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

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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

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
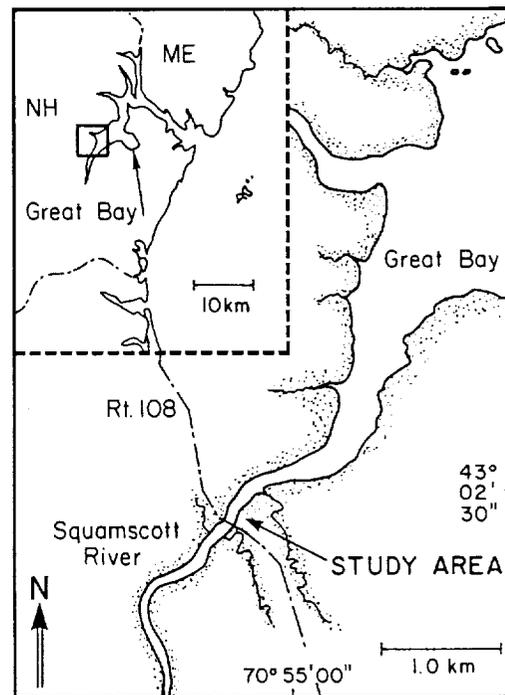

Fig. 1. Location of sampling sites in Chapman's Marsh, New Hampshire.

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.

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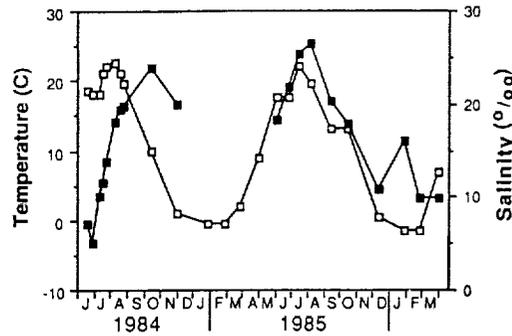
Fig. 2. Temperature (□) and salinity (■) in pore waters of Chapman's Marsh, June 1984–April 1986.

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.

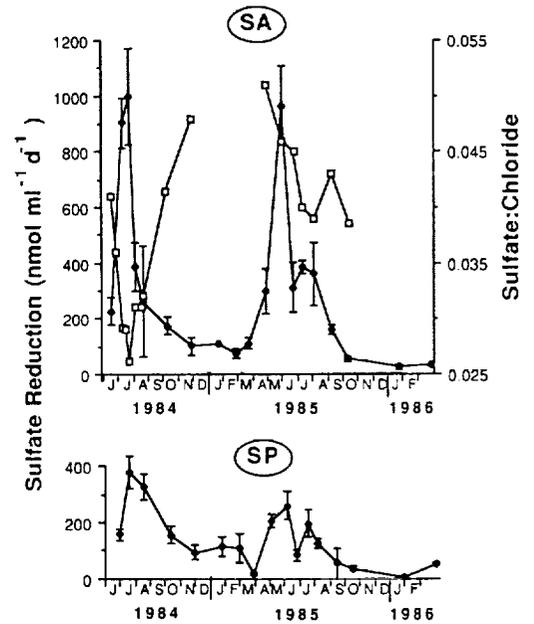During the 1984 growing season, weekly pore-water samples were collected from all three sites to determine the short-term temporal variability in pore-water chemistry. Sulfate reduction rates were determined at either the SA or SP site each week. All cores and pore-water samples were collected at midtide. 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 μmol 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
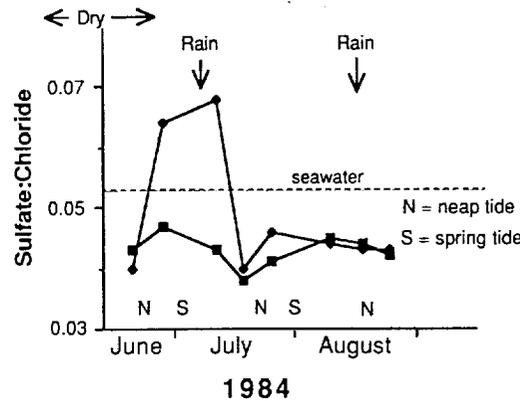
Fig. 4. Average SO_4^{2-} : Cl^- ratios in pore waters at sites T (■) and SP (♦) as a function of tidal regime and rainfall during summer 1984.
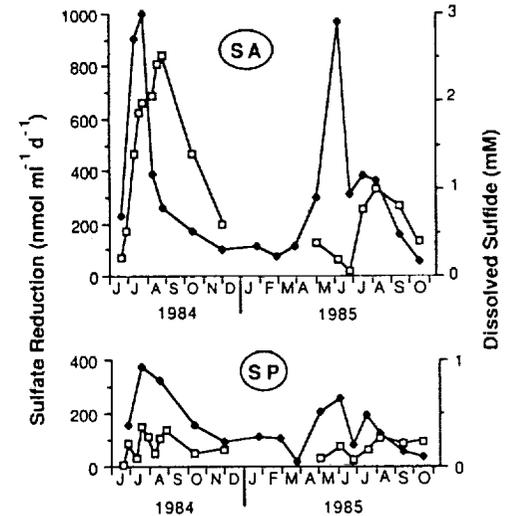

