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## The occurrence and distribution of methane in the marine environment\*

LARRY P. ATKINSON†‡ and FRANCIS A. RICHARDS†

(Received 29 August 1967)

**Abstract**—The distributions of methane dissolved in the sulfide-bearing waters of the Black Sea, the Cariaco Trench, and Lake Nitinat are reported. The gas was not detected in the oxygen-deficient water of the eastern tropical Pacific Ocean, in the Santa Barbara Basin, nor in the sulfide-bearing water of Saanich Inlet.

Maximum concentrations observed were 70  $\mu$ mole  $\text{CH}_4/\text{l.}$ , and the distribution tends to follow that of sulfide. The data indicate that methane is derived from organic compounds not containing nitrogen or phosphorus and that its formation is much slower than that of sulfide. The solubility coefficient in seawater (salinity = 40‰) is 0.021 l. (S.T.P.)/l. at 30°C and increases to 0.041 at 5°C.

The processes by which methane may be formed in the marine environment are discussed.

### INTRODUCTION

LITTLE is known of methane in marine environments. Although it is reportedly present, probably in large amounts, in the depths of the Black Sea (KRISSE, 1949, 1962), there are no data or references to substantiate the supposition. Large quantities of methane have been found in the saline, anoxic bottom water of a number of stranded fjords, including Rørholtfjord (STRØM, 1957), Tronstadvatn, and Birkelandvatn (HOLTEN, 1965) in southern Norway, Botnvatn (STRØM, 1961) in northern Norway, and Powell Lake on the southern coast of British Columbia (WILLIAMS, MATHEWS and PICKARD, 1961). These environments all contain relict seawater from which the sulfate has been removed by sulfate-reducing bacteria. KARABABA (1964) concluded, from the absence of bubbles in samples from depth in the Black Sea, that the gas was absent. Mass spectrometric analysis of gas extracted from Santa Barbara Basin sediments indicated the presence of methane, but it was apparently absent from the water column (EMERY and HOGGAN, 1958). REVELLE (1950) found appreciable amounts of an unidentified flammable gas in the lower parts of several cores of diatomaceous mud from the Gulf of California. Observations of the gas in Lake Nitinat, an anoxic fjord on Vancouver Island, British Columbia, Canada, were made by RICHARDS, CLINE, BROENKOW and ATKINSON (1965).

The occurrences reviewed above appear to concern methane that is still at or near the site of its origin in anoxic sediments or water. DUNLAP, BRADLEY and MOORE (1960) observed methane in seawater associated with oil or gas seeps—which they define as oil or gas present in sufficient quantities to appear as a distinct phase at the surface. These occurrences are of a different nature (although they may well be

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closely related) than those which are the subject of this paper, that is, occurrences close to the site of origin.

RICHARDS (1965b), considering a thermodynamic model for the decomposition of organic matter in seawater, concluded that methane formation by way of carbon dioxide reduction was unlikely in the marine environment because the sulfate ions in seawater should be a richer source of energy for microorganisms than carbon dioxide. Carbon dioxide reduction might be expected in the stranded fjords described by STROM (1957, 1961) and by WILLIAMS, MATHEWS and PICKARD (1961) because organic decomposition in these environments has reduced all the sulfate ions. RICHARDS ignored the possibility of anaerobic fermentation, but methane was observed in Lake Nitinat (RICHARDS, CLINE, BROENKOW and ATKINSON, 1965) in spite of the evident concurrence of sulfate ions. This suggested that methane can be formed in the marine environment by anaerobic fermentation (RICHARDS, CLINE, BROENKOW and ATKINSON, 1965) and prompted the investigation of the possible occurrence of the gas in other anoxic marine environments.

This report covers observations in Lake Nitinat, the Cariaco Trench, and the Black Sea, and is primarily concerned with the gas in solution in the water column. Waters from Saanich Inlet, that appears to flush annually (RICHARDS 1965a, b), from the Santa Barbara Basin (34° 10'N, 120°W) off California, and from the oxygen-deficient layers of the eastern tropical Pacific Ocean off the Mexican coast have also been examined for methane, but with negative results, except for one muddy water sample from Saanich Inlet.

