Tellus (1989), *41B*, 554–559

SHORT CONTRIBUTION

Climate-induced feedbacks for the global cycles of methane and nitrous oxide

By M. A. K. KHALIL and R. A. RASMUSSEN, *Institute of Atmospheric Sciences, Oregon Graduate Center, Beaverton, Oregon 97006, USA*

(Manuscript received 5 August 1988; in final form 20 December 1988)

ABSTRACT

Recent experiments have shown that the concentrations of methane dipped to between 300 and 350 ppbv during the ice ages some 20,000 and 150,000 years ago. Our data, spanning more recent times, show a proportionate decrease of methane (38 ± 19 ppbv) and also a decrease of nitrous oxide (about 6 ± 4 ppbv) during the little ice age between 1450 and 1750 AD. We believe that these decreases are a measure of the response of emissions from the earth's soils, oceans, and wetlands to global climatic change. In the future, as the earth warms from increasing levels of carbon dioxide, methane, nitrous oxide, and other trace gases, these feedbacks may produce more and more methane and nitrous oxide. Melting of the upper layers of permafrost in the high arctic could add still more methane and nitrous oxide to the atmosphere. The combination of the response of wetlands and permafrost may add as much or more methane and nitrous oxide to the atmosphere as expected from the increasing anthropogenic sources. Since adding methane is about 20 times more effective in increasing global temperatures as adding equal amounts of carbon dioxide, and nitrous oxide is perhaps more than 200 times as effective, even small increases in the emissions of these gases could be amplified into large effects on the earth's temperature and climate. The global warming that has apparently occurred over the past century may already have produced about 20% of the increase of nitrous oxide between the pre-industrial times and the present.

It is estimated that in the future, the build-up of long-lived trace gases, particularly methane, nitrous oxide, and the chlorofluorocarbons CCl_3F (F-11) and CCl_2F_2 (F-12), will cause a global warming as great as or perhaps even greater than expected from the increasing levels of carbon dioxide (Lacis et al., 1981; Ramanathan et al., 1985). Whether such a warming will occur depends on the ultimate atmospheric levels of these trace gases. By extrapolating emissions from the present anthropogenic sources, we can estimate the concentrations of CH_4 and N_2O in the years and decades to come. There is, however, a complicating factor: if the earth warms up, the large natural sources of CH_4 and N_2O in the soils, wetlands, and the oceans may emit more and more of these gases as biological productivity increases. This positive feedback could add considerable amounts of methane and nitrous oxide to the atmosphere by affecting the natural sources and may already be responsible for some of the increases being observed.

Recently, Stauffer et al. (1988) and Raynaud et al. (1988) have shown that concentrations of methane dipped to between 300 and 350 ppbv during the major ice ages some 20,000 years ago and 150,000 years ago. The concentrations during the warm periods, until a few centuries ago, had been between 650–750 ppbv (Rasmussen and Khalil, 1984; Stauffer et al., 1985). Now, methane concentrations exceed 1650 ppbv (Rasmussen and Khalil, 1986). Reports of the low concentrations of methane found during ice ages prompted us to re-analyze our methane and

