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Nitrous oxide emissions from desert region soils

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The University of Arizona, 1993

NITROUS OXIDE EMISSIONS

FROM DESERT REGION SOILS

by

Michael Roland Guilbault

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DEPARTMENT OF SOIL AND WATER SCIENCE

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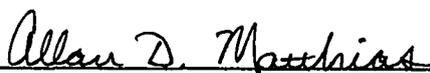

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Associate Professor of Soil and Water Science   Date

ACKNOWLEDGEMENTS

DEDICATION

This thesis is inscribed by way of compliment to the innumerable individuals who, by virtue of their exacting intellects, compelling actions, or exquisite spirits, have drawn forth my own vitality to actualize objectives of a far more ambitious order than would otherwise have been likely, or even possible.

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ABSTRACT

This study was conducted to determine emission rates of nitrous oxide (N_2O) gas from arid region locations. Fluxes were measured at an effluent-irrigated turfgrass location in Arizona, a Sonoran desert location, and a savannah location in Africa. Fluxes were measured by a closed chamber method at the Arizona locations on a weekly basis during the summer of 1991, and at the African location during two separate three day studies during the summer of 1992. Soils were sampled at each location during each sampling period and analyzed for water content, nitrate, pH, and total organic carbon content. Nitrous oxide fluxes in Arizona averaged approximately 13 and 0.7 kg N_2O-N ha^{-1} yr^{-1}, for the turf grass and desert locations respectively. The average fluxes from the African sites were 1.3, 1.6, and 1.3 kg N_2O-N ha^{-1} yr^{-1} for a millet field, fallow field, and "tigerbush" plateau, respectively. Diurnal and seasonal variability was observed.

CHAPTER 1

INTRODUCTION

Nitrous oxide (N_2O) is a radiatively active atmospheric trace gas implicated in many environmental problems including global warming and stratospheric ozone depletion. Produced primarily by microbial denitrification and to a lesser extent by nitrification, nitrous oxide emissions from soils constitute a significant source of atmospheric N_2O. Soil denitrification and nitrification are influenced by water content, oxygen content, temperature, pH, and the availability of carbon and nitrogen compounds in the soil. The major recognized sinks for atmospheric N_2O involves photodissociation and chemical reaction with atomic oxygen in the stratosphere.

It has recently been shown that the N_2O concentration is increasing at a rate of 0.2 to 0.3% per year in the global atmosphere. This indicates that an imbalance exists in the largely unquantified and uncertain sources and sinks of atmospheric N_2O.

Anthropogenic activities such as increasing use of nitrogen fertilizers, irrigation of arable lands, biomass burning and fossil fuel combustion have received much attention as potential sources of the increase in atmospheric N_2O concentration. Attention has also been focused on the uncertain role of disturbed tropical forest soils in the global N_2O concentration increase. Other natural ecosystems have, however, not been intensively investigated yet may play an important role in the global N_2O budget. Low-latitude desert ecosystems, in particular, have received little attention despite the favorable conditions for denitrification which arise from irrigation and fertilization of these lands.

Many low-latitude desert soils are irrigated and fertilized for agricultural, recreational or landscaping purposes. With the increasing scarcity of potable water in arid regions,

reclaimed sewage waters are more frequently being utilized for this irrigation. Since effluent water often contains larger amounts of nitrate and dissolved organic material than potable waters, replacing the latter with the former in irrigation applications further improves the conditions for nitrifying and denitrifying bacteria in the irrigated soils. This improvement in the microbial climate might be expected to lead to a pronounced N_2O emission increase in arid climates where microbial respiration rates are augmented by high temperatures.

Many parks, golf courses and recreational facilities in the southwestern United States already employ effluent water in irrigation, an option which in many places is becoming a mandate. Although the arguments for using municipal wastewater for irrigation of the turf grass facilities are many, the additional atmospheric pollution resulting from increased nitrous oxide emissions is a factor which must be quantified and included in any environmentally sound and forward-looking cost-benefit analysis of this irrigation option.

This study attempts to assess the emissions of nitrous oxide gas from the soils of an effluent-irrigated turf grass location in southeastern Arizona, an undisturbed Sonoran desert location adjacent to the turf grass location, and natural and agricultural locations in the Sahel region of Niger, West Africa. The flux of N_2O from the undisturbed Arizona desert location is considered the background level of emissions in order to estimate the increase in this flux resulting from the management practices employed at the turf grass facility. Samples of gas emissions from the Sahel were taken to assess the N_2O flux from a similar arid location

removed from the Arizona locations. The explicit objectives of this study are to assess the flux of N_2O gas from warm desert locations, including:

1. effluent-irrigated turf grass-covered soils in Arizona

2. undisturbed Sonoran desert soils in Arizona

3. natural and agricultural soils in the African Sahel

CHAPTER 2

LITERATURE REVIEW

Significance of Atmospheric Nitrous Oxide

Nitrous oxide (N_2O) is a radiatively and chemically active atmospheric trace gas implicated in global warming and stratospheric ozone depletion.

Connected with global warming primarily through its role in absorption and re-radiation of infrared (IR) energy, N_2O has a strong IR absorption band within the so-called "atmospheric window" at 7.7 microns. It also has IR absorption bands at 4.5 and 17 microns (Wang et al., 1976).

N_2O is also involved in the chemical destruction of stratospheric ozone (Cicerone, 1987). The ozone (O_3) concentration in the stratosphere, which accounts for 80% of all O_3, rises and falls in response to photochemical production and chemical destruction. Ozone protects the earth from UV radiation, with as little as a 10% drop in O_3 concentration accounting for as much as a 500% increase in UV flux (287 nm) through the atmosphere (Cicerone, 1987).

Reactions of N_2O in the Atmosphere

Large scale mixing in the tropical atmosphere injects tropospheric N_2O into the stratosphere, where it can interact with O_3. This N_2O often remains in the stratosphere for long time periods since its two major sinks, photochemical dissociation:

$$N_2O + hv ----> N_2 + O$$

and reaction with $O(^1D)$:

$$N_2O + O(^1D) ----> 2NO$$
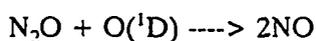
only serve to limit its atmospheric residence time to between 120 years (Cicerone, 1987) and

166 years (Prinn et al., 1990). The latter reaction accounts for 5% of N_2O destruction while

the former accounts for most of the remaining N_2O destruction (Cicerone, 1987). The two

reactions are estimated to consume 10.5 Tg^1 N_2O-N yr^{-1} (Bouwman, 1990).

The nitric oxide produced in the N_2O reaction with $O(^1D)$ is further involved in O_3

destruction by the catalytic reactions:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

and

$$NO_2 + O(^1D) \longrightarrow NO + O_2$$
$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
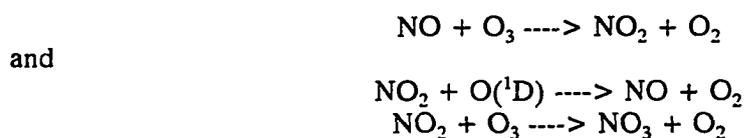
The total atmospheric sink for N_2O-N is estimated to be 13.3 Tg N_2O-N yr^{-1}. Since the

above reactions only account for 10.5 Tg N_2O-N yr^{-1}, a possible tropospheric sink for N_2O

also has been proposed (Wang et al., 1976). The disparity may be accounted for by N_2O

adsorption to tropospheric dusts and subsequent dry deposition (Khalil & Rasmussen, 1983).

N_2O concentration in the Atmosphere

The nitrous oxide concentration in the atmosphere has an influence on the degree

of global warming and ozone destruction which occurs. Estimates of present atmospheric

N_2O concentrations are variable, but range from 305 ppb (Cicerone, 1987) to 326.2 ppb

(Goldan et al., 1978), with a more recent N_2O concentration estimate being 302.9 ppb (Prinn

et al., 1990). In contrast, ice core samples estimating atmospheric N_2O from 500 BC to 1800

AD indicate a relatively constant concentration of 285-289 ppb (Pearman et al., 1986),

illustrating that the N_2O concentration has increased since pre-industrial times.

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[1] Note: 1 Terragram (Tg) = 1 x 10^{12} grams.

No appreciable seasonal cycling has been detected in the northern hemisphere (NH) by Wallace and Livingston (1990), or in the southern hemisphere (SH) by Scheel et al. (1990). However Khalil and Rasmussen (1983) report a 0.8 ppb higher NH N_2O concentration during April to June 1980-1983, which they attribute to a large anthropogenically-controlled source there. This higher NH N_2O concentration is in agreement with results from the Atmospheric Lifetime Experiment and Global Atmospheric Gases Experiment (ALE-GAGE) data (Prinn et al., 1990), based on more than 110,000 individual atmospheric measurements of N_2O over a 10 yr period. The ALE-GAGE study found that the NH concentration of N_2O was constantly 0.75 ± 0.16 ppb higher than SH concentration of N_2O and significantly more variable. The increased variability was attributed to growing tropical and mid-latitude NH sources. In possible disagreement with this data, Prinn et al. (1983) found that the N_2O concentration in the atmosphere lacked a substantial latitudinal gradient, indicating an even source distribution.

N_2O flux to the Atmosphere

The size of the atmospheric reservoir of N_2O-N is estimated to be 1500 Tg (Bouwman, 1990) with a steady-state total annual source (TAS) strength estimated at between 11 (±2.0) Tg yr^{-1} (Cicerone, 1987), and 20.5 (± 2.4) Tg yr^{-1} (Prinn et al., 1990). Cicerone (1987) estimated the annual increase in the TAS to be 2.8 Tg yr^{-1} (Bouwman, 1990), corresponding to an annual increase in N_2O concentration of 0.6 ppb. This estimation is lower than the 0.9 ppb N_2O concentration increase estimated by Khalil and Rasmussen (1983), but in agreement with the 0.6 ppb rate of increase estimated by Scheel et al. (1990). This latter figure indicates a 0.2% increase in N_2O concentration per year, slightly lower than the 0.3% annual increase measured by Prinn et al. (1990).

Global Circulation Model Predictions

Data which show an increasing N_2O concentration in the atmosphere are in agreement with the predictions of many global circulation models.

The Integrated Model for the Assessment of the Greenhouse Effect (IMAGE) developed by Rotmans et al. (1990) predicts future TAS strengths for N_2O. With 4 scenarios corresponding to completely unregulated through stringently regulated sources, IMAGE predicts a minimum 18 Tg to a maximum 60 Tg increase in TAS of N_2O by the year 2100 AD. All scenarios show some increase in N_2O due primarily to its long atmospheric lifetime. The IMAGE also predicts that N_2O rapidly becomes a "greenhouse gas" second only in importance to CO_2. Finally, the model predicts that even the most optimistic N_2O-emission scenario leads to a rise in the global temperature as a result of increases in atmospheric N_2O.

Unfortunately, the IMAGE ignores temperature feedbacks on microbial respiration rates, and the effects of cloud radiative properties on global warming. These factors, and the uncertainty of oceanic heat uptake and snow and ice cover at higher latitudes lend question to the validity of global circulation models in general (Dickinson, 1989).

Sources of Atmospheric N_2O

There are many suspected terrestrial and anthropogenic sources of atmospheric N_2O. Among the anthropogenic sources are fossil fuel and biomass burning (Dasch, 1992; Anderson et al., 1988), nylon production (Thiemens and Trogler, 1991), tropical land perturbation (Matson & Vitousek, 1987), and increasing irrigation and use of nitrogen fertilizers (Denmead, 1991). Of these sources fossil fuel burning is often considered the most significant. However, recent evidence (Muzio & Kramlich, 1988) shows that temporary storage of smoke from fossil fuel combustion results in spontaneous generation of N_2O in

sample containers. These findings cast doubt on studies quantifying the contribution of fossil fuel burning to the global N_2O budget.

Terrestrial sources of N_2O include chemical denitrification, biological nitrification and biological denitrification which take place primarily in soils. Although natural ecosystems are generally considered to be undersampled leading to high uncertainty in predictions, Bouwman (1990) estimates the N_2O TAS from soils to be 9 Tg N_2O-N yr^{-1}, 6 Tg N_2O-N yr^{-1} from natural ecosystem soils and 3 Tg N_2O-N yr^{-1} from cultivated soils.

Chemical denitrification results from the formation of unstable nitroso- groups in the presence of high concentrations of soil NO_2, which react to form N_2O. High NO_2 concentrations can be caused by nitrate respiration of soil microbes in the genera Bacillus and Clostridium, or NH_4 toxicity to Nitrobacter (Bouwman, 1990). The N_2O produced through this process is minimal in aerobic soils and insignificant in anaerobic soils (Bouwman, 1990).

Nitrous oxide emitted from soils is produced primarily through the processes of biological nitrification and denitrification (Amundson & Davidson, 1990). The nitrification process is accomplished primarily by autotrophic bacteria in the genera Nitrosomonas and Nitrobacter (Stevenson, 1982). Denitrification is performed by autotrophic bacteria of the genera Micrococcus and Thiobacillus, and by heterotrophs of the genera Pseudomonas, Micrococcus, Achromobacter and Bacillus (Stevenson, 1982). NH_4 availability is generally thought to limit nitrification activity, while the presence of O_2, and NO_3 and organic carbon (OC) availability are limiting factors in the denitrification reactions. Ideal denitrification produces orders of magnitude greater N_2O production than ideal nitrification in soils (Amundson & Davidson, 1990).

In biological nitrification, N_2O is produced by bacteria of the genus <u>Nitrosomonas</u> in oxygen limited conditions as a result of nitrate dissociation (Conrad et al., 1983). These processes take place in the soil surface layer principally (Staley et al., 1990). The general reaction of nitrification is:

$$NH_4^+ \dashrightarrow NO_2^- \dashrightarrow NO_3^-$$

The proportion of N_2O as a nitrification product is thought to be an inverse function of the nitrification rate (Amundson & Davidson, 1990).

In biological denitrification, soil nitrate is converted to N_2O and N_2 as denitrifying organisms utilize the nitrate as a terminal electron acceptor in their respiration processes (Amundson & Davidson, 1990). This process takes place primarily in the surface layers of soil and decreases with depth (Staley et al., 1990). Christensen et al. (1990) found that denitrification activity in the 15-30 cm layer of soil was only 2% of that in the 0-15 cm layer. Staley et al. (1990) found the greatest denitrification activity in the 0-3.8 cm layer of a silt loam soil. However, in desert region soils, Westerman and Tucker (1978) found maximum nitrate loss at depths between 10 and 15 cm with minimum losses between 25 and 30 cm. These nitrate losses in the desert soils were considered indicators of denitrification activity.

