The stability of tropospheric OH during ice ages, inter-glacial epochs and modern times

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ABSTRACT

Hydroxyl (OH) radicals remove many man-made and natural gases from the atmosphere and therefore play a key role in global tropospheric chemistry. Recent increases in CH_4 and CO have caused concern that the levels of OH may decrease, thus reducing the capacity of the atmosphere to remove and control man-made pollutants. We have calculated OH concentrations over a wide range of climatic conditions to examine its long term stability and to determine the major factors that may cause changes in its levels. We used a one-dimensional photochemical model, the concentrations of CH_4 and N_2O from polar ice cores and the current understanding of the sources and sinks of CO, NO_y and other gases involved in OH chemistry. We find that mean OH concentrations are stabilized against changes even though the climatic conditions and atmospheric trace gas composition change considerably between ice-ages, inter-glacial periods and the present. In these transitions, the more rapid destruction of OH from increased CH_4 and CO is compensated by increases in the production processes. Our calculations indicate that only a small part of the 5-fold increase of methane between the present and the peak of the last ice age, is due to changes in OH levels.

1. Introduction

Measurements of methane in ice cores taken at Dye 3, Greenland and Byrd Station in Antarctica indicate that atmospheric concentrations of CH_4 were about 350 ppbv during the Last Glacial Maximum (LGM) (about 18,000 yrs ago) and increased to 650 ppbv during the transition from glacial to inter-glacial conditions (Stauffer et al., 1988). The longer record from the Vostok ice core, which extends back to 160,000 years ago, indicates that CH_4 values during the penultimate glaciation (about 140,000 to 170,000 yrs B.P.) were also about 340 ppbv and in the following interglacial stage, rose to about 620 ppbv (Raynaud et al., 1988). In the last 300–400 years, methane concentrations have more than doubled to their current background level of about 1,650 ppbv (Khalil and Rasmussen 1982, 1985, 1987; Rasmussen and Khalil, 1984; Craig and Chou, 1982). Ice core measurements of N_2O show that pre-industrial

levels were about 285 ppbv and started increasing recently, perhaps after the turn of the century (Pearman et al., 1986; Khalil and Rasmussen, 1988). Concentrations during the LGM are still uncertain but were probably around 240 ± 30 ppbv (Khalil and Rasmussen, 1988).

The large changes observed for methane could be due to variations in its sources, which may be responding to increasing anthropogenic activities in recent centuries and changing climatic conditions, or in its loss processes or some combination of the two (Raynaud et al., 1988; Chappellaz et al., 1990). The dominant loss for methane is by reaction with OH radicals, whose variations in the past are largely unquantified. We will attempt to place constraints on possible variations in OH levels, thereby separating the contributions from sources and sinks in determining the observed increase in CH_4. Earlier estimates of the possible changes of OH due to anthropogenic activities were reported by Thompson and Cicerone (1986), Levine et al.

(1985) and Khalil and Rasmussen (1985). There are two new aspects included in this paper. First, we have extended the calculation of OH concentrations to the last ice age when atmospheric chemistry and climate are vastly different than at present. Second, and more importantly, we have included processes that increase production of OH in the transition from ice ages to inter-glacial periods and also in the transition from the clean pre-industrial atmosphere to the present atmosphere which is significantly affected by human activities. As discussed earlier by Khalil and Rasmussen (1989), increases in OH production rates caused by increases in ozone and water vapor may compensate partly the increased losses of OH from higher CO and CH_4 thus stabilizing OH concentrations during different climatic and environmental conditions. Consequently our present estimates suggest that during the last century, OH concentrations may have declined much less than previously calculated (see also Guthrie (1990)).

