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OCS, H₂S, and CS₂ Fluxes from a Salt Water Marsh

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Abstract. The diurnal-to-monthly behavior of the fluxes of OCS, H₂S, and CS₂ from a mixed-*Spartina* grass-covered site in a Wallops Island salt water marsh was determined through a series of experiments in August and September, 1982. Absolute flux values were determined for OCS and H₂S, while only relative values were determined for CS₂. The rates of emission of OCS and H₂S were observed to vary diurnally and to be strongly influenced by tides. The time-averaged flux values show that such mixed-*Spartina* stands are insignificant (<< 1%) global sources of H₂S or CS₂ and insignificant contributors to the global OCS cycle (< 1%). These results demonstrate that some marsh regions play a minor role in the global sulfur budget and, consequently, that the inclusion of such areas in extrapolations of measurements of more productive regions could lead to an overestimate of the role of salt water marshes in the global sulfur budget.

Key words. Carbonyl sulfide, hydrogen sulfide, carbon disulfide, fluxes, and salt water marsh *Spartina* grasses.

1. Introduction

A quantitative understanding of the global sulfur cycle and of regional sulfur cycles is an important goal in atmospheric chemistry. Two major categories of sulfur sources have been identified, namely anthropogenic and natural, and they are thought to contribute about equally to the global cycle. Interest in the natural or “background” sulfur cycle is in part motivated by a desire to understand the perturbations caused by anthropogenic sources. Both regional effects, such as acid rain, and possible global climatic effects, such as those induced by an increase in the stratospheric aerosol layer, are of concern. Global budget analyses suggest that natural sources are dominant (Kellogg *et al.*, 1972; Friend, 1973; Granat *et al.*, 1976; Moss, 1978; Ivanov, 1981). The importance of experimental studies that will help to quantify the contributions of the biogenic sources of sulfur is readily apparent.

Many researchers have speculated that anaerobic coastal marine environments such as salt water marshes are major biogenic sources of reduced sulfur gases (e.g., Kellogg *et al.*, 1972; Granat *et al.*, 1976; Ivanov, 1981; Várhelyi and Gravenhorst, 1981), and several investigators have made measurements of reduced sulfur gases over salt water marshes,

swamps and intertidal zones (Hill *et al.*, 1978; Hansen *et al.*, 1978; Schwarzenbach *et al.*, 1978; Aneja *et al.*, 1979a, b, c, 1980; Adams *et al.*, 1979, 1980, 1981; Goldberg *et al.*, 1981; Ingvorsen and Jørgensen, 1982; Steudler and Peterson, 1984, 1985). However, the deduced rates of emission for the various sulfur gases span several orders of magnitude. In part, this wide range of values undoubtedly reflects real seasonal variations. However, it may also be due to differences in specific local conditions (e.g., soil moisture, tidal influence, light intensity, soil temperature) and/or measurement techniques.

Quantitative experimental studies of the fluxes of reduced sulfur gases from natural sources are in their infancy. Although, as noted above, measurements of emissions of reduced sulfur species have been reported, the environments involved are sufficiently complex that many more studies are required to generalize the results to the global budget. Measurements to date are simply too sparse to accurately define the contribution of reduced sulfur gases to the global sulfur cycle. There may exist very important and as yet unidentified sources for these gases.

The primary goals of this research were to increase our understanding of the role of salt water marshes in the global carbonyl sulfide (OCS) cycle, and to establish the diurnal behavior of OCS from such a source. Secondary goals included the quantification of as many additional sulfur gases as could be resolved given the analytical instrumentation (optimized for OCS) and the constraints imposed by sample storage and analysis techniques. In particular, the absolute diurnal flux behavior of both OCS and hydrogen sulfide (H_2S) were determined from measurements along with the relative flux behavior for carbon disulfide (CS_2). The influences of light intensity, tides, and air and soil temperatures on the rates of emission of these three gases were also investigated.

Data were obtained during a field study at Wallops Island, Virginia. Wallops is a barrier island located off the eastern shore of the Delmarva (Delaware-Maryland-Virginia) Peninsula. The island is a part of the NASA/Goddard Space Flight Center/Wallops Flight Facility, and the northern part of the island consists primarily of isolated marsh and beach. This salt water marsh has been the site of several field investigations including, for example, flux measurements (e.g., Maroulis and Bandy, 1977 and Goldberg *et al.*, 1981) and studies of the local shark population (a project which was being conducted in the channel waters adjacent to the site chosen for this field study and which required a salt water environment). The field experiment was limited to studying the emissions of OCS, H_2S , and CS_2 from mixed stands of short *Spartina-alterniflora* and *Spartina-patens*. We will begin with a description of the field sites followed by a discussion of the sample collection and analysis procedures. Next, the details of the experimental conditions and a graphical representation of the results for each field study are presented. Finally, the global sulfur cycle is briefly discussed in light of the conclusions drawn from the experimental work described here.

2. Field Sites

Preliminary field experiments were conducted in June and July, during which time a survey was conducted to establish which marsh areas were routinely inundated by daily

tides and which areas would consistently be accessible through September. The marsh area studied is surrounded by channel water on three sides and is located on the northwestern side of Wallops Island, which faces the Delmarva Peninsula. Tall *S.-alterniflora* grasses grow along the water's edge and are replaced by short *S.-alterniflora* growth interspersed with small mud flats within approximately 5–10 m. *S.-patens* growth appears within another 10–15 m and then dominates the areas which are further landward. Flux measurements at the water's edge were not conducted due both to the extent of flooding by daily tides and the height of the tall *S.-alterniflora* grasses. The initial site chosen was approximately 10, 20, and 70 m from the water's edge to the east, west, and north, respectively, and approximately 200–300 m from the beginnings of brush and pine tree growth to the south. Growth at the site consisted of a mixture of *S.-alterniflora* and *S.-patens*, and the site bordered a small mud flat on the northwest. The site was observed to be inundated at high tide, with as much as 30 cm of standing water, during June and July. The sampling location was moved northward by approximately 20 m towards the water during mid-August because the site was very dry and had not been inundated by tides during the previous two weeks. The second and final site consisted of a stand of grass dominated by short *S.-alterniflora*, with lesser amounts of *S.-patens*, and the soil was significantly darker than that at the first site (typically a sign of greater organic content).

3. Sample Collection

The basic procedure was to measure the amount of sulfur gas emitted into air circulating continuously through a chamber covering a test plot. The on-site experimental apparatus is shown schematically in Figure 1. Ambient air was pulled through a carbon vane pump and its exhaust entered a regulating rotameter or was vented. The regulated flow (4 to 5 l min⁻¹) then passed through a series of plastic cylinders filled with Drierite prior to passage through a cryotrap consisting of two approximately 16 m lengths of 0.63 cm o.d. copper tubing which were coiled and immersed in liquid argon. The cryotrap was used to strip OCS, H₂S, and CS₂ from the ambient air. Without this step, the concentration of the sulfur gases entering and exiting the chamber was often comparable so that the fluxes were extremely difficult to discern. Hence, the use of sulfur-free purge air was necessary, and did not appear to enhance the rate at which gases flux from soils as evidenced by the measurement of concentrations which were much smaller than ambient values. After exiting the cryotrap, the air was reheated as it passed through tubing that was immersed in a warm water bath. The air then flowed through a second rotameter, which was used to identify any changes in the flow through the series of traps and driers and to confirm the flow rate before it entered the chamber. The air entering the chamber typically contained no detectable amount of H₂S (i.e., < 20 pptv), approximately 25 pptv of OCS, and a small amount of CS₂. OCS concentrations in the air exiting the chamber were always observed to be greater than or equal to incoming OCS values, thus allowing the observation that OCS fluxes were never negative.

