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The CH_4 concentration over the ocean and its possible variation with latitude

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ABSTRACT

Measurements of the CH_4 concentration over the North Atlantic and the Pacific are presented. The Pacific data indicate a difference of about 0.1 ppmv between Northern and Southern Hemispheres. From this difference and a plausible distribution of CH_4 sources a tropospheric CH_4 lifetime between 3.5 and 11 years is estimated.

1. Introduction

In most parts, the open ocean appears slightly supersaturated in CH_4 with respect to the partial pressure in the atmosphere (Lamontagne et al., 1973). It represents a source of CH_4 whose strength, however, is very weak and hardly significant for the global CH_4 budget (Ehhalt, 1974). Thus the danger of local contamination, which is always present over land surface, is greatly reduced in surface air over the open ocean. A latitudinal variation in the CH_4 concentration of surface air, if at all present, should be most easily detected over the ocean.

A latitudinal gradient or a difference between Northern and Southern Hemispheres would be not unexpected. CH_4 is mostly produced by the continental biosphere (cf. Ehhalt, 1974), and because of its larger land mass the Northern Hemisphere should have a much larger CH_4 production. Tropospheric removal of CH_4, which proceeds mainly through reaction with the hydroxyl radical, ought to be nearly the same for both hemispheres. Since CH_4 has a relatively short atmospheric lifetime of about 5 years, a gradient should be observable.

As part of a global survey we have measured the CH_4 concentration over the Atlantic and Pacific on three ship cruises. In the following these measurements are compared to oceanic data from other authors and investigated for a possible variation of the CH_4 concentration with latitude.

2. Technique

For the CH_4 analysis samples of air were collected in evacuated stainless steel containers of about 1 l volume. Fabrication and testing of the sample containers have been described previously (Heidt and Ehhalt, 1972). The test showed that air samples could be stored for a 1-year period without alteration of their CH_4 content. After collection the samples were shipped to the laboratory where their CH_4 concentration was measured by a gaschromatograph equipped with an FID detector. To improve precision an analysis consisted of repeated comparisons of the sample to a working standard (laboratory air with a known CH_4 concentration) alternating standard and sample runs until six comparisons were completed. (For details see Heidt and Ehhalt, 1972.) The mean standard deviation of these six comparisons is given as precision of the measurement in Table 1 and Fig. 2 below. It averaged 0.05 ppmv. To calculate the accuracy of the data, the error of the calibration of the working standard has to be included; it amounts to 0.03 ppmv.

3. Results

The first measurements were made over the mid-Atlantic. The samples were taken during June 1971

Table 1. *Measurements of the CH_4 concentration over the mid-Atlantic. The samples were taken during June, 1971, aboard the German research vessel Meteor*

Sample No.	Collection date	Latitude/longitude	CH_4 mixing ratio (ppmv)
57	June 8, 1971	38° 30′ N, 10° W	1.35 ± 0.03
62	June 10, 1971	38° 53′ N, 13° 55′ W	1.31 ± 0.04
63	June 11, 1971	39° 45′ N, 18° 40′ W	1.43 ± 0.04
64	June 12, 1971	40° 23′ N, 21° 24′ W	1.35 ± 0.03
65	June 14, 1971	42° 13′ N, 31° 13′ W	1.33 ± 0.05
66	June 15, 1971	42° 50′ N, 36° 23′ W	1.33 ± 0.04
67	June 16, 1971	43° 3′ N, 36° 49′ W	1.31 ± 0.05
83	June 16, 1971	43° 23′ N, 34° 23′ W	1.38 ± 0.05
75	June 17, 1971	43° 37′ N, 42° 18′ W	1.30 ± 0.02
74	June 18, 1971	43° 40′ N, 43° W	1.31 ± 0.06
73	June 19, 1971	45° 26′ N, 38° 26′ W	1.35 ± 0.04
72	June 19, 1971	46° 12′ N, 35° 42′ W	1.26 ± 0.05
68	June 20, 1971	47° 27′ N, 30° 34′ W	1.28 ± 0.04
71	June 21, 1971	48° 20′ N, 25° 41′ W	1.28 ± 0.04
70	June 22, 1971	49° 12′ N, 19° 8′ W	1.43 ± 0.06
12			1.25 ± 0.10
78	June 23, 1971	49° 33′ N, 12° 39′ W	1.19 ± 0.08
5			1.29 ± 0.06
77	June 24, 1971	49° 38′ N, 6° 28′ W	1.35 ± 0.04
76	June 24, 1971	49° 57′ N, 3° 22′ W	1.31 ± 0.06
			—
81	June 25, 1971	51° 39′ N, 2° 29′ W	1.34 ± 0.04
80	June 26, 1971	53° 44′ N, 6° 20′ E	1.44 ± 0.06
		Average $\bar{M}$	1.33 ± 0.012

