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Order Number 9230524

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Methane sources and sinks in upper ocean waters

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Tilbrook, Bronte David, Ph.D. University of Hawaii, 1992



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METHANE SOURCES AND SINKS IN UPPER

OCEAN WATERS

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

OCEANOGRAPHY

MAY 1992

by

Bronte Tilbrook

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Acknowledgements

As is the case with all dissertations, a large number of people contributed towards my finishing. First and foremost I would like to recognize the importance of my mother, Linda Tilbrook, for her continual support, and, by her own example, encouraging me to work hard. The dissertation committee exhibited a great deal of patience and offered many helpful suggestions and criticisms. I am especially grateful to my thesis advisor, Dr. Stephen Smith, who always made time to listen to me and contributed substantially to this work. Dr. David Karl also played a large part in allowing me to complete this research. He provided support for most of my time at the University of Hawaii, was always enthusiastic about my research, and provided many opportunities for me to participate in research cruises and attend scientific meetings. Dr. Francis Sansone allowed me to use his laboratory facilities, and was always interested in the research.

Dr. Lorenz Magaard was until recently the Chairman of the Department of Oceanography. He is genuinely interested in graduate students and made every effort to help them. He is no longer chairman of the department and has left some big shoes to fill. I would also like to thank Dr. Fred MacKenzie and Dr. Jane Tribble for providing some financial support.

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Field assistance was provided by David Jones during ADIOS, Deborah Burns during VERTEX, and Paul Haberstroh, Michelle Nawrocki and Georgia Tien during RACER. Ursula Magaard helped prepare for cruises on a number of occasions.

My final acknowledgement must go to the Graduate Division of the University of Hawaii. In the words of Rodney Dangerfield, "They seemed to care, about what I don't know."

Abstract

The mechanisms regulating the distribution of dissolved methane in ocean surface waters were investigated. Water column and sediment trap samples were collected in a various oceanic regions ranging from high productivity coastal California and Antarctic waters to the oliogotrophic ocean off Hawaii. The methane concentrations in most of the surface waters sampled were typically in the range of 5 to 75 per cent supersaturated with respect to atmospheric methane. Generally, the greatest supersaturations were found in nearshore areas. Methane concentrations varied between saturation and 15 per cent undersaturated in the offshore Antarctic waters of the Drake Passage.

The methane supersaturations off Hawaii are indicative of a net in situ methane production in the upper water column. In this region, the methane distributions are largely determined by in situ production and air-sea gas exchange. Closer to shore, sediment or near-bottom methane inputs become important as a source of methane to the water column.

Measurements in sediment trap solutions did show that methane accumulated in the traps. The accumulations were most apparent in the upper 200m of the water column and

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tended to increase towards the surface and with distance away from coastal California. The 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 open ocean surface waters.

Attempts to culture methane producing bacteria from samples of plankton and particulate material collected in sediment traps were largely unsuccessful, suggesting there is only a limited capacity for methanogenesis in the upper ocean.

The methane undersaturations observed in the Drake Passage surface waters resulted from the upwelling of methane-depleted Warm Deep Water. Methane was added to the waters flowing over the shelves around the Bransfield Strait and South Shetland Islands and methane supersaturations were a common feature in these nearshore waters. Air-sea methane flux estimates indicate that the net uptake of methane in the offshore waters of the Drake Passage is approximately balanced by the net methane release to the atmosphere in coastal Antarctic waters sampled.

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Chapter I

Introduction

General Overview

Methane is an important component of the biogeochemical carbon cycle. It is a major end-product in the anaerobic degradation of organic matter and provides a source of energy for certain bacteria. Although dissolved methane is typically only found at nanomolar concentrations in the open ocean, a number of studies have suggested that the microbial oxidation of methane and other reduced inorganic compounds may supply energy for bacterial chemoautotrophs present in sinking particles (Karl et al., 1984) and in deep-sea biotic communities associated with hydrothermal vents and hydrocarbon seeps (Welhan and Craig, 1979; Lilley et al., 1983; Jannasch and Mottl, 1985; Kennicutt et al., 1985; Paull et al., 1985; Kulm et al., 1985 and Karl et al., 1990). Descriptions of net methane production in the upper water column, presumably through anaerobic degradative processes (Scranton and Brewer, 1977), also imply that methane is a potentially useful indicator of the sites and conditions under which anaerobic processes occur in the oxygenated water column. Furthermore, Seiburth (1987) has proposed that the production and consumption of methane in anaerobic microzones is a key component in the upper ocean carbon cycle. Although these studies attest, at least on a small

scale, to the potential importance of methane in oceanic biogeochemical cycling, its sources and sinks are poorly known. The research described in the following chapters is aimed at understanding methane source and removal mechanisms in the oceans.

Methane Distributions in the Water Column

Dissolved methane in upper pycnocline and shallower oceanic waters is typically supersaturated relative to atmospheric equilibrium concentrations. A methane concentration maximum two or more times greater than equilibrium solubility is common in the upper pycnocline. The magnitude of the maximum generally decreases with distance offshore (Brooks et al., 1981; Burke et al., 1983; Lamontagne et al., 1973; Scranton and Brewer, 1977 and Traganza et al., 1979). The methane supersaturations have been attributed to in-situ biological methane production (Brooks et al., 1981; Burke et al., 1983; Lamontagne et al., 1973; Scranton and Brewer, 1977 and Traganza et al., 1979) and in part to methane inputs from sediments to coastal waters which are advected offshore (Scranton and Farrington, 1977).

Methanogenic bacteria are obligate anaerobes (Wolfe, 1971), yet methane production apparently occurs in oxygenated seawater. Potential sites for methane production in the oxygenated water column include reducing microenvironments in fecal pellets, suspended particulates,

and the intestinal tracts of zooplankton or other marine animals (Martens and Berner, 1974 and Scranton and Brewer, 1977). Reduced microzones have been identified in particulate aggregates and fecal pellets (Alldrege and Cohen, 1987; Pearl and Purfert, 1987), but whether or not the extreme anaerobic conditions believed necessary for methanogenesis are established is unknown. Scranton and Brewer (1977) have also suggested that methane in the euphotic zone could be a by-product of phytoplankton metabolism.

Traganza et al. (1979) reported a correlation between zooplankton biomass (measured as ATP on the 333 to 1800 μ m size fraction) and methane in the tropical North Atlantic, and suggested that the methane may be produced in association with zooplankton. Oremland (1979) measured net methane production in >164 μ m plankton samples and in the intestines of fish from San Francisco Bay that were incubated with known methanogenic substrates under anaerobic conditions. Oremland's plankton sample contained both zooplankton and particulate matter, and he could not determine which part of the sample was associated with the methane production. Cynar and Yayanos (1989) have also reported methane production occurring in association with plankton samples. Lamontagne et al. (1975) found no relationship between methane and chlorophyll-a measured in surface waters collected in the equatorial Pacific.

However, 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 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 (Tinkle et al., 1973; Bernard et al., 1976; Reed and Kaplan, 1977 and Cline and Holmes, 1977), organic rich sediments (Martens and Berner, 1974 and Martens and Klump, 1980), inputs of methane-rich freshwaters (Sackett and Brooks, 1975 and 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.

Below about 300 m depth, methane supersaturations have been found in association with submarine hydrothermal systems, seeps and anoxic basins. The fluids emitted at

hydrothermal vents have variable methane contents ranging from about 10^{-1} to 10^{-3} volumes of CH₄ per volume of sample (v/v) and are substantially enriched in methane relative to ambient waters which have contents of between 10^{-7} to 10^{-8} (v/v) methane (Welhan and Craig, 1979; Lilley et al., 1983; Welhan and Craig, 1983 and Welhan and Lupton, 1987). Active venting has been described at numerous locations including sites along mid-ocean spreading ridges (e.g. Corliss et al., 1979; Spiess et al., 1980; Ballard et al., 1984; and Rona et al., 1986), in the Mariana back-arc basin (Craig et al., 1987), and the Loihi seamount hot-spot (Karl et al., 1990). Plumes of methane-rich water resulting from the hydrothermal inputs have also been identified in many deep sea locations (Belviso et al., 1987; Gamo et al., 1987; Charlou et al., 1987 and Charlou et al., 1988). Welhan and Craig (1983) estimated that the hydrothermal methane flux is sufficient to replace all the deep sea methane in about 30 years.

Methane inputs to deep waters also occur in areas where methane-rich pore waters seep into the aerobic water column at rates sufficient to overwhelm consumption by methane oxidizing bacteria. Methane sources associated with deep sea seeps have been located on the Louisiana Shelf (Kennicutt et al., 1985), the Florida Escarpment (Paull et al., 1984), the Oregon subduction zone (Kulm et al., 1986), and the Nankai Trough and Japan Trench (Boulegue et al.,

1987). Seeps may also be the source for methane plumes located in the Gulf of Mexico (Brooks, 1979) and the Celebes Sea (Belviso et al., 1987).

Excluding the methane supersaturations associated with the above sources, methane distributions below about 300 m are generally uniform and undersaturated relative to atmospheric equilibrium (Lamontagne et al., 1973). The distribution is indicative of net methane consumption and suggests that at least on a regional scale, in situ methane production in the water column is not a particularly important source of methane to the deep sea. **Biogenic Methane Production and Consumption**

Methane is an end product in the anaerobic decomposition of organic matter. The conditions and substrates required by methanogens for growth and activity result from the metabolic activities of numerous organisms involved in the degradation of organic matter. The respiratory and fermentation processes that contribute to organic matter degradation and methane production are reviewed in Claypool and Kaplan (1974), Billen (1976), Rudd and Taylor (1980), Krumbein and Swart (1983), Frea (1984) and Large (1984).

Respiratory metabolism involves the oxidation of organic matter using oxygen, manganese, nitrate, iron oxides, sulphate and carbon dioxide as external electron acceptors. Competition among microorganisms for growth

substrates tends to select for the energetically most favourable metabolic system, and the electron acceptors are typically utilized in the order listed above (Claypool and Kaplan, 1974 and Froelich et al., 1979). Aerobic respiration yields the highest energy in the degradation of organic matter. Aerobic organisms typically dominate until oxygen is depleted, after which anaerobic degradation proceeds. Anaerobic respiration will utilize manganese, nitrate and iron oxides if they are available. Bacteria involved in sulphate and carbon respiration require substrates produced during fermentations. Factors such as the toxicity of electron acceptors to organisms, and the availability of electron acceptors and substrate also affect the sequence and extent of the various modes of respiratory metabolism. Carbon respiration, which produces methane by the reduction of carbon dioxide with hydrogen, yields the least energy and typically occurs after the other electron acceptors are depleted.

Apart from respiratory processes, certain bacteria use extracellular enzymes under anaerobic conditions to hydrolyze polymers (protein, carbohydrate and lipids) to monomers (amino acids, alcohols and long chain fatty acids). These are in turn degraded by fermenting bacteria to alcohols, carbon dioxide, hydrogen and short chain fatty acids including acetate. The more reduced products (alcohols and fatty acids such as propionate, succinate,

lactate and butyrate) may then be fermented to acetate, carbon dioxide and hydrogen by acetogenic bacteria (e.g. Krumbein and Swart, 1983). Methanogenic or sulphate reducing bacteria utilize many of these fermentation products in what represent terminal steps in anaerobic degradation.

Most natural methane is produced by the fermentation of acetate or by the reduction of carbon dioxide by hydrogen (Jeris and McCarty, 1965; Cappenburg and Prins, 1974; Bryant, 1976; Oremland and Taylor, 1978; Sansone and Martens, 1978 and Whiticar et al., 1986). However, utilization of hydrogen and acetate by sulphate reducers is thermodynamically and kinetically more favourable, and methanogenesis is typically inhibited if sulphate is available (Cappenburg, 1974; Claypool and Kaplan, 1974; Lovley et al., 1983 and Winfrey and Ward, 1983).

While methane supersaturations in oxygenated water suggest that the fermentations and extreme anaerobic conditions necessary for methanogenesis may occur there, the substrates used are unknown. In marine sediments, methane production is typically greatest in anoxic zones where sulphate reducing bacteria have depleted sulphate (Claypool and Kaplan, 1974; Martens and Berner, 1974 and Senior et al., 1982). Methanogenesis in sulphate-rich sediments is generally attributed to utilization of noncompetitive substrates such as methylated amines

(Oremland and Polcin, 1982; Oremland et al., 1982a and Winfrey and Ward, 1983). Iversen et al. (1987) have also suggested that non-competitive substrates may be the precursors of methane produced in the sulphate reducing zone of the Big Soda Lake, Nevada, water column. A similar situation is possible in the open ocean water column, where high sulphate concentrations are likely to inhibit methane production by either acetate fermentation or carbon dioxide reduction. By using non-competitive substrates, methane production in anoxic microenvironments would not be restricted to zones of sulphate depletion, and this should increase the number of potential sites for methanogenesis.

Methylated amines and dimethylsulfide (DMS) stimulate methanogenesis in sulphate rich sediments and these compounds may be important growth substrates for marine methanogens (Oremland and Polcin, 1982; Oremland et al., 1982a; Oremland et al., 1982b; Oremland et al, 1985 and Sieburth, 1987). Methylated amines are produced by the fermentation of choline, glycine betaine and other quaternary amino compounds, or by the reduction of trimethylamine oxide (Hippe et al., 1979; Fiebig and Gottschalk, 1983 and King, 1984). These molecules are common in many marine organisms (Beers, 1967; Blunden et al., 1982 and Fiebig and Gottschalk, 1983) and their degradation may also influence nitrogen remineralisation (King, 1984). Sieburth (1987) and Cynar and Yayanos (1989)

have recently reported methane production in plankton samples amended with methylamine. The major precursor of DMS appears to be dimethylsulfoniopropianate, which is common in marine algae (Challenger, 1959; White, 1982). DMS is released by marine algae and by zooplankton grazing algae (Vairavamurthy et al., 1985; Dacey and Wakeham, 1986), and DMS concentrations are typically in excess of atmospheric equilibrium concentrations in the upper water column (Bates et al., 1987). Other substrates that can support methanogenesis in the presence of sulphate include methionine and methanol (Hippe et al., 1979; Oremland and Polcin, 1982; Oremland et al., 1982a; Oremland et al., 1982b; King et al., 1983 and Sowers and Ferry, 1983).

A number of groups of bacteria are capable of utilizing methane as an energy or carbon source (e.g. Rudd and Taylor, 1980; Higgins et al., 1983; Higgins et al., 1984 and Large, 1984). Certain ammonia oxidizing bacteria can oxidize methane in seawater (Jones and Morita, 1983) and a methanotrophic bacterium has been isolated from waters collected in the Sargasso Sea (Sieburth et al., 1987). The potential for methane oxidation by other bacteria is unknown. However, studies in marine sediments and freshwater systems suggest that other bacteria involved in the marine nitrogen cycle (e.g. Rudd and Taylor, 1980) and sulphate reduction (Reeburgh, 1975) may also be capable of oxidizing methane.

The few published values of aerobic methane oxidation rates in the ocean typically show turnover times for dissolved methane of 100's to 1000's of days (Scranton and Brewer, 1978; Griffiths et al., 1982 and Ward et al., 1987). Higher oxidation rates corresponding to turnover times on the order of days were measured in Cape Lookout Bight waters (Sansone and Martens, 1978). However, this is a shallow enclosed basin with a large methane input from sediments (Martens and Klump, 1980) and is unlikely to be representative of open ocean conditions.

The factors controlling the oxidation of methane in the water column are not well defined. For Cape Lookout Bight waters, Sansone and Martens (1978) found that methane oxidation rates were inhibited by oxygen at dissolved inorganic nitrogen (DIN) concentrations below about 16 μ M. Above this DIN concentration, oxidation rates increased an order of magnitude and did not appear to be affected by oxygen concentrations. Rudd et al. (1976) reported a similar relationship for freshwater lakes. However, Griffiths et al. (1982) found no relationship between DIN, oxygen and methane oxidation rates in the Bering Sea. Weaver and Dugan (1972) have also proposed that oxidation rates may increase as suspended particle concentrations increase, but this was not evident in the Bering Sea (Griffiths et al., 1982).

Most of the methane produced under anoxic conditions in marine sediments is consumed by bacteria before diffusing into the overlying aerobic water column (Reeburgh and Heggie, 1977; Reeburgh, 1980; Martens, 1982 and Devol, 1983). By analogy, if methane is produced in reducing microenvironments in the water column, it may also be consumed before diffusing into the aerobic water column (Sieburth, 1987). Consequently, the long turnover times reported for dissolved methane may simply reflect that once methane diffuses into the water column, it is no longer readily available to methanotrophic bacteria. In this situation other processes including air-sea gas exchange and diffusive fluxes to the deep sea may be more important in determining dissolved methane distributions.

Research Objectives

The primary objectives of the research in this dissertation are to 1) establish the distributions of methane in a variety of oceanic environmments including the oligotrophic open ocean and high latitude coastal waters, and 2) investigate the major biological and physical controls on the distributions. The research is designed to provide an improved understanding of the sites and mechanisms of methane production in the water column, and to gain insights into the factors regulating the decomposition of organic matter in the oceans. A brief outline of the studies undertaken is given below.

The methods used to measure dissolved methane are described in chapter II. Chapter III describes the distribution of methane in oligotrophic North Pacific waters and the results of sediment trap experiments used to study a possible association between methane and particulate material caught in the traps. Chapter III also documents a study of methane distributions from coastal California to central North Pacific waters. This study was aimed at investigating how methane source/sink relationships vary between coastal and offshore locations. A study of methane distributions in Antarctic waters is described in chapter IV. Prior to this work, only a few measurements of dissolved methane had been reported for the entire Southern Ocean. The results provide a useful basis for estimating air-sea fluxes of methane in the Southern Ocean, and for determining how methane concentrations are influenced by the large spring blooms and the seasonal changes in sea-ice cover that characterise the region.

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Chapter II

Methods

Methane Concentration Measurements

Methane concentrations in water samples were measured by gas chromatography using a purge and trap technique similar to the one described by Swinnerton and Linnenbom (1967). The equipment allowed methane and other dissolved gases to be purged from a water sample and concentrated cryogenically before being injected into a gas chromatograph (Hewlett Packard 5890A) and quantified using a flame ionization detector. A schematic of the chromatography setup used is shown in figure 2.1.

The sample pipet (volume 171.6 ml) was made of Pyrex with teflon stopcocks at either end. The stripping chamber was also Pyrex and had a coarse fritted disc at its base to disperse bubbles through the sample. Trap T_1 was made of 3.2 mm o.d. stainless steel tubing packed with 80/100 mesh Porapak Q. The helium stripping gas was precleaned by passing the gas through trap T_2 (6.4 mm o.d. stainless steel tubing filled with activated charcoal and 80/100 mesh Porapak Q) which was immersed in liquid nitrogen. After about 10 hours of use, T_2 was regenerated by baking it at 200°C for several hours while passing helium through the trap. Trap T_d was used to remove water vapour and carbon dioxide from the purged gases and was made from 6.4 mm o.d. polypropylene tubing filled with Drierite and Ascarite. The



Figure 2.1. Schematic of the equipment used in this study to extract and analyse methane dissolved in seawater.

tubing between the sample pipet and T_d was 3.2 mm o.d. polypropylene and all other tubing was stainless steel with the exception of copper supply lines from the gas cylinders.

Samples were collected in 250 ml Pyrex glass bottles, poisoned with 1 ml of a saturated solution of mercuric chloride, and the bottles were sealed with ground glass stoppers. The stoppers were lightly greased with Apiezon M to ensure a good seal. In the laboratory, samples were transferred into the sample pipet by pressurising the sample bottles with helium and forcing the sample to flow through a tube connected to the bottom stopcock of the pipet and eventually out through a waste line at the top of the pipet. After flushing the sample through the pipet, the top and bottom stopcocks were turned to allow stripping gas to push the sample into the stripping chamber. Methane and other gases were then purged from the sample by flowing helium through the stripper at 100 ml min⁻¹ for 7 min. The purged gases passed through trap T_d to remove water vapour and carbon dioxide, and methane and other hydrocarbons were concentrated on T₁ which was immersed in liquid nitrogen. After the stripping procedure was completed, T₁ was heated with boiling water to release the trapped gases, and valve V, was switched to inject the gases into a Hewlett Packard 5890A gas chromatograph. A Porapak Q chromatographic column (3.2 mm x 2 m) separated methane from the other gases, and

hydrocarbons were quantified using a flame ionization detector. The response of the detector was calibrated by using valve V_2 to inject known volumes of a methane-in-helium standard (23 ppm; Air Products and Chemicals) into the gas chromatograph.

Long Term Storage of Samples

The samples used in this study were returned to shore for analysis, and tests were carried out to determine the effects of long term storage on the methane concentrations in the samples. For the tests, about 25 liters of surface seawater collected off Kaneohe Bay, Oahu, was tranferred from a 30 liter Niskin bottle into a carboy and subsamples were drained into 250 ml borosilicate glass sample bottles. During sampling care was taken to avoid trapping air bubbles, and the samples were poisoned and sealed as outlined above. The samples were stored in wooden boxes designed to block out light, and analysed over a period of one year. The measurements indicate that storage of up to one year had no discernable effect on the methane concentrations in the samples (Table 2.1). The standard deviation of all the measurements was \pm 2.6%, which compares well with the estimated analytical precision of ± 3% (1 s.d.) based on replicate analyses made throughout the study.

In a separate experiment, some bottles containing poisoned samples were covered by a few centimeters of

flowing seawater (T \approx 20-22°C) and exposed to sunlight for periods of up to four weeks. The methane content in these samples increased by as much as 300% over four weeks (data not shown), but there was a considerable variation between bottles. Bottles sealed with silicone grease instead of Apiezon M showed no changes in methane concentrations, indicating that a light-induced degradation of the Apiezon grease was the source of the methane increases. This light effect was only noticeable after the bottles had been exposed to surface light intensities for a few days. Therefore, all samples were kept in wooden boxes designed to block out sunlight to avoid any post-sampling alteration to the methane concentrations.

Storage Time (d)	Methane (nM)	Average (nM) ± 1 s.d.
0	2.43, 2.37, 2.46, 2.42, 2.46	2.42 ± 0.04
16	2.45, 2.42, 2.36, 2.35	2.40 ± 0.05
38	2.39, 2.41, 2.48	2.43 ± 0.05
93	2.36, 2.31, 2.35	2.34 ± 0.03
144	2.28, 2.43, 2.31	2.34 ± 0.08
368	2.27, 2.41	2.34 ± 0.10
Avera	age: 2.39 ± 0.06 (n=20)	

Table 2.1. Dissolved methane concentrations in stored water samples.

