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Journal
Atmospheric Environment (1967), 21(7)

ISSN
0004-6981

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Publication Date
1987

DOI
10.1016/0004-6981(87)90311-8

Atmospheric Environment Vol. 21, No. 7, pp. 1491–1495, 1987.
Printed in Great Britain.

0004–6981/87 $3.00 + 0.00

EMISSIONS OF BIOGENIC SULPHUR COMPOUNDS FROM SEVERAL WETLAND SOILS IN FLORIDA

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(*First received* 18 *September* 1986 *and in final form* 5 *December* 1986)

Abstract—Emission rates of the biogenic sulphur gases hydrogen sulphide, dimethyl sulphide, carbon disulphide and dimethyl disulphide have been measured from the exposed soils of five wetland plant communities in Florida. Dimethyl sulphide and hydrogen sulphide were the predominant species emitted. All the studied ecosystems showed diel variation in the emission rates of the biogenic sulphur gases with the highest emissions rates occurring early- to mid-afternoon, and the lowest emission rates occurring during the early morning. The relative magnitude of emissions from the individual ecosystems followed the trend *Distichlis spicata* > *Avicennia germinans* > *Batis maritima* ≅ *Juncus roemerianus* ≅ *Cladium jamaicense*. Only the emission rates from the peaty *D. spicata* site are comparable in magnitude to previous emission measurements in wetland ecosystems of *Spartina alterniflora* and associated mud flats.

Key word index: Biogenic sulphur emissions, dimethyl sulphide, hydrogen sulphide, carbon disulphide, dimethyl disulphide, wetland soils.

INTRODUCTION

Most models of the global sulphur cycle include biological sources of volatile S gases from continental areas as a significant input to the atmosphere. However, extensive studies using direct measurement of the emission rates of S compounds have centered largely on two distinct coastal environments, both of which have the potential for extremely high emission rates of reduced S gases. The first, *Spartina alterniflora* salt marshes (Aneja, 1984; Steudler and Peterson, 1985; and references therein) can be expected to release large quantities of dimethyl sulphide (DMS) as a result of the plant's high content of dimethylpropiothetin (Dacey *et al.*, 1986), whose hydrolysis or enzymatic cleavage leads to formation of DMS. The second, coastal mudflats (Jørgensen and Okholm-Hansen, 1985, and references therein), have the tendency toward anoxia, with concomitant production of H_2S via sulphate reduction. Tidal pumping mechanisms have been shown to enhance emissions of this gas in short, intense pulses (Aneja, 1984; Jørgensen and Okholm-Hansen, 1985; Cooper *et al.*, 1987, and references therein). Studies in more typical soil conditions generally show drastically lower emission rates of reduced S (Adams *et al.*, 1981).

The objective of the work reported here was to extend the studies of the emission of biogenic S gases to a variety of other wetland ecosystems. This paper reports measurements of the emission rates of the biogenic S compounds H_2S, DMS, carbon disulphide (CS_2) and dimethyl disulphide (DMDS) from four different wetland soil environments in the State of Florida, complementing measurements reported previously from a *S. alterniflora* zone using the same analytical methods (Cooper *et al.*, 1987; de Mello *et al.*, 1987). The sites comprised wetland areas with predominant plant communities of *Juncus roemerianus* (black needle rush), *Distichlis spicata* (spike grass), *Avicennia germinans* (black mangrove), *Cladium jamaicense* (sawgrass) and *Batis maritima* (saltwort), which are found extensively in marsh environments of the SE U.S.A.

SAMPLING SITES

The study was conducted during the months of April, May and October 1985 and January 1986. Geographic locations are shown in Fig. 1.

The *J. roemerianus* site was located at the St Marks National Wildlife Refuge, about 2 km inland from the coastline. The soil was an unconsolidated silica sand with an organic content of less than 2%, and was only flooded by extremely high tides. The height of the needle rush was approximately 50–80 cm.

The *D. spicata* site was located at the Merritt Island National Wildlife Refuge. The soil in this site was peat, to a depth of approximately 1.3 m, with the water table just below the soil surface during April and May 1985. It was above the soil on the later visits, with a salinity of less than 3 parts per thousand. Water levels were regulated as part of the Refuge water management program. The height of the emergent vegetation was always < 20 cm.

