THE MARINE GEOCHEMISTRY OF METHANE

by

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BIOGRAPHICAL NOTE

The author was born in Atlanta on February 28, 1950 and was raised there and in Chicago. She attended the University of Chicago Laboratory High School and graduated with a BA in Chemistry from Mount Holyoke College in 1972. Later in the summer of 1972 she entered the Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography. The author is a member of Phi Beta Kappa, Sigma Xi, the American Geophysical Union and the American Society of Limnology and Oceanography.

Publications

Scranton, M. I. (1976) Methane in the near-surface waters of the western subtropical North Atlantic. Trans. Am. Geophys. Union (Abstract), 57, 255.

Scranton, M. I. and P. G. Brewer (1977) Occurrence of methane in the near-surface waters of the western subtropical North Atlantic. Deep-Sea Res., 24, 127-138.

Scranton, M. I. and J. W. Farrington (1977) Methane production in the waters off Walvis Bay. Trans. Am. Geophys. Union (Abstract), 58, 422.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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ABSTRACT

In the highly productive coastal surface waters near Walvis Bay, methane is present in concentrations considerably above those which would be predicted from solubility equilibrium with the atmosphere. A one dimensional diffusive model and a one dimensional horizontal advection diffusion model were used to describe the methane distribution. Evaluation of the model fits to the data suggests that both advective supply of methane-rich coastal waters and in situ biological methane production are important sources for the mixed layer methane excess. The complexity of the hydrographic regime near Walvis Bay makes it impossible to make a quantitative estimate of the rate of methane production.

In the less productive Murray-Wilkinson Basin in the Gulf of Maine, a mixed layer methane excess is also observed. Methane concentrations are closely correlated with hydrographic parameters and the source of methane at a middepth maximum appears to be the highly anoxic sediments in the adjoining Franklin Basin. Diffusion of methane from the middepth maximum is probably adequate to maintain the surface methane excess against loss across the air-sea interface.

Coastal waters are frequently enriched in methane, and it has been shown that advective supply of these methane-rich waters may be a significant source of methane for the mixed layer near the coast. Thus the widespread occurrence of a methane maximum at the base of the mixed layer in the open ocean, coupled with surface waters typically 30-70% supersaturated with respect to solubility equilbrium, suggests that advective supply of methane might be an important methane source for the open ocean as well. However, a study of the western subtropical Atlantic shows that advective transport can probably supply only a fraction of the methane present in the maximum. Also the loss of methane across the air-sea interface was observed to be twenty times greater than the flux from the maximum. Thus in situ methane production must be very important to the open ocean methane distribution.

A series of phytoplankton culture experiments demonstrated that cultures of both Coccolithus huxleyi and Thalassiosira pseudonana

produce trace amounts of methane during logarithmic growth. (Because the cultures are highly oxygenated, anaerobic methane bacteria can be neglected as methane sources. However heterotrophic bacteria cannot be excluded as possible sources of methane to the cultures.) After three algal generations, the rate of methane increase closely parallels the growth curve suggesting that the methane is in fact coming from the algae. A methane production rate of 2×10^{-10} nmole methane/viable cell/hr was calculated from the data. This rate is three to four orders of magnitude slower than the rates of oxygen consumption and glutamate and glucose uptake measured by other workers for algae and bacteria. The methane production rate calculated from the culture experiments is the correct order of magnitude to account for the methane production occurring in the open ocean.

Methane is present in quite low concentrations in the deep ocean. By calculating water mass ages from GEOSECS and other data, it is possible to estimate methane consumption rates in the deep sea. Methane consumption is rapid at first (probably greater than 0.06 nmole/l/yr). At depth consumption appears extremely slow. This may be due to the fact that the methane concentrations in the deep sea are so low that methane oxidizing bacteria cannot use methane as a substrate, or due to reduced metabolic activity in the bacteria at the high pressures and low temperatures of the sea floor.

Methane is present in very high concentrations in anoxic basins, indicating that methanogenic bacteria are active. However, near the anoxic-oxic interface in both the Black Sea and the Cariaco Trench a one dimensional advection diffusion model predicts that methane consumption is occurring in the anoxic zone. In the Black Sea the methane depletion may be indicative of the presence of rapid methane oxidation near the Bosporus overflow. However in the Cariaco Trench the validity of such an explanation is difficult to evaluate since the overflow process is so poorly understood. A box model for the Trench has been developed which incorporates time dependence and supply of chemical species to the water from the sediments at all depths in the Trench. This model can explain the silica and sulfide data quite well, but methane depletion near the interface, relative to the model predictions, still occurs. Thus either anaerobic methane oxidation or decreased methane production in the sediments must be hypothesized.

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CHAPTER I

INTRODUCTION

The distribution of a dissolved chemical species in the marine environment is dependent on physical, chemical and biological source and removal mechanisms and their rates and on transport and mixing processes within the ocean. This thesis examines the distribution of methane in the marine environment in hopes of elucidating those processes of importance to the geochemistry of methane, and at the same time improving understanding of the phenomena which influence the distribution of other compounds with similar properties.

Methane is one of a number of reduced gases (H_2, CO, N_2O) present in the oceanic mixed layer in amounts considerably above that which would be calculated from solubility equilibrium with the atmosphere. Such a distribution suggests that an active supply mechanism must exist to maintain the excess surface concentration.

Another common feature in the distribution of many dissolved gases which are involved in biological cycles is depletion in the deep waters of the ocean. For oxygen, this depletion in primarily the result of consumption by organisms during respiration. By analogy, the depletion observed in methane, ethylene, and other gases is commonly attributed to biological utilization. However no rates of consumption have been calculated for gases in the deep ocean except for oxygen.

Finally investigations of anoxic sediments and waters have demonstrated that such environments strongly affect dissolved gas concentrations. The more oxidized constituents (oxygen, unsaturated hydrocarbons) disappear, while reduced species such as methane and hydrogen sulfide can attain high concentrations relative to those found in oxidizing environments.

Methane has a number of characteristics which make its study especially informative. It is present in the atmosphere in significant amounts and if the ocean and atmosphere were at equilibrium, methane concentrations in the ocean would be determined primarily by the temperature and salinity of the water and by the atmospheric methane concentration in regions of water mass formation. Deviations from predicted concentrations suggest that production or consumption processes are occurring.

In addition known biological sources and sinks for methane are restricted to very specialized classes of organisms. If conditions are not suitable for survival of these organisms, new sources and/or sinks must be hypothesized. The research presented in the following pages has been devoted to identification of anomalies in the distribution of methane and to attempts to understand the processes producing them.

A. Atmospheric Methane

Global budgets for methane (Hutchinson, 1949; Koyama, 1963; Robinson and Robbins, 1968; Ehhalt, 1974; Baker-Blocker _et al_., 1977- see Table I.1) estimate that all of the methane present in the atmosphere originates in reducing environments, most of which are on land. Methane is formed by bacterial fermentation of acetate, formate, or methanol or by reduction of carbon dioxide using hydrogen as an electron donor (Wolfe, 1971). Available atmospheric methane data (Ehhalt and Heidt, 1973; Prabhakara _et al_., 1974; Lamontagne _et al_., 1973; Lamontagne _et al_., 1974; Swinnerton _et al_., 1969; Cavanagh _et al_., 1969; Larson _et al_., 1972;

TABLE I.1

GLOBAL METHANE BUDGET

Sources	Flux (10^{14} g CH_4/yr)	Flux (10^{13} moles CH_4/yr)
Paddy fields	1.7 - 3.5	1.1 - 2.2
Swamps	1.5 - 5.7	0.9 - 3.5
Humid tropical areas	6.1	3.8
Enteric fermentation	0.45 - 2.2	0.3 - 1.4
Coal fields	0.20	0.12
Upland fields, grasses, etc.	0.1	0.06
Forests	0.004	0.0025
Total ≃	10.0 - 17.8	6.2 - 11.1

taken from

Koyama, 1963

Robinson and Robbins, 1968

Hutchinson, 1949

Baker-Blocker *et al.*, 1977

Ehhalt, 1974

Sink	Flux (10^{14} g CH_4/yr)	Flux (10^{13} moles CH_4/yr)
Hydroxyl radical oxidation	15.8	9.8

taken from

Levy, 1973

Williams and Bainbridge, 1973; Table III.1) suggest that atmospheric methane concentrations may range from 1.2 to greater than 2 ppmv (parts per million by volume). In unpolluted areas and areas not directly in contact with large methane sources, variations in atmospheric concentrations are small. The global time-average methane concentration is 1.4 ppmv with a variability of less than 0.3 ppmv (Prabhakara et al., 1974).

Although methane is thermodynamically unstable in the presence of oxygen, the reaction rate is slow and its residence time in the atmosphere is about two years (Levy, 1973). The major atmospheric sink appears to be oxidation by hydroxyl radicals to carbon monoxide (McConnell et al., 1971). Such a removal mechanism would not be important in the ocean and oceanic methane consumption is thus probably biological.

B. The Surface Ocean

If the atmosphere and ocean were at solubility equilibrium for methane, the amount of methane in the water would depend on the partial pressure of methane in the atmosphere and the solubility of the gas in seawater (see Appendix I.1). However observations have shown that an equilibrium distribution is uncommon (Brooks and Sackett, 1973; Brooks et al., 1973; Lamontagne et al., 1973; Swinnerton et al., 1969; Williams and Bainbridge, 1973; Scranton and Brewer, 1977; Scranton and Farrington, 1977; Chapters III and IV). In regions of significant organic pollution (the Louisiana-Texas shelf, the Potomac River) methane levels of up to 50 times those predicted from equilibrium with the atmosphere have been observed (Brooks and Sackett, 1973; Swinnerton et al., 1969).

A profile from the western subtropical North Atlantic, showing the most common features of the oceanic methane distribution is shown in Figure

I.1 (see Chapter IV for a more detailed discussion). Concentrations are generally somewhat above those predicted from solubility equilibrium in the mixed layer. Below the mixed layer, a subsurface maximum is often found, with the increase in concentration starting at the depth at which the density starts to increase. Because the profiles previously published in the literature generally do not extend to great depths, data are not always available to give the thickness of the maximum. Usually the maxima appear to be less than several hundred meters thick.

The maxima cannot be explained as the result of an inadequate knowledge of solubilities. Yamamoto _et al_. (1976) have presented very accurate and precise solubility data in distilled water and seawater and have shown that the logarithm of the solubility coefficient is approximately proportional to 1/T, where T is the absolute temperature. Similar relationships have been obtained previously by Weiss (1970) for N_2, O_2 and Ar. The methane concentrations predicted from Yamamoto _et al_. (1976) and from the temperature and salinity of the water are plotted in Figure I.1. They change quite gradually with depth and indicate that temperature variations are inadequate to explain the large variations in methane content that are observed.

Craig and Weiss (1971), among others, have pointed out several physical processes which might produce saturation anomalies of atmospheric gases. These include air-injection, atmospheric pressure changes and changes in water temperature after isolation from the atmosphere. While these processes are not well understood, it is possible to make some estimates of the importance of such phenomena in creating methane saturation anomalies. In Appendix I.2, it is calculated that saturation

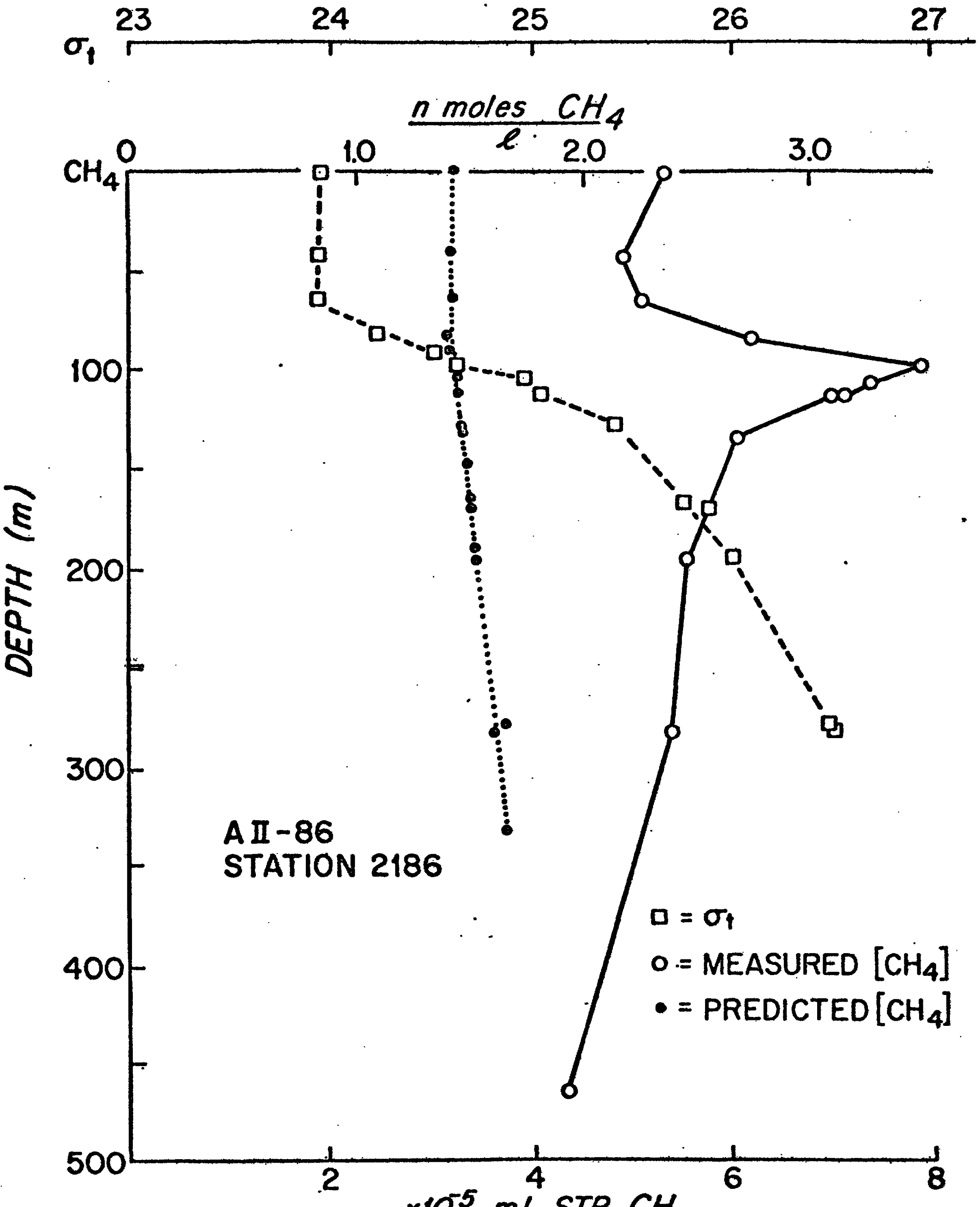

Figure I.1. Vertical profile of measured methane concentration, the methane concentration which would be predicted if the water and atmosphere were at equilibrium, and σ_t. Station AII86-2186 is located at 18°59'N 61°16'W.

anomalies of ± 10% for surface water and ± 30% for deep water might be attributable to physical processes of this sort. Argon, which has a solubility behavior very similar to that of methane, has saturation anomalies of only ± 5% (Craig and Weiss, 1968), indicating that this is a more realistic estimate for the effect of physical processes on methane concentrations. Thus the predicted anomalies are considerably smaller than the 30 to 70% surface water supersaturations and the up to 90% undersaturations observed in deep water. Processes other than those discussed by Craig and Weiss (1971) must be important for the marine geochemistry of methane.

Thus a source of methane for the surface ocean is required. Two possible sources come to mind. The first is physical transport of methane-rich coastal water into the open ocean. Sources for coastal methane include nearshore reducing sediments (Emery and Hoggan, 1958; Reeburgh, 1969; Reeburgh, 1972; Martens and Berner, 1974; Barnes and Goldberg, 1976), sewage from urban areas (Swinnerton _et al_., 1969), oil-gas seeps (Dunlap _et al_., 1960), seeps of biogenic gas (Bernard _et al_., 1976; Martens, 1976), petroleum production (Brooks _et al_., 1973) and anoxic basin waters (Atkinson and Richards, 1967; Swinnerton and Linnenbom, 1969; Hunt, 1974; Reeburgh, 1976; Chapter VII). Sediments under areas of extremely high productivity, such as off Walvis Bay, may also contribute significant amounts of methane (see Chapter III). If physical transport of methane-rich water is inadequate as an open ocean source, the only alternative is _in situ_ methane production. This is discussed in more detail in Chapters III, IV and V.

The sinks for methane in the surface ocean are loss to the atmosphere across the air-sea interface and biological oxidation of methane. Because the surface ocean has methane concentrations consistently above equilibrium, there will be a net flux into the atmosphere across the air-sea interface. Assuming an average mixed layer supersaturation of about 0.8 nmole/l and using the thin film model described by Danckwerts (1970), Liss and Slater (1974), Broecker and Peng (1974) and in Appendix I.1, the global flux of methane across the air-sea interface is about 2 x 10^{11} mole/yr. Although the flux is not significant in terms of the global budget of methane (see Table I.1), it is of importance to the distribution of methane in the ocean.

Methane oxidizing bacteria have been isolated from coastal surface seawater by Weaver (personal communication, 1974) and from marine sediments by Hutton and ZoBell (1949), so it appears likely that biological methane oxidation occurs in the mixed layer. However to date there is no quantitative information available.

C. The Deep Ocean

Below about 400 to 500 m, the ocean is markedly depleted in methane (Chapter VI; Lamontagne et al., 1973; Brooks and Sackett, 1973). Concentrations as low as 10% of the predicted atmospheric equilibrium value have been observed, and at depths greater than 1000 m, concentrations are generally less than 30% of saturation. Surface waters in areas known to be source regions for the deep water are close to equilibrium with the atmosphere (Lamontagne et al., 1973; Macdonald, 1976; Lamontange, personal communication, 1974) so the undersaturations observed at depth suggest that significant methane consumption takes place at some point after the water is removed from contact with the atmosphere.

It is possible that there is direct methane supply to the deep waters as well as an advective supply. Off Walvis Bay, it appears that slumping may be a result of sediment fluidization caused by very high gas (methane) contents within the sediment (Monroe, 1969; Summerhayes, personal communication, 1976). If this process does indeed occur in areas of rapid organic matter deposition, one might expect that large amounts of methane could be supplied to the deep water in such areas. It is difficult to determine how significant a source such a process would be. Under the high pressures and low temperatures of the sea floor, methane in high concentrations should form solid clathrates with water (van der Waals and Platteeuw, 1959; Katz, 1971; Katz, 1972). This would severely reduce the possible occurrence of fluidization. However the conditions under which methane clathrates would form in a seawater system in which many other gases are present are not well understood.

D. Anoxic Basins

Methane distributions have been measured in a variety of anoxic basins. These include the Cariaco Trench (Atkinson and Richards, 1967; Richards, 1970; Lamontagne _et al_., 1973; Reeburgh, 1976; Chapter VII), the Black Sea (Hunt, 1974; Bagirov _et al_., 1973; Chapter VII), Lake Kivu (Deuser _et al_., 1973), and Canadian Shield Lakes (Rudd and Hamilton, 1975; Rudd _et al_., 1974) among others. In general methane concentrations are low in the oxygenated zone in the upper water column. At or slightly above the sulfide/oxygen interface, methane concentrations begin to increase sharply and can attain very high levels. Over 20 mmoles methane/l were reported for Lake Kivu by Deuser _et al_. (1973). The high concentrations observed reflect both rapid methane production under anoxic conditions and the presence of strong density gradients in the water column which inhibit vertical transport.

Several workers (Rudd *et al.*, 1974; Rudd and Hamilton, 1975; Jannasch, 1975) have also found that rapid biological oxidation of methane occurs just above the sulfide/oxygen interface. At least in lakes, methane oxidation is most rapid at low oxygen concentrations and was observed in narrow lenses associated with the strong density gradient (Rudd *et al.*, 1974). The layer of oxidizing bacteria greatly reduces the amount of methane which eventually diffuses into the surface waters. Thus the importance of methane production in anoxic basins to the global budget for methane is far from well understood. The geochemistry of methane in two marine anoxic basins is discussed in detail in Chapter VII.

E. The Scope and Organization of the Research

As a part of this thesis, methane measurements have been made in the mixed layer and the deep and bottom waters of both the open and coastal ocean as well as in anoxic basins. In addition some laboratory phytoplankton culture experiments have been performed to examine biological production *in vitro*.

CHAPTER II

EXPERIMENTAL METHODS

A. Sampling

Water samples were taken from Niskin or Bodman bottles in a manner similar to that used for oxygen samples. Methane samples were drawn first, except at those stations where oxygen or tritium/helium-3 samples were being taken. In most cases, one liter standard taper ground glass stoppered bottles were used and were flushed by overflowing at least one volume from the bottom. The Black Sea samples were taken in 250 ml standard taper and 50 ml non-standard taper ground glass stoppered bottles. Care was taken to ensure that no bubbles were trapped. Before each bottle was stoppered, a small amount of mercuric chloride or sodium azide was added as a poisoning agent. The stopper was then tightly seated in the bottle. When refrigeration was available samples were kept cold until analysis. Where this was not possible samples were cooled for at least a few hours before analysis to reduce gas loss problems caused by bubble formation (air degassing). For those samples which were stored for longer than a few days, the stoppers were tightly taped with electrical tape. During cruises AII86-1A and AII86-2 in January and February of 1975 and for the Black Sea samples, Apiezon M grease was used on the stoppers. However, when the grease was used, it was hard to maintain a tight seal over an extended period of time so the practice was discontinued.

Measurements of atmospheric methane concentrations were obtained while the ship was steaming between stations. The air inlet was positioned on the top deck of the ship forward of the smoke stack and air samples were only taken while the ship was underway. Samples were collected by sucking air (using a vacuum pump in the main lab) through about 150 feet of copper tubing and then through an air sample loop (115 ml) for 10 minutes at 250 ml/min. Then the pump was shut off and the gas sample valve attached to the air loop was quickly switched, allowing carrier gas to flush the sample from the loop into a charcoal trap cooled to dry ice-acetone temperature. The remainder of the analysis was as described for water samples in section C.

B. Sample Storage

A number of the samples discussed in this thesis were stored for periods of from a few weeks to several months before analysis. In an effort to determine whether storage affected sample quality, duplicates were taken of all deep samples (below 350 m) from station AII86-2225 in the Cariaco Trench, of a number of samples taken at station AII86-2233 in the Caribbean, and of one sample from the Gulf of Maine. These samples were poisoned and refrigerated until analysis. Table II.1 compares the results obtained at sea with those obtained later in the lab. All samples with high methane concentrations lost methane. The deep samples from station AII86-2233, which had quite low methane concentrations, gained methane. Samples which were nearly at equilibrium with the atmosphere (station AII86-2233 at 198 m; station AII86-2151 at 99 m) seemed to store well. All the samples were in bottles with greased stoppers. It appears from these results that the best data for samples considerably out of equilibrium with the atmosphere are obtained if analysis is completed within a few days of sampling.

TABLE II.1

EFFECT OF STORAGE ON METHANE SAMPLES

Station	Depth (m)	(CH_4) (nmole/l)	Date analysed
AII86-2151	99	3.61	9 January, 1975
		3.78	7 April, 1975
AII86-2225	358	1700	21 February, 1975
		1230	8 April, 1975
	407	2070	21 February, 1975
		1520	8 April, 1975
	553	4370	21 February, 1975
		3110	8 April, 1975
	848	8010	21 February, 1975
		5390	8 April, 1975
	1142	8840	21 February, 1975
		6800	8 April, 1975
	1293	9080	21 February, 1975
		7340	8 April, 1975
AII86-2233	198	3.45	25 February, 1975
		3.41	7 April, 1975
	496	1.26	25 February, 1975
		1.86	7 April, 1975
	691	1.00	25 February, 1975
		1.32	7 April, 1975
	976	0.46	25 February, 1975
		1.08	7 April, 1975

A laboratory study has also been made of the effect of long term storage on poisoned and unpoisoned samples. A number of replicate samples were taken of water obtained at the ESL facility in Woods Hole and were stored in a refrigerator at 5.6°C. The stoppers were not greased. These samples were analysed at intervals over a period of about one year. Results appear in Table II.2. No systematic trend is observed in either the unpoisoned or poisoned samples. Thus it appears that, for water samples only slightly supersaturated with methane relative to solubility equilibrium with the atmosphere, storage does not alter the methane content if ungreased stoppers are used.

C. Extraction and Analysis

The method used for methane analysis is essentially that of Swinnerton et al. (1962a, b) and Swinnerton and Linnenbom (1967b). The extraction apparatus is shown in Figure II.1. Copper and stainless steel tubing and brass or stainless steel Swagelock fittings were used for most of the plumbing. For glass to metal connections, it was found that polypropylene or teflon fittings with teflon ferrules and polypropylene back ferrules greatly reduced breakage. Metal nuts and ferrules were used to attach the polypropylene fittings to the metal tubing.

Sample transfer was usually accomplished by seating the standard taper neck of the sample bottle on a standard taper inner joint on the extraction board. Positive pressure of methane-free helium was provided to the surface of the water through a heat exchanger tee attached to the inner joint. In this way, water was forced out of the bottle through a stainless steel tube extending to the bottom of the bottle and connected to a glass gas stripper.

TABLE II.2

LABORATORY STORAGE EXPERIMENT

Time since sampling (day)	P/U	(CH_4) (nmole/1)
0	U	7.89
	P	8.08
1	U	8.07
	P	8.14
7	U	8.17
	P	8.60
14	U	8.16
	P	8.19
26	U	8.04
	P	8.34
57	U	8.27
	P	8.27
134	U	8.59
	P	8.44
350	U	7.82
	P	7.47

U = unpoisoned sample
P = poisoned sample

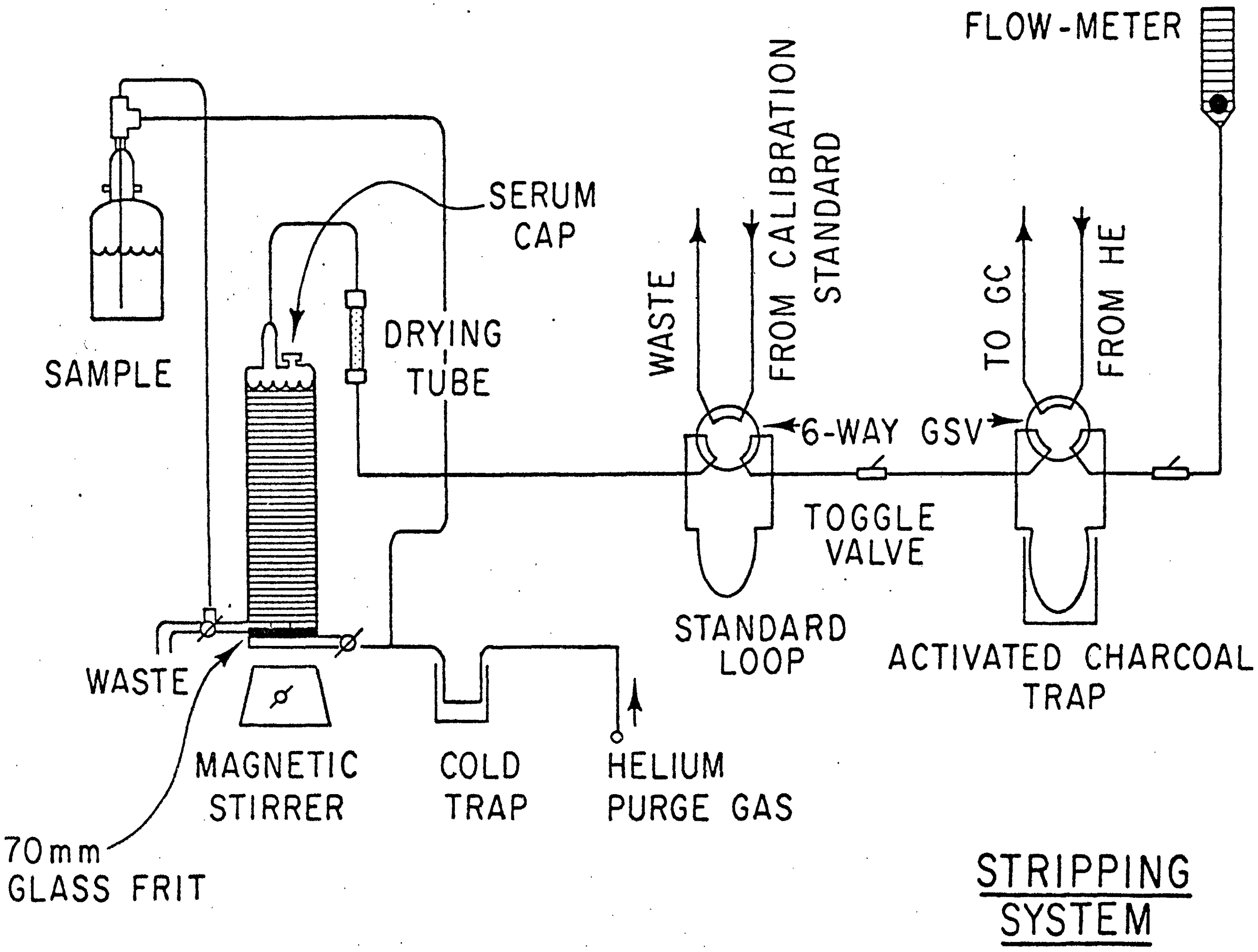

Figure II.1. Diagram of the stripping system used in methane analysis.

The volume of the stripper was about 1.7 liters. To add a typical sample of about 500 ml, an appropriate volume of water was forced from the stripper by methane-free helium. Then the transfer tubing was flushed and a new sample was added. This procedure maintained a constant head space free of methane above the water being stripped.

An alternative method of sample transfer was by syringe injection through the serum cap located at the top of the stripper. This method was used for samples taken in bottles without a standard taper joint, and in those cases where very high methane concentrations were anticipated (the Black Sea, the Cariaco Trench and off Walvis Bay). A gas-tight Hamilton syringe with a Luer-lock tip and provided with a needle with a Kel-F (teflon) hub was found to work best. A 26 gauge needle was used for the Cariaco Trench samples. The syringe was placed in the sample in such a way that the entire needle including the Luer-lock tip was submerged. The syringe was rinsed and a sample was taken. In the sampling of the Cariaco Trench samples, it was noted that bubbles occasionally appeared in the syringe. These could have been the result of degassing of the water, since air-leakage was unlikely with the syringe submerged. Therefore the bubbles were injected into the stripper along with the water sample. In determining the volume of water injected, a correction for the volume of the needle was added since the gas tight syringes are calibrated to leave water in the needle on injection. An 18 gauge needle was used for the Black Sea and Walvis Bay samples and bubble formation was not a problem.

After the sample was transferred to the stripper under helium or by syringe, helium (purified by passage through a molecular sieve 5A trap at dry ice-acetone temperature (-86°C)) was bubbled through the water. The gas passed first through a glass frit, producing finely dispersed bubbles. A magnetic stirring bar was placed on the frit to help increase dispersion. For the Gulf of Maine samples, stirring was not used due to the softness of the frit in the stripper. Instead samples were stripped twice and the peak areas summed.

Stripping time was 20 minutes for all analyses, at helium flow rates of from 55 to 65 ml/min. These flows were found to give good efficiency in a reasonable stripping time without the use of large amounts of gas. Using a 20 minute stripping time and a 55-65 ml/min flow rate, peak areas were reproducible to within ± 2 to 3%. The effect of variable stripping times and flow rates are shown in Figures II.2 and II.3.

The helium stripping gas containing dissolved gases from the sample first passed through a polycarbonate drying tube containing magnesium perchlorate. This removed all water vapor from the gas which then passed through a 3/16" O. D. stainless steel trap containing 60/70 mesh activated charcoal. This trap was maintained at -86°C by a dry ice-acetone bath. Methane is quantitatively adsorbed on the charcoal at these temperatures. Gases such as N_2 or O_2 are not adsorbed and are stripped from the trap by the helium carrier. Other low molecular weight hydrocarbons may be adsorbed, but were present in such small quantities and had such long retention times on the chromatographic column that they did not interfere with the methane analysis (see below).

When stripping was complete two toggle valves were closed isolating the trap from the rest of the system. The trap was heated for one minute using a hand-held hair dryer to desorb the methane from the

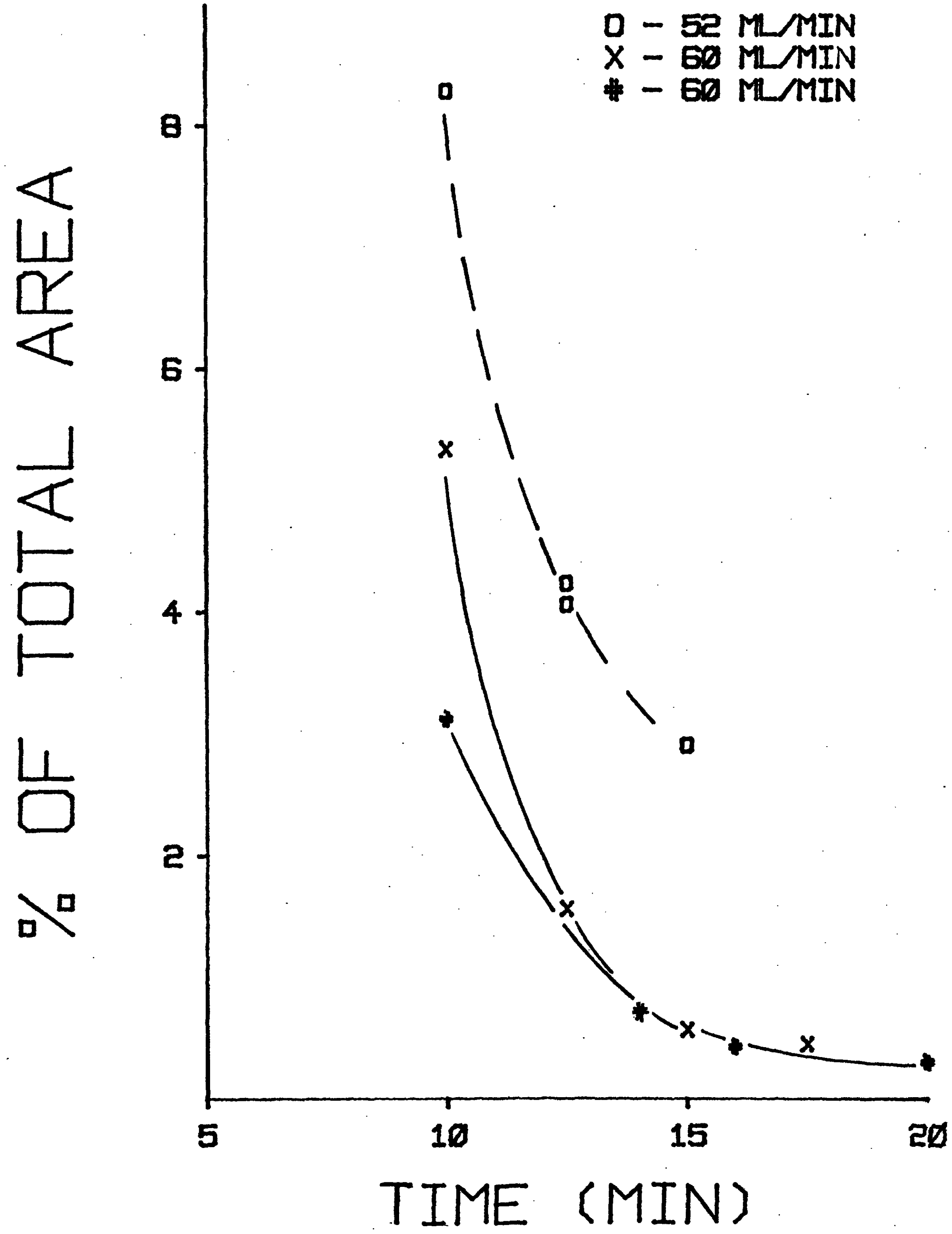

Figure II.2. Efficiency of methane extraction. Contribution of second strip to total area (first + second strip) in percent plotted as a function of stripping time. At 60-65 ml/min, extraction is complete after 15 minutes.

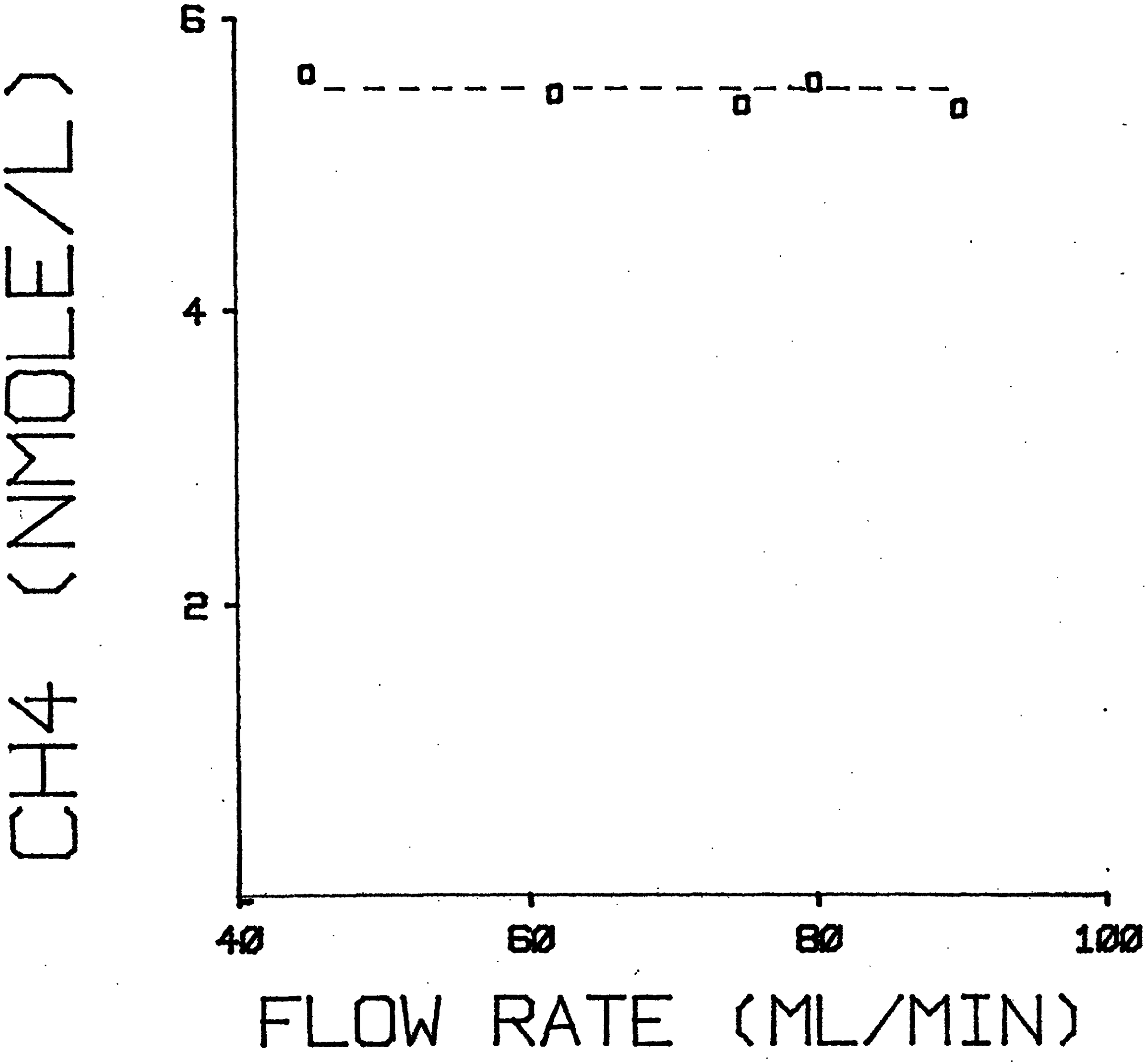

Figure II.3. Methane concentrations obtained from replicate water samples after stripping for 20 minutes at various flow rates. Stripping at flow rates between 40 and 90 ml/min gives constant results.

charcoal. The methane trap was attached to two ports of a 6-way gas sample valve, and injection of a sample into the chromatograph was accomplished by switching the valve so that helium carrier swept through the trap.

From the trap the sample was carried into a Varian 1400 gas chromatograph equipped with a hydrogen flame ionization detector. (This instrument was used for samples collected on AII86-1A and AII86-2.) The chromatographic column was a 4 ft. 1/4" O.D. stainless steel column containing 60/70 mesh chromatographic grade silica gel. The column was conditioned by heating to 150°C for several hours. A Speedomax G Leeds and Northrup recorder (1mV full scale) was used with a chart speed of two inches per minute. The high chart speed produced large peak areas aiding planimetry which was used for quantifying results. The column temperature during analysis was 55°C, the detector temperature was 130°C and carrier flow was about 60 ml/min.

System linearity was tested by injecting several different volumes of a single water sample into the stripper. Figure II.4 shows that peak area is a linear function of the amount of methane injected. From these data it can be concluded that the entire system, including the detector, gives a linear response with injected methane content up to at least 8.5 nmole methane. With one exception from the Cariaco Trench, sample volumes were always adjusted to stay within this range.

For the samples collected on cruises other than AII86, a Hewlett-Packard 5710A gas chromatograph with dual flame ionization detectors (set in the differential mode) was used. The column temperature was 50°C and detector temperature was 150°C. Carrier flow was about 60 ml/min

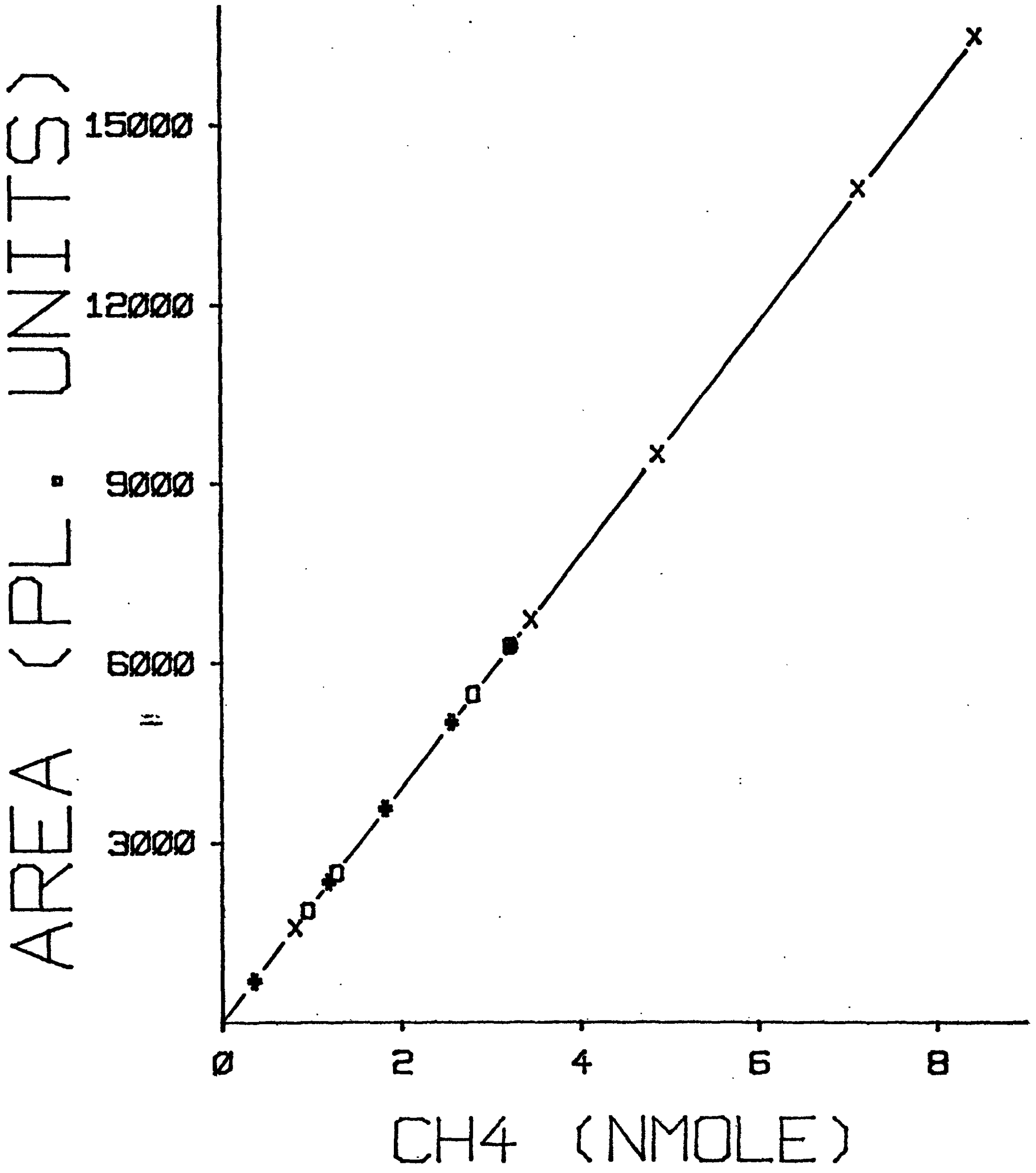

Figure II.4. Linearity plot for the Varian flame ionization detector. Variable volumes of replicate water samples were analysed to obtain variable amounts of methane. The various symbols represent three different water samples, each with different methane concentrations.

as with the Varian. Two 4 ft. 1/4" O.D. columns containing 60/70 mesh silica gel were used. System linearity was tested up to 7.5 nmole methane as with the Varian and data are presented in Figure II.5. With a few exceptions on the Walvis Bay cruise, sample size was always adjusted to give methane contents of less than 7.5 nmole.

The Varian was operated at sensitivities ranging from 2 x 10^{-12} amps full scale (1mV recorder) to about 64 x 10^{-12} amps full scale. The Hewlett-Packard was operated at sensitivities between 10 x 10^{-12} amps full scale to 160 x 10^{-12} amps full scale.

D. Standardizations

Standards were run after every one to two samples. The standard gas used was a Matheson primary standard calibration gas, 10 ppm ± 0.1 ppm methane in nitrogen. To confirm that the gas did contain the methane concentration reported, data were obtained for the concentration of methane in distilled water which had been equilibrated with the standard at a known temperature. The data show a scatter of about ± 5%, and it appears possible that the samples may not have been completely at equilibrium with the gas. The average methane concentration in the three samples was 15.8 nmole/l compared with 14.5 nmole/l which is the predicted concentration (Yamamoto _et_ _al_., 1976). If the data are accurate and the water was actually at equilibrium with the gas, the true methane concentration in the standard would be 9.1 ppmv. However the scatter in the solubility data is such that this discrepancy is within the error of the measurement. All further discussion will be based on the reasonable assumption that the standard concentration was 10 ppmv.

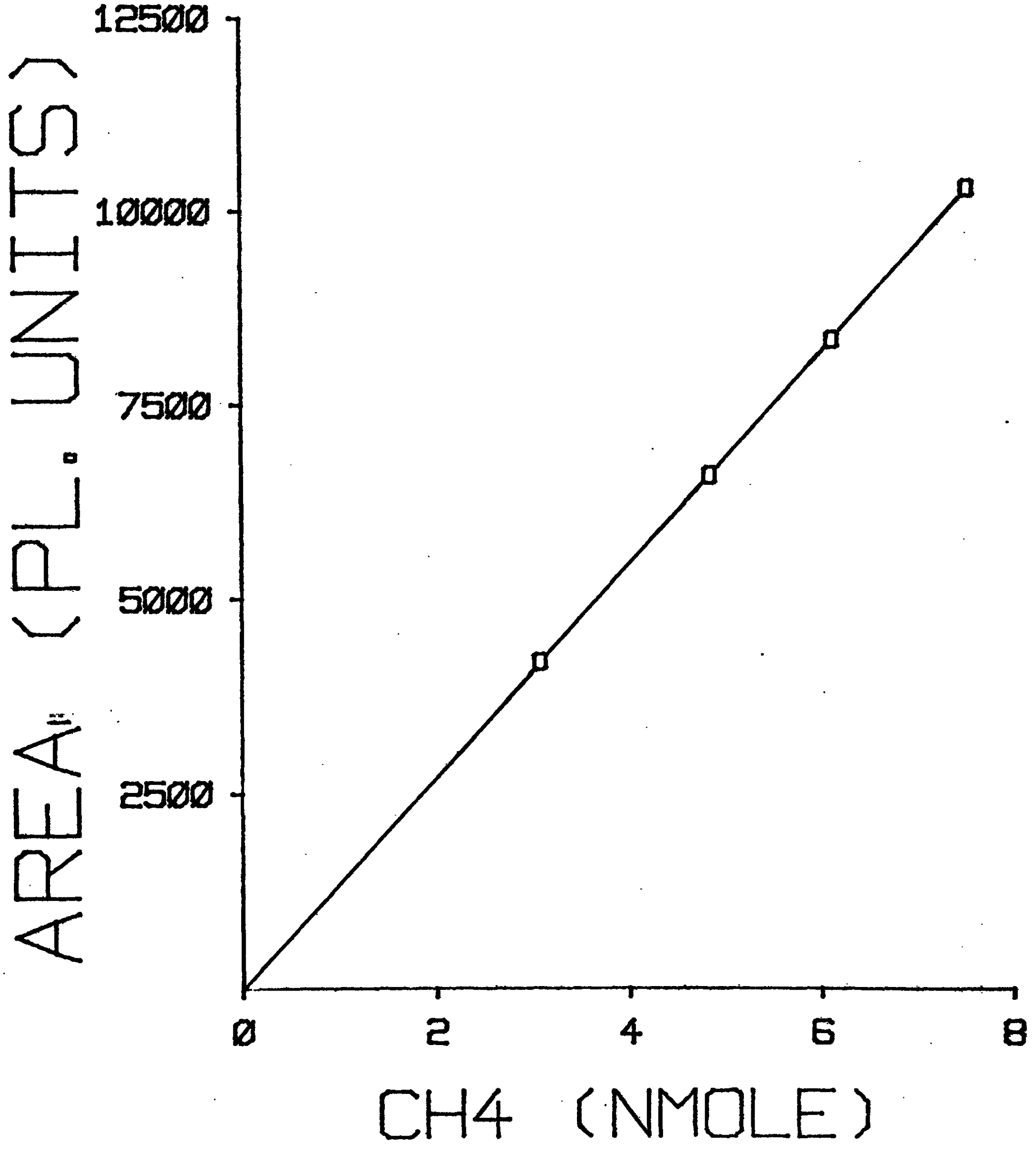

Figure II.5. Linearity plot for the Hewlett-Packard flame ionization detector. Variable volumes of replicate water samples were analysed to obtain variable amounts of methane. The detector is linear to at least 8 nmole methane.

