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Short-term nitrous oxide profile dynamics and emissions response to water, nitrogen and carbon additions in two tropical soils

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Abstract Tropical soils are potentially the highest and least studied nitrous oxide (N_2O) production areas in the world. The effect of water, nitrate and glucose additions on profile concentrations and episodic emissions of N_2O for two volcanic soils in Costa Rica was examined. Magnitudes of episodic N_2O pulses, as well as overall N_2O emissions, varied considerably and consistently, depending on soil texture, soil water content, and kind and availability of substrates. Emission pulses began within 30 min, peaking no later than 8 h after wetting. Production in the soil occurred mainly in the layer between 5 and 20 cm deep, but depended directly on the temporal dynamics of the water profile. Changes in soil NO_3^- were associated with soil N_2O concentration changes. Depending on the treatments, one episodic N_2O production event driven by one moderate rain could account for less than 15% to more than 90% of the total weekly production. Previous survey studies may have underestimated the contribution of N_2O emissions from tropical soils. In order to improve budgets and models of N_2O emissions, episodic emissions driven by rain events and amendments must be considered.

Keywords Nitrous oxide · Tropical soil · Profile dynamics · Episodic emissions

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Introduction

Nitrous oxide (N_2O), the third most important greenhouse trace gas in the troposphere and one important contributor to ozone destruction in the stratosphere, has had its concentration in the atmosphere increase steadily over the last few decades (Crutzen 1994). Of the presently known sources, soils are estimated to be the largest, contributing approximately 65% of total emissions (Prather et al. 1995). Comparative measurements have reported higher rates of denitrification and N_2O release in tropical than in temperate forests (Keller et al. 1986), with tropical forest soils thought to be the probable largest single source, followed by cultivated soils (Smith 1997). The increase in N_2O atmospheric concentration is directly associated with large-scale human interference in the N cycle (Prather et al. 1995) which is largely related to agriculture (Duxbury 1994). Tropical biomes cycle larger amounts of total N than temperate and boreal ecosystems (Vitousek and Matson 1993). As the tropical ecosystems are converted to agriculture, pasture or silviculture (Erickson and Keller 1997), where some form of N fertilization is used (Smith et al. 1997), there is an increasing potential for tropical soil N_2O emissions to become yet more significant (Duxbury 1994).

Production, consumption and diffusion of N_2O within the soil interplay to create dynamic changes of gas concentrations in the soil profile (Højberg et al. 1994). N_2O efflux from the soil surface is a function of timing and location of N_2O production in the soil profile. The N_2O production in soils is episodic in nature. Pulses of production associated with major transient changes in soil microsite environments have been shown to account for significant surges of emissions to the atmosphere in relatively short spans of time (Mosier et al. 1991; Brumme and Beese 1992). Most survey studies carried out for tropical soils in the past have not used high frequency (e.g. every few hours) sampling based on rain events to guide sampling. More commonly, daily sampling is conducted for only a short campaign (Keller et al. 1986; Matson et al. 1990). In some cases seasonal cycles are studied with

sampling approximately every week (Keller et al. 1993). Studies in dry tropical forest (Garcia-Mendez et al. 1991; Davidson et al. 1993) and savanna (Scholes et al. 1997) sampled rain-driven episodic events. These studies reported that the magnitude of the episodic events was a direct function of substrate accumulation during the dry season, and that the magnitude decreased with each successive rainfall until rain-associated emissions were not distinguishable from the background. This finding might be a good approximation for most of the relatively arid and infertile N-limited natural ecosystems, but might not represent well the fertile, non N-limited tropical systems.

Therefore, the main objectives of this work were to evaluate flux measurement frequency, particularly in response to changing environmental conditions, to examine the effects of water, available carbon and nitrate on the process of nitrous oxide production within the soil profile and emission to the atmosphere, and to supplement the meager amount of data available from tropical soils.

Materials and methods

Study site

La Selva, a 3,300-ha biological station of the Organization for Tropical Studies, lies in the province of Herédia (10° 26' N; 83° 58' W, 40 m approx. elevation above sea level), in the transition zone from the coastal plain to the steep foothills of the Costa Rican Cordillera Central. Annual climatic means are 25.8°C air temperature and 3,962 mm precipitation (Sanford et al. 1994). A dry season extends roughly from January to April, and the variation in air temperature is minimal throughout the year. The original vegetation of La Selva was wet tropical forest according to the Holdridge scheme. Two experimental sites were chosen in order to contrast different agroecosystems with distinct soil types. One site, Vegas, is located on an alluvial terrace at the confluence of the Puerto Viejo and Sarapiqui rivers. The original forest cover was converted in the 1950s to cacao (*Theobroma cacao*) cultivation, and abandoned ca. 1980 (Griffiths et al. 1993). In 1991 the area was cleared to bare soil for the establishment of the Huertos experimental plots. The marginal buffer zones among Huertos plots were left to regrow with wild pioneer plants. A regrowth strip (La Selva GIS grid –50/–375) was chosen for this experiment. One week prior to the beginning of the experiment the regrowth was cleared to bare soil, without removal of roots. The second experimental site, Flaminia, is located on the slope of a clayey terrain developed possibly from a higher river terrace. The area had been under long term pasture until abandonment several months prior to the experiment. An area covered with 1-m-tall grass (La Selva GIS grid –350/1,250) was chosen for this experiment. Three weeks before the beginning of the experiment the grass was cut down and the soil left bare.

The sandy lower-terrace soil in Vegas (Bambu consociation) is an Andic Fluventic Eutropept, rich in exchangeable bases, whereas the clayey pasture soil in Flaminia is a Typic Tropohumult, more weathered and poor in bases (Sollins et al. 1994). Table 1 shows selected data from the studied soils.

