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global warming
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SUMMARY

Source gases that affect the radiative balance of the Earth/atmosphere system and thereby climate, may be divided into three groups. First, we have the gases that have a *direct* effect on climate due to their radiative properties. Second, there are emissions of gases which have no or only a negligible radiative effect on climate, but which *indirectly* affect climate through impacting on chemical and physical processes in the atmosphere. Greenhouse gases (GHGs) and compounds interacting with solar radiation may thus be affected. Third, we have the source gases that possess the ability of affecting climate both directly and indirectly.

If an indirect effect increases the radiative forcing of climate, it is termed *positive*. On the other hand, if an indirect effect reduces this forcing, it is termed *negative*.

Methane (CH_4) and tropospheric and stratospheric ozone (O_3) are important radiatively active gases that will be affected by *indirect* effects through atmospheric chemistry. *Tropospheric ozone* is affected by emissions of nitrogen oxides (NO_x), carbon monoxide (CO), CH_4 and non-methane hydrocarbons (NMHC). Emissions of these gases also affect the atmospheric concentrations of *methane* through effects on the levels of the hydroxyl radical, OH , which is the main sink for CH_4 . Emissions of CH_4 therefore reduce the strength of its own sink, and this mechanism constitutes a feedback between concentration and loss of this gas. In other words, the relative increase in the *concentration* of methane is larger than the relative increase in *emissions*. In addition, the concentration of the greenhouse gas stratospheric water vapour increases in response to increased emissions of CH_4 . The levels of *stratospheric ozone* are affected by emissions of nitrous oxide (N_2O) and CH_4 , chlorine from chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), carbon tetrachloride (CCl_4), methyl chloride (CH_3Cl), methyl chloroform (CH_3CCl_3) as well as bromine from halons and methyl bromide (CH_3Br). Changes in stratospheric ozone will affect the radiative balance of the Earth/atmosphere system by changes in the fluxes of ultraviolet (UV) and infrared (IR) radiation. Since reductions in stratospheric ozone will increase the UV radiation into the troposphere, the levels of ozone and methane

in this part of the atmosphere will be affected. Emissions of SO_2 increase concentrations of sulphate aerosols in the atmosphere. These aerosols reflect solar radiation, and may also affect the radiation budget through changes in cloud optical properties and cloud chemistry.

There are large variations between the climatic effects of the different GHGs. In addition, the emissions of the gases vary considerably. The Global Warming Potential (GWP) concept was therefore introduced as a tool for policymakers to compare the different GHGs with respect to their warming effects, and for transforming the emissions to a common unit. In calculations of GWPs, emission of carbon dioxide (CO_2) is used as reference. There are, however, important limitations to the use of GWPs. They should only be used as indicators of the relative potentials of the gases to change climate and for a first order ranking of the importance of emissions. There are also significant uncertainties related to the estimated GWP-values, and these uncertainties vary between the different source gases.

In the GWP values published by the Intergovernmental Panel on Climate Change (IPCC) in 1992, only the direct effects on climate are included and no chemical interactions were quantified. The indirect effects were, however, considered in qualitative terms.

In this report the effects of emissions of CH_4 , NO_x and CO on the atmospheric concentrations of the greenhouse gases CH_4 and tropospheric O_3 are quantified and integrated into the GWP values for these source gases. For emissions of CH_4 , the effect on stratospheric water vapour is also included in the GWP values. No GWP calculations are done for NMHC, but the potential of these gases to affect the radiative balance is assessed by comparing them to emissions of CO . In addition, recent estimates of GWPs for CF_4 and C_2F_6 and SF_6 are given and discussed briefly.

Emissions of CH_4 increase the lifetime of CH_4 in the atmosphere (a positive feedback) as well as the levels of tropospheric O_3 and stratospheric water vapour. All these effects are positive, and our estimate shows that inclusion of these indirect effects

approximately doubles the GWPs for emissions of methane. The effects of **NOx emissions** on tropospheric ozone and methane are of opposite signs. NOx emissions increase the tropospheric levels of O₃ (a positive indirect effect). However, these emissions also increase the levels of OH, thereby reducing the levels of CH₄ (a negative indirect effect). For emissions of NOx from *airplanes*, the positive effect is significantly larger than the negative, and relatively high GWPs for NOx from airplanes are estimated. On the other hand, for NOx emitted from *surface sources*, these two indirect effects are of similar magnitude and uncertainty is still connected to the sign of the net effect on climate. These results should be considered preliminary given the uncertainties connected to the estimated effects of NOx emissions on the concentrations of O₃ and CH₄. **Emissions of CO** increase the levels of tropospheric O₃, and, through lowered levels of OH, they increase the levels of CH₄. Thus, emissions of CO have positive indirect effects on climate. **Emissions of NMHC** also have positive effects on climate since they increase tropospheric O₃ and CH₄.

The table below shows the GWPs for some of the gases considered in the report for three selected time horizons. These values are new or different from those given by IPCC (1992).

Gas	Time horizon		
	20 years	100 years	500 years
CO ₂	1	1	1
CH ₄ (direct and indirect)	71	23	8
CO	7	2	1
NOx from airplanes (NO ₂ basis)	253	68	25
CF ₄	3700	5100	8800
C ₂ F ₆	7300	10000	17300
SF ₆	14100	19000	31000

The estimated GWPs represent what we are able to quantify with the present model tools about indirect climatic effects of emissions through atmospheric chemistry. Extensive research is going on to quantify the importance of the indirect effects. It is therefore reasonable to expect that the GWPs will need updating due to new scientific knowledge. In addition, the GWP values will also need updating as the reference atmosphere is changing.

1. Introduction

Observations show that the composition of the atmosphere is changing. Several of the gases that are increasing in concentration are essential for the chemical transformation processes in the atmosphere as well as for physical properties of fundamental importance. Some of the gases are radiatively active in the spectral region where the Earth is emitting long-wave radiation to space (so-called greenhouse gases), or in the solar wavelength region, and changes in these gases may affect the radiative balance and thereby the climate of the Earth. In addition, some gases are able to affect the concentrations of the radiatively active gases through chemical interactions in the atmosphere. Such gases may therefore affect climate indirectly.

The *source gases* that affect the radiative balance of the Earth/atmosphere and thereby climate, may thus be divided into three groups. Firstly, we have the GHGs that have a *direct* effect on climate due to their radiative properties. Source gases as CO₂, CF₄ and C₂F₆ belong to this group. Secondly, there are emissions of gases which have no or a negligible direct greenhouse effect, but which are *indirectly* affecting climate through impacting on chemical and physical processes in the atmosphere. Greenhouse gases (GHGs) and compounds interacting with solar radiation may thus be affected. The source gases NO_x, CO and NMHC (non-methane hydrocarbons) are examples of such gases. Thirdly, we have the source gases that possess the ability of affecting climate both directly and indirectly. Methane (CH₄), chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) belong to this third group¹. The GHGs that will be affected by the indirect GHGs through atmospheric chemistry are mainly ozone (O₃) and CH₄, but also HCFCs and hydrofluorocarbons (HFCs). If an indirect effect increases the radiative forcing of climate, it is termed *positive*. On the other hand, if an indirect effect reduce this forcing, it is termed *negative*.

The potential of the various source gases for perturbing climate varies considerably,

¹ CO₂ can not affect the levels of other GHGs through chemical reactions in the atmosphere. It may however affect GHGs and gases interacting with solar radiation through effects on the thermal structure of the atmosphere. Such considerations are beyond the scope of this report.

and the concept Global Warming Potential (GWP) has been introduced as a tool for comparison of emissions. GWP estimates that include some important *indirect* effects of NO_x emissions from aircraft and ground sources, and CH₄ and CO emissions are given in this report. In addition, recent estimates of GWPs for CF₄, C₂F₆ and SF₆ from other studies are given and discussed.

The GWP estimates for NO_x, CH₄ and CO in this report are based on the results from a series of model studies of atmospheric chemistry interactions that has been published by Isaksen et al. (1992a) in WMO (1992), by Berntsen et al. (1992) and by Fuglestad et al. (1993).

GWPs for other gases with significant indirect effects (e.g. CFC, HCFC, and SO₂) are not estimated in this report. CFC and HCFC have significant indirect effects through their impact on stratospheric ozone. Emissions of SO₂ may affect climate through the formation of sulphate aerosols. These aerosols reflect solar radiation, and may also affect the radiation budget through changes in cloud optical properties, as well as cloud chemistry.

A compilation of GWPs for gases not considered in detail in this report are given in the last chapter. This is based on WMO (1992) and IPCC (1992).

It is important to be aware of the limitations to the use of GWPs. They should only be used as indicators of the potential of the ability of the gases to perturb climate and for a first ranking of emissions. GWP estimates are subject to extensive research activity and special focus is given to the role of the indirect effects. In the IPCC process, these effects are now quantified and taken into account for emissions of CH₄. For NO_x, CO and NMHC it is recognized that such effects may be important, but GWP estimates are at this stage left out until more results are available.

2. Direct effects of radiatively active gases on climate

Gases that absorb and re-emit terrestrial (longwave) radiation have the potential to affect the radiative balance of the Earth/atmosphere and thereby climate. In the atmosphere there are several gases that absorb IR in the spectral region where the Earth and the atmosphere emit most of the radiation to space ("the atmospheric window"). The most important gases are H₂O, CO₂, CH₄ and O₃. Clouds also absorb and re-emit IR. These constituents are the most important for the greenhouse effect. Increased levels of CO₂, CH₄ and tropospheric ozone, as well as new gases as halocarbons, have increased the greenhouse effect. While H₂O is still the dominating gas for the total greenhouse effect, the *enhancement* of the greenhouse effect due to other gases is found to be significant.

Three important parameters in estimates of the direct climate impact of GHGs are: 1) the spectral region in which the gas absorbs and emits radiation, 2) the strength of the absorption bands of the gas, and 3) the atmospheric concentration of the gas. The latter is not only a function of the emissions, but also of the lifetime of the gas. Gases with long lifetimes accumulate in the atmosphere. The location and the strengths of the bands, and especially the lifetime, are important for the the GWP values.

The radiative forcing that follows from a change in the concentration of a constituent is defined by the change in net radiative flux at the tropopause when all factors other than the concentration of the constituent under consideration are kept constant. Thus, the radiative forcing is the net change in radiative flux before the climate system has responded, which will lead to a new radiative balance of the Earth/climate system. The radiative forcing is interpreted as a gain or loss for the surface-troposphere system as one coupled system (IPCC, 1992). It has been found that the change in global average surface temperature can be related to the net radiative flux change at the tropopause (WMO, 1986). Therefore, the radiative forcing has been adopted as a convenient basis for estimating the potential effects on climate from changes in various constituents.

Source gases that enhance the greenhouse effect only through direct radiative effects are CO_2 , CF_4 , C_2F_6 , SF_6 and N_2O .

In addition, gases may have a direct impact on climate by affecting the fluxes of solar radiation (short wave). This mechanism is different from the greenhouse mechanism, and the most important gas in this context is ozone. Thus, ozone may affect climate directly through interaction with both long wave and short wave radiation.

Ozone and methane (and also HCF and HCFC) are affected by chemistry. Thus, gases affecting these species may therefore indirectly affect climate (see next chapter).

3. Indirect effects of source gases on climate through atmospheric chemistry interactions

3.1 Tropospheric interactions

Although tropospheric O₃ only makes up about 10% of all ozone in the atmosphere, it is essential for the oxidizing capacity of the troposphere, since photolysis of O₃ is the primary source of OH radicals as well as being an oxidizing species itself. Through the formation of OH ozone determines the cleansing efficiency of the troposphere. Therefore ozone ultimately controls the chemical composition of the atmosphere. In addition, ozone is an important gas with respect to the radiative balance of the Earth/atmosphere system due to its interactions with solar (short wave) and terrestrial (long wave) radiation (Wang et al. 1980; Lacis et al., 1990; WMO, 1992, Wang et al., 1993). Although tropospheric ozone makes up only a small fraction of the total ozone amount (~10%), it exerts a significant greenhouse effect (positive forcing). The sensitivity reaches a maximum for ozone changes in the upper troposphere (WMO, 1992).

The sources of tropospheric ozone are *in situ* chemical production and transport from the stratosphere. In the *stratosphere*, ozone is generated by photodissociation of O₂, followed by the combination of ground state oxygen atoms with O₂ :



The chemical production of ozone in the *troposphere* is driven by UV-radiation, NO_x, 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). HO₂ and peroxy radicals (RO₂), produced in the oxidation of CO and hydrocarbons, react with NO to give NO₂ (R3 and R4), which is then photolyzed (R5):



or

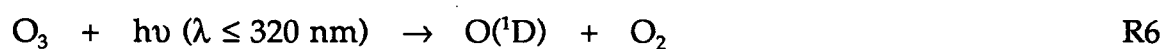


followed by



$\text{O}(^3\text{P})$ 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):



Only a small fraction of the $\text{O}(^1\text{D})$ produced through R6 goes through R7, but when the levels of water vapour are high, this mechanism represents a loss of ozone.

R7 represents a loss of ozone because in the absence of water vapour, $\text{O}(^1\text{D})$ will be energetically stabilized by an air molecule to $\text{O}(^3\text{P})$, which will react with molecular oxygen to give ozone again (R2).

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

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.

Ozone also reacts with NO₂ to give nitrate radicals, NO₃, which are stable only in absence of light.



NO₃, or the species N₂O₅ formed through the reaction



may be scavenged efficiently by deliquescent aerosols. This mechanism may be an important loss for NO_x during winter time and may thus lead to reduced O₃ production (Isaksen, 1988; Isaksen et al., 1989).

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

Most of the OH produced through R6 and R7 reacts with CO (~ 70%) :



In addition, a significant fraction of OH reacts with CH₄:



In both cases, HO₂ is formed through further reactions. OH is reformed when HO₂ reacts with NO or O₃, via R3 or R8, respectively.

The above set of reactions (mainly R3, R8 and R11) establishes a rapid equilibrium between OH and HO₂ in the troposphere. Changes in OH will therefore immediately lead to changes in HO₂. The ratio between OH and HO₂ may, however, change as a

result of changes in O₃, CO, CH₄, NO and/or NO₂. The strong coupling between OH and HO₂ is important since a major part of the loss of odd hydrogen (OH and HO₂) in the free troposphere proceeds via reactions involving both OH and HO₂:



or through the sequence



or



The loss rate of odd hydrogen (and thereby the loss of OH) is thus approximately quadratic in HO_x which is of importance for the responses in OH to perturbations.

Several factors related to change in atmospheric composition may affect the levels of OH. Tropospheric water vapour densities may have increased as a result of temperature increases in the troposphere. This may affect OH via the reaction between O(¹D) and H₂O (R7). The production of OH may also be affected by changes in the UV-flux through R6 and other photolytic reactions.

Several studies have examined the effects of source gases on OH. Increased emissions of NO_x tend to decrease the tropospheric levels of OH mainly due to a redistribution between OH and HO₂ (R3) and increased O₃ production. Increased emissions of CO and CH₄, on the other hand, generally lead to reduced levels of OH (Isaksen and Hov, 1987; Thompson et al., 1989; Isaksen et al., 1992a; Fuglestad et al., 1993). Table 1 gives the signs of the responses in O₃, OH, CH₄ and some other GHGs to increased emissions of some important source gases.

