

Atmospheric Environment 34 (2000) 4867-4878

ATMOSPHERIC ENVIRONMENT

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# Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere

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Received 16 December 1999; received in revised form 4 April 2000; accepted 12 April 2000

## Abstract

The exchange of carbonyl sulfide (COS) between lichens and the atmosphere was investigated under natural field conditions. Using dynamic enclosures flushed with ambient air, we demonstrate that lichens act as a major sink for atmospheric COS in the investigated ecosystem. Diel courses of the exchange are shown in an open oak woodland ecosystem at a rural site in central California. The measurements were distributed over a variety of weather conditions during the dry (May/June) and the wet season (Nov/Dec). The physiological parameters (CO<sub>2</sub> exchange and thallus hydration status) plus environmental variables (temperature, irradiance, atmospheric humidity and ambient COS mixing ratio) were recorded. Lichens are capable of continuous uptake of COS in the dark as well as in the light, depending mainly on their moisture status. Results indicate that the uptake is additionally dependent on temperature and COS ambient mixing ratio. Enzyme inactivation by high temperature denaturation demonstrate that the uptake is under physiological control. Light and thus photosynthetic activity do not have a direct influence on the uptake rate. Under these field investigations the COS uptake on a dry weight basis ranged between 0.015 and 0.071 pmol g<sup>-1</sup> s<sup>-1</sup>. On a thallus surface area basis the sink strength is comparable to the uptake by higher vegetation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbonyl sulfide; Lichens; Trace gas flux; Biosphere-atmosphere exchange; Vegetation

#### 1. Introduction

Carbonyl sulfide (COS) is the most stable and most abundant reduced sulfur gas in the atmosphere. It is photodissociated as well as photooxidized to form SO<sub>2</sub> (Chin and Davis, 1993). SO<sub>2</sub> is subsequently converted to sulfate aerosols. Aerosols directly cool the earth by reflecting sunlight, and the particles may act as seeds for cloud condensation (CCN) and thus increase the reflectivity or albedo of clouds in the lower troposphere (Andreae and Crutzen, 1997). In the stratosphere COS serves as an important source for the stratospheric aerosol layer (Crutzen, 1976; Meixner, 1984; Hofmann, 1990; Engel and Schmidt, 1994) which can intensify the destruction of the stratospheric ozone layer (Roche, 1994; Fahey et al., 1993; Solomon et al., 1993) and influences the earth's radiation budget (Turco et al., 1980). As a consequence it is important to assess global sinks and sources of COS.

The understanding of the global COS cycle is still poor, reflected by a seriously unbalanced budget with sources exceeding sinks by a factor of two (Chin and Davis, 1993; Johnson et al., 1993), although no temporal trend in the tropospheric mixing ratio of COS was observed during the past decade (Bandy et al., 1992; Rinsland et al., 1992; Thornton et al., 1996). Recently, Andreae and Crutzen (1997) proposed a correction towards a more balanced budget by changing the soil source strength into a soil sink strength, an assumption which was made owing to findings of Castro and Galloway (1991) and DeMello and Hines (1994) and which is

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supported by recent investigations of other research initiatives (Kuhn et al., 1999; Kesselmeier et al., 1999; Simmons et al., 1999). While vegetation is recognized as a major tropospheric sink (Taylor et al., 1983; Brown and Bell, 1986; Goldan et al., 1988; Chin and Davis, 1993; Kesselmeier and Merk, 1993, Kesselmeier et al., 1997, Andreae and Crutzen, 1997), recent laboratory investigations revealed that lichens possess the potential to take up COS in the same range as vascular plants, compared on the leaf versus thallus surface area according to Gries et al. (1994). Although some interspecific variation occurred among the 14 species investigated, deposition rates reached a relatively uniform level. In contrast to higher plants, the uptake of COS was dependent only on the thallus moisture content and thus on the physiological activity of the lichens. Because no investigations of lichens and COS exchange under natural field conditions have been carried out to our knowledge, considerable uncertainty exists about the potential role of lichens in the global COS budget, even though lichens may be dominant components on about 8% of the terrestrial land surface (Ahmadjian, 1995) and are important constituents of various ecosystems.

Lichens are not plants, but symbiotic associations consisting of populations of green algae and/or cyanobacteria (photobiont) and a fungal tissue (mycobiont). Because lichen dominated ecosystems cover extensive terrestrial habitats, their COS uptake may be important for the world's sulfur budget. The fruticose, epiphytic lichen species Ramalina menziesii occurs along the west coast of North America, covering an enormous latitudinal distance from southern Alaska to central Baja California (Rundel, 1974). Its reticulate thallus dominates the epiphytic community of central coastal California with a few stands as far east as the Sierra Nevada, often forming a dense, pendulous canopy and having biomasses as high as  $600-700 \text{ kg ha}^{-1}$  (Larson et al., 1985; Boucher and Nash III, 1990; Knops et al., 1996). The thallus morphology ranges from relatively coarse nets in sunny, inland areas to thin filaments in foggy, coastal regions (Larson, 1983; Larson et al., 1985; Rundel, 1974). During studies at a rural research station in California, we investigated the exchange of COS between lichens and the atmosphere using dynamic enclosures flushed with ambient air.

# 2. Methods

#### 2.1. Site description

This study was performed in an open oak woodland at the Hastings Natural History Reservation in Monterey County, central California (36°23'N, 121°33'W; 490 m asl). The reservation is located in a side valley of the Carmel Valley approximately 40 km from the coast. The area is characterized by a Mediterranean climate with hot, dry summers and a mean annual precipitation of 524 mm, which is restricted primarily (90%) to the wet season between November and April (Knops et al., 1996). The landscape includes a mosaic of mixed evergreen forest, deciduous oak woodland, oak savanna and chaparral (Griffin, 1977). The oak woodlands are composed of relatively even-aged trees that rarely exceed 5 m in height. Fruticose and foliose lichens are a conspicuous component of the ecosystem. According to Knops et al. (1996), Ramalina menziesii is the most common (78%), epiphytic, fruticose lichen followed by Usnea sp. (20%). They occur abundantly on oaks and a variety of other substrates. The vegetation found in the Hastings Reservation (in central Monterey County, California) is typical for the coastal mountain ranges. The region is regarded as rural to remote with minimal local anthropogenic influences.

COS exchange rates between lichens and the atmosphere were investigated in May/June and November/ December, 1994. Of the 11 sampling dates presented here, six were in winter and five in summer. Laboratory investigations with the same system as applied in the field were made at the Max Planck Institute for Chemistry in Mainz, Germany.

