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the direct measurement of the CO profile below the forest canopy, which gave a concentration gradient consistent with an upward flux of 4×10^{11} CO molecules $\text{cm}^{-2} \text{ s}^{-1}$.

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Surface Carbon Monoxide Measurements in Amazonia

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The concentration of atmospheric carbon monoxide, CO, was measured in the Amazonian rain forest. Air samples were collected at least three times a day during a continuous sequence of 36 days, from a height of 1.5 m above the ground. These surface CO measurements were part of a large binational field expedition to the Brazilian Amazon region, the ABLE 2B mission, a joint American-Brazilian effort to measure local concentrations of several species relevant to atmospheric chemistry. The time period of this experiment was April–May of 1987, in the local wet season. The measurement technique used was chromatographic separation followed by mercury vapor detection. The surface CO measurements obtained represent a comprehensive CO data set, unique in that the concentrations were measured immediately after collection, by a measurement system installed next to the sampling sites. The CO lab was set up at Ducke Forest Reserve, some 30 km north of the city of Manaus (3°S, 60°W). The results show a small but constant diurnal variation of the CO concentration, with a maximum around noon. The average CO mixing ratio for the period was 102.9 ± 11.4 parts per billion by volume (ppbv), with most samples giving concentrations between 95 and 105 ppbv. On six occasions in April, large CO concentrations were observed during relatively short periods, and these were classified as pollution episodes associated with unusual wind conditions which probably brought air into the forest that had contact with the city of Manaus. No such episodes were seen during May. Simultaneous sampling inside the forest, under the canopy, and in the Ducke Forest clearing, show larger concentrations in the forest, by a few ppbv. This result is consistent with the direct measurement of the CO profile below the forest canopy, which gave a concentration gradient consistent with an upward flux of 4×10^{11} CO molecules $\text{cm}^{-2} \text{s}^{-1}$.

INTRODUCTION

A sensitive CO instrument was installed in the middle of the Amazonian rain forest, in early April 1987, as part of a large field expedition to the Amazon region in which American and Brazilian scientists were involved. The aim was to measure several atmospheric constituents important for atmospheric chemistry. Coordinators were the National Aeronautics and Space Administration (NASA) and the Brazilian Institute for Space Research (Instituto de Pesquisas Espaciais, or INPE). Several atmospheric gases were measured on board NASA's Electra aircraft, especially equipped with scientific instruments, but several other measurements were also conducted from the ground. This field mission, the Amazon Boundary Layer Experiment (ABLE) [McNeal *et al.*, 1983], made its second visit to Amazonia in the 1987 wet season (April–May), and it was named the ABLE 2B mission. The previous campaign, the ABLE 2A experiment, took place in July–August of 1985, and several of its results were published in the *Journal of Geophysical Research* (volume 93, 1988). A general description of the ABLE 2A mission was presented by Harriss *et al.* [1988]. No specific, continuous-surface CO measurements were made in that first experiment, but CO profiles were obtained using a tethered balloon [Zimmerman *et al.*, 1988].

During ABLE 2B, surface ozone measurements and ozone soundings in the troposphere and stratosphere were made in addition to the CO measurements. These O_3 measurements are described by Kirchhoff *et al.* [this issue]. Measurements made from NASA's Electra are reported by Browell *et al.* [this issue] and Gregory *et al.* [this issue]. Grab samples of rain forest air were intensively collected at about 1.5 m above the ground and analyzed for CO in loco, almost

immediately after the sampling procedure. Continuous CO data were obtained in this way between April 6 and May 11, 1987, the local wet season. It is believed that this is the first comprehensive surface CO data set obtained for the Amazonian region. Carbon monoxide measurements were also made from the aircraft and are described by Harriss *et al.* [this issue].

Previous Work

It appears that the only CO measurements made in the rain forest prior to the ABLE 2B mission were those of the Crutzen *et al.* [1985] expedition [Delany *et al.*, 1985; Greenberg *et al.*, 1984] and the Sachse *et al.* [1988] and the Zimmerman *et al.* [1988] data of the ABLE 2A mission. Both were measurement campaigns performed on board aircraft during the dry season. The result of the Crutzen expedition was a thorough description of the effect of biomass burning on the atmospheric concentrations of ozone and carbon monoxide. Air samples collected over the Amazonian rain forest and over savannah areas detected large concentrations of CO (of the order of 300 and 400 parts per billion by volume (ppbv)) near the ground which were ascribed to nearby biomass burnings.

The later experiment of Sachse *et al.* [1988] confirmed the influence of biomass burnings on the atmospheric concentration of CO. These measurements were made using a laser-induced differential absorption technique. Concentrations as large as 300 ppbv were observed to heights of 2–3 km, in the Manaus area, during the pollution event of early August 1985, seen also in the surface ozone data [Kirchhoff, 1988]. The Sachse data set has also clearly shown the difference between the marine CO profile and the continental, midbasin profile, influenced by numerous continental sources. Nearground CO concentrations of about 90 ppbv were measured over the ocean, whereas 120–150 ppbv were more representative of the central Amazonian Basin area.

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A general survey of CO concentrations at Brazilian sites [Kirchhoff and Marinho, 1989] has revealed values between about 100 ppbv near the Atlantic shore, during September–October, to concentrations up to 700 ppbv at Cuiabá (15.6°S, 56.1°W), located very close to the major biomass-burning area of the Brazilian Amazon region. Thus it appears that the large effect of biomass burning on the atmospheric CO concentration is well established [Kirchhoff *et al.*, 1989]. The general expectation for ABLE 2B was to find much lower CO concentrations, since little biomass burning occurs in the rainy season.

