Methane oxidation associated with mid-depth methane maxima in the Southern California Bight

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Abstract—Methane concentration in the water column of the Southern California Bight exhibits two or more maxima. In the upper water column, a subsurface concentration maximum is often observed, usually near the bottom of the euphoric zone. Deeper maxima are often detected, well below the euphotic zone and separated from the sediments, which suggests an advective source from continental slope sediments. We measured methane concentrations and oxidation rates in an attempt to quantify the biological loss term for methane throughout the water column in the Santa Monica Basin, one of the semi-enclosed basins in the Southern California Borderland. The study site was in the central basin at a water depth of 900 m, which was sampled several times over 4 years, and an offshore transect of three stations, which was sampled once. Layers of methane rich water were detected in the mid water column (500-800 m depth) at the deeper stations, with concentrations exceeding those found in the subsurface maximum. Oxidation rates in these layers greatly exceeded rates associated with the subsurface maximum and represented turnover times on the order of a few months. The source of the methane at mid-depth is probably advection from petroliferous sediments in the margin of the borderland, rather than diffusion from underlying anoxic sediments in the basin. Relatively rapid oxidation rates and resulting turnover rates at depth imply the presence of a community adapted for the utilization of methane as a carbon source, a community which is not found in surface waters.

INTRODUCTION

The distribution of dissolved methane in surface waters from diverse locations in the world ocean is often reported as a characteristic subsurface maximum, typically reaching concentrations of several nanomolar, representing a supersaturation of several fold (LAMONTAGNE et al., 1971, 1973; SCRANTON and BREWER, 1977; BROOKS et al., 1981; BURKE et al., 1983; LILLEY et al., 1982; WARD et al., 1987, 1989). Fewer reports have described the distribution of methane below the surface layer. In the open sea, the gradual decrease in its concentration with depth has been used to compute an in situ methane consumption term (SCRANTON and BREWER, 1978), indicating the presence of methane oxidizing bacteria in the deep interior of the ocean. The concentration of methane in the deep water column was interpreted as a residual from methane input from surface waters (e.g. during deep water formation), with no in situ production or input from horizontal advection below the surface layer. That is, the subsurface methane maximum was seen as both the source of the

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small net flux of methane from the ocean to the atmosphere (Scranton and Brewer, 1977) and as the source of methane which underwent oxidation in the deep water.

Our study of methane distribution in the Southern California Bight addressed both the source and fate of methane in surface and deep waters of the California Borderland. The actual source of methane in the subsurface maximum remains problematic; other investigators (Cynar and Yayanos, 1991; Sieburth, 1987) are pursuing the possibility that conventional methanogenic bacteria are responsible for its production in situ, and we have collected hydrographic data in conjunction with methane distribution data to address the possible contribution of advection from shelf sources (Ward, 1992). Our approach to constraining the size of the in situ production term has been to assume that methane concentration in the water column is not increasing over time scales of less than a year or so, that is, that its production is approximately balanced by its consumption. Therefore, we measured methane consumption, making the simplest assumption that conventional methanotrophic bacteria were responsible for the consumption. Thus, the fate of methane via methane oxidation by methanotrophs is oxidation to carbon dioxide and incorporation into bacterial biomass. If methane is in quasi steady state in the Bight, then our measured oxidation rates should approximate in situ production rates and should provide an estimate of the turnover rate of methane in the water.

We reported elsewhere (Ward, 1992) that measured methane oxidation rates in the depth interval of the subsurface methane maximum were very slow, resulting in turnover times of many months to many years in the surface water. Since these times exceed the residence time of the surface water in the Bight, we concluded that in situ production and consumption by the known conventional bacterial processes were not the dominant factors determining methane distribution, but rather that advection from shelf sediments must be reconsidered as a source. In the course of this study, we also measured methane distributions and oxidation rates throughout the water column of the Bight, and report here on our findings for the deep water column.

