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Possible Variations in Atmospheric Methane

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A model coupling photochemistry and vertical transport in the troposphere has been used to investigate the magnitude of possible future perturbations to atmospheric CH_4. We have studied the response of atmospheric CH_4 to an increase in the concentration of CO or to a variation in stratospheric O_3. 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 CH_4 abundance. Our calculations imply that a perturbation of ~30–40% in atmospheric CH_4 could occur if stratospheric O_3 were perturbed by 10% or if man-made CO continued to increase. The possible consequences of a CH_4 perturbation may entail a perturbation in stratospheric photochemistry or in the thermal balance of the atmosphere.

INTRODUCTION

Atmospheric CH_4 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 CH_4 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 CH_4 from various soil types imply a global production rate of the order of 10^{11} CH_4 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 CH_4 atmospheric residence time of about 10 years.

The major sink of CH_4 is photochemical destruction via oxidation by OH [*Levy*, 1971]:

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad . \tag{1}$$
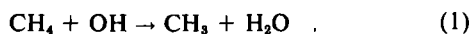
Calculations indicate that owing to destruction by reaction (1) in the troposphere, less than 10% of the CH_4 produced at the earth's surface enters the stratosphere. Note also that the oxidation of methane initiates a long series of reactions, known as the methane oxidation chain, which is believed to be a large source of tropospheric H_2 and CO and which may also play a major role in controlling the abundance of tropospheric ozone [*Levy*, 1972; *Wofsy et al.*, 1972; *Crutzen*, 1973, 1974a; *Chameides and Walker*, 1973, 1976]. There is, however, a possibility that the methane oxidation chain does not lead to CO exclusively; instead, the direct evolution of CO_2 may result, depending upon several formyl radical reaction paths (H. Niki, private communication, 1976).

The tropospheric CH_4 abundance is determined by a balance between biological production at the ground, transport upward, and destruction by reaction (1). In the steady state the CH_4 continuity equation may be written as

$$0 = -d/dz\, F(z) - k_1 n(OH) n(CH_4) \tag{2}$$

where F is the vertical methane flux, n is the number density, and k_1 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

$$F(0) - F(z_{tp}) = \int_0^{z_{tp}} [n(OH) n(CH_4) k_1]\, dz \tag{3}$$

where $F(z_{tp}) < 0.1 F(0)$. Since CH_4 has a constant mixing ratio, it follows from (3) that

$$X_{CH_4} = [F(0) - F(z_{tp})]/D \sim F(0)/D \tag{4}$$

where X_{CH_4} is the equilibrium CH_4 mixing ratio, and that

$$D = \int_0^{z_{tp}} n(OH) n_M k_1\, dz$$

where n_M is the background number density. Thus the tropospheric abundance of CH_4 is inversely proportional to the OH abundance.

As *Chameides and Walker* [1975] have pointed out, (4) implies that a perturbation in tropospheric OH will result in a change in the abundance of atmospheric CH_4. Since CH_4 takes part in several key stratospheric reactions [*Crutzen*, 1974b] and also contributes significantly to the atmospheric 'greenhouse effect' [*Wang et al.*, 1976], a perturbation in atmospheric CH_4 could result in perturbations to stratospheric O_3 and the thermal balance of the atmosphere. In this work, two possible causes of a perturbation to atmospheric CH_4 are investigated: an increase in the anthropogenic production rate of CO and a variation in stratospheric ozone. Both processes cause a change in tropospheric OH, which then results in a variation in CH_4. To determine the dependence of CH_4 upon these parameters, numerical calculations were made by using a steady state one-dimensional tropospheric model which couples photochemistry and transport, as described by *Chameides and Stedman* [1977] (their 'standard model'), with input data appropriate for 30°N latitude at equinox. In the calculations an iterative scheme with a 1% convergence test on all species was used to determine the mixing ratios of the long-lived gases, such as CH_4, as a function of stratospheric O_3 or anthropogenic CO, given a fixed flux condition at the earth's surface. Note that in these steady state calculations we calculated the equilibrium CH_4 abundance. Since CH_4 has a residence time of about 10 years, it would probably take a decade or so for CH_4 to adjust to its equilibrium value after a perturbation. We have also assumed that CH_4 is presently in equilibrium and that the CH_4 production rate is constant at 1×10^{11} cm^{-2} s^{-1}. Note also that in our model, for every CH_4 molecule oxidized, a CO molecule is produced.

