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The changing photochemistry of the troposphere

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ABSTRACT

The chemistry of the troposphere is substantially influenced by a wide range of chemical processes which are primarily driven by the action of solar ultraviolet radiation of wavelengths shorter than about 310 nm on ozone and water vapour. This leads to the formation of hydroxyl (OH) radicals which, despite very low tropospheric concentrations, remove most gases that are emitted into the atmosphere by natural and anthropogenic processes. Although tropospheric ozone only makes up about 10% of all atmospheric ozone, through the formation of OH, it determines the oxidation efficiency of the atmosphere and it is, therefore, of the utmost importance for maintaining the chemical composition of the atmosphere. Due to a variety of human activities, leading especially to increasing emissions of CH_4, CO and NO_x, it is conceivable that the concentrations of ozone are increasing in polluted and those of hydroxyl decreasing in clean tropospheric environments. The result is most likely an overall decrease in the oxidation efficiency of the atmosphere and consequently a buildup of several longlived trace gases that are primarily removed by reaction with OH. Here we discuss the most important processes that determine the oxidation efficiency of the atmosphere and give some examples of changes in O_3, CO, and OH concentration distributions that may have occurred as a result of human activities.

1. Introduction

Because of the great abundance and long lifetimes of the main atmospheric constituents N_2, O_2, and Ar, human activities certainly cannot affect their concentrations to any significant degree. Observations have shown, however, that these activities can much more readily increase the concentrations of much less abundant and shorter-lived gases. Examples are CO_2, CH_4, CO, O_3, NO_x ($NO + NO_2$), N_2O, and especially industrial chlorofluorocarbon gases, such as $CFCl_3$, CF_2Cl_2 and CCl_4. These gases are also of the greatest importance for the chemistry of the atmosphere (troposphere and stratosphere) and for the radiation budget of the earth-atmosphere system, and thus the earth's climate (e.g., Bolin et al., 1986; IPCC, 1990).

Most chemical constituents are emitted into the atmosphere at the earth's surface by natural, mostly biological, processes and increasingly also by Man's technological and agricultural activities. Through many millenia, growing populations of humans, all over the world, have been changing the earth's biosphere, e.g. through forest removal and other kinds of land use changes. Through the burning of large amounts of biomass, currently between 2×10^{15} and 5×10^{15} g C/yr (Crutzen and Andreae, 1990), tropical and subtropical agriculture produce large quantities of important trace gases. At temperate latitudes, industrial activities are perturbing the chemistry of the atmosphere to such an extent that, for instance, even globally averaged, the anthropogenic fluxes of the sulfur and nitrogen oxides are now larger than those due to natural processes.

The results of all this human diligence are now clearly visible on all scales in the atmosphere. For tropospheric background chemistry the increasing emissions and atmospheric concentrations of methane (CH_4), carbon monoxide (CO), and NO_x are of special importance, as they lead to changes in the concentrations of ozone (O_3) and the highly reactive hydroxyl (OH) radicals, which are responsible for the oxidation of almost all gases that are emitted by natural and anthropogenic activities in the atmosphere. As we will discuss, we envisage a gradual shift of photochemical activity

to occur from clean to more polluted atmospheric environments and an average decline in the atmospheric oxidation efficiency (global average hydroxyl concentrations).

In this paper, we will give a brief overview of the most important processes affecting global atmospheric chemistry, emphasizing those processes that control the oxidation efficiency of the atmosphere. We will show how these are increasingly controlled by human activities and present model calculations showing possible changes in the tropospheric concentrations of O_3, CO, and OH that have taken place over the past centuries.

2. Photochemistry of the background troposphere

Only about 10% of all atmospheric ozone is located in the troposphere. Ground level volume mixing ratios of ozone in the background troposphere range from 15 ppbv at low altitudes in the southern hemisphere to about 30 ppbv in the northern hemisphere (1 ppbv = 10^{-9} by volume). Even so, the relatively small amount of ozone in the troposphere is of fundamental importance for the composition of the earth's atmosphere, as the absorption of solar ultraviolet radiation of wavelengths shorter than about 310 nm by ozone leads to the generation of electronically excited $O(^1D)$ atoms, which can react with water vapour to form highly reactive hydroxyl radicals:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \ (\lesssim 310\,\text{nm}) \quad \text{R1}$$

$$O(^1D) + H_2O \rightarrow 2OH \quad \text{R2}$$

It is the attack by OH that initiates the oxidation of most trace gases in the atmosphere (Levy, 1971). This is of fundamental importance, because only few of the many gases that are emitted into the atmosphere at the earth's surface can be significantly removed by rainfall, while reactions with molecular oxygen are extremely slow. According to current estimates, the global, 24 h-average volume mixing ratio (mole fraction) of hydroxyl radicals in the troposphere is within 20% of 3×10^{-14}, corresponding to a concentration of about $7.7(\pm 1.5) \times 10^5$ molecules/cm^3 (Prinn et al., 1987). Therefore, although the atmosphere contains close to 21% molecular oxygen, it is the ultraminor constituent OH which acts as the "detergent" of the atmosphere, starting almost all atmospheric oxidation processes that lead to the removal of most natural and anthopogenic trace gases from the atmosphere. Thus, although ozone is phytotoxic and solar radiation below 310 nm is harmful to life, through the formation of OH radicals, they also counteract the accumulation of most gases in the atmosphere. Those trace gases that do not react with OH are generally removed by the action of short wave solar radiation in the stratosphere. This is e.g. the case with N_2O and the chlorofluorocarbons. Their photochemical breakdown leads to the formation of radical species, many of which act catalytically to destroy ozone.

In the background troposphere, remote from the direct effects of human activity, about 75% of the OH radicals react with CO, and most of the rest with CH_4 (Valentin, 1991). Smaller fractions react with various other gases. Since some decades the concentrations of CH_4 and CO have been increasing in the atmosphere: CH_4 by 0.7%–1% worldwide and CO by 0.85–1% in the troposphere above about 4 km at mid-latitudes in the northern hemisphere (Blake et al., 1982; Khalil and Rasmussen, 1988; Zander et al., 1989a, b). Clearly this alone can negatively influence the background tropospheric concentrations of hydroxyl and, therefore, also those of other atmospheric constituents. However, following the initial reactions a number of reaction chains are started which influence the production and destruction of ozone and hydroxyl. Good knowledge of these is required for a clear understanding of atmospheric chemistry and estimations of the past and future impact of human activities. In addition, through catalytic reactions, the concentrations of ozone and hydroxyl are affected by NO and NO_2, which have strong anthropogenic sources.

