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Methane oxidation potential in the water column of two diverse coastal marine sites

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Abstract. Methane oxidation in the water column was investigated at two nearshore marine environments with relatively high concentrations of dissolved methane. In the northern Gulf of Mexico, high methane oxidation rates were observed at the pycnocline, with the highest oxidation rate corresponding to the most negative bacterial δ^{13}C values. These low isotopic values occurred during the winter when overall bacterial productivity was low, suggesting that at this time of the year, methanotrophs in the Gulf could make up a significant portion of the overall bacterial assemblage. Although methane oxidation also occurred during more productive times (i.e., summer), the isotopic signal of methane oxidation was not observed in the bacterial biomass because of the higher overall bacterial productivity. The other site, Cape Lookout Bight, NC, is a small marine embayment where methane is produced in the organic-rich sediments. No measurable rates of methane oxidation in the water column occurred, and no anomalously low δ^{13}C values of the bacterioplankton were measured. In both environments, methane production and oxidation appear to be spatially coupled, occurring at/near the pycnocline in the northern Gulf of Mexico and at the sediment-water interface at Cape Lookout Bight, NC.

Introduction

The world's oceans are a source of methane to the atmosphere (Schlesinger 1997), since supersaturation of methane in surface ocean waters with respect to atmospheric mixing ratios is a consistent feature of most oceans. Most open ocean surface waters are 20 to 80% supersaturated with methane (Lambert and Schmidt 1993) relative to the saturation concentration in seawater of approximately 2 nM (Wiesenburg and Guinasso 1979). However, concentrations in nearshore shelf areas can be much higher. For example, dissolved methane concentrations in surface waters of the northern Gulf of Mexico average over 20-fold supersaturation (Swinnerton and Lamontagne 1974; Brooks et al. 1981). Recent studies have suggested that coastal shelf environments and estuaries contribute up to 75% of the total release of methane from the ocean to the atmosphere (Lambert and Schmidt 1993; Bange et al. 1994). This methane is thought to be derived from the decomposition of organic rich sediments underlying a shallow water column.

Once methane is produced in organic-rich sediments, it can diffuse up into the water column and eventually into the atmosphere. Methanotrophy at the sediment-water interface can substantially reduce the diffusive methane flux (Boehme et al. 1996). However, the high dissolved methane concentrations of coastal regions suggest that methane could also be an important carbon source for bacterioplankton in the water column.

Methane oxidation has been observed in many marine environments, from Framvaren Fjord, Norway (Lidstrom 1983) to the southern California Bight (Ward and Kilpatrick 1993) to the hydrothermal vents on Juan de Fuca ridge (de Angelis et al. 1993). In addition, methane oxidation has been inferred from stable carbon isotopic analyses. Sassen et al. (1999) suggested methane oxidation was associated with sea-floor gas hydrates on the Gulf of Mexico slope, while Kelley et al. (1998) gave evidence for an alternative microbial carbon source, perhaps methane, in the water column of the northern Gulf of Mexico that may be contributing to the bacterial production.

However, the relative importance of methane oxidation to total heterotrophic bacterial production is not known. Nor is the role of methane oxidation known with regards to air-sea exchange. Based on stable isotopic analyses, Holmes et al. (2000) suggest only a small percentage of the methane in the upper water column is oxidized. In this current paper, the role of methane oxidation in carbon cycling is compared at two coastal marine sites, the northern Gulf of Mexico and Cape Lookout Bight, NC. Both sites have relatively high dissolved methane concentrations, but differ in their physiographic setting and in the source of their organic matter input.

Site description

Although both field areas are coastal in nature, with relatively high concentrations of dissolved methane in the water column, their physiographic settings are quite different (Figure 1). Cape Lookout Bight, NC is a small semi-enclosed marine basin located about 105 km southwest of Cape Hatteras, NC. Cape Lookout forms the apex of a cuspate foreland consisting of two barrier islands situated at approximately 90 degrees from each other, separated by Barden Inlet. Barden Inlet serves as the conduit through which open seawater exchanges with sound water. Cape Lookout Bight (CLB) is a shallow (about 8 m deep), small embayment, approximately 2 km^2 in area, in which fine-grained sediments are rapidly (about 10 cm yr^{-1}) accumulating (Chanton et al. 1983). CLB is, in essence, a deep mudhole surrounded by shallower sandy sediments. Although the muddy sediment at this site supports high rates of anoxic organic matter remineralization, both sulfate reduction and methanogenesis (Crill and Martens (1983, 1987)), the water column remains mixed at seawater salinities and is well-oxygenated throughout the year (Bartlett 1981). The organic matter delivered to the site and contained in the surficial sediments is mainly algal and bacterial in nature (Canuel and Martens 1993). CLB has been studied extensively, both in terms of sedimentary carbon mass budgets (Martens et al. 1992) and stable carbon isotopes (Boehme et al. 1996).

