Tellus (1986), *38B*, 81–86

Characterization of emissions of biogenic atmospheric hydrogen sulfide

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(Manuscript received April 23; in final form January 14, 1986)

ABSTRACT

The emission rate measurements of H_2S into the atmosphere from coastal marine sediments were made by the use of an emission flux reactor (chamber) technique under deaerated (gaseous N_2) and aerated (ambient air) conditions. The emission rates of H_2S varied over a wide range (>0.05 to <100 gS m^{-2} yr^{-1}). The emission of H_2S was inversely related to the stage of tidal hydrology, with incoming and outgoing tidal hydrostatic pressure affecting the gaseous release at the locale. The diurnal studies showed an enhancement in the emission rates at night; however the emission rate of H_2S is unaffected by increasing light intensity (between 100 and 90,000 lux) at constant temperature. The emission rates of H_2S are greater in the deaerated chamber than in the aerated chamber. The measured marine fluxes of ~ 0.1 gS m^{-2} yr^{-1} seem to agree well with those derived from global marine sulfur budgets.

1. Introduction

The contribution of natural sulfur compounds to the atmospheric sulfur burden has been and remains an area of major concern. Natural sources are thought to constitute a large fraction (~ 0.1 to ~ 0.7) of the atmospheric sulfur burden (Conway, 1943; Eriksson, 1963; Junge, 1963; Robinson and Robbins, 1968; Kellogg et al., 1972; Friend, 1973; Granat et al., 1976; Ryaboshapko, 1983). Only recently (Aneja, 1975; Hill et al., 1978; Wilson et al., 1978; Aneja et al., 1979a, b; Adams et al., 1980; Jaeschke et al., 1980; Goldberg et al., 1981; Ingvorsen and Jorgensen, 1982; Barnard et al., 1982; Andreae and Raemdonck, 1983; Howarth and Giblin, 1983; Steudler and Peterson, 1985) experimental evidence has been reported in which earth-atmosphere fluxes of natural sulfur compounds were measured. Identification and characterization of sources of atmospheric natural sulfur compounds are essential for the rational formulation of emission control policies designed to limit the atmospheric sulfate burden, and for analysis of the origins of acid precipitation.

Biogenic sulfur is released from vegetation, produced by decomposition of organic matter and from bacterial sulfate reduction in the biosphere. Data on sulfur release by vegetation is scanty although some plants are known to emit hydrogen sulfide (H_2S) (Wilson et al., 1978), dimethyl sulfide (DMS), (Aneja et al., 1979a; Adams et al., 1980; Steudler and Peterson, 1985) and carbon disulfide (CS_2) (Aneja et al., 1979b; Adams et al., 1980; Steudler and Peterson, 1985). Many fungi and bacteria release sulfur compounds (Clarke, 1953; Pfennig and Widdel, 1982) during organic decomposition. Salt marshes, because of high sulfate reduction rates (Howarth and Teal, 1979; Howarth and Giblin, 1983) and concomitant production of H_2S, have been proposed as important sites of biogenic sulfur release to the atmosphere.

Field investigations of biogenic sulfur compounds have involved measurement of concentrations of compounds of interest in the ambient air (Natusch et al., 1972; Breeding et al., 1973; Maroulis and Bandy, 1977; Aneja et al., 1982; Hitchcock and Black, 1984). This paper explores the role of some physical properties, viz. light intensity, tidal hydrology, diurnal variations, deaerated (under gaseous N_2) and aerated (under ambient air) conditions on the release of biogenic sulfur compounds from a coastal marine salt marsh.

2. Emission flux measurements

Reported in this study are the results of the biogenic sulfur emissions using the emission flux reactor (chamber) method. The analytical instrument used was a gas chromatograph equipped with a flame photometric detector sensitive to sulfur compounds (details on the experimental methodology are published in Aneja et al., 1979). Experiments were carried out during fall at Cox's Landing, a privately owned salt marsh located near Long Beach, North Carolina on the east coast of the United States. The marsh is composed of mud flat and vegetated areas. The vegetation is predominantly *Spartina alterniflora*; much of it was flowering at the time. Towards the land, the *Spartina* is bordered by a fringe of *Iuncus roemerianus* (needle rush), sparse *Borrichia frutescens*, and *Spartina patens*. The tidal range is 1 to 1.5 meters and most of the marsh area is intertidal.