The Drierite (anhydrous calcium sulfate) cylinders were used to remove water vapor

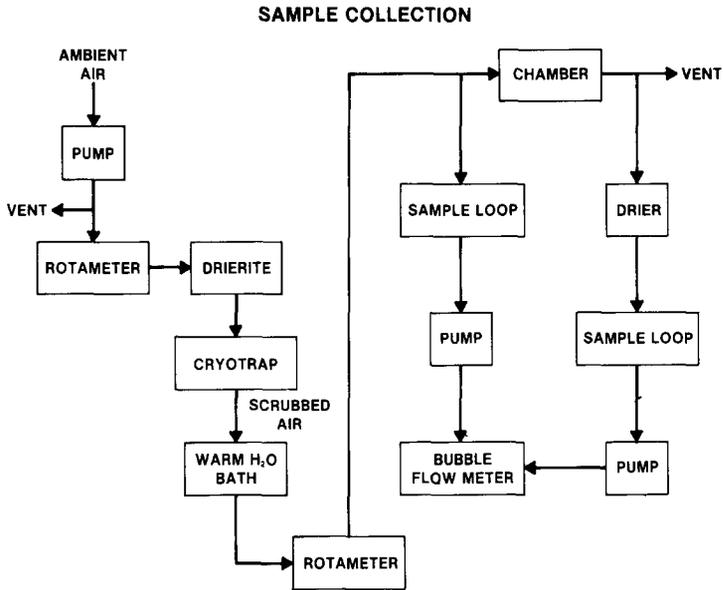


Fig. 1. Diagram of the components used in sample collection. Ambient air was pulled through a carbon vane pump and sent through various traps to remove as much of the water vapor and the sulfur species as possible before it entered the chamber. Samples of the air entering and exiting the chamber were collected simultaneously and cryogenically stored between collection and analysis.

from the air stream entering the cryotrap. Without this precaution, the cryotrap iced up within minutes. However, even in this configuration the cryotrap routinely became clogged after roughly 14 hrs at a typical 4 l min^{-1} flow rate. Exchanging used for fresh materials required approximately 15 min, and the chamber entrance was sealed during this brief interruption in the flow.

The flux chamber used in these field studies is outlined in Figure 2. The chamber

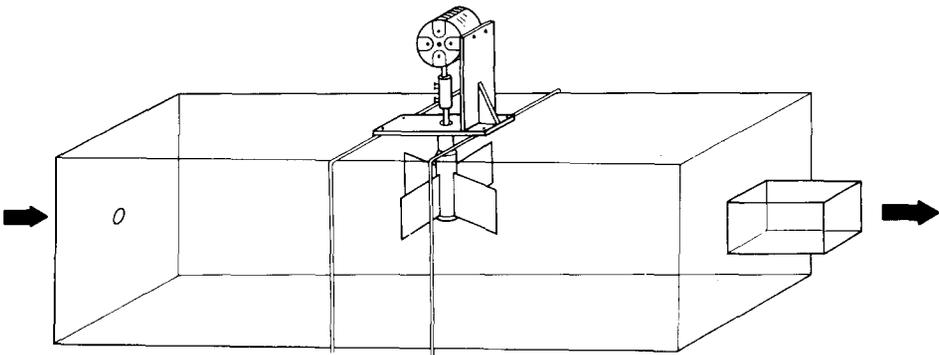


Fig. 2. The chamber was constructed of polycarbonate sheets and RTV adhesive. The dimensions were 0.41 m high by 0.41 m wide by 1.37 m long. The fan motor was mounted on an external aluminum frame, and the portion of the fan shaft inside the chamber was constructed of Teflon, as were the fan blades (only part of the external aluminum frame is shown in this diagram).

dimensions were 0.41 m high by 0.41 m wide by 1.37 m long with an internal volume of 230.2 l. The chamber was open-bottomed and was constructed of 0.32 m thick sheets of abrasion-resistant TUFFAK CM-2 polycarbonate and non-volatile DOW CORNING #3145 RTV adhesive. This material has been shown to be relatively inert to the sulfur gases of interest here (Adams *et al.*, 1980), and laboratory tests were conducted with OCS and CS₂ for confirmation (Carroll, 1983). Recent studies with humidified air have shown close to 100% recovery of OCS and CS₂ but only 60% recovery for H₂S (Kuster and Goldan, 1986). The polycarbonate material is clear and sturdy, and the flux chamber was easily positioned for a leak-free interface with the marsh surface. Due to the high reactivity of sulfur compounds, Teflon (Dupont) materials were used whenever possible where sample (or standard) gases came into contact with the components used for sample collection and analysis or for calibration (see later). Therefore, fan blades (8.3 by 12.1 cm) and a rotor shaft were machined from a block of virgin FEP Teflon and attached with #3145 RTV adhesive. A metal shaft connected the Teflon fan to a motor mounted on an aluminum frame over the chamber. Teflon washers were used to seal the chamber opening around the Teflon rotor shaft so that all internal chamber surfaces consisted either of Teflon or polycarbonate. The purpose of the fan was to circulate chamber air. Although no air velocity measurements were made inside the chamber, typical daytime winds appeared to be reasonably well imitated using the fan as evidenced by comparing grass-top motion both inside and outside the chamber. The chamber design included an exit port of sufficient size to minimize pressure buildup within the chamber.

The concentrations of OCS, H₂S, and CS₂ in the air immediately entering and immediately leaving the chamber were determined by cryotrapping the gases in sample loops followed by analysis. Sample loops were constructed of 63.5 cm lengths of 0.32 cm o.d. Teflon tubing ('bendable', NACOM) housed in 48.3 cm of aluminum tubing and equipped with Teflon plug valves (PFA, GALTEK). Extensive tests were conducted to determine cryogenic (liquid argon) trapping efficiencies (adsorption plus desorption), sample integrity during storage, and the degree to which low molecular weight hydrocarbons, fluorocarbons, nitrous oxide, and water vapor interfered with trapping and storage efficiencies or sample analysis for OCS and H₂S. The trapping and storage method was not calibrated for CS₂ because measurement of CS₂ was not the primary research goal. However, laboratory and field controls had confirmed that the materials and procedures employed were not sources of CS₂. In addition, the integrity of this sampling technique had previously been demonstrated for CS₂ measurements (Maroulis *et al.*, 1977). OCS and H₂S average trapping efficiencies (collection and desorption) were $72.4 \pm 2.9\%$ and $62.6 \pm 2.0\%$, respectively. A detailed discussion of the results of these tests is given elsewhere (Carroll, 1983).

