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March 28, 1984

Mr. John F. Royall
Grants Officer
NASA, Langley
Hampton, Virginia 23665

Dear Mr. Royall:

I enclose three (3) copies of our semi-annual progress report of research performed under NASA Research Grant NAG1-55 entitled "Sources and Sinks for Nitrous Oxide and Experimental Studies of the Source of Atmospheric COS, CS_2 and CH_3Cl.

Sincerely,

Michael B. McElroy

MBM/ffz
enc.

PROGRESS REPORT
NASA GRANT NAG1-55

N84-20030

MARCH 1984

"Sources and Sinks for Nitrous Oxide and Experimental Studies of the Source of Atmospheric COS, CS_2 and CH_3Cl.

We undertook an extensive series of atmospheric measurements in the tropical forest and savanna of Brazil, as well as adjacent marine areas. Data were obtained for N_2O, CH_4, and CO_2 with replicate analyses at NBS and at O region graduate centers. Measurements of CO in the flasks were made by Rei Rasmussen. A high degree of replication and tight quality controls were used to insure the highest possible precision, with 90% confidence intervals smaller than 1% for CH_4 and N_2O. The data showed that the tropical ecosystem is a major global source of these important trace gases, and the expeditions provided information needed to estimate the source strength using our 3-dimensional GCM/tracer model. The attached report gives a more complete description of this work. Soil fluxes of N_2O, CH_4 and CO_2 were made in conjunction with the atmospheric experiments. Large emissions were found for N_2O and CO_2. The fluxes of N_2O were consistent with the size of the source inferred from atmospheric data. Consumption by soils was observed for CH_4. Since the atmospheric data imply a large net source for the gas, this source must lie elsewhere, most likely in the extensive flooded regions of the Amazon and Paraguay river flood plains. Analysis of water samples from these areas showed very high concentrations of CH_4.

The work in Brazil included also studies of phosphorus distributions and chemistry in the estuary of the Amazon River. This study was intended to help understand the mechanisms controlling mobilization and transport of phosphorus from major rivers, an important problem for the NASA Global Habitability Concept and potential associated oceanographic satellites. The samples are currently being analyzed and experiments are being performed using sediments and water collected in the Amazon.

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March 20, 1984

Amazonian Atmospheric Studies: Preliminary Report

by

Steven C. Wofsy
Center for Earth and Planetary Physics
Harvard University

November, 1983

December 1, 1983

Preface

Studies of the air and water chemistry in the Amazon region of Brazil were initiated during the summer of 1982 in discussions between scientists at Harvard University, Capt. Jacques Y. Cousteau, and Dr. Henrique Bergamin Filho, director of the Institute Nacional de Pesquisas de Amazonia (INPA). As a result of these discussions, Harvard scientists were invited to participate in several experiments at INPA facilities, at other sites in Brazil, and aboard the RV Calypso of the Cousteau Society. Expeditions and participants are summarized in table I. We are indebted to the staff of INPA, to Director Dr. Henrique Bergamin Filho, and to the Cousteau Society for helping to create extraordinary opportunities for environmental research. The present preliminary data report deals with atmospheric studies. A subsequent report will present estuarine data.

December 1, 1983

Introduction

Table II summarizes the composition of the earth's atmosphere, for gases with concentrations greater than 0.1 parts per million by volume (ppmv). The major gases (N_2, O_2, Ar, H_2O, CO_2) were discovered before 1900 and their concentrations were measured accurately by manometric (pressure measuring) techniques. The trace gases (O_3, CH_4, N_2O, CO, H_2) were discovered and measured after 1930 primarily by scientists making spectroscopic observations of sunlight passing through the atmosphere. We now know that there are hundreds of additional minor trace gases (concentrations less than 0.1 ppmv) in the atmosphere. Measurements of these gases are made mainly by sensitive gas chromatographic techniques.

The major gases by themselves cannot participate in rapid chemical reactions, except inside lightning bolts or at the very top of the atmosphere. The trace gases however undergo a vast number of chemical reactions at all levels of the atmosphere. This chemical activity is responsible for removal of hydrocarbons, halocarbons, sulfur oxides, nitrogen oxides, and other pollutants which are emitted to the atmosphere by natural or anthropogenic sources.

The trace gases also play an important role in regulating the temperature of the atmosphere (climate) since they intercept infrared radiation (heat) at wavelengths where the major gases are transparent. For example, we expect the climate of the earth to warm up if the concentrations of N_2O or CH_4 should increase (Lacis et al., 1981). These gases also play important roles in the process which maintains a shield of stratospheric ozone around the earth. Increased levels of N_2O would decrease stratospheric ozone (McElroy et al., 1977). Such change in the abundance of stratospheric ozone could have significant ecological impact, because stratospheric ozone prevents damaging ultraviolet sunlight from reaching the earth's surface.

Atmospheric nitrous oxide (N_2O) became the subject of environmental concern during the 1970's, when it was pointed out that modern agriculture causes major perturbations to natural processes in the soil (McElroy, 1976; McElroy et al., 1977; Bolin and Arrhenuis, 1977; Ehhalt, 1978), leading to enhanced emissions of N_2O. Industrial processes (Weiss and Craig, 1976; Pierotti and Rasmussen, 1976) and biomass burning (Crutzen and Seiler, 1981) could also contribute potentially large sources of N_2O to the atmosphere.

Recent observations confirm that global concentrations of both N_2O and CH_4 are increasing at the present time (Weiss, 1981; Rasmussen and Khalil, 1983; Craig and Chow, 1983) by about 0.2% per year for N_2O and about 1% per year for CH_4. Atmospheric residence times for both gases are long, about 150 years for N_2O and 10 years for CH_4; a simple analysis of observed trends shows that present sources for each gas significantly exceed removal processes. It appears likely that present annual increases should continue, with important environmental consequences, over the next 10-50 years. Indeed data for CH_4 from polar ice cores indicates that the concentration of this gas has doubled since the 16th century (Craig and Chow, 1983) representing a massive perturbation to the atmosphere. The reasons for this increase remain unclear.

The present project was motivated by an urgent desire to determine where and how these gases are produced in nature and to measure emission rates to the atmosphere. Such data are required in order to understand the causes of the present observed changes in atmospheric concentrations. Early studies of N_2O sources focussed on bacterial production in soils

(Goody and Walshaw, 1953; Arnold, 1953), and it was recognized almost immediately that soils of the humid tropics could be especially important. Sources of methane were also expected to be large from tropical ecosystems, especially from seasonally flooded soils (cf. Ehhalt, 1974). The preliminary work reported here is the first to measure atmospheric concentrations and soil emission rates in equatorial ecosystems. The results indicate that the forests and flooded soils of South America are indeed very important sources to the atmosphere. Hence, these ecosystems appear to play a major role in global atmospheric chemistry.

Air Concentrations and Soil Fluxes for CH_4 and N_2O in Brazil

The experiments consisted of two components:

1. The main effort was to determine the differences in concentration of N_2O and CH_4 over the Brazilian landmass, as compared to adjacent oceanic and coastal locations. Higher concentrations over the land would indicate large sources whose magnititude could be estimated using a computer model for atmospheric motions.

2. We wanted also to make preliminary measurements of emission rates from soils in the moist equatorial forest. These data provide comparison with fluxes expected from the analysis in part (1) and serve as the basis for planning future work.

Air sampling and analysis methods are summarized in table III. We were expecting only small variations in the atmospheric concentrations of N_2O and CH_4. Therefore we collected a large number of samples at each station, in order to insure adequate data to compute precise average concentrations. Several different types of container were used to hold the samples, in order to be certain that no artifacts arose due to the influence of the sampling flask. The samples were independently analyzed in three laboratories: Harvard University, Cambridge, MA (Keller, Wofsy); National Bureau of Standards, Maryland; (Elkins); and Oregon Graduate Center (Rasmussen). Excellent agreement was obtained among the different sampling flasks and the various laboratories. We present below only those measurements made at Harvard University.

Results from the first experiment (December, 1982) are shown in table IV, for Manaus and four ocean stations. Comparison between Manaus and the most southerly marine station (0^o latitude) indicates excess N_2O, CH_4 and CO_2 in the Amazon basin.

Tables V-VII and Figures 1-5 show results of the atmospheric measurements for N_2O, CH_4, CO_2 and CO during March and April, 1983. (The CO measurements were made by R. Rasmussen, Oregon Graduate Center). Oceanic and coastal concentrations of N_2O, CH_4, and CO exhibit a gradual decrease from North to South. This trend has been observed many times in the past; it reflects excess biological and industrial sources of these gases associated with the large land masses, dense population and concentrated industrial development of the Northern hemisphere (cf. Logan et al., 1982). Data from oceanic and coastal sites are shown as open circles in figures 1 and 2; all stations except two fall on this gradual trend. The two anomalous sites are 0^o latitude (Amazon Mouth) and Recife (7.5^oS latitude). These two coastal stations and all interior stations show excess concentrations of N_2O, CO_2, CO, indicating that the two anomalous coastal sites were influenced by sources on land.

Contour maps of N_2O, CH_4 and CO concentrations in Brazil are shown in figures 3-5. Highest concentrations are found in the western parts of the Amazon basin and especially near Cuiaba, which is adjacent to the extensive wet lands of the Pantanal. The concentration excess near Manaus was relatively small in March, but larger in December and April. We believe these changes are due largely to atmospheric processes. Rains were very heavy in Manaus in March, which implies intense deep convection and rapid ventilation of the lowest layers of the atmosphere. This interpretation is supported by the computer simulation discussed below.