In constrast, the northern Gulf of Mexico is extremely affected by the Mississippi River, which transports large amounts of allochthonous materials to the Gulf.

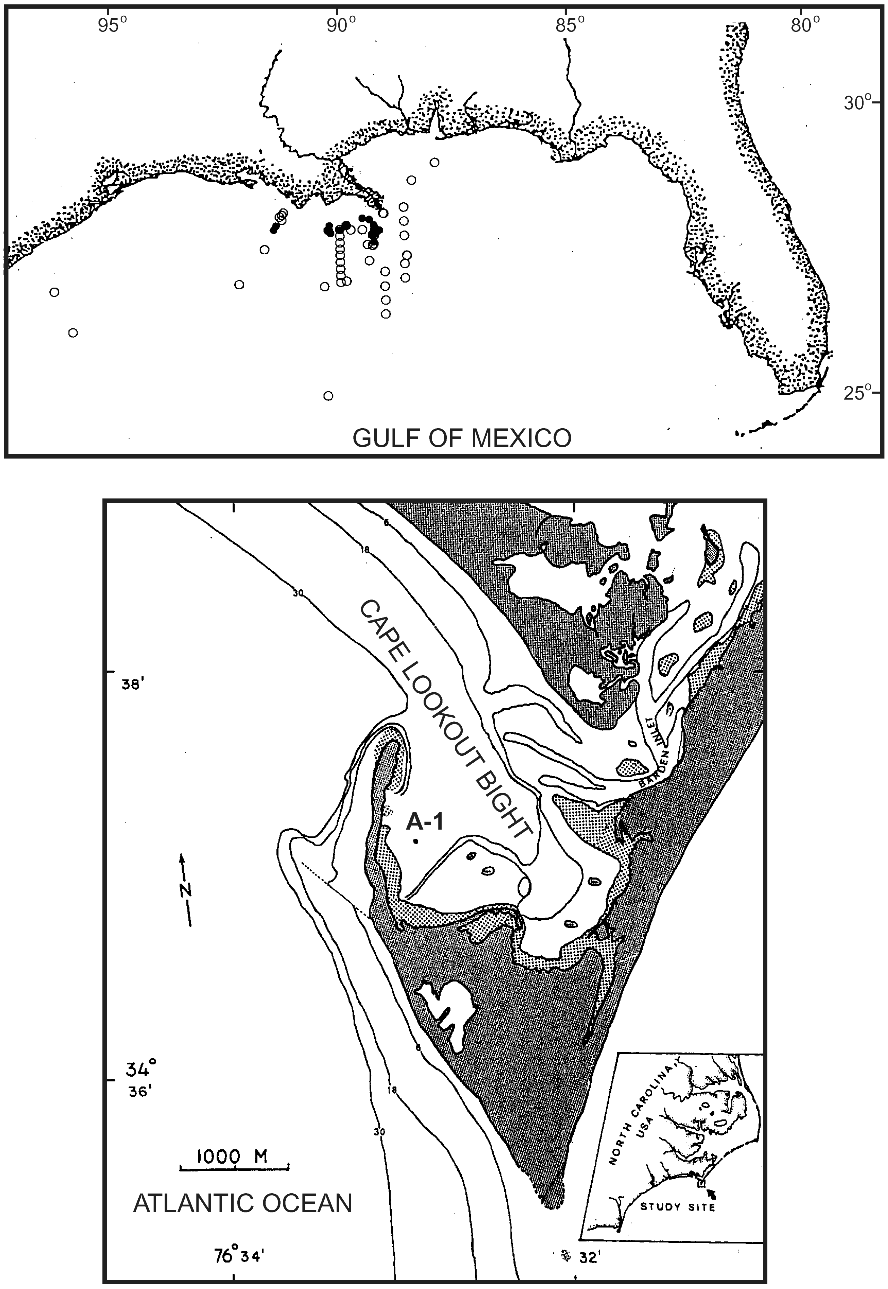


Figure 1. Maps of the study sites. In the Gulf of Mexico, the open circles represents stations at which methane concentrations were obtained and the filled circles are those at which both concentrations and methane oxidation rates were measured. At Cape Lookout Bight, NC, samples were obtained at Station A-1. Depth contours at CLB are in feet at mean low water.

The Mississippi River is the sixth largest river in the world, in terms of discharge, emptying 580 km^3 y^{-1} of water annually into the Gulf (Milliman and Meade 1983). This huge amount of freshwater has a profound effect on the biogeochemistry and bacterial metabolism of the region, as a plume of less saline water forms out from the delta leading to density stratification and the formation of a yearly hypoxic zone (Rabalais et al. 1994). In addition, both oil seeps and methane hydrates occur near the sediment surface in the Gulf of Mexico (Brooks et al. 1986).

