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Exchange of reduced sulfur gases between lichens and the atmosphere

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Abstract. Fourteen lichens, 10 green algal lichens and four cyanolichens, as well as a cyanobacterium emitted significant quantities of H_2S (0.01–0.04 pmol g dw^{-1} s^{-1}) and DMS (0.005–0.025 pmol g dw^{-1} s^{-1}), but were sinks for COS (0.015–0.14 pmol g dw^{-1} s^{-1}). In contrast, exchange of CH_3SH and CS_2 were sporatic and inconsistent. Although some interspecific variation occurred for the first three gases, exchange rates were relatively uniform and were not influenced by irradiance conditions. In contrast to DMS and H_2S emission, COS uptake was strongly influenced by degree of thallus hydration. Because lichen dominated systems cover extensive terrestrial habitats, COS uptake is potentially important in the world's sulfur budget.

Introduction

It is well accepted that higher plants are involved in the atmospheric sulfur cycle. Both, uptake and emission of volatile reduced sulfur compounds by plants have been identified (Taylor et al. 1983; De Kok et al. 1989, 1991; Rennenberg et al. 1990; Kesselmeier 1991; Kesselmeier et al. 1992, 1993). Recent estimates of total natural sulfur emissions including the share of plants and soils with 4–15 Tg S a^{-1} range around 65 (±25) Tg S a^{-1} (Andreae & Jaeschke 1992), which is equivalent to estimates of man-made sulfur emissions of 93 ± 15 Tg S per year (Cullis & Hirschler 1980). Due to differences in residence times (Warneck 1988), two groups of reduced sulfur compounds are recognized. One group contains the more labile compounds such as hydrogen sulfide (H_2S), methylmercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3, DMS) and carbon disulfide (CS_2), and the other group contains only the most stable compound carbonyl sulfide (COS) with a residence time in the atmosphere between 1 and 2 years. With the exception of CS_2, which is partly (50%) oxidized to COS, the labile compounds are mainly removed from the atmosphere by oxidization to SO_2 and sulfate, and thus brought back to the surface by dry and wet deposition. COS, the most abundant sulfur gas in the atmosphere and relatively inert in the troposphere, is transported into the stratosphere where photodissociation and photooxidation occurs. It is

believed to be the major source of stratospheric background sulfur aerosol ('Junge-layer'; Crutzen 1976; Turco et al. 1980; Hofmann 1990). Therefore, the understanding and quantification of its sources and sinks are of considerable importance.

COS has been shown to be a major sulfur compound emitted from vegetation (Lamb et al. 1987; Guenther et al. 1989). Other studies show that it is taken up by vegetation (Kluczewski et al. 1985; Brown et al. 1986; Brown & Bell 1986; Fall et al. 1988; Goldan et al. 1988). A few field studies support the deposition of COS (Goldan et al. 1987; Mihalopoulos et al. 1989; Hofmann et al. 1992; Bartell et al. 1993) and another found no evidence of COS uptake (Berresheim & Vulcan 1992). The principal problems in interpreting these experimental studies are the gaps in our knowledge on the production and consumption of the sulfur gases by vegetation and the use of purified air as an artificial environment in some studies may result in emission instead of deposition (Klesselmeier et al. 1993, Kesselmeier & Merk 1993). Such data may be partly responsible for the considerable uncertainties which still exist for the exchange of sulfur compounds (Andreae & Jaeschke 1992; Chin & Davis 1993).

As shown above, though insufficient, there are data on the exchange of reduced sulfur compounds between higher plants or soils and the atmosphere. Mosses, algae, fungi and symbionts like lichens may also play significant roles in some environments. The role of algae in the case of oceanic phytoplankton is quite well known (see Andreae & Jaeschke 1992). No such data exist for fungi and lichens, though these organisms may be of significant relevance for some ecosystems. For example lichens are dominant autotrophs in a number of coastal deserts (Kappen 1988) and polar systems (Longton 1988) and are major components as epiphytes in some forests (Boucher & Nash 1990). It may be assumed that they significantly influence the exchange of trace gases. This is especially true, as the lack of stomates and cuticles prevents a biological control of uptake and emission of gases. Compared to higher plant leaves most lichen species expose large surface areas per dry weight to the atmosphere. In a first approach, we investigated several lichen species for their uptake of reduced sulfur gases from ambient air or emission into ambient air. CO_2 gas exchange was measured in parallel to verify the physiological activity of the lichens and to allow assessment of potential relationships between trace sulfur gas exchange and CO_2 gas exchange as suggested by Protoschill-Krebs & Kesselmeier (1992).

Materials and methods

Materials

Experiments were conducted with 14 lichen species: 10 containing green algae as photobiont (*Cladonia rangiferina* (L.) Wigg., *Cladonia furcata* (Huds.)

Schrader, *Cladonia glauca* Flörke *Evernia prunastri* (L.) Ach., *Flavoparmelia caperata* (L.) Hale, *Hypogymnia physodes* (L.) Nyl., *Lobaria oregana* (Tuck.) Müll. Arg., *Parmelia sulcata* Tayl., *Pseudevernia intensa* (Nyl.) Hale and *Ramalina menziesii* Tayl.) and 4 cyanolichens (*Collema auriforme* (With.) Coppin & Laundon, *Peltigera collina* (Ach.) Schrad., *Peltigera praetextata* (Flörke *ex* Sommerf.) Zopf and *Pseudocyphellaria anthraspis* (Ach.) Magn.) In addition, the cyanobacterium, *Nostoc commune* L. was studied. The lichens were collected May, June and July 1993 (Table 1). Voucher specimens are deposited in the Arizona State University Harbarium (ASU).

