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MEASUREMENTS OF EMISSION RATES OF CARBON DISULFIDE FROM BIOGENIC SOURCES AND ITS POSSIBLE IMPORTANCE TO THE STRATOSPHERIC AEROSOL LAYER

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MEASUREMENTS OF EMISSION RATES OF CARBON DISULFIDE FROM BIOGENIC SOURCES AND ITS POSSIBLE IMPORTANCE TO THE STRATOSPHERIC AEROSOL LAYER

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Biogenic sources are thought to constitute a large fraction (~0.1 to ~0.7) of the atmospheric sulfur burden.¹⁻⁷ Identification and characterization of sources of atmospheric sulfur compounds are essential for the rational formulation of emission control strategies and to determine the relative importance of various terrestrial sources. Conway¹ had speculated that the principle volatile biogenic component of the sulfur cycle was hydrogen sulfide (H₂S). However, Lovelock *et al.*⁸ and Rasmussen⁹ suggested that dimethyl sulfide (DMS) rather than H₂S was contributing to the apparent source deficits.

Only recently¹⁰⁻¹² has this important inference been tested and the identity of some of the emitted sulfur compounds ascertained. Aneja *et al.*¹² have shown that both H₂S and DMS are emitted from salt marshes. Other gaseous sulfur compounds may also contribute to the sulfur burden of the atmosphere. Aneja¹⁰ and Hill *et al.*¹¹ observed and measured the emission rates of methyl mercaptan (CH₃SH), DMS, and dimethyl disulfide ((CH₃)₂S₂) from a salt marsh. Sandals and Penkett¹³ reported the measurement of carbonyl sulfide (COS) and carbon disulfide (CS₂), and Hanst *et al.*¹⁴ have reported COS measurement in the atmosphere. Lovelock¹⁵ has observed that CS₂ is widely distributed in coastal and ocean waters.

The inert sulfur gases COS and CS₂ are of interest because of their long tropospheric lifetimes. Hence, both COS and CS₂ are assumed to be of chemical significance in the stratosphere,^{13,16} where they may be photolyzed and thus explain the presence of sulfur dioxide (SO₂) and sulfates (SO₄²⁻). Since the stratospheric aerosol layer has an important effect on the global climate, it is imperative that the magnitude of the various sources be properly identified.

The present work reports the discovery of CS₂ emanating from a salt marsh and estimates its emission rates. Using these rates, it also discusses the possible transport of sulfur to the stratosphere as CS₂.

An emission flux reactor (chamber) for measuring earth-atmosphere fluxes of biogenic sulfur compounds was used. The chamber technique has the important advantage that the sensitivity for flux measurement is high without the necessity of

measuring very low concentrations. In addition, gas residence times in the emission flux reactor are on the order of minutes so that chemical transformations between emission and analysis may be minimized. The chamber used by Aneja¹⁰ and Hill, Aneja and Felder¹¹ was modified by making the walls from 5-mil thick FEP Teflon supported by an exterior aluminum frame. This design was chosen to afford negligible attenuation of ambient light.

The analytical instrument employed was a gas chromatograph equipped with a flame photometric detector. A 394 nm interference filter made the detector sensitive to sulfur compounds. A 36 foot (~11 meters) FEP Teflon column (1/8 inch (0.32 cm) o.d.) packed with 40–60 mesh Teflon coated with 5% polyphenyl ether and 0.5% phosphoric acid (H_3PO_4) was used at 50°C to separate gaseous sulfur species.¹⁷ The carrier gas was nitrogen with a flow rate of ~81 ml/min. The retention time for CS_2 under these conditions is ~14 minutes which allows a good separation from H_2S , SO_2 , CH_3SH , and COS . The overlapping DMS and CS_2 peaks were manually resolved into separate contributions. The gas chromatograph was calibrated in the laboratory and in the field using a dilution system and bag samples.

