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Journal
Limnology and Oceanography, 22(1)

ISSN
0024-3590

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Publication Date
1977

DOI
10.4319/lo.1977.22.1.0001

LIMNOLOGY
AND
OCEANOGRAPHY

January 1977
Volume 22
Number 1

Microbial methane consumption reactions and their effect on methane distributions in freshwater and marine environments[1]

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Abstract

A survey of reported methane distributions in sediments and the adjacent overlying water shows distinct differences between freshwater and marine environments. These differences may be explained by the activities of sulfate-reducing bacteria and appear to be the result of differences in sulfate concentration between freshwater and marine environments.

Measurements of methane in freshwater and marine environments have been reported by many workers over the past 20 years. Table 1 summarizes the studies that we have consulted for the water columns and sediments of both environments. Physical mixing processes are similar in lake and marine sediments, so a comparison of methane distributions is possible and should yield information on similarities and differences in chemical reactions occurring in these environments. Such a comparison is more difficult for the water column, as there are few marine circulation analogs of stratified lakes. Anoxic basins are the nearest analogs, so studies on the Black Sea, the Cariaco Trench, and Lake Nitinat are included in Table 1.

A great deal of emphasis has been placed on improving the precision and accuracy of gas measurements in sediments and explaining the formation of methane. Much less emphasis has been placed on methane consumption. No summary of the reported methane distributions has been attempted. Although an unusually wide variety of sampling and analytical techniques have been used in the sediment studies (e.g. Reeburgh 1968; Barnes 1973; Martens 1974), distributions from either freshwater or marine environments show reasonable internal consistency. Distinct differences in the methane distributions from freshwater and marine environments are also evident, suggesting that some general process must be responsible. We will use here the results from recent laboratory and field studies of the requirements, activities, and distributions of aerobic methane-oxidizing bacteria, as well as bacteria capable of anaerobic sulfate reduction, methane production, and methane oxidation, to point out the locations of the above bacterial reactions and to provide a general explanation of the differences in the freshwater and marine methane distributions.

Data

The results of the studies cited in Table 1 are too numerous to plot conveniently in a single figure, so representative examples of sediment methane distributions in

[1] This work was supported in part by National Science Foundation grants GA-19380 and GA-41209. Contribution 277, Institute of Marine Science, University of Alaska.

Table 1. Studies of methane in freshwater and marine environments.

Freshwater	Marine
Sediments	
Koyama 1953* (table 6)	Emery and Hoggan 1958† (table 2)
Reeburgh and Heggie 1974* (fig. 6)	Reeburgh 1969† (figs. 1-4)
Whelan 1974 (table 1)	Reeburgh and Heggie 1974 (figs. 1-4, 9)
Cappenberg 1974*a** (fig. 1, table 2)	Martens and Berner 1974† (fig. 1)
Rudd and Hamilton 1975*b** (fig. 4)	Reeburgh 1976† (fig. 2)
	Barnes and Goldberg 1976 (fig. 1)
Water column	
Koyama 1964 (table 4)	Atkinson and Richards 1967 (figs. 3-6)
Cappenberg 1972 (figs. 2, 3)	Lamontagne et al. 1973 (fig. 2)
Weimer and Lee 1973 (figs. 3-5)	Linnenbom and Swinnerton 1969 (fig. 1)
Cappenberg 1974*a* (fig. 1)	Wiesenburg 1975 (fig. 9)
Rudd and Hamilton 1975*b* (fig. 2)	Reeburgh 1976 (fig. 1)

*Plotted in Fig. 2 as typical examples.
†Plotted in Fig. 1 as typical examples.

freshwater and marine environments are plotted in Figs. 1 and 2. Schematic summary diagrams are shown as insets in each figure.

The marine sediment profiles (Fig. 1) are concave upward and have a gradient-free zone of low methane concentration ($\leq$0.05 mM) located between the sediment–water interface and depths ranging from 20 cm (Martens and Berner 1974) to 1 m (Emery and Hoggan 1958). Methane accumulates to much higher concentrations (5–15 mM) below this zone, sometimes reaching partial pressures high enough to permit its escape as bubbles (Reeburgh 1969; Martens and Berner 1974; Hammond 1975; Martens 1976). Reeburgh (1969) has suggested that the low-methane surface zone is the result of bioturbation and oxidation by molecular oxygen. Martens and Berner (1974) presented evidence, based on sequential analysis of sealed jars filled with natural sediments, indicating that methane was not produced in the presence of sulfate and favored lack of methane production as an explanation for the low methane concentrations.

