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Journal

Global Biogeochemical Cycles, 14(2)

ISSN

08866236

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Publication Date

2000-06-01

DOI

10.1029/1999GB001181

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Isotopic variability of N₂O emissions from tropical forest soils

T. Pérez,¹ S.E. Trumbore,¹ S.C. Tyler,¹ E.A. Davidson,² M. Keller,³ and P.B. de Camargo⁴

Abstract. We report measurements of the ¹⁵N and ¹⁸O signature of N₂O emitted from tropical rain forest soils at the La Selva Biological station in Costa Rica and in the Fazenda Vitoria in the State of Pará, Brazil. The δ¹⁵N values ranged from -34 to 2‰ with respect to atmospheric N₂, while δ¹⁸O values had a smaller range, from -4 to 18‰ with respect to atmospheric O₂. We attribute these large variations to differences in microbial production, consumption, and transport of N₂O. In general the δ¹⁵N of N₂O emissions from an Oxisol soil in Brazil were consistently enriched by ~20‰ in ¹⁵N compared to those from Ultisol and Inceptisol soils in Costa Rica. Denitrification is the most likely source of N₂O in both locations during the rainy season, and the ¹⁵N of nitrate was similar in both locations. We attribute the overall variability in emitted ¹⁵N to differences in the ratio of N₂O:N₂ escaping from the soil to the atmosphere, with a larger fraction of the N₂O reduced to N₂ at the Brazilian sites. We found light δ¹⁵N-N₂O values associated with high N₂O emissions in a fertilized agricultural site in Costa Rica and in a "hot spot" of high emissions in the forest site in Brazil. This result suggests that the increase of substrate availability might increase the fractionation associated with N₂O production. Overall, the Brazilian Oxisol soils had the most enriched δ¹⁵N-N₂O emissions yet measured from soils. If these are more representative of tropical soil emissions than the Costa Rica emissions, then the globally averaged δ¹⁵N-N₂O tropical rain forest soil source is more enriched than previously estimated. The large variations in isotopic signature for N₂O emissions demonstrate the potential utility of stable isotopes as tools for understanding the processes of N₂O production and consumption in soils.

1. Introduction

The concentration of nitrous oxide (N₂O) has increased in the atmosphere since pre-industrial times, and as a greenhouse gas, it contributes significantly to anthropogenic radiative forcing [Houghton *et al.*, 1995]. Its tropospheric mixing ratio is currently increasing annually by ~0.25% [Weiss, 1981]. The reason for this increase seems to be mostly dominated by agricultural intensification since 1500 [Kroeze *et al.*, 1999], with a smaller contribution from fossil fuel combustion, biomass burning, and industrial processes [Thiemens and Trogler, 1991]. Tropical forest soils are the largest natural source of N₂O to the atmosphere [Matson and Vitousek, 1990]. Conversion of tropical forest for pasture and agricultural use changes the rates of N₂O emission from soils; however, the net effect of changing tropical land use on the

N₂O budget is poorly known [Houghton *et al.*, 1995; Keller and Reiners, 1994; Luizão *et al.*, 1989; Veldkamp *et al.*, 1998; Verchot *et al.*, 1999].

The use of stable isotopes of N and O in atmospheric N₂O and its sources has been proposed as a way to better constrain the global N₂O budget [Cliff and Thiemens, 1997; Dore *et al.*, 1998; Kim and Craig, 1993; Naqvi *et al.*, 1998; Rahn and Wahlen, 1997; Yoshinari *et al.*, 1997; Yung and Miller, 1997]. Published data on the isotopic signature of N₂O emissions from tropical soils are limited to a total of six samples taken at two sites (in Costa Rica and Maui, Hawaii) [Kim and Craig, 1993] and the range is large (-25 to 0‰ for δ¹⁵N and 4 to 19‰ for δ¹⁸O relative to atmospheric N₂ and O₂), making it difficult to estimate the global isotopic signature from tropical soils.

Variations in the flux and isotopic signature of N₂O from tropical soils reflect microbiological processes that produce and consume N₂O and physical controls of the rate at which N₂O escapes from the soil pore space to the atmosphere [Firestone and Davidson, 1989]. N₂O is produced in soils during both nitrification and denitrification and is consumed by reduction of N₂O to N₂ in denitrification. The N₂O produced by nitrification is more depleted in ¹⁵N relative to substrates than that produced in denitrification [Barford *et al.*, 1999; Wahlen and Yoshinari, 1985; Webster and Hopkins, 1996; Yoshida, 1988; Yoshinari and Koike, 1994]. Denitrification selects light N₂O for reduction to N₂, enriching the remaining unreacted N₂O in ¹⁵N [Barford *et al.*, 1999]. If

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Paper number 1999GB001181.
0886-6236/00/1999GB001181\$12.00

N₂O escapes from the soil before reduction to N₂ by denitrification, then its isotopic signature will reflect the nitrification and denitrification processes that produce N₂O and that deplete the ¹⁵N in N₂O relative to ammonium or nitrate substrates. If the N₂O is subsequently denitrified (reduced to N₂), then more enriched δ¹⁵N values will be found in the remaining unreduced N₂O that escapes the soil.

Fewer data are available on ¹⁸O variability due to N₂O formation via nitrification and denitrification. The δ¹⁸O of N₂O formed by nitrification may reflect the oxygen isotopic signatures of several sources: hydroxylamine, molecular oxygen, and soil water. To date, no published data are available for oxygen isotopic fractionation associated with N₂O formation via nitrification. The δ¹⁸O of denitrification-derived N₂O should reflect the isotopic composition of the substrate (NO₃⁻). Only two studies are available that show ¹⁸O enrichment factors, and they differ by 60‰ [Barford, 1997; Wahlen and Yoshinari, 1985].

We report here measurements of the isotopic composition of N₂O emitted from tropical rain forest soils in the lowlands of Costa Rica and in eastern Amazonia during the rainy seasons of 1995 and 1998. By measuring the isotopic composition of N₂O precursors (soil organic matter and nitrate), we provide insights into the biogeochemical processes controlling N₂O emissions from tropical forest soils. The use of N₂O isotopic composition variability to explain N₂O production and consumption pathways in soils is limited by the lack of measured fractionation factors for nitrification and denitrification in situ. Fractionation factors are available only for pure bacteria cultures and a few soil studies. Despite this limitation, our study provides significant insights on the mechanisms influencing N₂O production and emission from tropical forest soils.

2. Site Description

We measured the isotopic composition of N₂O emitted from tropical rain forest soils during the end of the wet season of 1995 (Costa Rica and Brazil) and 1998 (Brazil). According to Sanford *et al.* [1994], the climate at La Selva, Costa Rica, is humid tropical, with an average temperature of 25.8°C and annual precipitation of 3962 mm. In Brazil the mean annual temperature is ~25°C, with little seasonal variation, and 80% of the annual precipitation (1850 mm yr⁻¹) falls between January and May [Jipp *et al.*, 1998].