aboard the German research vessel *Meteor*. The cruise track is indicated in Fig. 1. The measured CH_4 concentrations are listed in Table 1 as volume mixing ratio (ppmv) along with the precision of a measurement which averages 0.05 ppmv. From the frequency distribution of the data in Table 1, we find a standard deviation of 0.06 ppmv, hardly larger than the precision, which indicates that the natural variability around the average of 1.33 ppmv must have been small. Due to the large number of measurements the standard error of the mean CH_4 concentration is 0.012 ppmv.

Samples obtained on a Caribbean cruise during July 1973 were mainly intended for laboratory intercomparison. The sampling location is also shown in Fig. 1. The samples were collected by J. Swinnerton from the Naval Research Laboratory, Washington, D.C., who also took an aliquot from each sample and measured it aboard the ship. Our measurements are reported in Table 2. The average of 1.53 ppmv from the Caribbean is significantly higher than the data for the mid-Atlantic. The reason is not quite clear. It is conceivable that the samples from the Caribbean stations experienced contamination from the West Indies or Bahamas carried by the trade winds; another possibility is local seepage of natural gas.

More important for out present consideration is that the agreement with the measurements of Swinnerton (1974) was quite good, better than 1% for the average over all samples, which indicates that the absolute calibration of both laboratories is in good agreement. It is therefore possible to compare our Atlantic data directly with data published by the NRL group.

