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Methane Distribution and Production in the Georgia Salt Marsh

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Bacterial action in the anaerobic sediments of *Spartina* salt marsh produce large quantities of methane. Water in contact with the marsh has methane concentrations 200–300 times normal oceanic concentrations. The methane content of the water varies from maximum of 1.2 μl CH_4 l^{-1} in the summer to a minimum of 0.005 μl CH_4 l^{-1} in the winter. Methane production appears to be temperature dependent. Methane content of the sediment generally increases with depth to maximum observed concentrations of 2.8 ml CH_4 l^{-1} interstitial water. The flux of methane from the sediment is estimated by a variety of techniques to be about 0.21 ml CH_4 m^{-2} h^{-1} (1 g CH_4-C m^{-2} $year^{-1}$). Methane flux is higher in the high marsh than the low marsh.

Introduction

The salt marshes of the southeastern United States coast feature a sediment that is typically anoxic below a surface layer of a few centimeters. While it has been assumed, justifiably, that methane is produced in these sediments there has been little effort to determine the production rates, or spatial distribution. Questions such as the effect of this production on the world-wide methane budget (Hitchcock & Wechsler, 1972) and the role of methanogenesis in the biochemical cycles of the salt marsh ecosystem have been presented with little supporting experimental data. Over the past two years we have measured methane concentrations both in the field and in laboratory controlled experiments that aid in the analysis of the methane production system.

Study area

The salt marshes of the southeast U.S. Atlantic coast are concentrated in Georgia and the Carolinas. The characteristics of these marshes are comprehensively described in many publications (Teal, 1962; Reimold *et al.*, 1973). McIntire & Dunstan (1975) describe and summarize *Spartina* growth rates in this area. The area we examined (Figure 1) is typical of most salt marshes and is convenient to our laboratory. The salt marsh is characterized by the high marsh (upper part of tidal range relatively distant from tidal creeks) where *Spartina alterniflora* typically reaches heights of 0.5 m and low marsh (lower part of tidal range and near tidal creek banks) where *S. alterniflora* reaches heights of 1 m (Gallagher *et al.*, 1972; Christian *et al.*, 1975). As will be discussed later the root structure and sediment of these
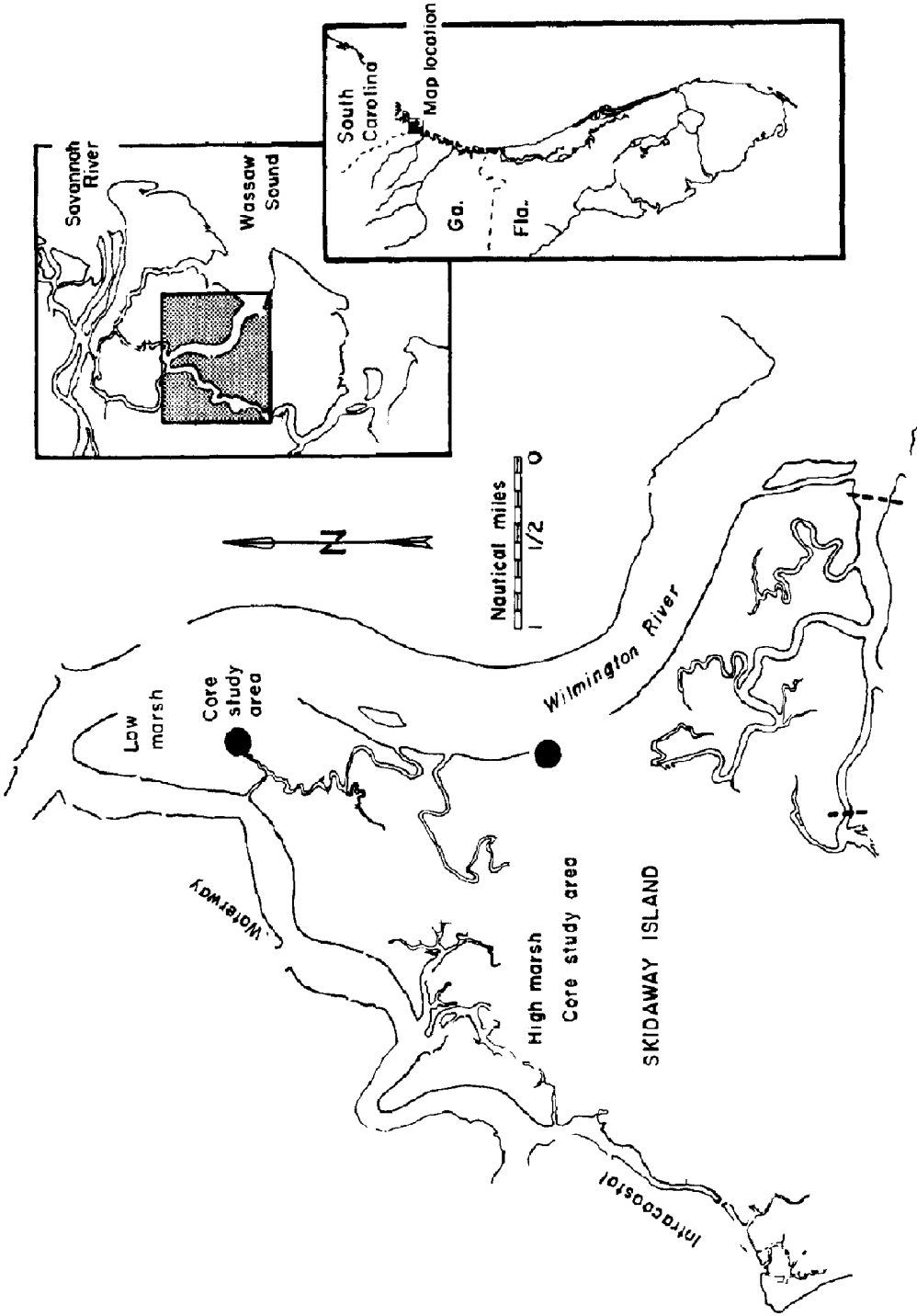
Figure 1. Location of Romerly Marsh Creek and Skidaway Cut sample locations.