A number of measurements were made of emission rates for N_2O and CH_4 from the soils of the INPA Bacia Modelo reserve, located 60 km north of Manaus. These data are shown in table VII. The N_2O fluxes measured here are more than a factor of ten larger than fluxes observed in Northern hardwood forests of North America. Forest soils in both ecosystems consume CH_4 from the atmosphere. These data indicate that tropical forest soils may be a major source for N_2O, but not CH_4, as discussed by Keller et al. (1983) (see the appendix to this report). Flooded soils are probably sources of the excess CH_4 found in the air over Brazil. This view is supported by measurements of gas concentrations in the water of <u>Varzea</u> lakes; (these samples were sent to us by Dr. Jeff Richey, University of Washington). <u>Varzea</u> waters contained enormous quantities of CH_4 but little N_2O, typical of carbon-rich, oxygen-poor environments (Elkins et al., 1978). The CH_4 is produced by anaerobic fermentation in these systems.

Discussion

We used a computer model of atmospheric motions to estimate the size of the source for N_2O which would be needed to account for excess concentrations observed in Brazil. Figures 6 and 7 show simulated atmospheric concentrations for a source of $7x10^6$ tons N_2O (as N) per year. Two different distributions were assumed for the sources, as shown in the right-hand panels of the figures; the 'swamp' source was associated with flooded soils, the 'forest' source with the equatorial rainforest ecosystem. Both simulations predict lower concentrations near Manaus in March than in December and both predict maximum excess concentrations in the range 4-6ppb, in agreement with observations.

Figure 8 shows observations of N_2O along the 60^o meridian, compared with model results for March 1983. The observed peak concentrations lie somewhat to the south of the simulations. This discrepancy could reflect an inadequacy of the computer model, since the simulated atmospheric motions are difficult to verify. However one should not rule out the possibility that seasonally dry forest and savannah areas, and industrial activity in southern Brazil, may provide important sources for N_2O, shifting the actual source distribution to the south of that assumed.

The source used in the computer simulation represents about 50% of the current global source of N_2O, and perhaps 70% of the source estimated for unperturbed conditions (i.e. pre-industrial, pre-agricultural). The corresponding values for CH_4 are 15% of the current source and 40% of the unperturbed source. These results indicate that the moist tropical ecosystems of Brazil play a central role in regulating the chemistry of the atmosphere. The present study is, of course, preliminary. Definitive work requires definition of seasonal changes and study of gas fluxes from major ecosystem types in Brazil. It would also be very helpful to make some measurements from an aircraft in order to acquire more representative samples of the atmosphere over a larger area.

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Figure Captions

Figure 1. Data for N_2O and CH_4 atmospheric concentrations in Brazil, plotted against latitude. Marine and coastal sites are shown as open symbols and inland sites are shown as solid symbols. Pv = Porto Velho, Ca = Cuiaba, Ba = Brasilia.

Figure 2. Same as Figure 1, for concentrations of CO in the atmosphere. These data by R. Rasmussen, Oregon Graduate Center.

Figure 3. The data of Figure 1 shown as contours of constant concentration, for N_2O in parts per billion by volume. There were four oceanic stations aboard RV Calypso and 11 stations in Brazil: Bv, Boa Vista; Ms, Manaus; Sm, Santarem; Bm, Belem; Fa, Fortaleza; Re, Recife; Sr, Salvador; Va, Vitoria; Ba, Brasilia; Ca, Cuiaba; Pv, Porto Velho. Manaus was visited in mid-March, while Bacia Modelo (value in parenthesis) was visited in late April.

Figure 4. Same as Figure 3, for CH_4 concentrations in parts per million by volume.

Figure 5. Same as Figure 3, for CO in parts per billion by volume.

Figure 6a. Distribution of equatorial moist forest used in the computer simulation. Seasonally dry areas are also shown.

Figure 6b. Distribution of N_2O in the atmosphere over Brazil, simulated by a computer model for the general circulation of the atmosphere. Contours show excess N_2O (ppb), as compared to the Atlantic Ocean, using a source of $7x10^6$ tons N in N_2O per year from the moist equatorial biome. The right panels show the computer simulation of the source distribution.

Figure 7a. Seasonally flooded soils ('swamp') in Brazil, as used in the computer simulation.

Figure 7b. Distribution of N_2O in the atmosphere of Brazil, simulated for the 'swamp' source.

Figure 8. Observed excess N_2O concentrations along the 60^oW meridian, as compared to marine air at the same latitude. Simulated profiles from the computer model are shown for comparison.

TABLE 1

DATE	LOCATION	OBJECTIVE	HARVARD PERSONNEL
December, 1982	R/V Calypso and Manaus	Amazon estuary, and preliminary air sampling.	Dr. Lewis E. Fox Dr. James W. Elkins
December, 1982	R/V Knorr	Amazon estuary.	Dr. Warren A. Kaplan Mr. Richard Porter
March-April 1983	R/V Calypso and ten Brazilian cities	Air sampling, preliminary soil fluxes.	Mr. Michael Keller Dr. Warren A. Kaplan
May, 1983	R/V Calypso and Belem	Amazon estuary, air sampling.	Dr. Steven C. Wofsy Dr. Lewis E. Fox
September, 1983 August, 1984 (ongoing)	Manaus, Fortaleza, and other cities.	Air sampling, atmospheric seasonal studies, soil fluxes.	Mr. Michael Keller * and others.

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* Mr. Keller's principal effort after September, 1983 was associated with the World Wildlife Fund ecological studies (Dr. Philip Fearnside and others).

TABLE II

ATMOSPHERIC COMPOSITION

GAS	ABUNDANCE		(excluding noble gases) DISCOVERY
N_2	78%		19th century-major gases (%)
O_2	21%		
Ar	1%		
H_2O	0-3%	* #	
CO_2	0.03%	* # @	
O_3	0.01-10 ppm	*	1930 Chapman
CH_4	1.6 ppm	* # @	1948 Migeotte
N_2O	0.3 ppm	* # @	1939 Adel
CO	0.05-0.2 ppm	* # ?	1949 Migeotte (telluric lines in solar spectrum)
H_2	0.5 ppm	* # ?	1951 Glueckauf

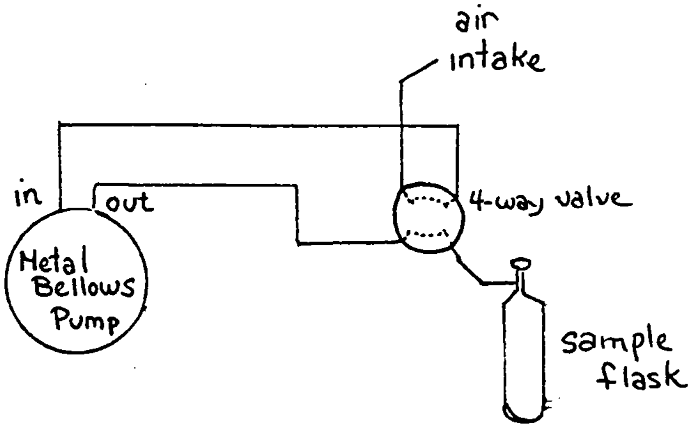
* affected by human activity   # biogenic   @ increasing atmospheric burden

TABLE III

AIR SAMPLING

(sampling)

. Pump arrangement



(sampling) . Redundant Flasks

MATERIAL	VALVE	VOLUME	# AT EACH STATION	SHIPPING
A. Glass (Harvard)	Ace;teflon/viton Young, glass/teflon	300 ml	5	N_2/air 1 atm
B. Glass (NBS)	Young, glass/teflon	300 ml	4	Vacuum packed in newsprint
C. Stainless Steel electropolished	Nupro stainless	4000 ml	1	Vacuum packed in wooden boxes

(analysis) . Simultaneous analysis (in parallel)

N_2O	electron capture gc	Perkin Elmer 3920B (Dec. 82) Shimadzu GC-6 (April)
CH_4	FID gc	Perkin Elmer 3920B
CO_2	ultrasonic detector	Tracor

TABLE IV

AIR SAMPLES FROM DECEMBER 1982

Station	N_2O(ppb)			CH_4(ppm)			CO_2(ppm)		
	c	s	n	c	s	n	c	s	n
1 Manaus 3°S	303.8	4.0	9	1.690	0.024	10	370.3	36	10
2 Ocean 0°S 48°W	300	2.6	9	1.648	0.023	9	351.1	7.0	9
3 Ocean 4°N 50°W	300.3	2.3	0	1.717	0.068	10	357.7	8.2	10
4 Ocean 8°N 58°W	298.0	3.9	13	1.680	0.039	13	361.5	16	14
5 Ocean 12°N 62°W	299.4	3.0	14	2.205*	1.05	13	355.4	11	14
Concentration Difference (Manaus)-(Sta. 2)	4±2 ppb			42±8 ppb			19.2±10 ppm		

90% confidence intervals

c = concentration
n = # measurements
s = standard deviation of the measurements

*contaminated by nearby Venezuelan oil operations.