Intensive measurements were made for biogenic sulfur species at Cox's Landing, Long Beach, North Carolina. This location is a salt marsh on the east coast of the

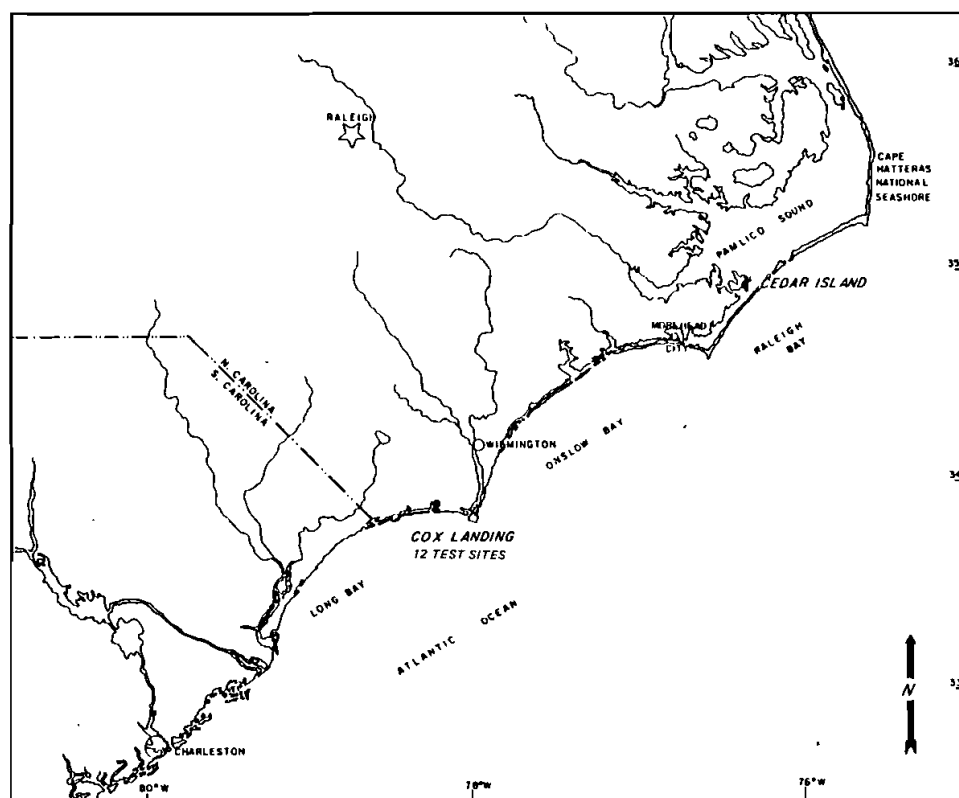


FIGURE 1 Location of the sites.

United States (Fig. 1). Experiments were performed during late summer at twelve (12) different test sites. At each test site, two identical emission flux reactors were placed adjacent to each other. One was flushed with pure gaseous nitrogen (deaerated) and the other with ambient air (aerated). This was done to gain information on the oxygen-depleted gaseous environment, as well as, to maintain the integrity of the emitted sulfur compounds in the deaerated case. Sampling was done over mud flats (Table I), over regions in close proximity to marsh grass where the vegetation was decaying (Table II), and over marsh grass (*Spartina alterniflora*) clipped to about one inch above ground level (Table III). Time-integrated bag samples were collected every thirty (30) minutes and were analyzed for various gaseous sulfur species. All the experiments described herein were performed to study the emission fluxes of CS₂ for diurnal and tidal variations. During the experiments, the ambient temperature ranged between 19.1°C and 33.4°C, sediment temperature with the tide out ranged from 24.2°C to 32.6°C, and the water temperature with the tide in was between 23.8°C and 31.2°C.

Figure 2 gives the recorder output for an injection into the gas chromatograph of sulfur gases emitted from a salt marsh. It establishes the presence and identity of CS₂ and various other biogenic sulfur species.

The emission rate of CS₂ at various test sites is tabulated in Tables I, II, and III. Twenty injections of the 172 aerated runs showed CS₂; however, CS₂ appeared only once in the deaerated case. All of the data in Tables I, II, and III are for the aerated case. These observations show that CS₂ is certainly produced in an aerated environment, and that it may be formed in a deaerated environment. Lovelock has observed¹⁵ that CS₂ can originate under anaerobic conditions on the sea floor, while, in the *Spartina* zone, we observe it more often under aerobic conditions. We currently cannot definitely explain the observational differences between the aerated and deaerated chamber runs.

