

Reduced sulfur compound exchange between the atmosphere and tropical tree species in southern Cameroon

JÜRGEN KESSELMEIER, FRANZ X. MEIXNER,
UWE HOFMANN, AYITÉ-LÔ AJAVON, STEPHAN LEIMBACH &
MEINRAT O. ANDREAE

Max Planck Institute for Chemistry, Biogeochemistry Department, PO Box 3060, D-55020 Mainz, Germany

Received 18 May 1993; accepted 9 September 1993

Key words: atmosphere, canopy top, carbonyl sulfide (COS), dimethyl sulfide (DMS), photosynthesis, reduced sulfur compounds, trace gas exchange, tropical rainforest, vegetation

Abstract. We measured the concentrations of reduced sulfur compounds in the atmospheric boundary layer over an equatorial African rain forest. Results obtained from a dirigible hot air balloon and a tethered balloon system in the early morning hours reflect a multilayered structure of the atmospheric boundary layer with gradients of COS and CS₂ indicating an uptake/production of these trace gases by the soil/vegetation system. In addition, we studied emission and deposition fluxes of volatile reduced sulfur compounds from tropical tree species using cuvettes to directly measure the exchange behavior of tree twigs. These cuvettes were operated at young trees in a forest clearing near ground level as well as at a mature tree species on top of the forest canopy, employing a specially designed tree top jungle raft ('Treetop Raft III, Dirigible version') placed on the canopy crown. The results show qualitative and quantitative disparities between different tree species as well as between individuals of the same species near ground level (young) and at the top of the canopy (mature). We found some correlations between photosynthetic CO₂ assimilation and emission of sulfur compounds. Comparison between measurements at the ground and at the canopy top show that the studied tree species adapts its photosynthetic CO₂ assimilation in response to the climatic conditions at the canopy top. This is accompanied by a quantitative change in trace gas emission. Lower CO₂ fixation rates are accompanied by an increase in the emission of reduced sulfur compounds. We propose the increase of DMS emission at the canopy top to be explained by a potential demand of nitrogen in the foliage resulting in an accumulation of sulfur.

Introduction

There is a continuous exchange of sulfur compounds between the biosphere and the atmosphere, both through emission and deposition. Estimates of the natural emissions range between 34 and 83 Tg (s) a⁻¹ (Andreae & Jaeschke 1992), a flux which is roughly equivalent to the

70–100 Tg (s) a^{-1} from man-made sulfur emissions. However, considerable uncertainty remains attached to these estimates (Kesselmeier 1991). Emissions of carbonyl sulfide (COS), carbon disulfide (CS_2), dimethyl sulfide (CH_3SCH_3 , DMS), methyl mercaptan (CH_3SH), and hydrogen sulfide (H_2S) from vegetation have been reported (c.f. Andreae 1985; Rennenberg 1991; Andreae & Jaeschke 1992). The volatile sulfur emissions from terrestrial plants are globally in the range of 7.4 Tg (s) a^{-1} (Filner et al. 1984) and 54 Tg (s) a^{-1} (Winner et al. 1981). According to a recent review by Andreae & Jaeschke (1992) the sulfur emission estimates from the entire soil/plant system range between 4 and 15 Tg (s) a^{-1} , of which tropical forests are responsible for 0.23–0.76 Tg (s) a^{-1} . Deposition of sulfur results mainly from the dry and wet deposition of sulfur dioxide, sulfuric acid, sulfate and methane sulfonate produced from reduced sulfur compounds through oxidation processes (Saltzman et al. 1986; Andreae & Andreae 1988; Andreae et al. 1990). Besides this deposition, a considerable uptake of carbonyl sulfide by vegetation has been reported (Taylor et al. 1983; Brown & Bell 1986; Brown et al. 1986; Goldan et al. 1987, 1988; Fall et al. 1988; Mihalopoulos et al. 1989; Berresheim & Vulcan 1992). A recent review on the exchange of COS and CS_2 describes our knowledge on the behaviour of these two sulfur gases and stresses the importance of the vegetation as a sink for COS (Chin & Davis 1993). Physiological studies point to enzymes of the CO_2 assimilation pathway being responsible for the uptake and consumption of COS in higher plants and algae (Protoschill-Krebs 1991; Protoschill-Krebs & Kesselmeier 1992).

During the 'Radeau des Cimes — Fondation ELF, Afrique 91' mission, the concentrations of reduced sulfur compounds in the atmospheric boundary layer over an equatorial African rain forest were investigated. We employed a dirigible hot air balloon and a specially designed mobile platform (Treetop Raft III, Dirigible version) which was placed on the top of the canopy to perform the measurements. In addition to vertical concentration measurements, emission and deposition fluxes of volatile reduced sulfur compounds from tropical tree species were studied with the help of cuvettes. These were employed near ground level on two young tree species at the edge of a forest clearing and on a twig of one mature species at the canopy top accessed from the mobile platform. This allowed a comparison between the gas exchange behavior of young tree twigs at ground level with that of mature twigs at the canopy top.

Materials and methods

Season, location and plant material

The experiments were performed at the end of the wet season from 11 November to 23 November 1991 in the wildlife reserve 'Reserve de Campo' (2.15–2.88°N, 9.8–10.38°E) in southern Cameroon (Equatorial Africa). The camp and the experimental site (2.622°N, 9.907°E) was located ≈ 10 km east of the coastline of the Atlantic ocean. The site position relative to the location of the Intertropical Convergence Zone (ITCZ) and the close vicinity of the site to the Atlantic ocean defined the general air flow pattern for this region. Between November 17–23, 1991, the ground track of the ITCZ (northern branch) was oriented more or less zonally at 5–15°N (DWD 1991). Therefore, the region of the South-Cameroon rainforest was seasonally part of the so-called 'transition zone' of surface winds separating the south-east trade winds (south of 5°S) from the 'equatorial westerlies' associated with the northern ITCZ (see Riehl 1979). The general south-westerly flow was modulated by a pronounced local land-sea breeze system (Kesselmeier et al. 1992). To characterize the local micrometeorological environment, relevant data on photosynthetic active radiation (PAR), air temperature and relative humidity during our sampling periods in close vicinity to the chamber are shown in Fig. 1. All data presented are 10 min averages.

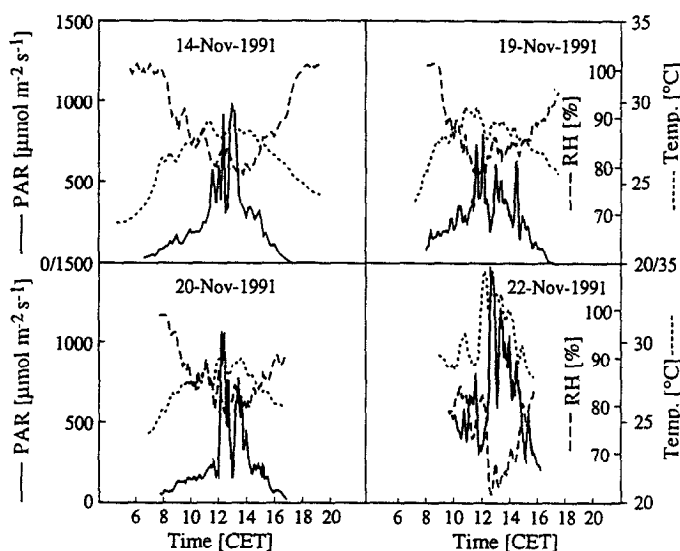


Fig. 1. Variation in photosynthetic active radiation (PAR, $\mu\text{mol photons m}^{-2} \text{s}^{-1}$), air temperature (°C) and relative humidity (%), Reserve de Campo, Cameroon, 14, 19, 20 Nov. 1991 (ground level, forest clearing) and 22 Nov. 1991 (canopy top).

