Measurements of methane in the troposphere and lower stratosphere

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ABSTRACT

Two profiles of air samples have been collected over Southern U.S.A. (30° N latitude) between ground level and 23 km and analysed for methane. The results show, with increasing altitude, a mixing ratio nearly constant to the tropopause and decreasing rapidly in the lower stratosphere. The results suggest that the troposphere is the major region of destruction of methane.

Introduction

Atmospheric methane is produced at the surface of the earth by biological reactions, and by industrial and geochemical processes. No known chemical reactions in the atmosphere can produce it, and its mode of destruction in the atmosphere is not yet determined. Determinations of atmospheric methane concentrations have been made in total air columns (GOLDBERG, 1951, GOLDBERG & MULLER, 1953; MIGOETTE, 1948; FINK *et al.*, 1964) and in surface air (SHAW, 1959; BOWMAN & SHAW, 1963) by optical spectroscopy. Attempts have been made to determine the methane mixing ratio as a function of altitude by measurements of total adsorbtion made at various angles of the sun; but, since most of the methane is in the lower atmosphere, vertical variations of concentration are difficult to determine by this method.

Atmospheric methane has four principal isotopic forms involving C^{13}, C^{14}, H^2 and H^3 (GLUEKAUF, 1951; BAINBRIDGE *et al.*, 1961; BISHOP *et al.*, 1962; BEGEMANN, 1963). The C^{14}/C^{12} ratios indicate that more than 75 % of the methane is produced by contemporary biological reactions while the remainder must be from fossil sources such as oil fields and volcanoes. This is in fair agreement with the rough estimates of KOYAMA (1963). However, the tritium content of atmospheric methane is 100–1000 times higher than the ground water from which the hydrogen in the methane is derived. Highest concentrations of CH_3T were found in the northern troposphere, indicating this to be the source region. The limited amount of data available as a function of time led MARTELL (1963) to propose atmospheric chemical reactions between methane compounds and tritiated molecular hydrogen, but as more experimental data became available (BEGEMANN, 1963) it was not clear that this mechanism was necessarily correct. The reactions proposed by Martell, however, suggest that the geochemistry of methane is a complex subject warranting further investigation. The present study is a part of a general survey of the variations of methane in the atmosphere.

Experimental

A gas sampling device, consisting of eight evacuated bottles (< 1 μ Hg residual pressure) which could be connected in turn to a sampling manifold by a rotary valve, was constructed in such a way that it would be carried to altitude either by a balloon or by an aircraft. Prior to opening the bottles to the atmosphere, the manifold was flushed about 20 times with ambient air by a small pump, and the residual pressure (if any) in the bottles was measured by thermocouple gauges. The bottles were constructed by welding the mouths of two 2 liter stainless steel beakers together. An inlet to this bottle was provided by a 0.63 cm ($\frac{1}{4}$ inch) outer diameter spigot and a small instrument type valve was used to isolate the bottles from the sampler. The material used was stainless steel.

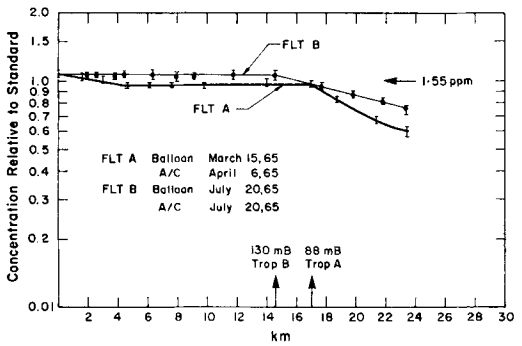

FIG. 1. Methane concentration as a function of altitude. Samples were collected from aircraft (below 9 km) and by balloon borne equipment. The sampling locations were in East Texas and Western Louisiana, U.S.A.

Sampling Details

On 15 March 1965 the gas sampler was installed on a balloon gondola to obtain a profile of air samples in the vicinity of Louisiana. The balloon was launched from the NCAR station in Palestine, East Texas. It ascended to a height of 24 kilometers where the surface of the balloon was allowed to degas for two hours. The balloon and gondola was then commanded to descend and samples were collected at selected altitudes between 24 and 9 km. The gondola was suspended 200 meters below the balloon, and the gas inlet was located a further 10 meters below. This long train was constructed in order to minimize the amount of contamination that could be carried from the troposphere adsorbed on the balloon and which could subsequently be released and collected by the sampling system.

The first balloon trajectory was approximately due east and the cutdown occurred in the vicinity of the Mississippi River. On 6 April 1965 a second profile of samples below 9 kilometers were collected aboard the National Center for Atmospheric Research "Queen Air" aircraft. The sampling line was located above the cabin of the aircraft in a region of free flow as previously determined by pitot tube measurements. Six samples were collected at intervals of approximately 1700 meters over Louisiana.

