

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 H₂S (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 CH₃SH and CS₂ were sporadic 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 H₂S 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 (H₂S), methylmercaptan (CH₃SH), dimethyl sulfide (CH₃SCH₃, DMS) and carbon disulfide (CS₂), 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 CS₂, which is partly (50%) oxidized to COS, the labile compounds are mainly removed from the atmosphere by oxidization to SO₂ 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. CO₂ 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 CO₂ 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.) Coppins & 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 Herbarium (ASU).

Table 1. Collecting locations for specimens.

| Species | collecting location |
|----------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| <i>Cladonia rangiferina</i> & <i>Lobaria oregana</i> | USA: southern Alaska: Tongass National Forest, Stikine Area |
| <i>Pseudocyphellaria anthraspis</i> & <i>Ramalina menziesii</i> | USA; California: Monterey County, Hastings National History Reservation on <i>Quercus</i> <i>chrysolepis</i> and <i>Q. lobata</i> |
| <i>Pseudevernia intensa</i> | USA: Arizona: Pima County, near the top of the SantaCatalina Mountains, on <i>Pseudotsuga</i> |
| <i>Peltigera collina</i> | Germany: Baden-Württemberg: Schwäbisch- Fränkischer forest near Gaildorf in Osterbachtal on <i>Quercus</i> |
| <i>Cladonia furcata</i> & <i>Nostoc commune</i> | Germany: Baden-Württemberg: Schwäbische Alb, ca. 10 km S of Urach on limestone |
| <i>Cladonia glauca</i> & <i>Flavoparmelia caperata</i> & <i>Parmelia sulcata</i> | Germany: Hessen: 15 km E of Lorch in Wispertal |
| <i>Collema auriforme</i> & <i>Hypogymnia physodes</i> | Germany: Hessen: top of ridge above Östrich near Herberge |
| <i>Evernia prunastri</i> | Germany: Hessen: 20 km E of Lorch in Wispertal, on roadside <i>Acer</i> |
| <i>Peltigera praetextata</i> | 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 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ 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 CO₂

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 $15\text{ }^{\circ}\text{C}$. With the light source turned on above the waterbath the air temperature inside the cuvettes was $16\text{ }^{\circ}\text{C}$ and the thallus temperature was $16.5\text{ }^{\circ}\text{C}$. 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 $14\text{ }^{\circ}\text{C}$. 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 $520\text{ }\mu\text{mol photons m}^{-2}\text{ s}^{-1}$ within the cuvettes ($170\text{ }\mu\text{mol photons m}^{-2}\text{ s}^{-1}$ 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 commercially 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 $30\text{ }^{\circ}\text{C}$ in a thermally controlled ($\pm 0.1\text{ }^{\circ}\text{C}$) 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 $-5\text{ }^{\circ}\text{C}$ to $85\text{ }^{\circ}\text{C}$ at $25\text{ }^{\circ}\text{C}$ 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 CS₂ 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 H₂S 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 H₂S 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 cm² g dw⁻¹ ± 6 s.d. in *Cladonia furcata* to 99 cm² 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 sporadically 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 H₂S 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 H₂S than the other species (Fig. 1). *Lobaria oregana* also emits high quantities of H₂S, 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) H₂S 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.