#### 2.2. Cuvette system

We applied an open, dynamic (flow-through) cuvette system consisting of two cylindrical chambers of 0.09 m in height and 0.145 m in diameter (internal volume of 1.5 l; Fig. 1), made of Teflon film supported by two external PVC skeletons. One cuvette acted as the sample (lichen) cuvette; an identical but empty one, as a reference. All surfaces in contact with the sample gas were made or covered by Teflon or Teflon film. Previous studies demonstrated that the applied Teflon film (FEP) shows no interference with trace gases tested such as organic acids (Schäfer, 1992), monoterpenes and isoprene (Kesselmeier et al., 1996), and reduced sulfur compounds (Kesselmeier et al., 1993, 1999) and is fully light permeable in the spectral range of 300–900 nm.

In order to obtain quasi-ambient conditions inside the enclosures, they were constantly flushed with outside air. The air flow was regulated and monitored using mass flow controllers. The air inside the chamber was well mixed by a Teflon propeller driven by a magnetically coupled motor attached outside. With a constant flow rate (Q) of 1 1 min<sup>-1</sup>, a complete turnover of the air within the cuvette was achieved approximately once every 1.5 min. Air and thallus temperatures within the cuvette were continuously recorded with teflonized thermocouples. Photosynthetically active radiation (PAR) was measured with a LiCor quantum sensor (LiCor, Lincoln, NE, USA) outside the chamber, and relative humidity recorded with a temperature-relative humidity



Fig. 1. Sectional view of the dynamic cuvette system.

probe (Model 133Y, Vaisala, Malmö, Sweden). For determination of the gas fluxes, air samples were taken continuously for COS analysis (0.11 min<sup>-1</sup>) and for CO<sub>2</sub> exchange. Both chambers were checked regularly for trace gas ad- or desorption.

The gas exchange rate (F) was calculated according to Eq. (1) from the measured concentration difference (lichen chamber:  $\Delta c = c_{\text{lichen}} - c_{\text{reference}}$ ), the chamber flush rate (Q) and the reference thallus dry weight (dw).

$$F = \Delta c \, \frac{Q}{\mathrm{dw}}.\tag{1}$$

Exchange rates obtained with enclosure techniques may not be extrapolated directly to the natural (undisturbed) field situation, as chamber measurements generally cause an alteration of the trace gas mixing ratio. For a quantitative description of this effect and for comparing measurements with different methods, the concept of the deposition velocity of a gas is used (see, e.g., Hicks et al., 1987). Deposition fluxes are assumed to be proportional to the ambient air concentration (c) and are therefore normalized to the so-called deposition velocity ( $v_d$ ):

$$v_{\rm d} = \frac{F}{c}.$$
 (2)

#### 2.3. Analysis of trace gases

Reduced sulfur compounds were sampled by cryogenic trapping and quantified by a gas chromatograph (GC) equipped with a flame photometric detector (Hofmann et al., 1992). Control measurements of the empty cuvettes were conducted regularly in order to evaluate possible chamber losses or contamination problems of COS inside the enclosure. No effect of the chambers could be detected within the precision of our system. The GC was calibrated with samples obtained from a permeation tube (VICI Metronics) device. Sampling efficiency for COS was 100% (Hofmann et al., 1992). The relative precision of the measurements was  $100 \pm 6\%$ , based on the reproducibility of consecutive samples over a 2-day period with 90 ppt (n = 26) and 710 ppt (n = 25) COS standards. The overall, absolute accuracy is estimated to be  $100 \pm 10\%$ , based on the standard deviation of calibrated samples (permeation device) injected on a daily basis (n = 60). The following assumptions were made to calculate the errors of the COS exchange rates: 6% error for the COS measurements of the reference cuvette ( $\sigma_r$ ) and of the lichen cuvette ( $\sigma_{\rm b}$ ), 5% error in the cuvette flow ( $\sigma_0$ ) determination, and 1% in the dry-weight ( $\sigma_{dw}$ ) determination. The total flux error ( $\sigma_{\rm F}$ ) from difference measurements can be obtained by using the error propagation method according to Doerffel (1984):

$$\sigma_{\rm F} = \sqrt{\frac{\left[(c_{\rm r}\sigma_{\rm r})^2 + (c_{\rm b}\sigma_{\rm b})^2\right]}{(c_{\rm r} - c_{\rm b})^2} + \sigma_{\rm Q}^2 + \sigma_{\rm dw}^2}.$$
 (3)

Quantification of  $CO_2$  and water vapor exchange was achieved by a standard infrared gas analyzer (Model 6262, LICOR, Lincoln, NE, USA) in the differential mode. It was maintained in a temperature-insulated box controlled at 40°C to prevent signal fluctuations due to temperature effects as well as water condensation. Furthermore, all tubings downstream of the cuvette were insulated and heated to 40°C.

### 2.4. Protocols employed

Because of their poikilohydric nature, metabolic activity of lichens varies greatly with the prevailing moisture content of the thalli (Lange and Tenhunen, 1981). During the field campaign, lichens were sampled and incubated in the cuvette, either moistened naturally by precipitation or wetted artificially with deionized water. Prior to incubation in the cuvette, surface water was removed by slightly shaking and blotting the thallus and the fresh weight was determined gravimetrically. Gas exchange measurements started 0.5 h after closing the cuvettes. The water content during the measuring period was then calculated according to the LiCor readings of water evaporation. Immediately after each measurement period, the lichen sample was weighed to determine its final water content and then oven-dried at 100°C for 24 h for dry-weight determination. All thallus-water content values were expressed as percent of oven dry weight. Conditions inside the cuvette did not exactly match the ambient conditions outside. Temperature increased during sunshine by  $< 2^{\circ}$ C, and the relative humidity inside the chamber was increased temporarily owing to evaporation from the wet lichen thallus. Consequently, the vapor pressure deficit as well as the water loss by the lichen decreased. The period of physiological activity due to a higher water content of the thallus was therefore extended inside the cuvette. Fig. 2 shows the delayed dehydration of *Ramalina menziesii* inside the cuvette (calculated from the LiCor readings) compared to the gravimetrically determined water loss of a reference thallus outside of the cuvette. During the summer periods, especially under conditions of high light intensity, we occasionally observed slight condensation on the inner surfaces of the chamber after incubation of a well-wetted thallus. In this case the calculated thallus-water content



Fig. 2. Diel cycle of the thallus-water content of a lichen inside the cuvette (calculated by means of the LiCor readings) compared with the waterloss of an extra thallus treated the same way but kept outside of the cuvette (resolved gravimetrically).

of the investigated lichen represents slower drying than actually occurring.

