

AN EXPERIMENTAL STUDY OF THE FLUXES  
OF REDUCED SULFUR GASES FROM A SALT WATER MARSH

by

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(1978)

Submitted to the Department of  
Earth and Planetary Science  
in Partial Fulfillment of the  
Requirements of the Degree of

DOCTORATE IN SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May 1983

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## ACKNOWLEDGMENTS

I would like to express sincerest gratitude to Ron Prinn, my thesis advisor at MIT, for his perpetually helpful advice, enthusiasm, support, and wit.

I am thankful for the opportunity extended to me by the Advanced Study Program at NCAR to develop my research interests as a UCAR Fellow (1978-79) and to conduct my thesis research as a Graduate Research Assistant (1981-83). I am deeply grateful to Ralph Cicerone for the opportunity to pursue research under his guidance and for his continued support throughout my tenure at NCAR. It has also been a pleasure to work closely with Leroy Heidt, and I have benefitted tremendously by this association.

I would also like to thank Ed Boyle at MIT for his continued interest and sound advice. Special thanks go to Kevin Brown, Ken Koehlert and Rich Freeman who participated in this research as Student Assistants under the MIT Undergraduate Research Opportunities Program.

I would like to acknowledge Paul Steudler at the Marine Biological Laboratory in Woods Hole, Massachusetts for the opportunity to share his laboratory and instrumentation as well as for providing access to his field site at the Sippiwissett Salt Marsh.

I would like to express my appreciation to Dr. Keller of the NASA/GSFC Wallops Flight Facility for the opportunity to conduct my field work at Wallops Island. I am especially grateful to Arnold Torres for generously sharing his laboratory and equipment. Special thanks to Rob Frostrom for facilitating my research requirements while I was a visitor at NASA/Wallops, to George Brothers for loaning equipment, to Bob Barnes for bringing me dinner during overnight analysis sieges, and to Rob Huey for being tremendously helpful and wonderously good-natured.

I would like to acknowledge Rich Lueb and Russ White at NCAR for lending their expertise during the developmental stages of this research. Thanks also to Electrical and Machine Shop, Graphics and Photographics personnel for their technical support, and to my ACAD colleagues for helpful conversations and equipment generously loaned. Thanks to Walt Pollack and Bruce Henry for being great lab-mates and to Med Medrud and Betty Wilson for all of their help. Special thanks to Mary Nuanes for secretarial support during my stay at NCAR and to both Mary and Ursula Rosner for typing this thesis.

I would like to express my gratitude to the Danforth Foundation for their support during my graduate studies. I am grateful not only

for their financial support but also for the opportunity to participate in several Danforth Conferences. Support for this research was also provided by NSF grants to MIT.

And, finally, it is with total appreciation that I acknowledge the extraordinary patience and support of my dear friends who have gifted me with the joys of humor, comfort, and love.

Dedicated to Pat

## ABSTRACT

In recent years there have been several attempts to model the earth's global sulfur cycle. Two major categories of sources have been identified as anthropogenic and biogenic, and they are thought to contribute 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 local effects such as acid rain and global effects caused by the flux of carbonyl sulfide to the stratosphere, are of concern. Most modelers have attributed a major role to biogenic sources due to an inability to otherwise balance their models. All have underlined the importance of experimental studies which will help to quantify the contribution of biogenic sources of sulfur.

The primary goals of this research were to determine the role of a salt water marsh in the global carbonyl sulfide (OCS) cycle, and to establish the diurnal and seasonal behavior of OCS from such a source. Secondary goals included the quantification of as many gases as could be resolved given the analytical instrumentation (optimized for OCS) and the constraints of sample storage and analysis requirements. Thus, the diurnal flux behavior of both OCS and hydrogen sulfide ( $H_2S$ ) were determined along with normalized concentration information for carbon disulfide ( $CS_2$ ). The influence of light intensity, soil moisture, and soil temperature on the rates of emission of these three gases was also monitored.

A TRACOR Gas Chromatograph (GC), equipped with a Flame Photometric Detector and a sulfur filter, and a SPECTRA PHYSICS programmable integrator comprised the analysis instrumentation. KINTEK and A.I.D. permeation devices were used to generate sulfur gas standards. Separation of the various sulfur gases was accomplished using a column made of specially treated Porapak-QS-packed Teflon tubing. A flux chamber was used to determine the rates of emission of OCS and  $H_2S$  from the marsh surface, and samples of chamber air were collected. After calibrating the GC response, sample loops were connected to the GC sample valve and desorbed by rapid transfer from liquid argon to boiling water. A composite calibration curve, made up of curves run before and after sample analysis, was used to determine sample concentrations. The fluxes of OCS and  $H_2S$  were then calculated from the difference between input and output chamber concentrations, the chamber flow rate, the chamber height, the chamber surface area, and the changes of concentration with time as estimated by mechanically fitting curves to the concentration plots.

The major data collection effort involved a field study conducted at Wallops Island, Virginia, a barrier island off the eastern shore of the Delmarva Peninsula. The island is a part of the NASA/Wallops Flight Facility, and the northern part of the island consists primarily of isolated marsh and beach. The field experiment was limited to studying the emissions of OCS,  $H_2S$ , and  $CS_2$  from mixed stands of Spartina-Alterniflora and Spartina-Patens found in the high marsh. Field experiments, each of 25-hour duration, were conducted weekly from mid-July through September 1982.

The mechanically-stirred, polycarbonate flux chamber was continually flushed with scrubbed ambient air. Ambient air was pulled through a carbon vane pump and its exhaust entered a regulating rotameter or was vented. The regulated flow was passed through a series of Drierite-filled plastic cylinders before the air passed through a series of two ~50' lengths of copper tubing coiled and immersed in liquid argon. Next, the air was warmed somewhat as it passed through tubing immersed in a warm water bath. The air then flowed through a second rotameter, 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. After an initial equilibrium period, the air entering and exiting the chamber was then collected simultaneously and stored for laboratory analysis to determine the amount of OCS, H<sub>2</sub>S, and CS<sub>2</sub> generated within the chamber. Sample loops made of Teflon tubing and housed in aluminum tubing were equipped with Teflon plug valves. A drier consisting of strands of Nafion (DUPONT) tubing with helium counterflow was employed on chamber exit samples.

Liquid argon was used to cryogenically trap and store samples which were pulled through the loops by FMI pumps. The pumping rate was constant and routinely checked to assure accuracy in the sample volume collected. Sample collection was conducted for 50-60 minutes every other hour over a period of 25 hours. Typical sample volumes were 1.5 to 2 liters of air. Light intensity and air and soil temperatures, both inside and outside the chamber, were also monitored. During the later six studies, a loosely-woven, lightweight, white cloth was used to shade the chamber which helped to reduce surface evaporation and thus condensation on interior chamber walls without significantly reducing the light which reached the chamber interior. Diurnal variation in fluxes and the strong influence of soil moisture upon the rates of emission of OCS and H<sub>2</sub>S were routinely observed. While the flux behavior of OCS and H<sub>2</sub>S followed similar patterns, CS<sub>2</sub> fluxes were routinely low except during some tidal flooding episodes.

Individual flux calculations during hot and wet conditions were often found to be very high but taken alone are misleading. For example, one could conclude that up to 12% of global OCS may be accounted for by salt water marshes from such measurements. Diurnally averaged flux values, however, show that high marsh mixed-Spartina stands are insignificant global sources of H<sub>2</sub>S or CS<sub>2</sub> and insignificant contributors to the global OCS cycle. This research suggests that it is erroneous to extrapolate fluxes determined from measurements made in low marsh or coastal areas to regions of the high marsh in calculations of global sulfur fluxes for H<sub>2</sub>S, OCS, or CS<sub>2</sub>.

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## CHAPTER 1

## INTRODUCTION

The research described here was motivated by the desire to better understand the earth's sulfur cycle. The sulfur cycle is of environmental interest due to current concerns about regional pollution effects such as acid rain and possible global climatic effects such as those induced by an increase in the stratospheric sulfuric acid "Junge" layer. Anthropogenic and natural sources of sulfur may contribute almost equally to its global atmospheric budget (Kellogg et al., 1972; Friend, 1973; Granat et al., 1976; Moss, 1978; Ivanov, 1981). Anthropogenic sources could increase rapidly due to future application of new technologies for coal liquefaction and gasification. Thus it is of utmost importance that we learn the magnitude of the contribution of the natural sources of sulfur and its compounds to the global sulfur cycle so that we may understand the degree to which anthropogenic sources perturb this cycle.

A schematic of the earth's global sulfur cycle is presented in Fig. 1. In many of the attempts to describe the natural circulation of sulfur (Eriksson, 1959, 1960, 1963; Junge, 1960, 1963a,b; Holser and Kaplan, 1966; Robinson and Robbins, 1968, 1970; Georgii, 1970; Kellogg et al., 1972; Rodhe, 1972; Friend, 1973; Levy, 1974; Goldhaber and Kaplan, 1974; Cadle, 1975; Granat et al., 1976; Zehnder and Zinder, 1980), the authors generally conclude that there must be a substantial oceanic source. For example, Eriksson (1963) balances his atmospheric sulfur budget with  $170 \text{ Tg S yr}^{-1}$  ( $\text{Tg} = 10^{12} \text{ g}$ ) from the ocean, Junge (1963a) requires a balancing oceanic source of

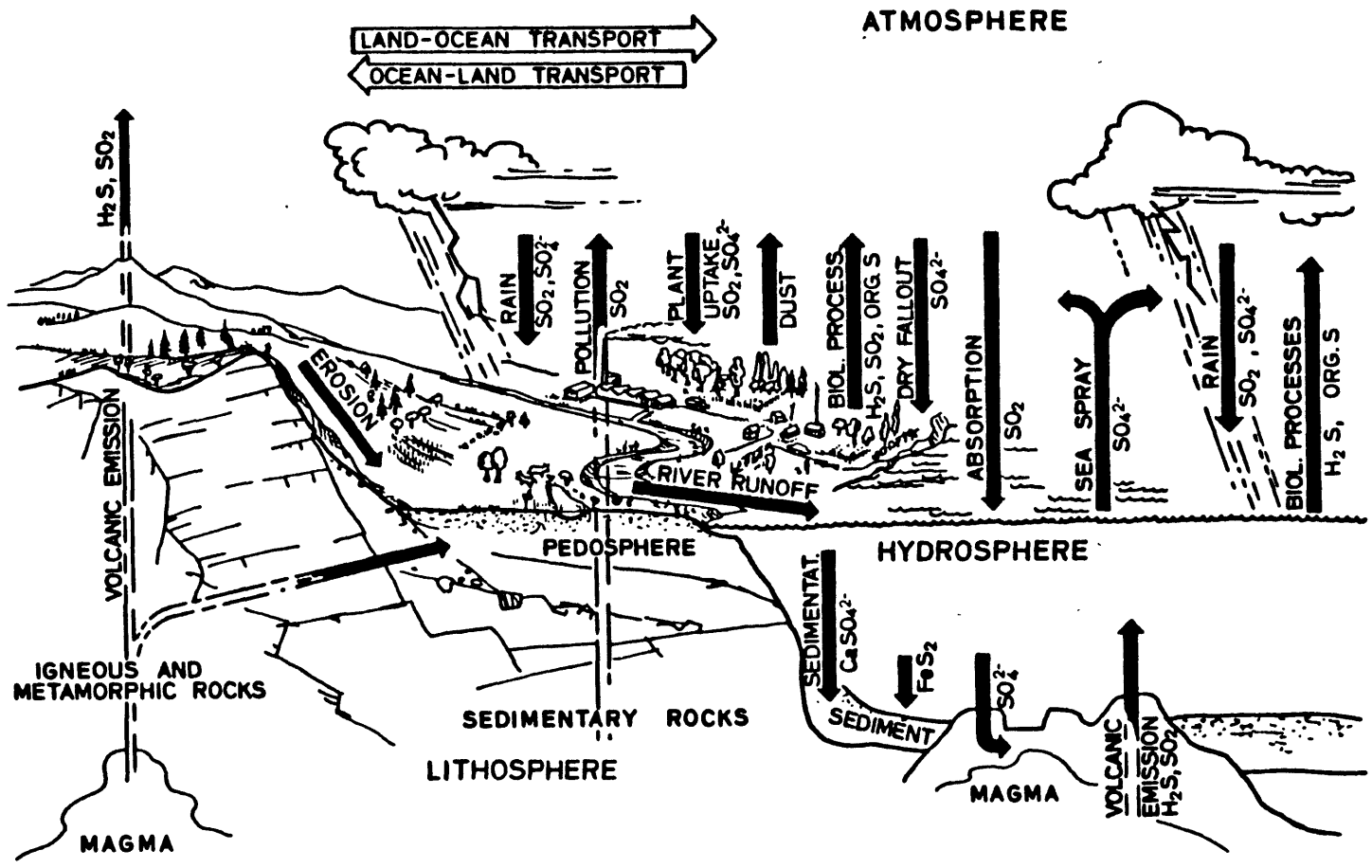


Fig. 1 Earth's global sulfur cycle (modified from Zehnder and Zinder, 1980)

A. J. B. Zehnder, S. H. Zinder



160 Tg S yr<sup>-1</sup>, and Robinson and Robbins (1968) balance their model with a much smaller oceanic source of 30 Tg S yr<sup>-1</sup>. Similarly, Kellogg et al. (1972), while they do not arrive at a separate oceanic source (89 Tg S yr<sup>-1</sup> land-ocean), suggest marshy areas, tidal flats, and the ocean surface as possible atmospheric sulfur sources, Friend (1973) assigns an oceanic source of 59 Tg S yr<sup>-1</sup> to balance his sulfur budget, Cadle (1975) balances his model with a land-ocean value of 87 Tg S yr<sup>-1</sup>, Granat et al. (1976) suggest an oceanic source for the 27 Tg S yr<sup>-1</sup> outstanding in their overall sulfur budget, and Zehnder and Zinder (1980) assign a balancing oceanic source of 48 Tg S yr<sup>-1</sup>. In contrast, rather than attribute the balancing role to oceans, Ivanov (1981) specifically calculates a total oceanic source of 79 Tg S yr<sup>-1</sup> (60 Tg S yr<sup>-1</sup> of marine sulfur with sea spray plus 12 Tg S yr<sup>-1</sup> of biogenic hydrogen sulfide (H<sub>2</sub>S) from coastal shallow sediments plus 7 Tg S yr<sup>-1</sup> of reduced sulfur emitted from the ocean's surface) based upon geochemical data for sulfur compounds and in situ experimental studies.

In spite of work by Ostlund and Alexander (1963) pointing out that H<sub>2</sub>S could not survive diffusion through an aerobic water column, authors continued to attribute to H<sub>2</sub>S the role of the missing oceanic link required to balance the global sulfur budget (e.g., Kellogg et al., 1972; Friend, 1973). Lovelock et al. (1972) also state that oceanic surface waters are too oxidizing to allow the emission of H<sub>2</sub>S in the amounts required to balance the aforementioned sulfur budgets, and they suggest that dimethyl sulfide ((CH<sub>3</sub>)<sub>2</sub>S) might replace H<sub>2</sub>S in this role. Lovelock (1974) reports observations of carbon disulfide

(CS<sub>2</sub>) in coastal and open ocean waters; however, he concludes that it is unlikely that oceanic CS<sub>2</sub> is a significant source of atmospheric sulfur based upon discussions with Liss, Broecker and Peng (Lovelock, 1974) regarding gas fluxes across the atmosphere-ocean interface. At the same time, he maintains the importance of (CH<sub>3</sub>)<sub>2</sub>S as a significant oceanic source of atmospheric sulfur. Rasmussen (1974) states that no measurements of H<sub>2</sub>S emitted from anaerobic environments have been reported. He questions the emission of H<sub>2</sub>S from anaerobic muds in quantities required to balance the postulated sulfur budgets, contending that the aerobic surface waters act as a physical barrier to H<sub>2</sub>S evolution. Rasmussen reports his analyses of H<sub>2</sub>S, methyl mercaptan (CH<sub>3</sub>SH), (CH<sub>3</sub>)<sub>2</sub>S, and dimethyl disulfide ((CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>) from aerobic habitats, suggesting that several organic sulfides are naturally released to the atmosphere from land and both ocean and fresh waters in amounts which well exceed that of H<sub>2</sub>S. Granat et al. (1976) also discuss the role of H<sub>2</sub>S as a marine source of atmospheric sulfur. Referencing a study of the kinetics of aqueous sulfide oxidation by Chen and Morris (1972), they suggest tidal flats, salt marshes, and shallow marine waters (which often experience anaerobic conditions) as possible oceanic sources. Several investigators have made measurements of reduced sulfur gases over salt water marshes, swamps and intertidal zones prior to this research effort (Hill et al., 1978; Hansen et al., 1968; Jaeschke 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 Jorgensen, 1982). However, the calculated emission rates for CS<sub>2</sub> span three orders of magnitude,

those for  $(\text{CH}_3)_2\text{S}$  span four orders of magnitude, those for  $\text{H}_2\text{S}$ , carbonyl sulfide (OCS), and  $(\text{CH}_3)_2\text{S}_2$  span five orders of magnitude, and those for  $\text{CH}_3\text{SH}$  span six orders of magnitude! In part, these ranges of emission rates undoubtedly represent seasonal variations. However, they may also be due to differences in measurement techniques and local conditions (e.g., soil moisture, tidal influence, light intensity, soil temperatures).

In addition to the aforementioned aquatic environments, soils (Bremner and Banwart, 1974; Banwart and Bremner, 1975a; Adams et al., 1979, 1981), animal waste (Bremner and Banwart, 1975b), volcanoes (Kellogg et al., 1972; Friend, 1973; Granat et al., 1976; Moss, 1978), biological decay and sea spray (Eriksson, 1960, 1963; Robinson and Robbins, 1968, 1970; Kellogg et al., 1972; Friend, 1973; Granat et al., 1976; Moss, 1978), geothermal areas and oil fields (Graedel et al., 1974), and forest fires (Hartstein and Forshev, 1974; Crutzen et al., 1979) complete the list of natural sources suspected or observed to emit sulfur gases.

Three of the apparently important reduced sulfur gases, namely  $\text{CS}_2$ ,  $(\text{CH}_3)_2\text{S}$ , and  $\text{H}_2\text{S}$ , are recognized as short-lived species in the troposphere. In particular,  $\text{H}_2\text{S}$  and  $(\text{CH}_3)_2\text{S}$  have lifetimes of only one or two days. They react with tropospheric hydroxyl radical (OH) to ultimately form sulfur dioxide ( $\text{SO}_2$ ) (Hales et al., 1974; Cox and Sandalls, 1974; Atkinson et al., 1978; Davis et al., 1979; Sze and Ko, 1980; Hatakeyama et al., 1982; Grosjean and Lewis, 1982) while  $\text{CS}_2$  may react with hydroxyl radicals to form OCS (Kurylo, 1978a,b; Atkinson et al., 1978; Sze and Ko, 1979; Sze and Ko, 1980, 1981; Bandy et al.,

1981; Jones et al., 1982). However, Wine et al. (1980) and Iyer and Rowland (1980) have shown the rate at which  $\text{CS}_2$  reacts with OH to be so low that this cannot be considered a viable sink for tropospheric  $\text{CS}_2$ . Wine et al. (1981) comment that the size of both the temporal variability (Maroulis and Bandy, 1980) and the vertical gradient (Bandy et al., 1981) found for  $\text{CS}_2$  suggests that the tropospheric lifetime of  $\text{CS}_2$  is quite short. They speculate that tropospheric photo-oxidation of  $\text{CS}_2$  may provide a considerable sink for  $\text{CS}_2$  with a corresponding lifetime of no more than one or two weeks.  $\text{SO}_2$ , the common oxidation product, may remain in the atmosphere or be further oxidized to sulfuric acid aerosol particles. Therefore, measurements of the concentrations of both the reduced and oxidized primary precursors of tropospheric sulfuric acid aerosols are needed to determine the formation and distribution of these aerosols. The role of these aerosol particles in the phenomenon of acid rain is being actively studied since the resulting pollution to forests, farmlands, water supplies, marble antiquities, etc., is of major concern.

Turco et al. (1980) have summarized the identified annual sources of OCS. Their estimated emission values include 1-9  $\text{Tg yr}^{-1}$  from the refining and combustion of fossil fuels, 1-5  $\text{Tg yr}^{-1}$  from the photochemical conversion of natural and manmade  $\text{CS}_2$  to OCS, 1  $\text{Tg yr}^{-1}$  from natural decay processes, 0.2  $\text{Tg yr}^{-1}$  from natural and agricultural fires, and smaller contributions from gasoline consumption, cigarette smoke, kraft mills, volcanoes, and fumaroles. This total annual global estimate of 1-10  $\text{Tg yr}^{-1}$  of OCS assumes, however, rapid reaction of  $\text{CS}_2$  with OH and the lack of any significant diurnal variation in the fluxes of OCS from natural environments.

The tropospheric lifetime of OCS is uncertain and estimates range from a few months to nine years (Breckenridge and Taube, 1970; Atkinson et al., 1978; Kurylo, 1978b; Sze and Ko, 1980; Ravishankara et al., 1980; Turco et al., 1981; Johnson, 1981). There has been debate (Atkinson et al., 1978 and Kurylo, 1978b; Ravishankara et al., 1980) over the reactivity of this compound with OH. The most recent measurements (Ravishankara et al., 1980) imply that OCS is relatively inert to attack by OH in the troposphere. Once OCS reaches the stratosphere, however, it becomes susceptible to photodissociation by solar ultraviolet radiation. The sulfur atoms produced by this dissociation are readily oxidized by molecular oxygen, OH, or hydroperoxyl radical ( $\text{HO}_2$ ) to  $\text{SO}_2$  and ultimately to sulfuric acid aerosol particles. This process was first suggested to explain the formation of the massive sulfuric acid clouds on Venus (Prinn, 1973) and later suggested to be important in the formation of the Junge layer on earth (Crutzen, 1976). Crutzen noted in particular that large increases in atmospheric OCS would lead to a significant enhancement of the Junge layer. A thickening of this layer would have important implications for the earth's radiation balance (Junge, 1963; SCEP, 1970) and thus for the global climate. Therefore, it is obvious that measurements of the concentrations of OCS are required to help us understand the formation of stratospheric sulfuric acid aerosols caused by the flux of this gas from the troposphere.

The first step in understanding the contribution of a particular sulfur gas to the global sulfur cycle is to identify and quantify its sources and sinks. The second step is the further investigation of these sources and sinks to understand their detailed mechanisms and

thus to understand their sensitivity to perturbations. In studying sources, it is expected that anthropogenic sources are more easily analyzed than biogenic sources. In particular, the detailed chemical and physical steps in industrial processes are readily definable and in many cases already fully analyzed. Natural sources, however, are more complicated. There are chemical and microbiological processes occurring, often simultaneously, and not all of these processes or their spatial and temporal variability are well understood. Extrapolation of a finding in the natural environment to other similar environments on a global scale therefore requires a more quantitative understanding of the chemical and microbiological processes involved.

Quantitative studies of the natural sources of  $\text{CS}_2$ ,  $\text{OCS}$ ,  $(\text{CH}_3)_2\text{S}$ , and  $\text{H}_2\text{S}$  are in their infancy. Gas chromatographic measurements of  $\text{H}_2\text{S}$  emission from a salt water marsh have recently been reported by Goldberg et al. (1979). Previous measurements of  $\text{H}_2\text{S}$  were obtained using more laborious wet chemical and filter matte techniques (Jaeschke, 1978 and Slatt et al., 1978). These techniques involve the use of, for example, silver nitrate-impregnated filters for the collection of  $\text{H}_2\text{S}$  as silver sulfide. While these studies and those mentioned earlier in this section are all important, the environments involved are sufficiently complex that many more studies are required. Measurements to date are simply too few in number 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. For example, Hanst et al. (1975), Maroulis et al. (1977), and Torres et al. (1979) have established the

ambient tropospheric distribution of OCS, but there has been no systematic study of potential natural and anthropogenic sources of this gas. These gaps in our knowledge are of sufficient extent and importance that a clear need exists to continue to initiate new experimental studies.

Consideration of these needs was foremost during the planning of the research reported here. The systematic study of a salt water marsh to determine the diurnal and seasonal behavior of the fluxes of OCS and H<sub>2</sub>S, and thus their contribution to the global sulfur cycle, was identified as the central goal of this research. Analytical techniques were developed and optimized for field studies which were conducted specifically for the measurement of these two reduced sulfur gases. In cooperation with Dr. Ralph Cicerone, preliminary instrument development and standard generation studies were carried out at the Scripps Institution of Oceanography, UCSD, La Jolla, California (June 1979-January 1980). Field studies were conducted during the summer of 1979 to monitor pH and the diurnal variation of dissolved oxygen in several shallow salt water environments near La Jolla, California. A micrometeorological flux study using adsorption traps and in situ wind measurements was proposed to intercompare with a chamber method used by investigators at the Marine Biological Laboratory (MBL) in Woods Hole, Massachusetts. Field studies conducted at MBL during the summer of 1980 included exploratory measurements of OCS, H<sub>2</sub>S, and (CH<sub>3</sub>)<sub>2</sub>S and simultaneous measurements of wind speed profiles in the first 2 m above the marsh surface. Instrumentation and sampling techniques were further developed and finally completed at the National Center for

Atmospheric Research (NCAR) in Boulder, Colorado (October 1980–October 1982). The field studies reported in this thesis were conducted through the courtesy of the NASA/GSFC Wallops Flight Facility at Wallops Island, Virginia. The diurnal behavior of the fluxes of OCS and H<sub>2</sub>S from a Wallops Island salt water marsh was determined through experiments conducted weekly in August and September 1982; relative (but not absolute) CS<sub>2</sub> concentrations were also determined. The influence of light intensity, soil temperatures, and soil moisture upon the rates of emission of OCS, H<sub>2</sub>S and CS<sub>2</sub> were also monitored. Aircraft measurements of OCS and CS<sub>2</sub> mixing ratios (20–26 kft) were conducted between San Juan, Puerto Rico and Albany, New York in July 1982, through the courtesy of the NASA/Langley Research Center and NASA/Wallops Flight Facility. Chapter 2, which follows, contains a description of the analytical instrumentation. Chapter 3 contains a description of the field sampling techniques and the sample collection and analysis procedures which were developed and routinely employed to determine the fluxes of OCS and H<sub>2</sub>S. The results of the various field studies conducted are presented in Chapter 4 and, finally, the global sulfur cycle is discussed in Chapter 5 in light of the conclusions from the experimental work described in this thesis.

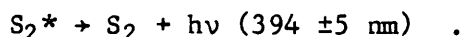


## CHAPTER 2

## ANALYTICAL INSTRUMENTATION

A TRACOR 560 Gas Chromatograph (GC) equipped with a Flame Photometric Detector (FPD) and a  $394 \pm 5$  nm band pass filter, along with a SPECTRA PHYSICS SP4100 programmable integrator, comprised the analytical instrumentation employed to identify and quantify concentrations of hydrogen sulfide ( $H_2S$ ), carbonyl sulfide (OCS), and carbon disulfide ( $CS_2$ ). Separation of these sulfur gases was accomplished using a column made of specially treated Porapak-QS-packed Teflon (DUPONT) tubing (Thornsberry, 1971; Pearson and Hines, 1977). Column preparation included the following steps: FEP Teflon tubing ( $6' \times 1/8''$ ) was serially washed with acetone and methanol and oven-dried before packing with acetone-washed, phosphoric acid-treated, 5% DC QF-1 on 80/100 mesh Porapak-QS. Porapak-Q is a porous polymer composed of ethylvinyl benzene cross-linked with divinyl benzene to form a uniform structure of a distinct pore size (Dow Chemical Company, Freeport, Texas). Porapak-QS, the silanized version of Porapak-Q, is chosen for work with highly reactive sulfur compounds because silanization reduces surface chemisorption. Acetone is used to clean the column support surfaces; the acetone wash is followed by treatment with phosphoric acid to minimize adsorptivity caused by the acetone wash. Silanization or treatment with phosphoric acid is routinely employed to enhance the degree to which silicone oil adheres to the support material. The Porapak-QS was then coated with 5% 2-1098 DC QF-1, a silicone oil. QF-1 was used as the stationary phase and provided improved  $H_2S/OCS$  peak resolution.

Following chromatographic separation, eluting compounds are combusted at the FPD. Sulfur-containing samples give rise to excited molecular sulfur,  $S_2^*$ . Theoretically, it is only the light given off by the decay of  $S_2^*$  which is monitored by the photomultiplier tube (PMT, EMI-GENCOM #9924A) abutting the detector cell:



If this were universally true, a square law relationship would always be observed between concentration and GC response. Indeed, the TRACOR 560 GC provides a "square root" mode option, the use of which implicitly assumes that such a relationship exists. Use of the TRACOR sulfur photometric response linearizer was however shown to be inappropriate for the analysis of OCS or  $CS_2$  because the slopes of these response versus concentration curves did not follow an exact square law. Use of this "square root" mode may be appropriate for  $H_2S$ , which was observed to routinely yield calibration curve slopes of approximately 2.0. However, reliable analysis should only be performed in the "+ polarity" rather than the "square root" mode. It is reasonable to speculate that the deviation from a slope of 2.0 for OCS and  $CS_2$ , or for very low concentrations of  $H_2S$  results from flame kinetics considerations or from column adsorption or conditioning effects. Column temperature and carrier and flame gas mixtures were both observed to influence this relationship for OCS.

The PMT's signal (anode current) is relayed to the GC's electrometer where it is converted to a voltage; the GC response is then out-

put to the SP4100 integrator. A serious drawback of the TRACOR 560 GC is that the GC response is limited by the GC attenuation setting. If the electronic signal exceeds the capacity of a particular setting, the electrometer saturates and the corresponding recorded signal is an artifact. This limitation requires careful calibration of the GC in the range (and over the appropriate attenuation settings) of concentrations expected for samples. Consequently, initial samples must routinely be sacrificed to determine approximate sample concentrations. Thus, unexpectedly high concentrations often are unresolved, and, in fact, disturb the GC's stability for following analyses. The GC calibration procedure involved generation of GC response versus standard concentration curves at various attenuation settings with the concentration values chosen to span anticipated sample concentrations. This enabled interpolation in calculating sample concentrations rather than extrapolation wherever possible. (Concentrations of the sulfur gases in the air which entered the flux chamber were, however, routinely obtained by extrapolation due to their extremely low values. See Chapter 4.)

Another serious limitation of the TRACOR 560 design is the lack of adequate flow controlling devices for carrier and flame gases. This resulted in changes in carrier and flame gas flow rates with changes in laboratory temperature. The GC response was fairly stable over typical laboratory temperature variations between 18 and 23°C. However, when temperatures deviated from this range, particularly when temperatures rose above 24°C, the GC response changed. In particular, the response decreased with increasing retention time, indicating a

reduction in sensitivity due to a change in the flame gas mixture. During initial instrument calibration studies, this behavior caused significant difficulties. Because the GC demonstrated such poor response stability, it made little sense to proceed to sample concentration prediction until establishing, with confidence, the detector's response to various standard concentrations. No clues were found upon examining the instrument's electrometer. The primary observable change was in species retention time. It became clear upon closer examination that the GC response varied although the standard concentration did not. A recording thermometer was employed to document laboratory temperature changes simultaneously with the continuous injection of the standard. The GC was automated and programmed to run and record chromatograms continuously over several 24-hour periods. While a 2-3°C change did not cause significant response instability (>1% standard deviation) when temperatures remained lower than 23°C, the instrument did demonstrate instability with the same 2-3°C temperature variation at temperatures higher than 23°C. Future instrument modifications should include housing carrier and flame gas flow controllers to assure thermal isolation.

The GC detector response was optimized by regulating carrier and flame gas flows to maximize signal to noise (S/N), simultaneously minimizing peak tailing and peak width. Once the response was optimized, column temperature could be set to enhance peak resolution and response, S/N improving with increasing oven temperature. The oven temperature was selected to resolve H<sub>2</sub>S and OCS peaks which coelute at temperatures >90°C on this column, and partially overlap at 70°C < T

< 90°C. After running laboratory standards with demonstrated resolution with an oven temperature of 70°C, it was found that desorbed field samples were not completely resolved at this temperature. Changing gas flows did not significantly reduce H<sub>2</sub>S peak tailing, so gas flows were returned to their previously optimized settings and the column was routinely temperature programmed starting at an oven temperature of 65°C rather than 70°C. This allowed for excellent peak resolution.

The TRACOR 560/Porapak QS column system showed conditioning effects. Doping with a small, continuous permeation flow of sulfur hexafluoride (SF<sub>6</sub>) helped to keep the column conditioned. However, as calibration curves were begun, seven standard injections were typically required before an equilibrated response was established (response with a standard deviation of <1% being defined as equilibrium).

Power interruptions which caused flameout episodes resulted in a significant reduction in detector S/N and stability. The return to previous response levels required a minimum of four days, with or without continuous standard injections. It was found that this return to previous response levels could be hastened slightly by injections of SF<sub>6</sub> directly onto the column in large amounts. The major benefit of this procedure was the improved response stability following bake-out. During the field study at Wallops Island this procedure was followed for the two flameout episodes with a significant improvement in stability. This allowed sample analysis within 30 hours of instrument startup, rather than the previous equilibrium period of four

days. The S/N remained relatively low, but the stability allowed reasonable estimates of sample concentration to be made. The maximum standard deviation of the GC response was 10%.

When the GC was running without interruption within a laboratory temperature range of 18-22°C, the stability was enhanced by using an "instrument bake" mode between periods of instrument use. The stability achieved via this procedure was excellent, with OCS calibration curves being essentially identical week after week. This assured a minimal uncertainty for the predicted sample concentrations.

The TRACOR 560 FPD exhaust port is unheated; consequently condensing water vapor causes pressure perturbations to appear in the GC response. This problem was eliminated by wrapping the exhaust port with heating tape. A Variac was employed to maintain heat tape temperatures to prevent condensation droplets at the port exhaust.

A Valco teflon-lined, 10-port sampling valve was mounted just above column entry to minimize dead volume. The "injection port" or point of column entry with the GC was maintained at 65°C. The 10-port valve facilitated switching from the standard/calibration mode to the sample analysis mode (see Fig. 2). A motor was mounted on the GC sample valve rotor shaft and the electronic components required to drive the motor were laterally mounted on the GC (see Figs. 3 and 4). The Spectra Physics SP4100 integrator is programmable and has the capacity to operate external functions. Therefore, a program was written to control this automated sampling valve in either the calibration or the sample analysis modes (the Spectra Physics program along with comments and variable definitions is listed in Appendix

## GC SAMPLE VALVE

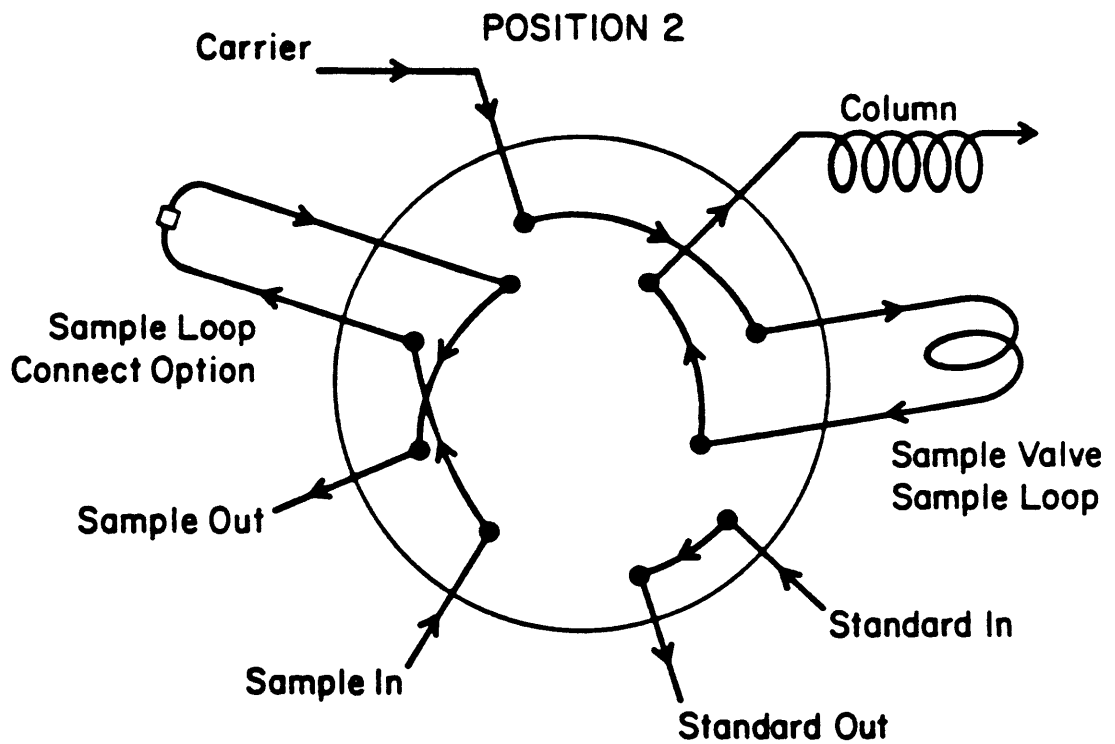
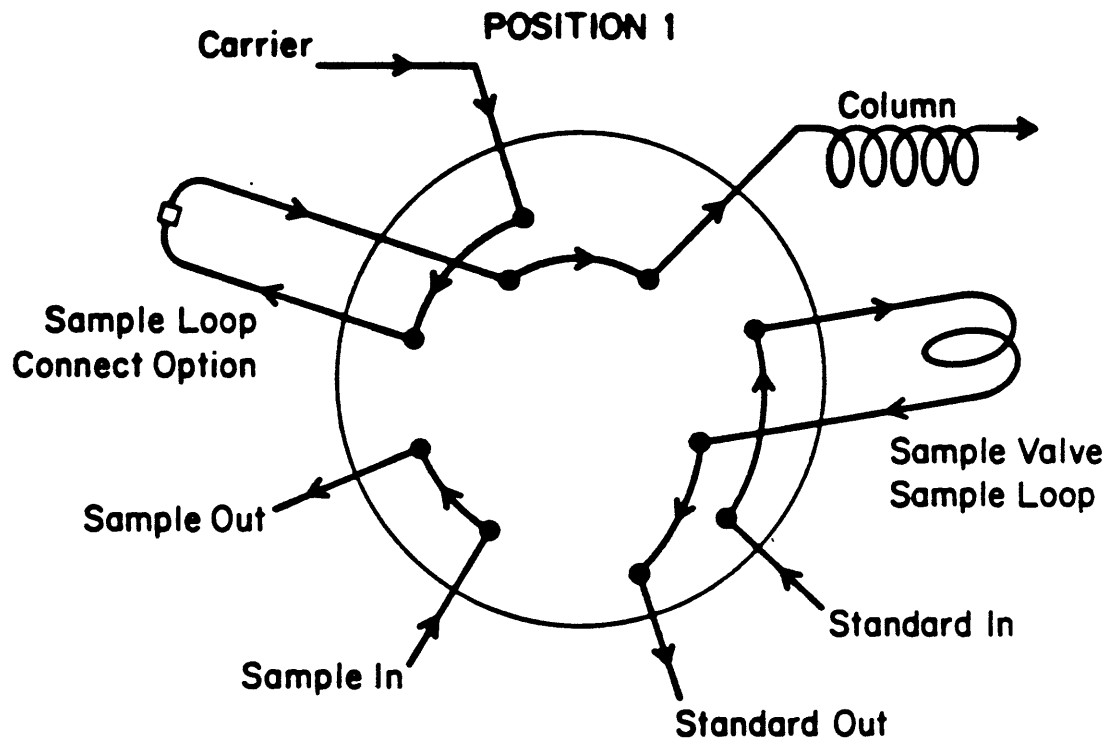


Fig. 2 VALCO 10-port sampling valve

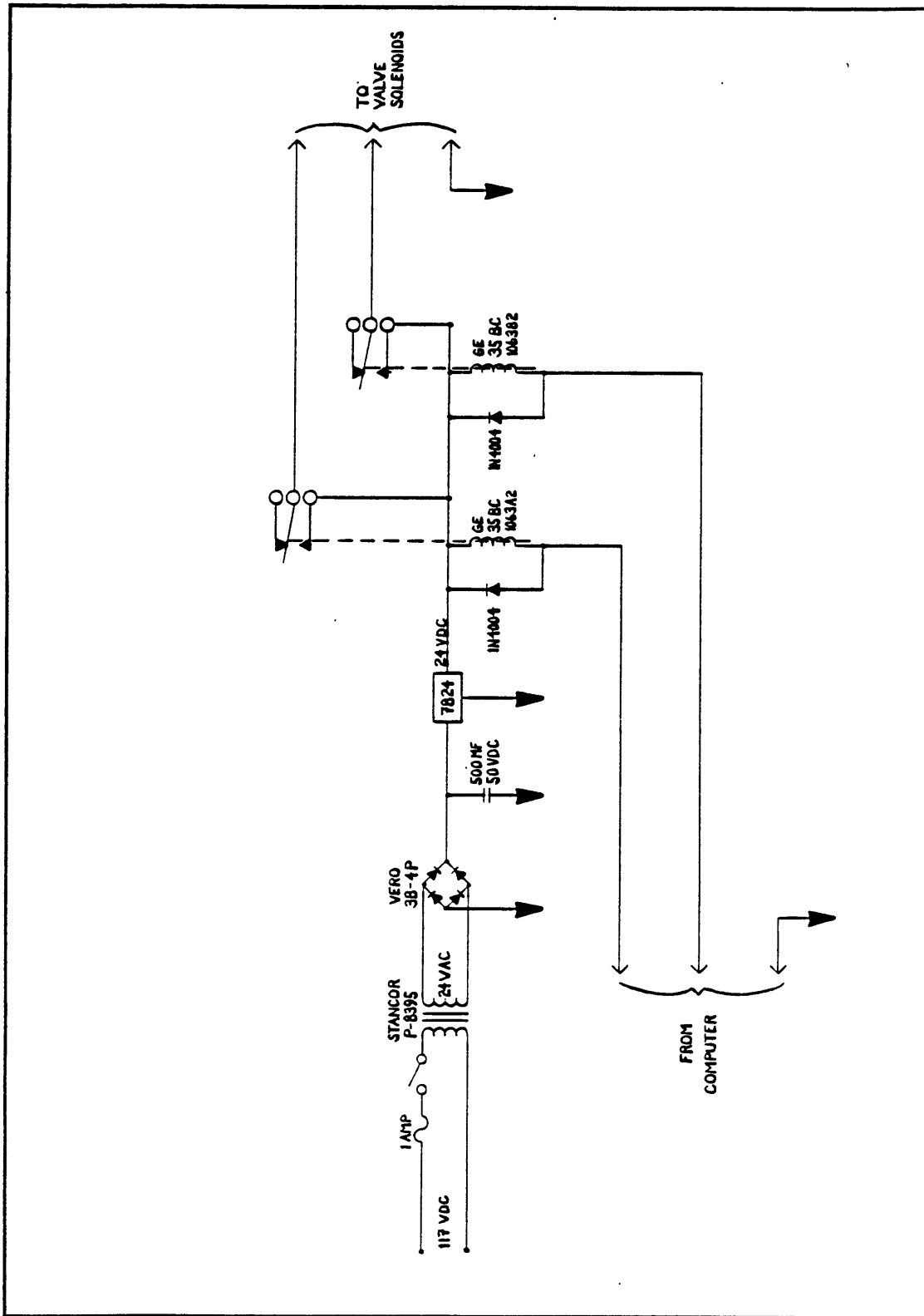


Fig. 3 Automatic sampling valve controller circuit diagram



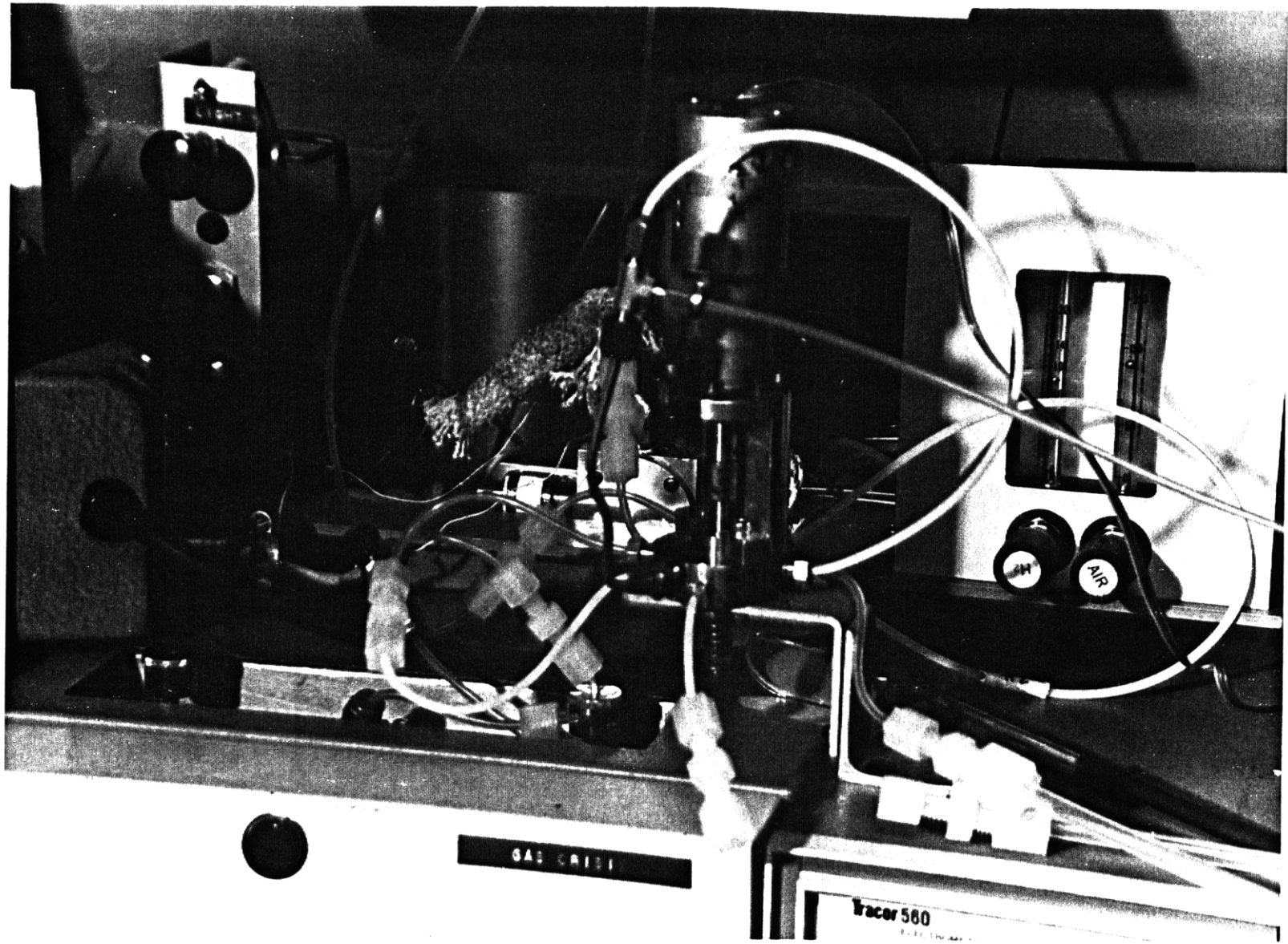


Fig. 4 Photograph of modified sample valve (Charles Semmer)

IV). This program was utilized to run calibration trials, to perform linear regressions on the GC response and standard concentration data, to graph calibration curves, to calculate sample loop trapping efficiencies, and to predict sample concentrations.

A.I.D. and KINTEK permeation tubes (PT's) were used as primary standards. PT's are constructed by sealing the compound of interest in aqueous form inside a Teflon tube. Careful thermostating of the tube at a precise temperature is required to ensure a constant permeation rate through the Teflon (tubes were refrigerated at 8-10°C when not in use). The PT's were maintained at a constant temperature of 30°C with continuously flowing diluent (dry, compressed air). The PT weight loss over time was monitored using a microanalytical balance to check the manufacturer's reported permeation rate whenever possible (this was not possible however during the Wallops Island field study). KINTEK standard generators were used as secondary standards. KINTEK markets a stainless steel cell with an operational concept which is, essentially, the reverse of a permeation tube (see Fig. 5). These devices were used as secondary standards because the permeation rate, although very stable, cannot be measured directly. Therefore, the absolute level is determined by comparison with the primary standard calibration curves (the KINTEK-reported OCS cell permeation rate was high by about 30%). However, these standard generators provide an excellent, constant standard source and thus were routinely used to calibrate the GC response. The range of mixing ratios which could be generated by the KINTEK OCS cell was approximately 25-1500 ppbv (parts per billion by volume). Teflon-lined stainless

**TRACE SOURCE™ 57S**  
**LOW EMISSION RATE**  
**GAS SOURCE PERMEATION DEVICE**

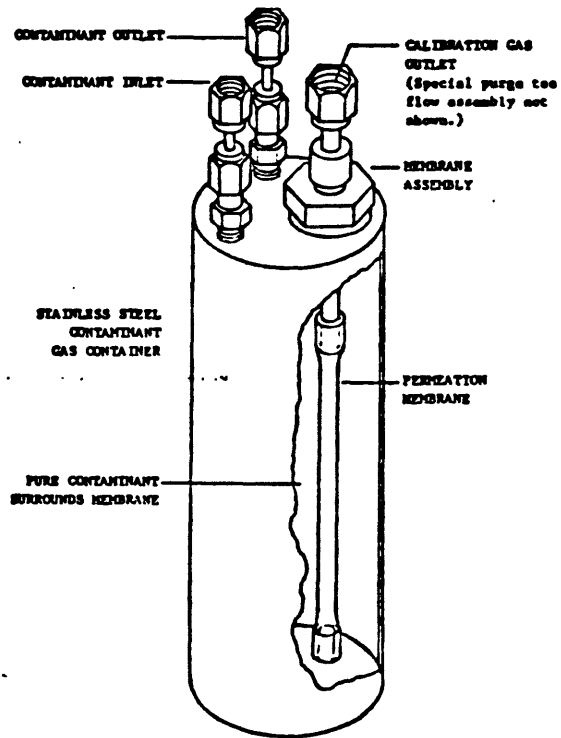


Fig. 5 KINTEK cell diagram

steel cylinders were used as dilution chambers to generate mixing ratios less than 25 ppbv. FMI-type pumps were used to pull samples through the GC sample valve's sample loop as well as in the dilution system described in Fig. 6. Calibrated HASTINGS flow meters (see Fig. 7) and bubble flow meters were used to determine diluent gas and pump flow rates.

Molecular sieve, indicator-treated silica gel, and activated charcoal traps were routinely employed in line with regulators for carrier and flame gases. At NCAR, liquid nitrogen ( $N_2$ ) vent gas was used as the  $N_2$  carrier gas while zero-grade  $N_2$  was used in the field. Hydrogen ( $H_2$ ) sources included an AADCO  $H_2$  generator or zero-grade  $H_2$ , while compressed or breathing (hospital grade) air comprised the air sources. Sample loops were routinely conditioned for one hour at  $120^\circ C \leq T \leq 130^\circ C$  in an oven with zero-grade  $N_2$  flowing at  $10-15 \text{ cc min}^{-1}$ . High ultra-purity helium (He) was used alternately for counterflow and as a purge gas in the Nafion driers used to remove water vapor from sample air (Nafion driers are discussed in Chapter 3).

In the field, air and soil temperatures were monitored using thermometers or a calibrated system consisting of an OMEGA Miniature Cold Junction, a battery powered, automatic cold junction compensator, and four Chromel-Alumel thermocouple circuits. Light intensity was monitored in arbitrary units which could be converted to foot candles of incident visible radiation, using a simple photographic light meter. Liquid argon was used to cryogenically trap and store samples and to "scrub" ambient air before it entered the flux chamber.

## STANDARD DILUTION SYSTEM

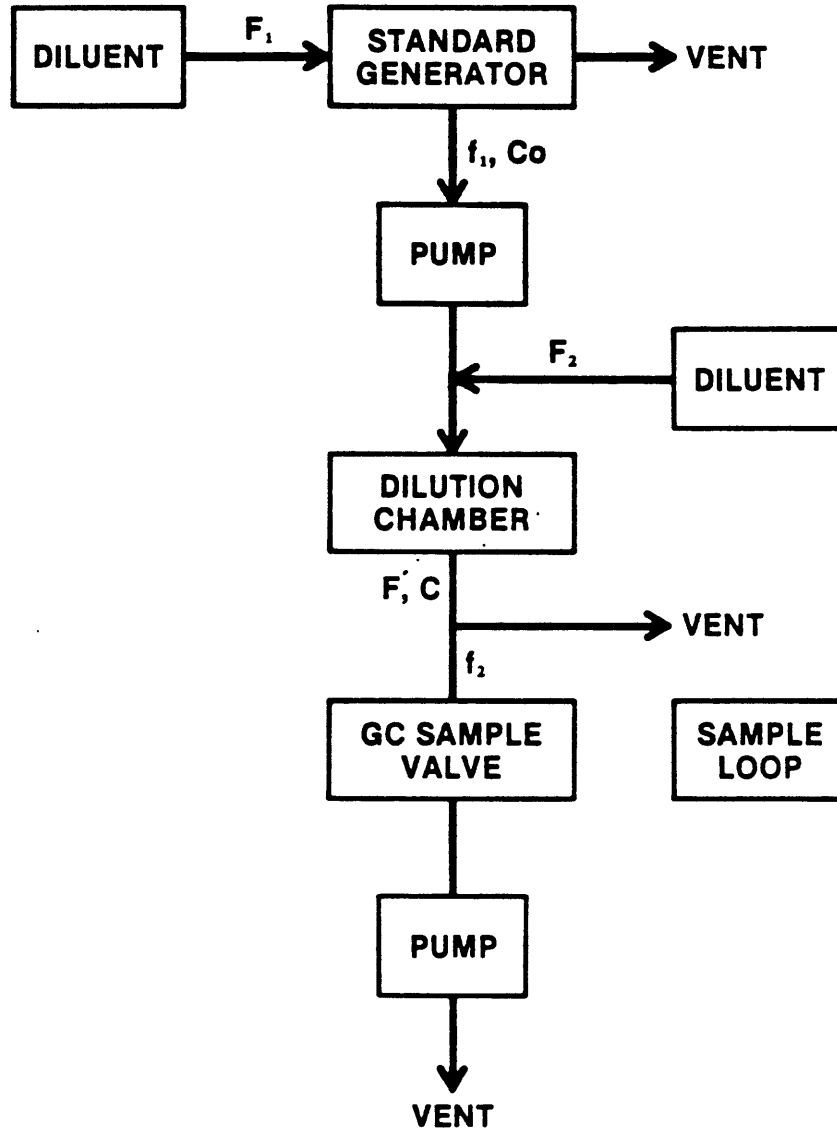


Fig. 6 Standard dilution system  
 $C_0$  = concentration exiting standard generator  
 $f_1$  = flow drawn from generator exhaust  
 $F_1$  = primary diluent flow  
 $F_2$  = secondary diluent flow  
 $F^1 = F_2 + f_1$   
 $C = (C_0)(f_1)/(F^1)$

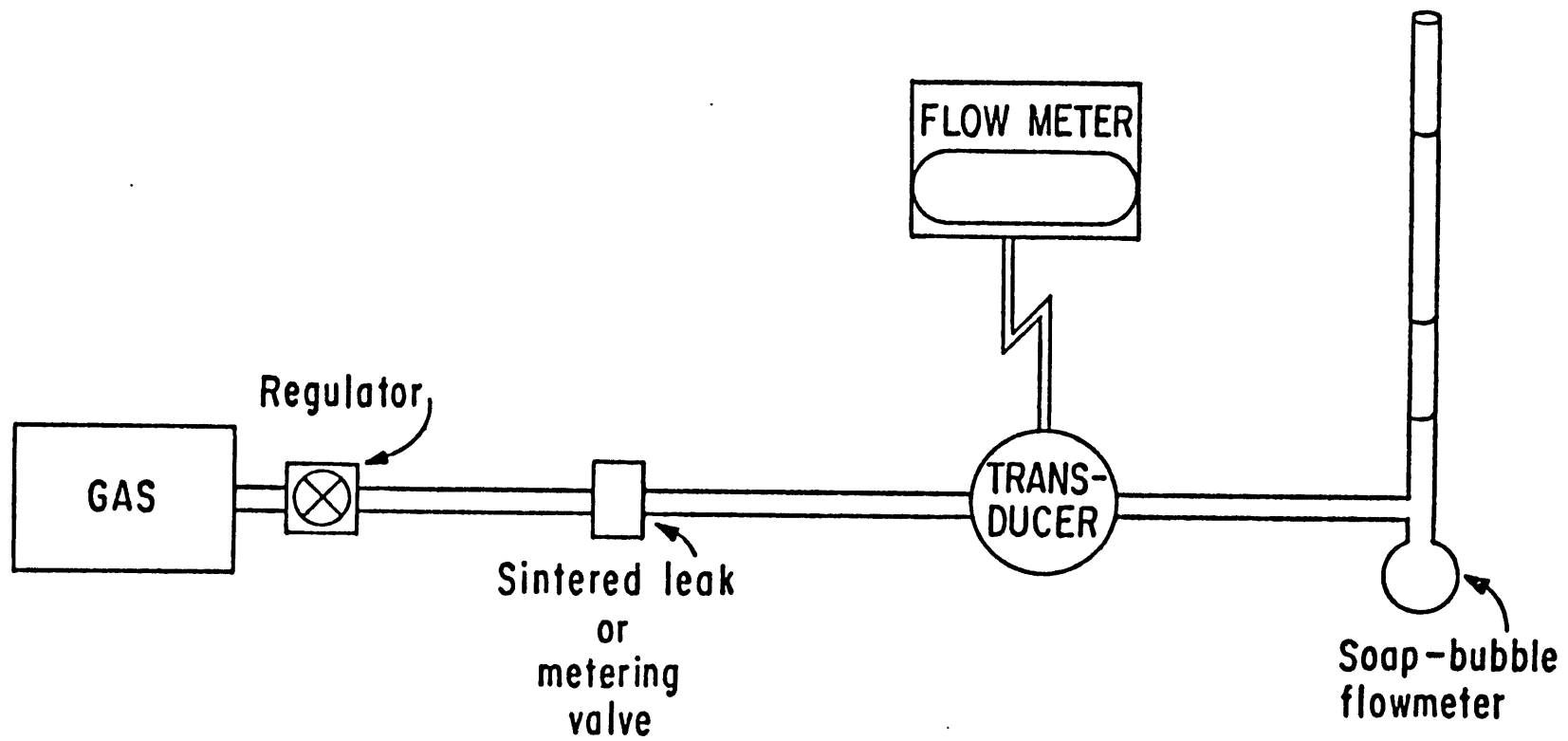


Fig. 7 Flow meter calibration system

Standard glass Dewars were used to contain the liquid argon used in the cryotrap and for sample collection while a larger stainless steel Dewar was used for sample loop storage. Drierite was used to dry air prior to its entering the cryotrap. Rotameters were calibrated and used to regulate and monitor the chamber air flow rate which was primarily controlled by a carbon vane pump. Electric immersion heaters were used to bring the water to boil and to ensure uniform temperature throughout the Dewar for the water used in desorbing the frozen samples.