Sediment Trap Experiments

In addition to analysing methane in water samples, methane concentrations in sediment trap solutions were measured to investigate a possible association between particulate material collected in the traps and microbial methane production. The association has been suggested previously because all known methanogens are obligate anaerobes and particulate material represents one of the few sites in oxygenated waters where anaerobic microenvironments are likely to occur (Scranton and Brewer, 1977; Alldredge and Cohen, 1988). This section describes the traps and summarises experiments conducted to evaluate the suitability of the traps for these measurements. An experiment was also conducted to establish background variability of oxygen and nutrients in trap solutions, and these results are also summarised below.

The traps (figure 2.2) were the same as the Multitrap arrays described in Knauer et al. (1979). For each depth of sampling, the multitrap arrays consist of up to twelve, 7 cm i.d., polycarbonate tubes hung from a PVC cross. The tubes are 65 cm long and were sealed at the bottom with polyethylene caps. The top, or mouth, of each tube was covered by a baffle made of fourteen small diameter (1.27 cm o.d. x 7.6 cm long) tubes glued together. In some tubes a 335μ m Nitex screen is placed at the base of the baffle to prevent large zooplankton from swimming into the solutions.



Figure 2.2. Schematic of the free-floating MULTITRAP arrays used in this study (after Knauer et al., 1979).

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All the tubes are filled to just below the baffle with an autoclaved salt solution (0.22 μ m filtered surface seawater with 27.1 g NaCl, 11.4 g MgCl₂.6H₂O, 0.74 g KCl added per liter). The salt solution is about twice the density of sewater and minimises the flushing of material from the traps during deployment and recovery.

For the experiments described here, the tubes were completely filled with salt solution 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 21 days). In all cases, the tubes were stored, acid cleaned and filled using the same methods as those used to prepare traps in the field. The tubes were exposed to surface light intensity or left in the dark to create the two extremes of light levels expected in the field. The 18% light level was chosen because it corresponds to the shallowest deployment depth (30 m) used for the multitrap array in the oligotrophic waters north of Hawaii. 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. Unfortunately, because of a need to collect sediment trap

material for other experiments, it was not possible to deploy sealed traps in the field on other occasions.

Dissolved methane did increase in the salt solutions of tubes exposed to direct sunlight, while tubes incubated in the dark or at the 18% light level showed only small and apparently random variations (figure 2.3). The solutions used to fill the traps were all autoclaved and the tubes were acid cleaned prior to use, making a biological source for the methane unlikely. Furthermore, the same trap solutions sealed in glass bottles and incubated in the light (data not shown) showed no measureable change in methane concentrations. These results imply that the source of the methane was associated with the tubes. The small changes in the darkened tubes relative to the tubes exposed to surface light intensity argues for some unknown photochemical source, although other processes such as adsorption and desorption onto the tube surfaces may also contribute to the changes.

The significance of the above results to the field measurements reported in the following chapters is not entirely clear. None of the traps were deployed in the field at light intensities above a depth corresponding to 18% of surface irradiance, whereas increases of methane in the experimental incubations were only observed at 100% irradiance. Furthermore, the increases in methane concentrations that were measured in these experimental



Figure 2.3. Methane concentration changes measured in sediment traps incubated for various periods. The traps were either kept in the dark, exposed to surface light intensities, or exposed to 18% of surface light intensity.

incubations were 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 field measurements. However, until traps can be constructed using inert materials such as glass, the data on methane concentration changes in sediment traps reported in the following chapters may be influenced by "blanks" and the results need to be interpreted with caution.

Oxygen and nutrient concentrations were also measured on a set of tubes incubated under light and dark conditions to determine if these parameters were influenced by abiological processes occurring in the tubes. Nutrients (NO₂, NH₄, and PO₄) were essentially zero both before and after a 16 day incubation (data not shown), but oxygen levels did decrease with the greatest change occurring in the tubes exposed to surface light intensities (Table 2.2). As reported above, the tubes used for the incubations were acid cleaned and the salt solutions used to fill them were filtered and autoclaved, suggesting that the processes causing the changes in oxygen concentrations were abiotic. Adsorption of oxygen onto the walls of the tubes could explain the decreases in oxygen in both light and dark tubes. However, the greater decreases measured in the light tubes indicate there was either a greater adsorption onto

the light tubes or that some other oxygen removal process, perhaps associated with photochemical reactions, was active in the light tubes. The resolution of the factors causing these changes is beyond the scope of this work, but the results do suggest that any oxygen changes measured in the tubes deployed in the field need to be interpreted with caution.

Table 2.2. Oxygen concentrations measured in the salt solutions of sediment trap tubes incubated for 16 days in darkness or at surface light intensities.

	Dissolved Oxygen (µmol l ⁻¹)				
Sample	Initial	Final	Change		
Dark-1	218.9	186.8	-32.1		
Dark-2	216.4	196.4	-20.0		
Light-1	209.3	156.2	-53.1		
Light-2	216.4	160.4	-56.0		

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Chapter III

Methane Distributions in the Upper Ocean of the North Pacific Gyre

Introduction

Here I present the results of field studies of methane in North Pacific waters. The studies were carried out to assess the distribution of methane in waters extending from coastal California to the oligotrophic North Pacific and included the use of sediment traps to consider possible associations of methane with sinking particles collected by traps. Incubations of plankton samples and particulate material collected in sediment traps were also made to test for the presence of methanogens in the plankton.

Methods

Water Column Sampling

Field samples were collected at a series of sites from Coastal California to the central North Pacific during the VERTEX and ONR cruises (figure 3.1) and in the central North Pacific during ADIOS (figure 3.2). The locations and times of sampling for the cruises are listed in Table 3.1.

All water samples were collected using PVC Niskin bottles mounted on a General Oceanics rosette which had been fitted with a Seabird CTD. Water samples for methane analysis were transferred from the Niskin bottles into 250 ml borosilicate glass bottles, poisoned with 1 ml of a saturated solution of mercuric chloride and sealed. All of



Figure 3.1. Location of sampling sites for the VERTEX and ONR cruises.





the methane samples were returned to shore for analysis. Experiments reported in chapter 2 have shown that poisoned samples can be stored for one year and possibly longer without producing any measureable change in the methane concentrations.

Cruise	Station	Location	Date
VERTEX	1	35.8N 122.6W	June 6, 1984
	2	35.8N 128.2W	June 24, 1984
	3	33.9N 133.8W	June 9, 1984
	4	33.3N 139.1W	June 26, 1984
ONR	1	36.3N 122.0W	June 7, 1985
	2	36.3N 122.2W	June 6, 1985
	3	36.3N 122.4W	June 5, 1985
	C	35.8N 122.6W	June 4, 1985
ADIOS	9	26.2N 155.1W	April 3, 1986
	11	26.4N 155.1W	April 5, 1986
	12	26.0N 155.0W	April 7, 1986
	17	26.0N 155.0W	April 16, 1986
	18	26.0N 155.0W	April 16, 1986

Table 3.1 Location, position and date of collection of water column samples.

Temperature data obtained from the CTD were calibrated using reversing thermometers and the CTD salinity data were calibrated with salinities measured using a Guildline salinometer. Oxygen concentrations were determined by modified Winkler titration (Strickland and Parsons, 1972), and nutrient concentrations were measured by AutoAnalyser (Strickland and Parsons, 1972). The methane concentrations in the water samples were determined by gas chromatography using the gas stripping method described in chapter 2. During the analysis of the ADIOS samples, contamination of the Porapak Q trap used to pre-concentrate the methane resulted in a slightly poorer precision (\pm 5%) than was usually obtained with this method (\pm 3%). The concentration of dissolved methane in equilibrium with the atmosphere was calculated from the temperature and salinity of the surface water using the solubility equations of Weisenburg and Guinasso (1979). In the following chapter, supersaturation refers to a dissolved methane concentration that exceeds the concentration expected if the water were in equilibrium with atmospheric methane.

Sediment Trap Sampling

Free-floating MULTITRAP arrays (chapter 2; Knauer et al., 1979) were used to collect sinking particulate materials during the ADIOS, ONR and VERTEX studies. During VERTEX methane samples were collected from traps deployed at three stations: Station 1: 4-17 June, 1984; Station 2: 5-27 June, 1984; Station 4: 7-29 June, 1984. The traps were set at a total of six depths between 50 m and 2000 m at each of the three VERTEX sites. At site C of the ONR cruise, traps were positioned at 80 m and 175 m depth between May 1 and May 13, 1985. For ADIOS the traps sampled were placed at depths of 30, 120 and 200 m and were

deployed for three periods: I: 24-31 March, 1986; II: 31 March-12 April, 1986; III: 14-17 April, 1986.

All the traps were filled with an autoclaved high density salt solution (0.22 μ m filtered surface seawater with 27.1 g NaCl, 11.4 g MgCl₂.6H₂0 and 0.74 g KCl added per liter) to prevent flushing of trap material during deployment and recovery. Baffles were fixed to the top of each trap to minimize mixing between the salt solutions and the ambient seawater, and a 335 μ m Nitex screen was placed at the base of each of the baffles to prevent large zooplankton and other organisms from swimming into the traps.

The concentration of dissolved methane in the trap solutions was measured to investigate the possible association of methane with particles settling into the traps. All the traps sampled in VERTEX were unpreserved, but for the ONR and ADIOS studies methane was measured in "unpoisoned" traps with no preservative and in "poisoned" traps with buffered formalin (5% v/v final concentration) or mercuric chloride (0.25% v/v of saturated solution) added to the trap solutions as a preservative. Immediately after recovery, seawater overlying the high density trap solutions was removed, and the solution was gently mixed using a polycarbonate plunger designed to prevent gas exchange with the atmosphere. Methane samples were then siphoned into 250 ml glass bottles and analysed as outlined

in chapter II. With the exception of the VERTEX study, initial methane concentrations were determined by sampling the trap solutions just prior to deployment.

Oxygen and nutrient concentrations were also measured in the ADIOS trap solutions using the analytical techniques described above. A blank correction of $-3.4 \ \mu mol \ 1^{-1} \ d^{-1}$ was applied to the oxygen data. The correction was calculated from the changes in dissolved oxygen measured in sealed traps exposed to sunlight (see chapter 2). Based on similar experiments with nutrients described in chapter 2, no blank corrections were necessary for nutrients.

After sampling for gases and nutrients, the remaining solution in the unpoisoned traps was processed for particulate carbon and nutrient analyses. The remainder of the solutions in the formalin-preserved traps was transferred into polycarbonate bottles for microscopic identification of organisms associated with the particles sinking into the traps.

The chloride concentrations of the ADIOS trap solutions were measured for the first deployment. The chloride concentration of the trap solutions were about twice that of seawater. Because chloride is unreactive, changes in the chloride concentration of the trap solutions during the deployment can provide an indication of the extent of exchange between dissolved material in the traps and the surrounding seawater. The chloride concentrations

were measured by potentiometric titration of the sample with a 0.1N AgNO₃ solution (Jagner and Aren, 1972). The amount of sample (\approx 0.2 ml) was determined by weight, and 1.0 ml of a 5 M solution of NaNO₃ was added to each sample to minimise changes in the ionic strenth of the solution due to 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 (chloride (g kg⁻¹) = salinity/1.80655).

Incubations of Trap Particulates and Plankton Samples

In order to evaluate the potential for sediment trap particulates producing methane, a series of incubations was carried out using unpreserved trap material collected at site C during the ONR cruise. Suspensions of the trap material were added to 60 ml serum vials and potential methanogenic growth substrates (methylamine, formate, acetate, glucose and methanol) were added to each bottle to a final concentration of 100 μ M. All air was displaced from the bottles and the bottles were sealed with black butyl rubber stoppers and incubated in the dark at 25°C for up to

26 days. Replicate samples were analysed at the beginning of the incubation and after 17 and 26 days. The sample analysis procedure was the same as for water samples described in chapter 2, but a smaller volume pipet (24.5 ml) and a smaller stripping chamber were used for the extraction of the methane.

As a test for methane production in the plankton, concentrated open ocean plankton samples (30-183 μ m and >183 μ m size ranges) were incubated with a variety of substrates utilized by methanogenic bacteria. The plankton samples were collected from the R/V Hokusei Maru at approximately 19° 50'N and 156° 15'W off the Island of Hawaii by making vertical net tows between 200 m and the surface. Immediately after each tow, the plankton collected in the nets were gently poured into polycarbonate bottles containing 500 ml of filtered (Whatman GF/F) seawater with resauzarin added (0.0001% wt/vol) as a redox indicator. The solution was gently swirled to distribute the plankton evenly, and subsamples of 10 ml were pipetted into glass Hungate tubes (Bellco Glass Inc., Vineland, N.J.). The air in the headspace of the tubes was replaced by a nitrogen atmosphere and the tubes were sealed with black butyl rubber stoppers.

The plankton samples were incubated with and without methanogenic substrates (acetate, formate, methanol, methionine, methylamine, dimethylamine, or trimethylamine).

The final concentration of each substrate was 10 mM and replicates were prepared for each sample treatment. Two of the replicates were incubated without further additions, while BES (2-Bromo-ethanesulfonic acid; 5 mM) was added to one replicate as a specific inhibitor of methanogenesis, and 100 μ l of a saturated solution of mercuric chloride was added to another as a killed control. For each of these samples, paired incubations with and without the reducing agent, cysteine-sulfide (final concentration of 0.025% wt/vol) were also made. All the samples were incubated in the dark at 25°C. Methane was determined in the headspace gas of the sample tubes by injecting 250 μ l of the gas into a HP5890 gas chromatograph equipped with a flame ionization detector. A 3.2 mm x 2 m Porapak Q chromatographic column was used to separate the methane from other gases. The detector response was calibrated using a 23 ppmv methanein-helium standard (Air Products and Chemicals).

Results

<u>Hydrography</u>

Sections of temperature, salinity, sigma-t and oxygen for VERTEX are shown in figure 3.3 and a salinity versus temperature plot (T-S) for the stations is shown in figure 3.4. Station 1 at 122.6°W is located in the California Current where salinities are typically less than about 33.1 per mil and temperatures range from about 12 to 17°C in the upper 100 m of the water column. The shoaling of T, S,



Figure 3.3. Temperature, salinity, sigma-t and oxygen sections along the VERTEX cruise track. Station numbers are given along the top of the figure.



Figure 3.4. Salinity versus temperature plot for stations sampled during VERTEX. The station numbers are given at top of each S-T line.

sigma-t, and oxygen isolines near station 1 is suggestive of upwelling along the California Coast. Station 2 at 128.5°W is towards the western edge of the California Current. The T-S plots for stations 1 and 2 (figure 3.4) are similar although some warming of the more westerly surface waters at station 2 are evident. West of station 2, mixed layer salinities increase up to about 34.5 per mil at station 4 (139.1°W) which is situated in the North Pacific Gyre. The waters between about 300 and 500 m at station 4 contain a salinity minimum (S = 34.00 per mil) associated with subarctic water (Martin et al., 1985). The 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 and cooler waters of the California Current and the warmer, saltier waters of the North Pacific Gyre to the west. Some interleaving of these two water masses is apparent in figures 3.3 and 3.4 for depths shallower than about 200 m (sigma-t < 26). Waters with a sigma-t greater than about 26.5 all have similar S-T properties. The oxygen section in figure 3.3 shows the upper water column is well oxygenated and a broad oxygen minimum (0, < 30 μ mol kg⁻¹) occurs between about 800 and 1000 m depth.

The waters sampled during the ONR cruise are situated in the California Current and extend from the position of station 1, VERTEX, towards the California Coast (see figure 3.1). The sigma- Θ section for the cruise (figure 3.5) shows little evidence for upwelling except for a slight uplift of isopycnals near the continental shelf at station 1, ONR. The waters at each of the stations have similar T-S properties (figure 3.6) indicating the ONR stations are all located within the same water mass.

The hydrography of the upper water column at the ADIOS sample site (figure 3.7) was 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 about 34.02 permil at about 570 m. The salinity minimum is associated with the minimum observed further east at station 4 of VERTEX. As mentioned above, the minimum results from the subduction of relatively fresh subarctic waters below more saline surface waters from the south. The surface mixed layer at the ADIOS site was characterised by fairly isothermal and isohaline conditions with temperatures between 20.0 and 20.4°C and a salinity of about 35.34 per mil. Nutrients were typically depleted down to the base of the mixed layer and oxygen concentration measurements indicate that 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 (Table 3.2).



Figure 3.5. Sigma- θ section along the ONR cruise track.

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Figure 3.6. Salinity versus temperature plot for stations sampled during the ONR cruise off coastal California. The station numbers are given at the bottom of each S-T line.



Figure 3.7. Salinity and temperature at the ADIOS (26N 155W) site.

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ADIOS Stat:	ion 9	26°	09.3'N	155° 06.8	~ W		1986	
Depth	Temp.	Sal.	Sigma-t	CH4	CH4eq	Oxygen	NO3	PO4
(m)	(C)	(g/kg)		(nM)	(nM)	(µmol/kg)	(µmol/kg)	(µmol/kg)
10	20.49	35.349	24.90	2.34	1.98	225.7	0.00	0.00
50	20.33	35.347	24.94	2.36	1.99	226.5	0.00	0.00
100	20.01	35.296	24.99	2.34	2.00	225.9	0.00	0.08
150	18.81	35.165	25.20	2.47	2.05	225.7	0.49	0.05
198	18.47	35.142	25.27	2.40	2.07	226.1	0.49	0.07
300	13.24	34.372	25.86	2.56	2.32	198.4	8.38	0.55
402	10.09	34.155	26.28	2.40	2.50	211.9	15.59	1.02
ADIOS Station 11 26° 21.1'N		21.1'N	155° 06.7	~w	5 April, 1986			
Depth	Temp.	Sal.	Sigma-t	CH4	CH4eq	Oxygen	моз	P04
(m)	(C)	(g/kg)		(nM)	(nM)	(µmol/kg)	(µmol/kg)	(µmol/kg)
10	20.48	35.344	24.90	2.51	1.98	228.9	0.00	0.02
49	20.44	35.348	24.91	2.46	1.98	229.1	0.00	0.00
98	20.34	35.347	24.94	2.30	1.99	228.0	0.00	0.00
150	19.43	35.228	25.09	2.48	2.02	219.9	0.68	0.05
200	18.31	35.091	25.27	2.51	2.07	223.5	0.98	
300	12.67	34.346	25.95	2.39	2.35	217.8	9.36	
400	10.36	34.162	26.24	2.80	2.49	212.8	14.52	0.92
567	6.31	34.003	26.73	1.52	2.75	119.5	30.97	2.23

Table 3.2 Methane and hydrographic data from ADIOS.

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ADIOS Station 12		26° 00.0'N		155° 00.0'W			7 April,	1986
Depth	Temp.	Sal.	Sigma-t	CH4	CH4eq	Oxygen	NO3	P04
(m)	(C)	(g/kg)		(nM)	(nM)	(µmol/kg)	(µmol/kg)	(µmol/kg)
8	20.44	35.354	24.92	2.38	1.98	227.7	0.00	0.00
50	20.41	35.352	24.92	2.43	1.98	228.3	0.00	0.05
100	20.40	35.348	24.93	2.43	1.98	228.1	0.00	0.05
151	19.44	35.248	25.10	2.48	2.02	222.3	0.29	0.00
203	16.70	34.799	25.43	2.58	2.15	208.6	3.51	0.25
303	12.60	34.296	25.93	2.51	2.36	217.1	9.16	0.66
399	9.63	34.115	26.33	2.38	2.53	207.1	15.98	1.00
568	6.53	34.021	26.71	1.24	2.74	112.7	32.14	2.28
ADIOS Stat	ion 17	26°	00.3'N	154° 59.9	Ŵ		16 April,	1986
Depth	Temp.	Sal.	Sigma-t	CH4	CH4eq	Oxygen	моз	PO4
(m)	(C)	(g/kg)		(nM)	(nM)	(µmol/kg)	(µmol/kg)	(µmol/kg)
10	20.30	35.354	24.97	2.40	1.99			
25	20.30	35.354	24.97	2.30	1.99			
80	20.29	35.352	24.97	2.35	1.99			
98	20.28	35.350	24.97	2.51	1.99			
119	19.54	35.256	25.10	2.75	2.02			
138	19.21	35.216	25.15	2.69	2.03			
157	18.92	35.178	25.20	2.52	2.05			
180	18.33	35.071	25.26	2.51	2.07			
200	17.80	34.975	25.32	2.39	2.10			
250	15.26	34.575	25.61	2.72	2.22			
300	12.79	34.307	25.92	2.68	2.35			

Table 3.2 (continued) Methane and hydrographic data from ADIOS.

AD:	ADIOS Station 18		25° 59.1'N		154° 59.8	~ W		16 April, 1986		
	Depth (m)	Temp. (C)	Sal. (g/kg)	Sigma-t	CH4 (nM)	CH4eq (nM)	Oxygen (µmol/kg)	NO3 (µmol/kg)	PO4 (µmol/kg)	
	10	20.32	35.360	24.95	2.20	1.99	224.3	0.00	0.00	
	50	20.31	35.360	24.96	2.22	1.99	224.8	0.00	0.01	
	100	20.97	35.357	24.96	2.28	1.96	224.8	0.00	0.00	
	150	19.17	35.218	25.15	2.32	2.04	220.9	0.49	0.07	
	200	18.04	35.034	25.29	2.32	2.09	214.8	1.85	0.11	
	300	12.77	34.325	25.92	2.56	2.35	211.2	9.45	0.56	
	400	9.89	34.158	26.32	2.61	2.52	208.5	15.49	0.96	
	530	6.81	34.013	26.67	1.43	2.72	130.5	28.83	2.00	

Table 3.2 (continued) Methane and hydrographic data from ADIOS.

hydrographic and nutrient data provided by R. Feely.

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The T and S structure at the ADIOS site remained coherent throughout the study, although a storm between March 31, 1986, and April 9, 1986, caused a deepening of the surface mixed layer from about 100 to 130 m (DiTullio, 1987). The storm coincided with increases in primary production and phytoplankton and total microbial biomass, which appear to be linked to the entrainment of nutrients into the surface layer during the storm (DiTullio, 1987; Jones, 1989; Laws et al., 1989). Increased fluxes of particulate carbon and nitrogen out of the mixed layer also occurred after the storm in apparent response to the changes in surface production and biomass (DiTullio, 1987; Laws et al., 1989; and Taylor, 1989).

Methane Profiles

Methane profiles obtained at stations 1, 2 and 4 of VERTEX are plotted in figures 3.8 to 3.10. The methane concentration data for these stations and for station 3 are listed in Table 3.3. Dissolved methane is at or above atmospheric equilibrium concentrations for waters shallower than 300 m and surface values range between 5% and 32% supersaturated. The largest supersaturations are found at station 1 where a distinct subsurface methane maximum is apparent in the upper pycnocline at about 150 m depth. Methane concentrations up to 5.42 nM (two times atmospheric saturation) were measured in the maximum. Station 2 also shows a methane maximum, but the maximum concentration is


Figure 3.8. Profiles of methane and sigma- θ at station 1, VERTEX (35.8N 122.6W) on June 14, 1984. CH₄eq is the predicted concentration of dissolved methane for water in equilibrium with the atmosphere.