With an internal volume of 230.2 l and a typical purge flow of 4.2 l min^{-1} , the chamber residence time was 54.8 min. Once set in the soil with all connections made, the chamber, mechanically stirred and continuously flushed with scrubbed ambient air, was typically allowed to equilibrate for 2 hrs at a purge flow rate of 4 to 5 l min^{-1} . After this initial equilibration period, air samples were collected simultaneously at the entrance and exit of the chamber and stored for laboratory analysis. Liquid argon was used to cryogenically

trap and store the samples, which were pulled through the Teflon sample loops by Fluid Metering Inc. pumps. The pumping rates were constant and were routinely monitored with a bubble flow meter to enable an accurate determination of the volume of air sampled. Sample collection was conducted for 50 to 60 min every other hour over a period of 25 hrs. Typical sample volumes were 1.5 to 2 l of air. Light intensity and air and soil temperatures, both inside and outside the chamber, were also monitored. During the last six (of the nine total) studies, a loosely woven, lightweight white cloth was used to shade the chamber, which helped to reduce the surface evaporation and thus the condensation rate on the cooler interior chamber walls without significantly reducing the light that reached the chamber interior ($\sim 5\%$ attenuation directly overhead).

The flow direction through the sample loops during both trapping and desorption was kept the same to minimize loss during desorption due to moisture. However, samples that showed evidence of water condensation still routinely displayed irreproducible behavior. Therefore, Nafion tubing driers (Foulger and Simmonds, 1979) were constructed and used in line upstream of the sample loops. The driers consisted of stainless steel tubes which housed 13 strands of Nafion tubing. Helium flowed countercurrently around the strands of Nafion as the sample gas was pulled through the Nafion tubes. Most of the water vapor was stripped from the sample gas stream by passage through the Nafion tubing and subsequently removed by the flowing helium. The driers were tested for adsorption and desorption of H_2S and OCS, and no enrichment or loss was observed for standard mixtures of air containing ambient levels of OCS (~ 500 pptv) or for standards containing 1 ppmv of H_2S . Continuous exposure to moist air caused a reduction in the efficiency of the Nafion driers; however, it was found that the driers could be effectively reconditioned between sample collection periods in the field by purging the Nafion tubes with He. Laboratory tests were also routinely conducted to check for OCS losses on the driers. Results from tests run after 150 hrs use showed 40% loss, suggesting that after considerable use ($100 \lesssim t \lesssim 150$ hrs), Nafion tubing may not remain inert to OCS and cannot be successfully reconditioned. Results from recent studies using humidified standards containing ambient levels of OCS, CS_2 and H_2S conflict with this assessment of Nafion tubing, showing neither loss nor degradation with time for OCS and CS_2 , and showing a consistent 20% loss of H_2S at the tens to several hundred pptv level (P. Goldan and W. Kuster, private communication, 1985).

4. Sample Analysis

A brief description of the analytical instrumentation and procedures used to conduct sample analysis is given here. Further details are given by Carroll (1983).

A Tracor 560 gas chromatograph (GC) equipped with a flame photometric detector (FPD) and a 394 nm band pass filter, along with a Spectra Physics SP4100 programmable integrator, comprised the analytical instrumentation employed to identify and quantify concentrations of H_2S , OCS, and CS_2 . Separation of these sulfur gases was accomplished using a column made of specially treated Porapak-QS-packed Teflon tubing (Thornberry, 1971; Pearson and Hines, 1977). Column preparation included the following

steps: FEP Teflon tubing (6 ft. long by 1/8 in o.d.) was serially washed with acetone and methanol and oven-dried before packing with acetone-washed, phosphoric acid-treated, 5% DC QF-1 silicone oil on 80/100 mesh Porapak-QS. QF-1 was used as the stationary phase and provided improved H₂S/OCS peak resolution, and the N₂-carrier gas was doped with SF₆ to continuously condition the column and detector. To eliminate the possibility of pressure perturbations in the FPD, the exhaust port was heated. The GC sample valve was automated for convenience in column conditioning and calibration studies, as well as for reproducibility in introducing samples to the GC column. Analytical Instrument Development permeation tubes were used as primary standards because the actual rates of emission were determined by weight loss over time using a microanalytical balance. Kintek standard generators were calibrated against the permeation tubes and used as secondary standards because a microanalytical balance was not available during field studies. When OCS mixing ratios less than 25 ppbv (parts per billion by volume) were required, Teflon-lined stainless steel cylinders were used as dilution chambers to generate the standards. Fluid Metering Inc. pumps were used to draw samples through the GC sample valve/sample loop and in the dilution system.

Calibrations were conducted both before and after sample analysis by recording GC response (peak area) versus standard mixing ratio curves at various GC attenuation settings with the mixing ratios chosen to span anticipated sample values. This enabled sample mixing ratios to be determined by interpolation rather than by extrapolation. The GC was temperature programmed for sample analysis as follows: the column temperature was held at 65 °C for 6 min followed by a ramp rate of 30 °C min⁻¹ for 2 min to a final temperature of 125 °C, which was held for 9 min. Sample loops were connected to the GC sample valve while still immersed in liquid argon. The integrator and temperature programs were begun simultaneously, and the valve configuration automatically switched to inject at 0.5 min. At this point the sample loop contents were desorbed onto the column by rapid transfer of the loop from the cryogen to boiling water.

Sample mixing ratios were calculated as follows: a linear regression was performed on the logarithms of the GC response and standard gas amount data, giving the relationship

$$\text{Log } R = \log(a) + b(\log X) \quad (1)$$

and, thus

$$X = (R/a)^{1/b}, \quad (2)$$

where $R = (\text{GC response}) \times (\text{GC attenuation})$, and $X = \text{gas amount in ppbv-cm}^3$ (parts per billion by volume-cubic centimeter), and b was typically 1.7 for OCS and 2.0 for H₂S. Next, this gas amount was adjusted for sample loop trapping efficiencies (e) and converted to a mixing ratio C , by dividing by the sample volume (v):

$$\bar{C}(\text{ppbv}) = X / \{(e)(v)\} (\text{ppbv-cm}^3), \quad (3)$$

where the bar over the C emphasizes that this value represents the average mixing ratio during the trapping period (typically 50 to 60 min), rather than an instantaneous measurement of the mixing ratio. The uncertainty in the average mixing ratio was determined by

standard propagation of errors, and was typically $\pm 20\%$. With \bar{C}_0 equal to the mixing ratio in the purge air entering the chamber and \bar{C} to the mixing ratio in the air leaving the chamber, $\bar{C} - \bar{C}_0$ represents the amount of gas entering the chamber from the test plot. The fluxes were calculated from the mixing ratios measured, as follows:

