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SPATIAL AND DIEL VARIABILITY IN THE EMISSIONS OF SOME BIOGENIC SULFUR COMPOUNDS FROM A FLORIDA *SPARTINA ALTERNIFLORA* COASTAL ZONE

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Abstract—Emission rates of the biogenic reduced sulfur gases dimethyl sulfide, dimethyl disulfide, carbon disulfide and hydrogen sulfide were measured from several environments within a Florida *Spartina alterniflora* coastal zone. Spatial and diel variability was observed in the emission rates of all the sulfur gases. The speciation and magnitude of sulfur emissions can be related to site elevation and the spatial variability of vegetation coverage. Dimethyl sulfide appears to be a metabolic byproduct of *S. alterniflora*.

Key word index: Dimethyl sulfide, hydrogen sulfide, dimethyl disulfide, carbon disulfide, biogenic sulfur emissions, *Spartina alterniflora*.

INTRODUCTION

In recent years, interest in the natural input of volatile sulfur gases to the atmosphere has increased because of their importance in balancing the global S cycle and their contribution to the acidity of rainfall. Emissions of biogenic S compounds have been measured directly over continental and coastal areas (Steudler and Peterson, 1985; Jørgensen and Okholm-Hansen, 1985; Cooper *et al.*, 1987; and references therein). Most of these measurements were conducted over salt marshes, in particular *Spartina alterniflora* marshes, and areas of mudflats. Dimethyl sulfide was usually found to be the predominant compound emitted from vegetated areas; from mudflats the major compound emitted was H_2S. Other than this broad generalization, however, there is a lack of data concerning diel or spatial variability in the reported emission rates.

Seasonal changes in the emission rates of reduced S compounds from a New England *S. alterniflora* marsh were reported by Steudler and Peterson (1985), and extremely short term, tidally induced, changes in H_2S emission rates from a Florida *S. alterniflora* zone were reported by Cooper *et al.* (1987). This report extends our previous data set of the emission fluxes of dimethyl sulfide (DMS), H_2S, carbon disulfide (CS_2) and dimethyl disulfide (DMDS) to include the effects of spatial variability and of temporal variability on a diel scale.

STUDY SITE

The present study was conducted during May and October 1985 and January 1986 at the St. Marks National Wildlife Refuge, Florida (Fig. 1). Stands of the saltmarsh cordgrass *S. alterniflora* ranged from 30 to 50 cm tall and occupied a zone about 15 m wide seaward of the extreme high tide mark. At this locale the substrate is a fine-grained quartz sand. Unvegetated areas within the cordgrass had a thin oxic top layer, about 0.5 cm thick, and an underlying dark layer characterized by a strong odor of H_2S. The thickness of the oxic layer within the cordgrass was variable but generally ranged between 5 and 10 cm. Samples were taken at two different locations in the *S. alterniflora*: a wet site flushed by at least one high tide each day; and a drier, more oxic, site close to the extreme high tide mark. Samples were also taken at an adjacent bare sand site within the wet *S. alterniflora* stand.

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

SAMPLING AND ANALYTICAL METHODS

The sampling and analytical techniques have been described in detail previously (Cooper *et al.*, 1987). Briefly, samples of S compounds emitted from the soil surface were taken using Teflon lined dynamic flow chambers. DMS, CS_2 and DMDS were trapped on Teflon loops at −183°C, and analyzed gas chromatographically using a Chromosil 330 column (Supelco, Inc., Bellefonte, PA) and a S specific flame

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photometric detector. H_2S was trapped on a silver nitrate impregnated filter and analyzed using the fluorescence quenching of dilute fluorescein mercuric acetate. Samples for H_2S were only taken at times of low tide in order to avoid the tidal effects reported by Cooper *et al.* (1987). These methods have detection limits for DMS, CS_2, DMDS and H_2S of 0.01, 0.03, 0.06 and 0.03 $\mu g\,m^{-2}\,h^{-1}$, except in the case of the bare sand site. Here, the sample volumes were limited to 500 cm^3, and the detection limits of DMDS and CS_2 increased to 0.1 and 0.2 $\mu g\,S\,m^{-2}\,h^{-1}$, respectively.

Soil surface temperature was recorded using a mercury thermometer. The difference between the soil temperature inside and outside the chamber was less than 1°C at night, but was as high as 6°C at the unvegetated site in the afternoon. Solar flux was monitored using a radiometer (The Eppley Laboratory, Inc., RI) equipped with a wide band solar spectrum filter (300–800 nm). Tide height was measured using a staff gauge.

