N₂O emissions from humid tropical agricultural soils: effects of soil moisture, texture and nitrogen availability

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Abstract

We studied soil moisture dynamics and nitrous oxide (N₂O) fluxes from agricultural soils in the humid tropics of Costa Rica. Using a split-plot design on two soils (clay, loam) we compared two crop types (annual, perennial) each unfertilized and fertilized. Both soils are of andic origin. Their properties include relatively low bulk density and high organic matter content, water retention capacity, and hydraulic conductivity. The top 2–3 cm of the soils consists of distinct small aggregates (dia. <0.5 cm). We measured a strong gradient of bulk density and moisture within the top 7 cm of the clay soil. Using automated sampling and analysis systems we measured N₂O emissions at 4.6 h intervals, meteorological variables, soil moisture, and temperature at 0.5 h intervals. Mean daily soil moisture content at 5 cm depth ranged from 46% water filled pore space (WFPS) on clay in April 1995 to near saturation on loam during a wet period in February 1996. On both soils the aggregated surface layer always remained unsaturated. Soils emitted N₂O throughout the year. Mean N₂O fluxes were 1.04 ± 0.72 ng N₂O-N cm⁻² h⁻¹ (mean ± standard deviation) from unfertilized loam under annual crops compared to 3.54 ± 4.31 ng N₂O-N cm⁻² h⁻¹ from the fertilized plot (351 days measurement). Fertilization dominated the temporal variation of N₂O emissions. Generally fluxes peaked shortly after fertilization and were increased for up to 6 weeks (‘post fertilization flux’). Emissions continued at a lower rate (‘background flux’) after fertilization effects faded. Mean post-fertilization fluxes were 6.3 ± 6.5 ng N₂O-N cm⁻² h⁻¹ while the background flux rate was 2.2 ± 1.8 ng N₂O-N cm⁻² h⁻¹. Soil moisture dynamics affected N₂O emissions. Post-fertilization fluxes were highest from wet soils; fluxes from relatively dry soils increased only after rain events. N₂O emissions were weakly affected by soil moisture during phases of low N availability. Statistical modeling confirmed N availability and soil moisture as the major controls on N₂O flux. Our data suggest that small-scale differences in soil structure and moisture content cause very different biogeochemical environments within the top 7 cm of soils, which is important for net N₂O fluxes from soils. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Soil moisture; Soil N₂O emissions; Fertilized soils; Automated field measurements; Low bulk density soils

1. Introduction

Nitrous oxide (N₂O) is an important atmospheric trace gas (Rhode, 1990). It is involved in many essential environmental processes in atmospheric (Crutzen, 1981; IPCC, 1996) and in biological systems (Galloway et al., 1992). Globally, soils are the major source of atmospheric N₂O. Forest soils in humid tropical regions are estimated to account for about 21% of the total global N₂O production on annual basis (Matson and Vitousek, 1990). For estimation of present and future N₂O emissions, it is critical to identify the sources and to understand the processes involved.

Soil microbes produce and consume N₂O during the processes of nitrification and denitrification (Williams et al., 1999). The conceptual model presented by Firestone and Davidson (1989) provides a simple approach to the complex processes of nitrogen oxide (NO and N₂O) production and consumption. In essence, the interplay between the amount of nitrogen cycling in soils and soil environmental conditions (mainly soil moisture, temperature, pH, oxygen and organic carbon concentration) governs microbial processes and thereby gaseous N production and consumption. In humid tropical soils temperature and moisture content are optimal
for biological processes most of the year, resulting in generally large production of gaseous N-oxides.

Soil moisture has multiple effects on N trace gas emissions. Water is essential for microbial survival and activity. Soil moisture dynamics determine the biogeochemical environment for microorganisms, affecting the availability of dissolved nutrients such as organic carbon, ammonium and nitrate. Rapid increases in soil moisture content may dilute nutrient concentration but also microbial populations in the water filled pore space. Soil water content affects the oxidation-reduction conditions in soils as well as gas diffusion. In relatively dry soils the predominantly aerobic environment favors microbial nitrification, producing mainly NO. In moist soils under more reducing conditions denitrification dominates, resulting in the production and consumption of reduced N forms (N₂O and N₂; Davidson, 1993). Denitrifiers are ubiquitous (Vermoesen et al., 1993) and denitrification in soils depends on substrate availability and oxygen deficiency. Field capacity is commonly used to distinguish between dominantly aerobic or anaerobic environments (Linn and Doran, 1984; Davidson, 1993). Micro-scale variability in soil moisture and nutrient distribution cause nitrification and denitrification to occur simultaneously in soils (e.g. Robertson, 1989; Davidson, 1993) and result in high variability of nitrogen oxide emissions.

Fertilization significantly increases the soil-atmosphere flux of N₂O on tropical soils (Matson et al., 1996; Veldkamp et al., 1998; Crill et al., 2000). Expansion and intensification of tropical agriculture is expected to be a major contributor to increasing atmospheric N₂O concentrations (e.g. Keller and Matson, 1994; Erickson and Keller, 1997). We performed a 2 year field experiment in the humid tropical lowland of Costa Rica to identify, quantify and evaluate the factors influencing N₂O emissions from tropical agricultural soils (Crill et al., 2000). We have studied the effects of soil moisture dynamics on N₂O fluxes from data measured at high temporal resolution and applied results in a statistical modeling approach.

2. Material and methods

2.1. Study area

We performed our field experiment at the La Selva biological station of the Organization for Tropical Studies in the Atlantic lowland of Costa Rica (10°N × 84°W). The climate is humid tropical with an average annual air temperature of 25.8°C (±0.69°C standard deviation). Mean annual rainfall is 3961.8 mm (±723.2 mm) (Sanford et al., 1994). Precipitation is well distributed throughout the year, with a slightly drier period from January through April. Over a 29 year period mean, monthly precipitation was lowest in March (152 mm) and highest in July (481 mm). We studied two soil types, a loam (fluventic Eutropept) and a clay (andic Dystropept) (Table 1). Both Inceptisols are of andic origin (Sollins et al., 1994). The clay is slightly more acidic than the loam. Both soils feature high organic matter content, low bulk density, high saturated hydraulic conductivity, and high water retention capacity.