Methods

Water samples for depth profiles of methane concentrations and for oxidation rates in the Gulf of Mexico were obtained using a CTD rosette equipped with 10 or 30 L GoFlo bottles. Water samples at CLB were obtained by pumping water into a 20 L carboy. In both cases, care was taken to avoid contamination with atmospheric methane. Salinity values were obtained with the CTD probe in the Gulf of Mexico, whereas at CLB, a hand held refractometer was used to obtain salinity measurements. Net methane oxidation rates were determined at all sites by incubating unfiltered water samples and determining changes in methane concentration with time. Generally six time points over the course of 48 hours were used to determine oxidation rates. The limit of detection with this method is approximately 5 nM d^{-1}. Control experiments were also performed using picolinic acid (~ 100 μM final concentration), which inhibits bacterial methane oxidation by blocking the initial uptake of methane catalyzed by the methane monooxygenase (Bedard and Knowles 1989). By using these control experiments, the possibility of methane production and gross methane oxidation could be determined.

The $\delta^{13}C$ values of the bacterial assemblages were also determined from water samples collected at depths corresponding to most of the methane oxidation experiments using the bioassay technique outlined in Coffin et al. (1989). Briefly, 20 L cubitainers were filled with 0.2 μm filtered sample water and inoculated with 0.8 μm or 1.0 μm filtered sample water (1% v/v). The cubitainers were incubated in the dark at about in situ temperatures. After approximately 48 hours, the water was filtered onto pre-combusted GF/F glass fiber filters and the filters were frozen. In the lab, the filters were fume acidified to remove inorganic carbon (Hedges and Stern 1984). The bacteria contained on the filters were analyzed by burning the filters and measuring the $^{13}C/^{12}C$ ratios of the CO_2 evolved.

The isotopic composition of the methane at CLB has been well-characterized (Martens et al. 1986). In the Gulf of Mexico, $\delta^{13}C$ values of the dissolved methane were determined during two cruises (November 1994, November 1997) by collecting about 4 L of seawater. KOH pellets (about 1 M final concentration) were added to the samples to stop or slow metabolic processes, as well as to keep the CO_2 in solution during later extraction of the dissolved methane. In the laboratory, the methane was extracted and oxidized to CO_2 on a flow-through vacuum line (Chanton et al. 1992), and analyzed for its $^{13}C/^{12}C$ content.

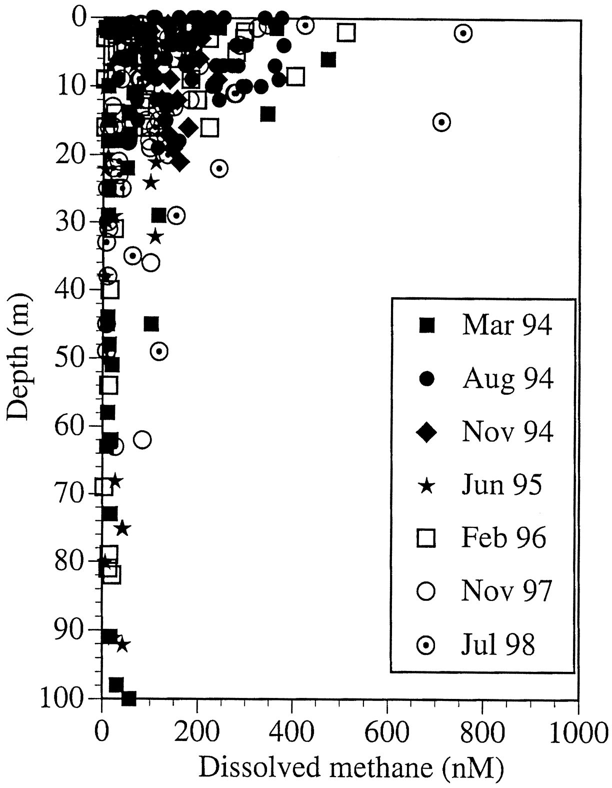


Figure 2. Methane concentration data from all the sites in the Gulf of Mexico for the upper 100 m of the water column.

Results

Methane concentration depth profiles were obtained during seven cruises in the northern Gulf of Mexico, near the Mississippi River plume, from March 1994 to July 1998 (Figure 2). Measurements of methane oxidation rates were obtained on the later six cruises, beginning in August 1994 (Table 1). Summer (August 1998) and winter (November, 1998) methane concentrations and oxidation rates were also obtained from CLB (Table 1).