areas are distinctly different. Our high marsh station was at Priest Landing and the low marsh station on Skidaway Cut (see Figure 1). In addition we took water samples in Romerly Marsh Creek (Figure 1) under various tidal conditions in an effort to determine the waterborne methane flux and characteristics of methane distribution in the marsh.

Analytical methods

Our analytical procedure is based on modification of the Swinnerton & Linenbom (1967) technique that incorporates continuous stripping (Atkinson, 1972). Either helium ionization or flame ionization gas chromatography is used for the analyses. Water samples are taken in 60-ml disposable plastic syringes, capped, stored in an ice chest and analyzed within 12 hours. For analysis, water is pumped by a peristaltic pump (Masterflex 7013) into a stripping chamber. Helium continuously flows up through the solution while the water is pumped in the top and out of the bottom. The flow rates are such that the methane is completely stripped from the solution before it leaves the stripping chamber. The helium+stripped gas flows through a drierite tube to remove H_2O then through a $\frac{1}{8}$ in×6 in (0·32×15·2 cm) activated charcoal trap immersed in a dry ice/acetone bath. The methane is adsorbed on the charcoal while other gases pass and leave the system. After the sample (20 ml typically) is stripped, the trap is isolated, placed in the gas chromatograph carrier gas stream with appropriate valving and heated. The methane peak is electronically integrated and is proportional to the methane present. Standardization is accomplished by injecting known methane–helium mixtures into the stripper and analyzing them as samples.