Experimental design

Each of the two experimental sites had one 3.2×3.2 m plot subdivided into four 2.56-m^2 sub-plots (treatments). Each sub-plot was a 1.6-m square with four basic components or installations: one PVC ring or collar inserted in the center of the square; one battery of stainless steel soil-gas-phase probes for sampling at depths of 2, 5, 10, 20 and 40 cm, installed to one side of the collar; one battery of tensiometers for sampling at the same depths; and one soil sampling pit. In addition to simulated rain events, several C and/or N solution additions were carried out. All the N and C sources were dissolved immediately before irrigation in stored rain water. The water or solutions were sprayed evenly onto the sub-plots over a period of 30 min, so that they would percolate into the soil without forming standing water. It was chosen to sample intensively in time rather than replicate in space. The time-steps used in the experiments for measurements were irregular, but followed a general scheme. For each simulated rain event, or solution addition, measurements were done preceding the additions and then 30 min, 2, 4, 8 and 24 h, and daily thereafter, until the next rain event or completion of the experiment. For event 1 there were two fertilizer treatments and water alone as a control. The fertilizers were sodium nitrate ($NaNO_3$) at a level of 50 kg $N \cdot ha^{-1}$ as the first fertilizer treatment, and $NaNO_3$ at 50 kg $N \cdot ha^{-1}$ plus glucose ($C_6H_{12}O_6$) at a level of 250 kg $C \cdot ha^{-1}$ as the second treatment. The 5:1 C:N ratio used was similar to those used in soil core incubation studies, and this nutrient proportion is suitable to measure denitrification potential (Schuster and Conrad 1992; Parsons et al. 1993). In Vegas there was also one dry control, and in Flaminia there was one glucose only treatment, at a level of 250 kg $C \cdot ha^{-1}$. Events 2 and 3 in Vegas were a continuation of the observation of treatments from event 1, with supplemental water additions on the two fertilizer and water treatments.

Field sampling

The enclosure technique used to quantify trace-gas exchange between soil and atmosphere has been widely used and discussed at

Table 1 Some physical and chemical properties of the studied soils

Site	Depth (cm)	Bulk density ($g \cdot cm^{-3}$)	Textural analysis [a]			pH (H_2O)	Mineral N		Total N (%)	Total organic C (%)
			Sand (%)	Silt (%)	Clay (%)		NO_3^- (mg $N \cdot kg^{-1}$ soil)	NH_4^+		
Vegas	2	0.7	66.5	26.5	7.0	6.4	19.6	12.6	0.4	3.9
	5	0.8	66.5	21.5	12.0	6.5	20.8	7.8	0.2	2.4
	10	0.9	69.5	18.5	12.0	6.6	5.8	1.4	0.2	2.0
	20	1.0	70.0	15.0	15.0	6.5	1.7	0.9	0.2	2.0
	40	1.0	66.5	23.5	10.0	6.4	0.5	0.2	0.1	0.7
Flaminia	2	1.4				4.6	12.1	20.3	0.4	3.7
	5	1.5				4.7	6.5	3.3	0.3	3.3
	10	1.5				4.8	8.1	4.6	0.3	2.8
	20	1.5				4.9	1.3	1.3	0.2	1.7
	40	1.4				4.9	0.5	1.8	0.1	1.3

[a] Textural analysis for clayey soil presented a resilient microaggregation problem, common to volcanic soils (Sollins et al. 1994)

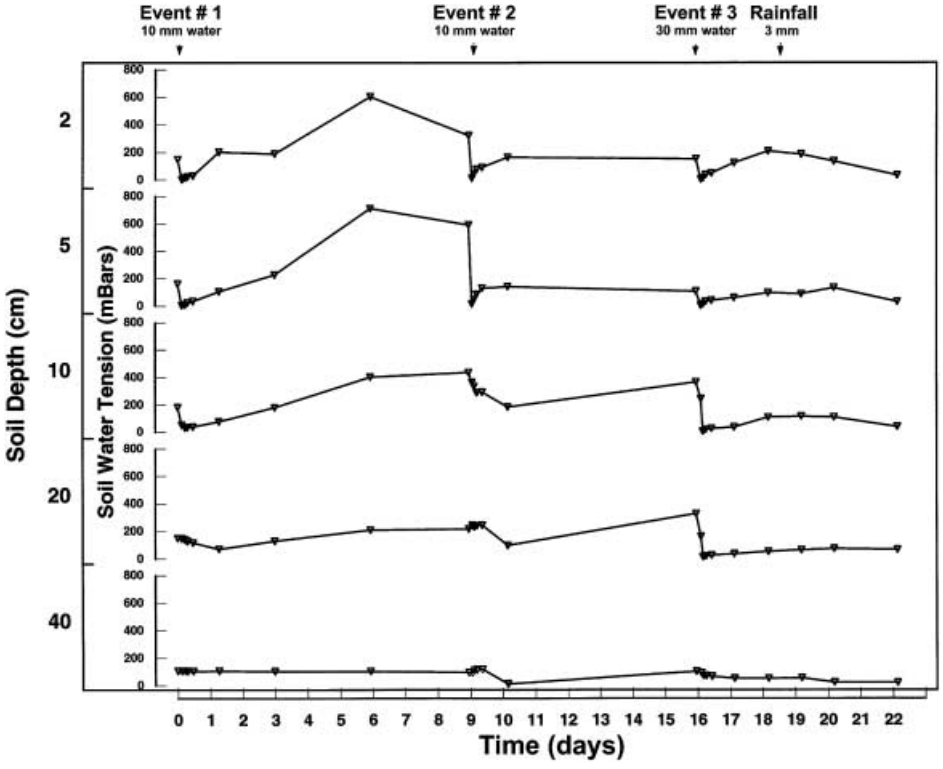


Fig. 1 Vegas soil profile time-series of water tensions in millibars. Average of the three treatments which received water. An *event* refers to the addition of water and/or substrate to the soil, and includes the subsequent drying period until the next event or until the end of the experiment

