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Sulfur Gases and Aerosols in and Above the Equatorial African Rain Forest

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We determined the distribution of gaseous and particulate sulfur compounds in the canopy of the tropical rain forest of northern Congo and the overlying atmosphere during February 12–25, 1988. Hydrogen sulfide and dimethylsulfide decayed exponentially with altitude from approximately 30–40 ppt at ground level to 3–5 ppt at around 3 km altitude. Emission fluxes from the forest to the atmosphere were estimated by fitting a one-dimensional time-dependent numerical model of chemistry and transport of the sulfur compounds to their observed vertical profiles. Emission fluxes of 0.6–1.0 nmol H₂S m⁻² min⁻¹ and 0.3–0.7 nmol DMS m⁻² min⁻¹ were consistent with the observed vertical profiles of H₂S and DMS. These fluxes compare well with fluxes reported previously for the Amazon rain forest during the dry season and support the view of a subordinate role of land biota in the global cycling of sulfur. The particulate sulfur concentration of 248 ppt was found below the forest canopy. Biomass burning is considered to be an important contributor to this particulate sulfur. Carbonyl sulfide was found to be enhanced above the 500 ppt tropospheric background throughout the mixing layer of 2–3 km depth, likely due to biomass burning.

INTRODUCTION

A variety of biogeochemical processes in the marine and terrestrial biosphere produces volatile sulfur compounds, which are then reallocated among biogeochemical reservoirs, with the atmosphere acting as a transport medium. Beyond being solely a transport medium, the atmosphere itself is affected by the reactive properties of the sulfur compounds, their products, and the interaction of these products with sunlight and cloud microphysics [Nguyen *et al.*, 1983; Shaw, 1983; Charlson *et al.*, 1987]. Deposition of the oxidized products at the Earth's surface supplies sulfur as a nutrient to the terrestrial biosphere but may also affect terrestrial ecosystems by their acidic properties.

While a fairly large data set on the role of marine ecosystems as a source of gaseous sulfur to the atmosphere has been established during recent years, information on the cycling of sulfur between terrestrial ecosystems and the atmosphere, in particular for tropical regions, still remains scarce. Consequently, global estimates on the emission of sulfur gases to the atmosphere by soils and terrestrial plants vary between 0.16 and 2.4 Tmol S yr⁻¹ [Frenay *et al.*, 1983; Andreae, 1990].

In the terrestrial biosphere, volatile sulfur compounds are produced by dissimilatory and by assimilatory sulfate reduction. Dissimilatory sulfate reduction by bacteria occurs in soils and wetlands under anaerobic conditions, producing H₂S. Through assimilatory sulfate reduction, bacteria, al-

gae, fungi, and higher plants synthesize the amino acid, cysteine, and various other compounds from sulfate. Sulfur compounds can be released to the atmosphere by plants through leakage of volatile intermediate metabolites, or as a mechanism to remove excess sulfur [Rennenberg, 1984]. The emission of hydrogen sulfide, DMS, and methyl mercaptan from plants has been documented [Filner *et al.*, 1984; Lovelock *et al.*, 1972; Lamb *et al.*, 1987]. Conversely, plants are reported to take up COS from the atmosphere, constituting a major sink for this gas [Goldan *et al.*, 1988; Mihalopoulos *et al.*, 1990b].

Until recently, studies on the emission of sulfur gases by soils and vegetation had, with a few exceptions, been confined to extratropical regions. H₂S fluxes of 4.2 nmol m⁻² min⁻¹ as an average from French oxalic lawn soils were measured by Delmas *et al.* [1980] and 0.06–65 nmol m⁻² min⁻¹ from marshland soils in Germany by Jaeschke *et al.* [1980]. Adams *et al.* [1981] report data from a field study on sulfur gas emissions from U.S. inland soils. By extrapolating their soil sulfur flux data to tropical latitudes, they arrived at a figure as high as 2 Tmol S yr⁻¹ for the global flux from terrestrial surfaces. Sulfur fluxes of 90 nmol m⁻² min⁻¹ as an average are reported by Delmas and Servant [1983] for forested soils and vegetation on the Ivory Coast of Africa, in support of these high flux estimates. Their data indicate fluxes to be a factor of 8 higher during the wet season (160 nmol m⁻² min⁻¹) than during the dry season (20 nmol m⁻² min⁻¹).

Much lower fluxes have been measured during recent studies. Goldan *et al.* [1987] and Lamb *et al.* [1987], revisiting some of the sites investigated by Adams *et al.* [1981], suggest a downward revision of those earlier flux estimates by as much as a factor of 10, mainly due to experimental errors in the original data for H₂S. Staubes *et al.* [1989] found fluxes of 0.2–0.5 nmol m⁻² min⁻¹ for DMS and 0.1–0.2 nmol m⁻² min⁻¹ for CS₂ at soil temperatures above 21°C from soils in Germany. Andreae and Andreae [1988] measured a flux of total short-lived sulfur species (H₂S, DMS, CH₃SH) from wet tropical forest soils during ABLE 2A in Amazonia in the dry season, which accords with the recent data from temperate regions quoted above. During

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the wet season (ABLE 2B), even lower soil emission values were found at the same site [Andreae *et al.*, 1990a]. The total emission of reduced sulfur gases from soils and the plant canopy was estimated to be about $2 \text{ nmol m}^{-2} \text{ min}^{-1}$ with little variation between seasons. Sulfur gas concentrations over Amazonia were about 10–40 ppt for DMS and H_2S in the canopy, decreasing to about 1–2 ppt for DMS in the free troposphere. CH_3SH was an order of magnitude lower. From the ABLE 2 data an internally consistent picture was established between low fluxes of the short-lived sulfur gases from the soil/canopy system to the atmosphere, their fluxes in the atmosphere above the canopy, their concentration and transformation in the atmosphere, the reaction products, and their removal from the atmosphere by dry and wet deposition [Andreae and Andreae, 1988; Andreae *et al.*, 1990a, 1990b]. This picture, if representative of the cycling of sulfur over remote continental ecosystems, indicates total fluxes of biogenic short-lived sulfur compounds to the atmosphere of about $0.15 \text{ Gmol S yr}^{-1}$, which falls at the very low end of existing global sulfur budgets [Frenay *et al.*, 1983]. In view of the large discrepancy between sulfur fluxes reported from tropical Africa and those from Amazonia, it was considered important to conduct measurements in Africa using the same methods that had been applied in Amazonia, in order to make possible a comparison of the cycling of sulfur compounds in the wet tropical ecosystems of South America and Africa. Here, we present the results of measurements made in and above the African equatorial rain forest during the 1988 Dynamique et Chimie de l'Atmosphère en Forêt Equatoriale (DECAFE) experiment.

