The Effects of Ammonium and Sulfate Additions on Methane Fluxes in Two Tidal Freshwater Wetlands of the Hudson River Estuary

by

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ABSTRACT

This study examined factors that control methane (CH_4) fluxes in two freshwater estuarine wetlands of the Hudson River (Tivoli North and South Bays). The importance of anaerobic CH_4 production and both anaerobic and aerobic CH_4 oxidation were examined in the sediments of the wetlands. The depth distribution, comparisons between the two wetlands, and the effects of ammonium (NH_4^+) and sulfate (SO_4^{2-}) additions on these processes were examined. The sediments from both wetlands were net methane producers. Production and consumption in the Tivoli South Bay was greater than in the Tivoli North Bay. Aerobic oxidation was not important in the sediments, but both wetlands exhibited anaerobic CH_4 oxidation. Anaerobic CH_4 oxidation decreased with depth, whereas CH_4 production did not vary with depth. Additions of 3 mM NH_4^+ and 5 mM SO_4^{2-} decreased both CH_4 production and consumption in both bays.

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INTRODUCTION

The concentrations of atmospheric methane (CH_4) have been increasing at about 1.1% y^{-1} over the past decade (Blake and Rowland 1988) and have shown a steady increase over the past 200 years (Rasmussen and Khalil 1984). The increase in atmospheric CH_4 concentrations could be due to either increases in the sources or decreases in the sinks of this gas. Along with rice paddies and the anoxic rumen of cattle, wetlands have been identified as one of the largest biogenic sources of atmospheric methane (Cicerone and Oremland 1988). Because CH_4 is a greenhouse gas, factors affecting CH_4 emissions in freshwater wetlands could affect global climate change.

The biogenic source of CH_4 is anaerobic bacteria, and wetland sediments are predominantly anaerobic. Because O_2 cannot diffuse quickly through waterlogged soils, only the first few millimeters of sediment are oxygenated. Aerobes in the surface sediment rapidly utilize any available O_2. Therefore, at the water-sediment interface there exists a thin layer of aerobic sediment and below that depth the sediment is anaerobic (Day et al. 1989; Rudd and Taylor 1980).

In anaerobic sediments, microorganisms decompose organic matter by using electron acceptors other than O_2, such as SO_4^{2-}, NO_3^-, Fe^{3+} and CO_2. These electron acceptors are utilized according to the amount of energy they can provide for the organism. Oxygen is the most energy yielding electron acceptor and CO_2 is the least. The electron acceptors are utilized in the order they appear in Figure 1.

HIGH ENERGY YIELD

AEROBIC PROCESSES $O_2 + CH_4 \text{ --> } CO_2 + H_2O$
DENITRIFICATION $NO_3^- + CH_2O + H^+ \text{ --> } N_2 + CO_2 + H_2O$
SULFATE REDUCTION $SO_4^{2-} + CH_2O + H^+ \text{ --> } HS^- + CO_2 + H_2O$
METHANOGENESIS $(CH_2O \text{ or } CO_2) + H_2 \text{ --> } CH_4 + CO_2$

LOW ENERGY YIELD

Figure 1. Several microbial processes found in wetland sediments. The processes occur according to the energy yielding potential of the electron acceptors.

Methanogenesis utilizes the least energy yielding electron acceptor and is the terminal step in the microbial food chain (Rudd and Talyor 1980). Because methanogenesis can occur after other microorganisms have depleted the electron acceptors on which they live, it is critical in continuing the carbon cycle of freshwater wetland ecosystems. Methanogenesis thus plays a key role in the biodegradation of organic matter and the release of nutrients for plant uptake (Iizumi et al. 1982; Kenworthy et al. 1982) in anaerobic sediments.

The net methane flux from a system is the combination of several complex processes. Methane is produced by methanogens in the anaerobic portion of the sediment, but it is also reoxidized, both anaerobically and aerobically. While little is known about anaerobic CH_4 oxidation, it has been observed to occur concomitantly with sulfate reduction (Reeburgh and Heggie 1977). Aerobic CH_4 oxidation occurs in the thin oxidized layer of the sediment at the water-sediment interface. Therefore, the net CH_4 flux from anaerobic sediment is the net sum of these three processes. Changes in any one of these processes could affect the net CH_4 flux from sediment.

The net CH_4 flux from a wetland is also controlled indirectly by interactions between different microbial populations. Because methanogens utilize the least energy yielding electron acceptors, they are easily outcompeted by any other organism that utilizes a more efficient electron acceptor, especially sulfate reducers which can utilize the same energy substrates as methanogens (Winfrey and Zeikus 1977).

Although most freshwater wetlands do not have high concentrations of

SO_4^{2-} and do not exhibit anaerobic CH_4 consumption (Reeburgh and Heggie 1977), Gould (1991) inferred the processes of methanogenesis, sulfate reduction and denitrification from porewater modelling in Tivoli South Bay. Therefore, it is possible that anaerobic CH_4 oxidation can occur in Tivoli South Bay. Because methanogens are highly susceptible to outcompetition by sulfate reducers, changes in SO_4^{2-} concentrations, which can be induced by land modifications and acid rain deposition, could alter C-cycling and nutrient availability to plants in the Tivoli Bays and other Hudson River wetlands.

Recently, several studies have shown links between soil nitrogen (N) availability and CH_4 oxidation in various ecosystems, including wetland sediments and rice paddies (Lindau et al. 1991, King 1990, Nesbit and Breitenbeck 1992). Lindau et al. (1991) found that CH_4 production from rice paddies enriched with N-fertilizers was higher than unfertilized paddies. King (1990) found decreased CH_4 oxidation rates with additions of NH_4^+ to wetland sediments. Ammonium (NH_4^+) is a known competitive inhibitor of methanotrophs in lab studies (Whittenbury et al. 1970; Bedard and Knowles 1989). Because CH_4 fluxes are a combination of CH_4 consumption and production, nitrogen additions to wetlands, which result from sewage inputs and atmospheric deposition, could increase the flux of CH_4 to the atmosphere by reducing the capacity of methanotrophs to oxidize methane.

In this study, I examined the importance of anaerobic CH_4 production and both anaerobic and aerobic CH_4 oxidation in Tivoli Bay sediments. The depth distribution of these processes and comparisons between the two bays were also

made. I also examined the effects of NH_4^+ and SO_4^{2-} additions on these processes. Three hypotheses were developed:

1) Aerobic CH_4 oxidizers should be active in the surface layers of the sediment, CH_4 production should increase, and anaerobic CH_4 consumption (if present) should decrease with depth due to the depletion of other electron acceptors, especially SO_4^{2-},

2) NH_4^+ additions will increase CH_4 emissions due to the inhibition of CH_4 oxidation in the aerobic portion of the sediment, and

3) SO_4^{2-} additions will decrease CH_4 production due to either inhibition of CH_4 production or stimulation of anaerobic CH_4 consumption.