In Costa Rica we sampled a total of three sites at the La Selva Biological Station (10°26'N, 84°0'W, Sarapiquí Cantón, Heredia Province, Costa Rica), including a primary tropical rain forest on Inceptisol (Andic Eutropept) and Ultisol (Typic Tropohumult) soils [Sollins *et al.*, 1994], and a fertilized papaya plantation on Inceptisol soil. Both N₂O and NO emissions have been studied at La Selva [Keller and Reiners, 1994; Parsons and Keller, 1995; Parsons *et al.*, 1993]. The papaya plantation at La Selva was a former Pejibaye palm (*Bactris gasipaes*, *palmae*) plantation, cleared in January 1994 and burned in March 1994 [Weitz *et al.*, 1998]. The plantation was fertilized in May 1995, and we fertilized two plots using a typical application of 67 kg-N/ha the day before collecting N₂O isotope samples. We used a

12:24:12 N-P-K granular fertilizer, in which the N source is ammonium nitrate (NH₄NO₃) with an ¹⁵N isotopic composition of -1.5±0.2‰ (± standard deviation, n=8).

In Brazil we sampled N₂O emissions from two sites within a primary forest on an Oxisol soil at the Fazenda Vitoria in Paragominas, State of Pará. The Fazenda Vitoria site (2°59'S, 47°31'W) is the location for a number of studies of C and N cycling [de Camargo *et al.*, 1999; Davidson and Trumbore, 1995; Nepstad *et al.*, 1994; Trumbore *et al.*, 1995; Verchot *et al.*, 1999]. Our sampling in May 1995 fell within the study period (February 1995 to May 1996) of monthly measurements of N₂O and NO emissions by Verchot *et al.* [1999]. We returned in May of 1998 to repeat sampling from the same sites. The strong El Niño of 1998 was marked by very low precipitation in northeastern Amazonia, so that soils at Fazenda Vitoria were significantly drier in 1998 than in 1995.

3. Methods

3.1. N₂O Isotopes and Fluxes

A minimum of 10 μL of N₂O (at STP) is required for analysis of isotopes using our method. For a sample with a N₂O mixing ratio of 310 ppm, it is necessary to trap and purify at least 60 L of air. We used a molecular sieve trapping system based on the one developed for atmospheric samples by Yoshida and Matsuo [1983] to concentrate N₂O in the field. The N₂O was trapped with a closed air circulation chamber system. The chamber (0.026 m³ volume, basal area 0.1 m²) was placed on a welded aluminum base that had been set in the soil for 24 hours previously. Four samples were taken by syringe at 10-min intervals after chamber closure and measured by electron capture detector (ECD) gas chromatography. The flux of N₂O was determined from the rate of increase of N₂O mixing ratio in the chamber headspace. After syringe sampling, air from the chamber was circulated through the trapping system using a portable vacuum/pressure pump with a flow rate regulated by a needle valve and measured by a mass flowmeter (Figure 1). The chamber had a vent and a tedlar bag inside to assure constant pressure while the air was circulating. The N₂O-free air exiting the molecular sieve 5A trap was passed through a bubbler with water to restore air humidity and then was recirculated into the chamber until N₂O from 60 L of air was collected (flow rate 0.4 L min⁻¹ during a period of ~2.5 hours). Because the initial air trapped in the chamber was included in our sample, we measured the mixing ratio and isotopic signature of below-canopy air and subtracted its contribution from the total N₂O sample. The contribution of initial air varied with the size of the N₂O flux, representing <10% of the total N₂O in samples taken during the rainy season of 1995 but between 23 and 45% during the rainy season of 1998.

At the Brazilian site, we also sampled N₂O isotopes from air in the soil pore space. Here, 10 L of air was pumped slowly (0.1 L min⁻¹) through the trapping system from tubes located at different depths (25, 75, 300, and 500 cm). The tubes were installed ~1 m into the side of a soil pit [Davidson and Trumbore, 1995].

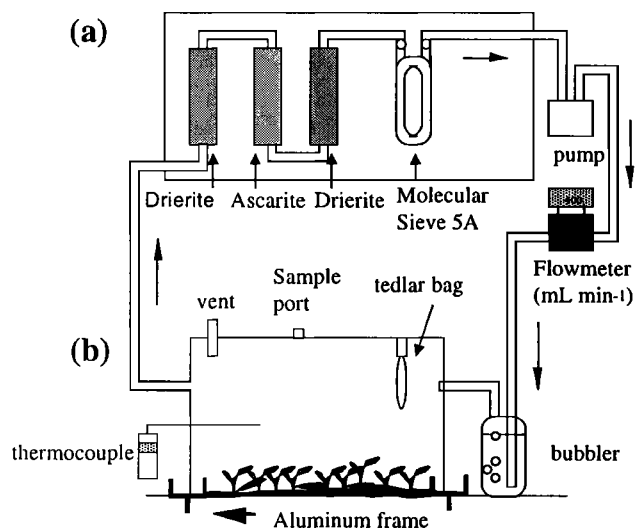


Figure 1. Field collection of N₂O: (a) trapping system and (b) closed chamber system.

3.2. N₂O Purification and Isotope Measurement

N₂O was desorbed from molecular sieve traps under vacuum at 250°C for an hour. The extract was purified using a vacuum line equipped with fine mesh ascarite to absorb CO₂ and silicalite to absorb low-molecular weight hydrocarbons [Rahn and Wahlen, 1997]. The purified N₂O was flame-sealed in Pyrex tubes and stored. We measured the isotopic composition of purified N₂O by direct injection mass spectrometry [Kim and Craig, 1993; Tanaka et al., 1995] on a Finnigan Mat model 252 Isotope Ratio Mass Spectrometer (IRMS). The working reference standard in our lab is a tank of pure N₂O calibrated against Albany N₂O reference gas prepared by Tadashi Yoshinari (New York State Department of Health) [Tanaka et al., 1995]. We measured mass to charge ratios 12/44 and 22/44 as indicators of CO₂ contamination remaining in the purified N₂O samples and correct the N₂O measurement for remaining CO₂ using the method of Rahn and Wahlen [1997]. We tested the yield and ability to quantitatively separate N₂O and CO₂ using known amounts of ultra high-purity N₂O (as a pure standard) and N₂O/CO₂ mixtures. Our measurement precision for dry N₂O working standards is $\pm 0.10\text{‰}$ for $\delta^{15}\text{N}$ and $\pm 0.40\text{‰}$ for $\delta^{18}\text{O}$. Reproducibility for N₂O recovered from actual air samples that have been trapped on the molecular sieve, purified, and measured is $\pm 0.3\text{‰}$ for $\delta^{15}\text{N}$ and $\pm 0.4\text{‰}$ for $\delta^{18}\text{O}$.

