

Methane emissions along a salt marsh salinity gradient

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Abstract. The seasonal flux of methane to the atmosphere was measured at three salt marsh sites along a tidal creek. Average soil salinities at the sites ranged from 5 to 17 ppt and fluxes ranged from below detection limits (less than $0.3 \text{ mgCH}_4 \text{ m}^{-2} \text{ d}^{-1}$) to $259 \text{ mgCH}_4 \text{ m}^{-2} \text{ d}^{-1}$. Annual flux to the atmosphere was $5.6 \text{ gCH}_4 \text{ m}^{-2}$ from the most saline site, $22.4 \text{ gCH}_4 \text{ m}^{-2}$ from the intermediate site, and $18.2 \text{ gCH}_4 \text{ m}^{-2}$ from the freshest of the three sites. Regression of the amount of methane in the soil with flux indicates that changes in this soil methane can account for 64% of the observed variation in flux. Data on pore water distributions of sulfate suggests that the activity of sulfate reducing bacteria is a primary control on methane flux in these transitional environments. Results indicate that relatively high emissions of methane from salt marshes can occur at soil salinities up to approximately 13 ppt. When these data are combined with other tidal marsh studies, annual CH_4 flux to the atmosphere shows a strong negative correlation with the long term average soil salinity over a range from essentially fresh water to 26 ppt.

Introduction

Methane (CH_4) is an important trace gas in the global atmosphere. In the troposphere for example, CH_4 is a sink for OH, a source of O_3 and CO, and by absorbing outgoing radiation in the infrared region, can act as a “greenhouse” gas as does CO_2 (Logan et al. 1981; Lacis et al. 1981). Recent evidence indicates that the concentration of CH_4 in the atmosphere is increasing on a global scale by 1–2% a year (Graedel & McRae 1980; Rasmussen & Khalil 1981; Khalil & Rasmussen 1986; Craig & Chou 1982; Stauffer et al. 1985). Known sources and isotopic measurements suggest that the majority of atmospheric methane is of biogenic origin (Stevens & Rust 1982; Ehhalt & Schmidt 1978). Primary biogenic sources are thought to include wetland soils—swamps, bogs, marshes, and rice paddies—where organic material is decomposed by bacteria under anaerobic conditions. The magnitude of the wetlands source is not well known however, and major environmental variables which can affect flux have rarely been examined outside of a laboratory setting. Reported methane emission rates from a

single type of wetlands such as salt marshes, for example, vary by seven orders of magnitude (Atkinson & Hall 1976; King & Wiebe 1978; Cicerone & Shetter 1981; DeLaune et al. 1983; Bartlett et al. 1985). Such problems lead to significant uncertainty in global estimates of fluxes from wetland habitats (Harriss & Sebacher 1980).

Although extensive laboratory work has been undertaken to examine the affect of a variety of environmental factors on methanogenic bacteria themselves (e.g. Balderson & Payne 1976; Mah et al. 1977; Zehnder 1978; Jones et al. 1982), little systematic work has been done to link methane emissions to the atmosphere with environmental variables. Where seasonal data exists, emission rates appear to be at least partially correlated with temperature, as might be expected for a biogenic gas (King & Wiebe 1978; DeLaune et al. 1983; Harriss et al. 1982; Bartlett et al. 1985). Measurements made in forested freshwater swamps by Harriss & Sebacher (1981) indicate that in these habitats, fluxes may also correlate with soil organic content or peat depth. Additionally, wetlands receiving nutrient enrichment in the form of compounds such as sewage effluent (Harriss & Sebacher 1981) or nitrogen fertilizers (Cicerone & Shetter 1981) appear to have higher emissions than similar habitats without such enrichment, although the relationship between increased nutrients and flux does not appear to be simple. The presence and type of wetland plants also appears to affect rates of CH_4 flux since they can serve as conduits passing the gas from the soil to the atmosphere (Dacey & Klug 1979; Cicerone & Shetter 1981; Seiler et al. 1984; Sebacher et al. 1985). Emission rates from some of these environments may then be correlated with life cycles and vigor of plants.

Considerable work in marine environments has examined the effect of sea water sulfate (SO_4^{2-}) and sulfate-reducing bacteria on methanogenesis and methanogenic bacteria (Martens & Berner 1974; Oremland & Taylor 1978; Abram & Nedwell 1978; Reeburgh & Heggie 1977; and others). Interactions between these two functional groups of bacteria are complex and a subject of some uncertainty. Sulfate reducers may compete with and/or inhibit methanogens in sediments (Abram & Nedwell 1978; Winfrey & Zeikus 1977; Oremland & Polcin 1982). They may also oxidize CH_4 (Rudd et al. 1974; Martens & Berner 1977; Devol 1983; Iverson & Jorgensen 1985; Alperin & Reeburgh 1985), resulting in low concentrations of methane in the soil or water column and subsequently little flux to the atmosphere. Distinct differences in methane distributions between freshwater and marine sediments led Reeburgh & Heggie (1977) to hypothesize that these differences were the result of sulfate concentration levels. They suggest that the presence of sulfate in marine environments and its near absence in fresh ones can determine the relative activities of sulfate reducing bacteria in consuming

methane, and can therefore be a controlling variable determining differences in the overall magnitude and distribution of CH_4 concentrations between these environments.

Although the use of varying techniques and a lack of seasonal data make generalization difficult, methane fluxes reported from a variety of wetland environments do suggest that fluxes from freshwater habitats tend to be greater than those from marine wetlands. DeLaune et al. (1983) have demonstrated large differences in annual CH_4 flux between a Gulf Coast saline wetland ($5.7 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$; 18.1 parts per thousand (ppt) soil salinity) and a fresh water marsh ($213 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$; 0.4 ppt soil salinity). A low salinity tidal marsh (1.8 ppt) had annual emissions intermediate between these extremes ($97 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$). Emissions from all sites were highly variable, both within a site and over time, but were at least partially correlated with temperature.

