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Preface

This report presents results from a series of model studies that have been published in part previously. Firstly, parts of this work were presented in Chapter 5, "Tropospheric Processes: Observations and Interpretation" by Isaksen et al. in the WMO report "Scientific Assessment of Ozone Depletion: 1991". There it formed, together with contributions from other researchers and groups, the basis for the discussion and the conclusions drawn. Secondly, parts of the results have been published in the paper "Chemical Dynamical Modelling of the Atmosphere with Emphasis on the Methane Oxidation" in "Berichte der Bunsen-Gesellschaft für Physikalische Chemie" by Berntsen, Fuglestvedt and Isaksen, 1992. This current report is meant to give a somewhat broader and more thorough presentation and discussion of the study and the results than was possible in the above-mentioned publications. We are thankful to Hans M. Seip and Jan E. Jonson for valuable comments.

RESPONSES IN TROPOSPHERIC O_3 , OH AND CH_4 TO CHANGED EMISSIONS OF IMPORTANT TRACE GASES

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Abstract

A two-dimensional (altitude vs. latitude) photochemical/transport model of the global troposphere is applied to study the effects of changed emissions of NOx, CH_4, CO and NMHC on the levels of O_3, OH and CH_4. On a mass basis, the efficiencies in increasing O_3 concentrations differs markedly between the source gases, with NOx having the largest effects. The sensitivity to increased emissions of NOx from airplanes is found to be significantly higher than for ground emissions of NOx (> a factor of 10). The tests also show that the efficiencies are larger for smaller perturbations and that the background levels of NOx are important for the efficiency in O_3 enhancement from NOx emissions. Increased emissions of CO, CH_4 and NMHC all reduce tropospheric OH, while increased NOx emissions increase OH. Through changes in OH these source gases also affect the distribution of CH_4. Since increased emissions of CH_4 reduce the strength of its own main sink, the relative increase in atmospheric levels is larger than the relative increase in emissions. The strength of this positive feedback is estimated to be approximately 35%. The results indicate that the indirect effects of emissions of CH_4, CO and NMHC on climate may be positive due to the positive effect on O_3 and the negative effect on OH, with the latter effect increasing the lifetimes of greenhouse gases removed by OH. The indirect effects of NOx on climate are of opposite signs; a positive through O_3 increases and a negative through OH increases. Thus, estimates of the net effect of the indirect effects of NOx emissions on climate require better knowledge of the NOx distribution and detailed radiative calculations.

CONTENTS

1. INTRODUCTION

For the first time since the industrial revolution and the rapid increase in the human population, mankind is able to alter the composition of the atmosphere on a global scale through large releases of chemical compounds. This has led to changed concentrations of trace gases which are of vital importance for the oxidative capacity of the atmosphere and for the radiative balance of the Earth/atmosphere.

The most interesting of the gases released by anthropogenic sources in this respect are the chemically active gases methane (CH_4), other hydrocarbons (so-called non-methane hydrocarbons, NMHC), carbon monoxide (CO) and nitrogen oxides ($NOx=NO+NO_2$). The atmospheric levels of methane have more than doubled since pre-industrial times. In the late 1970s the rate of increase was as high as ~20 ppb/yr (~1.3%/yr). In the mid-1980s the rate was about 12-13 ppb/yr (~0.75%/yr), while the growth rate for 1989 was possibly as low as 10 ppb/yr (~0.6%/yr) (IPCC, 1992, and references therein). The trends of NOx, CO and NMHC are more difficult to determine due to shorter lifetimes and a limited number of monitoring stations. But for ethane, Ehhalt et al., 1991, report a trend of 0.9±0.3%/yr in the Northern Hemisphere. Important sources for both CO and NOx are combustion of fossil fuel and biomass burning. The considerable intensification of these activities since pre-industrial times has caused a substantial increase in the emissions of NOx and CO. The global emissions of NOx from fossil fuel combustion are estimated to have increased by 3.4%/yr in the period 1860-1980 (Dignon and Hameed, 1989). As an indication of the development of the atmospheric NOx levels, changes in the content in ice of nitrate (NO_3^-), which is an end product for NOx in the atmosphere, may be used. The concentrations in ice in Greenland have increased by almost a factor of 2 since the end of the last century (Neftel et al., 1985), indicating anthropogenic contributions to the NOx budget at higher Northern latitudes. At the South Pole no such trend is observed for the same period (WMO, 1989). Mayewski et al., 1990, also find that anthropogenic emissions have significantly affected the nitrogen cycle of the remote atmosphere in the Northern Hemisphere by analysis of nitrate in ice in South Greenland. According to IPCC, 1992, the CO level in the Northern Hemisphere appears to be increasing at ~1%/yr, but there is no evidence of a significant trend in the Southern Hemisphere.

2. ESSENTIAL COMPONENTS AND REACTIONS IN THE CHEMISTRY OF THE TROPOSPHERE

Ozone (O_3) and the hydroxyl radical (OH) are key compounds in the atmospheric oxidation processes. Ozone is radiatively active and affects the radiative balance of the Earth/atmosphere. It is also absorbs UV radiation, and its photolysis initiates the production of OH in the troposphere and the stratosphere. In addition, ozone may cause damage to human health, plants and materials. OH is the most important oxidizing species in the troposphere. It is extremely reactive, and by destroying trace gases it prevents the accumulation of several gases in the atmosphere.

The sources of tropospheric ozone are *in situ* chemical production and transport from the stratosphere. In the *stratosphere,* ozone is generated by photodissociation of O_2, followed by the combination of ground state oxygen atoms with O_2 :

$O_2 + h\nu\ (\lambda \leq 243\ \text{nm}) \rightarrow 2O(^3P)$ R1

$O(^3P) + O_2 + M \rightarrow O_3 + M$[1] R2

The chemical production of ozone in the *troposphere* is driven by UV-radiation, NOx, CO and hydrocarbons. NO has a key role in the ozone chemistry because the level of this gas determines whether ozone will be produced or lost when CO and hydrocarbons are oxidated (Crutzen, 1987). HO_2 and RO_2 radicals, produced in the oxidation of CO and hydrocarbons, react with NO to give NO_2 (R3 and R4), which is then photolyzed (R5):

$HO_2 + NO \rightarrow OH + NO_2$ R3

or

$RO_2 + NO \rightarrow RO + NO_2$ R4

$NO_2 + h\nu\ (\lambda < 400\ \text{nm}) \rightarrow NO + O(^3P)$ R5

$O(^3P)$ reacts further with O_2 to give O_3 through R2.

Major loss reactions for ozone in the troposphere are photolysis in the presence of water vapour (R6 and R7), and reactions with unsaturated hydrocarbons and HO_2, (R8):

$O_3 + h\nu\ (\lambda \leq 320\ \text{nm}) \rightarrow O(^1D) + O_2$ R6

$O(^1D) + H_2O \rightarrow 2OH$ R7

R7 represents a loss of ozone because in the absence of water vapour $O(^1D)$ will be energetically stabilized by an air molecule to $O(^3P)$, which will react with molecular oxygen to give ozone again.

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[1] M represents the species that stabilizes the energized molecule by dissipating the energy. This prevents the energized molecule from decomposing back to reactants. In atmospheric chemistry the most important species acting as M are one of the most abundant molecules, i.e. N_2 or O_2. In some literature the role of M is indicated by appending an asterisk to M on the right side of the equation (M*). For a further discussion on termolecular reactions in atmospheric chemistry, see for instance Brasseur and Solomon, 1986, Finlayson-Pitts and Pitts, 1986, or Wayne, 1991.

R8 is important in the background troposphere, where the NO levels are low:

$HO_2 + O_3 \rightarrow OH + 2O_2$ R8

If sufficient levels of NO are present, the reaction between HO_2 and NO (R3) will dominate over R8, thereby leading to ozone production rather than destruction.

In addition to the loss mechanisms mentioned above, ozone is also lost by deposition at the Earth's surface.

Ozone also reacts with NO_2 to give nitrate radicals, NO_3, which are stable only in absence of light.

$NO_2 + O_3 \rightarrow NO_3 + O_2$ R9

Since NO_3 is readily photolyzed, it can only be of importance during night-time and in the polar night. Then OH is low, and NO_3 may then have the role as the main oxidating species. The reaction rates between NO_3 and hydrocarbons are generally much lower than for reactions between OH and hydrocarbons. But NO_3 reaches higher concentrations than OH does. (Typical levels of NO_3 during nighttime may be about 10^9 molecules/cm^3, while the daytime values of OH are in the order of 10^6 molecules/cm^3). NO_3 may therefore be important for the removal of primary organic pollutants in periods when sunlight is absent. NO_3 initiates oxidation chain reactions that produce HO_2 and RO_2 and thereby provides a source of OH (Wayne, 1991).

NO_3, or the species N_2O_5 formed through the reaction

$NO_3 + NO_2 + M \rightleftharpoons N_2O_5 + M$ R10

may be scavenged efficiently by deliquescent aerosols. This mechanism may be an important loss for NOx during winter-time and may thus lead to reduced O_3 production (Isaksen, 1988, Isaksen et al., 1989a). When the relative humidity is above approximately 50%, the lifetime of NO_3 is very short (minutes). This may be explained by the rapid heterogeneous removal of N_2O_5 and thereby also of NO_3 since the reaction between these two species reach equilibrium within minutes under conditions that are typical in the lower troposphere. Then the rate limiting process for the loss of NOx in the absence of OH will be R9 (Platt, 1986).

Since the release rates and the atmospheric concentrations of several precursors in ozone production have increased substantially the last decades, important changes in the chemistry of the atmosphere are likely to have taken place, and changes in the levels of tropospheric ozone are indeed reported. Bojkov, 1986, finds that the average of maximum values of surface ozone may have doubled in certain areas since the second half of the 19th century. Logan, 1985, reports results that indicate an increase of 20-100% since 1940 in summer concentrations of ozone near the surface in rural areas in Europe and Central and Eastern USA. She also reports good evidence for an increase in the middle troposphere over Europe and a weaker evidence for a similar increase over North America and Japan. Bojkov, 1988, reports an increase in surface concentrations by about 1%/yr from the late 1960s through 1986 for the Northern Hemisphere. He also finds that ozone is increasing in the free troposphere. Bojkov claims that the increase may have started earlier than the late 1960s. Kley et al., 1988, suggest that the ozone increase may have started around 1940. A recent analysis of time series from Switzerland shows statistically significant positive trends for the period 1967-1990 for all seasons up to 10-15 km. The trends are almost 15% per decade at 8 km (WMO, 1992). Anfossi et al., 1991, report results indicating that ozone levels in Europe have more than doubled; not only at the surface, but also in the free troposphere. Changes in the Southern Hemisphere are less well documented, but Sandroni et al., 1992, report that at Cordoba (30°S) and Montevideo (34°S) the recent levels are approximately twice as large as a century ago. London and Liu, 1992, have analyzed ozonesonde observations covering a period of 20 years. They conclude that the average of mid tropospheric trends in the Northern Hemisphere is +1.2%/yr.

Hov and Demerjian, 1992, have reviewed ozone trend data from several long-running measurement programs and historical data sets collected north of 20°N. The data sets include sonde data from Europe, North America and Japan, ground-based data from GMCC sites, Zugspitze and Whiteface Mountain, and recent historical analyses of data from Montsouris, Monscalieri and Pic du Midi. The authors conclude that the data sets indicate a broad horizontal spatial homogeneity of ozone in the free troposphere and that the mainly positive reported O_3 trends that they have reviewed, are representative of large portions of the troposphere north of the tropics. This is compatible with the expected long lifetimes of O_3 in this region of the troposphere (100 days).

Although OH is present in only very small concentrations in the troposphere (~1 part in 10^{13}), it is the main oxidating agent for trace gases, which usually are released from the Earth's surface in a reduced or not fully oxidized form. Due to this key role in the atmospheric oxidation processes, perturbations of the concentration and distribution of OH may have far reaching consequences. Gases which are controlled by OH (e.g. CH_4, HCFCs[2], HFCs[3]) are thus affected by changes in OH.

The main source of OH in the troposphere is the photolysis of ozone (R6) which gives the excited oxygen atom $O(^1D)$. This transient species reacts with water vapour to yield OH trough R7.

The source gases that may perturb OH are first of all NOx, CO, CH_4 and to a certain degree higher hydrocarbons. NO may lead to a redistribution among the HOx species (OH and HO_2) through R3, giving higher OH when the NO concentrations are

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[2] HCFC: Hydrochlorofluorocarbon

[3] HFC: Hydrofluorocarbon

increased. The reaction between OH and NO_2 removes OH out of the HOx system through the reaction

$NO_2 + OH + M \rightarrow HNO_3 + M$ R11

HNO_3 is efficiently scavenged by water droplets so this is an important loss mechanism for OH since only a small fraction of HNO_3 is photolyzed to give OH again. In addition to these mechanisms, NOx may also influence the production of OH through its important role in the ozone chemistry.

A number of factors may affect the concentration and distribution of OH and changes that affect the fluxes through R6 and R7 may be of special importance. Changed concentrations of O_3 in the stratosphere will lead to changed fluxes of UV into the troposphere, thereby affecting the photolysis of tropospheric ozone (R6), which will further affect the production of OH through R7. Climate changes affecting water vapour, and chemical, dynamical or radiative processes affecting ozone, may also lead to changed production and loss of OH.

The following reactions (R12-R14) are the initial steps in the interactions between OH and CO and hydrocarbons:

$CH_4 + OH \rightarrow CH_3 + H_2O$ R12

$CO + OH \rightarrow CO_2 + H$ R13

$NMHC + OH \rightarrow Products$ R14

Later in the degradation chain, there will be reactions where odd hydrogen (H, OH, HO_2, H_2O_2) are involved in such ways that the initial losses of OH through R12-R14 may be partly compensated or overcompensated.

Increased emissions of CO, CH_4 and NMHC, may, therefore, depending on other factors, lead to depletion of OH and an increase in other important gases. Again the NOx species have an important role. In addition to the direct (R3 and R11) and indirect (R6 and R7) control mechanisms shown above, NOx also controls the effect of CO and hydrocarbons on OH (Crutzen, 1987).

One of the main questions in atmospheric chemistry today is whether the OH levels have changed significantly over time or remained stable since the large anthropogenic emissions started. The behavior of OH through ice ages and interglacial periods is also of concern. Several model studies have addressed these questions, and many studies indicate that OH levels were higher in preindustrial time. The results of these model experiments are, however, critically dependent on model formulation as well as the emissions assumed. NOx levels are crucial for OH changes, and increased NOx-emissions counteract the OH reduction due to gases such as CO and CH_4 (Isaksen, 1988). The various models give different hemispheric levels and trends, and Prinn et al., 1992, estimate a positive trend in the global mean concentration of 1.0±0.8%/yr (1σ) for the period 1978-1990. Efforts have also been made to estimate the variations over larger time scales. Pinto and Khalil, 1991, used a one-dimensional (1D) photochemical model and observations from polar ice cores, and they found that average OH concentrations are stabilized against disturbances through the climatic transitions and after human perturbations. With a 1D multiregion model it is estimated that the reductions in global average OH concentration since last glacial maximum and since pre-industrial time are ~30% and 20%, respectively (Thompson, 1992).

Several attempts have been made over the last 20 years to measure OH in the atmosphere, but with limited success (Brune, 1992). Direct measurements of OH is difficult due to the short lifetime (< 1 second) and the low concentrations. The first measurements of tropospheric OH were based on laser-induced fluorescence of OH rotational lines in the UV part of the spectrum (Davis et al., 1976, Wang et al., 1976). These measurements were, however, hampered by many problems (Mount and Eisele, 1992). Later, long-path absorption of laser light in the UV region was applied to measure OH (Hubler et al., 1984, Platt et al., 1988, Hofzumahaus et al., 1991). More recently, two methods that use different principles gave similar results for the OH concentrations. The agreement of the measurements were generally within a factor of two. The first is a long-path absorption method, while the other is a point measurement based on the chemistry of OH (Eisele and Tanner, 1991, Mount, 1992, Mount and Eisele, 1992). According to Brune, 1992, the results give some indications that the description of the chemistry of OH may need revision, because the measured levels and the diurnal variation do not agree too well with what was expected from model calculations. The change in OH level from early morning to noon on a clear day was only a factor of two (Mount and Eisele, 1992). The measured concentrations of OH were in the range $\sim 0.5 - 8 \cdot 10^6$ molecules/cm^3. These measurements are, however, strongly influenced by the local conditions, and so far the results cannot give us information about the global levels of this important species.

Some indirect approaches have been applied. One approach is to use calculated OH fields and to recalibrate them with global tracer model experiments, using gases which has reaction with OH as the only loss and with known source strengths. This has been done for ^{14}CO and ^{12}CO in a global 2D model (Volz et al., 1981, Derwent and Volz-Thomas, 1990). Prinn et al., 1992, used methyl chloroform (MCF) to derive a global mean concentration for OH based on reported emissions of MCF and the assumption that the sinks for MCF are reaction with OH and oceanic uptake. There are however, some limitations to this method: A simple box model is used, and it is not capable of taking into account the redistribution of the MCF emissions that has occurred, which should affect the results (WMO, 1992). The rate constant for the reaction between OH and MCF, which is a crucial parameter in the approach, is later found to be different from what was assumed by Prinn et al., 1992. At 298 K and 277 K the rate constants were found by Finlayson-Pitts et al., 1992, to be respectively about 15% and 5% below the previously applied values, making corrections of the results necessary.

The global levels and distribution of OH may also be estimated by the use of photochemical models (Logan et al., 1981, Crutzen and Gidel, 1983, Isaksen and Hov, 1987, Valentin, 1990, Hough, 1991, Crutzen and Zimmermann, 1991, Kanakidou et al., 1991). There are, however, large uncertainties connected to the OH fields derived in this way. According to WMO, 1992, the uncertainties may be as large as 30-50%.

