The atmospheric cycle of methane

By D. H. EHHALT, *The National Center for Atmospheric Research,*[1] *Boulder, Colorado*

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ABSTRACT

The atmospheric distribution of CH_4 is rather uniform zonally and vertically but exhibits a slight gradient with latitude in the troposphere; in the stratosphere it shows a definite decrease with altitude. The average volume mixing ratio in the troposphere is 1.4 ppm which corresponds to a total amount of 4×10^{15} g of CH_4 present in the atmosphere. Most is of recent biologic origin. C^{14} analyses show that no more than 20 % is released by fossil sources. The various ecosystems producing CH_4 are discussed and the total annual production is estimated to lie between 5.5×10^{14} g/yr and 11×10^{14} g/yr. The corresponding turnover times for atmospheric CH_4 range from 4 to 7 yr. The destruction of CH_4 takes place mainly in the troposphere, most probably through the reaction $CH_4 + OH \rightarrow CH_3 + H_2O$. About 10 % of the CH_4 is destroyed in the stratosphere. The CH_4 cycle is strongly coupled to the H_2 and CO cycles and contributes also on the order of 1 % to the atmospheric carbon cycle.

Introduction

The presence of methane in the earth's atmosphere was discovered by Migeotte (1948), who identified it by its infrared absorption band in the solar spectrum. The early optical measurements indicated a uniform distribution throughout the atmosphere with an average volume mixing ratio of 2 ppm. Subsequent measurements lowered this value to 1.4 ppm (Fink et al., 1965). Our own measurements using gas chromatography give an average of 1.41 ppm for the troposphere and show a decrease in the stratosphere. (See also Bainbridge & Heidt, 1966.) These measurements also show that the CH_4 concentration may fluctuate significantly in individual tropospheric profiles (Ehhalt & Heidt, 1972). Interest in the CH_4 cycle has been recently stimulated by two developments. First, it was realized that CH_4 is important for the budget of hydrogen compounds in the stratosphere, contributing nearly one-half of the hydrogen compounds in the middle stratosphere and upon oxidation adding significant amounts of water vapor to the upper stratosphere (Ehhalt & Heidt, 1973). Second, it has recently been hypothesized that the oxidation of CH_4 yields CO as an intermediate step (McConnell et al., 1971), and may well be a major source of CO. Incidentally, the CH_4 cycle may also be coupled closely to the atmospheric H_2 cycle.

For these latter considerations the atmospheric distribution of CH_4 is the most important parameter, and since the CH_4 distribution is probably the best established part of the CH_4 cycle, we will start our discussion with this aspect.

Atmospheric distribution of CH_4

Surface measurements

There are now quite a number of measurements of CH_4 background concentration at the earth's surface. The older data, which are not always accurate, are reviewed by Junge (1963). More recent measurements have been made by Stephens & Burkson (1969) who report CH_4 concentrations close to 1.4 ppm for clear mountain air in southern California (35° N). Our own unpublished measurements in the Rocky Mountains close to Boulder (40° N) averaged 1.35 ppm. Cavanagh et al. (1969) report an average CH_4 concentration of 1.59 ppm at Point Barrow, Alaska ($\sim 60°$ N). This seems to indicate the possibility of higher CH_4 concentrations at northern latitudes, but the authors caution that

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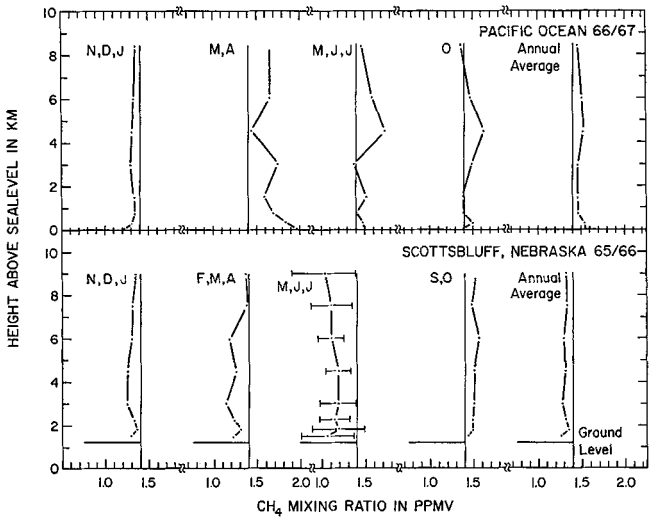

Fig. 1. Seasonally averaged profiles of the CH_4 mixing ratio in ppm by volume over the eastern Pacific and Scottsbluff, Nebraska. The letters indicate the months on which each profile has been averaged. The vertical lines represent the tropospheric average CH_4 mixing ratio: 1.41 ppm. The annual averages are given at the right.

the higher values could be local and due to seepage from natural gas wells and to release of CH_4 from tundra.

It is instructive to compare these numbers to measurements over the open ocean where the danger of local contamination is greatly reduced, since the open ocean is a weak source of CH_4. Swinnerton et al. (1969) found an average concentration of 1.24 ppm in the atmosphere over the southern Atlantic (22° N–35° N), our values from a 1971 cruise in the mid-Atlantic (40° N) average 1.33 ppm, and most recently Larson et al. (1972) measured an average of 1.4 ppm over the Norwegian and Greenland Seas (60° N–80° N). Again there seems to be a slight gradient of CH_4 with latitude. A decrease with lower latitude in the northern hemisphere is also exhibited by the North–South profile of CH_4 presented by Lamontagne et al. (1973). This profile also showed a significantly (5% to 10%) lower CH_4 concentration in the southern hemisphere.

