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METHANE CONSUMPTION IN CARIACO TRENCH WATERS AND SEDIMENTS

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Detailed measurements of CH$_4$ in the water column and sediments of the Cariaco Trench show that CH$_4$ is non-conservative in both environments. Concentration differences between the sediments and adjacent overlying water suggest that the sediments are the source of the water column CH$_4$. Co-metabolism of CH$_4$ by sulfate reducers appears to be the CH$_4$ sink in anoxic environments.

1 Introduction

Methane has been observed in the water columns of a number of anoxic basins [1–3], but no clear conclusions have been reached as to whether it is produced in the water column or whether it is supplied by the sediments. One of the reasons for this uncertainty is our inability in most instances to distinguish the effects of mixing from reactions in the water column. Steady-state vertical advection-diffusion models [4] have been applied in anoxic basins such as the Black Sea [5] and the Cariaco Trench [6,7] and offer a means of distinguishing the relative effects of mixing and reactions. Since some hope of steady-state conditions at the sediment-water interface is possible in these environments, anoxic basins appear to be reasonable places to attempt combining water column and sediment models. Detailed measurements of CH$_4$ in the water column and sediments of the Cariaco Trench are presented and discussed in this paper.

2 Previous work

The Cariaco Trench is a depression in the continental shelf off the coast of Venezuela containing two 1300–1400 m deep basins separated by a 900-m saddle and from the Caribbean by a 150-m sill. The waters are anoxic and contain sulfide below depths of 300 m. The environment has been studied extensively for 20 years, Richards [8] has summarized and reviewed these studies. Methane has been measured in the Cariaco Trench water column on several occasions [1–3]. Below 300 m, all of these studies showed approximately linear increases with depth. Methane in the sediments has been studied only once. During JOIDES leg 15, gas pocket samples were collected at site 147 and analyzed at ten depths ranging from 47 to 175 m [9,10].

Steady-state vertical advection-diffusion models have been applied to the Cariaco Trench water column by Broenkow [6] and Fanning and Pilsen [7], who differed in their assumptions regarding vertical transport terms and in their choice of boundaries. Broenkow considered an interval between 300 m and the bottom, set the vertical advection velocity equal to zero, and assumed a constant vertical eddy diffusivity of 0.5 cm$^2$ sec$^{-1}$. Fanning and Pilsen used vertical advection in their treatment and considered a linear $T$–$S$ region between 300 m and 1000 m. They considered the ratio of vertical eddy diffusivity (K) to vertical advection (w) constant over this interval and assumed $w = 0$ below 1000 m. Silica, sulfide and phosphate were linear functions of potential temperature, indicating they were conservative, i.e., neither produced nor consumed in the linear $T$–$S$ region. Fanning and Pilsen used silica fluxes to calculate a minimal vertical advection velocity of 0.75 m yr$^{-1}$. Their treatment, however, did not use least-squares fits and made no distinction between basins. Their work indicated that the sediments were
the source of silica in this environment. The same source was suggested for sulfide.

Methane, like sulfide, is formed by obligate anaerobes, but controversy surrounds the principal production mechanism in nature. CO₂ reduction is regarded as the principal production pathway by some workers [11,12], while acetate fermentation is favored by others [1,13]. Inhibition of CH₄ production by SO₄²⁻ has been suggested [14], but recent inhibition studies [13] and continuous culture work by Cappenberg [15] indicates commensalism between sulfate reducers and methane producers. The sulfate reducers require lactate and release acetate, which is fermented by the methane producers. The commensal relationship is complicated by sulfide inhibition of the methane bacteria at concentrations above 10⁻¹⁰ M. Cappenberg's observations are in accord with those of Lawrence and McCarty [16] who observed concurrent sulfate reduction and methane production in a sewage digester. Microbial oxidation of CH₄ with dissolved oxygen is reported to occur in lakes at rates up to 1 µmole l⁻¹ hr⁻¹ [17]. An oxidizer other than dissolved oxygen must be responsible for CH₄ consumption reactions in anoxic environments. Oxidation by SO₄²⁻ by the general reaction