We describe here a study with two primary objectives:

- to examine in more detail the dynamics of CH_4 flux and of sediment CH_4 and SO_4 pool sizes within the transitional range of estuarine salinities, 2–20 ppt
- to examine the seasonal relationship between flux and temperature in these environments by working within a homogeneous vegetation type in a marsh where annual temperature variations are more pronounced than that in DeLaune et al. (1983).

Materials and methods

A small tidal creek with similar vegetation and soil type along its banks was selected as a sampling site for our study. Queen's Creek near Williamsburg Virginia on the York River, is approximately 10 km in length (Fig. 1). The marsh along the banks of the creek covers 1.3×10^2 ha (Silberhorn 1981). It is vegetated largely by salt marsh cordgrass (*Spartina alterniflora*) near its mouth, with species less tolerant of high salinities such as *Spartina cynosuroides* and *Spartina patens*, gradually replacing *S. alterniflora* as one moves upstream. We selected three sampling sites along the creek, largely on the basis of soil and creek water salinities and similarity of vegetation.

Site 1 is located as far upstream as practical to reach by boat and is vegetated by *S. cynosuroides*. Creek water salinities at this site varied from 0 to 7.3 parts per thousand, depending upon tidal stage and rainfall, and averaged $2.6 \text{ ppt} \pm 0.55$ (standard error of the mean or SEM; $n = 16$). Seasonally, the average soil salinity in the top 50 cm varied between 1.4 and 8.0 ppt.

Site 2 is located in a mixed stand of *S. alterniflora* and *S. cynosuroides*.

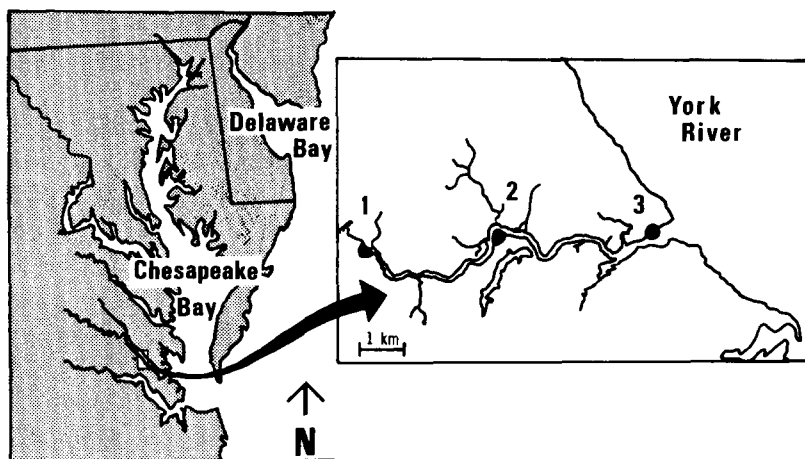


Fig. 1. Site map of Queen's Creek sampling locations near Williamsburg, Virginia, USA.

Measured creek salinities ranged from 1.5 to 11 ppt with a mean of 5.5 ± 0.55 ($n = 19$), and average soil salinity in the upper 50 cm varied from 8.0 to 17 ppt over the year.

Site 3, located near the mouth of the creek, is vegetated by a pure stand of *S. alterniflora*. Creek salinities in this area ranged from 8 to 12 ppt, with an average salinity of 8.8 ± 0.36 ppt ($n = 18$), while the average in the soil varied between 12 and 21.6 ppt.

A single flux measurement on two adjacent plots was made at each of the three sites on a monthly basis over the one year study period. Diurnal measurements made in another *S. alterniflora* marsh site indicate that methane flux varies little over a 24 hour period and that no consistent pattern with tide or time of day is observed (average flux = $57.7 \text{ mgCH}_4 \text{ m}^{-2} \text{ d}^{-1} \pm 1.90$ (SEM), $n = 19$; yielding a coefficient of variation of 14.4%). Duplicate measurements on two adjacent sites ($n = 4$) made two days earlier at this site are quite similar to those made over the 24 h period (average flux = $58.3 \text{ mgCH}_4 \text{ m}^{-2} \text{ d}^{-1} \pm 5.26$; yielding a coefficient of variation of 18%), indicating that a relatively small number of measurements should be representative of flux at a site over periods of at least several days.

Methane flux was detected by a non-dispersive infrared gas filter correlation analyzer (GFC) integrated with an aluminum chamber set over the sediment-air interface in a recirculating, continuous flow system. The details of this detection system can be found in Sebacher & Harriss (1982) and Sebacher (1985). Fluxes as low as $1\text{--}3 \times 10^{-4} \text{ gCH}_4 \text{ m}^{-2} \text{ d}^{-1}$ can be measured with the system in about 15 min. Due to the height of the vegetation at the sites (up to 2.0 m), two chambers (0.41 m^2 in area by 0.37 m height and

0.51 m² in area by 1.22 m height) were used during the study. Since it is possible that the marsh vegetation serves as a transport pathway for CH₄ emissions (e.g. Dacey & Klug 1979; Dacey 1981; Sebacher et al. 1985), measurements were made over undisturbed vegetated plots without clipping plants or other modification of natural conditions. Shading the chamber during measurements and the brief period required for a measurement serve to minimize the environmental perturbations that some chamber systems can induce (Matthias et al. 1980; Denmead 1979). Because our measurements are of short duration, the environment in the chamber does not change except for light level, during the measurement. Although changes in light intensity may affect gas transport in plants (see for example, Dacey 1981), measurements indicate that emissions of methane by *S. alterniflora* are relatively minor (Sebacher et al. 1985). Fluxes from plots in which the grass has been cut at ground level and sealed have not been found to be significantly different from undisturbed, vegetated plots.