The remoteness of Cox's Landing from anthropogenic sources was an important aspect in the site selection. Also, preliminary investigations performed with lead acetate treated tags (Metronics Associates, Inc.), indicated that it was a productive site of gaseous sulfur.

The emission flux experiments were conducted as follows: two similar emission flux reactors were placed adjacent to each other on the marsh over the surface of interest. In Reactor 1 (deaerated), a known volumetric rate of gaseous nitrogen from a cylinder was humidified at ambient temperature and then passed through the reactor. In Reactor 2 (aerated), a known volumetric rate of ambient air was passed through the emission flux reactor. These carrier gases swept the emitted gases into Teflon bags, where 15 to 30-minutes integrated samples were collected. Simultaneously, an inlet ambient air bag sample was also collected. A complete design of the field experimental apparatus is published in Aneja et al. (1982). The bags were collected every half hour during the course of the experiment. The three bags were analyzed for various gaseous sulfur species using a gas chromatograph equipped with a flame photometric detector. A 394-nm interference filter made the detector sensitive to sulfur compounds. A 36-foot ($\sim$11 m) FEP Teflon column ($\frac{1}{8}''$ (0.32 cm) o.d.) packed with 40-60 mesh Teflon coated with 5% polyphenyl ether (PPE) and 0.5% phosphoric acid was used at 50°C to separate gaseous sulfur species. The carrier gas was nitrogen with a flow rate of 81 ml $\min^{-1}$. The retention time for CS_2 in these conditions is 14 min which allows a good separation from H_2S+COS (1.5 min), SO_2 (3.1 min), and CH_3SH (5.0 min). The overlapping DMS (12.2 min) and CS_2 peaks were graphically resolved into separate contributions. This column did not resolve H_2S and COS, so these species were separated by incorporating a second 19-foot (5.8 m) FEP Teflon column ($\frac{1}{8}''$ (0.32 cm) o.d.) packed with 50/80 mesh Porapak QS in parallel with the first. The two columns were incorporated in the flow lines separately by a pneumatically controlled switching system. The carrier gas for the second column was nitrogen with a flow rate of 40 ml $\min^{-1}$. The retention time for COS in these conditions is 8 min, which allows a good separation from H_2S (retention time 5.5 min); however, this column retained CS_2. The gas chromatograph was calibrated for both columns in the laboratory and in the field using a dynamic dilution system and bag samples.

3. Results and discussion

The tidal flats of marine environment are areas of extreme complexity and activity. They serve as both sources and sinks of a wide variety of compounds and materials, produced by many complex processes. They are in a constant state of mass, energy and momentum flux with the surrounding environments. Here we present a systematic approach to study the release of biogenic sulfur compounds from intertidal marshes by examining chemical, physical and hydraulic factors. No doubt biological and microbiological factors are of equal importance, but they were not studied.

During the experiments, the ambient temperature ranged between $\sim$20°C to $\sim$32°C. The $[SO_4^{-2}]$ content of the solution under the emission flux reactor varied from ~2100 to ~2900 g ml^{-1} of solution. The dissolved oxygen concentration (D.O.) ranged from 3.6 to 13.5 ppm, and the locale was mostly alkaline.

The gaseous sulfur (H_2S) emission rate in the aerated chamber during day (light intensity > 100 lux) in the absence of a water column (tidal height ~0 cm), for emission rate measurements at similar temperature, was observed to be independent of light intensity. The most important biological source of atmospheric sulfur (free sulfide) is thought to originate within the anaerobic layer where it is produced primarily by heterotropic sulfate-reducing bacteria of the genera *Desulfovibrio*, *Desulfobacter*, and *Desulfobulbus* (Postgate, 1959; Stanier et al., 1970; Pfennig and Widdel, 1982). These anaerobes utilize sulfate and other inorganic sulfur compounds as specific hydrogen acceptors during the oxidation of organic energy sources. During this metabolic cycle, the original sulfur compounds are reduced to sulfides. These heterotropic sulfate-reducing bacteria are insensitive to light, suggesting increasing light intensity may not affect H_2S emissions.

