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Effect of greenhouse gas emissions on stratospheric ozone depletion

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PREFACE

The simulations discussed in this report were performed with the RIVM version of the 2-dimensional radiative-chemical transport model developed by Harwood and Pyle in the 1970s and 1980s. J. Pyle, A. Jones, K. Law and S. Bekki of the University of Cambridge provided us with a copy of the source code of the model.

ABSTRACT

Emissions of greenhouse gases can affect the depletion of the ozone layer through atmospheric interaction. In our investigation the increase in emissions of chlorine- and bromine-containing compounds, largely responsible for the depletion of stratospheric ozone at mid-latitudes, was found to be -5.8% per decade from 1980 to 1990. The increase in CH_4 emissions in the same period changes this ozone depletion by +1.4% per decade to -4.4% per decade, which is close to TOMS and Dobson measurements. The increase in N_2O emissions hardly affects this depletion. The decrease in stratospheric temperatures due to increased CO_2 emissions also diminishes the ozone depletion; the same may also happen when NO_x emissions are increased. The effect of these interactions in coming decades is to accelerate the recovery of the ozone layer. The trend in CH_4 emissions described in the business-as-usual scenario IS92a may yield 1980 ozone column levels in 2060 compared with 2080 with CH4 emissions fixed at 1990 levels. The temperature decrease in the stratosphere may initially also accelerate the recovery of the ozone layer by several years, ignoring a possible large extra ozone depletion by the extra formation of polar stratospheric clouds over large areas of the world.

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SUMMARY

The depletion of the ozone layer is caused mainly by the increase in emissions of chlorine-and bromine-containing compounds like CFCs, halons, carbon tetrachloride, methyl chloroform and methyl bromide. The effect of emissions of other compounds is usually ignored. This is valid for a first approximation, although especially CH_4, N_2O and CO_2 can have a direct or indirect effect on the ozone layer.

In this investigation we studied the interactions in the atmosphere between the greenhouse effect and stratospheric ozone depletion from the point of view of past and future emissions of the anthropogenic compounds: CFCs, halons, CH_4, N_2O, NO_x, CO and CO_2. The Cambridge/RIVM 2D model of the stratosphere was used for scenario simulations and quantification of the effects on the ozone layer.

The increase in emissions of CFCs and related compounds (carbon tetrachloride, methyl chloroform, halons, methyl bromide) was found responsible for a trend in the ozone column of -5.8% per decade at mid-latitudes from 1980 to 1990. The trend in CH_4 emissions in addition to this contributes +1.4% per decade (total -4.4% per decade) to the trend due to the increase of the chlorine reservoir HCl through the reaction CH_4 + Cl. The effect of the increase in stratospheric water vapour on the ozone column through the oxidation of CH_4 not only has the opposite sign but also a much smaller magnitude. The N_2O emission trend in addition to the CFC trend yields a +0.1% per decade contribution due to the increase in the chlorine reservoir $ClONO_2$. This effect of N_2O is currently larger than the additional catalytical destruction of ozone caused by the increase of NO_x from N_2O because of the current high chlorine levels in the stratosphere. The temperature decrease in the stratosphere this century, due to the increase in CO_2 emissions and stratospheric ozone depletion is estimated at 3 K for 1990. This temperature decrease results in an increase in ozone through a change in the thermal equilibrium of the odd-oxygen balance. The contribution from CO_2 emissions to the ozone column trend from 1980 to 1990 is estimated at +0.4% per decade.

Taking into account the effects of a trend in CH_4, N_2O and CO_2 emissions results in a good agreement between the calculated (-3.8% per decade) and measured (-4.0% per decade from TOMS and Dobson measurements) trend in ozone column at mid-latitude in the Northern Hemisphere from 1980 to 1990.

Anticipated increases in CH_4, N_2O and CO_2 emissions in the 21st century may affect the recovery of the ozone layer in coming decades. The Montreal Protocol, and amendments and adjustments, reduce the chlorine levels in the stratosphere, resulting in a thickening of the ozone layer. The ozone column may reach 1980 levels (taken as a measure for the recovery of the ozone layer) by approximately 2080. An increase in CH_4 emissions results according to the mid-range IPCC scenario IS92a in a faster recovery of the ozone layer, so that 1980 levels can be reached in approximately 2060. The corresponding IS92a N_2O emissions trend can slow this down slightly by five years. The increase in CO_2 emissions may decrease stratospheric temperatures and increase stratospheric ozone, so that 1980 levels are reached by approximately 2040, ignoring possible extra ozone depletion by the formation of PSCs (Polar Stratospheric Clouds). Large temperature decreases in the stratosphere might cause extra formation of PSCs in winter in polar areas and possibly also at mid-latitudes and in other seasons. This might cause a large depletion of stratospheric ozone through heterogeneous reactions on the surfaces of the PSCs. If this will happen is speculative, and if so it will probably only occur in winter at high latitudes and in the first half of the next century, when chlorine levels are still high.

Tropospheric CO and NO_x levels have increased this century but the exact magnitude of the increases are not well known. An estimated increase in tropospheric CO and NO_x concentrations contributes +0.1% per decade and +0.7% per decade, respectively, to the ozone column trend at mid-latitude from 1980 to 1990.

A thinner ozone layer (11% at 47°N) allows more UV radiation to reach the troposphere, which is responsible for a decrease in CH_4 lifetime and a calculated 6% globally averaged increase in oxidizing capacity of the atmosphere. This provides an illustration of the effect changes in the ozone layer can have on the troposphere and greenhouse effect. But past and expected future changes in stratospheric ozone levels are too small to have large effects in the composition of the troposphere. Changes in emissions of CO, NO_x and CH_4 can have much larger effects.

SAMENVATTING

De aantasting van de ozonlaag wordt voornamelijk veroorzaakt door de toename in emissie van chloor- en broomhoudende verbindingen als CFK's, halonen, koolstoftetrachloride, methylchloroform en methylbromide. De bijdrage van emissies van andere stoffen wordt meestal verwaarloosd hetgeen in eerste benadering correct is, maar vooral CH_4, N_2O en CO_2 kunnen direct of indirect de ozonlaag beïnvloeden.

In deze studie hebben wij de interacties in de atmosfeer onderzocht tussen het broeikaseffect en de aantasting van de ozonlaag vanuit het oogpunt van emissies van antropogene stoffen in het verleden en in de toekomst: CFK's, halonen, CH_4, N_2O, NO_x, CO en CO_2. Het Cambridge/RIVM 2D model van de stratosfeer is gebruikt voor scenariosimulaties en kwantificering van effecten op de ozonlaag.

De toename in emissies van CFK's en soortgelijke verbindingen (koolstoftetrachloride, methylchloroform, halonen, methylbromide) is verantwoordelijk voor een trend in ozon kolom van -5,8% per decennium op gematigde breedte van 1980 tot 1990. De trend in CH_4 emissies vermindert deze trend met +1,4% per decennium tot -4,4% per decennium, hetgeen wordt veroorzaakt door een toename in het chloorreservoir HCl via de reactie CH_4 + Cl. Het effect van de toename in waterdamp in de stratosfeer, door de oxidatie van CH_4, op de ozonlaag is klein en tegengesteld van teken. De trend in N_2O emissies boven op de CFK-emissietrend bedraagt +0,1% per decennium wat wordt veroorzaakt door een toename in het chloorreservoir $ClONO_2$. Dit effect van N_2O is op het moment groter dan de extra katalytische afbraak van ozon door de toename van NO_x in de stratosfeer omdat de huidige stratosferische chloorniveau's hoog zijn. De temperatuurafname in de stratosfeer in deze eeuw, veroorzaakt door een toename in CO_2 emissies en aantasting van de ozonlaag, wordt geschat op ongeveer 3K in 1990. Deze temperatuurafname resulteert in een toename van ozon door een verandering in het thermisch evenwicht van ozon en zuurstofatomen. De bijdrage van een CO_2-emissietrend aan de trend in ozonkolom van 1980 tot 1990 wordt geschat op +0,4% per decennium.

De totale trend in ozonkolom door de trend in emissies van CFK's en soortgelijke stoffen, CH_4, N_2O en CO_2 (-3,8% per decennium) komt goed overeen met metingen (-4,0% per decennium van TOMS en Dobson metingen) voor gematigde breedte voor het Noordelijk halfrond van 1980 tot 1990.

Een te verwachten toename in CH_4, N_2O en CO_2 emissies in de 21ste eeuw kan een effect hebben op het herstel van de ozonlaag in de komende decennia. Het Montreal Protocol, en de aanpassingen en aanscherpingen hierop, zal tot gevolg hebben dat de chloorniveaus in de stratosfeer zullen gaan dalen, met als gevolg een dikker wordende ozonlaag. De ozonkolom kan het 1980 niveau (beschouwd als een maat voor het herstel van de ozonlaag) bereiken in ongeveer 2080. Een toename in CH_4 emissies volgens het IPCC IS92a scenario (gemiddeld scenario) kan het herstel van de ozonlaag versnellen, waardoor 1980 niveaus in ongeveer 2060 bereikt kunnen worden. De corresponderende IS92a N_2O emissie trend kan dit met 5 jaar vertragen. Een toename in CO_2 emissies kan een afname in temperatuur en toename in ozon in de stratosfeer tot gevolg hebben, waardoor 1980 niveaus in 2040 bereikt kunnen worden. Hierbij wordt een mogelijke extra ozonafbraak door de vorming van PSC's (polaire stratosferische wolken) niet meegenomen. Grote temperatuur dalingen in de stratosfeer kunnen mogelijk voor een extra vorming van PSC's verantwoordelijk zijn in de winter in polaire gebieden en mogelijk ook op gematigde breedte en in andere seizoenen. Door heterogene reacties op de oppervlakken van de PSC's zou een grote extra ozonafbraak

kunnen optreden. Of dit gebeurt is speculatief, en als het gebeurt zal dit zich waarschijnlijk alleen in de winter voordoen op hoge breedtegraden en in de eerste helft van de volgende eeuw wanneer de chloorniveaus nog hoog zijn.

Troposferische CO en NO_x niveau's zijn deze eeuw toegenomen, maar de grootte van de toenamen zijn niet goed bekend. Een geschatte toename in de troposfeer van CO en NO_x concentraties draagt respectievelijk +0,1% en 0,7% per decennium bij aan de trend in ozonkolom op gematigde breedte van 1980 tot 1990.

Een dunnere ozonlaag (11% op 47°N) heeft tot gevolg dat meer UV straling de troposfeer kan bereiken. De UV straling bewerkstelligt een afname in de leeftijd van CH_4 en een berekende toename van 6% van het mondiaal gemiddelde zelfreinigend vermogen van de atmosfeer. Dit is een illustratie van het effect dat een verandering in de ozonlaag kan hebben op de troposfeer en het broeikaseffect. Maar de veranderingen in stratosferisch ozon die in het verleden plaatsvonden en de te verwachten veranderingen in de toekomst zijn te klein om een groot effect te hebben op de samenstelling van de troposfeer. Veranderingen in emissies van CO, NO_x en CH_4 kunnen veel grotere effecten veroorzaken.

1. INTRODUCTION

Depletion of stratospheric ozone and the enhanced greenhouse effect are two major global environmental issues receiving a lot of attention from the scientific community, the public and policy-makers. Both phenomena are usually considered independently, initially a valid approximation. Destruction of ozone in the stratosphere is caused mainly by elevated levels of active chlorine and bromine compounds in the stratosphere, which arise mainly from anthropogenic emissions of chlorofluorocarbons (CFCs) and halons. The enhanced greenhouse effect arises from a changing radiation balance in the atmosphere caused by anthropogenic emissions from carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and chlorofluorocarbons (CFCs). Tropospheric ozone, various types of aerosols, changes in clouds and emissions of minor trace gases also influence the enhanced greenhouse effect. The stratosphere interacts with the greenhouse effect, or climate change processes, in several ways. Some anthropogenic emissions cause chemical changes in both the troposphere and stratosphere, thereby affecting the concentration of greenhouse gases in the troposphere and also influencing the amount of active chlorine and bromine compounds in the stratosphere. The enhanced greenhouse effect causes changes in temperature of both the troposphere and stratosphere, which may affect the chemical composition of the atmosphere as well as its dynamics. It may also influence the exchange processes between the troposphere and stratosphere and thus the chemical composition. Changes in stratospheric ozone also cause changes in the amount of UV radiation reaching the troposphere, which affects the photolysis rates of several chemical reactions and thus changes the chemical composition of the atmosphere.

The enhanced greenhouse effect, with its social and economic impacts, are under study in the international framework of the Intergovernemental Panel on Climate Change (IPCC). This panel set up by the United Nations, reports frequently on the current state of the art on climate change (IPCC, 1994; 1995). This forms an important basis for international negotiations on climate change. In the last decade much scientific progress has been made while at the negotiation table the international community signed an agreement in Rio de Janeiro in 1992, the United Nations Framework Convention on Climate Change (UNFCCC), to reduce the adverse effects of climate change. In negotiations a start to formulate and implement policy measures to meet the goals set down in the UNFCCC has been made.

The case for the protection of the ozone layer is already much more advanced. In 1985 the Vienna Convention to protect the ozone layer was signed. This was followed by the Montreal Protocol in 1987 and several amendments and adjustments, i.e. London, Copenhagen and Vienna amendments in 1990, 1992 and 1995, respectively. These agreements were based on the research documented in WMO/UNEP reports, for example WMO (1991; 1994).

The atmospheric section of IPCC reports focuses on radiative forcing by greenhouse gases, while the WMO/UNEP reports mainly describe processes in the stratosphere. Both types of reports acknowledge interactions between the enhanced greenhouse effect and stratospheric ozone depletion, but do not address them extensively. In this report the focus will be on the interactions, not only qualitative but also quantitative from the point of view of trace gas emissions influencing stratospheric ozone and radiative forcing of the atmosphere. The emphasis will be on the effects these emissions have on the depletion and recovery of the ozone layer. The description of the interactions is based on information in the literature and calculations using a global atmosphere model.

In Chapter 2 the main interactions between processes in the troposphere and stratosphere are summarized. Chapter 3 and Appendix A contain a description of the emissions and a concise description of the global model used to quantify a number of the interactions. Chapter 4 discusses the results of simulations using the global model, followed in Chapter 5 by the conclusions.

2. INTERACTIONS BETWEEN OZONE DEPLETION AND GREENHOUSE EFFECT

The main interactions of stratospheric ozone depletion with the enhanced greenhouse effect are qualitatively described in this chapter and the theoretical background of the interactions explained. A quantitative overview of interactions will be given in Chapter 5. The radiative forcing (W/m^2) can be used as a quantitative measure of the enhanced greenhouse effect. Figure 1 and Table 1 show the major interactions between the chemical compounds, and processes and dynamics in both the troposphere and stratosphere from the point of view of anthropogenic emissions of trace gases.

The following compounds and processes were studied for their possible influence on stratospheric ozone and the radiative forcing of the atmosphere.

Emitted compounds:

CO_2 (carbon dioxide) is a major greenhouse gas causing an increase in the temperature in the troposphere by absorption of infrared (IR) radiation emitted by the surface. Since it is chemically inert it has a long chemical lifetime; its distribution in the atmosphere is fairly homogeneous up to 100 km altitude. In the stratosphere CO_2 emits IR radiation, resulting in a cooling effect. The current radiative forcing of the atmosphere is 1.56 W/m^2 (IPCC, 1995). CO_2 has no direct chemical effect on stratospheric ozone. CO_2 can affects ozone depletion indirectly by changing the temperature in the stratosphere. An increase in CO_2 causes a decrease in stratospheric temperatures. Large temperature decreases might initiate extra formation of PSCs which can cause a large depletion of the ozone layer. If this will happen is speculative, and if so it will probably only occur in winter at high latitudes and in the first half of the next century, when chlorine levels are still high. PSC effect are ignored in this study.

CFCs are greenhouse gases causing an increase in the troposphere temperature. The decrease in temperature in the stratosphere is very small because of its relatively low concentration. The current radiative forcing of the CFCs is 0.28 W/m^2 (IPCC, 1995). Because the lifetimes of CFCs in the atmosphere are long (50-100 yr) CFCs reach the stratosphere and are there the main contributors to active chlorine. The increase in CFC emissions last few decades is the main cause of stratospheric ozone destruction.