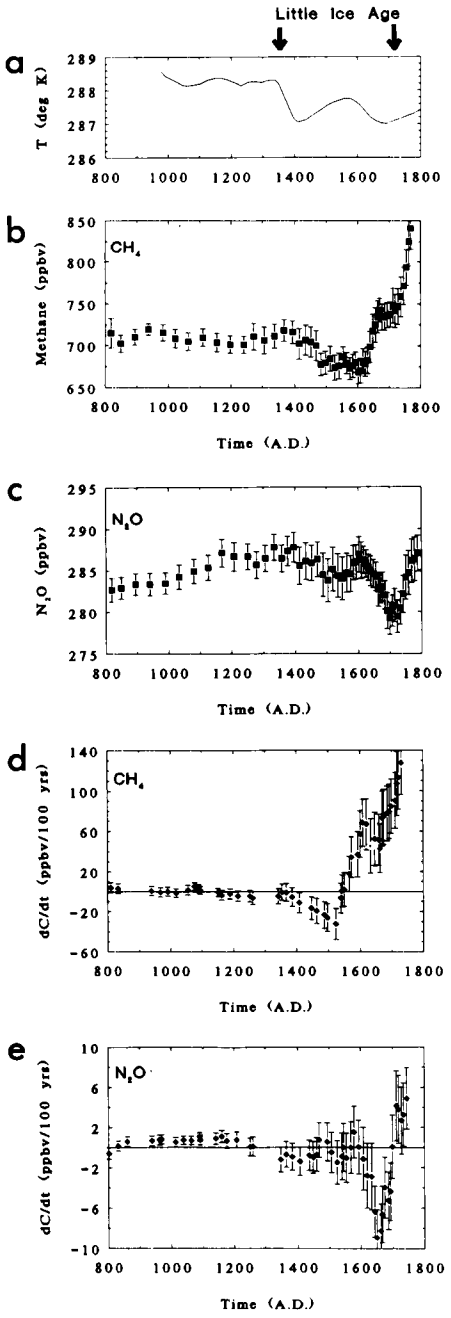

Fig. 1. (a) Estimated average northern hemisphere temperature around the little ice age (digitized from Watts, 1982). Smoothed concentration of (b) methane and (c) nitrous oxide in parts per billion by volume (ppbv). The cycle of methane may have been significantly affected by human activities after the rapid growth of population starting in the 17th century, thus compensating for the declining concentrations induced by the little ice age. In panels (d) and (e) the rate of change of methane and ntirous oxide are shown in ppbv/century ($\pm$ are estimates of 90% confidence limits). These panels reflect the imbalance of sources and sinks during the little ice age.

nitrous oxide data obtained from ice cores (Rasmussen and Khalil, 1984; Khalil and Rasmussen, 1988). Fortuitously, nearly half our measurements lie within the time of the little ice age, which lasted from about 1450 to 1850 AD (Fig. 1a) (Watts, 1982; Griffiths and Driscoll, 1982; Schneider and Londer, 1984).

We had 65 data between 400–1850 AD. We chose the simplest methods to look for the patterns in the data. A couple of data with high methane concentrations were suspected of being contaminated and were eliminated. The remaining uncertainties (all $\pm$ values) are reported as 90% confidence limits.

First, we corrected the methane data for the inter-hemispheric gradient of about 10% (Rasmussen and Khalil, 1984) by increasing concentrations from Antarctic cores by 5% and decreasing concentrations from Arctic cores by 5%. No correction was made to the nitrous oxide data. Then we took moving averages over each successive 9 data points and plotted these average concentrations at the average ages in Figs. 1b and 1c. Next we estimated the rates of change over each 20 points and plotted them in Figs. 1d and 1e at the middle of the times spanned by the 20 measurements in each series. The rates of change (dC/dt) are a direct measure of the imbalance between sources (S) and sinks (C/τ; τ = lifetime) of CH_4 and N_2O. Both these analyses show that the atmospheric levels of CH_4 and N_2O fell during the little ice age, corroborating the recent work on CH_4 during the major ice ages and showing the first evidence that atmospheric N_2O also responds to global temperature changes.

We analyzed the data to see whether the concentrations of nitrous oxide and methane were significantly lower during the cool period of the little ice age compared to the warmer times before. For nitrous oxide, the data are not as definitive. The greatest change occurred between the times just before the little ice age (1200–1450 AD) when concentrations were 288 $\pm$ 3 ppbv com-

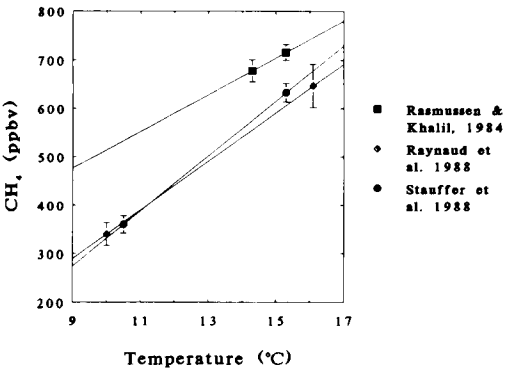

Fig. 2. Temperature and the concentration of methane. Data were corrected for the inter-hemispheric gradient during inter-glacial periods and during the little ice age but not during the major ice ages. The times represented by the three studies are very different. During the most recent times (past 2000 years or so) atmospheric concentrations of methane were probably higher than at earlier times as explained in the text.

pared with 281 ± 3 during the middle of the little ice age (1650 and 1750 AD). The change for nitrous oxide is 6 ± 4 ppbv. For methane we found that the average concentration between 800 AD and 1450 AD was 716 ± 16 ppbv and dipped to 678 ± 17 ppbv during the two hundred years of the little ice age between 1450 and 1659 AD. This corresponds to a change of 38 ± 18 ppbv.

