OBSERVATIONS OF AIR COMPOSITION IN BRAZIL BETWEEN THE EQUATOR AND 20°S DURING THE DRY SEASON.

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ABSTRACT

Field measurement programs in Brazil during the dry season months of August and September in 1979 and 1980 have demonstrated the great importance of the continental tropics in global air chemistry. Especially in the mixed layer, the air composition over land is much different from that over the ocean and the land areas are clearly large scale sources of many important trace gases. During the dry season much biomass burning takes place especially in the cerrado regions leading to substantial emission of air pollutants, such as CO, NO_x, N_2O, CH_4 and other hydrocarbons. Ozone concentrations are also enhanced due to photochemical reactions. Biogenic organic emissions from tropical forests play likewise an important role in the photochemistry of the atmosphere. Carbon monoxide was found to be present in high concentrations in the boundary layer of the tropical forest, but ozone concentrations were much lower than in the cerrado.

INTRODUCTION

For several reasons the tropics play a dominant role in atmospheric chemistry : they cover almost half of the earth's surface, they contain the tropical forests which are the most productive ecosystems of the earth, they have a large turnover rate   of biological material and they receive a maximum of visible and especially of photochemically active, ultraviolet solar radiation. Despite the obvious importance of   the tropics, very little is known about tropical air chemistry, particularly over the con-

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tinents. Most available information so far has been gathered during the GAMETAG air -
craft research flights over the Pacific Ocean and was mostly reported in the **Journal
of Geophysical Research** issue of December, 1980, while important additional information
has also been gathered by Seiler (1974) and Seiler & Fishman (1981) mostly from
aircraft flights along the coast of South America. Except for a few studies conducted'
by French research workers in the Ivory Coast (Marenco & Delaunay, 1980; Delmas **et al.**
1980), some early work by U.S. scientists in tropical Panama and Brazil (Lodge & Pate,
1966; Lodge et al., 1974) and studies by Brinkmann & de Santos (1974) and Stallard &
Edmond (1981), no information is available on the distribution of most trace gases in
the continental, tropical atmosphere.

The measurements which will be reported in this paper are therefore unique in
that they provide the first survey of the distribution of the photochemically active
trace gases O_3, CO, hydrocarbons and NO_x in one of the most important regions of the
continental tropical atmosphere. These measurements were made during the months of
August and September, i.e., during the dry season over equatorial and subtropical Bra
zil. Besides aircraft observations, air was also sampled on the ground for gas chromato
graphic determinations of such atmospheric constituents as hydrocarbons, nitrous oxide
and carbonyl sulfide.

The observations which will be reported in this study are not only important for
our understanding of global air chemistry in general, but are additionally important
because of the large changes which are taking place in the tropics in the agricultural
sector. The deforestation activities which are occurring in many tropical countries
have been much discussed in the press and in scientific circles (e.g., NAS, 1979) .
Through these activities the chemical composition of the air is changing, not only in
the tropics, but also worldwide. Up to now the most debated issue has been to what
degree the global carbon dioxide burden of the atmosphere has been influenced by
tropical forest cutting (e.g., Bolin **et al.**, 1979; Woodwell et al., 1978; Seiler &
Crutzen, 1980). However, carbon dioxide plays only a minor role in the photochemis -
try of the atmosphere. Less abundant gases are far more important. For instance,
it has been proposed by Zimmerman **et al.** (1978) that tropical forests are major produ-
cers of hydrocarbon gases which are oxidized in the atmosphere to carbon monoxide (CO).
CO plays an important role in the photochemistry of the global atmosphere as it is the
main constituent with which the important hydroxyl radical reacts in the troposphere(Le
vy, 1971, 1974; McConnell **et al.**, 1971). Theoretical investigations by Crutzen et
al., (1978), Crutzen & Gidel (1983) and Volz **et al**, (1981) have indicated that, most
likely, there is a large production of carbon monoxide in the tropics and hydrocarbon
oxidation is possible source. It was earlier shown by Crutzen & Fishman (1977) that
methane oxidation alone cannot account for this source, so that higher hydrocarbon ga
ses, especially isoprene, C_5H_8, and the terpenes, $C_{10}H_{16}$, may be important. Any
major change in the forest cover of the tropics can, therefore, have important conse-
quences for global air chemistry.

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The composition of the tropical and the global atmosphere can also be influenced by the burning of dead vegetation and wood during the dry season in many parts of the tropical world. This is normal agricultural practice and is done to free grasslands from dry and unpalatable vegetation with little nutritional value, to get rid of weeds or to clear primary or secondary forest in order to raise cattle or to grow agricultural and other cash crops for some period of time. Traditionally, in the forests the land was left to regrow, allowing nutrients gradually to return to the soil. After a period of several decades, this secondary forest was cut again and used for agriculture. This agricultural farming practice which goes under many names, most commonly shifting agriculture, slash and burn cultivation, forest farming or swidden cultivation, has been practiced in the tropics for many centuries, perhaps millenia and may be considered as the oldest form of agriculture. It was still common practice in parts of Europe in the last century. It was, or in many parts of the tropics still is the main cause of air pollution.

Analyses by Seiler & Crutzen (1980) and Crutzen **et al.** (1979) have shown that the burning of vegetation in the tropics can supply substantial amounts of important trace gases to the atmosphere, such as CO, N_2O, NO_x, CH_4, COS and CH_3Cl. In all cases the potential supply of these gases to the atmosphere was found to be of similar magnitudes as the industrial inputs.

We conducted two exploratory field programs in Brazil during the dry seasons of 1979 and 1980. The program employed research flights using the NCAR twin engine Sabreliner jet aircraft, mostly for continuous, simultaneous measurements of the meteorogical parameters, and the gases O_3, CO and NO_x. Also, evacuated cans were filled with air in the airplane or on the ground mainly to derive further information on gaseous emissions from biomass burning. Brazil was chosen for this work because of its relative proximity to our base in the U.S. and because this country combines both extensive forests (selva) and savanna-like (cerrado) ecosystems on its territory. In this paper, we report results from the fire emission sampling programs and aircraft flights in 1979 and 1980.
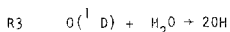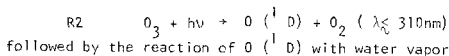
IMPORTANCE OF THE TRACE GASES SAMPLED

The gases CO, CH_4 and the other hydrocarbons, N_2O, NO_x, O_3 and COS all play important roles in air chemistry and climate. Carbon monoxide is the main gas which the hydroxyl radical reacts in the background troposphere, leading to the formation of CO_2:
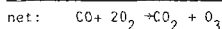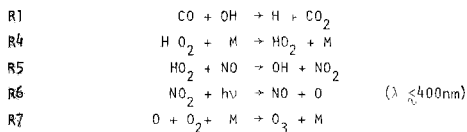
R1 $CO + OH \rightarrow H + CO_2$
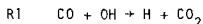
CO, therefore, limits the concentrations of OH in the troposphere (Wofsy, 1976).Many important atmospheric gases are mainly removed by reaction with OH, including most hydrocarbon gases (also those containing halogens and sulfur), carbon monoxide, hydro
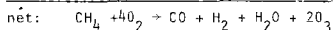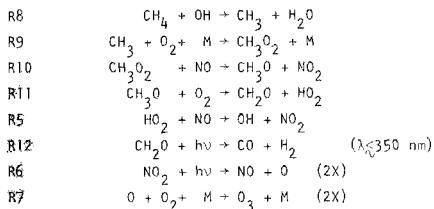
gen sulfide, nitric oxide and nitrogen dioxide (Levy, 1971, 1974; Crutzen **et al** ., 1978). Hydroxyl radicals play, therefore, an essential role in the cycling of many gases through the atmosphere. They are formed through the photolysis of ozone by ultra violet solar radiation below 319 nm, leading to the production of electronically exci-ted atomic oxygen:

R2 $\quad O_3 + h\nu \rightarrow O\ (^1D) + O_2\ (\ \lambda \lesssim 310nm)$

followed by the reaction of $O\ (^1D)$ with water vapor

R3 $\quad O(^1D) + H_2O \rightarrow 2OH$

This explains the large importance of tropospheric ozone in air chemistry. Ozone is, however, also depleted by the same and other reactions, so that rather little of it would be present in the troposphere, if additional reactions would not replenish the gas in the troposphere (Crutzen & Gidel, 1983). The oxides of nitrogen (NO and NO_2) play an important catalytic role in this tropospheric ozone production (Crutzen, 1983). The simplest set of reactions leading to ozone formation occurs during the oxidation of CO
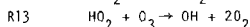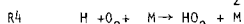
R1 $\qquad CO + OH \rightarrow H + CO_2$

R4 $\qquad H\ O_2 + M \rightarrow HO_2 + M$

R5 $\qquad HO_2 + NO \rightarrow OH + NO_2$

R6 $\qquad NO_2 + h\nu \rightarrow NO + O \qquad (\lambda \lesssim 400nm)$

R7 $\qquad O + O_2 + M \rightarrow O_3 + M$

$$\overline{\qquad net: \quad CO + 2O_2 \rightarrow CO_2 + O_3 \qquad}$$

Likewise, the oxidation of CH_4 may lead to ozone formation e.g. via

R8 $\qquad CH_4 + OH \rightarrow CH_3 + H_2O$

R9 $\qquad CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

R10 $\qquad CH_3O_2 + NO \rightarrow CH_3O + NO_2$

R11 $\qquad CH_3O + O_2 \rightarrow CH_2O + HO_2$

R5 $\qquad HO_2 + NO \rightarrow OH + NO_2$

R12 $\qquad CH_2O + h\nu \rightarrow CO + H_2 \qquad (\lambda \lesssim 350\ nm)$

R6 $\qquad NO_2 + h\nu \rightarrow NO + O \quad (2X)$

R7 $\qquad O + O_2 + M \rightarrow O_3 + M \quad (2X)$

$$\overline{\qquad net: \quad CH_4 + 4O_2 \rightarrow CO + H_2 + H_2O + 2O_3 \qquad}$$

Similar reaction paths are followed during the oxidation of other hydrocarbons and explain the formation of high ozone levels in urban enviroments during photochemi-cal smog episodes when much more reactive hydrocarbons than CH_4 are oxidized in a matter of hours or days. Hydrocarbons are produced in the tropics by natural processes and their oxidation leads to CO formation (Zimmerman **et al**., 1978), while nitric oxi-de, carbon monoxide and hydrocarbons are produced by biomass burning (Crutzen **et al** .,

Crutzen et al.

1979). In addition, NO is also produced by lightning and this source may be of particular importance in the continental, humid tropics. Although the oxidation of CO and CH_4 occurs much more slowly than that of other organics, these compounds are omnipresent in the atmosphere at much higher concentrations and their oxidation in the atmosphere can give rise to substantial ozone production in the presence of sufficient concentrations of NO. On the other hand, if the volume mixing ratio of NO near the surface is less than about 10 pptv (1 pptv = 10^{-12} by volume) the oxidation of CO leads to ozone loss via the reaction set:

$$R1 \qquad CO + OH \rightarrow H + CO_2$$
$$R4 \qquad H + O_2 + M \rightarrow HO_2 + M$$
$$R13 \qquad HO_2 + O_3 \rightarrow OH + 2O_2$$

$$\overline{\qquad CO \quad + O_3 \rightarrow CO_2 + O_2 \qquad}$$

The atmospheric distribution and the sources and sinks of NO and NO_2 play, therefore, important roles in the photochemistry of the atmosphere. Increasing concentrations of NO in the troposphere will lead to more ozone. We will see that the opposite is true in the stratosphere.