The sediment methane profiles from freshwater environments (Fig. 2) are much less consistent than the marine profiles and vary over a concentration range from $\ll$1 to >10 mM. The gradient-free low-methane surface zone has not been observed in freshwater environments; the upper 10–15 cm of these profiles generally have linear methane concentration gradients.

Marine water column methane concentrations have been summarized by Lamontagne et al. (1973). Concentrations in tropical open ocean areas range between 3×10^{-4} and 2×10^{-3} μM. Higher concentrations are found in polluted areas, areas of known gas seeps, and in an open ocean methane maximum at depths of around 100 m. Methane increases with depth to concentrations of $\simeq$7 μM in anoxic basins such as the Cariaco Trench and the Black Sea. Methane concentrations of 80 μM are reported for Lake Nitinat (Atkinson and Richards 1967).

Water column methane profiles in lakes are more variable than the marine distributions. Much higher methane concentrations (0.5–1.2 mM) than encountered in marine environments have been reported by Weimer and Lee (1973) and Cappenberg (1972). These distributions also show linear methane concentration gradients that approach zero concentration in the metalimnion.

Summarizing, methane appears to accumulate to higher concentrations in the hypolimnion of stratified lakes than in the ocean or in anoxic marine basins. Methane distributions in marine sediments show a low concentration surface zone overlying a zone where concentrations increase with

