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Factors controlling fluxes of volatile sulfur compounds in Sphagnum peatlands

William Zamboni de Mello
University of New Hampshire, Durham

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de Mello, William Zamboni, Ph.D.

University of New Hampshire, 1992

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FACTORS CONTROLLING FLUXES OF VOLATILE SULFUR COMPOUNDS IN *SPHAGNUM* PEATLANDS

BY

WILLIAM ZAMBONI DE MELLO
B.S., Universidade Federal Fluminense, 1980
M.S., University of Miami, 1986

DISSERTATION

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in

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This dissertation has been examined and approved.

Dissertation Director
Mark E. Hines, Research Associate
Professor of Earth Sciences

Robert C. Harriss, Professor of Earth Sciences

Patrick M. Crill, Research Associate
Professor of Earth Sciences

Barrett N. Rock, Associate Professor
of Natural Resources

Steven C. Wofsy, Senior Research
Fellow in Atmospheric Chemistry,
Harvard University

Sept. 11, 1992
Date

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

FACTORS CONTROLLING FLUXES OF VOLATILE SULFUR COMPOUNDS IN *SPHAGNUM* PEATLANDS

by

William Zamboni de Mello
University of New Hampshire, December, 1992

Exchange of DMS and OCS between the surface of *Sphagnum* peatlands and the atmosphere were measured with dynamic (S-free sweep air) and static enclosures. DMS emission rates determined by both methods were comparable. The dynamic method provided positive OCS flux rates (emission) for measurements performed at sites containing *Sphagnum*. Conversely, data from the static method indicated that OCS was consumed from the atmosphere.

Short and long-term impacts of increased S deposition on fluxes of volatile S compounds (VSCs) from *Sphagnum* peatlands were investigated in a poor fen (Mire 239) at the Experimental Lakes Area, Ontario, Canada. Additional experiments were conducted in a poor fen (Sallie's Fen) in Barrington, NH, USA. At Mire 239, emissions of VSCs were monitored, before and after acidification, at control and experimental sections within two major physiographic areas of the mire (oligotrophic and minerotrophic). DMS was the

predominant VSC released from Mire 239 and varied largely with time and space. Sulfur addition did not affect DMS emissions in a period of hours to a few days. DMS emissions in the experimental oligotrophic area of the mire was ~3-fold greater than in the control oligotrophic area, and ~10-fold greater than in the minerotrophic zones. These differences could be due to a combination of differences in types of vegetation, nutritional status and S input. At Sallie's Fen, DMS fluxes was not significantly affected by sulfate amendments, while DMS and MSH concentrations increased greatly with time in the top 10 cm of the peat column.

The major environmental factors controlling fluxes of DMS in a *Sphagnum*-dominated peatland were investigated in Sallie's Fen, NH. DMS emissions from the surface of the peatland varied greatly over 24 hours and seasonally. Temperature seemed to be the major environmental factor controlling these variabilities. Concentrations of dissolved VSCs varied with time and space throughout the fen. Dissolved DMS, MSH and OCS in the surface of the water table were supersaturated with respect to their concentrations in the atmosphere. *Sphagnum* mosses did not appear to be a direct source of VSCs, however they increase transport of DMS from the peat surface to the atmosphere.

CHAPTER I

Application of Static and Dynamic Enclosures in Determining DMS and OCS Fluxes in *Sphagnum* Peatlands

ABSTRACT

A static enclosure method was applied to determine the exchange of DMS and OCS between the surface of *Sphagnum* peatlands and the atmosphere. Measurements were performed concurrently with dynamic enclosure measurements with S-free air used as sweep gas. DMS emission rates determined by both methods were comparable between 5 and 500 nmol m^{-2} h^{-1}. The dynamic method provided positive OCS flux rates (emission) for measurements performed at sites containing *Sphagnum*. Conversely, data from the static method indicated that OCS was consumed from the atmosphere. Measurements using both techniques at a site devoid of vegetation showed that peat is a source of both DMS and OCS. Results suggested that OCS is produced in surface peat but it is taken up from the atmosphere by *Sphagnum* mosses. However, the net effect of both processes is that OCS uptake exceeds emission. The dynamic enclosure technique is adequate to measure rates of emissions of S gases which are produced in peatlands but not consumed, as long as attention is paid to the rate of sweep flow.

1. INTRODUCTION

Atmospheric S cycling is largely linked to the activities of various biological processes occurring on the Earth's surface. Dimethyl sulfide (DMS) and carbonyl sulfide (OCS) are the most relevant reduced volatile S compounds involved in these interactive processes. DMS is the major S gas emitted from oceans [Andreae, 1990] and several terrestrial environments [Aneja and Cooper, 1989]. In the marine troposphere, DMS is the principal precursor of cloud condensation nuclei (CCN) [Nguyen et al., 1983; Charlson et al., 1987], which are potentially important in regulating cloud optical properties and climate [Fitzgerald, 1991]. OCS contributes significantly to the formation of stratospheric sub-micron sulfate aerosol particles, during quiescent volcanic periods [Crutzen, 1976; Servant, 1986]. Considering the importance of S-containing atmospheric particles in regulating Earth's radiation balance and climate, a better understanding of the biospheric sources and fates of these compounds is required.

There are uncertainties concerning the role of the terrestrial biosphere in atmospheric S cycling. Estimates of global S emissions from continental natural environments have decreased by two orders of magnitude in the last eleven years [Adams et al., 1981; Andreae et al., 1990; Bates et al., 1992]. Confidence in the sampling methods employed in

determining S fluxes is crucial before other potential causes of those uncertainties are investigated.

There are primarily two methods which have been used to assess fluxes of volatile S compounds (VSCs) from continental environments; the dynamic enclosure method, employed in all investigations which have made direct measurements of S gas exchange [Hill et al., 1978], and, less commonly, the micrometeorological tower method [Andreae and Andreae, 1988; Andreae et al., 1990]. Most estimates of S fluxes in inland and coastal environments have employed the dynamic method which applies a constant flow of sweep air in enclosures. Of these, the majority have used S-free sweep air. However, it is possible that this method alters evolution of VSCs from soil. Since the flux strength of an S gas is a function of the gas concentration gradient between the soil (or water) and the overlying atmosphere, an alteration in the gas concentration within the enclosure head space should affect the natural emission rate. Also, the absence of carbon dioxide in the gas stream of a flow-through system could possibly influence S fluxes if production is controlled by vegetation and linked to photosynthesis [Dacey et al., 1987]. A less common technique employed for measuring S fluxes is a dynamic enclosure flushed with ambient air. The advantage of this technique is that it allows determination of S gas uptake by the soil surface [Castro and Galloway, 1991]. However, even with this technique, once gas concentrations within the enclosure head

space differ from ambient air, changes in the actual exchange rate may occur.

Static enclosures, in which the emitted gases are allowed to accumulate, have been employed to estimate emission and consumption of carbon dioxide, nitrous oxide and methane in a wide variety of continental environments [e.g., Keller et al., 1983; Barlett et al., 1985; Goreau and de Mello, 1985; Crill et al., 1988; Khalil et al., 1991]. This technique monitors gas concentration over time. However, it has never been used on studies of S fluxes in natural environments until recently when Hines and Morrison [1992] reported its use for determining OCS fluxes in Alaskan tundra. Possible reasons why this technique has not been employed routinely for measurements of S fluxes are: *(1)* low sensitivity of the analytical technique; *(2)* the relatively large number of samples required for each flux determination; and *(3)* entrapped S gases may undergo oxidation by O_3 and NO_x [Braman et al., 1978]. Therefore, the static method could not be properly employed for S fluxes unless these problems were overcome first.

The major goal of this study was to compare measurements of DMS and OCS fluxes made by S-free flow-through dynamic enclosures with measurements using static enclosures which entrap ambient air. Here, I report measurements of DMS and OCS fluxes made in *Sphagnum* peatlands.

2. EXPERIMENTAL

2.1. Sampling Sites

This study was conducted in two poor fens, in which S flux measurements were restricted to areas where *Sphagnum* mosses were the dominant ground level vegetation. Most of the measurements took place from the mid spring to late autumn of 1990 and 1991 at Sallie's Fen (1.7 ha), located in Barrington, NH (43°12'N, 71°04'W). The fen was dominated by *Sphagnum* spp.; *S. magellanicum*, *S. capillifolium* and *S. recurvum* were the dominant *Sphagnum* spp. present at the sites studied (David M. Lane, University of New Hampshire, personal communication). The ground level vascular component of the emergent flora at Sallie's Fen was dominated by sedges (mainly *Carex rostrata*) and leather-leaf (*Chamaedaphne calyculata*). A small number of flux measurements were made at Mire 239 (3.67 ha area), at the Experimental Lakes Area (ELA), northwestern Ontario (49°40'N, 93°43'W), in July 1990. *Sphagnum angustifolium*, *S. magellanicum* and *S. fuscum* were the major *Sphagnum* species found in Mire 239. The tree, shrub and herb communities were dominated by black spruce (*Picea mariana*), leather-leaf, Labrador-tea (*Ledum groenlandicum*), three-leaved false-Solomon's-seal (*Smilacina trifolia*) and *Carex trisperma* [Vitt and Bayley, 1984].

2.2. Sampling Design

Static and dynamic enclosure techniques were compared for determining S gas exchange between the surface of *Sphagnum* peatlands and the atmosphere. In Sallie's Fen, where most of the measurements were performed, S fluxes were first determined using the static method, which normally took place between 1100 and 1300 local time (LT). Cubic-shaped FEP Teflon enclosures (27 L volume) were applied. The enclosures were primarily built for dynamic measurements. Details on design and construction of the enclosures have been reported elsewhere [Morrison and Hines, 1990]. Enclosures were placed on Teflon-lined aluminum collars, which were installed in the sites before field campaigns had begun. Enclosures were shadowed by sun-screens during sampling procedure to minimize warming. A ~1 L ambient air sample was collected at 150 mL min^{-1} just after the enclosure was deployed, and three air samples (~300 mL each) were drawn from the enclosure head space at approximately 10, 20 and 30 minutes.

Once static measurements were accomplished, the enclosures were left on the site and flushed with S-free synthetic air (Liquid Carbonic, Specialty Gas Corp., Chicago, IL), at a flow rate of 3 L min^{-1}, for 1-1½ hours prior to sample collection. For the determination of each flux rate (dynamic), two replicate samples (~500 mL each) were taken from the enclosure head space, using a battery-powered pump, at a flow rate of 150 mL min^{-1}. Details of the

application of the dynamic enclosure method in *Sphagnum* peatlands are described in Chapter II. At the ELA, the same sampling procedure was applied for the determination of S fluxes, except that samples were collected at different times of the day.

Sulfur gases were trapped cryogenically in 0.32 cm diameter FEP Teflon tubes immersed in a dewar filled with liquid Ar. Flow rates and sample volumes were controlled by a mass flow controller/integrator system. After sampling, the cryotrap was immediately sealed by a Teflon-lined four-port distribution valve to prevent sample loss during transport to the laboratory. A PFA Teflon drier, placed in a Styrofoam container filled with dry ice, was used upstream of the cryotrap to minimize ice formation within the cryotraps.

During cryogenic enrichment of S gases from air, other atmospheric gases are simultaneously trapped, including strong oxidants, such as O_3 and nitrogen oxides (NO_x). During the thermal desorption, these oxidants react very effectively with some VSCs (e.g., H_2S, DMS, MSH and DMDS), decreasing their concentration greatly. Here, the loss of DMS during static enclosure measurement by co-trapping atmospheric oxidants was avoided by using a Na_2CO_3 scrubber [Braman et al., 1978; Ammons, 1980; Andreae et al., 1985]. Filters were held by two PFA Teflon filter holders in series and installed between the enclosure and the drier. The scrubber system, similar to that employed by Saltzman and

Cooper [1988], consisted of a pair of Whatman glass microfibre filters (47 mm diameter) coated with Na_2CO_3. Filters were dipped in a 5% (wt-vol) Na_2CO_3 solution and allowed to dry in an oven at 100°C. Saltzman and Cooper [1988] reported that the Na_2CO_3 scrubber were effective for sample volumes of ~12 L, even at conditions of very low levels of DMS in air (i.e., ~3 pptv) under the influence of a mixture of marine and continental air masses. They also mentioned that DMS spikes were recovered satisfactorily. In the present study, the same pair of Na_2CO_3 filters was never used to collect more than 7.5 L of air (ambient and from the enclosures head space), however, their efficiency in removing O_3 and NO_x were never tested. The Na_2CO_3 filters were not used when samples were collected from dynamic enclosures since the sweep gas was devoid of oxidants.

Before each sample acquisition (from either ambient air or enclosure head space), the whole sampling line was flushed with ~150 mL of air to avoid either dilution or contamination from the previous sampling. The inner volume of the drier, filter holders, and tubing comprised together a maximum volume of ~130 mL.

During sampling, ambient air and *Sphagnum* mat temperatures (in the shade) were simultaneously monitored. On average, the *Sphagnum* mat temperature was 4.5-5.0°C below the ambient air temperature.

2.3. Analytical

Analysis were performed with a Shimadzu GC-9A gas chromatograph equipped with a flame photometric detector, kept at 200°C. Separation of S gases was achieved using a 60/80 Carbopack B (1.5% XE-60, 1% H_3PO_5) column (Supelco, Inc., Bellefonte, PA) and carrier gas (He) flow rate of 30 mL min^{-1}. The detector flame was maintained with H_2 and air at flow rates of 45 and 40 mL min^{-1}, respectively. The oven temperature was programmed to start at 40°C, held for 1 min, and heated at 30°C min^{-1} to 90°C, and held for 4 min. To maximize detector sensitivity, the flame was doped with S by a CS_2 permeation tube kept in a copper cylinder attached to the H_2 fuel line. The cylinder was maintained in a water bath at room temperature.

Calibration curves for DMS and OCS were obtained by diluting known amounts of these S gases, released from permeation tubes (VICI Metronics, Santa Clara, CA) maintained at constant temperature (30°C), in He flow. Calibration curves (log peak area vs. log ng S) were linear between 0.1 and 6.5 ng S and DMS standards normally showed the best linearity, with correlation coefficient usually greater than 0.999. The detection limit under these conditions was ~0.4 pmol S, corresponding to minimum concentration of 0.4 nmol m^{-3} (10 pptv) for a 1 L air sample, and an emission rate of 1 nmol m^{-2} h^{-1}. The uncertainty of the S fluxes determined by the dynamic enclosure method was typically near ±10%.

2.4. Flux Calculation

The flux rate F of a S gas in the dynamic enclosure was calculated using the following equation

$$F = (V/A)(C_f - C_o) \quad (1)$$

where V is the steady volumetric flow rate of the sweep gas through the enclosure (3 L min^{-1}) and A is the soil surface area covered by the enclosure (900 cm^2). C_o is the S gas concentration in the inlet, which is equal to zero since a S-free sweep gas was employed. C_f is the S gas concentration in the outlet of the enclosure, which is equivalent to the concentration within the enclosure head space, assuming steady state and uniform mixing inside the enclosure.

When a static enclosure is employed, the S gas flux rate is calculated by the general expression

$$F = H[dC/dt]_{t=0} \quad (2)$$

where H is the enclosure geometry factor, i.e., the ratio of the enclosure volume to the enclosed soil area. For cylindrical and cubic enclosures, H equals the height (here, 30 cm). dC/dt is the slope of the curve of the gas concentration change in the enclosure head space, assuming a uniformly mixed condition therein (convective mixing), as a function of time (t), which is calculated from an exponential equation of the form

$$C(t) = a - be^{(-kt)} \qquad (3)$$

[Matthias et al., 1978].

The best exponential fits of the form of equation (3) were iteratively calculated by computer for the observed concentration vs. time data. The model applied calculated the constants a and k. The constant a (or C_{max}) corresponds to a concentration maximum which was reached when the S gas concentration within the enclosure head space equals the concentration of the soil micropores (soil atmosphere) or achieves equilibrium with respect to the dissolved gas concentration in water (e.g., soil pore water or standing water). Then, the S gas concentration change as a function of time at t = 0 was calculated by

$$[dC/dt]_{t=0} = k(C_{max} - C_{air}) \qquad (4)$$

to determine the S gas exchange rate using equation (2). C_{air}, in equation (4), is the ambient air concentration of the S gas measured at the time enclosure was deployed.

3. RESULTS

The majority of the DMS and OCS fluxes determined by the static enclosure method were calculated based on one ambient air and three head space air samples (i.e., N = 4)

with intervals of ~10 min and duration of ~30 min. The remainder were calculated from one ambient air and two head space air samples (i.e., N = 3). The best exponential fits for a non-linear change in DMS and OCS concentrations as a function of time (with N = 4) exhibited correlation coefficients above 0.980 and most above 0.990. Some examples of these curves, exhibiting positive slopes (DMS and OCS emissions) and negative slopes (OCS consumption), are displayed in Figure 1.

DMS concentrations always increased with time in the enclosure head space of static enclosures, indicating that in all circumstances DMS was released from the surface of the peatland to the atmosphere. Figure 2 shows DMS concentration changes as a function of time during experiments, at two different sites, in which samples were collected at 10 min intervals for 70 min. In this two experiments, the sampling period was extended with the purpose of following the evolution of the concentration vs. time curve for a period longer than the 30-min regularly measured. In both cases DMS concentrations increased exponentially from t = 0 to ~40 min, followed by a decrease for approximately 20 min thereafter. I was not able to explain this diversion from expected exponential trend. In the examples shown in Figure 2, the best exponential fits were determined for the entire data set (70 min, N = 8) and, also, for the initial 30 min (N = 4) only. Obviously, the

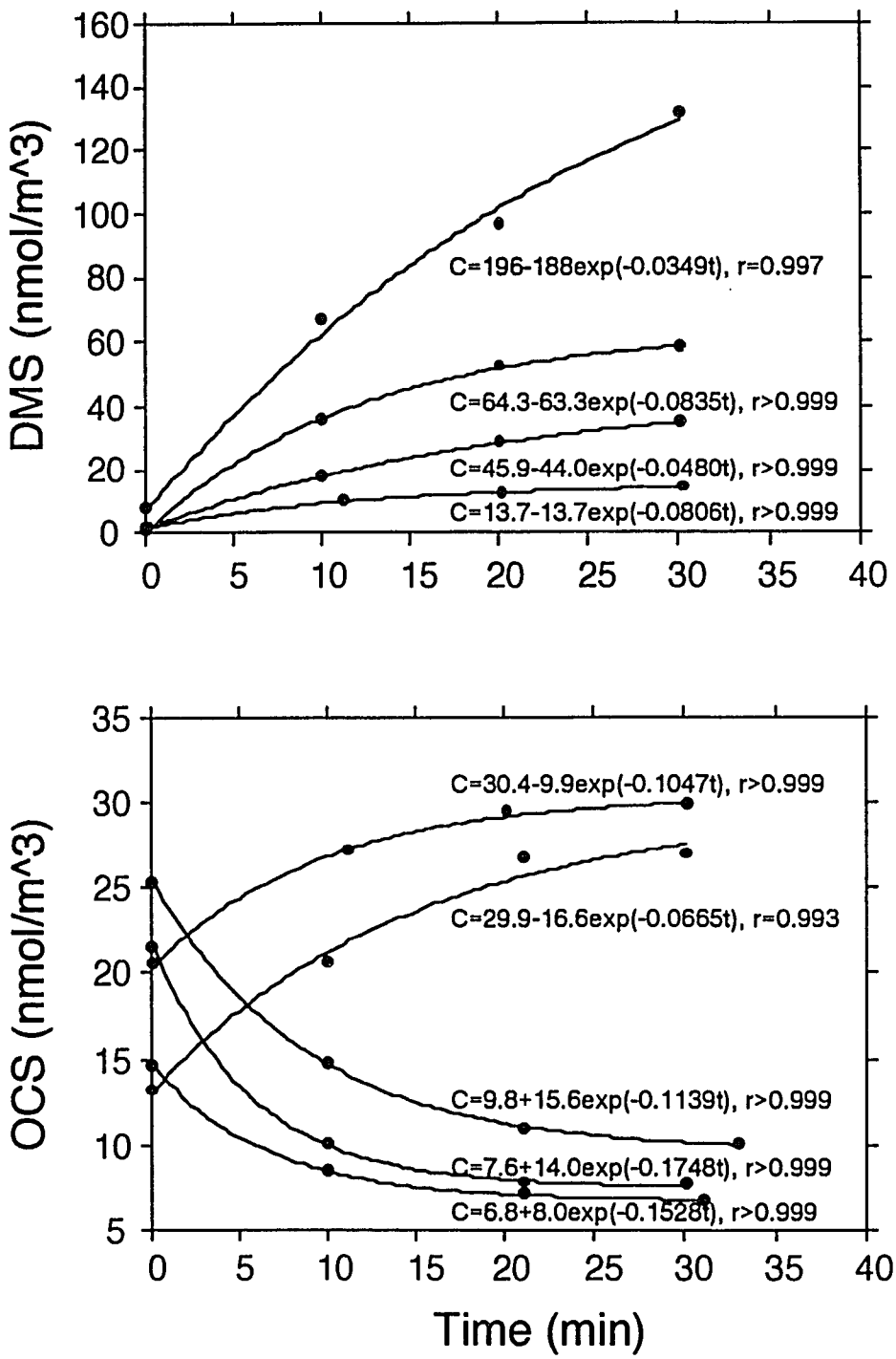

Figure 1. Typical DMS and OCS concentration vs. time curves during static enclosure measurements; best exponential fits and correspondent equations.

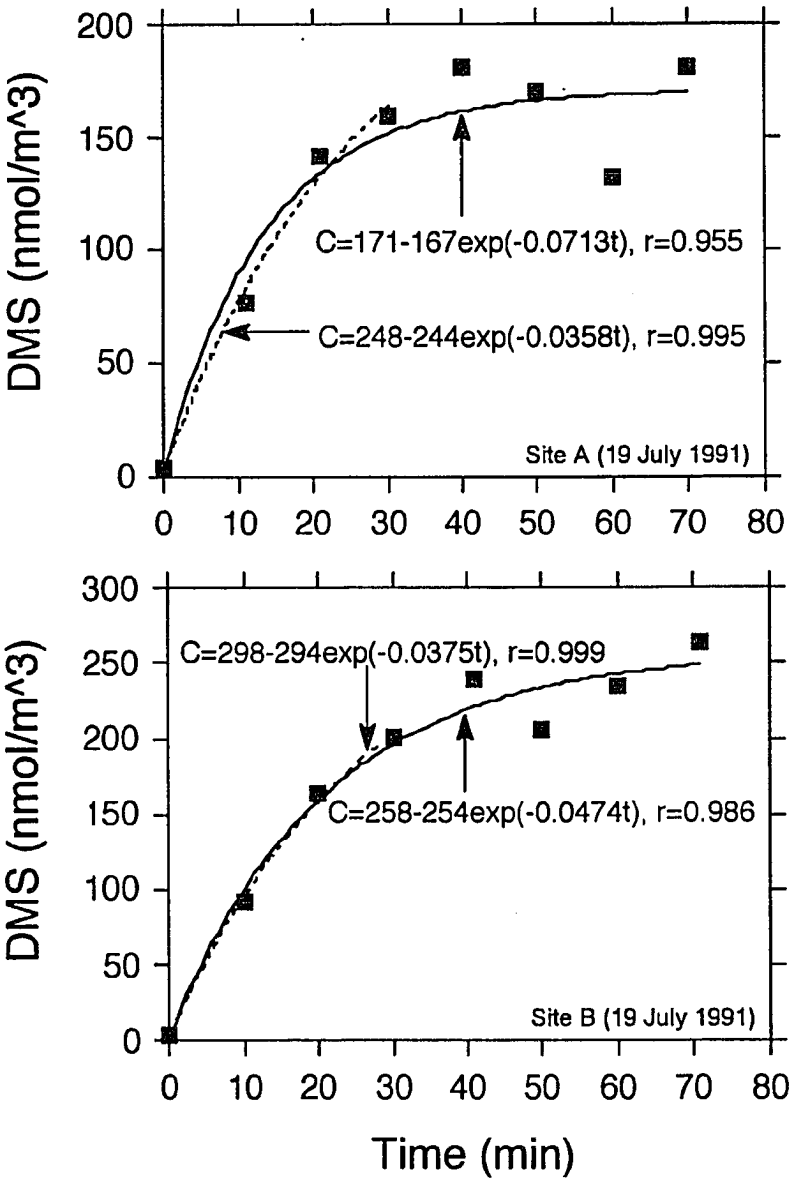

Figure 2. Static enclosure measurements of DMS concentration vs. time in 70-min sampling period, in sites containing *Sphagnum* mosses (Sallie's Fen, NH). Best exponential fits were determined for the entire 70-min sampling period (solid line) and for the first 30 minutes (dashed line) separetely.

correlation coefficients in Figure 2 indicate that the best fit was for data computed for the first 30 min.

Data from static enclosures indicated that OCS was either consumed or released in peatlands (Figure 1). Application of static enclosures on *Sphagnum*-covered surfaces displayed OCS consumption from the enclosure head space, i.e., OCS concentrations decreased with time. OCS concentration vs. time curves for these surfaces were less consistent than the DMS curves, which explains the smaller number of OCS flux data compared to DMS.