Sediment samples are taken by first digging a shallow trench through the root mass and then by taking a 4 in (10·2 cm) diameter core. Samples are taken from the trench wall and the extruded core with a 'microcorer' made of a 10-ml disposable plastic syringe with the Luer end cut off. The 10 ml 'core' is carefully injected into a 125-ml glass Erlynmeyer flask containing 75 ml of degassed distilled water. The flask is capped and stored in an ice chest with minimum agitation until analysis. For analysis the flask cap is carefully removed, a small stirring bar is placed in the flask and the cap pierced by a sparging tube with an exit tube in line with the trap previously mentioned; the flask replaced the stripping chamber. The sediment is stirred and sparged with helium for 30 min to remove all methane. The analysis is then identical to the water analysis.

The methane content of air is simply determined by injecting 500 µl into the gas chromatograph. Standard helium–methane mixtures are used for calibration.

Sediment samples for the methane flux measurements are taken with 12-cm diameter × 20-cm long fiberglass tubes. They are carefully capped with rubber corks and sealed with silicone grease. Two hyperdermic needles pierce the top cork to give access to the headspace above the sediment. They are kept sealed except during sampling when 500 µl of room air replaced the 500 µl sample removed. Some samples are maintained with helium in the headspace and during sampling helium replaces the removed sample.

pH, Eh, carbon content and water content are determined according to standard methods.

Results

Aqueous distributions

Our first attempts to determine methane flux were made in Romerly Marsh Creek (Figure 1) by differential advective measurements. Methane concentrations were determined every 15 min in the surface water at a fixed location in the mouth of the creek during the last of the

ebb and the beginning of the flood tide. The methane concentration increased steadily as the ebb brought water out from deeper in the marsh system (Figure 2). With the onset of the flood tide the concentration immediately began to decrease. Concentrations were always well above normal oceanic concentrations which average 0.01–0.05 µl $CH_4 l^{-1}$ (Swinnerton & Lamontage, 1974). The complexities of advective motion in the sound/tidal river system made this approach fruitless but the data yielded other useful insights that led to continued efforts to determine the methane flux.
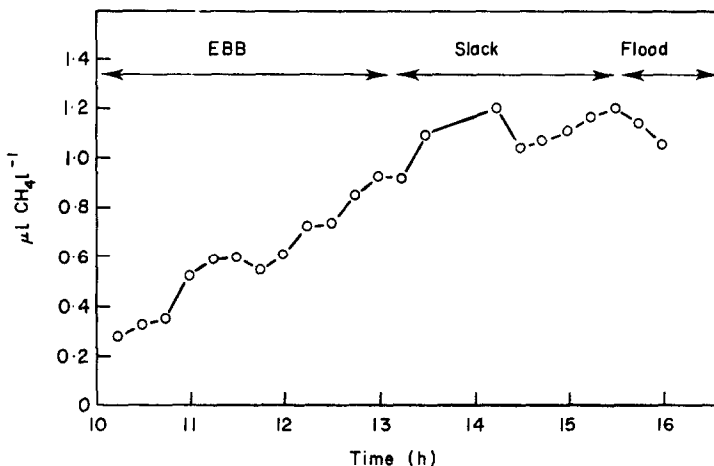
Figure 2. Methane in Romerly Marsh Creek during part of tidal cycle.

A second type of observation involved the measurement of methane concentrations in the waters of a small tidal creek (width = 2 m) in the center of Romerly Marsh. As the tide rises the adjacent marsh is flooded by water that has flowed up the creek, breeched the natural creek bank levee and moved across the high marsh. We sampled the creek water and the water in the adjacent marsh that was essentially the same creek water that had traversed 100–300 m of salt marsh surface. Figure 3 shows the results. The creek water contained about
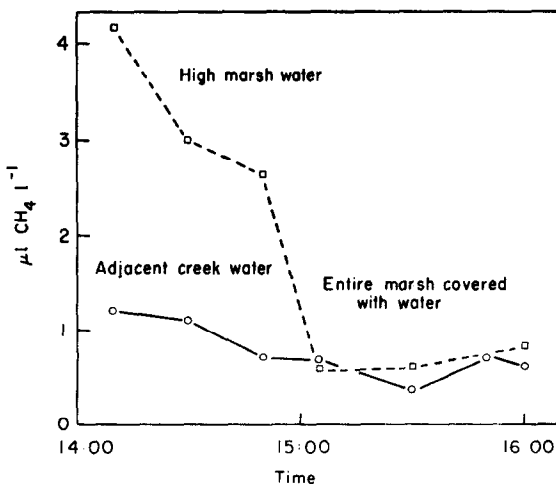
Figure 3. Methane in a small marsh creek and the adjacent marsh.

