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**Model studies of
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troposphere**

A summary of a
Dr.scient.-thesis

Jan S. Fuglestedt

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by

Jan S. Fuglestedt

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Model studies of indirect effects on climate through changes in the chemistry of the troposphere

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Jan S. Fuglestad

CICERO
Center for International
Climate and Environmental
Research - Oslo
University of Oslo
P.O. Box 1129 Blindern
N-0317 Oslo
Norway

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Acknowledgements

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The papers

Paper 1

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Paper 2

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Paper 3

Fuglestedt, J.S., Jonson, J.E. and Isaksen, I.S.A. 1994. Effects of reductions in stratospheric ozone on tropospheric chemistry through changes in photolysis rates. *Tellus*, 46B, 172-192.

Paper 4

Fuglestedt, J.S., Jonson, J.E., Wang, W.-C. and Isaksen, I.S.A. 1995. Responses in tropospheric chemistry to changes in UV fluxes, temperatures and water vapour densities. Presented at the NATO Advanced Research Workshop "Atmospheric Ozone as a Climate Gas", 19-23 June 1994, Lillehammer, Norway. Accepted for publication in the *NATO Advanced Science Institutes (ASI)* book "Atmospheric Ozone as a Climate Gas" (Eds. W.-C. Wang and I.S.A. Isaksen).

Paper 5

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INTRODUCTION AND SUMMARY

1. The role of atmospheric chemistry in the climate system - a short overview

The chemical composition of the atmosphere is a key factor in determining the global climate. Chemical constituents control the radiative balance of the Earth/atmosphere system due to interactions with both shortwave and longwave radiation. By absorption of terrestrial (longwave) radiation and re-emission at lower temperatures, the atmosphere is trapping radiative energy and thereby heating the surface-troposphere system. This mechanism keeps the surface about 33 °C warmer than it would otherwise be. The trapping of radiative energy, often referred to as "the greenhouse effect", is mainly due to the presence of water vapour, clouds and carbon dioxide (CO₂) in the atmosphere. Other gases such as methane (CH₄), nitrous oxide (N₂O) and ozone (O₃) also absorb and re-emit longwave radiation and contribute to the natural greenhouse effect. In addition to being radiatively active in the longwave region of the spectrum, ozone also absorbs solar (shortwave) radiation.

1.1 Changes in the concentrations of trace gases

Since pre-industrial times the atmospheric concentrations of several of these climate gases have changed significantly. Ice core analysis and direct atmospheric measurements indicate that the levels of CO₂ were approximately 280 ppmv at the end of the 18th century before the industrialisation, while the present levels are ~355 ppmv. Typical pre-industrial levels of CH₄ were 0.7 ppmv, but have now reached ~1.72 ppmv. The levels of N₂O have increased from about 275 ppbv to ~310 ppbv. The rates of change in the concentrations of CO₂, CH₄ and N₂O over the 1980s were 0.4, 0.8 and 0.25% per year, respectively (Intergovernmental Panel on Climate Change (IPCC), 1994) and the present levels of these gases are unprecedented for the last 200 000 years (Raynaud et al., 1993).

In addition to these changes, man's activities have introduced new gases to the atmosphere that significantly affect the fluxes of radiation. Of particular importance are the halocarbons containing fluorine, bromine or chlorine. For instance, the increases in the atmospheric concentrations of dichlorodifluoromethane (CFC-12) and chlorodifluoromethane (HCFC-22) in the 1980s were 4 and 7% per year, respectively (IPCC, 1994). In addition to their direct effect on the radiative balance, the weight of evidence suggests that the chlorine and bromine containing halocarbons also reduce the levels of ozone in the stratosphere. At mid-latitudes in the Northern and Southern Hemispheres the reductions in total-column ozone since 1979 are about 4 - 5% per decade according to observations (Bojkov, 1995). The reductions are higher during spring over the Antarctica where reductions in total ozone column up to 70% are reported (Bojkov, 1995). Heterogeneous chemical reactions involving halocarbon released chlorine and bromine and natural polar stratospheric particles are thought to be the main reason for the reductions in Antarctic ozone concentrations.

Observations of ozone in the *troposphere* are more scarce in time and space, but increases in free tropospheric ozone over the last 30 years are reported for several monitoring stations in the Northern Hemisphere (IPCC, 1994). There are also indications of increases in ozone since the early 1900s. Over the last decade, however, the trends are small or virtually zero. Observations and model studies together indicate that the amount of tropospheric ozone in the Northern Hemisphere may have doubled since pre-industrial times (IPCC, 1994). The enhancement is a result of increased emissions of the ozone precursors nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$), carbon monoxide (CO), methane and non-methane hydrocarbons (NMHC). In the Southern Hemisphere, observations are even more scarce, but reductions in tropospheric ozone since the mid-1980s are observed at the South Pole (IPCC, 1994).

The changes in the concentrations of CO_2 , CH_4 , N_2O , O_3 and halocarbons have increased the trapping of terrestrial radiation in the atmosphere and thereby enhanced the greenhouse effect above its natural level (IPCC, 1990, 1994). In addition, the fluxes in the shortwave region are affected by the changes in the concentrations of aerosols¹ and ozone. According to IPCC (1994) it is likely that the *net* effect of changes in stratospheric and tropospheric ozone since pre-industrial time also contributes to warming.

Model studies indicate that the concentrations of water vapour in the stratosphere may have increased since pre-industrial times. This is also supported by recent observations (Oltmans and Hofmann, 1995).

Increased concentrations of atmospheric aerosols have, according to model studies, reduced the amount of radiation reaching the surface due to scattering and absorption (Charlson et al., 1991; Kiehl and Briegleb, 1993; Taylor and Penner, 1994). Sulphur dioxide (SO_2) is chemically converted to sulphate that grow to sulphate aerosols. Increased emissions of SO_2 have therefore increased the atmospheric concentrations of aerosols, with additional contributions from other gases and aerosols from biomass burning and industry.

1.2 Radiative forcing of climate change

Several model studies indicate that longwave and shortwave changes in the radiative balance of the Earth/atmosphere may have significant effects on climate. A change in average net radiation at the tropopause, due to a change in the fluxes of either longwave or shortwave radiation, has been defined as a *radiative forcing of climate* (IPCC, 1990, 1994). A radiative forcing disturbs the balance between incoming and outgoing radiation at the tropopause, but over time a new balance is established as climate responds to the radiative forcing. A positive radiative forcing means that more energy is trapped by the troposphere, and this will have a warming effect on the coupled troposphere-surface climate system. A negative radiative forcing will have a cooling effect.

¹ Aerosols are gaseous suspensions of particles with diameter in the range 0.001 - 10 μm . These particles may or may not have water comprising a small to moderate fraction of their mass.

For a doubling of the atmospheric concentration of CO₂ from the pre-industrial level, a global mean radiative forcing of about 4 W/m² has been calculated (IPCC, 1994). When feedbacks in the climate system are taken into account, model studies indicate increases in global average surface air temperature at equilibrium between 1.5 and 4.5 °C (IPCC, 1990; 1992).

IPCC (1994) presents estimates of the direct radiative forcing from the changes in the individual gases since pre-industrial times, and these numbers are given in table 1. The total forcing from these changes are estimated to 2.45 (±15%) W/m².

Table 1. Contributions to direct radiative forcing since pre-industrial times (IPCC, 1994).

Gas	Radiative forcing from changes since pre-industrial times (W/m ²)
CO ₂	1.56
CH ₄	0.47
N ₂ O	0.14
CFC-11 (CCl ₃ F)	0.06
CFC-12 (CCl ₂ F ₂)	0.14
Other gases (mainly CCl ₄ , HCFC-22 and CFC-113)	0.08

Several studies have shown the importance of ozone as a climate gas through interactions with shortwave and longwave radiation, and through control of local stratospheric temperatures (e.g. Wang et al., 1980, and Lacis et al., 1990). There are some important differences between ozone and the greenhouse gases in table 1 as ozone itself is not emitted in significant amounts, but is produced through chemical reactions in the atmosphere. Furthermore, due to a lifetime in the order of a few weeks, there are, in contrast to long-lived gases such as CO₂ and N₂O, large spatial variations in the concentrations of ozone. The climate sensitivity to ozone changes reaches a maximum in the upper troposphere and lower stratosphere (Wang et al., 1980; Lacis et al., 1990). Estimates of global annual mean radiative forcing from changes in tropospheric ozone since pre-industrial times give a few tenths of a W/m² (IPCC, 1994, and references therein). Based on various results, a range of 0.2 to 0.6 W/m² is given by IPCC (1994). For example Hauglustaine et al. (1994a) have calculated changes in tropospheric ozone since pre-industrial times which result in a global annual average forcing equal to 0.55 W/m², with the largest contribution at Northern mid-latitudes. Wang et al. (1993) used ozone observations at Northern middle and high latitudes to study the climate implications of ozone changes. Their results indicate that increases in tropospheric ozone may give a local positive radiative forcing comparable to the effect of all other anthropogenically increased greenhouse gases. Berntsen et al. (1995) modelled the responses in ozone from increased emissions of NO_x, NMHC and CO in Asia. Using the 1980 emissions as reference, the anthropogenic emissions were doubled, which is expected to occur by the year 2000. From the changes in ozone they calculated a radiative forcing of

about 0.5 W/m^2 over large areas in Asia and a Northern Hemispheric average of 0.13 W/m^2 .

The radiative forcing from *observed* changes in stratospheric ozone during the period 1979 to 1990 is estimated to -0.08 to -0.09 W/m^2 (Ramaswamy et al., 1992; IPCC, 1992). Based on *model studies*, Hauglustaine et al. (1994a) calculate a positive forcing from changes in stratospheric ozone since pre-industrial times.

IPCC (1994) gives a radiative forcing of about 0.02 W/m^2 for the changes in stratospheric water vapour that may have followed from methane changes since pre-industrial times. This estimate is based on model calculations of changes in stratospheric water vapour and the confidence is low.

Increased concentrations of sulphate particles from SO_2 emissions have probably resulted in a negative forcing of climate. The increase in sulphate aerosols concentration since pre-industrial times has been estimated to result in a forcing in the range -0.3 to -0.9 W/m^2 (Charlson et al., 1991; Kiehl and Briegleb, 1993; Taylor and Penner, 1994). The direct effect due to aerosols from biomass burning is estimated to -0.05 to -0.6 W/m^2 (IPCC, 1994). There are large regional variations in the magnitude of the aerosol forcing. Aerosols may also affect the formation, lifetime and radiative properties of clouds (the *indirect* effect). For instance, aerosols may lead to a negative radiative forcing by enhancing cloud albedo. Quantifications of these effects are, however, highly uncertain. Preliminary estimates of changes in the radiative properties of clouds indicate a negative forcing that may be of similar magnitude to the direct forcing from the aerosols (IPCC, 1994).

1.3 Direct and indirect effects of emissions and climate feedbacks

Gases that are *emitted* to the atmosphere (hereafter source gases) may influence the radiative balance directly due to their radiative properties. Source gases may also give radiative forcing indirectly by changing the concentrations of other gases. The climatically relevant *source gases* may therefore be divided into three categories. Firstly, we have the gases that have a *direct* impact on climate due to their own radiative properties. Secondly, there are emissions of gases which have no or a negligible direct effect on climate, but which are *indirectly* affecting climate through impacts on chemical processes in the atmosphere. The concentrations of compounds interacting with shortwave and/or longwave radiation may thus be changed. Thirdly, we have the source gases that possess the ability of affecting climate both directly and indirectly. Table 2 shows examples of important source gases with direct and/or indirect impacts on climate.

Table 2. Overview of gases with direct and/or indirect effects on climate.