The oxides of nitrogen NO and NO_2 are removed from the troposphere by reactions with hydroxyl and ozone, leading to the formation of nitric acid,

$$R13 \qquad NO + O_3 \rightarrow NO_2 + O_2$$
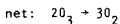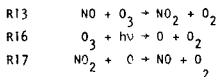$$R14 \qquad NO_2 + OH \;(+M) \rightarrow HNO_3 \;(+M)$$
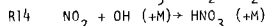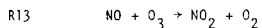
HNO_3 is removed from the troposphere in less than one week by rainfall. The main sources of carbon monoxide in the troposphere are oxidation of hydrocarbons, industrial emissions and biomass burning (Zimmerman **et al.**, 1978; Seiler, 1974; Crutzen **et al.** 1979; Logan **et al.**, 1981). Hydrocarbons, carbon monoxide, ozone and the nitrogen oxides interact, therefore, photochemically in intricate ways, with the hydroxyl radical acting as an important link. This radical is formed from ozone photolysis, carbon monoxide is removed by reaction with OH, but it is formed as an intermediate in the oxidation of the hydrocarbons which is initiated by reaction with OH. Ozone may be formed during the oxidation of carbon monoxide, methane and other hydrocarbons in the presence of sufficient amounts of nitric oxide, otherwise ozone may be destroyed.

Nitrous oxide (N_2O) and carbonyl sulfide (COS) play important roles in stratospheric photochemistry. The oxidation of N_2O by reaction with the $O\,(^1D)$ atom

$$R15 \qquad O\,(^1D) + N_2O \rightarrow 2NO$$
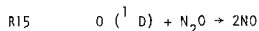
leads to the formation of nitric oxide in the stratosphere (Nicolet & Vergison, 1971 ; Crutzen, 1971; McElroy & McConnell, 1971) In the stratosphere powerful catalytic reactions lead to ozone loss via the reaction set:

R13 $NO + O_3 \rightarrow NO_2 + O_2$

R16 $O_3 + h\nu \rightarrow O + O_2$

R17 $NO_2 + O \rightarrow NO + O_2$

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net: $2O_3 \rightarrow 3O_2$

This is the main set of reactions limiting the abundance of ozone in the stratosphere (Crutzen, 1970). Several processes lead to the production of nitrous oxide at the earth's surface: denitrification and nitrification process in waters and soils (Conrad & Seiler, 1980; Bremner et al., 1981; Elkins et al., 1978), coal, oil and gas combustion (Pierotti and Rasmussen, 1976; Weiss & Craig, 1976) and biomass burning (Crutzen et al., 1979). No important sinks of N_2O have so far been identified in the trosposphere. In the stratosphere N_2O is mainly removed by the action of ultraviolet radiation with reaction R15 contributing about 10% of the total removal.

Carbonyl sulfide (COS) is important because it is probably the main precursor of the aerosol layer in the stratosphere during periods with low volcanic activity (Crutzen, 1976). This layer consists mainly of particulate sulfate (Junge et al., 1961) and is probably formed by the oxidation of SO_2, which in its turn is produced from COS by absorption of ultraviolet radiation and following reactions R19 and R20:

R18 $COS + h\nu \rightarrow CO + S$

R19 $S + O_2 \rightarrow SO + O$

R20 $SO + O_2 \rightarrow SO_2 + O$
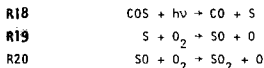
The stratospheric sulfate aerosol layer plays a role in the earth's radiation balance by reflecting a small fraction of the incoming solar radiation back to space (Turco et al., 1980), which will have the effect of a slight cooling at the earth's surface. Carbonyl sulfide has been detected in the stratosphere by Inn et al. (1979) and Mankin et al. (1979). Meixner (1981) has shown by measurements in the upper troposphere and lower stratosphere that COS is most likely the main gas which carries sulfur into the stratosphere. Hofmann & Rosen (1981) have claimed that the background stratospheric sulfate layer has been increasing over the last two decades and hypothesize that this may be due to an increase of COS or CS_2 with time. This may be due to anthropogenic activities and it is clearly important to monitor the concentrations of these gases in the atmosphere and to understand their sinks and sources. Absorption of ultraviolet radiation by ozone is the main source of energy in the stratosphere. This process also protects the biosphere from the penetration of harmful ultraviolet radiation. CO_2, N_2O, CH_4 and tropospheric ozone play important roles in the heat budget of the troposphere through the so-called greenhouse effect (Wang et al., 1976; Fishman et al., 1979). The gases which have been studied in Brazil are, therefore, both chemically and radiatively important.

The dry season in the equatorial and subtropical regions of Brazil lasts   from about June to October. During this period a strong anticyclonic subsidence stable layer often suppresses convection, especially in the subtropics, thereby   limiting rainfall and the upward transfer of gases and particulates from the boundary layer . During this time period extensive biomass burning takes place, so that high concentrations of gaseous and particulate effluents from the fires can accumulate in the lowest 2-3 Km of the atmosphere. Meteorological data from Brazil are available from   the collections of the National Meteorological Center, NMC) of the U.S.   Additional meteoro logical information was obtained on board of the research aircraft. A thorough climatological study of the meteorology of the Amazon region has been presented by Kousky & Kagano (1981).

Here we describe the circulation patterns and the vertical stability of   the atmosphere over Brazil for some arbitrarily selected dates during the expedition   of 1980. Height contours and observed winds for August 28, and August 31, 1980 for the 500 mb and 850 mb pressure levels respectively are presented in Figures 1 and 2. Hori - zontal plots are contoured from an octagonal grid data array provided by NMC on a South Polar stereographic map projection. The 850 mb pressure level may generally be conside red to represent mean conditions in the boudary layer which usually extended up   to about 750 mb ($\cong$ 2.5 Km) for most of the area of interest. The top of the boundary layer over the tropical forests is often difficult to define from the meteorogogical data Its location was, however, much more easily definable on the basis of the   chemical observations, especially those of water vapor and carbon monoxide. The average   flow patterns for the month of August are depicted in Figures 3 and 4, which show that the prevailing conditions on the days of August 28 and 31, 1980, as depicted in Figs.   1 and 2, did not differ appreciably from the mean. The same was true during 1979. These diagrams show that during the dry season, tropical Brazil, north of 10°S, experien - ces easterly flow up to mid-tropospheric levels while subtropical Brazil is more   frequently subject to mid-latitude circulation patterns. The mean resultant wind direc - tionin the boundary layer over South America in August is given in Figure 4. Anticyclonic circulation associated with the subtropical high pressure cells results in easterly trade winds throughout the boundary layer over much of Brazil. A significant consequence of the boundary layer flow coupled with the upper level circulation is a systematic decrease, poleward from the equator, in the vertical extent of the easterlies.

Vertical average profiles of dewpoint depression for tropical and   subtropical Brazil are presented in Figures 5 and 6. These figures suggest that the top of   the boundary layer over the tropical forests is located near 2 Km altitude (800 mb)   and near 2.5 Km (750 mb) in the cerrado. It is particularly marked in the subtropical cerrado region. The dry atmosphere above the mixed layer is related in part to large scale anticylonic subsidence. During August the intertropical convergence zone (ITCZ)   is situated at about 8°N. The stable subsidence layer over the cerrado is a   persistent

Observations of air ...

feature which is interrupted only occasionally by the northward extension of mid-latitu
de synoptic disturbances. In the Amazon Basin of tropical Brazil, however, such sta-
ble conditions are less pronounced and convective activity occurs more frequently. This
fact and the shorter transit time from the oceanic water vapor source explain   the
smaller dewpoint depressions above the boundary layer which were observed there   com-
pared to over subtropical Brazil.   During 1980 the anti-cyclonic circulation over Brazil
was so dominant that mid-latitude synoptic disturbances could not penetrate to subtropi
cal Brazil.   In 1979 more frequent occurrence of rainfall ocurred in the Brasilia re-
gion, sometimes leading to postponements of burning activities and hampering our sam -
pling program.

EXPERIMENTAL EQUIPMENT AND FLIGHT PATHS

        The NCAR twin-engine Sabreliner jet aircraft was instrumented to determine   the
concentration of O_3, CO, NO and NOX, as well as relative humidity,   temperature, alti
tude, position, wind speed and direction and to collect ambient air samples for subse
quent analysis of stable gases.

        Ozone was measured using a Dasibi 1008 AH ultraviolet absorption instrument (Da-
sibi, 1979) sampling from an intake via the aircraft environmental air system.   This
system was found to be somewhat compromised during full throttle ascents and so   ozone
values measured during ascent were later discarded. We are aware of the study   by
Huntzicker & Johnson (1979) who found an interference in the measurements of ozone   by
the Dasibi in forest fire plumes. All ozone data which will be reported in this paper
are, however, obtained outside plumes, so that the likelihood of interference   is
slim.

        During the 1979 measurement program, CO was measured by an infrared spectrosco-
pic method which utilized a high resolution Fourier transform spectrometer   (Mankin ,
1978), and a long path absorption cell (Mankin & Coffey, 1979) containing   the
atmospheric sample to be analyzed. The apodized spectral resolution was 0.06 cm^{-1}. For
measurements of CO, the region from 2150 to 2180 cm^{-1} was used, encompassing the   R
(1) through R(9) lines of the principal isotope. Typical smoke   plume   spectra   are
shown in Fig. 7. The system is designed to have a short reponse time ($\sim$ 10 S)   to
changes in CO amount so that the structure of smoke plumes could   be   determined   from
the fast moving aircraft.

        During the 1980 campaign carbon monoxide was measured with an instrument   based
on the HgO-Hg conversion and detection of Hg (Seiler, et al, 1980). This   instrument
shared the same intake as the ozone system, but because of the greater stability   of
CO there was no problem during ascents and so the full data set could be utilized.

        Nitrogen oxides (NO/NOX) were determined using two modified Thermo-Electron   14
B/E chemiluminescence analysers (Delany et al., 1982). A dedicated low pressure   in-
take supplied air to the instruments, one of which was operating to measure NO directly

while the other utilized a hot molydenum converter at 375° and measured NOX, the sum of most odd nitrogen compounds. A considerable ($\cong 0.75$ ppbv) NO signal was observed for these instruments which was possibly the effect of hydrocarbon interference. This rendered the clean air data suspect and NOX values have been utilized only for the cerrado boudary layer portions of the mission. Here the elevated (up to 10 ppbv) concentration of NOX tend to decrease the effect of the high background reading.

Data provided by these continuous instruments were displayed on chart recorders and recorded along with relative humidity, temperature, pressure, inertial navigation and aircraft attitude inputs on magnetic tape for subsequent computer analysis.

