Tellus (1987), *39B*, 271–285

Calculation of trends in the tropospheric concentration of O_3, OH, CO, CH_4 and NO_x

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(Manuscript received May 18; in final form November 10, 1986)

ABSTRACT

A 2-dimensional transport-photochemistry model of the global troposphere was applied to carry out long-term calculations of the effect of emission changes in nitrogen oxides, carbon monoxide, methane and nonmethane hydrocarbon, on ozone, hydroxyl and on the concentration of the precursors. For a model calculation for the 60-year period 1950–2010, where the tropospheric methane concentration was fixed to increase 1.5% per year, an average emission increase of only 1.05% per year was required to support the concentration increase. The 1.5% per year increase in methane, reduced hydroxyl by approximately 25%, over the period 1950–2010, while ozone increased by 0.45% per year. Increasing the emissions of carbon monoxide caused a slight reduction in hydroxyl. Increasing the NO_x-emission by 3% per year in the 30-year period 1965–1995, gave rise to a significant increase in both ozone and hydroxyl. If the emissions of carbon monoxide, nitrogen oxides and nonmethane hydrocarbons were increased by 3% per year and methane by 0.5% per year, the concentration of hydroxyl hardly changed over a 30-year period, while ozone increased by about 1% per year. If the emissions of carbon monoxide, nonmethane hydrocarbons and methane went up by 3, 3 and 0.5% per year, respectively, and the emissions of nitrogen oxides dropped by 3% per year, the concentration of hydroxyl declined markedly (−0.7% per year). As a consequence of the drop in the concentration of the hydroxyl radical, there was an increase in the concentration of methane which was more than twice the emission increase over the 1965–1995 time period.

1. Introduction

Increasing attention is being drawn to chemically active trace gases like ozone (O_3), carbon monoxide (CO), methane (CH_4) and nitrogen oxides ($NO_x = NO + NO_2$) as there is observational evidence of growing concentrations of O_3, CH_4 and perhaps CO in the free troposphere. For the period 1978–1983 Blake and Rowland (1986a) estimated the global CH_4 increase to be 1.1% per year. Recently, the concentration of CH_4 in the troposphere was deduced from infrared solar spectra recorded at Jungfraujoch in Switzerland in 1951, and it was found that the mean CH_4 mixing ratios had increased by $1.1 \pm 0.2\%$ per year for the time period 1951–1981 (Rinsland et al., 1985).

Increasing concentration of CO at some Northern Hemisphere locations has been reported. Khalil and Rasmussen (1984) believed that 3½ years of data from Cape Meares, Oregon, showed about 6% per year increase in CO. Dianov-Klokov and Yurganow (1981) reported data indicating a 2% per year increase in winter time CO at northern temperate latitudes, while the concentration seems to have remained constant in the summer. According to the authors the increase could be connected to the anthropogenic emission of CO, which they claim goes up by 4% per year. Using similar methods as for CH_4 (infrared spectroscopy), Rinsland and Levine (1985) estimated an average increase of 2% per year in the free tropospheric concentration of CO over Europe for the period 1950–1977. Fraser et al. (1986) could not detect any trends in the CO concentration in the Southern Hemisphere from

measurements at Cape Grim, Tasmania, for the time period 1978–1984 or from measurements in 1980–1984 at Mawson, Antarctica.

In a comprehensive review of the seasonal behaviour of tropospheric ozone, as well as of trends and anthropogenic influence, Logan (1985) concluded that there is evidence for an increase in ozone in the middle troposphere over Europe over the past 15 years. The increase over North America and Japan is less obvious. The upward trend in ozone over Europe is mainly judged from a very reliable record of ozone sonde observations over Hohenpeißenberg in Bavaria (Attmannspacher et al., 1984) and on the results from the ozone network in the German Democratic Republic (Warmbt, 1979). The ozone sonde records indicate a 50–70% increase in the concentration of ozone above the boundary layer from 1967–1982, while there is near doubling in the average concentration of ozone at clean air ground sites in the German Democratic Republic from the mid 1950's to the end of the 1970's.

The increase in abundance of tropospheric trace gases is important for several reasons.

(i) The potential climatic effect of radiatively active trace gases like O_3 and CH_4, is significant. Together with the change in atmospheric infrared absorption due to increasing concentrations of N_2O, $CFCl_3$, CF_2Cl_2 and other anthropogenic chlorinated hydrocarbons, Ramanathan et al. (1985) calculated that by 2030, these trace gases are potentially as important as CO_2 for the long-term climate trend.

(ii) O_3, CO and CH_4 are photochemically active species in the atmosphere. The increase in concentration of these species is partly due to changing emissions of NO_x, hydrocarbons and CO, and partly due to a likely change in the hydroxyl concentration. Levine et al. (1985) estimated that the tropospheric level of the hydroxyl radical may have decreased by about 25% since 1950 due to the change in CO and CH_4.

(iii) Increasing emissions of NO_x and HC have given rise to the increase in tropospheric ozone (Isaksen, 1979; 1980). The height distribution of the ozone change is important for the effect of ozone on infrared absorption. The longwave opacity of ozone increases with increasing pressure. A given percentage change in the tropospheric burden of ozone will result in 2 or 3 times higher surface warming (or cooling) than the same percentage change in stratospheric ozone, although about 90% of the atmospheric ozone content resides in the stratosphere. Furthermore, ozone changes in the lower stratosphere and upper stratosphere are more effective than changes in other regions of the atmosphere in causing a surface temperature change. On a per molecule basis, an ozone change at 10 km is 4–5 times more effective than the same change at 20 km in affecting the surface temperature (Ramanathan, 1979; Wang and Sze, 1980). Also, the magnitude of the change in radiative flux due to tropospheric ozone change, is latitude dependent (Ramanathan and Dickinson, 1979). The changes are larger in the tropics than at higher latitudes for the same absolute change in ozone. For climatic considerations, it is therefore important to keep in mind that a redistribution of atmospheric ozone may have a climatic effect even though the total column is unperturbed, and the climatic effect from ozone changes is latitude dependent.