Dissolved methane concentrations in the northern Gulf of Mexico were supersaturated with respect to atmospheric methane. Greatest concentrations occurred in the upper 50 m of the water column (Figure 2), reaching hundreds of nM's. Many profiles exhibited subsurface maxima, with the highest concentrations occurring near the pycnocline (Figure 3). Concentrations at CLB were similar to those measured in the northern Gulf of Mexico (Table 1).

Rates of methane oxidation for both the Gulf of Mexico and CLB are shown in Table 1. To account for differences in initial methane concentrations, the specific

Table 1. Dissolved methane concentrations and oxidation rates measured in unfiltered water samples from the northern Gulf of Mexico and Cape Lookout Bight, NC.

Station	Latitude Longitude	Water Depth (m)	Date sampled	Depth sampled (m)	Salinity (psu)	CH4 Conc. (nM)	CH4 Oxid. (nM d^{-1})	Specific Oxid. (d^{-1})	$\delta^{13}CH_4$ (‰)	δ^{13}C bacteria[1] (‰)
Northern Gulf of Mexico										
Gyre 1	28°54′N, 89°23W	18	10 Aug 94	13	31.4	154.8 ± 2.7	17.4	0.11	n.d.[2]	n.d.
Gyre 2	29°00′N, 89°30′W	15	11 Aug 94	2	18.8	235.0 ± 23.0	0	0	n.d.	n.d.
Gyre 3	29°06′N, 89°36W	15	12 Aug 94	2	20.4	321.6 ± 9.3	0	0	n.d.	n.d.
Gyre 4	29°07′N, 89°45′W	19	14 Aug 94	3	20.0	144.5 ± 2.7	0	0	n.d.	n.d.
Gyre 4			14 Aug 94	12	27.3	190.3 ± 3.7	50.6	0.27	n.d.	n.d.
Gyre 5	28°52′N, 90°27′W	16	15 Aug 94	15	32.2	142.2 ± 4.2	0	0	n.d.	n.d.
5b	29°00′N, 90°29′W	9	20 Nov 94	8	29.5	86.0 ± 5.2	0	0	−60.6	−24.0
8	28°57′N, 89°28′W	21	20 Nov 94	6	28.2	169.5 ± 9.1	0	0	−60.7	−25.6
8			20 Nov 94	19	35.7	169.0 ± 5.7	14.2	0.08	−58.8	−23.3
T1B	29°01′N, 91°40′W	10	11 Jun 95	2	23.5	46.7 ± 0.6	0	0	n.d.	−23.0
T1B			11 Jun 95	5	24.0	61.4 ± 3.8	0	0	n.d.	−27.9
T1D	28°42′N, 89°30′W	110	21 Feb 96	2	27.2	256.9 ± 7.7	10.0	0.04	n.d.	−25.0
T2D	28°57′N, 91°43′W	15	17 Feb 96	13	33.2	156.6 ± 1.8	0	0	n.d.	−26.3

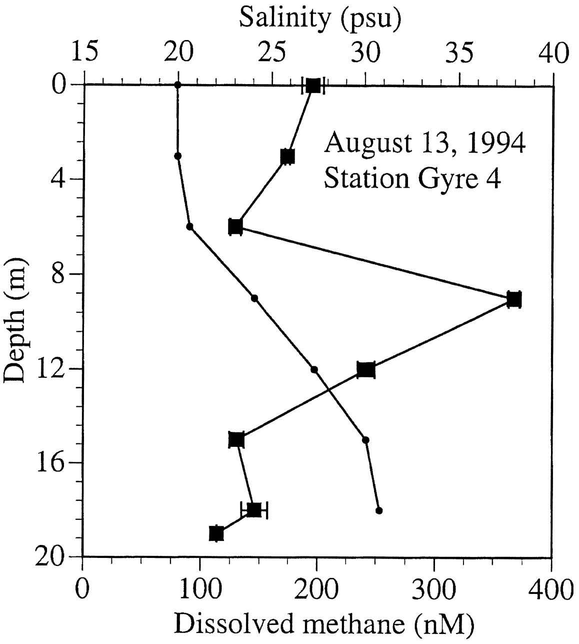
Table 1. Continued.