Since the 2D models suffer from the inherent limitation of zonally averaging (or meridionally averaging for the channel models), these models are not capable of treating some important non-linear effects. The OH and O_3 chemistry is very sensitive to the NO levels in a non-linear way, and the chemical lifetime for NOx is short enough (a few days) to give large zonal variations. When zonal mean values are applied in the chemistry calculations, these non-linear effects due to zonal variations in NO levels, are lost. This is probably the most serious consequence of the zonal averaging in the 2D models. Nevertheless, a 2D model gives a better description of the processes affecting the composition of the atmosphere than 1D or box models do. For a further discussion of the problem of zonal averaging, see Berntsen et al., 1992.

Kanakidou and Crutzen, 1992, used a 3D model to study the effect of zonal averaging. They assumed longitudinally uniform emissions of NOx and NMHC to imitate 2D models, and compared these results with results obtained by the same 3D model, but now with longitudinally varying emissions. They found that the "quasi 2D model" gave significantly higher levels of O_3 and OH, especially in the middle and low troposphere in the tropics and at northern mid-latitudes (see chapter 8).

The mechanisms that control the levels of OH and O_3 have been the subject of extensive research. The results harmonize qualitatively, but due to a large and complex set of chemical reactions that has to be simplified, and due to many processes affecting the chemistry (e.g. radiation, dynamics) which are treated in different ways, there are still serious uncertainties in the results. Especially for the calculated effects of increased NOx-emissions on ozone, the model results show large variations, ~ factor of 3 (WMO, 1992). The difference in temporal and spatial distributions is also large, and the results are very sensitive to the background concentrations.

In this report we use a 2D (altitude vs. latitude) photochemical-transport model for the global troposphere with extensive chemistry to study the effect of changed emissions of the source gases NOx, CH_4, NMHC and CO on the concentrations of O_3, OH and CH_4. Perturbations where the emissions are changed one by one are performed. We have also performed a perturbation in which the emissions of all these source gases were perturbed simultaneously. In addition, we have performed some tests to check the effects of the *degree* of perturbation and the sensitivity to the background concentration of the key compound NOx.

3. THE MODEL

The 2D model is a zonally averaged global model, with a meridional resolution of 10 degrees and a vertical resolution of 0.5 km below 3.25 km and 1.0 km above up to 16.25 km. The first version was developed by Isaksen and Rodhe, 1978, and then applied to study the distribution of SO_2 and sulphate in the troposphere. It has also been used in several later studies. It was applied by Rodhe and Isaksen, 1980, to estimate the tropospheric distribution of sulphur compounds resulting from natural and man-made emissions. The tropospheric ozone budget and possible man-made effects were studied by Isaksen, 1980. Isaksen et al., 1985, applied the model in an analysis of the measured concentration of organic gases in the Norwegian Arctic, and Isaksen and Hov, 1987, calculated trends in the concentrations of O_3, OH, CO, CH_4 and NOx for different assumptions about the development of source gas emissions. The model was also applied by Berntsen, 1989, to estimate the global source strength for methane and to estimate the distribution of the CH_4 emission on the different sources by the use of $\delta^{13}C$ for methane. Berntsen et al., 1989, used the model for calculations of past changes and for future scenarios, and Isaksen et al., 1989b, applied it for studies of the effects of aircraft on ozone. Finally, Berntsen et al., 1992, studied the methane oxidation and the role of NOx for the effects of changed methane emissions on OH.

The results presented here are calculated with a version using advective winds from Newell et al., 1972, and diffusion coefficients from Hidalgo and Crutzen, 1977, with some small modifications. The numerical scheme for the advection, given by Smolarkiewicz, 1983, is an upwind scheme with corrective steps to reduce implicit numerical diffusion. Meteorological data are seasonally averaged. The photodissociation rates (J-values) have a diurnal variation and the J-value sets are changed each month. The chemistry is gas-phase only, but first order heterogeneous scavenging of soluble species by rain and sticking on aerosols is included.

The chemical production term from a bimolecular reaction is given by:

$$P(t)=\sum_{ij} k_{ij} \cdot c_i(t) \cdot c_j(t) \qquad (1)$$

where c_i and c_j are the concentrations of species i and j.

Due to the non-linearity of the production term, and to a lesser degree of the loss term, a resolution of the diurnal variation of the short-lived species in the model is crucial. But to run such a detailed chemistry for each day would be very CPU-time consuming.

The scheme is therefore divided into two parts. In the first part, which is used during the first day of each month with a one hour time step, all species (49) are calculated. 42 species are transported, while 7 components have short enough chemical lifetime to assume that they are determined by the local chemical steady state.

The daily averaged production, $\bar{P}$, is calculated as follows:

$$\bar{P} = \frac{1}{n}\sum_{t=1}^{n} P(t) = \frac{1}{n}\sum_{t=1}^{n}\sum_{ij} k_{ij} \cdot c_i(t) \cdot c_j(t) \tag{2}$$

where n equals 24, the number of timesteps during the 24 h integration. The daily averaged loss, $\bar{Q}$, is calculated in an analogous way. This method makes it possible to take into account any large diurnal variations in concentrations of the species (c_i and c_j) because there may be important effects due to correlation over time.

These averaged production and loss terms are then used for the remaining days of the month with a timestep of one day to calculate diurnally averaged concentrations for 23 components. The remaining species have chemical lifetimes short enough to assume that a steady state is reached during the first day and that changes in concentrations the rest of the month would be small. At the end of the month, the noon values are adjusted according to the changes in the diurnal averages that have taken place during the month. The adjustments are done for the components that are included in both the one-day full chemistry calculations and in the simplified chemistry the rest of the month. These are components with intermediate chemical lifetimes (HCHO, H_2O_2, HNO_3, CO, NOx, etc.). The adjusted noon values are then used as initial values in the full chemistry calculations for the first day of the next month starting at noon, with new J-values.

This procedure allows us to resolve the diurnal variation in the concentrations of the short-lived species due to the diurnal variation in the photolysis rates, and thereby derive properly daily-averaged production and loss terms, which are important due to the non-linear terms in the chemical production and loss terms.

The numerical integration procedure applied to solve the set of time-dependent differential equations deduced from the chemical reaction scheme, is the quasi steady state approximation (QSSA) method described in Hesstvedt et al., 1978. For a further description of the model, see the references mentioned above.

The emissions of NOx, CO and CH_4 and their latitudinal distribution are taken from EPA, 1988. Tables 1 and 2 show the source strengths that are used in the reference calculations:

Table 1. NOx source strength used in the reference calculations (TgN/yr)

Ground sources	37
Lightning	6
Transport from the stratosphere	0.6
Airplanes	0.7

Table 2. Emissions of other gases than NOx (Tg/yr)

CO	1280
SO_2	140
CH_4 (see chapter 4)	484
C_2H_4	33
C_2H_6	33
C_3H_6	17
n-C_4H_{10}	33
m-xylene	17
n-C_6H_{14}	17
Isoprene	195

The last seven emission components in table 2 are chosen to represent all the organic species that are released to the atmosphere from natural and anthropogenic activities (see chapter 5). The input of O_3, NOx and HNO_3 from the stratosphere and the emissions of isoprene are changed each season. All other emissions are kept constant over the year.

4. ESTIMATION OF THE GLOBAL METHANE EMISSION

The global yearly source strength of methane is calculated by the model. It is assumed that the global emission is balanced by chemical loss (R12) in the troposphere and loss to the stratosphere. Any biological sink would give a corresponding increase in estimated source strength. The rate constant expression for R12 reported by Vaghjiani and Ravishankara, 1991, was applied in the calculations.

The procedure starts with assuming an emission value, E_0, that is similar to results from other studies (Crutzen, 1991, IPCC, 1992). The model calculations are fully coupled in the sense that in these calculations emissions of other source gases are included, and the distributions of 49 components are calculated in the model. The OH fields derived in these calculations are therefore based on an extensive and consistent set of atmospheric processes (chemical, radiative, dynamical).

The mixing ratio of methane is initially set to 1.72 ppm everywhere and the fully coupled model is run for 2 years, calculating the concentrations of all gases. The model is then run for 9 years with methane calculations only, using the monthly mean OH fields from the second year. This will give a tropospheric distribution of methane consistent with E_0. The source strength is then adjusted according to the following expression:

$$E_{i+1} = E_i \cdot \frac{1.72}{[CH_4]_i} = E_0 \prod_{n=0}^{i} \frac{1.72}{[CH_4]_n} \qquad (3)$$

where $[CH_4]_i$ is the tropospheric average mixing ratio of methane in iteration i. The procedure is then repeated until a steady state distribution of CH_4 occurs.

By this procedure we arrive at a global CH_4 loss of 484 $TgCH_4$/yr through R12 and through transport to the stratosphere. This is a steady state emission estimate that does not take into account the yearly increase in the atmospheric amount of methane. According to IPCC, 1992, this is 32 Tg/yr. The calculated emission of methane agrees well with other estimates. Crutzen, 1991, estimates a loss of methane by reaction with OH to be 420±80 Tg/yr (and 10±5 Tg/yr by reactions with $O(^1D)$ and Cl in the stratosphere). Fung et al., 1991, estimated a loss of 450±45 Tg/yr through the OH reaction. Prinn et al., 1992, estimated an average global source strength of 470 Tg/yr for the period 1978-1990.

The tropospheric distributions for the different components derived in this model run are used as references when we study the effects of various perturbations.

5. COMPARISON WITH OTHER MODEL RESULTS AND OBSERVATIONS

The fact that the estimated global source strength of methane is in agreement with the results from other studies with different approaches, indicates that the model-derived tropospheric OH fields are reasonable. The estimated annual tropospheric mean concentration of OH is $8.6 \cdot 10^5$ molecules/cm^3.

The obtained global mean OH concentration agrees well with other estimates. Based on observations of MCF concentrations for the period 1978-1990, estimated emissions and model calculations, Prinn et al., 1992, estimated a global average OH concentration of $8.7 \cdot 10^5$ molecules/cm^3. Inclusion of a loss of MCF to the ocean changed the inferred mean concentration to $8.1 \cdot 10^5$ molecules/cm^3. Kanakidou et al., 1991, calculated an overall annual tropospheric 24-hour mean OH concentration of about $8 \cdot 10^5$ molecules/cm^3 with a global 2D model. Hough estimated a global mean of $8.3 \cdot 10^5$ molecules/cm^3 also with a global 2D model. Crutzen and Zimmermann, 1991, used a global 3D tropospheric chemistry model, and their estimate of the global OH average was $\sim 7 \cdot 10^5$ molecules/cm^3. Thompson, 1992, gives an overview of calculated OH by different models (1D, 2D and 3D), and the estimates are in the interval $6 \cdot 10^5$-$9.5 \cdot 10^5$ molecules/cm^3. Our estimated value is thus in the range given by other studies.

Figure 1 shows the calculated diurnally-averaged OH field in the reference run for August. As can be seen, there are large variations in the OH concentrations. At higher latitudes, the concentrations are about $1\text{-}5 \cdot 10^5$ molecules/cm^3, while at the equator a maximum of $1.9 \cdot 10^6$ molecules/cm^3 is reached. The highest levels are found over the equatorial region because of minimum total ozone columns and small solar zenith angles, making the incoming solar radiation reach high values. In addition, there are high levels of water vapour in this region which increase the OH production through R7. NOx from lightning increases the OH levels in the middle troposphere through ozone production and redistribution among the HOx species through R3.

Due to the important role of solar radiation, ozone, and water vapour in the chemistry of OH, there are large seasonal variations in the OH distribution. At 50°N and 750 m, the diurnal average of OH changes from $1.4 \cdot 10^6$ molecules/cm^3 in August to $5.3 \cdot 10^5$ molecules/cm^3 in February. This is of importance for the overall oxidative capacity of the atmosphere, since the emissions of several manmade and natural gases reach maximum values at northern mid-latitudes.

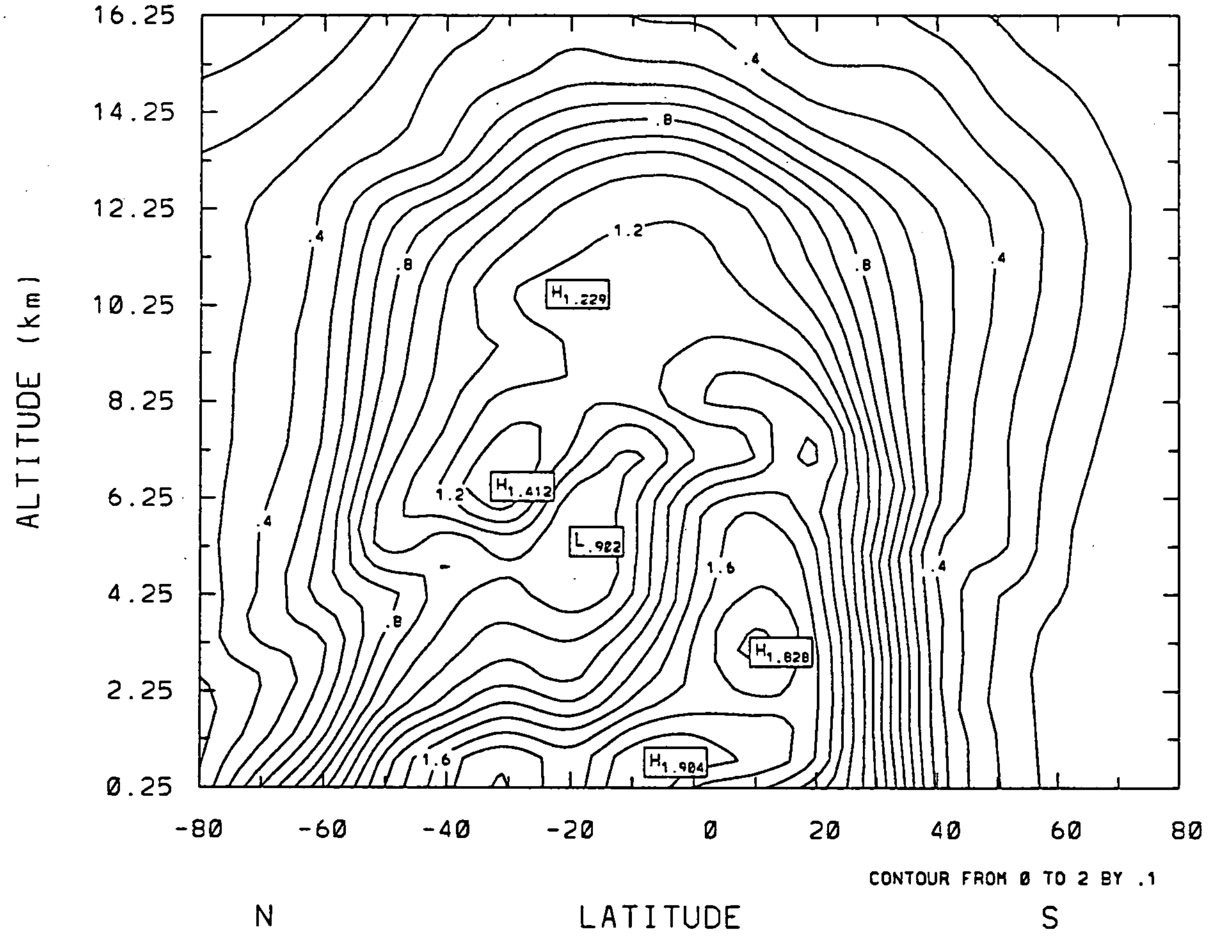

Figure 1. Diurnally-averaged OH concentrations as function of latitude and altitude for August. Unit: 10^6 molecules/cm^3.

There are serious uncertainties connected to the estimates of the global emissions of the various source gases and to the relative importance of the different sources. One of the most difficult sources to quantify is the lightning source of NO. Since NOx is a key compound in tropospheric chemistry, this may have significant effects on the results from models of tropospheric chemistry. Liaw et al., 1990, report values in the range 19-152 TgN/yr, while IPCC, 1992, gives the interval 2-20 TgN/yr. In the reference run we have used a lightning source of 6 TgN/yr. The lightning source has a maximum at 30°S and a secondary maximum at 10°N. The production decreases with altitude, but increases again to a local maximum at 10 km. To get an impression of the importance of this source strength assumption, we doubled the NOx production from lightning and applied the same method as described in chapter 4 to estimate the methane emissions. The result was an increase of 11% in estimated methane emissions, indicating an increase in the OH concentrations. The change in global mean OH was +16%.

Figure 2 shows a comparison between an average NO profile based on measurements between 40°N and 50°N (Drummond et al., 1988, Ehhalt, 1992) and calculated profiles (noon values) at the same latitudes. The model overestimates the concentrations in the boundary layer compared with these observations. But since the model is zonally averaged while the observations are from remote regions (oceans), it should be expected that the model will give higher values for the boundary layer. In the middle troposphere the agreement is good, but in the upper troposphere the model seems to underestimate NO significantly, probably since effective transport inside clouds is not included in the model. In the model the vertical transport is treated only as zonally averaged advection (slow) or eddy diffusion. In the real atmosphere a substantial part of the vertical transport occurs within deep convective clouds, which brings the air from the boundary layer to the upper troposphere on timescales of 10-15 minutes (Lelieveld et al., 1989). By this mechanism, air with high levels of NO and other source gases can be transported effectively to the upper troposphere.

Figure 2 also shows that the results are sensitive to the source strength for lightning and to the efficiency of heterogeneous removal of HNO_3. In the model the rate of the irreversible heterogeneous removal of HNO_3 was reduced by 50% (with 6 TgN/yr from lightning). This will allow for increased production of NO_2 through photolysis of HNO_3.

