Title
Short-term variability in biogenic sulfur emissions from a Florida Spartina Alterniflora marsh

Permalink
https://escholarship.org/uc/item/59q1k8j6

Journal
Atmos. Environ, 21

Authors
Saltzman, ES
Cooper, DJ
de Mello, WZ
et al.

Publication Date
1987

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, available at
https://creativecommons.org/licenses/by/4.0/

Peer reviewed
SHORT-TERM VARIABILITY IN BIOGENIC SULPHUR EMISSIONS FROM A FLORIDA SPARRINA ALTERNIFLORA MARSH

DAVID J. COOPER, WILLIAM Z. DE MELLO, WILLIAM J. COOPER*, ROD G. ZIKA, ERIC S. SALTMAN, JOSEPH M. PROSPERO and DENNIS L. SAVOIE

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida 33149, U.S.A. and *Drinking Water Research Center, Florida International University, Miami, Florida 33199, U.S.A.

(First received 18 November 1985 and in final form 27 June 1986)

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; Andreea and Raemdonck, 1983; Steudler and Peterson, 1984). Oxidation of these compounds leads to the formation of sulphate, which is precipitated as sulphuric acid in rainfall. Tidally influenced marine sediments and salt marshes are a major source of atmospheric H2S (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 H2S 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 (H2S), dimethyl sulphide (DMS), carbon disulphide (CS2) 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 H2S, 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
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 2.3-1.2 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, SO₂ 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 0.5-1.5 l min⁻¹ for H₂S analysis or 200 cm² min⁻¹ for DMS, CS₂ and DMDS analysis. H₂S emission measurements were made during a complete tidal cycle on 16-17 May 1985, while DMS, CS₂ 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. H₂S was analyzed by a method similar to that of Nausch et al. (1972). The sample gas stream was drawn through a silver nitrate impregnated filter, held in a 4.7-mm Teflon PFA filter holder (Cole-Parmer Instrument Co., Chicago, IL), quantitatively trapping the H₂S 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 fluorescam mercuric acetate. The method has a detection limit of 5 x 10⁻¹¹ moles, corresponding to a lower emission rate of 0.3 mg S(H₂S) m⁻² a⁻¹. Calibration was performed by standard addition of fresh dilute sodium sulphide solution to blank filters.

DMS, CS₂ and DMDS were trapped by passing the gas stream through a Teflon PFA loop (6.4 mm OD x 4 mm ID x 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 (Tracer Instruments, Austin, TX) with a 12 ft x 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 x 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 CO₂ and HCs in the early part of the chromatograms prevented use of the gas chromatographic method for H₂S or COS analysis.

RESULTS AND DISCUSSION

Emissions of hydrogen sulphide

The variations of H₂S 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 H₂S 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(H₂S) 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(H₂S) m⁻² a⁻¹ were measured from the sea surface. An enhancement in H₂S 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 H₂S 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 H₂S flux as the water approaches the chamber. An emission range of 0.005-1.04 g S(H₂S) m⁻² a⁻¹ was measured over the S. alterniflora, and 0.029-0.73 g S(H₂S) m⁻² a⁻¹ on the mudflat.

A similar enhancement of H₂S emissions from a North Carolina intertidal mudflat was reported by Anceja (1984), who suggested that hydrostatic pressure forced the release of gases. The above observations are in

Fig. 1. Sampling site location. St. Marks National Wildlife Refuge, Florida, U.S.A.
Short-term variability in biogenic sulphur emissions from *Spartina alterniflora*

The importance of the short-term enhancement in \( \text{H}_2\text{S} \) emission for the calculation of an atmospheric \( \text{H}_2\text{S} \) 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 ppm - 2, was 30 times greater than during the entire 7 h interval from 16:40 to 23:40 (31 ppm - 2).

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

The variations of the emission rates of DMS, \( \text{CS}_2 \) 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 dependence of flux on temperature for DMS from a *S. alterniflora* zone and for \( \text{H}_2\text{S} + \text{COS} \) 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 \( \text{CS}_2 \) 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 \( \text{CS}_2 \) and DMDS, in agreement with all the previous studies listed in Table I.

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 *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 prothetin, the most probable biological precursor of DMS, has been found in certain *Spartina* species (Larher et al., 1977).

**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.
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$_2$S 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$_2$S 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$_2$S 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 I) and Steudler and Peterson (1984). The higher flux of H$_2$S 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 chamber would be too short.

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.
Short-term variability in biogenic sulphur emissions from Sparrina alterniflora

Table 1. Measured range of sulphur emissions from Sparrina alterniflora marshes

| Sampling location       | H₂S (mg S m⁻² a⁻¹) | DMS (mg S m⁻² a⁻¹) | CS₂ (mg S m⁻² a⁻¹) | DMDS (mg S m⁻² a⁻¹) | 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                  | Aneja (1984) |
| Coastal marine marsh    | 0-100,000           | nr                  | nr                  | nr                  | Aneja (1979) |
| 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       | 400                 | 181                 | nr                  | nr                  | Aneja et al. (1981) |
| 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-hour period. Negative values indicate measured uptake.

| Sampling location       | Estimated emission rate (mg S m⁻² a⁻¹) |
|-------------------------|----------------------------------------|
| Sand in S. alterniflora | 756 55 19 104                         |
| Over S. alterniflora    | 25 448 31 13.4                        |
| Intertidal mudflat      | 21 nd nd nd                           |

nd = Not determined.