Station	Latitude Longitude	Water Depth (m)	Date sampled	Depth sampled (m)	Salinity (psu)	CH4 Conc. (nM)	CH4 Oxid. (nM d^{-1})	Specific Oxid. (d^{-1})	$\delta^{13}CH_4$ (‰)	$\delta^{13}C$ bacteria[1] (‰)
5	29°00′N, 90°06′W	23	16 Feb 96	16	35.5	58.5 ± 2.7	0	0	n.d.	−28.0
5			22 Feb 96	2	28.4	154.6 ± 3.2	0	0	n.d.	−25.3
5			22 Feb 96	17	35.7	80.4 ± 2.1	6.5	0.08	n.d.	−28.6
N1	28°55′N, 89°30′W	37	22 Nov 97	9	33.4	75.1 ± 3.0	56.9	0.76	−31.0	−34.4
N4	28°55′N, 90°15′W	20	23 Nov 97	15	34.9	114.1 ± 1.2	0	0	−57.2	n.d.
N6	28°50′N, 89°32′W	66	24 Nov 97	64	36.0	54.1 ± 0.9	9.5	0.18	−48.0	n.d.
N1	28°55′N, 89°30′W	37	28 Jul 98	20	35.1	9.9 ± 0.4	0	0	n.d.	n.d.
N4	28°55′N, 90°15′W	20	29 Jul 98	17	34.9	102.2 ± 15.2	0	0	n.d.	n.d.
N5	28°55′N, 90°30′W	15	29 Jul 98	7	30.4	343.3 ± 3.3	28.1	0.08	n.d.	−26.4
CLB, NC										
A-1	34°37′N, 76°33′W	7	8 Aug 98	2	35	156.6 ± 7.4	0	0	−57[3]	−23.0
			8 Aug 98	6	35	245.5 ± 5.3	0	0	−57	−22.0
A-1	34°37′N, 76°33′W	7	21 Nov 98	2	35	54.3 ± 1.4	0	0	−61	−22.6
			21 Nov 98	6	35	17.5 ± 0.9	0	0	−61	n.d.

[1] Bacterial isotope data from 1994 to 1996 are from Kelley et al. (1998).

[2] n.d. = not determined

[3] Methane isotope data for CLB are from Martens et al. (1986).



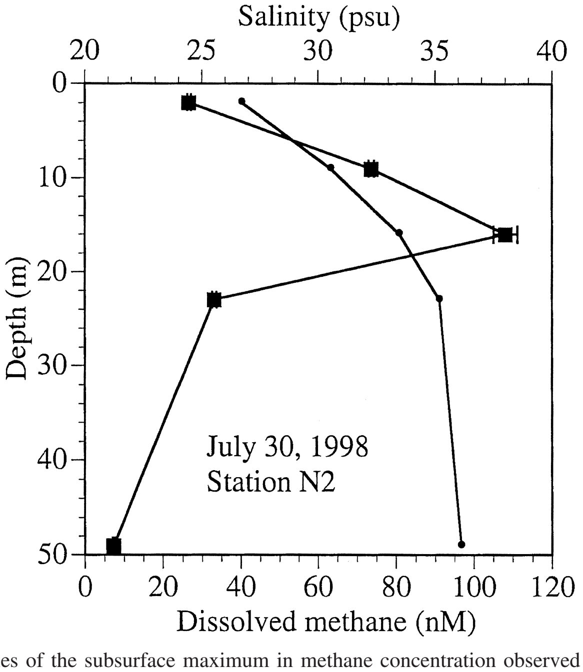


Figure 3. Examples of the subsurface maximum in methane concentration observed at the pycnocline for many of the profiles in the Gulf of Mexico. Methane concentrations are shown in the filled squares and salinity is shown in the small filled circles.

oxidation rates are also shown. The specific rate (d^{-1}) is the fraction of methane turned over per day and is calculated by dividing the oxidation rate by the initial methane concentration (de Angelis et al. 1991). The highest oxidation rate as well as the highest specific rate (56.9 nM d^{-1} and 0.76 d^{-1}, respectively) occurred at the pycnocline (salinity = 33.4 psu) of Gulf of Mexico Station N1 in November 1997. At this site, the methane concentration profile peaked at the surface and declined in concentration through the pycnocline (Figure 4). No measurable rates of methane oxidation occurred at CLB during the study (Table 1).

The isotopic composition of methane and the bacterial assemblages at the different stations are also shown in Table 1. In the Gulf of Mexico, methane isotopic values were obtained from two different time periods. The $\delta^{13}C$ value of dissolved methane from both time periods when no methane oxidation occurred averaged −59.5 ± 2.0‰ (n = 3). Where methane oxidation was observed, the methane $\delta^{13}C$ values correlated with methane oxidation rates. The most ^{13}C-enriched methane $\delta^{13}C$ value (−31.0‰) occurred at the site with the greatest oxidation rate (59.6 nM d^{-1}). This site also had the most ^{13}C-depleted $\delta^{13}C$ value of the bacterial assemblages (−34.4‰). The overall range of $\delta^{13}C$ values for the bacterial assemblages in the Gulf of Mexico was −23.3 to −34.4‰ (Table 1). The most ^{13}C-enriched values were observed when no methane oxidation occurred. The values obtained for the bacteria at CLB were consistent from summer to winter (Table 1) and averaged −22.5 ± 0.5‰ (n = 3).

