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Measurement of Biogenic Sulfur Emissions from Soils and Vegetation: Application of Dynamic Enclosure Methods with Natusch Filter and GC/FPD Analysis

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Abstract. Emission rates of reduced sulfur gases from vegetation and soils were measured in various regions of the United States during the summer of 1985. The predominant sulfur gases emitted were hydrogen sulfide, carbonyl sulfide and dimethylsulfide. Typically, vegetative (forests, crops, etc.) emission fluxes varied between approximately 10 and 60 ng S m^{-2} min^{-1}. Biogenic sulfur fluxes from mollisol and histisol soils averaged 15 and 217 ng S m^{-2} min^{-1}, respectively. Salt water marsh fluxes with a geometric mean of 293 ng S m^{-2} min^{-1} were the highest measured. These biogenic sulfur fluxes are somewhat lower than those measured during the SURE study at some of the same sites. The natural sulfur emission fluxes reported herein together with those data included in the two accompanying manuscripts provide the basis for developing a national inventory of reduced sulfur emissions from soils, crops and trees. When combined these data also will provide a foundation for deriving uncertainty limits associated with these flux estimates.

1. Introduction

Information concerning natural sulfur emissions to the atmosphere is of importance because of the potential role reduced sulfur gases play in the acidic deposition process. It is known that sulfur containing species such as hydrogen sulfide, carbonyl sulfide, dimethyl sulfide, carbon disulfide and dimethyl disulfide are emitted into the atmosphere by a combination of biological, geological and chemical processes. While the atmosphere fate of these reduced sulfur gases is not well known, it is very probable that a major portion is oxidized to sulfur dioxide and eventually to sulfate. Policy decisions regarding emission control strategies require an accurate assessment of the relative importance of natural and man-made sources. Clearly, benefits anticipated from a reduction in anthropogenic sulfur emissions could be over-optimistic if natural sources contribute significantly to acidic deposition.

As part of an overall program in our laboratory aimed at developing a gridded, biogenic sulfur emissions inventory for the continental United States, it

was necessary to establish emission rates from various terrestrial sources. In recent years, many research groups have attempted to qualify sulfur emissions from different biogenic sources. Adams and coworkers (1980, 1981) measured emission rates from soils at many sites in the eastern U.S. Their measurements included most of the volatile, reduced sulfur gases. In addition, several investigators have reported gaseous sulfur fluxes from coastal areas and salt marshes (Georgii, 1978; Jaeschke, 1978; Hansen *et al.*, 1978; Aneja *et al.*, 1981; Goldberg *et al.*, 1981; Carroll, 1983; Steudler and Peterson, 1985).

While there have been a number of flux determinations from soils and marshy surfaces, there is very little information concerning sulfur emissions from vegetation. Aside from a short communication by Lovelock *et al.* (1972) and an indirect measurement reported by Delmas *et al.* (1980), the literature is devoid of vegetative sulfur emissions data that are applicable for establishing ambient fluxes. There are some additional published reports that indicate when certain types of plants are irrigated with a sulfate rich medium hydrogen sulfide emissions occur. However, it is difficult to relate these emissions studies to real world conditions.

The primary objectives of the work reported herein were to measure emission rates of reduced sulfur gases from prominent types of vegetation and to try to obtain improved emissions data for hydrogen sulfide from soils. Secondary goals were to compare our emissions results with those determined simultaneously by two other research groups and with data collected at the same measurement sites some years earlier. Research teams from Washington State University (WSU), University of Idaho (UI) and NOAA's Aeronomy Laboratory measured sulfur emissions from biogenic sources at field sites during the summer of 1985. The sites selected for the field study in 1985 had been visited previously by Adams and coworkers (1981) during the SURE biogenic sulfur emissions measurement program. Thus, it was possible to compare gaseous sulfur emission rates as determined by three different groups simultaneously as well as with the reported SURE estimates six years earlier. These intercomparison data are important because they help to establish uncertainty limits associated with the reported biogenic emission rates.

2. Experimental Procedures

The experimental program consisted of a major field study at sites in the midwestern and eastern U.S. and supplementary measurements at sites in eastern Washington and northern Idaho.

2.1. *Sampling Sites*

Sulfur emission measurements from inceptisol, entisol, and alfisol soils were col-

lected during different seasons in 1984–85 at sites in northern Idaho, and alfalfa enclosure measurements were obtained within 5 km of Pullman, WA over a mollisol soil.

The major field sampling program during the summer of 1985 was conducted at three sites previously used in the SURE biogenic sulfur emissions study. The first location was the Iowa State University Hinds Research Farm 5 km north of Ames, IA. The soil at this site is an alluvial soil (Wabash loam) in the aquoll suborder of the mollisol order (Adams *et al.*, 1980). This type of soil is considered to be of modest to low potential for sulfur productivity. However, mollisol soils account for a relatively large fraction of the land area in the continental U.S. (30% of total area). The Iowa site has been intensively cultivated for a number of years with corn, soybeans and other crops. During 1985, samples were collected in fields planted with corn, soybeans, and oats. Deciduous trees at the research farm and in suburban Ames were also sampled for sulfur emissions.

The second field site was the Muck Branch Research Farm, Ohio State University, approximately 3 km south of Celeryville, OH. The soil at this site is a histisol (Rifle peat) which is extremely rich in organic matter. This Ohio farm ground has been heavily cultivated for many years with a variety of vegetables. Samples were collected over bare soil, bare soil with crops, and in a nearby fresh water marsh. Histisol soils are high in sulfur productivity, but these soils account for less than 6% of the U.S. land area. Deciduous trees were sampled in the vicinity of the farm.

The third field site was on Cedar Island, NC where samples were collected over salt water marshes, sandy tidal areas, an inland fresh water pond, inland soils, and from deciduous and coniferous trees on the island. The soil in the tidal zones is classified as a salt water swamp muck with marsh grass including species of the following three genera: rush (*Juncus*), cord grass (*Spartina*), and salt grass (*Distichlis*). The inland sampling sites were over a ultisol soil.

2.2. Dynamic Enclosure Sampling Methods

Sulfur emission measurements were obtained by passing sulfur-free air over an enclosed source and concentrating sulfur gases from the exhaust air using both cryogenic sampling loops and treated filters. Bare soils, soils and small crops, marshes, and open water were sampled with a rigid polycarbonate enclosure (used in the SURE study) or a rigid Teflon enclosure (described by Goldan *et al.*, 1987). Branches of large trees and the isolated biomass of crops (no soil) were sampled with a Teflon bag enclosure. In each case, a multi-bed absorbent cartridge was used to remove sulfur gases from the sweep air. The absorbents consisted of potassium permanganate-impregnated alumina pellets, activated charcoal, soda lime, and anhydrous calcium sulfate. Adams *et al.* (1980) used
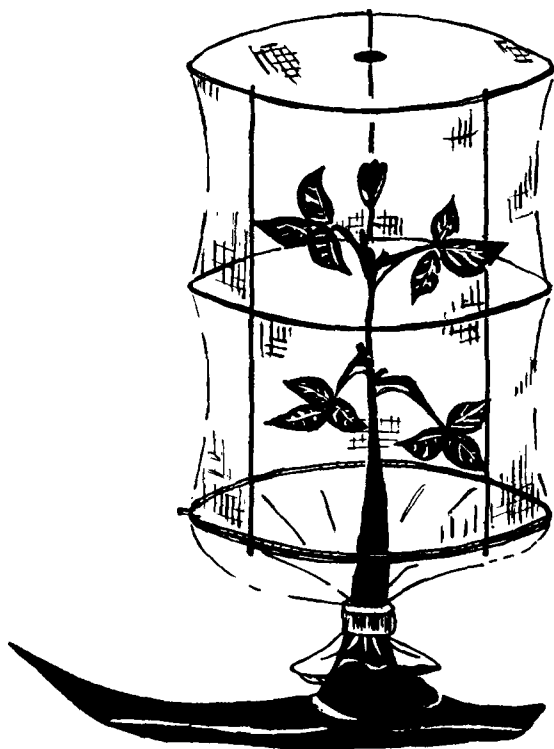
Fig. 1.   Schematic of vegetation enclosure.

this method to obtain 99% sulfur-free air in the SURE sampling program. Blank samples were collected routinely during the study to monitor the effectiveness of the air cleaning system.