Emission of	Direct effects *	Indirect effects
Carbon dioxide (CO ₂)	X	
Hydrofluorocarbons (HCF)	X	
Perfluoromethane (CF ₄)	X	
Nitrous oxide (N ₂ O)	X	X
Methane (CH ₄)	X	X
Chlorofluorocarbons (CFC)	X	X
Hydrochlorofluorocarbons (HCFC)	X	X
Nitrogen oxides (NO _x = NO + NO ₂)		X
Non-methane hydrocarbons (NMHC)		X
Carbon monoxide (CO)		X

*) CO₂ and other gases marked only under "direct effects" do not affect the levels of other climate gases through chemical reactions in the atmosphere. They may however affect climate gases and aerosols through effects on atmospheric temperatures and humidity.

The most important radiatively active compounds that are influenced by indirect effects through atmospheric chemistry are²:

- Tropospheric ozone (O₃)
- Stratospheric ozone (O₃)
- Methane (CH₄)
- Stratospheric water vapour (H₂O)
- Aerosols
- Hydrofluorocarbons (HFCs)
- Hydrochlorofluorocarbons (HCFCs)

In addition to the effects of atmospheric chemistry on climate, the chemical processes in the atmosphere will be affected by changes in climate. Such couplings may constitute feedback mechanisms if the levels of climate gases are altered.

² The CFCs are indirectly affected by chemical processes since they are photolysed by UV radiation which is controlled by the overlying ozone column.

Climate change may affect chemistry through several mechanisms. For instance, changes in temperatures, water vapour levels or clouds may have significant effects on atmospheric chemistry processes. Figure 1 shows the principles for direct and indirect effects of emissions on climate, as well as climate feedbacks through atmospheric chemistry.

Climate change will also influence atmospheric composition through impacts on source strengths of several gases. For instance, important sources of CH₄ are sensitive to temperature, soil moisture and the level of the water table. These mechanisms work through changes in factors external to the atmospheric chemistry system and are not addressed in this thesis.

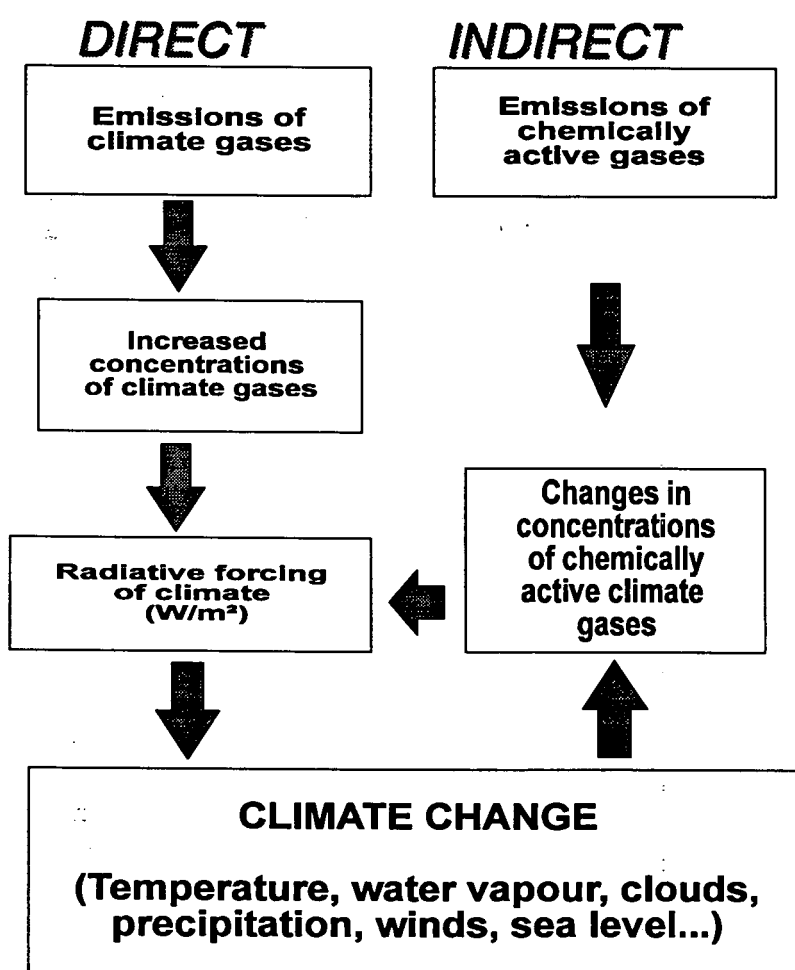


Figure 1. The principles for direct effects, indirect effects and climate feedbacks through atmospheric chemistry.

Indirect effects on climate are called *positive* if they result in a positive radiative forcing of climate. Correspondingly, they are termed *negative* if they lead to a negative forcing. Feedback mechanisms that *amplify* an initial perturbation of climate are termed *positive*, while those *dampening* the perturbations are called *negative*.

2. Climatically relevant compounds affected by chemical processes

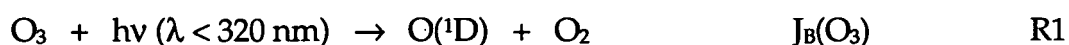
Chemical processes can affect the radiative balance and climate in several ways. In affecting the *oxidizing capacity of the atmosphere*, a feature of basic importance for the composition of the atmosphere is disturbed. Oxidation is necessary for the removal of gases from the atmosphere and prevents accumulation. Changes in the oxidation capacity may therefore affect the levels of climate gases. Furthermore, the levels of tropospheric and stratospheric *ozone* are controlled by chemistry, in addition to physical and meteorological processes. In the stratosphere, *water vapour* exerts a significant greenhouse effect, and the levels are controlled by transport from the troposphere and by chemistry. *Aerosols* are produced when SO₂ and other gases undergo chemical transformation in the atmosphere. A short overview of the mechanisms by which the oxidizing capacity and the levels of climatically relevant compounds may be affected by chemistry is given below.

2.1 Gases determining the oxidizing capacity of the atmosphere

Many of the gases emitted to the atmosphere are reduced (e.g. CH₄) or not fully oxidized (e.g. CO and NO). In the atmosphere, the source gases are oxidized and converted to forms that can be removed by dry and/or wet deposition. Thus, the atmosphere serves as an oxidizing component of the biogeochemical system. Consequently, the oxidizing capacity of the atmosphere determines the lifetimes of the reduced or partially oxidized species and is critical for sustaining the biogeochemical cycles. Several gases are also dissociated by solar radiation and are thereby converted to products that may undergo further transformation or removal. The oxidizing capacity of the atmosphere is determined by the concentrations of the reactive oxidants hydroxyl radicals (OH), ozone (O₃), nitrate radicals (NO₃), excited state atomic oxygen, (O(¹D))), hydroperoxyl radicals (HO₂), organic peroxy radicals (RO₂), hydrogen peroxide (H₂O₂), ground state atomic oxygen (O(³P)) and organic peroxides (ROOH). The concentrations of these oxidants are many order of magnitude lower than the concentration of O₂, but the high reactivities of these gases explain their importance for the oxidizing capacity.

The main oxidizing agent in the gas phase is the hydroxyl radical, OH. Other species such as the excited oxygen atom O(¹D)), the nitrate radical, NO₃, and ozone also contribute, but they are less important. The main mechanisms for degradation of gases in the stratosphere are photolysis or reactions with O(¹D)) or OH. For tropospheric species dissolved in the aqueous phase, the most important oxidizing species are O₃, H₂O₂ and OH.

OH is produced in the gas phase when ozone is photolysed in the presence of water vapour:

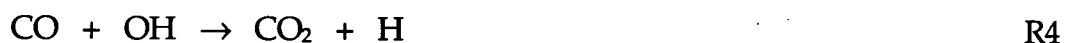


(where $J_{\text{B}}(\text{O}_3)$ is the photolysis rate.)

Most of the excited oxygen atoms that are produced from R1 are energetically stabilized by air molecules (mainly N₂ and O₂) to ground state oxygen, O(³P), which reacts with O₂ to yield ozone again. A few percent of the total loss of O(¹D), however, occur through the reaction with water vapour (R2) which yields two OH radicals.



The hydroxyl radical is extremely reactive. It is responsible for the transformation and initiation of the removal of many important atmospheric trace gases. For instance, the main sinks for CH₄ and CO are reaction with OH:



Since methane is an important greenhouse gas, changes in OH may indirectly lead to radiative forcing. Other gases with strong absorption characteristics, such as HCFCs and HFCs, are also degraded after reaction with OH. Several sulphur containing species also react with OH. Gas phase reaction between SO₂ and OH leads to production of sulphate aerosols.

The reaction between NO₂ and OH,



constitutes a main sink for NO_x since most of the HNO₃ undergoes rapid heterogeneous removal in the troposphere.

In the reactions between OH and CO (R4), CH₄ (R3) and NMHC the production of tropospheric ozone is initiated, since HO₂ and RO₂ radicals are produced in later steps (see next section). OH is re-produced when HO₂ reacts with NO or O₃. Thus OH and HO₂ are strongly coupled and this is important for perturbations of OH since a major part of the loss of odd hydrogen (H + OH + HO₂) in the free troposphere proceeds via reactions involving both OH and HO₂:



or through



followed by



or

$\text{H}_2\text{O}_2 \rightarrow$ heterogeneous removal

R9

In regions where the levels of NO_x are high, reaction R5 constitutes an important sink of OH.

HO_2 and RO_2 are not efficient oxidants in the gas phase, but by oxidizing NO to NO_2 they are prerequisites for the production of tropospheric ozone (see next section). RO_2 also produce organic nitrates in reactions with NO. These reactions may act as sinks of NO_x . There are however also indications that the RONO_2 species formed may act as reservoirs of NO_x .

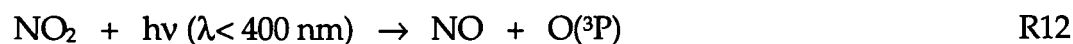
Nitrate radicals, NO_3 , are produced when ozone reacts with NO_2 :



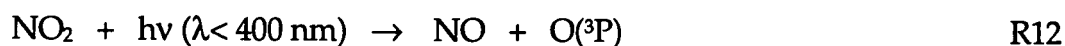
Since NO_3 is readily photolysed, it can only be of importance during night-time and in the polar night. Then the OH levels are very low, and NO_3 may have the role as the main oxidizing species. The reaction rates between NO_3 and hydrocarbons are generally much lower than for the corresponding OH reactions. But NO_3 reaches higher concentrations than OH does. NO_3 may therefore be important for the removal of hydrocarbons in the absence of sunlight. NO_3 initiates oxidation chain reactions that produce HO_2 and RO_2 , and thereby provides a source of OH at night.

2.2 Tropospheric ozone

A dominating way of oxidizing NO to NO_2 is through reaction with ozone. In the presence of radiation with wavelengths shorter than 400 nm, NO_2 is photolysed to NO and ground state atomic oxygen. The latter species may recombine with molecular oxygen to yield ozone:



In this sequence ozone is consumed and produced and the result is no net change in ozone. But if other gases than O_3 can accomplish the oxidation of NO to NO_2 , ozone may be produced in further reactions. Hydroperoxyl radicals (HO_2) or alkylperoxy radicals (RO_2), mainly produced from reactions between OH and CO, CH_4 or NMHC, may convert NO to NO_2 without loss of O_3 (R15 and R16 given below). Ozone will then be produced through the following sequence of reactions:

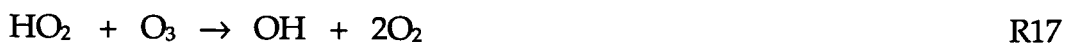


Alkylperoxy radicals convert NO to NO₂ by reaction R16 which is analogous to R15:



The sequence of reactions given above (S1) shows that NO, solar radiation (for photolysis of NO₂ and of O₃ to produce OH), and HO₂ or RO₂ (for NO/NO₂ conversion) are necessary for tropospheric production of ozone. OH is required since it provides HO₂ and RO₂ radicals.

