Possible Variations in Atmospheric Methane

W. L. CHAMEIDES

Department of Physics and Astronomy, University of Florida
Gainesville, Florida 32611

S. C. LIU AND R. J. CICERONE

Department of Atmospheric and Oceanic Sciences, University of Michigan
Ann Arbor, Michigan 48109

A model coupling photochemistry and vertical transport in the troposphere has been used to investigate the magnitude of possible future perturbations to atmospheric CH₄. We have studied the response of atmospheric CH₄ to an increase in the concentration of CO or to a variation in stratospheric O₃. Both of the above mechanisms, which could be caused by man's activities, arise because a change in the concentration of tropospheric OH will lead to a change in the CH₄ abundance. Our calculations imply that a perturbation of ~30-40% in atmospheric CH₄ could occur if stratospheric O₃ were perturbed by 10% or if man-made CO continued to increase. The possible consequences of a CH₄ perturbation may entail a perturbation in stratospheric photochemistry or in the thermal balance of the atmosphere.

INTRODUCTION

Atmospheric CH₄ is produced at the earth's surface primarily by biological fermentation in anaerobic environments such as swamps, tropical rain forests, and paddy fields [Koyama, 1963]. Tropospheric CH₄ is characterized by a well-mixed profile with a vertically constant mixing ratio of 1.4 ppm [Ehhalt et al., 1974]. Studies of the flux of CH₄ from various soil types imply a global production rate of the order of 10¹¹ CH₄ molecules cm⁻² s⁻¹ (420 Mt yr⁻¹ (420 million metric tons per year)) [Koyama, 1963; Baker-Blocker et al., 1977] and thus a CH₄ atmospheric residence time of about 10 years.

The major sink of CH₄ is photochemical destruction via oxidation by OH [Levy, 1971]:

\[ CH₄ + OH \rightarrow CH₃ + H₂O \]  (1)

Calculations indicate that owing to destruction by reaction (1) in the troposphere, less than 10% of the CH₄ produced at the earth's surface enters the stratosphere. Note also that the oxidation of methane initiates a long series of reactions, known as the methane oxidation chain, which is believed to be a large source of tropospheric H₂ and CO and which may also play a major role in controlling the abundance of tropospheric ozone [Levy, 1972; Wofsy et al., 1973; Crutzen, 1973, 1974a, Chameides and Walker, 1975, 1974a]. There is, however, a possibility that the methane oxidation chain does not lead to CO exclusively; instead, the direct evolution of CO may result, depending upon several formyl radical reaction paths (H. Niki, private communication, 1976).

The tropospheric CH₄ abundance is determined by a balance between biological production at the ground, transport upward, and destruction by reaction (1). In the steady state the CH₄ continuity equation may be written as

\[ 0 = -d/dz F(z) - k_n n(OH)n(CH₄) \]  (2)

where \( F \) is the vertical methane flux, \( n \) is the number density, and \( k_n \) is the rate coefficient for reaction (1), and we assume no net horizontal transport. Integrating (2) from \( z = 0 \) to \( z = z_{tp} \), the tropopause, we obtain

\[ F(0) - F(z_{tp}) = \int_{0}^{z_{tp}} [n(OH)n(CH₄)k_n] dz \]  (3)

Copyright © 1977 by the American Geophysical Union.

Paper number 6C0917.
According to (4) a decrease in the concentration of OH would lead to an increase in atmospheric CH$_4$. A major sink of tropospheric OH is believed to be reaction with atmospheric CO [Weinstock, 1969; Crutzen, 1974a; Wofsy, 1976]:

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$$

(5)