Figure 3 shows two typical examples of OCS depletion with time within the enclosure head space, for a sampling period longer than 30 min. Both examples show that 30 min after the enclosures were deployed, the OCS concentrations did not follow the exponential decreasing trend. Also, OCS data were less consistent than those observed for the DMS 70-min sampling. In the examples shown in Figure 3, the best exponential fits were determined for the entire 70-min sampling data and for the initial 30 min as well. Similarly to DMS, the exponential curves obtained for the 0-30 min sampling interval fit the data better than the total 70-min data.

Release of OCS from the peatland to the atmosphere was noted in a few measurements in which the static enclosure was deployed in a site where vegetation had been completely removed (bare site). OCS emissions at the bare site were

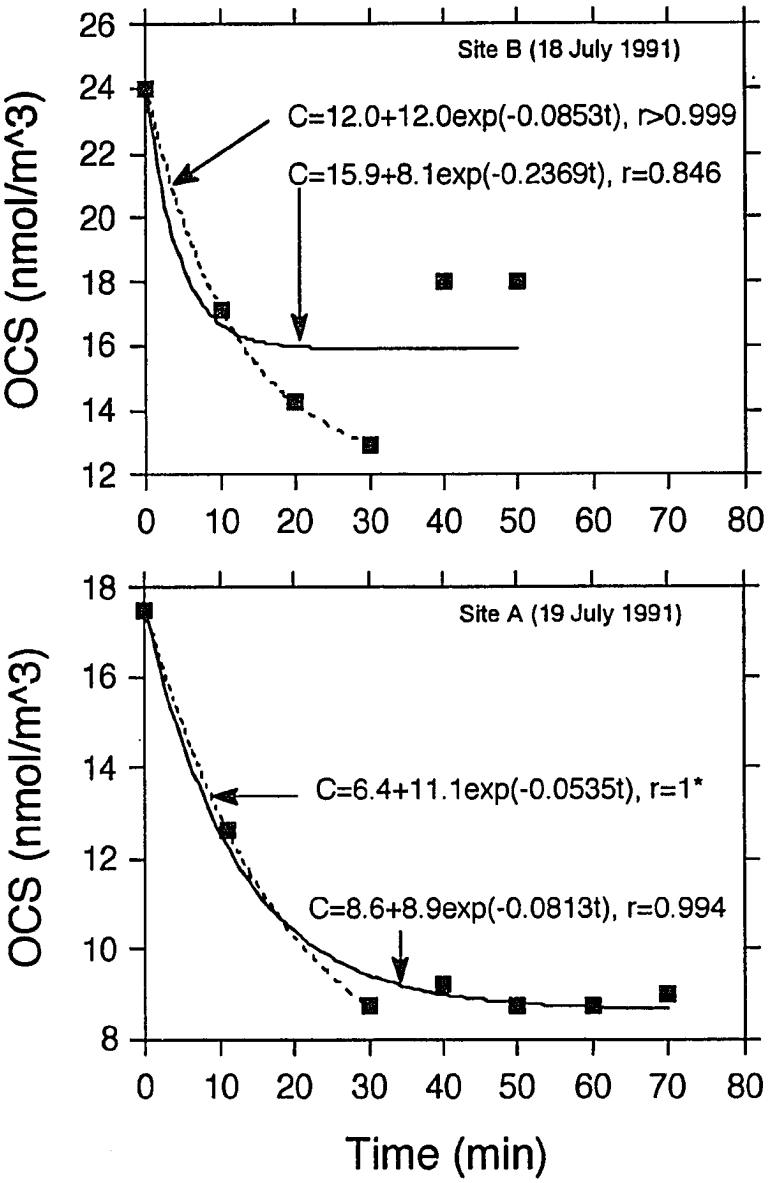

Figure 3. Static enclosure measurements of OCS concentration vs. time in 50 and 70-min sampling period, in sites containing *Sphagnum* mosses (Sallie's Fen, NH). Best exponential fits were determined for the entire 50 and 70-min sampling period (solid line) and for the first 30 minutes (dashed line) separately.

comparable to DMS emissions, measured by the static enclosure technique (Table 1).

Comparisons of DMS and OCS measurements using dynamic and static enclosures are shown in Figures 4 and 5. In these plots, the closer the points are to the 1:1 diagonal line the more similar are the results from both methods. The DMS data revealed considerable variability over the 1:1 line, however there was no apparent general trend toward any of the methods. The overall ratio of dynamic:static DMS emissions ranged from 0.21 to 2.08. That means that static DMS fluxes exceeded the dynamic fluxes (N = 24) up to ~400% and the dynamic exceeded the static (N = 23) up to ~100%. In two cases the dynamic:static ratio was equal to 1.00. This range was narrower than the 0.16-3.40 range reported by Moore and Roulet [1991] comparing dynamic and static enclosures for determination of CH_4 fluxes in a fen in Schefferville, Canada. However, my data are not directly comparable to theirs since their definition of a dynamic enclosure was one in which air was circulated with a fan and no sweep air was used. The large deviation from the 1:1 line for OCS data clearly demonstrate that static enclosures measure consumption while dynamic measure efflux.

Some of the largest differences between dynamic and static DMS fluxes observed in my work could possibly be due to influence of meteorological factors during measurements. For instance, on 13 June 1991 flux measurements were conducted under very windy conditions which might have

TABLE 1. OCS and DMS Emission Rates (nmol m^{-2} h^{-1}) From Peat Surface Devoid of Vegetation (Bare Site), Determined by the Static Method, Sallie's Fen, NH

Day (1991)	OCS	DMS
12 June*	20	17
25 June	19	32

* Water table was above the peat surface

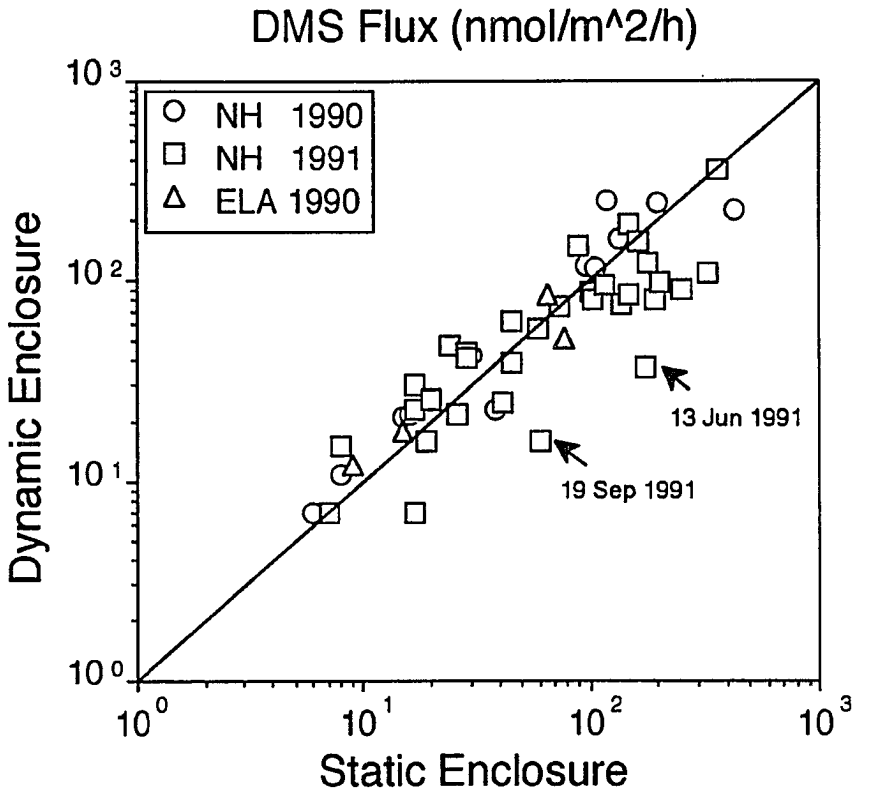

Figure 4. Comparison of DMS fluxes determined by dynamic and static enclosures.

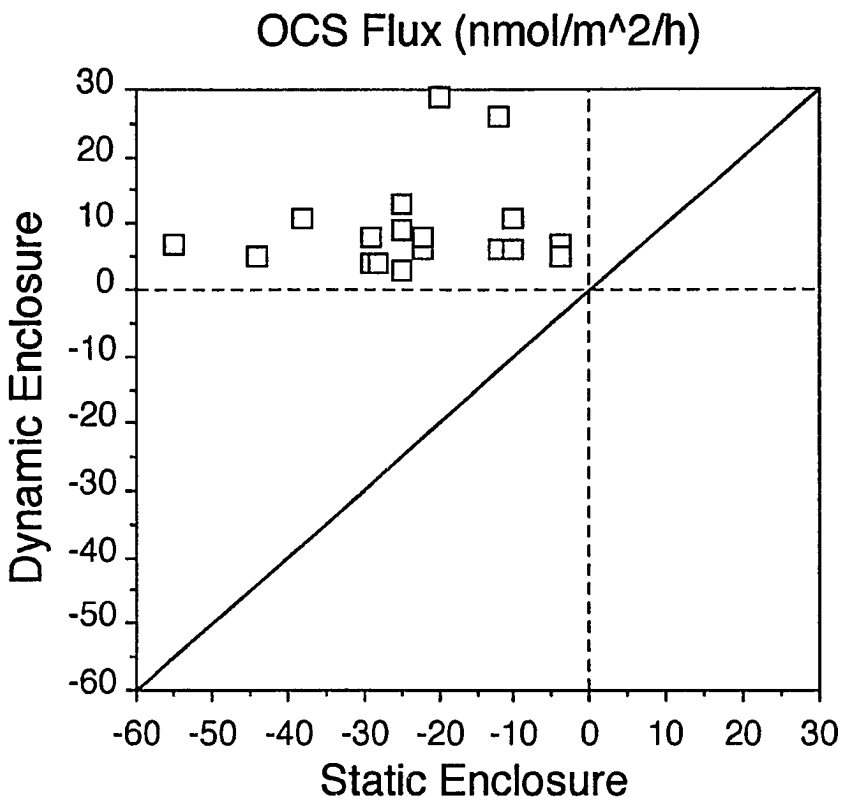

Figure 5. Comparison of OCS fluxes determined by dynamic and static enclosures.

forced oxidant-containing ambient air to penetrate enclosure causing a decrease in DMS concentration during dynamic mode, when oxidant scrubbers were not used. On 19 September 1991, it started to rain after enclosures were deployed and both ambient air and *Sphagnum* mat temperatures dropped ~4°C between the static and the dynamic measurements. Temperature strongly affects DMS fluxes in *Sphagnum* peatlands [Chapter III] and the 4°C decrease was sufficient to significantly decrease fluxes in the dynamic mode. The results of these two particular occasions are indicated by arrows in Figure 4.

Application of normality tests showed that the populations of both DMS and OCS flux data, determined either by static or dynamic enclosures, were not normally distributed. For instance, the cumulative frequency distribution (Figures 6a and b) showed significant departure from linearity and the limits for the skewness factor were superior to those accepted for a probability level of 5% [Taylor, 1990]. Therefore, a non-parametric method of hypothesis testing, the Wilcoxon matched-pair sign-rank test (an alternative to the matched-pair *t*-test) [Mattson, 1981], was applied to the overall DMS (N = 49) and OCS (N = 19) data to verify the consistency between both methods. The test was applied to *n* independent pair of flux measurements, each with two measurements (X_1, Y_1), (X_2, Y_2), ..., (X_n, Y_n), where (X_n, Y_n) represented the observed values for each

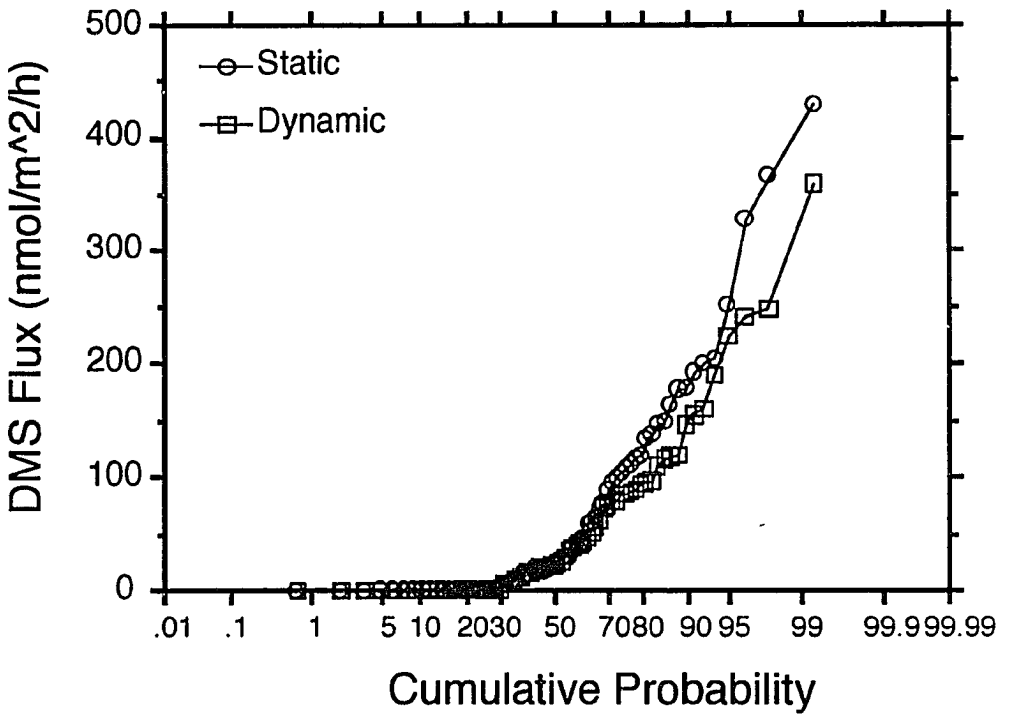

Figure 6a. Probability distribution plot of DMS fluxes.

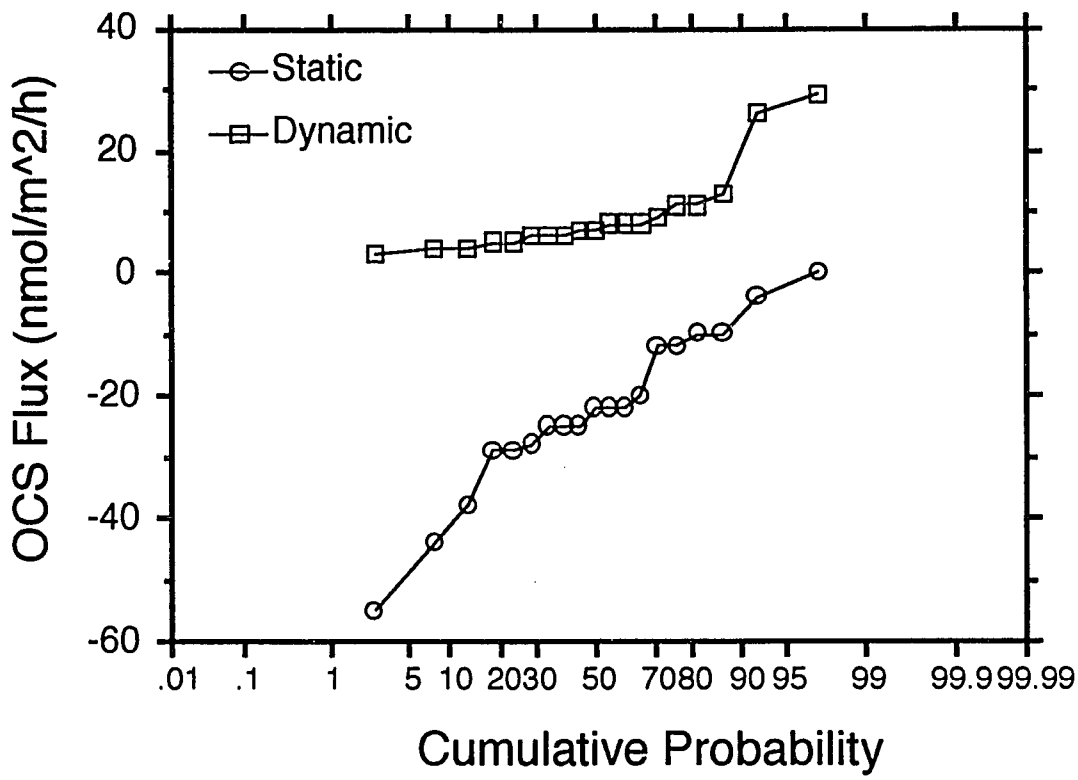

Figure 6b. Probability distribution plot of OCS fluxes.

member of the matched pair (i.e., static method, dynamic method).

Table 2 displays the results of the non-parametric test applied to the DMS and OCS data set. If results of both methods were comparable (i.e., the null hypothesis was true), the numbers of positive and negative ranks and the sum of ranks within each data set tended to be equal. The probability levels (P), based on the z scores (standard normal scores), shown in Table 1, indicate that DMS emissions determined by the static and dynamic methods were not significantly different. Conversely, the static and dynamic methods yielded results of OCS fluxes which were essentially divergent, i.e., the method indicated consumption of OCS from the atmosphere and the dynamic method indicated emission.

If a normal distribution of the DMS emission data was assumed, the application of the paired t-test would indicate also that there was no significant difference between methods for determination of DMS fluxes [i.e., t = 1.978, P = 0.0537 (2-tail)].

4. DISCUSSION

The significant correlation in results from both enclosure techniques indicated that DMS emissions using dynamic enclosure are correct in many instances. DMS

TABLE 2. Computed DMS and OCS Fluxes for the Wilcoxon Matched-Pair Signed-Rank Test

	Number of		Sum of		*z* score	P (2-tail)
	-ranks	+ranks	-ranks	+ranks		
DMS	23	24	459	669	-1.111	0.2665
OCS	19	0	190	0	-3.826	0.0001

emissions measured by the two enclosure methods were comparable in a wide flux range, i.e., approximately two orders of magnitude. This large variation resulted from several environmental factors which control S flux strength in *Sphagnum*-dominated peatlands, such as microbial activities, vegetation, nutrient status, temperature, and long-term atmospheric S input [Chapter II; Chapter III]. Although dynamic S-free enclosures have been widely used for determining exchange of VSCs between the soil surface and the atmosphere, this technique has been criticized because of the unnatural atmospheric composition established within the enclosure head space, especially when S gases are consumed from the atmosphere [Castro and Galloway, 1991]. In natural environments, the exchange rate of a particular S gas depends upon the concentration gradient between the soil surface (or sediment, peat or water) and the atmosphere, and the gas diffusion coefficient. Assuming that a particular S gas is supersaturated in the soil surface with respect to equilibrium with atmosphere, once a dynamic enclosure is deployed on the soil surface, flux is normally expected to rise if the steady concentration within the enclosure becomes lower than in the ambient air (i.e., the concentration gradient at the boundary soil-atmosphere inside the enclosure increases), and vice-versa. However, this deviation from the natural flux rate would occur only if the S gas concentration within the soil micropores (or dissolved in water) stays permanently constant, i.e., no

change toward equilibrium with the S concentration within the enclosure head space occurred.

In the present study, DMS concentrations within the enclosure head space, during dynamic measurements, ranged from 3.5 nmol m^{-3}(85 pptv) to 180 nmol m^{-3} (4340 pptv), which corresponded to the smallest and the greatest flux measurement, with a mean of 80 nmol m^{-3} (~1930 pptv). These values are considerably higher than the range of DMS concentrations in ambient air, measured approximately 50 cm above the peatlands, where the static enclosures were applied, i.e., from <0.4 nmol m^{-3} (<10 pptv) to 22 nmol m^{-3} (530 pptv), averaging 2.9 nmol m^{-3} (70 pptv). This range is close to the range of DMS concentrations in the marine atmosphere, 20-200 pptv, [Andreae, 1990] and much higher than ground level DMS concentrations over the Amazon Basin, 16±10 pptv, [Andreae et al., 1990]. Consequently, considering that DMS concentrations in ambient air over the peatlands were much lower than the range of DMS concentrations inside the enclosure head space during dynamic measurements, it would be expected that, the higher the natural DMS emission, the larger would be the error of the flux estimate (i.e., underestimation). However, as shown in Figure 4, DMS fluxes determined by the dynamic method did not exhibit any significant deviation from the corresponding fluxes determined by the static method.

An examination of the time course data in Figure 1 and 2 reveals a non-linear accumulation of DMS during static

enclosure deployments which is indicative of a negative feedback on flux as DMS accumulates within enclosures. This disagrees with the finding that static enclosure results agreed with dynamic enclosure data since the latter method produced a high level of DMS within enclosures before samples were collected. However, the time courses in Figure 2, which represent cases where fluxes were quit high, also show a relatively linear DMS accumulation up to >150 nmol m^{-3}. In most cases DMS concentrations within dynamic enclosures were in the lower range of the concentration vs. time curve in the corresponding static measurement. This was the most linear region of the curve where deviation of the static and dynamic methods would be expected to be minimal. Hence, the agreement between the two techniques may indicate that the equilibrium DMS concentration within the dynamic enclosures was always low enough to provide results that were similar to static enclosure results. This would also suggest that variations in the sweep flow rate would cause variations in the measured DMS efflux rate since the equilibrium concentration of DMS will increase with decreasing sweep flow rates. Therefore, if sweep flow is adjusted to maintain relatively low concentrations of DMS within enclosures, the dynamic enclosure technique is suitable for measuring fluxes of DMS from terrestrial habitats. Hence, previous data, all of which have been derived from dynamic methods, are probably correct.

An interesting aspect of the use of enclosures to estimate gas exchange at the soil surface is that changes in gas concentrations are normally assumed to take place only in the atmosphere inside the enclosure head space. Variations in gas concentration in the uppermost part of the soil profile (either in the micropores or dissolved in soil pore water) are normally not considered. Using a two dimensional numerical model, Matthias et al. [1978] demonstrated that the soil gradient of nitrous oxide concentrations was affected when enclosures were installed at the soil surface. Therefore, it is possible that changes in S gas concentrations inside the enclosure head space, during a dynamic measurement, do not influence gas exchange markedly, if equilibrium is reached between soil surface (or soil pore water) and air within the enclosure head space. However, this would occur only if the net production rate of the S gas in the soil is not affected by changes in gas concentration which takes place during sampling. This might partly explain why DMS fluxes measured by static and dynamic enclosures were comparable. If the production of precursors is a major factor controlling DMS flux then one would expect that the time courses in Figure 1 and 2 would become linear if the DMS production rate does not change. The non-linear data in Figures 1 and 2 suggested that if the production rate did not change, the decrease in flux over time was due to the inability of the dissolved DMS pool to equilibrate

quickly enough to keep up with the change in the head space DMS level.

The results for OCS differed greatly for the two techniques employed. OCS fluxes measured by dynamic enclosures showed emission from the peatland to the atmosphere, which varied from 2.3 to 29 nmol m^{-2} h^{-1}. Conversely, static measurements in vegetated areas indicated, in all instances, uptake of OCS, with consumption rates ranging from 3.7 to 55 nmol m^{-2} h^{-1}. Castro and Galloway [1991] reported a very similar result by using dynamic enclosures flushed with either S-free air or ambient air to measure OCS fluxes in unvegetated forest soils in Virginia. Their OCS emission rates were between 1.4-24 nmol m^{-2} h^{-1} (S-free air) and consumption rates between 5.2-30 nmol m^{-2} h^{-1} (ambient air).

Conversely, dynamic measurements using S-free sweep air resulted in OCS emissions from the surface of the peatlands. This implied that OCS concentrations in the peat surface were supersaturated with respect to OCS concentration within the enclosure head space. Since OCS in ambient air is usually ~500 pptv, it is possible that this efflux was simply due to the redistribution of OCS, which was originally in equilibrium with atmospheric OCS, once S-free air was passed over the peat surface. Hines and Morrison [1992] considered this redistribution in *Sphagnum*-dominated sites in tundra by calculating the efflux of OCS when ambient air was immediately replaced by S-free air. These

calculations showed that the efflux of OCS measured using dynamic enclosures was much higher than that due to the diffusional loss of OCS which had been in equilibrium with atmospheric OCS. This applies to the present data as well. In fact, I noted OCS supersaturation in the pore waters of Sallie's Fen [Chapter III]. Sites in which *Sphagnum* had been removed exhibited an efflux of OCS even when static enclosures were used. Therefore, OCS must have been produced in the decomposing peat, yet was consumed by the emergent vegetation (*Sphagnum* in this case). Several studies have determined that OCS is consumed by photosynthesizing vegetation [Brown et al., 1986; Fall et al., 1988; Goldan et al., 1988]. Since both peatlands studied here were completely vegetated, they must be considered as net sinks for atmospheric OCS, at least during daylight. These wetlands were both sources and sinks for OCS, but the rate of OCS consumption exceeded the source term.

The OCS decreasing time course data were not linear. This would be expected for a consuming system where the consumption rate is controlled largely by the concentration of reactants, i.e., OCS. Since OCS is consumed and produced in these systems, one would expect that the decrease in OCS consumption rate, as OCS levels decrease during time course measurements, would become balanced by OCS production leading to a leveling off of OCS concentrations at an equilibrium value. In addition, since it is likely that OCS consumption is controlled strongly by the OCS concentration

in enclosures, one would also expect that OCS consumption would be affected significantly in dynamic enclosures regardless of the composition of the sweep air. I have shown here that S-free sweep air is inappropriate for measuring the consumption of gases. Castro and Galloway [1991] also reported this finding. However, unless OCS is added to an enclosure at a rate identical to the net OCS consumption rate, the internal concentration of OCS will differ from ambient and the measured rate of OCS uptake will also be affected. For example, when ambient air is used as a sweep gas like in the studies by Castro and Galloway [1991], the internal OCS concentration will be lower than ambient and the OCS consumption rate will be underestimated. My static enclosure deployments avoided this artifact by extrapolating time course data to time zero. Another suitable approach would be to add OCS to static enclosures at a rate identical to its utilization. This approach has been used for photosynthesis rate measurements where CO_2 is continually monitored and added to the enclosures [G.J. Whiting, NASA, personal communication]. However, this is not feasible with current technology for measuring OCS.