First we note the identity

$$\frac{d(C - C_0)}{dt} = - \frac{u(C - C_0)}{AH} + \frac{E}{H}, \quad (4)$$

where C and C_0 are the instantaneous mixing ratios, t = time, u = chamber purge air flow rate, A = ground surface area, H = chamber height, AH = chamber volume, and E = the instantaneous flux (per unit area) of gas from the marsh surface. The mixing ratio (C_0) of OCS, CS₂, and H₂S in the air entering the chamber was essentially constant, thus $dC_0/dt = 0$. Note that the mixing ratio (C) of OCS, CS₂, and H₂S in the air exiting the chamber is not assumed to be constant, hence,

$$\frac{dC}{dt} = - \frac{u(C - C_0)}{AH} + \frac{E}{H} \quad (5)$$

and, integrating over the trapping time period (t_1 to t_2),

$$C_{(t_2)} - C_{(t_1)} = - \frac{u(\bar{C} - \bar{C}_0)}{AH} (t_2 - t_1) + \frac{\bar{E}}{H} (t_2 - t_1), \quad (6)$$

where \bar{E} refers to the average flux of gas during the trapping period. Defining $\delta C = C_{(t_2)} - C_{(t_1)}$, and $\delta t = t_2 - t_1$, we obtain

$$\bar{E} = \frac{H\delta C}{\delta t} + \frac{u(\bar{C} - \bar{C}_0)}{A}. \quad (7)$$

δC values were estimated by empirically fitting curves to the mixing ratio plots to determine $C_{(t_2)}$ and $C_{(t_1)}$, as shown in Figure 3. An estimate for the typical fractional error in δC ($\Delta\delta C/\delta C$) is 0.4.

5. Results

Field studies, each of 25-hr duration, were conducted in August and September, 1982. The first two field experiments were carried out at one site, while the remainder were carried out at a second site, as described earlier. For purposes of brevity, detailed results of only two of the field studies are presented here, followed by graphical summaries of all data sets. (Detailed discussions of each field study are contained in Carroll, 1983). In all cases, the H₂S values have not been altered to reflect possible losses discussed earlier. The two studies presented next demonstrate the strong influence of daylight and tides on the fluxes of OCS and H₂S.

(i) September 28–29, 1982. This field study was conducted two days after a storm had washed channel waters into the marsh. The marsh was noticeably soggy although

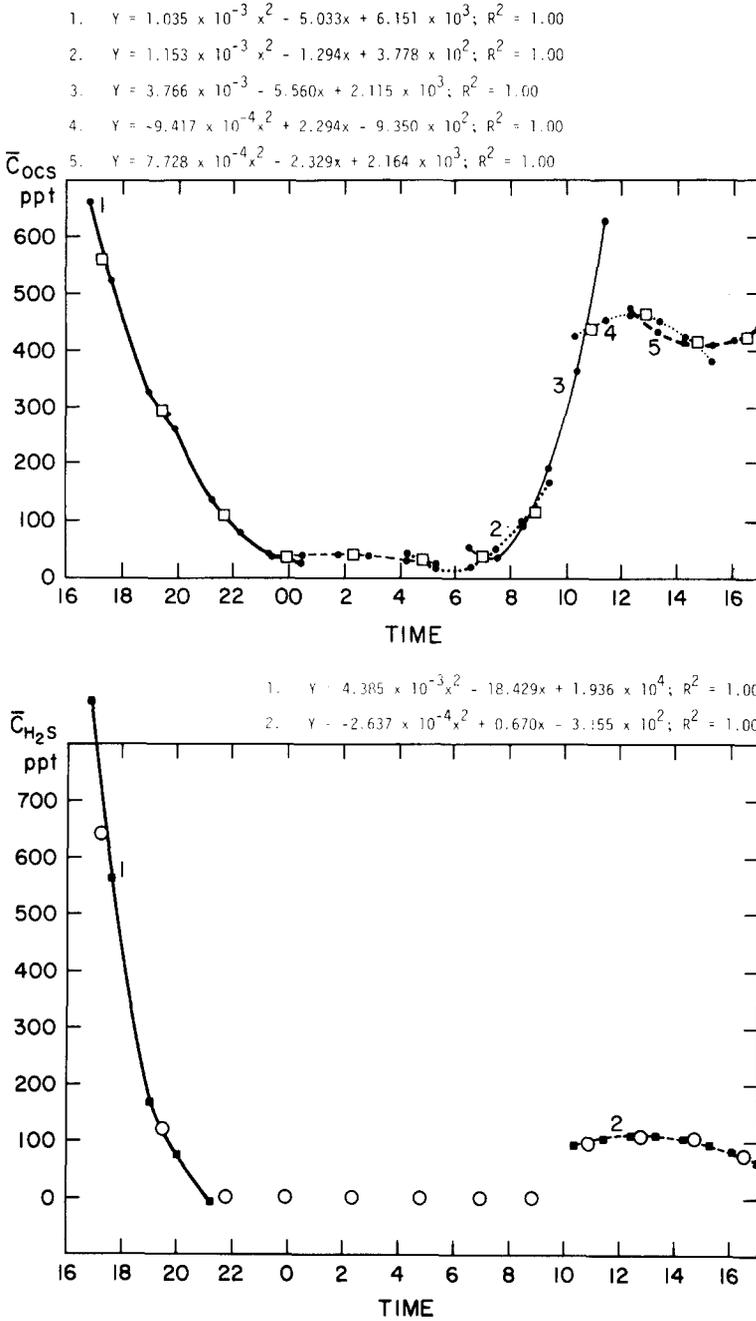
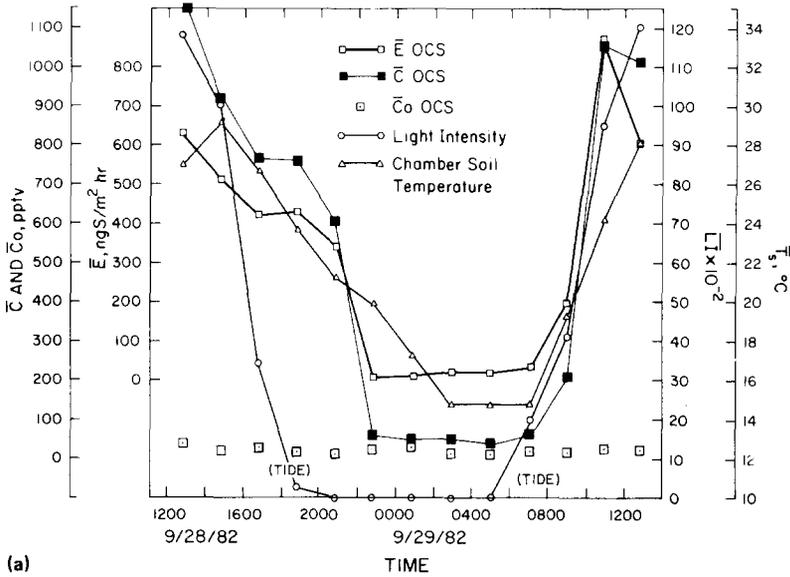