ANTHROPOGENIC CO AND ATMOSPHERIC CH$_4$

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]:

$$CO + OH \rightarrow CO_2 + H \qquad (5)$$
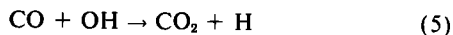
Thus an increase in CO could lead to an increase in tropospheric CH$_4$ by causing a decrease in the OH abundance. Atmospheric CO is produced in nature via the CH$_4$ oxidation chain [*McConnell et al.*, 1971] at a rate of about 1×10^{11} CO molecules cm^{-2} s^{-1} according to our one-dimensional model 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 [*Seiler*, 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 2.1×10^{11} cm^{-2} s^{-1} (1530 Mt yr^{-1}) and a CO production rate via CH$_4$ oxidation of 1×10^{11} cm^{-2} s^{-1} (730 Mt yr^{-1}) Since it is estimated that other natural CO sources produce about 3×10^{10} cm^{-2} s^{-1} (220 Mt yr^{-1}) [*Seiler*, 1974], this result implies that anthropogenic activities could produce as much as 8×10^{10} cm^{-2} s^{-1} (580 Mt yr^{-1}), or about 40% of the total CO production. This conclusion is supported by *Seiler*'s [1974] estimate that anthropogenic CO sources produce about 9×10^{10} cm^{-2} s^{-1} (640 Mt yr^{-1}). If we included a CO soil sink of about 6×10^{10} cm^{-2} s^{-1} (450 Mt yr^{-1}), as extrapolated from laboratory experiments and reported by *Seiler* [1974], an additional CO source would be needed, although in the southern hemisphere a soil sink of 2×10^{10} cm^{-2} s^{-1}, or 30% of the total sink, would not cause a significant imbalance in the southern hemispheric CO budget. However, as *Seiler* [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$_3$, CH$_3$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
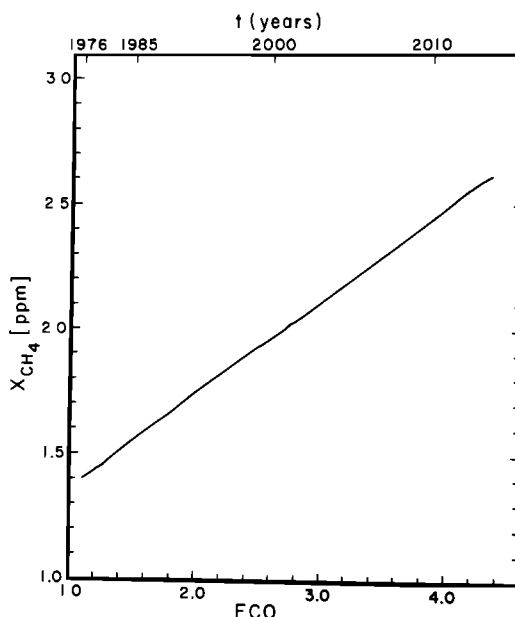

Fig. 1. The dependence of X_{CH_4}, the equilibrium CH$_4$ abundance, upon *F*CO, the non-CH$_4$ CO source strength, and upon time, where we assumed that $FCO = 3 \times 10^{10} + 8 \times 10^{10}(1.045)^{t-1976}$ cm^{-2} s^{-1}; i.e., the anthropogenic production rate is presently 8×10^{10} cm^{-2} s^{-1} and is increasing at an annual rate of 4.5%.

model calculations which determined the dependence of X_{CH_4} upon *F*CO, the non-CH$_4$ CO source strength, are presented in Figure 1, where $FCO = 1.1 \times 10^{11}$ cm^{-2} s^{-1} and $X_{CH_4} = 1.4$ ppm represent present-day conditions. These results confirm that as *F*CO 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 8×10^{10} 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 as 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:
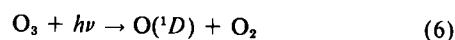
$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (6)$$

TABLE 1. The Equilibrium CH_4 Mixing Ratio, X_{CH_4} (ppm vol/vol), as a Function of $N(O_3)$ and $f(O_3)(11$ km)