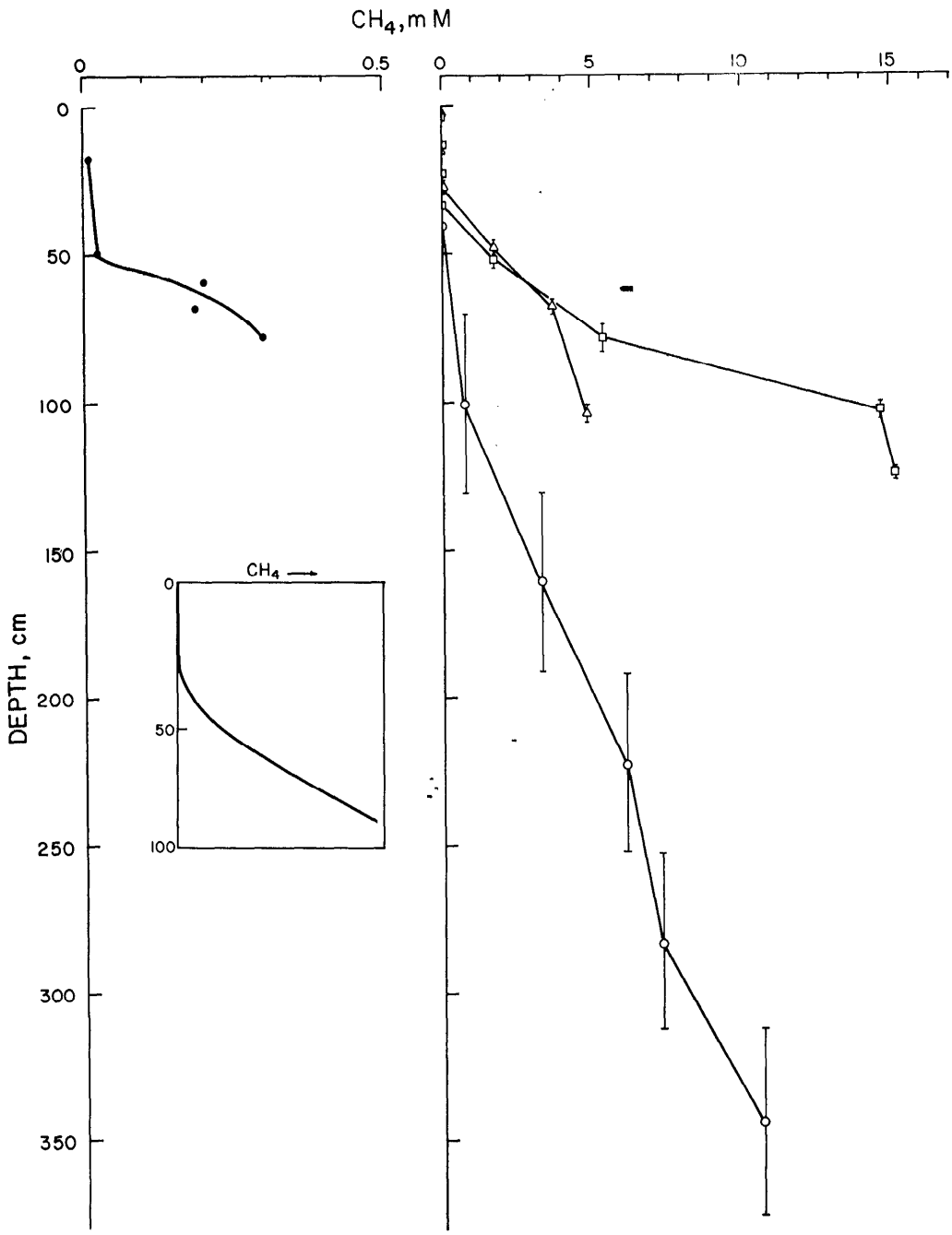

Fig. 1. Selected methane profiles († in Table 1) in marine sediments. ○—Emery and Hoggan 1958; △—Reeburgh 1969 (fig. 1); ●—Martens and Berner 1974 (BS-2 profile); □—Reeburgh 1976. Note differences in concentration scales. Vertical bars show reported depth interval of samples. Inset shows a schematic summary.