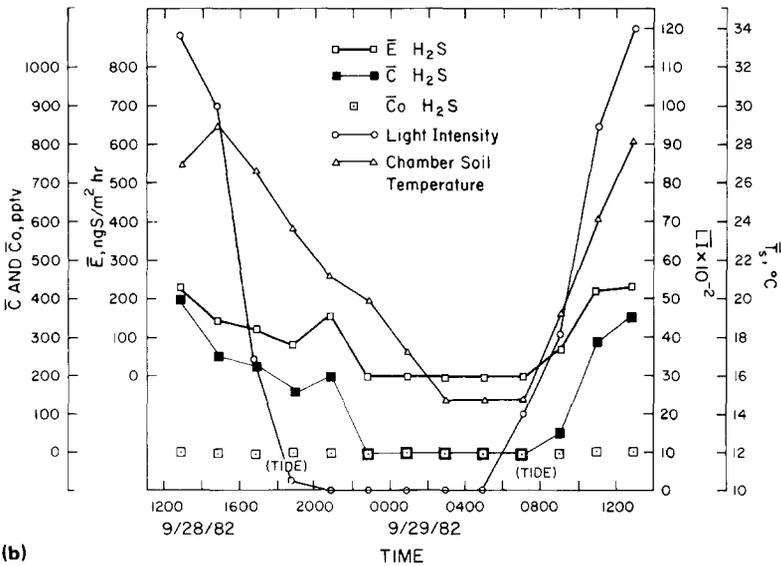
Fig. 3. Empirical fits to the plots of the mixing ratios of OCS and H₂S as a function of time were made to determine $C(t_1)$ and $C(t_2)$. The data shown are from the August 26–27 field study.

SEPTEMBER 28-29, 1982 FIELD STUDY
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,
 OCS MIXING RATIOS, AND OCS EMISSIONS VS. TIME



(a)

SEPTEMBER 28-29, 1982 FIELD STUDY
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,
 H_2S MIXING RATIOS, AND H_2S EMISSIONS VS. TIME



(b)

Fig. 4. For the September 28–29, 1982 field study: (a) soil temperatures, light intensities, and time-averaged OCS mixing ratios (\bar{C} and \bar{C}_0) and emissions (\bar{E}) are plotted as a function of time; (b) soil temperatures, light intensities, and time-averaged H_2S mixing ratios (\bar{C} and \bar{C}_0) and emissions (\bar{E}) are plotted as a function of time.

there was no standing water at the site or inundation during high tide. Outside soil and air temperatures ranged from 13 to 29 °C and 10 to 30 °C, respectively. The OCS and H₂S flux results are presented in Figures 4a and 4b, while CS₂ mixing ratios are shown in Figure 6c. Diurnal variations with nighttime minima were observed for all three gases.

(ii) September 14–15, 1982. This field study reflects the influence of tides on the rates of emission of OCS, H₂S, and CS₂. Although there had been no precipitation for a total of 18 days, the site had been flooded daily during high tide since September 9. The nighttime peak demonstrates the behavior regularly observed during or following tidal episodes. The maximum and minimum outside air temperatures were 29 and 12 °C, respectively, and outside soil temperatures ranged from 15 to 32 °C. Atmospheric conditions were hot and hazy. The OCS and H₂S flux results are presented in Figures 5a and 5b. The observed increase in CS₂, concurrent with standing tidal water inside the enclosure (see Figure 6c), was observed during some, but not all, tidal flooding episodes.

As shown in Figures 6a–6c, daytime emissions or mixing ratios were typically non-zero, while nighttime emissions were typically zero, except during or following tidal episodes. During two field studies, September 3–4 and September 9–10, daytime fluxes remained near or at nighttime zero levels. Both observations were made during extremely dry periods. In only one case did nighttime values remain at daytime levels, and this occurred during an extremely wet period (September 23–24).

As also displayed in Figures 6a–6c, nighttime zero levels were consistently interrupted by tidal influence at the site. Enhanced values were observed in all cases of actual site inundation, as well as when the tides approached to within several feet of the site.

6. Discussion and Conclusions

Table I summarizes the deduced fluxes for OCS and H₂S for the nine field studies of August and September, 1982 and lists relevant data concerning soil temperature and soil moisture. The major conclusions based upon the results of these field studies are:

- (1) OCS and H₂S undergo diurnal variations in emission, with daytime maxima and near-zero nighttime minima.
- (2) The diurnal variations in the fluxes of OCS and H₂S were similar in magnitude and pattern, whereas CS₂ fluxes (as indicated by their mixing ratios) were regularly much lower than those of OCS and H₂S except during periods of extreme tidal influence.
- (3) OCS and H₂S fluxes were observed to increase dramatically following tidal episodes, whereas CS₂ values were sometimes observed to increase during tidal episodes. Therefore, it is possible that CS₂ may have a more important oceanic water source than a *Spartina*-covered marsh source.
- (4) Tides and sunlight significantly influence the fluxes of OCS, H₂S, and CS₂ from marsh sites containing mixtures of the short *Spartina* grasses.

It is interesting to note that, although Rasmussen *et al.* (1982) found surface ocean waters to be supersaturated in OCS, OCS mixing ratios were not observed to dramatically

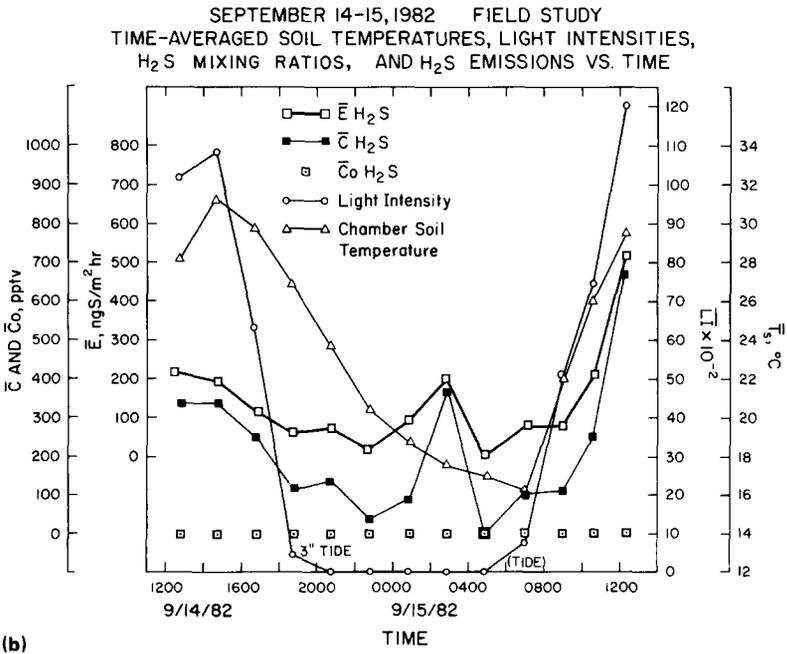
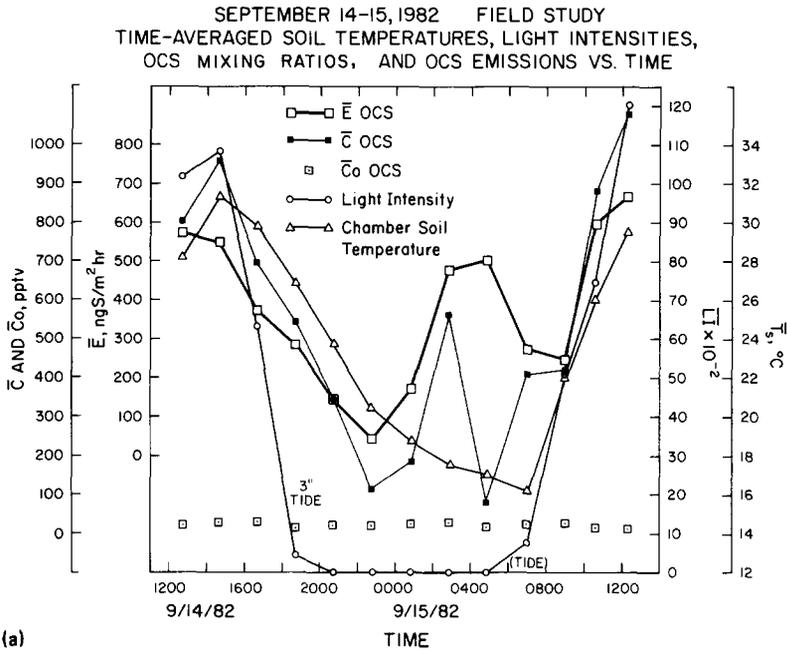


