C_1–C_4 hydrocarbons in the North and South Pacific[1]

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ABSTRACT

Low molecular weight hydrocarbons in the surface waters of the North and South Pacific have been measured. Methane concentrations average 4.2×10^{-5} ml/l, while the C_2–C_4 hydrocarbons averaged $1–5 \times 10^{-6}$ ml/l. A large broad peak was found between 10° N and 10° S for the unsaturated hydrocarbons. Large concentrations of the C_1–C_4 hydrocarbons were found in the different types of Antarctic sea ice. Atmospheric methane concentrations averaged 1.44 ± 0.04 ppm and decreased to 1.36 ± 0.04 ppm at the Intertropical Convergence Zone (ITC).

Introduction

In an attempt to elucidate the role of the oceans as either a sink or source of various gases, we at the Naval Research Laboratory have been making measurements of low molecular weight hydrocarbons (C_1–C_4) in a variety of ocean environments. The main sampling program has been in the open ocean where, in the upper layers, the mechanism of methane and unsaturated hydrocarbon production appears to be related to biological processes. We have also investigated restricted basins containing anoxic waters where hydrocarbons are produced mainly by the anaerobic decomposition of organic matter, and bays and rivers where the hydrocarbon concentration is affected by man-induced artifacts such as sewage. In conjunction with the water sampling program, atmospheric methane concentrations just above the ocean's surface have been measured.

Dissolved methane concentrations in open ocean areas range from 4 to 5×10^{-5} ml/l (Frank et al., 1970; Lamontagne et al., 1971; Swinnerton et al., 1969; Brooks & Sackett, 1972). Open ocean values for ethane, ethylene, propane, propylene, iso- and *n*-butane average $1–10 \times 10^{-6}$ ml/l (Linnenbom & Swinnerton, 1968; Frank et al., 1970; Brooks & Sackett, 1972).

Reported atmospheric concentrations for low molecular weight hydrocarbons (C_1–C_4) in non-urban areas, except for methane, are quite scarce. The few concentrations obtained average about 0.06 to 1.00 ppb (Behar et al., 1972; Cavanagh et al., 1969). Atmospheric methane concentrations made at ground level range from 1.2 to 1.7 ppm (Junge, 1963; Cavanagh et al., 1969; Bowman & Shaw, 1966). Methane measurements made over the open ocean have been reported ranging from 1.24 to 1.43 ppm (Swinnerton et al., 1969; Lamontagne et al., 1971; Ehhalt & Heidt, 1972). Atmospheric methane measurements along with measurements of atmospheric carbon monoxide have gained in importance since the postulation that methane oxidation is the major source of naturally-occurring carbon monoxide (McConnell et al., 1971; Weinstock & Niki, 1972).

This paper will be concerned primarily with methane concentrations in the air and surface waters on a cruise from Long Beach, California to McMurdo Station, Antarctica on board the USCGC *Glacier*. Surface water samples from Long Beach to the edge of the Antarctic ice field were obtained from the sea chest supplying the ship's evaporators. The water intake for the sea chest was located approximately 5 meters below the sea surface. All other water samples were taken with a Niskin water sampler. Air samples were obtained from an inlet mounted on the bow of the ship. All samples were analysed by gas chromatography (Swinnerton & Linnenbom, 1967).

