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Air Chemistry Over the Tropical Forest of Guyana

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The tropical forests of the world are hypothesized to be an important source and/or sink for a number of atmospheric gas and aerosol species. As part of the National Aeronautics and Space Administration's Global Tropospheric Experiment, an aircraft flight (June 27, 1984) was conducted over the wet tropical forest of Guyana for purposes of characterizing the forest boundary layer. Instrumentation on board the NASA Electra aircraft included measurement systems for a variety of chemical species, including ozone, carbon monoxide, dimethylsulfide, nonmethane hydrocarbons, and aerosols. The data reported represent the first comprehensive characterization of the wet tropical forest boundary layer from an aircraft platform. The data indicate that the boundary layer is a source of carbon monoxide, isoprene, and dimethylsulfide as well as being a sink for ozone. Reported aerosol data, including number density, mass concentration, and composition, indicate an increased aerosol presence in the boundary layer relative to the overriding troposphere. From an analysis of the aerosol composition this increase is the result of direct emissions from the forest as well as from various photochemical processes. The data are discussed in terms of their significance in the understanding of the wet tropical forest boundary layer as a source or sink for various species important to tropospheric chemistry.

1. Introduction

The tropical forests of the world are hypothesized to be an important source and/or sink for a number of atmospheric gas and aerosol species in the C-N-S-O family. Evidence is particularly strong in the case of carbon monoxide (CO), where measurements [Greenberg et al., 1984] and modeling calculations [Hameed and Stewart, 1979; Logan et al., 1981] show that the oxidation of biogenic hydrocarbons emitted by forest vegetation and biomass burning may be major sources to the global CO budget. Studies to date have focused on the production of nonmethane hydrocarbons (NMHC) and CO from biomass burning in tropical grasslands and subsequent photochemical production of ozone [Delany et al., 1985; Crutzen et al., 1985]. Ozone (O_3) is a secondary product of biomass burning when necessary photochemical precursors, particularly CO, NMHC, and nitrogen oxides (NO_x), are present at sufficient concentrations [e.g., Crutzen, 1973]. In contrast, there are preliminary data [Crutzen et al., 1985] which suggest that, while O_3 is clearly produced during burning in the dry grasslands, the lower atmosphere over wet tropical forest may be a sink for O_3. High concentrations of biogenic NMHC and low NO_x (<30 parts per trillion by volume (pptv)) may lead to in situ O_3 consumption. We report here a data set for CO, the predominant biogenic hydrocarbon isoprene (C_5H_8), and O_3 in and above the atmospheric boundary layer over the wet tropical forest of Guyana. These data support the hypothesis that the undisturbed wet tropical forest is a sink for O_3 and a source of CO and isoprene.

The role of tropical forests in supplying gaseous reduced sulfur compounds (which are subsequently oxidized to SO_2 and sulfuric acid) to the remote atmosphere still remains highly uncertain [Andreae, 1985]. Some evidence suggests that these fluxes may be substantial [Delmas and Servant, 1982], but existing data are limited to H_2S and may not be representative for the entire tropical region. We report here the first measurements of dimethylsulfide (DMS) from a tropical continental region. DMS is emitted by marine algae and terrestrial plants [Andreae, 1985]; its volatilization from the oceans is a major contributor to the atmospheric sulfur cycle. The measurements reported here were conducted in order to assess the contribution of DMS to continental biogenic sulfur emissions.

The role of the tropical forest as a source of primary and secondary aerosols is important to evaluating global budgets of chemical species such as sulfur and potassium [Lawson and Winchester, 1979; Andreae, 1983]. Biogenic aerosols may also be important components of atmospheric acidity in tropical nonurban air due to the presence of formic (HCOOH), acetic (CH_3COOH), and other carboxylic acids [Galloway et al., 1982]. Most of the particulate organic carbon (POC) over remote oceanic areas is of continental origin [Hoffman and Duce, 1977; Chesselet et al., 1981], with epicuticular vascular plant waxes derived from tropical forest vegetation accounting for a significant fraction of aerosol POC [Gagosian et al., 1981]. The release of these biogenic aerosols in tropical regions is particularly interesting, since these particles are known to be potential ice nuclei [Schnell and Vali, 1972] during rapid vertical transport to upper tropospheric and stratospheric altitudes (for example, in the intertropical convergence zone (ITCZ)). The data reported here are the first detailed comparison of the chemistry of aerosols in and above the atmospheric boundary layer over wet tropical forest.

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2. EXPERIMENTAL TECHNIQUE

In June 1984, NASA conducted, as part of its Global Tropospheric Experiment (GTE) program, a series of aircraft missions based at Barbados, West Indies. The primary objective of the GTE Atlantic Boundary Layer Experiment (GTE/ABLE) was the measurement and characterization of chemical species in the tropical marine boundary layer under various meterological conditions. A secondary objective was the characterization of the boundary layer over the wet tropical forest of Guyana. On June 27, 1984, flights were made over the forest at 3.5-km altitude and in the boundary layer at 450- to 150-m altitude. Instrumentation on board the NASA Wallops Electra aircraft included measurement systems for various chemical species, including ozone, carbon monoxide, dimethylsulfide, nonmethane hydrocarbons, and aerosols.

2.1. Ozone

The O_3 measurement system consisted of two simultaneously operating ozone detectors. The ozone detectors are state of the art, commercially available instruments, each having a different detection principle (C_2H_4 chemiluminescence and UV absorption). The ozone package has been used in numerous flight programs [Gregory et al., 1983, Gregory et al., 1984a, b]. Measurements from both instruments agreed, and only data from the faster-responding (2 s to 90% of reading) chemiluminescent detector are reported. Ozone measurements are accurate to 5% or 5 parts per billion by volume (ppbv), based on calibration accuracies using gas phase titration traceable to a National Bureau of Standards NO standard. Instrument precision is of the order of 2%, or 2–3 ppbv.