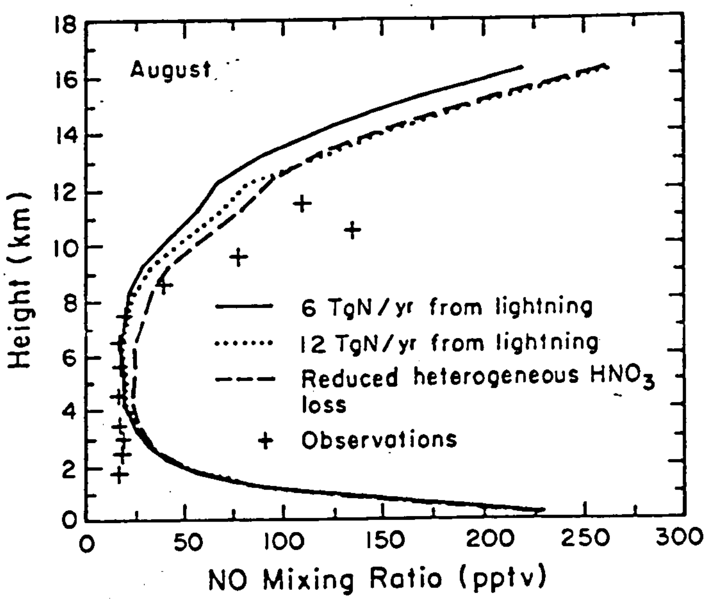

Figure 2. Calculated vertical profiles of NO at 45 °N for August in parts per trillion (ppt). Two different emissions from lightning and reduced wet removal rate for HNO_3 are used. Crosses indicate measured values from Drummond et al., 1988, as given in Ehhalt et al., 1992.

Berntsen, 1989, used CFCs[4] and MCF[5] to check the circulation in the model and found good agreement between observation and the modelled distributions. Isaksen et al., 1985, found fair agreement between the calculated annual variations and the measured concentrations of C_2H_2, C_2H_6, C_3H_8, C_7H_8 and C_2Cl_4 in the Norwegian Arctic. Isaksen and Rodhe, 1978, studied the water budget and found good agreement between observed and modelled precipitation, which is a good indication of an adequately modelled circulation pattern.

Due to the large number of species and the complex nature of the hydrocarbon chemistry, simplifications had to be done in the model. Ethane (C_2H_6), butane (C_4H_{10}) and hexane (C_6H_{14}) were chosen from the alkanes, while ethene (C_2H_4) and propene (C_3H_6) represent the alkenes. Of the aromatic hydrocarbons, only m-xylene (C_8H_{10}) is included (for emissions, see table 3). In this way we can include the effect of hydrocarbons on the chemistry of HOx, O_3, etc., without modelling the individual

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[4] CFC: Chlorofluorocarbon

[5] MCF: Methyl chloroform (1,1,1-thrichloroethane)

species explicitly. If we want to compare the calculated distributions of one of the mentioned species with observations, we will thus have to scale down the concentrations to get the concentrations for this species only. The mass fraction between ethane itself and the sum of species it is meant to represent (ethane, propane and acetylene) is 0.44. The modelled mixing ratios (noon values) for the artificial ethane are scaled down by this number and plotted for the lowest layer as a function of latitude in figure 3. Observations of ethane by Blake and Rowland, 1986, are given in figure 4. Taking into account that observations and calculations are for different months, the profile and general levels are well reproduced by the model.

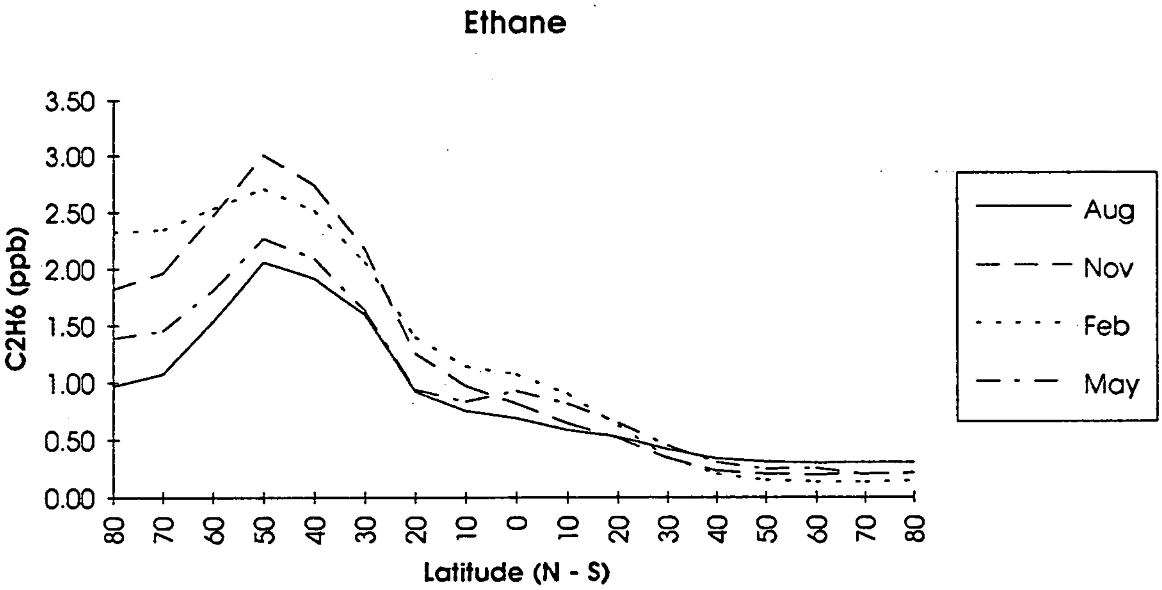

Figure 3. Calculated latitudinal distributions of ethane (C_2H_6) in parts per billion (ppb) for 0.25 km altitude.

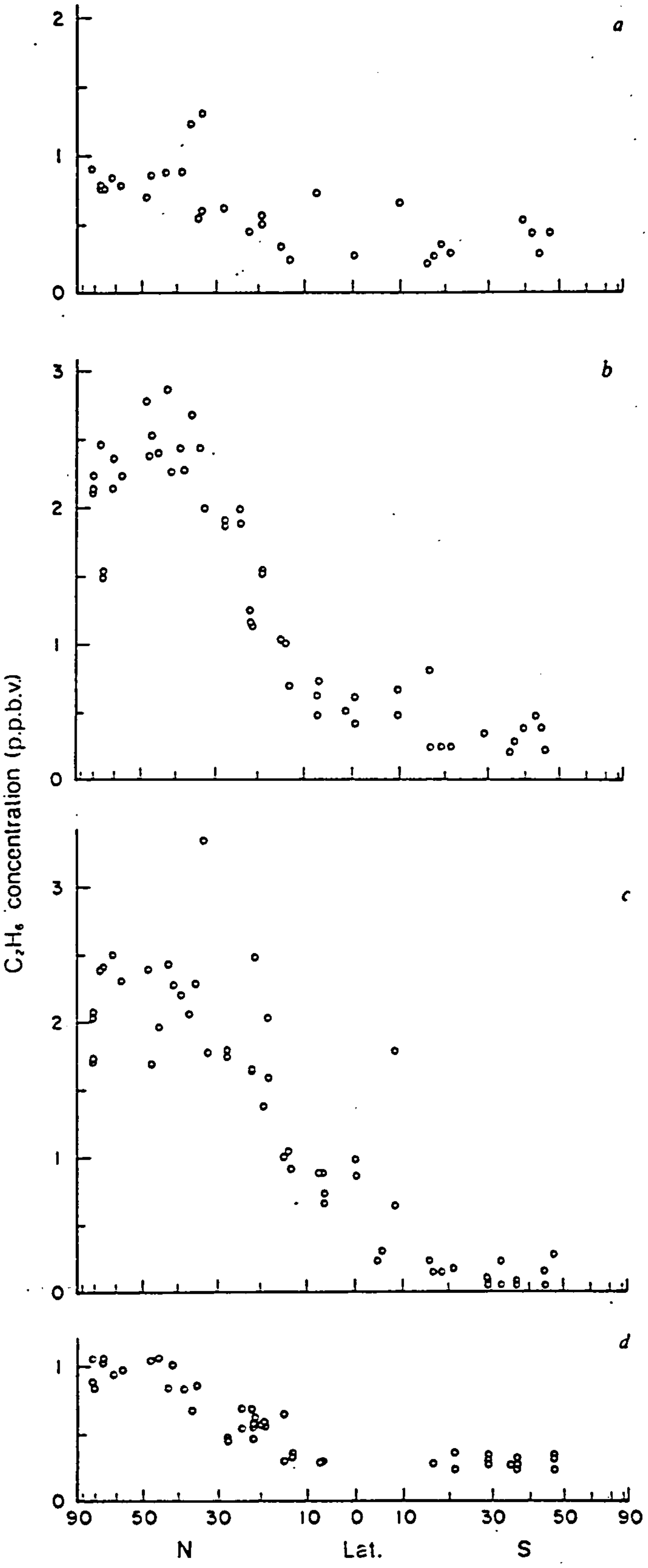

Figure 4. Surface observations of ethane (C_2H_6) in ppb for four different time periods, taken from Blake and Rowland, 1986. a) September 1984, b) December 1984, c) March 1985, d) June 1985.

The calculated noon values of CO for May and for four different altitude levels are plotted in figure 5. The levels are higher in the Northern Hemisphere than in the Southern, and they decrease with altitude. The profile may be compared to observational data in figure 6 from Heidt et al., 1980, as given in Cicerone, 1988. The modelled distributions show good agreement with the observations.

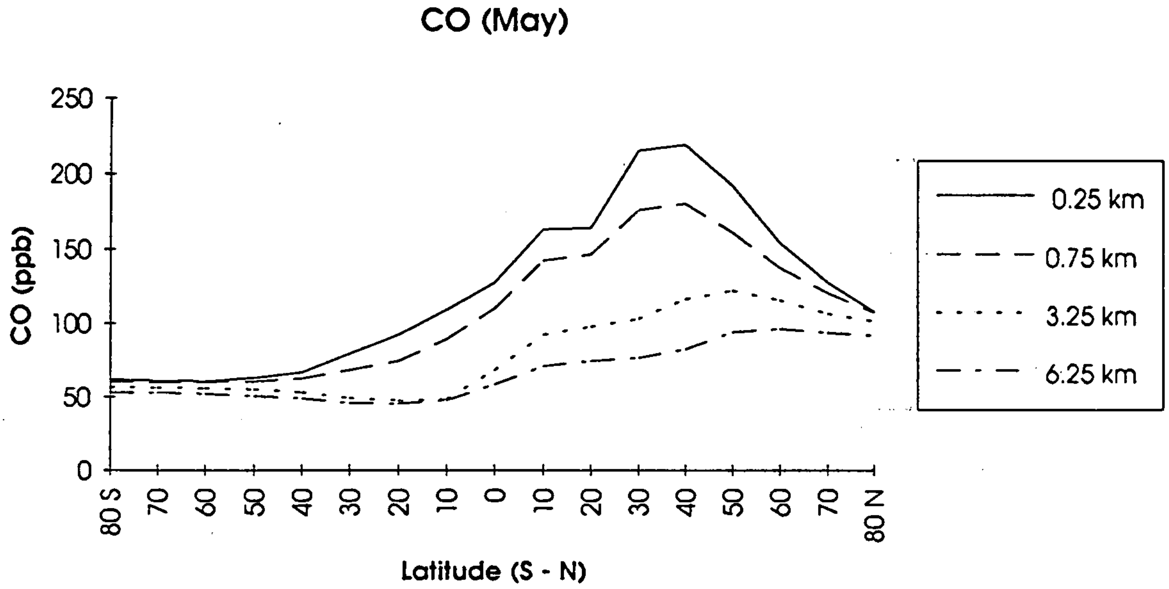

Figure 5. Calculated latitudinal distribution of CO (in ppb) for May and for four different altitude levels.

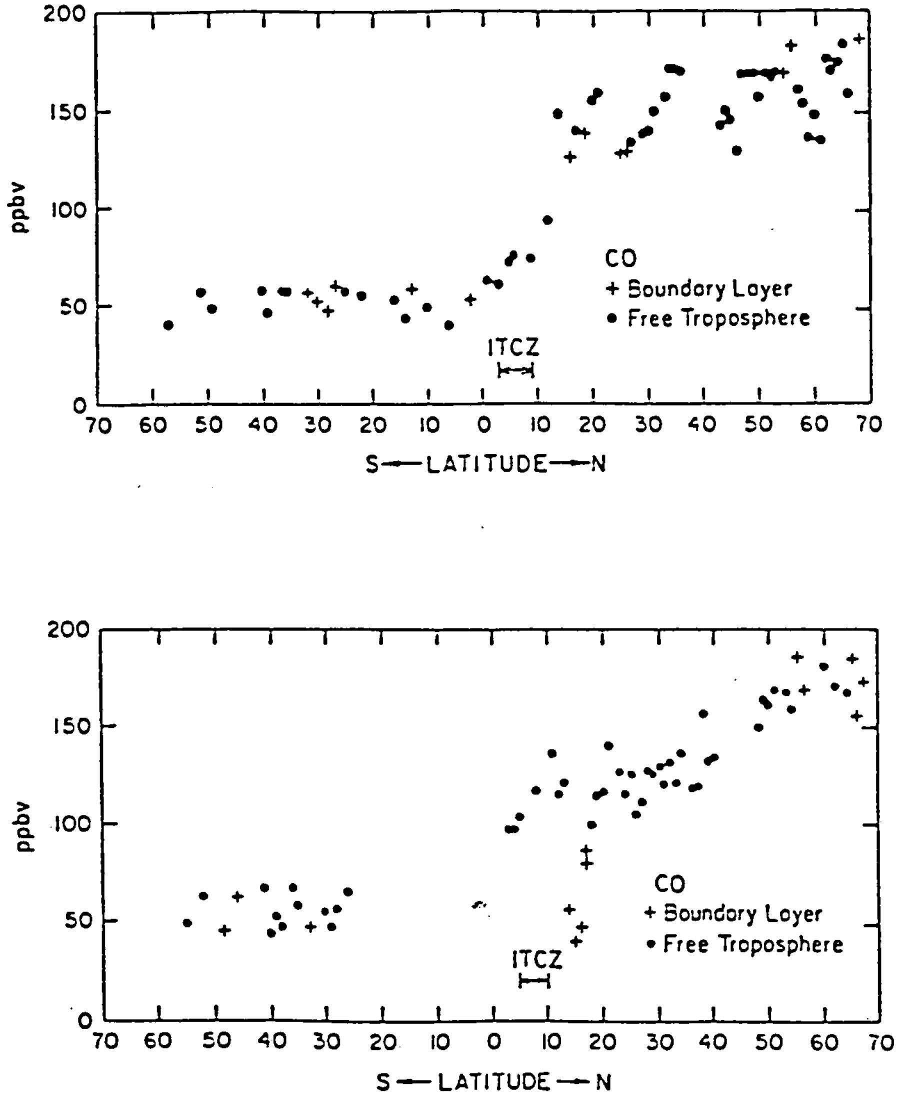

Figure 6. Observations of CO (in ppb) in the boundary layer and in the free troposphere from April and May 1978. From Cicerone, 1988, and Heidt et al., 1980.

The calculated noon values of O_3 for August as a function of latitude and altitude are given in figure 7. The distribution shows the effect of the Hadley circulation with rising motions over the equator bringing air masses with lower mixing ratios of ozone upwards. This circulation pattern gives subsidence at lower to middle latitudes, thereby bringing air with higher ozone levels downwards. In the Northern hemisphere, this picture is modified by the enhanced production of ozone due to the antropogenic emissions which give a maximum ozone level in the lowest layers at 40°N. The calculated ozone distribution may be compared to the observational distribution from London and Liu, 1992, given in figure 8. The figure is based on ozone sonde observations and represents June, July and August. (Note that the figure has pressure coordinates and that the North-South orientation is reversed). The enhanced concentrations in the free troposphere over the equator are not found in the modelled distribution. Between 19°N and 14°S there is only one observational site, Natal, Brazil. This makes it difficult to compare observations with results from a zonally-averaged model. At Natal there are large emissions of ozone precursors (CO, NMHC, NOx) from biomass burning during the dry season (May-September) which lead to significant *in situ* ozone production (Logan and Kirchhoff, 1986, Kirchhoff et al., 1991). The possibility of stratospheric intrusion due to deep convective clouds has not been ruled out as an explanation for the enhanced ozone levels. However, this mechanism is not included in the model. Outside the equatorial region the model reproduces the general pattern with the effects of the rising motions and of the subsidences. In addition, the enhanced levels at Northern mid-latitudes are in agreement.

