

Methane production, consumption, and air-sea exchange in the open ocean: An evaluation based on carbon isotopic ratios

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Abstract. The concentration of methane and its isotopic composition did not appear to vary significantly in the subtropical North Pacific during 1996-1997. Methane enters the atmosphere via the upper mixed layer at a rate of $1.6 \mu\text{mol m}^{-2} \text{d}^{-1}$ (± 0.1) with a $\delta^{13}\text{C}$ value of approximately -42‰ (± 1.5), with no apparent seasonal variation. In comparison, the sea-air flux of methane in the Sargasso Sea was between 1.6 and $4.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ with an isotopic composition between -43 and -45‰ . Excess methane in surface waters appears to be generated throughout the upper 300 m of the water column by bacterial methanogenesis. The methane concentration maxima occur at the pycnocline, suggesting that the maxima are supported by methanogenesis in suspended particles that accumulate at these depths. Particle incubation experiments show that methane production may occur in these microenvironments. The lack of a diurnal signal implies that methane production and consumption in the ocean is independent of day-night cycles such as photosynthesis, grazing and vertical migration of zooplankton. The flux to the atmosphere appears to be the main sink for methane in the upper ocean; microbial oxidation and downward eddy diffusion account for only 3 and 6%, respectively, of the total methane loss from the upper 300 m. Below that depth, concentrations decrease and isotopic ratios vary with depth due to bacterial oxidation and mixing of water masses of different ages and different histories of methane input.

1. Introduction

Concern about rising levels of greenhouse gases, such as methane, in the atmosphere has prompted reevaluation of the sources of these gases. The oligotrophic gyres of the North Pacific and the North Atlantic comprise vast areas which, by virtue of their size, may play an important role as sources of reduced gases to the atmosphere [e.g., Dore *et al.*, 1998]. Supersaturation of methane in surface water is a persistent feature of most ocean waters [Lamontagne *et al.*, 1973; Cicerone and Oremland, 1988]. The global oceanic source of methane to the atmosphere has been estimated at $5\text{-}50 \text{ Tg yr}^{-1}$, which is 3-30% of all natural sources of methane [Prather, 1995]. The large uncertainty in the estimates of the magnitude of the marine source of this gas, which is 3.7 times more effective per mole at trapping radiated heat than CO_2 [Lashof and Ahuja, 1990], emphasizes the need for better understanding of the temporal and spatial variations in the marine methane cycle.

However, the source of the methane excess in surface water remains poorly understood. River runoff and outgassing from sediments provide methane to the coastal and nearshore ocean [Lamontagne *et al.*, 1973; Sackett and Brooks, 1975; Sansone and Martens, 1981; Bugna *et al.*, 1996; Sansone *et al.*, 1999], but these sources cannot account for the presence of above at-

mospheric-equilibrium levels of methane observed in the open ocean far from land. Tracking of hydrothermal methane released from sources at the seafloor show that this methane is consumed near the source areas and does not generally reach the sea surface [e.g., Faber *et al.*, 1994; Mottl *et al.*, 1995]. In order to advance our understanding of the upper ocean methane cycle, this paper provides estimates of the amount and isotopic composition of methane entering the atmosphere from oligotrophic ocean regions.

2. Methods

Methane concentrations and isotopic ratios were measured in water column samples from Station ALOHA (A Long-term Oligotrophic Habitat Assessment) [Karl and Lukas, 1996], 100 km north of Oahu, Hawaii, in the North Pacific subtropical gyre (Figure 1a) and from the Sargasso Sea and Gulf Stream (Figure 1b). Water samples for methane analyses were collected at Station ALOHA during Hawaii Ocean Time-series (HOT) cruises in October 1996 (HOT 76) and January (HOT 79), April (HOT 82) and July (HOT 85) 1997. Sargasso Sea and Gulf Stream samples were collected in April 1997 on the Duke University/University of North Carolina Oceanographic Consortium cruise CH0497. Subsamples were transferred from 12-l. Niskin bottles to 230-mL serum bottles and preserved with 1 mL of supersaturated HgCl_2 solution, as described by Popp *et al.* [1995]. Atmospheric methane concentrations and isotopic compositions were also measured at Station ALOHA in April and July, 1997. Atmospheric samples from 5 m above the sea surface at the bow of the ship, with the bow headed into the wind, were collected in 250-mL glass

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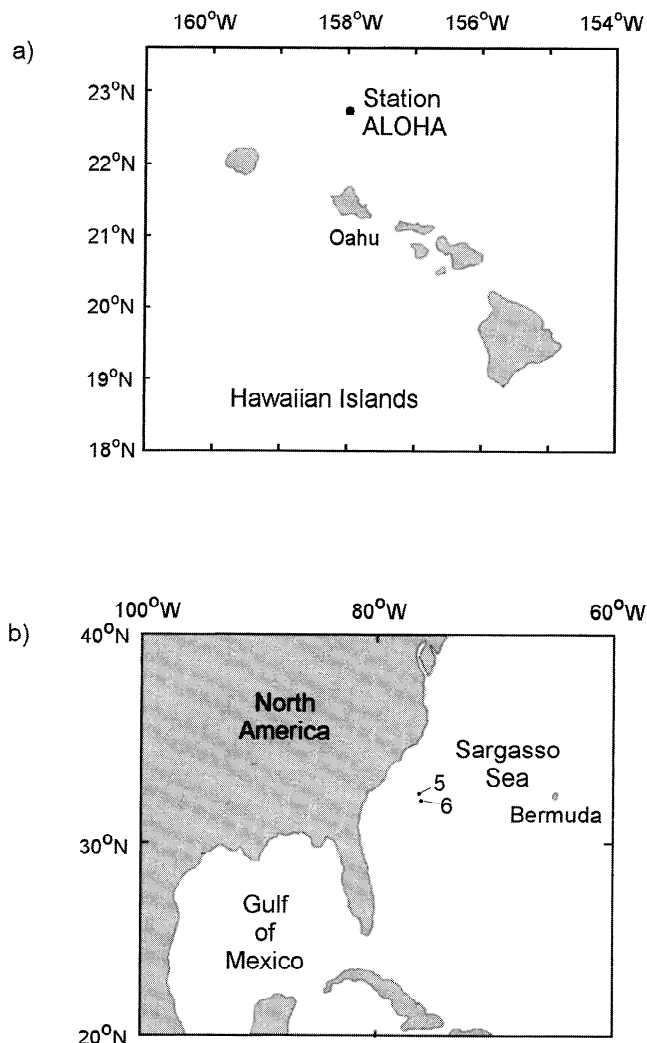


Figure 1. Maps indicating the location of (a) Station ALOHA (22°45'N, 158°0'W) in the North Pacific Ocean and (b) stations in the Gulf Stream (Station 5: 32°24'N, 76°32'W) and the Sargasso Sea (Station 6: 32°5'N, 76°22'W).

bulbs through which several volumes of air were pumped before the stopcocks were closed.