Discussion

Both methane-producing and methane-consuming processes fractionate carbon isotopes. Large fractionations are exhibited during methanogenesis resulting in biogenic methane being depleted in ^{13}C, with $\delta^{13}C$ values ranging from approximately −50 to −110‰ (Tyler 1992). Methanotrophy results in both the bacterial biomass, as well as the emitted CO_2, being more depleted in ^{13}C, by about 20‰, than the already depleted methane substrate, leaving behind methane somewhat enriched in the heavier isotope (Jahnke et al. 1998). By using measured rates of methane oxidation and isotopic composition of the bacterial assemblage and dissolved methane, we can start to constrain the role that methane plays in carbon cycling in coastal environments, such as the northern Gulf of Mexico, and CLB, NC.

Northern Gulf of Mexico

In the northern Gulf of Mexico, subsurface maxima of methane concentrations occur at the pycnocline (Figure 3) indicating a zone of production, perhaps due to higher particle concentration in this zone (Scranton and Farrington 1977; Brooks et al. 1981). Some evidence of methane production at the pycnocline was seen in the current study (Figure 5). Here, production was observed as an increase in methane concentration in the picolinic acid amended bottles. There was no statistical change

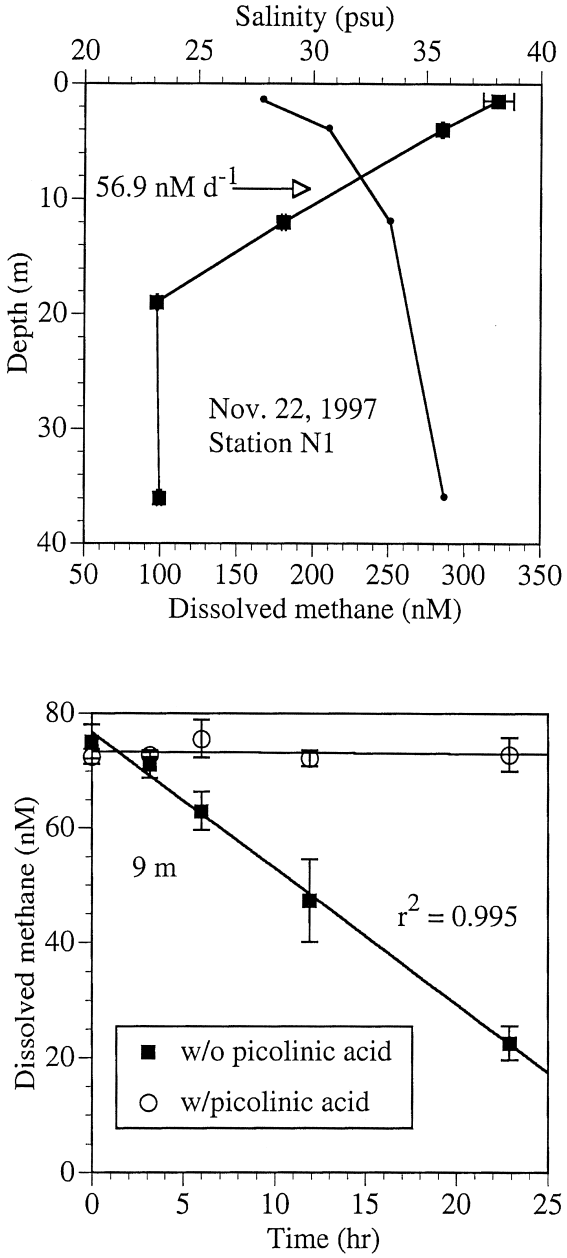


Figure 4. Concentration (large squares) and salinity profiles (small circles) and incubation data for Gulf of Mexico Station N1, November 1997. The arrow in the upper panel shows the depth at which the incubation water samples (lower panel) were obtained (9 m). These samples were obtained from a separate CTD water cast after the methane profile had been measured. When picolinic acid, a specific inhibitor of methane oxidation, was added, no change in methane concentration was observed, and the slope was not statistically different from zero ($p = 0.86$). In the unamended bottles, concentrations decreased linearly with time ($r^2 = 0.995$; $p = 0.0001$).

in concentration in the unamended bottles, indicating that all of the methane being produced was also oxidized. Apparently, both methane production and oxidation are coupled to this density interface. The highest methane oxidation rate was also observed near the pycnocline (Figure 4). This tight coupling between production and oxidation has been suggested by other workers (Scranton et al. 1995; Sieburth 1991).

