Methane sources, distributions and sinks from California coastal waters to the oligotrophic North Pacific gyre

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Abstract

The mechanisms regulating the distributions of dissolved methane in North Pacific Ocean waters were investigated. Water column and sediment trap samples were collected in representative oceanic provinces ranging from the high productivity coastal waters of central California to the oligotrophic ocean near Hawaii. Methane was supersaturated in surface waters throughout the study area with values ranging from 105 to 175%, relative to equilibrium with atmospheric methane. Generally, the greatest supersaturations were found in coastal areas. The methane concentrations in oceanic waters off Hawaii are largely determined by in-situ production and air–sea gas exchange. Near the California coast, sediment and near-bottom inputs become important as potential sources of methane to the water column.

Methane measurements in preserved and unpreserved sediment trap solutions documented a sinking particle-associated methane source that was most apparent in the upper 200 m of the water column, and that tended to increase towards the surface and with distance from shore. The exact source of the methane accumulating in the traps could not be determined, but the trap data are consistent with a net in-situ production occurring in surface water microhabitats and, perhaps, macrozooplankton intestinal tracts. In the oligotrophic waters near Hawaii, this novel methane source term may be the most important in-situ process and may help resolve the previously described upper water column methane supersaturation paradox.

1. Introduction

Dissolved methane concentrations in surface ocean waters are typically supersaturated with respect to atmospheric equilibrium. The magnitude of the “excess” methane generally decreases with distance offshore (Lamontagne et al., 1973; Scranton and Brewer, 1977; Traganza et al., 1979; Brooks et al., 1981; Burke et al., 1983). These methane supersaturations have been attributed to in-situ biological methane production

(Lamontagne et al., 1973; Scranton and Brewer, 1977; Traganza et al., 1979; Brooks et al., 1981; Burke et al., 1983; Cynar and Yayanos, 1991) and, in selected habitats, to methane inputs from sediments (Scranton and Farrington, 1977). Although methanogenic bacteria are obligate anaerobes (Wolfe, 1971), methane production apparently occurs in oxygenated seawater. This has recently been termed “the oceanic methane paradox” (Kiene, 1991).

Potential sites for methane production in the oxygenated water column include reducing micro-environments in fecal pellets, suspended particles,

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and the intestinal tracts of zooplankton or other marine animals (Scranton and Brewer, 1977; Alldredge and Cohen, 1987; Paerl and Prufert, 1987). Scranton and Brewer (1977) suggested that methane in the euphotic zone could be a by-product of phytoplankton metabolism, but it now appears likely that methanogenic bacterial consortia are responsible for this “algal” production (Sieburth, 1991).

Tragana et al. (1979) reported a correlation between zooplankton biomass (measured as ATP in the 333–1800 μm size fraction) and methane in the tropical North Atlantic, and suggested that methane may be derived from zooplankton metabolism. Oremland (1979) measured net methane production in $> 164 \mu\text{m}$ plankton samples and in the intestines of fish from San Francisco Bay that were incubated with known methanogenic substrates under anaerobic conditions. More recently, methane production has also been documented following anaerobic incubations of collections of suspended and sinking particles, and freshly egested zooplankton fecal pellets (Bianchi et al., 1992; Marty, 1993). In these latter studies, additions of methanogenic substrates generally enhanced methane production in these enrichment culture experiments. Cynar and Yayanos (1991) isolated a methanogenic bacterium, *Methanococcoides methylutens*, from plankton samples collected off Southern California. Methane, ATP and chlorophyll *a* maxima were sometimes correlated in profiles from the Gulf of Mexico (Brooks et al., 1981) and the eastern tropical North Pacific (Burke et al., 1983). Brooks et al. (1981) and Burke et al. (1983) also reported correlations between methane and total suspended matter for some water column profiles, and suggested that methanogenesis may be occurring in association with suspended particulate matter.

For waters overlying the continental shelves, sources other than in-situ production are likely to contribute to methane in the water column. Potential sources in these waters include seeps (Bernard et al., 1976; Reed and Kaplan, 1977), organic-rich sediments (Martens and Berner, 1974; Martens and Klump, 1980), inputs of methane-rich freshwaters (Sackett and Brooks, 1975; Cline et al., 1986) and inputs associated

with oil and gas production (Sackett and Brooks, 1975). Seasonal variations of methane concentrations in bottom waters of the Bering Sea shelf (Cline et al., 1986) and high methane concentrations in waters immediately above anoxic shelf sediments near Walvis Bay, Namibia (Scranton and Farrington, 1977) are considered indicative of methane inputs from sediments.

In spite of these numerous potential sources for the water column, the precise mechanism for the near-surface ocean methane supersaturations has been difficult to elucidate. Several recent studies have described the potential importance of rapidly sinking particles as a previously undescribed potential methane source term (Bianchi et al., 1992; Marty, 1993; Karl and Tilbrook, 1994). However, with the exception of the experiments conducted by Karl and Tilbrook (1994), in-situ rates of methane production have not been measured. This present study provides a more comprehensive analysis of their preliminary observations and presents a quantitative assessment of the importance of these processes to the upper water column methane cycle in the North Pacific Ocean.