Fig. 5. Concentrations of dissolved sulfide (□) in pore waters at sites SA and SP. Values represent averages over the upper 20 cm of soil. Sulfate reduction rates (♦) from Fig. 3 are included for comparison to sulfide data.

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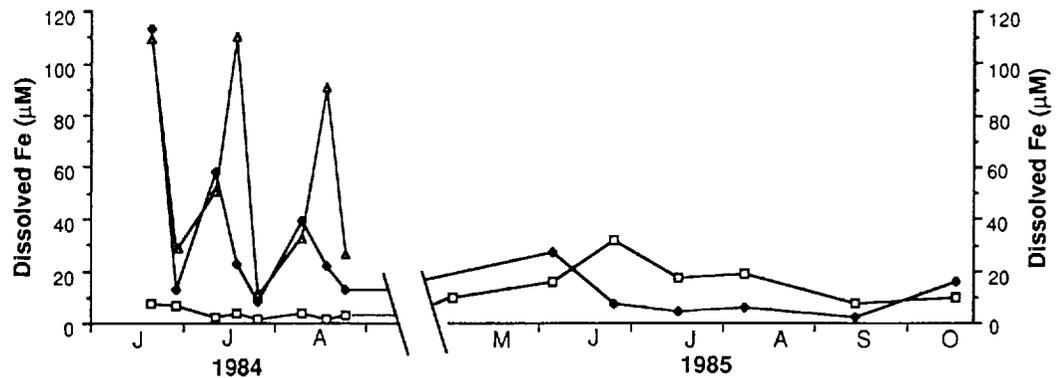
Fig. 6. Concentrations of dissolved iron in the pore waters at sites SA (□), T (△), and SP (◆). Values represent averages of the upper 20 cm of soil.

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 main-

tained 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
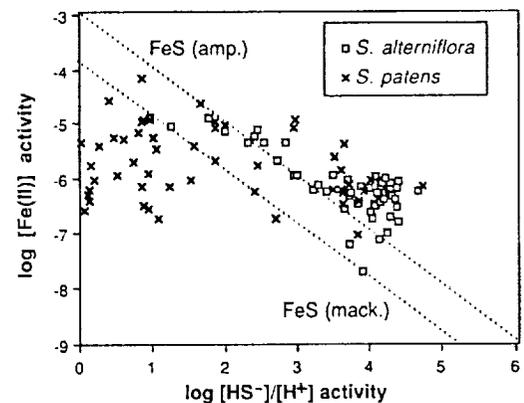

Fig. 7. Calculated values for the ion activity product of $(Fe^{2+})(HS^-)/(H^+)$ for pore waters collected from sites SA and SP during 1984 and 1985. Dotted lines represent pK_{sp} values for amorphous FeS and Mackinawite. Points above the dotted lines are supersaturated. Activity coefficients for Fe^{2+}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

duction 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

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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$_2$S 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$_2$S 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.