A synthesis of all the methane data on the response of atmospheric concentrations to climatic changes is shown in Fig. 2. The temperatures, which reflect average conditions in the northern hemisphere, are taken from Watts (1982). Fig. 2 shows that the magnitude of the decrease in CH_4 with decreasing temperature is very similar in all three studies. The estimated change dC/dT, in ppbv/K, and its uncertainties are 38 ± 19 (Rasmussen and Khalil, 1984), 57 ± 5 (Stauffer et al., 1988), and 50 ± 8 (Raynaud et al., 1988). The average response is about 48 ± 7 ppbv/K for methane. We are not able to assess all the potential errors, particularly those in estimating mean temperatures and potential errors in estimating the age of the air (see Schwander and Stauffer (1984)).

In Fig. 2, our measurements are somewhat higher than in the other two studies. It appears that the concentrations of methane in ice cores are higher over the past 2000 years compared with earlier times. It is not clear whether this represents an increase of atmospheric concentrations during recent pre-industrial times compared with earlier times, or an anomaly of ice core measurements. In the study of Stauffer et al. (1988) the two measurements representing the most recent times have a concentration of about 690 ppbv when corrected for the inter-hemispheric gradient, and the concentration in one sample from the D57 core reported by Raynaud et al. (1988) is about 680 ppbv when corrected for the inter-hemispheric gradient. Both these values are substantially higher than the average interglacial concentrations during earlier times which are 630 ppbv (Stauffer et al., 1988) and 620 ppbv (Raynaud et al., 1988). This 10% difference of concentrations during the past 2000 years compared with earlier times explains the systematically higher concentrations from our study shown in Fig. 2.

If the temperature at northern latitudes has risen by 0.5–1°K (Hansen and Lebedeff, 1987; Lachenbruch and Marshall, 1986) during the past century, then the feedback may already have contributed to the increased levels of CH_4 and N_2O. For methane this feedback would add about 50 ppbv, which is a small effect compared with the observed increase of about 900 ppbv over the last century. For N_2O, the net increase over the last 100 years has been only about 22 ppbv; therefore, the contribution from the climate-induced feedback may be of the order of 20%.

The declining concentration of methane during the little ice age was offset by growing anthropogenic sources. Concentrations started increasing rapidly after the middle of the 17th century AD, overtaking the declines caused by the climate feedback of the cooling earth. This increase from 1650 AD onward was probably caused by the rapid population growth and the simultaneous increases in cattle populations and rice production. Between 1650 and 1850 human population is estimated to have doubled, from 0.5 billion to 1 billion, a very fast increase compared with earlier times (Ehrlich et al., 1977). The concentrations of N_2O would not be much affected by this population growth since it would not be produced in large quantities by the agricultural practices of the time. In recent years, the increase

of N_2O has been attributed primarily to burning of fossil fuels and present use of nitrogen fertilizers (Weiss, 1981; Khalil and Rasmussen, 1983; Hao et al., 1987; Khalil and Rasmussen, 1988).

The reduced concentrations of N_2O and CH_4 are most probably related to the changes in the emission rates from the various ecosystems but may also be caused by possible changes in the atmospheric lifetimes. The change of concentration going from a steady-state in the warmer times to a steady-state at the cooler temperatures of an ice age is written as in eq. (1):

$$\Delta C/\Delta T = \tau_0 \Delta S/\Delta T + S_1 \Delta\tau/\Delta T, \quad (1)$$