Due to the highly reactive nature of sulfur compounds, Teflon tubing and fittings were used wherever sample or standard gases came into contact with the analytical components used for calibration or sample collection and analysis. Sample loops were constructed of "bendable" Teflon tubing (NACOM) housed in aluminum tubing and equipped with Teflon plug valves (GALTEK) (sample loops are discussed in detail in Chapter 3).

## CHAPTER 3

## SAMPLING TECHNIQUES

Tests of various adsorption and cryogenic trapping techniques were conducted, and procedures were established for sample collection and analysis. These three components of the sampling techniques employed in this research are described in this chapter.

### 3.1 Trapping Tests

Ambient atmospheric levels of OCS are ~500 pptv, a factor of 20 less than the Tracor FPD's detection limit, and a factor of 200 below the range of proven linearity between log (GC response) and log (concentration). Sample enrichment is therefore required to produce a detectable and reproducible signal. Several methods of sample enrichment were tested including trapping at ambient temperatures on Molecular Sieve, Molecular Sieve and Tenax-GC in series, and Porapak QS followed with desorption by heating to 250°C. Enrichment by cryogenic trapping using liquid nitrogen, liquid oxygen or liquid argon and Teflon loops containing glass beads, Teflon shavings or Teflon chips, were also tested before the empty Teflon loop was chosen as the most reproducible enrichment surface. Tests using Molecular Sieve in Pyrex glass tubing with Pyrex wool plugs at room temperature indicated 100% adsorption efficiency with no breakthrough over many hours (the term "breakthrough" here denotes the presence of the test sulfur gas in the air stream exiting the trap after an initial period of its absence in this air stream). Desorption tests, however, demonstrated low efficiencies when traps were heated to 250°C. While tests using Porapak-QS in Teflon tubing with Teflon wool plugs resulted in



breakthrough at room temperature, trapping under cryogenic conditions demonstrated 100% adsorption efficiency. However, problems again developed with desorption, possibly due to the Teflon tubing or the Porapak substrate beginning to decompose after extended exposure to high temperatures. Flow studies indicated a congealing effect from such exposure.

Sample enrichment tests were also conducted at the Marine Biological Laboratory using P. Steudler's Molecular Sieve/Tenax-GC traps. These traps were constructed of 6 mm O.D., 4 mm I.D. Pyrex glass tubing, 21.3 cm in length, packed with 9 cm (0.8 g) 60/80 mesh Molecular Sieve 5A and 11.5 cm (0.2 g) 60/80 mesh Tenax-GC with silanized Pyrex wool plugs (Steudler, private communication). Traps were preconditioned at 325°C for 12 hours with a continuous N<sub>2</sub> purge flow. After sampling, traps were stored in an ice box or in a freezer at -20°C until analysis, at which time they were placed into a desorption oven at 250°C for 15 s before the sample contents were injected onto the chromatographic column for analysis (see Appendix III for a description of the analytical instrumentation used at MBL). Steudler (1980) had reported ~80% adsorption/desorption efficiencies for all the sulfur gases of interest in his sulfur flux study (e.g., H<sub>2</sub>S, OCS, CS<sub>2</sub>, (CH<sub>3</sub>)SH, (CH<sub>3</sub>)<sub>2</sub>S) for these Molecular Sieve/Tenax-GC traps. Calibration studies conducted during the summer of 1980, however, did not produce similar results. While the lack of breakthrough indicated that adsorptivity was highly efficient, desorption studies were disappointing, often resulting in no detectable signal. Tests suggested that the reproducibility of the overall method was

±40% at best for the predicted concentrations with overall trapping (adsorption plus desorption) efficiencies estimated at <2%.

Use of liquid N<sub>2</sub> in cryogenic enrichment caused O<sub>2</sub> to be trapped along with the species of interest. The abundance of trapped O<sub>2</sub> routinely caused FPD flameout episodes upon desorption onto the chromatographic column. This problem was avoided by the use of liquid O<sub>2</sub> or liquid Ar. Preliminary cryogenic enrichment tests were conducted using liquid O<sub>2</sub>. Switching to liquid Ar in accordance with an NCAR safety decision did not, however, cause a significant change in test results.

The use of Teflon tubing packed with unpassivated glass beads or Teflon shavings proved to be reproducible to ±7-15% for an individual loop, with even greater variability between loops. Teflon sample loops packed with Teflon chips (~3.8 cm substrate) initially demonstrated the best overall trapping efficiencies (typically ~95% ±5% relative standard deviation for an individual loop) with good day-to-day reproducibility. The <100% efficiencies appeared to be due to desorption rather than adsorption inefficiencies. However, after repeated conditioning, reproducibility fell off drastically with use. These loops appeared to be especially sensitive to the presence of water vapor: trapping efficiencies fell off by 20 to 30% when H<sub>2</sub>O(g) was present.

The use of empty Teflon tubing was then tested and found to have much greater reliability although overall trapping efficiencies were only ~60-75% for OCS and H<sub>2</sub>S. Again, these <100% trapping efficiencies appeared to be due to retention on the loop after desorption

because tests for adsorption efficiencies (loops placed in series) showed no evidence of breakthrough during trapping. Tests using various tubing lengths (3-25" immersed in the cryogen) were conducted in the attempt to verify the theory of surface effects. The results, however, were not significantly different. Attempts to clean up ambient air for chamber-purging purposes later showed that utilization of greater lengths of tubing and varying flow rates (and thus the residence time of surface exposure) does indeed make a difference. However, flow rates ranging from  $\sim 10$ -250 cc min<sup>-1</sup> in the 12-25" tubing lengths showed no significant trapping behavior variance (empty Teflon tubing sample loop test results are given in Appendix V). Loop contents were desorbed simultaneously with sample loop transfer from cryogen to boiling water since tests showed that sample decomposition and peak broadening occurred with any length of heating. Rapid desorption, however, routinely resulted in sharp and well-resolved peaks (see Fig. 15 in Section 3.3). After trapping, samples could be stored without loss in liquid O<sub>2</sub> or Ar, with  $\sim 1.5$ " flexibility on Dewar top-off, for extended periods (<48 hours tested). Storage in liquid N<sub>2</sub> resulted in flameout episodes upon desorption presumably due to leaks at the sample loop Teflon plug valves which allowed room air to be trapped. Storage configurations which put the Teflon plug valves in close proximity with Dewar cryogen also resulted in flameout episodes (apparently due to leaky plug valves). This was avoided by extending the loop tubing 3" outside the Dewar before attaching the Teflon plug valves (see Fig. 7).

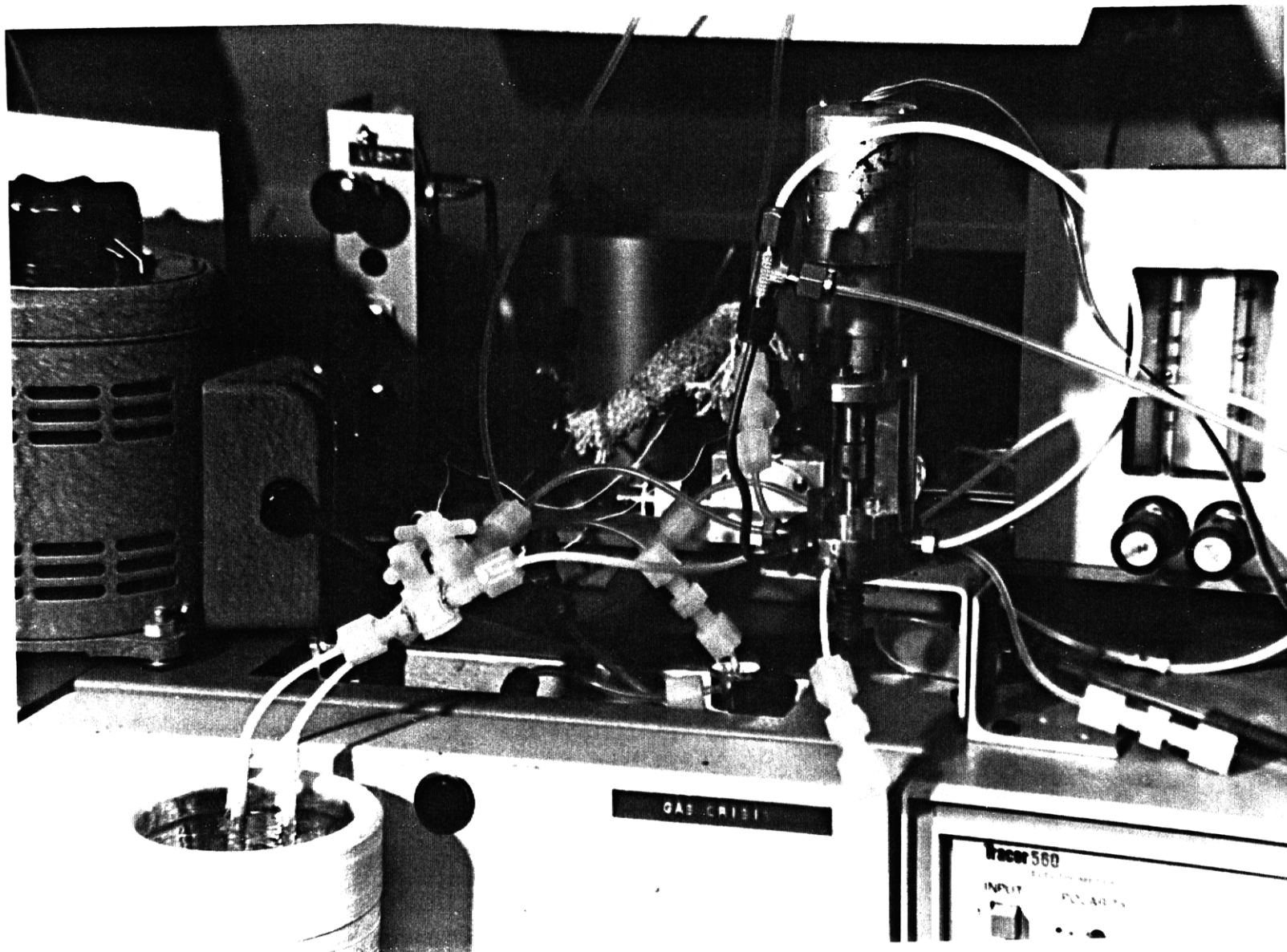


Fig. 8 Photograph of sample loop in cryogen (Charles Semmer)

Interference tests were conducted by doping standard mixtures with  $\text{H}_2\text{O}(\text{g})$ , trichlorofluoromethane ( $\text{CFCl}_3$ ), dichlorodifluoromethane ( $\text{CF}_2\text{Cl}_2$ ), 1,1,2-trichloro-1,2,2-trifluoromethane ( $\text{CFCl}_2\text{CF}_2\text{Cl}$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), and propane ( $\text{C}_3\text{H}_8$ ). The hydrocarbons listed were tested because  $\text{CH}_4$  and low-molecular weight non-methane hydrocarbons are also thought to be emitted from various soil and grass surfaces. Typically, coeluting hydrocarbons cause FPD flame quenching, thus necessitating interference studies for analysis techniques. Mixtures containing 0.5% each of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  in air (LINDE) were further diluted to test mixing ratios of ~4-7.5 ppmv and used to test for flame quenching. Calibration curves were run for OCS and  $\text{H}_2\text{S}$  followed by doping with hydrocarbons, and no flame quenching was observed for either gas. Fluorocarbons can also cause FPD flame quenching, so interference studies with mixing ratios of ~10-15 ppmv  $\text{N}_2\text{O}$ ,  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$  (diluted from mixtures containing 1% each (LINDE)) were conducted for OCS and  $\text{H}_2\text{S}$ . Again, no flame quenching was observed for either gas.

Introducing water vapor (see Fig. 9) to standard OCS or  $\text{H}_2\text{S}$  gas streams caused significant sample decomposition for  $\text{H}_2\text{S}$ . Low levels of humidity did not cause large losses in OCS or in OCS trapping efficiencies. Relative humidity values  $>20\%$ , however, caused almost immediate sample loop icing. Sample loops were marked so that the flow direction during trapping and desorption was the same to minimize loss during desorption due to moisture. However, samples which had begun to ice still routinely displayed irreproducible behavior. To elimi-

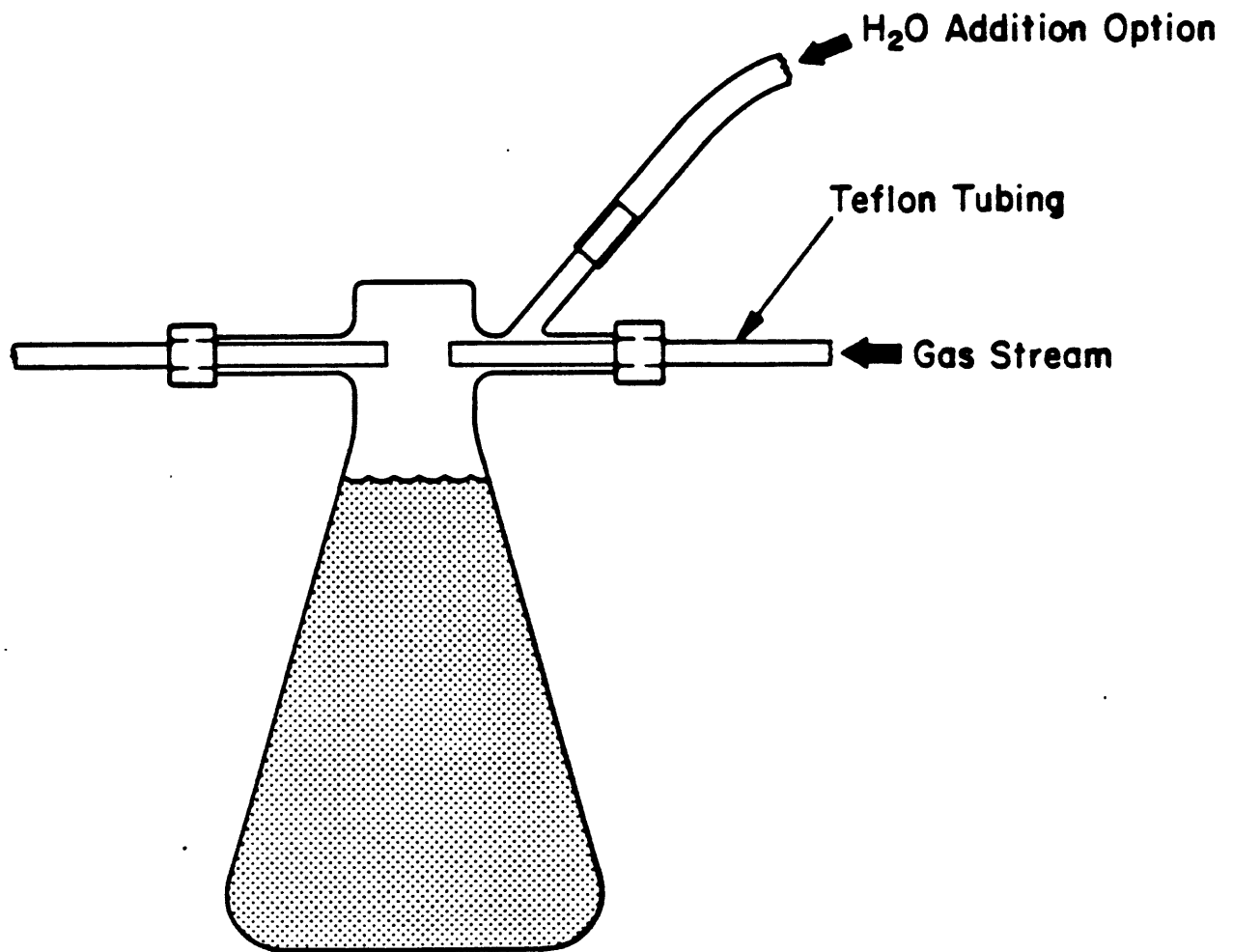


Fig. 9 Water vapor addition apparatus schematic

nate this problem, Nafion (DUPONT) tubing driers were constructed and used in line with sample loops (see Fig. 9). Nafion is a copolymer of tetrafluoroethylene and fluorosulfonyl monomer and acts as a permselective membrane. To effectively dry ambient air, ultra high-purity He was flowed countercurrently around 13 strands of Nafion tubing. These Nafion driers were tested for adsorption or desorption of  $H_2S$  and OCS. No enrichment or loss was observed from standard mixtures of air containing ambient levels of OCS (~500 pptv) or from standards containing ~1 ppm of  $H_2S$ . After considerable use, however, residual effects became obvious when air run through the traps was found to be enriched in its sulfur content. It was found that the driers could be effectively reconditioned between samples by purging the Nafion tubes with He. Tests were routinely conducted to check for OCS losses on the Nafion driers: Tests run after >100 hours use showed no evidence of loss; tests run after ~150 hours, however, showed ~40% loss, and tests run after an additional ~75 hours use showed that this had increased to a loss of ~45%. This research suggests that, with considerable use, Nafion tubing does not remain inert to OCS. Reconditioning efforts to restore the driers to their initial trouble-free behavior were unsuccessful.

### 3.2 Sample Collection

The sample collection procedure which was developed for and followed during the field study of the fluxes of OCS and  $H_2S$  from a salt water marsh (conducted at Wallops Island, Virginia) is outlined in the block diagram in Fig. 11. Ambient air was pulled through a carbon vane pump and its exhaust entered a regulating rotameter or was

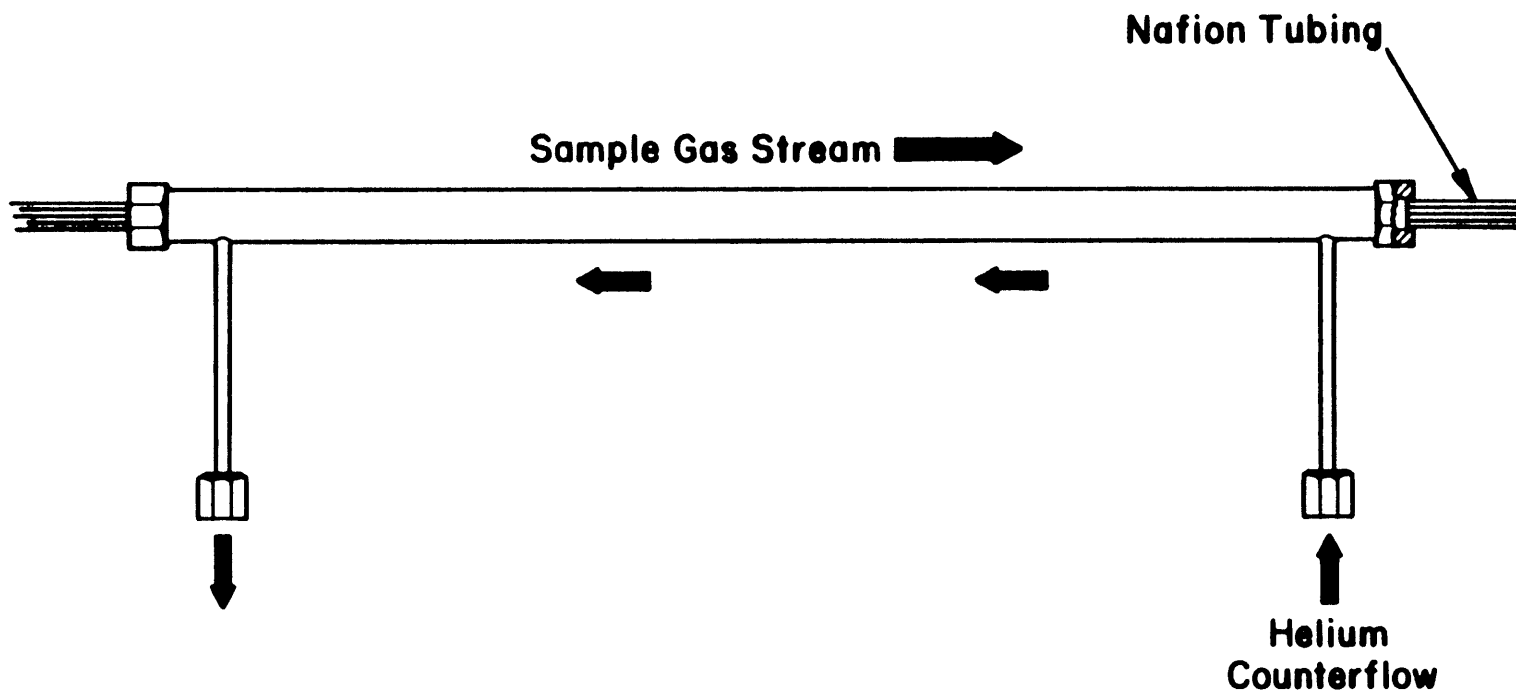


Fig. 10 NAFION drier schematic



# SAMPLE COLLECTION

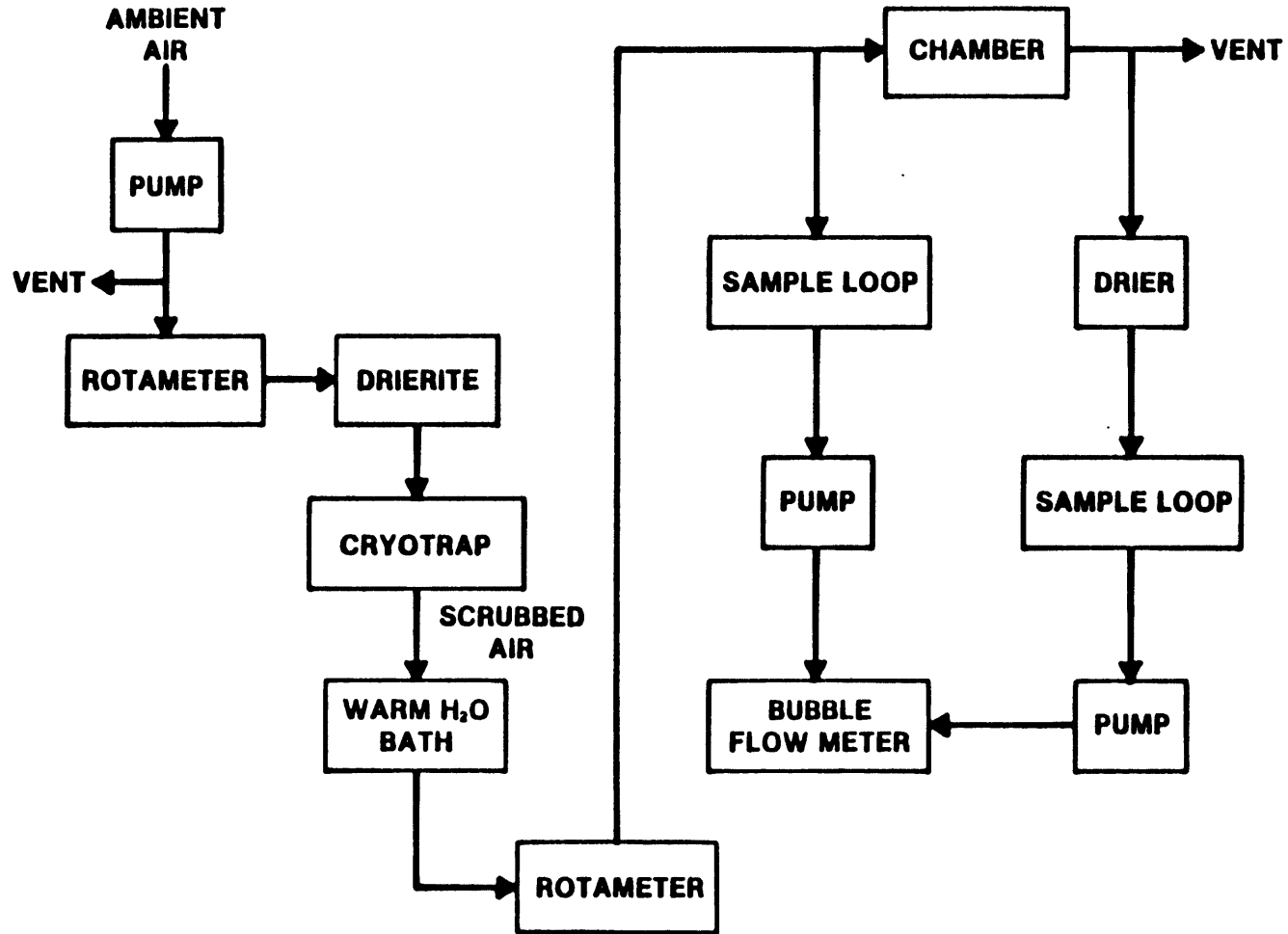


Fig. 11 Sample collection schematic

vented. The regulated flow ( $4-5 \text{ l min}^{-1}$ ) was passed through a series of Drierite-filled plastic cylinders before the air passed through a series of two approximately 50' lengths of 1/4" copper tubing coiled and immersed in liquid argon.

Drierite (anhydrous calcium sulfate) was used to remove water vapor from the air stream entering the cryotrap. Without this precaution, the cryotrap iced up within minutes. The Drierite-filled cylinders were configured so that the regulated flow entered three primary cylinders in parallel, each of which was connected to a secondary cylinder. Thus, the regulated flow was split into thirds and each air stream passed over a series of two Drierite-filled cylinders before the three dry air streams rejoined to enter the cryotrap. The three "primary cylinders" contained both indicating and non-indicating Drierite for ease in establishing when the Drierite was exhausted. However, this process was not 100% efficient in removing water vapor from ambient air, as the cryotrap routinely began to ice up after about ~14 hours at  $\sim 4 \text{ l min}^{-1}$ . The used Drierite in the "primary cylinders" was replaced with fresh Drierite, and the "icing" cryotrap was replaced with dry lengths of copper tubing before total icing occurred. It took approximately 15 minutes to exchange fresh for used materials, and the chamber entrance was sealed during this brief purge flow interruption.

After exiting the cryotrap, the air was warmed somewhat as it passed through tubing which was immersed in a warm water bath. The air then flowed through a second rotameter, 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.

Soda lime (Adams et al., 1980) was put in line between the Drierite and the cryotrap in order to strip sulfur gases, primarily OCS and CS<sub>2</sub>, from ambient air. This resulted in the cryotrap icing up in about 5 hours with a 4 l min<sup>-1</sup> purge flow. Although the soda lime used alone was fairly quickly exhausted, it was able to scrub ambient air of all but ~10% of its normal OCS level. The use of soda lime was discontinued because it caused cryotrap icing, it did not remove enough OCS when used alone, and it required the use of a Nafion drier on chamber inlet samples.

The chamber dimensions were 0.41 m × 0.41 m × 1.37 m, with an internal volume of 230.2 liters. The chamber was open-bottomed and was constructed of 1/8" sheets of abrasion-resistant TUFFAK CM-2 polycarbonate and non-volatile, DOW CORNING #3145 RTV adhesive (see Fig. 12). The polycarbonate material was chosen since it, like Teflon, has been shown to be relatively inert to sulfur gases (Adams et al., 1980) and since preliminary tests with a thin-film Teflon chamber proved to be unsuccessful. (These initial tests showed that, without a suitably-sized exit port, chamber purge air will exit through the ground which becomes the path of least resistance when positive pressure conditions dominate inside the Teflon chamber.) The polycarbonate material is clear, like glass, and sturdy, which facilitated sealing the chamber in the marsh soil. Tests were conducted to ensure the absence of leaks around the chamber-soil interface and to ensure that purge air exited through the chamber exit. A smaller, four-sided polycarbonate chamber was constructed in a similar fashion for laboratory tests to determine the degree to which the materials

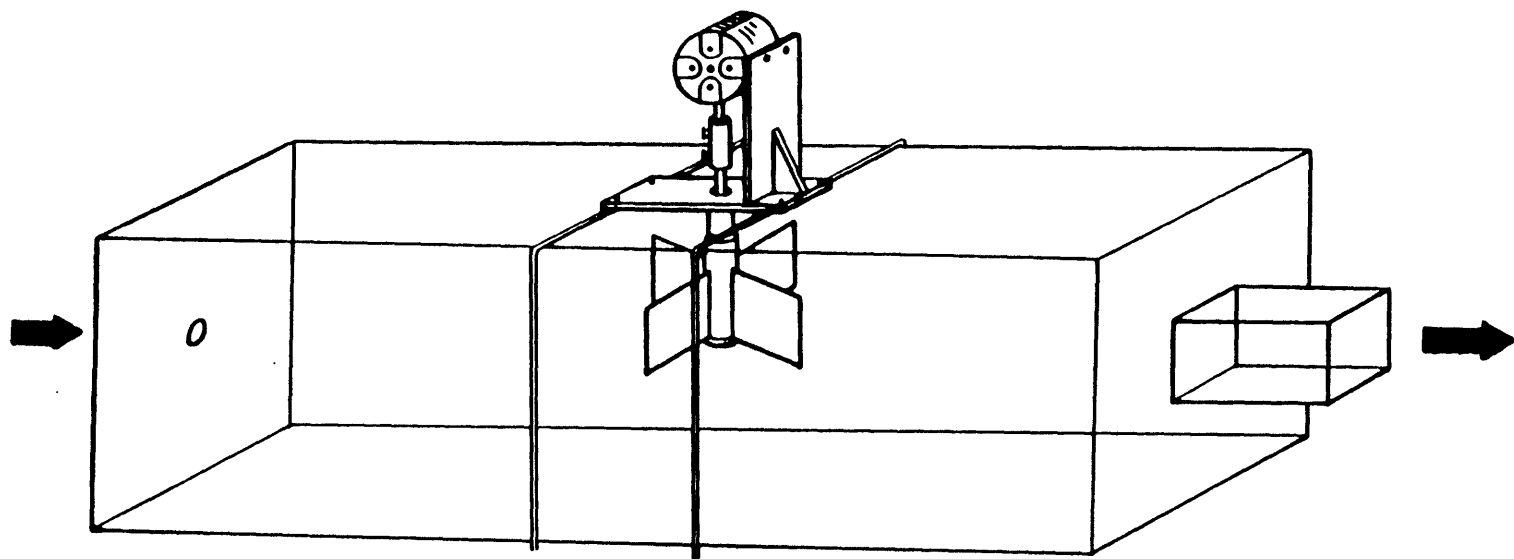


Fig. 12 Polycarbonate flux chamber

used in chamber construction adsorbed or desorbed the sulfur gases of interest. After a curing and equilibration period, this test chamber was purged with an air standard containing ~10 pptv OCS and a small amount of CS<sub>2</sub>. A portion of the air leaving the chamber was trapped, and analysis showed no significant change in either the GC response or the concentrations predicted. This confirmed an absence of significant outgassing from or adsorption onto the chamber materials. In addition, there were no unidentified peaks or indications of flame quenching. As noted, Adams et al. (1980) also used a polycarbonate flux chamber in their field studies, and their surface reactivity tests agree with these findings.

Fan blades (3.25" x 4.75") and a rotor shaft were machined from a block of 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 wind velocity measurements were made inside the chamber, typical daytime winds were reasonably well imitated as evidenced by comparing grass-top motion both inside and outside the chamber.

With an internal volume of 230.2 l and a typical purge flow of 4.2 l min<sup>-1</sup>, the chamber residence time was 54.8 minutes. Once set in the soil with all connections made, the chamber, mechanically stirred and continuously flushed with scrubbed ambient air, was allowed to equilibrate for 2-3 hours at a purge flow rate of 4-5 l min<sup>-1</sup>. After

this initial equilibrium period, the air entering and exiting the chamber was collected simultaneously and stored for laboratory analysis to determine the amount of OCS, H<sub>2</sub>S, and CS<sub>2</sub> generated within the chamber. Liquid argon was used to cryogenically trap and store the samples which were pulled through the loops by FMI pumps. The pumping rates were constant and were routinely checked with a bubble flow meter to ensure knowledge of the sample volume collected. Sample collection was conducted for 50-60 minutes every other hour over a period of 25 hours. Typical sample volumes were 1.5 to 2 liters of air. Light intensity and air and soil temperatures, both inside and outside the chamber, were also monitored. During the last six studies, a loosely-woven, light-weight white cloth was used to shade the chamber which helped to reduce surface evaporation and thus condensation on the cooler interior chamber walls without significantly reducing the light which reached the chamber interior.

### 3.3 Sample Analysis

A description of the analytical instrumentation which was used to analyze samples was given in Chapter 2. The analysis procedure included calibration of the GC response both before and after sample analysis. The GC response was initially calibrated for both OCS and H<sub>2</sub>S. Using the KINTEK Standard Generator, an OCS standard was generated by regulating the diluent air flow rate:

$$C_{\text{ppbv}} = \frac{(P_c + P)(PR)(0.975)(1000)}{(F) \left( \frac{P - P_{H_2O}}{760} \right) \left( \frac{273}{T} \right)}$$

where  $P_c$  = cell pressure (read in psi, converted to torr);  $P$  = laboratory pressure (torr);  $PR$  = permeation rate ( $\text{nl min}^{-1}$ ), 0.975 refers to 97.5% OCS cell gas;  $F$  = flow rate ( $\text{ml min}^{-1}$ );  $P_{H_2O}$  = water vapor pressure (torr);  $T$  = laboratory temperature (K). All flow measurements made using the bubble flow meter were corrected for water vapor pressure, and  $F$  was converted to standard cc/min, ( $P = 760$  torr,  $T = 0^\circ\text{C}$ ) in all calculations.

Using the A.I.D. Standard Generator to house a permeation tube, an  $\text{H}_2\text{S}$  standard was generated by regulating the diluent air flow rate around the tube:

$$C_{\text{ppbv}} = \frac{(PR)(k)(1000)}{(F) \left( \frac{P - P_{H_2O}}{760} \right) \left( \frac{273}{T} \right)}$$

where  $PR$  = permeation rate ( $\text{ng min}^{-1}$ ) and  $k$  = constant =  $22.4/\text{molecular weight}$ . Taking into account the volume of standard in the GC sample valve's sample loop ( $0.93 \times P/760$  std cc), injected amounts were recorded in the concentration units ppbvml. The flame gas flow rates were carefully monitored throughout each calibration and analysis period. Rotameter settings were chosen as a result of response-optimization studies:  $\text{H}_2$  at "85" and air at "125" (Tracor 560 rotameter calibrations in Appendix IV). The carrier  $\text{N}_2$  flow rate of 30 std cc  $\text{min}^{-1}$  was also carefully monitored although changes in flow rates appeared to be caused by changes in ambient temperature rather than actual setting changes. The Tracor 560 GC was run isothermally during OCS calibrations for convenience since tests had shown no

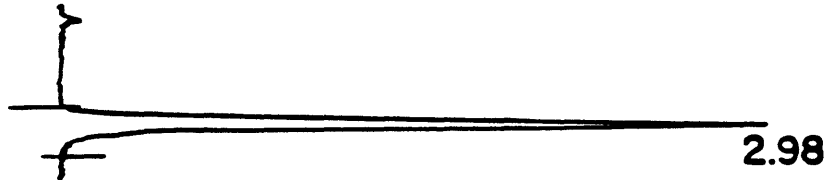
response change with temperature programming.  $\text{H}_2\text{S}$ , on the other hand, demonstrated temperature-dependent column conditioning effects. Therefore, the same T-programming regime which was used for sample analysis was required for calibration of the GC  $\text{H}_2\text{S}$  response: GC oven temperatures were held at  $65^\circ\text{C}$  for 6 min followed by a ramp rate of  $30^\circ\text{C min}^{-1}$  for 2 min to a final temperature of  $125^\circ\text{C}$  which was held for 9 minutes. Thus, chromatographic analysis required 17 minutes. The Tracor FPD temperature was constant at  $130^\circ\text{C}$  during all calibration and analysis periods. Retention times varied slightly between calibration and sample analysis chromatograms due to the time sequence used for sample desorption. The Spectra Physics and GC T-programming were begun simultaneously and the valve configuration automatically switched at 0.5 min. At this point, the sample loop contents were desorbed onto the column by rapid transfer from liquid argon to boiling water. Thus, sample chromatograms reflected this additional 0.5 min in compound retention times (see Table 1). Typical standard and sample chromatograms are shown in Figs. 13 through 16. OCS calibration curves run at the start of an analysis period consisted of a minimum of four standard concentrations, each run an average of four trials. For a GC response  $\geq 10,000$  (at any particular GC attenuation setting), typical GC response reproducibility was  $\leq \pm 1\%$  standard deviation. When regression analysis on the  $\geq 4$  calibration points showed a correlation coefficient  $< 0.995$ , additional points were run to assure GC response stability before beginning sample analysis. As mentioned, OCS standards were run isothermally, and each chromatogram took 4.5 min. The entire calibration curve therefore required 2-3 hours.



**Table 1**  
**Chromatographic Retention Times**

<u>Gas</u>	<u>Standard Retention Time (min)</u>	<u>Sample Retention Time (min)</u>
H <sub>2</sub> S	2.02	2.79
OCS	3.08	3.86
CS <sub>2</sub>	13.30	13.79

OCS STANDARD  
 INJECT TIME 29 17:57:29



PK#	RT	Area	Height	BC Code
1.	2.98	137152.	4157.3333	1.

INJECT TIME 29 18:02:04



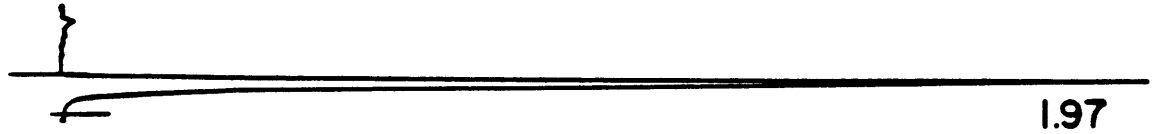
PK#	RT	Area	Height	BC Code
1.	2.97	137964.	4164.	1.

INJECT TIME 29 18:06:38

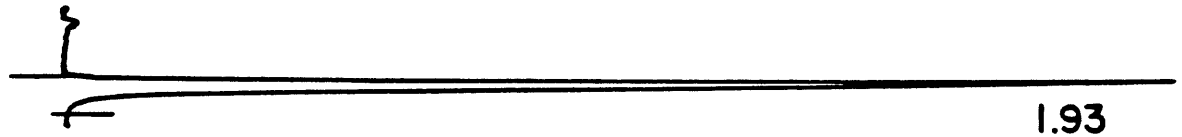


PK#	RT	Area	Height	BC Code
1.	2.97	138888.	4197.3333	1.

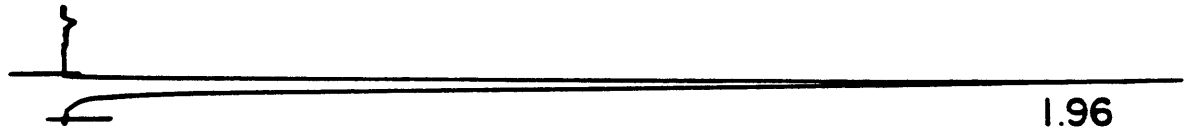
Fig. 13 OCS standard chromatogram

**H<sub>2</sub>S STANDARD****INJECT TIME 29 20:40:14**

PK#	RT	Area	Height	BC Code
1.	1.97	152352.	6330.6667	1.

**INJECT TIME 29 21:02:10**

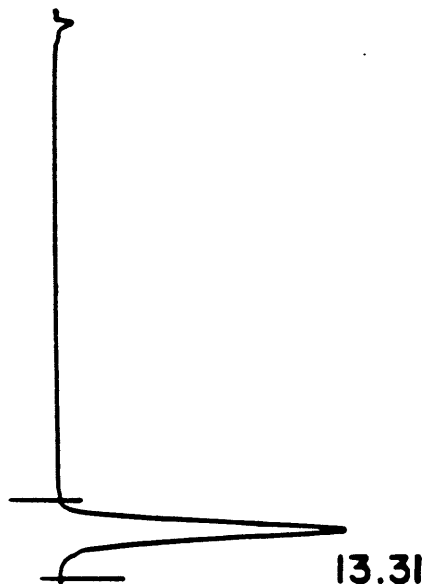
PK#	RT	Area	Height	BC Code
1.	1.93	155386.	6485.3333	1.

**INJECT TIME 29 21:25:09**

PK#	RT	Area	Height	BC Code
1.	1.96	157083	6528.	1.

Fig. 14 H<sub>2</sub>S standard chromatogram

CS<sub>2</sub> STANDARD  
INJECT TIME 27 19:16:17



PK#	RT	Area	Height	BC Code
1.	13.31	48007.	842.66667	1.

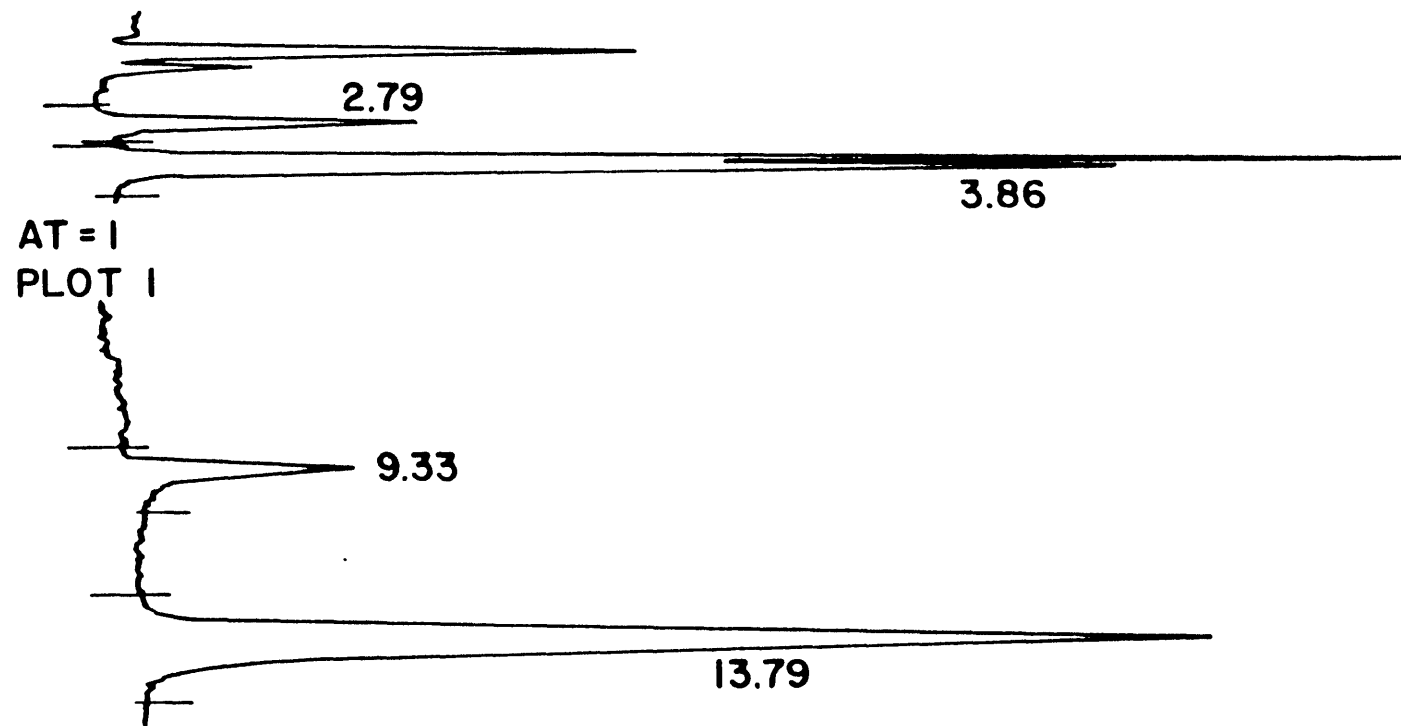
INJECT TIME 27 19:34:02



PK#	RT	Area	Height	BC Code
1.	13.3	46149.	820.	1.

Fig. 15 CS<sub>2</sub> standard chromatogram

REM LOOP #33  
 INJECT TIME 25 06:34:01



Pk#	RT	Area	Height	BC	GAS
1.	2.79	6237.	228.	1.	H <sub>2</sub> S
2.	3.86	98673.	2882.6667	1.	OCS
3.	9.33	7903.	162.66667	1.	?
4.	13.79	51390.	764.	1.	CS <sub>2</sub>

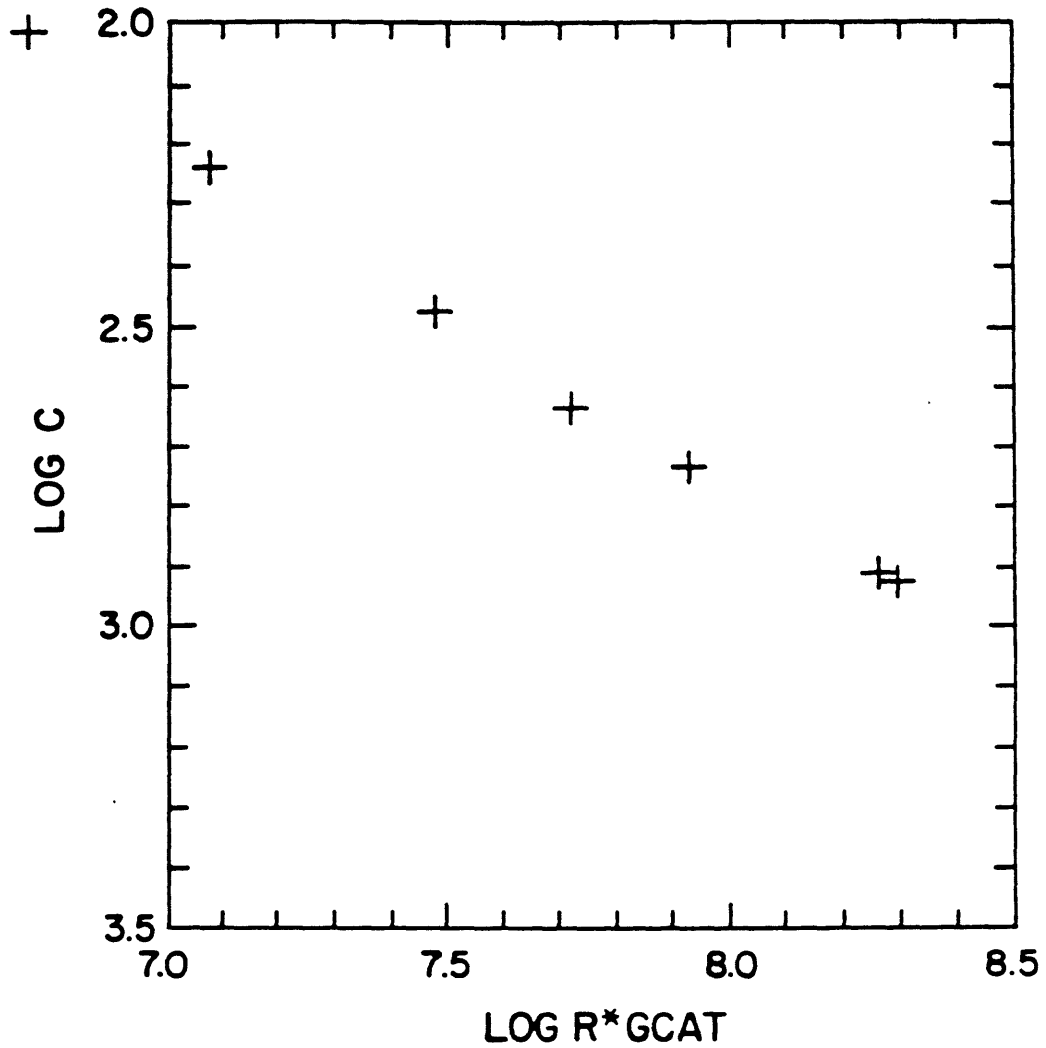
Fig. 16 Sample chromatogram

Initial H<sub>2</sub>S calibration curves also consisted of a minimum of four points, each run an average of three trials. Since chromatographic analysis required 17 minutes and oven cooling and re-equilibration took about 3 minutes, each point took a minimum of one hour. When GC response demonstrated week-to-week stability, H<sub>2</sub>S curves were sometimes checked with only three points. After determining the GC response to various standard OCS and H<sub>2</sub>S concentrations, the samples were analyzed. Typically, samples were analyzed as follows: "Air in" samples were analyzed in the order in which they were collected, followed by "air out" samples, also run in the order in which they were collected. For the Wallops Island weekly flux study, this typically involved 26 samples. At approximately 20 minutes per sample, analysis took about 8.5 hours. Occasionally "air out" sample contents caused the baseline to drift, necessitating an interruption to recondition the column. Column bakes were conducted at an FPD temperature of 165°C and an oven temperature of 150°C for 1-2 hours as required.

After sample analysis had been completed, a second OCS calibration curve of 4 points was run to determine the GC response drift during the >8.5 hr analysis period. When a change in the GC response was observed this was followed by a second H<sub>2</sub>S calibration curve. However, when the GC response was highly stable, a second H<sub>2</sub>S curve was not required as repeated tests showed it would be in excellent agreement with the first. Composite calibration curves, made up of curves run before and after sample analysis, were used to determine sample concentrations (see Fig. 17).

Fig. 17 Composite OCS calibration curve

SEPTEMBER 23-24, 1982 FIELD STUDY  
COMPOSITE OCS CALIBRATION CURVE



## CALIBRATION CURVE

Pt#	Conc	R*GCAT	Log C	Log R
1.	847.2	198198326	2.928	8.2971
2.	540.4	84004003	2.7327	7.9243
3.	297.9	29702977	2.474	7.4728
4.	104.3	5598865	2.0182	6.7481
5.	432.9	52650194	2.6364	7.7214
6.	174.3	11945380	2.2414	7.0772
7.	82.1	3561230	1.9143	6.5516
8.	823.2	183992444	2.9155	8.2648

Curve:  $R*GCAT = 1940.0071*conc^{**} 1.6995984$   
 Corr. Coeff.: 0.9990945

Concentrations were predicted as follows: A linear regression was performed on the log (GC response × GCAT) and log (standard concentration) data, giving the relationship

$$\text{Log } R = a + b \log C \quad \text{or} \quad R = 10^a C^b$$

and, thus

$$C = (R/10^a)^{1/b},$$

where  $R = (\text{GC response})(\text{GC attenuation})$  and  $C = \text{concentration in ppbvl}$ . Next, this initial concentration value must be adjusted for sample loop trapping efficiencies ( $e$ ) and sample volume ( $v$ ):

$$\bar{C}_{\text{ppbv}} = C_{\text{ppbvml}} / (e)(v) ,$$

where  $e = \% \text{ efficiency}/100$  and the sample volume (ml) is calculated from the trapping rate and the trapping time, both of which are closely monitored during sample collection. The bar over the  $C$  refers to the fact that this concentration represents the average concentration during the trapping period, rather than an instantaneous measurement of concentration.  $\bar{C}_0$  was used to denote the concentration in the air which entered the chamber, while  $\bar{C}$  refers to the concentration in the air which exited the chamber. Thus,  $\bar{C} - \bar{C}_0 = \Delta\bar{C}$  refers to the amount of gas generated within the chamber. The fluxes were calculated from the concentrations measured as follows:



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

where  $C$  and  $C_0$  refer to the instantaneous concentrations,  $t$  = time,  $u$  = chamber purge air flow rate,  $A$  = chamber surface area,  $H$  = chamber height;  $AH$  = chamber volume, and  $E$  = the instantaneous flux of gas from the marsh surface. The concentration ( $C_0$ ) of OCS, CS<sub>2</sub>, and H<sub>2</sub>S in the chamber purge air was essentially constant, thus  $dC_0/dt = 0$ . Defining  $\Delta C = C - C_0$ ,

$$\frac{dC}{dt} = -\frac{u\Delta C}{AH} + \frac{E}{H}$$

$$\int_{t_1}^{t_2} dC = \int_{t_1}^{t_2} \left( -\frac{u\Delta C}{AH} + \frac{E}{H} \right) dt$$

$$C_{t_2} - C_{t_1} = -\frac{u\bar{\Delta C}}{AH} (t_2 - t_1) + \frac{\bar{E}}{H} (t_2 - t_1)$$

where  $\bar{E}$  refers to the average flux of gas during the trapping period.