2.2. Experimental design

In February and March 1994 we cleared about 1 ha of secondary forest on each soil type (Weitz et al., 1998). We established a split-plot experiment comparing the two soils, each under two crop types (annual and perennial), and two agricultural treatments (unfertilized and fertilized; Fig. 1). Four experimental plots were installed on each cleared patch. Subplots were 26 × 26 m for the annual crops and 40 × 40 m for the perennial crops. An air-conditioned field laboratory (3 × 3 m), located in the center between subplots, housed the instruments. Chamber bases and soil sensors were installed in April (clay) and June (loam) 1994. We expect no chamber installation effect on N₂O measurements reported here, because chambers were installed about 7 months prior to sampling (Keller et al., 2000). Only one automated system

### Table 1

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Material and methods</th>
<th>Experimental design</th>
<th>Study area</th>
<th>Fertilization</th>
<th>Fertilized</th>
<th>Unfertilized</th>
<th>Fertilized</th>
<th>Unfertilized</th>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>Mean SD n</td>
<td>Mean SD n</td>
<td>Mean SD n</td>
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<td>0.45 0.05 28</td>
<td>0.53 0.11 28</td>
<td>0.54 0.08 28</td>
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<td>5.02 0.75 4</td>
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<td>6.64 0.20 4</td>
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<td>0.79 0.04 37</td>
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<td>0.69 0.06 36</td>
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<td>FC(6 kPa) [WFPS]</td>
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<td>0.68 0.11 8</td>
<td>0.82 0.03 8</td>
<td>0.83 0.03 8</td>
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<td>FC(30 kPa) [WFPS]</td>
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<td>0.52 n.a. 1</td>
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<tr>
<td>K(sat) [cm d⁻¹]</td>
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<td>502 103 6</td>
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</table>

*Note: Fertilization significantly increases the soil-atmosphere flux of N₂O on tropical soils.*
was available, therefore we switched the mobile above ground equipment between soil types after an individual cropping cycle of the annual crop was completed. Automated measurements were performed on the loam from 10 November 1994 to 15 March 1995, on the clay from 16 March 1995 to 8 January 1996, and again on the loam from 9 January 1996 to 23 August 1996.

2.3. Methods

We used an automated time domain reflectometry (TDR) technique (e.g. Dobson et al., 1985; Topp et al., 1988; Roth et al., 1990) to measure soil moisture dynamics. A cable tester (Tektronix 1502 B/C; Tektronix Inc., Redmond Oregon) was connected to 30 cm long TDR probes (Spaans and Baker, 1993). Probes were equipped with Belden 8219 RG-58 A/U coaxial cable, two parallel stainless steel rods, and a 1:1 balun, which is an impedance-matching transformer deployed to minimize signal loss at the connection between the coaxial cable and the rods. A 1:1 balun was reported to be preferable for measurements in wet soils (Spaans and Baker, 1993). TDR probes were installed horizontally into the soil to avoid introduction of artificial water pathways along the probes and to confine measurements to a relatively small depth interval (about 6–7 cm width; Ferré et al., 1998). On each subplot a total of nine TDR probes were installed at five depths (Fig. 1). We refer to the replicated measurements at 5 cm depth only. We used five multiplexers for 50 Ω coaxial cable (SDMX50; Campbell Scientific Inc., Logan, UT) in a two-level hierarchical design, to allow the measurement of multiple TDR probes by one cable tester. Communication between the cable tester and a CR10 data logger was permitted by a SDM1502 interface (both Campbell Scientific Inc.). We recorded the reflected waveform of the cable tester signal to derive the apparent dielectric number $K_a$. We modified the TRACE.41 program developed by E. Spaans and J. Baker (personal communication, 1994) for automated interpretation of $K_a$ from the measured TDR waveform. $K_a$ values were corrected for length of coaxial cable used for routine field measurements (A. Weitz, unpub. data). The soil moisture content was calculated using $K_a$, bulk density and soil temperature data in a 3-phase mixing model which was parameterized for the studied soils (Weitz et al., 1997). Soil moisture was expressed as the ratio of the water filled pore space (WFPS) in soils (Linn and Doran, 1984).

Our field system for automated sampling and analysis of $\text{N}_2\text{O}$ fluxes was described in detail by Crill et al. (2000). We installed two pneumatically operated chambers on each
subplot. A total of eight automated chambers were available. During routine operation each chamber was sampled for N$_2$O fluxes every 4.6 h. For measurements, one chamber at a time was closed for 23 min. to sample fluxes from a soil surface area of 0.187 m$^2$. During sampling the chamber headspace (approximately 0.039 m$^3$ volume) was connected in a closed loop to the instruments inside the field laboratory. A pump maintained continuous air circulation. We used a gas chromatograph with electron capture detection (GC-ECD, Shimadzu Mini-2) for N$_2$O analysis. Automated valves alternated gas flow from the chamber headspace and from standard gases to the GC.

We used commercially prepared working standard gases (Scott-Marin, Sunnyvale, CA) which had been calibrated against NIST (National Institute of Standards and Technology) and NOAA CMDL (National Oceanographic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, Boulder, CO) standards. Data were acquired and stored using a desktop computer. Fluxes were calculated from the linear increase of N$_2$O concentration in the chamber headspace during the time of chamber closure.

A tipping bucket (Model 6011, Qualimetrics Inc., Sacramento, CA) was installed in the vicinity of the field laboratory (Fig. 1). Soil temperature (°C) was measured using thermocouple sensors (T-type wire) connected to a CR10 data logger through a AM416 low level analog signal multiplexer (Campbell Scientific Inc.). We present soil temperature data measured at 5 cm depth only. The pulse output from the tipping bucket was stored as 30 min. rainfall totals, the data logger read thermocouple sensors per 2 min. and stored data as 30 min. averages. Soil moisture was measured once every 30 min.