Figure 3.9. Profiles of methane and sigma- θ at station 2, VERTEX (35.1N 128.2W) on June 24, 1984. CH₄eq is the predicted concentration of dissolved methane for water in equilibrium with the atmosphere.



Figure 3.10. Profiles of methane and sigma- θ at station 4, VERTEX (33.3N 139.1W) on June 30, 1984. CH₄eq is the predicted concentration of dissolved methane for water in equilibrium with the atmosphere.

Depth	Pot.	. Temp	•	Sal.	 \	Sigma-	Oxygen	CH4	Ch4eq
(111)		(0)		(0/00	, 	Liieta	(µM)	(11M)	(IIM)
Station	1	35.8N	122.	.6W	14	June, 19	84		
10		11.89		33.5	0	25.45	5 275	2.75	2.47
50		10.04		33.6	8	25.91	. 186	3.82	2.58
90		9.31		33.84	4	26.16	5 163	4.02	2.62
100		9.12		33.89	9	26.23	3 149	4.56	2.63
120		8.79		33.9	7	26.35	5 136	4.89	2.65
150		8.07		34.03	1	26.49	130	5.42	2.70
250		7.03		34.09	9	26.70) 87	3.09	2.77
450		5.31		34.2	1	27.01	. 36	1.73	2.89
600		4.77		34.34	4	27.18	24	1.12	2.93
700		4.42		34.39	9	27.26	22	0.92	2.96
800		4.12		34.44	1	27.33	23	0.61	2.98
900		3.88		34.5	1	27.41	. 25	0.83	3.00
1000		3.64		34.53	3	27.45	29	0.62	3.02
1100		3.46		34.50	5	27.49	35	0.54	3.03
1500		2.65		34.64	1	27.63	51	0.46	3.10
Station	2	35.1N	128.	2₩	24	June, 19	84		
20		16.28		33.08	3	24.21	243	2.96	2.24
60		14.57		33.06	5	24.57	238	3.18	2.33
100		13.55		33.17	7	24.87	233	3.59	2.38
125		12.58		33.29	}	25.24	216	3.97	2.43
150		11.04		33.43	3	25.55	202	3.72	2.52
200		9.34		33.71	L	26.06	159	4.07	2.62
250		8.53		33.94	l.	26.36	146	2.90	2.67
300		7.67		34.02	2	26.55	129	2.73	2.72
400		6.32		34.07	,	26.77	86	2.05	2.82
500		5.61		34.12	2	26.91	50	1.87	2.87
600		4.86		34.21	•	27.07	31	1.45	2.93
650		4.63		34.25	5	27.12	25	1.07	2.94
700		4.49		34.30)	27.18	21	0.87	2.96
750		4.42		34.34		27.22	18	0.80	2.96
800		4.23		34.39		27.28	17	0.92	2.97
850		4.08		34.42	2	27.32	16	0.77	2.99
900		3.97		34.46		27.36	17	0.66	2.99
950		3.79		34.48		27.40	19	0.45	3.01
1000		3.63		34.50		27.43	20	0.63	3.02
1050		3.49		34.51		27.45	22	0.51	3.03
1100		3.34		34.55		27.49	24	0.44	3.04
1300		2.93		34.60		27.57	33	0.47	3.08
1500		2.54		34.63		27.63	45	0.32	3.11

Table	3 .3 .	Dissolved	methane	and	hydrographic	data	obtained
			during	g VEI	RTEX		

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Depth (m)	Pot. Temp. (C)	Sal. (o/oo)	Sigma- theta	Oxygen (µM)	CH4 (nM)	Ch4eq (nM)
Station	3 33.9N	133.8W 9	June, 198	4		
125	15.84	34.31	25.18	208	2.37	2.25
175	11.47	33.71	25.69	193	2.89	2.49
300	8.55	34.00	26.40	170	2.70	2.67
500	6.17	34.12	26.84	58	1.40	2.83
650	4.99	34.22	27.06	30	1.17	2.92
750	4.26	34.26	27.17	24	0.94	2.97
950	3.82	34.44	27.36	18	0.87	3.01
Station	4 33.3N	L39.1W 26	June, 198	4		
100	16.26	34.35	25.19	205	2.63	2.23
150	13.72	34.11	25.56	194	2.53	2.36
200	11.53	33.92	25.84	198	2.57	2.48
250	10.09	33.96	26.13	185	2.79	2.57
300	9.12	34.02	26.34	182	2.55	2.63
400	7.44	34.00	26.57	161	2.66	2.74
500	6.03	34.00	26.76	111	1.32	2.84
600	4.92	34.09	26.97	58	1.41	2.93
650	4.65	34.15	27.04	45	1.22	2.95
700	4.42	34.19	27.10	34	1.20	2.96
750	4.22	34.26	27.17	26	0.89	2.98
800	4.12	34.34	27.24	20	1.02	2.98
850	3.99	34.36	27.27	18	1.02	2.99
900	3.86	34.40	27.33	17	0.56	3.00
950	3.74	34.43	27.36	17	0.56	3.01
1000	3.63	34,46	27.40	17	0.42	3.02
1100	3.39	34.51	27.46	22	0.52	3.04
1300	3.00	34.59	27.55	31	0.72	3.07
1500	2.57	34.62	27.62	41	0.34	3.11

Table 3.3 (continued) Dissolved methane and hydrographic data obtained during VERTEX

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only 4.07 nM (1.6 times atmospheric saturation). No subsurface maximum is apparent at station 4. A methane section between stations 1 and 4 (figure 3.11) shows that the methane concentrations in the upper 300 m of the water column decrease with distance offshore. Below 300 m, no inshore-offshore trends in concentration are apparent.

The methane profile along the cruise track for ONR is shown in figure 3.12, and the data are listed in Table 3.4. The highest methane concentration measured was 15.88 nM for a sample collected near bottom at the continental shelf break. The high concentrations in the near bottom around station 1 suggests methane has a near bottom or sediment source in the region. Offshore from station 2 a subsurface methane maximum is apparent at about 100 m. Station C is at the same location as station 1 of VERTEX V and the maximum concentrations were similar at both stations (5.42 vs. 5.44 nM for VERTEX V and ONR-1, respectively).

A composite plot of water column methane concentrations for hydrocasts made at the ADIOS sampling site is shown in figure 3.13, and the data are listed in Table 3.2. Samples collected in the mixed layer (0-100 m) ranged between 11 and 26% supersaturation relative to atmospheric equilibrium concentrations. This degree of supersaturation is consistent with values of 5 to 30% observed in other open ocean surface waters (Conrad and Seiler, 1988). The variations observed at the ADIOS site



Figure 3.11. Dissolved methane section contoured between stations 1 and 4 of VERTEX.



Figure 3.12. Dissolved methane section contoured between stations 1 and C of the ONR cruise.

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Station	ONR-1	36 18.7N	122 04.3W		June 7, 1	985
Depth	Temp.	Sal.	Sigma-	02	CH4	CH4ec
(m)	(C)	(0/00)	theta	(µM)	(MM)	(nM)
25	11.78	33.37	25.37	266	4.18	2.42
50	9.80	33.55	25.89	192	5.51	2.53
100	9.18	33.93	26.25	132	9.74	2.56
150	8.15	34.14	26.58	82	11.99	2.63
200					15.09	
200					15.88	
Station	ONR-2	36 20.0N	122 14.0W		June 6, 1	985
Depth	Temp.	Sal.	Sigma-	02	CH4	CH4ec
(m)	(C)	(0/00)	theta	(µM)	(nM)	(Mn)
30	11.51	33.34	25.39	255	4.09	2.43
80	9.38	33.54	25.92	172	4.68	2.56
130	8.61	33.87	26.29	134	4.70	2.60
180	8.21	34.03	26.48	111	3.41	2.62
220	7.60	34.10	26.62	104	2.83	2.66
300	6.60	34.18	26.83	60	2.55	2.73
500	5.74	34.35	27.07	28	1.79	2.79
600	5.09	34.40	27.19	23	1.55	2.84
700	4.71	34.47	27.28	22	1.53	2.86
Station	ONR-3	36 19.0N	122 23.0W		June 5, 19	85
Depth	Temp.	Sal.	Sigma-	02	CH4	CH4eq
(m)	(C)	(0/00)	theta	(Mu)	(nM)	(Mn)
50	10.81	33.28	25.47	234	3.38	2.46
100	8.91	33.70	26.12	153	5.08	2.58
150	8.38	33.95	26.39	110	4.04	2.61
200	7.87	34.02	26.53	124	3.43	2.65
250	7.24	34.06	26.65	125	3.11	2.69
300	6.63	34.08	26.75	85	2.91	2.73
400	5.76	34.17	26.92	52	1.89	2.79
600	4.89	34.38	27.20	23	0.99	2.85
800	4.40	34.50	27.34	23	0.63	2.89
1000	3.95	34.55	27.43	26	0.91	2.92

Table 3.4. Dissolved methane and hydrographic data collected between 5 and 7 June, 1985 off Point Sur, California

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Table 3.4. (continued) Dissolved methane and hydrographic dat collected between 5 and 7 June, 1985 off Point Sur, Californi

Station	ONR-C	35 50.0	N 122 36.0)W 2	June 4, 19	985
Depth (m)	Temp. (C)	Sal. (0/00)	Sigma- theta	О2 (µM)	CH4 (nM)	CH4eq (nM)
20	14.56	33.34	24.79	242	3.32	2.27
40	12.69	33.36	25.18	249	3.79	2.37
80	20.64	33.61	25.76	180	5.13	2.48
100	9.75	33.68	25.96	153	5.44	2.53
120	9.46	33.84	26.13	130	4.56	2.55
140	8.97	33.91	26.27	121	4.23	2.58
200	8.13	34.04	26.50	120	3.25	2.63
300	6.71	34.11	26.75	79	3.35	2.72
400	5.59	34.15	26.93	52	2.31	2.80
500	5.22	34.25	27.06	32	1.87	2.83
600	4.68	34.33	27.18	26	1.90	2.87
700	4.31	34.39	27.27	23	1.03	2.90
1000	3.79	34.55	27.45	26	1.49	2.94
1500	2.57	34.67	27.66	44	0.54	3.04
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Figure 3.13. Composite plot of dissolved methane measured at the ADIOS sample site (26N 155W) from 3/4/85 to 16/4/85.

show no trend with time and probably reflect a combination of analytical uncertainty and some natural variability in the methane distributions. The undersaturations observed below about 400 m are a characteristic feature of dissolved methane in deep ocean waters (Scranton and Brewer, 1978), with the exception of regions with bottom-derived inputs (Brooks, 1979 and Gamo et al., 1987).

Because of other sampling requirements, a detailed profile in the upper ocean could only be made at station 17 of ADIOS. The samples collected at this station (figure 3.14) show a small subsurface maximum at the base of the mixed layer with methane concentrations of up to 36% above saturation at 119 m. Larger subsurface maxima have been reported at other open ocean sites, but the maxima are not always present in the open ocean (Conrad and Seiler, 1989). Sediment Trap Data

<u>Chloride</u>

The concentrations of chloride measured in the formalin preserved trap solutions for the first deployment of ADIOS are given in Table 3.5. The decreases in chloride concentrations during the deployment were greatest in the shallow trap at 30 m, but only amounted to a 5.6% change. These data suggest that the high density salt solutions do not readily mix with overlying seawater, and that diffusion of dissolved constituents from the traps is minimal. However, it is important to realise that these measurements





Trap Depth (m)		Chloride (g kg ⁻¹)	2
 ,	Initial	Final	Change
30	40.9	38.6	-5.6%
120	40.4	40.0	-1.0%
200	40.4	40.0	-1.0%

Table 3.5 Chloride concentrations measured in the salt solutions of sediment trap deployed at three depths in the North Pacific between 3/24/86 and 3/31/86.

represent only the diffusive and mixing losses from the salt solutions that are recovered. When the traps are deployed they are filled with salt solution to within 7 cm of the top of the traps, and the rest of the trap is filled with distilled water. During deployment the distilled water is mixed out of the traps and replaced by denser seawater. When recovered, the interface between the salt solution and the overlying seawater is distinct, but the volume of the salt solution is always less than when the traps were deployed. For the traps used in this study, 15 to 35% of the original two liters of salt solution added to the traps was lost between deployment and recovery. Based on the chloride concentration measurements presented in Table 3.5, there does not appear to be much exchange between the

ambient seawater and the remaining salt solutions. However, the fraction of salt solution lost from the traps between deployment and recovery can affect the total accumulation of the dissolved constituents. For example, if the salt solution was lost from the traps during the initial deployment (before dissolved material such as nutrients and methane can accumulate in the traps), then the concentrations measured in the solutions will be representative of the total accumulation. If the "lost" salt solution is flushed from the trap during recovery, the amount of dissolved material originally in the trap will be underestimated by an amount equivalent to the fraction of salt solution lost, assuming the trap solution is well mixed. A situation in between the two extremes would result in an underestimation of between 0 and 35% of the total accumulation of dissolved material in the traps. Based on observations made from a submarine (G. Knauer, pers. comm.), most of the loss appears to occur during the initial trap deployment and the percent underestimation is likely to be at the lower end of this range. I have no direct evidence on when the salt solutions were lost from the ADIOS traps and I have not attempted to correct for this effect. For future studies, the use of opening and closing traps would help to avoid the loss of trap solution during deployment and recovery of the traps.

<u>Methane</u>

Methane concentration measurements made on sediment trap solutions showed that methane accumulated in the traps over time. Generally, the methane accumulations were greatest in the shallow traps and tended to increase with distance from shore.

Methane accumulations were greatest in the 30 m traps at the ADIOS site (Table 3.6), while concentrations in the

Table 3.6. Total accumulated methane (nmol trap⁻¹ d⁻¹) in formalin-preserved and unpreserved sediment traps deployed at the ADIOS sampling site (26N 155W). Deployment times were 6.9 days for station 1, 11.7 days for station II, and 3.1 days for station III.

Trap Depth	Methane (nmol trap ⁻¹ d ⁻¹)					
(m)	Preserved	Unpreserved				
Station I						
30	2.13	2.96				
120	0.62	0.78				
200	0.22	1.20				
Station II						
30	5.82	5.09				
120	0.97	1.32				
200	0.74	1.14				
Station III						
30	3.26	3.84				
120	1.23	1.06				
200	1.29	1.06				

120 and 200 m traps were similar for each deployment. The preserved and unpreserved traps at each depth also hadsimilar amounts of methane, implying that the methane increases were not the result of biotic production in the traps.

The preserved and unpreserved traps deployed at ONR site C also showed similar methane accumulations (Table 3.7). In addition, there does not appear to be any

Depth (m)	Trap	Preservative	Methane (nmol trap ⁻¹ d ⁻¹)
80	A-5 A-6 A-7	Formalin " HgCl ₂	0.93 0.74 0.66 Ave: 0.78 ± 0.14
80	A-8 A-9 A-10	None "	0.72 0.48 0.58 Ave: 0.59 ± 0.12
175	B-5 B-6 B-7	Formalin " HgCl ₂	0.47 0.48 0.58 Ave: 0.51 ± 0.06
175	B-8 B-9 B-10	None "	0.52 0.52 0.48 Ave: 0.51 ± 0.02

Table 3.7. Methane accumulations in preserved and unpreserved sediment traps deployed between 1/5/85 and 13/5/85 at the ONR site C. significant difference between the rates of methane increase between the 80 and 175 m traps.

Methane concentrations measured in the sediment traps deployed at stations 1, 2, and 4 during VERTEX V are shown in figure 3.15. As mentioned previously, the initial concentration of methane in the VERTEX traps was not determined and the data could not be corrected for the methane in the trap solutions at the time of deployment. The failure to correct for this "blank" makes a comparison between the VERTEX data and the samples collected on the other cruises difficult and I have not attempted to calculate a daily accumulation rate for methane. Nevertheless, the VERTEX data do reveal patterns of change in methane accumulation between coastal and offshore sites that are consistent with the variations observed at the ADIOS and ONR sampling sites as outlined below.

The VERTEX traps shallower than 300 m showed increases in methane concentration relative to deeper traps. Below 300 m the methane concentrations were 5.20 ± 1.06 nM (1 s.d.; n=14). The greatest methane increases in the near surface traps occurred at station 4, which had the smallest particulate matter fluxes of all the stations sampled (Martin et al., 1985). If the average methane concentrations of 5.20 nM observed in the deep traps 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 station 4 was 4.27 nmol trap⁻¹ d⁻¹. If the 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, which had the largest particulate matter fluxes of all the VERTEX stations (Martin et al., 1985). Station 1 is at the same location as the ONR sediment trap site and the data from both cruises indicate there is little variability with depth in the amount of methane accumulated in the traps at this site. Although the shallowest trap at station 2 is at 130 m, there appears to be a tendency for higher methane accumulations to occur in the traps closer to the surface compared with what was observed at station 1. The data collected at the VERTEX sites are consistent with the changes in methane accumulations observed at the ADIOS and ONR sites and suggest that methane accumulations in the traps increase towards the surface and with distance offshore.

Dissolved Nutrients and Oxygen

In order to provide an indication of the degradative processes associated with the particulate material collected in the traps, particulate and dissolved C and N and dissolved oxygen were measured in the traps. The flux

of particulate organic carbon and nitrogen (POC and PON) into the traps was greatest in the shallow 30 m trap for the first two deployments, while the greatest flux in the last deployment was measured in the trap set at 120 m (Table 3.8; Laws et al., 1989). For comparison, the methane accumulations accounted for 0.02% or less (mole/mole) of the particulate organic carbon collected in the traps. Dissolved nitrogen (DON + NH_4 + NO_3) in the trap solutions showed a pattern of change similar to particulate C and N, with the greatest concentrations tending to occur in the shallowest traps. The dissolved nitrogen accounted for between 16 and 37% of the total nitrogen accumulation, which is comparable to values of between 33 and 36% for identical traps deployed in near-surface waters off California (Karl and Knauer, 1989 and Taylor et al., 1986). The dissolved nitrogen was mostly DON and ammonium, with a small contribution from nitrate. The amounts of DON and NH₄ were comparable, but a greater fraction of NH₄ tended to occur in traps deployed the longest (station II).

Oxygen was consumed in the trap solutions. A maximum depletion of 140 μ mol was measured in the 30 m trap at station II, which is equivalent to the consumption of about 75% of the dissolved oxygen originally present in the solution. Generally, the longer the deployment time and the shallower the trap, the greater the oxygen depletion.

Table 3.8. Changes in dissolved and particulate components in Multitraps deployed at the ADIOS sampling site. All changes are in units of μ mol trap⁻¹, except for CH₄ (nmol trap⁻¹). The multitraps were deployed for 6.9 days at station I, 11.7 days at station II, and 3.1 days at station III.

Station	Trap Depth (m)	CH4*	0 ₂ **	POC¶	PON¶	DON	NH4 ^{**}	NO ₃ **	Total [§] N	%‡ DN
Station T										
	30 120 200	20.4 5.4 8.3	-60.6 -28.2 n.d.	155.6 112.0 120.6	15.5 9.7 10.9	5.15 3.35 1.58	3.27 2.31 0.39	0.05 0.05 0.16	24.0 15.4 13.0	35.3 37.0 16.4
Station II	E									
	30	59.6	-141.8	302.2	28.6	6.64	5.34	0.46	41.0	30.3
	120	15.4	-	241.5	25.8	4.72	5.67	0.20	36.4	29.1
	200	13.3	-25.6	168.2	13.1	2.08	1.17	0.26	16.6	21.1
Station II	II									
	30	11.9	-32.4	173.3	13.6	2.17	0.93	n.d.	16.7	18.6
	120	3.8	-26.4	230.9	20.2	6.07	1.04	n.d.	27.3	26.0
	200	4.0	-17.0	108.6	7.5	1.33	0.23	0.94	10.0	25.0

analytical precision ± 5%

** analytical precision (
$$\mu$$
mol trap⁻¹): 0, ± 3.0; NH, ± 0.08; NO₃ ± 0.03

$§$
 DON + NH₄ + NO₇ + PON

$$= [(DON + NH_{\ell} + NO_{\tau})/Total N] \times 100$$

n.d. no detectable change

Incubation of Trap Particulates and Plankton Samples Tests for methane production in plankton samples and in particulates caught in sediment traps were generally negative. The incubations of trap particulates (figure 3.16) and of plankton in the 30 to 183 μ m size range (data not shown) failed to produce any methane. Methane production was observed in one sample of plankton in the >183 μ m size range (Table 3.9) which had methanol and cysteine sulfide added as a substrate and reducing agent, respectively. However, a duplicate sample incubated under identical conditions failed to produce any methane. **Discussion**

The distribution of dissolved methane at the sampling sites is the net result of a number of processes including air-sea gas exchange, mixing, microbial methane oxidation, sediment inputs, and in situ production. Methane undersaturations are a common feature in the deep ocean (Scranton and Brewer, 1978) and the undersaturations observed in waters deeper than about 400m are suggestive of net methane consumption. At these depths, microbial oxidation of methane must exceed the rate of methane supply due to diffusion and advection from supersaturated surface waters, potential inputs from sediments, and in situ production (see chapter 1; Scranton and Brewer, 1977). The supersaturations in the surface layer require that inputs



Figure 3.16. Methane concentration changes (per cent) for samples of sediment trap particulates incubated for 17 and 26 days in serum bottles with various organic substrates added.

Table 3.9. Summary of the incubation of plankton samples with various substrates added to final concentrations of 10mM.

Sample Treatment	No added Substrate	Trimethyl -amine	Dimethyl -amine	Methyl -amine	Methanol	Methio -nine	Formate	Acetate
Sample	-	_	-	-	-	-	-	-
Sample + cysteine sulfid	-	-	-	-	+	-	-	-
Sample + BES	-	-	-	-	-	-	-	-
Sample + BES + cysteine sulfid	-	-	-	-	-	-	-	-
Sample + HgCl ₂ (control)	-	-	-	-	-	-	-	-

+ methane production- no methane production

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exceed losses. In some regions inputs from methane-rich coastal waters can influence the degree of supersaturation in the water column (e.g. Scranton and Farrington, 1977). Horizontal methane concentration gradients were not measured around the ADIOS site, but the VERTEX section (figure 3.11) to the east of the ADIOS site does not show any large horizontal methane gradients in open ocean waters of the central North Pacific. Consequently, horizontal diffusive and advective inputs of methane are unlikely to be important in effecting the methane distributions at the ADIOS site. The most probable cause of the supersaturations is in situ production, and previous investigations of methane distributions have also concluded that in situ production is required to support the supersaturations in the open ocean (Scranton and Brewer, 1977 and Brooks et al., 1981).

The relative importance of each of the sources and sinks in determining the surface layer methane concentrations at the ADIOS site is estimated below by applying a mass balance.