METHODS

Study Sites

The study sites for this project were the Tivoli Bays component of the Hudson River National Estuarine Research Reserve located on the east bank of the Hudson River just north of Kingston, NY (Figure 2). The two bays differ in several respects. Tivoli South Bay (TSB) is almost completely subtidal and is dominated by Trapa natans, whereas, Tivoli North Bay (TNB) is intertidal and dominated by such plants as Typha angustifolia, Lythrum salicaria, Phragmites australis and Nuphar advena.

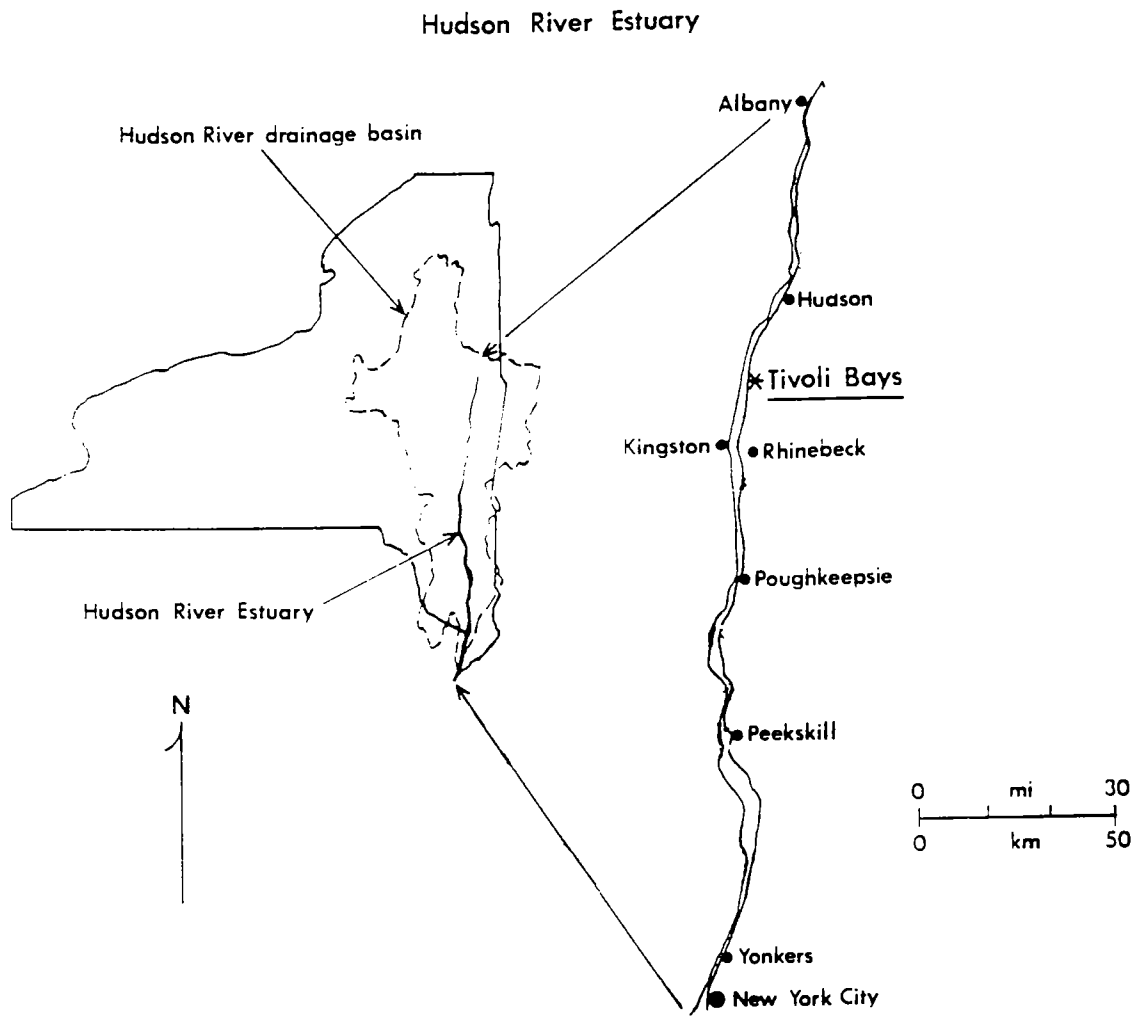

Figure 2. Location of the Tivoli Bays.

Experimental

Intact core samples were collected on July 7, 1993, July 21, 1993, and August 3, 1993. All samples came from a site in the middle of TSB or in a Nuphar advena-dominated site in TNB. All samples were collected with 30 cm long, 7.6 cm outer diameter polyvinyl chloride pipes bevelled at the bottom. Cores were collected either by a coring device, or by hand, when feasible. The cores where stoppered at the bottom with butyl rubber stoppers and a 3-10 mm layer of water was left on the surface. The tops were covered with parafilm to prevent spillage during transport. All cores were returned to an IES laboratory and analyzed within 24 h.

On the first sample date, July 7, 1993, one core from TSB was removed and then analyzed the next day. After the water was siphoned off, the core was sectioned under a nitrogen atmosphere in a Labconco glove box. The top 0-2 mm was gently scraped from the top of the core with a spatula (King 1990). The sediment was then extruded from the pipe and sectioned into depth ranges of 2-20 mm, 20-50 mm, and 90-100 mm. The various depth ranges were placed into aluminum dishes and were homogenized by stirring. Two 5 g samples of sediment from each depth range were placed into 100 mL serum bottles (total headspace of 125 mL). Another 5 g sample of each depth range was placed into a 125 mL Erlenmeyer flask (total headspace of 150 mL). One series of serum bottles (one bottle per each depth range) was removed from the glovebox and re-exposed to air. The rest of the serum bottles and Erlenmeyer flasks remained in the glove

box. Five mL of either deionized and deoxygenated water or deionized and oxygenated water were added to the 5 g of sediment in the incubation vessels (anaerobic vessels inside the glove box and aerobic vessel outside) to create anaerobic and aerobic slurries, respectively. The electrode potential (Eh) of each incubation was taken with a $Pt/AgCl_2$ combination electrode standardized with a 3mM $K_4Fe(CN)_6 \cdot 3H_2O/K_3Fe(CN)_6$ couple (Nordstrom 1977). The serum bottles were sealed with aluminum-crimped butyl rubber stoppers and the flasks were fitted with rubber stoppers. The anaerobic incubations were then evacuated for three minutes and refilled with N_2 to clear the headspace of CH_4, (CH_4 concentrations were as high as 30 ppm in the glove box) and to ensure anaerobic conditions (Yavitt and Lang 1990). The aerobic incubations were exposed to air, effectively clearing the headspace. The serum bottles and flasks were overpressurized with 20 mL of either air or N_2 for the aerobic and anaerobic incubations, respectively. The serum bottles and flasks were incubated at room temperature while shaking at 125 rpm. Five mL of headspace were removed with an airtight syringe from the bottles and flasks at 0, 1, 2.5, 4 and 24 hours. The samples were injected into a 2 mL sample loop for analysis by gas chromatography with a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector. A porapak Q column (6 ft long by 1/4 in wide) was used with helium carrier at a pressure of 2 kg cm^{-2}. Oven and injection port temperatures were 60°C and 110°C, respectively.