Soil pH was measured within a few hours after sampling bulk soil from 0–10 cm depth. We mixed 20 g field moist soil with 50 ml deionized water and measured after the solution was allowed to equilibrate for about 30 min. We used a laboratory Corning 245 pH meter (Corning Labware & Equipment, Corning, NY) calibrated with pH 4 and pH 7 buffer solutions. Analyses for total soil C and N were performed at the International Institute for Tropical Forestry (IITF), USDA Forest Service, in Rio Piedras, Puerto Rico. Air dried soil (0.2 g) was combusted for Tropical Forestry (IITF), USDA Forest Service, in Rio Piedras, Puerto Rico. Air dried soil (0.2 g) was combusted at 1300 °C in a LECO CNS-2000 C/N analyzer (LECO Corp., St. Joseph, MI); total N was measured by thermal conductivity and total C by an infrared technique (LECO, 1994).

Infrequently throughout the experiment we determined soil moisture gravimetrically (M. Keller and P. Crill, unpublished data). Using an auger (2 cm dia.) we sampled soil from 0–10 cm depth at eight different locations per subplot combining samples from four locations. Gravimetric moisture content was determined after weighting and oven drying at 105°C (Gardener, 1986) and converted into WFPS using bulk density (Mg m$^{-3}$) data measured at 5 cm depth on each sub-plot. We used metal cores of 300 cm$^3$ volume (7 cm height) to sample undisturbed soil columns and determined bulk density after drying of the soil at 105°C for 24 h (Blake and Hartge, 1986). Porosity was estimated assuming a soil particle density of 2.65 Mg m$^{-3}$. We evaluated soil structure studying bulk density changes within 0–7 cm depth on 48 core samples from the clay subplots. We carefully pushed the soil core out of the metal ring and subdivided it into three layers (0–2, 2–4, and 4–7 cm). Each subdivision was analyzed for bulk density and soil moisture content. This experiment could not be repeated on the loam because during sampling in August 1996 the soil was too wet to allow sub-sampling.

Soil water retention characteristics for the low suction range (0–30 kPa suction) were determined at the La Selva laboratory using undisturbed soil cores (300 cm$^3$) in a hanging water column device (Klute, 1986). Field capacity was estimated as WFPS at 6 kPa (FC$_{0.6}$kPa) and 30 kPa (FC$_{0.3}$kPa). Saturated and unsaturated hydraulic conductivity (cm d$^{-1}$) was measured in the field using undisturbed soil columns of about 300 cm$^3$ volume (0.1 m$^2$ flow area) in the modified crust test (Booltink et al., 1991).

2.4. Statistical methods

Statistical analysis was performed using JMP IN software (Sall and Lehman, 1996). Linear regression analysis was used to correlate the natural logarithm of mean daily N$_2$O flux data with soil moisture content. Inspection of measured flux time series while recognizing agricultural management information (Table 3) led us to distinguish empirically for post-fertilization phases (42 days post fertilization), weeding phases (28 days post weeding) and background phases (remaining measurement days). Statistical analysis confirmed the subdivision into management classes.

We developed an empirical regression model to simulate daily N$_2$O fluxes from soils for the measurement period 10 November 1994 to 20 August 1996. Recognizing the emission management phases the model describes N$_2$O emission as a function of soil water filled pore space (WFPS) and days (d) elapsed after a management event, fertilization or weeding, respectively. N$_2$O fluxes during background phases are modeled using zero for α and β. The general model is written as

\[
\text{flux ln}-\text{N}_2\text{O} = a + b \text{WFPS} + a \ln d + b d
\]

The moisture term affects the amplitude of the simulated flux. A positive slope of the linear regression ensures estimation of increasing fluxes with increasing WFPS. The term ($d^a * e^{bd}$) is the kernel of the gamma probability density function; α determines the shape and β the width of the simulated post-management flux response (Fig. 2). Negative β values ensure decay of simulated fluxes. Soil temperature was excluded from the analysis, because measured temperature variation was very small (Table 5). Simulation results
were evaluated by the root mean square error (RSME) criteria
\[
\text{RMSE} = \left( \sum (\text{flux} \ln N_2O \text{measured} - \text{flux} \ln N_2O \text{estimated})^2 / (n - p) \right)^{0.5}
\]
with \(n\) being the number of observations and \(p\) the number of regression parameters.

2.5. Agricultural management

Maize (Zea mays L.) was planted twice after land clearing (Table 2). Only maize cobs were harvested, therefore about 90% of the above ground biomass remained as mulch on the subplots. Following maize we cropped two cycles of taro (Colocasia esculenta L. Schott). After harvest of tubers in December 1995 all of the above ground biomass remained on the plots. When the field experiments ended in August 1996 the second taro crop was still growing. Papaya (Carica papaya L.) seedlings were planted in June 1994. After senescence plants were cut in November 1995, all of the aboveground biomass remained as mulch on the subplots. Balsa (Ochroma lagopus Swartz) seedlings were planted in December 1995. Trees reached about 10 m height by the end of the field experiment in August 1996.

Soils were never plowed during our experiment. Harvest of taro tuber caused the only notable disturbance of the topsoil layer. Mean bulk density of the top 2 cm in clay was 0.68 ± 0.06 Mg m\(^{-3}\) (mean ± standard deviation; \(n = 48\)) compared to 0.89 ± 0.05 Mg m\(^{-3}\) at 4–7 cm depth (\(n = 48\); Fig. 3). Mean porosity declined with depth from about 0.74 to 0.66; most of the reduction probably occurred in the inter-aggregate pore volume. In aggregated clay soil we measured much smaller moisture content in the surface layer than at 4–7 cm depth (0.4 ± 0.09 versus 0.88 ± 0.09 WFPS \(n = 48\) for each depth; Fig. 3).

Soil moisture content among probes installed at 5 cm depth on the same soil differed within a limited range (mean difference 0.15 WFPS), time series of soil moisture showed similar traces for replicated TDR probes with one exception. From November 1994 to March 1995 we measured about 30% lower water content by one of the replicated TDR probes installed in loam under fertilized annual crop. An air-filled animal burrow within the measurement volume of a TDR probe affects the TDR signal, and is a potential source for measurement error (Ferré et al., 1996; Weitz et al., 1997). Data from this sensor were excluded from subsequent analysis.