Although OH radicals react overwelmingly with CO and CH_4 in the background troposphere, these reactions do not necessarily lead to the removal of OH. They are merely the starting points for various, often lengthy, chains of reactions, which may compensate for the initial OH loss and which have important implications for the chemical composition of the troposphere. Some of these involve NO_x as catalysts, others do not; the net results for atmospheric chemistry are very different. For instance, in the presence of sufficiently

large concentrations of nitric oxide, the oxidation of carbon monoxide will lead to formation of tropospheric ozone, without loss of the catalysts OH, HO_2, NO, and NO_2 (Crutzen, 1973):

$$CO + OH \rightarrow H + CO_2 \quad \text{R3}$$
$$H + O_2 + M \rightarrow HO_2 + M \quad \text{R4}$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad \text{R5}$$
$$NO_2 + h\nu \rightarrow NO + O\ (\leqslant 400\ \text{nm}) \quad \text{R6}$$
$$O + O_2 + M \rightarrow O_3 + M \quad \text{R7}$$
$$\text{net: } CO + 2O_2 \rightarrow CO_2 + O_3$$

This catalytic reaction chain is propagated by the absorption of solar ultraviolet radiation with wavelengths shorter than 400 nm (reaction R6).

A competing chain of reactions, leading to ozone destruction in NO-poor environments:

$$CO + OH \rightarrow H + CO_2 \quad \text{R3}$$
$$H + O_2 + M \rightarrow HO_2 + M \quad \text{R4}$$
$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad \text{R8}$$
$$\text{net: } CO + O_3 \rightarrow CO_2 + O_2$$

likewise does not lead to the loss of OH and HO_2 radicals. The second reaction sequence is more important than the first one whenever the ratio of the concentrations of NO and O_3 is less than 2×10^{-4}. With ozone volume mixing ratios increasing from about $15–40 \times 10^{-9}$ (15–40 ppbv) at the earth's surface to 100 ppbv in the upper troposphere, the break-even point between the reaction chains R3-R7 and R3 + R4 + R8 is attained at nitric oxide volume mixing ratios in the lower troposphere of about 3 pptv (1 pptv $= 10^{-12}$ by volume) in the southern hemisphere to 8 pptv in the northern hemisphere, and 20 pptv at the tropopause. Although these values may appear very low, they may nevertheless not be exceeded in extensive regions of the troposphere in view of the very short residence times of NO and NO_2 due to the formation of highly water-soluble and chemically quite long-lived nitric acid via

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{R9}$$
$$NO_2 + OH\ (+M) \rightarrow HNO_3\ (+M) \quad \text{R10}$$

during daytime and

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{R11}$$
$$NO_3 + NO_2\ (+M) \rightarrow N_2O_5\ (+M) \quad \text{R12}$$

followed by the deposition of NO_3 and N_2O_5 on cloud droplets and wetted aerosol particles during nighttime. During daytime, the NO_3 which is formed through reaction R11 is immediately photolyzed to reproduce the original reactants NO_2 and O_3, so that N_2O_5 and NO_3 formation occurs only during night.

Because of the expected very short average lifetime of NO_x of the order of a few days in the troposphere, we may expect appreciable concentrations of NO and NO_2 only within one or two weeks' travel time from their main sources regions, i.e., the industrialized mid-latitude regions of the Northern Hemisphere, the tropical and subtropical continents during the dry biomass burning season, and the tropical and summer time middle and upper troposphere, in which significant amounts of NO are formed by lightning. In agreement with these thoughts, McFarland et al. (1979), Kley et al. (1981), Davis et al. (1987) and Drummond et al. (1988) have indeed measured background volume mixing ratios of NO of less than 10 pptv in remote atmospheric environments.

Besides reacting with NO and O_3 (reactions R5 and R8), HO_2 can also react with itself. Especially in NO-poor environments, this leads to the production of H_2O_2, which plays an important role in aqueous oxidation chemistry, especially through the oxidation of SO_2 to sulfuric acid (H_2SO_4) on wet aerosol particles or in cloud droplets. The most important reaction chain leading to the production of H_2O_2 is

$$CO + OH \rightarrow H + CO_2\ (2\times) \quad \text{R3}$$
$$H + O_2 + M \rightarrow HO_2 + M\ (2\times) \quad \text{R4}$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad \text{R13}$$
$$H_2O_2 + h\nu \rightarrow 2OH\ (\leqslant 350\ \text{nm}) \quad \text{R14}$$
$$\text{net: } 2CO + O_2 \rightarrow 2CO_2$$

This reaction sequence leads, therefore to the oxidation of carbon monoxide without affecting hydroxyl or ozone. The highly water-soluble H_2O_2 can, however, also be removed efficiently by

uptake in clouds and by precipitation, yielding the net result

$$2CO + 2OH + O_2 \rightarrow 2CO_2 + H_2O_2 \text{ (aqueous)},$$

thus leading to the loss of two OH radicals. Furthermore, H_2O_2 is involved in the reaction pair

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad \text{R13}$$
$$H_2O_2 + OH \rightarrow HO_2 + H_2O \quad \text{R15}$$
$$\text{net: } OH + HO_2 \rightarrow H_2O + O_2$$

which likewise removes OH and HO_2 radicals. Increasing CO concentrations in NO-poor environments, therefore, most likely leads to a decrease in OH and O_3 concentrations. In NO-rich environments, on the other hand, higher ozone and hydroxyl concentrations are favoured (Crutzen, 1973). Increases in the atmospheric emissions of NO will lead to higher O_3 and OH concentrations. Responsible for the latter is more ozone production, as well as a shift from HO_2 to OH via reaction R5 which strongly affect the OH concentrations, but only relatively little those of the much more abundant HO_2 radicals.

The oxidation of methane is likewise of substantial importance in background tropospheric photochemistry. One fourth of the hydroxyl radicals react with CH_4, starting several oxidation chains that strongly affect the atmospheric concentrations of hydroxyl and ozone (Crutzen, 1973). Again, the availability of nitric oxide plays an important role in determining the oxidation pathways:

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad \text{R16}$$
$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad \text{R17}$$
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad \text{R18}$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad \text{R19}$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad \text{R5}$$
$$NO_2 + h\nu \rightarrow NO + O \ (\leqslant 400 \text{ nm}) \ (2\times) \quad \text{R6}$$
$$O + O_2 + M \rightarrow O_3 + M \ (2\times) \quad \text{R7}$$
$$\text{net: } CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3$$

This sequence of reactions leads to the net production of two ozone molecules with various intermediates, in particular OH, HO_2, NO and NO_2, serving as catalysts.