The denitrification process becomes necessary only when oxygen is limiting, and 1% O_2 concentrations have been observed to suppress biological denitrification in some conditions (Westerman & Tucker, 1978). The general denitrification reaction is:

$$NO_3^- \dashrightarrow NO_2^- \dashrightarrow NO \dashrightarrow N_2O \dashrightarrow N_2$$

In this reaction, nitric oxide (NO) acts as a freely exchangeable intermediate (Amundson & Davidson, 1990) which may escape to be emitted from the soil due to its relative insolubility in water films. Atmospheric nitrogen is the end-product in this reaction, although often

nitrous oxide is a principal product. Factors such as the presence of denitrifying organisms (Christensen et al., 1990), pH, redox potential, OC, O_2 and NO_3 concentrations determine both the rate of, and the end-product of the denitrification reaction (Conrad et al., 1983). Because of soil chemical and physical heterogeneity, the differential solubility of NO, N_2O, and N_2, and the nature of the denitrification reaction, conditions may exist where N_2O is simultaneously produced and consumed in soils (Kaplan, 1984). N_2O is over an order of magnitude more soluble in water than either NO or N_2 (Weast, 1971), allowing water films in the soil to retain N_2O, and increasing contact of the dissolved N_2O with denitrifiers who may subsequently reduce it further. There is also evidence of soil uptake of N_2O in certain conditions (Cicerone, 1989), although more study is necessary to provide conclusive results.

The ratio of N_2O to N_2 produced by denitrification is affected by the ratio of oxidant (NO_x) to reductant (OC) in the soil. If the O:R ratio is low, N_2O and NO are the primary products whereas is the O:R is high, N_2 is the principal output (Amundson & Davidson, 1990). Nitrous oxide is produced in an Eh range from 200 to 620 mV while N_2 is the only product when the soil Eh is below 200 mV (Amundson & Davidson, 1990).

When soil pH is >6 N_2 is the dominant denitrification product although at soil pH <7 N_2O is not easily reduced (Westerman & Tucker, 1978).

Factors Affecting N_2O Emissions from Soil

Since the principal source of soil N_2O flux is bacterial denitrification, conditions in the soil which favor this reaction lead to increased N_2O flux from soil. These factors include poor soil drainage, soil temperatures at or above 25°C, soil reaction near neutral, a large supply of available organic matter, and a large concentration of soil nitrate and nitrite (Stevenson, 1982).

Poor soil drainage acts to elevate microbial activity and populations up to a certain point (Conrad et al., 1983), presumably through increasing contact of microbes with substrate, and augmenting solubility of necessary nutrients (Westerman & Tucker, 1978). By also limiting the rate of oxygen diffusion into the soil, high levels of soil moisture also contribute to anaerobic conditions in soils (Conrad et al., 1983). Anaerobic conditions promote biological denitrification, and are achieved rapidly with small elevations in moisture content, especially in finer textured soils (Amundson & Davidson, 1990).

In one study, a 10-fold increase in N_2O production in soil was observed as a result of increasing soil moisture from 10% to 20% (Conrad et al., 1983). This study also found the promotion of denitrification by rainfall on natural soils to be more pronounced after long periods on dryness. Another study (Christensen et al., 1990) indicated that denitrification activity was enhanced with increases in soil moisture content with peak activity occurring 0.5 hr after irrigation.

Soil temperatures between 2°C and 65°C are conducive to denitrification activity in soils, although temperatures above 70°C seem to inhibit it (Westerman & Tucker, 1978). Conrad et al. (1983) found that soil surface temperature at 3-5 mm depth correlated well with denitrification activity according to the Arrhenius equation. This correlation suggests not only that denitrification is influenced by temperature but also that it is taking place at the soil surface.

Soil temperature cycling has also been associated with diurnal cycling in the magnitude of N_2O flux. Conrad et al. (1983) found diurnal flux variation of one order of magnitude attributed to both vegetation and temperature effects. Matthias et al. (1979) also found diurnal cycling in the N_2O flux with highest emission in the early morning and lowest

during daylight hours. In contrast, Conrad et al. (1983) found maximum N_2O flux in grass-covered loess at 3:00-4:00 pm with minimum at 6:00 am. In comparison to the soil moisture effects, experiments with no-till (NT) and conservation-till (CT) plots in silt-loam cropped in maize produced higher N_2O fluxes in the former (Staley et al., 1990). Since NT plots were moister and cooler than CT plots, this suggests that moisture effects are more significant than temperature effects.

There is evidence that low soil pH adversely affects organisms involved in denitrification (Christensen et al., 1990), and denitrification may be insignificant in such soils. Evidence to support this theory includes very low flux values recorded from acidic soils (Bowden et al., 1990).

The presence of organic carbon in soils provides substrate for heterotrophic denitrifying bacteria to utilize, promoting their activity. Breakdown of these materials in soils affects the rate of O_2 consumption by non-denitrifiers as well, which may enhance anaerobic conditions in the soil (Westerman & Tucker, 1978). In some tests, addition of simple sugars and organic acids has increased N_2O flux from soils, but only when native OC was initially low (Westerman & Tucker, 1978). Laboratory tests have also shown that organic carbon can act as a limiting factor in denitrification (Artiola & Pepper, 1991).

Christensen et al. (1990) has identified what are termed "hot spots" of potential denitrification activity (PDA). These "hot spots" are associated with areas of large OC concentrations such as buried, rotting vegetation (Christensen et al., 1990) and may persist for periods of weeks. These "hot spots" give rise to short and long-term temporally stable ranking of field sites with regards to the magnitude of recorded N_2O flux (Christensen et al., 1990). Core studies of PDA support this finding by revealing that actual denitrification

activity may be traced to a very small volume of soil within a given core (Christensen et al., 1990). These PDA "hot spots" are particularly noticeable in aerobic conditions and are less affected by increases in soil moisture than the bulk soil (Christensen et al., 1990).

Related to the idea of PDA "hot spots" is the "islands of fertility" idea promoted by Schlesinger et al. (1990). In this scenario, soil resources in arid lands are concentrated under bushes and shrubs between which are large tracts of relatively infertile soils. This is partly due to erosional processes and partly due to the rhizosphere effect.

Spatial variability in N_2O flux resulting from differences in the previously discussed factors is insignificant compared to the effect of fertilization (Conrad et al., 1983). Strong increases in N_2O flux occurred 1 to 2 days after fertilization of a grass-covered loess soil in one study (Conrad et al., 1983), though total loss of nitrogen was less than 1% of that applied. Fertilizer type was also found to be important, with ammonium fertilizer having a more pronounced effect that nitrate fertilizer. This result suggests that nitrification had a more important influence on the N_2O flux than denitrification in this study. Staley et al. (1990) determined that nitrification controlled denitrification in a silt loam soil cropped with maize. The same situation may have occurred in the Conrad et al. (1983) study.

Nitrogen can also be supplied to land by rainfall, vegetation and bacterial activities. In virgin lands, nitrogen accumulation is influenced positively by the presence of vegetation, organic materials in the soil and fine soil texture (Stevenson, 1982). Large amounts of rainfall and cropping of soils tend to decrease nitrogen supplies (Stevenson, 1982). Since nitrogen is often found in combined form in soils, bound to organic and mineral matter, only a few kilograms per hectare are available at a specific time.

Rainfall and nitrogen fixation are estimated to account for approximately 12.8 kg N ha^{-1} yr^{-1} on average (Stevenson, 1982). This value is too high for desert lands, despite indications that N content of rainwater is inversely proportional to rainfall period (Stevenson, 1982). Nitrogen fixation including ammonification is estimated to account for 9.2 kg ha^{-1} yr^{-1} of the total.

Nitrogen in Desert Soils

Westerman & Tucker (1978) found the Sonoran desert to have an unexplained nitrogen deficit in a study considering N-removal by plants, leaching and runoff versus N-addition by dryfall, wetfall, fertilization and N-fixation. In agreement, a conservative estimate of input of atmospheric nitrogen to desert region soils indicated 77% of this input cannot be accounted for (Peterjohn & Schlesinger, 1990). According to this study, total atmospheric input of N to the southwestern American desert over a 10,000 year period is approximately 2.99 kg m^{-2}. This value is based upon 1.45 kg m^{-2} input due to wetfall, calculated from 50 measures over a four year period, and an estimated 1.54 kg m^{-2} due to dryfall. Nitrogen fixation by algal crusts, considered a primary mechanism of input, was ignored in this study adding to its conservativism.

Peterjohn and Schlesinger (1990) estimate storage of N within soils, based upon extant data from 212 locations throughout the southwestern United States to be 0.604 kg N m^{-2}. Vegetative storage is estimated at 0.036 kg m^{-2}, while vertical leaching over 10,000 years is estimated at 0.028 kg m^{-2}. Streamflow is considered negligible in desert regions.

The difference between input and storage is 2.32 kg N m^{-2} and may indicated gaseous loss due to nitrification and denitrification activities (Peterjohn & Schlesinger, 1990).

Although the authors indicate that deep seepage cannot be discounted, denitrification is likely to account for some of the loss.

The potential for denitrification in particular is high in the deserts of the southwestern United States compared to deserts in other parts of the world due primarily to organic carbon concentration, moisture and temperature (Westerman & Tucker, 1978). The Sonoran desert has more denitrification potential than the Great Basin desert, which in turn has more potential than the Mojave desert according to Westerman and Tucker (1978).

Measurements of Soil N_2O flux

Nitrous oxide fluxes from natural and managed-land soils have been extensively measured in recent years, showing an uneven source distribution. Among the unmanaged lands, tropical rain forest soils seem to be the largest terrestrial sources accounting for up to 40% of the present N_2O source or 75% of the pre-industrial source (Keller et al., 1986). The soils covered by tropical rain forest are estimated to be the source of 6.1 x 10^6 tons (6.1 Tg N) of atmospheric N_2O-N on an annual basis (Keller et al., 1986). Other unmanaged ecosystems are considered less significant in the global N_2O budget. The world's temperate steppes produce an estimated 1.1 x 10^{11} g N_2O-N yr^{-1} (Matson et al., 1991). Hao et al. (1988) estimate that burned and unburned savannah respectively contribute 1.9 x 10^{11} and 2.0 x 10^{12} g N_2O-N annually to the atmosphere, while Bowden et al. (1990) estimate that temperate mixed hardwood forests contribute <1% of the TAS of N_2O at 0.012 Tg N_2O-N yr^{-1}.

Tropical rainforest ultisols in the Amazon, and oxisols in Costa Rica were monitored by a closed-chamber method by Matson and Vitousek (1987). They found N_2O fluxes from

0 - 6.2 ng cm^{-2} h^{-1} N$_2$O-N with the highest fluxes associated with the Costa Rican rainforests. The fluxes were well correlated with mineralization and nitrification rates in the soil.

Keller et al. (1986) studied N$_2$O fluxes from rainforest soils using an open-chamber technique. They found fluxes in Brazil, Equador, and Puerto Rico averaged 17.4 x 10^{10} molecules cm^{-2} s^{-1} and arose mostly from contained areas of high flux which they termed "hot spots". Hot spots of N$_2$O flux along clayey-soil ridge tops were also found among sites near Manaus Brazil (Livingston et al., 1988). The mean emission rate from the Amazonian soils in this closed-chamber study was 1.3 ng N$_2$O-N cm^{-2} h^{-1}. Fluxes were reported to be highly variable and well correlated with soil nitrification rates.

Studies of the effect on N$_2$O flux of soil fertilization with NO$_3$ at another rainforest site near Manaus, Brazil showed a 20-fold increase in the ambient N$_2$O flux of 1.4 x 10^{10} molecules cm^{-2} s^{-1} one day after NO$_3$ application (Keller et al., 1988). The increased flux was thought to be due to soil denitrification activity.

Nitrous oxide flux from tropical savannah has also been studied by a closed-chamber method (Hao et al., 1988). The mean flux of N$_2$O varied from 2.5 x 10^9 to 3.0 x 10^{10} molecules cm^{-2} s^{-1} on undisturbed sites. The N$_2$O flux temporarily increased 4 to 5-fold after simulated rainfall, but was unaffected by burning of the grass layer.

The results of burning in the study by Hao et al. (1988) were consistent with results of a closed-chamber study of burned and unburned native tallgrass prairie in the midwestern United States (Goodroad & Keeney, 1984). Fluxes measured in this study were 0.6 - 0.7 ng N$_2$O-N m^{-2}s^{-1} throughout the year on both burned and unburned sites. Maximum N$_2$O flux was found after heavy rain during the summer months. In this study spatial variability was

minimal compared to temporal variability, and was related to changes in the soil moisture and temperature.

Closed-chamber studies of unburned native shortgrass prairie produced similar results (Mosier et al., 1991). Most (80%) of the 2.3 g N_2O-N ha^{-1} d^{-1} flux was caused by emissions immediately following rainfall events. Unfertilized, unburned shortgrass steppe in southern Colorado, USA was also studied by Mosier et al. (1991). Mean fluxes there by a closed-chamber method were 1.8 and 3.0 g N_2O-N ha^{-1} d^{-1} from midslope shortgrass and swale sites respectively.

Sagebrush steppe in south-central Wyoming was studied by Matson et al. (1991) using a closed chamber method. The mean flux detected from undisturbed sites at this location was 0.21 kg N_2O-N ha^{-1} yr^{-1}. In contrast, chapparel in southern California produced no detectable flux of N_2O in one closed-chamber study (Anderson & Poth, 1989). This was thought to be due to lack of sufficient soil moisture.

Wet meadowlands in Wisconsin produced N_2O fluxes of 8.5 ng N_2O-N m^{-2} s^{-1} in a survey by Goodroad and Keeney (1984). This study also measured fluxes of drained and undrained marshland, coniferous and deciduous forest. The mean fluxes were 18.0, 0.2, 1.5, and 7.7 ng N_2O-N m^{-2} s^{-1}, respectively, for these sites. N_2O fluxes from coniferous and deciduous forest soils in Massachusetts (Bowden et al., 1990) were similar to those found by Goodroad & Keeney (1984). The closed-chamber method flux values for a red pine plantation and mixed hardwood stand were 0.01 and 0.017 kg N_2O-N ha^{-1} yr^{-1} respectively. These low rates were attributed to low net nitrification rates in the soils studied.

Studies of N_2O flux from irrigated and fertilized fields have also taken place. These studies often show higher N_2O fluxes in managed soils than in similar unmanaged soils.

The N_2O flux from an irrigated northern Colorado clay-loam Maize (Zea mays) field soil was estimated using a closed chamber method by Mosier and Hutchinson (1981) to be 2.5 kg N_2O-N ha^{-1} (4 mo.)$^{-1}$. This flux represented 2% of the applied nitrogen fertilizer. A similar study by Hutchinson and Mosier (1979) indicated a N_2O flux of 4 kg N_2O-N ha^{-1} yr^{-1}.

Another study of a Maize (Zea mays) field soil (fine loam) in southern Wisconsin by a closed chamber method showed enhanced N_2O flux in N-fertilized fields over similar unfertilized fields. The N_2O flux values were 3.6 and 5.2 kg N_2O-N ha^{-1} yr^{-1} from the unfertilized and fertilized fields respectively (Cates et al., 1987). Consistent with the findings of Mosier and Hutchinson (1981), the N_2O-N losses from the fertilized field represented 2% of the N applied. Most of the N_2O flux in this study occurred in the summer or during the spring thaw.