\[
\text{CH}_4 + \text{SO}_4^{2-} + 2 \text{H}^+ \rightarrow \text{H}_2\text{S} + \text{CO}_2 + 2\text{H}_2\text{O},
\]

\[\Delta G^0 = -22.8 \text{ kcal/mole}\]

is thermodynamically possible [18] and sulfate reducers capable of oxidizing CH₄ and other hydrocarbons have been cultured [19]. However, jar experiments using coastal sediments showed no detectable CH₄ consumption [14] and Sorokin [20] found no evidence of CH₄ consumption in culture experiments with sulfate reducers. Sorokin [21] further reported that sulfate reducing activity in sediments is restricted to the uppermost layers. Whether the above reaction or a similar process provides a sink for CH₄ in nature remains a question.

3 Measurements

Sediment and water samples for this work were collected at two stations [22] in the Cariaco Trench during R/V "Trident" cruise 147 (STENCH 2). Methane in the water column was determined by gas chromatography using a modification [23] of the technique reported by Swinnerton and Linnenbom.
Samples were stored under refrigeration in glass-stoppered bottles with sodium azide until analysis at Old Dominion University. Precision of the water column measurements is estimated to be 3–4%. The data are shown in Fig. 1.

Methane and total CO₂ were determined on board using samples of freshly collected gravity cores. No core catcher was used in order to minimize disturbance of the sediment-water interface. Interstitial water was separated from samples of the cores [25] and analyzed for gases using techniques previously described by Reeburgh [26]. A thermal conductivity detector was used, duplicate measurements were precise to 3–5%. Figs. 2 and 3 show the depth distributions of CH₄ and total CO₂ in Carraco Trench sediments.

We encountered no significant problems with bubble formation and degassing of the cores on deck as reported previously [9]. Bubbles were observed in the vicinity of the deepest sample of the eastern basin CH₄ core (Fig. 2) as it was extruded, so we consider this sample unreliable. Ambient temperatures often exceeded the maximum use temperature (30°C) of the Aplezon N stopcock grease used on ball joints and stopcocks in the sediment gas analysis. Silicone grease was substituted, but non-wetting interior surfaces led to unreliable volume determinations for the water column total CO₂ measurements. When leaks were discovered, a CH₄ standard was run under the same flow conditions.

4 Discussion

4.1 Water column

For a stable non-conservative (SNC) parameter, the steady-state vertical profile has been shown by Craig [4] to be

\[ KC'' - wC' + J = 0 \]

where \( K \) is the vertical eddy diffusion coefficient (cm² sec⁻¹), \( w \) is the vertical advective velocity (length yr⁻¹), \( J \) is a reaction rate term (μmole 1⁻¹ yr⁻¹), \( C \) is the concentration (μmole 1⁻¹) and the primes derivatives with respect to depth, which is positive upward. Eq. 1 has the solution for constant \( J \):

\[ C - C₀ = (Cₘ - C₀) f(z) + (J/w) \left( z - zₘ f(z) \right) \]

where \( f(z) = (e^{z/z^*} - 1)/(e^{zₘ/z^*} - 1) \), \( C₀ \) is the concentration at the lower \( z = 0 \) boundary, \( Cₘ \) is the concentration at the upper \( z = zₘ \) boundary and \( z^* \) is the ratio \( K/w \). For a conservative parameter, \( J = 0 \).

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Fig. 3 Total CO₂ data versus depth in Carraco Trench sediments. Symbols for total CO₂ are as in Fig. 2.

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Fig. 4 Potential temperature-salinity diagrams for eastern and western basin Carraco Trench stations. Depths (m) shown for various points.
The $T_p$-$S$ plots for the eastern and western basins (Fig 4) are linear between 290 m and the bottom. The water column CH$_4$ profiles (Fig 1) show a homogeneous bottom layer below 1200 m. Boundaries of $z_m = 290$ m and $z_0 = 1200$ m were chosen for the mixing zone. The mixing parameter, $z^*$, was obtained for each basin by fitting the potential temperature and salinity data using nonlinear least-squares procedures similar to those of Craig [4]. The fitted profiles are shown with the data in Fig 5. The standard deviations of the temperature and salinity residuals are near the precision of the measurements.