A free-floating MULTITRAP array [Knauer *et al.*, 1979], consisting of individual collectors (0.0039 m²) affixed to a PVC cross, was deployed at Station ALOHA to collect sinking particles at 250 m water depth for 3 days. The three traps in the array were filled with 0.22- μm filtered seawater which was slightly more saline than ambient seawater and fitted with baffles at the tops of the traps to minimize trap flushing during recovery. The traps were retrieved after 3 days, and the water in the traps was partially siphoned off, leaving approximately 500 mL in each trap. The traps were gently mixed, and the particles were allowed to settle for a few seconds. The remaining water was siphoned into 230-mL glass serum bottles (leaving no headspace); 1 mL of supersaturated HgCl₂ solution was added, and the bottles were sealed with rubber septa and aluminum crimp-seals. These bottles represented the time-zero methane concentrations. The remaining water with particles was transferred to 230-mL serum bottles

in the same way. Two samples were sealed with no addition of HgCl₂, and one was sealed with 1 mL of HgCl₂ to function as a killed control. All samples were stored in the dark for 15 days.

Samples were analyzed by isotope-ratio-monitoring gas-chromatography/mass-spectrometry (irm gc/ms) using the methods described by Popp *et al.* [1995] and Sansone *et al.* [1997]. Analysis of triplicate water samples gave concentration analytical precisions of ± 0.2 nM, isotopic ratio analytical precisions were $\pm 0.3\text{‰}$ for samples > 2.5 nM and $\pm 0.7\text{‰}$ for samples < 2.5 nM. Comparison of duplicate samples measured for CH₄ concentration using the irm gc/ms method and conventional gas-stripping gas chromatography using a Varian 3300 gas chromatograph equipped with a Porapak Q packed analytical column and flame ionization detector showed that both methods yielded the same concentrations ($\pm < 0.1$ nM, $n=5$).

Equilibrium methane concentrations (C_{eq} ; the methane concentrations that would be expected if the water was in equilibrium with atmospheric methane) were calculated from the solubility data of Yamamoto *et al.* [1976]. In situ temperatures and salinities (Station ALOHA: Hawaii Ocean Time-series data set (see http://hahana.soest.hawaii.edu/hot/hot_jgofs.html) Atlantic Ocean Stations: C. Terry, personal communication, 1997) were used, and an atmospheric methane concentration of 1.7 ppm [Quay *et al.*, 1991; this work] was assumed.

Fluxes of methane from the sea surface to the atmosphere (shown in Table 1) were calculated using the following equation:

$$F = K_L(C_{\text{meas}} - C_{\text{eq}}), \quad (1)$$

where F is flux, K_L is the gas transfer coefficient, C_{meas} is the methane concentration in the surface mixed layer, and C_{eq} is the air-equilibrated gas concentration [Liss and Slater, 1974; Barber *et al.* 1988]. The gas transfer coefficient, K_L , used in calculating the flux was obtained from

$$K_L = U^* - 12.1 \text{ cm h}^{-1}, \quad (2)$$

where U^* is the friction velocity calculated from the wind speed 10 m above the sea surface [Barber *et al.*, 1988] ($K_L = 7.1\text{--}16.0 \text{ cm h}^{-1}$ at wind speeds of 5.3 to 8.2 m s⁻¹). Average monthly wind speeds were obtained from the National Data Buoy Center (Buoy 51001, located 400 km northwest of Station ALOHA; Buoy 41002, located 100 km west of Stations 5 and 6 in the North Atlantic).

3. Results

The mean atmospheric methane concentration and isotopic composition at Station ALOHA were 1.4 ± 0.01 ppm and $-47.35\text{‰} \pm 0.01\text{‰}$, respectively, in April 1997 ($n = 2$) and 1.7 ppm and -47.37‰ ($n = 1$) in July 1997. Methane concentration and isotopic-ratio profiles from the water column reveal that intra-annual variations were generally small at Station ALOHA (Figure 2). Methane exceeded atmospheric equilibrium concentrations in the upper 300 m, with subsurface maxima of 2.9–3.5 nM between 100 and 300 m (37–67% supersaturated relative to atmospheric equilibrium). Tilbrook and Karl [1995] reported similar concentrations at a site to the north of Station ALOHA ($\sim 2\text{--}3$ nM in the upper 400 m). The

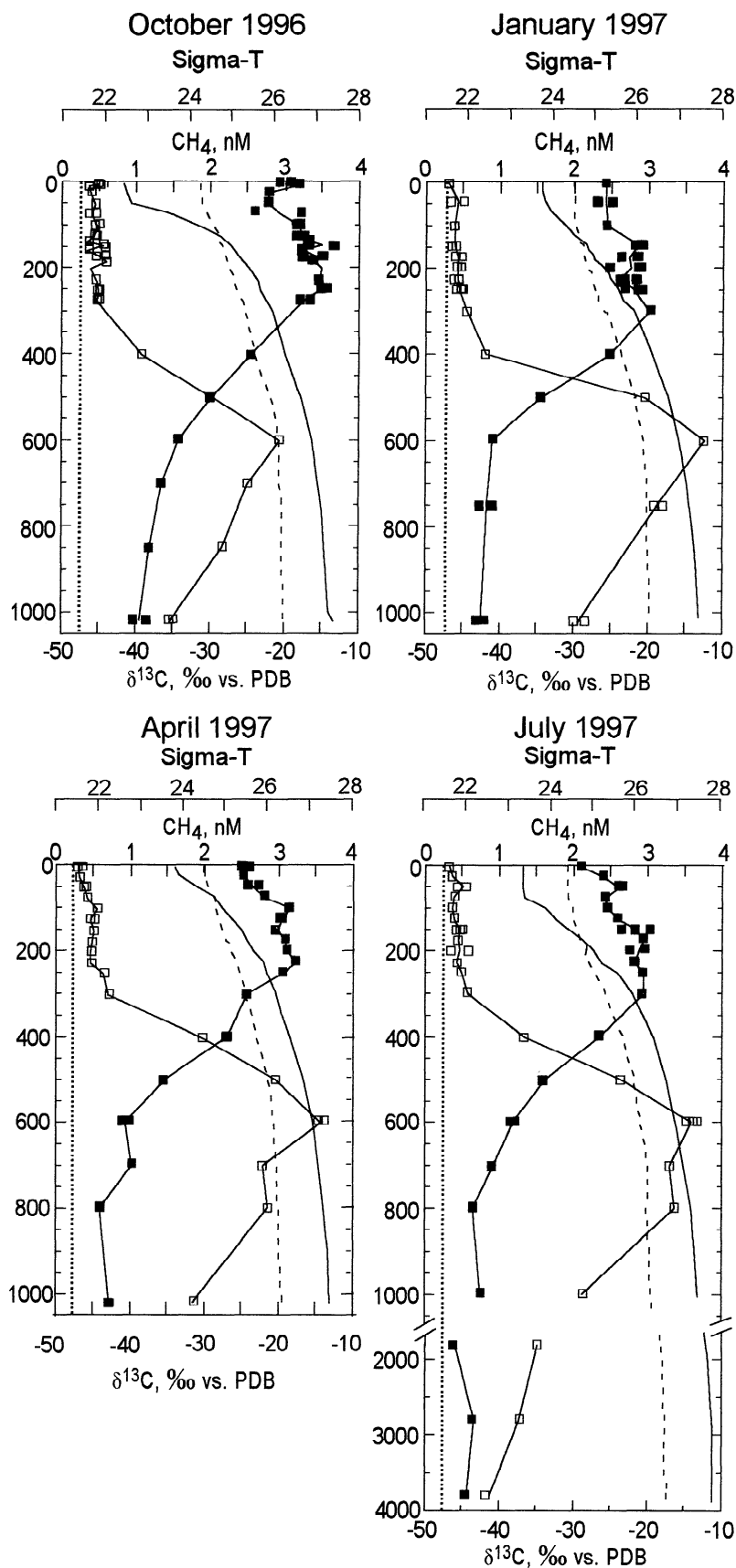


Figure 2. Methane concentrations (filled squares) and isotopic composition (open squares) at station ALOHA in October 1996, January 1997, April 1997, and July 1997. More than one symbol at a given water depth indicates duplicate or triplicate samples. The October and January profiles include samples from both day (1400 UT) and night (0100 UT) casts. The dashed lines indicate the concentrations expected at equilibrium with the atmosphere (1.7 ppm), the dotted lines denote the isotopic composition of atmospheric methane (-47.4‰), and the solid lines represent seawater density (sigma-*t*).