RESULTS

Results of the emission flux measurements are summarized in Table 1. Most of the data sets for the individual sites represent diurnal studies; sampling was only ceased at times of tidal inundation. Several general observations can be made concerning the range of emission measurements presented here. The most obvious are that DMS is the predominant species emitted from both the wet and dry *Spartina* sites and that the emissions of all compounds from the dry site are significantly higher than those from the wet site.

The wet *Spartina* and the wet sand sites in May, October and January were sampled with two identical chambers less than 1 m apart. Despite the proximity of the sites, the emissions of DMS were more than an order of magnitude higher from the vegetated than from the bare site. The emission rates of the other gases showed no systematic difference between the two sites. In contrast to the emission of H_2S, data from the October sampling trip (Cooper *et al.*, 1987) indicate that tidal changes do not significantly affect the emissions of the other S compounds on a short time scale.

In Fig. 2, we present data obtained in October from two dry sites, less than 1 m apart, in what appeared to be a homogeneous stand of *S. alterniflora*. Simultaneous sampling showed a two-fold difference (site 2 > site 1) in the emission rate of DMS between the two sites. The emission rate of CS_2, a factor of 10 lower, showed the reverse effect with Site 1 having twice the emission rate of Site 2. DMDS was comparable in magnitude at the sites. Careful inspection of the study sites later showed that although there was approximately equal *S. alterniflora* biomass above the soil, the root biomass was substantially greater at site 2.

It is evident in Fig. 2 that the variation in emission rates of DMS, CS_2 and DMDS follow the trend of both soil surface temperature and solar flux. There is, however, an interesting observation that was made when sampling was conducted at low tide during the night. Figure 3 shows data obtained at the wet *Spartina* site in May. A daytime maximum similar to that of Fig. 2 can be seen, but a second maximum also occurred in the emission flux of DMS at night, which does not follow the temperature data. At the same time that this effect was occurring, the salinity of the sediment porewater was decreasing as the tide receded, probably due to seepage of water from impounded marshland landward of the sampling site.

While temperatures on the May and October trips were comparable, it was significantly colder in January. Emissions of H_2S, CS_2 and DMDS were correspondingly lower, and the lowest emission rates of DMS from all three sites were found at this time. However, the upper emission rate of DMS measured from the two vegetated sites was not noticeably different than on previous occasions, despite a difference of 10–19°C in the upper temperatures of the individual sampling sites.

DISCUSSION

Spatial variability in the emission rates of the biogenic sulfur compounds DMS, CS_2 and DMDS within this sandy *S. alterniflora* zone appears to be related to two principle factors: (1) the amount of biomass enclosed by the chamber; and (2) the extent to which a site is influenced by daily tides. Diel variability, on the other hand, may be related either to temperature related changes in microbially mediated soil processes or to the transpiration/respiration cycle of the higher plants, i.e. photosynthesis in *S. alterniflora*.

The processes regulating the formation and release of the various S compounds probably differ substantially. H_2S is formed mainly by the anaerobic reduction of sulfate (Jørgensen and Okholm-Hansen, 1985, and references therein), and its major release appears to be a consequence of tidal pumping (Cooper *et al.*, 1987, and references therein). In contrast, previous studies (Bremner and Steele, 1978, and references therein) have shown that DMS, DMDS and CS_2 are formed by the microbial degradation of amino acids in waterlogged soils. The increase in emissions of both CS_2 and

Table 1. Range of reduced sulfur emission flux measurements from sampling locations within a Florida *Spartina alterniflora* zone

Site	Date	Temperature (°C)	Emission ($\mu g\,S\,m^{-2}\,h^{-1}$) DMS	CS_2	DMDS	H_2S*
Wet *Spartina*	12–13 Apr	18–22	nd	nd	nd	0.6–4.0
Wet sand	12–13 Apr	17–22	nd	nd	nd	1.6–3.9
Wet *Spartina*	16–17 May	23.0–36.5	19–59	< 0.2–0.6	< 0.2–0.5	0.6–4.6
Dry *Spartina*	17–18 May	22.0–33.3	97–556	< 0.2	< 0.2–2.5	1.2–5.5.
Wet sand	17 May	24.1–35.4	nd	nd	nd	1.2–9.1
Wet *Spartina*	7–8 Oct	21.4–29.5	30–70	< 0.2–18	< 0.2–3.8	nd
Dry *Spartina* 1	8–9 Oct	22.9–36.2	16–69	1.3–15	0.8–7.2	nd
Dry *Spartina* 2	8–9 Oct	22.8–31.5	66–147	< 0.2–8.0	< 0.2–8.3	nd
Wet sand	7–8 Oct	19.0–28.6	1.3–17	< 0.2–8.2	0.22–2.6	nd
Wet *Spartina*	23–24 Jan	10.0–19.0	17–96	< 0.2	< 0.1	0.17–1.2
Dry *Spartina*	23–25 Jan	9.0–17.2	10–188	< 0.2	< 0.1	0.07–1.9
Wet sand	23–24 Jan	10.0–16.7	0.5–1.7	< 0.2–1.0	< 0.1	0.09–1.5

nd, Not determined.
*, Data taken close to tidal inundation not reported.