The standard gas was injected into the system via a Varian 6-way gas sample valve with an attached 1.458 ml loop on it. Dead volume of the valve and fittings was 0.117 ml so the total volume of the injected standard was 1.575 ml. The standard loop volume was calibrated by weighing the loop empty and filled with mercury. The dead volume of the valve was determined by use of three calibrated loops. Standard gas was injected through each loop and the corresponding peak area was determined. A plot of peak area vs loop volume (Figure II.6) has a negative intercept on the loop volume axis corresponding to the amount of gas contributed by the valve dead volume.

An attempt was made to use syringe injection of 10 ppm and 100 ppm methane in helium Analabs standard calibration gases as well as injection by gas sample valve. The methane concentrations in some of the Analabs standards were considerably different from the quoted concentrations. For example, one 100 ppm standard was found to contain only 88 ppm relative to the 10 ppm Matheson standard. By calibrating the standards relative to the Matheson standard, it was possible to use these mixtures when the primary standard was not available.

Precision of analysis, based on replicate analyses of standards was ± 4% (1σ) for the Gulf of Maine, ± 2.5% for the stations of AII86-2, ±3% for the Walvis Bay cruise (AII93) and ± 2% for the samples analysed in the laboratory. Relative average deviations of samples based on duplicate analyses gave similar or better reproducibilities (see Table II.3). For deep water samples, where methane concentrations were very low, the precision of analysis was about ± 10%.

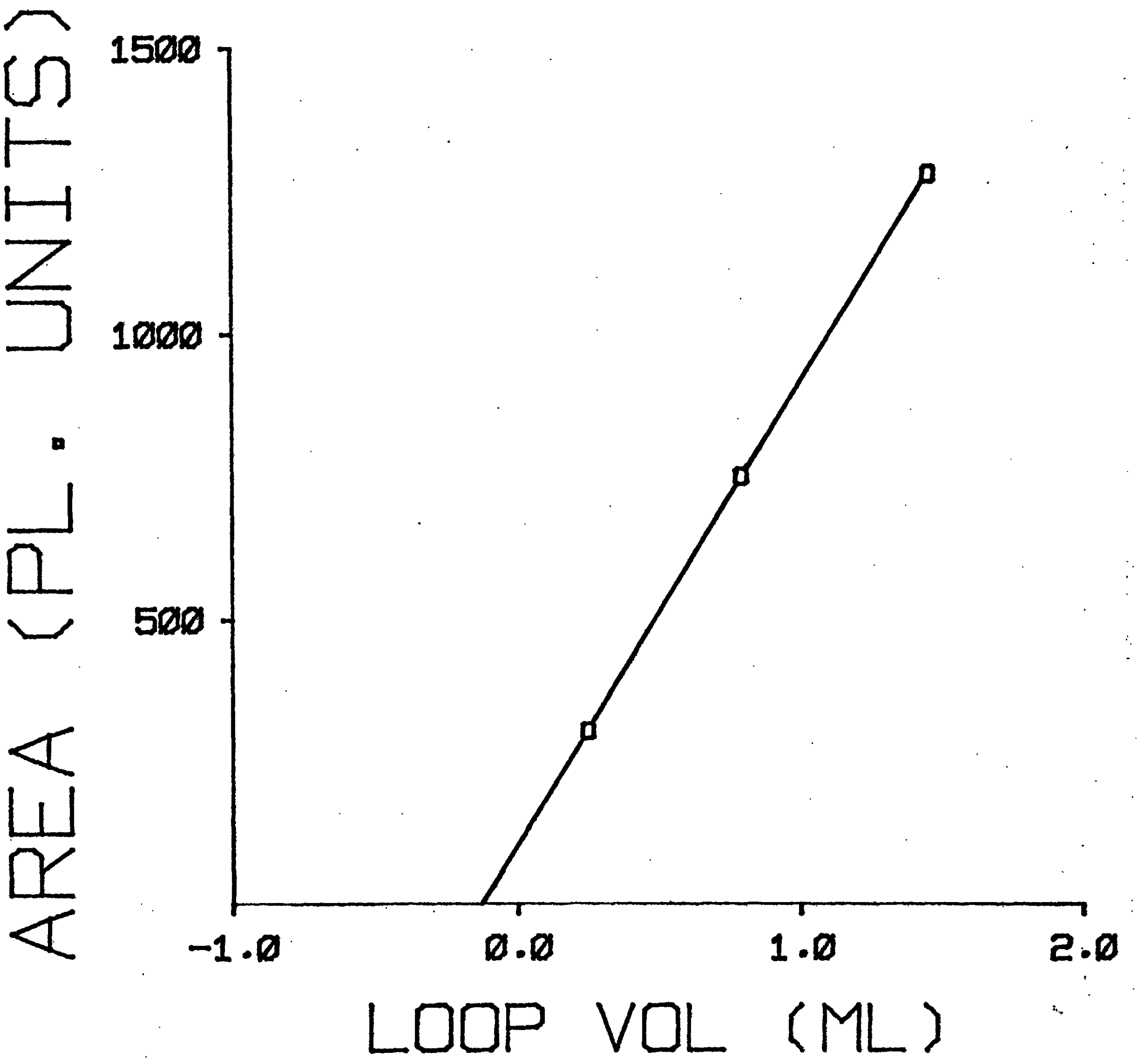

Figure II.6. Determination of valve dead volume. Peak areas obtained for injection of standard gas through gas loops of three calibrated volumes are plotted. The intercept on the loop volume axis represents the loop dead volume (volume of fittings and valve dead volume).

TABLE II.3

SHIPBOARD DUPLICATES

Station	Depth (m)	(CH_4) (nmole/l)	Avg. (nmole/l)	% difference from mean
AII86-2122	20	3.82 3.71	3.76	1.5%
	232	5.21 5.07	5.14	1.4%
AII86-2138	227	5.35 5.10	5.22	2.3%
AII86-2151	195	5.53 5.33	5.43	1.8%
AII86-2186	113	3.12 3.18	3.15	0.9%
AII86-2197	117	2.38 2.26	2.32	2.6%
AII86-2202	44	2.41 2.37	2.39	0.8%
AII86-2204	3000	0.44 0.54	0.49	10.2%
AII86-2220	100	4.40 4.52	4.46	1.3%
AII93-2242	0	2.86 3.02	2.94	2.7%
AII93-2244	120	2.54 2.56	2.55	0.4%
	168	2.50 2.36	2.43	2.8%
AII93-2246	53	3.83 3.57	3.70	3.5%

TABLE II.3

(continued)

Station	Depth (m)	(CH_4) (nmole/l)	Avg. (nmole/l)	% difference from mean
Oceanus06-743	1631	0.77 0.92	0.84	8.3%
	2628	1.15 1.10	1.12	2.7%

E. Retention Times

The retention time for methane in samples was about 1.6 minutes on both systems. This retention time was also obtained when gas standards were injected into the stripper by syringe and were subsequently treated like samples. However, when the gas standard calibration loop was used, different retention times were obtained. If the standard was merely injected via the charcoal trap without intermediate trapping, the methane retention time was about 2 minutes. During direct injection, a peak was also obtained for nitrogen which had a retention time of about 1 minute. (Although the flame ionization detector is not conventionally thought to be sensitive to nitrogen, the injection of 1.5 ml into the system as a part of the calibration standard does produce a small response.). If the standard gas is injected and trapped in the charcoal trap by using a dry ice-acetone bath, the resulting methane retention time is 1.8 minutes. Because the carrier flow rate varied slightly from day to day, retention times also varied somewhat. However, as only one peak was observed in seawater samples and as this peak was located at the position of the peak in seawater spiked with methane, variable retention time was not considered to be a problem.

The peak areas for the injection of a constant amount of methane by direct injection with and without trapping in the charcoal trap, and by injection via the stripper are the same. In general the method of direct injection without trapping was used as it was the fastest.

Retention times for ethane (eight minutes) and ethylene (fifteen minutes) were also determined, confirming that these compounds do not interfere with the methane analysis.

F. Other Sources of Error

The volume of water stripped was determined by measuring the volume of water drained out of the stripper with a graduated cylinder. The water was drained to a mark on the stripper each time and the stripper was also filled to a constant depth. The error contributed to the analysis was less than ± 10 ml out of 500 (± 2%). For samples of volumes significantly less than 500 ml, the relative error may have been higher.

The absolute limit of detection for the methane analysis was about 0.01 nmole/l. However after multiple strippings of one sample, a small methane peak is still present. This may be due to bleed of methane off the activated charcoal, since when new charcoal is added it takes numerous injections before reproducible peaks are attained. This suggests that the charcoal may have to be saturated with methane before replicable results can be obtained and some of this methane may be desorbed by multiple heating and refreezing cycles. The residual peak therefore is not a true blank for cases where all samples have approximately the same methane concentration. This conclusion is confirmed by the observation that trapped standards give the same peak areas as standards injected without trapping. Running a high level sample after several low level samples could give a slightly low result. Similarly running a low level sample after a high level one could give high results. This would be a serious problem only for the deep water samples where concentrations are only 10% or so of the surface values. However inspection of the methane concentrations in deep samples, many of which were analysed after shallow samples, suggests that any bleed problems are probably small. No blank corrections have been applied to any of the data presented in this thesis.

Finally it was noted that if the system was left for several hours without analyses being run, excessively high methane concentrations were observed. It was felt that this probably resulted from small amounts of air contamination. Before running the first sample in a series, the system was sparged for 45-50 minutes and, after long periods of disuse, a stripping blank was run to ensure that all air contamination had been eliminated. Repeated blanks indicated that, over the period of an analysis, air contamination was negligible.

CHAPTER III

METHANE IN COASTAL ENVIRONMENTS

As discussed in Chapter I, the presence of a persistent methane excess in the surface waters of the open ocean implies that a large and relatively constant methane source must exist. It is well known that methane is produced abundantly in anoxic paddy soils, swamps, salt marshes, and other highly productive environments (Barker, 1956 and references therein). One might expect, therefore, that methane production in the anoxic sediments associated with productive coastal regions, and subsequent mixing of methane-rich coastal water with low methane offshore waters could be a significant methane source for the open ocean. An alternative source might be biological methane production within the oxygenated open ocean water column. This is a report of the investigation of the source of methane for coastal waters, as these are the regions in which the effects of shallow water anoxic sediments should be most clearly seen.

A. Walvis Bay

Upwelling areas, such as the one near Walvis Bay, Namibia (formerly South West Africa) are known to be regions of extremely high biological productivity. In Walvis Bay, the high surface productivity is accompanied by rapid accumulation of organic matter in the sediments (Boon et al., 1975; Bremner, 1974) which thus become anoxic. The occurrence of both reducing sediments and high primary productivity near Walvis Bay suggested that a study of this area might permit the determination of the relative importance of methane input from coastal sediments and of in situ methane production in controlling the methane distribution in the water column of a productive coastal area.

The data which will be discussed here were collected on cruise 93 of the R/V ATLANTIS II to the Walvis Bay region during late December, 1975 and early January, 1976 (Scranton and Farrington, 1977). Station locations are shown in Figure III.1.

1. Methods

Temperature, salinity, oxygen, phosphate and methane measurements were made at all stations discussed. These data are presented in Appendix III.1. Temperatures were obtained from reversing thermometers and from XBTs made at the start of each station. At station 2245, the XBT data were used without correction as all thermometer data were bad. At five other stations (2241, 2242, 2247, 2248 and 2250), the temperatures recorded by the XBTs and by thermometers differed by up to 0.8°C. It was surmised that observed differences were due to ship drift in areas of strong horizontal temperature gradients and that the reversing thermometer measurements, taken at the time the water samples were being collected, were more appropriate for comparison with nutrient and methane measurements. XBTs were calibrated by shifting the traces to agree with the thermometer values. Salinity was determined by conductive salinometer in Woods Hole about six weeks after sample collection.

Oxygen concentrations were determined by a modification of the Winkler method (Carpenter, 1965). Phosphate concentrations were determined by the molybdenum-blue method of Murphy and Riley (1962). Oxygen,

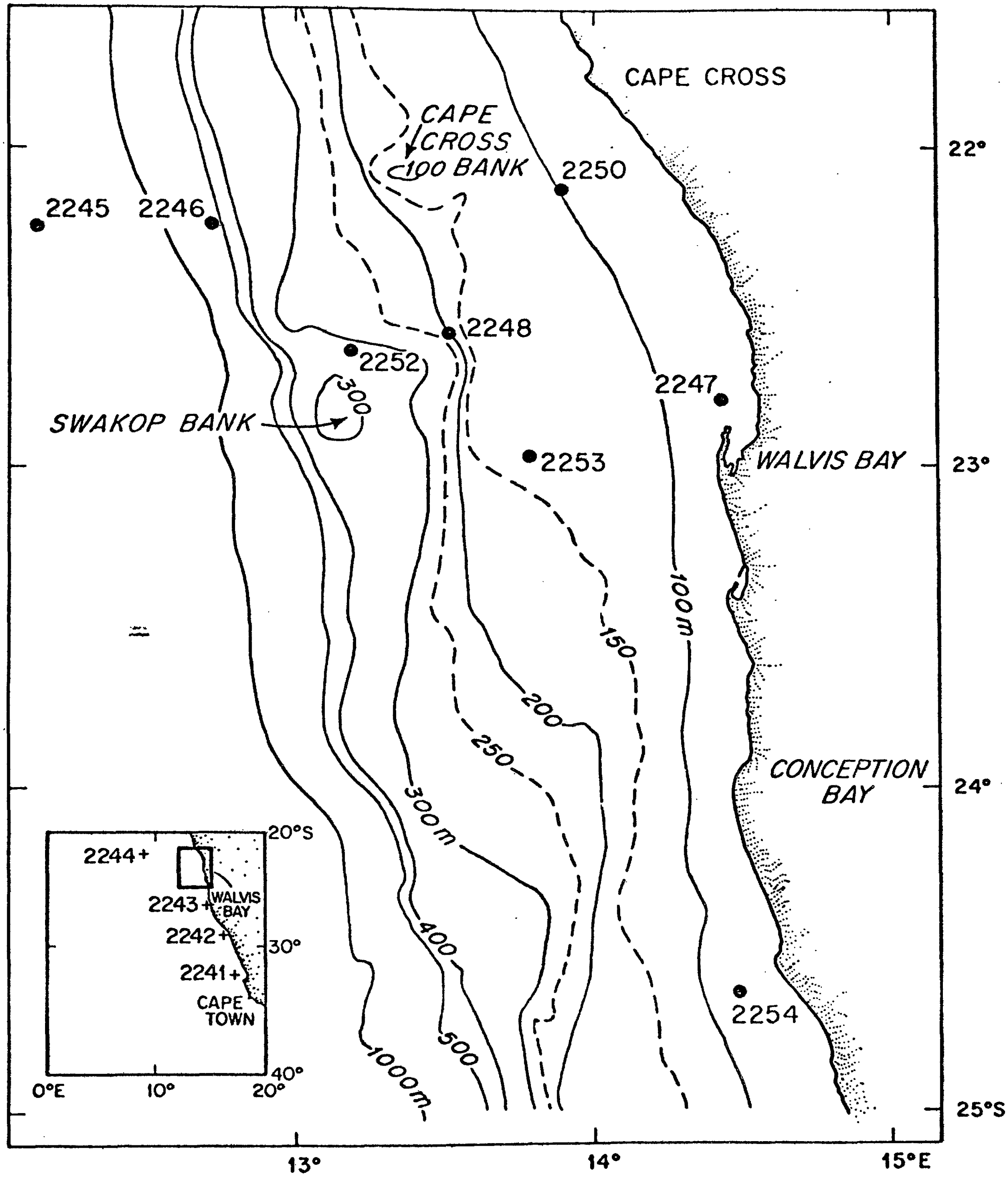

Figure III.1. Station locations for AII93.

phosphate and methane were measured within 24 hours of collection on unfiltered samples.

Methane measurements were made by a modification of the technique developed by Swinnerton et al. (1962a, b) and Swinnerton and Linnenbom (1967b) as described by Scranton and Brewer (1977) and in Chapter II. Measurements of atmospheric methane concentrations were obtained while the ship was steaming between stations also as discussed in Chapter II.

2. Discussion

The first three stations occupied on this cruise, 2241, 2242 and 2243, were located on the continental shelf between Cape Town and Walvis Bay off the Olifants River, the Orange River and Luderitz respectively (see Figure III.1).

Off the Olifants River at station 2241, the water column was strongly stratified (see Figure III.2). At about 30 m, the temperature dropped sharply from a mixed layer value of about 17°C to a 40 m temperature of 15°C and a bottom temperature of 8.3°C. Phosphate concentrations were high in the mixed layer (1.45 to 1.58 µmoles/l) suggesting that nutrient-rich upwelling water had only recently been isolated at the surface. Below the surface waters, phosphate concentrations increased to 3.05 µmole/l at 150 m. Mixed layer oxygen concentrations were about 5.6 ml/l and below the temperature break decreased to 4.0 ml/l. Surface methane concentrations were slightly above saturation (1.17 times that predicted from equilibrium with the atmosphere) and a methane maximum was observed within the mixed layer. At depth, methane concentrations decreased to about 3.5 nmoles/l (1.1 times equilibrium).

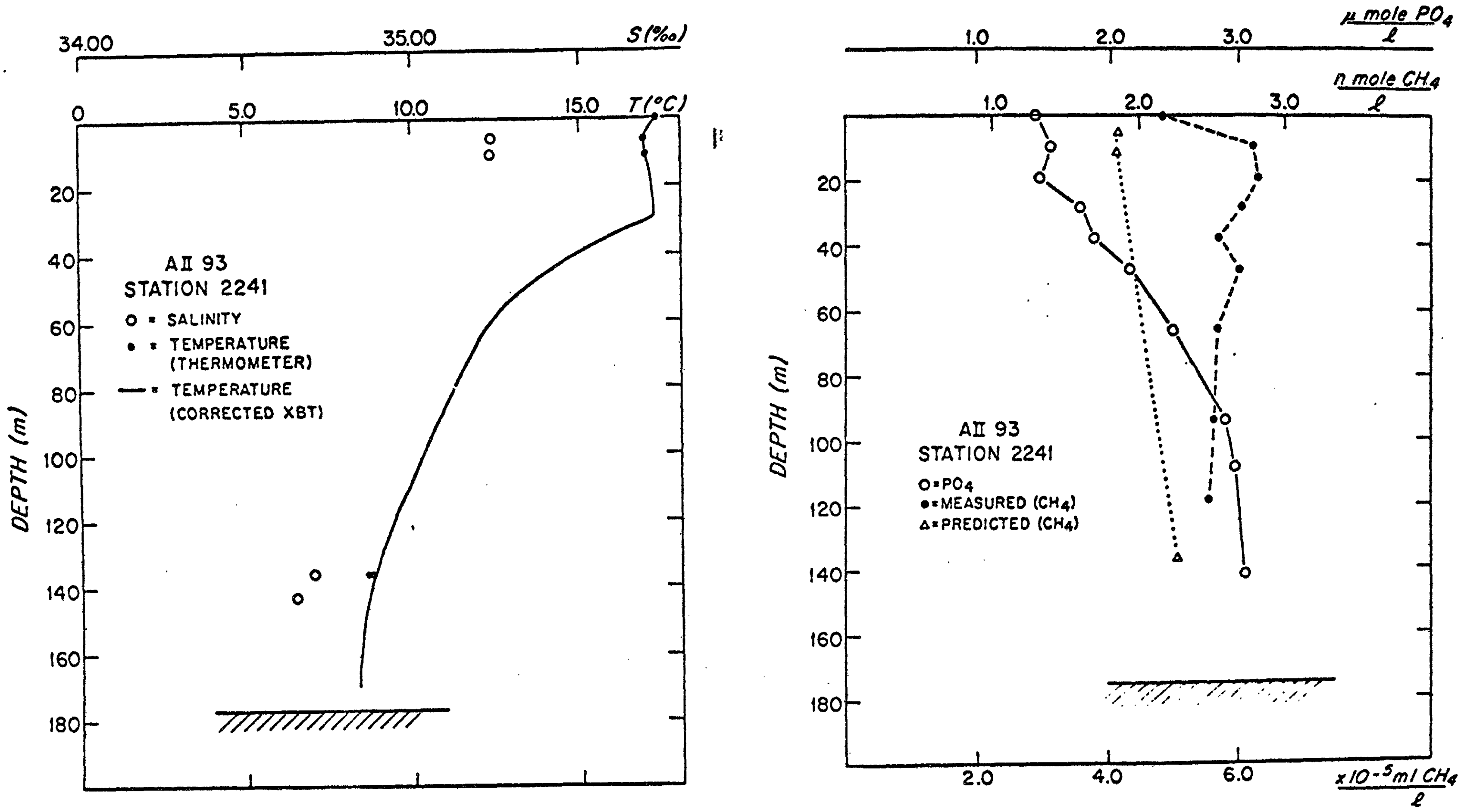

Figure III.2. Vertical profiles of temperature, salinity, methane and phosphate for station AII93-2241. Predicted methane concentrations are based on solubility data and an atmospheric methane concentration of 1.44 ppmv.

Near the Orange River, at station 2242 (see Figure III.3), the surface mixed layer extended to about 20 m, below which temperatures again decreased sharply. Phosphate concentrations in the surface were low, indicating biological removal. The presence of oxygen concentrations of up to 6.2 ml/l also suggested that photosynthetic activity was intense. Below the mixed layer oxygen concentrations decreased to 3.1 ml/l at the bottom and phosphate increased to 2.19 μmole/l. Surface methane concentrations were high (2.69 to 3.02 nmole/l or 1.4 to 1.5 times saturation), decreased to 2.41 nmole/l at middepths, and then increased to 3.78 nmole/l in the bottom waters.

Off Luderitz at station 2243 (Figure III.4) we encountered the best example of upwelling seen on the cruise; however, even here the waters were not completely isothermal. Above 50 m the temperature was uniformly 11.2°C while below 50 m it averaged 10.4°C. Above the temperature break, phosphate concentrations were high (about 1.4 μmole/l) and below the break increased to 2.2 μmole/l. Similarly, oxygen concentrations were quite constant at about 5.1 ml/l in the surface, but decreased sharply below the temperature break to about 1.6 ml/l. Methane concentrations were high in the surface water (2.90 to 3.13 nmole/l) and increased to 6.58 nmole/l at the bottom.

From these preliminary stations the methane distribution in the coastal waters of South Africa could be described as follows: Surface methane concentrations tended to be about 1.2 to 1.5 times that predicted from equilibrium with the atmosphere. Intermediate depths had somewhat lower methane concentrations than surface and bottom waters, but were

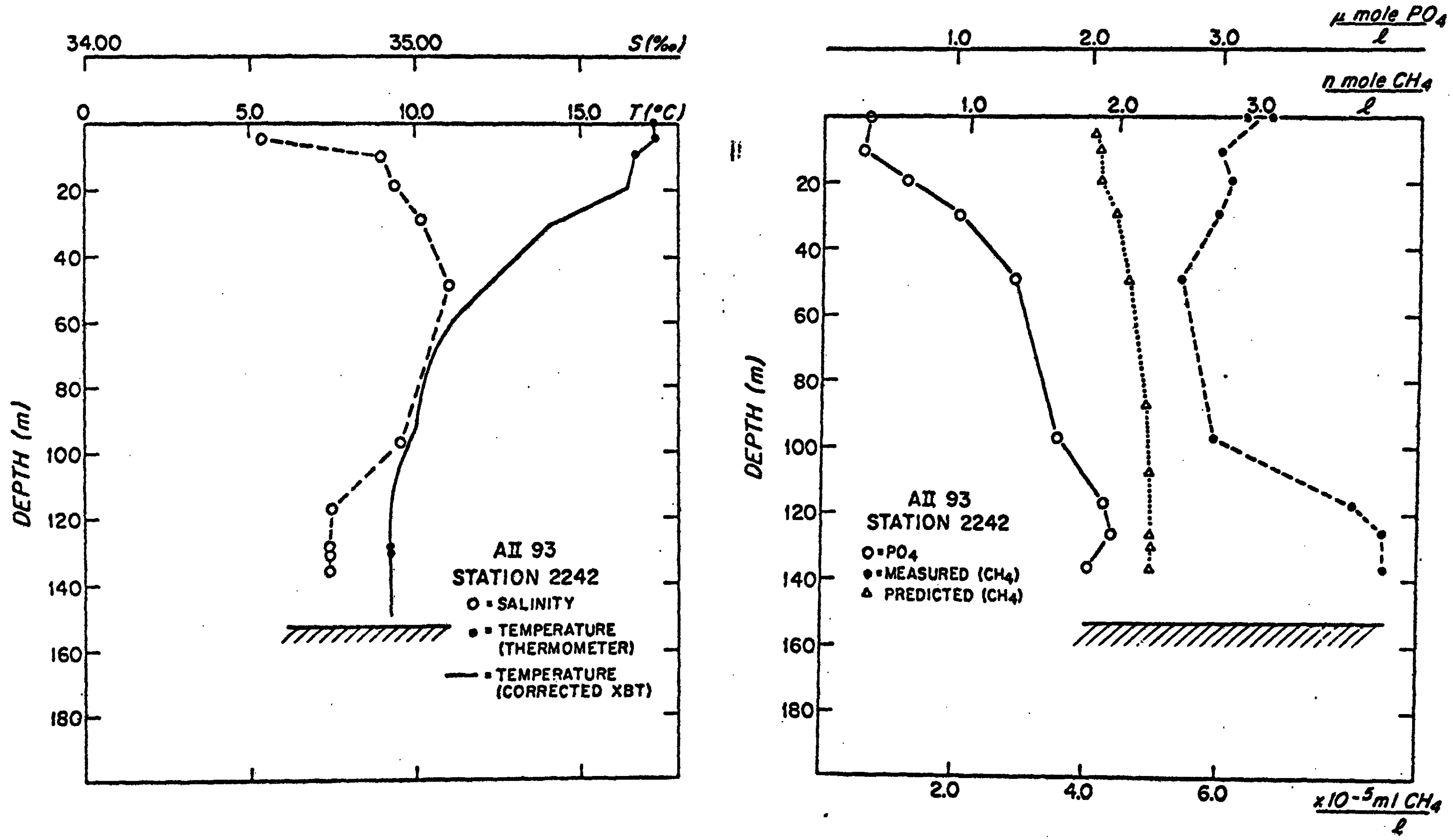

Figure III.3. Vertical profiles of temperature, salinity, methane and phosphate for station AII93-2242. Predicted methane concentrations are based on solubility data and an atmospheric methane concentration of 1.44 ppmv.

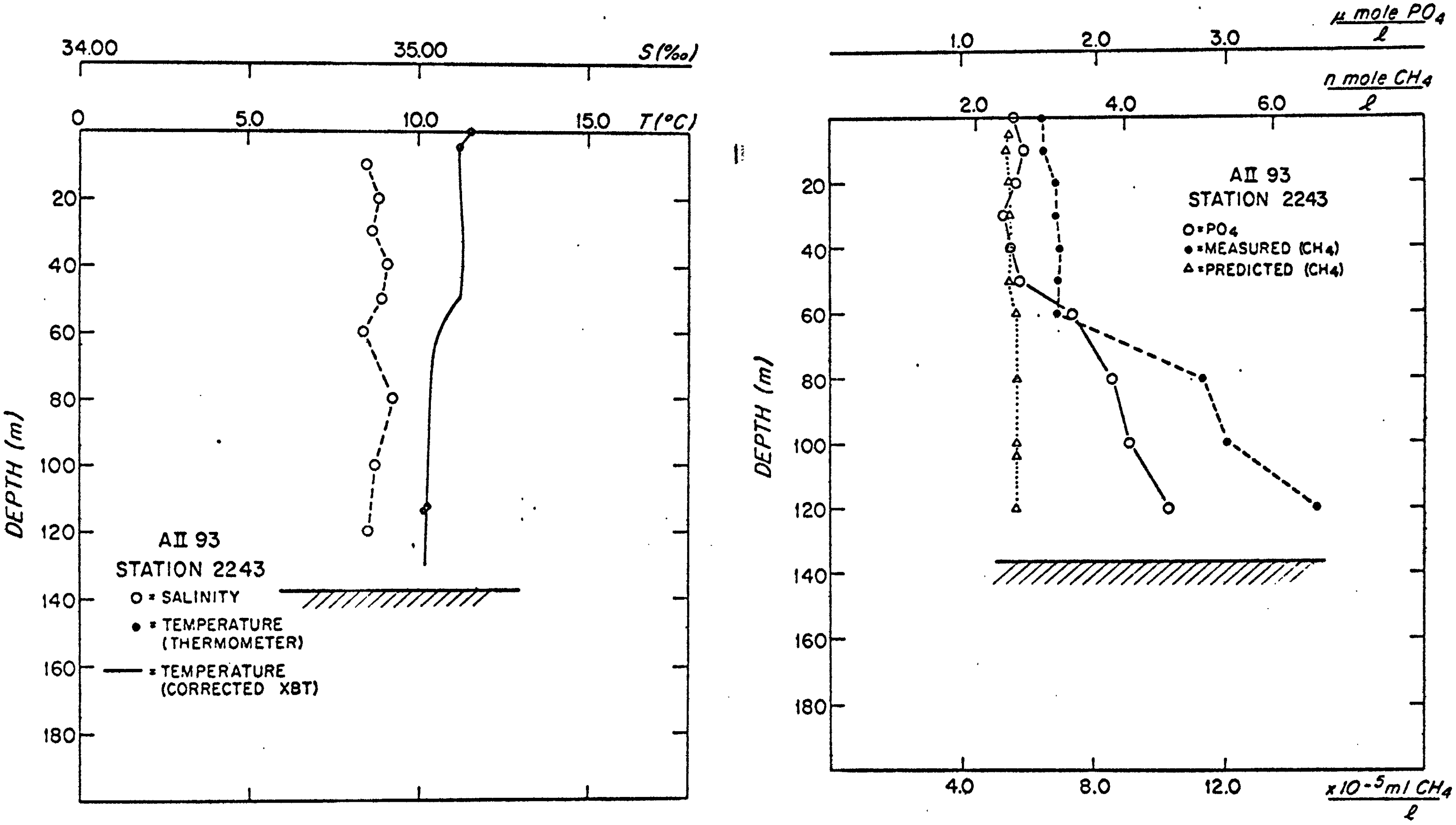

Figure III.4. Vertical profiles of temperature, salinity, methane and phosphate for station AII93-2243. Predicted methane concentrations are based on solubility data and an atmospheric methane concentration of 1.44 ppmv.

still enriched in methane with respect to solubility equilibrium. Bottom waters, especially in areas where surface productivity was high (Orange River and Luderitz), tended to have quite high methane concentrations suggesting that a sediment source might be important. Although these data give a qualitative picture of the methane distribution, they are not adequate to permit a quantitative assessment of the relative importance of physical transport and in situ methane supply. In Walvis Bay, the station density is sufficient to attempt such an exercise.

a. Circulation in the Walvis Bay region

The Walvis Bay region has been studied by a number of workers (Stander, 1964; Visser, 1969; Calvert and Price, 1971; Hobson, 1971). Based on these studies and others, it is known that upwelling is vigorous near Walvis Bay in the late winter and early spring but by mid-summer (January and February) is largely absent. The occurrence of upwelling is usually identified by the presence, at the surface and near the coast, of cool water with temperatures less than 15°C and with weak vertical temperature gradients, although not all upwelled water reaches the sea surface. The salinity of the upwelled water tends to be low, usually less than 35.00‰.

During December, 1975-January, 1976 it appeared that upwelling was either very weak or absent. The sloping isotherms which appear in the temperature section (Figure III.5) suggest that some residual upwelling may have been taking place. However, this upwelling could not have been vigorous as sharp vertical temperature gradients were found at 10-20 m in all stations occupied in this area. Indeed, some of the variability in

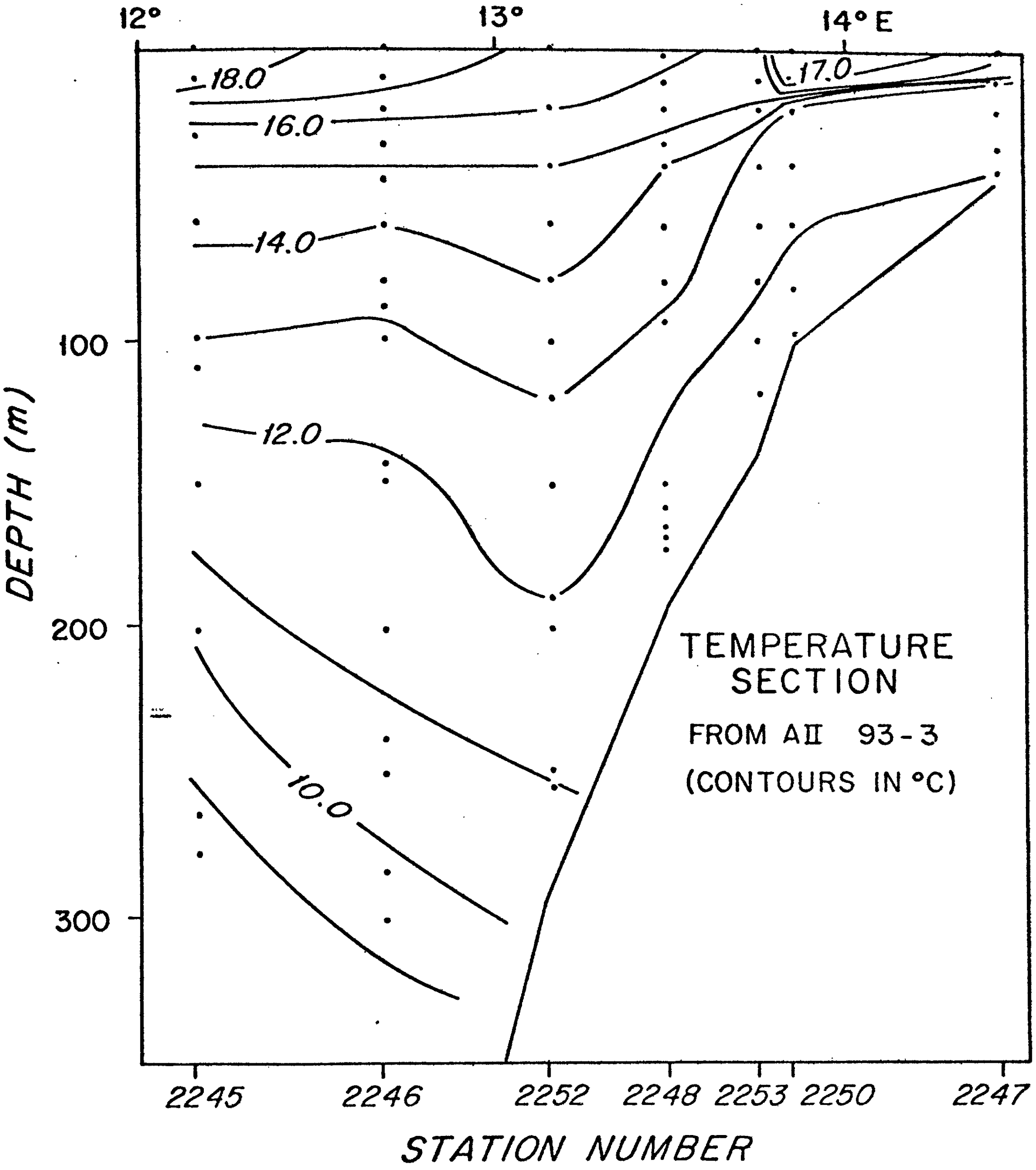

Figure III.5. Temperature section across the slope and shelf near Walvis Bay. Note the variations in the depths of the isotherms indicating the presence of complicated currents.

the depth of the isotherms might be due to the presence of eddies or meanders in the Benguela Current rather than to upwelling.

The salinity distribution (Figure III.6) also supports the idea that upwelling was weak or absent. The presence of a pool of low salinity water at the surface at stations 2246, 2252 and 2248 suggests either that remnant upwelled water was present but had been isolated from its source or that low salinity water was being advected into the area. These interpretations agree with those of Stander (1964) who has noted that moderate upwelling may occur in December, but that as summer progresses, greater vertical stability is achieved in surface water and upwelling is greatly reduced or ceases.

Oxygen concentrations on the shelf (Figure III.7) ranged from very low values at the bottom (0.0 ml/1 at station 2247) to very high values (>6.0 ml/1) in the surface. Between stations 2245 and 2246 the oxygen isolines deepened abruptly, and offshore the oxygen minimum was at about 400 to 500 m. Phosphate concentrations (Figure III.8) below the thermocline were very high, compared to offshore values at comparable depths. As was the case for oxygen, a sharp depth change in phosphate isolines was seen between stations 2245 and 2246.

A very noticeable feature in the oxygen and phosphate sections was the sharp concentration gradient observed at shallow depths between stations 2245 and 2246. Stander (1964) has found that a strong correlation exists between the presence of well-aerated (high oxygen) water and the presence of the Benguela Current and conversely, between poorly aerated water and a southward setting current. However, the low-oxygen water is

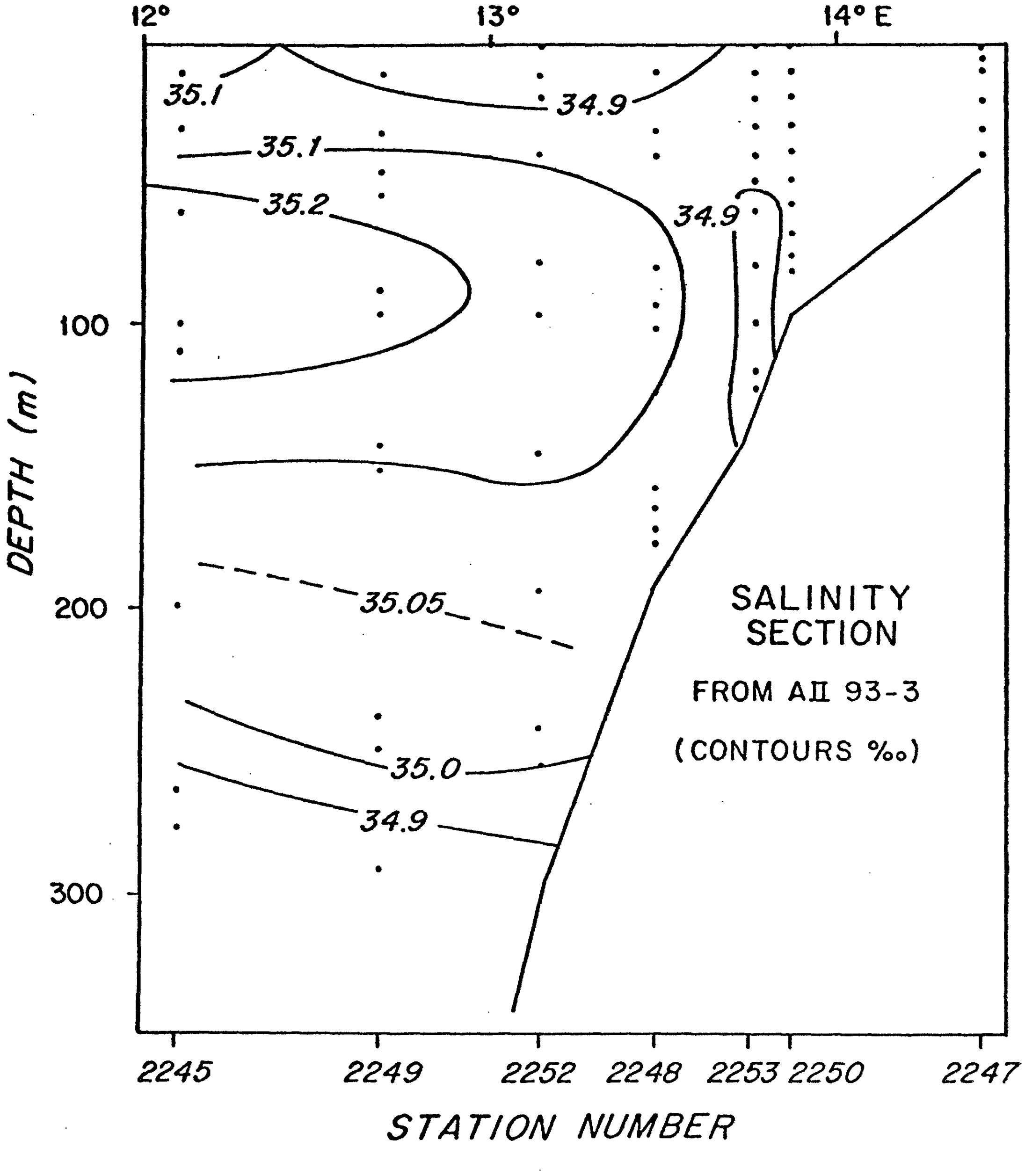

Figure III.6. Salinity section near Walvis Bay. The pool of low salinity water at the surface at stations AII93-2246, 2248 and 2252 indicates the possible presence of remnant upwelled water.

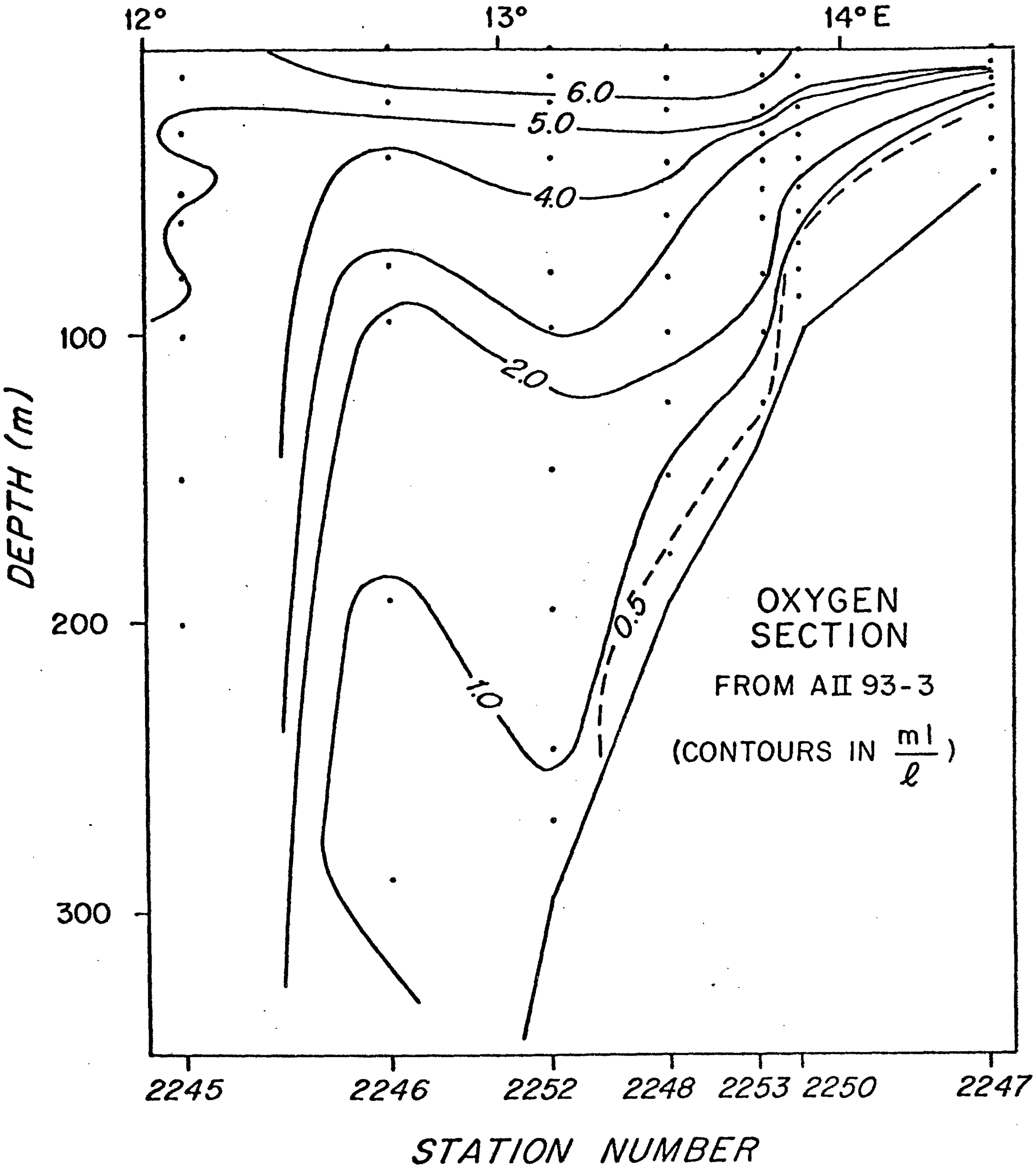

Figure III.7. Oxygen section near Walvis Bay. Note the formation of the oxygen minimum on the shelf.

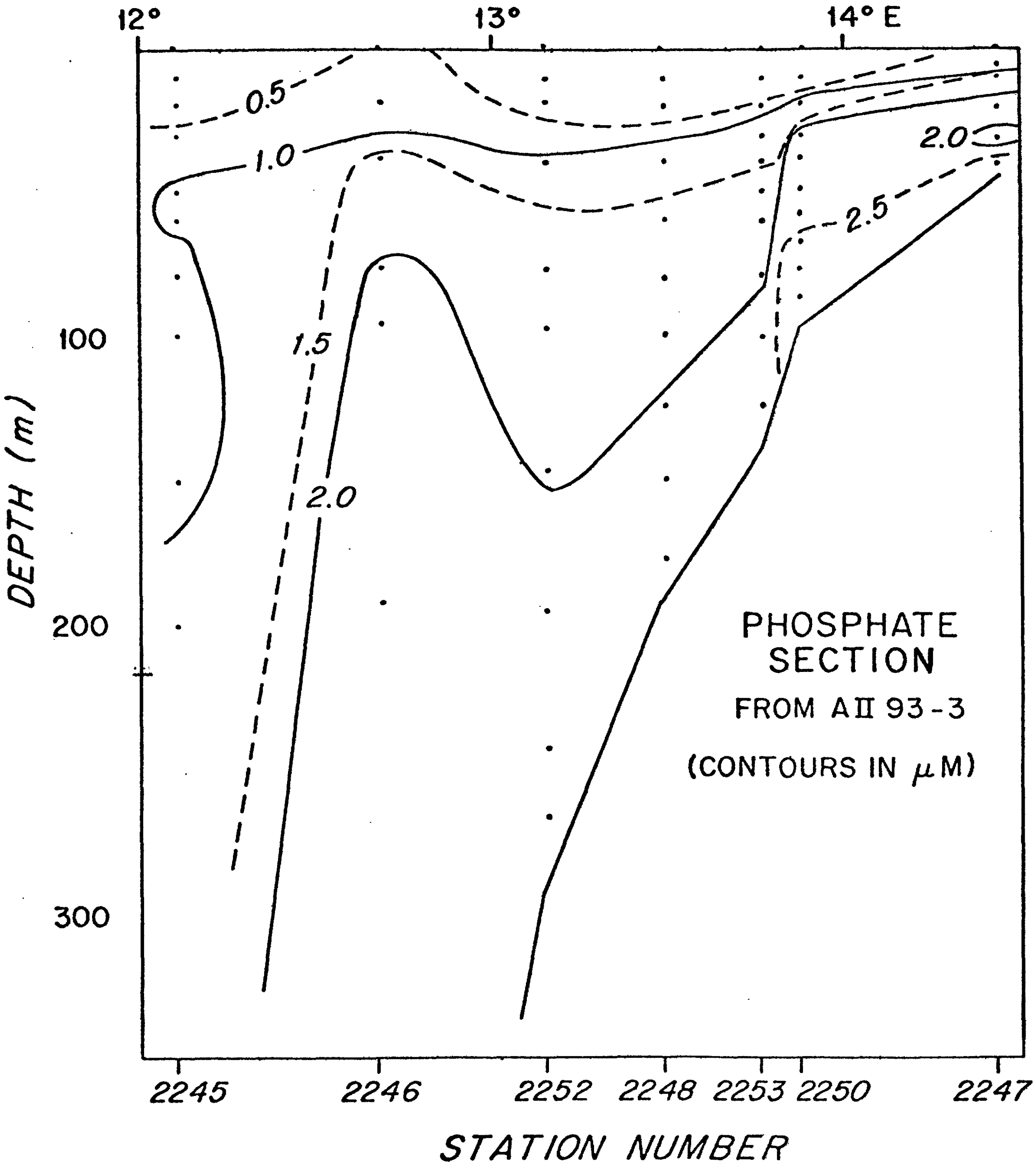

Figure III.8. Phosphate section from near Walvis Bay. A strong phosphate concentration gradient is found between stations AII93-2245 and 2246.

not necessarily an advective feature. Instead, the opposing currents may trap the coastal water in a region where sediments are highly reducing and where oxygen is rapidly removed from and phosphate added to the water.