METHODS

Measurements were made on three cruises to the Southern California Bight in October 1987, June 1988 and October 1988. Our main study site was one central basin station, number 305, located at 33°45′N, 118°47′W. We also sampled two other stations on a transect shoreward from the central basin station: the shelf station (Sta. 304) located at 33°50′N, 118°36′W, and the inshore station (Sta. 303) at 33°53′N, 118°31′W. Samples were obtained in 5-l Niskin bottles, equipped with Teflon-coated springs and silicone o-rings. Niskin bottles were deployed on a hydrowire, and were equipped with reversing thermometers.

Methane concentrations

Dissolved methane concentration was measured on 1-l samples by a gas extraction technique using flame ionization gas chromatography (Herr and Barger, 1978; as modified by M. I. Scranton, personal communication). We did not determine the detection limit, but concentrations less than 1 nM could be reproducibly assayed. In plots showing error bars, we indicate the error associated with repeated injections of a single extraction. The coefficient of variation associated with these injections ranged from less
than 1% to about 10%. Repeated assays on subsamples from the same 30-l Niskin yielded a coefficient of variation of 2.5% (for the means from several injections for each subsample).

**Methane oxidation rates**

A thick-walled Teflon tube was used to fill several 160-ml acid-cleaned and baked serum bottles (without introducing bubbles), each overflowed approximately 2 volumes, from Niskin samplers. Bottles were sealed without bubbles using solid black rubber stoppers (pre-boiled in NaOH to reduce toxicity) and aluminum crimp seals. Radiolabelled methane (200 µl of gas, mostly hydrogen, containing 6-8 µl CH₄; 24 µCi µmol⁻¹; biogenically produced by the method of DANIELS and ZEIKUS, 1983) was injected through the stopper using a second needle to accept overflow as the gas displaced liquid. Tracer additions formed a small bubble in the bottles, which were vigorously mixed following tracer addition. Dissolved methane concentrations in the bottles were computed from the corrected (Rudd and Hamilton, 1975b) equation of Rudd and Hamilton (1975a). The tracer addition resulted in an elevation of *in situ* concentrations up to 0.25 µM. At each time point (approximately 1, 4, 8 and 18 or 24 h) incubations were processed for labelled particulates (by filtration through 47 mm diameter 0.3 µm pore size nitrocellulose filters) and labelled CO₂ (by acidification and capture on phenethylamine soaked filters, with a recovery efficiency of 80%; WARD and Kilpatrick, 1990). Samples were shielded from light during all manipulations, and were incubated at approximately *in situ* temperature in running seawater incubators (for surface samples) or temperature controlled incubators (for deeper samples) in the dark. Filters were assayed by liquid scintillation counting within 1 week. Oxidation rates were calculated from the linear regression of the time course data (α ≤ 0.05). Measured oxidation rates have been found to be linearly dependent upon substrate concentration in this and other locations (WARD and Kilpatrick, 1990). We detected this response to substrate concentration in kinetic experiments performed at selected shallow and mid-water depths on every cruise (results not shown) and, therefore, results from standard time course experiments were corrected for altered substrate concentration due to label addition based on this linear relationship.

**Water chemistry and additional measurements**

Nitrate (Strickland and Parsons, 1972) concentrations were measured in frozen subsamples after the cruise by standard methods. Oxygen concentration was measured using the Carpenter modification of the standard Winkler titration (Carpenter, 1965). Temperature was measured and thermometric depth corrections were obtained using reversing thermometers on the Niskin samplers. Bacterial abundances were measured by acridine orange direct counting by epifluorescence (Hobbie et al., 1977) on preserved samples (2% formalin) immediately after each cruise.

**RESULTS**

**Mid-depth methane maximum**

During each cruise, data from several casts were combined to produce a composite methane profile. While short term variability in the surface layer meant that high
resolution in space and time was necessary to accurately describe the methane distribution in that region, temporal variability was less of a problem for distributions below the main thermocline. Methane concentrations throughout the water column varied from below saturation level to several times saturation. Methane concentration in equilibrium with the atmosphere as a function of temperature and salinity (Yamamoto et al., 1976) was computed to range between 2.2 and 3.0 nM (Fig. 1).