2. Calculations

We have used a one-dimensional photochemical model to estimate tropospheric O_3 and OH levels for three different cases corresponding to globally averaged conditions for the current atmosphere, the pre-industrial atmosphere (ca. 1850 A.D.) and the atmosphere during the last glacial maximum. The model extends from the surface to 80 km and uses absorption cross section and kinetic rate coefficient data from JPL 87–41 (Pinto et al., 1989). The effect of Rayleigh scattering on photolysis rates is treated using the method of Yung (1976). Boundary conditions for the major atmospheric trace gases at the surface are shown in Table 1 for the three cases. For most species the present concentrations were fixed according to globally averaged observations (CO, CH_4, H_2, N_2O and NO_y, or total reactive odd nitrogen species). For the pre-industrial and ice age atmospheres, surface values for CH_4 were set equal to 750 ppbv and 350 ppbv, respectively and N_2O concentrations were set equal to 285 and 235 ppbv based on the ice core data. The concentration of NO_y at the surface was taken to be 50 pptv, assuming that current background levels in the Southern Hemisphere can provide an analogue for the pre-

Table 1. *Calculated tropospheric hydroxyl radical and ozone concentrations during ice ages, inter-glacial epochs and modern times*

Concentrations of gases in ppbv:

	Modern	Pre-industrial	Ice age
CH_4	1650	750	350
N_2O	305	285	225
NO_y	0.1	0.05	0.05
CO	110	57	28
H_2	500	230	150

Calculated OH ($\times 10^{-5}$ molecules/cm^3) and O_3 (ppbv):

	Modern	Pre-industrial	Ice age
OH	9.2	9.6	11
O_3	22	14	12

industrial atmosphere. Ozone was calculated for all three time periods assuming a constant deposition velocity of 0.1 cm s^{-1} at the surface. For the pre industrial atmosphere, CO was calculated by imposing a flux at the lower boundary equal to the value calculated for the current atmosphere less 600 Tg yr^{-1} for the estimated emissions due to the combustion of wood and fossil fuels, (see review by Khalil and Rasmussen, 1990). For H_2, a deposition velocity of 10^{-3} cm/s was prescribed at the lower boundary. Because of the large uncertainties inherent in any attempt to characterize past emissions of trace gases, we also performed calculations to demonstrate the sensitivity of the results to assumptions made about the model inputs.

Temperature profiles for the modern and pre-industrial cases were taken from the midlatitude standard atmosphere. Relative humidity profiles for all cases were computed by the formulation given in Manabe and Wetherald (1967). For the construction of a nominal atmosphere during the LGM, we adopted globally averaged tropospheric temperatures 5°C lower than at present (Gates, 1976; Broccoli and Manabe, 1987).

Since no data for CO concentrations are available from ice cores, the construction of its global source during the LGM must rely on scaling current estimates of emissions. Surface temperatures of low and mid latitude continents were 5°–10° cooler than present, (Peterson et al., 1979), suggesting a substantial decline in non-methane hydrocarbon emissions from vegetation, if the temperature dependence found by Tingey (1981), is used. The contribution of natural forest fires as

a CO source could also have been much lower, because of the cooler temperatures. Pinto et al. (1983) have estimated potential CO sources from the oxidation of non methane hydrocarbons emitted by vegetation and biomass burning to be about 1300 Tg CO yr^{-1}. We removed 350 Tg yr^{-1} from this figure to estimate CO emissions during the last LGM. This figure roughly corresponds to a complete shut off of emissions from mid and high latitude vegetation during the LGM, while leaving tropical emissions alone. The production of CO from the oxidation of methane is also greatly reduced during the LGM. We have also lowered the value for the deposition velocity of H$_2$ during the last glacial maximum by 1/3, corresponding to a decrease in soil surface area due to the advance of the ice sheets.

We calculated upper limits on CO and H$_2$ levels during the LGM by imposing a zero flux for CO through the surface and a zero deposition velocity for H$_2$ at the surface. It should be noted, however, that this procedure will place somewhat extreme limits on their concentrations, since the existence

of CH$_4$ in the ice core record from the LGM does indicate the presence of biological activity, resulting in emissions of methane, at least.

3. Results

Calculated values for surface OH and ozone levels for the three major time periods outlined above are shown in Fig. 1 and in Table 1. The vertically averaged value for OH radicals, 6×10^5, we calculated for modern conditions is in good agreement with other analyses ($6-7 \times 10^5$), based on the seasonal behavior of tracers such as CH$_3$CCl$_3$ and ^{14}CO, see review by Altshuller (1989) and calculations by Lu (1990).

