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# SHORT-TERM VARIABILITY IN BIOGENIC SULPHUR EMISSIONS FROM A FLORIDA *SPARTINA ALTERNIFLORA* MARSH

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**Abstract**—Emissions of biogenic sulphur gases from a Florida *Spartina alterniflora* zone were measured over several tidal and diel cycles using a dynamic flow chamber technique, corroborating recently published information in the literature. The flux of hydrogen sulfide from individual measurements is shown to vary by over four orders of magnitude, and correlates primarily with the stage of the tidal cycle. In contrast, the fluxes of dimethyl sulphide, carbon disulphide and dimethyl disulphide vary by less than an order of magnitude and correlate primarily with the diurnal temperature changes in the sediment surface. These differences are discussed in terms of the various biological and physical parameters which may regulate the release of reduced sulphur compounds to the atmosphere.

*Key word index*: Biogenic sulphur emissions, salt marshes, hydrogen sulphide, dimethyl sulphide, carbon disulphide, dimethyl disulphide.

## INTRODUCTION

Recent studies on the problem of acid precipitation have focused largely on the biogeochemical cycling of sulphur-containing compounds. The contribution of biogenic reduced S gases to the atmospheric S burden has been and remains an area of major concern (Maroulis and Bandy, 1977; Adams *et al.*, 1981; Aneja *et al.*, 1981; Cline and Bates, 1983; Andreae and Raemdonck, 1983; Steudler and Peterson, 1984). Oxidation of these compounds leads to the formation of sulphate, which is precipitated as sulphuric acid in rainwater. Tidally influenced marine sediments and salt marshes are a major source of atmospheric $H_2S$ (Georgii, 1977; Hansen *et al.*, 1978; Jaeschke *et al.*, 1980; Ingvorsen and Jørgensen, 1982; Aneja, 1984; Hill *et al.*, 1978) as a result of anaerobic bacterial sulphate reduction and decomposition of organic material. Salt marshes have also been shown to be a major source of organosulphur compounds (Adams *et al.*, 1981; Aneja *et al.*, 1981; Steudler and Peterson, 1984). The range of reported emission rates is large, and extreme variability at a given sampling site is often found. Consequently, estimates of the annual emissions of $H_2S$ and organosulphur compounds are still very uncertain, and are, in fact, the major holdback in attempts to accurately quantify the atmospheric S cycle.

The spatial and temporal emission patterns of biogenic S compounds reflect the combined effect of numerous biological and physical parameters. Different metabolic pathways produce different S compounds (Aneja, 1984), and the ultimate release to the atmosphere may depend on both the efficiency of remineralization processes (Hansen *et al.*, 1978) and the effect of physical parameters such as tidal inundation (Aneja, 1984) and temperature (Hansen *et al.*, 1978). In this paper, we present flux measurements of four reduced S gases which were measured at three different environments within a *Spartina alterniflora* zone on the Gulf coast of Florida. The fluxes of hydrogen sulphide ($H_2S$), dimethyl sulphide (DMS), carbon disulphide ($CS_2$) and dimethyl disulphide (DMDS) are assessed in terms of the relative importance of tidal and diel cycles.

## EXPERIMENTAL

### *Study site*

Emission measurements were made on 16–17 May and 7–8 October 1985 at St. Mark's National Wildlife Refuge, Florida, U.S.A. (Fig. 1). A stand of short *Spartina alterniflora* (30–50 cm tall) extended about 15 m below the high tide mark. The substrate was fine-grained quartz sand with an organic content of < 1%. Measurements were made at three different locations; over the *S. alterniflora*, on bare sand adjacent to *S. alterniflora*, and on exposed mudflats below the *S. alterniflora* stand. Sediment temperatures ranged from 23°C at night to 36°C in the early afternoon in May, and from 19 to 29°C in October. The tidal range was 80–100 cm, exposing about 100 m of mud flats. The anaerobic zone in the sand, evidenced by black colouration, with the characteristic odour of $H_2S$, was typically less than 2 cm below the surface, and occasionally broke the surface. The depth of this anaerobic region was observed to be much deeper within the *S. alterniflora* stand (typically 5–10 cm).

