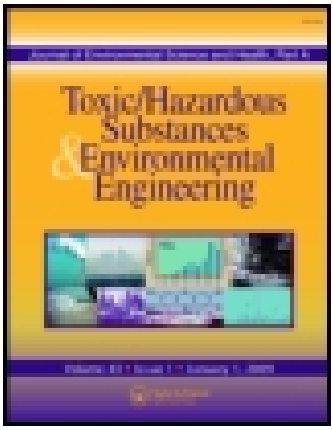

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A technique for measurement of biogenic sulfur emission fluxes

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A TECHNIQUE FOR MEASUREMENT OF BIOGENIC SULFUR EMISSION FLUXES

Key Words: Biogenic sulfur, hydrogen sulfide, organic sulfides, sulfur cycle, salt marsh

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ABSTRACT

Atmospheric sulfur compounds of biogenic origin are thought to constitute a significant fraction of the atmospheric sulfur burden. Determination of fluxes of these compounds into the atmosphere is desirable in order to permit accurate assessment of the relative roles of anthropogenic and biogenic sources in contributing to such phenomena as the atmospheric sulfate burden and acidity in precipitation.

In the present paper an emission flux measurement technique for biogenic sulfur compounds is described, and initial re-

sults of the use of the technique in a Long Island salt marsh are presented. These first known measurements of biogenic fluxes are compared to estimates of biogenic fluxes derived from global sulfur budgets and from calculations based on a simple mass transfer model. Comparison is also made with anthropogenic emission rates expressed as fluxes. Further steps in the development of the technique are suggested.

INTRODUCTION

A large fraction of the atmospheric sulfur burden is thought to be introduced into the atmosphere from biogenic sources. Evidence for this statement is inferential in nature. The statement is derived from observing what appears to be a major source deficit in the global atmospheric budget and from the notion that large sources of biologically-derived volatile sulfur compounds exist which may make up that deficit. The strength of the global biogenic source is held to be up to twice the global anthropogenic source. No direct, comprehensive experimental evidence has been reported which lends support to or discredits this important inference, in spite of intense current interest in a number of environmental problems associated with the sulfur cycle. Identification and characterization of sources of atmospheric biogenic 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.

In the present paper a technique for measuring earth-atmosphere fluxes of biogenic sulfur compounds is described. Initial results of use of the technique in a Long Island salt marsh are reported. The results, which constitute the first known measurements of biogenic fluxes, are compared to estimates of

biogenic fluxes obtained from global sulfur budgets and from calculations based on a mass transfer model. Comparison of the biogenic fluxes is also made with effective anthropogenic fluxes. Further steps in the development of the technique are suggested. Details on the experimental work are given by Aneja.[1]

BACKGROUND

Volatile compounds of sulfur identified with the label "biogenic sulfur" include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and no doubt others not yet identified. The early literature speaks of biogenic sulfur in terms of hydrogen sulfide only but the recent literature, following the work of Lovelock, et al.,[2] focuses interest on organic sulfur compounds as well.

Hill[3] has reviewed the available information on the processes of biogenic sulfur compound generation and release to the atmosphere and the fate of these compounds in the atmosphere. An updated summary of that review will now be presented.

The salient features of the overall process of generation, emission and atmospheric reactions for H_2S are as follows. Hydrogen sulfide originates from nonspecific bacterial reduction of organic sulfur and from sulfate reduction by specific sulfate reducing bacteria. The latter organisms are strictly anaerobic while nonspecific reducers may be found in anaerobic or aerobic environments. Both processes of H_2S production require the presence of organic material.

Hydrogen sulfide is produced in an aqueous medium such as a film of moisture in soil, interstitial water in sediments, or the bulk water of natural water bodies. Following its production it is transported to an air-water interface where it is released

to the atmosphere. Transport may occur by diffusion and convection and may lead to release as a soil gas or to release to the open atmosphere or to a rising gas bubble. While being transported to an air-water interface, H_2S is subject to transformation to nonvolatile forms by several processes, including oxidation by dissolved oxygen and by various kinds of bacteria, and precipitation as an insoluble metal sulfide. Within the atmosphere H_2S is oxidized either to sulfur dioxide and then to sulfate or directly to sulfate.