Tropospheric profiles

Since there is always the possibility that samples from the earth's surface are influenced by local sources or sinks, a program to measure CH_4 in the free troposphere was established at NCAR in 1965. One set of vertical CH_4 profiles was taken each month over Scottsbluff, Nebraska, during the period November 1965 to January 1967. Another set was taken over the Pacific 200 km offshore from Santa Barbara, California, from July 1966 to July 1967. Although some of the individual profiles show rather large scatter, the usual deviation from the mean tropospheric average, 1.41 ppm, is less than 20%. The data have been reported previously (Ehhalt & Heidt, 1972); the seasonally averaged profiles are shown again in Fig. 1. Most profiles represent an average of three or four profiles. Except for the spring profiles over the Pacific where we also observed large atmospheric CH_4 concentrations, the profiles are rather uniform and indicate that on a seasonal average the troposphere was rather well mixed vertically. The seasonal spring profiles over the Pacific are dominated by a few individual profiles with winds from the north and northwest and quite high CH_4 mixing ratios at all altitudes. Contamination from Los Angeles can be excluded based on air mass trajectories; probably a large-scale natural source of CH_4 is required to explain the high CH_4 concentration in the profiles (Ehhalt & Heidt, 1972). At present we do not know this source. There could be a local contribution as indicated by the high surface values in the profiles taken during March

and April. Generally, however, the ocean surface seems not to represent a strong source of CH_4.

The Scottsbluff profiles are slightly lower than the Pacific profiles and show a decrease in the very lowest layers, indicating a probable low level sink.

Otherwise, the average tropospheric CH_4 profiles show no significant gradients. The annually averaged profiles which are plotted at the right of Fig. 2 show a slightly higher CH_4 concentration for the Pacific. This is mainly due to the higher concentrations over the Pacific during spring and is probably not significant. We also measured a number of profiles over Death Valley, California, over East Texas; and over the Everglades in Florida. All fall well within the range of the profiles given here and show that although individual profiles might fluctuate significantly, the average free troposphere at mid latitudes is rather well mixed with respect to CH_4 both vertically and zonally. Averaging over all our measurements yields 1.41 ± 0.03 ppm for the troposphere during 1966 and 1967 in northern mid latitudes.

These data can also be investigated for a seasonal variation. Such a variation might be expected, since most of the atmospheric CH_4 is produced by bacteria whose activity is strongly temperature-dependent. If we consider only the Scottsbluff profiles, a systematic trend is apparent in the seasonal CH_4 concentration, with a maximum in September and October, followed by a decrease to minimum values in May, June and July. However, if we include the standard deviations which are indicated for the summer profile over Scottsbluff (and are the same for other profiles) it becomes obvious that the differences between the seasonal profiles cannot be considered significant at this stage. Solid confirmation of a seasonal variation would require several years of observation. The fact that the highest values were observed over the Pacific during spring, when the concentration over Scottsbluff was apparently at a minimum, indicates that the variation over Scottsbluff is not global. It should be noted in this context that the fall and winter periods over Scottsbluff and the Pacific do overlap, and that these profiles do show good agreement. The spring and summer profiles which disagree were determined from 1966 and 1967 samples, respectively, and these differences could signify

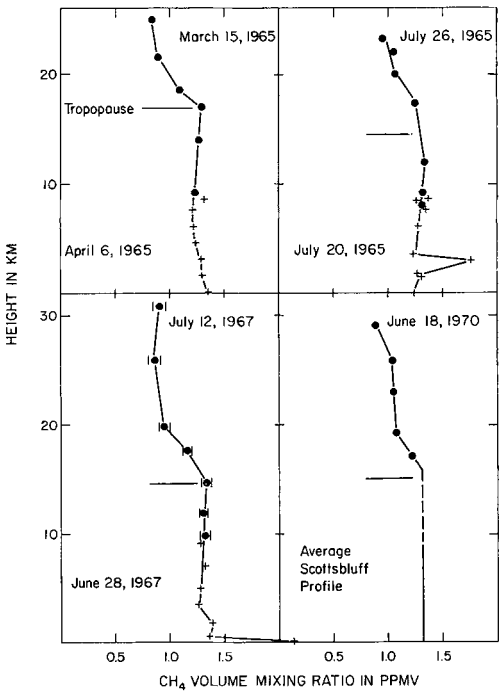

Fig. 2. Stratospheric profiles of the CH_4 mixing ratio in ppm by volume over Palestine, Texas. The circles represent samples collected by balloon on the date indicated in the upper right corner. The crosses represent samples from aircraft flights on the date indicated in the lower left corner. The balloon flights during 1965 are from Bainbridge & Heidt (1966). The standard error is indicated for the 1967 profile, and is about ± 5 % for the stratospheric samples.

yearly as well as local changes in the CH_4 concentration.