All previous data on fluxes of OCS from terrestrial habitats including wetlands, unvegetated soils, and agricultural plots have employed the dynamic enclosure technique. Except for the studies by Steudler and Peterson [1985] and Castro and Galloway [1991] who used ambient air as sweep, S-free sweep air has been used and net effluxes of

OCS from soil into the atmosphere have been reported. This data base has been used to calculate global emission rates for OCS and other VSCs from continents. My results indicate that these emission data are erroneous and that net OCS consumption might occur on vegetated terrestrial environments. Therefore, the total VSC emissions from continents needs to be reassessed. Previous studies using ambient sweep air [Castro and Galloway, 1991] have reported OCS consumption. However, my data suggest that this approach is also inappropriate and I recommend using static enclosures in the future to determine rates and direction of OCS exchange in continental habitats.

It appears that data for gases that are emitted from a surface, such as DMS, are not affected as much by their internal enclosure concentration compared to gases like OCS which are consumed. Therefore, previous emission data which have been derived from dynamic enclosures are probably correct for gases like DMS which are emitted. However, it appears that all dynamic enclosure data are erroneous for S gases which are consumed.

To the best of my knowledge, static enclosures have never been used to determine flux of organic VSCs in natural environments. According to my results, the method showed some advantages relative to the dynamic enclosure method, such as, *(a)* emission and uptake of different S gases can be determined simultaneously; *(b)* exchange rate is determined at an undisturbed environmental conditions (i.e., $t = 0$);

(c) reduction of sampling apparatus; and *(d)* shorter sampling period. Nevertheless, the inconveniences of the static method are: *(a)* a larger number of samples are needed for each exchange determination; *(b)* the sampling interval cannot be reduced due to the duration of each sample collection (~3 min); and *(c)* inner volume of the drier/Na_2CO_3 scrubber system might dilute samples taken from the head space of the enclosures and possibly contribute to the imprecision of the concentration vs. time curves before a steady concentration is achieved. Therefore, improvements of the static method are required in order to augment the precision of the results.

To minimize problems associated with the static method, both the sample volume and the inner volume of drier/scrubber system have to be reduced. The application of more sensitive detectors for S analysis (e.g., the sulfur chemiluminescence detector (SCD), [Shearer et al., 1990]) should aid in reducing the size of the sample. Hence, the sampling interval could be reduced and precision of the concentration vs. time curve improved. Also, once a more sensitive analytical technique becomes feasible for S analysis in natural samples, new techniques for sample collection (e.g., syringes) and storage systems should be tested for VSCs.

5. SUMMARY AND CONCLUSIONS

Based on the application of a static enclosure method for determining fluxes of VSCs between *Sphagnum*-dominated peatlands and atmosphere, the following conclusions can be drawn:

(1) DMS emissions from *Sphagnum* peatlands determined by the static and dynamic enclosures were comparable between 5 and 500 nmol m^{-2} h^{-1}. This suggests that previous DMS flux data are correct.

(2) In *Sphagnum* peatlands, OCS was released to the atmosphere from the surface of the peat, but it was consumed from the atmosphere by *Sphagnum* mosses. The net balance between both processes indicated that OCS consumption exceeds emissions. This is probably the case for most continental habitats indicating that previous OCS flux data are incorrect and global VSC exchange data need to be reassessed.

(3) Static enclosures are the most appropriate technique to estimate consumption of S gases from the atmosphere. S-free flow-through dynamic enclosures are inadequate for this application; and enclosures purged with ambient air should underestimate consumption because the concentration of the consumed gas inside the enclosure will be lower than ambient. However, dynamic enclosures are suitable for gases which do not exhibit a significant consumption term, e.g. DMS.

(4) The advantages of using the static enclosure technique in determining fluxes of S gases are: *(a)* it does not affect the environmental conditions at the time the exchange rate is determined, i.e., $t = 0$; *(b)* it allows simultaneous determination of emission and uptake of different S gases; *(c)* it minimizes transport of massive equipment (e.g., synthetic air cylinders) or intricate S gas scrubbers (and pump) and the use of tubing; and *(d)* it has a shorter sampling period since a pre-equilibrium period is avoided.

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CHAPTER II

Effects of Inorganic Sulfur Addition on Fluxes of Volatile Sulfur Compounds in *Sphagnum* Peatlands

ABSTRACT

Short and long-term impacts of increased S deposition on fluxes of volatile S compounds (VSCs) from *Sphagnum* peatlands were investigated in an artificially acidified (sulfuric and nitric acids) poor fen (Mire 239) at the Experimental Lakes Area (ELA), Ontario, Canada. Additional experiments were conducted in a poor fen (Sallie's Fen) in Barrington, NH, USA. At Mire 239, emissions of VSCs were monitored, before and after acidification, at control (unacidified) and experimental sections within two major physiographic zones of the mire (oligotrophic and minerotrophic). The experimental areas of the mire have received S amendments since 1983, in amounts equivalent to the annual S deposition in the highest polluted areas of Canada and US. Dimethyl sulfide (DMS) was the predominant VSC released from the mire and varied largely with time and space (i.e., from 2.5 to 127 nmol m^{-2} h^{-1}). Sulfur addition did not affect DMS emissions in a period of hours to a few days, although it stimulated production of DMS and MSH in the anoxic surficial regions of the peat. DMS emissions in the experimental oligotrophic area of the mire was ~3-fold greater than in the control oligotrophic area, and ~10-fold greater than in the minerotrophic zones. These differences could be due to a combination of differences in types of vegetation, nutritional status and S input. At Sallie's Fen,

DMS fluxes were ~8 times higher from a *Sphagnum* site than from a bare peat site. Fluxes of VSCs were not significantly affected by sulfate amendments at both sites, while DMS and MSH concentrations increased greatly with time in the top 10 cm of the peat column. My data indicated that although *Sphagnum* is not the direct source of DMS released from *Sphagnum* peatlands, it might play a role in regulating DMS emissions to the atmosphere.

1. INTRODUCTION

Sulfur gases are involved in several chemical and physical processes occurring in the troposphere and stratosphere. Reduced S gases are precursors of SO_2 and sulfate which are important in controlling the acidity of precipitation and the generation of atmospheric aerosols [Charlson and Rodhe, 1982]. It has been proposed that in the production and emission of dimethyl sulfide (DMS) could influence climate by affecting the density of cloud condensation nuclei (CCN), and influencing cloud albedo [Baldwin et al., 1976; Bolin and Charlson, 1976; Nguyen et al., 1983; Charlson et al., 1987; Legrand et al., 1988, 1991; Foley et al., 1991]. In the stratosphere, sulfuric acid aerosols, formed mostly from volcanic SO_2 and oxidation of carbonyl sulfide (OCS), provide sites for heterogeneous chemical reactions and influence the ozone budget [Tolbert et al., 1988; Hofmann and Solomon, 1989; Brasseur et al., 1990].

In the last decade, considerable attention has been directed toward determining the magnitude of oceanic contribution to the atmospheric S burden [e.g., Barnard et al., 1982; Andreae and Raemdonck, 1983; Erickson et al., 1990; Thompson et al., 1990]. In contrast, the role of terrestrial habitats in the production and consumption of atmospheric S gases have not been thoroughly investigated.

Consequently, recent determinations of the contribution of the continents to the global S burden are few and uncertain. For example, estimates of terrestrial sources of biogenic S gases since 1981 have decreased from 64 Tg S a^{-1} [Adams et al., 1981], to 40 [Möller, 1984], to 4 [Andreae et al., 1990], and most recently to 0.35-0.9 Tg S a^{-1} [Bates et al., 1992; Spiro et al., 1992]. This underscores the need to acquire additional data on terrestrial sources and sinks of volatile sulfur compounds (VSCs) to refine estimates of the continental contributions to regional and global atmospheric S cycling. Since S gases have a short atmospheric lifetime, they must be considered primarily on a local and regional basis. The diversity and complexity of terrestrial environments precludes an easy extrapolation of emission data to large spatial scales. Hence, studies are needed which describe S gas exchange in a variety of biomes.

Wetlands areas are particularly well suited to the production of reduced biogenic sulfur gases. They contain high concentrations of organic matter with anoxic regions which are in close proximity to the atmosphere. Wetlands are believed to be the major natural source of atmospheric methane [Harriss et al., 1985], and they have been cited as areas which are strong sources of S gases [Hines, 1992]. Bogs and fens occupy ~60% of the global wetland area, the majority of which are found in the boreal and subarctic regions of the northern hemisphere [Matthews and Fung, 1987; Aselmann and Crutzen, 1989]. Although these northern

peatlands dominate the high latitude landscape there are few studies of VSCs in these ecosystems. Hines and Morrison [1992] determined that S emissions from Alaskan tundra were very slow, which they attributed to low rates of atmospheric S input, the accumulation of organic matter and the spring run off of S deposited in arctic haze. Nriagu et al. [1987] reported that DMS emissions from boreal wetlands in Ontario, Canada, were similar in magnitude to those from oceanic regions and they suggested that those sources contribute to approximately 30% of the excess S in precipitation in the region. They suggested that biologically-mediated re-emission of previously deposited anthropogenic S could play an important role in the continuing acidification of the region for several years. However, their flux data were derived from DMS concentrations in standing water. No data are available which describe emissions from vegetated areas where the water table lies below the surface.

In this paper, I report mid-summer fluxes of VSCs from an experimentally manipulated *Sphagnum*-dominated poor fen, distant from major sources of pollutants, in the low boreal region of Canada. The major goal of this investigation was to examine the effects of increased S (as sulfuric acid) deposition on fluxes of VSCs, in part, to experimentally verify the hypothesis of Nriagu et al. [1987] that increased S deposition causes increased emission of biogenic S. Some of the environmental factors that might influence emission

rates were investigated, including mineral status throughout the fen and diel temperature variability.

2. METHODS

2.1. Sites Description

2.1.1. Mire 239

The majority of the study was conducted in July 1990 at a 3.67 ha poor fen (Mire 239), in the Experimental Lakes Area (ELA) of northwestern Ontario (49°40'N, 93°43'W) (Figure 7). The mire receives direct precipitation, runoff from the surrounding upland (6.91 ha of forested upland watershed), has no inflow stream, and has an outflow which is gauged with a weir. Groundwater seepage through bedrock is minimal [Bayley et al., 1986]. The mire has been used as an experimental site since 1983 for studies of the effects of acid deposition on boreal wetlands [Vitt and Bayley, 1984; Bayley et al., 1986; Bayley et al., 1987; Beaty, 1987]. Approximately 30% of the southern part of the mire was burned in 1974 and the black spruce (*Picea mariana*) trees were destroyed. The vegetation (excluding trees) was not altered by the fire [Vitt and Bayley, 1984].

Two major physiographic zones, based on vegetation type, are evident in the fen (Figure 7) [Vitt and Bayley, 1984; Bayley et al., 1987]: *1)* a slightly more mineral rich zone (comprising about 30% of the total area), along the

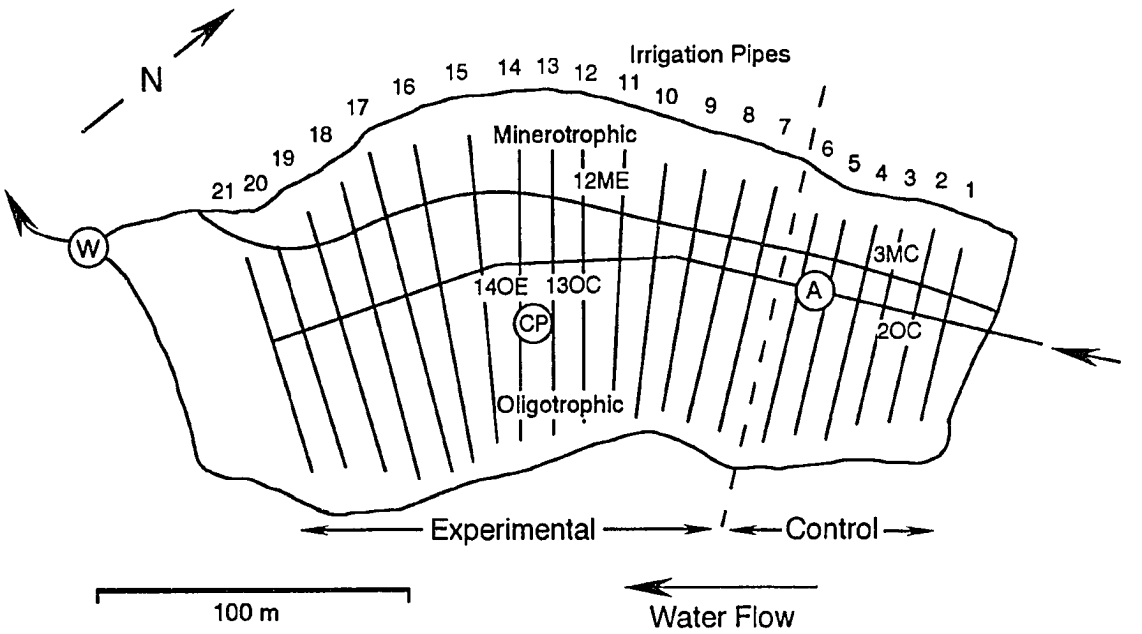

Figure 7. Mire 239 at the Experimental Lakes Area (ELA), Ontario, Canada. CP central pool; A acid addition; W weir. Acid application was made on irrigation pipes 7-21. Sites ME and OE received sulfuric acid. Sites MC and OC received lake water. Site 13OC received acid in the past but was excluded during July 1990.

northern and western fringes of the peatland, which receives runoff from the surrounding uplands and contains distinctly minerotrophic plant species, such a horse tail (*Equisetum sylvaticum*), willow (*Salix planifolia*), and alder (*Alnus crispa*); and *2)* an oligotrophic zone (about 70% of the total area), characterized by the lack of the above species and by the occurrence of typical nutrient-poor types of vegetation, such as pitcher plants (*Sarracenia purpurea*) and sundews (*Drosera rotundifolia*). *Sphagnum* spp. (*S. angustifolium* and *S. magellanicum*), dominate the ground layer vegetation in the entire peatland.

Mean annual precipitation at the ELA is approximately 680 mm, of which nearly 70% is rain. Monthly average air temperatures ranges from -18°C (January) to 19°C (July) and are above 0°C from April to October. On an annual basis, predominant winds are SW, followed by NW and NE, with a mean wind speed of 2.7 m s^{-1} at 10 m above the ground. See Beaty and Lyng [1989] for detailed ELA meteorological information.

Five sites were selected for the study of S gas emissions, distributed within the minerotrophic and oligotrophic portions of the mire (Figure 7). The mire was divided into experimental and control sections, the former received artificial acid rain while the latter received only lake water. Site numbers in Figure 7 are based on the nearest irrigation lateral pipe and the letters O, M, E and C denote oligotrophic, minerotrophic, experimental and

control, respectively. Letters A, B and C denote sub-sites within each habitat.

2.1.2. Sallie's Fen

Additional experiments were conducted in a 1.7 ha poor fen, Sallie's Fen, in Barrington (43°12'N, 71°04'W), NH, USA. The fen receives water from precipitation, upland runoff and ground water sources. The fen is a *Sphagnum*-dominated peatland although the distribution and speciation of *Sphagnum* have not been characterized well. The vascular component of the emergent flora is dominated by sedges (mainly *Carex rostrata*) and leather-leaf (*Chamaedaphne calyculata*). A few white pines (*Pinus strobus*) and black spruce (*Picea mariana*) are found in the southern-central part of the fen. The upland area is dominated by eastern hemlock (*Tsuga canadensis*), white pine (*Pinus strobus*), red maple (*Acer rubrum*), sugar maple (*Acer saccharum*) and white birch (*Betula papyrifera*).

2.2. Flux Measurement

Fluxes of S gases from the surface of the peatland were measured using dynamic enclosures. Details on construction and operation of the enclosures were described previously [Morrison and Hines, 1990; Hines and Morrison, 1992]. Briefly, cubic-shaped FEP Teflon enclosures (27 L volume) were placed on Teflon-lined aluminum collars (30 x 30 cm), which were inserted in selected sites at least a day before

the first samples were collected. Enclosures were shaded to avoid excessive increases in temperature and humidity. Sweep air, supplied from a cylinder of synthetic air (N_2 and O_2), was simultaneously distributed to three enclosures by 1/4" OD Teflon tubes through a mass flow controller/integrator system (Tylan Corp., Carson, CA), at a flow rate of 3 L min^{-1}. Sweep air flowed for one hour before sampling started. Air samples (~500 mL), from the enclosure head space, were withdrawn at 150 mL min^{-1}. Sulfur gases were trapped in a 60 cm (0.32 cm OD) FEP Teflon loop partially filled with Teflon wool (~15 cm long) and immersed in liquid Ar (-186°C). In 50% of the cases, three replicate samples were collected from each enclosure representing a single sampling time interval, and two replicates in the other 50%. Water vapor was removed using a Teflon drier (25 mL inner volume) surrounded by dry ice. Air temperature was measured, 1-1.5 m above the mire surface, using an Omega thermistor. *Sphagnum* mat temperature was also measured, ~5 cm below it surface. After collection, samples within loops were transported to the laboratory and analyzed within 6 hours.

2.3. Water Sampling and Gas Extraction

At Mire 239, pore water samples were collected near the flux sampling sites. Samples were collected 0-2 cm below the surface of the water table, usually 20-30 cm below the surface of the *Sphagnum* mat. The vegetation mat was spread carefully to expose the surface of the water table and

samples were immediately withdrawn with a 0.32 cm OD FEP Teflon tube, connected to a 20 mL glass syringe by a three-way stopcock. Water column samples were also collected in the small pool, located in the central part of the oligotrophic zone (Figure 7). Samples were collected without a head space after syringes were rinsed twice with ambient water. After collection, syringes were immediately stored in the dark at low temperature and analyzed within 6 hours. Water temperature was measured at the site. In the laboratory at the ELA, water *p*H was measured using an Orion Research 399A *p*H meter with a precision of ±0.02 *p*H units.

In the laboratory at the ELA, extraction of S gases from water samples was performed mostly in a 60 mL glass stripper connected in series to a 4-port Teflon valve and a rotameter. Known volumes (3-5 mL) of water were stripped with He at a flow rate of 40 mL min^{-1} for 5 minutes and S gases trapped cryogenically in a 0.32 cm OD Teflon loop, packed with Teflon wool, immersed in liquid Ar. After extraction, S gases were immediately desorbed from the trap by immersion into warm water and injected into the gas chromatograph (GC).

At Sallie's Fen, pore water samples were collected every 5 cm, from 1 cm below the surface of the water table to 26 cm. During the days the experiment was conducted (described below), the water table was ~4 cm below the peat surface. Pore water samples were collected using a 0.32 cm OD stainless steel tube, with millimeter-diameter

perforations near the tip, which was connected to a 20 mL glass syringe. Samples were stored at low temperature and analyzed within 7 hours. Water samples (5 mL) were sparged with He in a 10 mL glass stripper (Alltech Associates, Deerfield, IL) and cryogenically trapped. *p*H was measured in the laboratory.

2.4. Analysis of Sulfur Gases

In the laboratory, once sample loops were connected to a 6-port Teflon valve, they were transferred to a hot water bath and S gases swept into a Shimadzu GC-9A gas chromatograph (GC) equipped with a 60/80 Carbopack B (1.5% XE-60/1% H_3PO_5) column (1.8 m length x 0.32 cm OD) (Supelco Inc., Bellefonte, PA) and a S-specific flame photometric detector (FPD). Best resolution and maximum sensitivity was obtained with carrier gas (He), H_2 and air flow rates at 30, 45, and 40 mL min^{-1}, respectively. The FPD was maintained at 200°C. The oven temperature programmed at 40°C for 1 min, followed by an increase to 90°C at 30°C min^{-1}. Analysis took ~6 min. To maximize detector sensitivity, the fuel gas was doped with S by placing a CS_2 permeation tube into the H_2 line.

Calibration curves for hydrogen sulfide (H_2S), carbonyl sulfide (OCS), methane thiol (MSH), DMS and carbon disulfide (CS_2) were obtained by diluting known amounts of these S gases, from permeation tubes (VICI Metronics, Santa Clara, CA) maintained at 30°C, under a flow of He. The GC method

was quantitative for all these gases except H_2S due to co-elution of this species with CO_2 and CH_4, which quenched the FPD. Calibration curves (log peak area vs. log ng S) were linear between 0.1 and 6.5 ng S and DMS standards normally showed the best linearity of the gases studied ($r>0.999$). The detection limit for DMS under these conditions was ~0.3 pmol S, corresponding to a minimum emission rate of ~1 nmol m^{-2} h^{-1}. The precision for DMS emission was roughly ±10% (standard deviation expressed as a percentage of the mean).

2.5. Experimental Sulfur and Nitrogen Addition

2.5.1. Mire 239

Experimental acidification (addition of sulfuric and nitric acid) began in 1983, with the goal of simulating the acidification of wetlands in eastern North America. This constituted a decrease of 1.0 *p*H unit (average precipitation *p*H at ELA is ~5.0). The experimental area (2.66 ha) of the mire received loadings of concentrated sulfuric and nitric acids diluted in water from nearby Roddy Lake. The control area (0.85 ha) received only lake water. The mire was evenly irrigated by agricultural sprinklers over the 3.6 ha area.

The annual average bulk sulfate deposition at ELA was 10.8 mmol m^{-2} between 1973 and 1988. From mid-1983 to mid-1989, the experimental area of the mire 239 (lateral pipes 7 through 21) received 20 mmol m^{-2} a^{-1} of sulfuric acid (equally distributed between May and October), plus equal

amounts of nitric acid. From mid-1989 to mid-1990 the S load was twice as much, i.e., 40.8 mmol m^{-2} a^{-1}.

In 1990, before the start of my study, the fen had already received 13.6 mmol m^{-2} of S, half in May and half in June. In the afternoon of 18 July, 3 days after my sample collection started, the experimental sites were sprayed with sulfuric and nitric acids. The entire experimental area, except the area near the central pool (site 130C), received 3.4 mmol m^{-2} of sulfuric acid and 6.8 mmol m^{-2} of nitric acid. After the acid irrigation, which lasted ~5 hours, the mire was sprayed with lake water alone for ~30 min to mimic acid rain event. The mire received a substantial rainfall the day before the artificial acidification began.

The experimental design was selected to determine: *1)* the long term effects of S inputs (experimental vs. control sites prior to acidification); *2)* short term effects of S inputs (data collected before acidification and then for several hours after; site 130C acted as a further control which had receiving S for several years, did not for the experiment presented here); and *3)* differences between minerotrophic and oligotrophic areas.

2.5.2. Sallie's Fen

Two adjacent sites (30 x 30 cm each), containing only *Sphagnum fallax* (Bruce E. Burnham, University of New Hampshire, personal communication), at Sallie's fen were selected for the study of the effect of sulfate deposition

on S gases. In one of the sites, *S. fallax* was left within the collar (the same used for holding the dynamic flux enclosures). In the other site, *S. fallax* was removed when the collar was installed and regrowth was avoided by removal of new vegetation. However, roots of the adjacent vascular vegetation were observed within the underlying peat.

On 13 August 1991, pore water samples were collected at various depths and emissions of S gases were measured at both sites. Immediately after of the first day of sampling, a solution (900 mL) containing a total of 0.37 g of ammonium sulfate (solution *p*H = 5.6) was poured within the collars at each site. The amount of S added to the sites corresponded to a typical annual deposition of S (wet deposition) for the region. Flux measurements and pore water analyses were conducted in the following three days, at approximately the same time of the day, i.e., between 1000-1230 local time (LT). This experiment was conducted during a period with no precipitation in order to avoid effects of rain-induced lateral water movement.

3. RESULTS

3.1. Mire 239

3.1.1. Fluxes of VSCs

Dimethyl sulfide was the dominant VSC released (>90% of total VSC released) from the mire in mid-July, with fluxes ranging from 2.5 nmol m^{-2} h^{-1} (minerotrophic control area) to 127 nmol m^{-2} h^{-1} (oligotrophic experimental area) [Appendix A]. The mean DMS flux (± standard error of the mean) during the overall study period was 40±5 nmol m^{-2} h^{-1} (median = 33 nmol m^{-2} h^{-1}, N = 39). Fluxes of MSH and CS_2 ranged from <1.0 to 1.4 nmol m^{-2} h^{-1}, and from <2.0 to 8.1 nmol m^{-2} h^{-1}, respectively. In both cases, more than 90% of the measurements were below the detection limit.