For laboratory investigations the same procedure as described above was employed. Lichen thalli were transported in an air-dry state via airplane and stored at room temperature. They were moistened at least 1.5 h prior to experimentation.

#### 3. Results

We investigated the diel and seasonal behavior of COS exchange between lichens and the atmosphere, comparing measurements in May/June (dry season) and November/December (rainy season). Table 1 gives an overview of the exchange rates observed in the dry and rainy season. COS deposition was found in the range of 0.015–0.071 pmol  $g^{-1} s^{-1}$  on a dry-weight basis. Fluctuations can be related to the temperature and thallus-water content as shown below. Under summer conditions with nearly no rain, the lichens normally do not show any activity for a long time but recover quickly after moistening and reach similar exchange rates as found under winter conditions, when the organisms are more often wet enough to be physiologically active. Natural (rain/fog) and artificial moistening always sustained comparable activities. The gas exchange of lichens, which is dependent on physiological, morphological and anatomical features of the thallus, is above all a function of the eco-physiological characteristics of the (micro)habitat. Thus, out of the 11 days of measurement presented in Table 1, five diel courses are selected to represent the range of environmental conditions and the species variety of this habitat in further detail. (Figs. 3-7). The microclimatic conditions are characterized by

### Table 1

Ranges of COS uptake rates (pmol  $g^{-1}s^{-1}$ ) between lichens and the atmosphere on a dry weight basis measured under summer and winter conditions at the Hastings field site. Only periods with continuous data under stable conditions are listed. Nat., natural moistening by rain or fog; art., artificial moistening with deionized water

Date	Range (pmol g <sup>-1</sup> s <sup>-1</sup> )	Water content (%)	T (°℃)	Ambient COS (ppt)	Species	Remarks
06 June 1994	0.06 + 0.004	107 - 101	11 + 1	439 + 29	R. menziesii	Summer, nat.
14 June 1994	$0.04 \pm 0.005$	191 - 148	$6 \pm 2$	$424 \pm 55$	R. menziesii	Summer, art.
24 June 1994	$0.02 \pm 0.01$	147 - 80	$11 \pm 4$	$345 \pm 15$	R. menziesii	Summer, art.
25 June 1994	$0.02 \pm 0.004$	184 - 138	$11 \pm 1$	$348 \pm 7$	<i>U. sp.</i>	Summer, art.
15 June 1994	$-0.005 \pm 0.015$	22 - 15	$6 \pm 3$	$368 \pm 29$	R. menziesii	Summer, dry
07 June 1994	$0 \pm 0.005$	45 - 20	$12 \pm 5$	$483 \pm 48$	R. menziesii	Summer, dry
24 Nov 1994	$0.07 \pm 0.01$	262 - 148	$6 \pm 2$	$308 \pm 15$	R.menziesii	Winter, art.
03 Dec 1994	$0.03 \pm 0.006$	85 - 36	$9 \pm 4$	$358 \pm 41$	R. menziesii	Winter, art.
05 Dec 1994	$0.047 \pm 0.007$	202 - 83	$7 \pm 2$	$349 \pm 16$	R.menziesii	Winter, nat.
04 Dec 1994	$0.06 \pm 0.013$	144 - 80	$10 \pm 1$	$348 \pm 23$	<i>U. sp.</i>	Winter, art.
08 Dec 1994	$0.034 \pm 0.003$	128 - 116	$-3 \pm 1$	$273 \pm 9$	R. menziesii	Winter, art.
10 Dec 1994	$0.015 \pm 0.005$	104 - 60	$1 \pm 1$	$316 \pm 15$	<i>U. sp.</i>	Winter, art.



Fig. 3. Diel cycle of the COS uptake by *Ramalina menziesii* together with the thallus-water content and the eco-physiologically relevant parameters measured on 5 December 1994. Open squares represent test measurements of the empty cuvette system. Error bars of COS uptake indicate the total flux error derived from difference measurements according to Eq. (1). Error bars of the ambient COS mixing ratio indicate the precision of the system ( $\pm$  6%).

photosynthetically active radiation (PAR), relative humidity (rh), temperatures inside the cuvette and ambient COS mixing ratio; the physiology is represented by the thallus-water content and the assimilation/respiration of the lichen.

On a cold and rainy day in December (5 December 1994; Fig. 3), representative for the rainy season, relative humidity was close to 100% throughout the whole day, only slightly reduced during short periods of clear sky and rising temperatures during daytime. Dense cloud cover and fog events are reflected by the low light regime. A thallus of Ramalina menziesii, moistened to a water content of about 200% by preceding natural rainfall, was inserted into the cuvette the evening before (20:00 h). Owing to the high relative humidity, the water content decreased only slowly during the night; and the lichen remained well hydrated (upper diagram) even during a temporary increase in temperature (middle diagram) during daytime. The final water content was still > 80%when the thallus was taken out of the cuvette, sustaining physiological activity during the whole measuring period. The bold solid line in the middle diagram shows the CO<sub>2</sub> gas exchange rate, documenting respiration during



Fig. 4. Diel cycle of the COS uptake by *Ramalina menziesii* together with the thallus-water content and the eco-physiologically relevant parameters measured on 24 November 1994. Open squares represent test measurements of the empty cuvette system. Error bars as in Fig. 3.



Fig. 5. Diel cycle of the COS uptake by *Ramalina menziesii* together with the thallus-water content and the eco-physiologically relevant parameters measured on 6–7 June 1994. Error bars as in Fig. 3; note the different scales for the summer period.



Fig. 6. Reproduction of the diel cycle of the COS uptake by *Ramalina menziesii* with cuvettes covered by aluminum foil. The pattern without photosynthetically active radiation parallels those presented above indicating that COS exchange is not directly linked to photosynthesis. Error bars as in Fig. 3.

nighttime and photosynthesis during the daytime. Photosynthetic activity paralleled closely fluctuations in the light intensity (lower diagram). After sunset low respiratory activity was registered again.