Table 1. Collecting locations for specimens.

Species	collecting location
Cladonia rangiferina & *Lobaria oregana*	USA: southern Alaska: Tongass National Forest, Stikine Area
Pseudocyphellaria anthraspis & *Ramalina menziesii*	USA; California: Monterey County, Hastings National History Reservation on *Quercus chrysolepis* and *Q. lobata*
Pseudevernia intensa	USA: Arizona: Pima County, near the top of the SantaCatalina Mountains, on *Pseudotsuga*
Peltigera collina	Germany: Baden-Württemberg: Schwäbisch-Fränkischer forest near Gaildorf in Osterbachtal on *Quercus*
Cladonia furcata & *Nostoc commune*	Germany: Baden-Württemberg: Schwäbische Alb, ca. 10 km S of Urach on limestone
Cladonia glauca & *Flavoparmelia caperata* & *Parmelia sulcata*	Germany: Hessen: 15 km E of Lorch in Wispertal
Collema auriforme & *Hypogymnia physodes*	Germany: Hessen: top of ridge above Östrich near Herberge
Evernia prunastri	Germany: Hessen: 20 km E of Lorch in Wispertal, on roadside *Acer*
Peltigera praetextata	Germany: Rheinland Pfalz: 7 km N of Altstrimmig in a side valley of the Mosel River

Prior to trace sulfur gas measurements, the lichens were thoroughly cleaned. Any adhering plant material or soil was taken and washed off the thallus. Thereafter the lichens were maintained in a growth chamber with a 18 h day: 6 h night cycle, a photoperiod chosen to match the southern Alaskan habitat and to approximate that of the German collections. Light conditions were maintained at 300 µmol photons m^{-2} s^{-1} at 23 °C and a relative humidity of 70% and dark conditions at 18 °C and 75% relative humidity.

Sampling and analytical procedure for reduced sulfur gases and CO_2

An open flow-through system with two plexiglass cuvettes, similar to one employed by Lange & Redon (1983), was used. One chamber contained lichen material and the other was used as a reference. The system involved precise monitoring of air flow (1 l min^{-1}) with mass flow controllers (Walz Minicuvette system) through the two plexiglass cuvettes submerged in a temperature constant waterbath at 15 °C. With the light source turned on above the waterbath the air temperature inside the cuvettes was 16 °C and the thallus temperature was 16.5 °C. High air humidity in the air stream was achieved by leading the air through a washbottle and a measuring gas cooler (Walz) set at a dew point of 14 °C. This maintained the water content of the specimens at 150 to 200% for most species, but 220–280% for *Peltigera*, 350–380% for *Collema*, 1900–2100% for *Nostoc*, during measuring cycles of up to six hours. The setup allowed to measure CO_2 gas exchange simultaneously with collection of trace sulfur gases. CO_2 concentration was determined continuously with an infrared gas analyzer (Binos 100, Leybold-Heraeus, Hanau), employed in the differential mode (measuring sampling air vs. reference air stream). The gas analyzer was calibrated against certified standards. Net photosynthesis was measured under a 12V/75W light source (Walz) above the water bath, which resulted in 520 µmol photons m^{-2} s^{-1} within the cuvettes (170 µmol photons m^{-2} s^{-1} for *Peltigera* using gray filters). All measurements were stored in a data logger (Walz Minicuvette system) and subsequently processed with software programs on an IBM compatible computer.

For measurement of trace sulfur gases air samples were taken directly from the outlet ports of the gas exchange chambers at a flow rate of 100 ml/min. For precise sampling, mass flow controllers (100 and 500 ml min^{-1}, MKS Instruments, Germany) were used on the sampling lines from the two cuvettes. The samples were dried by commercialy available Nafion driers (Model 125, Permapure) and trace sulfur gases including CH_3SH, COS, CS_2, CH_3SCH_3 (DMS) and H_2S were cryogenically trapped into glass traps (volume ca. 25 ml) submerged in liquid argon (Hofmann et al. 1992).

Quantification in the pptv range of these gases (Hofmann et al. 1992) was accomplished with standard gas chromatography procedures. After calibrating the GC (DI200, Delsi France) with different-sized sample loops, where the calibration gases were obtained from permeation tubes (VICI Metronics, USA) incubated continuously at 30 °C in a thermally controlled (±0.1 °C) permeation device (Haunold, Frankfurt, Germany). Calibration was checked each day and performed approximately every three weeks. The GC was equipped with a flame photometric detector (Alementation FPD7, Delsi, France), had a column packed with Carbopack B/XE 60/H_3PO_4, and utilized He as carrier for the sulfur gases (flow rate 30 ml/min) and an H_2/air flame for combusting the gases at the site of the photodetector. Separation of the gases was achieved by increasing the operation temperature of the GC from –5 °C to 85 °C at 25 °C per minute. Processing and storage of data (peak heights, areas, etc.)

and calculation of concentrations according to calibration was accomplished by interfacing the GC with an MSDOS PC equipped with a GC analysis software (ELAB, OMS Tech, Miami, USA).

Ambient air was used for flushing the cuvettes. This resulted in fluctuations of actual mixing ratios for COS between 550 and 1100 pptv, for CS_2 between 100 and 400 pptv, and for DMS between 0 and 40 pptv. We are aware of possible influences on the exchange rates because of compensation points for these trace gases (Kesselmeier & Merk 1993). The present study was done for screening, influences of the compensation point will be subject of further studies.

