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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

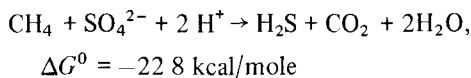
years, Richards [8] has summarized and reviewed these studies.

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 Pilson [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 $0.5 \text{ cm}^2 \text{ sec}^{-1}$. Fanning and Pilson 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 diffusion (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 Pilson 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. CO_2 reduction is regarded as the principal production pathway by some workers [11,12], while acetate fermentation is favored by others [1,13]. Inhibition of CH_4 production by SO_4^{2-} 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 $10^{-10.5} M$. 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 CH_4 with dissolved oxygen is reported to occur in lakes at rates up to $1 \mu\text{mole l}^{-1} \text{hr}^{-1}$ [17]. An oxidizer other than dissolved oxygen must be responsible for CH_4 consumption reactions in anoxic environments. Oxidation by SO_4^{2-} by the general reaction



is thermodynamically possible [18] and sulfate reducers capable of oxidizing CH_4 and other hydrocarbons have been cultured [19]. However, jar experiments using coastal sediments showed no detectable CH_4 consumption [14] and Sorokin [20] found no evidence of CH_4 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 CH_4 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

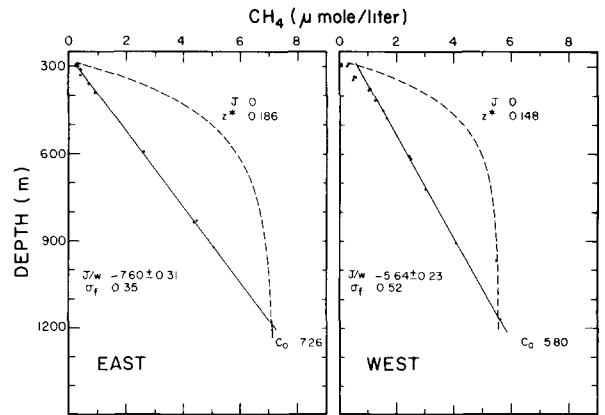


Fig 1 Methane data versus depth for eastern and western basin Cariaco Trench stations. Solid lines are linear SNC fits ($J \neq 0$) to the data using the average of points below 1200 m as C_0 . Dashed lines are SC ($J = 0$) profiles calculated using the mean of T_p^- and S^- derived z^* (Fig 5). Fits and calculations over the depth interval 290–1200 m. σ_f calculated from CH_4 residuals.

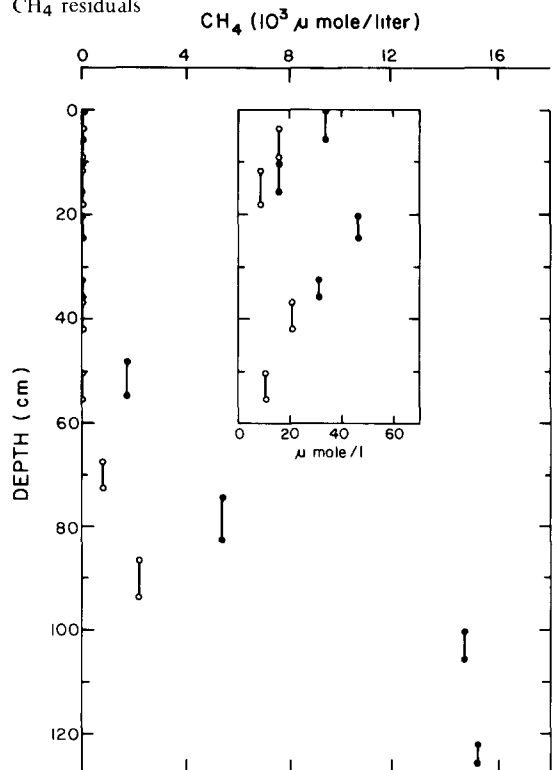


Fig 2 Methane data versus depth in Cariaco Trench sediments. Closed circles are eastern basin data, open circles are western basin data. Line connecting points is the depth interval of sediment core sampled. The inset shows CH_4 data from the top 60 cm of each core replotted on expanded concentration scale. Inset depth scale is unchanged.

