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Terminal Decomposition and Gaseous Sulfur Release from Tidal Wetlands

Principal Investigator

Mark E. Hines

Institute for the Study of Earth, Oceans and Space
University of New Hampshire
Durham, NH 03824

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Introduction

The following report is a summary of the results of a multi-year project which studied the release of biogenic sulfur gases from wetland habitats. This project also included an initial study of factors that control terminal decomposition in temperate salt marsh sediments. This preliminary research was used as a biogeochemical foundation for the interpretation of data collected during other aspects of this work. Although autonomous, the project was coordinated, to some extent, with other projects as part of the Wetlands Program of the Biospherics Research Program (formally the Global Biology Program). This coordination included the participation in various group-oriented endeavors, and in some instances these group efforts included personnel from other NASA programs; most notably the Global Tropospheric Experiment (GTE) within the Earth Sciences Division of NASA. Although the initial intent of the project was to investigate sulfur (S) emissions from salt water wetlands, as time progressed the research moved greatly into freshwaters since it became clear that these habitats had a greater influence on regional and global processes and these habitats were grossly understudied with respect to their role as producers and consumers of atmospheric S compounds. This report is a succinct summary of the project since more detailed information is provided as appendices here. These include reprints of most of the published work that arose from the research, abstracts of papers presented at professional meetings, abstracts of theses, and abstracts of manuscripts that are still in review. The reader is referred to this material throughout the text.

Salt Marsh Biogeochemistry

A detailed study of decomposition in salt marsh sediments was conducted. This included seasonal variations in pore water and solid phase chemistry, and measurements of rates of sulfate reduction and methanogenesis in the sediments. The results are summarized primarily in Hines et al. (1989) and Hines (1991a). However, several other

reports are listed in the appendices. Data were collected from three types of areas within the salt marsh which represented a gradient from the low to the high marsh, and included two species of marsh grasses. Techniques were developed to collect pore water samples without disturbing the sediment-plant system while maintaining sediment anoxia.

It was demonstrated that variations in plant activity and growth stage were the most important factors in controlling the rate of organic matter decomposition in the system. Plant activity also controlled the extent to which the sediments were oxidized and this activity, in turn, controlled the mobility of redox-sensitive chemical species within the sediments including hydrogen sulfide gas formation and mobility. There were dramatic differences in the biogeochemical dynamics of areas inhabited by tall or short forms of the cordgrass *Spartina alterniflora*, and in areas inhabited by *Spartina patens*. This study was the first to collect samples often enough to delineate the close and dynamic interaction between plant activity and sedimentary biogeochemistry. It also allowed us to decipher the dynamics of hydrogen sulfide production in salt marshes.

Release of Biogenic S Gases from Salt Marshes

A seasonal study was conducted to measure the exchange of biogenic S gases in salt marshes, and to investigate factors which control this exchange. The results are summarized primarily in Morrison (1988) and Morrison and Hines (1990). However, several other reports are listed in the appendices. Considerable effort was directed toward the development of technology which was appropriate for these types of measurements. It is difficult to accurately measure S gases, and this difficulty was compounded greatly by the need to develop sample acquisition equipment. Although the analytical system was continually modified throughout the duration of the project, it is the most sensitive and precise system currently in use to measure the simultaneous exchange of several S gases between natural habitats and the atmosphere.

The salt marsh emits extremely large quantities of S gases. This is dominated by dimethyl sulfide (DMS) but other gases such as methane thiol (MeSH), hydrogen sulfide (H_2S), carbonyl sulfide (OCS) and carbon disulfide (CS_2) are also present. The domination by DMS is due to the production of the osmolyte and DMS precursor, dimethylsulfoniopropionate (DMSP) by plants. DMSP is not produced by all salt marsh grasses and our work demonstrated extreme differences in the rates of emissions of DMS between areas dominated by different grasses. These results underscored the utility of remote sensing as a tool to quantify DMS emissions from coastal wetlands since there are such large differences in emission rates from different species of vegetation. The diel and seasonal studies also revealed the strong effects of temperature and hydrology on S gas exchange.

Release of Biogenic S Gases from Tundra

Sulfur gas exchange in tundra was measured during the joint expedition between the Wetlands Program of the Biospherics Research Program and GTE in Alaska in 1988 (ABLE 3A). These data are the first of their kind for tundra habitats. The results can be found in Hines and Morrison (1989, 1992). In brief, S gas fluxes from all of the freshwater sites were extremely slow. Wet sites emitted most while dry sites, inhabited primarily by lichens and Sphagna, emitted very little gas. Emissions were dominated by DMS, and tundra was a sink for OCS. Coastal habitats, which contained much more total S due to their proximity to the sea, emitted more S gas than the freshwater sites. However, the coastal fluxes were quite slow relative to temperate coastal wetlands. These data were used to calculate global emissions rates of S gases from tundra.

Release of Biogenic S Gases from the Florida Everglades

A study of S gas exchange in wetlands of the Florida Everglades was conducted to determine if fluxes could be extrapolated using vegetation information and remote

sensing. The results of this project appear in Hines et al. (1993). In brief, rates of S gas exchange were determined in each of several major habitats in the Everglades, including both freshwater and marine sites. Fluxes were highest in sites inhabited by red mangroves, particularly sites in which crabs had cleared the area of leaves and high fluxes of DMS were emanating from crab burrows as leaves decomposed therein. However, except for these high fluxes, many of the marine sites yielded fluxes which were similar in magnitude to some of the freshwater sites. The slowest fluxes occurred in the wet saw grass meadows which make up the bulk of the Everglades. Sites that had been burned within the last year exhibited higher fluxes than adjacent sites which were not burned.

The entire Everglades Park was divided into several vegetation classes and these were delineated visually using a Landsat thematic mapper (TM) image. Geographic information system software was used to "fine tune" the TM image and the fluxes of S gases were extrapolated for the entire park. With this procedure, it was possible to determine which habitats were most important as sources of biogenic S gases for the atmosphere.

Release of Biogenic S Gases from Northern Bogs and Fens

Although tundra was a very weak source of S gases, it was found that *Sphagnum*-dominated fens and bogs emit unusually large amounts of S gases, especially when considering the low amounts of S present in these systems . Emissions of S gases from a fen in New Hampshire were as high as 50 μmol m^{-2} d^{-1}. High fluxes were also encountered in wetlands in Ontario, Canada, and in other wetlands in the northeast US. Emissions are dominated strongly by DMS. Results of studies in these northern mires can be found in various papers and abstracts listed below. Some of the results are summarized in Hines (in press).

Experiments were conducted to determine the influence of changes in S deposition on S emissions. Amendments of sulfate to experimental plots increased the concentrations of dissolved S gases by several orders of magnitude but did not have a significant affect on fluxes over the short term. Chronic increases in S additions to an experimental wetland in Canada also caused an increase in dissolved S gases but had not affect on emissions. However, experimental sections of the wetland that had been receiving S amendments for several years emitted more S than did control regions.

The presence of *Sphagnum* greatly influenced S fluxes. Removal of the mosses decreased fluxes and sites devoid of mosses emitted much less S gases than moss-inhabited areas. It was hypothesized that the mosses enhance fluxes by acting as conduits of water through capillary action. Replacing mosses in a areas in which they had been previously removed resulted in an immediate increase in emission rate of DMS. It also appeared that highest DMS fluxes occur in sites that exhibit a low pH and are most devoid of nutrients. This result is counter to what occurs for other gases such as methane. The results also indicate that DMS is derived from the methylation of sulfide. This differs from marine habitats where DMS is derived from the cleavage of an S-C bond.

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Reprints and Preprints of Papers Published

Grant NAGW-0512

ABSTRACT

A PRELIMINARY STUDY OF THE VARIABILITY AND MAGNITUDE OF THE FLUX OF BIOGENIC SULFUR GASES FROM A NEW HAMPSHIRE SALT MARSH

by

Michael Cope Morrison
University of New Hampshire, December, 1988

Salt marshes have highly variable spatial and temporal fluxes of hydrogen sulfide, carbonyl sulfide, methane thiol, dimethyl sulfide, and carbon disulfide (H_2S, COS, MeSH, DMS, and CS_2 respectively). This variability was tested at nine emission sites in a New Hampshire, USA salt marsh: three replicates in each of three vegetation zones, *Spartina alterniflora*, *S. patens*, and a transition zone. Three sites were sampled simultaneously, either within or across vegetation zones, using a dynamic flux chamber technique. Difficulties with calibration and field equipment resulted in fluxes with maximum absolute uncertainties of greater than ±200%. However, the relative uncertainty between subsequent samples was closer to ±20%. Chambers are expected to affect the natural flux of gases by altering the humidity, temperature, and composition of the gas inside the chamber. Summertime fluxes are highest for all gases except COS which demonstrated evidence of a springtime peak. A summertime background flux of 5 to 100×10^{-9} g S m^{-2} min^{-1} was observed for all gases, while *S. alternifora* fluxes of MeSH and DMS were ~8 fold and ~100 fold higher than *S. patens*, respectively. DMS and MeSH fluxes were higher during the day than at night. Evidence of COS uptake by plants was observed. CS_2 appeared to be the quantitatively least important sulfur gas emitted. Improved laboratory and sample collection techniques and further data collection in the field will yield information on the details of salt marsh variability, will improve estimates of the error

associated with single flux measurements, and will allow a more accurate estimation of sulfur fluxes from salt marshes based on vegetation and area coverage data. Inability to control the temperature and humidity inside of the chamber remain significant problems with the chamber design.

Limnol. Oceanogr., 34(3), 1989, 578–590

Sulfate reduction and other sedimentary biogeochemistry in a northern New England salt marsh

Mark E. Hines, Stephen L. Knollmeyer,[1] *and Joyce B. Tugel*
Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham 03824

Abstract

Sulfate reduction rates, dissolved iron and sulfide concentrations, and titration alkalinity were measured in salt marsh soils along a transect that included areas inhabited by both the tall and short forms of *Spartina alterniflora* and by *Spartina patens*. Pore waters were collected with in situ "sippers" to acquire temporal data from the same location without disturbing plant roots. During 1984, data collected at weekly intervals showed rapid temporal changes in belowground biogeochemical processes that coincided with changes in *S. alterniflora* physiology. Rates of SO_4^{2-} reduction increased fivefold (to >2.5 μmol ml^{-1} d^{-1}) when plants began elongating aboveground yet decreased fourfold upon plant flowering. This rapid increase in rates of SO_4^{2-} reduction must have been fueled by dissolved organic matter released from roots only during active growth. Once plants flowered, the supply of oxidants to the soil decreased and sulfide and alkalinity concentrations increased despite decreases in SO_4^{2-} reduction and increases in SO_4^{2-} : Cl^- ratios. Sulfide concentrations were highest in soils inhabited by tallest plants.

During 1985, *S. alterniflora* became infested with fly larvae (*Chaetopsis apicalis* John) and aboveground growth ceased in late June. This cessation was accompanied by decreased rates of SO_4^{2-} reduction similar to those noted during the previous year when flowering occurred. After the fly infestation, the pore-water chemical profiles of these soils resembled profiles of soils inhabited by the short form of *S. alterniflora*.

The SO_4^{2-} reduction rates in *S. patens* soils are the first reported. Rates were similar to those in *S. alterniflora* except that they did not increase greatly when *S. patens* was elongating. Tidal and rainfall events produced desiccation-saturation cycles that altered redox conditions in the *S. patens* soils, resulting in rapid changes in the dissolution and precipitation of iron and in the magnitude and spatial distribution of SO_4^{2-} reduction.

Salt marshes are extremely productive and a large portion of their productivity occurs belowground as roots and rhizomes (Valiela et al. 1976; Schubauer and Hopkinson 1984). Their sediments are anoxic near the surface, and decomposition in the soil occurs primarily via dissimilatory SO_4^{2-} reduction (Howarth and Teal 1979; Howarth and Giblin 1983; Howes et al. 1984). The end products of SO_4^{2-} reduction are reactive and influence the chemical composition of sediments profoundly (Goldhaber and Kaplan 1975; Jørgensen 1977; Berner 1980).

Because of variations in tidal regime, temperature, sediment transport, topography, and hydrology, salt marsh productivity varies from one location to the next and within individual marshes (Shea et al. 1975; Howes et al. 1981; King et al. 1982; Wiegert et al. 1983). Temporal variations in plant physiology are evident, not only in the visible changes that occur, such as growth and production of reproductive organs, but in the allocation of carbon to various plant organs (Lytle and Hull 1980; Gallagher et al. 1984). Variations in tidal inundation and desiccation complicate attempts to predict the distribution of biogeochemically important compounds, particularly redox-sensitive species like those produced during SO_4^{2-} reduction (Carr and Blackley 1986; Casey and Lasagna 1987). Plant activity also can influence redox processes in marsh soils

[1] Present address: Analytics Environmental Laboratory, Portsmouth, N.H. 03301.

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by enhancing gas diffusion and transporting water from soils to leaves (Howes et al. 1981; Dacey and Howes 1984).

Most research related to belowground redox processes involving sulfur has been conducted in soils inhabited by the cordgrass *Spartina alterniflora*, particularly its short forms (e.g. Howarth and Teal 1979; Lord and Church 1983; Howes et al. 1984; Casey and Lasagna 1987). Much less is known of these processes in other grass species and in the tall form of *S. alterniflora*.

The present study describes the temporal sulfur and iron biogeochemistry of soils in a northern New England salt marsh including seasonal variations in SO_4^{2-} reduction and related biogeochemical processes in soils inhabited by *Spartina patens* and the tall form of *S. alterniflora*. During the first year of the study, samples were collected weekly, and the data revealed the dynamic nature of salt marshes. Furthermore, these temporal variations were coincident with temporal changes in the growth stages of the vegetation and demonstrated that changes in plant physiology were responsible for controlling biogeochemical redox conditions within marsh soils.

Area description and methods

Sampling location—Chapman's Marsh is a small marsh near the mouth of the Squamscott River in the upper regions of Great Bay, New Hampshire (Fig. 1). This marsh is dominated by *S. patens* with stands of *S. alterniflora* along creek- and riverbanks. Because of the steep slope of the banks the *S. alterniflora*-inhabited areas are generally <30 m and in some locations only a few meters wide. The tall form of *S. alterniflora* is often >2 m tall. The transition is abrupt from tall to short *S. alterniflora* and from *S. alterniflora* to *S. patens*. The tidal range at the marsh is slightly >2 m. These marsh characteristics are common in northern New England. The soil in the *S. alterniflora*-inhabited areas contains relatively fine-grained minerals in addition to roots and rhizomes. The *S. patens*-inhabited soils are composed primarily of decaying roots and rhizomes. During winter, *S. alterniflora*-inhabited regions are covered by ice which can become up to 1 m thick in some locations. The movement of ice tends to remove virtually all of the aboveground biomass from a large portion of the creekbank stands so that by spring much of the *S. alterniflora* region is barren except for very short remnants of grass stems. In these areas, the organic content of the soil is due mostly to belowground production.

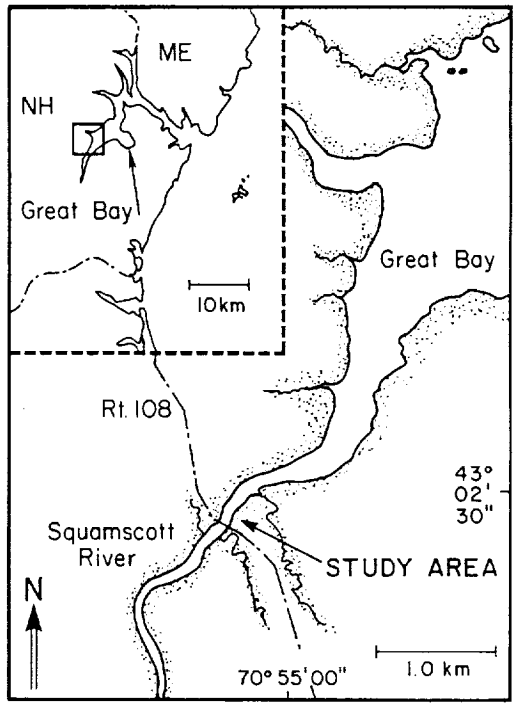

Fig. 1. Location of sampling sites in Chapman's Marsh, New Hampshire.

Sampling sites were chosen along a gradient perpendicular to the river in an area which was as far from drainage channels as possible. All drainage ditches in the marsh are natural since the marsh has not been altered for mosquito control. Three locations along this gradient were sampled: tall *S. alterniflora* (SA); *S. patens* (SP); and the transition zone (T) between these two grasses, consisting primarily of the short form of *S. alterniflora* interspersed with *S. patens*. The SA and SP sites were both sampled from June 1984 to June 1986. The T site was sampled only during the 1984 growing season. Boardwalks were installed in spring and personnel were restricted to them throughout the experiment.

Sample collection—Sediment cores were

collected with a Wildco handheld corer containing a polycarbonate liner, plastic or stainless steel core catcher, and a plastic nose piece. Cores were flushed with N_2 immediately after collection, capped, and transported back to the laboratory where they were extruded under N_2 in a glove bag.

Pore-water samples were collected with in situ "sippers" deployed during spring and removed in fall before ice formed. Sippers were identical in design to those described by Short et al. (1985) except that they were made from TFE Teflon. Sippers (lysimeters by definition) consisted of a cylinder which contained a 5-cm section covered by a porous Teflon collar. Two Teflon tubes were connected to the top of the device, one of which passed through to the bottom for sample removal. After deployment at the desired depth, a vacuum was applied by a hand pump, and the pore water was drawn into the sipper through the collar. Sippers were left full of water between sampling. On sampling days, the water within the sipper was removed by syringe. As water was withdrawn it was replaced with N_2 supplied by a gas-filled glass syringe flushed just before use. Care was taken to prevent oxygen from entering the sipper. This initial water was discarded and the sipper was filled again by applying a vacuum. After filling (~15–20 min), the pore water was removed with a precleaned glass syringe while N_2 was allowed to enter. Immediately after sample collection the syringe was connected to an acid-cleaned, N_2-flushed plastic Swinnex (Millipore Corp.) filter unit containing a 25-mm, 0.4-μm Nuclepore filter. The sample was filtered directly into an acid-cleaned plastic vial which was being flushed with N_2. Automatic pipettes that had been flushed with N_2 were used to divide the filtered sample into various vials for storage. Pore-water samples were therefore collected, filtered, and dispensed anoxically within 1–2 min in the field.

The sippers were left in place for several months at a time, so we were able to study temporal change unconfounded with varying sampling sites. In addition, the placement of the sippers before plant growth in the spring allowed nondestructive sampling. Howes et al. (1985) reported that damage to roots during centrifugation or sediment squeezing to obtain pore water caused drastic changes in pore-water chemistry, especially organic chemistry.

An individual sipper was used for each depth sampled. Four sippers were deployed at each location. Each set consisted of a near-surface sipper that contained a porous collar 2 cm long for a narrow sample interval at 1–3 cm in the soil. The remaining three sippers were placed in the remaining corners of a square array with ~10 cm on a side and at sample depths of 3–8, 9–14, and 15–20 cm. Studies comparing the concentrations of SO_4^{2-} and chloride in cores and sippers demonstrated that when the 5-cm porous collars were used, most of the sample obtained was drawn into the sipper from the upper 2 cm of the collar and that water was not drawn from above or below the sipper. Further comparisons demonstrated that in regions of live root material, dissolved sulfide concentrations were consistently higher in sipper samples than in pore waters collected by coring and squeezing even when extreme care was used to prevent oxidation of cores during processing. This latter result indicated that the sipper samples were not oxidized during collection.

Samples for sulfide analysis were mixed with an equal volume of 6% zinc acetate. Dissolved iron samples were stored in acid-cleaned plastic vials and acidified with HNO_3 to a final concentration of 1.0%. Pore water remaining in the original plastic vial was titrated for alkalinity (Gieskes and Rogers 1973) and then refrigerated for SO_4^{2-} analysis.

Chemical analyses—Sulfide was measured colorimetrically according to Cline (1969). Standards were prepared by dissolving and precipitating a weighed crystal of sodium sulfide in a solution of zinc acetate. This procedure precluded the need to use anoxic technique when preparing standards and the results were very reproducible. The stock zinc sulfide standard was stable for up to 7–9 weeks. Dissolved iron was determined colorimetrically with Ferrozine (Stookey 1970). Sulfate was determined turbidimetrically (Tabatabai 1974).

Sulfate reduction—Rates of SO_4^{2-} reduction were determined with ^{35}S according to

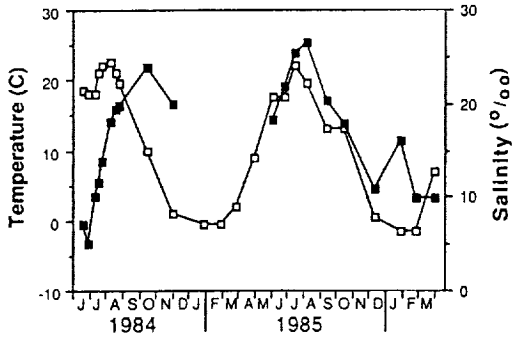

Fig. 2. Temperature (□) and salinity (■) in pore waters of Chapman's Marsh, June 1984–April 1986.

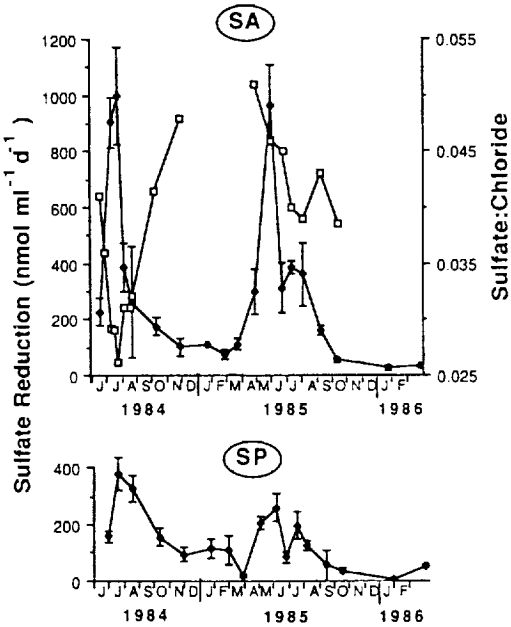

Fig. 3. Sulfate reduction rates (◆) in the sediments at sites SA and SP and SO_4^{2-} : Cl^- ratios (□) at SA, June 1984–April 1986. Values represent averages over the upper 20 cm of soil. Error bars equal ranges of duplicate cores.

Jørgensen (1978) as modified by Westrich (1983). Duplicate sediment cores were sliced into sections in a N_2-filled glove bag. Sliced portions were placed into 5-ml syringes sealed with serum stoppers. These subsamples were not homogenized before use. One microCurie of $^{35}SO_4^{2-}$ was injected into each syringe and samples were incubated in a dark N_2-filled jar overnight at ambient temperature. Activity was stopped by freezing to −80°C. Attempts to collect undisturbed small cores for direct core injection were unsuccessful due to the quantity of rhizome material present in the sediments.

^{35}S present in acid-volatile sulfides was determined by distilling sulfides into zinc acetate traps as described by Hines and Jones (1985). ^{35}S present in pyrite and elemental sulfur was determined by reducing these chemical species to sulfide with reduced chromium (Zhabina and Volkov 1978; Westrich 1983). Subsamples used for sulfide distillation were filtered and washed with distilled water to remove unused $^{35}SO_4^{2-}$, which otherwise resulted in a significant blank. Filters were stored dried in a desiccator until chromium reduction analyses. The reduction procedure liberated all of the sulfur when ground pyrite and reagent-grade elemental sulfur were used. The S : Fe ratio of the pyrite was 2.0 as determined by measuring the dissolved iron and SO_4^{2-} liberated from the mineral after oxidation and dissolution by aqua regia. The SO_4^{2-} reduction rate was calculated from the sum of radiolabel present in both the sulfide and chromium-reducible phases.

During the 1984 growing season, weekly pore-water samples were collected from all three sites to determine the short-term temporal variability in pore-water chemistry. Sulfate reduction rates were determined at either the SA or SP site each week. All cores and pore-water samples were collected at midtide. Samples were collected less frequently during the remainder of the study.

Results

The beginning and length of the growing season varied greatly from 1984 to 1985. During 1984, rainfall was abundant during spring and the salinity of the pore waters was <5‰ in May and June (Fig. 2). Salinity increased from 8 to 16‰ in July. Spring 1985 was unusually dry, and the salinity range in July was 25–32‰. Aboveground growth of marsh grasses in 1984 began in mid- to late June and continued until the first week in August, when *S. alterniflora* began to flower. *Spartina alterniflora* at site SA reached >2 m high during that 5–6-week period. *Spartina patens* at site SP began to grow a few days earlier than did *S. alterniflora*. In 1985, *S. alterniflora* began

to grow in mid-May and stopped at ~50 cm high in the last week of June. *Spartina patens* appeared to grow normally during that year. Examination of *S. alterniflora* in July 1985 revealed larvae of the ribbon-winged fly *Chaetopsis apicalis* John within the stems of the plants. This infection was evident in virtually all of the *S. alterniflora* plants in the marsh except for a narrow band along the creekbank. This narrow region was the only site flooded twice each day at high tide, including neap tides. An additional set of sippers was deployed in this tall creekside stand for comparison. The fly that attacked this marsh was the same species found previously in Great Sippewissett Marsh (J. Hartman and C. Cogswell pers. comm.).

Sulfate reduction—Rates of SO_4^{2-} reduction varied throughout the year and between sites (Fig. 3). Except for a period of ~2 months in summer when rates at site SA were considerably higher than at SP, rates were similar in magnitude at these sites. Sulfate reduction maxima at SA always occurred in the upper 2.0 cm of the sediment, and rates decreased several-fold with depth. During July 1984 this rate at 2.0 cm was $>2.5\ \mu mol\ ml^{-1}\ d^{-1}$. Sulfate reduction rates at site SP showed two maxima—one near the surface and one at 11.5 cm. The subsurface maximum usually exceeded rates measured near the surface.

Temporal SO_4^{2-} reduction maxima at site SA occurred during periods when plants were actively growing aboveground, i.e. from late June to early August 1984 and from late May to mid- to late June 1985 (Fig. 3). In 1984, there was nearly a fourfold decrease in depth-averaged SO_4^{2-} reduction rate at SA within a few days after flowering by *S. alterniflora* began. In 1985, vegetative growth ceased due to fly infestation, yet SO_4^{2-} reduction rates decreased as dramatically as they did during the previous year. Only one rate measurement was made during the period of active aboveground growth in 1985.

The SO_4^{2-} : Cl^- ratio at site SA decreased once plant growth began and increased after flowering began, thus coinciding with temporal variations in rates of SO_4^{2-} reduction (Fig. 3). Ratios of SO_4^{2-} : Cl^- in 1985 at SA were much higher than in 1984 despite the maximum in SO_4^{2-} reduction rate noted in May–June 1985. The occurrence of higher ratios in 1985 probably reflects the fact that even though the maximal SO_4^{2-} reduction rate at SA in 1985 was similar in magnitude to the maxima in 1984, the high rate in 1985 was probably too short lived to remove large quantities of SO_4^{2-}.

During summer 1984, ~80% of reduced ^{35}S in incubated samples from site SA was recovered as volatile and acid-volatile sulfides (data not shown). During winter, most ^{35}S in the upper few centimeters at SA was recovered in the chromium-reducible fraction; below 4 cm the chromium-reducible fraction accounted for ~40% of the label recovered. During summer 1985, the ^{35}S recovered in the chromium-reducible fraction at site SA was 40–70% of the total. The chromium-reducible ^{35}S fraction accounted for >90% of the label recovered in most of the samples collected at site SP during summer and winter. The acid-volatile fraction at SP was substantial (>50%), however, below 15 cm.

Other pore-water chemistry—Changes in the SO_4^{2-} : Cl^- ratios in the pore waters at site SP in 1984 coincided with variations in tidal regime and rainfall (Fig. 4). Occasionally, we were unable to collect sipper samples at certain depths at SP because sippers will not collect water unless the soils are saturated. SO_4^{2-} : Cl^- ratios at SP and T generally increased after these desiccation events and in some instances this ratio at SP exceeded the ratio in seawater. Soils at site SA were flooded at least once per day and did not experience periods of obvious desiccation. Sediments at site T appeared to be subjected to desiccation as at SP (Fig. 4). Desiccation events at site T were not severe enough, however, to produce SO_4^{2-} : Cl^- ratios higher than those of seawater. Since SO_4^{2-} : Cl^- ratios are altered greatly by tidal pore-water movements and by oxidation and reduction of sulfur (Howarth and Teal 1979; Casey and Lasagna 1987), the ratios reported here were instructive only for qualitative examinations of geochemical changes in the soils.

Dissolved sulfide concentrations were very high at site SA, and values averaged over the upper 20 cm of sediment increased

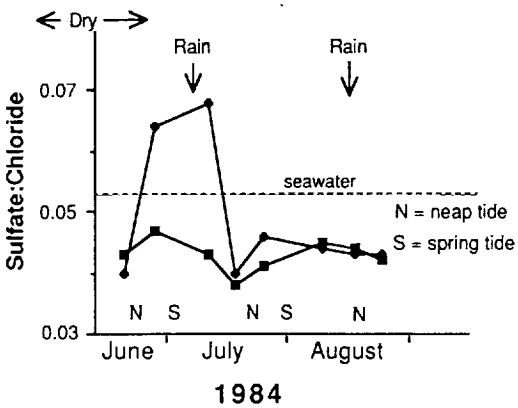

Fig. 4. Average SO_4^{2-} : Cl^- ratios in pore waters at sites T (■) and SP (◆) as a function of tidal regime and rainfall during summer 1984.

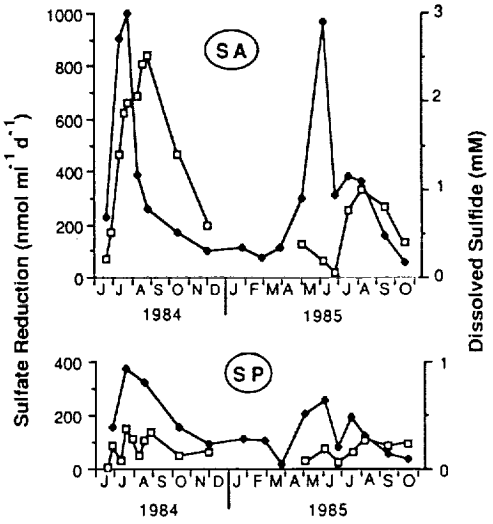

Fig. 5. Concentrations of dissolved sulfide (□) in pore waters at sites SA and SP. Values represent averages over the upper 20 cm of soil. Sulfate reduction rates (◆) from Fig. 3 are included for comparison to sulfide data.

to ~2.5 mM in August 1984 (Fig. 5). Sulfide concentrations in August at 2.0 cm were >1.0 mM and at 17.5 cm were >3.5 mM. These high concentrations of sulfide were prevalent in soils that supported stands of *S. alterniflora* 2 m or more high. Concentrations of sulfide at SA during 1984 began to level off near the end of the aboveground growth period in late July, but increased again in late August despite the fact that SO_4^{2-} reduction had decreased nearly fourfold and SO_4^{2-} : Cl^- ratios (Fig. 3) were increasing.

Dissolved sulfide concentrations were much lower at site SA during 1985 compared to the preceding year (Fig. 5), and the concentrations of sulfide decreased once the plants began to grow in May. Samples collected from the separate set of sippers deployed in the narrow band of tall *S. alterniflora* that was not affected by fly larvae in 1985 contained nearly 2 mM sulfide (data not shown) compared to concentrations of ~250 μM at SA (Fig. 5). High concentrations of sulfide were associated routinely with the tall form of the grass. Once plant growth ceased in June, sulfide concentrations increased at SA to 1.0 mM but never approached the >2.5 mM levels of 1984. This finding indicated that sulfide was removed from solution most effectively when plants were growing.

Dissolved sulfide concentrations at site SP were low compared to SA (Fig. 5). Values at site T were similar in magnitude to those at SP but did not vary as much (data not shown). Sulfide was never detected in the upper ~10 cm at either SP or T even though SO_4^{2-} reduction was routinely detected in this region at SP.

Alkalinity values varied from ~1.5 to >10 meq liter^{-1} and varied seasonally in a manner almost identical to dissolved sulfide concentrations (data not shown). The pH of the pore waters generally ranged from 6 to 7.5. Occasionally, we noted pH values at site SP of ~5.8.

Average dissolved iron concentrations were <10 μM at site SA during 1984, but were always detectable in the pore water even when sulfide concentrations were high (Fig. 6). Dissolved iron concentrations decreased at SA when plants were actively elongating and remained low throughout the remainder of 1984. The highest values at SA were in the upper 2 cm. The presence of high concentrations of dissolved sulfide and iron at SA during 1984 resulted in the supersaturation of Mackinawite and amorphous ferrous sulfide in pore waters (Fig. 7). The SA data points in Fig. 7 that represent undersaturation of FeS minerals were from samples collected in 1985.

During 1985, average dissolved iron concentrations at site SA increased to as high

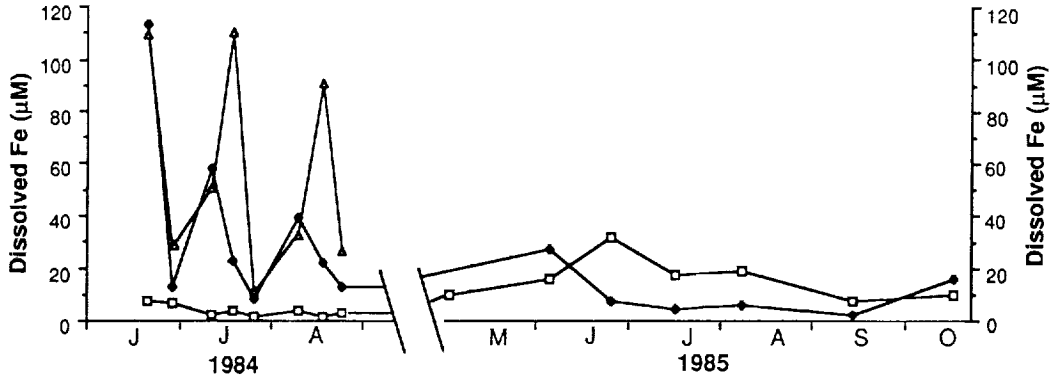

Fig. 6. Concentrations of dissolved iron in the pore waters at sites SA (□), T (△), and SP (◆). Values represent averages of the upper 20 cm of soil.

as 30 μM and were higher than values at SP (Fig. 6). The increase in iron occurred during the period of rapid SO_4^{2-} reduction in May–June, and dissolved iron concentrations remained relatively high once SO_4^{2-} reduction decreased in magnitude and sulfide increased (Fig. 5).

Dissolved iron concentrations at SP and T varied greatly throughout the study (Fig. 6). These variations were most prevalent in 1984 and in the upper 10 cm of sediment (depth data not shown). For example, dissolved iron at site SP decreased from 290 μM to <10 at 2 cm during an 8-d period in June 1984 and increased again to 140 in July. These large variations coincided roughly with changes in desiccation events and, therefore, with changes in SO_4^{2-} : Cl^- ratios (Fig. 4). For example, increases in SO_4^{2-} : Cl^- ratios (indicative of sediment oxidation) were accompanied by decreases in dissolved iron. Dissolved iron concentrations were relatively low and uniform below 15 cm in sediments where dissolved sulfide was detected. It appeared that sediment oxidation primarily was responsible for the removal of dissolved iron from solution in the upper 5–10 cm at SP while monosulfide precipitation was responsible for iron removal below 15 cm.

We routinely noted large quantities of ferric iron visually in the SP sediments when coring and often found large amounts of ferric iron in certain sipper samples before filtering. The ferric iron within sippers was not due to oxidation of ferrous iron as it entered the sipper, since the sippers maintained anoxia during sample collection. Ferric iron was not detected visually in sippers located at any sampling site except SP. The pore size of the sipper collar was 50 μm, which was large enough to allow visible ferric iron particles to pass.