Results

Overall patterns and interspecific variation

Essentially all lichens and the cyanobacterium evolved substantial quantities of H_2S and DMS, but took up COS (Figs. 1–3). When expressed on a dry weight basis the highly gelatinous cyanobacterium evolved the largest amounts of H_2S and DMS, reaching respectively almost 0.03 and 0.025 pmol g dw^{-1} s^{-1}. In contrast, the green algal lichens took up the most COS with several species taking up 0.06–0.1 pmol g dw^{-1} s^{-1} and *P. intensa* reaching almost 0.15 pmol g dw^{-1} s^{-1} (or 1.92–3.2 and 4.8 pg (S) g dw^{-1} s^{-1}, respectively). The surface area per gram dry weight ratio in these lichen species ranges from 45 cm^2 g dw^{-1} ± 6 s.d. in *Cladonia furcata* to 99 cm^2 g dw^{-1} ± 2 s.d. in *Evernia prunastri*. Accordingly, COS uptake expressed on the basis of thallus surface area ranges from 7 to 18 pmol m^{-2} s^{-1} (or 0.22–0.58 ng (S) m^{-2} s^{-1}). The other trace sulfur gases only occurred sporatically and rarely in concentrations substantially above detection limits (and hence are not plotted). Photosynthesis rates did not strongly correlate with trace sulfur exchange, but at least with the green algal lichens the highest evolution of H_2S occurred in the species with lower photosynthetic rates.

Within the lichen groups some interspecific variation was found based on Tukey's studentized range (hsd) comparisons. Among the green algal lichens *C. rangiferina* and *R. menziesii* emitted more H_2S than the other species (Fig. 1). *Lobaria oregana* also emits high quantities of H_2S, but the variability was so high that statistical differences with other species could not be detected. For COS uptake, *C. rangiferina* exhibited lower rates than all other species; and *P. intensa*, higher rates than all other species. For DMS essentially no significant differences were found, although *L. oregana* could be distinguished from *P. sulcata*. Among the cyanolichens (Fig. 2) H_2S emission was greater in *Collema* than the other three species. For COS *P. collina* exhibited higher uptake than either *Collema* or *P. praetextata*, but was indistinguishable from *Pseudocyphellaria*. No significant differences were found among the DMS emissions.

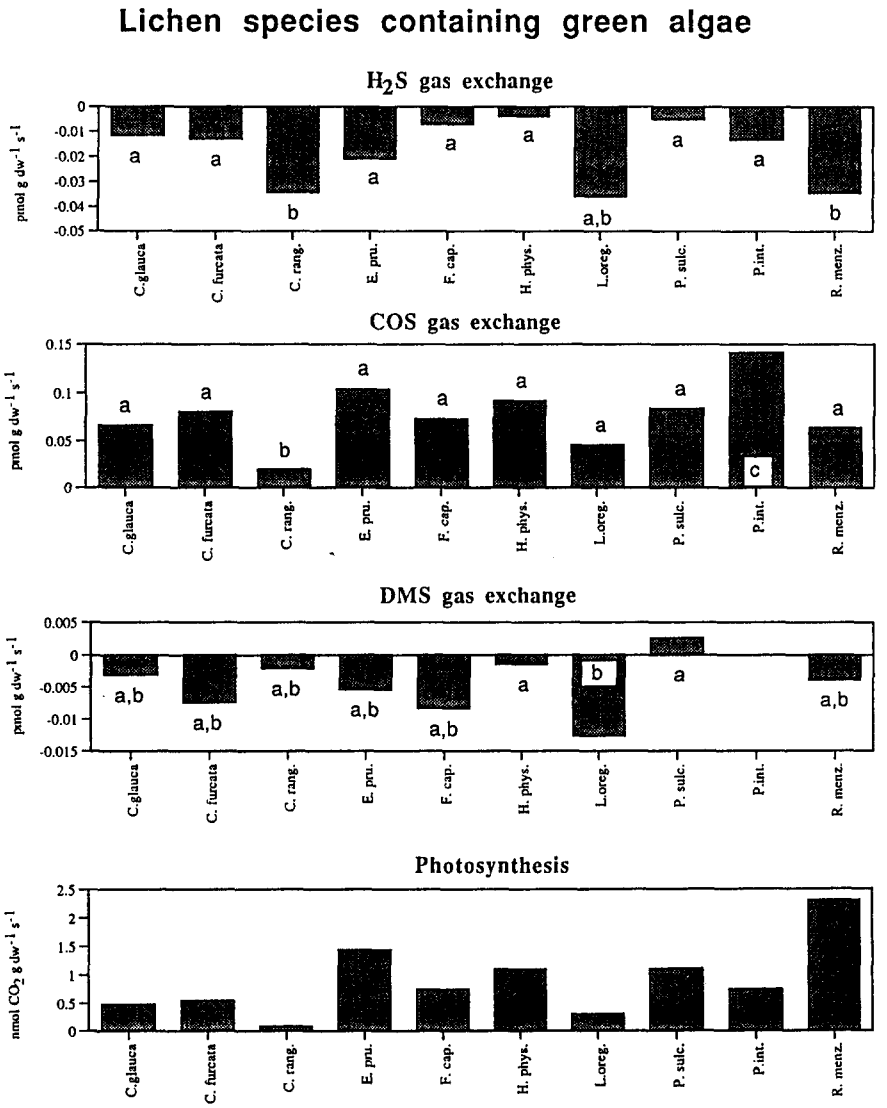


Fig. 1. Mean gas exchange (n = mostly 3, in pmol gdw^{-1} s^{-1}) of H_2S, COS and DMS of 10 green algal lichens at 15 °C under 520 µmol photons m^{-2} s^{-1} over a water content range of 150–200%. Means, which are not significantly different from each other as determined by Tukey's studentized range (hsd) for multiple comparisons, are indicated with the same letter (e.g. a, etc.).