Parallel to the physiological activity represented by the CO<sub>2</sub> exchange rate, Ramalina menziesii showed a high, persistent COS deposition rate during the whole day (Fig. 3, upper diagram). The uptake, already observed during nighttime, increased initially during daytime with only slight dehydration of the thallus, accompanied by an increase of temperature and ambient COS mixing ratio after sunrise (07:30 h). After a further rise of temperature the COS uptake declined gradually with dehydration of the thallus. Mean COS uptake values during the night  $(0.046 \pm 0.006 \text{ pmol g dw}^{-1} \text{ s}^{-1}; n = 6)$  did not differ significantly from the daytime values  $(0.048 \pm 0.008)$ pmolg dw<sup>-1</sup> s<sup>-1</sup>; n = 15) (*t*-test;  $\alpha = 0.01$ ). The ambient COS mixing ratio did not show a pronounced diel cycle during this day (middle diagram). Remarkably, the slight decrease in COS mixing ratio at 10:30 h was directly followed by a reduction of COS uptake.

Similar climatic conditions were found on the evening of 24 November 1994 (Fig. 4). Because there was no natural rainfall in spite of dense cloud cover, the lichen was artificially sprayed with deionized water to promote



Fig. 7. Diel cycle of the COS uptake by *Usnea spec.* together with the eco-physiologically relevant parameters measured on 4 December 1994. Error bars like in Fig. 3.

physiological activity, resulting in 250% thallus-water content. Owing to a low ambient relative humidity, dehydration was accelerated compared to the pattern described above. After sunrise with increasing temperature, the evaporation rate rose drastically, leading to a thallus-water content of ca. 30% shortly after 12:00 h. At first the CO<sub>2</sub> exchange responded similar to the pattern described above, but dropped sharply after 10:00 h owing to the on-going water loss. The COS deposition rate of  $0.063 \pm 0.008 \text{ pmol g dw}^{-1} \text{ s}^{-1} (n = 5)$  during nighttime was followed by a distinct increase directly after sunrise. A peak of COS deposition was then followed by a sharp decline of the COS uptake paralleled by a drop of photosynthesis. Again the temporary boost of COS deposition in the early morning hours was accompanied by an increase in temperature and ambient COS mixing ratio. During the winter as well as during the summer period, we frequently found significant diel cycles of atmospheric COS mixing ratios with high values during daytime and a drop by about 150 ppt during the night. Additionally, the mean COS daytime background mixing ratios were affected strongly by seasonal differences, with higher values during summer ( $465 \pm 77$  ppt) as compared to wintertime  $(375 \pm 56 \text{ ppt}; \text{ Kuhn et al.},$ 1999).

Owing to the climatological conditions in the summer period (e.g., little precipitation, high temperature and low relative humidity), the lichens of this ecosystem remain dry most of the time and are thus physiologically inactive (Matthes-Sears et al., 1986). The only natural precipitation event during our campaign was on 6 June 1994 (Fig. 5). After being moistened by a light nighttime drizzle, the lichen was inserted into the enclosure shortly before sunrise. Because of a dense cloud cover in the early morning hours, the commonly observed steep increase of light intensity to approximately 2000  $\mu$ mol m<sup>-2</sup>s<sup>-1</sup> (PAR) and an ambient temperature shift to almost 30°C was postponed until after 10:00 h on this specific day. Despite the short-term moistening after a long summer period of dryness, the CO<sub>2</sub> exchange (respiration/assimilation) started immediately within a range comparable to the winter values. Owing to the rapid drying, R. menziesii became inactive very soon as temperature rose during the day. Without any further wetting, the thallus-water content of the lichen increased only slightly because of the relative humidity at the subsequent nighttime. Lichens are able to utilize not only rain as source of water for hydration but also fog, dew, or even atmospheric water vapor to become physiologically active (Lange et al., 1986; Nash III, 1996). According to laboratory studies by Rundel (1974), the water content of R. menziesii in equilibrium with an atmosphere of 90% rh at 25°C reaches 34% of dry weight, a water content that is the approximate minimum for gross photosynthetic activity of this species in the field (Matthes-Sears et al., 1986). Our lichen barely reached this limit, reflected by the very low CO<sub>2</sub> exchange rate during the next morning (Fig. 5, middle diagram).

The same is the case for COS. An uptake rate of the well-hydrated thallus in the same range as for the winter period was followed by a sharp decline of the exchange activity with progressing dehydration. Under these conditions, a slight condensation effect at the inner surface of the chamber led to a delay of the calculated dehydration (calculated by LiCor readings) compared to the actual water loss by the lichen in the cuvette. For the rest of the day the lichen did not exchange any significant amount of COS, a behavior which was representative for most of the summer period (data not shown).

Gries et al. (1994) found in laboratory studies that the COS exchange is not influenced by irradiance conditions. To evaluate the effect of natural radiation and thus the impact of photosynthetic activity under field conditions, both cuvettes were covered by aluminum foil for one day. As shown in Fig. 6, the lack of photosynthetically active radiation is reflected by the lack of assimilation. The on-going respiration decreased during the night owing to very low temperatures  $(-5^{\circ}C)$  and was temporarily enhanced during a short period of higher temperature up to 18°C before dehydration started. However, even without photosynthetic active radiation, the normal COS uptake pattern could be observed; i.e., a moderately even uptake during the night, a temporary increase of the uptake paralleled by a rise in temperature and COS ambient mixing ratio during the morning, and a subsequent inactivity due to dehydration shortly afterwards. It is remarkable that not only the respiration is still significant at temperatures below 0°C (see, e.g., Lange, 1965; Kappen et al., 1995, 1996) but also the COS uptake mechanism is still operative, although the mean uptake values during this night of  $0.034 \pm 0.004$  pmol g dw<sup>-1</sup> s<sup>-1</sup> are somewhat lower than those reported above.

Besides *R. menziesii*, the second most frequent lichen species in this habitat, *Usnea sp.*, was investigated for its trace gas exchange behavior. This species is likewise



Fig. 8. Indication of the physiological background of the COS uptake by *Ramalina menziesii*. COS uptake as a function of water content of an active thallus (living control, closed symbols) compared to a dead thallus (inactivated, open symbols). The CO<sub>2</sub> exchange indicates the physiological state of the thallus. Error bars of COS uptake indicate the total flux error derived from difference measurements according to Eq. (1).

a fruticose one and, in general, it showed a similar COS uptake behavior in the same range as *R. menziesii*. An example of continuous activity over the period of one day during the winter campaign is shown in Fig. 7. There was high relative humidity even during daytime and no distinct diel cycle of temperature and COS ambient mixing ratio. The uptake value of the first-half of the day of  $0.069 \pm 0.01$  pmol g dw<sup>-1</sup> s<sup>-1</sup> is significantly different (*t*-test,  $\alpha = 0.05$ ) from the values of the second half of  $0.047 \pm 0.003$  pmol g dw<sup>-1</sup> s<sup>-1</sup>, most probably owing to the reduced thallus-water content decreasing below 100% after 11:00 h. Water content is a critical parameter for lichen activities showing an optimum behavior (Gries et al., 1994; Nash III, 1996).