where C is the global burden (g), T is the temperature (K), τ_0 is the lifetime in years during the warm period, and S_1 are the global emissions during the ice age (g/yr). S is the change of emissions between the warm periods and the ice ages, and τ is the change of atmospheric lifetime, which, for methane, could be caused by changing levels of OH radicals. We believe that changing sources are likely to be the main cause of the lowered concentrations of methane and N_2O ($\Delta\tau/\Delta T \sim 0$). For methane the sources most affected would be the natural wetlands, many located at high northern latitudes where the effects of past and future climate changes are likely to be the greatest. However, most other sources of CH_4 are also likely to be affected similarly by climatic changes. Warmer temperatures would increase biological activity leading to a greater production of methane in the wetlands and of N_2O from the soils. Cooling would have the opposite effect. Based on the estimates of $\Delta C/\Delta T$ given above, the response of the sources, primarily in the wetlands, that can explain the reduced concentrations of methane would be about 15 Tg/yr $- K$, taking the lifetime to be about 7 years. Similarly, the response of N_2O emissions, primarily from the soils and oceans, would be 0.5 Tg/yr $- K$, taking the lifetime to be 100 years. During the ice ages the high northern wetland sources of CH_4 may have been almost shut off.

Since reaction with OH radicals is the main mechanism for removing methane from the atmosphere, it is possible that some of the decrease during ice ages may have been caused by changes in the atmospheric OH concentrations and distributions. Hydroxyl radicals are produced when sunlight splits O_3 molecules into O_2 and excited $O(^1D)$ atoms. The $O(^1D)$ then react with water vapor to produce two OH molecules. The production of OH is balanced by reactions with CO and CH_4, and with other reactive hydrocarbons. In the atmosphere, undisturbed by human activities, plants and the oxidation of hydrocarbons, including methane, are the largest natural sources of CO as summarized by Logan et al. (1981), and Gammon et al. (1985). As the sources of CO and CH_4 start to shut down during the ice ages, the removal of OH would decrease; however, we speculate the production of OH may also decrease because of less water vapor and O_3 during the ice ages. CH_4, other hydrocarbons, and CO affect tropospheric O_3, and the earth's temperature affects water vapor. The competition between changes in production and destruction processes may cause OH concentrations to remain nearly constant or change very little. This reasoning, though speculative, suggests that the concentrations of OH radicals may be stable even though the climate may change. For instance, in the past century, CH_4 has doubled, and it is very likely that so has CO. Yet the concentrations of OH have probably declined by only a few % ($\leqslant 20\%$) (Khalil and Rasmussen, 1985; Levine et al., 1985; Thompson and Cicerone, 1986).

Although the various studies of CH_4 during ice ages are internally consistent, it is still impossible to accurately estimate the effect of these feedbacks for a much warmer earth in the future. It is likely that the increases of fluxes from the wetlands and other sources are non-linear and accelerate at warmer temperatures (Baker-Blocker et al., 1977), while the data we have is for a cool earth during ice ages. If the major middle and high northern latitude wetlands freeze, further cooling would not affect the fluxes of CH_4 during ice ages. The limits on the production of CH_4 and N_2O for a hotter earth are not known. Moreover, in a warmer earth, new feedbacks may be triggered that have no analogues in the ice ages.

For instance, besides the feedback from the wetland ecosystems, the cycles of both CH_4 and N_2O can also be greatly affected by the melting of the permafrost in the high arctic. Bell (1982) estimated that for a 10K increase of temperature at high latitudes, which can occur from a doubling of CO_2, some 300 Tg/yr of methane could be released from permafrost for a very long time. He did say, however, that this estimate

"... could be as much as a factor of 10 in error." Such a feedback could increase atmospheric concentrations by 800–1000 ppbv, assuming OH levels remain stable. If it occurs, concentrations of CH_4 may increase well beyond the levels expected just from the increasing anthropogenic sources. Moreover, we have found high concentrations of N_2O in permafrost, but the data are not yet sufficient to estimate the potential increase of N_2O if permafrost melts.

The climatic effects of even small increases of CH_4 and N_2O in the future can be substantial because at the present and expected concentrations, molecule for molecule, methane is about 20 times more effective than CO_2 for increasing the earth's temperature, and N_2O is 200 times more effective (based on the results in Lacis et al., 1981; Wang and Molner, 1985; Ramanathan et al., 1985). Moreover, for N_2O, because of its long lifetime of about 100 years, even a small increase in emission rate can lead to a slow but large increase in atmospheric concentration.