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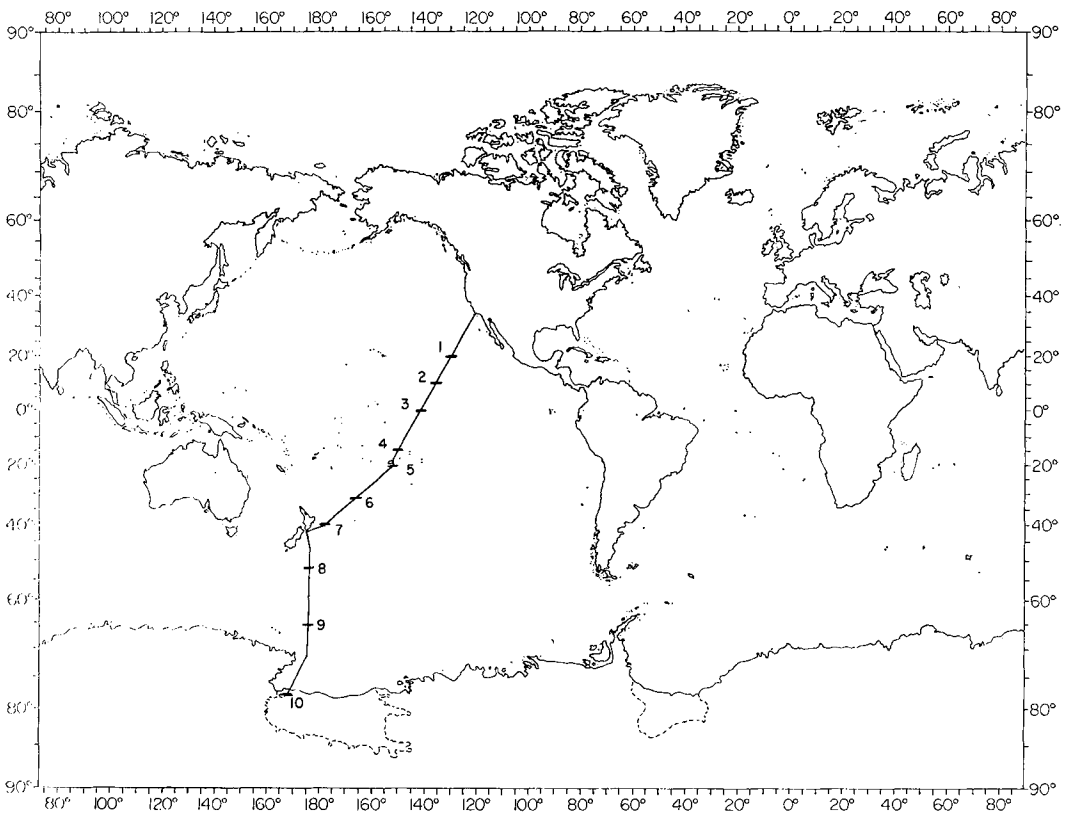

Fig. 1. Cruise track of the USCGC *Glacier* from Long Beach, California to McMurdo Station. Relative position of station samples taken is shown by the numbers.

Results

Fig. 1 shows the cruise track from Long Beach to McMurdo Station. Also listed are the relative positions of the stations occupied during transit. Fig. 2 shows the atmospheric and dissolved surface water methane concentrations along the cruise track. Along the abscissas are plotted the date, time, latitude, and longitude. As can be seen, the concentrations obtained from the sea chest and those from the water samplers agree quite well. Water and air samples were taken every three hours. The average surface water methane concentration is 4.2×10^{-5} ml/l down to about 35° S. The values increase after this point, due to the decreasing temperature of the water, and consequently the increasing solubility of methane. A peak is found at approximately 60° S in the area of the Antarctic convergence zone.

Atmospheric methane values averaged 1.44 ± 0.04 ppm (10^6 by volume) to about 10° N and then decreased to 1.36 ± 0.04 ppm and remained at this concentration throughout the remainder of the cruise. A calibration gas sample was run with each atmospheric sample.

Table 1 shows a comparison of the atmospheric methane concentrations we have found in various areas. The concentrations in the northern Pacific for 1970 between 20° N and 10° N average 1.43 ± 0.03 ppm (Lamontagne et al., 1971), and agree with those values obtained on this cruise (1972) between 35° N and 10° N of 1.44 ± 0.04 ppm. Samples collected in the Atlantic average approximately 1.36 ± 0.06 ppm, and agree with those values found in the Pacific between 10° N and 77° S. Sargasso Sea values are lower than our other atmospheric samples.