Defining  $\Delta C = C_{t_2} - C_{t_1}$ , and  $\Delta t = t_2 - t_1$ ,

$$\bar{E} = \frac{H\Delta C}{\Delta t} + \frac{u\bar{\Delta C}}{A}$$

The errors involved in the calculation of  $\bar{E}$  are as follows:

$$R = aC^x; \quad C = \left(\frac{R}{a}\right)^{1/x} = a^{-1/x} R^{1/x},$$

$$\frac{dC}{dR} = (a^{-1/x}) (1/x) R^{(1/x-1)} = \frac{1}{x} \frac{C}{R}$$

$$\frac{dC}{da} = (-1/x)(a^{-1/x-1})(R^{1/x}) = -\frac{1}{x} \frac{C}{a}$$

$$\frac{dC}{dx} = -\left(\ln \frac{R}{a}\right) \left(\frac{R}{a}\right)^{1/x} \frac{1}{x^2} = -\frac{\ln\left(\frac{R}{a}\right)}{x^2} C$$

$$\begin{aligned} \frac{\Delta C}{C} &= \left( \left( \frac{dC}{dR} \frac{\Delta R}{C} \right)^2 + \left( \frac{dC}{da} \frac{\Delta a}{C} \right)^2 + \left( \frac{dC}{dx} \frac{\Delta x}{C} \right)^2 \right)^{1/2} \\ &= \left( \left( \frac{1}{x} \frac{C}{R} \frac{\Delta R}{C} \right)^2 + \left( \frac{1}{x} \frac{C}{a} \frac{\Delta a}{C} \right)^2 + \left( \frac{\ln\left(\frac{R}{a}\right)}{x^2} \frac{C \Delta x}{C} \right)^2 \right)^{1/2} \\ &= \left( \left( \frac{1}{x} \frac{\Delta R}{R} \right)^2 + \left( \frac{1}{x} \frac{\Delta a}{a} \right)^2 + \left( \frac{\ln\left(\frac{R}{a}\right)}{x} \frac{\Delta x}{x} \right)^2 \right)^{1/2} \end{aligned}$$

$$\bar{C} \pm \Delta \bar{C} = (C \pm \Delta C) / (e \pm \Delta e)(v \pm \Delta v), \quad \Delta \bar{C} / \bar{C} = \Delta C / C + \Delta e / e + \Delta v / v$$

and

$$\bar{C}_0 \pm \Delta \bar{C}_0 = (C t_0 \pm \Delta C_0) / (e \pm \Delta e)(v \pm \Delta v), \quad \Delta \bar{C}_0 / \bar{C}_0 = \Delta C_0 / C_0 + \Delta e / e + \Delta v / v,$$

$$\begin{aligned} \bar{E} \pm \Delta \bar{E} &= \frac{((\bar{C} \pm \Delta \bar{C}) - (\bar{C}_0 \pm \Delta \bar{C}_0)) (u \pm \Delta u)}{A} \\ &+ \frac{H((C_{t_2} \pm \Delta C_{t_2}) - (C_{t_1} \pm \Delta C_{t_1}))}{((t_2 \pm \Delta t_2) - (t_1 \pm \Delta t_1))} \end{aligned}$$

The sample concentrations and the corresponding calculated flux values are presented with their errors in Appendix VI.

## CHAPTER 4

## FIELD STUDIES

The results of the field studies conducted in California, Massachusetts, and Virginia, along with the results of aircraft measurements of ambient atmospheric OCS and CS<sub>2</sub> concentrations, are presented in this chapter.

## 4.1 Dissolved Oxygen and pH Measurements

Preliminary work conducted at the Scripps Institution of Oceanography, La Jolla, California, included field studies to monitor the diurnal variations in dissolved oxygen in several Southern California salt-marsh and mud-flat environments. In particular, pH values were monitored and a diurnal dissolved oxygen cycle was identified in the Penasquitos Marsh (see Fig. 18). This variation of dissolved oxygen concentrations with sunlight was also observed in the Bataquitos Mud Flat and the Mission Bay Marsh.

## 4.2 A Micrometeorological Flux Study

In Massachusetts, measurements of reduced sulfur gas concentrations above regions of the Sippiwissett Salt Marsh near the Woods Hole Oceanographic Institution were planned. Scientists at the Ecosystems Center of the Marine Biology Laboratory at Woods Hole had expressed an interest in this investigation, and collaborative studies with P. Steudler at that laboratory were conducted during the summer of 1980.

A preliminary micrometeorological gas sampling experiment was conducted on April 11, 1980. Measurements taken included sample gas profiles, wind speed to a height of 2 m above ground, wind direction,

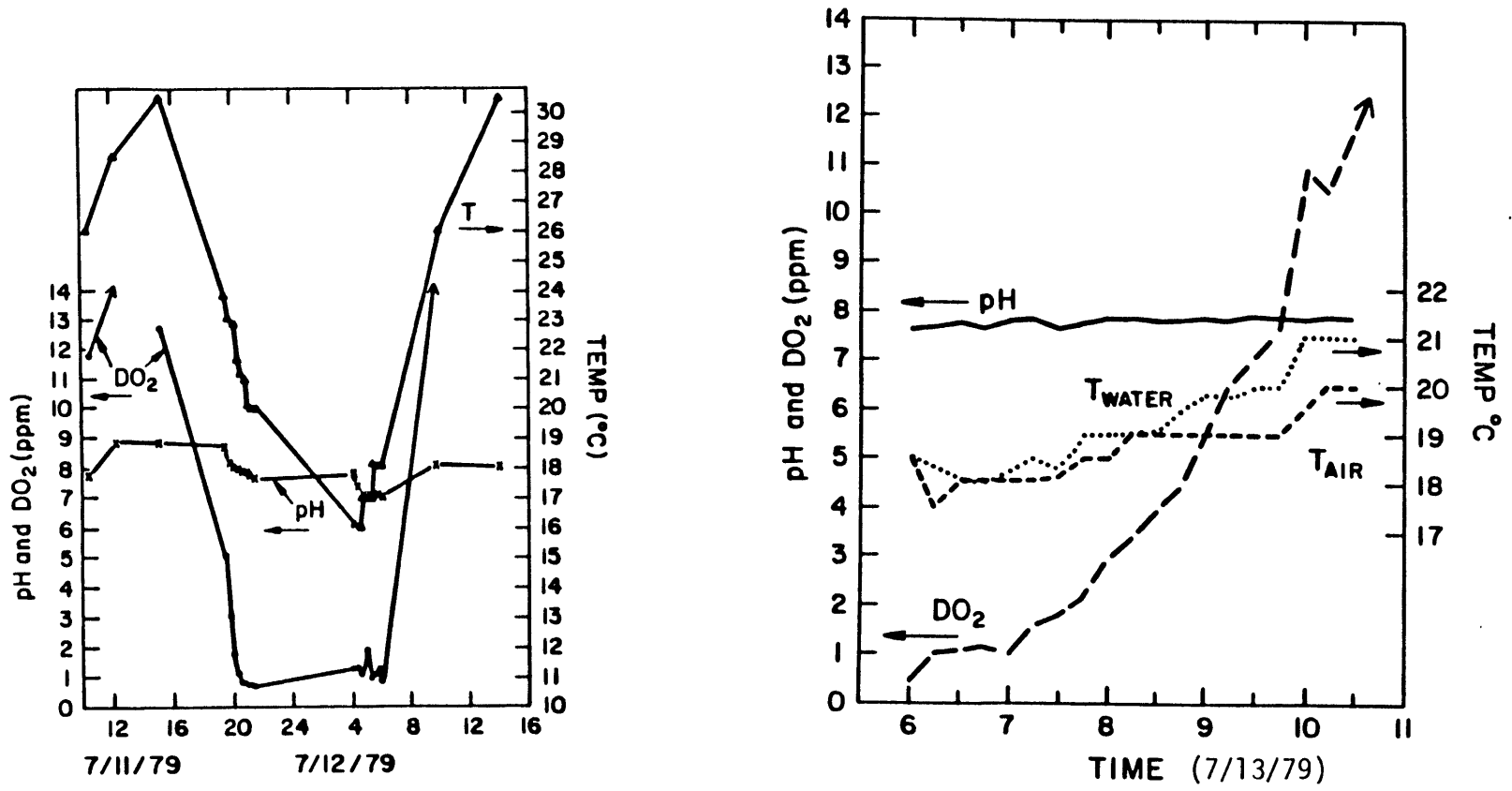


Fig. 18 July 1979 Panesquitos Marsh field studies results

light intensity, air and peat temperatures, and tide and sky observations. Reduced sulfur gases were trapped using three foil-wrapped "60/80 Molecular Sieve 5A-60/80 Tenax-GS" traps per 1.5 hr sampling period. The traps were positioned at 0.75 m, 1.25 m, and 2.0 m on a 3 m tower. Measurements were taken from 0900 to 1800, permitting the study of gas and wind data in conjunction with light intensity, temperature, and hydrological differences. Sample collection and gas analysis was carried out as described in Appendix III. The three Maximum #41 Generator anemometers had been calibrated in the Aeronautics and Astronautics Department's 5'x7' wind tunnel at MIT. Fluxes were calculated using the following general equations:

$$F_S = -K[M]\partial f_i/\partial z \quad (1)$$

$$K = k u_* z \quad (2)$$

$$u_* = k(z + z_0) \partial \bar{u}/\partial z \quad (3)$$

where  $[M] = 2.56 \text{ E}25 \text{ molecules/m}^3$ ,  $f_i =$  mixing ratio of species  $i$ ,  $k = 0.4$  (Von Karman's constant),  $u_* =$  friction velocity,  $\bar{u} =$  mean wind speed,  $z =$  height above ground, and  $z_0 =$  roughness length (~one order of magnitude  $<$  actual height of roughness elements, which for 20 cm grass is ~2 cm). Determination of the eddy diffusion coefficient,  $K$ , by use of the logarithmic wind profile (Eq. 3) included the assumption of neutral stability conditions, neglecting buoyancy. Variation of wind speed as a function of time and height is presented graphically (see Figs. 19 and 20). Gas data for the reduced sulfur

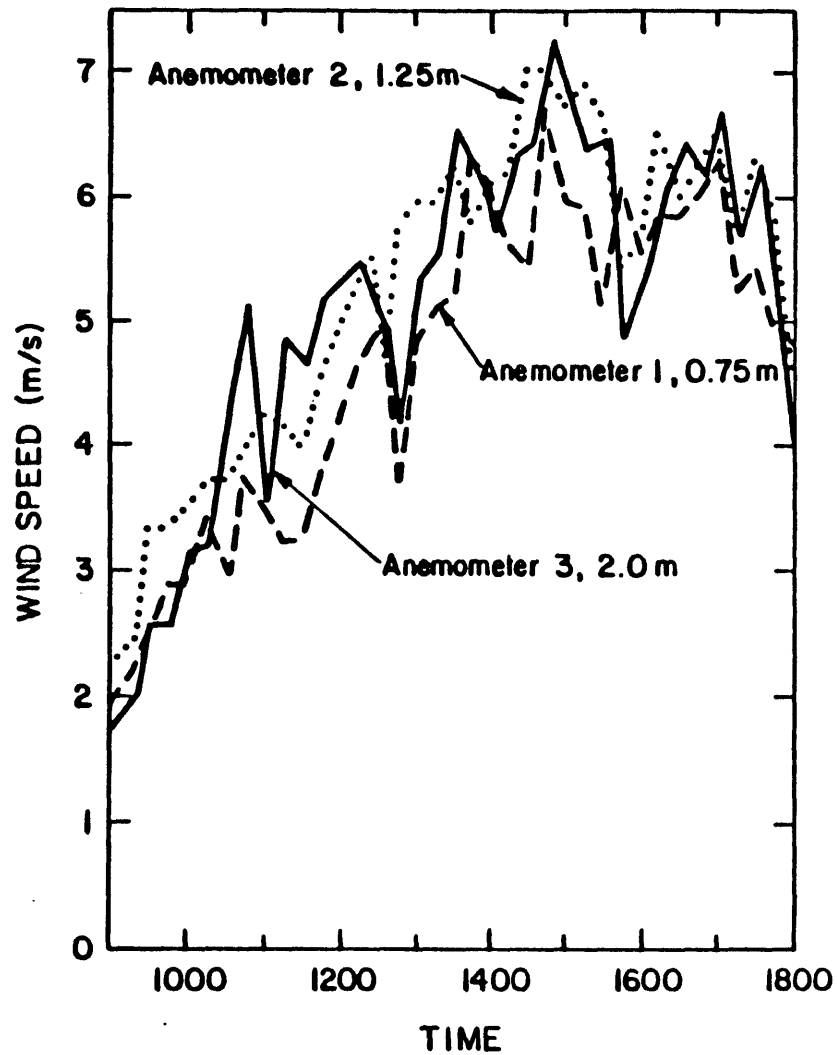


Fig. 19 April 1980 Sippiwissett Salt Marsh field study wind speed measurements

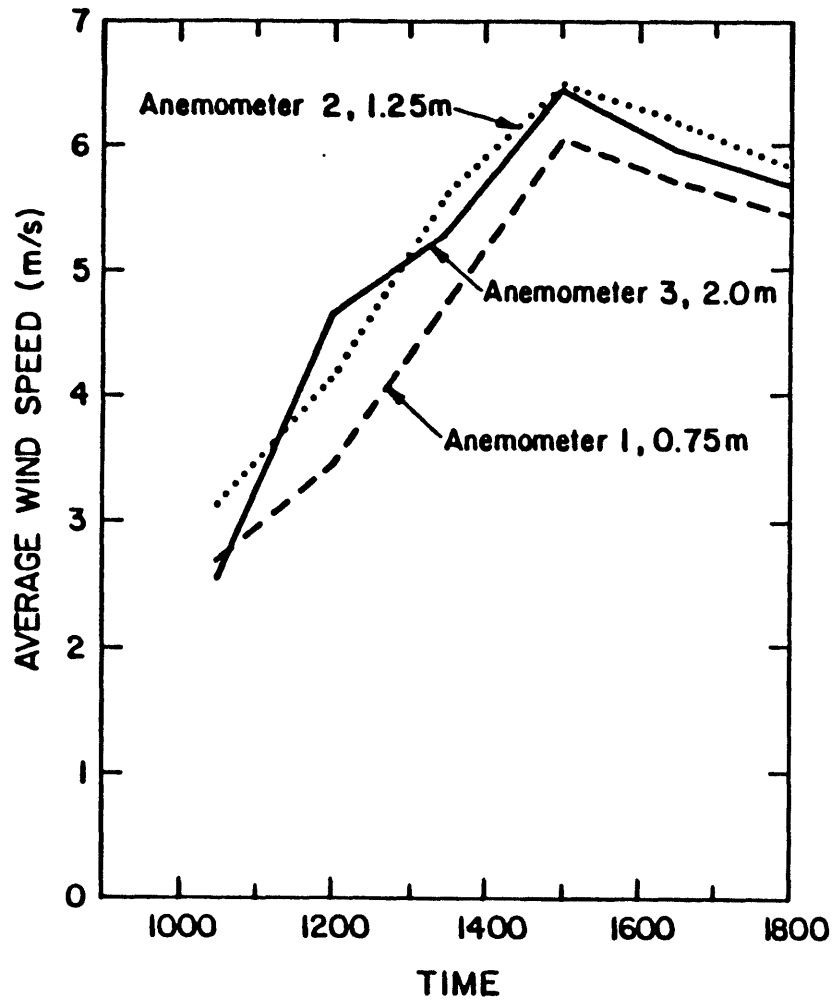


Fig. 20 April 1980 Sippiwissett Salt Marsh field study average wind speeds

gases carbonyl sulfide, hydrogen sulfide, and dimethyl sulfide are not presented here due to outstanding questions about the enrichment technique used (see discussion of Molecular Sieve/Tenax-GC traps in Chapter 3) and because it was found that  $\bar{\partial}u/\partial z$  was poorly determined within a vertical spatial resolution of only 2 m. The use of Priestley's (1974) formula to estimate convective fluxes by equating sulfur gas eddy diffusivity with the eddy diffusion coefficient for sensible heat was also explored:

$$K_H = hz^2(g/T|\partial T/\partial z + \Gamma|)^{1/2} \quad (4)$$

$$(\partial T/\partial z + \Gamma) = -(H/h\rho c_p)^{2/3}(T/g)^{1/3} z^{-4/3} \quad (5)$$

where  $\Gamma$  is the atmospheric lapse rate and H represents heat flux. However, the instrumentation to determine  $\partial T/\partial z$  accurately within a vertical spatial resolution of even 10 m does not exist. It was concluded that the use of Bellamy's triangulation method (1949) to determine the flux of sulfur gases from a salt water marsh was the only micrometeorological option available where poor vertical spatial resolution of wind speed and air temperature would not present difficulties. This method, however, is even more equipment and labor intensive than chamber flux studies. Consequently, a flux chamber method was developed to determine the fluxes of these sulfur gases from the marsh surface.

### 4.3 Wallops Island Flux Studies

The major data collection effort using the chamber technique involved a field study conducted at Wallops Island, Virginia, a barrier island off the eastern shore of the Delmarva Peninsula (see Figs. 21 and 22). The island is a part of the NASA/Wallops Flight Facility, and the northern part of the island consists primarily of isolated marsh and beach. The field experiment was limited to studying the emissions of OCS, H<sub>2</sub>S, and CS<sub>2</sub> from mixed stands of Spartina-alterniflora and Spartina-patens found in the high marsh. Grass height and the degree to which the lower marsh areas flooded during tidal episodes were the primary considerations involved in confining field studies to high marsh regions.

Instrumentation (described in Chapter 2) was set up in a laboratory located on the main base of the NASA/Wallops Flight Facility in mid-May 1982. After instrument equilibration, calibration studies were conducted through the first week in June. Three field experiments were conducted in June. These preliminary studies helped to identify changes required in the sample collection setup such as : (1) the use of He to transfer cryogen from large to hand-held sized dewars was excessive; (2) the amount of cryogen required to cover the ~30 hr field period plus sample storage up to ~30 hrs was almost twice that initially estimated; (3) wind barriers were required to reduce cryogen boil-off; (4) the initial plan to flow ambient air through the chamber would not work because the difference between two similarly-sized numbers ( $\bar{C} - \bar{C}_0$ ) was lost in the errors; and (5) the thin-film Teflon chamber did not seal easily, and, once properly



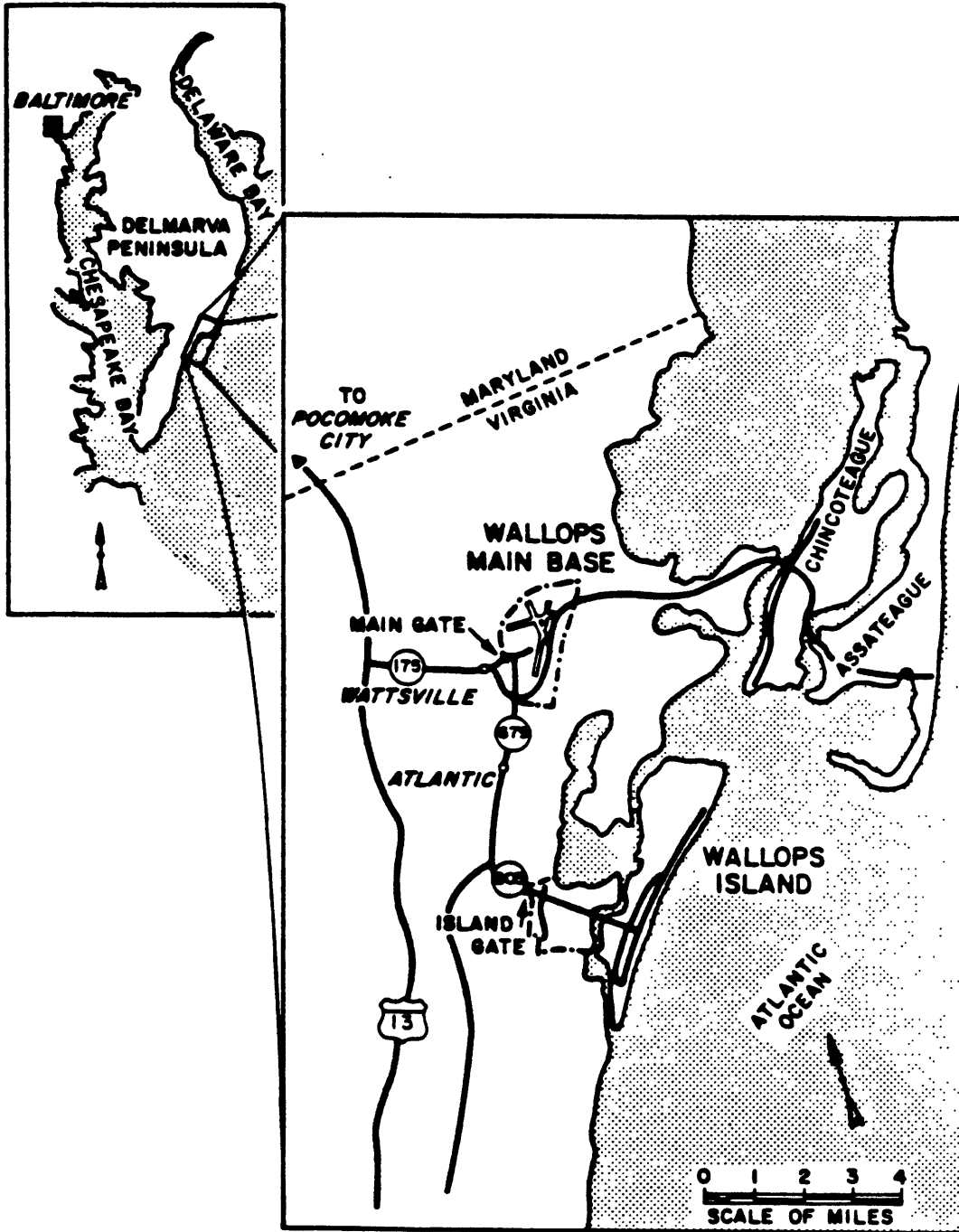


Fig. 21 Map describing location of Wallops Island, Virginia

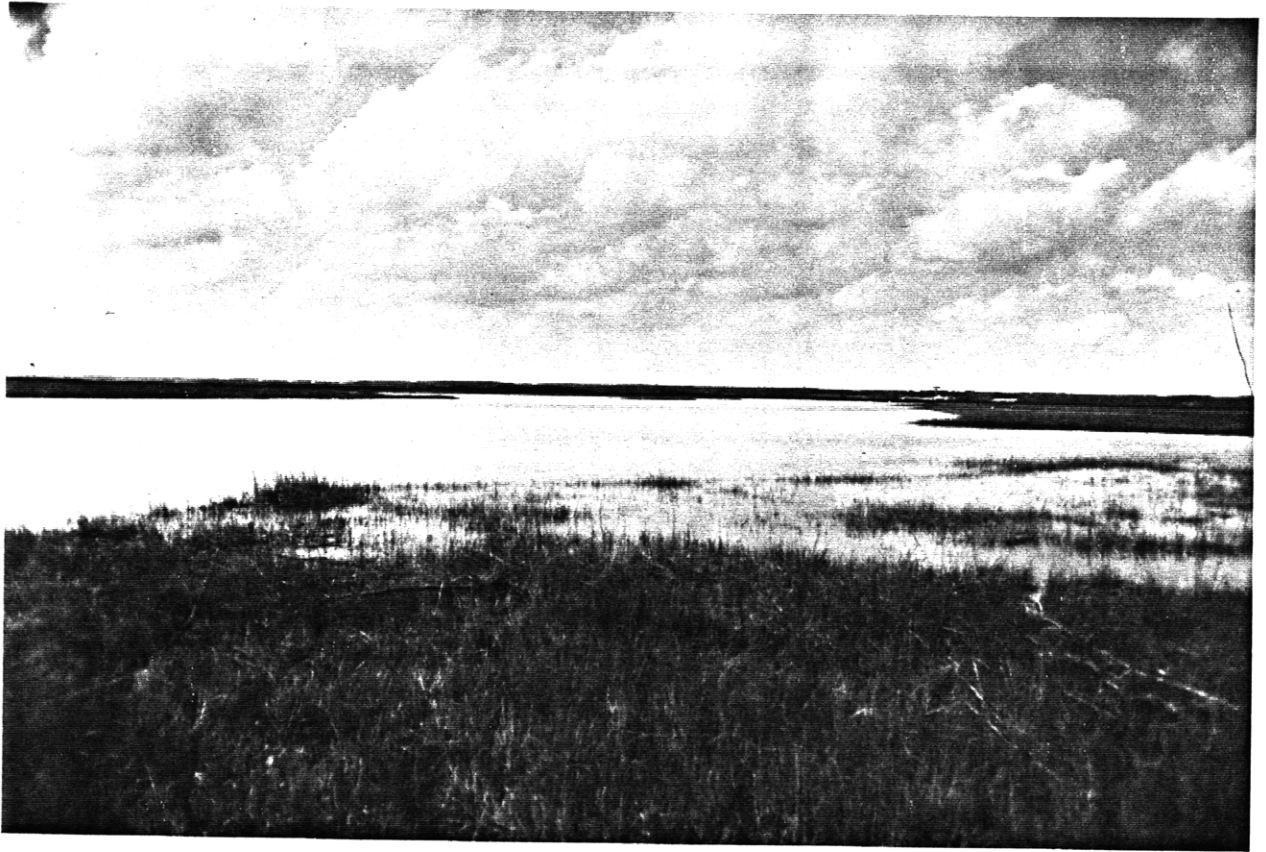


Fig. 22 Photographs of Wallops Island field site

sealed, the port sizes were too small to prevent the air from being pushed through the ground due to pressure buildup inside the chamber. Therefore, following the June field studies, the polycarbonate chamber was designed and built and revisions were made to the sampling procedure (the final sample collection procedure is discussed in Chapter 3). The twenty-five hour duration field experiments were conducted weekly from mid-July through September 1982. The two field experiments conducted in July also resulted in method adjustments: the July 20-21 field study consisted of a reproducibility study as well as a flux study. Unfortunately, the flux information was lost when the GC analysis was handled improperly (a contaminant created noise in the GC response, and a bakeout period should have been utilized to clean the column). The last study in July showed evidence of residual OCS and CS<sub>2</sub> on the Nafion driers used. Thus the values calculated then were suspect. For these reasons the results for the five preliminary studies conducted in June and July are not included here. However, the following points concerning these early studies are worth noting: (1) the results of the two reproducibility studies (see Appendix VII) demonstrated good overall method agreement loop-to-loop; (2) CS<sub>2</sub> values increased during tidal episodes. The results of the later nine field studies conducted in August and September are the ones specifically included in this thesis and discussed below.

Field studies were conducted on August 5-6, August 13-14, August 18-19, August 26-27, September 3-4, September 9-10, September 14-15, September 23-24, and September 28-29, 1982.

August 5-6, 1982. The August 5-6 field study was conducted in a region of high marsh adjacent to a sandy mud flat. The marsh surface inside the chamber consisted primarily of Spartina-patens with Spartina-alterniflora growth present in smaller amounts. Soil temperatures ranged from ~25 to 32°C, and the site was covered at high tide. Maximum and minimum air temperatures were ~30 and 23°C, respectively. The use of soda lime to scrub chamber purge air was being tested in line between the Drierite-filled cylinders and the cryotrap. However, the cryotrap became totally iced up after a period of ~5 hours (a 2-hour equilibration period plus two sampling periods 1 hour apart). The cryotrap was transported back to the laboratory and oven-dried. Once the cryotrap had been replaced and a second equilibration period begun using fresh soda lime, it became apparent that it was the soda lime that was causing the icing. The cryotrap was removed and the air was scrubbed by the soda lime trap only. The experiment was halted early because it was not clear that the soda lime would clean the air sufficiently, and because Nafion driers were in short supply and the moist inlet air required drying before it could be collected. Fortunately, the resulting  $\bar{C}_0$  values (~50 pptv) were low enough to distinguish a difference from  $\bar{C}$ . Figures 22 and 24 present the results of this flux study for OCS and H<sub>2</sub>S. Figure 25 shows the behavior of the concentrations measured for OCS, H<sub>2</sub>S, and CS<sub>2</sub>.

August 13-14, 1982. The August 13-14 field study was conducted at the same site as the August 5-6 experiment, with rain daily during the previous week (a total of 1.4" of rainfall). Soil temperatures

**AUGUST 5-6, 1982 FIELD STUDY  
SOIL TEMPERATURES, LIGHT INTENSITIES, AND TIME-AVERAGED  
OSC CONCENTRATIONS AND EMISSIONS VS. TIME**

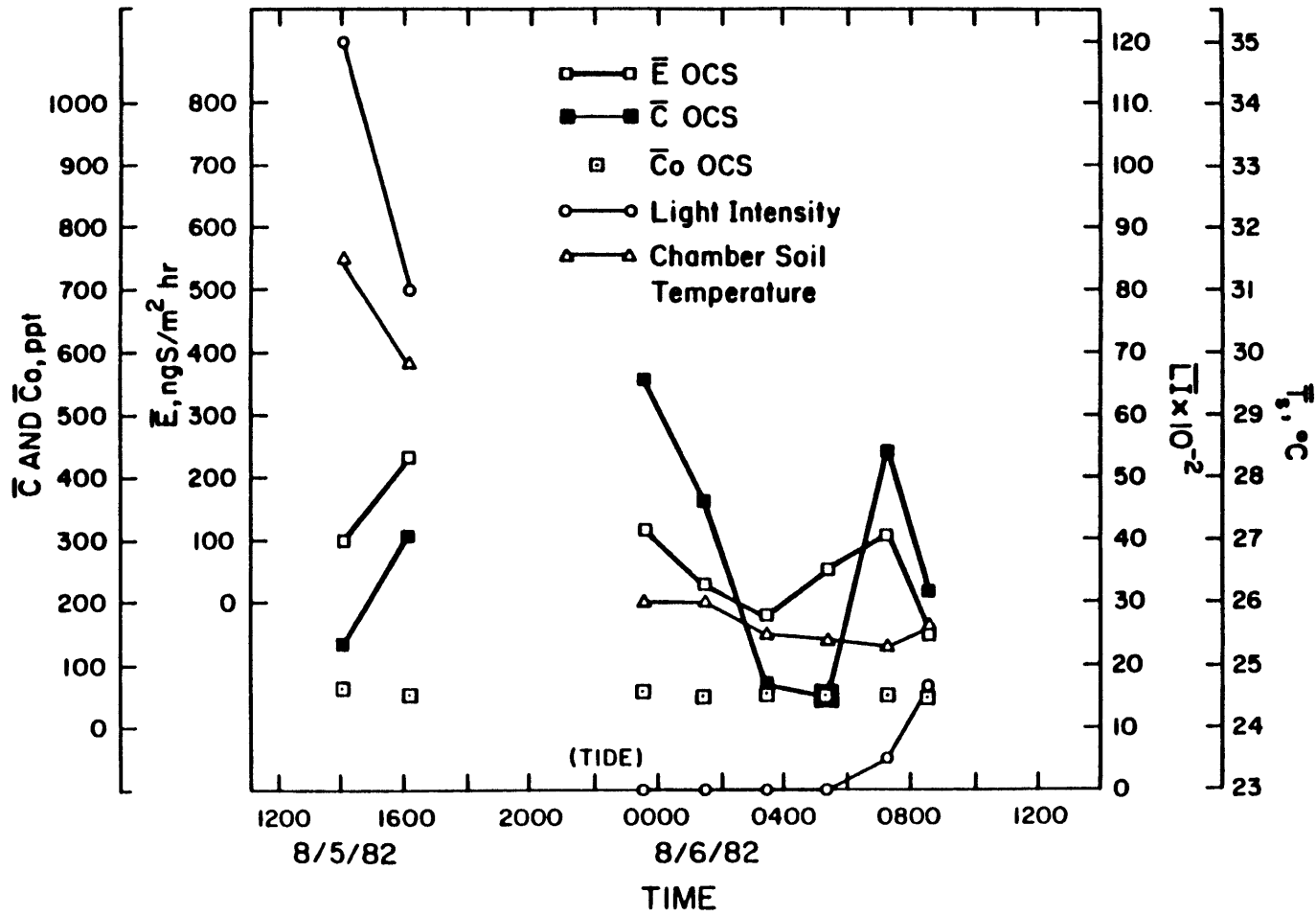


Fig. 23 August 5-6, 1982 field study: OCS fluxes

AUGUST 5-6, 1982 FIELD STUDY  
 SOIL TEMPERATURES, LIGHT INTENSITIES, AND TIME-AVERAGED  
 H<sub>2</sub>S CONCENTRATIONS AND EMISSIONS VS. TIME

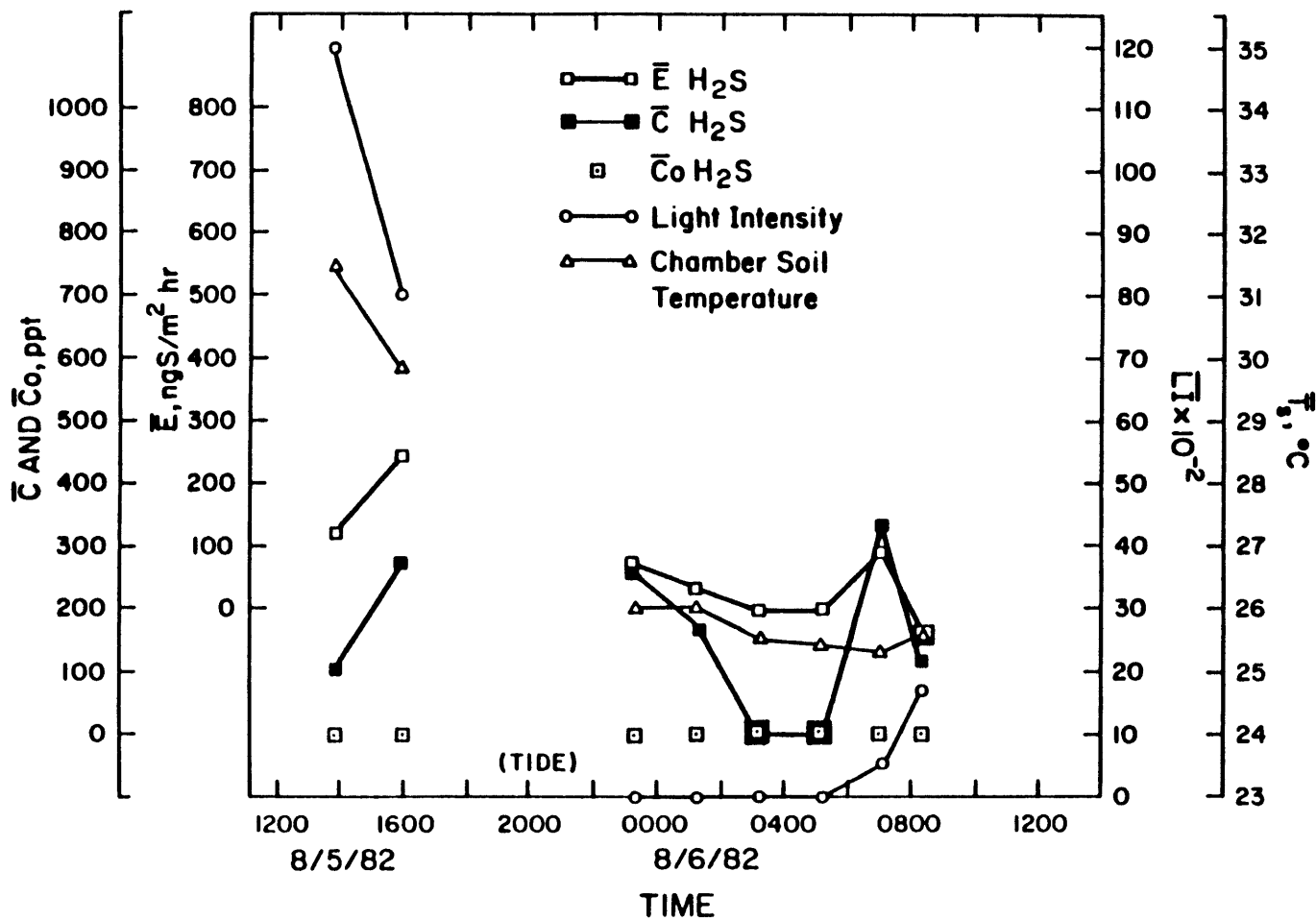


Fig. 24 August 5-6, 1982 field study: H<sub>2</sub>S fluxes

AUGUST 5 - 6, 1982 FIELD STUDY  
 TIME-AVERAGED CONCENTRATIONS  
 OF OCS, H<sub>2</sub>S, AND CS<sub>2</sub> VS TIME

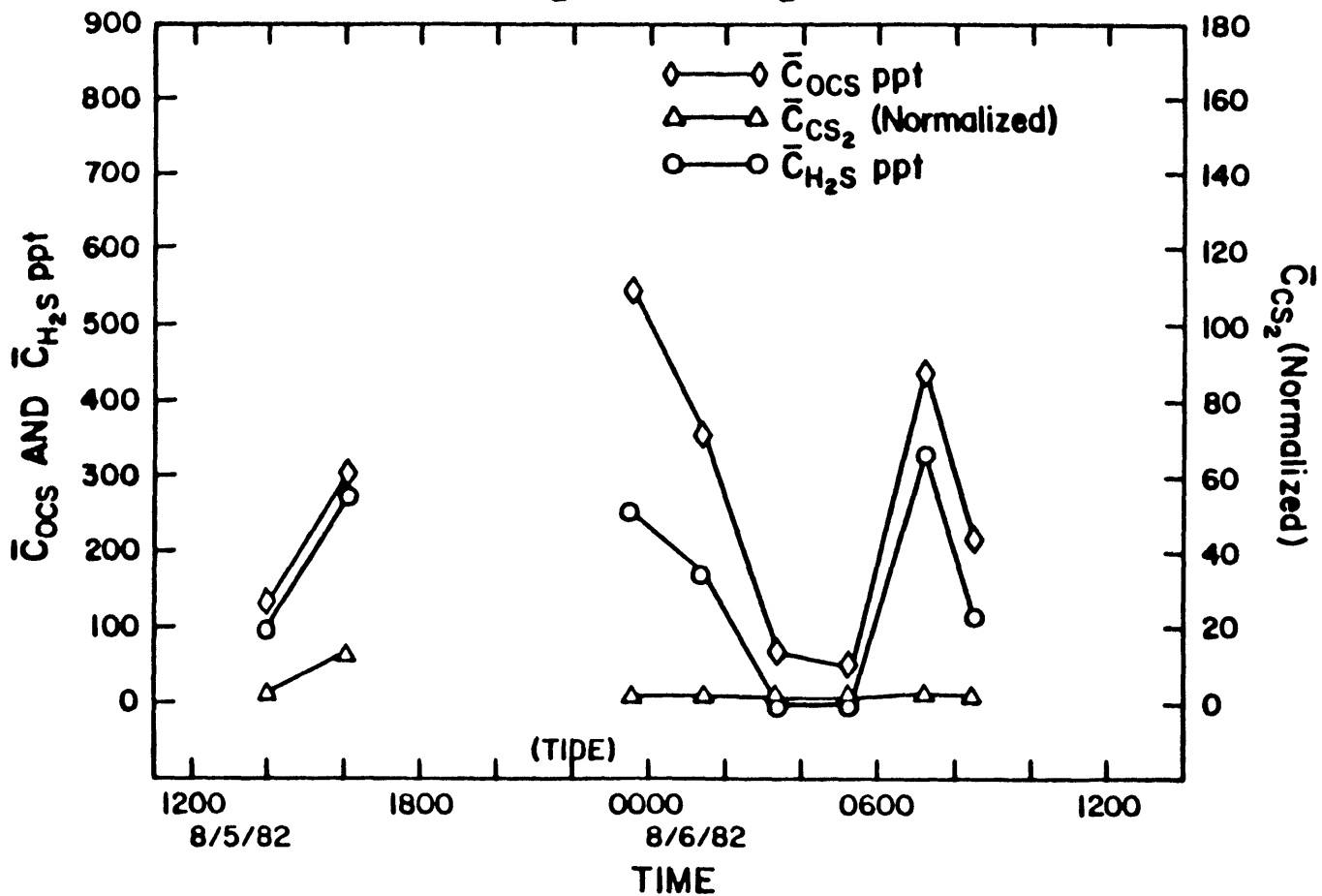


Fig. 25 August 5-6, 1982 field study: OCS, H<sub>2</sub>S and CS<sub>2</sub> concentrations

ranged from ~21 to 29°C, and air temperatures ranged from ~16 to 30°C. Soda lime was not used to scrub chamber air. After a 3 hr equilibration period at a chamber purge flow rate of 4.2  $\text{l min}^{-1}$ , samples were collected as described in Chapter 3. The calculated fluxes for OCS and H<sub>2</sub>S are presented in Figs. 26 and 27. The patterns of OCS, H<sub>2</sub>S and CS<sub>2</sub> concentrations are shown in Fig. 28.

August 18-19, 1982. The August 18-19 field study was conducted over a mixed-stand of S. alterniflora and S. patens, in an area of organic-rich soils (evidenced by the very dark soil color). The rest of the field studies were also conducted at this site. There had been heavy rainfall (.15") the previous night, and the site was covered (~5") during high tide. Soil temperatures ranged from ~22 to ~35°C and air temperatures ranged from ~18 to 29°C. A chamber/marsh equilibration period of 3 hrs with a chamber purge flow rate of 4.2  $\text{l min}^{-1}$  was allowed before sample collection was begun. Flux results for OCS and H<sub>2</sub>S are presented in Figs. 29 and 30. The behavior of OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations is shown in Fig. 31. Diurnal variations with nighttime loss except after site flooding were observed for all three gases.

August 26-27, 1982. August 26 and 27 were clear and warm days. There had been a total of .1" of precipitation within the previous week, and tides did not inundate the site. There had been no tidal influence for three or four days. Maximum and minimum air temperatures were ~28 and 14°C, respectively, and soil temperatures ranged from ~18 to 30°C. This week the equilibration period was 2 hrs with a chamber purge flow of ~5  $\text{l min}^{-1}$ . A loosely-woven, light-weight



**AUGUST 13-14, 1982      FIELD STUDY**  
**TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,**  
**OCS CONCENTRATIONS, AND OCS EMISSIONS VS. TIME**

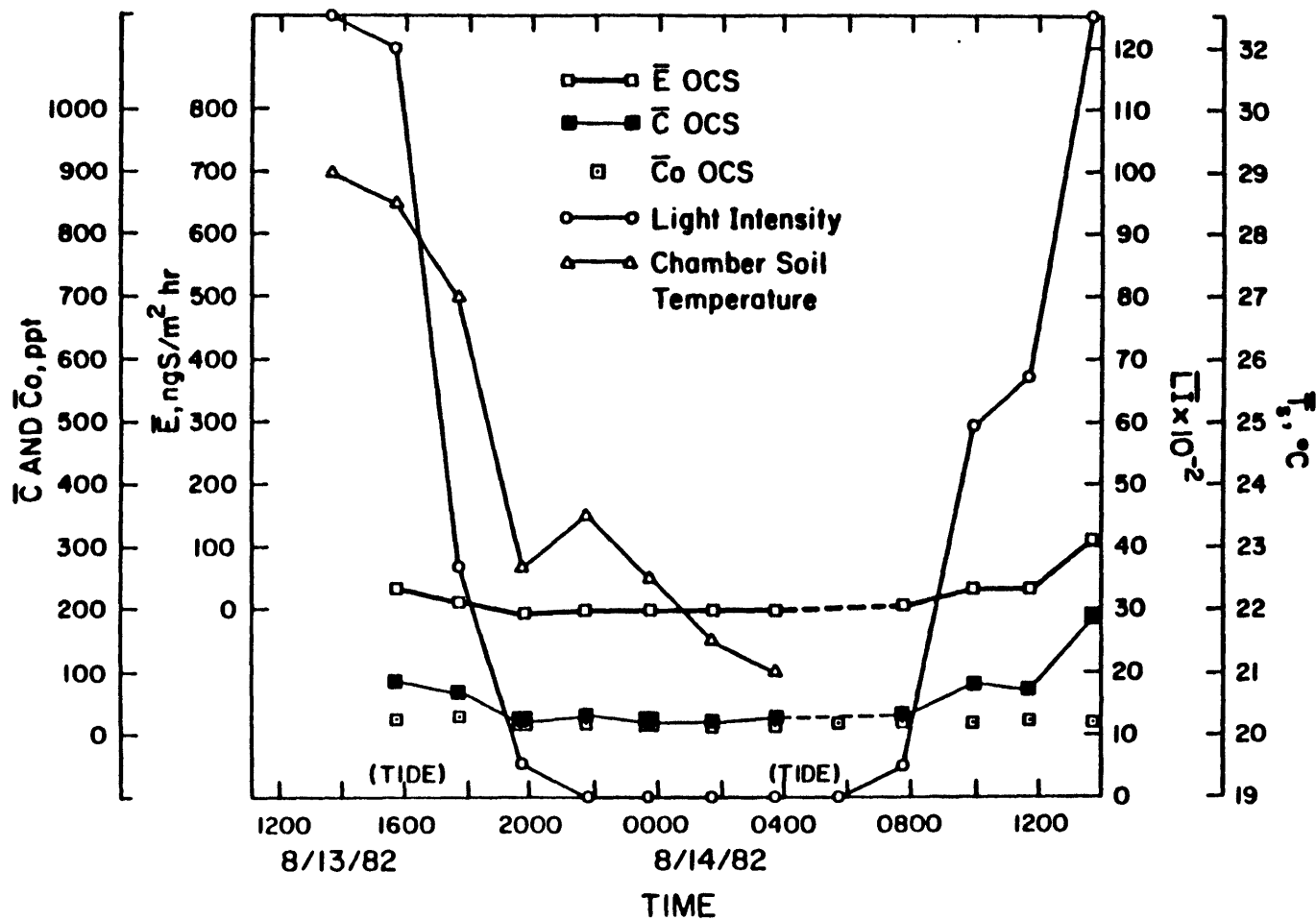


Fig. 26 August 13-14, 1982 field study: OCS fluxes

AUGUST 13-14, 1982      FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME

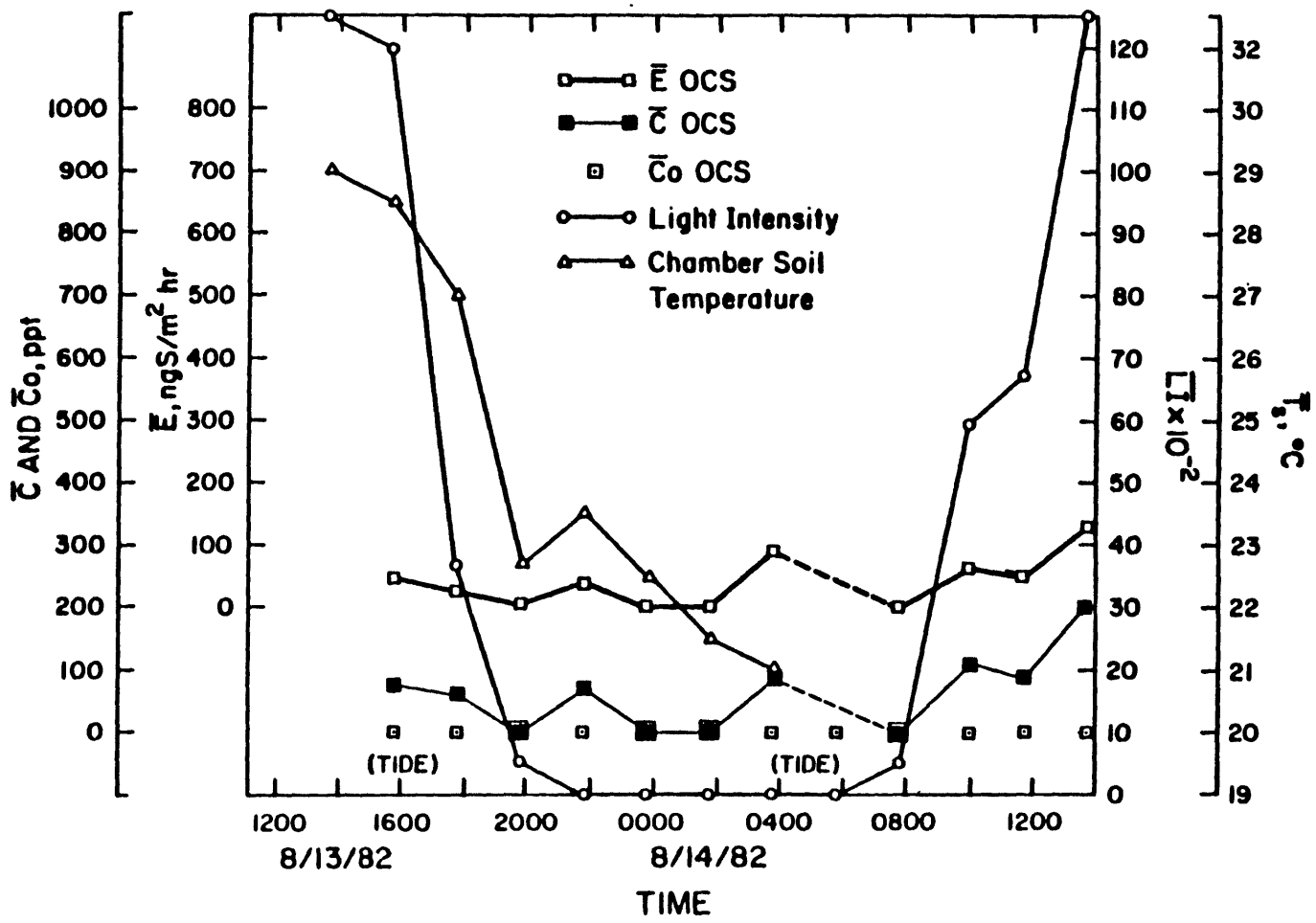


Fig. 27 August 13-14, 1982 field study: H<sub>2</sub>S fluxes

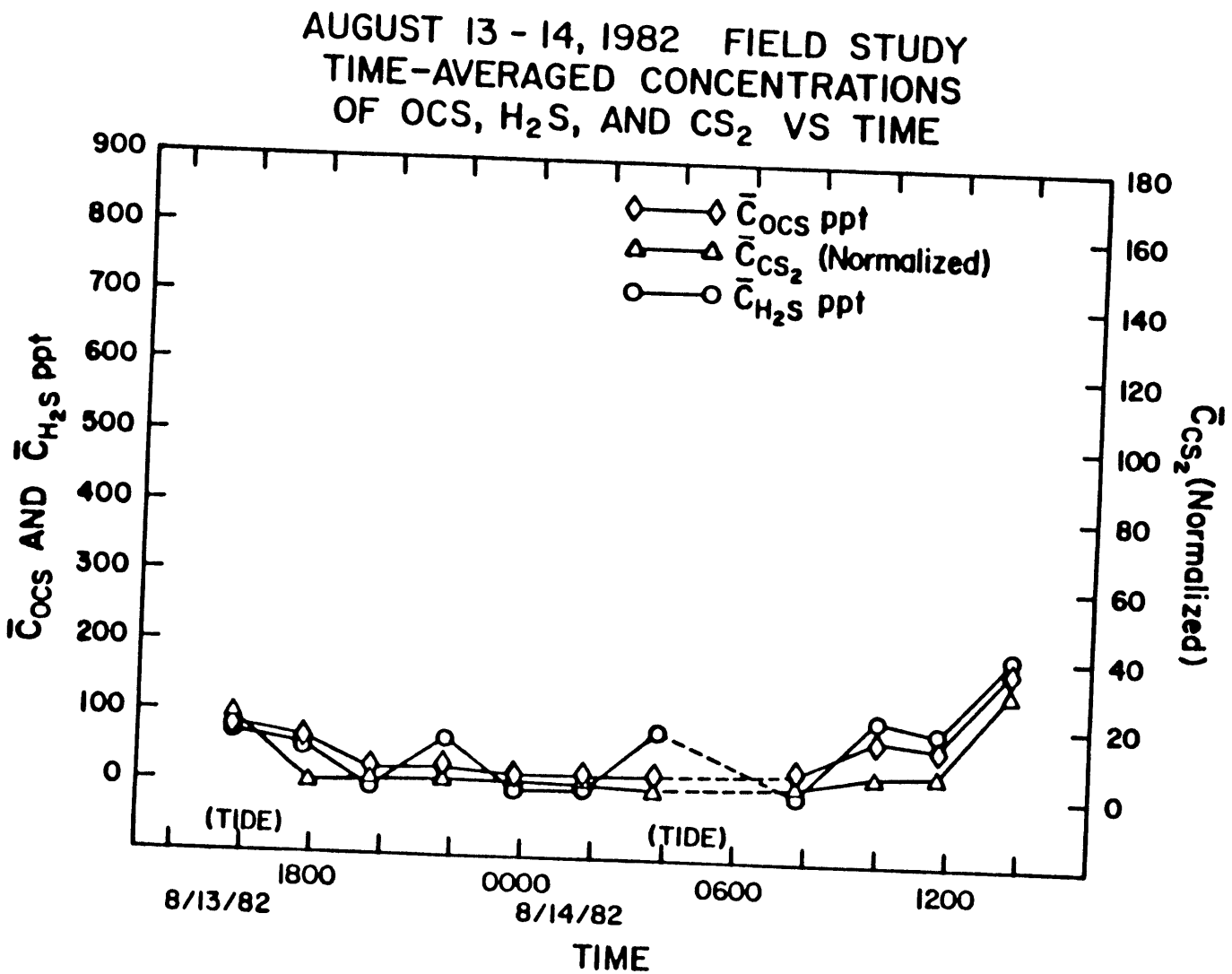


Fig. 28 August 13-14, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations

**AUGUST 18-19, 1982 FIELD STUDY**  
**TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,**  
**OCS CONCENTRATIONS, AND OCS EMISSIONS VS. TIME**

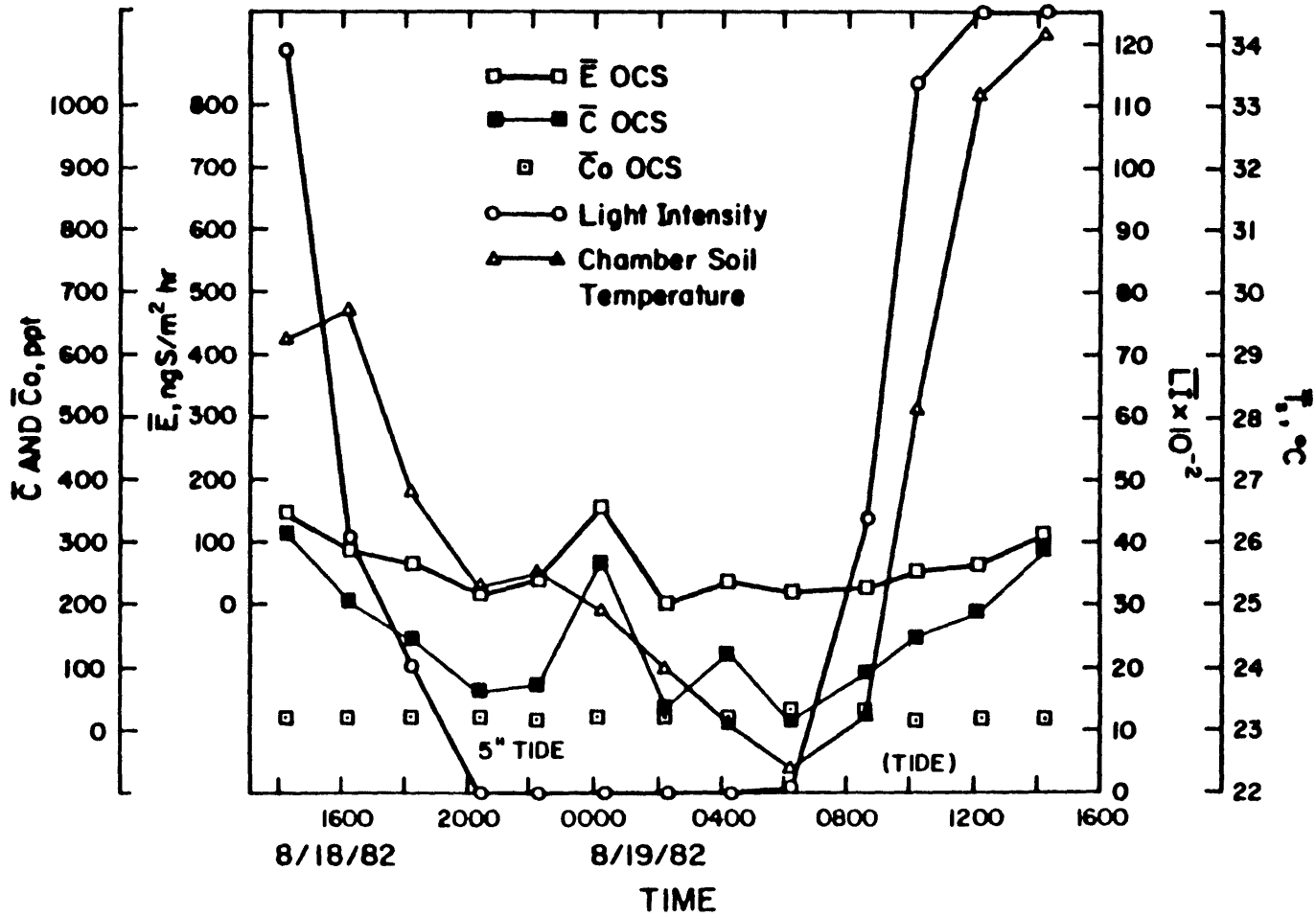


Fig. 29 August 18-19, 1982 field study: OCS fluxes

**AUGUST 18-19, 1982 FIELD STUDY**  
**TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,**  
**H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME**