H_2O (water vapour) is the most important greenhouse gas. Its abundance in the troposphere is almost completely determined by the temperature structure of the troposphere. The decrease in temperature with increasing altitude in the troposphere causes H_2O vapour to condense and form droplets and rain out of the atmosphere. There is no experimental evidence that the amount of H_2O in the lower troposphere is changing. A warmer climate might result in changes in the cloud cover and rainfall, which could change the amount of water vapour in the atmosphere (IPCC, 1995), but this is still speculative and no measurements are available to support this. There is an increase of H_2O in the stratosphere. Oltmans and Hofmann (1995) measured an increase in H_2O in the upper troposphere and lower stratosphere from 1% per year at 10-12 km to 0.34% per year at 24-26 km over the time period 1981-1994. This increase comes mainly from the oxidation of CH_4 but possibly also from climate-induced temperature changes.
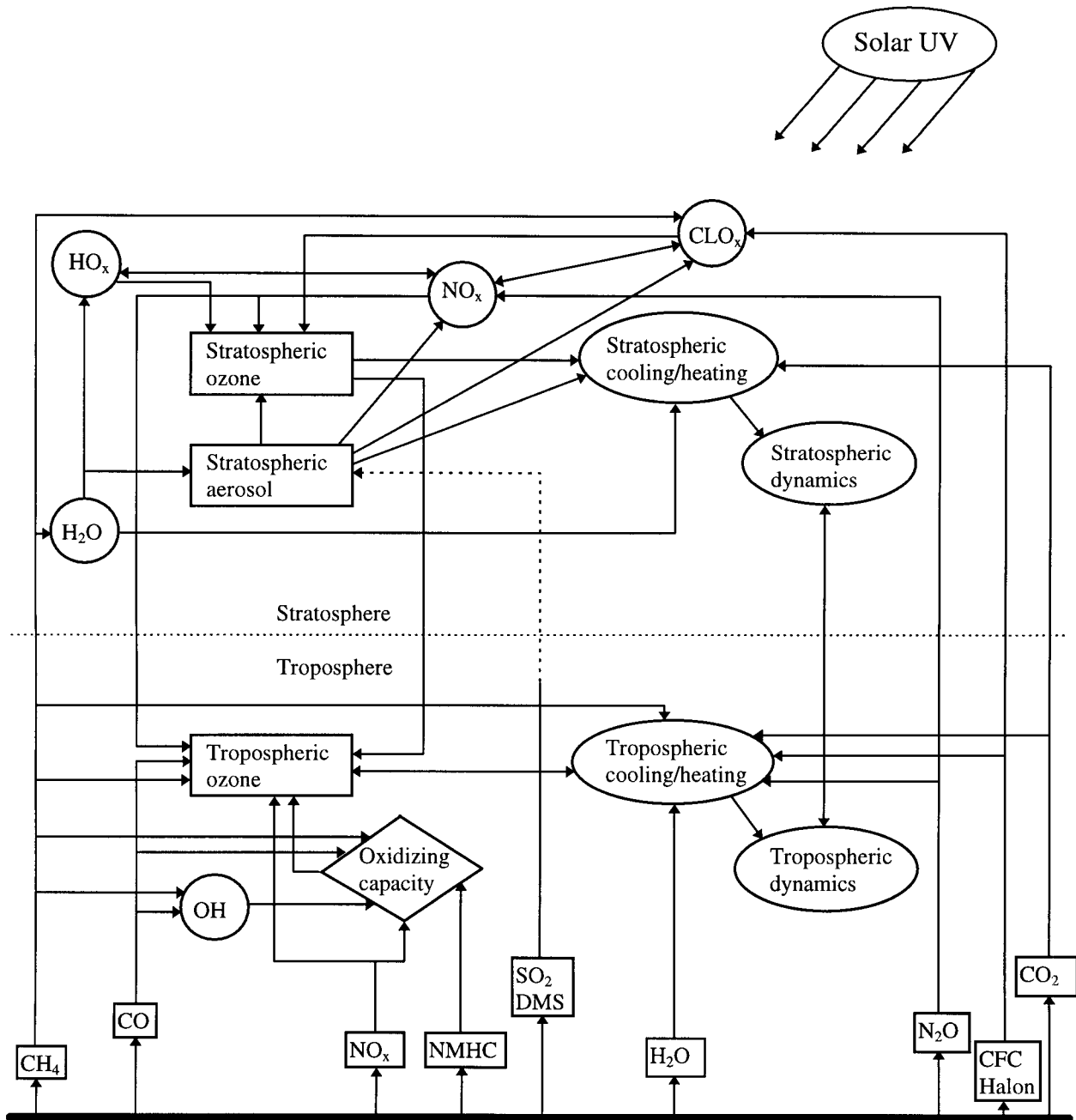
Figure 1. *Representation of the major interactions between stratospheric ozone depletion and the greenhouse effect. No specific boundary layer processes are described. DMS = dimethyl sulphide; NMHC = non-methane hydrocarbons; CFC = all chlorine compounds: CFCs, CCl₄, CH₃CCl₃, CH₃Cl; Halon = both the halons and CH₃Br. The hydrogen-containing chlorine and bromine compounds also react with OH. Solar UV radiation enters the stratosphere and a small fraction of it also reaches the troposphere. Terrestrial IR radiation affects heating and cooling through its absorption by greenhouse gases. Adapted from O. Hov (Wayne, 1991).*

Table 1. *Relation between emissions of trace gases and the enhanced greenhouse effect and stratospheric ozone.*

Compounds emitted at surface	Greenhouse effect			Stratospheric ozone column		
	direct	indirect	by:	direct	indirect	by:
CFCs	+			-		
Halons, CH_3Br				-		
CCl_4, CH_3CCl_3				-		
HCFCs	+			-		
HFCs	+					
N_2O	+			-		
NO_x		+	trop. O_3		+	trop. O_3
CO_2	+				+	temp.
					-	PSCs
CH_4	+	+	trop. O_3		-	HO_x
					+	HCl
CO		+	trop. O_3		+	trop. O_3
NMHC		+	trop. O_3			
SO_2/DMS	-				-	aerosols
H_2O	+					

N_2O (nitrous oxide) is a greenhouse gas causing an increase in temperature in the troposphere and a negligible decrease in the stratosphere. The current radiative forcing is 0.14 W/m^2 (IPCC, 1995). Its atmospheric lifetime is 120 yr, so large amounts can reach the stratosphere. In the stratosphere it is broken down mainly by photolysis, forming the major source of NO_x (= $NO + NO_2$) which can destroy ozone by catalytic reactions.

CH_4 is chemically important in both the troposphere and stratosphere. In the troposphere it reacts with OH and because of its large abundance affects in this way the amount of OH in the troposphere. The OH molecule is the most important oxidizer in the troposphere causing the removal of a large number of compounds from the troposphere. CH_4 thus affects the oxidizing capacity of the atmosphere, lifetimes of greenhouse gases and thereby the radiative forcing of several compounds. The lifetime of CH_4 can be regarded a measure for the oxidizing capacity of the atmosphere, i.e. a longer lifetime means a lower oxidizing capacity. The lifetime of CH_4 is 12 yr (IPCC, 1995), so it can reach the stratosphere in large quantities, where it produces a significant amount of H_2O. Stratospheric H_2O can be photolyzed to form HO_x (= H, OH, HO_2), which participates in catalytic cycles to destroy ozone. Another important role of CH_4 in the stratosphere is its function as the main reaction path for the formation of HCl, an important reservoir compound for chlorine in the stratosphere. Responsible for catalytic destruction of ozone are Cl and ClO. Chlorine in the form of HCl is not capable of destroying ozone. All chlorine compounds are collectively in photochemical equilibrium. This means that a concentration increase of HCl with increasing CH_4 emissions will result in a decrease in Cl and ClO and less ozone destruction by chlorine compounds. This does not hold for bromine compounds since the bromine reservoir HBr is not produced by the reaction Br + CH_4 but by Br + HO_2. Furthermore, HBr is a less stable compound than HCl and therefore a less effective reservoir. The lifetime of HCl in the lower stratosphere is

several weeks, after which it reacts with OH or is transported to the troposphere and removed out of the atmosphere by rain.

CO (carbon monoxide) is not a greenhouse gas. It has both natural and anthropogenic sources and is important in the formation of tropospheric ozone, contributing thereby indirectly to the radiative forcing of the atmosphere. It also affects the OH concentration in the troposphere, influencing the oxidizing capacity of the atmosphere.

NO_x (= NO + NO_2 , nitrogen oxides) are not greenhouse gases. They are mainly from anthropogenic origin and affect the formation of tropospheric ozone and so indirectly contribute to radiative forcing.

NMHC (non-methane hydrocarbons) are important for the formation of tropospheric ozone and the oxidizing capacity of the atmosphere.

SO_2 (sulphur dioxide) and DMS (dimethyl sulphide) are not greenhouse gases. When oxidized (by the reaction with OH) they form H_2SO_4 (sulphate aerosols), which have an estimated negative radiative forcing of -0.4 W/m^2 (IPCC, 1995). In the stratosphere the sulphate aerosols are important for heterogeneous chemistry. Chemical reactions can occur on the surface of sulphate aerosols, affecting the NO_x, ClO_x, BrO_x and HO_x concentrations in the lower stratosphere. This can change the destruction of stratosphere ozone by catalytic reactions of these compounds.

Compounds and processes in the troposphere:

OH in the troposphere reacts with a large number of compounds, causing them to disappear from the atmosphere, i.e. OH is the cleansing agent of the atmosphere. The abundance of OH in the troposphere is determined by the UV radiation reaching the troposphere and the abundance of CH_4, CO, NO_x and NMHC. Since OH is the most important oxidizer of the atmosphere, it determines the **oxidizing capacity**.

Heating and cooling in the troposphere are determined by the interaction of IR radiation with the greenhouse gases H_2O, CO_2, N_2O, CH_4, CFCs, HCFCs, HFCs and ozone, and by aerosols and clouds. They determine the dynamics and temperature distribution in the troposphere.

Tropospheric ozone is a greenhouse gas which is not directly emitted but formed in the troposphere by the chemical reaction $O + O_2$. The abundance of O atoms in the troposphere is determined by a number of compounds; CO, CH_4, NO_x and NMHC. The production and destruction of ozone in the troposphere are large but almost in balance. The influx of ozone from the stratosphere is therefore also important for its tropospheric abundance.

Compounds and processes in the stratosphere:

H_2O in the stratosphere is the main source of HO_x which is an important compound for catalytic ozone destruction. H_2O in the stratosphere comes from both transport through the tropopause and by oxidation of CH_4. It also plays a role in the formation of aerosols and in the heating and cooling of the stratosphere.

ClO_x in the stratosphere plays a major role in the destruction of ozone. Its source is the emission of CFCs, HCFCs, CCl_4, CH_3CCl_3 from anthropogenic sources and CH_3Cl from natural emissions from the oceans.

BrO_x is also important for the destruction of ozone. Approximately 70% comes from natural emissions of CH_3Br from the oceans, the rest from anthropogenic emissions of halons and CH_3Br. Bromine is on a per molecule basis more than 40 times more active in ozone destruction than chlorine but its abundance approximately 150 times less (Velders, 1995b).

NO_x in the stratosphere also reacts catalytically with ozone. It is formed in the stratosphere from photolysis of N_2O. The concentration of NO_x is affected by the presence of sulphate aerosols through heterogeneous reactions on the surfaces. Enhanced sulphate aerosol concentrations from the injection of SO_2 in the stratosphere by volcanic eruptions can therefore affect the NO_x abundance and influence the destruction of ozone.

Heating of the stratosphere is determined mainly by the amount and profile of ozone in the stratosphere, and the corresponding absorption of solar UV radiation. The stratosphere exists by virtue of the ozone layer. The heating/cooling is also affected by IR radiative properties of CO_2 and aerosols. The heating/cooling and dynamics of the stratosphere and troposphere are obviously strongly intertwined. Temperature changes in the atmosphere affect the chemical reaction rates and thereby the concentrations.

Stratospheric ozone determines the thermal structure of the stratosphere. It is formed from molecular oxygen under influence of UV radiation, and its abundance is strongly affected by catalytic reactions of HO_x, NO_x, ClO_x and BrO_x compounds.

Stratospheric aerosols are formed by the oxidation of SO_2 and subsequent reactions. Its abundance can increase by several orders of magnitude by injecting SO_2 from volcanic eruptions. Heterogeneous reactions on sulphate aerosols affect the NO_x chemistry in the lower stratosphere and thereby the ozone destruction. By the absorption of solar (UV) and terrestrial (IR) radiation, aerosols influence the heating/cooling and dynamics of the stratosphere.

Tropospheric and stratospheric dynamics are directly determined by heating and cooling in the atmosphere. The transport processes strongly affect the abundance and distribution of most compounds in the atmosphere.

Solar UV radiation is the driving force of almost all chemical reactions in the atmosphere. Most reactions are initiated by the photolysis of compounds, creating highly reactive radicals. Solar UV is absorbed in the stratosphere by both molecular oxygen and ozone. A small amount of UV (UV-A and -B) reaches the troposphere, where especially UV-B (280-315 nm) can photolyze several compounds. The photolysis of ozone in the troposphere creates excited oxygen atoms, $O(^1D)$, which react readily with H_2O to produce OH. Changes in stratospheric ozone affect in this way the amount of OH in the troposphere, influencing the oxidizing capacity of the atmosphere.

3. MODELS AND EMISSIONS

Two models are used for the scenario simulations. Changes in the radiative forcing and the temperature of the atmosphere are calculated with the OGI-1D radiative convective model and changes in the atmospheric composition and ozone layer thickness are calculated with the Cambridge/RIVM 2D model of the stratosphere. The emissions fields, both historical and future, used in the scenario simulations are described in this chapter.

3.1. The RIVM 2-dimensional stratosphere model

Chemical changes in the atmosphere are calculated with the RIVM version of the 2-dimensional stratosphere model (Velders, 1995a, 1995b) as originally developed by Harwood and Pyle; see also Harwood and Pyle (1975, 1977, 1980), Haigh and Pyle (1989) and Law and Pyle (1993a, 1993b). The main characteristics of this model are given in Appendix A.

3.2. OGI-1D Radiative convective model

The calculation of radiative forcings and temperature changes are performed using the OGI-1D radiative convective model from MacKay and Khalil (1991). This 1D model has 18 vertical layers from the surface to approximately 60 km and describes the transmission and absorption of IR and UV radiation, as well as convection in the atmosphere. Heating and cooling and the temperature profile of the atmosphere are calculated on the basis of given concentrations of the greenhouse gases: CO_2, CH_4, N_2O, O_3, CFCs and H_2O. The model has been extended to include the absorption of HCFCs and HFCs.

3.3. Historical emission data (1900-1990)

3.3.1. Chlorine and bromine compounds

The historical emission data (1900-1990) of chlorine- and bromine-containing compounds used for the simulations if from Kaye et al. (1994). Emissions from CFC-11, CFC-12, CFC-113, CFC-114, CFC-115, HCFC-142b are based on the emission inventory reports of AFEAS (1993, 1994). The major chemical manufacturers in the world participate in AFEAS (= Alternative Fluorocarbon Environmental Acceptability Study) by reporting their production figures of CFCs and related compounds. Not all emissions are covered by AFEAS. A number of countries in Eastern Europe (CIS), Asia (India, China), Africa and South America produce CFCs but their emissions are not included in the surveys of AFEAS or its predecessors. These countries are the so-called non-reporting countries. Kaye et al. (1994) improved the AFEAS emission inventories by taking into account emissions in the non-reporting countries. The emissions in the non-reporting countries are low compared with the emissions in the reporting countries, which are mostly the developed countries in the West. For most compounds the non-reporting countries emit less than 10% of the total world wide emissions, although their relative contribution is increasing. In coming decades it is expected that the contribution of the non-reporting countries to total emissions will increase since, following the Montreal Protocol and its amendments, a stricter (faster) phase-out of CFCs and related compounds applies to the developed (reporting) countries. They are also expected to comply better with the phase-out agreements than developing countries.

The historical HCFC-22 emissions are from AFEAS (1993, 1994), Kaye *et al.* (1994), Midgley and Fisher (1993) and Jesson (1979). Methyl chloride (CH_3Cl) emissions are taken from Kaye *et al.* (1994), methyl chloroform (CH_3CCl_3) emissions from Midgley (1989) and Prinn *et al.* (1987, 1992) and carbon tetrachloride emissions from Simmonds *et al.* (1983, 1988). The emissions of the bromine compounds halon 1211 and halon 1301 are taken from McCulloch (1992) and Kaye *et al.* (1994), while the natural and anthropogenic emissions of methyl bromide (CH_3Br) are taken from Singh and Kanakidou (1993) and Manö and Andreae (1994). For a more detailed description of the emissions that are used for the simulations see Velders (1995b). Since the emissions of the HFCs and HCFCs, except HCFC-142b and HCFC-22, are very low and emission inventories not available yet, the emissions of these have been ignored in the historical scenarios (i.e. before 1990).

The uncertainty in the emission data of the CFCs is caused by uncertainties in the reported levels of production, the levels of non-reported production and the time pattern of release for specific applications (Gamlen *et al.*, 1986; Kaye *et al.*, 1994). Fisher and Midgley (1994) estimated the uncertainty in the cumulative emissions through 1991 for CFC-11 and CFC-12 for different production and release scenarios. Adding up the uncertainties of the different categories, the uncertainty in the cumulative emissions ranges from -11.5% to +9.3% for CFC-11 and from -6.3% to +6.3% for CFC-12. The estimated uncertainty in the cumulative emissions from 1980 to 1990 for methyl chloroform (Kaye *et al.*, 1994) ranges from -2.5% to +5.7%, while the uncertainty for HCFC-22 (Midgley and Fisher, 1993) is larger (±10%). The uncertainty in the emissions of carbon tetrachloride is large since the principle use is feedstock for the production of CFCs, while the emissions come primarily from a few not very well quantified sources.