In NO-poor environments, other CH_4 oxidation pathways lead to CH_2O formation, such as

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad \text{R16}$$
$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad \text{R17}$$
$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \quad \text{R20}$$
$$CH_3O_2H + h\nu \rightarrow CH_3O + OH \ (\leqslant 330 \text{ nm}) \quad \text{R21}$$
$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad \text{R19}$$
$$\text{net: } CH_4 + O_2 \rightarrow CH_2O + H_2O$$

or the reaction sequence

$$CH_4 + OH \rightarrow CH_3 + H_2O \quad \text{R16}$$
$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad \text{R17}$$
$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \quad \text{R20}$$
$$CH_3O_2H + OH \rightarrow CH_2O + H_2O + OH \quad \text{R22a}$$
$$\text{net: } CH_4 + OH + HO_2 \rightarrow CH_2O + 2H_2O$$

which removes OH and HO_2.

This is also the result of the pair of reactions

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \quad \text{R20}$$
$$CH_3O_2H + OH \rightarrow CH_3O_2 + H_2O \quad \text{R22b}$$
$$\text{net: } OH + HO_2 \rightarrow H_2O + O_2$$

The photochemical breakdown of formaldehyde to carbon monoxide occurs along three pathways. One of these, taking place with a probability of about 40%, leads to the production of two HO_2 radicals:

$$CH_2O + h\nu \rightarrow H + CHO \ (\leqslant 350 \text{ nm}) \quad \text{R23a}$$
$$H + O_2 + M \rightarrow HO_2 + M \quad \text{R4}$$
$$CHO + O_2 \rightarrow CO + HO_2 \quad \text{R24}$$
$$\text{net: } CH_2O + 2O_2 \rightarrow CO + 2HO_2$$

The other pathways are:

$$CH_2O + h\nu \rightarrow CO + H_2 \ (\leqslant 350 \text{ nm}) \quad \text{R23b}$$

and

$$CH_2O + OH \rightarrow CHO + H_2O \quad R25$$

$$CHO + O_2 \rightarrow CO + HO_2 \quad R24$$

$$\text{net: } CH_2O + OH + O_2 \rightarrow CO + H_2O + HO_2$$

Altogether, the oxidation of CH_4, CH_2O and CO to CO_2 leads to a loss of OH and HO_2 in NO-poor environments and a gain of O_3 in NO-rich environments. In the latter case, up to 3.7 ozone molecules can be produced for each molecule of CH_4 that is oxidized to CO_2 (Crutzen, 1973).

3. Changes in global atmospheric photochemistry due to human activities

The amount of methane in the atmosphere has been increasing for considerable time, in agreement with the growth of various human activities. Observations during the past three decades indicate an average yearly increase by 0.7–1% (Khalil and Rasmussen, 1988; Blake et al., 1982; Steele et al., 1987; Zander et al., 1989b). Furthermore, analyses of air trapped in ice cores have shown that the atmospheric methane content during the holocene more than three hundred years ago was 2.5 times lower than at present (Rasmussen and Khalil, 1984; Craig and Chou, 1982). These global increases in methane should have caused increased production of ozone in NO-rich environments and lower hydroxyl concentrations in NO-poor environments. Especially over the past decades, the production of ozone in the northern hemispheric mid-latitude zone has been strongly enhanced by increases in NO emissions from industrial activities. In addition, carbon monoxide mean concentrations have also increased by 0.85–1% per year in the northern mid-latitude background troposphere (Khalil and Rasmussen, 1988; Zander et al., 1989a). Through reaction R3 the observed rise in CO concentrations would have lowered OH concentrations also at mid-latitudes in the northern hemisphere. However, enhanced ozone formation and higher nitric oxide concentrations which favour the conversion of HO_2 to OH via reaction R5, work in the other direction.

In the NO-poor atmospheric environments, the observed increase in background CH_4 concentrations should have led to lower hydroxyl and higher carbon monoxide concentrations. Contrary to the observations in the northern hemisphere, measurements at Cape Point in South Africa, however, do not indicate any significant trend (Brunke et al., 1990). This is surprising as in these regions one would expect the strongest feedbacks leading to lower OH and higher CH_4 and CO concentrations. A downward trend in OH concentrations would be significant, as lesser quantities of industrial and natural gases may become oxidized in the troposphere by reactions with hydroxyl, leading to a build-up of various important atmospheric trace gases, besides CH_4 and CO. Clearly it is very important to obtain much more information on trends in CO concentrations in background air in the northern and especially southern hemisphere.

4. Model simulations of present and pre-industrial O_3, CO and OH distributions

Indications of the potential changes that may have occurred in global tropospheric chemistry since pre-industrial times may be obtained by model calculations. Preliminary results showing these for tropospheric ozone were previously derived with two-dimensional models (Crutzen and Gidel, 1983; Isaksen and Hov, 1987; Hough and Derwent, 1990). Now the first results using three-dimensional models for tropospheric chemistry are becoming available (Spivakovsky et al., 1990; Levy and Moxim, 1989). As an example, we will compare carbon monoxide, ozone and hydroxyl distributions that are calculated for pre-industrial and industrial times using our global three-dimensional photochemical model that considers the chemistry of the background troposphere, driven by solar ultraviolet radiation and involving O_3, H_2O, CH_4, CO, NO_x, and products derived from these, as given by reactions R1-R25. Model transport is described by monthly average winds and an eddy diffusion parameterization derived from the standard deviations of the winds from the means (Oort, 1983). For more details about the model design the reader is referred to Zimmermann (1984), Zimmermann et al. (1989) and Feichter and Crutzen (1990).

For simulations of the chemical composition of

Table 1. *NO_x Emissions in TgN/month*

			Soils		Biomass burning $\|\phi\| < 30°$	
Month	Industry	Lightning	N	S	N	S
1	1.66	0.43	0.208	0.422	0.486	0.016
2	1.66	0.35	0.225	0.443	0.599	0.001
3	1.66	0.42	0.332	0.426	0.719	0.001
4	1.66	0.35	0.442	0.341	0.610	0.001
5	1.66	0.44	0.595	0.263	0.254	0.001
6	1.66	0.50	0.781	0.192	0.067	0.001
7	1.66	0.44	0.969	0.163	0.067	0.152
8	1.66	0.39	0.905	0.165	0.078	0.614
9	1.66	0.34	0.748	0.215	0.062	0.704
10	1.66	0.40	0.491	0.283	0.070	0.285
11	1.66	0.42	0.331	0.386	0.067	0.062
12	1.66	0.41	0.246	0.426	0.052	0.030
Σ			6.300	3.700	3.100	1.900
	20.0	5.00	N + S: 10.00		N + S: 5.00	

the present atmosphere, observed ground level CO and CH_4 concentrations (Dianov-Klokov and Yurganov, 1981; Dianov-Klokov et al., 1989; Steele et al., 1987), as well as estimated NO sources by industrial processes, lightning, soil emissions, and biomass burning were given as lower boundary conditions (see Table 1). The industrial source of NO_x has been taken to be equal to 20 Tg NO_x – N/yr (Logan, 1983; Ehhalt and Drummond, 1982), the same amount as provided by all other NO_x sources together. This anthropogenic emission was spatially distributed proportional to the industrial CO_2 emissions (Marland and Rotty, 1984), when possible readjusted by the NO_x-emission data published by World Resources Institute (1990).