As is evident from Table I, the emission rate of CS₂ over the mud flat zone was in all

TABLE I
Direct CS₂ emission rate measurements over mud flat zone

Date	Test Site			Stage of Tidal Cycle Cm	Light Intensity	CS ₂ Emission Rate* gmS/m ² /yr
	Location	No. of Runs	Characteristic			
8/23/77	1	4	Mud Flat	Low Tide, 0.0 Cm	Day	<0.05
8/25/78 & 8/20/77	2	56	Mud Flat	One Complete Tidal Cycle	Day & Night	<0.05
8/27/77	3	9	Mud Flat	Low Tide, 0.0 Cm	Night	<0.05
8/27/77	4	9	Mud Flat	Low Tide, 0.0 Cm	Day	<0.05
8/30/77	5	11	Mud Flat	Tide & Low Tide	Day	<0.05
8/31/77	6	8	Mud Flat	Low Tide, 0.0 Cm	Day	<0.05
9/2/77	9	3	Mud Flat	Low Tide, 0.0 Cm	Dawn	<0.05

*Emission Rate, n, = $F \cdot \Delta C / A$.

F = steady volumetric flow rate of gas through the chamber

ΔC = concentration increase

A = area of emitting surface covered by the chamber.

cases below the detectability of the gas chromatograph (emission rate <0.05 gmS/m²/yr). However, CS₂ is evolved over and in the vicinity of *Spartina alterniflora* (marsh grass) under the aerated emission flux reactor in the presence and absence of a water column (Table II and III). It may be that CS₂ is formed at a juncture of the carbon and sulfur cycles by either biogenic or chemical activity.

The emission rates in the vicinity of and over the *Spartina* zone are presented in Tables II and III and range from ~ 0.1 to ~ 0.3 gmS/m²/yr. These observations

TABLE II
Direct CS₂ emission rate measurements over decaying *Spartina* zone for individual runs

Date	Test Site			Stage of Tidal Cycle Cm	Light Intensity Lux	Temperature °C			CS ₂ Emission Rate* gmS/m ² /yr
	Location	No. of Runs	Characteristic			Ambient	Sediment	Water	
8/31/77	7	47	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Tide 12.7	Day 8500	31.2		20.8	0.18
8/31/77	7	47	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Low Tide 0.0	Day 2400	31.5	29.5		0.16
9/01/77	7	47	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Tide 7.6	Day 7700	29.8		29.8	0.23
9/01/77	7	47	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Tide 2.5	Day 7500	29.8		30.6	0.29
9/01/77	7	47	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Low Tide 0.0	Day 7300	31.0	30.4		0.28
9/01/77	8	6	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Low Tide 0.0	Day 3550	30.8	30.0		0.12
9/01/77	8	6	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Low Tide 0.0	Day 2550	30.4	29.8		0.09
9/02/77	10	8	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Tide 25.4	Day 4900	29.0		30.4	0.20
9/02/77	10	8	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Tide 15.2	Day 4600	29.8		30.6	0.20
9/02/77	10	8	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Tide 3.8	Day 4300	28.6		31.0	0.26
9/02/77	10	8	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Low Tide 0.0	Day 2500	28.8	30.0		0.20
9/02/77	10	8	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Low Tide 0.0	Day 1600	27.8	29.0		0.09
9/02/77	10	8	Decaying <i>Spartina</i> near <i>Spartina</i> zone	Low Tide 0.0	Day 205	26.0	28.0		0.12

*See Table I

TABLE III

Direct CS₂ emission rate measurements over *Spartina Alterniflora* zone for individual runs

Date	Test Site			Stage of Tidal Cycle Cm	Light Intensity Lux	Temperature °C			CS ₂ Emission Rate* gmS/m ² /yr
	Loca- tion	No. of Runs	Characteristic			Ambient	Sediment	Water	
9/3/77	11	5	<i>Spartina</i> zone	Low Tide 0 cm	Day 10,000	24.5	25.8	—	0.09
9/3/77	12	6	<i>Spartina</i> zone	Low Tide 0 cm	Day 1900	28.6	29.2	—	0.21
9/3/77	12	6	<i>Spartina</i> zone	Low Tide 0 cm	Day 650	27.8	29.0	—	0.21
9/3/77	12	6	<i>Spartina</i> zone	Low Tide 0 cm	Dusk 300	26.9	28.6	—	0.27
9/3/77	12	6	<i>Spartina</i> zone	Low Tide 0 cm	Dusk	26.6	28.4	—	0.27
9/3/77	12	6	<i>Spartina</i> zone	Low Tide 0 cm	Dusk	25.8	28.0	—	0.21
9/3/77	12	6	<i>Spartina</i> zone	Low Tide 0 cm	Dusk	25.6	27.5	—	0.21