2. Materials and methods

2.1. Water column sampling and analyses

Field samples were collected at a series of stations from coastal California to the central North Pacific during the Vertical Transport and Exchange (VERTEX) and Office of Naval Research (ONR) research programs, and in the central North Pacific gyre during the Asian Dust In Oceanic Systems (ADIOS) study (Fig. 1). All water samples were collected using PVC Niskin[®] bottles mounted on a General Oceanics[®] rosette that included a SeaBird[®] CTD. Temperature measurements obtained from the CTD were calibrated using reversing thermometers. Conductivity measurements were calibrated by discrete water sample measurements of salinity using a Guildline salinometer and IAPSO standard seawater. Oxygen concentrations were determined by modified Winkler titration (Strickland and Parsons, 1972),

Fig. 1. Location of the VERTEX, ONR, and ADIOS sampling sites.

and dissolved inorganic nutrient concentrations were measured by autoanalyzer techniques (Strickland and Parsons, 1972).

Water samples for methane determinations were transferred from Niskin[®] bottles into 250 ml borosilicate glass bottles using tygon tubing, preserved with 1 ml of a saturated solution of HgCl_2 , and sealed. All methane samples were returned to shore for analysis. Experiments, reported elsewhere, have shown that poisoned samples can be stored for at least one year without producing any measurable change in methane over the concentration range of samples analyzed in this study (Tilbrook and Karl, 1994). Methane was measured by gas chromatography, using a gas stripping and concentration method (Swinnerton and Linnenbom, 1967). Dissolved methane and other gases were purged from a predetermined volume (172 ml) of sample by bubbling with methane-free helium (7 min at 100 ml min^{-1}). The purged gases were passed through Drierite[®] and Ascarite[®] traps to remove water vapor and carbon dioxide, respectively. Methane was then concentrated onto a 80–100 mesh Porapak Q[®] filled stainless steel trap, cooled to liquid nitrogen temperature. After completion of the stripping procedure, the Porapak Q[®] trap was transferred from liquid nitrogen to a boiling water bath, and the released methane was automatically injected into a Hewlett-Packard 5890 gas chromatograph. A 80–100 mesh Porapak Q[®] chromatographic

column (3 m $\times$ 3.2 mm O.D.) and flame ionization detector (FID) were used for separation and detection of methane, respectively. The FID response was calibrated using a 23 ppm (by volume) methane-in-helium standard (Air Products and Chemicals). The detection limit for methane analysis using this system was approximately 0.05 nM, and the precision of repeated analyses of samples was $\pm 3\%$. The concentration of dissolved methane in equilibrium with the atmosphere was calculated from data on the temperature and salinity of the surface water, using the solubility equations of Wiesenburg and Guinasso (1979). Supersaturation refers to a dissolved methane concentration that exceeds the concentration expected if the water was in equilibrium with atmospheric methane.

2.2. Sediment trap sampling and analyses

Free-floating MULTITRAP arrays (Knauer et al., 1979) were used to collect sinking particles during each of the three separate field studies. During the VERTEX cruise, methane samples were obtained from traps deployed at the following Stations (and time periods):

- #1, 35.8°N, 122.6°W (4–17 June 1984);
- #2, 35.8°N, 128.2°W (5–27 June 1984);
- #4, 33.3°N, 139.1°W (7–29 June 1984).

For each array, traps were deployed at a total of six depths between 50 and 2000 m. At ONR Station #8 (35.8°N, 122.6°W), traps were positioned at 80 and 175 m between 1–13 May 1985 during a separate cruise just prior to the ONR expedition. ADIOS sediment traps were positioned at 30, 120 and 200 m, and were deployed at 26°N, 155°W during three consecutive periods: 24–31 March 1986 (A-I), 31 March–12 April 1986 (A-II) and 14–17 April 1986 (A-III).

For each deployment, the sediment traps were filled with an autoclaved high density salt solution (0.22 μm filtered surface seawater enriched with 27.1 g NaCl, 11.4 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and 0.74 g KCl l^{-1}) that was used to restrict diffusion losses of methane during deployment and to eliminate trap flushing during recovery. The chloride concen-

tration of the trap solutions, therefore, is about twice that of the surrounding seawater. Because chloride is unreactive, changes in the chloride concentration of the trap solutions over the deployment period can provide information on the exchange of dissolved material between the traps and the surrounding seawater.