Fig. 3 shows the ethylene surface water concentrations obtained between Long Beach and McMurdo Station. Date, time, and position are

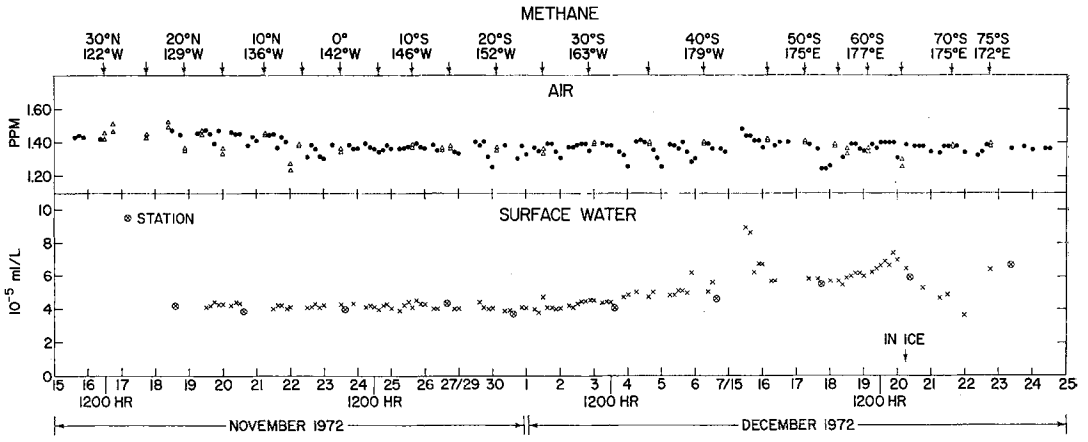

Fig. 2. Atmosphere and dissolved methane concentrations from Long Beach, California to McMurdo Station. × denotes those samples taken from the ship's evaporator sea chest, ⊗ denotes stations where the water samples were taken with a Niskin water sampler; Δ in the atmospheric samples represents duplicate samples.

Table 1. *Marine atmospheric methane concentrations (ppm)*

Pacific	(1970)	20° N – 10° N	1.43 ± 0.03
Pacific	(1972)	35° N – 10° N	1.44 ± 0.04
Pacific	(1972)	10° N – 77° S	1.36 ± 0.04
Atlantic	(1971)	55° N – 80° N	1.37 ± 0.05
Atlantic	(1969, 1970)	35° N – 10° N	1.36 ± 0.06
Sargasso Sea	(1971)	32° N – 20° N	1.30 ± 0.03

plotted along the abscissa. There is a definite latitudinal variation with a broad peak found between ≈10° N and 15° S with an average maximum value of $5.3 \pm 0.5 \times 10^{-6}$ ml/l. The next increase occurs near 40° S with a maximum value of 5.7×10^{-6} ml/l. There is no recognizable peak at 60° S, as was found for methane. The highest value obtained during the entire trip, 9.9×10^{-6} ml/l, was in the ice-covered region at ≈76° S.

Propylene concentrations (not plotted) follow the same general trend observed for ethylene with a broad peak between 10° N and 15° S. The average maximum concentration for this large broad area is 3.5×10^{-6} ml/l with the average low concentration ranging from 0.6–1.0×10^{-6} ml/l. A large peak is also observed at ≈40° S (3.7×10^{-6} ml/l) and ≈76° S (3.3×10^{-6} ml/l).

Ethane and propane remain fairly constant at 0.2×10^{-6} ml/l and 0.3×10^{-6} ml/l, respectively. Like ethylene and propylene, ethane and propane concentrations increase at ≈76° S to