Calvert and Price (1971) and others have noted that upwelled water on the shelf of an upwelling region commonly has nutrient concentrations much higher than water of similar T-S character off the shelf. The increased nutrient levels can best be attributed to regeneration from organic matter by bacterial action in the water column and sediments. Below the surface layer, phosphate concentrations are very high and increase to the bottom, while oxygen concentrations are low and decrease to the bottom. Concentrations also increase shoreward for phosphate and decrease shoreward for oxygen. The best explanation for the phosphate and oxygen distributions in the bottom water suggests production of nutrients either in or above the highly anoxic sediments.

In summary, the distribution of properties suggests that upwelling was weak or absent at the time of this study. Remnant upwelled water may have been present at the surface at some stations but was not being renewed. The coastal waters appeared to be trapped on the shelf, perhaps by the combined actions of the Benguela Current and the southward flowing counter current. Because the waters were retained over the reducing sediments off Walvis Bay, bottom phosphate concentrations had become very high and oxygen concentrations very low.

b. Observed methane distribution

With this picture of the circulation of the area in mind, an attempt to identify processes important in controlling the methane distribution in this coastal upwelling region can be made. These appear to be the first detailed methane data from such an environment.

Near Walvis Bay, there were a number of prominent features in the methane distribution (Figures III.9 and III.10). Mixed layer concentrations were high at the stations over the shelf and slope. Values ranged from only two times to greater than 300 times the concentrations predicted from solubility equilibrium with the atmosphere (as calculated from the solubility data of Yamamoto et al. (1976) and an average atmospheric methane concentration measured on this cruise of 1.44 ± 0.04 ppmv (Table III.1)). Methane maxima were present at most stations in the top of the thermocline, generally at about 10 to 20 m. In and below the thermocline on the shelf, concentrations decreased again and were approximately equal to concentrations at similar depths at the offshore stations. Near the bottom at shelf stations, concentrations increased again. At stations 2244 and 2245, in more oceanic environments, deep concentrations were quite low (decreasing to only 19% of solubility equilibrium with the atmosphere at 3000 m at station 2244). This has been observed in other oceans (Lamontagne et al., 1973; Brooks and Sackett, 1973; Chapter VI).

The methane distribution below the mixed layer on the shelf is consistent with some transport of offshore water with low methane concentrations onto the shelf. The high bottom water concentrations indicate that methane diffuses rapidly into the water from the sediments. The presence

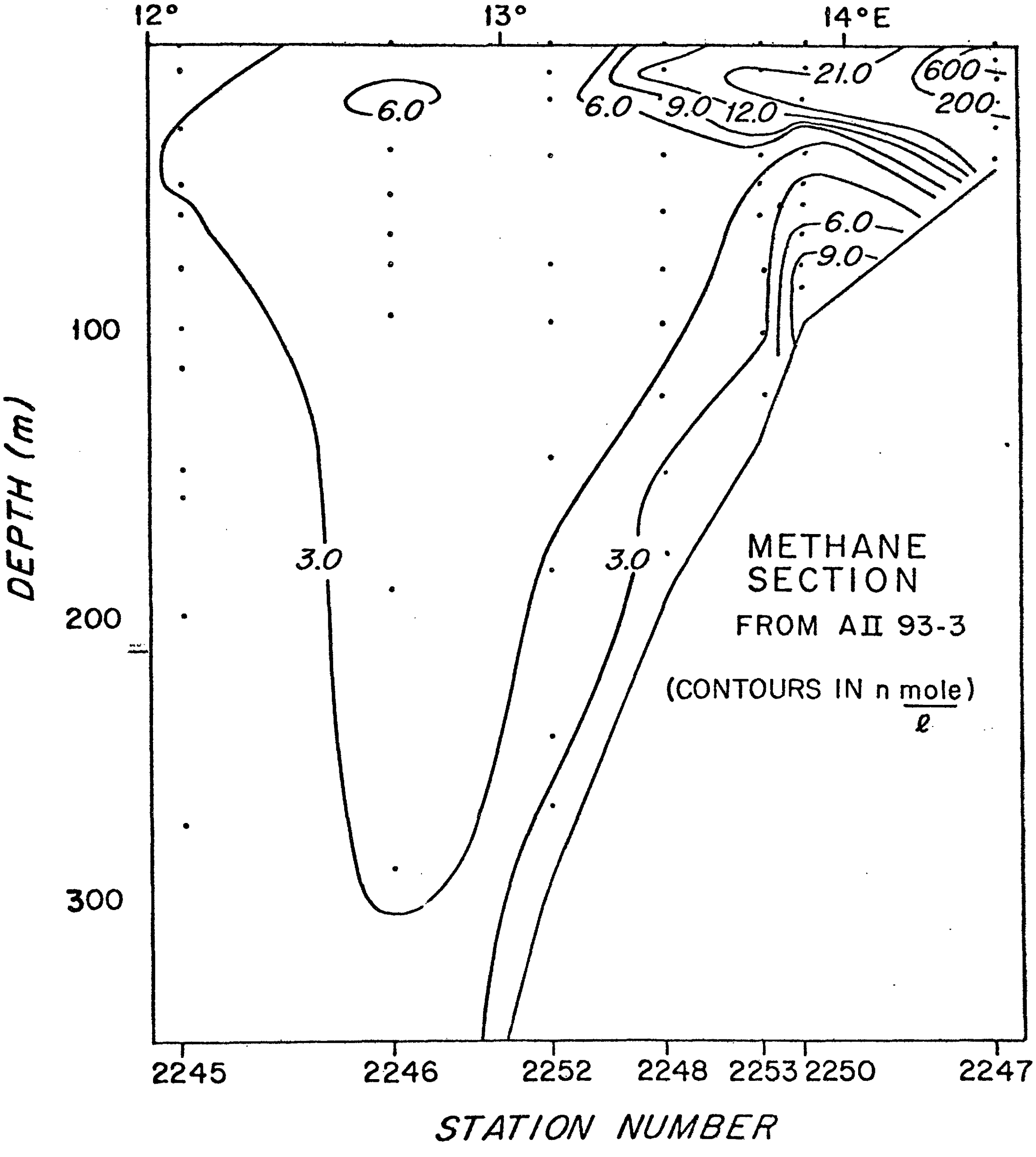

Figure III.9. Methane section from near Walvis Bay.

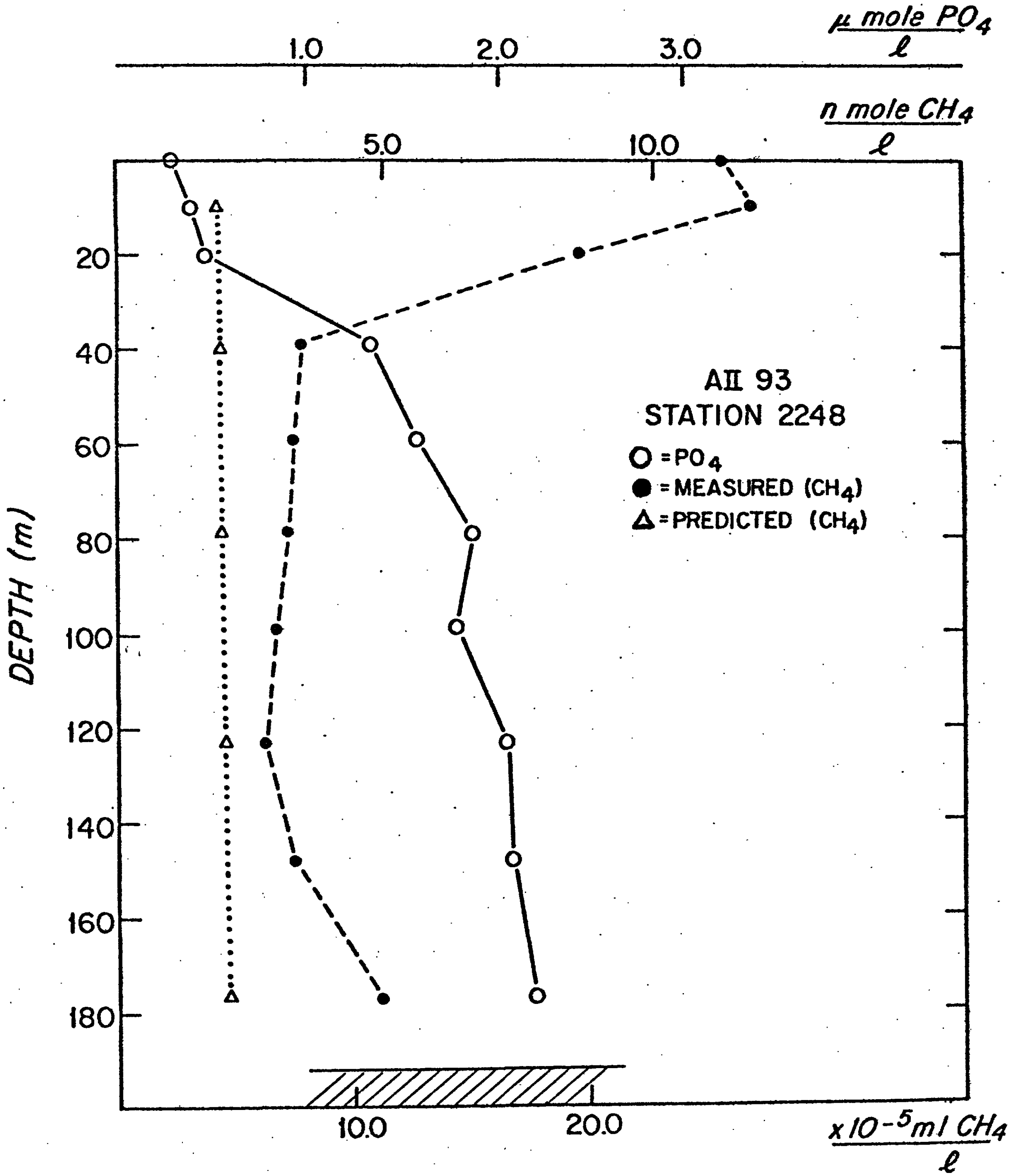

Figure III.10. Vertical profile of methane and phosphate from station AII93-2248. The predicted methane values are based on solubility data and an atmospheric methane concentration of 1.44 ppmv.

TABLE III.1

ATMOSPHERIC METHANE CONCENTRATIONS MEASURED ON AII93

Station	Methane concentration (ppmv)
AII93-2244	1.48
	1.45
	1.44
	1.50
AII93-2245	1.43
AII93-2246	1.40
AII93-2250	1.40
AII93-2252	1.37
	1.48
average	1.44 ± 0.04

All samples were taken while steaming onto or off of a station.

of a mid-depth minimum suggests that methane generation within this portion of the water column was not extensive.

The region in which sediment supply of methane was undoubtedly the highest was in Walvis Bay itself. At station 2247 (Figure III.11) we observed sulfide in the bottom water and methane concentrations as high as 0.88 μmole methane/l. In comparison, the deep waters of the Cariaco Trench have a methane concentration of 9.06 μmole/l and the Black Sea deep waters have a methane concentration of 12.2 μmole/l (see Chapter VII). Since no physical barriers to circulation such as are present in the Cariaco Trench and Black Sea are present in Walvis Bay, the high methane concentrations suggest extremely rapid methane supply from the sediments.

Sediments seem to be a principal source of methane to the bottom water on the shelf in the vicinity of Walvis Bay. However, the source of methane for the high concentrations in the mixed layer and upper thermocline cannot be the sediments directly beneath since there is an intermediate methane minimum at most stations.

c. Discussion of the methane data

I would like to determine if the primary source of methane for the surface waters near Walvis Bay is the water and sediments at very shallow depths. The surface water in the Walvis Bay region is isolated from the deeper waters below about 10 m by a sharp pycnocline. Some of the most methane-rich water is found in contact with the sediment. When sediment and bottom water are both above the thermocline, as in very shallow water, the methane-rich bottom water is able to exchange freely with waters further offshore and may provide a source of methane to the

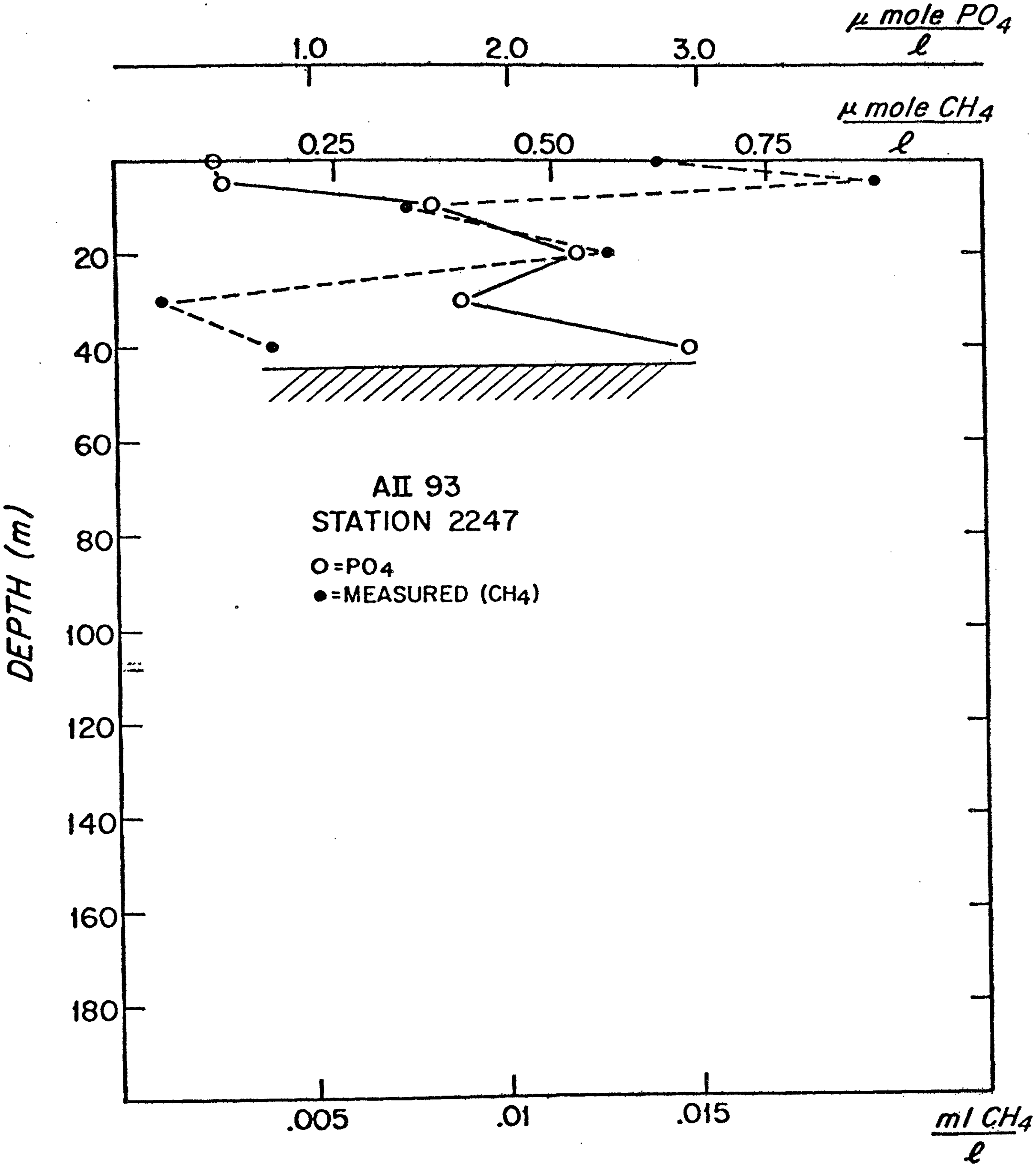

Figure III.11. Methane and phosphate data from station AII93-2247, the station within Walvis Bay. Note that methane concentrations are in μmole/l, while open ocean concentrations are nmole/l. No predicted methane concentrations are plotted as they would all be indistinguishable from zero.

mixed layer and upper thermocline. For example, station 2247 (Figure III.11) has a maximum methane concentration at 5 m, even though the bottom water at this station is anoxic below 30 m. The high methane concentrations seem to be supplied laterally rather than vertically.

3. One dimensional diffusive model

Brewer and Spencer (1975) have presented a model which attempts to describe the distribution of a species with a coastal source in terms of the relative contributions of horizontal mixing, first order loss and *in situ* production or consumption. As I am trying to determine the importance of a coastal source for the methane distribution in the surface waters off Walvis Bay, it seems appropriate that I attempt to use this model. I hope to determine if horizontal mixing processes alone can supply sufficient methane to the offshore surface waters to explain the observed surface distribution. If the model is applicable and if horizontal physical processes alone cannot describe the distribution, an *in situ* production term is probably important.

This discussion makes a number of assumptions about the physical situation. Firstly, offshore advection is neglected. The predominant currents in the Walvis Bay area flow to the north offshore at the surface (the Benguela Current) and to the south along the bottom at about 200 m (the coastal return flow). Upwelling was not active so this source for offshore advective transport can be ignored. However, the possibility of advective transport in eddies, in meanders, or by non-steady currents cannot be eliminated by the data I have available. Secondly, north-south gradients in methane concentrations are ignored. Undoubtedly there are geographical variations. However, the data suggest that both to the north and to the south of the immediate Walvis Bay region, surface water concentrations are roughly comparable for similar distances from shore. Unfortunately, the geographic coverage is not adequate to define the situation further. Bremner (1974) has noted that the only region in which high organic carbon is present in the sediments in very shallow water is in Walvis Bay. Thus we can at least ignore the possibility that high offshore concentrations are due to rapid southward advection of unusually methane-rich coastal waters further to the north. The only region which could potentially supply methane to surface coastal waters appears to be Walvis Bay itself.

A third basic assumption within the model is that mixing is taking place only between a near shore end member and an open ocean end-member. Because solar heating of the surface waters is important in the area near Walvis Bay (Calvert and Price, 1971; Stander, 1964), the T-S diagram for the surface waters in this area is not linear. However, since there are no rivers in this area, the sole source of low salinity surface water is probably upwelling at the coast. Evaporation can probably be considered to be negligible. The one case in which the assumption of two end-member mixing would be invalid would be if surface currents from the north or south were supplying waters of different properties to the region at different distances from shore. The data are not adequate to resolve the question, but from Stander (1964) it appears that some such water mass input may occur during periods of minimum upwelling. This makes the assumption of two end-member mixing more tenuous; however, I will try to use this model in the hope of clarifying the features most important for the methane distribution.

Mathematically, the model can be expressed by

$$K_h \frac{\partial^2 C}{\partial x^2} - \lambda(C - C_{eq}) + \alpha_o e^{-\mu x} = 0 \qquad (1)$$

where C = methane concentration in surface seawater

C_{eq} = methane concentration in a water sample at equilibrium with the atmosphere

K_h = horizontal eddy diffusion coefficient

λ = first order loss coefficient

α_o = production rate at $x = 0$

and μ = exponent determining the rate of decrease of production rate with distance from shore.

The solution to this equation is

$$C = C_o\, e^{-(\lambda/K_h)^{1/2} x} + \frac{\alpha_o}{\lambda - \mu^2 K_h}\left(e^{-\mu x} - e^{-(\lambda/K_h)^{1/2} x}\right) + C_{eq}\left(1 - e^{-(\lambda/K_h)^{1/2} x}\right) \qquad (2)$$

where C_o = concentration at the coast.

K_h can be estimated from the empirical results of Okubo (1971) who found that $K_h = 0.0103\ell^{1.15}$. The scale length in which I am interested is $\ell = 200$ km, indicating that K_h is about 2×10^6 cm^2/sec. λ can be estimated by assuming that this parameter represents loss to the atmosphere of excess methane in surface water (Appendix I.1) and that bacterial methane consumption is negligible. Assuming an average wind speed of about 4.5 m/sec and an average surface water temperature of 17°C, the gas transfer coefficient, D/z, for methane in the Walvis Bay region can be calculated to be 4.5 m/yr. If the thickness of the mixed layer underlying the laminar diffusion layer is M where M is 10 m, the first order rate constant for gas loss from the mixed layer is

$$\lambda = \frac{D}{zM} \tag{3}$$

Thus $\lambda = 45\ \text{yr}^{-1}$.

μ is the parameter which defines the rate of decrease of the production term with increasing distance from the coast. We have chosen μ equal to $0.014\ \text{km}^{-1}$, which would suggest that production at 70 km from shore is $\simeq 1/e$ times that at the coast. The phytoplankton biomass (determined from chlorophyll a data by Watson and coworkers (personal communication, 1976)) also gives this same exponential plot with distance from the coast.

The average value for C_{eq} (the concentration of methane in surface water which would be present if the seawater and atmosphere were in equilibrium) for the stations under consideration here is 1.85 nmole/l.

The methane data to be modelled are plotted in Figure III.12 as a function of distance from the coast. All values used were from the mixed layer and most were from samples taken at 0 m. If in situ production is neglected, the model can be fit to the data only if high K_h ($5 \times 10^7\ \text{cm}^2/\text{sec}$) and high coastal methane values (67 nmole/l) are

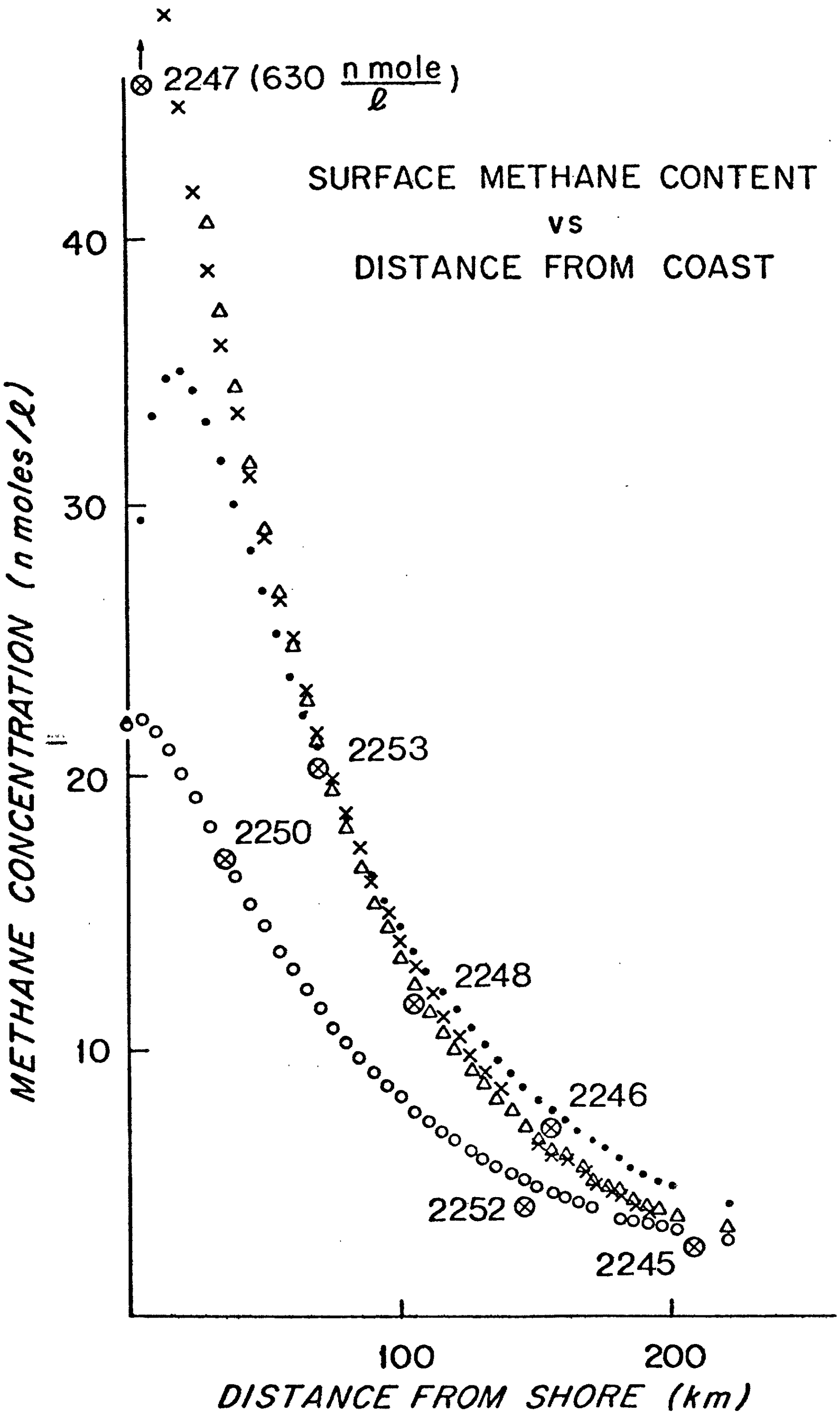

Figure III.12. Surface methane concentrations plotted vs distance from the coast, compared with curves calculated from the models discussed in the text. In situ production model: •, α_o = 2.2 μmole/l/yr; o, α_o = 1.1 μmole/l/yr for $K_h = 2 \times 10^6$ cm^2/sec and C_o = 22 nmole/l. x, α_o = 0 with $K_h = 5 \times 10^7$ cm^2/sec and C_o = 67 nmole/l. Advection diffusion model: Δ, $K_h = 2 \times 10^6$ cm^2/sec, C_o = 60 nmole/l and u = 10 cm/sec.

assumed. This fit is represented in Figure III.12 by the triangles. Based on Okubo's (1971) data, a K_h of 5×10^7 cm^2/sec appears to be more than a factor of 10 too large for the oceanographic region under consideration. In addition, coastal values (C_o) of 67 nmole/l or greater were observed at the surface only at the anomalous Walvis Bay station and not at any other coastal station we occupied. The value used in the model for C_o which appeared to be most representative is 22 nmole/l. This estimate agrees well with station 2250, our most shoreward station except 2247, but could be in error by a factor of two either way without making a significant difference to the following argument once K_h is chosen.

Since the parametric fit which ignores <u>in situ</u> production requires unreasonably high values of K_h and C_o, it appears necessary to include an <u>in situ</u> production term (α_o) in fitting the model to the data. The curves in Figure III.12 identified by open and closed circles respectively represent model calculations using two values for α_o (1.12 μmole/l/yr and 2.24 μmole/l/yr). These curves bracket all of the data except for the sample from station 2247 which appears anomalous in many ways.

If the production occurs uniformly throughout the 10 m thick mixed layer, it represents a methane supply of 1.1 to 2.2 μmole/cm^2/yr at the coast. At 100 km from shore, the production rate would be 0.4 to 0.8 μmole/cm^2/yr.

Until now <u>in situ</u> production rates have been treated as if they were representative of the absolute production of methane in the mixed layer and upper thermocline. In fact, it is probable that these rates are net production estimates. It is well known (Lamontagne et al., 1973; Brooks and Sackett, 1973; Chapter IV) that below about 500 m in the open ocean, methane concentrations are less than predicted from solubility equilibrium with the atmosphere. There are no known abiotic chemical processes which could consume methane at depth in the ocean at a significant rate, so the consumption is attributed to biological processes.

If methane oxidizing bacteria are present in the deep ocean, as deep methane data would indicate, it seems probable that similar organisms are also present in surface waters where methane concentrations are much higher. Indeed, Weaver (personal communication, 1974) has isolated methane oxidizing bacteria from seawater. Thus any production estimates made are measures of the net production only and actually underestimate the apparent ability of organisms to produce methane in a highly oxygenated environment.

4. Horizontal advection diffusion model

The production estimate discussed above was derived from a model neglecting offshore advection. Because the circulation pattern in Walvis Bay is extremely complex (Stander, 1964), it is not certain that this assumption is correct. Therefore, the methane data will also be described with a model which assumes that there is no in situ production and that loss of methane across the air-sea interface is balanced by eddy diffusion and horizontal advection of coastal water offshore. This model is of the same form as that used frequently for describing vertical profiles in the ocean (Craig, 1969; Wyrtki, 1962). Mathematically, it can be expressed as follows:

$$K_h \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} - \lambda C = 0 \qquad (4)$$

where K_h and λ have the same values as were substituted into equation (2). The model can be fit to the methane data if $u = 10$ cm/sec and C_o (the coastal concentrations) is 60 nmole/l. This curve is represented in Figure III.12 by the crosses. While it is conceivable that C_o could be as large as 60 nmole/l, an east-west current of 10 cm/sec in this region of strong northward flow seems unlikely. However, if the Benguela current meanders significantly, it is possible that rapid advective transport could carry coastal methane far offshore.

If advection were the sole source of the methane excess in offshore waters, it would be of interest to know the amount of methane which would have to be supplied by diffusion from coastal sediments. One way to estimate this is to calculate the amount of methane required to balance the air-sea loss in the preliminary model (equation 1). Advective transport may provide methane to offshore surface waters and, in the most extreme cases, all the methane initially ascribed to in situ production could actually be supplied by advection.

The in situ production term of the model (which represents the amount of methane not attributable to eddy diffusion) can be integrated over the two hundred kilometer section ${}_{0}\int^{200} \alpha_o e^{-\mu x}\, dx$. If the area under consideration is that between 22° and 23°S, the north-south distance is about 100 km. Using $\alpha_o = 1700$ nmole/l/yr as an average coastal in situ production and taking a 10 m thick mixed layer in which methane is being produced or to which methane is being supplied advectively, the total amount of methane to be accounted for is 1.14×10^{14} μmole/yr.

If all the excess methane is supplied advectively, 1.14×10^{14} μmole of methane must be produced each year in the coastal region in waters less than 10 m deep. Taking a coastline of 150 km (allowing for inlets and coastline irregularities) and assuming that the ten meter contour is about 5 km offshore, the maximum area of sediments which could supply methane to the mixed layer is 7.5×10^{12} cm^2. The flux out of the sediments which would be required is 15.2 μmole/cm^2/yr.

Reeburgh (1976) has published sediment data for the Cariaco Trench which suggest the sediment-water flux of methane there is 0.4 to 4 μmole/cm^2/yr (see Chapter VII). Thus if the supply of methane to offshore waters is completely advective, the sediments in the vicinity of Walvis Bay must supply 4 to 40 times as much methane to overlying waters as do the Cariaco Trench sediments.

A number of workers (Barnes and Goldberg, 1976; Reeburgh, 1976; Martens and Berner, 1977) have shown that a considerable percentage of the methane produced in anoxic marine sediments is consumed either at the sediment-water interface by oxygen-utilizing methane-oxidizing bacteria or deeper within the sediment by sulfate-reducing bacteria which oxidize methane while reducing sulfate. In a marine system such as Walvis Bay, both the presence of high sulfate and of significant oxygen concentrations in bottom waters would act to diminish the amounts of methane which could be supplied by the sediments, especially in comparison to the Cariaco Trench sediments where bottom waters are highly reducing. In Walvis Bay itself it is quite possible that very high rates of methane supply are present. However, for the coast as a whole, this is probably not true. An additional factor to be considered is that shallow sediments of very high organic carbon content (and thus high methane production potential) are restricted in extent to the immediate vicinity of Walvis Bay (Bremner, 1974). Thus the area of sediments used in the calculation of possible flux is probably a considerable overestimate, making the flux required from the suitable sediments even higher.

The in situ production model (equations 1 and 2) and the advective transport model (equation 4) seem mutually exclusive. However, the processes modelled by both are probably important. Advective transport of coastal methane to offshore surface waters probably supplies some, but not all, of the observed excess methane, while a significant amount of in situ methane production must also take place. Due to the great uncertainties in our understanding of the circulation pattern in this area, the rates of advective supply and in situ production cannot be fully quantified.

A number of other factors also prevent precise calculation of the rate of in situ production. Firstly, the value of K_h is only poorly known. Ideally a radioactive coastal tracer (such as ^{228}Ra) should be measured in conjunction with coastal methane studies to permit a more accurate estimate of the horizontal eddy diffusion coefficient to be made. Another parameter which is not precisely known is the thin film thickness, z. ^{222}Rn measurements would have permitted us to estimate this parameter directly. Unfortunately, facilities for these analyses were not available. The predictions of either model would be inaccurate if the values of the parameters used were greatly in error.

Finally upon close examination of the data, it appears that the physics of the situation off Walvis Bay is considerably more complex than that assumed by the models. In particular, the presence of a pool of low salinity water at the surface over the edge of the continental shelf suggests that the two end-member mixing assumption is probably unsound. It may be impossible to distinguish eddy-diffusive and advective transport from _in situ_ production of methane in a region where currents are complex and the circulation pattern is extremely time dependent. Nevertheless, the application of models such as those used above provides considerable insight into the types of processes which are important to the methane distribution in highly productive coastal environments and suggests the need for more interdisciplinary studies of such complex coastal regions.

No mention has been made of the nature of the _in situ_ production term. Presumably the production is biological, as abiological methane production in an oxidizing environment is unlikely. No obvious correlation between methane and ATP, chlorophyll or particulate organic carbon has been observed in Walvis Bay (Watson, personal communication, 1976; Gagosian, personal communication, 1977). However, the biological mechanism could be production of methane in reducing microenvironments by conventional methane bacteria or could be a hitherto unknown aerobic methane production process. These possibilities are discussed in detail in Chapter V.

5. Conclusions

Methane is supplied to the waters of Walvis Bay both from the sediments and by _in situ_ biological production. In the bottom waters diffusion from the sediments appears to be most important. In the surface waters, both _in situ_ production and lateral eddy diffusion and advection seem to act as sources for the excess methane which is rapidly lost across the air-sea interface. The mechanism(s) for methane production in an oxygenated environment are not well understood. However, the importance of _in situ_ methane production has been demonstrated for Walvis Bay. To provide more quantitative estimates of the _in situ_ production rates in upwelling regions, methane measurements will have to be coupled with measurements of other tracers and with extensive physical oceanographic studies.

B. Gulf of Maine

The relative importance of physical transport of methane produced in reducing sediments and of in situ production in supplying excess methane to surface waters has been discussed above for productive coastal waters such as those off Walvis Bay. It is also of interest to consider the processes important in less productive environments.

In January, 1975, during cruise 86 leg 1A of the R/V ATLANTIS II, methane data were obtained from three stations in the Murray-Wilkinson Basin in the Gulf of Maine. Salinity, temperature, dissolved oxygen, phosphate and silicate were also measured at these stations (Spencer, personal communication, 1975). The methods for oxygen and phosphate were those discussed in the methods section of Chapter III, part A. Silicate was determined using the reduced silicate-molybdate complex as described by Mullin and Riley (1955). Data from these hydrostations appear in Appendix III.2 and station locations are shown in Figure III.13. No productivity measurements were made, but the high nutrient concentrations observed in surface waters (up to 1.06 μmole/l PO_4 and over 10 μmole/l SiO_2) suggest that productivity was low at the time of sampling.

The Murray-Wilkinson Basin, in which the samples were taken, is an elongated depression about 120 miles east of Boston in the Gulf of Maine. It is about 80 km long and has a maximum depth of 285 m. The Murray and Wilkinson Basins are separated by the Wilkinson Divide extending to 250 m. In addition, there are several deep connections with other basins (185 m sills to the Rodgers and Franklin Basins and a 170 m sill to the Platts Basin). Above a broad sill at 160 m, the waters of the Murray-Wilkinson Basin can exchange freely with those of the Franklin Basin. The Murray-

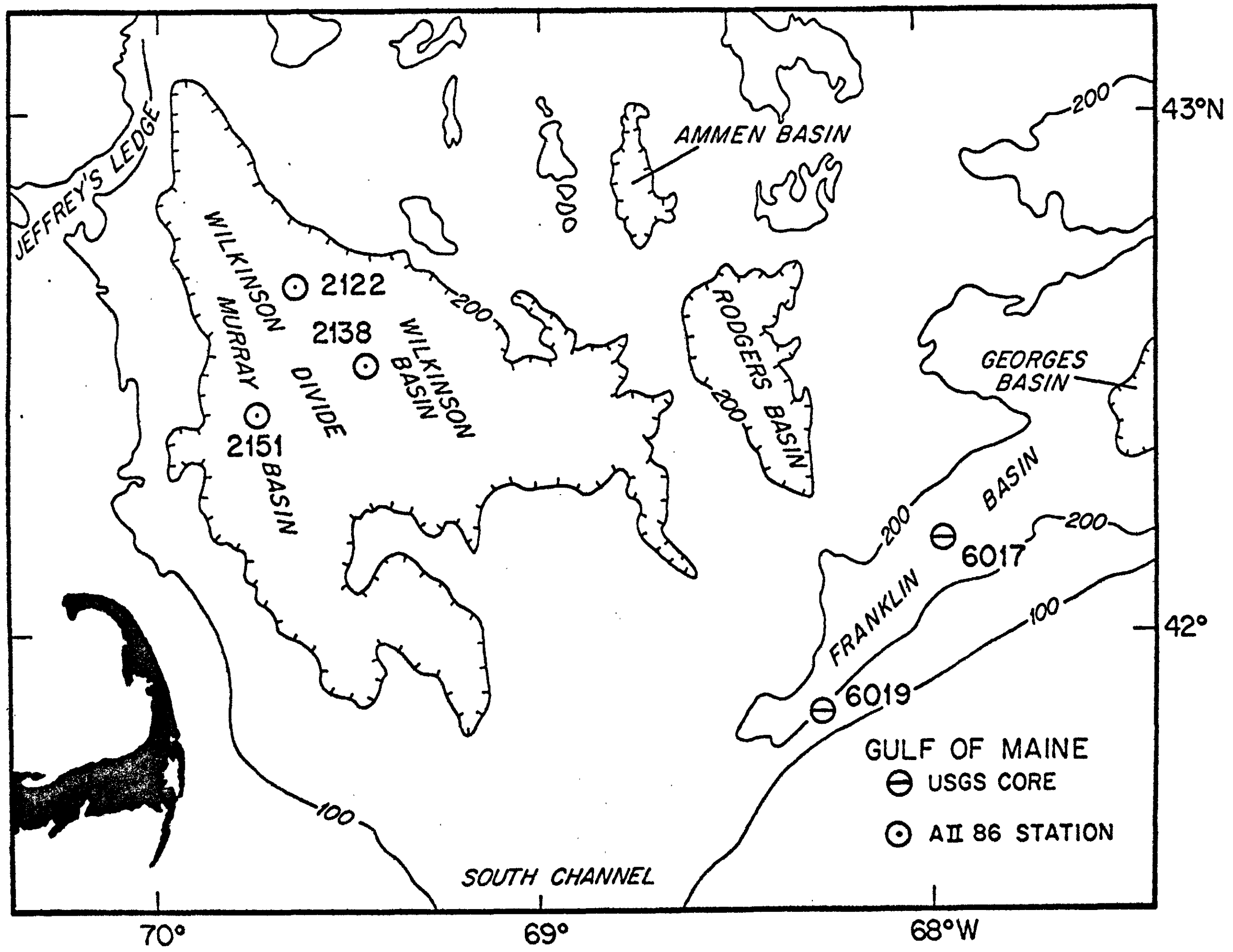

Figure III.13. Station and core locations for AII86 leg 1A, Gulf of Maine.

Wilkinson Basin is known to have a relatively stable deep water structure (Colton, 1968) being least affected of all the Gulf of Maine basins by variations in the amounts of Slope Water and Coastal Water introduced to the Gulf of Maine deep waters.

1. Results and Discussion

Methane analyses were performed at sea using the modified Swinnerton et al. (1962a, b) method described in Chapter II. Due to baseline fluctuations caused by a high sea state, to laboratory temperature fluctuations which affected the amount of standard gas injected via a gas sample loop, and to difficulties with the stripper which required two strippings per sample with summation of the results, the precision of analysis was reduced from a normal ±2% to about ±4% (based on replicate standard analyses).

A composite methane profile for the three Gulf of Maine stations is shown in Figure III.14. The methane distribution features a very uniform surface concentration extending to about 140 m, a sharp increase at 140 m or slightly below the top of the thermocline as shown in Figure III.15 and then a gradual decrease in methane content to the bottom below a mid-depth maximum.

In spite of minor analytical difficulties, the most striking aspect of the methane data is the high degree of uniformity observed in the mixed layer. Other properties (T, S, O_2, SiO_2 and PO_4) were also essentially constant to depths of 140 to 150 m, suggesting a very rapid rate of mixing within this zone. At station 2122, for example, the average

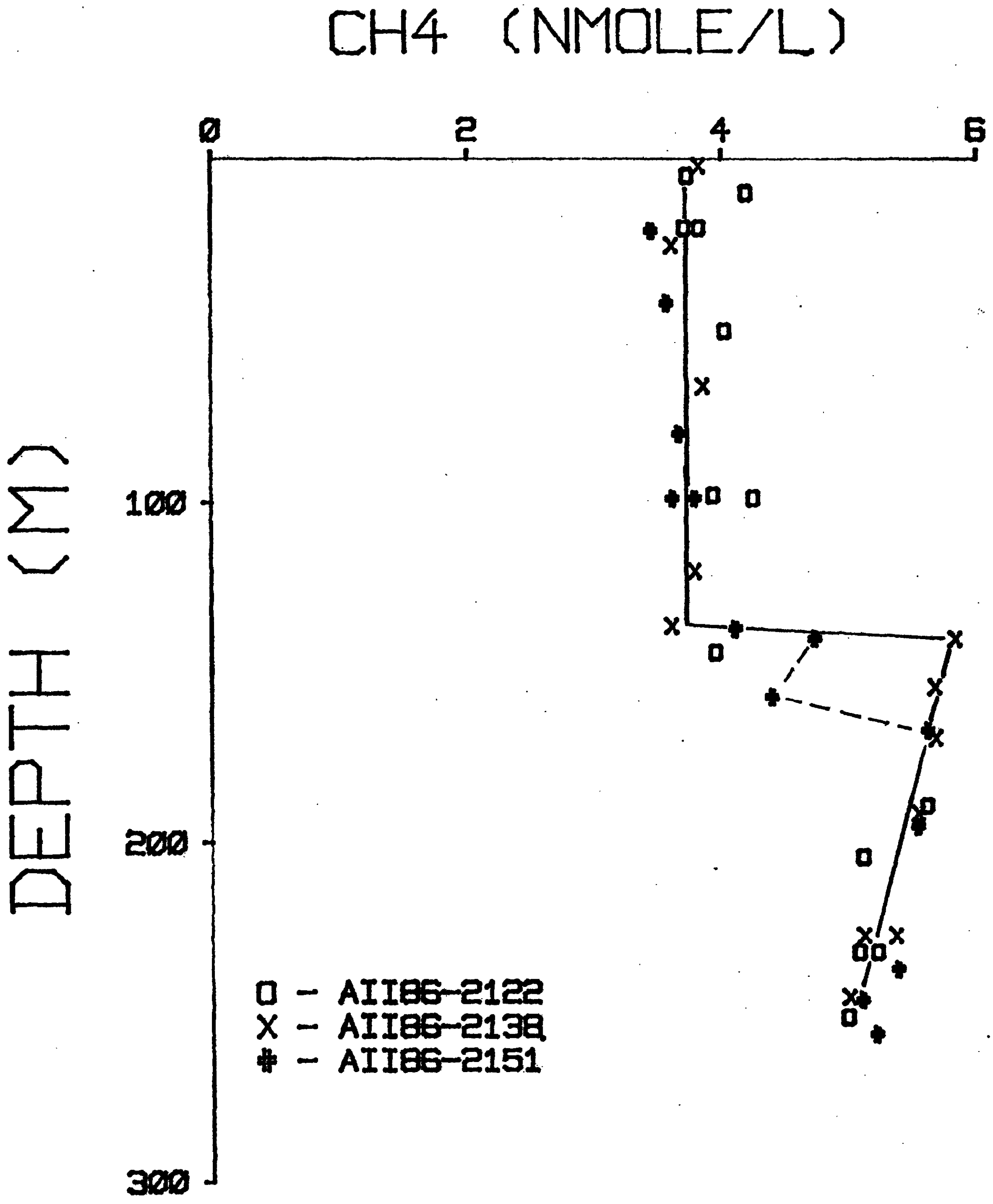

Figure III.14. Composite profile of methane concentrations in the three stations occupied in the Gulf of Maine during AII86 leg 1A.

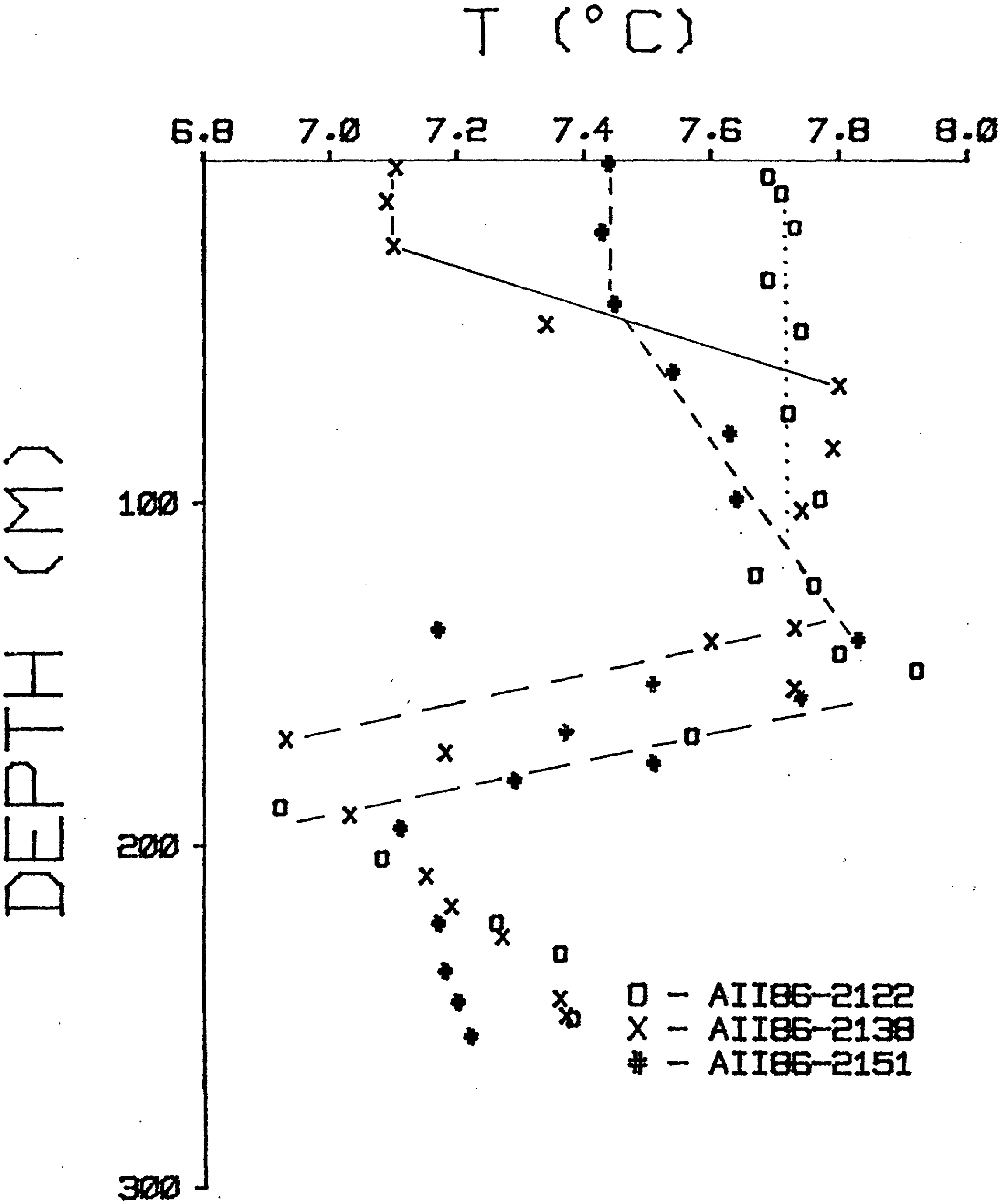

Figure III.15. Composite temperature profile for the three stations occupied in the Gulf of Maine during AII86 leg 1A.

methane concentration for all samples between the surface and 144 m was 3.95 nmole/l (±5%). The 5% variation observed is almost within the analytical error estimated for the cruise. At 2138 the average mixed layer value was 3.73 nmole/l (±3%) and for 2151 was 3.61 nmole/l (±3%). Within error these numbers are the same, indicating the Gulf of Maine surface waters are horizontally well mixed with respect to methane content.

An alternative explanation to analytical variability for the lower values obtained at stations 2138 and 2151 as compared with 2122 exists. A severe winter storm with freezing rain and high winds was encountered between stations 2122 and 2138, and it is possible that this caused an increase in mixing and thus an increase in the rate of gas exchange across the air-sea interface. Since the surface waters are supersaturated relative to solubility equilibrium with methane, an increased rate of exchange would result in decreased concentrations. Surface temperatures dropped from 7.7° to 7.1°C between station 2122 and 2138, but by the time 2151 was occupied, had risen again to 7.4°. This observation also suggests increased contact with the cool air.

One additional observation can be made about the amount of horizontal uniformity within the Murray-Wilkinson Basin. The erratic nature of the transition from surface to deep waters observed in 2151 is observed in all properties, and represents two hydrocasts which overlapped between 140 m and 176 m. All the high points belong to one cast and all the low points to the other. This suggests that horizontal uniformity, at least at depth in the western Wilkinson Basin, is not, in fact, very great.

The degree of horizontal uniformity observed in the surface water, coupled with the fact that the mixed layer contained from 1.6 to 1.9 times as much methane as predicted from solubility equilibrium, suggests that a significant methane source for the mixed layer exists. The size of the source can be estimated by determining the rate of methane loss across the air-sea interface if the system is in steady state. Unfortunately, no measurements were made of the concentration of methane in the atmosphere over the Gulf of Maine. Lamontagne et al. (1973) have determined values for the North Atlantic atmosphere of from 1.3 to 1.4 ppmv. Using this range the equilibrium methane content for the surface waters would be 2.10 to 2.32 nmole/l.