(iv) Ozone is a toxic gas for biological systems. The occurrence of pollution episodes with elevated ozone in the atmospheric boundary layer during the summer over Europe, North America, Japan and elsewhere in the world has caused concern. The episodic behaviour of ozone in the atmospheric boundary layer is superimposed on a background, "clean air" concentration which over Europe may have doubled in 25 years (Warmbt, 1979).

The following questions will be discussed in this paper: What is the relationship between the global source strength of CH_4, the long-term concentration change of CH_4, and the concentration of tropospheric hydroxyl (OH) and O_3? How will the long-term changes in emissions of NO_x, HC and CH_4, separately and together, affect the composition of the troposphere? What is the relationship between changes in the height distribution of tropospheric ozone and changes in the emission of NO_x, CO and CH_4?

2. Model description

The model was a two-dimensional, meridional model with 19 × 20 grid points. It was developed by Isaksen and Rodhe (1978) and applied by Isaken (1979, 1980), Rodhe and Isaksen (1980)

Table 1. *Upper and lower boundary conditions in the meridional 2-D model of the global troposphere. +, indicates a source for the troposphere; −, loss; and 0, no influence (zero flux).*

Boundary	Species	CO NMHC[1]	O_3	NO	NO_2	PAN	HNO_3	CH_3	Other species
top		0	+	+	+	0	+	–[2]	0
surface	emissions	+	0	+	+	0	0	+	0
	deposition	≈0	−	0	−	−	−	0	0

[1] Nonmethane hydrocarbons.
[2] 5% of the surface source.

and Isaksen et al. (1985). In the vertical two different grid steps were used: 250 m up to 3.25 km, and 1 km from there and up to 17 km. In the horizontal the grid size was 10° latitude. The field of mean motion was taken from Newell et al. (1972). The coefficients of turbulent diffusion were adopted from Hidalgo and Crutzen (1977), with some modifications. In the boundary layer, the vertical diffusion coefficients reported by Isaksen and Rodhe (1978), were used. Across the equator in the middle and upper troposphere, the horizontal diffusion coefficients were increased by a factor of 3 compared to the coefficients reported by Hidalgo and Crutzen (for heights above 4 km and between 20°N and 20°S latitude). This brought the K_y coefficients closer to the values reported by Hyson et al. (1980).

In the paper by Isaksen and Rodhe (1978) details about the numerical solution were given.

The boundary conditions were zero horizontal flux for all species across the vertical boundaries at 85°S and 85°N. At the lower boundary, fluxes and species were given either as emissions from natural or anthropogenic sources, or as ground removal. At the top boundary, fluxes were determined by the stratospheric transport into the troposphere as a function of season and latitude. In Table 1, the most important upper and lower boundary conditions are summarized.

The fields describing the mean motion, the temperature and pressure were changed every season in the model. December, January and February represented the first season, etc.

2.1. Chemistry

The distribution of tropospheric O_3, OH, CO, CH_4, formaldehyde (HCHO), peroxyacetylnitrate (PAN) and other trace gases containing O, H, C or N, is determined by gas chemical processes, precipitation, interaction with particulate matter and the ground, and by emissions of hydrocarbons and nitrogen oxides from natural and anthropogenic sources. In the chemistry calculation of ozone, hydroxyl and the other secondary species, the anthropogenic emissions of nonmethane hydrocarbons were divided into groups of species which were represented by C_2H_6, n-C_4H_{10}, n-C_6H_{14}, C_2H_4, C_3H_6 and m-xylene. The volume fractions were $\frac{2}{5}$, $\frac{2}{9}$, $\frac{1}{9}$, $\frac{2}{9}$, $\frac{1}{9}$ and $\frac{1}{9}$, respectively. The non-methane natural hydrocarbons are confined mainly to the atmospheric boundary layer at low latitudes. Only isoprene of the nonmethane natural hycrocarbons was assumed to be of importance for the gas phase chemistry, and of the products of the initial reaction, only 60% were assumed to go through further gas reactions. The rest was made up by photochemically rather long-lived oxygenated intermediates like alcohols and peroxides, which may be removed by tropical rain (Zimmerman et al., 1978). The decomposition of isoprene in the gas phase was assumed to follow the scheme suggested by Zimmerman *et al.* (1978) where about 3 HCHO, 1 CO_2 and 1 PAN-molecule were formed when one isoprene molecule was decomposed after the initial attack of OH with a reaction rate coefficient of nearly 1×10^{-10} $cm^3/(molecule \times s)$ (Kleindienst et al., 1982; Gu et al., 1985).

The diurnal variation in chemical species was calculated using a time-step of one hour in the numerical integration.

The photochemistry of the mixture of species resulting from emissions of HC, NO_x and CO in

tropospheric air followed to a large extent previously published schemes (see Isaksen et al., 1985 for further references). The calculation of photochemical processes, inclusion of an average cloud cover and numerical procedures were also described in the same paper. Dry deposition of O_3, NO_2, PAN and HNO_3 was treated in terms of a deposition velocity, and a simple parameterization was used to derive the deposition velocity to be used at the lowest grid point (250 m) from the velocity at the reference height (1 m), see Isaksen et al. (1985) and Isaksen and Rodhe (1978). The deposition velocities were weighted by the fraction of land and sea in each latitudinal zone of the model, and there was furthermore a shift with season due to a change in surface with much lower deposition velocities during the winter.

Scavenging by cloud or precipitation was of interest mainly for HNO_3 in this model, and a hemispheric mean value of 5×10^{-6} s^{-1} was used as the first order decay rate coefficient during summer. During winter the value was reduced by a factor of 4. The scavenging rate coefficient had a maximum around 50° N and 3 km height falling off to the north (Isaksen and Rodhe, 1978).

3. Emissions

Direct anthropogenic release of CO through the burning of fossil fuel was taken to be 640 Mt/y (Zimmerman et al., 1978), distributed with latitude from the anthropogenic source function (Fig. 1). Indirectly, there is a significant production of CO through the degradation of CH_4, isoprene and anthropogenic, nonmethane hydrocarbons.

The sources of methane are specified in Table 2.