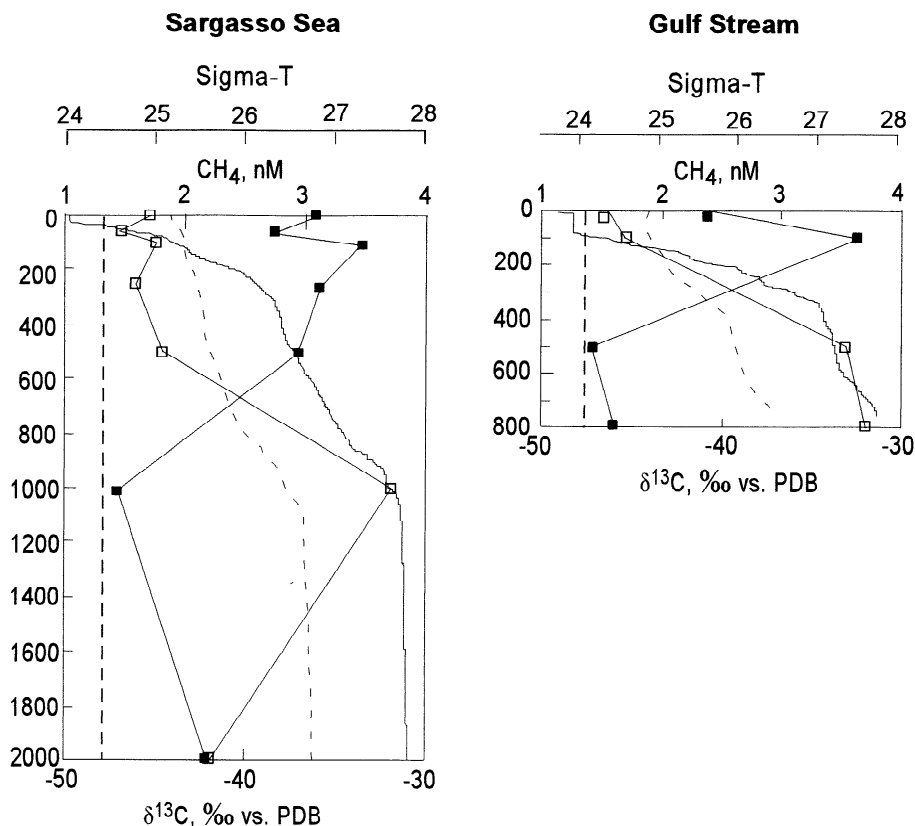


Figure 3. Methane concentrations (filled squares) and isotopic composition (open squares) at the Gulf Stream and in the Sargasso Sea. More than one symbol at a given water depth indicates duplicate or triplicate samples. The dashed lines indicate the concentrations expected at equilibrium with the atmosphere (1.7 ppm), the dotted lines denote the isotopic composition of atmospheric methane (-47.4‰), and the solid lines represent seawater density ($\sigma\text{-}t$).

$\delta^{13}\text{C}$ values were constant throughout 1996-1997 and ranged from -44 to -47‰ in the upper 300 m. Between 300 and 600 m, methane concentrations decreased rapidly to 0.9-1.6 nM and then more slowly to between 0.7 and 1.1 nM at 1000 m, or between 24 and 35% of atmospheric equilibrium values. Isotopic ratios increased below 300 m, with maxima at 600 m, decreasing again below that depth. During July 1997, the only data set that extends deeper than 1000 m, methane continued its slow decline in concentration and isotopic ratio to 3800 m (0.6 nM, -41.10‰).

The Sargasso Sea and Gulf Stream profiles were similar to those from Station ALOHA (Figure 3). Methane was supersaturated with respect to atmospheric concentrations by 25-90% in the upper 250 m (with a maximum concentration of 3.6 nM) and was isotopically heavier than atmospheric methane (-44.9 to -47‰). Below 250 m, concentrations decreased in the Sargasso Sea to a minimum at 1000 m of 1.4 nM (50% of the atmospheric equilibrium concentration) then increased at 2000 m to 2.2 nM. At the Gulf Stream, the concentration minimum (1.4 nM) occurred at a shallower depth of 500 m. Isotopic compositions mirrored concentrations, with a maximum of -31.9‰ at 1000 m in the Sargasso Sea and of -32.0‰ at 800 m at the Gulf Stream (the deepest sample). The $\delta^{13}\text{C}$ decreased below 1000 m in the Sargasso Sea to -41.9‰ at 2000 m. The concentrations measured in this work are slightly

higher than the values of 0.5-2.7 nM reported by Jones [1991] for the Sargasso Sea.

To compare nighttime and daytime methane concentrations and isotopic values, water samples were taken at 0100 and 1400 UT during the October and January Station ALOHA cruises (Figure 4). The data shown in Figure 4 is the same as in Figure 2 (HOT 76 and HOT 79), except the data shown in Figure 2 represent the average values of the night and day samples.

In the incubation experiments of water from Station ALOHA, methane concentrations in the bottles with particles increased over the 15-day incubation period by 0.23 and 0.24 nM (Figure 5). This increase is slightly greater than the error associated with these analyses. However, the $\delta^{13}\text{C}$ values of the samples increased by 1.1 and 1.8‰, a much larger change than the analytical margin of error ($\pm 0.3\text{‰}$). The control showed no significant change in either concentration or isotopic composition.

4. Discussion

4.1. Ocean-Atmosphere Methane Exchange

The overall methane surplus in the upper water column relative to atmospheric levels indicates that the North Pacific and Sargasso Sea/Gulf Stream regions supply this gas to the

