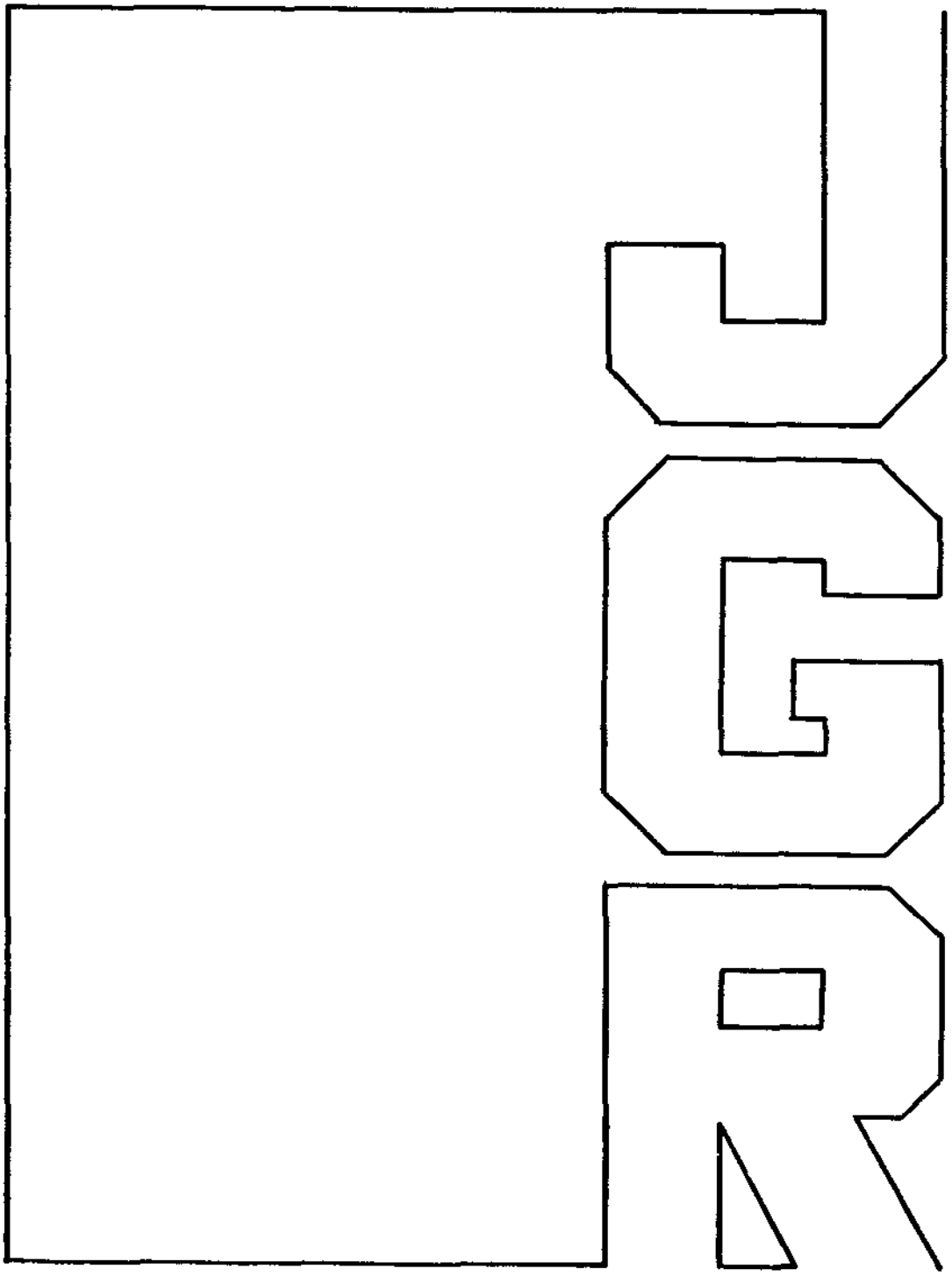
MFN= 007226
01 SID/SCD
02 5872
03 INPE-5872-PRE/2015
04 CEA
05 S
06 as
10 Kirchhoff, Volker Walter Johann Heinrich
10 Rasmussen, R.A
12 Time variations of CO and 03 concentrations in a region subject to biomass burning
14 7521-7532
30 Journal of Geophysical Research
31 95
32 D6
40 En
41 En
42 <E>
58 DGE/DIR
61 <PI>
64 May <1990>
68 PRE
76 GEOFISICA ESPACIAL
83 Carbon monoxide (CO) and ozone (O3) concentrations have been observed in the Brazilian Amazon region, at a site strongly affected by biomass burning (Cuiaba, 16 degrees S, 58 degrees W). Time variations are described for the first longterm program for studying the effect of biomass burning on O3 and CO over a complete seasonal cycle, including the seasonal maxima of 1987 and 1988. Concentrations of O3 are measured continuously, and CO samples are collected three times a week. In order to obtain elements for comparison, an identical observational program was maintained at a site totally outside of the direct influence of biomass burning (Natal, 6 degrees S, 35 degrees W). The biomass burning contribution to the Cuiaba concentrations of CO and O3 is very large. Diurnal maximum concentrations exceeded 90 ppbv (parts per billion by volume) O3 in 1987 and 120 ppbv O3 in 1988, in September. For the wet season, the monthly average ozone concentration in March-April is about 10 ppbv. During the month of maxima, September, the O3 concentration average was 41 ppbv for 1987 and 71 ppbv for 1988. The CO concentrations are about 90 ppbv in the wet season. In September, 460 ppbv and 660 ppbv of CO were observed for 1987 and 1988, respectively. At Natal the seasonal variaton is of the order of a factor of 2. For the biomass burning site this factor is 4 for 1987 and almost 7 for 1988. In contrast, during the wet season, the concentrations of CO and O3 at both stations are about the same.
90 b
91 FDB-19960401
92 FDB-MLR

TIME VARIATIONS OF CO AND O_3 CONCENTRATIONS IN A REGION SUBJECT TO BIOMASS BURNING

V. W. J. H. Kirchhoff and R. A. Rasmussen



Journal of Geophysical Research, vol. 95, no. D6, May 20, 1990

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 95, NO. D6, PAGES 7521-7532, MAY 20, 1990

TIME VARIATIONS OF CO AND O_3 CONCENTRATIONS IN A REGION SUBJECT TO BIOMASS BURNING

V. W. J. H. Kirchhoff

Instituto de Pesquisas Espaciais, São José dos Campos, São Paulo, Brazil

R. A. Rasmussen

Oregon Graduate Center, Beaverton

Abstract. Carbon monoxide (CO) and ozone (O_3) concentrations have been observed in the Brazilian Amazon region, at a site strongly affected by biomass burning (Cuiabá, 16°S, 58°W). Time variations are described for the first long-term program of studying the effect of biomass burning on O_3 and CO over a complete seasonal cycle, including the seasonal maxima of 1987 and 1988. Concentrations of O_3 are measured continuously, and CO samples are collected three times a week. In order to obtain elements for comparison, an identical observational program was maintained at a site totally outside of the direct influence of biomass burning (Natal, 6°S, 35°W). The biomass burning contribution to the Cuiabá concentrations of CO and O_3 is very large. Diurnal maximum concentrations exceeded 90 ppbv (parts per billion by volume) O_3 in 1987 and 120 ppbv O_3 in 1988, in September. For the wet season, the monthly average ozone concentration in March-April is about 10 ppbv. During the month of maxima, September, the O_3 concentration average was 41 ppbv for 1987 and 71 ppbv for 1988. The CO concentrations are about 90 ppbv in the wet season. In September, 460 ppbv and 660 ppbv of CO were observed for 1987 and 1988, respectively. At Natal the seasonal variation is of the order of a factor of 2. For the biomass burning site this factor is 4 for 1987 and almost 7 for 1988. In contrast, during the wet season, the concentrations of CO and O_3 at both stations are about the same.