TABLE V

BRAZIL AIR EXPERIMENT - MARCH 1983 (Harvard data)*

Station	N_2O(ppb)	CH_4(ppm)	CO_2(ppm)	CO(ppb)**
1 12°N,62°W	300.4 3.7(14)	1.649 0.002(14)	344.6 6.6(14)	195
2 9°N, 60°W	299.97 3.1(16)	1.642 0.19(16)	347.5 6.3(16)	190
3 4°N,50°W	299.2 3.1(8)	1.636 0.020(8)	344.8 3.4(8)	176
4 0°N,47°W	300.65 3.6(18)	1.680 0.028(18)	344.8 6.8(18)	219
5. Belem 2°S,48°W	301.8 3.3(14)	1.659 0.22(14)	349.9 6.3(15)	301
6. Santarem 2.5°S,55°W	302.9 3.3(15)	1.809 0.20(15)	379.0 27(15)	278
7. Manaus 3°S,60°W	300.5 3.6(13)	1.678 0.011(13)	395.2 5.8(13)	267
8. Brazilia 16°S,47°W	300.65 2.1(12)	1.666 0.016(12)	327.6 5.0(12)	228
9. Vitoria 20.5°S,40°W	299.08 3.7(21)	1.573 0.008(21)	325.67 2.7(21)	115,140
10. Salvador 13°S,37°W	298.38 4.0(17)	1.582 0.006(18)	328.9 6.0(18)	173
11. Recife 7.5°S,35°W	300.55 2.5(19)	1.683 0.019(19)	344.9 6.8(19)	302
12. Forteleza 3.5°N,37°W	299.0 4.8(20)	1.6665 0.016(20)	336.4 6.7(20)	175
13. Boa Vista 3°N,61°W	299.2 3.9(12)	1.666 0.27(12)	357 3.2(12)	191
14. Bacia Modelo 3°S	305.0 4.0(14)	1.669 0.030(14)	339.0 7.0(14)	No Data
15. Cuiaba 16°S,56.5°W	302.7 3.8(5)	1.8544 0.041(5)	385.3 12(5)	718
16. Porto Velho 8°S,63.5°W	303.6 2.8(5)	1.733 0.020(5)	367.7 9.1(5)	288

*numbers denote: concentration
standard deviation (# measurements)

**measurements by Oregon Graduate Center, R. Rasmussen

TABLE VI

SUMMARY OF CONTINENT/SEA CONTRASTS

Latitude/site	N_2O (ppb)	CH_4(ppb)	date	CO(ppb)+
Manaus 3°S	4.0±2	42±15	December 1982	
Manaus 3°S	0.6±1	72±10	March 1983	90
Boa Vista 3°N	1.0	33		75
Santarem 25°S	4.0	200		102
Belem 2°	2.8	50		130
*Recife 7.5°	1.4	86		125
Brazilia 16°S	1.8	80		50
Cuiaba 16°S, 56.5°W	4.0±1	278±10	April 1983	562
Porto Velho 8°S,63.5°W	5.0	136		110
Bacia Modelo 3°S	6.6	64		

*Coastal site with elevated concentrations. +Measured by R. Rasmussen, Oregon Graduate Center.

TABLE VII

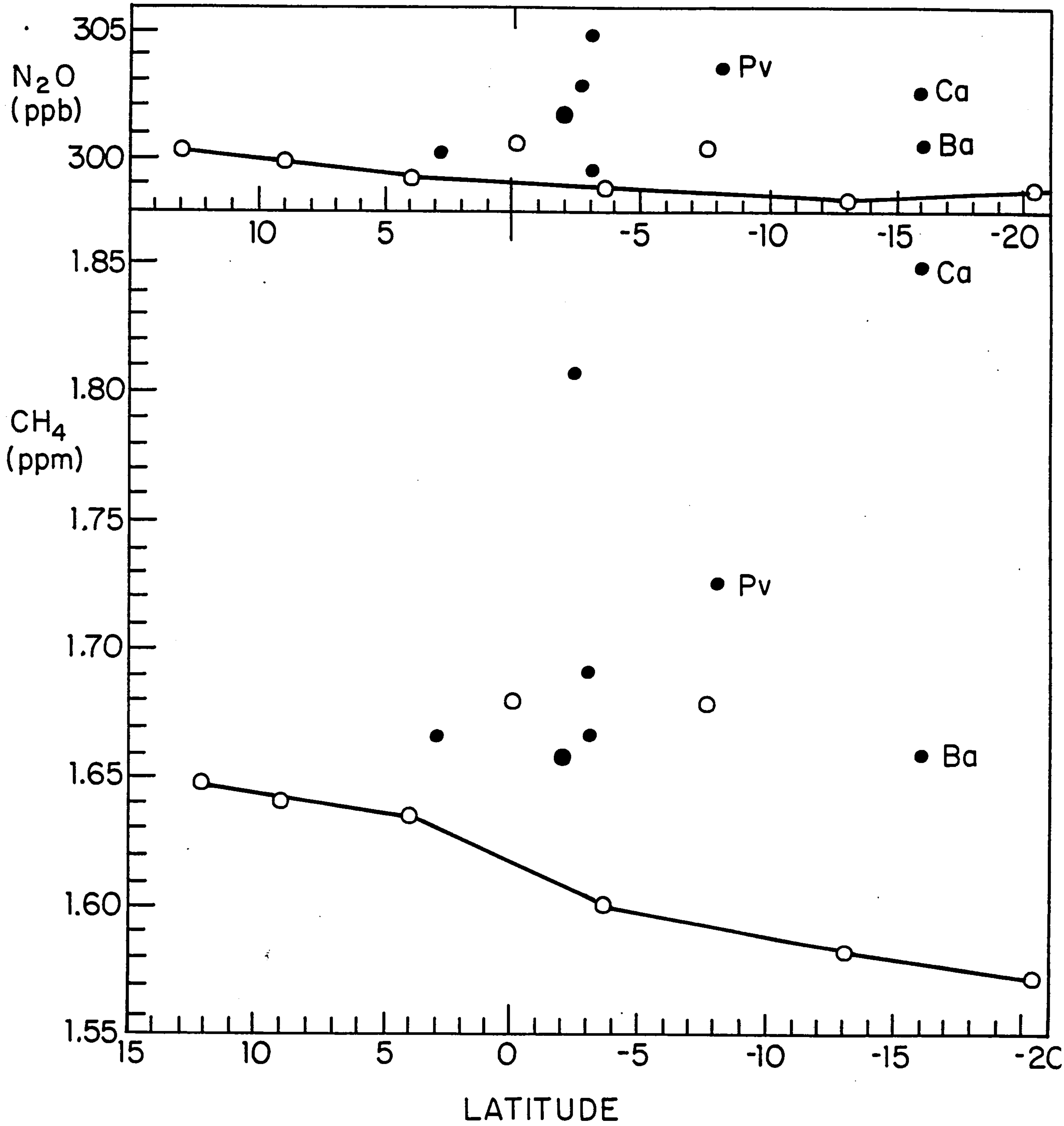
BACIA MODELO FOREST RESERVE 60 km NORTH OF MANAUS

$(10^{10} cm^{-2} sec^{1})$

Site	Flux Box #	N_2O Flux	CH_4 Flux
Base of slope	5	1.35	-2.69
	6	(204)	(-3.99)
On slope	5	2.10	-1.22
	6	2.79	-3.76
Top of hill	5	6.51	-2.03
	6	(3.23)	(-2.21)
Between trees	5	-*	-*
	6	(0.55)	(-7.86)
Tree butress	5	8.87	+1.33
	6	-*	-*
Second growth	5	1.09	-2.40
MEAN		+3.43	-1.92

*No change, box probably not sealed to soil.

FIG 1



305
300
N_2O (ppb)
Pv
Ca
Ba
10
5
-5
-10
-15
-20
1.85
1.80
1.75
1.70
1.65
1.60
1.55
CH_4 (ppm)
Ca
Pv
Ba
15
10
5
0
-5
-10
-15
-20
LATITUDE