On 20 June 1965 both the balloon and the aircraft flights were repeated except that the location of the profiles was over central Texas, 150 kilometers south of Dallas.

Results

Samples were analyzed for methane, neon, oxygen and nitrogen by a gas chromatographic technique to be published elsewhere. The concentrations of the latter three gases in all samples were the same as in ground level air to within the experimental error of 2 %. The results of the methane analyses are given in Figure 1.

In the first profile in the troposphere the concentration decreased from ground level to 4.5 km, but above this it remained constant to the tropopause. The stratospheric data show a decreasing mixing ratio with height which can be represented, to a good approximation, by an exponential relationship which decreased to 1/e of the initial value with an increase in altitude of 14.1 km. The second profile shows similar effects except that there was no statistically significant gradient at the lower level. The gradient in the stratosphere can be approximated to an exponential decrease with height, but in this case the distance for a 1/e decrease is 22 km.

By integrating the first and second profiles an abundance of 3.2×10^{19} and 3.4×10^{19} molecules of methane per square centimeter, respectively, are obtained, consistent with results obtained by GOLDBERG (1951) by optical spectroscopy over Michigan during the spring of 1950.

The vertical wind velocity was estimated to be 0.75 cm sec^{-1} for the second profile. For the first profile the value is uncertain (P. Julian, private communication).

Discussion

The lower troposphere

Between ground level and 4.5 km the concentration in flight A decreased from 1.60 ± 0.03 to 1.46 ± 0.03 ppmv, but did not change with altitude in flight B. Differences between the two flights show that the system is not in steady state, but such changes coupled with comprehensive wind and temperature data suggest that it may be possible to determine the average methane production rate over extended areas of the earth's surface.

The upper troposphere

Within the error of the measurements the methane concentration is constant between 4.5 km and the tropopause for both flights, showing that the region is well mixed without large sources or sinks. For the two profiles the total methane in the troposphere remains constant as the average height of the tropopause shifts. Since the average mixing ratio in flight B is higher than in flight A, then either the production increased or the destruction rate decreased between the time of the two flights. If the profiles are representative of the whole of the troposphere then thunderstorms, which occur mainly in the summer, as one source of energy for the destructive reactions of methane (MARTELL, 1963) does not seem to be likely. On the other hand, the biological production during the summer should also be at a maximum and so the problem remains unresolved.

The tropopause

Near the tropopause for flight A the methane gradient is -5.4×10^{-13} g g^{-1} cm^{-1} and K is about 2×10^{3} cm^{2} sec^{-1}, but decreases with height. At the tropopause (88 mB) then the transport in the vertical direction by eddy diffusion alone is (BOLIN, 1962) equal to 4.8×10^{-6} g cm^{-2} yr^{-1}. The gradient for flight B is -3.1×10^{-13} g g^{-1} cm^{-1} and this is equivalent to a transport by eddy diffusion at the tropopause (130 mB) of 4.2×10^{-6} g cm^{-2} yr^{-1}. Thus the transport of methane across the tropopause is about the same for each flight and is much less than the production estimated by Koyama indicating that the troposphere may be the major region for sinks of methane.

The lower stratosphere

The variations of the methane in this region can best be discussed using the following equation (BOLIN, 1962):

$$\partial q/\partial t + V \cdot \nabla q - (1/\varrho)\nabla \cdot (K\varrho \nabla q) - P + \lambda q = 0, \quad (1)$$

where q = mixing ratio (g g^{-1})
= 16 C/29
C = concentration (ppmv)
V = instantaneous wind vector (cm sec^{-1})
ϱ = density (g cm^{-3})
P = production rate (g g^{-1} sec^{-1})
λ = destruction rate (sec^{-1}) assumed to be first order
K = eddy diffusion coefficient (g cm^{-2} sec^{-1})

The first term accounts for the local time variations, the second and third terms for transport due to advection and eddy diffusion and the fourth and fifth terms for the chemical sources and sinks.

Below 25 kilometers K is decreasing with altitude (LETTAU, 1951). Thus it can be shown from the data in Table 1 that both vertical tranport terms (equation 1) and the variation of concentration with time are negative. No data on the possible chemical reaction (BATES & WITHERSPOON, 1952; ALTSHULLER, 1951; CADLE & ALLEN, 1965) could be found which would result in any significant production or destruction of methane in this region. Thus in order to balance equation 1 the horizontal components of the transport must be significant. If the net zonal transport is zero for trace substances (BOLIN, 1962) then the methane must be moving in a meridional plane, possibly in a similar manner as ozone (CRAIG, 1965).