The large variations and high concentrations of dissolved iron at site SP during 1984 were not noted in 1985 (Fig. 6). We may not have sampled during periods when dissolved iron concentrations were high, since we did not sample often during 1985. In addition, we did not note unusually high SO_4^{2-} : Cl^- ratios at SP during summer 1985. In most instances, ferrous sulfide minerals

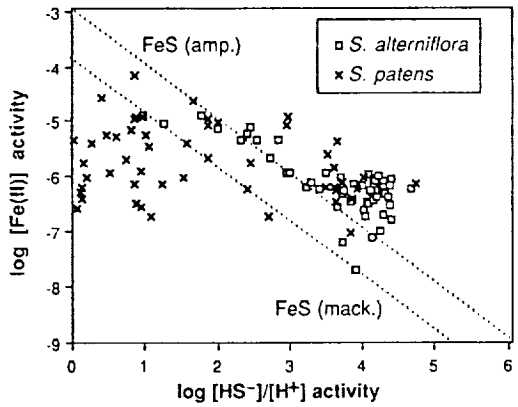

Fig. 7. Calculated values for the ion activity product of $(Fe^{2+})(HS^-)/(H^+)$ for pore waters collected from sites SA and SP during 1984 and 1985. Dotted lines represent pK_{sp} values for amorphous FeS and Mackinawite. Points above the dotted lines are supersaturated. Activity coefficients for Fe^{2+} and HS^- are from Davison (1980) and stability constants are from Berner (1967).

were undersaturated in the sediments at SP during 1984 (Fig. 7). The data points in Fig. 7 that represent supersaturated conditions with respect to FeS were from samples collected from the deepest sipper (15–20 cm).

Discussion

The high sampling frequency used during the growing season in 1984 provided data that demonstrated important relationships between plant processes and belowground biogeochemical transformations in *S. alterniflora* soils. Most important were the findings that SO_4^{2-} reduction responded quickly to changes in plant physiology and that redox processes within the sediments also were influenced by the growth cycle of the plants. During active vegetative growth, SO_4^{2-} reduction was stimulated while the soils were supplied with sufficient oxidants to cause a relatively rapid turnover of the sulfide produced by SO_4^{2-} reduction. Commencement of plant flowering in 1984 resulted in dramatic changes in the magnitude of SO_4^{2-} reduction and the redox conditions within the soil. The high frequency of sampling in the *S. patens* soils delineated the dynamic effects of desiccation-inundation cycles on redox reactions.

Biogeochemistry of soils inhabited by tall S. alterniflora—A likely explanation for the sensitivity of SO_4^{2-} reduction to plant growth was that during active aboveground elongation plants were leaking dissolved organic compounds into the soil and fueling anaerobic bacterial metabolism. Although the source of these compounds is unknown, there are two aspects of belowground plant metabolism that potentially influence leakage of DOC from rhizomes. First, it has been shown that production and redistribution of biomolecules in tall *S. alterniflora* follow a trend that coincides with the temporal variations noted here for SO_4^{2-} reduction. Rhizomes of tall *S. alterniflora* remobilize nonstructural carbohydrates once growth begins in spring, and these compounds (primarily sucrose) help to support early culm growth (Lytle and Hull 1980; Steen and Larrson 1986).

It has also been shown that new rhizomes are produced during the growth period in stands of tall grass (Lytle and Hull 1980). Once flowering occurs, carbohydrates are again immobilized rapidly in rhizomes and the sugar content increases more than twofold. Remobilization of sugars in rhizomes and downward translocation of current photosynthate for incorporation into new rhizomes only occurs during the period of aboveground growth (Lytle and Hull 1980). Hence, leakage of a portion of this material or of associated metabolites may serve as a source of DOC for SO_4^{2-} reduction.

The magnitude of carbohydrate loss from rhizomes studied by Lytle and Hull (1980) was insufficient to support the large increase in SO_4^{2-} reduction noted at site SA during summer 1984, particularly since most of the remobilized carbon was certainly used for plant growth and metabolism. Therefore, photosynthate transported from aerial plant parts during rhizome structural production must have contributed to DOC loss to the soil.

Short stands of *S. alterniflora* do not display the temporal trends in organic carbon distribution noted for tall stands. This discrepancy presumably occurs because short stands do not produce significant amounts of new rhizome material during aboveground growth and because shorter stands continue vegetative growth after the onset of flowering but tall stands do not (Lytle and Hull 1980; Steen and Larrson 1986). This distinction between tall and short stands of *S. alterniflora* may explain why previous studies have not noted the relationship between plant growth stage and soil microbial activity, since no previous studies have measured temporal changes in microbial activity in tall stands of *S. alterniflora* so frequently.

The second aspect of root metabolism that was probably important in regulating microbial activity in soils at site SA was the anaerobic metabolic activity of the roots. *Spartina alterniflora* roots have been shown to produce low-molecular-weight organic compounds such as ethanol and malate when roots metabolize anaerobically (Mendelssohn et al. 1981). Sulfate-reducing bacteria can use these compounds directly. It has been suggested that ethanol produced by roots diffuses into the surrounding pore

water (Mendelssohn et al. 1981; Mendelssohn and McKee 1987).

We did not measure redox potential, but the presence of high concentrations of dissolved sulfide in the soils at site SA must have kept the Eh quite low, and it is likely that anaerobic biochemical pathways were important in total root metabolism. Although anoxic conditions have been cited as necessary for the production of various low-molecular-weight dissolved organic compounds by rooted macrophytes (Mendelssohn et al. 1981; Kilham and Alexander 1984; Pregnall et al. 1984), our study noted that rates of SO_4^{2-} reduction decreased after plant flowering occurred even though sulfide concentrations increased. Therefore, since anoxia did not decrease following flowering it seemed that plant growth stage was more influential than anoxia in stimulating SO_4^{2-} reduction. Additional research is needed to determine the details of coupling between plant metabolism and activities of adjacent soil microflora.

Decomposition of solid-phase organic matter would not have resulted in such rapid changes in the rates of SO_4^{2-} reduction. Background rates of 200–400 nmol ml^{-1} d^{-1} before and after the period of active plant growth were probably due to decomposition of less labile solid-phase organic material produced belowground by the plants. This solid-phase material is relatively recalcitrant (Schubauer and Hopkinson 1984) and would not be responsible for rapid changes in the rates of soil microbial activity.

If we assume that the increase in the rate of SO_4^{2-} reduction in June–August 1984 was due to the utilization of *S. alterniflora* exudates by SO_4^{2-}-reducing bacteria and that the stoichiometry of carbon utilization during SO_4^{2-} reduction is $2C:SO_4^{2-}$, then the quantity of exudate C needed to fuel SO_4^{2-} reduction during the 42-d period of active plant elongation was ~140 g C m^{-2} or 17 mg C $liter^{-1}$ d^{-1}. Dissolved organic carbon concentrations during this period were 10–15 mg $liter^{-1}$ (Hines et al. in prep.), which is similar in magnitude to the amount of exudate C needed to fuel SO_4^{2-} reduction per day. Exuded C would have turned over rapidly and probably did not accumulate in the pore waters, while the DOC measured probably represented a less labile pool. If the labile organic C accounted for 2% of the total DOC (Meyer-Reil et al. 1980) then the labile C would have turned over every ~30 min. This rate is not unusually fast in bacterially active sediments where turnover times for labile organic monomers can be as short as minutes (King and Klug 1982).

Rates of SO_4^{2-} reduction may have been overestimated because of the stimulation of SO_4^{2-} reduction activity from leakage of organic material during coring. It is also possible that this artifact varied temporally with changes in plant physiology and that the relationship between plant growth and SO_4^{2-} reduction was spurious. Although it was not possible to determine whether SO_4^{2-} reduction was artificially stimulated during sampling, the temporal variations in SO_4^{2-} : Cl^- agreed with the temporal changes in SO_4^{2-} reduction, giving credence to the conclusion that SO_4^{2-} reduction responded to changing plant activity even if actual rates were overestimated. This ratio was measured using sipper samples and was not subject to coring artifacts.

Infiltration of tidal water and tidally mediated subsurface water flow in marshes (Hemond and Fifield 1982) prevented use of $SO_4^{2-}:Cl^-$ ratios to quantify rates of SO_4^{2-} reduction (Howarth and Teal 1979). Changes in $SO_4^{2-}:Cl^-$ ratios are good indicators of relative changes in SO_4^{2-} reduction, however, and the $SO_4^{2-}:Cl^-$ data in Fig. 3 clearly indicate that the rates of SO_4^{2-} reduction decreased at the end of July 1984. Furthermore, A. Giblin (pers. comm.) found that SO_4^{2-} reduction rates measured by injecting and incubating radiolabel directly into marsh soils in the field did not result in rates significantly different from those obtained by coring. Sediment oxidation was enhanced greatly during *S. alterniflora* growth. This oxidation would tend to increase $SO_4^{2-}:Cl^-$ ratios so that the differences in ratios noted during and after plant growth would have been even larger if they were controlled by differences in rates of SO_4^{2-} reduction alone.

The beginning of *S. alterniflora* flowering in 1984 and the end of vegetative growth in 1985 were accompanied by changes in

the oxidation of the soils as evidenced by increases in the concentrations of dissolved sulfide. Residence time of dissolved sulfide in pore waters can be calculated by dividing sulfide concentrations by rates of SO_4^{2-} reduction and correcting for sediment water content. During aboveground plant growth, sulfide was removed from pore water within 1–2 d (1984) or ~0.2 d (1985), whereas after growth ceased, sulfide was removed less rapidly or even accumulated. For example, following plant flowering at site SA in 1984, the concentration of sulfide increased ~40% and the residence time of pore-water sulfide increased to as long as 10 d. Therefore, the plants were instrumental in supplying oxidants to the soils during growth, and a major portion of the sulfide produced was removed rather quickly.

During 1985, sulfide was nearly completely removed from the soil during the short growing season yet increased severalfold once vegetative growth ceased. The constant presence of dissolved iron in the soils at site SA (albeit at low concentrations) would be expected if the plants were continuously supplying oxidants to the soil and therefore causing a subsurface redox cycle of iron and sulfur.

Previous studies (Dacey and Howes 1984; Howes et al. 1986) reported that the major mechanism for plant-mediated sediment oxidation was the movement of air into the soils as a result of removal of soil water by evapotranspiration. Apparently, evapotranspiration at site SA was most active when plants were growing aboveground. During rapid plant elongation in 1984, SO_4^{2-} reduction was rapid enough to provide considerably more sulfide and alkalinity to the pore water than were actually present. Certainly, any oxidation of the soil by plant activity would decrease the concentrations of both of these chemical constituents. If evapotranspiration at site SA during July 1984 was 10 liters m^{-2} d^{-1} (Howes et al. 1986 reported 9.1 liters m^{-2} d^{-1} for plants that were 102 cm tall), then ~90 mmol m^{-2} d^{-1} of oxygen entered the soil—a quantity sufficient to oxidize nearly half of the sulfide produced. Evapotranspiration rates at site SA in 1984 were probably higher since the plants quickly grew to heights of 2 m. A decrease in plant activity would result in decreased evapotranspiration and, therefore, soil oxidation; it would be expected that soil oxidation rates would decrease late in the growing season or earlier if plant activity was curtailed (e.g. June 1985 at site SA).

To our knowledge, the present results are the first to demonstrate such rapid change in redox status of marsh soils upon flowering. It is noteworthy that we sampled in a stand of tall, quickly growing plants frequently enough to delineate rapid changes. Further, a large percentage of tall plants generate flowers compared to short plants (Hull et al. 1976) and tall plants cease vegetative growth at the onset of flowering (Lytle and Hull 1980). Rapid reallocation of carbon to reproductive organs in most of the culms may have resulted in a rapid decrease in the entrance of oxygen into the soils presumably because of decreased evapotranspiration. Additional work is needed to determine whether flowering and associated photosynthate allocation result in changes in rates at which *S. alterniflora* supplies oxidants to soils.

Dissolved sulfide removal at site SA during July 1984 could have occurred by oxidation or by precipitation as an iron monosulfide mineral. It seemed unlikely that the rapid formation of pyrite was a significant sink for sulfide in the soils at site SA since the chromium-reducible fraction, which includes pyrite, accounted for only a small percentage of the total SO_4^{2-} reduction rate and solubility calculations indicated that iron monosulfides were supersaturated in the pore waters. These minerals were undersaturated in pore-water samples collected in 1985 at site SA and in most of the samples collected at site SP, suggesting that other minerals may have been the major end products of SO_4^{2-} reduction at those times. This conclusion was supported by the finding that the percentage of ^{35}S recovered by chromium reduction was much higher in these samples than in those collected at site SA during summer 1984. Howarth (Howarth and Teal 1979; Howarth and Giblin 1983) reported that pyrite was the major sink for sulfide produced in *S. alterniflora*-inhabited soils in Great Sippewissett

and Sapelo Island marshes. Our data indicate that the distribution of reduced sulfur varied annually and with depth and season.

The highest dissolved sulfide concentrations noted in these New Hampshire marsh soils were always associated with the tallest *S. alterniflora* plants. This contradicts the findings that even low concentrations of sulfide inhibit the growth of *S. alterniflora* (Howes et al. 1981; King et al. 1982). Several hypotheses have been advanced to explain why *S. alterniflora* grows taller along creekbanks, including the removal of sulfide and the flux of iron via groundwater movement (King et al. 1982) and the resupply of iron via internal redox cycling (Giblin and Howarth 1984). Howes et al. (1981, 1986) found higher Eh values in stands of tall *S. alterniflora* and suggested that more productive plants oxidize the soils more fully and that reducing conditions inhibit plant production.

Our data clearly demonstrated that the concentration of dissolved sulfide in marsh pore waters can be quite high in soils that support very tall *S. alterniflora* plants. In fact, sulfide concentrations decreased where plants were shorter. Although we did not measure Eh values in these soils, the Eh at site SA must have been low since dissolved sulfide concentrations were high. Teal and Kanwisher (1961) reported relatively low Eh values in creekside soils in a Georgia *S. alterniflora* marsh—in some instances more reducing than soils inhabited by short plants. They did note, however, that within the creekside soils tallest plants usually were present where Eh values were highest. Our data indicate that controls of plant productivity are still unclear.

Influence of fly infestation on biogeochemistry of tall S. alterniflora—Ribbon-winged fly larvae are introduced into the plants through holes bored into the stems by adult flies. The larvae consume the new shoots and therefore stop any new aboveground growth. The infestation of *S. alterniflora* by fly larvae was a natural experiment in marsh alteration and provided additional information and support of data from the previous year. First, comparison of data from 1984 and 1985 showed the close relationship between plant elongation and SO_4^{2-} reduction in both years despite extreme differences in growing seasons. Plant growth began several weeks earlier in 1985 than in 1984 and it is possible that total growth in 1985 may have surpassed growth in 1984 if fly infestation had not destroyed new production. Second, the transformation of tall grass to short grass by larval grazing confirmed that high concentrations of dissolved sulfide were found only where *S. alterniflora* was tall. Finally, the data demonstrated the changes in belowground geochemistry that occur immediately after an infestation by such herbivores. Once the larvae began to hinder aboveground growth, the plants failed to produce sufficient dissolved organic matter to support rapid anaerobic activity. A decrease in SO_4^{2-} reduction prevented the accumulation of high concentrations of sulfides in the soils, and the final result (June 1985 dissolved sulfide profiles) was a marsh environment similar geochemically to the short *S. alterniflora* site T. These results also showed that the belowground material that was present at site SA at the beginning of the 1985 growing season was insufficient to support rapid SO_4^{2-} reduction without the production of the dissolved organic component. Hence, in these soils, rapid productivity during the preceding year did not make the soils at site SA appear significantly different from other less productive soils.

Biogeochemistry of soils inhabited by S. patens—The subsurface biogeochemistry of *S. patens* soils has not been examined in any detail compared to *S. alterniflora*. On an area basis, however, *S. patens* is the dominant marsh grass in northern New England. The SO_4^{2-} reduction rates presented here are the first seasonal data reported for *S. patens* marshes. In general, SO_4^{2-} reduction was less rapid in the *S. patens* soils than in soils inhabited by *S. alterniflora* in this New Hampshire marsh and in other marshes where SO_4^{2-} reduction has been measured. SO_4^{2-} reduction proceeded at relatively high levels in the soils at site SP throughout the year, however, and the seasonal pattern followed changes in temperature. During summer, SO_4^{2-} reduction at SP reached levels as high as 780 nmol ml^{-1} d^{-1} with integrated rates of 75 mmol m^{-2} d^{-1}.

Unlike the depth profiles of SO_4^{2-} reduction at site SA, the maximum rate of SO_4^{2-}

reduction at SP was found at varying depths depending on the previous hydrologic conditions which affected desiccation of the soil. In general, the maximal rate was found at ~11 cm when the surface soils were oxidized and at ~1–2 cm when the soils were saturated with water and presumably reducing in character. Changes in the location of the SO_4^{2-} reduction maximum were rapid, depending on the desiccation history of the soil. As discussed below, this rapid change in the depth distribution of SO_4^{2-} reduction was accompanied by changes in concentrations of redox-sensitive chemicals.

Our results showed clearly that the soils at site SP were subjected to rapidly changing geochemical conditions mediated primarily by desiccation events. Desiccation caused the oxidation of reduced sulfur compounds and an increase in the SO_4^{2-} : Cl^- ratio in pore water in a manner similar to that reported for a Delaware marsh (Luther et al. 1986). This oxidation at site SP caused the removal of dissolved iron(II) and the oxidation of reduced iron associated with reduced sulfur minerals. Once the sediments became waterlogged after spring tides or rain, they again became anoxic, iron dissolution occurred, and SO_4^{2-} reduction increased. This cycle in oxidation and reduction of the soil at site SP occurred on time scales of days in some instances and must have resulted in a supply of iron(II) and (III) in the upper 10 cm at SP for reaction with sulfide, since sulfide was always depleted.

We detected rapid changes in redox conditions at site SP. For example, dissolved iron concentrations at the 2-cm depth varied from 5.9 μM on 27 June 1984 to 138 on 10 July to 9.9 on 17 July. The rate of SO_4^{2-} reduction at that depth varied from 170 to 780 μmol liter^{-1} d^{-1} during that same interval. Although no SO_4^{2-} reduction rate data were collected for the 10 July sample at this site, the SO_4^{2-} : Cl^- ratio on that date was even higher than on 27 June and decreased from 0.075 to 0.044 during the interval from 10 to 17 July. Therefore, the ~4.5-fold increase in SO_4^{2-} reduction between 27 June and 17 July probably occurred from 10 to 17 July. Although there was a dramatic decrease in dissolved iron during that week, the increase in SO_4^{2-} reduction was sufficient to remove that amount of iron more than 30 times. The decrease in dissolved iron quantified by the difference between values on 10 and 17 July thus represented only a small portion of the iron that must have been transformed to completely remove sulfide.

The above illustrates only one example of what must be a continuous desiccation-driven cycle of oxidation and reduction in this marsh and probably in many others. Wide variations in iron concentrations in the upper 10 cm and even in sulfide concentrations at 17.5 cm at site SP attest to the activity of the iron and sulfur cycles in these soils. These chemical variations were more rapid than those seen elsewhere (i.e. dissolved iron concentrations in Sippewissett as reported by Giblin and Howarth 1984), but may simply reflect our frequent sampling at site SP. The sippers both allowed this frequent sampling and avoided confounding variation in time with horizontal variation, which must be extreme in salt marshes.

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THE VARIABILITY OF BIOGENIC SULFUR FLUX FROM A TEMPERATE SALT MARSH ON SHORT TIME AND SPACE SCALES

MICHAEL C. MORRISON and MARK E. HINES*

Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824-3525, U.S.A.

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Abstract—Three emission chambers were deployed simultaneously to measure rates of emission of dimethyl sulfide, methane thiol and carbonyl sulfide within or across vegetation zones in a New Hampshire salt marsh. Short term (a few hours) variation in fluxes of all S gases from replicate sites were small within a monospecific stand of either *Spartina alterniflora* or *S. patens*. The quantity of emergent biomass and the type of vegetation present were the primary factors regulating the rate of emission. Dimethyl sulfide fluxes from the *S. alterniflora* soils ranged from 800 to 18,000 nmol $m^{-2} h^{-1}$ compared to emissions of 25–120 nmol $m^{-2} h^{-1}$ from *S. patens*. This difference was probably due to the presence of the dimethyl-sulfide precursor dimethylsulfoniopropionate which is an osmoregulator in *S. alterniflora* but not in *S. patens*. Methane thiol emissions from *S. alterniflora* were 20–280 nmol $m^{-2} h^{-1}$ and they displayed a similar diel trend as dimethyl sulfide, although at much lower rates, suggesting that methane thiol is produced primarily by leaves. Methane thiol emissions from *S. patens* were 20–70 nmol $m^{-2} h^{-1}$. Net uptake of carbonyl sulfide of 25–40 nmol $m^{-2} h^{-1}$ occurred in stands of *S. alterniflora* while net efflux of 10–36 nmol $m^{-2} h^{-1}$ of carbonyl sulfide occurred in stands of *S. patens*. In general, ranges of emissions of sulfur gases were similar to most other published values.

Key word index: Biogenic sulfur emissions, salt marshes, variability, carbonyl sulfide, methane thiol, dimethyl sulfide, *Spartina alterniflora*, *Spartina patens*.

INTRODUCTION

The existence of biogenic sulfur emissions has been recognized at least since the discovery of the atmospheric Junge layer in the early 1960s (Junge, 1963). The importance of these emissions as a component of the global cycle of sulfur (Möller, 1984; Andreae, 1985), their contribution to the pH of precipitation (Charlson and Rodhe, 1982), and their potential impact on global radiation balance and climate (Crutzen, 1976; Shaw, 1983; Bates *et al.*, 1987; Charlson *et al.*, 1987; Rampino and Volk, 1988) have spurred interest in the composition, magnitude and variability of these emissions from different sources.

The ability to estimate the annual emission of biogenic sulfur to the atmosphere on a global scale depends on a knowledge of the area of the emission surfaces and the magnitude of the flux. The area extent of emission surfaces may be determined from satellite imagery, maps and surveys. If emissions vary predictably with seasonal or diurnal cycles, or in response to the biota, then an estimate may be made of the per area emissions based on information about species composition, season length, temperature regime, day length, etc. However, if emissions vary widely and unpredictably, then much greater uncertainty must accompany these estimates. Such wide variability has characterized some emission measurements from salt marsh environments. Adams *et al.* (1981a) attributed this variability to 'hot spots', or the presence of localized, extremely active environments. Goldan *et al.* (1987) characterized salt marsh emissions as having greater variability than agricultural environments. Steudler and Peterson (1985) reported DMS fluxes which varied hourly by orders of magnitude. Cooper *et al.* (1987a) observed that changing tides caused a four order of magnitude variation in H_2S emissions from a non-vegetated site in a salt marsh. Despite the wide variation in reported S gas fluxes, the less than two-fold variation in S gas emissions from two flux chambers deployed simultaneously by de Mello *et al.* (1987) suggested that emission rates are not as unpredictable as previously thought. In addition, except for H_2S emissions, recent data tend to demonstrate that S emissions from tidal wetlands often vary in some predictable manner related to temperature, period of the day and the species of vegetation present. In this paper, we report an investigation of the short temporal (several hours) and spatial (several meters) scale variability of biogenic sulfur emissions from a New Hampshire *Spartina* sp. marsh using a multiple chamber approach. In addition, we report S emission rates from soils inhabited by *S. patents*, an abundant grass species in marshes of northern New England.

* To whom correspondence should be addressed.

METHODS

Study site

The salt marsh studied (Chapman's Marsh) was located in Stratham, NH, U.S.A., on the Squamscott River (Fig. 1). The marsh soils are poorly drained silts rich in organic material approximately 1 m thick overlying silty sand. Two vegetation species dominate the marsh: *Spartina alterniflora* for several m near the creek banks, and *S. patens* over much of the remainder of the marsh. Details of the marsh and its soils may be obtained from Breeding *et al.* (1974) and Hines *et al.* (1989).

Nine emission sites were chosen; three in each of three vegetation zones (Fig. 1). The first zone (sites A1–A3) was a uniform, nearly pure stand of *S. alterniflora* in the middle intertidal region ~ 2 m from the creek bank. The second zone (sites T1–T3) was located approximately 4 m from the creek in the transition between the *S. alterniflora* and *S. patens* zones but was dominated by *S. alterniflora*. The last zone (P1–P3) was located approximately 8 m from the creek bank and contained a uniform stand of *S. patens*.

Field sampling

Aluminum collars, 0.3 m × 0.3 m square, were installed at each emission site in early spring before the grasses began to grow insuring minimal disturbance to above and below ground portions of the plants during sampling. The inner surfaces of the collars were covered with an adhesive Teflon coating (Bytac) to prevent reactions of analytes with the aluminum.

Flux chambers were constructed with FEP Teflon film (0.127 cm thick) stretched over lexan frames (Fig. 2). The frames were assembled into boxes with open tops and bottoms, and continuous Teflon interiors. Several boxes could be stacked to form a chamber of any height necessary to enclose grasses. The addition of modified frames for sweep air inlet and vent, and a top frame, completed the chamber which fitted snugly over the collars in the field. Chambers were shaded to prevent excessive internal temperatures.

Sweep air was supplied from compressed gas cylinders of purified dry air (N_2 and O_2) (Fig. 2). Sweep air was delivered to the chambers via Tygon tubing (0.635 cm i.d.) at a rate sufficient to turn over the inside atmosphere every 10–15 min (3–9 ℓ min^{-1} depending on the number of chamber tiers needed to enclose a particular type of vegetation). Preliminary experiments determined that the addition of CO_2 to sweep air had no effect on short term S gas emissions. For the 1988 samples, sweep air flow to each chamber was controlled by a mass flow controller. Gilmont rotameters were used to control sweep flow for the 1987 samples.

Samples were drawn from the interior of the chamber near the vent frame via FEP Teflon tubing (0.165 cm i.d.) at a flow rate of 250 ml min^{-1} (Fig. 2). Laboratory tests demonstrated that samples could be collected at rates over 500 ml min^{-1} without measurable breakthrough. Samples of 0.3–3.0 ℓ were trapped cryogenically with liquid nitrogen in sample loops constructed of 60 cm lengths of 0.165 cm i.d. (1.285 ml internal volume) FEP Teflon tubing. Moisture was removed from sample air by passage through PFA Teflon pipe surrounded by dry ice. Recovery tests showed that S gases were not lost within the drier (Morrison, 1988).

Samples were obtained under a ~ 1/2 atm vacuum to prevent condensation of oxygen in the sample loops. The vacuum was generated using a vacuum pump with a PFA Teflon needle valve placed just upstream of the sample loop (Fig. 2). Each sample loop had a Teflon-lined four-port valve which allowed maintenance of the vacuum in the sample loop until analysis. Sample flow rate was determined using a mass flow controller situated downstream of the sample loop while an integrating circuit totalized the sample volume. Sample loops were stored in liquid nitrogen in the field until transportation to the laboratory for analysis. Storage of loops up to the maximum durations experienced in the field (8 h) had no effect on recovery of S gases (Morrison, 1988). The maintenance of a vacuum and the fact that oxygen did not enter the loops over time indicated that the loops did not leak during storage.

Blanks were obtained by sampling the sweep air just before it entered the chamber in the field with driers and full tubing lengths in place. Typical blank values (in 10^{-9} g S ℓ^{-1}) were 0.10 for DMS, 0.00 for MeSH and 0.25 for COS. The blanks remained relatively constant for several hours, however they did decrease slowly with time. Contamination of the sweep air with COS at near ambient levels allowed for the determination of consumption of this gas. Blank values for DMS were very low compared to samples collected from areas inhabited by *Spartina alterniflora*. However, the DMS blank was only 2–5-fold lower than DMS concentrations in chambers placed over *Spartina patens*. The blank values were due to contamination of the sweep air by the Tygon tubing. Although replacing the Tygon with Teflon tubing virtually eliminated

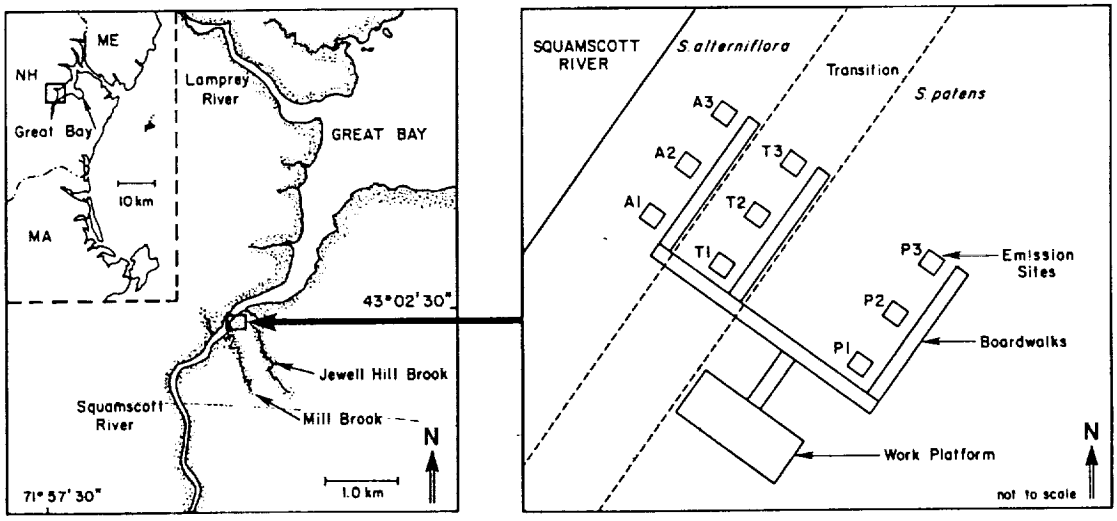
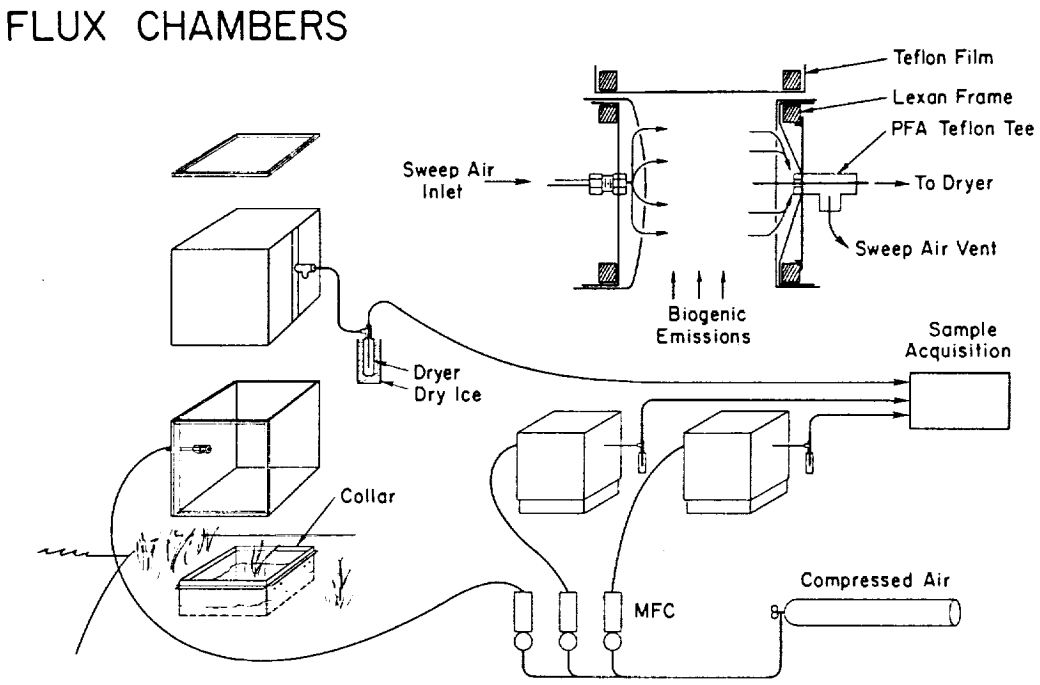
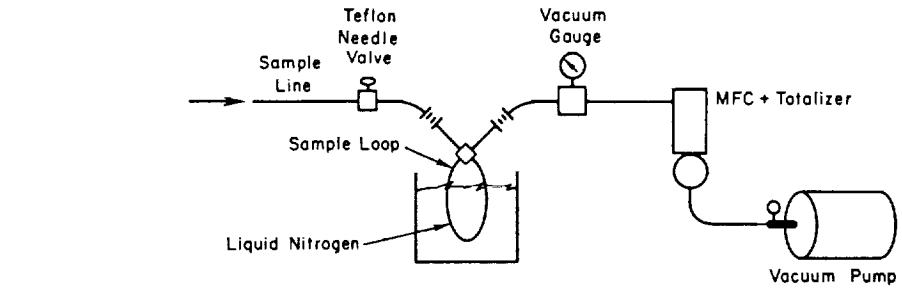


Fig. 1. Location of Chapman's Marsh in southern New Hampshire with a diagram of the sampling boardwalk and relative positions of replicate sampling sites.





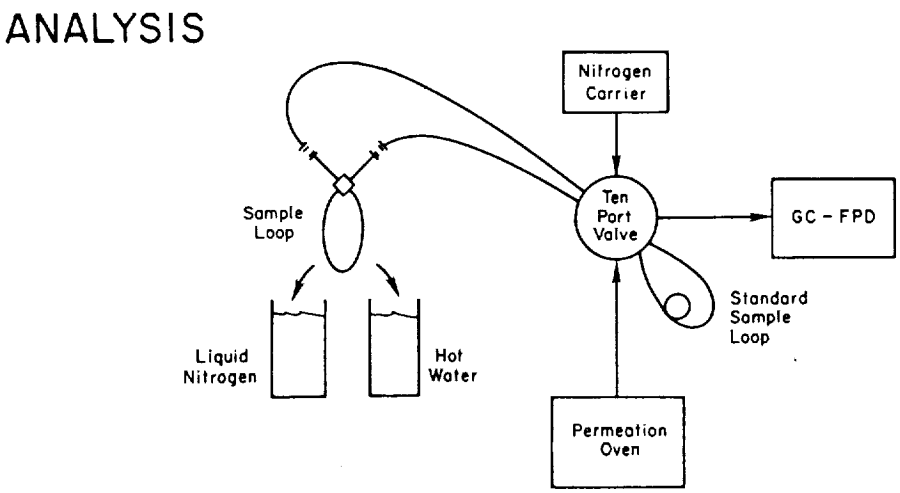


Fig. 2. Schematic diagram of flux chambers, sample acquisition system and analytical system used to measure rates of emission of biogenic sulfur compounds from wetlands.

the blank, we chose to use Tygon in the areas inhabited by *S. patens* to maintain continuity and to estimate COS uptake.

Three flux chambers were deployed simultaneously. To determine the intra-zone variability, all three chambers were deployed within one vegetation zone and several samples were collected over a short time period (3–4 h). On other occasions, one chamber was placed within each vegetation zone to determine inter-zone and diel variations. For sites which displayed very high fluxes of one particular S gas species (i.e. DMS), a small volume sample was collected just prior to a large one.

Analytical technique

Samples were analyzed on a Perkin-Elmer Sigma 300 gas chromatograph equipped with a sulfur dioxide doped, flame photometric detector and a 1.8 m × 0.3175 cm OD FEP Teflon column packed with 1.5% XE-60, 1% H_3PO_4, 60/80 Carbopack B (Supelco). Samples were remobilized by immersing the sample loops in a boiling water bath and loaded onto the column with a Teflon-lined ten-port valve (Fig. 2). The oven temperature of the gas chromatograph was programmed to begin at 50°C for 0.5 min, then ramp at 32°C min^{-1} to 90 °C, stay at 90 °C for 2.0 min, then ramp at 32 °C min^{-1} to 110 °C, remain at 110 °C for 1 min and then return to 50°C for the next sample. Sample analysis took approximately 6 min with a nitrogen carrier flow of 24 $cm^3 min^{-1}$. Chromatograms were integrated on a Perkin-Elmer LCI-100 plotter integrator.