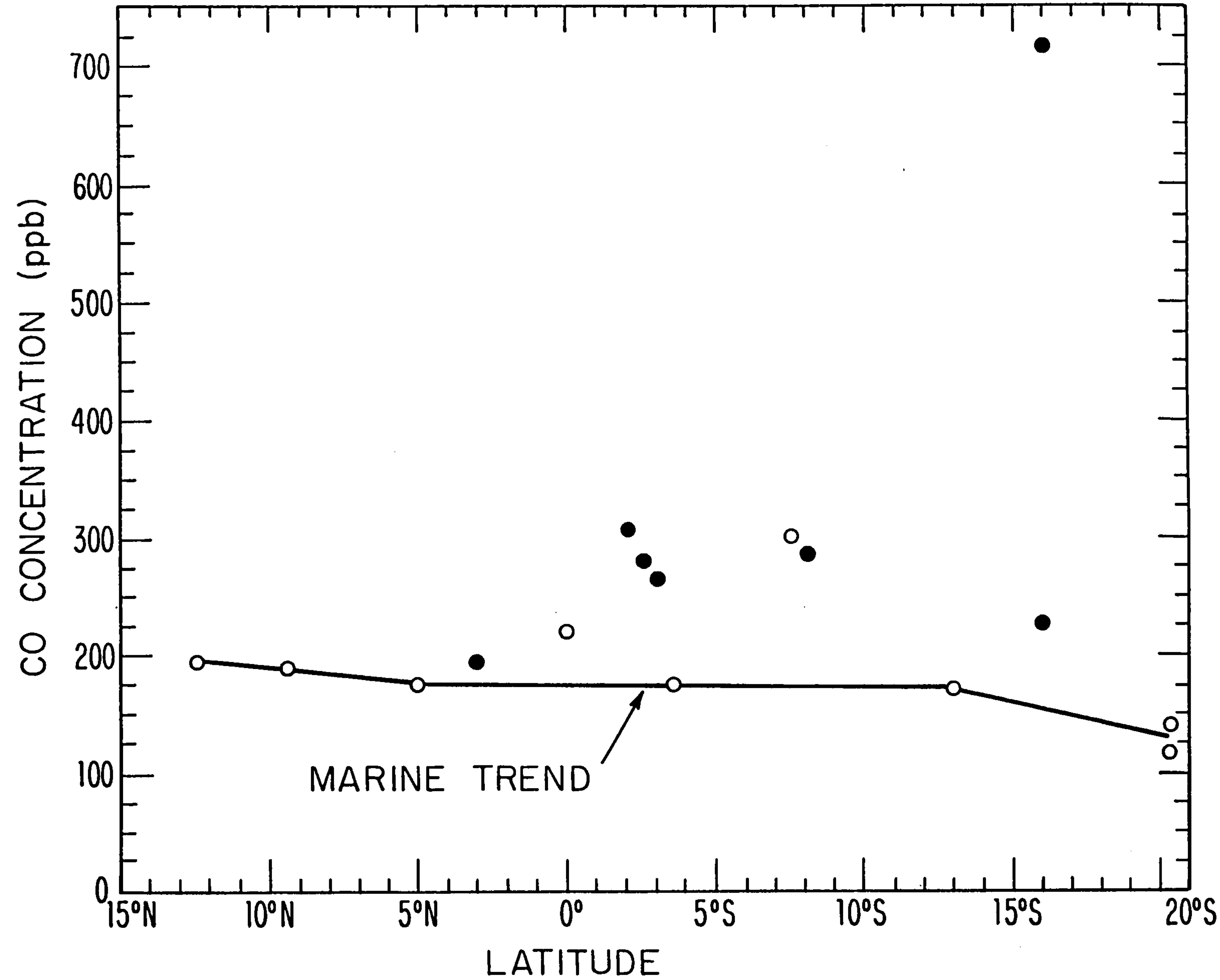

CO CONCENTRATION (ppb)
0
100
200
300
400
500
600
700
15°N
10°N
5°N
0°
5°S
10°S
15°S
20°S
LATITUDE
MARINE TREND

FIG 2

FIG 3

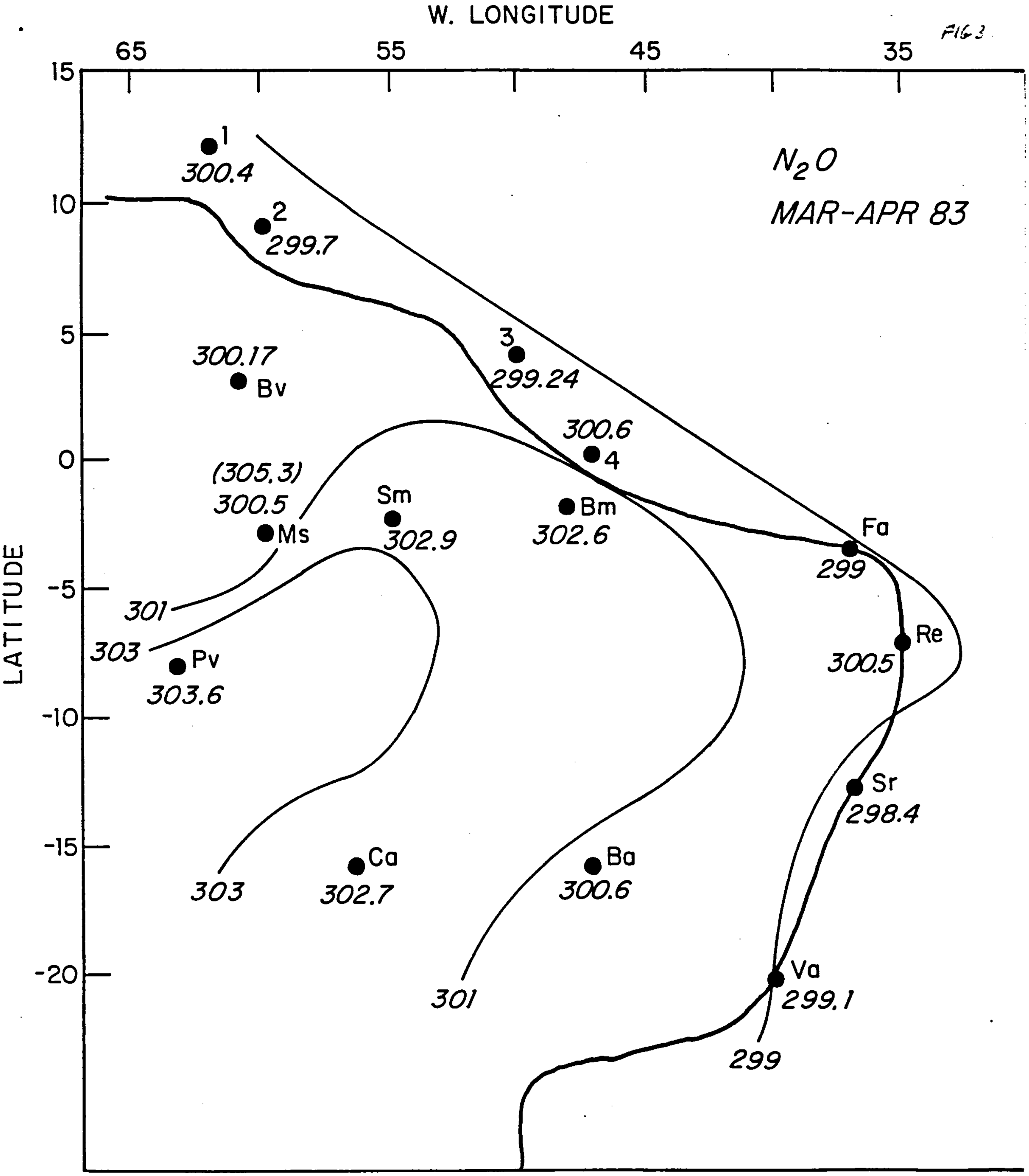