The air-sea flux can be estimated from the thin film model discussed by Danckwerts (1970) (see Appendix I.1). Broecker and Peng (1974) and Emerson (1975) have shown that there is a strong negative correlation between the square of the wind speed and thin film thickness. Since wind speeds during the cruise ranged from 5 to 30 knots, the thin film thickness can be estimated to range from 200 to 15 μm (Emerson, 1975). The flux across the air-sea interface would thus be in the range 8.9×10^{-5} nmole/cm^2/sec to 8.9×10^{-6} nmole/cm^2/sec. Since the winds were highly variable during the cruise, since the system undoubtedly requires a finite amount of time to reach a new equilibrium after the wind speed changes, and since wind speeds were not measured at the times at which the surface water samples were being taken, it seems unrealistic to attempt to define the flux more closely than this range of values.

The most likely source for the surface methane excess with which to balance the loss of methane across the air-sea interface is diffusion away from the mid-depth maximum observed in all three profiles. The methane increase correlates strongly with changes in other properties as noted earlier, and delineates the boundary between the well-mixed surface waters and the Gulf of Maine deep waters. This transition zone is only a few tens of meters thick. The methane maximum occurs at about 140-190 m, near sill depth of the Murray-Wilkinson Basin and near the depths at which the Basin is connected to the Rogers, Franklin and Platts Basins.

Taking the methane gradient inferred from the concentration profiles (Figure III.14) and assuming a vertical eddy diffusion coefficient of $0.2\ \mathrm{cm}^2/\mathrm{sec}$ (an estimate made for the thermocline by Rooth and Ostlund, 1972), the flux of methane away from the maximum is $K_v \frac{\Delta C}{\Delta z}$ and ranges from 8.9×10^{-6} to 8.9×10^{-7} nmole/cm^2/sec. Part of the variability undoubtedly results from inadequate sampling detail through the steep part of the methane gradient. Thus the real fluxes are probably larger than the ones calculated.

It is also quite possible that the vertical eddy diffusion coefficient is larger than $0.2\ \mathrm{cm}^2/\mathrm{sec}$, and, as mentioned above the values of the air-sea fluxes are also uncertain due to the stormy and variable nature of the winds. With this in mind, it seems likely that the air-sea flux is at least largely balanced by diffusion from the subsurface maximum.

The final question of interest is the source for the intermediate methane maximum. To answer this question we must first consider the hydrography of the area. Spencer (personal communication, 1975) has described the hydrographic data from the cruise in detail. Briefly, the surface water mass consists of cold, fresh water containing isolated parcels of residual "summer" water which is warm and salty. This layer is underlain by a warm water core present at about 130 m at all stations. In the deep water a cold water core was found to persist throughout the basin at 180-200 m. There is evidence that this cold water is part of the major counter-clockwise gyre in the Gulf of Maine and is a mixture of Labrador Coastal Water (LCW) and Slope Water (SW) advecting in from the Franklin Basin. The bottom water in the basin is somewhat isolated from upper layers as is seen by the lower oxygen and higher silica values associated with the LCW and SW.

The relationship between salinity and methane is shown in Figure III.16. This relationship and similar ones for $S‰-O_2$ and $S‰-SiO_2$ can be described as consisting of three linear sections representative of 1) mixing between surface water and the warm water core of salinity 33.5‰, 2) mixing of the warm core with the cold core of salinity 33.7‰ and 3) mixing between the cold core and the basin bottom water. The maximum methane concentrations are associated with the 33.7‰ cold core which, as was mentioned above, probably enters from the Franklin Basin.

The U.S. Geological Survey (Hathaway et al., 1976) has collected two cores from the Franklin Basin (see Figure III.13 for core locations). Both cores contained gassy surface sediments. Core 6019, at 174 m water depth, was anoxic soft clay containing numerous diatoms and large amounts of H_2S. Considering the correlation of the cold core water with the

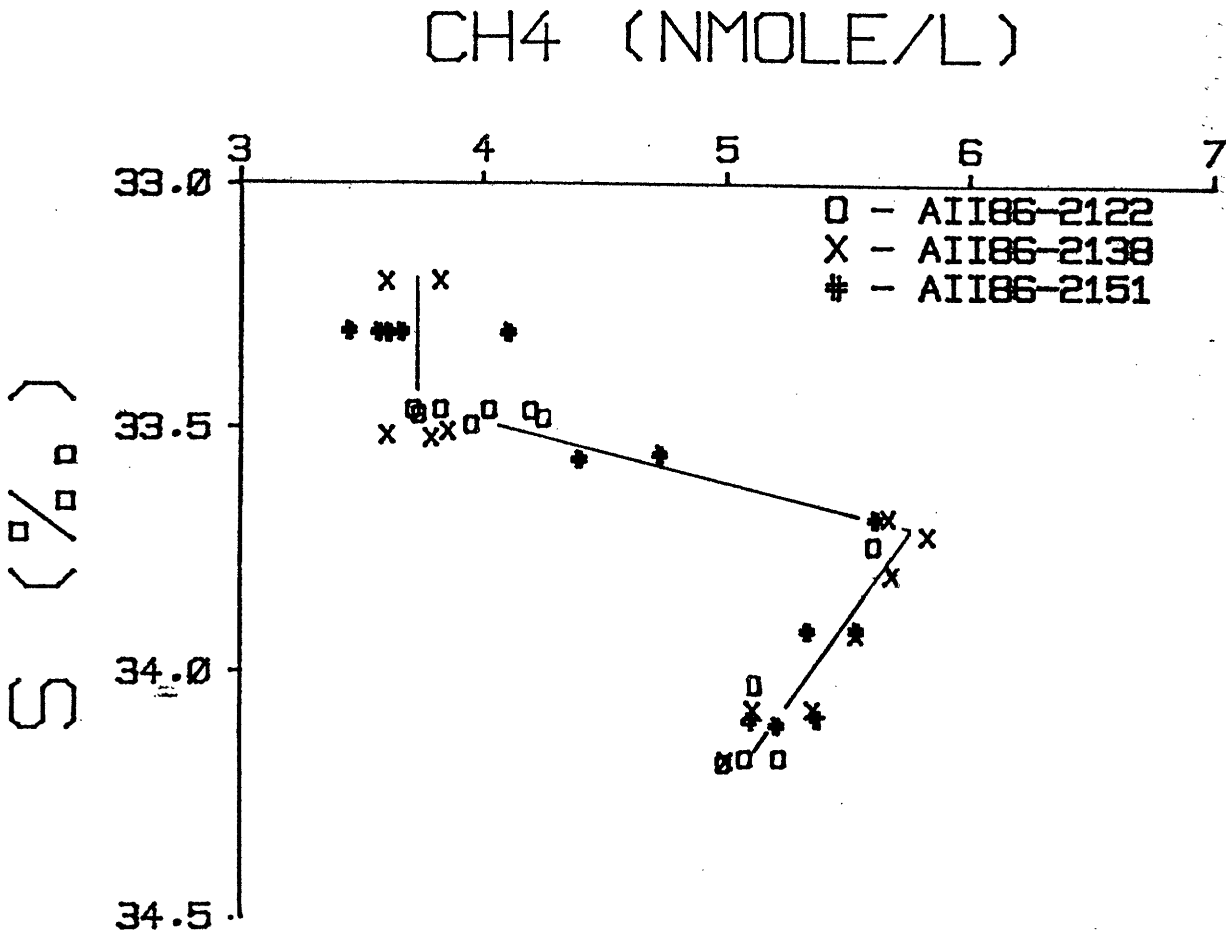

Figure III.16. Salinity vs methane plot for the three stations occupied in the Gulf of Maine during AII86 leg 1A. The four water types are surface water, warm core water, cold core water and bottom water.

methane maximum, it appears that the high methane concentrations in the surface waters of the Murray-Wilkinson Basin result from advective supply of methane from nearby anoxic sediments. The high methane concentrations in the deep waters of the Murray-Wilkinson Basin may be a result of downward diffusion of methane from the maximum and/or production within the sediments of the Murray-Wilkinson Basin itself.

C. Summary of Chapter III

Data from coastal waters near Walvis Bay and in the Gulf of Maine suggest that physical processes such as eddy diffusion and advection may transport significant amounts of methane from regions where methane is produced in anoxic sediments to surface waters. When this transport occurs predominantly below the thermocline, as in the Gulf of Maine, it is possible that lateral methane supply can provide enough methane to maintain surface supersaturations in spite of rapid loss across the air-sea interface. However, in regions where the methane supply is directly to the surface layer, horizontal transport of coastal methane is most important close to shore and in regions where strong offshore currents are present. In the waters further off the coast of Namibia, physical transport of methane rich coastal waters is insufficient to produce the observed methane excesses and thus *in situ* (biological) methane production must be occurring.

CHAPTER IV

METHANE IN THE NEAR-SURFACE WATERS OF THE OPEN OCEAN

Considerable data are available which indicate that the mixed layer of the open ocean is supersaturated with methane with respect to solubility equilibrium with the atmosphere (Lamontagne *et al*., 1971; Brooks and Sackett, 1973; Lamontagne et al., 1973; Williams and Bainbridge, 1973; Seiler and Schmidt, 1974). In some cases the excess clearly results from pollution by oil-gas production or sewage (Swinnerton et al., 1969; Brooks et al., 1973). In other cases the methane source has yet to be identified. This chapter will discuss the source of "excess" methane in "clean" ocean water.

In situ production of methane in the mixed layer appears to be a major methane source in highly productive coastal waters such as those off Walvis Bay (Scranton and Farrington, 1977; Chapter III). In less productive environments (for example, the Gulf of Maine), enough methane can be supplied by horizontal advection from sediment sources to maintain the mixed layer excess.

In the open ocean, the typical methane distribution includes a relatively uniform mixed layer where concentrations are generally 1.4 to 1.6 times solubility equilibrium, and a subsurface methane maximum lying in the very top of the thermocline. Below the methane maximum, concentrations decrease sharply and below about 400 to 500 meters the water is undersaturated with respect to equilibrium with the atmosphere. The presence of a subsurface maximum suggests that horizontal advective supply could be a source for the mixed layer excess. Based on the results from Walvis Bay, an *in situ* biological source also seems possible, although productivity is generally low in the open ocean.

In the present study, samples were taken in the western subtropical North Atlantic and Caribbean in an attempt to determine the relative importance of physical and biological processes in controlling the near-surface open ocean methane distribution.

A. Experimental Procedure

Temperature, salinity and methane concentrations were measured for all samples reported here. CTD profiles were available to aid in placement of sampling bottles. Occasional profiles using the Sachs-Spencer nephelometer (Meade *et al.*, 1975) were also made.

Methane analyses were performed at sea within one to two days of sample collection. Sampling and analysis were as described in Scranton and Brewer (1977) and in Chapter II. Based on calibrations made on shipboard using injections of a known volume of calibration standard gas, the precision of analysis was ± 2.5% for repeated measurements of the standard. The difference between the methane content of duplicate water samples ranged from 1.7 to 5.4% including errors in volume determinations, sampling reproducibility, and planimetry. The limit of detection for the analysis was about 0.01 nmole/l (about 0.45 nl/l).

B. Results

The samples discussed in the chapter were taken during Cruise 86, leg 2 of the R/V ATLANTIS II. The cruise track and station locations are shown in Figure IV.1. At all the stations made during this study, the top 400 to 500 meters of the water column were supersaturated with methane with respect to solubility equilibrium with the atmosphere (see

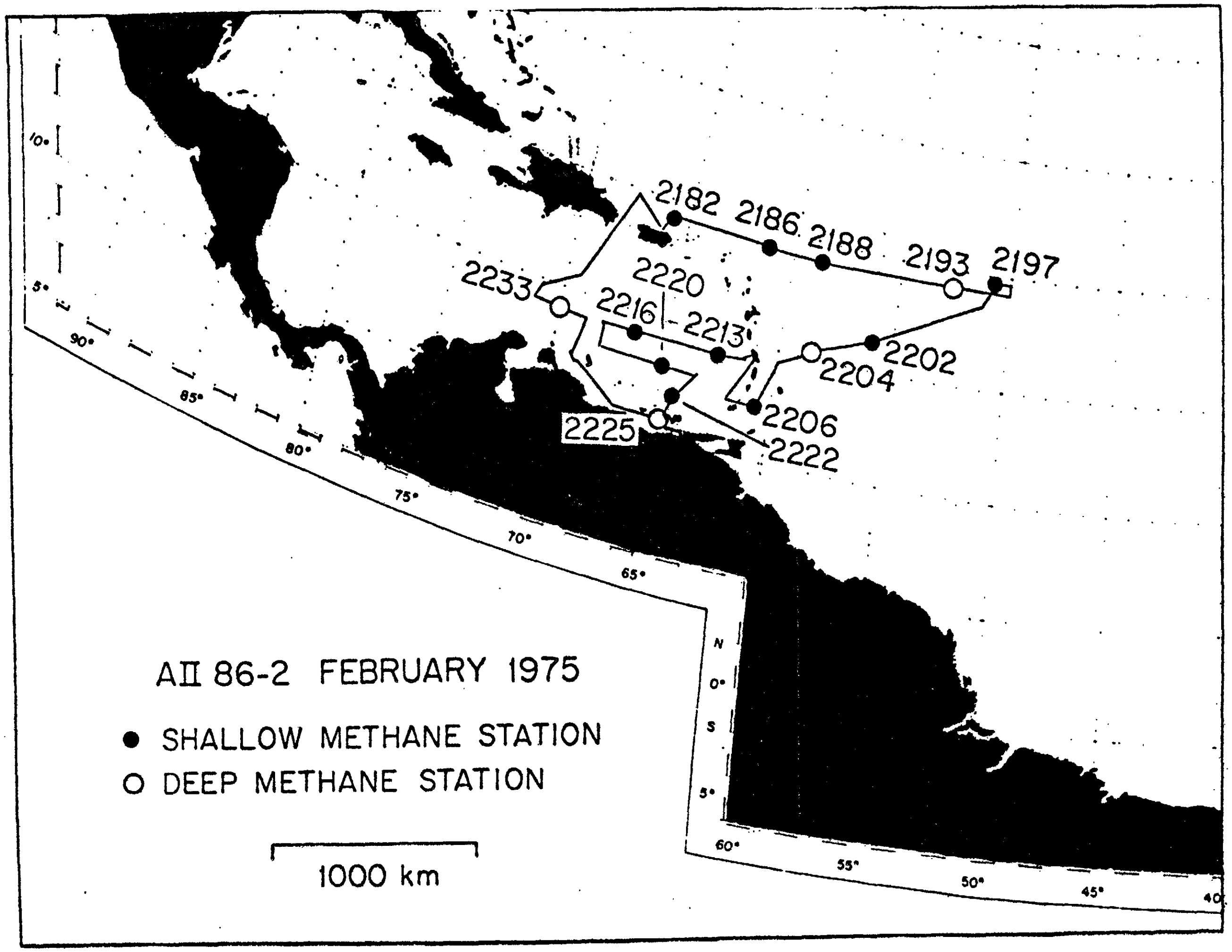

Figure IV.1. Cruise track for AII86 leg 2.

Appendix IV.1). Concentrations at the subsurface maximum ranged from about two times to 7.2 times solubility equilibrium. At depth, the concentrations steadily decreased and the water was undersaturated with respect to solubility equilibrium at depths greater than 400 to 500 m (Lamontange et al., 1973; Lamontagne and coworkers, personal communication, 1974; Chapter VI). The presence of excess methane in surface waters shows that a source of methane other than the atmosphere must be of considerable importance.

The goal of this investigation was to gain an understanding of the processes which control the distribution of methane in upper layers of the open ocean. Purely inorganic chemical processes are not important methane sources considering the conditions required for methane production (pure carbon and pure hydrogen at 1100°C-Pring, 1910; CH_3COONa and NaOH-Carroll, 1918); physical and biological processes are thus the important ones to consider.

C. The Western Subtropical North Atlantic

A well-defined maximum was found in all profiles from the western subtropical North Atlantic. In addition, methane sections (Figures IV.2 and IV.3) show that the maximum concentrations are relatively uniform over a large geographical area. The persistence of this feature over large horizontal distances in spite of losses occurring through vertical diffusion and gas exchange with the atmosphere suggests that there is a mechanism capable of rapidly supplying methane to the uppermost part of the pycnocline, in which the maxima are found.

One possible mechanism is physical transport of methane produced elsewhere (probably in near-shore reducing environments) into the oceanic

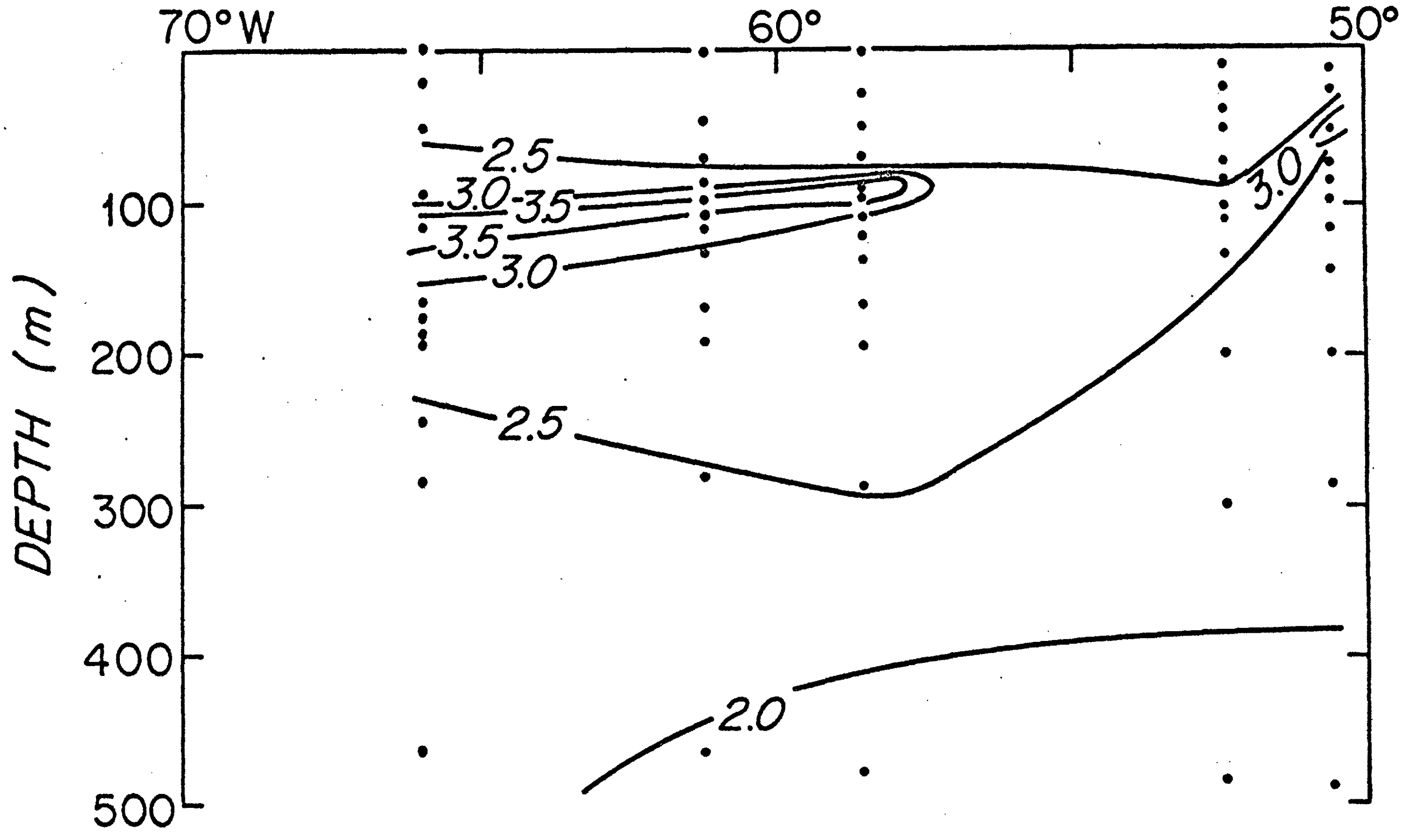

Figure IV.2. Section of methane concentrations from 65°W to 50°W along 19°N. Note the methane maximum at station AII86-2197. This occurs within a well-mixed layer which extends to 100 m. Methane contours are in units of nmole/l.

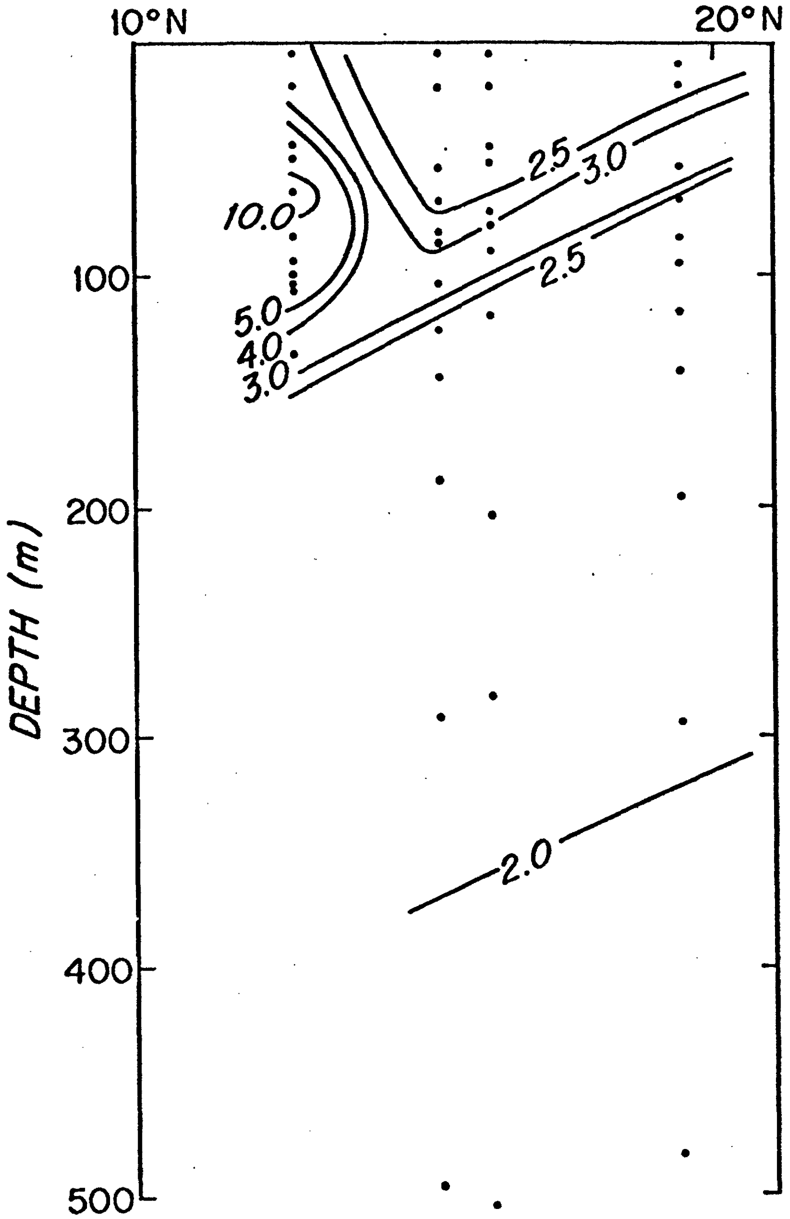

Figure IV.3. Methane section from near the Grenadine Islands to 19^{o}N 50^{o}W. Station AII86-2206, the station nearest the shore, has very high methane concentrations throughout the water column. It may represent a near-shore source for the methane in the oceanic methane maximum. Methane contours in units of nmole/l.

realm. Methane bacteria are known to be active in many anoxic environments and high levels of methane are found in anoxic basins such as the Cariaco Trench and the Black Sea (Lamontagne _et al._, 1973; Reeburgh, 1976; Hunt, 1974; Chapter VII) and in anoxic sediments such as those in Chesapeake Bay (Reeburgh, 1972) and Long Island Sound (Martens and Berner, 1974). The most landward station investigated in this study, station AII86-2206 (see Figure IV.4), had extraordinarily high methane levels, perhaps reflecting the presence of anoxic sediment in the coastal zone. Since a coastal source may be present, physical supply of methane to the open ocean must be considered.

A second supply mechanism could be _in situ_ biological production in the oxygenated mixed layer. In the following discussion I will show that _in situ_ biological production must indeed take place in the open ocean as well as in the coastal waters near Walvis Bay.

1. Physical Transport and Mixing

It is necessary to make a comparison of the relative importance of horizontal transport of methane by advective processes and vertical loss by eddy diffusion to determine whether near-shore reducing sediments could be a significant methane source for the subtropical North Atlantic. This comparison can be expressed mathematically as

$$u \frac{\partial C}{\partial x} = K_v \frac{\partial^2 C}{\partial z^2}$$

where u = horizontal advective velocity

K_v = vertical eddy diffusion coefficient

C = methane concentration, where methane is used as

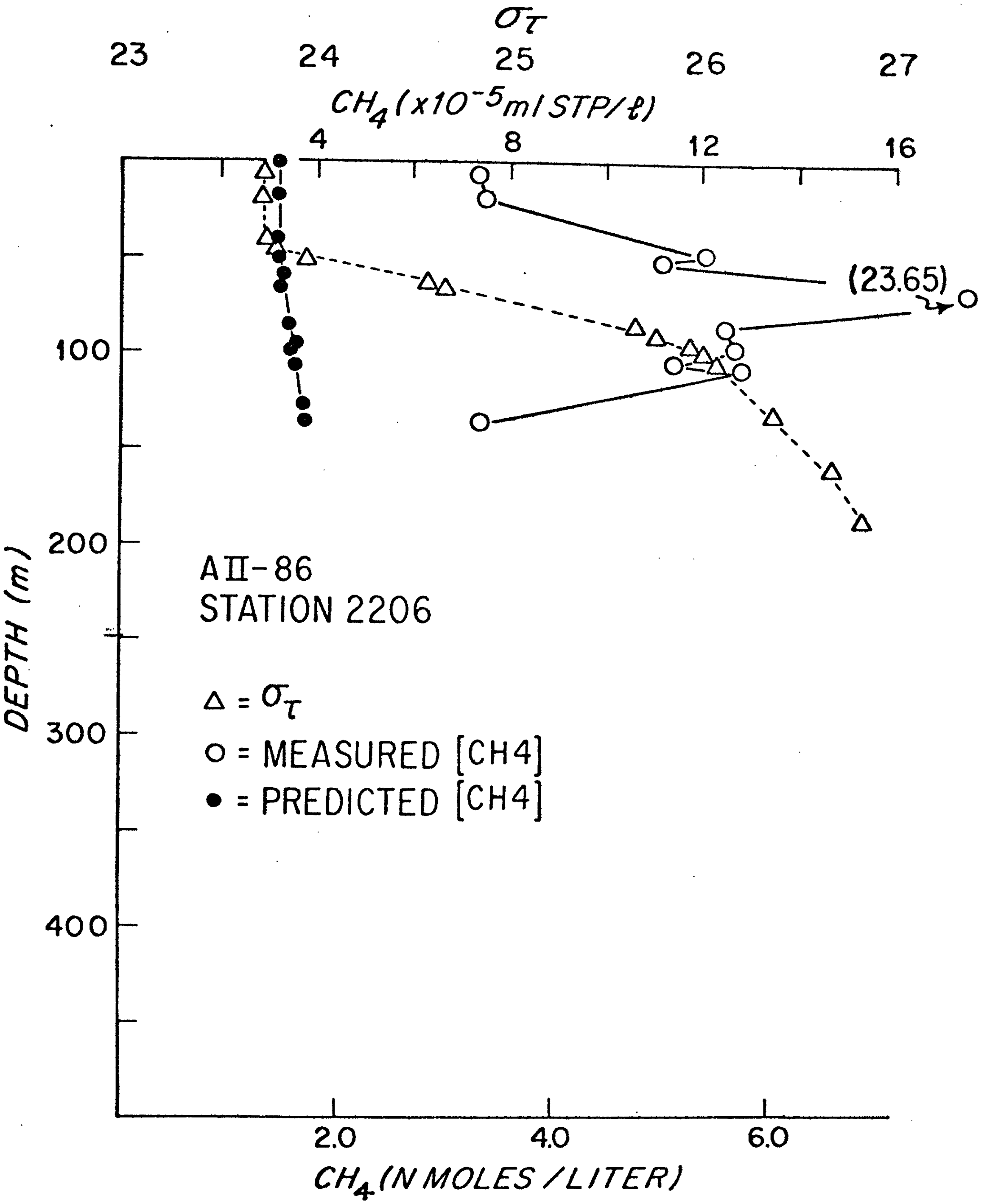

Figure IV.4. Vertical profile of methane concentration and σ_t at station AII86-2206. Predicted concentrations are those calculated from temperature and solubility data and are based on the assumption that the atmospheric methane concentration is 1.3 ppmv.

a conservative tracer

and z = depth (where $z = 0$ at the depth of the maximum and z is positive upward).

A solution to this equation is

$$C = C_0 + C_1 \exp(-K_v \pi^2 x/4L^2 u) \cos \pi z/2L$$

where L = depth scale (50 m).

Station AII86-2206, the station closest to the shore and exhibiting the highest methane concentration, is taken to be the source in the model (in other words, at $x = 0$, the methane distribution is as at station AII86-2206). A "background" methane concentration can be estimated by averaging the methane concentration at either 300 m or near the surface. Both estimates give C_0 equal to 2.3 nmole/l. This number has no apparent physical basis in a model involving only physical transport, but we have assumed arbitrarily that some outside force maintains the methane concentration at this level. Thus C_1 equals 8.3 nmole/l, the difference between the measured concentration and "background" at $x = 0$, $z = 0$. Table IV.1 shows some calculated values of C at $z=0$ for different values of K_v and u at several distances from the source. Table IV.1 also indicates that $K_v/u = 0.5$ cm gives reasonable agreement between the calculated concentration and the observed values. The fit is not excellent but considering the errors in the model and the fact that the parameters used are within the range of values considered appropriate for the circumstances, the model suggests that advective transport could supply some methane to the maximum at station AII86-2193, 1000 km from the coastal source.

TABLE IV.1

A COMPARISON OF SOME CALCULATED AND MEASURED METHANE CONCENTRATIONS IN THE WESTERN SUBTROPICAL NORTH ATLANTIC

Model: $C = C_0 + C_1 \exp(-K_V \pi^2 x/4L^2 u)\cos \pi z/2L$

or

$C = 2.3 + 8.3 \exp(-K_V \pi^2 x/10^8 u)\cos \pi z/10^4$

and at the maximum, $z = 0$ so $\cos \pi z/10^4 = 1$

K_V/u	x	calculated C	measured C	Sta. No.
0.1 cm	2.5×10^7 cm	8.8 nmole/l	3.14 nmole/l	2204
	5.0×10^7	7.4	3.21	2202
	1.0×10^8	5.4	2.82	2193
0.3	2.5×10^7	6.2	3.14	2204
	5.0×10^7	4.2	3.21	2202
	1.0×10^8	2.7	2.82	2193
0.5	2.5×10^7	4.7	3.14	2204
	5.0×10^7	3.0	3.21	2202
	1.0×10^8	2.4	2.82	2193
1.0	2.5×10^7	3.0	3.14	2204
	5.0×10^7	2.4	3.21	2202
	1.0×10^8	2.3	2.82	2193

However this model has a number of highly generous assumptions within it. Firstly, the methane distribution at x = 0 is not a perfect fit to a cosine function as suggested. Secondly, the above calculation uses u positive in the positive x direction (in other words from west to east). According to data of Mazeika (1973) the currents actually tend to flow from east to west through the BOMEX region (a square extending from about 50°W to 60°W and from 7°N to 18°N). This also agrees with the water movements discussed by Worthington (1976). Thus the coasts of the Lesser Antilles and South America may not be appropriate as near-shore source regions for the central subtropical Atlantic.

Thirdly, the importance of methane oxidation has been ignored. Observations have shown (Chapter VI) that water below 400 to 500 m in the ocean is undersaturated with respect to solubility equilibrium with the atmosphere. In fact, Lamontagne et al. (1973) have reported concentrations as low as 10% of equilibrium in the deep Pacific. Since the deep waters of the oceans were once in contact with the atmosphere and presumably in equilibrium with it, these observations suggest that methane oxidation is indeed important and, as discussed in Chapter VI, is probably most important in near-surface waters containing readily oxidizeable organic matter. Methane oxidizing bacteria have been observed in the ocean (Weaver, personal communication, 1974) and presumably are the agents of methane consumption. Thus the estimate presented for the importance of physical transport can only give an upper limit for a predicted concentration since consumption terms have been ignored.

Finally, the 50% supersaturation relative to solubility equilibrium, present in surface waters at every station, is not explained by the model. In order to give the most optimistic evaluation for the physical model, it was assumed that the supersaturation was maintained by an external process, presumably not related to physical transport. Thus even if physical processes can supply some methane to the open ocean maximum, an additional source must still be postulated.

2. *In situ* Production

The physical transport model presented in this chapter was designed to provide a generous estimate of the contribution physical processes could make to the methane budget of the mixed layer of the open ocean. From the above discussion, while it seems possible that some methane may be supplied from coastal waters, an *in situ* source must also be postulated. The nature of this source is discussed in more detail in Chapter V.

Several observations support the *in situ* production hypothesis. First consider the methane distribution of station AII86-2197. In Appendix IV.1 it can be seen that there is a methane maximum present at this station within a surface layer well mixed with respect to density. Although the maximum is only represented by a single point, profiles made by Lamontagne and coworkers (personal communication, 1974) show similar features-very narrow maxima in well mixed surface layers. A rapid *in situ* mechanism is required to maintain a maximum in such a situation where diffusive loss would be expected to be very fast.

The second line of evidence for *in situ* production of methane comes from a consideration of the source of the methane being lost to the atmosphere due to the supersaturation of surface waters with respect to the atmosphere. If physical transport of methane to the maximum were the source for all the excess methane in the surface waters of the western subtropical North Atlantic, the amount of methane diffusing away from the maximum into the mixed layer should equal the amount of methane being lost to the atmosphere. An imbalance would suggest that methane is being supplied at all depths above the maximum by an <u>in situ</u> process.

One can estimate the flux of methane away from the maximum by using a Fickian diffusion model where the flux, F, equals $K_v \frac{\Delta C}{\Delta z}$, where K_v is the vertical eddy diffusion coefficient and $\frac{\Delta C}{\Delta z}$ is the methane gradient. The fluxes calculated will be lower limits since methane consumption by methane oxidizers is being ignored. A reasonable estimate for K_v can be made from the data of Rooth and Ostlund (1972). These workers have found that K_v equals 0.2 to 0.3 cm^2/sec in the upper thermocline. (This value of K_v may serve as an upper estimate since it was calculated for the entire thermocline, and not for the narrow region of very high density contrast under investigation here.) Using the profile in Figure IV.5 (station AII86-2186) as an example, the upward flux from the maximum into the mixed layer is

$$F = K_v \frac{\Delta C}{\Delta z} = 4.1 \text{ nmole methane/cm}^2\text{/yr.}$$

This flux can now be compared with the loss of methane to the atmosphere across the air-sea interface.

The air-sea flux is determined by the extent to which the surface waters are supersaturated with respect to equilibrium with the atmosphere. A comparison of the measured and predicted methane concentrations as presented in Appendix IV.1 shows that open ocean surface waters in the subtropical North Atlantic contain methane excesses of from 48% to 67%.

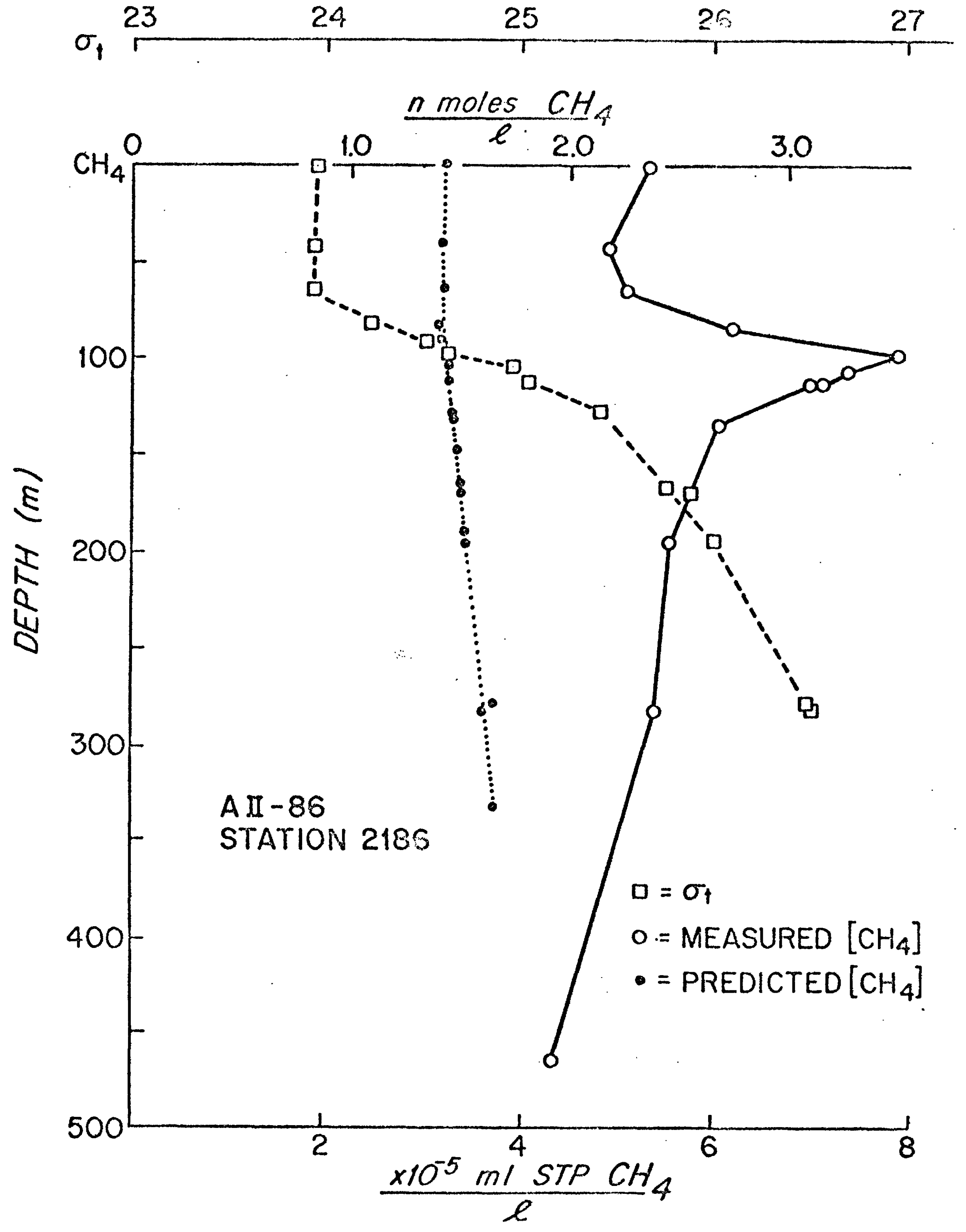

Figure IV.5. Vertical profile of methane concentration and σ_t at station AII86-2186. Predicted concentrations are those calculated from temperature and solubility data and are based on the assumption that the atmospheric methane concentration is 1.3 ppmv.

Lamontagne et al. (1973) found slightly lower excess methane levels.

Using an excess methane value of 0.93 nmole/l for station AII86-2186, the air-sea flux can be calculated from the thin film model described by Danckwerts (1970) and as discussed in Appendix I.1. An average film thickness of 50 μm was estimated using the wind speed/film thickness relationship of Emerson (1975) and an average wind speed of approximately 15 miles/hr as estimated from the ship's log. Using a diffusivity, D, appropriate for methane at an average temperature of 25°C (Witherspoon and Bonoli, 1969), the flux out of the sea surface is calculated to be

$$F = \frac{(C - C_{eq})D}{z} = 84 \text{ nmole methane/cm}^2\text{/yr.}$$

Clearly there is a large discrepancy between the flux to the mixed layer from the maximum (4 nmole/cm^2/yr) as compared to the loss to the atmosphere (84 nmole/cm^2/yr). This further supports the theory that physical transport is unimportant compared to in situ production.

D. Caribbean

During the second half of cruise 86, leg 2 of the R/V ATLANTIS II, five methane profiles were taken in the Caribbean (see cruise track, Figure IV.1). The data for these stations are presented in Appendix IV.1 and those for station AII86-2213, a typical station, are plotted in Figure IV.6. The most obvious characteristic of these profiles is that they are less smooth and have less well-defined maxima than the profiles made in the Atlantic. Also concentrations at several of the stations are considerably higher than observed in the Atlantic. One of the reasons for this may be the abundance of upstream shallow water regions (islands and the continental shelf of South America). These near-shore environments might be expected to have organic rich sediments in which

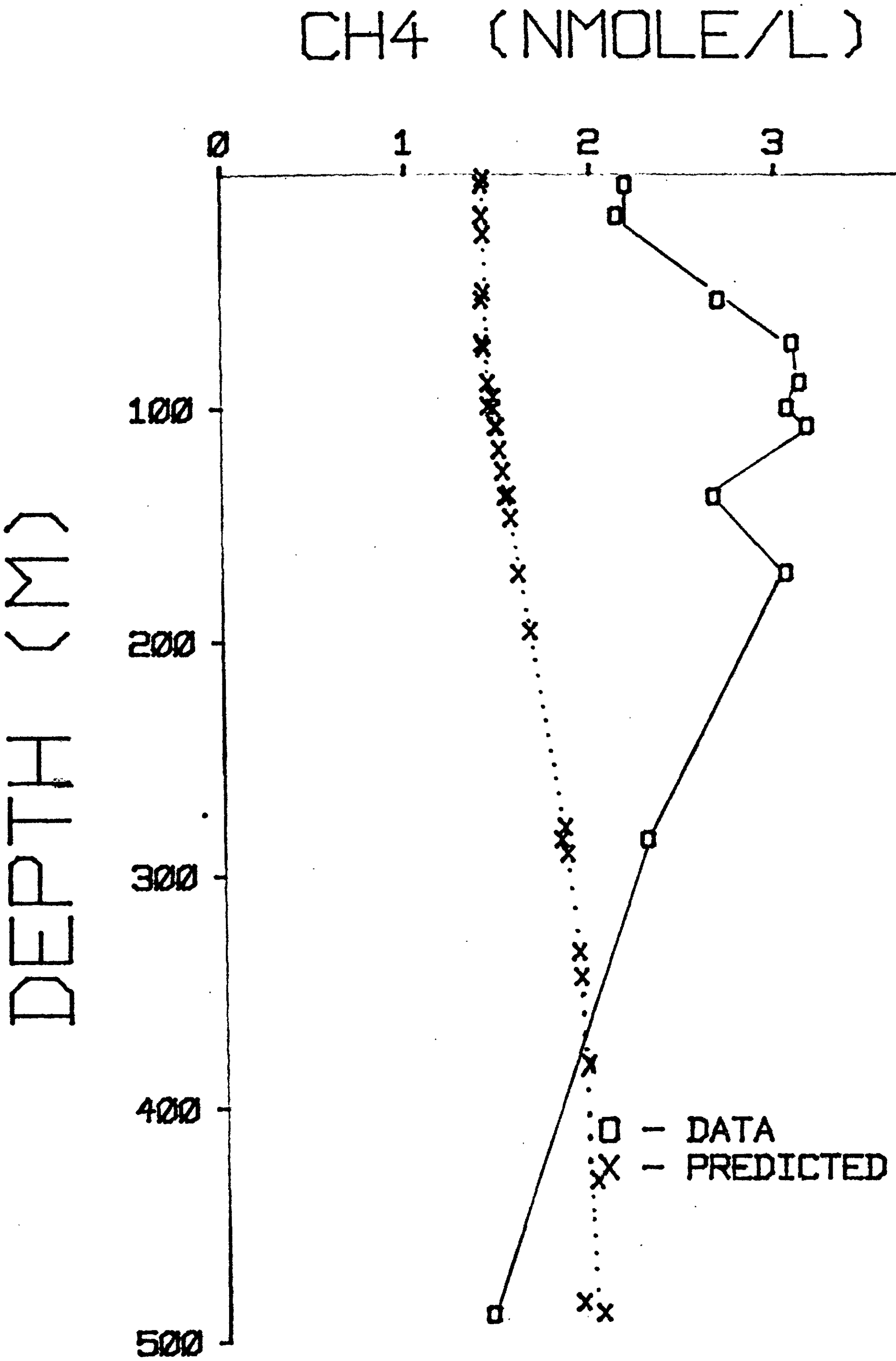

Figure IV.6. Vertical profile of methane concentrations at station AII86-2213. Predicted concentrations are based on solubility data and on an atmospheric methane concentration of 1.3 ppmv.

methane production is occurring. Then the methane-rich water could be carried offshore by currents. Such a phenomenon would explain the fact that the concentrations were higher for those stations nearer shore (stations AII86-2213, AII86-2220 and AII86-2222) than for the station in the center of the Caribbean (AII86-2216). The presence of maxima below the euphotic zone (for example at station AII86-2213) suggests that some of the high methane values may be related to advective features. Alternatively the coastal regions might be serving as nutrient sources and higher productivity may occur in near-shore regions than that observed in the open Caribbean. If methane production is related to productivity this process might also contribute to higher coastal methane concentrations.

Ortega (1972) has shown that there is an eddy in the eastern Caribbean at about the density of the salinity maximum, which would cause coastal waters to be carried offshore toward stations AII86-2220 and AII86-2222. Also station AII86-2213 is shown to be downstream from the Lesser Antilles. The extremely high values observed at station AII86-2233 are harder to explain on the basis of Ortega's acceleration potential plot, but could be due to the influence of the Venezuelan shelf, the Cariaco Trench or the Netherlands Antilles. Advective processes might be expected to extend coastal influence much further from shore than is predicted by the eddy diffusion model described for Walvis Bay in Chapter III.

Although physical transport processes may be important for the methane distribution in the Caribbean, especially in the near-shore regions, the biological processes which influence the distribution in the subtropical North Atlantic and in Walvis Bay are probably operating as well. This may be one of the reasons that the profiles are more complicated in the Caribbean than in the open ocean. The inland sea environment may be strongly influenced by both biological and physical processes, which then become difficult to separate.

If advective supply to the methane maximum is the source for the mixed layer methane excess, then the flux of methane from the maximum to the mixed layer should be greater than or equal to the flux of methane into the atmosphere across the air-sea interface as discussed earlier with respect to the subtropical North Atlantic. Taking station AII86-2213 (Figure IV.6) as a typical example of the Caribbean profiles, the flux from the maximum to the mixed layer is

$$F = K_v \frac{\Delta C}{\Delta z} = 1.26 \text{ nmole/cm}^2\text{/yr}$$

using the same value of K_v as was used for the subtropical Atlantic, and the methane gradient between 53 and 72 m.

In comparison the air-sea flux is 69.3 nmole methane/cm^2/yr. As was the case in the subtropical Atlantic, the flux from the maximum is considerably less than the air-sea flux indicating that an additional in situ process is probably present.

E. Conclusions

Near-surface methane data from the western subtropical North Atlantic and Caribbean indicate the consistent presence of high surface concentrations and methane maxima lying directly above the steep portion of the density gradient. Calculations show that horizontal physical transport may supply some methane to the open ocean from near-shore waters enriched in methane. However the loss of methane from the surface of the ocean is so much larger than the supply of methane to the mixed layer from the methane maximum that an *in situ* biological process is clearly of considerable importance.

CHAPTER V

LABORATORY CULTURE EXPERIMENTS

In Chapters III and IV, it has been shown that methane production occurs within the surface waters of the open ocean. Because of the strictly anaerobic environment required by methane producing bacteria (Stadtman, 1967; Wolfe, 1971; Mah _et al_., 1977; Zeikus, 1977) it appears unlikely that such organisms could survive unprotected in highly oxygenated ocean waters. To explain the occurrence of methane production in the mixed layer, it is necessary either to identify habitats in which methanogens can survive or to postulate a new process for methane formation.

One mechanism by which methanogens might survive in a macroscopically aerobic system would be to exist within reducing microenvironments (perhaps inside dead cells or fecal pellets). In order for such an environment to exist within an aerobic system, there must be active oxygen removal within the outer portions of the particle. Jørgensen (1977) has shown that, in oxygen saturated seawater, a microenvironment of a composition similar to a fecal pellet would have to be between 100 μm and 1 to 2 mm in diameter to have a totally anoxic center. In seawater, sulfate reducing bacteria, as well as methanogenic bacteria, would probably be present within the anoxic zone. (Sulfate reduction occurs in anaerobic microenvironments in the sediments as discussed by Jørgensen (1977) and as is shown by the presence of pyritized organic-rich particles in macroscopically aerobic sediments (Berner, 1969).)

Evidence from a number of workers (Winfrey and Zeikus, 1977;

Ferry, personal communication, 1977) suggests that sulfate reducers may effectively outcompete methanogens for hydrogen as an electron donor in natural environments. This results in a drastic reduction in methanogenesis in the presence of sulfate reduction. However, data of Winfrey and Zeikus (1977) show that some methane production does continue to occur. The source of this methane is unknown, but may be either methanogenic bacteria or sulfate reducers which produce methane as a trace byproduct (Postgate, 1969).