length by Livingston and Hutchinson (1995). In this study, the two-part static vented chambers were used which consist of a 25-cm internal diameter, 10-cm tall, polyvinylchloride (PVC) ring or collar and a molded acrylonitrile-butadiene-styrene (ABS) plastic top 10-cm tall with a gas sampling port, a pressure equilibration port, and a lip that fits over the PVC ring (Matson et al. 1990). The chamber top was ventilated before the beginning of each N_2O flux measurement. The lip was greased lightly with Apiezon and the collar capped tightly with the chamber top. Gas samples, withdrawn through the sampling port, were collected using 20-ml nylon syringes (S.E.S.I., VWR Scientific) fitted with butyl rubber o-rings, and polypropylene stopcocks (Baxter Scientific), at 1, 7, 14, 21 and 28 min after closure. Each five syringe sample set constituted one flux measurement, after which the chamber closure was opened. N_2O flux was calculated by regressing the N_2O concentration linear change over time in the chamber enclosure (Keller et al. 1986). One week prior to the experiment the collar was inserted approximately 2 cm into the top soil. The sampling of soil-gas was carried out using 10-cm-long perforated horizontal probes made of stainless steel tubing (3.17 mm outer diameter) formed in an "L" shape. The upper part of the "L" (2 cm) was bonded with epoxy resin to a capillary stainless steel tube leading upward out of the soil to a luer slip-lock fitting which was capped in between samplings. To monitor the soil water potential, porous-cup tensiometers (1-cm o.d. by 10-cm-long sensing porous-cup, 1 bar air entry value; Soilmoisture, Santa Barbara, Calif.) were installed horizontally in the soil about 25 cm away from the collars. They were placed at the same depths as the gas probes but offset laterally to avoid interference. Water tension inside the tensiometers was measured at each time step using a calibrated electronic pressure transducer (Soilmoisture) hooked to an ammeter. Soil samples to be chemically analyzed were collected for each time step, each treatment, and each depth and were obtained using a 25.4-mm o.d. steel tube soil sampler (Soilmoisture). The sampling scheme in the immediate vicinity of the experimental plots, consisted of digging one small pit (30 cm wide, 50 cm deep and 1 m long) for each treatment. Over the course of the experiment, the pits were progressively enlarged to up to 120 cm wide, to allow for the sequential soil samplings. To diminish the potential impact over the soil microclimate, especially due to evaporation, the sampling walls of the pits were kept covered during sampling intervals with sheets of plastic. The samples were then drawn horizontally, within the pit, from under the experiment area at the same depths as those used for gas probes and tensiometers. The amount of soil collected corresponded to about 200 g. Soil samples were frozen in the collection bags (–18°C) and stored until extraction was carried out.

Laboratory analysis

N_2O was determined using electron capture gas chromatography (Crill at al. 1995), with Poropak Q backflush column setup (Keller and Reiners 1994) and P5 carrier gas (5% CH_4 in Ar mixture). Standards (N_2O in N_2 mixture) used in the analysis (343.8, 543.7 and 808.7 ppbv; Scott Specialty Gases) were calibrated against NOAA (Climate Monitoring and Diagnostics Laboratory, Boulder, Colo.) secondary standards. Soil nitrate (NO_3^-) concentrations were determined colorimetrically in 2 N KCl extracts from soil samples using an autoanalyzer (Technicon Traacs 800).

Results and discussion

Alluvial soil (Vegas)

Vegas control treatment

The time series of water tension profiles (Fig 1), which are averages of three separate measurements of the treatments that received water, indicate the effects of each simulated rain event and subsequent drying period on soil water tension.

In the dry control treatment, N_2O fluxes remained close to background levels throughout the period