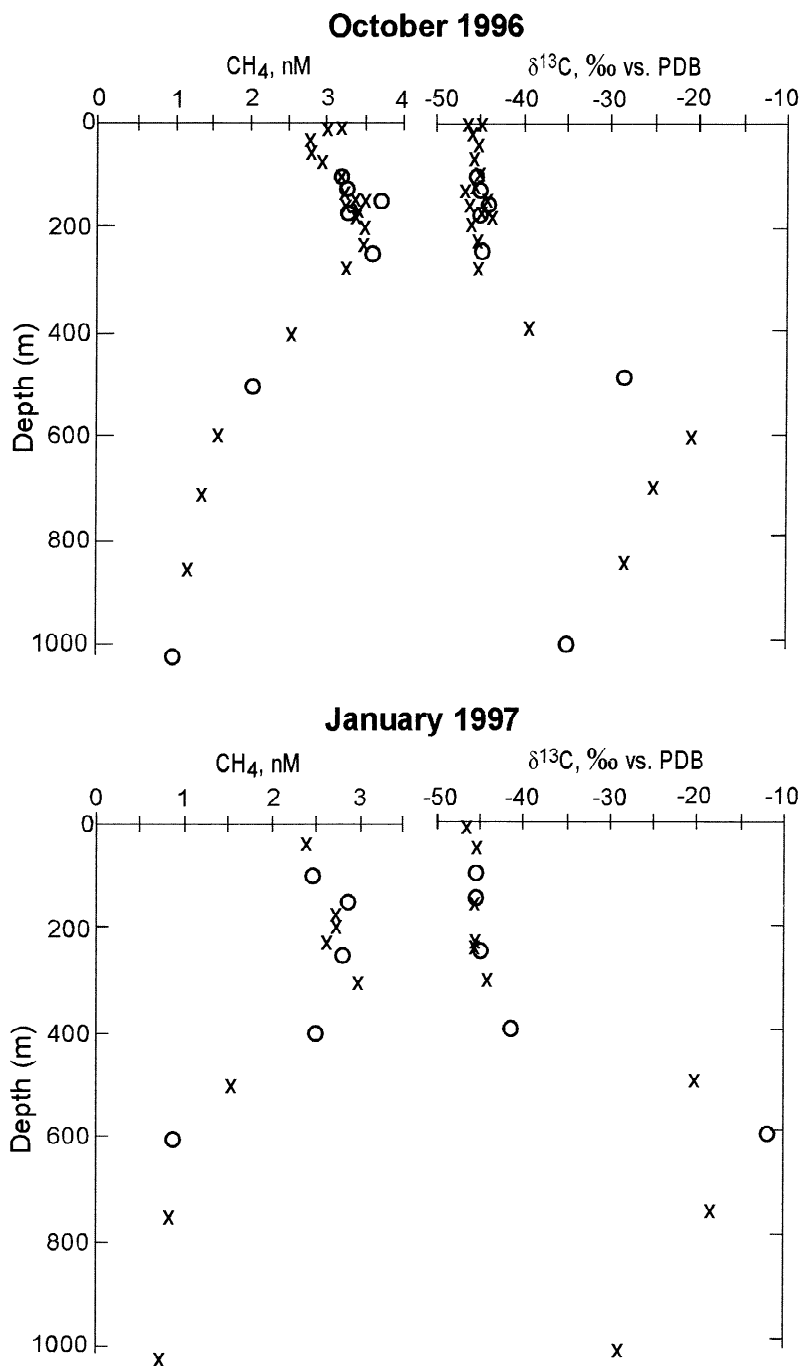


Figure 4. Daytime (circle) and nighttime (crosses) methane concentrations and isotopic composition at Station ALOHA during October 1996 and January 1997.

atmosphere. During the 1996-1997 samplings at Station ALOHA, we calculate that between 1.4 and 1.7 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ was degassed to the atmosphere (Table 1). These estimates for the flux to the atmosphere are similar to those of *Tilbrook and Karl* [1995], who calculated methane fluxes of 0.9-3.5 $\mu\text{mol m}^{-2} \text{ d}^{-1}$ at the ADIOS station a few hundred kilometers northwest of Station ALOHA. In the Sargasso Sea and Gulf Stream, the air-sea flux was 4.4 and 1.6 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, respectively. The larger flux in the Sargasso Sea was due mainly to the higher wind speed and surface methane

concentration, both of which were likely induced by a storm that occurred prior to and during the cruise. The storm probably deepened the surface mixed layer, bringing methane up from the subsurface maximum.

The eddy diffusive flux of methane from the subsurface maximum into the surface mixed layer was much smaller than the flux from the sea to the air (Table 1). In the North Pacific, the diffusive flux was calculated to be 0.09-0.13 $\mu\text{mol m}^{-2} \text{ d}^{-1}$, based on an eddy diffusion coefficient of 1.7 $\text{cm}^2 \text{ s}^{-1}$ [*Li et al.*, 1984] and concentration gradients of 0.006-0.009 $\mu\text{mol m}^{-4}$.

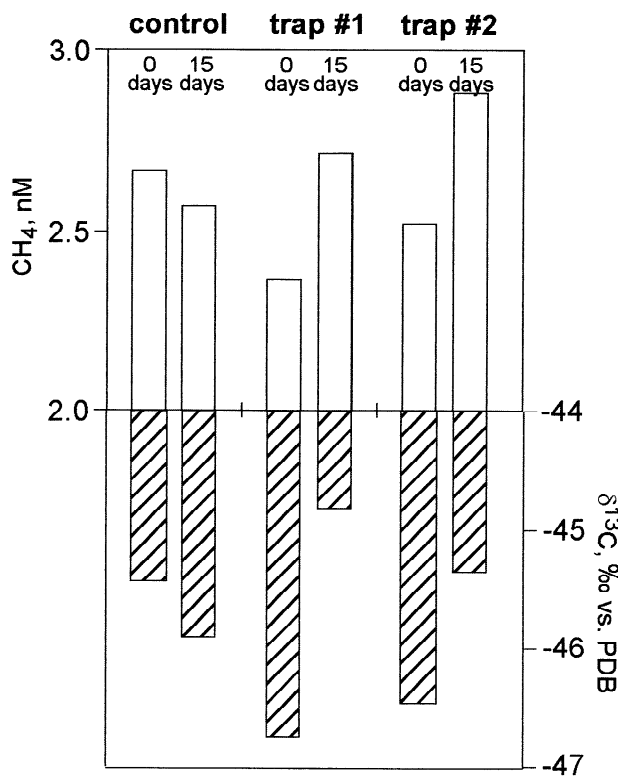


Figure 5. Methane concentration and isotopic changes during incubation of particles from 250 m at Station ALOHA.

In the North Atlantic, the calculated eddy diffusive flux was $0.26 \mu\text{mol m}^{-2} \text{d}^{-1}$ in the Sargasso Sea and $0.19 \mu\text{mol m}^{-2} \text{d}^{-1}$ in the Gulf Stream. These fluxes account for only 7-8% of the flux to the atmosphere from surface waters we calculated for the North Pacific and 6-12% of the flux for the North Atlantic, similar to the 5% estimates for the western subtropical North Atlantic [Scranton and Brewer, 1977] and 8% for the ADIOS site [Tilbrook and Karl, 1995]. As pointed out in the latter studies, the data suggest that methane is produced throughout the upper water column and is not supplied solely from the depth of the methane maximum.

The methane isotopic signatures in the upper ocean indicate that all three sampling sites are sources of isotopically heavy methane to the atmosphere. The ratio of the net gas fluxes of $^{13}\text{C}_{\text{CH}_4}$ to $^{12}\text{C}_{\text{CH}_4}$ to the atmosphere from the sea surface was calculated from [Quay et al., 1993]

$$\text{Flux}^{13}\text{C}_{\text{CH}_4}/^{12}\text{C}_{\text{CH}_4} = G \alpha_k [p\text{CH}_{4[\text{atm}]} R_{\text{atm}} \alpha_{\text{sol}} - p\text{CH}_{4[\text{ml}]} R_{\text{ml}}] / G [p\text{CH}_{4[\text{atm}]} - p\text{CH}_{4[\text{ml}]}], \quad (3)$$

where R_{atm} is the $^{13}\text{C}/^{12}\text{C}$ ratio in the atmosphere, R_{ml} is the $^{13}\text{C}/^{12}\text{C}$ ratio in the mixed layer, α_k is 0.9992 [Knox, et al., 1992; Happell et al., 1995], α_{sol} is 1.00033 [Fuex, 1980], $p\text{CH}_4$ is the methane partial pressure, and $\delta^{13}\text{C}-\text{CH}_{4[\text{atm}]}$ is -47.0 to -47.4‰ [Quay et al., 1991; this work]. The gas transfer rate values (G) cancel. The value assumed for α_k is based on $n = -2/3$ [Knox, et al., 1992]. The isotopic ratio of the net flux is relatively insensitive to the value of α_k or α_{sol} .