Table 1 summarizes all the measured fluxes reviewed here, converted to kg N_2O-N ha^{-1} yr^{-1} to facilitate comparison. A detailed summary of N_2O fluxes from agricultural lands is given in Eichner (1990).

Closed-chamber Flux Measurement Method

The closed-chamber flux-measurement method used in many studies, and variations similar to it have been used to evaluate soil gas emissions by many researchers. Several researchers have published performance evaluations of these chambers.

Hutchinson and Livingston (1991) and Rolston (1986) have identified several possible sources of measurement error which may result from using closed chambers to evaluate soil gas flux. They identify soil temperature perturbation, pressure differentials within the chamber, concentration effects, site disturbance during installation, and high spatial variability of fluxes as potential sources of error inherent in the closed-chamber method. Jury et al.

Table 1. Summary of nitrous oxide fluxes from selected studies of terrestrial sources.

Location of measurement and ecosystem	Reference	N_2O-N Flux (kg ha^{-1} yr^{-1})
So. America rain forest	Keller et al. (1986)	25.5
Arizona effluent-irrigated turf grass	This study	6.4
Wisconsin drained marsh	Goodroad & Keeney (1984)	5.7
Costa Rica tropical rain forest	Matson & Vitousek (1987)	5.4
Wisconsin fertilized Maize field	Cates et al. (1987)	5.2
Tropical region savannah	Hao et al. (1988)	4.4
Colorado Maize field	Hutchinson & Mosier (1979)	4.0
Wisconsin unfertilized Maize field	Cates et al. (1987)	3.6
Wisconsin wet meadowlands	Goodroad & Keeney (1984)	2.7
Wisconsin deciduous forest	Goodroad & Keeney (1984)	2.43
Brazil rain forest	Keller et al. (1988)	2.1
Niger laterite plateau	This study	1.7
Niger fallow Millet field	This study	1.6
Niger Millet field	This study	1.3
So. Colorado steppe	Mosier et al. (1991)	1.1
Brazil rain forest	Livingston et al. (1988)	1.1
Colorado shortgrass prairie	Mosier et al. (1991)	0.84
Arizona Sonoran desert	This study	0.7
Wisconsin coniferous forest	Goodroad & Keeney (1984)	0.47
Wyoming sagebrush steppe	Matson et al. (1991)	0.21
Colorado tallgrass prairie	Goodroad & Keeney (1984)	0.19
Wisconsin undrained marsh	Goodroad & Keeney (1984)	0.06
Massachusetts coniferous forest	Bowden et al. (1990)	0.01
Massachusetts hardwood forest	Bowden et al. (1990)	0.01
So. California chapparel	Anderson & Poth (1989)	0.0

(1982) state that since gases produced lower in the soil require longer to diffuse to the surface, accurate measurements of production require continuous, long-term measurements, particularly where source-depth may be variable. They conclude that the closed-chamber method is inadequate to quantify production rates of gases within the soil. Gas flux from moist soil, however, should not be affected by chambers since the diffusion rate is already low (Jury et al., 1982).

Studies of the chambers used in this study have shown that headspace air temperature commonly rises up to 10°C over ambient air temperature within several minutes of chamber placement on clear days. On cloudy days the effect is less pronounced. Chamber emplacement had no effect on soil temperatures at 2 cm or 12 cm depth of a sandy soil and caused a less than 1°C decrease in the temperature of a moist, loamy soil at the same depths (Guilbault, 1991, unpublished). Hutchinson and Livingston (1991) suggest using a reflective cover or other source of insulation to shield chambers from solar heating.

Pressure variations between the inside and outside of the chamber are not a large problem with closed chambers (Hutchinson and Livingston, 1991). Guilbault (1991) calculated a potential 5% increase in pressure within the chamber due to solar heating on sunny days and less of an increase on cloudy days. Romell (1922) calculated that no more than 1% of normal soil aeration can be attributed to pressure fluctuations, while wind action could not be responsible for more than .1% of normal soil aeration. Matthias et al. (1980) in experiments using a bellows to vary pressure within chambers concluded that this perturbation exerted a negligible effect on measured gas flux. These data suggest that wind and pressure variations have little effect on soil gas flux.

Decreases in the gas flux, which is primarily due to molecular diffusion (Jury et al., 1991), could conceivably be caused by gas buildup within the chamber headspace. Rolston (1986) considers concentration gradients an insignificant problem as long as chambers are not left in place for only 15 min to 3 hr. This time limit is in agreement with Jury et al. (1982) who states chamber placement times of less than 1 hr. are essential for accurate flux measurements.

Site disturbance has also been cited as a potential source of error inherent in this flux-measurement method. Matthias et al. (1980) found that chamber installation into soil accounted for a 250% increase in soil gas flux, immediately after installation. This disturbance, however, is due primarily to collar installation and probably doesn't pose serious limitations to flux determination if sites are left undisturbed for several days prior to initial measurements (Hutchinson & Livingston, 1991).

Finally, high spatial variability of gas flux from soils can be overcome by grouping areas or times of study into hypothetically similar associations (Hutchinson & Livingston, 1991). Random sampling within these associations is a well established sampling method.

Overall, if sites are left undisturbed for a period prior to initial flux determination, it is clear that concentration effects, pressure fluctuations, wind subduction, and soil shading would all contribute to underestimates of the soil gas flux by the closed-chamber method, if they had an effect. These errors, however, are probably insignificant.

CHAPTER 3

MATERIALS AND METHODS

Field Locations

Arizona

Nitrous oxide flux was measured at two southeastern Arizona locations. The Arthur Pack regional golf-course and a relatively undisturbed parcel of the surrounding desert roughly 25 miles north of the University of Arizona main campus were chosen for the study (approximately 32°N 111°W; elevation 648 m). The vegetation at the turfgrass location is predominantly bermudagrass (Cynodon dactylon) while the desert location is dominated by an upper storey of ironwood (Sideroxylon spp.), creosote (Larea tridentata), and palo verde (Parkinsonia aculeata) over an understorey of triangle burr sage (Salvia spp.), and various cacti (e.g. Sereus giganteus, Opuntia spp.) . Soil at the turfgrass location is a loamy sand. Soil at the desert location is also a loamy sand (Appendix C). These sites are located in a region characterized on the basis of its vegetation as the Arizona Upland portion of the Sonoran desert. Because of their mutual proximity, their climatic similarity, the effluent-irrigation of the golf course and the undeveloped nature of the desert, these sites were well-suited for the study.

The dimensions and features of the desert and turfgrass locations in Arizona were carefully determined using a simple orienteering technique, a compass and a manual odometer. From the information obtained using the technique, maps of each site were drawn. An artificial grid was superimposed over each map and its nodal points were assigned numbers. Using Lotus 123 @rand function, three numbers were chosen as sampling sites at

each of the turfgrass and desert locations. Sites were randomly chosen because with limited a priori chemical and subsurface physical information about the locations, a random selection of sites provided the most unbiased sample. Figures 1 and 2 show the Arizona turfgrass and desert sites respectively.

Africa

Nitrous oxide fluxes were measured at three locations in the Sahel region of Niger, Africa. The locations included a fallow field, uncropped for 10-20 years, vegetated with Guiera senegalensis bushes and a variety of grasses (Andropogon spp., Cenchrus biflorus, and Eragrostic tremula), an unvegetated plot designated as a millet (Pennisetum typhoides) field, and a "tigerbush" plateau area, all located within a 15 km^2 area of study (approximately 14°N 2°E; elevation 600 m). Soil at the fallow field and millet field location was sand, while soil at the "tigerbush" plateau location was a clay loam (Appendix C). The African field locations were chosen to correspond with areas studied by researchers working on the HAPEX-II-Sahel experiment in Niger, Africa. This area of the Sahel is characterized as subtropical steppe, with a morphology of ironstone plateaus separated by wide, sandy, gently sloping valleys. The location at the "tigerbush" plateau area, common to this region of the Sahel, is characterized by strips of vegetation (including Guiera senegalensis, Combretum micranthum, and Combretum gluttinosum) separated by barren inter-stripe areas of algal-crust, clay-crust and ironstone outcrop. The fallow and millet-field locations were located in inter-plateau areas characterized by sandy oxisols and ultisols. The three locations were chosen to be representative of the major landforms and anthropogenic uses of this region of Africa.
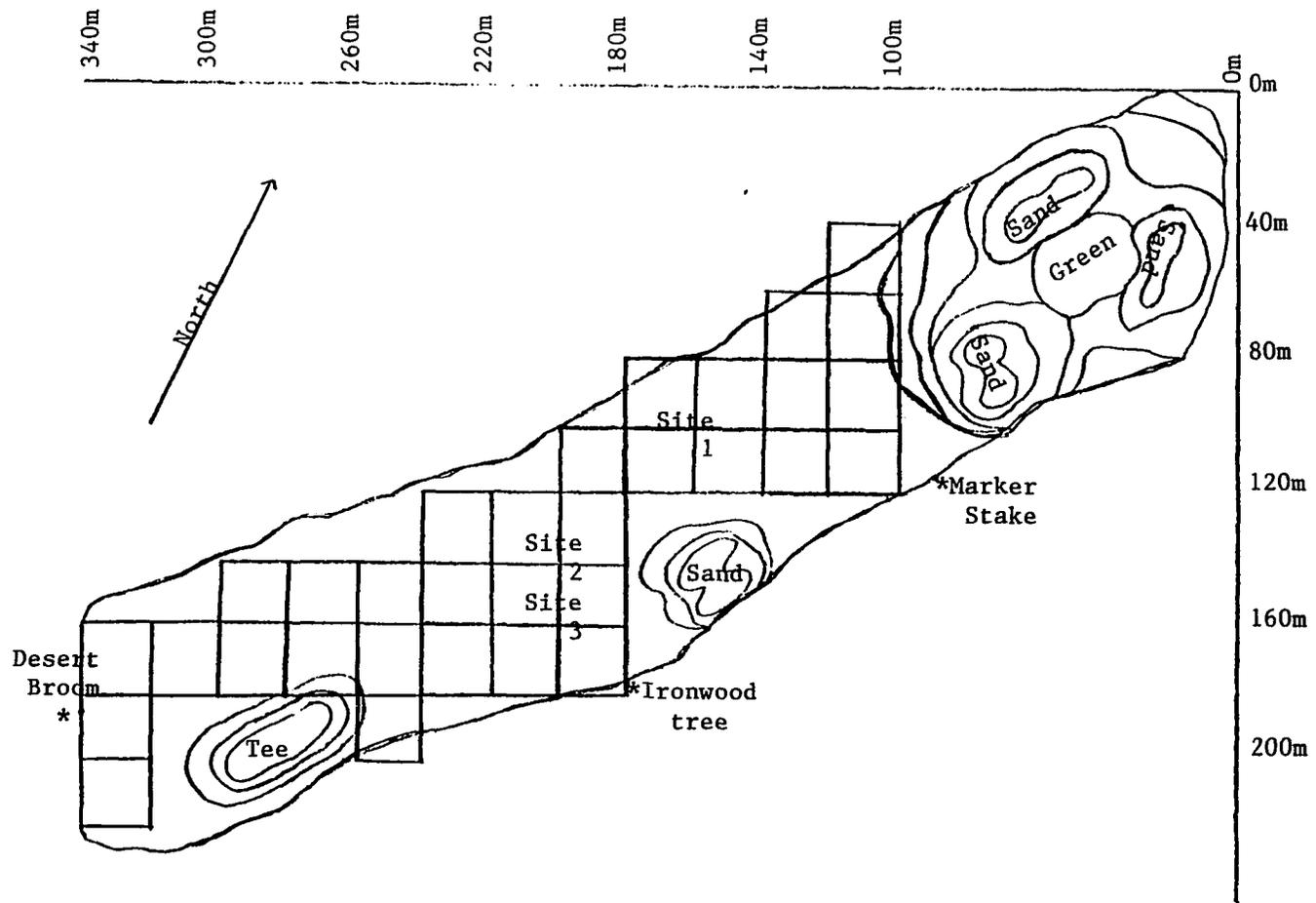
Figure 1.   The Arizona turf grass location.
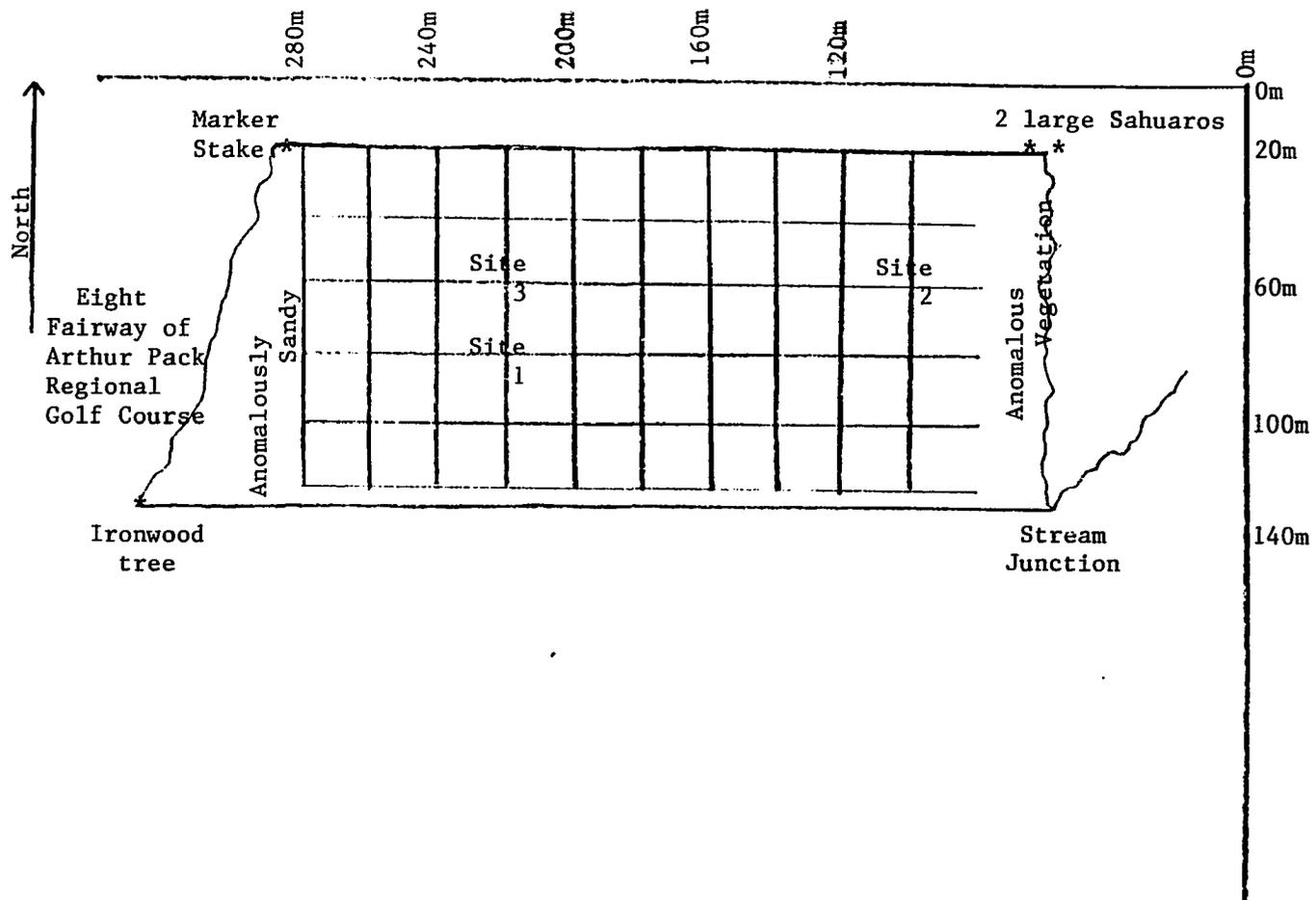
Figure 2.   The Arizona desert location.