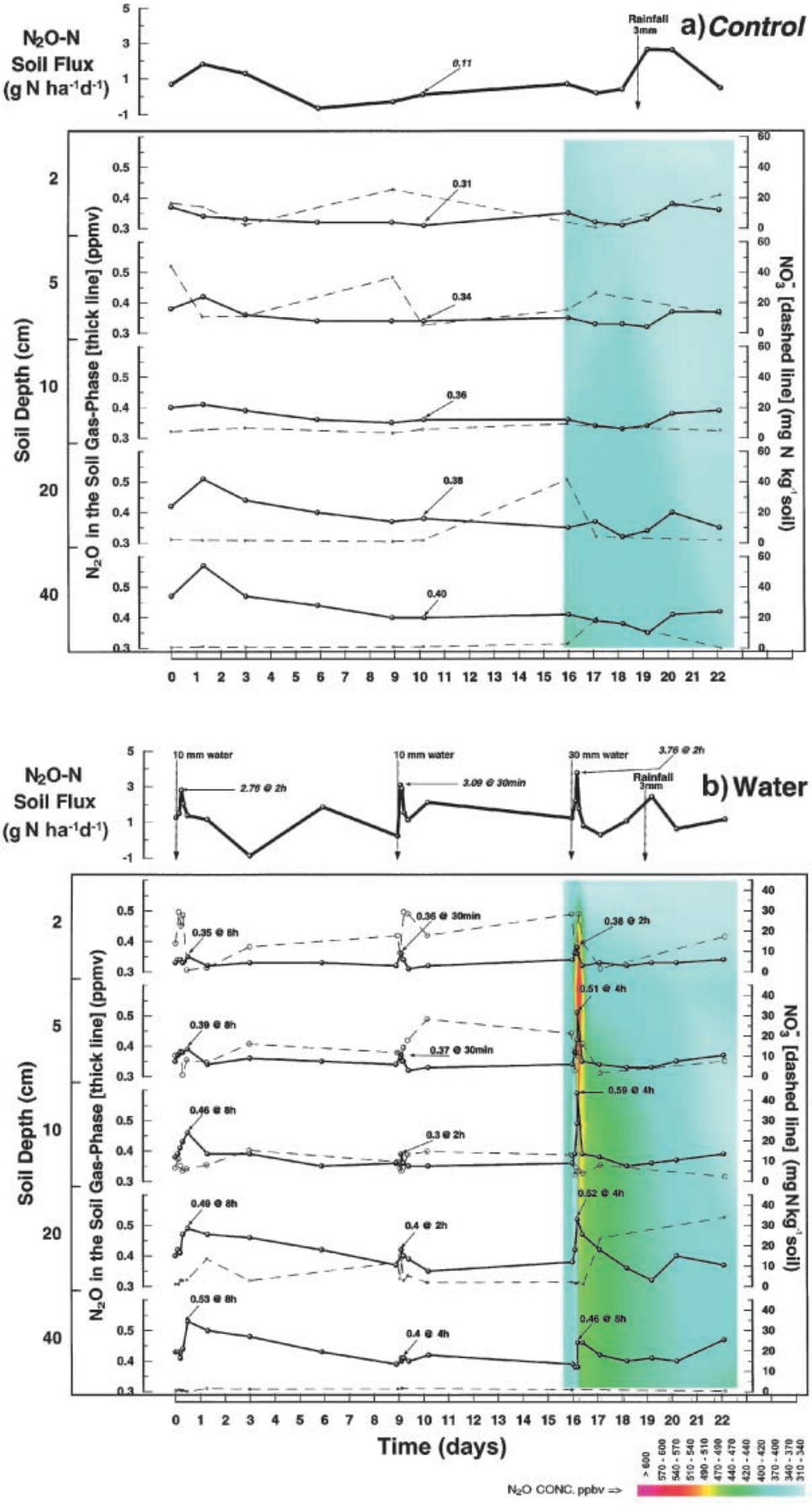


Fig. 2 Vegas soil profile time-series N_2O and NO_3^- data for dry control (**a**) and water (**b**) treatments. N_2O exchange flux with the atmosphere is shown on *top* of the soil profile, associated with soil gas-phase N_2O concentrations and soil extractable NO_3^- concentrations. *Color gradient* represents interpolated concentrations of N_2O in the soil gas phase for event 3

(Fig. 2a). The residual effects of moisture from some rainfall 3 days before the beginning of the experiments can be seen in the initial days as elevated N_2O concentrations at depths of 5, 20 and 40 cm. As the soils dried until day 20, the soil moisture to depths of 20 cm decreased progressively to tensions in excess of 1 bar. Changes in nitrate concentrations in the soil profile did not directly reflect changes in the associated N_2O concentrations. This could indicate that nitrification might be the main source for N_2O background emissions rather than denitrification, or that N_2O is diffusing up from deeper layers where it would have been produced either by denitrification or nitrification. Degassing from ground water is also a possible source. There is a consistent upward gradient in soil N_2O concentrations at all sampled depths, which supports the hypothesis of production at depth.

Vegas water treatment

Comparison of soil gas-phase N_2O concentrations of the control treatment with the first simulated rainfall event in the water treatment (Fig. 2b) shows the effect of water on increased soil N_2O concentrations. Griffiths et al. (1993), incubating similar soils to study denitrification potential, found that N_2O produced by denitrification was highest in the O_2-free headspace sample. Considering that water temporarily fills up pore space in the upper soil layers, diffusion of atmospheric O_2 into the soil could diminish, increasing the probability of a larger anaerobic fractional volume developing (Davidson 1992; Højberg et al. 1994), therefore allowing denitrification to proceed faster in layers beneath the saturated zone. Another possible explanation is that N_2O actively produced in upper layers diffuses downward. Gas diffusion from below would be inhibited. The N_2O peak for all depths happened around 8 h after the simulated rain, indicating a simultaneous response (no lag determined by diffusion constraints). Even though the magnitude of the second simulated rain event was the same as the first, the soil was much drier at that time. The wetting front percolated quickly to 5 cm, but moisture was soon lost to evaporation. The water added to the top 5 cm in this event kept water tension low until the third event, when a threefold larger simulated rain event percolated quickly to the drier layers underneath, reaching 20 cm, and producing strong pulses of N_2O to that depth. Lower water tensions might have induced lower O_2 partial pressure in the microbial microsites for a longer time than in previous events, leading to a further reduction of N_2O (already diffused from the liquid into the gas-phase) to N_2 (Højberg et al. 1994). In the "leaky-pipe" model (Firestone and Davidson 1989) this would mean a regulation at the third level, where diffusion and consumption of N_2O occur prior to escape from soil into the atmosphere. That would explain the sharp peaks at depths of 5 and 10 cm. From 20 cm downward, there could be less consumption after the peak, which would explain the skewed tails for those depths. The bigger pulses of soil gas-phase N_2O, compared with event 1 and 2, did not translate into bigger emissions at the soil surface. The NO_3^- data showed consistent patterns, especially the patterns associated with water additions and the resulting N_2O pulses. A progressive increase during low flux periods, like the one shown at 2 cm, could indicate two main processes: first, nitrification occurring during periods where O_2 is more plentiful, and also enhanced by moderate wetness; second, upward movement of soil solution from deeper layers to the surface by capillary action, due to surface evaporation, resulting in accumulation of NO_3^- at the uppermost layer and progressive loss of NO_3^- in deeper layers. There were NO_3^- oscillations associated with the N_2O pulses, with sudden NO_3^- decreases followed immediately by quick increases until stabilization around background concentration levels. This was similar to what was observed in tropical dry forest upon wetting (Davidson et al. 1993). This could suggest that with increased moisture, microbial communities bloom, consuming NO_3^- from the soil solution, leading to a decrease in NO_3^- concentration (Ellis et al. 1996). Then, either due to exhaustion of substrate or some other regulating factor, the recently grown biomass dies, liberating part of the N that was immobilized by the microbial mass. The subsequent stabilization in the NO_3^- concentrations during the dry periods suggested that the microbial community had reached a quasi-equilibrium.

After three simulated rain events over a 22-day period, 25 g N_2O-N·ha^{-1} was emitted (averaging 1.2 g N_2O-N·ha^{-1}·day^{-1}). The dry Vegas control treatment emitted 14 g N_2O-N·ha^{-1} (0.6 g N_2O-N·ha^{-1}·day^{-1}) over the same period. The episodic pulses of N_2O associated with water additions contributed approximately 20% of the total flux. The approximately 20 g N_2O-N·ha^{-1} attributable to background flux is still 1.4 times larger than the dry control background flux. This indicates that other N_2O-producing processes such as nitrification benefited from the increased soil moisture. The emission pulses in this treatment, 1 g N_2O-N·ha^{-1} for the first event, and 2 g N_2O-N·ha^{-1} for the last two events were evidence that water additions cannot be related to N_2O emissions in a linear way.