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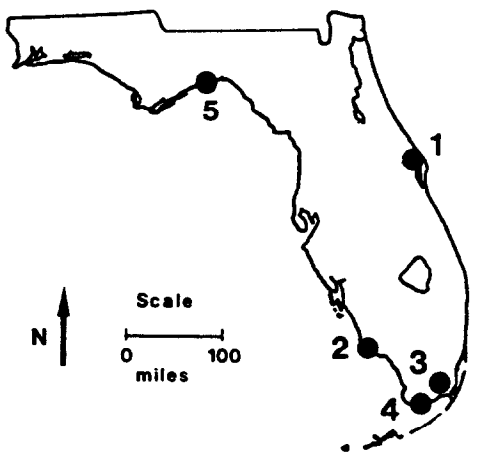

Fig. 1. Sampling site locations: 1. Merritt Island (*D. spicata*); 2. Rookery Bay (*A. germinans*); 3. Old Ingraham Highway (*C. jamaicense*); 4. Flamingo (*B. maritima*); 5. St. Marks (*J. roemerianus*).

The *A. germinans* site was located at the Rookery Bay National Estuarine Sanctuary, approximately 50 m from the shore, and was only occasionally flooded with salt water by extreme high tides. The substrate was peat with numerous mangrove pneumatophores.

The *C. jamaicense* site was an inland freshwater marsh located in the Taylor Slough area of the Everglades National Park. This region was dry from December to June. The substrate was a silty calcareous sediment (marl), with 15–20% organic matter. Standing water had a sulphate content of approximately 2.5 mg ℓ^{-1}. The height of the homogeneous vegetation surface was about 1 m.

The *B. maritima* site was also in the Everglades National Park, near Flamingo, approximately 20 m from the shore. The oxic calcareous substrate would not normally be flushed by tides, and was the driest site studied. The height of the plant growth was < 20 cm.

SAMPLING AND ANALYTICAL METHODS

Sulphur gases were collected over the soil surface in a rigid polycarbonate chamber, lined with Teflon FEP to provide an inert internal surface. Scrubbed ambient air, used as sweep gas, was introduced into the chamber at a flow rate ranging from 2.2 to 3.2 ℓ min^{-1} (Cooper *et al.*, 1987). The chamber was allowed to equilibrate for at least 30 min prior to sampling.

Sites were selected within an ecosystem such that the damage to the living plants was minimized when the chamber was placed on the surface. Soil surface temperatures, inside and outside the chamber, were taken with mercury thermometers. Insolation was measured using a radiometer (The Eppley Laboratory, Inc., RI) equipped with a wide band solar spectrum filter (300–800 nm). The radiometer was connected to a computer (IBM Corp., Armonk, NY) which averaged the solar flux every 10 min.

Samples were analysed for H_2S, DMS, CS_2 and DMDS as described in Cooper *et al.* (1987) and de Mello *et al.* (1987). Calibration was performed daily. These methods allowed the determination of a minimum emission rate of 0.03, 0.01, 0.03 and 0.06 $\mu g\ S\ m^{-2}\ h^{-1}$ for H_2S, DMS, DMDS and CS_2, respectively.

RESULTS

Table 1 shows a summary of all emission measurements made from the five ecosystems, together with the range of soil temperatures. H_2S and DMS were never below the detection limit of the methods, whereas CS_2 and DMDS were often not detected. In all cases where sufficient measurements were made, a diurnal cycle in

Table 1. Summary of biogenic S emission rates from five wetland soils characterized by different vegetation in Florida