Gas flow through the enclosure and the air sampling rates were controlled with calibrated gas rotameters. Flow through the polycarbonate enclosure was typically 2 l min^{-1} which provided a residence time of 8 min. The volume of the polycarbonate chamber was 16.7 l with an enclosure surface area of 0.069 m^2. Sweep air was introduced into the chamber through a Teflon diffusion ring fitted 4 cm above the sample surface and exhausted through a 2 cm port in the top of the chamber.

The vegetation enclosure system consisted of a 40 l flexible Teflon bag fixed to an aluminum frame designed to mount on a large tripod as shown in Figure 1. Sweep air was introduced at 2 l min^{-1} through a Teflon tube inserted into the bag and air was exhausted through a 2 cm hole in the opposite end of the bag.

For both enclosures, air samples were collected through 1/8 inch OD Teflon lines inserted into the exhaust port. Samples for analysis of carbonyl sulfide (COS), dimethyl sulfide (DMS), carbon disulfide (CS$_2$), dimethyl disulfide (DMDS), and higher molecular weight compounds were collected cryogenically

in passivated glass loops. Pyrex glass beads (60/80 mesh) were packed in the lower portion of the loops and held in place with glass wool plugs. The loops, beads, and glass wool were deactivated with a silylation procedure developed by Adams *et al.* (1980). Samples for hydrogen sulfide (H_2S) were obtained by drawing chamber air through silver nitrate impregnated filters (47 mm Whatman #4) in Teflon filter holders. Air flow through the glass cryogenic loop was 30 cm^3 min^{-1}, while air flow through the impregnated filters was 1 l min^{-1}. Usually both types of samples were collected simultaneously for 30 min. When the emission rates were expected to be very high, shorter sampling periods were used.

Samples were obtained by placing the enclosure over the source and allowing the system with sweep air flowing to equilibrate for more than 3 residence times (30 min for the rigid enclosure, 60 min for the Teflon bag). During the collection of the cryogenic and filter samples, ambient temperature, relative humidity, wind, and the general sampling conditions were recorded along with temperature and relative humidity measurements inside the enclosure. After the vegetative emissions collection was complete, the vegatation was cut, weighed, dried in an oven at 60 °C overnight, and reweighed to obtain dry biomass.

2.3. *Sulfur Sample Analyses*

2.3.1. *Gas chromatograpy methods.* The cryogenically collected samples were analyzed using a sub-ambient, temperature programmed gas chromatographic procedure employing a fused silica capillary column connected to a flame photometric detector (FPD). The FPD has a high selectivity to sulfur compounds compared to other non-sulfur gases. The sample collection loop was connected to a Carle micro sampling valve which was plumbed into the carrier gas line. The contents of the loop were transferred to the head of the capillary column where the sulfur compounds were focused in a narrow band, cryogenically. After a transfer period of 6 to 10 min., the glass loop was removed from the system, the capillary loop was immersed in heated water, and the gas chromatograph was programmed at 16 °C min^{-1} from −70 to 130 °C. This system yielded sulfur chromatograms nearly identical to those reported by Adams *et al.* (1980). Peak areas were measured using an electronic integrator. The detection limit with this system was approximately 0.01 ng S which corresponds to a lower bound sulfur flux of 0.3 ng S m^{-2} min^{-1} for rigid enclosure samples or 0.1 ng S g^{-1} min^{-1} for typical vegetation enclosure samples (assumes 100 g biomass).

The gas chromatograph was calibrated by transferring standards in dry air (3 cm^3) directly to the capillary loop. Standards for the various sulfur compounds were generated using sulfur-free air passed over low flow permeation devices (GC Industries, Chatsworth, CA). These gas-phase permeation tubes were maintained at 30 ± 3 °C in an air bath. Sulfur emission rates were shown to vary by approximately 0.3% for each 1 °C change in temperature. Thus, the air bath was

sufficient for maintaining a constant permeation rate during the field studies. The loss rates of the permeation devices were assigned by comparison (via gas chromatographic analyses) with high loss rate permeation tubes calibrated over the long term using gravimetric weighings. The low loss permeation devices were also tested against the dual flasher total sulfur analyzer described by McTaggert *et al.* (1987). Standards were analyzed periodically during each analysis period, and complete calibration curves were generated before and after the field sampling at each location.

2.3.2. H_2S filter methods. Filter samples collected for H_2S analyses were placed in clean plastic petrie dishes and stored inside sealed, aluminum cans. Cans containing exposed filters were periodically shipped via air freight to Pullman, WA for analysis. Typically, filters were returned and analyzed within 7 days of collection. Storage and shipping tests of filters generated from sulfur standards indicated that the filters were stable and remained uncontaminated for two weeks using these procedures. Laboratory tests for interferences from the other reduced sulfur gases showed no observable effects when a sample stream containing COS, CS_2, DMS, and DMDS, but no H_2S was passed through a filter.

The filters were prepared at WSU by immersion in a $AgNO_3$ solution followed by vacuum drying in a desiccator at room temperature. The preparation, sampling, and analysis procedure is a batch process and several filters in each batch were used to quantify background contamination. These blank filters were shipped to and from the field sites along with the sample filters.

Filters were analyzed following procedures similar to those given by Natusch *et al.* (1972), Axelrod *et al.* (1969), and Jaeschke and Herrman (1981). Each filter was leached with an alkaline cyanide solution, and an aliquot of the resulting mixture was combined with fluorescein mercuric acetate (FMA). Fluorescence quenching of the FMA by the sulfide was measured using a spectrofluorometer (Perkin Elmer LS-5). The instrument was calibrated prior to each analysis period using standard solutions prepared from sodium sulfide.

Results from these calibrations yielded a level of precision of approximately $\pm 11\%$. Analysis of replicate filters, both blanks and filters exposed to known H_2S concentrations, yielded scatter within each group ranging from $\pm 2\%$ to $\pm 24\%$. Intercomparison studies between WSU and the University of Idaho (Farwell, 1985) using very similar filter methods and the same H_2S sample stream gave agreement within approximately 20% for H_2S concentrations representative of real emissions samples. These results indicate that the uncertainty in H_2S measurements using the filter method is approximately $\pm 20\%$.