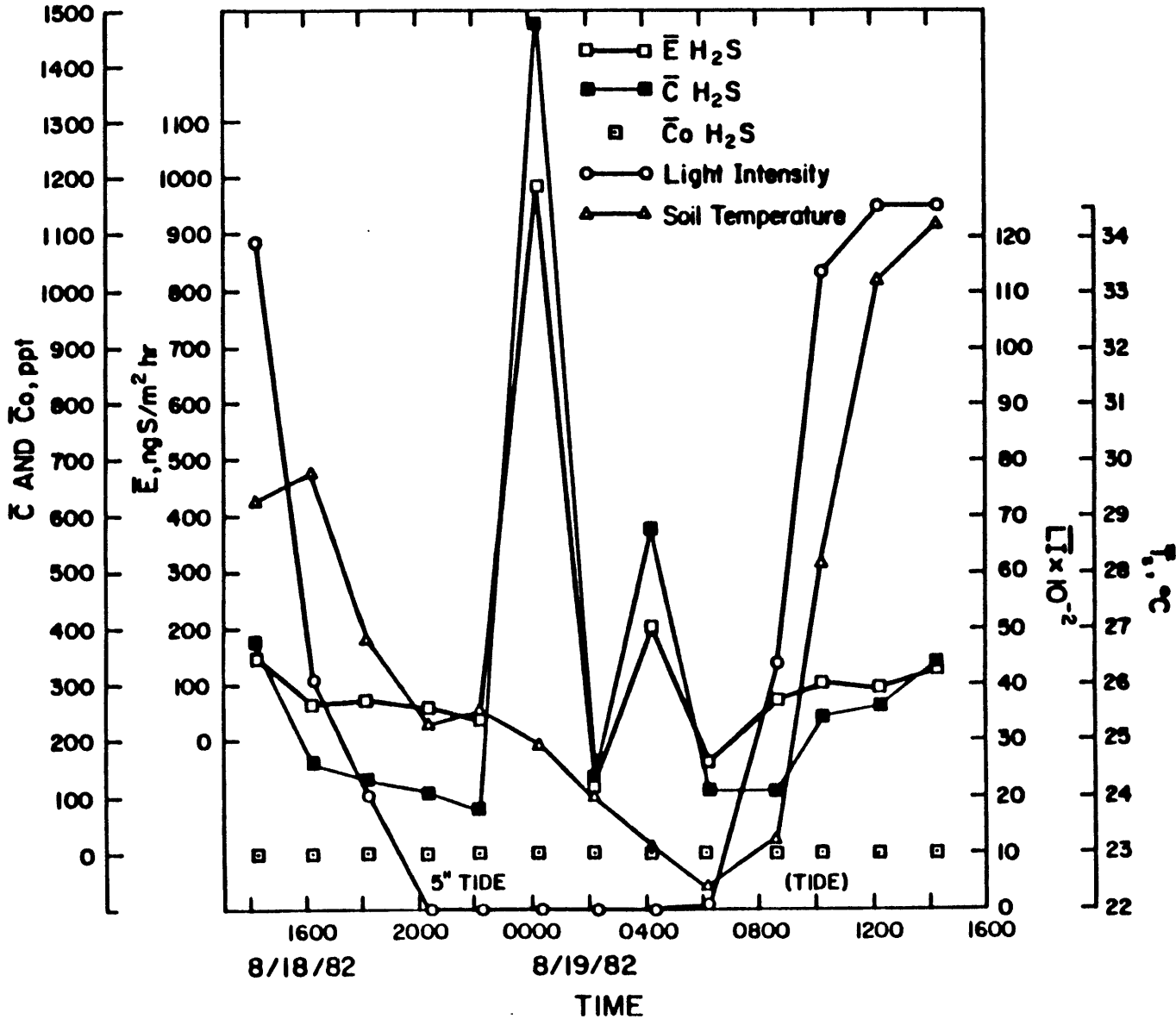


Fig. 30 August 18-19, 1982 field study: H<sub>2</sub>S fluxes

AUGUST 18-19, 1982 FIELD STUDY  
 TIME-AVERAGED CONCENTRATIONS  
 OF OCS, H<sub>2</sub>S, AND CS<sub>2</sub> VS. TIME

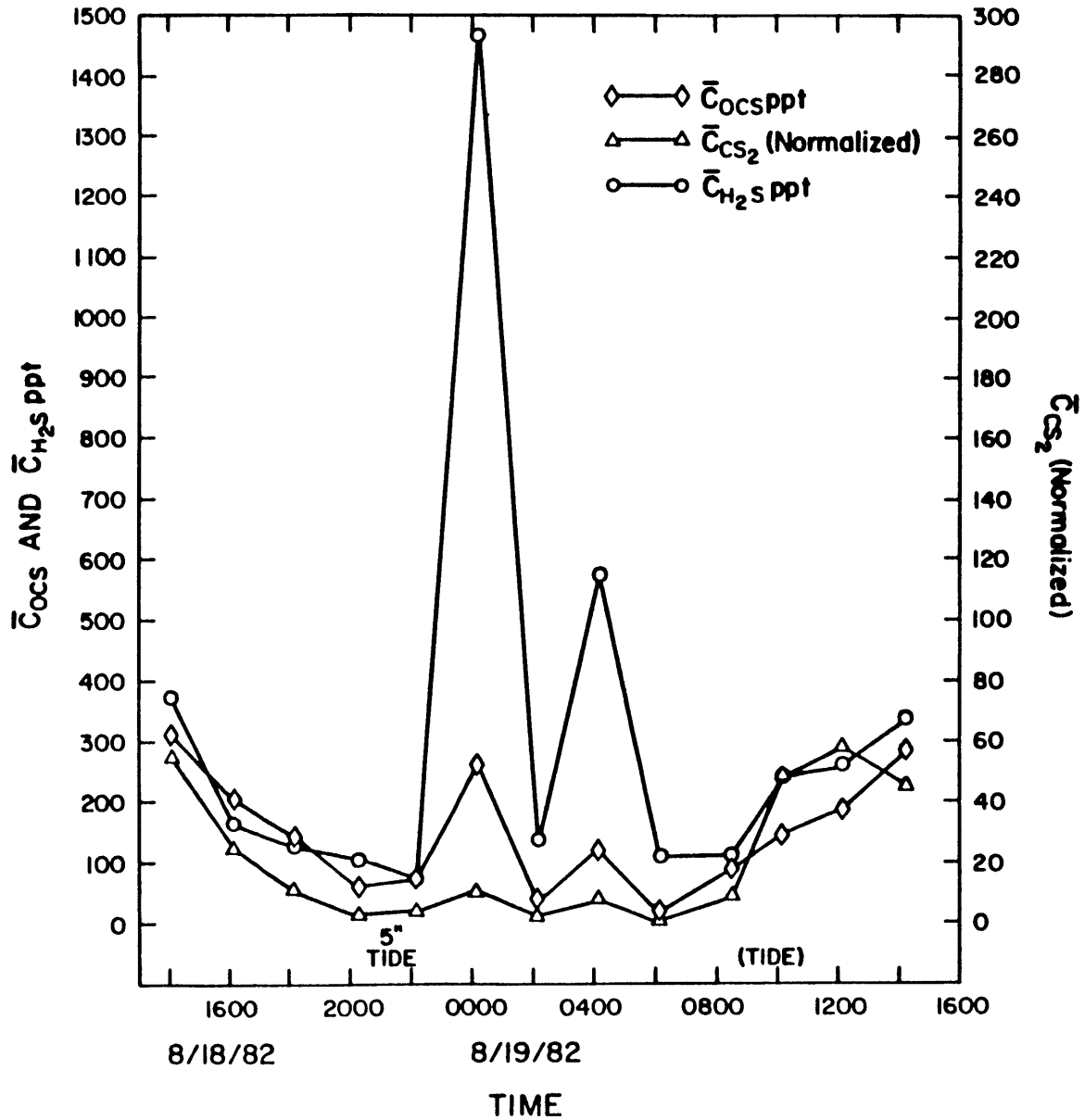


Fig. 31 August 18-19, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations

white cloth was used to shade the chamber during this experiment and during the remaining experiments. Calibrated thermocouples (see Appendix IV) were used to measure air and soil temperatures both inside and outside the chamber during this and all remaining field studies. The trend of OCS chamber outlet concentrations going to values  $\sim \bar{C}_0$  at night was again observed. The correlation between  $\bar{E}$  and light intensity appears to be stronger than the correlation between  $\bar{E}$  and soil temperature. For example, here  $\bar{E}$  was observed to fall to zero with light intensity equal to zero and soil temperature  $\sim 23^\circ\text{C}$ , whereas under daytime conditions at the same soil temperature,  $\bar{E}$  was observed to be greater than zero. Soil moisture appears to be as highly correlated with  $\bar{E}$  as light intensity. The OCS and  $\text{H}_2\text{S}$  flux results are presented in Figs. 32 and 33;  $\text{H}_2\text{S}$  and OCS concentrations followed similar patterns as shown, with  $\text{CS}_2$  concentrations, in Fig. 34.

September 3-4, 1982. The September 3-4 field study was conducted after one week without rain or tidal coverage. Soil temperatures ranged from  $\sim 19$  to  $35^\circ\text{C}$ , and air temperatures ranged from  $\sim 15$  to  $34^\circ\text{C}$ . This experiment's equilibration period consisted of 2.8 hrs at a chamber purge flow rate of  $4.2 \text{ l min}^{-1}$ . The OCS and  $\text{H}_2\text{S}$  fluxes are presented in Figs. 35 and 36. OCS,  $\text{H}_2\text{S}$ , and  $\text{CS}_2$  concentrations are shown in Fig. 37.

September 9-10, 1982. The conditions for the September 9-10 field study were a prior period of 13 days without precipitation and hot, sunny weather. There had been no tidal coverage of the site within the last two weeks until this date when the site was covered by

AUGUST 26-27, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 OCS CONCENTRATIONS, AND OCS EMISSIONS VS. TIME

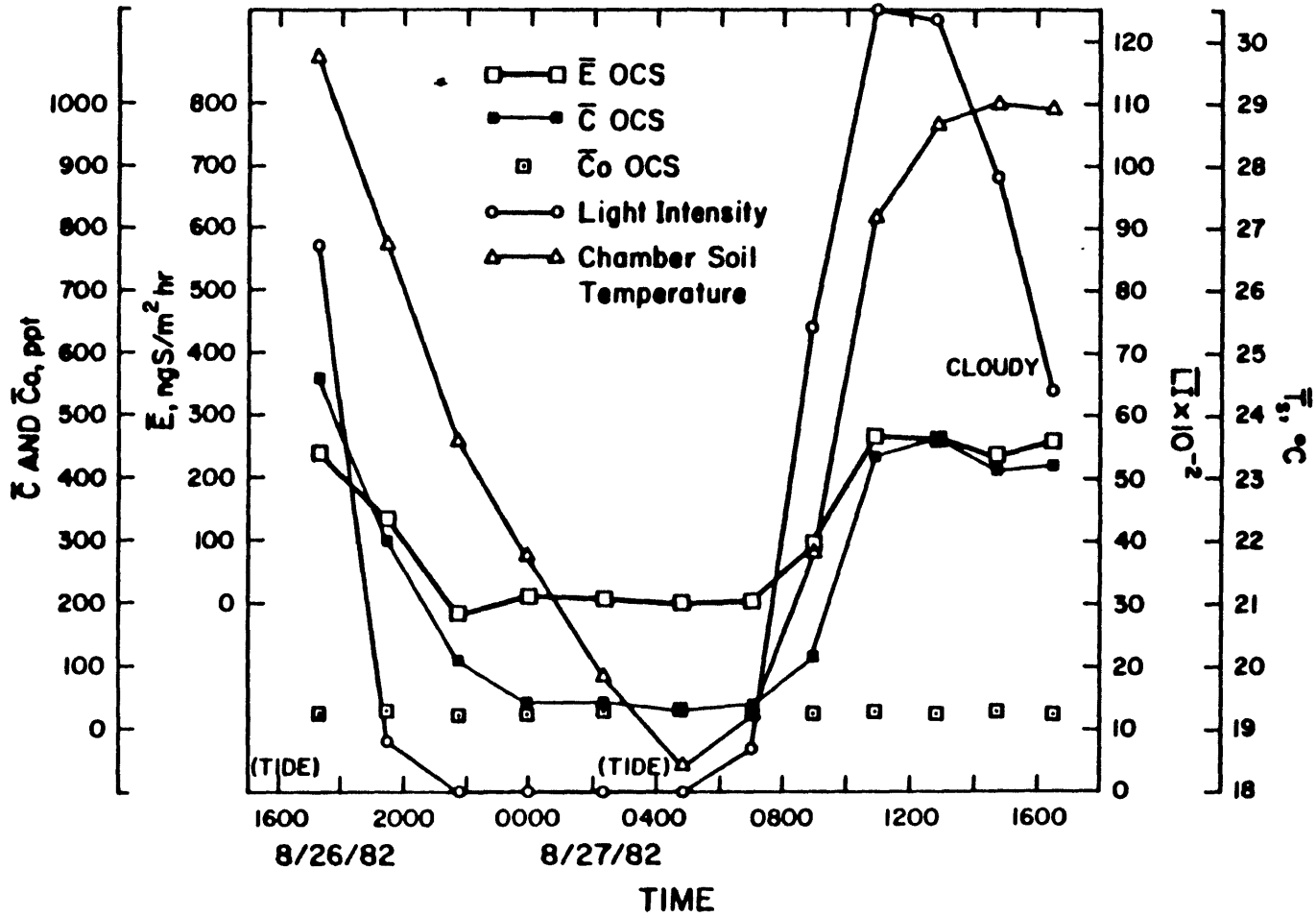


Fig. 32 August 26-27, 1982 field study: OCS fluxes



**AUGUST 26-27, 1982 FIELD STUDY**  
**TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,**  
**H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME**

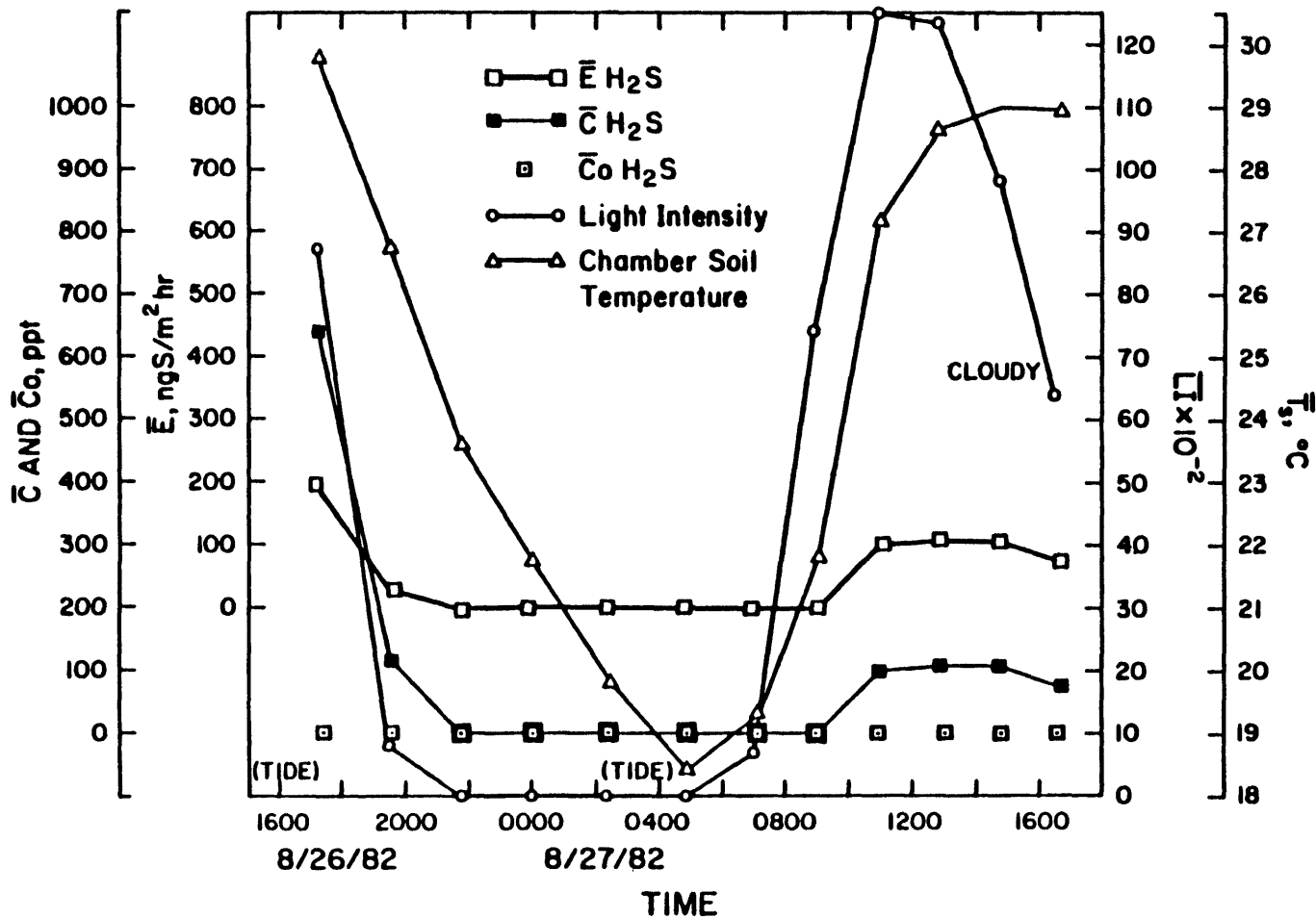


Fig. 33 August 26-27, 1982 field study: H<sub>2</sub>S fluxes

AUGUST 26 - 27, 1982 FIELD STUDY  
 TIME-AVERAGED CONCENTRATIONS  
 OF OCS, H<sub>2</sub>S, AND CS<sub>2</sub> VS TIME

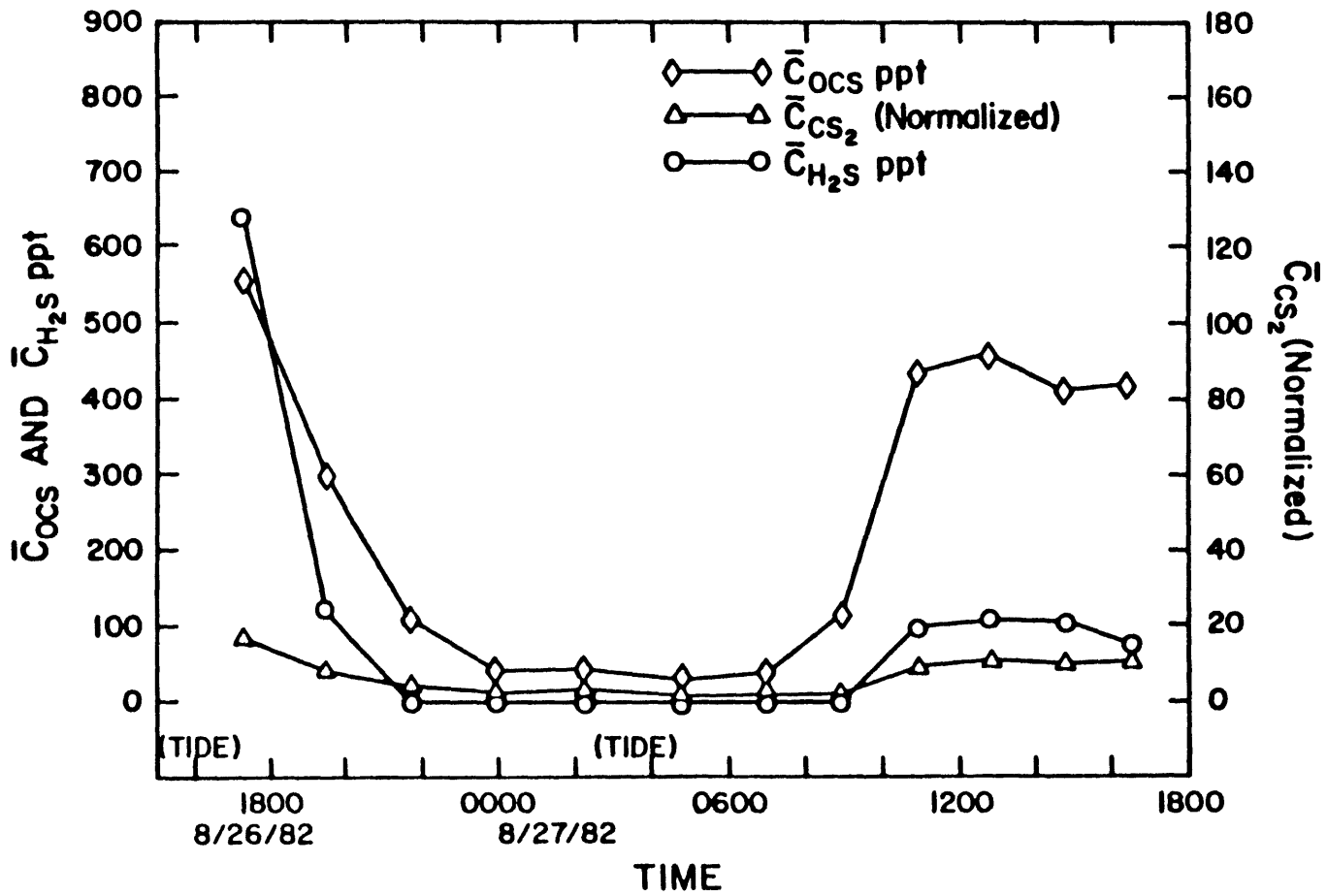


Fig. 34 August 26-27, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations

SEPTEMBER 3-4, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 OCS CONCENTRATIONS, AND OCS EMISSIONS VS. TIME

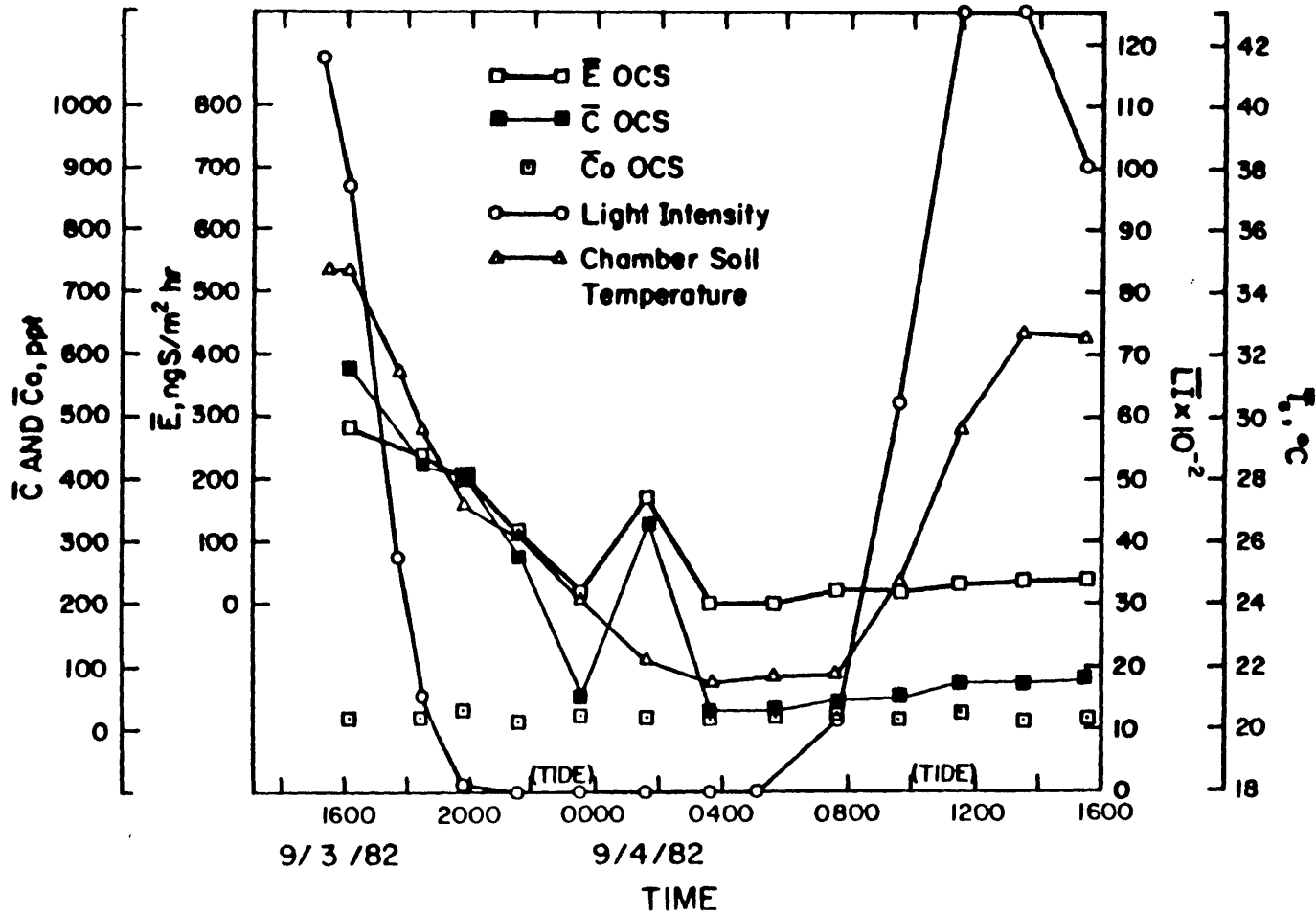


Fig. 35 September 3-4, 1982 field study: OCS fluxes

SEPTEMBER 3-4, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME

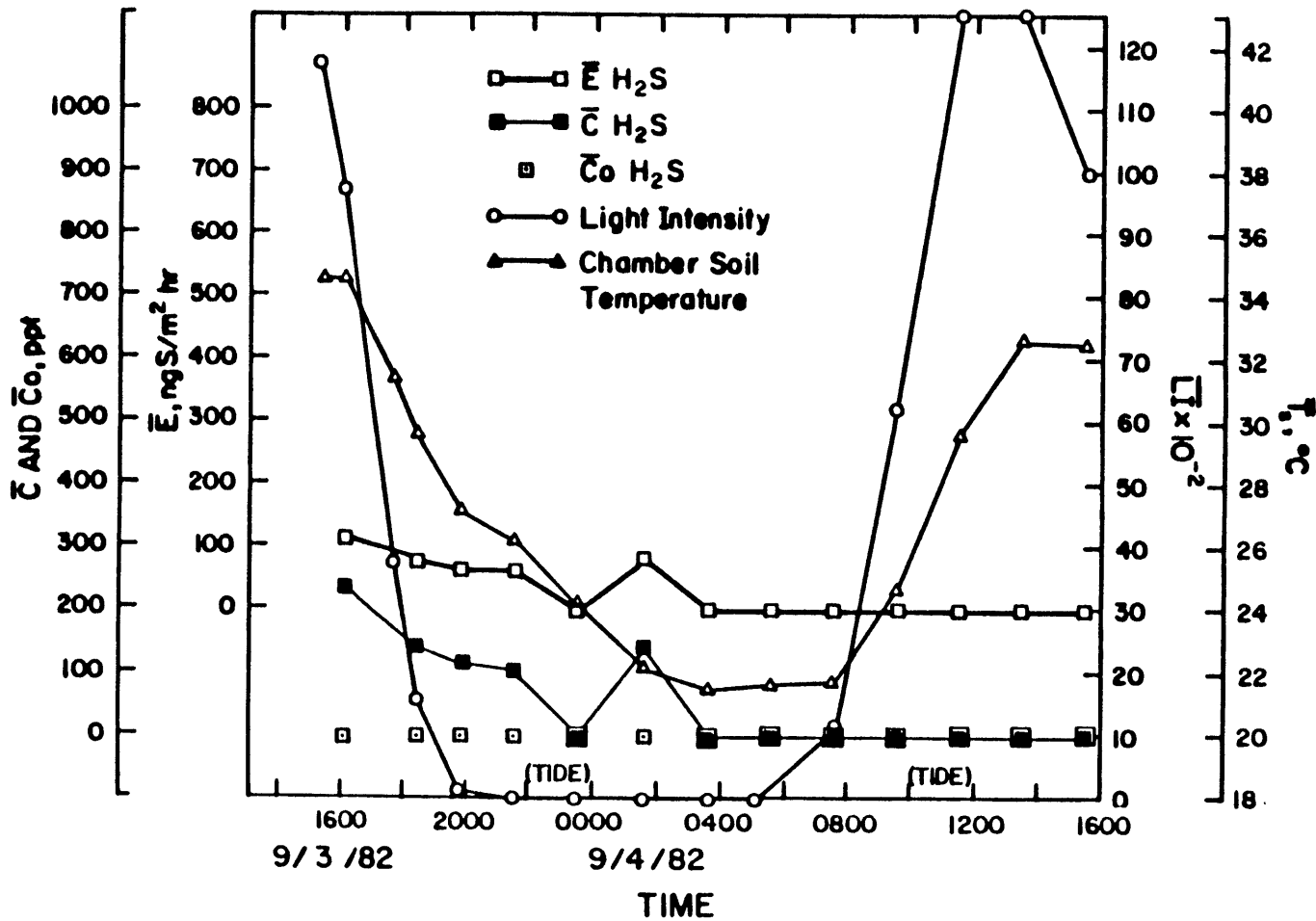


Fig. 36 September 3-4, 1982 field study: H<sub>2</sub>S fluxes

SEPTEMBER 3 - 4, 1982 FIELD STUDY  
 TIME-AVERAGED CONCENTRATIONS  
 OF OCS, H<sub>2</sub>S, AND CS<sub>2</sub> VS TIME

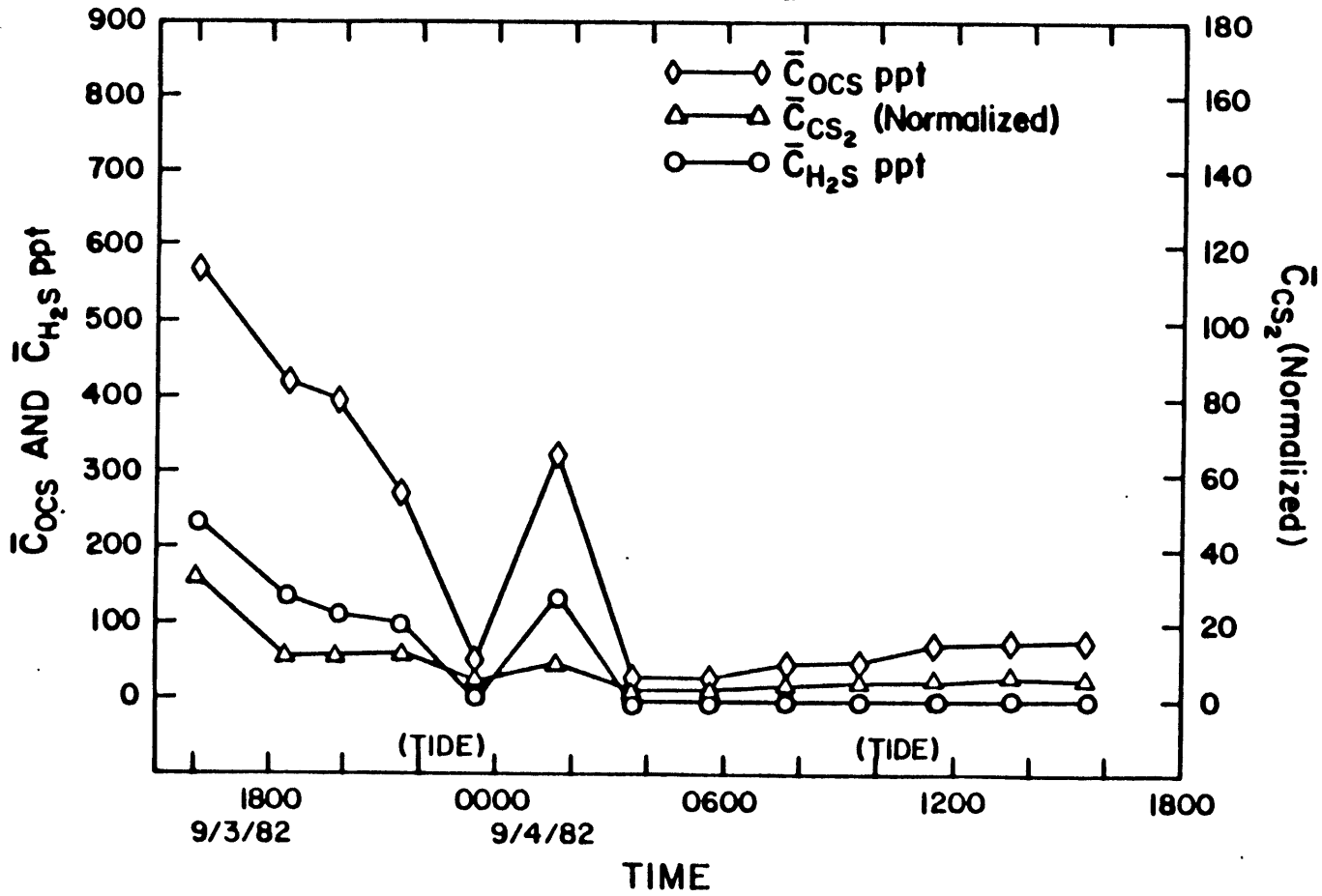


Fig. 37 September 3-4, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations

1"-1.5" of water during high tide. An equilibration period of 2 hrs with a  $\sim 5 \text{ l min}^{-1}$  chamber purge flow was allowed before sample collection was begun. Maximum and minimum air temperatures were  $\sim 29$  and  $9^\circ\text{C}$  respectively, and soil temperatures ranged from  $\sim 12$  to  $28^\circ\text{C}$ . The soil was dry and highly porous. It is not known if the bacterial activity which reduces  $\text{SO}_4^{=}$  to  $\text{S}^{=}$  halts with low moisture, the  $\text{S}^{=}$  formed is oxidized by the aerated soil, or both. The OCS and  $\text{H}_2\text{S}$  flux results are presented in Figs. 38 and 39. OCS,  $\text{H}_2\text{S}$ , and  $\text{CS}_2$  concentrations are shown in Fig. 40.

September 14-15, 1982. The September 14-15 field study was conducted 5 days later and reflects the influence of soil moisture on  $\bar{E}$ . 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 routinely observed during tidal episodes. Similar behavior was observed in all experiments where the tide influenced the site during the 25-hour study. The maximum and minimum air temperatures were  $\sim 29$  and  $12^\circ\text{C}$ , respectively, and soil temperatures ranged from  $\sim 15$  to  $32^\circ\text{C}$ . Conditions were hot and hazy. Chamber equilibration consisted of 2 hrs with a chamber purge flow rate of  $\sim 5 \text{ l min}^{-1}$ . The OCS and  $\text{H}_2\text{S}$  flux results are presented in Figs. 41 and 42, and OCS,  $\text{H}_2\text{S}$ , and  $\text{CS}_2$  concentrations are shown in Fig. 43. This type of behavior for  $\text{CS}_2$ , concurrent with standing water inside the chamber, was observed during several but not all tidal episodes.

September 23-24, 1982. The September 23-24 field study was conducted immediately following a four-day "nor'easter," a storm that

SEPTEMBER 9-10, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 OCS CONCENTRATIONS, AND OCS EMISSIONS VS. TIME

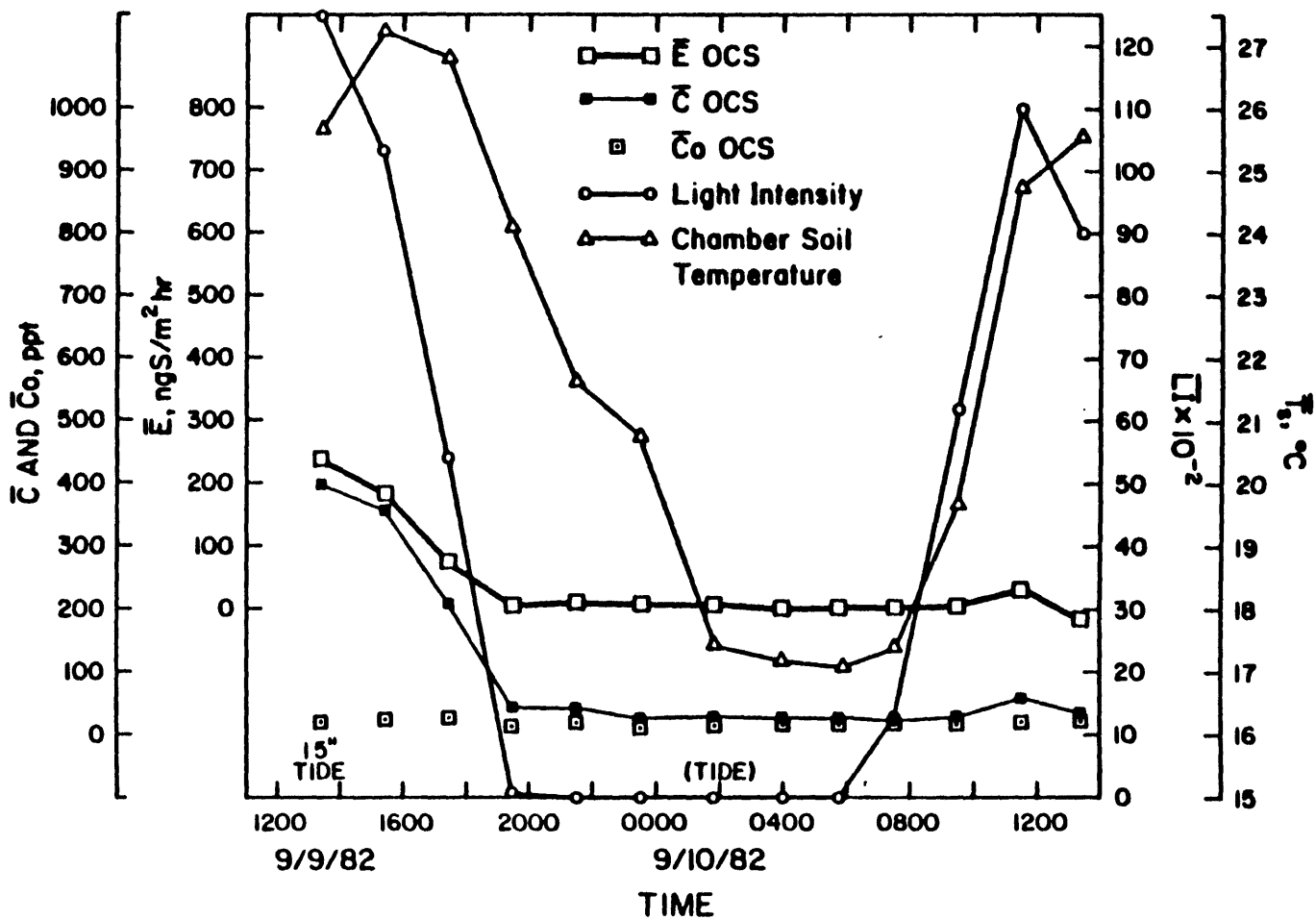


Fig. 38 September 9-10, 1982 field study: OCS fluxes

SEPTEMBER 9-10, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME

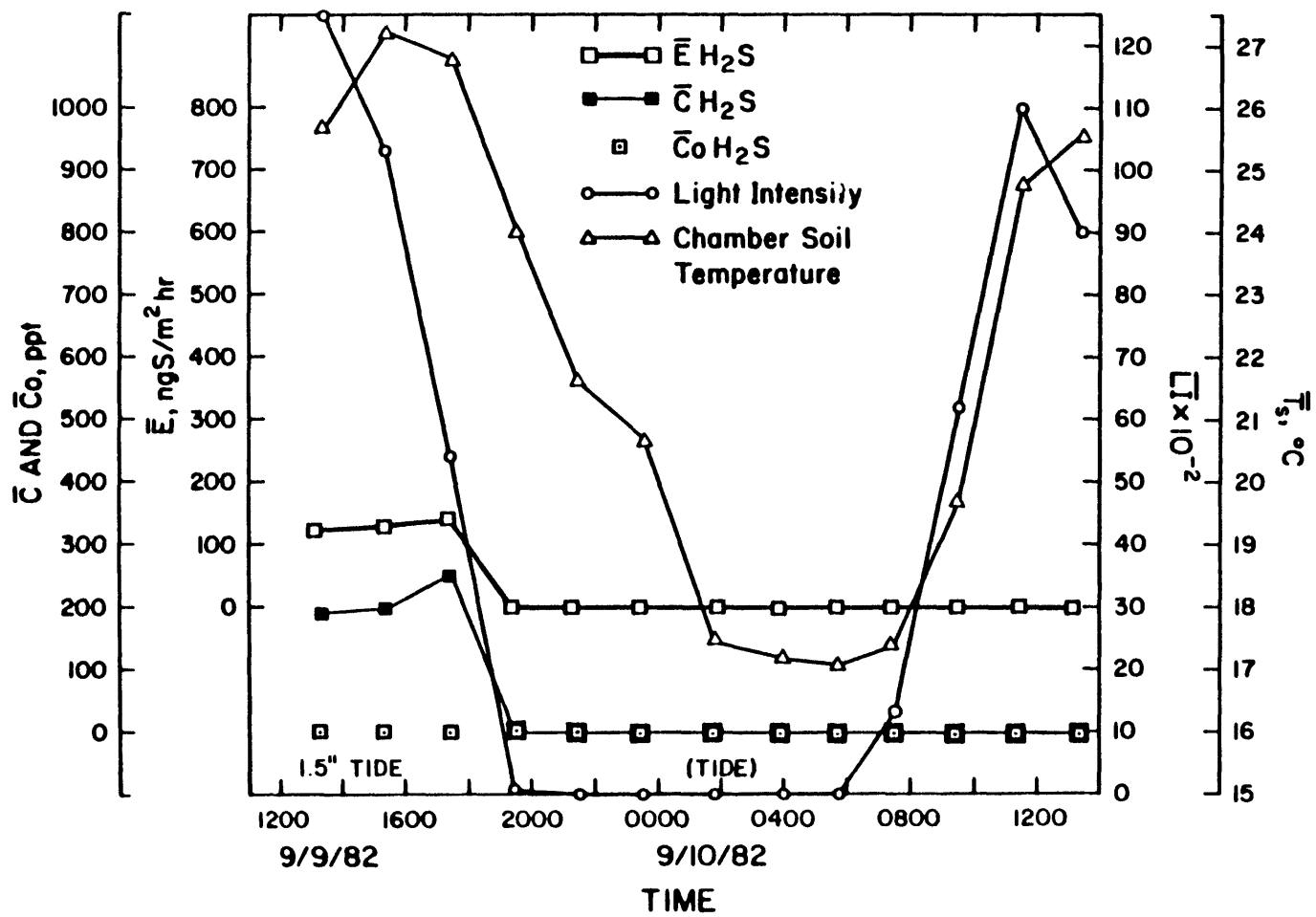


Fig. 39 September 9-10, 1982 field study: H<sub>2</sub>S fluxes



SEPTEMBER 9 - 10, 1982 FIELD STUDY  
 TIME-AVERAGED CONCENTRATIONS  
 OF OCS, H<sub>2</sub>S, AND CS<sub>2</sub> VS TIME

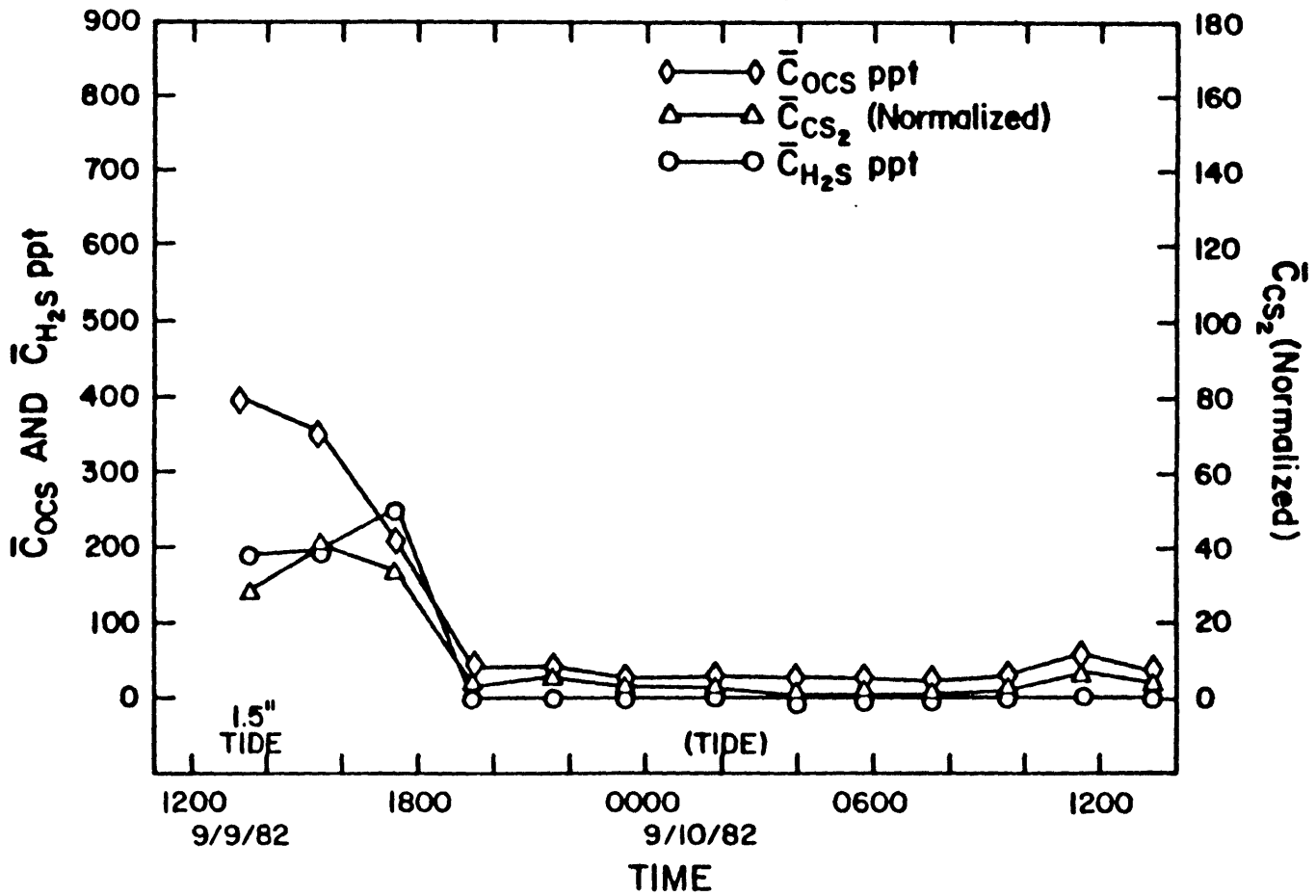


Fig. 40 September 9-10, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations

SEPTEMBER 14-15, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 OCS CONCENTRATIONS, AND OCS EMISSIONS VS. TIME

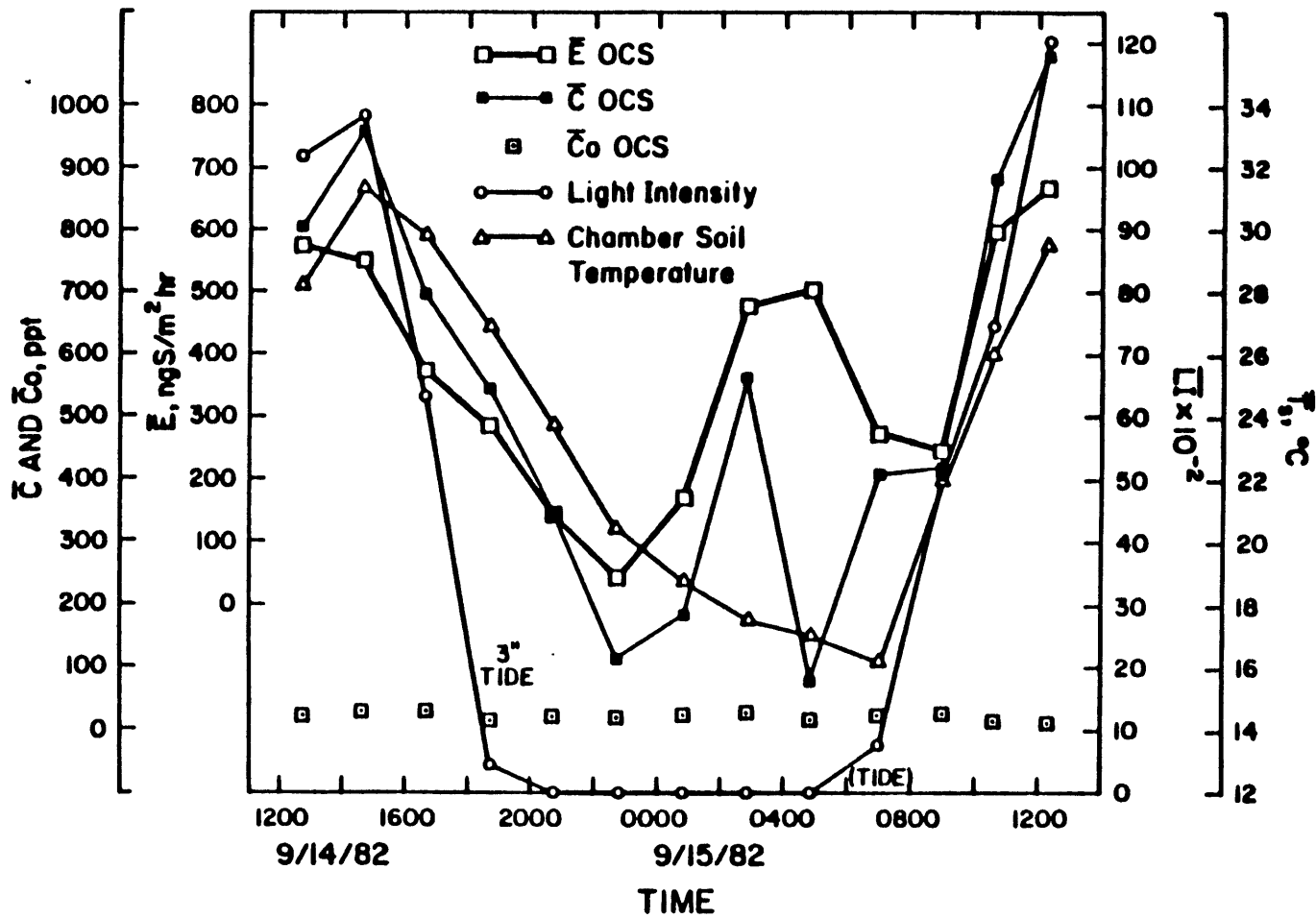


Fig. 41 September 14-15, 1982 field study: OCS fluxes

SEPTEMBER 14-15, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME

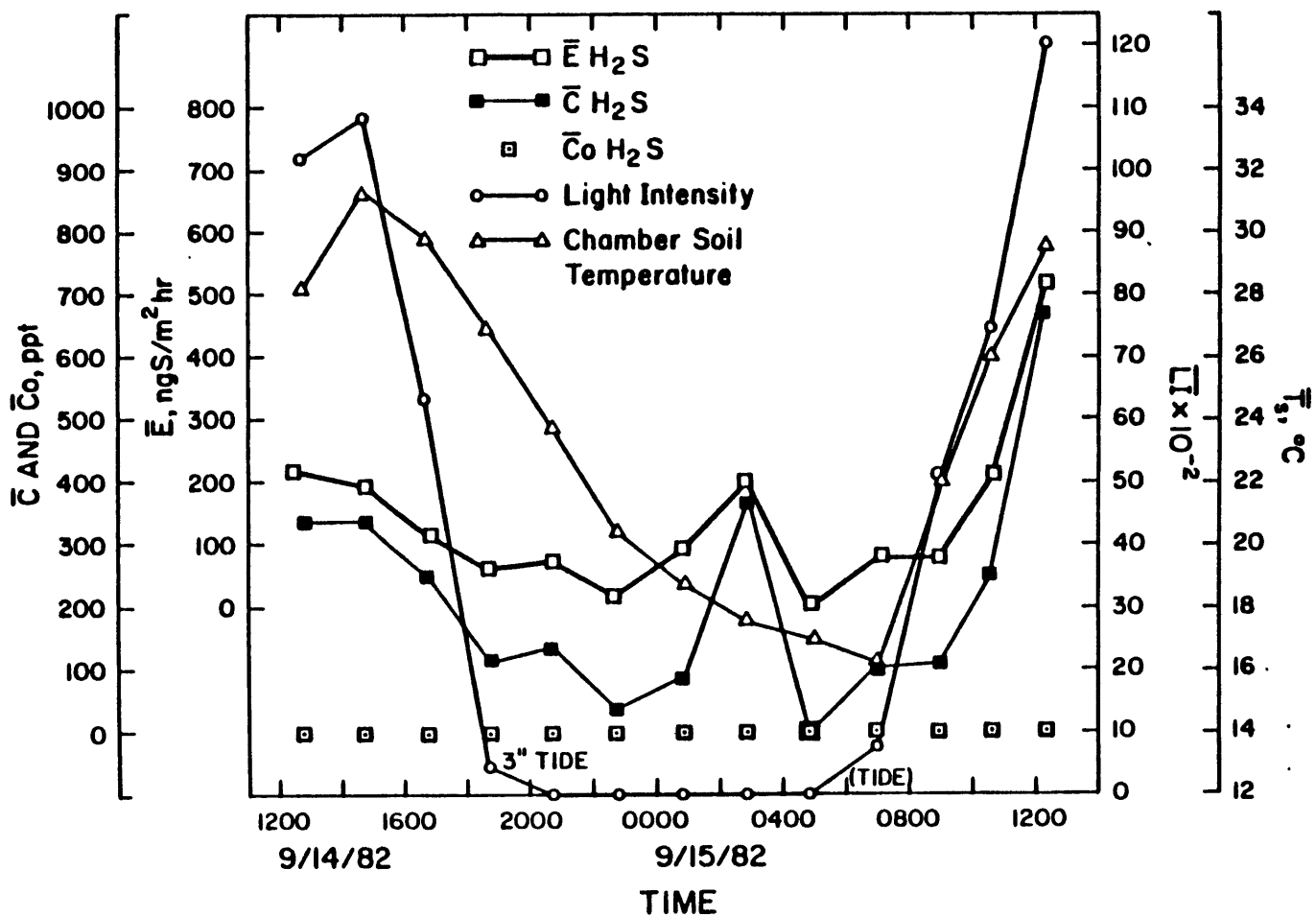


Fig. 42 September 14-15, 1982 field study: H<sub>2</sub>S fluxes

SEPTEMBER 14-15, 1982 FIELD STUDY  
 TIME-AVERAGED CONCENTRATIONS  
 OF OCS, H<sub>2</sub>S, AND CS<sub>2</sub> VS. TIME

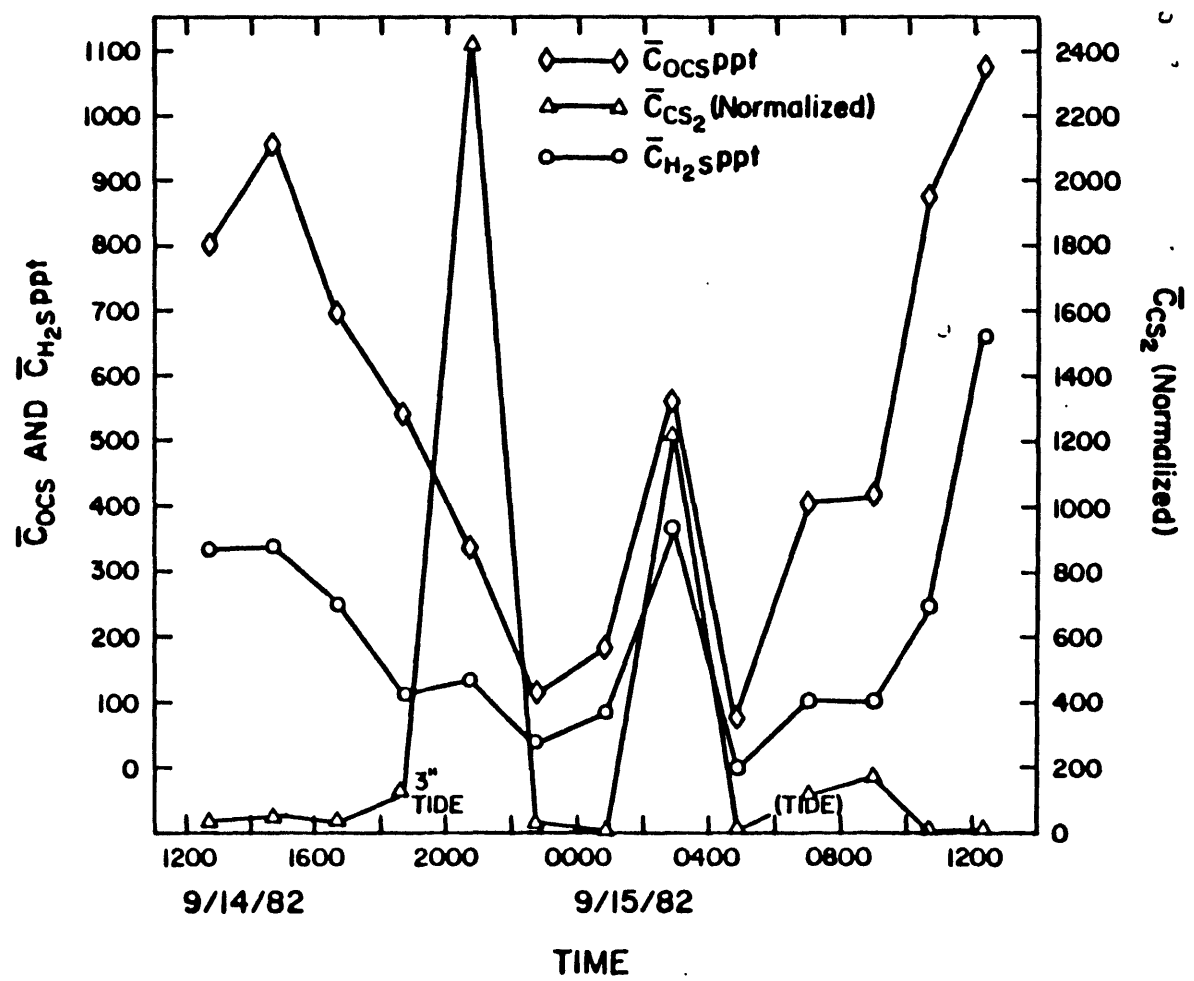


Fig. 43 September 14-15, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations

washed channel waters into the marsh and left the marsh inundated by from ~.25"-4" of water during the entire 25-hour sampling period. Standing water receded gradually, leaving the marsh the wettest it had been during this experiment. There was no obvious high tide site coverage, yet the emissions did not fall to zero overnight. Once again, this reflects the dramatic response of  $\bar{E}$  to soil moisture and to tidal influence. Air temperatures ranged from ~9 to 23°C, and soil temperatures ranged from ~12 to 25°C. Chamber equilibration consisted of 1 hr with a chamber purge flow rate of 10  $\ell$   $\text{min}^{-1}$ . Results for the OCS and H<sub>2</sub>S fluxes are presented in Figs. 44 and 45. As seen in Fig. 46, all three gases were emitted continuously with concentration values never approaching  $\bar{C}_0$ . CS<sub>2</sub> values were high and followed the patterns displayed by both OCS and H<sub>2</sub>S.