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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). Prelimi-

nary 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} gSℓ^{-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
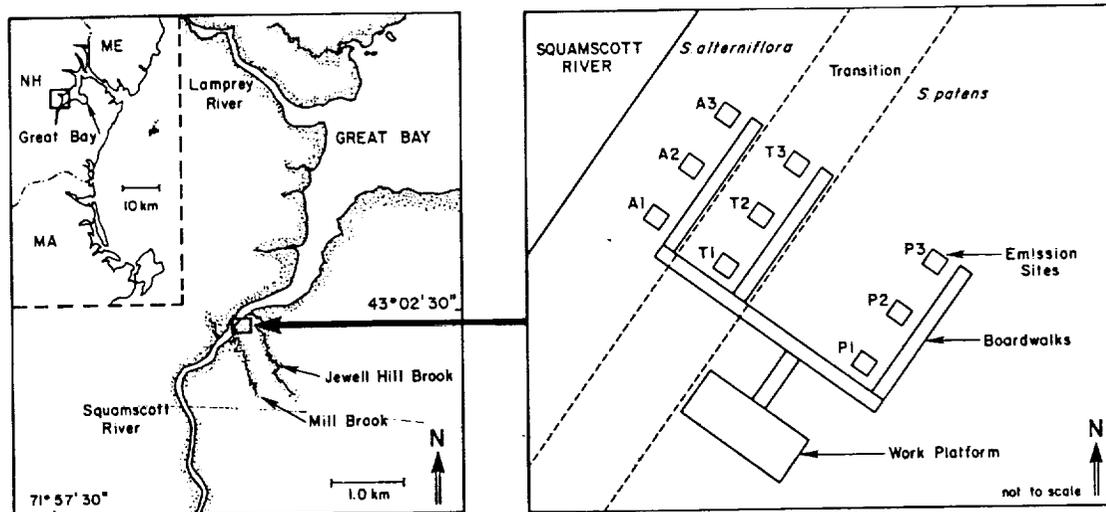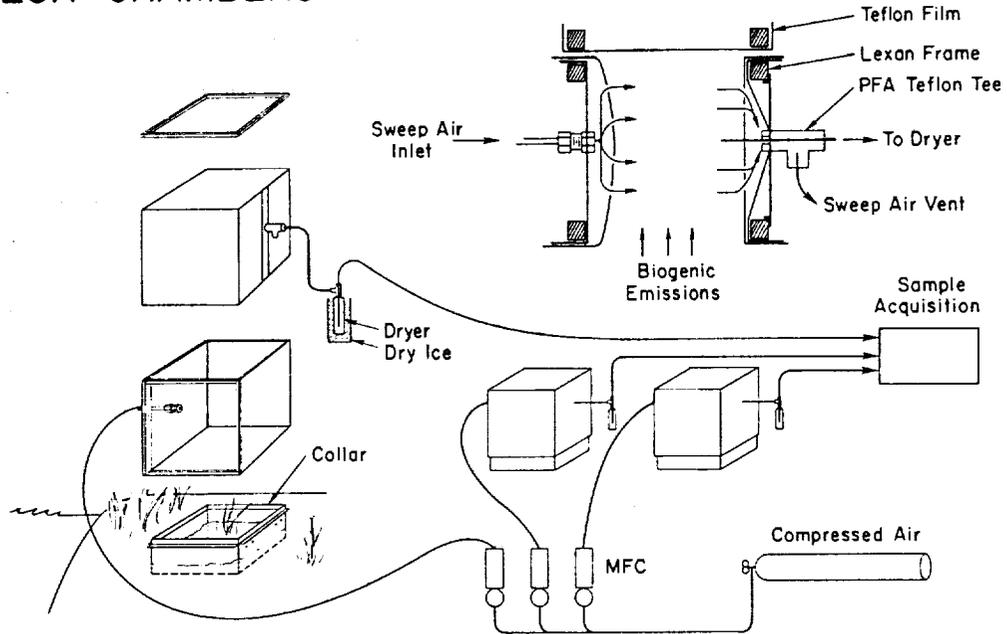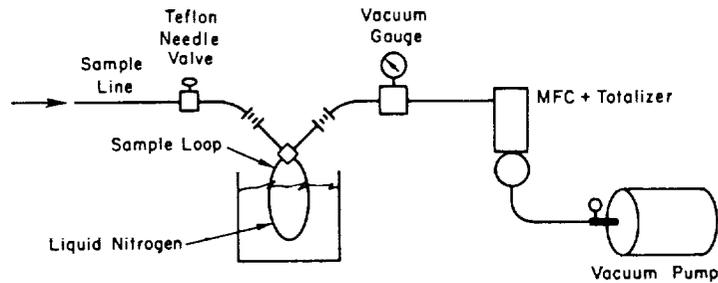

Fig. 1. Location of Chapman's Marsh in southern New Hampshire with a diagram of the sampling boardwalk and relative positions of replicate sampling sites.