It appears that although many uncertainties remain, the recent data on trace gases during ice ages are beginning to provide some measure of the feedbacks connecting emissions from the earth's ecosystems to climate change.

Acknowledgements

This work was supported in part by grants from the National Science Foundation (#DPP-8207470, #ATM-8414020), Department of Energy (#DE-FG06-85ER6031), and the National Aeronautics and Space Administration (#NAGW-280). Additional support was provided by the Biospherics Research Corp. and the Andarz Co.

REFERENCES

Baker-Blocker, A., Donahue, T. M. and Mancy, K. H. 1977. Methane flux from wetland areas. *Tellus 29*, 245–250.

Bell, P. R. 1982. Methane hydrate and the carbon dioxide question. In: *Carbon dioxide review: 1982* (ed. W. C. Clark). Oxford: Univ. Press, 401–406.

Ehrlich, P. R., Ehrlich, A. H. and Holdren, J. P. 1977. *Ecoscience: Population, resources, environment*. N.Y.: W. H. Freeman, 181–246.

Gammon, R., Wofsy, S. C., Cicerone, R. J., Delany, A. C., Harriss, R. T., Khalil, M. A. K., Logan, J. A., Midgeley, P. and Prather, M. J. 1985. Tropospheric trace gases. In: *Atmospheric Ozone: 1985* (World Meteorological Organization—GORAM project: report No. 16, Geneva), pp. 57–116.

Griffiths, J. F. and Driscoll, D. M. 1982. *Survey of climatology*. Columbus: Charles E. Merrill Publishing Co., 247–270.

Hansen, J. and Lebedeff, S. 1987. Global trends of measured surface air temperature. *J. Geophys. Res. 92*, 13345–13372.

Hao, W. M., Wofsy, S. C., McElroy, M. B., Beers, J. M. and Togan, M. A. 1987. Sources of atmospheric nitrous oxide from combustion. *J. Geophys. Res. 92*, 3098–3104.

Khalil, M. A. K. and Rasmussen, R. A. 1983. Increase and seasonal cycles of nitrous oxide in the Earth's atmosphere. *Tellus 35B*, 161–169.

Khalil, M. A. K. and Rasmussen, R. A. 1985. Causes of increasing methane: depletion of hydroxyl radicals and the rise of emissions. *Atmos. Environ. 19*, 397–407.

Khalil, M. A. K. and Rasmussen, R. A. 1988. Nitrous oxide: trends and mass balance over the last 3000 years. *Ann. Glaciology 10*, 73–80.

Lachenbruch, A. H. and Marshall, B. V. 1986. Changing climate: geothermal evidence from permafrost in the Alaskan arctic. *Science 234*, 689–696.

Lacis, A., Hansen, J., Lee, P., Mitchell, T. and Lebedeff, S. 1981. Greenhouse effect of trace gases. *Geophys. Res. Lett. 8*, 1035–1038.

Levine, J. S., Rinsland, C. P. and Tenille, G. M. 1985. The photochemistry of methane and carbon monoxide in the troposphere in 1950 and 1985. *Nature 318*, 254–257.

Logan, J. A., Prather, M. J., Wofsy, S. C. and McElroy, M. B. 1981. Tropospheric chemistry: A global perspective. *J. Geophys. Res. 86*, 7210–7254.

Ramanathan, V., Cicerone, R. J., Singh, H. B. and Kiehl, J. T. 1985. Trace gas trends and their potential role in climate change. *J. Geophys. Res. 90*, 5547–5566.

Rasmussen, R. A. and Khalil, M. A. K. 1984. Atmospheric methane in the recent and ancient atmospheres: concentrations, trends, and interhemispheric gradient. *J. Geophys. Res. 89*, 11599–11605.

Rasmussen, R. A. and Khalil, M. A. K. 1986. Atmospheric trace gases: trends and distributions over the last decade. *Science 232*, 1623–1624.

Raynaud, D., Chappellaz, J., Barnola, J. M., Korotkevich, Y. S. and Lorius, C. 1988. Climatic and CH_4 cycle implications of glacial–interglacial CH_4 change in the Vostok ice core. *Nature 333*, 655–657.