As can be seen, variations in surface OH levels are much smaller among the three cases, than the variations imposed in the concentrations of the major species, CH$_4$, CO and O$_3$. The effects of removing the surface fluxes of CO and H$_2$ result in an increase of the ice age OH value from about 1.1×10^6 to 1.5×10^6. In this case, because of the
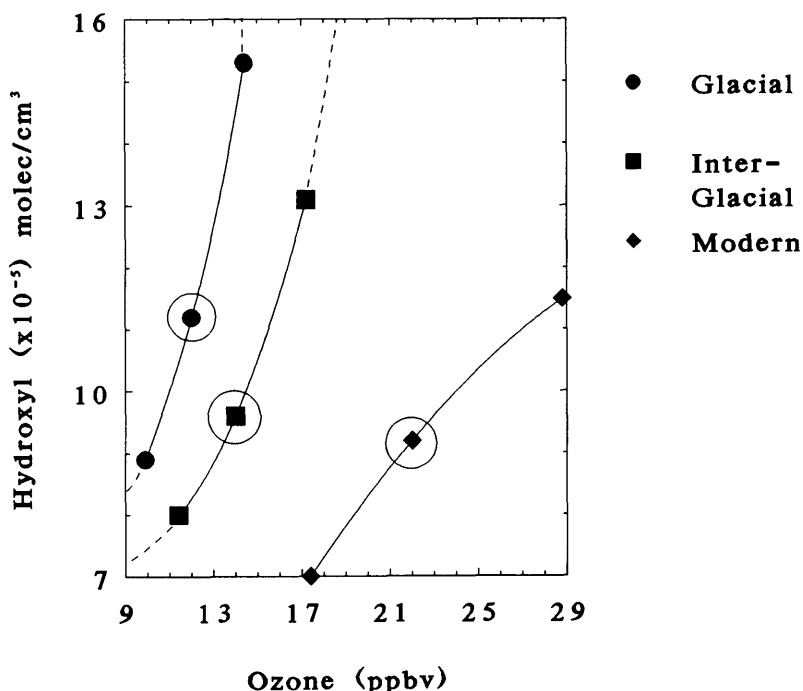

Fig. 1. Surface OH and O$_3$ values computed for the nominal modern, pre-industrial and ice age atmospheres. The sloping bars represent the effects of factor of two variations with respect to assumed background NO$_y$ levels. Central values were calculated for the conditions given in Table 1 and are circled.

lower concentrations of CO and H_2, the conversion of OH to HO_2 slows down. It should also be remembered that in addition to biogenic CO sources there are also soil emissions of NO which would also have been curtailed during the LGM resulting in a decreased rate of conversion of HO_2 back to OH radicals. The sloping lines in Fig. 1 demonstrate the sensitivity of the results to factor of two variations in assumed NO_y levels at the surface.

Because we have used a fixed profile of relative humidity to prescribe the vertical distribution of water vapor, changes in the temperature profile, as for instance from the transition between glacial and interglacial periods, result in changes in the water vapor mixing ratio through the Clausius–Clapeyron equation. Higher temperatures result in higher water vapor mixing ratios and higher production of OH radicals through the reaction

$$O(^1D) + H_2O \rightarrow OH + OH.$$
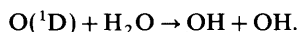
This water vapor temperature feedback operating by itself would tend to create higher OH levels during warm periods than during cold periods. However, the results shown in Fig. 1 do not reflect this behavior. Within our model framework, OH levels tend to be stabilized. There are two main reasons for the relative invariance in OH levels, we have calculated. First, variations in trace species tending to reduce OH levels (CH_4, CO) have been offset by variations in trace species tending to raise OH levels (odd-N, H_2O, O_3). Second, because of reactions such as $OH + HO_2$, a square root dependence for OH with respect to variations in either source or sink molecules can be derived which buffers the magnitude of OH variations. Additionally, during the LGM, a decrease in biological activity which lowers the input of CO to the atmosphere could also result in a drop in the microbial consumption of H_2. The combination of the two effects acts as a further buffer to changes in OH levels.