Finally, samples for our laboratory were collec-

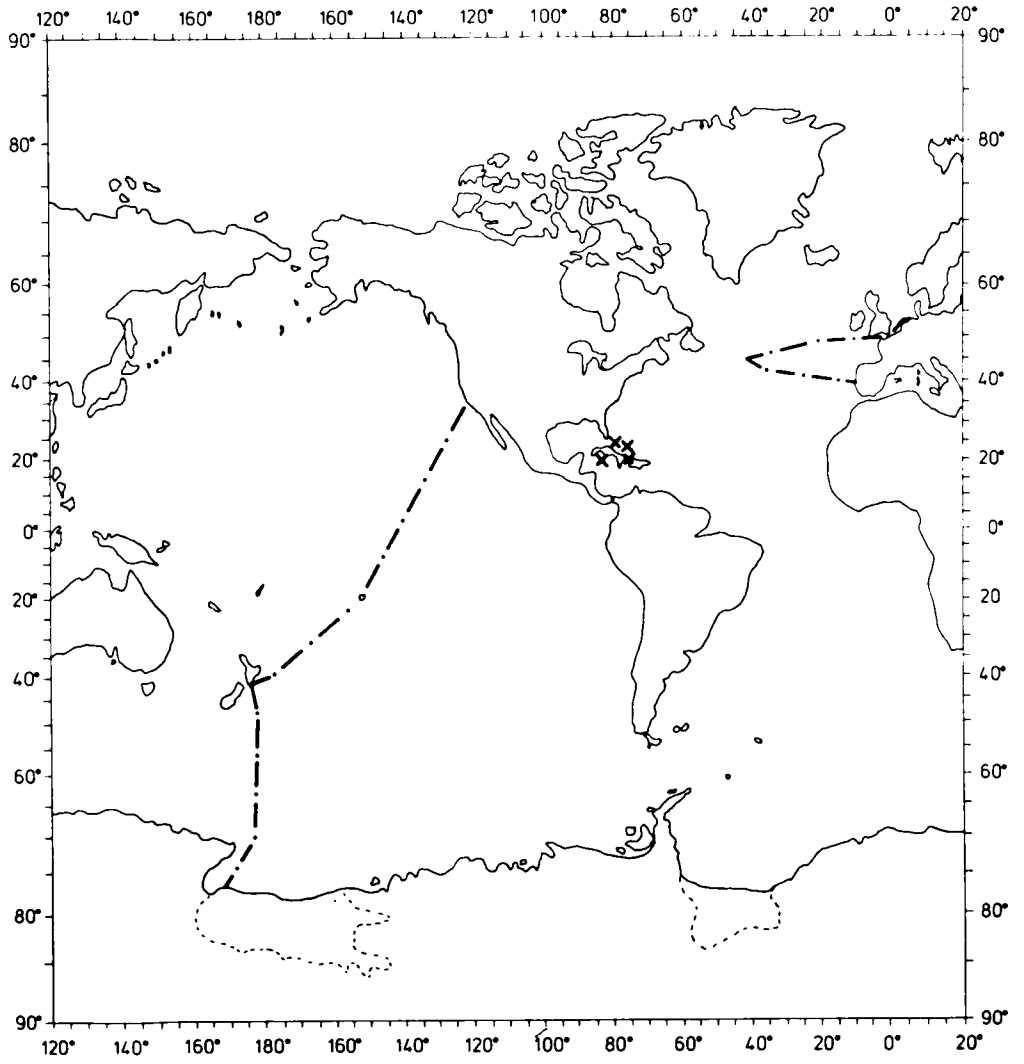

Fig. 1. Cruise tracks of the Pacific and mid-Atlantic cruises and sampling locations of the Caribbean cruise.

ted by J. Swinnerton on a cruise from Long Beach, California, to the McMurdo Station, Antarctica, on board the U.S.C.G.C. *Glacier*, during November and December 1972. The cruise track is also plotted in Fig. 1. The results are shown in Fig. 2. Plotted against latitude, the CH_4 concentration shows a drop in the Northern Hemisphere from 1.45 ppmv at 30° N to 1.33 ppmv at 5° N, followed by a slow decrease to a constant value of 1.30 ppmv in the Southern Hemisphere.

4. Discussion

Besides the present measurements, there are a number of data over the North Atlantic mainly published by the NRL group. The available data covering the North Atlantic between 80° N and 10° N are summarized in Table 3. They were mainly collected during late spring or early summer, and are therefore also comparable with regard to the season. Except for the lower value

Table 2. *Measurements of the CH_4 concentration over the Caribbean. Samples were taken during June/July, 1973, by J. W. Swinnerton*

Can. No.	Sampling date	Latitude/longitude	CH_4 mixing ratio (ppmv)
47	June 28, 1973, 170Z	20° 10′ N, 84° 37′ W	1.60
50			1.65
66			1.73
67			1.49
77			1.51
79			1.50
		Average $\bar{M}$ =	1.58 ± 0.04
62	July 2, 1973, 1430Z	19° 35′ N, 75° 32′ W	1.55
65			1.55
73			1.51
74			1.50
76			1.61
81			1.52
		Average $\bar{M}$ =	1.54 ± 0.016
43	July 6, 1973, 1515Z	24° 33′ N, 76° 14′ W	1.51
63			1.50
57			1.49
70			1.37
75			1.39
80			1.44
		Average $\bar{M}$ =	1.45 ± 0.024
44	July 8, 1973, 1315Z	25° 01′ N, 80° 02′ W	1.48
46			1.56
49			1.59
78			1.52
		Average $\bar{M}$ =	1.54 ± 0.02

between 33° N and 22° N which Swinnerton (1974) considers less reliable than the later data (and for which no standard deviation has been published), the average CH_4 concentrations at the different latitudes agree quite well. The data in Table 3 do now show any significant gradient over the North Atlantic. On the other hand the latitudinal resolution is rather poor, and a gradient, especially if concentrated in the tropical latitudes, could easily go undetected with the present data. Moreover there are no measurements over the Southern Atlantic so that an interhemispheric gradient cannot be determined from the Atlantic data.