#### *Environments where methane has been observed*

The physical and chemical features of Lake Nitinat have been described by NORTHCOLE, WILSON and HURN (1964) and by RICHARDS, CLINE, BROENKOW and ATKINSON (1965). The restricted entrance and freshwater influx result in a strong halocline that restricts vertical circulation so that anoxic conditions develop below about 30 m. Hydrogen sulfide concentrations increase with depth, reaching more than 300  $\mu\text{g-atom S}^{2-}$  - S/l. near the bottom (RICHARDS, CLINE, BROENKOW and ATKINSON, 1965).

The Cariaco Trench (RICHARDS and VACCARO, 1956; RICHARDS, 1965a, b) is a 1400-m deep depression in the continental shelf off the Venezuelan coast at 11° 40'N and 65°W. The deepest sill is at about 150 m and prevents horizontal exchange of deeper Caribbean Water. Water in the trench below 200 m is virtually isothermal and isohaline at 16.9°C and with a salinity of 36.2‰. Because of the restricted deepwater circulation and the permanent thermocline, the waters below about 400 m are devoid of oxygen. Sulfide concentrations reach 20  $\mu\text{g-atom S}^{2-}$  - S/l. near the bottom.

The restricted inflow of Mediterranean Water into the Black Sea through the Bosphorus and an excess of precipitation and runoff over evaporation result in strong vertical stability leading to anoxic conditions below 125-225 m. Sulfide concentrations reach 360  $\mu\text{g-atom S}^{2-}$  - S/l. near the bottom.

#### METHODS AND OBSERVATIONS

All samples were taken in nonmetallic water-sampling bottles built of high-impact polyvinyl chloride from a modification of the Emsworth design of CARRUTHERS, STUBBINGS and LAWFORD (1950).

During the Cariaco Trench (TT-001-15 and 17), eastern tropical Pacific Ocean (TT-001-58), Santa Barbara Basin (TT-001-73), June 1965 Nitinat (HH-196), May 1966 Nitinat, and the June 1966 investigations (see Table 1), a modification of the

Table 1. Summary of fieldwork.

General location	Date	Vessel	Station	Location	Method of analysis*
Black Sea	29-IX-64	<i>Candarli</i>	AGS-2-009†	41° 58'N, 30° 23'E	GE
Lake Nitinat	20-VI-65	R.V. <i>Hoh</i>	HH-196-3	48° 45'N, 124° 45'W	GE and GS
Cariaco Trench	2-XI-65	R.V. <i>Thompson</i>	TT-001-15	10° 31'N, 64° 38'W	GE and GS
Cariaco Trench	4-XI-65	R.V. <i>Thompson</i>	TT-001-17	10° 40.5'N, 65° 32.5'W	GS
Eastern tropical Pacific	29-XI-65	R.V. <i>Thompson</i>	TT-001-58	9° 9.5'N, 88° 59.7'W	GS
Santa Barbara Basin	11-XII-65	R.V. <i>Thompson</i>	TT-001-73	34° 16.0'N, 120° 42'W	GS
Lake Nitinat‡	21-V-66			48° 49'N, 124° 42'W	GS
Saanich Inlet‡§	4-VI-66			48° 35'N, 123° 30'W	GS

\*GE = gas extraction analysis, GS = gas stripper analysis.

†Samples taken in cooperation with the Turkish Navy Hydrographic Office.

‡Small unnamed boats used.

§Samples taken in cooperation with Pacific Oceanographic Group of the Fisheries Research Board of Canada.

gas stripping technique of SWINNERTON, LINNENBOM and CHEEK (1962) was used to remove dissolved gases from solution and introduce them into the gas chromatograph (ATKINSON, 1966). Samples from Cruises TT-001 and HH-196 were drawn into citrate bottles normally used for salinity samples. The bottles were completely filled in a way similar to that used for the Winkler oxygen analysis and stored at 1°C. The lower temperature increases the solubility of methane and therefore slows its loss from solution. Samples were analyzed usually within 1–2 hr of sampling. During cruises TT-001 and HH-196, samples were also collected for analysis in the laboratory. Ampoules (250 ml) fitted with stopcocks at both ends were slowly filled from the bottom to overflowing, about 1 ml of mercuric chloride slurry was injected to stop bacterial action, the stopcocks were closed securely, and the ampoules were stored in a cool, dark place. During the May 1966 Nitinat and June 1966 Saanich Inlet investigations, water samples were drawn in 6-oz (~170 ml) square bottles and 50 ml serum bottles, and about 0.5 ml of mercuric chloride slurry was injected to stop bacterial action. The bottles were sealed with serum caps and returned to the laboratory for analysis.