The mixed layer supersaturation was between 10 and 60%, and the $\delta^{13}\text{C}$ of methane in the mixed layer was between -45.5 and -46.6‰. The values of $\delta^{13}\text{C}$ for the methane flux were then calculated [Hoefs, 1987]:

$$\delta^{13}\text{C}_{\text{CH}_4\text{flux}} (\text{‰}) = \{ [R_{\text{flux}}/R_{\text{PDB}}] - 1 \} 10^3, \quad (4)$$

where R_{PDB} , the isotopic ratio of the PDB standard, is 0.011237 [Craig, 1957]. Averaging the air-sea flux rates in Table 1 yields a mean flux rate of $1.6 \mu\text{mol m}^{-2} \text{d}^{-1}$ for the North Pacific. If this flux is typical for the entire North Pacific oligotrophic gyre, whose area is $\sim 26.3 \times 10^6 \text{ km}^2$ [Wimm et al., 1994], 0.25 Tg y^{-1} of methane with an isotopic composition of between -42.5 and -43.0‰ is being supplied to the atmosphere from this oceanic region.

The isotopic ratios of methane in the upper ocean at Station ALOHA are less depleted in ^{13}C than previously published measurements of biologically produced methane (-50 to -110‰) [Whiticar et al., 1986; Krzycki et al., 1987; Alperin et al., 1992]. However, the oceanic depletion cannot be due to isotopic fractionation associated with oceanic methane equilibration with the atmosphere. This is because dissolved methane concentrations in the upper 300 m in 1996 and 1997 at Station ALOHA were on average 40% above equilibrium concentrations; in the North Atlantic the degree of supersaturation was 56%.

Alternatively, microbial consumption of methane in the upper ocean would lead to ^{13}C enrichment of the residual methane [Coleman et al., 1981; Whiticar, 1996; Reeburgh et al., 1997] and may explain the heavier than expected isotopic values of methane in surface waters. However, the long turnover time (5 to > 100 years) associated with microbial methane oxidation in the open ocean [Ward et al., 1987; Jones, 1991] indicates that this process is relatively unimportant in the removal of methane from surface waters. Approximately $0.03 \mu\text{mol CH}_4 \text{ m}^{-2} \text{d}^{-1}$ is consumed by microbes, assuming an average turnover time for methane in the upper ocean of 65 years [Ward et al., 1987; Jones, 1991]. This was estimated by dividing the average methane concentration in the upper 300 m (2.87 nM) by the turnover time and integrating this over 300 m. Thus microbial oxidation and downward eddy diffusion account for only 2 and 6%, respectively, of the total methane loss from the upper 300 m. Instead, flux to the atmosphere appears to be the main sink for methane in the upper ocean (Table 2). A downward flux out of the upper 300 m of $0.10 \mu\text{mol m}^{-2} \text{d}^{-1}$ is estimated based on the individual water column profiles in Table 1.

4.2. Upper Ocean Isotopic Budget

The isotopic composition of methane removed from the upper 300 m by in situ oxidation was calculated using published fractionation factors (α_k) and the following equation [Hoefs, 1987]

$$R_{\text{oxid}} = R_{\text{water}} / \alpha_k, \quad (5)$$

where R_{oxid} is the $^{13}\text{C}/^{12}\text{C}$ ratio in the methane oxidized in the upper 300 m and R_{water} is the $^{13}\text{C}/^{12}\text{C}$ ratio in the upper 300 m of the water column. The values of $\delta^{13}\text{C}_{\text{oxid}}$ were then calculated [Hoefs, 1987]:

$$\delta^{13}\text{C}_{\text{CH}_4\text{oxid}} (\text{‰}) = \{ [R_{\text{oxid}}/R_{\text{PDB}}] - 1 \} 10^3. \quad (6)$$

Table 1. Calculated Methane Sea-to-Air Fluxes in the North Pacific (Station ALOHA) and North Atlantic.

	Station ALOHA				North Atlantic ^a	
	Oct. 1996	Jan. 1997	April 1997	July 1997	Sargasso Sea	Gulf Stream
Average mixed layer conc., nM	2.9	2.4	2.5	2.4	3.0 ^b	2.4 ^b
Wind speed ^c , m s ⁻¹	5.3	7.8	6.7	7.5	8.2	8.2
Sea-air flux, $\mu\text{mol m}^{-2} \text{d}^{-1}$	1.6	1.7	1.6	1.4	4.4	1.6
Upward diffusive flux from subsurface maximum, $\mu\text{mol m}^{-2} \text{d}^{-1}$	0.11	0.13	0.12	0.09	0.26	0.19

Positive fluxes are upward.

^aSamples taken in April 1997.

^bSurface concentration.

^cFrom National Data Buoy Center (buoy 51001 for Station ALOHA and buoy 41002 for North Atlantic Stations) (<http://seaboard.ndbc.noaa.gov>).

The $\delta^{13}\text{C}$ value of methane consumed by bacteria is thus calculated to be between -50.3‰ ($\alpha_k = 1.005$) and -73.4‰ ($\alpha_k = 1.03$). The α_k values were taken from *Barker and Fritz* [1981] and *Coleman et al.* [1981].

The isotopic composition for the methane leaving the surface layer by eddy diffusion is taken to be the average isotopic composition (-45.6‰) of the methane in the upper 300 m (assuming no fractionation during eddy diffusion in water).

If $1.7 \mu\text{mol m}^{-2} \text{d}^{-1}$ methane is exiting the upper 300 m (upward and downward flux + removal by oxidation), the same amount must be produced to compensate for the diffusive and oxidative losses if the system is to maintain the relatively constant concentrations observed during 1996-1997. Similarly, the isotopic composition of methane produced in the upper 300 m should be equal to that exiting the upper 300 m by oxidation and eddy diffusion. The $\delta^{13}\text{C}$ of methane leaving the upper water column by flux to the atmosphere, eddy diffusion, and oxidation was estimated as follows:

$$\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-total}} = ((\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-flux}} L_{\text{flux}}) + (\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-diff}} L_{\text{diff}}) + (\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-oxid}} L_{\text{oxid}})) / \text{total loss}, \quad (7)$$

Table 2. Methane Fluxes in the Upper 300 m at Station ALOHA..