Nevertheless, if there is a seasonal variation it is not large. This lack of a conspicuous seasonal variation can have several causes. One is that there may be a number of sources whose seasonal variations are out of phase, so that only small and brief oscillations may occur globally. Another is that the seasonal variations of CH_4 production and destruction are similar. It has been recently proposed that the concentration of OH radical in the troposphere might be in the order of $10^6/cm^3$ (McConnell et al., 1971; Weinstock & Niki, 1972). If this is true, the reaction $CH_4 + OH \rightarrow CH_3 + H_2O$ in the troposphere will be the main destruction mechanism for CH_4. Since water vapor, ozone and solar radiation flux, which determine the con-

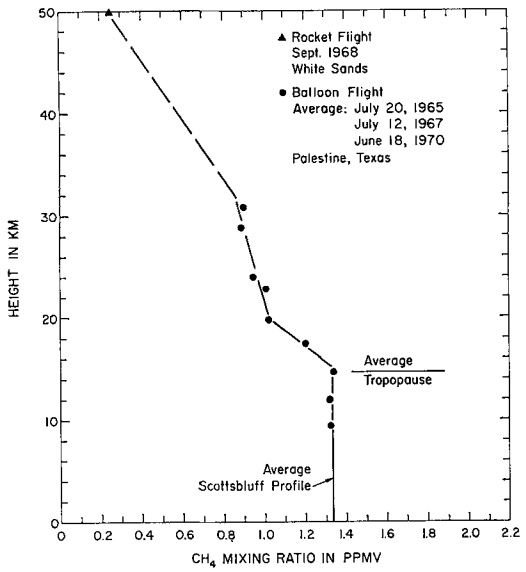

Fig. 3. Average stratospheric profile of the CH_4 mixing ratio in ppm by volume over Palestine, Texas during summer. The balloon flight on July 26, 1965 is from Bainbridge & Heidt (1966). The balloon data are supplemented by data from a rocket flight which collected an integrated sample at altitudes between 44 and 62 km. The weighted mean altitude of this sample is 50 km.

centration of OH radical, have maximum values in spring or summer, the destruction rate of CH_4 is at a maximum during the warmer seasons, as is the production rate. The two seasonal variations would tend to cancel each other and leave little imprint on the atmospheric CH_4 concentration.

Altogether we can conclude from both surface and aircraft measurements that the average CH_4 concentration varies little vertically, zonally, or seasonally. There is, however, a slight latitudinal gradient, and in particular, a significantly lower CH_4 concentration in the southern hemisphere as evident in data from Lamontagne et al. (1973).

Stratospheric profiles

We have also measured a number of stratospheric profiles from balloon and rocket flights. These profiles are from mid latitudes only and primarily during summer so that little information on horizontal and seasonal variation is revealed. The measurements do, however, show a strong decrease of the CH_4 mixing ratio with altitude, a fact already noted by Bainbridge & Heidt (1966). Our individual CH_4 profiles are shown in Fig. 2; included are the data from balloon flights made by Bainbridge & Heidt, with a slight correction introduced to compensate for their value for the standard which was too high. The profiles seem to indicate a relatively steep gradient between the tropopause and about 20 km, and a weaker gradient at higher altitudes. This is also illustrated in Fig. 3 which shows the average of the June–July flights. Here the balloon data are supplemented by data from a rocket flight in which an integrated sample was collected between 44 and 62 km altitude over White Sands, N. M. (32° N). The weighted mean altitude of this sample is 50 km, its CH_4 concentration 0.25 ± 0.02 ppm (Ehhalt et al., 1972). This concentration agrees well with the gradient observed at balloon altitudes. It should be noted that the mean standard deviations of the average balloon data lie between 5 and 10 %. It is, therefore, still possible to fit a more or less linear decrease to the average CH_4 mixing ratio in the stratosphere. However, all individual profiles show a steeper gradient in the lower stratosphere and we think it is probably real. The downward motions of the stratospheric branch of the Hadley circulation extend to 32° N, and it is possible that the gradient in the lower stratosphere is steepened by a mean downward motion. It is notable that in March, when the Hadley circulation is more pronounced, the CH_4 gradient was indeed steeper. In any case, it is obvious from Figs. 2 and 3 that the atmosphere above the tropopause acts as a sink for CH_4.

Last year two more stratospheric CH_4 profiles were published by Ackerman & Muller (1972) and Cumming & Lowe (1972), both pairs of researchers used optical methods. Although taken around 45° N, the profiles do confirm the decrease of the CH_4 mixing ratio beginning in the lower stratosphere.

Sources of atmospheric CH_4

It is generally agreed that CH_4 is too complicated a molecule to be synthesized within the atmosphere and that it is released mainly at the earth's surface. Even before detailed estimates of the CH_4 sources were available it was known that most of the atmospheric CH_4

must be produced by anaerobic decomposition of "recent" (i.e., recently alive) organic matter. This information was provided by the measurement of the radiocarbon content in the atmospheric CH_4. Any CH_4 derived from recent organic material has a C^{14} content very close to that of recent wood. In contrast, CH_4 derived from fossil fuels or volcanic activity contains essentially no C^{14}. The fuel deposits are so old that the originally present C^{14} has decayed. Several C^{14} analyses of atmospheric CH_4 made mostly by W. F. Libby, are available. They are summarized in Table 1. Most of these samples were collected before the atmosphere was contaminated with C^{14} from nuclear explosions and should represent the natural C^{14} level in CH_4. The average C^{14} content is 80% of that of recent wood, which indicates that 80% of the CH_4 is of recent biologic origin and 20% is "dead" CH_4. These 20% represent an upper limit. The measured CH_4 samples have been provided by air liquefaction plants, which are usually situated in heavily industrialized areas. Hence, these samples might have been subjected to local contamination by industrial (dead) CH_4.

The fact that most of the atmospheric CH_4 must be produced biologically by the decay of recent organic matter simplifies the search for its sources considerably. Biogenic CH_4 is produced by a group of anaerobic bacteria, living in anoxic environments rich in organic matter. Such environments are found in waterlogged soils, swamps, marshes, freshwater and marine sediments, as well as in the intestines of animals. In the following the strength of these sources and their importance for the global CH_4 production are estimated.