Several modifications were made to the gas chromatograph to improve its performance. The hydrogen fuel for the detector was doped with a SO_2 permeation tube at $\sim 7.6 \times 10^{-11}$ g S s^{-1} in 1987 and $\sim 6.9 \times 10^{-10}$ g S s^{-1} in 1988. Doping resulted in decreased detection limits, improved linearity of calibration curves and it allowed for the detection of detector interference from co-trapped hydrocarbons and CO_2. Both CO_2 and CH_4 eluted early from the column and did not interfere with any of the compounds of interest here. A typical chromatogram for sites inhabited by either *S. alterniflora* or *S. patens* are shown in Fig. 3. The temperature of the permeation tube used to dope the fuel was maintained in a water bath at room temperature. The detector jet was replaced with a quartz glass jet of identical configuration as the original steel jet. A baffled vent for the detector was also installed to prevent inadvertent air pressure changes from affecting the detector flame.

The gas chromatograph was calibrated by dilution of permeation tube (VICI Metronics) emissions. Permeation tubes for each subject compound were maintained at 30°C in a Tracor model 412 Mini-perm Permeation Tube Calibration System. Tube loss rates were determined gravimetrically. Routine primary calibration was conducted just before and after field sample analysis by varying the rate of diluent (N_2) flow across the permeation devices, injecting a known volume from a standard sample loop (Fig. 2) and correcting for temperature, pressure and flow rate. The rate of diluent flow was determined using a calibrated pressure gauge which was situated upstream of the chamber just prior to a critical orifice. The quantities of standard S, in ng, delivered to the analytical column from the sample loop were 0.26–23.3 for DMS, 0.134–11.87 for MeSH and 0.16–14.12 for COS.

Relative recoveries of S gases were determined occasionally using permeation standards and a laboratory flux chamber fitted with tubing, drier and a cryogenic system which were identical to the field apparatus. These tests were conducted using either high concentrations of S gases provided directly from the permeation devices or from S standards which were diluted within a secondary Teflon chamber. The secondary chamber consisted of an entry port from the primary chamber, an entry port which delivered diluent gas, an exit port which delivered diluted S gases to the laboratory flux chamber and a vent. The rates of diluent flow and vent loss were monitored directly with mass flow meters. The rate of flow from the secondary dilution chamber to the flux chamber was calculated by difference. The rate of diluent flow to the final flux chamber was also monitored with a mass flow meter. Mass flow meters never came in contact with the analyte compounds. The two chamber dilution system together with additional dilution provided by the flux chamber/sweep air system yielded concentrations of S gases within the chamber that were similar to those encountered in field samples (0.3–26.0 ng ℓ^{-1}). The addition of high humidity to the chamber had little to no effect on the recovery of S gases at both high and low concentrations of S. Recoveries using the cryotrapping system were 60–85% of results using the direct sample loop. The lowest recoveries were for compounds that eluted last from the column. Although the recovery of S gases was lower using the cryotrapping system, recovery percentages were consistent over all experimental conditions and were used to calculate the final fluxes. The coefficient of variation of triplicate standards of dimethyl sulfide (DMS), methane thiol (MeSH) and carbonyl sulfide (COS) handled identically to field samples were 1.6%, 2.1% and 1.5%, respectively at a simulated emission rate of ~ 3.0 nmol $m^{-2} h^{-1}$. However, we estimated that the error for field samples was closer to 15% (Morrison, 1988). The detection limits for the compounds of interest were 35–70 pg ℓ^{-1} at a signal to noise ratio of 2. The minimum emission rates that could be determined under typical field conditions for DMS, MeSH and COS, and were 1.4, 0.8 and 0.7 nmol $m^{-2} h^{-1}$, respectively. When Tygon tubing was used, the minimum emission rates for DMS and COS increased to 6.8 and 12.3 nmol $m^{-2} h^{-1}$, respectively.

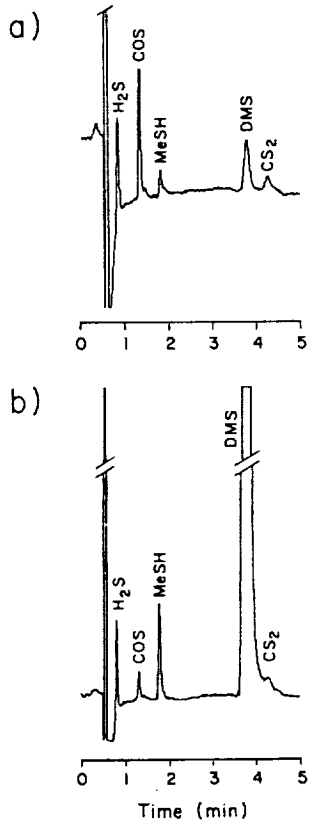


Fig. 3. Typical chromatograms of gaseous sulfur compounds in samples collected from flux chambers deployed over soils inhabited by *Spartina patens* (A) and *S. alterniflora* (B).

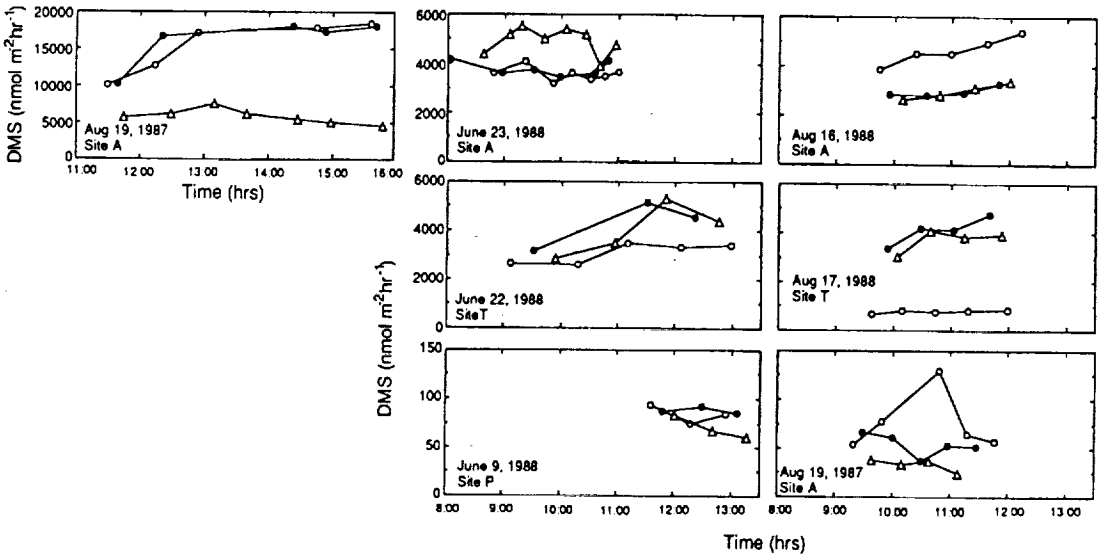


Fig. 4. Emission rates of dimethyl sulfide (DMS) from the various sites over short time scales on different dates. Replicate sites ○, 1; ●, 2; △, 3. Note that vertical and horizontal scales are identical for all plots except for 19 August 1987.

RESULTS

During 1987, the *S. alterniflora* at site A was approximately twice as tall as the *S. alterniflora* at site T. Although we did not measure the biomass within collars, there was a much lower density of culms within A3 compared to the other sites at A. In 1988, *S. alterniflora* plants at site A were shorter and less dense than in 1987. The *S. alterniflora* at site T during 1988 was nearly the same height as at site A. However, by mid-August 1987, the biomass within site T1 was considerably less than at the other T sites which remained similar to all of the A sites. Large annual variations in productivity and rates of biogeochemical processes within this marsh were noted previously for the period 1984–1986 (Hines *et al.*, 1989).

Dimethyl sulfide emissions

The variation in fluxes of DMS was a function of plant species and the apparent biomass of grass at each site. Fluxes of DMS from the *S. alterniflora* sites were the highest of all observed fluxes with rates generally 4000–6000 nmol m^{-2} h^{-1} (Figs 4 and 5). Emissions of DMS were extremely high at site A during mid-August 1987 when rates reached > 19,000 nmol m^{-2} h^{-1}. The fluxes of DMS from *S. patens*-inhabited sites (sites P1–P3) were much lower at 40–90 nmol m^{-2} h^{-1} (Figs 4 and 5).

During experiments of short duration, there was little temporal variation in DMS flux (Fig. 4). There was little variation in flux among replicate sites as well, except where there were marked differences in the quantity of biomass within collars. These exceptions were site A3 during 1987 and site T1 during 1988. These two locations had considerably less biomass than the others. Using a combination of column density and height, it was found that site T1 in mid-August

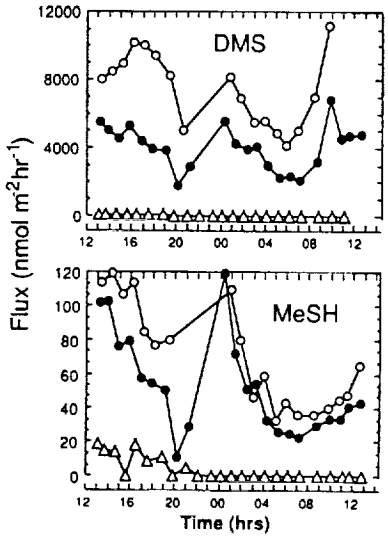


Fig. 5. Variations in dimethyl sulfide (DMS) and methane thiol (MeSH) emissions from sites A1 (○), T1 (●) and P1 (△) for a 24 h period in 1987. Site A soils were flooded from ~20:15 to 00:15. Site T soils were flooded from ~20:45 to 23:55.

1988 had ~ 15–20% of the emergent biomass as sites T2 and T3. Site T1 also displayed ~20% of the flux of DMS compared to the other sites at T. Earlier in the growing season (June) there were less noticeable differences in biomass at sites T1-3 and DMS fluxes were similar. In contrast with 1987, sites A and T in 1988 had similar quantities of emergent biomass and DMS fluxes from sites A1-3 and T2-3 were similar.

Fluxes of DMS varied by slightly more than a factor of two during a 24 h period in August 1987 (Fig. 5). Emissions were highest at site A and extremely low at

site P. Fluxes were highest during daylight hours and the temporal changes for the two sites inhabited by *S. alterniflora* showed similar trends. The differences noted on 5 August (Fig. 5) were similar to what was noted 6 days earlier during a shorter term preliminary study of these sites (data not shown). At both A and T, DMS fluxes increased after the marsh was flooded by tidal waters.

Methane thiol emissions

Fluxes of MeSH generally mimicked those of DMS, i.e. emissions were relatively constant for short time periods, highest from sites that contained the most biomass, highest during daylight hours and showed increases following tidal flooding (Figs 5 and 6). Rates of MeSH emissions were 100–150 nmol $m^{-2} h^{-1}$ during August 1987 and ~ 80 nmol $m^{-2} h^{-1}$ during 1988 in the *S. alterniflora* soils (sites A and T). Emissions of MeSH from the P soils were approximately one-third as rapid as those from the *S. alterniflora*-inhabited sites. The difference between the A and T sites and fluxes of MeSH at P were most evident during the 1987 studies when MeSH fluxes from the A and T sites were maximal.

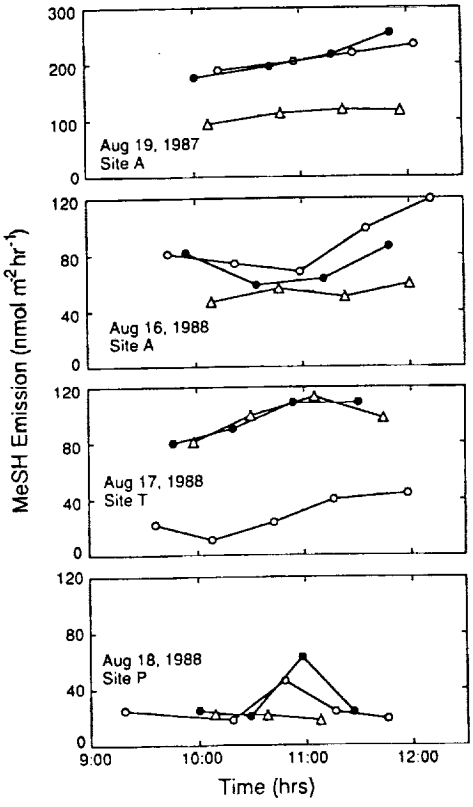


Fig. 6. Emission rates of methane thiol (MeSH) from the various sites over short time scales on different dates. Replicate sites ○, 1; ●, 2; △, 3. Note that vertical scales are identical except for 19 August 1987.

Carbonyl sulfide emissions

Quantification of COS emissions was affected by the Tygon tubing-imposed blank. Since blanks were not needed for the other gas species except for DMS in the *S. patens* soils, we did not measure them routinely on each sampling day. Figure 7 depicts results of a typical set of blank-corrected data for COS emissions from sites A and P. Although there was little variation in COS flux among sites within a particular vegetation type, there was net uptake of COS (~ 35 nmol $m^{-2} h^{-1}$) at site A as opposed to a net efflux of COS (~ 20 nmol $m^{-2} h^{-1}$) to the atmosphere from site P.

DISCUSSION

Emissions of DMS were controlled by plant species type and biomass. The finding that DMS flux was two orders of magnitude higher from *S. alterniflora* compared to *S. patens*, agreed with the fact that *S. patens* does not produce measurable quantities of the osmoregulatory compound dimethylsulfoniopropionate (DMSP) (Dacey *et al.*, 1987). The decomposition of this compound has been shown to be the primary precursor of DMS in marsh grasses and oceanic phytoplankton (Larher *et al.*, 1977; Dacey and Wakeham, 1986; Dacey *et al.*, 1987). The results presented here provide field confirmation that DMS emissions are a function of the presence of grass species that produce DMSP and that when calculating regional estimates of DMS flux one must consider the distribution and biomass of vegetation. Goldan *et al.* (1987) also found maximum fluxes of DMS from areas inhabited by *S. alterniflora* in a North Carolina marsh while DMS fluxes from *Juncus romerianus* were 10-fold lower.

The flux of DMS from *S. alterniflora* has been shown to occur from leaves rather than from the sediments (Dacey *et al.*, 1987). This explains our finding that DMS flux was related closely to the quantity of emergent biomass in the New Hampshire marsh. de Mello *et al.* (1987) also reported that DMS emissions were a function of biomass in a Florida *S. alterniflora* marsh. We also found that DMS emissions

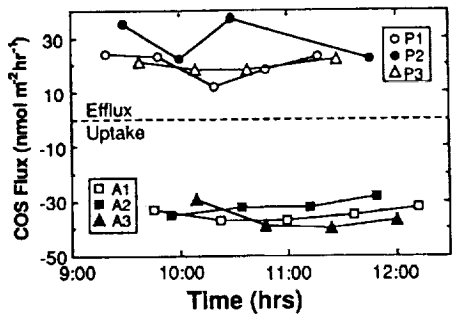


Fig. 7. Flux of carbonyl sulfide (COS) at sites A and P, August, 1988. Tidal water never flooded the soils when samples were being collected.

varied by a factor of ~ 2 over a 24 h period, probably in response to changes in light and temperature. Others have reported a close relationship between DMS flux and these physical parameters (i.e. Jørgensen and Okholm-Hansen, 1985; Goldan *et al.*, 1987; Cooper *et al.*, 1987a; Fall *et al.*, 1988). Our finding that DMS emissions increased during tidal flooding agrees with the conclusion of Dacey *et al.* (1987) that sediments are a sink for DMS and covering the sediments with water effectively blocks this sink. Goldan *et al.* (1987) also reported an increase in DMS flux rate from *S. alterniflora* soils once they were flooded with tidal water. This result is opposite to the fluxes of sediment-derived S gases, such as H_2S, which may display large maxima just prior to high tide due to tidal pumping (Hansen *et al.*, 1978; Jørgensen and Okholm-Hansen, 1985; Cooper *et al.*, 1987a). Insufficient data are available to ascertain if the increase in DMS flux during periods of flooding is due to physiological changes related to osmoregulation.

The data presented here support the notion that biomass and plant species distribution appear to be dominant controlling factors with light and temperature diel changes as secondary factors affecting the magnitude of DMS flux on a regional basis during the growing season. The obvious visual differences in the abundance of biomass within each collar and the coincident variations in gaseous S flux suggest that regional estimates of S emissions can be obtained from data that differentiate plant species and biomass. Remote sensors are currently available which have this capability such as the Airborne Imaging Spectrometer (Gross and Klemas, 1986).

Methane thiol emissions mimicked DMS emissions in the site inhabited by *S. alterniflora*, although at much lower rates. The coincidence of fluxes for these two S species was similar to what was reported for agricultural crops by Fall *et al.* (1988). As with DMS, MeSH appears to be produced by leaves of *S. alterniflora* and production is controlled, in part, by photosynthesis. The similarity in DMS and MeSH emission trends in the *S. alterniflora*-inhabited regions (A and T) suggests that MeSH could be a demethylation product of DMS. This does not seem to be the case for *S. patens* since the quantity of MeSH produced is large relative to the DMS flux rate, i.e. ~ 1:3 for *S. patens* and ~ 1:100 for *S. alterniflora*. Methane thiol is an intermediate in the methanogenic decomposition of DMS in anoxic marine sediments (Kiene *et al.*, 1986). Our finding that MeSH fluxes increased once the sediments were covered by tidal waters suggested that the sediments were a sink for MeSH.

Emissions of COS were also affected by plant species distribution with net uptake in the *S. alterniflora* soils and net efflux from the *S. patens* soils. Since COS uptake by vegetation is dependent on the COS concentration (Goldan *et al.*, 1988) it was not possible to calculate a natural rate of COS flux by these species. However, the quantity of COS introduced into the flux chambers by bleed from Tygon

Table 1. Ranges of emission estimates of biogenic sulfur compounds from vegetated areas of saline marshes

Location	Emission rate (nmol $m^{-2} h^{-1}$) DMS	MeSH	COS	Reference
Spartina alterniflora, NH, June, August	800–18,000	10–300	−25 to −40*	This study
S. alterniflora, MA, all year†	0–52,000	nr‡	94–2200§	Steudler and Peterson (1985)
S. alterniflora, Cedar Island, NC, August	560–1700	9–19	7–22	Goldan *et al.* (1987)
S. alterniflora, NC, Summer	640, 4700‖	nr	140¶	Aneja *et al.* (1979a,b)
S. alterniflora, FL, Jan., Oct., May	310–17,000	nr	nr	Cooper *et al.* (1987a); de Mello *et al.* (1987)
S. alterniflora, NC	1400¶	< 180	110¶	Aneja *et al.* (1981)
S. patens, June and August	0–130	0–60	10–36	This study
S. alterniflora and *S. patens*, VA, Aug., Sept.	nr	nr	0–28	Carroll *et al.* (1986)
Juncus romerianus, Cedar Island, August	100–650	5–75	17–41	Goldan *et al.* (1987)
Juncus romerianus, FL, April, May, Jan.	3–200	nr	nr	Cooper *et al.* (1987b)
Distichlis spicata, FL, April, May	19–720	nr	nr	Cooper *et al.* (1987b)
Marsh meadow, Denmark, July	100–1100	0–25	0–140	Jørgensen and Okholm-Hansen (1985)
Various saline marshes**	24–6600	1.1–780††	0.7–213‡‡	Adams *et al.* (1981b)

* Negative values indicate uptake.
† Range of 24 h mean values.
‡ Not reported.
§ Daily mean values were positive yet some hourly values were negative indicating uptake.
‖ Averages from Cox's Landing and Cedar Island, respectively.
¶ Mean values.
** Range of average values from 15 locations.
†† Most locations. Values up to 83,000 noted in some areas exhibiting high H_2S flux.
‡‡ Two locations in NC yielded rates of 3100 and 23,000.

tubing was approximately one-third of the typical concentration of COS in the troposphere (Carroll, 1985) so these rates may approach the natural rate.

Vegetation appears to act as a net sink for tropospheric COS (Kluczewski *et al.*, 1983; Brown and Bell, 1986; Fall *et al.*, 1988; Goldan *et al.*, 1988) and COS is probably taken up similarly to CO_2 (Goldan *et al.*, 1988). It appears, from the data presented here, that the rapidly growing *S. alterniflora* was a net daytime sink for COS compared to the less photosynthetically active *S. patens*. Previous studies have reported that salt marshes are sources of atmospheric COS (i.e. Steudler and Peterson, 1985; Carroll *et al.*, 1986; Goldan *et al.*, 1987). Steudler and Peterson (1985) did note periods of COS uptake in a *S. alterniflora* marsh but on a 24-h basis these episodes were overwhelmed by efflux events. Carroll *et al.* (1986) reported that COS emissions from a salt marsh were most rapid during the day, yet Fall *et al.* (1988) and Goldan *et al.* (1988) reported that COS uptake by laboratory-based agricultural plants occurred only in the presence of light. Therefore, it is unclear whether salt marshes are sources or sinks of COS. In addition, since COS is by far the most abundant S gas in the atmosphere, techniques that utilize S-free sweep air may be overestimating COS flux by enhancing the diffusional flux.

The emission rates of the S compounds presented here were similar to those published previously by others (Table 1). The comparison in Table 1 shows clearly that of the salt marsh species that have been studied, more DMS is emitted from *S. alterniflora* than from other grasses, a finding consistent with the presence of high concentrations of DMSP in *S. alterniflora*. It is interesting that the range of DMS fluxes measured in New Hampshire were very similar in magnitude to those measured by Cooper *et al.* (1987a) and de Mello *et al.* (1987) in a *S. alterniflora* marsh in Florida at the southern extent of the distribution of this grass species. Since the growing season of *S. alterniflora* is very short in New Hampshire (Hines *et al.*, 1989) compared to Florida, it is likely that the annual emission of DMS is greater in Florida. However, fluxes of DMS from a Massachusetts marsh located ~ 140 km south of New Hampshire were the highest ever recorded (Steudler and Peterson, 1985). Our MeSH flux data are also comparable to those of others (Table 1), however, relatively few field studies have measured MeSH fluxes. Although our MeSH emission rates from *S. alterniflora* were much higher than those of Goldan *et al.* (1987), the ratio of MeSH flux to DMS flux was very similar. In addition, the *S. alterniflora* that we studied at the SA site in New Hampshire was much taller than this species in the Cedar Island site studied by Goldan *et al.* (1987) underscoring the relationship between biomass and emission and the notion that MeSH is emitted primarily from leaves.

CONCLUSIONS

Emissions of DMS, MeSH and COS from saline marshes do not vary greatly over periods of a few hours. Horizontal variation in DMS and MeSH fluxes from *S. alterniflora*-inhabited regions is due primarily to differences in abundance of emergent biomass. Fluxes of DMS from *S. alterniflora* are two orders of magnitude higher than from *S. patens*, presumably because *S. patens* does not produce sulfonium compounds for osmoregulation. Emissions of MeSH from *S. alterniflora* mimicked those of DMS suggesting that MeSH is emitted primarily from emergent portions of these plants rather than from the marsh soil. The apparent release of DMS and MeSH from leaves and the relationships between emission rates, biomass and species distribution suggests that remote sensing techniques can be used to estimate S gas fluxes from saline marshes on regional scales. *Spartina alterniflora* appeared to take up COS, at least during the day, while *S. patens* was a net source of COS.

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J. BERTHELIN

C.N.R.S, B.P.5, 17, rue Notre Dame des Pauvres,
F-54501 Vandoeuvre-les-Nancy Cedex, France

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THE ROLE OF CERTAIN INFAUNA AND VASCULAR PLANTS IN THE MEDIATION OF REDOX REACTIONS IN MARINE SEDIMENTS

MARK E. HINES

Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824, U.S.A.

ABSTRACT

The mechanisms by which certain animals and plants affect redox processes in sediments was examined by studying three environments: (1) subtidal sediments dominated by the deposit-feeding polychaete *Heteromastus filiformis*; (2) a saltmarsh inhabited by the tall form of *Spartina alterniflora*; (3) tropical carbonate sediments inhabited by three species of seagrasses. ^{35}S-sulfide production rates were compared to pool sizes of dissolved sulfide and dissolved iron. In all of the sediments studied, rates of sulfate reduction were enhanced by macroorganisms while the rate of turnover of dissolved sulfide increased. The polychaete enhanced microbial activity and redox cycling primarily by subducting particles of organic matter and oxidized iron during sediment reworking. The *Spartina* species enhanced anaerobic activity by transporting primarily dissolved organic matter and oxidants. Although the final result of both animal and plant activities was the enhancement of subsurface cycling of sulfur and iron, decreased dissolved sulfide and increased dissolved iron concentrations, the mechanisms which produced these results differed dramatically.

Keywords: redox cycling, sulfate reduction, porewater chemistry, bioturbation, *Spartina alterniflora*, tropical seagrasses

INTRODUCTION

Plants and animals that live in or on sedimentary environments have considerable influence on the physical and chemical conditions of these sediments. Animals affect sediments by particle mixing due to movements during foraging for food or escaping from prey (Whitlatch, 1974; Cadée, 1976; Tevesz et al., 1980) or by the ingestion of particles during feeding and the transport of those particles to the sediment surface during defecation (Rhoads, 1967; Cadée, 1979; Taghon et al., 1984). Fecal pellets may be buried rapidly by new pellets as they are deposited at the surface.

Animals also influence sediments through irrigation of burrows (Aller et al., 1983). Both reworking and irrigation activities can have a profound effect on the microbiology of the sediments by transporting fresh organic matter to depth (Aller and Yingst, 1980, Hines and Jones, 1985), breaking down aggregates which can be colonized by microbes (Lopez and Levinton, 1978), transferring reduced compounds to oxidizing regions (Rhoads, 1974; Hines and Jones, 1985), and removing toxic metabolites while providing nutrients (Hargrave, 1970; Aller, 1977). Bioturbation has been reported to enhance rates of nitrification and denitrification (Sayama and Kurihara, 1978); Kristensen et al., 1985), SO_4^{2-} reduction (Aller and Yingst, 1980; Hines and Jones, 1985) and ammonification (Aller and Yingst, 1980).

Bioturbation affects sedimentary chemistry by disrupting vertical zonations of biogeochemical processes (Aller, 1977, 1982; Aller and Yingst, 1985). This results in redox gradients which may be situated horizontally and vertically as in the case of vertical, oxygenated burrows or more randomly as in microenvironments such as fecal pellets (Aller, 1977, 1982; Jørgensen, 1977). In general, the enhanced mixing of overlying water and porewater lowers the concentrations of most solutes in sediments. However, redox sensitive elements which change phases when reduced or oxidized may display increased porewater concentrations as a result of infaunal activity and subsurface redox cycling (Goldhaber et al., 1977; Hines et al., 1982, 1984).

Vascular plants such as marsh grasses and seagrasses can affect sedimentary chemistry in a manner which is similar to the effects of infauna. Although these organisms are not capable of particle movement, they influence the sediments by actively or indirectly transporting solutes and gases to the root zone (Wetzel and Penhale, 1979; Howes et al., 1981; Mendelssohn et al., 1981). In addition, rapid production by these plants can provide a subsurface source of organic matter to fuel microbial activity. Therefore, rapid subsurface redox cycles such as those in bioturbated sediments may be prevalent in sediments inhabited by active plant communities. The present communication compares sedimentary redox cycling in sediments subjected to active bioturbation by a subsurface deposit-feeding polychaete to temperate sediments inhabited by the salt marsh grass *Spartina alterniflora* and to tropical sediments inhabited by a variety of seagrasses. The net effect of the activities of these fauna and flora were similar, i.e., enhancement of subsurface anaerobic microbial activity, movement of oxidants to depth in the sediments and a rapid subsurface redox cycle of S and Fe. However, the infauna produced these events by transporting solid phase organic matter and oxidants into the sediment while the flora transported dissolved organic matter and molecular oxygen or dissolved oxidants.

MATERIALS AND METHODS

Sample locations

Bioturbated Site. Subtidal sediments in a shallow area of Great Bay, New Hampshire, U.S.A., were studied for several years. This site, which has been described by Hines and Jones (1985), is located just below the low tide mark in a ~0.7 ha cove. Mean tidal range is ~2 m and the temperature ranges from –0.5 to 25°C. The sediments are predominantly silts and clays with a large percentage of organic aggregates (Winston and Anderson, 1971). Cores collected for a 13 month period between 1984 and 1986 were examined for macroorganism content by P.F. Larsen (Bigelow Laboratory for Ocean Sciences, unpublished data) and revealed that the majority of the biomass in these sediments was attributable to the subsurface deposit-feeding polychaete *Heteromastus filiformis*. During summer, this organism reached population sizes as high as ~5000 individuals m^{-2}. Other infaunal species (36 total) were abundant but very small and restricted to the upper 1–2 cm of the sediment.

Salt Marsh Site. Chapman's Marsh is located near the mouth of the Squamscott River in the upper regions of Great Bay, New Hampshire and is described in detail

in Hines et al. (in review). This marsh is dominated by *Spartina patens* with stands of *S. alterniflora* along creek and river banks. Because of the steep slope of the banks the *S. alterniflora*-inhabited areas are generally less than 30 m wide and in some locations are only a few meters in width. The area sampled contained the tall form of *S. alterniflora* which reached over 2 m in height. The transition from tall to short *S. alterniflora* is abrupt and the tall *S. alterniflora* occupies a major percentage of the total *S. alterniflora*-containing soils. The tidal range at the marsh is ~2 m. The soil contained relatively fine grained mineral matter in addition to root and rhizome material.

Tropical Seagrass Site. Samples were collected from a shallow water site near the NE end of San Salvador Island, Bahamas. This location is described in Short et al. (1985). The sediments contained relatively fine-grained carbonate material and were inhabited by nearly pure seagrass stands of either *Thalassia testudinum, Syringodium filoforme*, or *Halodule wrightii* and sediment samples were collected from all three grasses. In addition, sediment samples were collected from a control site with no live seagrasses but with abundant remnants of seagrass roots and rhizomes. This control area was more affected by wave wash than in the vegetated areas.

Sample Collection. Sediment cores from the bioturbated site were collected using a hand-held plexiglas box corer (Hines and Jones, 1985). These were transported to the laboratory with the overlying water in place. Cores from the marsh site were collected using a Wildco corer which contained a plastic core liner and core catcher. Cores were flushed immediately in the field with N_2 and transported to the laboratory. Cores from the Bahamas sites were collected by hand using polycarbonate core liners. These latter samples were distributed into vessels in the field.

Porewaters from the bioturbated site were collected by centrifuging sediment horizons and filtering the supernatant under N_2 (Hines et al., 1984). Porewaters from both the marsh and tropical sites were collected using *in situ* "sippers" as described in Short et al. (1985) and Hines et al. (in review). These devices, which are deployed several days to weeks in advance of use, are lysimeters made of teflon which contain a porous teflon collar at the desired depth for water collection. Porewater is drawn into the sipper by application of a vacuum under N_2. Samples are immediately filtered under N_2 in the field and divided into storage vessels anoxically. Sippers are necessary to prevent artifacts due to the destruction of roots during sampling (Howes et al., 1985).

Sulfate Reduction Rates. Rates of sulfate reduction were determined using ^{35}S according to Jørgensen (1978) as modified by Westrich (1983). Sediment samples were placed into 5 cc syringes which were sealed with serum stoppers. One μCi of $^{35}S\text{-}SO_4^{-2}$ was injected into each syringe and samples were incubated in a dark N_2-filled jar overnight at ambient temperature. Activity was stopped by freezing. Sulfur-35 present in acid-volatile sulfides (AVS) was determined by actively distilling sulfides into Zn acetate traps as described by Hines and Jones (1985). Chromium-reducible sulfur-35, which represents largely pyrite and elemental sulfur, was determined by reducing these species to sulfide by refluxing with acidified Chromium (II) (Zhabina and

Volkov, 1978; Westrich, 1983). Only the AVS portion was determined in the bioturbated sediments.

Porewater Analyses. Sulfide was measured colorimetrically according to Cline (1969). Dissolved iron was determined colorimetrically using FerroZine (Stookey, 1970). Sulfate was determined turbidimetrically (Tabatabai, 1974).

RESULTS

Bioturbated site

Relative changes in bioturbation were determined using X-radiographs, abundances of infauna, and changes in sedimentary chemistry. In general, the influence of infaunal activity on sedimentary chemistry commenced in June during most years and was accompanied by an increase in rates of SO_4^{2-} reduction, an increase in the concentration of dissolved Fe, and a decrease in HS^- (Hines et al., 1984, 1985). Figure 1 demonstrates that dissolved Fe was abundant in JEL sediments throughout sedimentary regions that experienced relatively rapid rates of SO_4^{2-} reduction. Dissolved sulfide was never detected (detection limit 1–2 μM) in the upper 8–10 cm during the summers in which bioturbation was observed even though HS^- production increased to maximal levels during this time (Hines et al., 1985). The variations in dissolved Fe depicted in Fig. 1 were probably present at very low levels in these sediments but was maintained at undetectable concentrations by its rapid removal by FeS precipitation. The highest concentrations of dissolved Fe always occurred during the summer. For comparison, a relatively non-bioturbated site in Great Bay did not display an increase in dissolved Fe during the summer and rates of SO_4^{2-} reduction were much slower than at the bioturbated location (Hines and Jones, 1985).

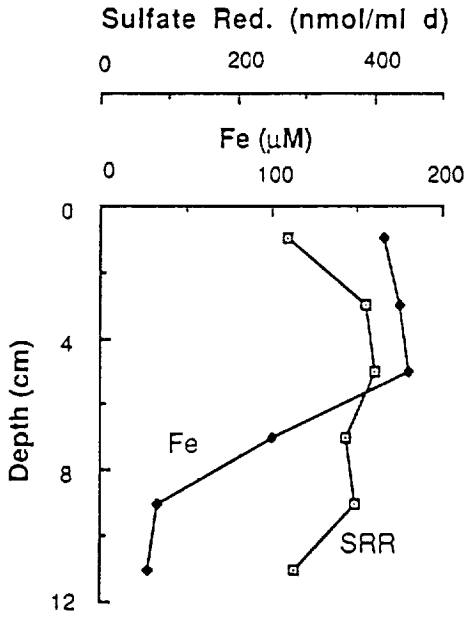

Fig. 1. Typical depth profile of dissolved Fe and rates of sulfate reduction (SRR) in the bioturbated sediments during summer. Dissolved sulfide concentrations were below detection (<2.0 μM).

Salt marsh site

Above-ground plant growth in the marsh soils studied began in mid-June and elongation ceased once the plants flowered in early August. Sulfate reduction was very rapid in the marsh soils and rates displayed sharp maxima when plants were actively elongating (Fig. 2). Once the *S. alterniflora* flowered, SO_4^{2-} reduction decreased ~4-fold within a few days. Temporal changes in SO_4^{2-} reduction rates agreed well with changes in SO_4^{2-}/Cl ratios (data not shown). However, as pointed out by Hines et al. (in review), SO_4^{2-}/Cl ratios in these

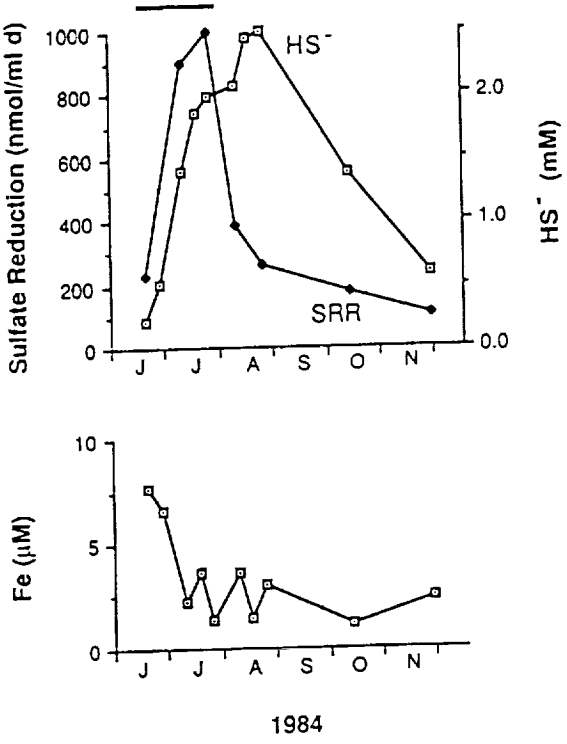

Fig. 2. Temporal variations in sulfate reduction rate (SRR) and concentrations of dissolved sulfide (HS^-) and dissolved Fe in the salt marsh sediments inhabited by the tall form of *Spartina alterniflora*. Values represent averages of upper 20 cm of sediment. Bar represents period when plants were actively elongating above ground. The detection limit for dissolved Fe was ~0.2 μM.

marsh sediments can only be used qualitatively because of the influence of vertical and lateral groundwater movement and the oxidation of the soils by plant activity.