It was not possible to calculate joint radiative-photochemical equilibrium profiles for stratospheric ozone. Variations in the total ozone column between the three cases amounted to less than 2%, without thermal feedbacks. Their introduction would have led to even smaller changes. Since the other factors considered here have had a much larger effect on tropospheric chemistry than

the changes in stratospheric ozone calculated for the non-interactive case, this neglect should not affect our conclusions.

4. Discussion

Understanding past variations in NO_y abundances is of critical importance for determining the response of tropospheric ozone and OH to anthropogenic activities. The large calculated increase in surface ozone between the pre-industrial and modern atmosphere is the result of increases in NO_y levels from fossil fuel combustion along with simultaneous increases in CH_4 and CO. Surface ozone values calculated for the pre-industrial atmosphere are quite similar to the recently re-evaluated series of Montsouri measurements from the past century (Volz and Kley 1988) and to the calculated glacial value. In both these cases, the troposphere acts as a net sink for ozone transported downward from the stratosphere. The rather close agreement between model results, over a wide range of NO_y values, suggests that the Montsouris values may also have been representative of global conditions a century ago.

Historical variations in the concentrations of CO and CH_4 could have been driven in part by positive feedbacks involving OH levels. Examples include increasing anthropogenic emissions of CO which can convert OH to HO_2, resulting in increases in the concentration of CH_4. These effects have been included in our calculations. However, this sort of feedback must be viewed within the context of changing levels of numerous atmospheric species (see also Hameed et al. 1979; Levine et al. 1985; Thompson and Cicerone, 1986; Thompson et al., 1989). On the basis of changes in the concentrations of the trace species shown in Table 1, our results indicate that the large changes in methane concentrations observed in the ice core record (and in the atmosphere) between the three cases simulated, largely reflect changes in CH_4 emissions rates. While it is not yet possible to verify the predictions for CO, H_2, NO_x and O_3 levels, the wide range of values used to test the sensitivity of the results show that changes in OH levels could not have been large enough to explain the observed changes in methane between the present and the last glacial maximum, or even

between the pre-industrial atmosphere and the LGM.

On the other hand, it would be not be entirely accurate to completely neglect the possible role of OH variations in the past. As indicated by the results presented in Fig. 1, a small fraction of the 5-fold concentration difference in CH_4 between the present and the LGM can be attributed to changes in OH levels, using our atmospheric reconstructions. A stringent upper limit on OH can be obtained by using the ice age OH value calculated assuming zero fluxes of CO and H_2 through the surface. In this case, we find that no more than about 30% of the change in methane concentrations is due to changes in OH removal.

Ice core data for CO would be useful in reducing the uncertainties in calculations of tropospheric chemistry in the past. In addition, isotopic data for CH_4 may help identify the causes for the variation in its abundance between glacial and interglacial times. Nitrate measurements within shallow ice cores from Dye 3, South Greenland (Neftel et al.,

1985) are consistent with increases in global NO_x concentrations over the past century. However, a much longer record is needed for quantifying global NO_x levels and details of glacial to interglacial changes in the nitrogen cycle.

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REFERENCES

Altshuller, A. P. 1989. Ambient air hydroxyl radical concentrations: Measurements and model predictions. *J. Air Pollution Control Assoc. 39*, 704–708.

Broccoli, A. J. and Manabe, S. 1987. The influence of continental ice, atmospheric carbon dioxide, and land albedo on the climate of the last glacial maximum. *Climate Dynamics 1*, 87–99.

Chappellaz, J., Barnola, J. M., Raynaud, D., Korotkevich, Y. S. and Lorius, C. 1990. Ice-core record of atmospheric methane over the past 160,000 years. *Nature 345*, 127–131.

Craig, H. and Chou, C. C. 1982. Methane: Record in polar ice cores. *Geophys. Res. Lett. 9*, 1221–1224.