### *Field sampling*

Emission measurements were made using a polycarbonate chamber (30.5 cm diameter × 30.5 cm height) lined with a thin film of FEP Teflon. Design and construction of the chamber was similar to Adams *et al.* (1980), and is described in more

Fig. 1. Sampling site location. St. Marks National Wildlife Refuge, Florida, U.S.A.

detail elsewhere (Cooper, 1986). The chamber was placed on the surface of interest, taking care not to damage any foliage, and depressed slightly in the sediment to ensure a good seal. Ambient air was used as a sweep gas at a flow rate of 2.2–3.2 $l\ min^{-1}$. This air was passed through gas scrubbers containing silica gel, molecular sieve, activated charcoal and palladium-coated molecular sieve in order to remove ambient reduced S compounds, $SO_2$ and atmospheric oxidants before entering the chamber. An equilibration time of 20 min was required before measurements were begun. Samples were drawn from the top of the chamber at a flow rate of 0.5–1.3 $l\ min^{-1}$ for $H_2S$ analysis or 200 $cm^3\ min^{-1}$ for DMS, $CS_2$ and DMDS analysis. $H_2S$ emission measurements were made during a complete tidal cycle on 16–17 May 1985, while DMS, $CS_2$ and DMDS were measured over two tidal cycles on 7–8 October 1985. Measurements were made during the rising tide until water surrounded the base of the chamber, and continued during the ebb tide until the water had receded below the sampling location. Tide height was recorded periodically during the study periods.

*Analytical*

The analytical equipment was housed in a self-contained mobile laboratory located close to the sampling site. This allowed samples to be analyzed immediately after collection. $H_2S$ was analyzed by a method similar to that of Natusch *et al.* (1972). The sample gas stream was drawn through a silver nitrate impregnated filter, held in a 47-mm Teflon PFA filter holder (Cole-Parmer Instrument Co., Chicago, IL), quantitatively trapping the $H_2S$ as silver sulphide. The sulphide was recovered by washing the filter in 0.1 M NaOH/NaCN solution, and analyzed fluorometrically by the fluorescence quenching of dilute fluorescein mercuric acetate. The method has a detection limit of $5 \times 10^{-11}$ moles, corresponding to a lower emission rate of 0.3 mg $S(H_2S)\ m^{-2}\ a^{-1}$. Calibration was performed by standard addition of fresh dilute sodium sulphide solution to blank filters.

DMS, $CS_2$ and DMDS were trapped by passing the gas stream through a Teflon PFA loop (6.4 mm OD × 4 mm ID × 40 cm length) packed with Teflon wool (Alltech Associates, Deerfield, IL), immersed in liquid oxygen. Total sample volume was monitored using a mass flow controller/integrator (Sierra Instruments, Inc. Carmel Valley, CA). The level of the liquid oxygen was raised at the end of the sampling period, and the loops capped to prevent loss of sample when returning to the mobile laboratory. The gases were analyzed with a Model 560 gas chromatograph (Tracor Instruments, Austin, TX) with a 12 ft × 1/8 in Chromosil 330 column (Supelco Inc., Bellefonte, PA) and a sulphur specific flame photometric detector. This method has a detection limit of less than $5 \times 10^{-12}$ moles of S injected, which corresponds to a lower emission rate of approximately 1–2 mg $S\ m^{-2}\ a^{-1}$. Calibration was performed by purging liquid standards onto the sample loop and, independently, by using permeation tubes (GC Industries, Chatsworth, CA). However, the latter method could only be used over short time scales due to long-term changes in the measured permeation rates of the tubes. Negative quenching of the FPD signal by $CO_2$ and HCs in the early part of the chromatograms prevented use of the gas chromatographic method for $H_2S$ or COS analysis.

## RESULTS AND DISCUSSION

*Emissions of hydrogen sulphide*

The variations of $H_2S$ emission rates from the wet site over *Spartina alterniflora*, the adjacent bare sand site within the *S. alterniflora*, and the intertidal mudflat site on 16–17 May 1985 are shown in Fig. 2. Tidal height data are plotted as the vertical distance from the minimum tide height recorded over the 2-day sampling period. Sampling was conducted during the times indicated by the broken lines on the tide height plot. Intersection of the solid and broken lines therefore represents the times of tidal inundation at the three sites.