On all three cruises, we detected elevated methane concentrations in the depth range between 400 m and approximately 800 m (Fig. 1) at the central station, number 305. The composite profiles from October 1987, June 1988 and October 1988 exhibit maxima centered around 550 m, which were detected in multiple bottles from more than one cast. The concentrations at these depths are in the range of 7–10 nM, with spikes reaching 32 nM, levels which, for the second and third dates, equal or exceed those measured in the subsurface methane maximum at the same time. The region of the water column between the maxima in the surface water and around 500 m has methane concentrations very close to equilibrium saturation values, and it is apparent that the two maxima are separated, i.e. unrelated to each other.

Minor methane concentration peaks near the sediment water interface were sometimes observed. The resolution of our vertical sampling was such that we did not usually detect enrichment in methane concentration due to release of methane from the sediments. The sediments at this location are indeed anoxic (Jahnke, 1990) and the water column itself is suboxic (Fig. 2). The decrease in nitrate concentration approaching the bottom indicates the presence of denitrification, certainly in the bottom sediments and perhaps in the
Methane oxidation associated with mid-depth methane maxima

Fig. 2. Dissolved oxygen (○, ●), nitrate (Δ, ▲) and temperature (+) distributions at station 305 measured in October 1988. Data from two casts (different symbols) were combined for the composite profile.

overlying water column. However, the bottom sediments are apparently not a large source of methane to the bottom water, since the near bottom water has methane concentrations below saturation level and the enhanced concentrations derived from the sediments, when detected, did not extend very far up into the water column.

**Methane oxidation rates**

Methane oxidation rates derived from time course incubation experiments were obtained in depth profiles at the central basin station (Fig. 3) and at two additional stations comprising a short cross shore transect perpendicular to the coast in October 1988 (Fig. 4). Although the subsurface maximum is a prominent feature of the concentration profile, there is very little oxidation activity associated with it (WARD, 1992). Rates in the vicinity of the subsurface maximum (between 0 and 125 m) were either undetectable (16 experiments) or negligible (two experiments) for 18 out of 19 incubation experiments carried out over five cruises. At the central station, turnover time for methane in the surface water was of the order of hundreds of years.

Methane oxidation rates increased, both in absolute terms and relative to the ambient concentration, in deeper water. Highest rates at the central station, approximately 3–4 pmol l\(^{-1}\) h\(^{-1}\), occurred around 600 m and near the bottom at around 900 m (Figs 3 and 4). Turnover times in this depth interval ranged from 2 to 15 months. Even after correction for the effect of elevated methane concentrations during incubation, highest rates occurred at depth, where methane concentrations were slightly elevated above surface values.
The shelf station, number 304, in water depth of 330 m, also exhibited a slight subsurface concentration maximum, which was associated with a small maximum in methane oxidation rates (Fig. 4B). In situ concentrations and measured oxidation rates at this station were similar in magnitude to those at the central station. No mid-depth maximum in concentration or rates was detected at Sta. 304, however, the bottom depth being shallower than the mid-depth feature in the central station. Maximum oxidation rates occurred at the deepest depth sampled. This activity may be associated with supply of methane from the anoxic sediments into the overlying water column, but our deepest sample was not very close to the sediment water interface and we did not detect elevated methane concentration at 220 m.

At the inshore station, number 303, both methane concentrations and oxidation rates were similar in magnitude to those at the deeper stations except for the near bottom sample in which both concentrations and oxidation rates were significantly elevated, again probably attributable to methane flux from anoxic sediments.

**DISCUSSION**

It was concluded from a study of the subsurface methane concentration maximum over three seasons using data from five cruises (WARD, 1992) that the subsurface maximum in the Southern California Bight was not predominantly a biologically controlled feature.
Methane concentration covaried on diel scales with changes in physical parameters, suggesting that water motion controlled the relative distribution of methane at different depths. Absence of detectable methane oxidation rates which were fast enough to affect the *in situ* methane concentration on relevant time scales was a second piece of evidence which implied that methane oxidation was not a significant flux in the carbon cycle in surface waters. These measurements addressed only the oxidation of methane by conventional methanotrophic pathways, yielding cellular carbon and CO₂. Alternative pathways of methane production and consumption cannot be ruled out.