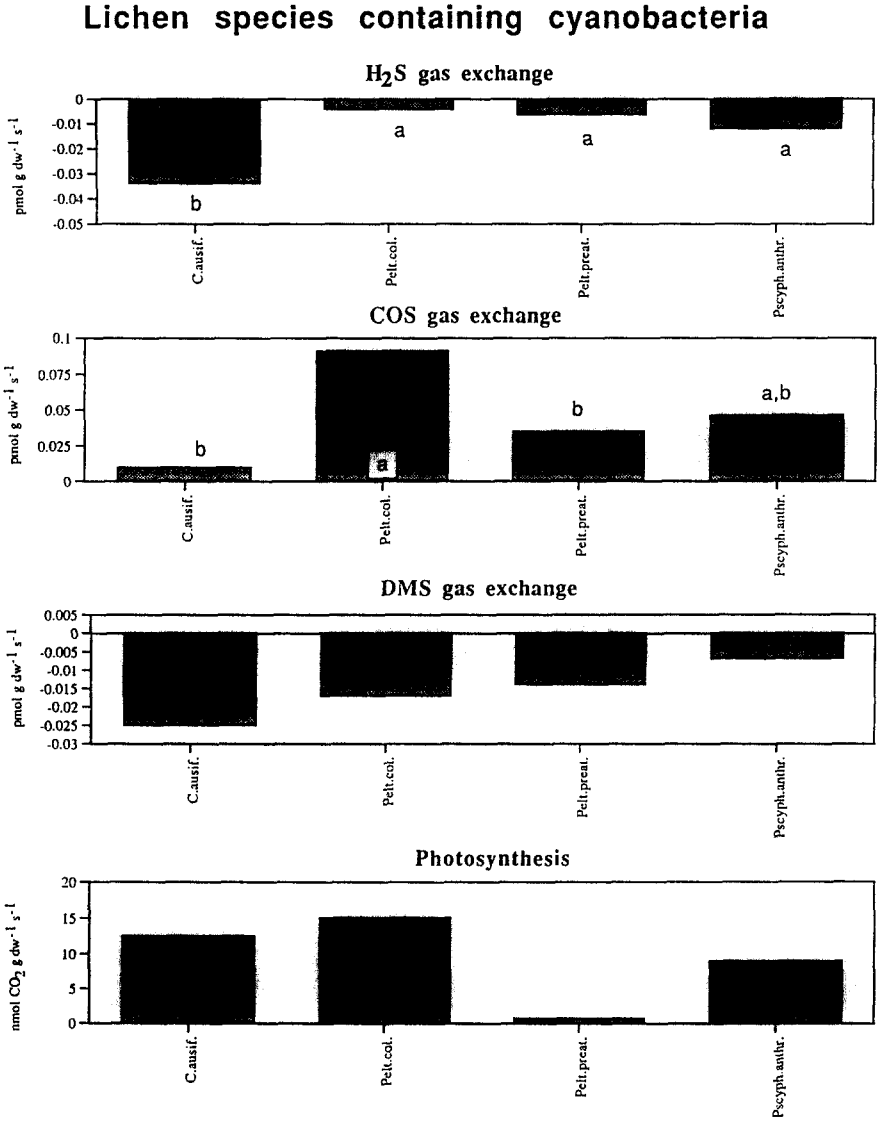


Fig. 2. Mean gas exchange (n = mostly 3, in pmol gdw^{-1} s^{-1}) of H_2S, COS and DMS of four cyanolichens at 15 °C under 170 (*Peltigera* spp.) or 520 µmol photons m^{-2} s^{-1} over a water content range of 170–200% (*Pseudocyphellaria*), 220–280% (*Peltigera* spp.), 350–380% (*Collema*). Means, which are not significantly different from each other as determined by Tukey's studentized range (hsd) for multiple comparisons, are indicated with the same letter (e.g. a, etc.). None of the DMS means were significantly different.

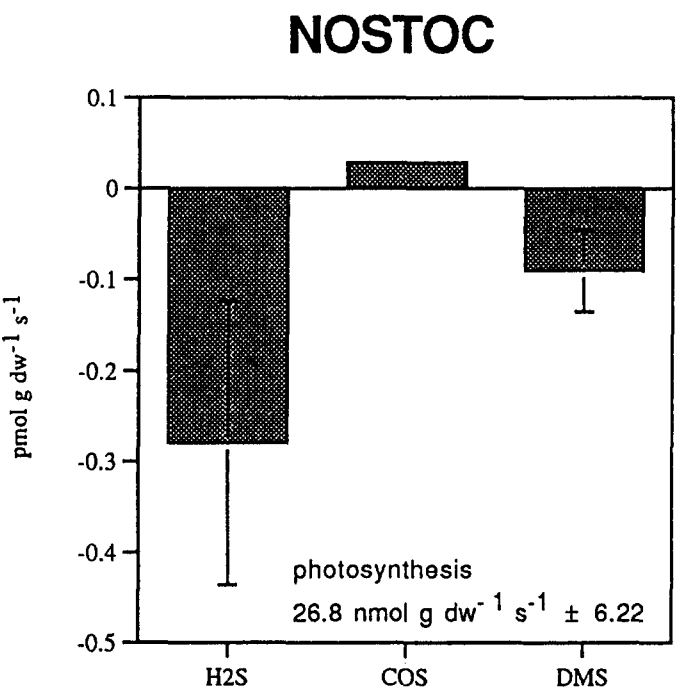
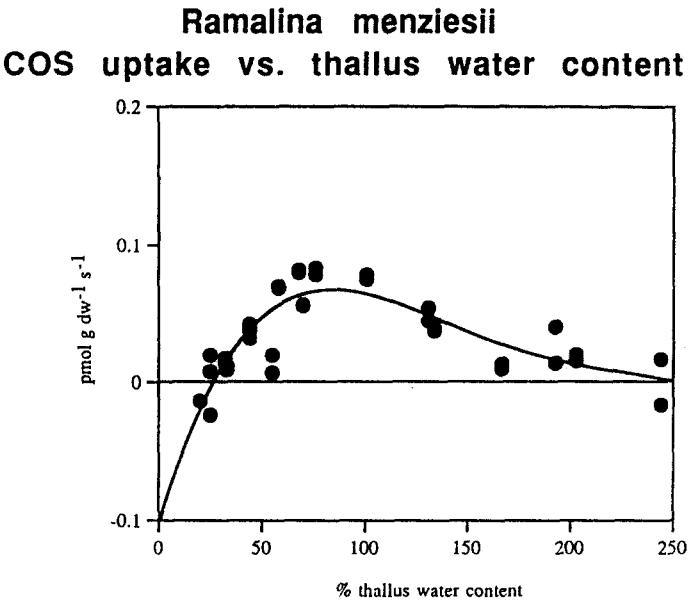