Ozone may also react with HO₂ which constitutes an important loss reaction for O₃:



Ozone is also lost through reaction R18 which is less important than R17:



Whether O₃ is lost or produced during daytime depends on the competition between the important ozone loss reaction R17 and reaction R15 which is the rate determining reaction in the ozone producing sequence S1. The levels of NO control which reaction will dominate, and thus NO plays a key role for the ozone budget (Crutzen, 1987). When the ratio [NO]/[O₃] is larger than the ratio between the reaction rate constants (k₁₇/k₁₅) there is a net production of ozone. If the ratio is smaller than this value, ozone loss through the sequence below is dominating:



For an ozone mixing ratio of 20 ppbv, there will be net O₃ production if NO is larger than approximately 5 pptv. This threshold value is temperature dependent and may also be larger due to other ozone loss reactions such as R1 and R2. However, in large parts of the troposphere the levels of NO are high enough to give net production of ozone when CO and hydrocarbons are oxidized.

If the levels of NO_x are very high, emissions of NO_x may lead to ozone loss due to removal of the oxidation initiating OH radicals through reaction R5. Consequently less NO₂ is available for photolysis and ozone production. Furthermore, since OH is lost, the production of HO₂ and RO₂ and thereby also ozone production will be inhibited. Ozone may also react with NO₂ to yield NO₃ (R10) which may be converted to N₂O₅ when sunlight is absent. This may represent an ozone loss since NO₃ and N₂O₅ may be scavenged and converted to HNO₃ which is rapidly removed heterogeneously. NO_x emissions may in this way also reduce the levels of ozone.

Ozone is also lost by deposition at the Earth's surface, through reaction with unsaturated hydrocarbons and through uptake and chemical reactions in the aqueous phase.

2.3 Stratospheric ozone

In the *stratosphere*, ozone is generated by photodissociation of molecular oxygen, O₂, followed by the combination of ground state oxygen atoms with O₂:



Stratospheric ozone is lost through reactions involving only oxygen species (Chapman chemistry) and through catalytic cycles involving nitrogen species from N₂O, odd hydrogen from CH₄ and H₂O, and chlorine and bromine species from halocarbons. Increased emissions of N₂O, CH₄, CFCs, HCFC, carbon tetrachloride (CCl₄), methyl chloride (CH₃Cl), methyl chloroform (CH₃CCl₃) as well as halons and methyl bromide (CH₃Br) may thus increase the loss of stratospheric ozone. Heterogeneous reactions taking place on particles (e.g. ice crystals in polar clouds or sulphate particles) have been found to increase the loss of ozone significantly. In these reactions chlorine is transformed from reservoir species to active forms with respect to ozone destruction. In addition, nitrogen species are removed, thereby reducing the damping effect of nitrogen compounds on the role of chlorine species. Enhanced levels of sulphate particles from the eruption of Mt. Pinatubo have increased the ozone depleting effect of chlorine species from halocarbons (McCormick et al., 1995).

As noted in section 1, the reductions in stratospheric ozone since the late 1970s have probably led to a negative radiative forcing of climate. Radiative forcing from ozone changes is very sensitive to the altitude profile of the changes. Changes in stratospheric ozone give radiative forcing through changes in absorption of solar

radiation, stratospheric temperatures and in absorption and emission of longwave radiation.

The reductions in stratospheric ozone may also affect climate through the impacts on tropospheric chemistry via changes in the UV fluxes reaching the troposphere. The rates of several photolytic reactions will be affected. The photolysis of ozone (R1) is very sensitive to changes in the overhead ozone column. Through the reactions R1 and R2, solar radiation is the driving force of tropospheric chemistry. By affecting the photolysis rate $J_B(O_3)$ for reaction R1, reductions in stratospheric ozone will increase the rate of OH production, which will propagate to changes in several other key species in the chemistry. The loss rate of methane and other climate gases will increase. The levels of tropospheric ozone will also be affected, mainly due to increases in the photolysis rate of ozone and higher levels of HO_2 .

This illustrates one of several linkages between the stratosphere and the troposphere. Furthermore, the oxidizing processes in the troposphere influence the amount of trace gases that reaches the stratosphere. In addition to these couplings through radiative and chemical processes, there are several important dynamical linkages. The input of stratospheric air rich in O_3 (and NO_x) at middle and high latitudes is important for the chemical properties of the troposphere. Likewise, the input of tropospheric air to the stratosphere at lower latitudes significantly affects the stratospheric chemical and radiative processes.

2.4 Stratospheric water vapour

Water vapour in the stratosphere contributes to the greenhouse effect. Water vapour is transported across the tropopause, and in the lower stratosphere this is the main mechanism controlling the H_2O levels. At higher altitudes, however, oxidation of methane is an important source. Approximately 2 water molecules are produced per CH_4 molecule oxidized. The climate sensitivity to changes in stratospheric water vapour is largest in the lower stratosphere, but at these altitudes the oxidation of methane is of minor importance, except at higher Northern latitudes in winter/spring. Estimates of the radiative forcing from increases in stratospheric water vapour due to CH_4 degradation show large variation between various models (from ~1% to almost 40% of the direct forcing from CH_4).

2.5 Aerosols

Several studies have emphasized the importance of aerosols in the context of climate change (e.g. Charlson et al., 1991; Taylor and Penner, 1994). Sulphate aerosols are formed when SO_2 or other sulphur containing gases are oxidized in the gas phase by OH, or when SO_2 is oxidized in the liquid phase where O_3 and in particular H_2O_2 are important oxidizing species. Higher levels of OH may therefore increase the gas phase production of sulphate that further leads to production of new sulphate aerosols. These aerosols also act as cloud condensation nuclei (CCN). It has been suggested that increases in OH may in this way affect the optical properties of clouds. Tuomi et al. (1994) modelled changes in the production of

CCN from the increases in OH that follow from enhanced UV-B radiation due to stratospheric ozone depletion. They found a negative forcing that could be of the same size as the forcing from the changes in stratospheric ozone. But, as pointed out by Isaksen (1994), the links between OH perturbations and climate effects of changes in cloud properties are very uncertain.

There are also other substances contributing to enhanced levels of tropospheric aerosols. Nitrates and organic matter from biogenic volatile organic carbon, and dust and soot from biomass burning also increase the concentrations of aerosols (IPCC, 1994).

As for tropospheric ozone, there are large regional variations in the changes of the aerosol concentrations. While the forcing from aerosols and tropospheric ozone are of opposite sign, the broad spatial pattern may be similar, due to the nature of the sources of SO₂ and ozone precursors.

2.6 Processes affecting climatically relevant compounds

The tropospheric concentrations of the *climatically relevant and chemically active compounds* considered above may change in response to several types of perturbations. They may be affected by *emissions* and the following chemical responses. They may also be affected by changes in the flux of *UV radiation* reaching the troposphere. Furthermore, the levels of radiatively and chemically active compounds may be altered as a consequence of *climate change*. This may occur through changes in atmospheric variables and processes (i.a. temperatures, water vapour, clouds, circulation pattern, precipitation), or through changes in source and sink strengths. While increased levels of the greenhouse gases CO₂, CH₄, N₂O and halocarbons warm the troposphere, they have a cooling effect on the stratosphere. In both cases, chemical reaction rates and meteorological processes may be affected. If an initial change in climate affects the concentrations of radiatively active gases or aerosols, such couplings form feedback mechanisms in the climate system. Both positive and negative feedbacks are conceivable when atmospheric chemistry or sources and sinks are affected.

3. Modelled effects of emissions, stratospheric ozone depletion and climate change on tropospheric chemistry

In this thesis the effects of emissions, stratospheric ozone depletion and climate change on tropospheric chemistry are studied (figure 2). Improved knowledge of such relations is necessary for the evaluation of which mechanisms that are important to build into models that include chemistry, radiation and dynamics. Main focus is given to the responses in tropospheric O_3 , OH and CH_4 and to how sensitive these gases are to the considered perturbations. In figure 2 the shaded arrows indicate the mechanisms studied in this thesis. The relations given by the white arrows are based on results from other studies.

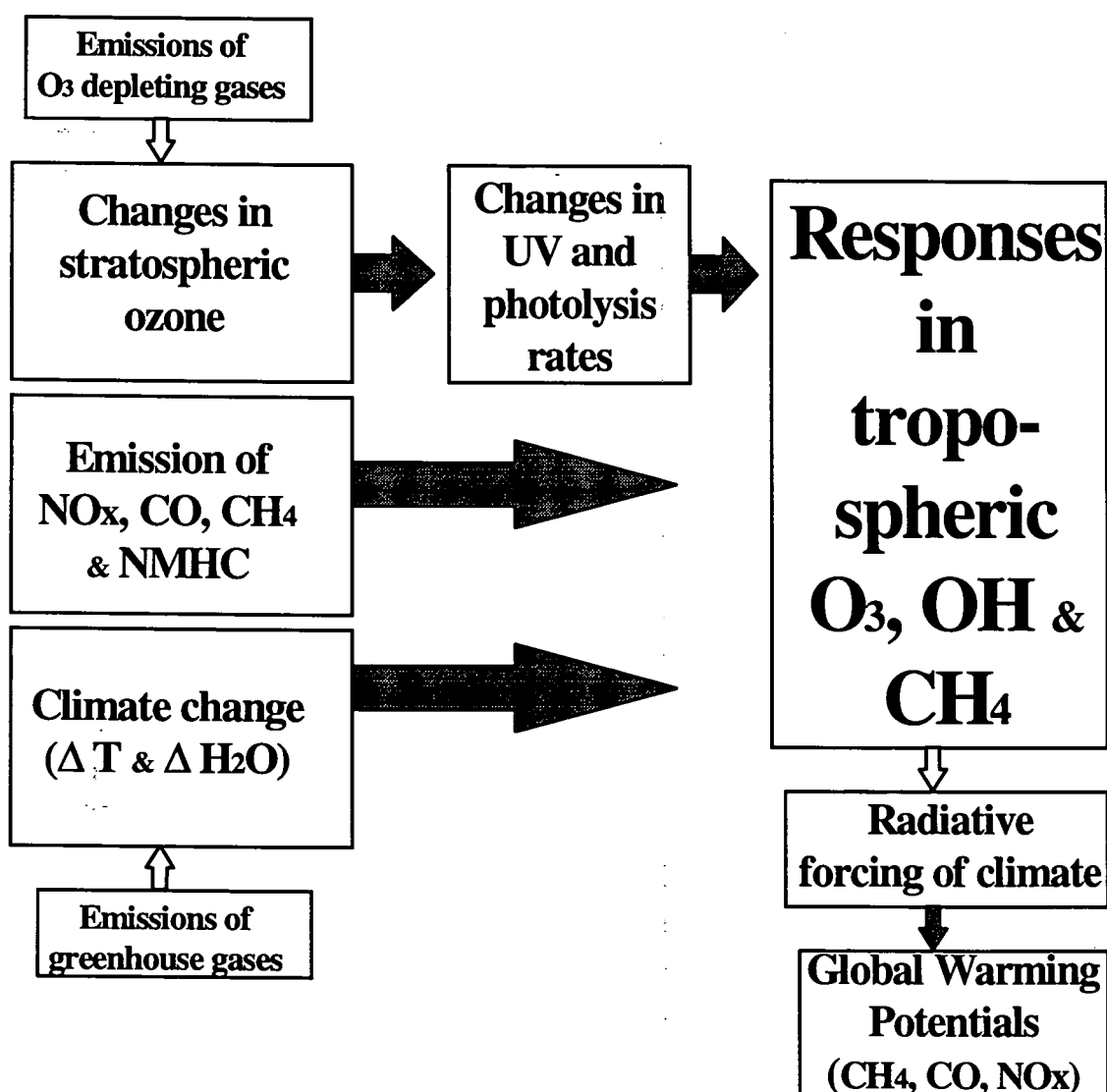


Figure 2. Considered mechanisms for perturbations of tropospheric chemistry.