Dissolved sulfide concentrations increased as plant height and rates of SO_4^{2-} reduction increased (Fig. 2). Concentrations of HS^- began to level near the end of the active elongation period. After *S. alterniflora* flowered in August, the concentrations of HS^- increased rapidly again even though rates of HS^- production had decreased dramatically. These concentrations decreased again in the Fall.

Dissolved Fe concentrations were low in these sediments when plants were elongating and decreased throughout the summer (Fig. 2). However, Fe was always detectable in the porewaters despite the occurrence of mM levels of HS^-.

Tropical seagrass beds

Sulfate reduction rates were ~10-fold lower in the sediments inhabited by seagrasses compared to the marsh soils described above (Fig. 3). Rates were most rapid in sediments occupied by *Halodule*, and slowest in sediments inhabited by *Thalassia*. Concentrations of HS^- were very low in the control sediments but reached values > 1 mM in seagrass sediments. The highest HS^- concentrations occurred in the *Syringodium* beds while concentrations were very low in the sediments inhabited by *Halodule*. Iron was not measured in these porewaters but presumably Fe concentrations were very low due to the carbonate composition of the island and of the sediments and the fact that this island in on the outer bank of the Bahamian islands.

There was no detectable decrease in SO_4^{2-} with depth in any of the tropical sediments examined (data not shown). This lack of SO_4^{2-} depletion has been noted in other carbonate sediments which exhibit SO_4^{2-} reduction which is even more rapid than rates noted for these Bahamian sediments (Hines and Lyons, 1982; Hines, 1985).

DISCUSSION

The production rates of HS^- (SO_4^{2-} reduction) in the bioturbated sediments in Great Bay were highest during the summer when temperatures were high and the sedi-

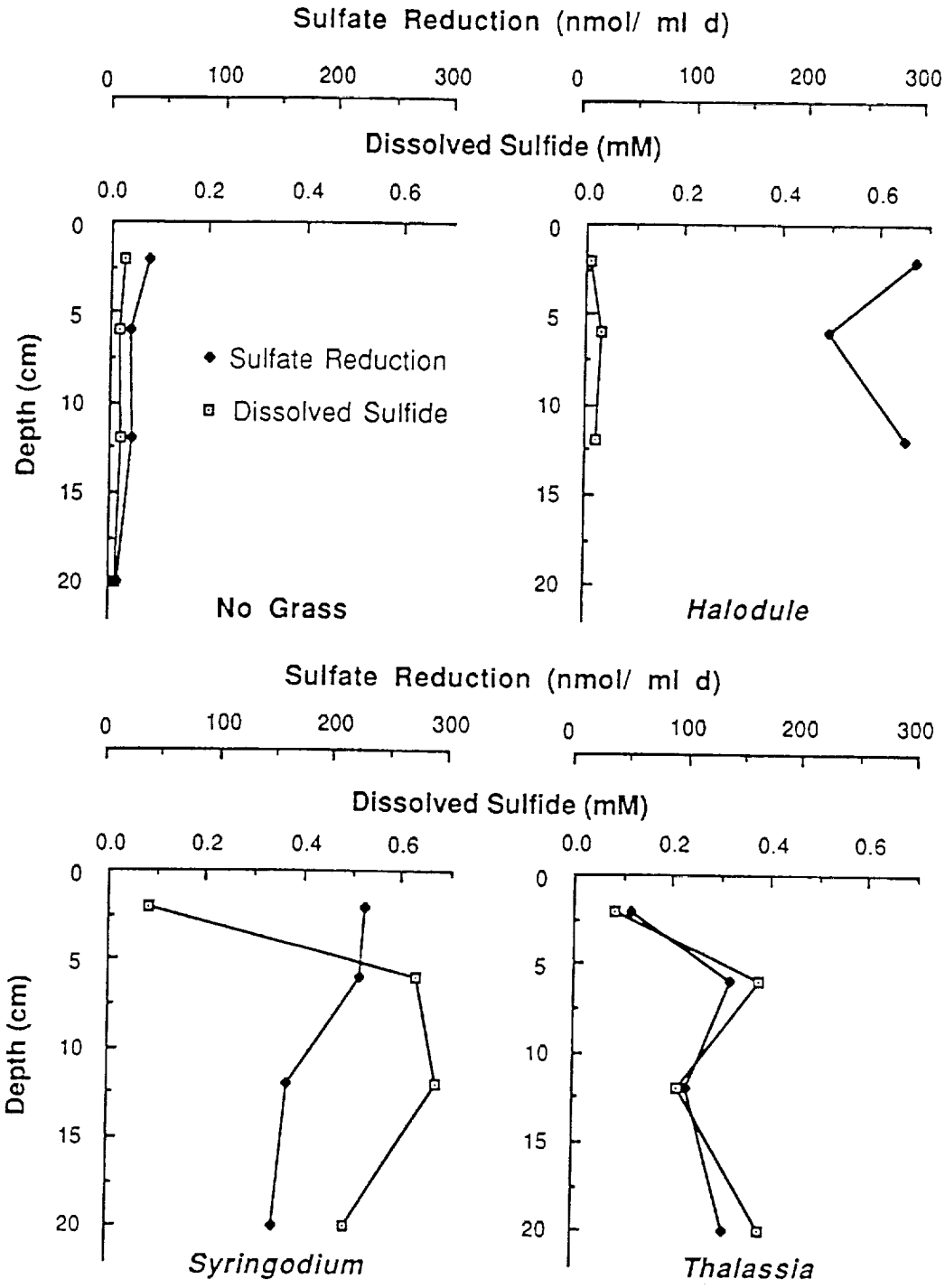

Fig. 3. Depth profiles of sulfate reduction rates and dissolved sulfide concentrations in various carbonate sediments from the Bahamas.

ments were subjected to active bioturbation (Hines and Jones, 1985). However, during this time of year, dissolved Fe was at maximal concentrations and HS^- concentrations were low or undetectable in the porewaters (Fig. 1). Although some Fe may have been complexed by organosulfur ligands (Boulegue et al., 1982), Fe cannot remain in solution at high concentrations in the presence of HS^- production since in anoxic sulfidic sediments the concentration of dissolved Fe is controlled primarily by the precipitation of Fe sulfide minerals (Lyons, 1979). To maintain high concentrations of dissolved Fe in these sediments which were experiencing rapid rates of HS^- production, it was necessary that the appropriate oxidants were continuously supplied to fuel a subsurface redox cycle of Fe and S which would result in the reduction and dissolution of Fe (Hines et al., 1982). Hence, Fe(III) had to be introduced into the sediments and reduced to Fe(II) at a rate which was at least fast enough to remove HS^- as it was generated microbially. One mechanism for providing the appropriate oxidant would be the introduction of O_2 into the sediments via burrow irrigation. However, a more plausible mechanism for the sediments studied here can be deduced from an examination of the lifestyle of the predominant bioturbator.

The infaunal community at JEL is dominated on a biomass basis by the subsurface deposit-feeding polychaete *H. filiformis*. This organism is a classic "conveyor-belt" feeder (Rhoads, 1974) which consumes fine anoxic sediment at 8–30 cm and passes it, through its gut, to the surface without oxidizing the reduced material (Cadée, 1979). Often, the fecal pellets are black (FeS) when deposited and they are then oxidized at the sediment surface (Cadée, 1979). The burrows are not ventilated and are not surrounded by a zone of oxidation (Pals and Pauptit, 1979). The worm is adapted physiologically to life in O_2-deficient environments (Pals and Pauptit, 1979).

The movement of fecal pellets by *H. filiformis* supplied the necessary oxidants to drive a subsurface redox cycle in the sediments studied. Reduced sediment in fecal material was oxidized at the sediment surface chemically and/or biologically. Additional pellet production buried the oxidized pellets into anoxic regions where they were reduced chemically and/or biologically, thus allowing for the dissolution of Fe. The Fe(II) produced was available for removing HS^- as FeS and HS^- never accumulated in the porewaters. In this way, a complete redox cycle of Fe and S occurred in deeper sediments without the need for the introduction of molecular O_2 into the sediments. Although particle reworking rates were not measured in these sediments, the population size of *H. filiformis* was sufficient to turn over the upper 10–15 cm of sediment several times during the summer (Cadée, 1979; Shaffer, 1983).

If the reduction of Fe(III) occurred chemically during HS^- oxidation then the production of FeS required two moles of HS^- for each mole of Fe since one mole of HS^- would have been consumed during the reduction of Fe(III). If Fe reduction was due to the use of Fe as an electron acceptor by bacteria then FeS precipitation required only one mole each of Fe and HS^-. Iron-reducing bacteria have been isolated from these sediments but the extent of Fe reduction that is strictly biological is unknown (Tugel et al., 1986).

The marsh and seagrasses studied also affected the subsurface redox chemistry in the sediments. One major difference be-

TABLE 1

Calculated resident times (days) of dissolved sulfide in the various sediments studied. Values equal the quotient of the concentration of sulfide divided by the rate of sulfate reduction

Bioturbated site	Marsh sediments		Tropical sediments			
	During growth	After flowering	*Halodule*	*Syringodium*	*Thalassia*	control
<.0067	1.5–2.0	5.1–10	0.16	2.7	2.4	1.2

tween the effects of bioturbation in Great Bay and the effects of the vascular plants was that the infaunal activities resulted in the complete removal of HS^- from solution while considerable HS^- remained in the plant inhabited porewaters. However, comparisons of the HS^- concentrations and rates of SO_4^{2-} reduction in the grass-inhabited areas revealed that plant activity had a strong influence on the redox chemistry of S in the sediments. The turnover time or residence time of HS^- in the porewaters was calculated by dividing the HS^- concentration by the rate of HS^- production or SO_4^{2-} reduction (Table 1). Since the rate measurements represent a value for the incubation period only and the concentration values are the result of previous and ongoing activity in the sediments, this calculation represents only an approximation of the reactivity of HS^- in the sediments. However, the wide range in values in Table 1 gives credence to use of these calculations for estimating the effect of the macroorganisms on S transformations.

Sulfide was not detected in the porewaters at the bioturbated site during summer so the HS^- residence times were calculated by using the detection limit of the method which is 2 μM (1 μmol^{-1} whole sediment at 50% porosity). Therefore, the residence time of HS^- during bioturbation was <10 min. This value represents removal of HS^- by all mechanisms and is not necessarily a measure of HS^- oxidation.

Although the HS^- concentrations in the marsh porewaters were high, the highest concentrations were encountered after SO_4^{2-} reduction had decreased greatly. Therefore, the calculations of HS^- residence times revealed a nearly 10-fold increase after the plants flowered (Table 1). The onset of flowering produced dramatic changes in the biogeochemistry of the soils including a ~4-fold decrease in SO_4^{2-} reduction and an increase in HS^- concentrations. The fact that the residence time of HS^- in the porewaters increased rapidly after flowering and was similar to values measured after the growing season ended (Table 1) demonstrated that the plants were able to oxidize the soils significantly only when they were elongating actively above ground. Although it was not clear whether the plant-mediated oxidation of the soil was due to molecular O_2 or to some other oxidized chemical species produced biochemically (Howes et al., 1981), it seems certain that the oxidizing agent was dissolved as opposed to the solid phase oxidant present in the bioturbated sediments at JEL. The possibility of O_2 as the oxidant in *Spartina* marshes has been discussed by Boulegue et al. (1982). Even though a decrease in residence time of HS^- does not indicate that HS^- is being removed ex-

clusively by oxidation in the soil, the introduction of an oxidizing agent is required to continually remove HS^- whether removal occurs via oxidation or precipitation as an Fe mineral.

The result of sediment oxidation by the *S. alterniflora* was not as apparent as that noted for the bioturbated sediments. However, the enhancement of SO_4^{2-} reduction by the plant was dramatic. The rapid increase in SO_4^{2-} reduction that occurred when plants were elongating above ground could not have been due to the utilization of solid phase organic matter. It was likely that dissolved organic exudates produced by the plants (Mendelssohn et al., 1981) were responsible for fueling the majority of SO_4^{2-} reduction. The "background" rates of ~200–300 nmol ml^{-1} d^{-1} which occurred before and after the occurrence of the SO_4^{2-} reduction maximum were probably due to the utilization of this solid phase material. Therefore, in contrast to the bioturbated sediments, when the plants were elongating, anaerobic microbial activity was fueled primarily by dissolved organic matter and the subsurface redox cycle was sustained by the production of dissolved oxidants.

The residence time of HS^- in the tropical seagrass-inhabited sediments were similar to those in the marsh soils. However, the rates of SO_4^{2-} reduction and the concentrations of HS^- were considerably less than in the marsh soils. *Halodule* tended to oxidize the soils much more than did the other grasses. In fact, these sediments were the only ones which yielded HS^- residence time data which were more rapid than the control. It was difficult to compare residence time data to the control since the low level of HS^- and SO_4^{2-} reduction in the control probably increased the importance of diffusional losses and oxidation in control sediments. The wave activity at the control site may have enhanced HS^- removal as well. A better control would have been obtained if vegetated areas had been cut to prevent photosynthesis. The enhancement of sediment oxidation in seagrass-inhabited sediments was most likely due to dissolved oxidants as in the marsh soils. Sulfate reduction was also most rapid in the sediments inhabited

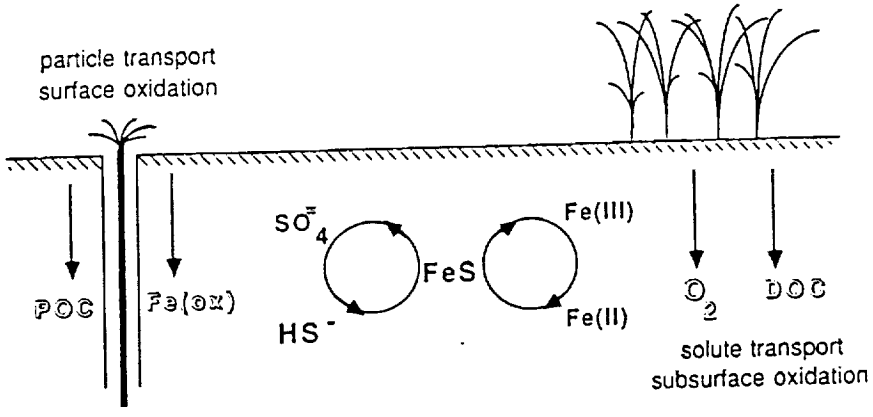

Fig. 4. Summary of the net result of bioturbation and plant activities on the redox conditions of the marine sediments studied. Both types of macroorganisms cause subsurface redox cycling but the mechanisms utilized are different.

by *Halodule* which may indicate that this species is active at providing oxidants and organic exudates to the sediments. Wetzel and Penhale (1979) demonstrated the capacity of seagrasses to release organic exudates from the root zone. However, the data from these Bahamian sediments were insufficient to determine whether SO_4^{2-} reduction was fueled primarily by dissolved (DOC) or particulate (POC) organic matter.

The net result of the occupation of the marine sediments studied by either infauna or flora was an enhancement of anaerobic microbial activity measured as sulfate reduction and the establishment of a subsurface redox cycle which caused high dissolved Fe and low HS^- concentrations. This process and the mechanisms by which these organisms produced these changes are summarized in Figure 4. The deposit-feeding polychaete community provided solid phase organic matter and oxidized Fe to subsurface sediments and were efficient at removing HS^-. Conversely, the flora studied enhanced anaerobic activity and maintained a subsurface redox cycle by providing dissolved organic matter and dissolved oxidants to the sediments. These HS^- removal mechanisms may be important for maintaining HS^- concentrations below levels which are toxic to macroorganisms.

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EMISSIONS OF BIOGENIC SULFUR GASES FROM ALASKAN TUNDRA

Mark E. Hines and Michael C. Morrison

Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham

Abstract. Fluxes of the biogenic sulfur gases carbonyl sulfide (COS), dimethyl sulfide (DMS), methyl mercaptan (MeSH), and carbon disulfide (CS_2) were determined for several freshwater and coastal marine tundra habitats using a dynamic enclosure method and gas chromatography. In the freshwater tundra sites, highest emissions, with a mean of 6.0 nmol m^{-2} h^{-1} (1.5-10) occurred in the water-saturated wet meadow areas inhabited by grasses, sedges and *Sphagnum* mosses. In the drier upland tundra sites, highest fluxes occurred in areas inhabited by mixed vegetation and labrador tea at 3.0 nmol m^{-2} h^{-1} (0-8.3) and lowest fluxes were from lichen-dominated areas at 0.9 nmol m^{-2} h^{-1}. Sulfur emissions from a lake surface were also low at 0.8 nmol m^{-2} h^{-1}. Of the compounds measured, DMS was the dominant gas emitted from all of these sites. Sulfur emissions from the marine sites were up to 20-fold greater than fluxes in the freshwater habitats and were also dominated by DMS. Emissions of DMS were highest from intertidal soils inhabited by *Carex subspathacea* (150-250 nmol m^{-2} h^{-1}). This *Carex* sp. was grazed thoroughly by geese and DMS fluxes doubled when goose feces were left within the flux chamber. Emissions were much lower from other types of vegetation which were more spatially dominant. Sulfur emissions from tundra were among the lowest reported in the literature. When emission data were extrapolated to include all tundra globally, the global flux of biogenic sulfur from this biome is 2-3 x 10^8 g yr^{-1}. This represents less than 0.001% of the estimated annual global flux (~50 Tg) of biogenic sulfur and <0.01% of the estimated terrestrial flux. The low emissions are attributed to the low availability of sulfate, certain hydrological characteristics of tundra, and the tendency for tundra to accumulate organic matter.

Introduction

Sulfur gases contribute to precipitation acidity [*Charlson and Rodhe*, 1982; *Nriagu et al.*, 1987], are involved in various important atmospheric chemical reactions, and have been implicated as potential regulators of climate by increasing global albedo [*Bates et al.*, 1987a; *Charlson et al.*, 1987]. A major question in our understanding of the natural sulfur cycle is the role of biogenic sulfur emissions in the atmosphere [*Andreae et al.*, 1990]. Although tremendous progress in delineating the sources and sinks of sulfur gases has been achieved recently, there remains considerable uncertainty as to the role of certain terrestrial environments as sources of biogenic sulfur gases [*Andreae*, 1985]. Recent work has contributed greatly to an understanding of the role of temperate soils and vegetation as sources and sinks of sulfur gases [*Goldan et al.*, 1987, 1988; *Lamb et al.*, 1987; *Fall et al.*, 1988]. Several studies have examined the emissions of sulfur gases from temperate salt marshes (see references listed in *Aneja and Cooper* [1989]) and recent studies have begun to examine the emissions of sulfur gases from tropical environments [*Andreae and Andreae*, 1988; *Andreae et al.*, 1990].

Nriagu et al. [1987] suggested that wetlands in Ontario, Canada, may emit quantities of biogenic sulfur which are similar in magnitude to oceanic fluxes of dimethyl sulfide (DMS). Although high latitude wetlands constitute a relatively large area of the terrestrial Earth [*Matthews and Fung*, 1987], no studies have directly determined the flux of sulfur gases from these environments. In this paper we present results of sulfur emission measurements made in freshwater and marine wetlands in Alaskan tundra during the Arctic Boundary Layer Expedition 3A (ABLE 3A) in July 1988. These data indicated that this type of tundra emits very small amounts of gaseous sulfur and accounts for a very small percentage of the global flux of biogenic sulfur to the atmosphere.

Methods

Sampling Locations

The freshwater sites studied were located near Bethel, Alaska, in the Yukon-Kuskokwim delta (Figure 1). In this area, flux measurements were made in various types of upland tundra vegetation including regions dominated by graminoids, labrador tea (*Ledum palustre*), *Sphagnum* mosses, and lichen species and in wet meadow sites dominated by *Sphagnum* spp., grasses (*Eriophorum* spp.) and sedges (*Carex* spp.). The wet meadow sites contained standing water while the upland sites were moist without standing water. Emissions from a lake surface were also measured.

In addition to the freshwater sites, emission measurements were made in a coastal area of the Delta at the mouth of the Tutakote River near Angyoyaravak Bay on the Bering Sea (Figure 1). Here, emissions were measured in an intertidal mud flat, an intertidal area inhabited by the sedge *Carex subspathacea*, and two supralittoral sites in monospecific stands of *Carex ramenskii* and *Elymus arenarius*. *Carex subspathacea* is grazed extensively by geese, and emission measurements were made in the presence and absence of goose feces. Samples and equipment were transported via float plane.

Sampling and Analysis

Net emission measurements were made using 30 x 30 x 30 cm dynamic FEP Teflon flux chambers placed on Teflon-lined aluminum collars which had been deployed previously in the various habitats. For the lake samples, chambers were placed on collars which were attached to Styrofoam floats. Three chambers were deployed simultaneously, each over a different vegetation mixture. Compressed synthetic air was used for sweep air at 2.0 L min^{-1} and 5.0 L gas samples were removed at 500 mL min^{-1} and trapped in Teflon loops immersed in liquid N_2. Laboratory studies demonstrated no measurable breakthrough of sulfur gases at this sampling rate [*Morrison*, 1988]. However, these tests were conducted using higher concentrations of sulfur gases than those encountered in the present study so it is possible that the rates reported here are underestimated. Oxygen condensation within loops was prevented by trapping gases under a slight vacuum. Rates of sweep air flow and sample air collection were regulated using

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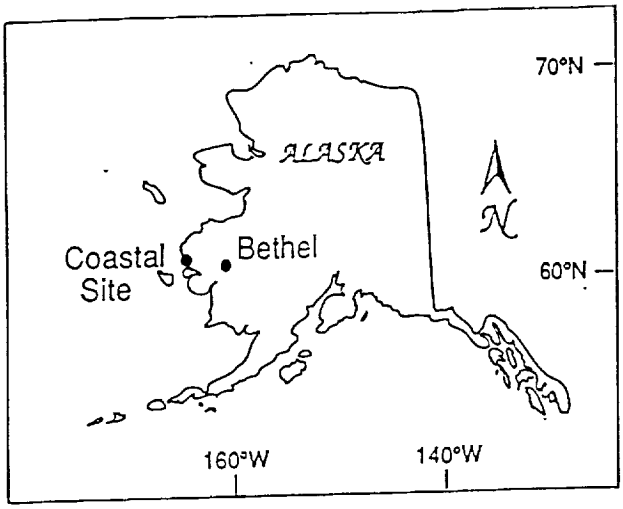

Fig. 1. Location in Alaska of the freshwater sampling site in Bethel and the coastal sampling site near Angyoyaravak Bay (165°36'W, 61°20'N).

mass flow controllers. Sample size was determined by integrating meter output. Samples were collected every 30-60 min for several hours. Diel experiments were not conducted. However, this area of Alaska in July receives sunlight for approximately 20 hours each day. For comparison, in some instances static chambers, which entrapped ambient air, were employed. Samples were collected every 30 min.

Sample loops were transported to a laboratory, where they were analyzed within at least 5 hours. In laboratory tests, samples could be stored in loops under liquid N_2 for over 8 hours without loss [*Morrison*, 1988]. Sulfur gases were remobilized by heating loops in a hot water bath, separated on a column packed with 1.5% XE-60, 1% H_3PO_4, 60/80 Carbopack B (Supelco) and quantified by a sulfur-doped flame photometric detector. Calibration was conducted using sulfur gases liberated from gravimetrically calibrated permeation devices maintained in a permeation oven. The minimum fluxes that could be detected under the conditions used were 0.15, 0.2, 0.25 and 0.3 nmol m^{-2} h^{-1} for carbonyl sulphide (COS), methane thiol [CH_3SH, (MeSH)], DMS and carbon disulfide (CS_2), respectively. Hydrogen sulfide (H_2S) could be detected but could not be quantified because it elutes on the tail of negative peaks due to hydrocarbons and carbon dioxide. For further analytical details, see *Morrison and Hines* [1990].

Results and Discussion

Rates of sulfur gas emissions were low at all of the freshwater sites (Table 1). Carbonyl sulfide was emitted from all sites and was the most dominant sulfur gas in many instances. Dimethyl sulfide emissions were also important and this gas was the dominant sulfur gas emitted from the wet meadow areas. Carbon disulfide was found less frequently and MeSH was detected only rarely at low concentrations and is not presented. Hydrogen sulfide was detected routinely but could not be quantified.

The data in Table 1 include replicate measurements from the same chamber made on the same day as well as measurements made on separate days. The collars remained in place throughout the experiment so the exact location could be sampled on several days. In most instances, variation within one day at one site was less than a factor of two. Fluxes were most variable in the upland sites. Fluxes increased from July 11 to 16, 1988. The highest increase of eightfold occurred in the lichen-dominated area, while emissions increased 2.8- to 4.5-fold in the wet meadow/slough areas. During this period the weather was unusually warm and dry. The midday ambient temperature ranged from 19 to 25° C throughout the experiment.

When employing the flow-through dynamic flux chambers, COS fluxes were 0.23 to 12 nmol m^{-2} h^{-1} with highest fluxes in the upland sites and lowest fluxes in the wet meadow (Table 1). These higher rates are rapid enough to double the COS concentration in an hour in our static chambers. However, when static chambers were used over an upland site, ambient COS concentrations decreased exponentially over time (data not shown) indicating that tundra vegetation was consuming COS. Others have reported the uptake of COS by photosynthesizing vegetation [*Fall et al.*, 1988; *Goldan et al.*, 1988].

TABLE 1. Summary of Sulfur Gas Emissions From Freshwater Tundra Near Bethel, Alaska

	Emissions, nmol S m^{-2} h^{-1}					
	COS		DMS		CS_2	
Site	Range*	Mean	Range*	Mean	Range*	Mean
Wet meadow grass and sedge	1.3-5.2	2.7	2.7-10	6.1	0-1.1	0.22
Wet meadow moss†	0.23-8.9	4.9	1.5-9.5	5.7	0-3.3	0.6
Upland mixed‡	2.3-12	7.6	0-5.0	2.6	0-1.2	0.4
Upland Labrador Tea§	2.9-10	6.5	0.5-8.3	3.5	0	0
Upland moss§	3.3-8.4	5.8	0-7.6	2.0	0	0
Upland lichen§	11-12	12	0.8-1.1	0.9	0	0
Lake¶	2.9	2.9	0.7-0.8	0.8	0-1.1	0.5

Methyl mercaptan (MeSH) was detected occasionally.
*All values including daily replicates and measurements made on separate days.
†Mixed with grass and sedge.
‡Variety of species including dwarf birch, graminoids, lichens, labrador tea, and mosses.
§Mixed tundra dominated by this type of vegetation.
¶Emission chamber floating on lake surface.

Emissions of COS measured using dynamic chambers did not vary significantly with time once equilibrium was established (~1.5 h). This indicated that the tundra soil was a source of COS since COS emissions , i.e., COS concentrations within the chamber, would have decreased with time if the only source of COS was that which was in equilibrium with the atmosphere. In addition, using the following equation [*Liss and Slater*, 1974], we calculated the expected flux of COS from water when the aqueous COS concentration was in equilibrium with the atmosphere and then the atmosphere was suddenly replaced by COS-free air:

$$F = k\Delta C \quad (1)$$

where F is flux in nmol m^{-2} h^{-1}, k is piston or exchange velocity in m h^{-1} and ΔC is COS concentration gradient. Since the atmosphere in the dynamic chamber was devoid of COS, ΔC equals the concentration of COS in water that is in equilibrium with ambient air. This concentration of COS in water was 9.2 pM as calculated as the quotient of an atmospheric concentration of COS of 500 ppt(v) divided by the Henry's law constant of COS in seawater at 20° C of 2.22 [*Johnson and Harrison*, 1986]. Hence, using equation (1), the flux of COS expected in the absence of COS production when COS-free sweep air is used is ~0.18 nmol m^{-2} h^{-1}. This is an underestimate, since the Henry's law constant used was determined for seawater. However, this emission rate is substantially lower than the rates actually measured using the dynamic chambers. This fact and the finding that the COS emission rates in dynamic chambers did not decrease over time indicated that these tundra soils were producing COS.

The discrepancy in the COS data between the dynamic and the static chambers was probably due to the uptake of ambient COS by vegetation when static chambers were employed. In the dynamic chambers, the concentration of COS, and, hence, the calculated flux, was a net result of emission from soils and consumption by vegetation. When using dynamic chambers, the most rapid COS emissions were from the lichen and other dry areas while COS fluxes were slower in the areas which were wet and contained much more biomass. These latter results suggested that the lower COS fluxes measured using dynamic chambers were not due to a smaller flux from wet meadow areas but to a faster rate of consumption. A similar conclusion was derived from our recent study of a temperate salt marsh [*Morrison and Hines*, 1990]. Therefore, we believe that the emission data for COS from these tundra sites, which were derived from dynamic chambers, do not represent the actual fluxes from the habitats and that it is possible that tundra is a net sink for COS. Unfortunately, since we only employed the static chambers on one occasion at two dry sites to test the utility of the dynamic enclosures for this gas, we were unable to quantify the uptake the COS thoroughly to make conclusions about the role of tundra in regulating atmospheric COS. We have included the COS flux data from dynamic chambers in Table 1 for comparison to other published COS emission data, most of which were derived from dynamic chamber deployments. In addition, it appears that of the sulfur gases quantified, DMS was the dominant S gas emitted from these habitats rather than COS.

Emissions of sulfur gases from the freshwater sites were highest in the wet meadow areas and slightly lower in most of the upland tundra sites (Table 1). Sulfur emissions were very low from upland areas dominated by lichens, and these fluxes were similar in magnitude to those from a lake surface.

Sulfur fluxes at the coastal sites were more rapid than the inland areas in most instances (Table 2). In addition, we were able to detect MeSH emissions from most of these sites. We did not utilize static chambers with ambient COS concentrations to test whether COS fluxes were artificial so the COS emission data, like those presented in Table 1, are suspect. Highest rates were noted in the intertidal area inhabited by *C. subspathacea*, and fluxes of DMS in this area more than doubled when goose feces were left within the flux chambers. Fluxes of DMS from *C. subspathacea* were six (vegetation alone) to 15 (vegetation plus feces) times faster than from the adjacent mud flat which was devoid of vegetation. The quantity of emergent biomass of *C. subspathacea* was low at ~10 g dry weight m^{-2}.

TABLE 2. Summary of Sulfur Gas Emissions at the Coastal Site on the Tutakote River, Alaska

Site	Range of Emissions, nmol S m^{-2} h^{-1}			
	COS	MeSH	DMS	CS_2
Carex subspathacea	5.7-10	1.6-2.6	70-81	5.0-9.7
C. subspathacea +feces	4.3-8.2	2.4-4.5	150-250	5.9-6.9
C. ramenskii	11-16	0-0.7	0-1.7	1.6-8.4
Elymus arenarius	18-21	1.2-2.7	75*	4.3-7.8
Mud flat	9.3-11	<0.2	10-16	2.1-4.2

All measurements made on July 18, 1988.
*Only one measurement.

Fluxes of sulfur gases from *E. arenarius* were similar in magnitude to those from *C. subspathacea* . Although we did not measure the biomass of *E. arenarius*, it was dense and over 30 cm tall and appeared to be at least 20 times more abundant in emergent biomass than *C. subspathacea*.

Except for CS_2, the rates of sulfur emissions from *C. ramenskii* were extremely low, even less than most of the inland freshwater sites examined (Tables 1 and 2). These low fluxes were surprising since the stand studied was only 2-3 m from the *C. subspathacea* site and, due to its close proximity to the ocean, this region must receive considerably higher inputs of sulfur than the Bethel sites. The *C. ramenskii* was dense, bright green, ~15 cm tall and we observed large areas of *C. ramenskii* from the air.

The highest sulfur emissions recorded in the freshwater tundra sites (exclusive of COS) were ~4% of those recorded for the average open ocean [*Barnard et al.*, 1982; *Andreae*, 1986; *Bates et al.*, 1987b], ~10% of fluxes from upland soils in the Amazon Basin during the dry season [*Andreae and Andreae*, 1988] and ~3.5% of estimates of sulfur emissions from waters in wetlands of southern and central Ontario, Canada [*Nriagu et al.*, 1987]. These must be considered lower estimates, since we were unable to quantify H_2S, which was always present. Fluxes of DMS from freshwater tundra were similar in magnitude to fluxes of DMS from decaying cattails, and native grasses in Ohio [*Goldan et al.*, 1987], fluxes of DMS from organic-poor soils in Germany [*Staubes et al.*, 1989], the lowest detectable rates of sulfur emissions from a freshwater wetland in southern Florida [*Cooper et al.*, 1987], and rates of emission of DMS from upland soils in the Amazon Basin during the wet season [*Andreae et al.*, 1990].

Although the sulfur emissions from the coastal sites were considerably higher than from the freshwater locations examined, the highest fluxes from the coastal sites were up to 100-fold lower than sulfur fluxes from stands of temperate salt marsh grasses [*Steudler and Peterson*, 1984; *Aneja and Cooper*, 1989; *Morrison and Hines*, 1990]. The biomass of *C. subspathacea* was only ~10 g m^{-2}, so the ratio of flux to biomass of 8-20 was similar to the ratio for temperate *S. alterniflora* of 10 (*Morrison and Hines* [1990] and our unpublished biomass data).

The enhanced DMS flux in the presence of *C. subspathacea* and the similarity between flux and biomass for this species

and *S. alterniflora* suggested that *C. subspathacea* produces a sulfonium compound like dimethylsulfoniopropionate (DMSP), a known precursor of DMS [*Dacey et al.*, 1987]. The only marsh species that have been previously shown to produce significant quantities of this compound are *Spartina alterniflora* [*Dacey et al.*, 1987] and *S. anglica* [*Larher et al.*, 1977]. The increased DMS flux in the presence of goose feces was probably due to the decomposition of DMSP after ingestion of *C. subspathacea* by geese. This is similar to the enhancement of DMS emissions when DMSP-producing marine phytoplankton are grazed by zooplankton [*Dacey et al.*, 1987] or when *S. alterniflora* is decomposed by microbes [*Kiene and Visscher*, 1987]. However, validation of the supposition that *C. subspathacea* is indeed a DMSP-producing macrophyte remains to be conducted. Despite the higher fluxes of sulfur gases from the coastal sites, the abundance of *C. ramenskii* and the fact that the coastal region is small relative to the freshwater wetlands in Alaska indicated that only the freshwater areas are of importance when considering the role of tundra in affecting the atmospheric sulfur cycle.

During the period of this study (July 1988), the wet deposition of sulfur in Bethel averaged 0.21 mg S m^{-2} d^{-1} (76 mg m^{-2} yr^{-1}) [*Talbot et al.*, this issue]. Hence, the measured loss of sulfur as gaseous efflux represented only 0.5% of the input during that period as compared to estimates of 30% for the Amazon Basin during the dry season [*Andreae and Andreae*, 1988].

There are several reasons why the fluxes of sulfur gases from Alaskan tundra are small. First, the supply of sulfate must be low since the rate of atmospheric deposition of sulfur to this locale is small even when compared to other remote areas [*Andreae and Andreae*, 1988]. The Canadian wetlands studied by *Nriagu et al.* [1987] were subjected to relatively high levels of pollutant sulfur with deposition rates up to 40-fold higher than those encountered in our Alaskan study. It is interesting that the calculated rates of sulfur emission from the Ontario bogs studied by *Nriagu et al.* [1987] were ~40-fold higher than those measured by us in Alaska. Hence, even when the rate of sulfur deposition is very low, the percentage that is re-emitted appears to be similar to areas experiencing higher deposition rates. Too few data are available to discern if this is a common phenomenon for high latitude wetlands or if reemission percentages are commonly high in tropical environments like those studied in the Amazon dry season.