In order to study the flux of H_2S versus time we plotted tidal and diurnal variations of the release of biogenic sulfur compounds under both aerated and deaerated conditions (Figs. 1, 2). In general, the emission rates of gaseous H_2S were strongly enhanced at night when compared with emission rates during the day. Similar conclusions were also arrived at by Hansen et al. (1978). This may be due to the suppression of the action of green and purple photosynthetic sulfur bacteria (Stainer et al., 1970), which oxidize H_2S to non-volatile forms and should in principle lead to lower fluxes in the daytime than at night. Another possible effect of light may involve photochemical action: an unknown mechanism involving rapid oxidation to particulate sulfate. However Hansen et al. (1978) observed that

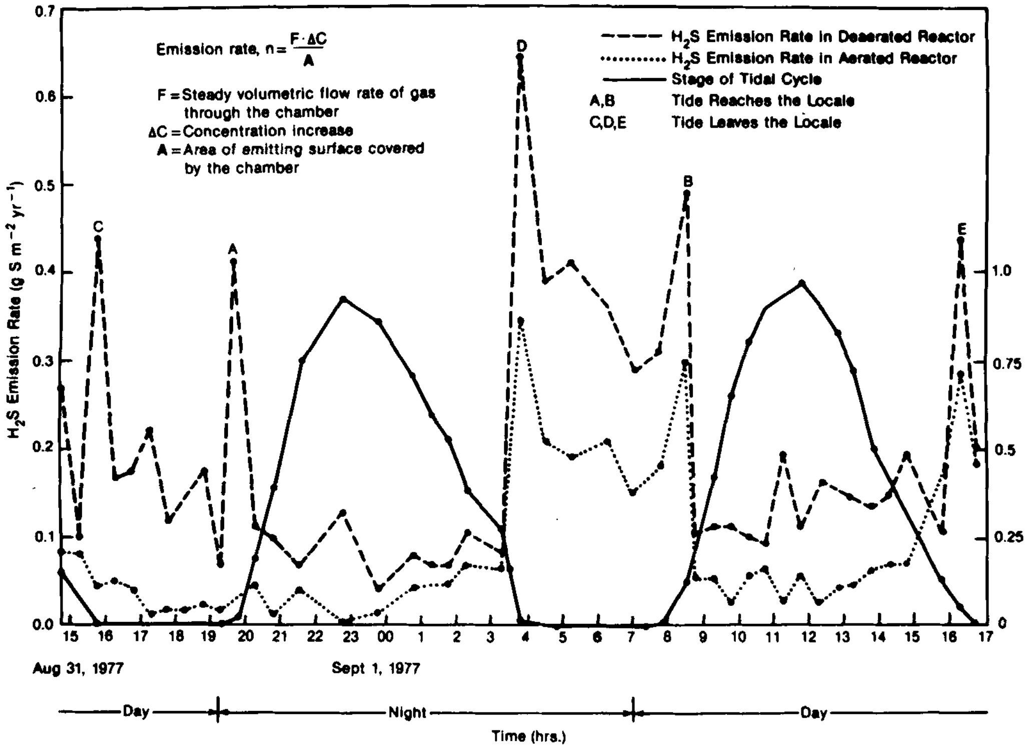

Fig. 1. Diurnal and tidal variation in the emission rate of hydrogen sulfide at Cox's Landing (a coastal marine marsh).