In terms of global distributions, the experiment of Reichle *et al.* [1986] should be mentioned. Mixing ratios of CO in the middle troposphere were measured by a gas filter radiometer carried on board the Space Shuttle during November 1981. Strong gradients in longitude and latitude were reported for the tropics.

Measurement Technique

Carbon monoxide concentrations in the ppbv range are usually measured using gas chromatography on whole air grab samples, temporarily stored in special containers, either glass or stainless steel cans, electropolished internally. It was decided to install the CO instrument as near to the sampling site as possible in order to avoid can storage periods longer than weeks or months. A small laboratory was installed in a forest preserve some 30 km north of the city of Manaus. All CO concentrations described in this paper were obtained in this improvised lab.

The basic CO measurement technique used is chromatographic separation followed by mercury vapor detection [Seiler, 1974]. This technique has much better resolution of the chromatographic peaks, as well as better measurement precision and linearity of response, as compared, for example, with the flame ionization detector (FID) technique, for low concentrations in the ppbv 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 temperature, are eliminated by chromatographic means on a routine basis, since the instrument is dedicated to the measurement 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 is, after extensive flushing with sample air, 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.

Site Description

The measurement site for atmospheric CO was established at the Ducke Forest Reserve, owned by the Brazilian Institute for Amazonian Research (Instituto Nacional de Pesquisas da Amazonia, or INPA). This is the same location used

Fig. 1. Measurement site at Ducke Forest Reserve. Samples were systematically taken at points M1 and M3, in the clearing, and at M2 and M4, within the forest. The clearing is surrounded by natural forests on one side (south) and by an area of cultivated trees on the other (north).

during the ABLE 2A campaign located some 30 km north of Manaus (3°S, 60°W), the capital of the Brazilian state Amazonas, and the largest city of the central Amazonian region. The prevailing winds at this site are easterlies, so that normally the effects of the big city are not transferred to the forest reserve.

The sampling site is located approximately in the center of the Brazilian legal Amazon region. This area, in Brazil, occupies about 5 million km². It reaches out into Peru, Colombia, and Venezuela in the west, and into Guyana, Surinam, and French Guyana in the north. The Amazon forest is the largest on Earth. The Amazon Basin is defined by the Amazon River and its tributaries and represents a unique ecosystem, important as potential sources or sinks for several atmospheric gases. Given its large size, this region is important not only in a regional sense, but also may have global importance in terms of atmospheric chemistry.

A sketch of the sampling site is shown in Figure 1. The clearing itself has an area of about 100 × 100 m. Its access road was kept closed to traffic at a point some 100 m away from the lab site. Samples were taken regularly at about 1.5 m above the ground, at the points marked M1 through M4. The first of these, M1, was the sampling point in the main clearing (the Met site [Kirchhoff, 1988]). At least three samples a day were collected at this point, between April 6 and May 11. M2 was a sampling point some 5 m inside the forest. Later during the experiment, M2 was abandoned in favor of point M22, further inside the forest by about 50 m. M3 was also a point in the clearing, close to a metallic tower which was used in the beginning of the experiment in an attempt to find vertical gradients. Finally, M4 was also a point inside the forest, with the difference that this site had a large contribution of nearby cultivated trees.

RESULTS

The sampling strategy was to sample three times a day at fixed times (9, 12, and 16 hours), since it was not expected to see variations at smaller time intervals. It was soon realized

TABLE 1. Summary of Surface CO Data Obtained Between April 6 and May 11, 1987

Sample Type	Site	Date
1. Morning, noon, afternoon	Ducke Forest	April 6-25
2. Hourly samples	Ducke Forest	April 26 to May 11
3. Day-night sequences	Ducke Forest	April 20, 26, and May 1, 6
4. Surface distributions		
City area	Manaus	April 7, 13, 15, 16
	airport	April 11, 22
	tropical	April 11
	INPA	April 22
Ducke Forest area	Emater	April 10, 18, 19
	ZF1 Tower	April 12, 16
	Met Tower	April 13, 18, 24, and May 5
Remote areas to the east	Careiro	April 25
	Rio Preto	April 19, 20, 28, 29, and May 4
	Embratel	April 19, 20, 28, 29, and May 4
	Rio Urubu	April 19, 20, 28, 29, and May 4

that this expectation was incorrect. Significant variations were noticed at time scales of hours, and therefore after a few days, hourly samplings were routinely made in the daytime. On five occasions, hourly samples were also taken at hourly intervals during the nighttime.

Table 1 shows a summary of all CO samples obtained at Ducke Forest or at other nearby sites. The data were analyzed in terms of day-to-day variations, diurnal variations, surface distributions, and forest-clearing comparisons. One vertical CO profile taken inside the forest will be discussed, since it provides the opportunity to calculate the vertical CO flux.

Day-to-Day Variations

The variability of the surface CO concentrations from day-to-day during the ABLE 2B experiment is shown in Figure 2, from April 6 to May 11. The values shown represent a diurnal average of three values derived from samples taken at 9, 12, and 16 hours of local time. On six occasions, one of these daily concentrations exceeded the average of the other two concentration values by more than three standard deviations, and were therefore excluded from Figure 2. The average CO concentration for this sequence of 36 days is 102.9 ± 11.4 ppbv.

Table 2 lists the days in April when the observed CO

concentrations were abnormally high. It appears that most of these can be attributed to pollution episodes that were also seen by colleagues, measuring other atmospheric species (for example, NO_y [Bakwin *et al.*, 1989]). The occurrence of these episodes was coincident with wind directions that were bringing air from the Manaus area to the forest site, that is, from the south, when the normal prevailing wind direction is from the east. These unexpected episodes were of 3-4 hours' duration each time, after which the concentrations of CO would settle to their normal values. This behavior was also seen in the NO_y data mentioned above. But although of short duration, these pollution episodes seen in April (none was observed in May) made us wonder about the appropriateness of Ducke Forest as a sampling site. With the unusual winds coming from the south, and having the option to drive eastward from Ducke Forest, it was decided to sample also more than 100 miles (160 km) to the east, outside of the Manaus plume thought to be responsible for the pollution episodes mentioned above. The results of these eastward excursions will be described in the next section.