1·2 µl CH_4 l^{-1} while the marsh water was initially over 4 µl CH_4 l^{-1} and decreased rapidly as it was diluted with increasing amounts of creek water. As high slack approached, the water in the creek breeched the levee and then the creek and marsh water samples were identical. With time the methane concentration slowly increased.

The methane content of Romerly Marsh Creek waters were also determined throughout a year. Samples were taken at high and low slack water at the mouth, middle and upper sections of the Creek. The values for high and low slack at the mouth of Romerly Marsh Creek (Figure 4) showed the general decrease in concentrations through the winter and the consistent differences between high and low slack as expected. During the winter the differences reached a minimum.

Data from the lower Romerly Marsh Creek at low slack are plotted against water temperature (Figure 5) to show the general decrease in observed concentration with decreasing
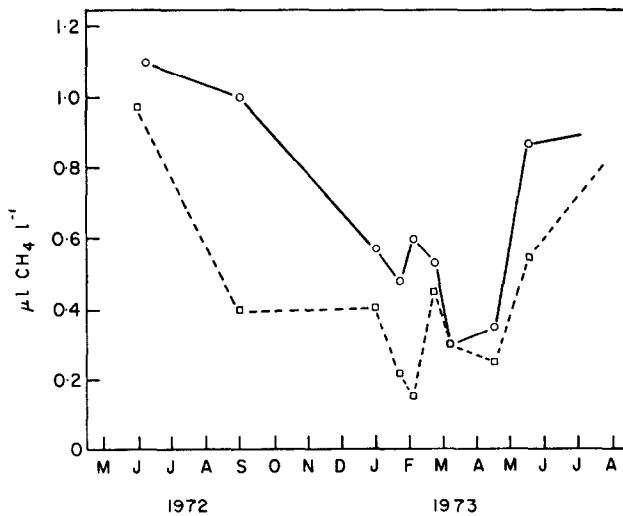

Figure 4. Methane in Romerly Marsh Creek at high and low water during 1972 and 1973. Dashed and solid lines are for low and high water samples, respectively.
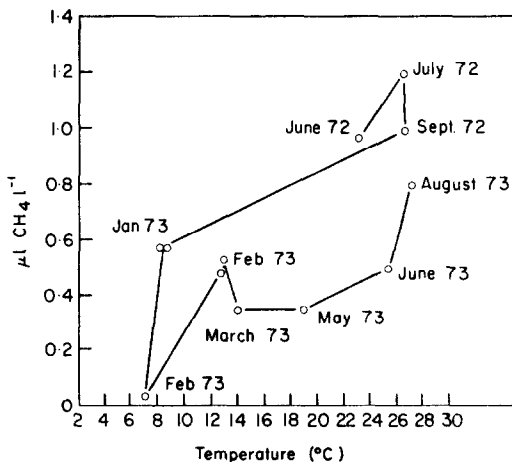

Figure 5. Methane in the lower part of Romerly Marsh Creek at low water *vs.* water temperature.

temperature. Methane tends to increase with increasing temperature. The line connects the points in chronological order demonstrating the annual change in methane production.