A Model 29 Fisher–Hamilton Gas Partitioner with modifications described by ATKINSON (1966) was used for gas chromatographic analyses. The stationary phase of the columns was molecular sieve (5 A) vacuum packed in a 6 ft × ¼ in. (3 m × 0.63 cm) column, and the moving phase was dry helium. The output from the detector was recorded on a Texas Instruments 1 mV recorder.

The gas extraction technique involves the vacuum extraction of gas from a known volume of seawater with a high-vacuum apparatus. The volume of the gas is then measured manometrically (BROENKOW, 1963). The extracted gas is transferred to a gas pipette and from the pipette to the partitioner, using a gas-tight syringe (see ATKINSON, 1966, for details).

### *Methane solubility measurement*

The solubility of methane in seawater was determined in the following manner: A 500-ml round-bottom flask with a vacuum-tight serum cap fitted near the bottom of the flask was attached to a rotating vacuum evaporator. The apparatus was arranged so that the flask could be immersed in a water bath ( $\pm 0.1^\circ\text{C}$ ). The stationary tube of the rotating evaporator was connected with high-vacuum tubing to a three-way stopcock. A source of highly pure methane was connected to one bore of the stopcock and a vacuum pump, mercury manometer, and dry ice-acetone water trap were connected to the other. Approximately 250 ml of Copenhagen Standard seawater ( $\text{Cl} = 19.00\text{‰}$ ) was placed in the flask. The entire system was then evacuated to the vapour pressure of the seawater ( $\sim 17$  mm Hg at  $20^\circ\text{C}$ ) and held there for 30 min with the flask rotating (after this time no detectable permanent gases remained). Methane was then slowly admitted into the system as the flask continued to rotate. The flask was then rotated for 100 min, during which time the methane pressure was maintained at 760 mm Hg (this time was found to be adequate to ensure equilibration). After equilibration, the rotation was stopped, and a 10 ml sample was withdrawn from the flask through the serum cap with a gas-tight syringe and analyzed by the method of SWINNERTON, LINNENBOM and CHEEK (1962) as modified by ATKINSON (1966). The remaining seawater was removed for salinity determination. The solubility coefficient of methane was calculated, using the combined gas laws and correcting for the vapour pressure of water.

## RESULTS

### *Methane distribution*

Two vertical profiles of methane and one of sulfides at Sta. 3 (Fig. 1) in Lake Nitinat in June 1965 are shown in Fig. 2. The differences in the methane profiles may reflect differences in the analytical methods as well as real differences in the samples, which were taken 8 days apart. Thus, methane may have been absent at 30 m on 20 June but present on 28 June. The errors in the methods are such that neither the maximum shown in the data from the gas stripper nor the slight increase in the bottom sample analyzed by extraction can be considered significant. The methane distribution in Lake Nitinat, observed at Sta. 1 in May 1966 and Sta. 3 in June 1965, and the oxygen and sulfide conditions observed in June 1965 are shown in Fig. 3.

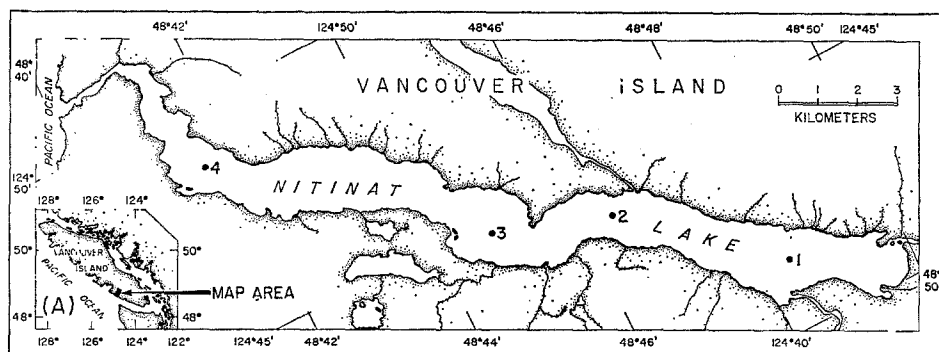


Fig. 1. Station plan, Lake Nitinat, June 1965 and May 1966.