Fig 1. N_2O concentrations in parts per billion

Fig 7

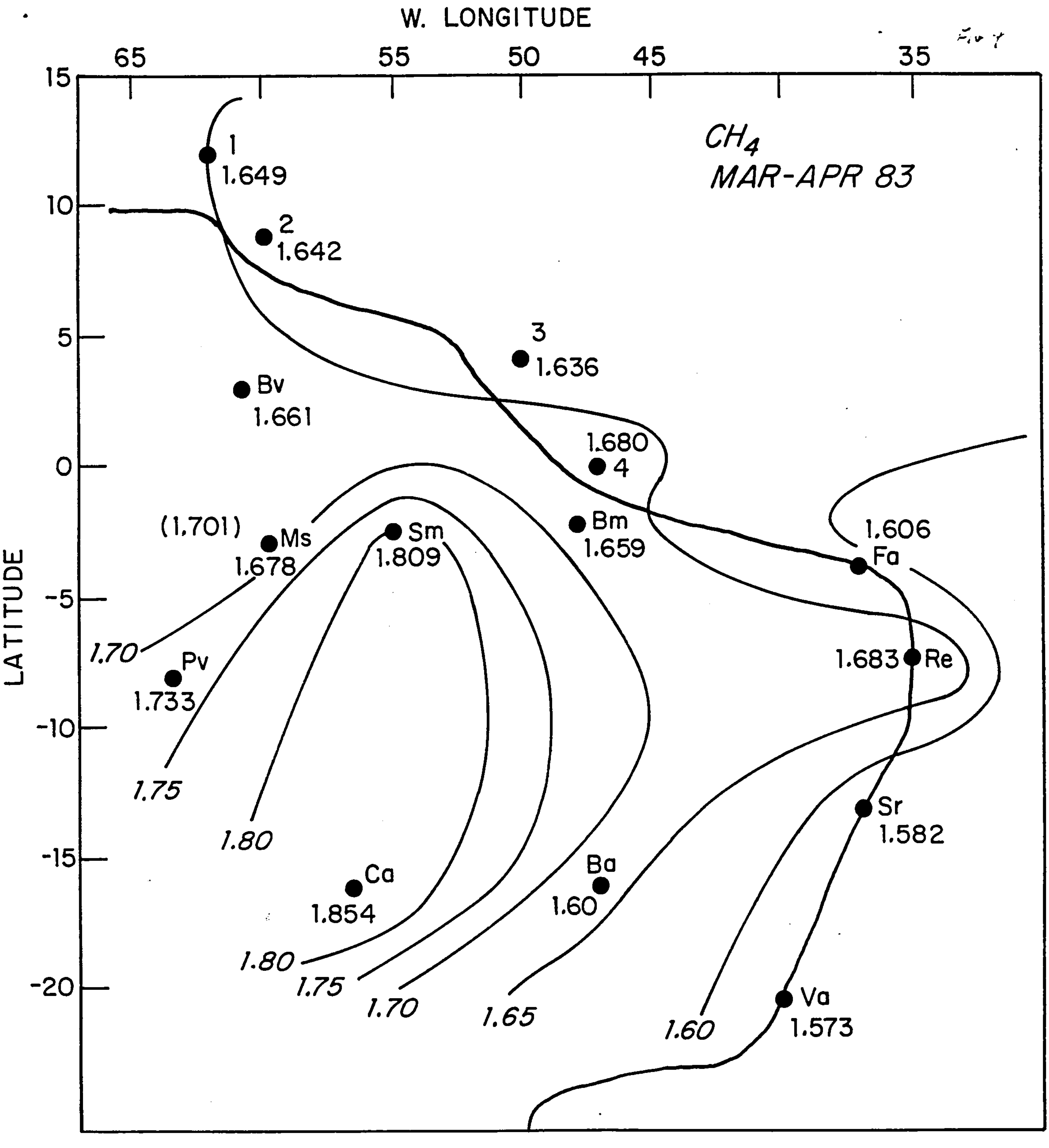
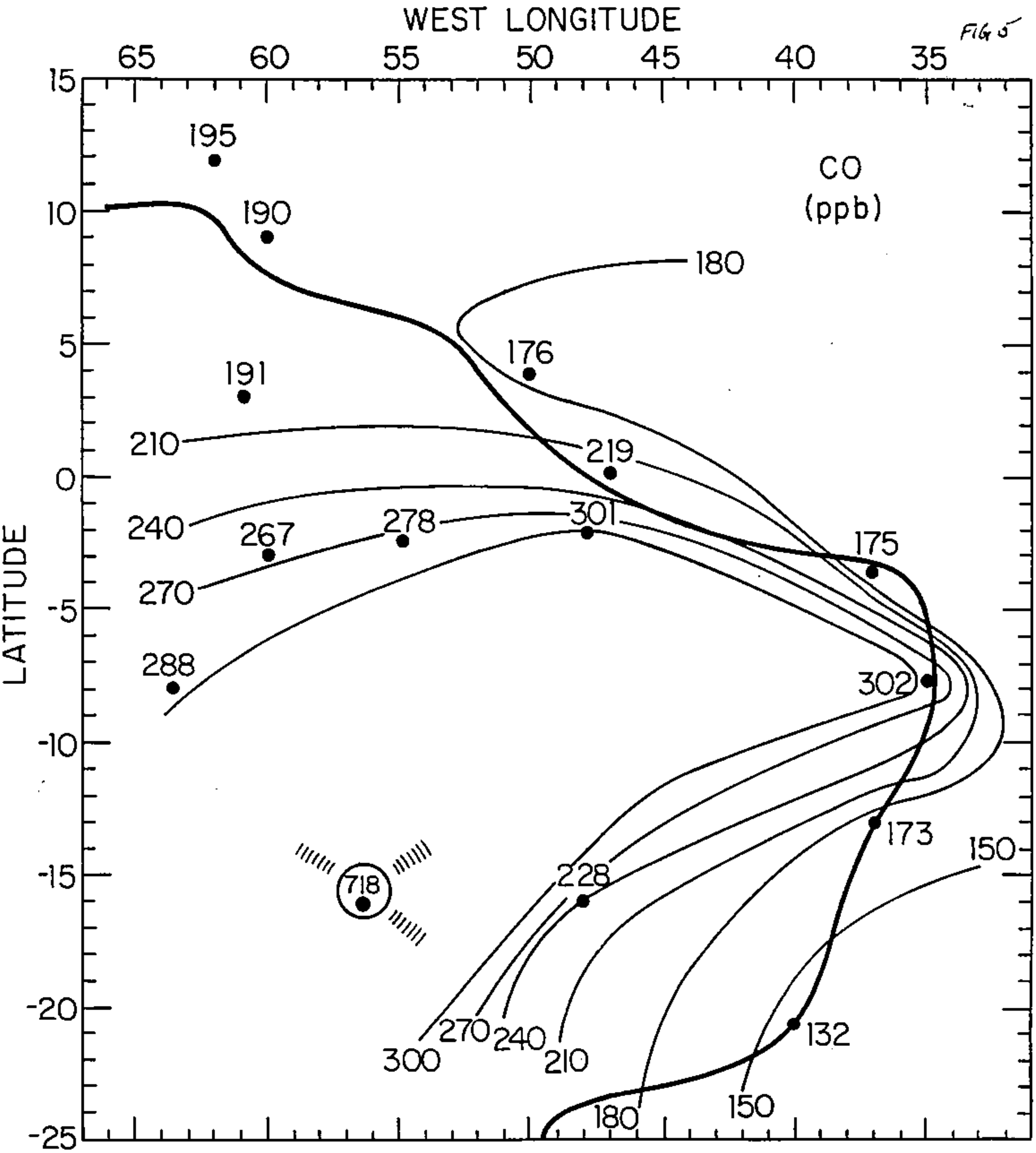


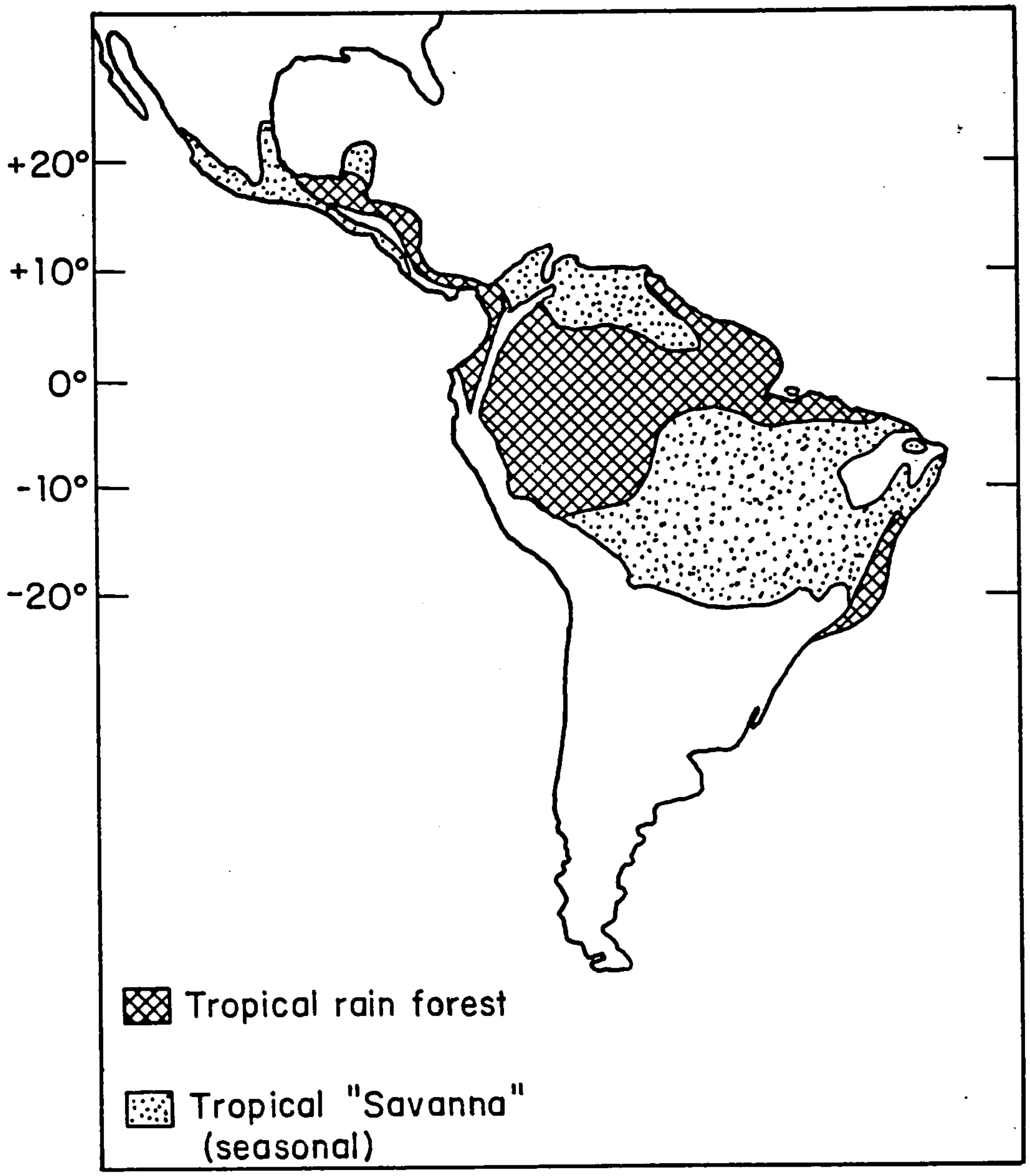
Figure 2. CH_4 concentrations
in parts per million