2.2. Carbon Monoxide

Carbon monoxide was measured in situ using a Trace Analytical gas chromatographic/mercury oxide detection system. Ambient air was injected into the system at approximately 2-min intervals. The analytical precision for the instrument was ±2%, based on multiple analyses of a CO gas standard. Carbon monoxide was also measured in cryogenically collected air samples, which were returned to the laboratory for trace gas analysis using gas chromatography.

2.3. Dimethylsulfide

Dimethylsulfide was sampled using a 5-mm ID stainless steel inlet tube and the gold surface preconcentration technique [Barnard et al., 1982; Andreae et al., 1985]. Air volumes were measured by an integrating mass flowmeter, and sample volumes ranged between 10 and 40 L. The samples were analyzed a few hours after the flight by thermal desorption from the gold surface, followed by gas chromatography with flame photometric detection [Barnard et al., 1982]. DMS is stable on the gold surface without detectable change for at least 18 hours.

2.4. Halocarbons and Isoprene

Integrated air samples were collected cryogenically by liquefying 12–15 L of air in internally electropolished 0.8-L stainless steel cans. The sampling time was generally 3 min, providing air samples over about 30% of the flight path in the boundary layer. Samples were shipped to the Oregon Graduate Center, where analyses were generally performed within a week of the collection time. The compressed air

samples obtained have shown excellent stability for a large number of atmospheric trace gases in the parts per trillion range [Kahlil and Rasmussen, 1983]. The air-sampling system has been used in numerous field studies [Rasmussen and Kahlil, 1982]. Quantitative analyses for approximately 20 trace gas species are routinely performed on the samples.

2.5. Aerosols

Three separate in situ aerosol systems and one remote sensor were flown on board the Electra aircraft. Aerosol mass concentration was measured as a function of particle size and time with a cascade impactor. Aerosols were sampled using an isokinetic inlet and separated according to their aerodynamic diameter in a low-pressure inertial impactor consisting of a series of piezoelectric quartz crystal microbalances (QCM). The 50% cutoff diameters of the various impactor stages are 21, 10.7, 5.4, 2.6, 1.3, 0.69, 0.33, 0.17, and 0.11 μm. Sampling times for the QCM system ranged from minutes to tens of minutes, depending upon ambient aerosol loadings.

A forward scattering spectrometer probe (FSSP) provided aerosol number density (aerosols per cubic centimeter) as a function of time and size. The FSSP, mounted external to the aircraft, counts (one-dimensional) and sizes (fifteen 0.5-μm-wide bins from 0.5- to 7.5-μm diameter) aerosols as they pass through the focused portion of an He-Ne laser beam. Integrated counting times ranged from 20 s to 90 s, which, considering the aircraft speed, equates to a horizontal spatial resolution of 2–10 km and a vertical resolution during ascents or descents of about 150 m. The FSSP, having an unconstrained sampling volume (that is, no inlet), was equally sensitive to liquid and solid aerosols.

The third in situ aerosol system consisted of a high-volume pump coupled to an isokinetic inlet and filters for collection of particulates [Sebacher et al., 1985]. Sample flow was typically 0.85 standard m^3/min, as monitored by a mass flowmeter. Filter collection time was of the order of 30 min. The filter medium was 10-cm-diameter Zefluor Teflon filter having a collection efficiency of >99% for ambient aerosols >0.01-μm diameter. These filters present minimal artifact problems in terms of sorption of gaseous species like HNO_3 [Appel et al., 1984]. Analysis of collected aerosol was by ion chromatography, using procedures described by Talbot et al. [1986]. Analyses included such species as NA^+, NH_4^+, K^+, Cl^-, PO_4^{3-}, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, $HCOO^-$, CH_3COO^-, $CH_3SO_3^-$, and F^-. Detection limits for the various species ranged from 0.05 to 7 ng/standard m^3 of sampled air [Talbot et al., 1986].

An airborne differential absorption lidar (DIAL) system was used on the aircraft to obtain continuous, remotely sensed aerosol distributions below each flight track. Aerosol profiles along the lidar line of sight are obtained in real time on the aircraft from analysis of backscattered laser light at wavelengths of 600 and 1064 nm. The spatial resolution for aerosol measurements is 15 m in the vertical and 20 m in the horizontal. A detailed description of the DIAL system has been given by Browell et al. [1983].

3. METEOROLOGY AND AEROSOL DISTRIBUTION

ITCZ cumulus convective activity was typically centered at approximately 5°N over the Atlantic Ocean during the period of the experiment (June 1984). Equatorial vortices, evident as regions of enhanced convective cloud activity on
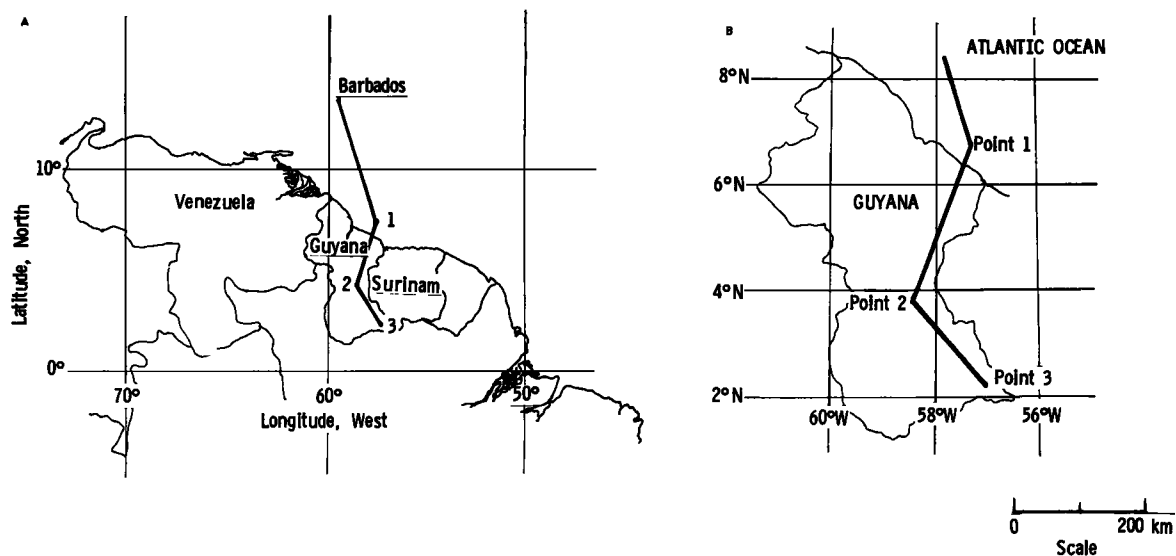
Fig. 1. Flight track for July 27, 1984, mission. (a) Overall mission. (b) Guyana overflight.