3.1 The main tool: A two-dimensional model of the global troposphere

A two-dimensional (2D) chemistry/transport model of the global troposphere is used in the studies of the chemical responses. The first version of the model was developed by Isaksen and Rodhe (1978) and then used to study the water budget and the distribution of SO₂ and sulphate in the troposphere. It was applied by Rodhe and Isaksen (1980) to estimate the tropospheric distribution of sulphur compounds resulting from natural emissions of H₂S and DMS and man-made emissions of SO₂. A more comprehensive chemistry scheme was developed by Isaksen et al. (1978a,b) and Hesstvedt et al. (1978) and used in studies of ozone generation in rural and urban regions as well as in comparisons of numerical schemes for modelling of oxidants. The chemistry module applied in these studies was later integrated to the global 2D model and Isaksen (1980) used the 2D model to study the tropospheric ozone budget and possible man-made effects. Isaksen et al. (1985) applied the model in an analysis of the measured concentration of organic gases in the Norwegian Arctic, and Isaksen and Hov (1987) calculated trends in the concentrations of O₃, OH, CO, CH₄ and NO_x for different assumptions about the development of source gas emissions. Berntsen et al. (1989) used the model for calculations of past changes and for future scenarios.

The model is zonally averaged with a meridional resolution of 10 degrees and a vertical resolution of 0.5 km below 3.25 km and 1.0 km above, up to 16.25 km. The results presented here are calculated with a version using advective winds from Newell et al. (1972) and diffusion coefficients from Hidalgo and Crutzen (1977), with some small modifications (see also Isaksen and Hov, 1987). The numerical scheme for advection, given by Smolarkiewicz (1983), is an upwind scheme with corrective steps to reduce implicit numerical diffusion. Meteorological data are seasonally averaged. The photodissociation rates have a diurnal variation (calculated each hour), and the J-value sets are changed each month. The chemistry is gas-phase with first order heterogeneous scavenging of soluble species by rain and clouds and adsorption on aerosols included. The chemistry scheme is divided into two parts. In the first part, which is used during the first day of each month, all chemical compounds (49) are calculated, with a one hour time step. At the same time, diurnally averaged production and loss terms are calculated based on the diurnal calculations. These averaged terms are then used for the remaining days of the month with a time step of one day in the calculations of the diurnal concentrations. In this way the model resolves the diurnal variation in the concentrations of the short-lived species due to the diurnal variation in the photolysis rates, and thereby derives properly diurnally averaged production and loss terms, which are important due to the non-linear terms in the chemical production and loss terms. The numerical integration procedure applied to solve the set of time dependent differential equations deduced from the chemical reaction scheme, is the quasi steady state approximation (QSSA) method developed by Hesstvedt et al. (1978).

The reaction rate constants were updated for the studies in paper 1, 2 and 5, and later the chemistry scheme was updated for paper 3 and 4 according to the latest compilations. The full set of chemical reactions with rate constants and references

used for paper 3 and 4 are given in Appendix A to paper 3. Deposition velocities for 6 components (O_3 , HNO_3 , NO_2 , PAN, CO and H_2O_2) are included, and Appendix B in paper 3 gives the deposition velocities for land, sea and snow/ice.

The input of NO_x , HNO_3 and O_3 from the stratosphere to the troposphere are calculated with a global two-dimensional (2D) chemistry/transport model extending from ground level to 50 km. For a description of the model see e.g. Stordal et al. (1985) or Isaksen and Stordal (1986). The fluxes from the stratosphere are changed each season. The emissions of isoprene also have seasonal variation, while all other emissions are kept constant over the year.

In some of the studies in this thesis input from other models have been used. The photolysis rates are calculated by the algorithm by Isaksen et al. (1977), and in paper 3 and 4 the modifications given by Jonson and Isaksen (1991) are taken into account. Vertical ozone distributions are calculated with the global stratospheric two-dimensional model mentioned above. The stratospheric model is run with heterogeneous chemistry between the gaseous phase and polar stratospheric clouds (PSCs) and background particles. In paper 3, time dependent calculations with the same 2D model are also performed to obtain changes in ozone column densities.

In the study of effects of increased temperatures and water vapour levels, model results from a work by Wang et al. (1992) were applied. The experiments were performed with a 3D climate model consisting of the National Center for Atmospheric Research community climate model (version one) for the atmosphere and a simple mixed-layer for the oceans (see Wang et al., 1991; 1992).

In the calculations of radiative forcing from changes in ozone and methane performed by Wang and his group (in paper 5) the same radiative model as in Wang and Molnar (1985) and Fisher et al. (1990) was applied.

3.2 Effects of emissions

The sensitivities of the chemical responses in the troposphere to changed emissions of source gases are studied in paper 1 and 2. While the former paper focuses on modelling the methane oxidation in a 2D model (together with a general discussion of models), the effects of isolated and combined changes in emissions of NO_x , CO, NMHC in addition to CH_4 were considered in paper 2. Parts of this work were also presented in Chapter 5, "Tropospheric Processes: Observations and Interpretation", by Isaksen et al. (1992) in the WMO report "Scientific Assessment of Ozone Depletion: 1991" (WMO, 1992). There it formed, together with contributions from other researchers and groups, the basis for the discussion and the conclusions drawn. Paper 2 gives a somewhat broader and more thorough presentation and discussion of the study and the results than paper 1 and Isaksen et al. (1992).

The model studies in paper 2 give increases in the tropospheric averages of O_3 in response to increased emissions of NO_x , CO, CH_4 and NMHC. The efficiencies in

increasing the tropospheric annual average of ozone differ significantly between the gases on a mass basis, with NO_x having the largest values (table 3).

Table 3. The efficiencies of the source gas emissions in increasing tropospheric annual average levels of O₃ given relative to the efficiency of doubling the methane emissions.

	2 x NO _x	2 x CH ₄	2 x CO	2 x NMHC	1.1 x NO _x	1.1 x CH ₄	1.1 x CO	1.7 x NO _x from aircraft
Efficiency relative to 2 x CH ₄	3.0	1.0	0.20	0.58	4.1	1.2	0.22	50

The sensitivities are larger for smaller increases in emissions. For NO_x, the efficiency in increasing ozone is almost 40% larger for a 10% increase in emissions compared to a doubling of the emissions. The corresponding numbers for CH₄ and CO are 20% and 10%, respectively. The sensitivity to increased *NO_x emissions from aircraft* are found to be much higher than for *ground emissions* of NO_x. Depending on whether the results are compared to a doubling or a 10% increase of the *ground emissions*, the increase in *aircraft emissions* is 12-17 times more effective in enhancing O₃. When the aircraft emissions were increased from zero to the present levels, the ozone enhancements were larger, owing to the non-linear effects of NO_x on ozone. In spite of the low contribution from aircraft to the global emissions of NO_x, this source may have significant effects on tropospheric ozone. Similar enhancements in the ozone production efficiency from aircraft emitted NO_x relative to surface emitted NO_x were also found by Johnson et al. (1992) and Hauglustaine et al. (1994b) (20 and 9 times more effective, respectively).

The spatial distributions of ozone changes from increased emissions of NO_x and CH₄ are quite different, with CH₄ having a more uniform effect on ozone throughout the troposphere. The effects of NO_x emissions are more confined to the regions where the emissions take place. This difference is due to the much shorter lifetime of NO_x (hours to a few days) than of methane (~10 years).

Paper 2 also focuses on the importance of the background levels of NO_x for the effects of changed emissions on ozone. Lightning is an important source of NO_x in the background troposphere and the significance of the NO_x levels was elucidated by assuming different strengths of the lightning source. The tests revealed that higher background levels of NO_x *reduce* the efficiency in ozone enhancement from increased NO_x emissions markedly. Enhanced emissions of methane increase ozone slightly *more efficiently* with higher background levels of NO_x.

The changes in the emissions of the various gases also affect the concentrations and distribution of OH. With respect to tropospheric mean values, increased emissions of CO, CH₄ and NMHC reduce OH, while increased emissions of NO_x increase

OH. Through the effects on OH, these changes also affect the concentration of methane: Increased emissions of CO, CH₄ and NMHC increase CH₄, while increased NO_x emissions decrease the CH₄ levels. In a test where all the emissions were changed simultaneously, these opposite effects balanced each other with respect to the *annual global tropospheric mean concentration* of OH, but gave significant changes in the spatial distribution of OH. In this test the NO_x emissions from aircraft and surface sources were reduced by 60% and 40%, respectively, CO and NMHC emissions by 20% each, while the CH₄ emissions were reduced by 15%.

Through the impacts on OH, methane affects the strength of its own main sink. This gives a feedback between concentrations and loss. For a 10% increase in emission the relative increase in the global mean concentration was estimated to be ~35% larger. For a doubling of the methane emissions, the feedback strength was estimated to ~50%. With a 2D model of the troposphere, stratosphere and the mesosphere that interactively couples dynamics, radiation and chemistry, Hauglustaine et al. (1994c) calculate a feedback strength of 40% for a doubling of the CH₄ emissions.

The signs of the effects on the concentrations of O₃ and OH and on the lifetime (τ) of climate gases controlled by OH are summarised in table 4.

Table 4. Impact of emissions on tropospheric annual averages of gases affecting climate. (+ gives increases in global averages, - gives decreases).

Emissions of	O ₃	OH	τ (CH ₄ , HCFC, HFC)
CH ₄	+	-	+
NO _x	+	+	-
CO	+	-	+
NMHC	+	-	+

The results indicate that the indirect effects of emissions of CH₄, CO and NMHC on climate may be positive. This is due to a positive effect on the ozone levels, and a negative effect on OH, thereby increasing the lifetimes and concentrations of greenhouse gases removed by OH. For NO_x, however, the effects on O₃ and OH work in opposite directions. Increased emissions of NO_x have a positive indirect effect through increased O₃ levels, but also a negative effect through increased OH levels and thereby reduced lifetime of CH₄.

In paper 1 and 2 the indirect effects of emissions were only quantified with respect to changes in the concentrations of O₃ and CH₄ and the following effects on the radiative balance were not considered. Later the results formed the basis for calculations of radiative forcing from the changes in these two climate gases in response to changes in emissions. These calculations were performed by the group

of Prof. Wei-Chyung Wang at State University of New York at Albany. Based on these results, Global Warming Potentials (GWPs) for emissions of CH₄, CO and aircraft emissions of NO_x that take into account the considered indirect effects were estimated. For NO_x from surface sources, only the radiative forcing from changes in O₃ and CH₄ were calculated, and not GWP values. Since the effects of NO_x on O₃ and OH (and thereby on CH₄) are highly dependent on the geographical location of the sources due to short lifetime and non-linear chemical responses, the GWP concept is not suited for NO_x from surface sources.

In addition to the indirect effects of CH₄ emissions mentioned above, the forcing from changes in stratospheric water vapour was also considered based on published results. All these indirect effects are positive, and our estimate in paper 5 suggests that the indirect effects added up are of the same magnitude as the *direct* radiative forcing from changes in CH₄.

For NO_x emitted from *aircraft*, the positive radiative forcing from ozone changes is significantly larger than the negative forcing from changes in CH₄. It was therefore concluded that the *net* effect of NO_x emitted from aircraft is positive. Our estimates also indicate that, per mass unit of emissions, the climate impact of NO_x emissions from aircraft is large compared to other source gases. Contrary to the emissions from aircraft, *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 reductions in CH₄ is therefore larger than in the case of NO_x emitted from aircraft. The estimated *net* forcing is slightly negative since the positive ozone forcing is somewhat smaller than the negative forcing from CH₄ reductions. This estimate depends on the geographical pattern of changes in NO_x emissions and may also be model dependent. These results should therefore be considered highly uncertain and preliminary. Nevertheless, the results point to the dual role of NO_x emissions on climate gases in the troposphere.

In the calculations of GWPs, sustained step function increases in emissions were applied and not pulses as in the definition of GWPs given by IPCC (1990, 1992). GWPs based on the sustained emission approach for the direct effect of CH₄ were taken from Wigley and Osborn (1994). The estimated GWP values are given in table 5.

Table 5. Calculated GWPs for CH₄, CO and NO_x for different time horizons.