Both biological and physicochemical parameters might potentially explain the observed COS deposition. To examine whether the uptake activity is dependent on a functioning physiology, a lichen was killed by heating it in an oven at 100°C for two days. Its trace gas exchange was investigated afterwards in the laboratory. The lichen was moistened and enclosed in the cuvette and then gently dehydrated under dark conditions over the course of several hours (Fig. 8). The control thallus showed a gas exchange behavior as expected, with high COS uptake and high respiration rates while being wet and decreasing activity during the course of dehydration. Conversely, the effect of overheating led to a complete physiological inactivity as demonstrated by the absence of any significant CO<sub>2</sub> exchange. Accordingly, there was no uptake of COS over the whole range of thallus-water content, excluding physicochemical deposition on the wet thallus surface as a significant contributor to the observed exchange.

Under field conditions in the natural habitat of the lichens, we never detected any significant exchange of sulfur compounds other than COS; i.e., hydrogen sulfide  $(H_2S)$  and dimethyl sulfide (DMS) exchange were not

detected. For both investigated lichen species, this is in contrast to laboratory investigations of Gries et al. (1994).

# 4. Discussion

The results of our studies clearly show that lichens are a considerable sink for COS under natural field conditions. The COS uptake rates of the two fruticose lichen species, Ramalina menziesii and Usnea sp., investigated under natural field conditions were found in the range of 0.015–0.071 pmol g dw<sup>-1</sup> s<sup>-1</sup> and confirm laboratory studies of Gries et al. (1994), though they found slightly higher values between 0.02 and 0.14 pmol g dw<sup>-1</sup> s<sup>-1</sup>. For a quantitative comparison between different types of COS consumers, we normalized the measured exchange rates to deposition velocities by dividing them by the COS mixing ratio inside the chamber. After conversion from a dry weight to a surface area basis according to Gries et al. (1997) deposition velocities were calculated (Table 2). A COS deposition velocity of up to  $0.28 \,\mathrm{mm \ s^{-1}}$ , observed under the actual conditions of the Hastings Reservation, is listed together with laboratory and field data of COS uptake by higher vegetation as found in the literature. On a leaf area versus thallus surface basis, the data are comparable to those for higher vegetation, which is considered as the main sink for COS on a global scale (Chin and Davis, 1993). This comparison shows the capacity of lichens as a sink for COS. However, as already shown in laboratory investigations (Gries et al., 1994), a high thallus-water content is crucial for the COS uptake as well as for the general physiology, i.e., the CO<sub>2</sub> exchange. In contrast to higher vegetation, lichen gas exchange is not under stomatal control. Lichens lack both stomates and the cuticle found in most vascular plant leaves and therefore exchange gases over

Table 2

Comparison of the COS uptake potential of lichens with some data for higher vegetation given as calculated deposition velocities related to projected leaf area surface or complete thallus surface

Species	Deposition velocity (mm s <sup>-1</sup> )	Reference	Type of measurement
Ramalina menziesii	≤ 0.28	This work	Field
Picea abies	0.5	Huber, 1994	Field
Phaseolus vulgaris	1.4	Taylor et al., 1983	Laboratory
Glycine max	3.1	ibidem	
Lycopersicon escul.	0.4	ibidem	
Vegetables <sup>a</sup>	0.25-0.6	Kluczewski et al.,1985	Laboratory
Grass	0.75	ibidem	
Crops	1.3-3.3	Goldan et al., 1988	Laboratory
Glycine max	1.25-1.7	ibidem	
Rapeseed	1.1-1.5	Kesselmeier, Merck, 1993	Laboratory
Corn	0.3-0.9	ibidem	

<sup>a</sup>Spinacea oleracea, Allium cepa, Lactuca sativa, Rhaphanus sativus, Brassica oleracea.

their entire surface (Nash III, 1996). Physiological inactivity of the lichen due to dehydration corresponds to the decline of its gas exchange, which is negligible over many hours of the day or many days. Desiccation of lichens is dependent on thallus morphology and the microtopography of their habitat. Their gas exchange is restricted to periods with high relative humidity, predominantly at low temperatures prevailing during the nighttime.

Although the thallus-water content appears to be the major limiting factor for the COS exchange, the ambient COS mixing ratio and the temperature are also important. Whenever the hydration status allowed optimal gas exchange, an increase in COS ambient mixing ratio coincided with a corresponding increase of COS uptake. In contrast, no direct influence of light and thus photosynthetic activity could be observed. The triggering function of water content, ambient COS mixing ratio, and temperature was also reported recently for the consumption of COS by soils in laboratory studies (Kesselmeier et al., 1999) as well as in the field (Simmons et al., 1999). The close relationship between physiological activity, water content, and COS uptake points to a biological basis for the consumption. Nevertheless, both, biological and physicochemical parameters, might be involved in the revealed COS exchange behavior, as governed by the amount of available water, ambient COS mixing ratio, and temperature.

To differentiate between a physiologically regulated COS uptake by the lichen and a physicochemical deposition on the wet surface, the exchange behavior of a dead thallus surface was examined. No significant uptake of COS was detectable over a wide range of thallus-water content, proving the physiological nature of the COS consumption. Hydration and hydrolysis are too slow to significantly account for the rates measured (Ferm, 1957), especially since hydrolysis of COS is only enhanced under alkaline conditions and the surface water pH of the investigated lichen was 4.3-4.7 (n = 7). Hence, the COS consumption process is assumed to be the biological hydrolysis of COS to H<sub>2</sub>S and CO<sub>2</sub>, enzymatically catalyzed by carbonic anhydrase (Protoschill-Krebs and Kesselmeier, 1992; Protoschill-Krebs et al., 1995, 1996; Kesselmeier et al., 1999). Carbonic anhydrase is ubiquitous in plants, animals and in bacteria (e.g., Atkins et al., 1972; Badger and Price, 1994; Karrasch et al., 1989). Therefore, we assume that the same enzyme also consumes COS in lichens, and thus provides a main metabolic pathway to supply sulfur to lichens growing in remote areas. Further experiments and a more detailed parameterization are needed to confirm this suggestion.