The aircraft was also fitted with sampling manifolds which allowed evacuated stainless steel cans to be filled with ambient air. These aircraft samples, together with ground samples, were analyzed for stable gases such as CO_2, N_2O, COS, CH_4 and many other hydrocarbons. Analyses of samples were in many cases conducted within a few days in our temporary laboratories in Brazil. Many samples were also taken back to NCAR in Boulder for further analysis   The hydrocarbon analyses from the 1979 work were all completed at NCAR. In 1979, when most of our efforts were devoted to biomass burning emissions in the cerrado regions of Central Brazil, a laboratory was set up in the Physics Deapartment of the University of Brasília. In 1980, the equip - ment, including instruments for hydrocarbon analysis, was installed at INPA, in Mana- us. Besides the aircraft air samples, many evacuated cans were filled on the ground , mostly to determine the production of effluents from biomass burning. A few cans were also filled above the clean forest canopy to obtain some information on the background concentration of the afore-mentioned gases. These samples provided some first informa tion on the distribution of gases in the clean environments of the tropical forests.The sampling and measurement techniques for CO_2, CH_4, CO, N_2O and COS have been previously described by Heidt (1978). All hydrocarbon analyses were performed on a Hewlett-Packard 5880 gas chromatograph equipped with flame ionization detectors.

The aircraft research flights and the ground sampling sites are displayed in Figure 8. In 1979 most of the ground sampling was in the Brasília-Cuiaba region, where- as in 1980 most ground sampling was in the Manaus region. The two most important ecosystems of Brazil are the tropical forests (selva) and the cerrado, which is a savanna-type vegetation mostly covered with grasses and scattered trees at most 10 m high. In the cerrado, extensive burning takes place during the dry season, mostly of grass and shrubs. This involves large areas. On limited size plots, burning takes place also in the forest areas to open new land for agriculture. The area which was most affected by land clearing was located in Mato Grosso near Cuiaba.

During 1979, the emphasis of the aircraft fligts was to investigate the composi tion of smoke plumes in the cerrado. Flight formats were designed to successively pass through a plume at various altitudes and to measure CO amounts adjacent to plumes. Flight formats were tailored to individual plumes, two examples being shown schematical ly in Figures 9 and 10. Locations of the plumes sampled are shown as A, B and C on

Figure 8. One flight was also devoted to determining the vertical distribution of CO in conditions free from smoke. The flight format was to descend from a high altitude (∿ 12 Km) and perform straight and level flights at a number of altitudes over the same location (denoted D on Figure 8).

During the 1980 aircraft flights, emphasis was on areas free of smoke plumes . Flights 7, 8 and 9, depicted in Figure 8, were flown to the northeast of Manaus in a non-developed area. Flights 10, 11, 12 and 13 made an excursion south into the cerrado. During the low altitude portions of these flights, care was taken to avoid the plumes from the large and numerous fires, although, of course, the entire boundary layer was filled with polluted air. Flights 14 and 15 were made specifically to investigate fires associated with the jungle clearing to the southwest of Manaus. Flight 16 was made to the west of Manaus, and a series of low level transits were made over a region of unperturbed jungle.

A typical flight profile for the 1980 flights is shown in Figure 11 showing 6 vertical profiles form the lower boundary layer to a little over 10 Km. Altogether ∿ 50 vertical profiles were obtained, about 20 over the clear jungle, 15 over the cer - rado with a further 15 either in the transition area or into fire smoke.

Because some of the instruments were operated at cabin pressure, it was the practice to hold pressure constant at 1 atmosphere when the aircraft operated at or below 6 Km and to change to a constant 0.8 atmosphere when the aircraft operated above this altitude. This practice accounts for the step-like character of the flight profiles.

RESULTS OF BIOMASS BURNING EXPERIMENTS AND BACKGROUND SAMPLES

During 1979 and 1980 a total of about 45 can samples obtained on the ground close to burning vegetation and on the aircraft in fire plumes were analyzed for atmospheric trace gases. In an earlier paper (Crutzen et al., 1979) we introduced a method to estimate the global emission rates of a particular gas from biomass by determining the ratio of the emission of the gas to that of CO_2 by the fires and multipling these ratios by the global CO_2 production rates as estimated by Seiler & Crutzen (1980). The emission ratios were determined by dividing the enhancement of the mixing ratio of the gas over background by the carbon dioxide mixing ratio enhancement. We occasionally sampled specific fires, e.g., above smoldering vegetation or directly above the fla - mes; most samples were integrated over about half a minute and were conducted by drawing in air from the top end of a three meter pole, which was swayed above or near the fires. Although we could have divided the data according to different categories of fires, e.g., fires of dead grass or forest material, first or second burn after slashing, etc., the data which we obtained were not dissimilar and numerous enough to justify detailed categorization at this stage. A more detailed analysis of the

physical and chemical factors which influence the emission rate ratios remains an important task in the future.

The emission rate ratios obtained from the fire samples in Brazil are presented in Table 1. The average emission ratios which were published in the earlier study, based on a much more limited data base (Crutzen et al., 1979), agree quite well for most gases with the exception of N_2O. The difference in N_2O yields by an order of magnitude is due to an earlier interference of the N_2O chromatographic peak by CO_2. It is clear that there is a wide range of possible emission ratios which stills needs to be narrowed down by more extensive and systematic research. The emission ratios of CO, CH_4 determined from the cannisters sampled during the aircraft smoke plume flights are also presented in Table 1. The agreement between the ratios derived by ground and aircraft sampling is encouraging.

During the Brazil experiments of 1979 and 1980, determinations were also made of non-methane hydrocarbon emissions by fires and the data are likewise listed in Table 1. We notice that alkenes constitute about 45% of the emissions, with ethylene the most important contibutor. Next in magnitude ($\approx 24\%$) are the emissions of alkanes, with ethane and propane as the most important gases. Especially the alkenes are photochemically reactive in the troposphere and their oxidation may lead to the formation of ozone, if sufficient NO is present in the atmosphere. This is likely in the cerrado re gion since NO is produced burning (Clements & McMahon, 1980). It may be mentioned that our CO and hydrocarbon emission factors do not deviate substantially from earlier determinations (see Table 2).

Some background air samples of natural atmospheric constituents are interesting because they were gathered at low altitudes over the tropical forest. One set of sam ples was taken at night on top of an approximately 40 meter high meteorological tower about 80 Km north of Manaus (unfortunately, a daytime sample was contaminated) and another set of data was obtained during flights between 30 and 360 meter altitude above the forest canopy. The data are shown in Table 3. All values are expressed as carbon atom volume mixing ratios, which means that e.g., for C_5H_8, the average volume mixing ratio is obtained by dividing the value in Table 3 by 5. Table 3 indicates that average daytime volume mixing ratio of isoprene from 5 datapoints up to 360 m altitude is equal to 1.7 ppbv (1.7×10^{-9}). During the night the measured, average hydrocarbon mixing ratio at canopy height is lower than during the day. Isoprene values have dropped on the average to 0.9 ppbv. This is in accordance with observation by Sanadze 1963 who found isoprene emission rates to be light dependent with no appreciable emissions occuring at night.

RESULTS OF AIRCRAFT FLIGHTS

Typical results of the 1979 flights are shown in Figures 9 and 10 which contain

the local concentrations of CO in smoke plumes. Shown in the figures are schematic representations of the smoke plumes and the aircraft passes through the plumes. The bar graphs show cross sections of the local concentrations of CO. Each bar represents approximately 10 s of measurement. The plume in Figure 9 was in relatively still air and was nearly vertical. The plume terminated in a cloud deck above which no smoke was visible. Passes were made above the cloud and at various altitudes through the smoke plume. The plume in Figure 10 exhibited a fairly coherent shape but was definitely tilted by the wind.

As may be seen in Figures 9 and 10, large concentrations of CO (up to 2 ppmv) may be found in the plumes. The effect of the large scale burning on CO amounts in the plume-free, well-mixed, cerrado boundary layer was to increase generally the concentration to 150-200 ppbv. It may be seen, however, from pass number 1 above the cloud deck in Figure 9 that some relatively clean air ($\sim$ 90 ppbv) had overridden the CO enriched layer below the cloud.

The results which were obtained on the 1980 aircraft flights can be divided up into the following three characteristic regions: 1) the boundary layer above the tropical forest, north of about 6° S; 2) the boundary layer above the cerrado, south of 9°S; 3) the free troposphere above the boundary layer.

The top of mixed layer was typically located at about 750 mb ($\sim$2.5 Km) in the cerrado and in the mean near 800 mb ($\sim$2 Km) above the forests. This can be most clearly identified particularly in the sub-tropical region by the dew point depression curves (Figs. 5 and 6) and in the relative humidity profiles of Figures 12 and 13 as the transition step to a deep layer of low relative humidities between 20% and 30% centered near 5-6 Km altitude. The profiles shown for the relative humidities and other profiles for CO and O_3 are average vertical profiles for all measurements during 1980 in the cerrado and in the tropical forest regions of Brazil. Individual profiles (Delany et al., 1985) showed sharper discontinuities between the boundary layer and the free troposphere. Plotted in Figures 12-20 is also the spread, expressed in one standard deviation, as the dotted curve on the righthand side of the average profiles. The potential temperature profiles for both regions are shown in Figures 14 and 15. These vary only slightly with altitude in the boundary layer of the cerrado region, indicating strong non-convective, thermal mixing. The average potential temperature profile over the tropical forests suggests the residual effects of moist adiabatic mixing related to convective activity or advection of air from regions with convective activity.

In order to separate clearly the air masses, which are polluted by biomass burning, from clean air, extensive trajectory analyses were perfomed for the flight program, adopting the isentropic package of Haagenson & Shapiro (1979). The trajectories which were so derived are shown in Figure 16. The profiles in unpolluted air masses are mainly located between the latitudes 2.1-6.2°S, while the profiles between 9.2-16.6°S were clearly affected by burning activities in the boundary layer. Between 6°S and 9°S, a transition region is situated and data from this region have not been

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Included in the present analysis. The average ozone and carbon monoxide vertical profiles for both regions are shown in Figures 17-20. Clearly the most remarkable features are the much larger, measured ozone concentrations in the lowest 3.5 Km in the cerrado regions and the drastic decrease of CO mixing ratios above the boundary layer in both tropical regimes. In comparing the measured O_3 concentrations over Brazil with data observed over the Pacific on GAMENTAG in August 1977 (Routhier et al., 1980) and along the westcoast of South America in August 1974 (Seiler & Fosham, 1981) at the same latitudes at 5-6.5 Km altitude, we notice almost two times higher ozone volume mixing ratios in the free troposphere above Brazil. From about 4 to 7 Km our measurements over both regions of Brazil show volume mixing ratios of about 40-50 ppbv (see Figures 17 and 18). Our measured ozone concentrations just above the tropical forest canopy decrease to about 20 ppbv, but the average value in the boundary layer is about 30 ppbv, which is slightly higher than the 20 ppbv measured during the GAMETAG flights in 1977 (Routhier et al., 1980). Seiler & Fishman (1981) reported values of only 10 ppbv. The measured ozone concentrations in the boundary layer over the cerrado of about 55 ppbv is, however, much higher than over the Pacific and also over the forest regions. Clearly, ozone is produced here by photochemical reactions.