Table 1. *C^{14} content of atmospheric CH_4 samples*

Sample origin	Collection date	C^{14} content (% of standard wood)
Wembley, England	December 1949	75 ± 2[a]
Wembley, England	April 1950	69 ± 2[a]
Tonawanda, New York	October 1950	102 ± 3[a]
Wembley, England	1959	90[b]
Gary, Indiana	January 1960	75.2[c]
Average		83

[a] Libby, W. F., private communication.
[b] Bishop et al. (1962); sample integrated over several months had 12.7 dpm/g carbon.
[c] Bainbridge et al. (1961).

Enteric fermentation of animals

The oldest estimate of CH_4 production is that of the enteric fermentation of animals. Hutchinson (1948) estimated the amount of CH_4 produced daily by various large herbivores (Table 2). From these figures and from estimated animal populations at that time he derived a global CH_4 production of 45×10^{12} g/yr. Mainly because of the doubling of the world cattle population to about 1.2×10^9 head in 1970 (Table 2), the present CH_4 production by enteric fermentation has increased to 101×10^{12} g/yr (Table 2). This value still represents a lower limit, since CH_4 production by a number of other domestic animals, wild herbivores, and possibly by herbivorous insects (some of which seem to need bacteria for cellulose digestion), are not included in Table 2. An upper limit can be derived from the following consideration. About 1.1×10^{17} g/yr of dry plant matter are produced on land, about 10% of which are eaten by herbivores (Woodwell, 1970). If all these animals produce CH_4 with the same food-to-CH_4 conversion ratio as cattle, which is about 0.02 g CH_4/g dry plant matter, and is the highest reported, we obtain an upper limit of 220×10^{12} g CH_4/yr for CH_4 production by enteric fermentation.

Table 2. *Production of CH_4 by enteric fermentation of animals*

	Rate of CH_4 production (g/day)	No. of animals in 1970 $\times 10^6$	Annual production (10^{12} g/yr)
Cattle	200[a]	1 198[b]	88.
Sheep	15.1[a]	1 026[b]	5.8
Horse	106[a]	125[c]	4.8
Goat	14.7[a]	384[d]	2.1
Total			101×10^{12} g/yr

[a] Hutchinson (1948).
[b] U.S. Dept. of Agric. (1971).
[c] United Nations FAO, 20, No. 9 (1971); includes mules and asses.
[d] United Nations FAO (1970).

Table 3. *Production rate of methane in various waterlogged paddy soils incubated at 30°C (from Koyama, 1964)*

Paddy soil	Production rate of CH_4 at 30°C (ml/day/100 g of dry soil)
Yamoto muck soil	3.91
Nishihata soil	3.75
Yoshida muck soil	3.59
Yashirota soil	2.97
Yoshida good soil	1.72
Anjo soil	1.57
Yoshida sandy soil	1.36
Nagano soil	1.10
Sanage soil	1.04
Average	2.33

Paddy fields

A rather careful estimate exists also for CH_4 production by paddy soils. Koyama (1963, 1964) measured the CH_4 production rate and its dependence on temperature for a number of Japanese paddy soils. His results are summarized in Tables 3 and 4. It is obvious from Table 3 that there is quite a spread in the productivity of different paddy soils, about a factor of 4 between the two extreme cases. Table 4 shows that the CH_4 productivity depends quite sensitively on temperature: production increases two fold per 5°C in the temperature range between 5 and 30°C.

From these data Koyama extrapolated the average CH_4 production of Japanese rice paddies to 2.3×10^{12} g/yr. This corresponds to an average productivity of 80 g CH_4/m^2 yr. In deriving this number he took into account the seasonal variation of the temperature, the depth of the paddy soils (15 cm in Japan), and the fact that the paddy soils are waterlogged for about 4 months only. Assuming that the paddy soils in other parts of the world (total area in 1964, 0.92×10^6 km^2) are similar to those in Japan, he deduced a global CH_4 production by paddy soils of 1.9×10^{14} g/yr. This corresponds to an average production rate of 206 g CH_4/m^2 yr which is over twice the Japanese average. Koyama does not attempt to explain the difference, but it is probably due to the higher annual temperatures in other rice-growing countries and possibly also to the fact that in tropical climates 2–3 crops are grown per year which means that the rice paddies are waterlogged throughout most of the year.

Table 4. *Average production rate of methane at various temperatures for the average paddy soils in Japan (from Koyama, 1964)*

Incubation temperature (°C)	Production rate of CH_4 (ml/day/100 g of dry soil)
5	0.04
10	0.10
15	0.24
20	0.38
25	0.73
30	1.86
35	2.2
40	2.8

By 1970 the global area of rice paddies had increased to 1.35×10^6 km^2 (*Monthly Bulletin of Agricultural Economics and Statistics 20*, No. 6, 1971). Therefore the present annual CH_4 production of paddy fields is 280×10^{12} g CH_4/yr. This figure might represent a slight overestimate for the CH_4 actually released to the atmosphere since Koyama determined the anaerobic CH_4 production of soils rather than the release of CH_4 to the atmosphere. In nature CH_4-oxidizing anaerobic bacteria will consume some of the CH_4 before it can reach the atmosphere. But Koyama showed also that the redox potential even at the depth of 0.5 cm from the paddy soil surface is already negative. Thus oxidation of CH_4 will take place mainly in the overlying water which, however, is very shallow (5 cm) and will remove only a small amount of CH_4 from the quickly rising bubbles.

