Pageoph, Vol. 116 (1978), Birkhäuser Verlag, Basel

Sources and Sinks of Atmospheric Methane

By D. H. EHHALT[1]) and U. SCHMIDT[1])

Abstract – In 1972 average mixing ratio of methane in the troposphere was 1.41 ppm and 1.3 ppmv for the northern and southern hemisphere, respectively, which corresponds to a total amount of 4 × 10^{15} g of CH_4 present in the atmosphere. Most is of recent biologic origin. ^{14}C analyses show that no more than 20 percent 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 yrs. The destruction of CH_4 takes place mainly in the troposphere, most probably through the reaction of $CH_4 + OH \rightarrow CH_3 + H_2O$. About 10 percent of the CH_4 is destroyed in the stratosphere. The CH_4 cycle contributes on the order of 1 percent to the atmospheric carbon cycle.

Key words: Trace gases; Atmosphere; Sources and Sinks; Methane.

1. Introduction

The presence of methane in the earth's atmosphere was discovered by MIGEOTTE (1948), who measured its infrared absorption bands in the solar spectrum. The early optical measurements indicated a uniform distribution throughout the atmosphere with an average mixing ratio of 2 ppmv. Subsequent optical measurements indicated a lower value of 1.4 ppmv (FINK *et al.*, 1965). More recent measurements by EHHALT and HEIDT (1973) and HEIDT and POLLOCK (1976) using gas chromatography gave averages around 1.41 ppmv and 1.63 ppmv, respectively, in the northern troposphere. These measurements also show that the CH_4 concentration may fluctuate significantly in individual tropospheric profiles. On the average the troposphere appears well mixed in the vertical with respect to CH_4. However, there seems to be a slight latitudinal gradient with lower CH_4 concentrations, about 1.3 ppmv, in the southern hemisphere as shown in Fig. 1 (EHHALT, 1977; cf. LAMONTAGNE *et al.*, 1974). In the stratosphere the CH_4 concentration decreases rapidly with altitude as indicated by Fig. 2.

Interest in the CH_4 cycle has been stimulated recently by several 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

---

[1]) Kernforschungsanlage Jülich GmbH. Institut für Chemie 3, Atmosphärische Chemie, D-5170 Jülich, BRD.

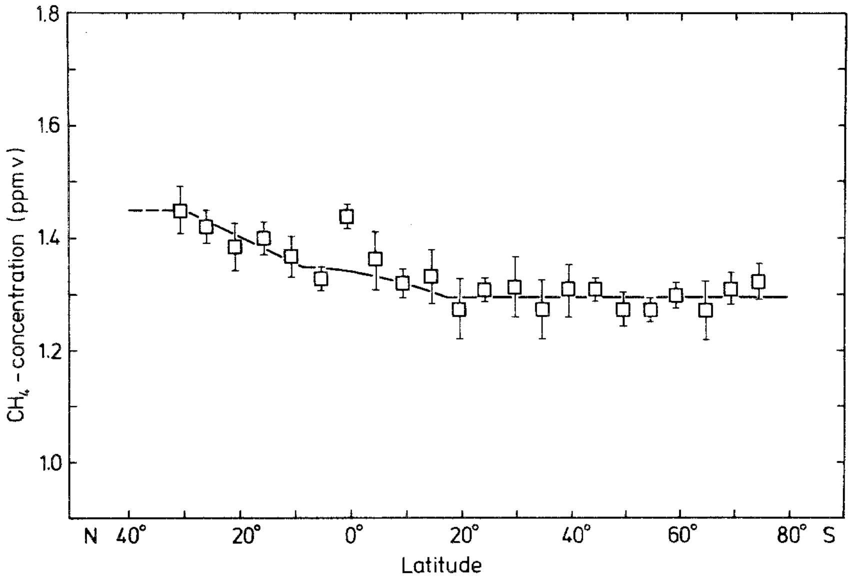

Figure 1
Latitudinal dependence of the CH_4 concentration. The samples were collected by J. Swinnerton aboard the USCGC Glacier during November and December 1972 and measured at NCAR (EHHALT, 1977).

middle stratosphere and upon the oxidation adding significant amounts of water vapor to the upper stratosphere. Second, the oxidation should yield CO as an intermediate product and may well be a major source of CO (MCCONNELL *et al.*, 1971) and of H_2 as well. In the following we will discuss the sources and sinks which govern the atmospheric CH_4 cycle. Since much of that material has been presented in detail previously (EHHALT, 1974, 1976) in the present paper only the major points of the CH_4 cycle will be reviewed. We will however update the data where new information has become available.