EXPERIMENT

Samples for the determination of H_2S , DMS, and COS were collected aboard a small aircraft from the boundary layer and the free troposphere. Air was sampled from an FEP Teflon manifold which was continuously flushed with outside air flowing in through Teflon tubing (8 mm ID) at a flow rate of approximately 15 L min^{-1} . The inlet was located about 15 cm upstream of the nose of the aircraft and brought to the manifold by about 3 m of Teflon tubing. Sample volumes were measured by integrating mass flowmeters (Teledyne-Hastings-Raydist). COS was sampled by filling evacuated stainless steel canisters. At ground level, samples were collected at various heights within the forest and a clearing nearby. Here, battery-powered pumps were used for drawing ambient air through the sampling devices, and gas sample volumes were determined from flow rates measured with rotameters and from sampling time. Throughout this paper, mixing ratios are reported in parts per thousand on a molar basis, whereby 1 ppt equals 10^{-12} mol of a species per mol of air.

Hydrogen sulfide was sampled and analyzed according to the method of Natusch *et al.* [1972], with the modifications recently developed by Saltzman and Cooper [1988] to overcome a positive interference created by atmospheric COS. For preconcentration of H_2S , air was drawn at a rate of $7\text{--}11 \text{ L min}^{-1}$ through silver nitrate impregnated filters (Whatman 41, 47 mm diameter) which were held in PFE Teflon filter holders. Sulfide collected on the filters was recovered by rinsing with 20 ml NaOH/NaCN solution and then determined fluorometrically by fluorescence quenching of dilute fluorescein mercuric acetate. We used a Turner Designs

model 10 series fluorometer with a blue lamp and 10 nm bandpass filters at 500 nm excitation and 520 nm emission wavelengths. Calibration in the field was performed using freshly prepared standard solutions of sodium sulfide [Natusch *et al.*, 1972]. After the expedition, in the laboratory, further calibration studies were made using solutions of anhydrous sodium sulfide (Alfa Research Chemicals, Karlsruhe, West Germany, Catalog 65122) and certified H_2S permeation devices (VICI Metronics, Santa Clara, California). The permeation devices were stored at 30°C and permeation rates were determined gravimetrically. They were placed in a temperature-controlled dynamic dilution system to produce gas streams with 50–300 ppt H_2S . Comparison between calibrations based on the dissolved sulfide standards and those based on the gas dilution system showed that the recovery from the gas phase was 89%. The field data from DECAFE 88 were corrected by this factor. Atmospheric COS presents a positive interference of the method, since approximately 1% of it hydrolyzes on the filters. It is recovered during analysis and thus produces an artifact (typically about 5–10 ppt) H_2S signal [Saltzman and Cooper, 1988]. To overcome this interference, two filters were used in tandem during sampling. The backup filters were used to obtain a measure of the COS artifact, which was then subtracted from the signal on the front filter, yielding a corrected H_2S value. The detection limit of the method (signal to noise of 2) is 13 ppt at 500 L sample volume. Under field conditions in Africa the precision at this level is 14%. All samples were analyzed in a field laboratory within 3–6 hours after sampling.

DMS was sampled by adsorption onto gold wool held in quartz glass tubes. Total sample volumes of 50–100 L were collected at a rate of up to 2 L min^{-1} . After sampling, the tubes were capped and stored in sealed containers. The samples were shipped back to the laboratory after the campaign, where DMS was desorbed thermally from the gold and analyzed by GC/FPD. This technique has been described in detail previously [Andreae *et al.*, 1985]. As a check, 24 blank tubes were stored together with the samples, and no significant contamination during storage was found. The analytical system was calibrated from a dilution system in which nitrogen was passed over a DMS permeation tube held at constant temperature. Samples of this gas stream were collected onto gold tubes and measured. The detection limit of the method is approximately 1.5 ppt DMS at a sample volume of 40 L. Precision and accuracy are typically near ± 10 and $\pm 20\%$, respectively, at 50 ppt DMS.

Atmospheric COS was sampled by filling evacuated 6-L electropolished stainless steel canisters with ambient air. The canister samples were shipped to France and analyzed in the CNRS laboratory. For analysis, COS was cryotrapped at -120°C on TENAX-GC from aliquots of the canister samples, desorbed thermally, separated on a Varian 3400 GC, and detected with a dual-flame FPD [Belviso *et al.*, 1987]. The samples were analyzed less than 1 month after they had been collected in the field.

To check for changes in sample composition due to storage, test samples of natural air were stored in the containers and analyzed over a period of 1 month. No significant variations of COS were observed. The precision of the analysis of COS in air samples is about 7% and the detection limit is 0.4 ng of COS. The reproducibility is better than 5%.

Aerosol was sampled at the forest site in the canopy about 5 m above the ground. Stacked filter units (SFU) were used to size-segregate coarse (2.0–15 μm) and fine (<2.0 μm) particles according to the procedure described by Artaxo *et al.* [1988]. Samples were loaded for 2 days at a flow rate of approximately 14 L min^{-1} . The SFU were stored in sealed containers before and after loading. Blank filters received the same handling as exposed filters before and after sampling. The samples were analyzed for 19 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Rb, and Pb) by particle-induced X ray emission (PIXE). A 2.4 MeV proton beam of the Van-der-Graaf accelerator from PUC University in Rio de Janeiro, Brazil, was used. The detection limit for elemental sulfur and potassium reported here was typically 5 ng m^{-3} and the precision of the PIXE analysis for these elements was better than 5%.

A single rainfall event was sampled at Impfondo. After a dry period of at least 10 days a thunderstorm brought heavy showers at around midnight on February 22. Rainwater was sampled with a polyethylene bucket in front of the field laboratory, at about 40 cm above ground. The bucket had been rinsed with deionized water and was exposed a few minutes before the rain began. The samples were stored in polyethylene bottles with a small amount of chloroform added to suppress microbial activity. The samples were analyzed in Mainz for sulfate using ion chromatography, with a DIONEX HPIC-AS4 column and 2.1 mM NaHCO_3 /1.9 mM Na_2CO_3 eluent.

RESULTS AND DISCUSSION

Sampling Environment and Meteorological Situation

The study area around Impfondo in northern Congo and the large-scale meteorological situation and micrometeorological conditions have been described in detail by Fontan *et al.* [this issue] and B. Benech *et al.* (unpublished manuscript, 1991). Impfondo is located near the northern edge of the humid equatorial rain forest belt of Africa. About 250 km north of Impfondo the vegetation changes from forest to savanna. The DECAFE 88 experiment was conducted during February and March, toward the end of the dry season of the region. The meteorological situation at this time of the year is characterized by two features: a low level southwesterly monsoon-type inland flow from the Gulf of Guinea and an overlying easterly or northeasterly dry continental "harmattan" current, originating from the arid savanna and desert regions of northern Africa. The dry season of northern Congo and its adjacent northward savanna regions originates mainly from the predominance of these northeasterly dry, continental winds, which diminish the convective properties of the underlying unstable humid southwesterlies [Bultot and Griffith, 1972]. With the exception of a thunderstorm which brought some rain on February 22, no precipitation occurred during the experiment. Cloud convection was usually restricted to approximately 4–5 km depth, but deep convective activity was occasionally observed from the research aircraft.