The CH$_4$ profiles (Fig 1) are very nearly linear with depth. Two interpretations are possible for a linear gradient: (1) it may represent a pure diffusion case ($w = 0$) for a conservative species, or (2) it may be the result of non-conservative behavior ($J \neq 0$). The temperature and salinity profiles (Fig 5) agree well with fits to the model assuming vertical advection and diffusion. Dissolved CH$_4$ cannot diffuse or advect independently, so the observed linear profiles can only result from net consumption of CH$_4$ in the water column. Conservative profiles are shown in Fig 1 for comparison.

The ratio $J/w$ for CH$_4$ may be obtained analytically from the depth profile. Craig [4,27] shows that for a linear profile

$$J/w = (C_m - C_0)/z_m$$  \hspace{1cm} (3)

The $C_0$ shown in Fig 1 is the average CH$_4$ concentration below 1200 m. The slope, $J/w$, was obtained by fitting linear least-squares line through $C_0$ at $z = 0$. The $J/w$ values for CH$_4$ in the eastern and western basins are $-7.60 \pm 0.31$ and $-5.64 \pm 0.23$ \textmu mole $1^{-1}$ km$^{-1}$. Vertical advective velocities may range between 0.0002 and 0.002 km yr$^{-1}$ [28], resulting in a possible range of CH$_4$ consumption rates of 1.13 $\times$ 10$^{-2}$ to 1.52 $\times$ 10$^{-2}$ \textmu mole $1^{-1}$ yr$^{-1}$.

The CH$_4$ flux from the homogeneous bottom layer through the lower boundary of the mixing interval can be determined using Craig and Clarke's [29] eq 2. Modifying this equation for use with absolute volume concentrations rather than saturation anomalies and mass fractions yields

$$\Phi = wC_0 - KC_0 = w[C_0 - z^*C'_0]$$  \hspace{1cm} (4)

where $K$, $w$, $z^*$ and the prime are identical to those in eq 1 and $C_0$ is the CH$_4$ concentration at the lower boundary of the mixing interval. The CH$_4$ gradient is linear, so $C_0 = J/w$ (eq 3) and

$$\Phi = w[C_0 - z^*J/w]$$  \hspace{1cm} (5)

Using the $J/w$, $z^*$ and $C_0$ values from Fig 1 and assuming the same range of vertical advective velocities as before yields an upward CH$_4$ flux ranging between 0.132 and 1.73 \textmu mole cm$^{-2}$ yr$^{-1}$.

The fraction of this upward CH$_4$ flux that transits the mixing interval may be estimated by considering fluxes into and out of the mixing interval. Since $C_m \rightarrow 0$ at $z_m$, $C_0 = -z_m J/w$. The upward CH$_4$ flux into the zone, $\Phi_0$, equals $-J(z_m + z^*)$. The upward CH$_4$ flux out of the zone, $\Phi_m$, equals $-J \cdot z^*$. CH$_4$ consumed in the mixing zone is the difference, $-J \cdot z_m$. Substituting the $z^*$ values from Fig 1 and appropriate $z_m$ values ($E = 0.930$ km, $W = 1.105$ km) shows that 85% of the CH$_4$ flux into the mixing zone is consumed there and that 15% transits the interval [30].