Soil moisture was determined by drying at 105°C for 24 h. All rates and concentrations are expressed on a soil dry weight basis (DW).

In the second experiment, three cores from TSB and three cores from TNB were taken on July 19, 1993. Because in the first experiment, Erlenmeyer flasks fitted with rubber stoppers behaved identically to serum bottles sealed with black butyl stoppers, Erlenmeyer flasks were used in the rest of the experiments.

The cores were sectioned as described above. The 0-2 mm depth was treated aerobically, and depth ranges of 2-20, 20-50, 90-100, and 190-200 mm (when available) were prepared and incubated anaerobically as described above. A 10 mL sample of flask headspace was taken at 0, 0.33, 0.67, 1.5, 4 and 8 hours. Air or N_2 (10 mL) was added after each sampling to maintain near atmospheric pressure in the flasks. The samples were placed into evacuated glass vials and analyzed by gas chromatography as described above.

The remaining sediment was placed into Whirlpak^{TM} sample bags and frozen until it could be analyzed for SO_4^{2-}, NH_4^+ and NO_3^- the next day. The Whirlpaks were returned to the glove box and two 5 g samples from each depth range (except the 0-2 mm range which only had enough sediment for 1 replicate) were placed into 125 mL Erlenmeyer flasks and extracted with 20 mL of 2N KCl. The extracts were analyzed for NH_4^+ and NO_3^- colorimetrically using an Alpkem Flow Solution Analyzer model # 35-90. Concentrations of NH_4^+ were quantified using the nitroprusside/phenolate method and NO_3^- was analyzed by cadmium reduction. The remaining sediment was placed in 50 mL plastic centrifuge tubes while in the glove box. The tubes were removed from the glove box and centrifuged at 1000 rpm for 10 min to separate the porewater. The tubes were returned to the glove box and the porewater was pored off and acidified with

1.2 N HCl. The porewater was analyzed for SO_4^{2-} using a Dionex Ion Chromatograph.

In the third experiment, two cores from TSB and two cores from TNB were taken on August 3, 1993. One core from TSB and one core from TNB were analyzed the following day and the second cores from TSB and TNB were analyzed two days after collection. The cores were sectioned anaerobically as described above into depth ranges of 0-20, 20-50, 90-100, and 170-190 mm. No aerobic incubations (0-2 mm depth range) were prepared.

For each depth range, six 5 g samples were placed in flasks. Two flasks received 5 mL of a 6mM NH_4Cl solution prepared in deoxygenated water, two flasks received 5 mL of a 10mM K_2SO_4 prepared in deoxygenated water, and the last two flasks received 5 mL of deoxygenated water.

The remaining sediment was placed directly into 50 mL centrifuge tubes with screw-on caps and was refrigerated under N_2 until they could be analyzed (within three days). The centrifuge tubes were then placed back into the glove box and samples were prepared and analyzed for SO_4^{2}, NH_4^{+} and NO_3^{-} as described above.

Rates of CH_4 production and consumption were determined by regressing the mass of CH_4 in the syringe against time from the production phase and the consumption phase of each profile. Production rates were often determined from only two points. If more points were available, linear regression was performed. Consumption rates were determined by fitting either linear or nonlinear regressions to the consumption phase (some of the consumption phases were

linear with time, others showed first order exponential decay). The consumption phases were fitted with both linear and nonlinear regressions and the regression that produced the best fit (the highest r^2) was chosen. Linear and nonlinear coefficients gave comparable results. For example, a linear regression with r^2 = 0.87 and a nonlinear regression with r^2 = 0.87 yielded rate coefficients of -0.0178 and -0.0125 respectively. Mixed rate coefficients have been used by others (Taylor and Parkinson 1988)

RESULTS

Methane Profiles

All profiles of the mass of CH_4 versus time for all experiments in the depth range of 0-10 cm showed a production phase and a consumption phase (Figure 3). In all profiles, the first one to three hours was dominated by CH_4 production. After this time, CH_4 consumption dominated. The consumption phase decreased with sediment depth and in the deepest sediments (19-20), this phase often disappeared completely.

Aerobic Consumption

In the first experiment all depth ranges were incubated both aerobically or anaerobically. Both the consumption phase and the production phase were less in the aerobic incubations than the anaerobic incubations (Figure 4). Oxygenated water did not stimulate CH_4 consumption, but in fact, reduced the overall CH_4 flux. The failure of these incubations to respond to higher O_2 concentrations

implies that the methanotrophic populations were too small to significantly contribute to the overall flux. As expected, increased O_2 availability adversely affected the methanogen population. Because aerobic CH_4 consumption was unmeasurable, the results presented here are from the anaerobic incubations only.

Methane Fluxes Over Depth

Both TSB and TNB sediments showed net CH_4 production; CH_4 production was greater than consumption for all depths (Figures 5 and 6). Although small, sediments from both bays showed anaerobic CH_4 consumption. Methane consumption decreased significantly with depth in both TNB (one way ANOVA, $p = 0.0003$) and TSB ($p = 0.0006$) while CH_4 production showed no significant trend with depth in either TNB or TSB in these experiments (Figures 5 and 6). Both CH_4 production ($p = 0.0091$) and consumption ($p = 0.0001$) were greater in TSB than in TNB (Figures 7 and 8). Data in Figures 5-8 are from the third experiment. Data for both CH_4 consumption and production showed the same trends in the second experiment, but the rates of consumption and production were lower in the second experiment than in the third experiment.

Methane Fluxes and Nitrogen and Sulfur Availability

The mean values of NH_4^+ (ng/g soil DW) and NO_3^- (ng/g soil DW) for three replicate samples from both TSB and TNB showed no variation with depth, although in individual cores, NH_4^+ generally increased while NO_3^- generally decreased with depth. Mean values for NH_4^+ ranged from 30.9 ng/g DW to 36.1

ng/g DW in TSB and 4.38 ng/g DW to 0 in TNB. Mean values for NO_3^- ranged from 1.2 ng/g DW to 0.62 ng/g DW in TSB and 0.88 ng/g DW to 2.26 ng/g DW in TNB. Sulfate concentrations were not determined due to oxidation of HS^- by accidental exposure to air.

If one TSB core with aberrantly high concentrations of NH_4^+ is not considered, methane production was positively correlated ($r^2 = 0.67$) with NH_4^+ concentrations (Figure 9). Methane consumption was not correlated to NH_4^+ concentrations. Neither CH_4 production or consumption correlated with NO_3^- availability.