Isotopic data are reported as δ values, where $\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1]1000$. $R = {}^{15}\text{N}/{}^{14}\text{N}$ or ${}^{18}\text{O}/{}^{16}\text{O}$. Delta values are reported as deviations from $\delta^{15}\text{N}$ of atmospheric N₂ and $\delta^{18}\text{O}$ of atmospheric O₂. The conversion for the $\delta^{18}\text{O}_{\text{atm}}$ standard to SMOW standard is $\delta^{18}\text{O}_{\text{atm}} = -23 + \delta^{18}\text{O}_{\text{SMOW}}/1.0235$ [Kim and Craig, 1990].

3.3. Soil Nitrate and Organic N

Ten soil samples were collected per site (~300 g of soil from 0-10 cm depth) each time we measured N₂O emissions.

The soil samples were mixed, and an aliquot was used to determine the nitrogen ion concentrations and ¹⁵N in KCl-extractable NO₃⁻ and total organic nitrogen (TON). Ten grams of soil were extracted with 100 mL of 2M KCl within 24 hours of collection using standard procedures. Extracts were filtered using KCl-rinsed Whatman 42 filters, stored at 4°C and transported to Irvine, California, to determine the ion concentration using conventional colorimetric techniques. Concentrations of NH₄⁺ and NO₃⁻ were determined using the salicylate-hypochlorite and modified Griess-Illosvay method, respectively [Mulvaney, 1996]. Reported NO₃⁻ concentrations are the sum of NO₃⁻ + NO₂⁻. Both ions were measured using a HACH DR/2010 spectrophotometer.

The stored KCl extracts were processed to determine ¹⁵N using the diffusion technique described by Sigman et al. [1997]. The final (NH₄)₂SO₄ salts fixed in the acid traps were placed in tin cups and analyzed for ¹⁵N content using combustion Continuous Flow IRMS (CF-IRMS) (Carol Kendall's Lab at U.S. Geological Survey, USGS, Menlo Park and Boston University Stable Isotope Lab). We report analyses of nitrate only because our ammonium samples were lost. Published values of organic N and extractable ammonia and nitrate in soils show that $\delta^{15}\text{N-NH}_4^+$ is usually between values for TON and NO₃⁻ [Binkley et al., 1985; Garten, 1993; Herman and Rundel, 1989; Koba et al., 1998; Nadelhoffer and Fry, 1994].

Organic matter samples were dried and stored. The ¹⁵N of total organic nitrogen was determined using combustion CF-IRMS (Carol Kendall's Lab at USGS Menlo Park and Boston University Stable Isotope Lab). Soil samples were also collected for gravimetric moisture analysis during each chamber measurement. Soil moisture at the Fazenda Vitoria site in Brazil was also monitored using time-domain reflectometry (TDR) probes, described by Nepstad et al. [1994]. Water-filled pore space (WFPS) [Linn and Doran, 1984] was calculated using bulk density values measured for each site.

4. Results

4.1. Soil Properties

Table 1 summarizes the soil properties and concentration of extractable soil N species for both years sampled. The most notable difference between soils from the two sampling locations is in bulk density, with higher values for the Oxisol soil in Brazil than for the volcanic material derived soils of Costa Rica. WFPS was >67% at most sites, although lower values were observed at one forest (site B) sampled in Brazil in 1998 (58%). Organic matter C and N contents were in accord with previous measurements made in tropical forest soils [Martinelli et al., 1999]. Ammonium concentrations were high only in the fertilized papaya plantation soil, and overall NO₃⁻ plus NH₄⁺ was lowest in the Brazilian Oxisol.

4.2. Surface N₂O Emissions

Table 2 summarizes the flux and isotopic signature of N₂O emissions for all sites in the 1995 and 1998 wet season. In 1995, N₂O emissions from the Oxisol in Brazil were consistently enriched in ¹⁵N (-3 to +2‰) compared to N₂O

Table 1. Soil Physical Properties, Elemental analysis and NH₄⁺ and NO₃⁻ Concentration at Each Studied Site

Site	Year	Physical Properties				Elemental composition and ion concentration				
		Bulk Density, g/cm ³	Water Content, cm ³ H ₂ O/cm ³ soil ^c	Pore Space cm ³ /cm ³	Water Filled Pore Space, WFPS,%	Total C g/kg ^d	Total N g/kg ^d	C/N	NH ₄ ⁺ , mg N/kg dry soil ^e	NO ₃ ⁻ , mg N/kg dry soil ^e
COSTA RICA										
	1995									
Inceptisol		0.76 ^a	0.60	0.71	83.9	52.3	4.5	11.69	2.5 (0.3)	12.6 (1.1)
Ultisol		0.69 ^a	0.52	0.74	70.7	57.1	4.6	12.32	12.0 (0.6)	8.9 (0.3)
Papaya plantation		0.79 ^a	0.67	0.70	95.3	63.3	4.6	13.86	71.3 (3.3)	5.5 (0.3)
BRAZIL, Oxisol										
Primary forest B	1995	1.02 ^b	0.41	0.61	66.9	30.6	2.8	11.05	4.2 (0.2)	1.3 (0.2)
Primary forest B	1998	1.02 ^b	0.35	0.78	57.6	23.7	2.2	10.68	3.3 (0.1)	7.7 (0.1)
Primary forest E		1.02 ^b	0.43	0.72	71.3	36.6	2.4	15.40	6.6 (0.1)	7.0 (0.7)

Bulk density and the percent of carbon and nitrogen in soils was measured on the top 10 cm of soil. Standard error is 0.01 (1σ).

^aAverage from 0 to 15 cm of depth [Sollins et al., 1994]. For the papaya site, *n*=29 is the average measured on 1995; values do not differ significantly throughout the year.

^bAverage from 0 to 15 cm of depth. Values do not differ significantly throughout the year.

^cAverage of two replicate sites (*n*=2) during the sampling period. Average standard deviation varied from 0.06 to 0.18.

^dHere *n*=2. Average standard deviation was 0.25 and 0.02 for %C and %N, respectively.

^eStandard error, *n*=3 (1σ).

emitted from Costa Rican soils (-34 to -23‰). N₂O was most depleted in ¹⁵N at the papaya plantation in Costa Rica, which had the highest N₂O emission rates (29-117 ng N cm⁻² hr⁻¹) and also the highest NH₄⁺ concentrations. At Fazenda Vitoria in 1995 the N₂O flux ranged from 28 to 47 ng N cm⁻² hr⁻¹, among the highest measured over the period of 1 year [Verchot et al., 1999], while emissions at the Costa Rican sites (8-26 ng N cm⁻² hr⁻¹) were typical of wet season values at these sites [Keller and Reinert, 1994].