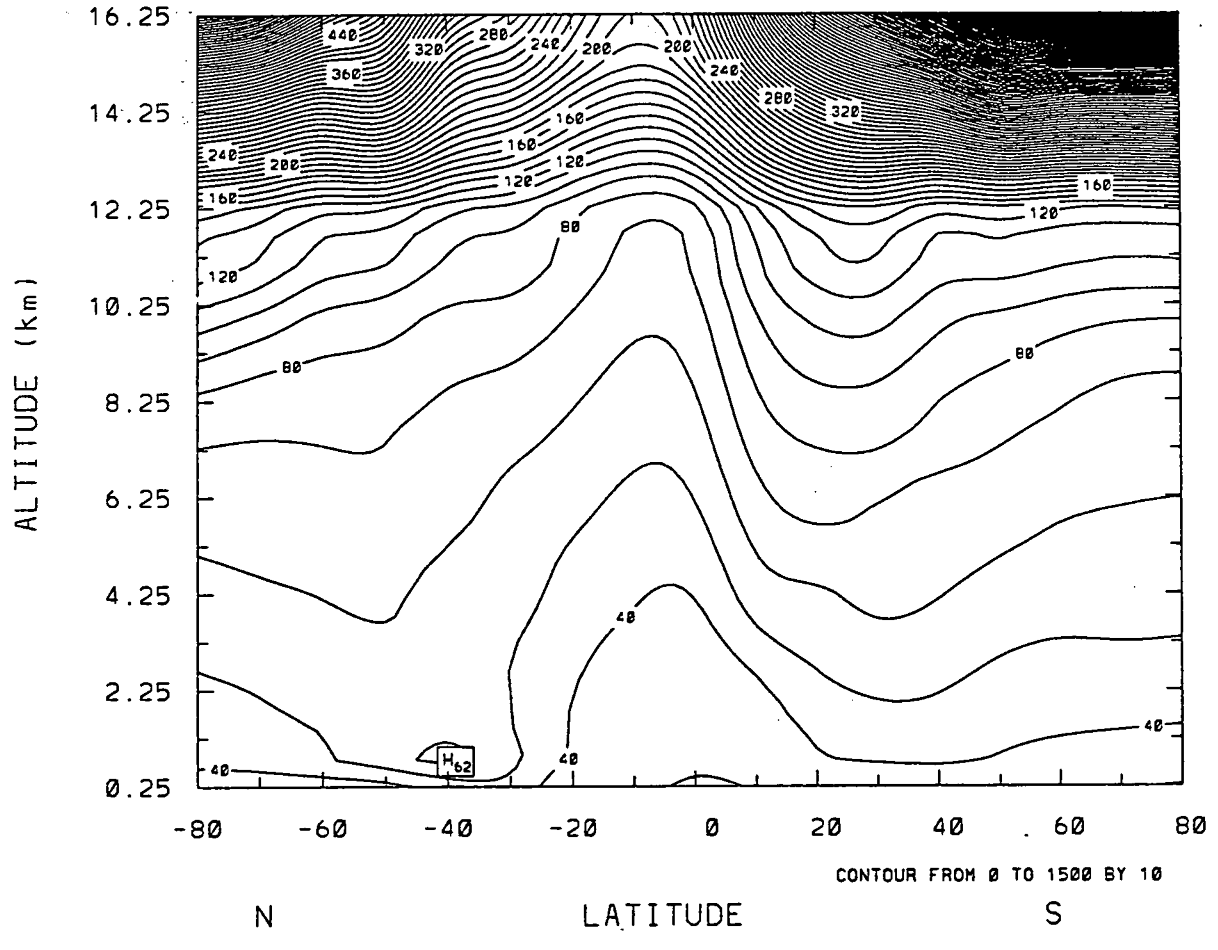

Figure 7. Calculated noon values of O_3 in ppb for August as a function of latitude and altitude.

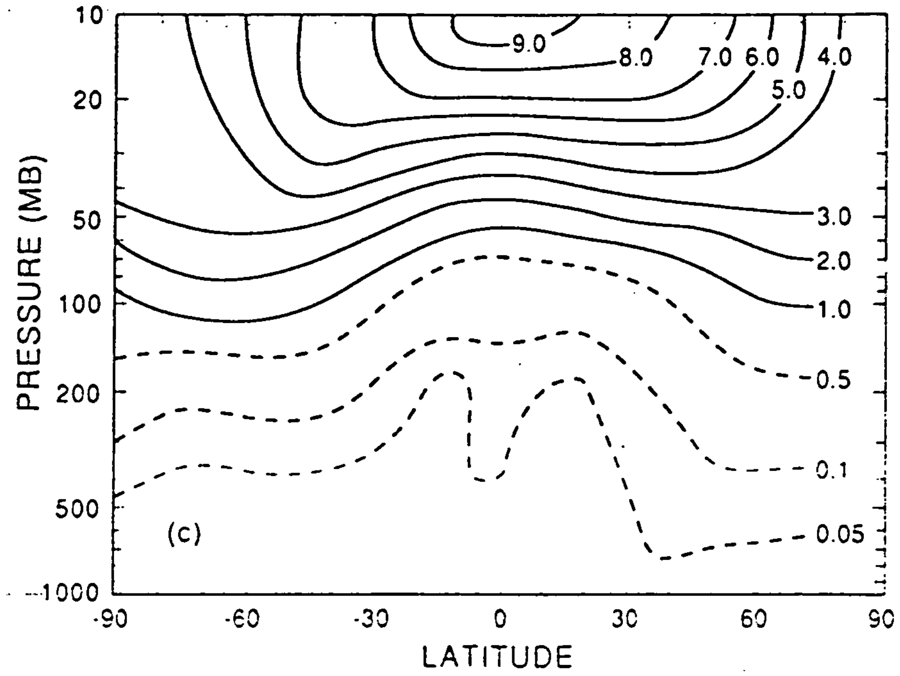

Figure 8. Observed pressure-latitude distribution of O_3 in ppm for May, June and August. From London and Liu, 1992.

The model gives concentrations of PAN (peroxyacetylnitrate) that are significantly higher in the Northern Hemisphere than in the Southern Hemisphere, and the concentrations in winter are higher than in summer. Figure 9 shows the latitudinal distribution of PAN in ppt (noon values) for August and February for 1.75 km altitude. Due to few observations and large variations in the results, it is difficult to find observations suited for comparisons with the meridionally-distributed results from the model, but the estimated concentrations are in the ranges reported from different studies (Singh et al., 1986, Ridley et al., 1990.) Since PAN is a tertiary species in the sense that it is produced by secondary species, one should expect large uncertainties in the calculated concentrations. Hough, 1988, made an intercomparison between different chemical schemes, and found very large variations for PAN. Any agreement between observations and calculations within a factor of 2 is, according to Hough, as good as can be expected and model calculations cannot be verified to a greater degree of accuracy when the results are compared with observations.

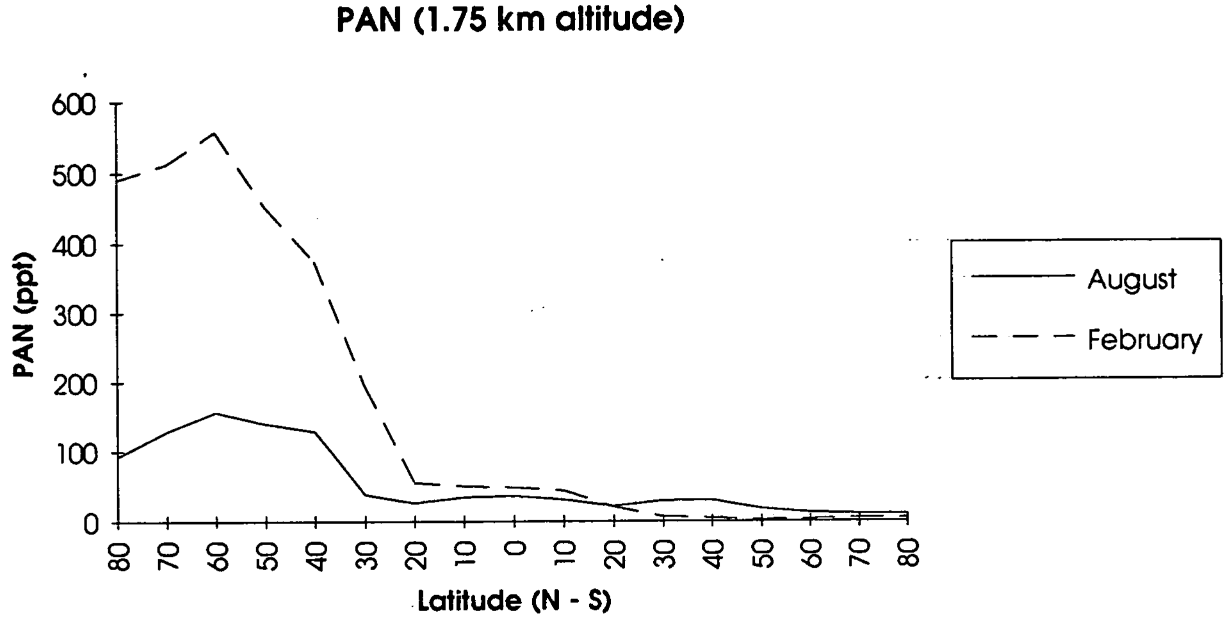

Figure 9. Latitudinal distribution of PAN in ppt (noon values) for 1.75 km altitude.

Based on observations from aircraft, Ridley et al., 1990, give PAN/NOx ratios vs. NOx for the middle free troposphere in August, figure 10. The corresponding calculated values from our model study are given in the same figure. As can be seen, the ratios are similar to what is reported by Ridley et al., but somewhat lower.

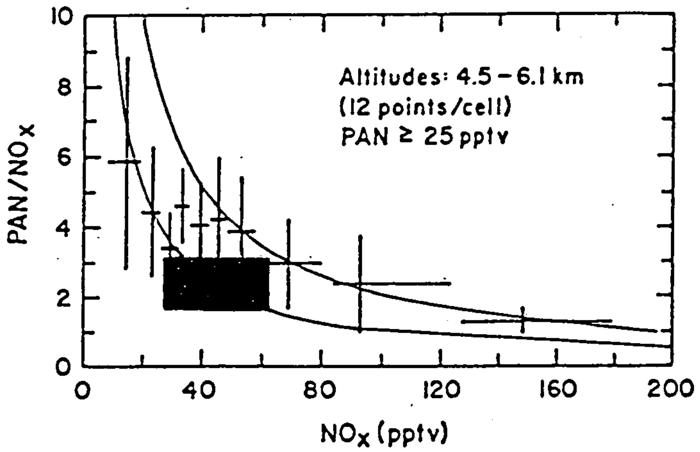

Figure 10. The variation of the PAN/NOx ratio vs NOx for August. Comparison between calculations and observations from Ridley et al., 1990. The calculated values are indicated by the black area.

Comparisons between model results and observations are hampered by the fact that zonal averages are calculated by the model, while observations usually are too few in space and in time to form a basis for calculating zonal averages. The comparisons performed here, however, indicate that the modelled distributions of important gases are in good agreement with observations and results from other calculations and model studies.

6. CHEMICAL PERTURBATIONS: RESULTS AND DISCUSSION

In order to study the potential for formation of tropospheric ozone by changes in emissions of NOx, CH_4, CO and NMHC, several perturbation studies have been done. The emissions of the source gases were changed one by one, and the effects on ozone, OH and CH_4 were studied.

6.1 Doubling of the ground emissions of NOx

For a doubling of the ground emissions of NOx (with unchanged latitudinal emission distribution), there was a substantial increase in O_3 at low altitudes over the Northern Hemisphere in August; the increase was as large as 20% between 0° and 10°N and 16% between 40°N and 70°N in the lowest levels (fig.11a).

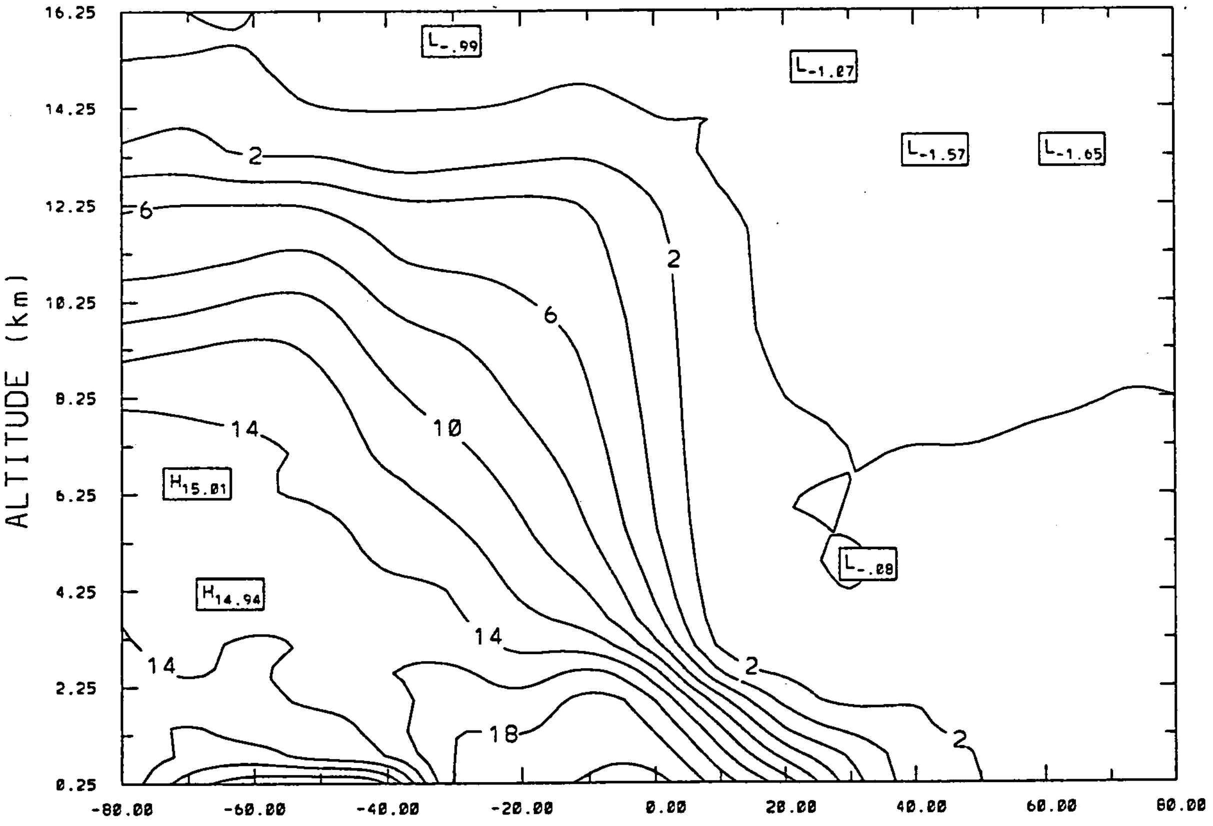

Figure 11a. Calculated percentage change in O_3 concentrations for August when the ground emissions of NOx are doubled.

In February the doubling of NOx emissions gave a somewhat different result. South of 30°N there was an increase, with the maximum near the equator (~20%), while north of 30°N there were reductions in O_3 up to 15% in the lowest few kilometers. These reductions in ozone at Northern mid latitudes in February can be explained by lower OH levels leading to lower levels of HO_2 and RO_2 which will result in reduced oxidation of NO to NO_2. The oxidation of NO to NO_2 will mainly take place through the reaction

$$O_3 + NO \rightarrow O_2 + NO_2 \qquad R15$$

which consumes ozone. Weaker solar radiation in winter-time will further make the photolysis of NO_2 (R5) less effective. In addition, PAN is more stable under colder conditions, thereby becoming more important as a NOx reservoir than in warmer periods.

The effect on OH in August was an increase at all latitudes below 9-14 km and reductions in the upper troposphere (fig.11b). The increase is due to a change in the distribution among the HOx species through R3 which may easily be seen by comparing figure 11b with figure 11c which shows the percentage change in HO_2. The largest increases in OH and the largest decreases in HO_2 are found in the lower troposphere in the Northern Hemisphere where the NOx levels are relatively high. HO_2 decreases throughout the entire troposphere in all seasons, except in a limited region over the equator. In addition to the effect through R3, there is increased OH production from photolysis of ozone (R6) followed by the reaction between $O(^1D)$ and water vapour (R7).

In February there was an OH reduction at higher northern latitudes in the lower troposphere and in the upper troposphere at all latitudes. The low altitude reductions can be explained by higher NO_2 (due to slower photolysis of NO_2) and therefore increased loss of OH through R11. Redistribution among the NOx species, (R3 and R4) will have less effect on the levels of OH since HO_2 and RO_2 are low in winter-time. In addition, the OH reductions in February take place in the same region as the ozone reductions do. This points to an effect on OH through R6 and R7.

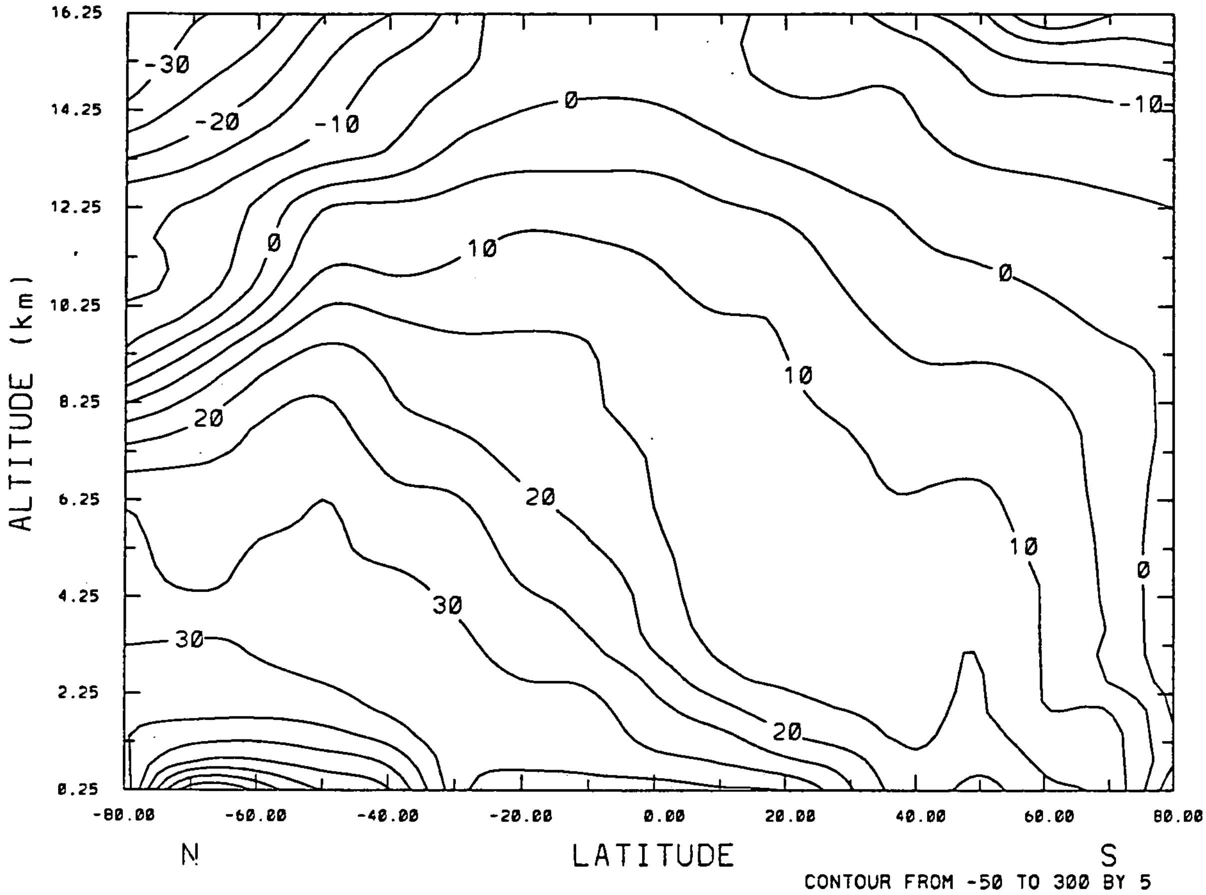

Figure 11b. Calculated percentage change in OH concentrations for August when the ground emissions of NOx are doubled.