Introduction

Ozone and carbon monoxide (O_3 and CO) are important constituents of the lower atmosphere, having active participation in a number of chemical reactions. Besides being a powerful oxidant, ozone is important through its photolysis, which produces the very reactive oxygen atom in the excited ^1D state, which can dissociate the otherwise very stable water vapor molecule, to produce the hydroxyl radical (Levy, 1971; Wofsy, 1976). This OH molecule starts most of the loss processes of relatively stable gases of the troposphere such as CO and CH_4, besides many man-made trace gases. In addition to its chemical importance, ozone concentrations seem to have increased in the lower atmosphere. Measurements of ozone during several years have indicated a positive trend for some stations in Germany (Feister and Warmbt, 1987; Logan, 1985), showing concentration increases between about 1 and 3% a year. Other stations in Europe seem to have measured much less ozone in the early half of the century than today, indicating also a trend for ozone concentration increases (Bojkov, 1986). Since ozone makes also a significant contribution to the greenhouse effect, and since high ozone concentrations can harm crop yields (Heck et al., 1984) the assessment of trends require not only very accurate measurements of ozone at several points on the globe, but also systematic long-term programs.

There has been much interest, in recent years, in studying ozone in the tropics, where the reaction rates are expected to be much faster because of the higher UV intensities that reach the equatorial troposphere (Crutzen et al., 1985). It has been shown that ozone can be produced in the troposphere (e.g. Fishman et al., 1979) by the reaction of CO with OH in the presence of the nitrogen oxides NO and NO_2, and ultraviolet light, and there is strong evidence that large forest fires can contribute to excess O_3 in the tropics (Crutzen et al., 1985; Fishman et al., 1986; Kirchhoff et al., 1988). In collaboration with NASA a long-term program is in effect to obtain ozone profiles at Natal (6°S, 35°W) twice a month since 1978 using Electro Chemical Concentration (ECC) sondes (Kirchhoff et al., 1981, 1983), and sporadic rocket campaigns have been made to study the upper stratosphere at Natal (Barnes et al., 1987). Despite the low latitude of Natal, this station shows a rather large seasonal variation of ozone in the troposphere, of the order of a factor of 2, and during local spring, ozone concentrations at Natal are comparable to values observed in Europe or the U.S.A. (Logan and Kirchhoff, 1986). Surface ozone has been measured in Venezuela (Sanhueza et al., 1985), in Asia (Ogawa and Komala, 1988), in Africa (Cros et al., 1987), in Hawaii (Oltmans and Komhyr, 1986), over the ocean (Winkler, 1988) and in the Amazon forest, where very small ozone concentrations are found (Kirchhoff, 1988; Kirchhoff et al., 1988; Gregory et al., 1988; Browell et al., 1988), and biomass burnings have been studied from aircraft over forest and savannah regions (Crutzen et al., 1985; Delany et al., 1985).

Carbon monoxide has been studied in detail by Seiler and co-workers, who have developed instrumentation capable of detecting small CO concentrations in the natural atmosphere of the order of parts per billion by volume (ppbv). They also established several measurement sites and organized field expeditions to measure CO globally showing CO concentrations much lower in the southern hemisphere (Seiler, 1974; Seiler et al., 1984). However, most survey measurements

Paper number 89JD03125.
0148-0227/90/89JD-03125$05.00

have been made over the ocean (Heidt et al., 1980). Only a few campaigns have been performed at continental sites (Kirchhoff and Marinho, 1989; Sachse et al., 1988), and these have shown larger concentrations over the continent than over the ocean. A surface survey of some atmospheric gases has also been made along the Brazilian coast, showing much larger concentrations of CO over the continent (S. Wofsy, private communication, 1985). Biomass burning produces large amounts of CO in the tropics (Crutzen et al., 1979; Seiler and Crutzen, 1980), and special field campaigns have been organized to study this CO source (Greenberg et al., 1984, 1985; Crutzen et al., 1985; Sachse et al., 1988; Marinho and Kirchhoff, 1988). On a global basis it is calculated (Crutzen et al., 1985) that a total of 8×10^{14} g of CO are emitted to the atmosphere every year by biomass burning activities, especially in the tropics. The industrial source, on the other hand, should be responsible for an emission rate of 6×10^{14} g of CO per year (Seiler, 1974).

Carbon monoxide is also very important from the photochemistry point of view, since it can generate ozone, in the presence of nitrogen oxides (Chameides and Walker, 1973, 1976; Crutzen, 1979) and it is of practical interest therefore to perform simultaneous measurements of CO and O_3. Specific field expeditions have recently been made into the Amazon region, with emphasis on CO and O_3 measurements (Kirchhoff and Marinho, 1989b; Kirchhoff et al., 1990; R. C. Harris et al., The Amazon Boundary Layer Experiment (ABLE-2B): Wet season 1987, submitted to Journal of Geophysical Research, 1989; E. V. Browell et al., Ozone and aerosol distributions over the Amazon basin during the wet season, submitted to Journal of Geophysical Research, 1989) which have special characteristics in the rain forest. The tropical rain forest has been shown to emit considerable amounts of isoprene and other hydrocarbons (Zimmerman et al., 1978), and these in turn can be oxidized by OH to produce CO (Rasmussen and Khalil, 1985, 1988).

The Brazilian northwest is covered by the large Amazonian rain forest, an area of about 3.5×10^6 km^2. Central Brazil is savannah land, about 1.2×10^6 km^2. Severe biomass burnings take place yearly in these regions during the dry season, July, August, and September. Most biomass burning of virgin forest is occurring around latitude 10°S.

Burning of phytomass is related to ancient agricultural practices. The type of agriculture most practiced in tropical lands is the so-called slash-and-burn or shifting agriculture. Vegetation is cut and trees are felled, and this is burned after drying in the sun. The cleared area is then used for a few years for crops. It is abandoned when the harvest yield becomes low, and a new clearing is made. Seiler and Crutzen (1980) give other details on this practice. In Brazil, in recent years, another type of biomass burning has increased considerably because of colonization and land development associated with deforestation and burning of virgin forest. It is estimated that perhaps one half of all burnings represent virgin forest. Estimates of land requirements for these practices by Seiler and Crutzen (1980) give values between 6.0 and 15.1×10^{10} m^2.

Objective

As was mentioned before, only sporadic measurement campaigns have been undertaken to study biomass burning in Brazil. This report describes the first effort to obtain data on a systematic, continuous basis. The objective of this paper is to report new observational results of simultaneous O_3 and CO concentrations, measured in a region subject to biomass burning activities. A long-term program has been started to monitor the O_3 and CO concentrations in order to evaluate detailed diurnal and seasonal variations. In order to understand the significance of the time variations in the biomass burning ecosystem, and to have parameters for comparison, a similar monitoring program is run simultaneously at a site that samples marine air on the Atlantic northeast coast of Brazil, a region not subject to biomass burning.

Results and Discussion

Sampling Sites

Biomass burning activities have been monitored at Cuiabá (15.6°S, 56.1°W) a city of about 600,000 inhabitants in the west central region of Brazil. The sampling site itself is outside the city limits, some 9 km in the northeast direction. The sampling site normally does not receive air masses that have been in contact with the downtown area. The prevailing winds bring air masses from the north, where a number of land development centers are active. The site is in a savannah environment, the local "campo cerrado" which extends to the east. The Amazonian rain forest starts to prevail a few hundred kilometers to the north.

Marine air from the northeast shore of Brazil has also been sampled, at Natal (6°S, 35°W). The prevailing winds are strong and always blow from the ocean. This site is well outside the direct biomass burning area of central Brazil and has been chosen for comparison with the Cuiabá results. Ozone is being measured continuously at the surface and sporadically in the troposphere and stratosphere using sondes (Barnes et al., 1987). A few samples have also been obtained in the Pantanal region. This is a remote and unique ecological system of marshlands, yearly flooded by the Paraguay river system, that occupies a large area of about 145,000 km^2 centered at 18°S, 57°W. It is covered by savannahlike grassland with spots of small trees and bushes. A temporary sampling site was established at Porto Jofre (17.3°S, 56.8°W), about 245 km from Cuiabá.

Air samples from the Amazon region will also be discussed. Measurements were made in a region near Manaus (3°S, 60°W), in a forest preserve some 30 km north of the city. The typical environment is the Amazonian rain forest. The wind regime prevails from the east, which means that normally the air masses sampled were in contact with the rain forest for several days. Table 1 shows the different sampling sites and their characteristics.