AFEAS divides the sales of the CFCs and HCFCs reported by them into hemispheric regions, northern hemisphere–southern hemisphere or 90°N–30°N, 30°N–Equator, Equator–90°S. This information is used to distribute the emissions over the latitude bands in the simulations. For CCl_4 and CH_3CCl_3, the distribution of the emissions over the different hemispheres is given by the original authors, Simmonds *et al.* (1983, 1988) and Midgley (1989), respectively. Where information about the hemispheric distribution of the emissions was available only for a limited number of years, the known distribution was extrapolated. Where no distribution was available at all, the following distribution for the anthropogenic emissions was assumed: 85% in 90°N–30°N; 10% in 30°N–Equator, 2.5% in Equator–30°S, 2.5% in 30°S–90°S. This assumed distribution agrees well with the known distributions and the atmospheric concentrations for long-lived compounds are not very sensitive to the hemispheric distribution of the emissions. The hemispheric distribution of Khalil *et al.* (1993) was used for the natural emission of CH_3Br, while for the (natural) emission of CH_3Cl we assumed: 10% in 90°N–30°N; 40% in 30°N–Equator, 40% in Equator–30°S, 10% in 30°S–90°S. The natural emissions of both CH_3Cl and CH_3Br are high compared with the anthropogenic ones, while there are also large uncertainties in the emissions (WMO, 1994; Kaye *et al.*, 1994).

In future the hemispheric distribution of the emissions is likely to change slightly as a result of the faster phase-out of the CFCs and related compounds by the developed nations than by the developing nations. The hemispheric distribution of CFC emissions and related compounds is relevant for the distribution in the troposphere of compounds with an atmospheric lifetime of only a few years. For compounds with long lifetimes and for distributions in the stratosphere, the hemispheric distributions is of only minor importance.

The assumptions made here for the hemispheric distributions will therefore hardly influence the calculated distribution of stratospheric ozone.

3.3.2. Methane and nitrous oxide

Chappellaz et al. (1993) reported that the global pre-industrial methane emissions amount to 180 Tg/yr, with a corresponding concentration of 650 ppbv. Putting these emissions in the RIVM 2D stratosphere model yields a CH_4 concentration in the troposphere of 570 ppbv in the Southern Hemisphere (SH) and 660 ppbv in the Northern Hemisphere (NH). Extrapolating these emissions to the 20th century, obtain a CH_4 emissions of 270 Tg/yr in 1900 with corresponding calculated concentrations of 900 ppbv (SH) and 1050 ppbv (NH). The emissions in 1990 are taken from The and Beck (1995) and yield 540 Tg/yr, with corresponding concentrations of 1580 ppbv (SH) and 1850 ppbv (NH) (January values). These values are close to the measurements in the NOAA/CMDL network (Fung et al., 1991; see also The and Beck, 1995) which yield 1630 ppbv (SH) and 1800 ppbv (NH) for January. The concentration in the NH is overestimated by the 2D model and in the SH is underestimated, which points to a small underestimation of the North-South transport in the 2D model. This can also be seen in a comparison of measured and modelled methyl chloroform concentrations (Velders, 1995a).

The 1990 global CH_4 emission of 540 Tg/yr is in very good agreement with the values reported by IPCC (1994); total atmospheric CH_4 sinks is 530 Tg/yr and the total emission from identified sources is 535 Tg/yr. These values are higher than previous estimates because of a faster chemical removal rate. An uptake of CH_4 by soils of 30 Tg/yr is also foreseen in the latest assessments, yielding a total CH_4 emission of 560 Tg/yr. A soil uptake of CH_4 is not taken into account in our model simulations so the total emission of 540 Tg/yr in 1990 used for the simulations agrees with the IPCC (1994) values.

The emissions from 1900 to 1990 are interpolated on the basis of the measured concentration and distributed over the months of the year and different latitudes using the CH_4 emission inventory of Müller (1992) (see also The and Beck, 1995).

The emissions of nitrous oxide (N_2O) are based on Kroeze (1994). She reports an emission of 8.8 TgN/yr in 1900 and 12.7 TgN/yr in 1990. The 1900 emission is based on estimated pre-industrial concentrations using too long an atmospheric lifetime of 170 yr. The current estimated lifetime of N_2O is 120 yr (IPCC, 1994). To obtain atmospheric N_2O concentrations in 1990 which are close to the measured values we added 2.05 TgN/yr to the emissions from Kroeze (1994). This yielded concentrations with the 2D model of 289 ppbv in 1900 and 307.5 ppbv in 1990. The pre-industrial concentration ranges from 260 to 285 ppbv (IPCC, 1994) and the measured 1990 concentration is 308 ppbv (IPCC, 1994; ALE/GAGE data, in Prinn et al., 1990).

The total N_2O emissions used for 1990 was 14.75 TgN/yr. IPCC uses an N_2O emissions of 12.9 TgN/yr in 1990 in their IS92 scenarios (Pepper et al., 1992), however since the IS92 fluxes are inconsistent with current lifetime and growth rate, 3.4 TgN/yr is added to all IS92 scenarios, yielding 16.3 TgN/yr in total (IPCC, 1994). Our emission of 14.75 TgN/yr is between the two IPCC values. This difference can be attributed to small differences in the specific model used to calculate the N_2O concentrations from the emissions.

3.3.3. Carbon monoxide and nitrogen oxides

For CO and NO_x the fixed surface concentrations are used instead of actual emissions. In most simulations the CO and NO_x surface concentrations are kept fixed. Only in a few sensitivity simulations is a CO and NO_x trend applied.

The fixed surface concentrations (month and latitude-dependent) for CO in 1990 are derived from measurements by Khalil and Rasmussen (1984, 1994) and correspond to the 1980s. These concentrations are approximately 45 ppbv (SH) and 125 ppbv (NH). The surface concentrations of CO have increased since the pre-industrial period. Khalil and Rasmussen (1988) argue that the CO concentrations may have doubled since pre-industrial times which also follows from calculations of Thompson and Cicerone (1986). When a CO trend was applied in the simulations, we used therefore a surface concentration half the levels of 1990 for 1900. The trend from 1900 to 1990 is taken proportional to the measured CO_2 concentration, since CO and CO_2 are of similar anthropogenic origin.

The fixed surface concentrations (month and latitude-dependent) for NO_x in 1990 are derived from model calculations from Law and Pyle (1993a), ranging from roughly 25-60 pptv (SH) and 0.3-4 ppbv (NH). Pre-industrial values for NO_x are very speculative, especially when applying them in a global atmosphere model. Thompson and Cicerone (1986) calculated boundary layer NO_x concentrations in pre-industrial times as low as 20-25 pptv. For an NO_x trend in the simulations we used 25 pptv in 1900, interpolating this to the 1990 concentrations using measured CO_2 concentrations.

3.4. Future emissions data (1990-2100)

3.4.1. Chlorine and bromine compounds

The IPCC IS92 scenarios (Pepper *et al.*, 1992) were used for the simulations from 1990 to 2100. These contain three different CFC scenarios, i.e. the IPCC cases 3, 4 and 6 with different levels of compliance to the Montreal Protocol. IPCC case 6 resembles the Copenhagen amendments to the Montreal Protocol. The IS92 scenarios contain the following CFC scenarios: IS92a (CFC case 3), IS92b (4), IS92c (3), IS92d (6), IS92e (6), IS92f (3). Simulations are performed with all these scenarios and also with different combinations of scenarios. The scenario IS92a is a mid-range, or business-as-usual, scenario with respect to the emission data for CO_2, CH_4 and N_2O. Since the current growth rates of most chlorine- and bromine-containing compounds are already declining (Montzka *et al.*, 1996) the IPCC case 3 and 4 scenarios for CFC are less likely to occur.

For these scenarios the latitudinal distribution of the emissions is kept fixed for all years and taken equal to the 1990 distribution of the historical emission scenarios. So, if possible, available information from AFEAS or another source on the hemispheric distribution of the emissions in 1990 is used, otherwise a distribution is postulated.

3.4.2. Methane and nitrous oxide

The IPCC IS92 scenarios (Pepper *et al.*, 1992) were used for the emissions of CH_4 and N_2O from 1990 to 2100. For the CH_4 emissions 34 Tg/yr is added to yield a 1990 value of 540 Tg/yr in accordance with the historical emission data. In the IPCC (1994) assessment 69 $Tg(CH_4)$/yr is added to the IS92 scenarios to be in agreement with the current lifetime and growth rate of methane. The emissions are distributed over the months of the year and

different latitudes using the CH_4 emission inventory of Müller (1992) (see also The and Beck, 1995). For N_2O we added 1.2 TgN/yr to the IS92 scenarios, yielding a start value in 1990 for the future emissions of 14.1 TgN/yr.

3.4.3. Carbon monoxide and nitrogen oxide

In the future scenarios the surface concentration of CO and NO_x will be held fixed (month and latitude-dependent). The CO concentration is derived from measurements by Khalil and Rasmussen (1984, 1994) and corresponds to the 1980s. The NO_x surface concentrations are derived from model calculations from Law and Pyle (1993a) and correspond to the current 1990 situation. No future trend is simulated for CO and NO_x.

4. SIMULATION RESULTS

A number of the interactions between the greenhouse effect and stratospheric ozone depletion, described qualitatively in Chapter 2, will be quantified in this chapter, beginning with the radiative forcing, a measure for the enhanced greenhouse effect, followed by the depletion of stratospheric ozone. The models and emissions used for this evaluation are described in Chapter 3 and Appendix A. Important tables and figures are shown here; others, indicated with a 'B', can be found in the Appendix B.

4.1. Concentrations

The atmospheric concentration of all the compounds (except CO_2) relevant for the greenhouse effect and stratospheric ozone depletion were calculated with the 2D stratosphere model. Carbon dioxide is chemically non-reactive and its concentration is determined not by chemical processes in the atmosphere, but by emissions and exchanges between the atmosphere, biosphere and the oceans. These processes are not taken into account in stratosphere models. The CO_2 concentration is therefore not calculated by the 2D stratosphere model but taken from the IPCC (1994) report. The mean global surface concentrations of a few relevant compounds are given in Figs. B1 to B6 (Appendix B).

The concentration of CO_2 increases considerably in the 21st century with possibly large consequences for the temperature in the troposphere and stratosphere. The CH_4 concentration increases in most scenarios, which will result in increases in radiative forcing. However this will also affect stratospheric ozone depletion through the formation of water vapour in the stratosphere and enhancement of the production of the reservoir compound HCl. N_2O also increases in concentration but relatively less than for CO_2 and CH_4.

CFC-11, being representative for all CFCs, methyl chloroform and carbon tetrachloride, decreases in concentration in all scenarios. These scenarios do not take proper account of the rapid, and difficult to time, changes in emissions occurring in the last few years. The decrease start after 2000. Measurements (Montzka et al., 1996; ALE/GAGE network, private communications) already show a decrease in concentration in methyl chloroform and carbon tetrachloride since a few years, while the concentration of CFC-11 has stabilized since approximately 1994. The concentration of CFC-12 still shows a small increase.

HCFC-22 and HFC-134a are the two respective compounds with the largest current and expected future emission of the whole class of HCFCs, HFCs. The trend in concentration is characteristic for all HCFCs, HFCs respectively. The scenarios IS92d and IS92e follow the Copenhagen amendments to the Montreal Protocol and show therefore a decrease in HCFC-22 concentration after 2010. The measured concentration of HCFC-22, but also of HCFC-141b and HCFC-142b, is increasing (Montzka et al., 1996). The HCFC-141b concentration was approximately 5 pptv and of HCFC-142b approximately 8 pptv in the Northern Hemisphere in 1995. The HFC-134a concentration increases for all scenarios. Montzka et al. (1996) have reported an increase in the concentration of HFC-134a, although the concentration is still low: < 3 pptv in 1995.

4.2. Temperature and radiative forcing changes

The IPCC (1994) assessment of radiative forcing of climate change gives two definitions of radiative forcing: 1) the instantaneous radiative forcing calculated with no changes allowed in stratospheric temperatures and, 2) the adjusted radiative forcing for which the temperature in the stratosphere has been allowed to re-adjust to instantaneous forcing. Both definitions yield only large differences in radiative forcing for changes in stratospheric ozone. The adjusted radiative forcing is usually considered the best measure for induced temperature changes in the atmosphere since it relates linearly to a change in surface temperature, with the same proportionality factor for all compounds.

The current (1994) radiative forcing calculated with the OGI-1D model agree reasonably well with the values reported by IPCC (1994), as can be seen in Table B1. The largest contribution to radiative forcing comes from CO_2. The depletion of stratospheric ozone results in a negative forcing relative to 1900. This forcing is somewhat larger than -0.1 W/m^2 reported by IPCC (1994) but within the uncertainty range, taking the change calculated for stratospheric ozone from 1980 to 1990 into account (see note of Table B1). Radiative forcing from changes in tropospheric ozone are not considered here. Figure 2 and Table B2 show the adjusted radiative forcing relative to 1900 for the IS92 scenarios calculated with the OGI-1D radiative convective model. The radiative forcing from scenario IS92a and IS92b can be considered as mid-range values, IS92e and IS92f are on the high end of the spectrum and IS92c and IS92d on the low end. The emissions of the greenhouse gases CO_2, CH_4 and N_2O increase continuously from 1990 to 2100 in all the future scenarios; consequently, radiative forcing from the compounds also increases continuously. This is not the case for the CFCs and stratospheric ozone. The emission and concentration of CFC, methyl chloroform carbon tetrachloride and halons in the atmosphere decrease in all scenarios after 2000 and so does the corresponding radiative forcing of these compounds. But these compounds are replaced by HCFCs and HFCs with larger radiative forcing that the compounds they replace. The total forcing from these compounds combined, e.g. from the sum of CFCs, HCFCs, HFCs and other chlorine and bromine compounds, does not decrease after 2000 but increases by approximately 65% for IS92d to 115% for IS92f in 2100 relative to 1990. Because of the lower emissions of chlorine and bromine compounds stratospheric ozone will increase and the corresponding negative radiative forcing will turn positive. Since the six IS92 scenarios contain three different CFC scenarios the change in radiative forcing from the change in stratospheric ozone differs for the various scenarios. The scenarios IS92d and IS92e have CFC scenario IPCC case 6 (Pepper et al., 1992), resembling the Copenhagen amendments to the Montreal Protocol, with the lowest CFC emissions and corresponding fastest increase in stratospheric ozone. The direct and indirect (by stratospheric ozone) changes in radiative forcing from CFCs, HCFCs, HFCs are approximately -0.1 W/m^2 in 1990 to -0.20 W/m^2 in 2000, and to 0.24 W/m^2 for IS92c and 0.48 W/m^2 for IS92e in 2100.

Radiative-forcing global-mean temperature changes in the atmosphere are calculated from these changes with the OGI-1D model from the surface to 60 km. These are shown in the Figs. 2 and 3 and in Table B3.