The spatial and temporal distribution of the lightning source is based on the observations of Turman and Edgar (1982) from the DMSP satellite. The total estimated source of 5 Tg N/yr (Noxon, 1976; Chameides et al., 1987) is distributed density weighted in vertical columns as recommended by Kowalczyk and Bauer (1982).

Another 5 Tg N/yr is assumed to be released by the burning of vegetation in the dry season in the tropics. The geographical and seasonal distribution of the burning events as well as the estimation of the release rate of NO_x was worked out by Hao et al. (1991).

The exhalation of NO from soils due to microbiological processes in this model was ascribed as a first guess to land areas, weighted according to precipitation amounts and temperature. No emissions were allowed at lower temperatures than 5°C and less precipitation than 10 mm/month in order to exclude polar regions and deserts. The total source was taken to be 10 Tg N/yr (Galbally and Roy, 1978; Johansson, 1989).

Observed or calculated concentrations of O_3 (Komhyr et al., 1989), HNO_3 (Gille et al., 1987) and NO_x (Valentin, 1991) at 100 hPa serve as upper boundary conditions. Latitude/altitude dependent photodissociation coefficients where provided by a two-dimensional model (Valentin, 1991) based on the method described in Brühl and Crutzen (1988). Together with ground deposition velocities for O_3, NO_2, HNO_3, CO and H_2O_2 as

Table 2. *Deposition velocities (cm s^{-1})*

Species	sea/snow	land	
O_3	0.1	0.4	Galbally and Roy (1980)
NO_2	0.1	1.0	Crutzen and Gidel (1983)
HNO_3	1.0	1.0	Crutzen and Gidel (1983)
H_2O_2	2.0	1.0	Crutzen and Gidel (1983)
CO	0.0	0.02	Seiler (1974)

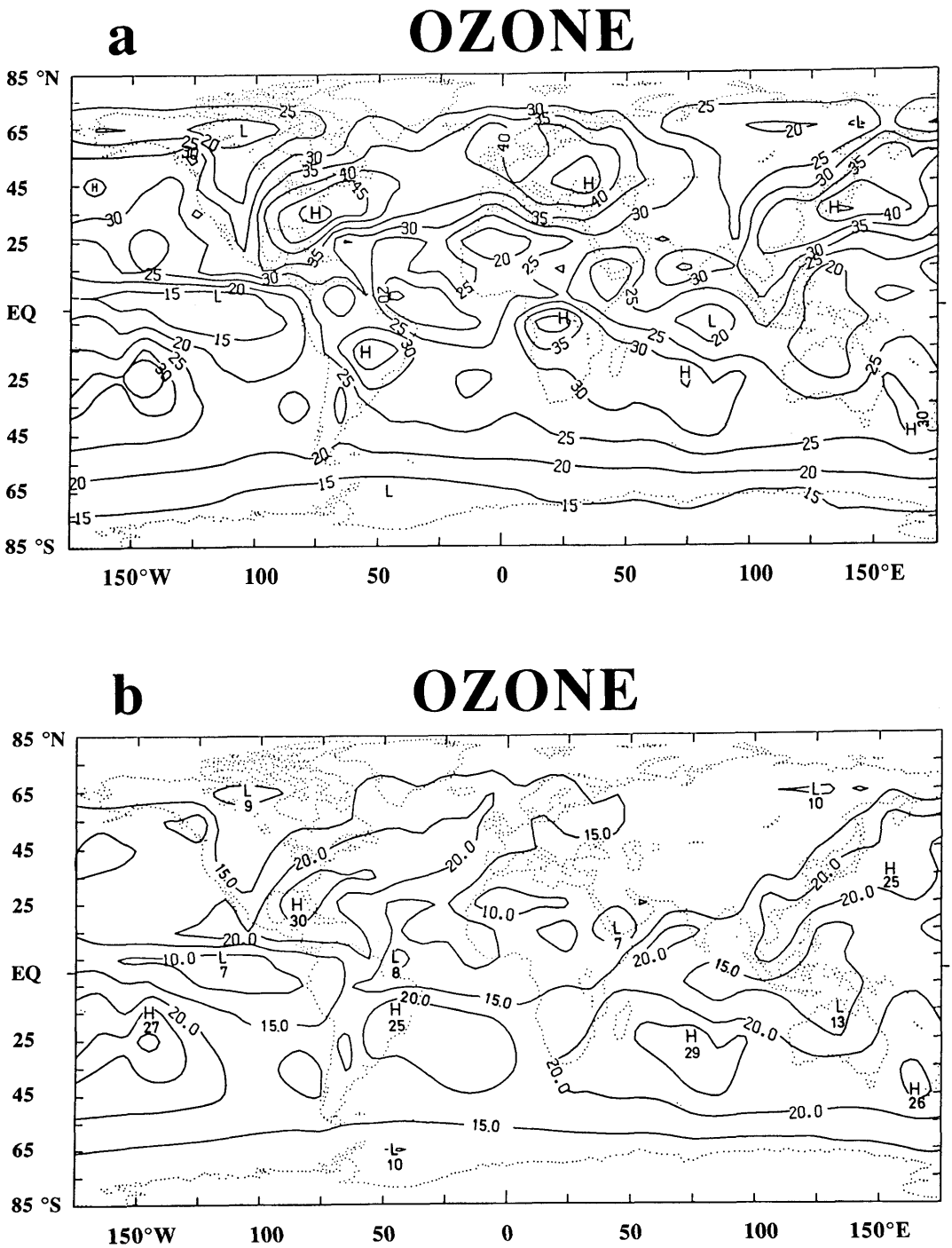

Fig. 1. Surface (1000 hPa) volume mixing ratios of O_3 for July for (a) the industrial period (year 1980) and (b) the preindustrial period, calculated with our three-dimensional tropospheric photochemical model. Units: ppbv.