Quantitative information on the steps in the overall process is limited. Information on time scales for oxidation in solution and in air is of particular present interest. Time scales for oxidation in solution have been reported to be from minutes[4] to days.[5] In the atmosphere H_2S is oxidized over times of the order of one day or less.[6, 7]

Knowledge of the generation, emission and atmospheric reactions of volatile organic sulfur compounds is meager compared to that for H_2S. Organic compounds are held to be derived from the protein component of decomposing plant material. Thus, for instance, CH_3SH and $(CH_3)_2S_2$ have been shown[8] to be produced in the dissimilation of methionine by bacteria and fungi. The gas phase photolytic decomposition of dimethyl sulfide in air has been studied by Bentley, et al.,[9] and by Cox and Sandalls.[10]

Field investigations of biogenic sulfur compounds have involved measurement of concentrations of compounds of interest in ambient air. Breeding, et al.,[11] found H_2S concentrations of 0.35 ppb and less in clean air in rural Illinois and Missouri whereas Natusch, et al.[12] in remote locations in Colorado found concentrations of the order of 0.04 ppb. Near known or sus-

pected strong sources much higher concentrations are found. Thus Hitchcock, et al.[13] measured concentrations of H_2S in air above a tidal marsh in North Carolina as high as 57 ppb. At a sampling station with industrial point sources 0.4 to 11.3 km away Graedel, et al.[14] measured long term average H_2S concentrations exceeding 1 ppm. Finally, Denmead[15] at a highly polluted shallow tidal harbor backwater found H_2S concentrations in air approaching 1 ppm. The finding of dimethyl sulfide (DMS) in seawater and in the gas phase above laboratory samples of soils and organic matter[2] led Maroulis and Bandy[16] to search for DMS in the atmosphere. At two sites along the coast of Virginia, average DMS concentrations as high as 0.058 ppb were found.

No direct measurements of emission fluxes of biogenic sulfur compounds appear to have been made prior to the present work.

EXPERIMENTAL

Two principal methods for measurement of earth-atmosphere fluxes of gases are in use. One may be referred to as the diffusion method, and the other as the emission flux chamber method. In the diffusion method, the vertical concentration profile of the gas of interest is measured in the atmosphere above a suspected source along with wind speed and direction. The average flux is determined by using the resulting data in an equation for the diffusion of a gas from an area source. The configuration of the source must be assumed. In the emission flux chamber method, a container or chamber with an open bottom is placed over an area of soil, mud or water. A sweep gas is passed through the chamber, serving to collect gases emitted from the surface covered by the chamber. The effluent gas is sampled and analyzed for content of the gas of interest.

We made a brief attempt to measure emission fluxes of biogenic H_2S at a shoreline site on Long Island, New York using the diffusion method.[17] At the site chosen the results of application of the diffusion method led to the conclusion that the emissions of H_2S were variable in space and time making assumptions about source configuration very tenuous and deductions of emission flux difficult. We were thus led to consider the emission flux chamber technique in which identification of an emission flux with a particular emission locale is conclusive.

Our first study of the emission flux chamber technique[17] was conducted in Flax Pond, a 59-hectare salt marsh in the village of Old Field on the north shore of Long Island, New York. Fig. 1 shows a map of Flax Pond and the areas of Spartina and other species which are found there. The first study involved an

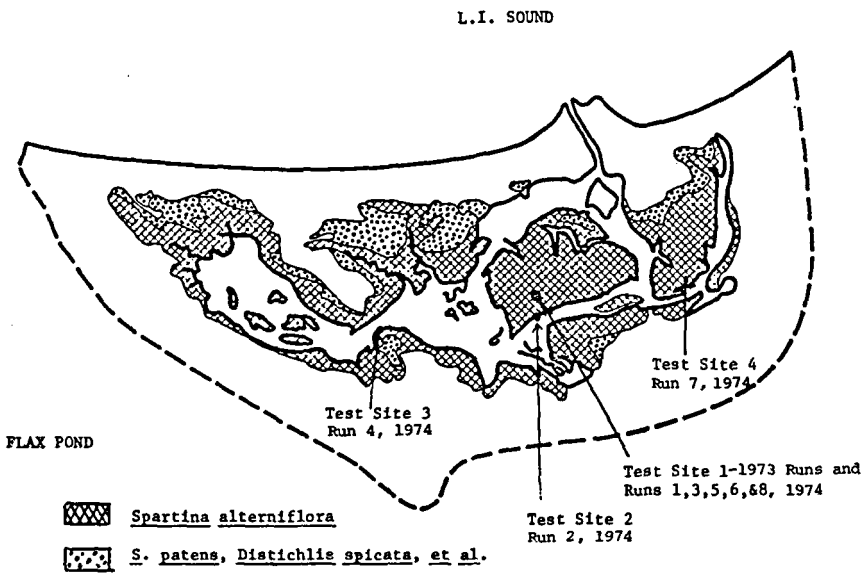

FIG. 1 Map of Flax Pond, Old Field, N. Y., showing vegetation types and experiment locations.

unstirred chamber and a sampling and analytical method sensitive only to H_2S. The present paper describes a study conducted at the same site with a refined chamber and an analytical technique sensitive in principle to a broad array of volatile sulfur compounds. The second Flax Pond study took place in October and November of 1974. Subsequently, during the period December 1974 through February 1975 a qualitative study of biogenic emissions was conducted there.

The emission flux chamber designed for this study is shown schematically in Fig. 2. The main body of the chamber was constructed of a Lucite cylinder, 34.3-cm i.d. × 25.4-cm high.