### Table 2

<table>
<thead>
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<th>Crop Type</th>
<th>Input Period</th>
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<td>Annual crop</td>
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</tr>
<tr>
<td>1st taro</td>
<td>May 1995–December 1995</td>
</tr>
<tr>
<td>2nd taro</td>
<td>January 1996–August 1996</td>
</tr>
</tbody>
</table>

Fig. 2. Effects of shape parameters in the statistical model.

3. Results

3.1. Soil physical properties

The surface soil remained well aggregated throughout the agricultural period. Mean bulk density of the top 2 cm in clay was 0.68 ± 0.06 Mg m\(^{-3}\) (mean ± standard deviation; \(n = 48\)) compared to 0.89 ± 0.05 Mg m\(^{-3}\) at 4–7 cm depth (\(n = 48\); Fig. 3). Mean porosity declined with depth from about 0.74 to 0.66; most of the reduction probably occurred in the inter-aggregate pore volume. In aggregated clay soil we measured much smaller moisture content in the surface layer than at 4–7 cm depth (0.4 ± 0.09 versus 0.88 ± 0.09 WFPS \(n = 48\) for each depth; Fig. 3).

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Mean moisture content measured by TDR was 0.86 ± 0.09 WFPS in loam (mean ± standard deviation \( n = 1355 \)) compared to 0.78 ± 0.08 WFPS in clay (\( n = 1102 \)). Means were calculated using daily mean WFPS data measured for two crop types on two agricultural treatments. High rain frequency and amount (about 4 m y\(^{-1}\)) together with high water retention capacity resulted in high soil water content over extended periods. For example, we observed 0.95 ± 0.03 WFPS at 5 cm depth on loam between 15 November and 15 December 1994, and 0.82 ± 0.03 WFPS on clay during July 1995. On days without rain, soils drained pore water rapidly with a mean rate of about 0.02 WFPS d\(^{-1}\) during five dry days on either soil. Drainage of surface soil was most rapid shortly after precipitation and slowed with elapsing time. The driest conditions measured in either soil were recorded in clay (0.46 WFPS) towards the end of the dry phase in April 1995.

High moisture content in the top 10 cm of soils was confirmed for both soils by gravimetric moisture measurements on bulk samples taken approximately once every 3 weeks between June 1994 and May 1996. Sampling all sub plots we calculated mean soil moisture content of 0.81 ± 0.12 WFPS on loam (\( n = 86 \)) and 0.74 ± 0.10 WFPS on clay (\( n = 88 \); M. Keller and P. Crill, unpub. data). Data from both TDR and gravimetric measurement techniques were available on 15 days between January 1995 and May 1996 (Fig. 4). The gravimetric moisture content reported for 6 May 96, appears to be very low. The loam

#### Table 3

<table>
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<tr>
<th>Crop</th>
<th>Fertilization</th>
<th>Fertilizer type</th>
<th>([\text{kg} \text{ N ha}^{-1}])</th>
<th>% N lost</th>
<th>Soil</th>
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<td>NH(_4)NO(_3)</td>
<td>11</td>
<td>ND</td>
<td>Clay</td>
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<td>CO(NH(_2))(_2)</td>
<td>46</td>
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</tbody>
</table>
received only 27.5 mm rain from 1 April to 26 April but a
total of 70.1 mm fell during the 10 days preceding the
measurement on 6 May. Small variability between gravi-
metric samples suggested that undetected problems in either
sampling method could have caused the large deviation. We
excluded the point from the analysis.

3.2. Nitrous oxide fluxes

Automated measurements documented increased mean
N₂O emissions from repeatedly fertilized soils, except for
clay under annual crops (Table 4). However, manual
measurements of N₂O fluxes, performed periodically
throughout the experiment, showed slightly larger emissions
from fertilized than from unfertilized clay (M. Keller,
unpub. data). We measured highest mean N₂O fluxes from
loam under perennial crop (Table 4). Within soil types mean
and variation of fluxes as well as proportion of fertilizer-N
lost as N₂O-N were greatest from plots that were fertilized at
the higher rate. N-loss was calculated from the difference of
mean fluxes from fertilized and unfertilized soils to estimate
the emissions due to fertilization only. This loss was smaller
from clay compared to loam.

We illustrate the relation between N₂O emissions and flux
controlling variables using time series measured from loam
under a balsa plantation (perennial crop; Fig. 5). This
measurement period covers a relatively dry phase from
January through April 1996, followed by a wet phase until
August 1996. It rained almost every day between 26 April
and 8 August 1996. The total rainfall within 105 days was
1591 mm, with a maximum daily sum of 126 mm on 14
May 1996. The temporal variation of mean daily soil
temperature was small (Fig. 5, Table 5). Rapidly infiltrating
precipitation increased mean moisture content measured at
5 cm depth instantly. Soil water content was generally high,
approaching 0.6 WFPS only during the relatively dry phase from 15 February through 20 March 1996 when the total rainfall was 55.5 mm.

Agricultural management affected temporal variability of N₂O fluxes from fertilized plots (Fig. 5). Fertilization increased emissions for several weeks. The amplitude and temporal dynamic of post fertilization fluxes was affected by soil moisture and the time elapsed after a fertilization event. N₂O emissions increased within a few hours when fertilizer was applied on wet soil (e.g. 28 March) and when precipitation transferred fertilizer N into the topsoil. When fertilizer was applied during a dry phase we measured increased post-fertilization N₂O fluxes only after the first rain rewetted the soil. For example, on 2 February 1996 we fertilized during the second half of a 5 day dry period. N₂O fluxes increased by 72% only after 24.3 mm of rain fell on 4 February. Whenever precipitation raised soil moisture content at 5 cm depth we observed briefly increased N₂O fluxes. The magnitude of post-fertilization peaks commonly decreased with elapsing time after a fertilization event. For example, average daily fluxes were 56.9 ng N₂O-N cm⁻² h⁻¹ on 13 February, 11 days post-fertilization, and 27.5 ng N₂O-N cm⁻² h⁻¹ on 16 July 29 days after fertilizer application. Mean background fluxes on fertilized loam under perennial crop were 1.4 ng N₂O-N cm⁻² h⁻¹ (Table 4; note: this value excludes fluxes measured in 1996 from soil under perennial crop, which were affected by the change from papaya to balsa crop). Repeated fertilization increased mean background fluxes compared to fluxes from unfertilized soils. Moisture dynamics contributed to the variation observed during background emission periods. High soil moisture content during the rainy period in June–July 1996 supported a longer period of high fluxes post fertilization.