Vegas nitrate-N treatment

Patterns of emissions from the soil surface were very consistent with patterns of changes in soil gas concentrations (Fig. 3a). There was an increase in N_2O and NO_3^- at 40 cm prior to any change in soil moisture. In this first amendment, the top three layers showed a large increase in NO_3^- with the arrival of a moisture front. The first peak of N_2O concentrations associated with NO_3^- additions exceeded the water alone treatment throughout the profile. The extra NO_3^- detected clearly stimulated higher denitrification activity. This is an indication that the soil ecosystem was limited in N, a result corroborated by soil core NO_3^- addition experiments with pasture and

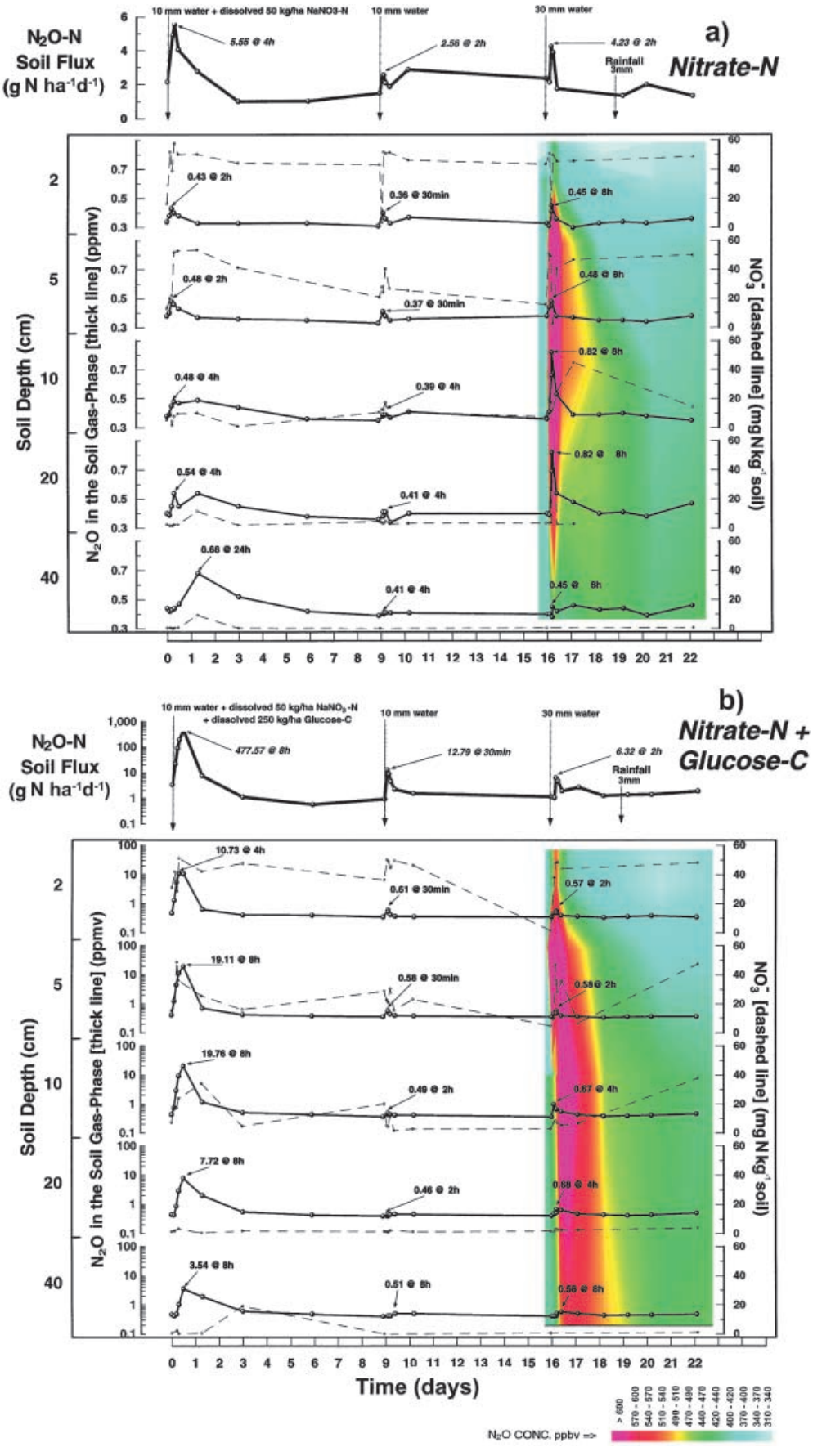


Fig. 3 Vegas soil profile time-series N_2O and NO_3^- data for nitrate-N (**a**) and nitrate-N + glucose-C (**b**) treatments (note logarithmic scales for the gas axes)

forest soils in the same region (Parsons et al. 1993), but contradicting results of another study (Keller et al. 1988). This treatment, with a 50 kg N·ha^{-1} amendment, emitted 45 g N_2O-N·ha^{-1} (2.0 g N_2O-N·ha^{-1}·day^{-1}), or 1.8 times the gas emitted by the Vegas water-alone treatment. That emission represented approximately 0.1% of the added N. Episodic emissions accounted for 22% of the total flux in this treatment.