2. *Sources of atmospheric* CH_4

It is generally agreed that CH_4 is too complicated a molecule with too high energy content to be synthesized within the atmosphere and that it must be 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 biologically. This information was provided by measurements of the radiocarbon content in atmospheric CH_4. Any CH_4 derived from recent organic material has a ^{14}C content very close to that of recent wood. In contrast, CH_4 derived from fossil fuels or volcanic activity contains essentially no ^{14}C. The fuel deposits are so old that the originally

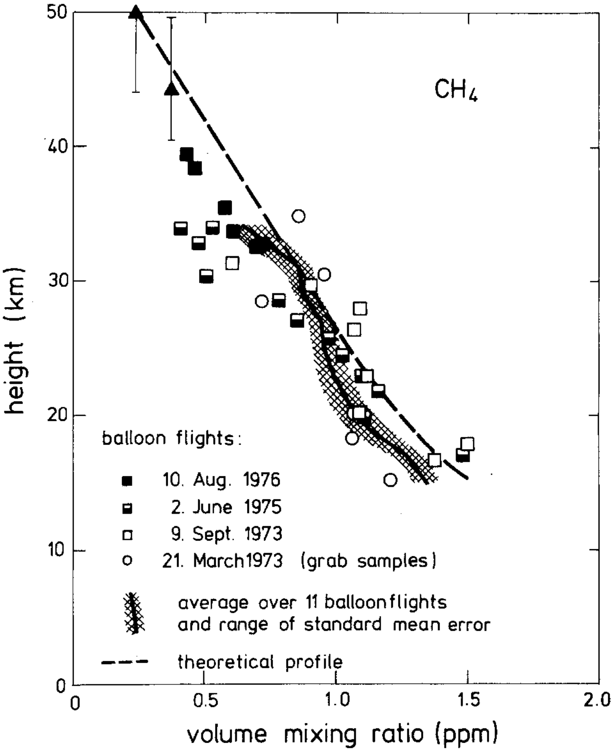

Figure 2
Stratospheric profiles of CH_4 concentrations. The data are mostly from measurements by NCAR (as summarized by VOLZ *et al.*, 1976).

present ^{14}C has decayed. Several ^{14}C analyses of atmospheric CH_4, made mostly by LIBBY (1973) are available. They are summarized in Table 1. Most of these samples were collected before the atmosphere was contaminated with the ^{14}C from nuclear explosions and should represent the natural ^{14}C level in CH_4. The average ^{14}C content was 80 percent of that of recent wood, which indicates that 80 percent of the CH_4 was of recent biologic origin and 20 percent was 'dead' CH_4. At that time, 1950, these 20 percent represented an upper limit. The measured CH_4 samples had 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.

Recent atmospheric CH_4 is contaminated by ^{14}C from nuclear explosions, so that this old estimate cannot be updated. But we also see from Table 4 below that the known anthropogenic sources add up to much less than 20 percent of the biogenic sources so that this old estimate should still represent a reasonable upper limit for '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.

Table 1

^{14}C *content of atmospheric* CH_4 *samples*

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

*) Libby (1973).

†) Bishop *et al.* (1962); sample integrated over several months had 12.7 dpm/g carbon.

‡) Bainbridge *et al.* (1961).

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. The strength of these sources and their importance for the global CH_4 production are summarized in Table 2.

In the following we will only discuss those sources which are important or which, because of their large area, might become important.

Table 2

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			100–220
Paddy fields	206*)	1.35**)	280
Swamps, marshes	50–100	2.6	190–300
Fresh water lakes	50–100	2.5†)	1– 25
Tundra	10	8††)	0.3– 3
Oceans	1.2×10^{-2}	361‡)	1.3– 16.6
		Total biogenic	570–850

*) Koyama (1963, 1964).

**) United Nations FAO (1971a).

†) Hutchinson (1948); only 1–10% of that area productive.

††) Whittaker (1971); only 1–10% of that area productive.