On unfertilized plots increasing N availability from weed- ing and from above and below ground litter may increase N₂O emissions temporarily when increasing soil moisture content supports N₂O fluxes (e.g. 22 March 1996; Fig. 5). Magnitudes of post-weeding fluxes were comparable on both soil types. We expect that weeding and litter were the major N inputs on unfertilized plots, since N deposition

Table 4
N₂O emissions and N-loss as % of applied fertilizer.  n = measurement days per phase

<table>
<thead>
<tr>
<th>Soil</th>
<th>Annual crop</th>
<th></th>
<th>Perennial crop</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unfertilized</td>
<td>Fertilized</td>
<td>Unfertilized</td>
<td>Fertilized</td>
</tr>
<tr>
<td>Mean N₂O flux</td>
<td>Clay</td>
<td>1.43 0.89 298</td>
<td>0.81 0.79 298</td>
<td>1.22 0.92 298</td>
</tr>
<tr>
<td>[ng N₂O-N cm⁻² h⁻¹]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background flux</td>
<td>Clay</td>
<td>1.00 0.49 170</td>
<td>0.41 0.15 84</td>
<td>0.91 0.53 129</td>
</tr>
<tr>
<td>Post-management flux</td>
<td>Clay</td>
<td>1.98 1.01 121</td>
<td>1.08 0.96 123</td>
<td>1.50 1.14 145</td>
</tr>
<tr>
<td>Mean N₂O flux</td>
<td>Loam</td>
<td>1.04 0.72 348</td>
<td>3.54 4.31 348</td>
<td>1.28 2.34 348</td>
</tr>
<tr>
<td>[ng N₂O-N cm⁻² h⁻¹]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background flux</td>
<td>Loam</td>
<td>0.78 0.68 150</td>
<td>1.62 1.73 64</td>
<td>0.64 0.25 55</td>
</tr>
<tr>
<td>Post-management flux</td>
<td>Loam</td>
<td>1.22 0.72 198</td>
<td>5.03 5.36 175</td>
<td>1.13 1.15 158</td>
</tr>
<tr>
<td>Mean N₂O flux</td>
<td>Clay Fertilizer (kg N ha⁻¹)</td>
<td>73 0.80 -0.60 260</td>
<td>0.52 0.18</td>
<td></td>
</tr>
<tr>
<td>[ng N₂O-N cm⁻² h⁻¹]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-fertilization</td>
<td>Clay</td>
<td>325 0.29 0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean N₂O flux</td>
<td>Loam Fertilizer (kg N ha⁻¹)</td>
<td>195 1.52 1.07</td>
<td>325 0.29 0.11</td>
<td>3.20 2.87</td>
</tr>
<tr>
<td>[ng N₂O-N cm⁻² h⁻¹]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-fertilization</td>
<td>Loam</td>
<td>1.08 0.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ₐ Post-weeding flux during 28 days following weeding on unfertilized soil; post-fertilization during 42 days following fertilization on fertilized soil.

₄ %N of applied fertilizer lost from fertilized soil using N₂O fluxes measured from fertilized soil for calculation.

₅ %N lost due to fertilization; for calculation using N₂O fluxes measured from fertilized soil corrected for fluxes from unfertilized soil.

Table 5
Mean soil temperature and water filled pore space ratio (WFPS) at 0.05 m depth

<table>
<thead>
<tr>
<th></th>
<th>Annual crop</th>
<th></th>
<th>Perennial crop</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clay</td>
<td>Loam</td>
<td>Clay</td>
<td>Loam</td>
</tr>
<tr>
<td>Mean soil temperature</td>
<td>27.9 1.0</td>
<td>27.8 1.2</td>
<td>27.1 1.3</td>
<td>27.2 1.3</td>
</tr>
<tr>
<td>WFPS</td>
<td>0.79 0.09</td>
<td>0.70 0.08</td>
<td>0.86 0.10</td>
<td>0.86 0.09</td>
</tr>
</tbody>
</table>
is representative for remote regions (5 \( \mu \text{eq l}^{-1} \); Eklund et al., 1997). Soil extractable nitrate concentrations measured from soil sampled from the top 10 cm of soils along with manual \( \text{N}_2\text{O} \) measurements showed no seasonal pattern (M. Keller and P. Crill, unpub. data).

We measured \( \text{N}_2\text{O} \) fluxes following 19 individual fertilization events. The observed post-fertilization fluxes varied considerably in magnitude and temporal pattern (Fig. 6(a)); soil moisture affected flux dynamics. \( \text{N}_2\text{O} \) emissions peaked within the first week post-fertilization (Fig. 6(b)), though in some cases we measured later fluxes exceeding initial peaks (Fig. 6(c),(d), thick line). Highest post-fertilization fluxes were measured from fertilized loam under perennial crop during a wet phase in June 1996 when 356 mm rain fell in 5 weeks (Fig. 6(c), thick line). Mean moisture content at 5 cm depth was 0.99 WFPS; 4.9% of applied fertilizer-N was lost as \( \text{N}_2\text{O} \)-N in the 42 days following fertilization (Fig. 7). In January 1995 we measured much lower fluxes from the same site that was fertilized at the same rate (Fig. 6(c), thin line). Then mean moisture content was 0.85 WFPS and only 0.77% of applied fertilizer-N lost as \( \text{N}_2\text{O} \)-N (Fig. 7). The lowest post fertilization fluxes were measured from clay under annual crop in June 1995 (Fig. 6(b)) when 443 mm of rain resulted in a mean moisture content of 0.73 WFPS. The fertilization rate was low and only 0.32% of applied fertilizer-N was lost as \( \text{N}_2\text{O} \)-N (Fig. 7).