Gas	Time horizon (years)				
	20	50	100	200	500
CH ₄ (direct) ^{a)}	35	24	16	10	6
CH ₄ (direct and indirect)	75	53	36	23	13
CO	10	6	3	2	1
NO _x from aircraft (N basis)	1576	751	441	268	148

a) From Wigley and Osborn (1994).

3.3 Effects of changes in stratospheric ozone

Emissions may also have indirect effects on climate through impacts on stratospheric ozone. In addition to the radiative forcing from changes in shortwave and longwave radiation induced by changes in stratospheric ozone, the enhanced fluxes of UV-B radiation will increase photolysis rates and lead to changes in tropospheric ozone and methane, as well as in other climatically relevant gases. Both mechanisms lead to indirect effects of ozone depleting source gases.

In paper 3 and 4 the sensitivity and the response of the tropospheric chemistry to changes in UV-B radiation from ozone depletion were studied. In paper 3, photolysis rates for 1970, 1980, 1990, 2000 and 2050 were calculated based on ozone column observations and model calculations of changes in stratospheric O_3 , and both steady state and time dependent calculations were performed in the studies of the tropospheric response. The time dependent calculations of the ozone column densities for 1980 and 1990 are based on reported emission data for gases affecting stratospheric ozone. The calculated ozone columns for the year 2050 are based on scenario A, described in chapter 8 in WMO (1992). For the year 2000 the scenario is adjusted to take into account the accelerated phase out of the ozone depleting substances which is expected to occur as a result of the agreement that was reached in Copenhagen in December 1992 by the parties to the Montreal Protocol. A linear interpolation is adopted for the intermediate years.

It was shown that reductions in stratospheric O_3 , and the following increase in the fluxes of UV-B into the troposphere, lead to significant increases in photodissociation rates for some gases. In particular, large increases were found in the photolysis rate of O_3 ($J_B(O_3)$) that initiates OH production. The relative increase in the photolysis rate is larger than the relative decrease in stratospheric ozone. The model studies showed that the effects of increased OH production through R1 and R2 are damped due to the coupling between OH and HO_2 (cf. section 2.1) and other interactions between tropospheric chemical key species.

The calculations gave reductions in tropospheric ozone in most regions in response to increased UV-B radiation, but the percentage reductions in tropospheric ozone are significantly smaller than the percentage increase in UV-B. However, at middle and high Northern latitudes during spring, there were increases in tropospheric O_3 in response to increased UV-B, which may be explained by high levels of NO_x and other ozone precursors accumulated during winter. The magnitude of the changes in ozone varies considerably with region and time of year.

Through increases in OH, the global level of CH_4 is reduced. But the relative changes in methane are found to be less than the relative changes in the global average of OH since the largest relative OH changes take place outside the region of most importance for the methane oxidation (low altitudes and low latitudes). Because of its long lifetime, the maximum effect on the methane level is delayed by ~10 years. The results indicate that increased UV-B fluxes due to reduced ozone columns may have contributed by approximately 1/3 of the observed reduction in

the growth rate of methane. Reduced emissions of methane itself is likely to be the dominating factor for the reductions in the growth rate.

In Figure 3 (from paper 3) the ratio between the global annual averages of total O_3 , $J_B(O_3)$, OH, CH_4 and tropospheric O_3 from scenarios with and without changes in stratospheric ozone and UV-B are plotted as function of time (i.e. $r_g(t) = c_g^*(t)/c_g(t)$, where the asterisk indicates that changes in UV-B are taken into account and g denotes the gas). The global levels of tropospheric O_3 and OH respond in the same year as the changes in total ozone and J-values take place, while the maximum response in CH_4 levels is delayed by ~ 10 years. The responses in tropospheric O_3 are generally delayed by some weeks relative to when the largest reductions in stratospheric O_3 take place. The response time at high Southern latitudes is ~ 2 months. At high and middle Northern latitudes the situation is different. Here the stratospheric reductions reach maximum in March and the increase in tropospheric O_3 reaches maximum in April. After that, the sign of the response is reversed, with the largest reductions occurring in June.

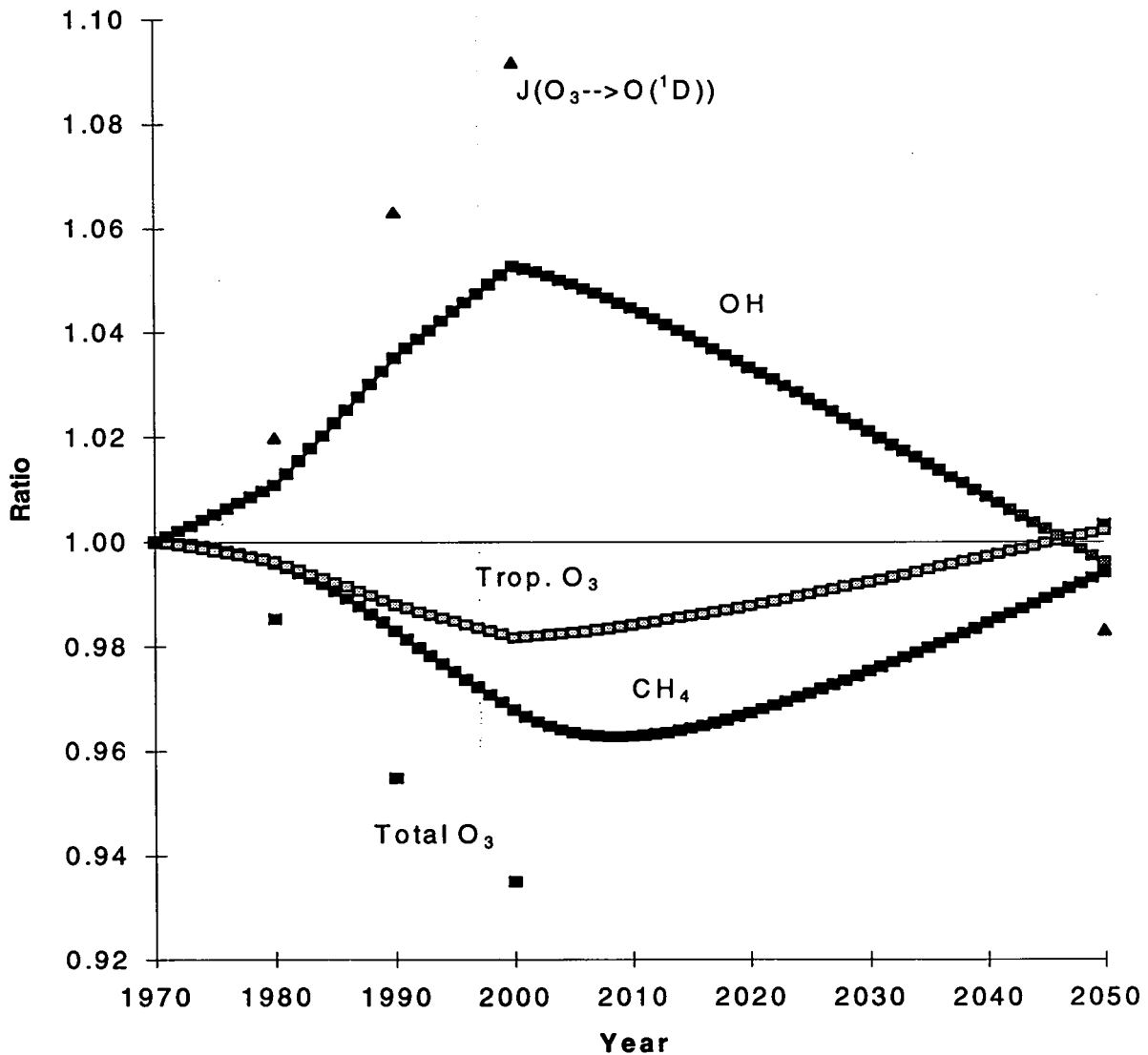


Figure 3. The ratio between the levels in total O_3 , $J_B(O_3)$, CH_4 , and tropospheric O_3 between a scenario with changes in UV-B and a scenario without such changes, as function of time.

Since significant changes in OH are calculated, it may be speculated that changes in UV-B radiation can increase the gas phase oxidation of SO₂ to sulphate particles, which may further affect the radiative balance. Increased levels of H₂O₂ are also calculated, but the magnitude of the responses varies considerably in space and time, with the largest responses during spring.

In paper 3 the changes in stratospheric ozone were calculated with a 2D chemistry/transport model of the stratosphere. In paper 4, on the other hand, the calculated changes in UV-B and photolysis rates were based on *observed* reductions in stratospheric ozone. Total ozone levels from TOMS (Total Ozone Mapping Spectrometer) measurements were applied, and the effects of changes over the period June 1979 through May 1994 were studied.

Figure 4 (from paper 4) shows the observed development in global total ozone and the calculated development in model domain average of the dissociation rate of O₃ that yields O(¹D). Both are given as annual averages normalized to 1979 levels.

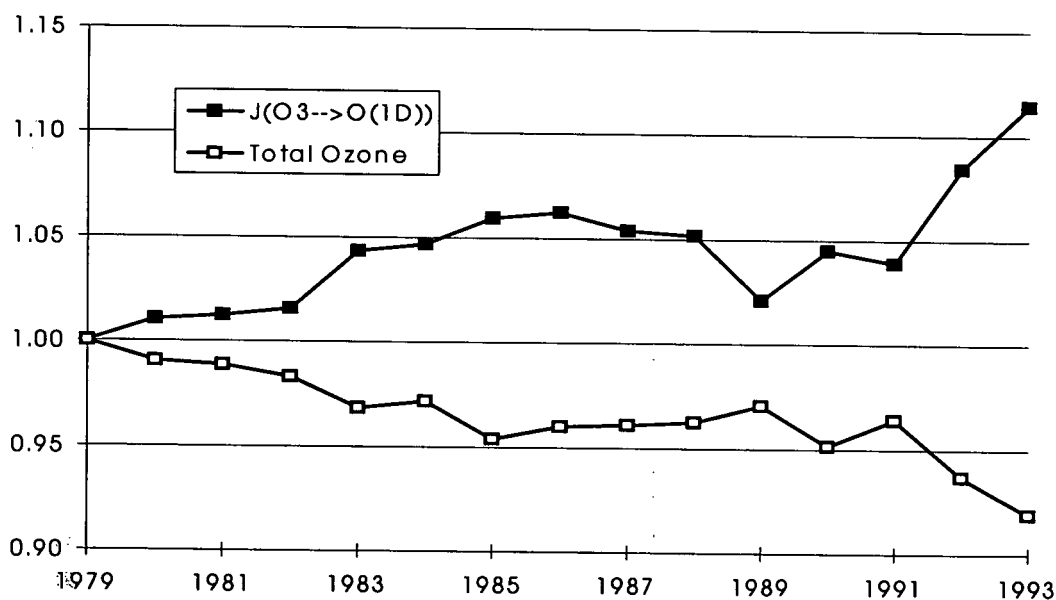


Figure 4. Development of observed global total ozone densities and calculated model domain average of $J_B(O_3)$, given as annual averages normalized to 1979 levels.

Also in paper 4 a moderate effect on the growth rate of methane was found; 1/4-1/3 of the observed reduction in growth rate could be explained by increases in UV-B radiation. Figure 5 (from paper 4) shows the calculated reduction in concentration and growth rate of CH₄.

Reductions in the emissions during recent years is likely to be the main reason for the decrease in the growth rate of methane. According to Dlugokencky et al. (1994) and Novelli et al. (1995) the observed reduction in the growth rate can be explained by a ~2% decrease in the total methane source.