15-min interval satellite imagery, were tracked across the Atlantic and into the continent of South America. Daytime convection over Guyana was enhanced during and immediately east of these cloud clusters, while convection ahead of the cluster (west) was suppressed. On June 27, the day selected for our research flight, Guyana lay in a region between two cloud clusters. For the previous day, satellite imagery showed Guyana to be engulfed in clouds, suggesting

Fig. 2. Cloud field from an altitude of 3.5 km at 1555:33 GMT and midway between points 2 and 3.
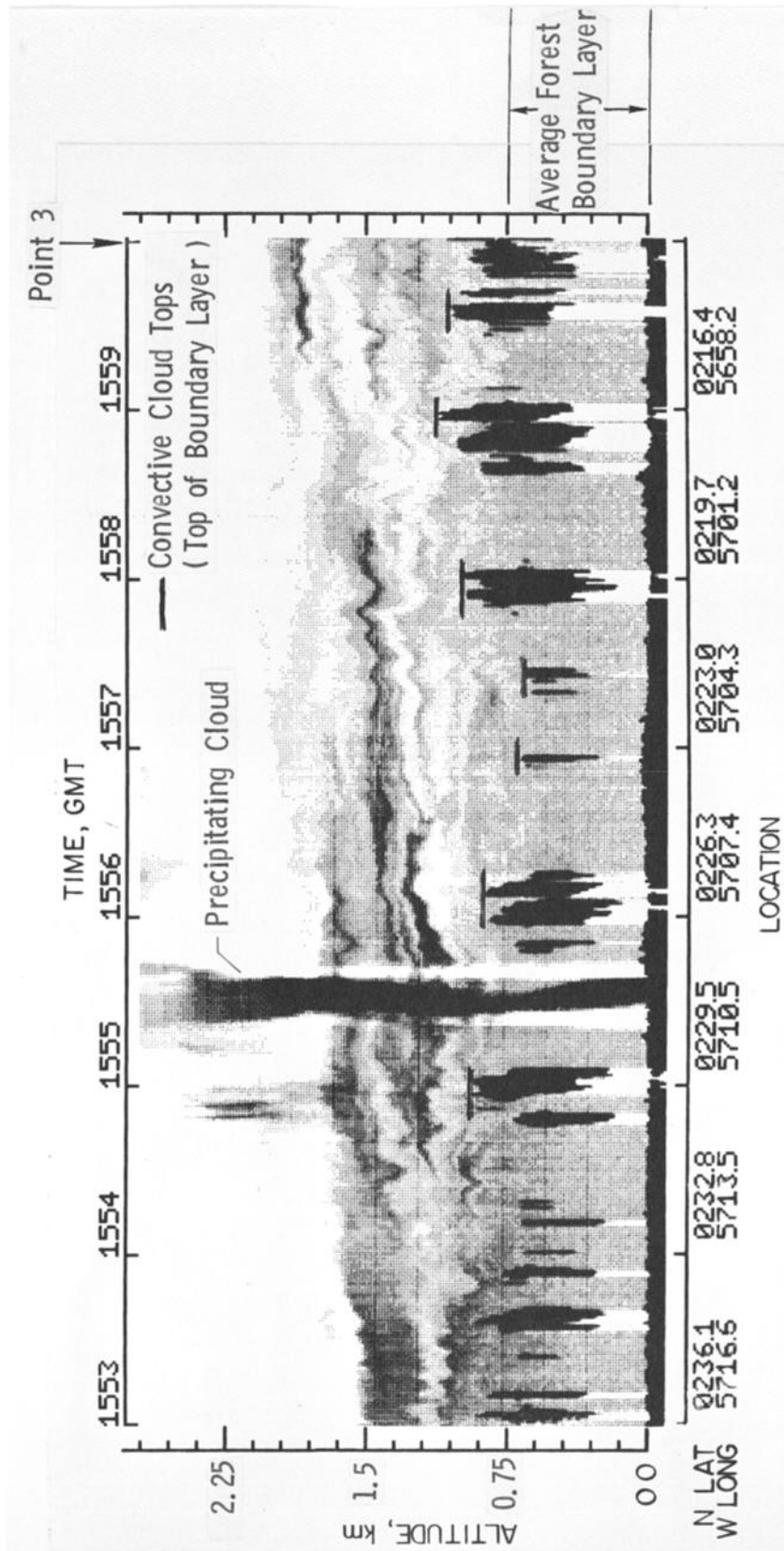
Fig. 3. Lidar aerosol measurements from just northwest of point 3 to point 3. Darker shades indicate higher aerosol concentrations. Black areas are clouds (note that the lidar does not penetrate through clouds and white areas below clouds indicate no data). The light areas above 0.75 km are a result of very low aerosol concentrations.
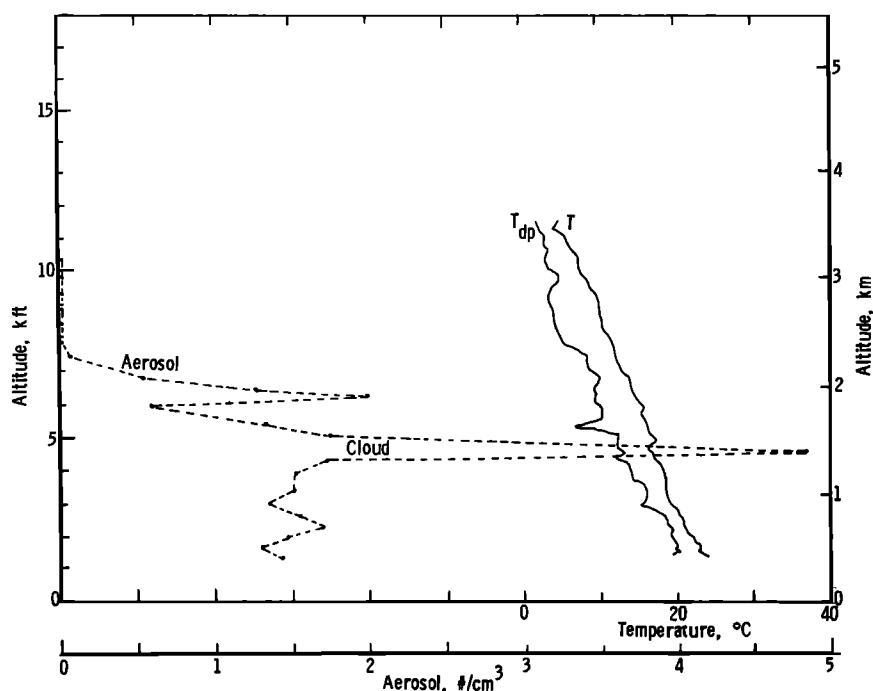
Fig. 4. Vertical distribution of aerosol (0.5- to 7.5-μm diameter), air temperature T, and dew point temperature T_{dp} at point 3 (2°15'N, 56°56'W) over the wet tropical forest.