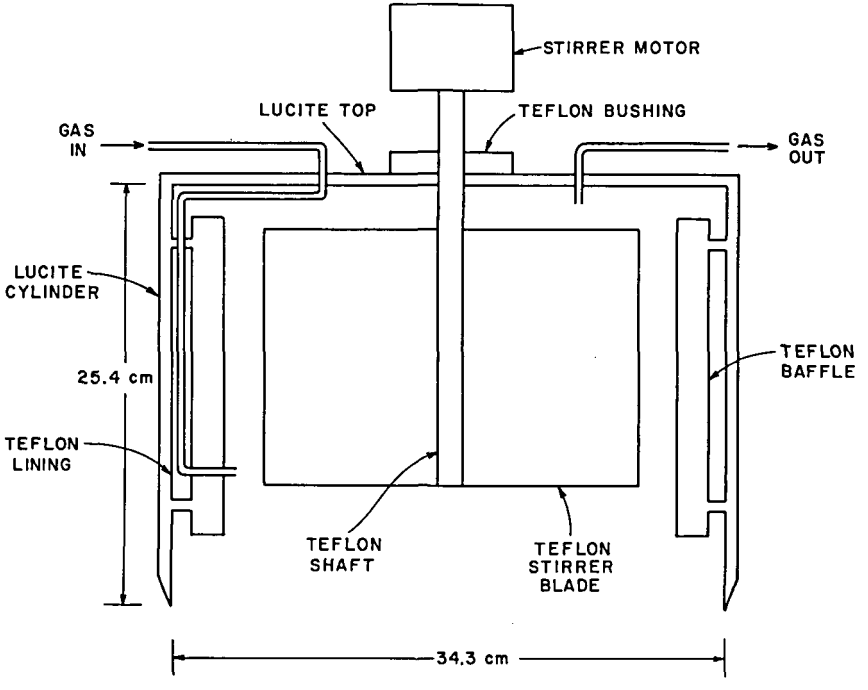

FIG. 2 Emission flux chamber used at Flax Pond, Old Field, N. Y.

One end of the cylinder was covered with a Lucite sheet. The entire inner surface of the chamber was coated with an adhesive Teflon sheet. Four Teflon baffles, 1.9-cm wide, were placed at 90° intervals. To prevent the formation of stagnation zones, the baffles were placed 1.3-cm away from the walls of the cylinder. A Honeywell continuous duty a. c. motor drove a Teflon stirrer with a Teflon shaft at 30 rpm. A Teflon bushing placed on the top surface of the chamber prevented the stirrer from wobbling. Another bushing clamped to the motor gripped the stirrer in place. The gas inlet and outlet were 3-mm i. d. FEP Teflon tubes. Thus all surfaces in contact with gas within the chamber were made of Teflon. The chamber was wrapped with 5-mm o. d. copper tubing (not shown in Fig. 2) on the sides and top. Water could be circulated through this tubing to provide a constant temperature inside the chamber close to the emission locale. Water cooling, however, was not used during the experiments described. The temperature inside the chamber was monitored by four thermocouples imbedded in the Lucite, one near the gas inlet and the other near the gas outlet, both on top, and two on the side near the top and bottom of the chamber. A 35.6-cm i. d. rubber inner tube encircling and attached to the chamber could be used to float the chamber on water. The bottom 2.5 cm of the chamber was beveled to form a knife-edge to facilitate formation of a seal between the inside and outside of the chamber.

The analytical device used with the chamber was a portable field-adapted gas chromatograph. It was an Analytical Instruments Development Corporation Model 513 and had a 183-cm Teflon column containing 15 percent Ucon HB-50 280x coated on a Teflon support. It was equipped with a flame photometric detector with a 394 nm interference filter making the detector sensitive to sulfur compounds.[18] We provided it with a six-port

Teflon sampling valve with a 15-ml sample loop. Because the oven insulation and heater were unable to cope effectively with some of the temperatures encountered in the field during the fall measurement period, we used the instrument placed in a large cardboard box filled with additional insulation.

The gas chromatograph was calibrated in the laboratory using permeation tubes. Its minimum sensitivity and elution time for five volatile sulfur-bearing gases are given in Table 1. Also given in Table 1 are the minimum values of the fluxes measurable at the minimum detectable concentrations given. These correspond to the nitrogen flow rate used in the experiments, namely, 2.6 l/min. (The method of calculating fluxes is given below.)

An emission flux experiment was conducted as follows. The chamber was placed over the surface of interest. A known volumetric rate of gaseous nitrogen from a cylinder was humidified and then passed through the emission flux chamber. This carrier gas swept the emitted gas into a six-port Teflon valve. The valve was used to inject samples every 20 minutes into the gas chromatograph. Runs were from 1 to 5 hr in duration. Af-

TABLE 1

Characteristics of Gas Chromatography Analysis

Gas	Elution Time, min	Minimum Sensitivity, ppb	Minimum Measurable Flux, gm S/m^2/yr
H_2S	1.67	10	0.20
CH_3SH	2.07	30	0.61
SO_2	2.33	10	0.20
$(CH_3)_2S$	2.5	50	1.02
$(CH_3)_2S_2$	10.0	8	0.33

ter every injection, temperatures of the air, sediment, and water outside the chamber were measured using a mercury-in-glass thermometer.