Fig. 5. For the September 14-15, 1982 field study: (a) soil temperatures, light intensities, and time-averaged OCS mixing ratios (\bar{C} and \bar{C}_0) and emissions (\bar{E}) are plotted as a function of time; (b) soil temperatures, light intensities, and time-averaged H_2S mixing ratios (\bar{C} and \bar{C}_0) and emissions (\bar{E}) are plotted as a function of time.

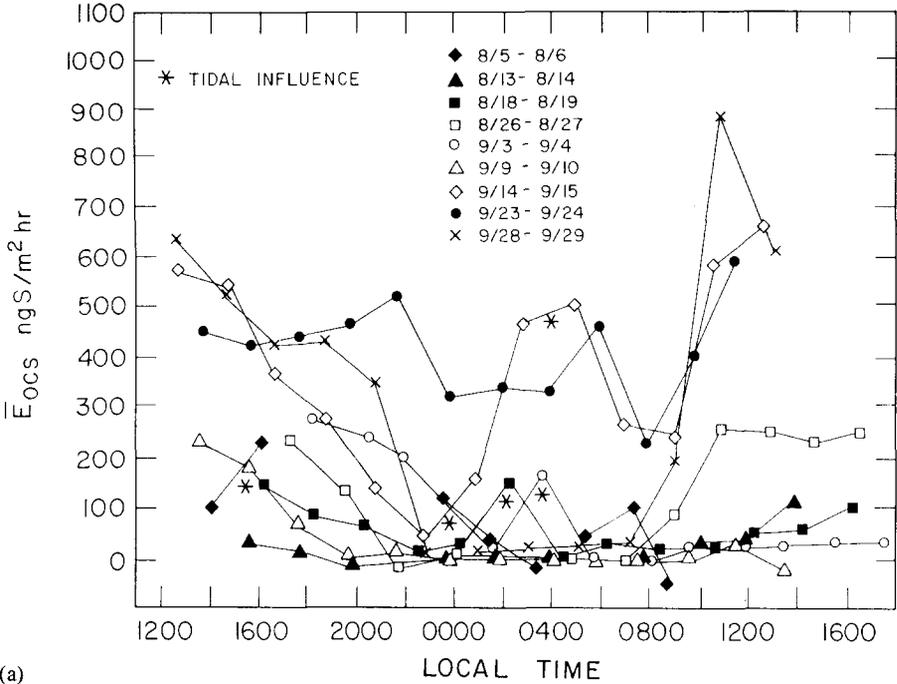


Fig. 6(a)

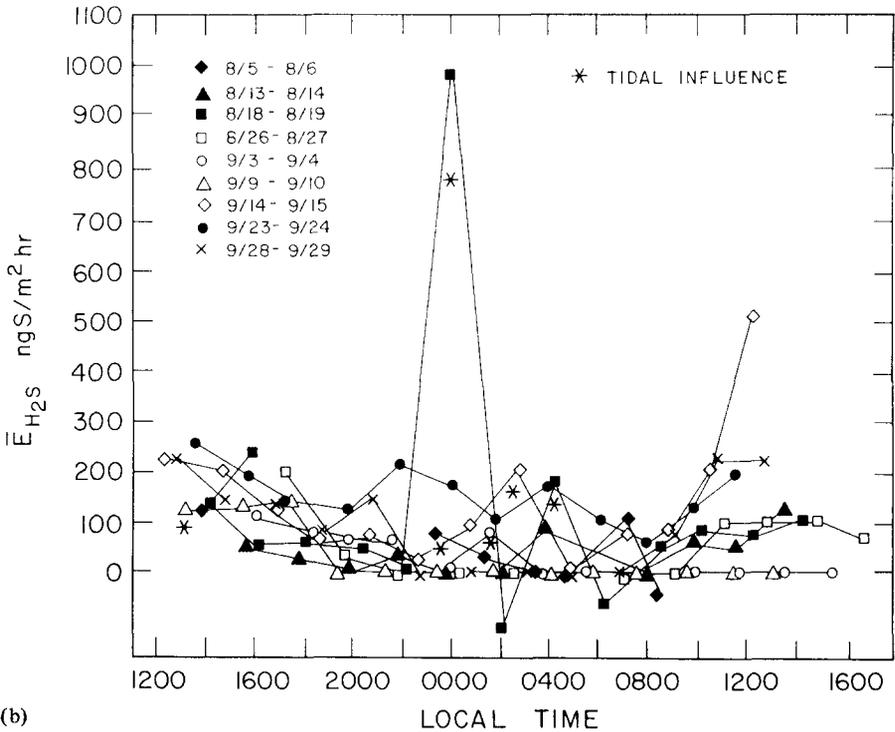


Fig. 6(b)

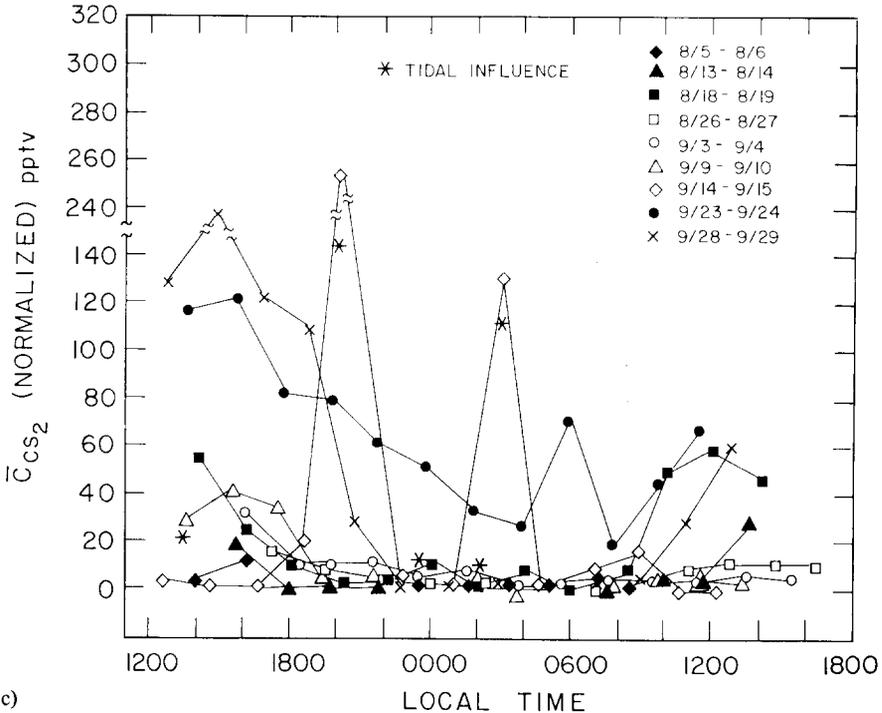


Fig. 6(c)