We sampled the boundary layer and free troposphere above the rain forest from the aircraft during a series of flights within a 50-km radius from Impfondo. Ground-based measurements were conducted at two sites in the forest and a nearby clearing, about 20 km west of the village of

Impfondo, as well as outside the field laboratory, at about 1-km distance from Impfondo. At one of the forest sites a pulley was erected, which allowed the sampling of vertical profiles of H_2S between the ground level and the top of the canopy. The vegetation around Impfondo is dominated by primary rain forest. At the forest sites the height of the canopy was around 35–40 m. The soil appeared to be well drained year-round at one site, whereas the site with the pulley was at a little creek, and the soil was moist. The site at the clearing was approximately 300 m distant from the forest sites; the clearing itself was about 150 m in diameter. It was sparsely covered by 2-foot-tall tussock grass.

Concentration of H_2S and DMS in and Above the Rain Forest

The H_2S measurements at 0.5 m height showed a clear difference between the concentrations present inside the forest (42 ± 16 ppt, $n = 12$) and those in the clearing (24 ± 15 ppt, $n = 9$). This difference becomes even more pronounced when only the data from the moist forest site are considered (50 ± 10 ppt, $n = 9$), as the values from the dry forest site (20 ± 8 , $n = 3$) are in the same range as those from the clearing. The air sampled at the clearing can be considered as representative for the situation above the top of the canopy, since vertical mixing is much more intense in the clearing where the ground is exposed to solar heating than it is in the forest, where turbulent fluxes are suppressed during much of the day [Monteith, 1976; B. Bonsang *et al.*, unpublished manuscript, 1991]. This is supported by the similarity between H_2S concentrations found at the clearing and the results taken from the aircraft at around 70 m during low altitude flights (Figure 1). The excess of H_2S in the forest as compared to outside can thus, as a first approximation, be interpreted as indicating a net transfer of H_2S from the soil/canopy system to the atmosphere. Because of the lack of data for diffusivities or bulk transfer coefficients between forest and atmosphere, our ability to quantitatively interpret this result is restricted.

A modeling approach to estimate H_2S fluxes from the Congo forest will be presented below. Vertical profiles of H_2S through the canopy were sampled by lifting the filters with a pulley to 10 m and 20 m above ground level. These profiles show H_2S to decrease from 50 ± 10 ppt at 0.5 m to 22 ± 14 ppt and 26 ± 8 ppt at 10 and 20 m, respectively (Figure 1), similar to the values outside the forest. The release of H_2S from the soil is obvious from the profile. The slight increase of H_2S between 10 and 20 m, which is within experimental variability, indicates some additional net release at the upper canopy level. Such an increase has also been frequently observed in the profiles through the canopy layer of the Amazon forest [Andreae and Andreae, 1988]. The existence of a light-dependent H_2S source at the upper canopy level may also be concluded from the diel cycle of H_2S at 10 and 20 m (Figure 2).

The diel variations of H_2S in the forest canopy as well as the vertical gradients in the canopy basically are in accordance with the diurnal cycle of the diffusivity of gases in the vertical below the canopy, K_{zc} . K_{zc} was derived by B. Bonsang *et al.* (unpublished manuscript, 1991) from measurements of the ^{222}Rn gas concentration gradient between the ground level and 20 m height. Diel variations of H_2S were measured on February 22 and 23 at 0.5, 10, and 20 m at the

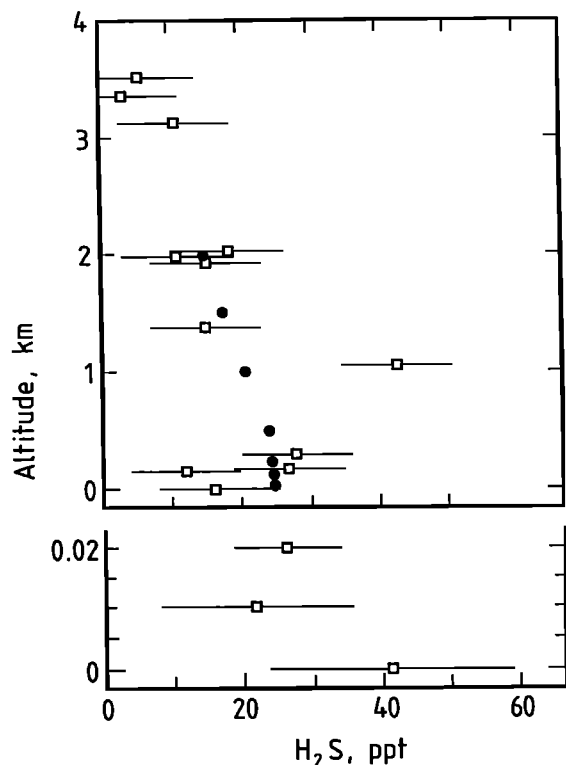


Fig. 1. Vertical distribution of H_2S , obtained during DECAFE 88: (upper part) from sampling on-board aircraft and (lower part) at 0.5, 10, and 20 m in the forest canopy. Error bars given represent analytical and sampling uncertainty ($1 s_m$). Solid circles represent the results of the model simulation with 0.4 ppb NO_x .

moist forest site. The highest mixing ratios were found at all three levels at around 1500 to 1600 LT in the afternoon, the lowest between 0100 and 0700 LT (Figure 2). The peak mixing ratios in the afternoon coincide with the largest

vertical gradient of H_2S of about 30 ppt between 0.5 m and the upper levels, whereas during the nocturnal H_2S minimum at 0100 LT, the vertical gradient did not exceed the analytical uncertainty of ± 6 ppt. This behavior can be explained through vertical mixing in the canopy, which is controlled by gain or loss of energy at the top of the canopy through radiation. During daylight, heat input from above stabilizes the layer below the top of the canopy, whereas cooling during the night produces instability in the layer below. This diurnal cycle of vertical diffusion is reflected by the difference between the ^{222}Rn gas concentration at ground level and at 20 m height, which increases during the day to a maximum at around 1700 LT and decreases rapidly from late afternoon to a minimum at around midnight (B. Bonsang et al., unpublished manuscript, 1991).