The locations were roughly surveyed and maps were created of each site. Single 20 m transects were established near the centers of the millet-field and fallow locations, by walking a pre-determined number of paces along randomly chosen compass bearings from the locations' peripheries. The fallow location transect was aligned with the contour of the land while the transect in the millet-field location was aligned against the contour. This was done in order to evaluate any hillslope position effects in the millet-field while controlling these effects in the fallow location. Greater interest was focused on effects brought on by proximity of sampling sites to bushes in the fallow field, where it was thought "hot-spots" of denitrification activity might be centered. Sampling sites were established at 2 m intervals along each of these transects.

At the "tigerbush" location a 20 m transect was taken across a randomly chosen "stripe" of vegetation. Sampling sites were established at the extreme upslope, center and extreme downslope of this transect. Figure 3 shows the African locations.

Site Preparation

Arizona

At each of the three turfgrass and desert sampling locations in Arizona, a 5 cm wide, 35 cm diameter steel anchor-ring (Figure 4) was inserted into the soil. Installation was accomplished using a board and hammer until the top of the ring was flush with the ground surface. After installation the sites were left undisturbed for one week before initial sampling. This was done to minimize the possible effects of soil disturbance on gas flux to the atmosphere. The turfgrass sites were labelled T1, T2, and T3, while the desert sites were labelled D1, D2 and D3.

North

To
Niamey

To
Niamey

*Hamdallay
(34 km to Niamey)

Site
A

Site
B

Fandou Beri
(55 km to Niamey)

Site
C

15 km

15 km
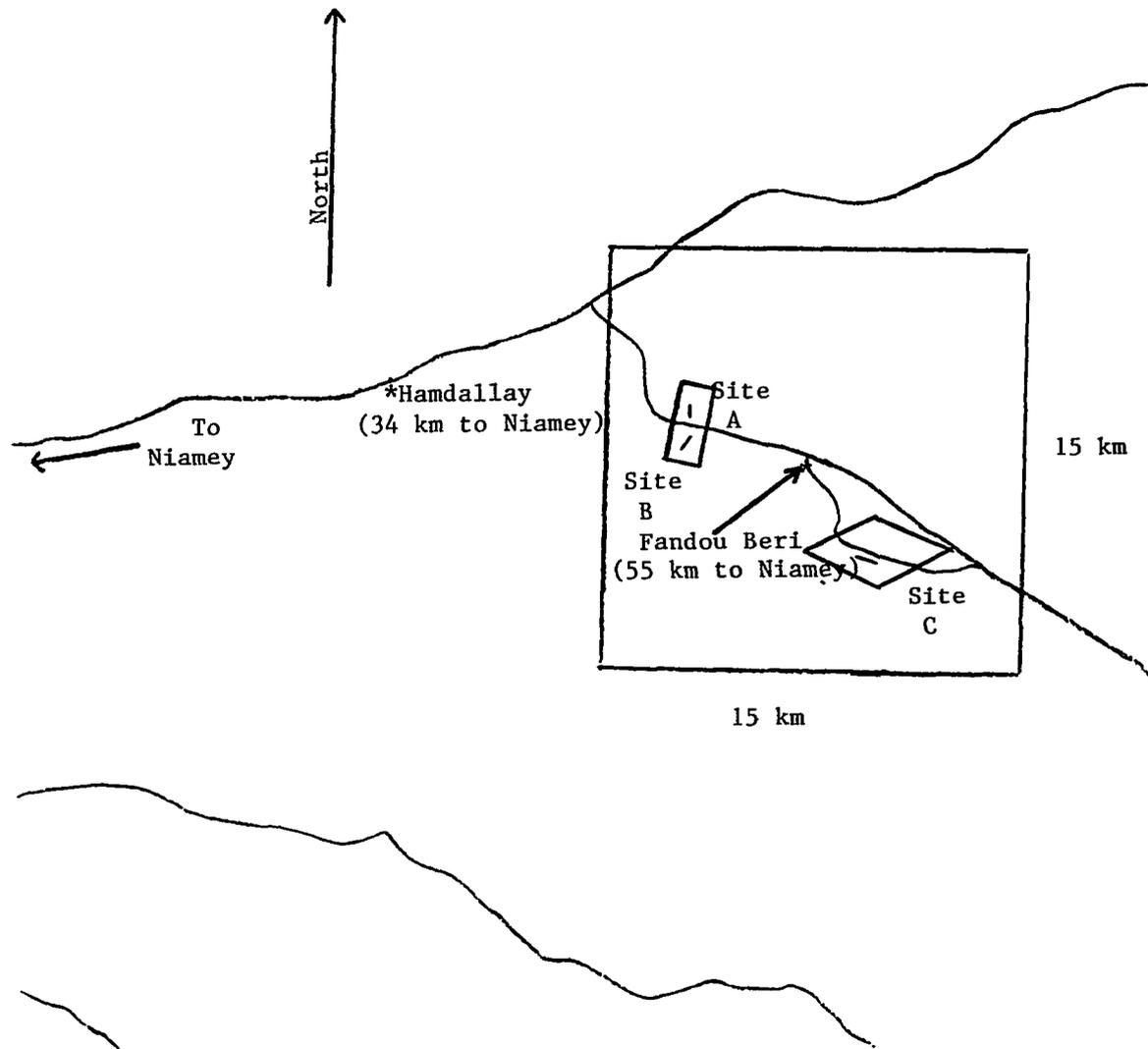
Figure 3.   The Africa Locations.

36
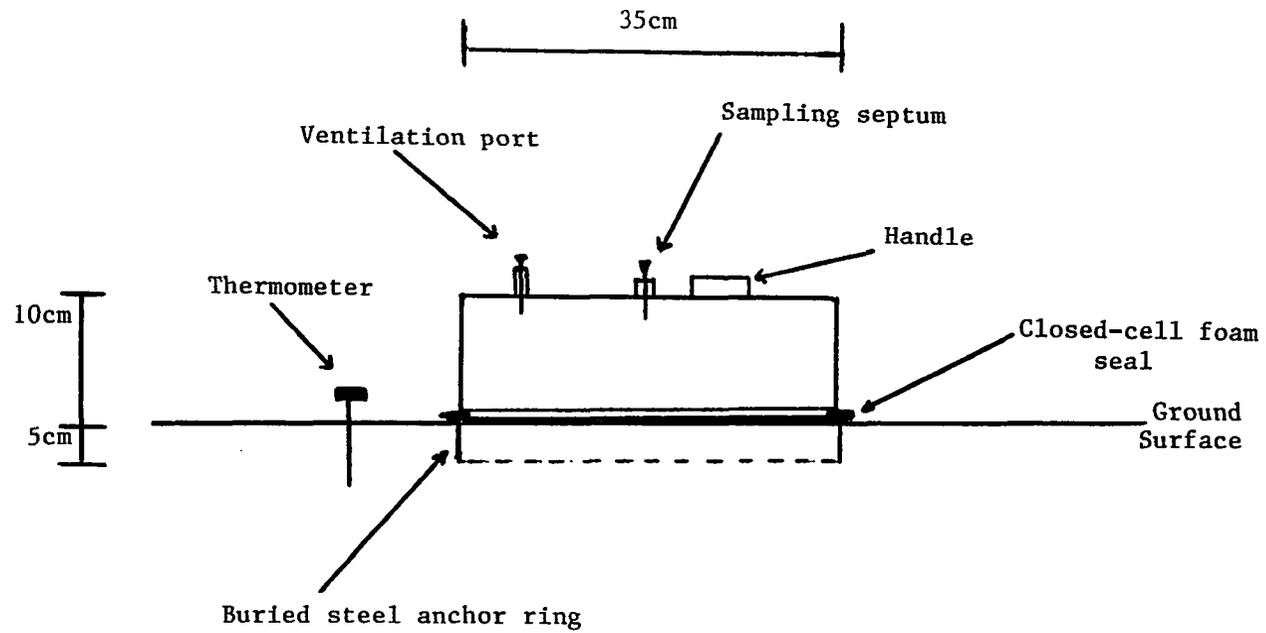
Figure 4.   The experimental setup, showing closed-chamber and anchor ring.

Africa

The 20 m transects in the fallow and millet-field locations of the African plots were marked with stakes and flags at 2 m intervals prior to sampling. These stakes were assigned numbers one through ten, consecutively, from the most southern to the most northern stake in each case. The "tigerbush" sites were marked with stakes and left undisturbed. The transect through the representative stripe was divided into three sampling sites, one on the upslope side of the stripe, another in the middle of the stripe, and a third on the downslope side of the stripe.

Sites were prepared on the day of sampling by turning an inverted anchor ring of the type previously described into the surface soil of each site, with the lip of the anchor in contact with the soil. This was done until an complete circular imprint of the ring could be seen on the ground, indicating that the ground was level enough to achieve good soil-chamber contact. A premium was placed on minimally disturbing the soil surface to prevent changes in the normal gas flux. After preparation all sites were left uncovered for several minutes to allow dissipation of any gases which had been released by this activity.

The millet field sites were labelled A1 through A10 from the northernmost to the southernmost sites, while the fallow sites were labelled B1 through B10 in the same manner. The "tigerbush" plateau sites were labeled "upslope stripe", "midslope-stripe", and "downslope-stripe" according to the physical position of the site.

Sampling Protocol

Arizona

N_2O flux and soil parameters were sampled during 10 early afternoons at one-week intervals between mid-June and mid-August of 1991. Diurnal and seasonal measurements were also made during the fall, winter and spring of 1991 and 1992.

Sites required no preparation immediately prior to sampling. In each case, cylindrical closed-chambers (Figure 4) 35 cm diameter and 10 cm in height, similar to those described in Matthias et al.(1980) were placed upon the anchor-rings at the desert and turfgrass sites. Two chambers were used to sample emissions from two sites simultaneously. The chambers were left in place on the anchor-rings at the turfgrass sites for 20 min and at the desert sites for 30 min. The longer chamber placement times at the desert location allowed smaller N_2O fluxes to be detected. Thirty mL air samples were removed at ten minute intervals via a needle inserted into a septum at the top-center of the chamber. Samples were collected using 30 mL polypropylene syringes (Luer-LOK brand, Becton Dickenson and Co. Rutherford, NJ). The syringes were fitted with Mininert standard luer hub valves (Precision Sampling Corp., Baton Rouge, LA) and 5 cm stainless steel needles. The needle was left in the septum during the intervals between air sample withdrawals. This was done to allow equalization of pressure between the inside and outside of the chamber. All filled syringes were numbered and transported to the University of Arizona in plastic bags for subsequent analysis by electron-capture gas chromatography (GC-ECD).

During the sampling period at a particular site, a Fisher Scientific digital thermometer (FS 15-078B) was inserted into the soil to a depth of 10 cm. After 20 to 30 min the soil temperature was recorded.

Samples of the soil surface horizon to a depth of 15 cm were also removed from within a 0.5 m radius of center of each sample site during each sampling period. Each soil sample was sealed within two 2 mm Zip-lok brand freezer bags in order to prevent drying. The soil samples were transported in an ice-filled Coleman brand 30 L cooler to the University of Arizona, where they were stored in a freezer maintained at temperatures below 4°C in order to minimize biological and chemical transformations of nutrient and carbon in the soils. Soil samples were later analyzed for total organic carbon, water content, pH, and nitrate concentration.

Africa

Each of the three African locations was sampled on two three-day-long periods that were separated by a two-week period in the late summer of 1992.

Sampling chambers of the type previously described were directly placed upon the soil surface at each sampling site. To improve the contact of the chamber with the soil surface, an extra layer of the closed-cell foam padding was added to the base of each chamber, large rocks were placed upon the chambers, and sand was piled around the emplaced chamber's sidewalls.

One location was sampled per day during each three day sampling period. At each location, two individual transect sites were sampled simultaneously until all had been sampled. During the first series of measurements, sites were sampled in order from one through ten. During the second sampling period two sites were sampled simultaneously from opposite ends of the transect converging on the center. This sampling procedure was introduced to minimize possible diurnal bias in the N_2O flux.

At all the sites, chambers were left emplaced for a one hour period, with air samples removed at 20 min intervals by the method previously described for the Arizona sites. Immediately after removal of air samples from a chamber, the sample was injected into a previously-evacuated 10 mL sampling bottles (Wheaton reorder #223739).

A total of 30 sampling bottles were filled with 513 ppb N_2O gas standards (Scott Specialty Gases, Plumsteadville, PA) throughout the duration of the study to evaluate possible leakage. During the second sampling period 36 bottles were also filled with ambient air at different times of day to evaluate possible diurnal changes in the N_2O concentration of the atmosphere.

All sampling bottles were fitted with natural red rubber straight plug stoppers (Wheaton reorder #224100-172) and unlined aluminum seals (Wheaton reorder #224178-01). Prior to installation, the red rubber stoppers were boiled in water for one hour then dried at room temperature in order to remove any residual nitrous oxide (Pamela Matson, 1992 Personal Communication). The bottles were sealed with Apiezon brand grease (GEC ALSTHOM LTD, Manchester, England) to improve the stopper-bottle seal. All sample bottles were transported by air to the University of Arizona, where they were stored at room temperature until analysis by GC-ECD. Storage ranged from 4 to 8 weeks.

Digital thermometers of the type previously described were inserted to a depth of 10 cm into the soils of each site for 30 min during each sampling occasion. The temperatures were noted and recorded for future reference.

Soil surface horizon samples to a depth of 15 cm were removed from three equally spaced locations along each transect on each sampling occasion. These soils were packaged, transported and stored as previously described. A soil pit was also excavated in close

proximity to each transect and examined. Soil samples were later analyzed for total organic carbon, water content, pH, and nitrate concentration.