\( \text{N}_2\text{O} \) flux time series (Fig. 5) and the percentage of fertilizer-N lost as \( \text{N}_2\text{O} \)-N during individual post-fertilization phases (Fig. 7) show the effects soil moisture dynamics on \( \text{N}_2\text{O} \) emissions. However, correlation between fluxes and WFPS were poor for individual sub-plots. We found a strong correlation \((r^2 = 0.64)\) for fertilized soils after distinguishing management phases and pooling data measured during post fertilization phase from all plots (Fig. 8(a)). Including background phase fluxes in the analysis reduced the strength of the correlation (thin line in Fig. 8(a)). \( \text{N}_2\text{O} \)
fluxes from unfertilized plots were only weakly correlated with WFPS (Fig. 8(b)).

3.3. Statistical modeling of N$_2$O fluxes

We employed multiple regression analysis to model N$_2$O fluxes from agricultural soils using measured soil moisture content, agricultural phases, and days after weeding or fertilization (Table 6). We estimated N$_2$O fluxes during post-fertilization, post-weeding, and background phases for the period November 1994–August 1996 (Fig. 9). Simulations confirmed that on our sites soil temperature was an unimportant determinant for N$_2$O fluxes. For both crop types simulated flux time series matched measured fluxes well when using linear relation between WFPS and ln-N$_2$O fluxes in the regression models. Weeding and soil moisture were weaker flux controls on unfertilized compared to fertilized soils. However, RMSE were similar for all crop-treatment combinations (Table 6). Structure in the residuals (data not shown) suggest that considerable autocorrelation remained after data analysis. Soil moisture content, nutrient availability and trace gas fluxes are correlated over time. Attempting to keep our empirical model simple, we disregarded terms describing lagged relations.

4. Discussion

4.1. Nutrient controls on N$_2$O emissions

Our measurement results are consistent with the conceptual model of microbial N-oxide production and consumption during nitrification and denitrification presented by Firestone and Davidson (1989) and Davidson (1993). Fertilization increased N availability for microbial processes. Post-fertilization N$_2$O fluxes increased after the applied granular fertilizer dissolved and leached into the soil. Fluxes from relatively dry soils increased only after precipitation increased soil moisture content. Post-fertilization N$_2$O fluxes and WFPS were positively correlated, despite generally high variability. During periods of lower nutrient availability (background phases) we found only a weak control of N$_2$O fluxes by soil moisture. Precipitation increased N$_2$O emissions only slightly (e.g. from 1–14 May in Fig. 5). Rainfall caused most of the variability in daily mean N$_2$O fluxes during these background phases.

Increased post-fertilization fluxes have been reported for different climate zones and land uses (e.g. Brumme and Beese, 1992; Crill et al., 2000). Generally, N$_2$O emissions are observed to be highest during the first weeks after a fertilization event and decline with elapsing time post-fertilization approaching background flux rates of a soil. We
encountered large variability in amplitude and temporal dynamics between individual post fertilization phases measured throughout 2 years at the Costa Rica site. Post-fertilization N₂O flux traces from a fertilized sugar cane plantation on Hawaii (Matson et al., 1996) appeared to be less variable between individual time series. Our high time resolution automated measurements indicated that dissolution of granular fertilizer and transfer of fertilizer-N into the soil by precipitation controls the timing of the appearance of initial post-fertilization peaks. Fluxes may increase within hours after fertilization of wet soil. On dry soil fluxes stay low until shortly after the first rain event post-fertilization. This precipitation effect on fluxes is similar to observations reported from other studies (e.g. Davidson, 1992).

Weeding increases surface and below-ground litter. Weeding may increase N₂O emissions after litter decomposition. For example, in January 1996 we measured weeding effects on N₂O fluxes from fertilized and unfertilized loam

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**Table 6**

Linear regression models. Subscripts for variables are b = background phase w = weeding phase and f = fertilization phase; \( d_w \) indicates day after a weeding event the day of weeding is 1; \( d_f \) indicates day after a fertilization event the day of fertilization is 1. Values in parenthesis are RMSE.

<table>
<thead>
<tr>
<th>Subtype</th>
<th>Equation</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual crop, fertilized</td>
<td>( \text{ln-N}_2\text{O} = -3.08 + 3.05 \text{ WFPS}_b + 2.96 \text{ WFPS}_w + 0.49 \text{ ln } d_w -0.03 \text{ d}_w + 5.66 \text{ WFPS}_i -0.13 \text{ ln } d_i -0.02 \text{ d}_i )</td>
<td>(0.63)</td>
</tr>
<tr>
<td>Annual crop, unfertilized</td>
<td>( \text{ln-N}_2\text{O} = -0.06 -0.47 \text{ WFPS}_b + 0.08 \text{ WFPS}_w + 0.33 \text{ ln } d_w -0.05 \text{ d}_w )</td>
<td>(0.66)</td>
</tr>
<tr>
<td>Perennial crop, fertilized</td>
<td>( \text{ln-N}_2\text{O} = -5.60 + 7.47 \text{ WFPS}_b + 7.42 \text{ WFPS}_w + 0.38 \text{ ln } d_w -0.03 \text{ d}_w + 8.60 \text{ WFPS}_i + 0.09 \text{ ln } d_i -0.02 \text{ d}_i )</td>
<td>(0.63)</td>
</tr>
<tr>
<td>Perennial crop, unfertilized</td>
<td>( \text{ln-N}_2\text{O} = -2.84 + 2.89 \text{ WFPS}_b + 2.80 \text{ WFPS}_w + 0.55 \text{ ln } d_w -0.07 \text{ d}_w )</td>
<td>(0.59)</td>
</tr>
</tbody>
</table>

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Fig. 7. Percentage of applied fertilizer-N lost as N₂O-N during the 42 days post fertilization period in relation with mean soil moisture content during that period. (For \( n \) used in daily figures see caption Fig. 5). Triangles are measured from clay soil, circles from loam, open symbols are measured from perennial crop, filled symbols from perennial crop. The regression line indicates loss as function of WFPS (‘loss’ = \(-5.7 + 8.36 \text{ WFPS}\)).
under balsa (Fig. 5). We are not aware of other investigators reporting a similar effect on N\textsubscript{2}O fluxes from agricultural soils. We did not distinguish surface litter and root decomposition effects on temporal variability of N\textsubscript{2}O emissions.