The source of methane depends on the latitude. An annual variation in the source strength for biomass burning and rice paddies was assumed in the model. The inclusion of an annual variation of the source strength did not make much difference to the methane-distribution since it takes approximately 10 years for CH_4 to reach steady state for a given emission intensity. Blake et al. (1982) estimated that an annual flux of 400 ± 130 Mt per year of CH_4 is required to maintain a steady state concentration at its present level of about 1.6 ppm.

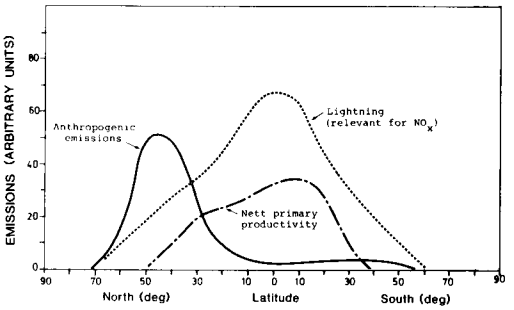

Fig. 1. Relative distribution with latitude of anthropogenic emissions, lightning and nett primary productivity (biomass).

Table 2. *Sources of methane (Mt per year)*

ruminants	100
termites	10
rice paddies	60
swamps and fresh water lakes	100
tundra	10
ocean	10
biomass burning	60
fossil fuel	100
total	450

The calculated meridional concentration profile for CH_4 for the northern hemisphere summer is shown in Fig. 2. Within the hemispheres the concentration is almost the same. At 1 km height the mixing ratio is 1.74 ppm in the northern and 1.655 ppm in the southern hemisphere, with an interhemispheric concentration ratio of 1.06, see Fig. 2. The calculated concentrations are approximately 5% higher than the measured average concentrations at the NOAA-GMCC stations (1.65 ppm for NH and 1.55 for the SH), but it should be kept in mind that the calculated CH_4-concentrations are steady state values obtained after 40 years of integration with present day's emissions and OH-concentration distribution (no feedback from CH_4 to OH in this case). Present atmospheric CH_4-levels are not in a steady state, as it will take more than 10 years to reach steady state if emissions and loss processes were kept constant.

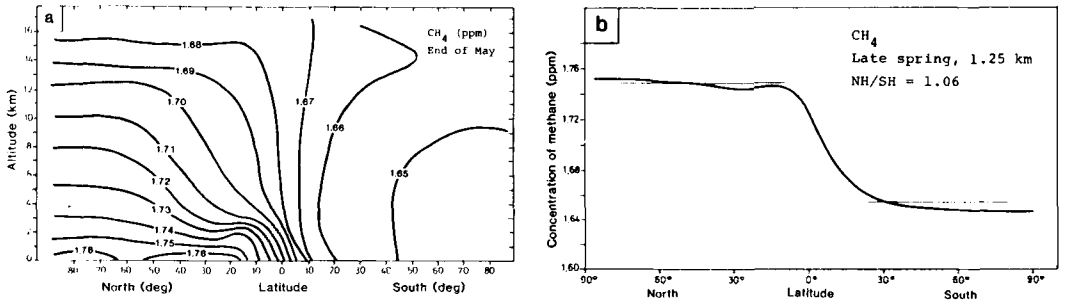

Fig. 2. (a) Steady state concentration distribution of CH_4 where model integration was carried out for 40 years with emission of CH_4 and distribution of OH representative of 1980. (b) Concentration distribution with latitude for CH_4 at 1.25 km height during late spring.

The calculated interhemispheric concentration ratio is consistent with the measurements made during Gametag in 1978 (Heidt et al., 1980) and the measurements reported by Singh and Salas (1982).

Several estimates of the global sources of NO_x have been reported in the literature. Logan (1983) concluded that the global NO_x-emissions range from 25–99 Mt(N) per year, specified as follows.

Fossil fuel combustion	21 Mt(N) per year(14–28)
Biomass burning	12 Mt(N) per year (4–24)
Lightning	8 Mt(N) per year (2–20)
Microbial activity in soils	8 Mt(N) per year (4–16)
Oxidation of ammonia	1–10 Mt(N) per year
Input from the stratosphere	~0.5 Mt(N) per year

Liu and Cicerone (1984) estimated global sources in the range 20–67 Mt(N) per year, specified as:

Fossil fuel burning	15–25 Mt(N) per year
Biomass burning	1–10 Mt(N) per year
Lightning	2–20 Mt(N) per year
Soil exhalation	1–10 Mt(N) per year
Subsonic aircraft	0.15–0.3 Mt(N) per year
Stratospheric intrusion	0.5–1.5 Mt(N) per year

In this study, the global emission of NO_x was taken as 29 Mt(N) per year, with 20 Mt(N) per year distributed as anthropogenic emissions, 4 Mt(N) per year from lightning and 5 Mt(N) per year from biomass burning. The relative distribution with latitude of the emissions is shown in Fig. 1. The lightning source NO_x is partly at low altitude and partly in the upper troposphere. Emissions from biomass burning has been given the same relative shape as "Nett primary productivity" in Fig. 1.

As indicated in Table 1, an additional stratospheric source of NO_x at the tropopause was assumed in the model calculations.

Anthropogenic, nonmethane hydrocarbon emission were taken to be 90 Mt per year, assuming 40% coming from automobile exhaust, 30% from solvent usage and 30% from natural gas exploitation and distribution (Isaksen et al., 1985). The nonmethane hydrocarbon emissions were distribued among six species as specified in the section on chemistry. The numbers of global NMHC-emissions reported in the literature, cover a wide range. Ehhalt and Rudolph (1984) estimated global anthropogenic NMHC-emissions to be 56 Mt per year, while the measurements and calculations of Tille et al. (1985) for the latitude belt 35–50°N pointed to a considerably higher global release rate of NMHC than 56 Mt per year. Looking at a single species only, Penkett (1982) suggested an annual release of C_2H_6 of 5 Mt, Ehhalt and Rudolph (1984) estimated 1.3 Mt, Isaksen et al. (1985) found that a 10 Mt source gave the best fit between measured and calculated values, while Blake and Rowland (1986b) estimated 13 $\pm$3 Mt for the annual atmospheric release of C_2H_6. This shows that there is a factor of 10 difference in the numbers published for the atmospheric C_2H_6 emissions, and the agreement is probably not much better for other species. On the other hand, it has been shown previously by us (Isaksen et al., 1985) that a global emission of 90 Mt per year of anthropogenic hydrocarbons gave reasonable agreement with the measured concentration of species like C_2H_6 and C_3H_8. This indicates that the global OH-distribution calculated using an

extensive photochemical reaction mechanism, is consistent with the emissions of NMHC. If the calculated OH-concentrations turn out to be wrong, however, the emissions are also incorrectly estimated.