Two six-volt, 52 ampere-hour batteries were used in series to produce a direct current which was in turn converted to 115 volts a. c. by a Powerverter (Tripp Lite Model PV-500FC). This source was used to provide power for a recorder, stirrer, gas chromatograph and heater and was sufficient for a 12-hour period of operation. All the equipment was carried to the work site in a 4-m shallow draft aluminum boat propelled by an air motor. Fig. 3 gives a block diagram of the layout of the field experiment.

The emission flux was calculated from the following equation.

$$n = \frac{F\Delta C}{A} \qquad (1)$$

where n is the emission flux of a particular compound, ΔC is the concentration increase in the gas leaving the chamber over its concentration in the gas entering the chamber, F is the steady volumetric flow rate of gas through the chamber, and A

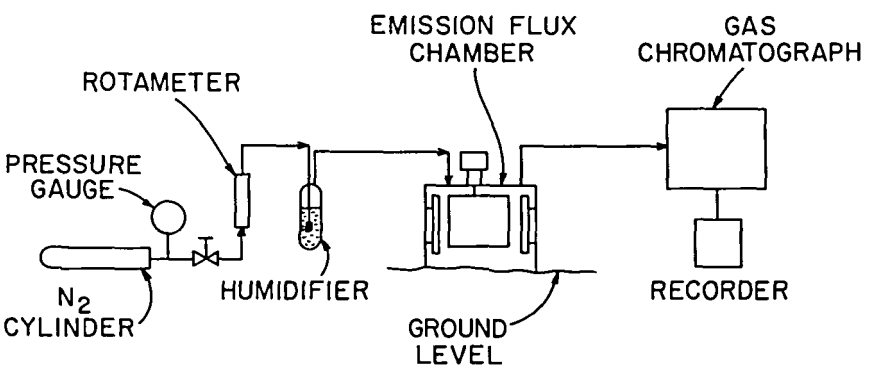

FIG. 3 Apparatus used at Flax Pond, Old Field, N. Y.

is the area of emitting surface covered by the chamber. It is assumed that n is constant with time and that the effluent concentration is the steady state value.

Eight runs were made, seven in the intertidal zone at low tide and one (Run 2) at high tide. Fig. 1 gives the position of the experimental sites. The sites were in Spartina alterniflora zones where the plants had been clipped to ground level to accommodate the chamber. In Run 2, conducted near high tide with the chamber floating on water, no emissions were detected. Of the other runs, in all conducted above a sediment temperature of 10°C, strong signals were obtained for H_2S while signals for other species were either very small or not clearly distinguishable from instrument baseline noise. The maximum fluxes of each compound measured in single injections are given in Table 2. Sulfur dioxide was detected only following the first two or three injections after putting the chamber in place, suggesting that this compound was present only in the ambient air. An unidentified compound was observed in most runs with an elution

TABLE 2

Maximum Sulfur Compound Fluxes Measured in Individual Gas Chromatograph Injections, Flax Pond, Old Field, N. Y., Fall, 1974

Gas	Maximum Flux, gm S/m^2/yr
H_2S	41.5
CH_3SH	1.92
SO_2	0.72
$(CH_3)_2S$	3.84
$(CH_3)_2S_2$	0.81

time of the order of 5 minutes. No H_2S was detected in Run 8 for which the sediment temperature was 6.6°C.

For all low tide runs, except Run 8, the average H_2S flux over a run was calculated and the results are plotted in Fig. 4 versus sediment temperature. The data are tabulated in Table 3. The value for Run 1 is seen to be anomalously high, a result for which we have no explanation. Two values are below the minimum sensitivity of 0.2 gm $S/m^2/yr$ reported in Table 1. These values were obtained by extrapolating the gas chromatograph calibration to values below the reported minimum concentration sensitivity, and the derived fluxes are thus subject to large error.

In general, the emission rate appears to increase strongly with increasing temperature. As stated above, no emissions were detected below 10°C. This result is consistent with the observation that microbial growth is often very slow or negligible at temperatures below 10°C.[19] Presumably substantially higher fluxes would be found at higher temperatures. The finding of no emissions in the winter (see below) and the implication of strong summertime emissions indicates a strong seasonal variation in emission flux.

Work conducted during the period December 1974 through February 1975 consisted of deploying lead acetate-treated tags in an inverted box in a Spartina zone in Flax Pond. Tags so treated darken upon exposure to H_2S. The box was arranged to float up and down with the tide. No evidence of emissions was found on tags so exposed during four periods of from 9 to 18 days during the three-month period.

Possible sources of error in these measurements are discussed in the next section of the paper.

