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# The atmospheric CH<sub>4</sub> increase since the Last Glacial Maximum

## (2). Interactions with oxidants

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### ABSTRACT

Two studies of the effect of changing CH<sub>4</sub> fluxes on global tropospheric oxidant levels, O<sub>3</sub>, OH, H<sub>2</sub>O<sub>2</sub>, have been performed with a multi-box photochemical model. (1) A sensitivity study is made by scaling back CH<sub>4</sub>, CO and NO emissions relative to present-day budgets. When the CH<sub>4</sub> ice core record is compared to calculated CH<sub>4</sub> abundances, corresponding CH<sub>4</sub> fluxes for the pre-industrial Holocene (PIH) and Last Glacial Maximum (LGM) are fairly well-constrained: 175–225 Tg CH<sub>4</sub>/yr for PIH and 100–130 Tg CH<sub>4</sub>/yr for LGM. Except for OH at fluxes of 100–200 Tg CH<sub>4</sub>/yr, preindustrial oxidant concentrations levels are not narrowly defined by the CH<sub>4</sub> record. The small range of CH<sub>4</sub> flux and OH abundance at the LGM is due to strong CH<sub>4</sub>–OH feedbacks. (2) Specific scenarios for CH<sub>4</sub>/CO/NO are selected to represent sources for the PIH and LGM. The CH<sub>4</sub> budget is taken from an evaluation of wetlands and other natural sources. For CO and NO, apparent O<sub>3</sub> levels and ice-core-derived H<sub>2</sub>O<sub>2</sub> for the PIH are used to constrain PIH CO and NO fluxes. These fluxes are further scaled back to simulate the LGM, and perturbed temperature, precipitation and stratosphere-troposphere exchange are prescribed according to the GISS GCM. For the PIH changes for global abundance relative to present day are: 44% less O<sub>3</sub>; 20% more OH and 56% less H<sub>2</sub>O<sub>2</sub>. For the LGM, with 120 Tg CH<sub>4</sub>/yr and surface temperature 4–5 K lower than today, global changes are 56% less O<sub>3</sub>, 32% more OH and 59% less H<sub>2</sub>O<sub>2</sub>. Calculated preindustrial oxidant changes are in reasonable agreement with other studies based on one-, two- and three-dimensional models, although differences among model physics preclude a definitive comparison. There is consensus that OH has decreased since the Last Glacial Maximum, in contrast to projections for future OH, on which models are in disagreement. Model validation of oxidant concentrations requires more ice-core data. Preindustrial OH would be inferred best by using a model with ice-core measurements of species that are uncoupled from the CH<sub>4</sub>–CO–OH–O<sub>3</sub> cycle. Candidates might be marine gases of moderately long lifetime, e.g., CH<sub>3</sub>Cl or OCS.

### 1. Introduction

It is well-known that concentrations of the three principal oxidants in the Earth's atmosphere, O<sub>3</sub>, the hydroxyl radical (OH), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), are affected by changes in atmospheric levels of methane and other trace gases (Sze, 1977; Chameides et al., 1977; Thompson and Cicerone, 1986; Thompson et al., 1989). It is essential to

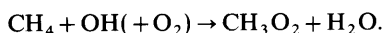
understand the past abundances of tropospheric oxidants in order to interpret changes in atmospheric chemical composition recorded in ice cores.

For example, it is known from analysis of ancient gas trapped in ice cores that the concentration of atmospheric CH<sub>4</sub> has increased greatly since the Last Glacial Maximum, roughly doubling from 18,000 years ago (18 KY BP, BP = Before Present) to the Early Holocene (9 KY BP), and more than doubling from the pre-industrial Holocene (700–200 years BP) to the present day (Rasmussen and Khalil, 1981, 1984; Craig and

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Chou, 1982; Pearman et al., 1986; Raynaud et al., 1988; Stauffer et al., 1985, 1988; Chappellaz et al., 1990). It is normally assumed that increases in CH<sub>4</sub> sources, driven by human influences are responsible for the CH<sub>4</sub> increase (Khalil and Rasmussen, 1985; Ehrlert, 1988). However, the lifetime of CH<sub>4</sub> may also be changing because the primary CH<sub>4</sub> sink, reaction with the OH radical,



is in turn a major sink for OH, making increases in CH<sub>4</sub> subject to a feedback effect. At the lower CH<sub>4</sub> levels associated with the Last Glacial Maximum, all other things being equal, OH would have been higher than at present, making the atmospheric lifetime of CH<sub>4</sub> shorter and reinforcing a tendency toward low CH<sub>4</sub> concentrations.

Recently Chappellaz et al. (1993) performed a detailed evaluation of methane fluxes from wetlands, the major natural CH<sub>4</sub> source, for the pre-industrial Holocene (PIH) and the Last Glacial Maximum (LGM, 18 KY BP). These and other CH<sub>4</sub>, CO and NO fluxes were used in a photochemical model to calculate atmospheric methane concentrations in good agreement with ice-core observations for these periods. From an evaluation of CH<sub>4</sub>-CO-OH-NO<sub>x</sub> feedbacks, it was concluded that 70% of the doubling of atmospheric CH<sub>4</sub> from the Last Glacial Maximum to the pre-industrial Holocene may have been caused by increasing CH<sub>4</sub> sources (mostly from wetlands), the rest by decreasing OH during that period.

In this paper, which is a companion to Chappellaz et al. (1993), we present model-computed concentrations of the oxidants, O<sub>3</sub>, OH and H<sub>2</sub>O<sub>2</sub>, based on estimates of CH<sub>4</sub>, CO and NO fluxes for the pre-Industrial Holocene and Last Glacial Maximum. Section 2 describes present-day oxidant levels and budgets for CH<sub>4</sub>, CO and NO, along with a sensitivity study of oxidant and CH<sub>4</sub> variations for reduced CH<sub>4</sub>, CO and NO fluxes. In Section 3 the ice-core records for CH<sub>4</sub>, HCHO and H<sub>2</sub>O<sub>2</sub> are used to prescribe more specific CH<sub>4</sub>, CO and NO emissions scenarios for the PIH and LGM. For the LGM, the model also simulates the effect of perturbed physical variables that can affect OH (temperature, precipitation, stratosphere-troposphere exchange). Section 4 compares the computed oxidant levels with other model studies of the PIH and LGM. In general, changes

in oxidant levels (relative to present-day) computed in this study agree qualitatively with those from other studies, although rigorous comparison is precluded by differences in model physics. In all cases, lack of preindustrial oxidant data is an obstacle to model validation.

## 2. Simulation of tropospheric composition at varying methane levels

### 2.1. Model description

A multi-box 1-dimensional photochemical model is used to simulate the trace gas chemistry of the troposphere (Thompson and Cicerone, 1986; Thompson et al., 1990). The model solves for 25 species: the standard complement of odd oxygen (O<sub>3</sub>, O(<sup>3</sup>P)); odd nitrogen (NO, NO<sub>2</sub>, NO<sub>3</sub>, HNO<sub>3</sub>, HO<sub>2</sub>NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>; odd hydrogen (H, OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>); stable carbon gases (CH<sub>4</sub>, CO, C<sub>2</sub>H<sub>6</sub>); and oxygenated hydrocarbons derived from CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub>CHO oxidation (CH<sub>3</sub>, CH<sub>3</sub>O<sub>2</sub>, CH<sub>3</sub>O, HCHO, CH<sub>3</sub>OOH, C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OOH, CH<sub>3</sub>CHO, CH<sub>3</sub>CO<sub>3</sub>, PAN (CH<sub>3</sub>CO<sub>3</sub>NO<sub>2</sub>)). The model domain spans 15 km with 24 altitude grid points; vertical transport is simulated by eddy diffusion. The kinetics scheme used in the model is described in Thompson and Cicerone (1982; 1986) with an updated rate coefficient for the reaction between CH<sub>4</sub> and OH taken from Vaghjiani and Ravishankara (1991). Only gas-phase reactions are considered except for the simulation of rainout for longer-lived gases (e.g., HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>) by a first-order scavenging coefficient. Heterogeneous removal of free radicals leading to O<sub>3</sub> formation may occur (Lelieveld and Crutzen, 1990), but is not included in this study.