It can be shown that methane production in fecal pellets is unlikely to be a significant source of methane for the mixed layer. Bishop (1977) has shown that, at a station in the equatorial Atlantic, the flux of fecal pellets past 400 m is about 0.9 g fecal pellet/cm^2/1000 years. Bishop (1977) presents data indicating that the mean diameter of these fecal pellets is about 100 μm, and that fecal pellet densities are about 1.5 g/cm^3. Thus it can be calculated that about 3 fecal pellets per day per cm^2 sink through the 400 m depth horizon. At a sinking velocity of 100 m/day (Smayda, 1969; Turner, 1977), there would be an average of three fecal pellets in each 100 m x 1 cm^2 volume of water, or three per 10 liters. Romesser and Balch (Taylor, personal communication, 1977) have measured a methane production rate of 50 ± 50 nmole methane/cm^3/day in the sediments of Little Sippewissett Marsh, a marine system in which oxygen and sulfate are present, and which therefore may mimic to some extent a reducing microenvironment. Using this methane production rate and assuming that fecal pellets are completely anoxic (an unrealistically generous assumption), the supply of methane by the fecal pellets to the mixed layer would be 7.9×10^{-6} nmole/l/day or 2.9×10^{-3} nmole/l/yr. The production in a 100 m thick mixed layer required to maintain the 80 nmole/cm^2/yr air-sea flux calculated for the western subtropical North Atlantic in Chapter IV would be 8 nmole/l/yr or four orders of magnitude larger than could be supplied by fecal pellets.

Nitrogen-fixing organisms which have their own active mechanisms for excluding oxygen, and any zooplankton which have reducing environments in their guts may be the most likely hosts for microenvironments of the sort necessary to maintain methane production.

An alternative methane source could be production of methane by microorganisms or algae as a metabolic byproduct. Macro- and perhaps microalgae produce CH_3Cl and CH_3I as well as other methylated compounds (Lovelock et al., 1973). Methane might be produced in association with these compounds or as a result of other incidental metabolic processes. Light attentuation measurements made by Clarke (1941) in the subtropical Atlantic indicate that one to two percent of the incident light is still available at the depth of the methane maximum in this area, and Raymont (1963) has shown that algae are still able to photosynthesize at these light levels.

The likelihood of trace methane production in organisms other than methane bacteria is supported by observations of trace methane production by biochemical pathways other than those used by methane bacteria. Postgate (1969) has found that sulfate reducing bacteria produce methane from the methyl carbon of pyruvate, a mechanism very different from that used by methane bacteria (Gunsalus et al., 1976). Thus it does not seem impossible that algal or other microbial incidental metabolism might yield traces of methane.

I have performed several experiments using cultures of marine algae to determine whether these organisms might be an important methane source. The algae used were <u>Thalassiosira pseudonana</u> (clone 13-1), a marine diatom, and <u>Coccolithus huxleyi</u> (clone BT-6), a coccolithophorid, both from Robert Guillard's culture collection. Both species are commonly found in the open ocean in temperate latitudes. Most work focused on BT-6 since it grew much more densely than 13-1.

Both cultures were tested for the presence of bacteria by inoculating the cultures in f/2 medium (Guillard and Ryther, 1962) enriched with 0.1% peptone, and by streaking the cultures onto plates made of the same medium solidified with 1% agar (Robert Guillard, personal communication, 1977). This is not a rigorous test and some heterotrophic bacteria may have been present in the cultures.

A. Experimental Details

The algae were grown in batch culture in 250 ml standard taper glass bottles which may be directly interfaced to the methane extraction system. f/2 medium (Guillard and Ryther, 1962) was prepared in large erlenmeyer flasks and autoclaved. 1.3 grams of sterile $NaHCO_3$ per liter were added to the medium after autoclaving to raise the pH and provide a carbon source for the algae. The sterile medium was dispensed into sterile culture bottles after addition of bicarbonate. Blanks consisted of uninoculated medium.

Enough algae were added to each culture bottle to provide an initial cell density of about 10^4 cells/ml. The cultures and blanks were tightly stoppered with standard taper ground glass stoppers and were placed in an incubator at 23.5°C and about 2000 foot candles (14 hour day, 10 hour night cycle) for periods of up to two weeks. The bottles were shaken daily. After a period of incubation, a direct cell count was made on a subsample of the culture and methane analyses were performed on the remainder (medium plus cells).

B. Results and Discussion

For both 13-1 and BT-6 cultures, significantly more methane was present in the culture medium after several days of incubation than was present in the blanks. The results from a representative experiment run with a BT-6 culture are shown in Table V.1 and Figure V.1. The increase in methane in each culture bottle was calculated as discussed in Appendix V.1. During the first few days of incubation, methane contents were not significantly different from those in the blanks. The occurrence of negative ΔCH_4 values reflects measurement and calculation errors of the order of ± 0.3 nmole. In all experiments performed with algae and f/2 medium, the methane content in the cultures at the end of a week of incubation was higher than that found in the algae-free blanks. Frequently, toward the end of the incubation period, the calculated ΔCH_4 decreased slightly and then remained constant. If the algae cease producing methane as they go into stationary phase, the apparent methane decrease in ΔCH_4 may simply reflect a decrease in the concentration in the liquid phase caused by a slow gas exchange rate between the gas and liquid in the culture bottles.

Oxygen concentrations in the bottles were at equilibrium with the atmosphere at the start of each experiment, and the rapidly

TABLE V.1

METHANE PRODUCTION IN ALGAL CULTURES

f/2 medium

Day	Cell Number (cells/culture)	ΔCH_4 (nmole)
1	4.6×10^6	-0.42
2	9.4×10^6	0.07
3	2.4×10^7	0.12
4	4.8×10^7	0.27
5	1.1×10^8	0.94
6	1.7×10^8	1.68
7	3.0×10^8	1.50

f/2 medium, N/20

Day	Cell Number (cells/culture)	ΔCH_4 (nmole)
1	3.2×10^6	-0.15
3	3.2×10^7	0.33
4	(9.9×10^7)	0.54
5	7.0×10^7	0.54
6	9.6×10^7	0.27
7	1.4×10^8	0.35
8	1.6×10^8	0.39

f/2 medium, N/200

Day	Cell Number (cells/culture)	ΔCH_4 (nmole)
2	5.1×10^6	0.06
3	(2.1×10^7)	0.04
4	7.7×10^6	0.14
5	1.0×10^7	0.07
7	3.1×10^7	0.11

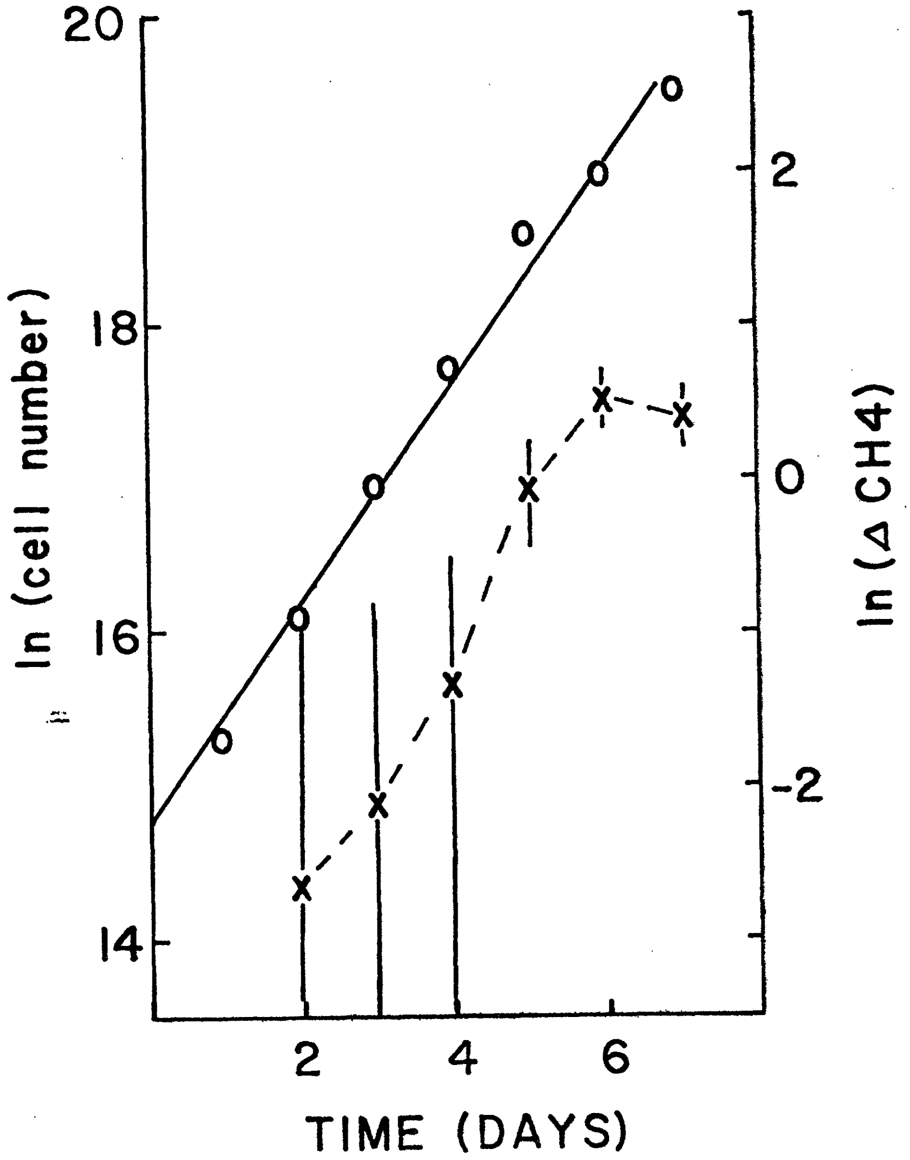

Figure V.1. Methane production in a culture of Coccolithus huxleyi. Note that the growth curve (o) and the methane curve (x) are approximately parallel after day 4 of incubation. The error bars give the ± 0.3 nmole uncertainty in ΔCH_4.

photosynthesizing algae produced more oxygen with time. In fact many of the dense cultures were positively pressurized, presumably due to large amounts of excess oxygen. It seems extremely unlikely that any anaerobic methane producing bacteria could survive in these systems. Thus it was hypothesized that the source of the methane was the algae, although the possible importance of heterotrophic bacteria cannot be completely excluded.

To test whether methane production was the result of algal metabolism, the change in methane content of the cultures and the total cell numbers in each culture were plotted against time (Figure V.1). Throughout the seven day incubation, the cultures appears to have been in exponential growth with a constant growth rate. A straight line fit to the plot of ln (cell number/culture) vs time gives a line with a slope equal to k ln 2 where k is the growth rate constant (day^{-1}). From Figure V.1, it can be determined that k for the culture under investigation was 1.02 day^{-1}. Also plotted in Figure V.1 is ln (ΔCH_4) against time where ΔCH_4 is the increase in methane content (nmole) in a culture bottle after a period of incubation (see Appendix V.1). As discussed by Taylor and Jannasch (1976), within the exponential growth phase, the rate of a metabolic function is proportional to the number of cells per unit volume. In the experiment under consideration, the total amount of methane produced after some period of time is measured. The equation appropriate to this situation is

$$TC = \frac{RN_0}{k\ \ln 2}\left(e^{kt\ln 2}-1\right)$$

where k = growth rate (day^{-1})

N_0 = initial cell number (cell/culture)

R = rate of methane production

($\text{nmole CH}_4\text{/cell/hr}$)

TC = total methane accumulated

(nmole/culture).

After approximately three generations ($kt \ln 2 \geq 3$), the rate of accumulation of methane should parallel the rate of increase of cell numbers if methane production is an algal metabolic process. In Figure V.1, it appears that this is indeed the case, as after day 4 (2.8 generations), the slope of the methane curve is approximately equal to that of the growth curve. By substitution of appropriate values into the above equation, a methane production rate of about 2×10^{-10} nmole methane/viable cell/hr was estimated.

To determine whether methane production is a major or minor metabolic pathway, it is of interest to compare the methane production rate to other rates obtained for important metabolic processes by other workers. Taylor and Jannasch (1976) obtained an oxygen consumption rate of 3×10^{-6} nmole O_2/viable cell/hr, a rate of incorporation of glutamate into cell polymers of 3.8×10^{-7} nmole/cell/hr and a rate of respiration of glutamate to CO_2 of 1.3×10^{-6} nmole/cell/hr for a marine bacterium. Ryther and Guillard (1962) determined an oxygen consumption rate of 3×10^{-7} nmole/cell/hr for _Thalassiosira pseudonana_ (a marine diatom). It appears that major metabolic processes occur at rates three to four orders of magnitude faster than does methane production.

An attempt was made to determine whether nutrient stress would cause the algae to produce methane at a greater rate than under optimum growth conditions. Cultures of BT-6 were inoculated into f/2 medium which had been prepared with 0.1 and 0.01 times the normal nitrogen content. The results from these experiments are also shown in Table V.1. Because the cultures were much less dense than those grown in f/2, it was not clear whether the rate of methane production (R) was the same in the two experiments. However, it was clearly not orders of magnitude higher in the low nitrogen case. This observation supports the contention that methane production is probably not the result of stress metabolism.

Due to the relatively low solubility of methane in water, most of the methane in the batch cultures was expected to be in the gas phase. Thus, in an attempt to increase sensitivity, an experiment was run in which ten ml of the gas phase, rather than the water, was analysed from each culture. The culture conditions were as described above except that butyl rubber, instead of ground glass, stoppers were used. Ten ml of seawater were injected into the culture by syringe before gas withdrawal to provide a positive pressure in the culture bottle.

The results from this experiment were quite surprising and are shown in Table V.2. There was no significant difference between the methane content in the gas phase in the blanks and cultures after a week of incubation. However when the water in the day 6 culture was analysed and compared to the day 6 blank, a significant difference in the

TABLE V.2

GAS SPACE ANALYSIS OF CULTURES

Day	Methane concentration (uninoculated medium)	Methane concentration (inoculated medium)
1	1.93 ppmv	1.66 ppmv
2	1.75	2.29
	1.89	
3	2.14	1.91
4	2.00	2.05
5	2.22	1.80
6	1.82	1.81
average	1.96 ppmv	1.92 ppmv

methane content was observed (3.27 nmole/l in the culture compared to 2.11 nmole/l in the blank).

It is known that a number of hydrocarbons are considerably more soluble in protein solutions than in water alone (Wishnia, 1962; Wishnia, 1963; Wetlaufer et al., 1964). In my work the cultures reached cell densities on the order of 10^6 cells/ml and undoubtedly contained very high organic carbon concentrations. Thus a solubility experiment was performed using dense (greater than 2 x 10^6 cells/ml) cultures of Coccolithus huxleyi (BT-6), medium to which no algae had been added, and distilled water. These solutions were equilibrated with standard gas containing 10 ppmv methane in nitrogen. The results are shown in Table V.3. The observed supersaturations are small (3-8%) and cannot be considered significant. Thus solubility anomalies cannot account for the observed increases in methane content in the liquid phase of a culture over that predicted from the gas phase methane concentrations.

It is apparent that gas exchange between the gas and liquid phases in the culture bottles was slow and that solubility equilibrium was not attained. During the gas-phase analysis experiment, the cultures were not vigorously shaken as was the common practice during the other culture experiments. Shaking was avoided in hopes of reducing methane supersaturations in the liquid. It appears that vigorous shaking is necessary to promote gas exchange.

To determine whether gaseous equilibrium was reached in the culture experiments in which the bottles were shaken, an experiment was

TABLE V.3

SOLUBILITY OF METHANE IN CULTURE MEDIUM

	Measured solubility (nmole/l)	Predicted solubility* (nmole/l)
Distilled water	13.87 14.00	13.37
Medium	11.72	10.88
Medium with algae	11.71 12.42 11.85	10.88

* Predicted solubilities are determined from the temperature and salinity of the water and the solubility data of Yamamoto _et al_. (1976).

performed in which seawater, equilibrated with air, was placed in 250 ml ground glass stoppered bottles and the gas phase was flushed with 10 ppm methane in nitrogen. Then the samples were tightly stoppered. Two samples were stirred using a magnetic stirring bar. The other samples were shaken vigorously one or more times to simulate the conditions in the culture experiments. Results are shown in Table V.4.

There is a considerable amount of scatter in the data, but it appears that shaking a sample vigorously at least twice produced a methane content in the liquid approximately equal to that which would be obtained by stirring. The concentration of methane in seawater in equilibrium with a gas phase containing 10 ppm methane is 10.88 nmole/l. It appears that none of the samples reached equilibrium during the few hours of the experiment; however, if the gas above the liquid was not completely replaced by the 10 ppm methane in nitrogen gas, a value lower than the predicted one would be expected. In any case it appears that two vigorous shaking episodes will significantly promote gas exchange in the culture vessels.

Equilibration was probably at least 70 to 90% complete during the culture experiments. However if significant gas exchange did not occur, the values for ΔCH_4 calculated in Appendix V.1 will be systematically too high. If the increase in methane in the liquid phase alone is considered (in other words, if it is assumed that no equilibration took place), the methane production rate calculated from the data is almost identical to that calculated earlier (2.9×10^{-10} nmole/cell/hr as

TABLE V.4

TEST OF SHAKING AS AN EQUILIBRATION TECHNIQUE

Sample treatment		Methane concentration (nmole/l)
equilibrated with air		2.4 ± 0.1
equilibrated with 10 ppmv methane in nitrogen		
stirred	(2 hours)	9.6 ± 0.5
	(3 hours)	8.4 ± 0.4
shaken	(1 time)	6.2 ± 0.3
	(2 times)	7.7 ± 0.4
	(3 times)	8.9 ± 0.4
	(3 times)	7.8 ± 0.4
predicted* for equilibration with 10 ppm methane in nitrogen		10.88

error estimates are ± 5%

* Predicted solubilities are determined from the temperature and salinity of the water and the solubility data of Yamamoto _et_ _al_. (1976).

compared to 2 x 10^{-10} nmole/cell/hr calculated assuming that equilibration occurred). This is due to the fact that the relative changes in methane content are very similar even though the absolute amounts differ by about a factor of three. Therefore a small degree of disequilibrium does not significantly alter the conclusions which can be made from the culture experiments.

If the methane production rate determined in these culture experiments is typical of that in oceanic algae, it is possible to compare the culture experiments to methane production rates estimated for the open ocean from data presented in Chapter IV. As was mentioned earlier in regard to the discussion about the importance of methane production in fecal pellets, methane production in the subtropical Atlantic must be about 8 nmole/l/yr to supply the methane lost across the air-sea interface. If we assumed a typical cell density in the open ocean of 10^3 cells/ml, the culture data would predict a production rate of 1.7 nmole/l/yr. These numbers are surprisingly close and suggest that, if the culture data indeed reflect algal methane production, this may be a significant methane source for the open ocean.

C. Summary

It seems improbable that methane production inside anaerobic microenvironments such as fecal pellets can be a major source of methane for the surface ocean. If zooplankton or larger organisms have anaerobic guts, these might prove to be habitats for anaerobic methane bacteria. Heterotrophic microorganisms may also produce trace amounts of methane.

In culture experiments performed as a part of this thesis, it has been shown that actively photosynthesizing algal cultures produce significant amounts of methane. The best explanation for the observed increases in methane content in the algal cultures appears to be that the algae themselves are producing methane, since the algal growth rates and the methane production rates are seen to be parallel. It appears that methane production is a metabolic process in algae. Further research in this area would profitably focus on algal cultures grown on medium sparged free of methane as one of the principal problems to date has been that relatively large amounts of methane were present in the medium at the start of the experiment. Laboratory and natural conditions are so different that it is difficult reliably to compare data from the two environments. However, the methane production rates calculated from the data presented here suggest that algae may be a significant oceanic methane source.

CHAPTER VI

METHANE CONSUMPTION IN THE DEEP OCEAN

One of the most interesting aspects of the marine geochemistry of methane is the presence of marked methane depletions at depths below about 500 m throughout the world's oceans. Similar distributions (high surface layer concentrations and low deep water concentrations) are observed for other organic compounds (sterols (Gagosian, 1976), dissolved combined amino acids (Lee and Bada, 1977)) and for other dissolved gases (oxygen, carbon monoxide (Seiler and Schmidt, 1974), possibly N_2O (Seiler and Schmidt, 1974), and ethylene (Swinnerton and Linnenbom, 1967a)). Of these, only oxygen has been studied in detail.

In this chapter I will present the methane data I have collected from the deep ocean (below 600 m) in conjunction with selected oxygen data. An attempt will be made to estimate the rates of methane and oxygen consumption based on interpolated $^3H/^3He$ and ^{14}C ages calculated from GEOSECS data. This discussion will assume that methane input only occurs at or near the air-sea interface. It is possible that gas seeps and/or anoxic sediments in deep waters may supply methane to the bottom waters as well. Such sources would be localized, and the methane introduced would probably be either rapidly oxidized by bacteria or rapidly mixed into the rest of the ocean. No evidence for this process is available from my data.

A. Methane Data

Deep water samples were collected from eight stations: four from the western North Atlantic, one from the eastern South Atlantic, one from the Caribbean, one from the Arabian Sea and one from the western North Pacific. All samples were poisoned immediately upon sampling. The samples were stored and analysed as discussed in Chapter II. The data from those samples which are not presented in the Appendices referring to the cruises on which the sample were taken are presented in Appendix VI.1. Most of these samples were analysed after some period of storage and, as noted in Chapter II, may therefore have been contaminated slightly. If any contamination (by air) has occurred, the results will be too high. As the discussion that follows is semiquantitative, inaccuracies of this sort will not change the arguments to be made.

B. Dating of Water Masses

An attempt has been made to estimate the water mass ages for both deep water methane and oxygen samples. For the South Atlantic, this was not possible due to the complex mixing occurring in this region and the lack of a well-defined initial value for the ^{14}C concentration in eastern South Atlantic bottom water. In addition the Oceanus 6 station was located very close to the continental margin, near the Gulf Stream, where North Atlantic GEOSECS data would not be expected to apply.

Thus the stations considered in the following discussion are stations KN51-716 and GEOSECS 3 (located just west of the Gibbs fracture zone), stations AII86-2193 and AII86-2204 at 19°N and 15°N respectively in the western North Atlantic, the suite of GEOSECS Atlantic stations for which Stuiver (1976) presents ^{14}C data, station AII86-2233 from the Caribbean, stations INDOPAC01-65D and GEOSECS 226 in the western North Pacific, and station AII93-2360 from the northern Arabian Sea.

Water mass ages were estimated in several ways. For station KN51-716, ages are based on $^3H/^3He$ ages determined for GEOSECS 3 as discussed by Jenkins and Clarke (1976). From these data it appears reasonable to assume an age of ten years for the entire water column below the main thermocline at GEOSECS 3. The age is certainly less than 25 years. Since KN51-716 is very close to GEOSECS 3, a ten year age has been assigned to all methane and oxygen samples from the deep waters at this station as well.

There were no GEOSECS stations close to AII86-2193 and AII86-2204 in the western subtropical North Atlantic. I have assigned an age of 150 years to the methane samples taken closest to the "Two Degree Discontinuity Water" (TDDW) as discussed by Stuiver (1976) and Broecker _et_ _al_. (1976). Oxygen data from the TDDW samples identified by Stuiver (1976) and Broecker _et_ _al_. (1976) were used directly with ages calculated from Stuiver's ^{14}C data and the assumption that the initial $\Delta^{14}C$ for TDDW was -80‰. The choice of age for the Caribbean deep water was based on the observation by Ribbat _et_ _al_. (1976) that Eastern Caribbean deep water has a turnover time, relative to exchange with the Atlantic, of 55 years. Thus the age of the deep water is between 55 and 200 years, since the deep water outside the Caribbean has an age of about 150 years (Stuiver, 1976).

Ages for station INDOPAC01-65D were calculated from ^{14}C data of Ostlund (unpublished data) from GEOSECS 226. Measured values of $\Delta^{14}C$ have been corrected for addition of ^{14}C by carbonate dissolution (Δ^{14}_{carb} assumed to equal -40‰) and by organic matter decomposition (Δ^{14}_{org} assumed to equal -80‰). Preindustrial prenuclear ^{14}C for the Pacific deep waters was assumed to be -50‰ and the preformed ΣCO_2 was assumed to equal 2076 μmole/l (Tsunogai, personal communication, 1976).

(The preformed ΣCO_2 represents the ΣCO_2 in very young Pacific deep water.) It has also been assumed that ages calculated for GEOSECS 226 are applicable to samples at the same depth at nearby INDOPAC01-65D. From Figure VI.1 it appears that this assumption may make the ages for INDOPAC01-65D systematically somewhat low; however, the errors in the age estimates are quite large. The ages used for the INDOPAC01-65D oxygens in Figure VI.1 are the same as are used for the INDOPAC01-65D methane samples in Figure VI.2. The age used for the deep Arabian Sea was derived from the calculations of Kuo and Veronis (1970) who obtained a model age of about 800 years for this region.

Figures VI.1 and VI.2 present plots of apparent oxygen utilization (AOU) and apparent methane utilization (AMU) versus calculated water mass ages for several stations. Also indicated are estimates of the errors both for concentration and for age.

Methane and oxygen data have been plotted from those depths at which it was felt that age estimates were relatively reliable. The value for apparent oxygen utilization calculated for the Caribbean station is based on the data of Ribbat et al. (1976) and is corrected for the entrainment of low oxygen water during the formation of bottom water. The oxygen concentration in the deep Arabian Sea appears to be extremely low (only 125 μmole/l) and may be influenced by the large overlying oxygen minimum. Therefore no point is plotted for this station in Figure VI.1. Additional methane data from other depths and from undated stations support the trend seen in Figure VI.2.

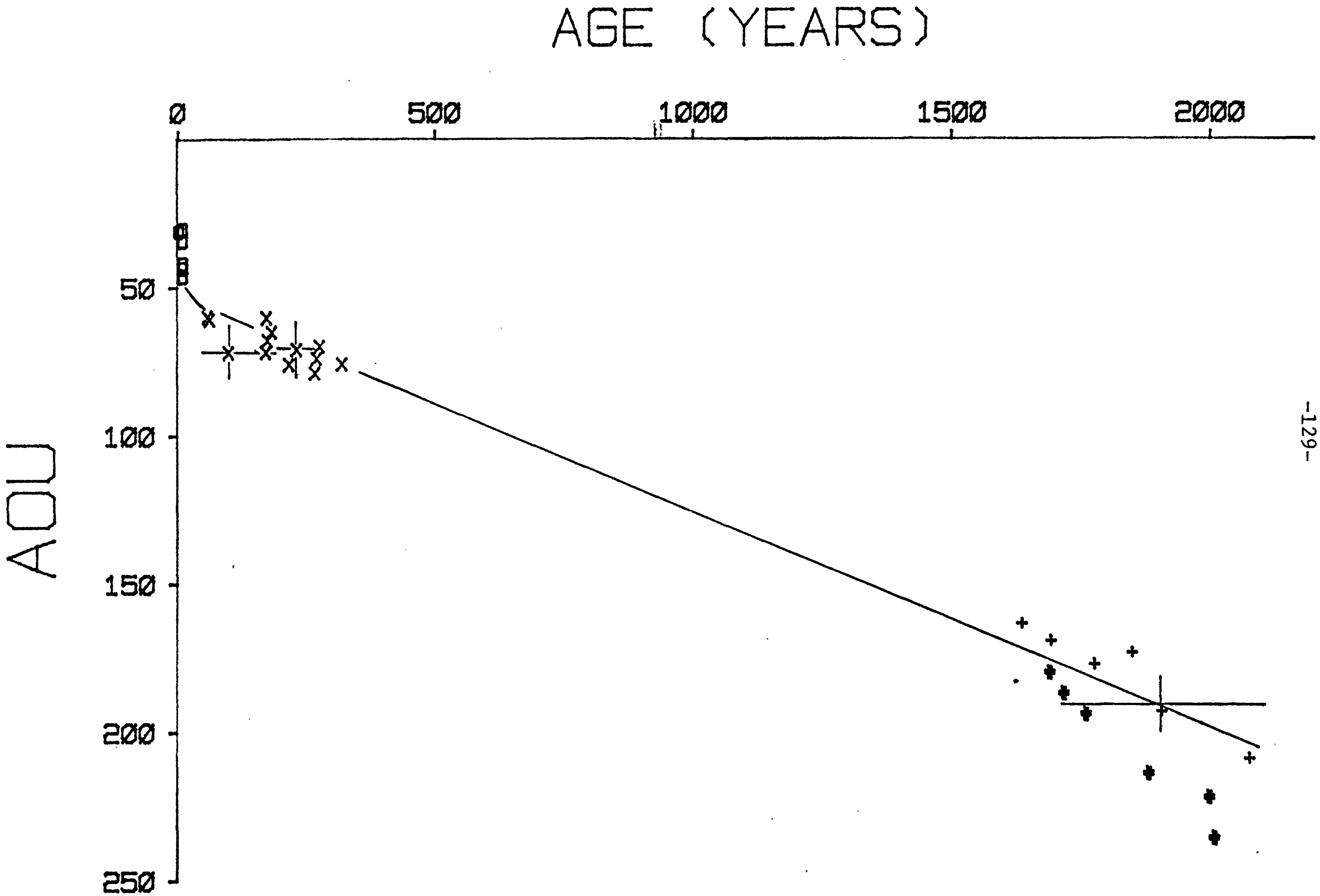

Figure VI.1. Apparent oxygen utilization (AOU) as a function of water mass age. ◻ = KN51-716; x = Atlantic GEOSECS stations; + = GEOSECS 226 (Pacific); # = INDOPAC01-65D.

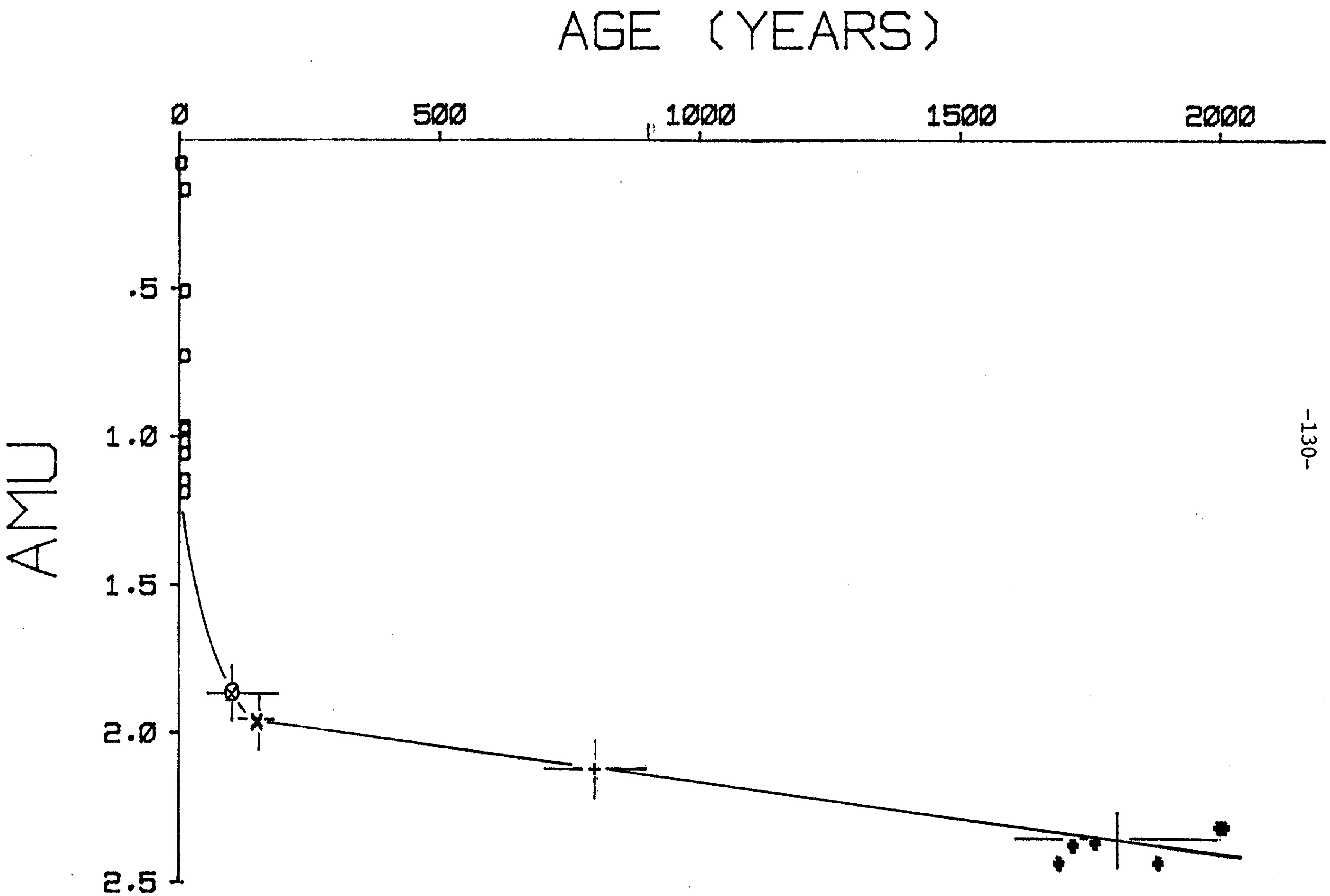

Figure VI.2. Apparent methane utilization (AMU) as a function of water mass age. □ = KN51-716; x = AII86-2193 and AII86-2204; ⊗ = AII86-2233; + = AII93-2360; # = INDOPAC01-65D.

C. Oxygen Utilization Rates

The availability of oxygen data from dated water masses makes it possible to obtain estimates of oxygen utilization rates. The plot of oxygen utilization versus age (Figure VI.1) gives results which are quite consistent with those obtained by other workers using a variety of methods. A line drawn by eye through the oxygen data yields a slope of 0.29 μmole/l/yr (6.5×10^{-3} ml/l/yr). Table VI.1 gives the rates of oxygen utilization calculated by other workers for both the deep waters and for intermediate depths, together with the rate calculated here. In deep water the estimates of other workers range from 4.5 nmole/l/yr to 3.4 μmole/l/yr with most estimates clustered around 0.04 to 0.22 μmole/l/yr. The crude estimate made using the ^{14}C ages and oxygen utilization values shown in Figure VI.1 gives a consumption rate in this range.

Wyrtki (1962) has assumed that oxygen consumption rates decrease exponentially with depth. Jenkins (1977) has also found that much higher oxygen consumption rates occur in Sargasso Sea 18° water (8.9 μmole/l/yr) than at depth. In agreement with this, Figure VI.1 shows that oxygen utilization is much more rapid in young, shallow water than in older, deep waters. If the 10 year age is correct for the deep samples at KN51-716, the oxygen utilization up to this point is 50 μmole/l or 5 μmole/l/yr, twenty times greater than the oxygen consumption rate in the deep water.

D. Methane Utilization Rates

Figure VI.2 shows that, unlike oxygen, methane is consumed very rapidly at first, but that at an early stage, methane consumption becomes

TABLE VI.1

OXYGEN CONSUMPTION RATES

Reference	Oxygen Consumption Rate (μmole O_2/l/yr)	Water Mass	Method
Jenkins (1977)	8.9	18° water	$^3H/^3He$ dating
Riley (1951)	0.05 - 13.4	100 - 1700 m	box model
Craig (1971)	0.18	deep Pacific	one dimensional advection diffusion model
Williams and Carlucci (1976)	0.004 - 0.62	2000 m	laboratory pressure incubation
Packard *et al.* (1971)	0.9 - 17.8	euphotic zone	electron transport system-respiration rate correlations
	0.2 - 0.9	100 - 500 m	
	0.02 - 0.2	500 m	
Skopintsev (1976)	0.13	1000 - 4000 m	incubations at *in situ* temperatures
Sorokin (1972)	1.1 - 3.4	4000 m	*in situ* incubations
Holm-Hansen and Paerl (1972)	0.04 - 0.22	1000 - 4000 m	ATP-respiration rate correlations
this work (1977)	0.29	abyssal ocean	AOU vs water mass age correlations

very slow. Almost all of the methane consumption which occurs in the deep ocean seems to take place within the first hundred years of water mass isolation from the atmosphere. This conclusion is still valid even if the KN51-716 samples (which were stored for two weeks prior to analysis) were slightly contaminated with air. All the AII86 samples were run within hours of collection and thus are reliable. It is difficult to calculate consumption rates for methane because of the scarcity of data. If 1.5 nmole/l of methane is removed from the water within the first 25 years of water mass isolation, as is suggested by Figure VI.2, the minimum consumption rate in NADW near its source is 0.06 nmole/l/yr. The true consumption rate may well be higher.

Methane consumption does not appear to occur to a significant extent in older waters. In Figure VI.2, very little change in apparent methane utilization is observed between 150 and 2000 years.

E. Discussion

Both methane and oxygen are rapidly consumed in 'young' water. The oxygen consumption rate decreases with increasing water mass age, but continues at a low rate throughout the ocean. In contrast methane consumption almost ceases within about 100 years of water mass isolation. It is of considerable interest to try and identify any differences in consumption mechanism. Deep waters are cold and are at considerably higher pressures than are shallower water masses. Jannasch *et al*. (1976) and Wirsen and Jannasch (1975) have demonstrated that substrate uptake rates decrease at high pressures. High pressure and low temperatures seem to have a different effect upon O_2 uptake and consumption of organic compounds

(Taylor, personal communication, 1977). This agrees well with the observation that methane uptake almost ceases, while oxygen uptake continues, in the deep ocean.

Methane oxidizing bacteria have been extensively studied in culture and in freshwater systems (Whittenbury et al., 1970; Patt et al., 1974; Ribbons et al., 1970; Rudd et al., 1974; Weaver and Dugan, 1972; and many other workers). Some work has also been done in saline lakes (Jannasch, 1975) and in seawater (Hutton and ZoBell, 1949; Weaver, personal communication, 1974). However data for the deep ocean are not available.

It is possible that methane uptake by methane oxidizing bacteria in the ocean is directly affected by pressure and temperature. Patt et al. (1974) and Hazeu (1975) have demonstrated that methane oxidizers may also take up other organic compounds during growth, and it may be that pressure also adversely affects this process.

Finally, Patt et al. (1974) and Rudd and Hamilton (1975) have noted that methane oxidizers are inhibited by the presence of high oxygen concentrations. Rudd et al. (1974) have shown that a requirement for low oxygen concentrations (less than 30 μmole/l) can be overcome if high nitrogen concentrations are present. It is difficult to know how applicable data from shallow freshwater lakes, where oxygen is less than 30 μmole/l, nitrate is about 40 μmole/l and methane is about 5 μmole/l, are to deep ocean systems where oxygen concentrations are 100 to 200 μmole/l, nitrate concentrations are 20 to 40 μmole/l, and methane concentrations are less than 1 nmole/l. At very low substrate levels, the absence of methane consumption in deep waters may simply reflect the fact that methane oxidizing bacteria are unable to grow at the methane concentrations found there (Jannasch, 1967). (Lee and Bada (1977) have suggested that constant low concentrations of dissolved combined amino acids in the Sargasso Sea also represent concentrations below a threshold value.)

One intriguing possibility supported by these sketchy data is that organic compounds exhibit variable rates of oxidation and attain characteristic minimum concentrations in the deep sea. Methane is oxidized by a relatively small class of organisms. Oxygen is utilized by many organisms. It may prove possible to constrain removal mechanisms for other organic compounds by systematically investigating their abyssal concentrations. It may also be possible to determine relative labilities. However this work points out the great need for data in "new" water masses, as concentrations of organic compounds may rapidly approach limiting values as the water mass ages.

CHAPTER VII

METHANE IN ANOXIC BASINS

Methane is present in anoxic basins in large quantities indicating that methane producing bacteria are active in such environments. There is also some evidence that methane oxidation occurs in anoxic basins. A number of workers (Martens and Berner, 1977; Barnes and Goldberg, 1976) have postulated that methane consumption by sulfate reducing bacteria is an important process in anoxic marine sediments. Reeburgh (1976) has suggested that this type of methane consumption is also important for the geochemistry of methane in the water column of the Cariaco Trench.

This chapter presents new methane data for the Cariaco Trench and the Black Sea which appear to be significantly more precise and accurate than previously available data. A one-dimensional advection diffusion model and a box model will be applied to these data in an attempt to confirm or refute the occurrence of anaerobic methane consumption.

A. The Black Sea

The Black Sea is the largest of the world's anoxic basins. It is almost completely isolated from the Mediterranean, with only a connection through the Bosporus (sill depth, 34 m-Gunnerson and Öztürgut, 1974) and the Dardanelles. Through this passage saline Mediterranean Sea water flows into the deep waters of the Black Sea while relatively fresh Black Sea water flows out at the surface. Some mixing between the inflow and outflow occurs during the passage through the Bosporus. The annual inflow from the Mediterranean has been estimated to be between 328 km^3 (Merz and Möller, 1928) and 0 km^3 (Ullyott and Ilgaz, 1946).

The value used previously in modelling discussions and considered to be the best estimate is 190 km^3/yr (Merz and Moller, 1928; Spencer and Brewer, 1971). The inflow is considerably more saline than the Black Sea deep water which has an average salinity of 20 to 22‰. Thus the inflow sinks and mixes with water in the basin at depths from 300 to 1700 m (Ostlund, 1974). The stability of the basin waters is controlled primarily by the salinity gradient as the temperature gradient becomes negative in winter (Brewer, 1971).

1. Sample Collection

In April, 1975, eighteen samples were taken for methane analysis in the Black Sea on cruise 120 of the R/V CHAIN (station CHAIN120-1355 at $42^{o}48'$N $33^{o}01'$E). These samples were taken in bottles with greased ground glass stoppers and were poisoned with mercuric chloride. The stoppers were firmly inserted and securely taped with electrical tape, and the samples were then kept refrigerated for two months until the ship returned to Woods Hole. The analyses were performed by a modification of the method developed by Swinnerton et al. (1962a, b) as described in Chapter II. For the methane-rich deep waters, instead of transferring the sample under methane free helium into the stripper, small volumes of liquid were removed from the sample bottles using gas tight syringes. The needle was placed as deeply into the water as was practicable, to reduce the possibility of sampling water which had been in contact with the atmosphere. The sample was then injected into the stripper through a serum stopper provided in the top of the the stripper. In this manner the amount of methane treated by the analytical method varied by only three orders of magnitude, a range over which the trapping efficiency of the system was known.

The methane data are presented in Figure VII.1 and in Appendix VII.1. The samples at 735 m and 1764 m, which appear to be low, both were in bottles which had very loose stoppers and have been ignored. As was discussed in Chapter II, it is not good practice to store methane samples with such high methane concentrations. Thus it is possible that all of the measurements are low. Some methane data from the Black Sea have been collected by others workers and are available for comparison (Hunt, 1974; Bagirov et al., 1973; Atkinson and Richards, 1967). Hunt's data are extremely noisy, while Bagirov et al. (1973) present their data in ambiguous units which cannot be reconciled with my data. Atkinson and Richards (1967) obtained methane concentrations of 10 μmole/l in the deep Black Sea, in close agreement with the data presented here.

2. Discussion of Data

The most common approach for the interpretation of data from anoxic basins has utilized a one-dimensional vertical advection diffusion model (Craig, 1969; Wyrtki, 1962). In this model horizontal advection and diffusion are ignored because horizontal concentration gradients are assumed to equal zero, and vertical eddy diffusion, vertical advection and in situ production or consumption are assumed to be the processes controlling the distribution of any chemical species in a steady state system. Boundary conditions are determined from the concentrations observed at the top and bottom of the mixing interval. Mathematically the model can be written as follows:

$$\frac{\partial C}{\partial t} = K_v \frac{\partial^2 C}{\partial z^2} - w \frac{\partial C}{\partial z} + J = 0$$

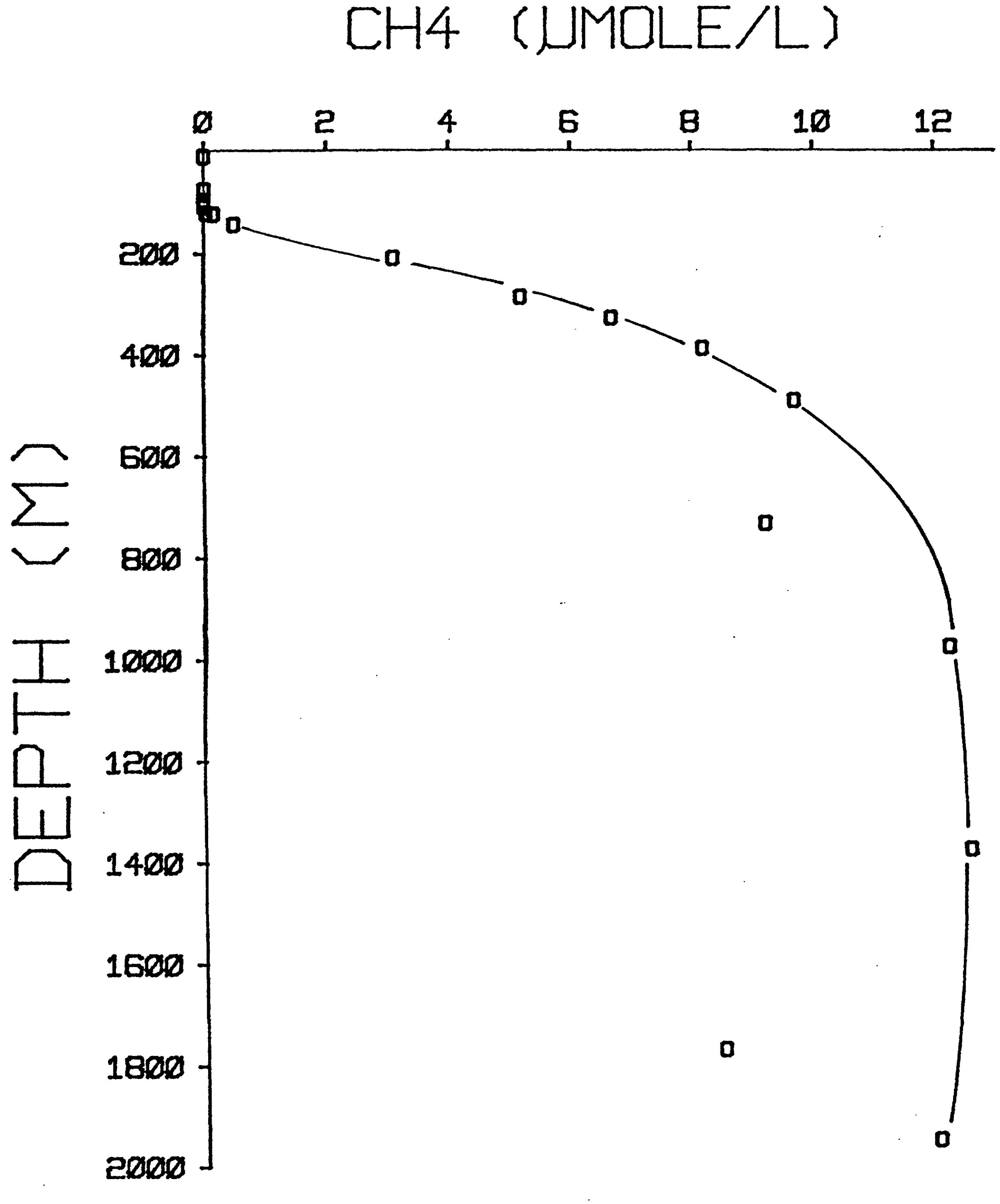

Figure VII.1. Methane profile at station CHAIN120-1355 in the Black Sea. The samples at 735 m and 1764 m are in error due to loose stoppers.

where C = concentration

K_v = vertical eddy diffusion coefficient

w = vertical advection velocity

J = *in situ* production or consumption rate

and z = depth.