A biological feature for an enzymatic process is the enhanced metabolism in correlation with the substrate concentration and the temperature, leading to either a saturation or optimum effect, respectively. Within our field data we found evidence for effects of both, temperature as well as ambient atmospheric mixing ratios. Temperature but also COS mixing ratios may vary significantly. As reported recently, a distinct diel cycle of the COS ambient mixing ratio with high concentrations during daytime and low values in the night was observed in summer as well as in winter. The COS mixing ratio regularly dropped by approximately 150 ppt during the night in both seasons (Kuhn et al., 1999). Ambient COS mixing ratios which are lower and more variable than those often cited in literature were also reported recently by Simmons et al. (1999). During daytime the atmospheric boundary layer is generally well-mixed owing to thermal convection and is therefore characterized by small concentration gradients and changes. In contrast, at night radiative cooling of the land surface creates a stable thermal stratification in the lower troposphere, and this has a strong damping effect on the turbulent vertical mixing. Together with frequently low windspeed, this leads to a limited height extension of the nocturnal boundary layer (NBL), i.e., the layer that is interacting with the surface through turbulent mixing. The regularly observed depletion of COS during night time was thus indicative of the existence of a strong regional nocturnal net sink.

The impact of lichens on the local COS budget compared to different compartments of the Hastings ecosystems is compiled by Kuhn et al. (1999). The authors concluded that, under optimal conditions, lichens represent a substantial sink strength beside the soil and the vegetation of the Hastings ecosystem. In contrast to more humid coastal regions, the physiological activity at Hastings is restricted almost entirely to the rainy months in winter (Matthes-Sears et al., 1986). Rain, dewfall and fog are the main moisture sources for the lichens. Though representing an important sink during the wet seasons, lichens cannot be considered to play a substantial role in the COS exchange in summer, when they rarely reach the minimum thallus-water content needed for a significant gas exchange. Taking into account the ranges of COS deposition found during the field experiments at Hastings, we may estimate the overall sink strength for this region. The biomasses of the most abundant lichen species R. menziesii and U. spec. in the Hastings reservation amount to 75.4 g m<sup>-2</sup> (Boucher and Nash III, 1990). The dry-weight-based exchange rates reported here, range between 0.015 and 0.071 pmol  $g^{-1} s^{-1}$ . For a calculation of the hours of total physiological activity, which depends mostly on the moisture content of the lichens, we took into account the seasonal and annual gross photosynthetic activity estimated by Matthes-Sears and Nash III (1986) for the lichens at the Hastings reservation and divided those values by a mean value of CO<sub>2</sub> uptake of  $4 \text{ mg CO}_2 \text{ g}^{-1} \text{ h}^{-1}$ , i.e. 50% of the maximum uptake rate measured under laboratory conditions (Matthes-Sears et al., 1987). COS is taken up also under dark conditions, only depending on the lichen moisture content. As the lichens are wetted by rain or dew, but will dry out early in

# Table 3

Ranges of estimated COS uptake in g ha<sup>-1</sup> a<sup>-1</sup> during the dry and rainy seasons for three consecutive years based on physiological data of gross photosynthetic CO<sub>2</sub> uptake according to Matthes-Sears and Nash III (1986). For details see discussion in the text

_	Dry season	Rainy season	Annual total
1981	1-5	4-21	5-26
1982	2-8	5-22	5-29
1983	2-11	6-29	8-40
Average	2-8	5-24	7–32

the morning under sunlight conditions, the time of general physiological activity is much higher than that of photosynthetic activity. Therefore, we multiplied the hours of photosynthetic activity by a factor of 4 (e.g. 8 h of dark activity following evening dewfall and 2 h activity in the light of the following day) to reach the total hypothetical physiological activity. This way, the estimates for the total annual COS uptake by the lichen biomass at the Hastings reservation ranges between 5 and 40 g ha<sup>-1</sup> a<sup>-1</sup> depending on the minimum/maximum rate of the determined COS uptake rates (Table 3). The predominant uptake occurs not in summer but in the rainy season under optimal conditions due to frequent rain and/or dewfall. This total annual range is in close accordance with the budget calculation by Gries et al. (1994), who calculated a COS uptake rate of 17-40 g  $ha^{-1}a^{-1}$  for this type of ecosystem based on laboratory COS exchange data.

Extrapolation to a global estimate of lichen COS uptake is impossible at this time. To our knowledge there are no estimates for global lichen biomass, although Ahmadjian (1995) claims approximately 8% of the earth's terrestrial surface is dominated by lichens. More importantly, physiological activity patterns of lichens in relation to environmental variables is known for relatively few locations (Kappen, 1988; Nash III, 1996). Nevertheless, taking into account all the lichen mats of the arctic and subarctic, all the forests with abundant lichen epiphyte biomass and all the open rock and soil surfaces covered by lichens, one can begin to build a case for lichens being important in the global COS budget. On global and regional scales, missing sinks for COS are often discussed in the literature. Intriguingly two examples occurred over regions where lichen dominant ecosystems are abundant. Johnson et al. (1993) documented an unexplained 19% reduction in ambient COS mixing ratios along a path immediately west of Hudson Bay, Canada, a region where Kershaw (1978, 1985) has investigated many lichen dominated ecosystems. According to Fried et al. (1993), peat, mosses and vascular plants were not sufficient to account for the observed depletion. The

second example is from Thornton et al. (1996), who documented a similar COS depletion in trophospheric air masses passing across arctic and subarctic regions of northeastern Siberia. Because of the abundance of lichens in such northern ecosystems, it would be interesting in the future to document the degree to which lichen mats in such ecosystems can assimilate COS.

# Acknowledgements

We acknowledge the fundamental support by the Max Planck Society and the additional financial supports by the Bundesminister für Bildung und Forschung (BMBF) as a project within the section "Biosphere Atmosphere Exchange (BIATEX)" of the European Environmental Program EUROTRAC and by the Deutscher Akademischer Austauschdienst (DAAD). The junior authors (T.H.N. and C.G.) also acknowledge support by the U.S. National Science Foundation (NSF) grant BSR-89-07405. We thank all people at the Hastings Natural History Reservation, especially Dr. M. Stromberg for the use of their facilities. Furthermore, we are grateful to K. Stevens, Salinas, CA, for his effort to deliver gases on short notice.