The measured CO concentration in the boundary layer of both regions of Brazil are very high compared to typical observations in marine or near coastal areas with values in the 50-100 ppbv range (Seiler, 1974; Heidt et al., 1980; Seiler & Fishman, 1981). In the boundary layer of the tropical forests measured CO concentrations average about 300 ppvb (Figure 19). Carbon monoxide mixing ratios were even higher in the cerrado boundary layer and very variable (Figure 20). Measured concentrations were higher than in rural areas at mid-latitudes in the northern hemisphere. In fact, the boundary layer values shown for the cerrado region in Figure 20 are underestimations, because CO concentrations larger than 400 ppbv could not be measured because of recorder setting limitations.

Above the boundary layer the measured CO concentrations are likewise substantially higher than those measured over the ocenas at similar latitudes and times of the year. The studies by Heidt et al. (1980), Seiler (1974) and Seiler & Fishman (1981) indicate volume mixing ratios of 50-150 ppbv in the marine, free troposphere. Our observations above 4 Km altitudes agree these values. However, they show much higher CO volume mixing ratios between the top of the boundary layer and 4 Km (600 mb). This is partly due to the averaging of several individual profiles, but also indicates upward transport from the boundary layer.

DISCUSSION
RESULTS OBTAINED FROM FIRE SAMPLING

The can sample data collected during the 1979 and 1980 experiments and presented in Table 1 indicate that the geometric mean of the emission ratios of CO and CH_4 compa-

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red to CO_2 from tropical biomass burning are close to 12% and 0.9% with uncertainties of factors of 2 and 2.5, respectively. The arithmetic means are 15.4% and 1.2% respectively with standard deviations of 10% and 1%. The plume flight ratios are 14.5% for CO and 1.7% for CH_4. These ratios agree closely with those derived by us for fires in temperate forests and grasslands, 14% and 1.6% respectively (Crutzen et al., 1979). We may, therefore, adopt values of about 13% for CO and 1.4% for CH_4 as the average ratios to use for discussions on the global emission rates of CO and CH_4 to the atmosphere. As done in the earlier study we can then derive the global production rates of CO and CH_4 and other species by multiplying these ratios with the estimated global production of CO_2 by biomass burning of 2.2-4 x 10^{15} g C per year mostly in the tropics (Seiler & Crutzen, 1980). The derived numbers which follow next remain, however, uncertain by at least a factor of three.

Biomass burning can lead to an annual release of 10^{15} g CO to the atmosphere, which should be compared to the input of 6 x 10^{14} g CO by industrial activities (Seiler, 1974). The calculated average emission rate of methane is 6 x 10^{13} g CH_4 or 4.5 x 10^{13} g C per year. This implies clearly a significant contribution to the atmospheric CH_4 budget, as it is currently estimated that about 3-4 x 10^{14} g CH_4 are broken down in the atmosphere by reaction with the OH radical, adopting an average OH concentration in the atmosphere of about 6 x 10^5 molecules/cm^3 (Crutzen & Gidel, 1983; Volz et al., 1981; Crutzen, 1983). Total emissions of non-methane hydrocarbons are calculated to reach 3.4 x 10^{13} g C/year, about equal to the methane emissions. The oxidation of all hydrocarbons which are produced by biomass burning has, therefore, the potential to produce 2 x 10^{14} g CO annually in the troposphere, which is about 25% of the direct production of CO by fires. The most prominant group of gases emitted among the non-methane hydrocarbons are the reactive alkenes ($\sim$45%) with ethylene being most abundant. Through these emissions there is the possibility of significant oxidant (ozone) formation. We will return to a discussion of this issue when we discuss the ozone observations. The next most abundant class of hydrocarbons emitted by the fires are the alkanes, especially ethane and propane. The composition of the non-methane hydrocarbons produced by the fires is shown in Table 1.

The geometric mean of the emission rate ratios obtained for COS is about 4.7 x 10^{-6}, and the arithmetic mean is 8.2 x 10^{-6}. These ratios are two to three times lower than the earlier derived average ratio of 1.6 x 10^{-5} (Crutzen et al., 1979), but the uncertainty in this ratio is very large. Adopting 6.5 x 10^{-6} as the average number, we can derive a global source of COS from biomass burning of 7 x 10^{10} g S annually Fortuitously, this production is equal to the stratospheric loss of COS by photolysis in ultraviolet sunlight (Crutzen 1976; Turco et al., 1980). Johnson (1981) has postulated that the ocean surface waters could remove about 2 x 10^{11} g S of COS annually by dissolution and hydrolysis, leading to the formation of H_2S and CO_2. On the other hand, Rasmussen et al. (1982) found seawater always to be supersaturated with regard to the atmospheric concentrations of COS and calculated a total, annual input of COS

from the oceans to the atmosphere of 4×10^{11} g S. In addition, the oxidation of CS_2 by reaction with OH has been shown by Jones et al. (1983) and Nike (personal communication) to proceed readily in air with a reaction coefficient of 2×10^{-12} cm^3 molecule^{-1} s^{-1}, leading to the formation of one COS and one SO_2 molecule. The global industrial release of CS_2 to the atmosphere is about 4×10^{11} g CS_2 annually (Peyton et al., 1976), so that the atmospheric oxidation of this amount of CS_2 in the atmosphere may yield COS at a rate of 1.7×10^{11} g S per year. Compared to these high input rates of COS to the atmosphere, the COS production from biomass burning may only account for 10%. Additional COS may be provided by coal burning and other industrial activities. It seems that a large sink of COS in the environment has not been identified. The terrestrial biosphere is the most likely possibility.

The new derived $N_2O : CO_2$ emission ratio rate has a geometric mean of 1.5×10^{-4}, with an uncertainty of about a factor of 3, the central value being roughly a factor of ten smaller than the earlier estimate of 2.2×10^{-3} (Crutzen et al., 1979). The arithmetic ratio is about two times higher. Adopting a value of 2.5×10^{-4} for this ratio, the global N_2O production from biomass burning can be estimated at 2×10^{12} g N per year with an uncertainty of more than a factor of 3. This value is significant as an anthropogenic source in comparison with the estimated production 1.6×10^{12} g N from coal and fuel oil burning (Weiss & Craig, 1976). The loss of N_2O in the stratosphere is in the range $6-11 \times 10^{12}$ g N per year, so that biomass burning can add a significant fraction of the total N_2O input in the atmosphere. Stratospheric reactions provide probably the only loss of atmospheric N_2O. The remaining atmospheric emissions of N_2O are probably due to denitrification and nitrification processes in the soils and waters (Weiss, 1981, Seiler, 1981; Elkins et al., 1978; Bremner et al., 1981) . The global burden of atmospheric N_2O is increasing by about 0.2% per year (Weiss, 1981)

An intercorrelation of CO and NOX concentrations from flights 10-13 was made to determine the CO/NOX emission from the large scale brushfires in the cerrado. During the portions of the 1980 flights in the cerrado boundary layer, the aircraft specifically avoided smoke plumes and so the ratios obtained relate to aged rather than fresh fire emission.

The results of a least squares fit for the CO versus NOX data was 73 ± 4 for the ratio of CO/NOX in the boundary layer over the cerrado and may be taken to be the emission ratio for the large scale fires. Given that a fairly constant value of 0.14 ± 0.02 for the CO/CO_2 ratio has been determined for all fire evissions measured in this study, a value of

$$\frac{CO_2}{NOX} = \frac{CO}{NOX} \times \frac{CO_2}{CO} = 535 \pm 95$$

may be obtained.

This compares with values of ≈ 1000 reported by Evans et al. (1977) on fresh smoke from prescribed burning in Australian fires. Laboratory burning experiments for a variety of fuels have given a CO_2 to NO_x volume emission ratio of about 400 (Clements

& McMahon, 1980). Tests on NO_x emissions from woodburning fireplaces indicate values of 2000 (Muhlbaier-Dasch, 1982) and 710 (DeAngelis et al., 1980). We believe that our measurements present an underestimate of the NOX production in open vegetation fires, because all our simultaneous in situ measurements of NOX and CO were made outside fire plumes so that we may suspect that some NOX may have been removed by photochemical reactions and dry deposition.
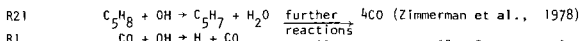
The determination of the NOX to CO_2 ratio of $\sim 2 \times 10^{-3}$ indicates the possibility of an NOX production of 7×10^{12} g N per year from biomass burning activities in the tropics. This compares to an industrial source of 20×10^{12} g N/year (Crutzen et al., 1979) and a lightning source of about 3×10^{12} g N/Year with an uncertainty of a factor of three (Crutzen, 1983). Consequently, the NOX emissions from biomass burning represent an important souce of nitrogen oxides to the tropical atmosphere with a strong potential for an impact on the photochemistry of the tropical, continental areas.

Our measurements in Brazil have, therefore, confirmed that agricultural burning activities can put substantial quantities of CO, CH_4, non-methane hydrocarbons, NOX and N_2O into the atmosphere and that these activities may very well be as important to global air chemistry as the industrial activities in the developed world. However, especially for NOX, N_2O (and COS) the variability in measured emission rate ratios are so large that there remain large uncertainties in the quantifications of the emission rates.

AIRCRAFT FLIGHT RESULTS - PROFILES OF OZONE AND CARBON MONOXIDE

The most interesting observations which we made concern the measured profiles of ozone (Figures 17 and 18) and carbon monoxide (Figures 19 and 20). They clearly point to a substantial production of carbon monoxide in the boundary layers of both the cerrado and selva regions, while ozone is clearly produced in the cerrado, but destroyed in the selva.

The production of carbon monoxide above the forests can be explained by the rapid oxidation of reactive hydrocarbons emitted by foliage in accordance with the proposal by Zimmerman et al. (1978). This can be shown by a simple calculation of the equilibrium volume mixing ratios of CO with the average measured isoprene (C_5H_8) concentrations of about 1.7×10^{-9} (1.7 ppbv) in the first 350 m above the forest canopy during one of our flights, assuming that the reactions with hydroxyl (OH) are important, so that

R21 $\qquad C_5H_8 + OH \rightarrow C_5H_7 + H_2O \xrightarrow[\text{reactions}]{\text{further}} 4CO$ (Zimmerman et al., 1978)

R1 $\qquad CO + OH \rightarrow H + CO_2$

Using reaction rate coefficients of 8×10^{-11} and 2.8×10^{-13} cm^3 molecule^{-1} s^{-1} for these reactions respectively (Atkinson et al., 1979; Baulch et al., 1981), the volume mixing ratio of CO in equilibrium with the observed isoprene concentrations is about

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equal to 2×10^{-6}, which is much larger than we observed. This shows clearly that the oxidation of isoprene and other hydrocarbon may very well be responsible for the high carbon monoxide concentrations in the boundary layer above the forests. *In reality* we must consider that the yield of CO *from* C_5H_8 oxidation may not be equal to 4, that the *measured* concentrations of 1.7 ppbv of C_5H_8 may not be characteristic for the boundary layer and that hydroxyl concentration may be so low over the tropical forests, that other chemical reactions may play a **role in the initiation** of the isoprene oxida-tion, e.g. the reaction with ozone. Likewise, the lack of knowledge of the reaction me chanisms which lead to the oxidation of hydrocarbons in the atmosphere, especially in the absence of NO, has been recognized (e.g., Zimmerman **et al.**, 1978) and it *was* pointed out that many oxygenated species may be *formed which* can be removed from the atmosphere by rainfall or uptake by vegetation. However, although it is clear that hydrocarbon oxidation may very well be the source of boundary layer CO in the forested regions, without further measurements, we cannot with certainty discount the possibi-lity that carbon monoxide is directly emitted by the forests in much larger rates than found by Seiler & Giehl (1977) for temperate vegetation. The limited amount of data available to us is not adequate to identify with certainty the source of carbon monoxi de over the tropical forest areas. In addition to C_5H_8 other hydrocarbons are emitted by the forests *which may likewise* be converted to CO by photochemical reactions (see Table 3).