During the A-I sediment trap experiment, chloride concentrations were measured by potentiometric titration of the sample with a 0.1 N AgNO_3 solution (Jagner and Aren, 1970). The amount of sample (~ 0.2 ml) was determined by weight, and 1.0 ml of a 5 M solution of NaNO_3 was added to each sample to minimize changes in the ionic strength of the solution caused by the addition of titrant. The sample was diluted to 50 ml with distilled water and a silver/silver sulphide electrode (Orion model #94-16) and a double junction reference electrode (Orion model #92-02) were used to measure the change in potential during the titration. The end-point was calculated by applying a Gran linearization to the data. IAPSO seawater was used as a standard, and the precision of repeated analyses was ± 0.1 per mil. Seawater chloride concentrations were calculated from salinity values assuming: $\text{chloride} [\text{g kg}^{-1}] = \text{salinity}/1.80655$.

Baffles were fixed to the top of each sediment trap to minimize mixing between the salt solutions and the ambient seawater. A 335 μm Nitex screen was placed at the base of each of the baffles to prevent zooplankton, and other large organisms, from swimming into the traps and potentially contaminating the traps with methane.

The concentrations of dissolved methane in the trap solutions after recovery were measured to assess the association of methane with particles settling into the traps. All the traps sampled during VERTEX were unpreserved, but for the ONR and ADIOS experiments methane was measured in both control traps with no preservative and in traps "poisoned" with either buffered formalin (5% v/v final concentration) or HgCl_2 (0.25% v/v saturated solution) added to the trap solutions prior to deployment (Karl and Tilbrook, 1994). Immediately after recovery, seawater overlying the high density trap solutions was removed, and the brine solutions were gently mixed using a polycarbonate

plunger assembly designed to prevent gas exchange with the atmosphere. Methane samples were then siphoned into 250 ml glass bottles and analyzed, as described above. With the exception of the VERTEX study, initial methane concentrations were also determined by sampling the trap solutions just prior to trap deployment (i.e. the time zero sediment trap solution methane concentration). For VERTEX we used a value of 5.2 nM to correct the final trap solutions for time zero methane concentration.

2.3. Abiotic methane production

Sediment trap collector tubes, identical to those used for the in-situ experiments, were acid washed and filled to just below the baffle with an autoclaved salt solution, as above, and sealed with end caps. The sealed tubes were then covered by a few centimeters of seawater and exposed to either direct sunlight, 18% of surface irradiance by shading with neutral density filters, or kept in the dark for periods that corresponded to trap deployment times in the field (up to 22 days). The 18% light level was chosen because it corresponds to the shallowest deployment depth (30 m) used for the ADIOS experiment. A similar experiment was carried out in the field by deploying sealed traps at 30 m depth for three days in the oligotrophic North Pacific at 23°N, 158°W. One half of the traps were covered with duct tape to exclude light and the other half were left clear.

Dissolved methane did increase in the salt solutions of tubes exposed to direct sunlight (5–8 nM increases over 14 d), while tubes incubated in the dark or at the 18% light level showed only small and apparently random variations. These results argue for some unknown photochemical source, although other processes such as adsorption and desorption onto the tube surfaces may also contribute to the changes.

The role of abiotic methane production in our field results is apparently negligible. None of the traps deployed in the field were positioned at light intensities above a depth corresponding to 18% of surface irradiance and most were below the euphotic zone. Furthermore, the increases in methane concentrations that were measured in

Fig. 2. Salinity (S) vs. temperature (T) plot for stations sampled during the VERTEX expedition. The station numbers are given at top of each S - T line.

these experimental incubations were, at most, only about 10% of those typically measured in the surface-most traps. Based on these results, it would appear reasonable to consider the background methane levels measured in the tubes exposed to surface light intensity as inconsequential to the interpretation of our field measurements.

3. Results

3.1. Hydrography

Station #1 of the VERTEX transect is located in the California Current where salinities are typically less than about 33.1‰ and temperatures range from 12 to 13°C in the upper 100 m of the water column (Fig. 2). The shoaling of temperature, salinity, σ_θ and oxygen isolines near Station #1 (data not presented) is suggestive of upwelling along the California Coast. VERTEX Station #2, located near the western edge of the California Current, has similar T - S characteristics although slightly warmer surface waters (Fig. 2). Further west, mixed-layer salinities at Station #4 increase to

Fig. 3. Salinity (S) vs. temperature (T) plot for stations sampled during the ONR cruise off coastal California. The station numbers are given at the bottom of each S - T line.

about 34.5‰ in the central North Pacific gyre (Fig. 2). The waters between about 300 and 500 m at Station #4 reveal a salinity minimum of approximately 34‰ that is associated with subarctic water (Martin et al., 1985). This low-salinity layer is produced by the subduction of relatively fresh waters from the northeastern portion of the North Pacific gyre below more saline waters to the south (Talley, 1985). The waters at Station #3 are in a transition zone between the fresher, cooler waters of the California Current and the warmer, saltier waters of the central North Pacific gyre to the west with some interleaving of these two water masses (Fig. 2).