Site (conditions)	Date	Temperature (°C)	Emission rate ($\mu g\ S\ m^{-2}\ h^{-1}$) H_2S	DMS	CS_2	DMDS
C. jamaicense	8–13 Nov. 84	17–28	0.4–0.8	nd	nd	nd
(freshwater,	28–29 Mar. 85	18–25	0.2–0.9	< 0.02–0.07	< 0.06	< 0.03
calcareous, moist)	21–23 May 85	24.2–37.3	0.4–4.7	0.6–7.1	0.2–0.5	0.1–0.7
	15–16 Jan. 86	12.0–23.4	0.1–1.0	0.2–0.9	0.07–0.2	0.03–0.2
D. spicata	15–16 Apr. 85	15†–21.5	8.3–152	nd	nd	nd
(moist, peaty)	14–15 May 85	19.9–32.5	nd	0.6–23	0.2–1.7	0.1–1.5
J. roemerianus	11–12 Apr. 85	19–24	0.6–1.5	0.1–0.3	nd	nd
(moist, sandy)	18 May 85*	24.1–37.9	2.0–2.8	3.3–6.4	< 0.06	< 0.03
	25–27 Jan. 86	6.8–14.5	0.1–1.3	0.1–0.9	< 0.06	< 0.03
A. germinans	3 April 85*	27–29	0.7–2.1	nd	nd	nd
(moist, peaty)	20 May 85*	29–34	4.9–7.9	nd	nd	nd
	20–22 Jan. 86	13.1–22.1	0.3–5.0	0.3–10	< 0.06–0.6	< 0.03–0.6
B. maritima (dry, calcareous)	17–19 Jan. 86	19.2–23.0	0.6–1.0	1.0–7.0	0.1–0.3	0.1–0.5

nd, Not determined.
*Measured during daytime only.
†Estimate, based on ambient temperature.

the emission rates of all compounds was found. Peak emissions were found in the early- to mid-afternoon, slightly later than the daily temperature and solar flux maxima.

Distichlis spicata *site*

Although this site was sampled four times over the entire study period, the soil was only exposed during the April and May visits. This site showed the highest fluxes of all compounds, up to 152 $\mu g\ S(H_2S)\ m^{-2}\ h^{-1}$ and 23 $\mu g\ S(DMS)\ m^{-2}\ h^{-1}$. A very strong odour of H_2S was often noticed in the early morning before the breakdown of the nocturnal atmospheric inversion. Ambient concentrations of H_2S at this time were measured at up to 86 $\mu g\ m^{-3}$ (62 ppbv), the highest recorded during the entire study. The high emission rates of reduced biogenic S compounds probably result from a combination of sulphate availability, soil moisture and the high organic content of the soil. The diurnal cycle in emission rates is best illustrated with data from this site, the most comprehensive of which is shown in Fig. 2 for DMS.

Avicennia germinans *site*

Lesser, but still considerable emission rates of all compounds were measured at the moist, peaty *A. germinans* site. The highest emissions of H_2S were found during daytime sampling in May 1985 (up to 7.9 $\mu g\ S\ m^{-2}\ h^{-1}$). All the S gases were measured over a period of 2 days at this site in January 1986. Diel variation was observed in the emissions of all gases, shown in Fig. 3. The emission rates of DMS and H_2S were similar in both magnitude and temporal variation, indicating that the processes affecting their emission from this environment, i.e. formation and release, may be similar.

Juncus roemerianus *site*

The moist, sandy *J. roemerianus* site was the site most affected by seasonal temperature changes, with a range from a high of 38°C in May 1985 down to a low of 7°C in January 1986. In May, a limited data set was obtained during the middle of the day, when the DMS and H_2S emission rates peaked at 6.4 and 2.8 $\mu g\ S\ m^{-2}\ h^{-1}$, respectively. In January 1986 the emissions were measured using two chambers placed within 20 cm of each other (Fig. 4, Chamber 1 and Chamber 2). The emission rates from the two chambers showed very little spatial variability and were considerably lower than the May visit, with maximum emissions of 0.9 and 1.3 $\mu g\ S\ m^{-2}\ h^{-1}$ DMS and H_2S, respectively on the first day. The second day was significantly colder (Fig. 4), and the observed maxima in emission rates correspondingly smaller (0.2 and 0.5 $\mu g\ m^{-2}\ h^{-1}$).