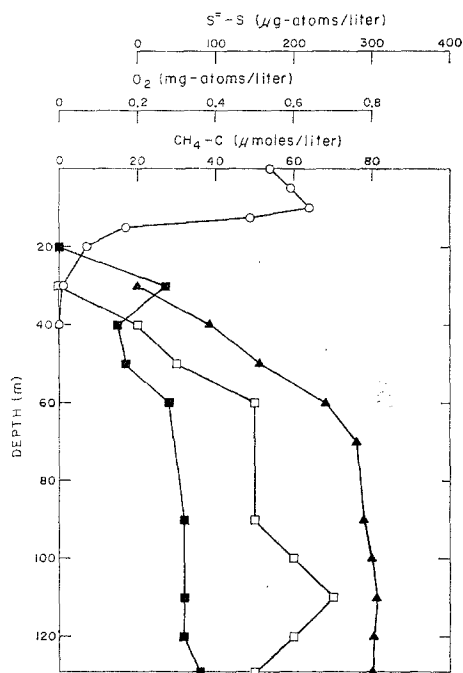


Fig. 2. Vertical distribution of oxygen (○), hydrogen sulfide (▲), and methane (gas extractor, ■; stripper, □), Lake Nitinat, June 1965.

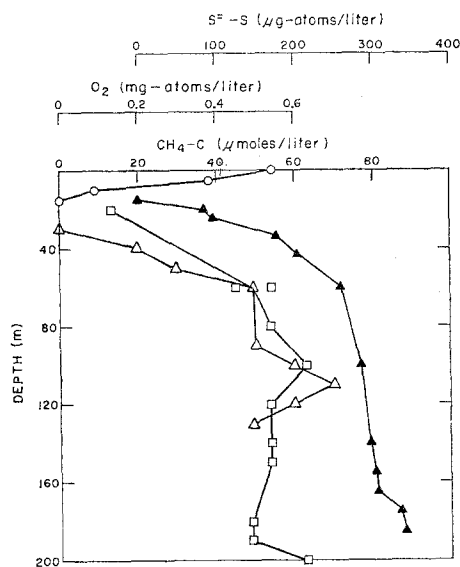


Fig. 3. Vertical distribution of oxygen (○) and hydrogen sulfide (▲) in Lake Nitinat, June 1965; and methane, determined using the stripping method, at Sta. 1, May 1966 (□) and at Sta. 3, June 1965 (△).

The surface conditions at these times may not have been the same, but those at depth probably were.

At Sta. TT-001-15 in the Cariaco Trench (Fig. 4), there was a steady increase of methane to the bottom, with fairly good agreement of the gas stripper and gas extractor data. The reason for the divergence below 900 m is not evident, especially since the values above 900 m agree. The gas stripping data were obtained at sea and very small amounts of methane were involved; therefore the analyses are probably less reliable than the gas extraction values. The precision of the gas extraction method at 800 m was  $5.2 \pm 0.4 \mu\text{mole CH}_4/\text{l}$ . *Thompson* Sta. 17 (Fig. 5) is generally similar to Sta. 15, except for the marked drop in methane in the lower 100 m that coincides with a decrease in sulfides. The large difference in the data from the stripper at 1000 m at *Thompson* Stas. 15 and 17 (Figs. 4 and 5) probably represents accidental loss during sampling or analysis. The negative gradient in the bottom 200 m at Sta. 17 coincides with the negative sulfide gradient and probably reflects an influx of new deep water over the western sill of the trench.

The methane, oxygen, and sulfide data from the Black Sea station are shown in Fig. 6. The methane concentration increases steadily with depth to a maximum of about  $10 \mu\text{mole CH}_4/\text{l}$ . Except for the value at 500 m, the methane and sulfide profiles are nearly parallel. These samples were stored for 9 months before analysis, so some leakage probably occurred and the reported methane concentrations may be less than the *in situ* values were.