A number of workers (Brewer and Spencer, 1974; Spencer and Brewer, 1971; Wong and Brewer, 1977; Brewer and Murray, 1973) have discussed data from the Black Sea in terms of this one dimensional advection diffusion model. The region of the water column modelled was the linear portion of the temperature-salinity regime between a salinity of 19.6‰ and of 21.7‰, or, in the case of species which are strongly affected by variations in the bacterial populations and by redox conditions, between the oxygen-sulfide interface and 21.7‰ salinity. In Figure VII.2 the methane data from the Black Sea are plotted together with the curves predicted from the one-dimensional model, first with $J = 0$ and second assuming that methane is consumed within the mixing zone. The predicted consumption rate, assuming a vertical advection velocity, w, of 0.5 m/yr (Spencer and Brewer, 1971) is $J = -15$ nmole methane/l/yr. Thus the model predicts that methane is being consumed within the anoxic zone of the Black Sea. This predicted consumption is a balance between methane production by anaerobic methane producing bacteria and consumption by some other process. All known methane oxidizers are obligately aerobic (Ribbons *et al*., 1970). However considerable geochemical evidence (Martens and Berner, 1977; Barnes and Goldberg, 1976) and a little bacteriological evidence (Davis and Yarbrough, 1966; Hanson, personal communication, 1976) is available suggesting that methane is

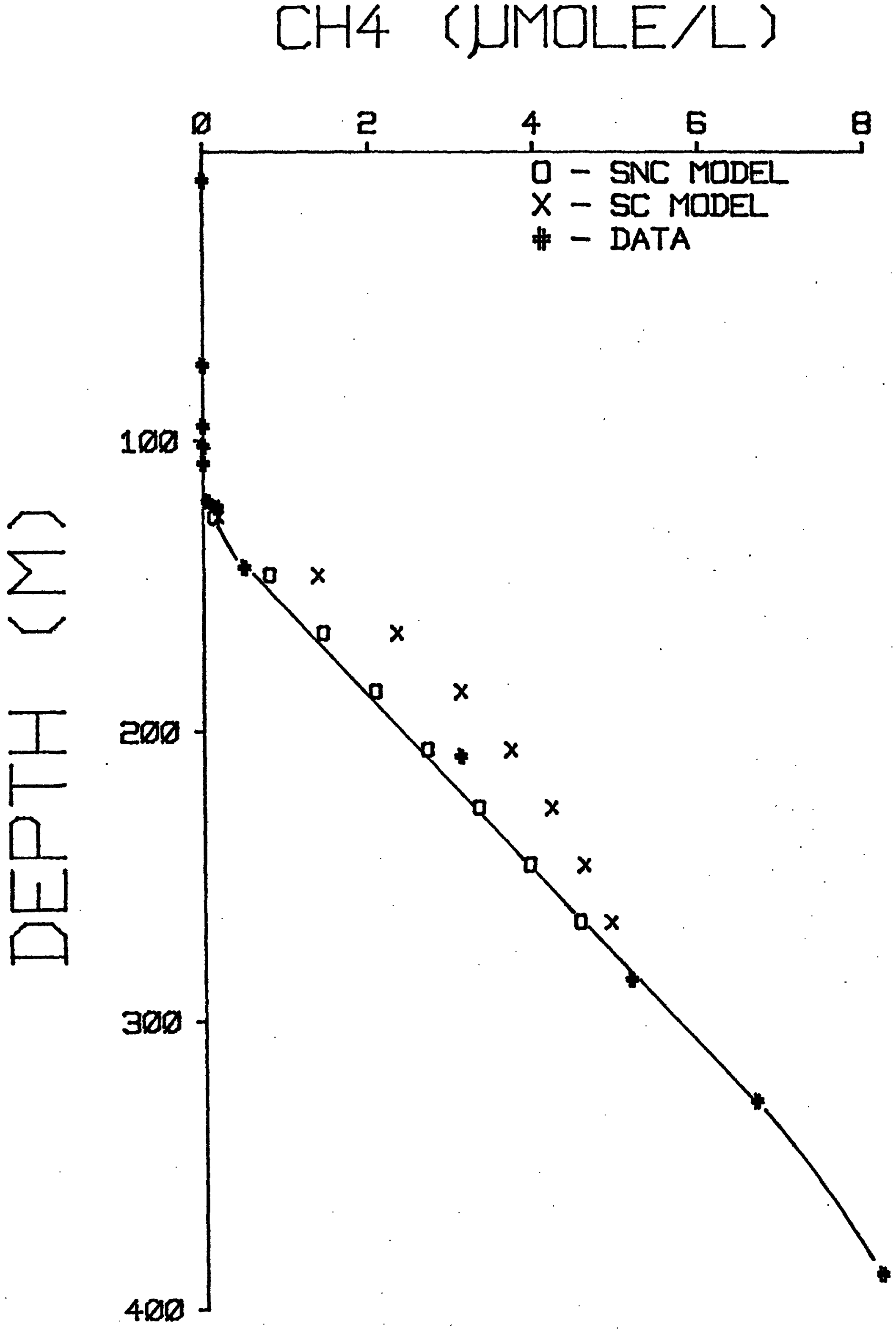

Figure VII.2. Fit of the one dimensional advection diffusion model to the Black Sea methane data. The best fit is obtained if an *in situ* consumption term is included.

consumed in anaerobic environments, probably by sulfate reducing bacteria which can mediate the thermodynamically feasible reaction

$$SO_4^{-2} + CH_4 \longrightarrow HS^- + HCO_3^- + H_2O.$$

My Black Sea data seem to provide an additional piece of indirect evidence for this phenomenon.

However the Black Sea is a complex system. Brewer and Murray (1973) have predicted that CO_2, ammonia and phosphate are consumed within the mixing zone, presumably by chemosynthetic bacteria. They also indicate that hydrogen sulfide consumption, in excess of the amount of oxygen which can diffuse down from the surface waters, occurs within the zone. Sulfide diffuses into the mixing zone from below at a rate of about 75 mmole/m^2/yr while oxygen diffuses in from above at a rate of only about 3 mmole/m^2/yr. Thus they were confronted with apparent sulfide consumption in the absence of oxygen. In their argument, Brewer and Murray (1973) ignored a major source of oxygen for the mixing zone. About 190 km^3 of Bosphorus water flows into the Black Sea each year, mixing with Black Sea water at depths from 300 to 1700 m. This inflow provides the water which drives an upward advection of 0.5 m/yr.

The inflowing Bosphorus water is at or near saturation with oxygen when it enters the Black Sea (Gunnerson and Öztürgut, 1974) suggesting that about 5 x 10^{10} moles of oxygen would be introduced to the deep waters each year by this pathway. This is equivalent to 138 mmoles O_2/m^2/yr if spread over the entire basin. Any reaction occurring within the inflow must take place very near the point at which the water sinks, as oxygen and sulfide were never measured within the same water sample throughout the seven week AII79 cruise (Brewer and Murray, 1973). Nevertheless since horizontal advection and eddy diffusion in the Black Sea are probably rapid, sulfide-depleted water from near the inflow could be mixed throughout the basin giving anomalously low sulfide values and suggesting in situ consumption. This argument resolves the question of how sulfide could be oxidized in the absence of oxygen. The process cannot, unfortunately, be quantified due to the large amount of scatter in both the sulfide and oxygen data.

If the oxygen introduced with the Bosporus water is important in oxidizing sulfide, it seems at least possible that it could also be involved in oxidation of methane, even though this process is biologically mediated and is probably slower than sulfide oxidation. Slower oxidation may ~~be~~ be compensated for by the fact that the rate of methane diffusion into the bottom of the mixing zone is only 1.6 mmole/m^2/yr as compared to 75 mmole/m^2/yr for sulfide. I feel that oxidation by aerobic (or microaerobic) methane oxidizing bacteria, utilizing oxygen from the Bosporus inflow, must be considered along with possible oxidation of methane by sulfate reducers in discussions of the methane geochemistry of the Black Sea. It would be extremely interesting to obtain sulfide, methane and oxygen data from near the Bosporus overflow as significant geographic variations would be expected if the model I have presented is realistic.

3. Summary

An apparent methane consumption rate of 15 nmole/l/yr is predicted for the Black Sea between the oxygen-sulfide interface and the bottom of the mixing zone (about 285 m at station CHAIN120-1355) from a one dimensional advection diffusion model. Previous workers would interpret this consumption to be a result of methane oxidation by sulfate reducing bacteria. However, at least in the Black Sea, it appears that the apparent consumption might be an artifact caused by mixing of water from the central Black Sea with water depleted of methane by methane-oxidizing bacteria near the Bosporus overflow.

B. The Cariaco Trench

The Cariaco Trench is the second largest of the world's anoxic basins. It is located on the Venezuelan continental shelf at about 10°30'N and 65°31'W, is about 200 km long, 50 km wide, has a maximum depth of about 1400 m and is separated from the rest of the Caribbean by a sill at about 150 m. Above this depth water can exchange freely with the water further offshore. The deep part of the basin is divided into two subbasins by a ridge extending to about 900 m.

Due to the geomorphology of the basin, horizontal circulation is greatly restricted at depth. Vertical mixing is also inhibited by the presence of a strong thermocline beneath the 100 m thick mixed layer. Salinity decreases with depth and the stability of the basin waters is due to the temperature structure. Because both horizontal and vertical exchange are limited, bottom water oxygen, utilized in respiration processes as an electron acceptor, is not replenished rapidly and the Cariaco Trench deep waters have become anoxic. The basin was first reported to be anoxic in 1956 by Richards and Vaccaro (1956), and at that time hydrogen sulfide was reported at all depths below about 450 m. In 1973, hydrogen sulfide was found at all depths below 270 m (Brewer, personal communication, 1974).

1. Collection of Data and Methods

The data to be discussed were collected on cruises 79 and 86 of the R/V ATLANTIS II in December, 1973 and February, 1975 respectively. The temperature, salinity, hydrogen sulfide and silicate data were collected in December, 1973 at two stations in the eastern basin at 10°32'N 64°46'W and 10°31'N 64°45'W. The methane data were collected in February, 1975 at a station in the eastern basin at 10°29'N 64°44'W (see Appendix VII.1). Although these two sets of data are not synoptic, the high quality of the nutrient and hydrographic data from the 1973 cruise makes them ideal for comparison with the detailed 1975 methane data. The assumption that the two sets of data are comparable may be in error as pointed out below. However it is assumed that changes over a period of 13 months will be relatively small and will not alter any conclusions in an important manner. Long term trends, however, are significant.

Temperatures were determined from reversing thermometers. Salinity was measured on board ship using an inductive salinometer. Silicate was determined colorimetrically by the metol-sulfite reduction of the silicomolybdate complex (Mullin and Riley, 1955) and sulfide by a methylene blue method (Cline, 1969). Temperature, salinity, sulfide and silicate analyses were all made within hours of the completion of each station. Sulfide data are all from samples taken in 30 liter PVC Niskin bottles as it was found that low values were obtained from samples taken in metallic Nansen bottles.

Methane samples were taken in one liter bottles with greased standard taper ground glass stoppers. All samples were poisoned with mercuric chloride and were refrigerated until analysis. One complete profile was analysed within one to two days of sample collection at sea, and a duplicate profile was analysed ashore seven weeks later.

2. Results

Salinity, potential temperature, sulfide and silicate data were obtained from Brewer (personal communication, 1974). The temperature vs salinity plot for the Cariaco Trench is linear between 16.8°C, 36.20‰ and 17.4°C, 36.30‰. In 1973 sulfide first appeared at 270 m in the eastern basin and below this depth increased rapidly until about 1200 m where the concentrations approached a value of about 35 μmole/l. The silicate concentration increased rapidly below the anoxic-oxic interface to a maximum of 66 μmole/l at the bottom.

A number of methane profiles obtained by previous workers in the Cariaco Trench are shown in Figure VII.3 together with my data. The data of Atkinson and Richards (1967) were obtained before a highly precise and accurate technique for methane analysis had been developed (Swinnerton and Linnenbom, 1967b). Lamontagne et al. (1973) and Wiesenburg (data presented by Reeburgh, 1976) used Swinnerton and Linnenbom's method but stored their samples for periods of up to several months before analysis. Comparison of my stored samples with those analysed at sea suggests that it is unwise to store samples of such high methane contents (see Chapter II). Previous methane data for the Cariaco Trench may be in error by as much as 30%.

3. Discussion-The One Dimensional Advection Diffusion Model

The one dimensional advection diffusion model described earlier for the Black Sea has also been used to interpret data from the Cariaco Trench. This approach has been applied to profiles of chemical species obtained in the Cariaco Trench by Wong and Brewer (1977), Fanning and Pilson (1972), and Reeburgh (1976) among others.

Reeburgh (1976) in particular has used this method in the interpretation of methane data from the Cariaco Trench. Using a mixing parameter $K_v/w = 0.186\ \mathrm{km}^{-1}$, determined from temperature and salinity data, he

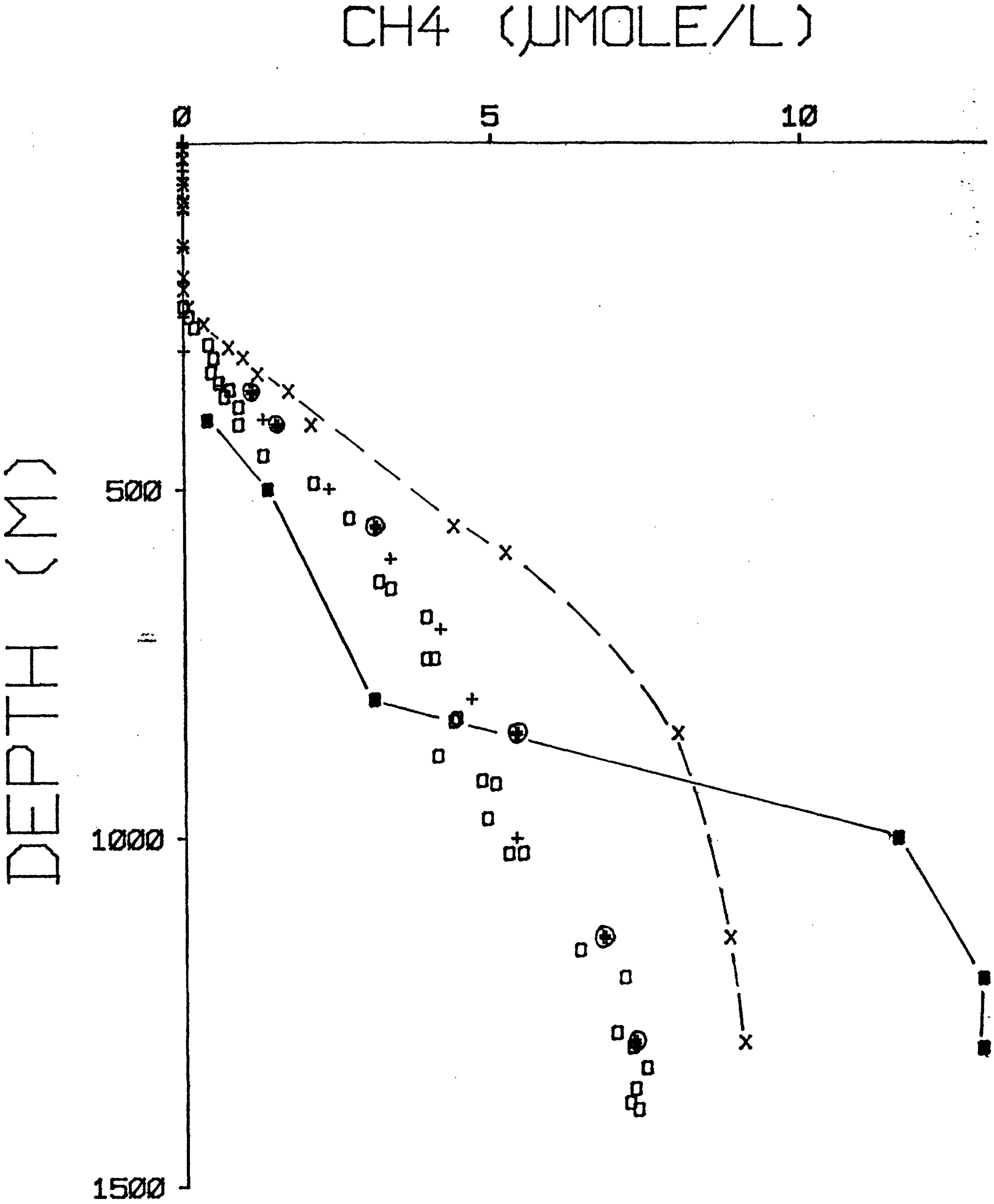

Figure VII.3. Methane data from the Cariaco Trench. x = this work, shipboard; ⌀ = this work, laboratory; ■ = Atkinson and Richards, 1967; + = Lamontagne et al., 1971; □ = Reeburgh, 1976. Note that stored samples from AII86-2225 agree well with stored samples from other workers.

found it necessary to include an in situ consumption term to fit the one dimensional model to the observed methane profile. For this data $J/w = -7.6$ μmole/l/km. Assuming that $w = 0.75$ m/yr (Fanning and Pilson, 1972), J is 5.7 nmole/l/yr. These data were obtained on stored samples and may be in error. I have also fitted the one dimensional model to my data (see Figure VII.4). Using $K_v/w = 0.23 \text{ km}^{-1}$ (determined from the precise hydrographic data collected on AII79), I also had to include a methane consumption term in order to fit the model to my methane data. Again assuming that $w = 0.75$ m/yr, J is 8.4 nmole/l/yr, a value very similar to that determined by Reeburgh (1976). Thus with accurate data, the one dimensional model suggests that in situ consumption of methane in the anoxic zone is important in the Cariaco Trench.

However there are difficulties associated with the use of the one dimensional advection diffusion model in the Cariaco Trench. Two assumptions are that the distribution of chemical species in the Trench has reached a steady state, and that a mixing zone exists within which concentrations are controlled solely by upper and lower boundary conditions and by in situ production or removal within the zone. Neither assumption is wholly correct in this instance.

Non-steady state conditions can be identified from several types of measurements. Richards and Vaccaro (1956) found the oxic-anoxic interface at a depth of 450 m. During the 1973 cruise, the interface was found to be at 270 m. Explorations made between the 1954 and 1973 cruises located the interface at intermediate depths (1971, 250 m, Brewer (unpublished data); 1968, 297 m, Fanning and Pilson (1972); 1965, 350 m, Richards (1970)). It appears that the interface has been

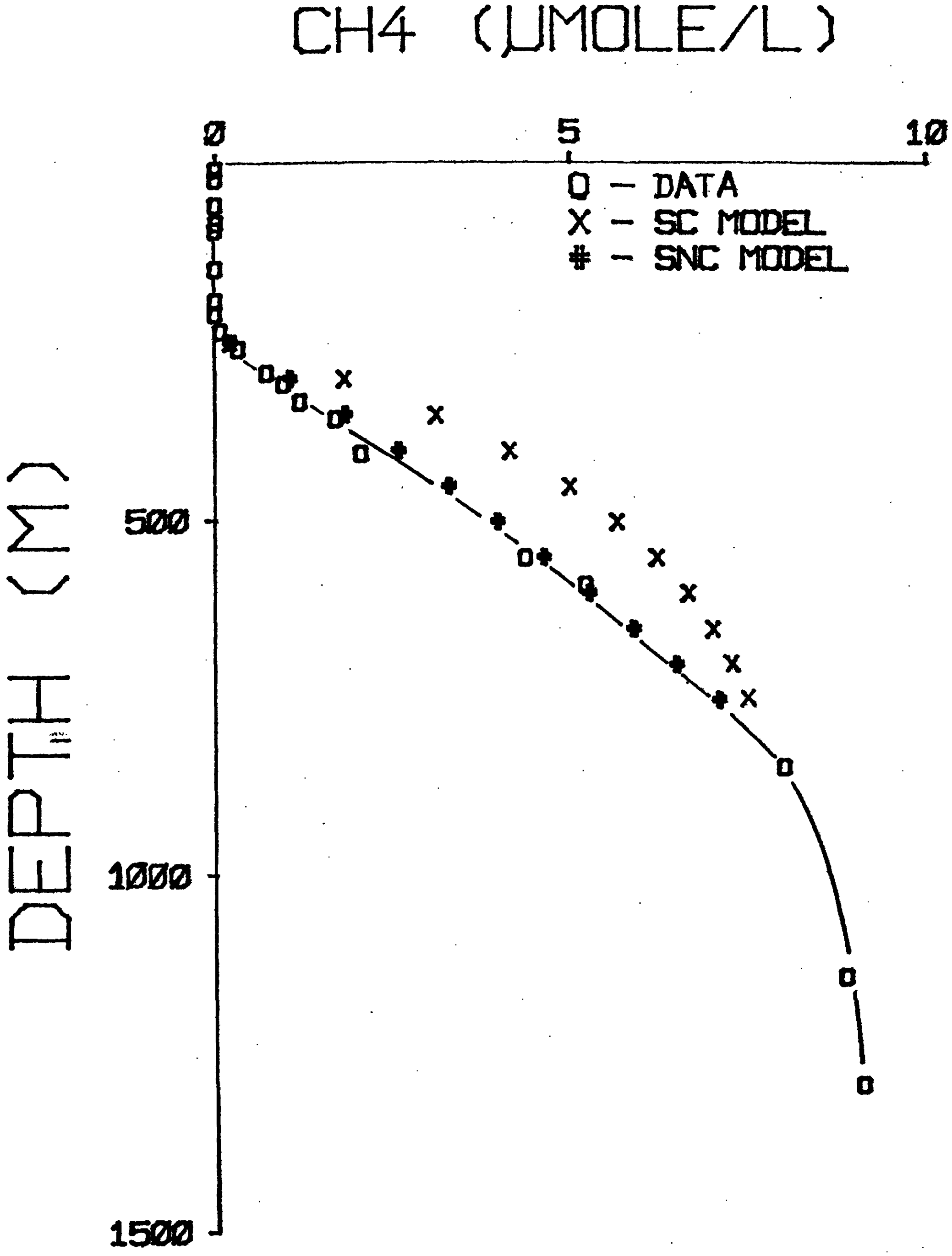

Figure VII.4. Fit of the one dimensional advection diffusion model to the Cariaco Trench methane data. The best fit is obtained if an in situ consumption term is included.

migrating upwards at a rate of about 10 m/yr, although data are insufficient to say whether the rate is constant. The temperature of the deep water has also been increasing at a rate of 0.004°C/yr (Brewer, personal communication, 1975; Herrera and Febres-Ortega, 1975).

In addition Richards (1975) has presented hydrogen sulfide data obtained by a number of workers since 1957. I have plotted the sulfide data available to me from the eastern basin in Figure VII.5. The data are, admittedly, quite noisy. However, ignoring the 1955 data there does appear to be a clear trend of increasing sulfide with time.

On the basis of these data it appears that the first assumption of the one dimensional model, that of steady state, is questionable at best. A relevant point to note here is that the time-dependent behavior observed over the past twenty years is very probably only a small portion of the variability in chemical composition of the basin which occurs over geological time. No oxidizing episodes are seen in the sediments more recently than 11,000 yrs BP (Gieskes, 1973). However as up to one-third of the organic carbon supply to the Trench is terrigenous (Deuser,1973), climatic variations along the coast could dramatically alter the input of organic matter. Climatic patterns may affect circulation patterns and either promote or inhibit overturn. These factors make model predictions over periods of hundreds to thousands of years tenuous. However for lack of information I shall assume that the chemical variability observed within the last 20 years is representative of that over the past several thousand years at least.

A second major assumption of the one dimensional model, that the only sources of a stable conservative chemical species are the upper

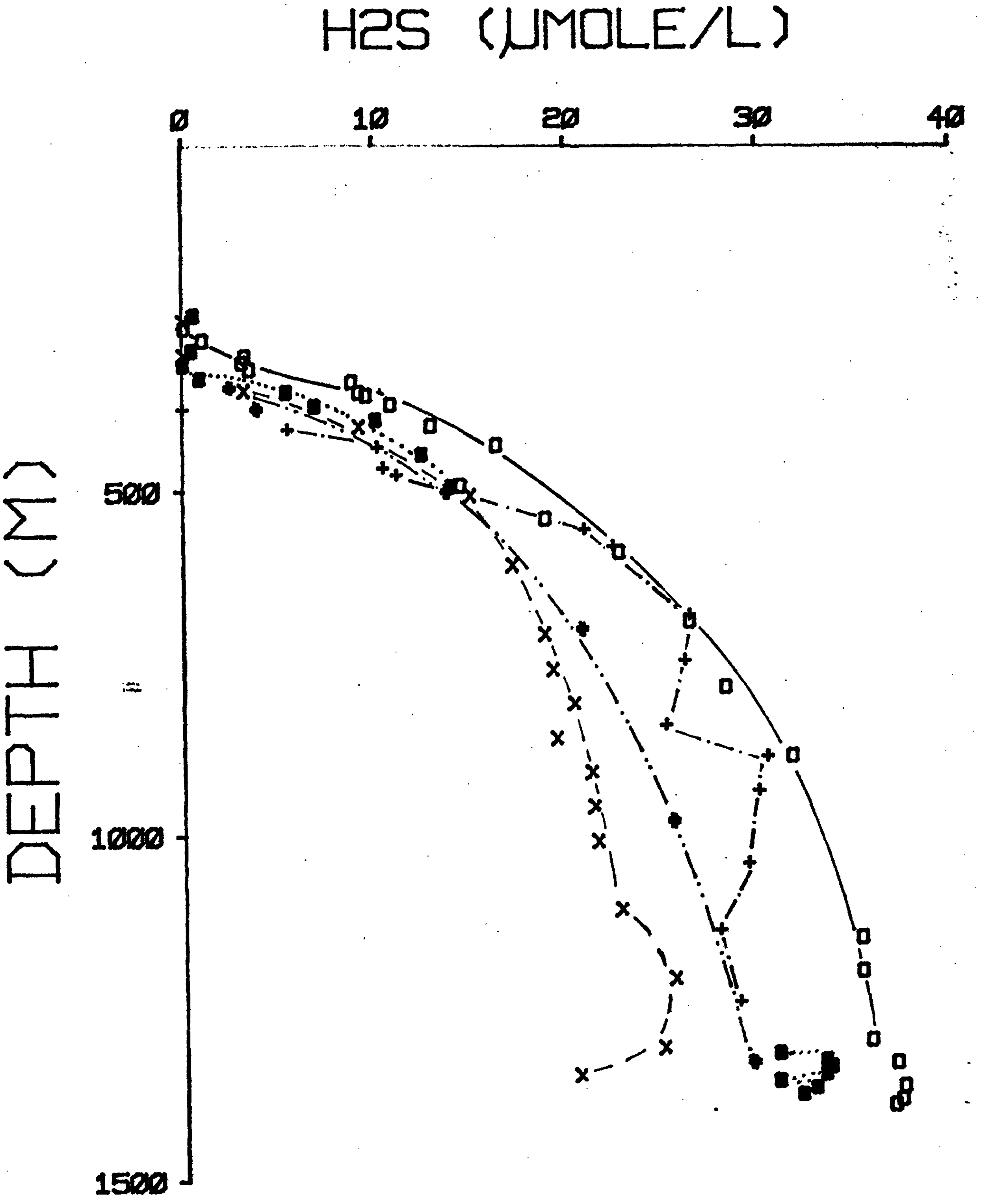

Figure VII.5. Sulfide data for the Cariaco Trench. □ , 1973 data, Brewer, personal communication, 1974; ■, 1971 data, Deuser, personal communication, 1975; #, 1970 data, Richards, 1975; x, 1965 data, Richards, 1970; +, 1955 data, Richards, 1975.

and lower boundaries, is also of doubtful validity. This assumption is equivalent to assuming that no chemical species can diffuse out of the sides of the basin, as the lower boundary is assumed to be only that part of the Trench floor lying at 1400 m. Since the Trench is only 50 km wide, the presence of sides clearly cannot be ignored; and since the Trench waters are anoxic below 270 m, it seems reasonable that reduced species and nutrients can be supplied from the walls as well as from the bottom.

Because of these violations of the assumptions of the one dimensional model, a box model may more exactly represent the situation in the Cariaco Trench. Hesslein (personal communication, 1975) has successfully modelled the distribution of chemical species in a small Canadian Shield lake using a similar model.

4. Discussion-The Box Model

The box model is schematically illustrated in Figure VII.6. A species, x, is added to or removed from a box, i, by transport across the upper and lower surfaces of the box, by diffusion out of the sediments and by vertical advective transport across the surfaces of the box. Within the box the concentration of x is assumed uniform (in other words, the horizontal eddy diffusion coefficient is assumed large compared with the vertical eddy diffusion coefficient). The model is made time dependent by iterating the calculation over some small time increment, Δt. In each time interval, species first diffuse and advect in a manner determined by the concentration distribution at the end of the previous time interval. Then a new concentration distribution is calculated and the next iteration is begun.

The various flux terms used in the box model are described

CARIACO TRENCH BOX MODEL

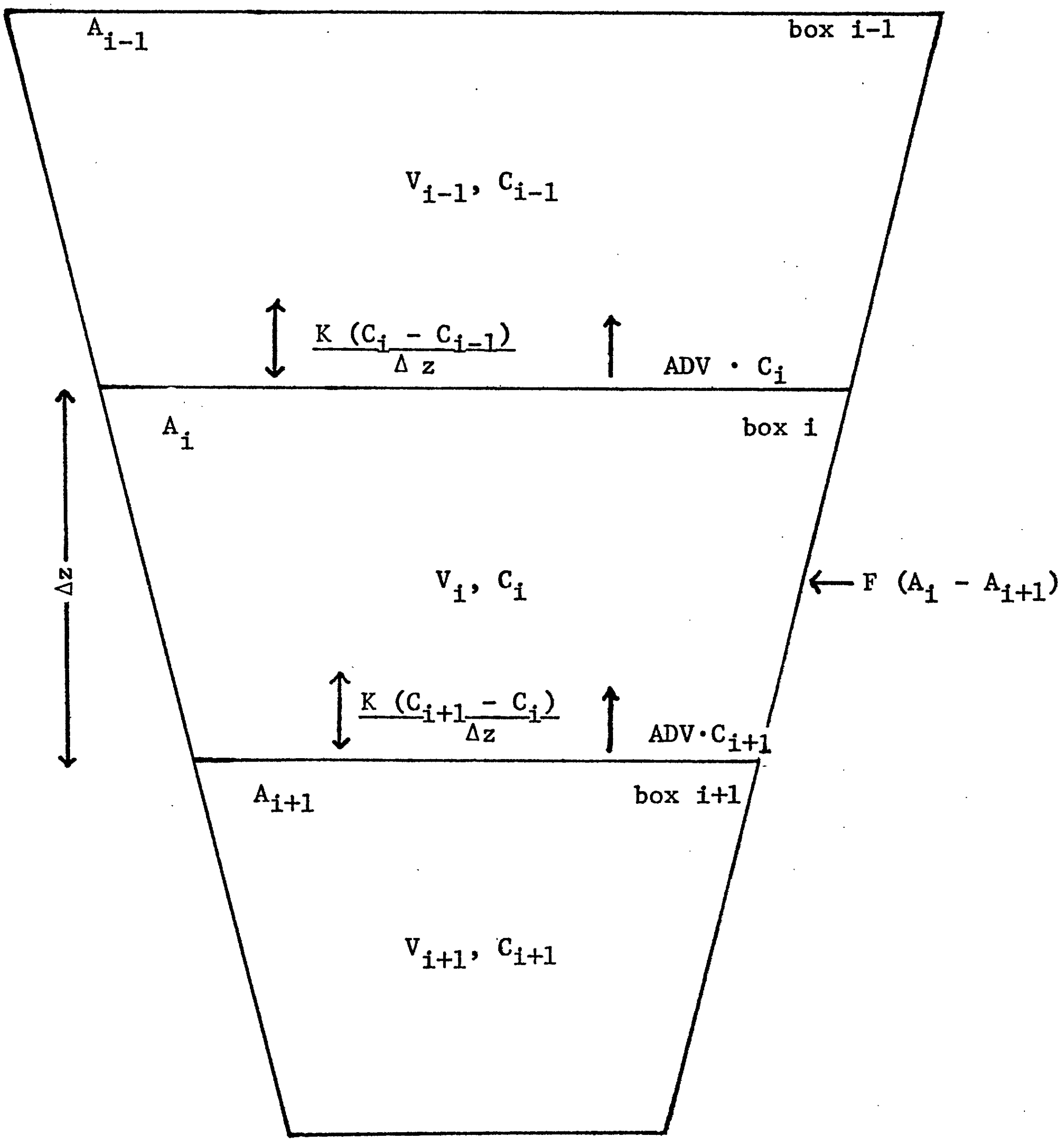

Figure VII.6. Schematic diagram of the box model used in describing the distribution of chemical species in the Cariaco Trench. The various parameters are discussed in the text.

mathematically in Table VII.1. For silica, sulfide and methane, the sole source is assumed to be the sediments. For silica the only sink is diffusion out of the basin. For hydrogen sulfide an additional factor, consumption by reaction with oxygen, has been taken into account. At time t = 0, it is assumed that the Trench has been completely flushed. An initial oxygen distribution is assumed in which oxygen concentrations are taken to be constant with depth and equal to the concentration present at sill depth in the Venezuelan Basin. Hydrogen sulfide is assumed to diffuse into the water from the sediments throughout the time period under consideration. (In other words, the sediments are assumed to be anoxic at t = 0.) The sulfide concentration in the water is assumed to equal zero until enough sulfide has diffused into the water to remove all the oxygen initially present. After the basin has become anoxic, the only sink for sulfide is diffusion across the oxic-anoxic interface. Methane is assumed to be absent from the water column until after sulfide appears. Methane is lost from the basin at the oxic-anoxic interface. Methane consumption by sulfate-reducing bacteria can also be included in the model by assuming that some fraction of the sulfide input is a result of methane oxidation in the water column.

In order to use the model, a number of parameters must be determined. Some of these can be estimated fairly accurately. Others can only be guessed at intelligently. The following discussion will describe the assumptions used in the choice of the model parameters.

a. Area and Volume: It is assumed that the Cariaco Trench can be represented by a series of layers, the surface and bottom areas of

TABLE VII.1

EQUATIONS FOR THE BOX MODEL OF THE CARIACO TRENCH

1. Sediment-water flux

Flux across the sediment-water interface is

$F\ (A_i - A_{i-1})$ where F = flux per unit area of species across interface

A_i = surface area of upper surface of box i.

The concentration change per unit time due this flux is

$$\frac{F\ (A_i - A_{i-1})}{V_i}$$ where V_i = volume of box i

2. Eddy diffusive flux across the box interface

Flux across upper boundary is

$$\frac{K_{v_i}\ (C_i - C_{i-1})}{z}$$ where K_{v_i} = eddy diffusion coefficient for box i

z = box thickness

C_i = concentration of species in box i.

3. Advective transport across box interface

Flux upward across the upper boundary is

$ADV \cdot C_i$ where ADV = volume per unit time of water advecting upward.

which can be obtained by planimetry of a bathymetric map (Maloney, 1966). This is valid if the slope of the basin walls is gradual. The maximum slope of the walls in the Cariaco Trench is about 18° indicating that the areas determined in this way will be in error by a maximum of 5%.

A layer thickness, z, of 92 m (50 fm) was selected. The volume of each layer was estimated using the prismoidal formula. Above the ridge dividing the eastern and western basins, the area and volume of the entire Trench were considered. Below this depth areas and volumes were determined for the eastern basin alone, as methane data are only available for the eastern basin. Values for A_i and V_i are shown in Table VII.2. Depths presented in this table represent the centers of the boxes used.

b. Time Increment: A time iteration step of 0.25 years was used. Smaller values for Δt did not change the calculated concentration values.

c. Initial Chemical Concentrations: At the start of the calculation, it was assumed that the waters of the Cariaco Trench had been completely overturned. Initial methane concentrations were assumed to equal air-saturation values for the temperature and salinity of the Cariaco Trench bottom waters. Initial silica concentrations were assumed to be equal to zero, typical of the oceanic mixed layer. The interface silica value was taken to be 27 μmole/l which is the current value. Since silica undoubtedly is supplied from sediments above the oxic-anoxic interface, as well as below, it is assumed that this concentration is maintained by diffusion from the shallow water sediments.

d. Eddy Diffusion Coefficient: In numerous attempts to use the model described above to fit observations in the Cariaco Trench, it was

TABLE VII.2

VALUES OF SOME PARAMETERS USED IN CARIACO TRENCH BOX MODEL

Depth* (m)	Area (10^9 m^2)	Volume (10^{11} m^3)	K_z (cm^2/sec)	Flux HS^- ** (10^5 μmole/m^2/yr)
320	8.22	10.50	0.80	0.69
412	7.60	9.90	1.30	0.68
503	6.97	9.07	1.60	0.85
595	6.31	8.05	1.70	1.1
686	5.70	6.90	1.80	1.3
778	5.03	5.55	2.00	1.4
870	4.40	3.55	2.40	1.1
961	1.35	2.01	2.60	2.2
1052	1.15	1.25	2.70	1.6
1144	0.92	0.72	2.70	1.1
1236	0.72	0.50	3.00	0.97
1327	0.51	0.45	3.60	1.3

* Represents the center of each 92 m thick box

** Flux of sulfide per unit area calculated from the change in sulfide in the basin between 1965 and 1973 found that the use of a constant eddy diffusion coefficient did not produce a good fit to the data. Briefly, curves predicted from constant eddy diffusivities and constant sediment-water fluxes increase too gradually at depth just below the interface. Therefore, a vertically varying eddy diffusion coefficient has been used. It was arbitrarily assumed that K_v was about 0.8 cm^2/sec at the center of the topmost box. Values similar to this have been calculated by several other workers using one dimensional advection diffusion models for the Trench. At the center of box 1, N (the Brunt-Vaisala frequency) was 0.18×10^{-2} sec^{-1}. It was assumed that K_v is proportional to 1/N, and that the proportionality constant was constant with depth. Sarmiento (personal communication, 1977) found that K_v is proportional to 1/N in lakes. The proportionality constant was calculated from the box 1 values of K_v and N. Values of N were calculated for the Trench using σ_t data from the AII79 cruise, and values of K_v for the other boxes were calculated using the inverse proportionality described above. The K_vs used in the model are presented in Table VII.2 and range from 0.8 cm^2/sec to 3.6 cm^2/sec.

e. Vertical advection: Neither in this nor in any previous model is an explanation offered for the mechanism of the inflow of water into the deep layers of the Trench. In this model and in others, a continuous inflow is required by the continuous upward advection included in the models. Unfortunately there is no evidence to suggest that dense water is continuously available at sill depth for the supply of new bottom water. In fact it is probable that the sinking phenomenon is an episodic one. However, like previous workers, I have found that the chemical data cannot be accurately described if an advective term is not included.

Before one can realistically postulate that vertical advective transport of water is important in a basin such as the Cariaco Trench, one must first confirm that water exists outside the Trench at appropriate densities such that the water can flow into the basin, sink to the bottom and displace the Trench water. The bottom waters of the Cariaco Trench have a σ_t of about 26.512. Outside the Trench, in the Venezuelan Basin, water of this density has been reported at depths greater than 200 m (Brewer, personal communication, 1974). However, considerable geographic and temporal variations may occur.

The greatest sill depth connecting the Trench and the Caribbean lies at a depth of slightly less than 150 m and is located at the far western end of the Trench. Water flowing over the sill would first enter the western basin. For deep water to be injected directly into the bottom of the eastern basin, it would probably have to enter by way of a 120 m sill between the islands of Tortuga and Margarita. It is probable that water of the appropriate density is only infrequently available at the appropriate depths. However, it is assumed that vertical advective transport and thus bottom water input is constant rather than episodic. This may not be realistic, but I have no data with which to model an episodic flow.

Another difficulty is associated with the chemical composition of the inflowing water. No model, including this one, is able to take into account the input of high oxygen, low nutrient water into the bottom of the Cariaco Trench without disrupting the vertical distributions of chemical properties. In the model this difficulty has been ignored.

Inflow probably occurs more frequently over the western, 150 m, sill than over the eastern, 120 m, sill. Thus the bottom waters of the western basin may be more frequently renewed than those of the eastern basin. However no significant interbasin differences were observed in the chemical species analyzed on AII79 (potential temperature, salinity, silica and sulfide).

Because the Cariaco Trench does not have vertical walls, it is inaccurate to assume a constant vertical advective velocity, w. Instead it has been assumed that a constant volume of water is advected upward across each box face. In the eastern basin, this volume was determined by a best fit to the silica data to be 4 x 10^9 m^3/yr. Above 900 m, the waters above both the eastern and western basins are considered. I have therefore assumed that water of the same composition as is present in the eastern basin at 900 m is advected upward across the surface of the western basin at a rate of 7 x 10^9 m^3/yr (the same advection velocity at 900 m, with the flow rate calculated by multiplying velocity by area) Without the inclusion of some vertical transport, it is very difficult to fit chemical species distributions which approach a constant concentration at depth, as is the case for silica, sulfide and methane.

f. Sediment-water fluxes: The final parameters to be constrained are the values of the sediment-water fluxes for silica, hydrogen sulfide and methane. Unfortunately very few reliable data exist for the Cariaco Trench to allow us to determine these values. The fluxes for the chemical species were chosen to best fit the observed data. However I will attempt to justify my choices by comparison with the data which are available. It has also been assumed that all sediment-water fluxes are constant with time even though the bottom water concentrations are increasing.

i) Silica: The bottom water silica concentration is about 66 μmole/l. Fanning and Pilson (1972) have measured silica in interstitial water in Cariaco Trench sediments and obtained values of about 400 μmole/l at about 5 cm depth in the core. This value was obtained on a core which had been warmed to room temperature before squeezing. Fanning and Pilson (1974) suggest that warm-squeezed cores give silica concentrations approximately 1.5 times that of cold-squeezed cores. If this relationship holds for the Cariaco Trench sediments, the actual 5 cm silica value should be 270 μmole/l. This is probably a minimum value since the Cariaco Trench sediments are warmer than those in the deep ocean. Assuming the diffusion coefficient (D) in the interstitial water to be about 3×10^{-6} cm^2/sec (Berner, 1974) and that there is a linear concentration gradient between 5 cm and the surface of the core, the flux across the sediment-water interface is

$$F = \frac{D\Delta C}{\Delta z} = 4.9 \times 10^4 \ \mu mole/m^2/yr.$$

However the flux used in Figure VII.7 to calculate the silica distribution best fitting the observed data was found to be one order of magnitude higher at 3.7×10^5 $\mu mole/m^2/yr$. If the physical parameters which give a good fit to the silica, methane and sulfide data are used, use of the lower sediment-water silica flux does not give a silica distribution which resembles the observed distribution.

Guinasso and Schink (1975) believe that low biological mixing rates for mixing of sediments by organisms will produce higher fluxes

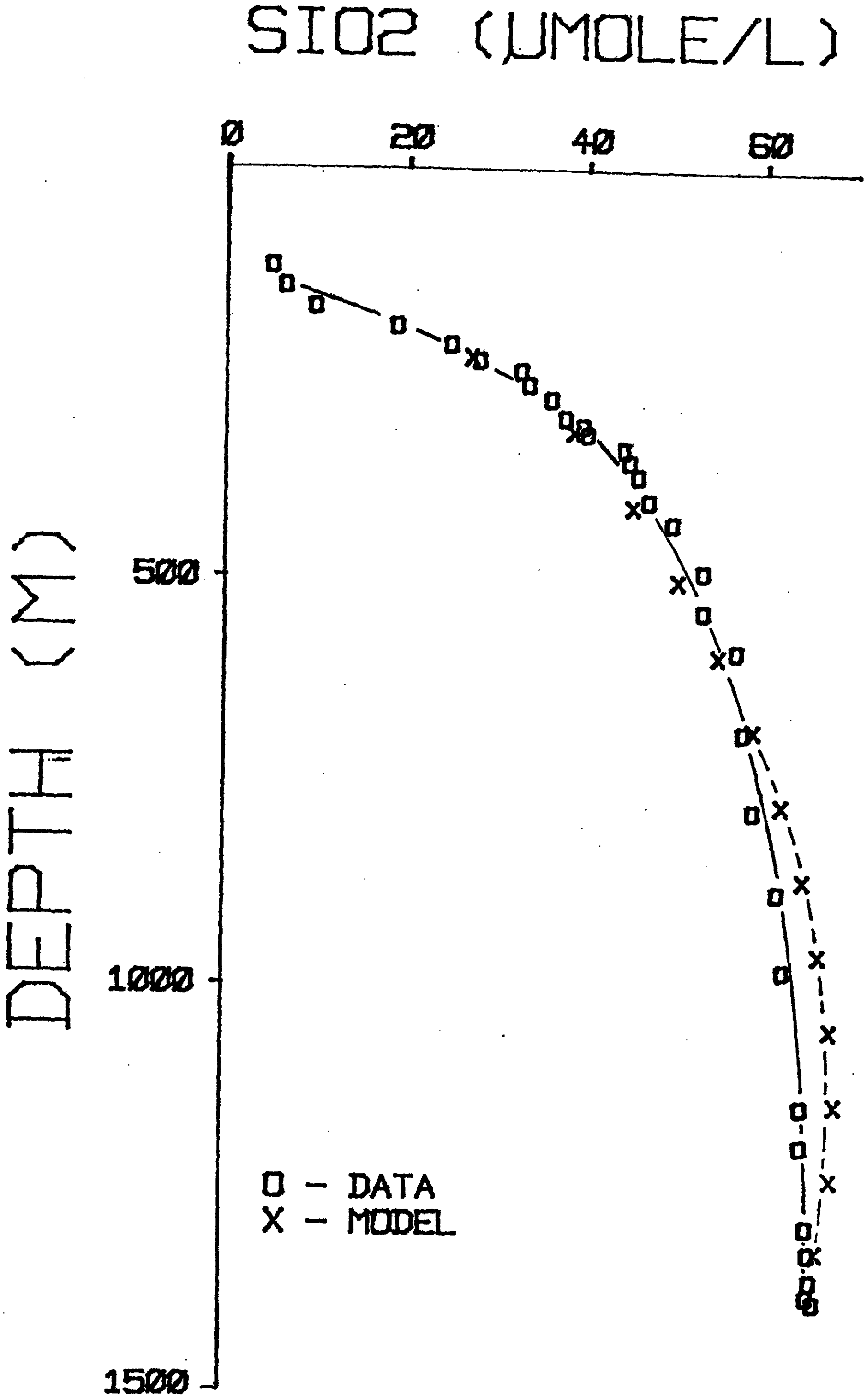

Figure VII.7. Silica profile for the eastern basin of the Cariaco Trench. The best-fit box model calculation is also shown.

since high interstitial concentrations can be built up close to the sediment-water interface. Because the Cariaco Trench waters are anoxic, biological mixing of the sediments should be absent. Since this would permit high silica concentrations to be present very close to the sediment-water interface, and thus increase the gradient across the interface, the true silica flux could be quite high.

An alternative explanation might be that much of the biogenic silica dissolves before it is buried in the sediments. In this case, the sediment supply of silica could be significantly higher than that predicted from interstitial water concentrations.

Using the values of the parameters discussed in the preceding pages, the silica distribution is found to reach a steady state in about 400 years. As will be discussed below, this is considerably shorter than the time period required for sulfide or methane distributions to equal those found at present and suggests that the silica distribution may in fact be in steady state at present.

ii) Hydrogen Sulfide: There are several discussions in the literature estimating rates of sulfide flux from anoxic sediments into a water column. Berner (1974) has presented a number of profiles of sulfate concentration with depth in pore waters and has fitted equations of the form

$$C = Ae^{-bx} + C_1$$

where C = concentration of sulfate

and A, b and C_1 are constants,

to his data. If the rate of sulfate diffusion into a sediment is assumed to be greater than or equal to the rate of sulfide diffusion out of a sediment (sulfide is removed by pyrite and elemental sulfur formation), an estimate of the upper limit for the sulfide flux can be obtained for the cases studied by Berner (1974). Differentiating Berner's concentration equations with respect to depth and evaluating the derivative at $x = 0$ (the sediment-water interface) gives fluxes of from 1.7×10^5 μmole sulfide/m^2/yr for the Santa Barbara Basin to 16.8×10^5 μmole/m^2/yr for Soames Sound, Maine.

Another estimate can be made from the data of Orr and Gaines (1973) who measured the rate of increase of sulfide in an anoxic basin in the Pettaquamscutt River. The sulfide production rate they obtained was about 4×10^6 μmole/m^2/yr. Considering the productive and shallow nature of the Pettaquamscutt basin, it is to be expected that this value is much higher than that obtained by Berner (1974) for deeper and less productive systems.

Sorokin (1964) measured the rates of sulfate reduction in surface sediments in the Black Sea and obtained production rates of from 0.15 to 12×10^5 μmole sulfide/m^2/yr. And finally Presley (1974) has calculated the rate of sulfate reduction in Cariaco Trench sediments based on measurements of total reduced sulfur in the sediments and the known sedimentation rate. His estimate is 3×10^5 μmole/m^2/yr.

Using the physical parameters obtained from the fit of the silica data, the hydrogen sulfide flux which gave the best fit to the data was determined to be 2.75×10^5 μmole/m^2/yr (see Figure VII.8). This estimate of the sulfide flux falls within the middle of the range of values determined by a number of other methods described above, and is extremely close to the value calculated by Presley (1974) for the Cariaco

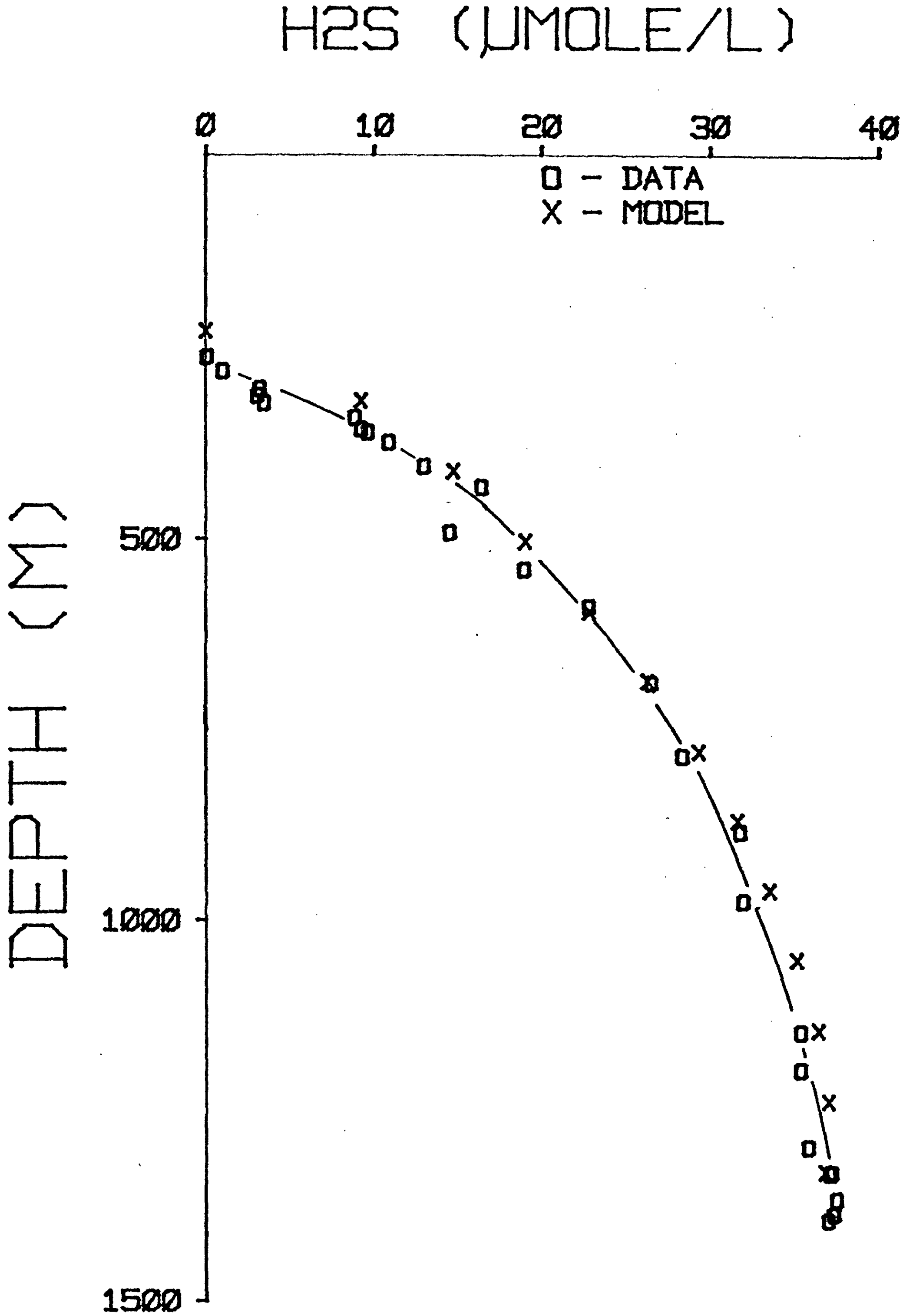

Figure VII.8. Sulfide profile for the eastern basin of the Cariaco Trench. The best-fit box model calculations are also shown.