In contrast to the data from the North Atlantic, the CH_4 measurements over the Pacific have a reasonably good resolution of 5° latitude. Indeed the CH_4 concentration shows a weak but distinct decrease already beginning in the Northern Hemisphere from 1.45 ppmv at 30° N to 1.30 ppmv at 20° S. This agrees well with the data of Lamontagne et al. (1974), who on the same cruise, with even better spatial resolution, found a decrease starting in the Northern Hemisphere and a lower average CH_4 concentration in the Southern Hemisphere (cf. their Fig. 2). Their data averages 1.44 ± 0.04 ppmv between 35° and 10° N, the location of the intertropical convergence zone (ITC), and 1.36 ± 0.04 between 10° N and 77° S. The ITC does not express itself in our data; they are therefore better averaged with respect to the equator and yield 1.40 ± 0.02 ppmv between 30° N and 0° and

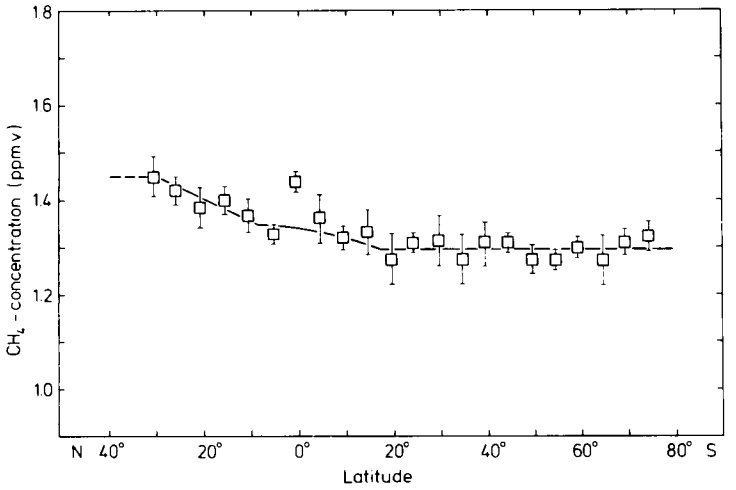

Fig. 2. CH_4 concentrations from the Pacific cruise, November, December 1972, plotted against latitude. Error bars give the precision of the CH_4 measurements as defined in text.

Table 3. *CH_4 concentrations over the north Atlantic. The error limits are those quoted by the various authors. The numbers in parentheses give the number of samples*

Latitude	Sampling date	Average mixing ratio (ppmv)	Author
80°–55° N	1971, August	1.37 ± 0.05 (13)	Larson et al., 1972
55°–35° N	1971, June	1.33 ± 0.03* (22)	this paper
33°–22° N	1968, June	1.24	Swinnerton et al., 1969
35°–10° N	1969, 1970	1.36 ± 0.06	Lamontagne et al., 1974

* Error includes that of standard calibration.

1.30 ± 0.01 between 5° S and 75° S. (If averaged over the same latitude intervals as the NRL data our averages would have to be increased by 0.01 and 0.02 ppmv, respectively.) Thus both data sets from the same Pacific cruise indicate a significantly lower CH_4 concentration by about 0.1 ppmv in the Southern Pacific.

Does this difference constitute a true interhemispheric asymmetry? For the Southern Hemisphere it can be plausibly argued that the data have been collected in the middle of the Pacific far away from any local CH_4 source, that the CH_4 concentration remains practically constant over a large latitude range, and that they should therefore represent a reasonable approximation of the average CH_4 concentration in the Southern Hemisphere. The same cannot be said from the data in the Northern Pacific. As the ship moved south it also moved away from the coast and it is conceivable that the observed gradient in the Northern Hemisphere is at least partly due to the increasing distance from coastal CH_4 sources. The possibility of such sources was revealed by earlier measurements of vertical CH_4 profiles in the atmosphere over the Pacific 200 km offshore Santa Barbara, which showed increased concentration in the surface air (Ehhalt and Heidt, 1973) possibly caused by the seepage of natural gas through the sea floor of the continental shelf. Although it is conceivable that the samples closest to the coast have been