4.2 Sediments

Fig 2 shows eastern and western basin sediment CH$_4$ profiles that are concave upward, have a low concentration CH$_4$ zone between the sediment-water interface and 35 cm (eastern basin) to 55 cm (western basin) and increase to much higher CH$_4$ concentrations below.
these depths. The inset shows the low CH$_4$ values from the upper 60 cm plotted on an expanded concentration scale. Such profiles can only result from CH$_4$ consumption in the surface sediments. Similar profiles have been reported in other marine environments [31,32,14], where they have been interpreted as resulting from CH$_4$ production at depth and oxidation in a biologically or physically mixed surface zone. Unlike the other environments, the waters overlying these sediments are permanently anoxic, so bioturbation and oxidation by molecular oxygen are precluded. Processes like in situ bubble formation, bubble formation during core retrieval, hydrate formation and physical mixing can be eliminated on physical grounds as causes of the low CH$_4$ surface zone. The CH$_4$ must be consumed by anaerobic biochemical reactions, resulting in an effective barrier to transfer of large quantities of CH$_4$ across the sediment-water interface.

The total CO$_2$ distributions (Fig 3) show linear gradients and slope changes at depths similar to those observed for CH$_4$. Presley [33] has measured SO$_4^{2-}$ depth distributions in eastern and western basin sediments and observed linear gradients and near complete reduction of SO$_4^{2-}$ at similar depths.

The similarity of the depths at which the CH$_4$, total CO$_2$ and Presley’s SO$_4^{2-}$ profiles change slope, combined with the directions of the nearly linear gradients for each suggest the presence of a diffusion-controlled CH$_4$ consuming zone located at the depth of the slope changes. Methane diffuses upward into the zone and is consumed, SO$_4^{2-}$ diffuses downward from the overlying water and is reduced, and increased amounts of CO$_2$ diffuse upward from the zone. We have no way of estimating the vertical extent of this zone, but the sample spacing and abrupt changes in the profiles suggest that it is probably not greater than 10 cm thick.

The CH$_4$ flux to the consuming zone may be calculated by applying the diffusion equation

\[ \Phi = -D_s \frac{dC}{dz} \]  

where \( \Phi \) is the flux (\( \mu \)moles cm$^{-2}$ yr$^{-1}$), \( D_s \) is an interstitial diffusion coefficient (molecular diffusion corrected for tortuosity) and \( \frac{dC}{dz} \) is the concentration gradient. Using CH$_4$ concentration gradients from Fig. 2 and Fanning and Pilson’s [34] interstitial diffusion coefficient for silica (\( 3 \times 10^{-6} \) cm$^2$ sec$^{-1} \) = \( 94.5 \) cm$^2$ yr$^{-1}$), CH$_4$ fluxes to the consuming zone in eastern and western basin sediments are estimated to be 159 and 548 \( \mu \)moles cm$^{-2}$ yr$^{-1}$. If consumption is uniform in a 10 cm thick zone, this flux corresponds to CH$_4$ consumption rates of 1.59 and 0.55 mmole 1$^{-1}$ yr$^{-1}$ for the sediments. This rate is sensitive to the choice of the consuming zone thickness and is \( 10^6 \) times greater than CH$_4$ consumption rates in the water column.

Eq. 1 may be used for steady-state sediment profiles by substituting a sediment diffusion coefficient \( D_s \) for \( K \) and a sedimentation rate \( \omega \) for \( w \). This gives an equation equivalent to Berner’s [35] eq 6-38. Considering the CH$_4$ gradient below the consuming zone to be linear, \( KC'' = 0 \) and \( J = \omega C' \). A sedimentation rate of 0.05 cm yr$^{-1}$ has been reported for the Cariaco Trench [36], maximum CH$_4$ production rates are 8.45 and 2.92 \( \mu \)mole 1$^{-1}$ yr$^{-1}$ for eastern and western basin sediments.