Vegas nitrate-N + glucose-C treatment

After addition, the profile of N_2O concentrations (Fig. 3b) indicated that denitrification was enhanced 30 times above levels measured in other treatments. The NO_3^- profile showed concentrations oscillating abruptly during gas peaks, as in other treatments which received water. Most of the NO_3^- was consumed during and soon after event 1 at depths of 5 and 10 cm, remaining constant in deeper levels. This suggests that microbial activity is most intense in those two layers, which increases the likelihood that N_2O is actively produced there (Firestone and Davidson 1989), diffusing upward and downward. In the surface layer, NO_3^- remained high, possibly due to the amendment, but also possibly due to the progressive loss of water by evaporation during the first interpeak period. Between events 2 and 3 NO_3^- progressively dropped to almost zero, possibly due to higher soil moisture conditions than the first interpeak. The N_2O concentrations reached in the first event of the NO_3^- + glucose additions were 25 times higher in the 2-cm-depth layer, 40 times higher in the 5- and 10-cm layers, 14 times higher in the 20-cm layer, and 5 times higher in the 40-cm layer, than in equivalent layers treated only with NO_3^-. Concentrations in the second event were only 1.2–1.7 times higher than the concentrations of the corresponding NO_3^- treatment. The third event had some concentrations which were even smaller than the corresponding NO_3^- treatment. This overwhelming response to added glucose, primarily in the layers wetted by the simulated rain, indicated the high potential for denitrification in this soil. This treatment emitted 303 g N_2O-N·ha^{-1} (13.7 g N_2O-N·ha^{-1}·day^{-1}), or 0.6% of the added N. During the episodic pulses 91% of the N_2O was produced, contrasting with the 22% in the NO_3^- treatment.

These results indicate that there might be a severe C limitation on denitrification in this soil (Parsons et al. 1993), or, perhaps, that glucose can stimulate aerobes to consume most of the available soil oxygen which increases the anaerobic fractional volume in the soil and then stimulates denitrification. Stoichiometric calculations showed that if glucose was totally respired aerobically, the amount added to the soil (250 kg of dissolved C·ha^{-1}) would have been enough to consume all of the atmospheric oxygen from the soil gas-phase down to almost 1 m deep, provided there was no diffusive replenishment from the atmosphere. The short time frame of intense reducing conditions is the key to understanding why N_2O emissions were so enhanced.

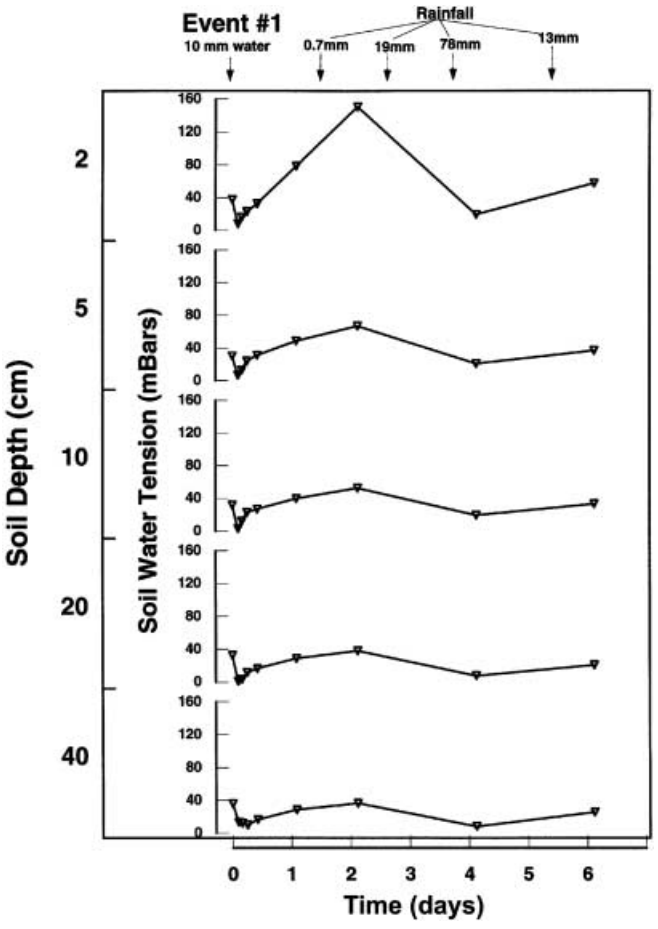


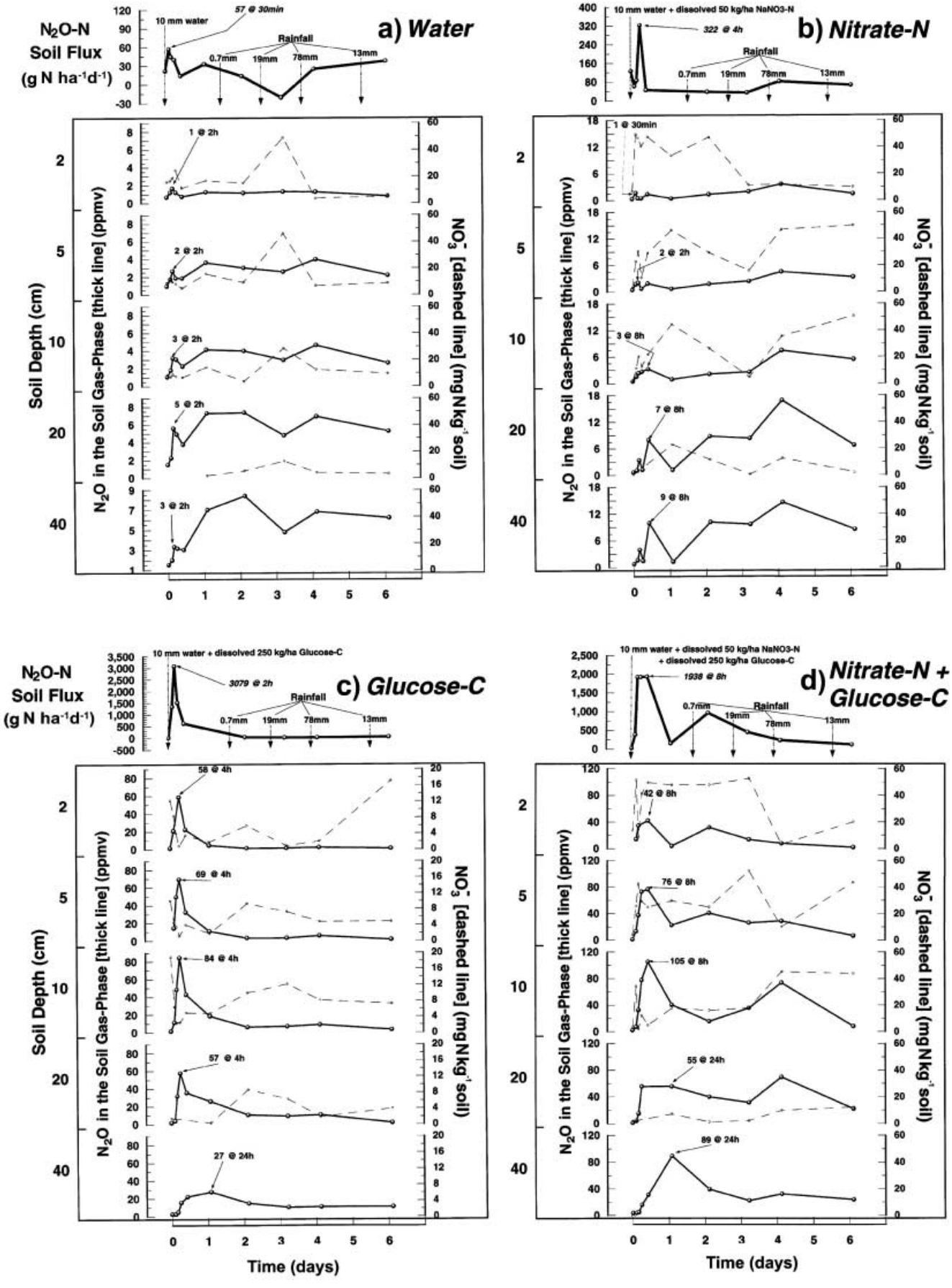
Fig. 4 Flaminia soil profile time-series of water tensions in millibars. Values are average of all treatments