The waters sampled during the ONR cruise are situated in the California Current and extend from the position of VERTEX Station #1 eastward toward the California Coast (see Fig. 1). The potential density section for this transect shows little evidence for upwelling, except for a slight uplift of isopycnals near the continental shelf (data not shown). The waters at each of the ONR transect stations have similar T - S properties indicating that all four stations are all located within the same hydrographic regime (Fig. 3).

Fig. 4. Vertical profiles of methane and water density (expressed as the density anomaly, σ_θ) at three VERTEX stations. CH_4eq is the predicted concentration of dissolved methane for seawater in equilibrium with the atmosphere. Station locations and sampling dates are: [Left] Station #1 (35.8°N, 122.6°W) 14 June 1984; [Center] Station #2 (35.1°N, 128.2°W) 24 June 1984; [Right] Station #4 (33.3°N, 139.1°W) 30 June 1984.

The hydrographic properties of the upper water column at the ADIOS sample site are typical of waters in the central North Pacific gyre. A broad shallow salinity minimum was evident between about 300 and 650 m depth with a core salinity of 34.02‰ at about 570 m. The surface mixed layer at the ADIOS site was characterized by fairly isothermal and isohaline conditions with temperatures between 20.0 and 20.4°C, and a salinity of about 35.34‰. Nutrients were typically depleted ($\text{NO}_3 < 0.05\mu\text{M}$, $\text{PO}_4 < 0.03\mu\text{M}$) to well below the base of the mixed layer. The upper 600 m of the water column was well oxygenated with a broad oxygen minimum zone extending between about 600 and 2000 m depth (data not shown).

3.2. Methane profiles

Methane concentrations in the near surface waters along the VERTEX transect were at, or above, atmospheric equilibrium concentrations with surface values ranging between 105 and 132% (Figs. 4 and 5). The largest supersaturations are found at Station #1, where a distinct subsurface

methane maximum is apparent in the upper pycnocline at approximately 150 m. Methane concentrations up to 5.42 nM (twice atmospheric saturation) were measured in this maximum. Station #2 also shows a methane maximum, but the maximum concentration is only 4.07 nM (160% atmospheric saturation). No subsurface maximum is apparent at Station #4. Below 300 m, no inshore–offshore trends in methane concentration are apparent (Fig. 5).

The methane concentrations along the ONR transect indicate only a weak onshore-to-offshore gradient (Fig. 6). The highest methane concentration measured was 15.9 nM for a sample collected near the seafloor at the continental shelf break. This suggests a near bottom or sediment source in the region. Offshore from Station #7, a subsurface methane maximum is apparent at about 100 m. ONR Station #8 is at the same location as VERTEX Station #1 and the maximum concentrations were similar (5.44 vs. 5.42 nM for ONR and VERTEX, respectively), despite the fact that they were sampled 1 year apart.

The methane concentrations for samples col-

Fig. 5. Dissolved methane concentration (nM) section for VERTEX Stations #1–4 (June 1984), for a transect from the coast of California to the oligotrophic North Pacific Ocean.

lected in the mixed layer (0–100 m) at the ADIOS sampling site ranged between 111 and 126% saturation of the respective atmospheric equilibrium values (Fig. 7). This degree of supersaturation is consistent with the 105–130% values observed in other open ocean surface waters (Conrad and Seiler, 1988). The variations measured at the ADIOS site show no trend with time over the 2 week period and, probably, reflect a combination of analytical uncertainty and natural variability. Below 500 m methane was undersaturated, as anticipated from previous studies (Scranton and Brewer, 1978; Cynar and Yayanos, 1991).

3.3. Sediment trap data

Chloride

The concentrations of chloride measured in the formalin preserved ADIOS trap solutions showed variable, but minimal, losses during the deployment period. Loss of chloride was greatest in the shallow trap (30 m), but amounted only to a 5.6% change. These data suggest that the high density salt solutions do not readily mix with overlying seawater. This conclusion is consistent with radiochemical mass balances of exogenous tracers measured in similar free-drifting sediment trap arrays (Karl and Knauer, 1984).

Methane

Methane concentration measurements made on

Fig. 6. Dissolved methane concentration (nM) section for ONR Stations #5–8 (June 1985), for a California coastal transect.

sediment trap solutions showed that methane accumulated in the traps over time. Generally, the methane accumulations were greatest in the shallow traps and increased with distance from shore

Fig. 7. Composite plot of dissolved methane concentrations in the upper 500 m of the water column at the ADIOS site (26°N, 155°W) measured during the period 3–16 April 1985. The station numbers refer to individual hydrocasts taken during this expedition.