Lichen species containing green algae

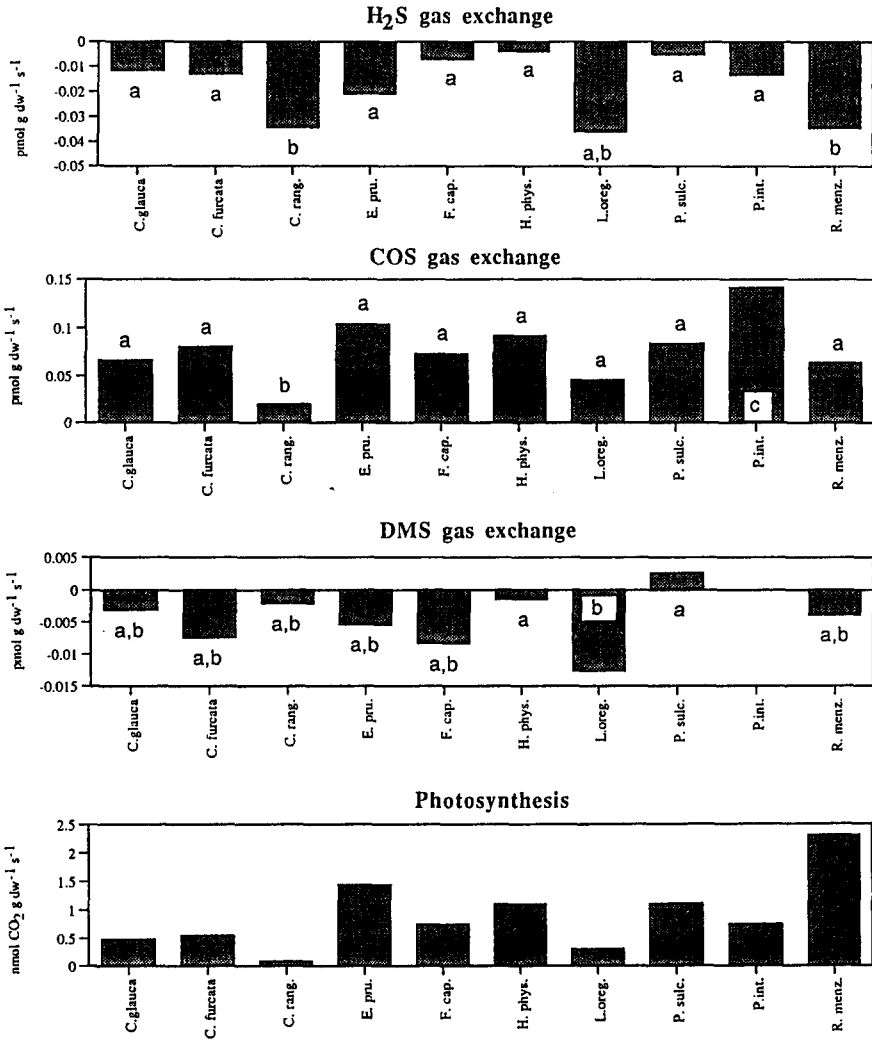


Fig. 1. Mean gas exchange ($n =$ mostly 3, in $\text{pmol g dw}^{-1} \text{ s}^{-1}$) of H₂S, COS and DMS of 10 green algal lichens at 15 °C under 520 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$ over a water content range of 150–200%. Means, which are not significantly different from each other as determined by Tukey's studentized range (hsd) for multiple comparisons, are indicated with the same letter (e.g. a, etc.).