It is clear that the high concentrations of CO in the cerrado boundary layer du-ring the dry season (see figure 20) are caused by the many fires in this region at that time of the year. Because of large emissions of smoke, visibility is often poor.

With the few available data on isoprene concentrations during daytime above *the* tropical forest, we may try to make a rough esti*mate* of the loss of ozone through reactions *with* C_5H_8 by tropical forests. The rate coefficient for the reaction O_3 + $C_5H_8 \rightarrow$ products has recently been determined by Adeniji et al. (1981) and for tropical conditions we may use as the value 2×10^{-17} cm^3 molecule^{-1}. With average O_3 volume mixing ratios of 30 ppbv in the boundary layer we calculate that the mean lifetime of isoprene against reaction with ozone is about 24 hrs. If reaction with ozone were the only sink for C_5H_8, the lifetime of this gas in the atmosphere would be long enough to allow thorough mixing through the mixed layer, so that the loss of ozone can be calculated to 10^{11} *molecules* cm^{-2}s^{-1} during daytime. It should be added, however , that ozone does also react with terpenes and C_2-C_7 alkenes, which are likewise abun-dant according to the observations listed in Table 3. Furthermore, ozone is destroyed by reactions with hydrocarbon fragments and with hydroperoxyl (HO_2) and by the two reac-tions

R2 $\qquad O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (\lambda \underset{\sim}{<} 310$ nm)

R3 $\qquad O(^1D) + 2OH$
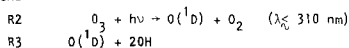
The electronically excited oxygen atom $O(^1D)$ is deactivated to ground state ato-mic oxygen mainly by reaction with atmospheric nitrogen and oxygen

R22 $O(^1D) + M \to O(^3P) + O_2$
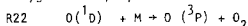
which leads back to ozone by reaction R7. Assigning typical calculated values to the photochemical, atmospheric parameters involved, we can calculate that the loss of ozone due to the pair of reactions R2 and R3 in the tropical forest boundary layer is about equal to 2×10^{11} molecules cm^{-2} s^{-1} during daytime. Therefore, the combined daytime loss of ozone in the forest boundary layer by chemical reactions certainly ex-ceeds 3×10^{11} cm^{-2} s^{-1}. Additional loss of ozone occurs through reactions on forest foliage, but this cannot be estimated from our observations. Extrapolating from the analysis of Lenschow et al. (1982) this sink is quite comparable to the chemical loss rate in the boundary layer, so that the total O_3 loss rate may be 5×10^{11} $cm^{-2}s^{-1}$ on the average.

We may continue the calculations for C_5H_8 and estimate the minimum effect of OH reactions on isoprene. As the reaction between isoprene and hydroxyl is very fast with a reaction rate coefficient of $8 \times 10^{11} cm^3$ molecule^{-1} s^{-1}, the minimum concentra-tion of OH in the boundary layer can be roughly determined by assuming that OH producti-on by reactions R2 and R3 and balanced by the reaction

R21 $OH + C_5H_8 \to C_5H_9O \to$ products
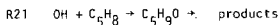
neglecting any recycling of OH in the following reactions. Adopting typical calculated values for the photochemical parameters in the tropics and $\mu(C_5H_8) = 1.7 \times 10^{-9}$ we can calculate (OH) $\geq 10^6$ molecules cm^{-3}. With this value of OH the photochemical lifetime of C_5H_8 becomes equal to 3 hours which may approach the dynamical mixing time in the boundary layer.

We can estimate approximately the minimum loss of isoprene in the boundary layer which must be supplied from the forests. The resulting isoprene flux is at least equal to about 6×10^{11} molecules cm^{-2} s^{-1}. For the entire 16×10^6 km^2 tropical forest area of the world (Bolin et al., 1979) this would extrapolate to a minimum annual produc-tion rate of isoprene of 1.5×10^{14} g C which is 60% of the value estimated earlier by Zimmerman et al., (1978). The resulting minimum CO production rate could be about 3×10^{14} g CO/year. This CO production rate in the mixed boundary layer above the tropical forests could lead to a buildup of at least 20 ppbv day. Referring to Figure 16 it can be seen that the air which reached Manaus, the center of most research flights, has travelled about 2 days in the forest boundary layer, allowing a minimum buildup of 40 ppbv of CO. It seems, however, that much more CO must have been produced in the airmass. Although, we do not know the composition of the air before it entered the forested area from the Atlantic (see Figure 4), it is probable that it contained about 100 ppbv of CO as seems to be typical for the composition of oceanic boundary layer air (Seiler, 1974; Seiler & Fishman, 1981). This means that about 75 ppbv of CO per day was formed in the forest boundary layer during transit to the Manaus region. This amounts to a production of 4×10^{12} molecules $cm^{-2}s^{-1}$ and is equivalent to 2-3% of the

net primary productivity of the tropical forests which is estimated at 1 kg C/m^2/ year (Bolin et al., 1979, page 24). This would indicate a much larger hydrocarbon emission efficiency in the tropical forests than in temperate ones (Zimmerman et al., 1978).

Carbon monoxide volume mixing ratios in the free troposphere in the cerrado and tropical forest areas are generally close to 100 ppbv above about 4.5 km altitude (Figure 20). These values are roughly equal to the concentrations measured by Seiler(1974), but much larger than the 50 ppbv reported by Heidt et al . (1980) on GAMETAG during the same season over the Pacific. Below this altitude there is a gradual transfer to the high measured concentrations of CO in the boundary layer both of the cerrado and selva ecosystems. Although this transition is to some degree a result of the averaging procedure, it is clear from the profiles that carbon monoxide does escape from the production region in the tropical boundary layer. Considering that CO volume mixing ratios in the equatorial free troposphere are higher over the continents than over the oceans, we have to conclude that in the tropics carbon monoxide is mainly formed in the boundary layer over the continents, that it probably escapes from it by convection and that it is transported in the free troposphere to the marine atmosphere where most of it is destroyed by reaction with hydroxyl. The production of carbon monoxide in the tropics satisfies the theoretical requirements by Crutzen & Gidel (1983) and Volz et al (1981).

The measured, average ozone vertical profiles over the savanna and tropical forest regions (Figures 17 and 18) clearly point to a production of ozone in the savanna boundary layer which is polluted by the effluents of biomass burning. This ozone production is probably made possible by the existence of substantial quantities of nitric oxide due to biomass burning and occurs when reactive hydrocarbons and carbon monoxide are oxidized by reactions which have been explained earlier in this article. Production of ozone in the plumes of forest fires has been documented by Evans et al. (1977) and Radke et al. (1978), so that it is not surprising that it also occurs on large scale during the dry season in the regions where much biomass burning takes place. Ozone is destroyed by reactions at the earth's surface and in the forest boundary layer by photochemical reactions involving UV radiation and water vapor and by reactions with hydrocarbons, especially isoprene, as discussed earlier in this chapter. Most likely, the ozone which is destroyed in the tropical surface layer is brought down form the free troposphere. To explain an average ozone loss of about 5×10^{11} molecules cm^{-2}s^{-1}, as derived before, a downward velocity at the top of the boundary layer (≈ 2 km altitude or 800 mb, pressure level) of about 0.5 cm/s is required, based on an average ozone volume mixing ratio of 40 ppbv form our measurements. This is not an unreasonable minimum value for tropical Brazil in the dry season. According to Kousky & Kagano (1981), the mean downward velocity at 800 mb during August for the triangle Belém (1°23'S, 48°29'W), Manaus (3°8'S, 60°1'W) and Vilhena (12°44'S, 60°8'W) can be estimated to be about 0.4 cm/s, so that a consistent picture for the ozone budget of the tropical forest boundary layer emerges.

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It is plausible that significant production of ozone takes place in the free troposphere of the continental tropics as there may be significant amounts of NO and NO_2 in the air due to the production of these gases in lightning. The concentrations of NO and NO_2 can be roughly calculated . A satellite study by Turman & Edgar (1982) reports the average number of lightning flashes over the tropical forest areas of Brazil to be equal between 20 and 40 per minute per 10^6 km^2 surface area during August. Assuming a production of at least 10^{26} molecules per lightning flash (Noxon, 1976, 1978) , the minimum production rate of NO_x ($NO + NO_2$) can be expressed as 5×10^9 molecules cm^{-2} s^{-1} . If we assume that most NO_x is generated between the ground and 12 km and that most NO_x is lost from the atmosphere by conversion to HNO_3 via the reaction.

R14 $OH + NO_2$ (+M) $\rightarrow$ HNO (+M)
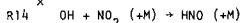
we may estimate an NO_2 volume mixing ratio of at least 50 ppbv for an average diurnal concentration of OH of 2×10^6 molecules cm^{-3} as currently calculated in photochemical models for the tropics (Volz et al., 1981; Crutzen & Gidel, 1983).

Due to the steady state between NO and NO_2 by the reactions

R13 $NO + O_3 \rightarrow NO_2 + O_2$

R6 $NO_2 + h\nu \rightarrow NO + O$ ($\lambda \lesssim 400$ nm)
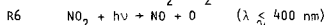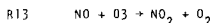
we may roughly calculate that the volume mixing ratio of NO in the free troposphere is about equal to that of NO_2. For such high mixing ratios of NO production of ozone will take place in the CO oxidation cycle, which was outlined before. The production rate of ozone is about equal to the loss rate of CO by reaction with OH. If we assume (OH) $\stackrel{\sim}{\sim} 2 \times 10^6$ molecules cm^{-3} and an average volume mixing ratio of CO of 200 ppbv above the surface layer, the average yield of O_3 between 2 and 5 km during one week is about equal to 70 ppbv and the column integrated, diurnally averaged ozone production and CO loss rate are equal to about 6×10^{11} molecules cm^{-2} s^{-1}, enough to balance the loss of ozone in the forest boundary layer. If the OH concentrations would be larger than 2×10^6 cm^{-3} more ozone production would take place and vice versa. The main point here is that ozone production of the right amount to balance the boundary layer loss of ozone can occur in the free troposphere. This production of ozone is concentrated over the continents, because that is where about 80% of all lightning occurs (Orville & Spencer, 1979; Turman & Edgar, 1982). This may well explain why ozone is more abundant in the continental than in the marine free troposphere (McFarland et al.,1979) It seems, therefore, that it is possible to derive rather consistent explanations for the ozone observations in Brazil. This hypothesis should be tested in future experimental studies.