major convective activity. On the basis of this observation we conclude that the forest boundary layer on the morning of June 27 was relatively "young," being of the order of 3–6 hours old.

Figure 1 shows the surface track for the flight. The aircraft approached the coast of Guyana at 5.4-km altitude and descended just east of the coast to 4.4-km altitude for transit to point 2. At point 2 (3°25'N, 58°03'W) the aircraft descended to 3.5 km for a straight and level sampling track over the forest between points 2 and 3. At point 3 (2°15'N, 56°56'W) the aircraft executed a spiral sounding to 400 m above the forest. The higher-altitude track was repeated from point 3 to point 1 at altitudes in the boundary layer just below convective cloud base (that is, 450- to 150-m altitude). Figure 2 illustrates that on the segment of track of most interest for this paper the weather was characterized by a 25 to 50% cover of fair-weather cumulus, with occasional deeper precipitating clouds.

The lidar aerosol backscatter distribution obtained along a portion (just northwest of and to point 3) of the 3.5-km flight leg is shown in Figure 3. The darker shades indicate higher relative aerosol concentrations, the black areas with tops between 600- and 1000-m altitudes represent clouds, and white areas below the clouds result from the laser beam not penetrating the optically thick clouds. The depth of mixed layer at point 3 is about 700 m, and the height of the predominant fair-weather cumulus tops, which represents the top of the planetary boundary layer, is about 800 m (Figure 3).

The lidar data are used to depict the general features associated with the distribution and height of clouds (including any precipitating clouds) in the forest area. As measured by the lidar data, the average mixing layer depth from point 2 to point 3 is 620 ± 90 (1σ) m, while the average boundary layer height is of the order of 700 ± 100 m. The major features of clean, low-aerosol air above 2 km and aerosol-

rich boundary layer air below 1.5 km are obvious. Between 0.75 and 1.5 km the lidar data provides evidence for a very heterogeneous distribution of aerosols, resulting from intermittent atmospheric mixing processes (for example, precipitating cloud penetration/evaporation and associated vertical transport). The combined effects of mixing processes and cloud evaporation apparently produced an irregular aerosol maximum between 0.75 and 1.5 km. A vertical profile of aerosol, static air temperature, and dew point temperature (Figure 4) provides a more detailed description of atmospheric structure at point 3. In the sounding we see evidence in the aerosol record of active mixing, probably from about 0.5 km to nearly 2 km. The indicated cloud is a partial sampling of a precipitating cloud which was penetrated during the descent. As was seen in the lidar data (Figure 3), the troposphere above 2.5-km altitude shows no evidence of any forest emissions.

