SHORT CONTRIBUTION

Direct measurements of emission rates of some atmospheric biogenic sulfur compounds

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ABSTRACT

Direct measurements of H_2S + COS and $(CH_3)_2S$ emission rates were made in two salt marshes on the coast of North Carolina during the summer of 1977. An emission flux reactor (chamber) technique was used to determine the emission rates of sulfur compounds into the atmosphere. The sulfur gases were identified and their concentrations in the flux reactor measured with a gas chromatograph equipped with a flame photometric detector specific for S. Flux measurements were made over salt marsh grass (*Spartina alterniflora*) and mud flats. The predominant gaseous sulfur species being emitted over the *Spartina* zone is $(CH_3)_2S$ (average flux is ~0.66 g S/m²/yr), and the predominant species over the mud flat zone is H_2S + COS (average flux is ~0.2 g S/m²/yr). In general, the emission rates of $(CH_3)_2S$ and H_2S + COS increase with increasing ambient temperature (in accordance with previously reported work over mud flats). Similar experiments were also performed in which the chamber was operated under deaerated (N_2) conditions. For deaerated conditions, the emission rates of both H_2S + COS and $(CH_3)_2S$ were increased.

1. Measurements and discussion

All global sulfur budgets which have appeared recently in the literature (Conway, 1943; Eriksson, 1963; Friend, 1973; Granat *et al.*, 1976; Junge, 1963; Robinson and Robbins, 1968; Kellogg *et al.*, 1968) require a substantial biogenic sulfur emission to balance the budget; however, the estimated magnitude of the global source strengths vary widely—from ~35 to ~280 Tg S yr⁻¹. Hydrogen sulfide (H_2S) has long been considered the principal volatile biogenic component of the sulfur cycle. For many years its emission into the atmosphere was thought to account for apparent emission deficits (Conway, 1943). H_2S is an attractive choice, since its fate is thought to be known and is consistent with other ideas about the sulfur cycle, i.e., it is

considered to be oxidized to sulfur dioxide (SO_2) and sulfate (SO_4^{2-}), the other principal forms of sulfur in the atmosphere. However, in possible contradiction of this view, recent papers (Lovelock *et al.*, 1972; Rasmussen, 1974) have suggested that other volatile compounds of biogenic sulfur, such as dimethyl sulfide (DMS), may serve in place of H_2S in contributing to the apparent source deficits.

The present work reports the direct measurements of emission rates of hydrogen sulfide plus carbonyl sulfide (H_2S + COS) and DMS from salt marshes. In addition, physical and chemical properties thought to influence the release of these compounds were also measured. An emission flux reactor (chamber) technique for measuring earth–atmosphere fluxes of biogenic sulfur compounds was used. The chamber used by Aneja (1975) and

Hill, Aneja and Felder (1978) was modified by making the walls from 5 mil thick FEP Teflon supported by an exterior aluminum frame. This design was chosen to permit negligible attenuation of light intensity and to minimize the "greenhouse" effect. Further experimental details will be published elsewhere. The analytical instrument employed was a gas chromatograph equipped with a flame photometric detector with a 394 nm interference filter making the detector selective to sulfur compounds. An 11-meter FEP Teflon column (0.32 cm o.d.) packed with 40–60 mesh Teflon coated with 5% polyphenyl ether and 0.5% phosphoric acid was used at ~50 °C to separate the sulfur gases (Stevens et al., 1971). However, this column did not separate H_2S and COS. The gas chromatograph was calibrated in the laboratory and in the field using permeation tubes and a dilution system.

Measurements were made for biogenic sulfur species at two sites on the east coast of the United States (Fig. 1). Test sites 1 and 2 were at Cedar Island Wild Life Refuge, North Carolina. Test sites 3, 4, and 5 were at Cox's Landing, Long Beach, North Carolina. At each of these locations sampling was done both over marsh grass (*Spartina alterniflora*) clipped to about one inch above ground level (test sites 1, 3, and 4) and over mud flats (test sites 2 and 5) under aerated (ambient air) condition. However, at Cox's Landing another emission flux reactor was placed adjacent to the first, and it was flushed with pure gaseous nitrogen. This was done to gain information on oxidation effects, as well as to maintain the integrity of the emitted sulfur compounds. Time-integrated bag samples were collected every thirty minutes and were analyzed for various gaseous sulfur species and total gaseous sulfur.