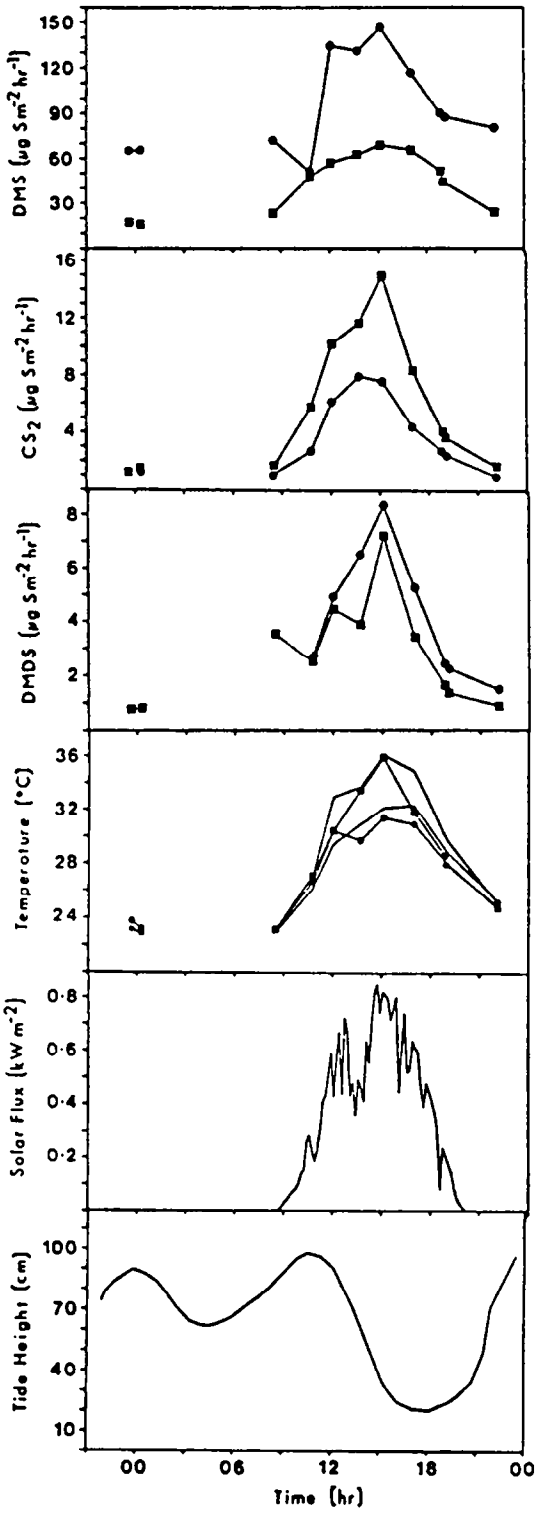

Fig. 2. Emission rate measurements of DMS, CS_2 and DMDS from adjacent chambers in an infrequently flooded site in a Florida *S. alterniflora* zone. ■ Chamber 1; ● Chamber 2. Temperature data without symbols measured inside the chambers, Chamber 1 data on upper plot.

DMDS, from the May–October sampling trips, reflects an increase in the organic content of the sediment. This region experienced two hurricanes between the two sampling trips which resulted in the deposition of considerable organic debris on the beaches and in the intertidal zone.