It is evident in Fig. 2 that the $H_2S$ emission at all three sampling sites increases dramatically as the water approaches the chamber, and is a maximum as the tide reaches the base of the chamber. The effect is most pronounced at the wet sand site, where the flux increases by > 4 orders of magnitude from about 0.01 to over 100 g $S(H_2S)\ m^{-2}\ a^{-1}$. The data between 12:30 and 16:00 represent time that the water covered the sampling site. The chamber was floated during this time, and emission of 76–272 mg $S(H_2S)\ m^{-2}\ a^{-1}$ were measured from the sea surface. An enhancement in $H_2S$ emission is also evident at the time that the water leaves the sampling site (after 16:00). In fact, because the chamber was re-equilibrated for 20 min after exposure of sediment prior to sampling, the enhancement on the falling tide was probably significantly greater than that shown in Fig. 2.

Complete tidal cycles were not studied in the case of the wet *S. alterniflora* site or the intertidal mudflat site. The plot of $H_2S$ emissions in Fig. 2 from the *S. alterniflora* site is a composite of measurements made over the entire 2-day period, 16–17 May, with the 17 May data plotted to show the correct tidal height at the time of sampling. Though less dramatic than at the wet sand site, the emission measurements at these sites show a similar tidally induced enhancement in the $H_2S$ flux as the water approaches the chamber. An emission range of 0.005–1.04 g $S(H_2S)\ m^{-2}\ a^{-1}$ was measured over the *S. alterniflora*, and 0.029–0.73 g $S(H_2S)\ m^{-2}\ a^{-1}$ on the mudflat.

A similar enhancement of $H_2S$ emissions from a N Carolina intertidal mudflat was reported by Aneja (1984), who suggested that hydrostatic pressure forced the release of gases. The above observations are in

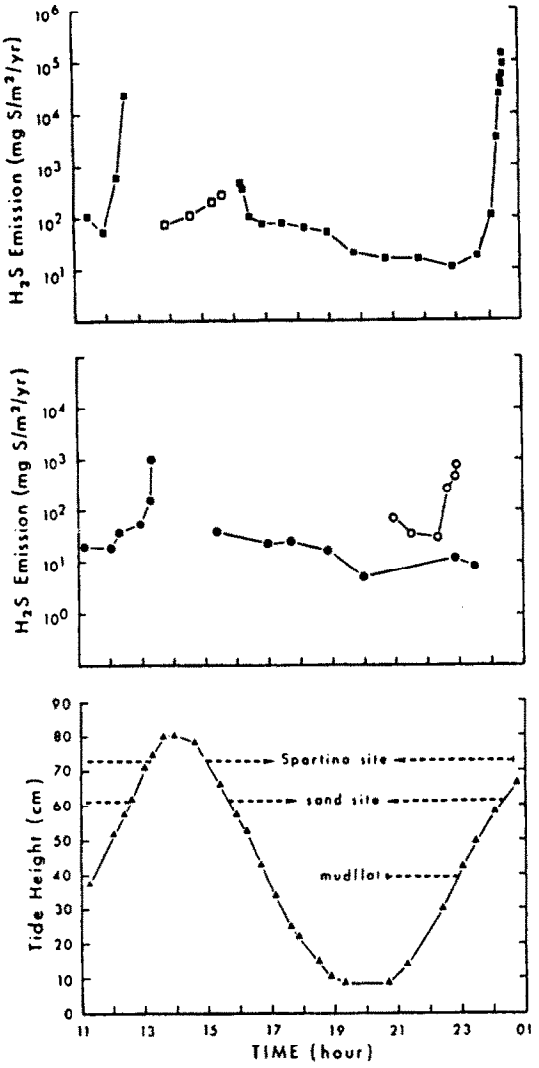


Fig. 2. Variation in the emission rate of hydrogen sulphide from a *Spartina alterniflora* marsh, St. Marks National Wildlife Refuge, Florida, 16–18 May 1985. ■ Bare sand site in *S. alterniflora*; □, sea surface above and in *S. alterniflora*; ●, site over *S. alterniflora*; ○, intertidal mudflat site; ▲, tide height measurement.

marked contrast to those made by Steudler and Peterson (1985) during a study of the diurnal cycle of reduced S emissions. Their data from a site over *S. alterniflora* not only showed no tidal enhancement in the $H_2S$ flux, but, on the contrary, actually indicated the reverse effect at the incidence of high tides.