CONCLUSIONS

In this work we have confirmed that large emissions of important atmospheric trace gases, such as CO, CH_4, hydrocarbons, NO_x and N_2O, take place due to biomass bur

ning especially in the dry tropics. These activities lead to high CO, O_3 and NO_x con - centrations in the boundary layer of the savanna regions of Brazil in comparison with concentrations measured in the marine boundary layer at the same latitudes. Concentrations of CO and O_3 are comparable to or higher than those at mid-latitudes in the northern hemisphere where industrial emissions play a large role. Similar conditions probable prevail during the dry season in many savanna regions on earth, which cover a total area of 19×10^2 km^2 (Bolin **et al.**, 1979). Agriculture-related activities are , therefore, the main source of photochemical air pollution in large parts of the conti nental tropics during the dry season and our work has confirmed that they are also of such a magnitude to be of importance in global air chemistry.

We have noticed that the concentrations of CO and O_3 over the continents are higher than over the oceans, not only in the boundary layer, but also in the free troposphere. The continental tropics are therefore the source regions of CO and O_3 and other trace gases which are found in the marine tropics. In the clean tropical troposphere there may well be enough NO_x present over the continents due to lightning to promote significant production of ozone.

A limited set of measurements of organic compounds over the tropical forest areas suggests an important role of organic compounds in global air chemistry. We have measured average isoprene volume mixing ratios of about 2 ppb in the forest boundary layer and have shown by simple calculations that its oxidation and that of other hydrocarbons may lead to carbon monoxide production of the same order as that derived from industrial and biomass burning activities. This explains the high concentrations of carbon monoxide which were measured in the tropical forest boundary layer and which are higher than in the rural areas of the mid-latitudes in the northern hemisphere. In fact, our studies point to the possibility that 2-3% of the carbon fixed in net primary productivity is returned to the atmosphere via CO. The hydrocarbon emission which would be responsible for this may be even larger.

Many areas in the tropics are undergoing rapid changes because of increasing development in the agricultural and industrial sectors. The findings of our work in Brazil therefore justify enhanced interest in studying tropical air chemistry. The tropics play a large role in global air chemistry.

RESUMO

Programa de medidas de campo no Brasil nas estações secas de 1979 e 1980, durante os meses de agosto e setembro, demonstraram a grande importância das regiões tropicais continentais na química atmosférica global. Especialmente na camada de mistura, a composição do ar sobre o continente e oceano é muito diferente e as regiões terrestres são fontes de produção em grande escala de muitos gases-traço importantes. Queimas de biomassa ocorrem durante a estação seca, especialmente nos cerrados, causando emissões substanciais de poluentes atmosféricos tais como CO, NO_x, N_2O, CH_4, e outros hidrocarbonetos. Concentrações de ozônio são também aumentadas devido a reações fotoquímicas. Emissões orgânicas biogênicas de florestas tropicais têm um papel importante na fitoquímica da atmosfera. O monóxido de carbono mostrou-se presente em altas concentrações na camada limite da floresta tropical e as concentrações de ozônio foram muito inferiores no cerrado.

Table 1. Emission rate ratios of CH_4, CO, N_2O, COS and non-methane hydrocarbons to CO_2 (n= number of samples, gm = geometric mean, gs = geometric standard deviation, am = arithmetic mean. σ = arithmetic standard deviation. Also give in this table is the average composition of the non-methane hydrocarbons [1] in the fires.

		CAN SAMPLE (GROUND)					PLUME FLIGHTS	
	n	gm	range	am	σ	n	am	σ
CH_4	36	0.9%	0.3-2%	1.2%	1%	4	1.7%	0.1%
CO	36	11.6%	6-24%	15.4%	10%	4	14.5%	3%
N_2O	38	1.8×10^{-4}	0.6.5.8%	3.1×10^{-4}	2.9×10^{-4}	3	1.3×10^{-4}	0.2×10^{-4}
COS	22	4.7×10^{-6}	1.5-15%	8.2×10^{-6}	7.5×10^{-6}			
NMHC	37	1.1%	0.4-2.8	1.7%	1.4%			

Composition of non-methane hydrocarbons as % C

45% alkenes (52% C_2H_4, 27% C_3H_6, 21% others)

24% alkanes (56% C_2H_6, 33% C_3H_8, 11% others)

13% aromatics (61% benzene, 27% toluene, 12% others)

8 % oxygenated

6 % C_2H_2

Table 2. Comparison between earlier compilations and our observations of hydrocarbon emission factors.

	Forest Fire Literature	Queimadas 1980 (our work)	Grass Fire Literature	Brushfire 1979 (our work)
(ΔHC /ΔCO_2) % Geometric Mean	1.2	2.3	1.8	1.7
(Range)	(0.4-8.0)	(0.5-5.8)	(0.6-10.3)	(0.7-15.3)
Reference	1,2,3,4		1,3,5	
(ΔCO /ΔCO_2) % Geometric Mean	6.2	11.9	7.1	11.3
(Range)	(3.2-21.0)	(1.1-39.1)	(3.6-24.6)	(3.1-54.9)
Reference	1,2,3,4,6		2,3,5,6	

References: 1. Darley et al., 1972; 2. Darley et al., 1966 3. Boubel et al., 1969; 4. Fritschen et al., 1970; 5. Gerstle & Kemnitz, 1967; 6. Crutzen et al., 1979

Table 3. Most frequently measured non-methane hydrocarbon in boundary layer
(below 2 km) over tropical forests obtained form five samples.

Compound	Volume Mixing Ratio of Carbon Atoms (ppbv C)	Number of Non-zero Determinations
Isoprene	8.3	5
Δ^4 Carene	15.4	2
β- Pinene	1.1	3
Myrcene	8.1	1
α- Phellandrene	8.7	1
α- Terpinene	0.9	1
Δ^3 Carene	6.1	1
α- Terpinene	0.3	1
α- Terpineol	2.4	1
Linanool	3.4	1

Percentage composition of hydrocarbons, except terpenes:

C_2 - C_7 Alkanes	25.2%
C_2 - C_7 Alkenes	29.1% (excl. isoprene)
Isoprene	20.4%
C_2, C_3 Alkynes	7 %
C_6- C_8 Aromatics	18.2%

500mb-HEIGHT CONTOURS

AUG 28, 1200 GMT
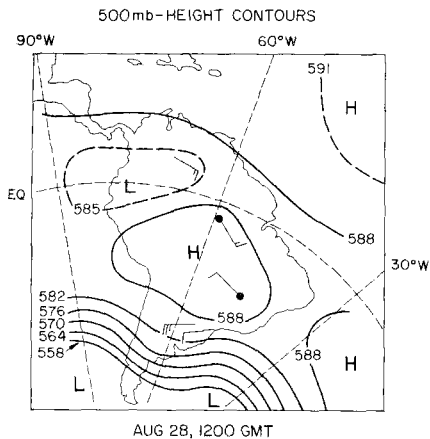
FIG. 1 - 500 mb height contours in decameters for Agust 28, 1980, 12:00 GMT. The black dots denote the locations of Manaus and Brasília, Brazil. Observed winds (direction and speed in kts) are given at selected radiosonde stations.

850mb-HEIGHT CONTOURS

AUG 31. 1200 GMT
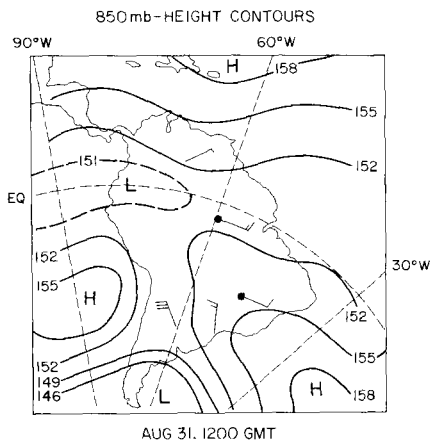
FIG. 2 - 850 mb height contours in decameters for August 31, 1980, 1200 GMT.

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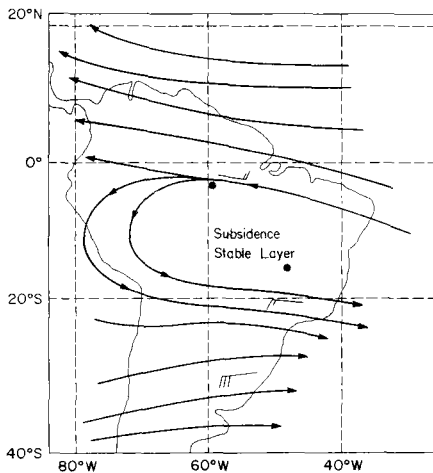
FIG. 3 - Mean climatological wind direction and speed at 500 mb over South America in August.
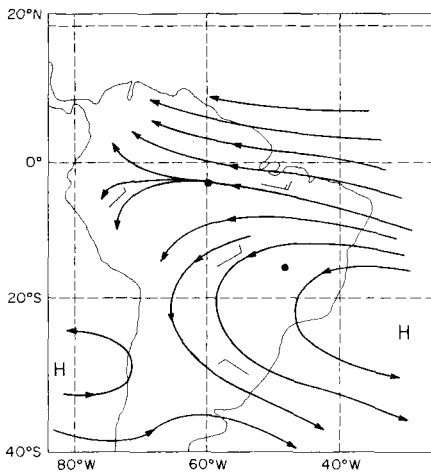
FIG 4 - Mean climatological wind direction and speed at 850 mb over South America in August.

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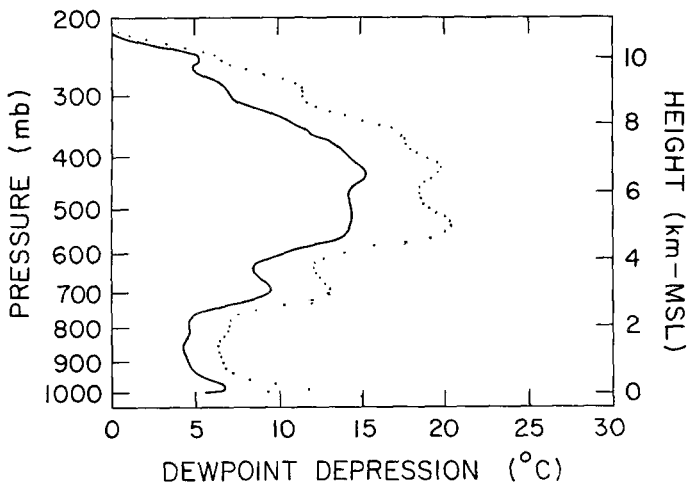
FIG. 5. Mean vertical distributions of dewpoint depression (solid curve) for the latitude range 2°S-7°S and longitude range 58°W-62°W over the tropical forests of Brazil. The horizontal distance between the solid and dotted curves marks the standard deviation of the measurements.
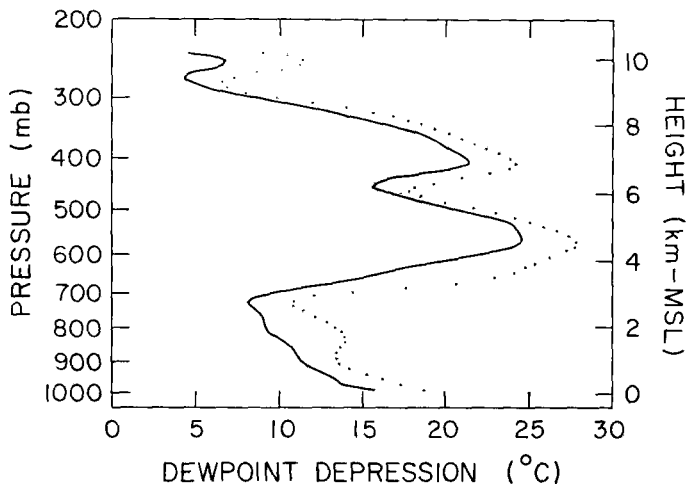
FIG. 6. Mean vertical distributions of dewpoint depression for the latitude 9°S-17°S and longitude range 48°W-58°W over the savanna regions of Brazil.