Conclusions

Samples of air collected up to altitudes of 23 km show the mixing ratio of methane to decrease systematically. The tropopause ap-

TABLE 1. *Summary of Analytical Data.*

Date	March 15, 1965	April 6, 1965	July 20, 1965
Tropopause level	88 mB	90 mB	130 mB
Concentration at			
Ground level		1.60 ± 0.03	1.60 ± 0.03
4.5 km		1.46 ± 0.03	1.60 ± 0.03
Upper Troposphere	1.46 ± 0.03		1.60 ± 0.03
24 km	1.05 ± 0.03		1.31 ± 0.03
Stratosphere Vertical Wind			0.75 cm sec^{-1}

pears to be the altitude at which the most significant changes occur. With the limited amount of meteorological and geochemical data available it is more likely that the decrease is caused by horizontal rather than vertical motion at the sampling location.

The transfer of methane across the tropopause is less than 10 % of the production estimates of KOYAMA (1963) and if this is taken as a global average it would indicate that the major region of destruction is in the troposphere. Significant changes in the troposphere also support this contention.

Several geochemical parameters critical to understanding the behavior of methane, especially its mode of production and destruction, are still not known. Of major importance is the effectiveness of bacteria as sources and sinks.

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REFERENCES

ALTSHULLER, A. P. (1951) "Natural sources of gaseous pollutants in the atmosphere". *Tellus*, **10**, 479–492.

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

BATES, D. R., and WITHERSPOON, A. E. (1952) "The photochemistry of some minor constituents of the atmosphere". *Monthly Notices of the Royal Astronomical Society*, **112**, 101–124.

BEGEMANN, F. (1963) "Tritium determinations in atmospheric gases and meteorites". *Final Report AF 61(052)-465 Air Force Cambridge Research Laboratories*, O.A.R.

BISHOP, K. F., DELAFIELD, H. J., EGGLETON, A. E. J., PEABODY, C. O., and TAYLOR, B. T. (1962) "The tritium content of atmospheric methane". *Tritium in the Physical and Biological Science*, I.A.E.A., Vienna, 55–62.

BOLIN, B. R. (1962) "Transfer and circulation of radioactivity in the atmosphere". *Nuclear Radiation in Geophysics* (H. Israel and A. Krebs, eds.) New York, Academic Press, 136–168.

BOWMAN, R. L., and SHAW, J. H. (1963) "The abundance of nitrous oxide, methane, and carbon monoxide in ground-level air". *Applied Optics*, **2**, 176.

CADLE, R. D., and ALLEN, E. R. (1965) "Kinetics of the reaction of $O(^3P)$ with methane in oxygen, nitrogen and argon mixtures". *J. Phys. Chem.*, **69**, 1611.

CRAIG, R. A. (1965) *The Upper Atmosphere, Meteorology and Physics*. New York and London, Academic Press.

FINK, U., RANK, D. H., and WIGGINS, T. A. (1964) "Abundance of methane in the earth's atmosphere". *J. Optical Soc. of Am.*, **54**, 572–574.

GLUEKAUF, E. (1951) *Compendium of Meteorology* (T. F. Malone, ed.). Boston, American Meteorological Society, 5–6.

GOLDBERG, L. (1951) "The abundance and vertical distribution of methane in the earth's atmosphere". *Astrophys. J.*, **113**, 567–582.

GOLDBERG, L., and MULLER, E. A. (1953) "The vertical distribution of nitrous oxide and methane in the earth's atmosphere". *J. Optical Soc. of Am.*, **43**, 1033–1036.

KOYAMA, T. (1963) "Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen". *J. Geophys. Res.*, **68**, 2971–2974.

LETTAU, H. (1951) *Compendium of Meteorology* (T. F. Malone, ed.). Boston, American Meteorological Soc., 320–333.

MARTELL, E. A. (1963) "On the inventory of artificial tritium and its occurrence in atmospheric hydrogen". *J. Geophys. Res.*, **68**, 3759–3769.

MIGEOTTE, M. V. (1948) "Spectroscopic evidence of methane in the earth's atmosphere". *Phys. Rev.*, **73**, 1948–1949 A.

SHAW, J. H. (1959) "A determination of the abundance of nitrous oxide, carbon monoxide and methane in ground level air at several locations near Columbus, Ohio". *Rept. AF* 19(604)-2259, *Air Force Cambridge Research Laboratories*.

ИЗМЕРЕНИЕ МЕТАНА В ТРОПОСФЕРЕ И НИЖНЕЙ СТРАТОСФЕРЕ

Получены два профиля проб воздуха над южной частью США (30° с. ш.) от уровня земли до 23 км. Анализируется содержание метана в пробах. Результаты показывают, что с увеличением высоты отношение смеси почти постоянно, вплоть до тропопаузы, и быстро убывает в нижней стратосфере. Результаты заставляют предположить, что тропосфера является основной областью распада метана.