The NMHC/NO_x ratio for the global, anthropogenic emissions is about 1.35 with 90 Mt and 20 Mt (N) as annual NMHC and NO_x-emissions, respectively, when NO_x is expressed as NO_2 in calculating the ratio.

The emissions of isoprene were taken to be 340 Mt/y, as estimated by Zimmerman et al. (1978). This source was distributed as the biogenic emissions in accordance with Lieth and Whittacker (1975), see Fig. 1. The isoprene emissions influence the photochemistry in the tropics considerably, while the impact at higher latitudes is slight. Terpenes are assumed to be of less importance for global tropospheric gas chemistry, and are not treated in the model calculations.

4. Calculations of concentration changes over decades

Three main questions were investigated in turn.

(a) There is a global increase in the concentration of tropospheric methane. What is the relationship between the concentration change, its effect on tropospheric chemistry (notably OH), and the global source strength of CH_4?

(b) What are the effects of long term emission changes (over 30 years) of CO, NO_x, HC and CH_4, separately and together, for different emission change scenarios, on the composition of the troposphere? Can an upward trend in the tropospheric ozone concentration be calculated on the basis of a realistic emission change scenario?

(c) For changes in the infrared opacity of the atmosphere, the concentration of ozone in the upper troposphere plays a crucial role. What is the relationship between changes in the height distribution of tropospheric ozone and emission changes of species like NO_x and CO? How does atmospheric transport influence the height distribution of tropospheric ozone?

Before the discussion of concentration changes due to emission changes over many decades, some results of the calculations with present day emissions will be shown. In Fig. 3 the distribution with latitude and height of O_3, OH, CO, HCHO, PAN and NO_x is shown for the end of May. The model was integrated for a sufficiently long time to approach an equilibrium annual cycle and to become self consistent. The concentrations given are diurnal mean values averaged over one month (May).

The calculation showed a maximum in O_3 at 40° and 50°N latitude. There was a decline in concentration towards the ground due to dry deposition. Measurements of the latitudinal distribution of O_3 show considerable variation, but usually there is a minimum in the tropics and maximum at 40°–50° latitude in both hemispheres. Measurements taken during northern hemisphere summer both in the free troposphere and the atmospheric boundary layer, consistently have a maximum in O_3 around 30–50°N with typical concentrations of 60–80 ppb ($1.5–2.0 \times 10^{12}$ molecules/cm^3) near the ground (Routhier et al., 1980; Logan, 1985).

The calculations for the end of May for ozone shown in Fig. 3 have much less latitudinal variation in the free troposphere than the measurements, e.g., by Seiler and Fishman (1981). Their results also indicate that the calculated ozone concentrations in the free troposphere are too high. There is a more pronounced tropical-free tropospheric minimum in ozone for other seasons in the calculations, more in agreement with the measurements. At the end of May, horizontal transport in the northern hemisphere has been too efficient, removing latitudinal gradients in the calculations, while stratospheric subsidence of ozone-rich air in the southern hemisphere winter has barely started. Also, the flux of ozone from the stratosphere may be over-estimated when establishing the boundary conditions in the model, giving too much ozone in the free troposphere. This may indicate that the calculated hydroxyl concentration is too high in the model; on the other hand, OH is highly dependent also on NO_x.

The maximum OH-concentration was found close to the ground at 40°N (close to 1.5×10^6 molecules/cm^3).

Recently the knowledge of atmospheric OH has been advanced through the measurements carried out by KFA-Jülich at three sites in the Federal Republic of Germany. Maximum OH-