The CO concentrations measured at Ducke Forest fall in the interval between 70 and 140 ppbv for most of the samples. This is shown by the histogram of Figure 3, where we show the number of samples in arbitrary concentration intervals of 5 ppbv. The majority of samples belong to the 100- to 105-ppbv interval. The small insert in Figure 3 shows the high concentration side in arbitrary intervals of 100 ppbv.

The whole data set, including the high concentrations

Fig. 2. Daily average surface CO concentrations from samples taken at point M1, between April 6 and May 11.

TABLE 2. List of Days When Abnormally High Concentrations of CO Were Observed

Day in 1987	Time, hours	Concentration, ppbv
April 13	16	265.3
April 17	12	231.2
April 19	9	174.7
April 23	9	192.8
April 25	12	163.1
April 26	9	191.0

Fig. 3. Histogram showing the distribution of samples in 5-ppbv concentration intervals, between 70 and 140 ppbv. The insert shows 100-ppbv intervals between 30 and 330 ppbv.

considered anomalous for the forest region, is shown in Figure 4. This figure shows the cumulative percentage of all concentration values plotted on probability paper. The curves show the actual distribution of the data points, whereas the straight line fits indicate a perfect normal distribution. The stronger slope straight line represents the anomalous data (except for one point), whereas the smaller slope distribution represents the great majority of the data, in a completely different statistical distribution. This seems to indicate again that the high CO concentration values have a different origin, probably linked to contaminated air masses.

Diurnal Variations

On the basis of large-scale emission rates and an average CO mixing ratio, Seiler [1974] derives an average tropospheric residence time for the CO molecule of $T_r = 36$ days.

Fig. 4. Cumulative probability plot showing the tendency for the CO data to follow two different slopes. The stronger slope is thought to contain contaminated data.

Fig. 5. The diurnal variation of surface CO concentrations measured at points M1, M2, and M4. The average concentrations inside the forest are slightly larger than the average concentrations in the clearing.

This may be compared to a chemical reaction loss time constant $T = ([OH][K]^{-1}) = 38.6$ days using $[OH] = 10^6 \text{ cm}^{-3}$ and $K = 3.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ [Hampson and Garvin, 1978]. Both time scales reflect the expectation that CO concentrations variations over time periods of a day should be small. One obvious exception to this rule would occur for measurements near sources or sinks, when time variations of these sources or sinks would modulate the concentrations. On this basis, only three samples a day were planned to be taken at the different sampling points at Ducke Forest Reserve: at 9, 12, and 16 hours of local time. The operation was extended to hourly samplings later during the experiment. Figure 5 shows the average behavior of these samples, for points M1, M2, and M4, for which data were available for the whole experiment. Slightly higher CO concentrations were observed during noon, and this tendency is most pronounced in the forest samples (M2 and M4). A tendency for slightly larger CO concentrations during midday hours was also noticed from samples taken nearby by another research group (R. Rasmussen, private communication, 1987).

Comparison of Forest and Clearing

Another interesting result of Figure 5 is that the concentrations at M2 and M4 are larger than those measured in the clearing (point M1). This result was noticed after a few days of measurements, and to test this finding further, a special comparison campaign was undertaken to determine whether this result was only fortuitous or a general feature of the forest.

It was thought that if the larger concentrations seen at M2 and M4 were in fact the result of the presence of the forest, then for further investigations it would be of interest to move the forest sampling points further inside the forest. Accordingly, a narrow 50-m-long path was opened in the forest, starting at M2 and in the southward direction away from the clearing. At this end point, called point M22, all samples for the special comparisons were taken, day and night. Figure 6 shows the results of the comparison. The data were separated between day and night cases. A total of 47 hourly simultaneous samples were available during daytime

Fig. 6. Comparison between concentrations of simultaneous samples taken in the clearing (M1) and within the forest (M22). For most samples the concentration difference falls in the 0- to 3-ppbv interval, that is, larger concentrations in the forest. Shown are 47 samples in the daytime and 19 samples in the nighttime.

hours at points M1 and M22. The concentration difference forest (M22) - clearing (M1) is shown in Figure 6. It shows a histogram for concentration intervals of 3 ppbv. It can be seen that most samples belong to the interval between zero and +3 ppbv. The average difference was 1.3 ± 4.3 ppbv. Higher concentrations in the forest were also observed at night. For 19 samples, the average difference was 2.5 ± 3.3 ppbv.

The forest-clearing comparison was also possible for the Micromet tower site. This was the working place of the Harvard group, away from M1 by about 2 hours' walking distance. Figure 7 shows the results for eight simultaneous samplings made at M1 (clearing) and MMT (the Micromet tower, well inside the forest). All comparisons were on the plus side, that is, again inside the forest, the CO concentrations were higher in comparison to the clearing. The average was 7.2 ± 6.4 ppbv. It seems therefore that the differences are not only consistently higher inside the forest, but the comparison of the averages is statistically significant.

Surface Distributions

As mentioned, there were days during the experiment when the wind was blowing from the south, which is a very unusual situation. Examination of the available meteorological record shows that the winds predominate from the east. Small north-south components are usually present but with much smaller amplitudes. Southerlies are therefore very unusual. Nevertheless, southerlies occurred during the ABLE 2B experiment.