4.3 Anaerobic CH$_4$ oxidation

The reaction responsible for anaerobic CH$_4$ consumption is of interest not only because of the apparent conflict in geochemical studies of anaerobic CH$_4$ oxidation [19,20] but also because anaerobic organisms capable of using CH$_4$ as the sole carbon source are unknown [37]. Davis and Yarbrough [19] and Sorokin [20] worked with pure cultures of sulfate reducers, but used very different media, the first used a lactate medium and observed oxidation of labeled hydrocarbons supplied as a minor carbon source while the latter used a mineral medium with CH$_4$ as the sole carbon source and observed no reaction. Mechalas [38] demonstrated that sulfate reducers may derive energy from the oxidation of recalcitrant molecules by co-metabolism, using isobutanol as an example. He further pointed out this group’s co-metabolic ability significantly broadens the spectrum of organic compounds available to them. The geochemical studies [19,20] are consistent with the notion of co-metabolism of CH$_4$, they show that CH$_4$ does not serve as the principal carbon source for sulfate reducers, but that it may be used as a secondary carbon source. Since sulfate reducers are active in the Cariaco Trench and SO$_4^{2-}$ is the only likely oxidant, co-metabolism by sulfate reducers must be responsible for the anaerobic consumption of CH$_4$ observed.

The CH$_4$ sediment profiles are maintained by diff-
fusion of SO$_2^{2-}$ and CH$_4$ into a subsurface zone where co-metabolism of CH$_4$ occurs at a much higher rate than the CH$_4$ production rate. The sedimentation rate and organic carbon flux to the sediments appear to control the depth of the CH$_4$ consuming zone.

In the following schematic summary the numbers in parentheses are fluxes in μmole cm$^{-2}$ yr$^{-1}$. The sediment CH$_4$ and CO$_2$ fluxes are from eastern basin sediments.

| Depth (m) | CH$_4$ (μmole cm$^{-2}$ yr$^{-1}$) | CO$_2$ (μmole cm$^{-2}$ yr$^{-1}$) | SO$_4^{2-}$ (μmole cm$^{-2}$ yr$^{-1}$) |
|----------|----------------------------------|----------------------------------|----------------------------------------|
| 300      | 0.02–0.26                        |                                  |                                        |
| 1200     | 0.13–1.73                        |                                  |                                        |
| Sediment-Water Interface | CH$_4$ (100) | SO$_4^{2-}$ (31) |                          |
| 45       | 15.9                             | 55.9                             | 0                                      |

4.4 Methane source

The water column discussion (subsection 4.1) showed clearly that net consumption of CH$_4$ takes place in the mixing zone of the Carriaco Trench and that the CH$_4$ source for this zone lies below 1200 m. The sediment discussion (subsection 4.2) also showed consumption of CH$_4$ in a subsurface consuming zone. Mixing in the lower 200 m of the water column cannot be assessed with our present data, but anything other than consumption of CH$_4$ here seems unlikely. Methane concentrations in the surface 45 cm of the sediments are between 3- and 10-fold higher than those in the adjacent overlying water, suggesting that the sediments are the water column CH$_4$ source. However, a distinct concentration gradient is not evident. With a linear concentration gradient, CH$_4$ concentrations between 60 and 800 μmole 1$^{-1}$ are needed at depths of 45 cm to maintain the range of water column fluxes. These concentrations are easily observed with the sediment gas measurements.

The levels to which CH$_4$ may be co-metabolised by sulfate reducers are unknown at present. This knowledge, as well as more detailed and sensitive CH$_4$ measurements in the surface sediments, is needed to fully understand the transfer of CH$_4$ across the sediment-water interface.

5 Summary

A summary of CH$_4$ behavior in Carriaco Trench waters and sediments may be obtained by combining fluxes for CH$_4$ and CO$_2$ estimated from this study with organic carbon and SO$_4^{2-}$ fluxes estimated by Presley [33]. In the following schematic summary the numbers in parentheses are fluxes in μmole cm$^{-2}$ yr$^{-1}$. The sediment CH$_4$ and CO$_2$ fluxes are from eastern basin sediments.

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SO\textsubscript{4}\textsuperscript{2-} profiles for inspection. J E Dryden did the computer fitting. D K Button, D M Nelson and D T Heggie read and discussed the manuscript at various stages. I gratefully acknowledge all of these contributions. This work was supported by NSF grant GA-41209. Contribution number 259 from the Institute of Marine Science, University of Alaska.

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