During 1998 we repeatedly measured emissions at four chamber bases using two pairs of chambers placed several meters apart at two sites located ~1 km apart in the primary tropical forest (site B and site E). One of the chambers placed at site B had consistently lighter δ¹⁵N values for emitted N₂O (-34 to -29‰) compared to the others (-9 to -5‰). The rate of N₂O emission was significantly higher for this chamber (9-15 ng N cm⁻² hr⁻¹) than for other chambers (2-5 ng N cm⁻² hr⁻¹). Overall, N₂O fluxes measured in 1998 were considerably lower than those measured at the same sites in 1995. In general, δ¹⁵N-NO₃⁻ at Costa Rica and Brazil was very similar (-2.9 to 0.1‰) whereas TON was ~4‰ lighter in Costa Rica than in Brazil.

The δ¹⁸O values of emitted N₂O sampled in both years (Table 2) ranged from -4 to +18‰ and were more variable within sites than between them. In general, N₂O emissions were more enriched in ¹⁸O in the following order: Oxisol > Ultisol > Inceptisol. We found heavier δ¹⁸O values in N₂O emitted from the Brazilian primary forest during the rainy season of 1998 than we did during the rainy season of 1995.

4.3. Profiles of N₂O in the Soil Atmosphere

Figure 2a shows the N₂O mixing ratios measured in soil air pore space at the primary forest sites in Brazil during the two wet season sampling periods in 1995 and 1998. Also shown

for comparison are mixing ratios measured in the dry season in October, 1995 [Verchot et al., 1999]. In 1995 N₂O mixing ratios were very high in the soil air, with maximum values of ~8 ppm at ~1 m depth. In contrast, samples taken during the wet season in 1998 showed much lower mixing ratios, increasing with depth to 1 m and then leveling off at ~1 ppm. Soil air N₂O mixing ratios for both wet seasons are larger than those in the dry season, though considerable differences are seen between 1995 and 1998 sampling periods.

The isotopic signatures of N₂O measured in soil air pore space in the primary forest sites at Fazenda Vitoria, Brazil, are given in Table 2. In 1995, δ¹⁵N-N₂O values measured to 1 m depth were similar to those of the emitted N₂O, while δ¹⁸O-N₂O values were enriched by ~10‰. In 1998 we sampled depth profiles more extensively. The heaviest ¹⁵N and ¹⁸O values were found at 100 cm depth, with isotopically lighter values at shallower and deeper levels (Figure 2b). The δ¹⁵N and δ¹⁸O of N₂O emitted from the soil surface was lighter in all cases than the shallowest soil air samples (25 cm).

5. Discussion

The data show large spatial variability in the δ¹⁵N of N₂O emitted from primary tropical forest soils from two locations with different soil types (Costa Rica and Brazil sampled in 1995) as well as at the very local scale of a few meters (differences between chambers sampled in Brazil in 1998). Comparison of the amount and isotopic ratio of soil N₂O emissions and soil N₂O profiles from two wet seasons (1995 and 1998) in Brazil show evidence for interannual as well as spatial differences. We attribute these variations to differences in the microbial processes controlling production and consumption within the soil and to physical processes affecting the transport of N₂O from the soil to the atmosphere.

Table 2. Isotopic Composition of N₂O, NO₃⁻, TON and N₂O Fluxes During the Sampling Time at Each Studied Soil.

Sample number: Date-site or depth	N ₂ O			NO ₃ ⁻	TON
	δ ¹⁵ N of N ₂ O Rel. to atm N ₂	δ ¹⁸ O of N ₂ O Rel. to atm O ₂	N ₂ O flux, ng N cm ⁻² hr ⁻¹	δ ¹⁵ N Relative to atm N ₂	δ ¹⁵ N Relative to atm N ₂
Costa Rica 1995					
090695-Ultisol chamber 1	-23.2	10.8	12.44	-2.9± 0.1	5.5±0.1
090995-Inceptisol chamber 2	-23.0	-1.9	8.17	1.3± 0.1	6.2±0.2
090995-Inceptisol chamber 2	-28.1	-0.7	25.81		
090795-Papaya chamber 2	-33.9	-2.2	28.91	2.2± 0.2	6.5±0.01
090795-Papaya chamber 1 ^a	-26.0	-2.2	117.17		
Average	-26.8± 4.5	0.8± 5.6			
Brazil 1995					
Primary Forest B:				-2.3± 0.4	9.7±0.9
052995-chamber 1	-1.8	-3.9	47.37		
053095-chamber 2	-1.2	7.1	47.12		
053195 chamber 1 ^a	1.9	7.3	40.43		
060195-chamber 2	-2.8	11.9	28.46		
Average	-0.97±2.0	5.6±6.7			
053095-25 cm ^b	-0.9	17.0			
053095-100 cm ^b	-1.8	16.5			
Brazil 1998					
Primary Forest B				-0.9± 0.2	11.6±0.1
050798-chamber 1 ^a	-34.1	2.2	9.26		
050998-chamber 1 ^a	-29.2	3.3	14.93		
051098-chamber 1 ^a	-30.5	4.5	13.67		
050798-chamber 2	-9.2	9.0	2.00		
050998-chamber 2	-6.9	13.9	3.36		
Average (chamber 1 excluded)	-8.1±1.6	11.5±3.5			
050898-25 cm ^b	4.5	19.7			
050898-75 cm ^b	4.4	24.8			
050898-300 cm ^b	0.3	17.7			
050898-500 cm ^b	-0.6	16.8			
Primary Forest E				0.1± 0.2	9.4±0.1
050798-chamber 1	-5.8	18.3	2.36		
050998-chamber 1	-9.9	15.9	4.07		
051098-chamber 1	-9.0	17.9	4.74		
050798-chamber 2	-4.8	14.4	3.08		
051098-chamber 2	-5.4	17.7	2.35		
Average	-7.0±2.3	16.8±1.7			
Air at 25 cm above forest Floor ^c	6.3±1.3	21.0±0.7			

All N₂O samples were corrected for CO₂ interference using beam intensity *m/Z* 22/44, the correction ranges from 0.02 to 0.5‰ and 0.04 to 0.9‰ for ¹⁵N and ¹⁸O, respectively. Standard deviation from trapped, purified, and analyzed samples is 0.3 and 0.4‰, for ¹⁵N and ¹⁸O, respectively, *n* = 10.

^aDuplicate samples. Standard deviation is 0.2 and 0.3‰ for ¹⁵N and ¹⁸O, respectively.