Second, the biologically active component of the tundra peat is a relatively thin section near the surface. Sulfur-containing waters which percolate through this region probably do not remain in contact with the active zone long before draining into deeper layers just above the permafrost (~50 cm). The upland tundra sites studied here were never saturated with water during the study period and meteoric waters must have drained into lower, wet meadow regions. These wetter areas are sites of increased nutrient accumulation because of drainage of nutrients from upland areas [*Matthes-Sears et al.*, 1988]. Wet meadows probably tend to accumulate more sulfur than upland areas as well and this may explain the higher fluxes of sulfur in the wet meadow sites. The wet meadow sites exhibited fluxes of methane which were approximately 100-fold higher than in the upland, drier sites [*Bartlett et al.*, this issue]. Substrate anoxia, which appears to enhance methane flux from the wet meadow areas did not enhance fluxes of sulfur gases similarly. During early spring thaw, a large portion of the precipitation runs off tundra rather quickly while flow is retarded during summer [*Matthes-Sears et al.*, 1988]. This surface flow probably also removes a large portion of any pollutant sulfur which is deposited during late winter by Arctic haze.

Third, tundra communities are characterized by organic matter accumulation with slow decomposition rates [*Chapin et al.*, 1978]. Tundra vegetation is active during the short summer season and tends to strongly sequester needed elements from the environment. Our flux measurements were made during the most productive period of the year and it is possible that sulfur emissions increased as plants began to senesce in August. Increases in DMS emissions in salt marsh soils in the fall have been reported [*Steudler and Peterson*, 1984]. In addition, there was a large increase in emissions from tundra during the final five to eight days of the experiment as the ecosystem became warmer and drier suggesting that emission rates are quite variable throughout the growing season. Others have reported good correlations between the log of sulfur emissions and enclosure temperatures with emissions increasing ~10-fold when temperature increase from 10 to 30° C in sites in Ohio [*Goldan et al.*, 1987; *Fall et al.*, 1988]. Unfortunately, too few emission data were collected and temperatures did not vary enough during our Alaska study to determine more than a semi-quantitative relationship between these variables. However, sulfur gas emissions from these tundra sites increased more per degree C than the increases reported for temperate sites [*Goldan et al.*, 1987].

If the global tundra area is 9×10^{11} m^2 (estimate for nonforested bog [*Matthews and Fung*, 1987]) and the active season is 100-150 days, then we estimate that the global flux of biogenic sulfur from tundra is 2.1-3.2 x 10^8 g yr^{-1}. This represents slightly less than 0.001% of the estimated global flux of biogenic sulfur (~50 Tg yr^{-1}) [*Möller*, 1984]. This value is probably smaller still since a large percentage of tundra is covered by lakes which we found emit very little sulfur compared to the vegetated terrestrial surfaces. Extrapolation of our data to northern wetlands in general, including both nonforested and forested bogs [*Matthews and Fung*, 1987], would increase this contribution by only a factor of ~3 which is still an insignificant contribution to the global atmospheric sulfur burden. *Andreae et al.* [1990] recently estimated the annual terrestrial flux of biogenic sulfur as ~4.2 Tg, making the tundra flux ≤0.01% of the global terrestrial emissions of biogenic sulfur. If our emission data were underestimated by as much as a factor of 10, the flux of biogenic sulfur from this ecosystem would still be very low. It should be pointed out that we were not able to quantify emissions of H_2S. If H_2S is a major component of the sulfur emissions from tundra, then these estimates of the importance of this ecosystem to the atmospheric sulfur burden may be significantly low.

There appears to be insufficient atmospheric sulfur input to expect a large increase in biogenic sulfur emissions from tundra and even a 100% recycling of atmospherically-deposited sulfur would contribute only slightly (<0.1%) to the global atmospheric sulfur burden. Although areas which receive high inputs of sulfur, such as coastal regions or locations subjected to anthropogenically derived sulfur, certainly contribute considerably more recycled sulfur to the atmosphere, the bulk of tundra globally, such as in Siberia and Alaska, probably emits too little biogenic sulfur to significantly affect the global atmospheric sulfur budget.

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M. E. Hines and M. C. Morrison, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824.

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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.

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Emissions of Sulfur Gases From Marine and Freshwater Wetlands of the Florida Everglades: Rates and Extrapolation Using Remote Sensing

MARK E. HINES

Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham

RAMONA E. PELLETIER

National Aeronautics and Space Administration, Science and Technology Laboratory, Stennis Space Center, Mississippi

PATRICK M. CRILL

Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham

Rates of emissions of the biogenic sulfur (S) gases carbonyl sulfide (COS), methyl mercaptan (MSH), dimethyl sulfide (DMS), and carbon disulfide (CS_2) were measured in a variety of marine and freshwater wetland habitats in the Florida Everglades during a short duration period in October using dynamic chambers, cryotrapping techniques, and gas chromatography. The most rapid emissions of >500 nmol m^{-2} h^{-1} occurred in red mangrove-dominated sites that were adjacent to open seawater and contained numerous crab burrows. Poorly drained red mangrove sites exhibited lower fluxes of ~60 nmol m^{-2} h^{-1} which were similar to fluxes from the black mangrove areas which dominated the marine-influenced wetland sites in the Everglades. DMS was the dominant organo-S gas emitted especially in the freshwater areas. Spectral data from a scene from the Landsat thematic mapper were used to map habitats in the Everglades. Six vegetation categories were delineated using geographical information system software and S gas emissions were extrapolated for the entire Everglades National Park. The black mangrove-dominated areas accounted for the largest portion of S gas emissions to the area. The large area extent of the saw grass communities (42%) accounted for ~24% of the total S emissions.

INTRODUCTION

Sulfur (S) gases are important components of the global cycle of S [*Andreae*, 1985; *Möller*, 1984]. Through their atmospheric oxidation to sulfate they influence the *p*H of precipitation [*Charlson and Rodhe*, 1982] and they affect global radiation balance and possibly climate [*Bates et al.*, 1987*a*; *Charlson et al.*, 1987; *Crutzen*, 1976; *Rampino and Volk*, 1988; *Shaw*, 1983]. Although anthropogenic emissions constitute a large source of gaseous S, mass balance considerations indicate that the release of biogenic S into the atmosphere makes up a significant percentage of S that enters the troposphere annually. Emissions of oceanic dimethyl sulfide (DMS) are a large source of this biogenic S gas [*Andreae*, 1986; *Bates et al.*, 1987*b*]. However, continental habitats are much more diverse and their role as producers of biogenic S gases remains as one of the most uncertain aspects of our understanding of the atmospheric S cycle [*Andreae*, 1985].

Waterlogged areas are conducive to the production and emission of reduced gases such as methane and reduced S compounds. When considered on an area basis, wetlands are strong sources of atmospheric S gases such as hydrogen sulfide (H_2S), DMS, methyl mercaptan (MSH), carbonyl sulfide (COS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS) [*Hines*, 1993]. The majority of previous work on continental S gas exchange was conducted in salt marshes which emit large quantities of H_2S and DMS [*Jørgensen and Okholm-Hansen*, 1985; *Morrison and Hines*, 1990; *Steudler and Peterson*, 1985]. However, it appears that high fluxes of DMS from salt marshes are restricted to regions inhabited by certain species of *Spartina* and that other marsh areas do not emit unusually large amounts of gaseous S to the atmosphere [*Dacey et al.*, 1987; *Morrison and Hines*, 1990]. In addition, the small spatial extent of salt marshes precludes them as major global sources of gaseous S [*Carroll et al.*, 1986]. Freshwater wetlands and organic rich soils, in some cases, emit relatively large amounts of gaseous S [*Adams et al.*, 1981; *Goldan et al.*, 1987; *Staubes et al.*, 1989], while other freshwater sites, such as Alaskan tundra [*Hines and Morrison*, 1992], emit very little. *Cooper et al.* [1987*b*] reported that several freshwater wetlands emitted S gases at rates similar to some marine habitats. Because of the uncertainty in the rates of emissions of biogenic S gases, global estimates of the annual emissions of S from terrestrial sources have decreased from ~25 Tg yr^{-1} in 1984 [*Möller*, 1984] to <0.4 Tg yr^{-1} today [*Bates et al.*, 1992].

One approach to refining estimates of regional and global emissions of biogenic gases is to utilize remote sensing data from airborne or orbital platforms to map the distribution and extent of various habitat types. These data, in conjunction with gas flux measurements in these habitats and geographic information system (GIS) software, can be used to derive estimates of gas flux at large spatial scales. *Matthews and Fung* [1987] used this approach with several habitat categories to calculate global CH_4 emissions. *Bartlett et al.* [1989] used a much higher resolution remotely sensed data set and a suite of actual flux measurements to examine variability in emissions of CH_4 from a region of the Florida Everglades.

The present study was conducted to determine the magnitude and range of emission rates of organo-S gases from a variety of

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Sample loops were transported to the South Florida Research Center where they were analyzed within a maximum of 5 hours. In laboratory tests, samples could be stored in loops under liquid N_2 for over 8 hours without loss [*Morrison*, 1988]. Sulfur gases were remobilized by heating loops in a hot water bath, separated on a column packed with 1.5% XE-60, 1% H_3PO_4, 60/80 Carbopack B (Supelco), and quantified by a CS_2-doped flame photometric detector on a Shimadzu model 9A gas chomatograph. The total GC run time was ~6 min with baseline separation of all compounds. Occasionally, when DMS concentrations were high, CS_2 eluted as a skimmed peak on the following edge of the DMS peak. Calibration was conducted using sulfur gases liberated from gravimetrically calibrated permeation devices maintained in a permeation oven. The minimum fluxes that could be detected under the conditions used were <0.4 nmol m^{-2} h^{-1}. Hydrogen sulfide (H_2S) could be detected but could not be quantified because it eluted on the tail of negative peaks due to hydrocarbons and CO_2.

REMOTE SENSING AND CALCULATION OF REGIONAL S FLUXES

To scale up S gas emissions for the Everglades system, we utilized an approach which was similar to that used by *Bartlett et al.* [1989] for CH_4 fluxes in the Shark River slough region of the central Everglades. The distribution of habitats (vegetation types) was inventoried using interpretation of orbital remote sensor data collected by the Landsat thematic mapper (TM) on November 2, 1985. The TM uses seven spectral bands encompassing the visible and infrared regions, and the pixels are 30 x 30 m cells. The TM scene covered much of South Florida, including most of the Everglades National Park, except for the very northwestern edge and some of the islands in Florida Bay to the south. All data processing was done with ELAS software [*Junkin et al.*, 1980]. A vegetation classification was developed to coincide with habitats from which the ground gas flux measurements were taken. Considering these habitats, a parallelepiped classification scheme [*Addington*, 1975] offered the best overall classification results when compared with several other classification procedures (e.g., maximum likelihood). Ground truthing of the classification was based on field inspections during the in situ sampling and partly by interpretation of color infrared photography for the more inaccessible locations. We also utilized vegetation maps provided by the National Park Service. The TM geographic information data base was combined with S emission data for the selected vegetation classes and a regional map was produced which was used to calculate S fluxes for the majority of the Everglades National Park.

RESULTS

Marine Sites

The marine sites exhibited a wide range in rates of S gas emissions (Figure 2). In all instances, except the site dominated by *Batis*, DMS emissions were highest. The well-drained sites (type 1) released the most S gas with summed fluxes of nearly 600 nmol m^{-2} h^{-1} at one location. At this site and the second most active site, enclosures were placed over bare soils that contained openings to crab burrows. The soils within an enclosure placed over a live mangrove in this area did not have any noticeable crab burrows and S emissions were

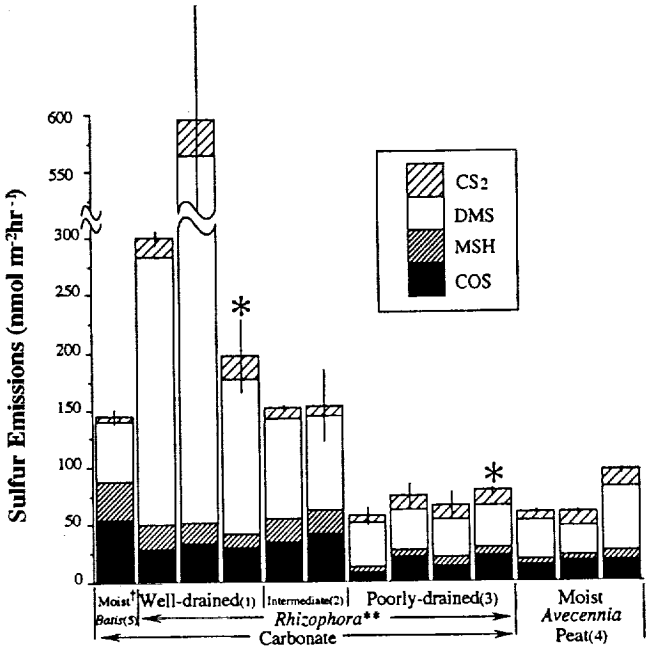

Fig. 2. Rates of sulfur gas emissions from the marine wetland sites in the Everglades. The three types of red mangrove areas (*Rhizophora*) and the *Batis* sites were in carbonate sediments, while the black mangrove sites (*Avecennia*) were in peat sediments. The asterisk represents sites where whole mangrove plants were entrapped within the emission chamber. Site numbers described in the text are included within parentheses. Error bars are standard deviations of replicate measurements at each site.

~200 nmol m^{-2} h^{-1} which were the lowest rates of the well-drained sites. All of these sites were within 2 m of open Florida Bay water.

The intermediate sites (type 2), which were considered transitional between the well drained coarser sediments and the less drained finer-grained sediments, exhibited S fluxes of ~150 nmol m^{-2} h^{-1} which was less than half of the average rate in the well-drained mangrove sites (Figure 2). Differences in S fluxes among all five of the drained sites were attributable to variations in DMS emissions.

Fluxes of S gases from the poorly drained mangrove sites (type 3) were <80 nmol m^{-2} h^{-1} (Figure 2). We noted little variation (<30%) in S gas emissions between these four sites despite the fact that one site included a live mangrove tree and one site was located over one kilometer away from the others.

Fluxes of S gases from the black mangrove sites (type 4) ranged from 60 to 95 nmol m^{-2} h^{-1} (Figure 2). These sites were located ~4 km from open water (Figure 1). Despite the extreme differences in soils between this site and the poorly drained sites described above, S emissions were similar in magnitude and speciation for both types of habitats.

Emissions of S gases from the *Batis*-dominated site (type 5) were twice those of the poorly drained mangrove area (which was ~3 m away) and similar in magnitude to the intermediate mangrove area at ~150 nmol m^{-2} h^{-1} (Figure 2). More than half of the S gas emission from *Batis* was due to COS, and COS and MSH fluxes were the highest recorded for all of the marine sites.

Freshwater Sites

Emissions of S gases from the freshwater sites were generally lower than the marine sites (Figure 3). The dwarf

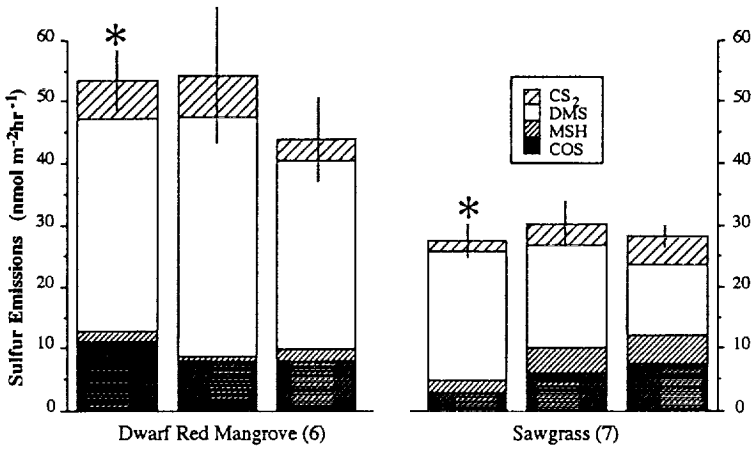

Fig. 3. Rates of sulfur gas emissions from the dwarf red mangrove and wet saw grass sites. The asterisks are sites where plants were entrapped within the emission chamber. At the dwarf mangrove site, the plants within the chamber were *Eleocharis* sp. Site numbers described in the text are included within parentheses. Error bars are standard deviations of replicate measurements at each site.

mangrove sites (type 6), which are influenced by marine waters, exhibited fluxes which were nearly identical in magnitude to the poorly drained red mangrove and the black mangroves sites, while the saw grass sites (type 7) emitted less S than any of the other sites studied. There was very little variation in emissions for each of the replicates examined at the two freshwater sites. The occurrence of plants within the flux chambers had no significant effect on flux rates at these sites (Figure 3). However, the plant biomass was quite low and bare areas (periphyton alone) were common.

Fluxes of S gases from the recently burned sites (type 8) were ~2-fold higher than from the adjacent unburned sites (Figure 4). Flux rates from the unburned site were similar to those in the saw grass site discussed above despite the fact that the emergent biomass was visually much more dense in the unburned area. Emissions from the burned area were similar to those in the dwarf mangroves. Burned and unburned sites containing live plants emitted nearly twice as much gaseous S as bare soils. Plant density at the burned sites was much lower than at the unburned sites and it was possible to place enclosures over areas containing solely hair grass or saw grass. The unburned site was a relatively well-mixed stand of both these species and both were included in enclosures.

Scaling S Emissions to the Region

A color-infrared simulated image of the park derived from TM bands 3, 4, and 5 is depicted in Plate 1. Red shades represent green vegetation (generally, the redder the shade the more vigorously growing or denser the vegetation). Blue and black shades represent water or significant wetness. Greyish shades represent inert materials such as roads, beach sands, rock outcrops, and in some cases yellowing grasses.

Several modifications were made to the initial vegetation classification obtained from the TM image and to the relative grouping of S flux data to provide a useful final categorization. Some of the vegetation classes were not easily discernible because of their small spatial extent and/or spectral similarity to other vegetation types. In some instances the water background predominated over vegetation in spectral response which resulted in mixed vegetation classes. Upland tree species were occasionally spectrally similar to mangroves. By considering the separation between the freshwater and the more saline environments, the upland pines and the hardwood hammocks were carefully regrouped differently from the mangroves. Widely spaced dwarf mangrove, *Eleocharis* sp., and other related plant communities that had a water-dominated background were also clustered together in a dwarf mangrove category. It was possible to separate other classes of vegetation spectrally, but these were clustered to obtain the six final classes examined during the S flux sampling.

Red mangroves did not spectrally separate consistently from black or white mangrove species. At least part of this was due to their tendency to border along waterways and fall within mixed pixel areas on a frequent basis. Therefore a red mangrove class was artificially incorporated as a border class along all open water bodies within the more saline regions of the image. Any larger clusters were incorporated into the black mangrove class. Since we observed that the well-drained red mangrove sites (type 1) occupied a very small region within a few meters of open water, fluxes from these areas were not used to calculate the regional flux of S gases. The red mangrove regional calculations were made using flux data derived from the mean of the intermediate drained sites (type 2) and the poorly drained sites (type 3).

Salt marsh grasses such as *Juncus* and *Spartina* spp. were moderately separable but were clustered with the *Batis* sp. and other coastal prairie plant communities just as was done in a generalized vegetation map published by the National Park Service. We did not measure emissions from areas dominated

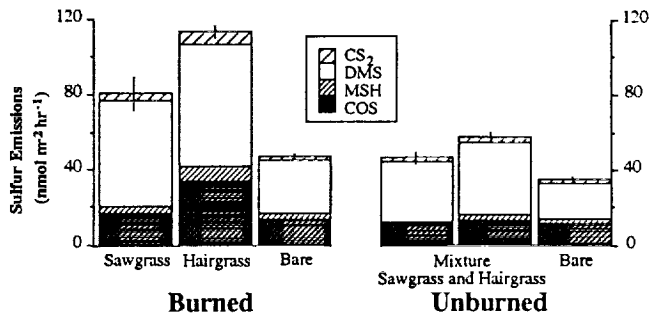

Fig. 4. Rates of sulfur gas emissions from the burned and unburned sites (site 8 in the text). Error bars are standard deviations of replicate measurements at each site.

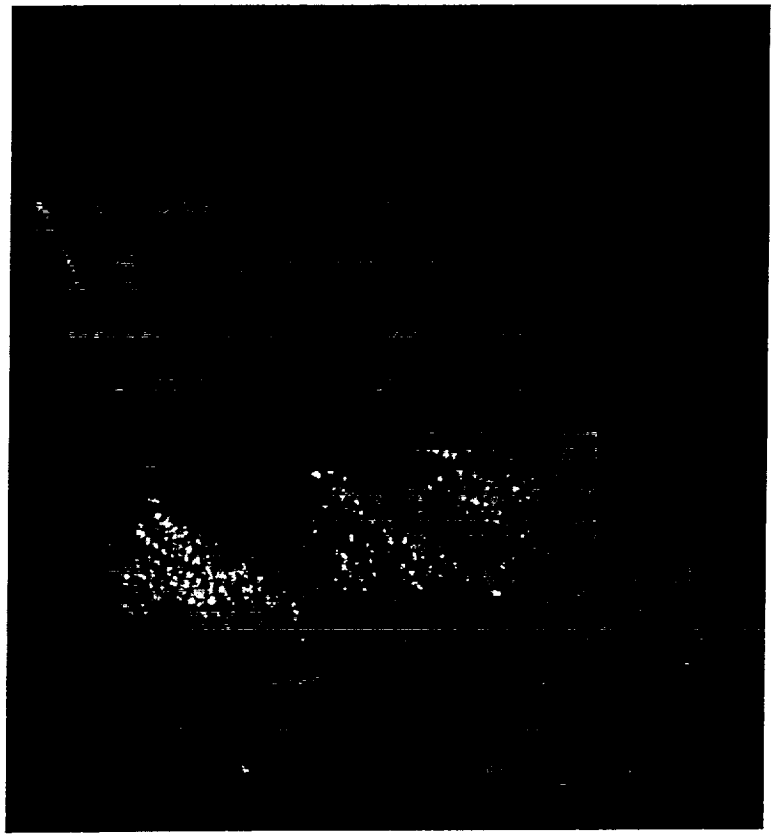

Plate 1. Thematic mapper image of the Everglades National Park taken on November 2, 1985. The image has been trimmed to include only the park.

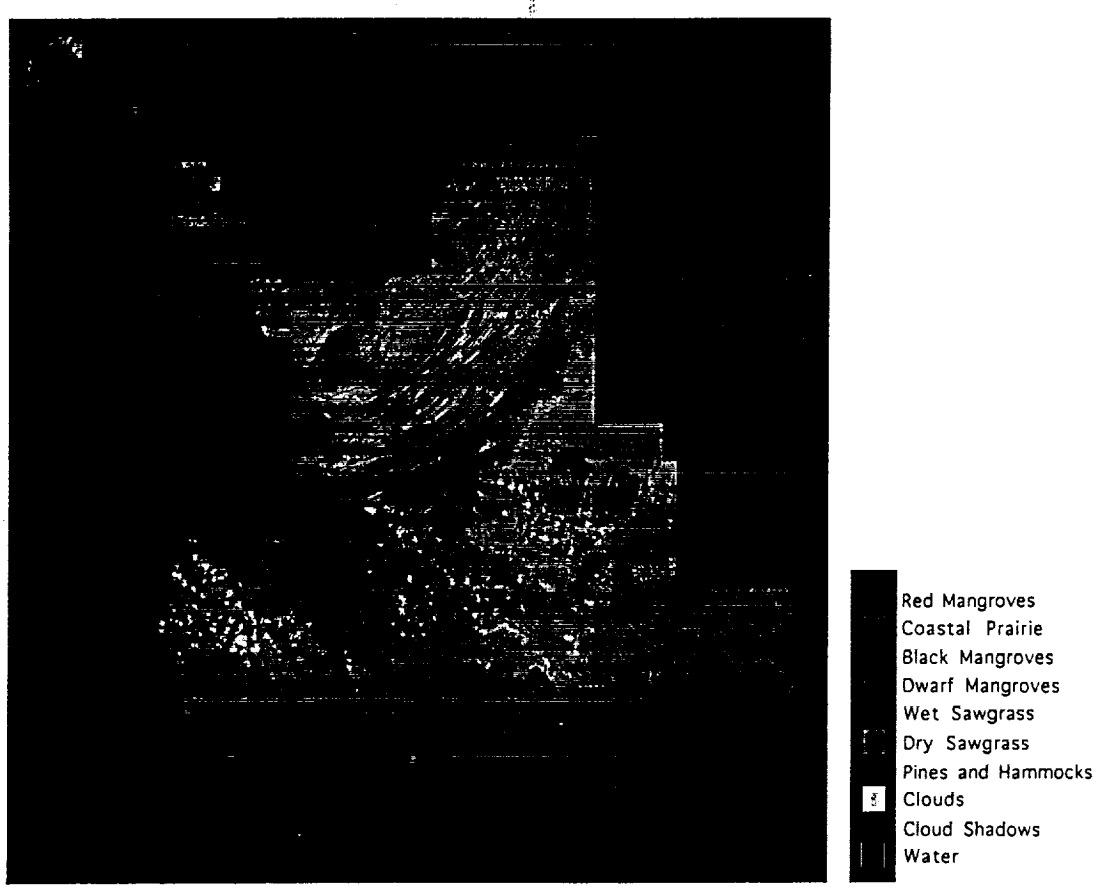

Plate 2. Map of the classes, derived from thematic mapper data, used for scaling up the S emissions for regional estimates.

TABLE 1. Regional Estimate of Sulfur Gas Emissions From Various Wetland Habitats in the Everglades

Vegetation Category (Site Type†)	No. of Samples	S Flux,* nmol m^{-2} h^{-1}, Mean (SE)	Category Area, km^2	Category Flux, moles h^{-1}	Total Flux, %
Red mangrove (2 and 3)	11	108 (14)	200	21.6	11.9
Black mangrove (4)	8	77 (5.9)	810	62.4	34.4
Coastal prairie (*Batis*) (5)	1	145	210	30.5	16.8
Dwarf mangrove (6)	6	51 (4.4)	470	24.0	13.2
Wet saw grass (7)	4	29 (6.7)	770	22.3	12.3
Dry saw grass (8)‡	6	46 (4.2)	450	20.7	11.4
Regional total	36	62	2940	181.5	100

*Total emission combining all four S gases measured.
†Refers to habitat types listed in study site section of text.
‡Emissions from unburned saw grass community.

by these former species which were restricted largely to areas northwest of where emission measurements were made. However, since these sites were mostly indistinguishable on the image and only occupied a small percentage of the scene, for scale up purposes, we used S flux data from the *Batis* site only. This grouping of classes is partially justified by the finding of *Cooper et al.* [1987*b*] that rates of S gas fluxes were similar for *Batis* and *Juncus* sites in Florida. However, sites dominated by *Spartina* can emit large quantities of DMS depending on the species of *Spartina* present [*Morrison and Hines*, 1990].

The saw grass sites were divided between those similar to the mahogany hammock sites (type 7) and the saw grass community represented by the unburned sites (type 8). The former contained less biomass with standing water and was designated as wet saw grass, while the latter canopies were more dense, devoid of standing water and designated as dry saw grass.

The final six vegetation classes selected from the TM image analysis and recategorized for scaling up S gas emissions were (1) red mangroves, (2) coastal prairie (*Batis* and salt marsh plants), (3) black mangroves, (4) dwarf mangroves, (5) wet saw grass, and (6) dry saw grass. A few other classes, e.g., clouds, cloud shadows, pines, hardwood hammocks, and water, were included in the mapping exercise to fill out the remainder of the image. We did not measure S fluxes from open water or upland habitats, so these areas were omitted from the scale up.

Plate 2 shows a color-coded distribution map of the vegetation classes utilized here for scaling up S emissions. These vegetation category areas and S gas fluxes were used to calculate gas flux rates for all of the Everglade wetlands (Table 1). Although individual fluxes varied 20-fold throughout the study area, the contribution of each vegetation category to the regional flux varied by a maximum of a factor of ~3 (Table 1). Black mangroves were the most abundant category on an area basis and accounted for the largest percentage of the S gas flux at ~34%. All the other categories accounted for 11 to 17% of the regional wetland flux. Combining both wet and dry saw grass areas accounted for 24% of the flux even though saw grass covered 42% of the total vegetated area considered.

As expected from data for individual sites, DMS dominated the flux of S gases from all sites regardless of whether they were marine or freshwater (Table 2). In fact, the highest percentages of DMS emitted were from the predominantly freshwater sites.

TABLE 2. Percentage of Total Regional Flux of S Gases Attributable to Individual Gases

Vegetation Category (Site Type*)	COS	MSH	DMS	CS_2
Red mangrove (2 and 3)	26	12	52	9.6
Black mangrove (4)	21	10	54	14
Coastal prairie (*Batis*) (5)	38	23	36	3.3
Dwarf mangrove (6)	18	2.8	69	11
Wet saw grass (7)	19	12	58	11
Dry saw grass (8)†	25	4.0	65	5.7
Regional total	26	13	58	9.7

*Refers to habitat types listed in study site section of text.
†Emissions from unburned saw grass community.

DISCUSSION

Rates of emissions of the sulfur gases studied varied between sites by a factor of ~25. However, spatial variation within sites was usually much less than a factor of 3 and in most instances less than 10%. The fact that all samples were collected within less than a 2-week period, at similar temperatures and during the same time of day made it possible to compare these data without severe complications due to seasonal, diel, or temperature variations. Hence variations were due primarily to spatial variability. This is an important consideration for studies of S gases since diel variations can be large and related to temperature variation [*Goldan et al.*, 1987].

The S flux rates reported here were similar in magnitude to those reported by others for a variety of marine and freshwater wetland habitats (Table 3). The notable exceptions are the rapid fluxes of S gases from salt marsh soils inhabited by *Spartina alterniflora*. In particular, DMS is emitted at high rates from *S. alterniflora* since the DMS precursor, dimethylsulfoniopropionate (DMSP), is abundant in this species [*Dacey et al.*, 1987]. However, when *S. alterniflora* areas are omitted, the sites that we studied emitted S gases at rates that were similar to other habitats regardless of whether they were marine or freshwater. Emissions from the Everglade wetlands were much higher than those from Alaskan tundra [*Hines and Morrison*, 1992] but similar to or less than fluxes of DMS from the ocean [*Bates et al.*, 1992].

Cooper et al. [1987*b*] measured emissions of gaseous S from some similar sites in the Everglades (Table 3). Their DMS fluxes at sites inhabited by black mangroves, *Batis*, and saw grass ranged from <0.5 to up to 5.5 times those reported here. Their data were collected over a 24-hour period which explains the wide range. Their chambers were not shaded during the day,

TABLE 3. Ranges of Emission Rates of Biogenic Sulfur Gases From Various Habitats

Location	Emission Rate, nmol m^{-2} h^{-1} DMS	MeSH	COS	CS_2	Reference
Marine subtropical wetlands					
red mangrove, *Rhizophora**, Oct.†	40 - 600	5 - 22	8 - 42	5 - 30	1
black mangrove, *Avicennia*, Oct.†	25 - 56	5 - 8	14 - 19	7 - 14	1
Avicennia, Jan.‡	9 - 310	NR§	NR	0 - 19	2
Batis, Oct.†	52	34	54	5	1
Batis, Jan.‡	31 - 220	NR	NR	3 - 9	2
Marine temperate wetlands					
Spartina alterniflora‡	0 - $2x10^4$	0 - 300	-40 to 140	0 - 700	3-7
S. patens‡	0 - 130	0 - 60	10 - 36	NR	5
Juncus romerianus	100 - 650	5 - 75	17 - 41	7 - 30	7,8
Distichlis spicata	19 - 720	NR	NR	6 - 53	7,8
Freshwater subtropical wetlands*					
Cladium, Oct.†	16 - 57	1.9 - 4	3.0 - 17	1.5 - 4	1
Cladium, Jan., March, May‡	0 - 220	NR	NR	0 - 16	2
Muhlenbergia, Oct.†	39 - 65	2.5 - 8	12 - 34	2.9 - 7	1
dwarf mangroves, Oct.†	34	1.7	11	6.2	1
Freshwater temperate wetlands					
swamps‖	14 - 700	NR	18 - 85	21 - 78	9
decaying cattails	0.4 - 3	NR	10 - 19	NR	7
Subarctic freshwater tundra¶	0 - 12	0	0.2 - 12	0 - 3	10
Subarctic marine tundra¶	0 - 250	0 - 5	6 - 21	2 - 10	10
Ocean average	170 - 340				11

(1) This study; (2) *Cooper et al.* [1987*b*]; (3) *Cooper et al.* [1987*a*]; (4) *de Mello et al.* [1987]; (5) *Morrison and Hines* [1990]; (6) *Steudler and Peterson* [1985]; (7) *Goldan et al.* [1987]; (8) *Aneja et al.* [1981]; (9) *Adams et al.* [1981]; (10) *Hines and Morrison* [1992]; (11) *Bates et al.* [1992].

*All sites in Florida.

†Samples collected midday.

‡Samples collected over a 24-hour period.

§Not reported.

‖Includes histosols (peat and muck), areas in Florida that may be subtropical, and one fen in Minnesota.

¶Midsummer values.

so depending on weather conditions, it was possible that temperatures inside the chambers were unusually high on some occasions. Although some of the sites studied by *Cooper et al.* [1987*b*] were in the Everglades, in some cases, such as the black mangrove sites, they sampled areas which were several kilometers from the sites we investigated. However, the flux rates measured in both studies were quite similar. This was surprising since the degree of inundation and the tidal and temperature regimes might have differed enough to cause large dissimilarities in fluxes for sites which were spatially separated and studied several years apart. The similarity noted may indicate that this type of habitat is relatively uniform with regard to emissions of S gases from soils.

The greatest variation in S emissions in the present study was due to the high DMS fluxes from the well-drained carbonate soils inhabited by red mangroves. When mangrove sediments were poorly drained and relatively fine grained, emissions were much slower. The bulk of this difference was due to DMS fluxes which were high in the well-drained carbonates. In addition, highest DMS fluxes occurred in sites containing crab burrows. *Smith et al.* [1991] found that these crabs transport virtually all of the mangrove leaf litter into their burrows where the leaves decompose. It appears that the decomposition of leaves in burrows was responsible for the high DMS fluxes noted. The presence of small (60 cm) mangroves within enclosures did not result in any increase in DMS flux relative to sediments alone. Hence the positive relationship between live plant biomass and DMS flux noted for *S. alterniflora* [*de Mello et al.*, 1987; *Morrison and Hines*, 1990] was not apparent in the red mangrove sites. However, the decomposition of dead leaves in burrows appeared to generate significant quantities of DMS.

Recently burned sites emitted twice the quantity of S gases as unburned sites which were only 10 m away. Photosynthesis and CH_4 emissions, which were measured at these sites within a few days of the measurements reported here, were twice as high in the burned areas as well [*Whiting et al.*, 1991]. Since the biomass in the burned areas was sparse compared to the unburned sites, the plant activity per unit of live biomass must have been much higher in the burned sites. It was unclear whether the enhancement in S fluxes from burned areas was due to enhanced plant metabolism or the sedimentary utilization of S that was liberated from biomass during burning. Within both the burned and the unburned sites, faster rates of S gas release occurred within enclosures placed over plants suggesting they were involved in S gas exchange. Because of the frequency of fires in the Everglades, burning should be considered when gas exchange is estimated.