Lichen species containing cyanobacteria

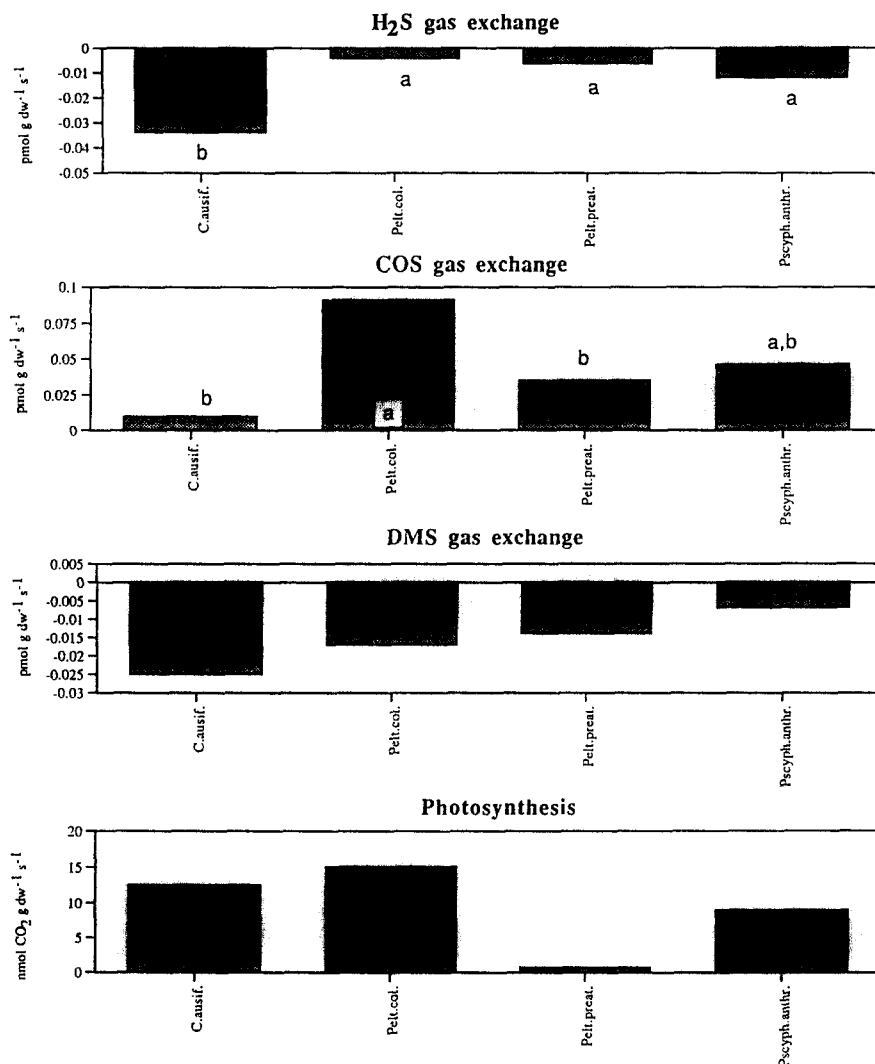


Fig. 2. Mean gas exchange ($n =$ mostly 3, in $\text{pmol g dw}^{-1} \text{ s}^{-1}$) of H_2S , COS and DMS of four cyanolichens at 15°C under 170 (*Peltigera* spp.) or $520 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$ over a water content range of 170 – 200% (*Pseudocyphellaria*), 220 – 280% (*Peltigera* 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.