2.4. Sample Collection Efficiencies

As a result of early work by Adams *et al.* (1980) and more recent studies by Farwell (1985), it is known that the cryogenic collection loops do not exhibit 100%

recovery efficiency for sulfur compounds in the sample air. In fact, the recovery efficiency appears to decrease dramatically for sample collection periods longer than 30 min. Our own measurement of recovery efficiencies yielded the following values: COS $24 \pm 7\%$, DMS $73\% \pm 12\%$, and DMDS $49 \pm 12\%$. We did not measure CS_2; results from Farwell gave a recovery efficiency at approximately 28% for CS_2. These efficiencies are for 30 min collection periods. The values represent averages obtained from multiple analyses of humidified standards passed through the enclosures and collected with the cryogenic sample system. As a result, the collection efficiencies include the effects of wall losses in the enclosures. However, there appeared to be no difference in collection efficiency between the rigid polycarbonate and Teflon sleeve enclosures. The emissions data for COS, DMS, and DMDS presented in this paper have been corrected using these recovery efficiencies. In addition, the data presented herein from the SURE program have been corrected using the recovery efficiency data from Farwell who conducted the tests using a GC system identical to that used in the SURE program.

3. Presentation of Results and Discussion

The sampling program in and around Pullman, WA was conducted during the fall of 1984, and spring of 1985. The major field sampling program during summer, 1985 consisted of a sample collection period at Ames, IA from July 3 to July 11 followed by Celeryville, OH from July 19 to July 29, and Cedar Island, NC from August 4 to August 12. A total of 279 emission samples were collected by WSU at the three sites in the following source categories: bare soils, soils with natural grasses, soils and crops, crops, trees, marshes, and open water. The major source types, the number of samples, and locations are summarized in Table I. Regression coefficients and fluxes predicted from the algorithm: $\ln F = a \pm bT$ where T is the enclosure temperature are listed in Table II for a number of sources.

3.1. *Emissions from Soils and Water*

Emission fluxes for different sulfur compounds are shown in Figures 2 and 3 for Iowa mollisol and Ohio histisol soils. In the case of H_2S, the emission fluxes from mollisol soils were in the range of 0.1 to 7 ng S m^{-2} min^{-1}, while for histisol soils the range was much higher at approximately 4 to 460 ng S m^{-2} min^{-1}. In both cases, there is a weak dependence of sulfur flux upon enclosure temperature as indicated by the regression lines through the data (see Table II). Emissions of DMS and COS from mollisol soils exhibit higher rates than the H_2S mollisol emission rates, and the emissions of DMS and COS from histisol soils were elevated to levels similar to those for H_2S emitted from histisol soils. For both soil types, emissions of CS_2 and DMDS were

Table I. Summary of biogenic sulfur emission measurements

Source	Location (state)	Month (1985)	Number of samples	Geo. mean emission (ng S m^{-2} min^{-1})	Mean sample temperature (°C)
Soils					
Inceptisol	ID	9, 10, 11, 3, 4	17	2.7	10.9
Entisol	ID	10, 3, 4, 5	11	10.1	11.9
Alfisol	ID	10, 5, 6	15	15.9	
Mollisol	IA	7	15	11.0	38.4
Histisol, bare	OH	7	18	204	32.9
Tidal shore	NC	8	8	224	36.3
Saline marsh					
(with grass)	NC	8	25	347	32.7
Salt water	NC	8	5	30.9	31.4
Fresh water	NC	8	4	158	29.6
Crops					
Oats (with soil)	IA	7	11	30.9	35.4
Misc. vegetables (with soil)	OH	7	6	74.1	29.3
				ng S kg^{-1} min^{-1}	
Corn	IA, OH	7	36	61.7	28.9
Soybeans	IA	7	16	126	32.8
Alfalfa	WA	9	6	107	22.4
Trees					
Deciduous	IA, OH, NC	7, 8	55	28.2	29.5
Coniferous	NC	8	13	18.6	29.2

lower than for emissions of H_2S, COS, and DMS. The fluxes of CS_2 and DMDS from mollisol soils were on the order of 1 ng S m^{-2} min^{-1} and the fluxes of these gases from histisol soils ranged from 0.1 to 5 ng S m^{-2} min^{-1}. During the initial sample collection period at the Ames site, a sun screen was not used and consequently the enclosure temperatures during the first day exceeded 40 °C. However, emission fluxes at these high temperatures did not decrease as might be expected if biological activity was disrupted by elevated temperatures.

The total emission fluxes from mollisol and histisol soils are also shown in Figures 2 and 3. Total sulfur fluxes from mollisol soil at the Iowa site ranged from 0.10 to 100 ng S m^{-2} min^{-1} in comparison to the total sulfur fluxes from histisol soils in Ohio which varied between 5 and 825 ng S m^{-2} min^{-1}. The combined sulfur fluxes at each site increase with increasing enclosure temperatures with correlation coefficients (r) of 0.52 for the Iowa data and 0.92 for the Ohio data. The enclosure temperatures at these sites varied from 26 to 55 °C in Iowa and from 6 to 43 °C in Ohio.

The emissions from mollisol and histisol soils in the midwestern U.S. can be

Table II. Regression coefficients and predicted fluxes for $\ln F = a + bT$

Source	No.	Enclosure temperature range (°C)	a	b	F (ng S m^{-2} min^{-1})	r	ε^a (%)
Mollisol					$T = 25.5$ °C		
H$_2$S	11	28–49	−1.11	0.041	0.38	0.95	71
DMS	13	16–49	−2.68	0.104	0.94	0.96	26
COS	11	26–49	−0.42	0.083	5.45	0.95	19
CS$_2$	11	26–49	−2.36	0.060	0.43	0.93	16
Total	14	26–49	−1.42	0.099	3.02	0.52	96
Histisol					$T = 22$ °C		
H$_2$S	16	6–43	1.63	0.055	17.22	0.66	65
DMS	16	29–43	−4.32	0.184	0.77	0.38	170
COS	16	29–43	−0.06	0.154	28.05	0.66	35
CS$_2$	14	29–43	−6.88	0.193	0.07	0.64	57
Total	17	6–43	1.13	0.127	50.23	0.92	40
Marsh					$T = 28$ °C		
H$_2$S	21	28–36	−6.87	0.366	29.44	0.50	227
DMS	21	28–36	1.18	0.120	93.33	0.26	99
COS	22	28–36	−1.70	0.157	14.72	0.45	74
CS$_2$	19	28–36	−4.24	0.173	1.81	0.36	172
Total	24	28–36	−2.60	0.258	102	0.44	148
Corn					(ng S kg^{-1} min^{-1}) $T = 28$ °C		
H$_2$S	27	6–38	2.26	0.028	20.8	0.21	104
DMS	20	26–38	2.72	0.074	119.7	0.36	80
Total	36	6–38	1.95	0.076	58.7	0.37	190

^{a} $\varepsilon = \dfrac{1}{N} \dfrac{\Sigma (S_o - S_p)}{S_p} \cdot 100\%$; $S_o \equiv$ observed and $S_p \equiv$ predicted from regression curve.

compared to emissions from salt water marshes at Cedar Island, NC which are shown in Figure 4. The H$_2$S emissions from salt water marshes ranged from less than 1 to more than 2300 ng S m^{-2} min^{-1} which far exceed the corresponding emissions from mollisol and histisol soils. The H$_2$S emissions also exceeded the maximum fluxes of the other observed compounds in the salt water marsh samples. DMS fluxes ranged to 700 ng S m^{-2} min^{-1} and COS fluxes reached 430 ng S m^{-2} min^{-1}, while CS$_2$ and DMDS fluxes were much less in the range 0.1 to 70 ng S m^{-2} min^{-1}. These limits encompass a slightly larger range compared to the fluxes for CS$_2$ and DMDS from mollisol and histisol soils.