A steady-state version of the model has been used for all simulations. This means that photochemical reaction rates are represented by diurnally averaged rates based on a time-dependent version of the model that exhibits 24-h periodic behavior (Thompson and Cicerone, 1982). When fluxes are reduced, as in sensitivity calculations or in the simulation of pre-industrial conditions, the steady-state model is used with the diurnally averaged rates computed for present-day conditions. Perturbed boundary conditions have also been run in a time-dependent version of the model to produce new diurnally averaged rates; the computed mixing ratios are virtually the same as with the original (unperturbed) rates.

Multiple boxes in the model permit specification of regionally varying emissions with non-interaction among the chemical species. Six regions are simulated, representing a range of mid- and low latitude environments, e.g., Northern Hemisphere urban and marine mid-latitudes, marine and continental low latitudes, Southern Hemisphere mid-latitude. The chemistry in the regions is initialized for 1990 ("present day") conditions by parameterizing fluxes of CH<sub>4</sub>, CO and NO to reproduce present-day surface mixing ratios of NO<sub>x</sub>, CO, CH<sub>4</sub>, and O<sub>3</sub> typical of each region. The 1990 CH<sub>4</sub>, CO and NO fluxes and surface concentrations of CH<sub>4</sub>, CO, NO, O<sub>3</sub>, OH and H<sub>2</sub>O<sub>2</sub> (both regional values and global means) are given in Table 1.

Global abundances are obtained by averaging over the six individual regions with area weights (Table 1). Total CH<sub>4</sub>, CO and NO budgets are given for the area of mid- and low latitude regions simulated (90% of the earth's area), scaled up to total Earth area. All three budgets are in good agreement with published budgets for CH<sub>4</sub>, CO (Seiler and Conrad, 1987; Khalil and Rasmussen,

1990) and NO (Logan, 1983, with updates). The CH<sub>4</sub> budget, 440 Tg CH<sub>4</sub>/yr, is near the low end of the commonly accepted range (400–600 Tg CH<sub>4</sub>/yr; Cicerone and Oremland, 1988; Khalil and Rasmussen, 1990 and references therein; Fung et al., 1991). The effects of omitting the highest latitude regions from explicit calculation can be estimated. No significant sources of CO and NO are usually assigned to these regions but adding 10% to the six-region budget does not put the CO and NO budgets beyond published limits; these are typically 30–50% uncertain. The effects of an additional 10% flux of CH<sub>4</sub>, CO or NO on O<sub>3</sub> and other oxidants are presumed small because photochemical rates of O<sub>3</sub> formation at high latitude conditions are slow. For CH<sub>4</sub>, the wetlands budget of Chappellaz et al. (1993) can be used to estimate the error in neglect of explicit high latitude sources. Assuming that CH<sub>4</sub> emissions scale with wetland area, and that wetlands are the only high-latitude CH<sub>4</sub> source, we calculate that emissions from Northern Hemisphere high-latitude wetlands account for 9% of the present-day CH<sub>4</sub> source. Thus, adding 10% to the six-

Table 1. Fluxes and mixing ratios for present day from 1-D multi-box model

Region	Area Weight %	Fluxes (cm <sup>-2</sup> s <sup>-1</sup> )			Mixing ratios (ppbv, 0 km)				Trop. column (cm <sup>-2</sup> ) (0–15 km)	
		NO	CO	CH <sub>4</sub>	CO	NO <sub>x</sub>	O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub>	OH
urban (NH) mid-lat.	3.7	1.3 (11)*	6.3 (11)	7.2 (10)	500	4.5	60	0.10	2.1 (18)	4.2 (11)
clean cont. mid-lat.	9.7	2.1 (10)	3.9 (11)	7.5 (10)	180	0.36	46	0.37	1.4 (18)	7.1 (11)
marine mid-lat.	7.7	5.1 (8)	1.0 (11)	3.3 (10)	100	0.023	25	0.28	8.1 (17)	4.2 (11)
marine low-lat.	32.9	1.2 (9)	1.1 (11)	1.2 (11)	70	0.030	16	0.64	6.3 (17)	1.1 (12)
cont. low-lat.	24.9	1.2 (10)	5.1 (11)	1.8 (11)	160	0.180	30	1.5	9.4 (17)	1.4 (12)
so. hem. mid-lat.	21.1	7.5 (8)	5.9 (10)	3.9 (10)	57	0.026	27	0.23	7.1 (17)	4.9 (11)
global average		1.01 (10)	2.5 (11)	1.1 (11)	120	0.26	27	0.68	8.7 (17)	9.3 (11)
total budget**		39 Tg N/yr	770 Tg C/yr	440 Tg CH <sub>4</sub> /yr	global mean CH <sub>4</sub> : 1.80 ppmv					

\* 1.3 (11) signifies  $1.3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ .

\*\* Six-region total scaled up by 10% to account for total Earth surface.

region total flux is a good estimate for the global CH<sub>4</sub> budget.

## 2.2. Sensitivity to CH<sub>4</sub>/CO/NO budget variations

In Chappellaz et al. (1993) CH<sub>4</sub> sources for pre-industrial conditions (800–200 years BP) are estimated at 190 Tg CH<sub>4</sub>/yr, ~40% those of today. To simulate the atmospheric consequences of reduced CH<sub>4</sub> emissions, the photochemical model is run with the 6-region CH<sub>4</sub> budget in 50 Tg CH<sub>4</sub>/yr decrements to a minimum source of 100 Tg/yr CH<sub>4</sub>. In performing these calculations, model fluxes in all regions are scaled back by the same fraction from present-day fluxes to give the specified total.

Methane mixing ratios are affected not only by changes in CH<sub>4</sub> emissions, but also by emissions of CO and NO, which determine O<sub>3</sub> and OH levels. Hence, the model is also used to calculate tropospheric composition with CO and NO budgets scaled back in decrements from present-day levels to a minimum of 1/8 present-day levels. For CO this means that emissions range from 800 Tg C (as CO)/yr for the six regions

(880 Tg C/yr globally), to 110 Tg C/yr globally. For NO the total source ranges from 44 Tg N/year globally to 5.5 Tg N/yr. For computations at a given level of CH<sub>4</sub> emissions, the CO and NO flux increments are covaried because CO and NO are both roughly half natural and half anthropogenic, with similar anthropogenic sources (combustion, biomass burning, soils, wood-burning). Strictly speaking, covariance of CO and NO sources is not physically realistic because lightning is a natural source only for NO, ~10–15% of the present-day budget and up to 50% of the pre-industrial NO budget. However, the assumed covariance has little effect on analysis of CH<sub>4</sub> sensitivity to CH<sub>4</sub>–NO–CO flux variations or on the selection of realistic PIH and LGM fluxes for these gases.

The calculations are made for a wide spectrum of CH<sub>4</sub>–CO–NO fluxes. For example, a model run is made with 110 Tg/yr CH<sub>4</sub> input with NO and CO at maximum fluxes, 110 Tg CH<sub>4</sub> with 7/8 maximum CO and NO fluxes and so on, down to 110 Tg CH<sub>4</sub> with 1/8 maximum CO and NO fluxes. The results for CH<sub>4</sub> mixing ratio variation as a function of global CH<sub>4</sub> flux are given in Fig. 1. Fig. 2 displays tropospheric O<sub>3</sub>, OH and H<sub>2</sub>O<sub>2</sub> abundances for the CH<sub>4</sub>/CO/NO flux variations shown in Fig. 1. The tendency toward increasing

## MODEL CALCULATED CH<sub>4</sub>

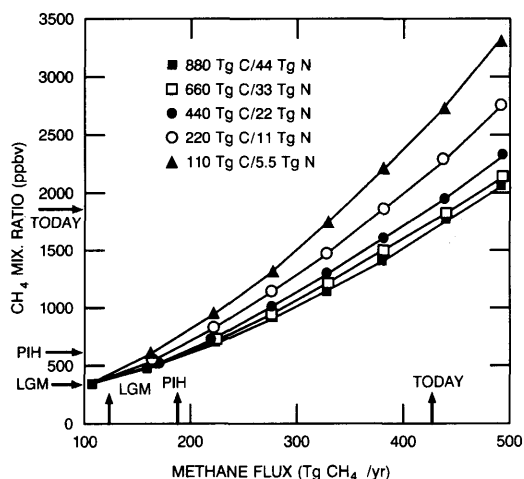
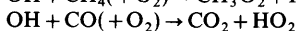
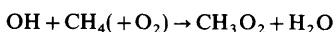


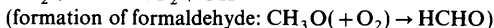
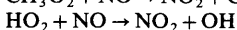
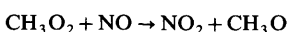
Fig. 1. Methane budgets (in Tg CH<sub>4</sub>/yr) and model calculated mixing ratios for five assumptions of CO (Tg C/yr) and NO (Tg N/yr) budgets. Marks for PIH and LGM refer to atmospheric methane concentrations for the Preindustrial Holocene and Last Glacial Maximum, respectively, as deduced from ice cores (Stauffer et al., 1988; Chappellaz et al., 1990).