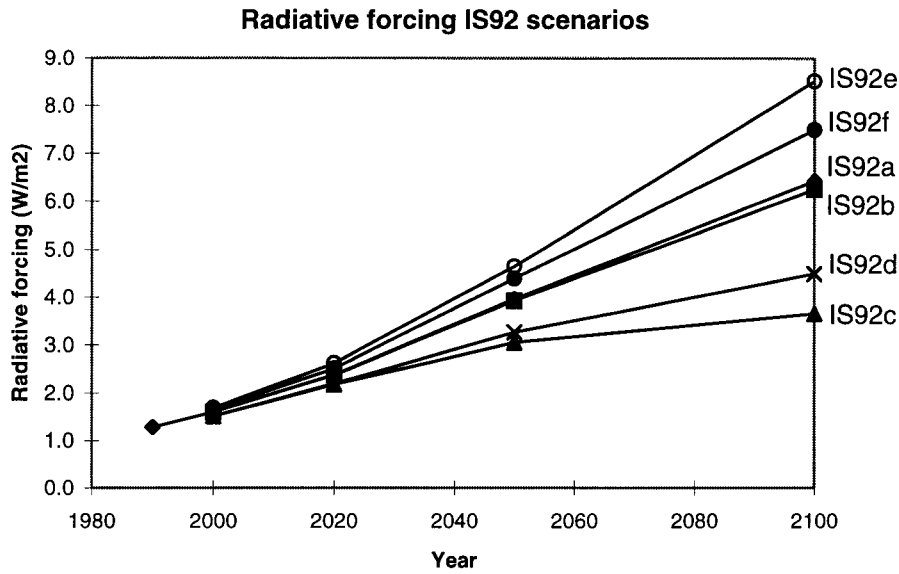**Figure 2.** *Adjusted radiative forcing (W/m²) for the IS92 scenarios relative to 1900. Contributions from CO_2, CH_4, N_2O, CFCs, HCFCs, HFCs and stratospheric ozone. The contributions of the various compounds to the radiative forcing are given in Table B2.*
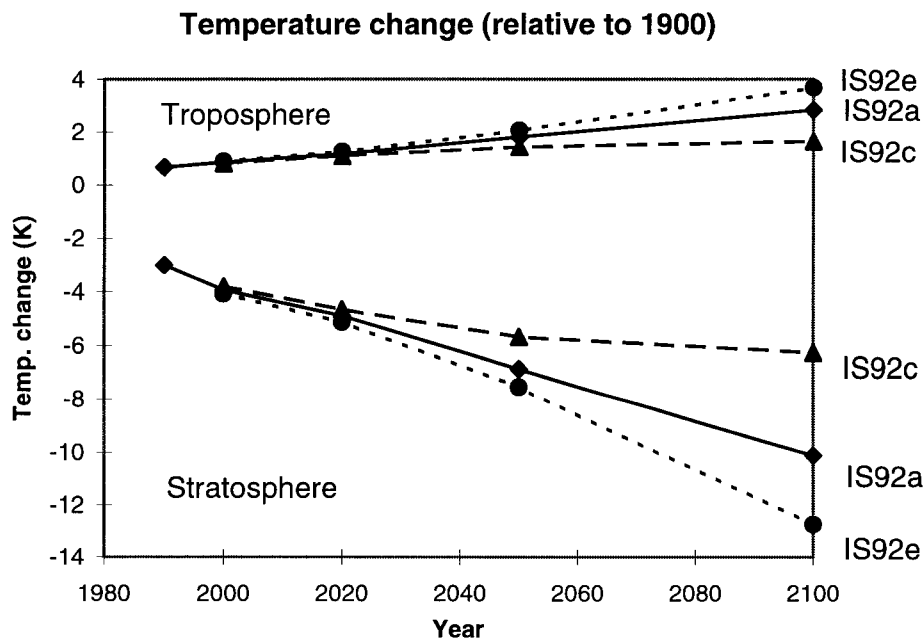

Figure 3. *Temperature change in troposphere and stratosphere calculated with the OGI-1D radiative model for IS92 scenarios.*
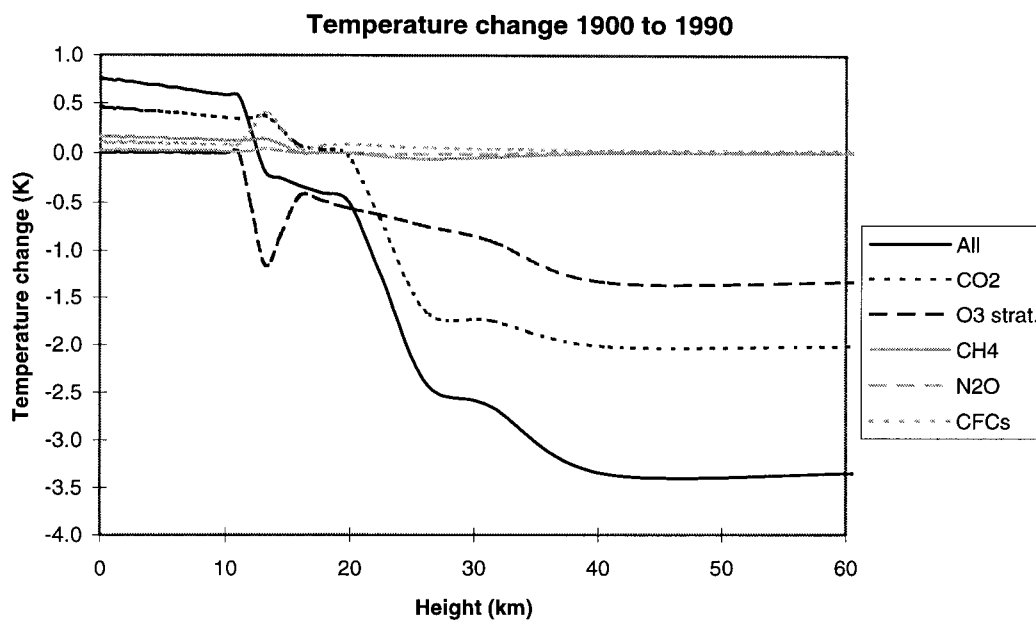
Figure 4. *Contributions of different compounds to the mean global temperature changes (K) from 1900 to 1990. Only stratospheric ozone is considered.*

The calculated temperature change for 1990 is 0.67 K for the troposphere, which is somewhat higher than the current analyzed global mean-surface temperature increase of 0.3 to 0.6 K (IPCC, 1994). The calculated tropospheric temperature changes in 2100 vary between 1.65 and 3.68 K relative to 1900 corresponding with 0.98 to 3.01 K relative to 1990. These values are very close to the best estimates from IPCC for the temperature change in 2100, ranging from 1 to 3.5 K relative to 1990. The largest contribution to the temperature change in the troposphere comes from CO_2, while CH_4 and the CFCs also contribute significantly, as can be seen in Fig. 4.

Larger temperature changes occur in the stratosphere. Our calculations reveal a large amount cooling in the stratosphere from CO_2 and a slightly smaller amount from ozone. The other greenhouse gases do not influence the temperature in the stratosphere significantly. Since the decrease in stratospheric ozone has occurred in the last few decades, while the increase in CO_2 takes place over a larger time frame, the relative contribution of stratospheric ozone to the temperature change in the stratosphere has increased in the last few decades. Randel and Cobb (1994) inferred a temperature trend from satellite observations. They found a decrease in temperature in the lower stratosphere ranging from -0.5 to -1.5 K from 1979 to 1990. Radio sonde measurements of the lower stratospheric temperature show a decrease of 0.25 to 0.4 K per decade over the last three decades. These observations are in agreement with the calculations of Table B3 and Fig. 4. Our calculations give a change in temperature in the lower stratosphere of approximately 0.45 K from 1980 to 1990. The future scenarios show large decreases in stratospheric temperatures in the 21st century. Relative to 1990, the temperature changes range from -3.26 K for IS92c to -9.75 K for IS92e. Since the radiative forcing from stratospheric ozone depletion decreases in the 21st century, the stratospheric temperature decrease originates mainly from changes in CO_2 emissions.

4.3. Historical changes in ozone: 1900-1990

This and the following sections form the heart of the report. The interactions described qualitatively in Chapter 2 will be quantified here. Table 2 shows the ozone column in 1990 and the trend in ozone column over the period 1980 to 1990 at 47°N for various scenario simulations. The emission trends, based on gradual continuous changes, do not take into account observed fluctuations in the concentration of some of the compounds in the last decade. All ozone levels are the result of simulations from 1900 to 1990, with conditions for the emission of compounds varying:

- trend in emissions from 1900 to 1990, indicated by 'Tr';

- emissions fixed at their 1900 values, indicated by '1900';

- emissions fixed at their 1990 values (default), indicated by a blank cell.

In most of the simulations summarized in Table 2 the emissions of CFCs and related chlorine and bromine compounds show a trend from 1900 to 1990; the effect of CH_4, N_2O, CO, NO_x and temperature changes are studied in addition to this chlorine trend. In the last column of Table 2 the atmospheric lifetime of CH_4 is given as a measure of changes in the troposphere based on changes in the emissions and ozone layer thickness. In other words, the CH_4 lifetime can be regarded as a measure of the oxidizing capacity of the atmosphere. A longer lifetime corresponds with a lower oxidizing capacity. The lifetime of CH_4 is largely determined by the OH concentration, which in turn depends on the CO, NO_x and CH_4 tropospheric concentrations and on the amount of UV radiation reaching the troposphere. The results of the simulations will be discussed and explained using both Table 2 and the Figs. B7 to B11 in Appendix B.

4.3.1. CH_4 trend

A trend in the emissions of CFCs and related compounds alone (simulation 1) gives an ozone column of 379.2 DU and a trend in ozone column of -5.8% per decade from 1980 to 1990. Applying a trend in CH_4 emissions in addition to this (simulation 3) yields a 3% thicker ozone column in 1990 and a smaller ozone trend of -4.4% per decade. That is, the trend in CH_4 emissions this century has reduced the destruction of the ozone layer from 1980 to 1990 by approximately 1.4% per decade. This positive trend comes clearly from the interaction of CH_4 with chlorine in the stratosphere. Figure B7 shows the increase in CH_4 of 80% in the whole atmosphere caused by the trend in CH_4 emissions from 1900 to 1990. The reaction CH_4 + Cl ==> HCl results in an increase in HCl of approximately 18% in the lower and 24% in the middle stratosphere. (These percentages are yearly averaged values over the designated areas.) The increase in HCl means that the photostationary equilibrium of active chlorine compounds (ClO_x) shifts more to the reservoir HCl, reducing the concentrations of Cl and ClO, which are the important compounds for catalytic destruction of stratospheric ozone. Cl and ClO are reduced by approximately 20% to 25% in the whole stratosphere (Fig. B7) resulting in an increase of 2% to 4% in ozone in the lower stratosphere. In the upper stratosphere the increase reaches 6% to 8% but this area hardly contributes to the ozone column.

Table 2. *Yearly averaged ozone column (DU) in 1990, ozone column trend from 1980 to 1990 (% per decade) at 47°N and methane lifetime (yr) with trends for CH_4, N_2O, CO, NO_x and temperature varying.*

Simulation	Characterization scenario[1]						Ozone[2] column (DU)	Relative[3] to run 4 (%)	Ozone trend (%/dec.)	CH_4 lifetime[8] (yr)
	CFC[4] halon	CH_4	N_2O	CO	NO_x	temp				
1 CH_4, N_2O fixed	Tr	1900	1900				379.2	-3.0	-5.8	11.1
2 N_2O trend	Tr	1900	Tr				379.4	-3.0	-5.6	11.1
3 CH_4 trend	Tr	Tr	1900				391.1	0.0	-4.4	11.5
4 CH_4, N_2O trend[3]	Tr	Tr	Tr				391.0	Referen.[3]	-4.3	11.5
5 CH_4 trend	1900	Tr	1900				435.5	11.4	0.1	12.2
6 N_2O trend	1900	1900	Tr				430.1	10.0	-0.2	12.0
7 CH_4, N_2O trend	1900	Tr	Tr				433.3	10.8	0.0	12.2
8 Temp. fixed	Tr	Tr	Tr			1900	381.1	-2.5	-4.2	11.7
9 Temp. trend	Tr	Tr	Tr			Tr[5]	390.9	0.0	-3.5	11.5
10 CO fixed	Tr	Tr	Tr	1900			390.6	-0.1	-4.5	8.3
11 CO trend	Tr	Tr	Tr	Tr			390.9	0.0	-4.4	11.5
12 NO_x fixed	Tr	Tr	Tr		1900		369.3	-5.5	-4.5	20.7
13 NO_x trend	Tr	Tr	Tr		Tr		391.1	0.0	-3.7	11.5
14 CO, NO_x fixed	Tr	Tr	Tr	1900	1900		375.2	-4.1	-4.6	15.0
15 CO, NO_x trend	Tr	Tr	Tr	Tr	Tr		391.0	0.0	-3.9	11.5
16 All 1900	Tr	1900	1900	1900	1900	1900	355.1	-9.2	-5.9	14.4
17 All trend	Tr	Tr	Tr	Tr	Tr	Tr	390.9	0.0	-3.2	11.5
18 T(no CFC)	Tr	Tr	Tr			Tr[6]	391.0	0.0	-3.8	11.5
19 1/2 × NO_x(1990)	Tr	Tr	Tr		1/2		383.2	-2.0	-4.2	17.3
20 H_2O fixed 1900[7]	Tr	Tr	Tr				391.5	0.1	-4.2	11.6
21 Gas-phase chemistry	Tr	Tr	Tr				395.6	1.2	-1.7	11.6
22 Heterogeneous/LL	Tr	Tr	Tr				398.7	2.0	-3.1	11.6

1) Tr = trend in emissions of CFCs, CH_4 and N_2O from 1900 to 1990. For CO and NO_x a trend in surface concentrations is applied; 1900 = fixed 1900 values are used; a blank cell means that fixed 1990 values are used.

2) Estimated total anthropogenic change in ozone column at 47°N in 1980 is -4.5% and in 1990 -8.6% relative to 1900.

3) Simulation 4 is considered as a reference scenario; the others are compared with this one.

4) CFC stands for all CFCs, HCFCs, methyl chloroform, carbon tetrachloride, halons, methyl chloride and methyl bromide.

5) Dynamical feedback and heterogeneous reactions on PSCs are not taken into account.

6) Temperature trend based on radiative forcing from increases of CO_2, CH_4 and N_2O. Changes in CFCs and ozone are not incorporated.

7) The H_2O concentration is kept fixed at the 1900 level.

8) The lifetime of CH_4 is considered a measure (inverse) of the oxidizing capacity of the atmosphere.

The increase in CH_4 concentration hardly affects the bromine compounds since the bromine reservoir HBr is not produced by the reaction $Br + CH_4$ but by $Br + HO_2$. Furthermore, HBr is a less stable compound than HCl and therefore a less effective reservoir. The increase in CH4 emissions in this century changed the Br concentration in the stratosphere by -4% and BrO by +0.1%.

The increase in CH_4 in this century causes an increase in H_2O of 1% in the lower, 8% in the middle and 15% in the upper stratosphere. OH, formed in the stratosphere by the reaction $O(^1D) + H_2O$, increases by approximately 7% in the lower and middle stratosphere. This causes extra ozone destruction by the catalytic HO_x cycles. This is only a small effect, as can be seen by simulation 20, in which the H_2O concentration is fixed in the atmosphere at its 1900 levels during the simulation. Comparing simulation 20 with 4 it can be seen that the increase in H_2O (simulation 4) causes a decrease in the ozone column in 1990 of 0.1% and an extra ozone trend of -0.1% per decade.

The increase in methane emissions this century results in less ozone destruction by chlorine compounds (+1.5% per decade) and slightly more destruction by increased H_2O (-0.1% per decade). The importance of the interaction between chlorine and CH_4 for ozone is also clear from simulation 5, in which a trend in CH_4 alone and not in CFC emissions is applied. The CH_4 emission result is a small positive trend in the ozone column of 0.1% per decade, while the much lower chlorine levels in the lower stratosphere, coming only from natural CH_3Cl emissions, yield an 11% thicker ozone column in 1990.

The effect of including a trend in CH_4 emissions in the calculation of the trend in ozone column results in a good agreement with measurements. The measured trend in ozone column at mid-latitude in the Northern Hemisphere from 1980 to 1990 is (-4.0 ± 2.1)% per decade from TOMS measurements and (-3.9 ± 0.7)% per decade from the Dobson network (WMO, 1994). These values are close to the -4.4% per decade resulting from the trend in emissions of CFCs and related compounds and CH_4.

The calculated CH_4 lifetime of 11.5 yr (simulation 4) is close to the IPCC (1995) figure of 12±3 yr. The increase in CH_4 emissions causes in increase in its lifetime through both the doubled CH_4 concentration and by the reduced amount of UV radiation passing through the thicker ozone layer. The emission of CFCs and related compounds caused a decrease of almost 11% in the ozone layer thickness (comparing simulation 7 and 4). The thinner ozone layer in simulation 4 allows more UV radiation to reach the troposphere, which is directly responsible for the decrease in lifetime of CH_4 from 12.2 to 11.5 yr. This is an illustration of the effect of changes in the ozone layer on the concentration of greenhouse gases. It should be noted that the change in atmospheric lifetime of CH_4 of 6% is determined by the global atmosphere and can therefore not be directly related to the change in the ozone layer of 10.8 % calculated for 47°N.

4.3.2. N_2O trend

The trend in N_2O emissions from 1900 to 1990 has a small effect on the ozone column and the ozone column trend. Comparing simulations 1 and 2 or 3 and 4 shows that the N_2O trend yields a trend in ozone of +0.2% per decade or +0.1% per decade, respectively. This positive contribution of N_2O comes from the interaction of nitrogen and chlorine compounds in the stratosphere. N_2O emissions on their own cause an increase in NO_x in the stratosphere which destroys ozone catalytically. Simulation 6 shows a trend in ozone of -0.2% per decade from

the trend in N_2O emissions alone (no CFC trend applied). But if CFC emissions also increase the interaction between NO_x and ClO in the stratosphere yields the chlorine reservoir $ClONO_2$, causing a shift in the photochemical equilibrium of chlorine compounds away from Cl and ClO yielding a smaller ozone destruction. This diminishing effect on ozone destruction by $ClONO_2$ formation is larger that the increasing effect by NO_x. Figure B8 shows that an increase in N_2O emissions this century results in a 6% larger N_2O concentration, an increase of NO_x of 5% and of $ClONO_2$ of 1% and a decrease of ClO of 4%, all in the lower stratosphere.

There is no large interaction between CH_4 and N_2O emissions which affects ozone formation as can be seen from the simulations 4 and 7 and when comparing them with the others.

4.3.3. Temperature trend

Simulations 8 and 9 show the effect of the trend in temperature on the ozone column as calculated with a radiative model described in section 4.2. The 3K temperature decrease in the stratosphere from 1900 to 1990 yields an increase in the ozone column of 2.5%, while the trend in the ozone column from 1980 to 1990 increases from -4.2% per decade to -3.5% per decade. The higher ozone levels with lower temperatures probably comes from the temperature dependence of the odd oxygen cycle, i.e. the Chapman cycle. Stratospheric ozone levels are, according to the Chapman cycle, proportional to the production of ozone by the reaction $O + O_2$, divided by the ozone destruction by the reaction $O + O_3$. The former reaction rate increases with decreasing temperature, while the latter decreases. So the increase in ozone production and decrease in ozone destruction with decreasing temperature yields higher ozone levels in the stratosphere. The increase in ozone is further assisted by a decrease in NO_x (-2%), OH (-3%) and ClO (-1%) in the lower stratosphere in 1990 relative to 1900 (Fig. B9), reducing catalytic destruction of ozone by these compounds.