Clayey soil (Flaminia)

Flaminia water treatment

The quick and homogeneous drop in soil moisture after a simulated rain event throughout the profile (Fig. 4) indicated higher infiltration, probably due to macropores. Except for the uppermost few centimeters which became drier, the rest of the measured profile behaved the same with respect to moisture. N_2O concentrations in the Flaminia pasture soil water treatment (Fig. 5a) showed a fourfold faster and 5–10 times larger response than the equivalent treatment on the soil at the Vegas site. Because of scattered rainfall during the experiment at Flaminia, it is not possible to compare background production with Vegas. N_2O formed after the first brief peak, accumulated progressively at depth. Because the rain events happened during the night, peak sampling was not done. Lack of sampling of the N_2O peaks makes it hard to evaluate the impact on the soil N_2O concentrations of different magnitudes of natural rainfall.

However, a few observations should be noted about the water treatment results. After 19+ mm of rain accumulated on the 3rd day, twice as much as the amount of


a) Water
b) Nitrate-N
c) Glucose-C
d) Nitrate-N + Glucose-C
N2O-N Soil Flux (g N ha-1d-1)
10 mm water
57 @ 30min
Rainfall
0.7mm
19mm
78mm
13mm
10 mm water + dissolved 50 kg/ha NaNO3-N
322 @ 4h
10 mm water + dissolved 250 kg/ha Glucose-C
3079 @ 2h
10 mm water + dissolved 50 kg/ha NaNO3-N + dissolved 250 kg/ha Glucose-C
1938 @ 8h
Soil Depth (cm)
N2O in the Soil Gas-Phase [thick line] (ppmv)
NO3- [dashed line] (mg N kg-1 soil)
Time (days)

the simulated rain in event 1, there was a drop in N_2O concentrations at almost all depths, associated with a big increase in NO_3^- concentration. On the 4th day, after 78 mm of rain, the situation reversed, with gas accumulating in the profile, and NO_3^- substrate diminishing abruptly. The first drop in gas concentrations was similar to the drop that happens after each episodic pulse, with the increased NO_3^- being the result of the increased mineralization-nitrification associated with the enhanced soil moisture. The increase in NO_3^- is associated with the first moisture peak for the three uppermost layers, and is proportional to the amount of water going through the soil. The increase in N_2O concentrations by the 4th day was probably caused by denitrification soon after the natural rain, which would also explain the drop in concentration of the NO_3^- substrate. This treatment emitted 116 g N_2O-N·ha^{-1} in 6 days, or proportionally 17 times more N_2O-N than observed in the equivalent treatment at Vegas. Considering that this kind of soil covers much larger areas and its use as pasture is much more common, these high emissions assume special significance (Keller et al. 1993; Reiners et al. 1994).

Flaminia nitrate-N treatment

The NO_3^- treatment (Fig. 5b) produced a significantly different response compared to the water treatment. Concentrations of N_2O are generally higher than those produced by water, but the dynamics of production and consumption were not symmetric as they were at the Vegas site. After the amendment, NO_3^- increased immediately in the uppermost layer, and showed a progressive lag for the increase at deeper levels. In contrast to the water treatment, NO_3^- in the three intermediate layers that accumulated during the 1st day began decreasing on the 2nd day, reaching its lowest concentration on the 3rd day, and recovering by the 4th day. Here, as in Vegas, NO_3^- in the surface soil remained high as the soil dried, but in contrast to Vegas, when more water was added, NO_3^- concentrations decreased and did not recover. The likely explanation is leaching of NO_3^- from the surface layer into layers beneath by the added water. The NO_3^- treatment, with a 50 kg N·ha^{-1} amendment, emitted 374 g N_2O-N·ha^{-1} (61 g N_2O-N·ha^{-1}·day^{-1}), or 0.7% of the added N. That emission is proportionally 30 times higher than the gas emitted at the Vegas NO_3^- treatment, and 3.2 times the gas produced at the Flaminia water treatment. The rate of N fertilization used in this experiment is relatively low compared to that used for agriculture in the area (e.g. banana plantations typically use 200 kg-N·ha^{-1}). Emissions associated with episodic fluxes increased from 15% of total flux in the water treatment, to 36% in this treatment.