^bSamples taken in a soil pit. These values are not included in the average. They might not be representative of the final N₂O that is emitted; see text for discussion.

^cAverage± standard deviation, *n* = 4. Brazil 1995 and 1998.

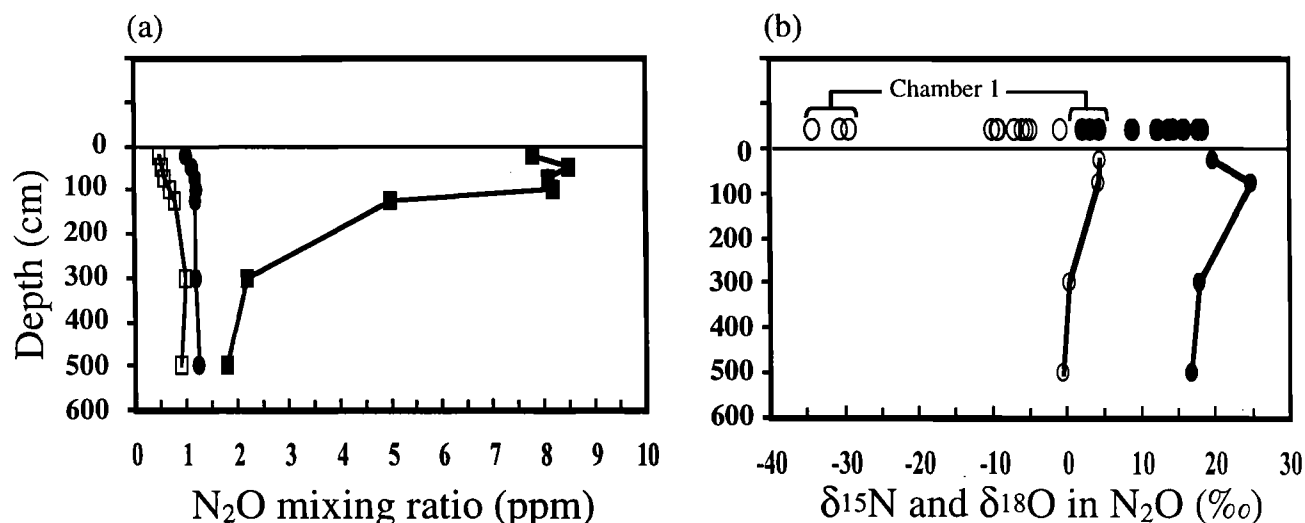


Figure 2. N₂O mixing ratios in soil air during May of 1995 and 1998, and δ¹⁵N and δ¹⁸O in N₂O from soil profile and N₂O emitted from the soil surface on May of 1998. (a) N₂O mixing ratios in soil depth profiles in primary forest in Paragominas, Pará Brazil. Results from 1995 are from Verchot *et al.* [1999] (filled squares, late wet season; open squares, mid-dry season). The 1998 results are measurements done on May 8th (filled circles, late wet season). (b) The δ¹⁵N-N₂O and δ¹⁸O-N₂O during May of 1998 are represented by open circles and filled circles, respectively. N₂O flux isotopic composition for 1998 is shown above ground level (not to scale with y axes).

The interpretation of our isotope results relies on very few published values for enrichment factors associated with N₂O production and consumption via nitrification and denitrification. We assumed enrichment factors of 60 to 68‰ [Yoshida, 1988] for nitrification (NH₄⁺ to N₂O) and 13 to 30‰ [Barford *et al.*, 1999, and references therein] for denitrification (NO₃⁻ to N₂O). This denitrification range is based on measurements done in soil incubation and pure culture studies. We assumed that the enrichment factors determined in these experiments for the overall denitrification process (NO₃⁻ to N₂) equal the enrichment factor for the NO₃⁻ conversion to N₂O [Barford *et al.*, 1999; Peterson and Fry, 1987], which is reasonable for incubation studies where N₂O accumulation is small compared to N₂. We have excluded a value of 30 to 40‰ for enrichment in denitrification by Cline and Kaplan [1975] because it was measured in the ocean and does not overlap with published data from soils. We recognize that these enrichment factors might not adequately represent all soil systems and therefore extrapolations of this discussion must be done cautiously. However, using published values, we are able to suggest plausible explanations for the large observed spatial variability of δ¹⁵N-N₂O emitted from tropical forest soils.

5.1. Differences in ¹⁵N in Emitted N₂O Between Costa Rican and Brazilian Sites in 1995

During the rainy season of 1995 the most likely source of the N₂O emitted from both Brazilian and Costa Rican soils was denitrification. At WFPS > 0.60, denitrification is assumed to be the dominant source of N₂O [Davidson *et al.*, 1993; Keller and Reiners, 1994; Parsons *et al.*, 1993]. N₂O/NO emission ratios >1 are characteristic of

denitrification as shown in biogeochemical studies and soil incubation experiments [Bollmann and Conrad, 1998; Davidson, 1991; Hutchinson and Davidson, 1993; Parsons and Keller, 1995; Parsons *et al.*, 1993]. Measured N₂O/NO ratios at our sites during the rainy season were 35 for primary forest sites in Costa Rica and 5 in Brazil, respectively [Keller and Reiners, 1994; Verchot *et al.*, 1999], also indicating that denitrification is the dominant source of N₂O.

As shown in earlier studies of ¹⁵N in soil inorganic nitrogen, it is likely that δ¹⁵N values of NH₄⁺ and NO₃⁻ are very close to each other [Binkley *et al.*, 1985; Garten, 1993; Herman and Rundel, 1989; Koba *et al.*, 1998; Nadelhoffer and Fry, 1994]. Using 0‰ as a representative value for measured δ¹⁵N-NO₃⁻ values (Table 2) and for assumed δ¹⁵N-NH₄⁺ values and assuming that published enrichment factors available for nitrification and denitrification [Barford *et al.*, 1999; Yoshida, 1988] are representative for our sites, we would expect N₂O produced from nitrification and denitrification to have δ¹⁵N ranges of -68 to -60‰ and -13 to -30‰, respectively. Comparison with the measured range of δ¹⁵N of emitted N₂O from primary forest soils (2 to -34‰) (Table 2) suggests that nitrification is unlikely to be a dominant source of the N₂O emitted from either Costa Rican or Brazilian soils, in accord with interpretations of N₂O/NO.

The lightest δ¹⁵N-N₂O value measured in 1995 (-34‰) was emitted from the fertilized papaya plantation in Costa Rica. Addition of ammonium nitrate fertilizer likely increased both nitrification and denitrification at this site. The applied fertilizer at this site had a δ¹⁵N value of -1.5 ± 0.2‰ (± standard deviation, n=8), close to the 0‰ assumed for NH₄⁺ and NO₃⁻ isotopic composition above. The N₂O/NO emission ratio was 0.08 averaged for the month we sampled [Keller *et al.*, 1998]. This suggests that nitrification contributed to N₂O production in the fertilized papaya plantation.