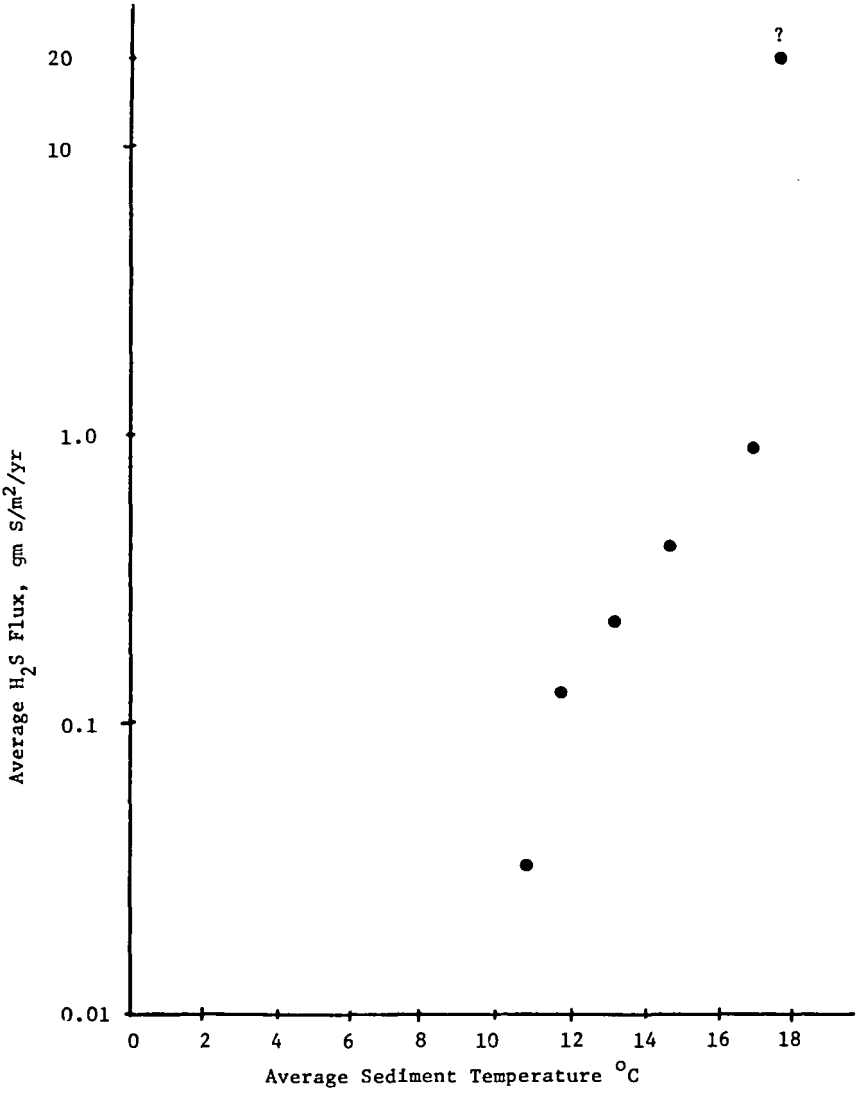

FIG. 4 Temperature dependence of average hydrogen sulfide emission fluxes, Flax Pond, Old Field, N. Y., Fall, 1974.

TABLE 3

Hydrogen Sulfide Emission Fluxes
from Spartina alterniflora Zones
in Flax Pond, Old Field, N. Y., Fall, 1974

Run No.	Site, Figure	Tidal Stage	Average Sediment Temperature, °C	Flux, gm S/m^2/yr
1	1	Low	17.6	20.6
2	2	High	n.a.	0.0
3	1	Low	13.2	0.23
4	3	Low	17.0	0.92
5	1	Low	14.7	0.44
6	1	Low	11.8	0.13
7	4	Low	11.2	0.03
8	1	Low	6.6	0.0

DISCUSSION OF THE CHAMBER TECHNIQUE

In this section we discuss briefly a number of advantages of the chamber technique and a number of problems with the technique that remain to be solved. The advantages are discussed while having diffusion methods in mind as alternates.

The chamber technique has the important advantage of association of a particular emission site and its measurable array of physical, chemical and microbiological properties with emissions of particular compounds or their reaction products. In addition, gas residence times in the chamber are of the order of minutes so that chemical transformations between emission and analysis may be minimized. Finally, the sensitivity for flux measurement is high without the necessity of measurement of very low concentrations.

As we shall see in the next section, the minimum global biogenic sulfur flux of interest is the marine flux, which may be

as small as 0.1 gm $S/m^2/yr$. Further, the average global flux of anthropogenic SO_2 is also of the order of 0.1 gm $S/m^2/yr$. To measure a flux equal to 10 percent of this value, we would have to be able to measure fluxes as small as 0.01 gm $S/m^2/yr$.