A latitude-longitude grid is shown in Figure 1 with the map of Brazil and the sampling sites at Cuiabá and Natal, shown by black dots. The other two sites that will be used can also be readily

TABLE 1. Sampling Site Locations and Characteristics

Site	Latitude, °S	Longitude, °W	Type
Cuiabá	15.6	56.1	savannah
Natal	5.9	35.2	Atlantic coast
Porto Jofre	17.3	56.8	Pantanal
Manaus	3.0	60.0	rain forest

identified on this map. The area most affected by biomass burning is shown inside a dashed rectangle, centered around 10°S, 55°W. This is the region where most burning took place in the dry season of 1987, as identified from satellite images. The dashed area covers part of the states of Mato Grosso (M), and Rondônia (R), in the south. Also shown are the sketches of three air mass trajectories, at three different pressure levels: 850, 500, and 300 mbar. These are shown in more detail in a later section when the Pantanal samples are analyzed.

Measurement Techniques

Ozone concentrations have been measured continuously at the surface, 1.5 m above ground, using the ultraviolet absorption technique.

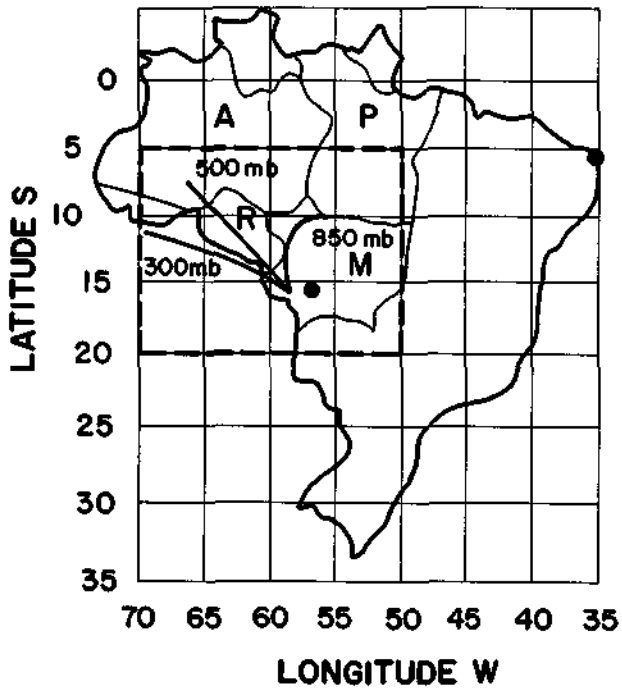


Fig. 1. Latitude-longitude grid showing the geographic position of Brazil. Black dots are Cuiabá (15.6°S, 56.1°W) and Natal (5.9°S, 35.2°W). The dashed rectangle shows the region where most of the biomass burnings have occurred in recent years. Air mass trajectories are sketched for three pressure levels. These and the dashed rectangular area are shown in detail in Figure 12.

Ozone profiles have also been obtained using ECC ozone sondes (Komhyr, 1969; Barnes et al., 1985) at Natal and Manaus. Performance characteristics are discussed by Torres and Bandy (1978) and Hilsenrath et al. (1986).

The basic CO measurement technique used is chromatographic separation followed by mercury vapor detection (Seiler, 1974). This technique has much better chromatographic resolution and measurement precision, as well as linearity of response, as compared, for example, with the FID (Flame Ionization Detector) technique, for low concentrations in the parts per billion by volume range. The carrier gas is dried and filtered to eliminate interference from reducing gases. Sulfur dioxide and hydrocarbons, which could react with mercuric oxide at the reaction chamber temperatures are eliminated on a routine basis because the instrument is dedicated to the measurements of CO only. Samples are individually injected, and the concentration is determined by comparison with calibration gases. Injection into the flow system is accomplished by initial transference to a 2-mL sample loop which, after extensive flushing with sample air, is introduced into the main flow using a six-port valve. The operation is very simple and fast and has excellent resolution and precision. Around 100 ppbv, typical precision is 0.2%. Each sample is analyzed in about 5 min. The samples are collected by a small portable air pump that pressurizes stainless steel cans of 800-mL volume, electropolished internally and especially manufactured for air sampling purposes, developed by R. Rasmussen, Oregon Graduate Center, Beaverton. For the present analysis, all samples were analyzed in the lab less than a week after sampling, and typically after 2 or 3 days.

Smoke and Fire Detection From Satellite

Being such a large area, the Amazon region is difficult to survey even by airplane. It is more convenient to use satellite images to localize large forest fires. The NOAA 9 satellite, for example, has a horizontal resolution at the surface of 1.1 km, at the nadir point. Its orbit is quasi-circular, quasi-polar, and sun-syncronous (Kidwell, 1985). The advanced very high resolution radiometer (AVHRR) on board NOAA 9 can transmit images by the high resolution picture transmission (HRPT) system in five spectral bands. In the visible band the image can detect clouds and smoke plumes in addition to the details on the terrain. In the infrared band 3 (3.55 to 3.93 m) the sensitivity is largest for temperature differences and can detect the fires themselves. The satellite signal is received and recorded on tape at the receiving station in Cachoeira Paulista, Brazil. The images are processed by a cluster synthesis automatic algorithm which provides grouping of elementary areas, pixels, of similar spectral characteristics. Only signals above a minimum threshold are classified as fires. To provide identification of smoke plumes and fires (and to discriminate clouds) and also to scale the size of the fires, the images of the visible and infrared bands can be compared on a video screen. In a separate paper, this identification of the fires is quantified in order to calculate burned areas.

Plate 1. NOAA 9 satellite image in the visible band showing patches of smoke in the area of Figure 12.

Plate 2. NOAA 9 satellite image in the infrared band showing hot spots in the same area of Plate 1 and Figure 12.

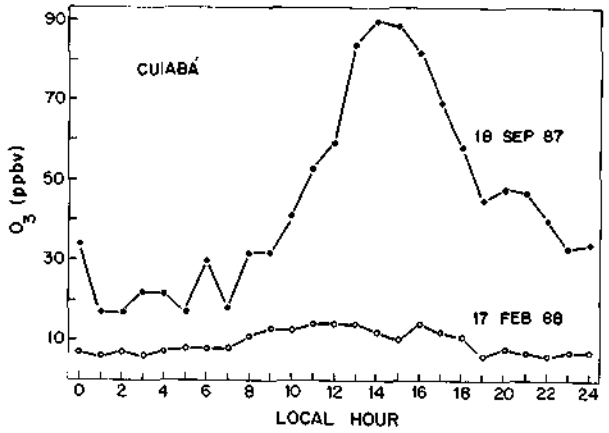


Fig. 2. Diurnal variation of ozone concentrations measured 1.5 m above the surface at Cuiabá. Two examples are shown, one for the dry season period (September 18, 1987) and one for the wet season period (February 17, 1988).

As an example of fire and smoke detection we show NOAA 9 images in Plates 1 and 2, for July 1987. A large number of fires can be clearly seen in Plate 2, the infrared channel. The details of these plates will be discussed later, but the fire density shown is not the largest observed during the dry season period. We have chosen to show this July day since the Pantanal sampling was done in this time frame and later, air mass trajectory calculations for this period will show the propagation direction of the gases produced in these fires. A total of 79 images were analyzed for the period between July 15 and October 2, 1987, which covers well the dry season period. Images were also analyzed for a few days in the wet season period to test the identification scheme. In the 1987 dry season, the highest fire density occurred in September. The average number of pixels varied from about 24,000 in July to 54,000 in August and 56.000 in September, being very close to zero outside of this interval. The actual precipitation rates in July, August, and September were less than 6 mm per month.

Diurnal Variations of Ozone

For low-latitude sites the annual variation of the solar zenith angle is relatively small, so that the conventional seasonal periods may not be very representative. More convenient, in the tropics, is the annual division in dry (low precipitation index) and wet (rainy) periods. These different periods can be easily identified. For Cuiabá the wet season extends from January to April, when precipitation rates of between 7 and 10 mm per day are usual. In contrast, during the dry season period, less than 2 mm/day of rain will fall during July, August, and September. For Manaus and Natal the maxima and minima are delayed by about 2 months.

Hourly average ozone concentrations are computed at all sites, every hour, by averaging individual measurements (three per minute) between 10 min. around the hour. The diurnal variation, in terms of these hourly averages, is shown in Figure 2 for Cuiabá. Two days are shown, one from the wet season period, and one from the dry season period, which shows much larger ozone concentrations in the daytime. In both cases, the maximum concentration occurs in the daytime.