Analysis of Samples

Gases

Analysis of gas samples was by electron-capture gas chromatography (GC-ECD) using a Varian (Walnut Creek, CA) model 3400 gas chromatograph fitted with a ^{63}Ni electron-capture detector. A Varian model 4290 integrator was used to determine chromatogram peak areas. The GC-ECD was fitted with a stainless steel sample valve (Valco Instruments Inc., Houston TX) equipped with a 1 mL sample loop. N_2 carrier gas flow rate was 23 mL min^{-1}. The column was 3 m long, 2.2 mm I.D. Poropak Q (80/100 mesh) type. Silica gel (0.5 g, 80/100 mesh) within an 80 mm long, 2.2 mm I.D. stainless steel tube was used as a sample drying agent between the injection port and sample loop. Temperatures were maintained at 80°C at the injector port, 50°C at the column, 300°C at the auxiliary detector oven housing the ECD, and 50°C at the standard detector oven. The 30 mL air samples were injected through the silica gel moisture trap to the sample loop which remained sealed at all times when not being flushed.

N_2O gas standards (Scott Specialty Gases, Plumsteadville, PA) at concentrations of 90.6, 513, and 971 ppb N_2O were used to calibrate the GC-ECD. Precision (coefficient of variation) of replicate samples of laboratory air (5 to 10 replicates) was generally 1.0 to 1.6% (Matthias et al., 1993).

Chromatograms consistently showed peaks at .9 min, 1.8 min, and 2.5 min, which corresponded to O_2, CO_2, and N_2O contents in the samples. The 2.5 min peak was integrated and used to determine N_2O concentration in a given sample.

Air in Wheaton bottles transported from Africa to the University of Arizona was removed by evacuation using a 30 cc syringe. After removal from the Wheaton bottles, these samples were immediately injected into the GC-ECD. Samples transported in syringes from Arizona sites were also injected directly into the GC-ECD.

Soils

Soil samples were dried at room temperature, ground and sieved. All samples were analyzed for total organic carbon (TOC), pH, NO_3, particle size, and moisture content.

Soil particle size distribution was determined by the hydrometer method. Moisture content was determined gravimetrically. The pH of a 1:1 soil:water extract was determined using a Fisher Scientific Accumet pH meter model 825MP. The TOC of 10% H_3PO_4-treated soil samples was determined by high-temperature combustion/thermal conductivity gas chromatography using a Carlo Erba model NA1500 NCS Analyzer fitted with a Poropak QS column. The NO_3 concentration was determined using 1:1 soil:water extracts and a Dionex model 20201 ion chromatograph with an electrical conductivity detector. All soil samples were analyzed at the University of Arizona's Soil, Water, Plant Analysis laboratory.

Calculations

Integrator output from the GC-ECD is in arbitrary area units under the N_2O peak. These values were converted to ppb N_2O using a regression equation (Appendix C) developed from the analysis of the standard gases. With the converted values, a simple

formula can be used to convert change in concentration within the headspace of the chambers over time into flux:

$$F = kh(\frac{273}{T})(\frac{\Delta C}{\Delta t})$$

where F is the flux of N_2O-N in kg ha^{-1} yr^{-1}, k is a units conversion factor (0.066 for the units given), h is the chamber height (m), T is the absolute temperature (K), and ΔC over Δt is the change in chamber headspace gas concentration (ppb) over change in time (min).

Statistical calculations including analysis of variance (ANOVA), linear regression, and stepwise multiple linear regression were performed using COSTAT statistical software (Cohort Software, Berkeley, CA). The ANOVA test was used to determine if N_2O emissions from the Arizona locations were significantly different from each other. The ANOVA test was also used to determine if individual sites within the Arizona locations were significantly different from one another. Linear regressions and stepwise polynomial regressions were used to determine the relationship between soil chemical and physical parameters and the measured N_2O emissions from the individual Arizona desert and turfgrass sites.

CHAPTER 4

RESULTS AND DISCUSSION

Arizona Emissions

Turfgrass location

The Arizona turf grass location produced relatively high, spatially and temporally variable N_2O emissions during the 10 week measurement period. The overall mean flux from all turf grass sites over all weeks was 40.2 ng N_2O-N m^{-2} s^{-1} with a standard deviation of 23.0 ng m^{-2} s^{-1}. These data are presented in Table 2.

The two highest fluxes were 274.7 and 92.8 ng N_2O-N m^{-2} s^{-1}, measured at site 3 during weeks 4 and 7 respectively. Both fluxes are over twice as large as the overall turf location mean. Similarly large temporal variability in N_2O flux has been reported by many authors (e.g. Christensen et al., 1990; Mosier et al., 1991), usually as a function of moisture or temperature cycling.

Chemical data from all sites and locations are provided in Appendix A. During weeks 4 and 7, total organic carbon (TOC) at site 3 was at its highest level during the study period at 1.58% and 1.81% respectively. Soil nitrate concentrations were below the ten week average during weeks 4 and 7. Soil nitrate levels decreased from week 4 to week 5 but increased from week 7 to week 8. No nitrate fertilizer was added to any of the sites during the 10 week study period. Soil moisture levels were slightly above average during weeks 4 and 7, probably as a result of recent rainfall. During week 4, soil temperature was the maximum recorded over the ten week period. During week 7 soil temperature was below the 10 week average.

Table 2.   Nitrous oxide fluxes (ng N_2O-N $m^{-2}s^{-1}$) from 3 Arizona turf grass sites during a 10 week interval from June 18, 1991 to August 20, 1991.

Week	Turf site #1	Turf site #2	Turf site #3
1	18.1	67.7	33.0
2	11.2	11.8	41.5
3	13.6	34.5	31.0
4	6.9	14.6	274.7
5	33.1	39.2	54.7
6	12.2	17.2	30.6
7	19.3	62.2	92.8
8	41.1	45.0	57.7
9	17.3	18.9	36.2
10	7.8	17.7	44.0
Mean:	18.1	32.9	69.6
StdDev:	10.4	19.3	70.6

The relatively large fluxes are not clearly explained by changes in soil chemical and physical parameters. High TOC and moisture levels and relatively high NO_3^- levels during week 4 provided favorable conditions for increased denitrification activity. Denitrification has been found in laboratory experiments to be partially carbon limited (Artiola and Pepper, 1991). Because of this, we would expect periods of high TOC in the soil to correspond with periods of high N_2O flux, consistent with observations. The drop in NO_3^- content from week 4 to week 5 may also indicate that denitrifiers were producing N_2O in the soil during this period. Denitrification only takes place in the absence of oxygen, thus would be more likely to take place at high soil moisture contents. Denitrification would also result in consumption of soil nitrate, again consistent with observations.

The high NO_3^- content of the soil at the time of data collection during week 4 could be a result of nitrification activity, also known to produce N_2O. Throughout the 10 week study period, conditions in the soil were mostly favorable for nitrification activity. From week 7 to week 8 at site 3, NO_3^- content of the soil increased from a relatively low level (44.7 mg/L) to a level of 106 mg/L, close to the 10 week site average. This may indicate that nitrifying bacteria were particularly active during this week, or may reflect changes in the content of NO_3^- in the effluent irrigation water. If high nitrification activity were occurring at this site during week 7, this activity could account for the large N_2O flux from the site, since N_2O is known to be produced during nitrification (Amundson & Davidson, 1990). Because TOC and moisture levels were very high during week 7, heterotrophic bacteria including denitrifiers would likely be active, accounting for some of the flux. Due to competition from heterotrophic bacteria and high moisture contents, autotrophic nitrifiers may not have been metabolizing at very high rates. Since production of N_2O during

nitrification is inversely related to nitrification rate (Amundson & Davidson, 1990), nitrifiers at this site may have produced more N_2O than average at this time.

The lowest fluxes, less than one quarter the magnitude of the turf grass mean, were found at site 1 during weeks 4 and 10. During week 4, soil nitrate levels at site 1 were much lower than average, but during week 10 a concentration over three times higher than average was recorded. Total organic carbon was close to the 10 week average, as was soil moisture. Soil temperature was above average during week 4, but below average during week 10. See Appendix A for weekly soil chemical and physical data.

During week 4, site 3 produced the highest recorded flux of the measurement period, while site 1 produced the lowest flux (Table 2). This may be explained by the higher temperature, higher NO_3^- and higher TOC of site 3 as well as its lower average pH when compared to site 1 (Appendix A). Although moisture levels at the two sites were comparable, the temperature and TOC of site 3 are more favorable to denitrification activity than temperature and TOC of site 1. Detailed statistical analyses are reported later in the chapter.

The oxidant (NO_3^-) to reductant (TOC) ratio (O:R) of site 1 was also higher than site 3 during week 4. Since high O:R values are associated with a greater proportion of N_2 than N_2O as a denitrification product, perhaps what is being seen between these sites is a change in the proportion of N_2O making up the total gas flux rather than a large change in the total amount of denitrification taking place. A simple linear regression was performed using COSTAT statistical software to analyze the relationship between chemical and physical parameters and the N_2O flux. Since high NO_3^- levels appeared to be only poorly linked with N_2O flux at the turf grass location ($r^2 = 0.06$), and NO_3^- is the primary oxidant in bacterial

denitrification reactions, denitrifiers organisms may be responsible for less of the flux than expected. However, nitrate is generally available at high enough concentrations in this soil that it is not limiting to denitrification even when concentrations are low (Artiola, 1993, personal communication). This fact may account for the low correlation between NO_3^- concentration and N_2O flux. Conditions at the turf grass location are generally favorable for denitrifying organisms, and despite the poor correlation with nitrate , denitrifiers are very likely to be responsible for a large portion of the N_2O flux.

Nitrous oxide flux at the turf grass sites displayed nearly stable temporal ranking during the 10 week study. At all times site 1 produced the lowest N_2O flux, while in all but two of the ten weeks, site 3 produced the highest N_2O flux. This results in a ranking of sites based on magnitude of emissions whereby site 1 < site 2 < site 3 in 8 of the 10 weeks comprising the measurement period. The mean fluxes from the individual sites and their associated standard deviations exhibit the same pattern. The coefficients of variation (CV) of the turf grass sites were 0.58, 0.59 and 1.01 for sites 1, 2, and 3 respectively.

My results may support the idea that "hot spots" of high denitrification potential exist in otherwise similar locations. A one-way completely randomized ANOVA test showed that sites 1 and 3 exhibit statistically significant differences in their 10 week mean fluxes at the 0.05 level of significance (P=.0452), while site 2 is not significantly different from either site 1 or site 3. The ANOVA test indicated that at the 95% level of confidence, a least significant difference (LSD) of 41.29 ng N_2O-N $m^{-2}s^{-1}$ between sites was required to consider site mean fluxes significantly different.

The mean nitrous oxide flux during the 10 week study period was approximately 40.2 ng N_2O-N m^{-2} s^{-1} which, with the limitations of my monitoring period in mind, may be

extrapolated to an estimated annual flux of 12.8 kg N_2O-N ha^{-1} yr^{-1}. The true annual flux is very likely to be lower than 12.8 kg N_2O-N ha^{-1} yr^{-1}. The 12.8 kg N_2O-N ha^{-1} yr^{-1} value is probably representative of the mean flux from the turf grass location during the 6 month period when the location is fertilized and irrigated with effluent water. The mean flux during the remaining 6 months is probably small. Measurements in late November, 1991, and in early April, 1992 indicated that fluxes were below the detection limit of our instruments during the time when there was no irrigation or fertilization.

If we consider the N_2O flux to be negligible for 6 months of the year and to average 12.8 kg N_2O-N ha^{-1} yr^{-1} for the remaining 6 months, the resulting annual flux from the turf grass location is about 6.4 kg N_2O-N ha^{-1} yr^{-1}. This value probably underestimates the true annual flux but is higher than most published fluxes for natural or agricultural ecosystems. No study of changes in N_2O flux immediately following fertilization was undertaken at this location, therefore it is likely that this estimate of N_2O flux is conservative. Table 1 shows that of selected studies I reviewed, only the South American rain forest produced a higher measured flux. Of agricultural ecosystems reviewed by Eichner (1990), only Ryden and Lund (1980) studying emissions from irrigated and fertilized soil cropped with celery, cauliflower and artichoke fields, and Duxbury and Bouldin (1982) studying emissions from irrigated, fertilized organic soils cropped with corn and onion reported annual fluxes higher than 6.4 kg N_2O-N ha^{-1} yr^{-1}.

It is difficult to make comparisons between the results of this study and those of other studies of turf grass due to the large variety of conditions and fertilization rates. Eichner (1990) summarizes the results of 26 such studies, with emissions ranging as high as 8.0 kg N_2O-N ha^{-1} yr^{-1} from grass fertilized at a rate of 400 kg N ha^{-1} (Webster & Dowdell,

1982), although most studies of grasslands found much lower fluxes. A study of a grass lawn in Andalusia, Spain (Slemr et al., 1984) found emissions ranging from 1 to 10 ng m^{-2} s^{-1}, a rate much lower than any of the turf grass sites in this study.

It is useful to express the amount of N_2O-N as a fraction of total N input to the turfgrass location in this study. Since the turf grass location was fertilized at a rate of 200 kg N ha^{-1} yr^{-1}, and effluent irrigation water contributes an estimated 108 kg N ha^{-1} yr^{-1} based on data by Hayes (1988), the total anthropogenic input of N to the location is approximately 308 kg N ha^{-1} yr^{-1}. If we add this to 3 kg N ha^{-1} yr^{-1} estimated to be added by dry and wet deposition to land in the desert southwest (Peterjohn & Schlesinger, 1990), the total N input is about 311 kg N ha^{-1} yr^{-1}. The measured N_2O-N flux is then calculated to be 2.1% of the total N inputs, a similar percentage to that found in previous studies of irrigated and fertilized lands (e.g. Mosier & Hutchinson, 1981; Cates et al., 1987).

Desert location

Table 3 displays the N_2O flux data from the three Arizona desert sites. The mean N_2O flux from all three sites over the entire observation period was 2.4 ng N_2O-N $m^{-2}s^{-1}$ with a standard deviation of 1.6 ng N_2O-N m^{-2} s^{-1}. These values were higher than expected considering the poor carbon and moisture status of the desert location compared to other natural ecosystems.

Similar to the turf grass location results, weeks 4 and 7 saw the highest fluxes from the desert location. In particular, site 1 produced the 3 highest fluxes of the study period during weeks 4, 7 and 10. Lowest fluxes were calculated to be negative, indicating that the soil was acting as a sink for atmospheric N_2O. Although soil sink activity is possible, the N_2O flux from these desert sites are also very close to the detection limit of the gas

Table 3.   Nitrous oxide fluxes (ng N_2O-N m^{-2} s^{-1}) from 3 Arizona desert sites during the 10 week interval from June 18, 1991 to August 20, 1991.

Week	Desert site #1	Desert site #2	Desert Site #3
1	-0.3	0.3	0.5
2	-0.9	2.0	-1.6
3	3.6	2.2	2.9
4	5.2	2.4	3.8
5	1.4	3.0	4.6
6	3.1	1.6	-1.3
7	7.3	2.7	2.9
8	2.7	1.6	-1.1
9	2.6	4.4	0.7
10	5.7	n/a	4.1
Mean:	3.0	2.2	1.6
StdDev:	2.4	1.1	2.3

n/a: Unable to calculate flux due to experimental difficulties.

chromatograph employed in this study. For this reason it is more likely that negative fluxes are a result of instrumental error rather than due to soil sink activity.