Figure 8 shows a sketch of the Manaus area with emphasis on the road system. As can be seen, Ducke Forest is to the north of Manaus and southerlies would bring city air masses to the forest area. Realizing the existence of a paved road to the east (state road AM010), several air samples were collected at the points shown in Figure 8 on several occasions, expecting to obtain air samples outside of the city plume on days when southerly winds were active, but also to obtain a few samples outside and away from the forest reserve.

RP is a small village, E is part of a local farm, and RU is a river crossing point by ferry boat, where the operators also

run a small primitive restaurant. Air sampling was always made far from human activity, and it is thought that this region may truly be considered a rural Amazonian environment. Traffic on the excellent AM010 road was very light, about three to six motorized vehicles per hour.

The results obtained for the CO concentrations from the samplings made along state road AM010 are shown in Figure 9. Five samples for RP five for E, and 17 for RU were analyzed, and the CO concentrations separated in intervals of 5 ppbv. The average for RP was 101.1 ± 6.5 ppbv, and for E was 99.5 ± 15.2 ppbv. RU had an average of 111.9 ± 12.0 ppbv of CO. These values are within the range of concentrations derived at Ducke's M1 site, where 102.9 ± 11.4 ppbv of CO were measured.

A much larger difference was seen on one of the perturbed days, April 10, 1987. This was one of those cases when unusual winds, blowing from the south, seem to have been responsible for bringing air remains that had contact with the city of Manaus to the forest area. Figure 10 shows the distribution of CO concentrations along the AM010 road, including Ducke Forest, where about 120 ppbv were observed. East of Ducke the concentrations were lower, 92 at RP, 82 at E, and 85 ppbv at RU. It seems therefore consistent with the idea that larger CO concentrations were observed in the southerly flow that came over Ducke Forest, but that sites eastward of Ducke were not affected. On the contrary, E and RU had concentrations somewhat lower than the average. The concentration shown for Ducke is the one sampled at noon. The morning sample gave 174 ppbv, and the afternoon, 100 ppbv.

It appears that, although the few pollution episodes provoked some concern, the Ducke Forest data base was not affected except as noted. For example, on three other days with simultaneous data, the Ducke Forest concentrations were smaller than the concentrations measured for RU, as shown in Figure 11. For the five samples taken per day on April 28, 29, and May 4, the concentrations at RU are about 10-15 ppbv higher than those at Ducke Forest Preserve.

Vertical Profile

The Micromet tower at Ducke Forest Preserve has been used by several groups to obtain data at several intermediate heights below the forest canopy. Almost simultaneous samples were obtained at three height levels of the forest on

Fig. 7. Comparison between concentrations of simultaneous samples taken in the clearing (M1) and within the forest, at the Micromet Tower (MMT). All eight cases show larger concentrations in the forest.

Fig. 8. The road system near Manaus. To determine the horizontal distribution of surface CO concentrations, air samples were taken along state road AM010 at sites D (Ducke), RP (Rio Preto), E (Embratel Tower), and RU (Rio Urubu).

April 24. The results of the CO concentrations are shown in Figure 12. The calculation of fluxes for NO and O₃ was discussed in detail by Kirchhoff *et al.* [1988]. Using the same formulation, the decreasing concentrations with height in the forest imply, in the present case, an upward CO flux given by

$$\Phi = Kdn/dz$$

where K is the eddy diffusion coefficient and dn/dz is the number density gradient. From Figure 12, the CO gradient near the surface is $1.2 \times 10^8 \text{ cm}^{-4}$, and using for K the value deduced by Kirchhoff *et al.* [1988], $K = 3.3 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$, the upward CO flux is

$$\Phi = 4 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$$

and if this result can be extrapolated to the whole region, it implies the forest to be a CO source.

DISCUSSION

The photochemistry of the lower atmosphere is especially interesting in the remote areas of Amazonia because of the strong interaction of especially CO, O₃, and OH, a result of the coupling of the strong UV radiation, typical of the equatorial region, and biogenic emissions from the forest and the surface.

Photochemistry

It appears that the most attractive feature of the Amazonian rain forest, with respect to the CO concentrations of the atmosphere, is the ability of the forest to emit several types of hydrocarbons [Greenberg *et al.*, 1984; Zimmerman *et al.*, 1988]. These are also emitted by other forests, but in smaller amounts [see Roberts *et al.*, 1983], especially terpenes and isoprene, which eventually may become oxidized by hydroxyl, producing CO. Photochemical interactions in the lower atmosphere have been studied extensively in the last decade. The importance of the hydroxyl radical OH was stressed in the photochemical models of Levy [1972] and Wofsy [1976], showing that the oxidation of methane by OH represents a source of CO. Crutzen [1987] shows how important the whole tropical region is in producing OH, given the availability of strong UV radiation. Chameides and Walker [1973, 1976] calculate the diurnal variation of ozone near the surface using another photochemical model, and Fishman and Crutzen [1977] and Crutzen [1979] describe the oxidation of CO by OH, in the presence of the nitrogen oxides NO and NO₂, to eventually produce ozone in the troposphere. This links together these two important atmospheric constituents: CO and O₃. It has been shown by several groups that larger O₃ concentrations were associated

Fig. 9. The CO concentration distribution for the sites along state road AM010.

Fig. 10. The CO concentration variation along state road AM010 on a perturbed day, April 19, 1987, showing higher concentrations at Ducke.