Table 1
Methane accumulations in unpreserved sediment traps deployed during the VERTEX cruise

Station #	Depth (m)	Methane accumulation ^c (nmol l ⁻¹)	Methane flux (nmol m ⁻² d ⁻¹)
V – 1 ^a	100	1.1	18.9
	225	1.2	19.8
	450	1.0	18.9
	900	0.1	1.8
	1500	< 0.1	< 1.5
V – 2 ^a	130	5.3	111.8
	300	2.2	47.5
	600	0.9	20.4
	750	< 0.1	< 1.5
	1000	1.1	24.2
	1500	< 0.1	< 1.5
V – 4 ^b	50	33.1	1097
	150	10.0	322.3
	275	4.2	135.4
	600	0.3	9.3
	750	< 0.1	< 1.5
	1000	1.3	39.5
	1500	0.2	6.4

^a Traps deployed for 21.75 d.

^b Traps deployed for 14 d.

^c Measured methane concentration corrected for the time zero methane blank which was determined to be 5.2 ± 1.1 ($n = 14$) nmol l⁻¹ of trap solution.

(Tables 1–3). The largest methane accumulations, 2–6 nmol trap⁻¹ d⁻¹, were measured in the 30 m traps at the ADIOS site (Table 3). A comparison of methane accumulations in preserved and unpreserved traps deployed at both the ONR (Station #8) and ADIOS sites showed comparable methane accumulations (Tables 2 and 3).

For the VERTEX transect, the greatest methane accumulation occurred in the surface trap at Station #4, which had the smallest particulate organic matter fluxes of all the stations sampled (Karl and Tilbrook, 1994; Table 1). If the average deep-water sediment trap methane concentration of 5.20 nM is taken as the methane initially in the solution (i.e. a “blank”), then the average daily methane accumulation in the 50 m trap at VERTEX Station #4 is 4.27 nmol trap⁻¹ d⁻¹. If a blank correction is not applied, then the accumulation would be 4.94 nmol trap⁻¹ d⁻¹. These methane accumulation rates are similar to the

average accumulation of 3.96 ± 1.07 nmol trap⁻¹ d⁻¹ for the 30 m traps at the ADIOS site, which is also situated in oligotrophic North Pacific waters. The smallest change with depth in the methane concentrations occurred at Station #1. VERTEX Station #1 is at the same location as the ONR sediment trap site (Station #8), and the data from both cruises indicate that there is little variability with depth in the amount of methane accumulated in the traps at this site (Tables 1 and 2). The data collected at the VERTEX sites are consistent with the methane accumulations observed at ADIOS and ONR sites, and suggest that methane accumulations in the traps increase towards the surface and with distance offshore.

4. Discussion

4.1. Onshore-to-offshore transect

The VERTEX methane section shows a plume of methane-enriched water extending from the California coast into the central North Pacific Ocean (Fig. 5). As with the ONR data, coastal methane inputs, which are probably sediment derived, are likely to influence the inshore–offshore gradients. With increasing distance from the source, air–sea gas exchange and diffusion decrease the methane concentrations, while some combination of in-situ methane production and diffusive or advective inputs from coastal waters supply methane to the upper ocean waters. The potential for advection having an influence on the methane distributions is perhaps best seen at VERTEX Station #3 (Fig. 5). At this location, a core of relatively fresh water from the California Current surrounded by saltier North Pacific gyre water occurs between about 125 and 225 m. The $T-S$ diagram (Fig. 2) also shows interleaving with the core of the cooler, and fresher, subsurface layer having a σ_θ of 25.7. Based on the regional methane distributions described above, the methane concentrations in the coastal waters of the region are greater than in the open ocean waters and the interleaving of these water masses may be responsible for producing the weak subsurface maximum in methane at Station #3 (Figs. 4 and 5).

Table 2

Methane accumulations in preserved and unpreserved sediment traps deployed between 1 and 13 May 1985 at the ONR Station #8

Depth (m)	Sediment trap #	Treatment	Methane accumulation (nmol trap ⁻¹ d ⁻¹)	Methane flux ^b (nmol m ⁻² d ⁻¹)
80	A-1	Formalin	0.93	238.5
	A-2	Formalin	0.74	189.7
	A-3	HgCl ₂	0.66	169.2
			0.78 ± 0.14 ^a	199 ± 36
80	A-4	None	0.72	184.6
	A-5	None	0.48	123.1
	A-6	None	0.58	148.7
			0.59 ± 0.12	152 ± 31
175	B-1	Formalin	0.47	120.5
	B-2	Formalin	0.48	123.1
	B-3	HgCl ₂	0.58	148.7
			0.51 ± 0.06	131 ± 15
175	B-4	None	0.52	133.3
	B-5	None	0.52	133.3
	B-6	None	0.48	123.1
			0.51 ± 0.02	130 ± 5

^a Mean value ± 1 sd for preserved (formalin and HgCl₂) and unpreserved treatments.^b Average for all treatments; cross-sectional area of trap collection surface is 0.0039 m².