During weeks 4 and 7, percent moisture was the highest recorded during the entire study, with the moisture level during week 4 nearly twice as high as during week 7 (see Appendix A). In the 4 days preceding week 4 sampling, 29 mm of measurable rain was recorded at the Marana AZMET (Arizona meteorological network) station, located approximately 15 km northwest of the Arizona sampling locations. During the same time period, 2 mm of measurable rainfall was recorded at the Tucson (Campus Agricultural Center) AZMET station, located approximately 10 km southeast of the Arizona sampling locations. On July 30, 1991, the day of the week 7 sampling, 9 mm of measurable rain fell at both of these AZMET stations. The only other measurable rainfall (21 mm at Marana, 20 mm at Tucson) during the 10 week measurement period occurred during the 5 days preceding the week 9 sampling, at which time site 2 produced a flux equal to twice its mean for the 10 week period.

The three highest NO_3^- levels of the measurement period were recorded during weeks 4 and 7 at site 1 (see Appendix A). The quantity of NO_3^- found at the three sites during weeks 4 and 7 followed the same trend as the N_2O fluxes, namely site 1 > site 3 > site 2. Levels of NO_3^- in the soil at site 1 dropped from week 4 to week 5 and from week 7 to week 8. In fact, in five out of six occasions, periods of the highest flux associated with higher moisture levels were followed by a drop in nitrate concentrations the following week (Appendix A).

The trend of high soil moisture and high soil nitrate concentrations measured during weeks of high N_2O flux can be observed at site 1 during weeks 4, 7, and 10, at site 2 during

week 7, and at site 3 during week 4. During weeks of low flux, sites often showed lower than average nitrate levels (Appendix A).

Although total organic carbon contents of the sites were near their ten week averages, site 1 which had the highest flux during weeks 4 and 7, also had the highest TOC, at 0.42% and 0.41% respectively. Site 1 was located adjacent to an intermittent wash within the desert location. A large cluster of vegetation in this area may have contributed to the higher average TOC level of this site. TOC levels at the desert sites were generally much lower than those at the turf grass sites and were not highly variable.

These data suggest that moisture, TOC and NO_3^- content regulate N_2O emissions from the desert location. Increases in the levels of these components are associated with increases in N_2O flux. Since the periods of the highest flux were also associated with high initial NO_3^- contents which decreased sharply the next week, and site 1 which had the highest flux also contained the highest TOC concentration, it is likely that heterotrophic denitrifying organisms were responsible for a large portion of the N_2O flux from the desert sites at these times, following rainfall.

Nitrifying organisms probably are primarily responsible for N_2O production at most times in the desert location, due to the relatively low soil moisture levels, low TOC, and limited competition from heterotrophic bacteria. Increases in soil moisture may act to mobilize NO_3^- accumulated during dry periods when nitrification activity predominates, enlarge the anaerobic volume of the soil, and activate denitrifying bacteria populations. The result is the measured increase in N_2O flux and depletion of soil NO_3^-, as denitrifiers begin contributing to the N_2O emissions.

Nitrifying bacteria, although able to produce N_2O, create orders of magnitude less

N_2O during ideal metabolism than do denitrifying bacteria during ideal metabolism (Amundson & Davidson, 1990). Nitrifiers also produce N_2O at a rate inversely proportional to their overall rate of metabolism (Amundson & Davidson, 1990). Although the desert soil is very dry, even small amounts of moisture result in soil pore space humidity levels near 100%, facilitating the activity of many aerobic bacteria including nitrifiers. Low soil organic carbon levels further improve the competitive advantage of N_2O-producing nitrifiers which are autotrophic. These factors, the probable existence of considerable amounts of available ammonium in the desert soil (Peterjohn & Schlesinger, 1990), and observed weekly increases in NO_3^- concentration, support the hypothesis that nitrification is readily occurring in the desert soils. Since conditions in the desert soils are not conducive to high rates of nitrification, and N_2O production by this mechanism is inversely proportional to nitrification rate, the nitrifying bacteria may be producing significant amounts of N_2O at times when denitrifiers may be relatively inactive. This may account for the low, but relatively consistent N_2O flux observed from the desert sites.

When moisture levels are increased, N_2O flux also increases, probably because denitrifying bacteria become active, producing N_2O at a much higher rate than the nitrifiers. At the same time, the rate of nitrification probably increases due to the beneficial effects of higher moisture levels, however, as the rate increases, the amount of N_2O produced by this mechanism decreases. Therefore, as we move from a dry soil to a moist soil condition in the desert location, the proportion of the N_2O flux resulting from denitrification activity increases while the proportion resulting from nitrification activity decreases.

During 3 of the 10 weeks of the study, fluxes from desert site 1 > site 3 > site 2. No other temporally stable ranking of the sites with regard to N_2O flux was observed during

the study. The mean flux (3.0 ng N_2O-N m^{-2} s^{-1}) from site 1 over the whole study period was the highest of the three. The coefficients of variation for the 3 sites were 0.8, 0.5 and 1.4 for sites 1, 2, and 3 respectively. However, a one-way completely randomized ANOVA test indicated that the mean fluxes from the 3 sites in the desert location were not statistically different at the 0.05 level of significance (P=.3161).

The mean flux from all three desert sites over the study period was 2.4 ng N_2O-N m^{-2} s^{-1} which corresponds to an annual flux of 0.74 kg N_2O-N ha^{-1} yr^{-1}. Flux measurements at these sites during mid-November 1991 and early April 1992, indicated fluxes below the level of detection. If we consider the N_2O flux to be negligible (i.e., 0 ng N_2O-N m^{-2} s^{-1}) for the six cooler months of the year, and represented by the 10 week mean flux for the six warmer months, we arrive at an annual flux estimate of about 0.4 kg N_2O-N ha^{-1} yr^{-1}. Considering the low nutrient and organic carbon status of the desert, this flux is relatively high. As displayed in Table 1, this value exceeds estimates of flux from tallgrass prairie, sagebrush steppe, two types of forested lands and Southern California chapparel.

The fractional amount of N inputs lost as N_2O-N is difficult to estimate for the desert location. Nitrogen inputs to natural desert ecosystems in the southwestern U.S. come primarily from wet and dry deposition (approximately 3 kg N ha^{-1} yr^{-1}, Peterjohn & Schlesinger, 1990) and nitrogen fixation (e.g. blue-green algae, rhizobia), which may contribute between 0.5 and 100 kg N ha^{-1} yr^{-1} (Peterjohn & Schlesinger, 1990). Given the large uncertainty in N input to the soil, I calculate N_2O evolution as a percentage of total input to be in the range of 0.4% to 10.6%. Peterjohn & Schlesinger (1990) estimate that 77% of atmospheric N inputs to southwestern U.S. deserts are lost to the atmosphere in gaseous forms. Although nitrous oxide is only one of several nitrogen gases which may be

evolved from desert soils, my data indicate that it may account for a significant portion of this unaccounted loss. Since at higher pH values, N_2 is considered the predominant denitrification product, the role of denitrification in N loss from deserts may be very significant. Other mechanisms of N gas production such as ammonia volatilization may also account for large amounts of N gas emissions from desert soils.

How important are the deserts in the atmospheric N_2O budget? My preliminary data certainly cannot fully answer this question. The data can, however, give an indication of the importance of emissions from deserts. If the value 0.4 kg N_2O-N ha^{-1} yr^{-1} is considered to be a representative rate of emission from upland Sonoran desert soils, the particular category of desert which the location represents, then the total annual source (TAS) of N_2O-N from this 62,700 km^2 area would be 2.32 x 10^6 kg N yr^{-1}. The entire Sonoran desert consists of 310,362 km^2 and extrapolation of my data to this area results in a TAS of 1.15 x 10^7 kg N yr^{-1}. If my data are considered to be representative of all the low latitude desert areas of the world, this TAS equals approximately 0.8 Tg N yr^{-1} for the 1/7 of the Earth's land area covered by these deserts (Note; 1 Tg = 1 x 10^{12} g). This low-latitude desert value is between 11% and 32% of the TAS reported for the world's tropical forests (Matson & Vitousek 1990), and exceeds estimated TAS strength of many other natural ecosystems. This emission value represents between 3.5% and 8.8% of the Earth's TAS strength for N_2O.

Emissions are likely to be underestimated in this study since no data was collected immediately following a rainfall event, all desert sites were located on vegetation-clear soil, and measurements were made in part during the dry part of the summer season. Upland Sonoran desert may be a stronger source of N_2O than previously believed.

Comparison of Arizona Locations

Figure 5 displays the mean N_2O fluxes from both Arizona locations during the 10 week measurement period beginning June 18, 1991. During each week of the study, N_2O emissions from turf grass sites were considerably higher than those from the desert sites. The mean N_2O flux from the desert site with the highest mean emission rate, desert site 1, was only 1/6 the mean emission rate of the turf grass site with the lowest mean flux, turf grass site 1. Also, the mean N_2O flux from all three desert sites over the ten week period was only 5.9% of the mean N_2O flux from all three turf sites over this period.

Tables 4 and 5, showing mean NO_3^-, TOC, pH, moisture and temperature values for all sites, provides some insight into the relative difference in N_2O emissions between the Arizona locations. The turf grass sites were higher in soil nitrate and total organic carbon, and lower in pH than any of the desert sites. If the six sites are grouped into sets of two according to the magnitude of N_2O flux, these sets also rank consistently with regard to chemical characteristics. Turf site 2 (T2) and turf site 3 (T3) have the highest flux, highest nitrate content, highest TOC, and lowest pH of all the sites. Desert sites D2 and D3 have the lowest fluxes, the lowest nitrate contents, lowest TOC and highest pH of all the sites. The sites with fluxes between these groups, sites T1 and D1, exhibit middle values in the chemical tests.

Statistical tests across all sites in both Arizona locations were performed using COSTAT to attempt to explain the spatial and temporal variability in the N_2O flux. Mean values for soil nitrate content, total organic carbon, pH, temperature and moisture levels were regressed against 10-week mean values for N_2O flux from the 6 Arizona sites. A multiple regression of nitrate, organic carbon and pH versus flux indicates strong correlation
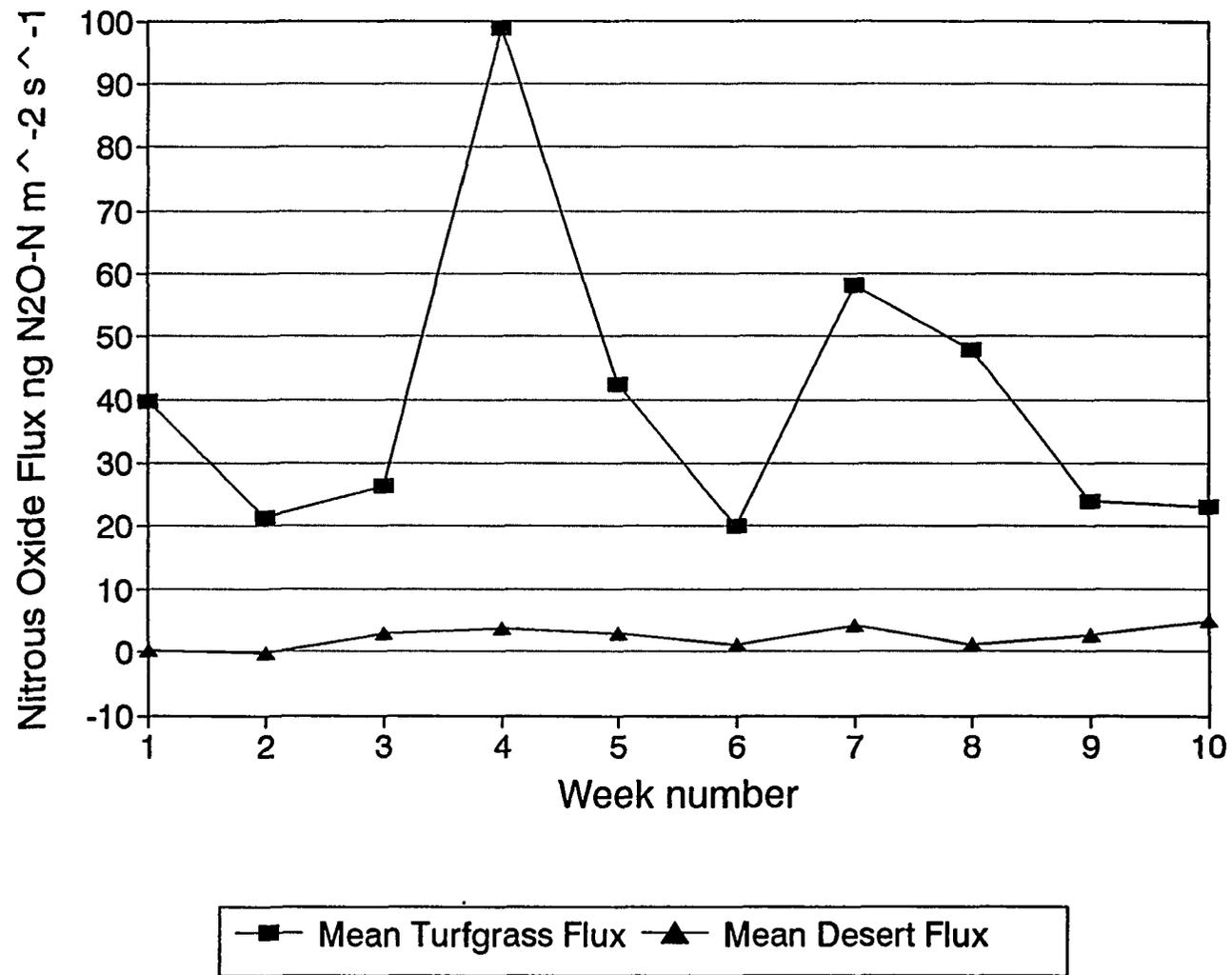
Figure 5.   Mean N$_2$O fluxes from Arizona locations.

Table 4.   Mean values for nitrate, total organic carbon and pH for all locations.

Location	NO3⁻ (mg/L)			TOC (%)			pH		
	Mean	Std.Dev.	n	Mean	Std.Dev.	n	Mean	Std.Dev.	n
Arizona Turf grass site #1	78.62	72.82	10	0.87	0.35	10	7.85	0.51	3
Arizona Turf grass site #2	117.05	102.54	10	1.48	1.04	10	7.39	0.27	3
Arizona Turf grass site #3	100.38	84.61	10	1.07	0.42	10	7.53	0.44	3
Arizona Desert site #1	13.33	8.68	10	0.41	0.06	10	7.97	0.37	3
Arizona Desert site #2	7.03	4.11	10	0.34	0.11	10	8.08	0.36	3
Arizona Desert site #3	8.55	5.44	10	0.22	0.03	10	8.28	0.33	3
Africa Fallow Field Location A	20.73	7.63	3	0.19	0.10	3	6.35	0.20	3
Africa Millet Field Location B	32.70	7.84	3	0.13	0.05	3	5.78	0.66	3
Africa Tigerbush Plateau Location C	90.27	28.02	3	0.76	0.29	3	5.81	0.71	3

Table 5.   Physical data for all soils.