influenced that way, certainly the sampling stations south of 20° N are sufficiently removed from the coast to exclude such contamination. In addition, Lamontagne et al. (1974) also measured the amount of CH_4 dissolved in ocean surface waters and always found low maritime CH_4 concentrations which seem to exclude a strong oceanic CH_4 source. On the other hand there is by now a rather large body of data indicating that the average CH_4 concentration in the Northern Hemisphere is at least 1.4 ppmv, the only notable exception being the Atlantic data quoted above. In a previous discussion an annual average of 1.41 ppmv was obtained for 1966 and 1967 from aircraft profiles over the North American continent (Ehhalt and Heidt, 1973). More recent flights from 1974 to 1976 gave CH_4 concentrations in excess of 1.5 ppmv (Heidt and Pollock, 1977). Various measurements in other years by different authors yield concentrations between 1.4 and 1.5 ppmv in clear surface air over North America (cf. Stephens and Burleson, 1969), and earlier measurements in 1970 over the Pacific between 20° and 10° N gave a mean concentration of 1.43 ± 0.03 (Lamontagne et al., 1974). For the present discussion we therefore adopt an average value of 1.40 ppmv for the Northern Hemisphere with an estimated error of ±0.05 ppmv. Accordingly the Southern Hemisphere CH_4 concentrations measured on the Pacific cruise appear significantly lower than the Northern Hemisphere average.

As mentioned above, based on the distribution of the CH_4 sources, such an interhemispheric difference is not unexpected. It can be readily estimated. For this purpose we divide the troposphere into two hemispheres and note that the air mass exchange between the hemispheres can be described by a characteristic time, τ_e, which is about 1 year (Nydal, 1968; Newell et al., 1969). We further assume steady state and the same loss rate of CH_4 in both hemispheres. With these assumptions we obtain two balance equations between the CH_4 production, the CH_4 flux between the hemispheres, and the CH_4 losses due to oxidation within the troposphere and transport to the stratosphere:

$$P_n - N\frac{M_n - M_s}{\tau_e} - N\frac{M_n}{\tau} = 0$$

$$P_s - N\frac{M_n - M_s}{\tau_e} - N\frac{M_s}{\tau} = 0 \qquad (1)$$

$$P_n = \alpha P_s \quad \alpha > 1$$

A third equation is obtained by fixing the ratio between the production in the Northern and Southern Hemispheres to a value α with $\alpha > 1$. P is the production; M is the mixing ratio. The subscripts refer to the hemispheres. N is the tropospheric air mass in a hemisphere. τ is the characteristic time for chemical reaction and loss to the stratosphere. Since we assume steady state, τ is also the characteristic time of global CH_4 production.

Eliminating P_n and P_s from eqs. (1) we obtain:

$$\tau = \tau_e \frac{\alpha M_s - M_n}{(\alpha + 1)(M_n - M_s)} \qquad (2)$$

With the help of eq. (2) we can calculate the expected difference. Inserting $\tau_e = 1$ year, $\tau = 5$ years; $M_n = 1.4$ ppmv and $\alpha = 2.4$, the ratio of the continental areas between 0° and 60° N, and 0° and 60° S respectively, we obtain $M_s = 1.3$ ppmv consistent with the measured value.

Conversely we can use eq. (2) to derive a new independent estimate of tropospheric lifetime of CH_4, τ, from the measured interhemispheric difference in CH_4 concentration. To do this we have to allow for possible errors in the parameters, mainly in α, but also in the interhemispheric difference of the CH_4 concentration. Since at least 80% of the atmospheric CH_4 is of biogenic origin and mostly from continents (Ehhalt, 1974), we assume as a first approximation that α equals the ratio of the continental areas in the Northern and Southern hemispheres. Counting all land α would be 2.06; discounting the land poleward of 60° N and 60° S respectively α becomes 2.4. Discounting more of the poleward land masses would lead to an α between 2 and 2.4. We might therefore assume that α should lie between 2 and 2.5. For the difference in the hemispheric CH_4 concentrations we have to allow a larger range. It is therefore introduced as an independent variable in Fig. 3 where eq. 2 is plotted for various α.

It is clear from eq. (2) and Fig. 3 that a small interhemispheric difference in the CH_4 concentration requires a long lifetime. Judging from the present CH_4 data the interhemispheric difference should fall between 0.05 and 0.15 ppmv. Correspondingly, one would deduce a tropospheric lifetime for CH_4 between 2.5 and 11 years, with a most likely value of about 5 years.