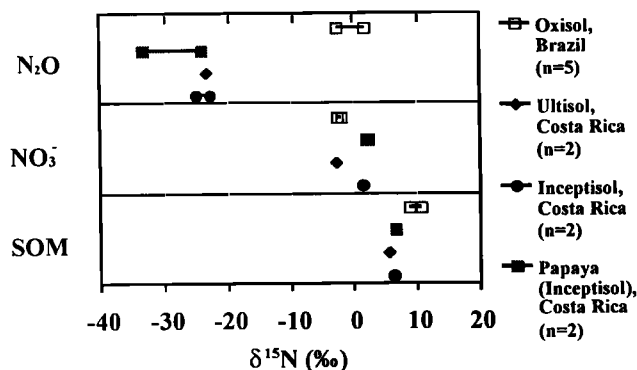


Figure 3. Measured $\delta^{15}\text{N}$ values of N_2O emission, NO_3^- and soil organic matter from Costa Rican and Brazilian soils during the rainy season of 1995.

Figure 3 compares $\delta^{15}\text{N}$ values for N_2O and its precursors for all sites measured in 1995. Values of ^{15}N in KCl-extractable NO_3^- were similar at all sites ($\sim 0\text{‰}$). These $\delta^{15}\text{N}\text{-NO}_3^-$ values were $\sim 5\text{‰}$ (Costa Rica) to $\sim 10\text{‰}$ (Brazil) less enriched in ^{15}N than nitrogen in soil organic matter. Given that denitrification is the likely source of N_2O at primary forest sites and that NO_3^- had similar isotopic composition across sites, we attribute the observed range in the $\delta^{15}\text{N}$ of emitted N_2O to differences in the processes of N_2O reduction during transport through the soil. This is illustrated in Figure 4 where to be able to model the isotopic fractionation associated with denitrification, the denitrification reaction sequence ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$) was assumed to be a two-step process ($\text{NO}_3^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$). This was done because

it has been found in incubation studies that extracellular NO is small [Schafer and Conrad, 1993; Yoshinari and Koike, 1994] and the net NO_2^- production rates are usually very small. Figure 4 shows that relatively depleted values ($\epsilon_1 = 13$ to 30‰) for $\delta^{15}\text{N}\text{-N}_2\text{O}$ are expected from the initial series of reactions leading to N_2O ($\text{NO}_3^- \rightarrow \text{N}_2\text{O}$). The large range of uncertainty associated with this term reflects the range of enrichment factors reported for denitrification in the literature. If N_2O formed in this step readily escapes to the atmosphere, the enrichment factor ϵ_1 fixes the $\delta^{15}\text{N}$ signature of the emitted N_2O . Otherwise, reduction of N_2O to N_2 removes the lighter isotope preferentially successively enriching the remaining unreacted N_2O in ^{15}N [Barford et al., 1999]. We infer that only a small fraction of N_2O was reduced to N_2 in the Costa Rican soils compared to a much larger fraction in the Brazilian soils in 1995 (Figure 4).

Both physical and microbial processes can explain why N_2O consumption might be more efficient in the Brazilian Oxisol than in the Costa Rican Inceptisol and Ultisol. First, Brazilian soils have higher bulk density (Table 1) and are finer textured than the Costa Rican soils. Soil texture affects the water-holding capacity and O_2 availability of a particular soil at the microsite level. Therefore reduction of NO to N_2O and of N_2O to N_2 is more likely in fine-textured soils that hold water better than coarse-textured soils [Bollmann and Conrad, 1998]. Second, reduction of N_2O to N_2 during denitrification is inhibited when the availability of electron acceptors (NO_3^- and NO_2^-) is high relative to the availability of electron donors (organic C), possibly through direct inhibition of N_2O reductase [Firestone et al., 1979; Nommik, 1956]. Extractable NO_3^- concentrations during 1995 were higher in Costa Rican sites compared to Brazilian sites (Table 1).

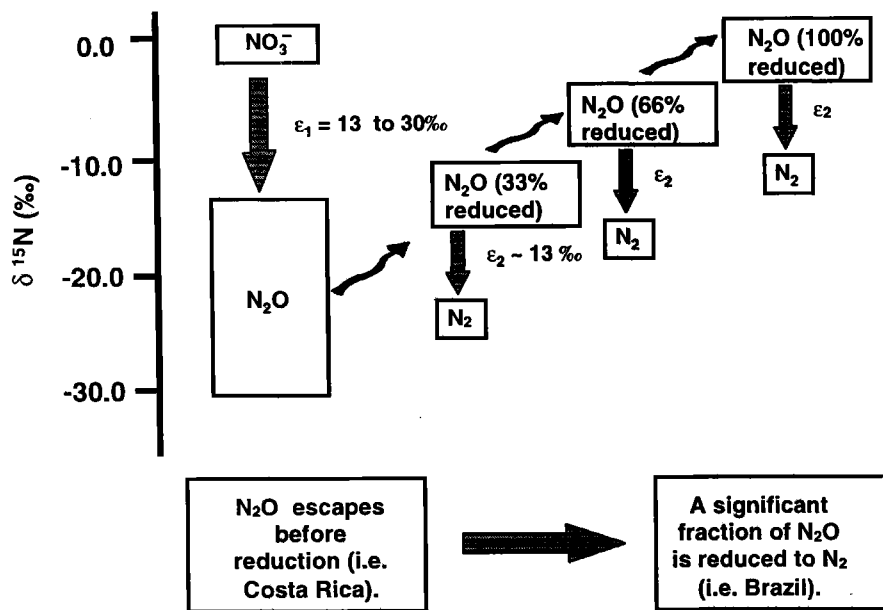


Figure 4. Variations in the $\delta^{15}\text{N}$ of N_2O produced by denitrification where either N_2O or N_2 is the dominant end product. The N_2O produced has characteristic enrichment factors ϵ_1 (NO_3^- to N_2O step) (range based on published enrichment factors by Barford et al. [1999] and references therein) and ϵ_2 (N_2O to N_2 step) [Barford et al., 1999], where $\epsilon = 1000(\alpha - 1)$ and α is the fractionation factor relative to the substrate.