4. ATMOSPHERIC CHEMISTRY OVER WET TROPICAL FOREST

Figure 5 shows the data obtained during the low-altitude flight from point 3 to point 1. The data of Figure 5 are useful for identifying the horizontal extent of the forest boundary layer. As shown, most species concentrations and meterological parameters changed as the coast was approached. In particular, O_3 and aerosols show an increase as the coast was approached, reaching typical marine values of 20 ppbv and 10/cm^3 (number density) at 50 km off the coast. The concentrations of the anthropogenic methylchloroform (CH_3CCl_3) increased as the aircraft approached the coast, in a pattern closely resembling the aerosol and O_3. Methylchloride (CH_3Cl) and methyliodide (CH_3I), which have large natural oceanic sources, were observed to be more concentrated over the ocean and the coastal transition zone, while substantially lower concentrations were observed over the forest. Finally, the concentrations of
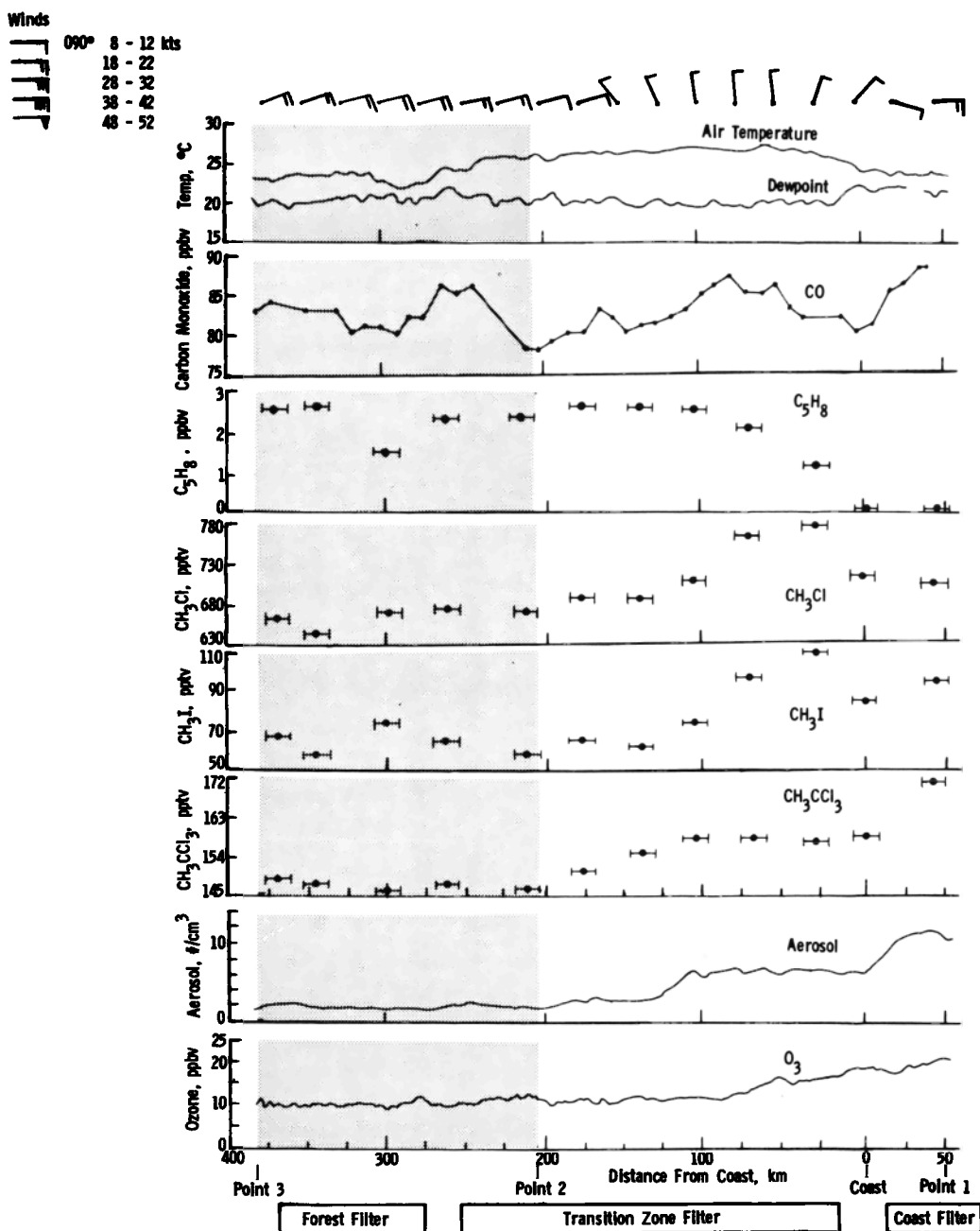
Fig. 5. Boundary layer data from the interior of the Guyana forest (point 3, 2°15'N, 56°56'W) to the coast.

isoprene further served to define the influence of forested regions on the tropical boundary layer in the horizontal. The pattern of isoprene is opposite to the patterns of O_3, aerosol, and trace gases. High levels are observed over the forested boundary layer, but concentrations fall to undetectable levels over the ocean. This pattern is consistent with the high flux of isoprene from the forests and its relatively short atmospheric lifetime that prevents substantial amounts to be transported to the marine boundary layer. The patterns of trace gases separate the forested and marine boundary layers. Trace gases emitted from the oceans (CH_3Cl and CH_3I) are more concentrated in the marine boundary layer and trace gases such as isoprene (C_5H_8) emitted from trees are more concentrated in the forest boundary layer.

As such, the data presented in Figure 5 suggest the presence of a "transition zone" between the forest and the

coast, a zone in which the boundary layer was composed on both marine elements and forest elements. The analyses of the three filter samples collected on this flight leg (see bottom of Figure 5) support the presence of a transition zone in that the coast filter showed enrichment of marine-related species (e.g., Na^+, Cl^-, K^+, SO_4^{2-}, and $CH_3SO_3^-$), the forest filter showed species associated with biogenic production of forest-related particles (e.g., SO_4^{2-}, PO_4^{3-}, CH_3COO^-), and the transition zone filter showed both marine and forest influences. While the extent of the transition zone is slightly different, depending upon the particular data used for that judgment, most data suggest that transitional effects are negligible at about 200 km inland from the coast. Thus in the following discussion, only data obtained 200 km or more inland from the coast (that is, from about point 2 to point 3 and the shaded area of Figure 5) are considered representa-

tive of the forest boundary layer chemistry. It is important to note (Figure 5) that most species concentrations in the forest boundary layer were horizontally homogeneous over the approximately 175-km data leg between points 2 and 3.