The dependence of sulfur flux upon enclosure temperature is less apparent in the marsh samples than in the inland soil samples. This is partly due to the smaller range of sampling temperatures encountered at Cedar Island and partly due to the added complexities of tidal effects upon sulfur emissions.
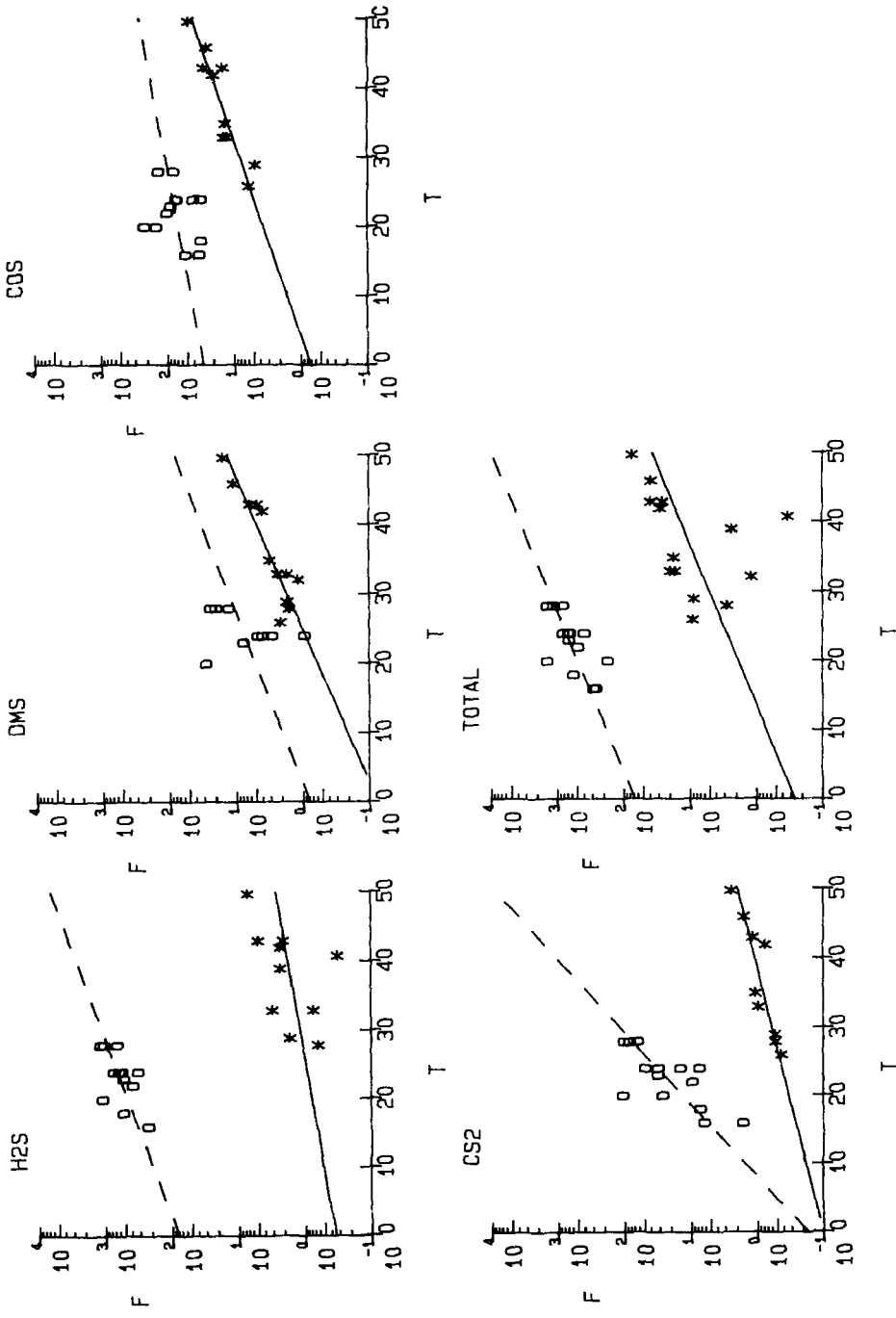
Fig. 2   Individual compound and total sulfur flux (ng S m^{-2} min^{-1}) vs. enclosure temperature (°C) from bare mollisol soil in Iowa: (○) SURE data. (∗) 1985 data.
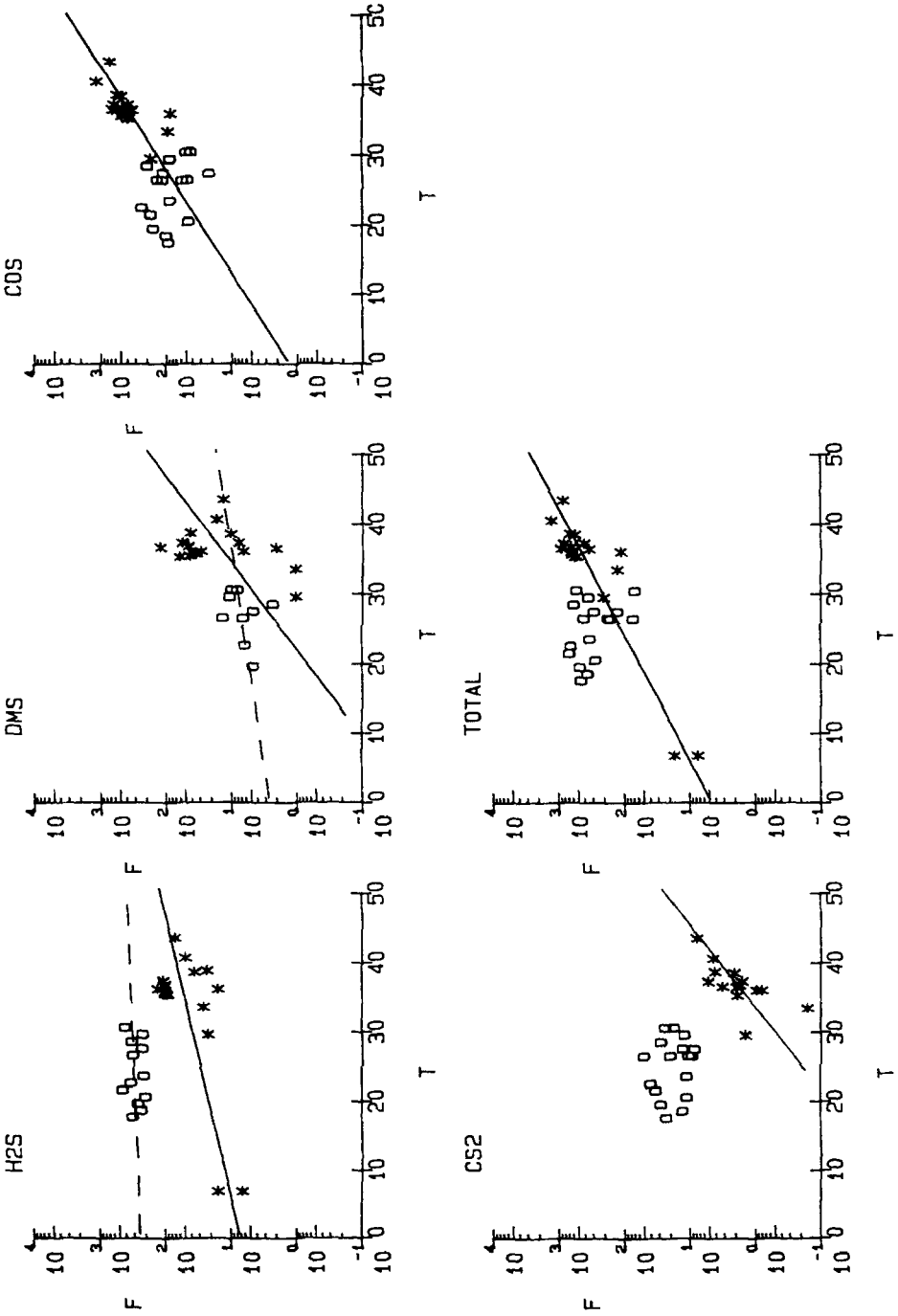
Fig. 3. Individual compound and total sulfur flux (ng S m^{-2} min^{-1}) vs. enclosure temperature (°C) from bare histisol soil in Ohio: (O) SURE data. (*) 1985 data.
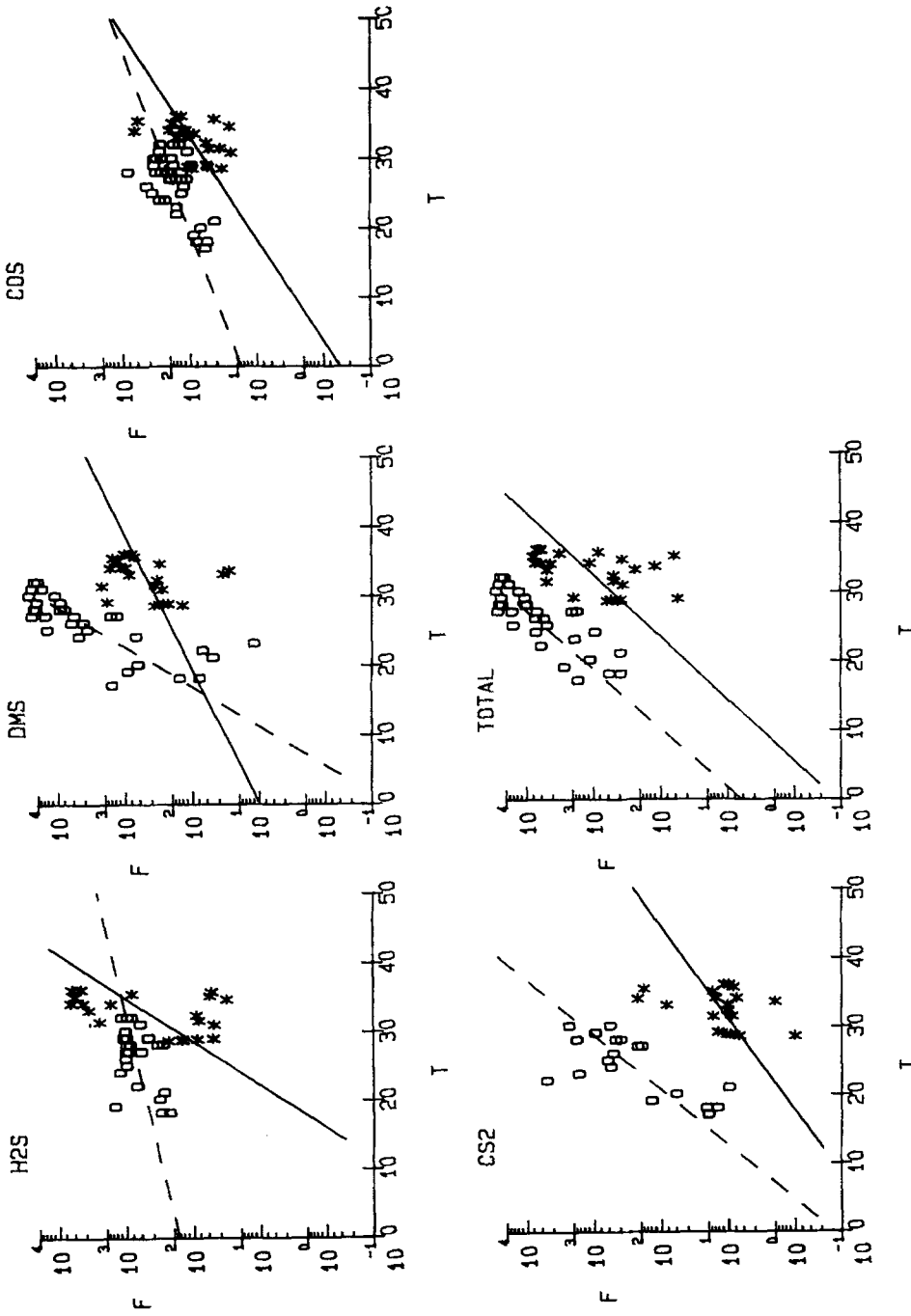
Fig. 4. Individual compound and total sulfur flux (ng S m^{-2} min^{-1}) vs. enclosure temperature (°C) from salt water marsh in North Carolina: (○) SURE data, (∗) 1985 data.