The Effects of Nitrogen and Sulfur Additions

As shown in Figures 10-13, both SO_4^{2-} and NH_4^+ additions reduced both CH_4 production and consumption rates in TSB and TNB. Both SO_4^{2-} and NH_4^+ additions were significantly different from the controls in TNB (3 way ANOVA comparing all depths, location and treatments with a Fisher's protected least significant difference multiple comparisions test to compare controls, NH_4^+ and SO_4^{2-} additions, $p = 0.007$) and TBS ($p = 0.0158$). Neither CH_4 consumption nor production rates correlated with SO_4^{2-}, NH_4^+ or NO_3^- in this experiment.

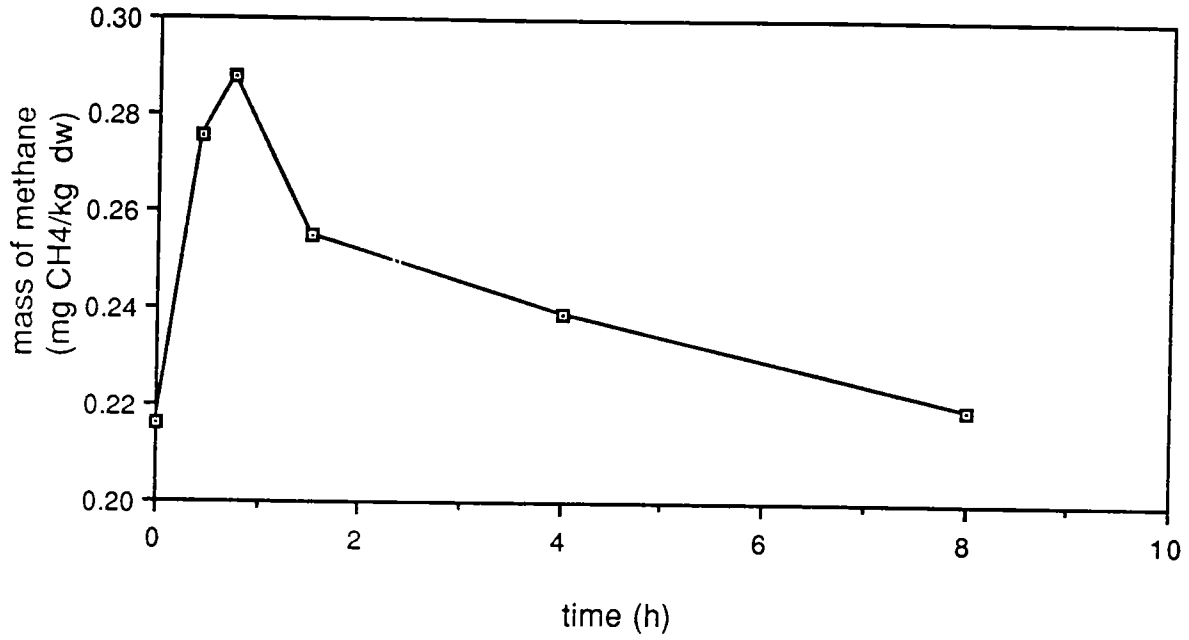

Figure 3: A typical methane profile showing the production and consumption phase.

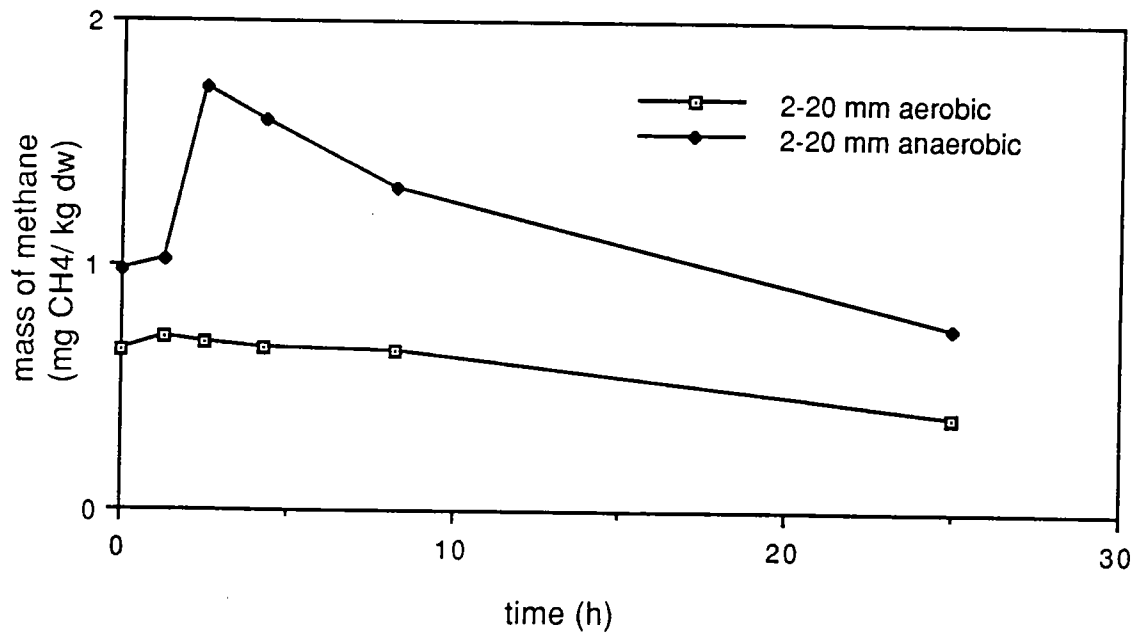

Figure 4: Methane profiles of an aerobic and anaerobic incubation of the 2-20 mm depth range.