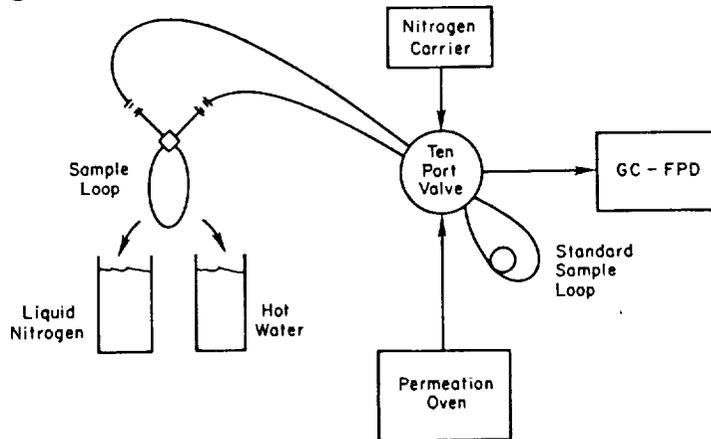# FLUX CHAMBERS

SAMPLE ACQUISITION

ANALYSIS

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.
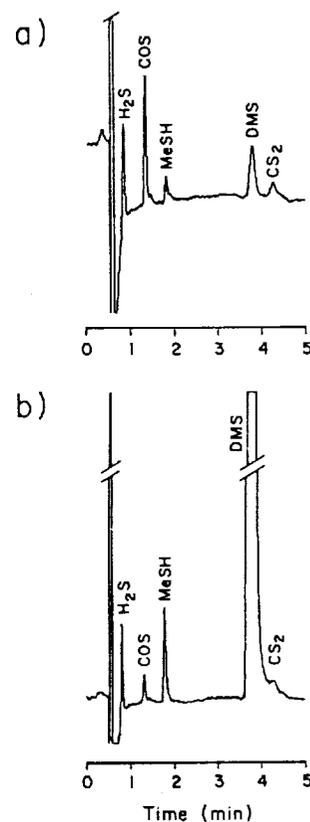

Fig. 3. Typical chromatograms of gaseous sulfur compounds in samples collected from flux chambers deployed over soils inhabited by *Spartina patens* (A) and *S. alterniflora* (B).
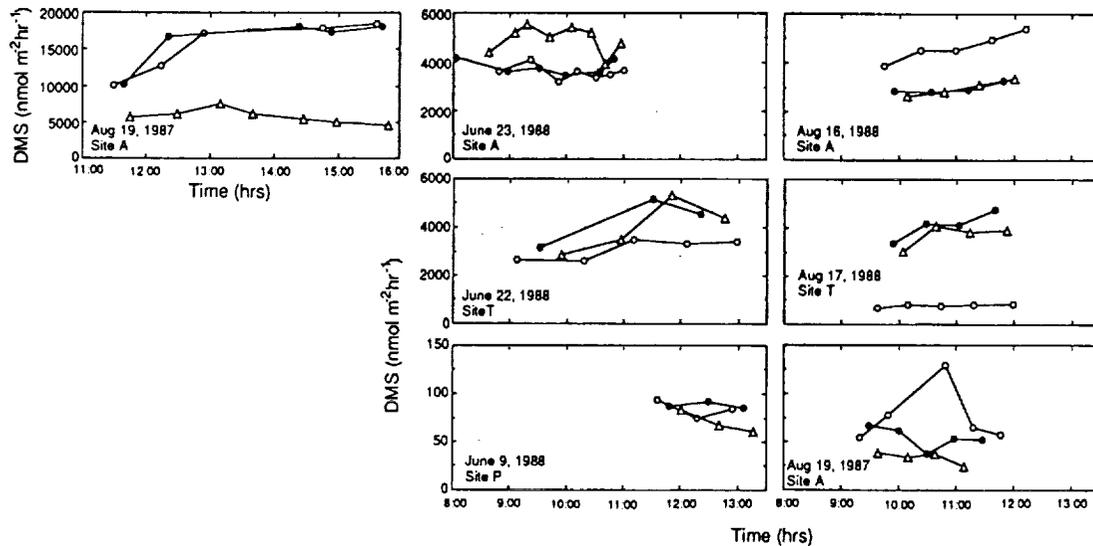
Fig. 4. Emission rates of dimethyl sulfide (DMS) from the various sites over short time scales on different dates. Replicate sites O, 1; ●, 2; △, 3. Note that vertical and horizontal scales are identical for all plots except for 19 August 1987.