Table 2. Photochemical reactions linking methane, CO and NO with O<sub>3</sub>, OH and H<sub>2</sub>O<sub>2</sub>

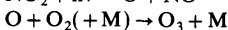
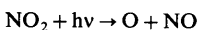
OH consumed by CO or CH<sub>4</sub>



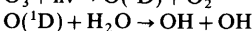
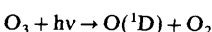
Conversion of NO to NO<sub>2</sub>



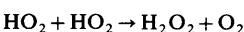
Formation of O<sub>3</sub>



Formation of OH



Formation of H<sub>2</sub>O<sub>2</sub>



$O_3$  and  $H_2O_2$  (Figs. 2a and 2c) with decreasing global OH as fluxes of  $CH_4$ , CO and NO increase has been described previously (Chameides et al., 1977; Sze, 1977; Thompson and Cicerone, 1986). Table 2 shows the sequence of reactions that cause increasing CO and  $CH_4$  levels to be accompanied by lower OH.

The processes determining OH response to changing  $CH_4$ , CO and NO emissions are non-linear. Thus, although lower fluxes of  $CH_4$  and CO allow OH concentrations to build up, reduced

levels of  $CH_4$  and CO oxidation products ( $HO_2$  and  $CH_3O_2$ , respectively), imply less  $O_3$  formation (and potentially lower OH). The fact that equilibrium levels of OH are higher at lower fluxes of  $CH_4$ , CO and NO means that having less OH removed by  $CH_4$  and CO is more important than the reduced supply of OH from lower amounts of  $O_3$ . Reduced  $O_3$  concentrations at lower fluxes of  $CH_4$ , CO and NO are obvious in Figure 2a. The conversion of OH to  $HO_2$  leads to more  $H_2O_2$  when two  $HO_2$  radicals combine (Table 2). Thus,

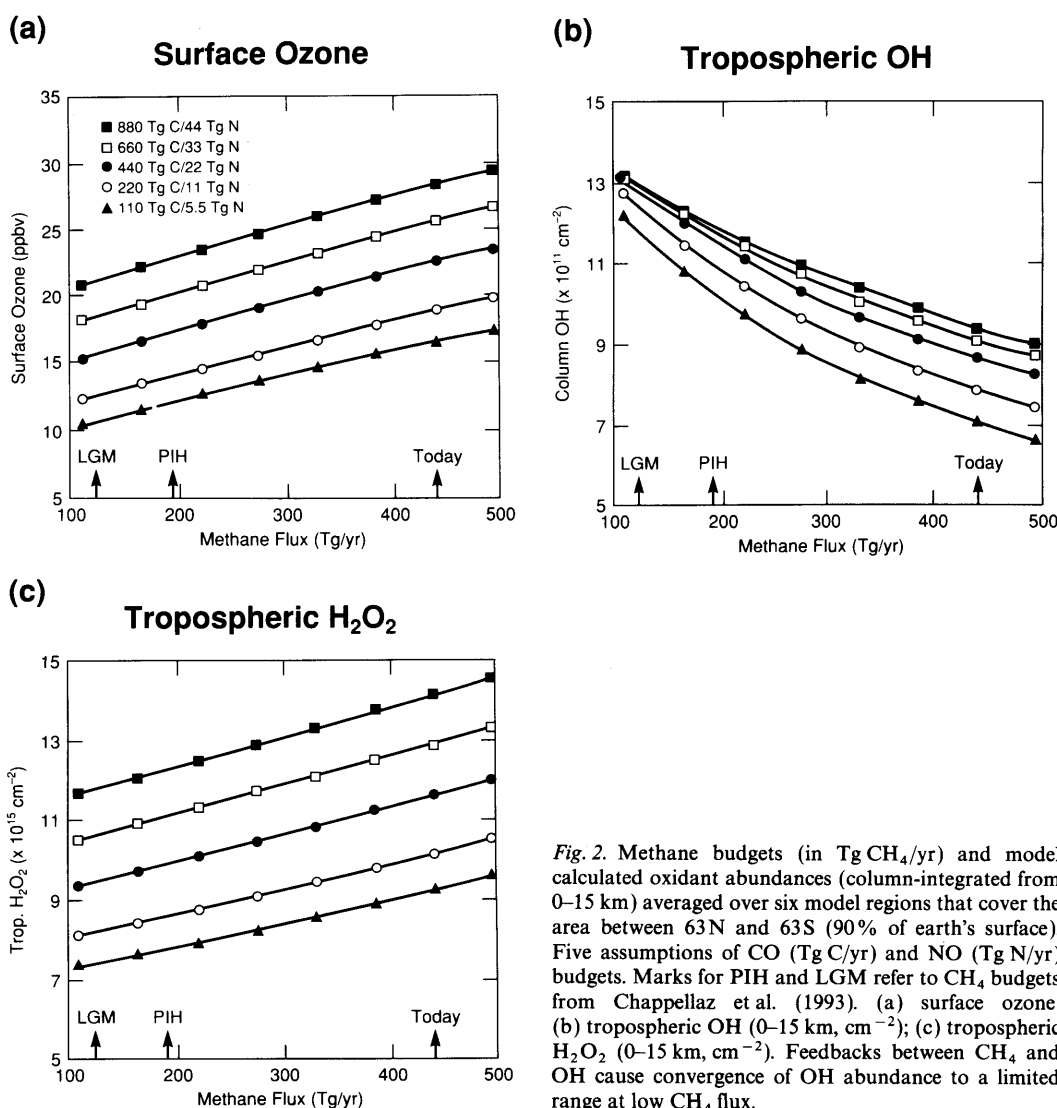


Fig. 2. Methane budgets (in Tg  $CH_4$ /yr) and model calculated oxidant abundances (column-integrated from 0–15 km) averaged over six model regions that cover the area between 63°N and 63°S (90% of earth's surface). Five assumptions of CO (Tg C/yr) and NO (Tg N/yr) budgets. Marks for PIH and LGM refer to  $CH_4$  budgets from Chappellaz et al. (1993). (a) surface ozone; (b) tropospheric OH (0–15 km,  $\text{cm}^{-2}$ ); (c) tropospheric  $H_2O_2$  (0–15 km,  $\text{cm}^{-2}$ ). Feedbacks between  $CH_4$  and OH cause convergence of OH abundance to a limited range at low  $CH_4$  flux.

higher fluxes of CH<sub>4</sub>, CO and NO lead to higher levels of H<sub>2</sub>O<sub>2</sub> (Fig. 2c).