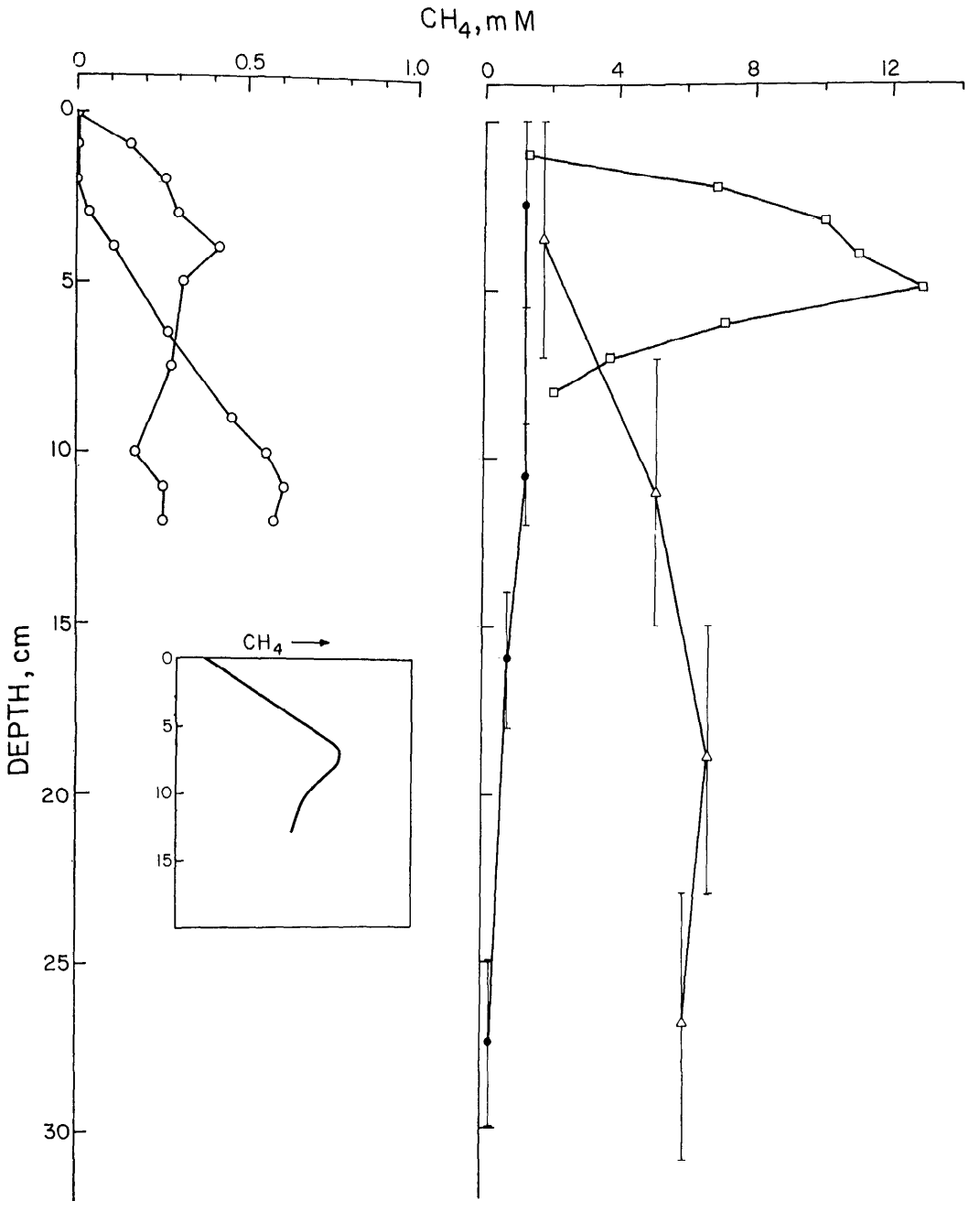

Fig. 2. Selected methane profiles (* in Table 1) in freshwater sediments. △—Koyama 1953 (table 6, L. Nakatsuna); □—Cappenberg 1974*a*; ●—Reeburgh and Heggie 1974; ○—Rudd and Hamilton 1975*b*. Note differences in concentration scales. Vertical bars show reported depth interval of samples. Inset shows a schematic summary.

depth. This feature is absent in freshwater sediments.

Microbial ecology

The distribution (Cappenberg 1972) and activities (Rudd et al. 1974, 1976; Rudd and Hamilton 1975*a*) of aerobic methane-oxidizing bacteria in lakes are restricted during summer stratification to a narrow depth interval in the metalimnion where both oxygen and methane are present. The reports just cited noted that these organisms function only in low (<1 ml liter^{-1}) oxygen concentrations and concluded that they were microaerophiles. Rudd et al. (1976) showed that they are able to function in high oxygen environments provided sufficient dissolved inorganic nitrogen is present and concluded that the restricted distribution of these organisms in the metalimnion during summer stratification was a result of nitrogen limitation in the epilimnion and their inability to function in the anoxic hypolimnion. These organisms are active throughout the water column during spring and fall overturn, when adequate quantities of oxygen and inorganic nitrogen are present, and appear to account for the bulk (>95%) of the annual whole-lake methane oxidation during fall overturn and shortly after winter ice cover. Rudd et al. (1974) measured the methane oxidation rates of these organisms with a ^{14}C-CH_4 tracer technique; Jannasch (1975) measured the methane decrease with time in sealed bottles of Lake Kivu metalimnion water to obtain similar results. The methane oxidation rates observed by these workers are in the μM day^{-1} range. Most of the work on aerobic methane oxidizers has been limited to freshwater environments, but Sansone and Martens (in prep.) have recently observed similar activity in marine systems.

Sulfate reducers and methane producers are well known as obligate anaerobes. Sulfate reduction requires a complex community of fermentative bacteria capable of degrading polymerized organic matter to simple molecules (Goldhaber and Kaplan 1974). Wolfe (1971) indicated that carbon dioxide reduction by hydrogen is an important methane-forming reaction, but showed that acetate is either a substrate or a requirement for several methane producers. Claypool and Kaplan (1974) used changes in the $\delta^{13}C$ of methane and carbon dioxide in sediments to suggest that some 30–50% of the methane is produced by carbon dioxide reduction. Until more is known of the individual activities of the methane producers, we cannot establish clearly whether carbon dioxide reduction and acetate fermentation are independent or sequential reactions, so the $\delta^{13}C$ results are not conclusive. Recent work by Cappenberg has elegantly clarified the situation regarding simultaneous sulfate reduction and methane production discussed by Claypool and Kaplan (1974) and Martens and Berner (1974). Cappenberg (1974*b*) used specific inhibitors to identify the principal substrates and products of sulfate reducers and methane producers and clearly demonstrated a commensal relationship between the two bacterial groups by continuous culture techniques (Cappenberg 1975). These studies showed that the sulfate reducers require lactate and produce sulfide and acetate, which is a precursor for methane production. Low redox potentials (<200 mV) are also provided by the sulfate reducers. Koyama (1964) presented data similar to Cappenberg (1972, 1975) showing an increase in acetate before methane production began.