The Campo National Reserve is covered by a lowland tropical rain-forest. The most common tree species were *Sacoglottis gabonensis* and *Dialium pachyphyllum*. *Sacoglottis* is relatively widespread in the rain forests of Western Africa. For a more detailed botanical description see Lösch & Kazda (1992) and Kazda & Lösch (1992). For the emission and deposition studies of reduced sulfur compounds, an example of two tree species were investigated. A pioneer tree, *Porterandia cladantha* (K. Schum.) Keay (Rubiaceae, Gardenieae; Herbarium Montpellier, France, No. FH4261) was growing at the edge of a forest clearing, which was a transition zone to an abandoned shifting cultivation area. This individual was analyzed by enclosing a twig approximately 2–3 m above ground (in the following 'near ground level'). The total height of the tree was around 6 m. We estimated the age between 4–8 years. The second species, *Sacoglottis gabonensis* (Humiriaceae), was investigated at the same site near ground level enclosing a branch of a young tree (estimated age between 4–8 years; height ca 7 m. In addition, an adult *Sacoglottis* tree (aged 30–50 years; height 45–50 m) in the middle of the forest was studied from a mobile platform (tree top raft) deposited on the canopy at a height of ca 45 m. Thus, we measured two individual *Sacoglottis* species, which, in addition to their age, were adapted to different local environments, and thus were of different developmental stage and height. Vertical profiles of trace gases obtained using a hot air dirigible supplemented the data obtained from the cuvette studies.

Plant cuvette

To measure the exchange of reduced sulfur compounds, a dynamic cuvette enclosed an intact twig of a living tree and was flushed with ambient air. The cuvette, a dynamic flow system, consisted of a PVC frame supporting a teflon bag (ID 30 cm; length 60 cm) from the outside. Previous studies with this cuvette system (Schäfer et al. 1992) showed that the teflon film (FEP) is fully light permeable in the spectral range tested (300–900 nm). We found no sulfur loss or emission due to adsorption or desorption from the cuvette material. Total air flow through the cuvette was of the order of 8 liters min^{-1} . Air samples for CO_2 and sulfur measurement were taken at the inlet and the outlet of the cuvette. Exchange was calculated from the difference between the inlet and outlet concentrations in relation to the photosynthetic CO_2 assimilation of the enclosed twig.

Determination of sulfur compounds and CO₂ assimilation

Air samples were taken in silanized glass vessels (250 ml) and transferred within 10 hours to cryo traps immersed in liquid nitrogen. Helium at a flow of 500 ml/min was used as the transfer gas to prevent the trapping of oxygen during transfer from the glass vessels to the cryo traps. The samples were analyzed by GC/FPD for carbonyl sulfide (COS), carbon disulfide (CS₂), dimethyl sulfide (CH₃SCH₃, DMS), methyl mercaptan (CH₃SH), and hydrogen sulfide (H₂S). For details of the analysis technique see Hofmann et al. (1992a). Though the collection efficiencies for all sulfur compounds are 100% (Hofmann et al. 1992a), due to the small volume of air sampled, the detection limits were 20 pptv (H₂S), 15 pptv (COS), 20 pptv (CH₃SH), 15 pptv (DMS) and 10 pptv (CS₂). Photosynthetic CO₂ assimilation was measured with a NDIR instrument (LICOR CO₂ analyser, model LI-6252).

Tethered balloon sounding system

From the launching square of the dirigible hot air balloon in a forest clearing, the tethered balloon system was launched and usually flew up to 0.5 km altitude. The tethered balloon sounding system (A.I.R. Inc., model TS-1A-1 Tethersonde™) consisted of a blimp-shaped balloon filled with helium, a (micro-) meteorological package, and an electrochemical ozone sensor (ECC ozonesonde, model 4A). Wind direction was recorded by electronic readout of a magnetic compass, wind speed by a cup anemometer, dry and wet bulb temperature by aspirated thermistors, and (relative) barometric pressure by an hybrid integrated circuit. Sensors of the meteorological and the ozone sonde were powered by airborne NiCd batteries, signals were serial time-multiplexed and transmitted by audio frequencies (3kHz ± 7.5%) to the ground receiving system. Altitude and speed control of ascent/descent of the balloon system was maintained by a powered winch allowing soundings up to 1000 m above ground with a typical ascent rate of 0.25 m/s. The cup anemometer was calibrated before and after the experiment in a windtunnel, dry and wet bulb temperature sensors were controlled in-situ (ground level, at least twice a day) by an hand-held Assmann-type psychrometer. Reagent solutions (Potassium iodide, KI) of the ozone sonde were prepared on the site. Several times a day the response time and the calibration of the ozone sonde were checked by means of an ozone generator/analysator (DASIBI, model 1008-RS).

Results and discussion

Measurements from a dirigible hot air balloon

Using an NDIR instrument (LICOR CO₂ analyser) on board of a dirigible hot air balloon, we were able to repeatedly trace the CO₂ mixing ratio from an altitude of 450 m to ground level (forest clearing) during the early morning hours. Unfortunately, it was not possible to continue measurements with the hot air dirigible later during the day due to flight safety considerations. Such experiments would have allowed rough integral estimates of trace gas exchange. Air samples were taken during ascent and/or descent against the prevailing wind 10 m below the balloon via a PTFE-tube. In Fig. 2 the vertical CO₂ distribution measured during ascent and descent on November 10, 07:23h–08:25h is shown. As expected for this time of the day, high CO₂ mixing ratios (420 and 490 ppmv, respectively) were encountered at ground level. At 60 m a strong decrease to \approx 390 ppmv was observed. Only a minor decrease to 360 ppmv was found between 60 m and 230 m. The decrease in the CO₂ mixing ratios at ground level between the take-off and the touch-down of the hot air balloon is of particular interest. During the intervening hour, the CO₂ mixing ratio decreased from 490 ppmv to 420 ppmv. This drop in the CO₂ mixing ratio may, to some minor extent, be due to turbulent mixing

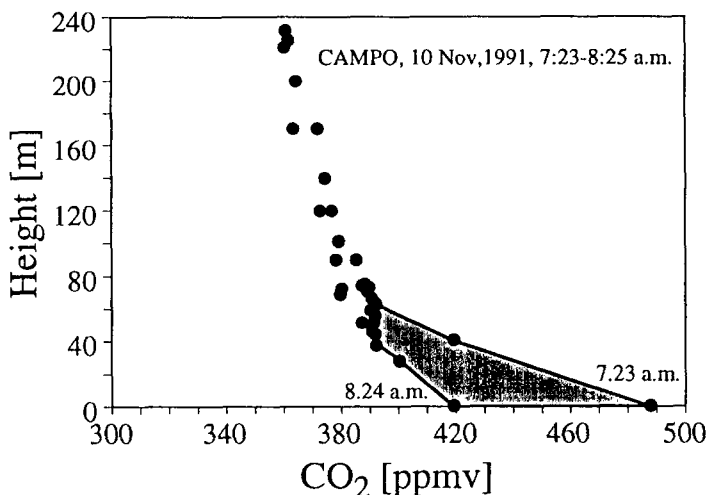


Fig. 2. Carbon dioxide profile measured during dirigible hot air balloon ascent/descent in the early morning hours (07:23h–08:25h), November 10, 1991. Note the decrease of CO₂ mixing ratio at ground level (forest clearing) between take-off and touch-down.

which slowly starts after sunrise, but it mainly reflects the photosynthetic activity of the vegetation.