Changes in the chemistry of one region affects the chemistry of a different region through the interaction between methane and OH. The reductions in O_3 in the *upper troposphere* can be explained by the OH increases in large parts of the troposphere (fig.11b). These increases lead to reduced upwards transport of methane and CO produced in the methane oxidation, thereby reducing the amount of HO_2 and RO_2 available for oxidation of NO to NO_2 (R3 and R4) which is a necessary step in ozone production (see fig.11c). Lower levels of ozone in the upper troposphere will further reduce the production of OH. In this way, increased levels of OH in one region of the troposphere may lead to reduced levels in another region.

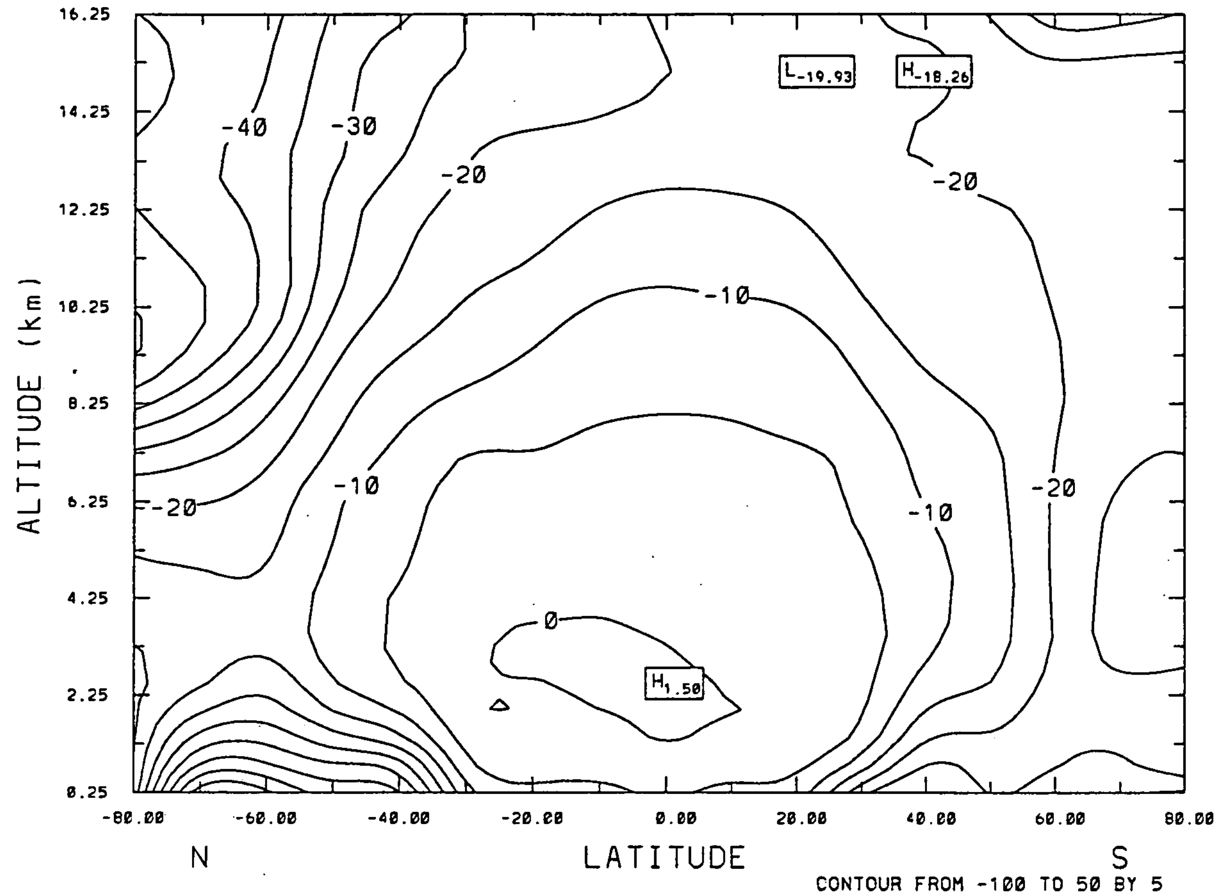

Figure 11c. Calculated percentage change in HO_2 concentrations for August when the ground emissions of NOx are doubled.

6.2 Doubling of the CH_4 emissions

Changes in the methane and NOx emissions from surface sources affect the ozone levels differently. The model experiment with a doubling of the methane emissions gave a more uniform effect on tropospheric ozone than a doubling of NOx. Increases in methane emissions lead to ozone increases everywhere in the model region (fig.12a). This is due to the longer lifetime for CH_4 (~10 years) than for NOx (a few days). In August the maximum increase of ozone was 23% at ca. 2 km above equator, while in February the maximum was 25-28% in the lowest levels at 40°S. The effects of methane on OH were substantial reductions (up to ~30%) in August below 8-12 km, depending on latitude (fig.12b). In the upper troposphere there was an increase in OH. This is due to the higher NOx concentrations in this region compared to the middle troposphere. When NO is above a certain level the oxidation of CH_4 will produce OH (Crutzen, 1987) (see chapter 7). In addition, there is a competition between the reactions R11 and R3 which give OH loss and production, respectively. Due to the pressure dependence of R11 and the negative activation energy of R3, which means that the rate constant increases with reduced temperature, the latter reaction dominates at higher altitudes, leading to a contribution to increased OH in this region (see chapter 7).

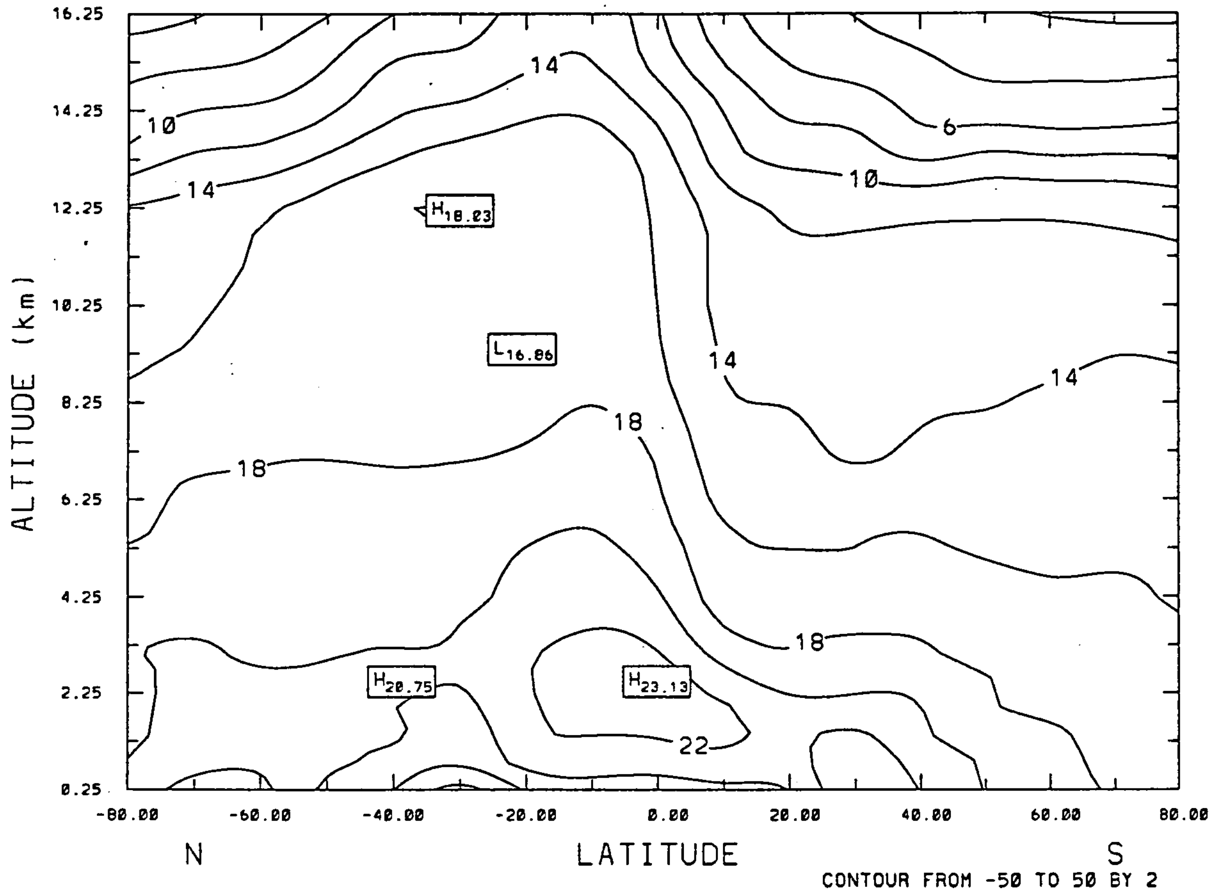

Figure 12a. Calculated percentage change in O_3 concentrations for August when the methane emissions are doubled.

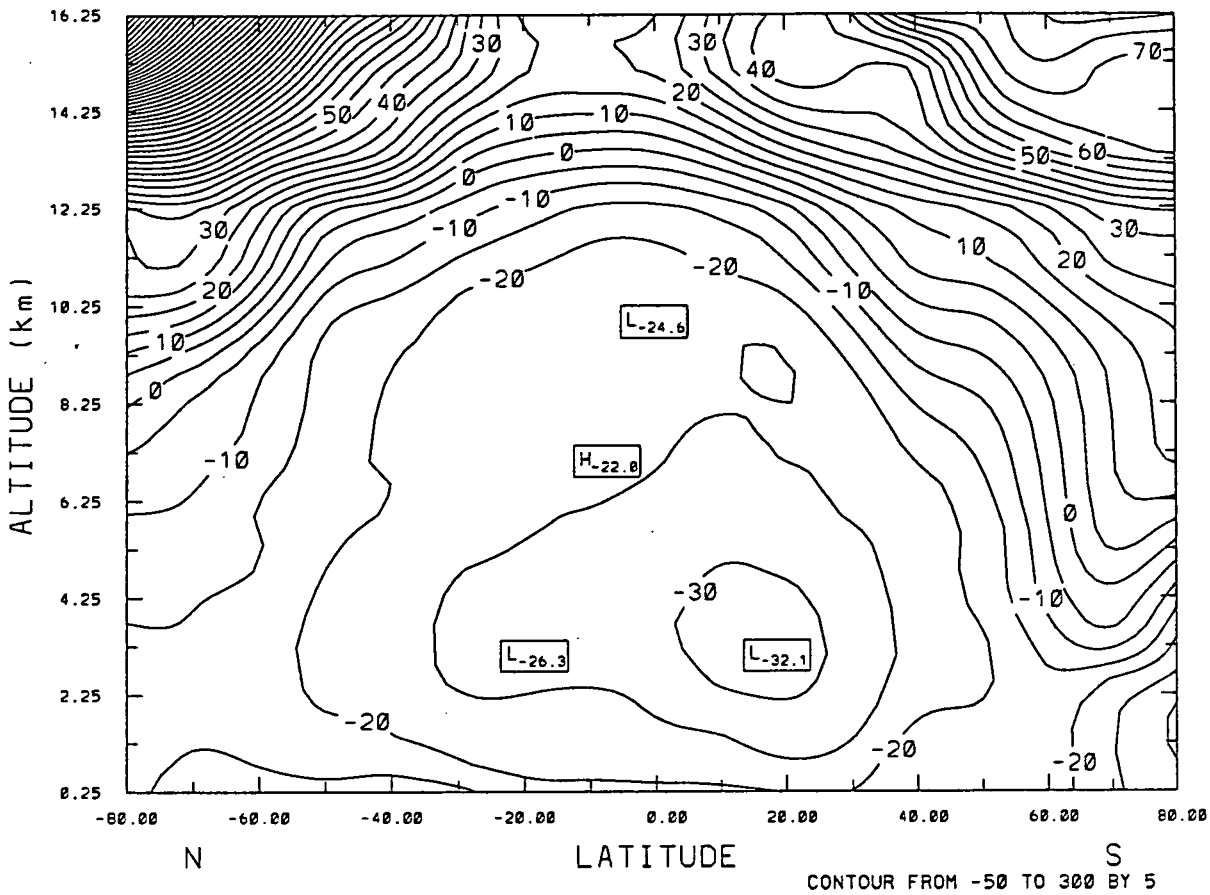

Figure 12b. Calculated percentage change in OH concentrations for August when the methane emissions are doubled.

6.3 Doubling of the CO emissions

The effect on ozone of a doubling of ground emissions of CO was an increase throughout the entire model domain that was most pronounced in the Northern Hemisphere (8-12%) where the CO (and NOx) emissions are largest (fig.13). Due to the relative long chemical lifetime (2-3 months), CO can be transported to regions in the remote troposphere. This is the reason for the local maximum ozone increase of ~10% at 12 km and 40°N in August. In this region the NOx concentrations are increasing with altitude due to input from the stratosphere (with an additional contribution from aircraft emissions). The relative high NOx concentrations make the ozone production from increased HO_2 effective.

The increase in HO_2 is due to the reactions between CO and OH (R13) followed by

$$H + O_2 + M \rightarrow HO_2 + M \qquad \text{R16}$$

The increase in HO_2 will further increase the fluxes through the ozone producing reactions R3, R5 and R2.

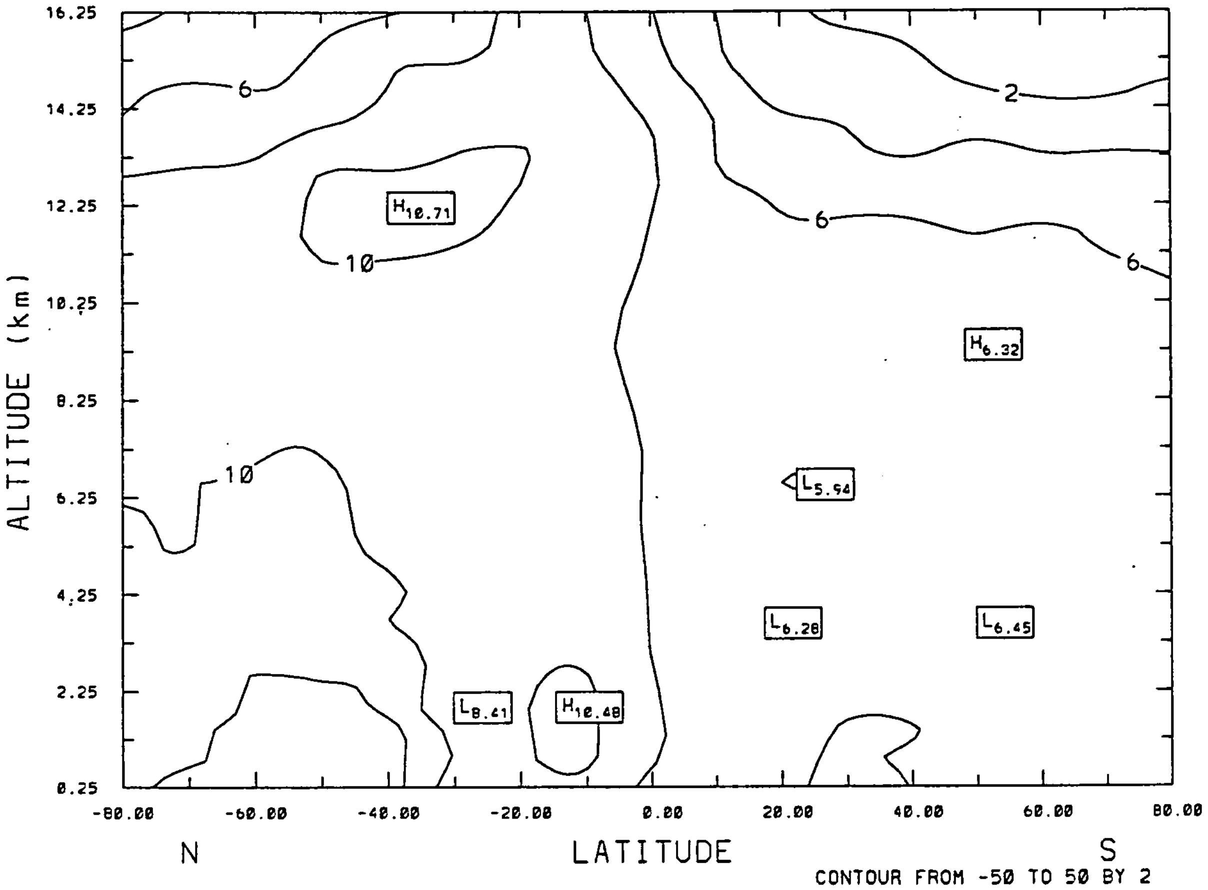

Figure 13. Calculated percentage change in O_3 concentrations for August when the CO emissions are doubled.