Adams *et al.* (1981) and others have commented upon the effects of tidal patterns upon diurnal changes in emissions from marshes.

Total sulfur emissions from the salt water marsh are dominated by the H_2S fluxes. The total fluxes vary from 0.2 to 2400 ng S m^{-2} min^{-1} for sampling temperatures of 28 to 36 °C. These levels are two or three times greater than the fluxes observed from mollisol and histisol soils.

Emissions from a fresh water pond were measured on Cedar Island. The emission flux of all compounds reached levels of 400 ng S m^{-2} min^{-1}.

The results collected for bare and naturally vegetated soils and for salt water marshes follow the trend expected for these types of sources. Emissions from the salt water marsh were dominated by H_2S and total sulfur emissions exceeded fluxes from the other types of sources by severalfold. In each source type, the emissions tended to be much higher for H_2S, DMS, and COS than for CS_2 and DMDS. Mollisol soils produced lower fluxes of sulfur gases than histisol soils or the fresh water pond.

3.2. *Biogenic Sulfur Emissions from Crops*

Measurements of sulfur emissions from crops are complicated by the fact that the rigid enclosure methods yield fluxes due to soil plus vegetation. Consequently, a Teflon bag system was developed to determine emission rates from the vegetation alone. In the case of crops like oats, only measurements with the rigid enclosures were obtained, so that the effects of soil are necessarily included in the results.

The emissions of sulfur from corn were measured in 30 samples using the vegetation enclosure bag and in 10 samples using the soil and vegetation rigid enclosure. Emissions from bare soil in the Iowa corn field were measured in 6 samples. The emission rates, in ng S kg^{-1} min^{-1}, from the vegetation enclosure samples are shown in Figure 5 for the dominant sulfur species and for the total sulfur emissions. In addition, data from the soil plus corn samples are shown in Figure 5. For these data, the regression curve from bare mollisol soils was used to subtract the contribution of the soil from the total emission flux, and the biomass of the enclosed corn plant along with the surface area of the rigid enclosure were used to convert the emission fluxes to emission rates. Emissions of H_2S and DMS dominated the sulfur flux from corn, and emission rates of DMS were higher than those of H_2S. Total sulfur emission rates from corn plants ranged up to 500 ng S kg^{-1} min^{-1} for enclosure temperatures between 6 and 38 °C.