Low $\delta^{13}C$ values of the total bacterial assemblages were also observed near the pycnocline (Table 1). Many of the bacterial $\delta^{13}C$ values are more ^{13}C-depleted than the range of previously measured values of dissolved organic carbon (DOC), −19.6 to −24.7‰, reported for the northern Gulf of Mexico (Eadie et al. 1978; Santschi et al. 1995). The bioassay method of obtaining these bacterial $\delta^{13}C$ values uses filtered water, and so may skew the isotopic values of the overall bacterial assemblages somewhat by eliminating particles that may be sites of active productivity. However, this method has given similar values (within 1–2‰) for sites that include the northern Gulf of Mexico (Kelley et al. 1998) as a nucleic acid extraction method (Coffin et al. 1990), which uses no incubation step with filtered water. Since both methods have given similar $\delta^{13}C$ values, the less labor-intensive bioassay method was used for this study.

The most depleted bacterial value, −34.4‰, corresponded to the highest rate of methane oxidation, 56.9 nM d^{-1} (Table 1). This very low bacterial $\delta^{13}C$ value occurred during the winter (November 1997). Chin-Leo and Benner (1992) measured bacterial production in the northern Gulf of Mexico, comparing summer to winter values. Bacterial productivity in the summer (2.56 ± 1.70 μM C d^{-1}) is about three times higher than the winter (0.85 ± 0.48 μM C d^{-1}), with the range in winter of 0.24 to 2.76 μM C d^{-1} (Chin-Leo and Benner 1992). If the methanotrophs incorporate about 25% of the methane carbon into biomass (de Angelis et al. 1993), then the highest methane oxidation rate measured (56.9 nM d^{-1}) would translate into 2% of the total bacterial production during winter, with a range of 0.5 to 6%. During the summer, because of the higher overall productivity, the highest methane oxidation (50.6 nM d^{-1}) would account for only 0.5% of the total productivity.

As mentioned earlier, methane oxidation fractionates carbon isotopes, with the bacteria incorporating methane carbon that is about 20‰ more depleted than the already depleted methane. The isotopic composition of the methane carbon incorporated into cell biomass in the northern Gulf of Mexico could be as depleted as −83.4‰. This is based on the isotopic composition of the dissolved methane when no methane oxidation was occurring, −59.5 ± 2.0‰, and the discrimination between dissolved methane and carbon incorporated into biomass, −23.9‰, as determined by Jahnke et al. (1998). Because of this very depleted incorporated methane carbon, the relatively low percent of methanotrophy to total bacterial productivity could shift the overall bacterial assemblage by a few tenths to −3.5‰. Greater shifts occur during the winter when overall productivity is lower; methanotrophy can make up a greater percentage of the total productivity at this time. During summer, although methane oxidation rates are comparable to what was observed during winter, the overall higher bacterial productivity makes the relative contribution of methane carbon to the total bacterial biomass much less.