The methane supersaturations observed in the mixed layer at the ADIOS site will cause a net flux of methane to the atmosphere. The magnitude of the flux, F, can be estimated using the equation

$$F(\mu mol m^2 d^{-1}) = K_L \cdot (C_s - C_{ed})$$
 (3.1)

where K_L is a gas transfer coefficient (m d⁻¹), C_s is the concentration of methane in the surface layer (μ mol m⁻³) and C_{eq} is the dissolved methane concentration (μ mol m⁻³) in seawater at equilibrium with the atmosphere. The latter property was calculated using the solubility equation of Weisenberg and Guinasso (1979) and an atmospheric methane concentration of 1.70 ppm. The atmospheric concentration was estimated by extrapolating data collected at a nearby monitoring site at Cape Kumukahi, Hawaii (Steele et al., 1990) to the time of the cruise. The gas exchange coefficient was estimated using:

 K_L (m d⁻¹) = 0.86U₁₀ - 2.9; 4.2 < U₁₀ < 18 m s⁻¹ (3.2) where K_L is normalised to methane at 20°C and U₁₀ is the wind speed at 10 m above sealevel. The expression for K_L is derived from Barber et al. (1988). The values were corrected to in situ temperatures by assuming K_L varies in proportion to Sc^{-0.5}, where Sc is the Schmidt number for methane (Jahne et al., 1987). During the sampling period average daily wind speeds varied between 8.4 and 15.1 m s⁻¹ (DiTullio, 1987). For the methane concentration and temperature data given in table 3.1, the calculated net sea to air flux of methane is between 0.9 and 3.5 µmol m⁻² d⁻¹. The time averaged flux of methane to the atmosphere is estimated to be 2.5 µmol m⁻² d⁻¹, using an average concentration of 2.39 µmol m⁻³ for the surface layer

(calculated from table 3.1) and the mean daily wind speeds given in DiTullio (1987).

The small methane maximum observed at the base of the mixed layer (figure 3.14) will cause a diffusive flux of methane into the surface layer. For an eddy diffusion coefficient of 1.8 $cm^2 s^{-1}$ (Li et al., 1984) and a methane concentration gradient of 0.0114 μ mol m⁻⁴ calculated between 98 and 119 m at station 17 (Table 3.1), the diffusive flux of methane will be about 0.2 μ mol m⁻² d⁻¹. This input only accounts for about 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 are often found in the open ocean (Scranton and Brewer, 1977). From the calculation above it is apparent that failure to consider this diffusive input to the surface layer should only affect the methane balance for the layer by less than 10%.

Dissolved methane in the surface layer should be consumed by microbial oxidation (Seiburth et al., 1987; Ward et al., 1987 and Jones, 1991). Turnover times associated with the microbial consumption of dissolved methane in the open ocean are long and vary from 5 to >100 years, with an average of about 65 years (Ward et al., 1987 and Jones, 1991). For an average methane concentration of 2.39 nmol 1⁻¹ in the upper 100 m of the water column, the

integrated methane consumption rate will be between 0.13 and 0.01 μ mol m⁻² d⁻¹ using the above turnover times. Based on the average turnover time of 65 years, the consumption rate is most likely to be on the order of 0.01 μ mol m⁻² d⁻¹. This rate is insignificant compared to the loss associated with air-sea gas exchange.

The above mass balance calculations suggest that the distribution of methane in the surface mixed layer at the ADIOS site is essentially a balance between in situ production, a small diffusive input through the base of the mixed layer, and loss by air-sea gas exchange; microbial consumption plays only a minor role in the mass balance. 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 μ mol m⁻² d⁻¹ occurs over the 100 m thick surface layer.

The source/sink relationships will change for waters below the mixed layer, where air-sea gas exchange will no longer directly affect methane concentrations. Here, the long subsurface residence times of deep water, combined with a decrease in methane production rates relative to methane oxidation rates would produce the undersaturations that are commonly observed in the deep ocean.

A net production is required to preserve the subsurface methane maximum at station 17. Because these subsurface waters cannot directly exchange methane with the

atmosphere, the rates of methane production needed to maintain the maxima can be 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 about 0.2 μ mol m⁻² d⁻¹. The diffusive flux from the maximum to deeper water will be about 0.06 μ mol m⁻² d⁻¹, given a methane gradient of 0.0039 μ mol m⁻⁴ (calculated from data in Table 3.1) and an eddy diffusivity of 1.8 $cm^2 s^{-1}$ (Li et al., 1984). The total diffusive flux away from the layer is then about 0.26 μ mol m⁻² d⁻¹. Assuming the production occurs over a 50 m thick subsurface layer, a net in situ production rate of 0.005 μ mol m⁻³ d⁻¹ could maintain the diffusive losses of methane from the maximum. In the surface mixed layer an average production rate of 0.023 μ mol m⁻³ d⁻¹ is needed to maintain the supersaturations (see above). Higher rates of production would be necessary if the subsurface methane production occurs over a narrower depth range. The 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, the maximum may simply result from air-sea gas exchange having no direct affect on the methane balance below the mixed layer.

The dissolved methane section for the ONR cruise (figure 3.12) suggests there is a near-bottom source of

methane to the water column near the continental shelf break off Point Sur, California. Sediments are the likely source of the methane and similar inputs have been found in a number of other locations (see chapter 1).

The ONR section (figure 3.12) also shows a methane maximum in the upper pycnocline of stations 3 and C. The slight minimum in methane concentrations at station 2 may simply be an indication of the variability in the methane content of waters that are advected down the California coast. Factors such as residence time of the water over the shelf, where sediments may be a source of methane, the upwelling of methane depleted waters near the shelf, and variations in the rates of in situ methane production could all introduce some variability in the methane distributions.

For station C of the ONR cruise, net production in the mixed layer can be calculated in a manner similar to the mass balance calculation for the upper water column at the ADIOS site. For the calculation I have assumed there are no net horizontal advective or diffusive inputs. As was the case for the ADIOS site, methane data are not available in all directions around site C, but water from station 3 is likely to be advected through the general area of site C by the southward flowing California Current. From figure 3.12 it is apparent that the horizontal gradients in methane concentrations between sites 3 and C are small and

neglecting any net horizontal inputs through diffusion and advection appears reasonable to a first order approximation. The net methane flux from the ocean to atmosphere at site C is calculated from wind speed data in the same way as for the ADIOS site and gives a net loss from the surface ocean of 3.08 μ mol m⁻² d⁻¹. For a vertical eddy diffusivity of 1.8 $cm^2 s^{-1}$ and a methane concentration gradient of 0.0155 μ mol m⁻⁴ (calculated from methane data in table 3.4), the net diffusive input to the mixed layer is 0.24 μ mol m⁻² d⁻¹. Methane oxidation is assumed to be insignificant as a sink in the mixed layer (see above). Using these flux terms, the resulting net production needed to maintain steady state methane concentrations in the mixed layer at site C is 2.84 μ mol m⁻² d⁻¹. This rate of net production is similar to the rate of 2.3 μ mol m⁻² d⁻¹ calculated for the oligotrophic waters at the ADIOS site and again suggests that net in situ production and gas exchange are the primary factors controlling the methane supersaturations in the mixed layer. However, this balance only applies to the mixed layer and the high methane concentrations in the methane maximum may be influenced by other factors. The increases in methane concentrations towards the shelf break (figure 3.12) suggest that other sources of methane, which may be related to sediment inputs, become important in coastal regions.

The methane section obtained on the VERTEX transect shows a plume of methane rich water extending into the central North Pacific gyre from the California coast. As with the ONR data, coastal methane inputs which are probably sediment derived are likely to influence the inshore-offshore gradients. With distance offshore, air-sea gas exchange and diffusion of methane from the subsurface maximum will act to decrease the methane concentrations, while some combination of in-situ methane production and diffusive and advective inputs from coastal waters will supply methane to the upper ocean waters. The potential for advection having an influence on the methane distributions is perhaps best seen at station 3 of VERTEX. At this station a core of relatively fresh water from the California Current occurs between about 125 and 225 m and is surrounded by saltier North Pacific gyre water (figure 3.3). The T-S diagram in figure 3.4 also shows this interleaving with the core of the cooler and fresher subsurface layer having a sigma- Θ of 25.7. Based on the methane distributions described above, the methane concentrations in the coastal waters of the region are greater than 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 (figure 3.11).

As mentioned above, in situ production appears to be the major source of the methane in open ocean surface waters. Methane is produced by methanogenic bacteria as an end product in the anaerobic diagenesis of organic matter. All known methanogens are obligate anaerobes (Wolfe, 1971); suggested sites for methane production in oxygenated surface waters include reducing microenvironments in fecal pellets, suspended particulates, and the intestinal tracts of zooplankton and other marine animals (Martens and Berner, 1974 and Scranton and Brewer, 1977). Scranton and Brewer (1977) have also suggested that methane may be a byproduct of algal growth.

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 (see chapter 1). No consistent associations have been observed, perhaps in part due to air-sea gas exchange which will influence methane distributions, but is unlikely to have any impact on biomass or particulate matter concentrations in the water column.

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 particulate aggregates in near-surface waters (Alldrege and Cohen, 1987; Paerl (1989)

and Paerl and Purfert, 1987), but it is not clear if the extreme reducing conditions needed for methanogenesis can exist in these or other aggregates. Other evidence for the existence of anoxic microzones is less direct. Shropp et al. (1987) have used an immunofluorescence technique to identify facultatively anaerobic "hydrogen-producing" bacteria in near-surface particulate material. While the presence of these bacteria suggests that anaerobic conditions may exist in particulate material, the same bacteria are also capable of growth under aerobic conditions and they are not an unequivocal indicator of anaerobic conditions. A number of reduced trace gases other than methane (e.g. carbon monoxide, hydrogen sulfide and ethylene) have also been found at concentrations in excess of equilibrium with respect to the atmosphere, and appear to have a source in the water column. These gases are known to form as products of the anaerobic degradation of organic matter, but other sources including photochemical reactions may also influence their concentrations (Elliot et al., 1987; Conrad and Seiler, 1980; Wilson et al., 1970). Overall, the above evidence suggests that anaerobic microenvironments can exist in the upper ocean, but the relevance to methane production is yet to be established.

If reducing microenvironments do exist in the upper ocean, the model calculations of Jorgenson (1979) and Jumars et al. (1990) indicate that high rates of oxygen

consumption would be needed to maintain the reducing conditions. Seiburth (1987) has proposed such a process where the microbial oxidation of methylated amines, derived from algae, reduces oxygen concentrations in particulate aggregates and permits the growth of methanogenic bacteria on the same methylated compounds.

The availability of suitable growth substrates is another important requirement for methanogenic bacteria. Most biogenic methane is produced in nature by the fermentation of acetate or the reduction of carbon dioxide by hydrogen (e.g. Whiticar et al., 1986). When sulphate is present in the environment, sulphate reducing bacteria tend to outcompete methanogens for acetate and hydrogen. The competition for the substrates generally results in methanogenesis being restricted to environments with low sulphate concentrations, or where non-competitive substrates such as methanol, methionine, dimethylsulphide and methylamine are available (e.g. see chapter 1 and references cited therein). The high sulphate content of seawater is likely to restrict methanogenic bacteria to growth on non-competitive substrates. Sieburth (1987) and Cynar and Yayanos (1989) have reported methane production in plankton samples incubated under anoxic conditions with methylamine added as a growth substrate. The only other report of methanogenesis in marine particulates was for plankton samples collected in San Francisco Bay and
incubated under reducing conditions (Oremland, 1979). No substrates were added to the San Francisco Bay samples and the substrates produced by the anaerobic degradation of the samples was presumably sufficient to support methanogenesis.

For the incubations carried out in this study, methane production was only observed in one >183 µm sized sample with methanol added as a growth substrate (Table 3.9). The sample included both particulate matter and zooplankton, and it is not possible to determine which component of the sample was associated with the methane production. Seiburth (1987) has suggested that methanol may be formed in microenvironments in the open ocean by the breakdown of algal polysaccharides. The other substrates tested, including methylated amines, did not produce methane although Cynar and Yayanos (1989) have reported successfully culturing a marine methanogen using methylamine as a growth substrate. The methane production observed in the incubation provides some evidence that methanogenesis may be occuring in planktonic or particulate material in the open ocean. However, the use of reducing agents and growth substrates for the incubations substantially alters the environment the samples are exposed to, and the observed methane production is merely an indicator of the potential for methanogenesis. Furthermore, lack of methane production in a duplicate

sample incubated under identical conditions suggests that the sampling procedures may have disrupted the microenvironments, or there is only a limited capacity for methanogenesis in the samples.

The incubations of particulate matter collected in sediment traps also failed to produce methane (figure 3.16), suggesting that the methane accumulations observed in the traps are unlikely to result form methanogenesis occurring in particles once they have fallen into the traps. This is supported by the similarity in methane accumulations in preserved and unpreserved traps deployed at either the ADIOS and ONR sites (Tables 3.6 and 3.7). These results do not preclude the possibility of methane production occurring in the particles prior to collecting them in the traps.

If the methane in the traps is assumed to be biologically derived, some constraints can be placed on the methane concentrations in the particles that are needed to produce the observed accumulations. This calculation is carried out for the ADIOS site because it had high methane accumulation rates and based on particulate carbon flux information (Martin et al., 1987) is expected to have much lower fluxes of carbon into the traps than the stations closer to shore (Martin et al., 1987). Consequently, the concentrations of methane in the particles that would be

necessary to account for the methane accumulations would be greater at the ADIOS site than the other trap locations.

The particulate carbon collected in the traps at the ADIOS site was predominantly amorphous organic material, and recognizable material (ciliates, sarcodines, fecal pellets and phytoplankton) accounted for less than 11 per cent of the total carbon flux (Taylor, 1989). For the 30 m trap at station II, the volume of recognisable material was about 6 mm³ (G. Taylor, personal communication). Fecal matter has a carbon:volume ratio of about 2.2 μ molC mm⁻³ (Urrere and Knauer, 1981). If we assume a similar carbon:volume ratio in the amorphous material in the trap, the volume of this material would be about 120 mm^3 (89% of POC accumulation of 302.2 μ molC divided by 2.2 μ molC mm⁻³). The methane accumulation in the same trap was 59.6 nmol (Table 3.8) and if the methane is evenly distributed throughout the particulates, the average methane concentration would be about 0.50 mmol 1^{-1} . The average concentration may actually be smaller because amorphous aggregates of organic matter are likely to have lower carbon:volume ratios than fecal pellets. For example, data on volumes and carbon concentrations of particulate aggregates of marine snow from coastal California (Hebel et al., 1985) can be used to estimate a carbon:volume ratio of between 0.001 and 0.01 μ molC mm⁻³. With these ratios the average methane concentration in the particles would range

between 0.2 and 2.2 μ mol 1⁻¹. The amorphous material in the traps appeared to be much less compacted than fecal matter, but there is no way to independently determine the volume of the material. The methane concentrations estimated in the same way for particulates collected in other ADIOS traps were less than the values given above.

The absolute methane concentrations in particles collected in the traps is likely to be influenced by bubbles which will form when the partial pressure of dissolved methane exceeds the hydrostatic pressure. Bubbles could disrupt the particles and might also make the particles bouyant and prevent their sinking into the traps. The solubility equation given in Weiss (1974) for a nonideal gas can be used to calculate the minimum concentrations at which bubbles will form. For the calculation, values of the second virial coefficient of methane used in the calculation were obtained from Dymond and Smith (1980) and the water temperature was 20°C. For a depth of 30 m, concentrations greater than 4.86 mmol 1^{-1} should result in bubble formation. At 200 m depth, bubbles will only begin to form when the methane concentration in the particles exceeded 24.13 mmol 1^{-1} . These concentrations are larger than the above estimates of concentrations needed to explain the methane accumulations in the traps. However, it is unlikely that methane production would occur evenly throughout the particles and locally higher

concentrations that approach these values may occur. Based on the above calculations, the estimated methane concentrations of up to 0.50 mmol 1⁻¹ in the particulates are possible. As mentioned previously, anaerobic microenvironments need to exist in the particles for bacterial methanogenesis to occur. Hence, oxygen diffusion into the particles must be at least matched by oxygen consumption in the particles or their interiors will become aerobic and methane production will cease.

Jorgensen (1977) used a sphere to represent a particle and constructed a simple steady state model of oxygen diffusion and consumption using the equation:

$$D_{g} \frac{1}{r^{2}} \frac{d}{dr} \left(r^{2} \frac{dC}{dr} \right) - \rho = 0$$
 (3.2)

where D_s is the molecular diffusivity of oxygen, r the distance from the center of the sphere, C the oxygen concentration, and ρ the rate of oxygen consumption which is assumed constant throughout the sphere. To obtain anoxic conditions in the center of the sphere at r=0, and for a sphere of radius, b, the equation solution is:

$$C_o = \frac{\rho}{6D_g} b^2 \tag{3.3}$$

At the ADIOS site the average oxygen concentration in the ambient seawater, C_{a} , was about 0.23 μ mol cm⁻³ (Table 3.1). The value of D is taken as 2.4 x 10^{-5} cm² sec⁻¹ (Jorgensen, 1977), and b is assumed to be 0.015 cm. The small radius was chosen because the screens covering the traps were a 333 µm mesh size. Based on these values, the center of a particle would only become anoxic if the oxygen consumption rate was equal to or exceeded 0.15 μ mol cm⁻³ sec⁻¹. Anoxic conditions have been reported for a fecal pellet with a radius of 210 μ m that was attached to marine snow (Alldredge and Cohen, 1987). The external oxygen concentration for this pellet was 0.5 μ mol 1⁻¹, and the oxygen consumption calculated using the above equation is 0.17 μ mol cm⁻³ sec⁻¹. This consumption rate is similar to the rate estimated to be necessary to maintain anoxic conditions in the 150 μ m radius particles. However, other particles sampled by Alldrege and Cohen (9187) showed only partial oxygen depletions and the anoxic conditions they described in the one fecal pellet may have be an unusual occurrence.

The oxygen depletions and nutrient enrichments in the trap solutions at the ADIOS site (figure 3.8) do indicate there is some capacity for oxygen-deficient microzones to develop in trap particulates. High ammonia concentrations

have been reported in suspended particulate aggregates and sediment trap solutions and in most cases result from nutrient regeneration by protozoan grazers (Alldrege and Silver, 1988; Glibert et al., 1988 and Taylor et al., 1986). Elevated DON concentrations have also been measured in traps and its release is also associated with particle decomposition (Taylor et al., 1986).

The initial stage of decomposition of organic matter consumes oxygen and produces ammonia by oxic respiration (e.g. Krumbien and Swart, 1983). A general equation can be written to describe this process by using the C:N:P ratio in the material being remineralized. The C:N:P ratio in the trap particulates of 155:16:1 was estimated by assuming the N:P ratio was the same as the Redfield ratio of 16:1 and a C:N ratio of 9.7:1 was calculated from the POC and PON data in Table 3.8. The C:N ratio is higher than the Redfield ratio of 6.6 and this is probably due to the high detrital component in the traps at the ADIOS site (>89%; Taylor, 1989). The general equation for the decomposition is:

$$(CH_2O)_{155}(NH_3)_{16}H_3PO_4 + 155O_2$$

 $\rightarrow 155HCO_3^- + 16NH_4^+ + HPO_4^- + 141H^+ (3.4)$

The ammonium ions produced in the equation can be oxidized to nitrite and then nitrate by the activity of nitrifying bacteria. Equations to describe these reactions are:

$$16NH_{4}^{+} + 240_{7} \rightarrow 16NO_{7}^{-} + 32H^{+} + 16H_{7}O$$
 (3.5)

$$16NO_{2}^{-} + 8O_{2} \rightarrow 16NO_{3}^{-}$$
 (3.6)

The ADIOS traps at or above 120 m depth had nitrate plus nitrite accumulations that were 10% or less of the ammonia increases. In the 200 m traps, the nitrate accounted for between 22% and 408% of the ammonia (Table 3.8). The pattern of increase in nitrate plus nitrite relative to ammonia is consistent with the activity of nitrifying bacteria increasing as particles sink or age (Karl et al., 1984 and Taylor et al., 1986).

If equation 3.4 describes the dominant process in the decomposition of the sediment trap organic matter, then a plot of oxygen utilization versus ammonia concentrations for the traps should give a line with a slope of about 9.7:1. However, the slope calculated from the data in Table 3.8 is about 24:1. The reason for the excess O_2 consumption relative to NH_4^+ production is not clear. Denitrification, the oxidation of reduced compounds produced in anoxic microenvironments, the absorption and desorption of ammonia and possibly oxygen from the trap walls, and oxygen consumption associated with photochemical reactions (e.g. Gieskes and Kray, 1982) are some processes that may cause a

change in the expected slope. Unfortunately, the data available do not make it possible to distinguish between these possibilities.

The oxygen depletion of 144 μ mol in the 30 m trap at station II (Table 3.8) can be produced with an average consumption rate of 6.9 x $10^{-4} \mu$ mol cm⁻³ sec⁻¹, if the carbon:volume ratio for the particles in the trap is 2.2 μ molC mm⁻³ (see above) and the total carbon collected in the trap is 444 μ molC (POC accumulation + O₂ depletion; Table 3.8). This rate of oxygen consumption is clearly too low to maintain anoxic conditions in particles with a 150 μ m radius. If the oxygen consumption rate is taken as 6.9 x $10^{-4} \mu mol cm^{-3} sec^{-1}$, and values of D_s and C_o are assumed the same as above, then a particle with a radius of 2.2 mm could become anoxic in its center. Decreasing the size of D_s could decrease the oxygen consumption rate needed to produce anoxic conditions. A decrease in D_s could result from solid matter in the particulates increasing the path length for diffusion of dissolved constituents into or out of the particles. 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 anoxic conditions necessary for bacterial methanogenesis cannot readily exist in the small (<150 μ m) particles collected in the traps. This conclusion is supported by the

similarity in methane concentrations in preserved and unpreserved traps and the lack of methane production in the trap particulates incubated with methanogenic substrates. 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 would most likely have occurred when the particles contacted the trap screens.

Alternatively, if the particles passed through the gut of organisms, high rates of oxygen consumption in the gut might produce anoxic conditions favourable for methanogenesis. After the particles are defecated, oxygen diffusion into the particles may make them aerobic depending on the rate of oxygen consumption. In this case, the most favourable conditions for methanogenesis would occur in the gut of organisms and perhaps immediately after defecation. 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 out to the surrounding water.