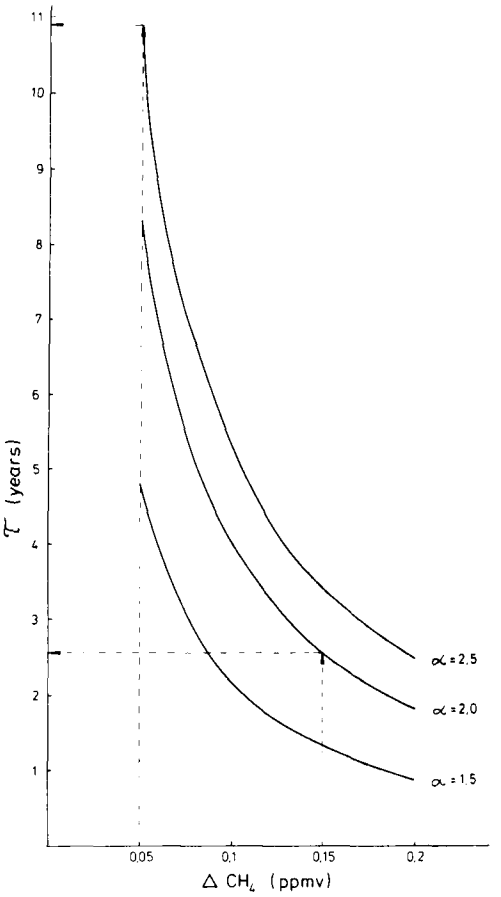

Fig. 3. Calculated tropospheric lifetime of CH_4 versus expected interhemispheric difference in CH_4 concentration, ΔCH_4.

5. Conclusions

It is interesting to note that the present consideration allows an estimate of the global CH_4 production without knowledge of the source strengths of the various ecosystems. The required information is reduced to knowing the interhemispheric difference in CH_4 concentration and the production ratio between Northern and Southern Hemispheres, α. The difference in concentration can be measured directly, and α can be estimated more easily and probably with higher accuracy than the global CH_4 production can be extrapolated from the few measured individual sources. From eq. (1) we calculate the global CH_4 production to be equal to the amount of CH_4 in the troposphere divided by τ. The CH_4 concentration averaged over both hemispheres is 1.35 ppmv and the mean height of the tropopause 13 km. The corresponding amount of tropospheric CH_4 is 3.3×10^{15} *g*. The tropospheric lifetimes given above correspond to production rates between 300×10^{12} and 1300×10^{12} *g* CH_4/yr with a most probable value of 660×10^{12} *g* CH_4/yr. Previous estimates of the global CH_4 production based on an extrapolation of the measured source strengths of various ecosystems gave values between 550×10^{12} to 1040×10^{12} *g* CH_4/yr (Ehhalt, 1974). The agreement is quite good. It can be expected that the range of possible τ (and that of the corresponding CH_4 production) can be reduced considerably as more CH_4 data, especially from the Southern Hemisphere, become available.

Finally, the chemical lifetime of CH_4 in the troposphere can be estimated by subtracting the loss to the stratosphere. Assuming an annual loss of 100×10^{12} *g* CH_4/yr to the stratosphere (Ehhalt, 1974), this chemical lifetime should lie between 2.7 and 15 years. Presently the only conceivable chemical sink of CH_4 in the troposphere is the reaction with the OH radical (Levy, 1971). The reaction rate is $5.5 \times 10^{-12} \exp(-1881/T)$ cm^3/molecule sec (Greiner, 1970). Weighing with the vertical temperature and density distribution, the average tropospheric reaction rate is about 5×10^{-15} cm^3/molecule sec. From this and the tropospheric lifetime of CH_4, we estimate a mean tropospheric OH concentration between 4×10^5 and 3×10^6 cm^{-3} with a most probable value of 1.5×10^6 cm^{-3}.

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КОНЦЕНТРАЦИЯ CH_4 НАД ОКЕАНОМ И ЕЕ ВОЗМОЖНЫЕ ВАРИАЦИИ С ШИРОТОЙ

Представлены результаты измерений концентрации CH_4 в атмосфере над Северной Атлантикой и Тихим океаном. Данные для Тихого океана указывают на разницу около 0.1 ppmv (10^{-7}) между концентрациями в Северном и Южном полушариях. Исходя из этой разницы и возможного распределения источников CH_4 время жизни метана в тропосфере оценивается величиной между 3.5 и П годами.