Above the canopy the average profile as sampled from the aircraft (Figure 1) shows H_2S to further decrease with altitude. In the planetary boundary layer, which was about 2–3 km deep and characterized by an accumulation of primary and secondary products from biomass burning [Andreae et al., this issue; B. Bonsang et al., unpublished manuscript, 1991; J. Rudolph et al., unpublished manuscript, 1991], 25 ± 16 ppt H_2S were found. Above this layer, H_2S dropped to values around 7–13 ppt, which is at the detection limit of the method under the sampling conditions on-board aircraft. These results can be compared to the data from Amazonia, where 47 ± 21 ppt were found in the boundary layer and 7 ± 7 ppt in the free troposphere. Assuming a similar source flux of H_2S from the soil/plant system in both regions, a somewhat lower H_2S concentration over the Congo forest would be consistent with higher OH concentrations over this region (see modeling section below). However, our data sets from both the Amazon and the Congo forest remain in striking contrast to the H_2S data reported from the Ivory Coast, where Delmas and Servant [1983] found a mean H_2S concentration of 420 ppt (range 35–2500 ppt). No explanation for this difference is apparent.

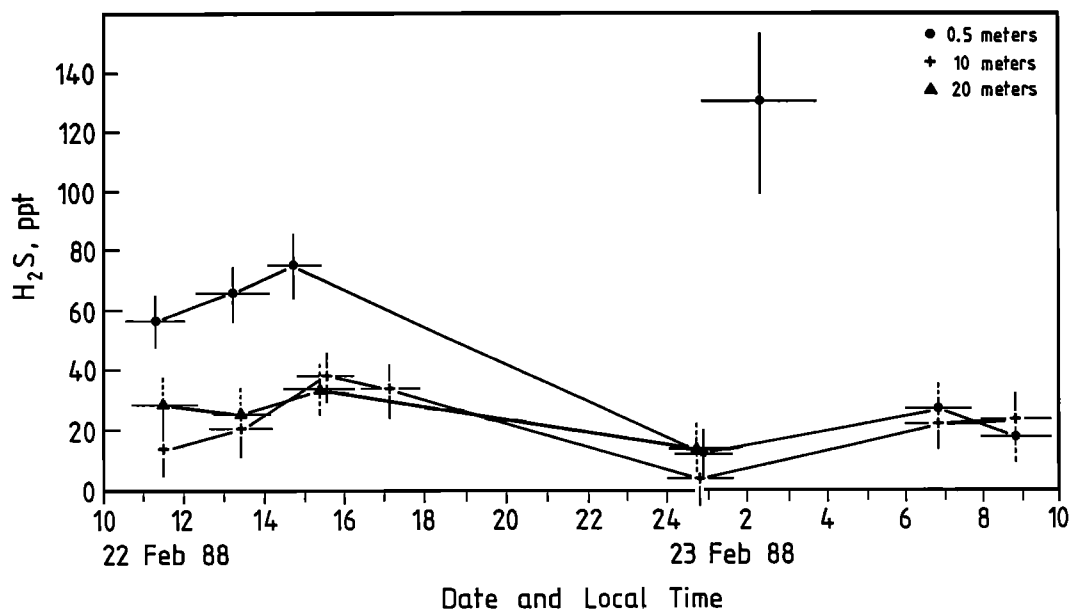


Fig. 2. Diurnal variation of H_2S in the rain forest canopy at 0.5, 10, and 20 m during February 22 and 23, 1988. Vertical error bars give analytical and sampling uncertainty (6 ppt if ≤ 40 ppt, 14% if ≥ 40 ppt); horizontal bars indicate the sampling interval.

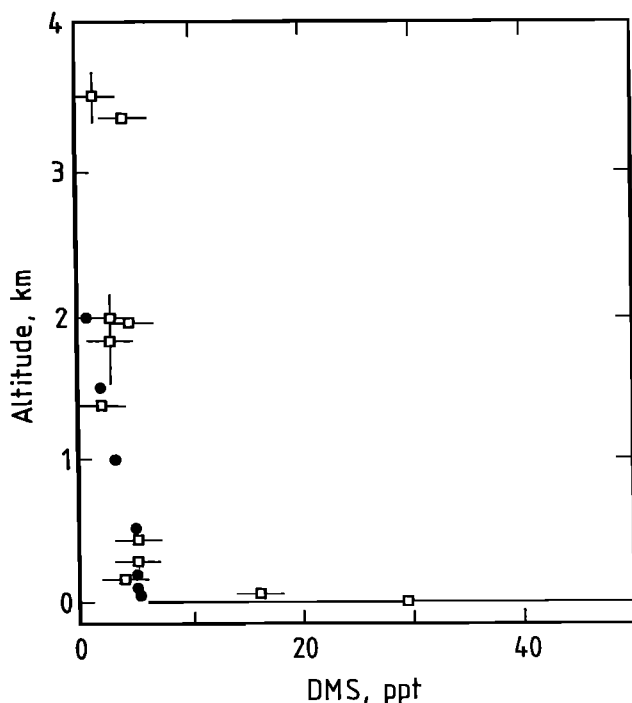


Fig. 3. Vertical distribution of DMS during DECAFE 88, obtained from aircraft and ground-based sampling. Data point at lowest altitude gives mean and range of DMS from ground-based measurements outside laboratory at Impfondo. Horizontal error bars of aircraft samples give standard error ($1 s_m$) of the measurement. Vertical bars give altitude interval of sampling. Solid circles represent the results of the model simulation with 0.4 ppb NO_x .

At ground level, DMS was sampled in an open area behind the field laboratory, about 1 km from the village of Impfondo. In 10 samples covering the period between 1300 and 1800 LT on March 24, mixing ratios ranged between 7 and 75 ppt, with an average around 30 ppt. The vertical profiles obtained from the aircraft (Figure 3) show a rapid decrease of DMS to values around 5 ppt at a few hundred meters height, much in accordance with the situation experienced above the Amazon forest. There, DMS decreased from 16 ± 10 ppt at ground level to 9 ± 7 and 7 ± 3 ppt at several hundred meters altitude, in the dry and wet seasons, respectively [Andreae et al., 1990a].

Emissions of H_2S and DMS from the Congo Rain Forest

The vertical decay of H_2S and DMS and the absence of pronounced maxima in the profiles, as was observed at around 2–2.5 km for primary and secondary burning products like CO , C_2H_2 , O_3 , and aerosols, reflects the dominance of biogenic emissions by the plant/canopy system for these gases as well as their short lifetimes. The biogenic emission fluxes of H_2S and DMS can be estimated by solving the continuity equation for the atmospheric concentrations of H_2S and DMS in the boundary layer over the forest and constraining the solutions to match the atmospheric concentrations observed from aircraft (Figures 1 and 3). We view the boundary layer over the forest as horizontally well mixed, which seems a reasonable assumption considering the homogeneity of the terrain and the undisturbed meteorological conditions observed throughout the experiment.