All the experiments described herein were performed during daytime in the intertidal zone at low tide. During the experiments over *Spartina*, the ambient temperatures ranged between 21 °C to
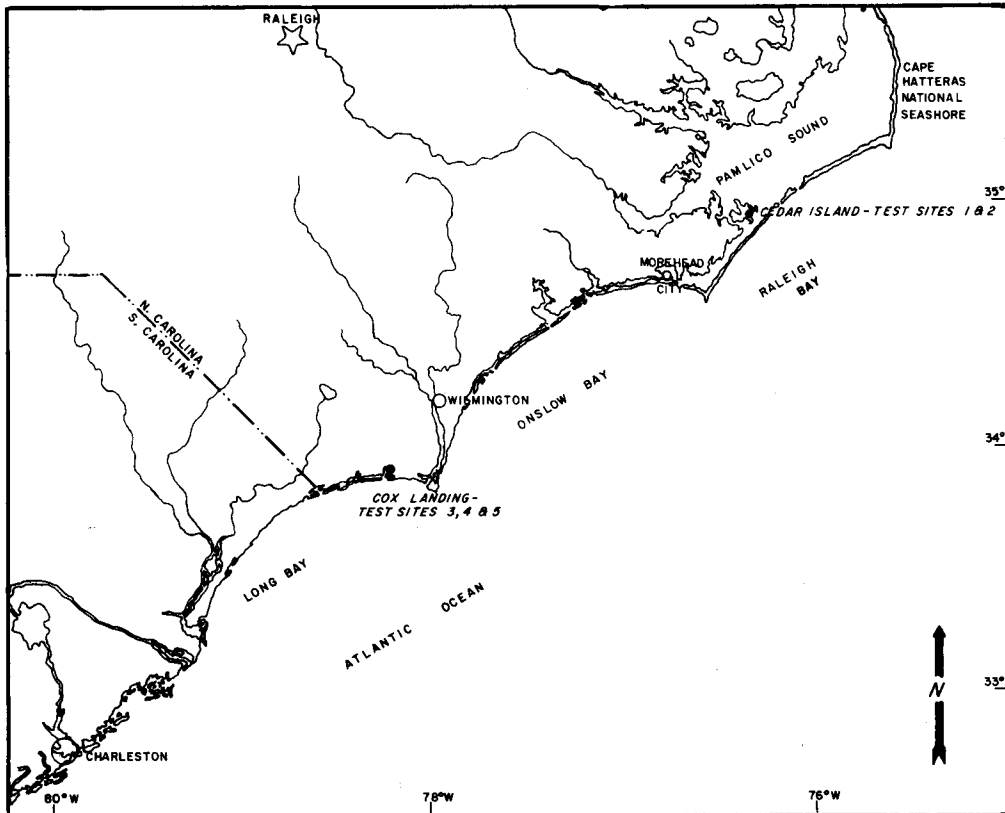

Fig. 1. Location of the sites.

Table 1. *Sulfur species emission rate (Aerated)*

Source	Average ambient temperature °C	Average H_2S + COS emission rate g S/m²/yr (±s.d.)	Average DMS emission rate g S/m²/yr (±s.d.)	No. of measurements
Cedar Island:				
Spartina zone Test site 1	31.3	0.19 (0.03)	1.31 (0.56)	6
Mud flat zone Test site 2	32.2	0.41 (0.05)	<0.04*	3
Cox's Landing:				
Spartina zone Test sites 3 and 4	25.2	0.04 (0.01)	0.18 (0.06)	8
Mud flat zone Test site 5	30.5	0.12 (0.04)	<0.04*	8

* These values were below the instrument detection limit.

Table 2. *Comparison of sulfur species emission rates under aerated and deaerated conditions Cox's landing*

Source	Average H_2S + COS emission rate g S/m²/yr (±s.d.)	Average DMS emission rate g S/m²/yr (±s.d.)	No. of measurements
Spartina zone Test sites 3 and 4			
Aerated	0.04 (0.01)	0.18 (0.06)	8
Deaerated	<0.03*	2.79 (0.98)	5
Mud flat zone Test site 5			
Aerated	0.12‡ (0.04)	<0.04*	8
Deaerated	0.17‡ (0.03)	<0.04*	8

* The values were below the instrument detection limit.
‡ Based on the assumption that at site 5 the two H_2S mean emission rates are equal, the result of a t-test is significant at the 0.05 level. This result strongly implies that the two means are different.

36 °C while the sediment temperatures ranged between 25.5 °C to 32.5 °C. For the experiments over mud flats, both the ambient and sediment temperatures ranged between 29.5 °C to 32.5 °C. The [SO_4^{2-}] content at the two locations is similar, ~2400 µg/ml of solution.

The averaged gaseous sulfur specie flux data at each site is tabulated in Table 1. We see that the predominant sulfur species being emitted over the *Spartina* zone is dimethyl sulfide while the predominant sulfur species emitted over the mud flat zone is hydrogen sulfide + carbonyl sulfide.