The diurnal variation of ozone concentrations at Cuiabá is similar to observations at other continental sites (Kirchhoff, 1988; Sanhueza et al, 1985; Feister and Warmbt, 1987; Ogawa and Komala, 1988), with maximum concentrations around noon and small values at night. This is true for both the wet season example (February, 17 1988) and the dry season one (September, 18 1987) shown

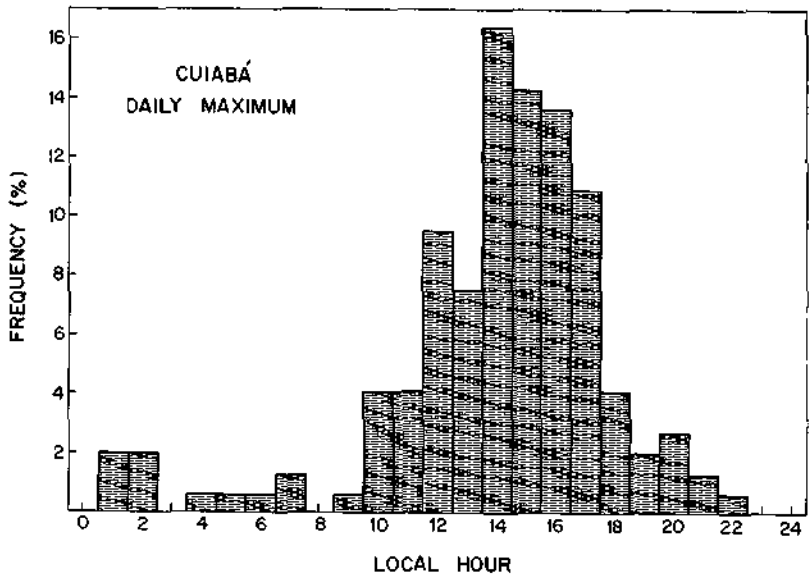


Fig. 3. Occurrence frequency of the daily maximum ozone concentration for Cuiabá as a function of local time.

in Figure 2. For the day in September the diurnal peak concentration occurs at a slightly later time of the day, about 2 hours later, than that of the February day, in the wet season, when the maximum occurs near noon. The daytime peak for September 18 is about 6 times larger. This is, however, an extreme case, not repeated very often. Results obtained in the African Congo, also a near equator station (4°S), show a very similar ozone concentration behavior. For October, Cros et al. (1987) report O_3 maxima of about 70 ppbv near 1500 LT (local time). For Asia, average measurements at 7°S, reported by Ogawa and Komala (1988), are of the order of 25 ppbv during the wet season and about 40 ppbv in the dry season.

The daily maximum, at Cuiabá, has occurred mostly at 1400 LT as shown by the histogram in Figure 3. More than 16% of all daily maxima analyzed fell in the 1400 LT hourly interval, followed by about 14% for the 1500 LT interval and over 13% for the 1600 LT interval. The diurnal maximum ozone concentration occurs only very rarely at night and then probably by a local perturbation, such as cumulonimbus downdrafts.

The average diurnal variation is computed every hour by calculating the average of all hourly averages in a given period, in general a month. The next figures show average diurnal ozone variations calculated for periods representative of the dry and wet seasons. The average diurnal variation for Cuiabá is shown in Figure 4. Ozone concentrations are shown in parts per billion by volume as a function of local time. The dry period average has been computed from 2 months of data, August and September 1987. For the wet season period, data for February and March 1988 were used. Almost 50 ppbv ozone are present in surface air at Cuiabá during the dry season, at the time of the diurnal maximum. In contrast, the wet season or rainy season air has only 15 ppbv, around noon. The ratio of maxima is 3.2. For 1988 this ratio is even larger. Using the monthly means of Figure 7, the ratio September/April becomes 6.4 (see Tables 2 and 3).

TABLE 2. Summary of CO Concentration Maxima and Minima at Cuiabá and Natal

Site	1987 Max	April Min	Max/Min Ratio	1988 Max	Max/Min Ratio
Cuiabá	460	90	5.1	660	7.3
Natal	120	85	1.4	120	1.4

Concentrations are in parts per billion by volume. (Max = Maximum; Min = Minimum)

TABLE 3. Summary of O_3 Concentration Maxima and Minima at Cuiabá and Natal

Site	1987 Max	April Min	Max/Min Ratio	1988 Max	Max/Min Ratio
Cuiabá	41	11	3.7	71	6.4
Natal	23	10	2.3	25	2.5

Concentrations are in parts per billion by volume. (Max = Maximum; Min = Minimum)

It appears that such large ratios between dry and wet seasons have not been reported for other stations; they appear to be the direct result of photochemistry, triggered by nearby biomass burning.

The average diurnal variation of surface ozone concentrations has also been computed for Natal and Manaus. These are shown in Figures 5 and 6, with the same scales used for Figure 4 (Cuiabá). The most striking difference for Natal, other than the much lower average (22 ppbv compared with 48) is the apparent absence of any diurnal variation for the marine air environment. A

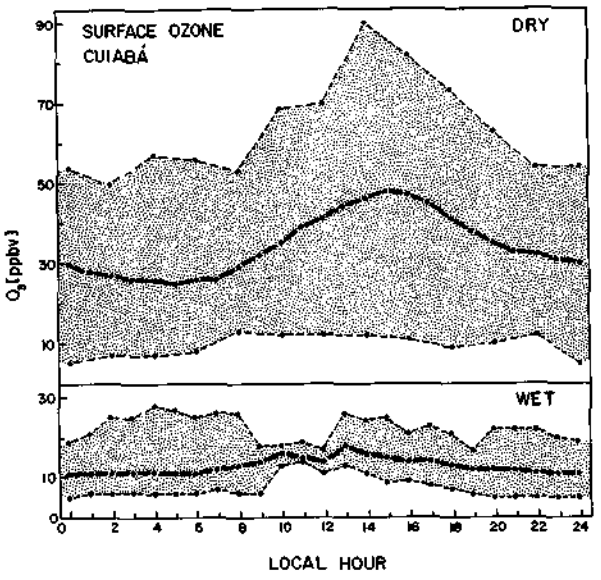


Fig. 4. Average diurnal ozone variation at Cuiabá computed for the dry season period and the wet season period. The hatched areas limit the minimum and maximum observed concentrations.

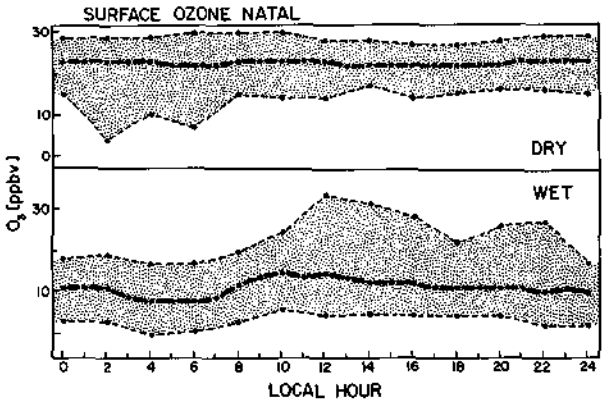


Fig. 5. Average diurnal ozone variation at Natal computed for the dry season period and the wet season period. The hatched areas limit the maximum and minimum observed concentrations.

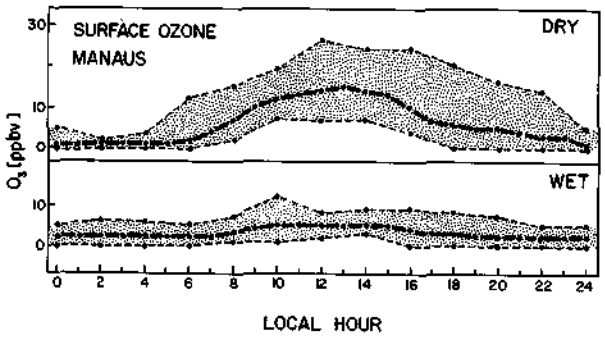


Fig. 6. Average diurnal ozone variation at Manaus (Ducke forest preserve) computed for a dry season period and a wet season period. The hatched areas limit the maximum and minimum observed concentrations.

behavior different from the continental pattern has also been reported for the Pacific region (Oltmans, 1981, Oltmans and Khomyr, 1986). The lack of diurnal variation of the ozone concentration in marine air is consistent with smaller photochemical activity (there are not so many sources of CO, CH_4, and NO_x) and less physical interaction of the air with the oceanic surface. The ozone flux to the marine surface is much lower than the flux over bare soil or soil covered with vegetation, of the order of 10^{10} cm^{-2} s^{-1} (Wesely et al, 1981) over ocean and about 10^{12} cm^{-2} s^{-1} over forest area. Since the time constant for loss of O_3 by contact with the surface is evidently inversely proportional to the flux, the loss time constant will be too large to allow a concentration change at the time scale of a few hours. It should be noted, finally, that even in the absence of photochemical activity, day-night concentration differences may be strongly influenced by the formation of the nocturnal inversion layer. Therefore the lack of a consistent diurnal variation in marine air could also result from the absence of significant nocturnal inversions in such environments.