The decrease in temperature in the stratosphere comes largely from CO_2 and the effect of a temperature trend can therefore also be viewed as resulting from the increase in CO_2 emissions in this century. In simulation 18 a trend in temperature caused only by the increase in CO_2, is applied. Comparing this simulation with 8 and 9 the contribution of CO_2 to the trend in the ozone column is +0.4% per decade. The temperature change from stratospheric ozone depletion is therefore estimated to be responsible for a +0.3% per decade ozone trend. It is clear that the effect of ozone destruction on the ozone trend is hard to estimate with a model that does not treat the temperature feedback interactively. The estimated +0.3% per decade contribution of ozone itself is therefore only an indication of the size of the feedback effect and will probably be smaller, since such feedbacks usually diminish the imposed changes.

4.3.4. CO trend

Changes in CO emissions from 1900 to 1990 have only a small effect on the ozone column as can be seen by comparing simulations 10 and 11. The ozone trend increases (less negatively) by 0.1% per decade. The CO trend this century causes an increase in ozone of 4% in the troposphere (global and yearly averaged) and a decrease in the lower stratosphere of -0.6% (Fig. B11). The decrease in tropospheric OH of 27% yields increases in CH_3Cl (39%) and CH_3CCl_3 (27%) giving less ClO_x in the stratosphere. At the same time the increase of CH_4 (27%), decreasing HCl (15%) in the lower stratosphere so that the abundance of ClO only changes by -5%, which lessens the ozone destruction. The decrease in OH is also visible in the increased lifetime of CH_4.

4.3.5. NO_x trend

The effect of the estimated increase in NO_x emissions (simulated with surface concentrations) on the ozone column from 1900 to 1990 is calculated in simulations 12 and 13 (Table 2). The imposed NO_x trend results in an increase in the ozone column of 5.5% and an increase in the ozone trend from -4.5% per decade to -3.7% per decade from 1980 to 1990. The origin of these increases can be derived from Fig. B10. The increase in NO_x results in a large increase in tropospheric ozone of approximately 38% (global and yearly averaged), which accounts for more than half of the increase in ozone column and trend. The increase of NO_x in the troposphere also gives an increase in tropospheric OH of 70% (global and yearly averaged), affecting the oxidizing capacity of the atmosphere. This causes a larger destruction and consequently smaller tropospheric abundance of, for instance, CH_3Cl, CH_3CCl_3 and CH_4. Although the total active chlorine content (ClO_x) of the stratosphere decreases by approximately 18%, the ClO abundance changes by only +4% in the lower and -3% in the middle stratosphere. This is probably because of the larger HCl decrease of 25% as a result of the CH_4 decrease. The amount of ClO and NO_x in the lower stratosphere will slightly decrease ozone, while the decrease in OH of 10% in the lower stratosphere increases ozone.

The large change in CH_4 lifetime comes completely from the NO_x concentration, since the ozone layer becomes thicker, allowing less UV to pass through and consequently less OH.

The effect of NO_x changes on ozone can also be seen in simulation 19. Because of the uncertainty in the NO_x concentrations in 1900, the NO_x surface concentration for 1900 in simulation 19 is fixed at half the 1990 levels. Comparing simulation 12 with 19 there is an increase in ozone trend of 0.3% per decade, which is less than that resulting from the previous NO_x trend of simulation 13, but shows that also moderate changes in NO_x concentrations can have significant effects.

4.3.6. Stratospheric sulphate aerosol

Very high stratospheric sulphate aerosol levels several months after a volcanic eruption can change the chemical balance in the stratosphere by induced local temperature changes resulting from the absorption of radiation. After the eruption of Mt. Pinatubo in June 1991 an increase in temperature of about 1 K (WMO, 1994) was observed in the lower stratosphere which could change the local ozone levels temporarily . On a time scale of several months or years sulphate aerosol can also influence the ozone levels by heterogeneous chemical reactions on the surfaces of the aerosols. Heterogeneous reactions on sulphate aerosols are taken into account in the simulations of Table 2 as the default. The default aerosol loading of the stratosphere corresponds with an estimated mean value over the last 20 years (WMO, 1991). In simulation 21 no heterogeneous reactions on aerosols are considered (only gas-phase chemistry); this gives a trend in ozone column of only -1.7% per decade. Using a low value for the aerosol loading, corresponding with a situation several years after a large volcanic eruption, yields an ozone trend of -3.1% per decade. Comparing this with the default aerosol loading (simulation 4), it is clear that changes in stratospheric aerosol can affect stratospheric ozone levels considerably.

There is little difference between CH_4 lifetimes calculated with and without heterogeneous chemistry. It is clear from Table 2 that the thickness of the ozone layer affects the oxidizing capacity of the atmosphere, as can be seen by the CH_4 lifetime, but the changes in stratospheric ozone are too small to cause large effects in the composition of the troposphere. Changes in emissions of CO, NO_x and CH_4 can have much larger effects.

4.4. Future changes in ozone: 1990-2100

The effects of a trend in emissions in CH_4, N_2O and CO_2 in future scenarios (1990 to 2100) are shown in Table 3 and Fig. 5. In simulation 23 to 30 the IS92a scenario is applied, a mid-range scenario of the IPCC (Pepper *et al.*, 1992) scenarios. In the original IS92a scenario the CFC emissions are much higher than can be expected regarding the development of these emissions in the last few years (Montzka *et al.*, 1996) and the emissions also do not agree with the latest international agreements as the Copenhagen amendments to the Montreal Protocol. For emissions of the CFCs and related compounds IPCC (Pepper *et al.*, 1992) case 6 scenario is used for all simulations mentioned in Table 3. This scenario, originally already part of the IS92d and IS92e scenarios resembles the Copenhagen amendments. In the IS92a scenario the emissions, and consequently concentration, of CH_4, N_2O and CO_2 increase continuously. Since after 2000 the ozone layer is expected to start to recover, which will increase stratospheric temperatures, and CO_2 concentration is projected to increase according to the IS92 scenarios, the decrease in temperature in the stratosphere can be attributed to CO_2.

Measurements of the ozone column do not show a depletion before the end of the 1970s. We will therefore use the ozone column in 1980 as a measure of the recovery of the ozone layer in the 21st century (WMO, 1994). The calculated total anthropogenic change in the ozone column since 1900 was -8.6% in 1990. The column of Table 3 named 'Recovery ozone layer' gives the year in which the ozone column reaches 1980 levels. Until approximately the year 2000 the thickness of the ozone layer will continue to decline because of the high chlorine levels in the atmosphere (Montzka *et al.*, 1996; WMO, 1994). According to our calculations (Table 3 and Fig. 5) the ozone column at mid-latitude will be 1.9% below 1990 levels in 2020 (simulation 23). From approximately 2040 onwards, ozone will reach 1990 levels (see also Velders, 1995b). This is with fixed 1990 emissions for CH_4 and N_2O. In approximately 2080 the ozone column will reach 1980 levels and in 2100 the ozone column will be 5.4% thicker than in 1990. An increase in N_2O emissions in addition to this causes the ozone layer thickness to increase less because of an increase of NO_x in the stratosphere. The lower chlorine levels in the next century reduce the interaction between the NO_x and ClO_x compounds to form the reservoir $ClONO_2$. As shown before, an increase in CH_4 emissions reduces the ozone destruction by ClO_x. The CH_4 increase causes a 1.5% thicker ozone layer in 2100 (comparing simulations 23 and 25). The recovery of the ozone layer will be reduced by 20 years from 2080 to 2060. The stronger interaction between CH_4 and chlorine, compared with NO_x and chlorine, is responsible for the continuous positive influence (thicker ozone layer) with increasing CH_4 emissions.

According to simulation 23 the ozone levels are expected to drop below 1980 levels in 2080, which is later than the year 2045 reported by Daniel *et al.* (1995) and WMO (1994). The difference is most likely caused by differences in the emission data in the phase-out period (1990-2010) of CFCs and related compounds, since the Montreal protocol and its amendments are based on production limitations and not on emissions. Further more, the steep slope in the calculated ozone column from 1970 to 1990 (Fig. 5) and the smaller slope from 2020 to 2100 influences the calculation of the moment 1980 ozone levels are reached again.

Table 3. *Change in yearly average ozone column (%) at 47°N and CH_4 lifetime (yr)*

Simulation	Characterization scenario:				Relative to 1990 (%)[1]			Recovery ozone layer	CH_4 lifetime[5] (yr)
	CFC[3] halon	CH_4	N_2O	temp.	2020	2050	2100[2]	1980 level	2050
IS92a[3]: Temperature fixed									
23 CH_4, N_2O fixed	Tr	1990	1990	1990	-1.9	1.9	5.4	2080	11.7
24 N_2O trend	Tr	1990	Tr	1990	-1.9	1.7	4.6	2095	11.7
25 CH_4 trend	Tr	Tr	1990	1990	-1.1	3.4	6.9	2060	11.9
26 CH_4, N_2O trend	Tr	Tr	Tr	1990	-1.1	3.2	6.1	2065	11.9
IS92a[3]: Temperature trend[4]									
27 CH_4, N_2O fixed	Tr	1990	1990	Tr	-0.4	5.4	12.5	2045	11.3
28 N_2O trend	Tr	1990	Tr	Tr	-0.4	5.2	11.7	2045	11.3
29 CH_4 trend	Tr	Tr	1990	Tr	0.4	7.0	14.2	2040	11.5
30 CH_4, N_2O trend	Tr	Tr	Tr	Tr	0.4	6.8	13.4	2040	11.5
Temperature fixed									
31 IS92c[3]	Tr	Tr	Tr	1990	-1.5	2.5	5.4	2080	11.8
32 IS92e	Tr	Tr	Tr	1990	-1.0	3.4	6.2	2060	12.0
Temperature trend[4]									
33 IS92c[3]	Tr	Tr	Tr	Tr	-0.1	4.9	8.5	2045	11.5
34 IS92e	Tr	Tr	Tr	Tr	0.8	7.6	16.4	2035	11.5

1) Yearly average ozone column in 1990 is 391.0 DU (simulation number 4 in Table 2)
2) Estimated total anthropogenic change in ozone column at 47°N in 1980 is -4.5% and in 1990 is -8.6% relative to 1900.
3) For the CFCs and related compounds not the original scenario is used but IPCC (Pepper *et al.*, 1992) case 6 scenario, which resembles the Copenhagen amendments to the Montreal Protocol.
4) The change in temperature is caused mainly by increases in CO2 emissions. Dynamical feedback and heterogeneous reactions on PSCs are not taken into account.
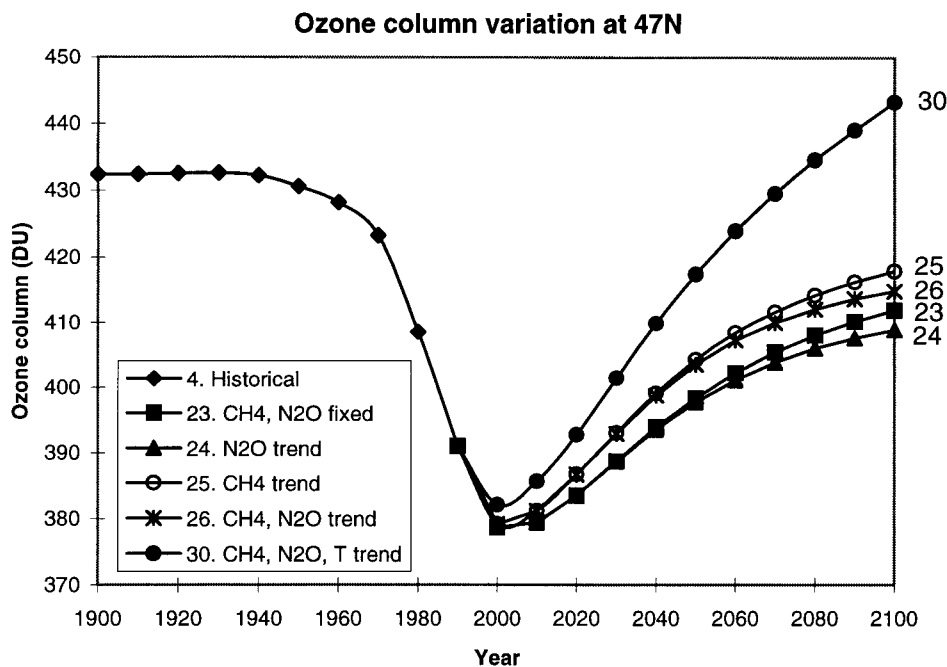5) The lifetime of CH_4 is considered as a measure (inverse) of the oxidizing capacity of the atmosphere.

Figure 5. *Thickness of the ozone layer (DU) at 47°N for various simulations.*

The larger H_2O and HO_x levels in the stratosphere from increased CH_4 emissions will cause some extra ozone destruction but this effect is, also in the next century, smaller than the diminished ozone destruction caused by the increase in CH_4. Applying a trend in both CH_4 and N_2O emissions (simulation 26) produces the average of the separate contributions of CH_4 and N_2O.

A decrease in temperature in the stratosphere of 7 K in 2100 relative to 1990, corresponding with scenario IS92a, has a large impact on the ozone layer in the next century. Comparing simulations 27 to 30 with 23 to 26, the effect of the temperature decrease since 1990 is more than a doubling of the ozone column change in 2100. The inclusion of the temperature trend in the simulations causes a faster recovery of the ozone layer: from approximately 6% to 12% in 2100 relative to 1990. The increase in ozone column thickness in 2100 with the incorporation of the temperature trend yield is larger than the total calculated anthropogenic change in ozone column (-8.6% in 1990). As mentioned before, the effects of temperature changes are difficult to model because of the nature of interactions between ozone and temperature itself. It can best be done using a model which calculates the temperature and ozone changes interactively instead of off-line with a separate model, as has been used here. The changes in ozone originating from temperature (CO_2) changes will be diminished with an interactive model. Large temperature decreases in the stratosphere might also cause extra formation of polar stratospheric clouds (PSCs) in winter in polar areas and possibly also at mid-latitudes and in other seasons. This might cause a large depletion of stratospheric ozone through heterogeneous reactions on the surfaces of the PSCs. If this will happen is speculative, and if so it will probably only occur in winter at high latitudes and in the first half of the next century, when chlorine levels are still high.
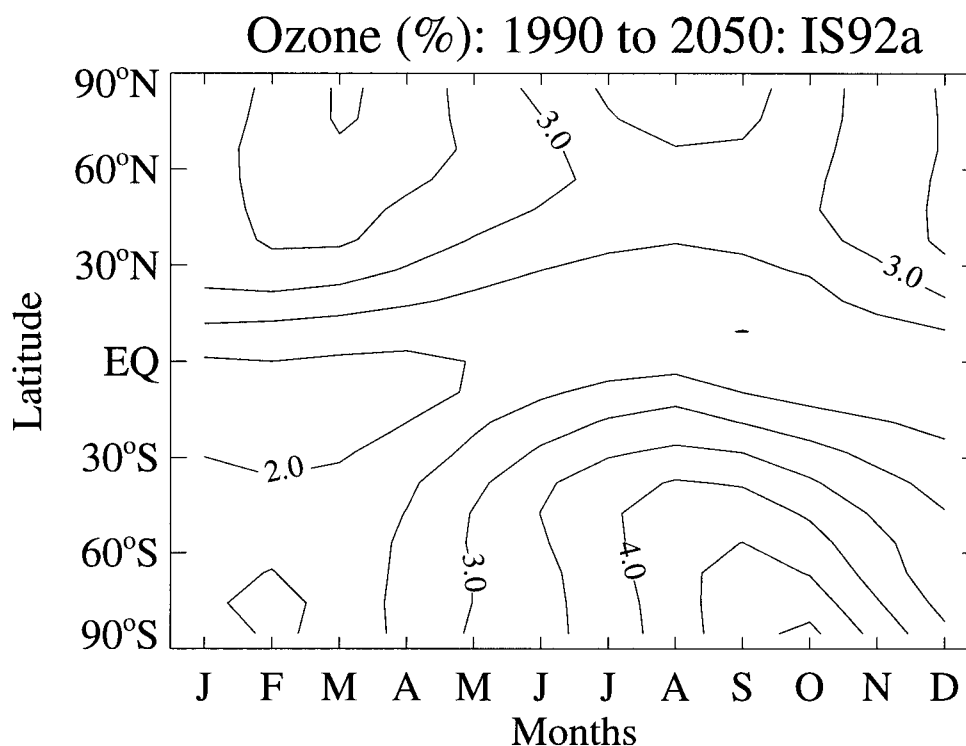
Ozone (%): 1990 to 2050: IS92a

Figure 6. *Change in ozone column (%) in 2050 relative to 1990 as calculated with simulation 26 and 4: trend in future CH₄ and N₂O emissions according to scenario IS92a.*

With a temperature trend in addition to a CH_4 emission trend the ozone column could reach 1990 levels just before 2020 and approximate 1980 values in 2040. The increase in CO_2 emissions, almost completely responsible for the temperature trend in the stratosphere after 2050, causes the ozone layer to reach pre-industrial levels by approximately 2070. A trend in N_2O emissions slows this recovery while a CH_4 trend accelerates it.