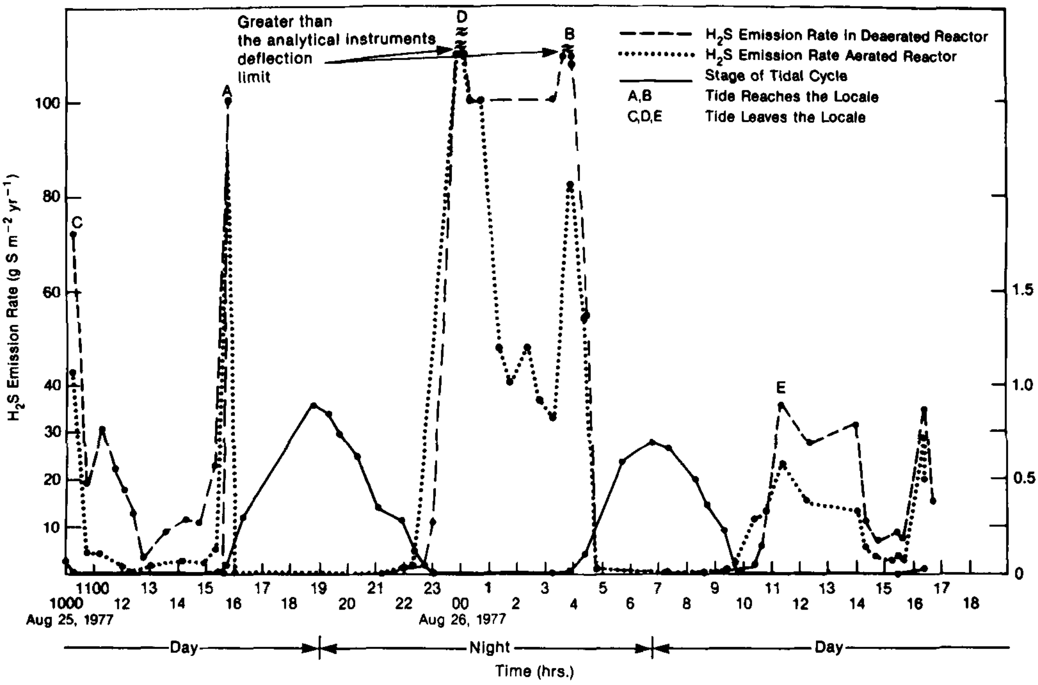

Fig. 2. See caption to Fig. 1.

increasing light made the locale more oxic which decreased the emissions of H_2S while during the night they observed essentially anoxic conditions leading to enhanced emissions of H_2S.

A comparison of fluxes derived from using gaseous nitrogen (deaerated conditions) and ambient air (aerated) as sweep gases show that the emission rate of gaseous sulfur (H_2S) are greater in the deaerated chamber than in the aerated chamber. This could be caused by loss of H_2S in the presence of oxygen or lack of oxygen also slows the rate of oxidation of H_2S in the aqueous phase or, by enhancement of the emission rates by lack of oxygen. 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 (Bremner and Steele, 1978).

It is interesting to observe from Figs. 1, 2 that there is 1 to 2 orders of magnitude variations in the sulfur flux between soil enclosure sites in the same marsh. This was perhaps caused by higher concentration of sulfate reducing microorganisms at the high sulfur emitting locale (Fig. 2), or it may be a temporal effect.

The release of gaseous sulfur (H_2S) appears to be inversely related to the stage of the tidal cycle, which is to say that at high tide, the release of gaseous sulfur was the lowest and vice versa. This is because the H_2S produced may diffuse upward in the water column until it encounters oxygenated water; where it is rapidly reoxidized to sulfate. A larger water column would provide larger quantity of dissolved O_2 and longer residence time for H_2S to be oxidized and recycled to sulfate, hence decreasing its release to the atmosphere. However, a very interesting phenomenon overlays this tidal variation (tidal pumping). We observe (Figs. 1, 2) that when the tide reaches the locale (A and B) or leaves the locale (C, D and E) there is a sudden enhancement in the release of H_2S emission for a short duration. We speculate that when the tide approaches the locale, hydrostatic pressure is created which forces the emitting gases into the atmosphere by convection. Alternately in the presence of a water column, the pressure exerted by it and the presence of dissolved O_2 on the locale may prevent the release of the emitting gases; and this pressure and much of dissolved oxygen are absent when the tide leaves the locale.