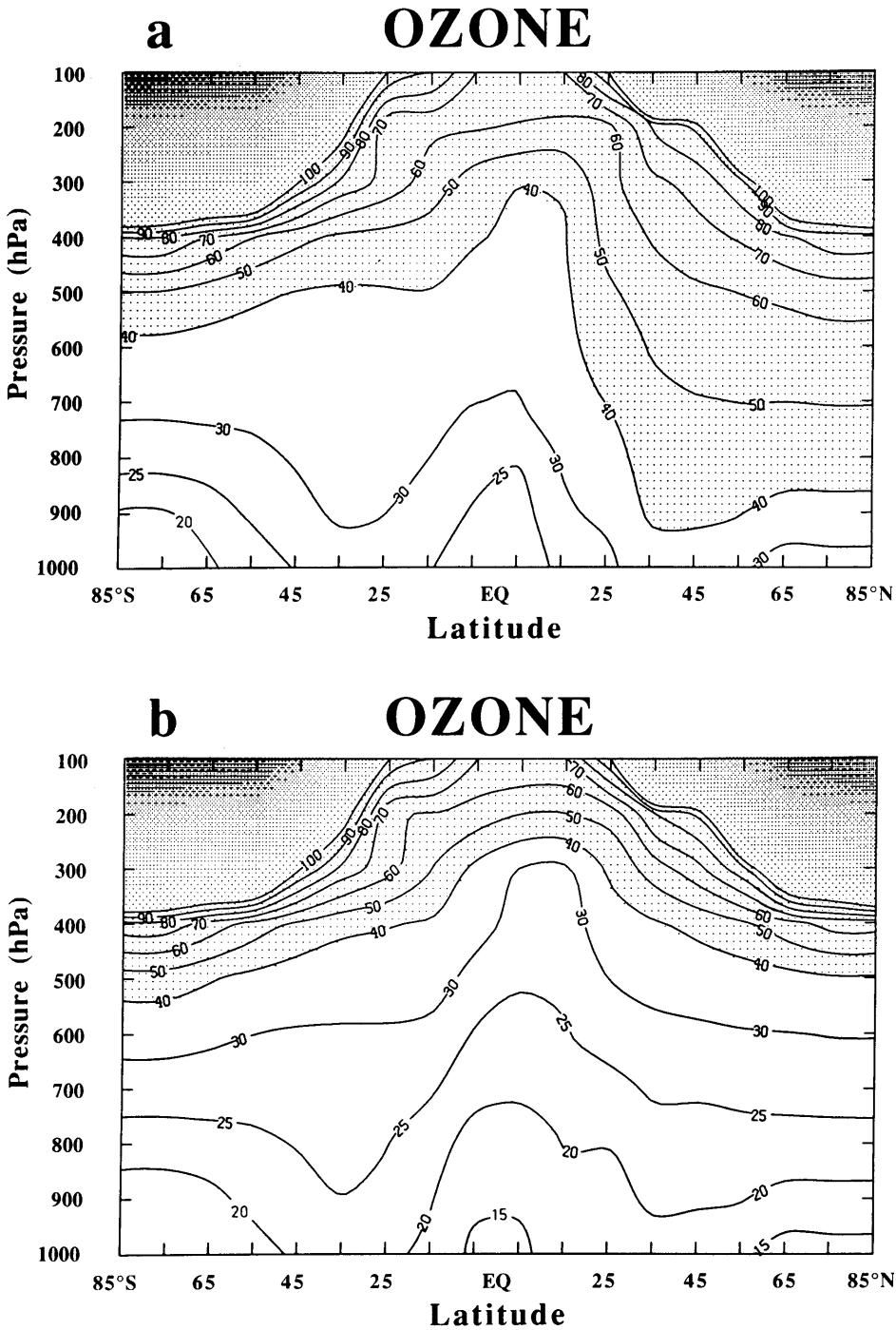

Fig. 2. Zonal average volume mixing ratios of O_3 for July for (a) the industrial period (year 1980) and (b) the preindustrial period, calculated with our three-dimensional tropospheric photochemical model. Units: ppbv.