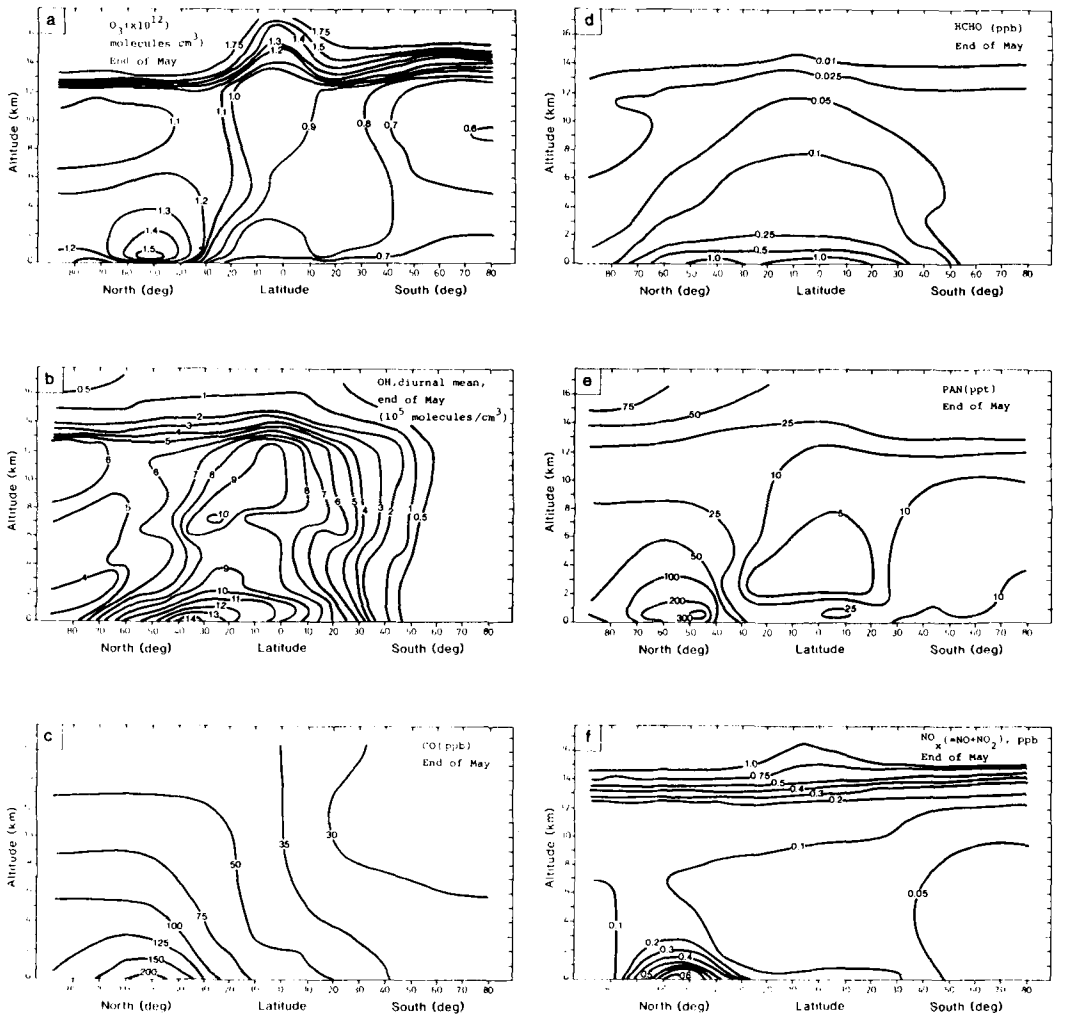

Fig. 3. Concentration distribution at the end of May (diurnal mean values averaged over one month) for O_3 (a), OH (b), CO (c), HCHO (d), PAN (e) and NO_x (f) for NO_x, CO, CH_4 and NMHC emissions representative for 1980.

concentrations ranged from less than 5×10^5 to 6×10^6 molecules/cm^3, and it was found that for high NO_x-concentrations (>2 ppb) the measured OH values could be described by model calculations using a state-of-the-art photochemical model and measured values for the precursors (aldehydes, CO, HC, NO_x), while for cleaner air, considerably higher OH-concentrations were calculated than measured (Hofzumahaus et al., 1985). The OH-concentrations in Fig. 3 are diurnal mean values, and the values calculated at 40°–50° N compare well with the measured values in FRG, although no direct comparison can be carried out.

For CO, the calculations gave a mid-latitude, northern hemispheric maximum of 212 ppb for the end of May, and there was typically a factor of 5 difference in mid-latitude concentrations in the northern and the southern hemisphere. This is also close to the annual average ratio. The computed latitudinal distribution compares quite well with the Gametag-measurements over the

Pacific where at the end of April 1978 was measured about 50 ppb in the free troposphere between 25 and 55°S and from 100 to 175 ppb going from the tropics and northwards to 60° N (Heidt et al., 1980). The calculated concentrations at 5 km are perhaps 30% lower than the observed values (Fig. 3). Comparing the measurements by Rasmussen and Khalil (1982) at Cape Meares (45°N) and the measurements by Fraser et al. (1986) at Cape Grim (41°S) indicate an interhemispheric ratio of about 3 on an annual basis and approximately the same during the spring.

The calculated CO concentrations may be lower than the measurements and the interhemispheric difference overestimated because the low latitude sources of CO in the model were 60 Mt/year of CO from biomass burning, as quoted by Zimmerman et al. (1978). Other authors (Greenberg et al., 1984) indicate that as much as 800 Mt/year of CO may be emitted from biomass burning. Such a source would increase the calculated tropospheric CO-concentration and lower the interhemispheric ratio.

A recent reevaluation of the reaction rate coefficient for the CO + OH reaction has given rise to slightly higher CO-concentrations than shown in Fig. 3. The calculated OH-distribution did not change much, however, since OH is to a large extent controlled by the NO_x-concentration.

The calculated CO-distribution and in particular HCHO-distribution, strongly reflected the isoprene-emissions in the tropics. The concentration of HCHO had a maximum of more than 1 ppb in the boundary layer both at mid latitudes in the northern hemisphere and in the tropics. Measurements in Jülich, FRG, in clean air conditions, gave 1 ppb as the most frequently sampled concentration (Lowe and Schmidt, 1983). Measurements on Atlantic cruises typically gave 0.2–0.3 ppb as HCHO-concentration between 40°S and 40°N (Lowe and Schmidt, 1983), or a factor 4–5 lower than the calculated concentration. There is probably a significant east-west gradient in the HCHO-concentration, since the precursor molecule in the tropics, isoprene, has a very short lifetime (a few hours only) and HCHO is also decomposed quickly compared to the characteristic time for zonal mixing, which is 1–3 weeks.

For PAN, the calculated monthly maximum for May was about 300 ppt in the boundary layer at 40°N. Penkett and Brice (1986) measured 353 ppt as the average clean air PAN-concentration at Harwell in the UK (clean air defined as air with less than the typical background atmospheric concentration of CFC-11; further screening was also undertaken using measurements of CH_3CCl_3). Clean air measurements by Singh and Salas (1983) and Meyrahn et al. (1984) showed more than 100 ppt of PAN at mid-latitudes in the northern hemisphere, while Rudolph et al. (1985) reported that during the June-1984 "Stratoz III"-flight, the concentrations in the southern hemisphere never exceeded 15 ppt, while in the northern hemisphere the concentrations were more variable (up to 50 ppt).

The concentration of NO_x was calculated to reach about 0.8 ppb close to the ground at 50°N latitude at the end of May. NO_x was mainly made up of NO_2, and the concentration of NO_2 was everywhere higher than the concentration of PAN at this particular time. There was a significant fall-off in concentration with height in the northern hemisphere, reflecting the limited lifetime of NO_x (determined by the reaction of NO_2 with OH through which more than 5% of NO_2 is converted to HNO_3 per hour when the concentration of OH is 1.5×10^6 molecules/cm^3). The concentration of NO_x increased towards the tropopause in response to the downward NO_x flux from the stratosphere where N_2O is broken up to yield NO_x through reaction with excited atomic oxygen.