Gates, W. L. 1976. Modeling the ice-age climate. *Science 191*, 1138–1144.

Hameed, S., Pinto, J. P. and Stewart, R. W. 1979. Sensitivity of the predicted CO–OH–CH_4 perturbation to tropospheric NO_x concentrations. *J. Geophys. Res. 84*, 763–768.

Khalil, M. A. K. and Rasmussen, R. A. 1982. Secular trends of atmospheric methane. *Chemosphere 11*, 877–883.

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

Khalil, M. A. K. and Rasmussen, R. A. 1987. Atmospheric methane: trends over the last 10,000 years. *Atmos. Env. 21*, 2445–2452.

Khalil, M. A. K. and Rasmussen, R. A. 1988. Nitrous oxide: trends and global mass balance over the last 3,000 years. *Ann. of Glaciol. 10*, 73–79.

Khalil, M. A. K. and Rasmussen, R. A. 1990. The global cycle of carbon monoxide: Trends and mass balance. *Chemosphere 20*, 227–242.

Khalil, M. A. K. and Rasmussen, R. A. 1989. Climate induced feedbacks for the global cycles of methane and nitrous oxide. *Tellus 41B*, 554–559.

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.

Lu, Y. 1990. *Modeling tropospheric OH chemistry*. M.S. Thesis, Oregon Graduate Institute, Beaverton.

Manabe, S. and Wetherwald, R. T. 1967. Thermal equilibrium of the atmosphere with a given distribution of relative humidity. *J. Atmos. Sci. 24*, 241–259.

Neftel, A., Beer, J., Oeschger, H., Zurcher, F. and Rinkel, R. C. 1985. Sulphate and nitrate concentrations in snow from South Greenland. *Nature 314*, 611–613.

Pearman, G. I., Ethridge, D., deSilva, F. and Fraser, P. J. 1986. Evidence of changing concentrations of CO_2, N_2O and CH_4 from air bubbles in antarctic ice. *Nature 320*, 248–250.

Peterson, G. M., Webb III, T., Kutzbach, J. E., van der Hammen, T., Wijmstra, T. A. and Street, F. A. 1979. The continental record of environmental conditions at

18,000 yr B.P.: An initial evaluation. *Quat. Res. 12*, 47–82.

Pinto, J. P., Yung, Y. L., Rind, D., Russell, G. L., Lerner, J. A., Hansen, J. E. and Hameed, S. 1983. A general circulation model study of atmospheric carbon monoxide. *J. Geophys. Res. 88*, 3691–3702.

Pinto, J. P., Turco, R. P. and Toon, O. B. 1989. Self-limiting physical and chemical effects in volcanic eruption clouds. *J. Geophys. Res. 93*, 11165–11174.

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*, 11,599–11,605.

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

Stauffer, B., Lochbronner, E., Oeschger, H. and Schwander, J. 1988. Methane concentration in the glacial atmosphere was only half that of the pre-industrial Holocene. *Nature 332*, 812–814.

Tingey, D. T. 1981. The effect of environmental factors on the emission of biogenic hydrocarbons from live oak and slash pine. In: *Atmospheric biogenic hydrocarbons, vol. 1*, (Eds: J. J. Bufalini and R. R. Arnts), Ann Arbor Science, Ann Arbor, MI. pp 53–79.

Thompson, A. M. and Cicerone, R. J. 1986. Possible perturbations to atmospheric CO, CH_4, and CO. *J. Geophys. Res. 91*, 10853–10864.

Thompson, A. M., Stewart, R. W., Owens, M. A. and Herwehe, J. A. 1989. Sensitivity of tropospheric oxidants to global chemical and climate change. *Atmos. Env. 23*, 519–532.

Volz, A. and Kley, D. 1988. Evaluation of the Montsouris series of ozone measurements made in the nineteenth century. *Nature 332*, 240–242.

Yung, Y. L. 1976. A numerical method for calculating the mean intensity in an inhomogeneous Rayleigh scattering atmosphere. *J. Quant. Spectros. Radiat. Transfer 16*, 755–761.