Vertical profiles of COS, CS₂, DMS and CO₂ over the rainforest were obtained during another flight (November 22, 1991) with the dirigible hot air balloon during a descent from 500 m (above ground) down to the launching square in the forest clearing (70 m above sea level). Cruising area of the hot air balloon was within 2 km of the camp. While CO₂ mixing ratio was measured online, discontinuous sampling of sulfur compounds (sampling interval 20 s) integrated over an altitude range of ca 10–15 m. For this particular descent mixing ratios versus altitude (above ground) are shown in the centre part of Fig. 3. Below 300 m DMS mixing ratio was below the corresponding detection limit (15 pptv). H₂S and CH₃SH atmospheric concentrations were always below the detection limit. Mixing ratios of the other trace gases are characterized by individual sequences of vertical increase, constancy and decrease, respectively. However, examining the structures of the individual vertical profiles more closely reveals the common existence of three different layers:

Layer 1, canopy level (35–50 m) to 85 m: COS mixing ratio is increasing from 480 to >550 pptv, CO₂ and CS₂ mixing ratios are decreasing (465 to 420 ppm, and 89 to <80 pptv, respectively),

Layer 2, 85 m to ≈ 300 m: there is only a small further vertical increase of COS (540 to 590 pptv); both, the CO₂ and the CS₂ mixing ratio reveal a sudden drop at 85 m (420 to 395 ppmv, and ≈ 80 to 55 pptv, respectively) followed by a small further decrease only (CO₂: 395 to 375 ppmv, CS₂: ≈ 55 to ≈ 45 pptv).

Layer 3, > 300 m: while the CO₂ mixing ratio seems to remain constant with altitude, both, the COS and the CS₂ mixing ratio increase to 695 pptv and 110 pptv at 430 m. Within this layer we detected DMS with mixing ratios above the detection limit of 15 pptv, which we interpret to be of maritime origin.

The existence of distinct layers (of limited thickness) in the atmosphere generally points to corresponding air masses of individual character. Close to the earth's surface, in the Atmospheric Boundary layer (ABL), this is mainly due to different exchange and/or transport processes. The close vicinity of the site to the ocean certainly has determined the multi-layered structure of the ABL as known for the trade wind zone over tropical oceans. According to Augstein (1979) the region below the trade wind inversion is subdivided in the surface layer ('SFL', 50–150 m deep), the following subcloud ('mixed') layer ('SCL', 100–400 m deep), and the uppermost cloud layer ('CL', 500–800 m deep) which is topped by the trade wind inversion. The three transitions (SFL/SCL, SCL/CL, CL/free

troposphere) are usually marked by discontinuities in air temperature and specific humidity and consequently in most trace substances.

The existence of a multilayered ABL structure over the rainforest may be demonstrated by the results of our vertical soundings of a tethered balloon system (for details, see Kesselmeier et al. 1992). The left and right part of Fig. 3 gives the vertical profiles of wind direction, air temperature, specific humidity, and ozone mixing ratio measured approx. 100 minutes before and after the hot air balloon descent. As shown in the left part of Fig. 3, the top of the nocturnal SFL over the rainforest canopy may be found at 86 (± 15) m, marked by a pronounced discontinuity of the vertical profile of specific humidity and air temperature. The following vertical constancy of specific humidity (and ozone mixing ratio) is typical for the tropical SCL and CL (see Augstein 1979), which may be topped at 239 (± 28) m, defined by the discontinuities of specific humidity, ozone mixing ratio and air temperature. It should be noted, that during these early morning hours, when cloud condensation starts immediately above the canopy of the rainforest, the SCL and CL are more or less amalga-

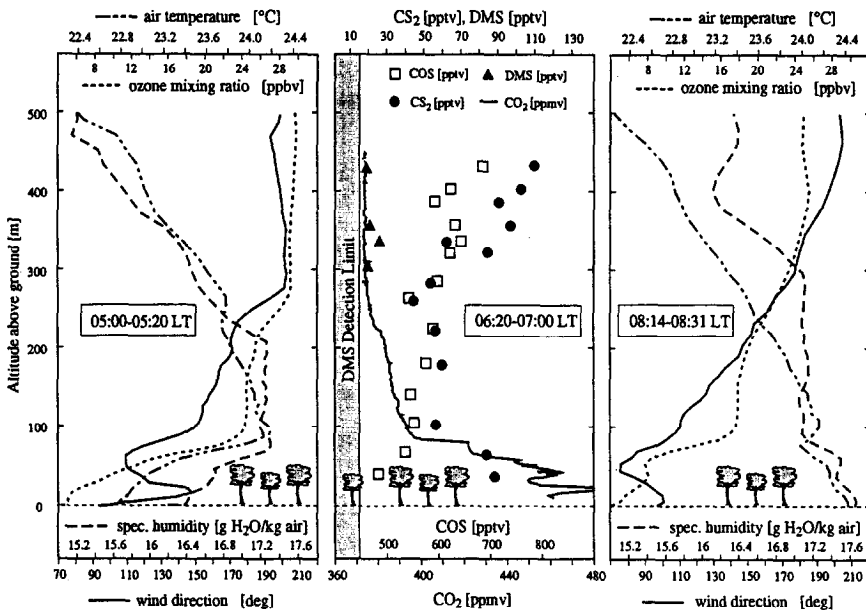


Fig. 3. Vertical profiles of air temperature, wind direction, ozone mixing ratio and specific humidity measured with the tethered balloon system before (05:00h–05:20h, left part) and after (08:14–08:31, right part) the hot air balloon descent. The centre part shows the vertical profiles of CO_2 , COS, CS_2 and DMS during the descent of the dirigible hot air balloon from 450 m a.g.l. to ground level (forest clearing) in the early morning (06:20h–07:00h, local time) on 22 Nov. 1991.

mated to one layer of uniform character. Decreasing specific humidity marks the following cloud-free layer which shows remarkably constant ozone mixing ratio and wind direction. The ceiling of the tethered balloon sounding was certainly much below the trade wind inversion (presumably 800–1000 m). The second sounding (Fig. 3, right part), which was performed 2 hours after sunrise, may define the transition between SFL and SCL/CL at $82 (\pm 23)$ m, and that between SCL/CL and the cloud-free layer at $346 (\pm 43)$ m by identical criteria as for the early morning sounding. Unfortunately, due to a data acquisition failure we have no tethered balloon data simultaneously to the hot air balloon descent. If we assume, for a first approximation, a temporally linear shift of the identified transitions, we may end at $84 (\pm 19)$ m for the top of the SFC, and at $293 (\pm 36)$ m for the top of the SCL/CL during the descent of the hot air balloon. These values deduced mainly from meteorological quantities agree considerably with those estimated from examination of the vertical profiles of the trace gases only.