The situation at the mid-depth concentration maximum appears to be different from the upper water column maximum. The methane distribution at depth at the central station was not correlated with simple hydrographic or nutrient distributions, but exhibited peaks and spikes in an irregular manner. Temperature data collected simultaneously with the methane concentration and oxidation measurements are available for October and June 1988 (Fig. 1). In both cases, the highest methane concentrations occurred at mid-depth and were associated with temperatures around 5–6°C (Fig. 5). The October data showed another high methane layer in slightly colder water. The 5°C water occurred at a depth above 700 m, which is just shallower than the sill depth of the Santa Monica Basin, 713 m (Jackson, 1986). Unfortunately, we do not have density data for these stations, and so are confined to using temperature alone as a correlate.

Temperature is the most important variable in determining solubility of methane in seawater. We used the solubility relationship of Yamamoto et al. (1976) and an atmospheric methane concentration of 1.7 ppm to compute the equilibrium solubility of methane with depth at the central station (Fig. 1). Unfortunately, complete depth...
coverage for temperature and salinity were not available from the cruises on which the rate measurements were made. Therefore, we used hydrographic data collected on a subsequent regional study (Ward, in preparation) to estimate the depth distribution of the equilibrium saturation value. This is a reasonable approach because the range in this value in July 1990, for example, was between 2.08 and 2.98 nM from surface to bottom water, and varied by less than 8% in the subsurface water between January and July. Methane concentration peaks in the 500–700 m interval often exceeded 3 nM, ranging up to more than five-fold greater than the equilibrium value.

The distribution and characteristics of oil and gas seeps in the Southern California Borderland are summarized by Reed and Kaplan (1977). Important gas seeps have been found near the coast around Santa Barbara (Coal Oil Point and Carpenteria), 100–150 km northwest of our sampling site. The isotopic composition and ratio of methane to other hydrocarbons in the gases indicates that their source is petroleum rather than in situ biochemical production (Stahl, 1974; Reed and Kaplan, 1977).

Elevated hydrocarbon concentrations have been reported in bottom water samples near the seeps described by Reed and Kaplan (1977), but little data on the distribution of hydrocarbons in the water column are present in the literature. Andreae (1979) published one profile of dissolved methane from the Santa Barbara Basin. That profile exhibits three features which we found in our study of the Santa Monica Basin site: a subsurface maximum in the region of the bottom of the euphotic zone; a mid-depth maximum (in the case of the Santa Barbara Basin station, between 200 and 350 m), and an increase near the sediment interface, indicating a source of methane from the underlying anoxic muds. The
Methane oxidation associated with mid-depth methane maxima

Santa Barbara Basin is an oil producing province, and evidence of natural seeps is obvious to the casual observer near shore. Known gas seeps close to shore in the Santa Barbara region (Coal Oil Point and Carpinteria) suggest that smaller gas seeps may be common in the region, and may be a source of methane to the water column, producing the mid-depth methane maximum reported by Andrae (1979).

Evidence of seeps is less obvious in the Santa Monica/San Pedro region. Our central station is approximately 46 km offshore of Redondo Beach, where Reed and Kaplan (1977) documented several oil and tar seeps close to shore, but did not comment on associated gas seeps. Reed and Kaplan also documented a known oil seep at 676 m depth in the borderland. We have not made independent measurements of hydrocarbon ratios or isotopic content of the methane we detected in the water column, but we hypothesize that its source is the seeps associated with petroliferous sediments in the nearby coast. This hypothesis will be examined in a regional study of methane distribution in the Southern California Bight (in preparation).

Brooks (1979) described high methane concentrations that occurred in discrete layers in the Caribbean Sea and Gulf of Mexico. While the subsurface maximum was attributed to a combination of advection and (predominantly) in situ production, the deeper maxima were attributed to seepage from the Jamaica Ridge in the depth interval of 250-600 m. The hydrocarbon composition of these gases implied a biogenic, rather than petrogenic, source. Subsequent discovery of thermogenic gas hydrates in the adjacent northwestern Gulf of Mexico (Brooks et al., 1984) provide yet another methane source in the 500-600 m interval.