[24] 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 Cariaco 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 ex-

ceeded the maximum use temperature (30°C) of the Apiezon 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

$$KC'' - wC' + J = 0 \quad (1)$$

where K is the vertical eddy diffusion coefficient ($\text{cm}^2 \text{sec}^{-1}$), w is the vertical advective velocity (length yr^{-1}), J is a reaction rate term ($\mu\text{mole l}^{-1} \text{yr}^{-1}$), C is the concentration ($\mu\text{mole l}^{-1}$) and the primes derivatives with respect to depth, which is positive upward. Eq. 1 has the solution for constant J

$$C - C_0 = (C_m - C_0)f(z) + (J/w)[z - z_m f(z)] \quad (2)$$

where $f(z) = (e^{z/z^*} - 1)/(e^{z_m/z^*} - 1)$, C_0 is the concentration at the lower ($z = 0$) boundary, C_m is the concentration at the upper ($z = z_m$) boundary and z^* is the ratio K/w . For a conservative parameter, $J = 0$.

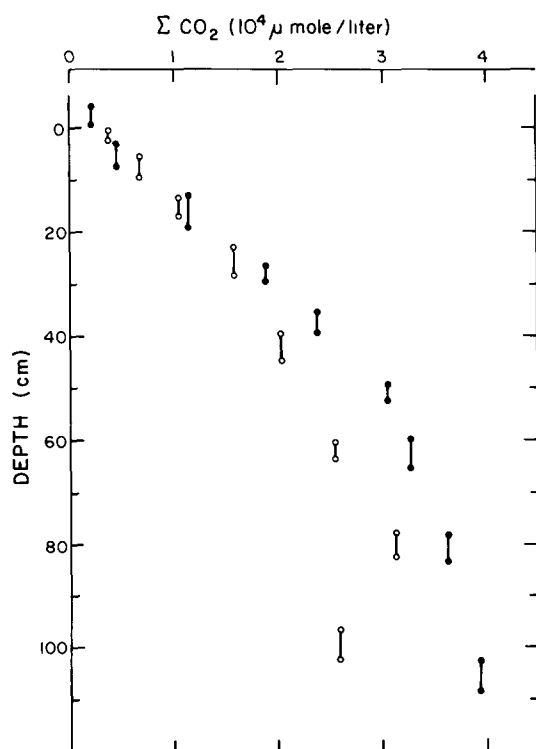


Fig. 3 Total CO₂ data versus depth in Cariaco Trench sediments. Symbols for total CO₂ are as in Fig. 2.

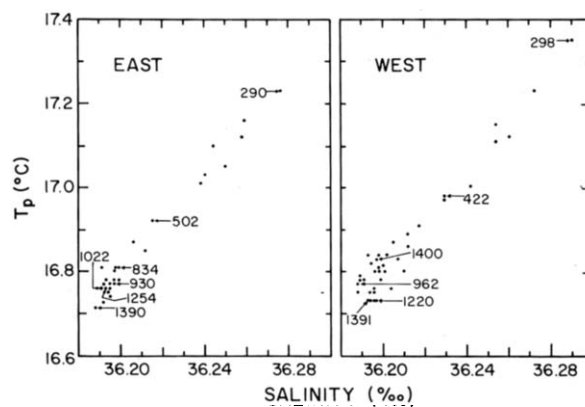


Fig. 4 Potential temperature-salinity diagrams for eastern and western basin Cariaco Trench stations. Depths (m) shown for various points.

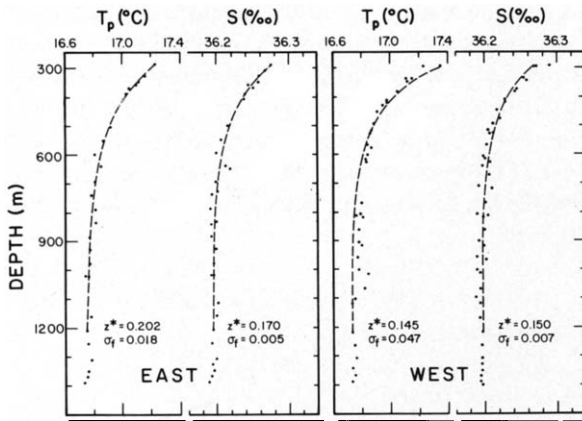


Fig 5 Potential temperature and salinity profiles versus depth for eastern and western basin Cariaco Trench stations. Dashed lines are least squares fits to the SC equation over the depth interval 290–1200 m. z^* values and σ_f calculated from the T_p and S residuals are adjacent to the plots