Batis maritima *site*

Emission rates of the reduced S gases from the dry *B. maritima* site were only measured in January 1986. DMS had a significant emission rate, peaking at

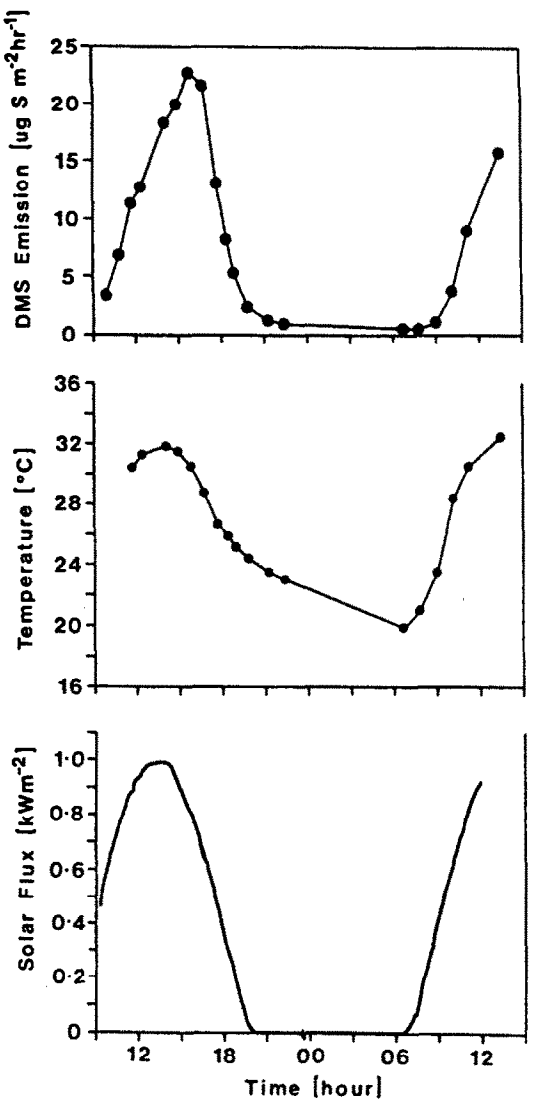

Fig. 2. Diurnal variation in DMS emission rate, soil temperature and solar flux, *D. spicata* site, Merritt Island, 14–15 May 1985.

7 $\mu g\ S\ m^{-2}\ h^{-1}$. Interestingly, while DMS, CS_2 and DMDS emission rates peaked in the early afternoon, coinciding with the highest soil temperature, the emission rate of H_2S was fairly constant throughout, possibly reflecting a deeper source less subject to surface temperature phenomena.

Cladium jamaicense *site*

The moist, calcareous *C. jamaicense* site is the only fresh water ecosystem characterized here. Emission rates of the reduced S gases are, however, comparable in magnitude to the drier salt water ecosystems (*J. roemerianus* and *B. maritima*) for all compounds. Peak emission rates were measured in May 1985, both the driest and the hottest visit, with 7.1 μg DMS $m^{-2}\ h^{-1}$ and 4.8 $\mu g\ H_2S\ m^{-2}\ h^{-1}$. In January 1986 this site was mostly flooded with a few higher areas of exposed soil. The temperatures were considerably lower than in