Although the methane accumulation rates in the traps were greatest at the offshore ADIOS site, this region typically has much lower particulate matter fluxes than the

more coastal waters around the ONR trap site (e.g. Martin et al., 1987). Given the methane is biogenic then it appears the methane production is not necessarily related to the amounts of particulate material present in the water column. Either the traps closer to shore are not collecting the particulates that contain microenvironments where methane production occurs, or there are more anoxic microenvironments in the particulates present in the offshore waters. The latter case could result from a more efficient cyling of organic matter in the offshore region. Here the particulate material may spend longer in the gut of organisms and be recycled through the gut more frequently (i.e. eaten more times before sinking to deeper water) which may tend to increase the liklehood of producing anoxic conditions in the particles. In the coastal regions, a more rapid passage of food through the gut of organisms due to a more plentiful food supply may not allow anoxic conditions to form in the particulates. Thus, given equal amounts of particulate matter there may be less capacity for methane production in coastal regions compared with offshore waters.

Unfortunately, the trap data presented here are not sufficient to identify the source of the methane. However, if the methane is produced in anaerobic microenvironments in the water column, the above calculations indicate that the conditions necessary for production will be most likely

to occur in millimeter and larger sized particles. In future studies, the measurement of methane concentrations and the stable isotopic composition of the methane in better designed traps (e.g. glass lined opening and closing traps), and measurements of oxygen concentrations in particulate matter would be useful for establishing the source of the methane.

Summary

The dissolved methane distributions measured at the ADIOS site indicate there is a net in situ production of methane in the upper water column. A mass balance of the upper water column suggests that the methane distributions are controlled primarily by in situ production and air-sea gas exchange. Closer to shore, sediment or near-bottom inputs become more significant.

Attempts to culture methane producing bacteria in plankton samples were generally unsuccessful. Methane production was observed in a single sample of plankton and particulate matter that had methanol added as a growth substrate, but this result was not duplicated. Based on this result there appears to be only a limited capacity for biogenic methane production in the upper ocean.

Measurements in sediment trap solutions did show an increase in dissolved methane over time, but the cause of the increases is unknown. Comparison of coastal and offshore trap sites showed there was a greater accumulation

of methane in the offshore sites even though the particulate matter fluxes tend to be lower offshore. The source of the methane in the traps is unknown, but the distributions measured are consistent with methane production occurring in upper ocean waters.

Overall, the data collected are consistent with bacterial methanogenesis occurring in the upper water column. However, the sites of methanogenesis appear to be limited and methane turnover in the water column is slow.

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Chapter IV

Methane distributions in the southwestern Drake Passage and the Bransfield Strait, Antarctica

Introduction

Since pre-industrial times atmospheric methane concentrations have increased more than two-fold (Rasmussen and Khalil, 1984) and are now increasing at a rate of about 1% per year (Steele et al., 1987). The increases are expected to contribute to global warming and influence atmospheric chemistry (e.g. Cicerone and Oremland, 1988). The rise in atmospheric methane appears to be linked to anthropogenic activities such as biomass burning and increases in rice paddy cultivation and livestock farming. However, the natural and anthropogenic methane sources and mechanisms controlling the sources are not sufficiently well known to construct accurate methane budgets.

Investigations have shown that the oceans are slightly supersaturated with respect to atmospheric methane, and are a small source of methane to the atmosphere (Lamontagne et al., 1973; Lamontagne et al., 1974; Scranton and Brewer, 1977; Ward et al., 1987; Conrad and Seiler, 1988). However, the magnitude of the oceanic source is uncertain because of sparse data coverage and a general lack of understanding of the processes that regulate methane distributions in the oceans. This is especially true for coastal regions where methane supersaturations tend to be the greatest and most

variable (Scranton and Farrington, 1977; Ward et al., 1989; Brooks, 1979; Cline et al., 1985).

The Southern Ocean is one region where methane data are particularly sparse, even though the region covers about 10% of the surface area of the world's oceans. A few dissolved methane measurements made in the vicinity of the Ross Sea indicate that during the early austral summer surface waters vary from saturated to slightly undersaturated, while closer to shore the concentrations increase above saturation (Lamontagne et al., 1974; Williams and Bainbridge, 1973). The undersaturations are a particularly unusual feature of the surface ocean and indicate that part of the Southern Ocean may actually be a net sink for atmospheric methane.

During the 1986/87 austral summer, methane distributions in Antarctic coastal waters of the Bransfield Strait and in the Southern Ocean waters of the Drake Passage were examined as part of the RACER program. The objectives of the study were to identify the factors controlling methane distributions in antarctic shelf and open ocean environments, and to evaluate the contribution these regions make to the sea-air flux of methane.

Methods

Station Locations

Sampling for the RACER program was carried out between December 15, 1986, and March 30, 1987, during a series of four cruises to the western Bransfield Strait and adjacent waters (figure 4.1). Each cruise consisted of a "fast grid" hydrographic survey of 69 stations over the entire region followed by more detailed "slow grid" water column sampling at selected stations. The water column profiles collected on the slow grid cruises are identified by a two-letter code followed by the station number. The first letter is an "S" to designate a slow grid cruise, and the second letter refers to the cruise (A-D). For example, "SA13" refers to slow grid cruise A, station 13.

Water column samples were collected down to a maximum depth of 200 m at five stations during the slow grid component of each cruise (figure 4.1). The sampling sites included shelf environments (stations 13 and 39), the Bransfield Strait (stations 43 and 48), and an open ocean site in the Drake Passage (station 20). Hydrocasts were not made at station 20 during the first cruise because of ice cover and at station 13 during the final cruise due to rough seas. Samples from 5 m depth were also collected at 61 stations throughout the study area during "fast grid" cruise C, from February 20 to 26, 1987. Samples were also collected from Port Foster, Deception Island (figure 4.2).



Figure 4.1. Map of the southwestern Drake Passage and the western Bransfield Strait (after Davey, 1972) showing the locations (\bullet) of the slow grid sampling sites during the 1986/87 RACER program.



Figure 4.2. Map of Deception Island in the Bransfield Strait, Antarctica showing the location (\bullet) of the water column profile collected on 2/27/87.

Methane Analyses

Dissolved methane samples were all collected using 10 liter PVC Niskin bottles mounted on a General Oceanics rosette fitted with a Seabird CTD (Holm-Hansen and Mitchell, 1991). The methane samples were transferred from the Niskin bottles into 260 ml borosilicate glass bottles, poisoned with 1 ml of a saturated solution of mercuric chloride, and the bottles were sealed with ground glass stoppers. All the methane samples were returned to shore for analysis. A small headspace (< 0.5 ml) developed in most of the sample bottles after they were sealed. Corrections for the partitioning of methane into the headspace were made based on the estimated headspace volume in each bottle. The correction typically amounts to about 5% of the dissolved methane concentration. No other storage effects were apparent; experiments indicated that poisoned samples can be stored for one year, and possibly longer, without producing any measureable change in the methane concentration (Chapter II).

Methane was measured by gas chromatography using the gas stripping method described in chapter II. The detection limit for the analysis was about 0.05 nM, and the precision of repeated analyses of samples was \pm 3%.

The solubility equations of Weisenburg and Guinasso (1979) were used to calculate the concentration of dissolved methane in equilibrium with the atmosphere.

Saturation ratios (R) were calculated by dividing the measured concentration by the calculated equilibrium concentration. Values of R less than 1.0 indicate the waters are undersaturated with methane relative to the atmosphere, and values of R greater than 1.0 indicate supersaturation.

Results

Physical Setting

The study area is located near the northern tip of the Antarctic Peninsula and covers a 100 km by 250 km region that includes the western Bransfield Strait and part of the southwestern Drake Passage (figure 4.1). The strait is considered to be an active back-arc basin (Barker and Dalziel, 1983) and forms an approximately 100 km wide trough-shaped depression that is bordered in the northwest by the South Shetland Island chain and in the southeast by the Antarctic Peninsula. The western entrance to the strait lies between Low and Brabant Islands. From there the strait extends for about 460 km to the northeast. To the west is the Bellingshausen Sea and to the east the Weddell Sea.

Tectonic activity combined with glacial and fluvial processes have produced a complex bottom topography in the region. A narrow shelf fringes the South Shetland Islands along the northern margin of the strait, while the shelf along the southern margin of the strait is broad and in many places is dissected by submarine valleys. A broad

shelf is also apparent along the northern margin of the South Shetland Islands. North of this margin, the seafloor slopes down into the South Shetland Island Trench.

Although the strait is considered to be an active back-arc basin (Barker and Dalziel, 1983), the only known site of volcanic activity in the study area is Deception Island. The last series of eruptions occurred on the island in 1970 (Barker et al., 1975), but since that time there have been numerous reports of seismic and fumarolic activity on the island (SEAN Bulletin, 1989). East of the study area, thermogenic hydrocarbons in sediments and water column δ^3 He anomalies below 2000 m depth indicate that volcanism and hydrothermal activity are occurring along the axis of the basin (Whiticar et al., 1985; Schlosser et al., 1988).

Hydrography

The physical oceanography of the Bransfield Strait and adjacent waters has been described in a number of studies (Clowes, 1934; Gordon and Nowlin, 1978; Stein, 1983; Heywood, 1985; Amos, 1987; Niiler et al., 1991). In the offshore region there is a general northeasterly drift of Bellinghausen Sea water along the Antarctic Peninsula. Some of the Bellinghausen Sea water is advected into the western Bransfield Strait and contacts colder, more saline, Antarctic Peninsula shelf water derived from the Weddell Sea to the east. The interaction of these waters combined

with local thermohaline alteration determines the T and S characteristics of the waters in the strait. For the RACER study (Dec. 1986 - Mar. 1987), descriptions of the surface water mass distributions and geostrophic flows in the region are presented in Niiler et al. (1991) and are outlined below.

The Drake Passage waters to the northwest have T and S distributions typical of summer stratification in offshore antarctic surface waters (Foster and Carmack, 1976; Gordon et al., 1977 and Heywood, 1985). A 50 m thick mixed layer that is seasonally warmed and slightly less saline caps a remnant of the low temperature surface layer present in winter (Winter Water). The remnant Winter Water is marked by a pronounced T-minimum and overlies warmer and saltier Warm Deep Water derived from Circumpolar Deep Water. A less pronounced T-minimum layer is also found in the Bellinghausen Sea waters in the southwest of the study area.

Abrupt changes in T and S distributions occur across a shelf-break front at the boundary between Drake Passage waters and shelf waters around Livingston and Low Islands. The waters surrounding the islands are derived from Bellingshausen Sea or Drake Passage waters and are modified as they flow over the shelves. For stations shallower than about 100 m, tide and wind mixing appear to have produced nearly isothermal and isohaline conditions, whereas deeper

stations generally show salinity and temperature changes with depth.

The influence of colder and more saline Antarctic Peninsula shelf waters becomes more apparent south of the Livingston and Low Island water masses. The shelf waters are derived from the Weddell Sea to the east and flow over the broad shelf on the north side of the Antarctic Peninsula before spreading into the Bransfield Strait (Heywood, 1985). A pool of well mixed shelf water is located around Trinity Island in the southeast of the study area. Similar T and S characteristics are also evident in water underlying the warmer and fresher surface layers in the northern Gerlache Strait and the central Bransfield Strait.

The transition between water derived from the Bellinghausen Sea or Drake Passage and the Antarctic Peninsula Shelf is marked by a frontal zone that is a consistent feature of the strait (Clowes, 1934; Stein, 1983; Heywood, 1985 and Niiler et al., 1991). The front extends from the western entrance of the Bransfield Strait (between Brabant and Low Islands) along the shelf break to the south of Livingston and Deception Islands. North of the front are the water masses surrounding Livingston and Low Islands and to the south are the waters of the Bransfield Strait. Within the front, a complex interleaving of the water masses is apparent.

Surface dynamic topography, relative to 200 db, implies geostrophic flow was greatest along the frontal zones described above, and was primarily to the northeast (Niiler et al., 1991). Generally, surface waters (0-50 m) flowing out of the Gerlache Strait are added to Bellinghausen Sea water flowing into the Bransfield Strait through the passage between Brabant and Low Islands. The waters are advected towards the northeast along the frontal zone south of Livingston and Deception Islands. The surface dynamic topography presented in Niiler et al. (1991) also suggests some branching of the flow to the north between Snow and Smith Islands. In the northern segment of the study area, flow occurs along the other frontal zone located at the boundary between the open ocean waters of the Drake Passage and waters overlying the Livingston Island shelf. The calculated mean surface flow is about 5 cm s⁻¹ within the frontal zones and decreases away from the fronts (Niiler et al., 1991).

Vertical Profiles of Dissolved Methane

The sampling sites for vertical methane profiles were selected to obtain information on upper water column methane distributions in most of the water masses in the region. Dissolved methane, salinity, temperature and sigma-t variations at stations 13, 20, 39, 43 and 48 are presented in figures 4.3 to 4.7 and are listed in Table A.2, Appendix A. Methane concentrations calculated for

Figure 4.3. Methane concentrations and hydrographic parameters measured at station 20 (61.95 62.3W) during the RACER program. CH₄eq is the calculated dissolved methane concentration for seawater in equilibrium with the atmosphere. The sampling dates were: SB20, 1/30/87; SC20, 3/3/87; SD20, 3/20/87. Hydrographic data were provided by B. G. Mitchell.



Figure 4.4. Methane concentrations and hydrographic parameters measured at station 39 (62.5S 61.5W) during the RACER program. CH₄eq is the calculated dissolved methane concentration for seawater in equilibrium with the atmosphere. The sampling dates were: SA39, 12/25/86; SB39, 1/31/87; SC39, 3/05/87; SD39, 3/25/87. Hydrographic data were provided by B. G. Mitchell.



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Figure 4.5. Methane concentrations and hydrographic parameters measured at station 13 (63.4S 62.4W) during the RACER program. CH₄eq is the calculated dissolved methane concentration for seawater in equilibrium with the atmosphere. The sampling dates were: SA13, 12/27/86; SB13, 1/28/87; SC13, 3/2/87. Hydrographic data were provided by B. G. Mitchell.

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Figure 4.6. Methane concentrations and hydrographic parameters measured at station 43 (64.2S 61.3W) during the RACER program. CH_4eq is the calculated dissolved methane concentration for seawater in equilibrium with the atmosphere. The sampling dates were: SA43, 12/22/86; SB43, 1/26/87; SC43, 2/28/87; SD43, 3/21/87. Hydrographic data were provided by B. G. Mitchell.


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Figure 4.7. Methane concentrations and hydrographic parameters measured at station 48 (63.25 61.0W) during the RACER program. CH₄eq is the calculated dissolved methane concentration for seawater in equilibrium with the atmosphere. The sampling dates were: SA48, 12/20/86; SB48, 1/25/87; SC48, 2/26/87; SD48, 3/30/87. Hydrographic data were provided by B. G. Mitchell.



waters in equilibrium with air are only shown for those samples where salinity and temperature data were obtained. Due to problems with the CTD, salinity and temperature data were not always available over the entire depth range of the casts. However, from the ranges of salinity and temperature observed in the region, the equilibrium methane concentrations should only vary between 3.0 and 3.3 nM.

The lowest methane concentrations were found at station 20 in the open ocean waters of the Drake Passage (figure 4.3). These waters were undersaturated relative to the atmosphere. Methane concentrations decreased with depth at this site and varied from 2.45 to 3.11 nM (R from 0.80 to 1.00) in the seasonally warmed surface layer, to values as low as 1.39 nM (R = 0.46) in Warm Deep Water at 200 m depth. Undersaturations are an unusual feature in the upper water column and have only previously been reported for samples collected in pack ice near the Ross Sea (Lamontagne et al., 1974) and in upwelled waters off Yucatan (Brooks et al., 1974).

High methane concentrations (4.86 to 8.90 nM; R from 1.58 to 2.87) were found at station 39, which is located in the water mass overlying the shelf around Livingston Island (figure 4.4). Subsurface maxima and minima were evident. The only near-bottom sample was collected at station 39 during cruise B, and showed methane increased towards the bottom, suggesting a possible near-bottom or sediment

methane source. However, if the methane supersaturations at this station result from sediment or near-bottom methane inputs, then lateral inputs from the sediments, intrusion of methane poor waters from offshore, or variable rates of methane consumption and production in the water column would also be required to account for the numerous maxima and minima observed at this site.

Station 13 is also located over a shelf. Unlike station 39, the waters at this site have a well defined surface mixed layer, about 40 m thick, with methane concentrations between 2.45 to 3.50 nM (R from 0.79 to 1.13; figure 4.5). Below the mixed layer, dissolved methane increased with depth to maximum concentrations in the range of 4.43 to 5.28 nM (R from 1.42 to 1.65) at 100 m depth. Although methane was not measured just above the sediment-water interface at this station, the observed increases in methane concentrations with depth are suggestive of a near-bottom or sediment derived methane source. This possibility has already been suggested for station 39. The near-saturated to undersaturated concentrations in the surface layer may be due to the admixture of methane depleted waters from offshore with the shelf waters.

The two stations located in the Bransfield Strait (station 43 and 48; figures 4.6 and 4.7, respectively) had different methane distributions. The water column at

station 43 was slightly supersaturated with methane (R from 1.07 to 1.31), and methane concentrations only ranged between 3.36 and 4.12 nM during the four months of sampling. On the other hand, station 48 showed large temporal changes in methane over the duration of the study. Methane was close to saturation (R from 0.99 to 1.21) in the upper 50 m of the water column, where concentrations ranged between 3.07 and 3.74 nM. Due to a lack of CTD data, equilibrium concentrations in the upper 50 m of the water column at station 48 are not available for cruises A and D. However, there appear to be layers of methane undersaturated near-surface waters present on both cruises with concentrations as low as 2.39 nM (R \approx 0.80). For cruises B and C, the surface water concentrations were at or above saturation (3.07 to 3.74 nM; R from 0.99 to 1.13). Below 50 m, large changes in methane concentration occurred during the study. The greatest changes were at 200 m depth, where the concentrations ranged between 3.47 and 13.20 nM (R from 1.10 to 4.25).

The overall variability of dissolved methane for the stations is apparent in a plot of methane concentrations versus the density of the water, sigma-t (figure 4.8).

The methane concentrations tend to converge towards atmospheric equilibrium values with decreasing sigma-t (decreasing depth), suggesting an air-sea gas exchange effect. Sigma-t values less than about 27.2 in figure 4.8



Figure 4.8. Variations in methane concentrations for all slow grid stations versus sigma-t.

generally correspond to a low density surface layer which was most apparent at stations 13 and 20 (figures 4.3 to 4.7). The presence of a low density surface layer is expected to enhance the effects of air-sea gas exchange by reducing mixing with deeper waters.

In higher density waters ($\sigma_t > 27.2$), three methane versus sigma-t trends are evident in figure 4.8. The undersaturated waters at station 20, the supersaturated waters of station 39, and the near saturated waters of station 43 all plot in distinct sigma-t versus methane fields. Station 13 has sigma-t versus methane characteristics similar to those at station 43, although a few samples overlap the station 20 and station 39 data. Each of the four stations is located in different water masses and based on the circulation of the region presented in Niiler et al. (1991) it is unlikely that significant mixing occurred between the stations over the duration of the study.

At station 48 located near the frontal zone that marks the boundary between the water mass surrounding Livingston Island and the waters of the Bransfield Strait, most of the methane data plot in the sigma-t versus methane field for station 43. The high methane concentrations measured in samples collected below 50 m depth during cruise D are offset from but have a trend similar to the station 39 data. If it is assumed that the methane versus sigma-t

trends observed at stations 39 and 43 are representative of their respective water masses, then much of the temporal variability in dissolved methane at station 48 could result from changes in the position of the water mass boundaries or an interleaving of the two water masses. The dynamic height contours presented in figure 9 of Niiler et al. (1991) indicate that at a depth of 150 m the position of the Bransfield Strait frontal zone had migrated south of station 48 by cruise D. On previous cruises the station was situated within the frontal zone. Therefore, the deep waters at station 48 during cruise D are likely to have belonged to the water mass surrounding Livingston Island, whereas deep Bransfield Strait waters appear to have been present at the station on the previous cruises. The offsets between the station 39 and 48 data in figure 4.8 could therefore be due to spatial variability of the methane concentrations in the water mass around Livingston Island, or to mixing at the boundary between the Livingston Island and Bransfield Strait water masses.

Surface Distribution of Dissolved Methane

The regional distributions of dissolved methane in surface waters (5 m) for fast grid C and the approximate boundaries of the major water masses (dashed lines; from Niiler et al., 1991) are shown in figure 4.9. The methane concentration data and calculated equilibrium methane concentrations relative to air are listed in Table A.2,



Figure 4.9. Contours of surface water (5m) methane concentrations (nM) for samples collected on fast grid cruise C between 2/20/87 and 2/26/87 with station locations (\bullet). The shaded arrows represent the major surface water flows in the region inferred from the surface dynamic topography relative to 200db determined during RACER (after Niller et al., 1991). The dashed lines are the approximate water mass boundaries determined by Niller et al. for fast grid cruise C. Appendix A. For comparison with the methane contours in the figure, equilibrium methane concentrations for all the surface samples averaged 3.08 ± 0.03 nM.

The methane distributions are closely related to water mass distributions in the region. The undersaturated waters measured at station 20 appear to be a general feature of Drake Passage surface water. Similarly, the supersaturated shelf waters at station 39 appear to be a general feature of the water mass around Livingston Island. The front that marks the boundary between the Drake Passage and Livingston Island water masses coincides roughly with the 3.0 nM contour located to the north of Livingston and Low Islands. South of the front, methane concentrations increase above saturation and are greatest over the Livingston Island shelf. High concentrations are also evident in the water mass around Low Island. South of Low and Livingston Islands, the methane concentrations decrease to values within about \pm 10% of saturation (2.8 to 3.4 nM) and then increase slightly (up to 4.0 nM) over the shallow waters of the Antarctic Peninsula shelf. A tongue of surface water with methane concentrations below 3.5 nM is also evident between Low and Deception Islands. This tongue appears to be an advective feature associated with branching from the predominantly northeasterly flow in the Bransfield Strait frontal zone.

Methane distributions and biological parameters

Methane supersaturations in the upper water column are often attributed to in-situ biological methane production, although the source is unknown (e.g. Scranton and Brewer, 1977; Burke et al., 1983). Associations are sometimes observed between dissolved methane profiles and biological parameters such as chlorophyll-a and particulate ATP, and these associations have been suggested as evidence in support of biological methane production in the upper ocean (Traganza et al., 1979; Brooks et al., 1981; Conrad and Seiler, 1988). To determine if similar relationships exist in the RACER study area, dissolved methane distributions were compared to indicators of production and biomass.