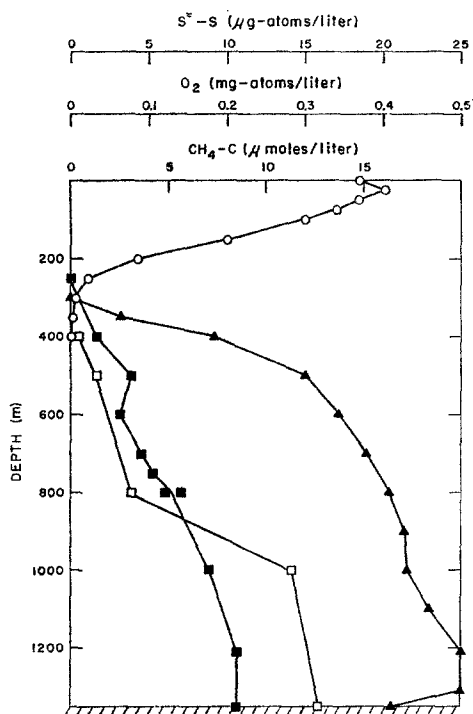


Fig. 4. Vertical distribution of oxygen ( $\circ$ ), hydrogen sulfide ( $\blacktriangle$ ), and methane (gas extractor,  $\blacksquare$ ; stripper,  $\square$ ), at Sta. TT-001-15, Cariaco Trench, November 1965.

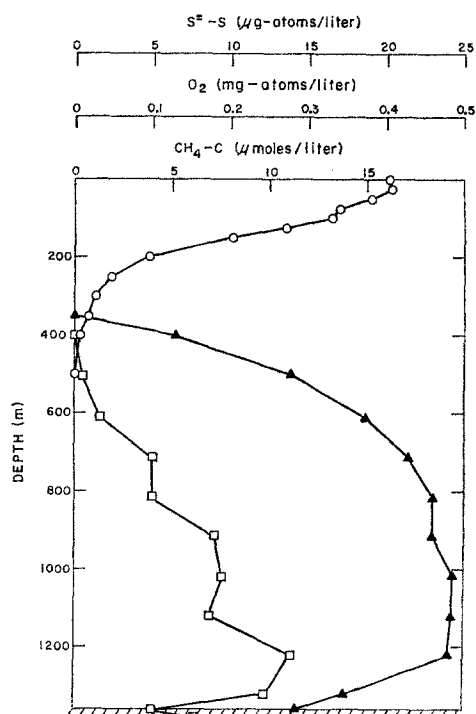


Fig. 5. Vertical distribution of oxygen ( $\circ$ ), hydrogen sulfide ( $\blacktriangle$ ), and methane determined by the stripping method ( $\square$ ), at Sta. TT-001-17, Cariaco Trench, November 1965.

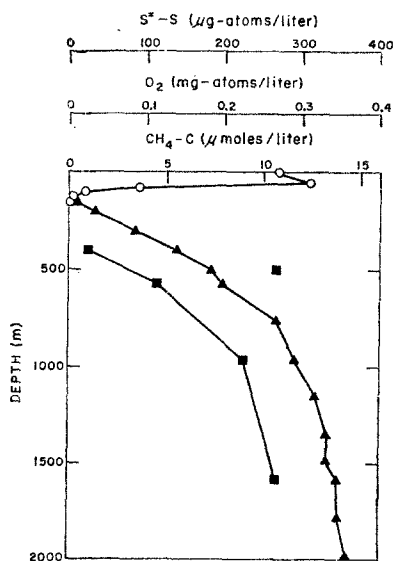


Fig. 6. Vertical distribution of oxygen ( $\circ$ ), hydrogen sulfide ( $\blacktriangle$ ), and methane determined by gas extraction ( $\blacksquare$ ), Black Sea, September 1964.

Because of interferences from the ship's electrical system, it would not have been possible to detect low concentrations of methane in the samples from the eastern tropical Pacific Ocean and the Santa Barbara Basin, had they existed. The lower limit of detection was around  $0.1 \mu\text{mole CH}_4/\text{l.}$

In Saanich Inlet in June 1966, a methane concentration of between  $0.01$  and  $0.04 \mu\text{mole CH}_4/\text{l.}$  was observed in a 230-m sample that contained mud. (Methane was never otherwise detected in the water samples from Saanich Inlet.) Sulfide was found in the lower 70 m in concentrations increasing from zero at 150 m to  $27 \mu\text{g-atom S}^{2-}\text{-S/l.}$  at 220 m.