September 28-29, 1982. The September 28-29 field study was conducted two days after a second storm had washed channel waters into the marsh. The marsh was noticeably soggy though there was no standing water at the site. Fluxes were high, apparently due to the influence of high soil moisture, and possibly due to the origin of the moisture (channel water is much higher in SO<sub>4</sub><sup>=</sup> than rain water, for example). Soil temperatures ranged from ~13 to 29°C, and air temperatures ranged from ~10 to 30°C. Chamber equilibration consisted of 2 hrs with a chamber purge flow of ~5  $\ell$   $\text{min}^{-1}$ . The OCS and H<sub>2</sub>S flux results are presented in Figs. 47 and 48, while OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentration information for this field study is shown in Fig. 49.

SEPTEMBER 23-24, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 OCS CONCENTRATIONS, AND OCS EMISSIONS VS. TIME

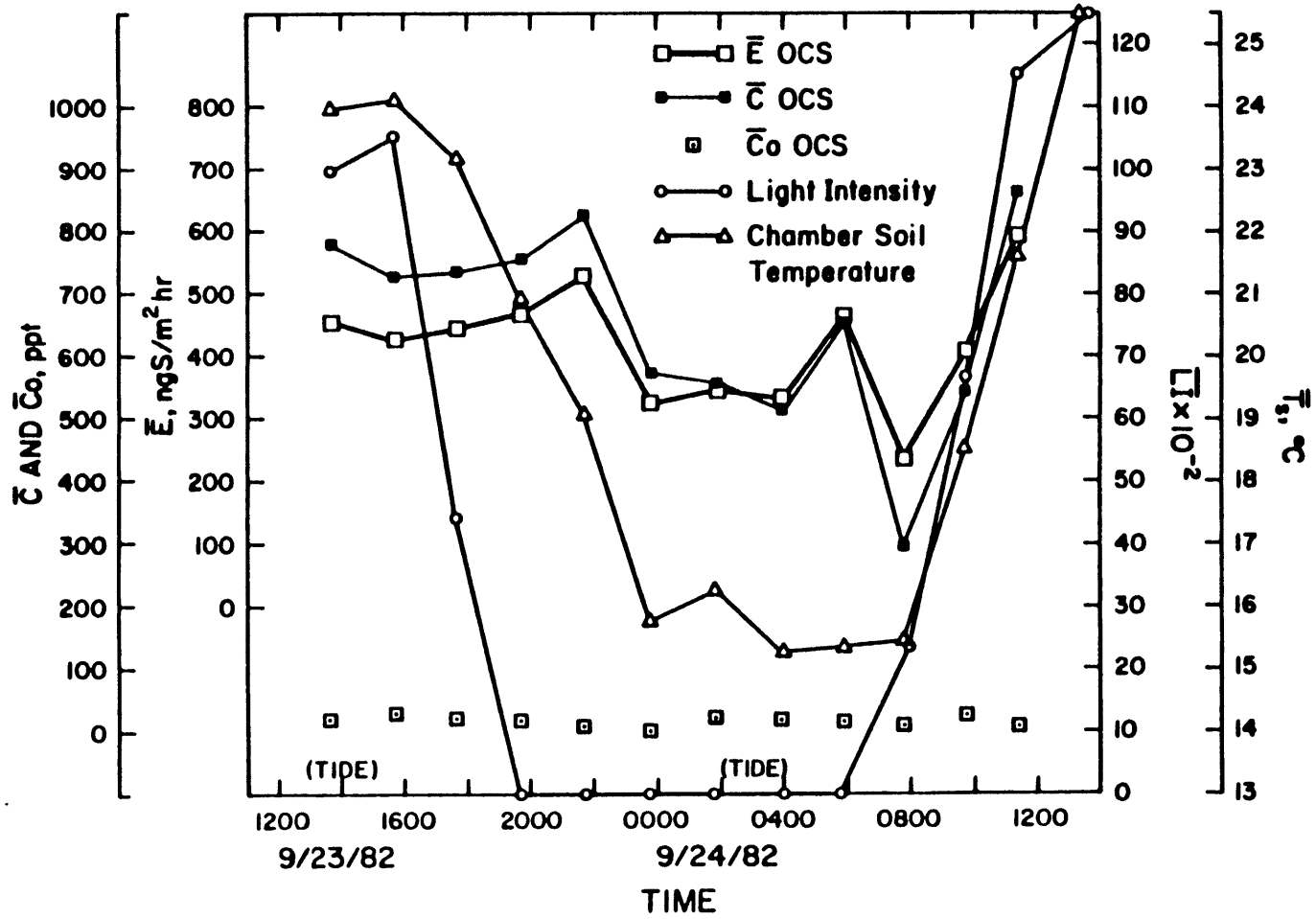


Fig. 44 September 23-24, 1982 field study: OCS fluxes

SEPTEMBER 23-24, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME

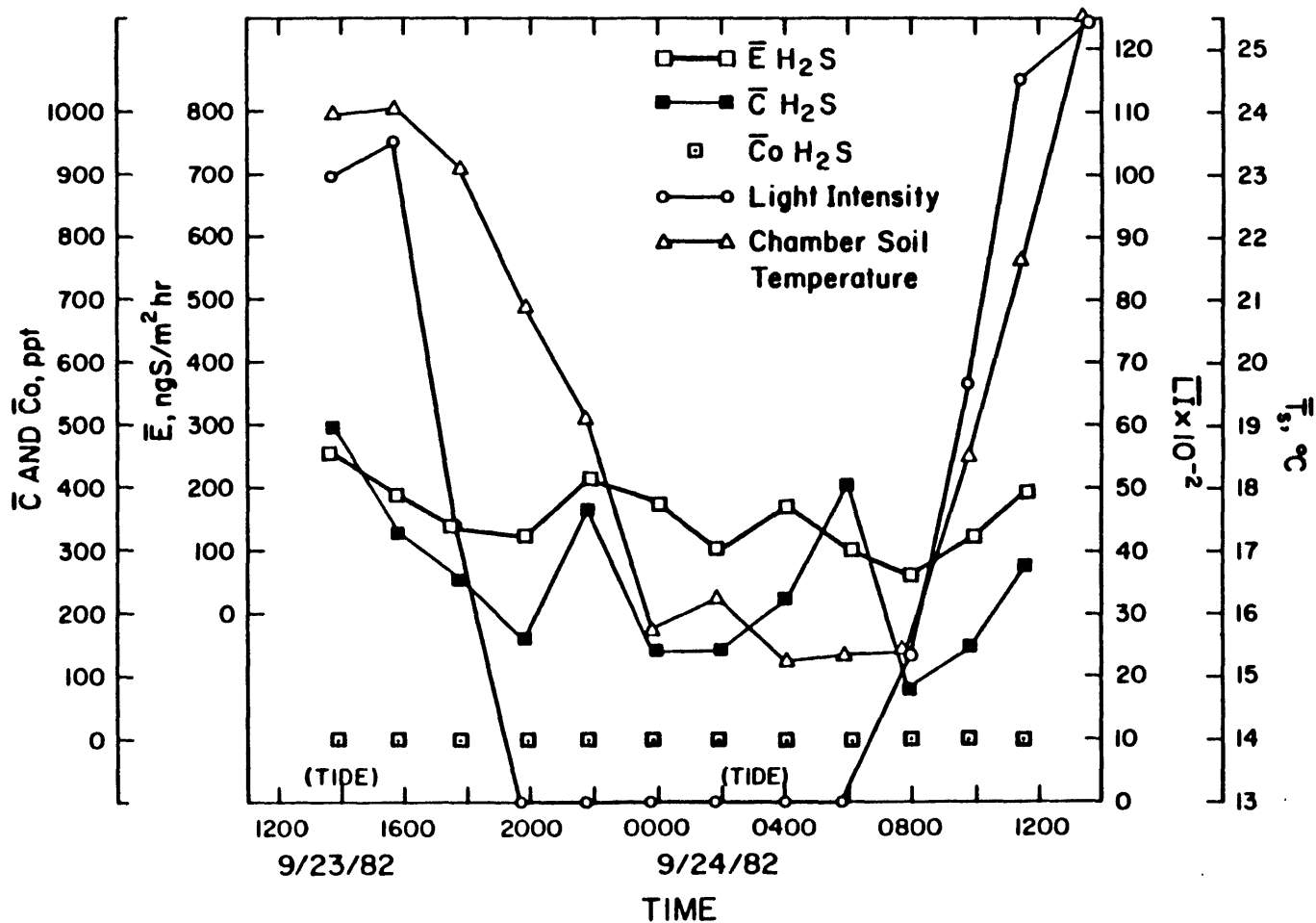


Fig. 45 September 23-24, 1982 field study: H<sub>2</sub>S fluxes

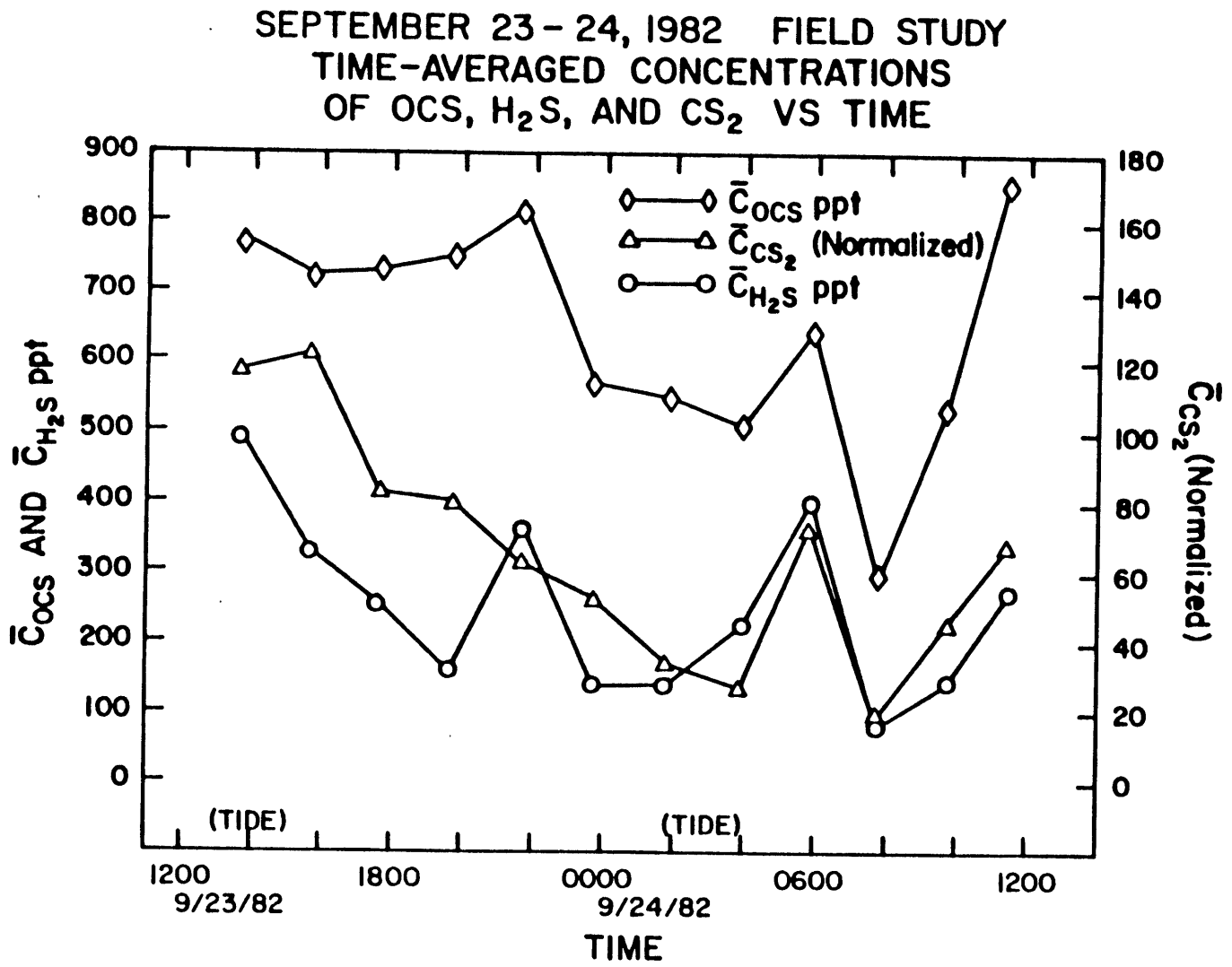


Fig. 46 September 23-24, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations



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

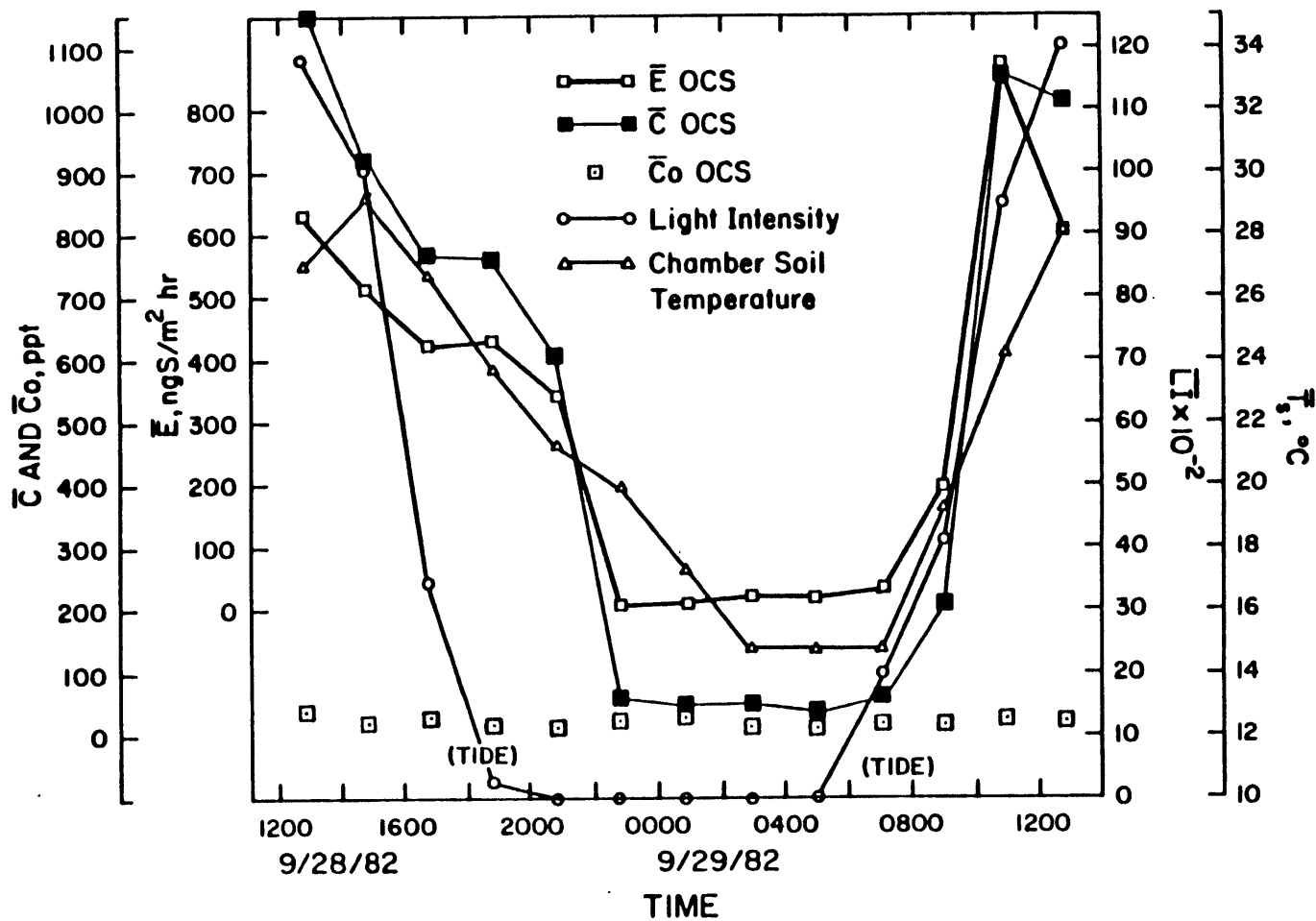


Fig. 47 September 28-29, 1982 field study: OCS fluxes

SEPTEMBER 28-29, 1982 FIELD STUDY  
 TIME-AVERAGED SOIL TEMPERATURES, LIGHT INTENSITIES,  
 H<sub>2</sub>S CONCENTRATIONS, AND H<sub>2</sub>S EMISSIONS VS. TIME

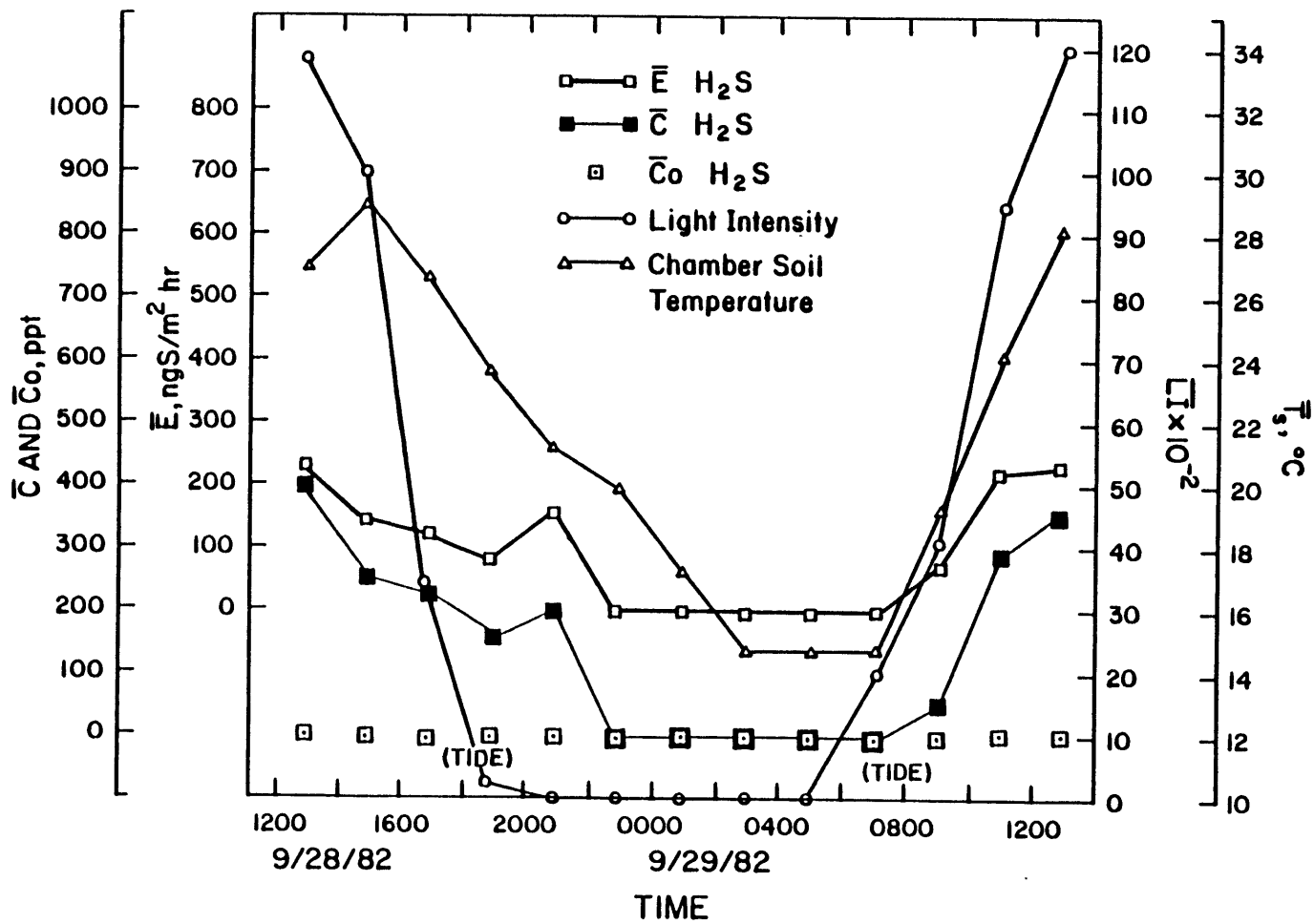


Fig. 48 September 28-29, 1982 field study: H<sub>2</sub>S fluxes

SEPTEMBER 28-29, 1982 FIELD STUDY  
 TIME-AVERAGED CONCENTRATIONS  
 OF OCS, H<sub>2</sub>S, AND CS<sub>2</sub> VS. TIME

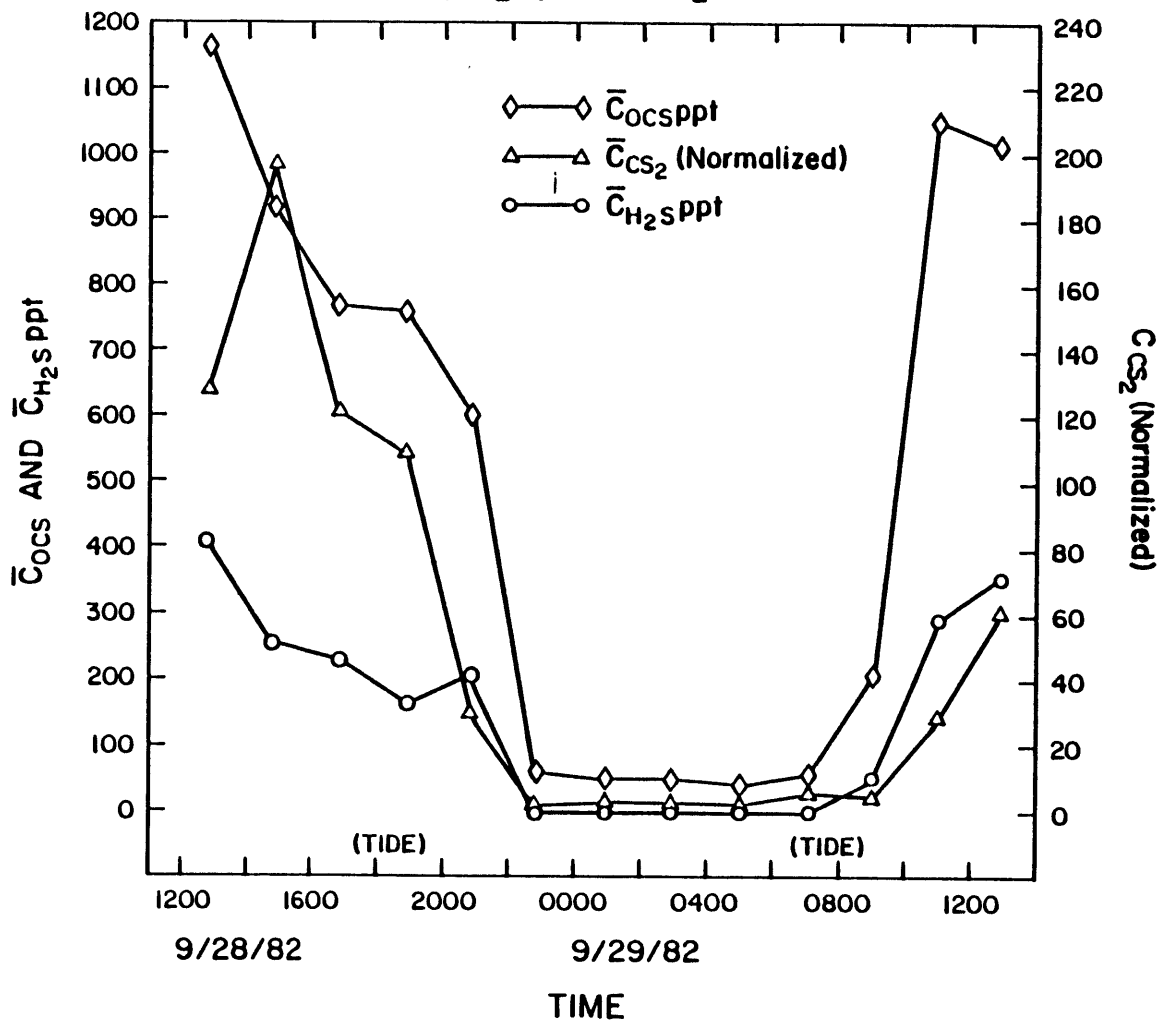


Fig. 49 September 28-29, 1982 field study: OCS, H<sub>2</sub>S, and CS<sub>2</sub> concentrations

#### 4.4 Aircraft Measurements

Samples of ambient OCS and CS<sub>2</sub> were cryogenically collected at 20-26 kft during a flight from San Juan, Puerto Rico to Albany, New York on July 11-12, 1982, through the courtesy of the NASA/Langley Research Center and the NASA/GSFC Wallops Flight Facility. During some prior preliminary tests conducted on a July 8-9 flight (Wallops Island, Virginia to San Juan, Puerto Rico) and a July 10-11 flight (San Juan, Puerto Rico to South America to San Juan, Puerto Rico), sample collection procedures were designed and revised, primarily to accommodate pressure changes. For example, it was found that the FMI pumps, used to trap samples at ground level, were incapable of pumping against a vacuum. A trapping period of 10 min was chosen after tests with and without Nafion driers in line showed that this would allow trapping without the driers in line with a minimal risk of icing. The sample collection procedure described in Fig. 50 worked well at the range of pressures encountered during sampling (322 to 246 torr). The OCS mixing ratios did not vary spatially but were constant at ~520 ppt within the analytical uncertainty of collection and analysis methods (517 ±12.6% relative standard deviation). CS<sub>2</sub> mixing ratios, on the other hand, showed considerable variability (concentration values for OCS and CS<sub>2</sub> are listed in Table 3). It is believed that these are the first measurements of ambient OCS at these altitudes. Since these OCS values are similar to those measured by others at lower altitudes, they support the belief that OCS is relatively inert in the troposphere. Therefore, a minimum lifetime for OCS in the well-mixed portion of the troposphere of about two months can be estimated using

## AIRCRAFT SAMPLE COLLECTION

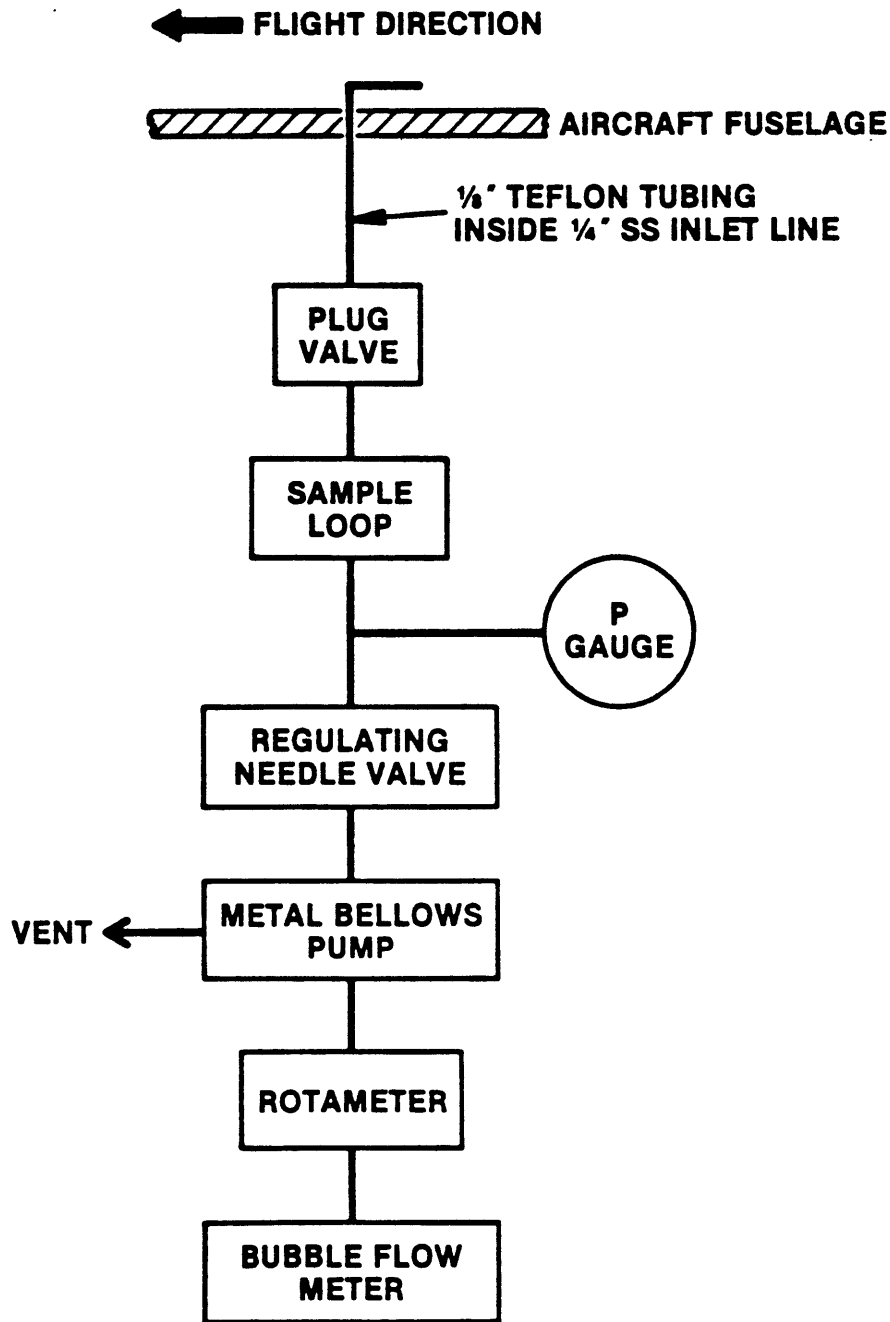


Fig. 50 Aircraft sample collection schematic

Table 2

## Aircraft Sample Collection

Loop #	Trap Time (hrs)	Cabin Pressure (torr)	Cabin Temperature (°C)	Loop Pressure (torr)	Comments	Altitude (kft)
5	2140-2146	655	19.2	321-315		20.0
6	2150-2200	655	18.5	321.3		20.0
7	2204-2211	655	18.5	320	turbulence	20.0
9	2216-2226	655	19.8	321		20.0
10	2231-2240	657	20.5	321		20.0
11	2245-2255	657	20.5	321		20.0
12	2300-2307	657	20.6	321	climbing	20.0&†
13	2313-2319	616&†	20.2	282-273		22-24
14	2323-2333	612	18.5	270		24.0
15	2337-2345	611	17.5	270-265		24.0
16	2350-0000	611	17.0	269		24.0
17	0005-0015	611	16.5	269	turbulence	24.0
18	0019-0029	611	15.7	269-270		24.0
19	0033-0043	611	15.0	270	turbulence	24.0
20	0050-0100	611	14.65	271		24.0
21	0104-0114	611	14.9	272.5		24.0
22	0118-0128	611	14.5	269		24.0
23	0132-0141	611	15.0	272-265	climbing	†to26.0
25	0149-0159	581.5	14.5	246		26.0
37	0204-0214	581.5	13.5	246		26.0
38	0218-0228	583	13.7	246		26.0

Table 3

Aircraft Measurements of OCS and CS<sub>2</sub>

Loop #	Mid-Time (hrs)	Altitude (kft)	Approx. Latitude	Approx. Longitude	OCS (ppt)*	CS <sub>2</sub> (ppt) (100% eff)*	CS <sub>2</sub> (ppt) (70% eff)*
5	2143	20.0	N25°08.9'	W68°01.1'	845.4	1970.2	2814.6
6	2155	20.0	N25°54.7'	W68°16.6'	639.9	554.9	792.7
7	2207.5	20.0	N26°51.2'	W68°36.1'	752.3	298.2	426.0
9	2221	20.0	N27°48.6'	W68°52.1'	523.7	141.0	201.5
10	2235.5	20.0	N28°57.9'	W69°11'	440.2	55.3	79.0
11	2250	20.0	N30°07'	W69°30.5'	561.9	95.4	136.3
12	2303.5	20.0&†	N31°14.4'	W69°49.8'	557.0	96.4	137.8
13	2316	22-24	N31°58.5'	W70°02.8'	601.0	99.3	141.9
14	2328	24.0	N33°07.7'	W70°22.2'	408.1	9.7	13.8
15	2341	24.0	N33°53.6'	W70°35.3'	623.3	23.7	33.9
16	2355	24.0	N34°57.3'	W70°53.9'	494.3	25.8	36.8
17	0010	24.0	N36°04.7'	W71°14.2'	459.5	19.8	28.3
18	0024	24.0	N37°09.3'	W71°53.8'	489.3	27.9	39.9
19	0038	24.0	N38°20.7'	W71°59.4'	436.4	18.4	26.2
20	0055	24.0	N39°23.1'	W72°35.3'	486.0	12.0	17.2
21	0109	24.0	N40°23.8'	W73°39.6'	489.7	14.3	20.4
22	0123	24.0	N41°38.5'	W73°44.3'	545.9	22.0	31.5
23	0136.5	†to26.0	N42°31.8'	W73°42'	652.3	39.3	56.2
25	0154	26.0	N41°23.4'	W73°43.9'	507.3	51.7	73.9
37	0209	26.0	N40°21.1'	W73°49.4'	509.0	11.8	16.8
38	0223	26.0	N39°19.7'	W74°31.8'	521.2	13.4	19.2

\*Cabin air contamination of inlet line present in first samples, residual may be present in samples Loop #s 5-7.

Average OCS mixing ratio Loop #s 9-38: 517.0 (±65.0) pptv (12.6% relative standard deviation).

$$\tau = Z^2/2D$$

where  $\tau$  = lifetime,  $Z = 10$  km, and  $D = 10^5 \text{ cm}^2 \text{ s}^{-1}$ .

The  $\text{CS}_2$  concentrations measured lie within the range of values reported in the literature and demonstrate significant spatial variability. The observed decrease of  $\text{CS}_2$  with altitude supports the current belief of a short photochemical lifetime for  $\text{CS}_2$  in the troposphere. Sample storage and analysis procedures have already been described in Chapter 3.



## CHAPTER 5

## SUMMARY AND CONCLUSIONS

## 5.1 Analytical Developments

A Tracor 560 Gas Chromatograph (GC) equipped with a Flame Photometric Detector (FPD) and a sulfur filter, along with a Spectra Physics programable integrator, comprised the analytical instrumentation. A specially treated Porapak-QS column was used to separate sulfur gases, and the  $N_2$ -carrier gas was doped with  $SF_6$  to continuously condition the column. A.I.D. and KINTEK permeation devices were used to generate standards of OCS,  $H_2S$ , and  $CS_2$  to calibrate the GC response. The GC response was observed to be extremely sensitive to flame gas makeup. The cause of the GC response instability was identified as inadequate flow-controlling devices which allowed flame gas flow rates to vary with variation in laboratory temperature. It was concluded the the carrier and flame gas flow-controllers should be thermally isolated. The Tracor FPD exhaust port was modified to eliminate the possibility of pressure perturbations in the GC signal caused by condensation in the port. 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. The Spectra Physics integrator was programmed to control the sample valve, to run calibration trials, to perform linear regressions on GC response and standard concentration data, to graph calibration curves, to calculate loop trapping efficiencies, and to predict sample concentrations.

Extensive tests were conducted to develop a reliable and portable sample collection technique. Various adsorbents (Molecular Sieve, Tenax-GC, Porapak-QS) were tested and found to be inefficient and unreliable in sulfur gas desorption. The cryogenic trapping of OCS on Pyrex beads and Teflon chips was also tested. The behavior of glass beads was not reproducible, and deterioration of collection efficiency and reproducibility was observed with extended use of the Teflon chip-packed sample loops. Empty Teflon tubing was chosen as the most reliable trapping surface, and sample loops consisted of Teflon tubing housed in aluminum tubing and Teflon plug valves. Extensive tests were conducted to determine cryogenic 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. Nafion tubing driers were placed in line with chamber output sample loops during sample collection. Laboratory studies were conducted to determine if an air stream containing OCS and H<sub>2</sub>S was depleted or enhanced in these compounds after it had passed through the Nafion tubing. No such loss or enhancement was observed during these initial tests. However, these driers became less efficient at removing water vapor and demonstrated losses of OCS as high as ~45% after extended use.

A cryotrap was made of two ~50'-lengths of 1/4" copper tubing which was coiled and immersed in liquid argon. This cryotrap was used to scrub ambient air in the field. The ambient air stream flowed through a series of Drierite-filled plastic cylinders before it

entered the cryotrap. Without this precaution, the presence of water vapor caused the cryotrap to rapidly clog with ice. The scrubbed air contained undetectable levels of  $\text{H}_2\text{S}$ , ~25 pptv OCS, and a small amount of  $\text{CS}_2$  and was used as the chamber purge air during the flux studies conducted at Wallops Island. The polycarbonate flux chamber was easily positioned for a leak-free interface with the marsh surface. Polycarbonate has been shown to be a relatively inert material and was chosen to minimize surface reactivity with the sulfur gases of interest. The chamber design included an exit port of sufficient size to minimize pressure buildup within the chamber, and a fan to circulate interior chamber air.

When flame-out episodes (caused by power failures) were not a problem, this system of sulfur gas collection and analysis demonstrated stability and yielded reproducible results for OCS,  $\text{H}_2\text{S}$ , and  $\text{CS}_2$ .

## 5.2 Field Studies

Preliminary field studies were carried out at the Scripps Institution of Oceanography, La Jolla, California. Temperature, pH, and dissolved oxygen were monitored in several Southern California salt marsh and mud flat environments. In the Penasquitos Marsh, pH values were found to vary from ~7 to 9, and a diurnal dissolved oxygen cycle was identified with daytime saturation values exceeding 14 ppmv and nighttime values falling to zero.

Field work was also conducted at the Marine Biological Laboratory in Woods Hole, Massachusetts. Measurements were made of the vertical wind profile in the first 2 m above the marsh surface along

with attempts to determine the fluxes of OCS, H<sub>2</sub>S, (CH<sub>3</sub>)<sub>2</sub>S, and CS<sub>2</sub> from Spartina-alterniflora-covered sections of the Sippiwissett Salt Marsh. Laboratory and field studies showed the choice of Molecular Sieve/Tenax-GC two-stage adsorbent traps to be inappropriate for reliable sulfur gas concentration determination. Field studies showed that wind and temperature variability within a spatial resolution of 2 m was too great to reliably establish  $\overline{du}/dz$  or  $dT/dz$ .

The major data collection effort involved a study of the fluxes of OCS and H<sub>2</sub>S from Spartina-alterniflora and Spartina-patens stands in a salt water marsh at Wallops Island, Virginia. Field studies were conducted weekly during August and September 1982. The fluxes of OCS and H<sub>2</sub>S were calculated from the difference between input and output chamber concentrations, the chamber flow rate, the chamber surface area, the chamber height, and the changes of concentration with time as estimated by mechanically fitting curves to the concentration plots. The diurnally averaged flux values calculated for OCS and H<sub>2</sub>S are presented in Table 4. The major conclusions which have been made based upon the results of these field studies are:

1. Diurnal variations with daytime maxima and nighttime chamber concentrations falling approximately to input concentrations were routinely observed for OCS, H<sub>2</sub>S, and CS<sub>2</sub>.
2. The OCS and H<sub>2</sub>S concentration variations were similar, and CS<sub>2</sub> concentrations were routinely much less than the concentrations of OCS or H<sub>2</sub>S except during periods of extreme soil moisture.

Table 4

## Summary: Wallops Island Flux Studies

Field Study	Diurnally Averaged Emissions (ng S/m <sup>2</sup> /hr)		$\bar{T}_{\text{Soil}}$ °C	$\bar{T}_{\text{Soil}}$ °C	Moisture Comments
	OCS	H <sub>2</sub> S	Maximum	Minimum	
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	34.17	22.38	Heavy rain previous night
8/26-27	124.75	37.0	29.73	18.42	Recent daily flooding at high tide
9/3-4	90.6	32.8	34.59	21.50	1 week without rain or tide coverage
9/9-10	30.4	32.5	27.24	17.09	2 weeks without rain or tide coverage
9/14-15	332.45	134.75	31.31	16.18	1 week of daily tide coverage
9/23-24	417.33	153.33	25.86	15.26	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)

3. OCS and H<sub>2</sub>S concentrations were observed to jump following tidal episodes whereas CS<sub>2</sub> concentrations were sometimes observed to jump during tidal episodes. Therefore, it is speculated that CS<sub>2</sub> may have a more important oceanic than marsh surface source.
4. Soil moisture significantly influences the fluxes of OCS, H<sub>2</sub>S, and CS<sub>2</sub> from the high marsh.

It is interesting to note that even though Rasmussen et al. (1982) found surface ocean waters to be supersaturated in OCS, OCS concentrations were not observed to dramatically increase during tidal episodes. Also, observations of increased CS<sub>2</sub> concentrations during tidal episodes support Lovelock's suggestion of an oceanic source for CS<sub>2</sub> (1974).

Grab samples were collected from aircraft at 20-26 kft between San Juan, Puerto Rico and Albany, New York to determine the ambient atmospheric concentrations of OCS and CS<sub>2</sub> (flight time was arranged through the courtesy of the NASA/Langley Research Center and the NASA/GSFC Wallops Flight Facility). No spatial variation was observed for OCS mixing ratios at these altitudes and latitudes. CS<sub>2</sub> values, however, demonstrated considerable variability.

### 5.3 The Global Sulfur Budget

In this section, the relative importance of salt water marshes to the global OCS cycle and as a source of H<sub>2</sub>S to the global sulfur cycle is discussed. The possibility of a significant oceanic source of CS<sub>2</sub>, and thus an atmospheric source of OCS, is raised, and the influence of water movement upon volatile sulfide concentrations in salt marsh soil pore waters is also discussed.

Table 5

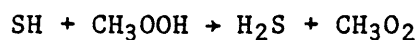
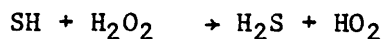
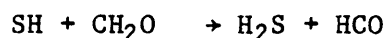
## Annual Global Fluxes of Sulfur from Biogenic Sources

(in Tg S yr<sup>-1</sup>)\*

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

\*1 Tg S = 10<sup>12</sup> g S

The biogenic component of the global sulfur cycle. Many authors have attributed a major role in their postulated global sulfur cycles to biogenic sources of sulfur (see Table 5). As previously discussed in Chapter 1, all except Ivanov (1981) have estimated the biogenic contribution to the global sulfur cycle by difference rather than from actual data. Even Ivanov (1981) calculated his land and oceanic fluxes of biogenic sulfur from the atmospheric content of reduced sulfur rather than from flux calculations derived from experimental studies. One possible problem with this approach is the assumption that reduced sulfur is only of biogenic origin. McElroy et al. (1980) suggest that the reaction of CS<sub>2</sub> (which has numerous anthropogenic sources) with OH provides a significant source for atmospheric SH and thus, perhaps, H<sub>2</sub>S via the following postulated reactions:



with removal of H<sub>2</sub>S by reaction with OH in turn regenerating SH:



A major problem associated with calculating global coastal emissions for H<sub>2</sub>S, for example, are the substantial uncertainties that result in the extrapolation of limited data to global environments



which are often dissimilar. The extent of diurnal and seasonal flux data available for the reduced sulfur compounds is extremely small. Global flux values which have been extrapolated from single daytime concentration measurements are most often all that is available. This research shows how completely inappropriate such calculations are. This research also suggests that it is invalid to attribute a significant role to salt water marshes for the primary biogenic source of  $H_2S$ , as most of these global models do. It may be reasonable to extrapolate  $H_2S$  fluxes calculated from studies of coastal shallow-water areas to other similar coastal regions in order to calculate a global flux. It would be erroneous, however, to include salt water marshes in such a calculation. Indeed, this research suggests that the higher regions of salt water marshes are relatively insignificant biogenic sources of OCS,  $H_2S$ , or  $CS_2$ .

OCS significance calculations. A range of values spanning  $\sim 2$  orders of magnitude have been calculated for the rate of destruction of OCS in the stratosphere (Crutzen, 1976; Sze and Ko, 1978; Turco et al., 1980). A relative quantification of the role of salt water marshes in the global OCS cycle can be achieved by equating the calculated rate of destruction of OCS in the stratosphere with its flux into the stratosphere combined with a knowledge of the relative global area of salt water marshes. With this information, one can calculate the rate of emission of OCS from salt water marshes which would be required if salt water marshes represented the only global source of OCS. The observed emissions of OCS can then be compared with this

predicted flux in order to calculate the actual relative importance of salt water marshes in the global OCS cycle.

Therefore, using the various values for the rate of destruction of OCS in the stratosphere calculated by the aforementioned authors, the relative global area of salt water marshes (0.0745%), and the assumption that salt water marshes represent the only global source of OCS, the following rates of emission of OCS from salt water marshes are required: (1)  $2.0 \times 10^{10}$  to  $2.0 \times 10^{11}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  ( $3.7 \times 10^4$  to  $3.7 \times 10^5$  ngS  $\text{m}^{-2} \text{hr}^{-1}$ ) is calculated using Crutzen's value of  $1.5 \times 10^7$  to  $1.5 \times 10^8$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  for the rate of stratospheric destruction of OCS (scaled to ~500 pptv ambient mixing ratio OCS), (2)  $3.9 \times 10^9$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  ( $7.2 \times 10^3$  ngS  $\text{m}^{-2} \text{hr}^{-1}$ ) is calculated from Sze and Ko's value of  $2.9 \times 10^6$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ , and (3)  $2.15 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  ( $4 \times 10^4$  ngS  $\text{m}^{-2} \text{hr}^{-1}$ ) is calculated using Turco et al.'s value for stratospheric OCS destruction of  $1.6 \times 10^7$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ . The maximum individual flux value of OCS observed during the Wallops Island field study ( $864 \text{ ngS m}^{-2} \text{hr}^{-1}$ ) then represents from 0.2 to 12% of the global OCS flux into the stratosphere, and the the maximum diurnally-averaged value observed for OCS ( $417 \text{ ngS m}^{-2} \text{hr}^{-1}$ ) represents at most 6% 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 ( $\sim 160 \text{ ng S m}^{-2} \text{hr}^{-1}$ ) represents no more than ~2% of global OCS emissions. This averaged value may represent an upper limit for this particular salt marsh for diurnally averaged OCS emissions because the

period studied is likely to be much more productive than winter months when low temperatures appear to cause microbial activity to halt (Ingvorsen and Jorgensen, 1982). Extrapolation of this value results in an annual global emission of only  $5.3 \times 10^8$  g S yr<sup>-1</sup>. 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<sup>-1</sup>, Granat et al., 1976).

H<sub>2</sub>S significance calculations. The maximum observed flux for H<sub>2</sub>S, 987 ng S m<sup>-2</sup> hr<sup>-1</sup>, translates to an annual global emission of H<sub>2</sub>S from salt marshes of  $3.3 \times 10^9$  g S yr<sup>-1</sup>. This observed maximum flux was an anomaly, however. The maximum diurnally-averaged H<sub>2</sub>S flux (153 ng S m<sup>-2</sup> hr<sup>-1</sup>) represents an annual global salt marsh contribution of only  $5.1 \times 10^8$  g S yr<sup>-1</sup>, and the average of the 9 August and September diurnally averaged flux values (80.7 ng S m<sup>-2</sup> hr<sup>-1</sup>) may represent an upper limit of H<sub>2</sub>S emissions from salt water marshes of only  $2.7 \times 10^8$  g S yr<sup>-1</sup>. Once again, this value is a factor of  $\sim 2 \times 10^4$  smaller than the 5 Tg S yr<sup>-1</sup> calculated by Granat et al. (1976), and a factor of  $\sim 10^4$  less than the 12 Tg S yr<sup>-1</sup> attributed by Ivanov (1981) to H<sub>2</sub>S emissions from shallow coastal regions.

CS<sub>2</sub> significance calculations. From the results presented in Chapter 4, it appears that diurnally averaged CS<sub>2</sub> fluxes from areas of the high marsh are much lower than those for H<sub>2</sub>S and OCS. However, GC-saturation due to high CS<sub>2</sub> concentrations sometimes occurred for samples taken during tidal episodes. Because high CS<sub>2</sub> concentrations only occurred concurrent with standing channel water inside the flux chamber, this raised the question of a significant oceanic source of

CS<sub>2</sub>, and thus of atmospheric OCS. Returning to the arguments used to calculate the relative importance of salt water marshes in the global OCS cycle, similar arguments can be presented to estimate the relative importance of an oceanic source of CS<sub>2</sub> to the global OCS cycle (here oceans represent approximately 70% of global area). If oceans were to represent the only global source of OCS, the required values for the oceanic fluxes of OCS would be  $4.1 \times 10^6$  molecules cm<sup>-2</sup> s<sup>-1</sup> (Sze and Ko's value for stratospheric OCS destruction) to  $2.1 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup> (Crutzen's upper limit rate of destruction of OCS in the stratosphere).

Near the end of September, after several weeks of excellent GC-response stability, a three-point, temperature-programmed calibration curve for CS<sub>2</sub> was run to roughly estimate absolute CS<sub>2</sub> mixing ratios and thus to enable rough flux estimates for CS<sub>2</sub>. Preliminary calculations to estimate maximum CS<sub>2</sub> fluxes observed during periods which caused GC-saturation result in minimum values of 1272 to 1817 ng S m<sup>-2</sup> hr<sup>-1</sup> ( $7 \times 10^8$  to  $9.7 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup>). (The range of values results from estimating trapping efficiencies (e) for CS<sub>2</sub> at  $70\% \leq e \leq 100\%$ .) If, as Jones et al. (1982) suggest, the atmospheric conversion of CS<sub>2</sub> to OCS by reaction with OH is 12% efficient, this would yield a comparable OCS input of  $8.4 \times 10^7$  to  $1.2 \times 10^8$  molecules cm<sup>-2</sup> s<sup>-1</sup>. The maximum individual flux value observed for CS<sub>2</sub> during a tidal episode then represents from 40-57% (calculated using Crutzen's upper limit) to ~2000-3000% (using Sze and Ko's value) of the global OCS flux into the stratosphere! Extrapolation of the maximum flux observed for CS<sub>2</sub> results in an annual global oceanic

contribution of  $\sim 4$  to  $6 \text{ Tg S yr}^{-1}$ , a factor of  $\sim 3$  to  $30$  less than the values in the literature for biological decay in oceans (see Table 5). It must be noted that this represents the highest rather than the average value observed for  $\text{CS}_2$  during tidal episodes and assumes that  $\text{CS}_2$  is fluxed from all ocean waters at this maximum rate.