Fig. 11. Comparison of CO concentrations at Ducke and RU.

with larger CO and NO amounts during ABLE 2A [Kirchhoff, 1988; Kirchhoff *et al.*, 1988; Sachse *et al.*, 1988; Torres and Buchan, 1988], but such correlations among CO, O₃, and NO, seen in the Amazonian data set, have also been observed elsewhere [Fishman *et al.*, 1979; Fishman and Seiler, 1983; Fehsenfeld *et al.*, 1983] and have been used as arguments to explain the seasonal variations of ozone in the tropics [Logan, 1985; Logan and Kirchhoff, 1986], with the implication that tropical ozone concentrations are not necessarily smaller in the southern hemisphere [Kirchhoff, 1984].

The importance of local sources and sinks has also been stressed by S. C. Wofsy (Amazonian Atmospheric Studies, unpublished report, 1984), on the basis of measurements of several trace gases, especially CO, CH₄, and N₂O, made in Brazil during the end of 1982 and beginning of 1983. This

data set shows conclusively larger CO concentrations over the continent as compared to the marine sites.

The present CO observations which show diurnal variations and a vertical gradient in the canopy are quite relevant to this issue. More than one CO molecule may be produced in the isoprene oxidation chain because of the intermediate products, which may produce CO as well [Zimmerman *et al.*, 1978, 1988; Crutzen *et al.*, 1985]. It is interesting to note that, as pointed out by Rasmussen and Khalil [1988], the removal of OH may be much more effective by reactions with C₃H₈ than with CO. Crutzen *et al.* [1985] point out that there are still some major uncertainties about the oxidation pathways and intermediate steps of the C₃H₈ oxidation chain. On the other hand, on the basis of reasonable assumptions, a consistent picture of the diurnal ozone variation has been obtained for the Amazonian data [Jacob and Wofsy, 1988, this issue] using this approach. For the wet season it is expected that this coupling becomes weaker, given the much larger cloud cover and the consequent changes of photolysis rates [Thompson, 1984].

The addition of artificial gases into the lower atmosphere may affect the tropospheric chemistry very strongly. Biomass-burning events cause the most spectacular artificial modifications of the lower atmosphere in rural areas and therefore have received much attention in recent years [Crutzen *et al.*, 1985; Delany *et al.*, 1985; Greenberg *et al.*, 1984, 1985; Andreae *et al.*, 1988]. Carbon monoxide is released directly from the fires [Crutzen *et al.*, 1979], whereas ozone is produced indirectly through chemical reactions as mentioned above. Biomass burnings were not important during the ABLE 2B mission, as reported by several investigators, in contrast to the ABLE 2A mission, when strong effects on CO [Sachse *et al.*, 1988], NO [Torres and Buchan, 1988], and O₃ [Kirchhoff, 1988; Kirchhoff *et al.*, 1988; Browell *et al.*, 1988; Gregory *et al.*, 1988] were reported.

Absolute Concentrations

Most atmospheric CO measurements performed in remote areas refer to marine sites, or areas near marine environments. It is therefore important to intercompare previous results with the Amazon data set for a possibly better understanding of the role of continental remote sites.

Absolute values of CO concentrations analyzed from whole-air grab samples are obtained by comparison to standards. Hoell *et al.* [1985] have described the results of an intercomparison campaign where several techniques of measuring CO were compared. The tests were performed with ambient air and CO-enriched ambient air at CO mixing ratios of 150–370 ppbv, and also with a nitrogen carrier, where CO was injected at mixing ratios of 20–380 ppbv. The results indicated a high degree of correlation between the measurements, suggesting a level of agreement among the different techniques of about 15%. Sporadic differences could be as high as 38%.

Surface CO concentrations in marine environments are much smaller than the values obtained at Ducke Forest Preserve. For such a marine site in Australia, Cape Point (34°S, 18°E), Seiler *et al.* [1984] report minimum CO concentrations of 53 ppbv during January–February, and maximum CO values of 87 ppbv during September–October. Other measurements reported by the same group show

Fig. 12. Vertical profile of the CO concentration within the forest canopy at the Micromet tower for April 24, 1987.

typical concentrations in the 50-ppbv range for the southern hemisphere [Seiler, 1974]. These results show a large hemispheric asymmetry with much larger concentrations in the north Atlantic region. Also, in contrast to larger variability found in the north, the CO mixing ratio at southern latitudes has been observed to be comparatively constant. Recent measurements made at Natal (6°S, 35°W), an Atlantic marine site, show concentration averages in the oceanic air masses of about 70 ppbv.

Mixing ratios over the Pacific Ocean are also of the order of 50 ppbv in the southern hemisphere. Measurements carried out during the Global Atmospheric Measurements Experiment of Tropospheric Aerosols and Gases (GAMETAG), reported by Heidt *et al.* [1980], show concentrations of about 50 ppbv between 0 and 60° with a latitudinal gradient between 0 and 20°N, after which latitude the concentration of CO remained in the 140- to 180-ppbv range, slightly lower than the north Atlantic values. In the southern hemisphere this pattern was also observed by Reichle *et al.* [1986], who deduce mixing ratios in the range of 55 ± 10 ppbv.

Measurements of the CO concentration in Cape Grim, Tasmania, Australia (41°S, 145°E) show yearly averages of 44 ppbv. Fraser *et al.* [1986] also report the same low concentration for the Antarctic station Mawson (68°S, 63°E) and for several other sampling points of the Southern hemisphere, using the Rasmussen CO calibration scale, the same used in this report. As pointed out by Fraser *et al.* [1986], there is a systematic scaling difference between the Seiler and the Rasmussen calibrations, the former being larger by about 30%. (Actually, Fraser *et al.* report a larger difference, but the value cited above 30% was actually obtained from a sample, courtesy of Seiler. For convenience, we have adopted the Rasmussen scale.)