Carbonyl sulfide emissions from Mire 239 ranged from <1.0 to 9.4 nmol m^{-2} h^{-1}. However, because the dynamic enclosure system used here employed S-free sweep air, it was unable to measure the consumption of S gases. Other studies using dynamic enclosures which utilize ambient air [Steudler and Peterson, 1985; Castro and Galloway, 1991] or OCS-spiked sweep air [Morrison and Hines, 1990], and studies which have employed static enclosures which entrap ambient air [Hines and Morrison, 1992], have shown that OCS is often consumed from the atmosphere. The study of Hines and Morrison [1992] found that OCS was consumed by vegetated tundra soils in Alaska. Uptake of OCS by several plant species has been

extensively reported in the literature [Brown et al., 1986; Brown and Bell, 1986; Goldan et al., 1987; Goldan et al., 1988; Fall et al., 1988; Mihalopoulos et al., 1989]. Therefore, it is likely that the OCS emission data, collected during the present study using dynamic enclosure techniques, were erroneous and will not be discussed further. However, I have determined consumption rates of OCS using static enclosure methods in *Sphagnum*-dominated peatlands and those data will be presented elsewhere [Chapter III].

3.1.2. Diel Variability of DMS Emissions

Diel variations in DMS fluxes were monitored at sites 130C-B, 140E-A and 140E-C from the late afternoon of 18 July (after acidification) to the late afternoon of the 19th (Figure 8). DMS fluxes increased with the temperature of the *Sphagnum* mat (Figure 9). A significant linear correlation between DMS flux and temperature was found for sites 130C-B ($r>0.99$, $N = 5$) and 140E-A ($r = 0.99$, $N = 5$). A weaker, but still significant, linear correlation was observed for site 140E-C ($r = 0.90$, $N = 5$). However, a better correlation coefficient ($r = 0.99$) was obtained when one value (measured on 19 July at 0712 LT) was excluded from the linear regression calculation.

In all instances, linear fits correlated better with the data than did the respective exponential correlation coefficients. A significant linear correlation was also

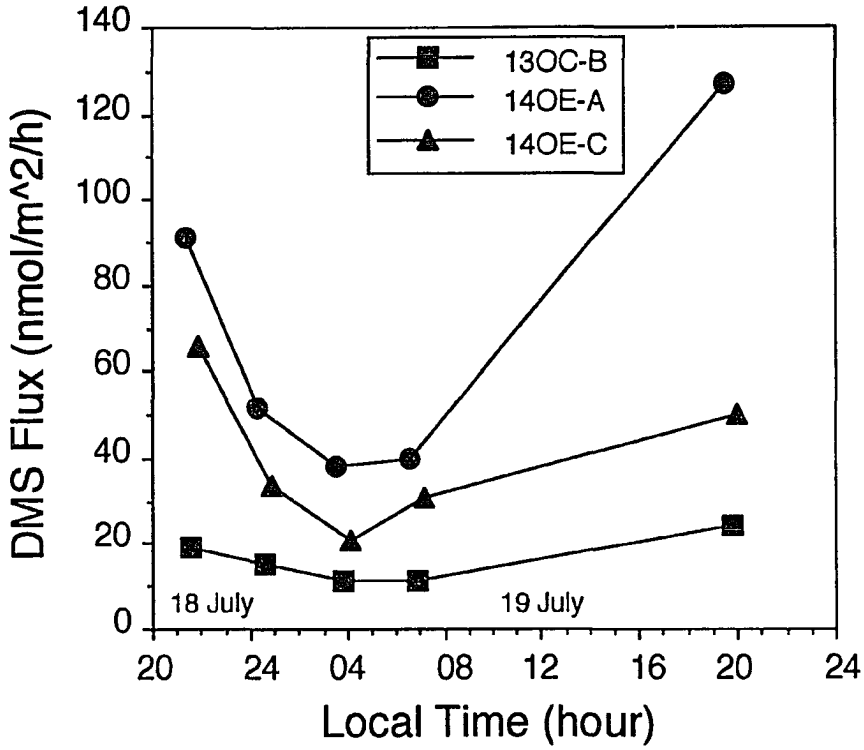

Figure 8. Diel variability of DMS fluxes at three sites in the oligotrophic area of Mire 239 (ELA). 13OC-B (control site); 14OE-A and 14OE-C (experimental sites).

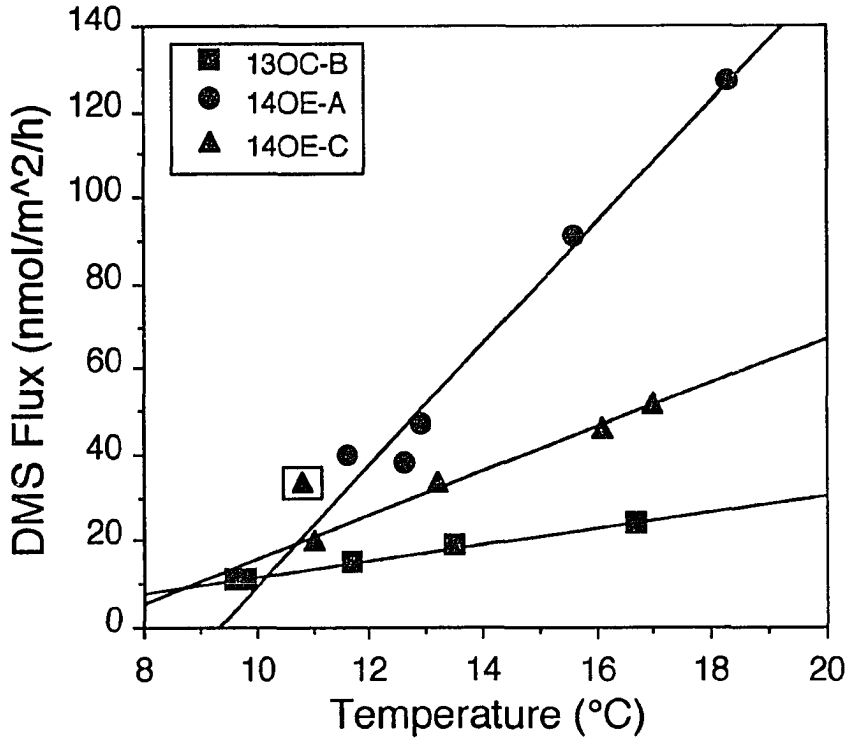

Figure 9. Regression of DMS fluxes vs. temperature of the *Sphagnum* mat at three sites in the oligotrophic area of Mire 239 (ELA). Temperature was measured 3-5 cm below the top of the *Sphagnum* mat. A flux value from site 14OE-C (within the square) was excluded from the regression.

found when data from the three sites were combined ($r = 0.72$, $N = 14$, $P<0.01$) (Figure 9). Others have reported that, over a larger range of temperature, emissions of VSCs from soils were related exponentially to temperature [Lamb et al., 1987; Goldan et al., 1987; Cooper et al., 1989]. The difference here may be due to my smaller temperature range, i.e., from 9°C to 19°C, and my smaller data set.

Table 3 lists the constants of the best linear least square fits of the data plotted on Figure 9. DMS fluxes normalized to 16°C (mean temperature of the *Sphagnum* mat during the study period) show a relatively large site-to-site (same physiographic zone) variability (Table 3), an indication that there are other environmental factors, besides temperature, which regulate DMS emissions from this mire.

3.1.3. Effects of Acidification on DMS Emissions

Because of the observed temperature dependence in DMS emission data, only DMS fluxes measured at temperatures between 15.0 and 18.0°C (*Sphagnum* mat temperature) were selected for comparisons of emissions occurring before and after acidification (Appendix A). I did not normalized the data to temperature because the equations in Table 3 indicated that the mathematical relationship between temperature and flux varied among sites. I also did not have diel data from all sites. Therefore, I chose to compare data that were collected at similar temperatures. Based on

TABLE 3. Constants for the best linear fit to the data derived from DMS fluxes in the oligotrophic zone and respective flux rates (F) normalized to 16°C - Mire 239 (ELA), 19-20 July

	$F(T) = a + bT$ (nmol m^{-2} h^{-1})		
Site	a	b	F(16°C)
13OC-B	-7.1	1.9	23
14OE-A	-132.7	14.2	95
14OE-C	-35.4	5.1	46
All combined	-73.5	8.5	63

T, Temperature (°C) of the *Sphagnum* mat.

equations in Table 3, DMS emissions at 18°C were less than 2-fold greater than at 15°C, so variations in flux that were greater than a factor of two were not due to temperature differences alone.

None of the sites studied exhibited an increase in DMS emissions immediately following acidification. Fluxes from the oligotrophic experimental area (sites 14OE-A and 14OE-C) were not significantly affected for the 24 hours; the mean emission rate prior to acidification, 72±10 nmol m^{-2} h^{-1}, was comparable to that after acidification, 75±13 nmol m^{-2} h^{-1}. In the minerotrophic experimental sites 12ME-A and 12ME-B, DMS fluxes were measured only once before and after acidification and fluxes actually decreased by more than a factor of two after acidification (Appendix A).

Table 4 summarizes DMS emissions from the experimental and control areas of the two major physiographic zones of the mire (data from before and after acidification). In the oligotrophic zone, DMS emissions were ~3-fold greater at the experimental area than at the control area, and significantly different to $P<0.01$. DMS emissions from the experimental and control areas of the minerotrophic zone could not be statistically treated due to insufficient data. However, they were nearly identical suggesting that acidification had no long term effect on DMS emissions from the minerotrophic region. These differences suggested that there might have been a long-term effect of acidification on the oligotrophic regions of the mire. It is interesting to

TABLE 4. Mean [±SE (N)] DMS fluxes, in nmol m^{-2} h^{-1}, from different physiographic zones of Mire 239 (ELA) - Only flux measured with *Sphagnum* mat temperatures between 15 and 18°C

	Experimental	Control
Minerotrophic	8±4(2)	8.5(1)
Oligotrophic	74±8(8)	22±3(4)

SE = $SD/N^{\frac{1}{2}}$.

note that the oligotrophic region of Mire 239 exhibited significantly higher fluxes of DMS than did the minerotrophic region. The oligotrophic experimental sites emitted ~10 times more DMS than all the minerotrophic sites.

3.1.4. Effects of Acidification on Dissolved VSCs

Prior to acidification, DMS was the most abundant VSC dissolved in the pore water at the top of the water table in Mire 239 (Table 5). Although few samples were collected, it appeared that before acidification DMS concentrations varied little throughout the mire. DMS concentrations were not substantially affected by acidification, except at the experimental area of the minerotrophic zone where DMS increased an order of magnitude following the acidification event.

MSH concentrations increased greatly after acidification in both the control and experimental areas of the oligotrophic zone (Table 5). MSH concentrations also increased in the minerotrophic zone but less than in the oligotrophic areas.

Although H_2S could not be quantified by my GC method, a large increase in the H_2S peaks was noticed after the acidification. Prior to acidification there were either traces of H_2S detected or no peaks were present at all. After acidification, broad peaks of H_2S were observed in the samples collected at all sites including the control. Like

TABLE 5. Surface (0-2 cm) pore water DMS and MSH concentrations (nM) and *p*H [±SE (N)] in Mire 239 (ELA)

	Oligotrophic		Minerotrophic	
	Experimental	Control	Experimental	Control
Before Acidification				
DMS	0.80±0.49(2)	0.75±0.38(4)	0.26 (1)	0.69 (1)
MSH	0.47±0.47(2)	0.28±0.14(3)	<0.2 (1)	0.68 (1)
*p*H	4.26±0.03(3)	4.22±0.06(5)	5.41±0.01(2)	5.02 (1)
After Acidification				
DMS	0.77±0.10(8)	0.68±0.16(7)	3.28±1.10(2)	0.31±0.08(2)
MSH	4.00±0.60(8)	2.29±0.33(7)	1.76±1.09(2)	1.52±0.76(2)
*p*H	4.20±0.03(8)	4.17±0.06(7)	4.74±0.16(2)	4.75±0.05(2)

SE = $SD/N^{\frac{1}{2}}$.
nd, not determined.

MSH, H_2S concentrations also increased in the control sites which were not acidified but received only lake water.

The *p*H of the waters at the surface of the water table decreased at all sites following the acidification event (Table 5). This was true even at the control sites which did not receive additional acid.

3.1.5. Dissolved VSCs in the Water Column in the Central Pool

Depth profiles of dissolved VSCs in the central pool waters were measured twice after the acidification event (20 and 22 July). The deepest sample was collected about 33 cm below the water surface, and about 7 cm beneath the bottom of the pool, i.e., in the interstices of the benthic peat. Dissolved DMS varied little with depth (Figure 4). MSH concentrations were lower than DMS and fairly uniform throughout the water column, except in the bottom peat, where concentrations were 35-fold greater than the average concentration in the overlying water (Figure 10). Although H_2S could not be quantified, like MSH, a very large H_2S peak was noted for the sample collected within the benthic peat of the central pool while the other pool samples exhibited very small or undetectable H_2S peaks.

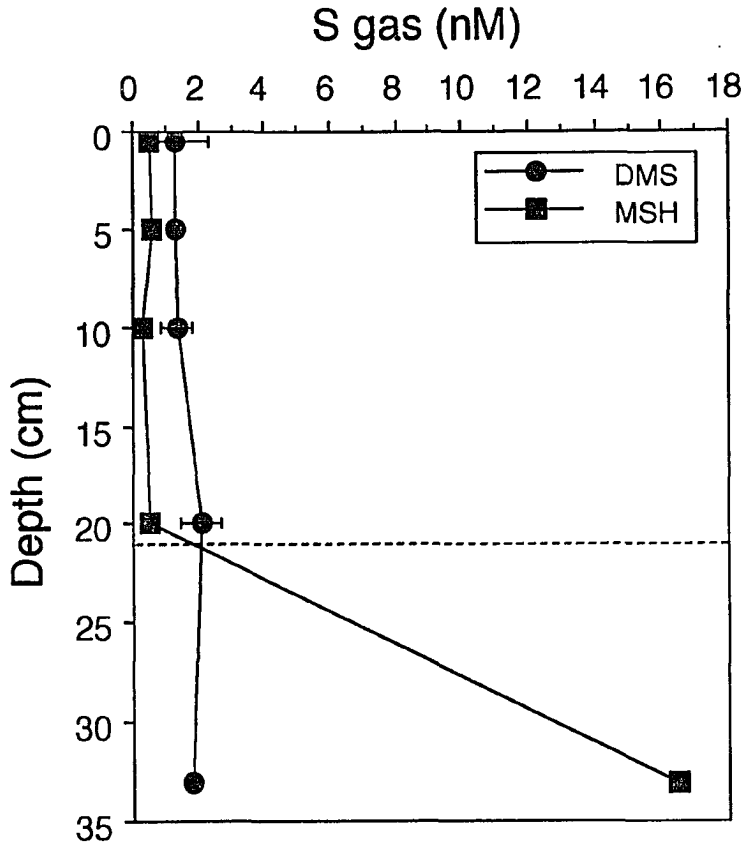

Figure 10. Vertical distribution of DMS and MSH in the oligotrophic central pool in Mire 239 (ELA). Dashed line is the interface water column/benthic peat. Dots without error bars represent one single sample, except for MSH at 20 cm depth, which error bar is very small to appear in the plot scale.

3.2. Sallie's Fen

3.2.1. Effects of Sulfate Addition on DMS and MSH Fluxes

Emissions of DMS and MSH from the surface of the experimental sites at Sallie's Fen were not affected by the addition of sulfate (Table 6). In the site covered by *Sphagnum*, DMS emissions did not vary significantly following the addition of sulfate. MSH emissions increased from undetectable levels, prior to sulfate addition, to 3.3 nmol m^{-2} h^{-1} in 24 hours following sulfate addition, and then decreased again to undetectable levels in the next 48 hours. In the bare site, emissions of both DMS and MSH were either undetectable or showed no temporal trend. These data agreed with those from Mire 239 (at the ELA) in that sulfate addition did not affect S gas fluxes in a period of a few days. However, these fluxes, in general, were much lower than those measured at several other locations in Sallie's Fen during a seasonal study [Chapter III].

3.2.2. Effects of Sulfate Addition on Dissolved DMS and MSH in the Peat Column

Although fluxes of VSCs were not significantly affected by the addition of sulfate, DMS and MSH concentrations in the top 10 cm of the peat column increased greatly following sulfate amendments (Figure 11). Prior to sulfate addition, DMS concentrations were <2 nM and <30 nM in the *Sphagnum* and bare sites, respectively. For 72 hours following the sulfate

TABLE 6. Flux of DMS and MSH (nmol m^{-2} h^{-1}) to the atmosphere in response to sulfate addition (13 August) in Sallie's Fen, Barrington (NH)

	Time (hours)			
	0*	24	48	72
Sphagnum Site				
DMS	7.8	10.1	10.2	10.9
MSH	<2.0	3.3	<2.0	<2.0
Bare Site				
DMS	2.2	<1.0	2.5	<1.0
MSH	<2.0	<2.0	<2.0	<2.0

* Measurement was performed prior to sulfate addition. After measurement 0.37 g of ammonium sulfate, dissolved in 900 mL of water, was spread over 900 cm^2 of both experimental sites.

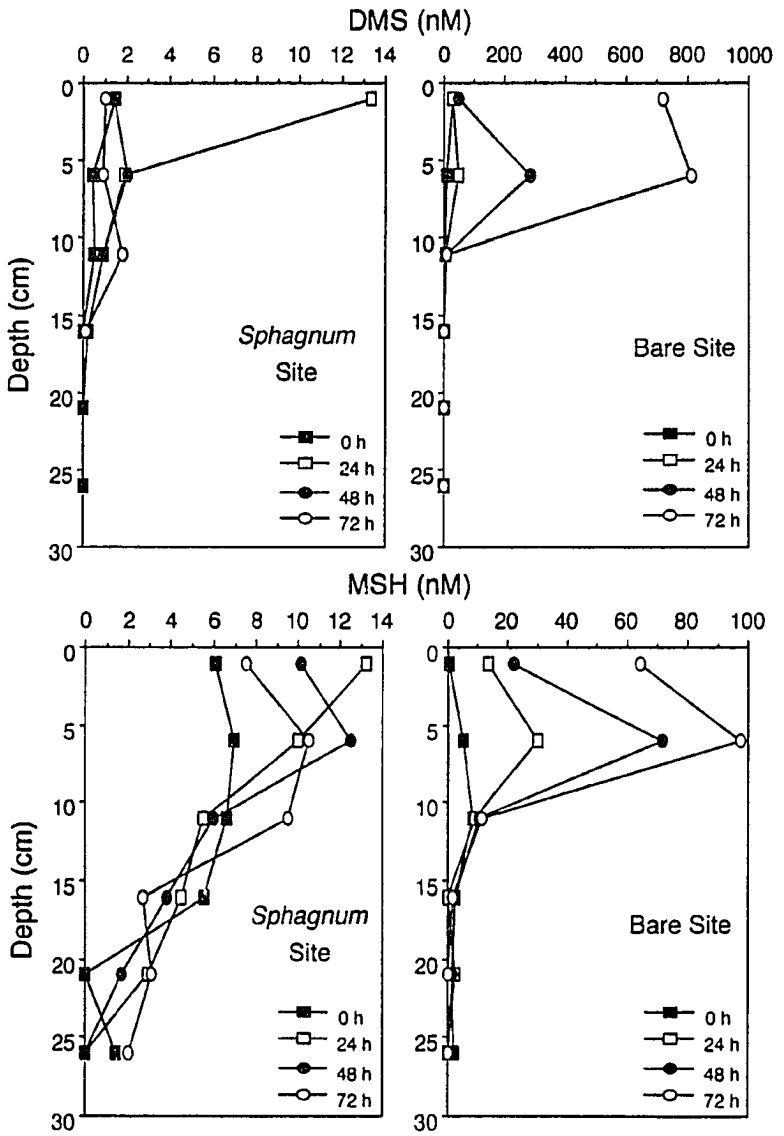

Figure 11. Concentrations of dissolved DMS and MSH in the peat profile of two adjacent experimental sites at Sallie's Fen, Barrington, NH, 13-16 August 1991. Depths were measured relative to the water table (about 4 cm below the peat surface). Numbers indicate time (hour) after sulfate addition. At time zero, measurement was performed prior to sulfate addition.

amendment, DMS concentrations at the bare site increased by 100 fold to >800 nM in the upper 10 cm. DMS concentrations at the *Sphagnum* site increased to only 13 nM for the first 24 hours in the upper 5 cm and then decreased again to previous levels during the next 24 hours.

MSH behaved similar to DMS. MSH concentrations were <9 nM in both the *Sphagnum* and bare sites prior to sulfate addition. Following the sulfate addition, MSH at the bare site increased more than 10 fold over 72 hours to nearly 100 nM in the upper 10 cm of the peat column. At the *Sphagnum* site, there was a 2-fold increase in MSH during the first 24 to 48 hours after the sulfate addition, followed by a decrease.

4. DISCUSSION

Previous studies of VSCs in high latitude aquatic environments have estimated fluxes using the concentrations of dissolved VSCs to and stagnant-film model of gas transfer across the water-air interface. The present study utilized direct flux measurements with enclosures. Richards et al. [1991] measured VSCs in ELA lakes and in the central pool of Mire 239. Direct DMS fluxes from Mire 239 were higher than those estimated by Richards et al. [1991] for the lakes at the ELA (16-24 nmol m^{-2} h^{-1}), except Lake 114 (104 nmol m^{-2} h^{-1}), which was experimentally acidified. My VSC data for

the central pool at Mire 239 were at the low end of the range of values reported by Richards et al. [1991]. Therefore, it is possible that the VSC concentrations, and the fluxes to the atmosphere, in Mire 239 were at a minimum level during the short period that my measurements were made.

Fluxes of DMS in Mire 239 were higher than emissions from Lakes Superior, Erie and Ontario (4.6-12.5 nmol m^{-2} h^{-1} [Nriagu and Holdway, 1989]) and from freshwater tundra habitats, including *Sphagnum*-dominated sites (0-10 nmol m^{-2} h^{-1} [Hines and Morrison, 1992]). Nevertheless, fluxes were lower than the mean flux from several acid-rain impacted freshwater wetlands in northern Ontario (290 nmol m^{-2} h^{-1}, [Nriagu et al., 1987]) and the global oceanic flux of 190-530 nmol m^{-2} h^{-1}, [Andreae, 1990].

4.1. Short Term Changes in VSCs in Response to Additions of Inorganic Sulfur

The fact that DMS fluxes from acidified areas did not increase after the acidification event, relative to controls, demonstrated that fluxes from *Sphagnum* peatlands do not increase quickly following a pulse of S deposition. Bayley et al. [1987] reported that dissolved sulfide increased greatly in the pore waters of Mire 239 after acidification with sulfuric acid. I noted a similar response in the present study. The data of Bayley et al. [1987] prompted us to investigate whether DMS emissions also

responded quickly to increases in S deposition, and my data indicated that this is not the case. Site 13OC was a necessary control for the present experiment because it had been receiving sulfuric acid similarly to the other sites in the oligotrophic experimental area of the mire. It is likely that short term responses of a system to a pulse of S are affected by the S deposition history. Hence, the lack of a significant response in S fluxes at sites 14OE-A and 14OE-C relative to site 13OC demonstrated that even sites exposed to chronic S deposition do not exhibit a short term emission response to individual S inputs.

It was interesting that pore waters at both Mire 239 and Sallie's Fen showed a short term response to S additions while fluxes, in both cases, did not. At Mire 239 I did not note an increase in dissolved DMS levels except perhaps in the minerotrophic experimental site. At Sallie's Fen there was an ephemeral appearance of DMS near the peat surface and concentrations decreased to prior levels 48 hours after the addition of sulfate. Pore water DMS samples at Mire 239 were collected later than 24 hours after the acid treatment. Therefore, it was possible that DMS levels increased after acidification but decreased again before water samples were collected. Dissolved MSH concentrations increased after the acid treatment at both Mire 239 and Sallie's Fen. Although maximum MSH levels in Sallie's Fen occurred after 24 hours, concentrations remained elevated for 72 hours. My finding that dissolved MSH concentrations increased greatly at Mire

239, while DMS did not, may simply be due to the fact that elevated MSH levels took longer to dissipate than did DMS.

Dissolved DMS and MSH concentrations in the bare peat at Sallie's Fen increased throughout the duration of the experiment (72 hours) to levels which were 10-100 times those in the *Sphagnum*-inhabited site. It appeared that the presence of *Sphagnum* greatly attenuated the accumulation of these compounds within the pore water. It was not clear how *Sphagnum* caused this decrease in VSC accumulation. Possible explanation include: *1)* removal of dissolved sulfate by *Sphagnum* prior to VSC production; *2)* increase in VSC oxidation; *3)* inhibition of VSC production; and/or *4)* enhancement of VSC exchange with the atmosphere. Although the fluxes of VSCs were small during the Sallie's Fen experiment, DMS emissions were much higher in the *Sphagnum*-inhabited site than in the adjacent bare site despite the high concentrations of dissolved DMS in the former. However, the higher DMS fluxes in the *Sphagnum*-inhabited site accounted for less than 1% of the DMS flux to the atmosphere required to explain the difference in dissolved DMS between the bare and *Sphagnum* sites. Therefore, the occurrence of *Sphagnum* must have influenced other aspects of the biogeochemistry of VSC besides gaseous loss.