Table 1. Impact of increased emissions on tropospheric averages of gases affecting climate. (+ gives increases, - gives decreases).

Increased emissions of ↓	O ₃	OH	Chemical lifetime of CH ₄ , HCFC and HFC
CH ₄	+	-	+
NO _x	+	+	-
CO	+	-	+
NMHC	+	-	+

Since reaction with OH is the main sink for methane, this coupling results in a positive feedback between CH₄ and OH. Increased emissions of CH₄ increase the atmospheric levels which will decrease the levels of OH. This will increase the chemical lifetime of CH₄, thereby further increasing the atmospheric levels of CH₄. For a 10% increase in emission, the relative increase in concentrations has been estimated to be ~35% larger than the relative increase in emissions of methane.

Figure 1 shows the relation between increase in emissions of CH₄ and increase in tropospheric mean concentration. (C₁ and E₁ are reference concentration and emission, respectively, and C and E are the perturbed levels.) The magnitude of the feedback increases with increasing perturbation in emission as methane becomes more important for the loss of OH at higher methane levels.

Although more than 90% of the emitted methane is removed by tropospheric OH and uptake in soils, the remaining fraction that is transported to the stratosphere may affect climate. The oxidation of stratospheric methane contributes by approximately 50% to the supply of water vapour to the stratosphere. Since water vapour is an important GHG in this part of the atmosphere, and to a large extent is controlled by the flux of methane from the troposphere, this mechanism constitutes an indirect effect of methane that should be taken into consideration.

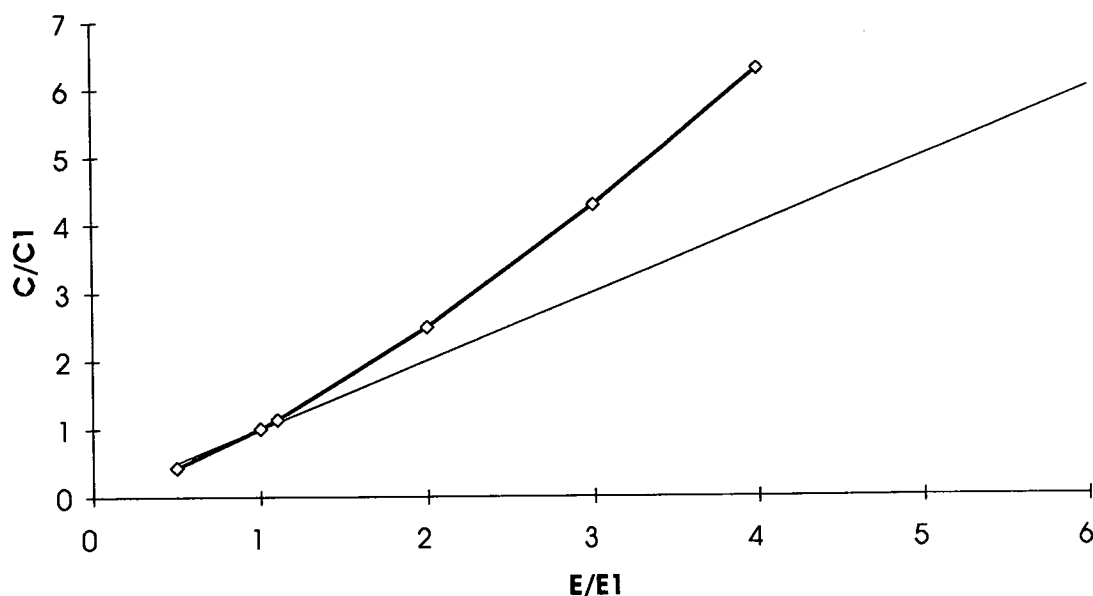


Figure 1. Calculated changes in concentrations of methane as a function of changes in emissions. The straight line represents no feedback between OH and CH₄.

Since CO₂ is the ultimate product when hydrocarbons and CO are oxidated, there is an additional indirect effect of emissions of NMHC, CH₄ and CO on climate from these gases if these source gases are of fossil origin.

3.2 Climatic effects of changes in stratospheric ozone

Changes in ozone affects both solar and longwave radiation. Reduction in *stratospheric* ozone leads to the following radiative effects (IPCC, 1992 and references therein):

1. Less solar radiation is absorbed in the stratosphere, which leads to an increase in the flux of solar radiation into the troposphere.

2. Less longwave radiation is emitted from the stratosphere into the troposphere.
3. Reduced absorption of solar radiation and longwave terrestrial radiation will decrease the stratospheric temperatures. Since the emission of longwave radiation is a strong function of temperature, the flux of longwave radiation downward into the troposphere will be reduced.

The net effect of these mechanisms is highly dependent on the altitude of the reductions in ozone. Model calculations of the changes in radiative forcing from the observed ozone changes give a decrease in radiative forcing which have large seasonal and latitudinal variations. Around the Equator, small increases in forcing is also calculated (IPCC, 1992, and references therein). Since it is highly probable that the observed decrease in stratospheric ozone may be explained by chlorine and bromine compounds, the estimated reductions in radiative forcing constitute an indirect effect of halocarbons on climate.

The flux of methane from the troposphere to the stratosphere has effects on stratospheric ozone. In the upper stratosphere methane leads to ozone destruction through the HOx catalytic cycle. In the middle stratosphere, however, methane gives increased levels of ozone. The latter is due to conversion of active chlorine to the inactive form HCl in the reaction between Cl and CH₄. In the lower stratosphere the degradation of methane also gives ozone production through the same reactions as those that produce ozone in the troposphere. Model calculations by Isaksen and Stordal (1986) have shown that ozone destructions take place for altitudes higher than approximately 40 km, while the total ozone columns increase by up to 6% at higher latitudes in response a doubling of the methane emissions. However, most of this increase in ozone takes place in the troposphere.

Since stratospheric ozone determines the UV flux which penetrate into the troposphere, it also controls the photodissociation rates for important chemical species in the troposphere and thereby also the oxidation processes. Changes in stratospheric ozone may therefore lead to changes in the tropospheric levels of

gases that are of importance for climate. In a model study by Fuglestad et al. (1994), the sensitivity of the responses in tropospheric chemistry to changes in total ozone column densities is studied. It is shown that reductions in stratospheric ozone lead to moderate reductions in the levels of tropospheric ozone in most areas and significant increases in OH at middle and higher latitudes in the spring. Through the changes in OH the levels of methane are reduced and the results indicate that increased UV fluxes due to reduced ozone columns may have contributed by approximately 1/3 to the observed reduction in the growth rate of methane over the period 1980-1990. Changes in tropospheric GHGs from increased UV radiation demonstrate one of the several linkages between the troposphere and the stratosphere, and another indirect effect from the CFCs on climate.

The thermal structure of the stratosphere is sensitive to changes in O₃ and CO₂. Changes in these gases may therefore affect stratospheric chemistry through temperature changes which may influence ice particle formation (Polar Stratospheric Clouds, PSCs) and chemical reaction rates. Through the latter mechanism, increased levels of CO₂ in the stratosphere leads to reduced ozone loss (Isaksen et al., 1980.) In addition, an increased flux of methane from the troposphere may, through the following enhancement in water vapour, lead to increased ice particle formation. Chemical reactions taking place between the gas phase and the ice particles are thought to be of great importance for the control of stratospheric ozone.

Due to the highly complex nature of atmospheric chemistry, physics and dynamics, there are several other possible indirect effects of trace gas emissions that have not been considered here that could be significant. The couplings and relationships that have been discussed here, however, are at present considered the most important.

4. The concept Global Warming Potential (GWP)

The Global Warming Potential index was introduced as a tool for policymakers to compare the potential of the various well-mixed source gases to affect climate. It is a *relative* measure since it expresses the climate effect compared to the effect of a reference gas. It is derived from the globally-averaged net radiative fluxes at the tropopause. Thus, it is a global measure that describes the effects on the whole surface-troposphere system. It expresses the cumulative radiative effect of the gases over a chosen time horizon. In IPCC (1990) this was defined as the time integrated commitment to climate forcing from the instantaneous release of 1 kg of a trace gas expressed relative to that from 1 kg of CO₂:

$$GWP = \frac{\int_0^n a_i \cdot c_i dt}{\int_0^n a_{CO_2} \cdot c_{CO_2} dt} \quad (1)$$

where a_i is the instantaneous radiative forcing due to a unit increase in the concentration of the GHG i , c_i is the concentration at time t , and n is the time horizon. The corresponding values for CO₂ are given in the denominator.

In this report we take into account some *indirect* effects that arise when source gases and secondary gases take part in the chemical reactions in the troposphere. Thus, some important *chemical* feedbacks are taken into account. Other indirect effects and feedbacks, such as changes in emissions, atmospheric chemistry, physics or dynamics in response to climate change, are not considered.

There are serious limitations to the use of GWPs which are discussed in detail in IPCC (1990), IPCC (1992) and WMO (1992). In short, some of these are:

- i) There are uncertainties connected to the modelling of radiative transfer in the atmosphere.
- ii) GWP is a measure of the global effect and is most appropriate for well-mixed gases.
- iii) GWP considers only the surface-troposphere radiative forcing, and not the *climatic response*. It is not appropriate for predicting regional climate responses.
- iv) The GWPs are sensitive to the applied residence times. For CO₂ there is not one single residence time and a carbon cycle model is used in the calculations of the time integrated forcing from the reference gas CO₂. Uncertainties are connected to this model.
- v) In the calculations of GWP, constant background concentrations at current levels is usually assumed. The radiative calculations depend on the assumed levels, but, so far, any changes in the composition of the atmosphere are not taken into consideration. This is most important for CO₂ (see chapter 11).

5. Estimated GWPs for CF₄ and C₂F₆²

5.1 CF₄ and C₂F₆ as greenhouse gases

The 1992 Scientific Assessment of Climate Change (IPCC, 1992) pointed out the importance of CF₄ and C₂F₆ as greenhouse gases. It was, however, recognized that there are large gaps in our understanding of the trends, distribution, sources, sinks, and the climate impact of these compounds. CF₄ and C₂F₆ are present in the atmosphere at ppt levels, with CF₄ the more abundant. Higher CF compounds are either present in very small quantities or are nonexistent in the atmosphere. For instance, recent analysis indicates that C₃F₈ probably is present in the atmosphere but in very small quantities.

The observations indicate a positive trend in the earlier CF₄ measurements (prior to 1985). Between 1985 and 1991 (the time of 1992 IPCC assessment) there were almost no studies of the atmospheric distribution of the two compounds and of their possible roles as climate gases.

Since 1990 it has been recognized that, although the overall global contribution to global warming from CF₄ and C₂F₆ is limited, the large emissions of CF₄ from the aluminum industry could contribute significantly to the global warming from countries which have a large aluminum industry (for instance Norway and Iceland). The significance of the above compounds as climate gases is due to their large GWPs.

A recent assessment of the role of CF₄ and C₂F₆ as greenhouse gases was performed by an international group of scientists (Isaksen et al., 1992b). This included a review of existing data on the distribution, trend, emission and atmospheric lifetime of the two compounds. Scientific studies were also performed of the radiative properties of the two compounds, and estimates of their GWPs were done. Recently, a few

² This chapter is taken from: "Study pertaining to preliminary measures to abate Polyfluorinated Carbons", by I.S.A. Isaksen. Report to the Swedish Environmental Protection Agency, 1994.

scientific articles have been published which deal with the atmospheric properties of CF_4 and C_2F_6 . The following is a summary of the present state of knowledge in the area.

5.2 Measurements of CF_4 and C_2F_6 in the atmosphere

A compilation of the atmospheric concentration of CF_4 made by Penkett et al. (1981) gives a value of 70 ± 7 ppt in 1979 in background air. The concentrations of C_2F_6 were approximately 4 ppt. The ratio of CF_4 to C_2F_6 in background air was estimated to be 0.057. These background observations cover sites in both hemispheres and should be representative for the global distribution. Measurements of the concentrations in aluminum plant plumes by the same authors showed enhanced levels of CF_4 and C_2F_6 , approximately a factor of two in both cases.

5.3 Atmospheric lifetimes

The conclusions of the studies are that there are no known sinks that are effective in breaking up CF_4 or C_2F_6 in the atmosphere, and that all known or likely loss processes that have been considered give lifetimes that are extremely long.

From the studies performed it seems likely to assume that the main destruction process occurs in the mesosphere and above (above approximately 60 km). At these heights the atmospheric densities are several orders of magnitude less than in the troposphere, and lifetimes will be limited by transport of molecules from below. This will result in lifetimes of 10 000 years or more.

5.4 Emissions of CF_4 and C_2F_6

The aluminium industry is believed to be the major contributor to the atmospheric burden, or to the observed increase in CF_4 during the beginning of the 1980s (Khalil and Rasmussen, 1985). Other sources are likely to be small, although the magnitude of their emissions is difficult to assess. Possible sources have been suggested, like electrolytic generation of F_2 , the reduction of UF_4 and UF_6 , the use of fluorospat in steelmaking, the burning of polyfluoroethylene and inadvertent production in fluorocarbon manufacture, as possible anthropogenic sources. Studies of the ratio of the two CF gases in emission plumes from aluminum plants compared to the ratio in atmospheric background air have so far not given any indications of any other significant anthropogenic sources. Studies are, however, underway to obtain a better understanding of the ratio in plumes from smelters in Norway and Canada (Schiff, 1993).

It is a relatively simple matter to calculate the total amount of CF_4 in the atmosphere from its measured atmospheric concentration. At present, approximately 1.6 Mt of CF_4 is in the atmosphere. This can be compared with the cumulative emission calculated from the published annual world-wide production figures and the value of the CF_4 emission per tonne of aluminium production. Based on measurements, one may assume a value of 1 Kg CF_4 emitted per tonne of aluminium, reasonable agreement is reached between these two calculations. However, the large uncertainties of the emission figures do not put any constraints on the existence of other sources.

5.5 Recommended values for the radiative forcing

The recommended values in the study performed by Isaksen et al., 1992b, for the radiative forcing are $0.10 \text{ Wm}^{-2}/\text{ppbv}$ for CF_4 and $0.30 \text{ Wm}^{-2}/\text{ppbv}$ for C_2F_6 . The error due to uncertainties in spectral resolution, the effect of overlapping gases and band strengths are, rather qualitatively, estimated to be about $\pm 20\%$.

These values were recommended in estimates of the global warming potential of the fluorocarbons. Their strength relative to CO₂, using the values for CO₂ in IPCC (1990, table 2.3), are given in table 2 on a per molecule and a per mass basis.

Table 2: Relative strength of CF₄ and C₂F₆ compared to the IPCC values of CO₂ on a per molecule and a per unit mass basis

Gas	Relative strength per molecule	Relative strength per unit mass
CF ₄	5 430	2 710
C ₂ F ₆	16 900	5 360

5.6 Recommended values for GWPs

As there is no single time horizon that is ideal for calculating GWPs, Isaksen et al. (1992b) used the same horizons as chosen by IPCC (1992) in the calculations of GWPs (table 3). These time horizons should cover the main range of interest for climate change.