In clean air, in the Rocky Mountains in North America the NO_x levels have been measured to be around 0.2 ppb (Kelly et al., 1980) and 0.4–0.5 ppb at Fritz Peak observatory west of Boulder in Colorado (Kley et al., 1981).

The lifetimes of OH, HCHO, PAN and NO_x ($= NO + NO_2$) are short, and the concentration of these species reflects the local conditions in terms of emissions and meteorology. The chemistry is furthermore non-linear. This means that the concentrations calculated in a zonally averaged model is different from the more realistic concentrations calculated from a model covering specific longitude bands and then averaged over all longitudes. Isaksen et al. (1985) found that in oceanic air with very litttle NO_x, OH in the lower atmosphere may be reduced by perhaps 50%

compared to the calculated concentration in a zonally averaged model.

4.1. The relationship between concentration and emissions of methane

Long-term calculations were carried out with 1980 as the base year. The calculations were speeded up by computing explicitly only the first year (usually 1965), the base year (1980) and the last year (usually 1995). If for instance a model calculation was to be done with a 3% emission increase in CO every year, the annual cycle was computed until convergence (negligible change in concentration distributions from one year to the next) with CO emissions at 64% of the base year ($0{\cdot}64 = 1.03^{-15}$), corresponding to 1965, and with emissions at 56% above the base year ($1.56 = 1.03^{15}$), corresponding to 1995. The response time to changes in the emissions was so fast that sufficient convergence was achieved already after one year of model simulation.

It is believed that methane emissions from the use of fossil fuels amount to more than 20% of the total methane emissions on a global basis (Table 2). Losses through production, distribution and consumption of natural gas probably make up a sizeable fraction of the anthropogenic methane emissions. The consumption of natural gas on a global basis, increased by nearly 4% per year as an average for the decade 1970–1980 (United Nations, 1983). Even if the natural emissions do not change, the increase in the anthropogenic fraction may cause an overall change in emission of 0·5% per year. Kahlil and Rasmussen (1983) estimated that the global source of methane may be going up by about 10 Mt per year, or about 2% per year if the annual emission is 450 Mt.

For a model calculation for the 60 year period 1950–2010, where the tropospheric methane concentration was fixed to increase by 1.5% annually, an average emission increase of only 1.05% per year was required to support such an increase. This is due to the suppression of OH as methane goes up. At 1.5% increase per year, the CH_4 concentration goes up approximately a factor 2.5 in 60 years. Assuming that the reaction with CH_4 for the base year (1980) accounts for 10% of the OH loss, the increase in CH_4 should reduce OH by approximately 25% without taking into account other feedback mechanisms, indicating that it is reasonable to expect that a 1.05% average increase in emissions per year is sufficient to support a 1.5% concentration increase per year.

4.2. Tropospheric chemical composition and long-term changes in the emissions of CO, NO_x, HC and CH_4

Anthropogenic CO is mainly emitted from mobile sources. Work in progress in OECD shows that the emissions of CO decreased significantly in North America and Japan from 1970–79, despite the constant increase in traffic volume. In the OECD countries in Europe, mobile CO sources have generally increased, or, at best, remained constant. North America contributes 64% of the anthropogenic CO emission within OECD. For the period 1978–1990 it is estimated that the CO emissions will decline by 50% in North America, while it is estimated a smaller decrease or no change (southern Europe) for other OECD countries.

The major part of the anthropogenic NO_x emission stems from transport sources. Trend analyses for the 1970–79 period from on-going OECD work indicate that there has been an increase in NO_x emissions in most of the OECD countries, although the total release of NO_x has increased slower than the gross national products. For the 1979 to 1984 period, however, the increase in the emissions of NO_x in Japan, North America and most of OECD-Europe has stopped or even decreased, with the possible exception of southern Europe. The changing trend in NO_x emissions reflects the combined effect of stagnation in economic growth, more economic fossil fuel use, and environmental controls on emissions starting to be efficient in the late 1970s.

Official documents from OECD (1982), based on reports and projections made by the individual member countries, indicate that the anthropogenic emissions of hydrocarbons have been increasing slightly over the last decade. A similar increase is anticipated also for the next decade (1–2% per year for most countries).

Estimates of the historical growth in the anthropogenic emissions of NO_x, HC, CO and CH_4 are uncertain. Projections into the future are of course based on speculation. To assess the impact of possible emission changes over a time

period of 30 years (1965–1995) on the concentration of ozone, hydroxyl, CH_4, NO_x and CO in the troposphere, the scenarios shown in Table 3 were set up.

Some results of the trend calculations are summarized in Table 4 and in Figs. 4–8. The concentration of CO increased much less than the direct emissions, indicating that the indirect production from methane and other hydrocarbons, which did not go up, is significant. The increase in CO is seen to reduce OH slightly, as is expected since the reaction

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2$$

is a major loss reaction for OH and thus is important for the HO_2/OH ratio.

Increasing NO_x-emissions is seen to give rise to a significant increase in both O_3 and OH. An important reaction for both O_3 and OH is

$$NO + HO_2 \rightarrow NO_2 + OH,$$

where NO_2 is broken up through photolysis to produce O_3.

In the global troposphere away from pollution sources, NO_x is believed to be a limiting factor in the production of ozone and constrain the hydroxyl concentration (Isaksen et al., 1985). The situation in polluted boundary layer air may be quite different. A decrease in the emission of NO_x may here enhance the production of photochemical oxidants (Hov et al., 1985).

Changes in the concentration of CH_4 have a pronounced effect on O_3 and OH throughout the troposphere. Increasing the CH_4-emissions by 1.5% per year gave rise to an average increase in

Table 3. *Emission scenarios for CO, CH_4, NO_x and NMHC to investigate the impact on O_3, OH, CO, NO and CH_4 over a 30-year period; 1980 is the base year, and calculations are carried out for the 1965–1995 period. All emission changes are in percent per year of the fraction which comes directly from anthropogenic emissions*

Scenario no.	Annual change in emission (%)			
	CO	NO_x	CH_4	NMHC
1	3	0	0	0
2	0	3	0	0
3	0	0	1.5*	0
4	3	3	0.5	3
5	3	−3	0.5	3

* In this case, the annual change in concentration is specified to be 1.5% for CH_4, and the calculation is carried out for the 60 years' period 1950–2010.