The described SCL/CL is the nocturnal residual of an entirely mixed layer extending from canopy level to > 500 m as observed in the afternoon of the day before by our continued soundings of the tethered balloon system from November 21, 11:20 LT to November 22, 04:40 LT (data not shown here). Therefore, average COS and CS₂ mixing ratios of 568 ppt and 52 ppt (as deduced from corresponding mixing ratios in the early morning SCL/CL) may be considered to be those determined by the exchange between the rainforest and the boundary layer during daytime including anthropogenic sources, which can not totally be ruled out, and assuming that there are no atmospheric sources/sinks due to chemical reactions in the SCL during the night. The decrease of COS mixing ratio and the increase of CS₂ mixing ratio in the SFL relative to that in the SCL/CL (see Fig. 3) could then be interpreted as consequences of corresponding nocturnal COS removal and CS₂ production processes, respectively.

Mixing ratios of reduced sulfur compounds at the ground (forest clearing) and at the top of the canopy

The exchange of trace gases is influenced by the ambient concentration of the compounds (Kesselmeier & Merk 1993). As we used ambient air for flushing the cuvette, we present the data on the mixing ratios of reduced sulfur compounds at the ground level and at the canopy top during our experiments, measured at the inlet of the cuvette (Fig. 4). The data for H₂S, CH₃SH and CS₂ are well within the ranges often observed (Andreae & Andreae 1988; Andreae et al. 1990; Berresheim & Vulcan 1992;

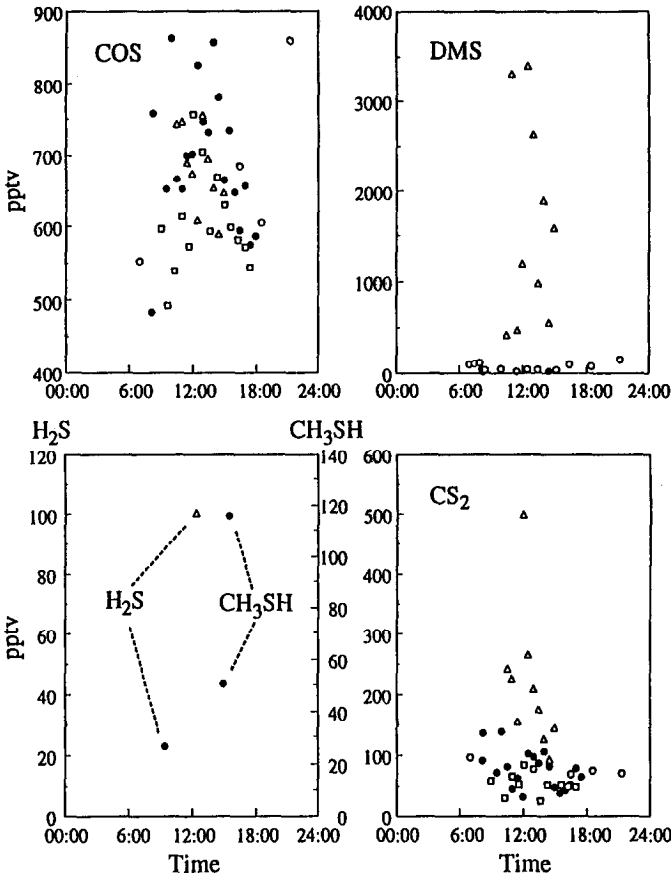


Fig. 4. Concentrations of reduced sulfur compounds in ambient air measured at the cuvette inlet at ground level (14–20 Nov. 1991, forest clearing) and at the top of the canopy (22 Nov. 1991). ○ Nov 14; ● Nov 19; □ Nov 20; △ Nov 22.

Berresheim 1993; Warneck 1988). COS shows an increase from 500 pptv to a maximum around 850 pptv observed at noon and then a subsequent decrease to 550 pptv. Such enormous fluctuations during the day with even higher maxima around noon have also been observed over wheat fields in temperate regions (Hofmann et al. 1992b) and are interpreted to result from a turbulent transport from aloft. DMS measurements at the ground level revealed concentrations between 20 and 160 pptv, however measurements at the canopy top in the air between the tree tops in the direct vicinity of *Sacoglottis* twigs showed very high values up to 3.5 ppbv. CS₂ exhibits a similar pattern as found with DMS, a behaviour which is not understood, whereas the high DMS levels can be explained by the high DMS emission rates of *Sacoglottis* (see next chapter). In contrast to

these high values are the low DMS concentrations (below or just above the detection limit of 15 pptv) in the atmosphere over the forest measured during the hot air balloon ascent (Fig. 3). We assume dilution by turbulent mixing mostly to be responsible for this gradient.

Reduced sulfur compounds and carbon dioxide exchange between vegetation and the atmosphere: Cuvette measurements at the canopy top in comparison to ground (forest clearing) measurements

As shown in Table 1, the tree species investigated show different exchange behaviours. Deposition of COS and CS₂ to both plant species was observed. However, *Porterandia* was found to emit significant amounts of methyl mercaptan in addition to DMS, CS₂, H₂S and COS, whereas only the latter four species were emitted by *Sacoglottis*. A qualitative difference was also observed between the emission from the younger *Sacoglottis* tree

Table 1. Exchange of reduced sulfur compounds in relation to CO₂ assimilation [pmol S-compound per μ mol CO₂ assimilated].

	----- Deposition -----				----- Emission -----			
	AVG	MIN	MAX	<i>n</i>	AVG	MIN	MAX	<i>n</i>
<i>Sacoglottis gabonensis</i> (measured at ground level; height of the tree ca 7 m)								
DMS	n.o.	—	—	—	15.6	0.5	37.5	25
CS ₂	-0.8	-0.03	-1.8	9	2.1	0.02	11.4	15
COS	-3.8	-0.3	-23.4	13	6.5	0.1	21.0	11
H ₂ S	n.o.	—	—	—	n.o.	—	—	—
CH ₃ SH	n.o.	—	—	—	n.o.	—	—	—
<i>Sacoglottis gabonensis</i> (measured at canopy top, height of the tree ca 45 m)								
DMS	n.o.	—	—	—	709	5.3	2374	12
CS ₂	-13	-0.4	-27.7	9	1.9	0.2	3.5	2
COS	-14.4	-0.8	-38.4	10	3.2	1.5	4.9	2
H ₂ S	n.o.	—	—	—	20.9	16.2	25.7	2
CH ₃ SH	n.o.	—	—	—	n.o.	—	—	—
<i>Porterandia cladantha</i> (measured at ground level; height of the tree height ca 6 m)								
DMS	-0.2	-0.2	-0.2	1	0.9	0.4	4.4	17
CS ₂	-0.4	-0.02	-1.2	10	1.2	0.08	7.3	8
COS	-1.7	-0.14	-6.0	12	1.6	0.4	2.2	7
H ₂ S	n.o.	—	—	—	1.6	0.9	2.6	8
CH ₃ SH	n.o.	—	—	—	2.7	0.4	4.3	15

S-exchange is given as actual emission/deposition on a 10 minute average of CO₂ assimilation; *n* = number of observations; n.o. = not observed.

located at the forest edge near the camp and emissions from an adult tree at the canopy top. *Sacoglottis* twigs investigated at the top of the canopy were found to emit H_2S , whereas this S-species was not emitted from the younger tree. Of special interest is that CS_2 and COS are both deposited and emitted by the trees. COS deposition caused by uptake (metabolization) of COS is a process which has been recently explained (Protoschill-Krebs 1991; Protoschill-Krebs & Kesselmeier 1992). On the other hand, the deposition of CS_2 and especially the emission of CS_2 and COS are, as yet, not understood and can only speculatively be linked with photochemical COS production, amino acid degradation or microbial activity in leaves.