Fig. 1 also shows that with low CH<sub>4</sub> sources, CH<sub>4</sub> mixing ratios show great sensitivity to CH<sub>4</sub> emissions and less sensitivity to CO and NO emissions: with 110 Tg CH<sub>4</sub>/yr, calculated CH<sub>4</sub> mixing ratios are 320–360 ppbv, regardless of CO and NO fluxes. This is more or less the measured uncertainty of LGM ice core CH<sub>4</sub> levels (Stauffer et al., 1988; Chappellaz et al., 1990). At present day CH<sub>4</sub> fluxes (400–450 Tg/yr), the effect of varied CO and NO scenarios is more pronounced. The “convergence” toward a relatively small range of CH<sub>4</sub> fluxes for a given atmospheric CH<sub>4</sub> level at lower CH<sub>4</sub> fluxes (Figure 1) is equivalent to a fairly narrow range of the CH<sub>4</sub> sink (OH radical). Fig. 2b shows that at a CH<sub>4</sub> flux of 100 Tg CH<sub>4</sub>/yr there is not much variation in OH compared to the range of OH for present-day CH<sub>4</sub> fluxes.

The small ranges of CH<sub>4</sub> and OH concentrations at low CH<sub>4</sub> flux are largely due to the CH<sub>4</sub>–OH feedback (Sze, 1977; Hameed et al., 1979). Several recent studies have made quantitative estimates of CH<sub>4</sub>–OH feedbacks (Guthrie, 1989; Thompson et al., 1989b; Lu and Khalil, 1992; Isaksen et al., 1992). For example, Lu and Khalil (1992) compare the byproducts of CO and CH<sub>4</sub> reaction with OH to show that for a given fixed level of NO, CH<sub>4</sub> has a greater effect on OH than does CO, even though CO “removes” OH 3–4 times faster than CH<sub>4</sub> does. The reason is that OH can be stored in the form of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> (other odd hydrogen species), following reaction with CO and CH<sub>4</sub>, eventually returning OH to the atmosphere, thereby “buffering” against OH loss. The buffering is more effective following CO reaction than CH<sub>4</sub> reaction where CH<sub>3</sub>O<sub>2</sub>, HCHO and CH<sub>3</sub>OOH tie up odd hydrogen, returning less OH to the atmosphere. Thus, reaction with CH<sub>4</sub> is more often a net loss for OH than CO is and CH<sub>4</sub> levels are more critical to OH abundance than CO is.

The degree of CH<sub>4</sub>–OH feedback is NO<sub>x</sub> dependent. Lu and Khalil (1992) find that total CH<sub>4</sub> losses can be up to 60 % larger than for CO at low NO<sub>x</sub> levels. Other studies reach similar conclusions about CH<sub>4</sub>–OH–NO<sub>x</sub> interaction. Evaluations of sensitivity coefficients of the type,  $(\partial \ln[\text{OH}]/\partial \ln[\text{flux}])$  show that for lower NO<sub>x</sub> conditions (in nonpolluted tropical and southern hemisphere regions, for example), OH may be

1.5–2 times more sensitive to CH<sub>4</sub> fluxes than to CO fluxes (Thompson et al., 1989b; Prather, 1989). An analysis of the dependence of OH (and other constituent) levels on reaction rate coefficients in our photochemical model shows that 1/3–1/2 of the computed species correlate highly with the rate coefficient for CH<sub>4</sub> and OH reaction, but only CO levels correlate with the rate for CO and OH reaction (Thompson and Stewart, 1991). The degree of correlation with the CH<sub>4</sub>–OH rate is greater at lower levels of NO<sub>x</sub>. Thus, atmospheric composition in general appears to be very sensitive to CH<sub>4</sub>–OH feedbacks, especially at low CH<sub>4</sub> (and NO) fluxes (Figs. 1 and 2b).

### 3. Simulating the pre-industrial holocene and last glacial maximum

#### 3.1. The ice-core record: constraint for sources and sinks

The ice-core CH<sub>4</sub> record can be used to deduce global CH<sub>4</sub> fluxes for the PIH and LGM. For the PIH (1200–1800 AD) the ambient CH<sub>4</sub> mixing ratio determined from replicate ice cores is  $700 \pm 30$  ppbv [Rasmussen and Khalil, 1984; Stauffer et al., 1985; Pearman et al., 1986; Raynaud et al., 1988; Despertis (personal communication) 1991]. Figure 1 shows that this CH<sub>4</sub> level implies a source strength of 180–200 Tg CH<sub>4</sub>/yr, in good agreement with that estimated directly from historical information (Chappellaz et al., 1993).

Using the ice-core LGM mixing ratio of  $350 \pm 30$  ppbv (Stauffer et al., 1988; Chappellaz et al., 1990) as guidance along with the photochemical model results (Figure 1) implies that the corresponding flux is in the range 100–130 Tg CH<sub>4</sub>/yr. Here too, the model-deduced CH<sub>4</sub> flux is within 20 Tg CH<sub>4</sub>/yr of the LGM CH<sub>4</sub> fluxes deduced from paleo-vegetation data (Chappellaz et al., 1993). Note, however, that the simulations shown in Fig. 1 have been made with present-day temperature profiles. With more realistic simulation of atmospheric conditions (Subsection 3.2), the model-derived source is reduced slightly.

Besides CH<sub>4</sub>, there is limited information on the atmospheric concentrations of shorter-lived species from the historical record. The record from Central Greenland ice cores over the past 700 years shows that the H<sub>2</sub>O<sub>2</sub> concentration increased by 50 % over the past 200 years, with

most of the increase occurring in the past 20 years (Sigg and Neftel, 1991). Within the uncertainty limits of the air-ice transfer coefficient, this is interpreted to represent a parallel atmospheric  $\text{H}_2\text{O}_2$  increase. Fig. 2c shows that with the  $\text{CH}_4$  source at 190 Tg  $\text{CH}_4/\text{yr}$  and CO and NO at 220 Tg C/yr and 11 Tg N/yr, respectively, the atmospheric  $\text{H}_2\text{O}_2$  concentration for the PIH would be 40% that of today (with 440 Tg  $\text{CH}_4/\text{yr}$ , 770 Tg C/yr from CO and 39 Tg N/yr from NO). With CO and NO at 330 Tg C/yr and 16.5 Tg N/yr, respectively, the PIH  $\text{H}_2\text{O}_2$  concentration would be 60% of today's levels. Thus, the ice-core  $\text{H}_2\text{O}_2$  for PIH conditions constrains CO to  $\sim 200\text{--}300$  Tg C/yr and NO to 11–15 Tg N/yr. We note a caveat in this interpretation because the Greenland ice core record may not be representative of mid- and low latitude  $\text{H}_2\text{O}_2$  changes. The lifetime of  $\text{H}_2\text{O}_2$  in our model is only 2–3 days at mid-latitude, which might be too short for significant transport to the latitude of Greenland. Measurements of  $\text{H}_2\text{O}_2$  ice cores dating to the LGM have been performed (Neftel et al., 1984) but their reliability is questioned because chemical decomposition of  $\text{H}_2\text{O}_2$  probably occurs on this timescale.

Some historic  $\text{O}_3$  data can be used to constrain PIH CO and NO. In-situ data at nonurban stations show a doubling of surface  $\text{O}_3$  from the mid-late 1800's to the 1980's in mid-latitudes of both Northern and Southern Hemisphere (Bojkov, 1986; Volz and Kley, 1988; Sandroni et al., 1992). Increases from 10–15 ppbv for the 19th century to 25–30 ppbv for today are typical. Looking at Fig. 2a shows  $\text{O}_3$  between 10 and 15 ppbv, with  $\text{CH}_4$  at 190 Tg/yr, CO at 110–330 Tg C/yr, and NO at 5.5–16.5 Tg N/yr (the 330 Tg C/yr curve is not depicted but falls halfway between the 220 Tg C/yr and 440 Tg C/yr curves). These CO and NO ranges overlap those that are consistent with the PIH ice-core  $\text{H}_2\text{O}_2$  data.