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

$$J/w = (C_m - C_0)/z_m \quad (3)$$

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 ± 0.31 and $-5.64 \pm 0.23 \mu\text{mole l}^{-1} \text{ km}^{-1}$. 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 1.13×10^{-3} to $1.52 \times 10^{-2} \mu\text{mole l}^{-1} \text{ yr}^{-1}$.

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

$$\Phi = wC_0 - KC'_0 = w[C_0 - z^*C'_0] \quad (4)$$

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

$$\Phi = w[C_0 - z^*J/w] \quad (5)$$

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 $\mu\text{mole cm}^{-2} \text{ yr}^{-1}$.

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, Φ_0 , equals $-J(z_m + z^*)$. The upward CH_4 flux out of the zone, Φ_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

$$\Phi = -D_s dC/dz \quad (6)$$

where Φ is the flux ($\mu\text{moles cm}^{-2} \text{ yr}^{-1}$), D_s is an interstitial diffusion coefficient (molecular diffusion corrected for tortuosity) and 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 ($3 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} = 94.5 \text{ cm}^2 \text{ yr}^{-1}$), CH_4 fluxes to the consuming zone in

eastern and western basin sediments are estimated to be 15.9 and 5.48 $\mu\text{mole cm}^{-2} \text{ yr}^{-1}$. If consumption is uniform in a 10 cm thick zone, this flux corresponds to CH_4 consumption rates of 1.59 and 0.55 $\text{mmole l}^{-1} \text{ yr}^{-1}$ 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 ω 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 $\mu\text{mole l}^{-1} \text{ yr}^{-1}$ 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. Mechals [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 dif-

fusion of SO_4^{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.

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 $\mu\text{mole cm}^{-2} \text{yr}^{-1}$. The sediment CH_4 and CO_2 fluxes are from eastern basin sediments.

	300 m	$\text{CH}_4 \uparrow (0.02-0.26)$		

	1200 m	$\text{CH}_4 \uparrow (0.13-1.73)$		

	sediment-water interface	organic C \downarrow (100)	$\text{SO}_4^{2-} \downarrow$ (31)	

	45 cm	$\text{CH}_4 \uparrow$ (?)	$\text{CO}_2 \uparrow$ (55.9)	
		$\text{CH}_4 \uparrow$ (15.9)	$\text{CO}_2 \uparrow$ (15.0)	$\text{SO}_4^{2-} \downarrow$ (0)
				CH_4 consuming zone

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 Cariaco 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 $\mu\text{mole l}^{-1}$ 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 Cariaco Trench waters and sediments may be obtained by combining

The upward fluxes of CH_4 and CO_2 below the CH_4 consuming zone are near equal, which is expected for formation of CH_4 by acetate fermentation. With carbohydrate as substrate, sulfate reduction releases 2 moles of CO_2 for each mole of SO_4^{2-} reduced, if CH_4 is oxidized, the stoichiometry is 1:1. Co-metabolism of CH_4 by sulfate reducers accounts for about half of the downward SO_4^{2-} flux and for 25% of the upward CO_2 flux in the surface sediments. This CO_2 may be an important source of isotopically light CO_2 to the deep waters of the Cariaco Trench [39]. It appears that about 40% of the organic carbon flux is preserved in the sediments. The upward flux of CH_4 to the water column, although not clearly identified, may be maintained by 1-10% of the CH_4 flux to the sediment consuming zone. Consumption reactions in the mixing zone of the water column require 85% of the water column flux. This anaerobic metabolism of CH_4 by sulfate reducers suggests that H_2S is probably not conservative in the water column.

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SO₄²⁻ 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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