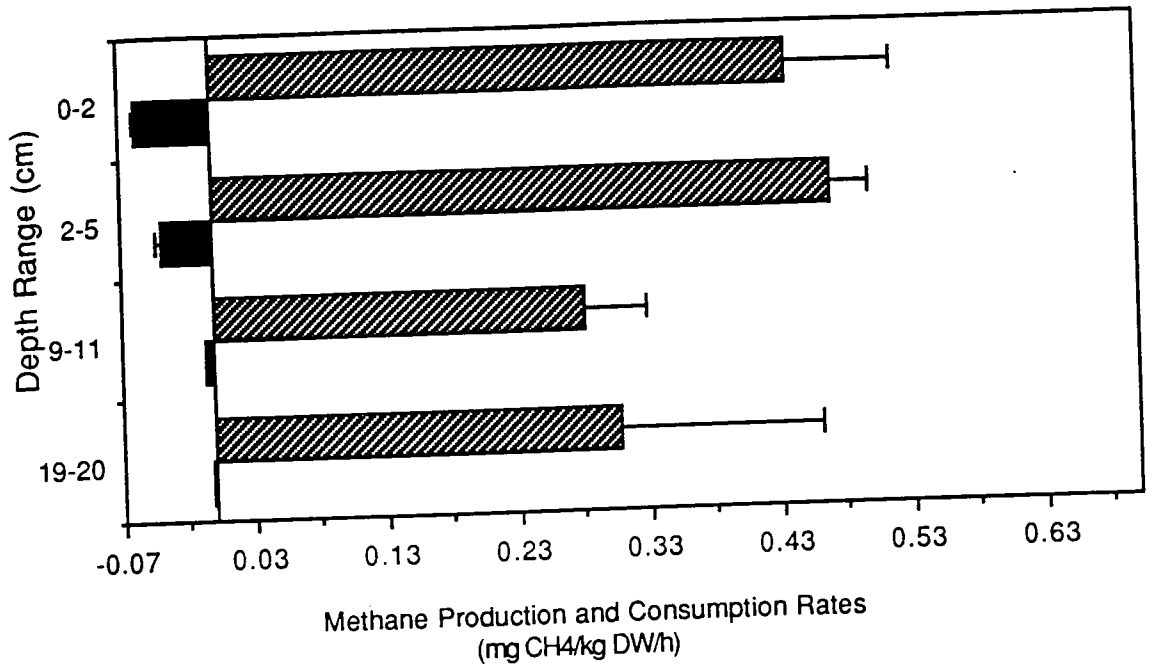

Figure 5: Methane consumption and production rates in several depth ranges of sediment from Tivoli South Bay. All rates are the means of duplicates.

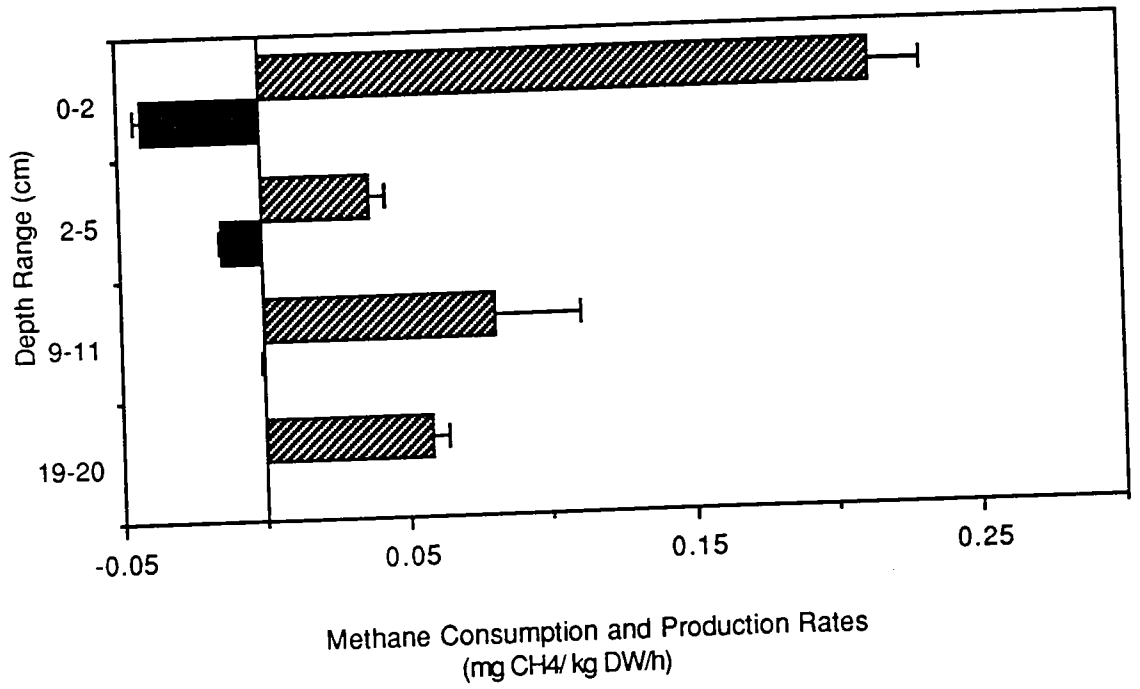

Figure 6: Methane production and consumption rates in several depth ranges of sediment from Tivoli North Bay. All rates are the means of duplicates.

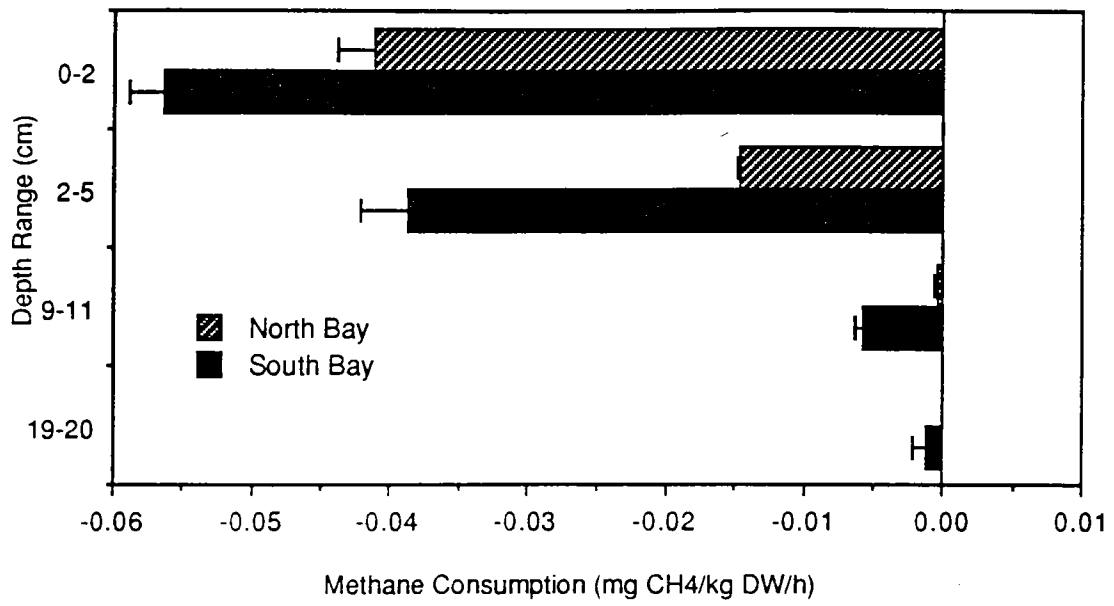

Figure 7: Methane consumption over depth ranges in both Tivoli North and South Bay.