Formaldehyde (HCHO) dissolved in Greenland ice was 30–90% lower 200 years ago (Staffelbach et al., 1991) and data from both Greenland and Antarctica show HCHO to be 10–20 times lower during the LGM compared to present day. Staffelbach et al. (1991) are able to reproduce the lower HCHO (and implied 10 times less OH) in a model calculation with reduced temperature, 350 ppbv  $\text{CH}_4$ , 40 ppbv CO and 1 pptv NO, but only by making additional assumptions about uv penetration into the lower atmosphere. Strato-

spheric  $\text{O}_3$  is assumed to be twice as great as today. When we specify the same temperature, CO, NO and uv conditions as Staffelbach et al. (1991) and a  $\text{CH}_4$  source at 120 Tg/yr, the lower OH in the LGM implies  $\text{CH}_4$  mixing ratios in excess of 2 ppmv; HCHO is 1/5 present-day levels. To reproduce a 350 ppbv  $\text{CH}_4$  mixing ratio under this scenario requires the  $\text{CH}_4$  source to be reduced to  $\sim 30$  Tg/yr. In other words, our analysis suggests that the LGM ice core records for  $\text{CH}_4$  and HCHO do not lead to a consistent set of constraints for the LGM  $\text{CH}_4$  source.

### 3.2. Model input for $\text{CH}_4/\text{CO}/\text{NO}$ budgets for PIH and LGM

Besides using the ice-core record to deduce sources and sinks, we also performed an ab initio evaluation of  $\text{CH}_4$  and CO sources for the pre-industrial Holocene and Last Glacial Maximum (Table 3). The  $\text{CH}_4$  budgets are essentially based on an evaluation of historical wetlands and other distributions, wetlands being the major natural source (Chappellaz et al., 1993). The CO budgets are based on reducing or eliminating anthropogenic sources and retaining natural ones. There is large uncertainty in the present partitioning of natural and anthropogenic CO budgets and our present-day value of 770 Tg C/yr (Table 1) is in the middle of the commonly accepted range (Khalil and Rasmussen, 1990). When this budget is scaled back, a PIH CO source of 250 Tg C/yr is obtained, consistent with what is deduced from the PIH ice-core  $\text{H}_2\text{O}_2$  record. For NO the same proportional change is assumed as for CO because many of the sources are similar; the main exception is lightning which may contribute significantly to the NO source. In performing model calculations with the  $\text{CH}_4$ , CO and NO fluxes in Table 3, the ratio between the PIH (or LGM) and present-day emissions (Table 1) is used to scale back fluxes for each period. The same scaling is used for all six regions.

Calculated  $\text{CH}_4$ , CO,  $\text{NO}_x$  and oxidant levels based on the PIH fluxes (Table 3) are presented in Table 4. Three sets of calculations are made: (1) only  $\text{CH}_4$  fluxes are scaled back; (2) only CO and NO fluxes are scaled back; and (3) all three fluxes are scaled back. In the second run lower values of pre-industrial NO lead to lower levels of ozone and OH, even though the CO loss alone would be consistent with higher OH and suppression of  $\text{CH}_4$  levels. This in turn yields a  $\text{CH}_4$  level



Table 3. CH<sub>4</sub> and CO budgets for PIH and LGM

Methane (Tg CH <sub>4</sub> /yr)		
Source	1200–1800 (PIH)	18 KY BP (LGM)
wetlands	145	75
wild animals	15	20
termites	20	20
wildfires	5	5
ocean	10	10
CH <sub>4</sub> hydrates	5	0
uptake by soils	–10	–10
total, Tg CH <sub>4</sub> /yr	190	120*
% 1990 flux (Table 1)	43 %	27 %
* Used for calculations in Table 5		
Carbon monoxide (Tg CO (or C)/yr)		
Source*	1200–1800 (PIH)	18 KY BP (LGM)
combustion	0	0
vegetation	75–100	75–100
biomass burning	68–100	68–100
ocean	40–100	40–100
NMHC Oxid.	285–370	140–185
soils	17	17
total, Tg CO/yr	485–687	340–500
(% 1990 flux, table 1)	(250 Tg C/yr) 32 %	(180 Tg C/yr) 23 %

for the 1200–1800 period that is higher than contemporary concentrations (2.2 ppmv, Table 4).

### 3.3. LGM oxidant levels

Fig. 3 shows CH<sub>4</sub>, CO, NO<sub>x</sub> and oxidant levels for the LGM calculated with 120 Tg CH<sub>4</sub>/yr, 180 Tg C/yr and 12.5 Tg N/yr (Table 3) with present-day temperature. Further calculations explore the sensitivity of CH<sub>4</sub> and oxidant levels to reduced temperature and other perturbations that might be associated with the Last Glacial Maximum. These specifications are as follows.

(1) LGM-4.5 K. LGM fluxes are used and all other model inputs are kept at present-day levels except for temperature. The regions representing mid-latitude conditions are 4.5 degrees colder than at present and the low latitude regions are 2.0 degrees colder than present-day (Hansen et al., 1984). (These specifications are made for the model surface temperature and are scaled with altitude until the difference at the tropopause is 0°). The effect of these temperature changes on photochemical reaction rates is nearly negligible. However, assuming that relative humidity is unchanged over time, lower temperatures cause boundary layer H<sub>2</sub>O mixing ratios to be reduced, giving less O<sub>3</sub> destruction and less OH:

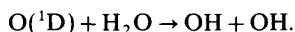
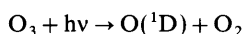


Table 4. Atmospheric composition for present day and three scenarios for Pre-industrial Holocene (PIH); globally averaged mixing ratios or column amounts

Species	Present-day mean mixing ratio	Pre-industrial (1200–1800)		
		reduce CH <sub>4</sub> *	reduce CO/NO**	reduce CH <sub>4</sub> /CO/NO***
CH <sub>4</sub>	1800 ppbv	590 ppbv	2230 ppbv	670 ppbv
CO	120 ppbv	86 ppbv	64 ppbv	36 ppbv
O <sub>3</sub>	27 ppbv	22 ppbv	19 ppbv	15 ppbv
NO <sub>x</sub>	260 pptv	260 pptv	37 pptv	67 pptv
Col-O <sub>3</sub> (cm <sup>-2</sup> )	8.7 (17)	7.0 (17)	7.2 (17)	5.7 (17)
Col-OH (cm <sup>-2</sup> )	9.26 (11)	1.19 (12)	8.0 (11)	1.11 (12)
Col-H <sub>2</sub> O <sub>2</sub> (cm <sup>-2</sup> )	8.5 (15)	6.7 (15)	5.4 (15)	3.7 (15)

\* Fluxes are 190 Tg CH<sub>4</sub>/yr, 770 Tg C (as CO)/yr and 38.5 Tg N (as NO)/yr.

\*\* Fluxes are 440 Tg CH<sub>4</sub>/yr, 250 Tg C (as CO)/yr and 12.5 Tg N (as NO)/yr.

\*\*\* Fluxes are 190 Tg CH<sub>4</sub>/yr, 250 Tg C (as CO)/yr and 12.5 Tg N (as NO)/yr.

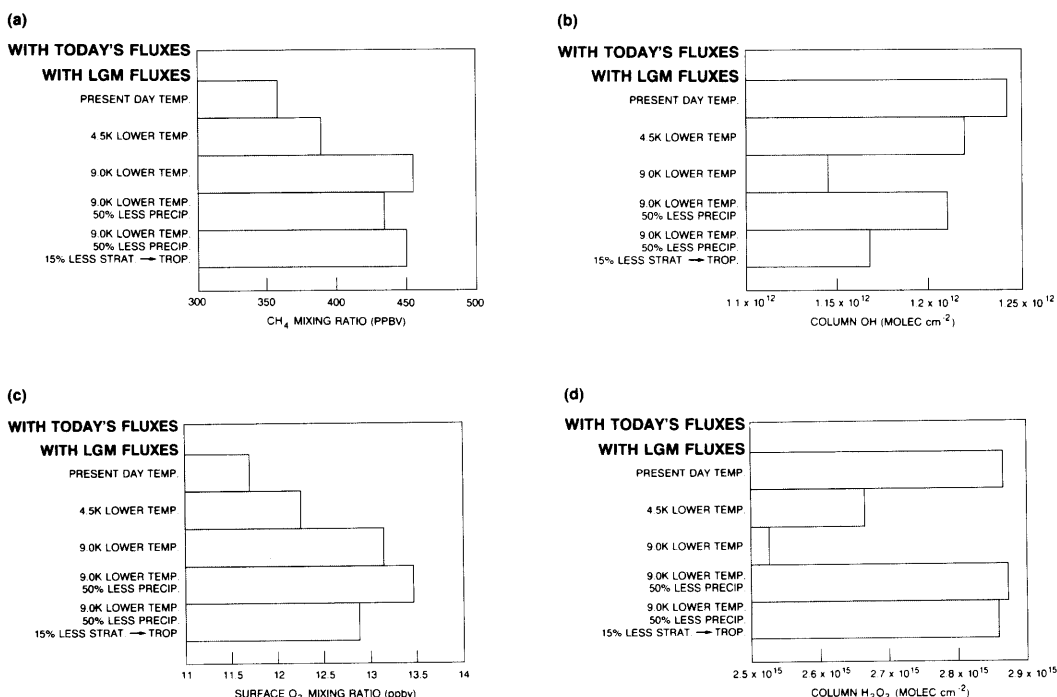
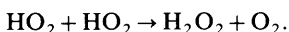
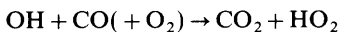