4.1. Carbon Monoxide, Isoprene, and Ozone

The vertical distribution of CO, C_5H_8, and O_3 over the Guyana forest are illustrated in Figure 6. These data were obtained during the descent at point 3. The symbols are averages and standard deviations for mixing ratios measured during the constant altitude legs at 3.5 km and in the boundary layer over the forest between points 2 and 3. Also depicted in Figure 6 (based on Figure 3) is the convective cloud tops of top of the boundary layer at point 3. The most striking features of these data are the threefold decrease in O_3 mixing ratio and the increase in CO and C_5H_8 in the tropical forest boundary layer relative to their values in the troposphere above 2.5-km altitude. The mixing ratios of C_5H_8 decreased tenfold from the mixed layer to the troposphere above 2.5-km altitude. No isoprene was detected above about 2-km altitude. If these measurements are representative of a relatively "young" boundary layer (as discussed in section 3), then these data suggest that the wet tropical forest boundary layer is a source of CO and C_5H_8 and a strong sink for O_3.

Oxidation reactions involving isoprene and other nonmethane hydrocarbon species emitted by vegetation are a likely source for production of CO in the forest. The concentration of isoprene over the Guyana forest was high, as indicated in Figure 6 and as discussed by Rasmussen and Khalil [1985] and, as a result, was probably a source of the enhanced CO levels in the boundary layer air [Kleindlenst et al., 1982; Zimmerman et al., 1978]. The nearly linear decrease (0.005 ppbv/m) in mixing ratio of CO between the convective cloud tops and 3 km suggests dilution was by

mixing, with no appreciable sources or sinks active at these altitudes.

The O_3 distribution over the Guyana tropical forest exhibited a decrease from values of 30 ± 7 ppbv at 3.5-km altitude to about 10 ± 2 ppbv at 0.4 km. Ozone mixing ratios decreased at an average rate of 0.005 ppbv/m from 3.5-km altitude to the convective cloud tops and 0.015 ppbv/m from the cloud tops to 0.4-km altitude. This increase in ozone depletion below the cloud tops (that is, within the boundary layer) and the nearly linear gradient from 800- to 400-m altitude suggest the presence of highly efficient boundary layer removal processes. Neglecting any existing near-surface or canopy layer, extrapolation of the 0.015 ppbv/m gradient to the surface results in a surface ozone mixing ratio of about 4 ppbv. These data do not enable distinction between in situ consumption (for example, NMHC oxidation) and surface deposition of O_3 to the forest canopy.

Our data for O_3 and CO support the hypothesis of Crutzen et al., [1985] that the boundary layer overlying the natural wet tropical forest is a sink for O_3 and a source for CO. Crutzen et al. [1985] attributed their observations of enhancement of boundary layer CO and depletion of O_3 to oxidation of isoprene and other hydrocarbons emitted by forest vegetation. Their studies lead them to speculate that 2–3% of the total carbon fixed in net primary productivity is returned to the atmosphere as CO. Theoretical investigations by Zimmerman et al. [1978], Volz et al. [1981], and Crutzen and Gidel [1983] also indicate that there should be a large production of CO from hydrocarbon oxidation in the tropics.

In contrast to wet tropical forest, dry tropical savannah areas appear to be a source of tropospheric O_3 as a result of photochemical processes associated with emissions from biomass burning [Delany et al., 1985]. Understanding the role of the tropics in the global ozone budget will require a careful assessment of the relative importance of these sources and sinks.

4.2. Dimethylsulfide

The results of the DMS measurements are presented in Figure 7. The values observed over the ocean (77 pptv in the boundary layer, 5–10 pptv at 5 km) are typical of those observed during other flights over the ocean off Barbados [Ferek et al., 1986] and reflect the input from the sea surface and the vertical transport of DMS in convective clouds. Over the forest region at 3.5 km and in the boundary layer, DMS values are about 4 times lower than over the ocean: 2.3 and 20 pptv, respectively. There are two possible explanations for the DMS levels observed over the Guyana region: (1) emission of DMS from the rain forest ecosystem or (2) advection of DMS from the marine boundary layer, over the continent. The latter explanation cannot not be excluded on the basis of the available meterological data but seems unlikely, based on the O_3 and aerosol distributions discussed above. If we assume that DMS is of local origin, we can obtain a rough estimate of the DMS input flux from the observed concentrations. The boundary layer thickness is about 700 m, and the age of the boundary layer air relative to exchange with the free troposphere is about 5 hours (section 3). This implies a lower limit for the surface input of DMS of about 4 μg S (DMS) m^{-2} h^{-1}. A higher flux would be required if significant removal of DMS by atmospheric reactions is taking place in the boundary layer. In view of the
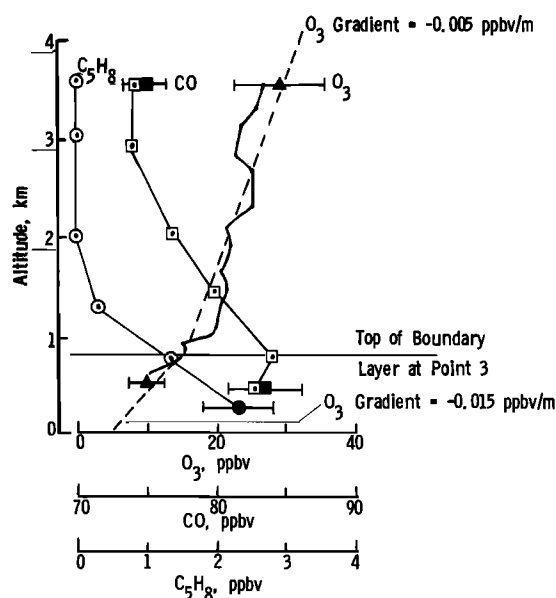