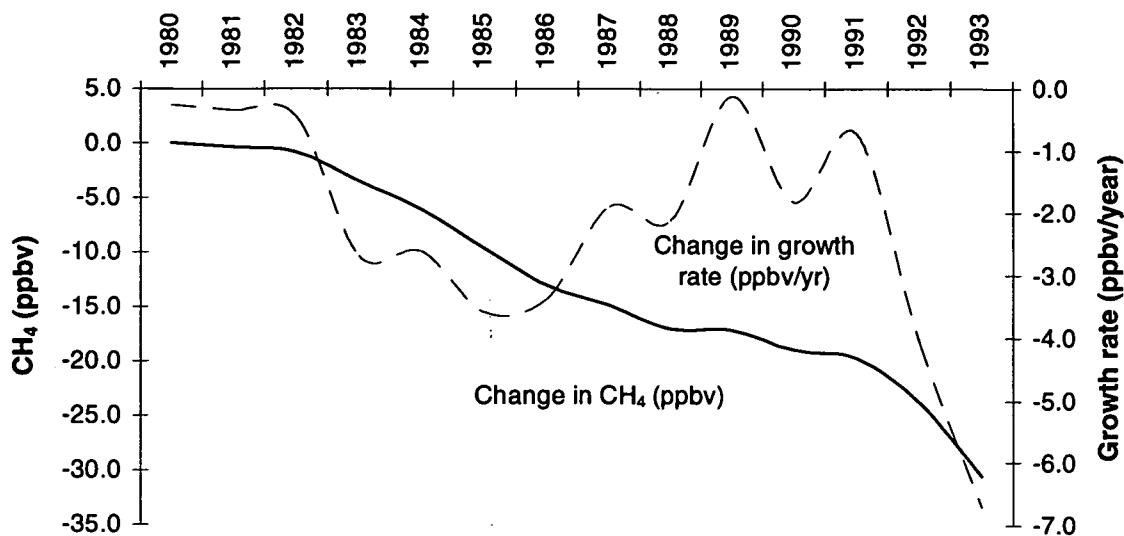


Figure 5. Changes in the global level and growth rate of CH₄ due to reductions in stratospheric ozone and UV-B increases.

Madronich and Granier (1992) estimated the effect of the observed reductions in total ozone between 1979 and 1989 on $J_B(O_3)$ and found a global average increase of about $4.0 \pm 2.8\%$ per decade which is comparable to our model-based estimate of 4.2% per decade for the period 1980 - 1990 (paper 3). Madronich and Granier (1992) assumed that the global average levels of OH and $J_B(O_3)$ are proportional and they presented the estimated increase in $J_B(O_3)$ as a first-order estimate of the changes in OH. When they applied this OH trend to the global average CH₄ level they estimated a reduction in the growth rate of CH₄ of 6.8 ± 4.8 ppbv/yr. This is substantially larger than our estimate. There are important differences between the approaches in their and our study. While we have used a global 2D model of tropospheric chemistry and transport with fully interactive chemistry in time-dependent calculations and changes in 16 different photolysis rates, Madronich and Granier (1992) inferred changes in the global levels of OH and CH₄ from changes in $J_B(O_3)$ through R1 and R2 by assuming the same trend for OH as they calculated for $J_B(O_3)$. In their calculations spatial and temporal variations in tropospheric ozone, water vapour and $J_B(O_3)$, as well as in the loss of methane, $k_3(T)[OH][CH_4]$, are neglected. With a global 2D model Bekki et al. (1994) estimated that almost half of the decrease in the growth rate of CH₄ was due to stratospheric ozone depletion and enhanced UV-B fluxes. In contrast to the results from Bekki et al. (1994), the results in paper 4 indicate that increased UV-B radiation is not likely to be an important factor behind the observed reductions in CO concentrations (Novelli et al., 1994).

The patterns of the modelled changes in tropospheric O₃, OH and H₂O₂ are similar in paper 3 and 4. But while the ozone increases at middle and high Northern latitudes calculated (in paper 3) for April 1990 at 60 - 70 °N reach 2 - 3% in response to the reductions in stratospheric ozone relative to the 1970 levels, the results for

April 1994 in paper 4 give 5 - 10% increase in response to the reductions in stratospheric ozone over the period 1979 to 1994. At lower latitudes and at higher Southern latitudes the reductions are larger in the latter case. The largest reductions in tropospheric ozone were calculated for the years 1992 and 1993 when the reduction in stratospheric ozone were largest. The calculated reductions in tropospheric ozone over high Southern latitudes in winter-time (paper 3 and 4) were found to be in agreement with observations.

The modelled responses in tropospheric ozone in paper 3 and 4 are in qualitative agreement with the results of Lui and Trainer (1988). They used a box model with fixed concentrations of NO_x, non-methane hydrocarbons (NMHC), CH₄ and CO to study the responses in O₃, OH, HO₂ and H₂O₂ in the boundary layer for summer conditions. They found that the response in tropospheric O₃ depends critically on the NO_x levels. In areas with high mixing ratios of NO_x (> 0.2 ppbv) the levels of tropospheric ozone increased in response to reductions in total ozone. For low NO_x levels (< 0.1 ppbv) they calculated ozone reductions.

The reductions in tropospheric ozone and methane lead to a negative radiative forcing of climate that may be attributed to the effects of ozone depleting substances. Bekki et al. (1994) included our estimate of the sensitivity of tropospheric O₃ changes to stratospheric O₃ depletion and calculated that the radiative forcing from reductions in tropospheric ozone and methane constitutes 30 - 50% of the forcing from changes in stratospheric ozone alone. Although their estimate is highly uncertain since the spatial and temporal patterns of the ozone changes were not taken into account, it may point to the importance of considering this mechanism when indirect effects of ozone depletion are studied.

3.4 Effects of changes in temperatures and water vapour densities

Temperature, water vapour densities, characteristics and distribution of clouds, precipitation and atmospheric circulation are examples of factors that have strong influence on the chemical properties of the atmosphere. In paper 4 the effects of increased *temperatures* and *water vapour densities* that may follow from enhanced greenhouse effect are studied. The initial effects will occur through temperature dependent reaction rate constants and through the water vapour dependent reaction R2.

To study this coupling between climate change and atmospheric chemistry, model results from a GCM study by Wang et al. (1992) were applied. They used the 1990 observed levels of CO₂, CH₄, N₂O, CFC-11 and CFC-12 in modelling the reference climate. Then the individual gas concentrations were based on the Business-as-Usual (BaU) scenario for 2050 from IPCC (1990) given in table 6. The modelled global annual mean radiative forcing of the troposphere-surface system is 3.1 W/m², while the increases in global annual mean surface temperature and column water vapour are 3.88 K and 27%, respectively (Wang et al., 1992). (No indirect effects from the CFCs through ozone changes were taken into account).

Table 6. Concentrations used in GCM calculations by Wang et al. (1992).

	CO ₂ ppmv	CH ₄ ppmv	N ₂ O ppmv	CFC-11 ppbv	CFC-12 ppbv
Reference (1990 levels)	354	1.72	0.31	0.28	0.48
Perturbed (BaU scenario for 2050)	539	3.24	0.37	0.55	1.07

The calculated temperature increase is 3 - 4 K below ~5 km south of 50 °N. Larger increases are found over Equator between 7 and 13 km (5 - 6 K) and at high Northern latitudes (up to 12 K in the lowest level). The calculated percentage changes in water vapour for January between 50 °N and 80 °S are generally in the range 20 - 40% below 5 - 8 km. The absolute increases are largest in the lower troposphere at lower and middle latitudes.

Changes in temperatures and water vapour give rise to a complex set of responses in tropospheric chemistry. Most of the reaction rate constants are temperature dependent; some are increasing with temperature and some are decreasing, and the degree of temperature dependence shows large variations. In a model run where only the temperatures were increased (the delta T case) the tropospheric annual average level of OH was reduced, while the level of CH₄ was reduced at the same time. This is due to a larger percentage increase in the reaction rate constant for the reaction between OH and CH₄ than the percentage reduction in OH levels. The net effect is an overall enhancement of the loss rate, given by $k_3(T)[OH]$, and thus reduced methane concentrations. The reductions in OH take place in the region of most importance for methane oxidation. There are, however, limited regions with small increases in OH (mainly at middle and high latitudes). The reductions in ozone are moderate (less than 7%) and they are largest between 2 and 3 km at low and middle latitudes.

When only the water vapour densities were changed (the delta H₂O case), the OH levels increased due to higher production through R1 and R2. As in the case of increased OH production from increased UV-B (paper 3 and 4), the OH perturbations were somewhat damped by the chemical interactions in the troposphere. The increases in OH reduce the levels of CO and CH₄. Higher OH levels further enhance the levels of HO₂, thereby increasing the loss of ozone through R17 and R18. In regions with low levels of NO_x, there will also be increased loss of O₃ through R1 and R2.

The ozone losses are larger at high Southern latitudes in summer than at high Northern latitudes in summer since higher levels of HO₂ also increase O₃ production through R15 which is more important for the O₃ budget at Northern latitudes. The ozone losses are usually largest at 3 - 5 km in the equatorial region due to the important role of the ozone destroying reactions with HO₂ and OH

here. In addition, the absolute increases in H₂O and thereby in OH and HO₂ are also relatively large here, increasing the importance of the loss reactions R1, R2 and R18 in addition to R17.

The ozone reductions in the delta T case are significantly lower than in the delta H₂O case. In the latter case O₃ reductions up to 20% are calculated in contrast to maximum reductions of ~7% in the delta T case. The changes in tropospheric annual mean values of O₃, OH, CO and CH₄ are given in table 7.

In the combined case (delta T and delta H₂O) ozone reductions are calculated in the entire model domain for all months. The reductions are usually largest around Equator at 4 - 5 km where they reach 20 - 22%. At 10 - 12 km the reductions are in the range 6 - 14% depending on month and latitude. In addition to the large reductions at Equator, there are also significant reductions at low altitudes at high Southern latitudes during the austral summer. The reductions are not so pronounced during summer at high Northern latitudes. The levels of NO_x and other ozone precursors are higher here, and thus the ozone producing reactions are more important for the ozone budget. Smaller relative reductions are generally calculated in the lower layers due to the increasing importance of surface deposition. In the upper troposphere, the small relative reductions is due to larger influence by input from the stratosphere and also smaller absolute increases in H₂O.

Table 7. Changes in tropospheric annual mean levels of O₃, OH, CO and CH₄ in response to increased temperatures and water vapour densities.

Case	O ₃	OH	CO	CH ₄
delta T	- 2.4%	- 1.8%	1.0%	- 7.2%
delta H ₂ O	- 8.0%	19.6%	- 10.4%	- 11.1%
delta T and delta H ₂ O	- 10.2%	17.1%	- 9.5%	- 17.6%

These studies indicate that the effect of changes in temperature and water vapour densities constitute a damping feedback in the climate system through the effects on the levels of tropospheric ozone and methane.

The regional and temporal patterns of the responses in OH to changes in temperature and water vapour densities are quite different from the pattern of response to changes in stratospheric O₃ and UV-B fluxes (paper 3 and 4). Changes in temperatures and H₂O give significant changes in OH in the region of most importance for the CH₄ oxidation (lower altitudes and latitudes), leading to a significant effect on the levels of methane.

Since significant increases in the OH levels were calculated, changes in temperatures and water vapour may also affect the sulphur chemistry. Due to the radiative properties of sulphate aerosols this mechanism may produce a feedback effect in the climate system.

4. Uncertainties, limitations and further work

One important limitation of the approach to the mechanisms and effects addressed in this thesis lies in the use of a two-dimensional model. The severity of this limitation, however, varies between the different tasks.