Trench.

A final check can be made by using the data presented in Figure VII.5 for the variation in sulfide concentration in the waters of the Cariaco Trench as a function of time. As is shown in Figure VII.5 comparison of the 1965 data presented by Richards (1970) and the accurate 1973 data obtained on AII79 by Brewer and coworkers (personal communication, 1974) indicates a significant change in sulfide content in the deep part of the Cariaco Trench in the past eight years. By calculating the increase in sulfide in each model box over the period of eight years, the average flux of sulfide from the sediments intersected by each box can be estimated. These numbers are presented in Table VII.2. The average sediment-water flux for the entire Trench determined in this way is 1.2×10^5 μmole/m^2/yr, and is almost equal to the flux rate estimated from the model fit (2.75×10^5 μmole/m^2/yr.

The model would predict that it takes about 600 years between the time the basin is completely flushed and the time when the sulfide distribution is as observed today. It is difficult to say how meaningful such an estimate is due to the various oversimplifications used.

iii) Methane: Unfortunately it is difficult to find good interstitial water methane data to permit a calculation of rates of methane supply from anoxic sediments. Most of the work has been done in areas where bottom waters are oxidizing. It is now widely accepted that rapid net methane accumulation occurs only in a zone below that in which sulfate reduction is occurring (Martens and Berner, 1977). Thus the presence of oxidizing bottom water is associated with a methane distribution in the sediments in which high methane concentrations are only observed fairly deep within a core (Reeburgh, 1972; Barnes and Goldberg, 1976). Because of the small sample size available for interstitial water studies, methane concentrations are only detectable if they are quite significantly above bottom water levels. Thus it is difficult to determine whether there is a gradient in methane concentrations near the sediment-water interface.

Estimates based on interstitial water values such as those of Reeburgh (1972) and Martens and Berner (1974) indicate that strict diffusive transport between tens of cms deep in the sediment and the sediment-water interface could give fluxes several orders of magnitude higher than our estimate. However, Barnes and Goldberg (1976) and Martens and Berner (1977) have suggested that most of the methane produced at depth in the sediment is reoxidized by sulfate reducers within the sediments. The flux in which I am interested would thus be a net flux, the flux of methane not oxidized.

Reeburgh (1976) has obtained interstitial methane concentrations for the Cariaco Trench sediments. He found a very low methane content to depths of 40 cm in his cores. Sayles et al. (1973) found high sulfate levels at depths of 4 m in a DSDP core taken on the ridge between the eastern and western basins, suggesting that sulfate reduction and perhaps methane consumption could be occurring to considerable depths. Taking Reeburgh's (1976) shallowest interstitial methane concentration for the Cariaco Trench sediments, 20 μmole/l, assuming this concentration was measured at 2 cm (the depth of the center of the uppermost sample) and assuming a diffusion coefficient for methane in interstitial water of 3×10^{-6} cm^2/sec, a sediment-water flux of 4.5×10^3 $\mu mole/m^2/yr$ can be calculated.

A flux of 7.5×10^4 $\mu mole/m^2/yr$ was found to give the best fit of the model to the data within the time interval for which the predicted sulfide concentrations attained a good fit to the data (see Figure VII.9). This is an order of magnitude more than the flux calculated from Reeburgh (1976). From the scatter of Reeburgh's data, it is clear that there are considerable analytical problems in working with such low concentrations. In addition the problem of sampling within a steep concentration gradient could easily result in a low estimate of the flux. High methane concentrations could continue almost to the interface. For example, if the concentration at 0.2 cm was 20 μmole/l, a flux of 4.5×10^4 $\mu mole/m^2/yr$ would be predicted.

The final parameter to be considered is that which determines the amount of methane oxidized during sulfate reduction. In Figure VII.9 the field data are plotted along with model curves representing the case of no methane oxidation and the case of oxidation of methane associated with 1% of the sulfide production. If 1% of the sulfide production occurs during methane oxidation, about 20 nmole/l/yr of methane is consumed, comparable with the consumption rate estimated from the one dimensional advection diffusion model (8.4 nmole/l/yr). For depths greater than 500 m, the model can be fit to the methane data within ± 5% using either the zero oxidation or the 20 nmole/l/yr hypothesis. The model is relatively insensitive to rather large changes in the methane oxidation rate. Therefore the mismatch between the predicted curve and

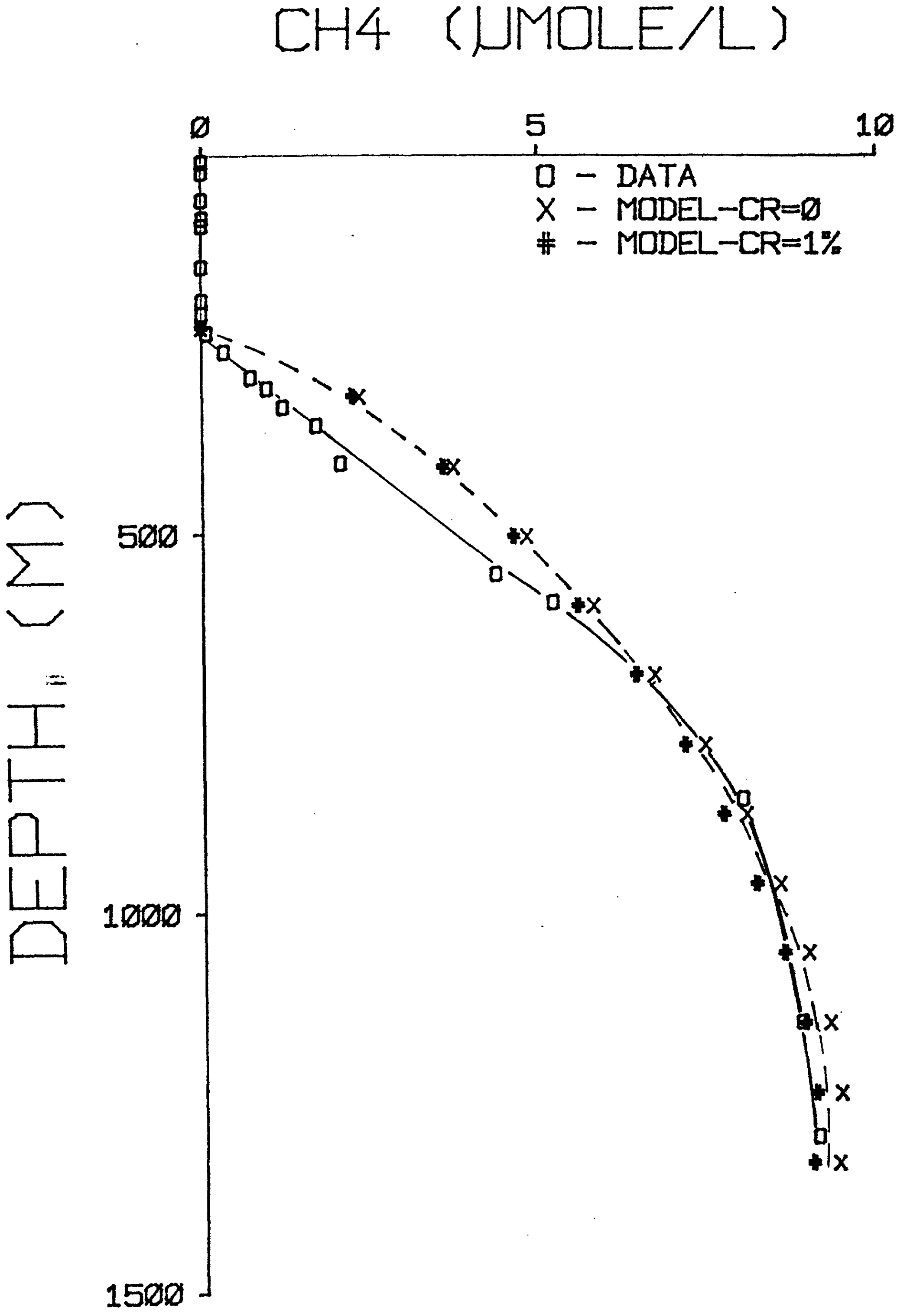

Figure VII.9. Methane data for the eastern basin of the Cariaco Trench. Box model fits are shown for the cases of no methane consumption and of methane consumption at a rate of about 20 nmole/l/yr.

the data at depths less than 500 m suggests that methane supply from the sediments may be significantly lower in this zone. Lower methane supply rates could be due to either lower production rates or to much higher methane consumption by sulfate reducers within the sediments.

It is also possible that the methane depletion may be a result of the same process which was hypothesized to account for the sulfide removal in the Black Sea; that is, that the inflowing water rapidly loses its oxygen as methane and sulfide are oxidized at the point of inflow. A slight sulfide deficit near the interface (Figure VII.8) may support this contention.

6. Summary

In using the one dimensional advection diffusion model to describe the methane distribution in the Cariaco Trench, one must assume that a large amount of methane is oxidized within the anoxic zone. Because several of the assumptions of the one dimensional model are not applicable to the Trench system, a box model was developed which incorporates both the time dependence of the system and supply of chemical species from the sediments at all depths in the Trench. To fit the model to the data, it is proposed that the silica flux out of the sediments is 3.7×10^5 μmole/m^2/yr, the sulfide flux is 2.75×10^5 μmole/m^2/yr and the methane flux is 7.5×10^4 μmole/m^2/yr. The predicted sulfide flux agrees well with fluxes calculated by other workers. Insufficient interstitial water data are available for silica and methane to determine whether the model fluxes are reasonable. The box model cannot explain a significant methane depletion at depths less than 500 m. Because the model is very insensitive to methane consumption, it seems probable that, near the oxygen-sulfide interface, much less methane is diffusing out of the sediments than at depth in the Trench. It is suggested that methane oxidation by sulfate reducers in the sediments, or decreased methane production by methanogenic bacteria, may be more important than methane consumption in the water. Oxidation by aerobic methane oxidizers utilizing oxygen from water flowing into the basin cannot be excluded either, largely due to the lack of information about the overflow process in the Cariaco Trench.

CHAPTER VIII

CONCLUDING REMARKS

It has been known for several years that the ocean and atmosphere are not at equilibrium with respect to the distribution of methane. The processes maintaining disequilibrium include both biological production and consumption and physical processes such as advection and diffusion.

In coastal regions where density stratification is strong, advective transport of methane below the mixed layer appears to be adequate to balance methane loss across the air-sea interface. In the mixed layer itself, however, both in some coastal and in open ocean regions, in situ biological production appears to be a major source of excess methane. Laboratory experiments have shown that algal metabolism may produce trace amounts of methane. Other possible sources are heterotrophic bacteria and methane bacteria present within reducing microenvironments in the mixed layer. Methane oxidation may also occur within the mixed layer, but no information is available about this.

In anoxic environments, methane is frequently present in large amounts due to the activity of obligately anaerobic methane-producing bacteria. The anoxic sediments found under the region of very high productivity in Walvis Bay appear to be a major local source for methane in the bottom waters. Methane production in anoxic sediments lying at very shallow depths also seems to be an important source of methane for Walvis Bay surface waters.

In anoxic basins such as the Black Sea and the Cariaco Trench, methane production undoubtedly occurs within the sediments. However a one dimensional vertical advection diffusion model predicts that consumption is taking place within the anoxic water column. In the Black Sea, consumption may be by methane oxidizing bateria which utilize oxygen introduced into the anoxic zone by the Bosporus overflow. In the Cariaco Trench, several of the assumptions of the one dimensional model are invalid. Thus a box model has been constructed to describe the distribution of chemical species in this environment. The box model predicts a silica flux of 4.9×10^5 μmole/m^2/yr out of the basin sediments, a sulfide flux of 2.75×10^5 μmole/m^2/yr and a methane flux of 7.5×10^4 μmole/m^2/yr. The sulfide flux has been determined accurately by other workers and the values they obtain and the value predicted by the model agree quite well. More detailed interstitial water studies on the Cariaco Trench sediments are needed before the accuracy of the silica and methane flux estimates can be evaluated. The box model for the Cariaco Trench cannot explain the significant methane depletion near the anoxic-oxic interface. It is possible that sulfate reducing bacteria which oxidize methane are active in this zone. However, it is more likely that the depletion results from a decrease in methane supply from the sediments. This may be due to decreased methane production or to increased methane oxidation by sulfate reducers in the sediments. The parameters used in the model need to be more accurately evaluated before these alternatives can be resolved.

The effect of methane oxidation is apparent in the deep ocean as well as in anoxic basins, and here it seems very probable that methane oxidizing bacteria are the cause of the reduced methane levels. Most of the methane depletion observed occurs within the first 100 years or so of water mass isolation. Methane consumption after that is very slow.

Deep water methane concentrations decrease less than 0.5 nmole/l during the entire journey of the deep waters from the North Atlantic to the North Pacific. It appears that either methane concentrations in the deep sea are too low for methane to act as a substrate for methane oxidizers or that the bacterial metabolic rates are severely reduced by the low temperatures and high pressures of the sea floor.

My work has identified several areas which should be studied in more detail.

1) The lack of data from which to calculate fluxes of silica and methane from Cariaco Trench sediments, points out the need for detailed sampling of interstitial water near the sediment-water interface in anoxic systems.

2) Methane data need to be obtained in water mass formation regions to define further the rates of methane removal in the initial stages of water mass isolation. A more extensive survey of abyssal methane concentrations in the world's oceans should also be made.

3) Laboratory experiments using methane-free medium and a variety of axenic phytoplankton algal cultures should be performed to evaluate further the role of algal metabolism in methane supply to the oceanic mixed layer. Experiments using heterotrophic bacteria would also be of interest, as would determination of the oxidizing or reducing nature of the guts of marine zooplankton.

4) Studies similar to that made in Walvis Bay but incorporating determination of more physical parameters could significantly improve estimates of the relative importance of physical transport and *in situ* biological consumption and supply in coastal regions.

REFERENCES

Atkinson, L. P. and F. A. Richards (1967) The occurrence and distribution of methane in the marine environment. Deep-Sea Res., 14, 673-684.

Bagirov, V. I., L. M. Zor'kin and L. V. Chertkova (1973) Hydrocarbon gases in bottom waters of the Black Sea. Dokl. Akad. Nauk. SSSR, 212, 216-217.

Baker-Blocker, A., T. M. Donahue and K. H. Mancy (1977) Methane flux from wetlands areas. Tellus, 29, 245-250.

Barker, H. A. (1956) Biological formation of methane. In: Bacterial Fermentations, CIBA Lectures in Microbial Biochemistry, John Wiley and Sons, Inc., New York, pp. 1-27.

Barnes, R. O. and E. D. Goldberg (1976) Methane production and consumption in anoxic marine sediments. Geology, 4, 297-300.

Benson, B. B. and P. D. M. Parker (1961) Nitrogen/argon and nitrogen isotope ratios in aerobic sea water. Deep-Sea Res., 7, 237-253.

Bernard, B. B., J. M. Brooks and W. M. Sackett (1976) Natural gas seepage in the Gulf of Mexico. Earth Planet. Sci. Lett., 31, 48-54.

Berner, R. A. (1969) Migration of iron and sulfur within anaerobic sediments during early diagenesis. Am. J. Sci., 267, 19-42.

Berner, R. A. (1974) Kinetic models for the early diagenesis of nitrogen, sulfur, phosphorus and silicon in anoxic marine sediments. In: The Sea, vol. 5, E. D. Goldberg, ed., Wiley Interscience, New York, pp. 427-450.

Bieri, R. H., M. Koide and E. D. Goldberg (1968) Noble gas contents of marine waters. Earth Planet. Sci. Lett., 4, 329-340.

Bishop, J. K. B. (1977) The chemistry, biology and vertical flux of oceanic particulate matter. PhD. Thesis, Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography, 292 pp.

Boon, J. J., J. W. deLeeuw, and P. A. Schenck (1975) Organic geochemistry of Walvis Bay diatomaceous ooze - I. Occurrence and significance of the fatty acids. Geochim. Cosmochim. Acta, 39, 1559-1565.

Bremner, J. M. (1974) Texture and composition of surficial continental margin sediments between the Kunene River and Silvia Hill, Southwest Africa. Joint Geological Survey/University of Cape Town Marine Geology Programme. Technical Report #6, pp. 39-43.

Brewer, P. G. (1971) Hydrographic and chemical data from the Black Sea. W. H. O. I. Reference No. 71-65, (unpublished manuscript).

Brewer, P. G. and J. W. Murray (1973) Carbon, nitrogen and phosphorus in the Black Sea. Deep-Sea Res., 20, 803-818.

Brewer P. G. and D. W. Spencer (1974) Distribution of some trace elements in the Black Sea and their flux between dissolved and particulate phases. In: The Black Sea-Geology, Chemistry and Biology, E. T. Degens and D. A. Ross, eds., AAPG Memoir 20, Tulsa, Okla., pp. 137-143.

Brewer, P. G. and D. W. Spencer (1975) Minor element models in coastal waters. In: Marine Chemistry in the Coastal Environment, T. M. Church, ed., ACS symposium series #18, ACS, Washington, D. C., pp. 80-96.

Broecker, W. S. and T.-H. Peng (1974) Gas exchange rates between air and sea. Tellus, 26, 21-35.

Broecker, W. S., T. Takahashi and Y.-H. Li (1976) Hydrography of the central Atlantic - I. The two degree discontinuity. Deep-Sea Res., 23, 1083-1104.

Brooks, J. M., A. D. Fredericks, W. M. Sackett and J. W. Swinnerton (1973) Baseline concentrations of light hydrocarbons in Gulf of Mexico. Environ. Sci. Technol., 7, 639-642.

Brooks, J. M. and W. M. Sackett (1973) Sources, sinks and concentrations of light hydrocarbons in the Gulf of Mexico. J. G. R., 78, 5248-5258.

Calvert, S. E. and N. B. Price (1971) Upwelling and nutrient regeneration in the Benguela Current, October, 1968. Deep-Sea Res., 18, 505-523.

Carpenter, J. H. (1965) The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. Limnol. Oceanogr., 10, 141-143.

Carroll, B. H. (1918) Alcohol and soda lime. J. Phys. Chem., 22, 128-149.

Cavanagh, L. A., C. F. Schadt and E. Robinson (1969) Atmospheric hydrocarbon and CO measurements at Point Barrow, Alaska. Environ. Sci. Technol., 3, 251-257.

Clarke, G. L. (1941) Observations on transparency in the southwest section of the North Atlantic ocean. J. Mar. Res., 4, 221-230.

Clarke, W. B., M. A. Beg and H. Craig (1969) Excess ^{3}He in the sea: evidence for terrestrial primordial helium. Earth Planet. Sci. Lett., 6, 213-220.

Claussen, W. F. and M. F. Polglase (1952) Solubilities and structures in aqueous aliphatic hydrocarbon solutions. J. Am. Chem. Soc., 74, 4817-4819.

Cline, J. D. (1969) Spectrophotometric determination of hydrogen sulfide in natural waters. Limnol. Oceanogr., 14, 454-458.

Colton, J. B., Jr. (1968) Recent trends in subsurface temperatures in the Gulf of Maine and contiguous waters. J. Fish. Res. Bd. Canada, 25, 2427-2437.

Craig, H. (1969) Abyssal carbon and radiocarbon in the Pacific. J. G. R., 74, 5491-5506.

Craig, H. (1971) The deep metabolism: oxygen consumption in abyssal ocean water. J. G. R., 76, 5078-5086.

Craig, H. and R. F. Weiss (1968) Argon concentrations in the ocean: a discussion. Earth Planet. Sci. Lett., 5, 175-183.

Craig, H. and R. F. Weiss (1971) Dissolved gas saturation anomalies and excess He in the ocean. Earth Planet. Sci. Lett., 10, 289-296.

Craig, H., R. F. Weiss and W. B. Clarke (1967) Dissolved gases in the equatorial and South Pacific ocean. J. G. R., 72, 6165-6181.

Danckwerts, P. V. (1970) Gas-Liquid Reactions, McGraw-Hill Book Co., New York, 276 pp.

Davis, J. B. and H. F. Yarbrough (1966) Anaerobic oxidation of hydrocarbons by Desulfovibrio desulfuricans, Chemical Geology, 1, 137-144.

Deuser, W. G. (1973) Cariaco Trench: oxidation of organic matter and residence time of anoxic water. Nature, 242, 601-603.

Deuser, W. G., E. T. Degens, G. R. Harvey and M. Rubin (1973) Methane in Lake Kivu: New data bearing on its origin. Science, 181, 51-54.

Dunlap, H. F., J. S. Bradley and T. F. Moore (1960) Marine seep detection-a new reconnaissance exploration method. Geophysics, 25, 275-282.

Ehhalt, D. H. (1974) The atmospheric cycle of methane. Tellus, 26, 58-70.

Ehhalt, D. H. and L. E. Heidt (1973) Vertical profiles of CH_4 in the troposphere and stratosphere. J. G. R., 78, 5265-5271.

Emerson, S. (1975) Gas exchange rates in small Canadian Shield Lakes, Limnol. Oceanogr., 20, 754-761.

Emery, K. O. and D. Hoggan (1958) Gases in marine sediments. Bull. AAPG, 42, 2174-2188.

Eucken, A. and G. Hertzberg (1950) Aussalzeffekt und Ionenhydratation. Z. Physik. Chem., 195, 1-23.

Fanning, K. A. and M. E. Q. Pilson (1972) A model for the anoxic zone of the Cariaco Trench. Deep-Sea Res., 19, 847-863.

Fanning, K. A. and M. E. Q. Pilson (1974) The diffusion of dissolved silica out of deep-sea sediments. J. G. R., 79, 1293-1297.

Gagosian, R. B. (1976) A detailed vertical profile of sterols in the Sargasso Sea. Limnol. Oceanogr., 21, 702-710.

Gieskes, J. M. (1973) Interstitial water studies, leg 15-alkalinity, pH, Mg, Ca, Si, PO_4 and NH_4. In: Heezen, B. C., *et al*., Initial Reports of the Deep Sea Drilling Project, vol. 20, Washington (U. S. Government Printing Office), pp. 813-829.

Guillard, R. R. L. and J. H. Ryther (1962) Studies on marine planktonic diatoms. I. *Cyclotella nana* Hustedt and *Detonula confervacae* (Cleve) Gran. Can. J. Microbiol, 8, 229-239.

Guinasso, N. L., Jr. and D. R. Schink (1975) Quantitative estimates of biological mixing rates in abyssal sediments. J. G. R., 80, 3032-3043.

Gunnerson, C. G. and E. Özturgut (1974) The Bosphorus. In: *The Black Sea-Geology, Chemistry and Biology*, E. T. Degens and D. A. Ross, eds., AAPG Memoir 20, Tulsa, Okla., pp. 99-114.

Gunsalus, R., D. Eirich, J. Romesser, W. Balch, S. Shapiro and R. S. Wolfe (1976) Methyl transfer and methane formation. In: *Microbial Production and Utilization of Gases*, H. G. Schlegel, G. Gottschalk and N. Pfennig, eds., Goltze Verlag, Göttingen, pp. 191-198.

Hathaway, J. C., J. S. Schlee, C. W. Poag, P. C. Valentine, E. G. A. Weed, M. H. Bothner, F. A. Kohout, F. T. Manheim, R. Schoen, R. E. Miller and D. M. Schultz (1976) Preliminary summary of the 1976 Atlantic Margin coring project of the U. S. Geological Survey. USGS open file report # 76-844, 217 pp.

Hazeu, W. (1975) Some cultural and physiological aspects of methane-utilizing bacteria. Antonie van Leeuwenhoek, *41*, 121-134.

Hellebust, J. A. and R. R. L. Guillard (1967) Uptake specificity for organic substrates by the marine diatom *Melosira nummuloides*. J. Phycol., *3*, 132-136.

Herrera, L. E. and G. Febres-Ortega (1975) Procesos de surgencia y de renovacion de aguas en la Fosa de Cariaco, Mar Caribe. Bol. Inst. Oceanogr. Univ. Oriente, *14*, 31-44.

Hobson, L. A. (1971) Relationships between particulate organic carbon and micro-organisms in upwelling areas off Southwest Africa. Inv. Pesq., *35*, 195-208.

Holm-Hansen, O. and H. W. Paerl (1972) The applicability of ATP determination for estimation of microbial biomass and metabolic activity. Mem. Ist. Ital. Idrobiol., *29* Supplement, 148-168.

Hunt, J. M. (1974) Hydrocarbon geochemistry of Black Sea. In: The Black Sea - Geology, Chemistry and Biology, E. T. Degens and D. A. Ross, eds., AAPG Memoir 20, Tulsa, Okla., pp. 499-504.

Hutchinson, G. E. (1949) A note on two aspects of the geochemistry of carbon. Am. J. Sci., 247, 27-32.

Hutton, W. E. and C. E. ZoBell (1949) The occurrence and characteristics of methane oxidizing bacteria in marine sediments. J. Bacteriol., 58, 463-473.

Jannasch, H. W. (1967) Growth of marine bacteria at limiting concentrations of organic carbon in seawater. Limnol. Oceanogr., 12, 264-271.

Jannasch, H. W. (1975) Methane oxidation in Lake Kivu (central Africa). Limnol. Oceanogr., 20, 860-864.

Jannasch, H. W., C. O. Wirsen and C. D. Taylor (1976) Undecompressed microbial populations from the deep sea. Appl. Environ. Microbiol., 32, 360-367.

Jenkins, W. J. (1977) Tritium-helium dating in the Sargasso Sea: a measurement of oxygen utilization rates. Science, 196, 291-292.

Jenkins, W. J., M. A. Beg, W. B. Clarke, P. J. Wangersky and H. Craig (1972) Excess ^{3}He in the Atlantic Ocean. Earth Planet. Sci. Lett., 16, 122-126.

Jenkins, W. J. and W. B. Clarke (1976) The distribution of ^{3}He in the western Atlantic ocean. Deep-Sea Res., 23, 481-494.

Jørgensen, B. B. (1977) Bacterial sulfate reduction within reduced microniches of oxidized marine sediments. Mar. Biol., 41, 7-17.

Katz, D. L. (1971) Depths to which frozen gas fields (gas hydrates) may be expected. J. Petrol. Technol., 23, 419-423.

Katz, D. L. (1972) Depths to which frozen gas fields may be expected-footnotes. J. Petrol. Technol., 24, 557-558.

Koyama, T. (1963) Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen. J. G. R., 68, 3971-3973.

Kuo, H. H. and G. Veronis (1970) Distribution of tracers in the deep oceans of the world. Deep-Sea Res., 17, 29-46.

Lamontagne, R. A., J. W. Swinnerton and V. J. Linnenbom (1971) Non-equilibrium of CO and CH_4 at the air-sea interface. J. G. R., 76, 5117-5121.

Lamontagne, R. A., J. W. Swinnerton and V. J. Linnenbom (1974) C_1-C_4 hydrocarbons in the North and South Pacific. Tellus, 26, 71-77.

Lamontange, R. A., J. W. Swinnerton, V. J. Linnenbom and W. D. Smith (1973) Methane concentrations in various marine environments. J. G. R., 78, 5317-5324.

Lannung, A. and J. Chr. Gjaldbaek (1960) The solubility of methane in hydrocarbons, alcohols, water and other solvents. Acta Chem. Scand., 14, 1124-1128.

Larson, R. E., R. A. Lamontagne, P. E. Wilkniss and W. I. Wittman (1972) Radon-222, CO, CH_4 and continental dust over the Greenland and Norwegian Seas. Nature, 240, 345-347.

Lee, C. and J. L. Bada (1977) Dissolved amino acids in the equatorial Pacific, the Sargasso Sea and Biscayne Bay. Limnol. Oceanogr., 22, 502-510.

Levy, H., II (1973) Tropospheric budgets for CH_4, CO and related species. J. G. R., 78, 5325-5332.

Liss, P. S. and P. G. Slater (1974) Flux of gases across the air-sea interface. Nature, 247, 181-184.

Lovelock, J. E., R. J. Maggs and R. J. Wade (1973) Halogenated hydrocarbons in and over the Atlantic. Nature, 241, 194-196.

McAuliffe, C. (1966) Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin and aromatic hydrocarbons. J. Phys. Chem., 70, 1267-1275.

McConnell, J. C., M. B. McElroy and S. C. Wofsy (1971) Natural sources of atmospheric CO. Nature, 233, 187-188.

Macdonald, R. W. (1976) Distribution of low-molecular-weight hydrocarbons in Southern Beaufort Sea. Environ. Sci. Technol., 10, 1241-1246.

Mah, R. A., D. M. Ward, L. Baresi and T. L. Glass (1977) Biogenesis of methane. Ann. Rev. Microbiol., 31, (in press).

Maloney, N. J. (1966) Geomorphology of continental margin of Venezuela. Part I. Cariaco Basin. Bol. Inst. Oceanogr. Univ. Oriente, 5, 38-53.

Martens, C. S. (1976) Control of methane sediment-water bubble transport by macroinfaunal irrigation in Cape Lookout Bight, North Carolina. Science, 192, 998-1000.

Martens, C. S. and R. A. Berner (1974) Methane production in the interstitial waters of sulfate depleted marine sediment. Science, 185, 1167-1169.

Martens, C. S. and R. A. Berner (1977) Interstitial water chemistry of anoxic Long Island Sound sediments. 1. Dissolved gases. Limnol. Oceanogr., 22, 10-25.

Mazeika, P. A. (1973) Circulation and water masses east of the Lesser Antilles. Deutschen Hydrographischen Zeitschrift, 26, 49-73.

Meade, R. H., P. L. Sachs, F. T. Manheim, J. C. Hathaway and D. W. Spencer (1975) Sources of suspended matter in waters of the Middle Atlantic Bight. J. Sed. Petrol., 45, 171-188.

Merz, A. and L. Möller (1928) Hydrographische Untersuchungen in Bosphorus und Dardanellen. Veröff. Inst. Meeresforsch., Berl. N. F., 18, 284 pp.

Monroe, J. N. (1969) Slumping structures caused by organically derived gases in sediments. Science, 164, 1394-1395.

Morrison, T. J. and F. Billett (1952) The salting out of non-electrolytes. Part II. The effect of variation in non-electrolyte. J. Chem. Soc., 1952, 3819-3822.

Mullin, J. B. and J. P. Riley (1955) The colorimetric determination of silicate with special reference to sea and natural waters. Anal. Chim. Acta, 12, 162-176.

Murphy, J. and J. P. Riley (1962) A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta, 27, 31-36.

Okubo, A. (1971) Oceanic diffusion diagrams. Deep-Sea Res., 18, 789-802.

Orr, W. L. and A. G. Gaines, Jr. (1973) Observations on rate of sulfate reduction and organic matter oxidation in the bottom waters of an estuarine basin of the Pettaquamscutt River (Rhode Island). Adv. Org. Geochem., 1973, 791-812.

Ortega, G. F. (1972) Isanosteric analysis of the eastern Caribbean waters during winter. Bol. Inst. Oceanogr. Univ. Oriente, 11, 19-34.

Östlund, H. G. (1974) Expedition "Odysseus 65"; Radiocarbon age of Black Sea Deep Water. In: The Black Sea - Geology, Chemistry and Biology, E. T. Degens and D. A. Ross, eds., AAPG Memoir 20, Tulsa, Okla., pp. 127-132.

Packard, T. T., M. L. Healy and F. A. Richards (1971) Vertical distribution of the activity of the respiratory electron transport system in marine plankton. Limnol. Oceanogr., 16, 60-70.

Patt, T. E., G. C. Cole, J. Bland, and R. S. Harrison (1974) Isolation and characterization of bacteria that grow on CH_4 and organic compounds as sole sources of carbon and energy. J. Bacteriol., 120, 955-964.

Peng, T.-H., T. Takahashi and W. S. Broecker (1974) Surface radon measurements in the North Pacific ocean station PAPA. J. G. R., 79, 1772-1780.

Postgate, J. R. (1969) Methane as a minor product of pyruvate metabolism by sulfate-reducing and other bacteria. J. Gen. Microbiol., 57, 293-302.

Prabhakara, C., G. Dalu and V. G. Kunde (1974) A search for global and seasonal variation of methane from Nimbus 4 Iris measurements. J. G. R., 79, 1744-1749.

Presley, B. J. (1974) Rates of sulfate reduction and organic carbon oxidation in the Cariaco Trench. Trans. Am. Geophys. Union, 55, 319-320.

Pring, J. N. (1910) The direct union of carbon and hydrogen at high temperatures. Part II. J. Chem. Soc., 97, 498-511.

Raymont, J. E. G. (1963) Plankton and Productivity in the Oceans, Pergamon Press, New York, 660 pp.

Reeburgh, W. S. (1969) Observations of gases in Chesapeake Bay sediments. Limnol. Oceanog., 14, 368-375.

Reeburgh, W. S. (1972) Processes affecting gas distributions in estuarine sediments. In: Environmental Framework of Coastal Plain Estuaries, B. W. Nelson, ed., GSA Memoir 133, GSA, Boulder, pp. 383-389.

Reeburgh, W. S. (1976) Methane consumption in Cariaco Trench waters and sediment. Earth. Planet. Sci. Lett., 28, 337-344.

Ribbat, B., W. Roether and K. O. Munnich (1976) Turnover of eastern Caribbean deep water from ^{14}C measurements. Earth Planet. Sci. Lett., 32, 331-341.

Ribbons, D. W., J. E. Harrison and A. M. Wadzinski (1970) Metabolism of single carbon compounds. Ann. Rev. Microbiol., 28, 135-158.

Richards, F. A. (1970) Physical, chemical and productivity data from a survey of the Caribbean Sea and the northeastern Pacific ocean. U. Washington Technical Report 249.

Richards, F. A. (1975) The Cariaco Basin (Trench). Oceanogr. Mar. Biol. Ann. Rev., 13, 11-67.

Richards, F. A. and R. F. Vaccaro (1956) The Cariaco Trench, an anaerobic basin in the Caribbean Sea. Deep-Sea Res., 3, 214-228.

Riley, G. A. (1951) Oxygen, phosphate and nitrate in the Atlantic Ocean. Bull. Bingham Oceanogr. Coll., 13, 1-126.

Robinson, E. and R. C. Robbins (1968) Sources, abundance and fate of gaseous atmospheric pollutants. Stanford Res. Inst. project PR-6755-final report. 101-104.

Rona, E. (1917) Diffusionsgrösse und Atomdurchmesser der Radiumemanation. Z. Phys. Chem., 92, 213-218.

Rooth, C. G. and H. G. Östlund (1972) Penetration of tritium into the Atlantic thermocline. Deep-Sea Res., 19, 481-492.

Rudd, J. W. M. and R. D. Hamilton (1975) Factors controlling rates of methane oxidation and the distribution of the methane oxidizers in a small stratified lake. Arch. Hydrobiol, 75, 522-538.

Rudd, J. W. M., R. D. Hamilton and N. E. R. Campbell (1974) Measurement of microbial oxidation of methane in lake water. Limnol. Oceanogr., 19, 519-524.

Ryther, J. H. and R. R. L. Guillard (1962) Studies of marine planktonic diatoms. III. Some effects of temperature on respiration of five species. Can. J. Microbiol., 8, 447-453.

Sayles, F. L., F. T. Manheim and L. S. Waterman (1973) Interstitial water studies on small core samples. Leg 15. In: Heezen, B. C., et al., 1973, Initial Reports of the Deep Sea Drilling Project, vol. 20, Washington (U. S. Government Printing Office), pp. 783-804.

Schröder, W. (1968) Beobachtungen an Lösungen von Gasen in Wasser. Naturwissenschaften, 55, 542.

Scranton, M. I. and P. G. Brewer (1977) Occurrence of methane in the near-surface waters of the western subtropical North Atlantic. Deep-Sea Res., 24, 127-138.

Scranton, M. I. and J. W. Farrington (1977) Methane production in the waters off Walvis Bay. J. G. R. (in press).

Seiler, W and U. Schmidt (1974) Dissolved nonconservative gases in seawater. In: The Sea, vol. 5, E. D. Goldberg, ed., John Wiley and Sons, New York, pp. 219-243.

Skopintsev, B. A. (1976) Oxygen consumption in the deep waters of the ocean. Oceanology, 15, 556-560.

Smayda, T. J. (1969) Measurements of the sinking rate of fecal pellets. Limnol. Oceanogr., 14, 621-625.

Sorokin, Y. I. (1964) On the primary production and bacterial activities in the Black Sea. J. Cons. internat. Explor. Mer, 29, 41-60.

Sorokin, Y. I. (1972) Microbial activity as a biogeochemical factor in the ocean. In: Changing Chemistry of the Oceans, Nobel Symposium 20, D. Dyrssen and D. Jagner, eds., Wiley Interscience, New York, pp. 189-204.

Spencer, D. W. and P. G. Brewer (1971) Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. J. G. R., 76, 5877-5892.

Stadtman, T. C. (1967) Methane fermentation. Ann. Rev. Microbiol., 21, 121-142.

Stander, G. H. (1964) The Pilchard of South West Africa: The Benguela Current off South West Africa. Adminstration of South West Africa Marine Research Laboratory Investigational Report #12, 44 pages plus 81 plates.

Stuiver, M. (1976) The ^{14}C distribution in west Atlantic abyssal waters. Earth Planet. Sci. Lett., 32, 322-330.

Swinnerton, J. W. and V. J. Linnenbom (1967a) Gaseous hydrocarbons in seawater: determination. Science, 156, 1119-1120.

Swinnerton, J. W. and V. J. Linnenbom (1967b) Determination of the C_1 to C_4 hydrocarbons in seawater by gas chromatography. J. Chromat. Sci. (J. Gas Chromat.), 5, 570-573.

Swinnerton, J. W. and V. J. Linnenbom (1969) Low molecular weight hydrocarbon analyses of Atlantis II waters. In: Hot Brines and Recent Heavy Metal Deposits in the Red Sea, E. T. Degens and D. A. Ross, eds., Springer-Verlag, New York, 251-253.

Swinnerton, J. W., V. J. Linnenbom and C. H. Cheek (1962a) Determination of dissolved gases in aqueous solutions by gas chromatography. Anal. Chem., 34, 483-485.

Swinnerton, J. W., V. J. Linnenbom and C. H. Cheek (1962b) Revised sampling procedure for determination of dissolved gases in solution by gas chromatography. Anal. Chem., 34, 1509.

Swinnerton, J. W., V. J. Linnenbom and C. H. Cheek (1969) Distribution of CH_4 and CO between the atmosphere and natural waters. Environ. Sci. Technol., 3, 836-838.

Taylor, C. D. and H. W. Jannasch (1976) A subsampling technique for measuring the growth of bacterial cultures under high hydrostatic pressures. Appl. Environ. Microbiol., 32, 355-359.

Turner, J. T. (1977) Sinking rates of fecal pellets from the marine copepod *Pontella meadii*. Mar. Biol., 40, 249-259.

Ullyott, P. and O. Ilgaz (1946) The hydrography of the Bosphorus: an introduction. Geog. Rev., 36, 44-60.

van der Waals, J. H. and J. C. Platteeuw (1959) Clathrate solutions. Adv. Chem. Phys., 2, 1-58.

Visser, G. A. (1969) Analysis of Atlantic waters off the west coast of southern Africa. R. S. A. Division of Sea Fisheries Investigational Report #75, pp. 1-26.

Weaver, T. L. and P. R. Dugan (1972) The eutrophication implications of interactions between naturally occurring particulates and methane oxidizing bacteria. Water Res., 6, 817-828.

Weiss, R. F. (1970) The solubility of nitrogen, oxygen and argon in water and seawater. Deep-Sea Res., 17, 721-731.

Wetlaufer, D. B., S. K. Malik, L. Stoller and R. L. Coffin (1964) Nonpolar group participation in the denaturation of proteins by urea and guanidinium salts: Model compound studies. J. Am. Chem. Soc., 86, 508-514.

Whittenbury, R., K. C. Philips and J. F. Wilkinson (1970) Enrichment, isolation and some properties of methane utilizing bacteria. J. Gen. Microbiol., 61, 205-218.

Williams, P. M. and A. F. Carlucci (1976) Bacterial utilization of organic matter in the deep ocean. Nature, 262, 810-811.

Williams, R. T. and A. E. Bainbridge (1973) Dissolved CO, CH_4 and H_2 in the Southern Ocean. J. G. R., 78, 2691-2694.

Winfrey, M. R. and J. G. Zeikus (1977) Effect of sulfate on carbon and electron flow during microbial methanogenesis in freshwater sediments. Appl. Environ. Microbiol., 33, 275-281.

Winkler, L. W. (1901) Die Löslichkeit der Gase in Wasser. Chem. Ber., 34, 1408-1422.

Wirsen, C. O. and H. W. Jannasch (1975) Activity of marine psychrophilic bacteria at elevated hydrostatic pressures and low temperatures. Mar. Biol., 31, 201-208.

Wishnia, A. (1962) The solubility of hydrocarbon gases in protein solutions. Proc. Natl. Acad. Sci., 48, 2200-2204.

Wishnia, A. (1963) The hydrophobic contribution to micelle formation: the solubility of ethane, propane, butane and pentane in sodium dodecyl sulfate solution. J. Phys. Chem., 67, 2079-2082.

Witherspoon, P. A. and L. Bonoli (1969) Correlation of diffusion coefficients for paraffin, aromatic and cycloparaffin hydrocarbons in water. I. and E. C. Fundamentals, 8, 589-591.

Wolfe, R. S. (1971) Microbial formation of methane. Adv. in Microbial Physiol., 6, 107-146.

Wong, G. T. F. and P. G. Brewer (1977) The marine chemistry of iodine in anoxic basins. Geochim. Cosmochim. Acta, 41, 151-159.

Worthington, L. V. (1976) On the North Atlantic Circulation. The Johns Hopkins Oceanographic Studies, no. 6, The Johns Hopkins University Press, Baltimore, 110 pp.

Wyrtki, K. (1962) The oxygen minima in relation to oceanic circulation. Deep-Sea Res., 9, 11-23.

Yamamoto, S., J. B. Alcauskas and T. E. Crozier (1976) Solubility of methane in distilled water and seawater. J. Chem. Engineering Data, 21, 78-81.

Zeikus, J. G. (1977) Biology of methanogenic bacteria. Bacteriol. Rev., 41, (in press).

APPENDIX I.1

AIR-SEA EXCHANGE

The rate of transfer of a gas across the air-sea interface can only be calculated if two parameters can be evaluated: the equilibrium concentration of the gas in seawater at the salinity and temperature of the water in question and the "piston velocity" or mass transfer coefficient which determines the rate of exchange of a gas across the air-sea interface.

A considerable amount of methane solubility data is available for distilled water (Eucken and Hertzberg, 1950; Morrison and Billett, 1952; Claussen and Polglase, 1952; Lannung and Gjaldbaek, 1960; Schröder, 1968; McAuliffe, 1966). Atkinson and Richards (1967) have presented an estimate of the solubility of methane in seawater, based on an interpolation between values determined for 40‰ seawater at temperatures between 0° and 30°C, and the distilled water solubility reported by Winkler (1901). However, highly precise and accurate measurements for seawater have only been available within the last few years (Weiss, personal communication, 1974; Yamamoto _et al._, 1976). Yamamoto and coworkers present their data in terms of Bunsen solubility coefficients (defined as the volume of gas at 0°C and 760 mm pressure which is absorbed by a unit volume of solvent at the temperature of measurement and under a total gas pressure of 760 mm). The dry gas pressure is equal to the total pressure minus the vapor pressure of the solvent at the temperature of interest. Yamamoto _et al._ (1976) have fitted to their data an equation of the form

$$\ln \beta = A_1 + A_2 (100/T) + A_3 \ln (T/100) + S (B_1 + B_2 (T/100) + B_3 (T/100)^2)$$

where the As and Bs are constants, T is the absolute temperature (^{o}K), and S is the salinity. Equations of this form have been used by Weiss (1970) for N_2, O_2 and Ar.

Using the solubility data presented by Yamamoto et al. (1976), the equilibrium concentration of methane in seawater is

$$C_{eq} = x_i^A \beta_i \frac{(P - p_v)}{P}$$

where x_i^A = partial pressure of methane in dry air

β_i = Bunsen coefficient for T and S of water

P = total atmospheric pressure

and p_v = vapor pressure of water at T and S of interest.

This equation gives C_{eq} in units of ml methane/liter seawater, since the Bunsen coefficient is in those units.

The second important parameter for gas exchange, the piston velocity, is calculated using a conceptual model of exchange across the gas-liquid interface known as the stagnant boundary layer model (Broecker and Peng, 1974; Liss and Slater, 1974; Danckwerts, 1970; Emerson, 1975). This model assumes the presence of two stagnant boundary layers, in the gas and liquid respectively, at the interface. Within these layers, gas transport is assumed to be by molecular diffusion alone. Outside of these layers, the two fluids are assumed to be uniformly mixed. The diffusion rates in the gas phase are so much higher than in the liquid phase that, except for a a few gases such as SO_2 which are extremely soluble in water, the gaseous diffusion layer may be ignored (Liss and Slater, 1974). Thus using Fick's law to describe diffusion through a stagnant film in the liquid, the flux of gas (F) is

$$F = D \frac{(C - C_{eq})}{z}$$

where C = measured bulk concentration in surface water
C_{eq} = concentration of gas at interface (equal to equilibrium concentration)
D = molecular diffusion coeff. coefficient
and z = stagnant film thickness.

This model probably does not accurately represent the true physical situation. In a system with waves, the concept of a uniformly thick stagnant film does not seem reasonable. However, Danckwerts (1970) has shown that the results of this model and of much more sophisticated ones are equal within a few percent for the conditions encountered in nature. Considering the error in our knowledge of the diffusion coefficients and even in the concentrations of some gases, the simplicity of the thin film model makes it the model of choice.

^{222}Rn measurements have been used extensively in connection with the boundary layer model, in particular to enable estimates of the boundary layer thickness to be made. Since the molecular diffusion coefficients for methane (Witherspoon and Bonoli, 1969) and for Rn (Rona, 1917) are known, the mass transfer coefficient determined for one gas can be used to estimate the coefficient for the other. Emerson (1975) and Peng _et al._

(1974) have shown that the thin film thickness, z, is proportional to the square of the wind speed. Knowing the wind speed, the atmospheric concentration of the gas in question and the temperature and salinity and methane content of the mixed layer, one can calculate the rate of exchange of gas across the air-sea interface.

APPENDIX I.2

PHYSICAL CONTRIBUTIONS TO GASEOUS SATURATION ANOMALIES IN SEAWATER

Craig *et al*. (1967), Bieri *et al*. (1968) and Craig and Weiss (1968) have noted that several of the noble gases (He, Ne and Ar) are present in deep ocean waters in concentrations different from those which would be predicted from solubility equilibrium with the atmosphere. Helium is produced by degassing at the ridge crests and by α-decay in the sediments (Clarke *et al*., 1969; Jenkins *et al*., 1972). However the saturation anomalies observed for argon and neon cannot be explained by production within the ocean basin.

Craig and Weiss (1971) have presented a model which explains the observed saturation anomalies for gases such as Ne as a result of physical processes which cause the actual concentration to deviate from that which would be produced by equilibration with the atmosphere at 760 mm pressure and the temperature measured in the water sample. Three processes may be involved: air injection (complete dissolution of bubbles), changes in temperature of the water since equilibration with the atmosphere, and atmospheric pressure variations over the sea surface (including partial dissolution of bubbles which gives almost the same result as increases in atmospheric pressure). Craig *et al*. (1967) and Benson and Parker (1961) have discussed these processes in a qualitative manner. Craig and Weiss (1971) have attempted to make quantitative estimates for the magnitudes of the anomalies to be expected from each process. The following is taken from Craig and Weiss (1971).

Δ_i can be defined as the 'wet' saturation anomaly equal to $(C/C_i^*) - 1$ where C_i^* is the equilibrium concentration defined at an atmospheric pressure of 760 mm. If ΔT is the change in water temperature since equilibration with the atmosphere and if a is the amount of injected air in ml/l, the predicted saturation anomaly is

$$\Delta_i = (P - 1) - P \frac{(d \ln C_i^*)}{dT} \Delta T + \frac{x_i^A a}{C_i^*}$$

where x_i^A is the volume fraction of the gas in dry air and P is the total pressure.

Writing Δ_i in percent

$$\Delta_i\ (\%) = \Delta_P - 100 \frac{(d \ln C_i^*)}{dT} \Delta T + \frac{x_i^A a}{C_i^*}$$

where Δ_P is the percentage deviation of the pressure component from one and x_i^A is in percent.

Craig and Weiss (1971) have estimated that the air injection component for the Atlantic is about 0.5 ml/l. The percent saturation anomaly which would result from such an air-injection component would be less than or equal to 2% for methane for all temperatures found in the Atlantic.

The effect of temperature changes after equilibration is much larger. Craig and Weiss (1971) give a rough estimate of the variation in ΔT in the Atlantic of from - 2°C to + 5°C. At 25°C this would result in a saturation anomaly for methane of from -0.1% to +0.3%. At 2°C the saturation anomaly from this process could be between - 14% and + 28%. (These large anomalies are due to the much greater temperature dependence of solubility at lower temperatures.)