The 1-day continuity equations for the atmospheric concentrations $C(z, t)$ of H_2S and DMS can then be written as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(K \frac{\partial C}{\partial z} \right) - kC \quad (1)$$

where $K(z, t)$ is the vertical eddy diffusivity ($\text{cm}^2 \text{ s}^{-1}$) and k is a rate constant (s^{-1}) representing chemical losses due to reactions with OH and NO_3 . Parameterization of vertical transport using eddy diffusivities appears to be appropriate for the conditions observed during the experiment (R. Lyra et al., unpublished manuscript, 1991). Rate constants for the reactions $\text{H}_2\text{S} + \text{OH}$, $\text{DMS} + \text{OH}$, and $\text{DMS} + \text{NO}_3$ are taken from Cox and Sheppard [1980], Atkinson [1986], and Dlugokencky and Howard [1988]. The reaction $\text{H}_2\text{S} + \text{NO}_3$ is negligibly slow [Dlugokencky and Howard, 1988].

We solve (1) over a vertical domain extending from the top of the canopy (40 m) to the top of the boundary layer (2000 m). Zero flux conditions ($K(z, t) = 0$) are assumed as upper boundary conditions at the top of the boundary layer. Lower boundary conditions are defined by the emission fluxes $\Phi(t)$ of H_2S and DMS at canopy top, which vary with time of day to reflect the dependence of vegetative emissions on sunlight and temperature [Fall et al., 1988]. We express this diurnal variation as

$$\Phi(t) = \Phi_0 \omega(t) \quad (2)$$

where Φ_0 is the 24-hour average flux and $\omega(t)$ is a diurnal weighting factor. Values for $\omega(t)$ are assigned to reproduce the diurnal variation of DMS fluxes previously reported by Andreae et al. [1990a] for the Amazon forest and range from 0.1 at night to 3.4 in early afternoon. The 24-hour average emission fluxes Φ_0 are adjusted to provide solutions to (1) which match the atmospheric concentrations observed from aircraft.

Eddy diffusivities in (1) are derived from boundary layer meteorological observations (R. Lyra et al., unpublished manuscript, 1991). These observations indicate a well-defined diurnal cycle of mixed layer growth and decay, with dry mixing depths (z_i) peaking at ≈ 600 m in early afternoon. The dry mixed layer was capped in the daytime by a cloud convective layer (CCL), which carried turbulent energy from the mixed layer aloft in shallow convective cells. The CCL grew in phase with the mixed layer, with CCL depths (z_c) peaking at ≈ 2000 m in early afternoon. The top of the CCL at z_c was marked by a strong persistent inversion. Midday values of z_i and z_c were highly reproducible from day to day over the course of the experiment (R. Lyra et al., unpublished manuscript, 1991). We compute $K(z, t)$ under unstable daytime conditions by using the bottom-up diffusion parameterization of Wyngaard and Brost [1984] for the mixed layer and a simple formulation based on dimensional analysis for the overlying CCL

$$K(z, t) = 2.5w^*z_i \left(1 - \frac{z}{z_i} \right) \left(\frac{z}{z_i} \right)^{3/2} + \alpha w^*z_i \quad z \leq z_i \quad (3a)$$

$$K(z, t) = \alpha w^*z_i \quad z_i < z \leq z_c \quad (3b)$$

$$K(z, t) = 0 \quad z > z_c \quad (3c)$$

where w^* (cm s^{-1}) is the convective velocity scale. The term αw^*z_i is added in (3a) for continuity of K at z_i . Values of z_i ,

TABLE 1. Summary of Model Results, 24-Hour Averages

Simulation	Emission Fluxes, nmol m ⁻² min ⁻¹			Sulfate Production Rate, ppt d ⁻¹	Concentrations, 10 ⁵ molecules cm ⁻³	
	H ₂ S	DMS	Isoprene		OH	NO ₃
(NO _x) = 0.2 ppb	0.60	0.26	500	8	4.1	37
(NO _x) = 0.4 ppb	0.63	0.33	600	12	5.6	82
(NO _x) = 2 ppb	0.98	0.69	1200	26	21	938

Results from simulations conducted with 0.2, 0.4, and 2 ppb NO_x (see text). Sulfate production rates and concentrations of OH and NO₃ are averages for the boundary layer air column (0–2000 m).

z_c , and w^* are specified from the observations of R. Lyra et al. (unpublished manuscript, 1991) as a function of time of day. We assign arbitrarily $\alpha = 10^{-2}$ in order to obtain reasonable midday values for $K(z, t)$ of order $10^5 \text{ cm}^2 \text{ s}^{-1}$ in the CCL. At night the boundary layer is assumed perfectly stratified; i.e., $K(z, t) = 0$ throughout the 40–2000 m air column.

The concentrations of OH and NO₃ needed to define the chemical loss rates of H₂S and DMS in (1) are computed with a one-dimensional photochemical model for the boundary layer. The model uses the detailed photochemical mechanism of *Lurmann et al.* [1986], modified for low NO_x conditions as described by *Jacob and Wofsy* [1988, 1990]. Vertical transport is simulated with the $K(z, t)$ parameterization described above. The UV radiation field is computed using a 6-stream code for the plane-parallel inhomogeneous Rayleigh atmosphere with an ozone column of 245 DU, an albedo of 0.1, and 25% opaque cloud cover above 2000 m. Fixed concentrations of CO, C₂H₆, C₃H₈, C₂H₄, and C₃H₆ are assumed and are specified from aircraft observations as a function of altitude (B. Bonsang et al., unpublished manuscript, 1991; J. Rudolph et al., unpublished manuscript, 1991). Water vapor mixing ratios, temperatures, and O₃ concentrations are specified from observations as a function of altitude and time of day (R. Lyra et al., unpublished manuscript, 1991). Isoprene is simulated in the same way as H₂S and DMS, i.e., by adjusting its emission rate to match the midday concentrations observed from aircraft (J. Rudolph et al., unpublished manuscript, 1991). Diurnal weighting factors $\omega(t)$ for isoprene emission are derived from the model results of *Jacob and Wofsy* [1990] for the Amazon forest and range from 0 at night to 4.7 at noon.

Measurements of NO_x made at ground level during the experiment indicate an upper limit of 2 ppb (B. Cros et al., unpublished manuscript, 1991); no NO_x measurements were made from aircraft. We estimate that sources from biomass burning would supply of the order of 0.2 ppb NO_x to the boundary layer over the forest, on the basis of the mean CO concentrations observed by J. Rudolph et al. (unpublished manuscript, 1991) and the NO_x/CO enrichment factors reported by *Andreae et al.* [1988] for biomass burning plumes over the Amazon basin. This contribution from biomass burning would be superimposed on the background NO_x concentration from soil emissions and thermal decomposition of peroxyacetyl nitrate (PAN), which we estimate at 0.2 ppb on the basis of model calculations for the Amazon forest [*Jacob and Wofsy*, 1988]. We therefore conducted model simulations with boundary layer concentrations of 0.2, 0.4, and 2 ppb NO_x, corresponding to the range of values that we think may be expected over the forest. The NO_x concentra-

tions in the model are assumed independent of altitude or time of day, but the partitioning of NO_x between its component species (NO, NO₂, NO₃, N₂O₅) is allowed to evolve as a function of the photochemical environment. Concentrations of PAN are constrained to remain in chemical equilibrium with NO_x at all times.