Figs. 2 and 3 are plots of the flux of DMS and

H_2S + COS in the *Spartina* zone vs ambient temperature. The data from Cedar Island show a logarithmic dependence of emission flux upon temperature in agreement with earlier work (Aneja, 1975; Hill et al., 1978). The data from Cox's Landing are more ambiguous in regard to temperature effect. The data are plotted together and, as a whole, seem consistent. This consistency may be merely fortuitous, especially in view of the great distance between the sites and easily perceived differences in soil coloration between the two locations. The data may imply, however, that, at least in a *Spartina* zone, sulfate concentration may
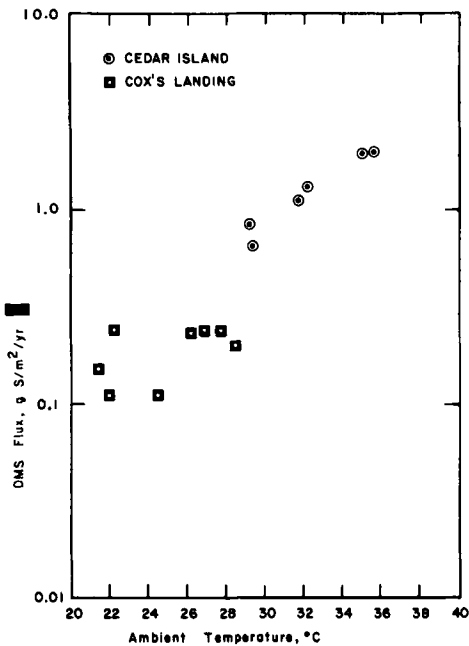
Fig. 2. Ambient temperature dependence of dimethyl sulfide flux over *Spartina* zone at Cedar Island and at Cox's Landing.
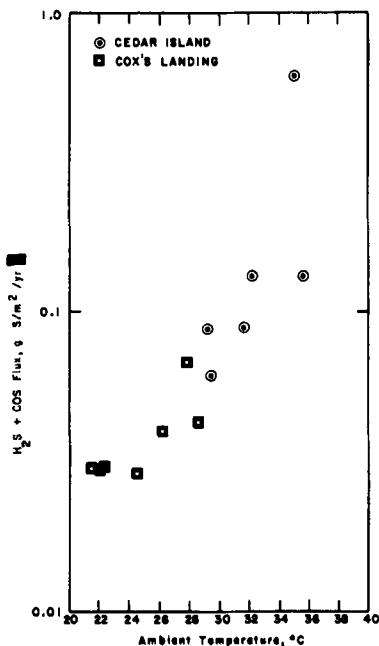

Fig. 3. Ambient temperature dependence of hydrogen sulfide plus carbonyl sulfide flux over *Spartina* zone at Cedar Island and at Cox's Landing.

be used to correlate diverse sites. Unfortunately, enough data are not yet available to draw a reliable conclusion. Table 1 shows that the emission rate of H_2S + COS over mud flats also appears to increase with increasing temperature.

Emission rates were also compared with other ambient conditions and light intensity; no correlation of emission fluxes and ambient concentrations of O_3 or NO_x was observed. Because temperature and light intensity are not totally independent it is impossible to separate these two effects based upon the limited data currently available.

A comparison of fluxes derived from using both nitrogen (deaerated conditions) and ambient air (aerated) as sweep gases is tabulated in Table 2. The emission rates of both H_2S + COS and DMS are greater in the deaerated chamber than in the aerated chamber. This could be caused by loss of H_2S + COS and DMS in the presence of oxygen or by enhancement of the emission rates by lack of oxygen. However, there is no evidence of oxidation of H_2S + COS or DMS in the aerated chamber to SO_2 or other gaseous products since the total gaseous sulfur flux approximately equaled the sum of the H_2S + COS and DMS fluxes. (Particulate sulfur was not monitored, however, and an unknown mechanism involving rapid oxidation to particulate sulfate cannot yet be ruled out.) As the soil becomes deaerated in the nitrogen-flushed chamber, one might anticipate enhancement of the H_2S emissions since the primary source of reduced sulfur (or sulfide) compounds is the anaerobic production of H_2S by bacteria (Postgate, 1959). There are several possible explanations of enhancement of DMS: the emission enhancement could be due to increased anaerobic microbial activity or due to a change in the metabolism of the *Spartina*.

The measured fluxes of about 0.5 g $S/m^2/yr$ are comparable to earlier direct emission rate measurements, also in a salt marsh, (Aneja, 1975; Hill *et al.*, 1978) of H_2S + COS of about 0.6 g $S/m^2/yr$. The measured DMS emission rates over *Spartina* exceed the indirectly-measured (Maroulis and Bandy, 1977) or theoretically-calculated (Liss and Slater, 1974) DMS emission rates over the ocean which have recently appeared in the literature. In addition, the data indicate that in coastal marsh lands one may find sites at which either H_2S + COS or DMS may be the predominant biogenic sulfur species emitted into the atmosphere.

A 5.7 meter FEP Teflon column (0.3 cm o.d.) of 50–80 mesh Porapak QS at $\sim 50\,°C$ was used for the separation of H_2S and COS in a preliminary investigation of the fluxes of these species. The results show that both H_2S and COS are being emitted by the marsh and that COS fluxes may be as great, and in some cases much greater than those of H_2S. These experiments are in progress and the data will be reported later.

2. Acknowledgements

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