Thus an increase in CO could lead to an increase in tropospheric CH$_4$ by causing a decrease in the OH abundance. Atmospheric CO is produced in nature via the CH$_4$ oxidation chain [McCormick et al., 1971] at a rate of about $1 \times 10^{10}$ CO molecules cm$^{-2}$ s$^{-1}$ according to our one-dimensional model calculations. While isotope data have been interpreted to indicate that at least 80% of the CO present in the atmosphere is produced by natural degradation of CH$_4$ [Stevens et al., 1972], other evidence implies a much larger role for anthropogenic CO sources, as was discussed by Wofsy [1976]. Measurements indicate that approximately 3 times as much CO is present in the northern hemisphere, where anthropogenic CO production is largest, as is present in the southern hemisphere [Seller, 1974]. Our model calculations, similar to the two-dimensional calculations of Wofsy [1976], indicate that in the southern hemisphere, with an average CO mixing ratio of 0.06 ppm, an approximate balance exists between CO production via CH$_4$ oxidation and CO destruction by reaction (1). In the northern hemisphere, however, with an average CO abundance of 0.15 ppm, a large imbalance was calculated between production and loss, possibly indicating the importance of anthropogenic CO production. For an average global CO mixing ratio of about 0.11 ppm we calculated a CO column destruction rate of $2.1 \times 10^{10}$ cm$^{-2}$ s$^{-1}$ (1530 Mt yr$^{-1}$) and a CO production rate via CH$_4$ oxidation of $1 \times 10^{10}$ cm$^{-2}$ s$^{-1}$ (730 Mt yr$^{-1}$). Since it is estimated that other natural CO sources produce about $3 \times 10^{9}$ cm$^{-2}$ s$^{-1}$ (220 Mt yr$^{-1}$) [Seller, 1974], this result implies that anthropogenic activities could produce as much as $8 \times 10^{8}$ cm$^{-2}$ s$^{-1}$ (580 Mt yr$^{-1}$), or about 40% of the total CO production. This conclusion is supported by Seller’s [1974] estimate that anthropogenic CO sources produce about $9 \times 10^{9}$ cm$^{-2}$ s$^{-1}$ (640 Mt yr$^{-1}$). If we included CO soil sink of about $6 \times 10^{9}$ cm$^{-2}$ s$^{-1}$ (450 Mt yr$^{-1}$), as extrapolated from laboratory experiments and reported by Seller [1974], an additional CO source would be needed, although in the southern hemisphere a soil sink of $2 \times 10^{9}$ cm$^{-2}$ s$^{-1}$, or 30% of the soil sink, would not cause a significant imbalance in the southern hemispheric CO budget. However, as Seller [1974] points out, since the uptake of CO by soils depends upon the CO density above the soil, the soil temperature, and the type of soil, the global uptake rate extrapolated from laboratory data is highly uncertain.

While further research is needed to determine more accurately the role of anthropogenic activities in the CO budget, models based on our present understanding of tropospheric photochemistry indicate that anthropogenic CO has already begun to perturb the atmosphere, and its effect will likely increase if anthropogenic CO production continues to grow. For instance, we calculated about 20% less OH in the northern hemisphere than in the southern hemisphere under present-day conditions owing to the enhanced CO concentration in the northern hemisphere, results similar to those of Wofsy [1976]. Since OH acts as a scavenger of many trace gases (e.g., NO$_x$, SO$_x$, NH$_x$, CH$_x$Cl), this diminution could be indicative of a serious problem.

As was discussed above, one likely effect of a decreasing OH density is an increase in atmospheric CH$_4$. The results of model calculations which determined the dependence of $X_{CH_4}$, the equilibrium CH$_4$ abundance, upon FCO, the non-CH$_4$ CO source strength, and upon time, where we assumed that FCO = $3 \times 10^{10} + 8 \times 10^{9}(1.045)^{-t/976}$ cm$^{-2}$ s$^{-1}$ and $X_{CH_4} = 1.4$ ppm represent present-day conditions. These results confirm that as FCO increases, thereby increasing CO and decreasing OH, the CH$_4$ abundance increases. Also illustrated in Figure 1 is the variation of $X_{CH_4}$ with time, where we assumed an anthropogenic production rate of $8 \times 10^{9}$ cm$^{-2}$ s$^{-1}$ in 1976 and an annual increase of 4.5%, similar to that of CO$_2$ [Broecker et al., 1971]. Given these assumptions, the photochemical model predicts that by the year 2000 the steady state CH$_4$ abundance will have increased by almost 40%. Of course, improved pollution control devices and/or a switch from fossil fuel burning to alternative power sources could slow the anthropogenic production of CO and thereby lessen a perturbation to atmospheric CH$_4$. In fact, pollution control in the United States has probably already slowed the global anthropogenic production of CO [Jaffe, 1973]. It is also possible that the CO abundance increases, the magnitude of the soil sink for CO will also increase, thereby moderating the effect of anthropogenic activities. Finally, it is possible that future increases in anthropogenic NO$_x$ emissions may also perturb OH levels and thus affect the CH$_4$ abundance. However, if CO production continues to grow, a significant increase in atmospheric CH$_4$ may result in the coming decades. Further measurements, especially of CO, CH$_4$, and OH, are needed to understand further the relationship between anthropogenic CO and atmospheric CH$_4$.