The importance of the short-term enhancement in $H_2S$ emission for the calculation of an atmospheric $H_2S$ flux can be clearly demonstrated by integrating the data presented in Fig. 2. The net emission during the brief 12 min period from 00:20 to 00:32 (942 $\mu g\,m^{-2}$) was 30 times greater than during the entire 7 h interval from 16:40 to 23:40 (31 $\mu g\,m^{-2}$).

*Emissions of dimethyl sulphide, carbon disulphide and dimethyl disulphide*

The variations of the emission rates of DMS, $CS_2$ and DMDS from the wet site over *Spartina alterniflora* and the adjacent bare sand site on 7–8 October 1985 are shown in Fig. 3. It is clear that there is no significant increase in the emission as the tide reaches the chamber, indicated by the broken line in Fig. 3. Instead, the predominant feature of the emission pattern from both sampling sites is the steady decrease on both days through the afternoon and evening. This follows the decrease in sediment temperature shown in Fig. 3, measured both inside (IN) and outside (OUT) the chambers.

The variation of emission rate with temperature is similar to that reported by Aneja *et al.* (1979), who demonstrated a logarithmic dependance of flux on temperature for DMS from a *S. alterniflora* zone and for $H_2S$ + COS from an intertidal mudflat at low tide. This relationship may be the result of several different factors. The metabolic activity of soil bacteria is a function of temperature, which is conveniently quantified by a $Q_{10}$ (temperature coefficient) factor. This factor, the increase in activity for a 10°C rise in temperature, is normally 2–3 for enzyme mediated processes. From the data presented here, the calculated $Q_{10}$ is significantly higher, greater than 10 in all cases. This suggests that other processes may also be contributing to the elevated emission of the S compounds. Two possible effects that may be important are the solubility of the S gases and the stability of their complexes. Both decrease with increasing temperature, but insufficient measurements were made to assess the magnitude of the effect.

It is evident from the emission plots in Fig. 3 that the emissions of DMS and $CS_2$ are greater from the *S. alterniflora* site than the bare sand site, while the flux of DMDS is similar from the two locations. DMS is the predominant species emitted from both sites, the flux being significantly higher than both $CS_2$ and DMDS, in agreement with all the previous studies listed in Table 1.

The only emission pattern that does not adhere closely to the temperature data in Fig. 3 is that of DMS from the *S. alterniflora* site. This suggests that the release of this compound may not be entirely related to bacterial processes in the soil, but may be related to the metabolism of the *S. alterniflora*. The same emissions pattern has been noted previously at the same study site and on a drier, infrequently flooded, site where the emission of DMS was found to be related to biomass of *S. alterniflora* inside the chamber (de Mello *et al.*, 1987). It is suggested that the release of DMS may be related to the osmotic regulation of the *S. alterniflora* in response to freshwater run-off from the interior of the marsh. Osmotic regulation with dimethyl propiothetin, the most probable biological precursor of DMS, has been found in certain *Spartina* species (Larher *et al.*, 1977).