There were 16 samples of soybeans plus soil, but only three samples with soybean vegetation alone. The regression curve for bare mollisol soil was again used to subtract the contribution of the soil, and the emissions due to soybean plants alone were obtained. These data were converted to emission rate units using the measured dry biomass of the enclosed vegetation. In a manner similar
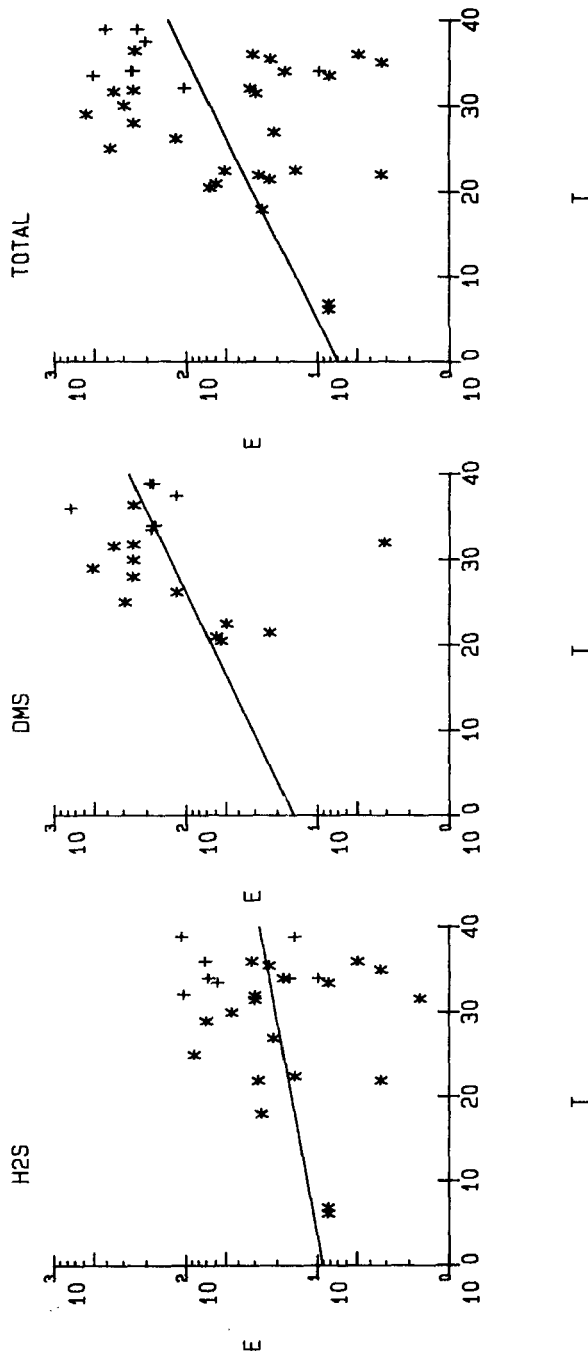
Fig. 5. H$_2$S, DMS, and total sulfur emission rate (ng S kg^{-1} min^{-1}) vs. enclosure temperature (°C) from corn in Ohio: (∗) rigid enclosure, (+) bag enclosure.

to corn, the emissions from soybean were dominated by DMS at levels near 80 ng S kg^{-1} min^{-1}.

Other crop samples were obtained for oats in Iowa; for celery, onions, and carrots in Ohio; and for alfalfa in Washington. Results from these measurements are listed in Table I in terms of the the geometric mean emission rates and corresponding mean sampling temperatures.

3.3. Biogenic Sulfur Emissions from Trees

A significant portion of this work was directed toward emission rate measurements from the dominant U.S. tree species. During the summer field program, 65 samples were collected from the deciduous species listed in Table III and 13 samples were obtained for loblolly pine (Pinus taeda) at Cedar Island.

There was no observable difference in emission rates or types of compounds from the different species of deciduous trees. The data for the dominant sulfur compounds and for total sulfur flux are shown in Figure 6. For deciduous trees, H$_2$S, COS, and DMS are the most significant species emitted. Emission rates of these compounds are similar and range from less than 2 to 80 ng S kg^{-1} min^{-1} for enclosure temperatures between 22 and 36 °C. There is no discernible trend in the data with respect to temperature.

The sulfur emissions from loblolly pine are predominately COS with measurable contributions of H$_2$S and DMS. The emission rates of COS vary from approximately 10 to 50 ng S kg^{-1} min^{-1} for temperatures between 24 and 35 °C. Dilts (1985) measured sulfur emissions from trees in the Pullman, WA area using the same procedures described herein. For Douglas fir (Pseudotsuga menziesii) and Norway spruce (Picea abies), Dilts obtained sulfur emission rates in the range 10 to 117 ng S kg^{-1} min^{-1} for enclosure temperatures between 8 and 24 °C.

Table III.   Trees sampled for biogenic emissions

| Common name	Scientific name	Location	No. of samples
Silver maple	Acer saccharinum	Ames, IA	5
Sugar maple	Acer saccharum	Ames, IA	5
White ash	Fraxinus americana	Ames, IA	7
Black walnut	Juglans nigra	Ames, IA	2
White oak	Quercus alba	Celeryville, OH	6
Hickory, Shagbark	Carya ovata	Celeryville, OH	6
Northern red oak	Quercus rubra	Celeryville, OH	5
Loblolly pine	Pinus taeda	Cedar Island, NC	13
Sweet gum	Liquidambar styraciflua	Cedar Island, NC	6
Red maple	Acer rubrum	Cedar Island, NC	11
Live oak	Quercus virginiana	Cedar Island, NC	9
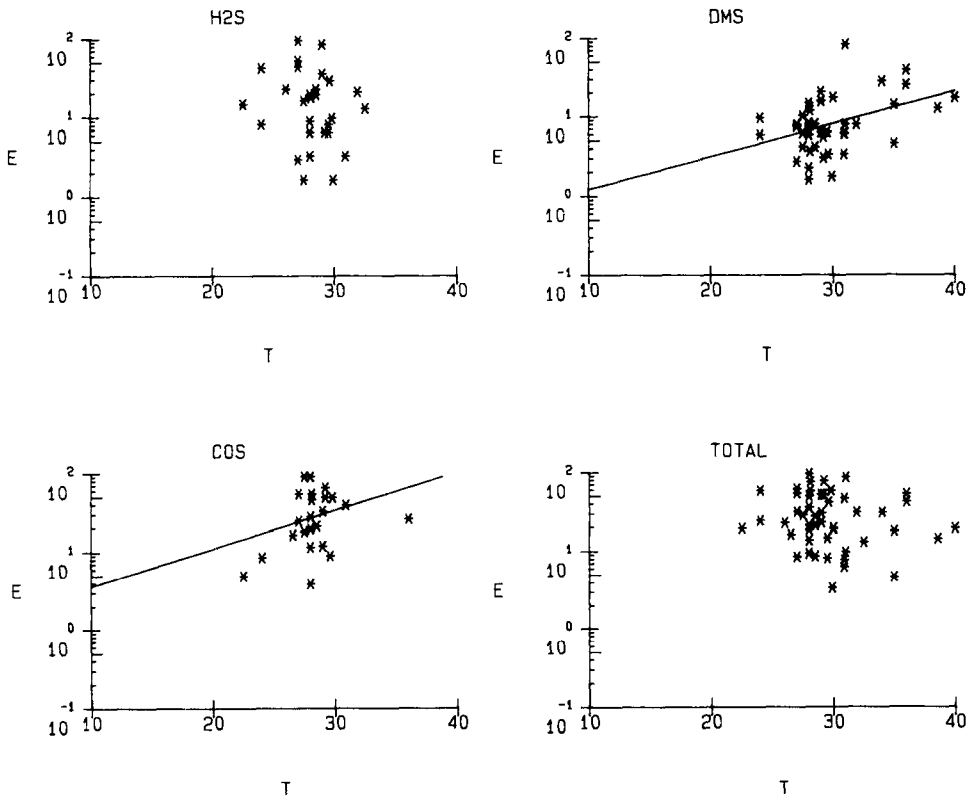
Fig. 6.   H₂S, DMS, and total sulfur emission rate (ng S kg⁻¹ min⁻¹) vs. enclosure temperature (°C) from deciduous trees in Iowa, Ohio, and North Carolina.