The CO mixing ratios observed in marine environments, in summary, are of the order of about 50 ppbv, which is about one half of the values observed in Amazonia during the wet season. These low CO concentration values observed in marine environments are commonly used in modeling studies. The results for Amazonia suggest that, over continental remote areas, even in the absence of obvious biomass-burning activity, the CO concentrations are probably much larger than the marine values, by as much as a factor of 2.

Vertical Profile

In the absence of biomass burning, it appears that the vertical profile of the CO concentration in Amazonia is approximately constant with height, between about 1.5 and 4.0 km. Below 1.5 km, the concentration increases downward, reaching about 100 ppbv at the surface. This result, which at the surface is in excellent agreement with the ground-based data of this work, was obtained in Amazonia by Sachse *et al.* [1988] during the ABLE 2A experiment in the early dry season period of July 1985, when apparently no biomass burning was in activity. During this time period, several days of early July had between 30 and 60 mm/d of rain, an indication that the CO profiles then obtained were probably representative of clean Amazonian air and therefore comparable to the present wet season results. The CO profiles were measured on board the Electra aircraft with the differential absorption CO measurement technique, which uses a totally independent calibration gas originated from the

National Bureau of Standards. It is encouraging to realize that the two measurement techniques give similar results.

On the basis of the CO profile measured at the Micromet tower, we calculate an upward CO flux of $4 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ CO molecules, implying that a CO source is active at the surface. This source strength represents an annual mass emission rate of $3.1 \times 10^{13} \text{ g CO/yr}$ just for Amazonia (estimated area of $5 \times 10^{16} \text{ cm}^2$) or even $1.05 \times 10^{14} \text{ g CO/yr}$, assuming an equal emission flux for all rain forest area (estimated at $17 \times 10^{16} \text{ cm}^2$). Following Crutzen *et al.* [1985], if the total emission of CO from biomass burning is $1.2 \times 10^{15} \text{ g CO/yr}$, then the forest emission flux represents between 2.5% and 8.5% of the biomass-burning source.

The Net Surface CO Source

The surface emission of CO in Amazonia may be the result of photochemical processes, especially effective in the lowest atmospheric layer, but other possibilities have also been proposed. Since CO is produced in living animals, probably by decomposition of hemoglobin, it is feasible that microbiological activity at the Earth's surface can also produce CO (see discussion by Seiler [1974]). A more recent study by Conrad and Seiler [1985], however, shows that the production of CO in the soil is an abiotic process, a result of chemical oxidation of soil organic matter, and that the presence of microorganisms in the soil is actually responsible for the consumption of CO, through metabolic biological processes. The production process is light independent, but the production rates reported by Conrad and Seiler [1985] were observed to correlate well with soil surface temperature. It should be noted that the CO concentrations observed in Amazonia, described in the present work, did show a small CO maximum during noon hours, but this effect could probably also be produced by photochemical effects.

In the absence of biomass burning, the most important source of CO in Amazonia may well be the oxidation of isoprene and terpenes, emitted from the forest through biogenic processes [Zimmerman *et al.*, 1978]. This situation has been investigated to some extent by the ABLE 2A mission [Zimmerman *et al.*, 1988; Rasmussen and Khalil, 1988] when large concentrations of isoprene were observed, showing a strong diurnal cycle for its concentration. Since the most powerful oxidant of the lower atmosphere, the hydroxyl radical OH, should also be copiously produced in the tropics, it is clear that there are reasons to expect some effects on the Amazonian CO concentrations as well.

In terms of chemical activity, the isoprene molecule C_5H_8 is the most important hydrocarbon in the Amazonian environment in the daytime [Rasmussen and Khalil, 1985]. Zimmerman *et al.* [1988] report typical daytime concentrations of between 2 and 5 ppbv, which amounts to about 20% of the gas phase carbon in nonmethane hydrocarbons (NMHC), but in terms of reactivity, C_5H_8 is dominant. Crutzen *et al.* [1985] suggest that NMHC may well be responsible in Amazonia for larger productions of CO, especially C_5H_8 , but that direct emissions of CO by the forest are also a possibility. Further details on the isoprene photochemistry are given by Brewer *et al.* [1984] and Killus and Whitten [1984].

Given the rather large C_5H_8 concentrations observed by Zimmerman *et al.* [1988] and Rasmussen and Khalil [1988], and the considerations above, it is very tempting to attribute

a local CO source to the oxidation of isoprene. However some of our observations of the behavior of CO may not be consistent with a C_5H_8 source [Jacob and Wofsy, this issue]. Nevertheless, careful calculations have not yet been made to further investigate this possibility.

As pointed out by Crutzen *et al.* [1985], the important reactions can be summarized by

In equilibrium of this simplified condition, the concentration of CO should be proportional to the concentration of C_5H_8 :

$$[CO] = [C_5H_8]k_1/k_2$$

and since a strong diurnal variation is observed in the C_5H_8 concentrations, this equation implies a proportional diurnal variation in (CO) as well, as is actually observed in the Amazonian CO data of the present work. Furthermore, if reaction (1) is assumed to be the primary production mechanism for atmospheric CO in Amazonia, where up to four CO molecules may be generated from the intermediate hydrocarbons that are formed in the oxidation process [Crutzen *et al.*, 1985], then a flux of isoprene of $2.5 \times 10^{-2} \text{ g m}^{-2} \text{ d}^{-1}$ [Zimmerman *et al.*, 1988] can produce as much as about 10 ppbv of CO per day, in the forest area, limited to a 3-km-deep boundary layer. It appears that all other possible sources cannot compete with such a strong production. It should also be noted that the average CO concentration observed in Amazonia as described in the present work, of 100 ppbv, corresponding to the wet season minimum, compares to about 60–80 ppbv observed east of the Amazon forest (Fortaleza and Natal), which is consistent with the previous discussion.