Fig. 3. Globally averaged (a) CH<sub>4</sub>; (b) OH; (c) O<sub>3</sub>; (d) H<sub>2</sub>O<sub>2</sub> for LGM fluxes as given in Table 3 with several variations of temperature (present day, 4.5 K colder, 9 K colder), precipitation (LGM-9 K with present day rainout rates and 50% of present day), and with reduced temperature (−9 K), rainout and 15% lower influx of O<sub>3</sub> and odd nitrogen from stratosphere to troposphere.

With less OH, there is less H<sub>2</sub>O<sub>2</sub> formation:



(2) LGM-9 K. This is similar to LGM-4.5 K except the surface temperature in regions representing mid-latitude conditions is 9 K colder than at present and low latitude regions are 4.5 K colder than present-day.

(3) LGM-9 K, and 50% less precip. This is the same as LGM-9 K, except that the model-specified rainout rate for soluble gases is reduced 50%.

(4) LGM-9 K, 50% less precip. and reduced stratosphere → troposphere influx. Temperature changes of this magnitude are likely to be accompanied by a variety of meteorological changes (Rind et al., 1990). For example, large scale circulation changes could affect stratosphere-to-troposphere exchange which would modify

background O<sub>3</sub> (and OH and H<sub>2</sub>O<sub>2</sub>) levels, i.e., CH<sub>4</sub> lifetime and feedback. This set of simulations reduces the model influx of O<sub>3</sub> and odd nitrogen 15% at the upper boundary for all six model "regions."

(5) LGM-20 K, and doubled overhead O<sub>3</sub>. This is an attempt to simulate greatly reduced HCHO and OH as Staffellbach et al. (1991) recently reported. We performed a similar sensitivity test, with NO and CO emissions adjusted to give 1 pptv NO and 40 ppbv CO at the surface for a nonpolluted marine region.

There are potentially other sources of atmospheric modification which have not been considered. One is the amount of lightning, which is a major source of NO in the nonpolluted atmosphere. Changes in cloudiness, which would perturb photodissociation rates and rates of heterogeneous reaction, also have not been considered.

#### 4. Discussion

We have already noted that mixing ratios of CH<sub>4</sub> calculated with a model CH<sub>4</sub> budget flux based on reduced CH<sub>4</sub> sources (Table 3) are in good agreement with observations for the pre-industrial Holocene and the Last Glacial Maximum (LGM), regardless of levels of CO and NO<sub>x</sub> (Fig. 1). In other words, although OH (and lifetime) changes for CH<sub>4</sub> are important, CH<sub>4</sub> changes appear to be driven primarily by changes in methane sources. This is the conclusion reached in published analyses of CH<sub>4</sub> increases over the past 200 years (Khalil and Rasmussen, 1985; Levine et al., 1985; Thompson and Cicerone, 1986).

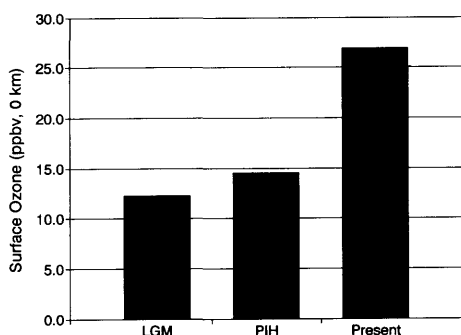
##### 4.1. Pre-industrial holocene

The fact that CH<sub>4</sub> flux changes are able to explain much but not all of the CH<sub>4</sub> increase from

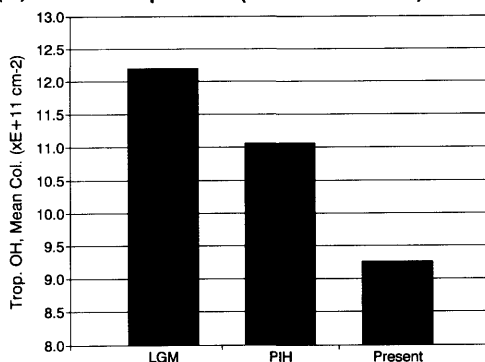
the PIH to the present is due to feedback effects involving atmospheric OH. The increase from 670 ppbv (PIH) to 1.80 ppmv (1990) is 169% (Table 4), whereas the specified flux increase between PIH and present day is 132% (Table 3). Thus, CH<sub>4</sub>-OH feedback accounts for about 1/4 of the CH<sub>4</sub> increase from the PIH to 1990.

The effect of CH<sub>4</sub> source reductions on PIH oxidant levels is significant. Table 4 shows that assuming only a reduction in methane flux in the pre-industrial Holocene could have meant a 29% higher global OH abundance and 20% less O<sub>3</sub>. Fig. 4 shows mean global abundances of O<sub>3</sub>, OH and H<sub>2</sub>O<sub>2</sub> at present-day, PIH and LGM conditions calculated assuming the CH<sub>4</sub>, CO and NO budgets given in Table 3. Individual region changes are not illustrated. However, with CH<sub>4</sub>, CO and NO scaled back, the model calculations for the region designated "Clean Continental mid-latitude" (Northern Hemisphere) show 20 ppbv

(a) Surface O<sub>3</sub> (Global Mean)



(b) Trop. OH (Global Mean)



(c) Surface H<sub>2</sub>O<sub>2</sub> (Global Mean)

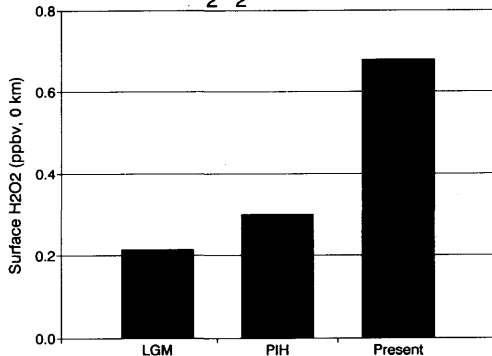


Fig. 4. (a) Surface ozone mixing ratio (global average); (b) tropospheric OH; and (c) surface H<sub>2</sub>O<sub>2</sub> at present-day, PIH and LGM conditions computed from fluxes in Table 3. LGM assumes that mid-latitude temperatures are 4.5 K colder than present day.

O<sub>3</sub> in the pre-industrial Holocene (1200–1800) compared to 40 ppbv in 1990. This change compares favorably with the factor of 2 increase that Volz and Kley (1988) report for background European O<sub>3</sub> levels between the 1860's and the present. With only CH<sub>4</sub> emissions scaled back, the Clean Continental region O<sub>3</sub> is 34 ppbv for the 1200–1800 period.

Depending on the assumed CH<sub>4</sub>, CO and NO emissions, hydrogen peroxide concentrations computed by the model are 21–56 % lower in the PIH than in 1990 in reasonable agreement with the recent report from Greenland ice cores by Sigg and Neftel (1991) (Table 4). Of course, the correspondence between atmospheric H<sub>2</sub>O<sub>2</sub> (in this case a model-computed global average) and ice-core H<sub>2</sub>O<sub>2</sub> is not clear. Soluble gases that have been measured in ice cores, e.g., hydrogen peroxide, nitric acid, formic acid, result from heterogeneous removal of the trace gas. Formation of H<sub>2</sub>O<sub>2</sub> in rain, snow and ice is possible and the transfer coefficient between snow and the atmosphere must be established before the peroxide ice-core record can

be used as an indicator of past atmospheric H<sub>2</sub>O<sub>2</sub> composition.