### *Methane solubility*

The equilibrium solubility of methane in seawater having a salinity of 40‰ was found to be a linear function of the temperature over the temperature range observed:

$$\alpha = 42.57 - 0.698 T$$

in which  $\alpha$  is the solubility of methane in ml (S.T.P.)/l. and  $T$  the Celsius temperature. Using this relationship and WINKLER'S (1891) values for the solubility of methane in distilled water, and assuming that the solubility is a linear function of salinity between 0 and 40‰, the solubility coefficients for seawater having a salinity of 36‰ would be

$T$ (°C)	0	5	10	15	20	25	30
$\alpha$	43.84	39.94	36.16	32.52	28.99	25.52	22.12

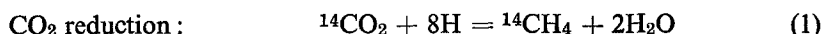
### DISCUSSION

The partial pressure of methane in the atmosphere is about  $2 \times 10^{-6}$  atmospheres (GLUECKAUF, 1951). Therefore the equilibrium concentration in seawater would be, from Henry's law,  $(2 \times 10^{-6}) \times (4 \times 10^{-2})$  or  $8 \times 10^{-8}$  liters of  $\text{CH}_4/\text{l.}$  of seawater at  $5^\circ\text{C}$  and 36‰. The analytical method used will only detect  $0.1 \mu\text{mole}$  ( $2.2 \times 10^{-6}$  l.) of methane, therefore the dissolved methane considered in this paper results from processes other than the solution of air.

### *Methane formation*

The methane found in anoxic environments can arise either from the bacterial decomposition of organic matter in the water column (or sediment), or from seepage from surrounding rock that may contain methane. Oil seeps occur along the southern California coast (EMERY, 1960) and presumably methane is released with the oil, but this is probably not a significant source of methane in the areas investigated.

Bacterially, methane can be formed either from carbon dioxide reduction or acetic acid fermentation (McCARTY, 1964; PINE and BARKER, 1956; KOYAMA, 1963) under anoxic conditions (the  $^{14}\text{C}$  indicates the pathway of the methyl carbon):



Methanol fermentation is a third possible source of methane (STADTMAN and BARKER,



1951), but methanol is not a common degradation product and therefore is probably a relatively minor source of methane.

ZOBELL (1939) and MCCARTY (1964) state that anaerobic fermentation of carbohydrates is the primary mechanism in methane production. ZOBELL pointed out that bacteria are known to ferment carbohydrates (including cellulose) anaerobically in Recent marine sediments. This fermentation results in a mixture of products that includes low-carbon fatty acids, carbon dioxide, and methane. Carbohydrates comprise about 1% of the total organic content of Recent sediments and are absent from ancient sediments, suggesting that anaerobic fermentation of carbohydrates to methane, fatty acids, and carbon dioxide takes place. MCCARTY (1964) stated that more methane arises from carbohydrate fermentation than from fatty acid or protein fermentation because of the additional energy available in the conversion of the carbohydrate to an organic acid. It is evident that methane can result from many fermentative and reductive pathways, with fermentative oxidation of carbohydrates being the most important.

MCKINNEY and CONWAY (1957) proposed a thermodynamic model in which organic matter is oxidized by bacteria first using free oxygen as a hydrogen acceptor, followed by nitrate, then sulfate, and finally acetate. The free energy yields of the reactions in which acetate is oxidized are shown in Table 2. Thermodynamically, the bacteria would obtain more energy from oxidation at the expense of free oxygen

Table 2. Free energy yield upon acetate oxidation using various reductants.

Energy source	Free energy yield (kg-cal/mole acetate)
O <sub>2</sub>	- 206.9
NO <sub>3</sub> <sup>-</sup>	- 187.0
SO <sub>4</sub> <sup>-2</sup>	- 11.2
Acetate fermentation	- 7.0

than from nitrate reduction and more energy from nitrate reduction than from sulfate reduction. RICHARDS (1965a, b) showed that this thermodynamic model partially explains the results of the decomposition of organic matter in oxygen-low and oxygen-deficient environments. The thermodynamic model predicts that methane will not be formed in the presence of sulfate. However, our data demonstrate that methane is present in sulfate-containing marine environments; there are three possible explanations:

(1) In microenvironments, for example around organic particulate matter where accelerated sulfate reduction has occurred because of the high concentration of substrate, the sulfate concentration may drop sufficiently to permit methane production.