In the presence of tide (Figs. 1, 2) we observe a gaseous H_2S exchange between water and air. The fluxes over water appear to be uniform and are observed to be ~ 0.075 gS m^{-2} yr^{-1} in the aerated mode, and ~ 0.12 gS m^{-2} yr^{-1} in the deaerated mode.

It is interesting to compare these fluxes and those derived from a mass transfer calculation across the air-sea interface. Estimates of mass transfer have been made by Liss and Slater (1974) based on a two-film theory of mass transfer. We use this approach here to estimate flux of H_2S from water to air under conditions corresponding to the air-sea interface. From our analysis, integrated over tidal and diurnal cycle, we can conclude that for air-sea exchange, the flux values in an abiotic environment are considerably higher (~ 5 gS m^{-2} yr^{-1}) than the emission rates for H_2S in natural biotic environment (~ 0.10 gS m^{-2} yr^{-1}). This could perhaps be due to either microbial or oxidation effects in the water column.

Average terrestrial fluxes calculated from recent global atmospheric sulfur budgets range from 0.4 to 0.7 gS m^{-2} yr^{-1}, while marine fluxes derived in the same way range from 0.1 to 0.5 gS m^{-2} yr^{-1} (Hill et al., 1978). We thus see that the measured marine fluxes of ~ 0.1 gS m^{-2} yr^{-1} seem to agree well with those derived from global marine sulfur budgets.

4. Acknowledgements

The data for the research described in this report were collected under U.S. EPA Contract No. 68-02-2566 to Northrop Services, Inc., Research Triangle Park, N.C., USA.

REFERENCES

Adams, D. F., Farwell, S. O., Robinson, E. and Pack, M. R. 1980. *Biogenic sulfur emissions in the SURE region*. Washington State University, Report No. EA-156, Research Project 8561, Electric Power Research Institute, Palo Alto, CA 94304, P.F-13.

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. 1975. *Characterization of sources of biogenic atmospheric sulfur compounds*. M.S. Thesis, Department of Chemical Engineering, North Carolina State University, Raleigh, NC, pp. 144.

Aneja, V. P., Aneja, A. P. and Adams, D. F. 1982. Biogenic sulfur compounds and the global sulfur cycle. *APCA Journal 32*, 8, 803–807.

Aneja, V. P., Corse, E. W., Cupitt, L. T., King, J. C., Overton, Jr., J. H., Rader, R. E., Richards, M. H., Sher, H. J. and Whitkus, R. J., 1979. *Biogenic sulfur sources strength field study*. Northrop Services, Inc., Report No. ESC-TR-79-22, Research Triangle Park, NC, p. 189.

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

Aneja, V. P., Overton, Jr., J. H., Cupitt, L. T., Durham, J. L. and Wilson, W. E. 1979b. Carbon disulfide and carbonyl sulfide from biogenic sources and their contribution to the global sulfur cycle. *Nature 282*, 493–496.

Barnard, W. R., Andreae, M. O., Watkins, W. E., Bingemer, H. and Georgii, H. W. 1982. The flux of dimethylsulfide from the oceans to the atmosphere. *J. Geophys. Res., 87*, C11, 8787-8793.

Breeding, R. J., Lodge, Jr., J. P., Pate, J. B., Sheeseley, D. B., Klonis, M. B., Fogle, B., Anderson, J. A., Englest, T. R., Haagenson, P. L., McBeth, R. B., Morris, A. L., Pogue, R. and Wortburg, A. F. 1973. Background trace gas concentration in the central United States *J. Geophys. Res. 78*, 7057.

Bremner, J. M. and Steele, C. G. 1978. Role of microorganisms in the atmospheric sulfur cycle. *Adv. Microb. Ecol. 2*, 155–201.

Clarke, P. H. 1953. Hydrogen sulfide production by bacteria. *J. Gen. Microbiol. 8*, 397.