The distribution of CH₄, SO₄²⁻, and salinity in the interstitial water of the soils at the three marsh sites was sampled on a monthly basis using plexiglas dialysis samplers similar to those developed by Hesslein (1976). The samplers were 62 cm in length with a sampling interval of 1.6 cm. They were filled with distilled water, covered with dialysis membrane (8000 mol. wgt. cut-off), and left in the marsh for an equilibration period of two weeks; a time period based on a previous time series study in a nearby marsh. It is possible that the cellulose acetate material of dialysis membrane may support bacterial growth. We conducted tests using side by side insertions of samplers having dialysis and teflon membranes to compare dialysis concentrations with those from biologically inert teflon. The tests did not show consistent differences in CH₄ concentrations between the two membrane types. Profile shapes were similar for both types of membranes and concentrations in samplers covered by dialysis membrane were not consistently higher or lower than those at similar depths using teflon membrane.

Equilibrated pore water was removed from the samplers within 10 min of retrieval using disposable glass syringes equipped with gas-tight polycarbonate stopcocks and was analyzed within 5 h (gases) or 24 h (sulfate and salinity). Dissolved CH₄ was analyzed by liquid stripping gas chromatography using a flame ionization detector (FID) and a 15 ft (4.6 m) molecular sieve column (McAuliffe 1971; Martens & Klump 1980). A 0.2 ml sampling loop was used for pore water samples. Analysis of pore water for sulfate concentration was performed using EPA standard colorimetric techniques on a Technicon autoanalyzer. Pore water salinities were determined using a handheld refractometer which measured dissolved chloride. Although the sulfate concentration in seawater varies as the chloride concentration changes, a constant molar ratio (5.17×10^{-2} , SO₄²⁻:Cl⁻) is maintained. Ratio

values less than this constant can indicate the loss of sulfate through bacterial sulfate reduction. The oxidation of reduced sulfur compounds to sulfate can increase values. Creek water temperatures and salinities were determined in the field using an induction salinometer.

Estimates of the net annual primary productivity (NAPP) of emergent macrophytes were made at the three sites to assess the importance of atmospheric losses of methane to the marsh carbon budget. Primary productivity was estimated by clipping vegetation at the sediment surface within 0.25 m^2 plots on a monthly basis. Above-ground production in a $\text{g dry wt m}^{-2}\text{ yr}^{-1}$ is calculated by changes in the live and dead biomass over the course of the growing season (Smalley 1959).

Results and discussion

Salinity/chloride

The distribution of a non-reactive species such as chloride in the sediment pore water should be controlled by hydrologic processes (tidal mixing, precipitation, and run-off), concentrating processes on the marsh (such as desiccation, evaporation, evapotranspiration), and diffusion. Since salinities in creek water, where the effects of plant evapotranspiration should not be significant, correlate well with pore water salinities, precipitation and run-off are suggested as major controls on marsh pore waters. Salinity variations in Queen's Creek tidal waters and in marsh interstitial waters appear to be correlated with precipitation over the drainage area, with a lag of approximately one month (correlation significant at the 95% confidence level). The importance of fresh water inputs to tidal waters in controlling pore water salinities is not surprising for frequently flooded locations such as these stations. Over the 12 month sampling period, pore water salinities in the top 50 cm were: 5.1 ± 0.6 ppt (mean \pm SEM) at Site 1; 12.8 ± 0.8 ppt at Site 2; 16.6 ± 0.8 ppt at Site 3. Salinity differences between sites were consistent throughout the sampling period.

Methane flux

Seasonal emissions of methane at the three sites are shown in Fig. 2. Peak fluxes are highest—an average of $259 \pm 72\text{ mgCH}_4\text{ m}^{-2}\text{ d}^{-1}$ (mean \pm SEM) at Site 1, the low salinity station and are lowest—a single measurement of $46.4\text{ mgCH}_4\text{ m}^{-2}\text{ d}^{-1}$ at the most saline Site 3. Seasonal patterns of flux appear to change along the gradient, with the period of near-peak fluxes