For the slow grid stations, the rates of primary production and glutamate incorporation, integrated to 50 m depth, and the water column inventories (0-50 m) of chlorophyll-a, particulate ATP, and methane are compared in figure 4.10 and table 4.1. The high rates of primary production and the large inventories of particulate ATP and chlorophyll-a during cruise A in December are indicative of a seasonal phytoplankton bloom that occurs in the region. By cruise D in March, the high values of all three parameters measured in the Bransfield Strait (stations 43 and 48) and in shallow coastal waters (stations 13 and 39) had decreased by up to 90%, and were similar to values measured offshore at station 20 in the oligotrophic waters

Figure 4.10. Water column inventories of dissolved methane and biological parameters integrated between the surface and 50m depth for the RACER slow grid cruise stations. ATP and glutamate incorporation rate data were provided by D. Karl. Primary productivity and chlorophyll-a data were provided by B. G. Mitchell and O. Holm-Hansen. N.D. - no data





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Station	Date	Methane	Chlorophyll-	Total** <u>a</u> * ATP	Glutamate** Incorporation	Daily [*] Production
<u></u>		(µmol m ⁻²)	(mg m ⁻²)	(mg m ⁻²) (1	mCi m ⁻² h ⁻¹) (mg	C m ⁻² d ⁻¹)
C 3 1 2	27-0-2-96	164	261	25 0	2 4	1950
CR12	27-Dec-00	104	201	25.9	3.4 1 /	1300
SC13	02-Mar-87	160	62.6	2.6	1.1	394
SB20	30-Jan-87	130	29.9	12.5	0.8	408
SC20	03-Mar-87	133	32.6	6.5	0.6	403
SD20	20-Mar-87	144	23.1	5.4	1.1	214
SA39	25-Dec-86	265	66.1	25.7	14.9	1700
SB39	31-Jan-87	263	32.2	10.3	1.5	243
SC39	05-Mar-87	321	43.9	3.5	1.4	130
SD39	25-Mar-87	318	23.1	2.2	1.7	73
SA43	22-Dec-86	191	372	49.5	10.8	1950
SB43	26-Jan-87	172	193	49.8	19.8	863
SC43	28-Feb-87	177	295	22.4	2.5	688
SD43	21-Mar-87	170	62.0	5.8	8.2	178
SA48	20-Dec-86	146	205	27.4	7.2	3440
SB48	25-Jan-87	168	178	26.5	8.3	1060
SC48	26-Feb-87	175	42.1	9.9	4.8	388
SD48	30-Mar-87	147	34.1	6.4	1.0	187

Table 4.1. Water column inventories of methane and biomass integrated to 50m depth and integrated rates of primary production and glutamate incorporation at the RACER slow grid stations.

* data provided by O. Holm-Hansen and B. G. Mitchell ** data provided by D. M. Karl

of the Drake Passage (Holm-Hansen et al., 1987; Karl et al., 1991). Glutamate incorporation is a measure of heterotrophic activity, and although these rates showed considerable variability, decreases were also apparent between the inshore stations and station 20. The changes in heterotrophic activity are expected to occur in reponse to changes in phytoplankton activity and a decline in glutamate incorporation rates was indeed observed to lag the decline in phytoplankton biomass and production at some locations (Bird and Karl, 1991).

In contrast to the large temporal changes in the water-column biological parameters that resulted from the phytoplankton bloom, methane inventories varied by less than about ± 10% of the average for each station, and showed no consistent trends with time. In addition, the high methane inventories at station 39 (170 to 210% saturation) and near-saturation inventories at the other stations (85 to 125% saturation) showed no obvious association with the spatial gradients of the biological parameters.

The methane concentration data for individual samples collected between the surface and 200 m at the slow grid stations also appear to be unrelated to particulate ATP, chlorophyll-a, or the rates of glutamate incorporation (figure 4.11). The elevated levels of ATP, chlorophyll-a, and glutamate incorporation in figure 4.11 are the result



Figure 4.11. Dissolved methane concentrations versus glutamate uptake rates, total ATP (both from D. Karl), and chlorophyll-a (from B. G. Mitchell and O. Holm-Hansen).

of the December bloom, and are associated mostly with samples collected between the surface and 50 m depth. Methane in these samples typically range between about 2.5 and 4.5 nM. However, samples collected at station 39 have concentrations clustered around 5 nM. Samples deeper than about 50 m, and samples collected during the low productivity post-bloom conditions on cruises C and D have low values of ATP, chlorophyll-a, and glutamate incorporation, but show a large range of methane concentrations (1.3 to 13.20 nM). The incorporation of the fast grid C surface data into this plot would have no affect on the distributions shown in the figure.

The general lack of a relationship between dissolved methane concentrations and the biological parameters does not preclude a net biological source or sink of methane in the water column. The parameters measured provide a general view of the bloom and post-bloom conditions in the region; they are not necessarily indicative of any population of methane producing or consuming organisms that may be present in the water column. However, the lack of relationship does suggest that other factors including air-sea gas exchange, mixing and alternative sources such as methane inputs from sediments may have a more significant impact on the methane distributions over the time and space scales being considered than net water column production.

Deception Island

Hydrothermal activity is a source of methane to the water column in many back-arc basins (Auzende et al., 1988; Horibe and Kim, 1986; Kim et al., 1983), and the volcanic activity at Deception Island suggests that some methane in the RACER study area may have a hydrothermal origin. To investigate the possibility of a hydrothermal methane source, dissolved methane was measured at a station in the center of Deception Island's partially submerged caldera, Port Foster (figure 4.2). The port is almost completely landlocked; water exchange with the Bransfield Strait occurs through a narrow passage called Neptunes Bellows where sill depth reaches 14 m (Heywood, 1985). The maximum water depth in Port Foster is about 180 m (Defense Mapping Agency, 1976).

Methane concentrations in Port Foster were high and ranged between 9.37 nM at the surface to a maximum of 22.45 nM at 125 m depth (figure 4.12; Table A.3, Appendix A). In comparison, methane concentrations between the surface and 14 m (the sill depth in Neptune's Bellows) at the nearby station 48 in the Bransfield Strait, only varied between 2.67 and 3.40 nM (Table A.1, Appendix A). These data clearly point to a methane source existing in the caldera. In view of the recent volcanic activity on the island (SEAN Bulletin, 1989) a hydrothermal source for the methane is possible, but biogenic methane may also contribute to the



Figure 4.12. Dissolved methane concentrations and hydrographic parameters measured in Port Foster, Deception Island of February 27, 1987.

high concentrations. Distinguishing between these sources generally requires information on the isotopic composition of the methane (Whiticar et al., 1986), which is currently unavailable. Whatever the source of the methane, the restricted circulation between Port Foster and the waters of the Bransfield Strait should prevent the methane-rich waters in the port from having a significant effect on methane distributions in the strait. Even if hydrothermal methane were injected into the strait at Deception Island, the general northeasterly flow of water past the island would quickly advect the methane out of the study area. Moreover, because Port Foster is the only reported site of volcanic activity in the study area (Barker and Dalziel, 1983), it is unlikely that hydrothermal methane sources are important to this region of the Bransfield Strait. Discussion

Dissolved methane in the Bransfield Strait and adjacent waters is characterized by concentrations above saturation levels in shallow coastal waters, with generally decreasing concentrations offshore to the undersaturated waters of the Drake Passage. The distributions are the result of interactions between the regional circulation and localized sources and sinks of methane. In the discussion below, I will briefly describe the processes expected to contribute to the input or loss of methane from the water column, and use this information in combination with the

hydrography of the region to determine the major controls on the distribution and the air-sea exchange of methane in the study area. Generally, mixing, coupled with air-sea gas exchange, and methane inputs to waters flowing over the shallow shelves around the Bransfield Strait, appear to be the most important factors controlling the methane distributions. Biological production and consumption in the water column may also affect methane concentration, but the processes mentioned above appear to mask these effects. Methane Sources and Sinks

Methane supersaturations are a common feature of upper ocean waters. The supersaturations are often attributed to the input of biogenic methane from sediments and production in the water column due to the activity of methanogenic bacteria (Scranton and Brewer, 1977; Scranton and Farrington, 1977 and Brooks et al., 1981). Riverine and anthropogenic methane inputs are also important in some nearshore regions (Sackett and Brooks, 1975; Cline et al., 1986 and DeAngelis and Lilley, 1987), but are absent from the RACER study area. As described above, the influence of hydrothermal methane inputs appears to be restricted to the caldera at Deception Island and will not be considered further.

Because all known methanogenic bacteria are obligate anaerobes (e.g. Large, 1984), the water column production is assumed to occur in anoxic microenvironments. Potential

sites for production include the gut of zooplankton, fecal pellets, and suspended particulate matter (Scranton and Brewer, 1977; Oremland, 1979; Traganza et al., 1983 and Seiburth, 1987). Scranton and Brewer (1977) have also suggested methane may be produced by phytoplankton as a metabolic by-product. In coastal waters, sediments provide an additional source of methane to the water column. The flux of methane out of the sediments occurs through diffusion and bubble ebullition, and is influenced to a large degree by the presence of dissolved sulfate in sediment pore waters (Martens and Berner, 1977 and Martens and Klump, 1980). The sulfate is utilized by sulfate reducing bacteria which compete with methanogens for common growth substrates and effectively retard methane production (Lovley et al., 1982 and Winfrey and Ward, 1982). The competition for substrates, combined with methane oxidation in oxic surface sediments (e.g. Martens, 1982) and perhaps in sulfate reducing sediments (Reeburgh and Heggie, 1977; Iverson and Jorgensen, 1985), tends to restrict large accumulations of methane to below the zone of sulfate reduction. Consequently, the greatest fluxes of methane are expected from organic-rich sediments where sulfate is rapidly depleted and high methane concentrations are found close to the seafloor.

The few reported rates of aerobic methane oxidation indicate that once methane is input to the water column,

bacterial consumption proceeds slowly. For oligotrophic surface waters, Ward et al., (1987) measured a turnover time of about 2.4 x 10^4 days; turnover times of between 3.0 x 10^2 and 3.0 x 10^3 days have been reported for coastal waters (Griffiths et al., 1982; Butler et al., 1987 and Ward et al., 1989). In all cases the turnover times were long relative to the residence times of the waters in the regions studied and relative to the turnover associated with air-sea gas exchange. For deep waters, however, these slow oxidation rates become significant relative to potential sources and methane undersaturations result (Scranton and Brewer, 1978).

Air-sea gas exchange will also affect the methane distributions. The gas exchange will drive surface water methane concentrations towards equilibrium with the atmosphere and will be a source of methane to the undersaturated waters of the Drake Passage and a sink to the supersaturated coastal waters in the region.

The net flux of gas across the air-sea interface can be estimated using,

$$F = k_{L} (C_{s} - C_{eq})$$

where F is the gas flux (mol $m^{-2} d^{-1}$), k_L is the gas transfer coefficient or piston velocity (m d^{-1}), C_s is the concentration of the gas in the surface water (mol m^{-3}), and C_{eq} is the concentration of gas in equilibrium with the atmosphere (mol m^{-3}). The equilibrium concentration can be

obtained from the solubility equation of Weisenburg and Guinasso (1979).

The major difficulty in calculating the air-sea gas flux lies in determining k. Various theoretical models suggest the transfer coefficient will vary as a function of the molecular diffusivity of the gas in water, the kinematic viscosity of the water, and wind speed. The models predict that k, is proportional to Scⁿ, where Sc (the Schmidt number) is the kinematic viscosity divided by the molecular diffusivity, and n varies between -1/2 and -1for the different models (e.g. Liss and Merlivat, 1986). Wind tunnel experiments indicate that an appropriate value for n is -2/3 for wave-free rigid surfaces and -1/2 after wave formation begins (Jahne et al., 1987). The gas exchange coefficient also varies in proportion to wind speed, and based on field and laboratory experiments a number of empirical equations have been proposed to relate these two parameters (Smethie et al. 1985; Hartman and Hammond, 1985; Liss and Merlivat, 1985 and Barber et al., 1988). Unfortunately, the gas exchange coefficients measured in the field are quite variable for a given wind speed and the values of k, calculated from the empirical equations can differ by 30% or more from the field measurements.

Values of k_{L} reported in this study were calculated using the relationship:

 k_{L} (m d⁻¹) = 0.86U₁₀ - 2.9; 4.2 < U₁₀ < 18 m s⁻¹ where k_{L} is normalised to methane at 20°C (Sc = 618) and U₁₀ is the wind speed at 10 m above sealevel. This relationship is taken from Barber et al. (1988), and the constants have been changed to express k_{L} in units of m d⁻¹ and the wind speed at 10 m height above the sea surface. The values of k_{L} were corrected to in situ temperatures using the Schmidt numbers for methane given in Jahne et al., (1987) and assuming k_{L} is proportional to Sc^{-1/2}. The above equation gives results similar to the relationship proposed by Smethie et al., (1985) and slightly higher values of k_{L} compared to the relationship of Liss and Merlivat (1986). <u>Offshore Methane Undersaturations</u>

The methane undersaturations in the surface waters of the Drake Passage are atypical of open ocean waters, where undersaturations are usually only found below about 300 m. Above this depth, net production in the water column generally produces methane supersaturations, and most surface waters of the open ocean are 10 to 30% above saturation (e.g. Lamontagne et al., 1973 and Conrad and Seiler, 1988). The unusual situation in the Drake Passage appears to be a function of the regional circulation. The Drake Passage waters are situated between the Polar Front and the shelf break front that borders the Antarctic

continent. Within this zone, the upwelling and entrainment of Warm Deep Water (WDW) into overlying surface waters provides an important source of heat and salt to offshore antarctic surface waters (Gordon et al., 1977 and Toole, 1981). The WDW is derived from Circumpolar Deep Water and low radiocarbon contents and oxygen undersaturations reported in WDW are indicative of its long residence time in the deep ocean (Weiss et al., 1979 and Schlosser et al., 1987). Because WDW is oxygen depleted relative to surface waters, the entrainment will lower surface water oxygen concentrations and can produce oxygen undersaturations (Gordon et al., 1984). Methane, like oxygen, is undersaturated in the deep sea, and the samples collected from WDW at station 20 (150 and 200 m samples) range between 46% and 68% of saturation. Consequently, the entrainment of WDW into the surface layer at station 20 is also expected to lower surface methane concentrations and produce undersaturated surface waters.

The entrainment of WDW into the surface layer occurs as a result of thermohaline convection associated with seasonal ice formation (e.g. Toole, 1981 and Gordon and Huber, 1984). For the period of sampling (Jan.-Mar.), the T and S profiles at station 20 (figure 4.4) show a seasonally warmed surface layer (0-50 m) above a T-minimum layer (51-100 m) of remnant Winter Water (WW). The WW is in turn underlain by the warmer and saltier WDW, and the two are

separated by a weak pycnocline. This water column structure is typical of summer stratification; exchange between the various layers occurs primarily by diffusion (Gordon et al., 1984). As winter approaches and ice formation begins, brine released from the ice drives thermohaline convection which mixes the warmed surface layer and the remnant WW. The mixing will eventually produce a homogeneous nearfreezing layer of WW under the sea-ice and will also entrain some WDW (Toole, 1981 and Gordon et al., 1984). Later in the year the thermohaline convection will cease as the melting of the sea-ice and surface warming reestablishes the summer stratification. Offsetting the tendency for the thermohaline convection to deepen the surface layer beneath the ice is the upwelling of WDW due to Ekman divergence (Gordon et al., 1977 and Toole, 1981).

A mass balance of methane in the water column can be used to estimate the annual entrainment of WDW into the surface layer. The calculation assumes that between the formation and subsequent melting of the seasonal ice cover, the changes in methane concentrations in the homogeneous WW layer beneath the sea-ice are due to the entrainment of methane-poor WDW. Implicit in this calculation is the assumption that the lateral diffusion of methane from the methane-rich waters around the South Shetland Islands has no significant effect on the methane concentrations at station 20. This assumption appears to be reasonable

because the Drake Passage waters are advected into the region from the Bellingshausen Sea in the west, and the flow is expected to continuously sweep the offshore portion of the study area, including station 20, with methane undersaturated open-ocean waters that originate far from any coastal regions. Presumably, methane that diffuses across the Drake Passage frontal zone will be advected with this general flow towards the northeast and away from station 20. This flow pattern is consistent with the surface methane concentrations shown in figure 4.9, which are fairly uniform in the Drake Passage water mass and only increase to methane supersaturated values across the Drake Passage frontal zone. Additional assumptions are that: the methane is not significantly influenced by net biological production or consumption on the seasonal time scales being considered; net diffusive fluxes of methane from coastal waters are insignificant; the winter ice cover is 100% effective in preventing air-sea gas exchange; and that the upwelling of WDW offsets entrainment effects and maintains a steady state with regard to the depth of the surface layer.

The minimum methane concentration in the 100 m surface layer just prior to complete ice cover was estimated to be 2.74 nM. This concentration assumes the layer is a mixture of a 50 m thick warm surface layer at equilibrium with the atmosphere ($CH_4 = 3.08$ nM), and a 50 m thick layer of

remnant WW layer ($CH_4 = 2.40 \pm 0.16$ nM; n=6). The warmed surface layer can exchange methane with the atmosphere during the ice free months and the methane concentration in this layer is likely to approach saturation by the end of the summer (see below). The concentration in the remnant WW (2.40 nM) is the mean of samples collected in the T-minimum layer at station 20 between January 30 and March 23 (Table A.2). The small variability in the WW concentrations over the 54 day period of sampling is consistent with biological and convective processes having a negligible effect on the methane concentrations in the ice-free period.

The estimated concentration of 2.74 nM is considered a minimum value and will apply only if the homogeneous WW layer that forms by mixing the warm surface and remnant WW layers is covered fast enough by sea-ice to prevent air-sea gas exchange. If the ice cover develops slowly and gas exchange becomes important, the concentration in the 100 m thick surface layer may reach saturation values of 3.08 nM.

The methane concentration in the WW at the time the sea-ice melted and thermohaline convection ceased is taken as 2.40 \pm 0.16 nM. Sea-ice still covered the Drake Passage waters on December 25, 1986, during slow grid cruise A, but had melted by January 20, 1987; samples were first collected at station 20 on January 30, 1987, during cruise B. The average of the concentrations for remnant WW collected during cruise B is 2.36 nM (n=2), which is not

significantly different from the mean for all the cruises $(2.40 \pm 0.16 \text{ nM})$. Consequently, it appears reasonable to assume that the remnant WW does provide a record of the mean methane concentration in the homogeneous WW layer just prior to melting of the seasonal ice.

Therefore, between the time the sea-ice formed and melted in the following summer, the mean methane concentration in the WW layer under the ice is estimated to have decreased from between 2.74 and 3.08 nM to 2.40 nM. For station 20, the average concentration of methane in the WDW (150 and 200 m samples) was 1.71 ± 0.31 nM (n=6). Thus, the incorporation of between 33 and 50% WDW into the WW will balance the methane budget. For a 100 m thick layer, this corresponds to an annual entrainment of between 33 and 49 m.

During the ice covered period, some methane will diffuse from the WW layer into the underlying WDW. For a vertical eddy diffusivity of 0.5 x 10^{-4} m² s⁻¹ (Gordon et al., 1984 and Schlosser et al., 1987) and an average gradient of 0.0086 µmol CH₄ m⁻⁴ (figure 4.4), the diffusive flux is about 0.037 µmol m⁻² d⁻¹. The duration of seasonal ice cover in the region is variable (Zwally et al., 1983), but if four months is assumed, then the diffusive flux would lower the calculated annual entrainment by about 4 m. Higher diffusivities would lower the amount of WDW entrainment even further.

Overall, the estimated entrainment is similar to a yearly WDW upwelling estimate of 31 m due to Ekman divergence in the 60-70°S latitude band (Gordon et al., 1977). As mentioned above, the average annual upwelling and entrainment should approximately balance if the average depth of the WW/WDW transition is to be maintained at a constant level over a year.

Calculations of WDW entrainment have been made for the Weddell Sea using mass balances of oxygen (Gordon et al., 1984) and ³He (Schlosser et al., 1987), and give annual values of 27 and 15 m to 35 m, respectively. The higher values obtained in the Drake Passage may be due in part to the methane concentration used for the WDW. Gordon et al. and Schlosser et al. (1987) used concentrations measured in the core of the WDW at about 450 m in the Weddell Sea to represent the composition of the WDW entrained into the surface layer. The core of WDW in the Drake Passage is at about 250 m (Heywood, 1985), and at this depth methane concentrations are probably close to the 1.41 nM average measured at 200 m. If 1.41 nM were used to calculate the annual entrainment rate, the range of values would decrease to between 24 and 40 m and diffusive losses would further reduce the value by about 4 m. However, the entrained waters most likely originate in the upper WDW rather than its core, and the 1.71 nM concentration should provide a more realistic estimate. A greater vertical eddy

diffusivity will also reduce the entrainment rates. Of course, some of the difference between the estimates may simply reflect geographic variability.

Although a number of factors can introduce uncertainty in the calculated amount of WDW entrainment, the general agreement between the three different gas balance calculations is remarkable. All three gases are influenced by mixing and gas exchange, but ³He is biologically inert whereas oxygen and methane have different biological source and sink terms. Thus, it appears that the methane distributions in the offshore region are primarily influenced by physical rather than biological processes. Obviously, biological methane consumption is important in producing the methane undersaturations in the WDW, but this occurs over a much longer time scale (10-100's years) than considered here.

The regional extent of the methane undersaturations is unknown, but the upwelling and entrainment of WDW into surface waters occurs around the Antarctic in the zone of seasonal ice formation (e.g. Toole, 1981). Oxygen undersaturations which are likely to be produced by these processes are a common feature of circum-antarctic waters (Gordon et al., 1982), and it appears reasonable to assume that methane undersaturations will also be a widespread feature of offshore antarctic waters. This is supported by the report of methane undersaturations in pack ice near the

Ross Sea (Lamontagne et al., 1974). The undersaturations would be most intense immediately after the sea-ice melts in the early summer and are likely to decrease over summer due to air-sea gas exchange.

The extent to which air-sea gas exchange, diffusion and biological processes will influence methane concentrations in the warmed surface layer during the icefree months can be investigated using a simple box model (figure 4.13). The equation describing the change in concentration for the surface layer is:

 $h \cdot dC_s/dt = k_L \cdot (C_{eq} - C_s) - k_z \cdot (C_s - C_{WW})/dz + J$ where C_s is the methane concentration (µmol m⁻³), C_{eq} is the methane concentration at equilibrium with the atmosphere (µmol m⁻³), and C_{WW} is the methane concentration in the remnant WW (µmol m⁻³), k_L is the gas exchange coefficient (m d⁻¹), k_z is the vertical eddy diffusivity (m² d⁻¹) between the surface layer and the WW layer, dz is the depth interval over which the methane concentration gradient between the surface and WW layers is determined (50 m), and h is the depth of the surface layer (50 m). J (µmol m⁻² d⁻¹) is a net production term when positive, or a net consumption term when negative.