Fresh water lakes, swamps and marshes

There are plentiful data showing that lake sediments, swamps and marshes produce CH_4 copiously, but only two quantitative studies of the CH_4 production rate. Both are in situ experiments measuring the amount of gas bubbling upward from the lake bottom. Conger (1943) measured the amount of CH_4 reaching the surface of Great Fresh Creek, a lake of about 2 m depth in Maryland (USA). His measurements for August (water temperature 24–27.5°C) averaged 0.32 g CH_4/m^2 day, which if maintained

throughout the year would correspond to a release of about 120 g CH_4/m^2 yr to the atmosphere. The other study was made by Howard et al. (1971) in Lake Erie, again during summer, when the water temperature was 25°C. These authors measured the CH_4 production of the lake mud by placing inverted funnels 15 cm above the lake bottom. They found an average CH_4 production rate of 1.75 g CH_4/m^2 day, which if maintained throughout the year would correspond to about 640 g CH_4/m^2 yr. However, most of that CH_4 does not reach the atmosphere. Earlier measurements of Rossolimo (1935) quoted by Hutchinson (1957), showed that gas bubbles formed at the bottom of Lake Beloye, Russia, about 10 m deep, had a CH_4 content of 74.1 to 83.5%. After their ascent to the surface the CH_4 content had decreased to 20 to 24% due to bacterial oxidation in the water. Assuming a similar oxidation in Lake Erie, the amount of CH_4 actually released to the atmosphere would be reduced to about 200 g CH_4/m^2 yr if summer time conditions prevailed throughout the year. Diffusion of dissolved CH_4 probably contributes very little to the upward transport because CH_4 is readily oxidized in lake water. Oxidation of dissolved CH_4 has also been measured by Howard et al. (1971). Their in situ measurements gave a CH_4 oxidation rate of 56×10^{-8} g CH_4/day/cc water between the lake bottom at 6 m and 4 m depth. The oxidation rate then decreased and was virtually zero in the upper 2 m.

Since the average global temperature is 15°C rather than 25°C, the average global CH_4 production must be lower by a factor of 3 than these measured production rates (Table 4). Thus we tentatively conclude from these studies, as well as from Koyama's numbers on CH_4 production, that swamps, marshes and lake sediments below a water column not deeper than 10 m do release 50–100 g CH_4/m^2 yr to the atmosphere on a global and annual average. These numbers are lower than Koyama's global average for rice paddies since the geographical distribution of rice paddies favors warmer latitudes. And in the case of lakes, more CH_4 is oxidized by the overlying waters. These production rates are nevertheless quite substantial. They amount to about 5% of the annual net production of dry organic matter which in a swamp of temperate latitudes averages 2 000 g/m^2 yr (Woodwell, 1970).

The global area of swamps and marshes has been estimated by Twenhofel (1951) to be 2.6×10^6 km^2, from which we obtain a global production of $130–260 \times 10^{12}$ g CH_4/yr.

The global area of fresh water lakes has been estimated by Hutchinson (1948) to be 2.5×10^6 km^2, about 0.1% of which he assumed to produce CH_4. This fraction is probably too low and we assume that about 1 to 10% of the fresh water lake areas overly sediments containing organic material and are shallow enough to release CH_4. Thus CH_4 released to the atmosphere from this source should lie between 1.25×10^{12} and 25×10^{12} g CH_4/yr.

Upland fields and forests

Koyama (1963, 1964) also measured the CH_4 production rates of upland soils and derived 0.44 g CH_4/m^2 yr for the annual global average. He estimated the global area covered by grassland, brushland, and cultivated areas to be 30×10^6 km^2 from which he obtained an annual global CH_4 production of 10×10^{12} h CH_4/yr. He found forest soils to produce even less CH_4: 0.9×10^{-2} g CH_4/m^2 yr; with a global area of 44×10^6 km^2 the total CH_4 production by forest amounts to 0.4×10^{12} g CH_4/yr.

There is an estimate by Robinson & Robbins (1968) who considered tropical humid areas separately and assumed a source strength of 0.1 that of paddy fields. Since the humid tropical region occupies 21×10^6 km^2, the resulting production would be quite large: 610×10^{12} g CH_4/yr. However, there are no measurements of atmospheric CH_4 concentration or production rates to substantiate this assumption of high CH_4 production. In fact, the humid tropical areas are already included in Koyama's estimate quoted above for forest and uplands which gives a much smaller CH_4 production. We therefore feel that this large number is unsupported and have not included it in our estimates in Table 5.

Tundra

There are a few measurements of the atmospheric CH_4 concentration which indicate that waterlogged tundra releases CH_4 (Benoit, 1973). Production rates are unknown. To determine

Table 5. *Biogenic sources of atmospheric CH_4 and their global production rate*

Source	Source strength (g CH_4/ m^2 yr)	Total area (10^6 km^2)	Annual production (10^{12} g CH_4/yr)
Enteric fermentation of animals			101–220
Paddy fields	206[a]	1.35[b]	280
Swamps, marshes	50–100	2.6	130–260
Fresh water lakes	50–100	2.5[c]	1.25–25
Upland fields	0.44[a]	30[a]	10
Forests	0.9×10^{-2}[a]	44[a]	0.4
Tundra	17	8[d]	1.3–13
Oceans			
(*a*) Open ocean	1.2×10^{-2}	361[e]	4–6.7
(*b*) Shelf	50–100	1.4[f]	0.7–14
Total biogenic			529–825

[a] Koyama (1963, 1964).
[b] United Nations FAO, 20, No. 6 (1971).
[c] Hutchinson (1948); only 1–10 % of that area productive.
[d] Whittaker (1971); only 1–10 % of that area productive.
[e] Sverdrup et al. (1961).
[f] Only 1–10 % of that area productive.

whether the tundra could constitute a major source we will try to estimate its CH_4 production by extrapolating from the measured production rates of lakes. Tundra thaws and is productive only during the 4 summer months. Despite low precipitation, waterlogged tundra is a common feature because of the bad drainage due to permafrost. For the summer period and for waterlogged tundra we assume a CH_4 production rate of about half that of swamps or lakes, i.e., 50 g/m^2 yr; we assume no CH_4 production for the rest of the year.