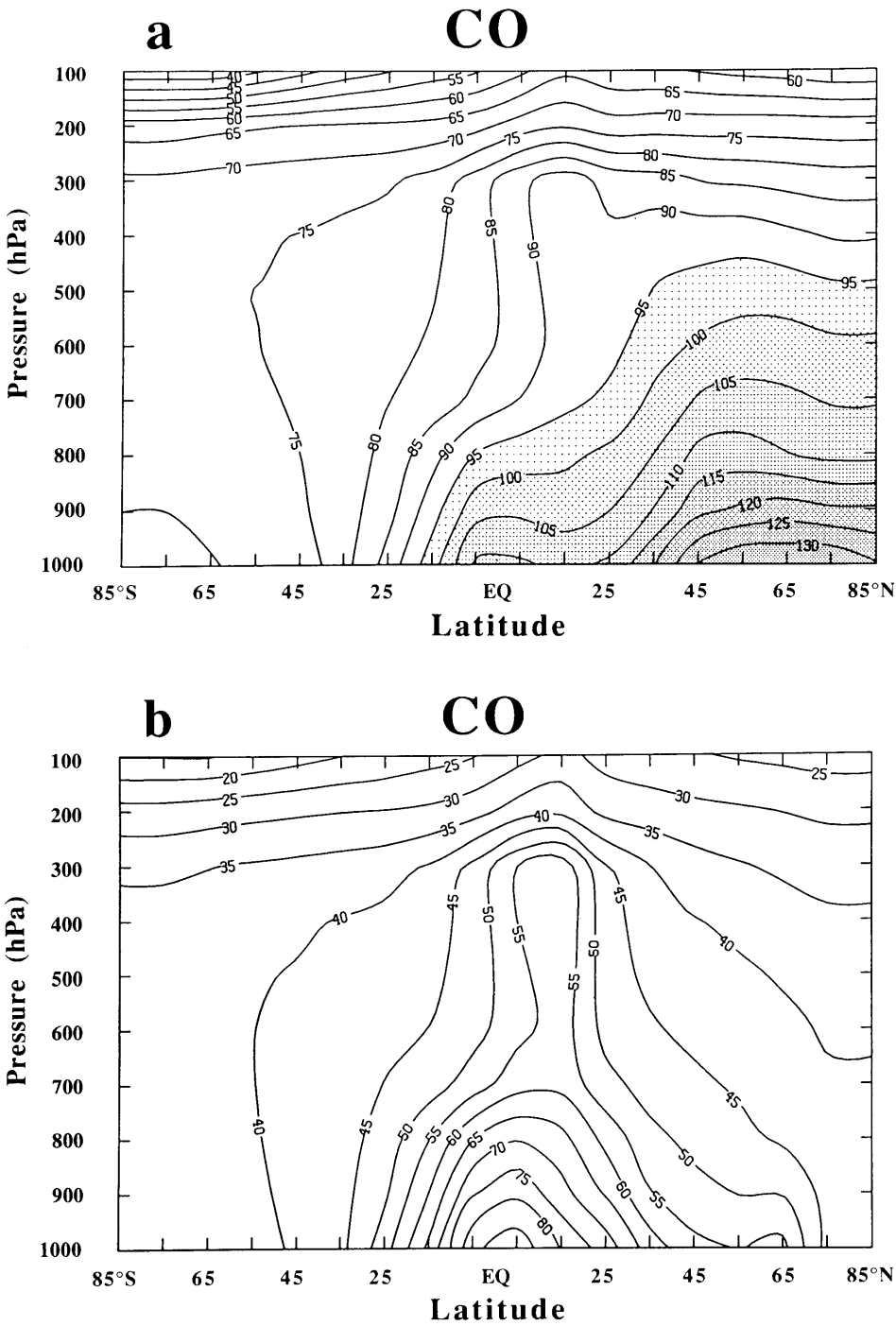

Fig. 3. Calculated zonal average volume mixing ratios of CO for July for (a) the industrial period (year 1980) and (b) the preindustrial period. Units: ppbv.

depicted in Table 2 and wet removal parameterization of HNO_3 and H_2O_2 based on climatological rainfall rates and scavenging efficiencies as proposed by Rodhe and Isaksen (1980), this information is sufficient to calculate the concentrations of ozone, hydroxyl and the other compounds. As examples, we show in Fig. 1a calculated 1980 July surface O_3 volume mixing ratios and in Figs. 2a, 3a and 4 the corresponding, longitudinally averaged distributions of O_3, CO and OH. The calculated O_3 field contains several features that are also observed (Logan, 1985) and clearly shows the influence of ozone production over and downwind from the main industrial regions, mainly due to the catalytic activity of the NO_x gases that emanate from them. As an outcome of these model calculations we estimate an amount of 2050 Tg CO/yr to be oxidized by OH (R3) and another 280 Tg CO/yr being lost due to surface uptake. 630 Tg CO/yr are produced via methane oxidation. The remaining input flux 1700 Tg CO/yr, which is required to maintain the currently observed CO distribution may be assumed to consist of 500 Tg CO/yr from industrial activities (Logan et al., 1981), 600 Tg CO/yr from tropical biomass burning (Crutzen and Andreae, 1990) and 600 Tg CO/yr from various natural sources, such as vegetation and oceans which either emit CO directly, or which emit hydrocarbons that are oxidized to CO in the atmosphere (Zimmerman et al., 1978; Seiler, 1974; Bonsang et al., 1988).

For the pre-industrial scenario, the above ground fluxes are reduced by the industrial source and by 90% of the biomass burning contribution, simulating a lower tropical population. The residual flux of 600 Tg CO/yr is increased by 20% to account for the effect of deforestation (World Resources Institute, 1990). Similarly we reduce the sources for NO by their anthropogenic contribution. Assuming that the pre-industrial methane concentrations were 60% lower than the present day concentrations, as known from the ice core

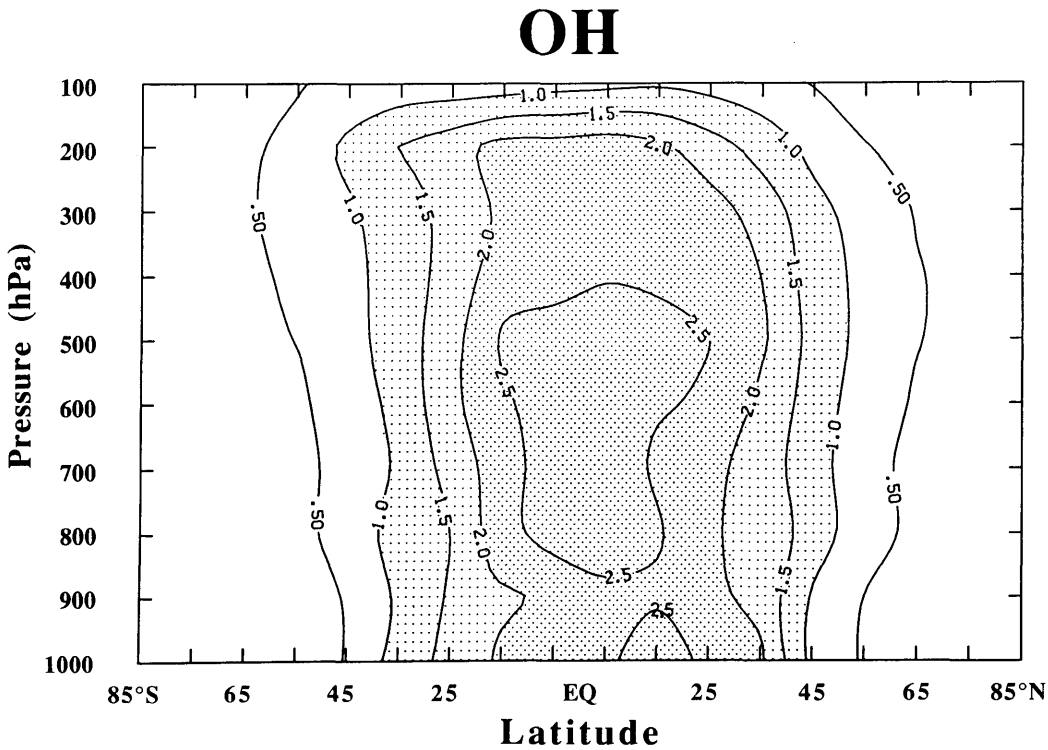

Fig. 4. Calculated daytime, zonal average, annual average concentrations of OH for the industrial period. Units: 10^6 molecules/cm^3.

Tellus A-B/43/4-10

measurements (Stauffer and Neftel, 1988), we can next calculate the chemical distributions of O_3, CO, and OH during the pre-industrial time. Figures 1b, 2b and 3b clearly show, compared to the results obtained for industrial conditions in Figures 1a, 2a and 3a, much lower O_3 concentrations in the northern hemisphere, as well as much lower CO concentrations everywhere, but especially in the northern hemisphere. As a result of the much lower CO and CH_4 concentrations during pre-industrial times, our model also indicates for most of the troposphere south of about 20° N, as shown in Figure 5, a decrease in OH concentrations by about 10-20%. To the north, the increase in tropospheric O_3 and NO due to anthropogenic activities may have caused an increase in hydroxyl concentrations.