It was noted above that the calculation in which pre-industrial NO and CO were reduced with no reduction of CH<sub>4</sub> sources suppressed OH levels relative to present-day so that corresponding CH<sub>4</sub> would have been higher in the PIH than today. Guthrie (1989) showed analytically that the OH feedback connecting CO and CH<sub>4</sub> demands a certain degree of CO and CH<sub>4</sub> covariance. The unrealistically high CH<sub>4</sub> obtained with the assumption of reducing CO–NO fluxes only (Table 4) may support Guthrie's conclusions that certain combinations of CH<sub>4</sub>, CO and OH will not occur and the CH<sub>4</sub>–CO–OH system is self-regulating.

Scaling back CH<sub>4</sub> emissions alone reduces CO substantially, but even a globally averaged 86 ppbv CO concentration for the PIH (Table 4, CH<sub>4</sub>-only flux reduction) is probably too high given current CO concentrations of 100–120 ppbv and rates of CO increase ~0.5–1 %/yr (Khalil and Rasmussen, 1984; Levine et al., 1985). The scenario

Table 5. *Model-calculated changes in global OH*

Model and type (Reference)	Current global OH (cm <sup>-3</sup> )*	% OH change PIH-today	% OH change LGM-today
Harvard (1D) (McElroy, 1989)	n/a	+ 60	+ 150**
U. Cambridge (2D) (Law & Pyle, 1991)	0.95 × 10 <sup>6</sup>	NH: + 50 SH: minus 20	—
AEA-Harwell (2D) (Hough & Derwent, 1990)	0.85 × 10 <sup>6</sup>	global mean: + 23	—
Max Planck Inst. (2D) (Valentin, 1990)	0.91 × 10 <sup>6</sup>	NH: minus 50–+ 40 SH: + (20–40)	+ 30–40
Max Planck Inst. (3D) (Crutzen & Zimmermann, 1991)	0.80 × 10 <sup>6</sup>	NH: minus (10–20) SH: + (10–20)	—
AREAL (1D) (Pinto & Khalil, 1991)	0.6 × 10 <sup>6</sup>	+ 4	+ 20
OGI (Multi-1D) (Lu & Khalil, 1991)	0.8 × 10 <sup>6</sup>	+ 11	+ 40
GSFC (Multi-1D) (This Study)	0.6 × 10 <sup>6</sup>	+ 20	+ 32

\* Global average refers to volume average over model domain.

\*\* LGM calculation neglected temperature effect on H<sub>2</sub>O vapor.

with reduced CH<sub>4</sub>, CO and NO emissions leads to a globally-averaged CO concentration of 36 ppbv for the PIH (Table 4).

#### 4.2. Last Glacial Maximum

Fig. 3 summarizes the results of simulations for the Last Glacial Maximum. Taking the CH<sub>4</sub> source to be 120 Tg CH<sub>4</sub>/yr (with the global CO and NO sources at 180 Tg C/yr and 9 Tg N/yr), the calculated CH<sub>4</sub> mixing ratio falls to 360–460 ppbv, depending on temperature. Mean surface CO is 25 ppbv, in contrast to 120 ppbv CO for present day and 36 ppbv CO for the PIH.

Global OH in the LGM is 32% greater than present day with the temperature 4.5 K less than present day (Figs. 3b and 4b). The difference between global OH with reduced CH<sub>4</sub>, CO and NO emissions and present-day temperature (LGM-PD Temp. in Fig. 3b) and the same emissions and 4.5 K lower temperature (LGM-4.5 K in Fig. 3b) is less than 2%, but the corresponding difference in atmospheric CH<sub>4</sub> is 8% (Fig. 3a). The difference in global OH at LGM-4.5 K and LGM-9 K is also small but it gives rise to a 13% difference in CH<sub>4</sub> (Fig. 3a).

The sensitivity of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> to the climatic factors simulated in the LGM calculations is not as small as it is for OH, but it is less than 15% in all cases (Figs. 3c and d). Reducing temperature (at constant relative humidity) lowers the OH (and H<sub>2</sub>O<sub>2</sub>) sources from H<sub>2</sub>O vapor. However, when less precipitation is assumed, i.e., less rainout for H<sub>2</sub>O<sub>2</sub>, some of the H<sub>2</sub>O<sub>2</sub> lost in a drier atmosphere is recovered (Fig. 3d).

#### 4.3. Comparison with other models

Several other models have simulated conditions for pre-industrial conditions. Table 5 summarizes OH changes calculated by other models that are constrained to reproduce the ice-core CH<sub>4</sub> record. All models show OH slightly higher at the Last Glacial Maximum than during the PIH and a loss in global OH since the start of pre-industrial times. In other words, there is agreement that human activities have led to a decrease in atmospheric oxidizing capacity (Isaksen, 1988; Thompson, 1992). In contrast, the models do not agree on the future course of OH and there are signs that globally averaged OH has increased over the past 12 years (Prinn et al., 1992).

The OH loss is not geographically uniform nor

do the models agree on the regional distribution of increases and decreases. For example, all of the regions simulated in our multi-box model show a negative trend in OH from PIH and LGM to present-day. The two- and three-dimensional models from Max-Planck Institut (Mainz) show OH increasing from the PIH up to present day in Northern Hemisphere regions of industrial growth (high NO<sub>x</sub> increases) and Southern Hemisphere OH losses because NO<sub>x</sub> levels remain small and CH<sub>4</sub> and CO increases suppress OH (Valentin, 1990; Crutzen and Zimmermann, 1991). The two-dimensional "Cambridge" model of Law and Pyle (1991) shows the opposite geographical pattern, at least for the time of year that is presented in their paper (December conditions; the Crutzen and Zimmermann (1991) report gives annually averaged daytime OH). The major reasons for the discrepancy between the Max-Planck and Cambridge models are presumably different geographical specification of CH<sub>4</sub>–CO–NO emissions increases over time. Law and Pyle (1991) assume quite low mean NO<sub>x</sub> for present day (10 pptv) and a factor of 10 less for the PIH; this tends to increase OH over time even as CH<sub>4</sub>–CO–NMHC increases would be depleting it. Other model characteristics that could be contributing to differing OH, transport parameterization, radiation, assumed stratospheric-tropospheric exchange, treatment of rainout, make it difficult to compare both present-day and perturbed model results. Unfortunately, an intercomparison of tropospheric two-dimensional models, comparable to that done for stratospheric models (Jackman et al., 1989) has only recently begun (Isaksen et al., 1992; Guthrie and Yarwood, 1991).

Table 4 shows 20–30% higher global OH for the PIH with scenarios for both CH<sub>4</sub> and CH<sub>4</sub>–CO–NO reduction. The two-dimensional calculations of Valentin and Crutzen (1990) show 20–70% more OH in the PIH relative to 1979 (the modern "reference year"), depending on region and season (Table 5). Their average tropospheric OH change is a decrease of 20–30% from the PIH to the present and the three-dimensional Max-Planck model shows zonally averaged 10–20% OH losses (Crutzen and Zimmermann, 1991). This agrees well with the 2D model result from the Harwell model (C. Johnson et al., personal communication, 1992; Hough and Derwent, 1990).

Global OH for LGM is also higher than pre-

sent-day, but not much greater than OH for the PIH (Table 5). There are several reasons. First, assumed changes in CO and NO sources between LGM and PIH are not much different (Table 3; also Valentin, 1990; Pinto and Khalil, 1991). Second, the tendency for lower CH<sub>4</sub> and CO to allow OH to build up in the LGM is offset by a cooler atmosphere with less H<sub>2</sub>O and OH formation from O<sub>3</sub>. Third, CH<sub>4</sub>-OH feedbacks and buffering effects of CH<sub>4</sub> and CO on OH at low CH<sub>4</sub> fluxes (Fig. 2b) limit the OH increase (Guthrie, 1989; Pinto and Khalil, 1991; Lu and Khalil, 1992). Thus, a factor of 3–4 decrease in CH<sub>4</sub> flux in the LGM (relative to today) means less than a factor of 2 higher OH.