**Stratospheric O$_3$ and Atmospheric CH$_4$**

Chameides and Walker [1975] have pointed out that a change in stratospheric O$_3$ can lead to significant perturbations in CH$_4$ by causing a change in the tropospheric OH density. The primary source of tropospheric OH radicals is believed to be the photodissociation of O$_3$ by radiation of wavelengths shorter than about 3100 Å, producing excited oxygen atoms:

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

(6)
4.2 \times 10^6 to 4.6 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}. Table 1 illustrates the calculated predict an approximate 30% decrease in $X_c$, if a 10% decrease 

Similarly, by changing $f(O_3)(11 \text{ km})$, the $O_3$ mixing ratio at 11 kin, from $1.30 \times 10^{-7}$ to $1.65 \times 10^{-7}$ and keeping $N(O_3)$ con-

tant we obtained an increase in the $O(D)$ production from $4.2 \times 10^6$ to $4.8 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$. 

Our calculations indicate that a 30-40% perturbation in atmospheric CH$_4$ may occur in the coming decades. The effects of a CH$_4$ perturbation are not clear, and further research is needed to understand fully the consequences of such a perturbation. Model calculations of the effects of CH$_4$ upon stratospheric O$_3$ are conflicting. The findings of Liu et al. [1976] and Rao-Vupputuri [1974] imply that an increase in CH$_4$ will result in a decrease in stratospheric O$_3$, while Crutzen [1971] and McElroy et al. [1974] apparently find the opposite effect. A careful reexamination of the importance of stratospheric CH$_4$ as an odd hydrogen source and of the photochemical role of odd hydrogen in the lower stratosphere is necessary to clarify this discrepancy.

Another possible consequence of a CH$_4$ variation is a perturbation to the thermal equilibrium of the atmosphere. Wang et al. [1976] have found that the infrared absorption bands of CH$_4$ in the 7- to 14-μm spectral region contribute to the atmospheric greenhouse effect. Their calculations using a one-dimensional radiative-convective model imply that a 0.3K increase in surface temperature will result from doubling the CH$_4$ concentration. Thus a 30-40% perturbation in atmospheric CH$_4$ could have a significant climatic impact. Further calculations are necessary to establish more accurately the magnitude and nature of this climatic effect.

It is interesting to note that other long-lived species, such as H$_2$, CH$_3$Cl, CHFCl$_2$, and CHF$_2$Cl, which are attacked by OH in the troposphere, should undergo variations similar to those discussed for CH$_4$. These variations are particularly significant in the case of the Cl-containing molecules, since they may affect stratospheric O$_3$ [cf. Cicerone et al., 1975].

In view of the remaining gaps in our understanding of the tropospheric photochemical system, large uncertainties are associated with our results, and our predictions should therefore be taken as rough estimates of possible future trends. In order to better understand tropospheric photochemistry and therefore the magnitude of future perturbations to atmospheric CH$_4$, further observational and theoretical research is necessary. A global program for measurement of OH, odd nitrogen, and CO levels is of primary importance.

**Acknowledgment.** This research was supported in part by the National Aeronautics and Space Administration under grant NSF-1363.

**REFERENCES**

Baker-Blocker, A., T. M. Donahue, and K. H. Mancy, Methane flux from wetlands areas, *Tellus*, in press, 1977.