Table 3: Global Warming Potentials (GWPs) for CF₄ and C₂F₆ (mass basis). Radiative forcing and lifetime (loss rates) for CO₂ are taken from IPCC (1992).

Time horizon (years)	20	100	500
CF ₄	3700	5100	8800
C ₂ F ₆	7300	10000	17300

Wuebbles and Grossman (1993) have estimated GWPs for the same time horizons as given in table 3 and their values agree with the values given in the table within 4%.

5.7 Contribution to global warming

The calculated radiative forcing, combined with the observed increases in atmospheric concentrations, can be used to estimate the global impact on climate by CF_4 and C_2F_6 . The increase in the latter compound is not known, however its atmospheric abundance is small compared to the abundance of CF_4 ; it is expected to have a much smaller climate effect than CF_4 . Although the estimated increase in CF_4 is also connected with uncertainties, the observations indicate an increase of approximately 2% per year in the beginning of the 1980s. If the trend continued throughout the decade, CF_4 mixing ratios could have increased by 15 ppt during the 1980s. If we compare this increase to the increase in CFCl_3 of approximately 100 ppt (WMO, 1992) during the same time period, and take into account the relative band strength of 0.44 (table 2) compared to CFCl_3 , we obtain a contribution to the greenhouse warming from CF_4 that is approximately 6% of the direct contribution from CFCl_3 . Since the direct contribution from CFCl_3 to the total greenhouse warming from man-made sources during the same period is approximately 6%, the contribution to the greenhouse warming from CF_4 and C_2F_6 together is less than 0.5%. However, CF_4 could contribute significantly to the national greenhouse budget in countries where the aluminium production per capita is large (e.g. Norway, Iceland).

6. Estimated GWPs for SF₆³

6.1 Atmospheric concentrations, increases and emissions SF₆

The 1985 ozone assessment (WMO, 1985) reports SF₆ concentrations in the atmosphere of 0.9 ppt in the Northern Hemisphere and 0.8 ppt in the Southern Hemisphere in 1981. More recent observations (Rinsland et al., 1990) give values of approximately 2 pptv. These observations are consistent with an observed rapid growth in the concentration of 6 to 7% per year. Such a trend in the mixing ratio has, for instance, been deduced from the long term series of spectroscopic data obtained at Jungfraujoch in Switzerland (Zander and co-workers, private communication, 1993).

Of a total global emission of polyfluorinated carbons (PFCs) presently at approximately 30 000 tonnes/year, it is estimated that 4.500 tonnes/year (15%) is emitted as SF₆ (Mocella, DuPont Electronics, 1993, private communications). Stordal (1993, private communications), estimates the yearly production in the range of 5000-8000 tonnes (1990), and indicates that emission could be approximately 50% of the production. Two main sources are given; metal industry and electric equipment with relative consumption of 20 to 80.

6.2 Radiative forcing and GWP for SF₆

Several groups have recently in two studies calculated radiative forcing and GWP for SF₆ (Ko et al., 1993; Stordal et al., 1993). A detailed discussion of the studies will not be given in this report, but rather an indication of the values. The relative strength of the radiative forcing for SF₆, is found to be substantially larger than for either of CF₄ and C₂F₆ (table 4).

³ This chapter is taken from: "Study pertaining to preliminary measures to abate Polyfluorinated Carbons", by I.S.A. Isaksen. Report to the Swedish Environmental Protection Agency, 1994.

Table 4: Relative strength of SF₆ compared to the IPCC values of CO₂, on a per molecule and a per unit mass basis (Stordal et al., 1993).

	Relative strength per unit mass	Relative strength per molecule
SF ₆	35 200	10 600

Table 5 gives the calculated GWPs by Stordal et al. (1993) for three different time horizons.

Table 5. Estimated GWPs for SF₆ from Stordal et al. (1993).

Time horizon (years)	20	100	500
SF ₆	14 100	19 000	31 000

6.3 Contribution to global warming

Due to the very long lifetime of SF₆, ~3200 years, (Ravishankara et al., 1993), its impact on climate will, in the same way as for CF₄ and C₂F₆, depend on the time horizon which is considered. Although the atmospheric abundancy of SF₆ is only a few pptv, it is increasing rapidly in the atmosphere, indicating significant sources. Its present contribution to global warming is estimated to be in the order of 0.1%. This fraction will increase in the future due to its rapid increase in atmospheric concentrations, if we assume that high emissions continue. The contribution could be in the order of 0.3% of the total global warming around 2010. Although these numbers are small on a global scale, the contribution in individual countries could be substantially larger.

7. HFCs as greenhouse gases

Hydrofluorocarbons (HFCs) were introduced as substitutes for the ozone depleting substances CFCs and HCFCs. The HFCs do not contain chlorine that may destroy stratospheric ozone. Ravishankara et al. (1994), have shown that any effects on ozone of the CF_3 radicals produced are negligible. Thus, according to the present state of knowledge, there are no indirect effects to take into account in the assessment of their potential climate impacts.

The dominant loss process for HFCs is reaction with tropospheric OH radicals, but photolysis and reaction with $\text{O}(^1\text{D})$ in the stratosphere is also significant. The lifetimes for the HFCs range from 1.8 (HFC-152a) to ~65 years (HFC-143a). The lifetimes are mainly controlled by the concentration of OH in the troposphere. Any changes in OH may therefore affect the GWPs for these gases. For a time horizon of 100 years, the GWPs vary from 150 for HFC-152a to 3800 for HFC-143a (see chapter 12).

Although increasing (e.g. HFC-134b), emissions of HFC are at present negligible, and their concentrations are not large enough to affect the levels of OH or O_3 . If any of the chemical species formed during the degradation of the HFCs have lifetimes larger than the HFC itself, such species may accumulate in the atmosphere. Any radiative, chemical or other environmental properties of the species may then become a problem.

8. Estimated responses in tropospheric O_3 and CH_4 to increased emissions of NO_x , CH_4 , CO and NMHC

A two-dimensional (altitude vs. latitude) photochemical-transport model for the global troposphere with extensive chemistry is applied to study the effect of changed emissions on O_3 , OH and CH_4 . For a description of the model see Isaksen and Hov (1987); Berntsen (1989), and Fuglestvedt et al. (1993). Model tests in which the emissions of the source gases are changed one by one has been performed. The latitudinal distribution of the emissions were kept constant. In each case the model was run for 5 decades to assure that steady state levels were reached. (For a further description of these model studies, see Fuglestvedt et al., 1993).

A doubling of the ground emissions of NO_x gave substantial increases in O_3 at low altitudes over the Northern Hemisphere in August; the increase was as large as 20% between 0° and $10^\circ N$ and 16% between $40^\circ N$ and $70^\circ N$ in the lowest levels. The percentage change in O_3 as a function of latitude and altitude is shown in figure 2.

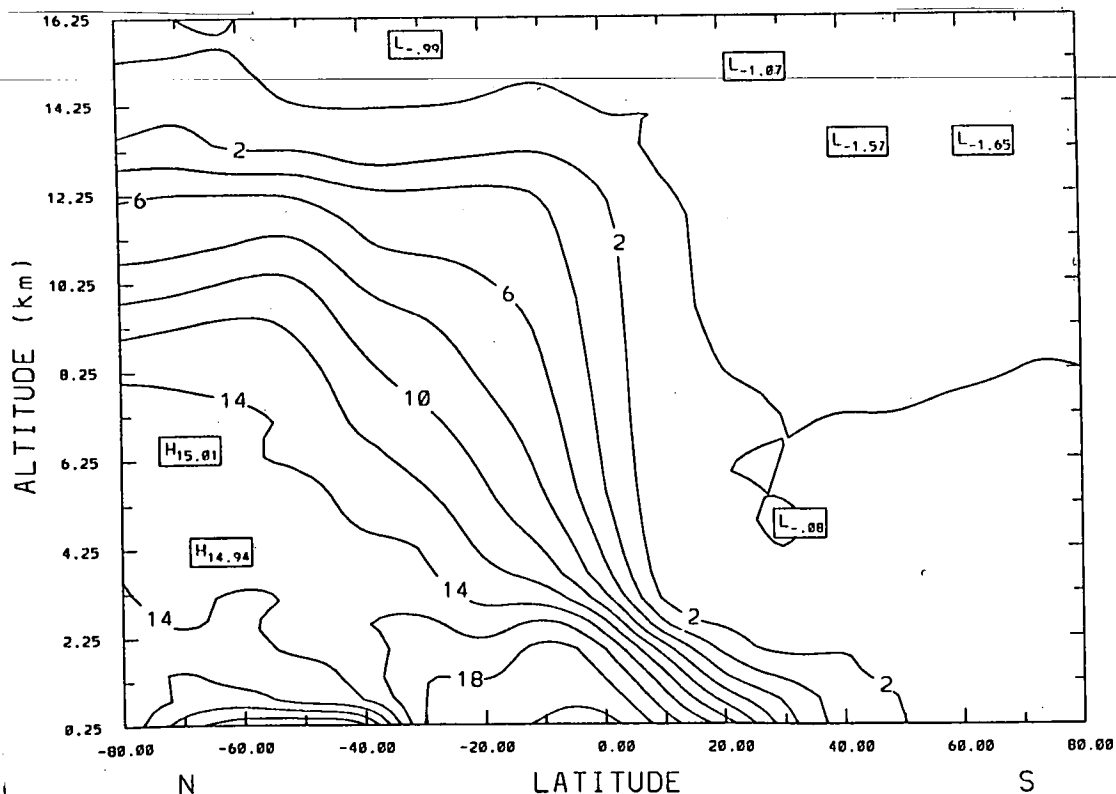


Figure 2. Calculated percentage change in O_3 concentrations in August when the ground emissions of NO_x are doubled.

In February, south of 30°N there was an increase, with the maximum near the equator (~20%), while north of 30°N there were reductions in O₃ of up to 15% in the lowest few kilometers.

The model experiment with a doubling of the methane emissions gave a more uniform effect on tropospheric ozone than a doubling of NO_x. This is due to the longer lifetime of CH₄ (~10 years) than of NO_x (a few days). Increases in methane emissions led to ozone increases everywhere in the model region (fig.3). In August the maximum increase of ozone was 23% at about 2 km above the equator, while in February the maximum was 25-28% in the lowest levels at 40°S.

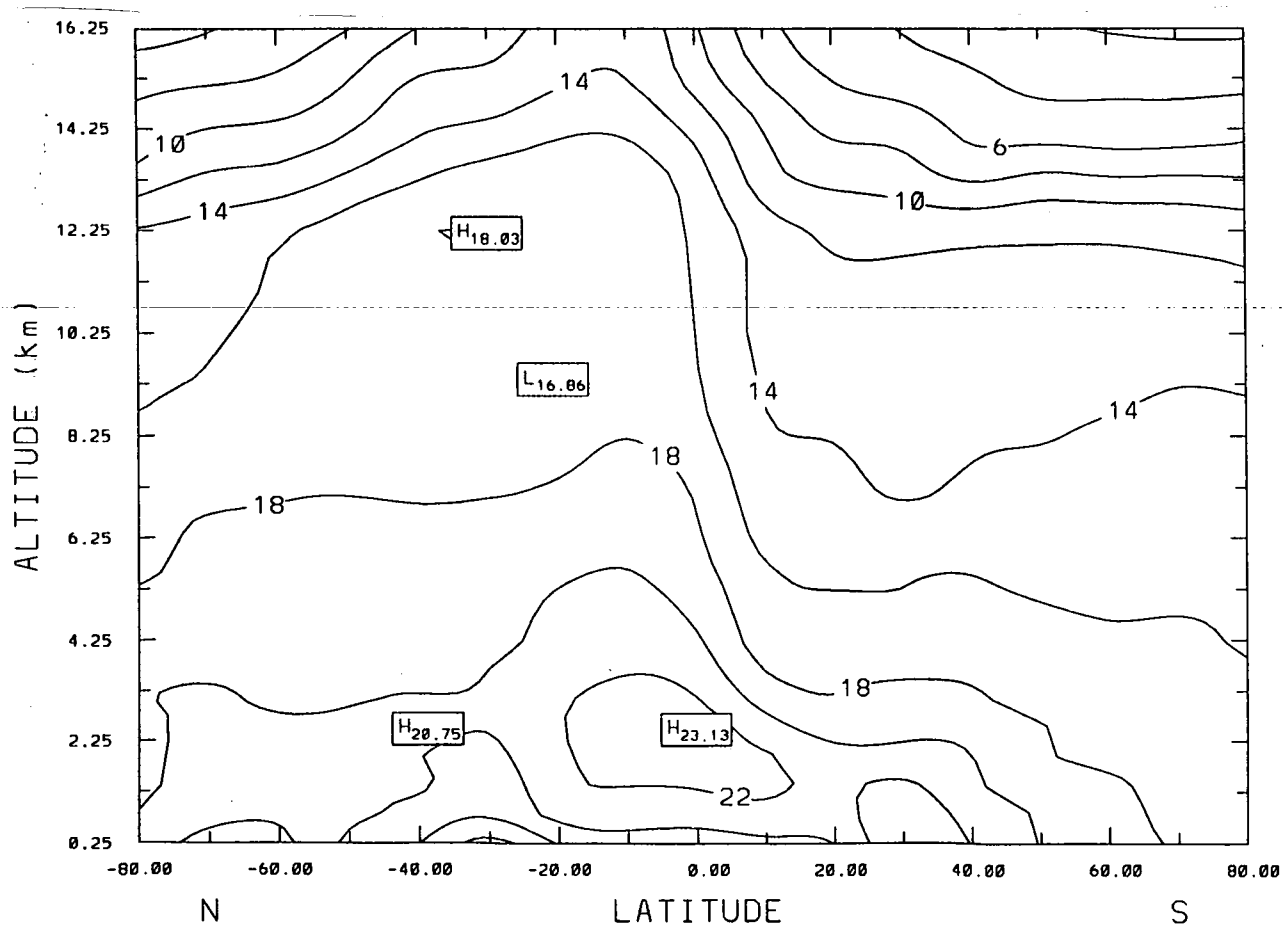


Figure 3. Calculated percentage change in O₃ concentrations in August when the emissions of CH₄ are doubled.

The effect on ozone of a doubling of ground emissions of CO was an increase throughout the entire model domain and was most pronounced in the Northern Hemisphere (8-12%) where the CO (and NO_x) emissions are largest (fig.4). 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 NO_x concentrations are increasing with altitude due to input from the stratosphere (with an additional contribution from aircraft emissions).