Let us require that this flux be measurable at an H_2S chamber concentration of 10 ppb, a value measurable with reasonable accuracy. The gas residence time in a chamber with height equal to diameter is given by

$$t_R = \frac{\pi}{4} D^3/F \qquad (2)$$

where t_R is the residence time, D is the chamber internal diameter, and F is the gas flow rate. If the emission flux is constant with time, approximately three residence times are required to elapse after chamber placement in order to attain a chamber concentration within 5 percent of the final steady value. Let this elapsed time be 20 min or t_R = 400 sec. Solving Equations (1) and (2) simultaneously with n = 0.01 gm $S/m^2/yr$, ΔC = 10 ppb, t_R = 400 sec, and T = 25°C, we find D = 9.1 cm and F = 89.3 cm^3/min. These represent a reasonable combination of flow rate and chamber size. The calculation thus indicates that the technique has adequate sensitivity at a practical size and flow rate without the necessity of measurement of very low H_2S concentrations.

Problems with the chamber technique which remain to be investigated are listed below.

1. Following use in Flax Pond, the interior surfaces of the chamber often were observed to have drops of water clinging to them. Absorption of the emitted gases by these drops may have been sufficient to result in an observed flux smaller than the natural flux. The drops may have originated through splash-

ing or condensation. Greater care in chamber placement or better temperature control may eliminate this problem.

2. The gas flowing through the chamber during the field study was nitrogen rather than air. This may have produced an increase in the metabolic activity of bacteria involved in sulfide production such that an enhanced flux would have been observed, or it may have produced an increase in activity of bacteria which oxidize H_2S, leading to diminished emission. It is not certain, however, that the time scale of the experiment was long enough to affect metabolic activity significantly. Also, and probably more importantly, the use of nitrogen may have resulted in enhanced emissions as a result of the reduction or elimination of chemical oxidation of dissolved H_2S to nonvolatile forms. Finally, the use of nitrogen would minimize air oxidation of emitted gases. A comparison should be made of fluxes derived from using both nitrogen and air as sweep gases.

3. The emission flux chamber technique has the advantage of producing concentrations within the chamber and the chamber effluent stream which are large compared to natural values and are therefore easy to measure. At the same time the elevated concentrations may be a disadvantage in that fluxes may be depressed below natural values. The following relation expresses the steady state rate of desorption of a volatile substance from a liquid into a gas:

$$n = K_L (C_{bl} - C_{bg}/H) \qquad (3)$$

where n is the flux of the substance into the gas, K_L is the overall mass transfer coefficient based on the liquid phase, C_{bl} and C_{bg} are the bulk liquid and gas phase concentrations of the substance, and H is the Henry' s law constant for the substance.

For present purposes we are interested in the concentration driving force term in parentheses in Equation (3) and not in the factor K_L. The maximum desorption flux for a given K_L will be found when $C_{bg} = 0$; and the flux will be zero when $C_{bg} = HC_{bl}$ or when the gas phase concentration is in equilibrium with the liquid phase concentration. The question of interest is for practical values of C_{bl} how large a value of C_{bg} is negligible compared to saturation? As a partial answer to this question, consider an acidic liquid phase (pH = 5) with an H_2S concentration of 1×10^{-10} mole/cm^3 = 3.4×10^{-9} gm H_2S/cm^3. Setting pH = 5 insures that substantially all of the H_2S present is in the molecular form. The H_2S concentration chosen corresponds approximately to the minimum sulfide concentration detectable with a silver-silver sulfide electrode. For H_2S at 25°C, H = 0.394.[20] Thus C_{bg} at saturation is $3.4 \times 10^{-9} \times 0.394 = 1.34 \times 10^{-9}$ gm/cm^3 which is 1340 μg/m^3 or approximately 1.3 ppm. In this situation if C_{bg} were 50 ppb, a value readily measurable with high accuracy, and the natural value of C_{bg} were essentially zero, then the flux n would be measured to within an accuracy of 5 percent. This argument indicates that the elevated concentrations associated with the chamber technique are not likely to depress natural fluxes significantly. However this point can be checked by measuring the flux as a function of carrier gas flow rate. For a fixed emission rate, a higher flow rate will result in a lower chamber concentration. The measured flux will increase with flow rate if concentration elevation significantly affects the driving force for desorption.

4. It may be expected that the gas phase fluid dynamics within the chamber will differ from the natural regime, perturbing K_L, the mass transfer coefficient in Equation (3), and thus

perturbing the flux from its natural value. However, calculations of K_L for turbulent water bodies, the results of which will be presented in the next section, show that over the pH range likely to be encountered in the environment mass transfer is liquid-phase controlled, and so will be little affected by gas phase flow patterns and turbulence. It should be even less affected by gas phase fluid dynamics in the case of desorption from a saturated soil surface. Again, this assertion may be checked experimentally, by measuring emission fluxes at a given gas flow rate as a function of stirrer speed. If mass transfer is controlled by the liquid or solid phase, the flux will not vary with stirrer speed and the measuring technique will not perturb the natural flux as a result of changed fluid dynamics.