In Mire 239, the increase in dissolved MSH and H_2S occurred in the unacidified controls as well as in the acidified plots. Bayley et al. [1987] noted an increase in dissolved sulfide in the experimental sites but not in the

controls. During the present experiment, it rained heavily prior to the artificial acidification. It is possible that rain was responsible for stimulating the production of VSCs. Bayley (personal observation) noted that dissolved H_2S in Mire 239 increased after rainfall in the control sites. The average rate of wet sulfate deposition at the ELA is ~30 μmol m^{-2} d^{-1} [Sirois and Barrie, 1988]. Assuming that this sulfate was totally reduced to sulfide in the top 10 cm of the water table and minimal H_2S removal took place, the calculated concentration of dissolved H_2S in the surficial pore water would have been ~3μM. Since it had not rained for several days prior to this rainfall, the total S deposited was probably greater than the summer average. Since dissolved sulfide has been shown to be a precursor of MSH and DMS [Drotar et al., 1987a,b; Finster et al., 1990], it follows that rainfall events could be responsible for increasing the accumulation of these gases in mire pore waters. Application of Roddy Lake water did not contribute to the increase of H_2S since the load of sulfate from this source was negligible relative to rainfall [Bayley et al., 1986; Bayley et al., 1987].

4.2. Long Term Changes in VSCs in Response to Additions of Inorganic Sulfur

Insufficient data were obtained to determine a long-term effect of S deposition on S emissions. The 3-fold difference in DMS fluxes between the experimental and the

control areas of the oligotrophic zone could, conceivably, be attributed to the chronic S input in the experimental section of Mire 239. This supports the hypothesis of Nriagu et al. [1987] that anthropogenic S, deposited in wetlands areas, is re-emitted as biogenic S. However, the oligotrophic areas of Mire 239 emitted more VSCs than did the minerotrophic regions. Even though the oligotrophic area was divided between the experimental and control sections, the oligotrophic experimental area, which was located in the center of the mire, was largely devoid of trees and was dominated by short vegetation, primarily *Sphagnum*. Therefore, the vegetation distributions demonstrated that the oligotrophic experimental sites were more oligotrophic than the oligotrophic control sites. Hence, it appeared that the difference between DMS emissions from the control and the experimental sites was more a function of the trophic status of the sites than it was the deposition of additional sulfate. However, emissions were only measured at a few small sites in a large wetland. Considerably more spatial data are needed to determine a long-term response to S addition.

It is surprising that the minerotrophic areas of Mire 239 would emit less gaseous S than the oligotrophic areas. This is certainly not the case for other biogenic gases like methane which exhibit largest fluxes from nutrient-rich areas [Crill et al., 1988; Williams and Crawford, 1984]. However, S fluxes are probably a function of the S needs of

the vegetation in relation to limitations by other nutrients. It is likely that oligotrophic regions of wetlands, that exhibit restricted growth due to nutrient limitation, would not require large amounts of S. This would result in increased availability of S relative to other nutrients and would increase the potential for S transformation into VSCs. Therefore, relative to carbon, I propose that oligotrophic areas of wetlands would be more likely to produce VSCs than mineral-rich areas where S would be sequestered by living biomass.

4.3. Sources of Methylated S Compounds in *Sphagnum* Peatlands

Richards [1992] incubated freshwater lake sediments with radiolabelled sulfate and observed that it stimulated production of organic S compounds. However, she did not note the production of VSCs during these experiments, only the production of compounds that yielded VSCs upon treatment with alkali. My experiments yielded different results since I observed VSCs directly upon the addition of inorganic S. I did not search for the production of VSC precursors, but my results indicated that VSCs are produced rapidly upon the addition of inorganic S to *Sphagnum* peatlands. My finding that peat sites, which are devoid of *Sphagnum*, produced large quantities of VSCs, supports the notion that depositional organic-rich habitats are strong producers of VSCs.

Although I was not able to measure H_2S directly, my data suggested that H_2S was a significant precursor of VSCs in *Sphagnum*-dominated wetlands. Drotar et al. [1987a,b] provided evidence that several heterotrophic bacteria isolated from terrestrial and marine environments were able to produce MSH by enzymatically methylating H_2S. Finster et al. [1990] observed that MSH and DMS were produced anaerobically in marine and fresh water sediments during microbial decomposition of methoxylated aromatic compounds (lignin-forming compounds) in the presence of inorganic sulfide. Lignin is a constituent of the cell walls of vascular plants. However, aromatic polymers (lignin-like compounds) are also present in cell walls of bryophytes, including *Sphagnum* spp., although it is controversial whether or not these polymers should be designated lignin [Hébant, 1977]. Hence, sulfide-linked demethoxylation could be a process regulating formation of volatile methylated S compounds in *Sphagnum*-dominated peatlands. Further investigations are needed to determine the significance of other possible sources of methylated S compounds in *Sphagnum* peatlands, such as microbial degradation S-containing amino acids, which seems to be an important source of VSCs in other natural environments [Segal and Starkey, 1969; Zinder and Brock, 1978; Kiene and Visscher, 1987]. *Sphagnum* mosses have some characteristics that are favorable to the formation of methylated S compounds through degradation of S-containing amino acids, e.g., the plant holds significant

amount of S and recycles S fairly rapidly [Urban et al., 1989]. However, the relatively rapid accumulation of VSCs at the bare site in Sallie's Fen must have been due to reduction of sulfate to sulfide, followed by the production of organo-S compounds, since sulfate was added to the plots and large amounts of VSCs were produced.

It was interesting that DMS dominated fluxes even though MSH was abundant in pore waters in many instances. It is possible that MSH was converted to DMS by methylation reaction [Drotar et al., 1987a; Finster et al., 1990] or that MSH was preferentially metabolized to CH_4, CO_2 and H_2S in the top layers of the peat by sulfate-reducing and/or methane-producing bacteria [Kiene and Visscher, 1987]. Microbiological processes affecting these VSCs deserve attention in the future.

4.4. A Potential Factor Controlling S Emissions in *Sphagnum* Peatlands

The accumulation of VSCs in peat indicated that *Sphagnum* is not the direct source of VSCs released from these peatlands, but that these gases are produced in the peat below the photosynthetically-active mosses. This differs from wetlands like salt marshes where DMS can be derived primarily from the leaves of certain grasses [de Mello et al., 1987; Dacey et al., 1987]. I have already shown here that *Sphagnum* exerts a strong influence on the accumulation of VSCs in peat, and that the presence of these

mosses enhances gaseous efflux of DMS. The enhancement in emissions by *Sphagnum* can also be examined by comparing my direct flux measurements with those calculated using dissolved DMS data.

A hypothetical DMS emission rate from Mire 239 was calculated using a stagnant-film model of gas transfer across an water-air interface [Broecker and Peng, 1974; Liss and Slater, 1974]. Assuming that the surface of the water table was directly exposed to the atmosphere and that the atmospheric DMS mixing ratio is negligible compared to pore water concentrations, emission rates were estimated as the product of the concentration of DMS in the pore water and the gas transfer coefficient (piston velocity). The latter, 3.3 cm h^{-1}, was computed for a wind speed of 2.7 m s^{-1} (average at ELA in July), based on the least-square equation from Upstill-Goddard et al. [1990] applied to wind speeds ranging ~2 to 9.5 m s^{-1}. The mean concentration of dissolved DMS in Mire 239 was 0.69±0.21 nM (samples collected before acidification) which yielded a flux of 23 nmol m^{-2} h^{-1}. This is ~1.8 times lower than the overall mean DMS emission rate measured with the dynamic enclosures. Comparisons between static and dynamic enclosures indicated that S-free sweep air did not stimulated DMS emissions from these peatlands [Chapter I]. Since the wind speed inside the enclosure was almost zero, calculated emissions should have been lower, which makes the discrepancy between the calculated and the measured fluxes even larger. In addition, this becomes

larger still when pore water and flux data from the oligotrophic experimental sites are used, since these sites exhibited the highest fluxes. This suggested that there must be mechanisms controlling transport of DMS from this peatland other than direct transfer from the peat surface to the air.

One hypothesis to explain the discrepancy between the calculated and the measured DMS fluxes is that *Sphagnum* mosses enhance gas emissions from the peat surface to the atmosphere. *Sphagnum* spp. have external capillary conducting structures (hyaline cells) which allow the transport of water to the outermost parts of the plant to balance evaporation [Proctor, 1979]. This results in an increased surface area of water exposed to the atmosphere per area of peatland, and possibly, accounts for the increased DMS emission within enclosures. If this morphological property of *Sphagnum* enhances the efflux of DMS, then biomass of *Sphagnum* and wind speed must contribute to these processes as well, suggesting that DMS emissions from *Sphagnum* might be even higher than what was measured using enclosures. The oligotrophic experimental sites, where highest DMS fluxes occurred, were dominated by *Sphagnum* and contained the lowest biomass of higher plants for the entire mire. These sites also exhibited the largest difference between measured and calculated fluxes. On the other hand, the minerotrophic sites (which have the most vascular plants) yielded measured fluxes which were less than those calculated from pore water

data. This suggests that a higher percentage of DMS was removed from these sites before escaping to the atmosphere compared to the oligotrophic sites. Therefore, it suggests that *Sphagnum* abundance and/or dominance was important in regulating the flux of DMS from these wetlands, and that data of dissolved gas alone are insufficient for estimating fluxes of DMS from vegetated regions of northern peatlands.

5. SUMMARY

DMS was the dominant VSC released from the boreal *Sphagnum*-dominated poor fen at ELA, Mire 239. DMS emissions varied largely with time and space. Temperature controlled diel variability in DMS emissions, with maximum fluxes occurring in the afternoon and minimum before dawn. DMS emissions were not affected by either acidification with sulfuric acid (Mire 239) or sulfate addition (Sallie's Fen) in a period of hours to a few days. However, both these treatments stimulated DMS and MSH production in the anoxic surficial regions of the peat column. Differences in DMS emissions between the two major physiographic zones of Mire 239, and their respective experimental and control areas, could be due to a combination of three major factors: vegetation, mineral status and S input. DMS emission determined using S-free flow-through enclosures were higher than that calculated by a stagnant-film model, suggesting

that the *Sphagnum* might play a role in regulating DMS emissions to the atmosphere.

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CHAPTER III

Environmental Factors Controlling Fluxes of Dimethyl Sulfide in a New Hampshire Fen

ABSTRACT

The major environmental factor controlling fluxes of DMS in a *Sphagnum*-dominated peatland were investigated in a poor fen in New Hampshire. DMS emissions from the surface of the peatland varied greatly over 24 hours and seasonally. Maximum DMS emissions occurred in summer with minima in the late fall. Temperature seemed to be the major environmental factor controlling these variabilities. There was also some evidence that that changes in water table height might have contributed to the seasonal variability in DMS emission. The influence of the water table was greater during periods of elevated temperature. DMS and MSH were the most abundant dissolved volatile sulfur compound (VSC) in the surface of the water table. Concentrations of dissolved VSCs varied with time and space throughout the fen. Dissolved DMS, MSH and OCS in the surface of the water table were supersaturated with respect to their concentrations in the atmosphere suggesting that the peat surface was a source of VSCs in the peatland. VCS in peatlands seemed to be produced primarily by microbial processes in the anoxic surface layers of the peat rich in organic matter and inorganic sulfide. *Sphagnum* mosses did not appear to be a direct source of VSCs, however they increase transport of DMS from the peat surface to the atmosphere.

1. INTRODUCTION

Short-lived volatile sulfur compounds (VSCs) emitted from freshwater wetlands in North America could be potentially important in regional atmospheric S cycling. Freshwater wetlands cover large areas of North America, Europe and Asia, in the region between 40-70°N [Matthews and Fung, 1987], and the magnitude of their S fluxes can be as rapid as those from the oceans [Nriagu et al., 1987; Chapter II]. Moreover, on all continents, a considerable part of these ecosystems are susceptible to the influence of atmospheric S input derived from industrial sources. Nriagu et al. [1987] suggested that emissions of dimethyl sulfide (DMS) from boreal wetlands receiving elevated atmospheric S input might give rise to approximately 30% of the atmospheric S burden in remote areas of Canada and that re-emission of anthropogenic S from natural environments could contribute in the continuing acidification of the environment. Based on the methanesulfonic acid (MSA) to sulfate ratios, Barrie et al. [1992] suggested that 3-18% of the sulfate in air of a remote area in Canada originated from DMS emitted from Canadian wetlands and from pulp mills along Lake Superior.

DMS is the major biogenic volatile organo-S compound released to the atmosphere from high productivity oceanic areas. Oceanic DMS has been studied in terms of its

production/consumption [Kiene, 1992] and loss to the atmosphere [Andreae, 1990]. However, relatively little is known of the factors that control emissions of DMS from continental habitats. Environmental variables controlling fluxes of DMS and other VSCs in coastal environments have been well-documented [e.g., Steudler and Peterson, 1986; Aneja, 1986; Carroll et al., 1986; Cooper et al., 1987a,b; de Mello et al., 1987; Dacey et al., 1987; Kiene, 1988; Cooper et al., 1989; Morrison and Hines, 1992]. High fluxes of DMS from salt marshes are restricted to areas which are inhabited by grasses (*Spartina alterniflora*) that produce the osmoregulant dimethylsulfoniopropionate (DMSP) [de Mello et al., 1987; Dacey et al., 1987; Hines and Morrison, 1990]. However, much less information is available on controls on emissions of DMS from freshwater wetlands despite the fact that these habitats occupy a large percentage of high latitude terrestrial environments. Temperature is a strong determinant which regulates diel and annual emissions of DMS from terrestrial environments [de Mello et al., 1987; Cooper et al., 1987b; Steudler and Peterson, 1985]. However, one would expect that other factors, such as controls on microbially-mediated decomposition processes, the degree of anoxia within a habitat, variations in vegetation type, and the rate of supply of S would also exert control on the magnitude of DMS fluxes.

The primary objective of this investigation was to identify the major environmental factors controlling fluxes

of DMS in a *Sphagnum*-dominated fen in New Hampshire. Although I have focused on the investigation of fluxes of DMS, which has been shown to be the dominant VSC emitted from *Sphagnum* peatlands [Chapters I and III], I also examined the spatial and temporal distributions of dissolved MSH, OCS and CS_2 in surficial waters throughout the fen.

2. METHODS

2.1. Study Area

This investigation was conducted in Sallie's Fen (1.7 ha area), in Barrington, NH (43°12'N, 71°04'W). The elevation of the fen is approximately 110 m. The peat thickness averages ~1.7 m, although it reaches more than 4 m in the center. The surface geology surrounding the fen is typically a glacial till with no bedrock exposure.

The closest meteorological station is in Durham (NH) which is approximately 15 km southeast of Sallie's Fen. The 30-years normal (1951-1980) mean annual precipitation in Durham is 1100 mm, with minima in June and July (75 mm/month) and maxima in November (120 mm). The 30-year normal monthly average temperature varies from -5°C (January) to 21°C (July), and is below 0°C from December to February; the mean annual temperature is 8.3°C [NOAA, 1982].

In Sallie's Fen, water is supplied by direct rainfall, surface runoff and seepage from the surrounding catchment, and from two ephemeral streams located in the northern and

southern margins of the fen (Figure 12). More water entered from the northern inlet stream. The southern inlet stream was more stagnant with algae found growing in puddles. The fen drained through an ephemeral stream. The water table was normally above the peat surface (referred as the brown layer underneath the living *Sphagnum* mosses) in the early spring and late fall, but it was below the peat surface during summer.

The dominant hummock-forming *Sphagnum* species over the fen were *S. magellanicum* and *S. capillifolium*. Hollows were predominantly occupied by *S. fallax*, but also *S. papillosum* and *S. cuspidatum* were found growing at and below the water level. There was a gradual increase in the abundance of *S. fallax* toward the northern part of the fen, and a decrease of *S. magellanicum*. *S. squarrosum* was sparsely present in shaded areas of the lagg and often submerged. Juniper moss [*Polytrichum juniperinum* var. *affine* (Funck) Brid.] was found occasionally associated with *Sphagnum* at the top of old hummocks. The ground level vascular component of the flora was dominated by leather-leaf (*Chamaedaphne calyculata*) and sedges (mainly *Carex rostrata*). The population of *Carex* spp. in the fen increased northward. Cat-tail (*Typha latifolia*) was present in a small area, between the boardwalk and the southern inlet (Figure 12). A few white pines (*Pinus strobus*) and black spruces (*Picea mariana*) were found in the southern-central part of the fen. The upland area was dominated by eastern hemlock (*Tsuga*

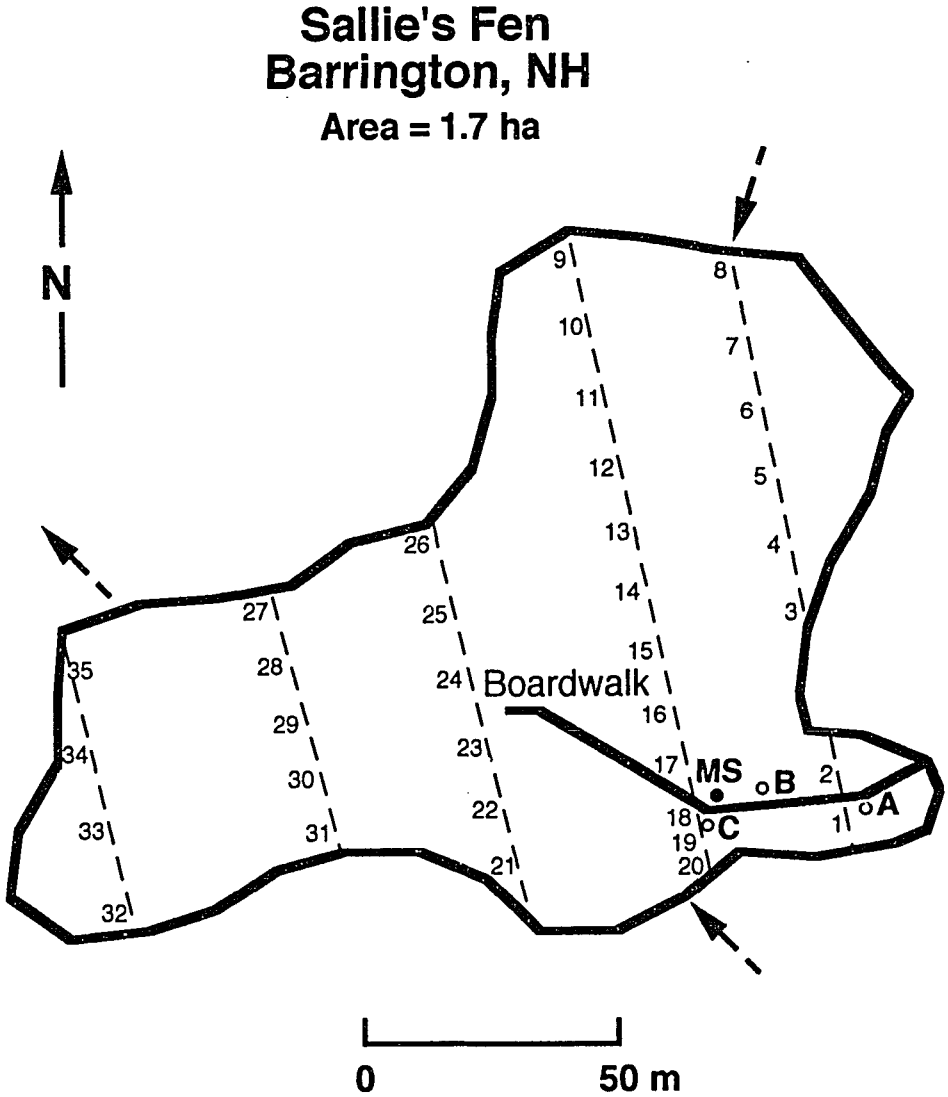

Figure 12. Sallie's Fen, Barrington, NH (43°12'N, 71°04'W). Arrows point out inlet and outlet streams (ephemeral). MS is a micro-meteorological station. A, B and C are sites where fluxes of VSCs were monitored between 1989-1991. Dashed lines depict locations of transects used for determining distribution of dissolved VSCs in the surface waters of the fen. Numbers (1 to 35) indicate sites where water samples were collected.

canadensis), white pine (*Pinus strobus*), red maple (*Acer rubrum*), sugar maple (*Acer saccharum*) and white birch (*Betula papyrifera*).

An elevated boardwalk allowed access to the central part of the bog from its southeastern margin. The first unit of the boardwalk (49 m length), which ends at the micro-meteorological station, was built in the early summer of 1989 and a second unit (39 m) in late summer of 1991. Herein, for purposes of reference, these units will be referred as the old and new boardwalks, respectively.

Water table height was monitored in five wells (supported by PVC perforated tubes) distributed along the old boardwalk between 13.5 and 45.5 m from the margin. Measurements (by meter stick) reported here were made relative to the peat surface.

2.2. Flux Measurements

Dynamic enclosures were used to measure fluxes of VSCs [Morrison and Hines, 1990; Hines and Morrison, 1992]. Flux measurements were normally made between 1200 and 1400 local time (LT). Enclosures were placed on collars and flushed with S-free synthetic air (Liquid Carbonic, Specialty Gas Corp., Chicago, IL) through a 0.64 cm OD FEP Teflon tube, at 3 L min^{-1} for 1-1½ hours before samples were collected. Enclosures were shaded during daylight measurements. Either two or three replicate samples of ~500 mL were drawn from within enclosures at 150 mL min^{-1}. Flow rates and sample

volume were determined by a mass flow controller/integrator system. Sulfur gases were cryogenically trapped in Teflon loops (0.32 cm OD x 60 cm length), filled with Teflon wool, immersed in liquid argon. Excessive moisture was removed by a FEP Teflon drier held between the enclosure and the trapping system. Samples were transported to the laboratory and analyzed within 5 hours after collection.

Temperature was measured in air (~1 m above the ground in the shade) and below the surface (~5 cm) of the *Sphagnum* mat.

2.3. Collection of Water Samples and Extraction of VSCs

Surficial waters were collected between 0-2 cm below the surface of the water table using glass syringes (20 mL). In drier sites, samples were taken through a 0.32 cm OD FEP Teflon tube (connected to syringes by a three-way stop cock), which was inserted through the peat surface until water table was reached. Syringes were rinsed with samples at least three times before collection. After collection, samples were immediately stored in a cooler. Surface water temperature was measured during sample collection.

In the laboratory, aliquots of the water samples (5 mL) were transferred to a 10 mL glass stripper (Alltech Associates, Deerfield, IL), sparged with ultrapure He (Liquid Carbonic, Specialty Gas Corp., Chicago, IL), at 40 mL min^{-1} for 5 minutes. S gases were trapped in a 0.32 cm OD Teflon loop, partially filled with Teflon wool, held in

liquid Ar. After extraction, the cold trap was quickly heated in hot water and S gases transferred to the gas chromatograph (GC).

Measurements of *p*H were performed in a sample aliquot using an Orion Research 399A *p*H meter with a precision of ±0.02 *p*H units.

2.4. Analysis of Sulfur Gases

Cryogenically-collected samples were analyzed using a Shimadzu gas chromatograph (GC) equipped with a 60/80 Carbopack B (1.5% XE-60/1% H_3PO_5) column (1.8 m length x 0.32 cm OD) (Supelco) connected to a flame photometric detector (FPD) [Morrison and Hines, 1990]. The oven temperature was programmed to increase at 30°C min^{-1} from 40°C (held for 1 min) to 90°C (held for 4 min). Detector sensitivity was enhanced by doping the flame with S from a CS_2 permeation tube installed in the H_2 fuel line. Peak areas were measured using a Shimadzu C-R34 integrator. The GC was calibrated by diluting known amounts of S gases from permeation tubes (VICI Metronics, Santa Clara, CA) in a He stream. The detection limit under these conditions ranged from 0.3 to 0.6 pmol S. For typical volumes of air (500 mL) and water (5 mL) analyzed, the detection limits were 1-2 nmol m^{-2} h^{-1} for flux and 0.1-0.2 nM for concentration in water. The precision for S fluxes and concentration in water were approximately ±10% and ±2% (standard deviation expressed as a percentage of the mean), respectively, based

on replicate analysis of air samples from the dynamic enclosure and from a single water sample.

2.5. Research Approach

2.5.1. Long Term Variability of Fluxes of VSCs.

Seasonal and annual trends of fluxes of VSCs were investigated simultaneously at three sites (A, B and C) distributed along the old boardwalk (Figure 12). Flux measurements of VSCs at Sallie's Fen began in 1989 at site B and at two other sites, adjacent to sites A and C, which will be referred to as sites A' and C'. Measurements were performed about every two weeks from July to September 1989, from June to November 1990 and from May to November 1991. The dominant vegetation within collars at each of these three sites is summarized in Table 7.

2.5.2. Diel Variability in Fluxes of VSCs.

Short-term (diel scale) temporal variability on fluxes of VSCs was investigated between 24 and 25 September 1991. Fluxes of VSCs were measured hourly over a 24-hour period. This information was required since investigations of seasonal and annual trends in fluxes of VSCs were always performed during daylight.

2.5.3. Spatial Variability of Fluxes of VSCs.

In early September 1991, nine more collars were installed along

TABLE 7. Dominant vegetation within collars, Sallie's Fen, NH

Site	Vegetation*
1	None W
A	*Sphagnum capillifolium*
3	*S. capillifolium*
4	*S. fallax*
B	*S. recurvum*
	S. magellanicum
6	*Chamaedaphne calyculata*
	Polytrichum juniperinum var. *affine*
C	*S. magellanicum*
	S. recurvum
	Carex rostrata
8	*S. magellanicum*
9	*S. papillosum*
10	*S. magellanicum*
11	*S. magellanicum*
	S. recurvum
12	*S. magellanicum*

* Identification made in July 1992

W Standing water

the old and new boardwalks. They where designated by numbers from 1 to 12, in increasing order from the margin toward the center of the fen. In this sequence, sites A, B and C corresponded to numbers 2, 5 and 7. From 11 to 19 September 1991, fluxes of VSCs were measured at the twelve sites. Water samples were also collected for measurements of dissolved VSCs and *p*H.