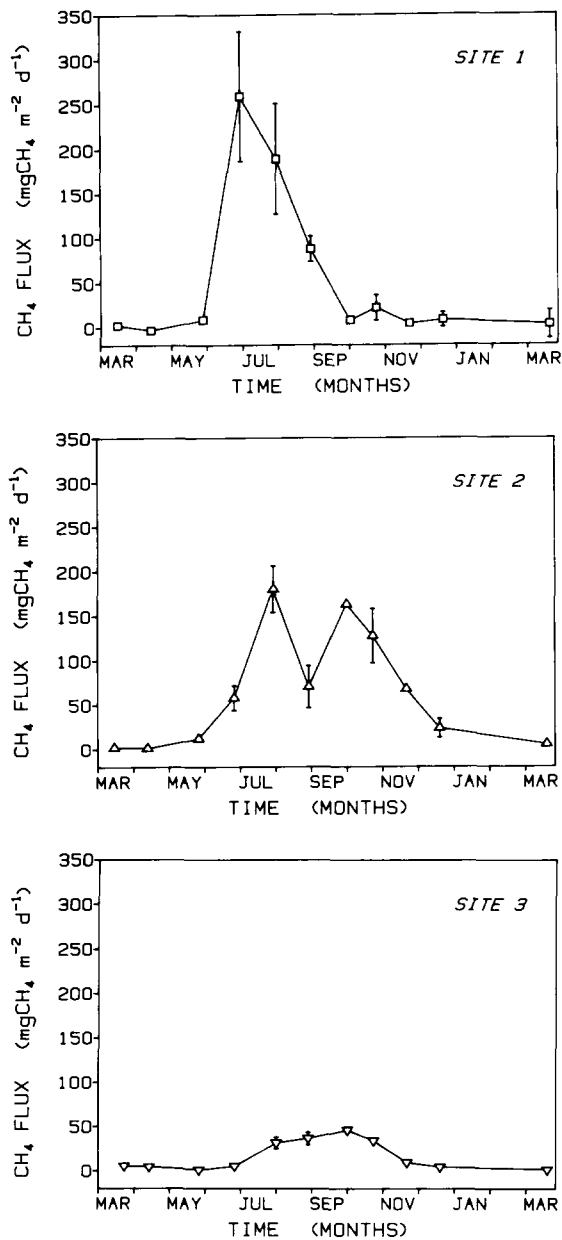


Fig. 2. Seasonal methane flux over the sampling period of March 1983 through March 1984. Values represent means \pm SEM. Aside from September values (a single measurement at each site), symbols without error brackets have errors smaller than the symbol. \square Site 1, \triangle Site 2, ∇ Site 3.

extending later into the fall at higher salinities. High fluxes occur over a comparatively short period of time at the low salinity site during the summer months (three months, June–August). Emissions drop below those of the other two sites from September to November. A pattern of relatively high emissions continuing well into autumn has been reported for other temperate saline marshes by DeLaune et al. (1983) and Bartlett et al. (1985).

Annual methane emissions were calculated from the three sites by integration under the curves of Fig. 2. Sites 1 and 2 had similar emissions (18.2 ± 5.8 and $22.4 \pm 3.4 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ respectively), with the annual rate at the more saline Site 2 somewhat higher than that at Site 1. Annual emissions were significantly lower from the most saline Site 3 ($5.6 \pm 0.7 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$). This value compares well with an annual flux of $5.7 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ from a site of similar salinity described by DeLaune et al. (1983). Annual emissions from Bay Tree salt marsh, a nearby, more saline marsh (soil salinity approximately 26 ppt) are lower than those reported here and range from 0.43 to $1.3 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ (Bartlett et al. 1985). Annual emissions from saline marshes in Georgia range from 0.4 to $1.3 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ for creek bank sites (Atkinson & Hall 1976; King & Wiebe 1978). Emissions reported by DeLaune et al. (1983) from lower salinity sites (less than 2 ppt) are higher than those reported here.

The distinct seasonal patterns of flux from the Queen's Creek sites result in annual emissions which are quite different from what would be predicted based on peak summer fluxes alone. Annual emissions at Sites 2 and 3 are much higher relative to Site 1 than are peak emission rates. This means that seasonal measurements of flux are important for accurate estimation of atmospheric source strengths.

Measured NAPP values permit calculation of annual plant above-ground carbon production lost as methane to the atmosphere. Losses are low, amounting to 1.2% at Site 3, 4.4% at Site 2, and 3.1% at Site 1. Methane lost from the sediments by advective transport (dissolved in porewaters and carried into Queen's Creek via porewater exchange) is likely to be on the same order (Bartlett et al. 1985). Other reports of carbon lost from salt marsh systems as CH_4 are similar to figures calculated here (King & Wiebe 1978; DeLaune et al. 1983; Howes et al. 1985; Bartlett et al. 1985). Calculating carbon released as methane on the basis of total plant production (above and below-ground), reduces loss figures further. Multiplying NAPP values by maximum and minimum values for reported root to shoot ratios (Gallagher & Plumley 1979; Schubauer & Hopkinson 1984; Good et al. 1982) results in methane carbon loss estimates between 0.1 and 2.2% of annual plant production at the three sites.

Methane in marsh pore waters

Methane concentrations in the sediment interstitial water at the three stations show large concentration changes with depth and over time (Fig. 3). Methane concentrations in the soils increase at mid-depths in the spring, resulting in well defined concentration peaks between 15 and 30 cm (Fig. 3). Later in the spring and summer at the fresher sites, concentration peaks disappear as concentrations throughout the sediment column increase. A general increase in concentrations also appears to occur at the more saline Site 3, although it takes place later in the season and a mid-depth (15–40 cm) concentration peak appears to be present throughout most of the year. At the fresher sites, methane concentrations decrease at shallow depths as soil temperatures fall in early autumn. During winter months, lower concentrations are found throughout the sediment column.