◀ **Fig. 5** Flaminia soil profile time-series N_2O and NO_3^- data for water (**a**), nitrate-N (**b**), glucose-C (**c**) and nitrate-N + glucose-C (**d**) treatments

Flaminia glucose-C treatment

The glucose-C treatment (Fig. 5c) was unique to the Flaminia site, and used to separate the effect of C alone from that of C plus N. The most evident effect of C alone, besides the brief enhancement of N_2O in the profile following amendment, was the consumption of NO_3^- at the lowest concentrations observed in any of the treatments. Similar to NO_3^- -N + glucose-C at Vegas, the N_2O production was most intense in the three upper layers. In these layers, NO_3^- reached zero at the same time as N_2O concentrations were peaking (at 4 h), indicating a shortage of N substrate for denitrification. If compared with N alone, the glucose treatment produced 3–30 times higher N_2O concentrations. Glucose is thus clearly the main driver of N_2O production associated with these amendments. However, glucose addition alone will deplete the system of NO_3^- after only 4 h of immobilization/denitrification. The glucose treatment at Flaminia emitted 1,273 g N_2O-N·ha^{-1} (208 g N_2O-N·ha^{-1}·day^{-1}), a response 11 times larger than the water treatment and 3.4 times larger than the NO_3^- treatment. The episodic part represented 91% of the measured emissions.

Flaminia nitrate-N + glucose-C treatment

The profile results for this treatment (Fig. 5d) confirmed the expectation from the results of the C alone treatment that an additional supply of N substrate would increase the production and accumulation of N_2O in the soil. The peaks in soil concentrations were equivalent in some layers, and much bigger in others, compared to those resulting from the glucose-C treatment. The enhanced N_2O peaks lasted much longer than in the glucose amendment. But even in this experiment, there seemed to have been some NO_3^- limitation, for at 10 cm, very low NO_3^- concentrations coincided with a decrease in the N_2O concentrations. It seems clear, as in the water treatment, that NO_3^- was leached from the surface layers into lower ones after an intense rainfall. However, it is unclear why, between 2 and 8 h, there was a plateau of concentrations in the upper two layers and also in the measured N_2O flux. N_2O concentrations in this treatment are 4–25 times larger than the concentrations for the equivalent treatment at Vegas. The enhanced peaks also lasted longer than at Vegas. In Flaminia, there was more soil moisture which was better distributed, but NO_3^- concentrations were similar at both sites. The key, we believe, were soil textural and structural differences. Larger bulk density (Flaminia pasture) with smaller porosity can influence infiltration and percolation rates, and very probably gas diffusivity rates (Reiners et al. 1994). The sandy Vegas soil had potentially much less space in micropores comparative to the clay soil in Flaminia. Consequently, the anaerobic fractional volume of the former could be much smaller. This treatment emitted 3,336 g N_2O-N·ha^{-1} (545 g N_2O-N·ha^{-1}·day^{-1}), or 38 times more than the equivalent treatment at Vegas. However, it was 20% less

than would be predicted by a simple multiplication of the individual treatments (nitrate and glucose). The episodic part represented 39% of the total emissions.

Patterns vs statistics

Although patterns of NO_3^- and N_2O concentrations in the soil profile were elusive and could indicate several potential relationships as noted before, very few statistical correlations between these two parameters were found significant (at $P<5\%$). The relationship between soil extractable NO_3^- and soil N_2O pass through dynamics of microbial communities, the complexities of soil microsites, the buffering effects of pools and lags, the transfer of ions and molecules across different interfaces and the interplay of different and concurrent substrates for denitrification, not to mention the complicating factor of nitrification generating both NO_3^- and N_2O. Therefore, we think that simple lack of direct statistical correlation between NO_3^- and N_2O can neither tell of the complexities of the biogeochemistry involved, nor can rule out a controlling relationship. Similarly, the relationships of the N_2O in the soil profile with the N_2O flux from the soil surface, as shown in these experiments, follows a complex interplay of production, consumption and gaseous transfer through the soil. Because N_2O is an intermediate product in the denitrification pathway, its transfer to the surface once produced depends on ensuing biogeochemical dynamics. The associated patterns seen in this experiment, notably for Vegas, illustrate well these complexities. To relate these parameters meaningfully one has to rely on mechanistic soil C and N biogeochemistry models that can capture the main drivers controlling sources, sinks and transfers of N_2O in the soil.

Conclusions

The series of experiments with the two volcanic tropical soils reported in this paper indicate that water additions and rainfall set the soil system to start emitting N_2O in intense pulses. The measurement of time-change concentration gradients for these soil profiles proved useful in delineating the timing and location of gas production. The general close relationship between patterns of N_2O concentration and water infiltration with substrate amendment, suggested an overwhelming importance of production in the upper soil layers, over production in deeper soil, in controlling the measured emissions. The effect of irrigation and amendment on the N_2O production was most dramatic in the short-term episodic peaks that followed additions, but also increased overall production of N_2O. The data in the soil profiles brought strong evidence of the connection between the movement of the wetting front into the soil and the change of N_2O concentrations at that level. Soil extractable NO_3^- showed remarkable and somewhat consistent patterns of oscillation associated with N_2O emission in transient pulses. The patterns associated with background emission also remained consistent with the conditions of the respective soil layer in many situations, even though the biogeochemical interpretation could not explain all the patterns observed. The fact that both N and C additions produced intense responses suggests that these soils were limited in both substrates. However, in only one instance was NO_3^- substrate observed to have been depleted as a result of supply of the glucose substrate.

Pulses of production can develop quite superficially in these soils, especially between depths of 5 and 20 cm, and can develop to a maximum emission strength (which can be several orders of magnitude greater than the background emission detected) within the range of 30 min to 8 h. Those episodic pulses associated with rain, liquid amendment or both, varied greatly in intensity and duration among treatments.

If the frequency and distribution of rainfall and amendments is shown to generate pulses throughout the year as intense as the pulses measured in these experiments, this episodic production should be taken into consideration to estimate N_2O emissions from tropical soils.

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