For the Manaus area, the magnitude of the maximum is rather small in comparison with Cuiabá, but a diurnal variation can be easily identified in both seasons. The diurnal variation for ozone has been calculated by Jacob and Wofsy (1988) for Manaus. The ratio of maxima for Natal is about 1.7, and for Manaus, about 2.0. As shown, the ratio for Cuiabá is much larger. Not only is the ratio larger, but, as is indicated in Figure 4, the variability between minima and maxima is much larger as well, reflecting the larger day-to-day variability expected in the biomass burning area. The variations for Cuiabá are much larger than those for the Venezuelan savannah (Sanhueza et al, 1985) where values between 16 and 24 ppbv of ozone have been observed. Largest O_3 concentrations are observed in the northern hemisphere in July. Fehsenfeld et al. (1983) report daily maxima around 60 ppbv, for a mountain site in Colorado. For rural sites in the western U.S.A., Logan (1987) reports ozone maxima in July of the order of 50 ppbv. It should be noticed that the seasonal maxima in Brazil occur in September, coincident with the peak burning season. The average maximum O_3 for September is therefore larger than our dry season example shown in Figure 4 (August-September average). Again, the daily maxima are much enhanced at the biomass burning site, in the dry season, compared to the other sites.

The later formation of peak daytime ozone concentrations at Cuiabá, about 1400 LT, as compared with noon in Manaus, is consistent with photochemical production of ozone as a result of the oxidation of CO by OH in the presence of the nitrogen oxides NO and NO_2, also produced in the combustion process. Fehsenfeld et al. (1983) show daytime peak concentrations forming at about 1500 LT, when the NO_x (=NO + NO_2) concentrations were above 0.6 ppbv, when about 60 ppbv of ozone were observed. The ozone concentrations observed in Brazil have a tendency to increase with height in the mixed layer, up to about 2 km. For example, in the ECC profiles for Natal (Logan and Kirchhoff, 1986), and for Manaus (Kirchhoff et al, 1988) and in the results of the field expeditions of Delany et al. (1985) and Crutzen et al. (1985), highly concentrated layers were observed. From the surface to about 2 km, the ozone mixing ratio may increase by as much as 15 to 20 ppbv. For Cuiabá this means that layers of the order of up to 100 ppbv ozone could result in the upper levels.

Seasonal Variation

Carbon monoxide concentrations have been measured from air samples collected three times a week at noon for the sites of Table 1. The monthly average O_3 concentrations are computed from the daily averages, which in turn are averages of the 24-hour hourly means. Figure 7

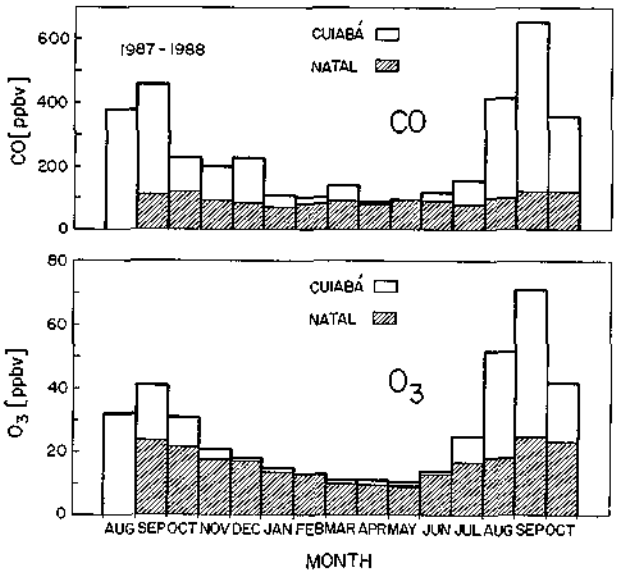


Fig. 7. Monthly average concentrations of CO and O_3 showing the seasonal variation between the two dry season maxima (September) and the wet season minimum (February-April). Cuiabá represents the biomass burning area whereas Natal, a marine site, is shown for comparison (hatched).

shows the monthly average CO and O_3 concentrations for Cuiabá and Natal, from August 1987 to October 1988 covering two periods of yearly maxima. The Natal concentrations are shown by the hatched bars. The maximum average concentrations for CO are seen in the month of September, for Cuiabá, with minima in the January-May period. The maximum CO for Natal is observed in September-October. The ozone concentration variation seems to follow the CO variation quite closely. Both Cuiabá and Natal have maximum concentrations in September. A seasonal variation is also clearly seen in the data reported by Cros et al. (1987) for equatorial Africa. The data obtained on board of ships show a more complex character, being different over different longitudinal belts (Winkler, 1988). The data for Asia (Ogawa and Komala, 1988) and the results for Australia

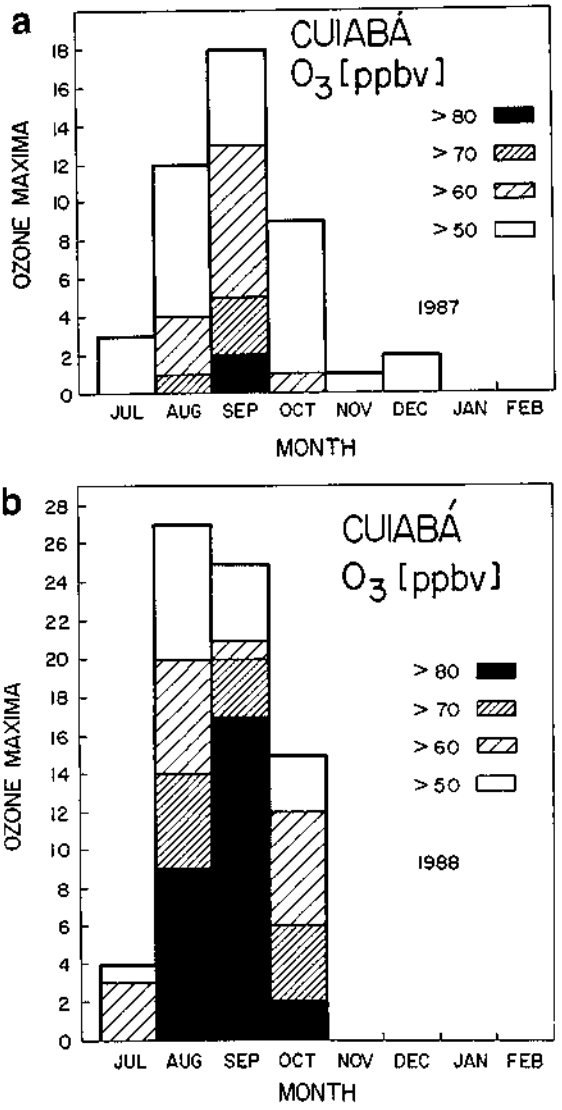


Fig. 8. Histogram showing the number of occurrences (number of days) in a given month when the maximum ozone concentration exceeded certain thresholds, here defined as 50, 60, 70, and 80 ppbv. (a) Dry season of 1987. (b) Dry season of 1988.