2.5.4. Spatial and Temporal Distribution of Dissolved VSCs Throughout the Fen Surface. Distribution of dissolved VSCs in surface and pore waters of the fen was investigated in the late spring (28-29 May), summer (27-28 August) and fall (5-6 November) of 1991. Samples (N = 35 total) were collected every ~15 m at five transects (Figure 1). Sampling time was usually between 0900 and 1100 local time (LT). Samples were always collected at the same sites which were marked by numbered flags. Waterlogged sites comprised lagg (all around the fen perimeter) and small puddles (wet hollows). The latter were mostly found in the northern and in the far eastern areas of the fen.

3. RESULTS

3.1. Seasonal and Annual Variability in DMS Emissions

Dimethyl sulfide was the most significant organic VSC released from the surface of sites A, B and C. In these

three sites, methane thiol (MSH) and carbon disulfide (CS_2) were always undetectable, i.e., fluxes <1.0 nmol m^{-2} h^{-1}. Although carbonyl sulfide (OCS) emissions have been determined in this fen using my dynamic enclosure technique, my measurements using static enclosures have determined that OCS is consumed [Chapter I].

DMS fluxes were variable over the year, with maximum emissions occurring between late June and August (Figure 13, top). This seasonal variability was rather irregular and exhibited some episodic discontinuities, which followed temperature variability (Figure 13, middle). Site-to-site variability in DMS fluxes was high. Highest fluxes were usually found at site B. Sites A' and A had the lowest DMS fluxes in 1989 and 1990, respectively, and site C the lowest fluxes in 1991.

Annual variability in DMS fluxes was also quite high (Figure 13). In 1989, maximum mean DMS flux was as high as 1080 nmol m^{-2} h^{-1}, while maxima in 1990 and 1991 were ~4 and ~7 times lower than in 1989, respectively. In 1989, only air temperature was measured and the relationship with DMS fluxes at sites A', B and C' was poor, i.e., not significant to $P<0.05$ ($r = 0.86$, $N = 5$; $r = 0.75$, $N = 6$; $r = 0.83$, $N = 5$). The small number of samples could be responsible for the poor correlation. More data were collected in 1990 and 1991, which were more appropriate for statistical analysis. Best fits for the relationship between DMS fluxes and temperature (*Sphagnum* mat), and respective regression equations, in 1990

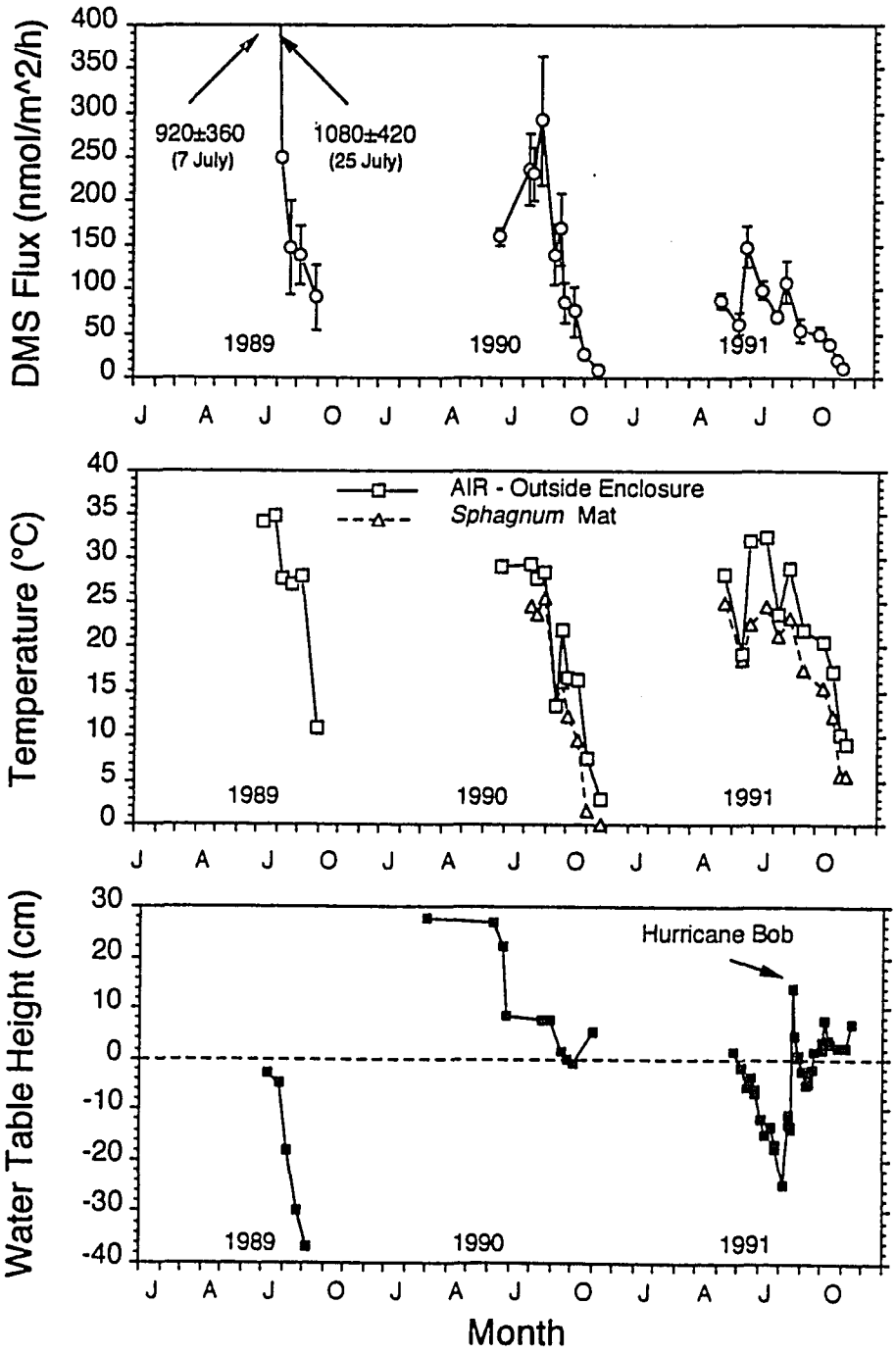

Figure 13. Seasonal patterns in DMS fluxes, temperature and water table. DMS fluxes were averaged over three sites (A, B and C); vertical lines represent the standard errors of the means. Temperature were measured during flux measurements. Water table height were averaged over five wells (SD = ±2 cm). The water table height is relative to the peat surface.

and 1991 are shown in Figure 14. In all instances the relationships were significant to $P<0.001$ (2-tailed test).

Variations in water table did not exhibit a consistent annual pattern between 1989 and 1991 (Figure 13, bottom). In 1990 a new beaver dam caused a major alteration in the normal annual water table pattern. At the end of the spring of 1990, the water level was almost 30 cm above the peat surface, and decreased twice during the course of that summer when the dam was lowered. On 19 August 1991, Hurricane Bob passed very close to New Hampshire bringing 170 mm of rainfall in Durham (78% on 19th and 22% on 20-21st September). In Sallie's Fen, during the hurricane the water table increased several centimeters, which took ~10 days to decrease to the level of the peat surface.

In September, 1991 the water table was not as low as it was in 1989. This was caused by both the incomplete removal of the beaver dam and an unusual large ground water input from the surrounding upland due to the hurricane. In spite of these large occasional variabilities on the water table, there were no indications of a major direct effect on DMS fluxes. Figure 10 displays averaged DMS fluxes (sites A, B and C) plotted as a function of water table height. Results showed that when the water table was above the peat surface DMS fluxes were did not exhibit any trend (scattered). On the other hand, when the water table was below the peat surface, increase in its height lead to increased fluxes. In 1989, an apparent normal year with regard to the hydrology

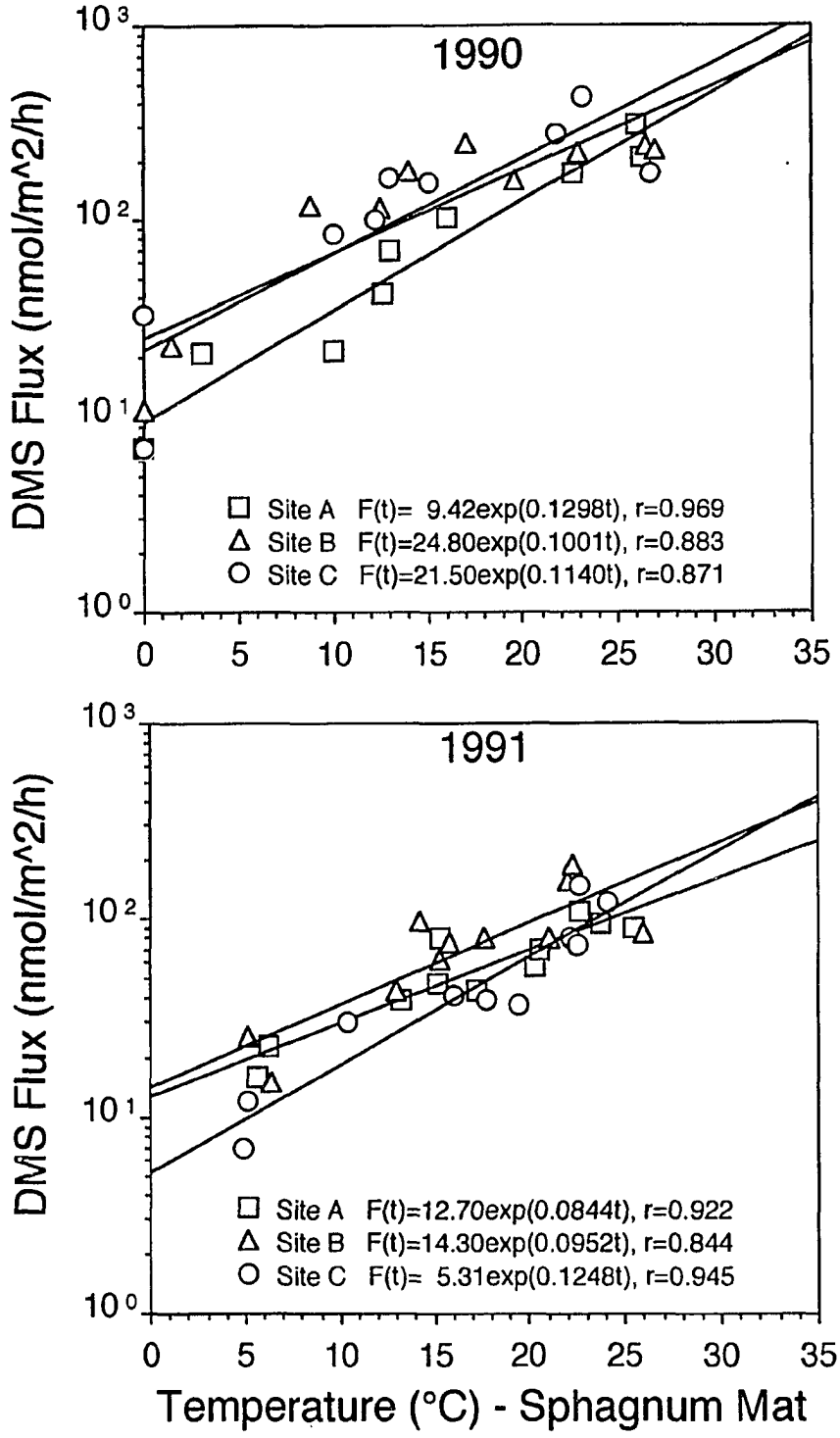

Figure 14. Regression of DMS fluxes vs. temperature from the seasonal variability data set.

of the fen (prior to beaver dam), the closer the water table was to the peat surface the greater was the DMS emissions (Figure 15). In 1990 and 1991, when the water table was below the peat surface, DMS emissions also tended to increase as the water table approached the peat surface.

3.2. Diel Variability in DMS Emissions

DMS emissions were variable over a 24-hour period (Figure 16). The highest DMS emissions (~160 nmol m^{-2} h^{-1}) occurred between 1200 and 1400 LT (local time), and the lowest (~30 nmol m^{-2} h^{-1}) between 0400 and 0600 LT. The mean DMS flux rate over the 24-hour period was 92 nmol m^{-2} h^{-1} (N = 25). Considering the frequency of DMS flux determinations, the product of this number by 24 hours would provide a suitable approximation of the daily integrated flux, estimated at ~1930 nmol m^{-2}.

Ambient air temperature ranged from 8.6 to 32.5°C while air within the enclosure head space varied from 7.2 to 33.7°C. Temperature within the *Sphagnum* mat (~5 cm below the mat surface) varied less than air temperature inside and outside the enclosure (Figure 16, bottom). There was a lag of 1-2 hours between the *Sphagnum* mat maxima and minima temperatures and the air maxima and minima.

Figure 17 displays DMS fluxes plotted as a function of temperature of the *Sphagnum* mat and air inside and outside the enclosure. DMS fluxes increased exponentially with increasing temperature within the range investigated.

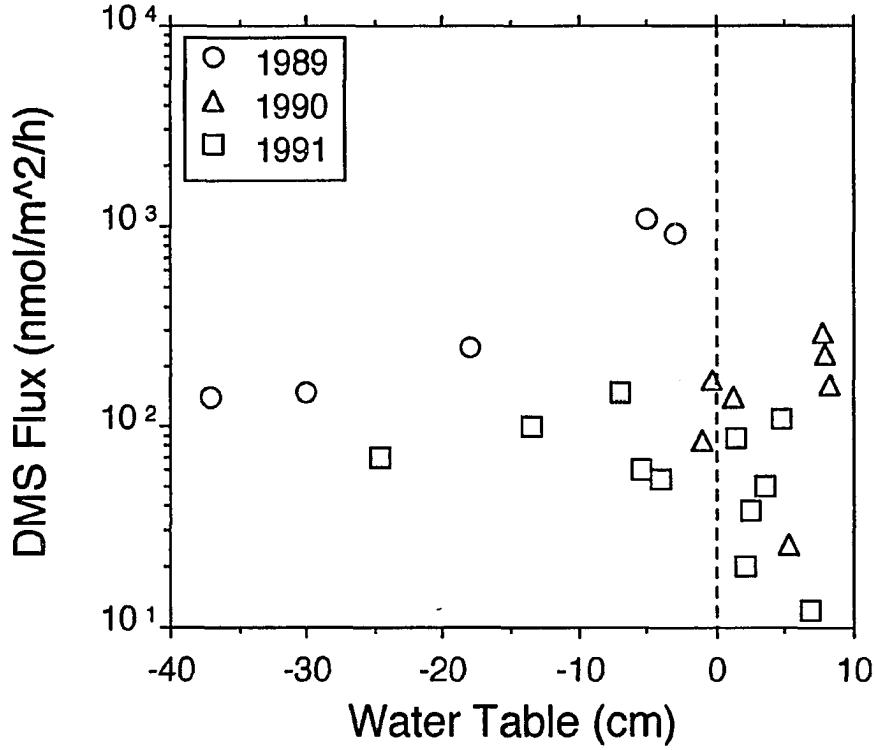

Figure 15. DMS emissions (sites A, B and C averaged) vs. water table height (five wells averaged). Dashed line denotes the peat surface.

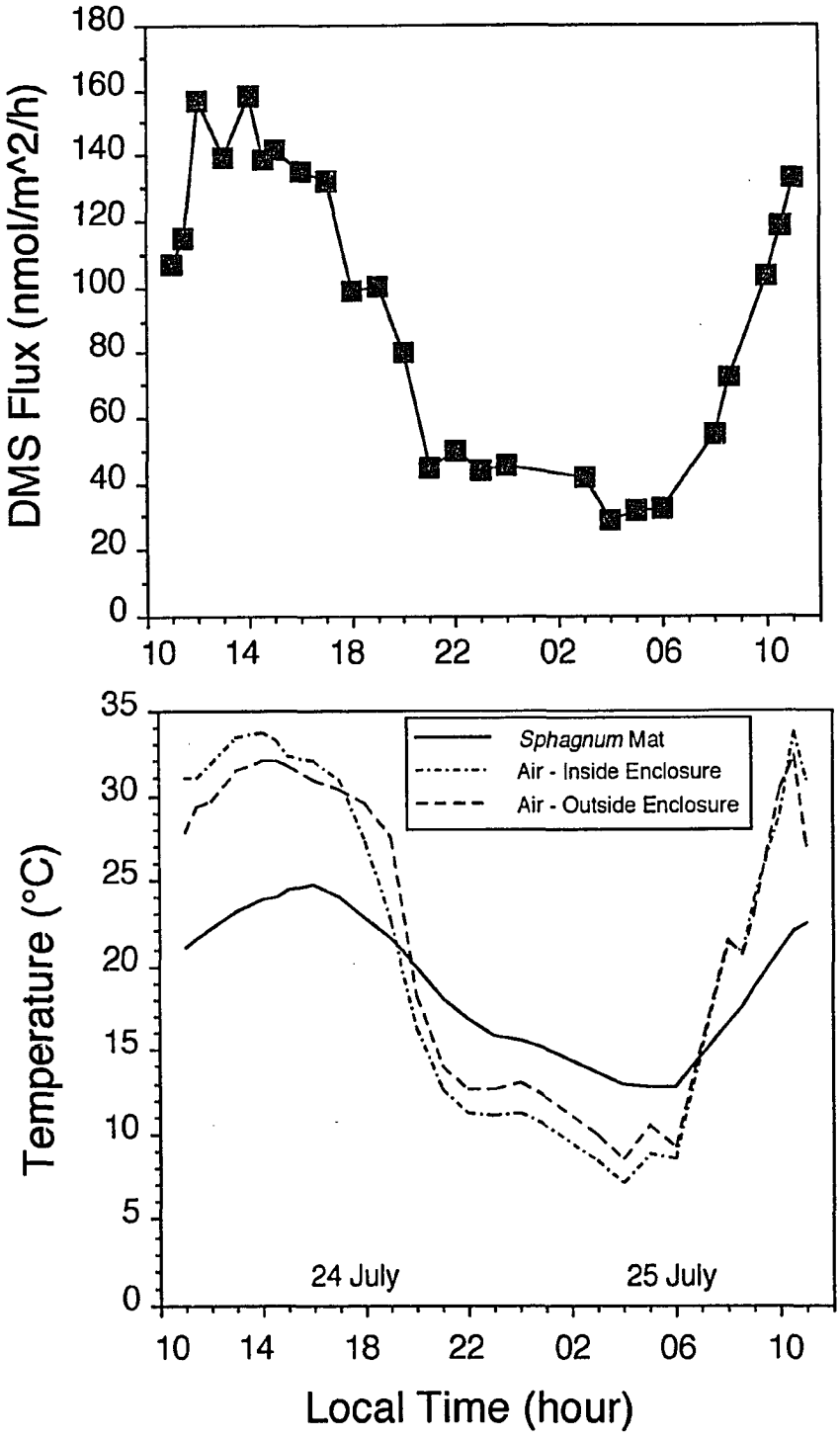

Figure 16. Diel patterns in DMS fluxes and temperature (at the *Sphagnum* mat, inside the enclosure head space and ambient air) on 24-25 July 1991, at site B.

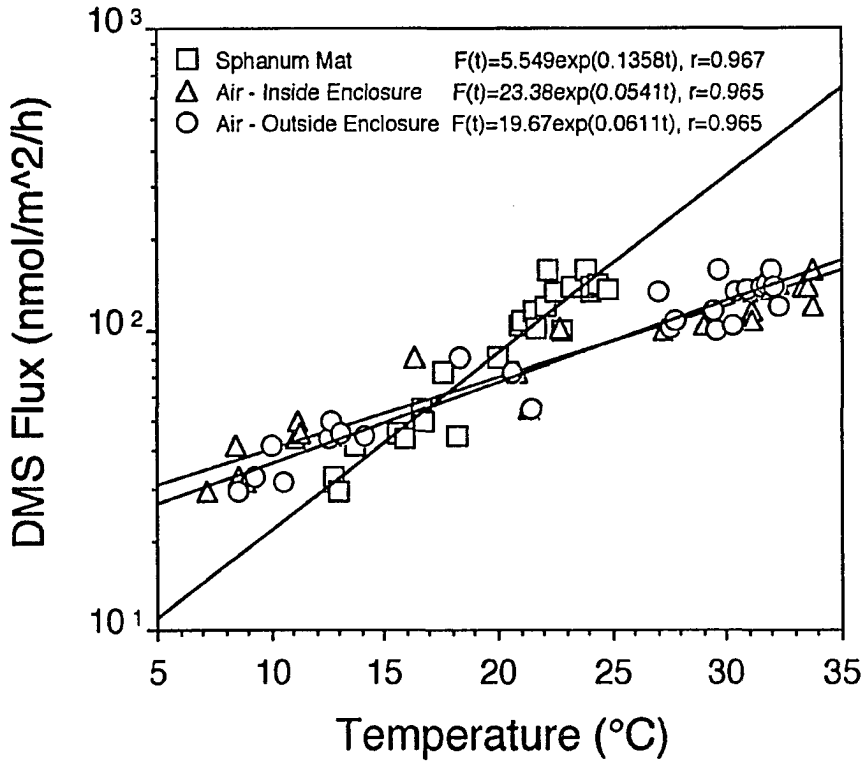

Figure 17. Regression of DMS fluxes vs. temperature from the diel variability data set.

Correlation coefficients for the best exponential fits were greater than 0.96 ($P<0.001$, $N = 25$), suggesting a highly significant effect of temperature on the diel variability of DMS emissions from this peatland.

3.3. Spatial Variability in DMS Emissions

DMS was also the most significant VSC emitted from the twelve sites surveyed for spatial variability. In this survey, three fourths of the MSH fluxes and all CS_2 fluxes were <1.0 nmol m^{-2} h^{-1}. Results of DMS and MSH emissions and selected environmental variables are summarized in Table 8.

Fluxes of VSCs were all measured between 1130 and 1430 LT. Therefore, results compiled in Table 8 represent the upper limit of VSCs emissions over a daily cycle. Undetectable DMS flux occurred only at site 1, located in the lagg. DMS emissions at site 4, which was inhabited only by *S. fallax*, was very close to the detection limit. The highest DMS emissions was found at site 6, a 30 cm hummock formed by *Chamaedaphne calyculata* and *Polytrichum juniperinum*, followed by site 9, the only site inhabited by *S. papillosum*.

Over the four days of spatial survey, the air temperature varied from 13.6 to 27.4°C and the *Sphagnum* mat temperature varied from 12.6 to 22.1°C (Table 8). Therefore, it was difficult to compare data from all sites since temperature variations strongly affect flux (Figures 14 and 17).

TABLE 8. Spatial variability in DMS and MSH fluxes (nmol m^{-2} h^{-1}), temperature, dissolved DMS and MSH (nM), and *pH*

Site	Flux		Temp. (°C)		Dissolved*		*pH*
	DMS	MSH	Mat	Air	DMS	MSH	
1	<1	<1	13.4[W]	16.6	1.4	<0.1	5.7
A	44	<1	17.2	22.5	2.4	<0.1	3.9
3	25	<1	15.3	17.5	0.9	0.9	4.0
4	1.5	<1	12.6	17.9	0.8	0.7	4.3
B	80	<1	17.6	22.0	0.8	0.1	4.1
6	359	3.8	19.2	27.4	1.7	1.3	4.3
C	39	<1	17.7	21.2	1.4	1.4	4.2
8	91	5.1	18.1	27.1	1.1	3.1	4.5
9	296	7.3	22.1	26.8	1.6	2.6	4.9
10	40	<1	18.4	15.2	1.1	1.5	4.3
11	99	<1	18.6	14.6	1.2	2.3	4.3
12	16	<1	17.2	13.6	5.6	2.4	4.3

Measurements were performed in September 1991 on days: 11th (sites A, B and C), 12th (sites 1, 3 and 4), 18th (sites 6, 8 and 9) and 19th (sites 10, 11 and 12).

* Arithmetic Mean (N = 2).

W Temperature of the water surface (there was no vegetation).

The correlation between air and *Sphagnum* mat temperatures was poor because changes in ambient air temperature were more rapid than in the *Sphagnum* mat. Statistical analyses of all data compiled in Table 8 suggested a reasonable correlation between DMS flux and the temperature of the *Sphagnum* mat ($r = 0.92$; $N = 10$; $P<0.001$), when data from sites 1 and 6 (non-*Sphagnum* inhabited sites) were excluded from the regression. However, the correlation was significant when DMS emission and temperature from site 6 was incorporated in the regression ($r = 0.90$; $N = 11$; $P<0.001$). Conversely, there was no significant correlation between DMS flux and air temperature ($r = 0.49$; $N = 10$).

Statistical analysis indicated that there was no relationship between DMS fluxes and dissolved DMS (Table 8). There was also no correlation between DMS fluxes and *p*H. Although MSH emission data were not sufficient to be statistically treated, two of the three detectable MSH fluxes occurred at sites where concentrations of dissolved MSH were high (Table 8).