Scenario IS92a is a mid-range scenario compared with IS92c (low) and IS92e (high). Simulations 31 to 34 of Table 3 show the ozone column changes of the latter two scenarios, with and without a temperature trend. The high-range scenario IS92e yields a faster ozone layer recovery than the low and mid-range scenarios, IS92c and IS92a respectively.

The seasonal and latitudinal dependence of the recovery of the ozone layer in the 21st century (Fig. 6) is similar to the destruction of the ozone layer in the last few decades of this century. Apart from the polar areas, the largest current decreases in ozone column occur at middle and high latitudes in spring. Figure 6 shows that in 2050 relative to 1990 the largest increases in ozone column take place in the same areas. All future scenarios show a similar latitudinal and seasonal dependence as is shown in Fig. 6.

The various future scenarios not only cause differences in the ozone layer thickness but also in the atmospheric lifetime of CH_4. The lifetime decreases when temperature changes are taken into account (compare simulation 26 with 30). The increase in CO_2 emissions in these scenarios causes a decrease in temperature in the stratosphere with corresponding thicker ozone layer, which should increase the CH_4 lifetime. But at the same time tropospheric temperature increases and this is responsible for the decrease in CH_4 lifetime or increased oxidizing capacity.

5. CONCLUSIONS

Emissions of greenhouse gases affect stratospheric ozone depletion
CFCs and other chlorine- and bromine-containing compounds are responsible for the main destruction of stratospheric ozone; however chemical interactions in the troposphere and stratosphere cause other compounds to affect the ozone column as well. The contribution of different gases to the trend in ozone column is summarized in Table 4.

Table 4. *Contributions to the trend in ozone column from 1980 to 1990 at 47°N and the recovery of the ozone layer as indicated by the year when 1980 ozone levels are reached*

Compounds emitted	Ozone column trend (% per decade)	Ozone recovery 1980 levels[2]	Mechanism	Remarks
CFCs, HCFCs, CCl_4, CH_3CCl_3, Halons, CH_3Br	-5.8	2080		
N_2O	+0.1[1]	+15[1]	NO_x, Formation of reservoir	
CH_4	+1.4	-20	Formation of reservoir	
CO_2	+0.4	-25	Temperature	Feedback and PSCs ignored
$CH_4 + N_2O$	+1.5	-15		
$CH_4 + N_2O + CO_2$	+2.0	-40		
NO_x	+0.7	n.a.[3]	Tropospheric ozone	Emissions uncertain
CO	+0.1	n.a.	Tropospheric ozone	Emissions uncertain
SO_2 sulphate aerosols[4]	-2	n.a.	Large volcanic eruptions	Magnitude uncertain

1) Contribution of the emissions of the compounds on top of the CFC, HCFC, CCl_4, CH_3CCl_3, halon and CH_3Br contribution (row 1).
2) Ozone layer recovered: the year the ozone layer reaches a level corresponding to the ozone layer in 1980.
3) n.a. = 'not assessed'.
4) Only the effect of the injection of aerosols from volcanic eruptions is calculated, not that of tropospheric aerosols.

The contribution of NO_x and CO is less certain because of the uncertainty in the trend in emissions and surface concentration in this century. The effect of the trend caused by temperature changes (CO_2 and ozone) does not take into account the dynamical feedback and will therefore probably overestimate the effect. The estimated temperature increase in this century in the troposphere is 0.67 K, while the estimated temperature decrease in the stratosphere is 3 K. Possible extra formation of PSCs by the temperature decrease and corresponding extra zone depletion is also ignored. The effect of the CH_4 and N_2O trend is

positive through the interaction of CH_4 and NO_x with Cl and the formation of the chlorine reservoir compounds HCl and $ClONO_2$.

Greenhouse gas interactions improve agreement with measurements

Taking into account the effects of a trend in CH_4 and CO_2 emissions results in a good agreement between the calculated (-3.8% per decade) and measured (-4.0% per decade from TOMS and Dobson measurements) trend in ozone column at mid-latitude in the Northern Hemisphere from 1980 to 1990.

CH_4 emissions accelerate the recovery of the ozone layer

The interactions between greenhouse gases and stratospheric ozone also have an effect on the recovery of the ozone layer in the 21st century. The international measures (Montreal Protocol and amendments and adjustments) are likely to reduce the chlorine levels in the stratosphere in the coming decades. The reduction in emissions of CFC and related compounds alone will result in 2050 in an ozone column 1.9% thicker than in 1990. Anticipating a business-as-usual scenario (IS92a) for N_2O and CH_4 in addition to the chlorine reduction yields 0.2% smaller and 1.5% larger increases, respectively. With fixed CH_4, N_2O and CO_2 emissions an ozone column corresponding with 1980 can be reached in approximately 2080. A methane trend as in scenario IS92a reduces this to approximately 2060, while an additional CO_2 trend (temperature decrease) reduces it to approximately 2040. A low-range (IS92d) or high-range (IS92e) scenario causes respectively slower and faster recovery of the ozone layer. The year 2080, calculated with fixed CH_4, N_2O and CO_2 emissions, for the recovery of the ozone layer is later than the 2045 reported by WMO. This probably caused by differences in the emission data used for CFCs and related compounds.

CO_2 increases can initially increase the ozone column

The CO_2 emission is largely responsible for a large decrease in temperature in the stratosphere in the 21st century: -7 K in 2100 relative to 1990. This results in an extra increase in ozone column of approximately 3.5% in 2050 relative to 1990. The temperature effect can be diminished if dynamical interactions in the atmosphere are taken into account interactively in a model. The decrease in temperature in the stratosphere might increase the occurrence of PSCs in winter, in polar regions but possibly also at mid-latitudes and in other seasons. If this happens a strong decrease in stratospheric ozone might occur from the temperature decrease. This effect is not considered here. A temperature decrease in the stratosphere, from an increase in CO_2 emissions will therefore, at least initially, yield a thicker ozone layer, as shown above.

Ozone depletion increases the oxidizing capacity of the atmosphere

A thinner ozone layer (11% at 47°N) allows more UV radiation to reach the troposphere, which is responsible for a decrease in lifetime of CH_4, or increase in oxidizing capacity of the atmosphere, of a globally averaged 6%. This is an illustration of the effect changes in the ozone layer can have on the troposphere and greenhouse effect. But past and expected future changes in stratospheric ozone levels are too small to cause large effects in the composition of the troposphere. Changes in emissions of CO, NO_x and CH_4 can cause much larger effects.

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APPENDIX A: THE RIVM 2-DIMENSIONAL STRATOSPHERE MODEL

The RIVM 2-dimensional stratosphere model has the following characteristics:

- Type: a classical Eulerian model where averages are taken over the longitude at fixed latitude, altitude and time. This makes the model a 2-dimensional or so-called 'zonally averaged model'.

- Horizontal resolution: the model extends from pole to pole in 19 latitude bands, i.e. a resolution of $9.47°$.

- Vertical resolution: the model extends from 0 to approximately 100 km (29 layers), although the chemistry is only modelled up to 60 km (17 layers). The vertical resolution is ~3.5 km (half-pressure scale height).

- Time step: the computational time step in the model is four hours. A daily cycle is not simulated so only diurnal averages are calculated.

- Dynamics: the dynamics of the model is represented by two terms; mean meridional transport using a mass-stream function and eddy transport using fixed monthly averaged K coefficients. The first term is responsible for the large-scale transport of air in the modelled atmosphere; the Brewer-Dobson circulation in the stratosphere and the Hadley, Ferrel and Polar cells in the troposphere. The second term, eddy diffusion, describes all subgrid processes originating from turbulent processes on scales smaller than the grid size of the model and is responsible for an averaging of concentrations.

- Chemistry: the model uses family chemistry, which means that several compounds converting rapidly into another compound are grouped together and transported as one family. The families are chosen so that their lifetimes are large compared with the time step of the model. The individual members of the families are assumed to be in a photochemical steady state within the model time step, and are therefore transported as one compound. With this approach the stiffness of the whole set of coupled differential equations can be avoided and rather large model time steps can be used. All important gas-phase and photochemical reactions between the compounds in the model are taken into account.

- Heterogeneous chemistry: The main heterogeneous reactions in the stratosphere are (Hanson and Ravishankara, 1991; Granier and Brasseur, 1992; Hanson et al., 1994, NASA, 1993; WMO, 1991):

$$N_2O_5 \text{ (g)} + H_2O \text{ (s)} \qquad \Rightarrow 2\, HNO_3 \text{ (s)}$$

$$ClONO_2 \text{ (g)} + H_2O \text{ (s)} \qquad \Rightarrow HNO_3 \text{ (s)} + HOCl \text{ (g)}$$

where (g) indicates gas phase and (s) a solid. These reactions convert the chlorine reservoir compounds (HCl and $ClONO_2$) into more reactive chlorine and nitrogen oxides into nitric acid. It is assumed that the reaction product, nitric acid, vaporizes immediately and contributes to HNO_3 in the gas phase. For the parameterization of the heterogeneous reactions, see Velders (1995b). Heterogeneous reactions on PCSs and possible heterogeneous chemical reactions on cloud droplets in the troposphere are not considered here.

- Aerosols layer: For the studies described in this report the WMO/UL aerosol surface area density distribution is used (WMO, 1991). This data set corresponds approximately to the

median aerosol distribution in the stratosphere of the past two decades. It includes the increases in stratospheric aerosol caused by volcanic eruptions. This averaged 2-dimensional (latitude versus altitude) data set (WMO, 1991) is based on analysis of SAGE II data and extends from 12 to 32 km in steps of 2 km, and from pole to pole in five latitude bands. Different data is used for the period January to June than for July to December. Since this data set is based on averaged SAGE II values it is very useful for scenario simulations over long time periods. For a direct comparison of observed values with modelled results, a time-dependent aerosol distribution has to be used.

- Compounds: the following compounds or groups of compounds (families) are simulated in the model:

Families:
O_x = O_3, $O(^3P)$, $O(^1D)$

NO_x = N, NO, NO_2, $ClONO_2$

CH_x = CH_4, CH_3, CH_3O, CH_3O_2, CH_3OOH, CH_2O, CHO

ClO_x = Cl, ClO, HOCl, HCl, OClO, ClONO2, Cl_2O_2

BrO_x = Br, BrO, HOBr, HBr, $BrONO_2$

HO_x = H, OH, HO_2

Long-lived compounds:

H_2O

H_2O_2

CO

HNO_3, N_2O_5, HO_2NO_2,

N_2O

CCl_4, CH_3CCl_3, CH_3Cl

CFC-11, CFC-12, CFC-113, CFC-114, CFC-115

HCFC-22, HCFC-123, HCFC-124, HCFC-141b, HCFC-142b,
     HCFC-225ca

HFC-125, HFC-134a, HFC-143a, HFC-152a

Halon 1211, Halon 1301, CH_3Br

- Radiation: the reaction rates of the photochemical reactions are calculated using a 2-stream radiative scheme, which includes a cloud parameterization, aerosol and Rayleigh scattering (Hough, 1988; Bruning, 1996).

- Degradation of (H)(C)FCs: the specific chemical degradation of the CFCs, HCFCs, HFC, and other chlorine and bromine compounds is not modelled for this study. In the first step of a CFC, HCFC or halon reaction, one chlorine or bromine atom is released immediately, but since the intermediate products of a chemical degradation of these compounds are often short lived the other chlorine or bromine atoms of the compounds are also released rapidly. For the study reported here, it is a good approximation to assume that all chlorine and bromine atoms are released immediately into the atmosphere in the case of a (photo)chemical reaction. For a different study, it might be necessary to model the degradation of these compounds with all the intermediate reaction products. At the moment there is still much uncertainty in the degradation schemes of most CFCs, HCFCs and HFCs (WMO, 1994).

- Deposition: the following compounds are removed from the modelled atmosphere by rainout in the troposphere: HCl, HBr, H_2O_2, HNO_3, HO_2NO_2, CH_2O and CH_3OOH. The

use of fixed surface concentrations for NO_x and CO simulates both emission and deposition of the compounds. Explicit deposition is not taken into account for other compounds.

- Interaction: dynamics, chemistry and radiation interact directly in the model, although in this version pre-computed fields of temperature and meridional winds, calculated in a fully interactive simulation, are used.

- Reaction rates: most reaction coefficients of the homogeneous and heterogeneous reactions come from the NASA JPL publication 94-26 (DeMore *et al.*, 1994). The absorption cross-sections are fitted to the recommended values of the NASA JPL 94-26 publication (DeMore *et al.*, 1994).

- Output: the interesting output variables are the volume-mixing ratios of the compounds with latitudinal, height and time dependencies.

- References: Harwood and Pyle (1975, 1977, 1980), Haigh and Pyle (1989), Law and Pyle (1993a, 1993b), Velders (1995a, 1995b).
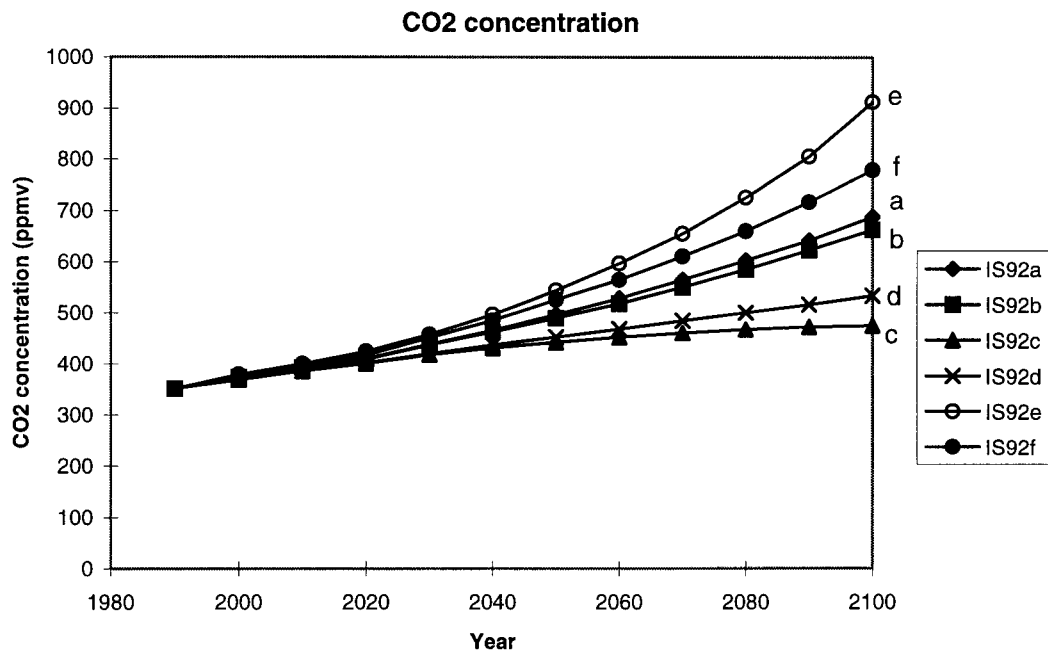
APPENDIX B: FIGURES AND TABLES

CO2 concentration

Figure B1. *Carbon dioxide concentration (ppmv) for the IS92 scenarios taken from IPCC (1994).*