Increased CO emissions have a particular pronounced effect on the OH distribution. Doubling the ground emissions of CO gave strong reductions in OH almost throughout the model region, with reductions up to 30%.

6.4 Doubling of the NMHC emissions

The impact on ozone and OH from increased NMHC emissions is strongly latitude and height dependent. Doubling the NMHC emissions gave substantial increases in ozone in the lower troposphere. In August the increase was up to 22% around 40°N, and in February up to 30%. The effect on ozone decreases markedly with altitude due to relatively short lifetimes for the NMHCs, and in the free troposphere above 3-4 km, the increase was less than 10%.

Doubling the NMHC emissions had significant effects on OH in the lowest layers in the model, with reductions up to 20% around the equator. In the free troposphere the changes were less than 10%. In February there was an increase in OH in the lowest layers north of 40°N and in the upper troposphere in both August and February. The positive effects on OH in these regions may be explained through the changes in PAN. The degradation of NMHCs will lead to production of peroxyacetyl radicals. When reacting with NO_2 they will form peroxyacetylnitrate, PAN,

$$CH_3C(O)O_2 + NO_2 \rightleftharpoons CH_3C(O)O_2NO_2 \qquad R17$$

This equilibrium is shifted to the right-hand side at lower temperatures. PAN may therefore be a stable species in the free troposphere and in the colder seasons.

In February, the PAN levels increased significantly (10-85%) in the regions where OH increased when the NMHC emissions were doubled. Increased $CH_3C(O)O_2$ and shifting of the equilibrium to the right in R17 will decrease the NO_2 level. Since the reaction between NO_2 and OH (R11) is a main sink of OH, the increased loss of NO_2 through R17 will have a positive effect on OH. In other words: The activity of the chemistry that removes OH in winter-time is reduced by the larger input of precursors of peroxyacetyl radicals. Since the levels of NOx and PAN are comparable, as figure 10 shows, this mechanism may affect the NOx levels significantly.

The effect of a doubling of CO did not have such a large effect on OH in the upper troposphere since there is no production of peroxyacetyl radicals from CO. There was an increase in PAN in the same region, but it was weaker than in the case of doubled NMHC emissions (5-20% increase in PAN). This increase in PAN from doubled CO emissions was due to a redistribution among the NOx species due to increased HO_2 (R3). This mechanism will also affect the PAN levels in the case of doubled NMHC. Changes in the NOx chemistry will affect OH through R3 and R11. In addition there will be higher order effects through changes in ozone. The net effect of all these mechanisms is given by the model result.

6.5 Increased NOx emissions from airplanes

Figure 14 shows the effect on ozone of an increase of 70% (or 0.5 TgN/yr) in *NOx emissions from airplanes*. The increase is largest around 10 km altitude at 40°N. The ozone production is less efficient in winter-time due to lower photodissociation rates. Due to the traffic pattern, with most of the emissions occurring in the Northern Hemisphere, airplanes are a source of free tropospheric ozone in the Northern Hemisphere.

The relatively strong effect on ozone is due to the low NOx concentrations in the altitude levels where the emissions take place (30-40 ppt), giving more efficient ozone production per NOx molecule (see section 6.9 and figure 15). Slower reaction between OH and NO_2 and no ground deposition increase the chemical lifetime of NOx in this region compared to lower altitudes. This makes it possible for NOx to take part in more conversions of NO to NO_2 through the reactions R3 and R4 before it is chemically converted and removed, thereby giving increased ozone production through R5 and R2. In addition, the chemical lifetime for O_3 itself is longer in this region compared to at lower altitudes, which permit more efficient buildup of O_3 in the region.

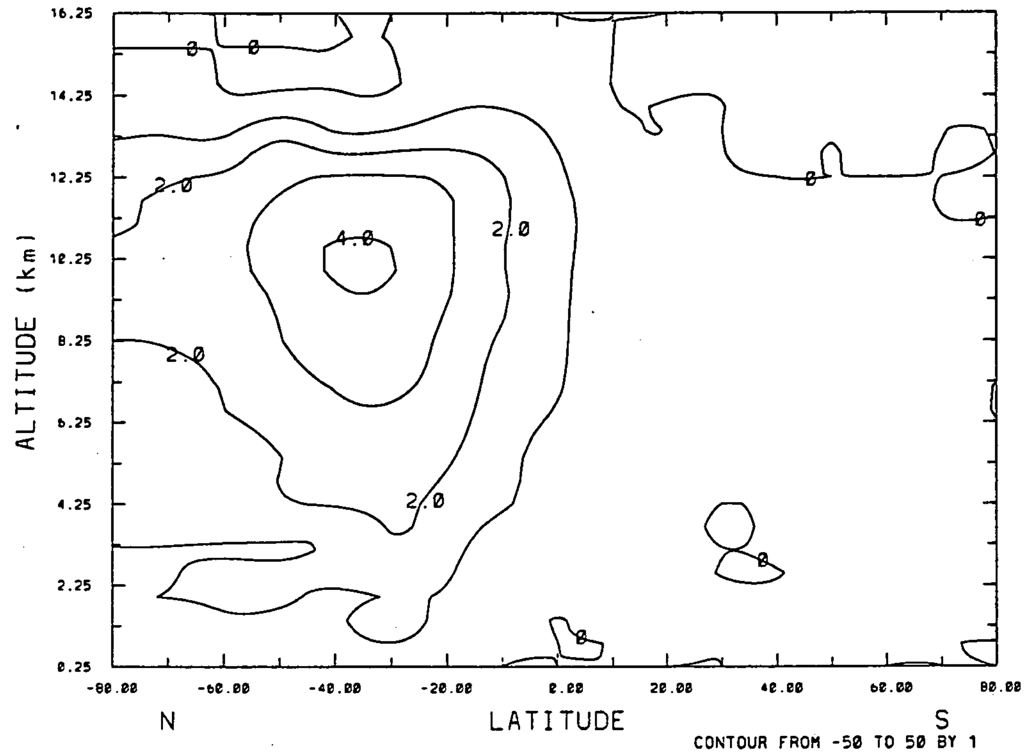

Figure 14. Calculated percentage change in O_3 concentrations for August when the NOx emissions from airplanes are increased by 0.5 TgN/yr.

The increase of ozone takes place at altitudes where ozone changes are very effective in perturbing the radiative balance of the Earth/atmosphere. Model studies by Lacis et al., 1990, show that the radiative forcing is largest for ozone changes taking place around altitudes of 10-12 km. The reason is that the climatic effect produced is directly proportional to the temperature contrast between the radiation absorbed and the radiation that is re-emitted. This contrast reaches a maximum near the tropopause (Wuebbles et al., 1989).

6.6 Comparison of the sensitivities in the effects on ozone

In these perturbation studies the source strengths of the different gases emitted are highly different. In order to make comparisons of the efficiencies in increasing ozone, all increases may be expressed relative to the increase in emission given in mass units. The numbers are given in table 3. The efficiencies have also been normalized to the impact on O_3 from a doubling of the methane emissions. Note that *annual tropospheric mean values of ozone* have been applied. If the radiative forcing from ozone is to be calculated, the vertical distribution of the change has to be taken into account.

Table 3. The efficiencies of the source gas emissions in increasing tropospheric O_3. (E: Emission in Tg/yr).

	2 x NOx	2 x CH_4	2 x CO	2 x NMHC	1.7 x NOx from airplanes
$\Delta O_3(\%)$	3.7	16.2	8.4	6.8	0.8
$\Delta O_3(\%)/\Delta E(Tg/yr)$	0.1005	0.0336	0.0066	0.0196	1.6797
$\frac{\Delta O_3/\Delta E}{\Delta O_3/\Delta E(CH_4)_{2x}}$	3.0	1.0	0.20	0.58	50

The numbers show that per mass unit of emitted NOx is approximately three times more effective in enhancing the tropospheric mean concentration of ozone than methane. The effect of CO is only one fifth of the effect of methane.

It may be surprising that NMHC has an ozone enhancement efficiency that is only approximately 60% of the efficiency of methane since for each NMHC that is degradated more NO to NO_2 conversions will take place, leading to higher ozone production. The estimated numbers would be different if the ozone changes were given per molecule and not per mass unit. The former alternative would increase the estimated numbers for the NMHCs. A further explanation for the lower number is the fact that, due to short lifetimes of the NMHCs, the ozone production from NMHC takes place at low altitudes where the deposition of ozone at the surface of the Earth is an important loss mechanism. Methane, on the other hand, has a long enough lifetime to permit dispersion to the entire troposphere, which will give ozone production in altitude regions where the lifetime of ozone is longer than at low altitudes. The ozone production efficiency is of course also dependent on the assumed composition of the NMHC emission, see chapter 3, table 2, and chapter 5.

From table 3 it can be seen that NOx emitted from airplanes is much more efficient in increasing ozone than NOx emitted at ground level. Compared to a doubling of the ground sources, NOx from airplanes is ~17 times more efficient with respect to ozone increases. Strongly enhanced effects on ozone production per unit of emission for airplane emissions of NOx were also obtained by Johnson et al., 1992, in a study where a 2D model was applied.

6.7 Nonlinear responses in ozone

Since a doubling of the ground emissions is an extreme perturbation, smaller increases in the emissions were also performed in order to elucidate the degree of non-linearity in the chemical responses. Similar comparisons were therefore made for NOx, CO and CH_4 emission increases of 10%. In table 4, the O_3 enhancement efficiencies are given relative to the effect on ozone of doubling CH_4, allowing for comparison with the numbers in table 3.

Table 4. The efficiencies of the source gas emissions in enhancing tropospheric O_3 for 10% increases in emissions. (E: Emission in Tg/yr).

	1.1 x NOx	1.1 x CH_4	1.1 x CO
$\Delta O_3(\%)$	0.5	2.0	0.9
$\Delta O_3(\%)/\Delta E$	0.1378	0.0403	0.0073
$\frac{\Delta O_3/\Delta E}{\Delta O_3/\Delta E(CH_4)_{2x}}$	4.1	1.2	0.22

Small increases in NOx emissions lead to more efficient ozone enhancement. The efficiency in ozone enhancement increases by ~40% when the NOx emission is increased by 10% compared to a doubling of the emissions. The increase in efficiency is somewhat less for methane (20%) and CO (10%).

As was shown in the preceding section, the aircraft emissions of NOx were ~17 times more effective in enhancing ozone than a doubling of the ground sources of NOx. When the effect is compared to a 10% increase in ground sources, the factor is ~12.

6.8 Comparison of the effects on methane

Since the various perturbations affect the tropospheric OH concentration, they will also affect the concentrations of gases that have reaction with OH as their main sink. The dominating sink of methane is the reaction with OH (R12) and changes in the distribution and levels of OH will therefore lead to changes in the levels of methane. As we have seen in the preceding sections, changes in the emissions of the source gases lead to changes in OH and these source gases may therefore further influence methane indirectly. Table 5 shows the effects of the various perturbations on the global level of methane.

Table 5. The effect on global mean concentration of methane in the various perturbations. (E: Emission in Tg/yr).

	1.1 x NOx	2 x NOx	1.1 x CO	2 x CO	Incr. NOx (airplanes)	2 x NMHC	1.1 x CH_4	2 x CH_4
ΔCH_4 (%)	- 1.7	- 16.4	3.0	23.4	- 0.1	8.0	13.7	148.7
$\frac{\Delta CH_4}{\Delta E}$	- 0.46	- 0.44	0.02	0.02	- 0.15	0.02	0.28	0.31

Increased emissions of NOx lead to reduced concentrations of methane, while increased emissions of CO give an increase in methane. The figures also show that increases in methane *emissions* lead to more than proportional increases in methane *concentrations*. This is often referred to as the CH_4-OH feedback (see chapter 7).

6.9 Sensitivity to background levels of NOx

Limited amounts of the NOx emitted at ground level reach the middle troposphere. NOx from lightning is therefore an important source of NOx in this region and will have a strong influence on the levels of NOx. An other source of NOx is decomposition of PAN, and, in the upper troposphere, input from the stratosphere is significant.

In order to test the significance of the background level of NOx, three perturbations were performed with 12 TgN/yr from lightning instead of 6 TgN/yr. Before the perturbations were done, a new reference run was made in order to get a global emission of methane that was consistent with this NOx production from lightning (see chapter 4). The estimated emission of CH_4 is then 11% higher, showing that the OH levels have increased. The figures below are again given relative to the effect on ozone of a doubling of methane with a lightning production of 6 TgN/yr by the expression:

$$\alpha = \frac{\left[\frac{\Delta O_3(\%)}{\Delta E}\right]_{12\,TgN}}{\left[\frac{\Delta O_3(\%)}{\Delta E(CH_4)_{(2x)}}\right]_{6\,TgN}} \tag{4}$$

The values of α for three perturbations are given in table 6.

Table 6. Ozone enhancement efficiencies for perturbations performed with 12 TgN/yr from lightning.

Perturbation	α
2 x NOx emissions	1.9
2 x CH_4 emissions	1.06
Increased NOx from airplanes (+ 0.5 TgN/yr)	27.6

The numbers show clearly that increases in tropospheric ozone from NOx are sensitive to the NOx levels already present. Higher background levels of NOx markedly reduce the efficiency of ozone enhancement from increased NOx fluxes (from 3.0 to 1.9, with the effect on ozone from a doubling of the methane emission as reference). Methane increases ozone slightly more efficiently (6%) at higher NOx background levels.

The tests also reveal that efficiencies in enhancing ozone are sensitive to the region where the emissions take place, e.g. NOx emitted in polluted regions gives a different O_3 enhancement efficiency than NOx emitted in less polluted regions. This is in agreement with the results from several other model studies. Berntsen and Isaksen, 1992, used a 3D eulerian model for Europe and showed that increased NOx emissions in background areas with large natural isoprene emissions from deciduous forests led to significantly larger ozone increases than similar changes in NOx emissions over more polluted areas.

Based on both observations and model calculations, Liu et al., 1987, concluded that the daily production of O_3 per amount of NO_2 removed by OH is larger for lower NOx levels. Model studies indicated that (for summer conditions at 40°N) a molecule of NOx emitted in an environment with 10 ppt NOx is ~10 times as effective in producing ozone as if it were emitted in an environment with more than 10 ppb NOx (WMO, 1992). Lin et al., 1988, used a box model to study the *net* production of O_3 (O_3 production minus O_3 loss) per NOx loss as a function of NOx levels. They assumed a constant relationship between the levels of NOx and NMHC but different compositions of NMHC. The results for summer condtions at 40°N for three different NMHC compositions are given in figure 15. The figure shows that, depending on the assumed NMHC composition, the net production of O_3 per NOx loss increases from less than 5 O_3 molecules produced per NOx molecule consumed at 100 ppb NOx to a maximum of 30-40 O_3 molecules produced per NOx molecule consumed at 0.2-0.4 ppb NOx. Below these NOx levels, the significance of the O_3 loss increases, and the net production of O_3 becomes negative at NOx levels below 80 ppt.

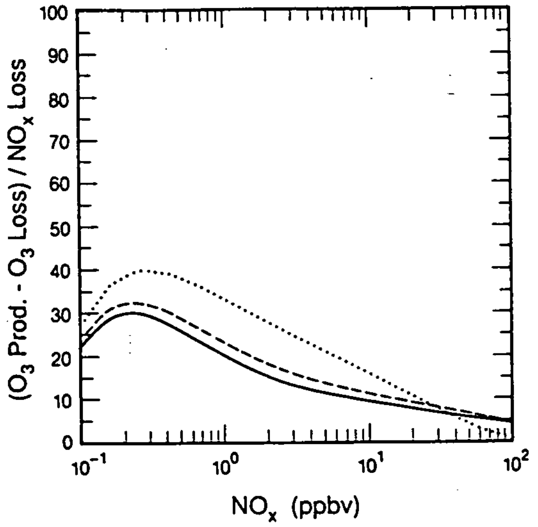

Figure 15. Net production of O_3 per loss of NOx given as a function of NOx level for three different compositions of NMHC. From Lin et al., 1988.

6.10 A combined perturbation

In addition to the model runs where the emissions were perturbed one by one, a combination model run was made in order to simulate the tropospheric conditions pertaining to a few decades ago. Table 7 shows the reductions in emissions in this model run relative to the reference run. The same latitudinal emission profiles as in the reference run were assumed. It is difficult to estimate a reasonable value for reductions in NOx emissions from ground sources. In the former Soviet Union the anthropogenic NOx emissions increased by approximately 60% between 1970 and 1993 (Dignon and Hameed, 1992). In North America the increase was ~10% from 1970 to 1985 (World Resources Institute, 1992), while in the OECD region the emissions increased by 12% during the same period (OECD, 1991a, 1991b). Data is unfortunately sparse for those parts of the world where significant changes in technology use and economic activity have taken place (South East Asia, Latin America). Futhermore, the natural emissions are uncertain (cf. chapter 8). In view of these difficulties this perturbation should primarily be regarded as a sensitivity test of how simultaneous changes in emissions may affect the atmospheric levels of the gases we are concerned with in this study.

Table 7. Reductions in emissions in the combined perturbation relative to the reference run.