3.4. Distribution of Dissolved VSCs

DMS and MSH were the most abundant dissolved VSC and concentrations were variable with time and space (Table 9). The concentration of dissolved DMS ranged from 0.2 to 26 nM. Concentrations were comparable in May and August, but were ~3 times lower in November. Three-dimensional (3-D) surface representations of dissolved DMS show that the gas had

TABLE 9. Concentrations (nM) of dissolved volatile sulfur compounds over five transects (N = 35) in Sallie's Fen; mean, median (between parenthesis) and range (below)

Time (1991)	DMS	MSH	OCS	pH	T(°C)
28-29 May	5.4(3.2) 0.4-26	9.9(0.5) <0.0-154	1.1(0.6) <0.0-5.6	4.9(4.9) 4.2-6.2	18(18) 12-26
27-28 Aug	5.4(4.1) 0.2-16	1.9(1.1) 0.0-7.7	1.9(1.5) 0.3-10	4.7(4.5) 4.0-5.8	19(19) 16-23
05-06 Nov	2.0(1.5) 0.3-11	2.0(0.9) <0.0-22	0.9(0.9) <0.0-2.5	4.7(4.7) 4.0-5.7	4.2(4.2) 1.0-6.6

several areas of maximum concentration and did not maintain a uniform distribution pattern over the year (Figure 18a).

Concentrations of dissolved MSH were more variable than DMS, i.e., ranging from <0.1 to ~150 nM (Figure 18b). There were five MSH concentration values greater than 10 nM in May, varying from 13 to 150 nM, and one in November (22 nM). In May, considering that 30% of the data were <0.1 nM, the five highest MSH concentration values were responsible for the large discrepancy found between the mean and the median. The major differences in MSH concentrations between May and August/November were restricted to areas near the northern and southern inlet streams (Figure 18b). Careful examination of the waters during sample collection indicated that high MSH levels were usually associated with organic-rich dark waters which appeared to be rich in H_2S (not quantified but detected).

The overall concentrations of dissolved OCS varied from <0.1 (less than 5% of the data) to 10 nM, but 60% of the data were between 0.1 and 1.0 nM (Table 9). Dissolved OCS concentrations were supersaturated with respect to equilibrium with atmospheric OCS concentration (~500 pptv), which is about one tenth of my OCS detection limit. Distribution of OCS concentrations exhibited similar characteristics in May and August (Figure 18c), i.e. OCS concentrations were lower and relatively constant over the southern area of the fen, and exhibited two sharp maxima over the northern area, one near the northern inlet stream

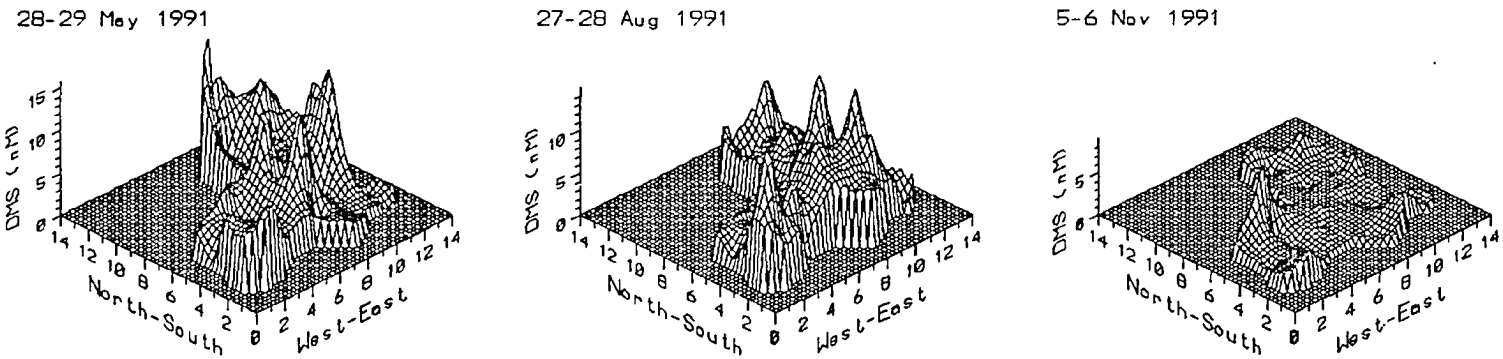

Figure 18a. Three-dimensional perspectives on distribution of dissolved DMS in the surface of the water table. Coordinates are arbitrary numbers, each unit is equivalent to 15 m.

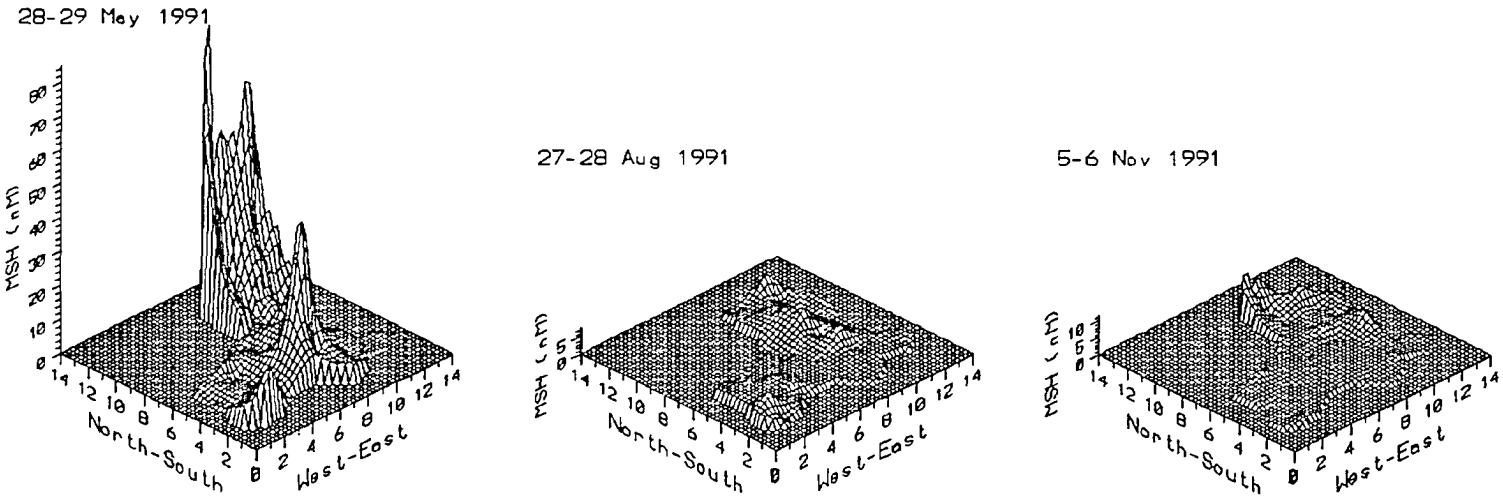

Figure 18b. Three-dimensional perspectives on distribution of dissolved MSH in the surface of the water table. Coordinates are arbitrary numbers, each unit is equivalent to 15 m.

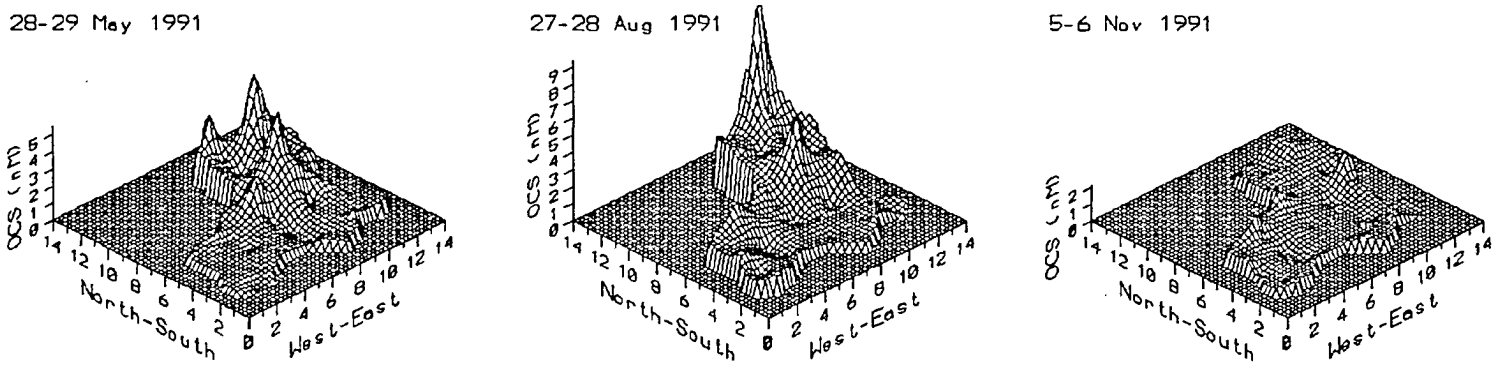

Figure 18c. Three-dimensional perspectives on distribution of dissolved OCS in the surface of the water table. Coordinates are arbitrary numbers, each unit is equivalent to 15 m.

and other between the end of the boardwalk and the northern inlet. In November, OCS concentrations were uniformly low throughout the peatland.

3.5. Surface Water *p*H Distribution

The spatial variability in *p*H followed a very uniform distribution pattern (Figure 19). The northern waters were less acidic with a *p*H of ~5.2 (Table 10). In the central part of the fen there was an abrupt decrease in *p*H with the southern area of the fen exhibiting the most acidic waters (~4.4 average). There was no apparent temporal variation in *p*H (Table 10).

4. DISCUSSION

4.1. Major Factors Controlling Diel and Seasonal Variabilities of DMS Fluxes

Temperature was the major factor controlling the variability of DMS emissions from the surface of the peatland on a time scale ranging from hours to months. Emissions tended to increase logarithmically with increasing temperature. This temperature dependence has also been observed for emissions of DMS and other VSCs from several natural environments and cultivated areas [i.e., Hill et al., 1978; Adams et al., 1981; de Mello et al., 1987; Goldan

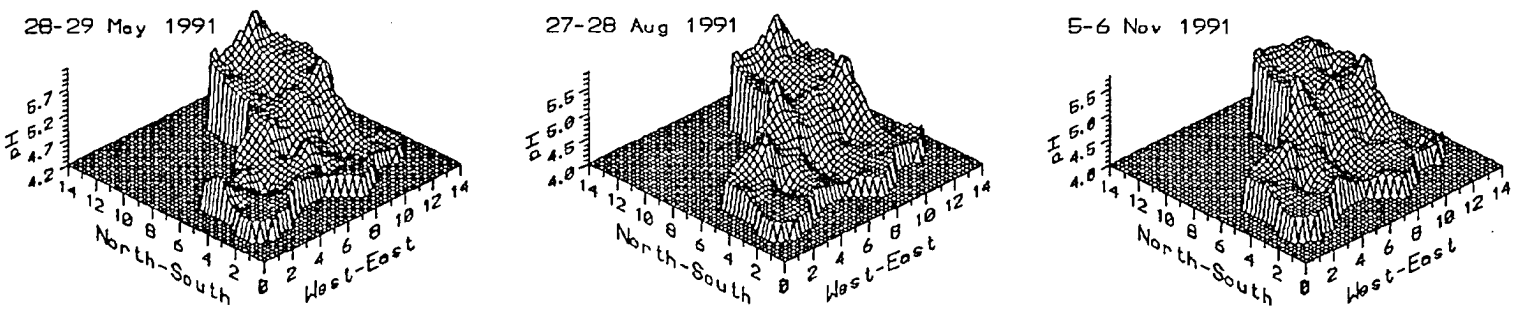

Figure 19. Three-dimensional perspectives on *p*H distribution in the surface of the water table. Coordinates are arbitrary numbers, each unit is equivalent to 15 m.

TABLE 10. Surface water *p*H means (±SD) in Sallie's Fen

Time	Whole fen*	Northern zone	Southern zone
28-29 May	4.9 (±0.5)	5.4 (±0.3)	4.5 (±0.2)
27-28 Aug	4.7 (±0.5)	5.1 (±0.3)	4.3 (±0.2)
5- 6 Nov	4.7 (±0.5)	5.2 (±0.3)	4.3 (±0.3)

* Whole fen N = 35; northern zone N = 15; southern zone N = 20.

et al., 1987; MacTaggart et al., 1987; Lamb et al., 1987; Fall et al., 1988].

Diel DMS fluxes at Sallie's Fen (site B, September 1991) varied by a factor of ~5 over a temperature range of 12.8-24.8°C (*Sphagnum* mat). Similar temperature dependence has also been observed in the diel variability of DMS emissions from a boreal *Sphagnum* peatland [Chapter II]. It has been reported that diel variability in DMS emissions in coastal wetlands were regulated strongly by temperature whether the sources of the S gas were vegetation (*Spartina alterniflora*) or soil microbial activity [de Mello et al., 1987; Cooper et al., 1989].

Maximum DMS fluxes occurred in summer and minima in the late fall. However, I have no data from the early winter throughout mid spring. In late November 1991, temperature of the *Sphagnum* mat was 0°C, and the ambient air ~3°C, but fluxes ranged from 7-11 nmol m^{-2} h^{-1}. Therefore, it is possible that DMS emission were measurable throughout much of the winter. Emissions of methane from Sallie's Fen were low but still measurable during winter [P.M. Crill, personal communication].

In July 1989, DMS fluxes in Sallie's Fen were ~10 times higher than fluxes in July 1991. No measurements were made in July 1990 because the fen was flooded by the beaver dam. However, DMS fluxes in August and September 1989 were very similar in magnitude to those during the corresponding period in 1990. Ambient air temperatures on 7 and 25 July

1989 were the highest of my entire data set, i.e., 34.1 and 34.9°C, respectively. Since DMS fluxes were similar in August-September 1989 and 1990, I estimated fluxes in July 1989 using equations from 1990 that defined DMS fluxes as a function of temperature (ambient air). The calculated DMS fluxes for July 1989 were almost half of the observed fluxes. Therefore, it is unlikely that temperature was the only variable responsible for such high emissions.

Results also indicated that DMS fluxes tended to increase with an increasing water table as long as the latter remained below the peat surface (Figure 15). Methane emissions have been shown to respond similarly to changes in water table height [Moore et al., 1990]. It is possible that the high DMS fluxes in July 1989 was caused by a combination of high temperature and the position of the water table relative to the peat surface. Since production of DMS in *Sphagnum* peatlands is related to the microbial activity in the anoxic layers of the peat surface [Chapter II], a high water table might contribute metabolizable substrates for the microbial population (see discussion below) while decreasing the penetration of oxygen. These July 1989 fluxes are among the highest ever recorded for freshwater habitats.

4.2. Potential Factors Controlling Annual DMS Emissions

The daily average ambient air temperature during my survey of the diel variability of DMS fluxes was 22.6°C. Applying this temperature to the equation determined for the

best non-linear fit for the relationship between DMS flux and ambient air temperature, shown in Figure 17, yields a flux of 1880 nmol m^{-2} day^{-1}. This is only 3% lower than the estimated daily integrated DMS flux. Therefore, I used the equations determined for the seasonal relationship between DMS emission and ambient air temperature to estimate the annual DMS emission in 1990 and 1991 at each site (Table 11). These were calculated using the average annual air temperatures in Durham, i.e. 9.6°C and 9.4°C, respectively. The estimated annual DMS fluxes at sites A, B and C indicated that, in general, DMS emissions in Sallie's Fen decreased from 1990 to 1991. However, the data indicated that the annual changes were not consistent over the three sites, i.e., changes at site C were greater than site B, and no change occurred at site A (Table 11).

The 0.2°C difference between the annual average temperatures for 1990 and 1991 was too small to account for the observed variation in DMS fluxes. This indicated that the decrease in DMS emissions was due to changes in other environmental factors. It is possible that the decrease in DMS emission was caused by a decrease in the atmospheric S input or/and changes in the nutritional status of the fen as a result of the beaver dam built in 1990.

Sulfur deposition was never monitored directly at Sallie's Fen. Therefore, I used sulfate deposition data (wet deposition only) provided by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) to

TABLE 11. Annual DMS fluxes (μmol m^{-2} yr^{-1}) as a function of temperature at Sallie's Fen

	F(t) = Aexp(Bt)*		Ratio 1990/1991
Site	1990	1991	
A	174	180	1.0
B	369	196	1.9
C	279	95	2.9
Average	274	157	1.7

t Temperature (°C).
* Annual average air temperatures [t = 9.6°C (1990) and t = 9.4°C (1991)] were applied to equations from the non-linear regression of DMS fluxes vs. ambient air temperature:
1990,
Site A, F(t) = 5.90exp(0.1262t), r = 0.924
Site B, F(t) = 15.43exp(0.1046t), r = 0.888
Site C, F(t) = 9.51exp(0.1259t), r = 0.892
1991,
Site A, F(t) = 10.18exp(0.0746t), r = 0.948
Site B, F(t) = 10.02exp(0.0854t), r = 0.935
Site C, F(t) = 3.81exp(0.1112t), r = 0.967

examine the relationship between DMS emissions and atmospheric S input. Table 12 summarizes sulfate deposition data for 1989 to 1991 at the four NADP/NTN stations closest to Sallie's Fen. From 1989 to 1990 there was no indication of a significant decrease in S deposition in the region since only one station showed a decrease of ~ 10%. From 1990 to 1991, S deposition decreased 8-18% in three stations and increased by 20% in the other. In sites B and C, DMS emissions from 1990 to 1991 (Table 11) decreased much more than the decrease in S input via wet deposition, indicating that changes in S deposition were not responsible for the decrease in DMS emissions. However, this was inferred without any information on dry deposition, a parameter which can vary greatly [Likens et al., 1990].

The increased water table height, caused by the beaver dam in 1990, might have enhanced uptake of dissolved nutrients and minerals by plants by bringing water-born materials into the oligotrophic surface areas of the fen. Enhanced productivity and S uptake by plants could result in a decrease in availability of S for the microbial population responsible for DMS production. I noted that DMS fluxes in a boreal poor fen in Canada were more rapid in oligotrophic areas than in minerotrophic ones [Chapter II]. These results contrast what has been observed for methane, i.e., increased productivity yields more methane [Whiting et al., 1991]. However, in the case of methanogenesis, gas production is limited by organic carbon availability which increases with

TABLE 12. Annual sulfate deposition* (mmol m^{-2} yr^{-1}) at the closest NADP stations to Sallie's Fen, Barrington, NH

Station	Deposition*			State	County	Dist. from Barrington (km)
	1989	1990	1991			
Hubbard Brook	25	25	23	NH	Grafton	80
Bridgton	16	17	14	ME	Cumberland	100
Bennington	24	25	30	VT	Bennington	175
East	28	25	22	MA	Middlesex	80

* Annual deposition values were originally reported in kg SO_4 ha^{-1} (wet deposition only) in the NADP/NTN database.

plant production. DMS production may be limited by S availability which could decrease as plant production increases.

4.3. Potential Factors Controlling Distribution of Dissolved VSCs

Concentrations of dissolved DMS and MSH in Sallie's Fen were greater than in the surficial waters of an artificially acidified boreal fen at the Experimental Lakes Area (ELA), in northwestern Ontario, Canada [Chapter II]. In Sallie's Fen, DMS, MSH and OCS concentrations were also greater than in several unpolluted lakes in Canada [Richards et al., 1991]. DMS concentration were also greater than in the surface waters of the Great Lakes [Nriagu and Holdway, 1989] and as high as those in surficial waters of several wetlands receiving elevated anthropogenic S input from the atmosphere [Nriagu et al., 1987]. In May and August, average DMS concentrations in Sallie's Fen were close to the average DMS concentration in the oceanic coastal and equatorial upwelling regions, i.e., 4.9 nM [Andreae, 1990]. OCS concentrations in the surface water of Sallie's Fen were higher than in oceanic waters (~0.03-1.0 nM) [Ferek and Andreae, 1983, 1984; Turner and Liss, 1985].

The mechanisms of DMS and MSH production in *Sphagnum* peatlands are still unknown. Hence, it appeared that production of methylated S compounds in *Sphagnum* peatlands was linked to the activity of sulfate-reducing bacteria. It

is possible that other microbially-mediated processes, such as degradation of S-containing amino acids [Segal and Starkey, 1969; Bremner and Steele, 1978], might also contribute to the production of methylated S compounds in peatlands. However, the rapidity in which methylated S compounds were formed after sulfate addition in Sallie's Fen [Chapter II] suggests that sulfide formation precedes S methylation. Finster et al. [1990] suggested that the production of these methylated S compounds in anoxic environments is linked to the biogeochemistry of organic compounds and inorganic sulfide. They observed that the production of DMS and MSH in sulfide-containing marine and freshwater sediments was stimulated by addition of methoxylated aromatic compounds (constituents of lignin and lignin-like compounds). These types of compounds are present in *Sphagnum* and in other vegetation within and surrounding Sallie's Fen. I noted rapid increases in DMS and MSH concentration in the surficial anoxic layers of peat in Sallie's Fen following additions of large quantities of sulfate to a plot in which vegetation had been removed [Chapter II]. Drotar et al. [1987a,b] demonstrated the occurrence of microbial enzyme systems which are capable of using other methyl donors for methylating sulfide to form MSH and DMS. The majority of DMS formed in marine habitats appears to be derived from the cleavage of the plant osmoregulant dimethylsulfoniopropionate (DMSP). Although, DMS fluxes reported here were higher than those measured in

salt marsh areas inhabited by non-DMSP producing grasses [Morrison and Hines, 1990], it is not expected that this compound would be present at significant levels in Sallie's Fen which has a low ionic strength.

Table 13 displays apparent activation energies (E_a) for DMS production using data for DMS fluxes and temperature (*Sphagnum* mat) measured at Sallie's Fen during diel and seasonal surveys. These E_a values are similar to those estimated for sulfate reduction in sediments from a waterlogged alder swamp (54-67 kJ mol^{-1} [Westermann and Ahring, 1987]), a saltmarsh (85 kJ mol-1 [Abdollahi and Nedwell, 1979]) and in Lake Mendota (75 kJ mol^{-1} [Ingvorsen et al., 1981]). Nielsen [1987] found an E_a of 85 kJ mol^{-1} for sulfate reduction in biofilms of wastewater treatment plants as well. This similarity may be because sulfate reduction is potentially involved in production and consumption of methylated sulfides in the fen, as has been shown in sediment incubation studies [Finster et al., 1990; Kiene and Visscher, 1987]. Most E_a values calculated from DMS fluxes and those from sulfate reduction were smaller than those determined for methanogenesis, 92-116 kJ mol^{-1}, [Westermann and Ahring, 1987] and methane fluxes from peatlands, 116-177 kJ mol^{-1}, [Crill et al., 1988], providing further evidence for the importance of sulfate reduction in DMS and MSH production.

The water supplied through the ephemeral streams might have been a source of sulfate to the fen which contributed

TABLE 13. Arrhenius activation energy (E_a) based on the effect of temperature (*Sphagnum* Mat) on DMS emissions over diel and seasonal time scales

Site	Time Period	E_a kJ mol^{-1}
B	24 hr Sep 91	95
A	Aug-Nov 1990	89
B	Jun-Nov 1990	69
C	Aug-Nov 1990	80
A	May-Nov 1991	58
B	May-Nov 1991	66
C	Jun-Nov 1991	85

to production of methylated sulfides. The large MSH concentrations found in areas near the northern and southern inlet streams in May, a period of high water flow, could have been due to this sulfate input. In August, MSH concentrations were more uniformly distributed throughout the fen and MSH concentrations near inlet streams were comparable to the rest of the fen. Streams were dry at that time of the year, so surficial S input would have been minimal. In August, the overall median MSH concentration was ~2-fold higher than in May, which might have been due to an elevated sulfate input during Hurricane Bob or enhanced S cycling at the higher temperature. In November, there was again some stream water inflow, but MSH distribution was comparable to that in August. However, temperature was much lower in November which probably attenuated MSH production and consumption.

In May, surficial concentrations of dissolved DMS did not exhibit the same distribution pattern as MSH, i.e., DMS concentrations were not as variable as MSH nor were DMS levels as high. The difference in the distribution of these compounds could be due to the kinetics of MSH and DMS production. A sequential methylation pathway (via microbial processes) starting from H_2S yields MSH which is a direct precursor for DMS. It is possible that in May, there was sufficient H_2S to produce large quantities of MSH without producing DMS. In August DMS concentrations were higher than MSH suggesting that MSH methylation was dominant. In

November, DMS concentrations were more than 2-fold lower than in May and August, indicating that, like MSH, DMS production was attenuated by low temperatures.

Photooxidation of dissolved organo S compounds is believed to be the major source of OCS in seawater [Ferek and Andreae, 1984]. However, it is unlikely that photochemistry is the dominant process forming OCS in the surface waters of Sallie's Fen. Surface waters are barely exposed to sunlight over the fen. At the lagg, waters visibly rich in dissolved organic matter are normally shaded by trees and bushes. When the level of the water table was above the peat surface, the area of the fen where waters were more exposed to sunlight was in the far eastern part of the fen. This was a very open area, dominated by *Sphagnum* mosses growing very close to water level (or wet peat level). In this area OCS concentrations were normally low. Hence, the supersaturation of OCS in Sallie's Fen was probably due to biological production.

The relationship between concentration and temperature also indicates a biological source of OCS in the fen. Kelly and Smith [1990] reported production of OCS from oxidation of CS_2 by *Thiobacillus thioparus* TK-m, a microorganism also capable of oxidizing also DMS, MSH, DMDS (dimethyl disulfide) and H_2S [Kanagawa and Mikami, 1989]. Bremner and Steele [1978] also provided evidence that OCS is produced microbially during the decomposition of S-containing organic compounds. I did not observe any change in either CS_2 or OCS

throughout the upper 25 cm of a peat column when sulfate was added to the surface of Sallie's Fen [Chapter II]. This suggested that, if OCS in Sallie's Fen was produced by microorganisms, its production was not related to DMS or MSH production.