Sediment distribution

A different phase of our observational scheme was to determine the methane concentration gradients and related parameters in the sediments. All profiles are from the lower marsh since we found it difficult to properly sample high marsh cores due to the high density of root masses. An example of the data is shown in Figure 6. Figure 7 shows all the methane profiles together. It is noted that in all cores methane increased to 50–100 cm below the surface. Below this depth the methane content, in all but one core, decreased slightly. No dramatic subsurface methane maximum has ever been observed as might be expected from a shallow methane source.
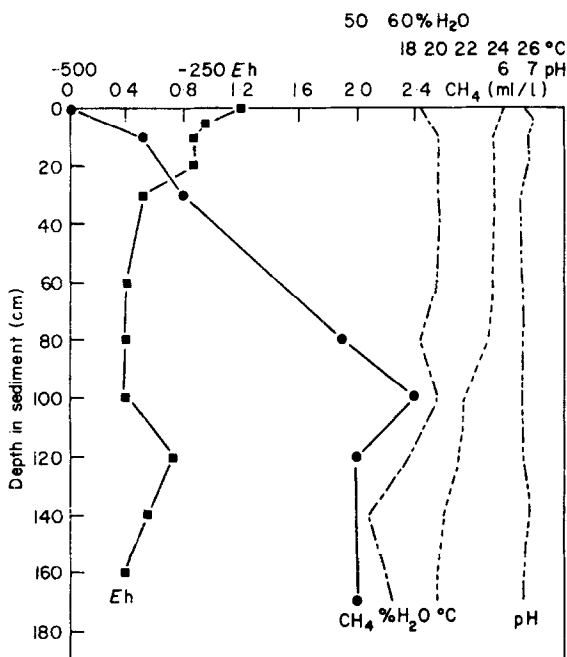

Figure 6. Typical methane, temperature, H_2O, Eh, pH in low marsh core.

Core flux measurements

The flux of methane out of core samples in the laboratory was determined to quantify the flux of methane from the sediment. Short cores (10 cm diameter × 40 cm deep) were taken in the high and low marsh locations and treated as previously described and capped with about 100 ml of headspace. The upper centimeter of sediment was removed ('scraped') from half the cores and a helium atmosphere was maintained in the headspace. The methane concentration was measured over a period of days and flux calculated. The data are presented in Table 1. The flux from the high marsh is nearly 40 times greater than that from the low marsh. In addition the scraping and helium treatment had a noticable effect on the low marsh samples and relatively little effect on samples from the high marsh.
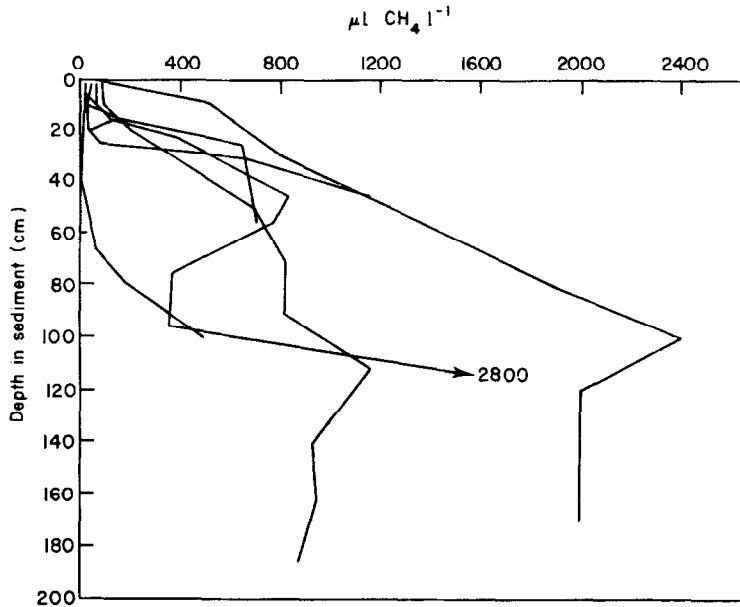
Figure 7. All methane profiles from cores in the low marsh.