It should be noted that recent reports have suggested that vetatation can serve as a sink for COS (Brown and Bell, 1986; Goldan *et al.*, 1987). During our field studies described herein, no attempt was made to determine whether the tree species sampled would serve as a net source or sink for COS. Our measurement procedure, which utilized sweep air devoid of COS, did not permit detection of COS uptake by vegetation.

3.4. *Comparison with SURE Biogenic Sulfur Measurements*

This research is directed toward the development of regional inventories of biogenic sulfur emissions for use in models of the natural component of acid precipitation. The SURE biogenic sulfur program produced the most comprehensive data base available for development of natural emissions inventories. As a result, a major focus of the present work has been to determine the limits of uncertainty asociated with the SURE data base. The selection of sites in the midwestern and eastern U.S. was made to allow direct comparison of new

measurements using several independent methods with the existing SURE data from the same sites.

During the SURE program, sulfur flux measurements were made using the rigid polycarbonate enclosure; no isolated vegetation measurements were conducted. Cryogenic samples were collected in a manner similar to that described herein. These samples were analyzed using capillary column gas chromatography for H_2S and the remaining sulfur compounds considered in this work. Measurements were made over bare soils, soils with natural grasses, and soils with small crop plants.

As part of our analysis of the uncertainties in making sulfur emission measurements, we have completed a detailed analysis of the uncertainties involved in each step of the SURE sampling and analytical procedures. The types and estimated level of uncertainty from this analysis include (1) variability in the gravimetric calibration sources, $\pm 35\%$; (2) scatter about the logarithmic calibration curve, $\pm 13\%$; (3) scatter about the collection efficiency vs. sample time curve, $\pm 32\%$; and (4) reproducibility of the enclosure procedure based upon paired enclosure measurements, $\pm 86\%$ (this includes the effects of (2) and (3) above). Together, these estimates of uncertainty yield approximate bounds on the SURE emission measurements. However, this analysis of uncertainty does not address the true contribution of H_2S and methyl mercaptan (MeSH) since the reported recovery efficiencies for these gases could only be determined for dry air as opposed to the moist sample air used in the efficiency tests for the other gases. This difficulty in cryogenically collecting and analyzing for H_2S in a moist sample stream is the reason for the use of the H_2S filter method in the 1985 field measurements.

With the above estimates of reproducibility in mind, the SURE data for bare soils from Iowa and Ohio and for the marsh in North Carolina can be compared to the data collected in 1985. The SURE results are shown in Figures 2 and 3 for bare mollisol and histisol soils and in Figure 4 for the salt water marsh. Most of the SURE data for these sites were collected during July and August so that the time of year is essentially identical for the 1985 and SURE data sets.

Emissions of the H_2S from mollisol soil in Iowa measured during the SURE program were three orders of magnitude larger than the H_2S emissions measured during the 1985 field study. The difference between emission fluxes of H_2S from histisol soil in Ohio is less with SURE data yielding emission fluxes in the range 100 to 300 ng S m^{-2} min^{-1} and the 1985 H_2S data in the range 1 to 400 ng S m^{-2} min^{-1}. At the salt water marsh on Cedar Island, the 1985 H_2S emission estimates encompass the SURE emissions data within the range 1 to 2300 ng S m^{-2} min^{-1}. The trend toward better agreement between the two data sets for increasing production of H_2S might be an indication that the cryogenic collection and GC analysis for H_2S achieves better results at higher H_2S concentrations.

Emission estimates for COS in the two data sets follow a pattern similar to that for H_2S. For the Iowa mollisol soil, the SURE COS emission estimates ex-

ceed those from the 1985 data by one to two orders of magnitude. For the Ohio histisol soil, the results from the SURE and 1985 studies essentially lie along the same regression curve although the SURE data appear to have more scatter about the line. Emission estimates of COS from the salt water marsh based upon the SURE data overlap the COS estimates from the 1985 work, but the SURE data yield a regression curve which lies approximately an order of magnitude above the curve through the 1985 COS data.

The flux of DMS from mollisol soil is larger in the SURE data than in the 1985 data by approximately an order of magnitude. The DMS estimates from the two data sets show relatively good agreement for the histisol soil in Ohio just as for the case of COS estimates from histisol soil. Emissions estimates of DMS from the salt water marsh exhibit considerable variability in both data sets. It appears from Figure 4 that the SURE estimates tend to exceed the 1985 measurements by approximately an order of magnitude.

Emissions of CS_2 in the SURE data set exceed the estimates in the 1985 data by one to two orders of magnitude for all three sites. In part, this difference can be attributed to the lack of correction for recovery efficiency in the 1985 data set. However, even with a correction for a typical recovery efficiency of 20%, the CS_2 emissions in the SURE data would exceed the emission estimates from the 1985 data by more than a factor of five. The emission fluxes of CS_2 are quite low in both data sets for histisol soil, of moderate strength for mollisol soils and reasonably large for the salt water marsh.

There were no DMDS emissions reported in the SURE study for the Iowa mollisol soil and only one sample for the Ohio histisol. DMDS emission estimates for the salt water marsh were quite comparable for the SURE and 1985 studies. The differences between the two data sets for DMDS emissions are less than a factor of three at emission fluxes very near 1 ng S m^{-2} min^{-1}.

Total sulfur fluxes reported for the two studies reflect the differences described above. For mollisol soil where the SURE H_2S estimates were extremely high, the total sulfur fluxes for mollisol soil in the SURE data exceeds the total sulfur fluxes in the 1985 data by two orders of magnitude. For histisol soil where the differences for each compound were less, the total sulfur fluxes from the SURE study lie approximately along the regression curve through the 1985 total sulfur flux data. For the salt water marsh, where both data sets exhibited considerable scater and the SURE emissions tended to be greater than the 1985 emissions, the total sulfur fluxes from the SURE data are generally greater than the corresponding fluxes from the 1985 data through there is some overlap.

This comparison of the SURE and 1985 data sets for Iowa, Ohio, and North Carolina sites can be summarized as follows. The differences between H_2S emission estimates in the SURE and 1985 data sets decrease from three orders of magnitude as the emission fluxes increase from mollisol to histisol to the salt water marsh sources. Estimates of DMS emissions for histisol soil and for the salt water marsh show relatively good agreement, but the SURE estimates of

DMS emissions from mollisol soil are larger than the 1985 estimates by an order of magnitude. This pattern is roughly the same for COS estimates where the two data sets show good agreement for histisol soil, moderate agreement for the salt water marsh, and poor agreement for the mollisol soil. The estimates of CS_2 emissions in the SURE data exceed the estimates in the 1985 data at all three sites. Where DMDS emissions were reported in the SURE data, the agreement with the 1985 study is relatively good.