Conway, E. J. 1943. Mean geochemical data in relation to oceanic evolution. *Proc. R. Irish Acad. A 48*, 119–159.

Eriksson, E. 1963. The yearly circulation of sulfur in nature. *J. Geophys. Res. 68*, 4001–4008.

Friend, J. P. 1973. The global sulfur cycle. In: *Chemistry of the lower atmosphere*, S.I. Rasool, ed. Plenum Press, New York, 177–201.

Goldberg, A. B., Maroulis, P. J., Wilner, L. A. and Bandy, A. R. 1981. Study of H_2S emissions from a salt water marsh. *Atmos. Environ. 15*, 11–18.

Granat, L., Rodhe, H. and Hallberg, R. O. 1976. The global sulfur cycle (B. H. Svensson and R. Soderlund, eds.). *Nitrogen, phosphorus and sulfur-global cycles, 22*, 89–134. SCOPE Report 7, Ecological Bulletins, Stockholm.

Hansen, M. H., Ingvorsen, K. and Jorgensen, B. B. 1978. Mechanism 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. *Environ. Sci. Health 13* (3), 199–225.

Hitchcock, D. R. and Black, M. S. 1984. $^{34}S/^{32}S$ Evidence of biogenic sulfur oxides in a salt marsh atmosphere. *Atmos. Environ. 18*, 1–17.

Howarth, R. W. and Giblin, A. 1983. Sulfate reduction in the salt marshes at Sapelo Island, Georgia. *Limnol. Oceanogr. 28*, 70–82.

Howarth, R. W. and Teal, J. M. 1979. Sulfate reduction in a New England salt marsh. *Limnol. Oceanogr. 24*, 999–1013.

Ingvorsen, K. and Jorgensen, B. B. 1982. Seasonal variation in H_2S emission to the atmosphere from Intertidal sediments in Denmark. *Atmos. Environ. 16*, 855–865.

Jaeschke, W., Claude, H. and Herrmann, J. 1980. Sources and sinks of atmospheric H_2S. *J. Geophys. Res. 85*, 5639–5644.

Junge, C. E. 1963. *Air chemistry and radioactivity*. Academic Press, New York, 1963 38 pp.

Kellogg, W. W., Cadle, R. D., Allen, E. R., Lazrus, A. L. and Martell, E. A. 1972. The sulfur cycle. *Science 175*, 587–596.

Liss, P. S. and Slater, P. G. 1974. Flux of gases across the air-sea interface. *Nature 247*, 181–184.

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

Natusch, D. F. S., Klonis, M. B., Axelford, M. D., Teck, R. J. and Lodge, Jr., J. P. 1972. Sensitive method for the measurement of atmospheric hydrogen sulfide. *Anal. Chem. 44*, 2067.

Pfennig, N. and Widdel, F. 1982. The bacteria of the sulfur cycle. *Philos. Trans. R. Soc. London, Ser. B, 298*, 433–441.

Postgate, J. R. 1959. Sulfate reduction by bacteria. *Ann. Rev. Microbiol 13*, 505–520.

Robinson, E. and Robbins, R. C. 1968. *Sources abundance, and fate of gaseous atmospheric pollutants.* SRI Project Report PR-6755, prepared for American Petroleum Institute, New York, 123 pp.

Ryaboshapko, A. G. 1983. The atmospheric sulphur cycle. In *The global biogeochemical sulfur cycle* (ed. by M. V. Ivanov and J. R. Freney). John Wiley and Sons, New York, 470 pp.

Stainer, R. Y., Dondoroff, M. and Adelberg, E. A. 1970. *The microbiol world.* Prentice-Hall, Englewood Cliffs, New Jersey.

Steudler, P. A. and Peterson, B. J. 1985. Annual cycle of gaseous sulfur emissions from a New England *Spartina Aeterniflora marsh. Atmos. Environ. 19*, 1411–1416.

Wilson, L. G., Bressan, R. A. and Filner, P. 1978. Light-dependent emission of hydrogen sulfide from plants. *Plant Physiol. 61*, 184.