‡) Sverdrup *et al.* (1961).

3. *Enteric fermentation of animals*

The oldest estimate of CH_4 production is that of the enteric fermentation of animals. Hutchinson (1948, 1954) estimated the amount of CH_4 produced daily by various large herbivores (Table 3). From these numbers and from the 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 heads in 1970, the present CH_4 production by enteric fermentation has increased to 100×10^{12} g/yr (Table 3). 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. 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 percent of which are eaten by herbivores (Woodwell, 1970). Cattle consume a minimum of about 10 kg of dry plant matter per day from which they produce 200 g of CH_4. The resulting food-to-CH_4 conversion ratio of 2.0×10^{-2} g CH_4/g dry plant matter is the highest of all large herbivores (Table 3). If all these animals produce CH_4 with this ratio, we obtain an upper limit of about 150×10^{12} CH_4/yr (Table 2) for CH_4 production by enteric fermentation.

Table 3

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	200.0*)	1198**)	88.0
Sheep	15.1*)	1026**)	5.8
Horse	106.0*)	125†)	4.8
Goat	14.7*)	384††)	2.1
		Total	100×10^{12} g/yr

*) Hutchinson (1948).

**) U.S. Dept. of Agric. (1971).

†) United Nations FAO (1971b); includes mules and asses.

††) United Nations FAO (1970).

4. *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. From these data he 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 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 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.

By 1970 the global area of rice paddies had increased to 1.35×10^6 km^2 (UNITED NATIONS FAO, 1971a). Therefore the present annual CH_4 production of paddy fields is 280×10^{12} g CH_4/yr (Table 2). 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.

5. *Fresh water lakes, swamps and marshes*

There are plentiful data showing that lake sediments, swamps, and marshes copiously produce CH_4, but very few quantitative studies of the CH_4 production rate have been made. CONGER (1943) measured the amount of CH_4 reaching the surface of Great Fresh Creek, a lake of about 2 m depth in Maryland (U.S.A.). His measurements for August (water temperature 24–27.5°C) averaged 0.32 g CH_4/m^2/d, which if maintained throughout the year would correspond to a release of about 120 g CH_4/m^2/yr to the atmosphere.

Another 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/d, 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 the gas bubbles formed at the bottom of Lake Beloye, U.S.S.R., about 10 m deep, had a CH_4 content of 74.1 to 83.5 percent. After their ascent to the surface the CH_4 content had decreased to 20 to 24 percent 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/d/cm^3 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.

The most recent and most extensive studies of ebullient gases from wetlands have been made by BAKER-BLOCKER *et al.* (1977). Fluxes between 9.2×10^{-6} and 1.1×10^{-4} g CH_4/cm^2/d corresponding to 33 and 401 g/m^2/yr were found. From their data these authors also determined the dependence of the local CH_4 flux as function of the air temperature T to be $F = 4.6 \times 10^{-5} - 5.6 \times 10^{-6} \cdot T + 2.6 \times 10^{-7} T^2$ g/cm^2/d which allows a more reliable extrapolation to other swamp and marsh areas. From this relation they calculated the source strength of some of the major swamp systems: Pripet Marshes in the U.S.S.R.: 40 g/m^2/yr, the Sudd region in the Sudan: 400 g/m^2/yr, the Everyglades in U.S.A.: 170 g/m^2/yr and the swamps in Uganda: 230 g/m^2/yr. The total annual production from these regions amounts to 68×10^{12} g CH_4/yr. Still these swamps occupy only about 10 percent of the global area of swamps and marshes and a further extrapolation is necessary. Using the temperature dependence for CH_4-release from BAKER-BLOCKER *et al.* (1977), as well as that found by KOYAMA (1964), further assuming a more or less uniform distribution of swamp, marshes and lakes with latitude and therefore a mean global temperature of 15°C we tentatively adopt a mean CH_4 flux of 50–100 g CH_4/m^2/yr for the remaining swamps as well as for lake sediments below a water column not deeper than 10 m.