5.2. Isotopic Variability Within a Forest Site

Chamber measurements of N₂O emissions from tropical forest soils regularly show the presence of "hot spots" with elevated emissions. Our 1998 sampling in primary forest in Fazenda Vitoria, Brazil, captured one such "hot spot," with one of the four chambers we deployed showing 3-5 times higher N₂O emissions. The emitted N₂O was 20-25‰ lighter in ¹⁵N than in the other three chamber sites. These differences were sustained over a period of 4 consecutive days (Table 2). The association of high emissions with extremely light N₂O isotopic signatures indicates a difference in the way N₂O was produced, consumed, or transported at this "hot spot," rather than just an intensification of existing processes. It is possible that an enhanced surface source of N₂O (local fertilization increasing both nitrification and denitrification) could be responsible for producing lighter N₂O emissions. This interpretation is also supported by the results obtained in the soil profile. Figure 2b shows the ¹⁵N isotopic composition of the emitted N₂O and the N₂O in soil air at different depths during 1998. The δ¹⁵N-N₂O values in the soil profile are closer to the values measured in the other chambers during 1998 (Figure 2b), whereas that of the "hot spot" chamber (chamber 1) is significantly lighter. This suggests that the N₂O emitted in this "hot spot" was probably derived from surface soil layers.

5.3. Differences Between 1995 and 1998 Wet Seasons in Brazilian Primary Forest

Overall, ¹⁵N signatures of emitted N₂O were lighter (-10 to -5 ‰, excluding "hot spot" values) in the 1998 wet season than in the 1995 wet season (-3‰ to +2‰). The year 1998 was marked by very low rainfall in eastern Amazonia related to a strong El Niño event. Precipitation at the Brazilian site during the month of May was 630 mm in 1995 but only 87 mm in 1998 [Verchot *et al.*, 1999; E.A. Davidson, unpublished data, 1998]. It rained 2 times during the sampling period in 1998, whereas in 1995 rain fell on each sampling day. Several explanations may be offered for the differences in the δ¹⁵N-N₂O between 1995 and 1998. Wetter surface soils in 1995 may have resulted in increased reduction of N₂O before it was emitted, either because of more sluggish diffusion or because more anaerobic microsites were present. Extractable nitrate was higher in May 1998, which may have inhibited reduction of N₂O.

5.4. Implications of N₂O Isotope Values in Soil Profiles

Profiles of N₂O in soil air space show that values at depths above 1 m are greater than the atmospheric value of ~0.3 ppm (Figure 2a). Our isotopic data suggest that at these depths N₂O is likely produced closer to the surface during the wet season and diffuses downward and upward. Isotopic data of N₂O deeper than 1 m are available only for May 1998. At this time, the mixing ratios of N₂O increased from the surface to ~75 cm depth then remained constant at deeper layers (Figure 2a). Maximum δ¹⁵N values for N₂O are also observed at ~75 cm depth, with lighter values of δ¹⁵N and δ¹⁸O both above and below (Figure 2b).

The peak in N₂O concentration at about 1 m depth during 1998 suggests that N₂O could diffuse either upward or

downward along a diffusional gradient from this depth. Because N₂O concentrations were constant with depth below 75 cm in 1998, either N₂O production at depth exactly equals consumption or both fluxes are insignificant. The gradient observed in δ¹⁵N-N₂O and δ¹⁸O-N₂O below 75 cm should reflect molecular diffusion plus any N₂O isotopic change due to fractionation during N₂O production and consumption in deeper soils. We calculated the enrichment factor associated with molecular diffusion of N₂O in air [Jost, 1960] for ¹⁵N and ¹⁸O to be 4.35 and 8.56‰ for δ¹⁵N and δ¹⁸O, respectively (with N₂O isotopes more depleted by these quantities at depth). The measured δ¹⁵N-N₂O for deeper layers (300 and 500 cm) in comparison with the value obtained at 75 cm of depth is lighter by 4.6±0.6‰ and 7.7±0.7‰ for ¹⁵N and ¹⁸O, respectively. This isotopic difference agrees remarkably well with the theoretical values for molecular diffusion, suggesting that there is no other process (production or consumption) affecting N₂O isotopes below 75 cm (Figure 2b).

In contrast to downward diffusion, upward diffusion of N₂O from 1 m depth is also likely to be affected by production and consumption. We estimated the contribution of N₂O produced at 1 m depth to the total surface N₂O emissions using Fick's law: Flux = -D_{eff}d[C]/dz, where D_{eff} is effective diffusivity in the soil, d[C]/dz is the concentration gradient, and z is the dimension along which the net flux takes place (soil depth, here 1 m). It is assumed that the soil N₂O profile and surface fluxes are in steady state on the timescale required for gases to diffuse from 1 m to the surface (<30 min in all cases) and that the soil is horizontally uniform. The N₂O mixing ratio inside the chambers is assumed to be the mixing ratio at surface. We used a range of diffusivities (0.013 - 0.029 cm² s⁻¹) for the top 1 m of soil in wet and dry seasons of a nearby forest site [Davidson and Trumbore, 1995].

The result of this calculation shows that for both years a significant portion (5-56%) of the observed surface flux in Brazil was the result of upward diffusion of N₂O produced at roughly 1 m. The range in the estimated contribution reflects the differences in the N₂O concentration gradients for both years and the range of effective diffusivities used. While the source of N₂O produced deep in the soil contributes significantly to the surface flux, much of that deep N₂O is probably consumed before it escapes the soil. Fractionation due to diffusion should result in δ¹⁵N values of soil N₂O mixing ratios at 1 m deep ~4.4‰ heavier than surface emissions [Cerling *et al.*, 1991], but the differences we observed are greater and therefore also reflect the isotopic signature of production and consumption above 1 m depth. This calculation also implies that N₂O reduction in the Brazilian soil may result from the long distance N₂O travels from the site of production to the soil surface.

5.5. The δ¹⁸O Signature in N₂O Emitted From Soils

It is difficult to interpret the observed δ¹⁸O-N₂O without more information of the isotopic composition of oxygen sources. Because we consider that the N₂O produced in the forest soils is derived from denitrification, the δ¹⁸O-N₂O should reflect the isotopic composition of NO₃⁻ and intermediates (NO₂⁻, NO) and the oxygen isotope enrichment factors associated with each denitrification step. Barford

[1997] estimated an ϵ_o of 105‰ (assuming that exchange between N₂O and H₂O is ignored and that the fractionation is assumed to be constant over all Barford's experimental treatments). *Wahlen and Yoshinari* [1985] determined that during N₂O reduction via denitrification (N₂O → N₂) the remaining N₂O gets heavier in ¹⁸O by a range of 37 to 42‰. Our measured $\delta^{18}\text{O}$ range of N₂O emitted from Brazilian soils is only -4 to 18‰, not much more enriched than the N₂O emitted from Costa Rican sites which have a range of -2 to 11‰. This suggests that either the enrichment factors reported in the literature for ¹⁸O are too large, or these emission factors do not describe the processes affecting the ¹⁸O of N₂O emitted from these soils. We conclude that more work is needed to understand the sources of ¹⁸O in N₂O in soils, which include $\delta^{18}\text{O}$ in H₂O, NO₃⁻ and O₂.