Whittaker (1971) estimates the global area covered by arctic and alpine tundra to be 8×10^6 km^2. To obtain a first estimate we make the assumption that between 1 and 10% of that area is waterlogged at any given time in the warm season. The resulting average global production by tundra then lies between 1.3×10^{12} and 13×10^{12} g CH_4/yr.

Oceans

There are a few published measurements of CH_4 dissolved in ocean water, indicating a supersaturation of about 1.3 with respect to the atmosphere (Swinnerton & Linnenbom, 1967; Lamontagne et al., 1973). These measurements also show an increase of CH_4 with depth. The increase is relatively strong in the Gulf of Mexico and weak in the open Atlantic; both nevertheless indicate that the oceans might be a source of CH_4. Their release of CH_4 can be estimated by calculating the rate of molecular diffusion of CH_4 through the stagnant water film at the air–sea boundary. Assuming a diffusion coefficient of 20×10^{-6} cm^2/sec, a thickness between 30 and 50 μ for the stagnant film (Broecker and Peng, 1973), a supersaturation of 1.3 and a concentration of 4.7×10^{-5} ml CH_4 (gas)/l water at the surface (Swinnerton & Linnenbom, 1967), we obtain between 1.2×10^{-2} and 2×10^{-2} g CH_4/m^2 yr for the molecular diffusion flux of CH_4 from the open ocean. The total ocean area is 361×10^6 km^2 (Sverdrup et al., 1961) and the resulting global CH_4 release due to upward diffusion in the open ocean lies between 4 and 6.7×10^{12} g CH_4/yr. (There is a possibility that upwelling sweeps deep, CH_4-rich water to the surface in certain areas of the ocean, thus increasing the total CH_4 release, but no numbers are available at present.)

Another possibility is CH_4 production along the continental shelf and tidal flats. Wherever the sediments contain organic material and the overlying water is not deeper than 10 m, we might expect CH_4 production similar to that in fresh water lakes, i.e., 50–100 g CH_4/m^2 yr on the global average. From the slope of the shelf which averages 0.2% (Sverdrup et al., 1961) and from the area of the shelf 127×10^6 km^2 less than 200 m deep we estimate that the area of the shelf at less than 10 m depth is 1.4×10^6 km^2. Assuming, as for fresh water lakes, that 1 to 10% of the area produce CH_4 we obtain a global production of atmospheric CH_4 between 0.7×10^{12} and 14×10^{12} g CH_4/yr from that source.

This concludes our list of biogenic sources, each is entered in Table 5. It is reemphasized that the estimates are tied to very few measured production rates and that the extrapolations are necessarily large. It is, therefore, possible that future, more detailed studies will show that

some productions have been under or overestimated. The best present estimates for the lower and upper limits of the total biogenic CH_4 production are 530×10^{12} and 850×10^{12} g CH_4/yr.

In addition to biogenic sources, there are a number of sources which produce C^{14}-free CH_4. These are listed in Table 6. These sources of "dead" CH_4 total between 15.6×10^{12} and 49.4×10^{12} g CH_4/yr. An upper limit can also be obtained from the C^{14} content in CH_4 since C^{14} measurements indicate that the emission of "dead" CH_4 could be at most 25% of the biogenic production, or 210×10^{12} g CH_4/yr. The relatively large discrepancy between these numbers is due either to strong local contamination of the sampling sites used for C^{14} analysis or to underestimation of the global emissions of "dead" CH_4. With the emission of "dead" CH_4 included, the total annual production of CH_4 lies between 546×10^{12} and $1\,060 \times 10^{12}$ g CH_4/yr (Table 7).

It is instructive to compare the total biogenic production to the other production figures listed in Table 7. We find that the release of biogenic CH_4 to the atmosphere equals or exceeds the annual production of CH_4 from natural gas wells. We further find that the biogenically released CH_4 may amount to as much as 0.5% of the annual production of dry organic matter. Since the energy content of CH_4 is about 3 times that of cellulose, about 1 to 2% of the solar energy fixed by photosynthesis is lost to the atmosphere as CH_4 and escapes the biologic food chain. Finally, by dividing the total amount of CH_4 present in the atmosphere by the total production rate of CH_4 we obtain a CH_4 turnover time of 4 to 7 years.

Table 6. *Anthropogenic and other sources of C^{14} free CH_4 and their global production rate*

Source	Annual global production (10^{12} g CH_4/yr)
Coal mining	6.3–22[a]
Lignite mining	1.6–5.7[a]
Industrial losses	7–21[a]
Automobile exhaust	0.5[a]
Volcanic emissions	0.2[a]
Total "dead" CH_4	15.6–49.4[a]
Total "dead" CH_4 from C^{14} content of CH_4	210

[a] Hitchcock & Wechsler (1972).