The solution to the equation is:

$$C_{s}(t) = A/B + (C_{0} - A/B) \cdot e^{-Bt}$$

where C_0 is the initial methane concentration in the



Figure 4.13. Box model representation of the methane exchange between the atmosphere, warm surface layer and remnant Winter Water during ice free conditions in offshore antarctic waters. The surface layer and the remnant WW layer are 50m thick. $k_{\rm L}$ is the gas exchange coefficient (m d⁻¹) and $k_{\rm L}$ is the vertical eddy diffusivity between the water layers.

surface layer, $A = (k_L \cdot C_{eq} + k_z \cdot C_{WW}/dz + J)/h$, and $B = (k_1 + k_2/dz)/h$. In order to calculate the changes in the methane concentration the initial value for the surface layer is taken as 2.40 nM, the same as the concentration in the WW layer, and C_{eq} is 3.08 nM. Both C_{eq} and C_{uu} are held constant with time. A constant methane concentration in the WW layer implies that the net diffusive input from the overlying warm surface layer will be balanced by losses to the WDW, assuming no significant biological effects. A net diffusive flux of 0.037 μ mol m⁻² d⁻¹ (see above) from the WW to the WDW would decrease methane concentrations in the WW layer by about 0.18 nM over eight months. The actual change should however be less because the loss is likely to be offset by a diffusive input from the overlying surface waters. In addition, the observed temperature range of -1.3 to 1°C in the study area will only cause about a ± 0.1 nM variation in C_{eo}.

The influence of the various coefficients on temporal changes in methane concentrations in the surface layer is shown in figure 4.14. The concentrations in the figure are plotted against the number of days since the sea-ice melted. The mean of the concentrations observed at station 20 are also plotted. The horizontal error bars for each of the station 20 points represent the uncertainty in the length of time since the ice melted. The vertical error
Figure 4.14. Predicted changes in methane concentrations in the warm surface layer of the offshore antarctic waters as a function of time since the seasonal ice cover melted, and average concentrations (\oplus) measured in the warm surface layer at station 20. A). $k_{\rm L}$ variable and $k_{\rm L}$ constant at 0.5 x 10⁻⁴ m² s⁻¹. B). k variable and $k_{\rm L}$ constant at 0.90 m d⁻¹. C). $k_{\rm L}$ of 0.90 m d⁻¹ and $k_{\rm W}$ of 0.5 x 10⁻⁴ m² d⁻¹, P variable. The horizontal line at 3.08nM is the approximate methane concentration in surface waters at equilibrium with the atmosphere.



bars represent the uncertainty in the concentration measurements (±3%).

The balance between the diffusive flux of methane out of the surface layer to deeper waters and the uptake of methane by air-sea gas exchange is apparent in figures 4.14a and 4.14b. For both figures, biological effects are assumed to be negligible. In figure 4.14a the vertical eddy diffusivity, k_z , is held constant at 0.5 x 10⁻⁴ m² s⁻¹ (Gordon et al., 1984) and the gas exchange coefficient is varied. A k_1 of 0.90 m d⁻¹ is the estimated gas exchange coefficient at an in-situ temperature of 0.6°C and an average wind speed (Dec.-Feb.) of 5.2 m s⁻¹ obtained from the US Navy Climatic Atlas of the World (1965). As mentioned above, this value of the gas exchange coefficient is calculated from the relationship between wind speed and k, of Barber et al. (1988). Other equations have been proposed by various authors and if these equations were used to calculate k, the value would only vary between 0.96 m d⁻¹ (Smethie et al., 1985) and 0.75 m d⁻¹ (Liss and Merlivat, 1986). The effect of variations in k, over this range is small, although the lower value does provide a slightly better fit to the data. In figure 4.14b, k, is held constant at 0.90 m d^{-1} and k, is varied about the estimated value of 0.5 x 10^{-4} m² s⁻¹ to determine the influence of k, on the methane concentrations. For the range of parameters used, the surface methane

concentrations have still not achieved steady state after 240 days. Both figures also show that changes in the methane concentrations of the surface layer are initially dominated by gas exchange, and with time the diffusive flux into deeper waters becomes important in controlling the concentrations. Diffusion to the WW layer has a greater impact on the surface layer concentrations with time because the air-sea gradient that drives the net uptake of atmospheric methane diminishes, and the concentration gradient between the surface and WW layer increases over the ice-free period.

Net methane production will cause more rapid increases in the methane concentrations of the surface layer (figure 4.14c). Direct measurements of methane production have not been made in the ocean, but Ward et al. (1987) used a mass balance to estimate a minimum net production equivalent to $6 \times 10^{-4} \mu mol m^{-3} d^{-1}$ in the surface waters of the Cariaco Basin. At this rate, the steady state methane concentration would increase only about 1% above the concentration expected if there were no production. This effect would not be discernible at the precision of the methane analysis. A ten-fold greater production would result in a more rapid increase in the concentrations, and after about 50 days the surface waters would become supersaturated with methane. However, based on the observed data, a net production greater than $6 \times 10^{-4} \mu mol m^{-3} d^{-1}$ appears unlikely. Due to

the long turnover times associated with biological methane consumption in the open ocean (2.4 \times 10⁴ days; Ward et al., 1987), net biological consumption would also appear to have a negligible impact relative to mixing and gas exchange.

Overall, the changes in methane concentrations observed at station 20 are consistent with the temporal variations predicted by the model, although the average concentration for cruise C is less than expected. The low concentration observed for cruise C may result from lateral inhomogeneities in the methane concentrations of the surface waters advected into the region, or could reflect some other inadequacy in the model. Complexities such as seasonal and short term changes in wind speed, and the possibility of erosion of the top of the WW layer during storms are not incorporated into the model and may cause changes in the concentrations. More extensive sampling over a longer period of time is required to determine if these or other processes including biological factors have an important effect on the concentrations. Nevertheless, the results of the model do indicate that the increases in concentration observed over summer in the surface layer at station 20 can result solely from air-sea gas exchange and mixing processes.

Coastal Dissolved Methane Distributions

South of the Drake Passage frontal zone, dissolved methane concentrations typically increase above saturation,

and the distributions appear to be strongly influenced by the addition of methane to waters flowing over the shelves in the region. The greatest supersaturations were associated with the Livingston Island water mass. This water mass is derived from the undersaturated waters of the Drake Passage (Heywood, 1985), and there is clearly an input of methane to the water column overlying the shelf around the island. The supersaturations are less pronounced over the shelves along the Antarctic Peninsula and around Low Island, but the concentrations also tend to increase over the shelves.

The variability in the methane concentrations in the shelf waters is presumably a function of the rate of input of methane to the water column, and of the extent of mixing with the relatively methane-poor waters that surround the shelves. The frontal zones that border the Livingston Island water mass limit exchange with the surrounding waters, and the surface dynamic topography of the region indicates there is little net flow over the shelf surrounding the island (Niiler et al., 1991). In comparison the dynamic topography indicates a more vigorous net flow exists over the Antarctic Peninsula and Low Island shelves, and a greater exchange is likely with the surrounding waters. Consequently, the high concentrations measured around Livingston Island may result in part from the waters

having a longer time to accumulate methane compared with the other shelf locations.

In the deeper parts of the Bransfield Strait most of the samples analysed had concentrations near saturation. However, at station 48 in the Bransfield Strait frontal zone the interleaving or mixing of methane-rich shelf waters with near saturated off-shelf waters appears to cause a complex pattern of methane concentration changes with depth. Similar processes may have also produced the slight undersaturations observed in the surface layer at station 13. The surface waters are a low density layer of slightly undersaturated water that probably originated offshore in the Bellingshausen Sea and has been advected over more methane rich shelf waters at the station.

The variations in methane concentrations at station 39 to the north of Livingston Island (figure 4.4) indicate the inputs to the shelf waters are complex. However, the variability only amounts to be \pm 16% (\pm 1 s.d.) of a mean of 6.1 nM, and it appears reasonable to assume steady-state conditions in order to calculate a methane input to shelf waters around station 39. The mean methane concentration of 6.1 μ M at station 39 was assumed to be the concentration of a uniform layer of water overlying a 20km x 20 km area of shelf with an average depth of 100 m (figure 4.15). The southern boundary of the shelf waters is formed by Livingston Island and methane exchange through this



Figure 4.15. Schematic diagram of methane exchange between shelf waters to the north of Livingston Island and the surrounding waters. The shelf waters are 100m deep and cover a 20km x 20km area. The arrows indicate the direction of net flux and the flux values (x $10^8 \ \mu mol \ d^{-1}$) are shown in the boxes next to the arrows. The diffusive fluxes were calculated from observed methane concentration gradients (dC/dy; $\mu mol \ m^{-4}$) given in the figure. The sea-to-air flux of methane was calculated for a gas exchange coefficient of 1.46 m d⁻¹ and a saturation concentration of 3.08nM.

boundary is assumed to be zero. Methane exchange across the other boundaries was assumed to occur solely by diffusion. This appears to be a reasonable assumption because the surface dynamic topography shows there is little net flow in this region (Niiler et al., 1991). The net diffusive fluxes across the boundaries were calculated using concentration gradients given in figure 4.15, and a horizontal eddy diffusivity of 20 $m^2 s^{-1}$ estimated for a scale length of 20 km (Okubo, 1971). The concentration gradients were determined from the surface water methane concentrations shown in figure 4.9. Using the methane concentration gradients in this manner assumes the surface concentrations around station 39 reflect changes in methane throughout the water column. If the concentration changes were produced by air-sea gas exchange in a layer of surface water, the horizontal diffusion of methane away from the station and the net input to the station 39 waters will be overestimated. For a gas exchange coefficient of 1.46 m d^{-1} , calculated for an averaged summer wind speed of 6.3 m s⁻¹ measured at Deception Island (Burdecki, 1957), the net methane input needed to offset losses through gas exchange and diffusion is about 5.6 μ mol m⁻² d⁻¹. It is important to realize the calculation only provides a rough estimate of the integrated input needed to maintain the observed supersaturations over this portion of the shelf. The changes in methane concentrations at station 39 and in the

surface methane distributions indicate that the actual inputs are likely to be variable in space and time. Nevertheless, it appears reasonable to expect the input is somewhere on the order of 6 μ mol m⁻² d⁻¹.

The calculated flux does not distinguish between water column production or sediment derived methane inputs. However, the tendency for high methane concentrations to occur over the shelves, and the previously described poor correlation between methane concentrations and biotic variables, indicates that sediments are probably the major supplier of methane to region. Even if the entire flux of about 6 μ mol m⁻² d⁻¹ is from sediments, this input is small compared to methane fluxes reported for other coastal sediments. For example, Scranton and Farrington (1977) estimated a maximum sediment-water flux of 416 μ mol m⁻² d⁻¹ was necessary to maintain methane supersaturations in the waters off Walvis Bay, Namibia. Their estimate was considered a maximum because water column production may have contributed to the flux. Sediment-water fluxes of 1,200-60,000 μ mol m⁻² d⁻¹ have also been reported for the anoxic sediments of Cape Lookout Bight, North Carolina (Martens and Klump, 1984).

The comparatively small flux for the Livingston Island shelf is consistent with the low organic carbon contents (0.4-0.6%) reported for sediments around the Bransfield Strait (DeMaster et al., 1987). The low sedimentary organic

carbon contents are presumably the result of low seasonally averaged fluxes of sinking particulate organic matter to the seafloor (Karl et al., 1991 and Wefer et al., 1986) and dilution by terriginous material (Dunbar et al., 1985). The low organic carbon contents should restrict the development of anoxic conditions and the availability of substrates necessary for methanogenesis, and thereby limit the sediment-water methane flux. Cline et al. (1986) has also noted that methane production in the sediments of the Bering Sea may be retarded at near-freezing temperatures, and the uniformly low temperatures in the study area may provide an additional control on the sediment-water methane flux.

The uncertainty in the net water flows over the shelves along the Antarctic Peninsula and around Low Island prevents the application of a mass balance to calculate methane inputs at these locations. Niller et al., (1991) estimated the average flow in the frontal zones that border the South Shetland Islands to be about 5 cm s⁻¹, and the flow is probably less over the shelves. Assuming water flows over a 100 m deep and 20 km wide shelf at a maximum speed of 5 cm s⁻¹, then a methane input of about 6 μ mol m⁻² d⁻¹ would cause an increase in methane concentrations of about 0.3 nM, averaged over the water column. Because the transit time of the water over this segment of shelf is only about 5 days, potential gas exchange and oxidation

effects can be neglected. The observed increases over the shelves range from about 0.1 to 3.0 nM, relative to offshelf waters, suggesting that methane inputs of the same order of magnitude as estimated for the Livingston Island shelf can produce the increases found over the Antarctic Peninsula shelf and around Low Island.

An estimate of methane inputs to Port Foster, Deception Island, can also be made using the exchange coefficient of 1.46 m d⁻¹ given above. For a methane concentration of 9.37 nM and an atmospheric equilibrium concentration of 2.96 nM (Table A.3), the estimated flux of methane from the sea to air will be 9.36 μ mol m⁻² d⁻¹. Some loss may also occur by the exchange of methane-rich water in Port Foster with the waters surrounding Deception Island. However, this exchange will only occur through the narrow and shallow passage called Neptunes Bellows (figure 4.2). For the purposes of this calculation I have assumed the exchange has no effect on the methane balance. In order to maintain the calculated methane loss by gas exchange, there must be an equivalent input of 9.36 μ mol m⁻² d⁻¹ to the waters in Port Foster. This input does not distinguish between bottom-derived or water column methane sources. The general increase in methane concentrations towards the seafloor (figure 4.12) indicates the source is likely to be bottom derived and is perhaps associated with hydrothermal activity.

Air-Sea Methane Fluxes

The surface water methane concentration data were used to calculate averaged air-sea fluxes of methane for three regions (Table 4.2), which were separated based on the water mass distributions shown in figure 4.9. The Drake Passage region refers to the open ocean waters north of the Drake Passage frontal zone, the South Shetland Island region is the coastal zone covered by the Low and Livingston Island water masses, and the Bransfield Strait region refers to the coastal water masses south of the Bransfield Strait front. The fluxes are representative of the summer months. The negative fluxes indicate a net uptake of atmospheric methane by undersaturated surface waters, while positive fluxes indicate a net flux to the atmosphere from supersaturated surface waters.

Compared to other coastal waters, the methane fluxes from the South Shetland Island and the Bransfield Strait waters are small, and are more typical of open ocean fluxes (Table 4.3). The area weighted flux for both regions is $0.69 \ \mu mol \ m^{-2} \ d^{-1}$. The small fluxes are a consequence of low water temperatures and seasonally low wind speeds resulting in a small gas exchange coefficient, combined with a low rate of methane input to the water column. Meteorolgical records for Deception Island (Burdecki, 1957) indicate the mean monthly wind speed in the Bransfield Strait increases to a maximum of about 8.2 m s⁻¹ in June, and these windier

Region	Area	U	к	Dissolved	Methane (nM)	Flux (μ mol m^{-2} d^{-1})	
	(x10 ^{'2} m ²)	(m s ⁻¹)) (m d ⁻¹)	Average	Range	Average	Range
Drake Passage	3.4	5.2	0.90	2.69	2.22 to 3.09	-0.35 -	0.77 to 0.01
South Shetland Islands	5 14.4	6.3	1.46	3.80	2.80 to 7.09	1.05 -	0.41 to 5.86
Bransfield Strait	9.5	6.3	1.46	3.18	2.71 to 3.97	0.15 -	0.54 to 1.30

Table 4.2. Dissolved methane concentrations and air-sea gas exchange fluxes for surface waters in the RACER study area during the 1986/87 Austral summer.

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	Flux (µmol m	-2 d')	Source
Location	Range	Average	
Coastal:			
Walvis Bay, Namibia	1.09 to 816	n.r.	Scranton and Brewer (1977)
Bering Sea	5.08 to 70.2	27.5	Cline et al. (1985)
Oregon Estuary	2.05 to 1312	181	DeAngelis and Lilley (1987)
Saanich Inlet, Canada	n.r.	57.0	Lilley et al. (1982)
Saanich Inlet, Canada	n.r.	2.27	Ward et al. (1989)
Tampa Bay, Florida	27.4 to 603	137	Barber et al. (1988)
Boca Ciega Bay, Florida	110 to 685	219	Barber et al. (1988)
Bransfield Strait	-0.54 to 1.30	0.15	This study
South Shetland Islands	-0.41 to 5.86	1.05	This study
Open Ocean:			
Carribean Sea	n.r.	0.23	Ward et al. (1987)
subtropical Atlantic	n.r.	0.08	Scanton and Brewer (1977)
Atlantic Ocean (50N-35S)	0.09 to 4.65	0.23	Conrad and Seiler (1989)
Open Ocean	2.05 to 3.46	n.r.	Ehhalt (1974)
Drake Passage	-0.77 to 0.01	-0.35	This study

Table 4.3. Methane fluxes to the atmosphere from the surface ocean.

n.r. - not reported.

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conditions should enhance the sea-to-air flux. However, the higher winds will only increase the average methane fluxes to about 1.71 and 0.24 μ mol m⁻² d⁻¹ (area weighted flux of 1.13 μ mol m⁻² d⁻¹) for the South Shetland Island and Bransfield Strait regions, respectively. Therefore, the antarctic coastal waters sampled in this study do not appear to be as significant a methane source as most coastal regions.

In the offshore waters, methane fluxes into the water from the atmosphere should decrease between the summer and winter months as the surface layer approaches equilibrium with the atmosphere. Assuming the model given above to describe methane exchange in the offshore waters is valid, the net annual uptake can be estimated by substituting the expression for the change in methane concentrations in the surface layer, C_{e} , into the equation:

$$Flux = k_{L} \cdot (C_{eq} - C_{s})$$

and integrating over a 240 day ice-free period. The temperatures in the region remain near freezing throughout the year and C_{eq} can be assumed to remain constant (3.08 nM). For a k_{l} of 0.90 m d⁻¹ and an initial C_{s} of 2.40 nM (see above), the annual average methane uptake is 41 μ mol m⁻². The total uptake is primarily determined by the amount of methane-poor WDW entrained into the surface layer, and about 15% of the total represents a net diffusive flux of methane to deeper water. Seasonal changes in wind speed

will cause only small changes in the total methane uptake. For example, the estimated average wintertime wind speed in the Drake Passage is about 11 m s⁻¹ (U.S. Navy Climatic Atlas of the World, 1965), and the net annual uptake only increases to 46 μ mol m⁻² when recalculated with a gas exchange coefficient corresponding to this higher wind speed. The slightly greater flux occurs because at higher wind speeds (greater k_l) the methane concentration will approach saturation more rapidly, causing the methane concentration gradient between the surface and WW layers that drives the diffusive flux to deeper water to increase more rapidly than under calmer conditions.

These flux data provide a basis for estimating the contribution of the Southern Ocean waters to the total oceanic flux of methane to the atmosphere. For the calculation I have assumed that area weighted average fluxes of between 0.69 and 1.13 μ mol m⁻² d⁻¹ for the coastal waters in the study area are representative of the fluxes from all antarctic coastal waters. For an area of 2.1 x 10^{12} m² (Mackintosh, 1973), the total coastal flux to the atmosphere will be between 5.3 x 10^8 and 8.7 x 10^8 mol CH₄ yr⁻¹. In the offshore waters the ice concentration curves of Zwally et al., (1983) show that the seasonal ice zone covers a maximum area of about 17 x 10^{12} m², although only about 9 x 10^{12} m² of the surface is blanketed by greater than 85% cover. The entrainment of WDW that drives the net

methane uptake should occur throughout the zone of seasonal ice cover, but the uptake is probably less in the partially ice covered waters than in regions where complete ice cover has developed. Consequently, a range in net uptake was calculated using both the maximum extent of the ice cover and the smaller area that encompasses greater than 85% cover. For an annual uptake of between 41 and 46 μ mol m⁻², the total flux into the seasonal ice zone will vary between 3.7 x 10^8 mol CH₄ yr⁻¹ and 7.8 x 10^8 mol CH₄ yr⁻¹. This range can be checked using the 31 m yr⁻¹ upwelling rate estimated by Gordon et al. (1977) for the 60-70°S latitude band. In a steady state situation the upwelling rate will equal the entrainment rate. If the WDW is assumed to have a concentration of 1.71 nM, then the methane deficit relative to an assumed saturation concentration of 3.08 nM will be 42.5 μ mol m⁻² over the entire surface layer, irrespective of the depth of the layer. Only about one half of this deficit will influence the methane uptake because, during summer, the formation of the warm surface layer restricts mixing with the underlying remnant WW layer which contains a portion of the entrained WDW. The net uptake required to re-establish equilibrium with the atmosphere will be 24.4 μ mol m⁻² which includes the 21.2 μ mol m⁻² methane deficit in the surface layer, plus a 15% correction for diffusive losses to deeper water. If the surface layer methane concentration is less than saturation at the onset of ice

formation, then the uptake will be slightly greater. The $60-70\,^{\circ}$ S latitude band over which the upwelling estimate was derived covers 16.8 x 10^{12} m², and the total uptake over this area amounts to 4.1 x 10^8 mol CH₄ yr⁻¹. This estimate agrees well with the range of values derived above for the offshore waters.

The uptake of methane in the offshore waters tends to compensate for the net flux of methane to the atmosphere in the coastal waters. The combination of the ranges of gas flux estimates above will produce a net exchange of between -2.8 x 10^8 and 5.0 x 10^8 mol yr⁻¹, which corresponds to a flux of between about -0.04 to $0.07 \ \mu$ mol m⁻² d⁻¹ out to the edge of the seasonal ice (total area of 19.1 x $10^8 \ m^2$). This range in flux is less than is normally observed in the open ocean (Table 4.3), and indicates that at least out to the edge of the seasonal ice zone, the Southern Ocean has little impact on the total flux of methane between the surface ocean and atmosphere.

Summary

Dissolved methane concentrations were measured in the upper water column (0-200 m) of the western Bransfield Strait and southwestern Drake Passage on four cruises between December, 1986 and March, 1987. The methane distributions were similar on all four cruises and showed distinct geographic variations. In contrast to most open ocean surface waters, the waters of the Drake Passage were

undersaturated with methane relative to atmospheric equilibrium. The degree of the undersaturation varied from about 0-15% in the seasonally warmed surface layer to about 46% at 200 m. The undersaturations result from the entrainment of methane-poor Warm Deep Water into the surface layer, and from seasonal ice cover restricting airsea gas exchange in winter.

South of the Drake Passage, a shelf-break frontal zone marked a distinct transition to coastal waters that were typically supersaturated with methane. The highest methane concentrations were generally associated with the shelf waters surrounding the Bransfield Strait and the South Shetland Islands. In the deeper waters of the central Bransfield Strait concentrations tended to decrease to near-saturation values, although the interleaving or mixing of the near-saturated waters with methane-rich shelf waters resulted in a complex pattern of concentration changes at some locations in the strait. Overall, the methane distributions appear to be largely controlled by mixing, coupled with the addition of methane to waters flowing over the shelves in the region. Sediments are the most likely source of the methane, but production in the water column may also contribute some methane.