	Flux, $\mu\text{mol m}^{-2} \text{d}^{-1}$	$\delta^{13}\text{C}\text{-CH}_4$, ‰
CH₄ Loss From Upper 300 m		
Upward	1.57 ± 0.1	-42.1 ± 1.5
Downward	0.10 ± 0.02	-45.0 ± 0.6
Oxidation	0.03 ± 0.003	-73.4 to -50.3 ± 0.6
Input to Upper 300 m		
Methanogenesis	1.70	-43 to -42.5 ± 1.4

Average concentrations were 3.0 nM for the upper 300 m and 2.57 nM for the mixed layer. Average isotopic compositions were -45.6‰ for the upper 300 m and -46.2‰ for the mixed layer.

where L_{flux} is the fraction of the overall methane loss due to sea-air flux, L_{diff} is the fraction of the overall methane loss due to eddy diffusion, and L_{oxid} is the fraction of the overall methane loss due to oxidation. Here $\delta^{13}\text{C}_{\text{CH}_4 \text{ exit-oxid}}$ was set equal to -50.3‰ for the upper estimate of $\delta^{13}\text{C}$ exiting the upper 300 m via oxidation and to -73.4‰ for the lower estimate. According to these mass balance calculations, the isotopic composition of newly produced methane at Station ALOHA should be around -43‰. These calculations show that the heavier than expected isotopic signature of methane in the surface layer does not reflect the residual effect of microbial oxidation but suggest instead that some process associated with methanogenesis controls the isotopic ratio. *Tilbrook and Karl* [1995] found that although methane may be produced photochemically in water exposed to direct sunlight, abiotic methane production was unimportant in water exposed to lower light levels. Therefore we conclude that most of the methane is produced biogenically.

4.3. Methane Production and Oxidation in the Upper Ocean

Although it is evident that methane is produced in the upper ocean, it is not clear by what mechanism methanogenesis occurs. Previous studies have reported a correlation between methane and zooplankton-ATP (adenosine triphosphate), chlorophyll, and/or density [*Traganza et al.*, 1979; *Brooks et al.*, 1981; *Conrad and Seiler*, 1988]. However, methane concentrations and isotopic compositions at Station ALOHA did not correlate with either ATP or chlorophyll a (Hawaii Ocean Time-series data set). One exception is the April 1997 profile, in which the chlorophyll a maximum at 100 m coincided with a shallow methane concentration maximum and a slight elevation in $\delta^{13}\text{C}$ at this depth. Instead, methane dynamics appear to be related to density, since concentration maxima occurred at the pycnocline ($\sigma_t = 25.5 - 25.9$) during all four cruises in the North Pacific (Figure 2). In the Sargasso Sea the maximum concentration coincided with $\sigma_t = 25.2$ and at the Gulf Stream with $\sigma_t = 24.3$ (Figure 3). Similarly, methane maxima occur primarily in a range of σ_t from 24 to 26 in the Gulf of Mexico [*Brooks et al.*, 1981]. This suggests that the observed methane maxima were supported by methanogenesis in sus-

pended particles that accumulate at the pycnocline [e.g., *Sieburth et al.*, 1987].

It has been suggested that diurnal variations in dissolved gases in the pycnocline of the ocean might occur in tandem with other biologically mediated parameters such as bacterial activity. We compared methane profiles (0-1000 m) from samples taken at 0100 and 1400 UT during the October and January ALOHA cruises and found no significant diurnal differences in either methane concentration or isotopic composition (Figure 4). The lack of a diurnal signal implies that methane production and consumption in the ocean is independent of day-night cycles such as photosynthesis, grazing, and vertical migration of zooplankton.

One explanation for the high $\delta^{13}\text{C}$ values is that the methane is produced in microniches in which methanogenic substrates may become limiting, driving the $\delta^{13}\text{C}$ of the methane toward heavier values. Potential microniches for strictly anaerobic methanogens in an oxygenated water column in the open ocean include fish guts, fecal pellets, and detrital particles [*Oremland*, 1979; *Marty*, 1993; *de Angelis and Lee*, 1994; *Karl and Tilbrook*, 1994], which could become depleted in methanogenic substrates, as suggested by *Marty* [1993].

Alternatively, the nature of the methanogenic pathway may contribute to the higher than expected $\delta^{13}\text{C}$ values. Carbonate reduction is believed to be the primary means of methane formation in marine sediments [*Whiticar*, 1996]. However, high fractionation factors ($\alpha = 1.05 - 1.1$) are associated with this pathway, which has been found to result in methane with $\delta^{13}\text{C}$ values of -60 to -110‰ [*Whiticar et al.*, 1986]. Laboratory estimates of α for fermentation of methylated compounds such as acetate and methylamines, however, are lower (1.025 - 1.055) [*Blair and Carter*, 1992; *Whiticar*, 1996]. If these methanogenic substrates have initial isotopic compositions that are not too different from that of bulk marine organic matter (approximately -20‰), this mechanism for methane formation could yield $\delta^{13}\text{C}$ - CH_4 values as heavy as -44‰. Because sulfate-reducing bacteria outcompete methanogens for acetate where there is abundant sulfate, it is likely that methane production in the upper ocean occurs via fermentation of methylamines, as suggested by *Sieburth* [1987] and *de Angelis and Lee* [1994]. Further, *Cynar and Yayanos* [1991] and *Sieburth* [1993a, b] have isolated methylamine-utilizing methanogens from the upper ocean. Thus bacterial consortia in the water column producing methane via different pathways (e.g., methylotrophy) than those in sediments could lead to the relatively heavy methane isotopic signature measured in the upper ocean.

Preliminary experiments to determine methane production potential in particulate matter, and its isotopic composition, were carried out in July 1997 (Figure 5). The ^{13}C enrichment of 1.1 and 1.8‰ observed in the methane after incubation supports the prediction by mass balance calculations that the $\delta^{13}\text{C}$ values of methane produced in the upper water column are higher than expected for biogenic methane not because of oxidation but because of substrate limitation and/or the methanogenic pathway used. Although sample size was small, the results suggest that methane may be produced in sinking particles and encourage future research into particle-associated methanogenesis. *Karl and Tilbrook* [1994], how-

ever, found that methane was not produced in particles collected in sediment traps and concluded that methane formation was associated with the sinking particles and perhaps originated in larger particles which could break up during settling through the water column and in the traps. Their traps had 335- μm screens near the tops of the traps which prevented large particles from entering the traps. Screens were not used in our traps, and the particles which we collected were perhaps large enough for the maintenance of the anaerobic conditions believed necessary for methanogenesis.

4.4. Intermediate and Deep Water

The progressive enrichment of methane in ^{13}C with depth, in tandem with decreasing concentration, is most likely related to the oxidation of the methane with little or no new production of the gas. Below the euphotic zone, variations in methane concentration and isotopic composition at Station ALOHA correspond to the depths of different water masses. The core of North Pacific Intermediate Water (NPIW) is located at 500 m [*Hasunuma*, 1978; *Bingham and Lukas*, 1996]. Below this, Antarctic Intermediate Water (AAIW) extends to around 1500 m, with its core at 800 m [*Bearman*, 1989; *Bingham and Lukas*, 1996]. Part of the NPIW interacts with the North Pacific gyre system and circulates around the western boundary of the Pacific [*Reid and Mantyla*, 1978]. By the time this water mass, known as modified NPIW, reaches the central North Pacific, it has interacted with other water masses and currents and is older than the water above or below it [*Wyrki*, 1977]. This is evident in the high $\delta^{13}\text{C}$ values at 600 m which likely reflect isotopic fractionation associated with in situ methane oxidation. Below this depth, $\delta^{13}\text{C}$ - CH_4 decreases, probably reflecting mixing between the modified NPIW and the AAIW below it. The deepest water mass in our profiles (July 1997) is North Pacific Deep Water (NPDW), located between 3000 and 4000 m [*Mantyla*, 1975]. The continuing decrease in $\delta^{13}\text{C}$ - CH_4 to 4000 m may reflect mixing between NPDW and the water masses above.