*See Table I

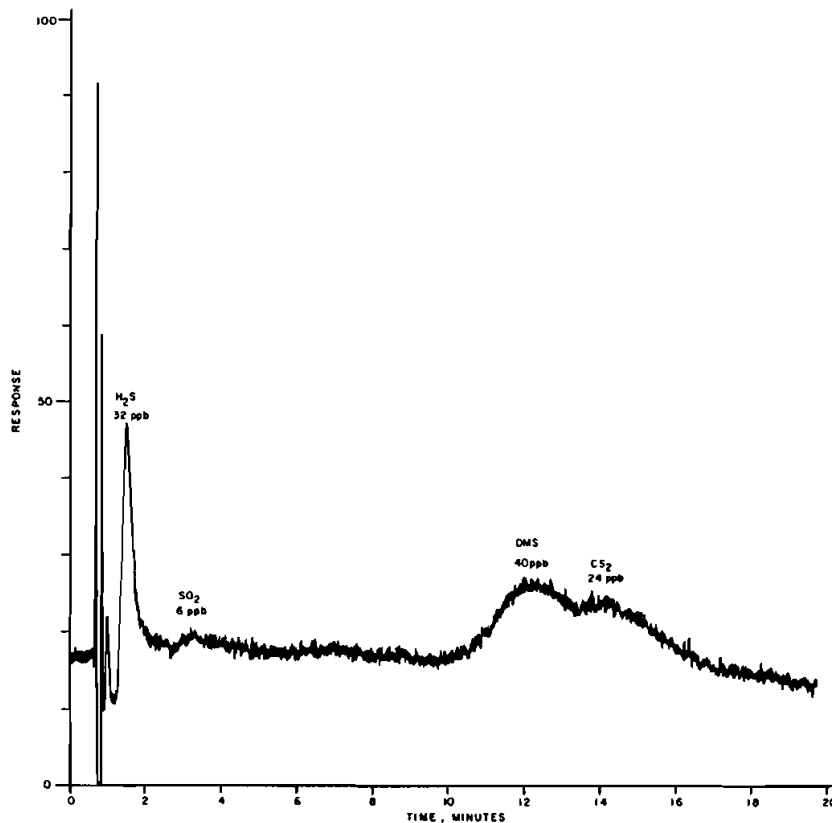


FIGURE 2 Salt marsh emitted volatile sulfur compounds.

suggest that *Spartina alterniflora* plants are in some way related to the production of CS₂.

To estimate the percentage of biogenic contribution of CS₂ to the global sulfur cycle, we assumed that all marshes emit uniformly, took the total marsh area¹⁸ as 3.8×10^5 km² and assumed that 100×10^6 tons of gaseous sulphur are emitted per year from the biosphere by natural processes.⁴ Based on our CS₂ emission rates (~ 0.022 gmS/m²/yr averaged over 172 aerated runs) and the above assumptions, the contribution of CS₂ from marshes is a small portion ($<0.07\%$) of the biogenic sulfur. Obviously, more data is needed to characterize adequately a global process.

We also estimated the contribution of CS₂ emissions to the stratospheric sulfate aerosol layer. According to Crutzen's¹⁶ estimates, a flux of $\sim 1.8 \times 10^{-4}$ gmS/m²/yr into the stratosphere will account for the entire stratospheric sulfate aerosol layer. Based on Junge's¹⁹ one-dimensional eddy diffusion model under steady-state conditions and first order reactions, and using the present CS₂ average emission rate for global marshes and a CS₂ atmospheric lifetime of one year,¹³ the contribution of marsh CS₂ to the stratospheric sulfate aerosol layer is less than 8%. However, if land plants emitted CS₂ at rates comparable to those measured for *Spartina alterniflora* the biogenic emissions of CS₂ could account for the entire Junge layer. Experiments are in process to test for CS₂ emissions for land vegetation.

In summary, we have discovered that the environs of salt marshes are a source of CS₂ and its average emission rate is ~ 0.022 gmS/m²/yr. The observed emissions do not contribute substantially to either the natural atmospheric sulfur cycle or the sulfate aerosol layer. Hence, the source of the persisting layer of stratospheric sulfate aerosol particles during extended periods of little or no volcanic activity still remains to be found.

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