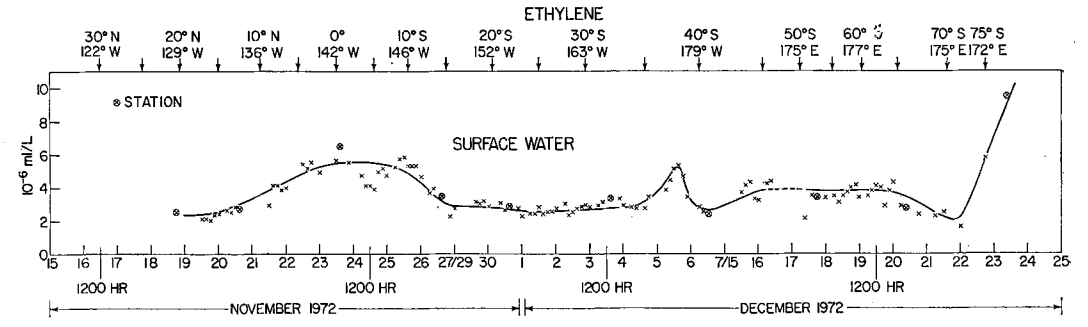

Fig. 3. Ethylene concentrations in the surface waters between Long Beach, California and McMurdo Station. × represents the same terms listed for methane in Fig. 2.

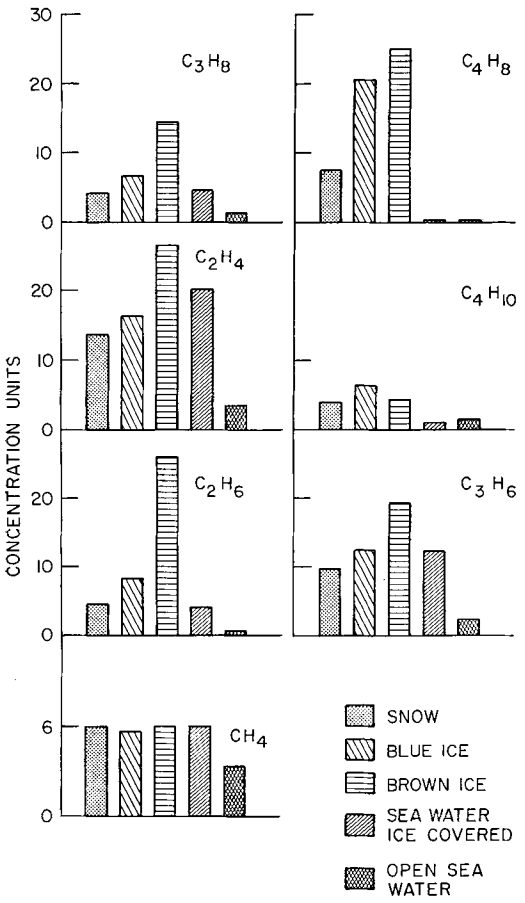

Fig. 4. Hydrocarbons in Antarctic sea ice.

1.9×10^{-6} and 1.2×10^{-6} ml/l, respectively. Iso- and *n*-butane are present in trace amounts (10^{-7} ml/l) in the surface waters with increases in the ice-covered regions.

Fig. 4 shows the hydrocarbons in Antarctic Sea ice and snow. The concentration units are relative units, but give a perspective of the concentrations between the various environments encountered. Open sea water concentrations are listed as a reference point. Methane in the open sea water listing for Fig. 4 is 5.9×10^{-5} ml/l, while the concentrations in the snow and ice average 8.1×10^{-5} ml/l. The maximum ice concentrations observed for each of the remaining hydrocarbons are as follows:

C_2H_6, 11.9×10^{-6}; C_2H_4, 11.2×10^{-6}; C_3H_8, 4.3×10^{-6}; C_3H_6, 5.3×10^{-6}; C_4H_8, 5.5×10^{-6}; C_4H_{10}, 1.7×10^{-6} ml/l.

Discussion

Methane concentrations in the surface waters of the Pacific between 20° N and 77° S agree quite well with previous measurements made in the north Pacific and Atlantic. Supersaturation of the surface water with respect to atmospheric methane is approximately 30% (water temperature variations have been taken into consideration) as found in the majority of our other data. Brooks & Sackett (1972) have reported undersaturation in upwelled surface waters in the Gulf of Mexico. In agreement with Brooks & Sackett's (1912) findings, undersaturation has been found in all of our deep water samples obtained in freely circulating open ocean areas. Undersaturation of ≈20% was found in the ice-covered section of our cruise track. However, samples obtained in the Greenland ice pack exhibited values of ≈30% supersaturation (Lamontagne et al., 1972). Consequently, the surface waters of the north and south Pacific Oceans are acting as a source for methane in the ice-free areas. However, in the partially ice-covered areas of Antarctica, in the vicinity of the Ross Sea, the ocean is acting as a sink. During the time spent in the vicinity of ice, the wind was calm with a minimum amount of disturbance at the air–sea interface. It may be that during these quiescent times, the presence of methane utilizing bacteria may become a major factor in the observed undersaturation.