Air Mass Trajectories

The air mass circulation over the Amazon region in Brazil has been described in detail in the ozone paper [Kirchhoff *et al.*, this issue], and other transport aspects are discussed by Martin *et al.* [1988] and Scala *et al.* [this issue]. Our interest here is to investigate whether it was possible at all that unusual wind systems might have brought downtown pollution products from the Manaus area over Ducke Forest. As shown in Table 2, there were three cases between the period April 23–26, when high CO concentrations were observed. Air mass trajectories have been calculated for three occasions, backward from 3°S, 60°W, for periods of 48 hours. As described by Kirchhoff *et al.* [this issue], the trajectories are calculated at four pressure levels (950, 850, 700, and 500 mbar), and new positions are calculated at intervals of 3 hours. Figure 13 shows the progression of the wind vectors from an easterly direction on April 21 to a southerly direction April 24. The largest changes, almost 90°, occur near the surface at 950 and 850 mbar. The trajectories at 700 and 500 mbar are more stable, extending from the east and southeast, but for clarity, these are not shown in Figure 13. It appears, therefore, that air masses may be transported from the south, occasionally. On the other hand, trajectory calculations for specific cases did not show contaminations from the south. For April 13, for example, the 24-hour backward air mass trajectories, shown in Figure 14, certainly did not have

Fig. 13. Backward air mass trajectories showing the progression from east to south.

any contact with air in the Manaus area. Another case, for April 26, also shows air masses that originated from the north and northeast. This seems to indicate that the high CO events may also have been originated by smaller local anthropogenic centers, such as cattle farms, chicken farms, and agricultural centers.

SUMMARY AND CONCLUSIONS

Carbon monoxide concentrations have been analyzed from Amazonian air samples collected near the ground. The experiment was conducted during the wet season period of the rain forest in the central part of the Brazilian Amazon region. It appears that these measurements were unique in at least two aspects: they were analyzed close to the sampling sites, and they represent the first CO data set taken during the wet season. The major sampling site was Ducke Forest Reserve located some 30 km north of the city of Manaus, but complementary samples were also taken outside of the forest reserve. Data were obtained during a continuous period of 36 days. Major conclusions are as follows.

Fig. 14. Backward air mass trajectories for April 13, 1987.

Diurnal variations. A small diurnal variation was shown with a maximum near local noon. This result is probably related to the CO source, and suggests correlations either with temperature, UV light intensity, or both.

Day-to-day variations. These were within about 20% for most cases, but, on six occasions in April, CO peaks of up to 200–300 ppbv were observed and attributed to unusual pollution air masses, transported to Ducke by rare wind systems. The period's average CO concentration was 102.9 ppbv.

Vertical gradient. A consistent vertical gradient was observed, with CO concentrations decreasing upward. On one occasion this gradient was measured directly. Other measurements were made by simultaneous sampling within the forest and in the clearing. Both methods gave consistent results, showing slightly larger CO concentrations inside the forest. The calculated upward vertical flux that corresponds to these gradients is $4 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$.

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REFERENCES

- Andreae, M. O., et al., Biomass-burning emissions and associated haze layers over Amazonia, *J. Geophys. Res.*, **93**, 1509–1527, 1988.
- Bakwin, P. S., S. C. Wofsy, and S.-M. Fan, Measurements of reactive nitrogen oxides (NO_x) within and above a tropical forest canopy in the wet season, *J. Geophys. Res.*, this issue.
- Brewer, D. A., M. A. Oglaruso, T. R. Augustsson, and J. S. Levine, The oxidation of isoprene in the troposphere: Mechanism and model calculations, *Atmos. Environ.*, **18**, 2723–2744, 1984.
- Browell, E. V., G. L. Gregory, R. C. Harriss, and V. W. J. H. Kirchhoff, Tropospheric ozone and aerosol distributions across the Amazon Basin, *J. Geophys. Res.*, **93**, 1431–1451, 1988.
- Browell, E. V., G. L. Gregory, R. C. Harriss, and V. W. J. H. Kirchhoff, Ozone and aerosol distributions over the Amazon Basin during the wet season, *J. Geophys. Res.*, this issue.
- 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.
- Conrad, A., and W. Seiler, Influence of temperature, moisture, and organic carbon on the flux of H_2 and CO between soil and atmosphere: Field studies in subtropical regions, *J. Geophys. Res.*, **90**, 5699–5709, 1985.
- Crutzen, P. J., The role of NO and NO_2 in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Planet. Sci.*, **443–472**, 1979.
- Crutzen, P. J., The role of the tropics in atmospheric chemistry, in *The Geophysiology of Amazonia*, edited by R. E. Dickinson, pp. 107–130, John Wiley, New York, 1987.
- Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. H. Pollock, and W. Seiler, Biomass burning as a source of atmospheric gases CO , H_2 , H_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. Kelly, 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.
- Fishman, J., and P. J. Crutzen, A numerical study of tropospheric photochemistry using a one-dimensional model, *J. Geophys. Res.*, **82**, 5897–5906, 1977.
- Fishman, J., and W. Seiler, Correlative nature of ozone and carbon monoxide in the troposphere: Implications for the tropospheric ozone budget, *J. Geophys. Res.*, **88**, 3662–3670, 1983.
- 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.
- 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 carbon monoxide in African savannah air, *Geophys. Res. Lett.*, **12**, 113–116, 1985.
- Gregory, G. L., E. V. Browell, and L. S. Warren, Boundary layer ozone: An airborne survey above the Amazon Basin, *J. Geophys. Res.*, **93**, 1452–1468, 1988.
- Gregory, G. L., E. V. Browell, L. S. Warren, and C. H. Hudgins, Amazon Basin ozone and aerosol: Wet season observations, *J. Geophys. Res.*, this issue.
- Hampson, R. F., and D. Garvin, Reaction rate and photochemical data for atmospheric chemistry—1977, *NBS Spec. Publ. US*, **513**, 1978.
- Harriss, R. C., et al., The Amazon Boundary Layer Experiment (ABLE 2A): Dry season 1985, *J. Geophys. Res.*, **93**, 1351–1360, 1988.
- Harriss, R. C., G. W. Sachse, G. F. Hill, L. O. Wade, and G. L. Gregory, Carbon monoxide over the Amazon Basin during the wet season, *J. Geophys. Res.*, this issue.
- Heidt, L. E., J. P. Krasnec, R. A. Lueb, W. H. Pollock, B. E. Henry, and P. J. Crutzen, Latitudinal distribution of CO and CH_4 over the Pacific, *J. Geophys. Res.*, **85**, 7329–7336, 1980.
- Hoell, J. M., Jr., G. L. Gregory, D. S. McDougal, G. W. Sachse, G. F. Hill, E. P. Condon, and R. A. Rasmussen, An intercomparison of carbon monoxide measurement techniques, *J. Geophys. Res.*, **90**, 12,881–12,889, 1985.
- Jacob, D. J., and S. C. Wofsy, Photochemistry of biogenic emissions over the Amazon forest, *J. Geophys. Res.*, **93**, 1477–1486, 1988.
- Jacob, D. J., and S. C. Wofsy, Budgets of reactive nitrogen, hydrocarbons, and ozone over the Amazon forest during the wet season, *J. Geophys. Res.*, this issue.
- Killus, J. P., and G. Z. Whitten, Isoprene: A photochemical kinetic mechanism, *Environ. Sci. Technol.*, **18**, 142–148, 1984.
- 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., 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., A. W. Setzer, and M. C. Pereira, Biomass burning in Amazonia: Seasonal effects on atmospheric O_3 and CO, *Geophys. Res. Lett.*, **16**, 469–472, 1989.
- Kirchhoff, V. W. J. H., I. M. O. da Silva, and E. V. Browell, Ozone measurements in Amazonia: Dry season versus wet season, *J. Geophys. Res.*, this issue.
- Levy, H., II, Photochemistry of the lower troposphere, *Planet. Space Sci.*, **20**, 919–935, 1972.
- Logan, J. A., Tropospheric ozone: Seasonal behavior, trends, and anthropogenic influence, *J. Geophys. Res.*, **90**, 10,463–10,482, 1985.
- Logan, J. A., and V. W. J. H. Kirchhoff, Seasonal variations of