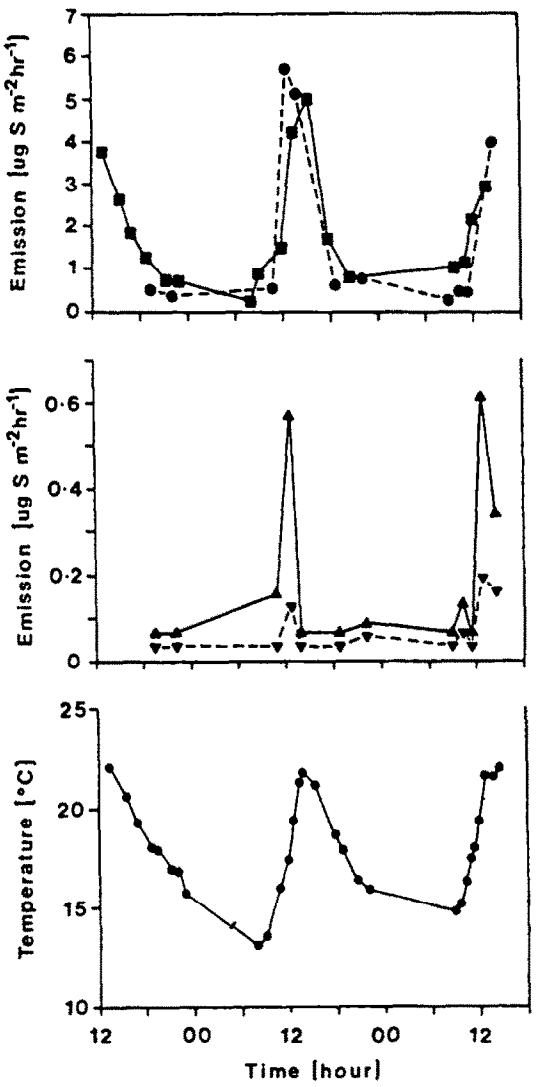

Fig. 3. Diurnal cycle of reduced S gas emissions from the *A. germinans* site, 20–22 January 1986. ● DMS, ■ H_2S, ▲ CS_2, ▼ DMDS, • soil temperature.

May, leading to much lower emission rates of all the S gases, a factor of eight lower in the case of DMS, five for H_2S.

DISCUSSION

There is much uncertainty about the mechanisms controlling the observed diel variation in the emission rates of biologically generated S gases. This study was not designed for mechanistic work, but we can make some inferences based on our limited data. It is obvious from Table 1 that there is considerable variability in the emission rates of DMS, H_2S, DMDS and CS_2 from the wetland soils studied. H_2S and DMS emissions were generally comparable and were normally more than an order of magnitude greater than those of CS_2 and DMDS, as found in previous studies conducted in *S. alterniflora* marshes. The relative magnitude of

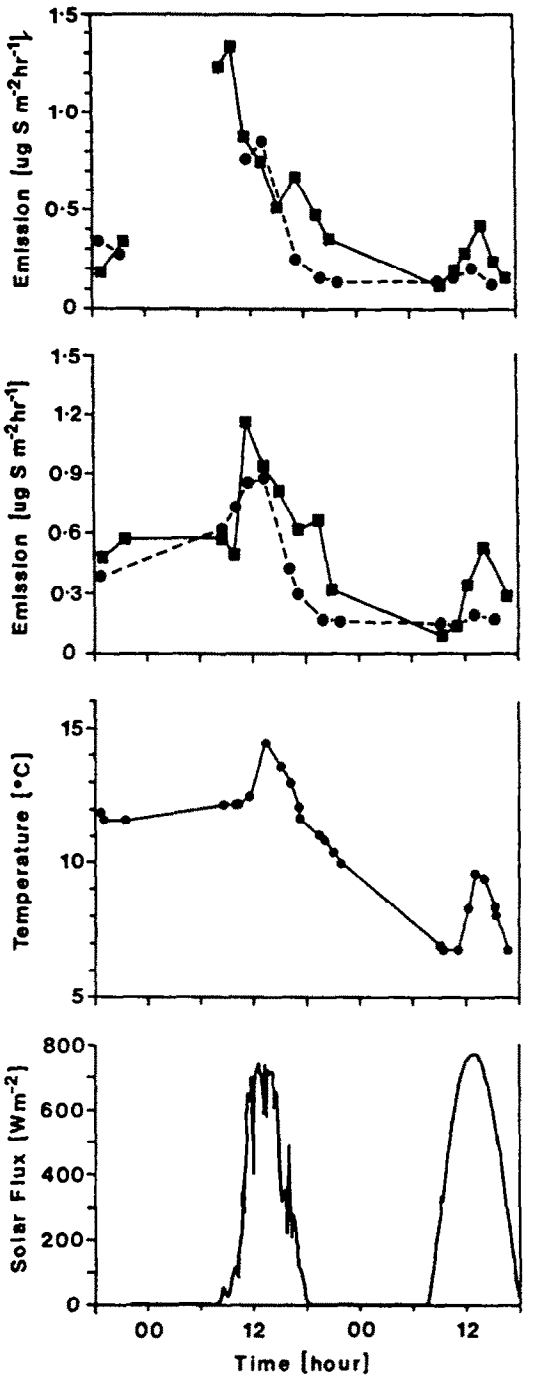

Fig. 4. Diurnal cycle and spatial variability of DMS and H_2S emissions from the *J. roemerianus* site. ● DMS, ■ H_2S, • soil temperature, — solar flux.

emission rates from the different sampling sites probably reflects the availability of both sulphate and organic substrate. Most H_2S is formed by dissimilatory sulphate reducing bacteria under anoxic conditions, e.g. *Desulphovibrio* and *Desulphotomaculum* (Jørgensen and Okholm-Hansen, 1985, and references therein), whereas DMS and DMDS originate through microbial degradation of methionine, and CS_2 from

cysteine and cystine, all under waterlogged conditions (Bremner and Steele, 1978, and references therein).