Finally Craig and Weiss (1971) estimate that Δ_P is about ± 8% for the Atlantic.

Thus the saturation anomaly for methane is probably between - 6% and

+10% at 25°C and between -34% and +24% at 2°C. The data on which the result is based (Craig and Weiss, 1971) are very uncertain. I feel sure that the ranges of ± 10% for 25°C and ± 30% for 2°C are generous estimates, and probably overestimates, of the possible contribution of physical processes to the saturation anomalies of methane in the oceans. The surface waters are consistently supersaturated with methane by 30 to 60% (see Chapters III and IV). The deep waters are consistently undersaturated by up to 90% (see Chapter VI). It seems very unlikely that these results are due to predominantly physical effects.

APPENDIX III.1

DATA FROM R/V ATLANTIS CRUISE 93 LEG 3 TO WALVIS BAY

Equilibrium methane concentrations were calculated from the equation presented by Yamamoto *et al*. (1976) using the temperature and salinity of the sample in question. The atmospheric methane concentration was taken to be 1.44 ppmv as measured on the cruise (see Chapter III). The precision of the phosphate analyses was ± 0.05 μmole/l except where otherwise indicated. Parentheses around a value indicate that its accuracy is in question. Single parentheses to the left of methane values indicate that the two values are from duplicate samples taken from the same Niskin bottle.

Station AII93-2241 31°48.7'S 17°12.7'E Taken 23 December 1975

Depth: 177m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0			2.18		5.61	1.45
6	16.93	35.240		1.86		
9			2.79		5.66	1.58
11	16.95	35.233		1.86		
19			2.83		5.60	1.50
28			2.71		5.10	1.80
38			2.55		4.76	1.90
47			2.68		4.54	2.17
66			2.54		4.48	2.50
94			2.52		3.98	2.90
118			2.48		3.92	2.97
136	8.72	34.707		2.26		
136	8.80	34.712		2.25		
141					4.37	3.05
143		34.654				

Station AII93-2242   28°43.6'S 15°51.7'E   Taken 24 December 1975

Depth: 153m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0			) 2.86		6.06	0.37
			) 3.02			
5	17.29	34.542		1.85		
10		34.902	2.69	1.87	6.22	0.32
10	16.70					
15		(34.829)				
19		34.937	2.74	1.89	6.22	0.64
29		35.022	2.66	1.98	4.77	1.05
49		35.102	2.41	2.07	4.26	1.48
97		34.953	2.64	2.20	3.64	1.77
117		34.748	3.58	2.22	3.25	2.16
126		(34.835)	3.79	2.23	3.14	2.19
129	9.22	34.740		2.23		
131	9.21	34.737		2.23		
136		(34.812)	3.78		3.08	2.02
136		34.740				

Station AII93-2243 26°36.2'S 14°53.5'E Taken 25 December 1975

Depth: 137m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0			2.90		5.16	1.40
5	11.23	34.860		2.12		
10		34.849	2.93	2.12	5.10	1.48
10	11.73	34.848		2.10		
20		34.884	3.08	2.12	5.10	1.43
30		34.868	3.09	2.12	5.07	1.33
40		34.913	3.13	2.12	4.88	1.38
50		34.895	3.10	2.12	4.44	1.44
60		34.845	3.10	2.16	3.20	1.84
80		34.931	5.05	2.16	2.05	2.15
100		34.874	5.37	2.17	1.91	2.27
113	10.26	34.896		2.17		
114	10.19	34.850		2.17		
120		34.856	6.58	2.17	1.57	2.33
120		34.878				

Station AII93-2244
Depth: 4240m

Shallow cast: 22°18.5'S 08°59.7'E
Intermediate cast: 22°14.9'S 08°59'8'E
Deep Cast: 22°13.2'S 08°59.2'E

Taken 26-29 December 1975

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/1)	CH_4eq (nmole/1)	O_2 (ml/1)	PO_4 (µmole/1)
0			2.57		5.57	0.41
10	19.22	35.310		1.78		
11		35.326	2.43	1.78	5.63	0.45
22		35.328	2.39	1.78	5.61	0.34
27	19.29	35.329		1.77		
30	18.48	35.325		1.80		
30		35.335				
34		35.341	2.59	1.79	5.66	0.36
39	18.37	35.378		1.80		
44		35.394	2.50	1.81	5.66	0.40
47	17.95	35.366		1.82		
54		35.390	2.52	1.85	5.44	0.37
55		35.353				
64		35.402	2.53	1.87	5.49	0.53
69	16.28	35.398		1.89		
72	16.15	35.377		1.89		
77		35.386				
83		35.416	2.44	1.90	5.44	0.61
93	15.89	35.418		1.90		
99		35.381				
102		35.404	2.42	1.92	5.33	0.59
117	15.10	35.400		1.93		
120			) 2.54			
			) 2.56			
144	13.95	35.229		1.98		
146		35.321	3.06	1.98	3.53	1.73
162	13.58	35.195		2.00		
168			) 2.50			
			) 2.36			
169		35.174				
183	13.05					
184	13.17	35.206		2.03		

...continued

Station AII93-2244 (continued)

192		35.175	2.76	2.03	3.03	1.71±.2
226	11.61	35.048		2.10		
233		34.995				
288		34.908	2.34	2.16	3.14	1.93±.2
384		34.719	1.98	2.26	1.96	2.51
432		34.640				
435	7.75	34.642		2.31		
442		34.613				
480		34.567	1.68	2.35	2.35	2.70
576		34.506	1.39	2.42	2.41	2.65±.2
623	5.33	34.473		2.47		
628	5.30	34.479		2.47		
630		34.474				
672		34.467	1.24	2.48	2.92	2.51±.2
734	4.56	34.461		2.52		
759	4.47	34.454		2.52		
766		34.453				
768		34.451	1.22	2.52	3.25	2.61
864		34.465	1.11	2.56	3.48	2.57
914	3.94	34.486		2.56		
960	3.80	34.528		2.56		
967		34.533				
1126	3.47	34.601		2.59		
1133		34.606				
1152		34.628	1.03	2.59	4.04	2.31
1169	3.45	34.638		2.59		
1282	3.37	34.705		2.59		
1452	3.28	34.784		2.59		
1458		34.785				
1478	3.32	34.781		2.59		
1776		34.870	0.84	2.59	5.05	1.59±.2
1799	3.15	34.872		2.60		
1933	3.04	34.886		2.61		

...continued

Station AII93-2244 (continued)

1940		34.888				
2073		34.890	0.86	2.62	5.30	1.66
2359		34.893	0.70	2.64	5.44	1.60
2380	2.66	34.892		2.64		
2481	2.54	34.884		2.64		
2488		34.882				
2682		34.881	0.54	2.67	5.42	1.58
3002		34.872	0.50	2.68	5.41	1.55±.2
3138	2.20	34.878		2.67		
3142		34.871				
3322		34.872	0.66	2.68	5.38	1.68
3345	2.17	34.865		2.67		
3597			0.52	2.68	5.38	1.71
3833	1.65	34.827		2.72		
3840		34.824				
3863		34.832	0.60	2.71	5.27	1.95
4143	1.15	34.774		2.76		
4305			0.78	2.78	5.01	2.06±.2
4317	0.88	34.752		2.78		
4336	0.80	34.742		2.78		
4341		34.740				

Station AII93-2245 1st cast 22°16.3'S 12°03.3'E Taken 30 December 1975
2nd cast 22°13.9'S 12°09.4'E
Depth: 1885m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0						0.23
10		35.123	2.46	1.78	5.87	0.31
20						0.19
30		35.062	3.03	1.82	4.77	0.51
50			4.36		5.05	1.12
60		35.256	2.79	1.97	4.77	1.10
80			2.69		5.05	0.80
100		35.219	2.40	2.04	4.77	0.82
109	(13.60)	35.203		2.00		
114			2.50			
150			2.37		4.60	0.94
160			2.51			
200		35.026	2.40	2.18	4.23	1.26
265	(10.28)	34.874		2.16		
274			2.24			
278		34.805				
381		34.623	1.92		3.06	2.17
478		34.523	1.65		2.88	2.30
574		34.510	1.42		2.37	2.61
671		34.478	1.39		2.72	2.60
769		34.465	1.36		3.12	2.54
847	4.19	34.478		2.53		
867			1.05		3.45	2.44
963		34.516	1.35		3.64	2.40
1154		34.644	0.91		4.04	2.30
1347		34.785	1.00		4.37	2.02
1712	3.18	34.889		2.59		
1732			1.00		4.93	1.70

Station AII93-2246 22°14.7'S 12°41.6'E Taken 31 December 1975

Depth: 660m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/1)	CH_4eq (nmole/1)	O_2 (ml/1)	PO_4 (μmole/1)
0					6.17	0.59
10		34.983			5.27	0.77
10		34.981			3.98	1.68
19			6.92			
32	15.14	35.026		1.93		
38		(35.274)	3.76	1.95		
45	14.22	35.130		1.97		
53			) 3.83			
			) 3.57			
53		35.181				
67			4.07			
76			3.73		2.13	2.03
89	13.08	35.215		2.02		
95		35.188	3.65	2.03	1.85	2.02
96		35.195				
143	11.82	35.102		2.09		
151		35.080				
191			3.32		0.81	2.38
239	10.92	35.010		2.13		
250	10.88	35.010		2.13		
284	9.99					
288			3.40		0.75	2.40
291		34.882				
385		34.740	2.23	2.27	1.37	2.54
430	7.68	34.663		2.32		
437		34.632				
484			1.70		1.91	2.63
583			1.48		2.27	2.65
591	5.89	34.527		2.43		
592	5.88	34.526		2.43		
620	5.63	34.507		2.44		
627		34.506				

Station AII93-2247 22°47.5'S 14°25.7'E Taken 1 January 1976

Depth: 44m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/1)	CH_4eq (nmole/)	O_2 (ml/1)	PO_4 (μmole/1)
0		35.049	629	1.91	7.32	0.57
5		35.048	879	1.98	7.34	0.56
9	13.01	35.050		2.03		
10		35.053	330	2.04	2.52	1.62
20		35.051	567	2.07	0.35	2.38
30		35.091	54	2.08	0.10	1.78
32	11.92					
40		35.091	174	2.08	0	2.97
40		35.091				

Station AII93-2248 22°35.4'S 13°29.2'E Taken 2 January 1976

Depth: 192m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0			11.5		6.45	0.34
10		34.941	12.1	1.92	6.39	0.40
10	15.85	34.940		1.90		
20			8.81		5.94	0.47
31	14.37	35.027		1.97		
31		35.057				
39		35.072	3.51	1.98	4.15	1.35
59			3.36		3.11	1.60
79		35.170	3.26	2.02	2.64	1.89
93	12.78	35.160		2.03		
99			3.02		2.18	1.81
101		35.146				
123		35.098	2.83	2.08	1.65	2.07
148			3.33		0.78	2.10
158	11.61	35.082		2.10		
165	11.62	35.083		2.10		
167	11.64					
172	11.62	35.084		2.10		
177		35.089	5.00	2.10	0.50	2.23

Station AII93-2250 22°08.5'S 13°52'E Taken 3 January 1976

Depth: 97m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0		35.069	16.9	1.84	5.61	0.26
10		35.069	19.1	1.85	5.61	0.33
19		35.024	32.8	2.03	3.53	1.42
29		35.066	5.60	2.05	2.07	2.12
38		35.092	2.94	2.06	2.07	1.98
48		35.088	3.20	2.06	1.46	2.12
57		35.091	3.43	2.07	1.29	2.21
67		35.087	6.26	2.08	0.34	2.70
76		35.083	9.28	2.09	0.17	2.82
81	11.78	35.086		2.09		
86			10.2		0.17	2.86

Station AII93-2252 22°39.0'S 13°09.6'E Taken 3 January 1976

Depth: 294m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0		34.937	3.98	1.86	6.00	0.34
10		34.932	4.46	1.87	6.11	0.40
19		34.931	4.85	1.88	5.98	0.37
39		35.041	4.05	1.94	4.79	1.03
77		35.179	5.49	1.98	3.70	1.66
97		35.183	5.14	2.01	3.06	1.83
145		35.152	3.64	2.04	1.76	1.93
194		35.095	2.75	2.06	1.09	2.13
242		35.011	2.49	2.13	1.20	2.22
256	10.83	35.000		2.14		
256	10.84	34.998		2.14		
266			3.58		0.67	2.39

Station AII93-2253 22°58.9'S 13°45.8'E Taken 4 January 1976

Depth: 139m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0		35.051	20.3	1.93	6.39	0.43
10		35.075	21.4	1.93	6.34	0.47
20		35.071	13.8	1.97	5.44	0.88
30		35.102	10.5	2.02	3.84	1.44
39		35.086	3.08	2.05	2.97	1.58
49		35.059	2.94	2.05	2.80	1.70
59		34.931	2.62	2.06	2.80	1.60
79		34.912	2.57	2.08	2.47	1.82
99		34.939	2.65	2.09	1.57	2.04
118	11.60	35.065		2.10		
123		34.938	4.79	2.10	0.78	2.20

Station AII93-2254 24°38'S 14°29'E Taken 5 January 1976

Depth: 34m

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	PO_4 (μmole/l)
0		34.965	10.7	1.95	7.88	0.13
5		34.958	14.5	1.95	6.14	0.48
10			20.2		4.29	1.13
15		34.927	26.9	2.04	3.28	1.63
20			32.9		2.92	1.83
25		34.910	60.9	2.08	1.01	2.54
30			63.4		0.62	2.77

APPENDIX III.2

DATA FROM R/V ATLANTIS II CRUISE 86 LEG 1A
TO THE GULF OF MAINE

Equilibrium methane concentrations were calculated from the equation presented by Yamamoto _et_ _al_. (1976) using the temperature and salinity of the sample in question. The atmospheric methane concentration was assumed to be 1.4 ppmv. Parentheses around a value indicate that its accuracy is in question. Single parentheses to the left of methane values indicate that the two values are from duplicate samples taken from the same Niskin bottle.

Station AII86-2122 42°35.5'N 69°41.5'W Taken 4 January 1975

Depth: 272m

Depth (m)	T (°C)	S (‰)	σ_τ	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	SiO_4 (μmole/l)	PO_4 (μmole/l)
0		33.464				6.25	10.20	0.87
5	7.69	33.476	26.144	3.73	2.27	6.47	9.13	0.82
10	7.71	33.468	26.135	4.19	2.27	6.24	8.84	0.82
20	7.73	33.463	26.128	) 3.82	2.25	6.19	9.52	0.89
				) 3.71				
35	7.69	33.465	26.135		2.27	6.16	8.93	0.91
50	7.74	33.465	26.128	4.02	2.26	6.18	8.84	0.92
74	7.72	33.472	26.136		2.27	6.17	9.13	1.00
98		(33.441)		3.93	2.26	6.14	9.22	1.02
99	7.77	33.484	26.139	4.24	2.26	6.18	8.84	0.95
121	7.67	33.460	26.134		2.27		8.84	1.05
124	7.76	33.486	26.142		2.26	6.15	8.54	0.95
144	7.80	33.495	26.143	3.95	2.26	6.10	8.54	1.05
149	7.92	33.637	26.237		2.25	5.02	12.53	1.14
168	7.57	33.671	26.314		2.27	4.76	13.40	1.30
189	6.92	33.746	26.464	5.60	2.31	4.68	15.34	1.25
204	7.08	34.026	26.662	5.10	2.29	4.24	19.23	1.48
223	7.26	34.112	26.704		2.28	4.19	18.64	1.56
232	7.36	34.178	26.742	) 5.21	2.28	4.09	18.55	1.59
				) 5.07				
242		34.184				4.04	18.74	1.63
251	7.38	34.188	26.747	4.98	2.28	3.94	18.64	1.67

Station AII86-2138 42°32.0'N 69°31.0'W Taken 7 January 1975

Depth: 272m

Depth (m)	T (°C)	S (‰)	σ_τ	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	SiO_4 (μmole/l)	PO_4 (μmole/l)
2	7.104	33.200	26.009	3.82	2.31	6.42	8.84	1.06
12	7.09	33.200	26.011		2.31	6.59	8.84	0.94
25	7.10	33.201	26.011	3.60	2.31	6.40	8.84	0.96
48	7.34	33.321	26.072		2.29	6.46	8.84	0.95
66	7.80	33.510	26.155	3.85	2.26	6.38	8.74	0.88
84	7.79	33.515	26.160		2.26	6.19	8.64	1.00
102	7.74	33.512	26.165		2.26	6.16	8.64	0.98
120		33.523		3.78	2.26	6.13	8.64	0.97
136	7.73	33.517	26.170	3.60	2.26	6.08	8.16	0.87
140	7.60	33.726	26.353	5.82	2.27	4.72	14.27	1.26
154	7.73	33.687	26.304	5.66	2.26	4.96	13.50	1.28
169	6.93	33.803	26.507	5.67	2.31	4.50	16.99	1.36
173	7.18	33.793	26.465		2.29	4.43	14.57	1.42
191	7.03	33.924	26.588	5.53	2.30	4.43	17.19	1.39
209	7.15	34.049	26.670		2.29	4.34	17.77	1.47
218	7.19	34.083	26.691		2.29	4.19	18.35	1.45
227	7.27	34.077	26.675	) 5.35	2.28	4.18	18.35	1.40
				) 5.10				
236		34.160				4.12	18.35	1.47
245	7.36	34.182	26.745	4.99	2.28	4.08	18.64	1.47
250	7.37	34.187	26.748		2.28	4.07	18.64	1.52

Station AII86-2151 42°26'N 69°45'W Taken 7 January 1975

Depth: 270m

Depth (m)	T (°C)	S (‰)	σ_τ	CH_4 (nmole/l)	CH_4eq (nmole/l)	O_2 (ml/l)	SiO_4 (μmole/l)	PO_4 (μmole/l)
1	7.44	33.304	26.045		2.29	6.44	8.64	0.93
21	7.43	33.304	26.046	3.45	2.29	6.58	8.84	0.93
42	7.45	33.305	26.044	3.57	2.28	6.43	8.84	0.95
62	7.54	33.305	26.031		2.28	6.49	10.10	0.95
80	7.63	33.306	26.019	3.66	2.28	6.52	10.10	0.95
99	7.64	33.307	26.019	) 3.61	2.28	6.37	9.13	0.95
				) 3.78[+]				
137	7.17	33.307	26.084	4.10	2.30	6.20	9.22	1.00
140	7.83	33.559	26.189	4.72	2.26	5.65	11.75	1.07
153	7.51	33.653	26.308		2.28	4.93	14.57	1.26
157	7.74	33.567	26.208	4.39	2.26	5.52	10.49	1.15
167	7.37	33.691	26.358	5.61	2.28	4.82	14.66	1.34
176	7.51	33.598	26.265		2.28	5.35	12.72	1.31
181	7.29	33.780	26.439		2.29	4.72	15.15	1.42
195	7.11	33.917	26.572	) 5.53	2.29	4.56	16.90	1.49
				) 5.33				
209		34.031			2.29	4.30	18.06	1.53
223	7.17	34.069	26.683			4.33	18.45	1.57
237	7.18	34.098	26.704	5.37	2.29	4.51	19.52	1.60
246	7.20	34.102	26.705	5.09	2.29	4.30	19.52	1.60
256	7.22	34.109	26.707	5.20	2.29	4.28		

[+] sample analyzed 7 April 1975

APPENDIX IV.1

DATA FROM R/V ATLANTIS II CRUISE 86 LEG 2
TO THE SUBTROPICAL ATLANTIC AND CARIBBEAN

Equilibrium methane concentrations were calculated from the data presented by Yamamoto *et al*. (1976) using the measured temperature and assuming a salinity of 34 ‰. The atmospheric methane concentration was assumed to be 1.3 ppmv. Parentheses around a value indicate that its accuracy is in question. Single parentheses in the right margin of the table indicate that the methane analyses are from duplicate samples taken from the same Niskin bottle.

Station 2182 19°02'N 65°59'W Taken 29 January 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$ nmole/l	σ_θ
1	25.041	35.493		1.44	23.73
1		35.481	2.52	1.44	
19		35.487	2.20	1.44	
25	25.046	35.500		1.44	23.73
44		35.495	2.29	1.44	
92	25.081	36.478	2.67	1.44	24.46
99	24.668	36.461		1.45	24.57
112	24.930	36.764	3.57	1.44	24.72
147	23.626	36.762		1.48	25.11
160		36.850	2.81	1.50	
175		36.960	2.86	1.53	
184		36.922	2.80	1.54	
189	21.212	36.916	2.57	1.55	25.91
238	19.221	36.500	2.32	1.62	26.13
286	17.885	36.504	2.20	1.66	26.48
465	14.336	35.893		1.80	26.84
470		35.861	2.20	1.81	
656	9.558	34.957		2.01	27.03
922	6.106	34.184		2.18	26.94

Station 2186 18°59'N 61°16'W Taken 31 January 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ	
1			2.37	1.44		
1	24.892	35.713		1.44	23.94	
25	24.987	35.713		1.44	23.91	
42	24.987	35.751	2.20	1.44	23.94	
42	24.983	35.755		1.44	23.94	
66	24.970	35.755	2.28	1.44	23.95	
83	25.454	36.333	2.76	1.43	24.24	
93	25.328	36.660		1.43	24.52	
98		36.825	3.52	1.44		
99	25.310	36.120		1.43	24.12	
104	24.206	36.799	3.30	1.47	24.96	
108	24.212	36.802		1.52	24.97	
113		36.961	3.12	1.46		) duplicates
113		36.961	3.18	1.46		)
127	23.678	37.155		1.48	25.39	
128	23.544	37.151		1.48	25.43	
133		37.169	2.70	1.48		
147	23.637	37.103		1.48	25.36	
166	22.246	37.102		1.52	25.76	
171		36.992	2.60	1.52		
189	21.096	36.943		1.55	25.96	
194		36.831	2.48	1.54		
277	17.707	36.475		1.66	26.50	
282		36.453	2.41	1.62		
333	17.570	36.460		1.67	26.52	
460		35.868				
465		36.653	1.94			
667	9.016	35.070		2.02	27.21	
713		35.028		2.11		
790	7.498	34.891		2.09	27.30	
865	6.491	34.794		2.15	27.37	

Station 2188 18°59'N 58°41'W Taken 1 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$ nmole/l	σ_θ
1		35.731	3.12	1.45	
24		35.728	2.33	1.45	
48		35.749	2.48	1.45	
52	24.637	35.759		1.45	24.05
71		35.901	2.24	1.45	
86		37.010	3.52	1.45	
90	24.588			1.45	
91	25.591	37.029		1.42	24.72
96		37.168	3.71	1.45	
109		35.735	2.58	1.45	
114	24.628	35.734		1.45	(24.04)
116	24.298	37.288		1.46	25.31
121		37.332	2.45	1.47	25.3
129	23.784	37.333		1.47	25.49
134		37.352	2.96	1.47	
164	23.125	37.339		1.49	25.69
169		37.285	2.58	1.51	
191	21.868	37.155		1.52	25.911
196		36.067	2.55	1.53	
285	17.831	36.520		1.66	26.50
290		36.483	2.55	1.64	
472	12.731	35.600		1.86	26.95
477		35.544	1.82	1.85	

Station 2188 18°59'N 58°41'W (continued) Taken 1 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4)eq nmole/l	σ_θ
1	24.715	35.714	1.45	23.99
25	24.741	35.712	1.45	23.99
50		25.709		
75	24.698	35.733	1.45	24.01
99		37.070		
109	24.851	37.232	1.44	25.10
119	24.252	37.277	1.46	25.31
124		37.303		
129	23.893	37.328	1.47	25.46
139	23.593	37.349	1.48	25.56
144	23.513	37.338	1.48	25.51
149	23.456	37.339	1.48	25.60
157		37.337		
173	22.574	37.236	1.51	25.77
188		37.194		
197	21.506	37.110	1.54	25.98
207	21.058	37.039	1.55	26.05
230		36.815		
253		36.673		
277		36.527		
323		36.298		
370	15.255	36.059	1.76	26.76
416		35.785		
463	12.420	35.546	1.87	26.97
510	11.913	35.513	1.90	27.04
557	10.625	35.304	1.95	27.12
604	10.043	35.269	1.98	27.19
651		35.118		
672	8.424	35.006	2.05	27.25

Station 2193 18°59'N 52°28'W Taken 3 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ
1		36.700			
6		36.731	2.15	1.45	
20		36.734	2.13	1.45	
34		36.734	2.24	1.45	
46	24.617	37.009		1.45	25.00
51		37.022	2.15	1.45	
69		37.025	2.19	1.45	
83		37.155	2.22	1.45	
95	24.640	37.162		1.45	25.11
100	24.295	37.325		1.46	25.34
103		37.323	2.82	1.45	
105		37.329	2.77	1.45	
125	22.663	37.295		1.51	25.79
130		37.250	2.54	1.49	
190	19.956	36.873		1.59	26.22
195		36.804	2.21	1.58	
289		36.392			
294		36.330	2.27	1.68	
479	12.066	35.546		1.89	27.04
484		35.538	1.46	1.86	
675	8.810	35.075		2.03	27.25
680		35.052	0.86	2.03	
832	6.513	34.811		2.15	27.38
837		34.806	0.45	2.17	
1458	4.358	34.976		2.27	27.77
1463		34.975	0.53	2.27	
1872		34.960	0.45		
2917		34.906		2.34	
2922		34.905	0.37	2.34	
3995	1.919	34.863		2.39	27.90
4000		34.863	0.36	2.39	
5000		34.831	0.38		

Station 2193 18°59'N 52°28'W (continued) Taken 3 February 1975

Depth (m)	θ (°C)	S (‰)	$(CH_4)_{eq}$ nmole/1	σ_θ
1	24.369	36.648	1.45	24.80
25	24.383	36.647	1.45	24.80
100	23.837	37.323	1.47	25.47
150	21.994	37.209	1.52	25.92
199	20.157	36.904	1.58	26.19
396	14.655	35.965	1.78	26.82
782	6.845	34.837	2.14	27.35
877	5.911	34.769	2.19	27.42
970	5.714	34.830	2.20	27.49
1455	4.405	34.976	2.27	27.76
1940	3.451	34.961	2.34	27.85
(1946)		34.969		

Station 2197 19°22'N 50°47'W Taken 5 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$ nmole/l	σ_θ	
1	24.111	37.365		1.47	25.42	
10		37.375	2.43	1.47		
20		37.366	2.24	1.47		
25		37.362				
50	24.136	37.366		1.46	25.42	
55		37.360	3.48	1.47		
68		37.358	2.34	1.47		
69	24.084	37.358		1.46	25.42	
83		37.360	2.26	1.47		
89	24.061	37.406		1.47	25.47	
94		37.333	2.22	1.47		
100	24.033	37.355		1.47	25.44	
117		37.368	2.38	1.48		) duplicates
117		37.368	2.26	1.48		)
142		37.249	2.56	1.51		
149	22.027	37.235		1.52	25.93	
192	20.720	37.091		1.56	26.18	
197		36.959	2.42	1.56		
199	20.641	37.080		1.56	26.19	
289	17.055	36.410		1.69	26.61	
294		36.381	2.22	1.66		
395	14.864	36.001		1.78	26.80	
481	12.838	35.688		1.85	26.99	
486		35.545	1.68	1.86		
782	6.909	34.926		2.13	27.41	
875	6.136	34.866		2.18	27.47	
971	5.719	34.817		2.20	27.48	

Station 2202 16°10'N 56°13'W Taken 8 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ	
1	24.767	35.546		1.44	23.85	
5		35.569	2.15	1.44		
19		35.761	2.18	1.44		
25	24.106	36.123		1.47	24.48	
39	25.165	36.381		1.43	24.36	
44		36.589	2.41	1.44		duplicates
44		36.589	2.37	1.44		
52		36.586	2.33	1.44		
71	25.166	37.206		1.43	24.98	
76		37.237	2.94	1.44		
81		37.235	3.00	1.44		
90		37.304	3.21	1.44		
99	23.455	37.297		1.48	25.56	
113	23.377	37.318		1.48	25.60	
118		37.264	2.72	1.49		
149	21.560	37.116		1.54	25.97	
198	19.223	36.749		1.62	26.32	
200	19.462	36.790		1.68	26.29	
205		36.726	2.27	1.64		
281	16.334	36.242		1.72	26.65	
286		36.204	2.26	1.71		
392	13.488	35.751		1.83	26.91	
500	11.547	35.447		1.90	27.06	
505		35.432	1.47	1.93		
776	6.385	34.785		2.16	27.37	
873	5.737	34.766		2.20	27.44	
970	5.488	34.821		2.21	27.51	

Station 2204 15°17'N 58°50'W Taken 9 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ	
5		35.409	2.35	1.41		
20		(35.440)	2.35	1.41		
50	25.741	35.403		1.41	23.45	
55		35.408	2.25	1.41		
70		35.409	2.46	1.41		
83		36.774		1.40		
85		36.731	2.66	1.41		
88		36.915	2.70	1.41		
105		37.132	3.14	1.42		
125		37.094	2.49	1.44		
141	23.185	37.192		1.49	25.56	
146		37.283	2.28	1.47		
185	20.168	36.846		1.58	26.14	
190		36.719	2.31	1.53		
288	16.533	36.281		1.71	26.63	
293		36.243	2.15	1.66		
493	11.964	35.547		1.89	27.06	
498		35.525	1.42	1.90		
677	7.708	34.958		2.08	27.32	
682		34.911	0.82	2.09		
824		34.811	0.36			
1451	4.407	34.973		2.27	27.76	
1456		34.969	0.43	2.27		
1948	3.348	34.964		2.34	27.86	
1953		34.948	0.46	2.34		
2995	2.331	34.899		2.40	27.90	
3000		34.893	0.44	2.40		) duplicates
3000		34.893	0.54	2.40		)
3708	2.036			2.42		
3713		34.882	0.72	2.42		

Station 2204 15°17'N 58°50'W (continued) Taken 9 February 1975

Depth (m)	θ (°C)	S (‰)	$(CH_4)eq$ nmole/1	σ_θ
1	25.860	35.409	1.41	23.42
25	26.010	35.407	1.41	23.37
99	26.262	36.911	1.40	24.43
148	23.376	37.165	1.48	25.49
196	21.184	37.040	1.55	26.01
388	14.383	35.884	1.79	26.82
760	7.093	34.892	2.11	27.36
851	5.879	34.776	2.19	27.43
942	5.496	34.803	2.21	27.50

Station 2206 12°44'N 60°39'W Taken 11 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ
1	25.902	35.837	3.25	1.41	23.73
4		35.778	3.26	1.41	
18		35.801	3.34	1.41	
41	25.895	35.871		1.41	23.76
46		35.902	5.39	1.41	
47	25.784	35.885		1.42	23.80
50		35.887	4.98	1.41	
61	23.924	36.182		1.48	24.58
66		36.509	10.55	1.47	
68	23.366	(36.122)		1.48	
86		36.543	5.56	1.53	
89	21.077	36.663		1.55	25.76
96		36.661	5.68	1.56	
97	20.180	36.662		1.54	26.00
102		36.662	5.10	1.58	
105		36.594	5.72	1.60	
130	17.574	36.266		1.67	26.37
131	17.514	36.271		1.68	26.39
136		36.179	3.29	1.68	
158	15.135	35.949		1.77	26.70
184	12.990	35.547		1.85	26.85

Station 2213 14°02'N 63°01'W Taken 14 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$ nmole/l	σ_θ
1	25.702	35.459		1.42	23.50
4		35.465	2.19	1.41	
17		35.459	2.14	1.41	
25	25.722	35.455		1.42	23.50
48		35.717			
50	25.858	35.713		1.42	23.65
53		35.795	2.69	1.41	
60		36.209			
72		36.873	3.09	1.41	
74	25.835	36.105		1.42	23.95
89		36.926	3.13	1.44	
95	24.022	36.883		1.47	25.08
99	23.952	36.872		1.44	25.10
100		36.923	3.06	1.47	
103	(22.216)	36.924			
108		36.871	3.17	1.48	
108	23.200	36.909		1.49	25.34
118	22.934	36.963		1.50	25.46
127	21.891	36.899		1.52	25.71
133	(23.050)	36.857			
137	21.050	36.812		1.55	25.88
138		36.843	2.66	1.53	
147	20.881	36.891		1.56	25.98
166	(16.822)	36.211			
171		(35.289)	3.05	1.60	
196	17.637	36.386		1.66	26.45
245		35.984			
280	13.229	35.581		1.84	26.83
285		35.539	2.29	1.82	
291	12.998	35.553		1.85	26.86
333	11.575	35.320		1.91	26.96
344	11.296	35.274		1.92	26.97
382	10.418	35.141		1.96	27.03

Station 2213 14°02'N 63°01'W (continued) Taken 14 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)_{eq}$ nmole/l	σ_θ
393		35.116			
431	9.405	34.992		2.00	27.09
483	8.697	34.899		1.92	27.13
488		34.880	1.43	2.03	

Station 2216   14°00'N 66°00'W   Taken 15 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$ nmole/l	σ_θ
1	25.971	35.598		1.41	23.53
19	(25.691)	35.512		1.42	
24		35.527	2.25	1.41	
24	25.950	35.590		1.41	23.53
48		35.529	2.24	1.41	
49	25.841	(35.590)		1.41	23.56
67	(25.705)	35.559		1.42	23.58
71		35.585	2.21	1.41	
74	25.813	35.593		1.42	23.57
86		35.663	2.43	1.41	
88	(25.876)	35.965		1.41	23.83
93		36.661	3.17	1.41	24.53
93	25.300	36.741		1.43	
105		36.872	2.85	1.43	
109	24.646	36.971		1.45	24.96
116		36.964	2.86	1.45	
118	24.629	36.948		1.45	24.95
133	23.325	37.095		1.48	25.45
135	23.268	37.090		1.49	25.46
140		37.104	2.82	1.50	
148	22.829	37.102		1.50	25.60
156	(23.711)	37.055		1.48	25.30
157	21.976	37.015		1.52	25.77
190		36.615	2.87	1.60	
196	18.696	36.518		1.63	26.28
245		36.124			
290		35.771	2.48	1.78	
294	14.027	35.733		1.81	26.78
295	14.090	35.752		1.81	26.78
344	12.625	35.507		1.86	26.90
392	11.290	35.316		1.92	27.01

Station 2220 12°59'N 64°55'W Taken 17 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ	
1	25.974	35.554		1.41	23.49	
24	25.931	35.565		1.41	23.51	
25		35.561	2.48	1.43		
48	(24.730)	35.561				
48	25.907	35.563		1.41	23.52	
53		35.563	2.63	1.43		
72	25.859	35.588		1.41	23.55	
75		35.642	3.08	1.43		
86	24.725	35.897		1.45	24.13	
91		36.522	3.63	1.45		
96	24.721	36.629		1.45	24.68	
100		36.657	4.40	1.46		) duplicates
100		36.657	4.52	1.46		)
105	24.512	36.656		1.45	24.77	
110		36.773	4.53	1.47		
114	23.983	36.784		1.47	25.02	
119	23.962	36.760		1.47	25.01	
124		36.968	4.09	1.48	25.31	
124	23.472	35.992		1.48		
133	22.404	36.877		1.52	25.55	
143	22.186	36.915		1.52	25.64	
150		36.726	5.38	1.54		
155	20.760	36.736		1.56	25.90	
161	20.426	36.702		1.57	25.96	
166		36.607	4.98	1.57		
186	18.376	36.506		1.64	26.35	
191		36.462	2.86	1.62		
192	18.435	36.512		1.64	26.34	
214		36.278	2.76	1.66		
243		36.058				
287	14.276	35.801		1.80	26.78	

Station 2220 12°59'N 64°55'W (continued) Taken 17 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ
292		35.759	2.63	1.81	
292	14.172	35.780		1.81	26.78
341	12.402	35.483		1.87	26.92
393	11.473	35.338		1.91	26.99

Station 2222 12°05'N 64°23'W Taken 18 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq nmole/l	σ_θ
1	25.363	35.444		1.43	23.60
20		35.466	9.48	1.43	
25		35.501			
30		35.522			
35		36.489	3.17	1.43	
49	25.580	35.660		1.42	23.69
56	25.117	36.820		1.44	24.71
61		36.967	2.92	1.45	
69	24.431	36.961		1.45	25.02
79	23.155	36.962		1.49	25.40
80	22.771	36.922		1.50	25.48
85		36.865	3.65	1.50	
88	22.241	36.868		1.52	25.59
98	21.997	36.863		1.52	25.65
108	21.046	36.801		1.56	25.87
117		36.713	2.98	1.58	
117	20.234	36.692		1.58	26.01
135		36.585		1.62	
140		36.577	3.98	1.62	
147	19.065	36.570		1.62	26.22
166		36.514	3.01	1.66	
190		36.285			
195		36.217	3.03	1.69	
196	17.014	(36.268)		1.70	
216		36.211	2.48	1.71	
240		35.985	2.60	1.75	
244	15.165	35.955		1.77	26.70
246		36.046			
296	13.209	35.613		1.84	26.86
297		35.531	2.21	1.83	
345	11.673	35.345		1.90	26.96
346	11.879	35.377		1.89	26.94
388		35.190	1.63	1.94	

Station 2233 13°59'N 69°57'W Taken 25 February 1975

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$ nmole/l	σ_θ
10		35.992	2.51	1.43	
37	25.569	36.003		1.48	23.96
42		36.243	2.87	1.46	
74		36.627	3.70	1.50	
88		36.718	6.12	1.52	
93	23.122	36.781		1.50	25.27
98		36.847	5.78	1.54	
108	21.275	36.846		1.54	25.84
113			4.62	1.56	
127		36.860	4.21	1.58	
156		36.600	3.83	1.62	
193	(22.971)	36.410			
198		36.347	3.45	1.66	
292	13.777	35.691		1.82	26.80
297		35.674	2.73	1.81	
496	9.144	34.982	1.26	2.02	27.12
686	6.167				
691		34.698	1.00	2.19	
971	4.819	34.893			27.65
976		34.892	0.46	2.25	
1244	3.981	34.939			27.78
1249		34.939	0.40	2.30	
4413		34.945			
4418		34.943	0.40		

Station 2233 13°59'N 69°57'W (continued) Taken 25 February 1975

Depth (m)	θ (°C)	S (‰)	$(CH_4)_{eq}$ nmole/l	σ_θ
1	25.662	35.993	1.42	23.92
97	23.001	36.832	1.50	25.34
146	19.564	36.603	1.60	26.12
193	(22.971)	36.410	1.50	
195	17.869	36.395		26.40
294	13.782	35.684	1.82	26.79
344	12.624	35.512	1.86	26.90
394	11.265	35.303	1.92	27.00
686	6.167	35.703	2.00	28.13
971	4.819	34.893	2.25	27.65
1244	3.980	34.939	2.30	27.78

APPENDIX V.1

CALCULATION OF ΔCH_4 IN ALGAL EXPERIMENTS

Let us first assume that in all bottles containing culture medium before inoculation, the gas and liquid phases are in equilibrium. From analysis of the liquid phase in the blanks, it is possible to calculate the concentration of methane in the gas phase

$$CH_{4_{gas}} = \frac{CH_{4_{liq}}}{\alpha}$$

where α = Bunsen solubility coefficient (ml gas/l liquid)

$CH_{4_{gas}}$ = Concentration of methane in gas (ml CH_4/ml gas)

$CH_{4_{liq}}$ = Concentration of methane in liquid (ml CH_4/l liquid).

From the initial gas and liquid methane concentrations and the volumes of liquid (V_1) and gas (V_g) in each culture bottle, a "predicted" methane content for the culture vessel (m) can be calculated.

$$m = CH_{4_{gas}} V_g + CH_{4_{liq}} V_1.$$

The total methane content in each culture vessel after incubation is calculated from the assumuption that the gas and liquid phases are in equilibrium at this point as well. In this case

$$m^* = CH_{4_{liq}}^* V_1 \frac{(V_g + \alpha V_1)}{\alpha V_1}$$

where m^* = total methane content after some period of incubation

$CH_{4_{liq}}^*$ = methane concentration in liquid after incubation.

Thus $\Delta CH_4 = m^* - m$, or the increase in total methane content of the culture bottle after incubation.

APPENDIX VI.1

DATA FROM SEVERAL DEEP STATIONS

Data from other stations discussed in Chapter VI can be found in Appendix III.1 for stations from AII93 and in Appendix IV.1 for stations from AII86. Equilibrium methane concentrations were calculated from the equation presented by Yamamoto *et al*. (1976) and from the temperature and salinity data from the sample in question. Atmospheric methane concentrations used are indicated in individual tables.

KNORR 51-716 51°41.5'N 35°59'W

Taken: 1 October 1975
Analyzed: 14 October 1975

Depth (m)	θ °C	S ‰	(CH_4) nmole/l	(CH_4)eq* nmole/l	O_2 ml/l
surf.	11.570	34.360	2.72	1.98	6.18
192	4.975	34.795	3.27	2.32	6.12
386	4.431	34.908	2.56	2.36	5.85
582	4.116	34.930	2.46	2.37	6.15
771	3.733	34.904	2.49	2.40	6.62
972	3.657	34.913	2.25	2.40	6.43
1167	3.532	34.908	2.17	2.41	6.48
1287	3.571	34.929	2.05	2.41	6.43
1462	3.536	34.947	1.83	2.41	6.36
1640	3.450	34.948	1.62	2.41	6.33
2121	3.139	34.949	1.37	2.44	6.27
2628		34.950	1.23		6.34
3208	2.428	34.944	1.43	2.49	6.31
3400		34.942	1.42		6.42
3447	2.256				6.34
3497		34.933	1.34		6.41
3547	2.215				6.39
3596		34.932	1.21		6.38

*assuming $\chi_i^A = 1.35$ ppmv

OCEANUS 6-743 34°40.3'N 70°00.6'W Taken: 20 May 1976
Analyzed: 25 May 1976

Depth (m)	θ °C	S ‰	(CH_4) nmole/l	(CH_4)eq** nmole/l
1128		35.001	1.21	
1631	3.538	34.981	0.77	2.41
			0.92*	2.41
2115		34.972	0.62	
2135	3.104			
2628	2.591	34.975	1.15	2.47
			1.10	2.47
3100		35.045	1.05	
3120	2.120			2.50
3600		34.911	0.74	
4000		34.899	0.63	
4080		34.895	0.59	2.53
4090	1.816			

*small air bubble on collection

**assuming $\chi_i^A = 1.35$ ppmv

AII93-2360 20°52.8'N 63°13.0'E

Taken: 13 February 1977
Analyzed: 30 & 31 May 1977

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	(CH_4)eq* nmole/l	O_2 ml/l	SiO_2 μmole/l	PO_4 μmole/l	NO_3 μmole/l
218	17.441	35.878	4.30	1.78	0.11	20.5	2.52	23.5
234	16.530	35.811	3.61	1.81	0.13	21.9	2.58	23.1
3170		34.707	0.83					
3261	1.494		0.53	2.65	2.87	120.9	2.71	36.3

* assuming $\chi_i^A = 1.4$ ppmv

AII93-2365 25°02.6'N 57°46.0'E

Taken: 16 February 1977
Analyzed: 30 May 1977

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$** nmole/l	O_2 ml/l	SiO_2 µmole/l	PO_4 µmole/l	NO_3 µmole/l
1	22.739	36.438	6.42	1.60	4.10	2.8	1.00	8.8
121	22.734	36.434	6.06	1.60	4.08	2.3	1.00	7.9
195*	19.992	36.114	11.38*	1.68	0.11	14.0	2.39	23.3
291	19.154	36.881	9.63	1.71	1.08	15.3	2.00	17.0
338	16.612	36.412	7.64	1.80	0.22	24.2	2.45	20.6
384	15.716	36.315	13.66	1.84	0.20	25.8	2.53	21.4
486	13.527	35.958	3.41	1.93	0.13	33.0	2.78	22.4
573	12.060	35.700	2.02	2.02	0.09	40.7	2.92	25.2
772		35.492	11.20		0.11	56.3	3.39	30.2
960	8.707	35.372	1.47	2.18	0.13	64.9	3.22	33.2

*possible contamination during analysis

**assuming $\chi_i^A = 1.4$ ppmv

INDOPAC 01-65D 34°59.8'N 174°01.4'E Taken: 16 April 1976
Analyzed: 19 May 1976

Depth (m)	θ (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$* nmole/l	O_2 ml/l
32	15.35	34.607	2.31	1.88	5.799
126	15.00	34.607	2.31	1.90	5.545
400	11.02	34.328	2.51	2.08	5.413
696	5.00	34.056	1.81	2.43	2.633
991	3.46	34.275	0.81	2.52	0.787
1143	3.05	34.350		2.55	0.830
1542	2.26	34.498	0.65	2.60	0.966
1944	1.85	34.572	0.46	2.63	1.540
2336	1.55	34.625	0.41	2.65	2.256
2732	1.44	34.640	0.42	2.66	2.579
3126	1.33	34.651	0.29	2.67	2.792
3522	1.24	34.663	0.36	2.67	3.258
3913	1.17	34.672	0.37	2.68	3.422
4154	1.11	34.679	0.32	2.68	3.595

*assuming χ_i^A = 1.4 ppmv

APPENDIX VII.1

DATA FROM THE CARIACO TRENCH AND THE BLACK SEA

Cariaco Trench

Equilibrium methane concentrations were calculated from the data of Yamamoto _et_ _al_. (1976) using the measured (1973) temperature of the water and assuming a salinity of 34‰. The atmospheric methane concentration was assumed to be 1.3 ppmv. Parentheses around a value indicate that its accuracy is in question.

CARIACO TRENCH

Station AII-86-2225 10°29'N 64°44'W Taken 20 February 1975

Depth (m)	θ + (°C)	S (‰)	(CH_4) nmole/l	$(CH_4)eq$ nmole/l
10		36.775	4.56	1.49
18		36.809		1.50
23		36.844	4.42	1.50
59		36.812	5.63	1.54
84		36.692	15.53	1.56
89		36.697		1.58
94		36.692	4.61	1.57
148		36.516	8.29	1.62
188		36.389		1.66
193	18.00	36.376	5.76	1.66
211		36.334	9.68	1.66
236	17.53	36.339	85.5	1.66
261	17.37	36.265	330	1.66
290		36.251		1.66
295	17.23	36.242	734	1.66
309	17.20	36.241	964	1.66
334	17.12	36.230	1210	1.66
358	17.10	36.222	1700	
358*		36.222	1230	
407	17.00	36.212	2070	
407*		36.212	1520	
553	16.85	36.183	4370	
553*		36.183	3110	
584		36.178		
591	16.83	36.169	5220	
848	16.78	36.166	8010	
848*		36.166	5390	
1142	16.76	36.161	8840	
1142*		36.161	6800	
1288		36.168		
1293	16.76	36.161	9080	
1293*		36.161	7340	

Depth (m)	θ (°C)	S (‰)
1	23.521	36.807
24	22.797	36.857
48	21.268	36.793
73	21.506	36.709
96	20.239	36.718
146	18.941	36.518
165	18.486	36.446
174	18.249	36.432
183	18.170	36.411
200	17.993	36.387
210	17.817	36.382
213		36.338
223		36.320
242		36.295
291		36.281
340		36.247
388		36.214

+ θ estimated from 1973 data - most of 1975 temperatures bad

* samples measured 8 April in lab

BLACK SEA

Station CHAIN 120-1355 42°48'N 33°01'E

Taken 21/22 April 1975
Analyzed 26 June 1975

Depth (m)	θ (°C)	S (‰)	CH_4 nmole/l	O_2 ml/l	H_2S
10		18.371	4.05		
31	7.858	18.483			
43	7.643	18.562			
68	7.992	19.654			
74		19.785	6.92	2.29	
89	8.310	20.240			
95		20.431	2.45	0.41	
95	8.438	20.599			
101	8.467	20.633			
102		20.690	3.68	0.34	3.28
102	8.495	20.732			
108		20.829	3.91	0.34	0.50
114	8.546	20.850			
117	8.545	20.907			
121		20.913	51.7	0.27	28.03
123		20.975	163		0.39
134	(8.453)	21.036			
137	8.597	21.092			
143	8.652	21.156			
144		21.140	496		33.20
149		21.191			12.57
157	8.665	21.281			
163		21.325			28.03
178	8.711	21.392			
180	8.744	21.415			
194	8.704	21.460			
203	8.745	21.506			
209		21.533	3100		7.90
233	8.775	21.583			
237	8.789	21.638			
255	8.825	21.675			
281	8.881	21.742			
286		21.773	5170		151.3

Station CHAIN 120-1355 (continued)

Depth (m)	θ (°C)	S (‰)	CH_4 (nmole/l)	H_2S (μmole/l)
297	8.824	21.784		
323	8.843	21.836		
328		21.843	6680	215.2
335	8.867	21.864		
359	8.822	21.894		
382	8.870	21.948		
388		21.950	8190	292.0
444	8.873	22.004		
482	8.886	22.053		
483	8.865	22.054		
488		22.058		359.3
490		22.225	9700	
580	8.900	22.131		
726	8.895	22.216		
732		22.222	9230	496.2
971	8.948	22.300		
967	8.963	22.228		
973		22.295	12200	525.0
1365	8.981	22.335		
1371		22.328	12600	510.6
1472	8.934	22.335		
1758	9.069	22.342		
1764		22.338	8540	545.0
1794	9.085	22.341		
1937	9.116	22.336		
1943		22.347	12100	522.8
2042	9.105	22.340		

Station CHAIN 120-1355 (continued)

Depth (m)	H_2S (μmole/l)
100	0.39
112	0.72
124	0.95
136	3.73
148	8.34

Depth (m)	S (‰)
10	18.374
10	18.376
37	18.526
49	18.777
107	20.782
142	21.114
184	21.416
186	21.440
200	21.488
229	21.620
243	21.653
261	21.703
303	21.802
341	21.850
365	21.903
450	22.010
586	22.137
977	22.334
1478	22.336
1800	22.343
2048	22.343