Source gas	**Reductions relative to reference**
NOx (ground)	40%
NOx (airplanes)	60%
CO	20%
NMHC	20%
CH_4	15%

The effects on ozone, when going *from low to high emissions,* were significant increases in the entire troposphere in all seasons. The increase in tropospheric annual mean was almost 10%. The increases were up to 23% in August in the lowest layers at 50°N and just a few percent in the upper troposphere. The enhancements were strongest at northern mid-latitudes (fig.16a). where the emissions reach their highest values. The effect of the NOx emissions was, due the short lifetime, confined to the regions where the emissions took place. Methane, on the other hand, has a lifetime long enough to allow good mixing throughout the troposphere, thereby giving a more uniform effect on ozone, as the individual perturbations have shown. The perturbations also showed that increased emissions of CO (and NMHC) will affect ozone the strongest in the Northern Hemisphere where the emissions are largest.

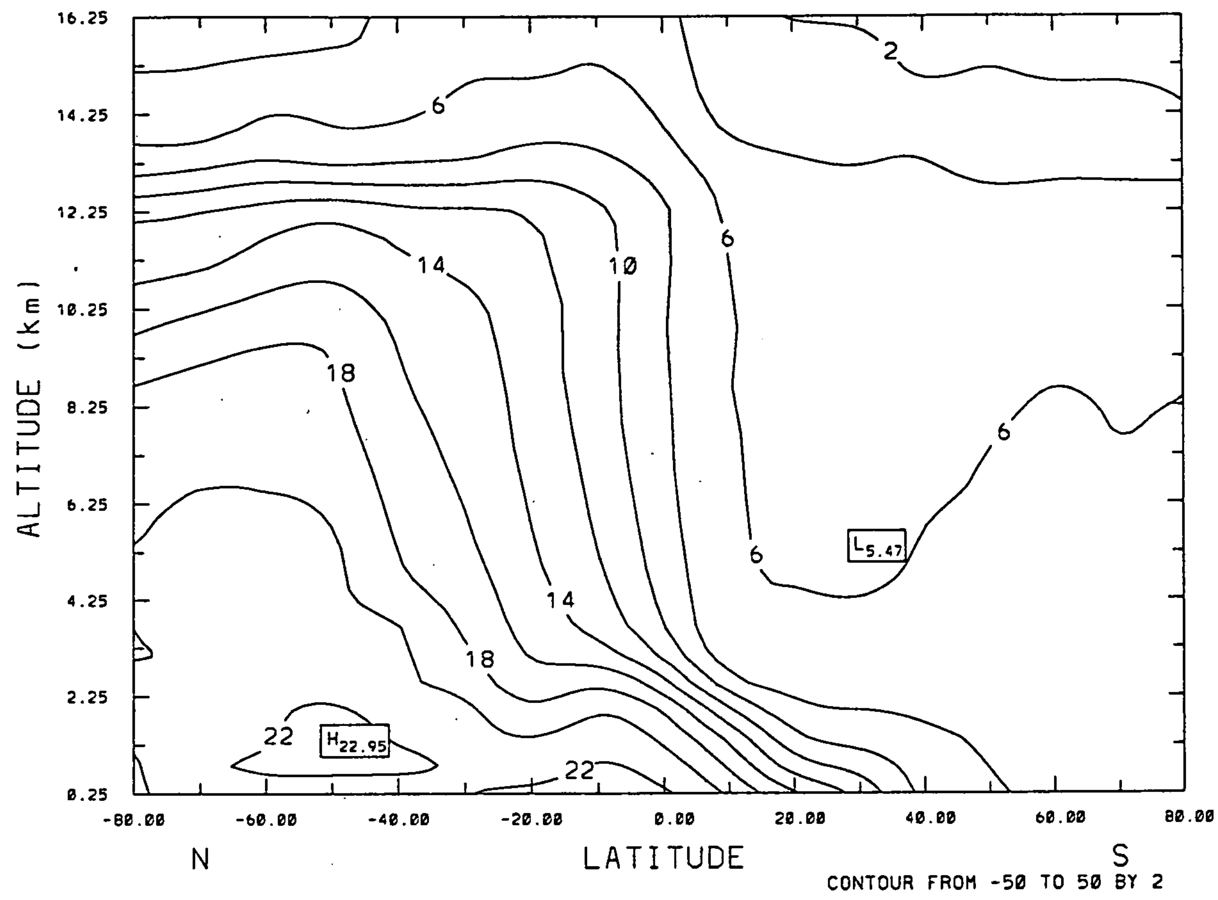

Figure 16a. Calculated percentage change in O_3 concentrations for August when going from low to high emissions in the combined sensitivity test.

The effect on OH was small with respect to the tropospheric mean concentration (<1%), but regionally there are significant changes. In the Northern Hemisphere in August the model gives an increase of about 10-15% in OH (fig.16b). From the perturbation where the ground sources of NOx were doubled, we can infer that the OH increase in this part of the troposphere is due to the increase in NO emissions which increases the OH fraction of HOx through R3. In addition, there is enhanced OH production through R6 and R7 since O_3 increases. The effects from CH_4, CO and NMHC counteract the effect from NOx, but is suppressed. On the other side, these gases contribute to increased O_3 production, which will enhance OH levels. The negative effects on OH from CO, CH_4 and NMHC are not suppressed in the Southern Hemisphere where the emissions and levels of NOx are relatively low.

For winter-time conditions the model also gives an increase in OH over Northern Hemisphere, but the changes are smaller due to lower fluxes through R6 and R7.

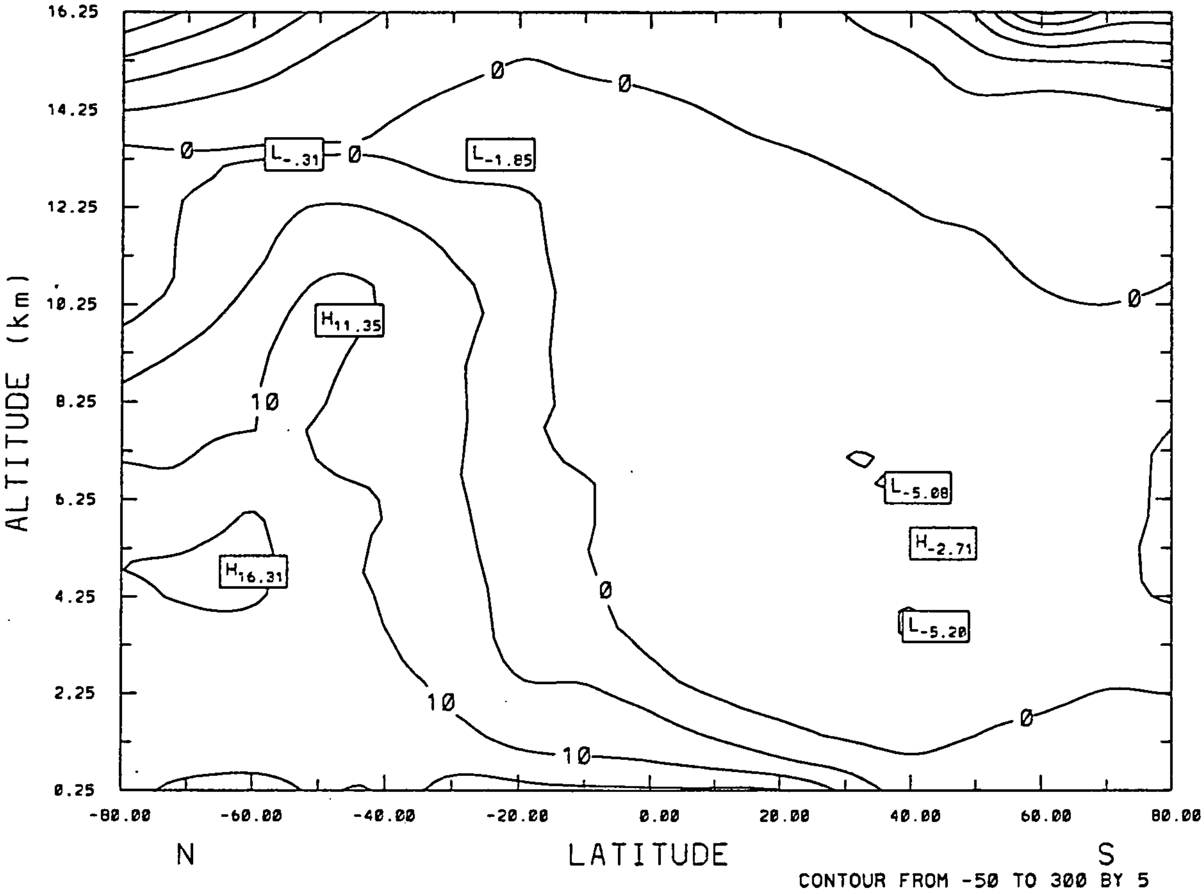

Figure 16b. Calculated percentage change in OH concentrations for August when going from low to high emissions in the combined sensitivity test.

The effect on PAN, when going from low to high emissions, was large increases throughout the entire troposphere of 10-50%. Higher emissions of NOx and higher levels of peroxyacetyl radicals from degradation of hydrocarbons are the main reasons. The higher levels of ozone will also contribute to higher PAN, since ozone oxidizes NO to NO_2 through R15. Enhanced production of PAN will lead to more transport of PAN into cold regions of the troposphere where PAN is a reservoir species for NOx. This makes wider dispersion of NOx possible and thereby efficiently increases the ozone production in parts of the troposphere where NOx is low.

7. THE CH_4-OH FEEDBACK

Because the oxidation of methane has a strong influence on OH concentration on a global scale, there exists the possibility of a positive feedback:

Enhanced CH_4 emissions → enhanced concentrations → reduced OH concentrations → increased chemical lifetime → further enhanced CH_4 concentrations

This is what our calculations show. Figure 17a shows the relation between increased fluxes and increased mean concentration of CH_4 in the troposphere. The strength of the feedback increases with increasing perturbation as methane becomes more important for the OH loss at higher methane values since the magnitude of this feedback depends on, among other things, how important R12 is for the loss of OH. A significant part of the increase in atmospheric methane could be due to this positive feedback imposed by increasing methane on the OH concentrations (Chameides et al., 1977, Sze, 1977, Isaksen, 1988).

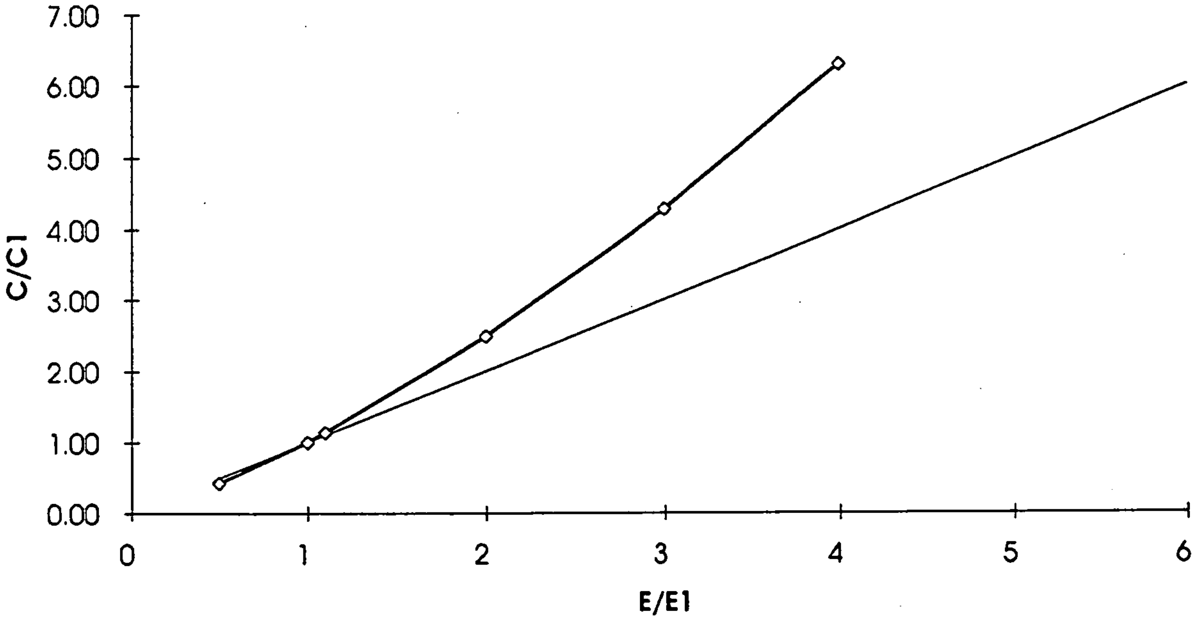

Figure 17a. Calculated changes in global mean concentration of CH_4 as a function of changes in emissions. The straight line represents no feedback between OH and CH_4.

The total feedback effect is a combination of several chemical responses. The feedback is often described as the effect on OH from methane oxidation that may be seen from purely stoichiometric considerations. Whether there will be a loss or gain of OH as methane is oxidated is, to a large extent, controlled by NO. According to Crutzen, 1987, 0.5 OH radicals are produced in the oxidation of one molecule of CH_4 to CO_2 in environments where the NO levels are above 5-10 ppt. In "NO-poor" environments (NO < 5-10 ppt), odd hydrogen radicals are lost instead of gained. According to Crutzen, 3.5 HOx radicals are lost per CH_4 molecule oxidated. Cicerone and Oremland, 1988, estimated a loss of 1-2 HOx radicals depending on the OH level, the heterogeneous removal rate for CH_3O_2H and the pathways of CH_3O_2H reactions.

There is also a feedback through the NO/NO_2 system. The increase in methane will through increase of HO_2 and O_3, increase the oxidation of NO to NO_2. The net effect of this on OH will be the result of the competition between increased formation of OH through increased HO_2 reacting with NO (R3) and increased loss through R11.

The effect of these two reactions on OH may be illustrated qualitatively by assuming that changes in OH are controlled by these two reactions only. The steady-state concentration of OH in such a system, OH_{NOx}, would then be:

$$OH_{NOx} = \frac{k_3 \cdot NO \cdot HO_2}{k_{11} \cdot NO_2} \tag{5}$$

The change in OH caused by changes in NO, NO_2 and HO_2 when methane emissions are doubled may then be expressed by:

$$\Delta OH_{NOx} = \frac{\left[\frac{k_3 \cdot NO \cdot HO_2}{k_{11} \cdot NO_2}\right]_{2\,x\,CH_4} - \left[\frac{k_3 \cdot NO \cdot HO_2}{k_{11} \cdot NO_2}\right]_{ref}}{\left[\frac{k_3 \cdot NO \cdot HO_2}{k_{11} \cdot NO_2}\right]_{ref}} \cdot 100 \tag{6}$$

ΔOH_{NOx} for August is plotted in figure 17b. In the lower tropical atmosphere there is a decrease in OH_{NOx} due to the increased levels of NO_2. Due to the pressure dependence of k_{11}, and the negative activation energy of k_3, reaction 3 dominates at higher altitudes.

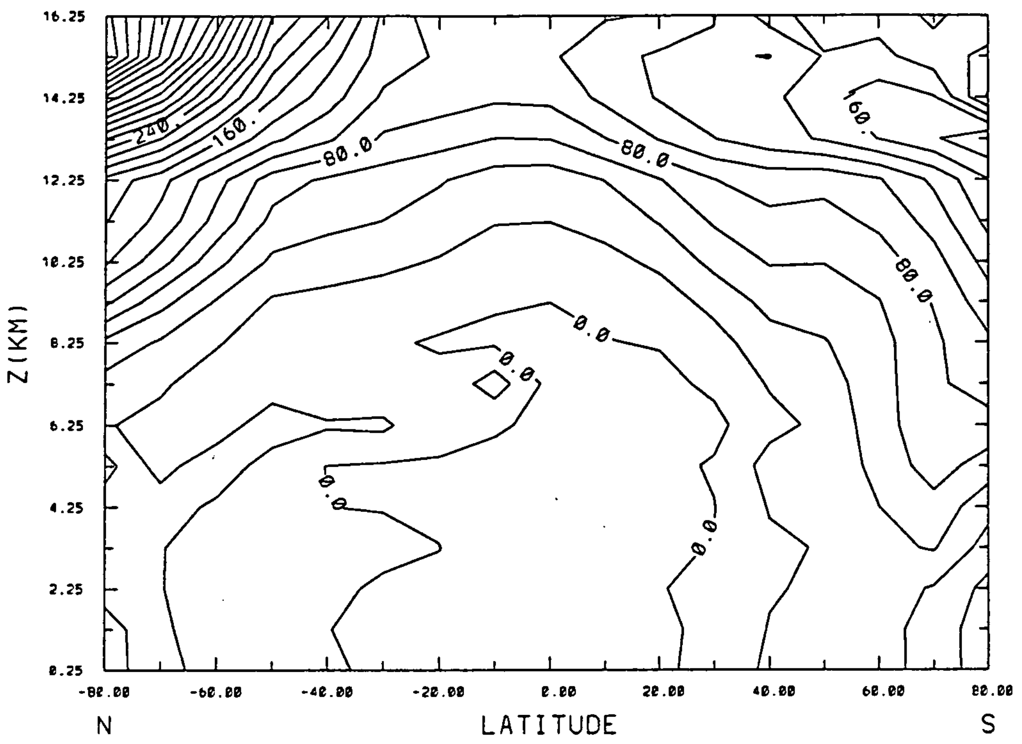

Figure 17b. Calculated percentage change in OH_{NO_x} when the methane emissions are doubled (August).