NO is a key component in the chemistry of the troposphere. There are large zonal variations in the emission intensity of NO and thereby also in the atmospheric concentrations since the lifetime of NO is only a few days, while the zonal transport time is approximately 2 weeks. By assuming zonal homogeneity, the ability to model some important non-linear effects in tropospheric chemistry is reduced. Kanakidou and Crutzen (1992) studied the effects of zonal averaging. They used a global three-dimensional (3D) chemistry/transport model and assumed longitudinally uniform emissions of NO_x and NMHC ("2D mode") and compared the results obtained with results from the same 3D model, but now with longitudinally varying emissions. They found that in 2D mode the model overestimated the middle and the low tropospheric levels of O₃ and OH in the tropics and middle Northern latitudes compared to the 3D case. Their study also gave an overestimation in the amount of methane oxidized by approximately 20% in the 2D case relative to the 3D case. This may point to uncertainties in the estimates of the feedback strength in paper 1 and 2. The use of a 2D model in the study of the CH₄/OH feedback is discussed in paper 1. It is concluded that the main effect of performing a CH₄/OH feedback study in a 3D model compared to a 2D model is to increase the fraction of the troposphere where the NO levels are so low that OH is lost in the oxidation of CH₄. This will contribute to increased strength of the feedback. The fact that these low NO environments are mainly found in the tropics and sub tropics, which are the most important regions for methane oxidation, will further strengthen the feedback.

The chemical processes included in the model are of course highly simplified compared to the real atmosphere; only approximately 100 reactions are modelled. However, the selection of reactions have during the development and refinements of the chemistry scheme (e.g. Isaksen et al. 1978a,b; Isaksen, 1980; Isaksen and Hov, 1987; Fuglestvedt et al., 1994; Berntsen and Isaksen, 1994) been thoroughly evaluated in order to include the reactions that are most important in modelling the chemistry of the troposphere. One limitation, however, is the omission of reactions occurring in the aqueous phase and between the gaseous and aqueous phase. But first order heterogeneous scavenging of soluble species by rain and clouds and adsorption on aerosols are included. Other potentially important reactions that are omitted are the oxidation of hydrocarbons by the NO₃ radical. The formation of RONO₂ from reactions between NO and various RO₂ radicals is included and this constitutes an additional sink of NO_x. In the calculations it is assumed, as suggested by Finlayson-Pitts and Pitts (1986), that the RONO₂ compounds are stable end products that are removed by scavenging and/or deposition. There are, however, indications that these gases are not stable, but are degraded by photolysis or by reaction with OH (Roberts, 1990). If the organic nitrates are not stable, but have a chemical lifetime long enough to be transported over larger distances before

they decompose and give NO_x, the nitrates may act as reservoir species of NO_x in a manner analogous to the role of PAN. If so, NO_x may be transported as RONO₂ to remote areas where it may contribute to ozone formation more efficiently than in the source region.

Another potentially important process that is not included in the model is heterogeneous loss of NO₃ and N₂O₅. With a global 3D model Dentener and Crutzen (1993) studied the impact of these reactions and found 80% and 20% reductions in NO_x in winter and summer, respectively. The tropospheric averages of OH (weighted with the amount of CH₄ reacting with OH) and O₃ were reduced by 9% each. The levels of these gases were most sensitive in the Northern Hemisphere to the heterogeneous losses of NO₃ and N₂O₅.

But uncertainties in the results are not only due to the simplifications that models necessarily have to adopt. The quality of the results is of course also affected by uncertainties in the input data. The reaction rate constants, quantum yields and absorption cross sections, as well as deposition velocities are examples of such input data. Using a Monte Carlo technique, Thompson and Stewart (1991) studied how imprecisions in chemical rate constants propagate to uncertainties in calculated concentrations in a 1D photochemical model for the troposphere. They found that the most critical kinetic processes were the photodissociation of O₃ and NO₂. The reaction between OH and CH₄, and the rate of nitric acid formation (which removes NO_x and odd hydrogen) were also found to be critical. The results show that the uncertainties are highly dependent on which gas is studied and the general level of pollutants. Under clean background conditions the 1σ imprecision of OH, HO₂, and H₂O₂ in the mixed layer were as low as 20, 15 and 25%, respectively. Under conditions with high NO_x, NMHC and O₃, the numbers were as high as 70, 70 and 90%, respectively. For O₃, the uncertainty was calculated to be ~15% in both cases. By averaging over regionally differing results, they estimated that a typical mean value for OH calculated by their model is ~25% uncertain due to imprecisions in the kinetics. Although the results are dependent on model formulation, the chemistry scheme and numerical methods, the study indicates the level of uncertainty and which reactions that are critical with respect to uncertainty.

Uncertainties are also connected to the emission numbers. The total emission of methane is reasonably well constrained from source estimates, observations of concentrations and lifetime estimates. There are however large uncertainties related to the estimates for the individual sources and thereby also for the latitudinal distribution of the sources. The emissions of NMHC and NO_x are highly uncertain, especially the natural emissions of hydrocarbons, and the lightning emissions of NO_x. There is also a great need for better data on the atmospheric distribution of NO_x which can be used for evaluation of the modelled distributions. Due to the short lifetimes and highly inhomogeneous distribution of the NO_x sources, there are very large variations in the levels of nitrogen oxides between highly polluted regions and remote regions.

In many two-dimensional models the transport processes and their large temporal and spatial variations are treated in a highly simplified manner. One mechanism

that affects the distribution and budget of tropospheric O₃, is the effective transport of air inside clouds from lower tropospheric layers. This transport mechanism is not included in the model. The vertical transport is treated only as zonally averaged advection and slow eddy diffusion. A substantial part of the vertical transport occurs, however, within deep convective clouds, which bring air from the boundary layer to the upper troposphere on timescales of 10 - 15 minutes (Lelieveld et al., 1989). In this way, air with high levels of NO_x and other source gases can be transported effectively to the upper troposphere. This mechanism was found to have a large effect on upper tropospheric ozone in a 3D model study by Bernsten et al. (1995).

As pointed out by Lelieveld and Crutzen (1994), inclusion of this mechanism also increase the ozone loss through surface deposition due to more downward transport of ozone through subsidence. They found that omission of convective transport leads to significant overestimates of the upper tropospheric levels of NO_x and O₃, and they calculated 20% and 30% reductions in total tropospheric ozone and NO_x, respectively, when convective transport was included. Inclusion of this mechanism also increased the tropospheric chemical production and loss of O₃, as well as the ground deposition of O₃. They also found that the oxidation capacity of the atmosphere increases due to higher O₃ concentrations near the surface which increase the production of OH through R1 and R2. Since this occurs in the lower troposphere where the temperatures and the concentrations of the gases reacting with OH are higher, this mechanism has a significant effect on the oxidation capacity. An increase of 20% in the oxidation of CH₄ was calculated.

The results of Lelieveld and Crutzen (1994) may point to an important limitation to the model applied in this thesis and the results obtained. In modelling the reference distributions of the gases, too high levels of O₃ and NO_x in the upper troposphere may have been calculated. The results from Lelieveld and Crutzen also indicate that the contribution to the ozone concentrations in the lower layers from ozone of stratospheric origin may be underestimated. Since the production of hydroxyl radicals is controlled by ozone, the OH production may also be too low.

The effects of surface emissions on upper tropospheric chemistry (e.g. ozone levels) due to less transport of source gases upwards may also have been underestimated. In addition, the impact of the fractions of the surface emissions that reach the upper troposphere by advection or eddy diffusion will be different since these gases will influence the chemical processes there with background concentrations that may be overestimated. Too high levels of NO_x for instance, give lower O₃ production per NO_x molecule added. The estimated effects of aircraft emissions may also be affected by too high background levels of NO_x and O₃ in the altitude region where these emissions take place. Since the O₃ levels at lower altitudes are to a larger extent controlled by subsidence when convective transport is included, too low concentrations in the lower layers may have been calculated and the modelled *relative* effects of emissions on the O₃ levels here may be uncertain.

Few measurements of UV trends are available and at present there is insufficient basis for drawing firm conclusions about global trends in UV radiation. Increased fluxes of UV are reported for several locations while decreases are also observed (Kerr and McElroy 1993; Smith et al., 1993; Madronich, 1993; IPCC, 1994; World Meteorological Organization (WMO), 1995). Reductions in UV fluxes are probably due to effects of SO₂, NO₂, aerosols and tropospheric ozone. Effects of changes in the concentrations of aerosols on the UV-B fluxes and J-values were considered and found insignificant during the studies presented in paper 3 and 4, which is in agreement with Bekki et al. (1994) who also found that this effect is of minor importance.

The assumptions about cloud fractions, occurrence, their optical properties and vertical distributions were found to have large effects on the calculated J-values. Above the clouds, reflections from the clouds will enhance the upward solar flux, and the calculated J-values will be higher compared to J-values based only on the direct solar radiation. In the upper part inside the clouds, the J-values will also increase due to multiple scattering by cloud droplets, which will increase the optical path length. Depending on the type of clouds, the J-values will decrease at a certain distance below the cloud top since the solar fluxes are reduced due to the scattering in the layers above (Jonson and Isaksen, 1991). In terms of global averages, the inclusion of clouds increases the J-values (Berntsen and Isaksen, 1994). This will give higher production of OH through the reactions R1 and R2.

But clouds do not only affect the OH levels through the photolysis rates. Inclusion of aqueous phase chemistry reduces the tropospheric levels of odd hydrogen and the omission of aqueous phase chemistry contributes to overestimating the odd hydrogen levels (Jacob, 1986; Berntsen and Isaksen, 1994). The processes leading to lower OH levels are direct uptake of OH and HO₂ in the droplets, and lower concentrations of O₃ due to loss reaction with O₂(aq) and reduced O₃ production in the gas phase due to separation of HO₂ and NO.

In addition to the sources of uncertainty mentioned above, there may also be potentially large errors due to unknown processes that could change the model simulations significantly. An example of the importance of previously unknown processes is the role of heterogeneous chemistry between gas phase and particles in stratospheric ozone chemistry.

The ability of the applied 2D chemistry model to reproduce observed distributions of various gases in the atmosphere was evaluated in paper 2. Comparisons between model results and observations are difficult because the model applies climatological average values and calculates zonal averages while observations usually are so few in space and time that large uncertainties are related to calculations of zonal averages. The comparisons, however, indicate that the observed atmospheric distributions are generally well reproduced by the model, especially for species with lifetimes of weeks or longer. The modelled effects of stratospheric ozone depletion on tropospheric ozone are also supported by the observations by Schnell et al. (1991), who found significant reductions in surface ozone during winter time over the period 1979 to 1990. In paper 2 the calculated

tropospheric OH average were compared to other estimates based on various approaches, and good agreement was found.

In WMO (1995) calculated ozone fields for July and January for the current atmosphere from eight models (2 and 3 dimensional) were compared. Results from the model studies presented in paper 4 were included in this comparison. Tropospheric ozone fields from the scenario with changed UV-B fluxes were then used. Table 8 gives an overview of the eight models with references. All the plotted ozone fields represent the current atmosphere, but there are differences in the applied boundary conditions as well as in the emissions.

There is broad agreement in the general feature of the zonally averaged ozone distributions. The flux of ozone from the stratosphere and the loss of ozone through surface deposition are reflected in the vertical distributions showing maximum values in the upper troposphere and minimum values in the lowest layers. This picture is however modified by enhanced ozone production at middle and higher Northern latitudes during summer-time relative to summer-time at the Southern Hemisphere. In WMO (1995) it is concluded that these models are able to reproduce the gross features of observed ozone distributions. Figure 6 shows the calculated ozone fields given in mixing ratios (ppbv) for January and July as function of latitude and altitude.

Table 8. Chemistry-Transport Models included in the comparison of ozone fields.

Model	References
2D models	
UK Met Office	Derwent (1994)
University of Oslo	Fuglestad et al. (1994, 1995a)
University of Bergen	Strand and Hov (1993; 1994)
TNO	Roemer and v d Hout (1992)
NCAR/CNRS	Hauglustaine et al. (1994a)
LLNL	Wuebbles et al. (1993); Patten et al. (1994)
3D models	
Images	Müller and Brasseur (1994)
University of Oslo	Berntsen and Isaksen (1994)

The modelled mixing ratios are in the range 40-60 ppbv at 10 km and about 10-30 ppbv in the boundary layer. In July, the modelled mixing ratios are 30-50 ppbv in the lowest few kilometers at middle Northern latitudes. In the Southern Hemisphere in January the corresponding values are in the range 10-30 ppbv. The 2D model applied in this thesis calculates ozone fields that are similar to the LLNL 2D model, and to the 3D model at the University of Oslo. The latter model has a chemistry scheme that is almost identical to the scheme in the 2D model, and a certain degree of agreement between these two models is not surprising. The 3D model, however, includes effective cloud transport, which, in addition to the 3D feature of the model, leads to important differences relative to a 2D model calculation.