Fig. 3. Mean gas exchange (n = 3, in pmol gdw^{-1} s^{-1}) of H_2S, COS and DMS of the cyanobacterium *Nostoc commune* at 15 °C under 520 µmol photons m^{-2} s^{-1} over a water content range of 1900–2100%. Confidence intervals (vertical line) are ±1 standard deviation.

Patterns in relation to thallus water content and light regime

Both photosynthesis and COS uptake are strongly influenced by the hydration status of the lichens (Figs. 4 & 5). At very low water contents no uptake occurs, but as water content values increase above the 20–30% range COS uptake increases markedly until maximal rates in the 60–100% range occur. However, at the higher water contents, above 150%, COS uptake declines markedly, as does photosynthesis in the case of *R. menziesii*. For the other gases no obvious trends with water content (data not shown) were found, although slightly higher emissions may occur at the higher water contents.

For all the gases remarkably similar emission (or uptake in the case of COS) rates were found in the light versus dark for all 7 species (*C. furcata, C. glauca, E. prunastri, F. caperata, H. physodes, P. sulcata and P. collina*) tested. No significant differences (t-test) were found; the most extreme t-value calculated had an associated probability of 0.17.



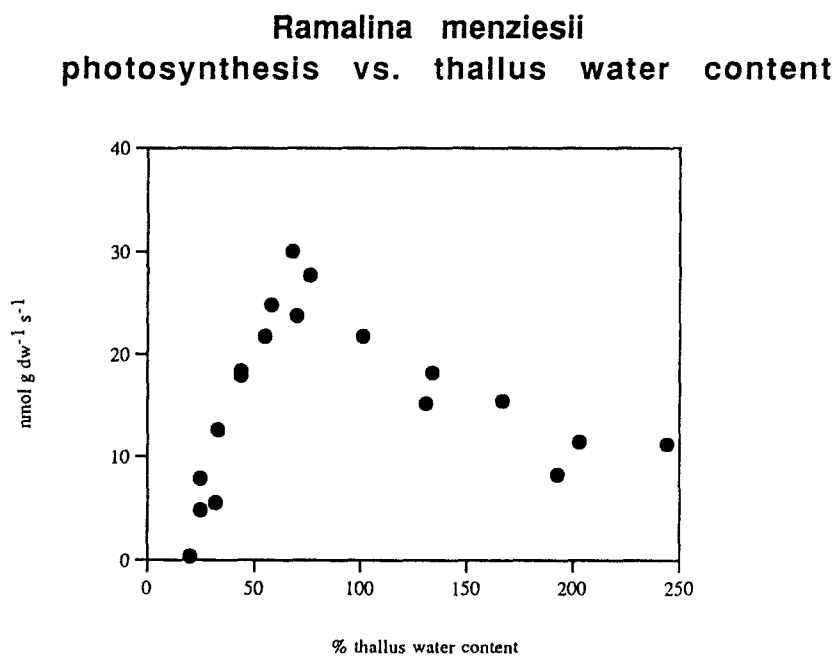


Fig. 4. The relationships of COS and CO_2 gas exchange to thallus water content in *Ramalina menziesii* under 520 µmol photons m^{-2} s^{-1} at 15 °C. A fourth order polynomial equation is fitted to the curve (r^2 = 0.727).