TABLE 1. Methane flux values (ambient temperatures: 24 °C low marsh; 18 °C high marsh; laboratory temperature 25 °C)

Area	Core	Treatment	Observed flux ml CH_4 m^{-2} h^{-1}	g CH_4-C m^{-2} yr^{-1}	Comments
Low marsh	1	Normal	0	0	
Low marsh	2	Normal	0.4×10^{-4}	0·0002	
Low marsh	3	Normal	3.9×10^{-4}	0·0018	
Low marsh	4	Normal	11×10^{-4}	0·0052	
Low marsh	5	Scraped and He	54×10^{-4}	0·025	
Low marsh	6	Scraped and He	35×10^{-4}	0·016	crab and 3 holes
Low marsh	7	Scraped and He	16×10^{-4}	0·0075	
Low marsh	8	Scraped and He	26×10^{-4}	0·012	crab
High marsh	9	Normal	1800×10^{-4}	0·84	H_2S smell
High marsh	10	Normal	160×10^{-4}	0·075	
High marsh	11	Normal	890×10^{-4}	0·42	
High marsh	12	Normal	610×10^{-4}	0·29	H_2S smell
High marsh	13	Scraped and He	350×10^{-4}	0·16	
High marsh	14	Scraped and He	1300×10^{-4}	0·61	
High marsh	15	Scraped and He	1300×10^{-4}	0·61	
High marsh	16	Scraped and He	670×10^{-4}	0·31	

*a*Comments refer to the presence of crabs, crab-holes, H_2S.

Discussion

As the methane laden water is advected away from the sediment-water interface the methane content decreases because of degassing to the atmosphere, diffusion and possibly bacterial degradation. We had originally hoped that these observations would allow calculation of the methane flux from the salt marsh but the complexities of the salt marsh circulation patterns made this impossible; not to mention uncertainties in the rates of other processes listed above!

Measurements in the small tidal creek and adjacent marsh dramatically demonstrate the rapid rate that flood tide water absorbs methane from the marsh sediment surface. The same exchange rates could be assumed for other soluble compounds found in the sediment.

An estimation of methane transfer can be calculated by dividing the difference in methane concentration between the creek and adjacent marsh water by the time that the collected marsh water was in contact with the marsh sediment. The contact time is estimated from visual observation of the flow patterns to be from 0·25–0·75 h. A methane difference of about 3 μl CH_4 l^{-1} implies a rate of increase of 0·004–0·012 ml CH_4 l^{-1} h^{-1}. The marsh water depth was 10 – 40 cm as it flowed over the marsh surface implying an areal flux of 0·04–0·48 ml CH_4 m^{-2} h^{-1} (0·18–2·2 g CH_4-C m^{-2} year^{-1}). This will be compared to other flux measurements later in the discussion.

The seasonal change in the aqueous methane concentration (Figures 4–5) illustrates two phenomena. The overall concentration decreases about sixfold from summer to winter presumably because of the effect of decreased temperature on bacterial metabolism. Secondly, the difference between high and low slack values reach a minimum in the winter indicating that in the winter the methane production rates nearly equal the short-term diffusive loss to the atmosphere. It is noted that the concentrations are lower despite the greatly increased methane solubility resulting from the lower temperatures.

In low marsh sediment methane concentrations increase with depth at a rate not clearly dependent on Eh (Figures 6 and 7). If it is assumed that the gradient in the Eh curve reflects the activity of the sulfate reduction system then methane production reaches maximum rates at depths greater than the sulfate reduction.

The rates of methane production given in Table 1 imply a maximum seasonal methane flux of 0·089 ml CH_4 m^{-2} h^{-1} (0·42 g CH_4-C m^{-2} year^{-1}). The technique used to determine the flux could result in high observed rates. The process of taking the core could create channels along the side of the core that would increase degassing from the mud. However, if boundary channels were created the flux should increase quickly then decrease as steady state is approached. When the core is taken the headspace is exposed to air flow for 3–5 min during which the initial methane loss due to side channeling would occur. Since methane increased linearly over several days, it can be concluded that the system was in steady state and the initial degassing had already occurred. Thus there is no methodological reason to suspect these values. We must conclude that methane flux is much less than other metabolic processes in the high marsh and less so in the low marsh. These rates are further substantiated by the flux calculation based on the creek and marsh water observations.