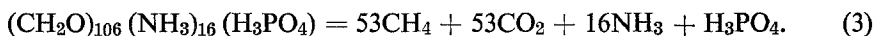
(2) Sulfate may be absent from the sediment as a result of sulfate reduction and the restricted replenishment of sulfate-rich water from the water column. In such an environment, methane production would be thermodynamically favorable. The methane produced could then diffuse and be advected, perhaps by means of bubbles, or diffuse into the water column.

(3) One could ignore the thermodynamic model and assume that a bacterial species will use any available mechanism by which it can live and reproduce. The

natural environment will not contain a single species of bacteria that, when presented with several choices of energy sources, will select the most advantageous. If this were the case, the thermodynamic model should apply strictly. The sulfate reducers oxidize the organic substrate incompletely and commonly produce short-chain fatty acids as by-products (LEBAN and WHITE, 1963). The methane bacteria generally require short-chain fatty acids as substrate. If these acids are produced during sulfate reduction, the methane bacteria must be present and respond to the anoxic and substrate-rich conditions. Conversely, if the sulfate reducers oxidized their substrate completely to carbon dioxide and water, there should be no methane production. Therefore it appears that methane is produced by the anaerobic fermentation of the low-molecular-weight fatty acids produced during sulfate reduction.

*Effect of methane fermentation on the ratios of CO<sub>2</sub>, S<sup>2-</sup>, NH<sub>3</sub>, and PO<sub>4</sub><sup>3-</sup> in the water column*

Methane formation will alter the chemical characteristics of the water column either by liberating or consuming carbon dioxide, ammonia, phosphate, and methane. RICHARDS, CLINE, BROENKOW and ATKINSON (1965) proposed that one representation of methane production might be



During this process the  $\Delta\text{CO}_2 : \Delta\text{CH}_4 : \Delta\text{NH}_3 : \Delta\text{H}_3\text{PO}_4$  ratios would be 53 : 53 : 16 : 1, by moles. Equation (3) represents the anaerobic fermentation of average planktonic organic matter (RICHARDS, CLINE, BROENKOW and ATKINSON, 1965) in which methane is formed from the carbohydrate (CH<sub>2</sub>O) units. This representation seems reasonable because the primary source of methane probably is the anaerobic fermentation of carbohydrates (ZOBELL, 1939; MCCARTY, 1964). During sulfate reduction, the ratios  $\Delta\text{CO}_2 : \Delta\text{S}^{2-} : \Delta\text{NH}_3 : \Delta\text{H}_3\text{PO}_4 = 106 : 53 : 16 : 1$ , by moles (RICHARDS, 1965b). Methane production according to equation (3) would alter the ratios obtained from sulfate reduction alone by an amount depending on the relative amounts of methane and sulfide production. In Lake Nitinat, the ratio of methane to sulfide is 1 : 6, by moles. Therefore, taking a weighted average of the two ratios gives a corrected ratio of :



This mechanism for methane production does not alter the ammonia-phosphate ratio. During the proposed methane formation, both carbon dioxide and ammonia would be added to the water in a ratio of  $\Delta\text{CO}_2 : \Delta\text{NH}_3 = 53 : 16$ , which reduces the  $\Delta\text{CO}_2 : \Delta\text{NH}_3$  ratio to 104 : 16, lower than the 106 : 16 ratio expected from sulfate reduction alone and much lower than the ratio of 141 : 16 observed by RICHARDS, CLINE, BROENKOW and ATKINSON (1965). The proposed methane formation would contribute ammonia to the system and thereby alter the  $\Delta\text{S}^{2-} : \Delta\text{NH}_3$  ratio to 48 : 16. In Lake Nitinat, RICHARDS, CLINE, BROENKOW and ATKINSON (1965) observed  $\Delta\text{S}^{2-} : \Delta\text{NH}_3 = 50 : 16$ , a ratio lower than the 53 : 16 expected from sulfate reduction alone and higher than the 48 : 16 predicted by equation (4). The  $\Delta\text{CO}_2 : \Delta\text{NH}_3$  ratio indicates that methane formation is not contributing ammonia to the system, whereas the  $\Delta\text{S}^{2-} : \Delta\text{NH}_3$  data indicate it may be contributing a small amount. The ratios appear to indicate that the primary source of methane is not organic material of the type proposed,  $(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)$ , but the