4.2. Oligotrophic gyre processes

Horizontal methane gradients were not measured around the ADIOS site but, based on the oceanic extension of the VERTEX section (Fig. 5) to the ADIOS site, there does not appear

to be a detectable horizontal methane concentration gradient in the central North Pacific Ocean. Consequently, horizontal diffusive and advective inputs of methane are probably negligible at the ADIOS site. The most probable cause of the supersaturations is in-situ production, and

Table 3

Total accumulated methane in formalin preserved and unpreserved sediment traps deployed at the ADIOS sampling site (26°N, 155°W)

Trap experiment #	Deployment period (d)	Trap depth (m)	Methane accumulation ^a (nmol trap ⁻¹ d ⁻¹)		Methane flux ^b (nmol m ⁻² d ⁻¹)
			Preserved	Unpreserved	
1	6.9	30	2.13	2.96	652.6
		120	0.62	0.78	179.5
		200	0.22	1.20	182.1
2	11.7	30	5.82	5.09	1399
		120	0.97	1.32	293.6
		200	0.74	1.14	241.0
3	3.1	30	3.26	3.84	910.3
		120	1.23	1.06	293.6
		200	1.29	1.06	301.3

^a Corrected for time zero methane concentrations.^b Average of preserved and unpreserved treatments; cross-sectional area of trap collection surface is 0.0039 m².

previous investigations of methane distributions have also concluded that in-situ production is required to support the supersaturations observed in the open ocean (Scranton and Brewer, 1977; Brooks et al., 1981).

The relative importance of each of the sources and sinks in determining the surface layer methane concentrations can be estimated by the application of a mass balance model. The methane supersaturations observed in the mixed layer support a net flux F ($\mu\text{mol m}^{-2} \text{d}^{-1}$) of methane to the atmosphere calculated as:

$$F = K_L \cdot (C_s - C_{\text{eq}}) \quad (1)$$

where K_L is a gas transfer coefficient (m d^{-1}), C_s is the concentration of methane in the surface layer ($\mu\text{mol m}^{-3}$), and C_{eq} is the estimated methane concentration ($\mu\text{mol m}^{-3}$) at equilibrium with the atmosphere. The value C_{eq} was calculated using the solubility equation of Wiesenburg and Guinasso (1979) and an atmospheric methane concentration of 1.70 ppm. The gas transfer coefficient (K_L) was calculated as:

$$K_L = 0.86U_{10} - 2.9; 4.2 < U_{10} < 18 \text{ m s}^{-1} \quad (2)$$

where K_L is normalized to methane at 20°C and U_{10} is the wind speed 10 m above the ocean surface (Barber et al., 1988). Based on averaged daily wind speeds of 8.4–15.1 m s^{-1} measured during ADIOS and an air–sea methane difference of 0.21–0.53 $\mu\text{mol m}^{-3}$, the calculated net sea-to-air flux of methane is 0.9–3.5 $\mu\text{mol m}^{-2} \text{d}^{-1}$, with a time averaged flux of methane to the atmosphere of 2.5 $\mu\text{mol m}^{-2} \text{d}^{-1}$.

The small methane maximum observed at the base of the mixed layer (Fig. 7) will result in a diffusive flux of methane into the surface layer. For an eddy diffusion coefficient of 1.8 $\text{cm}^2 \text{s}^{-1}$ (Li et al., 1984) and a methane concentration gradient of 0.0114 $\mu\text{mol m}^{-4}$ calculated between 98 and 119 m at Station #17, the diffusive flux of methane would be 0.2 $\mu\text{mol m}^{-2} \text{d}^{-1}$. This input accounts for only 8% of the estimated net flux of methane to the atmosphere. The samples were too widely spaced on other hydrocasts to determine if the subsurface maximum is a persistent feature, but subsurface methane maxima have been reported in other oceanic habitats (Scranton and Brewer, 1977).

Dissolved methane in the surface layer is consumed by microbial oxidation processes (Sieburth et al., 1987; Ward et al., 1987; Jones, 1991). Turn-over times associated with the microbial consumption of dissolved methane in the open ocean are long, and vary from 5 to > 100 yr, with an average of about 65 yr (Ward et al., 1987; Jones, 1991). For an average methane concentration of 2.39 nmol l^{-1} in the upper 100 m of the water column, the integrated methane consumption rate will be between 0.13 and 0.01 $\mu\text{mol m}^{-2} \text{d}^{-1}$ using the above-referenced turnover times. Based on an average turnover time of 65 years, the consumption rate is most likely to be on the order of 0.01 $\mu\text{mol m}^{-2} \text{d}^{-1}$. This rate is negligible compared to the losses associated with air–sea gas exchange.

The above mass balance calculation suggests that the distribution of methane in the surface mixed layer in the oligotrophic North Pacific is controlled by inputs from in-situ production and diffusion through the base of the mixed layer, and loss by air–sea gas exchange. Adding the various terms in the mass budget indicates that the methane supersaturations at the ADIOS site can be maintained if an integrated net methane production of 2.3 $\mu\text{mol m}^{-2} \text{d}^{-1}$ occurs over the approximately 100 m thick surface layer.