FIG 5



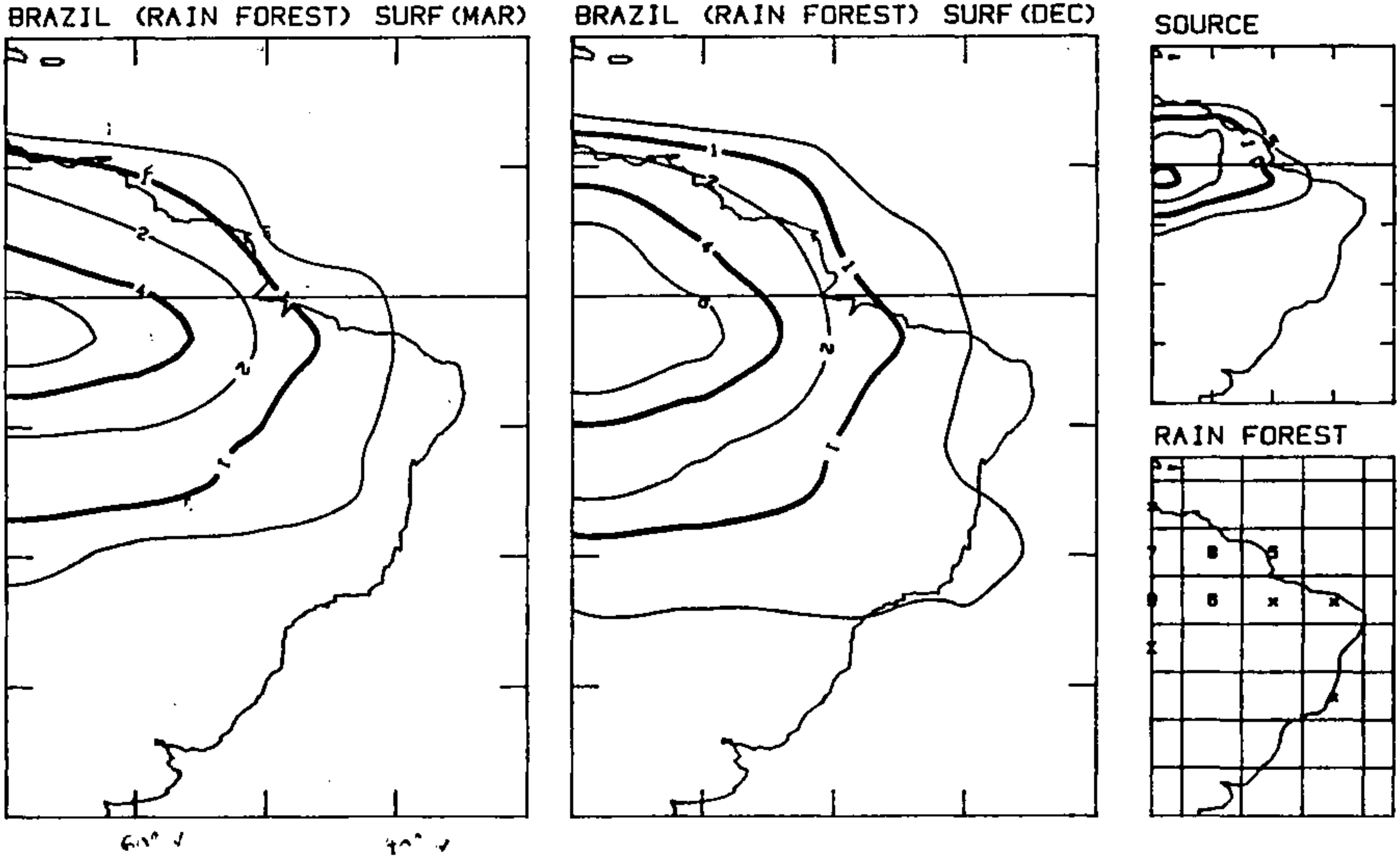
WEST LONGITUDE
65
60
55
50
45
40
35
LATITUDE
15
10
5
0
-5
-10
-15
-20
-25
CO
(ppb)
195
190
180
176
191
210
219
240
267
278
301
175
270
288
302
173
150
718
228
300
270
240
210
132
180
150

FIG 6



+20°
+10°
0°
-10°
-20°
▩ Tropical rain forest
▨ Tropical "Savanna" (seasonal)

FIG 6b


BRAZIL (RAIN FOREST) SURF (MAR)

BRAZIL (RAIN FOREST) SURF (DEC)

SOURCE

RAIN FOREST

FIG 7

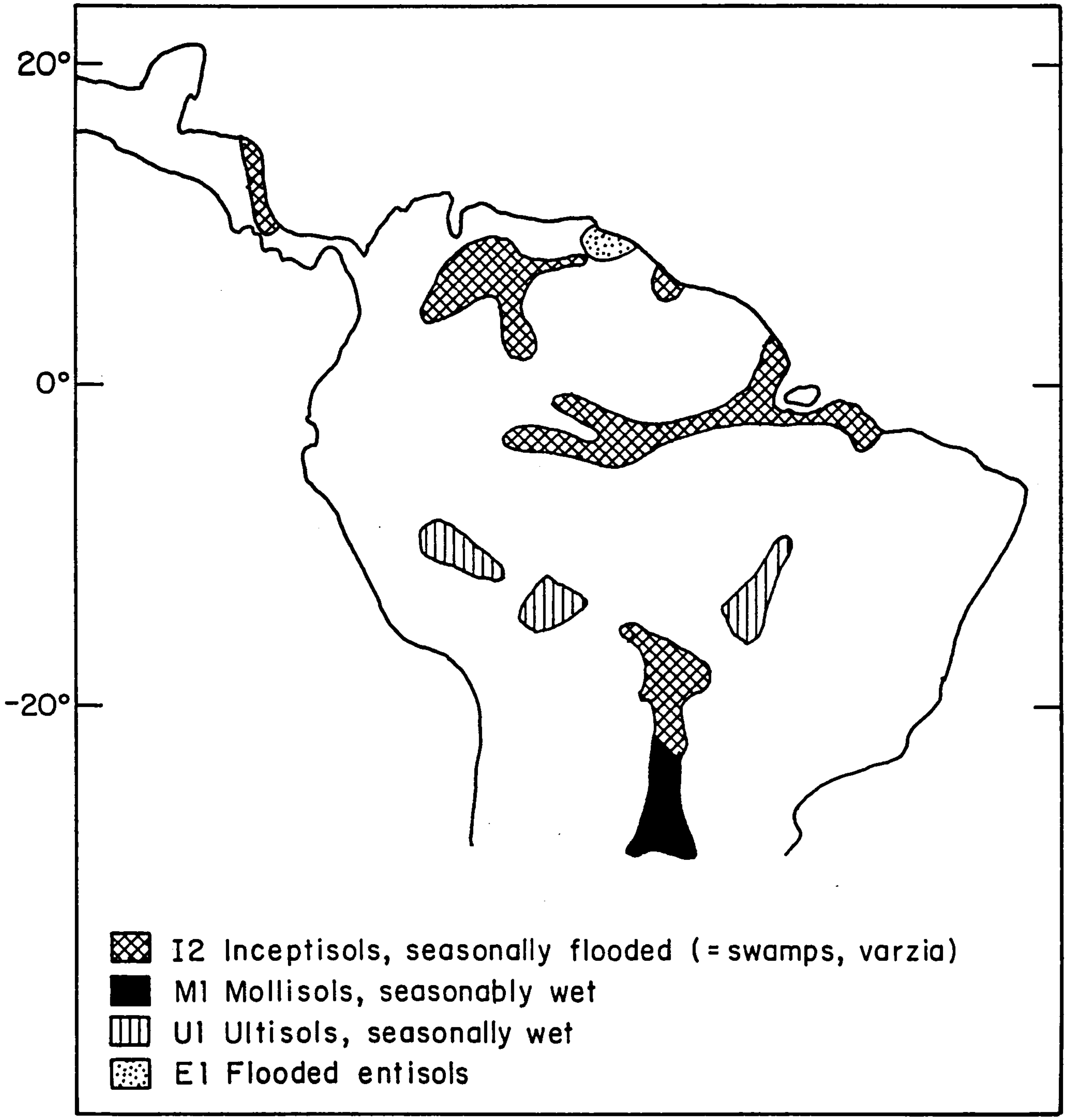
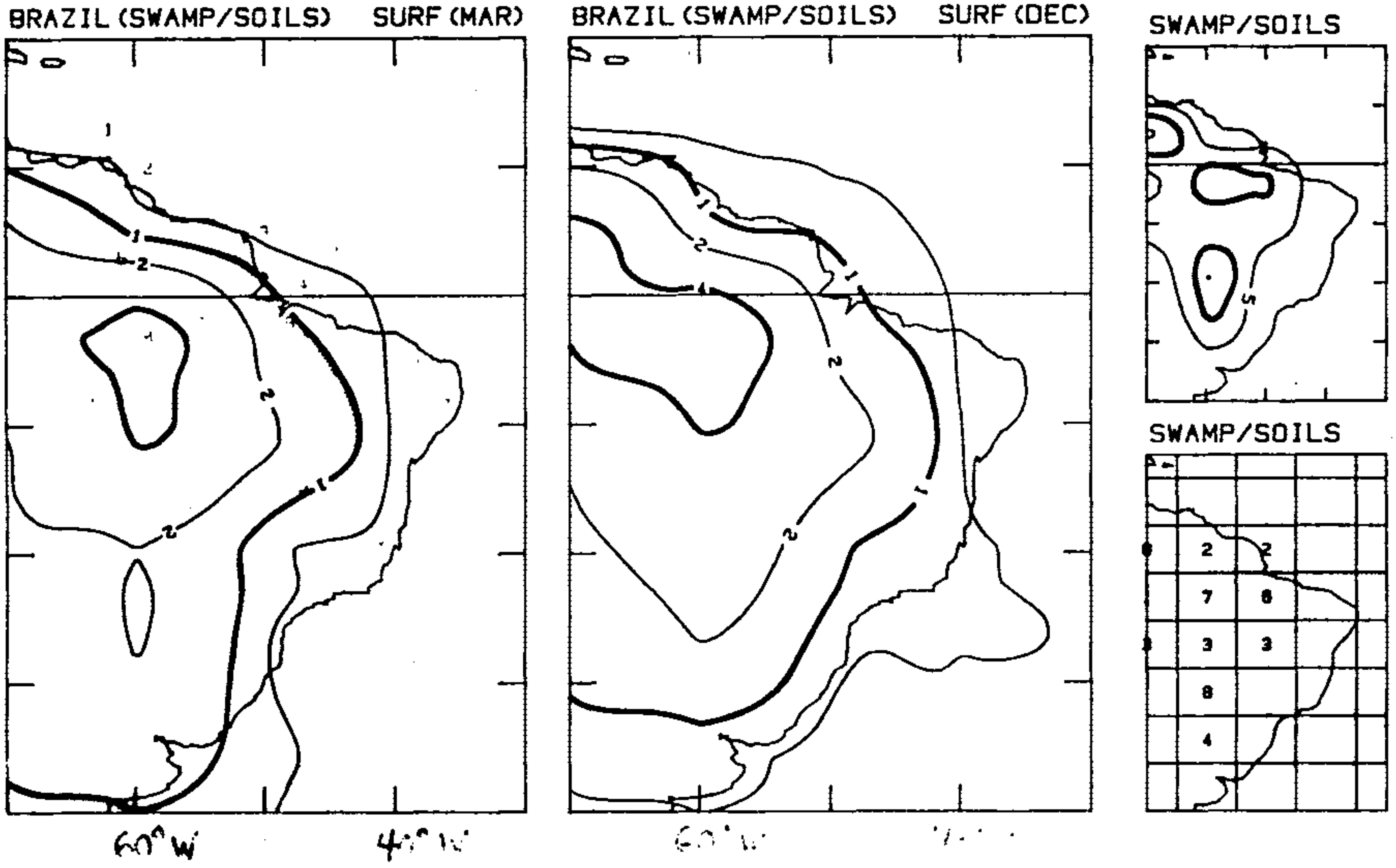

20°
0°
-20°
I2 Inceptisols, seasonally flooded (= swamps, varzia)
M1 Mollisols, seasonably wet
U1 Ultisols, seasonally wet
E1 Flooded entisols

FIG 7b.