Large increases in tropospheric ozone concentrations have indeed been observed at the Hohenpeißenberg station in Southern Germany during the period 1967–1982, implying more than a doubling in the lower troposphere (Attmannspacher et al., 1984). Observations of surface ozone at the clean air stations of Mauna Loa, Hawaii and Point Barrow, Alaska (Oltmans et al., 1989) likewise suggest variable upward trends by 0.5–1.5% per year over the last 15 years, most pronounced during the summer months. Several examples of observed ozone trends on the American and European continents have also been given by Logan (1985) and Crutzen (1987). Finally, Volz and Kley (1988), by rechecking the old measurement techniques, have shown that ozone measurements carried out during clean air conditions by Levy and coworkers at the outskirt of Paris during the last decades of the past century should have produced reliable results. The old data show that ozone volume mixing ratios were about equal to 10 ppb or less year round, indicating that surface ozone concentrations have increased 2–4 times since the end of the past century. Unfortunately, trend analyses for other

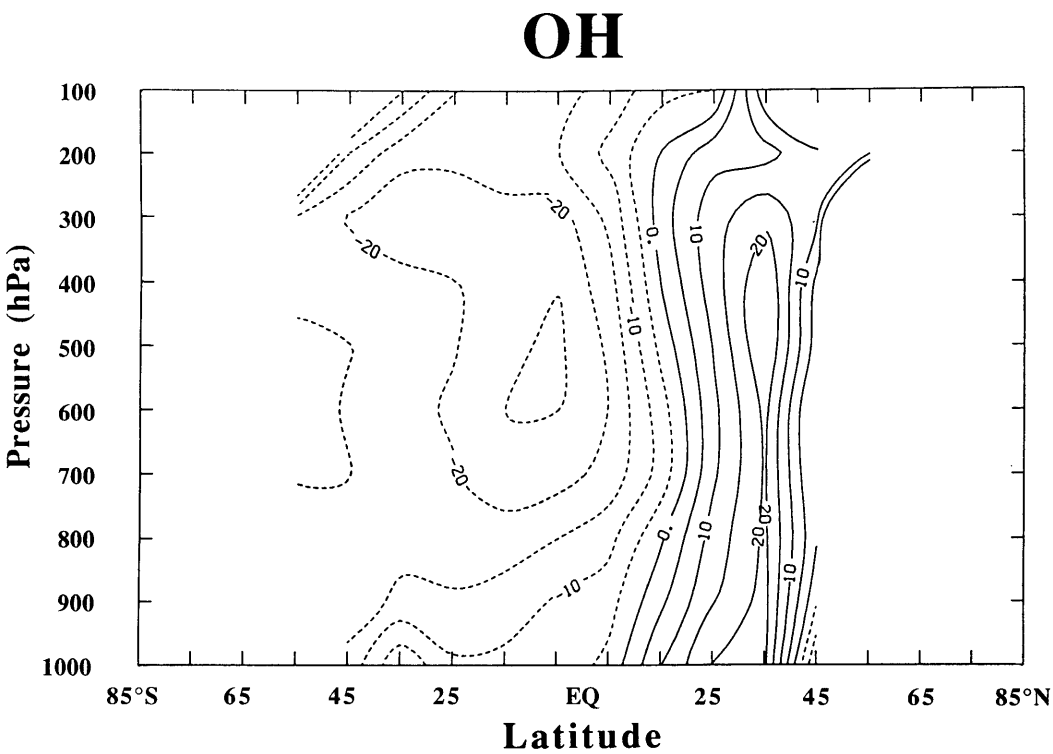

Fig. 5. Percent changes in the calculated daytime, zonal average, annual average concentrations of OH since the preindustrial times. Units: percent.

parts of the world can not be made due to lack of data.

5. The importance of the tropics in atmospheric chemistry

In photochemical models highest, OH concentrations are calculated to occur in the tropics (see Fig. 4). This is to be expected, as the flux of solar ultraviolet radiation peaks there, because of minimum overhead ozone amounts and small solar zenith angles. From these calculations, the global average concentration of hydroxyl in the troposphere is estimated to be about 7×10^5 molecules/cm^3. The few direct observations of hydroxyl radical concentrations that are available (Dorn et al., 1988; Hard et al., 1986; Perner et al., 1989; Platt et al., 1988) have been made in rather

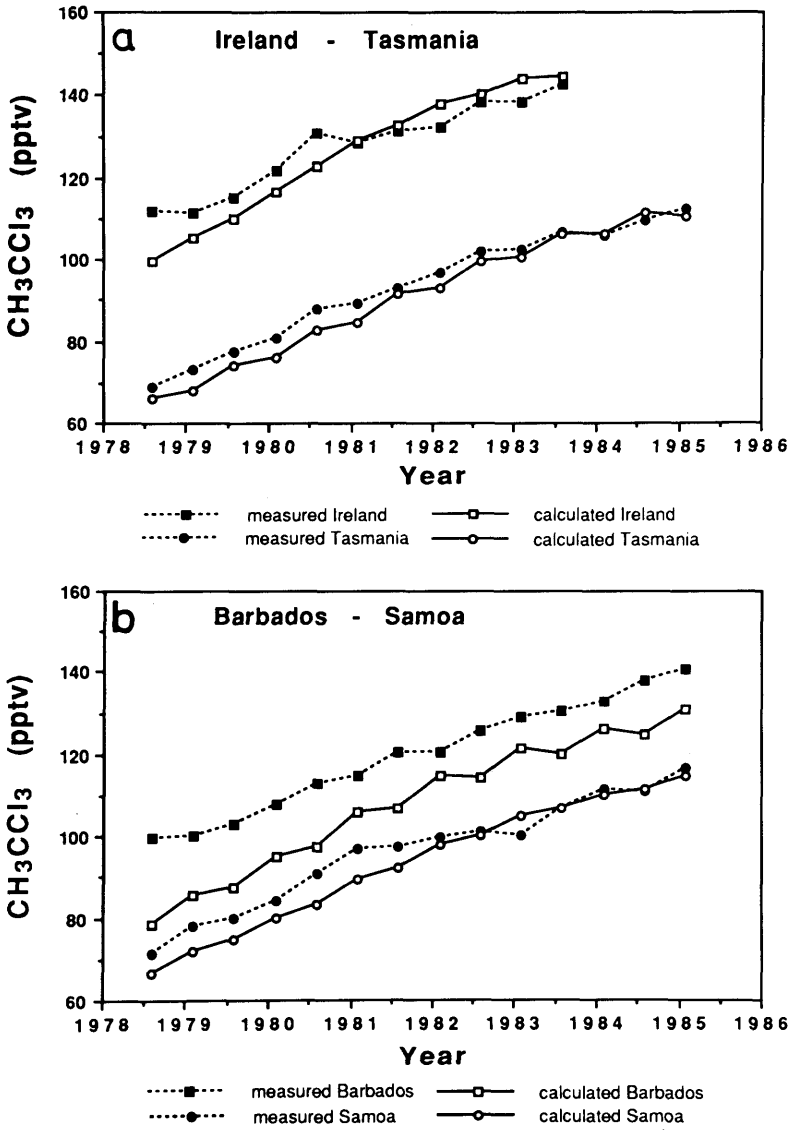

Fig. 6. Calculated and observed methylchloroform (CH_3CCl_3) volume mixing ratio for selected stations. Units: pptv.