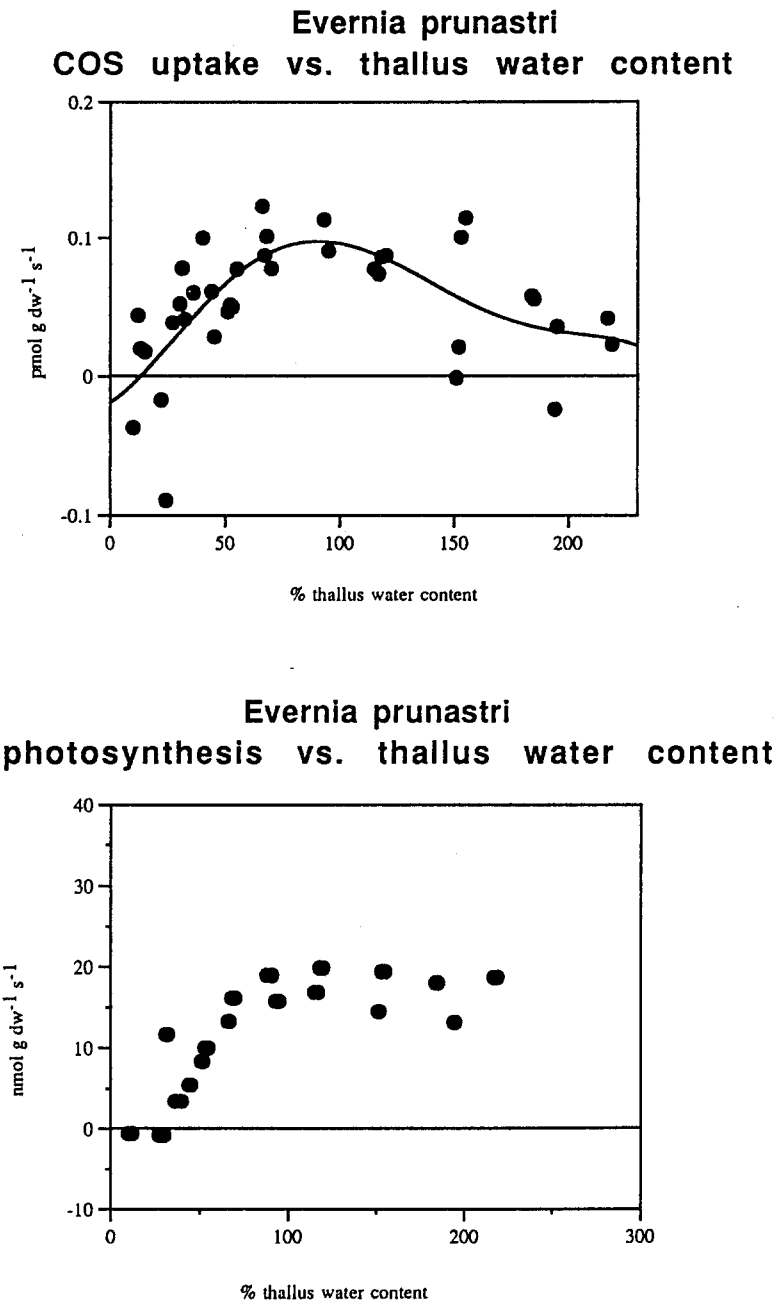


Fig. 5. The relationships of COS and CO_2 gas exchange to thallus water content in *Evernia prunastri* under 520 µmol photons m^{-2} s^{-1} at 15 °C. A fifth order polynomial equation is fitted to the curve (r^2 = 0.447).

Discussion

To our knowledge this is the first study on the exchange of volatile reduced sulfur compounds between lichens and the atmosphere. Clearly under the experimental conditions employed all lichens collected from relatively pristine field sites emitted significant quantities of H_2S and DMS and were sinks for large quantities of COS. The strong dependence of COS uptake on thallus water content, a pattern strongly paralleling CO_2 uptake by RUBISCO, provides circumstantial evidence that the process is under metabolic control within the lichen. In contrast, the lack of dependency of H_2S or DMS emission on thallus water content implies either a lack of physiological control or processes centered within the surficial fungal tissue. The physiological basis for COS uptake by the lichen is not fully understood, but it should be at least partly related to the carbonic anhydrase system in the chloroplast of the photobiont as proposed for higher plants (Protoschill-Krebs & Kesselmeier 1992). In vascular plants carbonic anhydrase is a light independent enzyme either regulating the CO_2/HCO_3^- equilibrium in aqueous systems or splitting COS to CO_2 and H_2S. Carbonic anhydrase is a widespread enzyme found in higher plants as well as in algae, cyanobacteria and animal tissue (Chengelis & Neal 1980; Lamb 1977; Maren 1967; Poincelot 1979; Tsuzuki et al. 1985; Tsuzuki & Miyachi 1989). Thus, this enzyme system might be also responsible for the consumption of COS by a lichen through fungal or algal carbonic anhydrase. An enhancement under light conditions should then only be observed if the lichen species is more dominated by the algal partner, leading to a more intensive consumption of CO_2 by the photosynthetic pathways and thus accelerating the equilibrium. Such an interpretation is in accordance with the model of Protoschill-Krebs & Kesselmeier (1992).

The uptake of COS ranged between 0.02 and 0.14 pmol g^{-1} dw s^{-1} (or 7 and 18 pmol m^{-2} s^{-1}). These data are in the range of those found for higher plants (see Table 2). In contrast to higher plants, all lichen species showed a nearly permanent uptake of COS in the dark as well as in the light, depending only on the moisture content and thus the physiological activity. In part this may be explained by the fact that gas assimilation is not under stomatal control in lichens. Lichens lack both stomates and the cuticle found in most vascular plant leaves, and therefore absorb gases over their entire surface.

Lichens as a potential COS sink had not been documented heretofore. Thus our results may have implications for the global COS budget estimates and may partly explain a recently observed 19% COS depletion in air masses originating from boreal to arctic regions of central and northern Canada and traveling for at least 2000 km across tundra and transitional forest (Johnson et al. 1992; The National Atlas of Canada 1993) in central and northern Canada along the west coast of Hudson Bay. The sudden decrease of COS concentrations in these air masses implies that a large unknown sink of COS exists in this region with extensive lichen dominated communities (Kershaw 1985). Studies by Fried et al. (1993) with bog microcosms showed that peat,

Table 2. Sulfur-compound exchange on a leaf area basis of some higher plants, crops and trees.