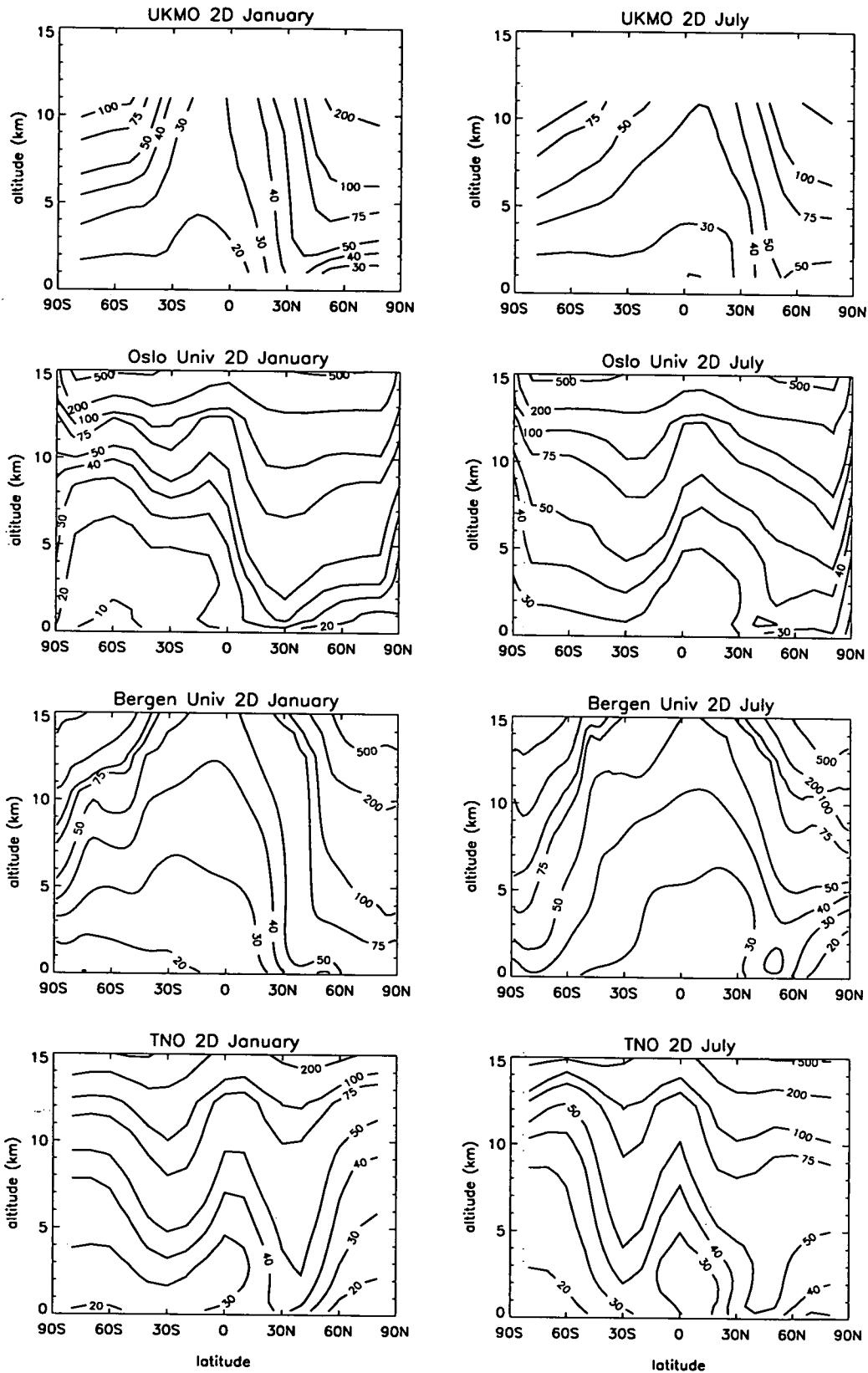
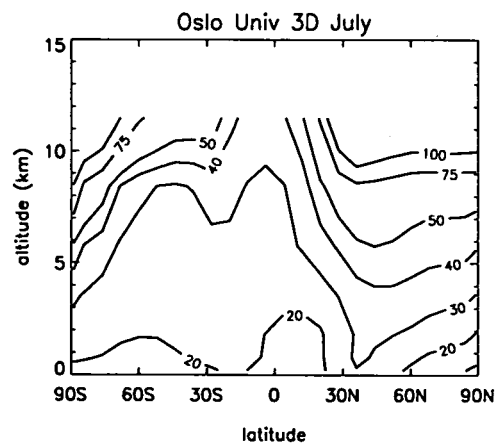
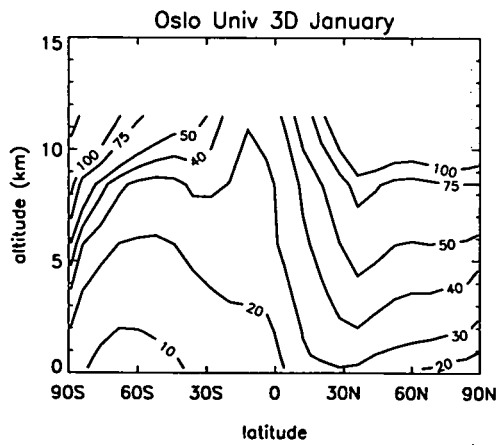
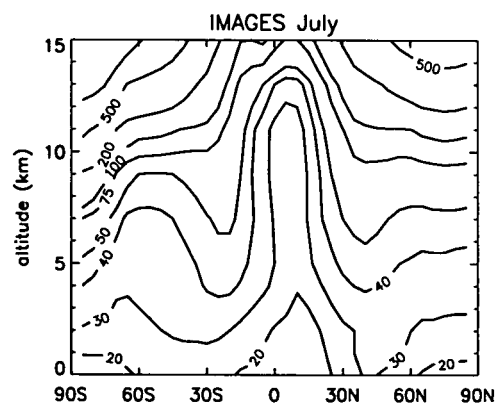
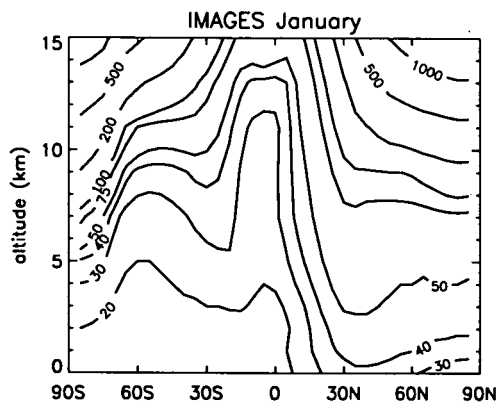
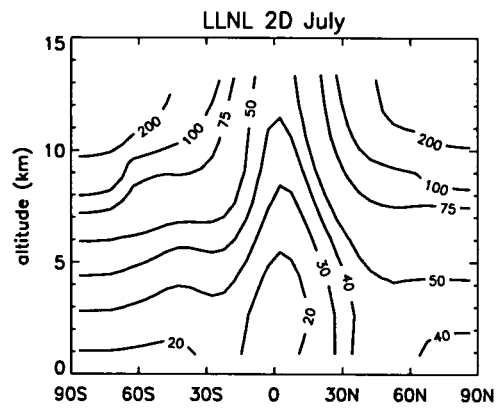
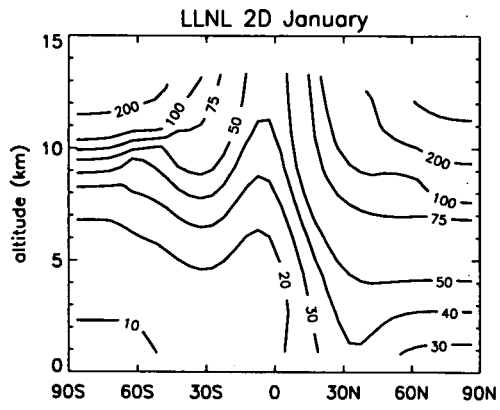
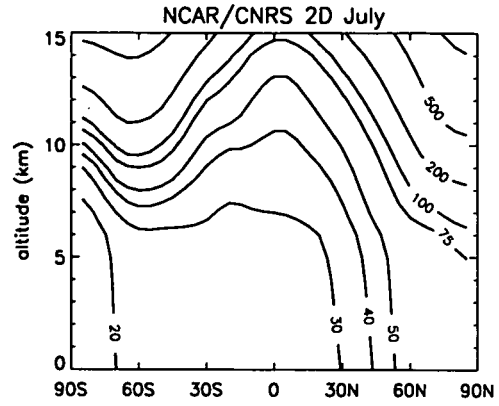
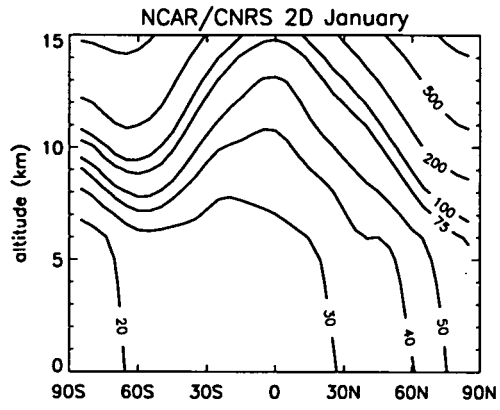


Figure 6. Latitude by altitude contours of zonally averaged ozone mixing ratios as calculated in eight global models (WMO, 1995).



On the background of the uncertainties and limitations discussed in this section, it may be concluded that the applied two-dimensional model is best suited for process and sensitivity studies. If the results are to be used as a basis for policy-making, they should be used with caution. The results obtained should only be regarded as indications of levels of the various compounds, or of chemical regimes that one may expect from changes in various factors taking part in the complex interplay of atmospheric chemistry. The model is best suited for studies of changes in long-lived tropospheric gases such as methane, and in this case it is also a good tool for providing information for decision-makers.

Due to the rapid improvements regarding computer resources, several of the studies performed with this 2D model may soon be performed with 3D models with chemistry schemes of similar extent. The results obtained with 2D models should then be compared to results obtained with 3D models to obtain knowledge of which studies that can be performed with a 2D model, and which requires a 3D approach. The effects of NO_x from surface sources on tropospheric ozone and methane is a kind of study that preferably should be performed with a 3D model (cf. section 2.2 and 3.2 and the results of Kanakidou and Crutzen, 1992).

If the 2D model is to be used as a tool for process studies and for studies of gases with too long lifetimes for a 3D study, one should develop further the competitive advantage of the model: The possibility to include a rather extensive chemical scheme. In particular the following improvements will significantly better the ability of the model to predict changes in tropospheric chemistry in response various perturbations:

- Inclusion of convective transport inside clouds.
- Inclusion of heterogeneous loss of NO₃ and N₂O₅.
- Inclusion of a scheme for interactive heterogeneous chemistry (e.g. the scheme developed by Jonson and Isaksen, 1993).
- Inclusion of nitrate radical oxidation in the chemistry scheme.
- Inclusion of photolysis and OH reaction for RONO₂.

Furthermore, it may also be useful to perform the following tasks:

- The effects of various assumptions about distribution and properties of clouds should be studied, not only focusing on the effects on the J-values, but also on the sensitivities of tropospheric chemistry to the various assumptions.

- Evaluate the effects of introducing seasonal variation for more of the source gases.
- Make the chemistry scheme identical to the scheme in the 3D model developed by Berntsen and Isaksen (1994), and then compare results to obtain knowledge of which types of studies the 2D model is suitable for.

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