5. Exclusion of solar radiation from the emission flux chamber may perturb the natural flux. This perturbation may result from suppression of the action of green and purple photosynthetic sulfur bacteria,[19] which oxidize H_2S to nonvolatile forms and should in principle lead to lower fluxes in the daytime than at night. Whether the flux is measurably perturbed when an opaque chamber is put in place should be tested experimentally. Another possible effect of light involves photochemical action: photo-oxidation of H_2S may lead to reduced observed fluxes of this compound and to increased apparent fluxes of oxidation products. Designing a chamber which is transparent to solar radiation and whose temperature may be satisfactorily controlled may present some problems. It should be noted that Hitchcock, et al.[13] measured higher H_2S concentrations in air over a North Carolina marsh at night than during the day, but this variation was attributed to meteorological influences.

COMPARISON OF EXPERIMENTAL AND ESTIMATED FLUXES

It is interesting to compare the fluxes reported in the present work with other values of biogenic fluxes, such as those derived from global sulfur budgets and those derived from a mass transfer calculation. Further, it is of value to compare biogenic fluxes with anthropogenic emissions expressed as fluxes. These comparisons are made in this section.

In making estimates of global quantities we took the area of the globe to be 5.1×10^{18} cm^2 with land and ocean areas being 1.5×10^{18} cm^2 and 3.6×10^{18} cm, respectively.

Average terrestrial fluxes calculated from recent global atmospheric sulfur budgets[6, 21-24] range from 0.4 to 0.7 gm $S/m^2/yr$, while marine fluxes derived in the same way range from 0.1 to 0.5 gm $S/m^2/yr$.

Estimates of mass transfer rates across the air-sea interface have been made by Liss and Slater[25] based on a two-film theory of mass transfer. We use their approach here to estimate fluxes of H_2S and also SO_2 from water to air under conditions corresponding to the air-sea interface.

The fluxes are calculated from Equation (3). The overall mass transfer coefficient, K_L, is given by

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Hk_G} \tag{4}$$

where k_L and k_G are the liquid and gas film mass transfer coefficients, respectively, and H is the Henry's law constant for the gas in question. Liss and Slater used an expression for the liquid film coefficient derived by Hoover and Berkshire.[26] This expression accounted for the augmentation of the coefficient resulting from ionization of the desorbing gas or from the reaction of the gas with water. The rate of ionization or reaction was

taken to be finite. For H_2S and SO_2, the rates of these reactions are very fast and thus to a good approximation can be taken to be locally at equilibrium in the liquid film. We note that when this is true Hoover and Berkshire's expression for the liquid film coefficient becomes

$$k_L = k_L^o \left(1 + \frac{K_1}{C_{H^+}}\right) \tag{5}$$

Here k_L^o is the liquid film mass transfer coefficient for the desorbing gas when considered inert with respect to ionization or reaction, K_1 is the equilibrium constant for ionization or reaction with water, and C_{H^+} is the hydrogen ion concentration.

We calculated maximum desorption fluxes for H_2S for the liquid phase total sulfide concentration which is just at the limit of detection using the silver-silver sulfide electrode, namely, 1×10^{-10} mole/cm^3. Sulfur dioxide fluxes were calculated for the same total sulfite concentration. Our object is to determine the maximum value of these fluxes which may exist when neither H_2S nor SO_2 can be detected by reasonably sensitive analytical methods. For both gases the gas phase concentration was zero corresponding to the maximum desorption rate. Data used in the calculation and the results are given in Table 4.

In the case of H_2S, desorption is liquid phase-controlled at the lower pH values. Gas and liquid phase resistances are equal at a pH slightly less than 9. Consequently decrease in the concentration of the un-ionized species with increasing pH is approximately balanced by increase in the overall coefficient resulting from increase of the liquid film coefficient with pH. Fluxes for SO_2 were calculated to illustrate how small such fluxes might be. There has been speculation that biogenic sulfur emissions might actually occur from water as SO_2 derived from

TABLE 4

Maximum Desorption Fluxes of H_2S and SO_2 from Turbulent Water Bodies

Total bulk liquid sulfide or sulfite concentration = 10^{-10} mole/cm^3

For H_2S, H = 0.0394,[20] $K_1 = 9.5 \times 10^{-11}$ (moles)/(cm^3)[5]

For SO_2, H = 3.32×10^{-2}, $K_1 = 1.3 \times 10^{-5}$ (moles)/)cm^3)[29]

k_G = 3000 cm/hr, k_L^o = 20 cm/hr

pH	n, gm S/m^2/yr	
	H_2S	SO_2
5	5.51	2.14×10^{-2}
6	5.50	2.15×10^{-3}
7	5.42	2.15×10^{-4}
8	4.76	2.15×10^{-5}

sulfide oxidation in water. For SO_2, the gas film resistance is controlling over the entire pH range shown. Thus the overall mass transfer coefficient does not vary appreciably with pH, but the concentration of the desorbing species, SO_2, does decrease exponentially with increasing pH. Thus the fluxes fall off in a corresponding manner.