In the present study, we focused on the oxidation of methane in order to determine the significance of methane to the carbon cycle of nearshore waters. The contribution of oil seeps to benthic metabolism has been supported by the finding of elevated organic carbon content of sediments and elevated microbial metabolism in sediments near seeps (Montagna et al., 1987; Bauer et al., 1988) and by 14C isotopic evidence that fossil carbon contributes to meio- and macrofaunal diets near seeps (Bauer et al., 1990). Seeps also support symbioses between methanotrophic symbiotic bacteria and several invertebrate hosts near hydrocarbon seeps in the Louisiana slope (Brooks et al., 1987). The concentration of dissolved methane in the water column of the Bight is much lower than the hydrocarbon content of coastal sediments near seeps, but the amount of water in which elevated methane concentrations are likely to occur make it worth considering the possible impact of methane as a carbon source at the base of a microbial food web in the mid to deep water. This can be addressed when better spatial coverage in methane concentration data are available for this depth interval.

If methane were a significant carbon input to the food web at depth, its contribution might be reflected in greater total biomass in this depth interval. Our present data on biomass distributions within the water column are restricted to enumeration of bacteria (Fig. 6). The main feature in the abundance distribution is a maximum within the euphotic zone and there is little indication of increased abundance in the interval of the deep methane maxima. When those depths within the subsurface methane maximum were excluded from the analysis, a significant relationship between bacterial numbers and methane concentration was detected for June 1988 ($R^2 = 0.370, N = 14, P = 0.021$) but not for October 1987 ($R^2 = 0.230, N = 11, p = 0.136$). Thus a small percentage of the variability in bacterial abundances might be explained by variation in methane concentration, but this idea requires further investigation. Higher resolution sampling for
enumeration of bacteria and bacterivores and measurement of indicators of microbial activity might also be considered in the future.

Scranton and Brewer (1978) argued that methane concentrations below saturation in the old deep water of the ocean implied that methane was slowly consumed by microorganisms as the water aged. They concluded that methane consumption virtually ceased within 100 years of water mass isolation; in these older waters, methane concentration was significantly below the equilibrium saturation level and was in the range of less than 0.5 nM. Scranton and Brewer (1978) suggested that the residual methane persisted because either pressure and temperature effects prevent its utilization by methanotrophic bacteria present in the seawater, or because the low concentrations were below the threshold utilization level for bacteria. Methane concentrations in the Santa Monica Basin are below saturation both above and below the mid-depth maximum (Fig. 1). Based on our measured rates of methane oxidation, methane consumption in these layers is very slow, but may be sufficient to maintain low concentrations.

Oxidation rates were much faster in the depth interval in which methane concentration was also elevated (Figs 3 and 4). Total oxidation rates and specific oxidation rates both exceeded activity near the surface by several orders of magnitude. Computed turnover times (2–15 months) are shorter than the estimated residence time of the water in this depth interval, which is on the order of 17 months (Jackson, 1986). These results imply that production and consumption of methane in deeper water contributes to methane turnover and carbon fluxes that are not coupled with ocean/atmosphere exchange of methane. Recent computation of sea–air methane fluxes (e.g. Cynar and Yayanos, in press a; Ward, 1992) in this region confirm that the ocean as a whole is a minor source of methane to the atmosphere on a global basis. As shown here, however, this does not

Fig. 6. Depth distribution of bacterial abundance in October 1987 (●) and June 1988 (○).
Methane oxidation associated with mid-depth methane maxima

preclude a role for methane in the carbon cycle of the sea, independent of its role in the atmosphere or surface ocean. The magnitude of this role must be addressed in terms of the regional seep methane input, integrated methane oxidation rates and overall carbon production rates or vertical fluxes in the water column.

Whether the microbial community responsible for the observed activity developed in situ or was advected and developed along with the advecting methane cannot be determined from the present data. Either way, these oxidation rates indicate the presence of a community in deep water which is either not present or not active in surface water. The shallow methane maximum, although close to the photic zone, usually occurs well below the 1% light level, implying that light inhibition of the methane oxidizing organisms is not likely to prevent their utilization of the methane present at that depth. Although the shallow subsurface methane maximum is almost always present in Southern California Bight waters (WARD, 1992; CYNAR and YAYANOS, in press b), perhaps the lower concentrations are insufficient to support an active methane oxidizing population, such as found at depth.

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REFERENCES