The differences between the measurements at ground level in comparison with those at the canopy top become even more pronounced when we compare quantitatively the exchange behaviour of the examined trees. Data in Table 1 have been processed on a photosynthetic basis, i.e. they show the amount of sulfur compounds emitted by or deposited to the twig as pmol per $\mu\text{mol CO}_2$ assimilated by the leaves. These data show the pioneer tree *Porterandia* to be a tremendous methyl mercaptan emitter, though emissions of all other compounds were found as well. *Sacoglottis*, however, seems to be a prolific DMS emitter, especially at the top of the canopy with maximum values around 2.4 nmol DMS emitted per $\mu\text{mol CO}_2$ assimilated. These values are consistent with our observations of relatively high DMS concentrations of up to 3 ppbv in the air between the tree crowns in the direct vicinity of *Sacoglottis* twigs. Furthermore, *Sacoglottis* emitted H_2S from the older twigs at the canopy top but not from those younger twigs at the ground level. These examples demonstrate that it is important to measure the exchange of reduced sulfur compounds at the top of the canopy as this is the most active exchange site in the forest, an observation which is highlighted by the data on photosynthesis (Fig. 5, Table 2). *Sacoglottis* typically shows light saturation around 300 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ for CO_2 assimilation at the ground level; however, even at levels as high as 1400 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ light saturation was never reached by the twig at the top of the canopy (Fig. 5). This result indicates the ability of this tropical tree species to adapt to disparate environments (i.e. canopy top). We were not able to measure at the ground and at the canopy top at the same time. However, at least for the ground measurements there is a data set covering a period of three days. For the canopy top only one day is available. We basically cannot rule out that the temporal component is not important, however, the difference for DMS between ground and canopy top is so striking, that we believe that the temporal component is of minor importance.

How can we explain this emission/deposition behaviour of plants? The

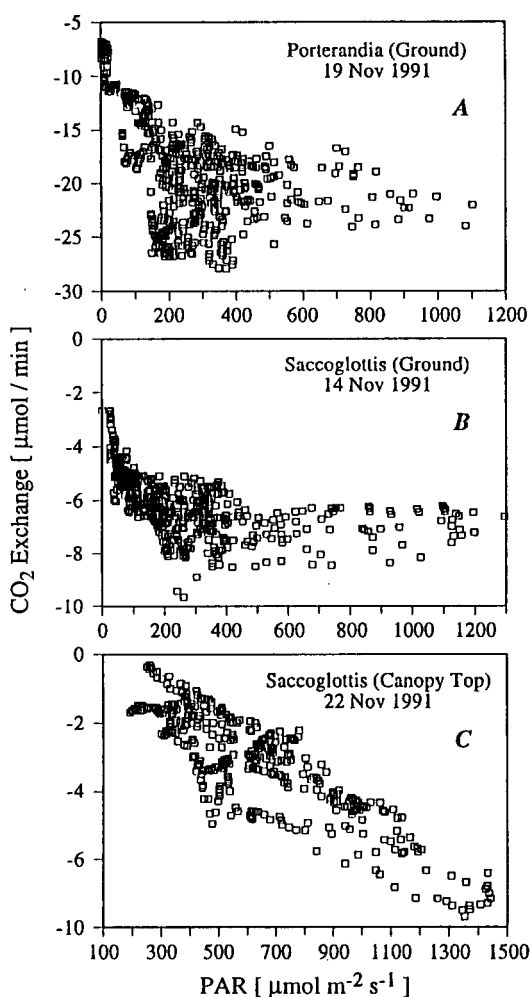


Fig. 5. Light dependent CO₂ assimilation (a) of *Porterandia*, (b) *Sacoglottis* at ground level (forest clearing), and (c) *Sacoglottis* at the canopy top. Note light saturation at the ground (a/b) and continuing increase of the CO₂ assimilation with light intensity at the canopy top (c).

metabolic pathways leading to the production and emission of COS and CS₂ have not yet been identified in plants nor in microorganisms. Methyl mercaptan emission may be assumed to be due to methionine degradation (Schwenn et al. 1983; Schmidt et al. 1985). Some salt marsh species of higher plants possess dimethyl sulfoniopropionic acid (Larher et al. 1977; Reed 1983; van Diggelen et al. 1986; Dacey et al. 1987), the biological precursor for DMS, and thus may emit DMS. Whether this ability may be

Table 2. Daily averages of photosynthetic carbon fixation and sulfur emission per m² leaf or ground area and hour (Reserve de Campo, Cameroon, Nov. 1991).

	----- Leaf area basis -----		----- Ground area basis* -----	
	$\mu\text{mol CO}_2 \text{ m}^{-2} \text{ h}^{-1}$	$\text{nmol S m}^{-2} \text{ h}^{-1}$	$\text{mmol CO}_2 \text{ m}^{-2} \text{ h}^{-1}$	$\text{nmol S m}^{-2} \text{ h}^{-1}$
	fixed	emitted	fixed	emitted
Sacoglottis gab. forest edge at ground level [§]	369/654	12.1/33.5	2.95/5.23	96.8/268
Sacoglottis gab. in the forest canopy top (45 m) ^{§§}	130	267	1.04	2136
Porterandia clad. forest edge near ground ^{§§}	1221	14.9	9.77	119

[§] 2 days of measurement. ^{§§} 1 day of measurement. * Leaf Area Index (LAI) = 8.

attributed to all higher plants, is uncertain. In addition we are only able to extrapolate knowledge on DMS production in bacteria and algae to higher plants (see Warneck 1988). The emission of H_2S had been explained although some uncertainties remain (Rennenberg 1991) and the H_2S uptake may be assumed to be linked closely to the pathways discussed for the emission of H_2S . The uptake of COS by the carboxylating enzymes and the carbonic anhydrase has recently been demonstrated by Protoschill-Krebs & Kesselmeier (1992). During our measurements, COS exchange showed a poor correlation to CO_2 assimilation (Fig. 6). Only under conditions which favour high photosynthetic activity (see *Porterandia* Fig. 6) we found some relation between CO_2 assimilation and COS uptake. Limited CO_2 assimilation, however, was often accompanied by an emission of COS. In contrast to the uptake of COS, the emission is not understood. A COS production process might mimic the consumption of COS and as long as we do not understand both processes we cannot interpret the observed exchange behaviour. DMS emissions from *Porterandia* and *Sacoglottis* seem to correlate with light, temperature and photosynthetic

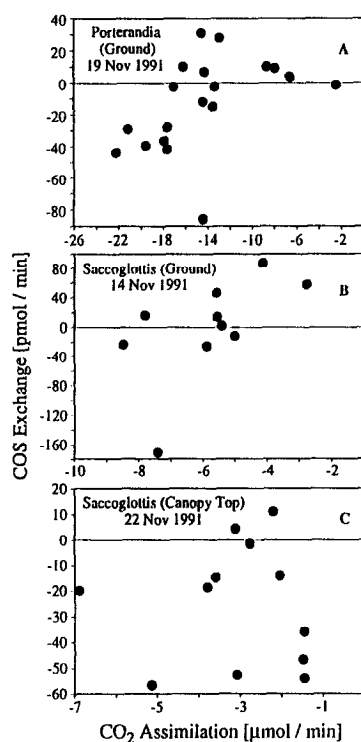


Fig. 6. Correlation of COS exchange with CO_2 assimilation. (a) *Porterandia*, (b) *Sacoglottis* at ground level (forest clearing) and (c) *Sacoglottis* at the canopy top.