Methane concentrations do not decrease noticeably below around 800 m, probably because consumption of methane all but stops in older, deeper waters [*Scranton and Brewer*, 1978]. However, isotopic ratios will vary with depth due to mixing of water masses of different ages and different histories of methane input. For example, a water mass that has had a significant input of methane, such as from mid-ocean hydrothermal venting [e.g., *Mottl et al.*, 1995], should have a relatively heavy isotopic ratio due to fractionation during oxidation of this added methane. This history of methane input and oxidation, however, may not be evident from the methane concentrations alone because older waters have fairly uniform low concentrations.

5. Conclusion

Methane concentrations were supersaturated (up to 90%) with respect to the atmosphere in the upper 300 m in both the North Pacific and North Atlantic study sites in 1996 - 1997. Although it has been well known for some time that the upper part of the oceans are supersaturated with methane, the constancy of the elevated concentrations and upper ocean $\delta^{13}\text{C}$ values (approximately -45‰) over a 1 year annual cycle has been shown here.

On the basis of the concentrations and isotopic ratios, we conclude that methane production and consumption processes in the North Pacific gyre region varied little on a seasonal basis in 1996 - 1997. Methane with a consistently heavier isotopic value than atmospheric methane was transferred from the sea surface to the atmosphere at Station ALOHA at an apparently uniform rate throughout the year. The excess methane in the surface waters appears to be generated throughout the upper 300 m of the water column by bacterial methanogenesis and is not supplied solely from the depth of the methane maximum. The methane concentration maxima occur at the pycnocline, suggesting that the maxima are supported by methanogenesis in suspended particles that accumulate at these depths. In support of this, experiments showed that methane concentrations increased in water in which particles collected at 250 m water depth were incubated. The lack of a diurnal signal implies that methane production and consumption in the ocean is independent of day-night cycles such as photosynthesis, grazing, and vertical migration of zooplankton. The flux to the atmosphere appears to be the main sink for methane in the upper ocean; microbial oxidation and downward eddy diffusion account for only 2 and 6%, respectively, of the total methane loss from the upper 300 m. Below the upper 300 m, methane concentrations and isotopic compositions reflect methane oxidation and mixing of different water masses.

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References

- Alperin, M.J., N.E. Blair, D.B. Albert, T.M. Hoehler, and C.S. Martens, Factors that control the stable carbon isotopic composition of methane produced in an anoxic marine sediment, *Global Biogeochem. Cycles*, **6**, 271-291, 1992.
- Barber, T.R., R.A. Burke, and W.M. Sackett, Diffusive flux of methane from warm wetlands, *Global Biogeochem. Cycles*, **2**, 411-425, 1988.
- Barker, J.F., and P. Fritz, Carbon isotope fractionation during microbial methane oxidation, *Nature*, **293**, 289-291, 1981.
- Bearman, G. (Ed.), *Ocean Circulation*, 238 pp., Pergamon Press, New York, 1989.
- Bingham, F.M., and R. Lukas, Seasonal cycles of temperature, salinity and dissolved oxygen observed in the Hawaii Ocean Time-series, *Deep Sea Res., Part II*, **43**(2-3), 199-213, 1996.
- Blair, N.E., and W.D. Carter Jr., The carbon isotope biogeochemistry of acetate from a methanogenic marine sediment, *Geochim. Cosmochim. Acta*, **56**, 1247-1258, 1992.
- Brooks, J.M., D.F. Reid, and B.B. Bernard, Methane in the upper water column of the northwestern Gulf of Mexico, *J. Geophys. Res.*, **86**, 11,029-11,040, 1981.
- Bugna, G.C., J.P. Chanton, J.E. Cable, W.C. Burnett, and P.H. Cable, The importance of groundwater discharge to the methane budgets of nearshore and continental shelf waters of the northeastern Gulf of Mexico, *Geochim. Cosmochim. Acta*, **60**, 4735-4746, 1996.
- Cicerone, R.J., and R.S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochem. Cycles*, **2**, 299-327, 1988.
- Coleman, D.D., J.B. Risattiand, and M. Schoell, Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria, *Geochim. Cosmochim. Acta*, **45**, 1033-1037, 1981.
- Conrad, R., and W. Seiler, Methane and hydrogen in seawater (Atlantic Ocean), *Deep Sea Res.*, **35**, 1903-1917, 1988.
- Craig, H., Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Acta*, **12**, 133-149, 1957.
- Cynar, F.J., and A.A. Yayanos, Enrichment and characterization of a methanogenic bacterium from the oxic upper layer of the ocean, *Curr. Microbiol.*, **23**, 89-96, 1991.
- de Angelis, M.A., and C. Lee, Methane production during zooplankton grazing on marine phytoplankton, *Limnol. Oceanogr.*, **39**, 1298-1308, 1994.
- Dore, J.E., B.N. Popp, D.M. Karl, and F.J. Sansone, A large source of atmospheric nitrous oxide from subtropical North Pacific surface waters, *Nature*, **396**, 63-66, 1998.
- Faber, E., P. Gerling, U. Berner, and E. Sohns, Methane in ocean waters: Concentration and carbon isotope variability at East Pacific Rise and in the Arabian Sea, *Env. Monit. Assess.*, **31**, 139-144, 1994.
- Fuex, A.N., Experimental evidence against an appreciable isotopic fractionation of methane during migration, *Phys. Chem. Earth*, **12**, 725-732, 1980.
- Happell, J.D., J.P. Chanton, and W.J. Showers, Methane transfer across the water-air interface in stagnant wooded swamps of Florida: Evaluation of mass-transfer coefficients and isotopic fractionation, *Limnol. Oceanogr.*, **40**, 290-298, 1995.
- Hasunuma, K., *Formation of the Intermediate Salinity Minimum in the North-Western Pacific Ocean*, vol. 9, 47 pp., Ocean Res. Inst., Tokyo, 1978.
- Hoefs, J., *Stable Isotope Geochemistry*, 241 pp., Verlag Springer, New York, 1987.
- Jones, R.D., Carbon monoxide and methane distribution and consumption in the photic zone of the Sargasso Sea, *Deep Sea Res., Part A*, **38**, 625-635, 1991.
- Karl, D.M., and R. Lukas, The Hawaii Ocean Time-series (HOT) program: Background, rationale and field implementation, *Deep Sea Res., Part I*, **43**, 129-156, 1996.
- Karl, D.M., and B.D. Tilbrook, Production and transport of methane in oceanic particulate organic matter, *Nature*, **368**, 732-734, 1994.
- Knauer, G.A., J.H. Martin, and K.W. Bruland, Fluxes of particulate carbon, nitrogen and phosphorus in the upper water column of the northeast Pacific, *Deep Sea Res.*, **26**, 97-108, 1979.
- Knox, M., P.D. Quay, and D. Wilbur, Kinetic isotopic fractionation during air-water gas transfer of O_2 , N_2 , CH_4 and H_2 , *J. Geophys. Res.*, **97**, 20,335-20,343, 1992.
- Krzycki, J.A., W.R. Kenealy, M.J. DeNiro, and J.G. Zeikus, Stable carbon isotope fractionation by *Methanosarcina barkeri* during methanogenesis from acetate, methanol or carbon dioxide/hydrogen, *Appl. Environ. Microbiol.*, **53**, 2597-2599, 1987.
- Lamontagne, R.A., J.W. Swinnerton, V.J. Linnenbom, and W.D. Smith, Methane concentrations in various marine environments, *J. Geophys. Res.*, **78**, 5317-5324, 1973.
- Lashof, D.A., and D.R. Ahuja, Relative contributions of greenhouse gas emissions to global warming, *Nature*, **344**, 529-531, 1990.
- Li, Y.-H., T.-H. Peng, W.S. Broecker, and H.G. Ostlund, The average vertical mixing coefficient for the oceanic thermocline, *Tellus*, Ser. B, **36B**, 212-217, 1984.
- Liss, P.S., and P.G. Slater, Flux of gases across the air-sea interface, *Nature*, **247**, 181-184, 1974.
- Mantyla, A.W., On the potential temperature in the abyssal Pacific Ocean, *J. Mar. Res.*, **33**, 341-354, 1975.
- Marty, D.G., Methanogenic bacteria in seawater, *Limnol. Oceanogr.*, **38**, 452-456, 1993.
- Mottl, M.J., F.J. Sansone, C.G. Wheat, J.A. Resing, E.T. Baker, and J.E. Lupton, Manganese and methane in hydrothermal plumes along the East Pacific Rise, 8°40' to 11°50'N, *Geochim. Cosmochim. Acta*, **59**, 4147-4165, 1995.