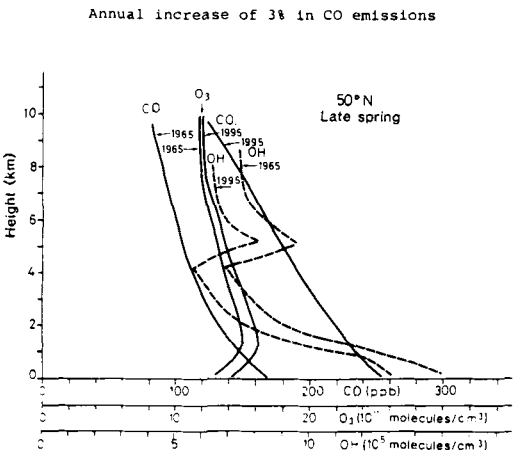

Fig. 4. The distribution of the concentration of O_3, CO and OH with height at 50°N, late spring (end of May) for 1965 and 1995 in a model calculation with an annual increase in CO-emissions of 3%.

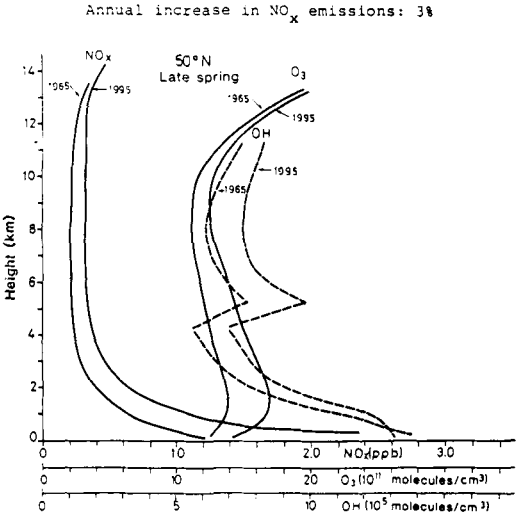

Fig. 5. Same as Fig. 4 for NO_x, O_3 and OH with the NO_x-emissions increasing by 3% per year.

Table 4. *Results of trend calculations where the global emissions of CO, NMHC and NO_x and the concentration of CH_4 changed as specified for the scenarios in Table 3. The calculation was carried out for the 30-year period 1965–1995, with 1980 as the base year. All numbers are given as change per year for the 1965–1995 period in per cent of the concentration calculated at the start of the period for the height and latitude indicated*

Scenario		1		2		3	4					5				
Latitude	Height (km)	CO	O_3	O_3	NO_x	O_3*	O_3	CO	OH	NO_x	CH_4	O_3	CO	OH	CH_4	NO_x
50°N	1.25	1.95	0.27	0.67	2.05	0.29	1.39	2.50	0.17	2.86	0.48	−0.28	2.47	−1.13	1.30	−1.40
	4.25	1.67	0.18	0.63	1.57	0.51	1.18	2.36	0.11	2.70	0.40	−0.42	2.27	−1.51	1.26	−0.99
30°N	1.25	1.66	0.25	0.64	1.31	0.20	1.22	2.17	0.19	2.39	0.47	−0.39	2.33	−1.33	1.28	−0.53
	4.25	1.20	0.08	0.35	1.15	0.38	0.94	1.97	0.06	1.99	0.38	−0.26	1.83	−0.89	1.22	−1.00
30°S	1.25	0.72	0.10	0.41	0.93	0.63	0.62	1.54	0.31		0.25	−0.43	1.07	−0.98	1.18	−1.05
	4.25	0.36	0.03	0.15	0.20	0.79	0.48	1.39	0.17		0.24	−0.14	0.80	−0.57	1.17	−1.23

* Increase in O_3 in % per year for the period 1950–2010.

Change in the hemispheric average OH-concentration for the summer, in % per year for the 1965–1995 period

Scenario	1	2	3*	4	5
northern hemisphere	−0.29	0.29	0.29	≈ −0.05	−0.67
southern hemisphere	−0.11	0.28	0.34	0.06	−0.72

* Average for the 1950–2010 period.

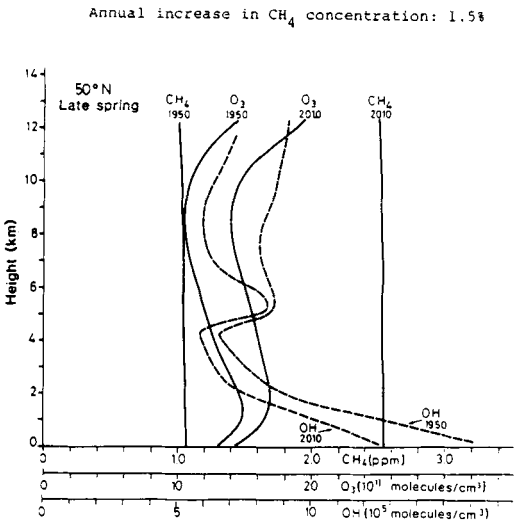

Fig. 6. Same as Fig. 4 for CH_4, O_3 and OH in a model calculation where the annual increase in the CH_4-concentration was 1.5% for the time period 1950–2010.

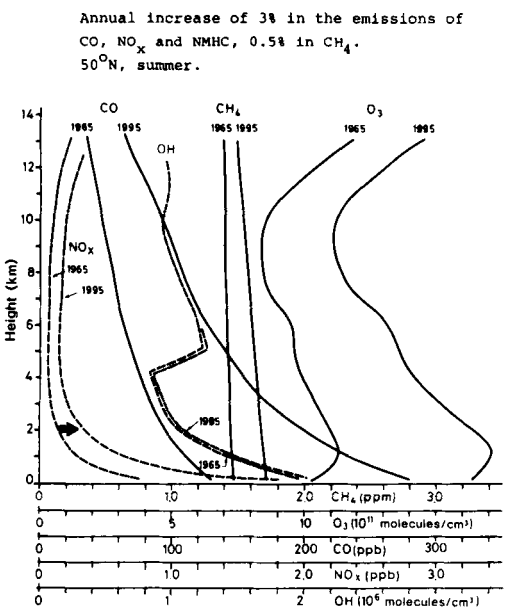

Fig. 7. Same as Fig. 4 for CO, CH_4, O_3, NO_x and OH where the annual emission of CO, NO_x and NMHC went up 3% and CH_4 0·5% for the period 1965–1995. The arrows indicate the direction of change with time.