O_3 Mixing Ratio at 11 km, $f(O_3)(11$ km)	Value of the O_3 Column Above 10 km, $N(O_3)$, cm^{-2}				
	7×10^{18}	8×10^{18}	9×10^{18}	10×10^{18}	11×10^{18}
6.5×10^{-8}	1.2	1.5	1.8	2.1	2.5
9.5×10^{-8}	1.1	1.3	1.6	1.9	2.3
1.3×10^{-7}	0.96	1.2	1.4*	1.7	2.0
1.65×10^{-7}	0.84	1.0	1.2	1.5	1.7
2.0×10^{-7}	0.74	0.90	1.1	1.3	1.5

*Present-day conditions are given by $N(O_3)$ = 9×10^{18} cm^{-2}, $f(O_3)(11$ km) = 1.3×10^{-7}, and X_{CH_4} = 1.4 ppm.

followed by

$$H_2O + O(^1D) \rightarrow 2OH \qquad (7)$$
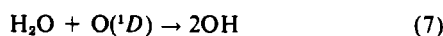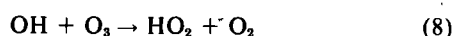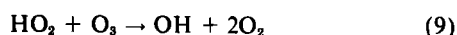
[*Levy*, 1971].

Since the $O(^1D)$ density can be altered either by changing the flux of near-UV radiation or by changing the local O_3 density, a perturbation to stratospheric O_3 can affect the OH and therefore also the CH_4 tropospheric abundance in two ways: by changing the flux of near-UV radiation penetrating the tropopause and by changing the O_3 density in the lower stratosphere and thus the injection rate of stratospheric O_3 into the troposphere. (Note that in our model, approximately 60% of the ozone found in the troposphere originates in the stratosphere, the remainder being produced locally by photochemical processes [*Chameides and Stedman*, 1977].) For instance, for equinoctial conditions at 30°N near the ground we calculated that a change in $N(O_3)$, the ozone column above 10 km, from 9×10^{18} to 8×10^{18} cm^{-2} resulted in a change in the production of $O(^1D)$ from 4.2×10^6 to 4.8×10^6 cm^{-3} s^{-1}. Similarly, by changing $f(O_3)(11$ km), the O_3 mixing ratio at 11 km, from 1.30×10^{-7} to 1.65×10^{-7} and keeping $N(O_3)$ constant we obtained an increase in the $O(^1D)$ production from 4.2×10^6 to 4.6×10^6 cm^{-3} s^{-1}. Table 1 illustrates the calculated dependence of X_{CH_4} upon both $N(O_3)$ and $f(O_3)(11$ km). These results, which could be incorporated into stratospheric model calculations as a lower boundary condition upon CH_4, indicate that a significant CH_4 perturbation could result from a change in stratospheric O_3. For example, our calculations predict an approximate 30% decrease in X_{CH_4} if a 10% decrease in $N(O_3)$ is accompanied by a 25% increase in $f(O_3)(11$ km). Note that stratospheric model calculations predict that a decrease in $N(O_3)$ is generally accompanied by an increase in the ozone density near the tropopause due to photolytic healing. However, *Liu et al.* [1976] found the opposite effect when they used a combination of rate coefficients which maximized the odd hydrogen density in the lower stratosphere.

Since stratospheric CH_4, which originates in the troposphere, takes part in several key photochemical reactions, the possibility exists for feedback effects whereby an initial O_3 perturbation is reduced or enhanced by a subsequent variation in atmospheric CH_4. CH_4, as a source of stratospheric odd hydrogen via reactions (1) and (7), may act to increase or decrease stratospheric O_3 [*Crutzen*, 1971; *McElroy et al.*, 1974; *Rao-Vupputuri*, 1974; *Liu et al.*, 1976]. While reactions
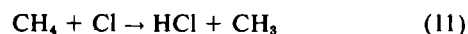
$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (8)$$

and

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (9)$$

act as an O_3 sink,

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad (10)$$

tends to enhance O_3 by removing an odd nitrogen molecule from the catalytic chain which destroys O_3. Similarly, in a stratosphere with chlorine, CH_4 can enhance O_3 by removing Cl from its catalytic O_3-destroying chain

$$CH_4 + Cl \rightarrow HCl + CH_3 \qquad (11)$$

Whether CH_4 acts to decrease or increase stratospheric O_3 and thus whether the system described above will stabilize or destabilize stratospheric O_3 depend upon the importance of reactions (8) and (9) relative to reactions (10) and (11). Further study, both in the laboratory and with numerical models, is needed to help clarify this point.

CONCLUSION

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 0.3°K 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_3Cl, $CHFCl_2$, and CHF_2Cl, 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.

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