Soil moisture and volatile sulfide concentrations. As noted in Chapter 1, it has been speculated that anaerobic coastal marine environments such as salt water marshes are major sources of  $\text{H}_2\text{S}$ . 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) (see Fig. 51). The sulfide yield appears to depend upon the carbon source (Postgate, 1965; Goldhaber and Kaplan, 1974), and volatile sulfide concentrations in salt marsh soil pore waters have also been found to vary considerably from coastal regions to areas of high marsh (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 the attempt to determine what parameters regulate volatile sulfide concentrations and Spartina-alterniflora productivity. 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 differences in the rates of sulfate reduction between these same types of sites at the same marsh. According to Cappenberg

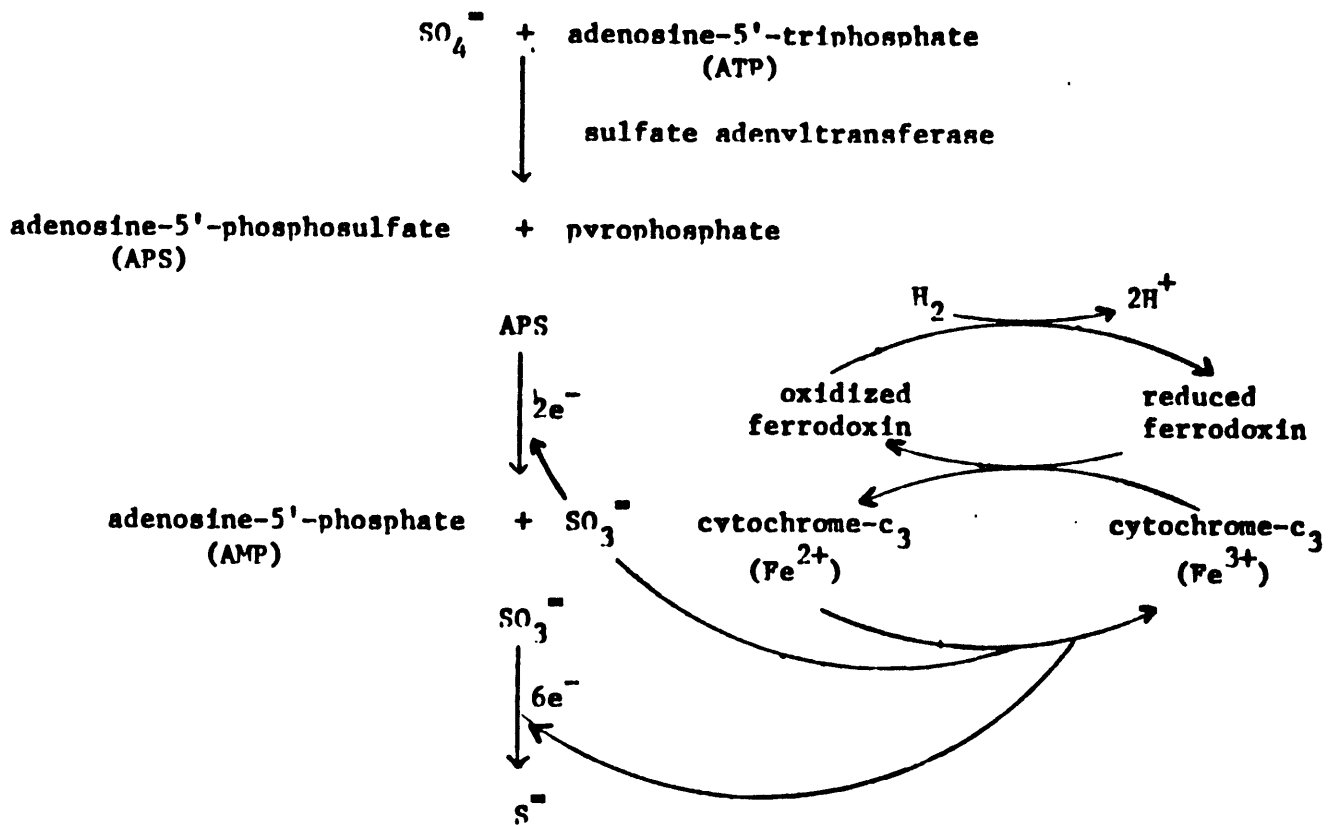


Fig. 51 Dissimilatory Sulfate Reduction: the obligate use of sulfate as the terminal electron acceptor for anaerobic respiratory metabolism in the species of Desulfovibrio and Desulfotomaculum.

(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) suggest that the lower rates of sulfate reduction they observed in the high marsh are thus in agreement with the observations of high rates of methanogenesis in the same region made by King and Skyring (1977) and King and Wieke (1978). At the same time, most researchers agree that volatile sulfide concentrations are much higher in short Spartina (SS) soils than in tall Spartina (TS) soils. Several authors speculate that Spartina growth is inhibited by soil anaerobiosis, per se (e.g., Linthurst and Seneca, 1980; Mendelssohn and Seneca, 1980), and regulated by oxygen transport within plants and by the volatile sulfide concentrations and redox potentials of the marsh soils (Howes et al., 1981; King et al., 1982). All of these researchers have observed a strong positive correlation of Spartina growth with soil water movement, and a similarly significant negative correlation of volatile sulfide concentration with Spartina growth and, thus, water movement. King et al. (1982) speculate that regions of poor soil drainage or low water movement are observed to have much higher volatile sulfide concentrations than marsh regions which flood regularly due to the differences in interstitial iron concentrations found between these regions. According to King et al. (1982), pools of dissolved iron are universally related to those of dissolved sulfide, and the highest concentrations of dissolved iron were found in the low marsh or TS soils. Because iron is not readily available for sulfide precipi-

tation in high marsh or SS soils, high concentrations of volatile sulfide may accumulate in these areas.

It is interesting, however, that such low values of  $H_2S$  were observed to be emitted from the regions of the high marsh studied in this research. While volatile sulfide concentrations in the high marsh may exceed those of lower marsh soils, SS soils are much more highly aerated due to the same lack of water movement which enhances the volatile sulfide concentrations. Perhaps this degree of aeration exerts considerable influence upon the flux of  $H_2S$  or other reduced sulfur compounds from these soils. The results of the field studies conducted at Wallops Island certainly indicate that this is true since maximum fluxes of  $H_2S$  and OCS were only observed during periods of high soil moisture in these regions.

Returning to the relative importance of the high marsh as a global source of biogenic sulfur, the sum of the average diurnally averaged  $H_2S$  and OCS fluxes observed may represent an upper limit of annual global salt water marsh contributions of only  $\sim 8 \times 10^8$  g S  $yr^{-1}$ . This represents at most  $\sim 0.02\%$  of the global biological decay from land (Granat et al., 1976, Table 5). Therefore, if these areas 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  $(CH_3)_2S$  (Goodwin et al., 1982). It would be especially interesting to measure in situ volatile sulfide, OCS,  $H_2S$ , and  $(CH_3)_2S$  concentrations in salt marsh soil pore waters simultaneously with the determination of their rates of emission from both the TS and SS soils.



This research represents a beginning in the effort to quantify natural sources of reduced sulfur gases. Although flux chambers currently comprise the only option available to determine the source and amount of emissions from heterogeneous environments, their use could significantly alter the rates at which gases are emitted in an undisturbed setting. Hitchcock (1978) has warned that the use of stagnant flux chambers creates artificial concentration gradients above a source and thus disturbs the potentially fragile balance, perhaps halting or reversing fluxes. Dynamic flux chambers may not be adequate since most do not mimic in-situ wind motions and variability, and increased humidity may enhance losses and surface effects. Another potential source of interferences are the compounds used to scrub ambient air, such as soda lime and Drierite. The continuation of efforts to quantify natural sources of sulfur compounds is necessary and should include multiple seasonal studies and analytical improvements to enhance instrument stability, to insure minimal disruption of natural settings, and to provide the option of conducting in situ measurements wherever possible.

## BIBLIOGRAPHY

- Adams, D. F., S. O. Farwell, M. R. Pack, and W. L. Bamesburger, 1979: Preliminary measurements of biogenic sulfur-containing gas emissions from soils, J. Air Pollution Control Assoc., 29(4), 380-383.
- Adams, D. F., S. O. Farwell, E. Robinson, M. R. Pack, 1980: Assessment of Biogenic Sulfur Emissions in the SURE Area, EPRI Final Report, No. EA-1516, Electric Power Research Institute, Palo Alto, CA, Sept. 1980.
- Adams, D. F., S. O. Farwell, E. Robinson, M. Pack, W. L. Bamesberger, 1981: Biogenic Sulfur Source Strength, Paper No. 81-15.3 presented at the Annual Meeting of APCA, Philadelphia, PA.
- Aneja, V. P., E. W. Corse, L. T. Cupitt, J. C. King, J. H. Overton, Jr., R. E. Rader, M. H. Richards, H. J. Sher, R. J. Whitkus, 1979: Biogenic Sulfur Sources Strength Field Study, Northrop Services, Inc. Report No. ESC-TR-79-22, Research Triangle Park, NC, p. 189.
- Aneja, V. P., J. H. Overton, Jr., L. T. Cupitt, J. L. Durham, W. E. Wilson, 1979: Direct measurements of emission rates of some atmospheric biogenic sulfur compounds, Tellus 31(2): 176.
- Aneja, V. P., J. H. Overton, Jr., L. T. Cupitt, J. L. Durham, W. E. Wilson, 1979: Carbon disulfide and carbonyl sulfide from biogenic sources and their contribution to the global sulfur cycle, Nature, 282(5738): 493.
- Aneja, V. P., J. H. Overton, Jr., L. T. Cupitt, J. L. Durham, W. E. Wilson, 1980: Measurements of emission rates of carbon disulfide from biogenic sources and its possible importance to the stratospheric aerosol layer, Chem. Eng. Communications 4(6): 721.
- Atkinson, R., R. A. Perry, and J. N. Pitts, Jr., Rate constants for the reaction of OH radicals with COS, CS<sub>2</sub>, and CH<sub>3</sub>SCH<sub>3</sub> over the temperature range 299-430K, Chem. Phys. Lett., 54, 14-18, 1978.
- Baas Becking, L. G. M., and E. J. F. Woods, 1955: Biological processes in the estuarine environment. I and II. Ecology of the sulfur cycle. Koninkl. Ned. Akad. Wetenschap Proc. U., B48, 160-181.
- Bandy, A. R., P. J. Maroulis, L. Shalaby, and L. A. Wilner, 1981: Evidence for a short tropospheric residence time for carbon disulfide, Geophysical Research Letters, 8(11), 1180-1183.
- Banwart, W. L. and J. M. Bremner, 1975a: Volatilization of sulfur from unamended and sulfate-treated soils. Soil Biol. Biochem., 8, 19-22.

- Banwart, W. L. and J. M. Bremner, 1975b: Identification of sulfur gases evolved from animal manures, J. Envir. Qual., 4, 363-366.
- Bellamy, J. S., 1949: Objective calculations of divergence, vertical velocity and vorticity, Bull. Amer. Meteorol. Soc., 30(2), 45-49.
- Black, M. S., R. P. Herbst, and D. R. Hitchcock, 1978: Solid adsorbent preconcentration and gas chromatographic analysis of sulfur gases, Analytical Chemistry, 50(7), 848-851.
- Breckenridge, W. H., and Taube, H., 1970: Ultraviolet Absorption Spectrum of Carbonyl Sulfide, The Journal of Chemical Physics, 52(4), 1713-1715.
- Bremner, J. M., and W. L. Banwart, 1974: Identifying volatile S compounds by gas chromatography, Sulphur Inst. J., 10, 6-9.
- Broecker, W. S., and T. H. Peng, 1974: Gas exchange rates between air and sea, Tellus, 26, 21-35, 661.
- Cadle, R. D., 1975: The sulfur cycle, in: Parker, H. S. (ed.) Sulphur in the Environment, pp. 1-13. St. Louis, Missouri: Missouri Botanical Garden and Union Electric Company, St. Louis, Missouri.
- Cappenberg, T. E., 1974: Interrelations between sulfate-reducing and methane-producing bacteria in bottom deposits of a fresh water lake. I. Field observations, Antonie van Leeuwenhoek, 40, 297-306.
- Chen, K. Y., and J. C. Morris, 1972: Kinetics of aqueous oxidation of sulfide by O<sub>2</sub>, Environ. Sci. Technol., 6, 529-537.
- Cox, R. A., and F. J. Sandalls, 1974: The photo-oxidation of hydrogen sulphide and dimethyl sulphide in air, Atmospheric Environment, 8, 1268-1281.
- Crutzen, P. J., 1976: The possible importance of CSO for the sulfate layer of the stratosphere, Geophys. Res. Lett., 3, 73-76.
- Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. H. Pollack, and W. Seiler, 1979: Biomass burning as a source of atmospheric gases W, H<sub>2</sub>, N<sub>2</sub>O, NO, CH<sub>3</sub>Cl, and COS, Nature, 282, 253-256.
- Davis, D. D., A. R. Ravishankara, and S. Fischer, 1979: SO<sub>2</sub> oxidation via the hydroxyl radical: Atmospheric fate of HSO<sub>x</sub> radicals, Geophys. Res. Lett., 6, 113-116.
- Eriksson, E., 1959: The yearly circulation of chloride and sulfur in nature; meteorological, geochemical, and pedological implications, 1, Tellus, 11, 375-403.

- Eriksson, E., 1960: The yearly circulation of chloride and sulfur in nature; meteorological, geochemical, and pedological implications, 2, Tellus, 12, 63-109.
- Eriksson, E., 1963: The yearly circulation of sulfur in nature, J. Geophys. Res., 68, 4001-4008.
- Ferry, J. G., and H. D. Peck, Jr., 1977: Relationships between sulfate reduction and methane production in salt marsh sediments, Bacteriol. Proc. 236.
- Foulger, B. E., and P. G. Simmonds, 1979: Drier for field use in the detection of trace atmospheric gases, Analytical Chemistry, 51, 1089-1090.
- Friend, J. P., 1973: The global sulfur cycle, in: S.I. Rasool (ed.) Chemistry of the lower Atmosphere, pp. 177-201, New York: Plenum Press, 1973.
- Garrels, R. M., F. T. Mackenzie, and C. Hunt, 1973: Chemical Cycles and the Global Environment, William Kaufmann, Los Altos, California.
- Georgii, H. W., 1970: Contribution to the atmospheric sulfur budget, J. Geophys. Res., 75, 2365-2371.
- Goldberg, A. B., P. J. Maroulis, L. A. Wilner, and A. R. Bandy, 1981: Studies of H<sub>2</sub>S emissions from a salt water marsh, Atmospheric Env., 15, 11-18.
- Goldhaber, M. B., and I. R. Kaplan, 1974: The sulfur cycle, in: Goldberg, E.D. (ed.) The Sea, vol. 5, Marine Chemistry, pp. 569-655. New York: John Wiley and Sons, 1974.
- Gooch, E. L., 1968: Hydrogen sulfide production and its effect on inorganic phosphate release from the sediments of the Canary Creek marsh. M.S. Thesis, University of Delaware, Newark, Del.
- Goodwin, J. T., S. G. Wakeham, J. W. H. Dacey, and B. C. Howes, 1982: Dimethyl Sulfide in Salt Marsh Pore Waters, presented at the Biogeochemistry of Particulates and Sediments Section of the Fall AGU Meeting, San Francisco, California.
- Graedel, T. E., B. Kleiner and C. C. Patterson, 1974: Measurements of extreme concentrations of tropospheric hydrogen sulfide, J. Geophys. Res., 79(30), 4467-4473.
- Graedel, T. E., 1977: The homogeneous chemistry of atmospheric demic sulfur, Rev. Geophys. Space Phys., 15, 421-428.
- Graedel, T. E., 1978: Chemical Compounds in the Atmosphere, Academic Press, Inc., New York, N.Y., 440 pp.

- Granat, L., H. Rodhe, and R. O. Hallberg, 1976: The global sulphur cycle, in: Svensson, B. H. and R. Soderlund (eds.) Nitrogen, Phosphorus and Sulphur - Global Cycles, SCOPE Report 7, Ecol. Bull. (Stockholm) 22, pp. 89-134.
- Grosjean, D., and R. Lewis, 1982: Atmospheric photooxidation of methyl sulfide, Geophys. Res. Lett., 9, 1203-1206.
- Hales, J. M., J. O. Wilkes, and J. L. York, 1974: Some recent measurements of H<sub>2</sub>S oxidation rates and their implications to atmospheric chemistry, Tellus, 26, 277-282.
- Hansen, M. H., K. Ingvorsen, and B. B. Jorgensen, 1978: Mechanisms of hydrogen sulfide release from coastal marine sediments to the atmosphere, Limn. and Oceanogr., 23(1), 68-76.
- Hanst, P. L., L. L. Spiller, D. M. Watts, J. W. Spence, and M. F. Miller, 1975: Infrared measurements of fluorocarbons, carbon tetrachloride, carbonyl sulfide, and other atmospheric trace gases, J. Air Pollut. Contr. Assoc., 25, 1220-1226.
- Hartstein, A. M., and D. R. Forshey, 1974: Coal mine combustion products: Neoprenes, polyvinyl chloride compositions, urethane foam, and wood, U.S. Bur. Mines Rep. Invest., 7977, 15.
- Hatakeyama, S., the late M. Okuda, and H. Akimoto, 1982: Formation of sulfur dioxide and methanesulfonic acid in the photooxidation of dimethyl sulfide in the air, Geophys. Res. Lett., 9, 583-586.
- Hill, F. B., V. P. Aneja, R. M. Felder, 1978: A technique for measurement of biogenic sulfur emission fluxes, Environ. Sci. Technol., 13, 199.
- Hitchcock, D. R., 1978: A problem with flux chamber measurements of biogenic sulfur emissions, unpublished manuscript.
- Holser, W. T., and I. Kaplan, 1966: Isotope geochemistry of sedimentary sulphates, Chem. Geol., 1, 93-135.
- Hoshika, Y., and Y. Iida, 1977: Gas chromatographic determination of sulfur compounds in town gas, J. Chromatography, 134, 423-432.
- Howard-Smith, I., and G. J. Werner, 1976: Coal Conversion Technology, Noyes Data Corporation, Park Ridge, N.J., 133 pp., 1976.
- Howes, B. L., R. W. Howarth, J. M. Teal, and I. Valiela, 1981: Oxidation-reduction potentials in a salt marsh: Spatial patterns and interactions with primary production, Limnol. Oceanogr., 26, 350-360.
- Ingvorsen, K., and B. B. Jorgensen, 1982: Seasonal variation in H<sub>2</sub>S emission to the atmosphere from intertidal sediments in Denmark, Atmos. Env., 16, 855-865.

- Inn, E. C. Y., J. F. Vedder, and B. J. Tyson, 1979: COS in the stratosphere, Geophys. Res. Lett., 6(3), 191-193.
- Ivanov, M. V., 1981: The global biogeochemical sulfur cycle, in: Likens, G.E. (ed.) Some Perspectives of the Major Biogeochemical Cycles, SCOPE Report 17, Chapter 4, John Wiley and Sons.
- Iyer, R. S., and F. S. Rowland, 1980: A significant upper limit for the rate of formation of OCS from the reaction of OH with CS<sub>2</sub>, Geophys. Res. Lett., 7, 797-800.
- Jaeschke, W., 1978: New methods for the analysis of SO<sub>2</sub> and H<sub>2</sub>S in remote areas and their application to the atmosphere, Atmos. Environ., 12, 715-721.
- Jaeschke, W., H. M. Georgii, H. Claude, and H. Malewski, 1978: Contributions of H<sub>2</sub>S to the atmospheric sulfur cycle, Pure and Appl. Geophys., 116(2/3): 463.
- Johnson, G., C. Matthews, M. Smith, and D. Williams, 1970: Distribution of sulfur species in the burnt gas of fuel-rich propane-air flames, Combust. and Flame, 15, 211-214.
- Johnson, J. E., 1981: The lifetime of carbonyl sulfide in the troposphere, Geophys. Res. Lett., 8, 939-940.
- Jones, B. M. R., J. P. Burrows, R. A. Cox, and S. A. Penkett, 1982: OCS Formation in the reaction of OH with CS<sub>2</sub>, Chemical Physics Letters, 88, 372-376.
- Jorgensen, B. B., 1978: A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments, I-III, Geomicrobiol. J., 1(1), 11-64.
- Jorgensen, B. B., N. P. Revskeh, T. H. Blackburn, and Y. Cohen, 1979: Diurnal cycle of oxygen and sulfide microgradients and microbial photosynthesis in a cyanobacterial mat sediment, Applied and Environmental Microbiology, 38(1), 46-58.
- Jorgensen, B. B., 1977: The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark), Limnol. Oceanogr., 22(5), 814-832.
- Junge, C. E., 1960: Sulfur in the atmosphere, J. Geophys. Res., 65, 227-237.
- Junge, C. E., 1963a: Sulfur in the atmosphere, J. Geophys. Res., 68, 3975-3976.
- Junge, C. E., 1963b: Air Chemistry and Radioactivity. New York: Academic Press, 382 pp., 1963b.
- Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus, and E. A. Martell, 1972: The sulfur cycle, Sci., 175, 587-596.

- King, G. M., and G. W. Skyring, 1977: A seasonal study of methanogenesis in a Georgia salt marsh, Bacteriol. Proc., 243.
- King, G. M., and W. J. Wiebe, 1978: Methane release from soils of a Georgia salt marsh., Geochim. Cosmochim. Acta, 42, 434-348.
- King, G. M., M. J. Klug, R. G. Wiegert, and A. G. Chalmers, 1982: Relation of soil water movement and sulfide concentration to Spartina alterniflora production in a Georgia salt marsh, Science, 218(4567), 61-63.
- Kurylo, M. J., 1978a: Flash photolysis-resonance fluorescence investigation of the reaction of OH radicals with dimethyl sulfide, Chem. Phys. Lett., 58(2), 233-237.
- Kurylo, M. J., 1978b: Flash photolysis-resonance fluorescence investigation of OH radicals with OCS and CS<sub>2</sub>, Chem. Phys. Lett., 58(2), 238-242.
- Levy II, H., 1974: Photochemistry of the Troposphere, in: Advances in Photochemistry, Vol. 9, 369-524, New York: Wiley and Sons, 1974.
- Linthurst, R. A., 1979: The effect of aeration on the growth of Spartina alterniflora Loisel, Am. J. Botany, 66, 685-691.
- Linthurst, R. A., and E. D. Seneca, 1980: The effects of standing water and drainage potential on the Spartina Alterniflora-substrate complex in the North Carolina salt marsh, Est. and Cstl. Mar. Sci., 11, 41-52.
- Liss, P. S., and P. G. Slater, 1974: Flux of gases across the air-sea interface, Nature, 247, 181-184.
- Lovelock, J. E., 1974: CS<sub>2</sub> and the natural sulphur cycle, Nature, 248, 625-626.
- Lovelock, J. E., R. J. Maggs, and R. A. Rasmussen, 1972: Atmospheric dimethyl sulfide and the natural sulphur cycle, Nature, 237, 452-453.
- Maroulis, P. J. and A. R. Bandy, 1977: Estimate of the contribution of biologically produced dimethyl sulfide to the global sulfur cycle, Science, 196, 647-648.
- Maroulis, P., A. Torres, and A. Bandy, 1977: Atmospheric concentrations of carbonyl sulfide in the southwestern and eastern United States, Geophys. Res. Lett., 4, 510-512.
- McElroy, M. B., S. C. Wofsy, and N. D. Sze, 1979: Photochemical sources for atmospheric H<sub>2</sub>S, Atmos. Environ., 14, 159-163.

- Mendelssohn, I. A., and E. D. Seneca, 1980: The influence of soil drainage on the growth of salt marsh cordgrass Spartina alterniflora in North Caroline, Estuarine and Coastal Marine Science, 11, 27-40.
- Moss, M. R., 1978: Sources of Sulfur in the Environment; The Global Sulfur Cycle, in: Sulfur in the Environment, Part I: The Atmospheric Cycle, J. O. Nriagu, Ed., New York, John Wiley & Sons, 23-50, 1978.
- Nriagu, J. O., Ed., 1978: Sulfur in the Environment, Part I: The Atmospheric Cycle, New York, John Wiley & Sons, 1978.
- Oshrain, R. L., 1977: Aspects of Anaerobic Sulfur Metabolism in Salt Marsh Soils, Masters Thesis, University of Georgia, Athens, Georgia.
- Ostlund, G., and J. Alexander, 1963: Oxidation rate of sulfide in sea water, a preliminary study, J. Geophys. Res., 68, 3995-3997.
- Pearson, C. D., and W. J. Hines, 1977: Determination of hydrogen sulfide, carbonyl sulfide, carbon disulfide, and sulfur dioxide in gases and hydrocarbon streams by gas chromatography/flame photometric detection, Anal. Chem., 49(1), 123-126.
- Postgate, J. R., 1965: Recent advance in the study of the sulfate-reducing bacteria, Bacteriol. Rev., 29, 425-441.
- Priestley, C. H. B., 1974: Turbulent Transfer in the Lower Atmosphere, University of Chicago Press, Chicago, 130 pp., Midway Reprint, 1974.
- Prinn, R. G., 1973: Venus: Composition and structure of the visible clouds, Science, 182, 1132-1135.
- Rasmussen, R. A., 1974: Emission of biogenic hydrogen sulfide, Tellus, 26, 254-260.
- Rasmussen, R. A., M. A. K. Khalil, and S. D. Hoyt, 1982: The oceanic source of carbonyl sulfide (OCS), Atmos. Environ., 16(6), 1591-1594.
- Ravishankara, A. R., N. M. Kreutter, R. C. Shah, and P. H. Wine, 1980: Rate of reaction of OH with COS, Geophys. Res. Letters, 7(11): 861.
- Robinson, E., and R. Robbins, 1968: Emissions, concentrations and fate of gaseous atmospheric pollutants, Stanford Research Inst., Menlo Park, California, 110 pp.
- Robinson, E., and R. Robbins, 1970: Gaseous sulphur pollutants from urban and natural sources, J. Air Pollut. Control. Assoc., 20, 303-306.



- Rodhe, H., 1972: A study of the sulphur budget for the atmosphere over Northern Europe, Tellus, 24, 128-138.
- Sandalls, F. J., and S. A. Penkett, 1977: Measurements of carbonyl sulphide and carbon disulphide in the atmosphere, Atmos. Environ., 11, 197-199.
- SCEP, 1970: Man's Impact on the Global Environment, Report of the Study of Critical Environmental Problems, sponsored by M.I.T., Cambridge: The MIT Press, 319 pp.
- Schwarzenbach, R. P., R. H. Bromund, P. M. Gischwend, and O. C. Zafiriou, 1978: Volatile organic compounds in coastal seawater, Organic Geochemistry, 1, 93-107.
- Skyring, G. W., R. L. Oshrain, and W. J. Wiebe, 1979: Sulfate reduction rates in Georgia marshland soils, Geomicrobio J., 1(4), 389-400.
- Slatt, B. J., D. F. S. Natusch, J. M. Prospero, and D. L. Savoie, 1978: Hydrogen sulfide in the atmosphere of the Northern Equatorial Atlantic Ocean and its relation to the global sulfur cycle, Atmos. Environ., 12, 981-991.
- Sivanesaw, A., and J. G. Manners, 1972: Bacteria of muds colonized by Spartina townsendii and their possible role in Spartina die back, Plant and Soil, 36, 349-361,
- Stedman, D. W., T. J. Kelly, R. E. Shetter, J. D. Shetter, and R. J. Cicerone, 1978: Feedback flow and permeation system for the calibration of very low gas concentrations, Air Quality Meteorology and Atmospheric Ozone, A.S.T.M., Spec. Tech. Pub. 653, 563-571.
- Stuedler, P., 1980: Conference of the Amer. Poll. Control Assoc.
- Sze, N. D., and M. K. W. Ko, 1978: Stratospheric sulfur cycle: A theoretical model, unpublished manuscript.
- Sze, N. D., and K. W. Ko, 1979: Is CS<sub>2</sub> a precursor for atmospheric COS, Nature, 278, 731-732.
- Sze, N. D., and M. K. W. Ko, 1980: Photochemistry of COS, CS<sub>2</sub>, CH<sub>3</sub>SCH<sub>3</sub> and H<sub>2</sub>S: Implications for the atmospheric sulfur cycle, Atmos. Environ., 14, 1223-1239.
- Sze, N. D., and M. K. W. Ko, 1981: The photochemistry of carbon monosulfide: A possible source for atmospheric OCS, Geophys. Res. Lett., 8, 765-768.
- Thornsberry, W. L., Jr., 1971: Isothermal gas chromatographic separation of carbon dioxide, carbon oxysulfide, hydrogen sulfide, and sulfur dioxide, Anal. Chem., 43(3), 452-453.

- Torres, A. L., P. J. Maroulis, A. B. Goldberg, and A. R. Bandy, 1979: Atmospheric OCS measurements on Project GAMETAG, J. Geophys. Res., 85, 7357-7360.
- Turco, R. P., R. C. Whitten, O. B. Toon, J. B. Pollack, and P. Hamill, 1980: OCS, stratospheric aerosols and climate, Nature, 283, 283-286.
- Turco, R. P., R. J. Cicerone, E. C. Y. Inn, and L. A. Capone, 1981: Long Wavelength Carbonyl Sulfide Photodissociation, J. Geophys. Res., 86, 5373-5377.
- Wine, P. H., R. C. Shah, and A. R. Ravishankara, 1980: Rate of reaction of OH with CS<sub>2</sub>, J. Phys. Chem., 84, 2499-2503.
- Wine, P. H., W. L. Chameides, and A. R. Ravishankara, 1981: Potential role of CS<sub>2</sub> photooxidation in tropospheric sulfur chemistry, Geophys. Res. Lett., 8, 543-546.
- Winfrey, M. R., and J. G. Zeikus, 1977: Effect of sulfate on carbon and electron flow during microbial methanogenesis in freshwater sediments, Appl. Environ. Microbiol., 33, 275-281.
- Zehnder, A. J. B., and S. H. Zinder, 1980: The Sulfur Cycle, in: Vol. 1 part A, Handbook of Env. Chem., "The Natural Environment & the Biogeochemical cycles", pp. 105-145, Springer-Verlag Berlin Heidelberg, 1980.
- Zobell, C. E., and S. E. Rittenberg, 1948: Sulfate-reducing bacteria in marine sediments, J. Mar. Res., 7, 602-617.

## APPENDIX I

Curriculum Vita

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## EDUCATION:

B.A. (Chemistry), 1978, University of Massachusetts/Boston  
Doctoral Candidate (Atmospheric Chemistry), Department of Earth  
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anticipated completion date: April 1983.

## PROFESSIONAL EXPERIENCE:

University Corporation for Atmospheric Research Fellow,  
June 1978 - May 1979

NCAR Graduate Research Assistant, June 1981 - present.

## RESEARCH EXPERIENCE:

Worked with Dr. Paul Crutzen and Dr. Louis Gidel on a two-  
dimensional model of the troposphere, summer 1978 at NCAR as UCAR  
Fellow.

Thesis research with Dr. Ronald Prinn (MIT) and Dr. Ralph  
Cicerone (NCAR): Conducted an experimental study of the flux of  
carbonyl sulfide from a salt water marsh (at Wallops Island,  
June-October 1982); developed analytical procedures to measure  
sulfur concentrations and determine fluxes of various reduced  
sulfur gases. Research with Dr. Cicerone at the Scripps Insti-  
tution of Oceanography, La Jolla, California, June 1979 - January  
1980. Research at the Marine Biological Laboratory, June 1980 -  
September 1980. Research with Dr. Cicerone and Mr. Leroy Heidt  
at NCAR, October 1980 - present.

## HONORS:

University of Massachusetts/Boston: Graduated Summa Cum Laude  
with University and Chemistry Departmental Honors, Outstanding  
Senior Chemistry Award, Phi Beta Kappa Book Award, Nomination,  
John F. Kennedy Award, and Nomination, Danforth Fellowship compe-  
tition.

Danforth Fellow, 1978 - present.

## PROFESSIONAL SOCIETIES:

American Association for the Advancement of Science  
American Geophysical Union  
Association for Women in Science (AAAS)  
Sigma Xi  
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## RESEARCH INTERESTS:

Atmospheric and Analytical Chemistry

Biogeochemical cycling of compounds: Method development and application for measuring natural and anthropogenic source contributions of chemical species as well as species concentrations in clean and polluted ambient air.

## PUBLICATIONS:

Carroll, M. A., An Experimental Study of the Fluxes of Reduced Sulfur Gases from a Salt Water Marsh, Doctoral Thesis, 1983.

Carroll, M. A., L. E. Heidt, R. J. Cicerone, and R. G. Prinn, Carbonyl Sulfide Fluxes from a Salt Water Marsh, Paper No. A22A-03, presented at the Tropospheric Chemistry section of the Fall American Geophysical Union Meeting, San Francisco, California, 1982.

Carroll, M. A., Sources of Reduced Atmospheric Sulfur Gases, in "Interaction of the Biota with the Atmosphere and Sediments," Eds. M. N. Dastoor, L. Margulis, and K. H. Nealson, Final Report, NASA Workshop on Global Ecology held October 18-20, 1979, p. 28.

Consultant to the Space Science Board, Committee on Planetary Biology and Chemical Evolution, National Academy of Sciences, National Research Council: "Scientific Strategy for the Decade 1980-1990. Origin and Evolution of Life: Implications for the Planets," 1980.

Alper, J. S., M. A. Carroll, and A. Gelb, Classical Trajectory Study of Rotationally Inelastic Scattering of Two HF Molecules, Chemical Physics, 32, 471-479, 1978.

## APPENDIX II

Analytical Instrumentation Used at the  
Scripps Institution of Oceanography

The Tracor 560 gas chromatograph, discussed in Section II, along with a linear chart recorder comprised the initial analytical instrumentation employed in developmental work conducted at the Scripps Institution of Oceanography. Primary standards were generated by housing A.I.D. permeation tubes in temperature-controlled cells with diluent-N<sub>2</sub> flowing continuously. Permeation rates were determined by weight loss over time, monitored with a microanalytical balance. Secondary standards were generated by a routine static dilution method, using a calibrated pressure gauge and a calibrated regulator. A vacuum system was employed in the transfer of the gas of interest to an evacuated cylinder (see Fig. 52). This transfer was followed by successive dilutions with zero grade N<sub>2</sub> gas. Dissolved oxygen and pH measurements were made using a portable Orion Research Ionalyzer (model 399A/F), and Orion KCl gel-filled combination pH electrode (model 91-005), and an Orion oxygen electrode (model 97-08). Salinity, required to adjust dissolved oxygen values, were determined by chlorinity titration, where  $(1,80655)(\text{o}/\text{o}\text{o Cl}^-) = \text{o}/\text{o}\text{o S}$ , and by using a salinity hydrometer. Research grade chemicals and twice-distilled water were used to make the required buffer and electrode test solutions.

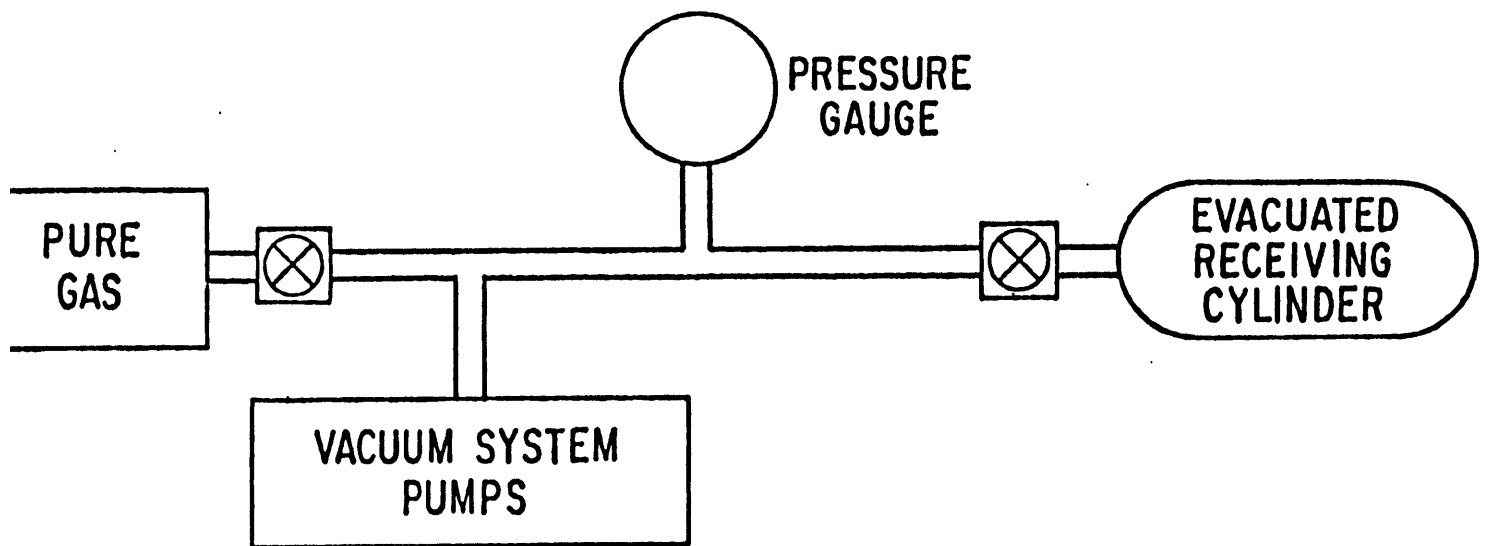


Fig. 52 Primary standard generation by dilution method

## APPENDIX III

Analytical Instrumentation Used at the Marine Biological Laboratory

The chromatographic system used at the Marine Biological Laboratory consisted of Hewlett-Packard model 5730 gas chromatograph equipped with a Tracor Flame Photometric Detector. The data acquisition system consisted of a Dohrmann 1 mv recorder and a Columbia Scientific Instrument model 3A integrator. The photomultiplier tube and part of the detector has been surrounded by a cooling coil maintained at 10°C to improve the signal to noise ratio (Steudler, unpublished manuscript, personal communication). A 6' x 1/8" O.D. FEP Teflon chromatographic column packed with Chromosil 330 (Supelco) was employed for calibration and sample analysis. Column conditioning consisted of an overnight bake at 120°C with a continuous zero N<sub>2</sub> purge flow, with the column disconnected from the detector. Separation of the sulfur compounds was achieved by temperature programming the column from 25°C to 100°C at 8°C/min with an initial 4 min delay (Steudler, unpublished manuscript, private communication). Wind speed data was collected using Maximum #41 Generator anemometers in conjunction with an integrating voltmeter. Samples were trapped using foil-wrapped 60/80 molecular sieve 5A-60/80 Tenax GC traps (see Chapter 3).

## APPENDIX IV

SP4100 Program and Rotameter and Thermocouple Calibrations

Table 6

## SP4100 Program

```

5 ECHO Ø: INPUT "LOOP #" G1
10 !"OCS(Ø) H2S(1)": INPUT G2
20 !"INPUT CURVE R = A*C**B?": INPUT I
25 IF I = Ø THEN 30 ELSE INPUT "A" G3: INPUT "B" G4
30 INPUT "TRAPRATE" G5; INPUT "TRAPTIME" G6; G7 = G6*G5
35 INPUT "LOOPEFF" G8; G9 = G8/100
40 INPUT "CHAMBERF" M1; INPUT "GCAT" M2; INPUT "RESPONSE" M3
45 M4 = (M3*M2/G3)**(1/G4); M5 = M4/G9; M6 = M5/G7
85 INPUT "CONCIN" M7; M8 = M6 - M7; M8 = M8*1.36184;
M9 = M8*M1*60/0.5574
100 !"LOOP #": G1
110 !"COMPOSITE CURVE:" G3"*C**"G4
115 !"TRAPPING RATE:" G5"Std.cc/min"
120 !"TRAPPING TIME:"G6"MIN"
125 !"VOLUME TRAPPED:"G7"ML"
130 !"LOOP EFFICIENCY:"G8"%
135 !"CHAMBER FLOW:"M1"Stnd.cc/min"
136 IF G2 = 0 THEN 140 ELSE 141
140 !"CONCENTRATION:"M6"ppb OCS"
141 !"CONCENTRATION:"M6"ppb H2S"
145 !FLUX:"M9" ngS/m2-hr"
150 END
500 J1=1: ECHO Ø: INPUT *AN*AN: INPUT *GCAT*G2
505 INPUT *UVI*H1: INPUT *DET1*H2: INPUT *INJ1*H3
510 INPUT *RH2*H7*: INPUT *RH1R*H8: INPUT *FLTR*H5: INPUT *ZERO*H6
515 !*STANDARD (Ø) SAMPLE(1)*: INPUT D5
520 IF D5 THEN !*FLD(1) STD GEN (Ø)*: INPUT D4
525 IF D4 THEN 780
531 INPUT *TLAB*85: 85=85+273
532 INPUT *PH20*86
533 INPUT *PLAB*84: 84=84-86
535 !*KINIE(Ø) FF(1)*: INPUT D6: !*H2S(Ø) OCS(1)*: INPUT L1
536 IF L1 THEN C5=60 ELSE C5=34
537 IF D6 THEN Z6=*RID* ELSE Z6=*KINIE*
538 INPUT *TBUX*U1: U1=U1+273
540 IF D6 THEN INPUT *GHS*O1: ELSE 595
545 IF D6 THEN INPUT *PT*O3: ELSE 595
550 INPUT *PR*88
555 INPUT *FLOW*87: GOTO 625
561 INPUT *F1*O8: INPUT *F*O9: GOTO 631

```



```

595 !*CELL(0) PT(1)*: INPUT Z4: IF Z4 THEN 605
596 IF L1 THEN B1=*COS* ELSE B1=*H2S*
600 INPUT *CELL#*B2
601 INPUT *PSTD*B3: B3=B3/.019337
602 INPUT *PR*B8: INPUT *Z*B9: B9=B9*10
605 INPUT *FLOW*B7: IF Z4 THEN 620
610 E7=((B3+B4)/760)*B8*B9/(E4*.35921*B7/B5)
615 E8(J1)=E7*.93*B4/760: GOTO 635
620 IF L2 THEN 630 ELSE INPUT *PT#*B2: INPUT *PR*B8
625 E6=B5*62358.97/C5*B4
630 E7=E6*B8/(B7*E4*.35921/B5): E8(J1)=E7*.93*B4/760
631 IF L4 THEN E7=E7*C8/C9 ELSE 635
632 E8(J1)=E7*.93*B4/760
635 !*FLOWING*;*E7*;*PPB*:* IF D5 THEN 784
636 !*DILUTION?*: INPUT *D?*L4
637 IF L4 THEN 561 ELSE 640
640 !*INJECTING*;*E8(J1)*;*PPBML*
645 !*# OF TRIALS AT THIS CONC?*: INPUT *RH*RH: IX=0
646 N1=0: N3=0
650 !*STAB CHECK? Y(1) N(0)*: INPUT C: IF C=0 THEN 660
654 ECHO 1
655 INPUT *FLAME*:* INPUT *RH2*:* INPUT *RHIR*:* INPUT *OTHER*
660 IF D5 THEN FI=2 ELSE FI=1
665 Z2=2PEEK#C399: Z3=3PEEK#C398: RUN 2600: END
670 FOR C=1 TO 500: NEXT : IF IX THEN 715
672 IF D6 THEN B1=C1
675 !*FILENAME*:*$5.03NM;NM(1);NM(2),*ANALYST*:*$5.03HN
680 H=3PEEK#C396
685 !*DATE*:*$5.03MY(1);MY(2);A;$5MY
690 !*TIME*:*$5.0322;Z3
691 !*TLAB(K)*:*B5,*PLAB*:*B4,*PH20*:*B6
692 IF D6=0 AND Z4=0 THEN !*PSTD(TORR)*:*B3,*ZGAS*:*B9
693 !*STD GEN*:*$5.03 Z6;Z6(1),*SGT*:* $5.01 U1,*PR*:*B8
694 !*CELL/PI#*:*B2
695 !*CONC*:*E8(J1)*;*PPBML      GAS*:*$5.03B1
696 IF L1 THEN B1=*CUS*ELSE B1=*CUS*
700 !*RH2*:*H7,*RHIR*:*H8,*POLARITY*:*
705 !*FILTER*:*$5.03H5,*ZERO*:*$5.03H6
706 !*UV T*:*H1,*DET T*:*H2,*INJ T*:*H3,*GCAT*:*C2
710 !*BLPK RESPONSE*:* !*PN*PN,*PT*PT,*PH*PH,*SPAT*AT
715 H4=SIZE*PS*
720 !*PK#*THB12*RT*THB 22*AREH*THB32*HEIGHT*THB42*BC CODE*
724 FOR N=1 TO H4: IN;PS(N);PSR(N);PSH(N);PSF(N): NEXT
725 IF D5=1 THEN 815
726 S=RH-IX: IF S>3 THEN 728
727 N1=N1+PSR(1): N3=N3+PSR(1)*PSR(1)
728 IX=IX+1: IF IX=RH THEN N1=N1/3 ELSE 665
729 N2=SQR((N3-3*N1*N1)/2): N4=N3*100/N1
730 !*STATISTICS REPORT ON LAST THREE TRIALS*
732 !N1;N3;N4
734 !*STORE DATA FOR CURVE?*: INPUT A

```

```

735 IF H THEN 740 ELSE 645
740 N5(J1)=N1*C2
741 !*NEW CONC?*: INPUT *NC*L2
742 IF L2=0 THEN 744 ELSE J1=J1+1
743 IF D6 THEN 555 ELSE 605
744 FOR I=1 TO J1: M1(I)=I: NEXT
745 !TAB18*CALIBRATION CURVE*: S1=0: S2=0: S3=0: S4=0: S5=0
746 !!*PT* TAB15*CONC* TAB26*R*GCAT* TAB37*LOG C* TAB47*LOG R*
747 FOR I=1 TO J1: Z=M1(I)
748 X5(I)=LGT(E8(Z)): Y5(I)=LGT(N5(Z)): X=X5(I): Y=Y5(I)
749 !Z; $10.2 E8(Z); $12 N5(Z); $10.5 X5(I); $10.5 Y5(I)
750 S1=S1+X: S2=S2+X*X: S3=S3+Y: S4=S4+Y*Y: S5=S5+X*Y
751 NEXT
752 S6=(J1*S5-S1*S3)/(J1*S2-S1*S1)
753 S7=(S3-(S1*S6))/J1: S7=10**S7
754 !!*CURVE: R*GCAT=*; S7; *CONC**; S6
755 X1=J1*S5-S1*S3
756 X2=SQR((J1*S2-S1*S1)*(J1*S4-S3*S3))
757 X2=X1/X2: !*CURR. COEFF. *: X2: IF H=1 THEN 777
758 !*ADVANCE PAPER TO DESIRED ORIGIN*: GRAPH0,0,1: END
759 R8=S7: Z8=S6: !TAB 26*LOG R*GCAT*
760 !TAB7*7.0* TAB21*7.5* TAB35*8.0*, TAB49*8.5* TAB63*9.0*
761 GRAPH0,900,1: GRAPH0,100,0
762 FOR I=100 TO 900STEP 40GRAPH0,I,1
763 GRAPH50,I,0: NEXT
764 GRAPH0,100,1: GRAPH3000,100,0
765 FOR I=3000TO 0STEP -200GRAPH I,100,1
766 GRAPH I,115,0: NEXT
767 FOR I=1 TO J1X=(X5(I)-2)*2000: Y=(Y5(I)-7)*400+100
768 GRAPH X+50,Y,1: GRAPH X-50,Y,0
769 GRAPH X,Y+13,1: GRAPHX,Y-13,0: NEXT: S7=LGT(S7)
770 X=2000*((7-S7)/S6-2): Y=2000*((9-S7)/S6-2)
771 GRAPHY,900,1: GRAPH X,100,0
773 GRAPH 0,0,1: !TAB3*2.0*: GRAPH875,0,1: !TAB3*2.5*
774 GRAPH 1200,0,1: !TAB1*LOG C*: GRAPH 1600,0,1: !TAB3*3.0*
775 GRAPH 2500,0,1: !TAB3*3.5*
776 H=1: GOTO 745
777 !!!*ANOTHER CURVE?*: INPUT J2: IF J2=0 THEN 781
778 !*INPUT # OF POINTS*: INPUT J1
779 !*INPUT PT*'S*: FOR I=1 TO J1 INPUT M1(I): NEXT
780 GOTO 745
781 !!!*RUN TRAPPING TESTS?*: INPUT K: IF X=0 THEN END
782 D5=1: GOTO 605
784 !*INPUT CURVE R=A*C**B?*: INPUT I
785 IF I=0 THEN 790 ELSE INPUT *A*R8: INPUT *B*Z8
790 FI=2: IF D4=1 THEN 665
795 INPUT *F2*R1: INPUT *TRAP I*R2: R1=R1+E4*.35921/B5
800 R3=R1*R2*E7: R2=R2+1: TT(5)=R2: R2=R2+.04
804 TT(6)=R2: R2=R2+2: TT(7)=R2: R2=R2+4: TT(8)=R2
805 !*C THEOR: *R3*PPBML F2C:*R1
810 END
815 R4=1/Z8: FOR I=1 TO R4

```

```

820 R5=(PSR(I)*C2/R8)**R4
825 !'CONC=':R5
830 R5=100*R5/R3: !'2 EFF:C/C=':R5
835 END
870 RUN 670
871 END
900 !'PLOT FROM EXTERNAL DATA'
905 !'INPUT # OF POINTS': INPUT J1
910 FOR I=1 TO J1 INPUT 'LOG C*X1: E8(I)=10**X1
915 INPUT 'LOG R*GCAT*Y1: NS(I)=10**Y1: NEXT
920 GOTO 744: END
1000 RUN 870
1001 END
2050 RUN 759: END
2082 RUN 900: END
2690 RETURN
2711 GOTO 4820
2712 END
2715 R=0
4450 GOTO 4820
4841 RUN 870
8780 RUN 870
8781 END

```

Table 7

## SP4100 Program Variable List

<u>Name</u>	<u>Variable</u>	<u>Units</u>
OV T	A1	°C
DET T	A2	°C
INJ T	A3	°C
RH2	A7	ML/MIN
RAIR	A8	ML/MIN
FLTR	A5	S,M,F
ZERO	A6	OFF,L,M,H
STD.GEN	D6	0 = KINTEK, 1 = FF
GAS	B1	
PLAB	B4	TORR
PH20	B6	TORR
PLAB-PH20	E4	TORR
TBFM	B5	°C (converted to K)
LV	C1	ML
GCAT	C2	INPUT * OUTPUT
PT#(FF)	C3	
PR(FF)	C4	NG/MIN
MWT	C5	G/MOL
TBOX(FF)	C6	°C
F2(FF)	D1	ML/MIN
FPT(FF)	C7	VOLTS
VF1(FF)	C8	VOLTS
VF(FF)	C9	VOLTS
F2C(FF)	D1	ML/MIN
FPTC(FF)	C7	ML/MIN
F1(FF)	C8	ML/MIN
F(FF)	C9	ML/MIN
K*1000	E6	
INIT CONC(FF)	E6	PPB
FLOWING CONC	E7	PPB
INJ. CONC	E8(J1)	PPBML
CONC. INDEX	J1	
CELL OR PT (KIN)	Z4	0 = CELL, 1 = PT
CELL#	B2	
PSTD	B3	PSI (converted to TORR)
PR	B8	NG/MIN
%	B9	
FLOW	B7	ML/MIN
TUBE#	Z5	
# OF TRIALS	E9	
TLAB	C6	°C (converted to K)
EXT. STD. FLAG	Z1	0 = NOT STD, 1 = EXT.STD.
TIME	Z2; Z3	HR:MIN:SEC
INJ. TIME	G3	TIME BASE UNITS
% DRIFT	F5	
DRIFT RATE	F5	%/HR

<u>Name</u>	<u>Variable</u>	<u>Units</u>
FILENAME	NM,NM(1),NM(2)	
ANALYST	AN	
DAY	A	
TRIAL INDEX	IX	
# OF PEAKS	A4	
RT	PST( )	
AREA	PSR( )	
HEIGHT	PSA( )	
BL CODE	PSF( )	
TRIAL#1 AREAS	E1( )	
TRIAL#2 AREAS	E2( )	
TRIAL#3 AREAS	E3( )	
MEAN	N1( )	
$\sigma$	N3( )	
%RSD	N4( )	
$\Sigma$ LOG AREA	S1( )	
$\Sigma(\text{LOG AREA})^2$	S2( )	
$\Sigma$ LOG CONC	S3( )	
$\Sigma(\text{LOG CONC} \times$ LOG AREA)	S5( )	
$\Sigma(\text{LOG CONC})^2$	F9( )	
CORR. COEFF.	U	
NUMBER OF VALUES	NV	3*#CONC.
PRED. AREA	F4	
	R*GCAT =	
	A*CONC**B	
A	R8	
B	Z8	
CORR FOR DRIFT	Z	%/HR*HR
STD OR SAMPLE	D5	0-STD 1-SAMP
STDGEN SAMP OR		
FIELD	D4	0-STD GEN 1-FIELD
PUMPING RATE	R1	ML/MIN
SAMPLING TIME	R2	MIN
TRAPPED CONC		
(IF 100%)	R3	PPBML
PREDICTED CONC.	R5	PPBML
%EFF. R/R	R6	%
%EFF C/C	R5	%

Table 8

## Main Program

<u>Line #</u>	<u>Comments</u>
<u>500-533</u>	<u>INITIALIZATION, INPUT PARAMETERS</u>
500	INITIALIZE CONC. COUNTER, TURN OFF PRINTER
501	ZERO STATISTICS REGISTERS
505,510	INPUT GC PARAMETERS
515-525	SELECT STD. OR SAMPLE, IF SAMPLE (L FD) TRANSFER TO TRAPPING SUB-R
531	INPUT TLAB, CONVERT TO K
532,533	INPUT PRESSURES + CORRECT FOR H <sub>2</sub> O VAPOR
535,536	SELECT KINTEK OR FF, H <sub>2</sub> S OR COS. SET PROPER MWT.
<u>545-560</u>	<u>PERMEATION TUBE OPTION</u>
545	IF KINTEK GO TO KINTEK CALC SUB-R(595)
555	CORRECT "F2" FLOW FOR T, P, H <sub>2</sub> O VAPOR
560	INPUT FLOW METER VOLTAGES. RETURN POINT FOR NEW CONC.
<u>595-630</u>	<u>KINTEK CALCULATIONS</u>
595	SELECT CELL OR PERM. TUBE. IF TUBE GO TO PT CALC (605)
601	INPUT RAW GAS PRESSURE (PSI). CONVERT TO TORR.
605	INPUT FLOW. IF PERM. TUBE THEN GO TO PT CALC (620). RETURN POINT FOR KINT. NEW CONC.
610	CORRECT FLOW FOR P, T, H <sub>2</sub> O VAPOR. CALCULATE FLOWING CONC.
615	CALCULATE INJECTED CONC. GO TO 635 TO PRINT CONCS.
620	KINTEK PT CALC. IF NEW CONC, CALCULATE AT 630 ELSE INPUT PARAMETERS.
625	INTERMEDIATE RESULT IN CONC. CALC.
630	CALCULATE FLOWING CONC, INJECTED CONC.