What conclusion can be drawn about pre-industrial levels of OH? Almost certainly it was greater than today, probably less than a factor of 2 greater in the LGM, although none of the models in Table 5 can be selected as the "best" quantitative evaluation. All of the models simulate the ice-core CH<sub>4</sub> record successfully because they have been forced to do so. Note, however, the wide range of corresponding fluxes for the PIH and LGM (Fig. 5). If consistency between the Chappellaz et al. (1993) flux and calculated mixing

ratios is the criterion for the most likely OH level, then the present study and Pinto and Khalil (1991) would be preferred. Besides CH<sub>4</sub>, however, there are not sufficient ice core chemical data to provide a benchmark for deduction of OH. Estimates of the natural component of preindustrial NO, CO and NMHC fluxes could be made analogously to the Chappellaz et al. (1993) evaluation for CH<sub>4</sub>. However, the partitioning of emissions for those gases are less certain than for CH<sub>4</sub> and the magnitude (possibly the direction) of climate-induced feedbacks on NO, CO and NMHC emissions in a cooler climate is unknown. Thus, instead of improving flux estimates for model input, it would be preferable to have ice-core measurements of a trace gas uncoupled from the terrestrial CH<sub>4</sub>-CO-NO<sub>x</sub>-OH-NMHC-O<sub>3</sub> cycle in order to deduce historic levels of OH. A trace gas of marine origin with moderately long lifetime and an exclusive OH photochemical sink (also stable in ice-trapped air) would be a good candidate. Many marine gases (OCS, H<sub>2</sub>S, CS<sub>2</sub>, CH<sub>3</sub>Cl) appear feasible, but their sources would be difficult to quantify if they are subject to biogenic-climate feedbacks.

Table 6 summarizes model simulations of O<sub>3</sub>

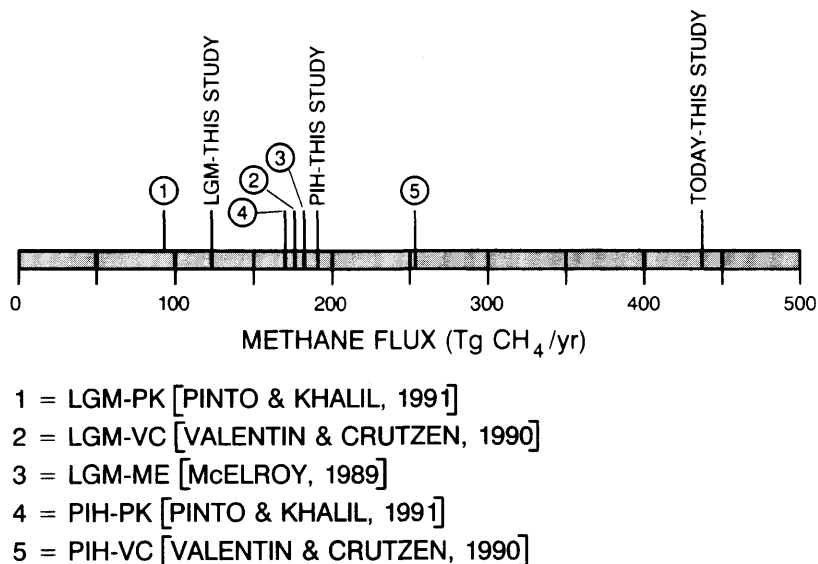


Fig. 5. Comparison of CH<sub>4</sub> budgets from five studies: VC = Valentin and Crutzen (1990); PK = Pinto and Khalil (1991); ME = McElroy (1989); LK = Lu and Khalil (1991). Note that for McElroy, adjustment was made for budget required with revised rate for CH<sub>4</sub> + OH reaction (Vaghjiani and Ravishankara, 1991).

Table 6. *Model-calculated ozone and CO*

Model and type (Reference)	Ozone (mean, ppbv)			CO (mean, ppbv)		
	Today	PIH	LGM	Today	PIH	LGM
Cambridge U. (2D) (Law & Pyle, 1991)	NH: 60 SH: 20	10–15 7–8	— —	150	50	—
Max Planck-Mainz (2D) (Valentin, 1990)	NH: 30–40 SH: 15–30	15–20 15–20	15–20 15–20	100–150 50–60	30–40 20–25	15–20 10–15
Max Planck-Mainz (3D) (Crutzen & Zimmermann, 1991)	NH: 30–40 SH: 20–30	15–20 20–25	— —	120 75	60 40	— —
AREAL/OGI (1D) (Pinto & Khalil, 1991; Lu and Khalil, 1991)	22	14	12	110	57	28
GSFC (Multi-1D) (This Study)	27	15	12	120	36	23

\* Global average refers to volume average over model domain.

and CO levels. In general, the agreement between published models and this study is very good. This is especially gratifying when one considers that two and three-dimensional models are more finely resolved with respect to sources than the six-box, one-dimensional model used here. Our calculations show regional PIH O<sub>3</sub> mixing ratios ranging from 9–23 ppbv O<sub>3</sub>, with a mean of 15 ppbv O<sub>3</sub> (Table 4) in good agreement with the Max Planck 2-D and 3-D models simulating the same period (Valentin and Crutzen, 1990; Crutzen and Zimmermann, 1991).

## 5. Summary and conclusions

Incorporation of assumed changes in CH<sub>4</sub>, CO and NO sources for the preindustrial Holocene and Last Glacial maximum periods into a photochemical model shows pronounced changes in atmospheric concentrations of CH<sub>4</sub>, CO, OH, O<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>. The principal results are as follows.

Model estimates of pre-industrial O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> show levels considerably lower than present-day. PIH H<sub>2</sub>O<sub>2</sub> and CH<sub>4</sub> concentrations from ice cores together imply CO and NO sources of 200–300 Tg C/yr and 11–15 Tg N/yr, respectively. This is in good agreement with an estimate based on scaling back present-day CO and NO budgets according to reduced sources. Using values of 250 Tg C/yr and 12.5 Tg N/yr with 190 Tg CH<sub>4</sub>/yr for the PIH

implies a 20 % greater level of global OH and 44 % less O<sub>3</sub> with roughly half the O<sub>3</sub> reduction due to lower CH<sub>4</sub>. At the low CH<sub>4</sub> fluxes appropriate for LGM, strong feedback between CH<sub>4</sub> and OH limits the sensitivity of OH to CO and NO fluxes.

Our best supposition for CH<sub>4</sub>, CO and NO fluxes for the Last Glacial Maximum (120 Tg CH<sub>4</sub>/yr, 180 Tg C/yr (as CO) and 9 Tg N/yr (as NO)) gives global OH 32 % greater than at present. This gives good agreement with the ice-core CH<sub>4</sub> record but not with the other LGM ice-core measurement reported, HCHO, which suggests that OH was much lower than at present (Staffelbach et al., 1991).

Methane levels calculated from reduced fluxes based on estimated CH<sub>4</sub> source changes (cf., Chappellaz et al., 1993) are in good agreement with the ice-core CH<sub>4</sub> record for the period 1200–1800 and for the Last Glacial Maximum, 18 KY BP. Our direct flux estimates (120 and 190 Tg CH<sub>4</sub>/yr, respectively, for LGM and PIH) are bracketed by those reported in the literature and deduced from models. The range of deduced sources is wide, however, a factor of two for the LGM (Fig. 5).

Other photochemical models reach qualitatively similar conclusions about preindustrial OH and O<sub>3</sub> but the magnitude of the OH decrease to present-day varies considerably. In order to pin down global OH changes from the ice core record of other constituents, it will be necessary

to measure something that reacts with OH but is uncoupled from the OH–CO–CH<sub>4</sub>–O<sub>3</sub> cycle. Potential candidates might be gases with moderately long lifetimes and an oceanic source, e.g., OCS and CH<sub>3</sub>Cl.

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