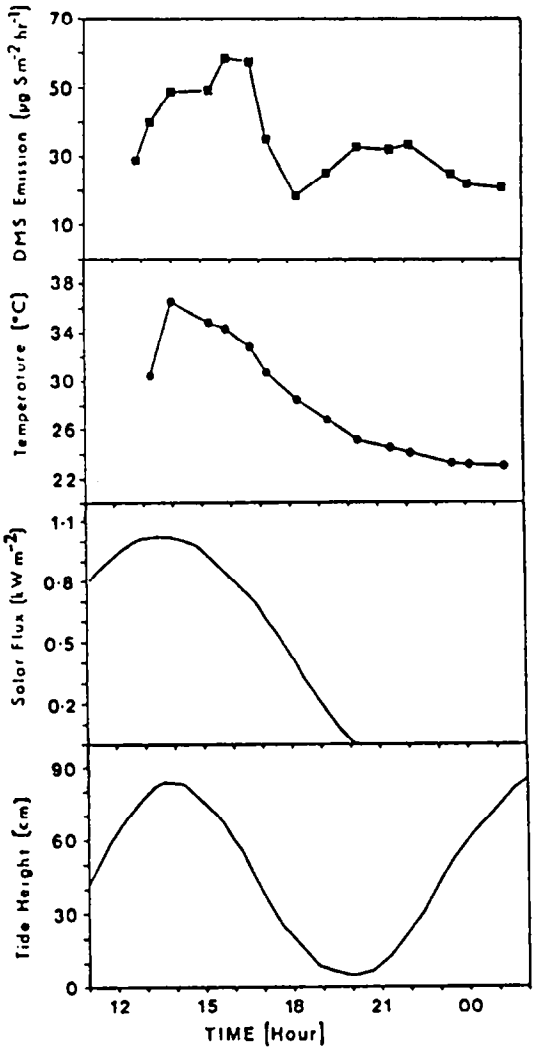

Fig. 3. Emission rate measurements of DMS from a tidally flushed site in a Florida *S. alterniflora* zone. ■ DMS; ● Temperature.

The data presented here, however, are not consistent with the production of DMS solely by these microbial processes in the soil. If this was the only process producing DMS, the drier site would be expected to emit less DMS than the wet site, and the seasonal variability should be greater, i.e. more similar to that of the other compounds. The relationship between *S. alterniflora* biomass and DMS emission and the fact that seasonal variability was evident at the unvegetated site suggest that emissions of this gas are related to the physiology of the macrophyte, *S. alterniflora*.

The ionic sulfur containing compound, dimethylpropiothetin (DMPT), whose base catalyzed or enzymatic cleavage leads to DMS (Cantoni and Anderson, 1956) has been found in other species of *Spartina* (Larher *et al.*, 1977; Storey and Wyn Jones, 1978) and its concentration has been observed to change with NaCl stress (Stewart *et al.*, 1979). Recent results of Wakeham (1986, Personal Communication) have shown that DMPT is present in *S. alterniflora* and is distributed throughout the plant. DMPT is widely used in marine organisms for the purpose of osmoregulation (Cantoni and Anderson, 1956; Dickinson *et al.*, 1982; Vairamurthy *et al.*, 1985), with concomitant release of DMS. Our data for the

emissions of DMS can be explained by postulating an analogous role in *S. alterniflora*.

To put the effect of tidal variation on H_2S emissions in context here, our study of spatial and diel variability precluded the use of H_2S emissions data measured close to tidal inundation of the wet sites. For this reason the data of Table 1 do not clearly indicate the magnitude of the total flux of this gas. Cooper *et al.* (1987) showed variation over four orders of magnitude at a bare sand site, with over 90% of emissions occurring in less than 10% of the tidal cycle. Similarly in January, at times of approaching inundation, the emission flux at the wet sand site increased from 0.6 to 8151 $\mu g\,m^{-2}\,h^{-1}$ in less than 15 min. However, this effect is only significant when calculating an integrated emission flux from unvegetated areas in the *S. alterniflora*.

While the data presented here do not change the overall picture of biogenic emissions from *S. alterniflora* salt marshes, it can be used to explain the large range of emission rates which have been reported in previous studies. The observed variability may be related mainly to the commonly used method of estimating emissions. The use of an encapsulating chamber is necessary to isolate the area of interest from other influences, but experimental and logistical constraints are such that relatively small areas are enclosed at any one time (less than 0.1 m^2 in this study). These small areas are not necessarily representative of the larger ecosystem.

SUMMARY AND CONCLUSIONS

Spatial, diel and seasonal variability are clearly evident in the emission rates of DMS, H_2S, DMDS and CS_2 from coastal *S. alterniflora* sites in Florida. Aside from direct tidal influences, the spatial variability of vegetation coverage and site elevation have a large impact on the speciation and magnitude of the reduced sulfur gas emissions. Superimposed on this variability within the larger ecosystem, the diel variability at individual sub-sites is related to fluctuations in surface temperature or insolation.

Dimethyl sulfide was the predominant sulfur gas emitted from vegetated sites. In addition to soil microbial processes, its production and release seems to be related to the metabolism of the macrophyte, possibly in response to osmotic stress.

CS_2 and DMDS emissions are apparently related to the concentration of organic matter in the sediment. In contrast, H_2S emissions, which occur in brief pulses, are largely governed by tidal flushing.

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