The range of measured fluxes is compared to that of hydrogen sulphide in Table 1, together with previous measurements made in *Spartina alterniflora* marshes. With the exception of the upper value for $H_2S$ emission from the bare sand site, the majority of fluxes

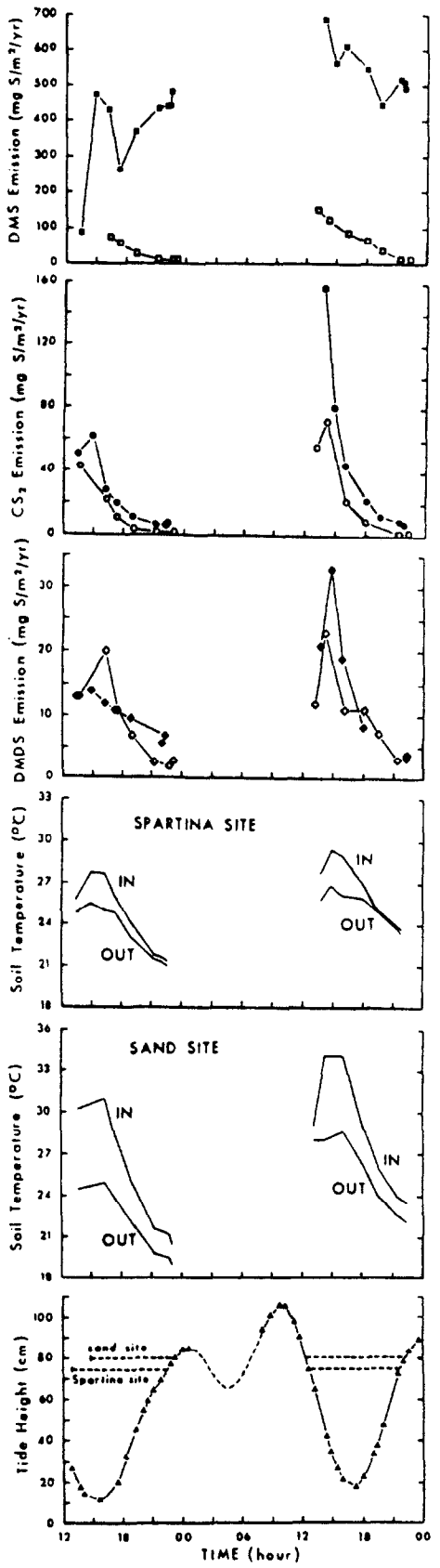


Fig. 3.

measured in this study fall toward the lower extreme of earlier studies.

N Florida is the southern extreme of *Spartina* species habitation, and the sampling site at St. Marks Refuge is well flushed tidally and very low in organic matter. Steudler and Peterson (1985) reported emissions of approximately an order of magnitude higher from a peaty New England *Spartina* marsh. This difference in substrate could explain both their higher emission rates of organosulphur compounds and lack of observed tidal effects. The peaty substrate would hold water more efficiently than a sandy substrate, minimizing the effect of the incoming tide flushing out pore waters or accumulated gases, while at the same time acting as a rich source of biodegradable organic matter.

*Calculation of an atmospheric sulphur flux*

Each of the plots in Figs 2 and 3 can be integrated to obtain an atmospheric flux of reduced S compounds over the sampling period. Because different processes are found to explain the emission patterns, it is necessary to use different methods of calculation to arrive at a mean flux. The $H_2S$ data need to be integrated over a tidal cycle, while the DMS, $CS_2$ and DMDS must be integrated over a diurnal cycle. Mean flux estimates calculated in this manner are presented in Table 2. These calculations assume two equal tidal cycles per day; a diurnal flux is thus obtained by simply doubling the $H_2S$ emissions seen in Fig. 2 for the single tidal cycle.

Table 2 shows that the predominant emission from the *S. alterniflora* site is DMS (448 mg S $m^{-2}$ $a^{-1}$) being almost an order of magnitude greater than the combined flux of the other gases. The situation is markedly different at the unvegetated site in the *S. alterniflora*, where the $H_2S$ emission (756 mg S $m^{-2}$ $a^{-1}$) is more than an order of magnitude greater than the combined organosulphur emission. This is in agreement with the results of Aneja *et al.* (1981) (Table 1) and Steudler and Peterson (1984). The higher flux of $H_2S$ from the sand relative to the other gases calculated here is probably a consequence of our complete study of the tidal cycle giving a greater integrated flux than the steady low tide measurements.