Higher Plants	[pmol m^{-2} s^{-1}] S-Species and Flux Direction
Corn (*Zea mays*)	2.6–21* COS uptake[1], light
Rapeseed (*Brassica napus*)	13–21* COS uptake[1], light
Peas (*Pisum sativum*)	1.7–26* COS uptake[1], light
Corn (*Zea mays*)	7# DMS emitted[2], light
	3# DMS emitted[2], light
Alfalfa (*Medicago sativa*)	2.3# DMS emitted[2], light
	0.7# DMS emitted[2], dark
	0.2# H_2S emitted[2], dark + light
	0.6# CH_3SH emitted[2], light
	0.2# CG_2SH emitted[2], light
Spruces (*Picea abies*)	0.6±0.04 †H_2S emitted[3], light
	0.3±0.05 †H_2S emitted[3], dark
Tropical Trees	
Saccoglottis gabonensis (young tree)	10±4.5[$] DMS emitted[4], light
Saccoglottis gabonensis (old tree, canopy top)	90±80[$] DMS emitted[4], light
Porterandia cladantha	0.6±0.2[$] DMS emitted[4], light
	2.6±1.4[$] CH_3SH emitted[4], light
Forest and cropland	0.4–12 (S)[@,†]DMS, H_2S, COS emitted[5]

[1] Kesselmeier and Merk (1993); [2] Fall et al. (1988); [3] Rennenberg et al. (1990); [4] Kesselmeier et al. (1993); [5] Bates et al. (1992). * depending on light; # after adaptation switched from dark to light and *vice versa*; † cuvette flushed with S-free air; [$] emission observed between 10:00 and 16:30 local time, Cameroon; [@] assuming a leaf area index of 4–12 for croplands or forests.

mosses and vascular plants within this bog system cannot account for such a large sink. If we do not assume that trees within the boreal ecotypes are specialists for the consumption of COS, why not assume that lichens may play a major role, especially as, if they are wet, they may act as an excellent sink independent from light triggered activities? Calculations on the basis of data from Moser et al. (1983) for biomass per area ground surface (*C. rangiferina*: 310 g dw m^{-2}) and hours the lichens had a water content above 50% in 1978 at Anaktuvuk Pass, Alaska, (311 hours per season) we estimate an annual COS uptake by *Cladonia rangiferina* of 1.32 µg COS gdw^{-1} a^{-1} or 0.42 mg COS m^{-2} ground surface a^{-1}. *C. rangiferina* represents here about 23% of the total biomass. Since *C. rangiferina* takes up significantly less COS than the other *Cladonia* species tested we estimated an annual COS uptake of approximately 6.0 mg COS m^{-2} a^{-1} for the area of consideration in Canada. This takes into account the hours during which the lichens are active, an average COS uptake for *Cladonia* and a biomass of *Cladonia* species of 1.1 to 1.4 kg m^{-2} found in many arctic regions.

Similar estimates can be made for *Ramalina menziesii* growing as epiphytes in blue oak (*Quercus douglasii*) woodlands occupying ca. 6.5% of California

along the Pacific coast (Boucher & Nash 1990). Biomass of *R. menziesii* amounts to 706 kg ha^{-1} and hours during which they are active are approximately 1852 per year (Nash & Knops unpubl.) for a location 40 km inland from Monterey and up to 4380 along the coast. Therefore, the COS uptake ranges from 17 g COS ha^{-1} a^{-1} to 40 g COS ha^{-1} a^{-1} (or 1.7–4 mg COS m^{-2} a^{-1}) for *R. menziesii* in California. Obviously, these numbers are uncertain as long as no data of field measurements exist. However, they may be used as an initial estimate.

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References

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

Bartell U, Hofmann U, Hofmann R, Kreuzburg B, Andreae MO & Kesselmeier J (1993) COS and H_2S fluxes over a wet meadow in relation to photosynthetic activity: An analysis of measurements made on 6 September 1990. Atmosph. Environ. 27A: 1851–1864

Bates TS, Lamb BK, Guenther A, Dignon J & Stoiber RE (1992) Sulfur emissions to the atmosphere from natural sources. J. Atmos. Chem. 14: 315–337

Berresheim H & Vulcan VD (1992) Vertical distribution of COS, CS_2, DMS and other sulfur compounds in a loblolly pine forest. Atmos. Environ. 26A: 2031–2036

Boucher, VL & Nash III TH (1990) The role of the fruticose lichen *Ramalina menziesii* in the annual turnover of biomass and macronutrients in a blue oak woodland. Bot. Gaz. 150: 114–118

Brown KA & Bell JNB (1986) Vegetation – the missing sink in the global cycle of COS. Atmos. Environ. 20: 537–540

Brown KA, Kluczewski SM & Bell JNB (1986) Metabolism of [^{35}S]-carbonyl sulphide in perennial ryegrass (*Lolium perenne* L.) and radish (*Raphanus sativus* L.) Environ. Exp. Bot. 26: 355–364

Chengelis CP & Neal RA (1980) Studies of carbonyl sulfide toxicity: Metabolism by carbonic anhydrase. Toxicol. Appl. Pharmacol. 55: 198–202

Chin M & Davis DD (1993) Global sources and sinks of OCS and CS_2 and their distributions. Global Biogeochem. Cycles 7: 321–337

Crutzen PJ (1976) The possible importance of COS for the sulfate layer of the stratosphere. Geophys. Res. Lett. 3: 73–76

Cullis CF & Hirschler MM (1980) Atmospheric sulfur: Natural and man-made sources. Atmos. Environ. 14: 1263–1278

De Kok LJ, Stahl K & Rennenberg H (1989) Fluxes of atmospheric hydrogen sulphide to plant shoots. New Phytol. 112: 533–542