The source/sink relationships change radically for waters below the thermocline, where air–sea gas exchange does not directly influence methane concentrations. A net production is required to preserve the subsurface methane maximum sampled during ADIOS. Because these subsurface waters cannot directly exchange methane with the atmosphere, the rates of methane production needed to maintain the maxima are smaller than those in the surface mixed layer. For example, the diffusive flux of methane to the mixed layer from the maximum was calculated, above, to be 0.2 $\mu\text{mol m}^{-2} \text{d}^{-1}$. By comparison, the diffusive flux from the maximum to deeper water is 0.06 $\mu\text{mol m}^{-2} \text{d}^{-1}$, given the observed methane gradient of 0.0039 $\mu\text{mol m}^{-4}$ and an eddy diffusivity of 1.8 $\text{cm}^2 \text{s}^{-1}$ (Li et al., 1984). Consequently, the total diffusive flux away from the layer is 0.26 $\mu\text{mol m}^{-2} \text{d}^{-1}$. Assuming that production occurs over a 50 m thick subsurface

layer, then a net in-situ production rate of $0.005 \mu\text{mol methane m}^{-3} \text{ d}^{-1}$ could maintain the diffusive losses from the maximum. In the surface mixed layer, an average production rate of $0.023 \mu\text{mol m}^{-3} \text{ d}^{-1}$ is needed to maintain the observed supersaturations (see above). Higher rates of production would be necessary if the sub-surface methane production occurs over a narrower depth range. These calculations demonstrate that the methane concentration maxima that are often found at the base of the mixed layer in the open ocean are not necessarily the result of greater in-situ methane production rates. Instead, these maxima may simply result from air–sea gas exchange having no direct effect on the methane balances below the mixed layer.

4.3. Particle-associated methane

As emphasized above, in-situ production appears to be the major source of methane in open ocean surface waters. A number of studies have attempted to determine the sites of methane production by correlating dissolved methane distributions with variables such as total suspended matter, zooplankton biomass and chlorophyll *a*. However, no consistent associations have been observed, which could result in part from an air–sea exchange influence on the dissolved gas distributions. This physical process would not be expected to affect biomass or particulate matter distributions.

The requirement for anaerobic microenvironments is crucial to the survival of methanogenic bacteria in the well-oxygenated waters of the upper ocean. Oxygen depletions have been reported for aggregates in near-surface waters (Alldredge and Cohen, 1987; Paerl and Prufert, 1987; Paerl, 1989), but it is not clear if the extreme reducing conditions needed for methanogenesis can exist in these aggregates. Other evidence for the existence of anoxic microzones is less direct. Recent investigations demonstrating the presence of methanogenic bacteria (i.e. the “potential” for methane formation) in sediment trap-collected particulate matter and in fecal pellets (Bianchi et al., 1992; Marty, 1993) support the potential for a local methane source but cannot be extrapolated to

methane production rates. In-situ accumulations of methane in preserved and unpreserved sediment traps (Karl and Tilbrook, 1994; Tables 1 and 2), however, provide evidence that methane production does occur within particles in the epipelagic zone of the ocean. For the 50–100 m depth interval of the oligotrophic North Pacific gyre site, a conservative estimate of the input of methane from sinking particles to the water column is $4\text{--}8 \text{ nmol m}^{-3} \text{ d}^{-1}$ (Karl and Tilbrook, 1994). This minimum value is approximately 15–30% of the total required to sustain the mass balance, discussed above, and it is probable that methane production from all suspended and sinking particles exceeds this estimate (Karl and Tilbrook, 1994). This result does not resolve the production mechanism, but does help identify a possible source for methane for the upper water column.

4.4. Establishment and maintenance of the prerequisite anaerobic conditions

Although it now appears that the methane supersaturations that are ubiquitous in the world ocean may be controlled, in part, by sinking particle-associated methane, both the site and mechanism of initial methane production are still open to question. Model calculations of Jørgensen (1977) and Jumars et al. (1989) indicate that high rates of oxygen consumption are needed to maintain anaerobic conditions in oceanic particulate matter. Jørgensen (1977) used a sphere to represent a hypothetical particle, and constructed a simple steady-state model of oxygen diffusion and consumption as:

$$D_s(1/r^2)(d/dr)[r^2(dC/dr)] - p = 0 \quad (3)$$

where D_s is the molecular diffusivity of oxygen, r is the radius of the sphere, C is the oxygen concentration, and p is the rate of oxygen consumption. The latter was assumed constant throughout the sphere. To obtain anaerobic conditions in the center of the sphere at $r = 0$, and for the sphere of radius $= b$, the equation solution is:

$$C_0 = (p/6D_s)b^2 \quad (4)$$

If we solve this equation for conditions character-

Table 4

Changes in dissolved and particulate components in MULTITRAPS deployed at the ADIOS sampling site