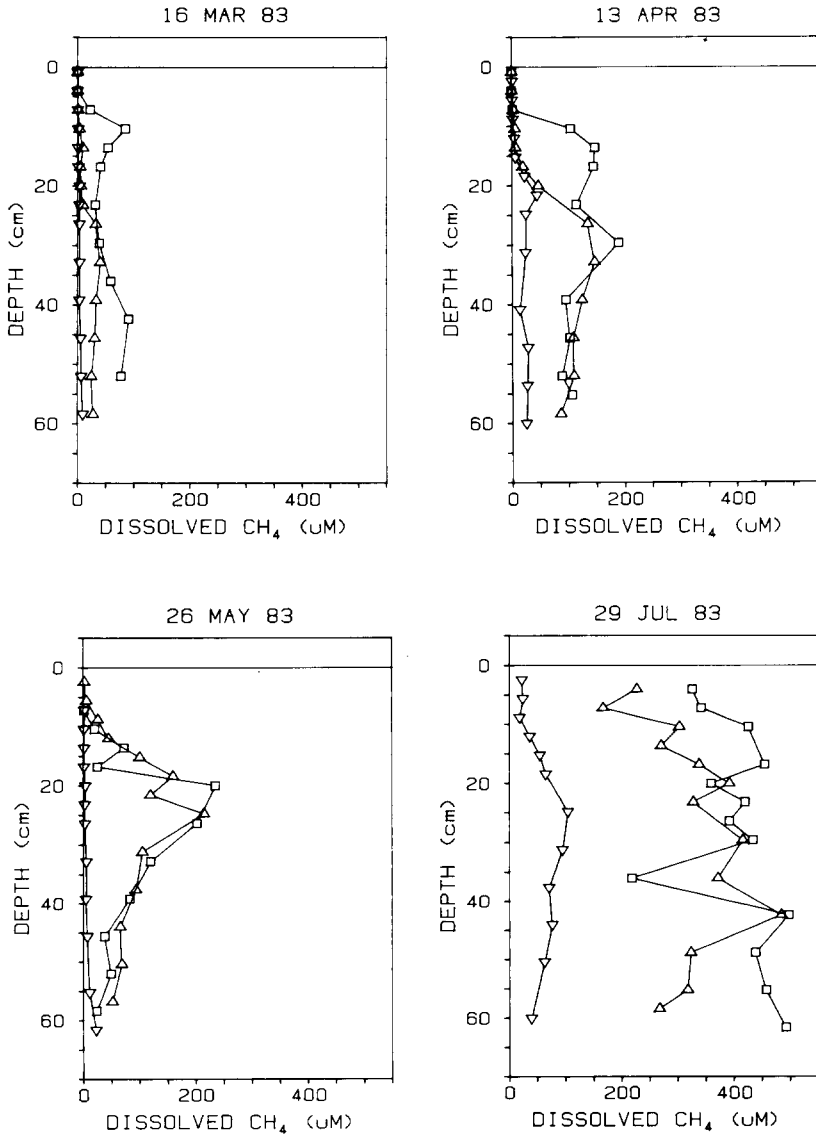
Flux across the air-soil interface should be related to the concentration difference across the interface (Liss & Slater 1974; Berner 1980). By integration of the methane profiles with depth, and by assuming a soil dry bulk density of 0.3 g cm^{-3} (Nixon 1979) and a soil porosity of $0.7 \text{ gH}_2\text{O g soil}^{-1}$, a “standing stock” or amount of dissolved methane in a volume of soil can be calculated. These “standing stocks” of methane exhibit systematic seasonal changes at the three stations (Fig. 4), strongly resembling the trends in flux (Fig. 2), and methane flux is found to be strongly correlated with the log of CH_4 in near-surface soils ($r = .801$, $p < .01$). Seasonal changes in soil methane pools therefore can account for 64% of the observed variation in flux. Within each station, fluxes are well correlated with soil methane, but yield different slopes for the relationship. Regression slopes were quite similar at Sites 1 and 2, but were greater at Site 3 (regression model slopes: Site 1, 0.527; Site 2, 0.564; Site 3, 1.671). Differences in slope could reflect differences in transport pathways or diffusivities between the most saline Site 3 and the two fresher stations.

The near-surface slopes of methane depth profiles were modelled to both linear and logarithmic fits, with the log form providing the best fit to the data. Although fluxes correlate significantly with these slopes ($r = .513$, $p < .05$), calculated standing stocks of methane are better statistical predictors of flux. More closely spaced sampling near the air-soil interface may result in more accurate slope calculations and improved correlations between flux and CH_4 gradients. Multiple regression of flux with the near-surface standing stock of CH_4 and the calculated CH_4 gradient indicates that inclusion of the gradient data does not significantly improve the ability to predict flux over using only CH_4 standing stocks. High correlation between sediment methane stocks and flux from marsh soils indicates that emissions

are driven by the dynamic balance between production and consumption of the gas in the bulk soils.

Controls on pore water methane

Temperature. Rates of methane production and consumption in soils can be controlled by a variety of parameters including temperature, organic substrate supplies, the availability of nutrients and electron acceptors, and



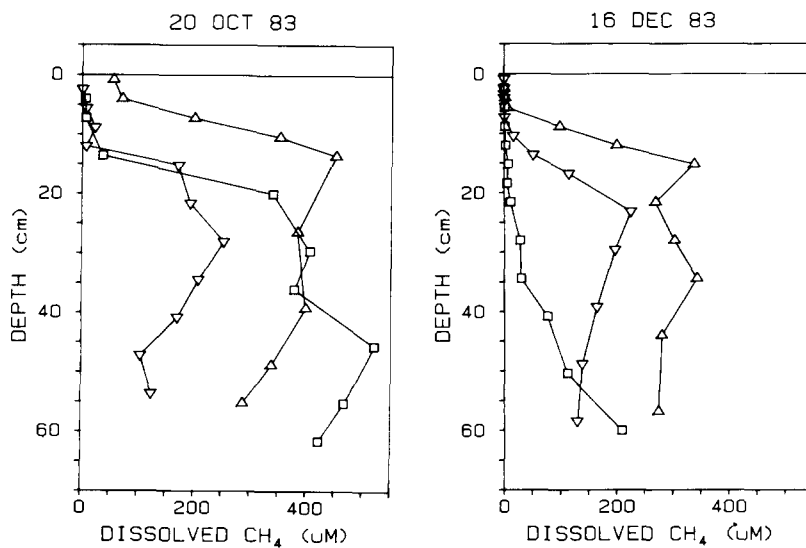


Fig. 3. Selected methane profiles with depth in Queen's Creek tidal marsh soils. Site designation as in Fig. 2.