The remaining areas occupy about 90 percent of the global area of swamps and marshes which has been estimated by TWENHOFEL (1951) to be 2.6×10^6 km^2. They are assumed to reduce CH_4 with the above rate. The corresponding annual production lies between 117×10^{12} and 234×10^{12} g CH_4/yr to which we have to add Baker-Blocker's estimate of 68×10^{12} g CH_4/yr for the mentioned areas. Thus the total production from marshes and swamps falls between 190×10^{12} and 300×10^{12} g CH_4/yr (Table 2).

The global area of fresh water lakes has been estimated by HUTCHINSON (1948) to be 2.5×10^6 km^2, about 0.1 percent of which he assumed to produce CH_4. This fraction is probably too low and we assume that about 1 to 10 percent of the fresh water lake areas overlie 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 1×10^{12} and 25×10^{12} g CH_4/yr (Table 2).

6. *Tundra*

There are a few measurements of the atmospheric CH_4 concentration, which indicate that waterlogged tundra releases CH_4 (BENOIT, 1973). 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. CH_4 production rates for tundra have been published by SVENSSON (1973) and SVENSSON *et al.* (1975). For waterlogged tundra the production rate was highest, about 10 g $CH_4/m^2/yr$.

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 percent of that area is waterlogged at any given time in the warm season. The resulting average global production by tundra then lies between 0.3×10^{12} and 3×10^{12} g CH_4/yr (Table 2).

7. *Oceans*

There are a few published measurements of CH_4 dissolved in ocean water, indicating supersaturations from about 1.1 to 1.8 with respect to the atmosphere (SWINNERTON and LINNENBOM, 1967; SWINNERTON *et al.*, 1969; LAMONTAGNE *et al.*, 1973, 1974). 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. The release of CH_4 can be estimated by calculating the rate of molecular diffusion of CH_4 through the stagnant water film of the air–sea boundary. Assuming a diffusion coefficient of 20×10^{-6} cm^2/sec, a thickness between 30 μ and 50 μ for the stagnant film (BROECKER and PENG, 1974), a solubility coefficient of 0.03 ml CH_4 (STP)/ml $H_2O\cdot$ at (YAMOMOTO *et al.*, 1976) and an average atmospheric CH_4 mixing ratio of 1.4 ppm, we obtain between 0.4×10^{-2} and 4.8×10^{-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 1.3 and 16.6×10^{12} g CH_4/yr (Table 2). Previous estimates by several authors differ by a factor of 5 (EHHALT, 1974; LISS and SLATER, 1974; SEILER and SCHMIDT, 1974), but fall into the same range. Since all of those estimates are derived from the same data base, the differences are due to discrepancies in the assumed values for diffusion coefficients, film thickness and solubility data, that were used in the calculations.

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.

8. *Anthropogenic* CH_4 *sources*

In addition to biogenic sources, there is a number of sources which produce ^{14}C-free CH_4. They are listed in Table 4. These sources of 'dead' CH_4 total between

Table 4

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

Source	Annual global production in 10^{12} g CH_4/yr
Coal mining	6.3– 22.0*)
Lignite mining	1.6– 5.7*)
Industrial losses	7.0– 21.0*)
Automobile exhaust	0.5*)
Volcanic emissions	0.2*)
Total 'dead' CH_4	15.6– 49.4*)
Total 'dead' CH_4 from ^{14}C content of CH_4	140.0–210.0

*) HITCHCOCK and WECHSLER (1972).

15.6×10^{12} and 49.4×10^{12} g CH_4/yr. An upper limit can also be obtained from the ^{14}C-content in CH_4 since ^{14}C measurements indicate that the emission of 'dead' CH_4 could be at most 25 percent of the biogenic production or 140–210 × 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 ^{14}C 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 590×10^{12} and 1060×10^{12} g CH_4/yr (Table 5).

It is instructive to compare the total biogenic production to the other production figures listed in Table 5. We find that the release of biogenic CH_4 to the atmosphere equals or exceeds the 1965 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 percent of the annual production of dry organic matter. Since the energy content of CH_4 is about three times that of cellulose, about 1 to 2 percent of the solar energy fixed by photosynthesis is lost to the atmosphere as CH_4 and escapes the biologic food chain. Finally, by

Table 5

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	$590 \times 10^{12} - 1060 \times 10^{12}$ 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*)
Amount of CH_4 present in the atmosphere based on a mixing ratio of 1.41 ppmv	4.0×10^{15} g

*) WOODWELL (1971).

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.