BRAZIL (SWAMP/SOILS)
SURF (MAR)
BRAZIL (SWAMP/SOILS)
SURF (DEC)
SWAMP/SOILS
SWAMP/SOILS
1
2
2
2
1
1
2
2
1
2
1
5
2
2
7
8
3
3
8
4
60°W
40°W
60°W

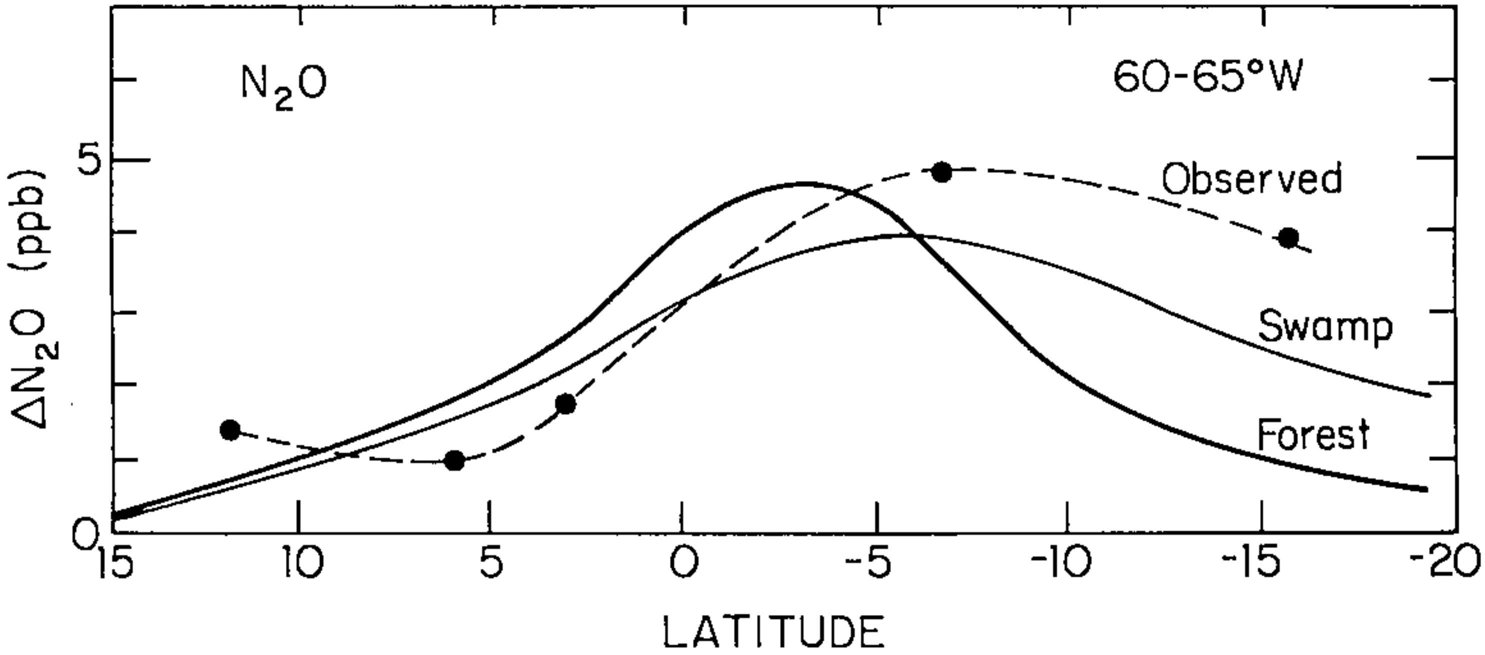

N$_2$O
60-65°W
Observed
Swamp
Forest
ΔN$_2$O (ppb)
5
0
15
10
5
0
-5
-10
-15
-20
LATITUDE

Fig. 8

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PRODUCTION OF NITROUS OXIDE AND CONSUMPTION OF METHANE BY FOREST SOILS

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Abstract. Soils in an Amazonian rainforest are observed to release N_2O at a rate larger than the global mean by about a factor of 20. Emissions from a New England hardwood forest are approximately 30 times smaller than Brazilian values. Atmospheric methane is consumed by soils in both systems. Tropical forests would provide a major source of atmospheric N_2O if the Brazilian results are representative.

Introduction

Nitrous oxide and methane play significant roles in the chemistry and radiative budget of the atmosphere (McElroy and McConnell, 1971; Ehhalt, 1974; Chameides et al., 1977; Crutzen, 1970; Wofsy et al., 1972; Lacis et al., 1981). It appears that the concentrations of both gases are increasing at the present time, nitrous oxide by about 0.2% per year (Weiss and Craig, 1976; Weiss, 1982), methane by between 1 and 2% per year (Graedel and McRae, 1980; Rasmussen and Khalil, 1981; Blake et al., 1982). The increase is believed to be associated with human activity but the underlying chemical and biological controls are incompletely determined. Field studies to date have emphasized the ocean and perturbed fresh water and terrestrial environments. This paper reports results from exploratory investigations of selected undisturbed soils in mid latitude and equatorial forests.

Microbial processes are important both as sources and sinks for N_2O and CH_4. Nitrous oxide is a by-product of the oxidation of NH_4^+, nitrification (Yoshida and Alexander, 1970; Goreau et al., 1981), and is formed also by reduction of NO_3^-, denitrification (cf. Payne, 1982). Nitrification proceeds under aerobic conditions. Denitrification requires that the oxygen concentration should be very low. Anoxic conditions allow further reduction of nitrogen, from N_2O to N_2. The quantity of N_2O released from, or taken up by, anoxic environments depends on a complicated balance of physical and biological processes.

It appears that similar competition may occur for CH_4. Methane is produced by methanogenic bacteria functioning under strictly anaerobic conditions. It is consumed by a separate class of organisms requiring O_2 as electron acceptor. As we shall see, consumption in soils dominates exchange of CH_4 with the atmosphere for the environments studied here. In contrast soils provide a signficant source for atmospheric N_2O.

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Experimental Methods

Data were taken at six sites in an undisturbed stand of hardwoods at Hubbard Brook, New Hampshire (Likens et al., 1977), and at a similar number of locations in the Bacia Modelo Reserve of the Instituto Nacional de Pesquisas de Amazonia (INPA). The data from Hubbard Brook were acquired at approximately two week intervals during the growing seasons of 1980 and 1981. Measurements in Brazil were made during April 1983.

The forest at Hubbard Brook is an aggrading stand, 65 years old, classified as part of the Northern Hardwood Forest ecosystem (Bormann et al., 1970). The forest floor is composed of partially decomposed leaf litter with underlying soils developed from granitic glacial till. Annual precipitation averages about 1300 mm. Soil temperatures vary seasonally from about 6°C in May to 17°C in June 21. The six sites included a variety of drainage conditions at a mean elevation of 580 m.

All samples from the Bacia Modelo Reserve (elevation 50 m), approximately 60 km north of Manaus, were collected beneath the canopy (28 m high) of a mature, upland (terra firme) tropical moist forest. The sites were located on a transect leading uphill from a small stream. Soils were yellow-grey oxisols characteristic of this region, with scant surface organic material. Precipitation averages 2000 mm per annum, with heaviest rains from December to May (>200 mm month^{-1}). Soil temperature (at 5 cm) for the six sites on the date of sampling averaged 25.8°C.

A closed chamber technique (Goreau, 1982) was used to measure fluxes of gas across the soil-air interface. Duplicate adjacent aluminum chambers, dimensions 40x20x10 cm (lxwxh), were inserted into the forest floor to a depth of 1 cm. Four or five 40 ml gas samples were removed from the chambers over a period of 30 to 60 minutes using 50 ml glass syringes. Pressure equilibrium was maintained with the atmosphere during sampling by admitting outside air through a large-bore syringe needle. Gas diffusion along the barrel of the syringe was inhibited by wetting the barrel with a small amount of distilled water, allowing preservation of gas concentrations for at least two weeks.