Photochemical rates in the model are computed at seven altitudes (60, 100, 200, 500, 1000, 1500, and 2000 m), with vertical fluxes computed at intermediate altitudes. The distributions of H₂S and DMS are determined as part of the model simulation by solution to (1). The model simulation consists in following the chemical evolution of the boundary layer over the forest during a 3-day period, corresponding to the residence time of air over the forest as inferred from trajectory analyses for the flight days [*Fontan et al.*, this issue]. Low background concentrations are assumed as initial conditions for all variable species, including <1 ppt for H₂S and DMS. Comparisons of model results with observations (Figures 1 and 3) use results from the third model day. The simulated concentrations of DMS are relatively insensitive to the choice of initial conditions because of the short lifetime of DMS (<1 day). Concentrations of H₂S are more sensitive because of the longer lifetime of H₂S (1 to 7 days depending on the NO_x levels). The fluxes of H₂S and DMS computed from the model must be viewed as upper limits to account for the possibility that high concentrations of the two species may be present upwind of the forest (in particular along the coast).

Results from the simulations with 0.2, 0.4, and 2 ppb NO_x are summarized in Table 1. Vertical profiles of OH and NO₃ concentrations at noon and midnight, respectively, are shown in Figure 4 for the simulation with 0.4 ppb NO_x. In the low NO_x simulations we find that 24-hour average H₂S and DMS fluxes of 0.6 and 0.3 nmol m⁻² min⁻¹, respectively, provide good fits to the observed aircraft concentrations (compare Figures 1 and 3). The simulation with 2 ppb NO_x requires somewhat higher fluxes (1.0 and 0.7 nmol m⁻² min⁻¹ for H₂S and DMS, respectively) in order to match the observed atmospheric concentrations, because the concentrations of OH and NO₃ increase with increasing NO_x. The emission fluxes in Table 1 do not scale linearly to the average OH and NO₃ concentrations in the boundary layer, partly because the H₂S and DMS concentrations at midday are most sensitive to the OH concentrations in the mixed layer (below 600 m) which are less dependent on NO_x levels than the boundary layer average. Also, the high emission fluxes of H₂S and DMS at midday tend to bring the atmospheric concentrations of these species out of steady state with their chemical sinks. For completeness we list in Table 1 the computed 24-hour average emission fluxes for isoprene;

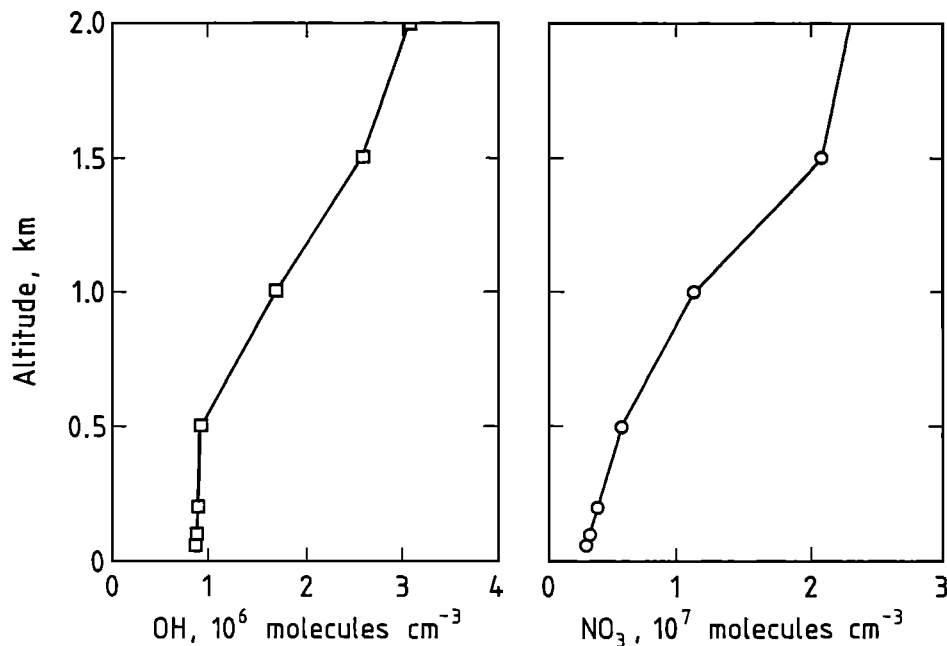


Fig. 4. Simulated vertical distribution of OH (noon) and NO₃ (midnight) in the atmosphere over the Congo rain forest.

these fluxes lie in the range 500–1200 nmol m⁻² min⁻¹, much higher than the value of 90 nmol m⁻² min⁻¹ estimated for the Amazon forest by *Jacob and Wofsy* [1990].

Our computed H₂S and DMS fluxes from the Congo rain forest can be compared to the values from the Amazon forest reported by *Andreae et al.* [1990a], which were 1.1 and 0.2 nmol m⁻² min⁻¹ for H₂S and DMS, respectively. Fluxes of reactive sulfur from the Congo rain forest are therefore of similar magnitude as those from the Amazon forest. The source of atmospheric sulfate from oxidation of H₂S and DMS over the Congo rain forest is in the range 8–26 ppt d⁻¹ (Table 1), whereas the aerosol sulfur concentrations measured during the experiment averaged 248 ppt. We conclude that biogenic sulfur emissions from the forest made only a small contribution to the aerosol sulfur budget.

Aerosol Sulfur

Total aerosol mass concentrations and abundances of crustal elements like aluminum, silicon, and iron indicate heavy loading of the atmosphere with mineral dust throughout the DECAFE 88 experiment [*Artaxo et al.*, 1990]. The concentrations of these elements in the fine and coarse mode during DECAFE 88 were 4–40 times higher than during the ABL 2A and 2B experiments in the Amazon in the dry and wet seasons [*Artaxo et al.*, 1988, 1990]. This clearly reflects that the study area is located downwind of the Earth's largest arid region during this time of the year.