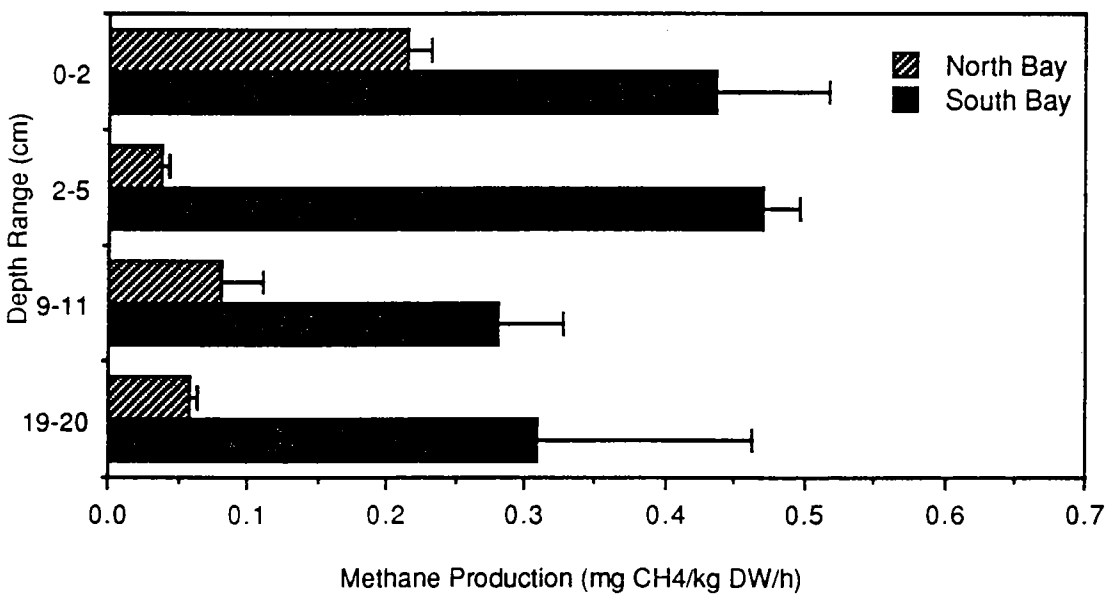

Figure 8: Methane Production over depth ranges in both Tivoli North and South Bays.

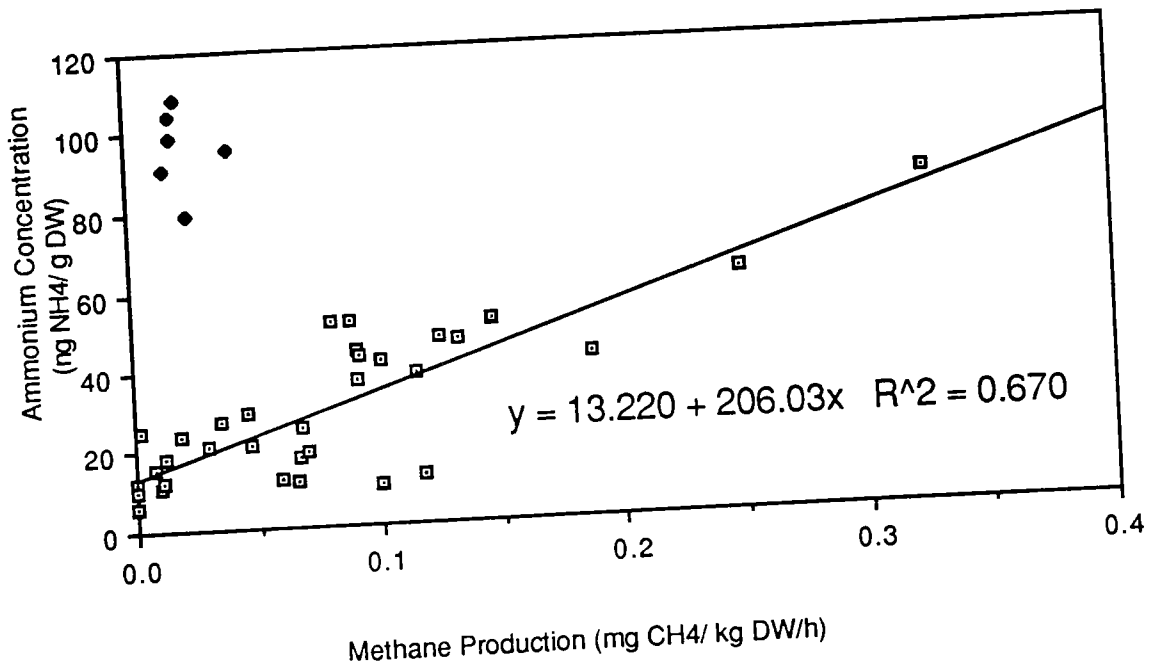

Figure 9: Methane production rates vs. ammonium concentration. Production rates from all depth ranges from both TNB and TSB are included. The (♦) symbols are not included in the regression analysis. These points are from one TSB core.

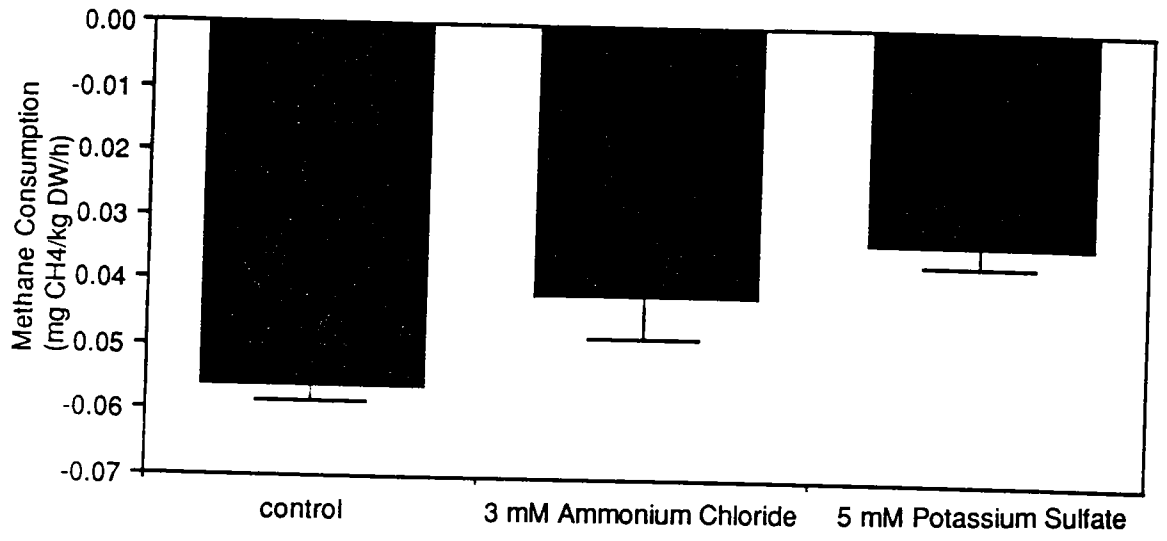

Figure 10: Methane consumption rates vs. ammonium and sulfate additions in the 0-2 cm depth range of sediment from Tivoli South Bay. All rates are the means of duplicates.