Our field data suggest that a suite of factors other than those addressed explicitly by our regression modeling also contributed to spatial and temporal variability of N\textsubscript{2}O fluxes. For example, we observed that ant activity affected post-fertilization fluxes measured by one of the replicated automated chambers located on loam (Fig. 10). Starting about February 1996, ants invaded parts of the soil beneath chamber number 3. Ants are not expected to produce N\textsubscript{2}O, and we did not account for soil chemical effects due to the intrusion. Ant activity disturbed the original soil structure in parts of the chamber flux area, making organic material, previously protected within aggregates, accessible to roots soil fauna and microbial populations. Changed soil structure and bulk density probably affected soil moisture locally. Another potential effect on N\textsubscript{2}O fluxes that we did not consider in our modeling may be due to decomposition of roots (Keller et al., 2000). Papaya plants were cut in November 1995. We measured slightly increased N\textsubscript{2}O fluxes from unfertilized perennial crop during the wet period from June to July 1996. Root decomposition probably contributed to high net fluxes from the fertilized plot.

Fig. 8. Linear regression between ln-N\textsubscript{2}O fluxes and soil moisture content (WFPS) for post-fertilization (upper panel) and for unfertilized soils (bottom panel). Triangles are data measured from clay, circles from loam; open symbols are measured from perennial crop, filled symbols from annual crop. The thick regression line in the upper panel is derived for data measured during post fertilization phases only (ln-N\textsubscript{2}O = −6.11 + 8.79 WFPS; r\textsuperscript{2} = 0.65), including all data measured from fertilized plots weakens the correlation between fluxes and WFPS (thin regression line, ln-N\textsubscript{2}O = −4.67 + 5.66 WFPS; r\textsuperscript{2} = 0.43. Data points measured during background phases are not printed). The regression line shown for the unfertilized plots is calculated using all data measured during 28 days post weeding (ln-N\textsubscript{2}O = −0.86 + 0.99 WFPS; r\textsuperscript{2} = 0.01).
Fig. 9. Daily mean N₂O fluxes from perennial crop. Dark lines are measured fluxes, the gray lines are simulated fluxes using the statistical model. The top panel shows data from fertilized plots, the bottom panel from unfertilized plots. Horizontal bars indicate post-fertilization or post-weeding phases, respectively. (For n used in daily figures see caption Fig. 5). Measurements started in 1994 on loam, continued on clay in 1995 and were performed on loam again in 1996.

Fig. 10. Daily mean N₂O flux measured with two replicated automated chambers from loam under annual crop. For each chamber daily fluxes were calculated from five individual measurements given uninterrupted sampling. An ant nest expanded under chamber 3, starting in about mid February 1996 (observation recorded in field notebook). We believe this accounts for the increased N₂O fluxes.
4.2. Soil moisture controls on N₂O emissions

Soil moisture content measured at 5 cm depth was above 0.6 WFPS for most of the experiment due to high soil water retention and high rainfall rates. Soil water retention measurements for the low bulk density soils delivered high field capacity estimates (Table 1), suggesting an abundance of fine pores. Small pores (<0.1 μm) hold water below 1.5 MPa suction. Radulovich et al. (1992) studied soils at the La Selva Biological Station similar to our experimental soils. They reported that small pores, which account for about 60% of the total porosity, were continuously water filled and that meso- and fine pore space at 5 cm depth remained saturated throughout long periods. The generally high moisture content probably contributed to the high denitrification rates from La Selva soils (Radulovich et al., 1992). We observed slight hydromorphic staining in our experimental soils, which suggested an intermittently reducing biogeochemical environment.

We find the strongest correlation between soil WFPS and N₂O gas fluxes within 6 weeks post fertilization of agricultural soils; unfertilized soils show only a weak dependency of soil N₂O fluxes from increasing soil moisture content (Fig. 8). Keller and Reiners (1994) measured soil WFPS and N₂O fluxes from soils under old growth and secondary forest in Costa Rica. They report a stronger relation between fluxes and WFPS from relatively nitrate rich soil under old growth forest compared to the poorer soil under secondary forest. These results compare to our findings, however Keller and Reiners measured generally higher fluxes and slopes of regression lines are steeper than derived for our agricultural soils. Similarly, Dobbie et al. (1999) report a strong, positive correlation between WFPS and N₂O fluxes from soils under pasture in Scotland, and a weaker relation and lower fluxes from less nitrogen containing pasture soil. This study also shows higher N₂O fluxes than measured from our sites (Fig. 8).

Soil moisture content is a critical determinant of soil microbial activity (Skopp et al., 1990; Linn and Doran, 1984; Williams et al., 1992; Firestone and Davidson, 1989). Davidson (1991) estimated the relative contribution of nitrification and denitrification to net N₂O fluxes from soil moisture content. He predicted the maximum of net N₂O flux to occur at about 0.6 WFPS, with nitrification and denitrification contributing equally to the flux. With increasing soil moisture content nitrification decreases and is predicted to cease at about 0.7 WFPS. Reduction of N₂O to N₂ is expected to start at 0.7 WFPS and to increase rapidly with increasing soil saturation. Net N₂O fluxes should decrease rapidly above 0.7 WFPS and are predicted to cease at about 0.9 WFPS. This generally acknowledged model was developed mainly from studies on temperate zone soils. Doran et al. (1990) found that in andic soils with high water retention the optimal WFPS for CO₂ production and probably field capacity was higher than in other soils. Hence the threshold values for N₂O production and consumption in our highly porous predominantly wet soils of andic origin may need to be shifted towards higher WFPS (E. Davidson, pers. comm., 1999). Recognizing this argument, we still use the model as presented originally as a framework to discuss our measurement results.