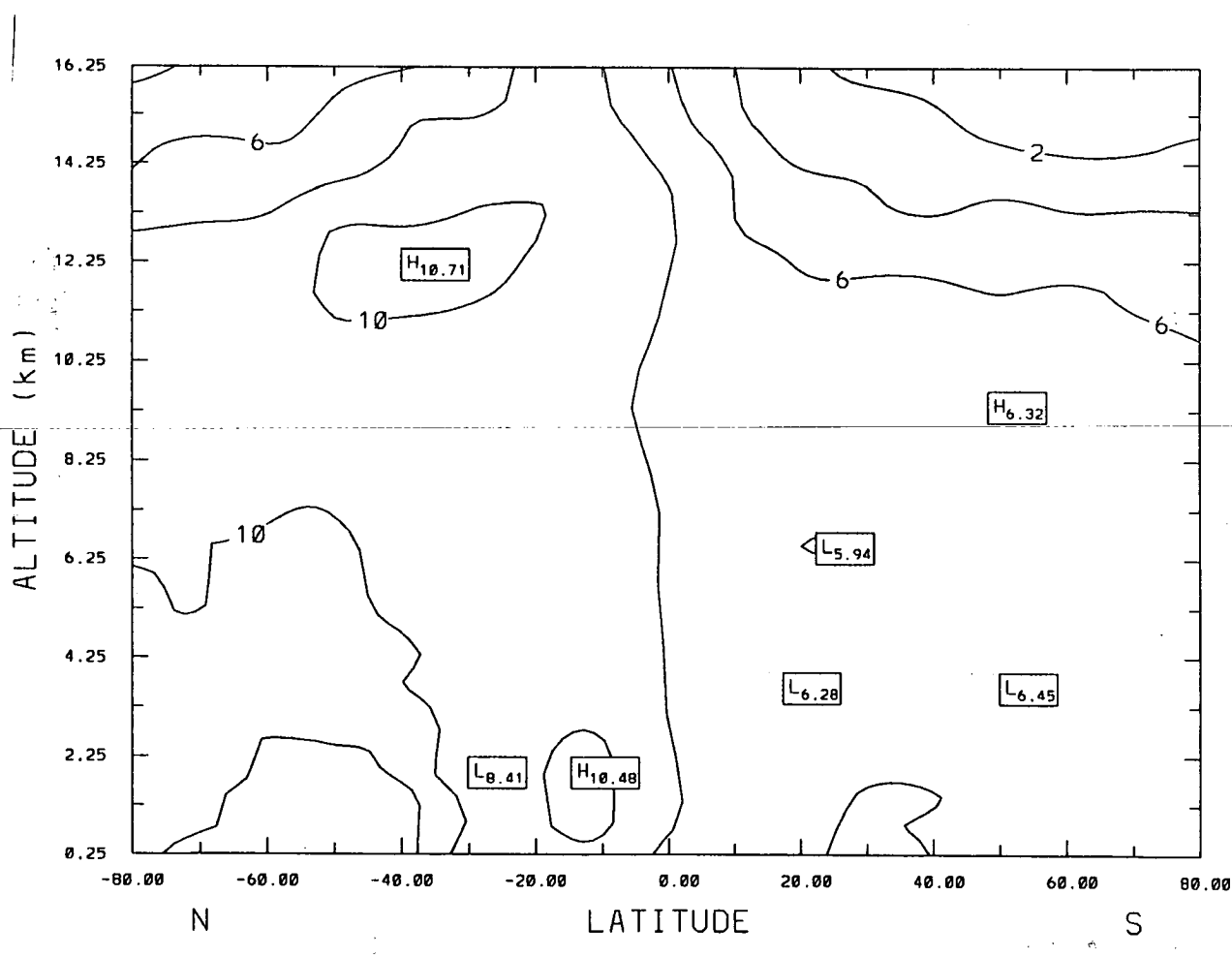


Figure 4. Calculated percentage change in O₃ concentrations in August when the emissions of CO are doubled.

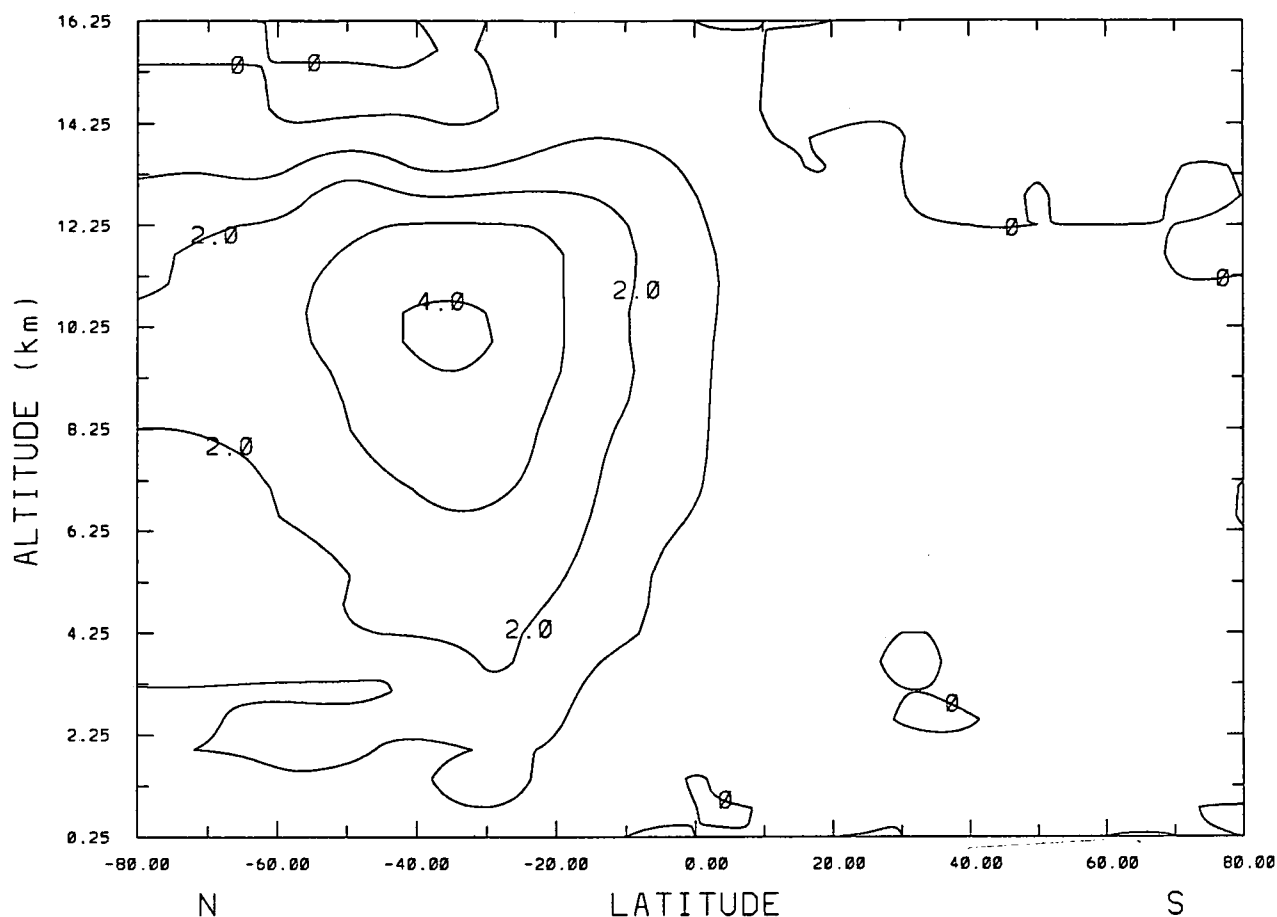


Figure 6. Calculated percentage change in O_3 concentrations in August when the emissions of NO_x from airplanes are increased by 0.5 TgN/yr (or 70%).

The relatively strong effect on ozone is due to the low NO_x concentrations in the altitude levels where the emissions take place (30-40 ppt), giving more efficient ozone production per NO_x molecule emitted. Slower reaction between OH and NO_2 and no ground deposition increase the chemical lifetime of NO_x in this region compared to lower altitudes. This makes it possible for NO_x 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 permits more efficient buildup of O_3 in the region.

The increase of ozone from increased airplane emissions takes place at altitudes where ozone changes are very effective in perturbing the radiative balance of the Earth/atmosphere. Model studies by Wang et al. (1980) and 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 difference between the radiation absorbed and the radiation that is re-emitted (Wuebbles et al., 1989). This contrast reaches a maximum near the tropopause.

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 are expressed relative to the increase in emission given in mass units. The numbers are given in table 6. The efficiencies are normalized to the impact on O_3 from a doubling of the *methane* emissions. Note that *annual tropospheric mean values of ozone* are given in this table. In the calculations of the radiative forcing from ozone (chapter 9), the seasonal variations and the vertical distribution of the change are taken into account.

Table 6. 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
$\Delta O_3(\%)/\Delta E(\text{Tg/yr})$	0.1005	0.0336	0.0066	0.0196	1.6797
$\frac{\Delta O_3/\Delta E}{\Delta O_3/\Delta E(\text{CH}_4)_{2x}}$	3.0	1.0	0.20	0.58	50

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

The calculations show that NOx emitted from airplanes is much more efficient in

increasing ozone than NO_x emitted at ground level. Compared to the case where the ground sources are doubled, NO_x from airplanes is ~17 times more efficient with respect to ozone increases.

The chemistry controlling tropospheric ozone is highly non-linear. Model tests with smaller increases in the emissions were therefore performed to elucidate the degree of non-linearity in the chemical responses. Similar comparisons are made for the results of model tests where the NO_x, CO and CH₄ emissions were increased by 10%. In table 7, the O₃ enhancement efficiencies are given relative to the effect on ozone from a doubling of CH₄ emissions, allowing for comparison with the numbers in table 6.

Table 7. The efficiencies of the source gas emissions in enhancing tropospheric O₃ for 10% increases in emissions. (E: Emission in Tg/yr).

	1.1 x NO _x	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 NO_x emissions lead to more efficient ozone enhancement. The efficiency in ozone enhancement increases by ~40% when the NO_x 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 mentioned, the aircraft emissions of NO_x are ~17 times more effective in enhancing ozone than a doubling of the ground sources of NO_x. When the effect is compared to a 10% increase in ground sources, the factor is ~12.

Since the various perturbations affect the tropospheric OH concentration, they will also affect the concentrations of gases that have reactions with OH as their main sink. Methane is one of these gases and table 8 shows the effects of the various

perturbations on the global level of methane. (For a discussion of the spatial variations in the response in OH, see Fuglestad et al., 1993).

Table 8. The effect on global mean concentration of methane in the various perturbations. (E: Emission in Tg/yr).

	1.1 x NO _x	2 x NO _x	1.1 x CO	2 x CO	Incr. NO _x (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
$\frac{\Delta\text{CH}_4}{\Delta\text{E}}$	- 0.46	- 0.44	0.02	0.02	- 0.15	0.02	0.28	0.31

Increased emissions of NO_x lead to reduced concentrations of methane, while increased emissions of CO and NMHC give increases in methane. The figures also show that increases in methane *emissions* lead to more than proportional increases in methane *concentrations*. This is a consequence of the feedback between CH₄ and OH (see chapter 3). The feedback will also affect the CH₄ levels when the emissions are *reduced*; the reduction in concentration will be larger than the reduction in emissions. But the feedback effect will become less significant at lower concentrations.

The performed calculations show that both ozone and methane are affected by changes in the emissions of source gases. Since ozone and methane are GHGs with different effects on the radiative balance of the Earth/atmosphere, it is necessary to calculate the effects on the radiative forcing from the changes in these gases in order to be able to estimate the *net climatic effects* of the emissions.

9. Estimated changes in radiative forcing from changed levels of O₃ and CH₄

In the estimates of GWPs in this report, the changes in UV radiation at the tropopause are not included in the calculations. This is due to the fact that the surface, the boundary layer and the free troposphere is a tightly coupled system because of the transport processes taking place here. Changes in the fluxes of UV should be included if ozone changes in the stratosphere are also taken into consideration.

Radiative calculations are performed for the latitude bands 60°N, 40°N, Equator, 40°S and 60°S for four months representing the four seasons. This is an approximative approach, but, seen in relation to the precision of the two-dimensional tropospheric model which has been used in the chemical calculations, this is reasonable.

Due to the highly non-linear properties of atmospheric chemistry, the degree of perturbation may have significant effects on the results. This is shown and discussed in chapter 8. Against this background, we have chosen to use the smallest perturbations for the estimates of GWPs.

In the calculations of radiative forcing stemming from the changes in the levels of one gas, all the other gases are kept at constant levels. These levels are given in table 9:

Table 9. Reference and background levels of important GHGs.

CO ₂	CH ₄	CFC-11	CFC-12	N ₂ O
353 ppm	1.72 ppm	280 ppt	484 ppt	310 ppb

Data for tropospheric temperatures and water vapour are taken from the 2D chemistry/transport model, while data for stratospheric temperature, water vapour, ozone and methane are taken from the 2D chemistry/transport model of the stratosphere (Isaksen et al., 1990).

Figures 7, 8 and 9 show the calculated changes in IR radiative forcing from changes in tropospheric ozone in response to a 10% increase in emissions of CH_4 , CO and NO_x (from surface sources), respectively, for the selected months and latitudes. In figure 10 the corresponding numbers are shown for increases in tropospheric O_3 in response to increased emissions of NO_x from airplanes.

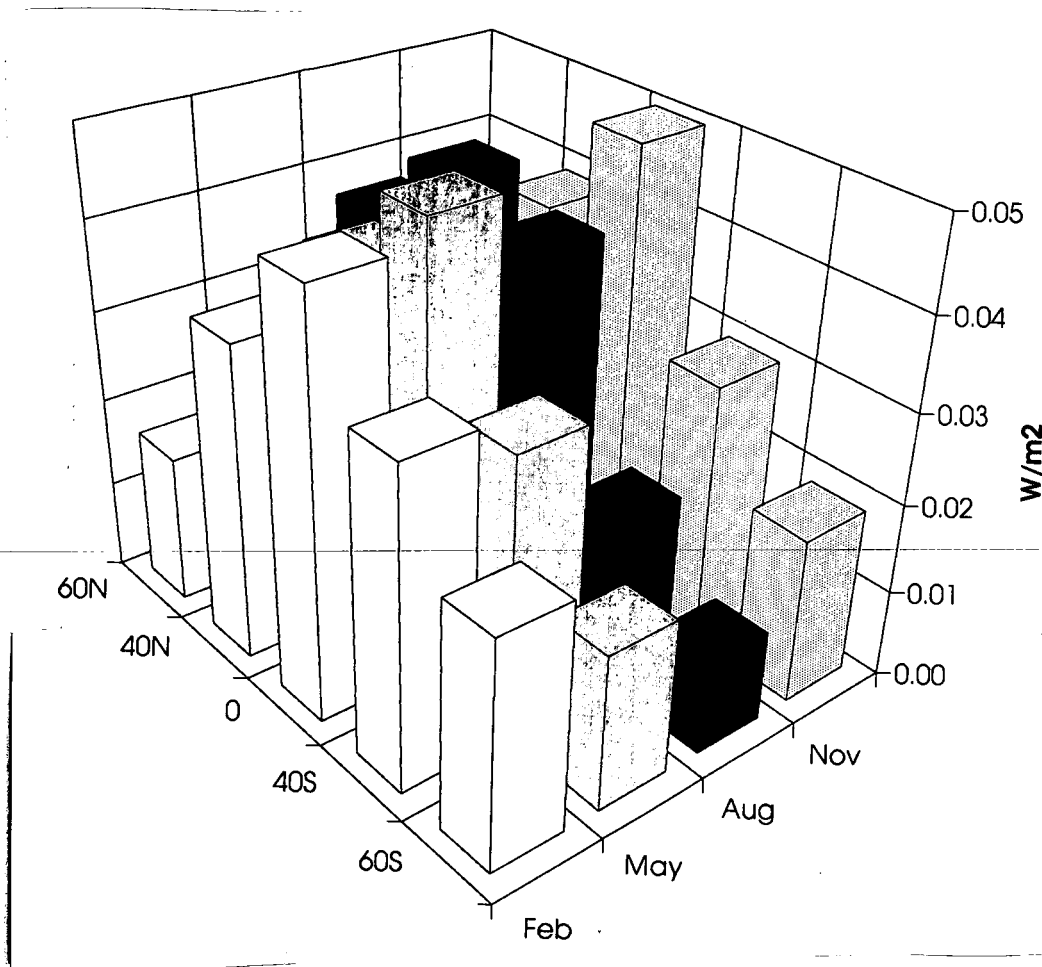


Figure 7. Calculated changes in IR radiative forcing from O_3 changes in response to 10% increase in methane emissions as function of latitude and month.