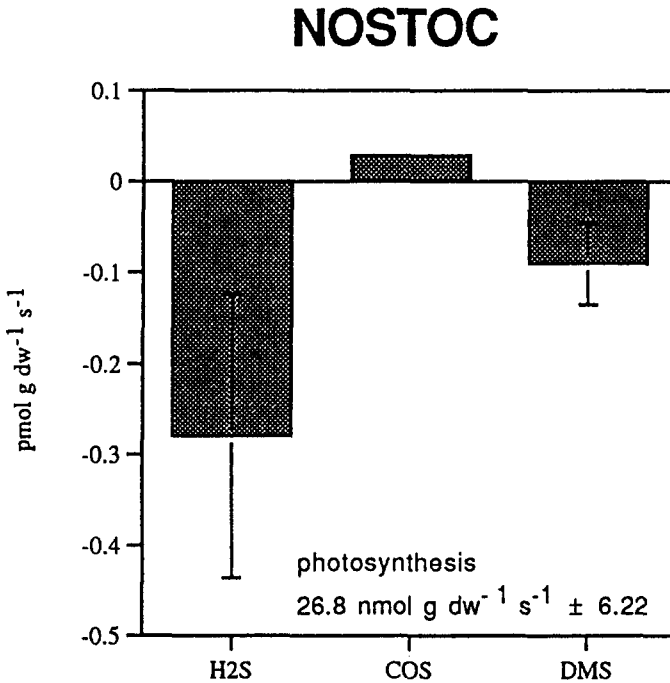


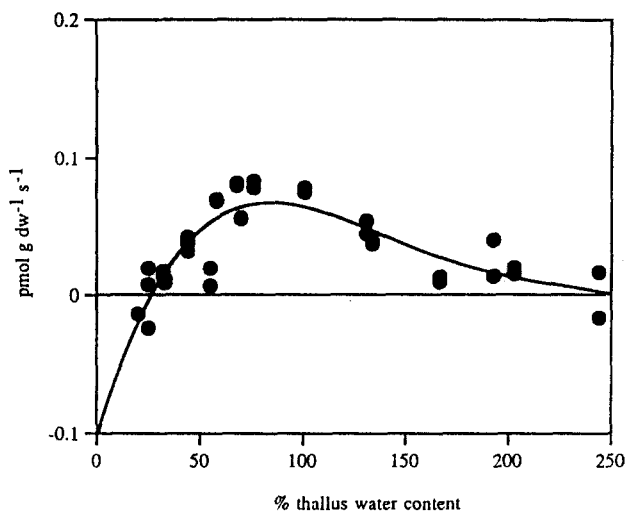
Fig. 3. Mean gas exchange ($n = 3$, in pmol g dw⁻¹ s⁻¹) of H₂S, COS and DMS of the cyanobacterium *Nostoc commune* at 15 °C under 520 μmol photons m⁻² s⁻¹ over a water content range of 1900–2100%. Confidence intervals (vertical line) are ±1 standard deviation.

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.

Ramalina menziesii
COS uptake vs. thallus water content



Ramalina menziesii
photosynthesis vs. thallus water content

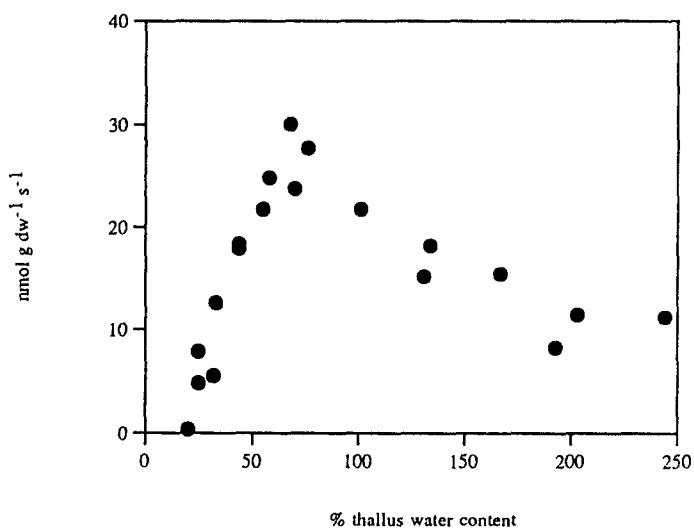
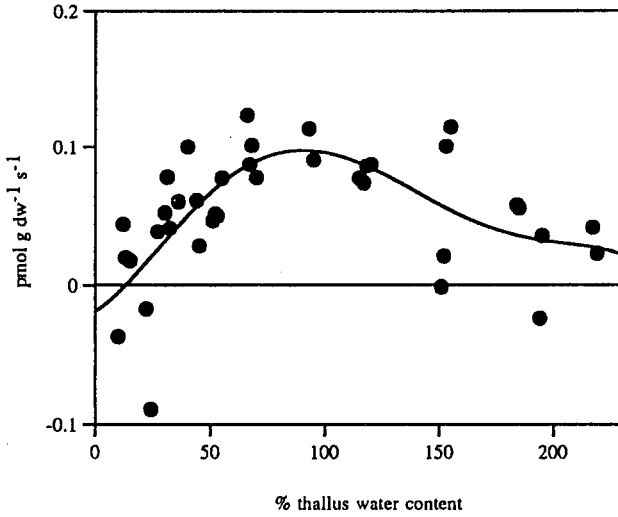


Fig. 4. The relationships of COS and CO₂ gas exchange to thallus water content in *Ramalina menziesii* under 520 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ at 15 °C. A fourth order polynomial equation is fitted to the curve ($r^2 = 0.727$).