However, the oxidation of methane will also lead to other chemical responses that will affect the fractionation between OH and HO_2. Increasing the methane emissions will increase the level of odd hydrogen, HOx. (For a doubling of the methane emissions the annual tropospheric average concentration of HO_2 increased by ~30%.) But due to the other changes that will follow from the increase in methane emissions, there will be a redistribution in the HOx system in a way that lowers the OH/HO_2 ratio. If we assume HO_2 to be in steady state and determined by the reactions R3, R7, R8, R11, R12 and R13, the ratio OH/HO_2 may be expressed as:

$$\frac{OH}{HO_2} = \frac{k_3 \cdot NO + k_8 \cdot O_3 + 2 \cdot k_7 \cdot O(^1D) \cdot (\frac{H_2O}{HO_2})}{k_{12} \cdot CH_4 + k_{13} \cdot CO + k_{11} \cdot NO_2} \tag{7}$$

The expression shows that the OH/HO_2 ratio will decrease when methane emissions increase since the increases in the numerator will not compensate the increase in the denominator. The ratio between the tropospheric annual mean concentrations of OH and HO_2 calculated by the model was reduced by almost 40% when the methane emissions were doubled. The changes in the species included in this expression will contribute to reduced levels of OH when the methane emission is increased. (For a doubling of the methane emissions the methane level increases by almost 150%, CO increases by approximately 50% and NO_2 increases by 12%. NO decreases by 12%, while O_3, and thereby $O(^1D)$, increases by only 16%).

In the lower atmosphere there are other factors controlling the HOx budget that may be more important than the oxidation of methane. The formation of water soluble species as HNO_3, H_2O_2 and CH_3O_2H and subsequent scavenging by rain become more important since the scavenging rate is higher in the lower troposphere (maximum around 2 km at mid latitudes). The formation of H_2O_2 is probably of special importance since the rate of formation is quadratic in HO_2. The loss of HO_2 and CH_3O_2 by sticking to aerosols will also contribute to lowered HOx levels in this part of the troposphere.

There is also a sub-cycle that affects the HOx level, and, depending on the importance of other loss reactions for OH and HO_2, the cycle may also affect the OH/HO_2 ratio (Crutzen, 1987):

$$CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \qquad R18$$
$$CH_3O_2H + OH \rightarrow CH_3O_2 + H_2O \qquad R19$$

$$OH + HO_2 \rightarrow H_2O + O_2$$

This cycle, however, cannot be viewed in isolation from the rest of the chemical processes. CH_3O_2H may photodissociate through the reaction

$$CH_3O_2H + h\nu \rightarrow CH_3O + OH \qquad R20$$

CH_3O reacts further with O_2 to produce HO_2 and formaldehyde:

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad R21$$

Formaldehyde may photodissociate to either CO and H_2 or to H and HCO. The latter two species will react with O_2 to give HO_2. Predicting the net effect of these mechanisms when the methane emissions are increased requires a model that can take into account all the chemical changes that propagate through the complex interactions.

When the overall feedback strength is calculated (fig.17a), it is not only a function of the percentage alteration of OH. The total feedback strength is determined by the change in the oxidation rate of methane given by the product $k \cdot OH$, which means that the percentage change in OH has the largest impact in regions of the atmosphere where $k \cdot OH$ is high. Due to high absolute humidity and solar fluxes, the formation and concentration of OH is at a maximum in the tropics. Combined with the strong temperature dependence of k, this leads to a maximum in the methane oxidation rate in the warm and humid tropical troposphere, which makes it clear that the changes in the lower tropical atmosphere is the most important region for the CH_4-OH feedback. Our calculations show that the decrease in OH has a maximum in this region (fig.12b).

The strength of the feedback can be expressed as:

$$f = \left[\frac{\frac{c-c_1}{c_1}}{\frac{E-E_1}{E_1}} - 1\right] \cdot 100 \tag{8}$$

where c_1 and E_1 are reference concentrations and emissions, respectively, and c and E are the perturbed levels.

The overall global and yearly feedback strength amounts to, according to this model study, 35% at present for a 10% increase in emissions. For a doubling of the methane emissions the feedback strength is 50%. In a similar way the feedback mechanisms will affect the concentrations when the methane emissions are reduced (as indicated in fig.17a). When the emissions are reduced by 50%, the global mean concentration of methane is reduced by 57%.

8. LIMITATIONS AND UNCERTAINTIES

In the perturbation tests we have performed, unchanged relative distributions of the emissions along latitude are assumed. This is not a very realistic assumption, but on the other hand, it is not straightforward to predict where any changes in emissions may take place in the future. For the purpose of testing sensitivities in the atmospheric chemistry, such an approach is reasonable. For the effects of NOx, however, one should be aware of the fact that the geographical location of the emissions is of importance because of the relative short lifetime and the non-linear features of the NOx chemistry.

The important role of NOx in tropospheric chemistry has been emphasized several times in this report. It is a key compound in the production of ozone; it determines whether ozone is produced or lost when CO and hydrocarbons are oxidated. The background levels of NOx also determine the magnitudes of the chemical responses. Furthermore, it is a key component in the processes taking part in the feedback between methane and OH. As was shown in section 6.7, the estimated source strength for methane also depends on what source strength is assumed for NOx from lightning. Unfortunately, the present knowledge of NOx in the troposphere is limited. Firstly, there are large uncertainties in the emissions. According to the IPCC, 1992, the emission from soils is 5-20 TgN/yr, while the emission from biomass burning is between 2.5 and 13 TgN/yr. As the tests in this study have shown, the assumed NOx production from lightning is of great importance due to the fact that this is probably the only large source of NOx in the background troposphere (other sources are airplanes, decomposition of PAN and input of NOx at the top of the troposphere). The large range in production of NOx from lightning, 2-20 TgN/yr, given by the IPCC, 1992, introduces large uncertainties in the modelling of tropospheric chemistry.

Secondly, due to its short lifetime, NOx concentrations are highly variable in space and in time, which makes it difficult to obtain a good knowledge of the distribution in the troposphere. The processes that control the "filtering" of NOx through the boundary layer are important. A large fraction of the emitted NOx is removed by chemical transformations and deposition before the rest is able to escape the boundary layer. Once in the free troposphere, however, it may be able to influence the chemistry on a larger scale. It is therefore of great importance to model these mechanisms as well as possible. According to Hov and Demerjian, 1992, it is likely that less than 20% of the surface emissions of NOx is transported into the free troposphere as NO or NO_2.

But it is not only the emissions that introduce uncertainties in the modelling. Uncertainties are also connected to the kinetics. Thompson and Stewart, 1991, studied how the imprecisions in chemical rate constants propagate to uncertainties in computed concentrations in a 1D photochemical model for the troposphere. This was done by using a Monte Carlo technique. They found that the most critical kinetic processes were the photodicossiation of O_3 and NO_2. The reaction between OH and CH_4, and the rate of nitric acid formation (which removes NOx and odd hydrogen) were also found to be critical. The results show that the uncertainties are highly dependent on which gas is studied and the general level of pollutants. Under clean background conditions the 1σ imprecision of OH, HO_2, and H_2O_2 in the mixed layer were as low as 20, 15 and 25%, respectively. Under conditions with high NOx, NMHC and O_3, the numbers were as high as 70, 70 and 90%, respectively. For O_3, the uncertainty was calculated to be ~15% in both cases. By averaging over regionally differing results, they estimated that a typical mean value for OH calculated by their model is ~25% uncertain due to imprecisions in the kinetics. Although the results are dependent on model formulation and the chemistry scheme and how it is solved, the study shows the level of uncertainty and the reactions that play critical roles with respect to uncertainty.

A comparison of 20 chemical schemes published within the last 20 years was performed by Hough, 1988. The schemes were implemented in the same box model. An important finding in Hough's comparison and analysis was that the calculated concentrations of ozone and HNO_3 were in good agreement (less than 10% difference between the most recent schemes). For other species like PAN and H_2O_2 the difference was as large as a factor of 2.

In Chapter 5 by Isaksen et al., in the report "Scientific Assessment of Ozone Depletion: 1991" (WMO, 1992), a comparison between the results from this study and the results from two other models was performed. The two other models are the "multiregion 1D model" from NASA/Goddard Space Flight Center and the Harwell 2D model. It was concluded that there are large variations between the models. This is especially the case for the response in O_3 to increased emissions of NOx (~ factor of 3). In addition to the spatial and temporal variations, the model results are highly sensitive to the background concentrations. Model differences and spatial variations in the O_3 increase in response to increased CH_4 are moderate (both within 50%).

In this study only gas phase chemistry is modelled, but first order heterogeneous scavenging of soluble species by rain and sticking on aerosols are included. Some atmospheric chemistry models are now capable of including exchange processes between the gaseous and aqueous phase, as well as aqueous phase chemistry (Lelieveld and Crutzen, 1990, 1991, Jonson and Isaksen, 1993). The results obtained so far give reduced ozone levels. Jonson and Isaksen report reductions in the ozone levels of 10-30% compared to when the aqueous phase is excluded, with the largest reductions taking place in the remote middle troposphere. An important mechanism behind the results is the separation of the soluble species HO_2 from the insoluble NO in clouds. This will lead to lower flux through the gas phase reaction R3, thereby leading to reduced O_3 production. In the aqueous phase, HO_2 will dissociate to H^+ and O_2^-. The latter species will react with O_3 in the aqueous phase through R22 and thereby increase the loss of ozone:

$$O_3 + O_2^- \xrightarrow{H_2O} OH + 2O_2 + OH^- \qquad R22$$

Another important mechanism that may affect the ozone levels is the conversion of N_2O_5 to HNO_3 once it comes in contact with deliquescent aerosols or comes into a cloud, followed by rainout. Since this process is a sink for NOx, it will reduce the ozone production, as explained in chapter 2.

As Finlayson-Pitts and Pitts, 1986, and Atkinson, 1990, point out, organic nitrates may be formed through R23b:

$$RO_2 + NO \rightarrow f\cdot[NO_2 + RO] \qquad R23a$$
$$\rightarrow (1\text{-}f)\cdot RONO_2 \qquad R23b$$

where f is the fraction that goes through the branch which produces NO_2 and RO. The formation of nitrates, or (1-f), increases with the number of carbon atoms in RO_2 and with pressure, while it decreases with increasing temperature. For compounds and conditions in our model domain, (1-f) is usually less than 0.2.

If these organic nitrates are stable, as suggested by Finlayson-Pitts and Pitts, 1986, and are removed from the atmosphere only by scavenging and/or deposition, this mechanism may provide an additional sink for NOx. The mechanism is not included in this study, which may lead to underestimates of the NOx loss, and thereby overestimates of ozone production. On the other hand, if the organic nitrates are not stable, but have a chemical lifetime long enough to be transported over larger distances before they decompose and give NOx, the nitrates may act as reservoir species of NOx in a manner analogous to the role of PAN. If so, NOx may be transported as $RONO_2$ to remote areas where it may contribute to ozone formation more efficiently than in the source region.

As pointed out in chapter 2, under night-time conditions, the NO_3 radical may act as an important oxidizing species. Such mechanisms are not included in the present chemistry scheme. There is limited knowledge of the role of this species on a global scale, and it is difficult to quantify the effect of omitting such oxidation processes.

In this study we have used a model which assumes zonal homogeneity. Species with a chemical lifetime of a week or more can be assumed to be zonally well mixed and the 2D approximation is justified. Several chemical species have lifetimes considerably shorter than this. Important among these is NOx, which has a chemical lifetime in the order of a few days. NOx levels show therefore strong variations zonally. This reduces the ability to model some non-linear effects in the chemistry connected to the role of this key compound. 3D models are better suited for modelling the variations in NOx and its role in the chemistry. As mentioned in chapter 2, a model experiment performed by Kanakidou and Crutzen, 1992, indicated that 2D models tend to overpredict the OH and O_3 levels, especially in the middle and low troposphere in the tropics and at northern mid-latitudes. Their study also gives an overestimation by ~20% of the amount of CH_4 oxidized in the atmosphere in the 2D case compared to the 3D case. This effect was not globally uniform, and in the low tropical troposphere and around 45°N, the amount of CH_4 oxidized was overestimated by up to a factor of two in the 2D case relative to the 3D case. According to the authors, a consequence of this may be that 2D models not only overestimate the global source strength for methane, but also fail to estimate their latitudinal distribution. However, even the 3D model is very coarse (10° x 10°) which implies a considerable degree of averaging. It is therefore possible that improvments to a finer grid could change the results significantly. It is further possible that their results depend significantly on the chemistry scheme applied.

Our estimate of the feedback strength for CH_4 should be considered only as a preliminary estimate since a 2D model is applied and because aqueous chemistry is not included. Owing to the short atmospheric lifetime of NOx a fine spatial resolution is required to model the role of NOx. Due to the complexity and the important role of NOx in the CH_4-OH feedback, estimation of this feedback requires a model with comprehensive dynamics and chemistry.

The condition for a positive CH_4-OH feedback, as it is given by Crutzen, 1987, will to a limited extent be met in the model applied in this study. This is due to the zonal averaging which often leads to NO values above the threshold value given by Crutzen. Another important difference is that in these model calculations we are able to include several dynamic interactions in the chemistry that are not taken into account in the more static stoichiometric considerations done by Crutzen. However, increased HOx is consistent with the threshold value and the description of the feedback by Crutzen. The feedback through the NO/NO_2 system, as described in chapter 7, is necessary to explain the calculated feedback.

In addition to changes in emissions of source gases there are numerous other factors that may alter the chemistry of the troposphere in terms of concentrations, spatial distributions, oxidizing capacity and turnover. Important among such factors is the stratospheric ozone layer which exerts an important control over the flux of UV radiation penetrating downward into the troposphere. Changes in the UV flux are expected to have taken place as a consequence of the significant reductions in stratospheric ozone that are reported (WMO, 1988, Crutzen, 1992, Madronich and Granier, 1992). The intensity of this flux is of fundamental importance since radiation with wavelengths shorter than 320 nm photolyses ozone (R6) giving $O(^1D)$ which further produces OH in the reaction with water vapour (R7), thereby driving the chemical transformation processes in the troposphere. An increase in UV radiation is therefore expected to result in higher levels of OH. Increased UV flux may also increase ozone in regions where NOx and hydrocarbons are abundant, while the opposite is the case in regions where NOx and hydrocarbons are present in low concentrations. Reductions in tropospheric O_3 due to increased UV have been observed in the NOx and hydrocarbon poor troposphere over the South Pole where large reductions in stratospheric ozone have taken place (WMO, 1992, Schnell, et al., 1991, Thompson, 1991).

Tropospheric water vapour densities are likely to have increased as a result of temperature increases in the troposphere. Such changes may affect OH due to the reaction between $O(^1D)$ and H_2O (R7) which is the main source of OH.

The increased use of fossil fuels has enhanced the amount of sulphate aerosols in the atmosphere. In addition, volcanic eruptions may increase the loading temporarily. Enhanced levels of aerosols may, through scattering (and absorption), affect the UV radiation penetrating downward into the troposphere, thereby affecting the production of OH through changed photolysis rate of ozone. Increased number density of aerosols may also affect the NOx levels via scavenging of N_2O_5, thereby further affecting ozone.

9. CONCLUSIONS

The sensitivity in the chemical responses in the troposphere to changed emissions of source gases is the main focus of this report. The results of the model study should be considered as indications of levels of essential components or of chemical regimes that one may expect from such changes in factors taking part in the complex interplay of atmospheric chemistry.

The study gives increases in the tropospheric averages of O_3 in response to increased emissions of NOx, CO, CH_4 and NMHC. However, the efficiencies in increasing ozone differ significantly between the gases on a mass basis, with NOx having the largest value (table 3). The sensitivities (in terms of annual tropospheric mean values) to increased emissions are larger for smaller increases in emissions. For NOx, the efficiency in increasing ozone is 40% larger for a 10% increase in emissions compared to a doubling in emissions. The corresponding numbers for CH_4 and CO are 20% and 10%, respectively. The sensitivity to increased *NOx emissions from airplanes* are found to be significantly higher than for *ground emissions* of NOx. Depending on whether one uses a comparison of a doubling or a 10% increase of the *ground emissions*, the increase in *airplane emissions* is 12-17 times more effective in enhancing ozone. In spite of the low contribution from airplanes to the global emissions of NOx, this source may significantly affect the chemistry of the atmosphere.

The results indicate that the background levels of NOx are of significant importance when the effects of changed emissions on ozone are studied. Lightning is an important source of NOx in the background troposphere and, by assuming different source strengths, the significance of this factor has been elucidated. The tests reveal that higher background levels of NOx *reduce* the efficiency in ozone enhancement from increased NOx emissions markedly, while enhanced emissions of methane increases ozone slightly *more effectively* with higher background levels of NOx.

The changes in the emissions of the various gases also affect the concentrations and distribution of OH. With respect to tropospheric mean values, increased emissions of CO, CH_4 and NMHC reduce OH, while increased emissions of NOx increase OH. Through the effect on OH, these changes also affect the concentration of methane: Increased emissions of CO, CH_4 and NMHC increase CH_4, while increased NOx emissions decrease the CH_4 levels. In a test where all the emissions were changed simultaneously, these opposite effects balanced each other with respect to the *annual global tropospheric mean concentration* of OH, but gave significant changes in the spatial distribution of OH.

Through the effect on OH, methane affects the strength of its own main sink. This gives a feedback between changed emissions and concentrations. The relative increase in the global mean concentration was ~35% higher than the relative increase in emission.

The sign of the effects on O_3 and OH and on the lifetime (τ) of climate gases controlled by OH are summarized in table 8. (+ gives increases in global averages, - gives decreases).

Table 8. Impact of increased emissions on tropospheric averages of gases affecting climate.

Increased emissions of ↓	O_3	OH	τ(CH_4,HCFC, HFC)
CH_4	+	-	+
NOx	+	+	-
CO	+	-	+
NMHC	+	-	+

The results indicate that the indirect effects of emissions of CH_4, CO and NMHC on climate may be positive. This is due to a positive effect on the ozone levels, and a negative effect on OH, thereby increasing the lifetimes and concentrations of greenhouse gases removed by OH. For NOx, however, the effects are of opposite signs. Increased emissions of NOx have a positive indirect effect through increased

O_3 levels, but also a negative effect through increased OH levels. Thus, estimates of the net effect of the indirect effects of NOx on climate require better knowledge of the atmospheric NOx distribution and detailed radiative calculations.

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