- Oremland, R.S., Methanogenic activity in plankton samples and fish intestines: A mechanism for in situ methanogenesis in oceanic surface waters, *Limnol. Oceanogr.*, *24*, 1136-1141, 1979.
- Popp, B.N., F.J. Sansone, T.M. Rust, and D.A. Merritt, Determination of concentration and carbon isotopic composition of dissolved methane in sediments and nearshore waters, *Anal. Chem.*, *67*, 405-411, 1995.
- Prather, M., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou, Other trace gases and atmospheric chemistry, in *Climate Change 1994: Relative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, edited by J.T. Houghton et al., pp. 73-126, Cambridge Univ. Press., New York, 1995.
- Quay, P.D., S.L. King, J.M. Landsdown, and D.O. Wilbur, Carbon isotopic composition of atmospheric CH_4 : Fossil and biomass burning source strengths, *Global Biogeochem. Cycles*, *5*, 25-47, 1991.
- Quay, P.D., S. Emerson, D.O. Wilbur, C. Stump, and M. Knox, The $\delta^{18}\text{O}$ of dissolved O_2 in the surface waters of the subarctic Pacific: A tracer of biological activity, *J. Geophys. Res.*, *98*, 8447-8458, 1993.
- Reeburgh, W.S., A.I. Hirsch, F.J. Sansone, B.N. Popp, and T.M. Rust, Carbon kinetic isotope effect accompanying microbial oxidation of methane in boreal forest soils, *Geochim. Cosmochim. Acta*, *61*, 4761-4767, 1997.
- Reid, J.L., and A.W. Mantyla, On the mid-depth circulation of the North Pacific Ocean, *J. Phys. Oceanogr.*, *8*, 946-951, 1978.
- Sackett, W.M., and J.M. Brooks, Origin and distribution of low-molecular-weight hydrocarbons in Gulf of Mexico coastal waters, in *Marine Chemistry in the Coastal Environment*, *ACS Symp. Ser.*, vol. 18, edited by T.M. Church, pp. 211-230, Am. Chem. Soc., Washington, D. C., 1975.
- Sansone, F.J., and C.S. Martens, Methane production from acetate and associated methane fluxes from anoxic coastal sediments, *Science*, *211*, 707-709, 1981.
- Sansone, F.J., B.N. Popp, and T.M. Rust, Stable carbon isotopic analysis of low-level methane in water and gas, *Anal. Chem.*, *69*, 40-44, 1997.
- Sansone, F.J., M.E. Holmes, and B.N. Popp, Methane stable isotopic ratios and concentrations as indicators of methane dynamics in estuaries, *Global Biogeochem. Cycles*, *13*, 463-474, 1999.
- Scranton, M.I., and P.G. Brewer, Occurrence of methane in the near-surface waters of the western subtropical North-Atlantic, *Deep Sea Res.*, *24*, 127-138, 1977.
- Scranton, M.I., and P.G. Brewer, Consumption of dissolved methane in the deep ocean, *Limnol. Oceanogr.*, *23*, 1207-1213, 1978.
- Sieburth, J.McN., Contrary habitats for redox-specific processes: Methanogenesis in oxic waters and oxidation in anoxic waters, in *Microbes in the Sea*, edited by M.A. Sleight, pp. 11-38, Harwood, New York, 1987.
- Sieburth, J.McN., C_1 bacteria in the water column of Chesapeake Bay, USA, I, Distribution of sub-populations of O_2 -tolerant, obligately anaerobic, methylotrophic methanogens that occur in microniches reduced by their bacterial consort, *Mar. Ecol. Prog. Ser.*, *95*, 67-80, 1993a.
- Sieburth, J.McN., C_1 bacteria in the water column of Chesapeake Bay, USA, II, The dominant O_2 - and H_2S -tolerant methylotrophic methanogens, coenriched with their oxidative and sulfate reducing bacterial consort, are all new immunotypes and probably include new taxa, *Mar. Ecol. Prog. Ser.*, *95*, 81-89, 1993b.
- Tilbrook, B.D., and D.M. Karl, Methane sources, distributions and sinks from California coastal waters to the oligotrophic North Pacific gyre, *Mar. Chem.*, *49*, 51-64, 1995.
- Traganza, E.D., J.W. Swinnerton, and C.H. Check, Methane supersaturation and ATP-zooplankton blooms in near-surface waters of the Western Mediterranean and the subtropical North Atlantic Ocean, *Deep Sea Res., Part A*, *26A*, 1237-1245, 1979.
- Ward, B.B., K.A. Kilpatrick, P.E. Novelli, and M.I. Scranton, Methane oxidation and methane fluxes in the ocean surface layer and deep anoxic waters, *Nature*, *327*, 226-229, 1987.
- Whiticar, M.J., Isotope tracking of microbial methane formation and oxidation, *Mitt. Internat. Verein. Limnol.*, *25*, 39-54, 1996.
- Whiticar, M.J., E. Faber, and M. Schoell, Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation - Isotope evidence, *Geochim. Cosmochim. Acta*, *50*, 692-709, 1986.
- Winn, C.D., F.T. Mackenzie, C.J. Carrillo, C.L. Sabine, and D.M. Karl, Air-sea carbon dioxide exchange in the North Pacific Subtropical Gyre: Implications for the global carbon budget, *Global Biogeochem. Cycles*, *8*, 157-163, 1994.
- Wyrtki, K., *Water Masses in the Oceans and Adjacent Seas*, *International Dictionary of Geophysics*, Pergamons, New York, 1977.
- Yamamoto, S., J.B. Alcauskad, and T.E. Crozier, Solubility of methane in distilled water and seawater, *J. Chem. Eng. Data*, *21*, 78-80, 1976.

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