Fig. 6. For all field studies conducted in August and September, 1982: (a) OCS emissions are plotted as a function of time; (b) H₂S emissions are plotted as a function of time; (c) CS₂ mixing ratios ($\bar{C} - \bar{C}_0$) are plotted as a function of time.

increase during tidal episodes. Also, observations of increased CS₂ mixing ratios during tidal episodes support the concept of an oceanic source for CS₂, even though Lovelock (1974) argues that the ocean-atmosphere interface is not conducive to such emissions.

The influence of water movement upon volatile sulfide concentrations in salt marsh soil pore waters is also of interest. As stated earlier, many researchers have speculated that anaerobic coastal marine environments such as salt water marshes are major sources of H₂S. Such environments are rich in sulfate, and the dissimilatory sulfate-reducing bacteria, *Desulfovibrio* and *Desulfotomaculum*, are thought to be primarily responsible for transforming sulfate to sulfide in anoxic waters and sediments (Zobell and Rittenberg, 1948; Baas-Becking and Wood, 1955) and in salt marsh soils (Gooch, 1968; Sivanesaw and Manners, 1972). Also, volatile sulfide concentrations in salt marsh soil pore waters have been found to vary considerably from regions bordering the water's edge to more landward areas (Oshrain, 1977; Linthurst, 1979; Skyring *et al.*, 1979; Linthurst and Seneca, 1980; Mendelssohn and Seneca, 1980; King *et al.*, 1982). Several studies have been conducted in an attempt to determine the parameters that regulate volatile sulfide concentrations and *Spartina-alterniflora* productivity. For example, Skyring *et al.* (1979) found varying rates of sulfate reduction between tall and short *Spartina* marsh soils at Sapelo Island, Georgia. However, King *et al.* (1982) found no significant differ-

TABLE I. Summary: Wallops Island field studies

Field study	Diurnally-averaged		\bar{T}_{soil} °C Maximum	\bar{T}_{soil} °C Minimum	Moisture comments
	Emissions OCS	(ng S m ⁻² - hr) H ₂ S			
8/5-6	71.25 (8)	64.6 (8)	31.5	25.3	Site covered at high tide (1° S. Patens)
8/13-14	19.6	39.9	29.0	21.0	1 entire week of rain (1° S. Patens)
8/18-19	60.9	142.75	34.2	22.4	Heavy rain previous night
8/26-27	124.75	37.0	29.7	18.4	Recent daily flooding at high tide
9/3-4	90.6	32.8	34.6	21.5	1 week without rain or tide coverage
9/9-10	30.4	32.5	27.2	17.1	2 weeks without rain or tide coverage
9/14-15	332.45	134.75	31.3	16.2	1 week of daily tide coverage
9/23-24	417.33	153.33	25.9	15.3	After 4-day storm, marsh inundated with channel water
9/28-29	291.25	88.9	29.0	14.8	Marsh soggy from second storm (channel water)

ences in the rates of sulfate reduction between these same types of sites at the same marsh. According to Cappenberg (1974), Winfrey and Zeikus (1977), and Ferry and Peck (1977), high rates of sulfate reduction are generally associated with low rates of methanogenesis and vice versa. Skyring *et al.* (1979) suggested that the lower rates of sulfate reduction that they observed in the high marsh are thus in agreement with the high rates of methanogenesis in the same region observed by King and Skyring (1977) and King and Wiebe (1978). Most researchers also agree that volatile sulfide concentrations are much higher in short *Spartina* soils than in tall *Spartina* soils. Several authors (e.g., Linthurst and Seneca, 1980; Mendelssohn and Seneca, 1980) speculate that *Spartina* growth is inhibited by soil anaerobiosis and regulated by oxygen transport within the plant and by the volatile sulfide concentrations and redox potentials of the marsh soil (Howes *et al.*, 1981; King *et al.*, 1982). All of these researchers have observed a strong positive correlation of *Spartina* growth with soil water replenishment rates, and a similarly significant negative correlation of volatile sulfide concentration with *Spartina* growth.

It is interesting, however, that only relatively small amounts of H₂S were observed to be emitted from the regions of the marsh studied in this research. While volatile sulfide concentrations in short *Spartina* soils may generally exceed those in tall *Spartina* soils, the short *Spartina* soils studied were highly aerated. Because soils with low moisture content experience lower amounts of sulfate reduction than soils having a high water content, aeration limits the flux of H₂S or other reduced sulfur compounds from these soils. The results of the field studies at Wallops Island certainly indicate that this is

true because maximum fluxes of H_2S and OCS were only observed during periods of high soil moisture in these regions. It would be useful to conduct a global survey of salt water marshes to establish which portions are waterlogged, and the percentage of the time that they are waterlogged, in order to determine what fraction of short *Spartina* stands are often aerated.

A major problem in calculating global budgets for sulfur and other gases is the substantial uncertainty that results from the extrapolation of limited data for a few localities to apparently related localities over the globe. The diurnal and seasonal flux data available for the reduced sulfur compounds are extremely sparse. Global flux values have sometimes been extrapolated from single daytime emissions measurements (e.g., Adams *et al.*, 1981). Our results suggest that such extrapolations are misleading because they do not take diurnal and seasonal variations into account. Further, while it is reasonable to extrapolate fluxes calculated from studies of coastal shallow-water areas to other similar coastal regions in order to calculate a global flux, it may be invalid to include other marsh regions in such calculations. Indeed, this research suggests that frequently-aerated regions of salt water marshes are relatively insignificant biogenic sources of OCS , H_2S , or CS_2 .

If we assume that 75% of the global area of salt water marshes can be considered to encompass regions which experience some degree of aeration ('landward') and that all such areas emit sulfur gases at equal rates throughout the entire year, we can arrive at a rough estimate of the contribution of such marsh regions to the annual global sulfur cycle. The following paragraphs address possible global contributions from landward regions of salt water marshes for OCS and H_2S , and from ocean waters for CS_2 .

A range of values spanning ~ 2 orders of magnitude has been calculated for the rate of destruction of OCS in the stratosphere (e.g., Crutzen, 1976; Sze and Ko, 1978; Turco *et al.*, 1980; Gravenhorst, 1983). An estimate of the potential role of landward marsh areas in the global OCS cycle can be obtained by comparing the calculated rate of stratospheric destruction of OCS with the extrapolated OCS flux from 75% of the world's salt water marshes. For this purpose, we can calculate the required rate of emission of OCS per unit area from this portion of the world's salt water marshes to balance stratospheric OCS destruction. The extrapolation of our observed emissions of OCS can then be compared with this hypothetical flux to determine the relative importance of landward regions of salt water marshes in the global OCS budget.