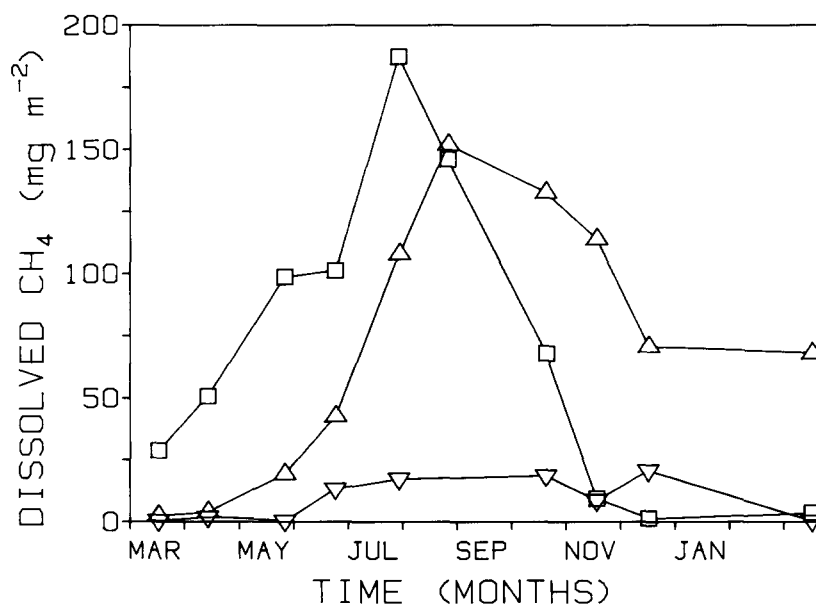


Fig. 4. Pools of dissolved methane in near-surface (top 15 cm) of marsh soils. Site designation as in Fig. 2.

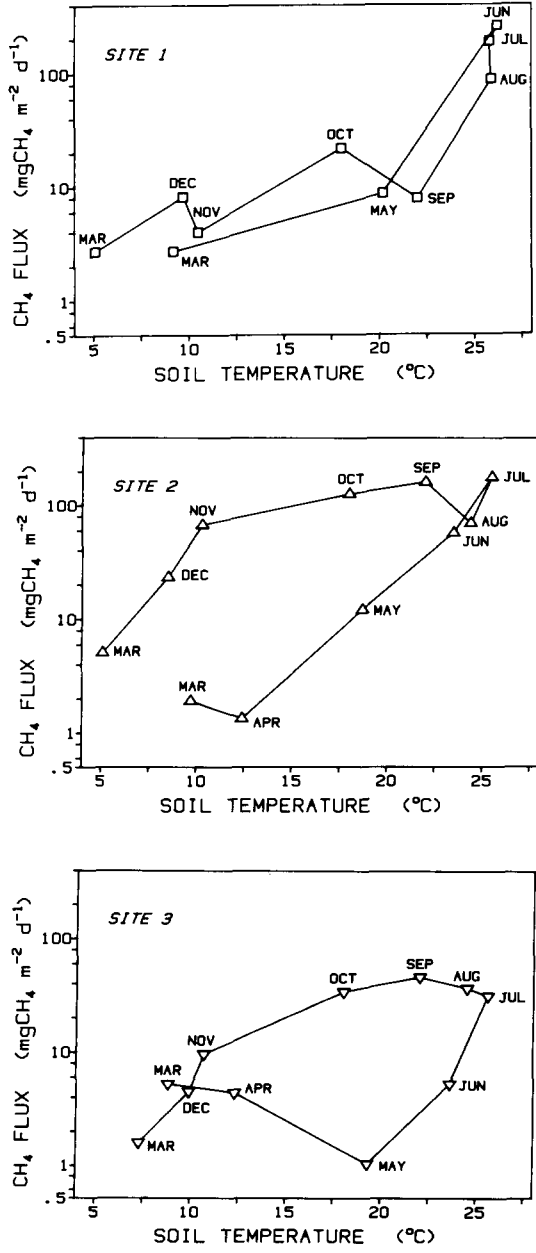


Fig. 5. Average methane flux and soil temperature (15 cm depth).

interactions with other microbial communities (see for example, Zeikus & Winfrey 1976; Martens & Goldhaber 1978; Rudd & Taylor 1980; Kelly & Chynoweth 1981). Although flux to the atmosphere at Queen's Creek is logarithmically correlated with soil temperature ($r = .668$, $p < .01$), it is clear from Fig. 2 that the sites differ significantly in seasonality. Variation in flux to the atmosphere as well as in the amount of CH_4 in Queen's Creek soils correlates well with soil temperatures at only one of the three stations, the freshest Site 1. Figure 5 demonstrates that although CH_4 emissions are clearly related to soil temperature, other variables create higher fluxes in the autumn than the spring for equivalent temperatures. At the freshest site, the seasonal trajectory is compressed, with fluxes in the spring and fall much more similar, resulting in a good correlation with temperature. Stocks of CH_4 in pore waters form similar seasonal temperature trajectories at the three sites. Such temporal trajectories have been reported in salt marshes elsewhere for rates of bacterial sulfate reduction (Howarth & Teal 1979) and CO_2 production (Howes et al. 1985). In these studies, higher autumn rates were hypothesized to be caused by the release of readily metabolized organic substrates as marsh plants mature and die. Trajectories observed at our sites may be caused by similar factors; however, since amounts of methane in the sediments are a function of both production rates and rates of consumption and loss, a change in the variables controlling either can result in a change in standing stock and flux. Average $\text{SO}_4:\text{Cl}$ ratios in pore waters, an indirect relative measure of the activity of sulfate reducing bacteria, have seasonal temperature trajectories similar in form to those of CH_4 flux and CH_4 concentration. These trajectories however, are opposite in direction to those for CH_4 with higher ratios at cooler temperatures, lower ratios at higher temperatures, and lower ratios than might be expected for equivalent temperatures in the autumn. These data suggest that either the two functional groups of bacteria are closely linked or that similar environmental factors are operating on both.