Location	Gravimetric Moisture (%)			Temperature (^{o}C)		
	Mean	Std.Dev.	n	Mean	Std.Dev.	n
Arizona Turf grass site #1	14.5	4.2	8	28.5	1.2	10
Arizona Turf grass site #2	15.6	9.7	8	28.4	1.4	10
Arizona Turf grass site #3	13.0	1.5	8	28.8	1.3	10
Arizona Desert site #1	2.1	2.0	8	45.9	4.0	10
Arizona Desert site #2	2.2	2.5	8	45.6	4.2	10
Arizona Desert site #3	2.4	3.3	8	44.8	2.8	10
Africa Fallow Field Location A	5.9	3.1	6	35.6	3.6	20
Africa Millet Field Location B	4.6	1.7	6	34.1	3.1	20
Africa Tigerbush Plateau Location C	14.3	4.7	6	31.2	3.0	20

(R^2 = 0.94), as did other combinations of three parameters versus N_2O flux. The R^2= 0.94 for nitrate, TOC, and moisture level versus N_2O flux, R^2= 0.84 for TOC, pH and temperature versus N_2O flux, and R^2= 0.99 for pH, temperature and moisture versus N_2O flux. Linear regressions of individual chemical and physical characteristics of the soil versus N_2O flux show lesser correlation. The r^2 values from these linear regressions were 0.65, 0.53, 0.64, 0.59 and 0.51 for nitrate, TOC, pH, temperature, and moisture level versus N_2O flux respectively. These regressions may indicate that the chemical and physical factors examined in the study are involved in regulating N_2O flux from the soils studied, as expected.

The regressions described above are based upon weekly mean values of chemical and physical parameters and weekly mean N_2O flux values. These simple linear regressions also do not exclude the influence of other variables when calculating the regression of interest. For these reasons, a stepwise polynomial regression was performed on the individual values for the chemical and physical parameters versus the individual weekly values for the N_2O flux from all Arizona sites. This stepwise regression indicated that the effects of total organic carbon and temperature on the N_2O flux from individual sites over the 10 week measurement period were very highly significant (r^2=.19, P.05=.0006; r^2=.20, P.05=.0007, respectively). Having a lesser influence were moisture content and pH (r^2=.14, P.05=.0131; r^2=.07, P.05=.0434, respectively). Nitrate content of the soil was not significantly correlated with N_2O flux (r^2=.06, P.05=.0665). These results are in contrast to the findings of Matson et al. (1991) for semi-arid shrubland in southeastern Wyoming. In that study N_2O flux was significantly related to mean soil nitrate content (r^2=.042, P<.02).

Correlation does not necessarily indicate causation in this study. Factors such as temperature and pH of the desert location may not be causally involved in regulating N_2O

flux to a great extent. Since the flux values between the desert and turf grass locations are so different in magnitude, any large difference between these locations would correlate well with N_2O flux, yet may have no causal influence on N_2O flux. For example, the correlation of temperature with bacterial activity is known to be positive, with increases in temperature generally causing increases in the rate of bacterial metabolism. In this study, increases in temperature were very highly correlated with decreases in N_2O flux. The very highly significant correlation between TOC and N_2O flux was expected. The carbon content of the soil is considered a limiting factor in denitrification (Artiola & Pepper, 1991). The test results provide strong evidence that denitrification activity is responsible for some of the N_2O flux observed here.

Diurnal Studies

Diurnal studies of N_2O flux from turf grass site 1 and desert site 3 were conducted on two occasions (August 9, 1991 and August 16, 1991) during the 10 week study period. A large variation in flux was found at both sites during each of these studies. Appendix B shows all the fluxes taken over both days of the study at both sites. Appendix B contains data from the diurnal studies.

At the turf grass site, N_2O fluxes ranged from 3.5 ng N_2O-N m^{-2} s^{-1} at 19:00 to 41.5 ng N_2O-N m^{-2} s^{-1} at 11:30 on August 9, 1991. On August 16, 1991, this same site produced N_2O fluxes ranging from 4.5 ng N_2O-N m^{-2} s^{-1} at 17:00 to 39.3 at 9:30. Highest rates of emission were found in the mid-morning to early afternoon during both studies, while the lowest rates of emission were generally found in the early evening. There was no clear relationship found between N_2O flux and soil temperature, but the flux increase occurred in response to irrigation. It is well known that soil temperature and N_2O flux are related

(Conrad et al., 1983), and might be expected to be the major diurnal influence on N_2O flux. The effect of irrigation in this study was apparently strong enough to mask the effect of temperature on N_2O flux. Although no soil moisture data is available for direct correlation to N_2O flux, pre-dawn irrigations at this site were followed with periods of high N_2O flux. A late afternoon irrigation also occurred during the second study, and was followed by high fluxes that evening.

The N_2O fluxes from the desert site followed no recognizable pattern during the first diurnal study. During the second diurnal study, a relatively high flux of 1.1 ng N_2O-N m^{-2} s^{-1} occurred at 9:35, and a low of -1.5 ng N_2O-N m^{-2} s^{-1} occurred at 17:05. During both studies the fluxes from the desert site were very close to the detection limit. Because of this, only the periods of high and low flux are reported. Further interpretation of the data is not possible.

Africa Emissions

Table 6 shows the calculated fluxes for all the sites of the three Africa locations studied during two weeks in the summer 1992. Figure 6 displays the mean weekly emissions from each of the three African locations in graphical form.

Fallow field

Emissions of N_2O in location A, the fallow field, were the middle of those found during the first week, but ranked highest in magnitude during week 2. Moisture levels more than doubled at this site from the first to the second week, while the magnitude of the flux dropped. The mean flux from all sites in the fallow field over the two week measurement period was 5.1 ng N_2O-N $m^{-2} s^{-1}$ with a standard deviation of 1.6 ng N_2O-N m^{-2} s^{-1}.

Table 6.   Nitrous oxide flux (ng N_2O-N m^{-2} s^{-1}) from 3 Africa locations during a 2 week interval in July/August 1992.

Week	Site #	Fallow field	Millet field	Tigerbush
1	1	6.9	3.0	
1	2	4.0	5.0	
1	3	n/a	2.6	
1	4	6.1	9.7	5.9
1	5	3.0	4.0	4.1
1	6	9.9	4.2	9.4
1	7	5.0	5.4	
1	8	6.9	9.1	
1	9	6.3	3.3	
1	10	6.0	3.4	
Mean:		6.0	5.0	6.5
StdDev:		1.9	2.4	2.2
2	1	3.4	2.3	
2	2	3.4	3.0	
2	3	2.4	3.2	
2	4	2.6	3.0	1.5
2	5	5.9	5.0	2.2
2	6	8.1	4.2	1.2
2	7	6.1	3.7	
2	8	5.7	2.9	
2	9	3.5	3.7	
2	10	3.9	2.4	
Mean:		4.5	3.3	1.6
StdDev:		1.8	0.8	0.4

n/a: Unable to calculate flux due to experimental difficulties.

Site 6 produced the highest measured fluxes of any site in any African location during both weeks. This site was located beneath a <u>Guierra senegalensis</u> bush, and bacteria in the soil may have experienced enhanced levels of metabolism resulting from the rhizosphere effect. No other temporal trends were observed, although the sites were only studied on two occasions. Moisture contents in the vicinity of sites 5 and 6 were higher than at any of the other sites both weeks. The mean temperature was highest of the African sites. Nitrate content was low at the location and TOC content was very low. Also, pH was slightly acidic (Appendix A).

Moisture content and the rhizosphere effect may have influenced the magnitude of the flux at site 6, but not enough soil samples were analyzed to provide conclusive evidence.

Millet field

Location B, the millet field, produced the lowest flux during week 1 and the middle flux during week 2. In contrast to the moisture level of location A, there was a drop in percent moisture from week 1 to week 2, and a corresponding drop in the magnitude of the N_2O flux. The 2-day mean N_2O flux from this site was 4.2 ng N_2O-N m^{-2} s^{-1} with a standard deviation of 1.2 ng N_2O-N m^{-2} s^{-1}.

Moisture content of this location was the lowest of the African locations, as was TOC and pH. Nitrate concentration was intermediate of the locations. No temporally stable trends could be detected, since there was only a limited amount of data available.

Tigerbush plateau

Location C, the tigerbush plateau, produced the highest flux during week 1 and the lowest flux during week 2. The 2-day mean flux (of n=3 measurements each day) from this

location was 4.0 ng N_2O-N m^{-2} s^{-1} with a standard deviation of 1.3 ng N_2O-N m^{-2} s^{-1}.

Moisture levels were twice as high as the highest of the other sites during week 1 but unavailable for week 2. Nitrate concentrations at this location were comparable to those found at the Arizona turf grass location, while TOC was significantly higher than the other African locations. The soil at this location was acidic, with a mean pH of 5.81. No temporally stable trends were detected in the very limited data sets.

<u>Comparison of Africa Locations</u>

Figure 6 shows the weekly mean N_2O flux from the 3 Africa locations for 2 weeks in the summer of 1992. Because of the limited amount of data, only minimal comparison of the African sites is possible. The three African locations rank in the order C > A > B based on magnitude of N_2O flux. This ranking is consistent with the TOC and moisture contents of the locations, but is inconsistent with the amounts of NO_3^-, pH and temperature of the locations, which follow a different trend. The small number of samples does not favor statistical analysis.

Since denitrification activity is carbon limited, and takes place only in anaerobic conditions which may be brought on by increases in soil moisture, it is possible, however unlikely, that this mechanism may be responsible for the observed fluxes. Moisture contents of the millet and fallow fields are so low that anaerobic conditions in a large portion of the soil are unlikely. However, acidic conditions are known to inhibit nitrification.

A study by Hao et al. (1988) of a tropical savannah, found a mean N_2O flux of 4 kg N_2O-N ha^{-1} yr^{-1}, about two to three times the mean flux found in this study for the three African subtropical savannah locations.
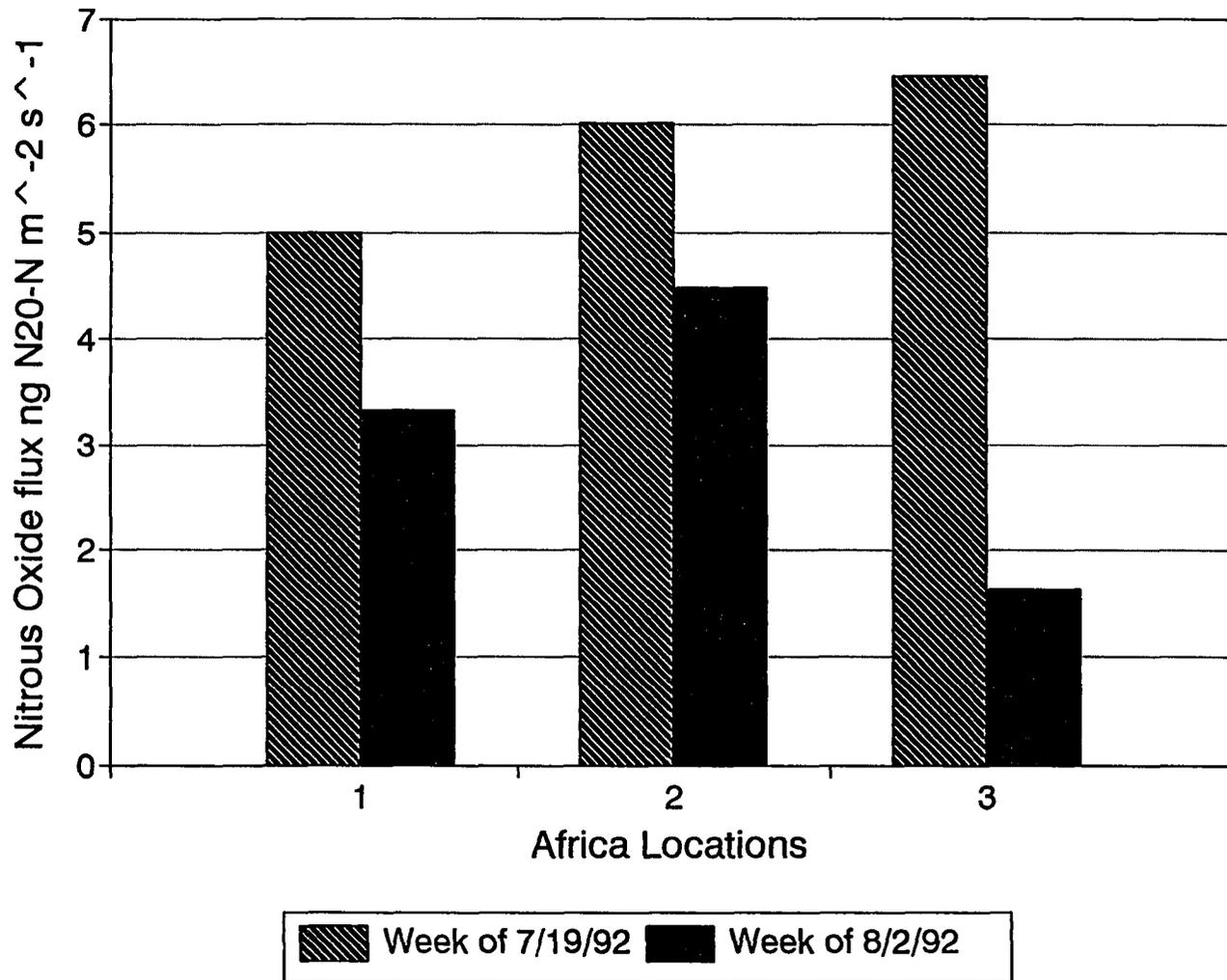
Figure 6.   Mean N₂O fluxes from Africa locations; 1: Millet field, 2: Fallow field, 3: Tigerbush plateau.

Since all the sites in a given location in Africa were sampled during the same day, any variability that is noticed is principally spatial variability. In contrast, sites from a given Arizona location were sampled several times over the course of a 10 week period. Variability in the flux from an individual site in Arizona was solely temporal. Variability in the fluxes taken in any one week from an Africa location was almost solely spatial. When the coefficients of variation for individual sites in the Arizona locations are compared to those for individual weeks at the Africa locations, the latter show consistently lower values. These lower values indicate that fluxes from the African locations during an individual study period were generally less variable than the individual Arizona sites over the 10 week measurement period. Although Arizona sites also showed larger CV differences between themselves than did Africa locations, this may indicate that there is generally less spatial than temporal variability in N_2O flux.

CHAPTER 5

CONCLUSION

These data are among the first from long-term studies of N_2O emissions from desert

soils and soils irrigated with effluent water. Mean nitrous oxide emission from the effluent-

irrigated Arizona turf grass location was estimated to be 40.2 ng N_2O-N m^{-2} s^{-1} during a 10

week measurement period during summer 1991. Mean N_2O flux from the Arizona upland

Sonoran desert location was estimated to be 2.4 ng N_2O-N m^{-2} s^{-1} during the same

measurement period. The N_2O flux from the turf grass location was nearly 17 times larger

than the flux from the desert location. Statistical tests revealed that emissions from the two

locations were significantly different at the 95% level of confidence and were significantly

correlated with total organic carbon content of the soil and soil temperature at 10 cm depth.