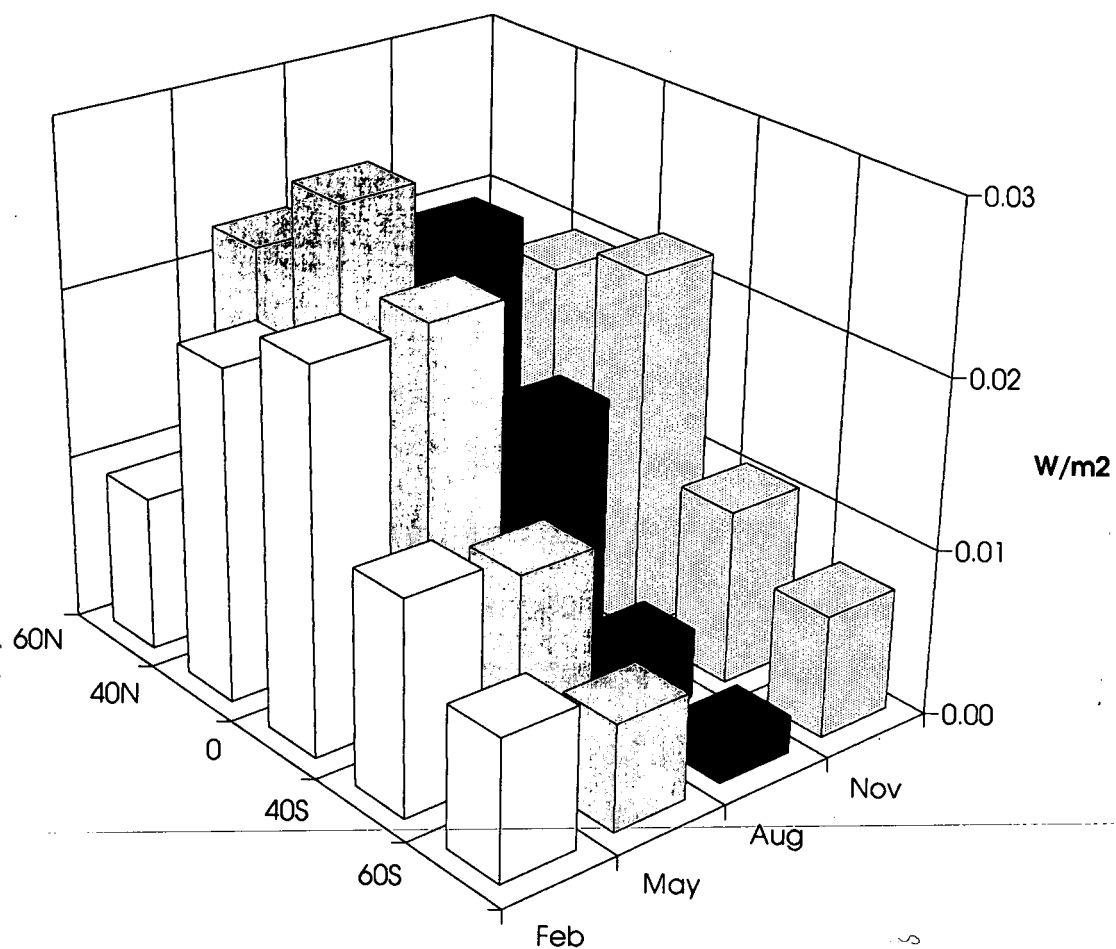


Figure 8. Calculated changes in IR radiative forcing from O_3 changes in response to 10% increase in CO emissions as function of latitude and month.

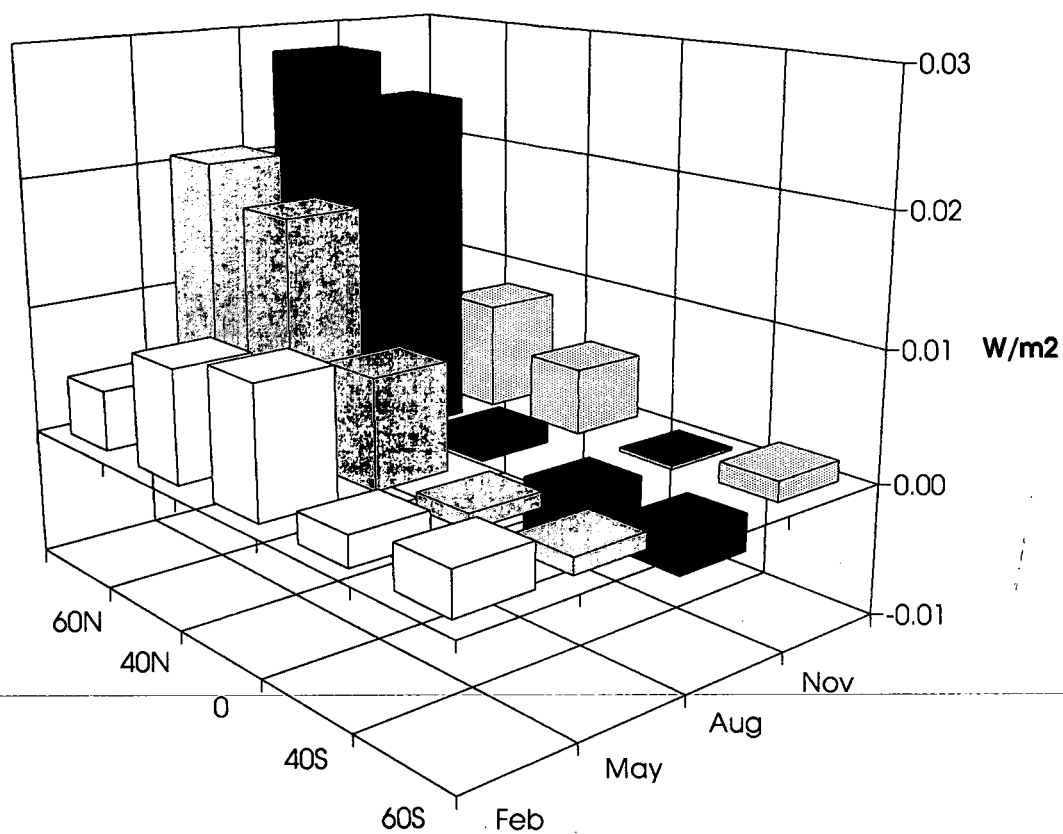


Figure 9. Calculated changes in IR radiative forcing from O_3 changes in response to 10% increase in surface emissions of NO_x as function of latitude and month.

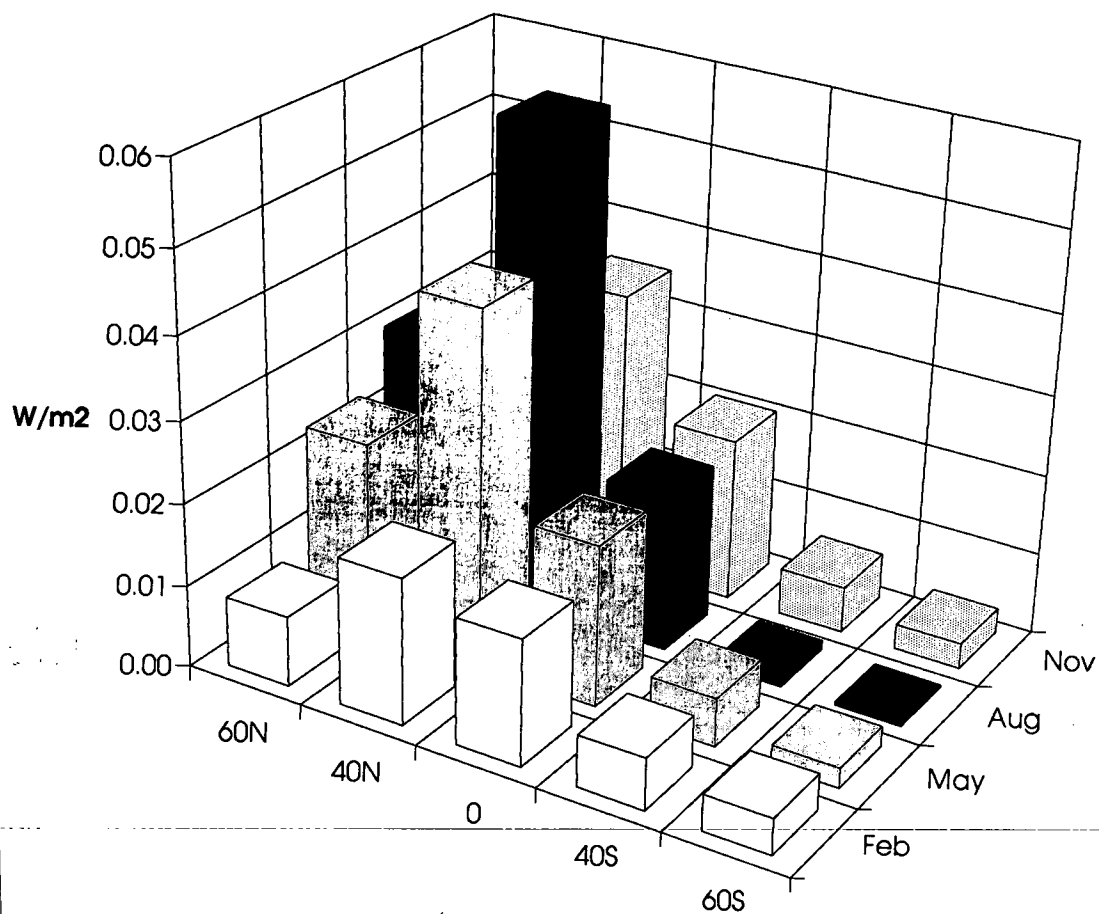


Figure 10. Calculated changes in IR radiative forcing from O_3 changes in response to increases emissions of NO_x from airplanes as function of latitude and month.

The figures show that the latitudinal distribution of changes in radiative forcing from increased emissions of CH_4 is more uniform than changes in forcing due to changed emissions of NO_x . The effects of NO_x is largest around 40°N where the emissions are largest. The change in radiative forcing from NO_x is slightly negative at higher southern latitudes in August due to the modelled reductions in ozone here.

In addition to the radiative forcing through the effects on tropospheric ozone, the emissions also affect radiative forcing through changes in methane. Ozone and methane do not have spectral overlaps and the *total* radiative forcing is simply the sum of the two numbers.

The contribution from changes in ozone and methane to the net radiative forcing at steady state from increased methane emissions is illustrated in figure 11. Corresponding figures for CO and NO_x from airplanes and surface sources are shown in figures 12, 13 and 14.

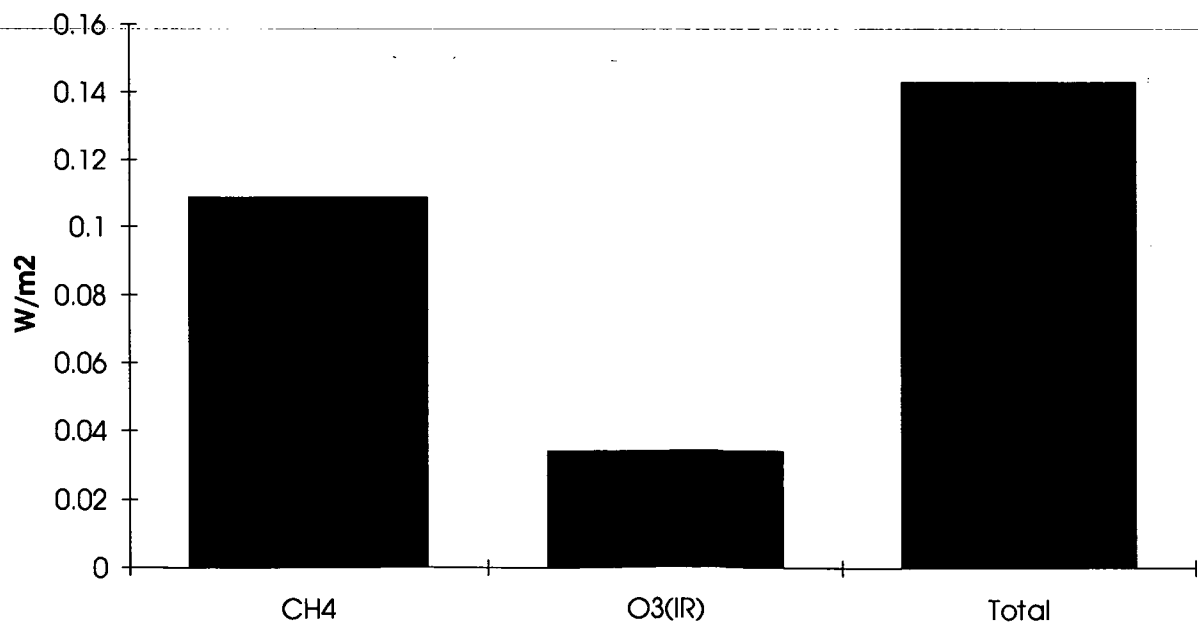


Figure 11. Calculated radiative forcing from changes in methane and ozone at steady state in response to a 10% increase in CH_4 emissions.

Figure 12. Calculated radiative forcing from changes in methane and ozone at steady state in response to a 10% increase in CO emissions.