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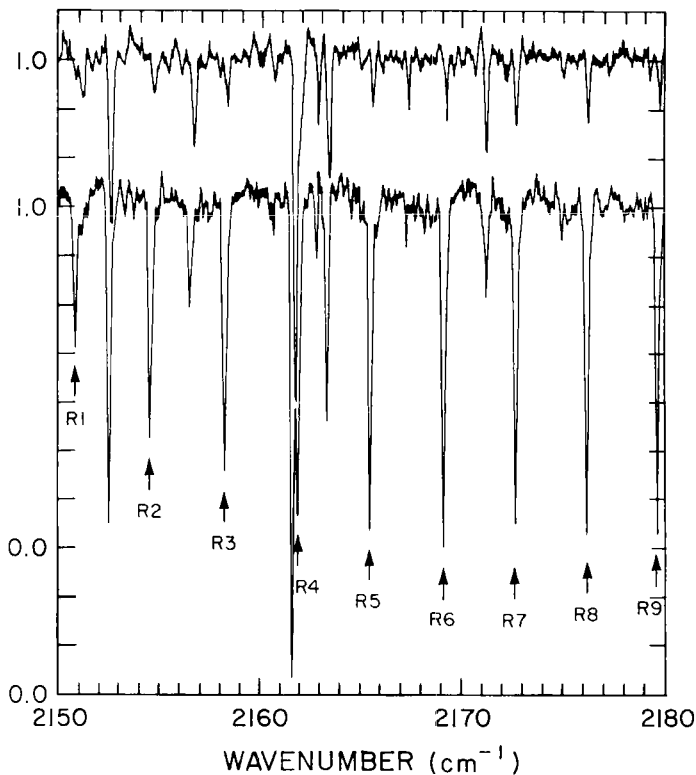
FIG. 7. A portion of the absorption spectrum in the CO fundamental. Lines (1) through R(9) of CO are marked as well as prominent lines due to H_2O, N_2O and O_3. The two spectra were recorded 30 s apart as the aircraft passed through a plume and have been displaced for clarity. The upper spectrum corresponds to 250 ppbv and the lower to 2000 ppbv. The path length was 120 m and the flight level was 939 mb.
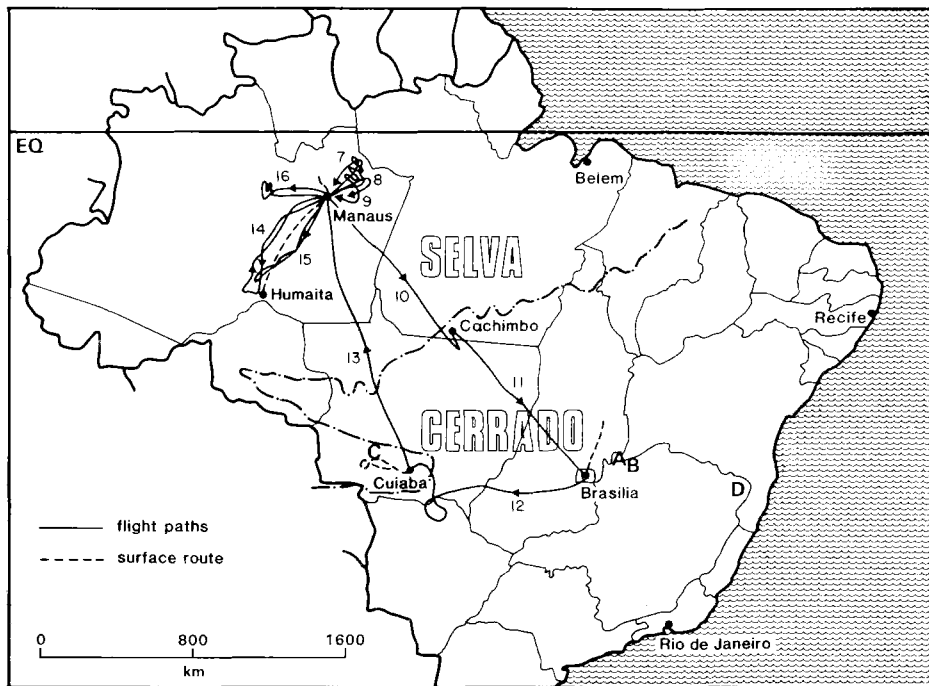
FIG. 8 – Aircraft flight routes and surface sampling locations during the 1979 and 1980 expeditions in Brazil. Plume locations the 1979 flights are denoted A, B, C and D.
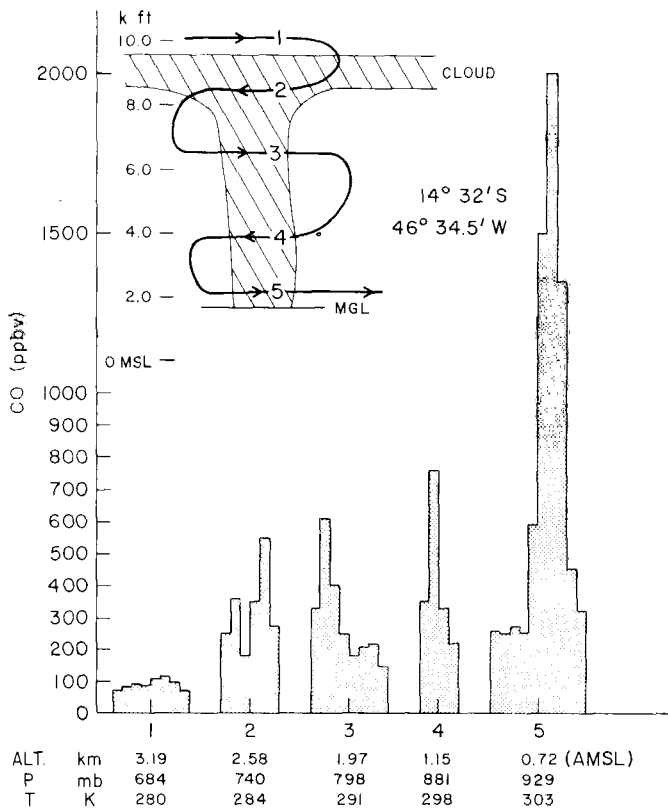
FIG. 9. Vertical distribution of CO amount for the plume shown in schematic. Each bar represents a 10 s measurement which corresponds to ∿ 1 km in the horizontal. The plume was near $14°32'S$ and $46°35'W$ on 1 September 1979.
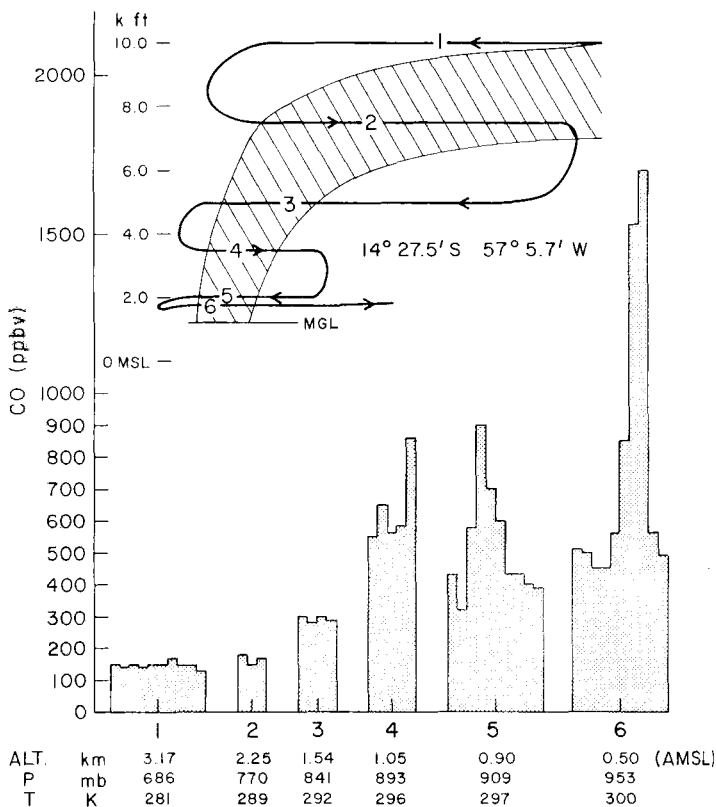
FIG. 10. As Figure 9 for a plume near $14°27'$S and $57°6'$W on 6 September 1979.

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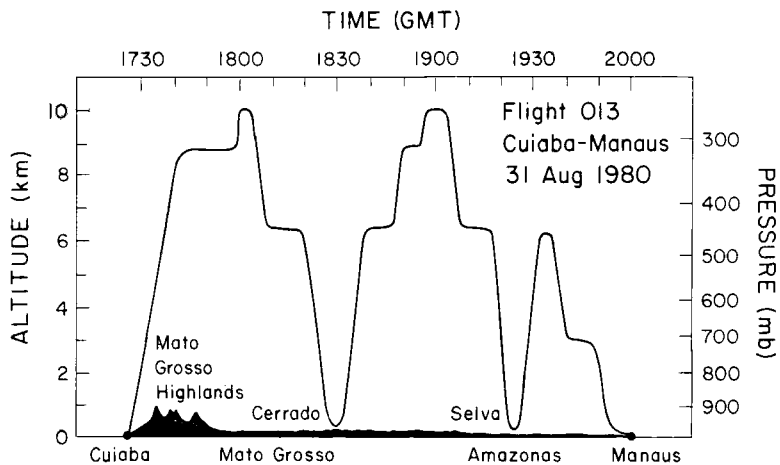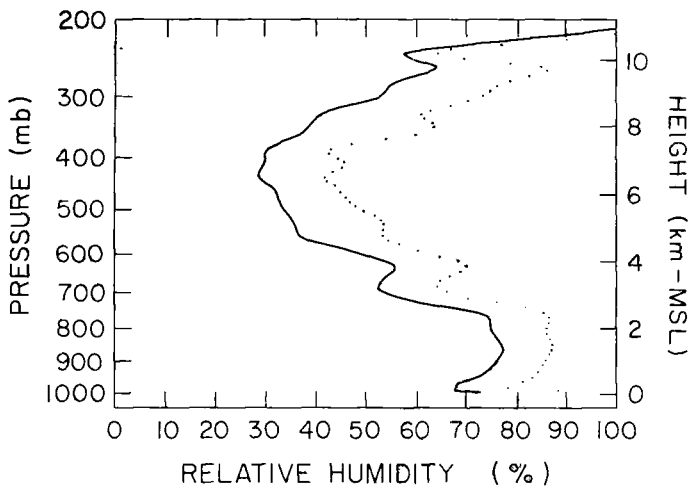
FIG. 11. Example of typical compositions of a flight leg.