A possible source of error in this study is the enhancement of emissions by the use of S-free sweep gas in the chamber. In practical terms, however, the short-term changes in emission rates found at this site would make the use of ambient air as sweep gas impossibly complicated, since the residence time in the

Fig. 3. Variation in emission fluxes of dimethyl sulphide, carbon disulphide and dimethyl disulphide from a *Spartina alterniflora* marsh, St. Marks National Wildlife Refuge, Florida, 7–8 October 1985. ■, DMS from *Spartina* site; □, DMS from sand site; ●, $CS_2$ from *Spartina* site; ○, $CS_2$ from sand site; ◆, DMDS from *Spartina* site; ◇, DMDS from sand site; —, temperature; ▲, tide height measurement.

Table 1. Measured range of sulphur emissions from *Spartina alterniflora* marshes

| Sampling location | Range of emission rates ($mg\ S\ m^{-2}\ a^{-1}$) $H_2S$ | DMS | $CS_2$ | DMDS | Reference |
|---|---|---|---|---|---|
| Sand by *S. alterniflora* | 11–130000 | 11–152 | 13–72 | 19–23 | This study |
| Over *S. alterniflora* | 5–1040 | 89–687 | 57–157 | 58–33 | This study |
| Intertidal mudflat | 29–732 | nr | nr | nr | This study |
| Coastal marine marsh | 0–100,000 | nr | nr | nr | Aneja (1984) |
| Cedar Island, NC* | 2–6 | 7–1575 | 9–60 | 0.4–0.5 | Adams *et al.* (1981) |
| Cedar Island, NC† | 191‡ | 1311 | nr | nr | Aneja *et al.* (1979) |
| Cox's Landing, NC | 40‡ | 181 | nr | nr | Aneja *et al.* (1979) |
| NC saline marsh mudflat† | 500 | <10 | <50 | <50 | Aneja *et al.* (1981) |
| NC *S. alterniflora* marsh† | <10 | 400 | 150 | <50 | Aneja *et al.* (1981) |
| Falmouth, MA§ | −12,000–18,000 | 0–14,500 | −200–660 | −180–320 | Steudler and Peterson (1985) |

* Mean values, measured in May, July and October, respectively.
† Mean value.
‡ Includes carbonyl sulphide (COS) flux.
§ Hourly measurements over 24-h period. Negative values indicate measured uptake.
nr = Not reported.

Table 2. Mean flux estimates of biogenic sulphur compounds to the atmosphere from a Florida *Spartina alterniflora* marsh

| Sampling location | Estimated emission rate ($mg\ S\ m^{-2}\ a^{-1}$) $H_2S$ | DMS | $CS_2$ | DMDS |
|---|---|---|---|---|
| Sand in *S. alterniflora* | 756 | 55 | 19 | 10.4 |
| Over *S. alterniflora* | 25 | 448 | 31 | 13.4 |
| Intertidal mudflat | 21 | nd | nd | nd |

nd = Not determined.

chamber is long (7 min) compared to the sampling time at peak emission rates (30 s).

## CONCLUSIONS

The data presented in this paper indicate that the major emission of $H_2S$ from the intertidal regions studied is not a steady release from the sediment surfaces exposed at low tides, but is concentrated in a narrow region at the water's edge as the tide rises and falls. The higher fluxes measured at a given sampling site occur for very brief periods of time. Consequently, comprehensive flux data on a short time scale are required in order to calculate average emissions on a longer time scale. By conducting emission measurements on expanses of exposed mudflats or marshlands at times of low tide, previous studies may have significantly underestimated $H_2S$ fluxes to the atmosphere. A mean flux of $0.756\ g\ S(H_2S)\ m^{-2}\ a^{-1}$ from bare sand in a *S. alterniflora* zone is obtained by integration of the emissions data measured over a complete tidal cycle. While this may be an underestimate due to the lack of data at the beginning of the cycle, it is still more than an order of magnitude higher than the directly determined flux for the steady emissions over 7 h of tidal exposure, which represents 92% of the sampling time.

DMS is the predominant species being emitted from the *S. alterniflora* stand, with an estimated annual emission of $0.448\ g\ S\ m^{-2}\ a^{-1}$. The emission of DMS, $CS_2$ and DMDS can largely be explained by variation in sediment temperature.

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