9. *Sinks of atmospheric* CH_4

Measurements over the past 20 years have indicated that the tropospheric CH_4 concentration was practically constant until 1970. The atmospheric turnover time of CH_4 is about 5 yr, and assuming the CH_4 cycle to be in a steady state, the CH_4 production must be matched by an equivalent destruction. It turns out that soil microorganisms do not present a significant sink for the CH_4.

Laboratory measurements made at NCAR, in which about 40 l air in a closed system had been exposed to natural soil (2000 cm^2) did not show any detectable decrease of the CH_4 mixing ratio (1.5 ppmv) within one day. With an experimental error of 5 percent, this means that the CH_4 deposition velocity was less than 10^{-5} cm/sec. Since the oceans seem to act as a slight source, the sinks of CH_4 must lie within the atmosphere.

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 acts as a sink for CH_4 as shown by the vertical profiles in Fig. 2. However the stratospheric sink is by far too weak to match the surface production. The simplest way to calculate the total destruction of CH_4 in the stratosphere is to calculate its flux into the stratosphere. The main transport process is upward eddy diffusion, driven by the CH_4 gradient in the lower stratosphere. The vertical diffusion flux is given by:

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

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/cm^3. If we take K_z to lie between 3×10^3 and 10^4 cm^2/sec in the lower stratosphere and use the gradient from Fig. 2 which is 0.2×10^{-12} g CH_4/g air/cm, as an upper limit for the global average, we obtain a global loss between 25 and 85×10^{12} g/yr by upward eddy diffusion (Table 6). Since our estimated global CH_4 production lies between 590×10^{12} and 1060×10^{12} g/yr, the stratospheric sink can account for at most 15 percent of the atmospheric CH_4 destruction, and a tropospheric sink is required.

The only mechanism which can supply a sink strength of the required magnitude is the reaction of CH_4 with OH:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

Table 6

Destruction of tropospheric CH_4

Sink	Annual destruction 10^{12} g CH_4/yr
Uptake by soil microorganisms	<1
Loss to stratosphere	25–85
Reaction with OH in troposphere	450–1800
Total	475–1885

with a reaction rate of $5.5 \times 10^{-12} \exp(-1900/T)$ cm^3/molecule/sec (GREINER, 1970). Average tropospheric OH-concentrations have been estimated by a number of authors to lie around 10^6 cm^{-3} (LEVY, 1971; CRUTZEN, 1974; WARNECK, 1975; WOFSY, 1976). Weighing with the vertical temperature and density distribution, the average tropospheric life time of CH_4 against reaction with OH is 4.5 yr. The corresponding global destruction rate is 900×10^{12} g/yr. Unfortunately the average concentration of OH in the troposphere is a very uncertain quantity. Although a few measurements of its concentration exist, which are in general agreement with model calculations (WANG *et al.*, 1976; PERNER *et al.*, 1976; DAVIS *et al.*, 1976), they are by far too spotty and we have to rely on the numbers predicted from chemical models. The range of uncertainty for the OH concentration predicted by the model calculation has never been reliably estimated, but from the scatter of the published data it must be at least a factor 2. Thus the sink strength is not better known than the source strength, and the turnover time of the CH_4 cycle is certainly not better known than by a factor of 2.

10. Conclusion

Atmospheric CH_4 originates at the earth's surface, at least 80 percent resulting from the aerobic decay of recent organic matter. The CH_4 production must be balanced by destruction in the troposphere, most probably by the reaction of CH_4 with the hydroxyl radical. A small fraction (at most 15 percent) of the CH_4 enters the stratosphere and is destroyed there mainly by the same reaction. The resulting 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.

REFERENCES

BAINBRIDGE, A. E., SUESS, H. E. and FRIEDMAN, I. (1961), *Isotopic composition of atmospheric hydrogen and methane*, Nature *192*, 648–649.

BAKER-BLOCKER, A., DONAHUE, T. M. and MANCY, K. H. (1977), *Methane flux from wetlands areas*, Tellus *29*, 245–250.

BENOIT, R. (1973), Private communications.

BISHOP, K. F., DELAFIELD, H. I., EGGLETON, A. E. J., PEABODY, C. O. and TAYLOR, B. T. (1962), *The tritium content of atmospheric methane*, Proc. Sym. Tritium Phys. Biol. Sci., Vienna, Austria, May 3–10, 1961, Vol. 1, p. 55.