<u>Line #</u>	<u>Comments</u>
635	PRINT FLOWING CONC. IF TRAPPING TEST GO TO TRAPPING SUB-R (780)
645	INPUT # OF TRIALS. RESET INDEX.
646	RESET STATISTICS REGISTERS.
<u>650-655</u>	<u>STABILITY CHECK</u>
654	TURN PRINTER ON
655	PRINT COMMENTS ON FLAME, GAS FLOWS, OTHER.
660	SELECT FILE. IF SAMPLE, FILE 2. IF STANDARD FILE 1.
<u>665</u>	<u>INJECT</u>
	GET INJECT TIME VALUES. TRANSFER PROGRAM CONTROL TO ROM PROGRAM AT LINE 2600. END EXECUTION OF "MAIN PROGRAM"
	ON 2ND "INJECT/STANDBY" OR "ERØ" CONTROL IS TRANSFERRED FROM LINE 4841 OF ROM PROGRAM TO LINE 870 OF "MAIN PROGRAM" MORE INFO ON TRANSFER IN "ROM PATCHES"
<u>670-725</u>	<u>REPORT</u>
670	DELAY LOOP TO AVOID OVER PRINTING CHROMATOGRAM. IF NOT FIRST RUN AT THIS CONC, PRINT ABBEREVIATED REPORT AT LINE 715.
680	GET VALUE OF DAY FROM MEMORY
685-710	PRINT PARAMETERS
715	ASSIGN # OF PEAKS IN CHROMATOGRAM TO USER VARIABLE
720,725	ABBREVIATED REPORT, PM#, RT, AREA, HEIGHT, BC CODE
726	IF SAMPLE RUN GO TO TRAPPING CALCS AT 815. IF ONE OF LAST THREE RUNS USE DATA FOR STATICS ELSE 728.
<u>727-732</u>	<u>STATISTICS CALCULATIONS</u>
727	ADD DATA TO $\Sigma$ AREA + $\Sigma$ (AREA) <sup>2</sup> REGISTERS
728	INCREMENT INDEX, IF INDEX $\neq$ # OF TRIALS INJECT AT 665 ELSE CALCULATE MEAN.
729	CALCULATE STD. DEV. AND %RSD
730,731	PRINT HEADER FOR STATISTICS REPORT

<u>Line #</u>	<u>Comments</u>
732	PRINT STATISTICS DATA
<u>734-757</u>	<u>CALIBRATION CURVE</u>
734-735	CHECK FOR GOOD DATA. IF YES STORE DATA (740) IF NO GO TO # OF TRIALS AT SAME CONC (645).
740	STORE $\bar{R} \times \text{GCAT}$
741,742 743	ASK FOR NEW CONC IF YES* INCREMENT CONC. COUNTER INPUT VFPT ETC (560) OR FLOW (605). IF NO CONTINUE WITH CALIBRATION CURVE CALCULATIONS.
744,745	PRINT CALIBRATION CURVE HEADER
746-748	LOOP TO PRINT CONC, $R \times \text{GCAT}$ , LOG C, LOG R
749-751	STORE DATA AS $\Sigma \text{ LOG CONC}$ , $\Sigma (\text{LOG CONC})^2$ , $\Sigma \text{ LOG}(R \times \text{GCAT})$ , $\Sigma (\text{LOG } R \times \text{GCAT})^2$ , $\Sigma (\text{LOGC} \times \text{LOGR} \times \text{GCAT})$
752	CALCULATE SLOPE
753	CALCULATE INTERCEPT, $10^{\text{INTERCEPT}}$ .
754	PRINT CURVE PARAMETERS
755-757	CALCULATE AND PRINT CORR. COEFFICIENT
779	IF NO SAMPLE, END
<u>780-845</u>	<u>TRAPPING CALCULATIONS</u>
780-785	INPUT CURVE PARAMETERS
790	SET FILE 2 FOR ANALYSIS. IF FIELD SAMPLE, END. (MANUAL INJECT)
795	INPUT "F2", CORRECT FOR T, P, H <sub>2</sub> O.
800-805	CALCULATE THEORETICAL CONC., SET TIME FUNCTION TIMES BASED ON TRAPPING TIME.
810	END "MAIN PROGRAM" (MANUAL INJECT).
815-830	CALCULATE CONC. AND % EFF.
835	NEW CONC. IF YES GO TO 795. IF NO END (MANUAL INJECT).



<u>Line #</u>	<u>Comments</u>
870	LINK FROM ROM PROGRAM 4841 TO REPORT AT 670.
871	END
<u>2690-8781</u>	<u>ROM PATCHES</u>
2690	BEGIN ROM PATCH (ALLOWS STATEMENTS TO BE PLACED IN ROM FOR CALLS BY "MAIN PROGRAM")
2711	ON 2nd "INJECT STANDBY" OR "ERØ" TRANSFERS TO "END OF REPORT"
2712	PREVENT FURTHER EXECUTION OF ROM PROGRAM.
4450	TRANSFERS TO "END OF REPORT"
8780	TRANSFERS CONTROL TO "MAIN PROGRAM" AT LINE 870..
8781	PREVENTS FURTHER EXECUTION OF ROM PROGRAM.

Table 9

## Plotting Subprogram

<u>Line #</u>	<u>Comments</u>
758-759	PRINT LABEL + SCALE FOR Y-AXIS
760	DRAW Y-AXIS
761-762	DRAW HASH MARKS AT 0.1 UNIT INTERVAL
763	DRAW X-AXIS
764-765	DRAW HASH MARKS AT 0.1 UNIT INTERVAL
766	CALCULATE X + Y POSITION IN PLOTTER UNITS
767-768	PLOT POINTS WITH "+"
769	CALCULATE END POINTS OF LINEAR REGRESSION CURVE
770	DRAW LINE BETWEEN END POINTS: MOVE PRINT HEAD TO ORIGIN: PRINT SCALE OF X-AXIS
771-772	CONTINUE PRINTING X-AXIS SCALE + LABEL
777	ASK IF TRAPPING TESTS WILL BE RUN: IF NO END
778	IF YES, SET SAMPLE FLAG TO 1: TRANSFER TO LINE 520 TO ASK FOR FIELD OR STANDARD GENERATED SAMPLE

Table 10

## Tracor Rotameter Calibrations

P(psi)	Reading	Flow Rate (ml min <sup>-1</sup> )
Carrier Control #1		
60	1.0	18.0
	~1.8, 1.9	29.0
	3.1	41.9
	4.0	54.2
	5.0	67.1
	6.0	80.1
50	1.0	15.3
Carrier Control #2		
50	0.9	24.8
60	1.0	29.8
80	1.0	37.0
	2.0	47.4
	4.0	72.2
	6.0	106.7
Air		
20	*~60	55.4
	100	90.9
	150	152.0
	200	206.7
	250	263.45
40	**100	94.6
	150	151.4
	200	200.1
	250	247.8
H <sub>2</sub>		
20	~30	26.5
	60	57.2
	100	94.1
	140	128.3
	200	203.3

\* will not go below 50 easily  
 \*\* will not go below 100 easily

Table 11  
Chromel-Alumel Thermocouple Calibration

Temperature (°C)	#1	mv Reading		#4
		#2	#3	
42.7	1.69	1.69	1.69	1.69
34.2	1.34	1.34	1.34	1.34
26.85	1.05	1.05	1.05	1.05
21.9	0.86	0.86	0.86	0.86
12.7	0.49	0.49	0.49	0.49
47.05	1.87	1.87	1.87	1.87

Linear regression:  $T^{\circ}\text{C} = 24.94 (\text{voltage}) + 0.55$

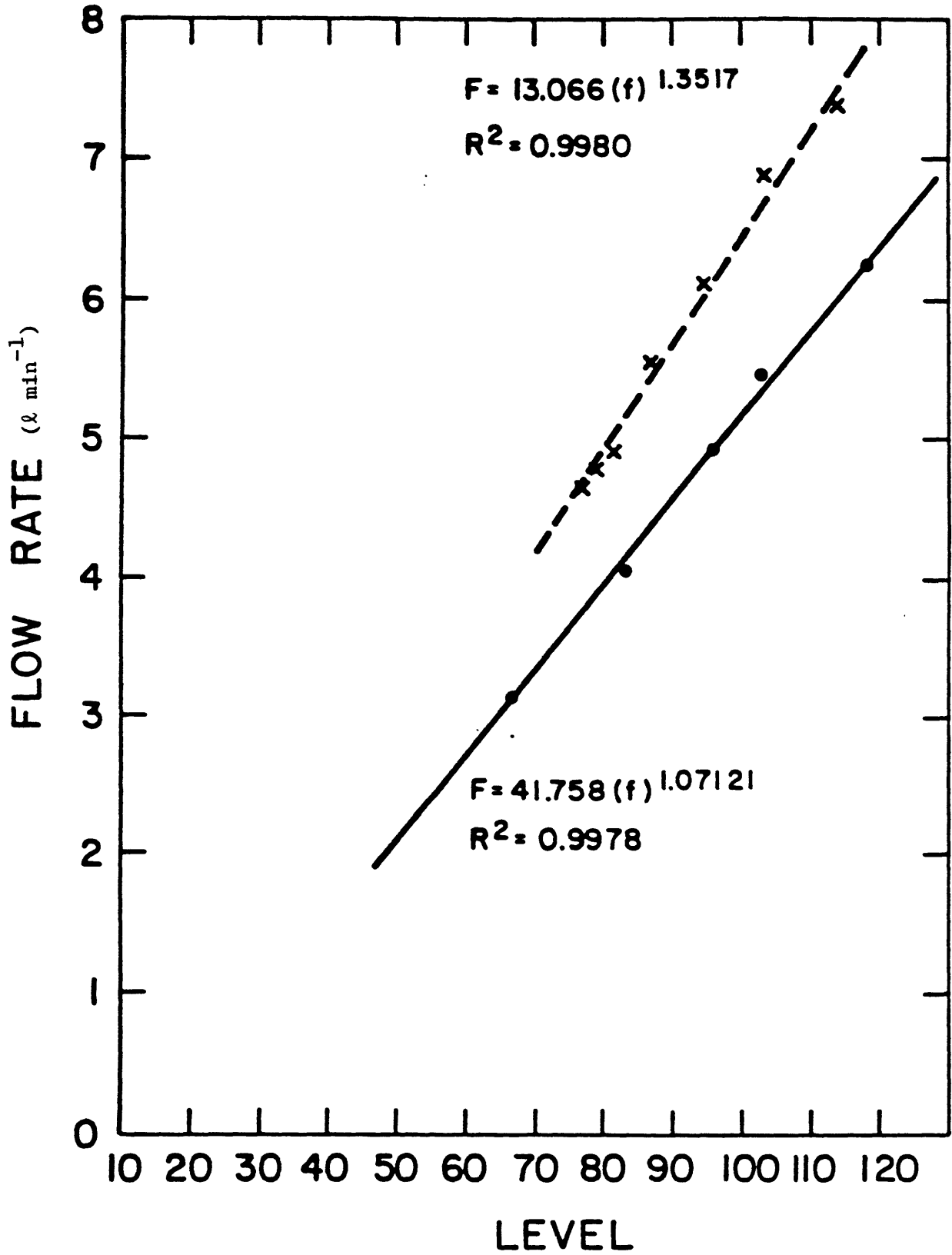
Intercept =  $0.5503681 \pm 0.1770746$

Slope =  $24.94490 \pm 0.1356055$

$R^2$  = 0.9998818

$S_{y \cdot x}$  = 0.1575087

Fig. 53 Rotameter calibrations .



APPENDIX V

Empty Teflon Sample Loop Efficiencies

Table 12

## Empty Teflon Sample Loop Trapping\* Efficiency Tests

Loop #	% Efficiency $\pm$ Standard Deviation (# Trials)		
	OCS		H <sub>2</sub> S
1	71.79	$\pm 0.04$ (3)	62.29 $\pm 1.33$ (6)
1	69.95	$\pm 2.31$ (4)	
2	70.90	$\pm 0.54$ (3)	60.71 $\pm 0.49$ (3)
3	69.98	$\pm 1.07$ (3)	59.60 $\pm 4.82$ (3)
4	73.60	$\pm 3.03$ (3)	62.84 $\pm 2.10$ (3)
5	74.74	$\pm 0.09$ (3)	62.00 $\pm 0.62$ (3)
5	75.94	$\pm 0.25$ (3)	
6	76.10	$\pm 0.075$ (3)	65.14 $\pm 1.57$ (3)
7	72.03	$\pm 1.98$ (3)	63.12 $\pm 0.28$ (3)
8	74.15	$\pm 0.30$ (3)	65.32 $\pm 0.52$ (3)
9	73.57	$\pm 0.35$ (3)	
10	72.26	$\pm 0.90$ (3)	
11	69.38	$\pm 0.67$ (3)	
11	71.73	$\pm 0.51$ (3)	
11	68.33	$\pm 0.30$ (3)	
12	73.34	$\pm 0.73$ (3)	
12	69.42	$\pm 0.57$ (3)	
13	74.21	$\pm 0.51$ (3)	
14	72.395	$\pm 4.56$ (4)	
14	74.71	$\pm 0.57$ (3)	
14	66.34	$\pm 0.40$ (3)	
15	73.52	$\pm 0.27$ (3)	
16	75.36	$\pm 1.06$ (3)	
17	70.95	$\pm 0.37$ (3)	
18	74.51	$\pm 1.89$ (5)	
19	76.48	$\pm 0.14$ (3)	
20	70.05	$\pm 0.41$ (3)	
20	67.33	$\pm 0.55$ (3)	
21	65.93	$\pm 1.37$ (3)	
21	65.39	$\pm 0.77$ (3)	
22	71.28	$\pm 1.84$ (3)	
22	65.24	$\pm 0.84$ (3)	
22	68.67	$\pm 0.15$ (3)	
23	71.36	$\pm 0.24$ (3)	
24	72.97	$\pm 0.11$ (3)	
25	78.66	$\pm 0.52$ (3)	
26	73.78	$\pm 0.76$ (3)	
27	74.12	$\pm 0.45$ (3)	
28	73.40	$\pm 0.18$ (3)	
28	69.21	$\pm 0.74$ (3)	
29	72.97	$\pm 1.51$ (3)	
30	73.94	$\pm 0.42$ (3)	
31	74.64	$\pm 0.73$ (3)	
32	71.37	$\pm 1.16$ (3)	

Loop #	% Efficiency $\pm$ Standard Deviation (# Trials)		
	OCS		H <sub>2</sub> S
33	75.72	$\pm 0.20$	(3)
33	77.55	$\pm 0.12$	(3)
34	67.57	$\pm 0.94$	(3)
35	73.01	$\pm 1.44$	(3)
35	74.55	$\pm 0.55$	(3)
36	70.36	$\pm 4.74$	(4)
36	65.21	$\pm 0.44$	(3)
37	71.67	$\pm 1.09$	(3)
38	67.13	$\pm 2.74$	(3)
38	73.44	$\pm 0.55$	(3)
39	72.46	$\pm 0.20$	(3)
39	77.89	$\pm 0.23$	(3)
40	70.40	$\pm 0.60$	(3)
41	74.55	$\pm 4.89$	(4)
41	72.84	$\pm 0.61$	(3)
42	66.76	$\pm 2.07$	(4)
42	74.57	$\pm 0.38$	(3)
43	69.10	$\pm 0.40$	(3)
43	76.34	$\pm 0.23$	(4)
44	67.67	$\pm 0.64$	(3)
45	74.84	$\pm 0.36$	(3)
46	73.91	$\pm 2.21$	(3)
46	76.91	$\pm 0.59$	(3)
47	66.57	$\pm 1.38$	(3)
48	76.97	$\pm 0.33$	(3)
48	69.91	$\pm 0.23$	(3)
49	76.04	$\pm 0.52$	(3)
50	73.99	$\pm 0.19$	(3)
50	76.62	$\pm 1.17$	(3)

\*Trapping  $\equiv$  collection plus desorption

Average of 50 "1st tests" for OCS: 72.37  $\pm$ 2.862% efficiency (3.95% relative standard deviation). Total error = 53.88 or  $\pm$ 1.49%.

Average of 8/50 H<sub>2</sub>S tests: 62.63  $\pm$ 1.97% efficiency (3.45% relative standard deviation). Total error = 12.33 or  $\pm$ 2.46%.



APPENDIX VI

Mechanical Fits to Plots of  
Concentrations to Determine  $C(t_i)$  for  
Wallops Island Flux Studies and Concentration and  
Flux Results, Reported With Their Errors,  
for  $H_2S$  and  $OCS$

Fig. 54 Mechanical fits to OCS concentrations for August 5-6, 1982 field study

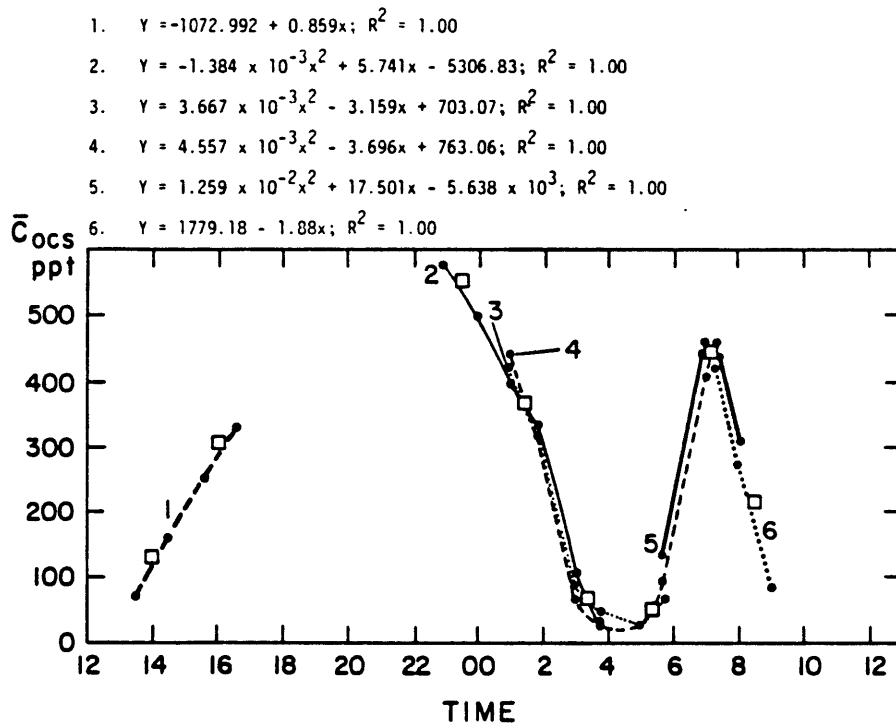


Fig. 55 Mechanical fits to H<sub>2</sub>S concentrations for August 5-6, 1982 field study

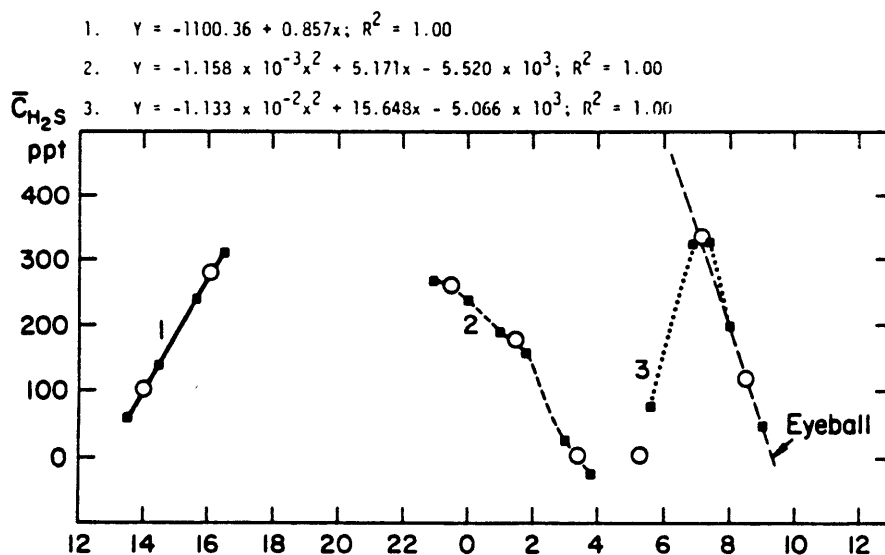


Fig. 56 Mechanical fits to OCS concentrations for August 13-14, 1982 field study

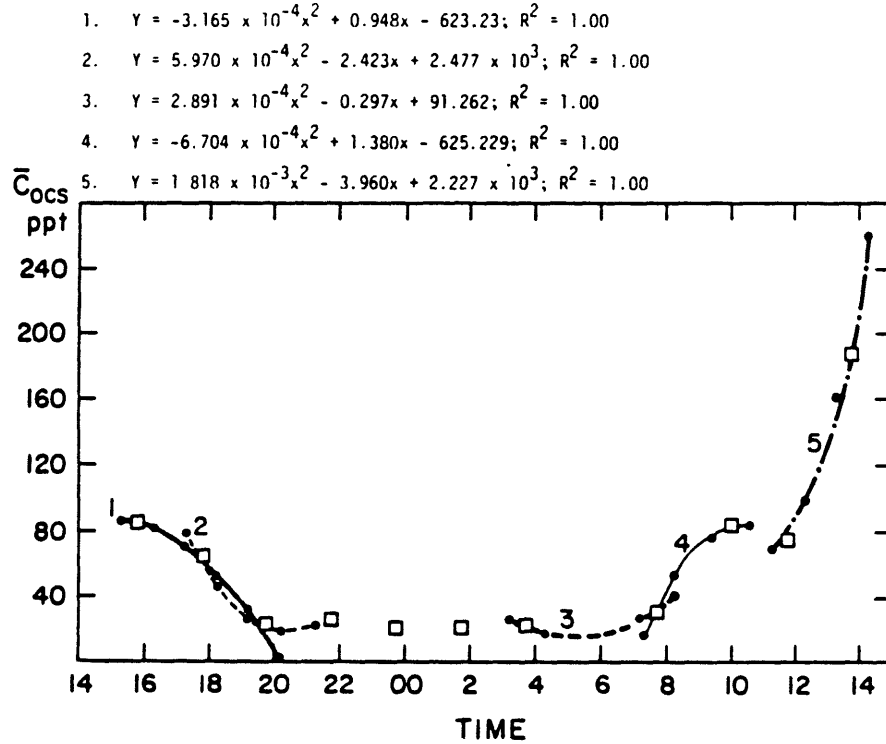


Fig. 57 Mechanical fits to  $H_2S$  concentrations for August 13-14, 1982 field study

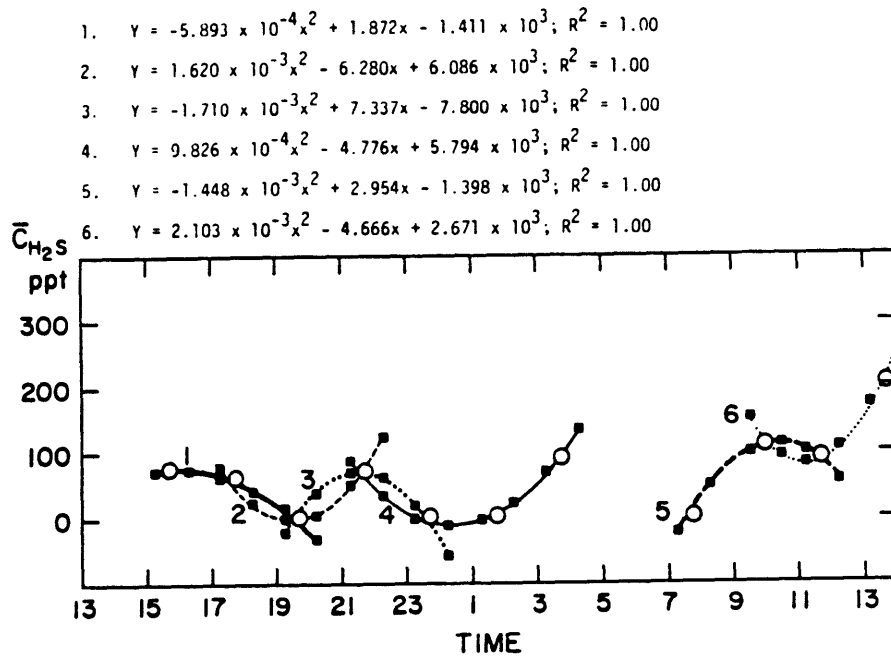


Fig. 58 Mechanical fits to OCS concentrations for August 18-19, 1982 field studies

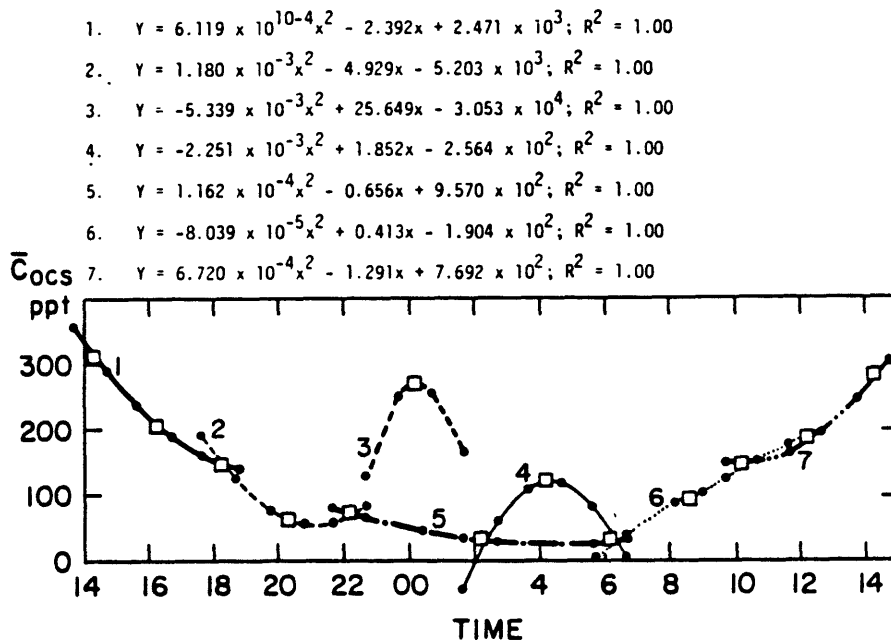


Fig. 59 Mechanical fits to H<sub>2</sub>S concentrations for August 18-19, 1982 field studies

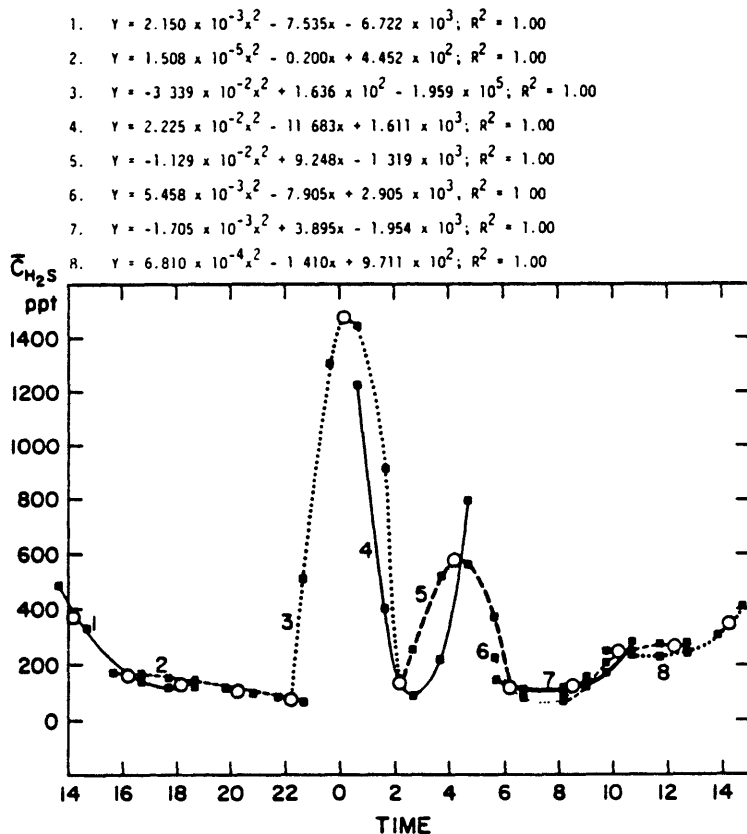


Fig. 60 Mechanical fits to OCS concentrations for August 26-27, 1982 field study

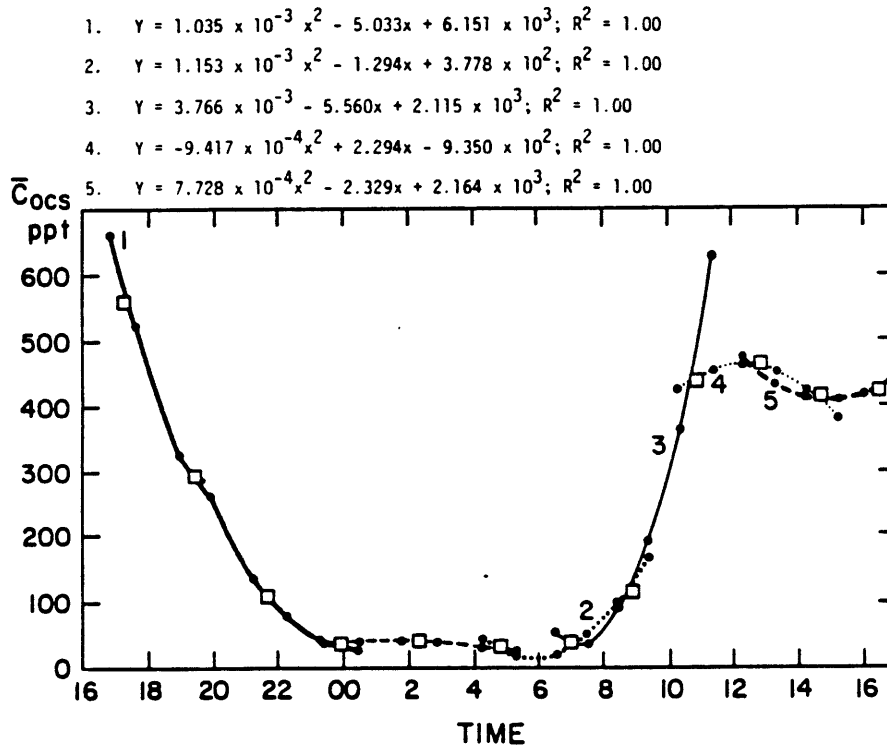


Fig. 61 Mechanical fits to H<sub>2</sub>S concentrations for August 26-27, 1982 field study

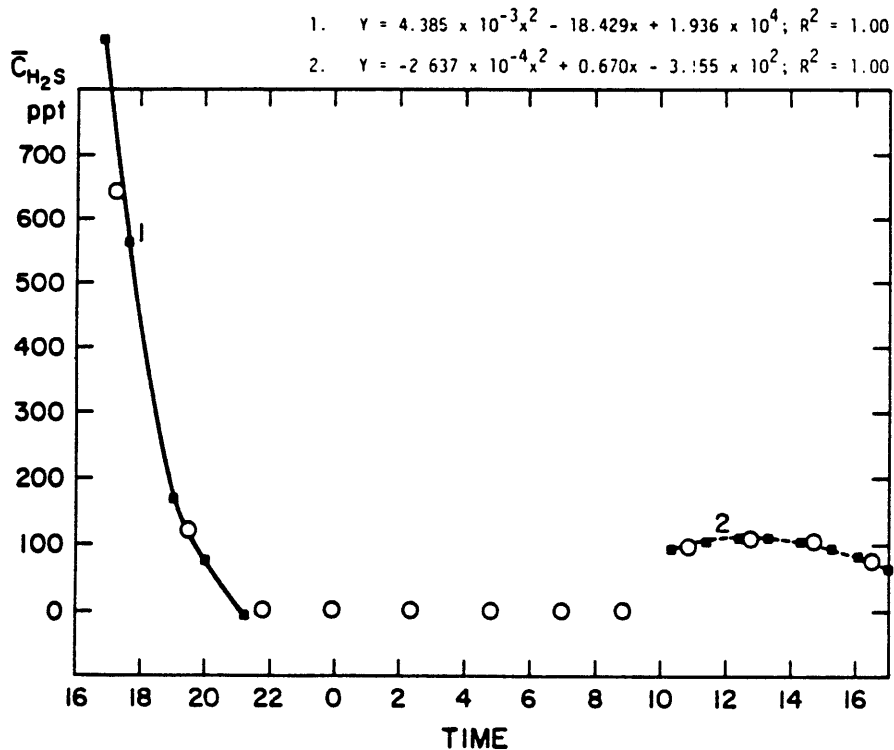


Fig. 62 Mechanical fits to OCS concentrations for September 3-4, 1982 field study

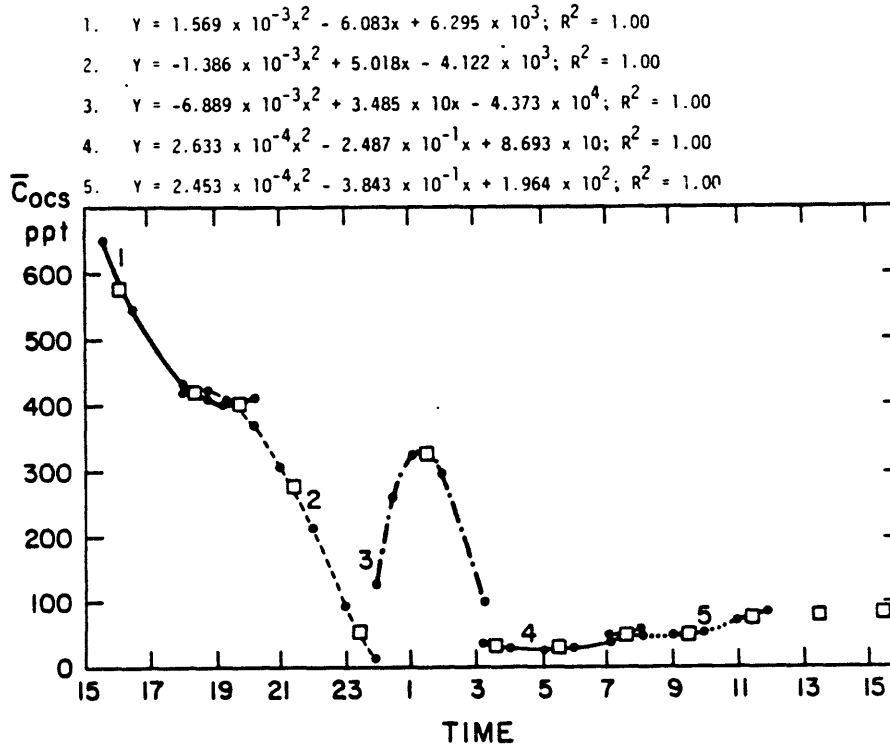


Fig. 63 Mechanical fits to H<sub>2</sub>S concentrations for September 3-4, 1982 field study

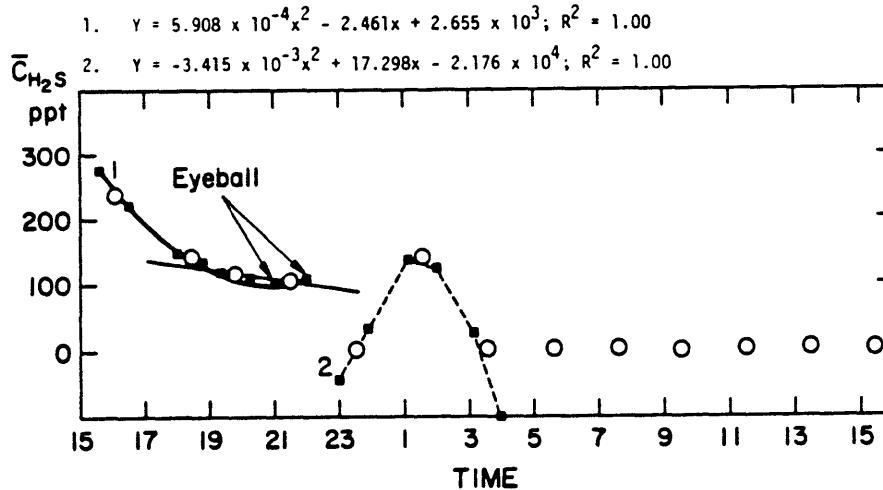


Fig. 64 Mechanical fits to OCS concentrations for September 9-10, 1982 field study



Fig. 65 Mechanical fits to H<sub>2</sub>S concentrations for September 9-10, 1982 field study

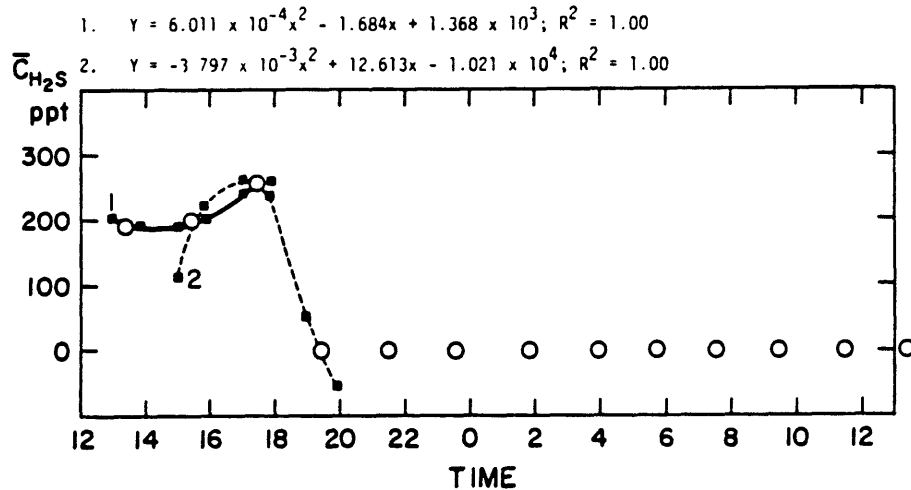


Fig. 66 Mechanical fits to OCS concentrations for September 14-15, 1982 field study

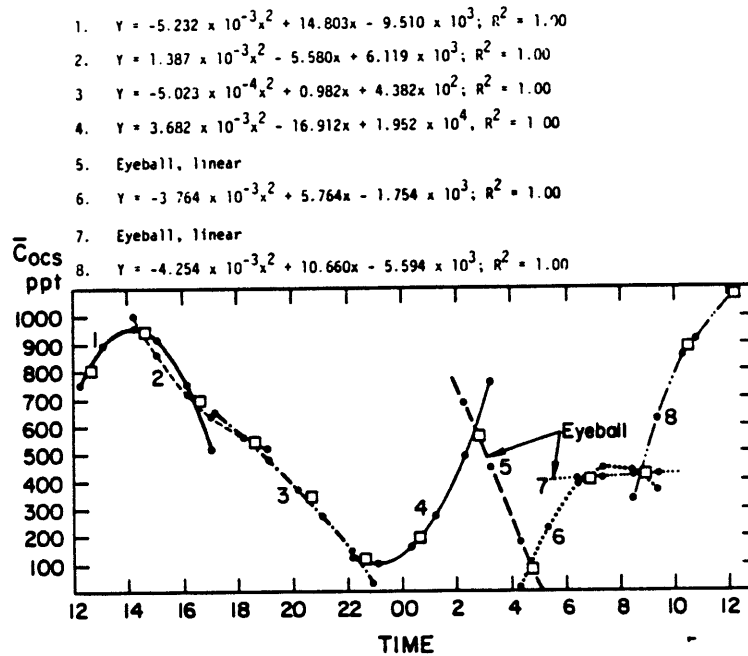


Fig. 67 Mechanical fits to  $H_2S$  concentrations for September 14-15, 1982 field study

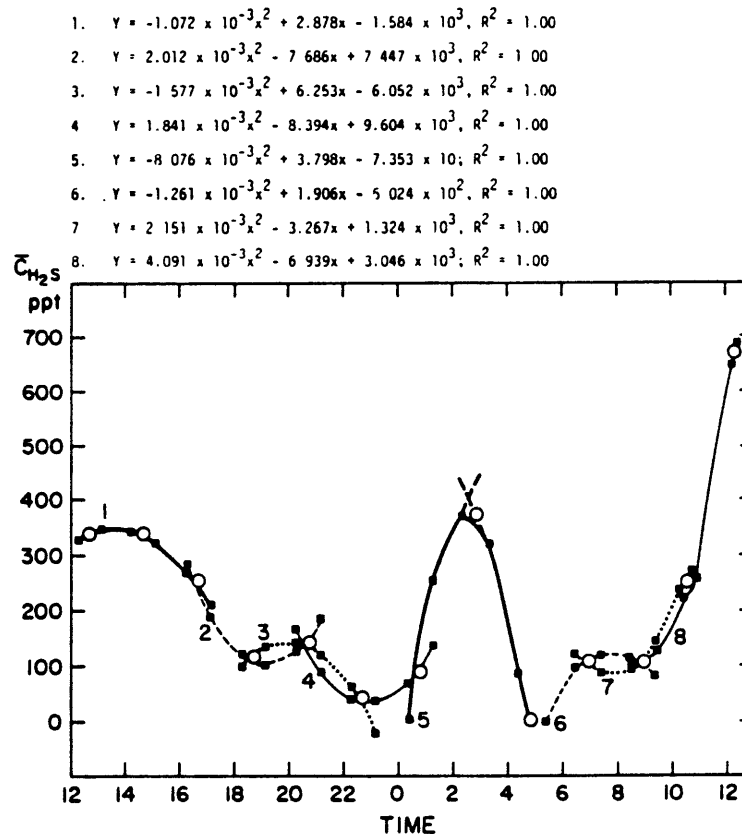




Fig. 68 Mechanical fits to OCS concentrations for September 23-24, 1982 field study

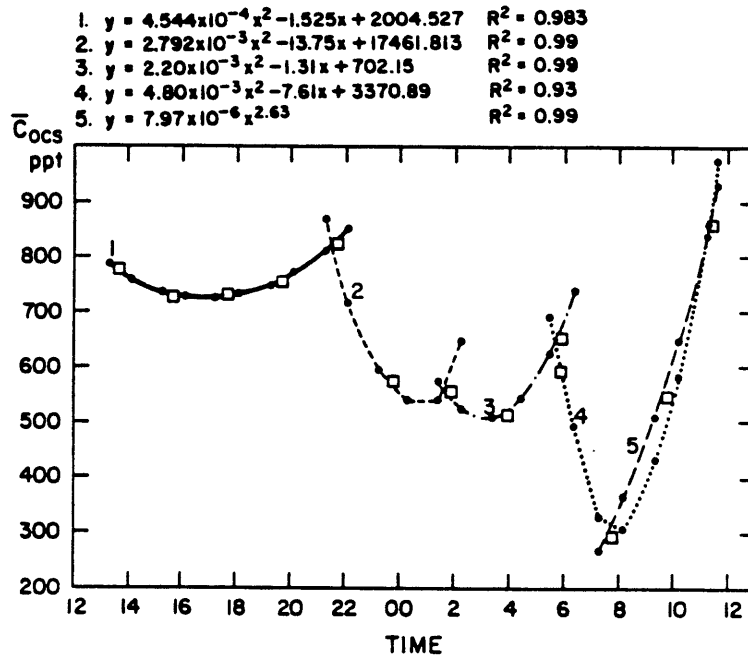


Fig. 69 Mechanical fits to H<sub>2</sub>S concentrations for September 23-24, 1982 field study

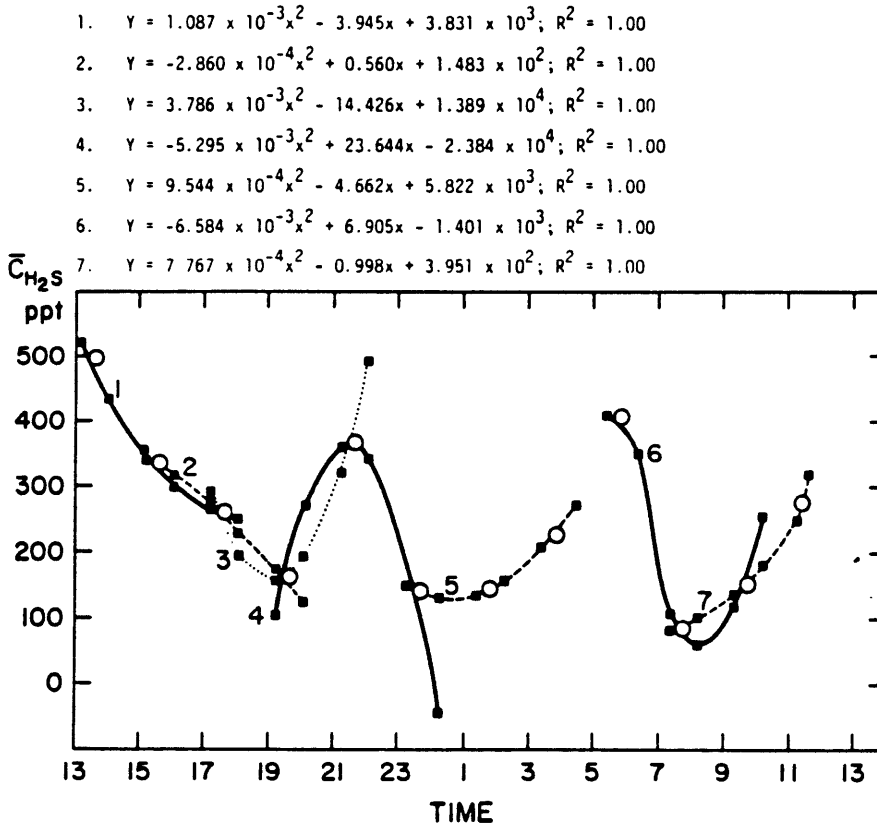


Fig. 70 Mechanical fits to OCS concentrations for September 28-29, 1982 field study

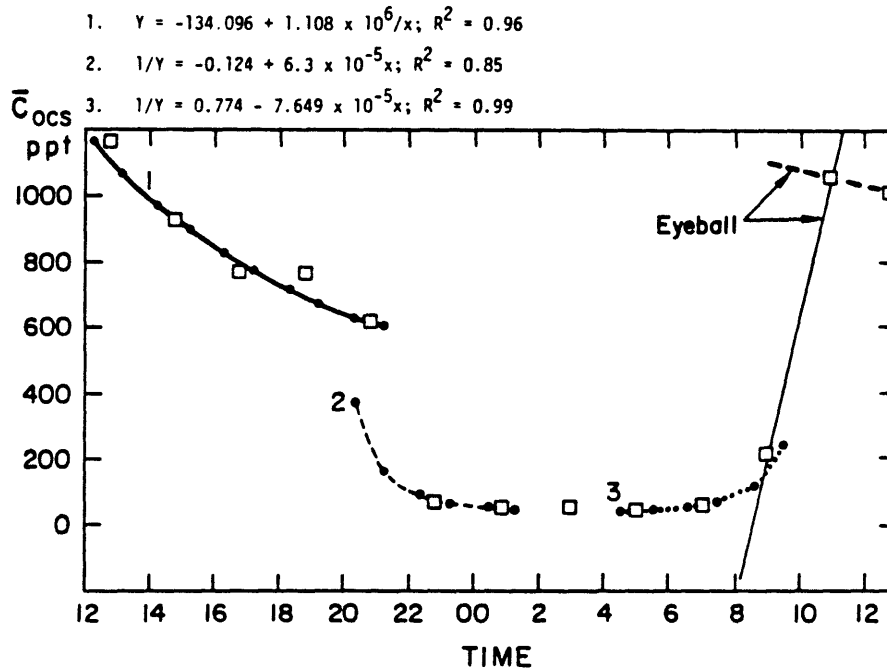
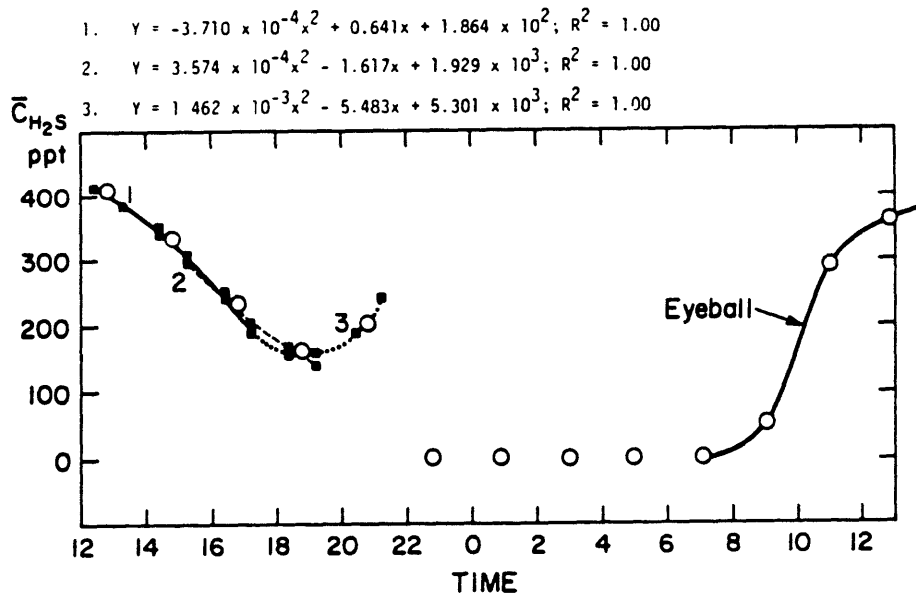


Fig. 71 Mechanical fits to H<sub>2</sub>S concentrations for September 28-29, 1982 field study



The numerical results for OCS and H<sub>2</sub>S are presented next.  $\bar{C}$  refers to the average output chamber concentration during a sampling period,  $\bar{C}_0$  refers to the average input chamber concentration during a sampling period, and  $\bar{E}$  refers to the average flux calculated for a particular sampling period.

In these tables  $\Delta$  refers to standard deviation,  $E1 = (\bar{C} - \bar{C}_0)(u)/A$ ,  $E2 = (C(t_2) - C(t_1))(H)/(t_2 - t_1)$ , and  $\bar{E} = E1 + E2$ .

The  $\bar{C}$  values presented graphically for OCS and H<sub>2</sub>S in Chapter 4 for the September 14-15, September 23-24, and September 28-29 field studies were corrected for loss on the NAFION drier (33.9%) whereas the values presented here have not been adjusted.

Individual  $\bar{C}$  and  $\bar{C}_0$  values typically have relative standard deviations of ~20%.  $E1$  values were typically reliable to ~30%.  $E2$  values, however, have much greater uncertainty and therefore represent most of the uncertainty reported in  $\bar{E}$ .