5.6. Global Budget Implications

Figure 5 shows that the tropospheric N₂O isotopic signature reflects a balance between ¹⁵N-enriched N₂O mixing downward from the stratosphere with ¹⁵N-depleted surface sources such as soil emissions. This study has increased the available information for the soil source by a factor of 3. Overall uncertainties in determining N₂O isotopic budget are large and the isotopic signatures of several N₂O sources are as yet unknown. Figure 5 shows large variations in the isotopic signature of N₂O from the soil source indicating that it may be

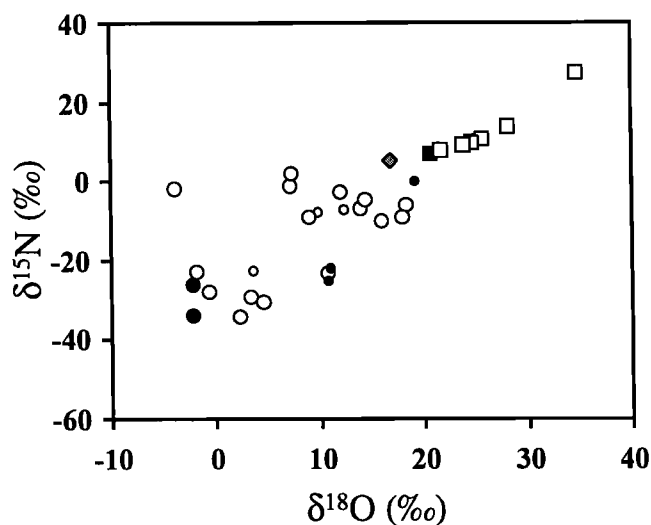


Figure 5. N₂O isotopic composition of the stratosphere, the troposphere and N₂O sources. Tropical rain forest and agricultural soils are represented by open and filled circles, respectively. From the 25 soil points, 19 belong to this study. The six smaller circles are *Kim and Craig* [1993] results from agricultural and primary forest soils. The surface ocean N₂O isotopic composition (shaded diamond) [*Dore et al.*, 1998] is displayed as representative of the dominant oceanic contribution to the atmosphere (the relative contribution from upwelling waters is not well understood). N₂O isotopic composition values of the troposphere (average) and stratosphere [*Rahn and Wahlen*, 1997] are represented by filled and open squares, respectively.

difficult to determine a global average value for the most important natural source of N₂O.

Our measurements of ¹⁵N₂O emitted from primary forest soils in Brazil are ~13‰ enriched compared to a recent estimate of the global average for tropical soils [*Kim and Craig*, 1993]. Oxisols cover ~39% of the Brazilian Amazon, which represents ~31% of global rain forest area [*Richter and Babbar*, 1991]. Globally, Oxisols are more common throughout the tropics than are volcanic ash soils like those in Costa Rica and Maui, where the previous isotopic measurements of N₂O were made. However, Oxisols also include a wide range of soil texture classes, and soil texture appears to be a key factor in determining the fate of in situ N₂O production (escape to the atmosphere versus reduction to N₂) and hence the isotopic composition of N₂O. While our site in Brazil may not adequately represent the wide range of tropical Oxisols, our data suggest the global average isotopic signature for N₂O emitted from soils may be more enriched in ¹⁵N than previously estimated. If, however, isolated spots with high emissions and low- $\delta^{15}\text{N}$ values are an important component of the regional N₂O flux to the atmosphere, the global isotopic signature may be weighted to more negative values.

Rahn and Wahlen [this issue] use estimates of the stratospheric and oceanic sources to predict the globally averaged isotopic signature of N₂O emitted from terrestrial sources. In their mass balance model the terrestrial source prediction was always lighter than the tropospheric N₂O but with a wide range of N₂O isotopic values. Clearly, the uncertainties in determining the globally averaged soil source are large, and more sampling of sources, coupled with mechanistic understanding of how microbial and physical controls affect the isotopic signature of emitted N₂O, are needed. The one agricultural site we sampled had the lightest $\delta^{15}\text{N}$ values we measured for emitted N₂O. Fertilized agricultural fields are an increasing N₂O terrestrial source over the last 100 years. If the N₂O emissions from this source are also isotopically light, then a temporal trend in the isotopic composition of tropospheric N₂O is expected owing to anthropogenically emitted N₂O, as predicted by *Rahn and Wahlen* [this issue].

6. Conclusions

In soils where denitrification is the main source of N₂O, consumption of N₂O by its reduction to N₂ can potentially produce a wide range of values in the $\delta^{15}\text{N}$ of emitted N₂O. Spatial variations in isotopic signature of emitted N₂O at scales of ~1 m are as large as those between very different soil types, and variation among soil types is also large. Having measured a large range of isotopic signatures, it now appears that the source of N₂O from tropical forest soils may be more enriched in ¹⁵N than indicated by previous studies. However, if "hot spots" are associated with isotopically light N₂O, then its relative contribution to the isotopic composition of the global emitted N₂O needs to be determined. The results of this work show the potential to differentiate N₂O biological processes if the current published enrichment factors are representative for tropical rain forest soils.

We want to reemphasize that the interpretation of our results is based on few published isotopic enrichment factors that are generally determined using cultures of pure bacteria. These enrichment factors might not be representative of the bacteria populations present in the soils we have studied. In situ determinations of fractionation factors would allow us to quantitatively link signature of emitted N₂O to the processes involved in its production, consumption, and transport from the soil to the atmosphere.

Acknowledgments. We thank the Instituto de Pesquisa Ambiental da Amazonia (IPAM) and Organization for Tropical Studies (OTS), La Selva Biological Station for logistical support in Brazil and Costa Rica; Carol Kendall, Cecily Chang, and Steve Silva for isotope analysis at USGS Menlo Park; Elizabeth Belk of the Woods Hole Research Center for assistance with gas chromatography in Brazil; Thom Rahn of SIO for his advice with the direct injection measurements method; Tadashi Yoshinari for kindly providing the N₂O standard, and two anonymous reviewers for their helpful comments. We acknowledge funding from the A. W. Mellon foundation and National Science Foundation NYI program (S.E.T.), the California Space Intsitution (S.C.T. and S.E.T.), the CONICIT-Venezuela for Graduate Scholarship award (T.P.), the Terrestrial Ecology Program under NASA grants NAGW-3772 and NAG5-6277 (E.D. and M.K.), the interagency Agreements from NASA (2849-EDBECO-0014), and the U.S. EPA (DW12935643) to the USDA Forest Service (M.K.). This work was done in cooperation with the University of Puerto Rico.

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(Received May 26, 1999; revised October 22, 1999; accepted November 9, 1999.)