- tropospheric ozone at Natal, Brazil, *J. Geophys. Res.*, **91**, 7875–7881, 1986.
- Martin, C. L., D. Fitzjarrald, M. Garstang, A. P. Oliveira, S. Greco, and E. Browell, Structure and growth of the mixing layer over the Amazonian rain forest, *J. Geophys. Res.*, **93**, 1361–1375, 1988.
- McNeal, R. J., J. P. Hugler, R. C. Harriss, and J. M. Hoell, Jr., NASA Global Tropospheric Experiment, *Eos Trans. AGU*, **64**, 561–562, 1983.
- Rasmussen, R. A., and M. A. K. Khalil, Atmospheric isoprene, *Eos Trans. AGU*, **66**, 39, 1985.
- Rasmussen, R. A., and M. A. K. Khalil, Isoprene over the Amazon Basin, *J. Geophys. Res.*, **93**, 1417–1421, 1988.
- Reichle, H. G., Jr., V. S. Connors, J. H. Holland, W. D. Hypes, H. A. Wallio, J. C. Casas, B. B. Gormsen, M. S. Saylor, and W. D. Hesketh, Middle and upper tropospheric carbon monoxide mixing ratios as measured by a satellite-borne remote sensor during November 1981, *J. Geophys. Res.*, **91**, 10,865–10,888, 1986.
- Roberts, J. M., F. C. Fehsenfeld, D. L. Albritton, and R. E. Sievers, Measurements of monoterpene hydrocarbons at Niwot Ridge, Colorado, *J. Geophys. Res.*, **88**, 10,667–10,678, 1983.
- 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.
- Scala, J. R., et al., Cloud draft structure and trace gas transport, *J. Geophys. Res.*, this issue.
- Seiler, W., The cycle of atmospheric CO, *Tellus*, **2**, 116–135, 1974.
- Seiler, W., H. Giehl, E. G. Brunke, and E. Halliday, The seasonality of CO abundance in the southern hemisphere, *Tellus*, **36**, 219–231, 1984.
- Thompson, A. M., The effect of clouds on photolysis rates and ozone formation in the unpolluted troposphere, *J. Geophys. Res.*, **89**, 1341–1349, 1984.
- Torres, A. L., and H. Buchan, Tropospheric nitric oxide measurements over the Amazon Basin, *J. Geophys. Res.*, **93**, 1396–1406, 1988.
- Wofsy, S. C., Interactions of CH₄ and CO in the Earth's atmosphere, *Annu. Rev. Earth Planet. Sci.*, **4**, 441–469, 1976.
- Zimmerman, P. R., R. B. Chatfield, J. Fishman, P. J. Crutzen, and P. L. Hanst, Estimates on the production of CO and H₂ from the oxidation of hydrocarbon emissions from vegetation, *Geophys. Res. Lett.*, **5**, 679–682, 1978.
- Zimmerman, P. R., J. P. Greenberg, and C. E. Westberg, Measurements of atmospheric hydrocarbons and biogenic emissions fluxes in the Amazon Boundary layer, *J. Geophys. Res.*, **93**, 1407–1416, 1988.
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