O_3 of 0.45% per year, while the hydroxyl radical concentration dropped by about 0·4% annually. Future changes in tropospheric methane will have a strong bearing on tropospheric ozone.

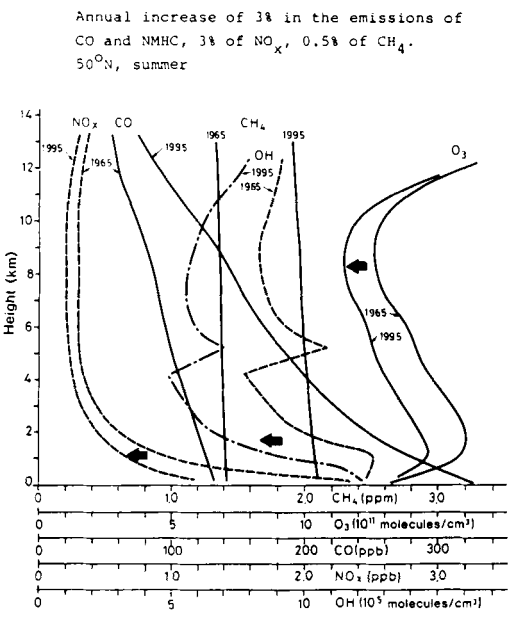

Fig. 8. Same as Fig. 7 with changes in annual emissions of CO, NMHC, NO_x and CH_4 of 3%, 3%, −3% and 0·5%, respectively. The arrows indicate the direction of change with time.

The vertical profile of OH is structured between 2 and 6 km height, dependent on latitude, due to the effect of cloud cover on photolysis rates.

In the fourth scenario, the emissions of CO, NO_x and HC all went up by 3% per year, while methane went up by 0.5% per year. It can be seen from Table 4 and Fig. 7 that the concentration of the hydroxyl radical hardly changed during the period 1965–1995, although there were significant annual growths for species like NO_x and CO due to the increase in emissions. This shows that the positive effect on the hydroxyl radical concentration from the increase of the NO_x-emissions, was counterbalanced by the decline in OH due to higher concentrations of CO and CH_4. In scenario 5, the importance of future NO_x-emission changes for the concentration of hydroxyl was demonstrated. A decline in the emissions of NO_x was introduced (Table 4 and Fig. 8), with a marked decline in the OH-concentration with time as a result, and an increase in the methane concentration which was much larger than the emission increase (a factor

2–3 difference). The concentration of CO increased more slowly than the emissions, indicating that the indirect sources from the oxidation of anthropogenic and biogenic hydrocarbons have been much reduced. The effect on ozone is striking, as its concentration is seen to drop. One may speculate that global emissions were represented by scenario 4 until about 1978–1980, with a significant growth in tropospheric ozone (~1% per year), while CH_4 did not go up as fast as the direct emissions. After 1978–1980, a scenario like No. 5 may be more realistic, which should imply larger than proportional increase in CH_4 compared to the change in emission, while there is a decline in tropospheric O_3. It seems difficult to accommodate increases both in the tropospheric burden of ozone and of methane at the same time within the frame of scenarios 1–5 and a 2-dimensional global model calculation.

4.3. *Emission changes of NO_x, CO and CH_4 and the height distribution of tropospheric ozone*

From Figs. 4–8 it is quite obvious that emission changes of CO and NO_x mainly affected ozone in the lower troposphere, while the change in the methane concentration had an impact throughout the troposphere (Fig. 6), and most marked in the upper troposphere where the climatic consequences are greatest. Methane has an average tropospheric lifetime of about 7 years, leaving sufficient time for the gas to mix well in the troposphere, while CO and in particular NO_x, are more short lived.

In the northern hemisphere summer, the production of ozone is much higher in the atmospheric boundary layer in the latitude band with the highest anthropogenic emissions (40–50°N), than in the free troposphere. If a more stable atmosphere is introduced in the model by reducing all diffusion coefficients by $\frac{2}{3}$, the calculations showed a significant drop in the concentration of ozone throughout the free troposphere. Less ozone and precursors were transported out of the boundary layer, at the same time as the increased accumulation of NO_x and NMHC in the boundary layer did not enhance the ozone concentration at 50°N (Fig. 9). The flux of precursors out of the boundary layer was reduced, at the same time as the downward flux of ozone from the free troposphere was reduced. Thus, the calculated ozone distribution in the free troposphere is quite dependent on the parameterization of vertical exchange between the atmospheric boundary layer and the free troposphere.

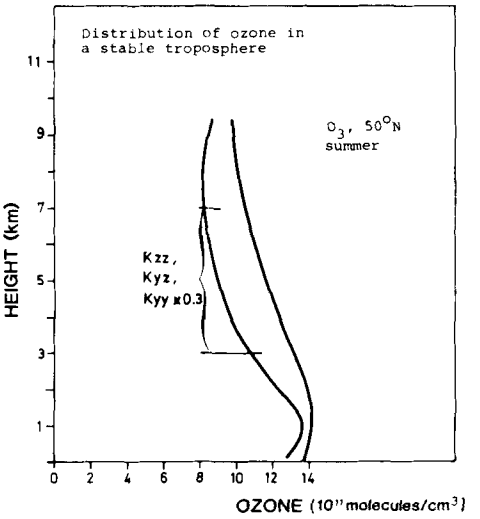

Fig. 9. The calculated influence on O_3 of reducing K_{zz}, K_{yy} and K_{yz} by about 70% in the height interval 3–7 km at 50°N, summer (July).

5. Acknowledgement

This work was partly funded by The Royal Norwegian Research Council for Science and Technology through a research contract with ØH (No. FK03.15772).

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