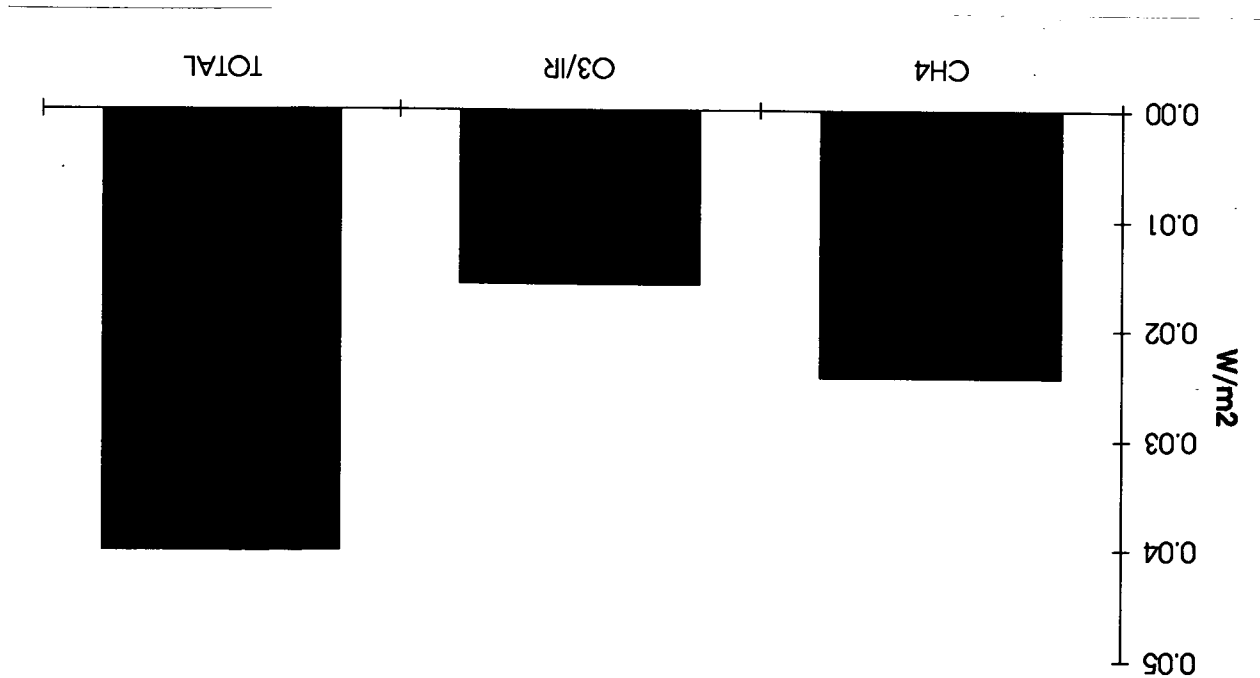
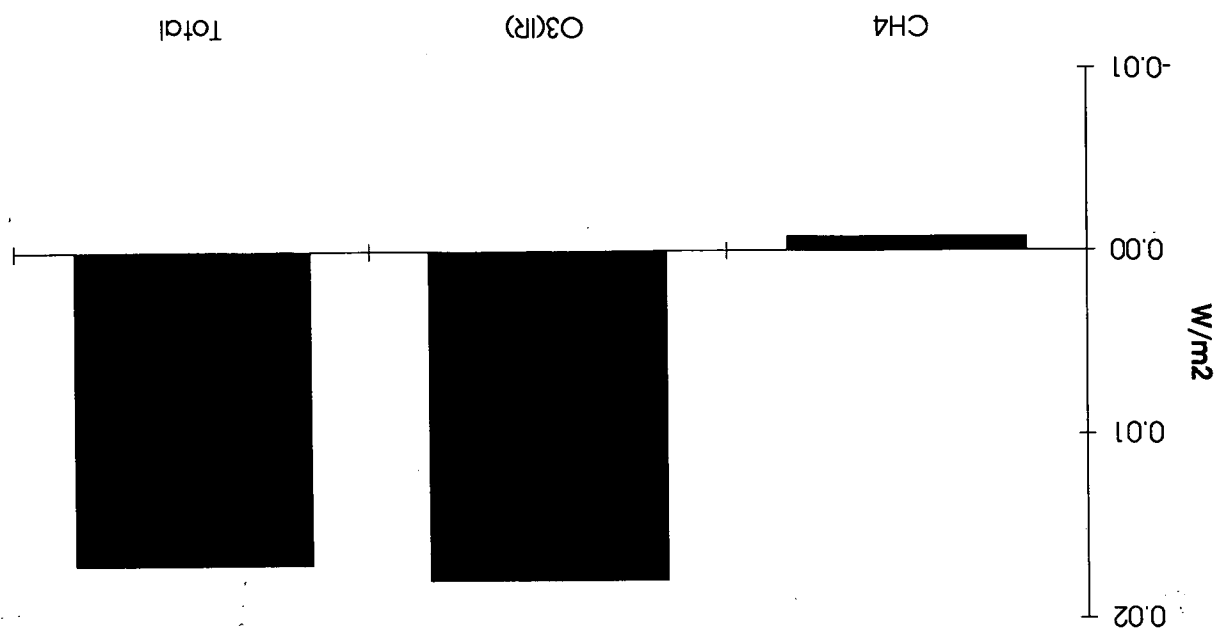


Figure 13. Calculated radiative forcing from changes in methane and ozone at steady state in response to increased NOx emissions from airplanes.



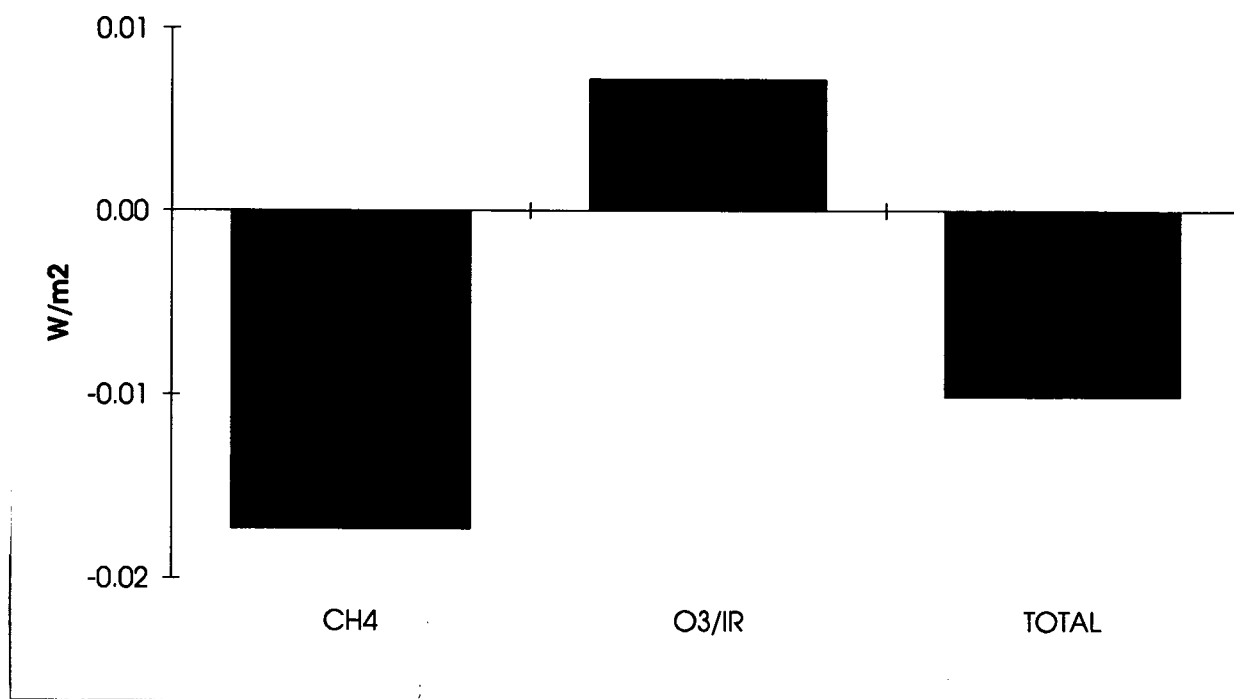


Figure 14. Calculated radiative forcing from changes in methane and ozone at steady state in response to a 10% increase in NO_x emissions from surface sources.

In the chemical calculations continuous emissions are applied and not pulses of emissions as in the definition of the direct GWP. The two approaches, however, give the same result. This is a necessary approach when the *indirect* effects through the interactive atmospheric chemistry is to be taken into account. The response times of these effects are generally significantly shorter than the shortest time horizon applied (20 years). Responses in the methane levels are exceptions, and this is taken into account in the calculations (see chapter 10).

In the definition of the direct GWP the lifetime of the trace gas determines how much is remaining at time t , and the lifetime is therefore an important parameter. When continuous emissions are applied this parameter is equally important as it determines to what degree the gas accumulates in the atmosphere and thereby the steady state level of the gas under consideration.

10. Estimated total GWPs for CH₄, CO and NO_x

In this chapter, the effects of emissions on the radiative balance through changes in tropospheric ozone and methane will be included in the estimates of GWP values. The contribution from increases in stratospheric water vapour, based on published results from other groups, will also be taken into account for methane.

The inclusion of the indirect effects from methane emissions will be done by relating the magnitude of the forcing through changes on ozone and methane to the *direct* radiative effect of methane itself. Since NO_x and CO do not have any significant direct radiative impact on the energy balance of the atmosphere, the indirect effects of these components will be related to the direct effect of methane.

Methane has a chemical lifetime of ~10 years in the atmosphere. Thus, for a time horizon of 20 years, the methane levels have not reached the new steady state after the perturbation, but have achieved 86% of their replacement from the old to the new steady state level. This is taken into account and in Appendix A it is shown how the correction factor is deduced.

The oxidation of CO, CH₄ and NMHCs in the atmosphere yields CO₂. For sources with carbon of fossil origin, this will add to the GWP values. When applying the GWPs to emission inventories one must, however, be sure to avoid double counting the contribution to CO₂, since emission estimates of CO₂ often are based on the total carbon content in the fuels. In this work, the contribution to increased CO₂ levels is *not* included in the estimated GWPs given in the tables. The increase in the GWP values are given in the text.

10.1 Total GWPs for CH₄

The oxidation of methane gives a significant contribution to the levels of H₂O in the stratosphere. To include this contribution to radiative forcing, results from estimates

in WMO (1992) are used. The following relation is given there:

$$RF(H_2O \text{ from } CH_4) = f_{H_2O} \cdot RF(CH_4 \text{ direct})$$

f_{H_2O} is the enhancement in the GWP of methane, while RF is radiative forcing. The following values for f_{H_2O} are given:

0.3	(IPCC, 1990)
0.22	(WMO, 1992)
0.31 - 0.38	(WMO, 1992)
0.05	(Lelieveld and Crutzen, 1992)

In our estimate of the total GWP, the value 0.3 is chosen.

Due to the chemical feedback between CH_4 and OH the direct radiative effect of increased mixing ratios of methane should be divided into a "direct chemical" and "indirect chemical". For a 10% increase in methane emissions, the feedback has been estimated to be 35% (Fuglestad et al., 1993), i.e. the relative increase in *concentration* is 35% larger than the relative increase in *emission*. The factor $f_{CH_4/OH}$ (defined in an analogous manner as for stratospheric H_2O) is therefore set equal to 0.35.

The change in IR radiative forcing from increased tropospheric O_3 is estimated to be 42% of the direct effect (f_{O_3} equals 0.42). The changes in ozone in response to increased emissions vary between models, but these variations are moderate (see chapter 11).

The total (direct and indirect) GWP is then given by:

$$GWP_{total} = GWP_{dir} \cdot f_{total} = GWP_{dir} \cdot \sum_{i=1}^4 f_i \quad (2)$$

The values for f_i and f_{total} are given in table 10.

Table 10. The ratio f between the different indirect effects and the direct effects.

CH ₄ (direct)	CH ₄ (indirect)	O ₃	Stratospheric water vapour	TOTAL
1.00	0.35	0.42	0.3	2.1

Thus, it may be concluded that the indirect effects of methane are of the same sign and magnitude as the direct effect. The contribution from the various effects (at steady state) to the total GWP of methane is illustrated in figure 15.

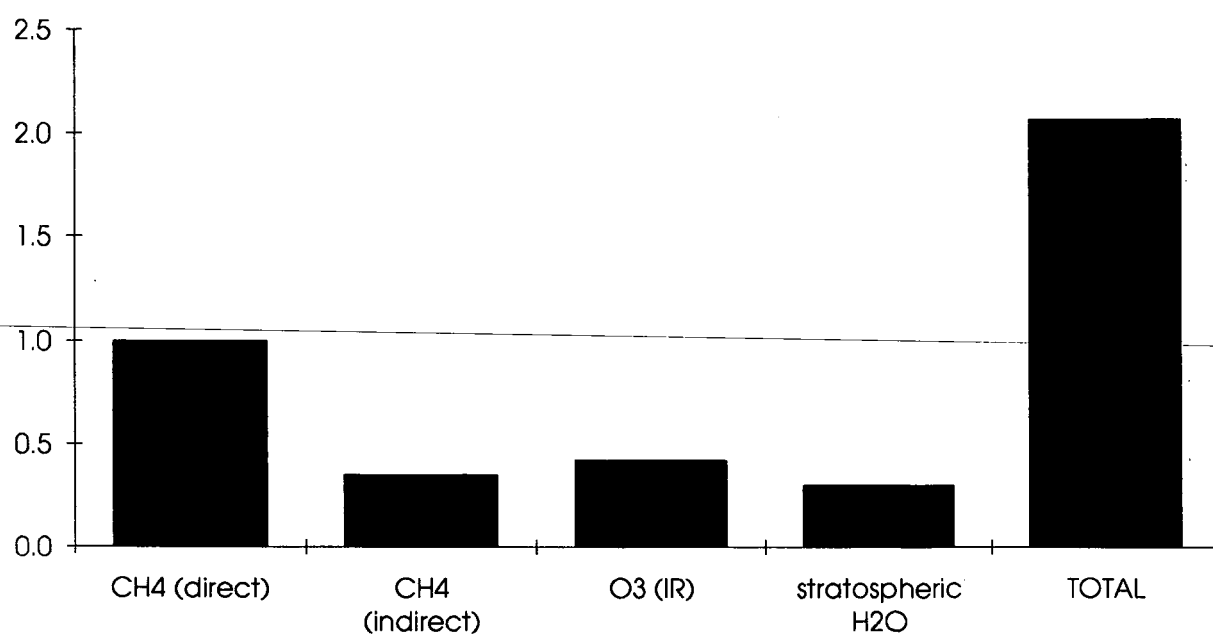


Figure 15. Contribution from the various effects to the total GWP for methane.

The *direct* GWP values for five time horizons are given in table 11 (WMO, 1992; IPCC, 1992).

Table 11. Direct GWP values (from WMO, 1992; IPCC, 1992).

Horizon (years)	20	50	100	200	500
Direct GWP	35	19	11	7	4

The factor 2.1 is multiplied by the direct GWPs given in table 11 (according to equation 2) and the numbers in table 12 give the total GWPs for methane emissions.

Table 12. Total GWP values for methane for different time horizons.

Horizon (years)	20	50	100	200	500
Total GWP	71	39	23	15	8

The main reason for the decline of the GWP values with larger time horizons is the increasing importance of CO_2 relative to CH_4 . (The CO_2 level, which is in the denominator of the expression for the GWP calculations (eqn. 1), has a slower approach to a new state level than CH_4 .) After 20 years (approximately $2 \times \tau_{\text{CH}_4}$), the level of methane has reached ~86% of the difference between the old steady state level and the new steady state level that the concentration is approaching asymptotically. After 50 years, the methane concentration has reached 99% of the difference. The response times of the indirect effects through tropospheric O_3 and stratospheric H_2O are short compared to the time horizons applied above. This implies that these effects have reached their full effects within the time horizons. The full response in O_3 is reached within a few months, while the effect on stratospheric water vapour is reached within approximately 5 years. The magnitude of the effects through the CH_4/OH feedback between OH and CH_4 is multiplied with 0.86 to take

into account that steady state has not been reached when a time horizon of 20 years is applied.