Table 7. *Total global production of CH_4 and plant matter, and the amount of CH_4 present in the atmosphere*

Annual production of atmospheric CH_4	$545 \times 10^{12} - 1\,035 \times 10^{12}$ g CH_4/yr
Annual output of CH_4 from natural gas wells in 1965	520×10^{12} g CH_4/yr
Annual production of dry organic matter	1.65×10^{17} g/yr[a]
Amount of CH_4 present in the atmosphere based on 1.41 ppm mixing ratio	4.0×10^{15} g

[a] Woodwell (1971).

Sinks of atmospheric CH_4

Measurements over the past 20 years have indicated that the tropospheric CH_4 concentration is practically constant with time. Since the atmospheric turnover time of CH_4 is about 5 years, the CH_4 cycle is in a steady state, and CH_4 production must be matched by an equivalent destruction. It is well known that CH_4 reacts with atomic oxygen, especially with the excited O^1D atom, and with the OH radical. These radicals are known to be present in the stratosphere and the stratosphere, as shown by profiles in Fig. 2, acts as a sink for CH_4.

The simplest way to calculate the total destruction of CH_4 in the stratosphere is to calculate its flux into the stratosphere. There are two transport processes to be considered. The first is the Hadley cell circulation which penetrates into the lower tropical stratosphere. Newell (1970) estimated that the mean rising motion in the tropics has a velocity of about 0.02 cm/sec. From that he deduced a flux of 2.4×10^{12} g air/sec into the stratosphere. This flux leaves the stratosphere at about 30° N. The flow of this meridional circulation is so slow that it takes about 1.6 years to replenish the air in the lower tropical stratosphere to 5 km above the tropopause. The characteristic time with respect to chemical oxidation of CH_4 is about 5 years. Thus about 30% of the CH_4 entering the stratosphere will be destroyed be-

Table 8. *Destruction rates of atmospheric CH_4*

	10^{12} g/yr
Reaction with OH in troposphere	⩽2 200
Loss to stratosphere in Hadley circulation	⩽60
Loss to stratosphere by eddy diffusion	45–150
Uptake by soil microorganisms	Probably negligible
Total destruction	⩽2 450

fore the air reenters the troposphere. To obtain a conservative upper limit of this CH_4 loss, we assume that all CH_4 entering the stratosphere in the Hadley circulation is destroyed. The resulting loss is 60×10^{12} g CH_4/yr (Table 8).

The second transport process is upward eddy diffusion, driven by the CH_4 gradient in the lower stratosphere (Fig. 3). The vertical diffusion flux is given by:

$$J = -\varrho K_z \frac{\partial M}{\partial z}$$

where ϱ is the density, K_z is the vertical eddy diffusion coefficient, and $\partial M/\partial z$ is the vertical gradient of the CH_4 mixing ratio at the tropopause.

The hemispherically averaged height of the tropopause is 13 km and the corresponding density is 2.7×10^{-4} g/cm³. If we take K_z to lie between 3×10^3 and 10^4 cm²/sec in the lower stratosphere and use the gradient from Fig. 3, 0.34×10^{-12} g CH_4/g air/cm, as an upper limit for the global average, we obtain a global loss between 45 and 150×10^{12} g/yr by upward eddy diffusion (Table 8). The total loss of CH_4 to the stratosphere therefore lies between 100 and 200×10^{12} g/yr where the larger value is a rather conservative upper limit. The actual loss to the stratosphere is probably less than 100×10^{12} g CH_4/yr. Since our estimated global CH_4 production lies between 545×10^{12} and $1\,035 \times 10^{12}$ g/yr, the stratospheric sink can account for at most 37% of the atmospheric CH_4 destruction, and a tropospheric sink is required.

It has been speculated that atmospheric CH_4 might be oxidized by soil microorganisms. Indeed, the tropospheric profiles over Scottsbluff (Fig. 3) do show a decrease in CH_4 concentration close to the surface, which might indicate a low level sink. However, experiments in our laboratory, in which we measured soil uptake of CH_4 at atmospheric concentrations under aerobic conditions, gave very low values. These measurements have been confirmed by Ingersoll & Inman (1973). Thus it appears that soil microorganisms cannot utilize the low CH_4 concentrations of the atmosphere and that soil is probably not a significant sink for atmospheric CH_4.

Apparently we need an atmospheric sink mechanism. Such a mechanism is provided by a reaction cycle which has been recently proposed by Levy (1971). This cycle is expected to maintain an OH concentration of about 2.5×10^6/cm³ in the troposphere (McConnell et al., 1971). With such an OH concentration the destruction of CH_4 in the troposphere becomes very important. Although only the first step in the oxidation of CH_4 is of importance here, the whole sequence is of interest because CO and H_2 appear as intermediate products. Thus the CH_4 cycle is coupled to the CO and H_2 cycles.

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad (1)$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \quad (2)$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (3)$$

$$CH_3O + O_2 \rightarrow H_2CO + HO_2 \quad (4)$$

$$H_2CO \xrightarrow{+OH} CHO + H_2O \quad H_2CO \xrightarrow{+h\nu} H_2 + CO \quad H_2CO \xrightarrow{+h\nu} CHO + H \quad (5)$$

$$CHO + O_2 \rightarrow CO + HO_2$$

OH is eventually regenerated by the reaction

$$HO_2 + NO \rightarrow NO_2 + OH \quad (6)$$

It should be pointed out that reaction (3) is not supported by laboratory evidence. This is a minor detail however, because there is general agreement that CH_3O_2 will eventually react to form H_2CO (Crutzen, 1972).