The relatively higher measured flux in the high marsh supports the conclusions of Christian *et al.* (1975) who found much higher microbial activity in the high than in the low marsh sediment.

It is possible by indirect techniques to place a limit on the flux of methane from the sediment. Although it is difficult to calculate the exchange of methane from the sediment to the air or water the calculation for water/air transfer is relatively simple. When the increased ambient concentrations are known and the areal distribution assumed, air/sea gas flux is defined by the equation

$$F = \frac{\varDelta s}{d} (p - p_0)$$

where $\varDelta$ = gaseous diffusivity which is about $2 \cdot 0 \times 10^5$ cm^2 s^{-1},

         s = Bunsen solubility coefficient (1 gas l^{-1} atm^{-1}),

$p-p_0$ = partial pressure of a gas in the air minus the partial pressure of that same gas in the water (atm),

d = laminar layer thickness (cm).

d is determined empirically and Δ/d, the transport coefficient is typically 0.0005 cm s^{-1} (Atkinson, 1974; Liss, 1973). The concentration in the water typically ranges up to 1 μl CH$_4$ l^{-1} and since the Bunsen solubility coefficient is about 40 ml CH$_4$ l^{-1} atm^{-1} (Atkinson & Richards, 1967), the partial pressure p_0 is 0.000025 atm. The ambient partial pressure is about 1×10^{-6} atm in air (Hitchcock & Wechsler, 1972), thus $p-p_0 = 24 \times 10^{-6}$ atm. Using these values the flux is a maximum of 0.17 ml CH$_4$ m^{-2} h^{-1} (0.81 g CH$_4$-C m^{-2} year^{-1}). The uncertainties in this calculation lie in the value used for Δ/d and the $p-p_0$ value. Because of the uncertainties the calculated value cannot be assumed to be very accurate. However, the value is of the same order of magnitude as other flux estimates.

TABLE 2. Estimates of methane flux by various techniques

Technique	Methane flux	
	ml CH$_4$ m^{-2} hr^{-1}	g CH$_4$-C m^{-2} year^{-1}
Headspace in core		
Low march	0.0021	0.0099
High marsh	0.0890	0.42
Creek/marsh water		
High marsh	0.04–0.48	0.18–2.2
Gas exchange	0.17	0.81

The various estimates of methane flux are given in Table 2. The flux from the high marsh is much higher than that from the low marsh which agrees with Whelan (1974). This also agrees with the CO$_2$ observations of one of us (Hall, unpublished data). He found CO$_2$ flux to be 440 and 110 g CO$_2$-C m^{-2} year^{-1}, in the high and low marsh, respectively. These CO$_2$ values are more than 100 times the average measured methane flux value.

We conclude that the average methane flux from the salt marsh is about 1 g CH$_4$-C m^{-2} year^{-1} with a great amount of variability. This is compared to other calculated flux in Table 3. To our knowledge these are the only reasonably direct measurements of methane flux. Most other estimates of methane flux are based on Koyama's data (cf. Ehhalt, 1973). The world methane flux from salt marshes based on our data is 3.8×10^{11} g CH$_4$-C year^{-1} using estiamtes of world salt marshes (3.8×10^{11} m^2) by Woodwell *et al.* (1973), which are rough estimates. This value is one hundred times smaller than other sources of methane (Ehhalt, 1973) on the earth's surface. For example the release of natural gas from wells is estimated to be 5.2×10^{14} g year^{-1} (Ehhalt, 1973).

TABLE 3. Comparison of methane flux estimates

Source	Value g CH$_4$-C m^{-2} yr^{-1}	Reference
Spartina salt marsh	1	This study
Shallow freshwater lakes	5	Hutchinson (1954)
Rice paddies	25	Koyama (1963)
Maryland marshes	105	Conger (1943)

Acknowledgements

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