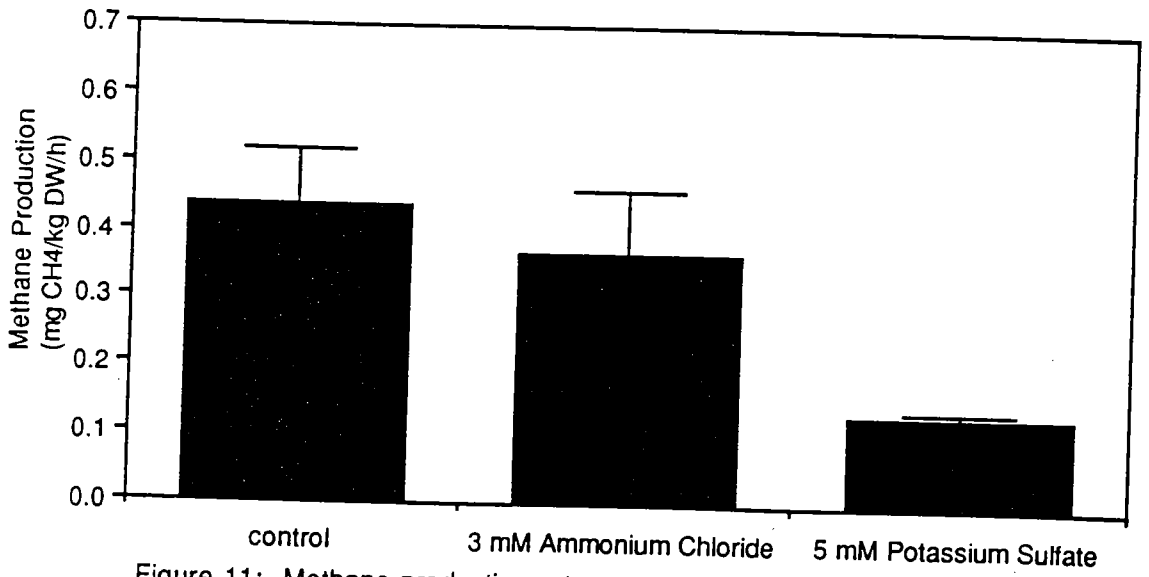

Figure 11: Methane production rates vs. ammonium and sulfate additions in the 0-2 cm depth range of sediment from Tivoli South Bay. All rates are the means of duplicates.

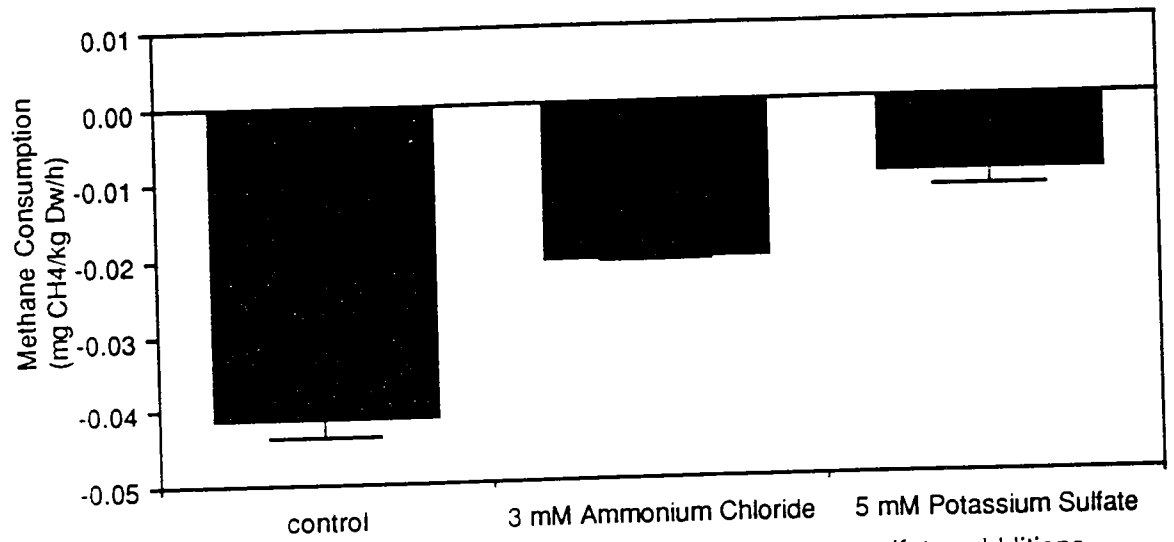

Figure 12: Methane consumption rates vs. ammonium or sulfate addditions in the 0-2 cm depth range of sediment from Tivoli North Bay. All rates are the means of duplicate.

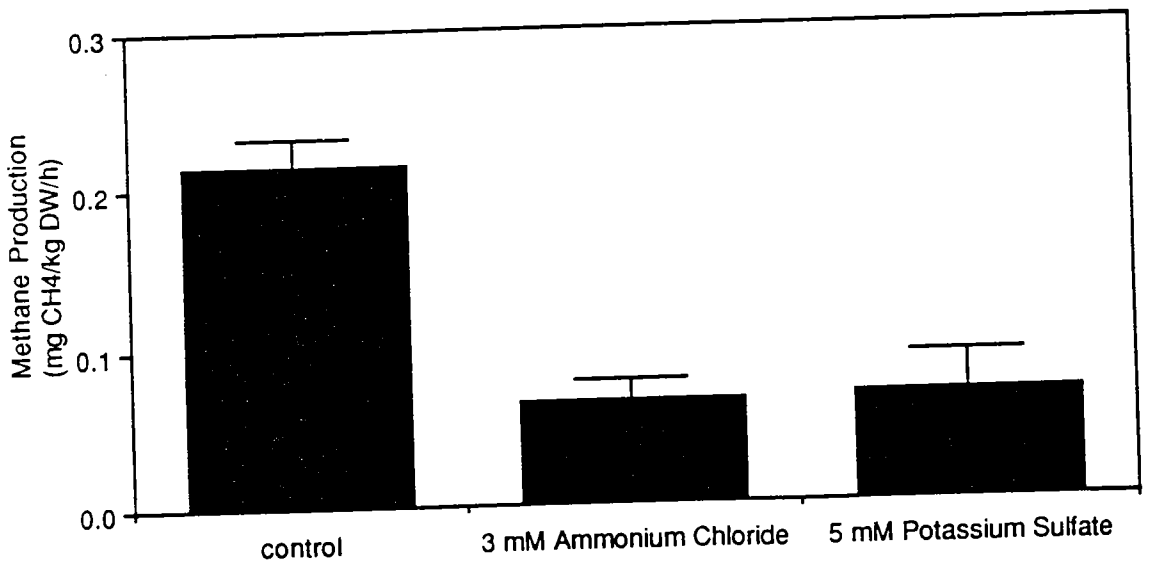

Figure 13: Methane production rates vs. ammonium or sulfate additions in the 0-2 cm depth range of sediment from Tivoli North Bay. All rates are the means of duplicates.