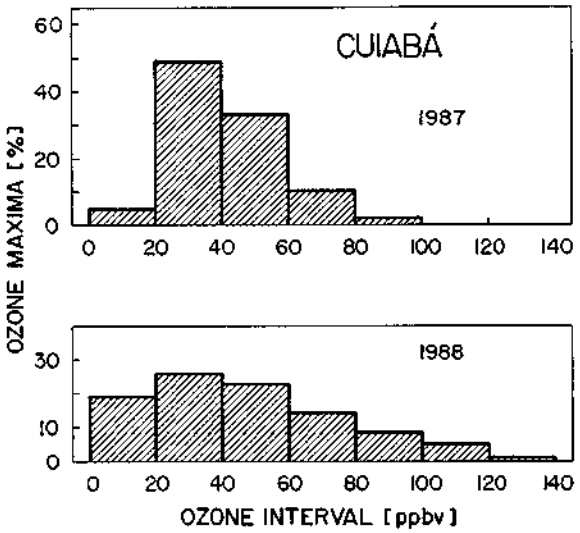


Fig. 9. Histogram of maximum ozone concentrations in intervals of 20 ppbv for Cuiaba, comparing 1987 and 1988 results.

(Fraser et al, 1986) and data for much higher latitudes (Feister and Warmbt, 1987) all show seasonal variations near the surface of the order of a factor of 2 or less. The O_3 seasonal variations of daily average values are usually not much larger than a factor of 2 in either eastern or western sites of the USA (Logan, 1987). For Cuiabá the ratio between maxima and minima (Figure 7) is of the order of a factor of 4 for 1987, and of more than a factor of 6 for 1988. The seasonal ratios are summarized in Tables 2 and 3.

The distribution of the ozone daily maximum is examined in Figures 8 and 9, for the dry season period of 1987 and 1988. Figure 8 shows how often the maximum ozone concentration exceeds certain thresholds in a given month. The 1987 season is shown in Figure 8a. During September, two cases were observed when O_3 in excess of 80 ppbv were observed. Concentrations larger than 70 ppbv were seen in August (one case), and September (five cases); concentrations larger than 60 ppbv were seen in August (four cases), September (thirteen cases), and October (one case). Concentrations above 50 ppbv occurred in July (three cases), August (twelve cases), September (eighteen cases), October (nine cases), November (one case), and December (two cases). For 1988 a much larger number of cases with O_3 concentrations above 80 ppbv have been observed, as is shown in Figure 8b: nine cases in August, seventeen cases in September, and two cases in October. The distribution is similar to that of the previous year but the concentrations are larger. For example, only 18 days in September 1987 had O_3 larger than 50 ppbv. In 1988 there were 25 days in this month with values above 50 ppbv.

Another way of comparing the distribution of maxima in the dry season is shown in Figure 9, where the percentage of cases is plotted in intervals of 20 ppbv. It can be seen that the tail at the higher concentration side is much larger for 1988 than for 1987. Figure 9 shows

that only about 3% of all cases were between 80 and 100 ppbv. In terms of cumulative percentage, 98% of the cases were below 80 ppbv in 1987. For 1988, 78% of all cases were below 80 ppbv. The cumulative percentages, when plotted on probability paper, follow a straight line when a Maxwellian distribution is represented. For the data in Figure 9, the largest deviation from a Maxwellian distribution starts at about 80 ppbv. Figure 10 shows the seasonal variation of the monthly maxima, observed at 1400 and 1300 LT, and the hourly averages at these times. The largest values occur in September, and the lowest concentrations are observed in February-March, following the variations already shown in Figure 7. Comparing this to results shown by Logan (1987), the Cuiabá results are similar to the "eastern site" characteristics, where the average of the daily maxima vary from 80-90 ppbv during the seasonal maximum to about 25-30 ppbv in the seasonal minimum.

It is interesting to note that the seasonal variations for O_3, described for these surface

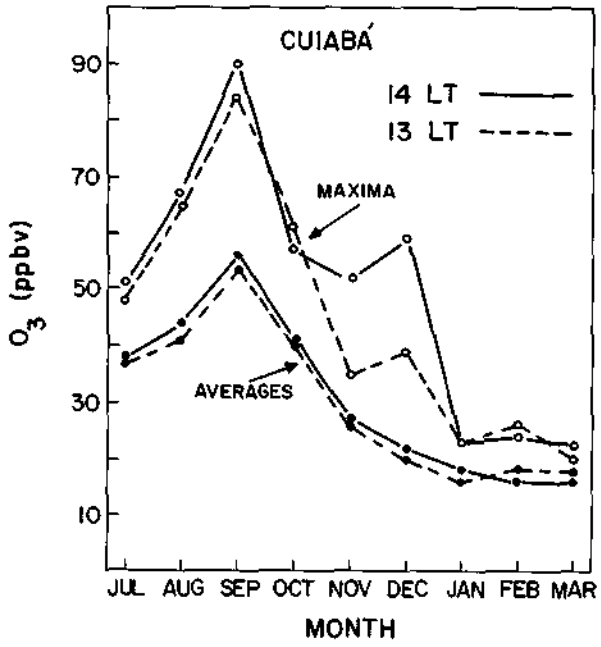


Fig. 10. The variation of monthly maxima O_3 at 1400 LT (continuous curve) and 1300 LT (dashed curve) showing the seasonal variations between the dry season peak (September) and the wet season minimum (February-March). The hourly averages are also shown, for comparison.

observations, are very likely similar at the upper levels of the troposphere. Extensive measurements at Natal (Logan and Kirchhoff, 1986) show that the seasonal variations seen at the surface are in phase and only slightly decreasing in magnitude with height. This seems to be true also for the Manaus region, where two large field expeditions have sampled O_3 profiles in the dry season and the wet season. It is therefore reasonable to expect large seasonal variations of O_3 at various levels above the surface in the Cuiabá area as well.

Several hypotheses have been raised to explain the factor of 2 seasonal variation seen at Natal, which might be considered unexpectedly large given the small latitude of the station, and the constancy of the prevailing easterly winds (Kirchhoff, 1984; Logan and Kirchhoff, 1986; Kirchhoff and Nobre, 1986). It seems possible that even here biomass burning is responsible, in a very diluted way in comparison to the Cuiabá data, but nevertheless partly responsible for the seasonal variation at Natal. Kirchhoff and Nobre (1986) discuss the details of possible transport mechanisms, either from the central region of Brazil through the troposphere and stratosphere, or direct transport of burning products from equatorial Africa over the Atlantic ocean, when dilution could be minimized by strong subsidence. Biomass burning is also very common in the African savannah region, around the equator, but the results of Cros et al. (1987) were concentrated on the rainy season and do not show large concentrations directly related to biomass burning. There is, however, an increase of a factor of 2 between December 1983 and October 1984. A clear increase in the dry season can also be seen in the results for Asia, given by Ogawa and Komala (1988), which are very near a factor of 2.

CO Measurements in the Pantanal

Air samples have also been taken far away from any direct burning activity, 245 km south of Cuiabá, in the Pantanal region, at Porto Jofre. Three samples a day were collected during a 1-week period in July 1987. The results for CO are shown in Figure 11. During the sampling period no evidence of fires or smoke was noticed in the Pantanal region itself. The relatively large CO concentrations are probably the result of long range transport. Observing NOAA 9 images for the period of the Pantanal sampling, it is apparent that burning activities were effective to the north, at distances of the order of 500 km away from Cuiabá. Plates 1 and 2 show several fires around 10°S, for July 28, 1983. Plate 1 shows the visible band of a NOAA 9 image made July 28,

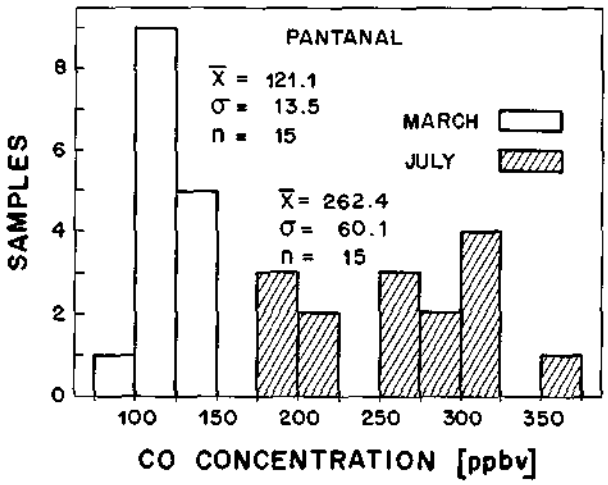


Fig. 11. CO concentrations measured in the center of the Brazilian Pantanal region (Porto Jofre). The distribution of samples in 25-ppbv intervals is shown, for March (wet) and July (dry) periods.