Data on emissions of COS must be viewed with caution since it was likely that the dynamic enclosure system used here resulted in data which made it appear that all sites were net sources of this gas. However, data from enclosure systems which contain ambient or COS-supplemented air demonstrated that some habitats are net sinks for COS [*Hines and Morrison*, 1992; *Morrison and Hines*, 1990; *Steudler and Peterson*, 1985]. Plants are known to consume COS [*Fall et al.*, 1988; *Goldan et al.*, 1988; *Kluczewski et al.*, 1983, 1985] and it has been proposed that this consumption is a major global sink for the gas [*Brown and Bell*, 1986; *Goldan et al.*, 1988]. However,

since COS is abundant in the atmosphere compared to other S gases, when dynamic chambers use S-free sweep air, there can be an increase in COS concentration within the chamber relative to the S-free sweep gas which is interpreted as a net flux even though a net removal may be occurring at ambient COS levels [*Hines and Morrison*, 1992]. We have not observed this artifact for the other S gases measured. If COS is indeed consumed by the system rather than emitted by it, which is likely, then the total organo-S gas fluxes from the Everglades will be ~25% lower than calculated in Table 1. The percentage of flux due to the other S gases will also increase accordingly (Table 2), making DMS account for over 70% of the total flux.

The scaling of S gas emissions to a regional area using vegetation classes and remote sensing data was intended to provide a "snapshot" of S flux and to help decipher which habitats, if any, deserve attention in future work. It was not intended that the regional data would serve as benchmark of S fluxes in this system, particularly with the small data set employed. Unlike CH_4, S flux data are difficult and tedious to obtain and relatively large data bases, such as those used for regional estimates of CH_4 flux by *Bartlett et al.* [1989], are not available. Furthermore, biogenic S fluxes from terrestrial sources, including the Everglades [*Cooper et al.*, 1987*b*, 1989], exhibit strong diel variability. Emissions of CH_4 apparently do not vary greatly throughout a 24-hour period unless plants actively transport gas. In addition, the present study was conducted over a relatively short time period with measurements made over a small portion of the day. Since all of the measurements here were determined under similar climatic conditions for each of the sites, it was assumed that flux data for each site could be compared. However, the scaling exercise yields a regional estimate of flux for the conditions of this study only and are not applicable to nighttime or any other season.

We had insufficient data to adequately address the variability within each habitat. In all sites except *Batis*, chambers were deployed in more than one location and the variation between these local sites was usually less than 15% (expressed as percent of the standard error/mean). However, the individual emissions chambers were never more than 36 m apart. *Bartlett et al.* [1989] reported that sample sizes greater than 20 were needed to achieve a variability of <15% (calculated as above) for CH_4 fluxes along a 1 km transect in a particular freshwater habitat in the Everglades. The lower variability noted here for S gases may be due simply to the fact that all the samples for a particular habitat type were collected in close proximity to each other. Hence the S gas data probably provided a much cruder estimate of regional flux than the variability alone indicated. In addition, *Bartlett et al.* [1989] found no correlation of flux with temperature and *Harriss et al.* [1988] found that CH_4 flux in the Everglades was not sensitive to seasonal changes in temperature. However, *Cooper et al.* [1987*b*] found that DMS emissions from a saw grass site in the Everglades increased ~10-fold from January to May.

The "snapshot" approach to estimating regional S gas emissions suggested that over half of the S flux from regions harboring emergent vegetation in the Everglades was from marine-influenced wetlands, i.e., mangroves and the *Batis*/salt marsh sites. The saw grass sites were less important because of the low area flux from saw grass areas with standing water such as those at mahogany hammock. However, if emissions of S gases from open waters (depths greater than 30 cm) were significant then the freshwater areas could have been similar to the marine sites. We did not determine S gas emission rates for open water sites. However, other studies have demonstrated that both marine [*Bates et al.*, 1987*b*] and fresh [*Richards et al.*, 1991] open water sites can emit significant quantities of S gases to the atmosphere. Although open water sites deserve some attention in the future, the Landsat thematic mapper sensor is designed for delineating terrestrial vegetated habitats and is not suited for discriminating water bodies on the basis of variations in water color. Since emissions of S gases from water should vary depending on their particular chemistries and productivities, our scaling up exercises were restricted to sites with emergent vegetation. In addition, if the burned saw grass areas were to occupy a large area of the Everglades then S fluxes for the whole region would increase slightly as well.

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P. M. Crill and M. E. Hines, Institute for the Study of Earth, Oceans and Space, Morse Hall, University of New Hampshire, Durham, NH 0382+3525.

R. E. Pelletier, NASA, Science and Technology Laboratory, Stennis Space Center, MS 39529.

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Emissions of Sulfur Gases from Wetlands

Mark E. Hines

Institute for the Study of Earth, Oceans and Space
University of New Hampshire
Durham, NH 03824, USA

Abstract

Data on the emissions of sulfur gases from marine and freshwater wetlands are summarized with respect to wetland vegetation type and possible formation mechanisms. The current data base is largest for salt marshes inhabited by *Spartina alterniflora*. Both dimethyl sulfide (DMS) and hydrogen sulfide (H_2S) dominate emissions from salt marshes, with lesser quantities of methyl mercaptan (MeSH), carbonyl sulfide (COS), carbon disulfide (CS_2) and dimethyl disulfide (DMDS) being emitted. High emission rates of DMS are associated with vegetation that produces the DMS precursor dimethylsulfoniopropionate (DMSP). Although large quantities of H_2S are produced in marshes, only a small percentage escapes to the atmosphere. High latitude marshes emit less sulfur gases than temperate ones, but DMS is still the dominate. Mangrove-inhabited wetlands also emit less sulfur than temperate *S. alterniflora* marshes.

Few data are available on sulfur gas emissions from freshwater wetlands. In most instances, sulfur emissions from temperate freshwater sites are low. However, some temperate and subtropical freshwater sites are similar in magnitude to those from marine wetlands which do not contain vegetation that produces DMSP. Emissions are low in Alaskan tundra but may be considerably higher in some bogs and fens.

Keywords: Biogenic sulfur gases, wetlands, hydrogen sulfide, dimethyl sulfide, carbonyl sulfide, carbon disulfide, dimethyl disulfide, methyl mercaptan

Introduction

Gaseous sulfur compounds are intermediate metabolites or end products of biological processes in natural environments. Although the majority of hydrogen sulfide (H_2S) is probably produced through dissimilatory sulfate reduction, other reduced sulfur gases appear to be generated 1) during a variety of anaerobic respiratory or fermentative processes which may be complex; 2) as a cleavage product during decomposition of a biologically-produced compound or; 3) photochemically (Kadota and Ishida 1972; Bremner and Steele 1978; Khalil and Rasmussen 1984; Jørgensen and Okholm-Hansen 1985). It appears that waterlogged areas are conducive to the production and emission of sulfur gases and, when considered on an areal basis, wetlands are strong sources of atmospheric sulfur compounds such as H_2S, dimethyl sulfide (DMS), methyl mercaptan (MeSH), carbonyl sulfide (COS), carbon disulfide (CS_2) and dimethyl disulfide (DMDS) (Jørgensen and Sorensen 1985; Steudler and Peterson 1985; Cooper et al. 1987b; Morrison and Hines 1990).

Much of the recent information concerning sulfur gases in wetlands has been derived from studies of rates of gaseous sulfur emissions from these habitats in response to a need to balance the atmospheric sulfur budget and concerns about acid precipitation (Maroulis and Bandy 1977; Möller 1983). However, studies of gas emissions have provided insights into some of the mechanisms of formation and release of sulfur gases. Research on sulfur gas emissions from wetlands, especially those from higher latitudes, and mechanisms which may be responsible for the production of some of these gases will be emphasized in this paper. The reader is referred to recent reviews by Aneja and Cooper (1989) and Giblin and Wieder (in press) who tabulated rates of biogenic sulfur gas emissions from various habitats including salt marshes and freshwater wetlands.

Marine-Influenced Wetlands

Temperate Salt Marshes

Rates of emission of sulfur gases from salt marshes vary diurnally, from one location to the next and from one type of vegetation to another (Table 1). Until the mid-1970's it was thought that salt marshes were a significant global source of gaseous sulfur because they contained large quantities of sulfide (Kellogg et al. 1972; Ivanov 1981). During the last five years it has been demonstrated that the small areal extent of salt marshes precludes them from being an important global source of gaseous sulfur.

The majority of salt marsh work was conducted in stands of *Spartina alterniflora* which is the predominant grass in many temperate salt marshes. Emissions of DMS usually dominate the flux of sulfur from areas inhabited by this grass (Table 1). Fluxes of H_2S can be high as well. The high rates of DMS emissions from *S. alterniflora* are undoubtedly due to the presence of high concentrations of the DMS precursor dimethylsulphoniopropionate (DMSP) in all parts of the plant (Dacey et al. 1987). This compound is an osmoregulant in certain marine algae and higher plants. Its enzymatic cleavage yields DMS plus acrylic acid (Cantoni and Anderson 1956; Larher et al. 1977; Stewart et al. 1979; Dacey et al. 1987). Although the turnover of only a small portion of the endogenous pool of DMSP would be needed to produce a large DMS flux, recent investigations supported the premise that the bulk of DMSP cleavage to DMS occurs through microbial decomposition of plant tissue or possibly exuded DMSP rather than by the metabolism of *S. alterniflora* (Kiene, this volume).

It was demonstrated in laboratory studies that the bulk of DMS loss from soils inhabited by *S. alterniflora* occurs from the emergent portion of the plant and that the sediments act as a sink (Dacey et al. 1987). Field emission studies showed increased DMS fluxes from sites with the most aboveground biomass (Hines et al. 1989). Conversely, de Mello et al. (1987) reported a two-fold difference in DMS emissions from sites that contained essentially equal quantities of aboveground biomass but contained a

large difference in the amount of belowground biomass. Although roots and rhizomes of *S. alterniflora* contain large quantities of DMSP (Dacey et al. 1987), concentrations of DMS in marsh sediment pore waters are low (≤ 100 nM; Howes et al. 1985). Apparently, DMS released from DMSP in marsh soils is utilized rapidly by soil microflora. Methanogenic and sulfate-reducing bacteria have been shown to decompose DMS in marsh soils (Kiene et al. 1986; Kiene 1988; Kiene and Capone 1988).

Only three species of *Spartina* have been shown to contain high levels of DMSP: *S. alterniflora*, *S. anglica* (Larher et al. 1977; Dacey et al. 1987) and *S. foliosa* (J.D.H. Dacey, pers. comm.). Field emission studies by Morrison and Hines (1990) demonstrated rates of DMS flux from *S. alterniflora* which were 100-fold faster than emissions from an adjacent stand of *Spartina patens*, another common marsh grass. *Spartina patens* does not produce DMSP (Dacey et al. 1987) which underscores the dominant role of DMSP as a precursor of DMS in these environments.

It is beyond the scope of this paper to address the biogeochemistry of H_2S in salt marshes. Considerable work has been conducted on sulfate reduction in salt marshes (eg. (Howarth and Teal 1979; Howes et al. 1983; King 1983; Hines et al. 1989). Even though sulfide concentrations can be very high (mM levels) in marsh sediment pore waters (King 1983; Hines et al. 1989), only a minor portion escapes to the atmosphere (Jørgensen and Okholm-Hansen 1985). Emissions of H_2S are affected strongly by tidal pumping which can increase flux rates by as much as four orders of magnitude (Jørgensen and Okholm-Hansen 1985; Cooper et al. 1987a). Emissions of H_2S generally increase at night (Hansen et al. 1978; Jørgensen and Okholm-Hansen 1985; Castro and Dierberg 1987). During the day certain anaerobic photosynthetic microorganisms at the sediment surface consume sulfide while other oxygenic microorganisms increase the depth distribution of oxygen which oxidizes sulfide before it escapes. However, Carroll et al. (1986) reported daytime maxima in H_2S emissions from a *Spartina* marsh. The distribution of dissolved sulfide is influenced strongly by iron geochemistry, and it would be expected that

emissions would be higher in iron-poor soils such as carbonates. Vegetated soils also tend to prevent the release of H_2S compared to organic-rich sulfureta-type sediments (Jørgensen and Okholm-Hansen 1985) because marsh plants deliver oxygen to roots which enhances sulfide oxidation. Periodic dessication during neap tides also tends to oxidize the sediments (Howes et al. 1981; Dacey and Howes 1984; Hines et al. 1989) . Sulfureta-type sediments emitted 20-90% of the sulfide produced from sulfate reduction compared to non-sulfureta sediments which emitted <0.02% (Hansen et al. 1978; Jørgensen and Okholm-Hansen 1985).

Emissions of MeSH, CS_2, COS and DMDS from salt marshes are considerably slower than the fluxes of DMS or H_2S (Table 1). Although emissions of MeSH from a *S. alterniflora*-inhabited area in New Hampshire were less than DMS emissions they also varied in a similar fashion throughout the day (Morrison and Hines 1990). This suggested that MeSH flux was related mechanistically to DMS emissions or that the demethylation of DMS was responsible for the bulk of the MeSH released. The coincidence between MeSH and DMS emissions was reported for other *S. alterniflora* soils (Goldan et al. 1987), for agricultural plants grown in the laboratory (Fall et al. 1988) and for certain sites in a Danish estuary (Jørgensen and Okholm-Hansen 1985). The similarity between the daily variation in flux of these gases was not noted for sites dominated by *S. patens* (Morrison and Hines 1990) or *Juncus romerianus* (Goldan et al. 1987) and the emission ratio MeSH:DMS was 30-fold higher in *S. patens* soils compared to sites inhabited by *S. alterniflora*.

Emissions of COS from salt marshes are also much lower than DMS emissions from *S. alterniflora*-inhabited sites (Table 1). Laboratory studies revealed that vegetation consumed COS in the daylight similarly to CO_2 (Fall et al. 1988; Goldan et al. 1988). When flux measurements were made using chambers that employed sulfur-free sweep air only an efflux of gaseous sulfur was determined. However, studies using ambient sweep air containing COS (Steudler and Peterson 1985) or sweep air with COS added (Morrison

and Hines 1990) demonstrated uptake of COS by *S. alterniflora*. Conversely, light stimulated the emission of COS from sediment cores devoid of vegetation (Jørgensen and Okholm-Hansen 1985).

Emissions of CS_2 and DMDS were detected in many studies of salt marshes (Table 1). Rates of emission of both these compounds were generally very low and DMDS fluxes were usually lower than those for CS_2 (Steudler and Peterson 1985; Cooper et al. 1987a; de Mello et al. 1987). The low emission rates and the often inconsistent temporal trends noted for the emissions of these compounds make interpretations of possible production and emission mechanisms difficult.

Subarctic Salt Marsh

Emissions of sulfur gases from a salt marsh on the Alaskan coast in the Bering Sea were much slower than for temperate salt marshes (Table 1) (Hines and Morrison in press). Unlike temperate marshes, subarctic regions are devoid of vegetation throughout the majority of the intertidal zone with various grasses situated near the high tide line. Hines and Morrison (in press) measured sulfur emissions from sites inhabited by various plants and from a bare mud flat. The site exhibiting the highest flux of sulfur contained the sedge *Carex subspathacea*. This *Carex* sp. which emits primarily DMS is grazed thoroughly by geese during the summer. Emissions of DMS doubled when geese feces were left within the emission chamber. Although the DMS emissions were low from this site, the ratio of flux to emergent biomass was similar to data for temperate *S. alterniflora*. This similarity suggested that *C. subspathacea* produces a sulfonium compound like DMSP and that emission of DMS from geese feces is analogous to the enhancement of DMS emissions when DMSP-producing marine algae are grazed by zooplankton (Dacey and Wakeham 1986). Supralittoral vegetation (*C. ramenskii*) at the Alaskan site was orders of magnitude more abundant than *C. subspathacea* yet emitted little to no DMS.

Subtropical

Emissions of sulfur gases from mangrove-dominated wetlands (Table 2) were reported in three studies (Castro and Dierberg 1987; Cooper et al. 1987b; Hines et al. in prep.). Cooper et al. (1987b) reported data for soils inhabited by black mangroves (*Avicennia germinans*) where DMS and H_2S emissions were similar in magnitude and varied greatly in response to soil temperature. Emissions of CS_2 and DMDS were an order of magnitude lower than DMS or H_2S. The fluxes all of these gases were much lower than fluxes from *S. alterniflora* in Florida (Cooper et al. 1987a; de Mello et al. 1987). Hines et al. (in prep.) also found that sulfur emissions from black mangrove peatty soils were much lower than those for *S. alterniflora* soils and that their measurements of mid-day rates were nearly an order of magnitude less than those rates reported by Cooper et al. (1987a).

Emissions from salt-tolerant red mangrove (*Rhizophora* sp.) were also measured by Hines et al. (in prep.). These were consistently higher at sites that were frequently flooded, well drained at low tide and directly adjacent to open water. Areas with a few cm of standing water over fine-grained carbonate material had surprisingly low emissions compared to drier well-drained sites. Emissions of DMS were dominant. Fluxes of MeSH and CS_2 were often relatively high especially from the well drained areas near open water. Emissions of COS were much higher from the well-drained areas as well. There was no significant increases in fluxes when intact *Rhizophora* sp. plants were included within the enclosures. Sulfur gas fluxes from all of these marine subtropical sites seem to indicate greater emissions from the soil rather than plants. Castro and Dierberg (1987) reported highly variable H_2S fluxes from areas dominated by red mangroves. Emissions of sulfur gases have also been determined by Castro and Dierberg (1987) and Cooper et al. (1987a) for regions inhabited by *Distichlis* sp. and *Juncus* sp. (Table 1) and by Cooper et al. (1987a) and Hines et al. (in prep.) for the *Batis* sp. (saltwort) in Florida (Table 2). Temperature variations strongly affected the measured gas fluxes.

It appears that emissions of sulfur from subtropical marine wetlands are not as high as those from temperate *S. alterniflora* soils. The major difference is probably the high flux of DMS from *S. alterniflora*. Even when the year round growing season in the tropics is taken into consideration, these environments do not seem to be significant global sources of atmospheric sulfur. This is in contrast to the estimates made by Adams et al. (1981b) who reported that emissions of sulfur gases increased exponentially along a north to south gradient. More recent work by Andreae et al. (in press) indicated that tropical soils are not unusually high sources of atmospheric gaseous sulfur. However, they sampled only upland soils. As pointed out by Aneja and Cooper (1989), most of the data reported recently appear to indicate that terrestrial sulfur emission rates are as much as 20-fold lower than those reported nearly a decade ago (i.e. Adams et al. 1981a,b). Although a portion of this descrepancy is probably due to methodogical improvements and a larger data base, recent data suggested that emissions do not increase exponentially from temperate to the tropical regions.

Freshwater Wetlands

Temperate to Subtropical

Few studies have addressed the production and emission of sulfur gases in freshwater environments (Table 3). The majority of emission data for inland sites are from soils. However, some of these studies also measured emissions from wetlands. Adams et al. (1981b) found that sulfur emissions were relatively slow in swamps and several peatty "muck" areas throughout the eastern U.S.A. Aneja et al. (1981) reported that emissions of H_2S from a freshwater marsh in North Carolina were relatively high but that fluxes of DMS, COS, CS_2, MeSH and DMDS were less than their detection limit of ~175 nmol m^{-2} hr^{-1}. Goldan et al. (1987) found that emissions of COS, H_2S and DMS from decaying cattails were low and 10 to 1000-fold less than those from a salt marsh site . Although H_2S fluxes were similar to those from grasses and clover, COS fluxes from cattails (*Typha*

sp.) were ~10-fold higher and DMS fluxes were ~10-fold lower than fluxes from grasses and clover.

Emissions of sulfur gases from freshwater subtropical wetlands were measured by Cooper et al. (1987b), Castro and Dierberg (1987) and Hines et al. (in prep.) (Table 3). Emissions from sawgrass (*Cladium* sp.)-dominated areas were similar in magnitude to emissions from some of the marine areas investigated. In fact, emissions from freshwater sites studied by Hines et al. (in prep.) were similar to those from the wet and peatty mangrove sites sampled within a few days of the freshwater areas. Cooper et al. (1987b) found much higher emissions of sulfur during the hottest times of the year. Unlike the marine sites inhabited by mangroves, fluxes of sulfur gases from various freshwater sites doubled when enclosures were placed over sawgrass and/or *Muhlenbergia* sp. plants (Hines et al. in prep.). The lower total fluxes and the larger leaf areas of these freshwater habitats may result in an increased importance of direct leaf emission of sulfur from freshwater wetland grasses compared to the marine mangrove sites situated within this same large wetland system in the Everglades. Many types of terrestrial plants have been shown to directly release sulfur gases (Rennenberg 1984, 1989; Fall et al. 1988).

Emissions of sulfur from Everglades freshwater sites were twice as high from locations that had burned five months previously compared to adjacent unburned sites (Hines et al. in prep.). Fires are common in wetlands like the Everglades where they contribute to natural species succession and preservation. The recycling of sulfur through plant organic matter, ash, soil microorganisms and plants may influence the natural emissions of sulfur from these environments, or perhaps the enhanced productivity of newly-growing species accounts of the enhanced fluxes. The aboveground biomass was much smaller at the burned sites but its photosynthetic activity was higher (G.J. Whiting, pers. comm.).

Higher Latitudes

Wetlands are important features in high latitude terrestrial environments. Bogs, fens and non-forested tundra, which remain wet throughout the warmer months, occupy a large percentage of the terrain. Nriagu et al. (1987) found that DMS, and perhaps H_2S, concentrations were relatively high in standing waters within bogs in Ontario. His calculated fluxes of DMS were similar in magnitude to average oceanic fluxes (Table 3). On the basis of isotopic data he suggested that some of the sulfur emitted from industrial activity that was deposited in these bogs was biologically transformed into DMS and H_2S which was re-emitted to the atmosphere.

Recent data for Alaskan tundra (Hines and Morrison in press) demonstrated that emissions of gaseous sulfur from this environment are very low and similar to rates of sulfur emissions from temperate cattails, native grasses and organic-poor soils (Goldan et al. 1987; Lamb et al. 1987; MacTaggart et al. 1987; Staubes et al. 1989) (Table 3). Using enclosures, emissions from tundra were highest from wet meadows and slough areas which contained grasses and some standing water. Sulfur fluxes were slowest from sites dominated by lichens. Emissions from all sites were dominated by DMS; however, H_2S could not be quantified with the techniques used at the tundra sites. Since complete water inundation appeared to enhance emissions from tundra it was postulated that low fluxes of sulfur were due in part to hydrological changes in water levels. Tundra environments also tend to accumulate organic matter that is never completely decomposed. However, this environment receives very little input of sulfur from the atmosphere (Talbot et al. in press), of which approximately 0.5% is re-emitted as DMS.

Contrary to the Alaskan tundra data, emissions of sulfur gases from bogs and fens in New Hampshire were among the highest ever measured for freshwater environments (Hines unpublished data; Table 3). Emissions of DMS which appeared to originate from below the water table in the New Hampshire fen clearly overwhelmed the other quantified gases. Even though H_2S was not determined quantitatively, it was routinely noted. There

are some indications that sulfur gas emissions are strongly influenced by the position of the water table relative to the surface of the mosses. It appears that DMS is produced under anaerobic conditions in bogs as opposed to its possible aboveground source in salt marshes. The fluxes of sulfur gases from the New Hampshire bogs/fens were greater than the calculated emissions reported from bogs in Ontario (Nriagu et al. 1987) even though atmospheric sulfur deposition is probably substantially higher at the Ontario sites. One reason for this discrepancy may be that the Canadian rate data were derived from measurements of DMS in standing water while those in New Hampshire were measured directly at the vegetated sites. From these studies it is unclear 1) if sulfur emissions are relatively rapid from bogs and fens in general; 2) if this emission is regulated primarily by the amount of atmospheric sulfur deposition and is, thus, only rapid in polluted areas and; 3) how sulfur gases are produced in bog environments. Adams et al. (1981b) reported very low emissions of sulfur gases from a fen in Minnesota. The sulfur budget for a bog in Minnesota was nearly balanced indicating that the the loss of gaseous sulfur had to be small on an annual basis (Urban et al. 1989). In addition, Morgan et al. (this volume) found that the concentrations of sulfur gases in the pore waters of a New Jersey fen were quite low and dominated by H_2S and DMS.

Conclusions

Considerable progress has been made in the last 10-15 years in the quantification of rates of emissions of sulfur gases from wetland habitats. However, the only habitats that have been characterized fairly well are temperate salt marshes and, even there, data are sparse, especially results from seasonal studies. It appears that earlier studies of the role of terrestrial environments in the global sulfur cylce overestimated their importance by as much as a factor of ten. The low latitudes probably emit much less gaseous sulfur to the atmosphere while the high latitudes may be a larger source of these gases than previously thought. The paucity of data underscores the need to include all of the major habitats when assessing the importance of wetlands as sites for production and recycling of gaseous

sulfur. In addition, studies are needed which address the mechanisms of production and transformation of sulfur gases within the various terrestrial ecospystems.

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Table 1. Emissions of biogenic sulfur compounds from vegetated areas of saline marshes. Absolute detection limits varied greatly between studies. 0 = below detection.

Location	Emission Rate (nmol m^{-2} hr^{-1}) H_2S	DMS	MeSH	COS	CS_2	DMDS	Ref.
Spartina alterniflora, NH, June, August	nr[Ω]	800-18,000	10-300	-25 to -40[*]	nr	nr	1
S. alterniflora, MA, all year[@]	-6000-18,000	0-52,000	nr	94-2200[∞]	0-1600[∞]	0-38,000[∞]	2
S. alterniflora, NC, August	10-620	560-1700	9-19	7-22	4-9	nr	3
S. alterniflora, NC, Summer	1800	640, 4700[¥]	nr	140[§]	700[§]	nr	4, 5
S. alterniflora, FL, Jan., Oct., May	2-3500	310-17,000	nr	nr	0-560	0-120	6, 7
S. alterniflora, NC	0	1400[§]	0	110[§]	530[§]	0	8
S. patens, June and August	nr	0-130	0-60	10-36	nr	nr	1
S. alterniflora & S. patens, VA, Aug., Sept.	0-30	nr	nr	0-28	45	nr	9
Juncus romerianus, August	25-20,000	100-650	5-75	17-41	7-30	nr	3
J. romerianus, FL, April, May, Jan.	3-90	3-200	nr	nr	0	0	10
J. romerianus, FL, August	11-54	nr	nr	nr	nr	nr	11
Distichlis spicata, FL, April (H_2S), May	260-4800	19-720	nr	nr	6-53	3-50	10
Marsh meadow, Denmark, July	nr	100-1100	0-25	0-140	nr	nr	12
Various saline marshes[&]	70-2,000,000	24-6600	1.1-83,000	0.7-23,000	4-5000	1.5-5800	13
Spartina, Juncus, Distichlis , NC, summer	0-4300	1-1300	nr	1-800	1-180	nr	14
Alaska, July[**]							
Carex. subspathacea	nr	200	3.2	6	6.5	nr	15
C. ramenskii	nr	0.9	0.3	13	4.8	nr	15
Elymus arenaria	nr	75	2.2	20	6.2	nr	15

[Ω]not reported
[*]negative values indicate uptake
[@]range of 24 h mean values
[∞]daily mean values were positive yet some hourly values were negative indicating uptake
[¥]averages from Cox's Landing and Cedar Island, respectively
[§]average values
[&]range of average values from 15 locations
[**]average values

1. Morrison and Hines (1990)
2. Steudler and Peterson (1985)
3. Goldan et al. (1987)
4. Aneja et al. (1979a)
5. Aneja et al. (1979b)
6. Cooper et al. (1987a)
7. de Mello et al. (1987)
8. Aneja et al. (1981)
9. Carroll et al. (1986)
10. Cooper et al. (1987b)
11. Castro and Dierberg (1987)
12. Jørgensen and Okholm-Hansen (1985)
13. Adams et al. (1981b)
14. Lamb et al. (1987)
15. Hines and Morrison (in press)

Table 2. Emissions of biogenic sulfur compounds from subtropical areas inhabited by mangroves and from sites adjacent to mangroves inhabited by saltwort.

Location	Emission Rate (nmol m^{-2} hr^{-1}) H_2S	DMS	MeSH	COS	CS_2	DMDS	Ref.
Red mangroves (*Rhizophora*), June, July†	0-970	nr	nr	nr	nr	nr	1
Red mangroves, Oct*	nr	40-550	5-22	8-42	5-30	nr	2
Black mangrove (*Avicennia*), Oct*	nr	25-56	5-8	14-19	7-14	nr	2
Black mangrove, Jan‡	9-160	9-310	nr	nr	0-19	0-19	3
Saltwort (*Batis maritima*), Jan‡	18-31	31-220	nr	nr	3-9	3-16	3
Saltwort, Oct*	nr	52	34	54	5	nr	2

†some samples collected mid day, others over 24 hr period
*all samples collected mid-day
‡samples collected over 24 hr period

1. Castro and Dierberg (1987)
2. Hines et al. (in prep.)
3. Cooper et al. (1987b)

Table 3. Emissions of biogenic sulfur gases from freshwater wetland habitats.

Location	Emission Rate (nmol m^{-2} hr^{-1}) H_2S	DMS	MeSH	COS	CS_2	DMDS	Ref.
Temperate							
Swamps* (many locations, eastern USA)	4-570	14-700	nr	18-85	21-78	4	1
Decaying cattails, OH, summer	9-16	0.4-3.0	nr	10-19	nr	nr	2
Freshwater marsh, NC, summer and fall	360-2100	0	0	0	0	0	3
Subtropical†							
Cladium , Jan., Mar., May‡	3-150	0-220	nr	nr	0-16	0-22	4
Cladium, Oct.¢	nr	16-57	1.9-3.5	3.0-17	1.5-4.0	nr	5
Muhlenbergia, Oct.¢	nr	39-65	2.5-8.0	12-34	2.9-7.3	nr	5
Eleocharis, Oct.¢	nr	34	1.7	11	6.2	nr	5
Eleocharis, Mar.‡	190-390	nr	nr	nr	nr	nr	6
Swamp, brackish, Aug., Sept.‡	3.5-21	nr	nr	nr	nr	nr	6
Higher latitudes							
Tundra, wet meadows∞, AK, July	nr	1.5-10	trace	nr	0-3.3	nr	7
Tundra, upland¶, AK, July	nr	0-8.3	trace	nr	trace	nr	7
Bogs and Fens, Ontario, Canadaœ	nr	300	nr	nr	nr	nr	8
Fens§, NH, July, Aug.	nr	240-1700	2-30	4-10	2-21	nr	9

*includes histosols (peat and muck), areas in FL that may be subtropical and one fen in MN

†all sites in Florida

‡samples collected over 24 hr period

¢samples collected mid-day

∞standing water with emergent grasses, sedges and *Sphagnum* mosses

¶variety of areas with mosses, lichens, graminoids and grasses

§dominated by *Sphagnum* mosses and/or various short woody plants

œcalculated from DMS concentrations in standing water

1. Adams et al. (1981b)
2. Goldan et al. (1987)
3. Aneja et al. (1981)
4. Cooper et al. (1987b)
5. Hines et al. (in prep.)
6. Castro and Dierberg (1987)
7. Hines and Morrison (in press)
8. Nriagu et al. (1987)
9. Hines (unpublished)

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Acetate concentrations and oxidation in salt marsh sediments

Abstract

Acetate concentrations and rates of acetate oxidation and sulfate reduction were measured in S. alterniflora sediments in New Hampshire and Massachusetts. Pore water extracted from cores by squeezing or centrifugation contained >0.1 mM acetate and, in some instances, >1.0 mM. Pore water sampled non destructively contained much less acetate, often less than 0.01 mM. Acetate was associated with roots, and concentrations varied with changes in plant physiology. Acetate turnover was very low whether whole core or slurry incubations were used. Radiotracers injected directly into soils yielded rates of sulfate reduction and acetate oxidation not significantly different from core incubation techniques. Regardless of incubation method, acetate oxidation did not account for a substantial percentage of sulfate reduction. These results differ markedly from data for unvegetated coastal sediments where acetate levels are low, oxidation rate constants are high and acetate oxidation rates greatly exceed rates of sulfate reduction. The discrepancy between rates of acetate oxidation and sulfate reduction in these marsh soils may be due either to the utilization of substrates other than acetate by sulfate reducers or artifacts associated with measurements of organic utilization by rhizosphere bacteria. Care must be taken when interpreting data from salt marsh sediments since the release

of material from roots during coring may affect the concentrations of certain compounds as well as influencing results obtained when sediment incubations are employed.

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Anaerobic decomposition is an important component of the cycling of carbon in sediments. Acetate is a significant intermediate in this decomposition, both as a fermentation product and a substrate (Lovley and Klug 1986). It is generally assumed that acetate is an important precursor for bacteria, such as sulfate-reducing and methane-producing bacteria, which are situated at the terminal step in the anaerobic decomposition pathway. In fact, acetate accumulates in sediments in which these processes have been inhibited (Smith and Klug 1981; Michelson et al. 1989). In subtidal marine sediments, the measured rate of acetate oxidation often exceeds the rate of sulfate reduction (Sansone 1986). However, it has been proposed that the discrepancy between these two rate measurements is due to the presence of an acetate pool that is not bioavailable (Christensen and Blackburn 1982; Novelli et al. 1988) leading to an overestimation of acetate oxidation.

Sulfate reduction accounts for more than half of the decomposition that occurs in salt marsh sediments and rates of sulfate reduction in marsh sediments are among the highest recorded (Howarth and Hobbie 1982). These high belowground rates are due to high rates of primary production in salt marshes and the fact that a large fraction of this productivity is allocated to growth belowground (Schubauer and Hopkinson 1984). Studies of the utilization of organic substrates in these sediments could potentially be hampered by the fact that common techniques such as coring, squeezing

and centrifugation of sediments destroy root and rhizome material. Howes et al. (1985) reported that dissolved organic carbon concentrations in Spartina alterniflora sediments were as much as 7 times higher in samples collected using destructive techniques than concentrations in pore waters obtained using non-destructive methods. Since the actual concentration of a substrate is multiplied by a rate constant (obtained using radiotracers) to obtain actual rates of bacterial utilization of a compound (Wright 1978), erroneously high natural concentrations due to destructive sampling should yield erroneous rates of organic uptake.

Although several previous studies have investigated acetate cycling in freshwater and marine sediments, sediments inhabited by vascular plants have not been examined similarly even though it has been shown that anaerobic bacterial metabolism is high in vegetated sediments relative to unvegetated habitats (Hines 1991). The present study was conducted to determine the potential role of acetate in salt marsh sediments. In particular, the objective was to examine the effects, if any, of the release of acetate during sediment processing on the use of acetate by microbes in vegetated sediments.

Samples were collected from two New England salt marshes from 1983 through 1988. The first was Chapman's Marsh in southern New Hampshire (Hines et al. 1989) where sediments were sampled in a creekside stand of tall S. alterniflora and in a stand of S. patens. Samples were also collected in

adjacent areas in which S. alterniflora had been recently killed by wrack. The second site was in a stand of short S. alterniflora in Great Sippewissett Marsh in Massachusetts (Howarth et al. 1983). Samples here were also collected in areas in which the S. alterniflora had been killed by covering grasses with wooden planks.

Sediment cores from Chapman's Marsh were collected and handled anoxically as described previously (Hines et al. 1989). Sediment samples from Sippewissett Marsh were obtained using a 6.4 cm diameter corer which was immediately capped.

Pore waters were collected anoxically by destructive and non-destructive methods. For destructive samples from Chapman's Marsh, core sections were centrifuged at 5,000 x g. Core material was chopped for placing into centrifuge tubes when necessary. In one set of Chapman's Marsh samples, cores were sliced vertically and one half was processed as described above. The other half was sectioned and the sediments separated from root and rhizomes by washing with seawater. The remaining plant material was chopped and placed into centrifuge bottles similarly to whole core material, mixed with artificial sea water and then centrifuged. The resulting water was then processed similarly to other pore-water samples. The non-destructive pore water samples from Chapman's Marsh were collected anoxically using in situ Teflon sippers (Hines et al. 1989) which were deployed several days prior to the first sampling.

For pore-water sampling in Sippewissett Marsh, cores were extruded, sections were immediately placed in a Reeburgh press (Reeburgh 1967) and pore water pressed out. For non-destructive sampling, core sections were placed within a Reeburgh press and pore water collected without applying pressure using a syringe with a 12-gauge needle inserted into the sediment.