Studies of the two Arizona locations during the cooler season indicated emissions below the

level of detection. Diurnal variability in the emissions from the desert and turf grass location

was large. Diurnal variability in the N_2O flux at the turf grass location was related to

irrigation. Diurnal variability in N_2O flux at the desert location was not significantly linked

to any measured soil physical and chemical parameters.

The mean N_2O flux from the turf grass location was larger than flux estimates for

most agricultural and turf grass locations previously reported, and represented about 2% of

N inputs. The emissions from the desert location were extrapolated to annual fluxes of areas

for which these fluxes may be representative. If the measured flux is representative of flux

from Upland Sonoran desert, the estimated annual N_2O emission from this part of the

Sonoran desert is 2.32 x 10^6 kg N yr^{-1}. Extrapolation to the entire Sonoran desert area gives

a total annual source strength of 1.15×10^7 kg N yr^{-1}. Extrapolation to the total area of the world's low latitude deserts gives a total annual source strength of 0.8 Tg N yr^{-1}. This rate of emission is highly uncertain and is approximately one order of magnitude smaller than the estimated flux from the world's tropical rain forests. It is, interestingly, nearly one order of magnitude larger than a recent estimate (Matson et al., 1991) of the flux from the world's temperate shrublands.

Locations in the Sahel region of Africa were sampled on two occasions in the summer of 1992. The means of N_2O fluxes measured along transects at the locations in Africa were 5.1, 4.2, and 4.0 ng N_2O-N m^{-2} s^{-1} for a fallow field, millet field and laterite plateau area respectively. The Africa locations were studied during the same season (summer) as the Arizona locations. The N_2O emissions from the Africa locations were slightly higher than the emissions measured at the Arizona desert location.

Recommendations for Future Research

Future research is necessary to clearly determine the magnitude of the diurnal variation in N_2O flux from both desert and turf grass locations. Further research to determine the climatic, chemical and physical factors influencing the N_2O flux on a diurnal basis is also needed. Knowledge of the magnitude of diurnal variability in N_2O flux and its causes allow researchers to confidently use carefully timed single measurements to accurately estimate daily N_2O flux. A more precise estimate of short-term flux from a given site will also lead to more accurate estimates of long-term fluxes based upon a minimum number of samples.

More research in the area of potable water irrigation of southwestern turf grasses would also be helpful. A study of N_2O flux from turf grass plot irrigated with potable water

adjacent to a plot irrigated with effluent water would provide information about the effect of nitrogen compounds and organic matter in the effluent water on the N_2O flux from soil. Other studies could examine changes in denitrification potential and in bacterial populations between plots. An evaluation of the effects of fertilizer type and quantity on N_2O flux from turf grass is also needed.

A detailed study of the desert as a source of N_2O is definitely called for. There are many unanswered questions about the N_2O flux from this ecosystem. These include queries about the spatial distribution of N_2O fluxes in proximity to plants and to various morphological features of the desert. A transect study across a large variety of desert features, or a study in which sampling sites are located close to nitrogen fixing plants and algal crusts would provide important insight into the influence of vegetation and microflora on N_2O flux. Studies of the desert location after rainfall during the summer monsoon season are also called for. Of particular interest are changes in the N_2O flux following the first rain after a lengthy dry period. Measurements of the N_2O flux in proximity to intermittent washes in the desert would also provide valuable information. These washes frequently contain different soil types and higher moisture levels than the surrounding desert and should be investigated as a source of N_2O emissions. Core studies should also be done to determine the depth distribution of potential denitrification activity in the desert soils, and to determine the soil chemical and physical conditions which best promote emission of N_2O from these soils.

Finally, other natural ecosystems should be more thoroughly studied over a long time period, including other deserts in the southwestern U.S. and similar zones throughout the world. The deserts have long been assumed to be an insignificant source of N_2O, but this

assumption may not be fully justified. More research is needed to more precisely quantify this largely uncertain source.

APPENDIX A:

SOIL CHEMICAL AND PHYSICAL DATA

Site	Week	Nitrate (mg/L)	TOC (%)	pH	Moisture (%)	Soil Temp
D1	1	3.73	0.41	8.42	0.7	49.1
D1	2	6.70	0.37		0.4	47.3
D1	3	3.87	0.39		0.3	52.3
D1	4	24.50	0.42		8.3	47.0
D1	5	4.75	0.48	7.63		47.8
D1	6	15.00	0.51		0.7	45.9
D1	7	17.30	0.41		4.9	38.0
D1	8	15.90	0.35		1.4	46.0
D1	9	15.70	0.34	7.87		46.0
D1	10	25.80	0.40			39.4
	Mean:	13.33	0.41	7.97	2.38	45.9
	StDv:	8.68	0.06	0.37	3.33	4.0
D2	1	2.89	0.20	8.53	1.2	47.9
D2	2	4.19	0.52		0.8	48.3
D2	3	1.35	0.34		0.6	54.5
D2	4	8.40	0.24		2.9	47.3
D2	5	13.50	0.34	7.82		45.6
D2	6	7.83	0.49		1.5	45.1
D2	7	11.30	0.35		7.2	39.6
D2	8	4.03	0.26		1.4	45.3
D2	9	7.02	0.37	7.88		43.4
D2	10	9.80	0.30			39.4
	Mean:	7.03	0.34	8.08	2.21	45.6
	StDv:	4.11	0.11	0.36	2.53	4.2

Site	Week	Nitrate (mg/L)	TOC (%)	pH	Moisture (%)	Soil Temp
D3	1	2.57	0.27	8.51	1.2	46.9
D3	2	3.10	0.25		0.5	47.3
D3	3	5.02	0.23		0.5	44.8
D3	4	14.40	0.23		4.3	46.3
D3	5	5.15	0.20	8.47		45.6
D3	6	6.93	0.19		1.3	46.8
D3	7	16.80	0.18		5.0	39.8
D3	8	9.63	0.22		1.7	44.7
D3	9	15.00	0.22	7.87		46.9
D3	10	6.89	0.24			39.2
	Mean:	8.55	0.22	8.28	2.08	44.8
	StDv:	5.44	0.03	0.33	1.99	2.8
T1	1	31.90	0.37	8.33	12.2	26.7
T1	2	45.60	0.87		13.9	26.6
T1	3	114.00	1.68		11.9	29.1
T1	4	45.70	0.85		13.4	30.2
T1	5	40.20	0.79	8.00		29.6
T1	6	41.10	0.71		12.0	29.7
T1	7	22.20	0.89		15.7	27.6
T1	8	49.50	0.97		12.0	28.8
T1	9	167.00	0.65	7.23		29.0
T1	10	229.00	0.89			27.7
	Mean:	78.62	0.87	7.85	13.00	28.5
	StDv:	72.82	0.35	0.51	1.53	1.2

Site	Week	Nitrate (mg/L)	TOC (%)	pH	Moisture (%)	Soil Temp
T2	1	30.70	0.81	7.74	10.9	27.4
T2	2	31.20	0.53		9.8	26.4
T2	3	278.00	4.01		35.0	26.5
T2	4	84.50	1.92		16.6	31.0
T2	5	79.00	1.46	7.20		28.8
T2	6	48.50	1.41		10.6	29.3
T2	7	43.00	0.90		10.9	27.9
T2	8	94.60	1.67		15.4	29.6
T2	9	260.00	1.30	7.24		29.2
T2	10	221.00	0.80			27.9
	Mean:	117.05	1.48	7.39	15.62	28.4
	StDv:	102.54	1.04	0.27	9.67	1.4
T3	1	51.10	0.87	8.08	8.7	29.1
T3	2	59.30	0.56		11.6	26.0
T3	3	55.50	0.92		21.0	28.4
T3	4	82.60	1.58		14.5	31.3
T3	5	74.90	0.94	7.35		29.2
T3	6	54.70	0.95		14.9	29.0
T3	7	44.70	1.81		13.9	28.2
T3	8	106.00	1.39		17.1	29.6
T3	9	174.00	0.65	7.17		29.6
T3	10	301.00	0.98			27.9
	Mean:	100.38	1.07	7.53	14.53	28.8
	StDv:	84.61	0.42	0.44	4.22	1.3

Site	Week	Nitrate (mg/L)	TOC (%)	pH	Moisture (%)	Soil Temp
MILLET	1a	39.50	0.11	5.81	3.1	
	1b				4.5	
MILLET	2a	26.80	0.17	5.22	2.4	
	2b				8.6	
MILLET	3a	31.80	0.10	6.30	8.8	
	3b				7.8	
	Mean:	32.70	0.13	5.78	5.9	
	StDv:	7.84	0.05	0.44	3.1	
FALLOW	1a	16.60	0.29	6.45	7.4	
	1b				5.0	
FALLOW	2a	17.70	0.15	6.44	4.3	
	2b				2.8	
FALLOW	3a	27.90	0.14	6.16	3.8	
	3b				4.2	
	Mean:	20.73	0.19	6.35	4.6	
	StDv:	7.63	0.10	0.20	1.7	
TIGER	1	66.40	0.52	5.40	10.3	
TIGER	2	112.00	1.00	5.55	14.7	
TIGER	3	92.40	0.77	6.47	18.0	
	Mean:	90.27	0.76	5.81	14.3	
	StDv:	28.02	0.29	0.71	4.7	

APPENDIX B:

DIURNAL STUDY DATA

Site	Date	Time	Flux kg ha^{-1} yr^{-1}	Flux ng m^{-2} s^{-1}
T1	8/9/91	6:57	2.85	9.0
T1	8/9/91	8:30	5.96	18.9
T1	8/9/91	10:00	10.97	34.8
T1	8/9/91	11:30	13.07	41.5
T1	8/9/91	13:00	12.06	38.2
T1	8/9/91	14:15	9.17	29.1
T1	8/9/91	16:06	2.69	8.5
T1	8/9/91	17:30	2.93	9.3
T1	8/9/91	19:00	1.11	3.5
T1	8/10/91	1:30	1.39	4.4
T1	8/10/91	7:15	5.65	17.9
		Mean:	6.17	19.56
		StDv:	4.65	14.75
D3	8/9/91	7:01	0.25	0.8
D3	8/9/91	8:35	-0.69	-2.2
D3	8/9/91	10:05	0.38	1.2
D3	8/9/91	11:35	0.28	0.9
D3	8/9/91	13:05	-0.24	-0.8
D3	8/9/91	14:20	0.42	1.3
D3	8/9/91	16:08	-0.29	-0.9
D3	8/9/91	17:35	-0.03	-0.1
D3	8/9/91	19:05		
D3	8/10/91	1:25	0.05	0.2
D3	8/10/91	7:20	0.05	0.2
		Mean:	0.02	0.06
		StDv:	0.36	1.15

Site	Date	Time	Flux kg ha^{-1} yr^{-1}	Flux ng m^{-2} s^{-1}
T1	8/16/91	00:30	8.68	27.5
T1	8/16/91	08:00	8.18	26.0
T1	8/16/91	09:30	12.40	39.3
T1	8/16/91	11:00	7.66	24.3
T1	8/16/91	12:30	5.05	16.0
T1	8/16/91	14:00	3.10	9.8
T1	8/16/91	15:30	2.71	8.6
T1	8/16/91	17:00	1.43	4.5
T1	8/16/91	18:30	1.77	5.6
T1	8/16/91	20:00	1.65	5.2
		Mean:	5.26	16.69
		StDv:	3.98	12.61
D3	8/15/91	23:53	-0.51	-1.6
D3	8/16/91	08:05	-0.14	-0.5
D3	8/16/91	09:35	0.35	1.1
D3	8/16/91	11:05	0.17	0.5
D3	8/16/91	12:35	-0.15	-0.5
D3	8/16/91	14:05	-0.07	-0.2
D3	8/16/91	15:35	-0.14	-0.4
D3	8/16/91	17:05	-0.48	-1.5
D3	8/16/91	18:35	-0.32	-1.0
D3	8/16/91	20:05	0.17	0.5
		Mean:	-0.11	-0.36
		StDv:	0.30	0.94

APPENDIX C:

REGRESSION EQUATIONS

AND

SOIL PARTICLE SIZE DISTRIBUTION DATA

1. Standard curve formula used for N_2O quantification by gas chromatography.
    Based upon repeated analysis of 3 Scotty II gas standards of different concentrations (90.6 ppb(v/v), 502 ppb(v/v), and 971 ppb(v/v))

$$[N_2O \text{ ppb}] = -13.55 + 0.0121*(\text{Area Count})$$
$$r^2 = 0.9995$$

2. Statistical relationships of chemical/physical properties to measured N_2O flux at 6 Arizona sites.

Simple Linear Regressions:

TOC (%) vs. N_2O flux (ng N_2O-N m^{-2} s^{-1})
Flux = 26.995*(TOC) + 1.62
P= 0.0006, r^2= 0.19

Temp(°C) vs. N_2O flux (ng N_2O-N m^{-2} s^{-1})
Flux = -1.999*(Temperature) + 96.84
P= 0.0007, r^2= 0.20

Moisture (%) vs. N_2O flux (ng N_2O-N m^{-2} s^{-1})
Flux = 2.324*(%Moisture) + 3.94
P= 0.0131, r^2= 0.14

pH vs. N_2O flux (ng N_2O-N m^{-2} s^{-1})
Flux = -12.969*(pH) + 194.97
P= 0.0434, r^2= 0.07

Nitrate (mg/L) vs. N_2O flux (ng N_2O-N m^{-2} s^{-1})
Flux = 0.129*(NO$_3^-$) + 14.56
P= 0.0665, r^2= 0.06

Stepwise Multiple Regression

N_2O flux (ng N_2O-N m^{-2} s^{-1}) =   -85.844 + 2.046*(TOC)
                                               + 0.184*(NO$_3^-$)
                                               - 1.509*(%Moisture)
                                               + 4.294*(Temperature)
                                               + 2.022*(pH)

3.   Soil particle size distribution (PSD) data.

Location/Site	Texture	Sand (%)	Silt (%)	Clay (%)
Arizona Turfgrass/ T1	Loamy Sand	75.9	17.4	6.7
Arizona Turfgrass/ T2	Loamy Sand	79.9	15.9	4.2
Arizona Turfgrass/ T3	Loamy Sand	81.1	13.6	5.3
Arizona Desert/ D1	Loamy Sand	77.3	16.2	6.6
Arizona Desert/ D2	Loamy Sand	74.5	22.4	3.1
Arizona Desert/ D3	Loamy Sand	84.9	11.0	4.1
Africa Fallow Field	Sand	96.6	2.2	1.3
Africa Millet Field	Sand	91.4	5.8	2.8
Africa Tigerbush Plateau	Clay Loam	43.9	18.7	37.4

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