Broecker, W. S., Y.-H. Li, and T.-H. Peng, Carbon dioxide—Man's unseen artifact, in *Impingement of Man on the Oceans*, edited by D. W. Houghton, pp. 287-324, John Wiley, New York, 1971.
Chameides, W. L., and D. H. Stedman, Tropospheric ozone: Coupling transport and photochemistry, J. Geophys. Res., 82, in press, 1977.
Chameides, W. L., and J. C. G. Walker, A photochemical theory of tropospheric ozone, J. Geophys. Res., 78, 8751–8760, 1973.
Chameides, W. L., and J. C. G. Walker, Stratospheric ozone: The possible effects of tropospheric-stratospheric feedback, Science, 190, 1294–1295, 1975.
Chameides, W. L., and J. C. G. Walker, A time-dependent photochemical model for ozone near the ground, J. Geophys. Res., 81, 413–420, 1976.
Cicerone, R. J., D. H. Stedman, and R. S. Stolarski, Estimate of late 1974 stratospheric concentration of gaseous chlorine compounds (CIX), Geophys. Res. Lett., 2, 219–222, 1975.
Crutzen, P. J., Ozone production in an oxygen-hydrogen-nitrogen oxide atmosphere, J. Geophys. Res., 76, 7311–7333, 1971.
Crutzen, P. J., Gas-phase nitrogen and methane chemistry in the atmosphere, in Physics and Chemistry of the Upper Atmosphere, edited by B. M. McCormac, D. Reidel, Dordrecht, Netherlands, 1973.
Crutzen, P. J., Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air, Tellus, 26, 47–57, 1974a.
Crutzen, P. J., A review of upper atmospheric photochemistry, Can. J. Chem., 52, 1569–1581, 1974b.
Ehhalt, D. H., L. E. Heidt, R. H. Lueb, and N. Roper, Vertical profiles of CH₄, H₂, CO, N₂O, and CO₂ in the stratosphere, Proceedings of the Third Conference on CIAP, Rep. DOT-TSC-OST-74-15, pp. 390–402, U.S. Dep. of Transp., Washington, D. C., 1974.
Jaffe, L. S., Carbon monoxide in the biosphere: Sources, distribution, and concentration, J. Geophys. Res., 78, 5293–5305, 1973.
Koyama, T., Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen, J. Geophys. Res., 68, 3971–3973, 1963.
Levy, H., Normal atmosphere: Large radical and formaldehyde concentrations predicted, Science, 173, 141–143, 1971.
Levy, H., Photochemistry of the lower troposphere, Planet. Space Sci., 20, 919–935, 1972.
Liu, S. C., T. M. Donahue, R. J. Cicerone, and W. L. Chameides, Effect of water vapor on the destruction of ozone in the stratosphere perturbed by CIX or NOₓ pollutants, J. Geophys Res., 81, 3111–3118, 1976.
McConnell, J. C., M. B. McElroy, and S. C. Wofsy, Natural sources of atmospheric CO, Nature, 235, 187–188, 1971.
McElroy, M. B., S. C. Wofsy, J. E. Penner, and J. C. McConnell, Atmospheric ozone: Possible impact of stratospheric aviation, J. Atmos. Sci., 31, 287–303, 1974.
Rao-Vuppaturi, R. K., A zonally averaged circulation model of the stratosphere incorporating radiative heating and ozone photochemistry in an oxygen-hydrogen-nitrogen atmosphere, Proceedings of the Third Conference on CIAP, Rep. DOT-TSC-OST-74-15, pp. 390–402, U.S. Dep. of Transp., Washington, D. C., 1974.
Seiler, W., The cycle of atmospheric CO, Tellus, 26, 116–135, 1974.
Stevens, C. M., L. Krout, D. Walling, and A. Venters, The isotopic composition of atmospheric carbon monoxide, Earth Planet. Sci. Lett., 16, 147–165, 1972.
Wang, W. C., Y. L. Yung, A. A. Lacs, T. Mo, and J. E. Hansen, Greenhouse effects due to anthropogenic perturbations, Science, 194, 685–690, 1976.
Weinstock, B., Carbon monoxide: Residence time in the atmosphere, Science, 166, 224–225, 1969.
Wofsy, S. C., Interactions of CH₄ and CO in the earth’s atmosphere, Annu. Rev. Earth Planet. Sci., 4, 1976.
Wofsy, S. C., J. C. McConnell, and M. B. McElroy, Atmospheric CH₄, CO, and CO₂, J. Geophys. Res., 77, 4477–4493, 1972.

(Received June 1, 1976; revised December 6, 1976; accepted December 6, 1976.)