The commensal relationship (Cappenberg 1975) is complicated by sulfide inhibition of the methane producers at pS^{2-} values below 10.5. These findings are consistent with those of Lawrence and McCarty (1965), who found that sulfate reduction and methane production proceeded simultaneously in a sewage digester, even at seawater sulfate levels. The onset of methane production has been linked with the disappearance of sulfate by Claypool and Kaplan (1974) and Martens and Berner (1974); Cappenberg's work suggests that sulfide is the sulfur species responsible for inhibition of methane production. Electrode measurements of sulfide should

be distinguished from colorimetric measurements of total sulfide. At pH values encountered in marine systems, total sulfide can reach mM levels before sulfide ion approaches concentrations of $10^{-10.5}$ M.

Anaerobic oxidation of methane by sulfate is thermodynamically possible (Feely and Kulp 1957) and laboratory studies (Davis and Yarbrough 1966) have shown that sulfate reducers were able to oxidize methane at low rates in a lactate medium. Sorokin (1957), however, found no evidence of the reaction using sulfate reducers and methane as the sole carbon source. Recent work on Cariaco Trench waters and sediments (Reeburgh 1976) and on Santa Barbara Basin sediments (Barnes and Goldberg 1976) shows that anaerobic methane oxidation occurs in nature and suggests that the studies of Davis and Yarbrough and of Sorokin represent end members of a range of possible reaction conditions.

Reeburgh (1976) used arguments based on a steady state vertical advection-diffusion model (Craig 1969) to demonstrate that methane is consumed in the Cariaco Trench water column. This treatment indicated that anaerobic methane oxidation was uniformly distributed with depth in the anoxic water column and proceeded at rates between 10^{-2} and 10^{-3} μM yr^{-1}, consuming some 85% of the upward methane flux through the anoxic zone.

The sediment methane profiles in Cariaco Trench sediments are like those from other marine environments (Fig. 1). Unlike the other marine environments plotted in Fig. 1, the waters adjacent to these sediments are permanently anoxic, so aerobic methane oxidation or dilution by bioturbation are precluded as causes of the profile. Lack of methane production (Martens and Berner 1974) also fails to explain the uniform methane concentrations in the surface zone; a consumption process is required to dispose of the methane flux from depth in the sediments. In order to produce the concave upward distributions and the low-methane concentration surface zone, the anaerobic methane-oxidizing activity must be located in a narrow depth interval at the base of the surface zone (Reeburgh, 1976). Changes in the gradients of sulfate and total carbon dioxide profiles are consistent with the presence of a narrow zone. The distribution of $\delta^{13}C$ in the sediment carbon dioxide also supports the notion of a narrow zone. Claypool and Kaplan (1974, fig. 6) show a $\delta^{13}C$ minimum at the suggested location of the anaerobic methane oxidation zone. The minimum reflects the addition of isotopically light carbon dioxide from anaerobic methane oxidation; the increase toward positive values below the minimum reflects isotope fractionation during methane formation. Although the depth scales and sample spacing are large, figs. 8 through 10 of Claypool and Kaplan (1974) also indicate a $\delta^{13}C$ minimum with a similar origin.

The consumption appears to be due to cometabolism of methane by sulfate reducers (Mechalas 1974) and occurs at rates 10^6 times greater than those in the water column. How completely methane may be cometabolized is not known, but low and variable methane concentrations in the surface zone suggest that the process is not complete. Too little is known of anaerobic methane oxidation to determine whether a distinct group of organisms is responsible or whether the process represents another commensal or possibly a symbiotic link between sulfate reducers and methane producers.

Discussion

A general explanation of the freshwater and marine methane distributions as well as the differences between them is possible when the locations, substrate requirements, and reaction rates of the previously described bacteria are considered. Consumption reactions rather than production reactions emerge as the most important processes controlling methane distributions.