CH4 concentration

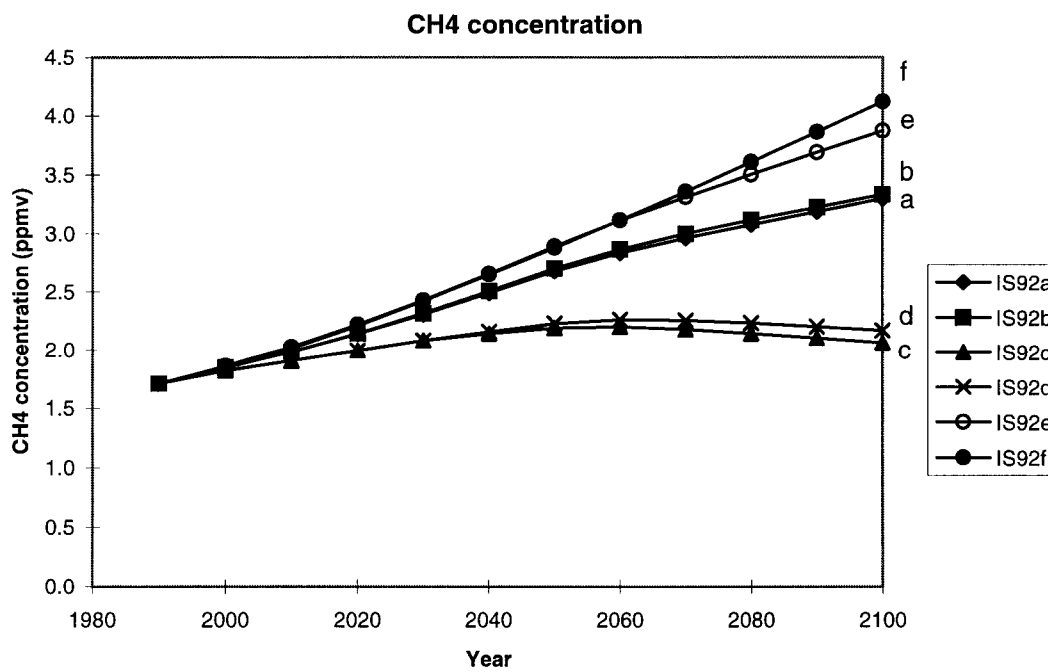**Figure B2.** *Global mean surface concentration of methane (ppmv) for the IS92 scenarios calculated with the 2D stratosphere model.*
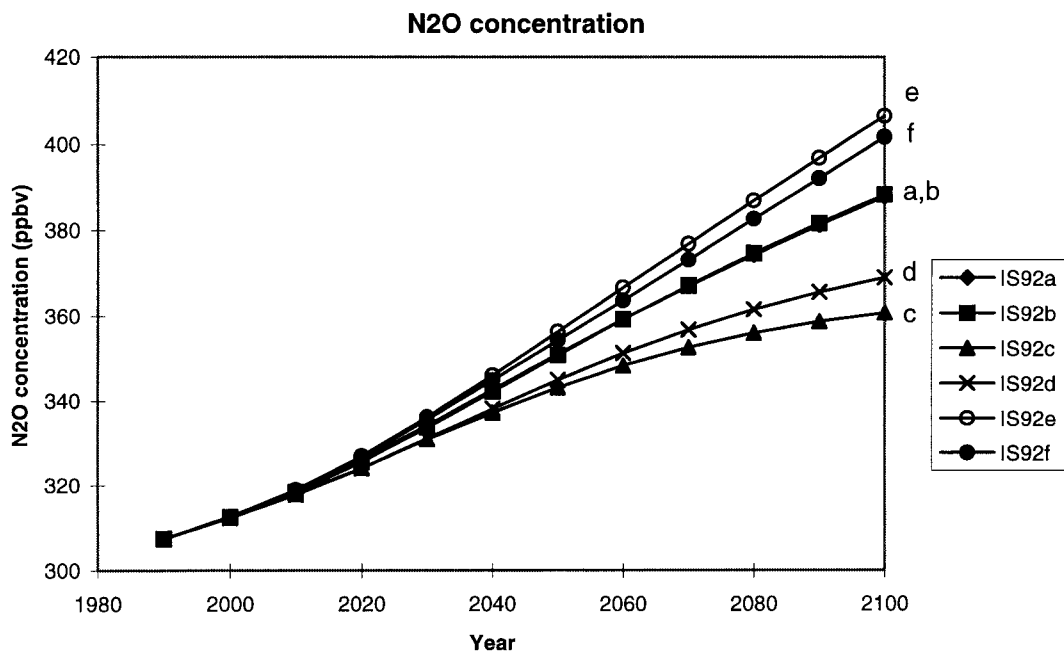
N2O concentration

Figure B3. *Global mean surface concentration of nitrous oxide (ppbv) for the IS92 scenarios calculated with the 2D stratosphere model.*

CFC-11 concentration

Figure B4. *Global mean surface concentration of CFC-11 (pptv) for the IS92 scenarios calculated with the 2D stratosphere model.*

HCFC-22 concentration

Figure B5. *Global mean surface concentration of HCFC-22 (pptv) for the IS92 scenarios calculated with the 2D stratosphere model.*

HFC-134a concentration
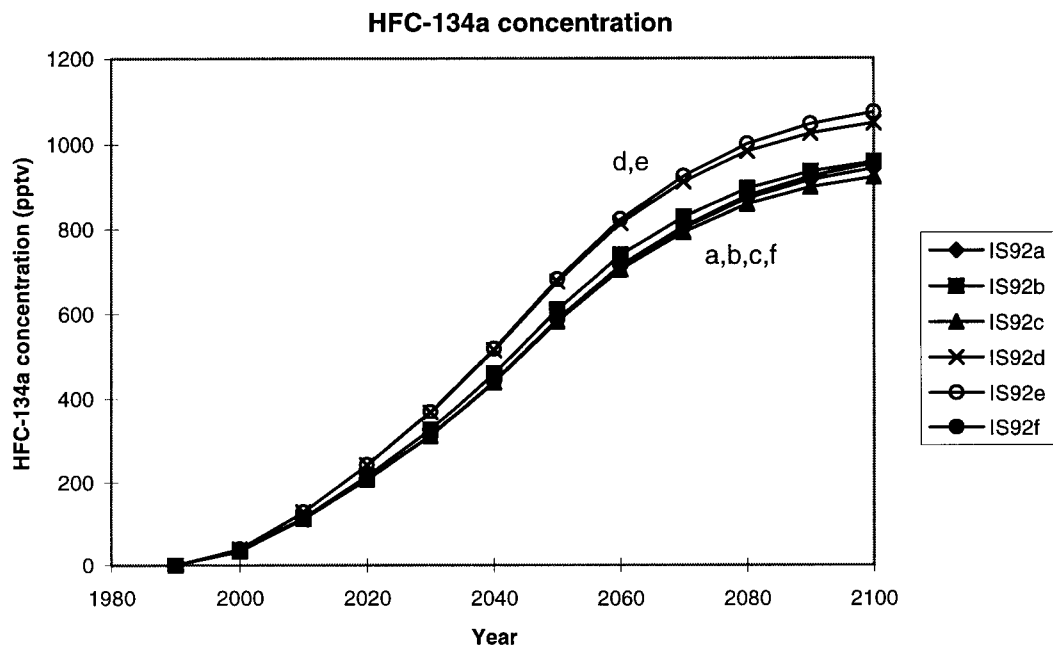
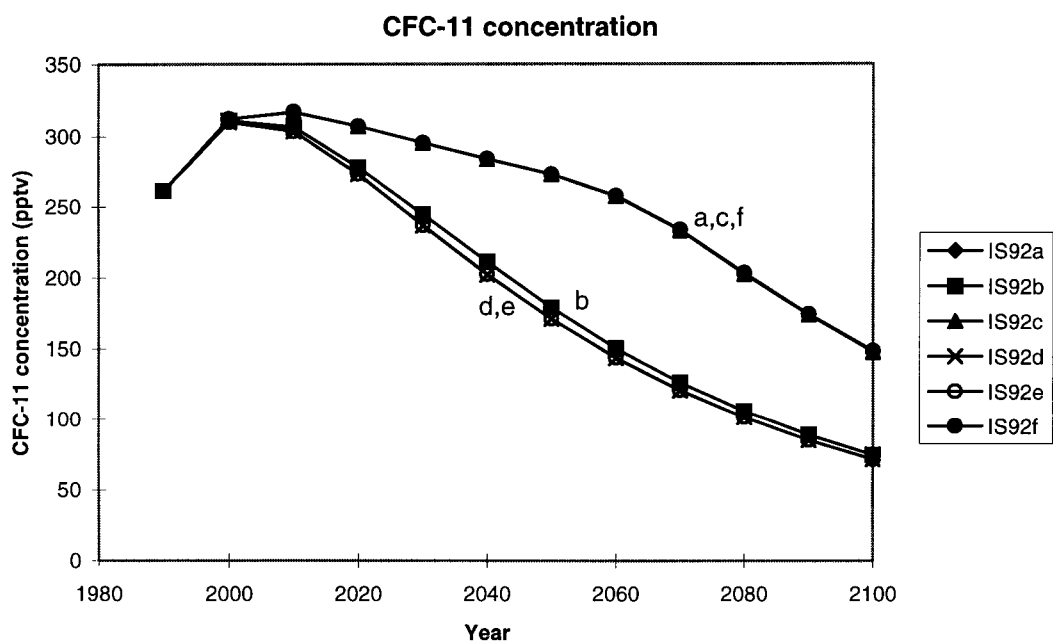**Figure B6.** *Global mean surface concentration of HFC-134a (pptv) for the IS92 scenarios calculated with the 2D stratosphere model.*

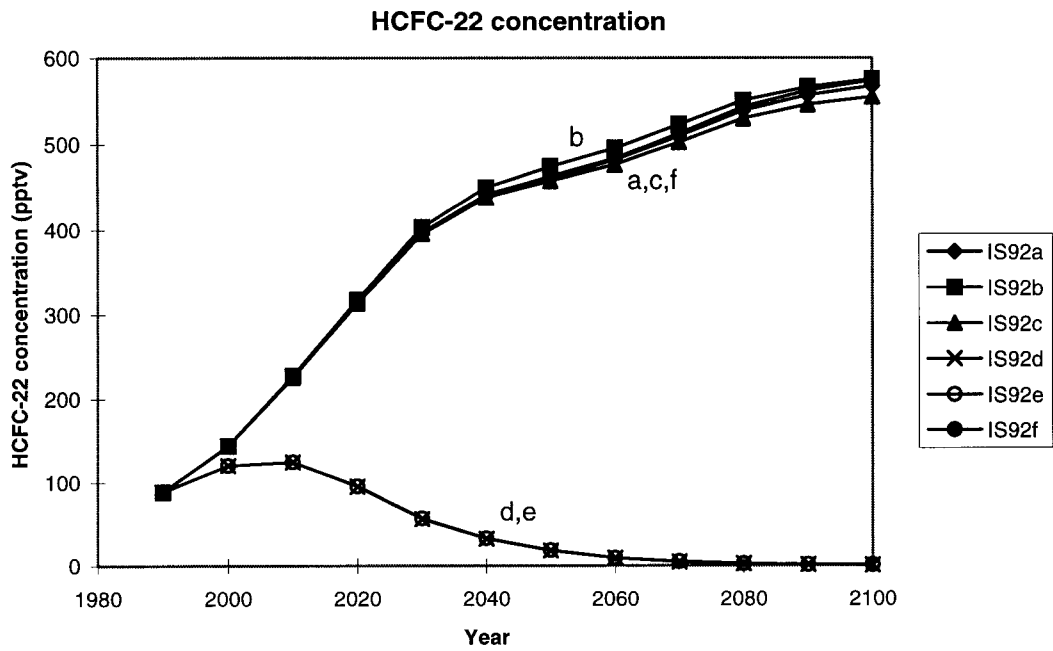## Simulation: CH$_4$ emissions trend

Figure B7. *Relative contribution (in %) to the concentrations of O$_3$, CH$_4$, H$_2$O, HCl, OH and ClO in January 1990 caused by the trend in CH$_4$ emissions from 1900 to 1990. Fixed 1990 surface concentration of CO and NO$_x$ and a trend in emissions from 1900 to 1990 for N$_2$O and all chlorine and bromine compounds. Simulation 4 minus 3 of Table 2.*

Simulation: N₂O emissions trend

Figure B8. *Relative contribution (in %) to the concentrations of O₃, N₂O, NOₓ, and ClO in January 1990 caused by the trend in N₂O emissions from 1900 to 1990. Fixed 1990 surface concentration of CO and NOₓ and a trend in emissions from 1900 to 1990 for CH₄ and all chlorine and bromine compounds. Simulation 4 minus 2 of Table 2.*
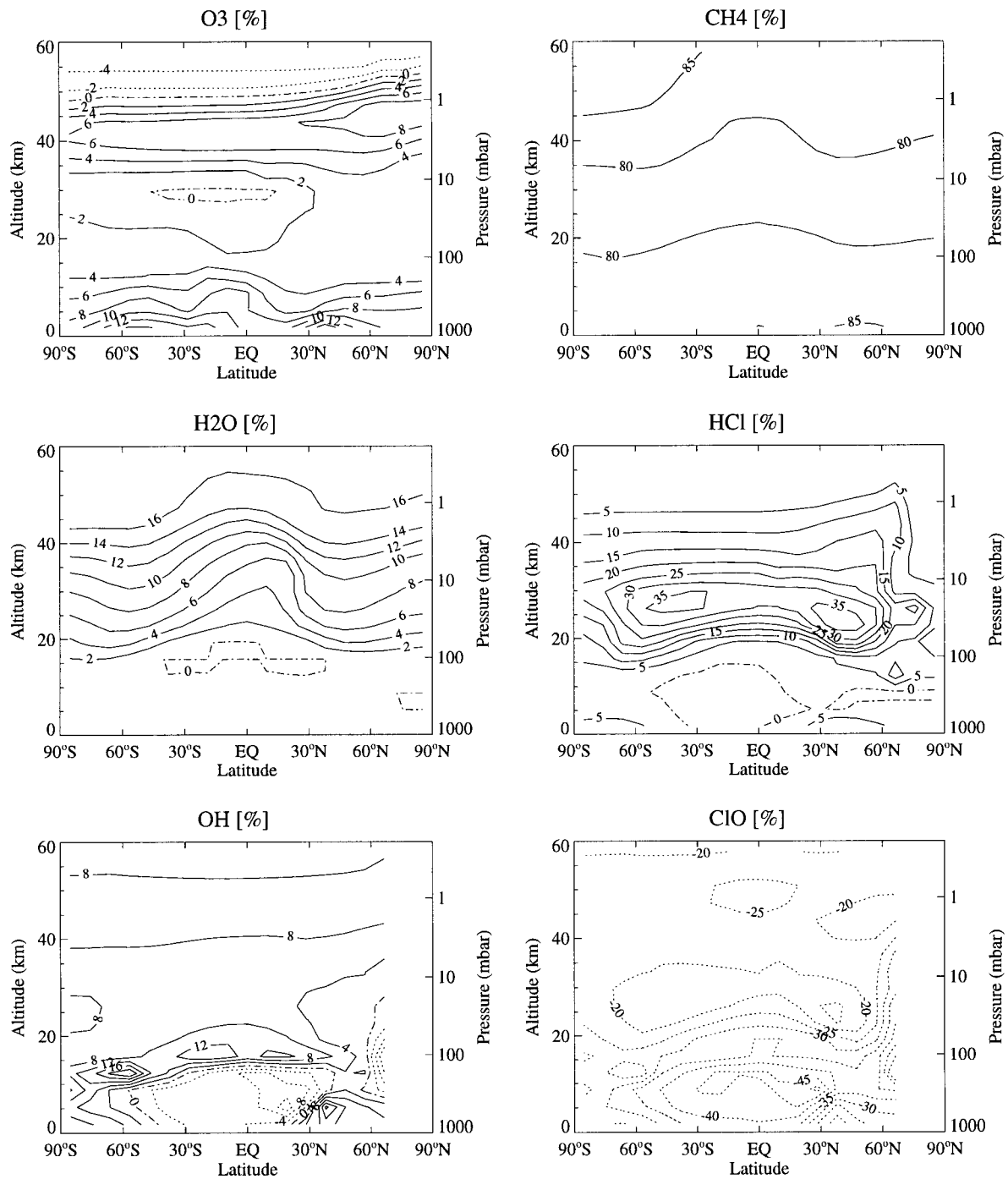
Simulation: temperature trend

Figure B9. *Relative contribution (in %) to the concentrations of O_3, NO_x, OH and ClO in January 1990 caused by the trend in tropospheric and stratospheric temperatures from 1900 to 1990. Fixed 1990 surface concentration of CO and NO_x and a trend in emissions from 1900 to 1990 for CH_4, N_2O and all chlorine and bromine compounds. Simulation 9 minus 8 of Table 2.*

Simulation: NO$_x$ concentration trend

Figure B10. *Relative contribution (in %) to the concentrations of O$_3$, NO$_x$, OH and CH$_4$ in January 1990 caused by the trend in the surface concentrations of NO$_x$ from 1900 to 1990. Fixed 1990 surface concentration of CO and a trend in emissions from 1900 to 1990 for CH$_4$, N$_2$O and all chlorine and bromine compounds. Simulation 13 minus 12 of Table 2.*
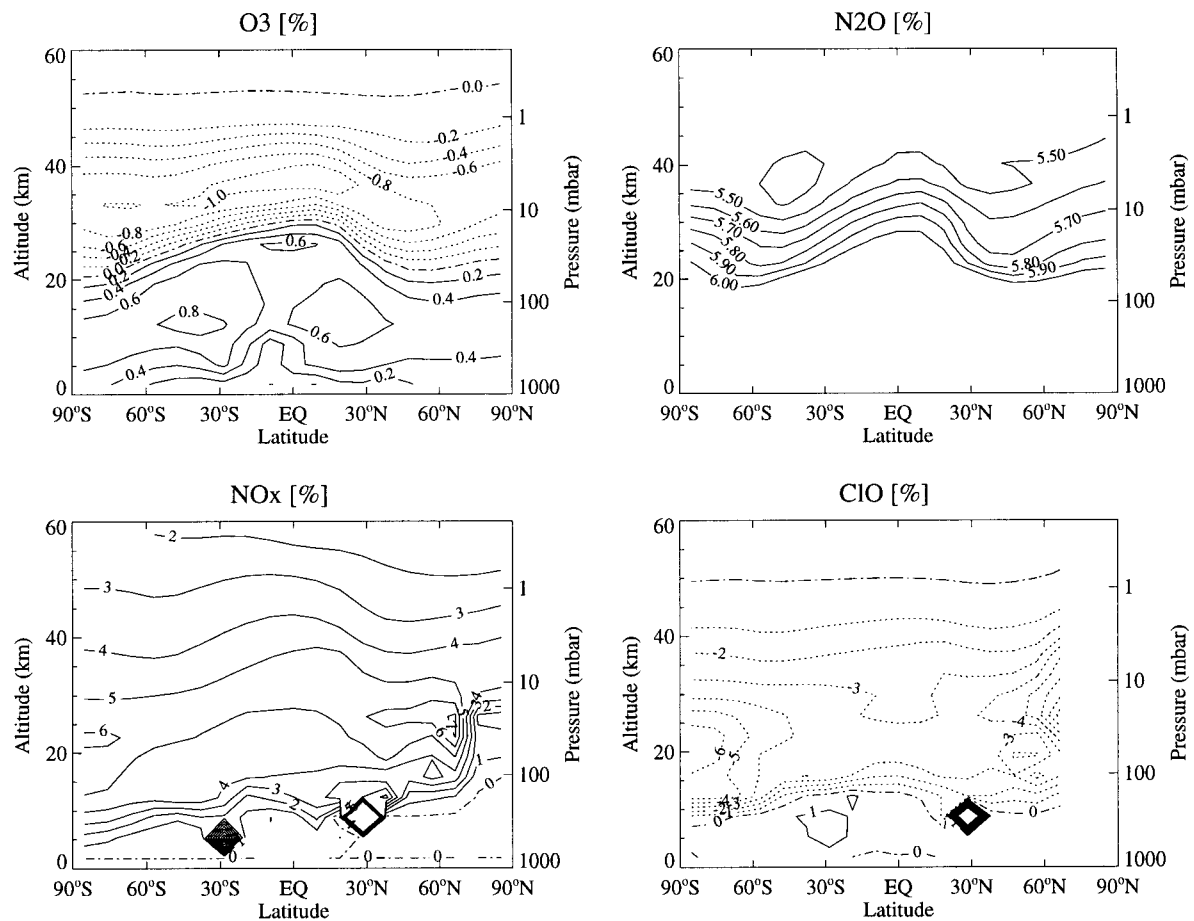
Simulation: CO concentration trend