Most important for the present discussion is the destruction of CH_4 by reaction (1). Its reaction rate is $5.5 \times 10^{-12} \cdot \exp(-1881/T)$ cm³/molecule sec (Greiner, 1970). Weighing with the vertical temperature and density distribution, the average tropospheric reaction rate is 7 ×

10^{-15} cm³/molecule sec. From this and the estimated OH concentration of 2.5×10^6/cm³ we would obtain a tropospheric turnover time of 1.8 yr. The corresponding destruction rate is $2\,200 \times 10^{12}$ g CH_4/yr (Table 8). This is more than enough to match the CH_4 production. In fact, the CH_4 cycle could be closed by a tropospheric destruction between 500 and 900×10^{12} g CH_4/yr. This means that an OH concentration between 5×10^5 and 10×10^5 cm^{-3} in the troposphere would be sufficient to maintain a steady state CH_4 cycle.

Obviously a reaction cycle like the one proposed by Levy (1971) and McConnell et al. (1971) could very well balance the CH_4 cycle. It is furthermore important, because the proposed cycle converts CH_4 quantitatively into H_2CO and then into CO. Previous estimates indicated that this source of CO could be as large as $3\,900 \times 10^{12}$ g CO/yr. Based on the present CH_4 cycle, we estimate a lower tropospheric CO production of 880 to $1\,600 \times 10^{12}$ g CO/yr. CH_4 oxidation should also produce $\frac{1}{2}$ to one H_2 molecule per CH_4 molecule (Ehhalt & Heidt, 1973). Finally more radicals like HO_2 are produced than consumed in that cycle.

We may ask how well this possibly quite important theoretical chemical cycle is supported by experimental facts. At present there is no direct experimental evidence of the importance of this reaction scheme in nature; in particular, there are no measurements of tropospheric OH concentrations. But there are two facts which provide circumstantial evidence: first, the above CO production implies a tropospheric CO residence time of about 3–5 months, which is in agreement with the tropospheric residence time derived from measurement of the C^{14} content in CO (Weinstock & Niki, 1972). Second, supporting evidence is also provided by tracer observations. Atmospheric CH_4 has a relatively high content of tritium (T), about 2×10^4 T.U., which is probably due to the release of tritiated CH_4 from nuclear industry (Begemann & Friedman, 1968). Thus reaction products of CH_4 which contain hydrogen should also have a high tritium content. Atmospheric molecular H_2 unfortunately has a high T content anyway because of the release of tritiated H_2 from thermonuclear explosions and nuclear industry. But formaldehyde, another reaction product, is longlived enough to be collected and analyzed for T. H_2CO is washed out and enriched in rain to 0.5 μg H_2CO/l water (Junge, 1963). Musgrave (1966) separated H_2CO from large amounts of rain and indeed observed T contents comparable to those of CH_4 (Shearer, 1969). This finding provides some solid support for the idea that H_2CO is derived from CH_4, but provides little information about the destruction rate of CH_4 or the production rate of CO. Thus more measurements, especially on the tropospheric OH concentrations, are needed before the chemistry of the tropospheric CH_4 destruction mechanism is fully established. Nevertheless the reaction cycle proposed by Levy should provide a good working hypothesis in the search for the tropospheric CH_4 sink.

Conclusion

Atmospheric CH_4 originates at the earth's surface, at least 80% resulting from the anaerobic decay of recent organic matter. The CH_4 production must be balanced by destruction in the troposphere, and the reaction of CH_4 with the hydroxyl radical may seem to be a likely mechanism. This and subsequent reactions seem to constitute the major sink of CH_4 and a major source of CO. A small fraction (about 10%) of the CH_4 enters the stratosphere and is destroyed there mainly by the same reaction. The resulting reaction products are important to the water and ozone budgets and to the overall chemistry of the stratosphere. The CH_4 cycle is closed at the earth's surface, where CO_2 and H_2O (the ultimate reaction products of CH_4) are photosynthesized to plant matter. Some of the plant matter enters the soil as litter, a fraction of which is eventually decomposed anaerobically with the release of CH_4. The CH_4 cycle makes a small but significant contribution to the carbon cycle. Between 1.5×10^{15} and 2.9×10^{15} g CO_2/yr pass through it annually. This amounts to a few percent of the annual CO_2 uptake by land plants which is about 130×10^{15} g/yr.

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АТМОСФЕРНЫЙ ЦИКЛ МЕТАНА

Распределение CH_4 в атмосфере довольно однородно в зональном направлении и по вертикали, но выявляет слабый широтный градиент в тропосфере; в стратосфере оно имеет определенное уменьшение с высотой. Среднее объемное отношение смеси в тропосфере равно $1{,}4 \cdot 10^{-6}$, что соответствует общему количеству CH_4 в атмосфере, равному $4 \cdot 10^{15}$ г. Большая часть его недавнего биологического происхождения. Анализ на C^{14} показывает, что ископаемые источники дают не более 20 % метана. Обсуждаются различные экосистемы, производящие CH_4, и общий годовой выход его оценивается в пределах от $5{,}5 \cdot 10^{14}$ г до $11 \cdot 10^{14}$ г. Соответствующее время кругооборота атмосферного CH_4 лежит между 4 и 4 годами. Разрушение CH_4 происходит в основном в тропосфере, наиболее вероятно путем реакции $CH_4 + OH \rightarrow CH_3 + H_2O$. Около 10 % метана разрушается в стратосфере. Цикл CH_4 сильно связан с циклами H_2 и CO и дает вклад порядка 1 % в цикл атмосферного углерода.