Fig. 6. Vertical distribution of CO, C_5H_8, and O_3 over wet tropical forest. The vertical profiles were obtained at point 3 (2°15'N, 56°56'W). The average mixing ratio, and standard deviation for CO (solid square), C_5H_8 (solid circle), and O_3 (solid triangle) measurements along the flight legs at 3.5- and/or 0.4-km altitude illustrate the variability in and above the boundary layer.
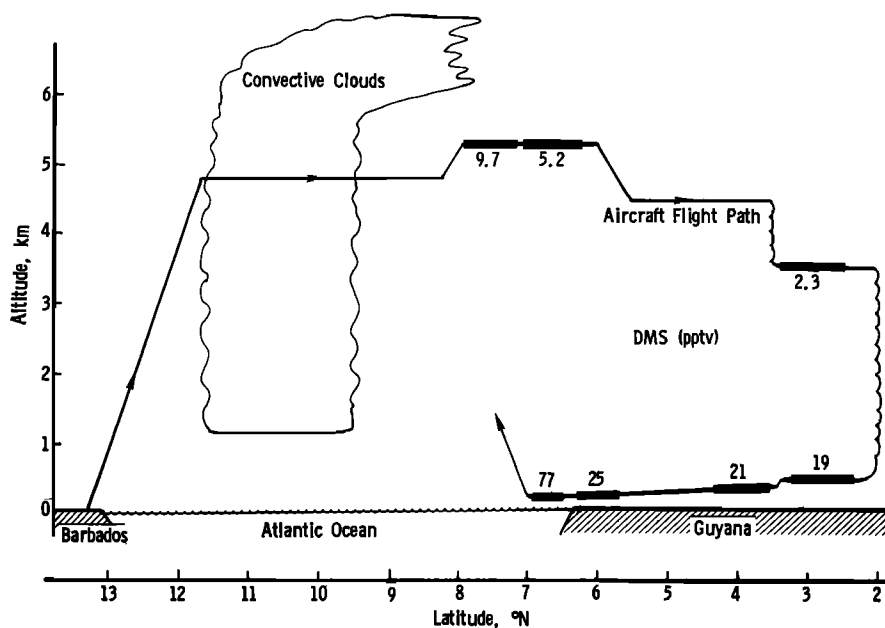
Fig. 7.   Spatial variation of dimethylsulfide over the coast and tropical forest of Guyana.

uncertainty of the reaction rate of DMS in continental air, we can use a lifetime of about 1 hour as a lower limit, which results in an upper limit for the DMS flux of about 20 $\mu g\ m^{-2}$ h^{-1}. This value range is remarkably similar to the marine DMS emission rate, which has been estimated to be near 10 $\mu g\ m^{-2}\ h^{-1}$ on average [Andreae, 1985]. Clearly, measurements of DMS concentration in air masses of unambiguously continental history are needed to resolve the problem of continental DMS emission rates.

4.3. Aerosol Chemistry

Particulate material in the boundary layer over tropical forests can originate from emission of primary and secondary aerosols from vegetation, wind erosion of local soils, and atmospheric transport from distant sources. The composition of selected chemical species in the water-soluble fraction of boundary layer and free tropospheric aerosols over Guyana are presented in Table 1. We were especially interested in the water-soluble composition, since this fraction contains many species biogeochemically active in forest metabolism processes.

The forest boundary layer aerosol showed enrichments of Na^+, NH_4^+, NO_3^-, SO_4^{2-}, $CH_3SO_3^-$, PO_4^{3-}, F^-, $C_2O_4^{2-}$, and CH_3COO^- relative to the clean tropospheric levels. Scanning electron micrographs of aerosols collected in the forest boundary layer revealed the presence of numerous organic particulates (for example, vegetation-derived particulates), many with diameters approaching 20 μm. We hypothesize that organic particulates derived from forest vegetation were a major source for aerosol chemical species in the boundary layer over the Guyana wet tropical forest. Lawson and Winchester [1979] analyzed total aerosol composition of ground-based samples from South American tropical forests and postulated that sulfur, potassium, and phosphorus were most likely associated with biogenic particulates.

Aerosol chemical species in the forest boundary layer can also originate as secondary products of biogenic gases released from forest soils. Recent studies in humid forests of the Ivory Coast have demonstrated that wet season tropical forest soils can be a significant source of H_2S [Delmas et al., 1980; Delmas and Servant, 1983]. These results suggest that SO_4^{2-} in the boundary layer over the Guyana forest may have been derived in part from H_2S emitted from anaerobic sites in forest soils. The oxidation of DMS may also make a significant contribution to the observed levels of aerosol sulfate. Another aerosol sulfur species, methyl sulfonate ($CH_3SO_3^-$), also most likely originated from the photooxidation of DMS. Similarly, the aerosol NO_3^- and NH_4^+ concentrations can be attributed partially to release of reduced nitrogen gases (for example, NO and NH_3).

Carboxylic acids, formic and acetic acids in particular, are believed to be major contributors to rainwater acidity in tropical areas [Galloway et al., 1982]. However, the atmospheric concentrations of particulate formate and acetate over the Guyana forest were very low. Galloway et al. [1982] measured substantial rainwater concentrations (that is, mg/kg levels) of these species a few hundred kilometers to the west of the Guyana forest at San Carlos, Venezuela.

TABLE 1.   Chemical Compositon of the Water-Soluble Fraction of the Atmospheric Aerosol Collected at 3.5- and 0.4-km Altitude Over Wet Tropical Forest in Guyana, June 27, 1984

Species	Free Troposphere, 3.5 km	Forest Boundary Layer, 0.4 km
Na	51	162
K	13	20
NH_4	8	105
Cl	69	74
NO_3	3	13
SO_4	22	256
CH_3SO_3	0.91	2.7
PO_4	20	157
F	0.74	5.1
C_2O_4	4	25
HCOO	1	<0.5
CH_3COO	2	11

Concentrations are reported as nanograms per standard cubic meter.

These results, combined with our aerosal measurements, appear to suggest that formic and acetic acids may be primarily in gaseous phase in tropical forest atmospheres, at least in northern South American forests. However, in-cloud heterogeneous production of formate and acetate may also be an important source of these species in rainwater [*Chameides and Davis*, 1983].