CO₂ assimilation (Figs. 7, 8). However, a close relation between DMS emission and photosynthesis is not certain. Similar correlations were found between the emission of methyl mercaptan and photosynthesis in the case of *Porterandia* (Fig. 9). These correlations are not understood and expose our lack of understanding of the metabolic background.

Flux calculations for tropical rainforests

Though our data are limited by both the number of experiments and tree species investigated, we assess our values in comparison to recently published data. A comparison between our data on photosynthetic CO₂ assimilation of the tree species investigated and those found in the literature for tropical rainforests should offer some insight into the reliability of our cuvette measurements. Introducing an average leaf area index (LAI) of 8 for tropical rainforests (Whittaker & Likens 1975) we can extrapolate our leaf area based data to a ground area basis. Thus, our deposition flux estimates (Table 2) range between 1 and 10 mmol CO₂ m⁻² h⁻¹ on a ground area basis and are comparable to CO₂ deposition around 37 mmol

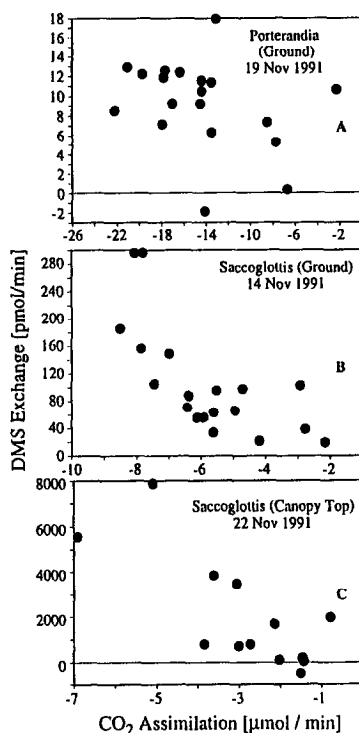


Fig. 7. Relation between DMS emission and photosynthesis.

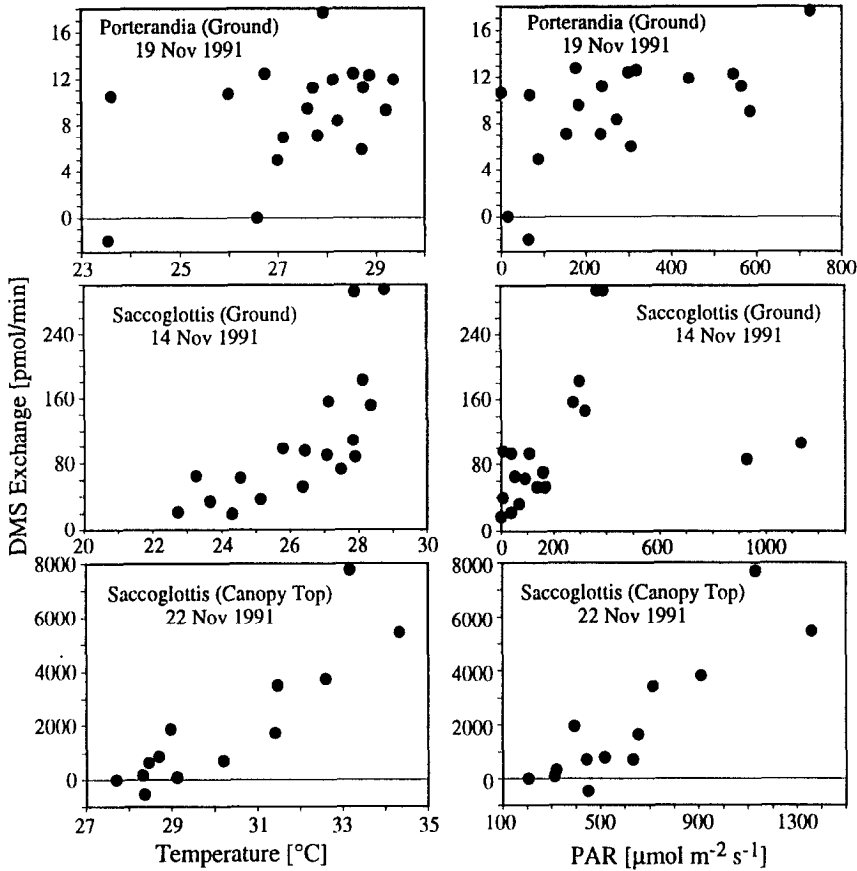


Fig. 8. Exchange of DMS in relation of light and ambient temperature.

$\text{CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ ($4.4 \text{ kg C ha}^{-1} \text{ h}^{-1}$) observed by Fan et al. (1990) over the central Amazon forest. Interestingly, the pioneer tree *Porterandia* showed the highest CO_2 fixation rates. The young *Sacoglottis* individual studied at the forest edge and the older one observed from the top of the canopy in the middle of the forest displayed fundamental differences. CO_2 assimilation on a leaf area basis of the younger individual ranged between daily averages of 369 and $654 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ h}^{-1}$, whereas the values from the top of the canopy (only one day) showed an average of only $130 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ h}^{-1}$. This pattern indicates that adaptation of *Sacoglottis* to strong light at the canopy top (i.e. no light saturation up to the maximum light value measured, see Fig. 5) is accompanied by a decrease in photosynthetic CO_2 assimilation. The adapted individual needs more light to achieve a given CO_2 fixation rate, however it is able to exploit higher light

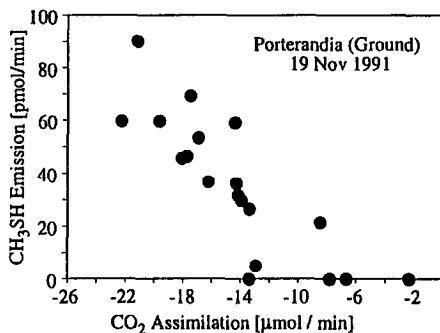


Fig. 9. Emission of methyl mercaptan from *Porterandia* in relation to photosynthetic CO₂ assimilation.

intensities to further increase its fixation rates in contrast to the non-adapted individuals at ground level.

In analogy to CO₂, the sulfur fluxes can be calculated on a leaf and ground area basis. On the still limited data set available, Andreae & Jaeschke (1992) predict a sulfur emission flux from the wet tropics of 0.23–0.76 Tg (S) a⁻¹ based on fluxes of about 60 to 190 nmol S m⁻² h⁻¹ (Andreae & Andreae 1988; Andreae et al. 1990; Bingemer et al. 1992) and related to an area of 14.5×10^{12} m² (Cicerone et al. 1984). The data from the present work on the Cameroon trees lead to flux emission estimates between 100 and 270 nmol S m⁻² h⁻¹ on a ground area basis (Table 2) for the tree species measured near the ground level, consistent with the above mentioned previous estimates. However, the *Sacoglottis* species measured at the canopy top emitted an hourly mean of more than 2000 nmol S m⁻² h⁻¹. This points to the great variability in sulfur flux between different species and sites. Our measurements of sulfur gases in the boundary layer are consistent with fluxes in the order of 100 nmol S m⁻² h⁻¹, suggesting that the emission rate of the mature *Sacoglottis* is higher than that of other rainforest species.