The global average fraction of the emitted methane that is of fossil origin is estimated to be 20% (IPCC, 1992, and references therein). That is, in average, only 20% of the CO_2 formed from the atmospheric oxidation of methane represents a *net* contribution to the atmospheric levels of CO_2 . For methane sources with fossile carbon (coal mining, oil and natural gas production) this represents only a small additional effect and is not taken into account in the GWPs estimated here. The ratio between the molecular weights for CO_2 and CH_4 is 2.7. Thus, for fossil sources, this may add 2.7 to the GWPs for methane since one CO_2 molecule is produced for each CH_4 molecule that is broken down.

10.2 GWPs for CO

Since CO is not a direct GHG itself with a direct GWP that the indirect effects may be related to, a somewhat different approach has to be applied for this component. The two indirect chemical effects that are taken into account are the effects on methane, and the effect on tropospheric ozone.

Emissions of CO increase tropospheric levels of ozone, and, through negative effects on the OH levels, it increases the levels of methane. The radiative forcing from changes in tropospheric ozone and methane at steady state in response to a 10% increase in emissions of CO was shown in figure 12. The effects are of the same sign and of comparable magnitude. The total radiative effect ΔRF (W/m^2) (i.e. through changes in O_3 and CH_4) is normalized to the increase in emissions in mass units (ΔU). The ratio α , between this number and the change in radiative forcing from increased emissions of methane (the direct effect) is then calculated and multiplied by the total GWP of methane to give the GWP for CO emissions:

$$GWP_{CO}^{total} = \frac{(\frac{\Delta RF}{\Delta U})_{CO}^{total}}{(\frac{\Delta RF}{\Delta U})_{CH_4}^{dir}} \cdot GWP_{CH_4}^{dir} \quad (3)$$

The GWP values for the different time horizons are given in table 13.

Table 13. GWPs for CO.

Horizon (years)	20	50	100	200	500
GWP (CO-basis)	7	4	2	1	1

For a time horizon of 20 years, it is taken into account that the O₃ levels are at steady state while the level of methane has only reached 86% of the difference between old and new steady state levels. This has to be taken into account since the change in radiative forcing from O₃ changes is related to the change in radiative forcing from changes in methane.

The contribution to increased CO₂ levels is *not* included in the numbers. For CO emissions of fossil origin, the GWPs increase by 1.5.

10.3 GWPs for NOx emitted from airplanes

NOx is not a direct GHG itself with a direct GWP that the indirect effects may be related to, and the indirect effects will be related to the direct effect of methane. The two indirect chemical effects that are taken into account are, again, the effects on methane through changes in OH and the effect on tropospheric ozone.

The effect on methane is *negative*. Through increased levels of OH, the loss of methane is increased when the NO_x emissions are increased. However, this effect, in terms of change in radiative forcing, is small compared to the effect of increased ozone levels. The absolute value of the change in radiative forcing through methane changes at steady state is approximately 5% of the radiative forcing from ozone increases. Figure 13 shows the radiative forcing from reduced levels of methane and increased levels of O₃ at steady state in response to increased emissions of NO_x from airplanes.

The radiative effect ΔRF (W/m²) is normalized to the increase in emissions in mass units (ΔU). The ratio α between this number and the change in radiative forcing from increased emissions of methane (the direct effect) is then calculated and multiplied by the total GWP of methane to give the GWP for NO_x emissions from airplanes:

$$GWP_{NO_x}^{total} = \frac{\left(\frac{\Delta RF}{\Delta U}\right)_{NO_x}^{total}}{\left(\frac{\Delta RF}{\Delta U}\right)_{CH_4}^{dir}} \cdot GWP_{CH_4}^{dir} \quad (4)$$

The total GWPs for NO_x emitted from airplanes, are given in table 14.

Table 14. GWPs for NO_x emitted from airplanes.

Horizon (years)	20	50	100	200	500
GWP (NO ₂ -basis)	253	118	68	44	25
GWP (N-basis)	833	388	225	143	82

For a time horizon of 20 years, it is taken into account that the O_3 levels are at steady state while the level of methane has only reached 86% of the difference between new and old steady state levels. This has to be taken into account since the change in radiative forcing from O_3 changes is related to the change in radiative forcing from changes in methane.

10.4 GWPs for NO_x emitted from surface sources

As in the case of NO_x emitted from airplanes, the indirect effects that are taken into account are effects on methane (through effects on OH) and on tropospheric ozone. Equation 4 is used to estimate the GWP-values for the different time horizons.

NO_x from surface sources has a larger effect on the levels of methane than NO_x emitted from aircraft (see table 8). The reason for this is that the levels of OH are affected in a region that is much more important for the oxidation of methane than is the case for the region of the airplane emissions.

The radiative effect through changes in methane is comparable to the effect on radiative forcing through changes in tropospheric ozone, but is of opposite sign, as was shown in figure 14 for steady state conditions after an increase of 10% in the NO_x emissions. The negative radiative forcing through reduced levels of methane is larger than the positive forcing from increased ozone levels, giving a net radiative forcing that is negative. As shown in chapter 8, the responses in O_3 to increased emissions of NO_x depend on the magnitude of the perturbation. How this affects the GWPs is discussed in chapter 11. The calculated GWP values for NO_x for different time horizons are given in table 15.

Table 15. GWPs for NO_x emitted from surface sources.

Horizon (years)	20	50	100	200	500
GWP (NO ₂ -basis)	-16	-9	-5	-3	-2
GWP (N-basis)	-51	-31	-18	-11	-7

For a time horizon of 20 years, it is taken into account that the O₃ levels are at steady state while the level of methane has only reached 86% of replacement from the old steady state level. This has to be taken into account since the change in radiative forcing from O₃ changes is related to the change in radiative forcing from changes in methane.

It is important to note that there are large uncertainties connected to the estimated GWP values for NO_x from surface sources. The results may depend on the model that is applied (see discussion in chapter 11).

10.5 GWPs for NMHC: Order of magnitude

No separate radiative calculations were performed for the modelled changes in O₃ and CH₄ in response to increased emissions of NMHC. From the chemistry model studies (chapter 8) we can, however, compare the effects of NMHC and other source gases on O₃ and CH₄. We may therefore relate the effects of NMHC to those of CO, for which we have radiative calculations of the effects through changes in O₃ and CH₄.

The radiative forcing from increases in CH₄ due to increased CO emissions is multiplied by 8/3 which is the ratio between the effects of NMHC and CO emissions

on the CH_4 levels (table 8). The radiative forcing from increases in O_3 is scaled by $6.8/0.9$, the ratio between the effects on O_3 (tables 6 and 7). The latter effect is further increased by 10% to take into account that a 100% perturbation was performed for NMHC, while a 10% perturbation would give approximately 10% higher O_3 production efficiency. These estimated numbers for radiative forcing through O_3 and CH_4 are then added together and divided by the increase in emission of NMHC. The ratio between this number and the corresponding number for CO is then multiplied with the GWP for CO for the different time horizons.

From these very rough considerations, we assess the GWP for NMHC to be approximately 80% larger than the GWP for CO. This number, however, represents an upper limit due to the different height distributions of the ozone changes between the case where CO emissions are increased and the case where NMHC emissions are increased (fig.4 vs. fig.5).

It is important to note that the effects of NMHC emissions on O_3 and CH_4 depend on the composition of the NMHCs. Appendix B gives the composition of the NMHC emission that is assumed in the chemistry modelling.

11. Limitations and uncertainties

The estimated GWPs should be used with caution due to limitations in the methods applied as well as in the GWP concept itself. It is referred to the discussions of the limitations of GWPs in Chapter A2 in IPCC 1992 and in Chapter 7 in WMO (1992).

11.1 Limitations and uncertainties in the chemical calculations

The ability of the applied 2D chemistry model to reproduce observed distributions of various gases in the atmosphere has been evaluated by Fuglestvedt et al. (1993). Comparisons between model results and observations are difficult because the model applies climatological average values and calculates zonal averages while observations usually are too few in space and time to form a basis for calculating zonal averages. The comparisons performed by Fuglestvedt et al. (1993), however, indicate that the observed atmospheric distributions of species with lifetimes of weeks or longer generally are well reproduced by the model.

Since the applied two-dimensional model suffers from the inherent limitation of zonal averaging, the capability of the model to treat some important non-linear effects is limited. Species with a chemical lifetime of a week or more can be assumed to be zonally well mixed and the two-dimensional approximation is justified. But several chemical species have lifetimes considerably shorter than this. Important among these is NO_x, which has a chemical lifetime in the order of hours to days. The NO_x levels show, therefore, strong variations zonally and in time. 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 NO_x and its role in the chemistry. The OH and O₃ chemistry is very sensitive to the NO levels in a non-linear way. 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.

Kanakidou and Crutzen (1992) used a 3D model to study the effect of zonal averaging. They assumed longitudinally *uniform* emissions of NO_x 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 O₃ and OH, especially in the middle and low troposphere in the tropics and at northern mid-latitudes. This test was done for the surface emissions of NO_x and NMHC as well as for lightning emissions of NO_x. The representativeness of these results is, however, difficult to assess. It may be expected that the effect of zonal averaging is less critical for emissions from airplanes due to the faster zonal transport and thereby better zonal mixing at the altitudes where these emissions take place. Sub-grid processes that are not taken into account may modify the results. In a study by Arnold et al. (1992) it is, however, shown that at a distance of 2 km behind the jetliner, only 0.05% of the emitted reactive nitrogen were converted to inactive forms with respect to ozone production.

It has earlier been found that the *relative* effects on O₃ of increased emissions, especially of NO_x, is dependent on the background concentrations of NO_x (Isaksen et al., 1992a; Fuglestvedt et al., 1993). Several factors determine the levels of NO_x in the background troposphere. Important among these are convective transport from the boundary layer, production of NO_x from lightning, input from the stratosphere and decomposition of PAN. Lightning is probably the most important among these. In order to test the sensitivity of the results to the background concentration of NO_x, the lightning production of NO_x was increased. It was found that higher background levels of NO_x reduce the efficiency of ozone enhancement from increased emissions of NO_x, both relative and absolute. The O₃ levels are higher in the reference case with higher NO_x production from lightning and it is the ozone increase in number of molecules that is of interest when the effect on radiative forcing is under consideration. It is therefore relevant to consider the *absolute* increase in ozone (in molecules/cm³), not the relative increase. Depending on season, the absolute increase in ozone between 8 and 12 km was typically between 20% and 40% lower in the case of higher NO_x production from lightning relative to the case with lower production. The increase in tropospheric mean concentration was 40% lower in the case with high

NO_x production from lightning. Methane emissions increase the tropospheric average of ozone only slightly more efficiently at higher background levels of NO_x.

The magnitude of the perturbation also affects the efficiency with which the emitted NO_x increases the ozone levels. Small increases in NO_x emissions give more efficient O₃ enhancements. The efficiency increases by approximately 40% when the NO_x emission is increased by 10% compared to a doubling of the emissions.

Effective transport of air from the lower layers in the troposphere 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 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. This means that increased emissions from surface sources may increase ozone in the upper troposphere more efficiently than that which our model is able to estimate. Since ozone is an efficient GHG in this part of the troposphere, the omission of this mechanism is likely to affect the GWP values for NO_x from surface sources.

In Chapter 5 by Isaksen et al., in the report "Scientific Assessment of Ozone Depletion: 1991" (WMO, 1992), a comparison between the results from the study by Fuglestvedt et al., 1993 (which this work is based upon) 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 O₃ to increased emissions of NO_x (~ 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 O₃ increase in response to increased CH₄ are moderate (within 50%). Figure 16 shows the calculated increases in annual global average of ozone due to a doubling of the *emissions* or the *mixing ratio* of CH₄. It is seen that the variations between the models

are moderate. The results from the OSLO model (which is applied in this work) are given with and without the effect of the CH_4/OH feedback. This was done to make it possible to compare the results with those of the models that have doubled the mixing ratio of methane instead of the emissions of methane (Harwell and NASA/GSFC). The difference between our model and the LLNL (Wuebbles and Tamerisis, 1993) and the NASA/GSFC models increase in the upper troposphere. This is a region where ozone increases efficiently affect the radiative forcing of climate.

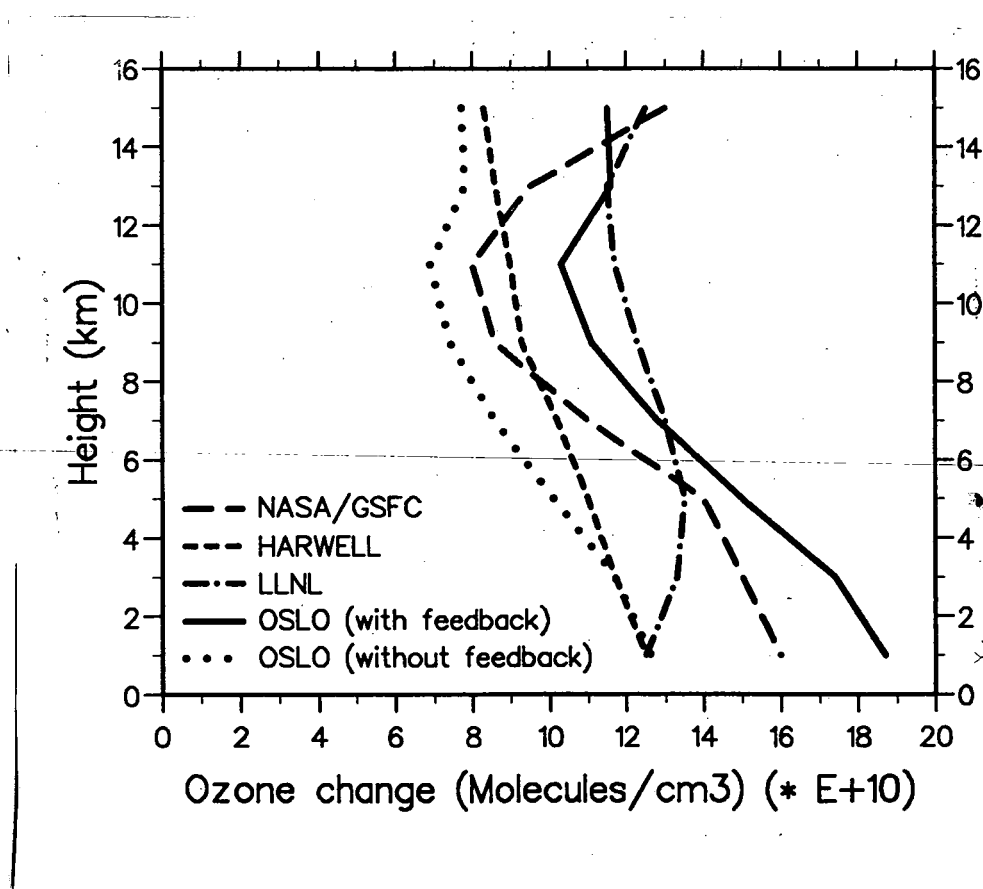


Figure 16. Calculated increases in ozone ($\text{molecules}/\text{cm}^3$) in response to doubling the emissions or doubling the surface mixing ratios of methane.