Our data also show changes in the water-soluble chemical composition of the atmosphere aerosol along the boundary layer transect from the forest to the coast which reflect spatial variation in source relationships. A comparison (Figure 8) of the three boundary layer aerosol samples collected over this flight transect is difficult because of confounding effects of the transition zone. However, there is a clear trend of increasing atmospheric concentration of Na^+, K^+, Cl^-, SO_4^{2-}, and MSA as the coast is approached, indicative of the strong marine source for these species. The NO_3^- and $HCOO^-$ concentrations were also highest near the coast, which may reflect enrichment of these species in Saharan dust [see *Talbot et al.*, 1986]. (It is noted that a layer of
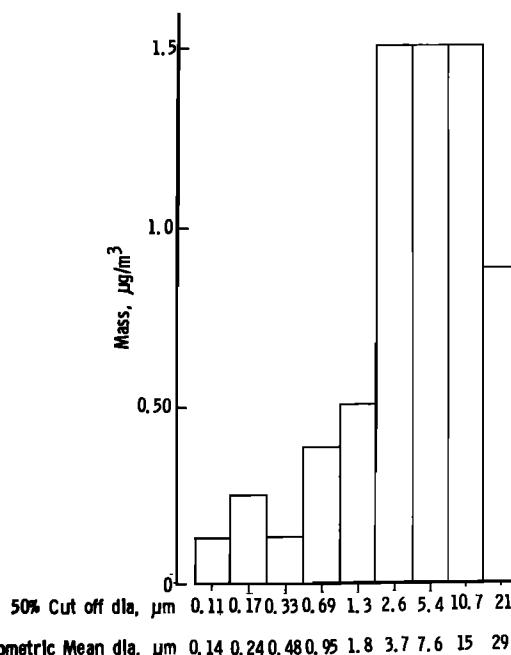
Fig. 9. Mass-size distribution of forest boundary layer aerosol. Data represent the average of 8 samples collected with the QCM impactor. Average total mass concentration was 6.8 ± 3 (1σ) g/standard m^3.

Saharan dust at about 3-km altitude was tracked from Barbados to just east of the coast of South America.) On the other hand, the data indicate that the tropical wet forest may be a source of reduced nitrogen gases, such as NO, which can serve as a source for secondary aerosol NO_3^-. The aerosol NH_4^+ data indicate that the forest may also be a source of NH_3, presumably related to biogenic decomposition processes. The source of aerosol SO_4^{2-} is most likely biogenically produced reduced sulfur gases and organic particulates, as suggested by *Lawson and Winchester* [1979].

The size distribution of particulates in the forest boundary layer, as measured with the QCM impactor, is shown in Figure 9. These data represent the average of eight samples collected between points 2 and 3. The average aerosol mass concentration was 6.8 ± 3 (1σ) $\mu g/m^3$, with the majority of the mass in the 2- to 10-μm-diameter range. The large particle dominance of the mass-size distribution most likely reflects organic particulates originating from forest vegetation.

5. CONCLUSIONS

Synoptic sampling of CO, O_3, DMS, halocarbons, isoprene, and aerosols over an extensive area of tropical forest in Guyana demonstrated that the wet tropical forest has a pronounced influence on the chemistry of the atmospheric boundary layer. Results of this study support the hypothesis that forest vegetation emits nonmethane hydrocarbons, particularly isoprene, which are subsequently oxidized in the boundary layer via photochemical reaction and provide a source of CO. Ozone is most likely a major participant in these oxidation processes, and as a result, the forest boundary layer acts as a substantial O_3 sink. DMS was found to be present in significant concentrations in the boundary layer over the Guyana rain forest. While advective transport from the oceans cannot be excluded, the data do
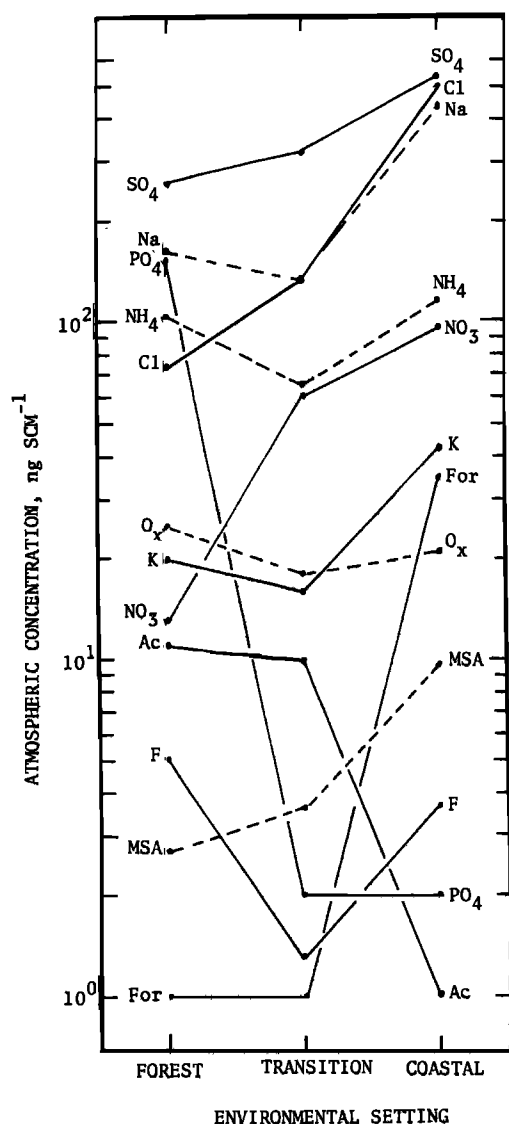
Fig. 8. Spatial variation of selected water-soluble chemical species in the boundary layer aerosols collected from the forest to the coast of Guyana. See Figure 5 for the locations at which the forest, transition, and coastal filter samples were collected.

suggest emission of DMS from the rain forest ecosystem. The wet forest also appears to be a source of nutrient-rich boundary layer aerosols, probably being associated with organic particulates released from vegetation.

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