Pore waters from Chapman's Marsh were filtered through 0.4-μm Nuclepore filters, the pH was adjusted with 2 N NaOH and they were stored frozen in acid-washed serum vials sealed with Teflon-lined septa. Samples from Sippewissett Marsh were filtered through 0.45-μm Millipore filters and the pH adjusted with 1 N NaOH.

Acetate was measured using gas chromatography (GC). For Chapman's Marsh, thawed pore water samples were concentrated by evaporation at 80° C, mixed with 100 μl of 10% H_3PO_4, and desalted using a microdistillation system (Christensen and Blackburn 1982). The efficiency of distillation was determined using standards and [^{14}C]acetate. Most samples collected by centrifugation contained sufficient acetate such that preconcentration by evaporation was not necessary. Desalted samples were immediately mixed with an equal volume of 1% formic acid in a microliter syringe and injected into a Perkin Elmer model Sigma 300 gas chromatograph equipped with a 1-m, 4-mm-diameter glass column packed with 0.3% Carbowax 20 M, 0.1% H_3PO_4 on 60/80 mesh Carbopack C (Supleco, Inc.) and a flame ionization detector. The injector was 200° C,

the oven was 120° C, the detector was 130° C and the N_2 flow rate was 80 ml min^{-1}. Standard mixtures of volatile fatty acids (Supleco, Inc.) were put through the entire procedure. The detection limit was ~10 μM. Sippewissett Marsh samples were analyzed similarly to those above and as described by Novelli et al. (1988).

Acetate oxidation rate constants were determined using ^{14}C. Anoxic subsamples (1.0 ml) from Chapman's Marsh cores were mixed with an equal volume of deoxygenated (N_2) artificial sea water in a serum vial and then sealed with a Teflon-lined septa. Slurries were injected with 0.1 or 1.0 μCi of uniformly labeled [^{14}C]acetate. After incubation for 2-24 h, bacterial activity was stopped by injection of 0.25 ml of 10% formaldehyde. Production of $^{14}CO_2$ from acetate oxidation was determined by acidifying killed slurries, stripping with N_2, and trapping CO_2 in vials containing a 1:1:2 mixture of methanol, phenethylamine and a scintillation cocktail, respectively. Replicate control samples were killed with foramldehyde prior to incubation with ^{14}C and were treated similarly. An insignificant quantity of [^{14}C] acetate was carried over from the slurry to the traps. The efficiency of recovery of CO_2 was determined by adding a solution of [^{14}C]bicarbonate to killed controls. Radioactivity was determined by scintillation counting. Rate constants were calculated using a linear equation. Because uptake was very slow in most instances, there was no significant difference between rate constants calculated this

way and constants calculated using natural log transformed data. Acetate oxidation rates were calculated as the product of the rate constants and the pore-water concentrations of acetate corrected for sediment porosity.

Acetate oxidation in Sippewissett samples was determined by injecting uniformly labeled [^{14}C]acetate directly into subcores held within syringes. Sample processing was similar to that described by Novelli et al. (1988). Briefly, after 2-3 h the incubation was terminated by extruding samples into jars containing formaldehyde and NaOH. After mixing, the jars were fitted with phenethylamine impregnated glass fiber filters, the samples were acidified with H_2SO_4, and the trapped $^{14}CO_2$ determined by scintillation counting.

Rates of sulfate reduction were determined using ^{35}S (Howarth and Merkel 1984; Hines et al. 1989). In all cases, except the in situ experiment described below, sediment cores were subcored and sections in syringes were injected with ^{35}S and incubated in the dark for 12-18 h at in situ temperatures. Reactions were stopped by either injection of 10% zinc acetate followed by freezing (Massachusetts samples) or by rapid freezing alone (all other samples). The incorporation of ^{35}S into the acid-volatile (HS^- and iron monosulfides) and chromium-reducible (S° and pyrite) phases were determined for all samples.

On one occasion, rates of sulfate reduction and acetate oxidation were measured in the field by injecting $^{35}SO_4$ or [^{14}C]acetate directly into undisturbed Sippewissett Marsh

sediments at depths of either 5 or 10 cm. The experiment was carried out at low tide and inside very large diameter core tubes which had been placed in the marsh a month previously. After incubation, cores containing the radioisotope were collected using 6.4-cm-diameter core tubes and sulfate reduction rates determined as described above. Cores for sulfate reduction were frozen using Dry Ice after injecting zinc acetate. Cores for acetate oxidation were immediately sectioned and placed in a solution of formaldehyde and NaOH. All the sediment within the tubes was removed from the field for disposal as radioactive waste. Parallel experiments were run on marsh samples collected near the experimental site but with the incubations conducted in situ in syringes as described above for acetate oxidation and sulfate reduction rates in Sippewissett Marsh.

Dissolved acetate concentrations were highest in samples collected using destructive techniques (Tables 1 and 2). The highest concentrations (>1.5 mM) were in the tall S. alterniflora in Chapman's Marsh during vegetative growth (i.e. June 1986) (Table 1). The disturbed (cored) samples yielded acetate levels that were greater than undisturbed samples by as much as 500-fold or more. When cores were washed free of sediment and the remaining root material was processed like an intact core, ~75% of the acetate found in intact cores was recovered (Table 1). In addition, acetate concentrations in squeezed Sippewissett samples collected

during summer were 5–10 fold higher than in pore-water samples removed using a syringe and needle (data not shown).

In most instances, acetate concentrations were much higher than other volatile fatty acids such as propionate and butyrate. The GC techniques used were not able to detect formate, but 67 μM formate, 245 μM acetate, and 27 μM propionate were found in Sippewissett pore waters in the summer using a derivatization GC method (D.G. Shaw pers. comm.). Subtidal unvegetated marine sediments generally contain low concentrations of acetate (14-70 μM) (Novelli et al. 1988; Michelson et al. 1989) compared to these vegetated sediments, even when destructive techniques are used to collect pore water.

Acetate concentrations using destructive techniques during the growing season were highest in the upper 5 and 15 cm in S. patens and S. alterniflora sediments, respectively (Table 1), corresponding to the depths where live roots and rhizomes generally existed. Below the live root zone, acetate concentrations decreased and were usually similar in samples collected by non-destructive or destructive techniques. These data indicated that acetate was associated with root and rhizome material and that ambient pore water acetate levels were low. Although samples from destructive techniques were collected rapidly, in many instances the acetate concentrations were very high. This result indicated that acetate was probably released directly from roots rather than from precursors released from roots during processing.

The latter could only occur if acetate production from a precursor was extremely fast.

Acetate concentrations in marsh sediments varied greatly throughout the year and these variations, in samples collected destructively, corresponded to major changes in the physiological state of marsh grasses (Table 1). Highest acetate concentrations were noted in S. alterniflora sediments when plants were growing rapidly aboveground, i.e., June 1986 when levels exceeded 1.5 mM (Table 1). After flowering in August, acetate levels were ~10 times less than during June. However, the June and August data are not directly comparable since samples were collected in different years. In September 1985 when plants were senescing, acetate concentrations increased in S. alterniflora sediments in New Hampshire, decreased by December, and were at the lowest recorded levels prior to the initiation of growth in May 1986. The only New Hampshire samples that contained significant concentrations of VFA other than acetate were those collected in September when S. alterniflora was senescing. The lowest acetate concentrations were in sipper samples collected during the summer.

Acetate oxidation rate constants in vegetated marsh sediments ranged from 0.002 to 1.8 d^{-1} (Table 3). The highest values were obtained in sediments in which S. alterniflora had been previously killed while the lowest values were in S. patens sediments. Rate constants did not vary consistently with depth. Triplicate subsamples

generally varied by less than 20%. The rate constants in these vegetated sediments were 5 to several thousand-fold lower than in unvegetated subtidal sediments studied by others (Table 3). The inverse of the rate constants yields turnover or residence times of acetate of 0.5–500 d in vegetated sediments. Because of the slow turnover in the marsh sediments, it was often difficult to obtain data which were linear over time. Some of the lower values in Table 3 were obtained using data from only the 0 and ~20 h time points.

Figure 1 depicts acetate oxidation as a function of sulfate reduction for the salt marsh sediments studied. The acetate oxidation rates (acetate concentration * rate constant) were calculated using acetate concentrations obtained from destructive techniques. The 1:1 line represents a situation where all of the sulfate reduction could be due to acetate utilization using the 1:1 stoichiometry of acetate oxidized to sulfate reduced. Values above this line indicate that processes other than sulfate reduction were responsible for acetate oxidation while values below this line indicate that sulfate-reducing bacteria were utilizing substrates other than acetate. Acetate did not appear to be an important substrate for sulfate reduction. This lack of imporatnce was most pronounced in the S. patens sediments where often less than 1% of the sulfate reduction was due to acetate oxidation. For comparison, the unvegetated Buzzards Bay data of Novelli et al. (1988) are

included in Fig. 1. These sediments are typical of unvegetated sediments in that they exhibited high rates of acetate oxidation compared to sulfate reduction activity.

There were no significant differences in rates of sulfate reduction and acetate oxidation when measured using either in situ or core incubation techniques (Table 4). Therefore, sediment disturbance during sampling did not affect these processes. Unfortunately, this experiment was conducted in October when plant and microbial metabolic activity and acetate concentrations in pore water were relatively low. Therefore, we did not anticipate a large stimulation of acetate uptake. However, despite the lack of difference in acetate concentrations using the two pore water collection methods, the large discrepancy between sulfate reduction and acetate oxidation persisted.

Acetate concentrations in marsh samples collected using destructive techniques were much higher than those reported for unvegetated coastal marine sediments (<70 μM) (Novelli et al. 1988; Michelson et al. 1989). The destructive techniques also yielded acetate concentrations that were much higher than those obtained using sippers in the marsh. We previously noted a 5-fold increase in acetate concentrations in centrifuged samples of unvegetated subtidal sediment compared to samples obtained using sippers (Hines and Tugel, unpublished). In addition, Shaw and McIntosh (1990), working in subtidal coastal sediments, reported that the first 5 ml of pore waters obtained from sediment squeezers was enriched

~10-fold in acetate compared to the remaining water obtained. However, this enrichment in acetate in unvegetated sediments was small relative to our marsh results. Obviously, the higher concentrations in vegetated sediments were due to the presence of roots.

Acetate concentrations in disturbed samples of marsh sediments were highest when plants were at their peak of physiological activity. In addition, acetate in S. alterniflora sediments was found closely associated with root material devoid of sediments. Since pore water samples were collected rapidly, these findings indicated that the bulk of the sedimentary acetate, or its precursor, was produced by roots. Acetate has been shown to be a fermentation end product of unicellular algae (Gfeller and Gibbs 1984) and certain lower animals (Crawford 1980). To our knowledge, the production of acetate by roots of marine vascular plants has not been previously determined, nor have data on the abundance of root-associated acetate been reported. It remains unclear how acetate is produced in the Spartina rhizosphere.

Acetate oxidation rate constants in the salt marsh sediments were often extremely low (Table 3) compared to constants reported for unvegetated coastal sediments (Novelli et al. 1988; Michelson et al. 1989). These low rate constants also persisted in samples that were not disturbed prior to or during incubation, including the experiment where radiotracers were injected directly into the sediment in the

field. Hence, the unusually slow acetate turnover in the marsh was not an artifact of acetate liberation from roots by coring and sample processing.

Sulfate reduction rates in salt marsh sediments greatly exceeded rates of acetate oxidation (Fig. 1). This result differed greatly from studies of unvegetated marine sediments where acetate oxidation rates exceeded rates of sulfate reduction in some cases by several-fold (Novelli et al. 1988; Michelson et al. 1989). We noted a few instances in the salt marsh sediments where rates of these processes approached the 1:1 stoichiometry expected if acetate were an important substrate for sulfate reduction. However, none of the rates in the marsh samples exhibited a ratio of acetate oxidation to sulfate reduction that was as high as in the majority of samples collected from unvegetated sediments (Fig. 1). Ratios were low in marsh samples regardless of the type of incubation used, be it sediment slurries or direct injection of tracer in the field. This discrepancy persisted even when incubations for measuring acetate oxidation were as long as those used for measuring sulfate reduction, i.e., overnight. If acetate was a significant substrate for sulfate reduction, then any effects of coring on the acetate pool would have affected sulfate reduction and acetate oxidation similarly. Therefore, the low ratio noted here was probably not due simply to the release of large quantities of acetate during sample handling.

It was unclear why there was such a large mismatch between acetate oxidation rates and sulfate reduction and why it was more pronounced in S. patens than in S. alterniflora. One explanation is that acetate was simply not a major substrate for sulfate reduction. Other compounds which are produced by Spartina roots, such as malate and ethanol, are known to be utilized directly by sulfate-reducing bacteria. Hines et al. (1989) suggested that seasonal changes in the allocation of carbon in S. alterniflora were responsible for much of the temporal variations in sulfate reduction activity. Aquatic vascular plants are known to excrete significant quantities of organic carbon from roots and this carbon can be utilized by the sediment microflora (Moriarty et al. 1986). However, it is not known whether these exudates from S. alterniflora are capable of replacing acetate as the primary substrate for sulfate-reducing bacteria in the marsh.

Another more likely explanation for the mismatch between acetate oxidation and sulfate reduction is the possibility that the radio-acetate used for measuring acetate oxidation did not thoroughly reach the microsites of active acetate oxidation. Roots and rhizomes supply acetate (or its precursor) to the sediments and provide three dimensional diffusional gradients. Therefore, it is unlikely that sediment incubations involving injections, cores or slurries could mimic the in situ chemical conditions and the physical juxtaposition of microorganisms and substrates. Our

inability to mimic natural rhizosphere conditions may be similar to problems encountered in studies of mycorrhizal nutrition in the rhizosphere of terrestrial plants (Coleman et al. 1978). One would not expect this type of artifact to affect measurements of sulfate reduction rates since sulfate is abundant and derived from overlying waters.

Another reason for the mismatch may be that during the slow utilization of tracer substrates by bacteria there is a delay in the release of terminal products (CO_2) because of differences in the relative turnover times of intracellular intermediates (King and Berman 1984). This artifact is severe for substrates like glucose which also yield extracellular fermentation products which must be further oxidized to CO_2 (King and Klug 1982). The artifact also should be most pronounced in environments exhibiting relatively slow rates of substrate turnover such as the marsh sites presented here. We measured only the production of CO_2 and did not include the uptake of acetate into intracellular pools or into biomass. It is conceivable that a significant percentage of ^{14}C had yet to be released as CO_2 when the incubations were terminated and that the actual rates of acetate consumption were substantially faster.

We still do not know whether to use acetate concentrations in cores or from sippers to calculate acetate oxidation rates; an uncertainty that complicates our interpretation. Since acetate oxidation rate constants were determined using cores, we chose to use acetate

concentrations from core samples for calculating acetate oxidation rates. If sipper data had been used, the difference between acetate oxidation and sulfate reduction would have been much larger. We believe that the sipper values are the true pore-water concentrations. However, regardless of the acetate concentrations used, the calculated acetate oxidation rates were a small percentage of sulfate reduction.

It has been proposed that a significant portion of the acetate in marine sediments is not bioavailable (Christensen and Blackburn 1982; Novelli et al. 1988). If a portion of the acetate extracted from the marsh samples was not bioavailable, then the acetate oxidation rates in the marsh sediments were even lower than those presented here, and the differences between the rates of acetate oxidation and sulfate reduction would be even larger. Therefore, the acetate bioavailability argument that has been used to explain the discrepancy in acetate oxidation and sulfate reduction in unvegetated sediments tends to widen the gap between these processes in these salt marsh sediments.

The release of acetate during coring may have stimulated sulfate reduction. Therefore, it is possible that previously reported rates of sulfate reduction in salt marshes, all of which have utilized coring techniques, may have been overestimated. This notion is counter to the sulfate reduction data obtained from the direct field injection experiment where undisturbed and disturbed samples yielded

similar rates of sulfate reduction. However, since acetate levels were low when this experiment was conducted, these data are probably not representative of what would occur in samples collected during the growing season when large quantities of acetate are present in the root zone. Hence, the experiments to verify whether coring yields erroneous sulfate reduction rate data in marshes remain to be conducted. However, when surficial unvegetated marine sediments were amended with acetate 5 to 50-fold over in situ concentrations, sulfate reduction activity increased ~2-fold (Hobbie et al. unpublished data). These results are not directly comparable to marsh sediments but they demonstrate the potential for stimulation of sulfate reduction during coring. This enhanced sulfate reduction phenomenon cannot be used to reduce the discrepancy between acetate oxidation and sulfate reduction since any stimulation of sulfate reduction by acetate release would also increase the rate of acetate oxidation. However, a 2 or even 5-fold change in sulfate reduction would not eliminate the majority of the difference between the rates of these processes.

In conclusion, acetate concentrations in salt marsh sediments are much higher than in unvegetated sediments. Acetate is released during coring and increases pore water acetate levels several fold. Acetate turnover and oxidation rates in salt marsh sediments are much lower than in unvegetated sediments. In addition, unlike unvegetated sediments, acetate oxidation in salt marsh sediments accounts

for only a small percentage of the sulfate reduction activity. The discrepancy between acetate oxidation and sulfate reduction in marsh sediments may be due to compounds other than acetate acting as major substrates for sulfate reduction, to artifacts from an inability to introduce radio-acetate into the appropriate bioactive pool, or to intracellular pool artifacts. Investigators studying salt marshes must be careful in interpreting results from samples obtained from destructive sampling techniques such as coring when compounds are released from roots.

Mark E. Hines

Institute for the Study of Earth, Oceans and Space
University of New Hampshire
Durham, NH 03824

Gary T. Banta
Anne E. Giblin
John E. Hobbie

The Ecosystems Center
Marine Biological Laboratory
Woods Hole, MA 02543

Joyce B. Tugel

Institute for the Study of Earth, Oceans and Space

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Table 1. Acetate concentrations (μM) in sediments from Chapman's Marsh, New Hampshire on various dates using destructive (core) and non-destructive (sipper) sampling techniques.

Depth (cm)	*Spartina alterniflora*		*Spartina patens*		Dead *S. alt.**	*S. alt*
	Core	Sipper	Core	Sipper	Core	Roots†
August 1985						
2	144	0.2	115	0.8		
5.5	147	0.7	9	5		
11.5	271	2	17	2		
17.5	25	11	22	1		
September 1985						
2	417	3	101	unsaturated‡		
5.5	338	<0.1	50	2		
11.5	159	1	7	3		
17.5	61	1	44	29		
December 1985						
2	115	14	4	7		
5.5	53	9	12	2		
11.5	8	59	9	3		
17.5	86	7	1	2		
May 1986						
2	115		8		18	
5.5	53		5		23	
11.5	8		6		18	
17.5	86		11		4	
June 1986						
2	1600		240			970
5.5	1500		160			
11.5	870		23			630
17.5	870		36			

**S. alterniflora* killed by wrack during previous summer.

†half of core washed free of sediment and roots processed like whole core (see text). 5.5 cm value = 0-8 cm, 17.5 cm value = 9-20 cm.

‡neap tide, upper few cm not saturated with water so unable to collect sipper sample.

Table 2. Acetate concentrations in short *Spartina alterniflora* soils in Sippewissett Marsh on various dates using destructive (core) techniques.

Date	Depth (cm)	Acetate (μM)
Jun 1983		
	1.2	290
	4	300
	7	170
	15	63
Oct 1983		
	1.2	390
	4	270
	7	250
	15	230
Oct 1983 (dead)*		
	1.2	250
	4	230
	7	130
	15	130
Aug 1984		
	2	77
	6	130
	10	52
	15	44
	20	18
	25	26
Aug 1984 (dead)*		
	2	35
	6	95
	10	23
	15	19
	20	15
	25	21

*Grass killed during summer of 1982 by covering with plywood.

Table 3. Acetate oxidation rate constants for salt marsh sediments. Data from unvegetated marine sediments included for comparison

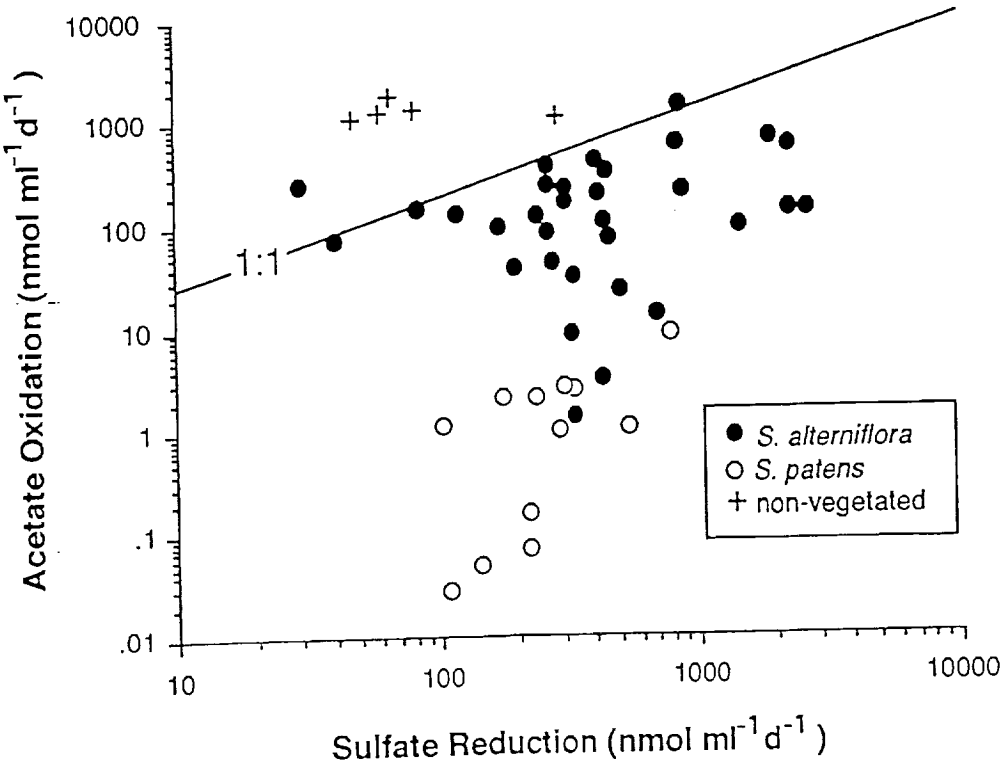
Site	Date	Depth (cm)	n	Rate constant (d^{-1})
Chapman's Marsh, NH				
Tall *S. alterniflora*	Jun-Aug	1.0-20	20	0.068 - 0.48
Spartina patens	Jun-Aug	1.0-20	12	0.002 - 0.12
Sippewissett Marsh				
Short *S. alterniflora*	Jun, Oct	1.2-15	8	0.31 - 2.9
Dead *S. alterniflora*	Oct	1.2-15	4	0.48 - 4.0
Unvegetated				
Novelli et al. 1988	Aug	0.0-16		12 - 48
Michelson et al. 1987	Apr	0.0-10		7.9 - 31

Table 4. Sulfate reduction and acetate oxidation in Sippewissett Marsh in samples incubated either by direct injection of radiotracers into sediments in the field (Field) or injection of tracers into previously retrieved cores (Laboratory). Included are acetate concentrations and rate constants. All acetate data are for 5 cm depth.

Parameter	Field	Laboratory
SO_4^{2-} reduction (nmol ml^{-1} d^{-1})		
5 cm	339 ± 112 (n=3)	200 ± 79 (n=3)
10 cm	118 ± 12 (n=2)	64 ± 64 (n=3)
Acetate (μM)	46*	23-75†
Acetate oxidation rate constant (d^{-1})	<0.144	<0.144
Acetate oxidation (nmol ml^{-1} d^{-1})	<5	<10
Acetate oxidation:SO_4^{2-} reduction ratio	<0.01	<0.01

*Pore water removed with syringe.

†Pore water removed by squeezing in Reeburgh press.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Acetate Oxidation (nmol ml^{-1} d^{-1})
Sulfate Reduction (nmol ml^{-1} d^{-1})
S. alterniflora
S. patens
non-vegetated

Figure Legend

Fig. 1. Acetate oxidation rates vs. sulfate reduction rates in sediment samples from various salt marsh sediments. The non-vegetated sediments are from Buzzards Bay, Massachusetts as reported in Novelli et al. (1988).

Abstracts of Manuscripts Submitted or in Preparation

Grant NAGW-0512

To: Journal of Geophysical Research

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

William Z. de Mello and Mark E. Hines

Institute for the Study of Earth, Oceans and Space
University of New Hampshire, Durham, NH 03824, USA

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.

To Journal of Geophysical Research

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

William Z. de Mello[1], Mark E. Hines[1] and Suzanne E. Bayley[2]

[1]Institute for the Study of Earth, Oceans and Space
University of New Hampshire, Durham, NH 03824, USA

[2]Department of Botany, University of Alberta, Edmonton, Alberta T6G 2E9, CANADA

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 segments 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 segment of the mire was ~3-fold greater than in the control oligotrophic segment, 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. Our 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.

To: Global Biogeochemical Cycles

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

William Z. de Mello and Mark E. Hines

Institute for the Study of Earth, Oceans and Space
University of New Hampshire, Durham, NH 03824, USA

ABSTRACT

The major environmental factors 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 was 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 were not a direct source of VSCs. However they increased transport of DMS from the peat surface to the atmosphere.

Abstracts of Papers Presented at Professional Meetings

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Sulfur Transformations in the Sediments of a New Hampshire Salt Marsh

M.E. HINES, S.L. KNOLLMEYER, A. ELDRIDGE, D. LUKEN, J.B. TUGEL and W.B. LYONS (Jackson Estuarine Laboratory, Univ. New Hampshire, Durham, NH 03824)

Summer sulfate reduction and sulfide and iron chemistry were monitored in marsh soils along a gradient from a creekside Spartina alterniflora region to an inland area dominated by S. patens. Sulfate reduction rates measured using ^{35}S increased from 0.4 in June to as much as 4.5 μ mole $ml^{-1}d^{-1}$ in July in S. alterniflora soils with most rapid rates occurring in the upper few cm. Rates in S. patens soils were ≅ 5-8 fold slower with the most rapid rates occurring generally in soils deeper than 10 cm. The recovery percentage of reduced ^{35}S sulfur varied with depths at both locations; dissolved and acid-volatile sulfides dominating S. alterniflora regions while chromium-reducible solid phases were abundant in S. patens soils. Dissolved sulfide in S. alterniflora soils increased throughout the summer to ≅ 2.8mM while sulfide in S. patens soils was abundant only in soils deeper than 15 cm. Dissolved sulfide covaried inversely with iron. Diel studies demonstrated that sulfide and iron varied ≅ two-fold in response to a semi-diurnal tide. Dissolved sulfide turnover was most rapid during periods of active plant growth.

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3. (a). Mark E. Hines
   Jackson Estuarine Lab
   Univ. New Hampshire
   Durham, NH 03824

   (b) 603-862-2175
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BIOGEOCHEMICAL FACTORS WHICH REGULATE THE FORMATION AND FATE OF SULFIDE IN WETLANDS

Mark E. Hines*, W. Berry Lyons and H.E. Gaudette
University of New Hampshire
Durham, New Hampshire 03824

Coastal wetland areas occupy a small percentage of the terrestrial environment yet are extremely productive regions which support rapid rates of belowground bacterial activity. Wetlands appear to be significant as biogenic sources of gaseous sulfur, carbon and nitrogen. These gases are important as tracers of man's activities, and they influence atmospheric chemistry. The interactions among wetland biogeochemical processes regulate the anaerobic production of reduced gases and influence the fate of these volatiles. Therefore, spatial and temporal variations in hydrology, salinity, temperature and speciation and growth of vegetation affect the type and magnitude of gas emissions thus hindering predictive estimates of gas flux. Our research is divided into two major components, the first is the biogeochemical characterization of a selected tidal wetland area in terms of factors likely to regulate sulfide flux; the second is a direct measurement of gaseous sulfur flux as related to changes in these biogeochemical conditions. Presently, we are near completion of phase one.

The New Hampshire marsh under investigation is subject to a 3m tidal range, seasonal salinity variations of ~20 ppt, contains a productive creekside stand of Spartina alterniflora and a nearby high marsh stand of Spartina patens. We have been conducting a seasonal study of pore water and solid phase chemistry in conjunction with measurements of rates of sulfate reduction and methanogenesis along a gradient between both grass species. Pore waters were collected using in situ "sippers" to prevent artifacts due to the destruction of plant material. Microbial activity rates were determined using radiotracers. Samples were collected weekly during summer to establish the influence of plant growth on biogeochemical processes. The S. alterniflora inhabited sediments which received no detrital input year round were influenced strongly by plant growth. Microbial activity, for example, increased drastically once alterniflora growth began and decreased again in August as the grass began to flower. Dissolved sulfide increased to > 4.0 mM during this period. Sulfate reduction was less active in the S. patens soils and sedimentary biogeochemistry was influenced strongly by variations in tidal regime and rainfall. Sulfide was produced throughout the S. patens sediment column but only accumulaed below 15 cm because the changing hydrologic conditions caused sulfide removal by the enhancement of iron cycling. The alterniflora soils were sulfide rich while the anoxic patens soils were Fe^{3+} rich. This discrepancy affected the fate of ^{35}S during rate measurements. Methanogenesis was slow in the alterniflora soils even when the salinity was low. Methanogenesis was absent in patens soils. Attempts to delineate the important methane precursors were hindered by slow rates and the possibility of gross artifacts due to sampling techniques. Diel studies of pore water chemistry demonstrated that the concentrations of certain solutes changed dramatically in response to tides. Dissolved sulfide and organic carbon varied inversely by as much as 2.0 and 0.5 mM respectively in a 6 h period. The interactions among plant activity, bacterially-mediated processes and hydrologic regime produced a rapidly changing and biogeochemically dynamic system which potentially will alter rates of production of biogenic gases and influence the immediate fate of these gases.

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REGULATION OF SULFIDE FORMATION IN NEW HAMPSHIRE TIDAL WETLANDS.

Mark E. Hines, Stephen S. Knollmeyer, Audrey L. Eldridge and W. Berry Lyons. University of New Hampshire, Durham, NH.

Salt marshes are productive and support active belowground anaerobic microbial populations which produce reduced gases. To better understand the regulation of sulfide formation, a study of soil biogeochemical processes was conducted along a marsh gradient from a riverside stand of Spartina alterniflora into a stand of S. patens. Rates of sulfate reduction and methanogenesis were compared to pore water data obtained using in situ samplers. Sulfate reduction was most rapid in S. alterniflora soils but only during periods of active plant growth. Dissolved sulfide reached 4 mM in soils inhabited by S. alterniflora which was 2.5 m tall. Variations in tidal flooding and rainfall strongly affected sulfur and iron cycling in patens soils which restricted sulfide to sediments deeper than 15 cm. Pore water concentrations of sulfide and organic carbon varied as much as two-fold in response to tidal variations. The belowground production and fate of sulfide was influenced primarily by plant growth, redox cycling due to irregular dessication events, and the large tidal range encountered.

Gas cycling in wetlands

Mark E. Hines and David S. Bartlett

THE ROLE OF CERTAIN INFAUNA AND VASCULAR PLANTS IN THE MEDIATION OF REDOX REACTIONS IN MARINE SEDIMENTS.

M.E. HINES, INSTITUTE FOR THE STUDY OF EARTH, OCEANS AND SPACE, UNIVERSITY OF NEW HAMPSHIRE, DURHAM, NEW HAMPSHIRE, USA.

Bioturbation by deposit-feeding infauna affects certain redox processes in sediments in a manner which is similar to what occurs when plants transport oxygen into the anaerobic root zone. The mechanisms by which these macroorganisms do so was examined by studying three differing sedimentary environments: 1) subtidal temperate estuarine sediments dominated by the subsurface deposit-feeding polychaete *Heteromastus filiformis*; 2) a temperate saltmarsh inhabited by *Spartina sp.*; 3) and tropical carbonate sediments inhabited by three species of seagrasses. ^{35}S-sulfide production rates were compared to pool sizes of dissolved sulfide, other solid phase S species, dissolved iron and data related to animal and plant abundance and activity. In all of the sediments studied, rates of sulfate reduction were enhanced by macroorganisms while the rate of turnover of dissolved sulfide increased. The polychaete enhanced microbial activity primarily by subducting particles of organic matter and oxidized iron during sediment reworking. Rates of sulfate reduction were ~5-fold faster in sediments inhabited by the polychaete compared to similar sediments which did not support a deep-feeding infaunal community. Sulfide was removed from solution primarily by interactions with dissolved iron. The *Spartina* species enhanced anaerobic activity by transporting primarily dissolved organic matter during periods of active leaf elongation. Rates of sulfate reduction increased more than 5-fold as soon as plants began to grow aboveground and rates decreased again within a few days of the cessation of growth as plants flowered. Molecular oxygen transported to roots caused the oxidation of reduced species within the sediment. In addition, iron was remobilized and a portion of the sulfide generated was precipitated as iron sulfide. The turnover of dissolved sulfide slowed ~5-fold once the plants flowered. The tropical seagrasses, which grew more slowly than the *Spartina*, oxidized the sediments but to a lesser degree. Dissolved sulfide turned over every 2-4 days in grass-inhabited sediments compared to >20 days in control areas. The enhanced turnover of sulfide in the seagrass sediments was due primarily to oxidation by oxygen since these sediments were nearly devoid of iron. The final result of both animal and plant activity was subsurface cycling of sulfur and iron, decreased dissolved sulfide and increased dissolved iron concentrations. The magnitude of the enhancement of subsurface redox cycling was polychaetes > *Spartina* > tropical seagrasses. Sulfide turnover times decreased from greater than 30 days in control sediments to seconds in some experimental sediments. All three sites displayed dramatic seasonal changes in this activity. Although the final result was the same, the animals affected redox conditions by transporting particulate organic material and Fe(III) while plants transported dissolved organic material and molecular oxygen.

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BIOGEOCHEMISTY AND GASEOUS SULFUR RELEASE IN TIDAL WETLANDS

Mark E. Hines

University of New Hampshire

Institute for the Study of Earth, Oceans and Space

Science & Engineering Research Building

Durham, NH 03824 U.S.A.

Phone: (603) 862-4725

The production and flux of biogenic gases from terrestrial ecosystems is a function of several interrelated conditions and processes including floral speciation and physiology, soil chemistry, salinity, temperature and the duration and vigor of the growing season. Tidal wetlands are especially influenced by the physical environment since they act as an interface and buffer between the aquatic and terrestrial environments. Hence, these ecosystems are unusually complex and productive and can act as a source of biogenic compounds which greatly exceeds an averaged ecosystem.

Because of the juxtaposition to the sea and the varying redox gradients, salt marshes have an abundant source of sulfur and potentially can generate an unusually large quantity of biogenic sulfur gases. To fully understand the role of wetlands in atmospheric chemical budgets it is necessary to study the total environment, including the soil, to clarify the effects of physical factors on gaseous emissions. The present study has been examining the short and longer term changes in the biogeochemistry of tidal wetlands in terms of sulfur cycling and the production and flux of sulfur gases to the atmosphere.

Two temperate East Coast marsh systems have been studied during the past three years. The New Hampshire marsh under investigation is dominated by Spartina plant species particularly S. patens with a narrow but productive stand of S. alterniflora along river and creek banks. The Great Marsh in Lewes Delaware was investigated during June of 1986 as part of an interdisciplinary study to examine the flux of various gases from tidal wetlands along a salinity gradient. The Delaware marsh contained a variety of grass species but was dominated by S. alterniflora and S. patens.

Sedimentary pore water samples were collected using in situ samplers which were deployed several days prior to use and which minimize disturbance to the plant root-rhizome system. Rates of bacterial sulfate reduction were determined using radioisotopes. Solid phase analyses were conducted on core samples which were handled anoxically. Emission rates of the gaseous sulfur compounds methane thiol (CH_3SH), hydrogen sulfide (H_2S), dimethyl sulfide (DMS), carbonyl sulfide (COS) and carbon disulfide (CS_2) were determined using a dynamic flow-through teflon flux chamber. Gas samples were concentrated in cryogenic traps and, after remobilization, were analyzed using a gas chromatographic system with a flame photometric detector.