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, CS₂ and DMDS can largely be explained by variation in sediment temperature.

Acknowledgements—The authors thank Joe D. White and Culver S. Gidden of St. Mark’s National Wildlife Refuge for assistance. The work was partially supported by the Florida Electric Power Coordinating Group, Inc. Florida acid deposition study through Environmental Science and Engineering, Inc. Support was also received from the Florida International University Drinking Water Research Center, the University of Miami Rosenstiel School of Marine and Atmospheric Science, and NSF Grant No. ATM 84-03921.

CONCLUSIONS

The data presented in this paper indicate that the major emission of H₂S 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 H₂S fluxes to the atmosphere. A mean flux of 0.756 g(S(H₂S)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.

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

| Sampling location       | Estimated emission rate (mg S m⁻² a⁻¹) |
|-------------------------|----------------------------------------|
| Sand in S. alterniflora | 756 55 19 104                         |
| Over S. alterniflora    | 25 448 31 13.4                        |
| Intertidal mudflat      | 21 nd nd nd                           |

nd = Not determined.

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, CS₂ and DMDS can largely be explained by variation in sediment temperature.

REFERENCES

Adams D. F., Farwell S. O., Pack M. R. and Robinson E. (1981) Biogenic sulfur gas emissions from soils in eastern and south-eastern United States. J Air Pollut Control Ass. 31, 1035–1140.

Adams D. F., Farwell S. O., Robinson E. and Pack M. R. (1986) Biogenic sulfur emissions in the SURE region. EPRI Report EA-1516.

Andreae M. O. and Raemdonck H. (1983) Dimethyl sulfide in the surface ocean and the marine atmosphere: a global view. Science 221, 744–747.

Aneja V. P. (1984) The role of tidal and diurnal variations on the release of biogenic sulfur compounds. In Environmental Impact of Natural Emissions (edited by Aneja V. P.), pp. 1–20. Air Pollution Control Association, Pittsburgh, PA.

Aneja V. P., Overton J. H. and Aneja A. P. (1981) Emission survey of biogenic sulfur gas emissions from terrestrial surfaces. J Air Pollut Control Ass. 31, 256–258.

Aneja V. P., Overton J. H., Cupitt L. T., Durham J. L. and Wilson W. E. (1979) Direct measurements of some atmospheric biogenic sulfur compounds. Tellus 31, 174–178.

Cline J. D. and Bates T. S. (1983) Dimethyl sulfide in the equatorial Pacific Ocean: a natural source of sulfur to the atmosphere. Geophys. Res. Lett. 10, 949–952.

Cooper D. J. (1986) Variability in biogenic hydrogen sulfide emissions from selected Florida ecosystems. M. S. thesis, University of Miami.

de Mello W. Z., Cooper D. J., Cooper W. J., Saltzman E. S., Zita R. G., Savoie D. L. and Prospero J. M. (1987) Spatial and diel variability in the emissions of some biogenic sulfur...
compounds from a Florida *Spartina alterniflora* coastal zone. *Atmospheric Environment* (in press).

Georgii H.-W. (1977) Large-scale spatial and temporal distribution of sulfur compounds. *Atmospheric Environment* 12, 681-690.

Hansen M. H., Ingvorsen K. and Jørgensen B. B. (1978) Mechanisms of hydrogen sulfide release from coastal marine sediments to the atmosphere. *Limnol. Oceanogr.* 23, 68-76.

Hill F. B., Aneja V. P. and Felder R. M. (1978) A technique for measurement of biogenic sulfur emission fluxes. *J. Environ. Sci. Health* 13, 199-225.

Ingvorsen K. and Jørgensen B. B. (1982) Seasonal variation in H₂S emission to the atmosphere from intertidal sediments in Denmark. *Atmospheric Environment* 16, 855-865.

Jaeschke W., Claude H. and Herrmann J. (1980) Sources and sinks of atmospheric H₂S. *J. geophys. Res.* 85, 5639-5644.

Larher F., Hamelin J. and Stewart G. P. (1977) L’acide dimethyl sulphonium-3-propanoique de *Spartina anglica*. *Phytochemistry* 16, 2019-2020.

Maroulis P. J. and Bandy A. R. (1977) Estimates of the contribution of biologically produced dimethyl sulfide to the global sulfur cycle. *Science* 196, 647-648.

Natusch D. F. S., Klonis H. B., Axelrod H. D., Teck R. J. and Lodge J. P., Jr. (1972) Sensitive method for the determination of atmospheric hydrogen sulfide. *Analyst. Chem.* 44, 2067-2070.

Steudler P. A. and Peterson B. J. (1984) Contribution of gaseous sulphur from salt marshes to the global sulfur cycle. *Nature* 311, 455-457.

Steudler P. A. and Peterson B. J. (1985) Annual cycle of gaseous sulfur emissions from a New England *Spartina alterniflora* marsh. *Atmospheric Environment* 19, 1411-1416.