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
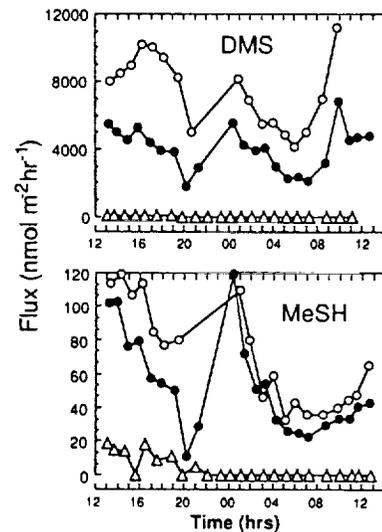

Fig. 5. Variations in dimethyl sulfide (DMS) and methane thiol (MeSH) emissions from sites A1 (O), T1 (●) and P1 (△) for a 24 h period in 1987. Site A soils were flooded from ~20:15 to 00:15. Site T soils were flooded from ~20:45 to 23:55.

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 $\sim$ 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.
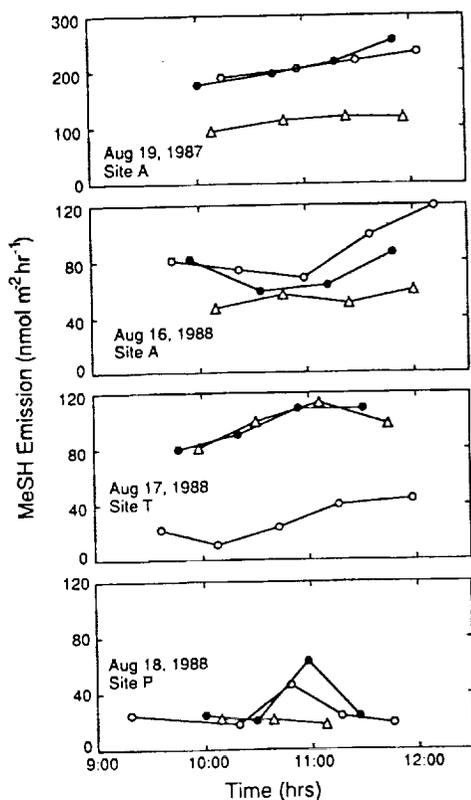

Fig. 6. Emission rates of methane thiol (MeSH) from the various sites over short time scales on different dates. Replicate sites ○, 1; ●, 2; △, 3. Note that vertical scales are identical except for 19 August 1987.

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 ($\sim$ 35 nmol m^{-2} h^{-1}) at site A as opposed to a net efflux of COS ($\sim$ 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
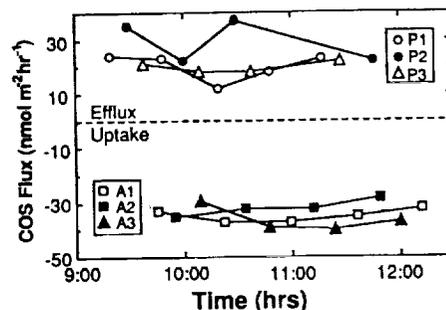

Fig. 7. Flux of carbonyl sulfide (COS) at sites A and P, August, 1988. Tidal water never flooded the soils when samples were being collected.

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})			Reference
	DMS	MeSH	COS	
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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6

DIVERSITY OF ENVIRONMENTAL BIOGEOCHEMISTRY

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