Sulfate. In pore water depth profiles, CH_4 and SO_4^{-2} concentrations (or $\text{SO}_4:\text{Cl}$ ratios) are inversely related (Fig. 6), as has been found elsewhere in salt marsh and subtidal marine sediments (Reeburgh & Heggie 1977; Winfrey & Zeikus 1977; Hines & Buck 1982; Bartlett et al. 1985; and others). These profiles suggest a coupling between methanogenesis and sulfate reduction in these sediments. Correlation between average $\text{SO}_4:\text{Cl}$ ratios in near-surface soils and CH_4 flux to the atmosphere is good ($r^2 = .679$) and suggests that the activity of sulfate reducing bacteria is one of the primary controls on these emissions (Fig. 7). Assuming constant supply rates of sulfate and abundant organic material, seasonal changes in reduction rates can create changes in the depth of the sulfate reduction zone in environ-

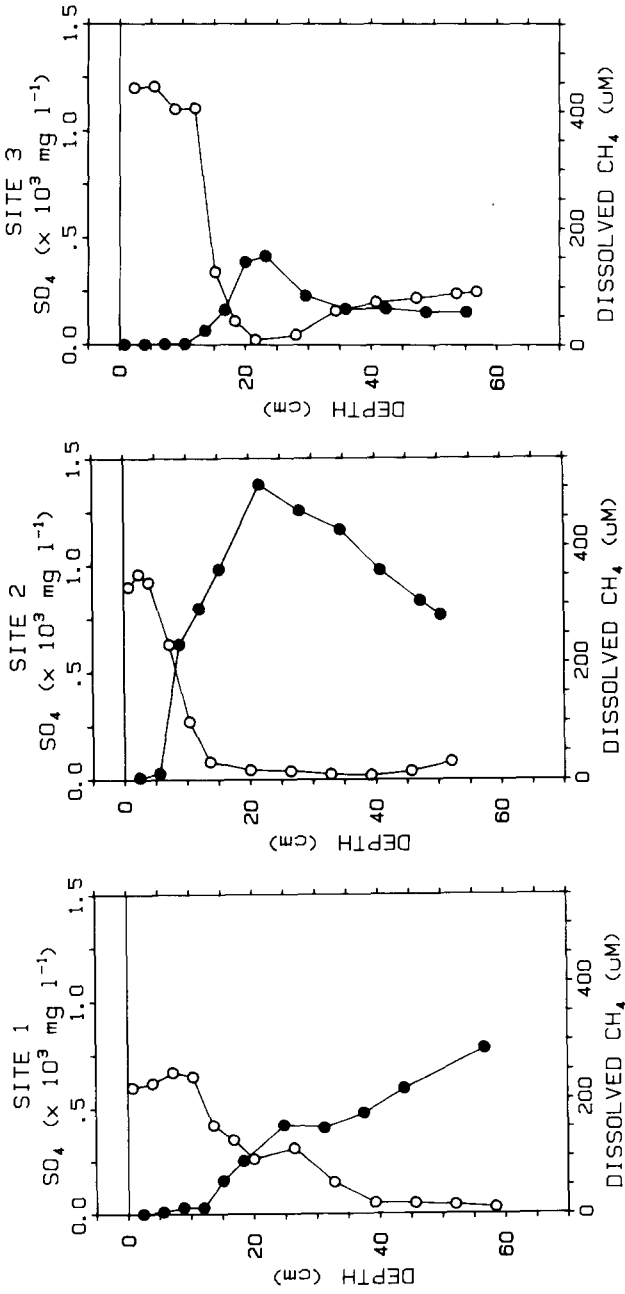


Fig. 6. Methane and sulfate concentrations in marsh pore waters, 19 November 1983. ● CH_4 , ○ SO_4^{2-} .

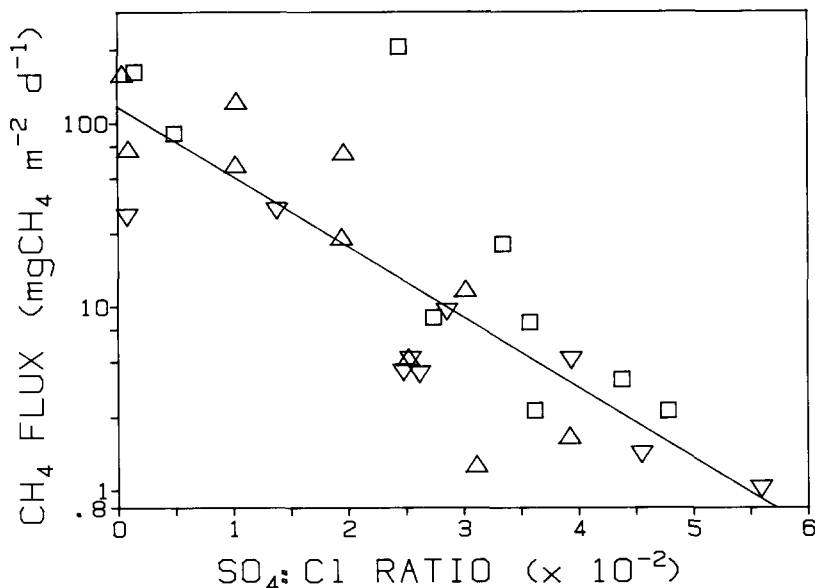


Fig. 7. Average SO_4 :Cl ratios in the top 15 cm of marsh soils and methane emissions across the air-soil interface. ($r = -0.824$, $p < .01$). Site designation as in Fig. 2.