Table 13

Concentration and Flux Results for  
Wallops Island Flux Studies of OCS and H<sub>2</sub>S

AUGUST 5 - 6 , 1982 FIELD STUDY OCS

LINEAR REGRESSION

$$\text{LOG}(R * \text{GCAT}) = M + B \text{ LOG}(C)$$

$$M = 3.84308 \pm 6.40219E-02$$

$$B = 1.61964 \pm 2.30337E-02$$

LP#	PPT		PPT	
	$\bar{C} \pm \Delta \bar{C}$	$\bar{C} \pm \Delta \bar{C}$	$\bar{CO} \pm \Delta \bar{CO}$	$\bar{CO} \pm \Delta \bar{CO}$
49	138.229	21.1738		
2			60.3282	8.7958
48	326.331	50.8969		
36			50.183	7.17806
38	540.113	87.9713		
33			60.8621	8.88451
7	363.734	57.0619		
1			47.7097	6.80051
11	64.2894	9.27987		
14			51.7379	7.36272
39	52.3643	7.43238		
28			49.256	6.95344
12	449.011	67.2341		
5			76.4043	10.6287
20	210.29	32.2788		
19			70.7485	9.89637

SET#	NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR	
	$\bar{E}_1 \pm \Delta \bar{E}_1$	$\bar{E}_1 \pm \Delta \bar{E}_1$	$\bar{E}_2 \pm \Delta \bar{E}_2$	$\bar{E}_2 \pm \Delta \bar{E}_2$	$\bar{E} \pm \Delta \bar{E}$	$\bar{E} \pm \Delta \bar{E}$
1	58.6967	24.6881	44.3325	22.3378	103.029	47.0259
2	195.523	48.1364	47.9342	63.3902	243.458	111.527
3	149.642	41.0192	-39.2464	90.693	110.395	131.712
4	98.6757	27.0469	-70.6339	72.3121	28.0418	99.359
5	3.9191	5.47874	-24.7451	13.2291	-20.826	18.7078
6	.970555	4.56174	52.9025	11.9822	53.873	16.5439
7	116.343	32.6907	-11.1534	220.024	105.19	252.715
8	43.5704	16.3067	-96.9622	33.8453	-53.3918	50.152

AUGUST 5 - 6 , 1982 FIELD STUDY H2S

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=2.29866 \pm .146314$$

$$B=2.02649 \pm 5.25758E-02$$

LP#	$\bar{C} \pm \Delta \bar{C}$	PPT $\bar{C} \pm \Delta \bar{C}$	$\bar{CO} \pm \Delta \bar{CO}$
49	101.763	25.5992	
48	276.678	73.4127	
38	259.579	69.4052	
7	176.181	45.354	
12	332.944	83.9802	
20	116.803	29.6683	

SET#	NGS/M <sup>2</sup> -HR $E1 \pm \Delta E1$		NGS/M <sup>2</sup> -HR $E2 \pm \Delta E2$		NGS/M <sup>2</sup> -HR $E \pm \Delta E$	
1	76.6765	22.0404	44.244	26.9504	120.921	48.9908
2	195.899	59.0096	47.8385	91.3049	243.737	150.315
3	81.0511	27.5083	-13.1484	71.4456	67.9027	98.9539
4	55.0109	18.1231	-20.7836	57.263	34.2273	75.3861
5	103.959	33.7089	-13.3683	274.822	90.5904	308.531
6	36.4707	11.8902	-77.2881	31.0372	-40.8174	42.9274

## AUGUST 13 - 14 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R * \text{GCAT}) = M + B \text{ LOG}(C)$$

$$M = 3.71789 \pm .206702$$

$$B = 1.65467 \pm 7.55778E-02$$

LP#	$\bar{C} \pm \Delta C$	PPT $\bar{C} \pm \Delta C$	$\bar{CO} \pm \Delta CO$	PPT $\bar{CO} \pm \Delta CO$
49	89.3415	35.5574		
41			28.8712	10.5966
9	69.9447	27.3581		
47			32.3577	11.9588
22	24.7162	9.01465		
50			23.3517	8.45106
21	28.5636	10.5248		
40			25.7369	9.3791
35	23.4278	8.52251		
37			20.708	7.44452
3	23.4808	8.52324		
43			24.7668	8.98202
46	24.6504	8.99364		
6			15.9616	5.64892
8	32.4986	12.0663		
19			22.5602	8.1496
25	87.5727	34.7413		
23			20.661	7.41289
34	78.7677	31.0801		
15			24.9252	9.06361
39	194.164	81.4288		
7			22.4202	8.09046

SET#	NGS/M <sup>2</sup> -HR $E1 \pm \Delta E1$		NGS/M <sup>2</sup> -HR $E2 \pm \Delta E2$		NGS/M <sup>2</sup> -HR $E \pm \Delta E$	
1	37.408	29.8942	-0.694841	37.1069	36.7132	67.0011
2	23.252	25.1566	-8.87932	28.6493	14.3727	53.806
3	.844078	10.8349	-4.07647	9.49278	-3.23239	20.3277
4	1.74862	12.3757	0	0	1.74862	12.3757
5	1.68256	9.93789	0	0	1.68256	9.93789
6	-.795548	10.8005	0	0	-.795548	10.8005
7	5.37506	9.25106	0	0	5.37506	9.25106
8	6.14809	12.7266	7.55984	12.6716	13.7079	25.3982
9	33.0554	22.5767	3.37017	37.2062	36.4256	59.7829
10	21.9422	17.9398	14.3087	32.3804	36.2509	50.3202
11	61.1785	36.2943	52.2023	86.4327	113.381	122.727

AUGUST 13 - 14 , 1982 FIELD STUDY H2S

LINEAR REGRESSION

LOG(R\*GCAT)=M + B LOG(C)

M=1.52889 ± .273382

B=2.21755 ± 9.71528E-02

LP#	$\frac{\text{PPT}}{\bar{C}} \pm \Delta \bar{C}$		$\frac{\text{PPT}}{\bar{CO}} \pm \Delta \bar{CO}$	
49	73.5039	28.6379		
9	63.5948	24.5424		
21	69.1474	26.8489		
46	88.3009	34.8239		
25	108.453	43.2839		
34	86.6279	34.1273		
39	199.954	83.2622		

SET#	NGS/M <sup>2</sup> -HR E1 ± ΔE1		NGS/M <sup>2</sup> -HR E2 ± ΔE2		NGS/M <sup>2</sup> -HR E ± ΔE	
1	45.4708	19.3478	1.37118	29.8907	46.842	49.2385
2	39.3409	16.5943	-10.9349	25.7185	28.4061	42.3128
3	42.7759	18.1443	-3.53806	27.7912	39.2378	45.9356
4	54.6246	23.5031	34.2645	36.4956	88.8891	59.9987
5	53.5772	24.2225	5.99304	46.3656	59.5702	70.5881
6	35.3031	16.4502	12.2051	35.534	47.5082	51.9842
7	71.2274	34.7892	56.0124	88.3945	127.24	123.184

AUGUST 18 - 19 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=3.7846 \pm 5.87733E-02$$

$$B=1.64079 \pm 2.19216E-02$$

LP#		$\frac{\text{PPT}}{\bar{C}} \pm \Delta \bar{C}$	$\frac{\text{PPT}}{\bar{CO}} \pm \Delta \bar{CO}$
46	313.87	46.2573	
25			24.429 3.18676
19	205.597	29.5041	
15			24.2376 3.1618
43	146.276	20.5406	
37			23.0514 2.9994
40	61.7074	8.4845	
1			18.3684 2.36561
9	73.712	10.2294	
7			18.8775 2.4331
39	269.972	39.3914	
12			24.4972 3.19535
26	35.0147	4.66114	
5			23.4301 3.04951
41	124.459	17.2891	
20			24.4742 3.19209
50	33.7853	4.49233	
8			17.2739 2.21695
31	94.1169	13.0601	
2			24.3594 3.17768
35	150.548	21.1809	
34			16.6888 2.1383
13	190.836	27.2612	
6			21.5781 2.79932
30	287.392	41.9553	
21			22.8877 2.96742

SET#	NGS/M <sup>2</sup> -HR E1 ± ΔE1		NGS/M <sup>2</sup> -HR E2 ± ΔE2		NGS/M <sup>2</sup> -HR E ± ΔE	
1	179.053	37.0129	-35.9778	48.5808	143.075	85.5937
2	112.192	24.2341	-23.002	30.7459	89.1901	54.98
3	76.2292	17.298	-10.3222	21.4029	65.9071	38.7009
4	26.8103	7.67425	-10.6399	8.73145	16.1704	16.4057
5	33.9216	9.05062	12.4355	10.6666	46.3571	19.7172
6	151.856	31.7948	5.60334	41.4284	157.459	73.2232
7	7.16646	5.02714	-2.84729	4.91527	4.31917	9.94242
8	31.2194	8.6436	4.56464	18.1738	35.784	26.8174
9	5.15556	2.4662	16.4925	4.75469	21.648	7.22089
10	21.7812	6.63872	8.87169	17.3443	30.6529	23.983
11	41.7963	10.2913	13.1732	22.0523	54.9695	32.3436
12	52.8492	13.1922	11.4792	28.2654	64.3284	41.4576
13	82.5891	19.9746	31.0748	46.7362	113.664	66.7108



AUGUST 18 - 19 , 1982 FIELD STUDY H2S

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=1.54224 \pm .380473$$

$$B=2.16432 \pm .135313$$

LP#	$\bar{C} \pm \Delta\bar{C}$	PPT $\bar{C} \pm \Delta\bar{C}$	$\bar{CO} \pm \Delta\bar{CO}$
46	368.996	222.413	
19	162.493	92.4899	
43	127.699	71.4562	
40	105.518	58.334	
9	74.4886	40.1705	
39	1472.32	980.202	
26	133.87	75.0973	
41	573.758	356.936	
31	109.262	59.477	
35	251.607	147.738	
13	261.864	154.234	
30	338.85	202.282	

SET#	NGS/M <sup>2</sup> -HR $\bar{E}1 \pm \Delta\bar{E}1$		NGS/M <sup>2</sup> -HR $\bar{E}2 \pm \Delta\bar{E}2$		NGS/M <sup>2</sup> -HR $\bar{E} \pm \Delta\bar{E}$	
1	228.268	145.781	-81.005	233.033	147.263	378.814
2	100.521	60.8235	-35.7647	96.1647	64.7566	156.988
3	78.9966	47.0392	-7.60512	74.2864	71.3915	121.326
4	65.2756	38.4291	-7.15738	59.6358	58.1182	98.0649
5	46.08	26.5039	-6.82296	40.8294	39.2571	67.3333
6	910.807	639.058	75.439	1030.51	986.246	1669.56
7	82.8142	49.4286	-164.932	79.9062	-82.1179	129.335
8	179.151	124.352	20.6873	374.758	199.838	499.11
9	34.1161	21.0281	38.4481	78.976	72.5642	100.004
10	78.5619	51.7877	26.5673	153.425	105.129	205.212
11	81.7646	54.0468	10.7209	159.59	92.4855	213.637
12	105.803	70.7805	26.0752	224.59	131.878	295.37

AUGUST 26 - 27 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R*\text{CCAT})=M + B \text{ LOG}(C)$$

$$M=2.87547 + .103873$$

$$B=1.70495 + 3.82558E-02$$

LP#	PPT		PPT	
	$\bar{C} \pm \Delta\bar{C}$		$\bar{CO} \pm \Delta\bar{CO}$	
40	557.813	130.337		
35			41.5189	8.36321
32	299.083	67.8441		
17			27.6293	5.41433
14	108.961	23.3804		
7			23.4546	4.56344
48	39.7139	7.98802		
25			23.8033	4.63128
20	40.8521	8.27307		
5			30.0429	5.95686
41	29.4506	5.83516		
2			32.5468	6.46864
45	25.6579	5.0199		
43			37.5809	7.50566
34	114.974	24.679		
15			27.4115	5.36628
31	435.997	102.286		
26			27.6561	5.44895
50	460.531	107.717		
19			24.3126	4.73039
37	412.953	95.9037		
21			29.0935	5.72165
9	422.152	97.9136		
8			24.9675	4.8578

SET#	NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR	
	$E1 \pm \Delta E1$		$E2 \pm \Delta E2$		$\bar{E} \pm \Delta\bar{E}$	
1	319.389	97.2649	-88.4686	172.675	230.921	269.94
2	167.926	51.3456	-32.6541	73.7626	135.272	125.108
3	52.8961	19.1849	-69.7655	24.6374	-16.8695	43.8223
4	9.8426	8.15977	0	0	9.8426	8.15977
5	6.68674	9.04287	0	0	6.68674	9.04287
6	-1.9154	7.54262	0	0	-1.9154	7.54262
7	-5.82023	5.8059	0	0	-5.82023	5.8059
8	54.1679	20.5305	38.6979	27.0685	92.8658	47.5991
9	252.607	75.7123	13.8133	99.73	266.42	175.442
10	269.852	79.2467	-5.27727	115.771	264.575	195.017
11	237.463	71.3894	-3.36195	102.377	234.101	173.766
12	245.706	72.3942	11.9838	108.894	257.689	181.288

AUGUST 26 - 27 , 1982 FIELD STUDY H2S

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=2.79475 \pm .142667$$

$$B=1.81485 \pm 5.31033E-02$$

LP#	$\bar{C} \pm \Delta \bar{C}$	PPT $\bar{C} \pm \Delta \bar{C}$	PPT $\bar{CO} \pm \Delta \bar{CO}$
40	639.633	194.301	
32	120.3	33.178	
31	98.7294	27.0646	
50	107.293	29.3831	
37	105.199	28.7848	
9	74.7764	19.9527	

SET#	NGS/M <sup>2</sup> -HR $E1 \pm \Delta E1$		NGS/M <sup>2</sup> -HR $E2 \pm \Delta E2$		NGS/M <sup>2</sup> -HR $E \pm \Delta E$	
1	395.688	134.399	-206.659	257.865	189.03	392.263
2	74.42	23.1953	-47.3003	36.2603	27.1196	59.4556
3	61.0758	18.9346	5.27752	26.3981	66.3533	45.3326
4	66.3732	20.559	0	0	66.3732	20.559
5	65.078	20.1424	-5.43431	30.7543	59.6437	50.8966
6	46.2581	14.0032	-10.8669	22.2407	35.3912	36.2439

SEPTEMBER 3 - 4 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=3.26143 \pm 8.84584E-02$$

$$B=1.68545 \pm 3.42733E-02$$

LP#	PPT		PPT	
	$\bar{C} \pm \Delta C$		$\bar{CO} \pm \Delta CO$	
38	575.546	121.936		
15			45.7472	8.29829
11	421.033	85.5918		
33			41.0234	7.40464
26	449.417	93.206		
5			34.7318	6.16833
32	277.351	56.4047		
17			14.0662	2.38297
48	52.8501	9.68396		
36			22.7699	3.95306
50	328.112	66.7306		
19			23.3745	4.03674
14	33.0731	5.83123		
8			20.1378	3.44364
45	29.216	5.13631		
43			22.4878	3.88612
7	46.4915	8.4326		
41			22.8608	3.96273
31	51.4404	9.35975		
21			16.0274	2.71522
25	75.2568	14.0812		
2			31.3467	5.53555
40	74.4436	13.9254		
34			15.1405	2.56498
47	79.6325	15.		
18			17.8874	3.0647

SET#	NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR	
	$E1 \pm \Delta E1$		$E2 \pm \Delta E2$		$E \pm \Delta E$	
1	327.743	92.3277	-61.3304	150.47	266.413	242.798
2	235.081	65.9659	-10.9044	137.176	224.177	203.142
3	256.532	70.6813	-23.6422	108.006	232.89	178.687
4	162.873	42.2123	-48.9993	59.4893	113.873	101.702
5	18.6081	9.10393	-4.57176	10.7034	14.0364	19.8073
6	188.516	50.75435	-20.0237	82.9227	168.492	133.466
7	8.00201	6.02478	-3.42877	7.43807	4.57325	13.4629
8	4.16216	5.73081	0	0	4.16216	5.73081
9	14.6183	8.1926	8.0442	9.62547	22.6625	17.8181
10	21.9071	8.25601	0	0	21.9071	8.25601
11	27.1636	13.1102	5.31594	16.1036	32.4795	29.2138
12	36.686	11.5179	0	0	36.686	11.5179
13	38.1967	12.546	0	0	38.1967	12.546

## SEPTEMBER 3 - 4 , 1982 FIELD STUDY H2S

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=2.31718 \pm .11118$$

$$B=1.98005 \pm 4.09525E-02$$

LP#		$\overline{C} \pm \Delta \overline{C}$	$\overline{PPT} \pm \Delta \overline{PPT}$
38	237.452	50.8143	
11	139.667	28.6733	
26	127.957	26.473	
32	103.377	21.3826	
50	141.409	29.5143	

SET#	NGS/M <sup>2</sup> -HR $\overline{E1} \pm \Delta \overline{E1}$		NGS/M <sup>2</sup> -HR $\overline{E2} \pm \Delta \overline{E2}$		NGS/M <sup>2</sup> -HR $\overline{E} \pm \Delta \overline{E}$	
1	146.892	36.7063	-32.5832	62.7472	114.309	99.4536
2	86.4005	20.8386	-9.46042	45.9891	76.9401	66.8277
3	79.1565	19.2175	-7.379	30.6807	71.7775	49.8981
4	63.9511	15.5228	-2.62369	22.4563	61.3274	37.9791
5	87.4785	21.3975	-8.58145	36.6743	78.8971	58.0718

SEPTEMBER 9 - 10 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=3.44279 \quad + \quad 9.20853E-02$$

$$B=1.63541 \quad + \quad 3.67508E-02$$

LP#	PPT		PPT	
	$\bar{C} \pm \Delta C$	$\bar{C} \pm \Delta C$	$\bar{CO} \pm \Delta CO$	$\bar{CO} \pm \Delta CO$
44	398.823	88.837		
3			45.4566	8.73535
28	357.652	78.9925		
1			23.9631	4.41761
15	211.173	44.7918		
14			26.661	4.9429
38	44.2589	8.53536		
32			11.9558	2.12014
50	44.0217	8.49082		
26			18.7883	3.41997
35	26.8509	5.05712		
21			10.4096	1.84595
46	28.4919	5.32987		
18			16.0816	2.89571
8	25.0325	4.63044		
43			19.2519	3.49032
47	27.0414	5.056		
41			18.913	3.4471
45	22.8488	4.219		
34			18.203	3.30419
36	27.8448	5.21055		
9			21.	3.84787
48	57.4393	11.3604		
11			20.6842	3.8111
17	34.0252	6.42316		
2			24.8012	4.57292

SET#	NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR	
	E1 $\pm \Delta E1$	E1 $\pm \Delta E1$	E2 $\pm \Delta E2$	E2 $\pm \Delta E2$	E $\pm \Delta E$	E $\pm \Delta E$
1	218.599	68.2052	5.49981	107.191	224.099	175.396
2	206.426	59.0073	-22.7058	95.8759	183.72	154.883
3	114.143	34.8631	-38.4202	55.3817	75.7223	90.2448
4	19.9833	7.30886	-13.1495	10.0906	6.83381	17.3994
5	15.6148	7.92862	-4.08311	9.91018	11.5317	17.8388
6	10.1709	4.63538	0	0	10.1709	4.63538
7	7.67722	5.36402	0	0	7.67722	5.36402
8	3.57599	5.15199	0	0	3.57599	5.15199
9	5.02842	5.44063	0	0	5.02842	5.44063
10	2.87396	4.75713	0	0	2.87396	4.75713
11	4.23437	5.75567	2.61534	6.10478	6.84971	11.8604
12	22.7374	10.2014	11.3743	12.01	34.1117	22.2114
13	5.7061	7.00716	-7.81841	8.05058	-2.11231	15.0577

SEPTEMBER 9 - 10 , 1982 FIELD STUDY H2S

LINEAR REGRESSION

$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$

$M=2.31718 \pm .11118$

$B=1.98005 \pm 4.09525E-02$

LP#		PPT $\bar{C} \pm \Delta \bar{C}$	PPT $\bar{CO} \pm \Delta \bar{CO}$
44	191.454	40.8233	
28	197.13	42.0983	
15	251.965	54.1622	

SET#	NGS/M <sup>2</sup> -HR $E1 \pm \Delta E1$		NGS/M <sup>2</sup> -HR $E2 \pm \Delta E2$		NGS/M <sup>2</sup> -HR $\bar{E} \pm \Delta \bar{E}$	
1	118.437	29.5045	2.41248	49.2569	120.849	78.7614
2	121.948	30.4193	6.87531	51.0647	128.823	81.484
3	155.87	39.0996	-15.4078	66.7812	140.462	105.881

SEPTEMBER 14 - 15 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=3.3276 \pm 9.06593E-02$$

$$B=1.68052 \pm 3.59518E-02$$

LP#		PPT		PPT	
		$\bar{C} \pm \Delta \bar{C}$		$\bar{CO} \pm \Delta \bar{CO}$	
21	538.48	117.624			
18			48.684	9.04645	
30	647.232	143.759			
22			27.2009	4.88289	
7	464.267	100.351			
3			28.5746	5.13296	
50	353.845	75.2693			
26			13.5068	2.32615	
45	225.471	46.4449			
8			19.9613	3.52291	
46	70.9398	13.5584			
14			17.4101	3.03531	
36	465.171	100.869			
35			77.0632	14.8163	
47	373.44	79.99			
39			25.0107	4.48163	
23	48.2821	9.08981			
1			13.468	2.33514	
13	268.391	56.0101			
10			22.5591	4.01108	
20	275.573	57.361			
6			23.1886	4.11595	
38	347.301	71.9356			
16			13.419	2.30244	
40	690.528	136.8			
33			11.9759	2.05484	

SET#	NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR	
	E1 $\pm \Delta E1$		E2 $\pm \Delta E2$		$\bar{E} \pm \Delta \bar{E}$	
1	302.997	89.2346	89.4603	145.847	392.457	235.082
2	383.563	105.718	-26.3098	170.263	357.253	275.982
3	269.527	74.9271	-38.3847	123.542	231.143	198.469
4	210.54	55.5579	-48.7117	89.9487	161.828	145.507
5	127.132	35.4735	-58.7568	53.6264	68.3755	89.1
6	33.1145	11.4536	-13.7809	16.8066	19.3337	28.2602
7	240.091	80.1815	68.9349	119.321	309.026	199.502
8	215.545	59.9912	145.76	90.2933	361.304	150.285
9	21.5366	7.84059	114.165	10.2178	135.702	18.0584
10	152.076	42.588	35.4736	64.2955	187.55	106.883
11	156.13	43.634	1.82482	69.7938	157.955	113.428
12	206.546	53.3376	58.1729	196.124	264.718	249.462
13	419.765	100.963	8.65264	819.211	428.417	920.173



SEPTEMBER 14 - 15 , 1982 FIELD STUDY H2S

LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=2.31718 \pm .11118$$

$$B=1.98005 \pm 4.09525E-02$$

LP#	$\bar{C} \pm \Delta\bar{C}$	PPT $\bar{C} \pm \Delta\bar{C}$	PPT $\bar{C} \pm \Delta\bar{C}$
21	222.84	47.5129	
30	223.228	47.734	
7	166.934	35.249	
50	75.3208	15.1808	
45	92.5612	18.9252	
46	25.2663	4.77885	
36	215.162	45.911	
47	245.773	53.08	
13	70.0752	14.0919	
20	69.3358	13.8838	
38	98.642	19.8156	
40	441.762	89.835	

SET#	NGS/M <sup>2</sup> -HR $E1 \pm \Delta E1$		NGS/M <sup>2</sup> -HR $E2 \pm \Delta E2$		NGS/M <sup>2</sup> -HR $\bar{E} \pm \Delta\bar{E}$	
1	137.853	34.3396	9.63894	58.7545	147.492	93.0941
2	138.093	34.485	-14.0046	56.5659	124.088	91.051
3	103.268	25.5118	-38.2156	43.5433	65.0528	69.0551
4	46.5948	11.0633	-10.6826	18.1465	35.9123	29.2098
5	57.26	13.7624	-13.5675	21.7893	43.6925	35.5517
6	15.6302	3.51723	-3.43919	5.91523	12.191	9.43245
7	133.103	33.1782	37.8762	54.3484	170.979	87.5266
8	152.04	38.2927	-29.4896	59.5137	122.55	97.8064
9	43.3498	10.2733	10.5484	16.1862	53.8982	26.4595
10	42.8924	10.1281	13.7124	16.9727	56.6048	27.1008
11	61.0217	14.4483	47.7437	54.2155	108.765	68.6638
12	273.282	65.3812	90.8682	538.478	364.15	603.859

SEPTEMBER 23 - 24 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=3.28776 \pm 7.45567E-02$$

$$B=1.69961 \pm 2.97118E-02$$

LP#	PPT		PPT	
	$\bar{C} \pm \Delta C$	$\bar{C} \pm \Delta C$	$\bar{CO} \pm \Delta CO$	$\bar{CO} \pm \Delta CO$
47	514.518	94.2035		
46			19.9294	2.98627
38	480.348	87.6008		
35			27.8978	4.26547
33	484.808	88.3937		
1			20.9757	3.15229
36	497.728	90.8175		
32			18.633	2.77915
43	543.557	99.8704		
8			7.83569	1.11952
26	378.397	68.5829		
6			6.5995	.942904
50	367.223	65.6227		
7			22.9286	3.46122
30	340.604	61.4107		
13			17.8192	2.68334
37	431.384	78.4086		
31			17.373	2.59447
12	193.493	33.0882		
48			7.6277	1.06981
16	359.148	63.9825		
5			25.6889	3.90062
21	570.305	98.7072		
10			6.33894	.905676

SET#	NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR	
	E1 $\pm \Delta E1$	E1 $\pm \Delta E1$	E2 $\pm \Delta E2$	E2 $\pm \Delta E2$	$\bar{E} \pm \Delta \bar{E}$	$\bar{E} \pm \Delta \bar{E}$
1	305.962	71.1038	-16.0218	115.267	289.94	186.371
2	279.894	66.8751	-5.82612	105.702	274.068	172.577
3	286.935	66.9296	4.09737	107.978	291.033	174.908
4	296.377	68.537	14.3579	112.885	310.735	181.422
5	331.407	74.3678	24.2853	123.012	355.692	197.38
6	230.001	51.2643	28.277	71.2331	258.278	122.497
7	212.987	50.3803	14.2674	81.0776	227.254	131.458
8	199.68	46.8159	17.6558	61.5891	217.336	108.405
9	256.115	59.3014	65.5552	89.1533	321.67	148.455
10	114.979	25.2695	59.0751	39.8351	174.055	65.1046
11	206.284	49.3969	88.1995	80.4956	294.484	129.892
12	348.88	74.143	62.8635	293.623	411.743	367.766

SEPTEMBER 23 - 24 , 1982 FIELD STUDY H2S

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=2.31718 \pm .11118$$

$$B=1.98005 \pm 4.09525E-02$$

LP#	$\bar{C} \pm \Delta \bar{C}$	PPT $\bar{C} \pm \Delta \bar{C}$	PPT $\bar{CO} \pm \Delta \bar{CO}$
47	327.745	71.6626	
38	219.836	46.8767	
33	170.51	36.0457	
36	104.668	21.4468	
43	241.034	51.6387	
26	91.1935	18.7349	
50	92.5404	18.836	
30	147.393	31.2597	
37	267.168	57.9241	
12	54.9583	10.863	
16	52849.3	10903.	
21	179.723	36.0963	

SET#	NGS/M <sup>2</sup> -HR E1 $\pm$ $\Delta E1$		NGS/M <sup>2</sup> -HR E2 $\pm$ $\Delta E2$		NGS/M <sup>2</sup> -HR E $\pm$ $\Delta E$	
1	202.749	51.6081	-54.7847	87.9417	147.964	139.55
2	135.994	33.8794	-18.2756	56.6539	117.719	90.5333
3	105.481	26.0841	-24.7965	44.1707	80.6842	70.2548
4	64.7494	15.5911	23.698	26.7799	88.4474	42.371
5	149.108	37.2959	-13.3415	63.609	135.766	100.905
6	56.414	13.6144	-7.6725	19.4586	48.7415	33.0729
7	57.2472	13.7068	13.7414	23.33	70.9886	37.0368
8	91.1799	22.6101	32.5242	31.4917	123.704	54.1018
9	165.275	41.7644	-35.4845	65.7842	129.79	107.549
10	33.9982	7.94016	10.6171	13.0253	44.6153	20.9655
11	123956.	30021.3	28.2656	13627.	123985.	43648.3
12	111.18	26.3199	23.4549	107.378	134.635	133.698

SEPTEMBER 28 - 29 , 1982 FIELD STUDY OCS

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=3.19766 \pm 3.87642E-02$$

$$B=1.73277 \pm 1.48093E-02$$

LP#	PPT		PPT	
	$\bar{C} \pm \Delta\bar{C}$	$\bar{C} \pm \Delta\bar{C}$	$\bar{C} \pm \Delta\bar{C}$	$\bar{C} \pm \Delta\bar{C}$
47	770.063	83.6428		
36			38.2884	3.74422
41	408.497	42.7973		
30			23.6438	2.26842
41	609.42	65.3731		
1			32.9362	3.20243
16	507.799	53.869		
14			19.2853	1.83446
50	504.048	53.4176		
6			16.6805	1.5772
38	41.1256	4.03818		
37			25.6002	2.46294
8	35.6607	3.4792		
5			26.6886	2.5713
48	34.8083	3.4504		
12			14.7357	1.39332
32	26.6865	2.58513		
3			14.5711	1.37775
40	39.2568	3.84369		
13			19.59	1.86368
33	139.335	13.6931		
23			16.6366	1.57305
26	811.195	87.5824		
18			25.4658	2.44814
35	670.453	72.3543		
25			22.7209	2.17697

SET#	NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR		NGS/M <sup>2</sup> -HR	
	$\bar{E}1 \pm \Delta\bar{E}1$	$\bar{E}1 \pm \Delta\bar{E}1$	$\bar{E}2 \pm \Delta\bar{E}2$	$\bar{E}2 \pm \Delta\bar{E}2$	$\bar{E} \pm \Delta\bar{E}$	$\bar{E} \pm \Delta\bar{E}$
1	452.689	70.3054	-68.3877	122.609	384.302	192.915
2	238.077	36.4226	-42.8184	52.7344	195.259	89.157
3	356.624	55.2207	-33.3717	80.8363	323.252	136.057
4	302.203	45.3047	-26.8677	67.2452	275.336	112.55
5	301.495	44.8409	-21.9744	67.5928	279.52	112.434
6	9.60432	4.36639	-14.3337	5.08661	-4.72937	9.45301
7	5.55031	3.94214	-5.14937	4.36359	.400932	8.30573
8	12.4174	3.44196	0	0	12.4174	3.44196
9	7.49481	2.72049	3.74595	2.87484	11.2408	5.59533
10	12.1662	3.96731	10.463	4.91401	22.6293	8.88132
11	75.9034	12.1679	76.7259	17.726	152.629	29.8939
12	486.067	73.1386	228.065	111.427	714.132	184.565
13	400.699	60.4868	-119.77	88.8761	280.929	149.363

SEPTEMBER 28 - 29 , 1982 FIELD STUDY H2S

## LINEAR REGRESSION

$$\text{LOG}(R*GCAT)=M + B \text{ LOG}(C)$$

$$M=2.31718 \pm .11118$$

$$B=1.98005 \pm 4.09525E-02$$

LP#	$\bar{C} \pm \Delta \bar{C}$	PPT $\bar{C} \pm \Delta \bar{C}$
47	269.562	58.0007
41	161.807	34.0313
16	154.474	32.3831
50	106.022	21.703
21	134.902	28.002
33	33.4193	6.39581
26	223.977	47.5479
35	235.779	50.8014

SET#	NGS/M <sup>2</sup> -HR $E1 \pm \Delta E1$		NGS/M <sup>2</sup> -HR $E2 \pm \Delta E2$		NGS/M <sup>2</sup> -HR $\bar{E} \pm \Delta \bar{E}$	
1	166.756	41.8649	-13.1086	84.8156	153.647	126.68
2	100.097	24.6447	-16.4178	41.8273	83.6791	66.472
3	95.5607	23.4623	-22.031	40.0759	73.5297	63.5382
4	65.5871	15.7797	-.574952	27.0306	65.0121	42.8103
5	83.4529	20.3175	-19.611	35.4813	63.8419	55.7988
6	20.6738	4.69851	13.1603	8.14345	33.8341	12.842
7	138.556	34.3865	16.3361	59.848	154.892	94.2345
8	145.857	36.6613	12.7933	61.9739	158.651	98.6351

APPENDIX VII

Reproducibility Studies

Table 14  
Reproducibility Studies

July 20-21, 1982				
Test #	Drier- $\phi_1$ Loop #	$\phi_3$ Loop #	Drier- $\phi_1$ OCS (ppt)	$\phi_3$ OCS (ppt)
1	30	28	658.0	582.5
2	29	31	-	742.1
3	34	32	486.3	534.7
4	9	6	604.4	653.2
5	25	7	692.1	675.8
6	38	23	588.8	714.7
7	19	18	562.2	591.4
8	20	17	494.6	690.9
9	21	2	621.3	703.7
10	5	37	651.8	868.5

Average " $\phi_3$ " OCS mixing ratio: 675.75 ( $\pm 94.5$ ) ppt  
(14% relative standard deviative)

Average "drier- $\phi_1$ " OCS mixing ratio: 595.5 ( $\pm 71.1$ ) ppt  
(11.9% relative standard deviative)

June 15-16, 1982

Test #	OCS (Loop #)(ppt)	OCS (Loop #)(ppt)
1	598.2(1)	605.1(2)
2	1157.4(3)	1207.5(4)
3	580.3(5)	502.2(6)

APPENDIX VIII

Wallops Island Field Studies:

Light Intensities and Air and Soil Temperatures



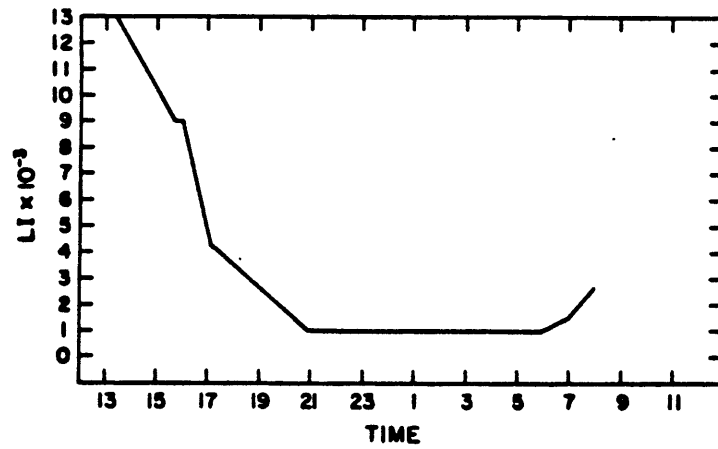


Fig. 72 August 5-6, 1982 field study: Light intensities versus time

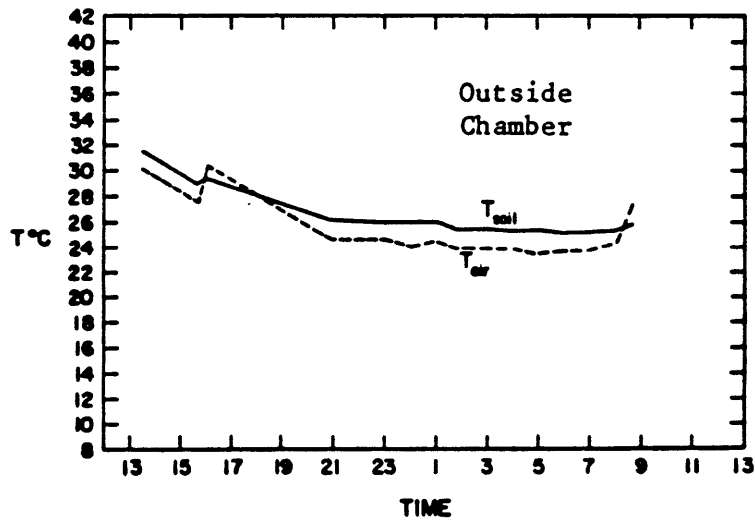


Fig. 73 August 5-6, 1982 field study: Air and soil temperatures versus time

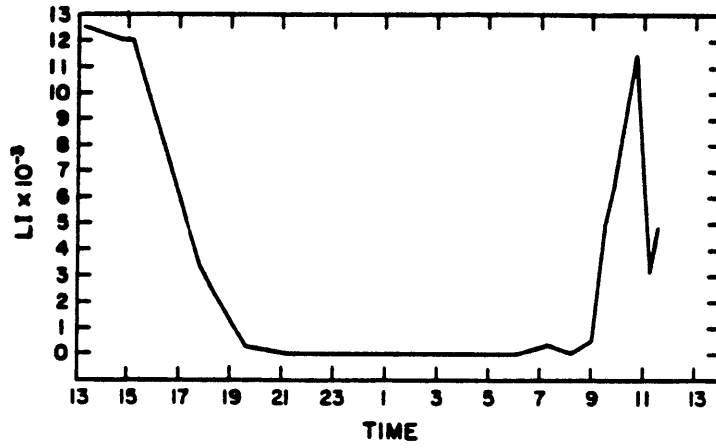


Fig. 74 August 13-14, 1982 field study: Light intensities versus time

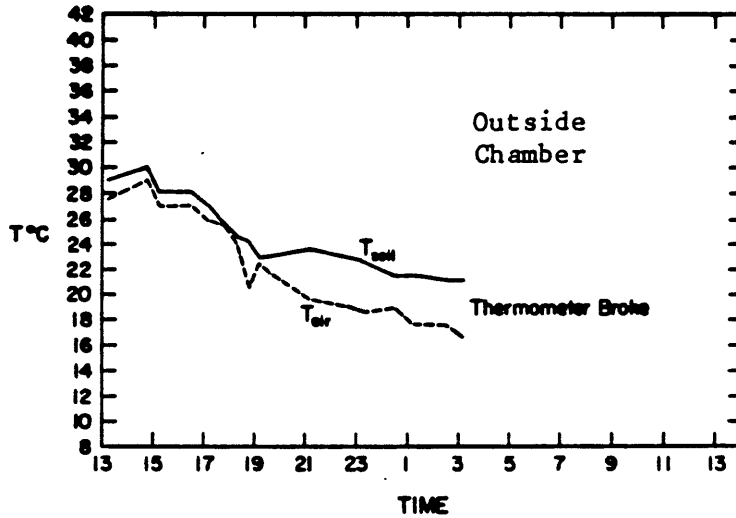


Fig. 75 August 13-14, 1982 field study: Air and soil temperatures versus time

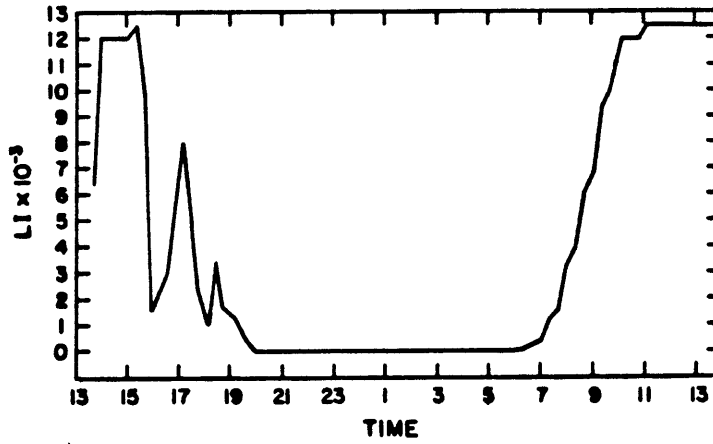


Fig. 76 August 18-19, 1982 field study: Light intensities versus time

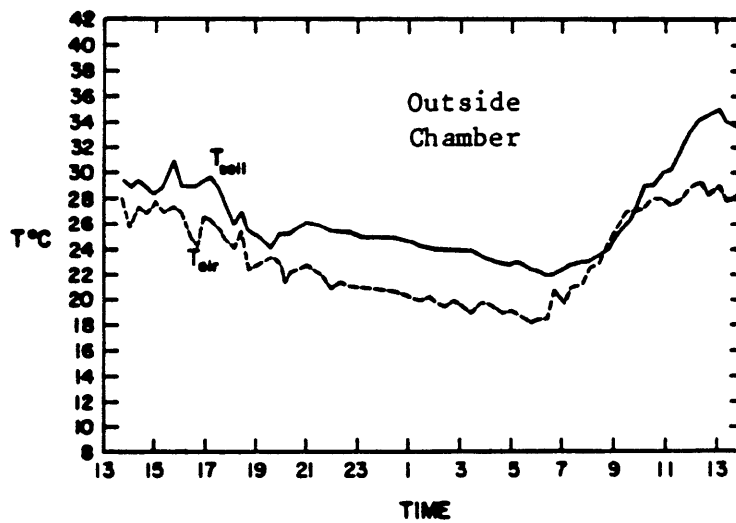


Fig. 77 August 18-19, 1982 field study: Air and soil temperatures versus time

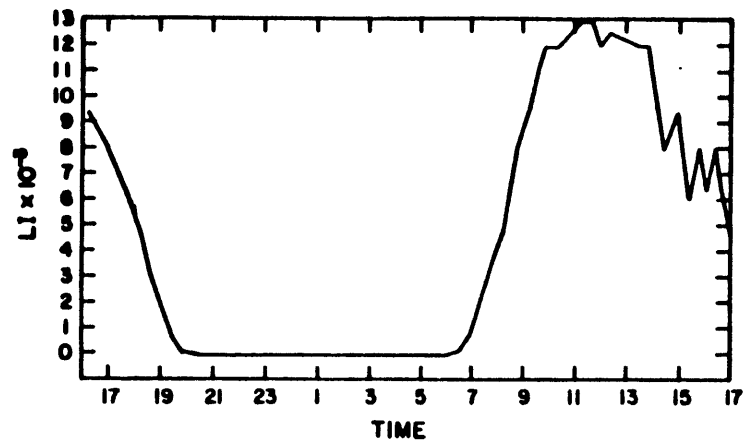


Fig. 78 August 26-27, 1982 field study: Light intensities versus time

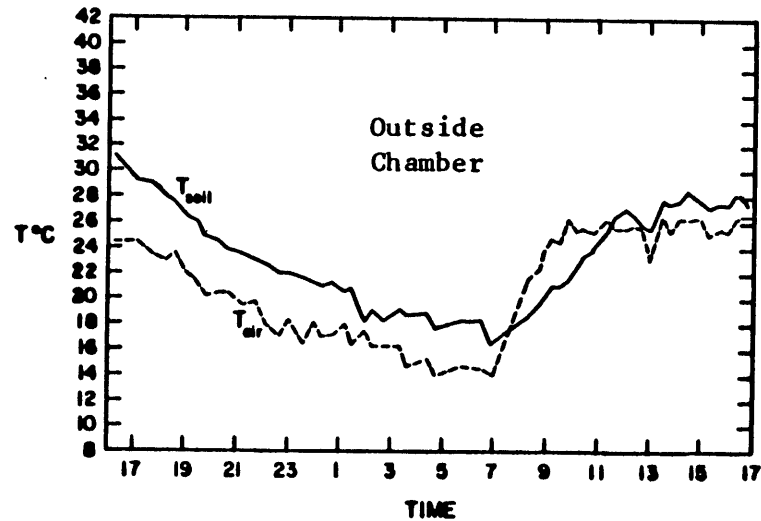
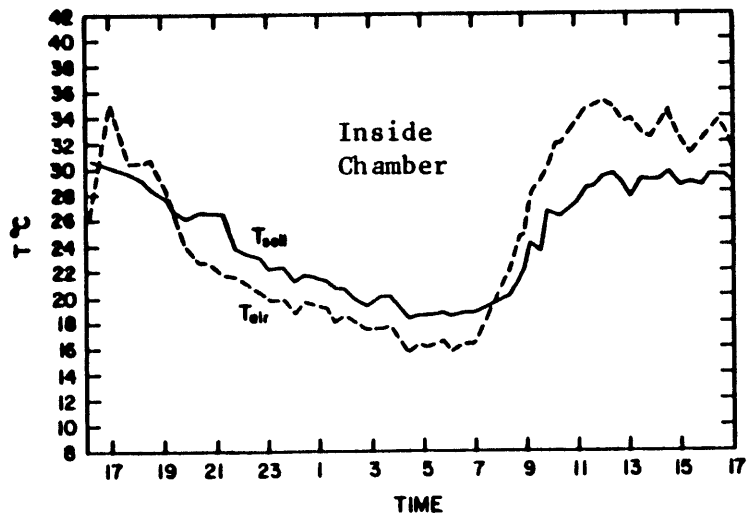


Fig. 79 August 26-27, 1982 field study: Air and soil temperatures versus time

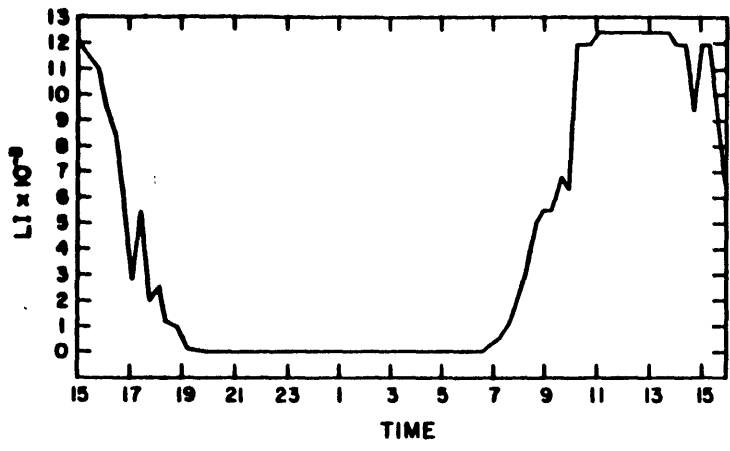


Fig. 80 September 3-4, 1982 field study: Light intensities versus time

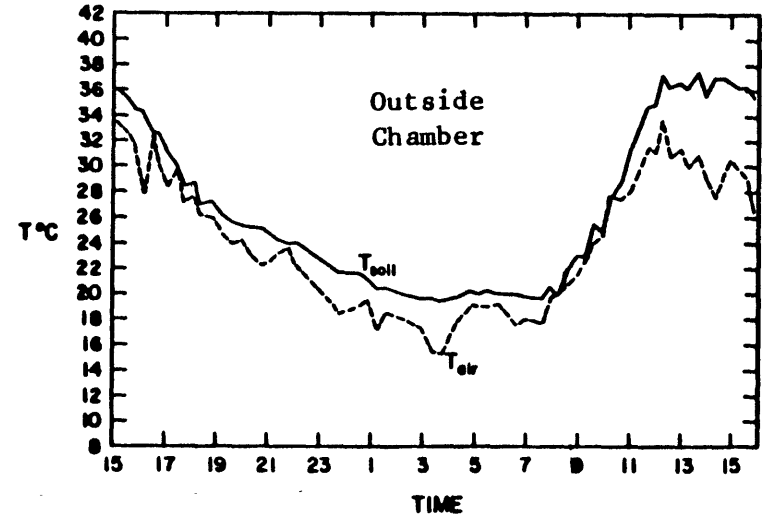
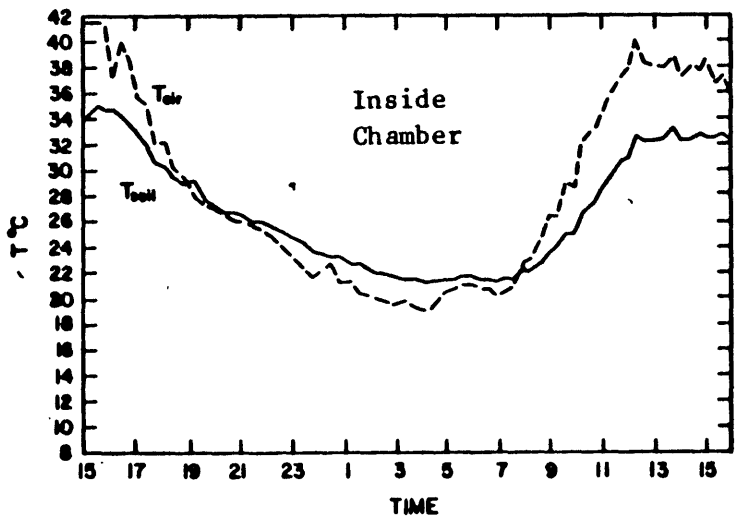


Fig. 81 September 3-4, 1982 field study: Air and soil temperatures versus time

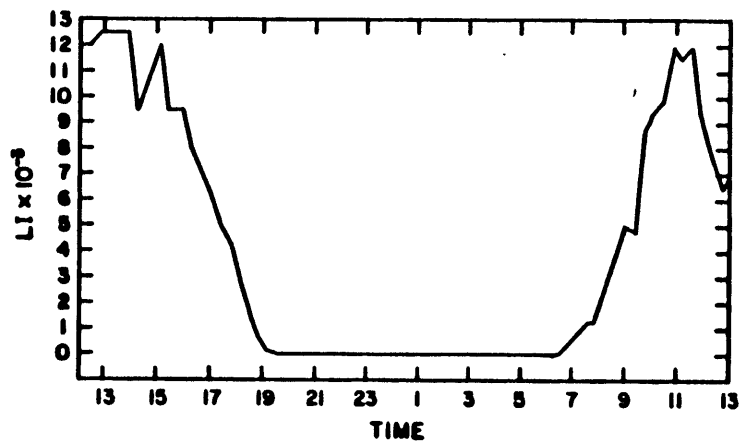


Fig. 82 September 9-10, 1982 field study: Light intensities versus time

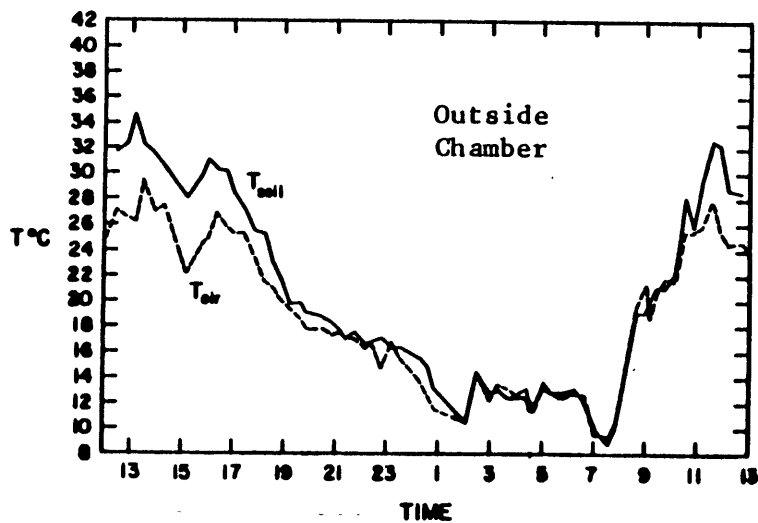
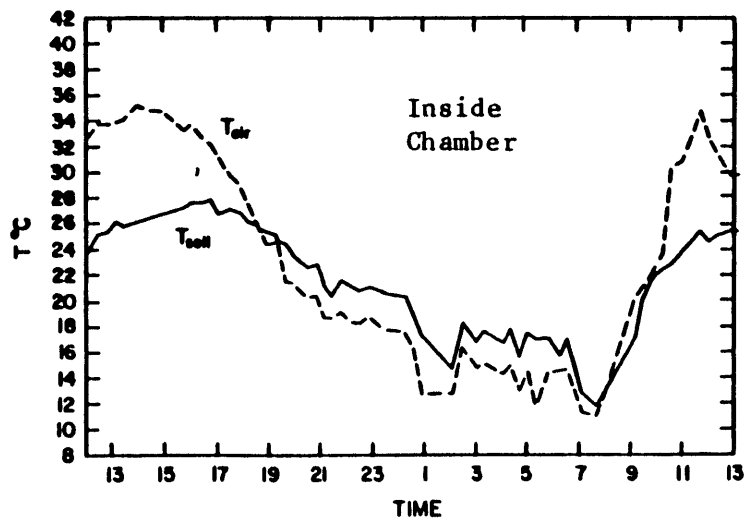


Fig. 83 September 9-10, 1982 field study: Air and soil temperatures versus time

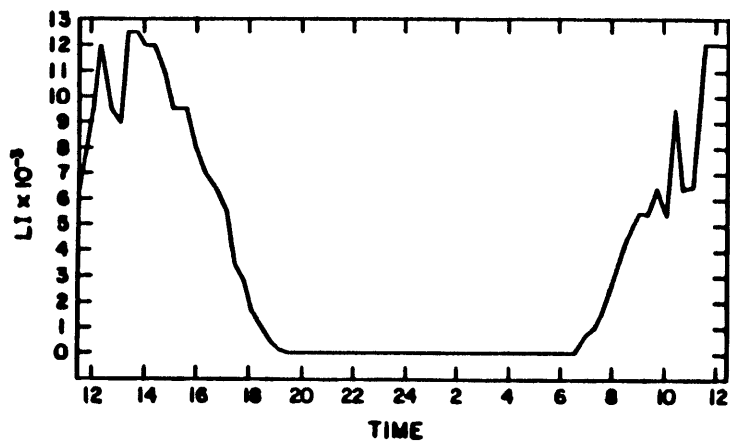


Fig. 84 September 14-15, 1982 field study: Light intensities versus time

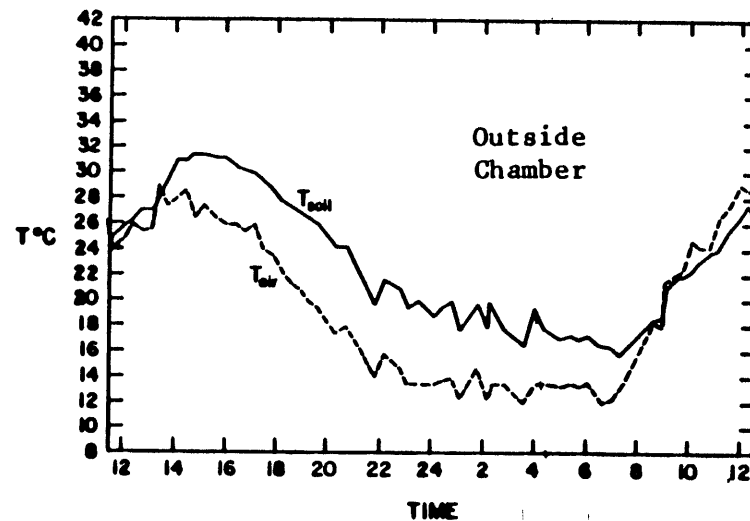
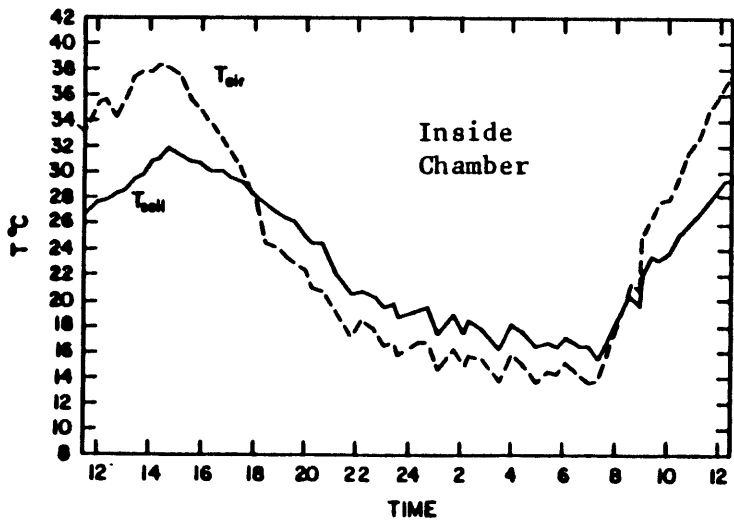


Fig. 85 September 14-15, 1982 field study: Air and soil temperatures versus time

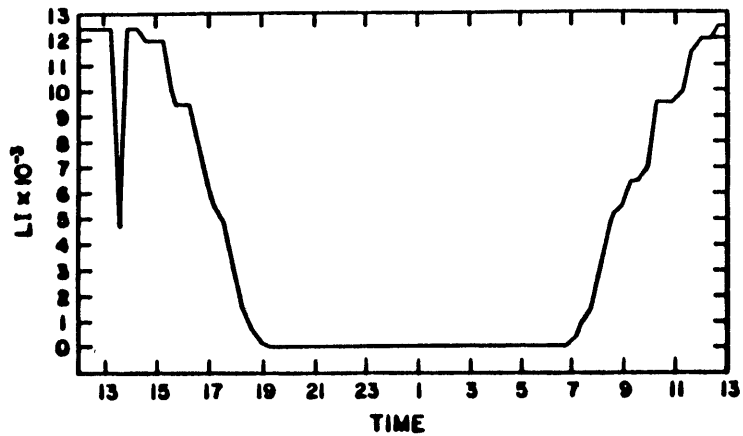


Fig. 86 September 23-24, 1982 field study: Light intensities versus time

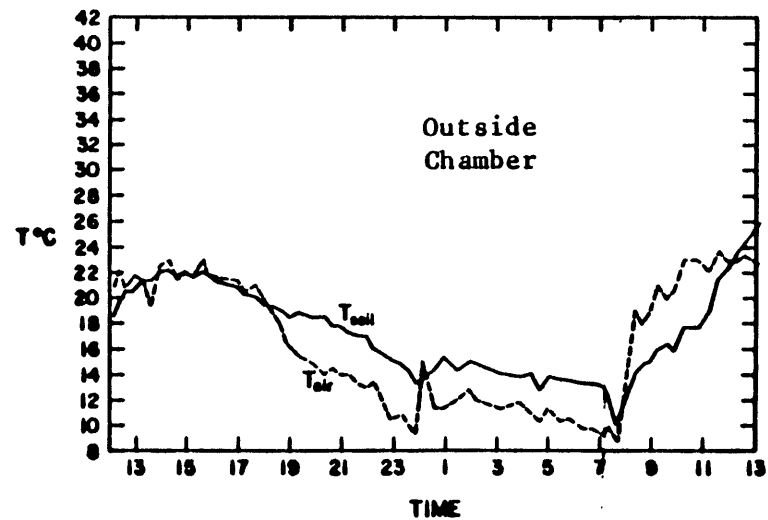
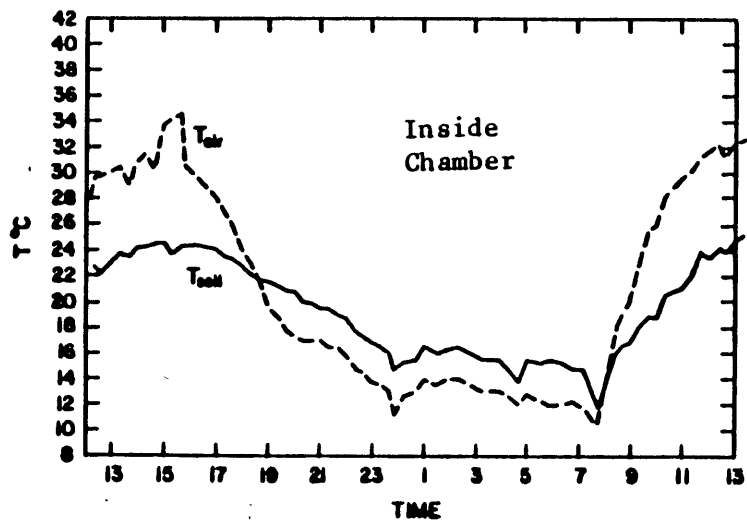


Fig. 87 September 23-24, 1982 field study: Air and soil temperatures versus time



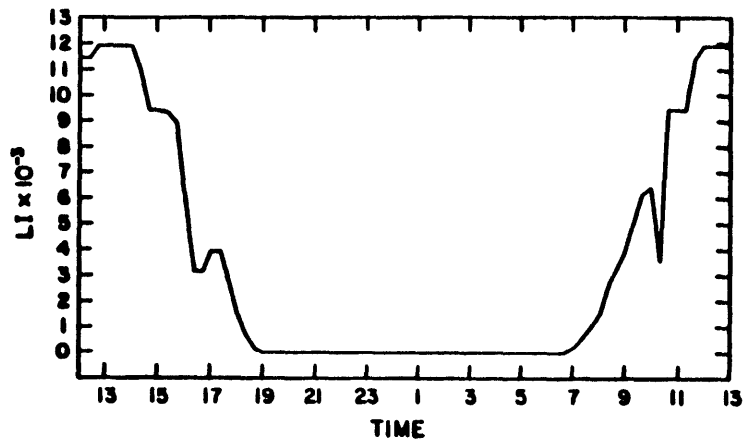


Fig. 88 September 28-29, 1982 field study: Light intensities versus time

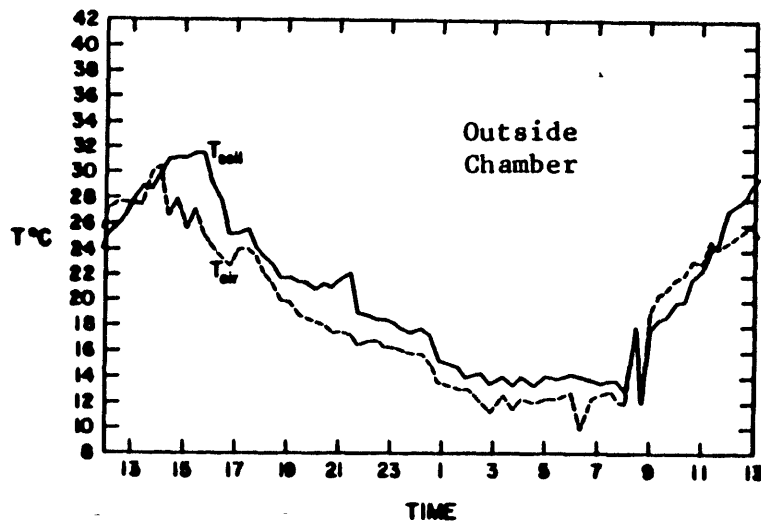
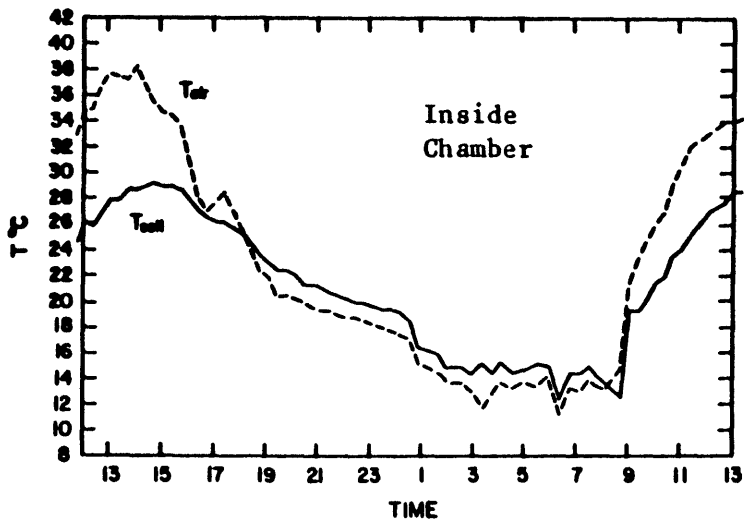


Fig. 89 September 28-29, 1982 field study: Air and soil temperatures versus time