In the chemistry model tests, the emissions of the gases were changed one by one. Due to the interactions in the chemistry, the atmospheric response may be different from what is expected when the emissions of several gases are changed simultaneously. When the emissions are increased, the same relative latitudinal distribution of the emissions is applied. Due to the short lifetime of NO_x, the chemical response to increased emissions of NO_x, CO and hydrocarbons may depend on the geographical location of the emission. In particular, the response may vary with respect to net production of ozone, and this may therefore be of importance for the GWP estimates.

In this study gas phase chemistry is modelled with first order scavenging of soluble species by clouds, rain and aerosols included. Chemistry/transport models of the troposphere that include aqueous phase chemistry and exchange processes between the gaseous and the aqueous phase, give lower levels of ozone (Lelieveld and Crutzen, 1990; Lelieveld and Crutzen, 1991; Jonson and Isaksen, 1994; Jonson and Isaksen, 1993). Jonson and Isaksen (1994) report up to ~20 % lower levels in ozone when heterogeneous chemistry is included. The largest reductions take place in the remote middle troposphere. But the omission of heterogeneous chemistry in the troposphere in our study may constitute only a small error since we are focusing on *changes* in the levels of the gases.

Necessary further work to improve the calculations would be to use a 3-dimensional chemistry/transport model in order to take into account the large zonal variations in NO_x and the chemical effects of these variations. Inclusion of convective transport and heterogeneous chemistry would also make the results more realistic.

11.2 Limitations and uncertainties in the GWP calculations

The uncertainty in the radiative calculations in this work is assessed to be less than 5%. However, a recent comparison of 15 Global Circulation Models showed substantial variations between the models in the calculated forcing from a doubling

of the CO₂ concentration (Cess et al., 1993). The mean value was 4 W/m², with a coefficient of variation of 10.2% (standard deviation divided by the mean) and a range (100*(max-min)/mean) of 34%. The largest contribution to the variation was from the CO₂ radiation parameterization of the models.

In the GWP calculations performed by WMO (1992) and IPCC (1992), a carbon cycle model was used to calculate the integrated radiative forcing from CO₂ in order to avoid using a single lifetime for CO₂. The overall loss of CO₂ is composed of several loss processes, with the ocean being dominant, and an approximate lifetime is 120 years. The lifetime of CO₂ is not constant but increases over time since the capacity of the ocean to absorb excess CO₂ from the atmosphere will be reduced as more carbon is absorbed in the ocean. On the other hand, the radiative forcing for each additional unit of atmospheric CO₂ will decrease due to the saturation of the absorption bands. Each of these effects will influence the calculated radiative forcing from future CO₂ emissions. Future increases in CO₂ will lead to reduced efficiency in radiative forcing from CO₂ per unit increase over long time horizons. Interactions will also apply to CH₄ and N₂O, but these are less significant.

In a study by Caldeira and Kasting (1993), however, these two effects compensate for each other, and the net result is that the GWP for CO₂, relative to other radiatively active gases, is almost independent on the future emissions of this gas.

How the lifetime of CO₂ varies with the level of CO₂ is subject to extensive research. In the IPCC process it has been so far concluded that the revised lifetime of CO₂ will not change by more than ±20% relative to the lifetimes applied so far in the calculations of GWPs.

The calculated GWPs apply to the present atmospheric conditions in terms of concentrations of the various chemically and radiatively active gases. With continued emissions of such gases, the effects on the radiative balance will change over time. The absolute GWP for CO₂ will decrease by up to 30% for a time horizon of 100 years and somewhat less for 500 years in a scenario with emissions required to stabilize

CO₂ at 650 ppm. In addition, the chemical response to emissions is dependent on the concentrations of various gases that take part in the chemical interactions. For instance, as the levels of NO_x increase, the chemical effect of each additional unit of emissions of NO_x will change.

Due to radiative overlapping between H₂O and the other greenhouse gases, the GWPs will change as global warming occurs since H₂O will increase in response to higher temperatures. This may lower the effects of the non-H₂O gases, and the magnitude of this effect will vary between the gases.

Due to the factors mentioned above, the GWPs will need updating as the reference atmosphere changes. Updated values will also be needed due to new scientific knowledge. Recent estimates indicate increases in the radiative forcing from HCF and CH₄ by ~20%. Our estimated total GWPs for methane may thus increase by somewhat less. New estimates for the lifetime of N₂O give 120 years instead of 132, which will give somewhat lower GWPs for this gas.

The calculations of radiative forcing in this work are performed for clear sky conditions. The presence of clouds will reduce the values for radiative forcing in the order of 20-30%. The GWPs are given in relative units and will change very little.

Changes in the flux of UV is not considered when the net change in radiative forcing is estimated since we focus on changes in the *tropospheric* levels of ozone (see chapter 9). Changes in methane will, however, also affect the stratospheric levels of ozone.

In the upper stratosphere increased methane emissions leads to ozone depletion, while in the middle and lower stratosphere the result is ozone increases. The total ozone column increases in response to increased emissions of methane.

The estimated net change in radiative forcing from emissions of NO_x from surface sources is estimated to be negative; the negative effect through changes in CH₄ is larger than the positive through changes in O₃. These effects are of the same absolute

magnitude and the *net* effect is probably model dependent. In this study, a 10% increase in NO_x emissions was used as basis for the estimated GWPs for NO_x from surface sources. The chemistry calculations have shown that NO_x has a lower ozone production efficiency for larger increases in the emissions. This will reduce the positive component of the GWP. On the other hand, the effect on methane (the negative component) shows a much lower levelling off tendency with increasing perturbation. Thus, for a 100% increase, the GWP would be slightly more negative than for a 10% perturbation.

Since convective transport inside clouds is not included in the model, the effect of NO_x from surface sources on ozone in the middle and upper troposphere may, as already mentioned, be underestimated. Thus, the positive component of the GWP for NO_x from surface sources may be larger in the real atmosphere, and the net effect may be positive.

No separate radiative calculations are done for the effects of increased emissions of NMHC and the magnitude of the GWP values are only assessed by comparison to the effects of CO emissions on methane and ozone. Our calculations indicate that the indirect effects of NMHC through changes in O₃ and CH₄ are positive and that the GWP is in the order of 80% larger than the GWPs for CO. This may be an overestimate since NMHC affects O₃ at lower altitudes than does CO, which is of importance since the radiative forcing from O₃ is height dependent. It is also important to note that the effects of NMHC emissions on tropospheric O₃ (as well as on OH and CH₄) are dependent on the chemical composition of NMHCs.

In the calculation of GWPs for methane, three indirect effects have been taken into account; the CH₄/OH feedback and the effects on tropospheric O₃ and stratospheric water vapour. Of these, the latter is the effect with largest variations between different models. The magnitude of this effect, given in change in radiative forcing relative to the direct effect, varies from 0.05 to 0.38 (see. section 7.1 and WMO, 1992). The magnitude of the CH₄/OH feedback is often estimated to be in the range of 20-45%.

Table 16 shows the results of some very simple sensitivity tests. First, the effects of changes in the radiative forcing from stratospheric H₂O is tested. Assuming the lowest reported effect, the GWPs are reduced by 12%. Increasing the effect to the largest reported value increases the values by ~4 % relative to the applied values.

An increase in the strength of the CH₄/OH feedback from 35 to 50% increases the GWPs by approximately 5%. The same increase in GWPs is obtained when the effect through O₃ enhancements is increased by 30%.

Table 16. GWP values for methane estimated for different assumptions about the strength of the various indirect effects.

Time horizon	20 years	50 years	100 years	200 years	500 years
f (strat. H₂O) = 0.05	62	35	20	13	7
Applied estimate	71	39	23	15	8
f (strat. H₂O) = 0.38	74	41	24	15	9
OH feedback 50%	75	42	24	16	9
O₃ enhancement increased by 30%	75	42	24	15	9

As mentioned above, the change in the concentration of ozone as a result of NO_x emissions from airplanes is 20-40% lower between 8 and 12 km when the background levels of NO_x are increased by doubling the NO_x production from lightning. This will decrease the positive component of the total effect on climate from such NO_x emissions. The ozone increases that have been calculated here are lower than what has been calculated with the Harwell 2D model (WMO, 1992), especially in the region where O₃ changes have the largest effects on climate. In the Harwell model

calculations, NO_x emitted from aircraft is more than 20 times as effective in enhancing ozone (Johnson et al. (1992). The differences may be explained by an unrealistic modelling of the transport in the upper troposphere by the Harwell model.

We rank the source gases with respect to their uncertainty in estimated GWPs as follows:

NO_x (surface) > NMHC > CO > NO_x (airplanes) > CH₄

Three-dimensional chemical calculations and radiative calculations with higher resolution in time (not only for four months) and space (more latitude bands) would significantly improve the quality of the calculations.

12. Conclusions and compilation of GWPs

Global Warming Potentials for emissions of CH₄, CO and NO_x that take into account indirect chemical effects have been estimated for five time horizons. The indirect effects of methane emissions that have been considered are the ability of methane to increase its own lifetime (through the CH₄/OH-feedback) and the effects on the levels of tropospheric ozone and stratospheric water vapour. All these effects have positive signs, and our estimate shows that the indirect effects together are of the same magnitude as the *direct* radiative effect of methane.

For emissions of NO_x, the picture is somewhat more complicated. Emissions of NO_x generally increase the levels of tropospheric ozone. Ozone is an important GHG and therefore this mechanism constitutes a *positive indirect effect*. On the other hand, NO_x emissions increase the levels of OH, thereby reducing the lifetime of gases that are removed by OH. Of these, methane is the most important in this context. The effect on CH₄, through changes in OH, constitutes a *negative indirect effect* on climate. Difficulties may therefore be connected to estimating the *net* effect of these opposing effects. However, for NO_x emitted from airplanes the radiative forcing from changes in ozone is significantly larger than the radiative forcing from the changes in methane. We may therefore conclude that the *net* effect of NO_x emitted from airplanes is positive. Our estimates also indicate that the climate impact of NO_x emissions from airplanes, expressed as GWPs, is relatively large. One should, however, bear in mind that while the GWPs for NO_x from airplanes are relatively large, the emissions are small compared to the surface emissions of this component.

For NO_x emitted from surface sources the picture is not so clear. Contrary to the emissions from airplanes, surface emissions of NO_x affect OH in a region of the troposphere that is very important for the oxidation of CH₄. The negative effect through reduced CH₄ levels are therefore more important than in the case of NO_x emitted from airplanes. The estimated *net* effect is slightly negative since the positive effect through increased O₃ levels is somewhat smaller than the negative effect. This estimate may be model dependent and should only be considered a preliminary

finding.

Emissions of CO increase the tropospheric levels of ozone, and, through lowered levels of OH, CO increases the levels of methane. Thus, the considered indirect effects of CO are positive.

The effects of NMHC emissions on the radiative balance are assessed by comparison with the effects of CO. This assessment is dependent on the chemical composition of NMHC.

In the IPCC assessment from 1992, only the direct GWPs for methane were given and the estimates of the indirect GWP from the 1990 assessment were abandoned. In IPCC 1990, GWPs for NO_x from surface sources were also given, but only the effect through increased levels of tropospheric ozone were considered. This estimate was also left out in the 1992 report.

There are large uncertainties connected to the estimates of the indirect GWPs. The estimated GWPs represent what we are able to infer with the present model tools, and they should be considered as preliminary results which will change. Efforts should be made to develop these model further and to refine the methods for estimating the GWPs.

The GWPs for CF₄ and C₂F₆ given in this current report are also different from earlier estimates (WMO, 1992 and IPCC, 1992). The estimates are taken from Isaksen et al. (1992b), and a summary of the present state of knowledge in this area is also given. In addition, a short review of the knowledge of SF₆ is also given. CF₄, C₂F₆ and SF₆ all have very long atmospheric lifetimes and strong absorption of IR, giving very high GWP values.

In table 17 the GWPs are given for different time horizons. GWPs for gases not considered in this report are also given and these are taken from WMO (1992) and IPCC (1992).

Table 17. Global Warming Potentials for selected gases and time horizons. The values are taken from WMO (1992), IPCC (1992) Stordal et al. (1993), and this work.

Gas	20	50	100	200	500
CO ₂	1	1	1	1	1
CH ₄ (direct only)	35	19	11	7	4
CH ₄ * (incl. indirect effects)	71	39	23	15	8
N ₂ O	260	270	270	240	170
CFC-11	4500	4100	3400	2400	1400
CFC-12	7100	7400	7100	6200	4100
CFC-13	11000		13000		15000
CFC-14 (CF ₄) *	3700		5100		8800
HCFC-22	4200	2600	1600	970	540
CFC-113	4600	4700	4500	3900	2500
CFC-114	6100	6700	7000	7000	5800
CFC-115	5500	6200	7000	7800	8500
CFC-116 (C ₂ F ₆) *	7300		10000		17300
SF ₆	14100		19000		31000
HCFC-123	330	150	90	55	30
HCFC-124	1500	760	440	270	150
HFC-125	5200	4500	3400	2200	1200
HFC-134a	3100	1900	1200	730	400
HCFC-141b	1800	980	580	350	200
HCFC-142b	4000	2800	1800	1100	620
HFC-143a	4700	4500	3800	2800	1600
HFC-152a	530	250	150	89	49
CCl ₄	1800	1600	1300	860	480
CH ₃ CCl ₃	360	170	100	62	34
CF ₃ Br	5600	5500	4900	3800	2300
CHCl ₃	92		25		9
CH ₂ Cl ₂	54		15		5
CO	7	4	2	1	1
NOx (airplanes) □	253	118	68	44	25

* Different from the values given in IPCC, 1992.

□ Represents the net effect of changes in radiative forcing from reduced CH₄ and increased O₃ (see chapter 10). The GWPs for NOx are given on NO₂ basis.

APPENDIX A

The change in concentration of a gas with time due to production (photochemical and/or emissions) and loss (photochemical, deposition, heterogeneous loss) may be described by:

$$\frac{dC}{dt} = P - L \cdot C$$

where

C: Concentration

P: Production

L : Loss

τ : chemical lifetime

and $L = 1/\tau$

If P and L are assumed to be constant over the time of integration, this equation can be integrated to give:

$$C(t) = \frac{P}{L} + (C_0 - \frac{P}{L}) e^{(-\frac{t}{\tau})}$$

which equals

$$C(t) = C_1 + (C_0 - C_1) e^{(-\frac{t}{\tau})}$$

since $P/L = C_1$ at steady state ($t \gg \tau$).

Rearrangement yields:

$$C(t) - C_I = \frac{C_0 - C_I}{e^{\left(\frac{t}{\tau}\right)}}$$

At $t = 2\tau$

$$C(t) - C_I = \frac{C_0 - C_I}{e^2} \rightarrow$$

$$\frac{C(t) - C_I}{C_0 - C_I} = \frac{1}{e^2} \Rightarrow$$

$$\frac{C_I - C(t)}{C_0 - C_I} = -\frac{1}{e^2}$$

$$\frac{C_0 - C_I}{C_0 - C_I} + \frac{C_I - C(t)}{C_0 - C_I} = 1 - \frac{1}{e^2} \Rightarrow$$

$$\frac{C_0 - C(t)}{C_0 - C_I} = 1 - \frac{1}{e^2} \approx 0.86$$

Appendix B

Composition of the emissions of Non-Methane Hydrocarbons in the chemistry calculations (Tg/year).

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

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