The differences that do exist between the two data sets may be the result of differences in the measurement procedures or the differences may be caused by changes in environmental conditions between the SURE study years of 1977–80 and the 1985 study. Because the mechanisms of sulfur emission from biogenic sources are very poorly known, it is difficult to determine the effects of environmental conditions for comparison of the two data sets. This is further exacerbated by the lack of precision in the measurement methods.

3.5. Comparison of Biogenic Sulfur Emissions with Other Estimates

As indicated in the introduction, there have been a number of studies of biogenic emissions reported in the literature. Most of these studies have been concerned with high productivity sources such as salt water marshes and tidal areas. Steudler and Peterson (1985) summarized these studies in terms of the mean sulfur flux by compound for different sites and times of the year for comparison with their measurements over marsh grass (*Spartina*) on the coast of Massachusetts. The data from Steudler and Peterson (1985), the studies cited in their work, and the results from our 1985 study at Cedar Island are listed in Table IV. The mean, standard deviation, geometric mean, and the range within one geometric standard deviation of the geometric mean are included from our results.

For each compound there is a large range of emission fluxes extending as much as two to three orders of magnitude. Our data for H_2S, COS, and DMS lie within the range of reported fluxes. For H_2S, our estimate is lower than that from Steudler and Peterson, but comparable to those from Adams et al. (1981) and Aneja et al. (1979). Measurement of DMS emissions in 1985 yielded values which were also quite low compared to Steudler and Peterson. This is also true of our COS emission measurements. In the case of CS_2, our estimates are less than any of the reported values. Our results for DMDS are approximately the same as reported by Adams et al. (1981) for Cedar Island and for a marsh in Delaware, but these DMDS emission rates are very small compared to the other reported emission fluxes.

As Steudler and Peterson indicated in their discussion, the variability among these different emission estimates may be related to differences in measurement techniques or to differences in environmental conditions. While this lack of agreement cannot be easily explained, it is of interest to note that natural varia-

Table IV. Estimates of biogenic sulfur emissions from salt water marshes

Reference	Location	Month (1985)	Emission (ng S m^{-2} min^{-1})				
			H$_2$S	COS	DMS	CS$_2$	DMDS
Adams *et al.* (1981)	NC	5, 7, 10	63	23	1024	66	0.92
	DE	8	182	23	913	133	1.00
	MA	8	–	7.7	1142	53	11
	VA	–	–	57	3550	2633	76
Aneja *et al.* (1979)	NC	7	362[a]	a	2492	–	–
	NC	9	76[a]	a	343	–	–
Aneja *et al.* (1981)	NC	7, 8	19	57	762	285	95
Goldberg *et al.* (1981)	VA	8	18,000	–	–	–	–
Carrol (1983)	VA	8, 9	2.5	2.7	–	–	–
Steudler and Peterson (1985)	MA	1 yr	3900	572	5470	305	798
This study	NC	8					
Mean			630	98.9	158	3.23	1.21
Standard deviation			891	119	152	1.66	1.71
Geo. mean			166	30	155	3.98	0.87
Range: –1 std. dev			21	12	47	1.07	0.24
+1 std. dev			1,288	72	513	14.8	3.16

[a] H$_2$S + COS

bility in biogenic emissions is not restricted to sulfur emissions. Measurements of natural hydrocarbon emissions from vegetation also cover several orders of magnitude for different species, different locations, and different environmental conditions.

Our estimates of biogenic sulfur emissions from trees cannot be compared to other measurements because of the lack of data. It is worth noting, however, that typical sulfur emission rate from trees (20 ng S kg^{-1} min^{-1}) is more than three orders of magnitude smaller than typical hydrocarbon emission rates which range from 20 to 2 × 10^5 μg kg^{-1} min^{-1}. This is probably not too surprising in view of the relative abundance of hydrocarbons compared to sulfur in vegetation. The low sulfur emission level from trees can also be compared to sulfur emissions from crops and soils. Total sulfur emissions from corn, soybeans, and alfalfa were each approximately 30 ng S kg^{-1} min^{-1}. On an area basis, biomass densities for forests are typically 0.5 kg/m^2 and biomass densities of crops typically range from 0.5 to 2.0 kg/m^2. Total sulfur fluxes from forests will be approximately 10 ng S m^{-2} min^{-1} while fluxes from crops will range between 15 and 60 ng S m^{-1} min^{-1}. These fluxes are comparable to the emissions from mollisol soil, but the crop and forest fluxes are much less than those from histisol soil or the salt water marsh.

4. Summary and Conclusions

Estimates of reduced sulfur gas emissions from soils, crops, and trees were

obtained from more than 270 enclosure samples collected at three sites – previously used in the SURE biogenic sulfur study – in Iowa, Ohio, and North Carolina. The WSU results follow the expectation that emission fluxes from a salt water marsh are greater than emissions from a histisol (organic) soil which, in turn, are greater than emissions from a mollisol soil. The predominate sulfur gases emitted from these sources were H_2S, DMS, and COS. Smaller amounts of CS_2 and DMDS emissions were also recorded. Emission rates from crops, including corn, soybeans, oats, alfalfa, and miscellaneous vegetables were also measured. Total sulfur emission rates from corn, soybean, and alfalfa were each approximately 30 ng S kg^{-1} min^{-1}. Emission rates from a variety of deciduous trees and from loblolly pine were also in the range of 15 to 30 ng S kg^{-1} min^{-1}. At these rates and with typical biomass densities, forest and crop emission fluxes will be on the order of 10 and 60 ng S $^{-2}$ min^{-1}. For comparison the emission fluxes from mollisol, histisol, and salt water marsh were 15, 217, and 293 ng S m^{-2} min^{-1}, respectively, in terms of the geometric mean flux for each source type. Forest and crop emissions are thus comparable to mollisol soil emission fluxes and much less than histisol soil or salt water marsh emission fluxes.

The emission estimates for bare soils and for the salt water marsh were generally less than the emission estimates for the same sites from the 1977–80 SURE program. In the case of H_2S emissions from mollisol soils, the SURE emission data exceeded the 1985 results by as much as three orders of magnitude. However, the differences in reported H_2S emission fluxes were less for the histisol soil, and there was little difference between the two data sets for H_2S emissions from the salt water marsh.

Emission estimates of COS and DMS from the SURE study were larger than the estimates from the 1985 study by one to two orders of magnitude for mollisol soil. The emission estimates of COS and DMS were in better agreement for the histisol soil and salt water marsh, although the SURE estimates were generally larger than the 1985 estimates. CS_2 emissions from the SURE study were also larger than those from the 1985 study, but a portion of the difference can be attributed to the lack of a correction for recovery efficiency for CS_2 in the 1985 data set. Where DMDS emissions were reported in the SURE data, the agreement with the 1985 study was relatively good.

As has been discussed by Steudler and Peterson (1985), there is a large range of sulfur emission estimates for salt water marshes in the U.S. Our emissions measurements for H_2S, COS, and DMS lie near the low end of the range of emission estimates for these compounds. In the case of CS_2 and DMDS, the emission measured in North Carolina during 1985 were much less than most of the reported values.

The results of the 1985 field study will be compared in detail with the measurements by NOAA and UI in a later paper. These data will also serve as the basis for the further development of a national inventory of reduced

sulfur emissions from soils, crops, and trees. This inventory will be used in regional acid deposition models to determine the natural component of acid precipitation in the U.S.

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