ments with limited sulfate supplies. Crill & Martens (1983) demonstrate that a decrease in the depth of sulfate reduction allows methanogenesis to proceed at shallower depths and for CH_4 to accumulate at depths closer to the sediment-water interface, resulting in enhanced emissions. Although we have no direct measurements of sulfate reduction rates, we believe this general model of the spatial interactions between sulfate reducing bacteria and methanogens can explain seasonal changes in flux at the Queen's Creek sites. Figure 3 illustrates accumulations of CH_4 in near-surface soils during summer months, changes that are paralleled by low SO_4 concentrations and low SO_4 :Cl ratios such as in Fig. 6. The abrupt decrease in flux in the late summer and fall at Site 1 is mirrored simultaneously by SO_4 :Cl ratios that are higher than those at Sites 2 and 3. Methane flux and SO_4 :Cl ratios correlate with soil temperature at Site 1 and may reflect a diminished impact of a pulse of organic substrate during plant senescence. Although environmental factors such as organic matter supplies and temperature exert ultimate controls on these systems, it is apparent that complex biological influences such as those observed in these soils are crucial to our understanding of atmosphere-biosphere links.

Salinity and methane emissions from estuarine marshes

Data now exist to examine annual methane flux from temperate tidal marshes and its relationship to average pore water salinities on an ecosystem

basis. DeLaune et al. (1983) have reported annual emissions from marsh sites having salinities of 0.4, 1.8, and 18 ppt (annual fluxes of 213, 97, and $5.7 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ respectively). Bartlett et al. (1985) found an average annual emission of $1.0 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ from a more saline marsh (26 ppt soil salinity) in Virginia. Adding data from the three Queen's Creek sites provides reasonably comprehensive coverage of annual marsh fluxes over a salinity range of 0.4 to 26 ppt. As shown in Fig. 8, soil salinity is a strong correlate of the logarithm of methane flux over this range. Although this relationship neglects other important variables affecting methane release, it is clear that it alone can account for much of the difference in flux from these transitional estuarine areas. This suggests that soil salinity does not function as a simple switch for methane flux, with high emissions from fresh water marshes and negligible emissions from areas with measurable salinity. Significant emissions of $20 \text{ gCH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ or more can occur at salinities of 5–15 ppt. Emissions of this magnitude have been reported from fresh water wetlands (Harriss et al. 1982; Wilson et al. in prep.). Given the correlation between annual emissions and salinity, it should be possible to derive first order estimates of methane flux from large estuarine areas if data on soil salinities are available.

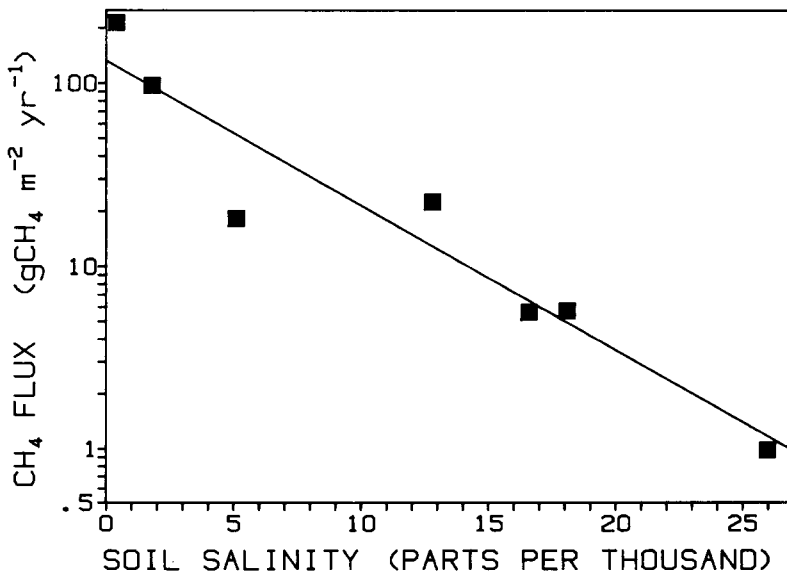


Fig. 8. Annual methane flux and average soil salinity; least squares fit to the equation: $\log y = -0.079x + 2.123$ ($r = -.953$, $p < .01$). Data from Queen's Creek Marsh, VA (this study), Louisiana Gulf Coast (DeLaune et al. 1983) and Bay Tree Marsh, VA (Bartlett et al. 1985).

Summary

Methane flux to the atmosphere changed both seasonally and spatially along a temperate salt marsh salinity gradient. Largest peak fluxes occurred at the lowest salinity site. Fluxes at the most saline site were relatively low year-round. The period of high flux extended later into the autumn at the more saline sites, enhancing their annual emissions over what would be expected by comparison of peak flux values. Thus, annual flux at the mid-salinity station was slightly larger than at the freshest site, 22.4 ± 3.4 (SEM) $\text{gCH}_4 \text{m}^{-2} \text{yr}^{-1}$ and $18.2 \pm 5.8 \text{gCH}_4 \text{m}^{-2} \text{yr}^{-1}$ respectively. Annual emission at the most saline station was significantly lower, $5.6 \pm 0.7 \text{gCH}_4 \text{m}^{-2} \text{yr}^{-1}$. We calculate that carbon lost as methane from the marsh surface accounts for a small percentage of the annual emergent macrophyte production at these sites. Seasonal changes in the sediment CH_4 pool can account for 64% of the variation observed in flux. Methane and sulfate concentrations in pore waters are inversely related and support the coupling between methanogenic and sulfate reducing bacteria suggested by prior studies. Correlation between average near-surface $\text{SO}_4:\text{Cl}$ ratios and CH_4 release to the atmosphere is strong and further supports the hypothesis of the activity of sulfate reducers as a primary control on CH_4 flux. Annual emissions of CH_4 in this and other studies are strongly related to average ambient pore water salinities in the range from 0.4 to 26 ppt, permitting first order estimation of emissions from large areas based on salinity data.

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