Concentrations of CH_4 were determined using flame ionization gas chromatography (Perkin Elmer model 3920). Samples were passed through a trap maintained at -78°C, in order to remove water vapor, then into a 1 ml sampling loop attached to a 6-way Carle valve. Concentrations of methane in dry air were determined by comparison with commercially prepared standards. Precision for repeated analyses was better than one percent. Concentrations of N_2O were measured simultaneously with those for CH_4 using gas chromatography

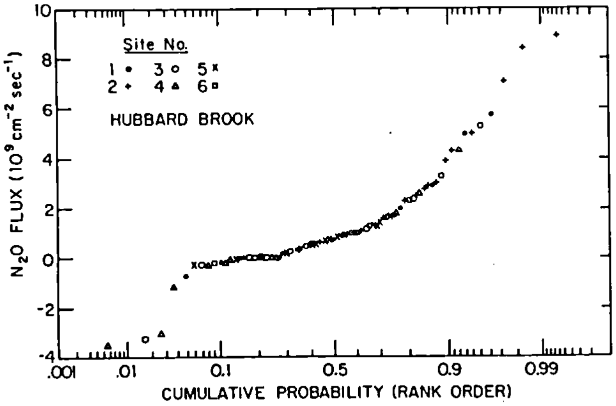

Fig. 1a. Flux of N_2O from the forest floor at Hubbard Brook, N.H., during the 1981 growing season. Observations are plotted in ascending order on probability paper, such that normally distributed data would fall on a straight line. The annual mean flux is less than 10^9 molecules cm^{-2}sec^{-1} with 90% confidence limits about the mean of approximately $\pm 5x10^8$.

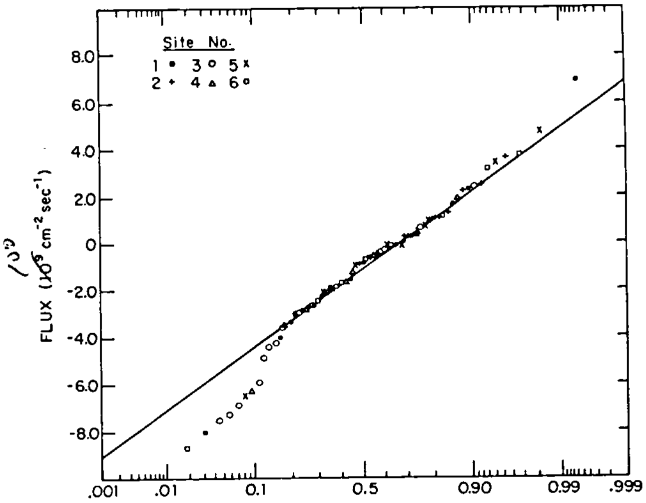

Fig. 2a. Fluxes of CH_4 observed from forest soils during the growing season of 1981 at Hubbard Brook, N.H., showing mean consumption. The straight line is drawn as a visual guide.

with electron-capture detection. The flux of gas across the soil-air interface was calculated by fitting a line to data defining concentration as a function of time in the chamber. The magnitude of the minimum detectable flux for CH_4 is about $2x10^9$ molecules cm^{-2}sec^{-1} (~40 μg CH_4 m^{-2}day^{-1}), corresponding to a change of concentration in the chamber of 0.02 ppm in 30 min. The minimum detectable flux for N_2O is about $3x10^8$ molecules cm^{-2}sec^{-1} (~12 μg N in N_2O m^{-2}day^{-1}). By comparison, the global mean source of CH_4 (500 Tg yr^{-1}) corresponds to a planetary average emission of $2x10^{11}$ molecules cm^{-2}sec^{-1} while that for N_2O (12 Tg yr^{-1}) equals $1.6x10^9$ molecules cm^{-2}sec^{-1} (cf. Logan et al., 1978, 1981).

Results and Discussion

Flux of gas from forest soils at both locations was quite variable. Fluctuations in the rate for exchange between soil and atmosphere can be studied conveniently using an approximate probability distribution function. Fluxes are arranged in order of ascending magnitude. The probability of finding a value less than F_i is approximated by $(i-1/2)/N$, where i is the rank of F_i in the list and N is the total number of observations (Blank, 1980, p. 428 ff). Results are plotted on probability paper such that normally distributed data define a straight line. Probability distributions for nitrous oxide are shown in Figure 1.

The observed probability distribution deviates from normal, with high fluxes of N_2O observed in rare events. Similar fluctuations have been observed for agricultural systems by McKenney et al. (1978), Bremner et al. (1980), and Hutchinson and Mosier (1979). Emission rates are much higher at the tropical sites than at Hubbard Brook, in some instances by as much as 2 orders of magnitude. The mean flux of N_2O at Bacia Modelo is $2.6x10^{10}$ molecules cm^{-2}sec^{-1}. The annual mean flux at Hubbard Brook was less than $1.0x10^9$ molecules cm^{-2}sec^{-1}.

Tropical evergreen forests cover about $10x10^6$ km^2 at present, having originally occupied about $15x10^6$ km^2 (Meyers, 1980). If the observations at Bacia Modelo are assumed typical of such ecosystems, soils of tropical moist forests could provide a major fraction of the present global atmospheric input of N_2O; the source from tropical seasonal forests could be comparable. As will be discussed elsewhere, concentrations of N_2O over Brazil are appreciably higher than the global background. These data support the view that tropical terrestrial ecosystems play a significant role in the budget of atmospheric N_2O. Tropical forests are now rapidly exploited for timber harvest and for agriculture (Meyers, 1980), a development likely to lead to significant future change in the source for N_2O.

Data for CH_4 at Hubbard Brook in 1981, some 79 measurements, are displayed in Figure 2a. Soils at Hubbard Brook appear to provide a net sink for atmospheric methane. The observed flux has a mean value of $-1.2x10^{10}$ molecules cm^{-2}sec^{-1} with

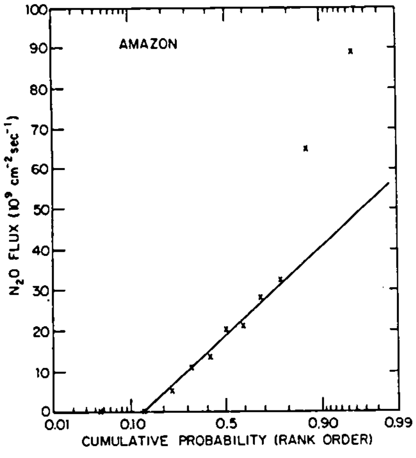

Fig. 1b. Flux data for N_2O from the forest floor at Bacia Modelo.

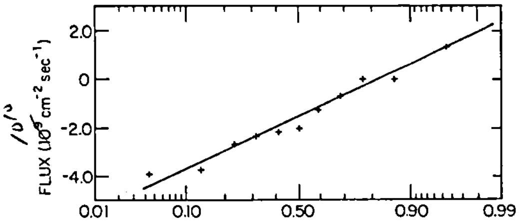

Fig. 2b. Same as 3a, for CH_4 at Bacia Modelo in equatorial Brazil.

a standard deviation of $3.5x10^{10}$ molecules cm^{-2} sec^{-1}. Ninety percent confidence intervals about the mean are $-1.83x10^{10}$ and $-0.65x10^{10}$ molecules $cm^{-2}sec^{-1}$. The distribution deviates from normal for the largest consumption rates, suggesting a distinct subpopulation corresponding to intense uptake of methane. The warmest and driest site (site 3) accounts for 7 of the 13 observations in this subpopulation.

Net consumption of CH_4 was observed on all seven sampling dates. No significant trends were detected either with season or with soil temperature. Site 2, a seep where groundwater emerged at the surface, accounts for 9 of the 26 observations with positive flux. If site 2 were excluded from the analysis mean consumption would be $-1.7x10^{10}$ molecules cm^{-2} sec^{-1}.

Figure 2b shows the methane flux data for Bacia Modelo. The mean flux here is $-1.6x10^{10}$ molecules $cm^{-2}sec^{-1}$, about the same as for Hubbard Brook during the growing season, with 90 percent confidence limits of -2.51 to $-0.71x10^{10}$ molecules $cm^{-2}sec^{-1}$. The data base for the Amazon is much more limited than for Hubbard Brook: consumption patterns appear similar, however.

These data demonstrate a capacity of soils to take up atmospheric methane at a mean rate of about $2.5x10^{-4}$ g CH_4 m^{-2} day^{-1}. In contrast, Sheppard et al. (1982) reported emission from forest soils at rates from $3.8x10^{-2}$ to $6.5x10^{-2}$ g CH_4 $m^{-2}day^{-1}$. The contradiction appears to result from a difference in sampling methodology. Sheppard et al. (1982) employed a chamber filled with methane-free zero-air. Zero-air was allowed to flow through the chamber during the sampling interval, a technique expected to induce transfer of CH_4 from the soil pores to the headspace within the chamber. Fluxes derived on the basis of these data are consequently suspect.

Uptake of atmospheric methane by soils represents a small fraction (<1%) of the global sink due to reaction with OH (cf. Logan et al., 1981). Nevertheless consumption in soils may play a major role in modulating release of methane to the atmosphere from biological systems. Methane-oxidizing bacteria are widespread in soils (Hanson, 1980), with conditions for growth particularly favorable at the interface between the atmosphere and the anaerobic environments where CH_4 is produced. Harriss et al. (1982) observed vigorous production of CH_4 by waterlogged anaerobic soils in the Great Dismal Swamp of Virginia. On occasions when the surface of the soil dried out, however, and the upper soil layers became aerobic, methane was rapidly consumed (flux ~ $-2x10^{11}$ $cm^{-2}sec^{-1}$). Present results indicate that the capacity for efficient oxidation of CH_4, detected by Harriss et al. (1982), is not restricted to unusual environments, but is widespread in aerobic soil systems.

In summary, it appears that soils of tropical rainforests provide a gobally significant scurce of N_2O. Methane was consumed by soils in both temperate and tropical forests.

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