The sedimentary biogeochemistry of the New Hampshire marsh was influenced primarily by the growth of marsh plants and the desiccation of marsh soils by periodic precipitation events and the cycling of the tide. Rapid bacterial anaerobic activity occurred only during periods of rapid plant growth. However, this vigorous growth of marsh vegetation also caused an oxidation of marsh soils which enhanced the turnover of sulfide in the sediments. The high marsh soils were subjected to severe desiccation during neap tides and periods of drought which caused a reoxidation of iron and the recycling of iron and sulfur. This prevented the accumulation of reduced sulfur compounds in the high marsh soils.

Diel measurements of sulfur gas fluxes revealed that the total S flux rate was similar at S. alterniflora-containing locations which differed tremendously in terms of sedimentary chemistry. A large portion of the Delaware marsh contained sediments which were oxidizing and low in pH due to sulfur oxidation within the soil. However, the

flux of DMS from these sites was similar in magnitude to the flux noted at a site which exhibited reducing, neutral soils rich in dissolved sulfide. Conversely, H_2S fluxes were influenced strongly by subsurface chemistry and a rapid flux was noted only at sites rich in dissolved sulfide.

Sulfur gas fluxes varied greatly throughout the day. DMS flux rates were most rapid at night and appeared to be enhanced by the condensation of water on grass leaves. H_2S fluxes also increased at night but decreased rapidly at dawn, presumably because of the pumping of photosynthetically-generated oxygen to roots. H_2S fluxes also increased very quickly as a result of tidal pumping of sedimentary pore waters. The fluxes of CS_2, COS and CH_3SH were much slower than the fluxes of DMS and H_2S and fluxes of the former gases varied throughout the day. DMS was the major S gas emitted from S. alterniflora-containing soils. However, DMS fluxes from S. patens were slow. The results suggested that DMS is emitted from the leaves of marsh plants while H_2S is emitted directly from soils. Although the sites studied were marine, the flux of sulfur gases amounted to $\sim$ 2% of the flux of methane from the same locations.

Extrapolation of flux data revealed that salt marshes contribute $\sim$ 1.5 Tg of S globally to the atmosphere. This estimate is a maximum since measurements were made during an active period of the year and only rates for S. alterniflora were considered in the calculation.

compensated by either condensation or evaporation of the solid phase ammonium nitrate. The system was modelled to investigate these relaxations under different conditions to ascertain the effect of these conditions on the measured fluxes of all three components. Numerical simulations incorporating differing atmospheric concentrations, surface fluxes, system equilibration relaxation times and turbulent transport parameters have been carried out. Comparison with the field experimental results have been made.

A41A-05 0915H

Measurements of Concentrations and Surface Fluxes of Atmospheric Nitrates in the Presence of Ammonia Vapor

W. LUKE (Department of Chemistry, Univ. of Maryland, College Park, MD 20742),
B.J. HUEBERT (Center for Atmospheric Chemistry Studies, Grad. School of Oceanography, Univ. of Rhode Island, Narragansett, RI 02882-1197)
A.C. DELANY, R. BROST (NCAR, Boulder, CO 80307)

We measured summertime gradients of nitrate aerosol and vapor at the BAO tower, in the presence of occasionally high ammonia vapor concentrations from nearby agricultural facilities. The nitrate vapor gradients were much flatter than expected, based on earlier field work and on theoretical considerations. In some cases the apparent vapor concentration was actually greatest near the surface, implying an upflux of nitric acid and a negative deposition velocity! Aerosol nitrate sometimes showed more of a gradient than the vapor.

We believe that the data is consistent with nitric acid vapor deposition which is coupled to the evaporation of NH_4NO_3 aerosol. Aerosol evaporation flattens the vapor gradient by resupplying vapor to the depleted air near the surface. In such a situation, the total nitrate flux is conserved, but the vapor and aerosol fluxes vary with height.

The deposition velocity/concentration method for estimating surface fluxes may result in gross errors (even sign errors) when a phase equilibrium is coupled to the deposition.

The time scale for the evaporation of ammonium nitrate aerosol must be small compared to the vertical eddy-transport time, to have the observed effect on the vertical gradients.

A41A-06 0930H

Trace Gas Emissions from Prescribed Chaparral Fires

WESLEY R. COFER III (Atmospheric Sciences Division, NASA Langley Research Center, Hampton, VA 23665-5225)
JOEL S. LEVINE
DANIEL I. SEBACHER
EDWARD L. WINSTEAD (ST Systems Corporation, Hampton, VA 23666)

Gas samples were collected from smoke plumes over the San Dimas Experimental Forest in the San Gabriel Mountains of southern California during prescribed chaparral fires on December 12, 1986, and on June 22, 1987. A helicopter was used to collect the samples over areas of vigorous flaming combustion and over areas of transitional and smoldering combustion. Sampling was conducted at altitudes as low as 35 m and as high as 670 m above ground level. Samples were collected in pairs, then returned by helicopter to our field laboratory and immediately analyzed for carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), methane (CH_4), total nonmethane hydrocarbons (TNMHC), and nitrous oxide (N_2O). Samples of gas were also collected upwind of the burn and analyzed to determine ambient background levels.

Emission ratios ($\Delta X/\Delta CO_2$; X = each species; V/V) determined for these gases relative to CO_2 were generally lower (except for N_2O) than the emission ratios reported in the literature for other large biomass burning field experiments. Relatively insignificant differences in CO_2 normalized emission ratios (except for N_2O) for these gases were determined when samples from vigorously flaming and smoldering stages of combustion were compared.

The very high surface-to-volume fuel ratio typical of chaparral fires (which minimizes the smoldering aspects) may have accounted for both the consistency in the emission ratios and the overall lower emission ratios of the measured gases.

A41A-07 0944H

Sulfur Gas Emissions from a Temperate Salt Marsh: Flux Controls and Variability.

M. C. Morrison
M. E. Hines (Both at: Institute for the Study of Earth Oceans and Space, University of New Hampshire, Durham, NH 03824)

Dynamic flux chambers were used to determine the emission rates of reduced sulfur gases (H_2S, COS, CH_3SH, DMS, CS_2) and the variability resulting from spatial, biological and physical heterogeneity. Zero-grade sweep air with controlled CO_2 concentration was passed through three teflon flux boxes simultaneously within and across species ranges.

DMS emissions from tall *Spartina alterniflora* were greatest with rates from 1000 to >5000 ng S m^{-2} min^{-1}. Fluxes from short *S. alterniflora* were about half that of the tall form and emissions from *S. patens* were negligible. Photosynthetic rate and humidity appear to be the primary controlling factors.

The remaining gases were emitted in the range from 0 to 80 ng S m^{-2} min^{-1} with COS fluxes being higher in *S. patens* than *S. alterniflora* and CH_3SH higher in *S. alterniflora*. Tide and temperature appear to be the primary controlling factors for these gases.

Spatial variability within species ranges was observed to be less than the experimental error.

A41A-08 1018H

Ozone Budgets in the Cloud-Topped Marine Boundary Layer

S. R. Kawa and R. Pearson, Jr., (Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523)

Fast-response, high-sensitivity ozone (O_3) measurements were obtained from aircraft in summer, 1985, during the Dynamics and Chemistry of Marine Stratocumulus Experiment (DYCOMS) off the California Coast. Concurrent measurement of winds and atmospheric scalars allowed the vertical O_3 flux to be calculated by eddy correlation. The O_3 flux and mean concentration measurements are used to estimate the rate of destruction of O_3 at the sea surface and the net rate of chemical production or destruction in the marine boundary layer. These are important quantities in the global O_3 budget. The surface destruction rate for the DYCOMS regime compares reasonably well with previous measurements but shows significant variability from flight to flight which does not correlate with any other measured or observed variables. The net chemical production or destruction rate is calculated as the residual of measured terms in the conservation equation. Values of this rate for individual cases are near zero and of either sign. The mean rate for the entire experiment is consistent with with photochemical model predictions for pristine marine air.

A41A-09 1032H

IR Laser Absorption Eddy Correlation Instrument for Atmospheric Methane

P.L. KEBABIAN, S. ANDERSON, A. FREEDMAN, M.S. ZAHNISER and C.E. KOLB (Center for Chemical and Environmental Physics, Aerodyne Research, Inc., Billerica, MA 01821)

The development of open path IR absorption instrumentation for atmospheric trace gas flux measurements is discussed. The principle of eddy correlation is used to measure surface emission or uptake of trace gases without enclosures or traps that would disturb the local environment. Fluctuations in trace gas concentration are correlated with fluctuations in the vertical component of the wind. The IR laser is coupled to an open-path (atmospheric pressure) multipass absorption cell which provides adequate sensitivity (at 10 Hz) and permits simultaneous measurement of gas concentration and windfield parameters in the same volume of air.

The instrument for methane measurements employs a HeNe laser for which an accidental coincidence between molecular absorption and the laser line occurs (2947.9 cm^{-1}). The natural laser frequency is Zeeman-split using permanent or electromagnets with a commercial laser tube. With a demonstrated available tuning range of 1.6 GHz for the 2947.9 cm^{-1} line, we estimate that 1% fluctuations in the 1.6 ppm ambient methane concentration can be measured at 10 Hz without interference from atmospheric water vapor. Transmission of the 3.39 μm laser light to and from the multiple pass cell can be accomplished using fiber optics, reducing the complexity of the optical train. Results of preliminary testing and field measurements will be reported.

A41A-10 1046H

On the Lack of Equilibrium of Ammonia Species Over the Ocean

PATRICIA K. QUINN and ROBERT J. CHARLSON (Dept. of Chemistry, University of Washington, Seattle, WA 98195)
TIMOTHY S. BATES (NOAA/Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, WA 98115)

Ammonia exists in five phases in the remote marine environment: in seawater as ammonium and dissolved ammonia, NH_4^+ (s) and NH_3 (s), in atmospheric gas and particulate phases, NH_3 (g) and NH_4^+ (p), in cloudwater, NH_4^+ (c), and in rainwater, NH_4^+ (r). The ammonia species NH_4^+ (s) + NH_3 (s), NH_3 (g), and NH_4^+ (p) were sampled simultaneously along with particulate non-seasalt sulfate, xs $SO_4^=$ (p), to investigate the equilibrium of ammonia between these phases during non-cloudy conditions in the marine troposphere. Concentrations of NH_3 (s) were derived from seawater equilibrator measurements of NH_3 (g). Samples were collected concurrently at a coastal mountaintop site, Cheeka Peak which is located on the northwest tip of Washington State, and aboard the NOAA research vessel, McArthur, operating 0 to 140 km off the coast of Washington State.

Concentrations were found to range between 0.21 and 2.4 umol l^{-1}, 10 and 53 nmol l^{-1}, 0.1 and 2.8 nmol m^{-3}, 1.6 and 15 nmol m^{-3}, and 1.2 and 14 nmol m^{-3} for NH_4^+ (s), NH_3 (s), NH_3 (g), NH_4^+ (p), and xs $SO_4^=$ (p), respectively. Comparison of the gas and particulate phase data through a simple equilibrium model indicates that NH_3 (g) and NH_4^+ (p) are not in equilibrium. The seawater and gas phase data suggest that a Henry's Law equilibrium does not exist between the ocean surface and the atmosphere for ammonia and that the ocean in this region is a source of NH_3 (g) to the marine troposphere.

A41A-11 1100H

Fine Scale Temporal Variability in the Atmospheric Deposition of Be-7

Jack E. Dibb (University of Maryland, Center for Environmental and Estuarine Studies, Chesapeake Biological Laboratory, Solomons, MD 20688)

The cosmogenic radionuclide Be-7 can be a useful tracer of a variety of mixing and transport processes operating on time scales of weeks to months on the earth's surface. Atmospheric deposition is generally the dominant input of Be-7, therefore, knowledge of the atmospheric flux is essential in studies employing Be-7 as a tracer. In situations where it has not been possible to measure the atmospheric deposition of Be-7 some researchers have estimated the flux on the basis of published regressions of Be-7 deposition against precipitation.

On the basis of the first 15 months of an ongoing observation program at a site on the western shore of the Chesapeake Bay (Solomons, MD) it is apparent that such an estimation technique can yield serious overestimates of Be-7 flux. The intensity of a precipitation event, the time interval since the previous event, and the time of year (and, presumably, several other factors) alter any simple relation between Be-7 deposition and total precipitation. A simple estimation technique that considers Be-7 flux to be a function of seasonal variation in Be-7 production and the timing and amount of precipitation provides improved estimates of Be-7 atmospheric deposition.

A41A-12 1114H

ATMOSPHERIC INPUT OF METALS INTO THE MEDITERRANEAN REGION

STEFANO GUERZONI, FENZO LENAZ and GIANNI QUARANTOTTO (Istituto di Geologia Marina, CNR, Via Zamboni n.65, 40127 Bologna, Italy)
(Sponsor: D.E. Hammond)

To study atmospheric transport of eolian dusts and trace metals into the Mediterranean Sea, samples were collected at the seawater-air interface, with the contemporary use of an impingment catching system on nylon mesh panels and a high volume (75 m3/h) filtration system. During ship cruises meteorological data are collected, by means of an automatic portable meteo station, together with "true wind" velocity and direction. Samples collected with the impingment catching system mainly consist of silty clays or clayey silts, with a modal class of 4-8 μm or 2-4 μm, and with a low sand content.

Observed amounts of dust-loading range from 15 to 35 μg/m3, with no correlation with the average wind speed recorded onboard during the sampling period (10-12 hours).

Preliminar results on trace metals show values ranging from 5 to 76 ng/m3 for Pb, 0.1-1.3 for Cd, 10-80 for Zn, 3-12 for Ni, 2-11 for V and 8-94 for Mn.

A rough estimate of dry deposition into the basin (based on a deposition velocity of 1 cm/sec), gives the following: Pb = 160-2400 (avg. 700) ng.cm-2.y-1, Cd = 3-42 (avg. 15), Zn = 315-2520 (avg. 885).

The aerosols over the Mediterranean Sea have concentrations of Fe, Ni, Mn and V similar to those of continental crust. In contrast, non-crustal sources govern the concentrations of Cd, Pb and Zn; dust samples show EF(crust) values as follows: Zn = 15 (5-62), Pb = 49 (7-236), Cd = 71 (32-149), with the maxima in the Eastern Mediterranean.

A41A-13 1128H

The Effect of Light, Dark and CO_2 on Short-term Measurements of Methane Flux.

G.J. WHITING (N.R.C./NASA Langley Res. Cen., Hampton, VA 23665), P.M. CRILL (College Of William and Mary, Williamsburg, VA 23185), J.P. CHANTON (Univ. of North Carolina, Chapel Hill), K.B. BARTLETT (College of William and Mary) and D.B. BARTLETT (NASA Langley Res. Cen.)

Methane fluxes from wetlands are commonly measured using static chambers sealed to the ground with flux rates calculated from the accumulation of methane within the trapped air space. The chambers are usually dark boxes of varying complexity that are placed over plants. Rarely has the effects of containment on the flux been evaluated. We report here on an experiment

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Emissions of Biogenic Sulfur Compounds from Alaskan Tundra

M E Hines and M C Morrison (Institute for the study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824; 603-862-4725; OMNET M.HINES.UNH; NASAMAIL MHINES)

Fluxes of COS, DMS, CS_2 and MeSH from a variety of habitats in the Yukon-Kuskokwim Delta were measured using Teflon, dynamic flux chambers. Sampling sites included upland tundra, wet meadow tundra and lake waters near the town of Bethel and several locations within and directly adjacent to an intertidal region on the southwest Alaskan coast. Concentrations of S gases in sedimentary bubbles and stems of emergent macrophytes were also determined. Gas samples were cryogenically trapped and measured using GC-FPD.

Sulfur gas fluxes were extremely low in the inland sites with highest rates of ~10 nmol S m^{-2} h^{-1} in wet meadow areas inhabited by grasses and sedges. Upland areas with a mixture of grass, berries and dwarf birch averaged ~3 nmol S m^{-2} h^{-1}, Labrador Tea ~5 and regions dominated by lichens ~1. Sulfur emissions from lake water was <1 nmol S m^{-2} h^{-1}. Fluxes were dominated by DMS with lesser amounts of MeSH and occassionally CS_2. Small amounts of hydrogen sulfide (H_2S) were detected routinely but could not be quantified. Lake sediment bubbles contained, in pmols S l^{-1}, 350 COS, 425 DMS and 350 CS_2. Only COS was detected within plant stems. Using 10^{12} m^2 as the global area of non-forested bog and a 150 day season, the global flux of biogenic S to the atmosphere from tundra is 4 x 10^8 g yr^{-1} or 0.001% of the estimated global flux of biogenic S.

Emissions of S from the marine sites were more rapid but still 50-fold lower than fluxes from temperate salt marshes. Rates of DMS flux from sites inhabited by the intertidal sedge *Carex subspathacea* were 80 nmol m^{-2} h^{-1} and more than doubled when geese feces were left within the flux chamber. When normalized to aboveground biomass, DMS fluxes from this species were equal to fluxes from temperate cordgrass suggesting that the former uses DMSP during osmoregulation. Emissions were extremely slow from *Carex* sp. which dominated the supralittoral. Another salt-tolerant species, *Elymus*, emitted modest quantities of DMS.

Emissions of Dimethyl Sulfide and Related Biogeochemistry in Northern *Sphagnum*-Dominated Wetlands.

Mark E. Hines*, William Z. de Mello*, Georgia L. Murray*, Suzanne E. Bayley†, Joyce B. Tugel* and Patrick M. Crill*.

Institute for the Study of Earth, Oceans and Space
University of New Hampshire, Durham, NH 03824*
Department of Botany, University of Alberta, Edmonton, Alberta T6G 2E9†

Sulfur gases are important components of the global cycle of S. They contribute to the acidity of precipitation and they influence global radiation balance and climate. The role of terrestrial sources of biogenic S and their effect on atmospheric chemistry remain as major unanswered questions in our understanding of the natural S cycle. We have been investigating the role of northern wetlands as sources and sinks of gaseous S by measuring rates of S gas exchange as a function of season, hydrologic conditions and gradients in trophic status. In addition, we have been examining the processes of methanogenesis and sulfate reduction.

Experiments have been conducted in wetlands in New Hampshire, particularly a poor fen, and in Mire 239, a poor fen at the Experimental Lakes Area (ELA) in Ontario. Emissions were determined using Teflon enclosures, gas cryotrapping methods and gas chromatography (GC) with flame photometric detection. Dynamic (sweep flow) and static enclosures were employed which yielded similar results. Dissolved S gases and methane were determined by gas stripping followed by GC. Depth profiles of sulfate reduction were determined by ^{35}S and methanogenesis was determined by peat incubations.

Emissions of dimethyl sulfide (DMS) dominated S gas fluxes from all sites. In New Hampshire, DMS fluxes were >1.6 μmol m^{-2} d^{-1} in early summer, 1989 when temperatures were warm and the water table was ~5 cm below the surface. These rates are several-fold faster than average oceanic rates of DMS emission. Despite continued warm temperatures, a rapid drop in the water table resulted in a 6-fold decrease in DMS emissions in late July. In 1990, a new beaver dam kept water levels above the surface of the fen for the bulk of the season and S gas emissions were much lower than during 1989. However, emissions of methane were ~3-fold higher during that period compared to 1989. Concentrations of methane and DMS in surface waters co-varied closely until the water table dropped below the surface. The elimination of the beaver and a drop in the water table in August produced a rapid increase in S gas emissions. However, the low temperatures in late August prevented S gas fluxes from being as high as those noted in 1989. Emissions of DMS were highest in the most oligotrophic areas. Using static chambers, we observed that these fens are sinks for atmospheric COS.

Similar measurements were made at the ELA in July, 1990. Mire 239 was irrigated with sulfuric and nitric acids to simulate acid rain. Sulfur gas emissions,.dissolved S gas and methane concentrations, and rates of methanogenesis and sulfate reduction were determined before and after an acidification event in control and experimental areas in both minerotrophic and oligotrophic regions of the fen. Emissions of DMS dominated the S gases and fluxes followed a smooth diel pattern. Emissions of DMS were higher in the acidified areas compared to unacidified controls. Emissions were also much higher in the oligotrophic regions compared to the minerotrophic ones. Despite the wide differences in S gas fluxes (20-fold), it was difficult to determine if acidification or variations in trophic status were most responsible for differences in S gas emissions. DMS dissolved in the surface of the water table (25 cm below the fen surface) did not vary throughout the fen. DMS emitted into the atmosphere was not derived from the water table but originated in peat situated above the water table. Measurements using only dissolved concentrations of DMS may grossly underestimate fluxes. Following a rain event, dissolved methane

decreased greatly while dissolved sulfide concentrations increased. However, rates of methanogenesis did not decrease after rain or the acidification event.

Highest S gas emissions (DMS) occurred in the most oligotrophic regions of mires despite the fact that these locations received the smallest S input. Our preliminary data from Alaska to the northeastern US suggest that DMS emissions correlate with atmospheric S depositions and complications from terrestrial inputs may be insignificant in affecting these fluxes. If this is true, then scaling up using remotely sensed information would be greatly facilitated. However, hydrologic variations influence emissions by perhaps orders of magnitude and this and other influences need to be addressed in detail.

Emissions of Biogenic Sulfur Gases from *Sphagnum*-Dominated Wetlands

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de Mello, W.Z.[1], M.E. Hines[1] and S.E. Bayley[2]

[1] Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824, USA

[2] Department of Botany, University of Alberta, Edmonton, Alberta T6G 2E9, CANADA

ABSTRACT

Our research focuses on understanding the role of *Sphagnum*-dominated peatlands as sources and sinks of atmospheric reduced sulfur gases, such as dimethyl sulfide (DMS), hydrogen sulfide (H_2S), carbonyl sulfide (OCS), methane thiol (MSH) and carbon disulfide (CS_2). These reduced sulfur species are precursors of tropospheric acid sulfate and stratospheric sulfuric acid aerosols, which control the acidity of rain and are potential climate regulators.

This research is being conducted in a poor fen in Barrington, NH, where fluxes of reduced sulfur gases are systematically being monitored. Last summer, an intensive one-week study also took place in a poor fen in the Experimental Lakes Area (ELA) of northwestern Ontario. Three distinct methods were used to determine and estimate fluxes: dynamic chambers, static chambers and a stagnant-film model. Other physical and chemical parameters are measured simultaneously, such as 1) temperature in the atmosphere, in the *Sphagnum* cushion, and at various depth below the peat surface, 2) concentrations of reduced sulfur gases and methane in the surface of the water table, 3) dissolved oxygen, 4) pH, and 5) water table level.

Emission of reduced sulfur gases varied in space and time. Spatial variability occurred on small and large scales, i.e. within the same physiographic area and latitudinally. Temporal variability occurred on daily and annual scales. Fluxes were higher during the day and lower during the night. Fluxes were higher in summer and decreased toward the end of the fall. Fluxes in NH were higher than at the ELA. There was some evidence that the surface of the peatland may, in fact, consume OCS from the atmosphere. Although investigations on the potential factors controlling fluxes from peatlands still continue, it seems that capillary transport of water from the peat surface by the *Sphagnum* is the principal factor regulating reduced sulfur gas emissions in these environments.

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THE EFFECTS OF ACID DEPOSTION ON SULFATE REDUCTION AND METHANE PRODUCTION IN PEATLANDS

Georgia L. Murray and Mark E. Hines, Department of Earth Sciences and Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824

Suzanne E. Bayley, Department of Botany, University of Alberta, Edmonton, Alberta T6G 2E9

Peatlands, as fens and bogs, make up a large percentage of northern latitude terrestrial environments. They are organic rich and support an active community of anaerobic bacteria, such as methanogenic and sulfate-reducing bacteria. The end products of these microbial activities, methane and hydrogen sulfide, are important components in the global biogeochemical cycles of carbon and sulfur. Since these two bacterial groups compete for nutritional substrates, increases in sulfate deposition due to acid rain potentially can disrupt the balance between these processes leading to a decrease in methane production and emission. This is significant because methane is a potent greenhouse gas that effects the global heat balance.

A section of Mire 239 in the Experimental Lakes Area, in Nortwestern Ontario, was artificially acidified and rates of sulfate reduction and methane production were measured with depth. Preliminary results suggested that methane production was not affected immediately after acidification. However, concentrations of dissolved methane decreased and dissolved sulfide increased greatly after acidification and both took several days to recover. The exact mechansim for the decrease in methane was not determined. Analyses are under way which will be used to determine rates of sulfate reduction. These results will be available by spring and will be discussed.

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DMS Emissions from *Sphagnum*-Dominated Wetlands

M E Hines and W Z de Mello (Both at: Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824; 603-862-4725; OMNET M.HINES.UNH)
S E Bayley (Department of Botany, University of Alberta, Edmonton, Alberta T6G 2E9)

The role of terrestrial sources of biogenic S and their effect on atmospheric chemistry remain as major unanswered questions in our understanding of the natural S cycle. We have been investigating the role of northern wetlands as sources and sinks of gaseous S by measuring rates of S gas exchange as a function of season, hydrologic conditions and gradients in trophic status.

Experiments were conducted in wetlands in New Hampshire (NH), and in Mire 239, a poor fen at the Experimental Lakes Area (ELA) in Ontario. Emissions were determined using Teflon enclosures, gas cryotrapping methods and GC with flame photometric detection.

Emissions of DMS dominated fluxes. In NH, DMS fluxes were >1.6 μmol m^{-2} d^{-1} in early summer, 1989 when temperatures were warm and the water table was ~5 cm below the surface. These rates are several-fold faster than average oceanic rates of DMS emission. A rapid drop in the water table resulted in a 6-fold decrease in DMS emissions in late July. In 1990, a new beaver dam kept water levels above the surface and S emissions were much lower than during 1989. The elimination of the beaver and a drop in the water table in August produced a rapid increase in S gas emissions. Emissions of DMS were highest in the most oligotrophic areas.

Mire 239 (ELA) was irrigated with sulfuric and nitric acids to simulate acid rain. S emissions were determined before and after an acidification event in control and experimental areas in both minerotrophic and oligotrophic regions. Emissions of DMS were higher in the acidified areas compared to unacidified controls. Emissions were also much higher in the oligotrophic regions compared to the minerotrophic ones. Despite the wide differences in S gas fluxes (20-fold), it was difficult to determine whether acidification or variations in trophic status was most responsible for differences in S gas emissions. DMS emitted into the atmosphere was not derived from the water table but originated in peat in the unsaturated zone.

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EMISSIONS OF BIOGENIC SULFUR GASES FROM NORTHERN BOGS AND FENS.

W. Z. DE MELLO[1], M. E. HINES[1] AND S. E. BAYLEY[2]. Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampsire, USA,[1] and Department of Botany, University of Alberta, Edmonton, Alberta, Canada[2].

Sulfur gases are important components of the global cycle of S. They contribute to the acidity of precipitation and they influence global radiation balance and climate. The role of terrestrial sources of biogenic S and their effect on atmospheric chemistry remain as major unanswered questions in our understanding of the natural S cycle. We have been investigating the role of northern wetlands as sources and sinks of gaseous S by measuring rates of S gas exchange as a function of season, hydrologic conditions and gradients in trophic status.

Experiments have been conducted in wetlands in New Hampshire, particularly a poor fen, and in Mire 239, a poor fen at the Experimental Lakes Area (ELA) in Ontario. Emissions were determined using Teflon enclosures, gas cryotrapping methods and gas chromatography (GC) with flame photometric detection. Dynamic (sweep flow) and static enclosures were employed which yielded similar results. Dissolved S gases and methane were determined by gas stripping followed by GC.

Emissions of dimethyl sulfide (DMS) dominated S gas fluxes from all sites. In New Hampshire, DMS fluxes were >1.6 μmol m^{-2} d^{-1} in early summer, 1989 when temperatures were warm and the water table was ~5 cm below the vegetation surface. These rates are several-fold faster than average oceanic rates of DMS emission. Despite continued warm temperatures, a rapid drop in the water table resulted in a 6-fold decrease in DMS emissions in late July. In 1990, a new beaver dam kept water levels above the surface of the fen for the bulk of the season and S gas emissions were much lower than during 1989. Concentrations of methane and DMS in surface waters co-varied closely until the water table dropped below the surface. Emissions of DMS were highest in the most oligotrophic areas. Using static chambers, we observed that these fens are sinks for atmospheric COS.

Similar measurements were made at the ELA in July, 1990. Mire 239 was irrigated with sulfuric and nitric acids to simulate acid rain. Sulfur gas emissions, dissolved S gas and methane concentrations, and rates of methanogenesis and sulfate reduction were determined before and after an acidification event in control and experimental areas in both minerotrophic and oligotrophic regions of the fen. Emissions of DMS dominated the S gases and fluxes followed a smooth diel pattern. Emissions of DMS were higher in the acidified areas compared to unacidified controls. Emissions were also much higher in the oligotrophic regions compared to the minerotrophic ones. Despite the wide differences in S gas fluxes (20-fold), it was difficult to determine if acidification or variations in trophic status were most responsible for differences in S gas emissions. DMS dissolved in the surface of the water table (situated ~25 cm below the vegetation surface) did not vary throughout the fen. Estimates of S gas flux using dissolved concentration data were significantly lower than directly measured fluxes. This discrepancy may have been due to enhanced diffusivity of S gases from water sequestered during capillary action by *Sphagnum* mosses. Measurements using only dissolved concentrations of S gases may grossly underestimate fluxes when the water table is below the vegetation surface.

Highest S gas emissions (DMS) occurred in the most oligotrophic regions of mires despite the fact that these locations would be expected to have the smallest S input. Our preliminary data from Alaska to the northeastern USA suggest that DMS emissions correlate with atmospheric S depositions. If this is true, then scaling up using remotely sensed information would be greatly facilitated. However, hydrologic variations influence emissions by perhaps orders of magnitude and this and other influences need to be addressed in detail.

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Hines, M. E., J. B. Tugel, University of New Hampshire, Durham, NH, A. E. Giblin, G. T. Banta and J. E. Hobbie, Ecosystems Center, Woods Hole, MA.

ELEVATED ACETATE CONCENTRATIONS IN THE RHIZOSPHERE OF *SPARTINA ALTERNIFLORA* AND POTENTIAL INFLUENCES ON SULFATE REDUCTION.

Acetate is important in anaerobic metabolism of non-vegetated sediments but its role in salt marsh soils has not been investigated thoroughly. Acetate concentrations, oxidation (^{14}C) and SO_4^{2-} reduction (^{35}S) were measured in *S. alterniflora* soils in NH and MA. Pore water from cores contained >0.1 mM acetate and in some instances >1.0 mM. Non-destructive samples contained <0.01 mM. Acetate was associated with roots and concentrations were highest during vegetative growth and varied with changes in plant physiology. Acetate turnover was very low whether whole core or slurry incubations were used. Radiotracers injected directly into soils yielded rates of SO_4^{2-} reduction and acetate oxidation not significantly different from core incubation techniques. Regardless of incubation method, acetate oxidation did not account for a significant percentage of SO_4^{2-} reduction. These results differ markedly from data for non-vegetated coastal sediments where acetate levels are low, oxidation rate constants are high and acetate oxidation rates greatly exceed rates of SO_4^{2-} reduction. The discrepancy between rates of acetate oxidation and SO_4^{2-} reduction in marsh soils may be due either to the utilization of substrates other than acetate by SO_4^{2-} reducers or artifacts associated with measurements of organic utilization by rhizosphere bacteria.

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de Mello, W.Z. and M.E. Hines, University of New Hampshire, Durham, NH 03824; S.E. Bayley, University of Alberta, Edmonton, Alta T6G 2E9, Canada

FACTORS CONTROLLING SULFUR GAS EXCHANGE IN *SPHAGNUM*-DOMINATED WETLANDS

Atmosphere-peatland exchange of reduced sulfur gases was determined seasonally in a fen in NH, and in an artificially-acidified fen at the ELA in Canada. Dimethyl sulfide (DMS) dominated gas fluxes at rates as high as 400 nmol m^{-2} hr^{-1}. DMS fluxes measured using enclosures were much higher than those calculated using a stagnant-film model, suggesting that *Sphagnum* regulated efflux. Temperature controlled diel and seasonal variability in DMS emissions. Use of differing enclosure techniques indicated that vegetated peatlands consume atmospheric carbonyl sulfide. Sulfate amendments caused DMS and methane thiol concentrations in near-surface pore waters to increase rapidly, but fluxes of these gases to the atmosphere were not affected. However, emission data from sites experiencing large differences in rates of sulfate deposition from the atmosphere suggested that chronic elevated sulfate inputs enhance DMS emissions from northern wetlands.

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SULFUR GAS EXCHANGE IN *SPHAGNUM*-DOMINATED WETLANDS

Mark E. Hines, William Z. de Mello and Carolyn A. Porter
Institute for the Study of Earth, Oceans and Space
University of New Hampshire
Durham, New Hampshire 03824

Sulfur gases are important components of the global cycle of S. They contribute to the acidity of precipitation and they influence global radiation balance and climate. The role of terrestrial sources of biogenic S and their effect on atmospheric chemistry remain as major unanswered questions in our understanding of the natural S cycle. We have been investigating the role of northern wetlands as sources and sinks of gaseous S by measuring rates of S gas exchange as a function of season, hydrologic conditions and gradients in trophic status. We have also investigated the effects of inorganic S input on the production and emission of gaseous S.

Experiments have been conducted in wetlands in New Hampshire, particularly a poor fen, fens within the Experimental Lakes Area (ELA) in Ontario, Canada and in freshwater and marine tundra. Emissions were determined using Teflon enclosures, gas cryotrapping methods and gas chromatography (GC) with flame photometric detection. Dynamic (sweep flow) and static enclosures were employed. Dissolved gases were determined by gas stripping followed by GC.

Emissions of dimethyl sulfide (DMS) greatly dominated S gas fluxes from all sites. In New Hampshire, DMS fluxes were >1.6 μmol m^{-2} h^{-1} in early summer, 1989 which were several-fold faster than average oceanic rates of DMS emission. After construction of a dam by a beaver in 1990, DMS fluxes decreased for the next two years to ~150 nmol m^{-2} h^{-1}. Fluxes displayed a smooth diel pattern which followed temperature. Dissolved DMS and methyl mercaptan (MSH) concentrations varied throughout the fen both temporally and spatially. Concentrations were highest in the most minerotrophic areas and in the spring.

Additions of SO_4^{2-} caused a rapid increase in dissolved DMS and MSH concentrations in pore waters. However, emissions of gases were not affected. Dissolved S gases were 100-fold higher in a site in which vegetation was removed. Conversely, emissions of DMS were higher in the vegetated sites. Although dissolved MSH concentrations increased in response to SO_4^{2-} additions, MSH efflux did not occur. The results suggested that DMS and MSH were formed from the methylation of sulfide.

S gas emissions in a Canadian wetland varied greatly along a transect running from the central pond to the upland. Emissions of S gases were slow in the floating *Sphagnum* mat next to the pond and were dominated by hydrogen sulfide (H_2S). Fluxes a few meters away from the pond were much higher and restricted to DMS, whereas sites adjacent to the upland exhibited low to undetectable fluxes of all S gases. Emissions from the lake surface were insignificant.

Carbonyl sulfide (COS) was consumed by *Sphagnum* wetlands in both the light and dark. However, when *Sphagnum* was removed, COS was emitted to the atmosphere. Dissolved COS concentrations varied from <0.1 to 10 nM and were highest in the summer and in minerotrophic areas.

Emissions of S gases (DMS) from these wetlands were much faster than expected from the low S content of the ecosystem. *Sphagnum* appeared to greatly enhance S gas flux compared to other types of vegetation, and fluxes were often highest in ombrotrophic regions. Fluxes calculated from S gas concentrations in standing water pools or in pore waters will often greatly underestimate rates compared to direct measurements using chambers. Emissions of S gases from northern wetlands probably do not contribute greatly to the global burden of atmospheric S. However, they may affect regional budgets. More importantly, investigations of controls on these relatively rapid fluxes may be useful for understanding S cycling in northern, continental areas.