During DECAFE 88 the average particulate sulfur concentration was 248 ppt, of which 156 ppt was found in the fine mode and 92 ppt in the coarse mode (Figure 5). This agrees well with the average of 227 ppt S found in the dry season at Ducke in the Amazon during ABL 2A, consisting of 181 ppt S in the fine mode and 46 ppt S in the coarse mode. Gas-to-particle conversion of SO₂ from biomass burning and

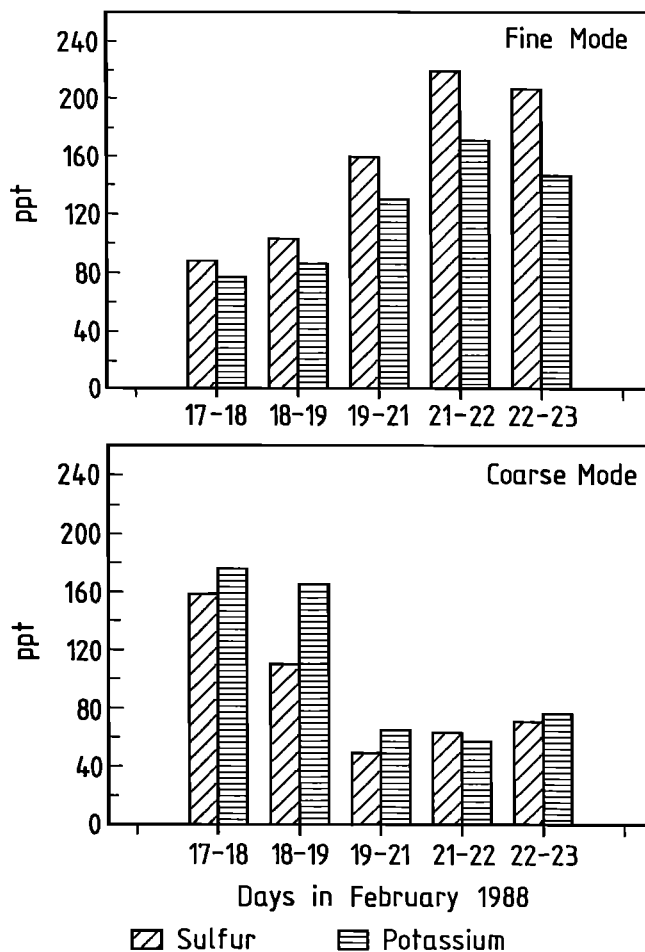


Fig. 5. Concentration of sulfur and potassium in fine and coarse mode aerosol sampled in the rain forest canopy at 5 m height.

TABLE 2. Sulfur and Potassium (ppt) in Fine Mode Aerosol From the Rain Forest Canopy During DECAFE 88 and ABLE 2A

	S	K	S _x *	K _x *	K _x /S _x	n
DECAFE 88	156	123	155	67	0.43	5
ABLE 2A	181	92	181	89	0.49	25

*Excess fractions.

long-range transport of burning-derived sulfate as well as the conversion of DMS and H₂S are likely the most substantial contributors to fine mode sulfur. The coarse mode sulfur may include a terrigenous fraction due to long-range transport. Local soil dust is unlikely to contribute substantially, since the forest soils are densely covered by several centimeters of plant debris.

Potassium, a major constituent of plants which is released both during burning [Andreae, 1983] and possibly from live plants [Beaufort et al., 1977], may serve as an indicator of pyrogenic and biogenic contributions to atmospheric aerosol. Fine mode sulfur and potassium present in excess of their terrigenous components were derived by subtracting soil-derived potassium and sulfur from the observed concentrations (Table 2), using iron as a tracer for the soil component together with Bowen's composition of crustal rock [Bowen, 1979]. Both fine particulate S and K and their excess fractions S_x and K_x agree well with the corresponding data from the Amazon dry season (Table 2). The ratio of K_x to S_x of 0.43 from DECAFE 88 is close to the 0.49 found during ABLE 2A, indicating a similar composition of the sources which contribute to their abundance in fine mode aerosol of Amazonia and of equatorial Africa.

A detailed breakdown of the contribution from individual sources, like oxidation of biogenic H₂S and DMS, biomass burning, oxidation of pyrogenic SO₂, and long-range transport, to the 248 ppt of S_x found below the forest canopy is not possible, since vertical profiles of S_x and SO₂ between the forest and mixing layer above are not available. However, a crude estimate on the potential contribution of pyrogenic sources to the particulate sulfur below the forest may be possible through a comparison of our S_x data with those predicted on the basis of emission ratios ΔS/ΔCO obtained from plume studies above the Amazon forest and the CO mixing ratios observed by us below the forest canopy during the DECAFE 88 experiment. The geometric mean emission ratio ΔS/ΔCO from flights through plumes and unpolluted boundary layer air over Amazonia was 1.04 × 10⁻³ [Andreae et al., 1988]. With 249 ppb of CO as the geometric mean of four samples from the forest site of DECAFE (J. Rudolph et al., unpublished manuscript, 1991) this calculation yields 260 ppt of particulate S below the canopy derived from burning. Provided that the emission ratio from Brazil is representative for the situation below the forest canopy during DECAFE 88, the 248 ppt particulate S sampled in the forest could be attributed to burning. This value is comparable to the 160 ppt S reported by Delmas et al. [1978] for Lamto in the savanna of the Ivory Coast, during February to April in the dry season.

In our rainwater samples from Impfondo, sulfate ranged between 5.1 and 11.9 μmol L⁻¹ (n = 5). The geometric mean of 7.4 μmol L⁻¹ is higher than the average sulfate concentration in rainwater of 4.5 μmol L⁻¹ obtained in the

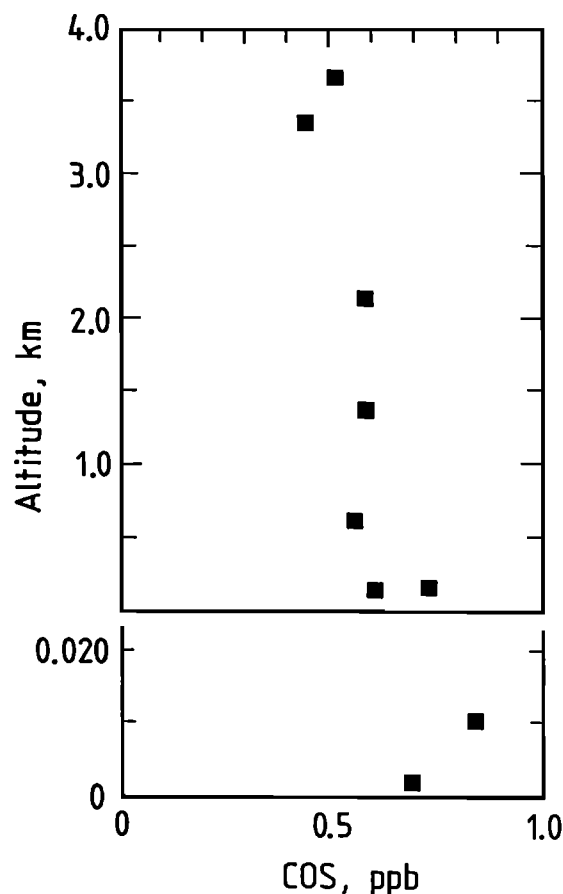


Fig. 6. Vertical distribution of COS during DECAFE 88 (composite of data from several flights and ground-based samples).