These conditions are certainly found at the peaty *D. spicata* and *A. germinans* sites, where the highest emission rates were found. In addition, whilst the emission rates were not as great from the *D. spicata* site as those reported from a Florida *Spartina alterniflora* stand (Cooper *et al.*, 1987; de Mello *et al.*, 1987), it is conceivable that the *Distichlis* may use sulphonium compounds in its osmoregulatory system in a similar way to *Spartina* species (Larher *et al.*, 1977).

The relatively low emissions observed at the *J. roemerianus* and *B. maritima* sites may be explained by the fact that they are low in organic matter, and that their elevation (upper marsh) is such that they are only inundated by extreme high tides, limiting the availability of sulphate.

Previous studies have shown that release of H_2S can be controlled by a tidal pumping mechanism (Aneja, 1984; Jørgensen and Okholm-Hansen, 1985; Cooper *et al.*, 1987), but this effect is not important in this study due to the upper marsh elevation or the impounded nature of all sites here. The only site where such a mechanism could be important is the *J. roemerianus* site, which may be periodically flushed by extreme high tides. Release of microbial metabolites can be correlated with soil temperature (Adams *et al.*, 1981; de Mello *et al.*, 1987), but this daily cycle is necessarily correlated with solar irradiation. It is therefore impossible to distinguish between the effects of increasing microbial activity and photosynthetic activity of the plant community without further investigation. In addition, where S compounds are involved in the osmoregulatory system of the plants, release can be a result of plant response to changes in the pore water salinity (de Mello *et al.*, 1987).

Our study on the emissions of the S gases at the *J. roemerianus* site in January 1986 (Fig. 4) shows even though temperatures dropped to below 10°C, emissions were never completely shut off, in contrast to the findings of Hill *et al.* (1978). This may, however, simply reflect the lower detection limit of our method.

The major sources of error in this study are the unavoidable changes made to the environment by the use of an enclosure. The emissions of S compounds may be enhanced both by the use of a S-free sweep gas and by the daytime warming of enclosed soils relative to the surroundings.

SUMMARY AND CONCLUSIONS

Emission rates of the biogenic S gases H_2S, DMS, CS_2 and DMDS have been measured from the exposed soils of five wetland plant communities in Florida.

The emission rates of DMS and H_2S are generally 10–100 times higher than those of DMDS and CS_2. All the studied ecosystems showed diel variation in the emission of rates of biogenic S gases, which is correlated loosely with the diurnal cycle in soil temperature and solar irradiation.

The measured emission rates of total reduced S from the individual ecosystems followed the trend *Distichlis spicata* > *Avicennia germinans* > *Batis maritima* ≅ *Juncus roemerianus* ≅ *Cladium jamaicense*.

Only the emission rates from the *D. spicata* site are comparable in magnitude to previous emission measurements in wetland ecosystems, most of which were conducted over *Spartina alterniflora* or areas of mud flats.

Acknowledgements—The authors thank Stephen Vehrs and Stephen Gard of the Merritt Island National Wildlife Refuge; Arthur Graham, Canaveral National Seashore; Dr Ross Hinkle, Bionetics, Kennedy Space Center; Joe D. White and Culver S. Gidden, St Marks National Wildlife Refuge; Dr Kris Thoemke and Ken Gyorkos, Rookery Bay National Estuarine Sanctuary for valuable assistance at the research sites; The Florida Department of National Resources, National Audubon Society, Collier County Conservancy and the Nature Conservancy, and Lee Casey, David Odum and Tom Snowdon for technical assistance. This work was partially supported by the Florida Electric Power Coordinating Group, Inc. through Environmental Science and Engineering, Inc., Gainesville, FL; Drinking Water Research Center, Florida International University; Rosenstiel School of Marine and Atmospheric Science, University of Miami and NSF grant ATM 84-05921 to the University of Miami.

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