Using an average calculated value of 8×10^7 molecules cm^{-2} s for the rate of destruction of OCS in the stratosphere and 75% of the fractional area of the globe covered with salt water marshes ($0.75 \times 0.0745\%$), a rate of emission of OCS from landward marsh regions of 1.5×10^{11} molecules cm^{-2} s (4.8×10^5 ng S m^{-2} hr) is required to balance stratospheric destruction. Our maximum individual flux value of OCS observed during the Wallops Island field study (864 ng S m^{-2} hr) therefore represents only 0.2% of the required global OCS flux into the stratosphere, and the maximum diurnally averaged value observed for OCS (417 ng S m^{-2} hr) represents less than 0.1% of global OCS emissions.

If one averages the nine diurnally averaged values calculated for the flux of OCS for the August and September field studies, the result (~ 160 ng S m^{-2} hr) represents less

than 0.05% of global OCS emissions. Furthermore, this averaged value may represent an upper limit for this particular salt marsh for diurnally averaged OCS emissions because the summer/fall period studied may be more productive than most winter months when low temperatures appear to cause microbial activity to halt (Ingvorsen and Jørgensen, 1982). If we extrapolate our averaged value to salt marshes world-wide, the result is an annual global emission of only 4×10^8 g S yr⁻¹. This is four orders of magnitude less than even the lowest annual global flux value in the literature attributed to biological decay on land (5 Tg S yr^{-1} from all reduced sulfur gases, Granat *et al.*, 1976).

The maximum observed flux for H₂S, 987 ng S/m² hr, translates to a maximum annual global emission of H₂S from landward marsh areas of 2.5×10^9 g S yr⁻¹. This observed maximum flux was an anomaly, however. The maximum diurnally-averaged H₂S flux (153 ng S m⁻² hr) represents a maximum annual global contribution of only 3.8×10^8 g S yr⁻¹, and the average of the nine August and September diurnally averaged flux values (80.7 ng S m⁻² hr) represents an average global H₂S emission of only 2.7×10^8 g S yr⁻¹. Even if our H₂S observations were low by as much as 60% (which would result in a global contribution of 3.4×10^8 g S yr⁻¹), they are still 1.5×10^4 times smaller than the 5 Tg S yr^{-1} calculated by Granat *et al.* (1976), and a factor of 3.5×10^4 less than the 12 Tg S yr^{-1} attributed by Ivanov (1981) to H₂S emissions from shallow coastal regions.

Our results suggest that diurnally averaged CS₂ fluxes from landward marsh areas are much lower than those for H₂S and OCS. However, GC-saturation was observed for the high CS₂ mixing ratios which sometimes occurred for samples taken during tidal episodes. Because high CS₂ values only occurred with standing channel water inside the flux chamber, this raised the question of a significant oceanic source of CS₂.

Near the end of September, after several weeks of excellent GC-response stability, the instrument was calibrated for CS₂ in order to estimate absolute CS₂ mixing ratios, and, thus, to enable rough flux estimates for CS₂. Preliminary calculations to estimate maximum CS₂ fluxes (observed during periods which caused GC-saturation) result in minimum flux values of 1272 to 1817 ng S m⁻² hr (7×10^8 to 9.7×10^8 molecules cm⁻² s). The quoted range of values results from an estimated trapping efficiency for CS₂ ranging from 70 to 100%. (Based upon the physical properties of CS₂ and OCS, it is expected that CS₂ will behave similarly to or demonstrate desorption efficiencies greater than OCS.) If, as Jones *et al.* (1982) suggested, the atmospheric conversion of CS₂ to OCS by reaction with OH is 12% efficient, this would yield a comparable OCS input of 8.4×10^7 to 1.2×10^8 molecules cm⁻² s. The maximum individual flux value observed for CS₂ during a tidal episode then represents roughly 100 to 150% of the global OCS into the stratosphere. Extrapolation of the maximum flux observed for CS₂ to all oceans results in an annual global oceanic contribution of 4 to 6 Tg S yr⁻¹, a factor of 3 to 30 less than the values in the literature for biological decay in oceans for all sulfur gases (see Table II) and a factor of 6 to 10 less than the global sea-to-air flux calculated by Andreae and Raemdonck (1983) from their global weighted average concentration of (CH₃)₂S in surface seawater. It must be noted that this represents the highest rather than the average value observed for CS₂ during tidal episodes and assumes that CS₂ is emitted from all ocean waters at this maximum rate.

TABLE II. Annual global fluxes of sulfur from biogenic sources (in Tg S yr⁻¹)*

	Biological decay (land)	Biological decay (ocean)
Eriksson (1960, 1963)	110	170
Junge (1963a, b)	70	160
Robinson and Robbins (1968, 1970)	68	30
Kellogg <i>et al.</i> (1972)		90
Friend (1973)	58	48
Garrels <i>et al.</i> (1973)	56	35
Granat <i>et al.</i> (1976)	5	27
Zehnder and Zinder (1980)	33	48
Ivanov (1981)	23	19
Várhelyi and Gravenhorst (1981)		3.3–35.5

* 1 Tg S = 10¹² g S.

In addressing the topic of landward areas of salt water marshes as global sources of biogenic sulfur, we note that the sum of our measured average H₂S and OCS fluxes provides an upper limit to the annual global contribution of only 6 × 10⁸ g S yr⁻¹. This represents at most 0.01% of the global sulfur emissions attributed to biological decay from land (Granat *et al.*, 1976, Table II). Therefore (assuming that the marsh areas studied are representative), if these regions are to remain of interest to the global sulfur cycle, it appears that the primary role must be attributed to other reduced sulfur compounds, perhaps, for example, (CH₃)₂S (Goodwin *et al.*, 1982). It would be particularly interesting to measure in situ the SO₄²⁻, OCS, H₂S, and (CH₃)₂S concentrations in salt marsh soil pore waters simultaneously with the determination of their rates of emission into the atmosphere from both tall and short *Spartina* soils.

Finally, although flux chambers currently comprise the only option available to determine the source and amount of emissions from heterogeneous environments, this method is far from ideal. The use of flux chambers could significantly alter the rates at which gases are emitted in an undisturbed setting. Hitchcock (1978) has warned, in particular, that stagnant chambers create artificial concentration gradients above a source and thus disturb a potentially fragile balance, perhaps halting or reversing fluxes. Dynamic flux chambers of the type we have used may also be inadequate since most do not mimic in situ wind motion variability. Also, the use of cryogenically scrubbed, rather than ambient, air may perturb natural rates of emission, and increased humidity may enhance losses and surface effects. Another potential source of interference are the compounds used to scrub ambient air, such as soda lime and Drierite. A continuation of efforts to quantify natural sources of sulfur compounds is necessary and should include both diurnal and seasonal studies, analytical improvements to enhance precision and accuracy, and, finally, minimal disruption of natural settings.

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