#### References

- Ahmadjian, V., 1995. Lichens are more important than you think. BioScience 45, 124.
- Andreae, M.O., Crutzen, P.J., 1997. Atmospheric aerosol: biogeochemical sources and role in atmospheric chemistry. Science 276, 1052–1058.
- Atkins, C.A., Patterson, B.D., Graham, D., 1972. Plant carbonic anhydrase. I. Distribution of types among species. Plant Physiology 50, 214–217.
- Badger, M.R., Price, G.D., 1994. The role of carbonic anhydrase in photosynthesis. Annual Review of Plant Physiology and Plant Molecular Biology 45, 369–392.
- Bandy, A.R., Thornton, D.C., Scott, D.L., Lalevic, M., Levin, E.E., Driedger III, A.R., 1992. A time series for carbonyl sulfide in the northern hemisphere. Journal of Atmospheric Chemistry 14, 527–534.
- Boucher, V.L., Nash III, T.H., 1990. The role of the fruticose lichen *Ramalina menziesii* in the annual turnover of biomass and macronutrients in a blue oak woodland. Botanical Gazette 151, 114–118.
- Brown, K.A., Bell, J.N.B., 1986. Vegetation the missing sink in the global cycle of carbonyl sulfide (COS). Atmospheric Environment 20, 537–540.
- Castro, M.S., Galloway, J.N., 1991. A comparison of sulfur-free and ambient air enclosure techniques for measuring the exchange of reduced sulfur gases between soils and the atmosphere. Journal of Geophysical Research 96, 15427–15437.
- Chin, M., Davis, D.D., 1993. Global sources and sinks of OCS and CS<sub>2</sub> and their distribution. Global Biogeochemical Cycles 7, 321–337.

- Crutzen, P.J., 1976. The possible importance of CSO for the sulfate layer of the stratosphere. Geophysical Research Letters 3, 73–76.
- De Mello, W.Z., Hines, M.E., 1994. Application of static and dynamic enclosures for determining dimethyl sulfide and carbonyl sulfide exchange in Sphagnum peatlands: implications for the magnitude and direction of flux. Journal of Geophysical Research 99, 14601–14607.
- Doerffel, K., 1984. Statistik in der analytischen Chemie, 3rd Edition. Verlag Chemie, Weinheim.
- Engel, A., Schmidt, U., 1994. Vertical profile measurements of carbonyl sulfide in the stratosphere. Geophysical Research Letters 21, 2219–2222.
- Fahey, D.W., Kawa, S.R., Woodbridge, E.L., Tin, P., Wilson, J.C., Jonsson, H.H., Dye, J.E., Baumgardner, D., Borrmann, S., Toohey, D.W., Avallone, L.M., Proffitt, M.H., Margitan, J., Loewenstein, M., Podolske, J.R., Salawitch, R.J., Wofsy, S.C., Ko, M.K.W., Andreson, D.E., Schoeberl, M.R., Chan, K.R., 1993. In situ measurements constraining the role of sulfate aerosols in mid-latitude ozone depletion. Nature 363, 509–514.
- Ferm, R.J., 1957. The chemistry of carbonyl sulfide. Chemical Review 57, 621–649.
- Fried, A., Klinger, L.F., Erickson III, D.J., 1993. Atmospheric carbonyl sulfide exchange in bog microcosms. Geophysical Research Letters 20, 129–132.
- Goldan, P.D., Fall, R., Kuster, W.C., Fehsenfeld, F.C., 1988. Uptake of COS by growing vegetation: a major tropospheric sink. Journal of Geophysical Research 93, 14186–14192.
- Gries, C., Nash III, T.H., Kesselmeier, J., 1994. Exchange of reduced sulfur gases between lichens and the atmosphere. Biogeochemistry 26, 25–39.
- Gries, C., Sanz, M.-J., Romagni, J.G., Goldsmith, S., Kuhn, U., Kesselmeier, J., Nash III, T.H., 1997. The uptake of gaseous sulfur dioxide in non-gelatinous lichens. The New Phytologist 135, 595–602.
- Griffin, J.T., 1977. Oak woodland. In: Barbour, M.G., Major, J. (Eds.), Terrestrial Vegetation of California. Wiley-Interscience, New York, pp. 383–414.
- Hicks, B.B., Baldocchi, D.D., Meyers, T.P., Hosker Jr., R.P., Matt, D.R., 1987. A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. Water, Air and Soil Pollution 36, 311–330.
- Hofmann, D.J., 1990. Increase in the stratospheric background sulfuric acid aerosol mass in the past 10 years. Science 248, 996–1000.
- Hofmann, U., Hofmann, R., Kesselmeier, J., 1992. Cryogenic trapping of reduced sulfur compounds using a nafion drier and cotton wadding as an oxidant scavenger. Atmospheric Environment 26A, 2445–2449.
- Huber, B., 1994. Austausch flüchtiger Schwefelverbindungen in land- und forstwirtschaftlichen Ökosystemen. Ph.D. Thesis, University of Munich.
- Johnson, J.E., Bandy, A.R., Thornton, D.C., Bates, T.S., 1993. Measurements of atmospheric carbonyl sulfide during the NASA chemical instrumentation test and evaluation project: implications for the global COS budget. Journal of Geophysical Research 98, 23443–23448.
- Kappen, L., 1988. Ecophysiological relationships in different climatic regions. In: Galun, M. (Ed.), CRC Handbook of Lichenology, Vol. 2. CRC Press, Boca Raton, pp. 37–100.