All estimates show that the mature *Sacoglottis* individual measured on the top of the canopy emits more DMS than the younger individual measured near the ground. This high emission at the canopy top has to be discussed in relation to the low photosynthetic CO₂ assimilation found (Table 2). At the canopy top, *Sacoglottis* seems to emit high amounts of sulfur during low CO₂ fixation. This could mean that the intensive photosynthetic electron flow driven by the light cannot be used for the reduction of CO₂, for reasons which are not understood. The strong emission of reduced sulfur, however, might be explained by an insufficient nitrogen supply. Normally the sulfur to nitrogen ratio is given by 0.030 (mol/mol)

for a balanced nutrition (Kelly & Lambert 1972; Johnson et al. 1982). As shown by Kazda & Lösch (1992) leaves of several tree species at the investigated site, including *Sacoglottis gabonensis*, showed significantly higher values up to 0.11 (mol/mol), due to low nitrogen contents. This indicates sulfur accumulation in the foliage on the one hand, and a potential demand for nitrogen on the other hand (Kazda & Lösch 1992). Such an excess of sulfur may result in an increased sulfur reduction (Rennenberg 1984). Thus, sulfur accumulation in addition to an intensive light driven electron flow may be the reason for a high emission of reduced sulfur compounds. To consume the reductive force, the plant metabolism may switch to a reduction of, for example, sulfate and production of organic sulfur compounds, thus leading to an excessive emission of DMS. The emission of DMS as a consequence of sulfur accumulation is additionally facilitated by the high average leaf conductances around 0.8 cm sec^{-1} found for *Sacoglottis gabonensis* at this site by Lösch & Kazda (1992). Furthermore, the authors showed that the older leaves of *Sacoglottis* have lost their restrictive regulation of water losses, as found for younger leaves. Thus mature leaves, due to open and poorly regulated stomata, show higher transpiration rates and consequently higher emission rates of trace gases produced by the leaf. More field data are required to confirm the cuvette flux calculations, notably measurements at the canopy top. It is of interest to look for correlation between the emission of sulfur and the photosynthetic capacity of the plant species or ecotype, especially as a decrease in photosynthetic yield, due to an adaptation to extreme conditions, seems to be accompanied by an increase in S-emission.

Conclusions

The observations during this experiment in and over the tropical rain-forest in Cameroon reveal our lack of understanding of the metabolic background of the exchange of sulfur between vegetation and atmosphere. Such knowledge is necessary to understand these exchanges and to counterbalance variances between direct measurements from different sites on the globe. In this context, experiments determining exchange processes in the tropics are necessary for two main reasons: 1) to estimate fluxes of climatically relevant trace gases to and from the atmosphere and 2) to obtain data from use in further investigations of and comparison with metabolic processes. Similarly, a better understanding of the metabolic background is needed to obtain more reliable data for global flux calculations. Data obtained in the course of this experiment clearly demonstrate the importance of measuring directly at the top of the canopy. As shown

in Table 1, emissions from the mature tree tops may be significantly higher than from younger trees near the ground. A platform on the canopy top therefore proves very useful for cuvette measurements allowing insight into the correlation between plant physiology and trace gas exchange under natural conditions. Nevertheless, it would be of interest to supplement such cuvette measurements with gradient measurements over the canopy using, for example, a dirigible hot air balloon. Thus flux estimates over larger regions could be made to supplement calculations made on a physiological basis.

Acknowledgements

We thank the ELF Foundation for its parts in the funding of this work and its great help in solving logistic problems. We acknowledge the support of the entire raft team. In particular we want to express our gratitude to Prof. Dr. Francis Hallé, Dr. Olivier Pascal and Gilles Ebersolt for their organisational efforts, and the pilots Dani Cleyet-Marrel (dirigible hot air balloon), J. M. Morio and J. M. Lopinot (helicopter) for their enthusiastic cooperation during the experiments. We are grateful to the government of the republic of Cameroon for permission to conduct our investigation. We also thank Cathy Harris for help with the manuscript.

References

- Andreae MO (1985) The emission of sulfur to the remote atmosphere: Background paper. In: Galloway JN, Charlson RJ, Andreae MO & Rodhe H (Eds) *The Biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere* (pp 5–25). Reidel, Dordrecht
- Andreae MO & Andreae TW (1988) The cycle of biogenic sulfur compounds over the Amazon Basin, 1. Dry season. *J. Geophys. Res.* 93: 1487–1497
- Andreae MO & Jaeschke WA (1992) Exchange of sulphur between biosphere and atmosphere over temperate and tropical regions. In: Howarth RW, Stewart JWB & Ivanow MV (Eds) *Sulphur Cycling on the Continents* (pp 27–61). Scope, John Wiley & Sons Ltd.
- Andreae MO, Berresheim H, Bingemer H, Jacob DJ, Lewis BL, Li SM & Talbot RW (1990) The atmospheric sulfur cycle over the Amazon basin. 2. Wet season. *J. Geophys. Res.* 95: 16813–16824
- Augstein E (1979) The atmospheric boundary layer over the tropical oceans. In: Shaw DB (Ed) *Meteorology over the Tropical Oceans* (pp 73–103). Royal Meteorological Society, J. Glaisher House, Grenville Place, Bracknell, Berkshire RG12 1BX, UK
- Berresheim H & Vulcan VD (1992) Vertical distribution of COS, CS₂, DMS and other sulfur compounds in a loblolly pine forest. *Atmos. Environ.* 26A: 2031–2036