Station #	Trap depth (m)	Deployment period (d)	CH ₄ (nmol trap ⁻¹)	O ₂ (μmol trap ⁻¹)	POC ^a (μmol trap ⁻¹)
A – I	30	6.9	20.4	–60.6	155.6
	120		5.4	–28.2	112.0
	200		8.3	0 ^b	120.6
A – II	30	11.7	59.6	–141.8	302.2
	120		15.4	– ^c	241.5
	200		13.3	–25.6	168.2
A – III	30	3.1	11.9	–32.4	173.3
	120		3.8	–26.4	230.9
	200		4.0	–17.0	108.6

^a POC data from Laws et al. (1989).^b Less than 3.0 μmol trap⁻¹.^c Sample lost.

istic of the ADIOS site (i.e. $C_0 = 0.23 \mu\text{mol cm}^{-3}$ and $b = 0.015 \text{ cm}$) and assume D_s is $2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Jorgensen, 1977), then the center of a particle would only become anaerobic if the oxygen consumption rate was equal to, or exceeded, $0.15 \mu\text{mol cm}^{-3} \text{ s}^{-1}$.

Anaerobic conditions have been reported for a fecal pellet with a radius of 0.021 cm that was attached to marine snow (Alldredge and Cohen, 1987). The external oxygen concentration in their experiment was $0.5 \mu\text{mol l}^{-1}$, and the oxygen consumption calculated using the above equation is $0.17 \mu\text{mol cm}^{-3} \text{ s}^{-1}$. This consumption rate is similar to the rate estimated to maintain anaerobic conditions in the 0.015 cm radius particles. However, other particles sampled by Alldredge and Cohen (1987) showed only partial oxygen depletions and the anaerobic conditions they described in the one fecal pellet may not have been entirely representative.

We estimated the net oxygen consumption rates of the sedimenting particulate matter at the ADIOS site by direct measurements of the dissolved oxygen concentrations in unpreserved sediment trap solutions following three consecutive short-term (3–12 d) deployments (Table 4). The largest oxygen depletion measured, 142 μmol in the 30 m trap during deployment II, implies an average consumption rate of $6.9 \times$

$10^{-4} \mu\text{mol cm}^{-3} \text{ s}^{-1}$, if the carbon: volume ratio for the particles in the trap is $2.2 \mu\text{mol C mm}^{-3}$ and the total carbon collected in the trap is 444 μmol C (POC accumulation + O₂ depletion; Table 4). This rate of oxygen consumption is clearly too low, by several orders of magnitude, to maintain anaerobic conditions in particles with a 0.015 cm radius. If the oxygen consumption rate is taken as $6.9 \times 10^{-4} \mu\text{mol cm}^{-3} \text{ s}^{-1}$, and values of D_s and C_0 are assumed to be the same as above, then only particles with radii $\geq 0.22 \text{ cm}$ could become anaerobic. A decrease in D_s , as might result from solids in the particulate matter causing an increase in the path length for diffusion of dissolved constituents into or out of the particles, could theoretically decrease the oxygen consumption rate required to produce anaerobic conditions. However, even sediments with a high tortuosity rarely show decreases in D_s of more than a factor of two (Berner, 1980).

Based on the above calculations, it appears that the anaerobic conditions necessary for bacterial methanogenesis cannot readily exist in the small ($< 150 \mu\text{m}$), freely-suspended particles that are present in the ocean and that we collected in our in-situ sediment trap experiments. This conclusion is supported by the similarity in methane concentrations in preserved and unpreserved traps (Tables 2 and 3; Karl and Tilbrook, 1994). The calculations

also suggest that if the methane in the traps is biogenic, then the methane production probably occurred in larger particles which fragmented before falling into the traps. The fragmentation could have occurred when the particles contacted the trap screens. If so, our estimates of downward particle-associated methane flux must be revised upward.

Alternatively, if the particles passed through the gut of organisms, high rates of oxygen consumption in the gut might produce anaerobic conditions favorable for methanogenesis. The potential for methanogenic bacterial activity in association with freshly egested fecal pellets (Bianchi et al., 1992; Marty, 1993), and the well-established role of intestinal methanogenic fermentations in the animal kingdom provide support for this hypothesis. After fecal pellets are released, oxygen diffusion into the particles is likely to exceed the rate of oxygen consumption. In this case, the most favorable conditions for methanogenesis would occur in the gut of organisms and perhaps immediately after defecation. Oxygen diffusion into the particles would probably restrict methanogenesis to progressively larger particles unless oxygen consumption rates can be maintained at high levels. At the same time, the methane in the particles would diffuse into the surrounding water or, if intercepted by a sediment trap, into the brine solution. This conclusion is consistent with the model calculations of Jumars et al. (1989) and supports their conclusion that most of the fecal pellet derived solutes, including dissolved gases, are probably exchanged within a zone 10–100 m within the zone of fecal pellet formation. In our study, the most intense zone of pellet formation is the epipelagic zone and should coincide with the greatest particle-to-water column methane flux.

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