De Kok LJ, Rennenberg H & Kuiper PJC (1991) The internal resistance in spinach leaves to atmospheric H_2S deposition is determined by metabolic processes. Plant. Physiol. Biochem. 29: 463–470

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

Fried A, Klinger LF & Erickson III DJ (1993) Atmospheric carbonyl sulfide exchange in bog microcosms. Geophys. Res. Lett. 20: 129–132

Goldan PD, Kuster WC, Albritton DL & Fehsenfeld FC (1987) The measurement of natural sulfur emissions from soil 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 COS uptake of growing vegetation. A major tropospheric sink. J. Geophys. Res. 93: 14186–14192

Guenther A, Lamb B & Westberg H (1989) US national biogenic sulfur emissions inventory. In: Saltzman ES & Cooper WJ (Eds) Biogenic Sulfur in the Environment (pp 15–30). American chemical Society, Washington DC

Hofmann DJ (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 under the influence of a NAFION dryer and cotton wadding as an oxidant scavenger. Atmos. Environ. 26: 2445–2449

Johnson JE, Bandy AR, Thornton DC & Bates TS (1993) Measurements of atmospheric carbonyl sulfide during the NASA CITE-3 project: implications for the global COS budget. J. Geophys. Res. 23443–23448

Kappen L (1988) Ecophysiological relationships in different climatic regions. In: Galun M (Ed) Handbook of Lichenology, Vol II (pp 37–100) CRC Press, Boca Raton, USA

Kershaw KA (1985) Physiological Ecology of Lichens. Cambridge University Press, Cambridge, UK

Kesselmeier J (1991) Emission of sulfur compounds from vegetation and global scale extrapolation. In: Sharkey TD, Holland EA & Mooney HA (Eds) Trace Gas Emissions from plants (pp 261–265) Academic Press, San Diego, USA

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 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, Reserve de Campo, Cameroun (pp 247–263)

Kesselmeier J, Meixner FX, Hofmann U, Ajavon A, Leimbach St & Andreae MO (1993) Reduced sulfur compound exchange between the atmosphere and tropical tree species in southern Cameroon. Biogeochemistry 23: 23–45

Kesselmeier J, Merk L, Bliefernicht M & Helas G (1993) Trace gas exchange between terrestrial plants and atmosphere: Carbon dioxide, carbonyl sulfide and ammonia under the rule of compensation points. In: Slanina J, Angeletti G & Beilke S (Eds) General assessment of

biogenic emissions and deposition of nitrogen compounds, sulphur compounds and oxidants in Europe, CEC Air Pollution Research Report 47 (pp 79–88). E. Guyot, Brussels

Kluczewski SM, Brown KA & Bell JNB (1985) Deposition of [^{34}S]-carbonyl sulphide to vegetable crops. Radiat. Protect. Dosim. 11: 173–177

Lamb JE (1977) Minireview – Plant carbonic anhydrase. Life Sci. 20: 393–406

Lamb B, Westberg H, Allwine G, Bamesberger L & Guenther A (1987) Measurement of biogenic sulfur emissions from soils and vegetation: Application of dynamic enclosure methods with Natusch filter and GC/FPD analysis. J. Atmos. Chem. 5: 469–491

Lange OL & Redon J (1983) Epiphytische Flechten im Bereich einer 'Nebeloase' (Fray Jorge). II. Ökophysiologische Charakterisierung von CO_2-Gaswechsel und Wasserhaushalt. Flora 174: 245–284

Longton RE (1988) Biology of Polar Bryophytes and Lichens. Cambridge University Press, Cambridge, UK, 391 pp

Maren TH (1967) Carbonic anhydrase: Chemistry, physiology and inhibition. Physiol. Rev. 47: 595–781

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

Moser TJ, Nash III TH & Link SO (1983) Diurnal gross photosynthetic patterns and potential seasonal CO_2 assimilation in *Cladonia stellaris* and *Cladonia rangiferina*. Can. J. Bot. 61: 642–655

Poincelot RP (1979) Carbonic anhydrase. In: Gibbs M & Latzko E (Eds) Photosynthesis II, Encyclopedia of Plant Physiology. New Series Vol 6 (pp 230–238). Springer Verlag, Berlin, Heidelberg, New York

Protoschill-Krebs G & Kesselmeier J (1992) Enzymatic pathways for the metabolization of cabonyl sulphide (COS) by higher plants. Botanica Acta 105: 206–212

Rennenberg H, Huber B, Schröder P, Stahl K, Haunold W, Georgii H-W, Slovik S & Pfanz H (1990) Emission of volatile sulfur compounds from spruce trees. Plant Physiol. 92: 968–971

Taylor GE, McLaughlin SB, Shriner DS & Selvidge WJ (1983) The flux of sulfur-containing gases to vegetation. Atmos. Environ. 17: 789–796

The National Atlas of Canada 5th edition (1993) Vegetation Cover. Canada Map Office, Energy, Mines and Resources Canada. MCR 4182

Turco RP, Whitten RC, Toon OB, Pollac JB & Hamill P (1980) OCS, stratospheric aerosols and climate. Nature 283: 283–286

Tsuzuki M & Miyachi S (1989) The function of carbonic anhydrase in aquatic photosynthesis. Aquat. Bot. 34: 85–104

Tsuzuki M, Miyachi S & Edwards GE (1985) Localization of carbonic anhydrase in mesophyll cells of terrestrial C_3 plants in relation to CO_2 assimilation. Plant Cell Physiol. 26: 881–891

Warneck P (1988) Chemistry of the National Atmosphere. In: Dmowska R & Holton JR (Eds) International Geophysics Series Vol 41 (p 492). Academic Press, San Diego, USA