carbohydrate and fatty acid by-products of other processes, probably sulfate reduction. During fermentation, carbon dioxide, water, and methane would be released to the water column, while ammonia and phosphate might be removed from the water column.

#### *Consideration of the low concentrations observed*

Too little is known of the biochemical mechanisms of methane production to explain the relatively low concentrations that are observed. It is evident from the solubility of methane that the observed concentrations do not represent methane-saturated seawater. MCCARTY (1964) found that the generation time of anaerobic bacteria is greater than that of aerobic bacteria. *The methane-producing bacteria, specifically, have a very slow generation time, which averages 4-5 days* (an average generation time for aerobic bacteria is 20 min-3 hr), with a maximum of 15 days. MCCARTY suggests that low energy yields and generally low substrate utilization rates contribute to the slow generation time, and hence to the slow rate of methane accumulation.

The June 1966 data from Saanich Inlet are indicative of the slow rate of methane accumulation. Saanich Inlet probably flushes during the fall and therefore any methane or sulfide present was formed in the period following flushing. By June 1966, sulfide and methane concentrations reached 25-30  $\mu\text{g-atoms S}^{2-}\text{-S/l.}$  and 0.01-0.04  $\mu\text{mole CH}_4\text{-C/l.}$  in a water sample that contained mud. These observations indicate that in Saanich Inlet sulfide production is relatively much faster than methane production. This apparently slow rate of methane formation suggests that, following flushing, the growth of a methane-producing flora is slow, possibly because some biochemical or physical parameter, such as temperature, pH, Eh, or suitable substrate, is not favorable or available for growth of methane-producing bacteria.

#### *Spatial sources of methane*

The data are inadequate to judge whether the methane is formed in sulfate-deficient sediments and then diffuses and is advected into the water above, or whether it is formed in the water column. In the absence of advective replacement of bottom water, a negative gradient near the bottom would rule out diffusion from the bottom into the water column. Negative gradients near the bottom have been observed both in Lake Nitinat and in the Cariaco Trench, but whether they were the result of the greater production of methane in the water column than in the sediments or of the intrusion of an increment of newer bottom water is uncertain. The latter mechanism is almost certain to have been the case in Lake Nitinat (HAMILTON and HOPKINS, in press). A positive gradient near the bottom would allow diffusion processes to transport methane from the sediment into the water, and such gradients have been observed. However, pure diffusion of methane from the sediment to the water column would result in a linear increase in the methane concentration with depth, and this has not been observed.

The transport of methane from the sediment to the water column in bubbles probably takes place. Echo-sounder traces sometimes show what appear to be bubbles rising from the bottom of Saanich Inlet (MCCARTNEY and BARY, 1965) and Lake Nitinat (unpublished data). The kind of distribution this type of transport would produce is unknown.

The data do not indicate whether the methane is formed in the water column, the sediment, or both. More detailed sampling at the water-sediment interface would be necessary to clarify this point.

#### *Contribution to atmospheric methane*

It is doubtful if the methane produced in the anoxic environments investigated adds substantially to the atmospheric methane. As the methane diffuses upwards out of the anoxic zone, it becomes an energy source for the methane-oxidizing bacteria. The only way for methane to traverse the oxygenated layer would be by way of bubbles. In swampy and sludge-bed environments, the anoxic zone is very near or at the surface and the methane does escape into the atmosphere.

#### SUMMARY

The distribution of methane in several anoxic marine environments is described. Its determination involves the gas chromatographic analysis of gas stripped from the water by the carrier gas or extracted under a vacuum. The distribution of methane seems to parallel that of sulfide. The data indicate that the gas is derived from organic compounds not containing nitrogen and phosphorus, such as carbohydrates and fatty acids. The data from Saanich Inlet suggest that methane accumulates slowly.

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