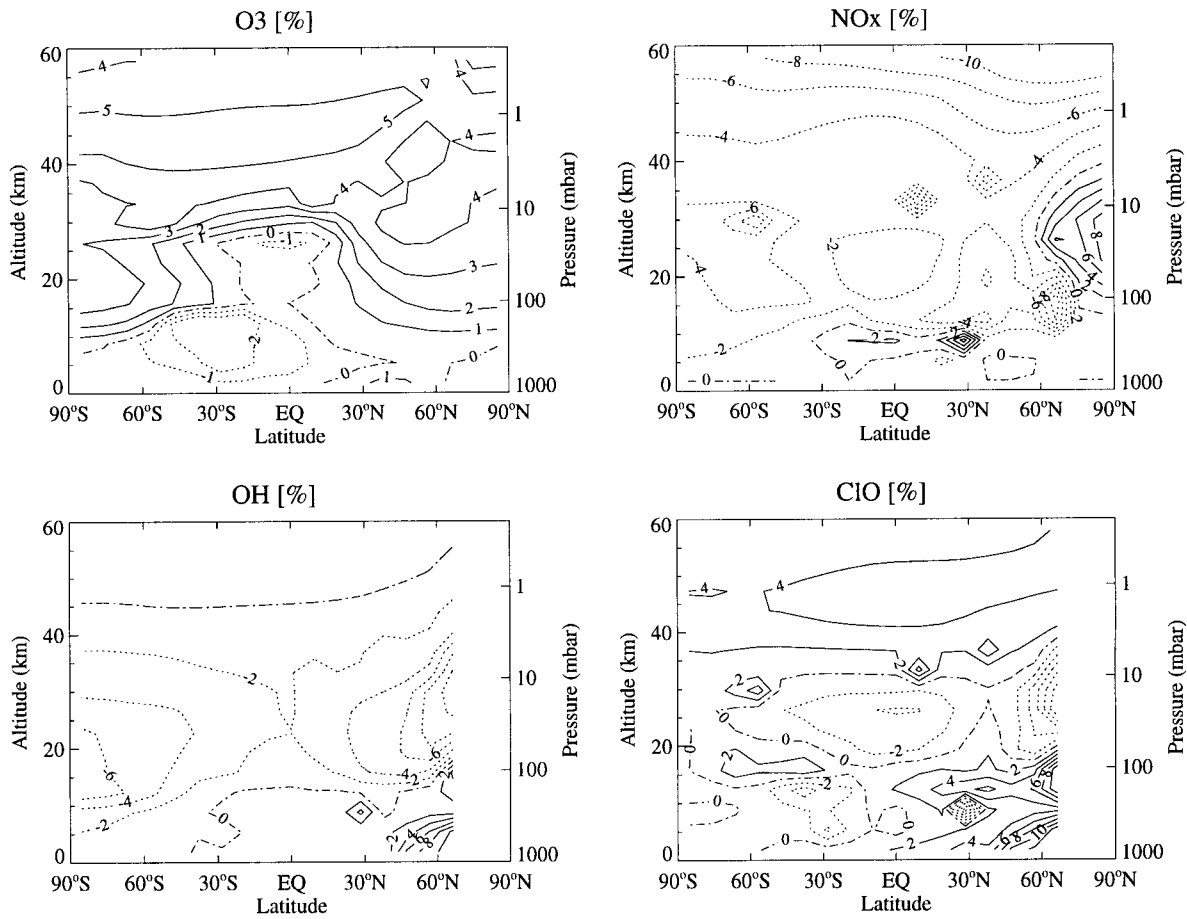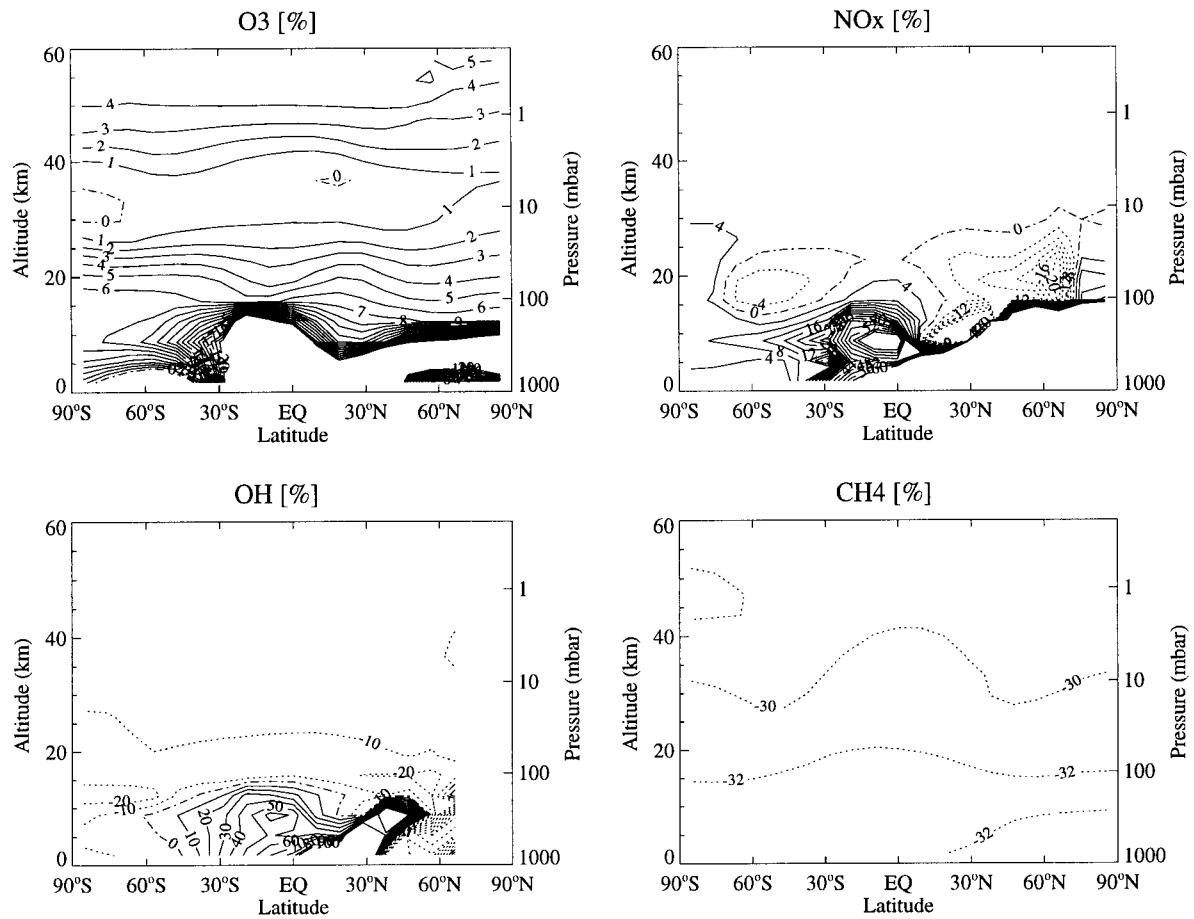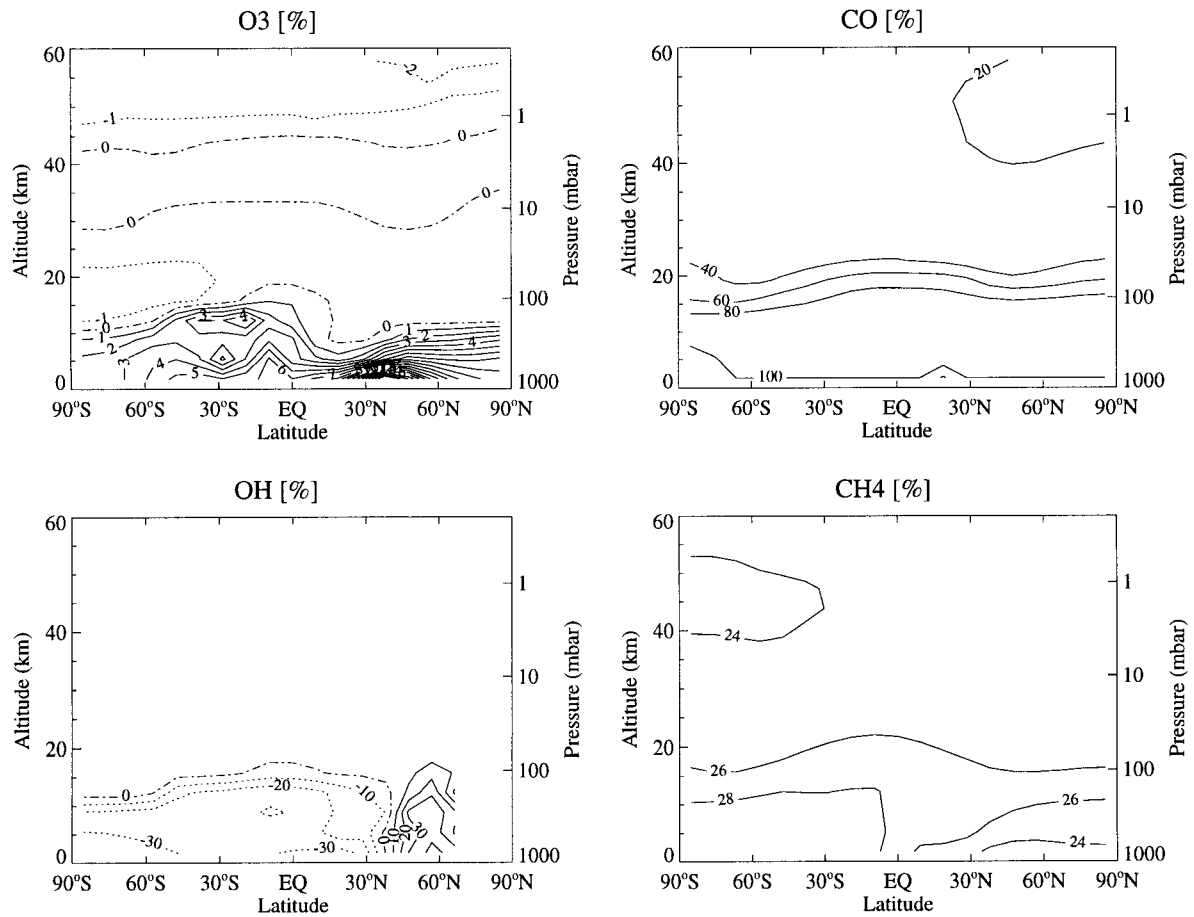**Figure B11.** *Relative contribution (in %) to the concentrations of O_3, CO, OH and CH_4 in January 1990 caused by the trend in the surface concentrations of CO from 1900 to 1990. Fixed 1990 surface concentration of NO_x and a trend in emissions from 1900 to 1990 for CH_4, N_2O and all chlorine and bromine compounds. Simulation 11 minus 10 of Table 2.*

Table B1. *Current adjusted radiative forcings (W/m^2) calculated with the OGI-1D radiative convective model*

	Calculated OGI-1D		IPCC
	1900 to 1990	Pre industrial to 1994	Pre industrial to 1994
CO_2	0.991	1.390	1.56
CH_4	0.339	0.515	0.47
N_2O	0.048	0.082	0.14
CFC*[1]	0.226	0.226	0.28
Strat.[2] O_3	-0.320	-0.320	-0.1[3]
Total[4]	1.284	1.893	2.25[3]

1) CFC* stands for all CFCs, HCFCs, HFCs, methyl chloroform, carbon tetrachloride, halons, methyl chloride and methyl bromide.

2) Only stratospheric ozone is considered.

3) The radiative forcing from ozone is calculated for a change in stratospheric ozone from 1980 to 1990. The uncertainty range for this number is -0.05 to -0.2 W/m^2. The model calculations with the 2D stratosphere model reveal that this change is half the total change in stratospheric ozone since 1900. The forcing since pre industrial times is therefore estimated at -0.2 W/m^2 with a range from -0.10 to -0.40 W/m^2. This number is used for the total forcing.

4) Total is the sum of the forcings from the five compounds.

Table B2. *Adjusted radiative forcings (W/m^2) for the IS92 scenarios relative to 1900 calculated with the OGI-1D radiative convective model*

		IS92a	IS92b	IS92c	IS92d	IS92e	IS92f
2000	CO_2	1.351	1.351	1.271	1.271	1.430	1.398
	CH_4	0.391	0.391	0.381	0.381	0.395	0.393
	N_2O	0.060	0.060	0.060	0.060	0.060	0.060
	CFC*[1]	0.280	0.280	0.280	0.276	0.275	0.280
	Strat. O_3	-0.477	-0.476	-0.479	-0.474	-0.470	-0.476
	Total[2]	1.605	1.606	1.513	1.514	1.690	1.655
2020	CO_2	1.899	1.885	1.766	1.781	2.100	2.000
	CH_4	0.494	0.495	0.444	0.444	0.520	0.517
	N_2O	0.093	0.092	0.088	0.088	0.095	0.094
	CFC*	0.338	0.319	0.337	0.295	0.295	0.338
	Strat. O_3	-0.442	-0.414	-0.460	-0.410	-0.386	-0.435
	Total	2.382	2.377	2.175	2.198	2.624	2.514
2050	CO_2	3.045	2.959	2.350	2.484	3.594	3.389
	CH_4	0.663	0.670	0.512	0.524	0.726	0.722
	N_2O	0.150	0.150	0.133	0.137	0.161	0.157
	CFC*	0.438	0.376	0.436	0.333	0.337	0.441
	Strat. O_3	-0.329	-0.221	-0.375	-0.209	-0.169	-0.314
	Total	3.967	3.934	3.056	3.269	4.649	4.395
2100	CO_2	5.034	4.806	2.784	3.481	6.797	5.810
	CH_4	0.840	0.848	0.470	0.508	0.986	1.036
	N_2O	0.227	0.228	0.173	0.191	0.262	0.253
	CFC*	0.482	0.422	0.469	0.376	0.399	0.489
	Strat. O_3	-0.140	-0.037	-0.231	-0.055	0.077	-0.079
	Total	6.443	6.267	3.665	4.501	8.521	7.509

1) CFC* stands for all CFCs, HCFCs, HFCs, methyl chloroform, carbon tetrachloride, halons, methyl chloride and methyl bromide.
2) Total is the sum of the forcings from the five compounds.

Table B3. *Calculated average tropospheric and stratospheric global temperature changes (K) for different scenarios relative to 1900 using the OGI-1D radiative convective model*

	Past	IS92a	IS92b	IS92c	IS92d	IS92e	IS92f
Troposphere							
1960	0.26						
1970	0.37						
1980	0.51						
1990	0.67						
2000		0.85	0.85	0.82	0.82	0.89	0.87
2020		1.17	1.16	1.09	1.08	1.26	1.23
2050		1.82	1.77	1.44	1.47	2.06	2.00
2100		2.83	2.72	1.65	1.95	3.68	3.28
Stratosphere							
1960	-0.93						
1970	-1.37						
1980	-2.13						
1990	-3.00						
2000		-3.94	-3.94	-3.80	-3.79	-4.07	-4.03
2020		-4.88	-4.80	-4.66	-4.58	-5.14	-5.06
2050		-6.87	-6.51	-5.67	-5.59	-7.54	-7.46
2100		-10.12	-9.57	-6.26	-7.16	-12.75	-11.41