DISCUSSION

Methane Profiles

Because I was not able to obtain killed controls, degassing of CH_4 dissolved in the incubation flasks cannot be ruled out as an explanation for the initial increase in CH_4 in the headspace of the flasks. Degassing was unlikely, however, considering the rigorous treatment the flasks received. The sediment was broken up and slurried, the headspace was evacuated, and the incubations were performed on a shaker table at 125 rpm. This should make any degassing effects extremely rapid and would not account for the increase in CH_4 in the headspace over time. Furthermore, degassing would have been the same for both aerobic and anaerobic treatments of the sediment. However, the aerobic treatments showed lower CH_4 production, suggesting that the production phase was biogenic.

Aerobic Oxidation

One of the objectives of this project was to examine the effects of NH_4^+ additions on aerobic CH_4 consumption. However, aerobic consumption was never isolated. Aerobic consumption may have been undetectable for several reasons. First, possibly due to the methods employed, the aerobic CH_4 oxidizing sediment was never isolated. Because the process of extruding cores from the bays disturbed the surface of the core and possibly mixed the surface layer with deeper sediment, these incubations may have had sufficient methanogen populations from the deeper (i.e., greater than 2 mm) sediment to override any consumption by the

methanotrophic population.

Another possibility for the absence of observed aerobic CH_4 consumption is the lack of a discrete layer of methanotrophic activity. De Angelis and Scranton (in press) found CH_4 oxidation occurred in the water column of the Hudson River. If methanotrophs live not only in the surface sediment, but in the water column directly above the sediment, there may not be a discrete region of methanotrophic activity exclusive to the sediment surface. This may be true especially if the upper sediments are mixed with the water column by bioturbation.

Anaerobic Oxidation

All incubations exhibited net CH_4 production, as is expected from anaerobic sediments. Unexpectedly, anaerobic CH_4 consumption was also observed in sediment to depths of 10 cm. In freshwater wetlands, SO_4^{2-} concentrations are usually too low to sustain appreciable anaerobic CH_4 oxidation (Rudd and Taylor 1980). Usually, aerobic CH_4 oxidation predominates in freshwater wetlands and anaerobic CH_4 oxidation predominates in marine ecosystems (Reeburgh and Heggie 1977). However, Gould (1991) inferred sulfate reduction and net CH_4 production in TSB from porewater modeling studies; therefore, anaerobic CH_4 oxidation linked to sulfate reduction may be possible. The results reported here are consistent with Gould's findings; net CH_4 production is far greater than anaerobic CH_4 consumption.

Because CH_4 fluxes are a combination of CH_4 production and CH_4

consumption, anaerobic CH_4 oxidation was not evident until after 1 to 3 hours of incubation. Anaerobic CH_4 consumption only became evident when some critical change, which altered the balance between net production and consumption, occurred in the incubation vessels. These changes could include the buildup of toxic end products, depletion of substrates or a rise in reduction potential. In the 17-19 cm depth range, either CH_4 production was so great that anaerobic consumption remained obscured, or there was no significant anaerobic consumer population. Unfortunately, the extent to which anaerobic CH_4 occurs in situ cannot be determined from these experiments. These experiments only suggest the existence of anaerobic CH_4 consumption.

Because anaerobic CH_4 consumption was present in both TNB and TSB, one must consider factors that may influence the rates of anaerobic CH_4 oxidation when considering overall C budgets or C-cycling in these ecosystems. For example, SO_4^{2-} additions from sources such as acid rain or sewage inputs could dramatically affect the extent of anaerobic CH_4 oxidation.

Methane Production and Consumption with Depth

Methane production did not vary significantly with depth. Previous research has shown that CH_4 production rates vary with depth in a number of ways. Yavitt and Lang (1990) found CH_4 production rates increased with depth, where as, Williams and Crawford (1984) found CH_4 production rates to decrease with depth. Thebrath et al. (1993) found CH_4 production was concentrated at a subsurface maximum. Therefore, lack of correlation between CH_4 consumption

rates and depth is not unprecedented.

As expected, anaerobic CH_4 consumption rates decreased with depth. If anaerobic consumption is related to SO_4^{2-} reduction, then as the SO_4^{2-} concentrations decreased with depth, so should the anaerobic consumer populations.

Methane Consumption and Production in TSB vs.TNB

Methane production and consumption rates were higher in TSB than TNB. This result is consistent with Findlay et al. (1990), who found higher rates of organic matter decomposition in TSB than TNB. If there is more substrate available for methanogenesis and CH_4 consumption in TSB than TNB, then methanogenesis and methane consumption should be greater in TSB.

Furthermore, CH_4 production rates were positively correlated to NH_4^+ availability. TSB also had higher NH_4^+ concentrations than TNB. Pastor et al. (1984) found that NH_4^+ availability was an index of substrate quality. If TSB had not only more, but higher quality substrates for microbial consumption, then CH_4 production should be higher in TSB than TNB.

The Effects of NH_4^+ and SO_4^{2-} on CH_4 Production and Consumption

Sulfate and NH_4^+ additions decreased both CH_4 consumption and production rates. One would expect SO_4^{2-} additions to decrease CH_4 consumption rates, since sulfate reducers outcompete methanogens for energy substrates and SO_4^{2-} additions stimulate sulfate reducing populations (Winfrey

and Zeikus 1977). However, it is unknown why NH_4^+ would decrease either CH_4 production or anaerobic consumption. Furthermore, one would expect SO_4^{2-} additions to stimulate anaerobic CH_4 consumption. The opposite result was obtained; SO_4^{2-} additions decreased anaerobic consumption.

Nesbit and Breitenbeck (1992) and Adamsen and King (1993) have suggested that methanogen populations may be particularly sensitive to changes in osmotic potential. If this is true, 6 mM NH_4^+ and 10 mM SO_4^{2-} additions would greatly alter osmotic potentials. Changes in osmotic potential could at least partially explain the observed decrease in CH_4 production and oxidation rates.

CONCLUSIONS

This research has two implications for management practices. If SO_4^{2-} and NH_4^+ additions reduce both CH_4 consumption and production in the bays, SO_4^{2-} and NH_4^+ enrichment from sewage inputs or acid deposition could reduce the overall carbon cycle in both the bays. Methanogenesis regulates not only the carbon cycle but ultimately the rate of organic matter degradation and nutrient recycling. A reduction in methanogenesis could decrease the overall carbon and nutrient cycling in these ecosystems. These could affect the overall productivity of the bays. Secondly, SO_4^{2-} additions could change the dynamics of the system from a CH_4 based system to a sulfur based system. If sulfate reducing populations are stimulated by SO_4^{2-} additions, methanogens may be outcompeted. Sulfate based systems produce H_2S which is toxic to many organisms. Suggestions for further research include obtaining rates for sulfate reduction and methanogenesis in situ.

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