BROECKER, W. S. and PENG, T. H. (1974), *Gas exchange rates between air and sea*, Tellus *26*, 21–35.

CONGER, P. S. (1943), *Ebullition of gases from marsh and lake waters*, Pub. *59*, Cheasapeake Biol. Lab. Solomons Island, Maryland, U.S.A., pp. 1–42.

CRUTZEN, P. (1974), *Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air*, Tellus *26*, 47–57.

DAVIS, D. D., HEAPS, W. and MCGEE, T. (1976), *Direct measurements of natural tropospheric levels of OH via an airborne tunable dye laser*, Geophys. Res. Letters *3*, 331–333.

EHHALT, D. H. and HEIDT, L. E. (1973), *Vertical profiles of* CH_4 *in the troposphere and stratosphere*, J. Geophys. Res. *78*, 5265–5271.

EHHALT, D. H. (1974), *The Atmospheric Cycle of Methane*, Tellus *26*, 58–70.

EHHALT, D. H., *The Atmospheric Cycle of Methane*, in: *Microbial Production and Utilization of Gases* (H. G. Schlegel, G. Gottschalk, N. Pfennig, eds.), (E. Goltze KG, Göttingen, 1976), pp. 13–22.

EHHALT, D. H. (1977), *The* CH_4 *concentration over the ocean and its possible variation with latitude*, Tellus, in press.

FINK, U., RANK, D. H. and WIGGINS, T. Q. (1965), *Abundance of methane in the earth's atmosphere*, Techn. Rept. on Office of Naval Research Contract NONR-656 (12), NR 014-401, Penn. State University, University Park, Pennsylvania, U.S.A.

GREINER, N. R. (1970), *Hydroxyl radical kinetics by kinetic spectroscopy, VI. Reactions with alkanes in the range 300–500K*, J. Chem. Phys. *53*, 1070–1076.

HEIDT, L. E. and POLLOCK, W. H. (1976), *Measurements of* N_2O, CH_4, H_2, CO *and* CO_2 *in the non urban troposphere*. Proceedings Symp. on 'The Non-Urban Tropospheric Composition' Hollywood, Florida, U.S.A.

HITCHCOCK, D. R. and WECHSLER, A. E. (1972), *Biological cycling of atmospheric trace gases*, Final rept, NASW-2128, 117–154.

HOWARD, D. L., FREA, J. I. and PFISTER, P. M. (1971), *The potential for methanecarbon cycling in Lake Erie*, Proc. 14th Conf. Great Lakes Res. Int. Assoc., Great Lakes Research, pp. 236–240.

HUTCHINSON, G. E. (1948), *Circular casual systems in ecology*, Ann. New York Acad. Sci. *50*, 221.

HUTCHINSON, G. E., *The biochemistry of the terrestrial atmosphere*. In: *The Solar System; II. The Earth as a Planet* (G. P. Kniper, ed), (Chicago Press, 1954), pp. 371–433.

HUTCHINSON, G. E., *A Treatise on Limnology* (New York, John Wiley, 1957), pp. 631–632.

KOYAMA, T. (1963), *Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen*, J. Geophys. Res. *68*, 3971–3973.

KOYAMA, T., *Biogeochemical studies on lake sediments and paddy soils and the production of atmospheric methane and hydrogen*, In: *Recent Researches in the Field of Hydrosphere, Atmosphere and Nuclear Geochemistry* (Y. Miyake and T. Koyama, eds.), (Marucen, Tokyo, 1964), pp. 143–177.

LAMONTAGNE, R. A., SWINNERTON, J. W., LINNENBOM, V. J. and SMITH, W. D. (1973), *Methane concentrations in various marine environments*, J. Geophys. Res. *78*, 5317–5324.

LAMONTAGNE, R. A., SWINNERTON, J. W. and LINNENBOM, V. J. (1974), C_1–C_4 *hydrocarbons in the north and south pacific*, Tellus *26*, 71–77.

LEVY, H. (1971), *Normal atmosphere: large radical and formaldehyde concentrations predicted*, Science *173*, 141–143.

LIBBY, W. F. (1973), Private communication.