Amazon during ABLE 2A in the dry season [Andreae and Andreae, 1988]. This suggests a greater impact of biomass burning on sulfur fluxes in equatorial Africa than in Amazonia. Assuming that the observed sulfate concentration of 7.4 μmol L⁻¹ is representative of the average monthly precipitation of 63 mm for February in this region [Müller, 1982], we arrive at a wet deposition flux of 12 nmol SO₄²⁻ m⁻² min⁻¹ for dry season conditions, which is 50% higher than the wet deposition flux of sulfur reported for the dry season in the Amazon [Andreae and Andreae, 1988].

Carbonylsulfide

Unlike the sulfur compounds discussed above, COS undergoes no chemical transformations in the troposphere. Its long tropospheric lifetime of approximately 2.5 years [Khalil and Rasmussen, 1984] is reflected by a large-scale variability in its mixing ratio of only about 10–40% (relative standard deviation) around the global tropospheric background average of approximately 510 ppt [Torres et al., 1980; Johnson and Harrison, 1986; Bingemer et al., 1990; Mihalopoulos et al., 1990a]. However, small-scale variations such as seen in the vertical profiles obtained during DECAFE 88 can help to identify sources, sinks, and the direction of net fluxes. Our COS profile from northern Congo (Figure 6), which compiles the data from six individual flights, shows mixing ratios above the 500 ppt background concentration from ground level up to 2.5 km. About 600 ppt were found in the layer between 600 and 2500 m, which carried the bulk of biomass

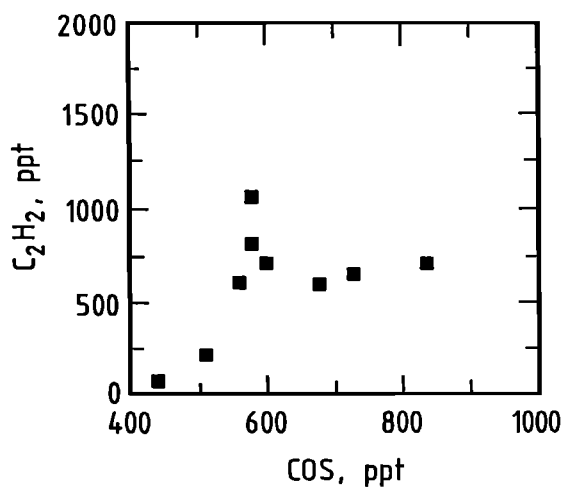


Fig. 7. Scatter plot of atmospheric COS against acetylene (both COS and C₂H₂ analyzed from the same can samples).

burning products according to the profiles of CO, hydrocarbons, and aerosols [Andreae *et al.*, this issue; J. Rudolph *et al.*, unpublished manuscript, 1991]. Above this layer, COS approaches the global background of 500 ppt. From ground level up to 100 m, mixing ratios even higher than 600 ppt were found. The overall structure of the profile downward to the canopy presents no evidence for the significant sink function of the plant canopy for atmospheric COS which had been suggested by other authors [Goldan *et al.*, 1988; Brown and Bell, 1986; Mihalopoulos *et al.*, 1990b]. However, any effect of COS uptake by the canopy on the gradient of COS toward this sink may have been compensated by COS from biomass burning. This view is supported by the concentration of particulate sulfur below the canopy, which can largely be attributed to biomass burning emissions.

The relationship of atmospheric COS to other gases of known pyrogenic origin, such as acetylene [Ehhalt *et al.*, 1986] and CO₂, is of special interest. Nguyen *et al.* [1990], sampling the plumes of African savanna fires, previously demonstrated the role of fires as a source of COS by its correlation with atmospheric acetylene. In the canister samples from DECAFE 88, acetylene has been analyzed by B. Bonsang *et al.* (unpublished manuscript, 1991). The regression between COS and acetylene (Figure 7) yields a correlation coefficient of $R = 0.43$. Because of the small number of samples ($n = 9$) this correlation is not significant and allows no firm conclusion about the role of fires as a source of COS from these data.

Emission factors for COS in plumes, relating its excess above the background of the free troposphere to that of CO₂, could be derived only for the flight on February 20, 1988, from which simultaneous data on COS and CO₂ in and above the boundary layer exist (Table 3). CO₂ was measured from air collected in stainless steel canisters by J. Rudolph *et al.* (unpublished manuscript, 1991). The COS emission factors of 6×10^{-6} and 42×10^{-6} agree reasonably well with those of $5\text{--}29 \times 10^{-6}$ reported from forest fires in Colorado [Crutzen *et al.*, 1979] and $1.5\text{--}15 \times 10^{-6}$ obtained from Brazil [Crutzen *et al.*, 1985], supporting the view of burning as a source of this gas.

TABLE 3. COS and CO₂ Mixing Ratios and Emission Factors During Flight, February 20, 1988

	Altitude, m	COS, ppt	CO ₂ , ppm	$\Delta\text{COS}/\Delta\text{CO}_2$
Boundary layer	150	600	354.3	6.1×10^{-6}
Boundary layer	1370	580	341.3	41×10^{-6}
Free Troposphere	3660	510	339.6	

CONCLUSIONS

The vertical profiles of the short-lived sulfur species H₂S and DMS from the ground level up to the free troposphere are both in their structure and numerical values remarkably similar to those found over Amazonia during the dry season. Thus no evidence of drastic differences in the cycling of biogenic sulfur between the equatorial forest ecosystems of South America and those of Africa could be demonstrated. Airborne particulate sulfur and rainwater sulfate were found to be slightly higher than during the Amazon's dry season, most likely due to a substantial contribution to the abundance of the longer-lived sulfur species SO₄⁻ and SO₂ by burning activities in the vast arid regions north of equatorial Africa. This might explain some of the discrepancies which currently exist between the high sulfur deposition fluxes reported from equatorial Africa [Delmas and Servant, 1983] and recent estimates for equatorial South America [Andreae and Andreae, 1988; Andreae *et al.*, 1990a]. On the basis of the vertical distribution of COS and its relationship to other gases derived from burning, a substantial contribution of biomass burning to the abundance of atmospheric COS appears likely. Our data set shows no obvious evidence for uptake of COS through the plant canopy, probably because COS emissions from fires mask any effect of sinks on the vertical profile.

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