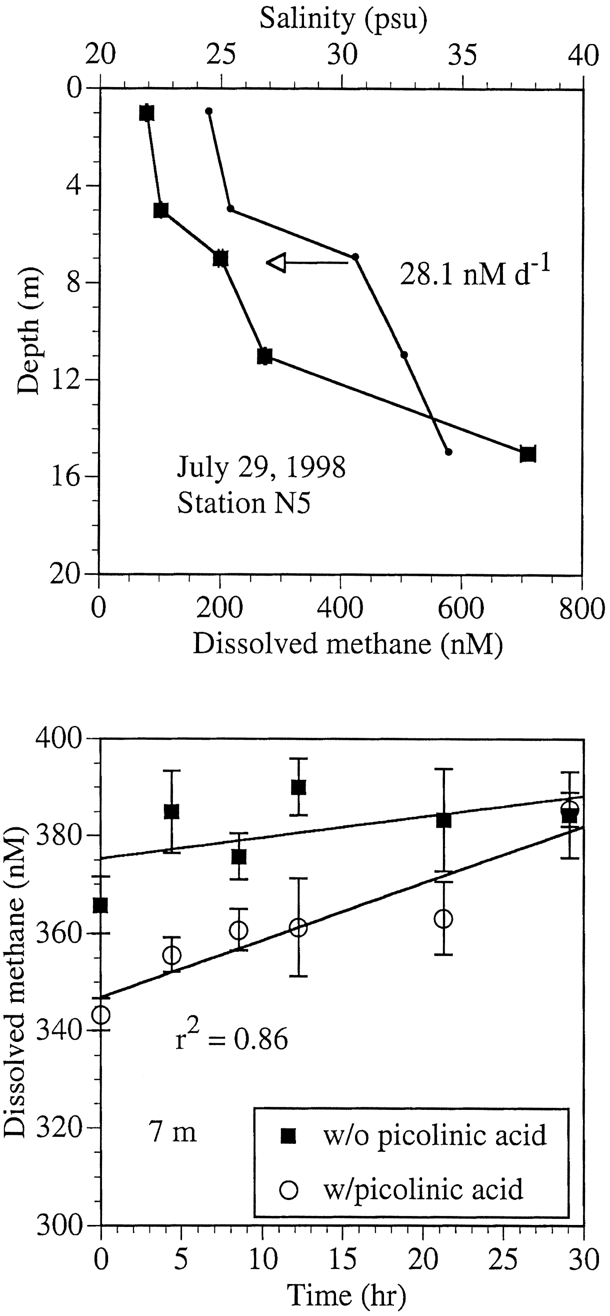


Figure 5. Concentration (large squares) and salinity profiles (small circles) and incubation data for Gulf of Mexico Station N5, July 1998. The arrow in the upper panel shows the depth at which the incubation water samples (lower panel) were obtained (7 m). In the samples with picolinic acid, methane concentrations increased linearly during the incubation time, indicating production (r^2 = 0.86; p = 0.008). In the unamended bottles, no change in methane concentration was observed, and the slope was not statistically different from zero (p = 0.27).

CLB may appear similar to the northern Gulf of Mexico. It is a coastal marine site with seawater salinities. In addition, methane is produced at all times of the year in the organic-rich marine sediments of CLB promoting relatively high methane concentrations in the water column (Martens and Klump 1980). However, unlike the Gulf of Mexico, no measurable methane oxidation occurred in the water column during the study period.

Because of its small size, the residence time of water within in the bight can be important when determining the role of dissolved methane to carbon cycling in CLB's water column. Current velocities in Barden Inlet, as well as in the bight itself, can be substantial. Typical speeds are in the order of 25 to 50 cm s^{-1}, with instantaneous current measurements often exceeding 150 cm s^{-1} (Wells 1988). In addition to these typical current velocities, the effects of storms, and the subsequent flushing due to higher currents, on methane concentrations are considerable (Martens and Klump 1980). These authors report that a rainsquall featuring greater than 20 knot winds dropped bottom water methane concentrations by almost 90%. Winds in the 30 to 40 knot range occur during every month of the year (Wells 1988). Apparently, residence time of water in this system is short and the dissolved methane concentrations at CLB can be controlled by flushing of water through this system.

As mentioned in the site description, sediment is accumulating at CLB at very high rates. Marine snow dominates particle transport in the water column and can account for the high sedimentation at this site (Wells and Shanks 1987). In most oceanic environments, marine snow is an aggregate of organic matter, typically discarded larvacean houses, phytoplankton remains, and fecal material (Alldredge 1998). DOC concentrations in marine snow aggregates are one to two orders of magnitude greater than the surrounding seawater (Alldredge 2000). However, at CLB, the marine snow particles appear to be packed with mineral grains, especially quartz particles, rather than organic matter (Wells 1988). The platey nature of the quartz allows for very little resuspension of sediment to occur once deposited in the bight, despite high bottom current speeds. Because of this core of mineral grains, rather than organics, methane is probably not produced in these sinking particles to any great extent, as have been thought to occur at other sites (Marty 1993), such as the northern Gulf of Mexico.

Measurements of methane oxidation from this study indicate that methane is not used by the bacterioplankton in the water column at CLB (Table 1). The stable isotopic composition of the bacterial assemblage (−22‰), which is within 1‰ of the measured isotopic composition of the DOC (Marc Alperin, pers. comm.), also indicates that methane is not used by the bacteria in the water column. However, bacteria capable of oxidizing methane occur at the site, being concentrated at the sediment-water interface, rather than up in the water column. Based on a stable isotopic mass balance, as much as 76 ± 21% of the methane diffusing across the sediment-water interface is oxidized (Boehme et al. 1996). In addition, there is also evidence for anaerobic methane oxidation occurring within the sediment column (Hoehler et al. 1994).

Conclusions

At both sites, methane oxidation and production appear to be coupled spatially. In the northern Gulf of Mexico, the processes occur up in the water column near the pycnocline. At this density interface, particles may accumulate promoting both methane production and methane oxidation. When overall low rates of bacterial production occur, such as during the winter, methanotrophs may make up a significant portion of the bacterial assemblage, as indicated by the very low bacterial δ^{13}C values. At Cape Lookout Bight, NC, methane production occurs only within the sediment column, with oxidation occurring anaerobically in the sediment (Hoehler et al. 1994) or aerobically at the sediment-water interface (Boehme et al. 1996). Methane oxidation was not observed to occur in the water column, despite relatively high methane concentrations and the presence of large amounts of marine snow. Because of the inorganic nature of the marine snow, the small size and the rapid flushing of water through the bight, there may be little chance for a methanotrophic population to develop in the water column at CLB.

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