Evernia prunastri
COS uptake vs. thallus water content



Evernia prunastri
photosynthesis vs. thallus water content

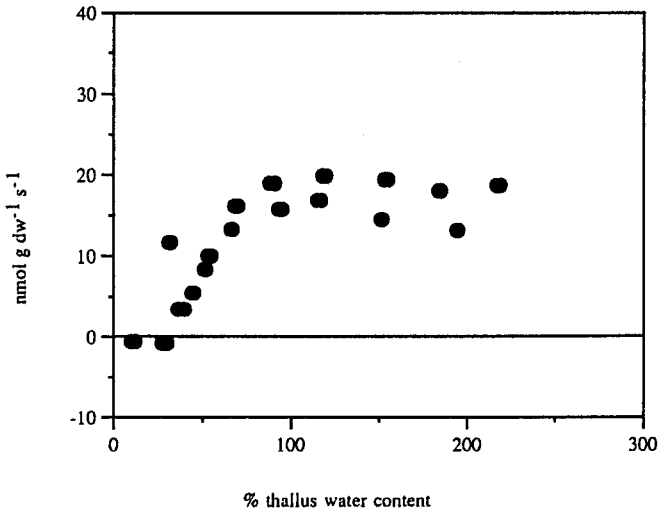


Fig. 5. The relationships of COS and CO₂ gas exchange to thallus water content in *Evernia prunastri* under 520 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ at 15 °C. A fifth order polynomial equation is fitted to the curve ($r^2 = 0.447$).

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 H₂S and DMS and were sinks for large quantities of COS. The strong dependence of COS uptake on thallus water content, a pattern strongly paralleling CO₂ uptake by RUBISCO, provides circumstantial evidence that the process is under metabolic control within the lichen. In contrast, the lack of dependency of H₂S 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 CO₂/HCO₃⁻ equilibrium in aqueous systems or splitting COS to CO₂ and H₂S. 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 CO₂ 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 (<i>Zea mays</i>) | 2.6–21* COS uptake ¹ , light |
| Rapeseed (<i>Brassica napus</i>) | 13–21* COS uptake ¹ , light |
| Peas (<i>Pisum sativum</i>) | 1.7–26* COS uptake ¹ , light |
| Corn (<i>Zea mays</i>) | 7 [#] DMS emitted ² , light |
| | 3 [#] DMS emitted ² , light |
| Alfalfa (<i>Medicago sativa</i>) | 2.3 [#] DMS emitted ² , light |
| | 0.7 [#] DMS emitted ² , dark |
| | 0.2 [#] H ₂ S emitted ² , dark + light |
| | 0.6 [#] CH ₃ SH emitted ² , light |
| | 0.2 [#] CG ₂ SH emitted ² , light |
| Spruces (<i>Picea abies</i>) | 0.6±0.04 ¹ H ₂ S emitted ³ , light |
| | 0.3±0.05 ¹ H ₂ S emitted ³ , dark |
| Tropical Trees | |
| <i>Saccoglottis gabonensis</i> (young tree) | 10±4.5 ⁵ DMS emitted ⁴ , light |
| <i>Saccoglottis gabonensis</i> (old tree, canopy top) | 90±80 ⁵ DMS emitted ⁴ , light |
| <i>Porterandia cladantha</i> | 0.6±0.2 ⁵ DMS emitted ⁴ , light |
| | 2.6±1.4 ⁵ CH ₃ SH emitted ⁴ , light |
| Forest and cropland | 0.4–12 (S) ^{@,1} DMS, H ₂ S, 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*; ¹ cuvette flushed with S-free air; ⁵ 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 H₂S 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, CS₂, 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 [³⁵S]-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 CS₂ 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 H₂S 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 [³⁴S]-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 CO₂-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 CO₂ 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 carbonyl 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 & Pfanzen 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 C₃ plants in relation to CO₂ 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