LISS, P. S. and SLATER, P. G. (1974), *Flux of gases across the air–sea interface*, Nature *247*, 181–184.

MCCONNELL, J. C., MCELROY, M. B. and WOFSY, S. C. (1971), *Natural sources of atmospheric CO*, Nature *223*, 187–188.

MIGEOTTE, M. V. (1948), *Spectroscopic evidence of methane in the earth's atmosphere*, Phys. Rev. *73*, 519–520.

PERNER, D., EHHALT, D. H., PÄTZ, H. W., PLATT, U., RÖTH, E. P. and VOLZ, A. (1976), *OH-radicals in the lower troposphere*, Geophys. Res. Letters *3*, 466–468.

ROSSOLIMO, L. (1935), *Die Bodengasausscheidung und das Sauerstoffregime der Seen*, Verh. Int. Ver. Limnol, *7*, 539–561.

SEILER, W. and SCHMIDT, U., *Dissolved nonconservative gases in seawater*, in: *The Sea*, Vol. V (E. D. Goldberg, ed.), (Wiley, New York, 1974), pp. 219–243.

SVENSSON, B. H. (1973), *Production of Methane and Carbon Dioxide from a subarctic Mire*, Tech. Rep. 16 Swedish Tundra Biome Project.

SVENSSON, B. H., VEUM, A. K. and KJELVIK, S., *Carbon losses from Tundra Soils*, in: *Ecological Studies. Analysis and Synthesis, 16* (F. E. Wielgolaski, ed.), (Springer Verlag, Berlin, Heidelberg, New York, 1975).

SVERDRUP, H. U., JOHNSON, M. W. and FLEMING, R. H. (1961), *The Oceans, their Physics, Chemistry and General Biology* (Prentice Hall, Englewood Cliffs, N.J., 1961), p. 21.

SWINNERTON, J. W. and LINNENBOM, V. J. (1967), *Gaseous hydrocarbons in sea water: determination*, Science *156*, 119–120.

SWINNERTON, J. W., LINNENBOM, V. J. and CHECK, C. H. (1969), *Distribution of methane and carbon monoxide between the atmosphere and natural waters*, Environ. Sci. Tech. *3*, 836.

TWENHOFEL, W. H., *Principles of Sedimentation* (McGraw-Hill, New York, 1951), p. 78.

UNITED NATIONS FOOD AND AGRICULTURAL ORGANIZATION (1971a), Monthly Bulletin of Agricultural Economics and Statistics, *20*: 6, 18.

UNITED NATIONS FOOD AND AGRICULTURAL ORGANIZATION (1971b), Monthly Bulletin of Agricultural Economics and Statistics, *20*: 9, 20.

UNITED NATIONS FOOD AND AGRICULTURAL ORGANIZATION (1970), *Production Yearbook*, p. 335.

UNITED STATES DEPARTMENT OF AGRICULTURE (1971), *Agricultural Statistics*, Washington, D.C., Government Printing Office.

VOLZ, A., EHHALT, D. H., HEIDT, L. E. and POLLOCK, W. (1976), *Vertical profiles of* CH_4, CO *and* CO_2 *in the stratosphere*, Proc. Joint Symposium on Atmospheric Ozone (IAOC/ICACGP), Dresden, GDR.

WANG, C. C., DAVIS, L. I., WU, C. H. and JAPAR, S. (1976), *Laser-induced dissociation of ozone and resonance fluorescence of OH in ambient air*, Appl. Phys. Letters *28*, 14–16.

WARNECK, P. (1975), *OH production rates in the troposphere*, Planet. Space Sci. *23*, 1507–1518.

WHITTAKER, R. H. (1971), *Communities and Ecosystems*, New York, The MacMillan Company, p. 84.

WOFSY, S. C. (1976), *Interactions of* CH_4 *and* CO *in the Earth's atmosphere*, Atm. Rev. Earth Planet. Sci. *4*, 441–469.

WOODWELL, G. M. (1970), *The energy cycle of the biosphere*, Sci. Am. *223*, 64–74.

YAMAMOTO, S., ALCAUSKAS, J. B. and CROZIER, T. E. (1976), *Solubility of methane in distilled water and seawater*, J. Chem. Eng. Data *21*, 78–80.

(Received 29th July 1977)