- Berresheim H (1993) Distribution of atmosphere sulphur species over various wetland regions in the southeastern USA. *Atmos. Environ.* 27A: 211–221
- Bingemer HG, Andreae MO, Andreae TW, Artaxo P, Helas G, Mihalopoulos N & Nguyen BC (1992) Sulfur gases and aerosols in and above the equatorial African rainforest. *J. Geophys. Res.* 97: 6202–6217
- Brown KA & Bell JNB (1986) Vegetation — the missing sink in the global cycle of carbonyl sulphide (COS). *Atmos. Environ.* 20(3): 537–540
- Brown KA, Kluczewski SM & Bell JNB (1986) Metabolism of (³⁵S)-carbonyl sulphide in perennial ryegrass (*Lolium perenne* L.) and radish (*Raphanus sativus* L.). *Environ. Exp. Bot.* 26(4): 355–364
- Chin M & Davis DD (1993) Global sources and sinks of OCS and CS₂ and their distributions. *Global Biogeochemical Cycles* 7: 321–337
- Cicerone RJ, Delwiche CC, Harriss R & Dickinson R (1984) Critical processes affecting the distribution of chemical species: Biological and surface sources. In: *Global Tropospheric Chemistry: A Plan for Action* (pp 55–68). National Academy Press, Washington DC
- Dacey JWH, King GM & Wakeham SG (1987) Factors controlling emission of dimethylsulphide from salt marshes. *Nature* 330: 643–645
- DWD (German Weather Service) (1991) *European Meteorological Bulletin*, 16, Nov. 1991, Deutscher Wetterdienst, Offenbach, Germany
- Fall R, Albritton DL, Fehsenfeld FC, Kuster WC & Goldan PD (1988) Laboratory studies of some environmental variables controlling sulfur emissions from plants. *J. Atmos. Chem.* 6: 341–362
- Fan SM, Wofsy StC, Bakwin PS & Jacob DJ (1990) Atmosphere-Biosphere exchange of CO₂ and O₃ in the central Amazon forest. *J. Geophys. Res.* 95: 16851–16864
- Filner P, Rennenberg H, Sekiya J, Bressan RA, Wilson LG, Le Cureux L & Shimel T (1984) Biosynthesis and emission of hydrogen sulfide by higher plants. In: Koziol MJ & Whatley FR (Eds) *Gaseous Air Pollutants and Plant Metabolism* (pp 291–312). Butterworth, Stoneham, MA
- Goldan PD, Kuster WC, Albritton DL & Fehsenfeld FC (1987) The measurement of natural sulphur emissions from soils and vegetation: Three sites in the Eastern United States revisited. *J. Atmos. Chem.* 5: 439–467
- Goldan PD, Fall R, Kuster WC & Fehsenfeld FC (1988) The uptake of COS by growing vegetation: A major tropospheric sink. *J. Geophys. Res.* 93: 14186–14192
- Hofmann U, Hofmann R & Kesselmeier J (1992a) Cryogenic trapping of reduced sulfur compounds using a Nafion drier and cotton wadding as an oxidant scavenger. *Atmos. Environ.* 26: 2445–2449
- Hofmann U, Hofmann R & Kesselmeier J (1992b) Field measurements of reduced sulfur compounds over wheat during a growing season. In Schwartz SE & Slinn WGN (Eds) *Precipitation Scavenging and Atmosphere-Surface Exchange. Volume 2 — The Semonin Volume: Atmosphere-Surface Exchange Process* (pp 967–977). Hemisphere, Washington DC
- Johnson DW, Turner J & Kelly JM (1982) The effects of acid rain on forest nutrient status. *Water Research* 18: 449–461
- Kazda M & Lösch R (1992) Element dynamics in canopy leaves of a tropical rain forest in Cameroon. In: Hallé F & Pascal O (Eds) *Biologie d'une Canopée de Forêt Équatoriale — II. Rapport de mission: Radeau des Cimes Octobre/Novembre 1991* (pp 217–230). Reserve de Campo, Cameroun, ISBN-No 2-950 6703-1-8
- Kelly JM & Lambert JM (1972) The relationship between sulphur and nitrogen in the foliage of *Pinus radiata*. *Plant Soil* 37: 395–407

- Kesselmeier J (1991) Emission of sulfur compounds from vegetation and global-scale extrapolation. In: Sharkey ThD, Holland EA & Mooney HA (Eds) *Trace Gas Emissions from Plants* (pp 261–265). Academic Press, San Diego, USA
- Kesselmeier J, Meixner, FX, Hofmann U, Ajavon A, Leimbach St & Andreae MO (1992) Distribution of ozone over a tropical rain forest and exchange of reduced sulfur compounds between tropical tree species and the atmosphere: Investigations from the atmospheric boundary layer, at ground level and from the top of the canopy. In: Hallé F & Pascal O (Eds) *Biologie d'une Canopée de Forêt Équatoriale — II. Rapport de mission: Radeau des Cimes Octobre/Novembre 1991* (pp 247–263). Reserve de Campo, Cameroun, ISBN-No 2-950 6703-1-8
- Kesselmeier J & Merk L (1993) Exchange of Carbonyl Sulfide (COS) between Agricultural Plants and the Atmosphere: Studies on the Deposition of COS to Peas, Corn and Rapeseed. *Biogeochemistry* 23: 47–59
- Larher F, Hamlin J & Stewart GR (1977) L'acide dimethylsulfonium 3-propanoïque de *Spartina anglica*. *Phytochemistry* 16: 2019–2020
- Lösch R & Kazda M (1992) Water turnover of leaves in the rainforest canopy, the understorey and in a regrowth site of the Reserve De Campo/S. Cameroon. In: Hallé F & Pascal O (Eds) *Biologie d'une Canopée de Forêt Équatoriale — II. Rapport de mission: Radeau des Cimes Octobre/Novembre 1991* (pp 206–216). Reserve de Campo, Cameroun, ISBN-No 2-950 6703-1-8
- Mihalopoulos N, Bonsang B, Nguyen BC, Kanakidou M & Belviso S (1989) Field observations of carbonyl sulfide deficit near the ground: Possible implication of vegetation. *Atmos. Environ.* 23: 2159–2166
- Protoschill-Krebs G (1991) Untersuchungen zur Aufnahme und zum Metabolismus von Carbonylsulfid in Pflanzen. Ph.D. Thesis, Johannes-Gutenberg-University of Mainz, FRG
- Protoschill-Krebs G & Kesselmeier J (1992) Enzymatic pathways for the consumption of carbonyl sulphide (COS) by higher plants. *Botanica Acta* 105: 206–212
- Reed RH (1983) Measurements and osmotic significance of dimethylsulfoniumpropionate in marine macro-algae. *Mar. Biol. Lett.* 4: 173–181
- Rennenberg H (1984) The fate of excess sulfur in higher plants. *Ann. Rev. Plant Physiol.* 121–153
- Rennenberg H (1991) The significance of higher plants in the emission of sulfur compounds from terrestrial ecosystems. In: Sharkey ThD, Holland EA & Mooney HA (Eds) *Trace Gas Emissions from Plants* (pp 217–260). Academic Press, San Diego, USA
- Riehl H (1979) *Climate Weather in the Tropics*. Academic Press, London, New York, San Francisco
- Saltzman ES, Savoie DL, Prospero JM & Zika RG (1986) Methanesulfonic acid and non-sea-salt sulfate in Pacific air: Regional and seasonal variations. *J. Atmos. Chem.* 4: 227–240
- Schäfer L, Kesselmeier J & Helas G (1992) Formic and acetic acid emission from conifers measured with a 'cuvette' technique. In: Angeletti G, Beilke S & Slanina J (Eds) *Field Measurements and Interpretation of Species Related to Photooxidants and Acid Deposition, CEC Air Pollution Research 39* (pp 319–323). Guyot SA, Brussels
- Schwenn JD, Schriek U & Kiltz HH (1983) Dissimilation of methionine in cell suspension cultures from *Catharanthus roseus* L. *Planta* 158: 540–549
- Schmidt A, Rennenberg H, Wilson LG & Filner P (1985) Formation of methanethiol from methionine by leaf tissue. *Phytochemistry* 24: 1181–1185
- Taylor GE, McLaughlin SB, Shriner DS & Selvidge WJ (1983) The flux of sulfur-containing gases to vegetation. *Atmos. Environ.* 17: 789–796

- van Diggelen J, Rozema J, Dickson DMJ & Broekman R (1986) β -3-Dimethylsulfonio-propionate, proline, and quaternary ammonium compounds in *Spartina anglica* in relation to sodium chloride, nitrogen and sulphur. *New Phytol.* 103: 573–586
- Warneck P (1988) Sulfur compounds in the atmosphere. In: Warneck P. (Ed) *Chemistry of the Natural Atmosphere* (pp 484–542). Academic Press Inc., San Diego
- Whittaker H & Likens GE (1975) The biosphere and man. In: Lieth H & Whittaker H (Eds) *Primary Productivity of the Biosphere*. Ecological Studies 14 (pp 305–328). Springer Verlag, Berlin
- Winner WE, Smith CL, Koch GW, Mooney HA, Bewley JD & Krouse HR (1981) Rates of emission of H_2S from plants and patterns of stable sulfur isotope fractionation. *Nature* 289: 672–673