FIG. 12 – Average profile of relative humidities and standard deviation from all flights over the tropical, humid forest regions of Brazil between 2°S and 7°S.
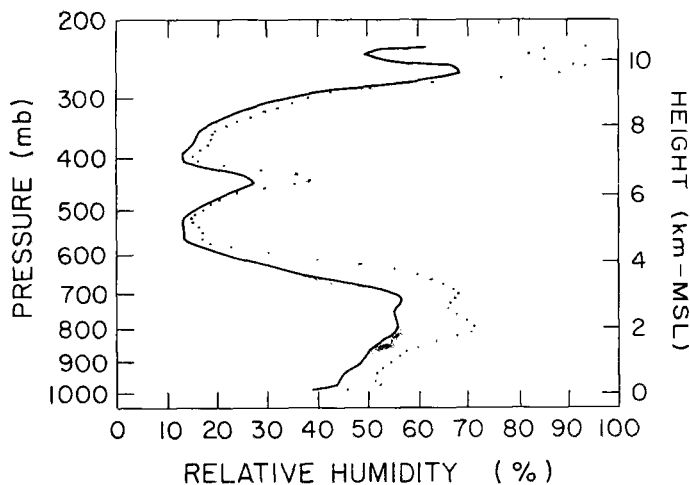

FIG. 13 – As figure 12, but for the savanna regions.
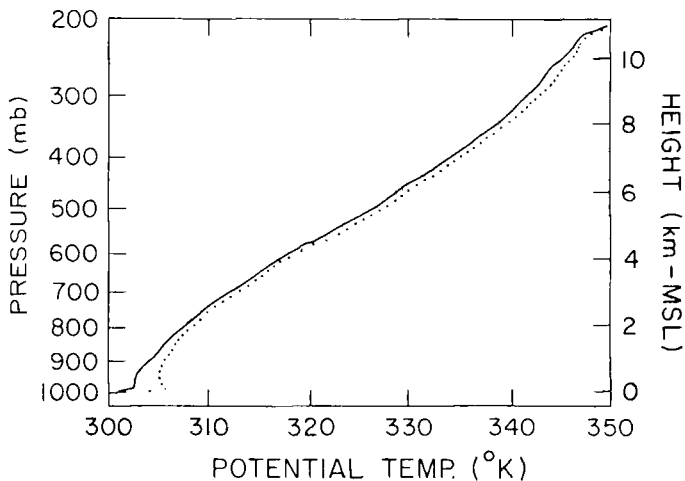
Crutzen et al.

FIG. 14 - Average profile of potential temperature over the tropical, humid forest areas of Brazil. The distance between the solid ans dotted curve marks the standard deviation of the measurements.
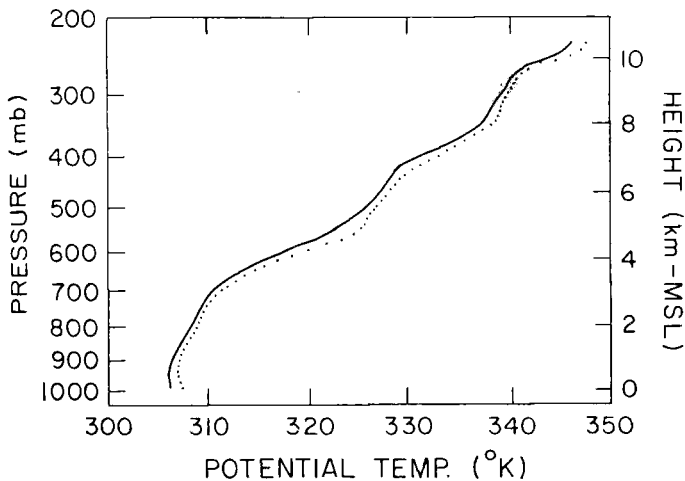

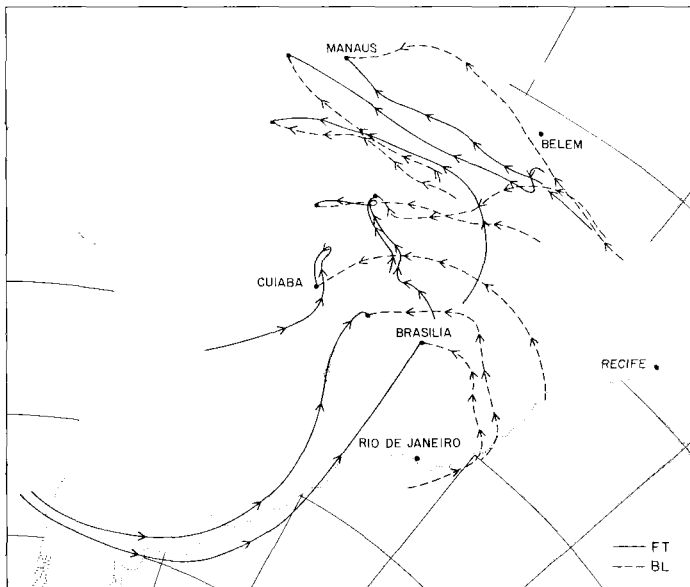FIG. 15 - As Figure 14, but for savanna regions.

FIG. 16. Backward isentropic trajectories for boundary layer air parcels
(dashed lines) and free-troposphere air parcels (solid lines ;
∿ 400–500 mb) sampled by an aircraft in the vicinity of   the
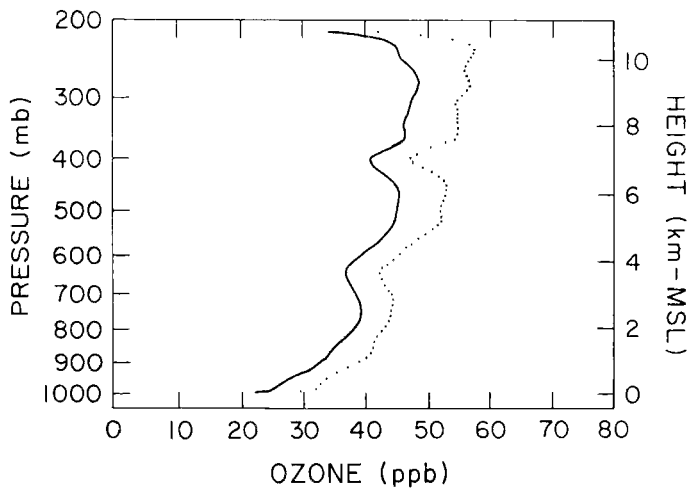trajectory end points. Each arrow segment represent 12 hr tran-
sit time.

FIG. 17 - Average profile of ozone volume mixing ratios and standard deviation (dotted curve) over the tropical, humid forest areas of Brazil.
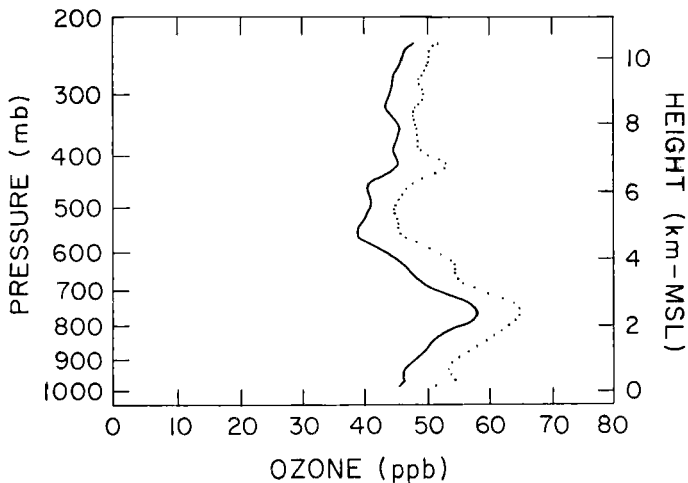

FIG. 18 - As figure 17, but for the savanna regions.
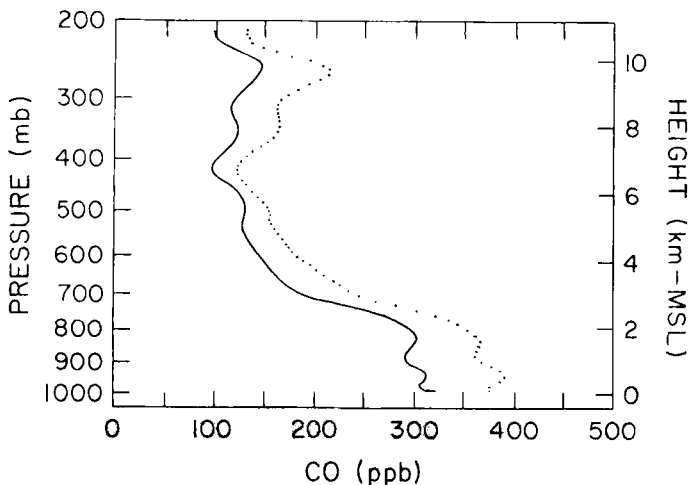
FIG. 19 – Average 1980 profile of carbon monoxide volume mixing ratios and standard
deviation (dotted curve) over the tropical, humid forest areas of Brazil.
The dotted curve indicates the standard variation of the measurements.

FIG. 20 – As figure 19, but for the savanna regions. The squares and circles are from
infrared absorption measurements in 1979. Squares are from a clear air des-
cent at 16°S. Circles are from two flights near 14°S in the vicinity   of
burning but avoiding visible smoke plumes.

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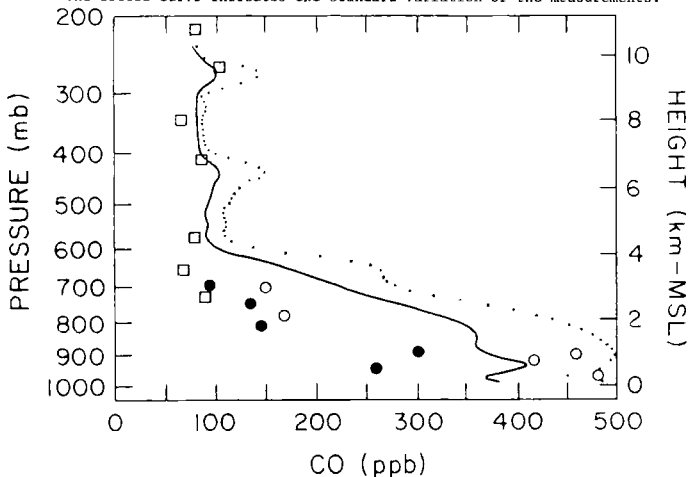Adeniji, S. A.; Kerr, J. A.; Williams, M. R. – 1981. Rate constants for ozone alkene reactions under atmospheric conditions. **Int. J. Chem. Kin.** 13: 209–217.

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