N₂O fluxes and soil moisture content generally agree with the expected model, however at high soil saturation our results do not entirely match with previously reported observations and theoretical concepts. During post-fertilization phases our data do not confirm the expected reduction of net N₂O fluxes from highly saturated predominantly anaerobic soils (Davidson, 1993). Inhibition of N₂O reduction to N₂ in the presence of high soil nitrate concentrations (Monaghan and Barraclough, 1993; Van Cleemput et al., 1994) may explain the measured high post-fertilization N₂O fluxes from very wet soil. In contrast, emissions measured at high soil saturation from unfertilized plots and during the background phase from fertilized plots were highly variable (Fig. 8), thus results were ambiguous with respect to the predicted reduction of net N₂O fluxes.

Crill et al. (2000) reported evidence for decreasing N₂O fluxes when WFPS exceeded about 0.8 on our sites. Seemingly different results from the present and the previous study are due to different sub-sampling and analysis approaches. Crill et al. (2000) presented data measured during the second annual cropping period on loam only (Table 2). They related N₂O fluxes to binned rather than distinct soil water data, and did not distinguish management phases. We used linear regression analysis on post fertilization fluxes measured from two soil types over 2 years, and correlated fluxes with daily mean moisture data. By emphasizing post-fertilization phases we reduce variability in fluxes and exclude mostly low fluxes from periods of low nutrient availability.

4.3. Effects of soil structure on N₂O emissions

Surface soil aggregation was maintained throughout the agricultural period due to high soil biological activity and lack of tillage. Aggregates were more stable on clay than on loam, primarily because of texture and mineral composition. This may also be a remnant of high temperature effects on clay aggregates due to burning during forest conversion. The distinct aggregation of the 2–3 cm thick surface soil layer may have affected N₂O fluxes throughout our experiment. The measured large differences in structure, bulk density and soil water content within the upper 7 cm of clay suggest that very different biogeochemical conditions may be established in the surface 0–10 cm of our soils.

In the well aggregated surface soil, large macro-pores contribute to a major portion of the inter-aggregate pore space. Large macro-pores are expected to drain rapidly after precipitation and are dominantly air filled at 0.2 kPa (TomSELLA and Hodnett, 1996). Abundant finer pore sizes in the soil at 4–7 cm depth resulted in higher water holding capacity compared to the aggregated surface soil. The soil moisture
content measured in the aggregated upper 2 cm of clay soil supported aerobic nitrification, while the WFPS measured at 4–7 cm depth supported anaerobic denitrification (Fig. 3). Manual measurements of trace gas fluxes from clay during relatively dry phases showed high emissions of nitrogen oxide that may be produced by both processes, while concomitantly measured soil moisture content suggested dominantly denitrification (M. Keller, unpub. data).

Nitrification and denitrification may occur simultaneously in the aggregated surface soil layer during wet phases. Denitrification probably dominates within anaerobic aggregate interiors while nitrification dominates on aerobic aggregate surfaces and inside small aggregates (Smith, 1990). Slowly draining small macro-pores at 4–7 cm depth may temporarily hold water during periods of frequent rains. TDR measurements showed that soils at 5 cm depth frequently remained saturated above field capacity for several days. Possibly, during that time this depth contributed little to the net N₂O flux compared to the aggregated, mainly aerobic surface soil.

High effective diffusivity in aggregated soil supports rapid escape of produced nitrogen oxides. From laboratory experiments Bandidas et al. (1994) reported nitric oxide production by aerobic processes in the drier near surface soil, while N₂O production occurred in largely saturated pore space at 3 cm depth and inside wet soil aggregates. Arah et al. (1991) reported significant N₂O consumption in the upper 5 cm of poorly aerated soils. Similarly, highly saturated, unstructured pasture soils studied by Veldkamp et al. (1998) showed low net N₂O fluxes. Even though exposed to similar precipitation, strongly aggregated surface soils under banana plantation were much drier than pasture soils and emitted relatively little N₂O. Surface soil aggregation in soils under banana plantation extended slightly deeper compared to the agricultural soils we studied.

4.4. Conclusions and implications for future studies

Robust daily averaging of data measured automatically at high temporal resolution allowed the identification of rapid responses of N₂O fluxes to soil moisture dynamics. Substrate availability for microbial processes together with soil moisture dynamics controlled the temporal variability of N₂O fluxes from agricultural soils. Fertilization effects were strongest on wet soils and weak on relatively dry soils. Fertilization increased emissions for about 6 weeks after fertilization. Intensive measurements throughout the post-fertilization phase combined with less frequent sampling during background phases will probably allow the reliable characterization of N₂O fluxes from agricultural soils.

For data analysis and regression modeling we correlated soil-atmosphere N₂O fluxes and soil moisture content measured at 5 cm depth. However, field data suggested that soil moisture content may differ at the centimeter scale between the strongly aggregated surface layer and soil at 5 cm depth. Acknowledging a soil structure effect on soil moisture and N₂O flux dynamics, then net N₂O fluxes probably result from mixed effects in multiple soil layers, where large differences in soil water content and redox conditions exist in a small depth interval. Simultaneous aerobic nitrification and anaerobic denitrification may occur in the aggregated surface layer, while high moisture content measured at 5 cm depth supports anaerobic denitrification. Reduced N₂O conversion to N₂ after fertilization possibly due to increased nitrate concentration also may have been important for net N₂O fluxes.

TDR probes were installed as close as technically possible to the soil surface, measuring soil moisture content from about 2–8 cm depth. Ultimately, this design failed to distinguish the centimeter scale differences in moisture content between the aggregated soil surface layer and the more homogeneous soil at 5 cm depth. Improved depth resolution for soil moisture data should reduce uncertainty in the correlation of net fluxes and WFPS.

Our simulations using empirical regression models confirmed that soil nutrient availability and moisture content were the major flux controlling variables. The empirical model traced the measured flux time series well in spite of the observed variability in the soil moisture to flux relation. We expect that the general form of the model may be applied on any site, given the required data are available. A temperature effect should probably be incorporated when studying fluxes from temperate zone soils. However, the model parameters are site-specific and should not be applied to other than the experimental sites.

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