The principal methane-consuming reaction in freshwater environments, aerobic methane oxidation, is located in the water column at the methane–oxygen boundary during summer stratification, so methane

distributions below this sink are governed by production and transport. Sulfate concentrations in freshwater systems range between 1 and 10 μM; in marine systems they usually exceed 10 mM. In view of this 10^3-fold concentration difference, the controls exerted on methane by sulfate reducers—inhibition of methane production by sulfide and anaerobic methane oxidation—will not operate when the small quantities of sulfate present in freshwater systems are exhausted. Accumulation to concentrations larger than those observed in marine environments is possible in the absence of other consumption reactions. The range of methane concentrations observed in freshwater environments must be due to differences in the redox conditions in the individual environments as well as the nature and quantity of the organic carbon supply. Although production of methane in the water column should be possible, the linear methane gradients reported in the water columns suggest minimal methane production there. The water column methane must primarily originate by diffusion from the sediments.

Although aerobic methane oxidation probably occurs at the surface of sediments overlain by oxic waters, the process governing methane distributions in marine systems appears to be anaerobic methane oxidation. This process occurs in a narrow zone within the sediments as well as throughout the anoxic portions of the water column. Sulfate is never limiting in the water column of marine systems. It may become limiting in sediments when consumption by sulfate reducers exceeds the rate of supply from overlying waters (Goldhaber and Kaplan 1974). Anaerobic methane oxidation in the sediments produces the low methane surface zone and serves as an effective barrier to transfer of methane across the sediment–water interface. Only 1–10% of the upward methane flux from the sediments in the Cariaco Trench escapes oxidation in the sediments and enters the water column (Reeburgh 1976). Sulfide concentrations in the surface sediments, where sulfate reduction rates are highest (Goldhaber and Kaplan 1974), and in the anoxic water column are high enough to inhibit methane production in either of these locations. The effectiveness of the anaerobic oxidation in the sediments and the absence of methane sources other than the deep parts of the sediments account for the low methane concentrations observed in marine water columns. The thickness of the low-methane surface zone in marine sediments is dependent on the sedimentation rate, the organic carbon flux, the sulfate reduction rate, and mixing by organisms. Mixing by organisms will compress the sequence of reactions vertically, increasing the methane gradients. Ebullition from shallow water marine sediments is possible when the methane production rate exceeds the anaerobic oxidation rate and methane accumulates to partial pressures exceeding the in situ pressure.

These relationships clarify the results of several studies and point the way to further work. Reeburgh and Heggie (1974, fig. 9) observed no methane in *Zostera* bed sediments of Izembek Lagoon: those sediments contained large quantities of sulfide, which must have inhibited methane production. Whelan's (1974) study of Louisiana marsh sediments further illustrates the freshwater-marine differences. He observed that lakes with high sulfate contents had low methane concentrations and vice versa. The water column methane concentrations of Lake Nitinat (Atkinson and Richards 1967), which are high for a marine environment (80 μM), can be explained by a high sedimentation rate and organic carbon flux resulting in a thin sulfate-reducing zone; anaerobic oxidation of methane would be less effective here in limiting the upward methane flux, so a larger fraction of the methane would escape oxidation in the sediments and accumulate in the water column. The subsurface methane maximum of the open ocean (Lamontagne et al. 1973) may result from either coastal sources or from local production. The magnitudes of the reported aerobic methane consumption rates suggest

the latter as the more likely explanation. Anaerobic methane oxidation in marine sediments will also require re-examination of the $\delta^{13}C$ data of Nissenbaum et al. (1972) and Claypool and Kaplan (1974) for sediments as well as Deuser's (1973) water column $\delta^{13}C$ measurements. Anaerobic methane oxidation provides a means of introducing isotopically light carbon dioxide, leading to underestimates of methane production in the first two studies and to an overestimate of terrestrial carbon input in the last study. A sulfate-rich or sulfate-dosed lake or laboratory system would be an ideal environment for confirming these relationships. In the presence of high sulfate concentrations and sulfate reduction, methane distributions similar to those observed in marine environments would be expected. Future work should also include attempts to measure methane in longer cores from bubble-free marine environments. Knowledge of the shapes of methane distributions below the anaerobic oxidation zone is needed to determine which of several possible models are most appropriate.

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Submitted: 12 February 1976
Accepted: 12 July 1976