Using our measured partial pressure difference between dissolved methane and atmospheric methane, 1.80–1.40 ppm, and using

Table 2. *Marine atmospheric ratios of CH_4 and CO*

Location	Position	CH_4 (ppm)	CO (ppm)	Ratio CH_4/CO
Atlantic (1969, 1970)	10° N – 35° N	1.36	0.114	11.9
Pacific (1970)	10° N – 20° N	1.43	0.123	11.6
Atlantic (1971)	55° N – 80° N	1.37	0.111	12.3
Pacific (1972)	35° N – 10° N	1.44	0.128	11.3
Pacific (1972)	10° N – 77° S	1.36	0.040	34.0

the transfer coefficient for carbon monoxide (Linnenbom et al., 1973, corrected for the difference in solubility between methane and carbon monoxide), a flux of 4×10^{-3} mg/cm^3 yr from the oceans to the atmosphere can be estimated for methane. This flux must be regarded as the upper limit, since the carbon monoxide transfer coefficient used is an upper limit. In the northern hemisphere, this corresponds to approximately 6×10^{12} g/yr. This is only about 1 % of the overall production rate for methane given by Ehhalt & Heidt [1972]. Consequently, the role of the ocean as a major source or a sink for methane is insignificant.

Performing a student's *t*-test on the atmospheric methane data (Fig. 2) indicates that the decrease from 1.44 ppm to 1.36 ppm occurring in the vicinity of the intertropical convergence zone (ITC) is significant. The ITC was located at 7° N during our cruise (Machta, 1973). Atmospheric carbon monoxide measured at the same time also decreased in concentration from 0.128 ppm to 0.036 ppm at the ITC. This leads us to believe that the values found on this recent cruise (1972) are real and that the decrease at the ITC is not an artifact.

An interesting aspect of this recent data is a comparison of the ratio of atmospheric methane to carbon monoxide (Table 2). In all of these ratios, the methane and carbon monoxide were measured from the same air samples collected in the marine environment. If the oxidation of methane to carbon monoxide takes place as postulated, then one would expect the ratio of methane to carbon monoxide to be fairly constant throughout the world, especially in areas where man-made pollution does not have an immediate impact. The ratio for all of our CH_4/CO measurements in the Atlantic and in the Pacific down to $\approx 10°$ N, ranges from 11.3–12.3, while the ratio for the Pacific below 10° N to 77° S averages 34. If one assumes that the background level of atmospheric carbon monoxide is not increasing, then the destruction of carbon monoxide must be equal to its formation. Also, if methane oxidation is the major source of naturally occurring carbon monoxide (as postulated), then

$$\frac{-d(CH_4)}{dt} = K_1(CH_4)(OH)$$

where $CH_4 + OH = CH_3 + H_2O$ is the first step towards formation of CO, and

$$\frac{-d(CO)}{dt} = K_2(CO)(OH)$$

where $CO + OH = CO_2 + H$ is the disappearance mechanism for CO, then

$$CH_4/CO = K_2/K_1 \quad \text{or} \quad \frac{1.40\ \text{ppm}}{0.12\ \text{ppm}} = 12$$

Using values of 9.2×10^{-15} cm^3 molecule^{-1} sec^{-1} and 1.5×10^{-13} cm^3 molecule^{-1} sec^{-1} for K_1 and K_2, respectively (Grenier, 1969, 1970), one obtains $K_2/K_1 = 16$.