The calculated fluxes of methane across the air-sea interface varied from -0.77 to +5.86 μ mol m⁻² d⁻¹, throughout the study area. The average uptake of atmospheric methane

in the Drake Passage was 0.35 μ mol m⁻² d⁻¹, while the average flux from the coastal waters to the atmosphere was 0.69 μ mol m⁻² d⁻¹. The coastal and offshore fluxes tend to compensate each other. The net effect is that air-sea methane fluxes in the Southern Ocean out the edge of the seaonal ice zone are small and will have no significant impact on the current estimates of the oceanic source of methane to the atmosphere.

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Chapter V

Summary

The factors regulating the distribution of dissolved methane in upper ocean waters were investigated in various ocean environments including coastal temperate and Antarctic waters and the open ocean waters of the central North Pacific gyre. All the surface waters sampled in the North Pacific were supersaturated with methane relative to atmospheric equilibrium concentrations. The surface waters sampled in the central North Pacific gyre (26.0N 155.0W) were slightly supersaturated (11 to 26%) with methane, while supersaturations of up to 72% were observed in coastal California waters (36.3N 122.1W). Methane concentrations were more variable in coastal Antarctic waters and ranged between about 10% undersaturated and 74% supersaturated. The open ocean waters of the Drake Passage, Antarctica, were typically between 0 and 15% undersaturated.

Mass balance calculations indicated the methane distributions in the surface waters of the central North Pacific gyre were primarily controlled by a net in situ methane production and a net flux of methane to the atmosphere from the surface ocean. Closer to shore, nearbottom or sediment derived methane sources became more important and a subsurface plume (100 to 200 m) of methane-

rich water was found to extend from near the coast of California and out into the North Pacific Gyre.

The source of the methane produced in the open ocean surface waters could not be determined. Incubations of open ocean plankton samples with methanogenic substrates were largely unsuccessful, suggesting there is only a limited capacity for methanogenesis in the surface waters. Incubations of particulates collected in sediment traps deployed in coastal California waters also failed to produce any methane.

Measurements made in sediment trap solutions showed that methane did accumulate in sediment traps. The greatest methane accumulations were typically found in the shallowest traps, and the accumulations tended to increase with distance offshore for traps deployed in the upper 200m of the water column. Methane accumulations were not significantly different in paired preserved and unpreserved traps, indicating that biological activity within the traps was not the source of the methane. Assuming the methane is biogenic, the most likely sites of production are within the gut of organisms or in large particulate aggregates. Although the source of the methane in the trap solutions could not be determined, the trap data are consistent with a small net methane production occurring in the upper water column.

Open ocean surface waters are typically supersaturated with methane and undersaturations observed in the offshore waters of the Drake Passage are an unusual feature. The undersaturations resulted from the entrainment of methane depleted Warm Deep Water into the surface layer and from seasonal ice cover restricting air-sea gas exchange in the winter. The entrainment process is driven by the seasonal formation and melting of sea-ice. Small increases in the methane concentration of the surface layer occurred over summer after the sea ice had melted. The increases were largely due to a net uptake of atmospheric methane through air-sea gas exchange. Although the extent of the surface methane undersaturations is unknown, the entrainment of Warm Deep Water occurs around Antarctica and methane undersaturations are likely to be a common feature of offshore Antarctic surface waters.

In the nearshore waters of the Bransfield Strait and South Shetland Islands methane was added to the waters flowing over the shelves in the region. The mixing of methane-rich shelf waters with offshore waters advected into the Bransfield Strait produced a complex pattern of methane supersaturated waters over the shelves and nearsaturated methane concentrations in the central Bransfield Strait. Furthermore, the interleaving of the shelf waters with undersaturated waters derived from offshore produced

complex patterns of methane concentration changes with depth in the frontal zones that separate these waters.

The average uptake of atmospheric methane in the Drake Passage was calculated to be 0.35 μ mol m⁻² d⁻¹, while the average flux from the coastal waters to the atmosphere was 0.49 μ mol m⁻² d⁻¹. These fluxes tend to compensate each other and indicate that methane fluxes in the Southern Ocean, out to the edge of the seasonal ice zone, do not significantly effect current estimates of the net oceanic flux of methane to the atmosphere. Appendix

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RACER SA13		63.4S 62.4W		12/27/86					
Depth (m)	Temp (C)	Sal (o/oo)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/1)	Glutamate Incorporation (nCi/1/hr)
1.5	-0.45	33.776	27.16	2.85	3.18	0.90	5.77	571	48
5.0	-0.44	33.776	27.16	3.12	3.18	0.98	6.93	715	51
15.0	-0.51	33.780	27.17	2.96	3.18	0.93	7.62	591	72
30.0	-0.65	33.787	27.18	3.17	3.20	0.99	6.46	545	98
40.0	-1.28	33.829	27.23	3.56	3.26	1.09	5.08	322	58
50.0	-0.93	33.904	27.28	4.36	3.22	1.35	3.50	331	37
75.0	-0.75	34.071	27.41	4.12	3.20	1.29	1.95	159	22
100.0				5.28			1.35	141	17
RACER SB13		63.4S 62.4W	, 	01/28/87					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.0	0.41	33.514	26.91	2.94	3.10	0.95	3.57	502	16
10.0	0.36	33.517	26.91		3.11		3.81		40
15.0	0.35	33.534	26.93	3.08	3.11	0.99	3.44	526	37
20.0	0.31	33.544	26.94		3.11		3.64		
40.0	-0.36	33.694	27.09	2.95	3.17	0.93	4.44	520	· · 23
50.0	-0.46	33.797	27.18	3.23	3.18	1.02	3.83	401	24
60.0	-0.57	33.871	27.24	3.93	3.19	1.23			
75.0	-0.70	33.899	27.27	3.86	3.20	1.21	1.74	142	21
100.0				4.58			0.57	84	19

Table A.1. Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.
RACER SC13		63.45 62.4W		03/02/87					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/1)	Glutamate Incorporation (nCi/l/hr)
5.4	0.36	33.705	27.06	2.45	3.10	0.79	1.43	50	37
10.7	0.36	33.703	27.06	3.16	3.10	1.02	1.36		
14.9	0.36	33.705	27.06	3.50	3.10	1.13	1.28	45	19
20.4	0.36	33.705	27.06	3.29	3.10	1.06	1.33		
30.2	0.37	33.705	27.06	3.34	3.10	1.08	1.24	68	29
41.1	0.35	33.717	27.07	3.35	3.10	1.08	1.22	48	7
75.4	0.18	33.857	27.20	3.92	3.11	1.26	0.59	41	26
100.0	0.14	33.998	27.31	4.43	3.12	1.42	0.33	10	9
RACER SB20 Depth (m)	Temp (C)	61.9S 62.3W Sal (0/00)	Sigma-t	01/30/87 CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.0	1.08	33.385	26.77	2.68	3.04	0.88	0.49	260	15
15.0	1.05	33.391	26.77	2.45	3.05	0.80	0.51	261	12
30.0	0.70	33.399	26.80	2.69	3.08	0.87	0.67	276	21
40.0	0.61	33.397	26.80		3.08		0.66	232	18
50.0	-0.14	33.572	26.98	2.54	3.15	0.81	0.59	170	. 13
75.0	-1.23	33.921	27.31	2.39	3.25	0.74	0.29	65	· 11
100.0				2.33			0.20	61	9
125.0				2.21					
150.0				2.02			0.08	39	7
200.0				1.51			0.02		24

Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

RACER SC20		61.9S 62.3W		03/03/87					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.3	0.97	33.482	26.85	2.78	3.05	0.91	0.65	129	7
15.0	0.95	33.486	26.85	2.73	3.05	0.89	0.68	128	17
29.6	0.96	33.484	26.85	2.65	3.05	0.87	0.65	146	14
39.4	0.91	33.488	26.86	2.46	3.06	0.80	0.64	133	16
50.1	0.14	33.599	26.99	2.59	3.12	0.83	0.44	85	3
75.3	-0.89	33.956	27.32	2.53	3.22	0.79	0.25	39	13
100.6	-0.21	34.096	27.41	2.15	3.15	0.68	0.11		29
150.1	0.83	34.254	27.48	1.86	3.05	0.61	0.04		3
203.1	1.61	34.381	27.53	1.40	2.97	0.47	0.01		5
RACER SD20		61.9S 62.3W		03/23/87					
Depth (m)	Temp (C)	Sal (o/oo).	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.6	0.40	33.572	26.96	3.11	3.10	1.00	0.49	98	18
14.9	0.39	33.579	26.96	2.71	3.10	0.87	0.46	107	15
29.5	0.37	33.575	26.96	2.96	3.10	0.95	0.43	100	34
40.3	0.34	33.581	26.97	2.71	3.11	0.87	0.46	125	. 26
50.5	0.27	33.604	26.99	2.76	3.11	0.89	0.45	106	16
75.5	-0.51	33.809	27.19	2.60	3.18	0.82	0.28	80	34
99.7	-0.94	34.025	27.38	2.38	3.22	0.74	0.17	14	96
149.8	0.07	34.246	27.52	2.06	3.12	0.66	0.06	17	51
202.0	1.13	34.414	27.59	1.39	3.02	0.46	0.03		9

Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

RACER SA39		62.5S 61.5W		12/25/86					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Ch1-a (ug/1)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
1.3	-0.06	34.004	27.33	5.06	3.13	1.62	0.85	610	117
5.0	-0.06	33.998	27.32	4.97	3.13	1.58	0.68	531	119
15.0	-0.06	34.002	27.33	5.29	3.13	1.69	0.60	845	70
30.0	-0.07	34.005	27.33	5.30	3.13	1.69	0.62	532	186
40.0	-0.14	34.044	27.36	5.47	3.14	1.74	0.47	206	793
50.0	-0.18	34.081	27.40	5.55	3.14	1.77	0.46	182	527
75.0	-0.21	34.098	27.41	8.40	3.15	2.67	0.48	110	103
100.0				7.07			0.40	79	59
RACER SB39		62.5S 61.5W		01/31/87					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/1)	Glutamate Incorporation (nCi/l/hr)
5.0	0.88	33.978	27.25	4.86	3.05	1.60	0.51	207	24
15.0	0.75	34.015	27.29	4.95	3.06	1.62	0.66	221	26
30.0	0.64	34.037	27.32	5.39	3.07	1.76	0.66	205	37
40.0	0.62	34.042	27.32	5.80	3.07	1.89	0.70	207	. 31
50.0	0.60	34.046	27.33	5.40	3.07	1.76	0.64	179	. 39
75.0	0.52	34.077	27.35	5,96	3.08	1.94	0.43	140	46
100.0				4.88				153	30
116.0				6.13					_ ~

Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

RACER SC39		62.55 61.5	Ŵ	03/05/87					
Depth (m)	Temp (C)	Sal (o/oo)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
4.2	0.52	33.929	27.24	7.09	3.08	2.30	0.62	69	34
14.9	0.57	33.944	27.25	6.62	3.08	2.15	0.64	70	48
30.0	0.56	33.980	27.28	5.99	3.08	1.95	0.62	84	21
40.2	0.48	34.032	27.31	6.58	3.08	2.14	0.46	73	10
49.6	0.47	34.038	27.33	5.92	3.08	1.92	0.40	35	12
75.1	0.39	34.081	27.37	6.89	3.09	2.23	0.36	36	23
RACER SD39		62.55 61.5	W	03/25/87					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.1	0.25	33.965	27.28	6.32	3.11	2.04	0.49	39	25
15.1	0.25	33.964	27.28	7.60	3.11	2.45	0.48	46	42
30.0	0.27	33.968	27.28	5.86	3.10	1.89	0.48	37	24
40.6	0.27	33.977	27.29	5.79	3.10	1.86	0.48	54	55
40 E	0.26	33.995	27.30	6.47	3.10	2.08	0.47	52	21
49.5									
49.5	0.32	34.126	27.41	5.87	3.10	1.90	0.32	51	22

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Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

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ACER SA43		64.25 61.3	Ŵ	12/22/86					
Depth (m)	Temp (C)	Sal (o/oo)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.0	1.83	33.952	27.17	3.65	2.96	1.23	10.50	1144	169
15.0	0.99	33.966	27.24	3.71	3.04	1.22	11.20	1375	263
30.0	0.68	34.165	27.42	3.86	3.06	1.26	7.62	660	249
40.0	0.07	34.329	27.58	3.96	3.11	1.27	9.52	890	184
50.0	-0.24	34.335	27.60	4.07	3.14	1.30	8.25	769	191
75.0	-0.22	34.387	27.64	4.06	3.14	1.29	4.68	453	112
100.0				3.70			2.72	395	119
150.0				4.12			1.62	263	53

Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

RACER SB43 64.2S 61.3W

Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
1.5	1.34	33.534	26.87	3.49	3.02	1.16	4.96	1393	480
5.0	1.31	33.552	26.88	3.39	3.02	1.12	5.25	1311	295
15.0	1.80	33.793	27.04	3.45	2.97	1.16	2.77	967	619
30.0	1.05	34.067	27.31	3.32	3.03	1.09	3.54	957	410
40.0	0.33	34.178	27.45	3.56	3.09	1.15	5.55	863	· 215
50.0	-0.02	34.249	27.52	3.53	3.12	1.13	6.08	767	253
75.0	-0.13	34.309	27.58	4.10	3.13	1.31	3.06	351	110
100.0				3.73			3.21	383	114
150.0				4.06			1.55	162	47
200.0				3.61			0.91	82	37

01/26/87

RACER SC43	64.25 61.3W			02/28/87					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
4.5	0.39	33.712	27.07	3.63	3.10	1.17	8.79	961	73
14.1	0.01	34.233	27.51	3.39	3.12	1.09	6.00	391	55
29.6	0.07	34.250	27.52	3.81	3.12	1.22	3.41	263	47
39.5	0.01	34.244	27.52	3.41	3.12	1.09	3.71	281	35
49.6	-0.06	34.233	27.51	3.65	3.13	1.17	3.86	287	34
76.2	-0.26	34.310	27.58	3.43	3.15	1.09	4.31	270	65
99.6	-0.17	34.339	27.60	3.74	3.14	1.19	2.16	140	36
150.3	-0.25	34.369	27.63	3.63	3.14	1.16	0.85	97	32
200.3	-0.34	34.395	27.66	3.84	3.15	1.22	0.71	66	24

Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

03/21/87

Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
3.4	-0.13	33.964	27.30	3.49	3.14	1.11	0.80	148	105
15.4	-0.11	33.981	27.31	3.36	3.14	1.07	0.76	144	249
30.9	-0.07	34.090	27.40	3.34	3.13	1.07	0.59	113	179
40.2	0.01	34.160	27.45	3.43	3.12	1.10	0.50	91	94
50.2	-0.02	34.243	27.52	3.39	3.12	1.09	0.37	59	141
75.1	-0.07	34.298	27.56	3.56	3.13	1.14	0.40	95	35
100.1	-0.07	34.335	27.59	3.59	3.13	1.15	0.43	75	18
150.0	-0.10	34.393	27.64	3.38	3.13	1.08	0.14	52	48
200.4	-0.14	34.442	27.68	3.53	3.13	1.13	0.09	44	43

RACER SA48		63.2S 61.0W		12/20/86					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
1.0				3.10			5.08	753	87
5.0				3.15			5.02	648	115
15.0				3.40			4.73	613	117
30.0				2.39			4.33	525	137
40.0				2.72			3.45	514	226
75.0				3.50		- -	1.06	100	127
100.0				4.11			0.23	58	24
150.0				4.87			0.70	98	22
200.0				5.34			0.30	39	11
RACER SB48		63.2S 61.0W		01/25/87					
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/1)	Glutamate Incorporation (nCi/l/hr)
5.0	0.58	33.068	26.54	3.07	3.10	0.99	4.76	833	190
15.0	0.56	33.448	26.85	3.15	3.09	1.02	4.10	602	283
30.0	0.69	34.103	27.37	3.61	3.06	1.18	5.98	452	79
40.0	0.51	34.213	27.47	3.38	3.08	1.10	1.46	303	·129
50.0	0.34	34.243	27.50	3.74	3.09	1.21	1.59	281	123
75.0	-0.01	34.314	27.57	3.97	3.12	1.27	0.87	187	55
100.0				3.60			0.31	82	26
150.0				4.34			0.14	34	9
200.0				4.26			0.11	21	21

Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

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RACER SC48		63.2S 61.0W							
Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.2	0.92	33.848	27.15	3.23	3.05	1.06	1.08	241	53
29.8	0.65	33.956	27.25	3.58	3.07	1.17	0.77	170	152
40.3	0.59	34.003	27.29		3.07		0.53	154	118
50.9	0.52	34.046	27.33	3.51	3.08	1.14	0.34	119	54
75.5	0.20	34.183	27.46	4.37	3.11	1.41	0.19	89	46
100.4	0.04	34.260	27.53	5.47	3.12	1.75	0.11	65	17
150.4	-0.24	34.392	27.65	3.78	3.14	1.20	0.10	51	8
200.2	-0.20	34.430	27.68	3.47	3.14	1.10	0.07	42	4

Table A.1. (continued) Dissolved methane, hydrographic, and biological data collected on RACER slow grid cruises A through D.

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RACER SD48	63 25 61 OW	03/30/87
VUCPV DD40	00.20 01.00	03/30/07

Depth (m)	Temp (C)	Sal (0/00)	Sigma-t	CH4 (nM)	CH4eq (nM)	Saturation Ratio	Chl-a (ug/l)	Total ATP (ng/l)	Glutamate Incorporation (nCi/l/hr)
5.0				2.71			0.68	145	16
15.0				2.67			0.67	134	18
30.0				3.05			0.67	118	23
40.0				3.24			0.67	117	20
50.0				3.26			0.62	116	• 23
73.9	-0.11	34.070	27.38	5.12	3.14	1.63	0.35	60	13
100.4	-0.11	34.175	27.47	4.83	3.13	1.54	0.11	11	12
150.3	-0.06	34.240	27.53	7.19	3.13	2.30	0.07	3	8
199.2	0.14	34.355	27.60	13.20	3.11	4.25	0.04		7

ATP and Glutamate incorporation data from D. Karl.

Chlorophyll-a data from B. G. Mitchell and O. Holm-Hansen.

TABLE A.2. Dissolved methane and hydrographic data for surface waters (5 m) collected during RACER fast grid cruise C

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STA	LAT. (°S)	LONG. (°W)	DATE	TEMP (C)	SAL (0/00)	SIGMA-t	CH4 (nM)	CH4eq (nM)	Satn. Ratio
42344567 44567 44552355567 5589012 665667 665667 665667	$(^{\circ}S)$ $61^{\circ}56.25^{\circ}$ $64^{\circ}14.00^{\circ}$ $64^{\circ}2.90^{\circ}$ $63^{\circ}49.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}12.75^{\circ}$ $63^{\circ}25.50^{\circ}$ $62^{\circ}47.25^{\circ}$ $62^{\circ}21.75^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}37.70^{\circ}$ $63^{\circ}37.70^{\circ}$ $63^{\circ}37.70^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}37.70^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}37.70^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}37.70^{\circ}$ $63^{\circ}25.50^{\circ}$ $63^{\circ}37.70^{\circ}$	$(^{\circ}W)$ $61^{\circ}24.00'$ $61^{\circ}17.00'$ $61^{\circ}10.00'$ $61^{\circ}5.00'$ $61^{\circ}2.75'$ $61^{\circ}2.75'$ $61^{\circ}2.75'$ $61^{\circ}2.00'$ $61^{\circ}1.00'$ $60^{\circ}59.00'$ $60^{\circ}59.00'$ $60^{\circ}59.00'$ $60^{\circ}59.00'$ $60^{\circ}59.00'$ $60^{\circ}35.00'$ $60^{\circ}37.25'$ $60^{\circ}37.25'$ $60^{\circ}35.50'$ $60^{\circ}35.50'$ $60^{\circ}35.50'$ $60^{\circ}35.50'$ $60^{\circ}34.40'$ $60^{\circ}31.00'$ $60^{\circ}22.50'$ $60^{\circ}9.50'$ $60^{\circ}8.50'$	2/21/87 2/24/87 2/24/87 2/24/87 2/24/87 2/24/87 2/24/87 2/24/87 2/22/87 2/22/87 2/22/87 2/24/87 2/24/87 2/24/87 2/24/87 2/24/87 2/24/87 2/24/87 2/26/87 2/22/87 2/25/87 2/25/87 2/25/87	$(C) \\ 0.44 \\ 1.17 \\ 1.05 \\ 0.10 \\ -0.10 \\ 0.68 \\ 0.72 \\ 0.56 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.77 \\ 0.63 \\ 0.76 \\ 0.56 \\ 0.55 \\ 0.44 \\ 0.76 \\ 0.27 \\ -0.12 \\ -0.38 \\ 0.20 $	(0/00) 33.503 33.557 33.860 34.317 34.380 34.091 33.934 33.934 33.929 34.029 33.719 34.290 34.298 34.251 34.060 33.842 33.940 33.939 33.914 34.350 34.180 34.180	26.90 26.90 27.20 27.57 27.63 27.32 27.23 27.22 27.24 27.05 27.56 27.56 27.56 27.56 27.33 27.15 27.24 27.24 27.24 27.25 27.56 27.56 27.56 27.61 27.46	(nM) 2.91 3.97 3.24 1.98 3.07 3.23 3.40 3.91 4.88 3.92 3.06 2.89 3.98 3.98 3.98 3.98 5.27 4.22 3.98 3.08 3.98 3.08 3.98 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.06 3.08	(nM) 3.10 3.03 3.04 3.11 3.13 3.06 3.07 3.06 3.08 3.08 3.07 3.06 3.08 3.07 3.06 3.08 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.07 3.06 3.08 3.08 3.09 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.10 3.113 3.113 3.10 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.113 3.114 3.114	Ratio 0.94 1.31 1.07 0.64 0.98 1.06 1.11 1.27 1.60 1.28 1.00 0.94 1.05 1.26 0.93 1.11 1.30 1.71 1.37 1.26 0.99 1.15 0.89 0.98
69	62°47.25′	60° 5.75'	2/25/87	0.63	33.949	27.25	3.55	3.07	1.16

TABLE A.2. (Continued) Dissolved methane and hydrographic data for surface waters (5 m) collected during RACER fast grid cruise C

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DEPTH (m)	TEMP (C)	SAL (0/00)	SIGMA-t	CH4 (MM)	CH4eq (nM)	Satn. Ratio
0.6	1.93	33.77	27.01	9.37	2.96	3.17
8.1	1.15	33.83	27.12	9.90	3.03	3.27
37.0	0.82	33.83	27.14	12.87	3.06	4.21
74.4	-0.29	33.98	27.31	18.14	3.16	5.75
107.1	-1.16	34.08	27.43	19.34	3.24	5.97
125.4	-1.28	34.10	27.45	22.45	3.25	6.91
149.1	-1.45	34.12	27.47	20.79	3.27	6.36

Table A.3. Dissolved methane and hydrographic data collected on 02/27/87 at 62°57.9'S 60°39.3'W in Port Foster, Deception Island.