4.4. *Sphagnum* as a Control of DMS Fluxes in Peatlands

The magnitude of DMS concentrations in the surface of the water table was not proportional to DMS emissions (Table 8). In fact, during the present study on the spatial variability of DMS fluxes, I noted that the rate of DMS flux from surface water in the lagg, which contained 1.4 nM DMS, was <1 nmol m^{-2} h^{-1}. On the other hand, DMS fluxes ranged from 25 to 99 nmol m^{-2} h^{-1} from sites covered by *Sphagnum* mosses and which contained DMS concentrations in the water table of <1.4 nM (excluding site 4). Site 4, which had a thin mat of *Sphagnum fallax*, exhibited a DMS flux rate very close to the limit of detection. However, all other *Sphagnum*-containing sites yielded rapid DMS fluxes even when dissolved levels of DMS were lower than in sites containing standing water.

Concentrations of dissolved DMS in water squeezed from *Sphagnum* leaves in Sallie's Fen were always identical or smaller than DMS concentrations in the peat pore water (Table 14). No data have been published which demonstrate the production of VSCs by *Sphagnum* mosses. Therefore, the DMS held by the *Sphagnum* leaves probably arose from the

TABLE 14. Mean dissolved DMS concentration (nM) in water squeezed from *Sphagnum* leaves and pore water from the peat surface underneath the *Sphagnum* mat

Site	*Sphagnum*				Water				Date 1991
	DMS	*p*H	T(°C)*	N	DMS	*p*H	T(°C)¤	N	
A¥	0.5	4.4	15.3	6	0.6	4.7	8.7	3	7 May
A	0.9	4.0	12.5	2	4.3	4.4	9.1	2	10 May
B	1.2	4.1	12.0	2	4.0	4.4	7.8	2	10 May
C	3.1	3.8	12.2	1	5.0	4.5	8.8	2	10 May

* Temperature of the *Sphagnum* mat.

¤ Temperature of the water.

¥ Area near site A.

transport of peat water through the plant capillary system formed by hyaline cells. Lower DMS concentrations found in the *Sphagnum* leaves compared to concentrations in the water table might be due to DMS oxidation during water transport through the plant capillary system. Higher DMS diffusion from the plant-water system compared to evapo-transpiration, which is regulated by temperature and wind speed, could also explain lower DMS concentrations in the *Sphagnum* leaves.

In another report [Chapter II] I utilized pore water DMS levels and direct flux data to demonstrate that *Sphagnum* mosses probably enhance DMS fluxes by creating a three dimensional diffusion gradient for the gas. The average DMS flux from all *Sphagnum*-containing sites (N = 10) reported in Table 8, was 73 nmol m^{-2} h^{-1} which was higher than the flux of 29 nmol m^{-2} h^{-1} calculated using a stagnant-film model [Liss and Slater, 1974]. The latter estimate utilized an exchange coefficient of 1.7 cm hr^{-1} for a wind speed of zero [Sebacher et al., 1983]. The difference between actual fluxes and calculated fluxes supports my hypothesis that *Sphagnum* mosses enhance DMS emissions from peatlands [Chapter II]. The observed high DMS flux at site 6, a site located on the top of a hummock of ~30 cm height and dominated by leather-leaf and juniper moss, indicated that there are other plants in the peatland responsible for DMS emissions (or controlling emissions) other than *Sphagnum*.

4.5. Comparison with Different Regions

My present and previous observations [Chapters I and II] suggested that DMS is the major organic volatile S compound emitted from *Sphagnum* peatlands. Since previous studies on S fluxes in *Sphagnum* peatlands and *Sphagnum*-containing environments were conducted in July [Chapter II; Hines and Morrison, 1992], I first need to normalize my present data to temperature for adequate inter-comparison. The same equations applied to determine the annual DMS flux as a function of temperature (Table 11) were used to estimate DMS emissions in Sallie's Fen in July. Using the average July temperature in Durham (21.2°C), DMS fluxes ranged from 40 to 142 nmol m^{-2} h^{-1} (86 nmol m^{-2} h^{-1} average, 1990-1991). DMS fluxes from an experimental boreal fen in northwestern Ontario (49°40'N) averaged 40 nmol m^{-2} h^{-1} [Chapter II]. Lower DMS fluxes, 5.7 nmol m^{-2} h^{-1}, were reported from a *Sphagnum* containing wet meadow in Alaskan tundra (61°20'N) [Hines and Morrison, 1992]. These results suggest that DMS emissions from *Sphagnum* peatlands in North America tend to decrease with increasing latitude.

Annual DMS emissions from Sallie's Fen ranged from 95 to 369 μmol m^{-2} yr^{-1} (1990-1991). Using a temperature dependent S emission algorithm, Guenther et al. [1989] estimated total S emission from New England deciduous forests as 100 to 345 μmol m^{-2} yr^{-1}, of which 15% of the total emission was DMS and 60% was OCS. Hence, their DMS flux was 15-52 μmol m^{-2} yr^{-1}. Their U.S. national average

emission rate from all terrestrial biogenic S sources was 66 μmol m^{-2} yr^{-1} of which 23 μmol m^{-2} yr^{-1} was DMS and 25 μmol m^{-2} yr^{-1} OCS. Using an identical algorithm, Bates et al. [1992] estimated a total S flux from the world wetlands between 35-50°N of 28 μmol m^{-2} yr^{-1}, of which 6.2 μmol m^{-2} yr^{-1} was DMS and 15 μmol m^{-2} yr^{-1} was OCS. This is considerably lower (15-60 fold) than my estimates for Sallie's Fen (43°N).

Recent studies, applying ambient air flow-through enclosures and static enclosures, have shown that OCS is consumed at the surface of vegetated and unvegetated soils [Castro and Galloway, 1991; Hines and Morrison, 1992; Chapter I]. Although OCS concentrations in the surface of water table of *Sphagnum* peatlands are supersaturated with respect to concentrations in the atmosphere (section 4.3), the net flux of the gas in these environments showed consumption [Chapter I]. This suggests that OCS might not be the major S gas emitted from terrestrial environments as have been proposed by U.S. National and global inventories on S emissions from natural sources [Guenther et al., 1989; Bates et al., 1992]. Therefore, if sites were revisited for new estimation of S fluxes in terrestrial environments using adequate enclosure techniques and inventories were reviewed, results would lead to a conclusion that DMS is the major S gas released from terrestrial environments.

5. CONCLUSION

DMS was the dominant volatile organo S compound emitted from the surface of the peatland. DMS emissions varied greatly over 24 hours and seasonally. Temperature seemed to be the major environmental factor responsible for these variabilities. However, 1989 data indicated that there was a synergistic effect between temperature and water table height on DMS emissions. Disturbance of the annual regular vertical movement of the water table might have been the cause of observed long-term decreases in DMS emissions from Sallie's Fen during the warmer periods of the year. Changes in atmospheric S input during the period studied was insignificant compared to changes in DMS emissions which would exclude the former variable as a major control during that period.

Dissolved DMS, MSH and OCS in the surface waters were supersaturated with respect to their concentrations in the atmosphere indicating that surface waters were sources of VSCs in the peatland. It appeared that all three S gas were produced primarely by microbial processes in the surficial anoxic layers of the peat and standing waters rich in organic matter and sulfide. Although *Sphagnum* mosses did not seem to be a source of S gases, they enhanced DMS fluxes by transporting surficial waters throughout an interlinked system of opened cells (hyaline cells) to the upper most parts of the plant.

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APPENDICES

APPENDIX A

Fluxes of DMS in Mire 239 at ELA, Ontario, Canada

Site	Day	Local Time	Temperature, °C *Sphagnum* mat	Temperature, °C Ambient air	DMS flux nmol m^{-2} h^{-1}
Oligotrophic					
20C-A	16	1857	15.2	25.7	15
	21	1730	17.7	19.1	18
20C-B	16	1909	12.3	25.6	33
	21	1642	17.4	19.3	30
130C-A	16	1607	18.2	25.2	16
130C-B	16	1619	19.9	27.3	48
	18	2136	13.5	10.8	19
	19	0036	11.7	nd	15
	19	0350	9.8	nd	11
	19	0652	9.6	13.9	11
	19	1945	16.7	18.8	24
	20	1156	14.2	nd	18
	22	1229	20.1	23.2	43
130C-C	16	1633	13.5	27.4	77
140E-A	15 (b)	1917	18.8	23.1	60
	16 (b)	1145	15.4	23.0	85
	18	2124	15.6	11.6	91
	19	0019	12.9	12.4	47
	19	0334	12.6	6.5	38
	19	0634	11.6	7.2	40
	19	1928	18.3	21.4	127
	20	1140	15.3	nd	117
140E-B	15 (b)	1929	nd	nd	19
	16 (b)	1107	20.4	25.8	12
140E-C	15 (b)	1938	17.4	22.0	52
	16 (b)	1120	15.3	23.7	79
	18	2150	16.1	10.5	46
	19	0055	13.2	9.0	34
	19	0408	11.0	12.1	20
	19	0712	10.8	14.2	34
	19	2001	17.0	18.9	52
	20	1212	15.4	nd	71
	22	1343	19.5	25.5	76
Minerotrophic					
3MC-A	16	1923	16.4	24.9	8.5
	21	1700	19.9	18.5	2.5
12ME-A	17 (b)	1105	13.5	22.3	25
	20	1538	17.3	nd	12
12ME-B	17 (b)	1121	9.9	20.3	21
	20	1557	17.7	nd	4.1

(b) Before acidification.
nd, Not determined.

APPENDIX B

Seasonal study.
Dynamic emclosure technique.

Date	Temperature (°C)		DMS flux (nmol m^{-2} h^{-1})		
	Sphagnum mat	Ambient air	Site A	Site B	Site C
27 Jun 90	nd	29.0	nd	160	nd
09 Aug 90	24.6	29.3	315	224	173
16 Aug 90	23.6	27.8	176	241	277
28 Aug 90	25.4	28.4	212	230	435
17 Sep 90	13.8	13.5	70	179	167
26 Sep 90	16.0	21.8	103	247	156
02 Oct 90	12.4	16.5	42	116	99
17 Oct 90	9.6	16.4	22	118	85
30 Oct 90	1.5	7.5	21	23	33
21 Nov 90	0.0	3.0	7	11	7
22 May 91	25.1	28.1	80	97	nd
13 Jun 91	18.6	19.3	70	76	37
26 Jun 91	22.5	31.9	110	190	146
17 Jul 91	24.6	32.3	94	85	120
06 Aug 91	21.3	23.7	57	79	74
23 Aug 91	23.2	28.8	90	155	79
11 Sep 91	17.5	21.9	44	80	39
11 Oct 91	15.5	20.5	47	63	41
24 Oct 91	12.2	17.2	39	44	30
07 Nov 91	5.5	10.3	23	26	12
14 Nov 91	5.6	9.2	16	15	7

nd, not determined

APPENDIX C

24-25 July 1991.

Local time	DMS flux nmol m^{-2} h^{-1}	Temperature (°C) *Sphagnum* mat	Head space	Ambient air
1100	107	21.1	31.1	27.8
1130	115	21.6	31.1	29.4
1200	157	22.2	31.9	29.7
1300	139	23.2	33.5	31.5
1400	158	23.9	33.7	32.0
1430	139	24.1	33.3	32.1
1500	142	24.4	32.3	31.7
1600	135	24.8	32.0	30.9
1700	132	24.1	30.9	30.4
1800	99	22.8	27.2	29.5
1858	101	21.7	22.7	27.6
2000	81	20.0	16.3	18.3
2100	45	18.2	12.7	14.1
2200	50	16.8	11.2	12.7
2300	44	15.9	11.1	12.6
2400	45	15.6	11.3	13.1
0050	nd	15.2	10.7	12.3
0300	42	13.7	8.5	10.0
0400	29	13.0	7.2	8.6
0500	32	12.8	8.9	10.6
0600	33	12.8	8.6	9.3
0800	55	16.6	21.4	21.5
0830	72	17.6	20.8	20.6
0900	nd	18.7	23.9	23.0
1000	103	20.9	29.0	30.3
1030	119	22.1	33.7	32.3
1100	133	22.5	30.9	27.0

APPENDIX D

Concentrations of dissolved OCS, MSH, DMS and CS_2 (nM).

Transect I - 28-29 May 1991.

Site #	T(°C)	pH	OCS	MSH	DMS	CS_2
1	16.8	4.4	0.7	0.0	0.4	nd
2	18.0	4.4	0.7	0.0	1.3	nd
3	16.0	5.1	0.7	0.0	15	nd
4	16.1	5.7	2.3	0.0	13	nd
5	16.6	5.4	1.4	0.0	0.6	nd
6	17.2	5.5	1.1	0.0	4.1	nd
7	15.8	5.6	5.6	13	10	nd
8	15.4	6.2	0.0	68	8.2	nd
9	18.1	6.0	0.0	154	26	nd
10	20.3	5.3	4.3	0.5	4.8	nd
11	16.9	5.3	1.3	0.3	1.3	nd
12	21.1	5.2	0.4	1.5	2.3	nd
13	15.3	5.0	0.7	0.4	1.3	nd
14	20.1	5.3	5.2	9.2	3.8	nd
15	17.2	5.2	2.7	4.7	7.2	nd
16	14.9	4.5	0.4	3.4	0.8	nd
17	15.5	4.3	0.6	0.0	1.7	nd
18	15.6	4.4	0.6	0.0	1.9	nd
19	14.7	4.5	1.1	1.7	0.8	nd
20	12.3	4.6	0.4	1.0	2.4	nd
21	23.5	4.6	0.6	5.4	3.2	nd
22	18.0	4.4	0.0	4.9	1.6	nd
23	16.0	5.0	0.0	45	15	nd
24	15.0	4.4	0.3	0.5	4.4	nd
25	18.3	5.2	2.8	0.5	13	nd
26	19.0	5.2	0.7	0.3	0.7	nd
27	21.7	4.4	0.9	6.6	7.5	nd
28	18.1	4.7	0.4	0.3	2.0	nd
29	17.8	4.2	0.3	0.8	1.5	nd
30	20.5	4.5	0.6	2.4	nd	nd
31	18.0	4.9	0.5	0.3	3.2	nd
32	20.8	4.6	0.0	16	9.6	nd
33	25.9	4.6	0.4	5.1	6.9	nd
34	21.4	4.5	0.4	0.0	7.3	nd
35	20.2	5.0	0.4	0.0	1.2	nd
Minimim	12.3	4.2	0.0	0.0	0.4	--
Maximum	25.9	6.2	5.6	154	26	--
Average	17.9	4.9	1.1	9.9	5.4	--
SD	2.8	0.5	1.4	29	5.7	--
SE	0.5	0.1	0.2	4.8	1.0	--

nd, not determined

Concentrations of dissolved OCS, MSH, DMS and CS_2 (nM).

Transect II - 27-28 August 1991.

Site #	T(°C)	pH	OCS	MSH	DMS	CS_2
1	16.1	4.3	0.3	0.8	0.2	0.0
2	19.0	4.3	0.5	1.9	3.0	0.0
3	17.1	5.1	2.8	0.0	4.4	0.2
4	18.0	5.5	2.4	0.0	3.1	0.2
5	17.4	4.9	1.9	0.0	0.6	0.2
6	17.3	5.1	1.7	0.0	1.6	0.2
7	18.1	5.1	3.3	0.0	2.0	0.0
8	17.5	5.8	10	6.7	9.7	1.3
9	18.3	5.6	3.1	0.4	10	0.4
10	18.5	5.2	2.4	0.0	2.6	0.2
11	17.9	4.9	2.9	1.5	1.0	0.3
12	19.9	4.8	2.3	3.6	5.5	0.3
13	17.2	4.7	2.9	6.4	7.7	0.5
14	17.6	5.1	5.3	7.7	4.2	0.0
15	19.9	4.8	2.0	0.6	15	0.1
16	20.2	4.2	0.5	6.0	2.9	0.0
17	20.8	4.3	0.7	1.0	15	0.0
18	20.0	4.2	0.7	1.7	11	0.0
19	18.2	4.4	0.9	2.1	5.1	0.0
20	18.1	4.5	1.5	0.5	1.0	0.0
21	20.4	4.3	0.8	0.6	6.4	0.0
22	18.3	4.0	0.6	1.1	8.3	0.0
23	19.7	4.0	0.9	1.2	11	0.0
24	18.4	4.2	0.6	1.3	9.3	0.0
25	18.5	5.0	1.3	0.0	1.7	0.1
26	18.8	5.6	2.2	0.0	2.1	0.1
27	19.6	4.8	3.2	0.0	4.1	0.1
28	18.7	5.1	1.8	1.3	1.6	0.2
29	21.7	4.0	0.3	3.6	3.7	0.0
30	18.4	4.1	0.5	3.8	8.8	0.0
31	18.9	4.4	1.2	0.3	0.7	0.0
32	19.1	4.2	1.5	0.7	4.6	0.1
33	23.2	4.3	0.8	7.0	16	0.1
34	20.9	4.3	1.9	2.6	2.7	0.2
35	19.8	4.5	1.4	2.9	1.3	0.2
Minimim	16.1	4.0	0.3	0.0	0.2	0.0
Maximum	23.2	5.8	10	7.7	16	1.3
Average	18.9	4.7	1.9	1.9	5.4	0.1
SD	1.4	0.5	1.8	2.3	4.4	0.2
SE	0.2	0.1	0.3	0.4	0.7	0.0

Concentrations of dissolved OCS, MSH, DMS and CS_2 (nM).

Transect III - 5-6 November 1991.

Site #	T(°C)	pH	OCS	MSH	DMS	CS_2
1	4.2	4.3	0.3	0.0	0.8	0.0
2	4.6	4.0	0.3	0.0	0.7	0.0
3	6.2	4.9	1.0	5.7	1.8	0.1
4	3.1	5.5	2.5	3.3	3.8	0.1
5	4.0	5.0	0.7	0.0	0.3	0.0
6	4.3	4.8	1.3	0.0	1.4	0.1
7	4.8	5.4	1.9	5.2	4.2	0.2
8	6.2	5.3	1.9	1.2	1.3	0.1
9	6.6	5.6	0.0	22	3.3	0.2
10	4.7	5.3	1.2	4.1	3.4	0.1
11	5.6	5.1	0.9	0.4	0.4	0.1
12	4.3	5.0	1.4	0.0	1.7	0.1
13	4.5	4.8	1.0	0.9	0.5	0.0
14	5.6	5.3	0.9	2.9	1.5	0.1
15	3.8	4.9	0.4	0.0	2.0	0.0
16	4.9	4.2	0.5	0.8	0.7	0.0
17	4.1	4.4	0.3	0.6	1.1	0.0
18	nd	nd	nd	nd	nd	nd
19	4.1	4.2	0.5	2.2	3.6	0.1
20	1.2	4.3	1.3	0.9	3.9	0.1
21	1.5	4.4	1.1	0.6	0.8	0.0
22	4.1	4.1	0.7	1.6	1.5	0.1
23	1.0	4.1	0.7	1.9	1.5	0.0
24	3.1	4.2	0.6	1.6	2.3	0.1
25	2.2	5.1	1.0	0.7	2.2	0.1
26	3.9	5.7	1.9	0.9	1.3	0.1
27	3.6	4.8	2.3	3.3	10.7	0.1
28	5.7	5.0	0.8	1.2	0.5	0.0
29	4.9	4.0	0.3	0.4	0.6	0.0
30	3.7	4.1	0.3	0.6	0.6	0.0
31	3.9	4.7	1.0	1.1	0.8	0.1
32	3.6	4.4	1.0	2.0	4.1	0.1
33	3.4	4.4	0.6	0.6	2.0	0.0
34	5.6	4.4	0.4	0.0	0.6	0.0
35	5.7	4.6	1.2	1.7	1.4	0.1
Minimim	1.0	4.0	0.0	0.0	0.3	0.0
Maximum	6.6	5.7	2.5	22	11	0.2
Average	4.2	4.7	0.9	2.0	2.0	0.1
SD	1.4	0.5	0.6	3.8	1.9	0.1
SE	0.2	0.1	0.1	0.6	0.3	0.0

nd, not determined

DMS fluxes (nmol m^{-2} h^{-1}) - Static vs. Dynamic.

Date	Site	C_o	C_{max}	k	Sta.	Dyn.	Location
27Jun90	B	13.3	103	0.0826	134	160	NH
16Jul90	14A	5.4	70	0.0562	66	85	ELA
19Jul90	14C	4.6	212	0.0206	77	52	ELA
20Jul90	12MA	2.7	18	0.0342	9	12	ELA
21Jul90	2A	2.3	15	0.0657	15	18	ELA
09Aug90	B	16.9	235	0.1089	428	224	NH
16Aug90	B	21.9	279	0.0433	200	241	NH
26Sep90	B	7.9	196	0.0350	119	247	NH
	A	0.6	60	0.1033	111	95	NH
02Oct90	B	1.6	115	0.0522	107	116	NH
	A	6.4	34	0.0618	30	42	NH
17Oct90	B	1.1	64	0.0833	95	118	NH
	A	1.1	9	0.1069	16	22	NH
30Oct90	B	1.9	46	0.0480	38	23	NH
	A	4.6	19	0.0572	15	21	NH
21Nov90	B	0.0	56	0.0078	8	11	NH
	A	0.0	18	0.0192	6	7	NH
22May90	B	1.6	61	0.1921	204	97	NH
	A	3.1	84	0.0720	104	80	NH
12Jun91	Bare	2.5	14	0.1732	17	7	NH
13Jun91	B	0.0	47	0.1607	137	76	NH
	C	0.0	29	0.3350	177	37	NH
26Jun91	B	0.0	170	0.0485	148	190	NH
	A	0.0	103	0.1763	327	110	NH
	C	0.0	127	0.0388	89	146	NH
17Jul91	B	1.4	60	0.1392	147	85	NH
	A	3.2	113	0.0590	117	94	NH
	C	0.9	108	0.0920	178	120	NH
06Aug91	A	3.3	49	0.0720	59	57	NH
	C	3.4	54	0.0821	74	74	NH
23Aug91	B	0.0	92	0.0993	164	155	NH
	A	3.3	93	0.1546	251	90	NH
	C	7.4	122	0.0934	192	79	NH
10Oct91	B	0.3	52	0.0492	45	63	NH
	A	0.0	39	0.0342	24	47	NH
	C	0.3	52	0.0314	29	41	NH
24Oct91	B	1.3	201	0.0081	29	44	NH
	A	1.3	26	0.1011	45	39	NH
	C	1.3	36	0.0271	17	30	NH
07Nov91	B	0.0	33	0.0345	20	26	NH
	C	0.0	21	0.0452	17	23	NH
14Nov91	B	0.9	152	0.0029	8	15	NH
	A	0.0	14	0.0751	19	16	NH
	C	0.9	10	0.0422	7	7	NH

DMS fluxes (nmol m^{-2} h^{-1}) - Static vs. Dynamic continued.

Date	Site	C_o	C_{max}	k	Sta.	Dyn.	Location
11Sep91	B	1.8	46	0.1259	100	87	NH
	C	2.7	98	0.0155	26	22	NH
12Sep91	3	0.0	69	0.0327	41	25	NH
	4	0.0	4	0.0634	4	2	NH
18Sep91	6	1.9	286	0.0714	365	359	NH
19Sep91	12	4.5	76	0.0477	61	16	NH

OCS fluxes (nmol m^{-2} h^{-1}) - Static vs. Dynamic

Date	Site	C_o	C_{max}	k	Sta.	Dyn.	Location
20Jul90	12MA	25.8	10.0	0.1018	-29.0	4.2	ELA
09Aug90	B	16.0	7.6	0.0247	- 3.7	6.6	NH
16Aug90	B	16.6	5.9	0.1155	-22.2	7.9	NH
02Oct90	B	30.1	6.1	0.1281	-55.4	6.5	NH
21Nov91	B	25.4	9.5	0.0992	-28.4	3.7	NH
12Jun91	Bare	13.3	29.6	0.0691	20.2	12.7	NH
26Jun91	C	24.3	20.0	0.2604	-19.9	28.9	NH
06Aug91	A	21.6	7.7	0.1748	-43.9	4.8	NH
	C	21.2	10.4	0.1261	-24.6	8.7	NH
10Oct91	B	18.1	2.3	0.0780	-22.3	8.2	NH
07Nov91	A	12.5	5.5	0.0924	-12.0	5.8	NH
14Nov91	B	14.7	-0.7	0.0147	- 4.1	5.4	NH
	A	16.0	2.2	0.0383	- 9.5	5.5	NH
11Sep91	B	14.8	6.8	0.1528	-21.8	5.5	NH
12Sep91	1				0.0	7.8	NH (water)
	3	16.7	7.8	0.1812	-28.9	7.9	NH
18Sep91	4	16.7	7.6	0.1521	-24.8	2.6	NH
	6	18.2	7.7	0.2006	-37.9	10.8	NH
19Sep91	8	19.3	10.0	0.0715	-12.0	26.0	NH
	10	12.9	7.4	0.0996	-9.8	10.6	NH
	11	19.3	11.4	0.1738	-24.7	12.9	NH