1987. The Xingu river system, in the north of the state of Mato Grosso, Brazil, can be clearly seen in the center of Plate 1. Although this band cannot show the fires with enough clarity, it is important to identify surface features for the horizontal scaling of Plate 2. Individual fires can be readily identified in Plate 2, which shows the same region of Plate 1. It is impressive to realize the large number of fires that are active in the region. The area of the plates is centered at about 10°S, being about 4.5° wide by 4° high. A closer examination of plates 1 and 2 allows one to estimate sizes. This is not an easy task, since the horizontal resolution of the satellite sensor is rather large, and therefore a very hot but small size fire could, in principle, saturate the sensor, leaving the impression of a much larger fire area. From the plates, the individual fires vary in size but a rough average size seems to be around 5 km in diameter. This is much larger than the horizontal resolution of 1.1 km, which may be an indication that most of the fires are in fact larger than the resolution capacity of the sensor. In this case, the fire size estimates and burned land areas would be good estimates, probably better than so many guesses found in the literature. Continuing this exercise, there are about 150 fires of this size in Plate 2, with a total area of 2945.2 km^2. This gives for the area shown a ratio fire area over total area of 1.3%. This compares with 1 and 2.5%, quoted by Seiler and Crutzen (1980). The larger fire slightly to the right of the center of the plates is located at 10.3°S, 52.5°W, near the village of Palmeira in the north of the state of Mato Grosso, in a region of large agricultural developments. It has a length of about 22 km and a width of about 11 km. The smoke area generated by this fire system has a size of about 70 x 30 km.

Figure 12 shows an enlargement of the burning area between 5 and 20°S, indicated by the dashed lines of Figure 1. For a point near Cuiabá and Porto Jofre, three air mass trajectories have been calculated to show the long-range transport characteristics of the region. Between 850 and 500 mbar, air masses from the heavy burning area are brought to the Cuiabá region. At 850 mbar, in the mixed layer, the air is transported towards Cuiabá and Porto Jofre from the north-northeast, near the area where numerous fires are seen (Plates 1 and 2). Each arrow represents the transit time of 6 hours. At 500 mbar the air masses come from the direction of Rondônia, another state where much burning takes place. The high pressure center of anti-cyclonic circulation that is present over central Brazil in July, in the case shown, is responsible for the transport of air masses to the south. It is possible, however, through a relatively small displacement of this center, to produce north-northwest air transport, as described for example by Browell et al. (1988) and Kirchhoff et al. (1988).

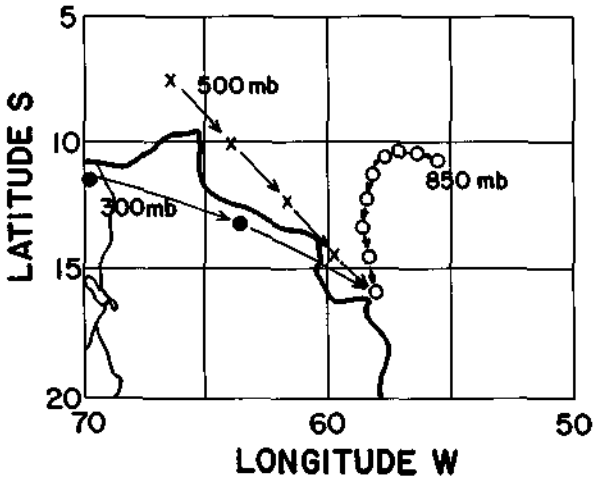


Fig. 12. The region around 15°S, 60°W, which is most severely subject to biomass burning yearly. The rectangular area of Figure 1 is shown, with backward air mass trajectories near Cuiabá calculated for three different pressure levels. The size of each arrow represents a time period of 6 hours. Air masses at the lower heights reach the Cuiabá area coming from regions of severe burnings, as shown in Plates 1 and 2.

Summary and Conclusions

A comprehensive analysis is presented on the diurnal and seasonal variations of the concentrations of CO and O_3 in surface air from samples collected at a site in Amazonia subject to nearby biomass burning. For the first time, from a simultaneous analysis program that uses a site outside the biomass burning area it has been determined by how much the burning activity has an influence on the composition of the lower atmospheric gases O_3 and CO.

The concentration of O_3 follows well the variations of CO, a result that is probably the consequence of photochemical activity. At Cuiabá the CO maximum monthly average was 460 ppbv for 1987, and 660 ppbv for 1988. In contrast, the maxima at Natal did not reach more than 120 ppbv. For ozone, Cuiabá had 41 and 71 ppbv in September for 1987 and 1988, respectively, when Natal had only 23 and 25 ppbv. This difference between the two stations, so strong in the dry season, is practically absent in the wet season, when both stations observe the same concentrations.

Acknowledgments. At the sampling sites, thanks are due to Geraldo Garcia, Adilson Palone, and Homero dos Santos, at Cuiabá; Adauto Motta, José Alves, and Francisco da Silva at Natal; Maria A. de Jesus in São José dos Campos; and Herbert Schubart and the INPA staff in Manaus. NASA has provided partial support for the Natal ECC measurements, with constant support of Arnold Torres and the Wallops Island team, and the surface measurements at Ducke forest preserve, near Manaus, with support from the NASA GTE-ABLE project. Calibration gas for CO was also provided by W. Seiler, who sent us a special 800-mL tank (can 26) of his calibration gas nº 1178328. We thank A. Setzer and M. Pereira for the NOAA 9 plates.

References

Barnes, R. A., A. R. Bandy, and A. L. Torres, ECC ozonesonde accuracy and precision, J. Geophys. Res., 90, 7881-7888, 1985.

Barnes, R. A., A. C. Holland, and V. W. J. H.

Kirchhoff, Equatorial ozone profiles from the ground to 52 km during the southern hemisphere autumn, J. Geophys. Res., 92, 5573-5583, 1987.

Bojkov, R. D., Surface ozone during the second half of the nineteenth century, J. Clim. and Appl. Meteorol., 25, 343-352, 1986.

Browell, E. V., G. L. Gregory, R. C. Harriss, and V. W. J. H. Kirchhoff, Tropospheric ozone and aerosols distributions across the Amazon Basin, J. Geophys. Res., 93, 1431-1451, 1988.

Chameides, W., and J. C. G. Walker, A photochemical theory of tropospheric ozone, J. Geophys. Res., 78, 8751-8760, 1973.

Chameides, W., and J. C. G. Walker, A time dependent photochemical model for ozone near the ground, J. Geophys. Res., 81, 413-420, 1976.

Cros, B., R. Delmas, B. Clirac, J. L. Mdembi, and J. Fontan, Survey of ozone concentrations in an equatorial region during the rainy season, J. Geophys. Res., 92, 9772-9778, 1987.

Crutzen, P. J., The role of NO and NO_2 in the chemistry of the troposphere and stratosphere, Ann. Rev. Earth Planet. Sci., 7, 443-472, 1979.

Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. L. Pollock, and W. Seiler, Biomass burning as a source of atmospheric gases CO, H_2, N_2O, NO, CH_3Cl, and COS, Nature, 282, 253-256, 1979.

Crutzen, P. J., A. C. Delany, J. Greenberg, P. Haagenson, L. Heidt, R. Lueb, W. Pollock, W. Seiler, A. Wartburg, and P. Zimmerman, Tropospheric chemical composition measurements in Brazil during the dry season, J. Atmos. Chem., 2, 233-256, 1985.

Delany, A. C., P. Haagenson, S. Walters, A. F. Wartburg, and P. J. Crutzen, Photochemically produced ozone in the emission from large-scale tropical vegetation fires, J. Geophys. Res., 90, 2425-2429, 1985.

Fehsenfeld, F. C., M. J. Bollinger, S. C. Liu, D. D. Parrish, M. McFarland, M. Trainer, D. Kely, P. C. Murphy, D. L. Albritton, and D. H. Lenschow, A study of ozone in the Colorado Mountains, J. Atmos. Chem., 1, 87-105, 1983.

Feister, U., and W. Warmbt, Long-term measurements of surface ozone in the German Democratic Republic, J. Atmos. Chem., 5, 1-21, 1987.

Fishman, J., S. Solomon, and P. J. Crutzen, Observational and theoretical evidence in support of a significant in situ photochemical source of tropospheric ozone, Tellus, 31, 432-436, 1979.