Global average anthropogenic fluxes of SO_2 derived from the global sulfur budgets cited earlier range from 0.08 to 0.14 gm S/m^2/yr. When account is taken of the fact that 93 percent of this release occurs in the northern hemisphere,[27] then the average fluxes in this part of the globe range from 0.15 to 0.26 gm S/m^2/yr.

It is of interest to compute a regional anthropogenic flux for the eastern United States. Sulfur dioxide emissions in this region for the year 1980 have been projected to reach 2.2 x 10^6

metric tons S per year.[28] If we take the area of this region to be 3×10^{16} cm^2, then the average regional flux is calculated to be 7.4 gm S/m^2/yr. We assume that urban fluxes of SO_2 may equal or exceed 100 gm S/m^2/yr.

Table 5 summarizes the measured and estimated fluxes. In this table it may be seen that the measured fluxes range up to approximately two orders of magnitude larger than global fluxes, terrestrial or marine. Hydrogen sulfide fluxes from turbulent water bodies may be an order of magnitude larger than global fluxes even though the H_2S concentration is not detectable. A necessary condition for this latter finding is that the lifetime of H_2S with respect to oxidation is long. This will be so at small sulfide concentrations if the oxidation proceeds in accordance

TABLE 5

Emission Fluxes of Biogenic and Anthropogenic Sulfur Compounds, gm S/m^2/yr

Measured biogenic H_2S fluxes in a Long Island salt marsh (Flax Pond)	0 to 42
Global average terrestrial biogenic flux	0.4 to 0.7
Global average marine biogenic flux	0.1 to 0.5
Maximum H_2S flux, turbulent water to air, sulfide concentration = 10^{-10} mole/cm^3, pH = 5 to 9, from Table 4	5.5 to 2.1
Maximum SO_2 flux, turbulent water to air, sulfite concentration = 10^{-10} mole/cm^3, pH = 5 to 9, from Table 4	2.1×10^{-2} to 2.1×10^{-6}
Global average SO_2 flux	0.1
Average SO_2 flux, northern hemisphere	0.2 to 0.3
Average SO_2 flux, eastern United States, 1980	7.4
Urban SO_2 flux	100 (?) +

with the rate expressions of Chen and Morris.[5] These authors found the oxidation rate to be proportional to $(S_T)^{1.34}$, where (S_T) is the total sulfide concentration. The H_2S half-life would then be proportional to $(S_T)^{-0.34}$ and would increase with decreasing (S_T). Sulfur dioxide fluxes from turbulent water bodies in which the SO_2 concentration is near the limit of detection are always small compared to global average biogenic sulfur fluxes. Finally, the measured fluxes span the range of anthropogenic fluxes, from global almost to the presumed range of urban values. As seen from earlier discussion of the sensitivity of the emission flux measurement technique, measurement of biogenic fluxes which are significant with respect to anthropogenic fluxes is not difficult even for the global scale.

SUMMARY

A chamber technique for the determination of emission fluxes of biogenic sulfur compounds was described. Initial use of the technique was made in a Long Island, N. Y., salt marsh. Fluxes of H_2S measured in the fall months with an agitated Teflon-lined chamber provided with a field-adapted gas chromatograph were strongly temperature-dependent, indicating a large seasonal variation in the sulfur emission rate. A refined gas chromatographic technique is required for the unequivocal measurement of fluxes of organic sulfur compounds. A number of additional problems in flux measurement with the chamber technique were pointed out along with suggested solutions. The technique was shown to be sensitive enough to permit convenient measurement of fluxes in the range of expected biogenic sulfur compound fluxes which are in turn significant with respect to effective anthropogenic fluxes.

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NOTATION

An illustrative consistent set of units is given.

A	emission area covered by chamber, cm^2.
C_{bg}, C_{bl}	bulk gas and bulk liquid concentration, respectively, of desorbing species, $mole/cm^3$.
C_{H^+}	hydrogen ion concentration in liquid, $mole/cm^3$.
ΔC	increase in concentration of desorbing species across chamber, $mole/cm^3$.
D	inside diameter of chamber, cm.
F	gas flow rate through chamber, cm^3/sec.
H	Henry' s law constant for desorbing species, $(mole/cm^3)$ gas/$(mole/cm^3)$ liquid.
k_G, k_L	gas and liquid film mass transfer coefficients, respectively, cm/sec.
k_L^o	liquid film mass transfer coefficient for chemically inert species, cm/sec.
K_L	overall mass transfer coefficient based on the liquid phase, cm/sec.
K_1	first ionization constant of desorbing species, *mole*, cm^3.
n	emission flux of desorbing species, $mole/cm^2/sec$.
(S_T)	total sulfide concentration, $mole/cm^3$.
t_R	chamber average residence time, sec.
T	temperature, °C

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