polluted environments; no measurements have yet been made in background air. Because modeling of short-lived gases like NO_x that strongly affect OH concentrations is extremely difficult, the correctness of the calculated OH distribution is hard to judge. Fortunately, the OH concentration distributions shown in Fig. 4 have been successfully tested against global observations of methylchloroform (CH_3CCl_3), which is removed from the atmosphere by reactions with OH and which has no other sources than the industrial emissions which are known to within 20%. Using this approach, the global, 24 h-average OH concentrations are estimated to be equal to $7.7 \pm 1.4 \times 10^5$ molecules/cm^3 (Prinn et al., 1987). The observed time series of methylchloroform mixing ratios at the ALE stations (Prinn et al., 1987) could be reproduced by the model generally within 10%, as shown in Fig. 6. Fig. 4 should, therefore, contain the main features of the annual average meridional distribution of OH radicals. This is extremely useful, because it allows some rough estimation of the global distribution of the sinks of CH_4 and CO, which are removed from the atmosphere by reaction with OH. The results are shown in Fig. 7.

Containing such high concentrations of OH, the tropical regions contribute most strongly to the destruction of CO and CH_4. Consequently their production also peak in the tropics. The most important tropical sources for carbon monoxide are biomass burning and the oxidation of hydrocarbon gases, especially methane (CH_4), isoprene (C_5H_8) and other reactive hydrocarbon gases that are emitted by the vegetation (Zimmerman et al., 1978). For the same reason, methane too is mostly formed in the tropics, mainly by the decay of organic matter in the anaerobic sediments

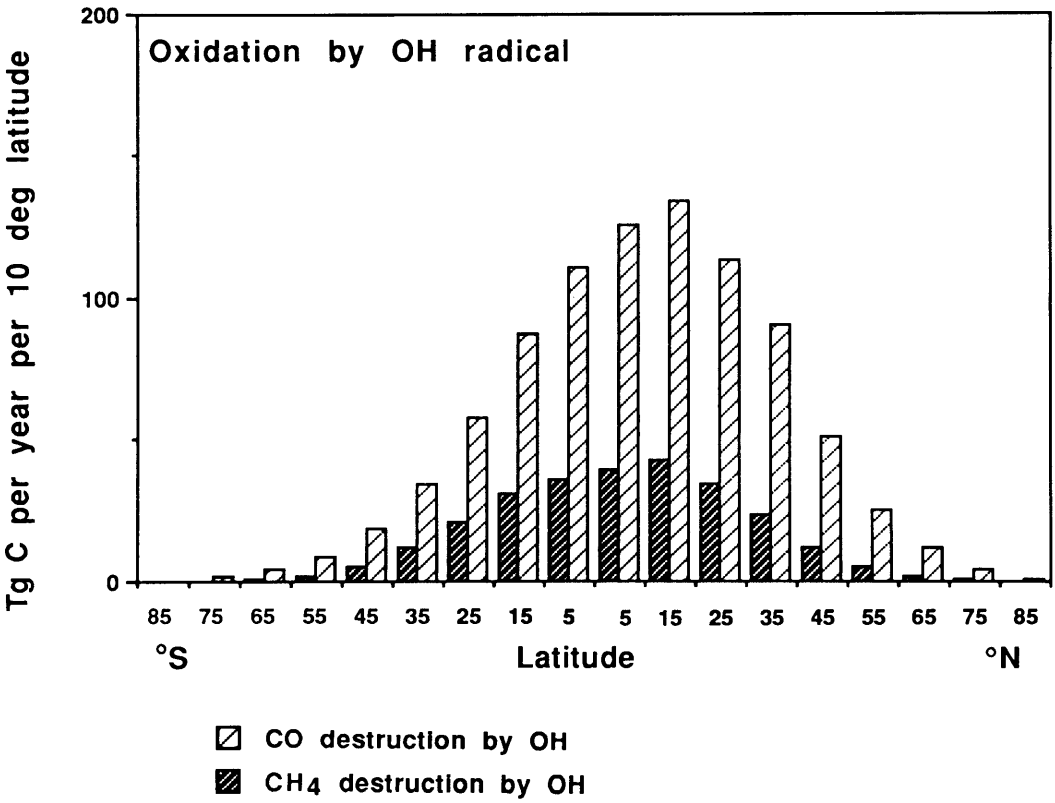

Fig. 7. Estimates of annual CO and CH_4 oxidation amounts by reaction with OH for 10° latitude belts. The calculated total tropospheric destructions are 2050 Tg CO/yr and 360 Tg CH_4/yr. Units: Tg C/yr.

of natural wetlands and rice fields, in the rumen of cattle, and by biomass burning. At higher latitudes CH_4 emissions from wetlands, cattle, landfills, fossil fuel production and leaks in natural gas distribution systems, as summarized e.g. by Cicerone and Oremland (1988) and Aselmann and Crutzen (1989) are the most important contributions. Altogether, the tropics dominate the sinks and sources of CO and CH_4. Considering that the greatest industrial and agricultural developments will occur in these regions of the world, it is of the utmost importance that much study is devoted to tropical photochemistry.

6. Conclusions

In this paper we have presented a short overview of the main processes that determine the chemistry of the background atmosphere, emphasizing reactions taking place in the O_3–HO_x–NO_x–CO–CH_4 photochemical system. Due to human activities this global photochemical system has been changing considerably since pre-industrial times. The changes probably imply a gradual shift of the oxidation processes from unpolluted to more polluted environments of the atmosphere, with growing ozone concentrations in the latter. Three-dimensional model calculations indicate a strong growth of ozone and carbon monoxide concentrations especially in the northern hemisphere and a decrease in hydroxyl concentrations since pre-industrial times. Also in the southern hemisphere CO concentrations most likely were substantially smaller during pre-industrial times than at present. It will thus be particularly interesting to obtain information of past atmospheric CO levels from the ice core records.

For the globe as a whole the oxidation efficiency of the atmosphere (globally averaged OH concentrations) may have been gradually decreasing due to increasing concentrations of CH_4 and CO, although for the extratropical regions in the northern hemisphere this tendency may have been opposed by the strong growth in anthropogenic NO emissions and the resulting increase in tropospheric ozone. The overall loss of OH implies the possibility of an increase in the many atmospheric trace gases that are removed by reactions with hydroxyl.

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