Fishman, J., P. Minnis, and H. G. Reichle, Jr., Use of satellite data to study tropospheric ozone in the tropics, J. Geophys. Res., 91, 14,451-14,465, 1986.

Fraser, P. J., P. Hyson, R. A. Rasmussen, A. J. Crawford, and M. A. K. Khalil, Methane, carbon monoxide and methylchloroform in the southern hemisphere, J. Atmos. Chem., 4, 3-42, 1986.

Greenberg, J. P., P. R. Zimmerman, L. Heidt, and W. Pollock, Hydrocarbon and carbon monoxide emissions from biomass burning in Brazil, J. Geophys. Res., 89, 1350-1354, 1984.

Greenberg, J. P., P. R. Zimmerman, and R. B. Chatfield, Hydrocarbons and carbons monoxide in African savannah air, Geophys. Res. Lett., 12, 113-116, 1985.

Gregory, G. L., E. V. Browell, and L. S. Gahan, Boundary layer ozone: An airborne survey above the Amazon Basin, J. Geophys. Res., 93, 1452-1468, 1988.

Heidt, L. E., J. P. Krasnec, R. A. Lueb, W. H. Pollock, B. E. Henry, and P. J. Crutzen, Latitudinal distributions of CO and CH_4 over the Pacific, J. Geophys. Res., 85, 7329-7336, 1980.

Heck, W. W., W. W. Cure, J. O. Rawlings, L. J. Zaragoza, A. S. Heagle, H. E. Heggestad, R. J. Kohut, L. W. Kress, and P. J. Temple, Assessing impacts of ozone on agricultural crops: I, Overview, J. Air Pollut. Control. Assoc., 34, 729-735, 1984.

Hilsenrath, E., W. Attmannspacher, A. Bass, W. Evans, R. Hageneyer, R. A. Barnes, W. Komhyr, K. Mauersberger, J. Mentall, M. Proffitt, D. Robbins, S. Taylor, A. Torres, and E. Weinstock, Results from the Balloon Ozone Intercomparison Campaign (BOIC), J. Geophys. Res., 91, 13,137-13,152, 1986.

Jacob, D. J., and S. C. Wofsy, Photochemistry of biogenic emissions over the Amazon forest, J. Geophys. Res., 93, 1477-1486, 1988.

Kidwell, K. B., NOAA polar orbiter data (TIROS-N, NOAA-6, NOAA-7, NOAA-8, NOAA-9) user guide, Natl. Environ. Satellite Data and Inf. Serv. Suitland, Md., 98 pp., May 1985.

Kirchhoff, V. W. J. H., Are northern hemisphere tropospheric ozone densities larger? Eos Trans. AGU, 65, 449, 1984.

Kirchhoff, V. W. J. H., Surface ozone measurements in Amazonia, J. Geophys. Res., 93, 1469-1476, 1988.

Kirchhoff, V. W. J. H., and E. V. A. Marinho, A survey of continental concentrations of atmospheric CO in the southern hemisphere, Atmos. Environ., 23, 461-466, 1989.

Kirchhoff, V. W. J. H., and E. V. A. Marinho, Surface carbon monoxide measurements in Amazonia, J. Geophys. Res., in press, 1990.

Kirchhoff, V. W. J. H., and C. A. Nobre, Atmospheric chemistry research in Brazil: Ozone measurements at Natal, Manaus, and Cuiabá, Geofísica, 24, 95-108, 1986.

Kirchhoff, V. W. J. H., Y. Sahai, and A. G. Motta, First ozone profiles measured with ECC sondes at Natal (5.9°S, 35.2°W), Geophys. Res. Lett., 8, 1171-1172, 1981.

Kirchhoff, V. W. J. H., E. Hilsenrath, A. G. Motta, Y. Sahai, and R. A. Medrano-B., Equatorial ozone characteristics as measured at Natal (5.9°S, 35.2°W), J. Geophys. Res., 88, 6812-6918, 1983.

Kirchhoff, V. W. J. H., E. V. Browell, and G. L. Gregory, Ozone measurements in the troposphere of an Amazonian rain forest environment, J. Geophys. Res., 93, 15,850-15,860, 1988.

Kirchhoff, V. W. J. H., E. V. Browell, and I. M. O. da Silva, Ozone measurements in Amazonia: Dry season versus wet season, J. Geophys. Res., in press, 1990.

Komhyr, W. D., Electrochemical concentration cells for gas analysis, Ann. Geophys., 25, 203-210, 1969.

Levy, H., II, Normal atmosphere: Large radical and formaldehyde concentrations predicted, Science, 173, 141-143, 1971.

Logan, J. A., Tropospheric ozone: seasonal

behavior, trends, and anthropogenic influence, J. Geophys. Res., 90, 10,463-10,482, 1985.

Logan, J. A., The ozone problem in rural areas of the United States, in NATO Workshop on Tropospheric Ozone, proceedings, pp.1-18, D. Reidel, Hingham, Mass., 1987.

Logan, J. A., and V. W. J. H. Kirchhoff, Seasonal variations of tropospheric ozone at Natal, Brazil, J. Geophys. Res., 91, 7875-7881, 1986.

Marinho, E. V. A. and V.W.J.H. Kirchhoff, Surface CO results from the ABLE-2B expedition to Amazonia (abstract), Eos Trans. AGU, 68, 322, 1988.

Ogawa, T., and N. Komala, Diurnal and seasonal variations of the tropospheric ozone in tropical Asia, paper presented at Quadrennial Ozone Symposium, Göttingen, Federal Republic of Germany, Aug, 4-13, 1988.

Oltmans, S. J., Surface ozone measurements in clean air, J. Geophys. Res., 86, 1174-1180, 1981.

Oltmans, S. J., and W. D. Komhyr, Surface ozone distributions and variations from 1973-1984 measurements at the NOAA Geophysical Monitoring for Climatic Change Baseline Observatories, J. Geophys. Res., 91, 5229-5236, 1986.

Rasmussen, R. A., and M. A. K. Khalil, Atmospheric isoprene (abstract), Eos Trans. AGU, 66, 238, 1985.

Rasmussen, R. A., and M. A. K. Khalil, Isoprene over the Amazon Basin, J. Geophys. Res., 93, 1417-1421, 1988.

Sachse, G. W., R. C. Harriss, J. Fishman, G. F. Hill, and D. R. Cahoon, Carbon monoxide in the atmosphere over the Amazon Basin during the 1985 dry season, J. Geophys. Res., 93, 1422-1430, 1988.

Sanhueza, E., K. H. Octavio, and A. Arrocha, Surface ozone measurements in the Venezuelan tropical savannah, J. Atmos. Chem., 2, 377-385, 1985.

Seiler, W., The cycle of atmospheric CO, Tellus, 26, 117-135, 1974.

Seiler, W., and P. J. Crutzen, Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning, Clim. Change, 2, 226-247, 1980.

Seiler, W., H. Giehl, E. G. Brunke, and E. Halliday, The seasonality of CO abundance in the southern hemisphere, Tellus, 36, 219-231, 1984.

Torres, A. L., and A. R. Bandy, Performance characteristics of the electrochemical concentration cell ozonesonde, J. Geophys. Res., 83, 5501-5504, 1978.

Wesely, M. L., D. R. Cook, and R. M. Williams, Field measurement of small ozone fluxes to snow, wet bare soil, and lake water, Boundary Layer Meteorol., 20, 459-471, 1981.

Winkler, P., Surface ozone over the Atlantic Ocean, J. Atmos. Chem., 7, 73-91, 1988.

Wofsy, S. C., Interactions of CH_4 and CO in the earth's atmosphere, Annu. Rev. Earth Planet. Sci., 4, 442-469, 1976.

Zimmerman, P. R., R. B. Chatfield, J. Fishman, P. J. Crutzen, and P. L. Hanst, Estimates on the production of CO and H_2 from the oxidation of hydrocarbon emissions from vegetation, Geophys. Res. Lett., 5, 679-682, 1978.

V. W. J. H. Kirchhoff, Instituto de Pesquisas Espaciais, INPE/MCT, C.P. 515, 12201 São José dos Campos, SP, Brazil.

R. A. Rasmussen, Oregon Graduate Center, 19600 N.W. Von Neumann Drive, Beaverton, OR 97006.

(Received May 3, 1989;
revised September 20, 1989;
accepted October 5, 1989.)