Assuming no significant difference between 16 and 12, but a significant difference between 12 and 34, then in the southern hemisphere, the production of carbon monoxide from methane is not taking place as postulated, or there is some additional destruction mechanism for carbon monoxide, which is not present in the northern hemisphere. It must be kept in mind that all this is based on the assumption that the large decrease in carbon monoxide and the small decrease in methane is real, and that the difference between 16 and 34 is significant. However, with the supporting low values of Robinson & Robbins (1968) for carbon monoxide in the south Pacific (0.04 ppm) and those of Seiler for the south Atlantic (1973, symposium in Mainz 0.03–0.05 ppm), we feel that the atmospheric carbon monoxide values are real. Only additional data from the southern hemisphere and confirmation that the destruction of CH_4 by OH leads to CO formation in the troposphere will help to explain the situation.

Ethylene (Fig. 3) and propylene concentrations show a very large broad peak between 10° N and 15° S. This corresponds to the area of the south equatorial current sweeping biologically-rich upwelled waters away from the South American coast (Fleming & Laevastu, 1956). It has been shown by Wilson et al. (1971) in the laboratory that unsaturated hydrocarbons increase with biological activity, while there is very little production of saturated hydrocarbons. The ethane and propane concentrations remain relatively constant, and in no case undergo the large broad increase found between 10° N and 15° S. Both ethylene and propylene show an increase around 40° S, and this is probably due to the influence of the continental shelf around New Zealand. There is

no variation in the ethane, propane, iso- and *n*-butane in this area.

One finds large increases in all the hydrocarbons (C_1–C_4) in the different types of sea ice and snow. The brown ice observed in Antarctica was ice that had large amounts of algae entrained on the bottom. Taking samples of this ice (frozen algae), we found our highest concentrations of hydrocarbons. This is undoubtedly due to the presence of the algae. Surprisingly, in most cases, the sea water immediately under this brown ice does not have correspondingly high concentrations. This may be in part due to the dilution which occurs when these hydrocarbons are released to the water from the ice.

Blue ice and clean snow had much higher concentrations than the open sea water; this had not been expected. Possibly, the snow acts as a scavenging agent during its formation. The blue ice concentrations are probably due to the inclusion of scattered algal debris, which was not percolated out with the brine during aging. We have not taken profiles through the ice, and we therefore are unable to determine if there is a gradient present from the algae incrusted bottom to the relatively clean-looking top. We feel that these high concentrations are probably the result of biological activity.

In conclusion, atmospheric methane concentrations over the Pacific between 35° N and 77° S agree with values obtained in other oceanic areas. However, a significant decrease occurs in the vicinity of the ITC. Methane surface water concentrations average 4.2×10^{-5} ml/l with little variation until approximately 60° S where a concentration peak is observed. The ratio of CH_4/CO as an indicator of CO formation from CH_4 oxidation suggests that this proposed mechanism may not exist in the southern hemisphere. Ethylene and propylene exhibit latitudinal variations, which may be the result of biological activity. Ethane, propane, iso- and *n*-butane are extremely small (10^{-7} ml/l) in the open ocean, but along with ethylene and propylene, increase quite dramatically in areas where ice conditions prevail.

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C_1–C_4 ГИДРОКАРБОНАТЫ В СЕВЕРНОЙ И ЮЖНОЙ ЧАСТЯХ ТИХОГО ОКЕАНА

Измерялось содержание низкомолекулярных гидрокарбонатов в поверхностных водах в северной и южной частях Тихого океана. Концентрация метана составляла в среднем $4{,}2 \cdot 10^{-5}$ *мл/л*, в то время как для C_2–C_4 гидрокарбонатов было $(1-5) \cdot 10^{-6}$ *мл/л*. Большой и широкий пик для концентраций ненасыщенных гидрокарбонатов был найден между 10° с. ш. и 10° ю. ш. Большие концентрации C_1–C_4 гидрокарбонатов были найдены в различных типах антарктического морского льда. Концентрация атмосферного метана составляет в среднем $(1{,}44 \pm 0{,}04) \cdot 10^{-6}$ и уменьшается $(1{,}36 \pm 0{,}04) \cdot 10^{-6}$ в Междутропической зоне конвергенции.