- Kappen, L., Sommerkorn, M., Schröter, B., 1995. Carbon acquisition and water relations of lichens in polar regions – potentials and limitations. Lichenologist 27, 531–545.
- Kappen, L., Schröter, B., Hestmark, G., Winkler, J.B., 1996. Field measurements of photosynthesis of umbilicarious lichens in winter. Botanica Acta 109, 292–298.
- Karrasch, M., Bott, M., Thauer, R.K., 1989. Carbonic anhydrase activity in acetate grown Methanosarcina barkeri. Archives of Microbiology 151, 137–142.
- Kershaw, K.A., 1978. The role of lichens in boreal tundra transition areas. Bryologist 81, 294–306.
- Kershaw, K.A., 1985. Physiological Ecology of Lichens. Cambridge University Press, Cambridge, UK.
- 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.
- Kesselmeier, J., Meixner, F.X., Hofmann, U., Ajavon, A.-L., Leimbach, S., Andreae, M.O., 1993. Reduced sulfur compound exchange between the atmosphere and tropical tree species in southern Cameroon. Biogeochemistry 23, 23–45.
- Kesselmeier, J., Schäfer, L., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Jacob, V., Denis, J., Fugit, J.L., Dutaur, L., Torres, L., 1996. Emission of monoterpenes and isoprene from a Mediterranean oak species *Quercus ilex* L. measured within the BEMA (Biogenic Emissions in the Mediterranean Area) project. Atmospheric Environment 30, 1841–1850.
- Kesselmeier, J., Schröder, P., Erisman, J.W., 1997. Exchange of sulfur gases between biosphere and the atmosphere. In: Borrel, P., Borrel, P.M., Cvitas, T., Kelly, K., Seiler, W. (Eds.), Transport and Chemical Transformation of Pollutants in the Troposphere Vol. 4, Biosphere–Atmosphere Exchange of Pollutants and Trace Substances. Slanina, J. (Ed). Springer, Heidelberg, pp. 176–198.
- Kesselmeier, J., Teusch, N., Kuhn, U., 1999. Controlling variables for the uptake of atmospheric carbonyl sulfide by soil. Journal of Geophysical Research 104, 11577–11584.
- Kluczewski, S.M., Brown, K.A., Bell, J.N., 1985. Deposition of (35S)-carbonyl sulfide to vegetable crops. Radiation Protection Dosimetry 11, 173–177.
- Knops, J.M.H., Nash, T.H., Schlesinger, W.H., 1996. The influence of epiphytic lichens on the nutrient cycling of an oak woodland. Ecological Monographs 66, 159–179.
- Kuhn, U., Ammann, C., Wolf, A., Meixner, F.X., Andreae, M.O., 1999. Carbonyl sulfide exchange on an ecosystem scale: soil represents a dominant sink for atmospheric COS. Atmospheric Environment 33, 995–1008.
- Lange, O.L., 1965. Der CO<sub>2</sub>-Gaswechsel von Flechten bei tiefen Temperaturen. Planta 64, 1–19.
- Lange, O.L., Kilian, E., Ziegler, H., 1986. Water vapor uptake and photosynthesis of lichens: performance differences in species with green and blue-green algae as phycobionts. Oecologia 71, 104–110.
- Lange, O.L., Tenhunen, J.D., 1981. Moisture content and  $CO_2$  exchange of lichens. II. Depression of net photosynthesis in *Ramalina maciformis* at high water content is caused by increased thallus carbon dioxide resistance. Oecologia 51, 426–429.
- Larson, D.W., 1983. Morphological variation and development in *Ramalina menziesii*. American Journal of Botany 79, 668–681.

- Larson, D.W., Matthes-Sears, U., Nash III, T.H., 1985. The ecology of *Ramalina menziesii*. I. Geographical variation in form. Canadian Journal of Botany 63, 2062–2068.
- Matthes-Sears, U., Nash III, T.H., 1986. The ecology of *Ramalina menziesii*. V. Estimation of gross carbon gain and thallus hydration source from diurnal measurements and climatic data. Canadian Journal of Botany 64, 1698–1702.
- Matthes-Sears, U., Nash III, T.H., Larson, D.W., 1986. The ecology of *Ramalina menziesii*. III. In situ diurnal field measurements at two sites on a coastal-inland gradient. Canadian Journal of Botany 64, 988–996.
- Matthes-Sears, U., Nash III, T.H., Larson, D.W., 1987. The ecology of *Ramalina menziesii*. VI. Laboratory responses of net CO<sub>2</sub> exchange to moisture, temperature and light. Canadian Journal of Botany 65, 182–191.
- Meixner, F.X., 1984. The vertical sulfur dioxide distribution at the tropopause level. Journal of Atmospheric Chemistry 2, 175–189.
- Nash III, T.H., 1996. Photosynthesis, respiration, productivity and growth. In: Nash, T.H. (Ed.), Lichen Biology. Cambridge University Press, Cambridge, pp. 88–120.
- Protoschill-Krebs, G., Kesselmeier, J., 1992. Enzymatic pathways for the consumption of carbonyl sulfide (COS) by higher plants. Botanica Acta 105, 206–212.
- Protoschill-Krebs, G., Wilhelm, C., Kesselmeier, J., 1995. Consumption of carbonyl sulfide by *Chlamydomonas reinrardtii* with different activities of carbonic anhydrase (CA) induced by different CO<sub>2</sub> growing rates. Botanica Acta 108, 445–448.
- Protoschill-Krebs, G., Wilhelm, C., Kesselmeier, J., 1996. Consumption of carbonyl sulfide (COS) by higher plant carbonic anhydrase (CA). Atmospheric Environment 30, 3151–3156.

- Rinsland, C.P., Zander, R., Mahieu, E., Demoulin, P., Goldman, A., Ehhalt, D.H., Rudolph, J., 1992. Ground-based infrared measurements of carbonyl sulfide total column abundances: long-term trends and variability. Journal of Geophysical Research 97, 5995–6002.
- Roche, A.E., 1994. Observations of lower-stratospheric CINO<sub>2</sub>, HNO<sub>3</sub> and aerosol by the UARS CLAES experiment between January, 1992, and April, 1993. Journal of Atmospheric Science 51, 2877–2902.
- Rundel, P.W., 1974. Water relations and morphological variation in *Ramalina menziesii* Tayl. Bryologist 77, 23–32.
- Schäfer, L., 1992. Untersuchungen zur Abgabe von organischen Säuren durch Pflanzen an die Atmosphäre. Diploma Thesis, Johannes Gutenberg University, Mainz.
- Simmons, J.S., Klemedtsson, L., Hultberg, H., Hines, M.E., 1999. Consumption of atmospheric carbonyl sulfide by coniferous boreal forest soils. Journal of Geophysical Research 104, 11569–11576.
- Solomon, S., Sanders, R.W., Garcia, R.R., Keys, J.G., 1993. Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mount Pinatubo. Nature 363, 245–248.
- Taylor, G.E., McLaughlin, S.B., Shriner, D.S., Selvidge, W.J., 1983. The flux of sulfur-containing gases to vegetation. Atmospheric Environment 17, 789–796.
- Thornton, D.C., Bandy, A.R., Blomquist, B.W., 1996. Impact of anthropogenic and biogenic sources and sinks on carbonyl sulfide in the North Pacific troposphere. Journal of Geophysical Research 101, 1873–1881.
- Turco, R.P., Whitten, R.C., Toon, O.B., Pollack, J.B., Hamill, P., 1980. OCS, stratospheric aerosols and climate. Nature 283, 283–286.