Climate Change Research: Evaluation and Policy Implications
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ASSESSMENT REPORT ON NRP SUBTHEME

"ATMOSPHERIC PROCESSES & UV-B RADIATION"

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Contents

ABSTRACT

The atmosphere is a very complex, open, dynamic and multi-causal relation system in which non-linear processes and feedback mechanisms play an important role. Research within this subtheme in NRP-1 focused on uncertainties in our understanding of three issues i.o.

- the role of clouds and aerosols on the radiation budget
- the role of atmospheric ozone in global change and the effect of atmospheric change on UV-B climatology
- tropospheric budgets of non CO2 greenhouse gases

These issues are being dealt with in 12 projects.
On average good progress has been made in many of the projects and through there are some weaknesses, the overall quality of science and technological developments is good and in some cases even excellent in comparison to international standards.

Links with international programmes such as IGBP, CEC, EUREKA/EUROTRAC are well established.

1. INTRODUCTION

Many different gases can interfere with the earth's radiation budget. Some are highly stable and have residence times of decades or even a century or more. The most important of these gases are water vapour (H_2O); carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), ozone (O_3) and the (H)CFC's (hydrogen-containing chlorofluorocarbons).
Other atmospheric constituents, including certain aerosols and notably clouds, may also affect radiation regimes. Most scientists agree that this may have significant effect on regional climates.

A model of global warming simulates the effects of various policy strategies on the built-up of greenhouse gases in the atmosphere (see Figure 1.1). First the built-up of radiation influencing constituents is linked to emission scenarios, which are based on assumptions about future population levels, global and regional energy resources, energy and material use, land-use changes (e.g. due to deforestation, regrowth and biomass burning), agricultural activity, industrial activity, certain policy dependent assumptions about taxes, income and price elasticities of demand, and other economic factors. In Table 1.1 an overview of activities and emissions of radiatively active compounds are given.

Input & assumptions	Demographics; Technical & Macro-economics; Policy etc.
Productions & emissions	Anthropogenic / Natural (biogenic)
Atmospheric concentrations	Atmospheric (retention) models N_2O, CO_2, (H)CFC's, O_3, CH_4, aerosols (SO_2/DMS) Clouds, H_2O-vapour; radiation
Radiative effects	Equilibrium radiative forcing models ↓ ↓ Estimated global warming

Figure 1.1
Schematic structure of the model of global warming

In the second stage of analysis, atmospheric retention models are used to simulate chemical and biophysical processes by which the relevant emitted compounds are removed from the atmosphere, resulting in projections of their future concentrations.

Table 1.1
Anthropogenic activities and emissions of radiatively active compounds

1: *Fossil-fuel combustion*
- a: CO_2 emission (infrared IR trapping)
- b: CH_4 emission by natural gas leakage (IR trapping and O_3 changes, which on its turn leads to changes in UV absorption and IR trapping)
- c: NO_x emission (alters O_3)
- d: Carbonaceous soot emission (efficient solar absorption)
- e: SO_2-sulfate emission (solar reflection and IR trapping)
- f: VOC/CO emission (alters O_3)

2: *Land-use changes*
- a: Deforestation (releases CO_2 and increases albedo)
- b: Regrowth (absorbs CO_2 and decreases albedo)
- c: Biomass burning (releases CO_2, NO_x and aerosols)

3: *Agricultural activity*
- a: Release of CH_4 (IR trapping and changes O_3)
- b: Release of N_2O (IR trapping and changes O_3)

4: *Industrial activity*
- a: Release of CFC's and their substitutes (IR trapping and O_3 destruction)
- b: Release of SF6, CF4 and other ultra-long lived gases (IR trapping virtually forever)
- c: Release of VOC (O_3 changes)

In the third stage, radiative effects of the projected concentration changes are estimated and translated into equilibrium global and regional radiative forcing, which may be translated into temperature changes. The effects of the radiatively active constituents will not register immediately as a change in surface temperature. The oceans large thermal mass will cause a lag in warming effects. Nonetheless radiative active constituents will cause an eventual or "equilibrium" warming after some time, perhaps several decades after a certain atmospheric concentration has been reached. Since the industrial revolution an additional global average radiative forcing, due to an increase in atmospheric CO_2, N_2O, CH_4, stratospheric water vapour, CFC's and tropospheric O_3 of 2.4 W/m^2 has been calculated in this way, which is equivalent to a temperature increase of about 0.7 K.

The subtheme "Atmospheric processes and UV-B radiation" focuses on atmospheric processes. The atmosphere is a very complex, open, dynamic and multi-causal relation system in which nonlinear processes and feedback mechanisms play an important role. One should note that the feedback mechanisms themselves might influence the emissions in a direct way. The major problems we are faced with can be summarized as follows:

- Radiative forcing by gases is a function of their concentration. The relation between emissions and concentration is usually not a linear one, but is determined by chemical processes in the atmosphere. The chemistry of the atmosphere, however, will change if the composition of the atmosphere, as is the case, changes. The consequence e.g. being that changes in the atmosphere's methane concentration since the turn of the century does not reflect changes in its emission pattern. This means that for projections of atmospheric concentrations of radiatively active gases for different emission scenarios, one should also take into account the chemical processes occurring in the atmosphere.
- Aerosols may change the earth's albedo in a direct way through absorption and backscatter of solar radiation and indirectly as condensation nuclei in cloud formation. Aerosol cloud condensation nuclei (CCN) may namely increase cloud droplet concentration and cloud reflectance (albedo) of incoming solar radiation. Atmospheric aerosol particles of concern are both biogenically derived from dimethylsulphide (DMS) oxidation and by anthropogenic activities, particularly sulphates from SO_2 emissions, organic condensates and soot from biomass burning.

  Recent applications of coupled atmospheric chemical/radiative transfer models, by utilizing empirical aerosol scattering properties, have shown that anthropogenically derived sulphate aerosols cause clear-sky climatic forcing, that when averaged over the globe is comparable in magnitude, but opposite in sign, to forcing by CO_2. Unlike CO_2, anthropogenically derived aerosol particles are not uniformly distributed over the globe but are mainly found over industrialized areas in the Northern Hemisphere. As a matter of fact the present day aerosol forcing in many regions of the Northern Hemisphere, as an annual average, may offset the combined greenhouse effect of CO_2; CH_4; N_2O; CFC's, and O_3 (Figure 1.2).

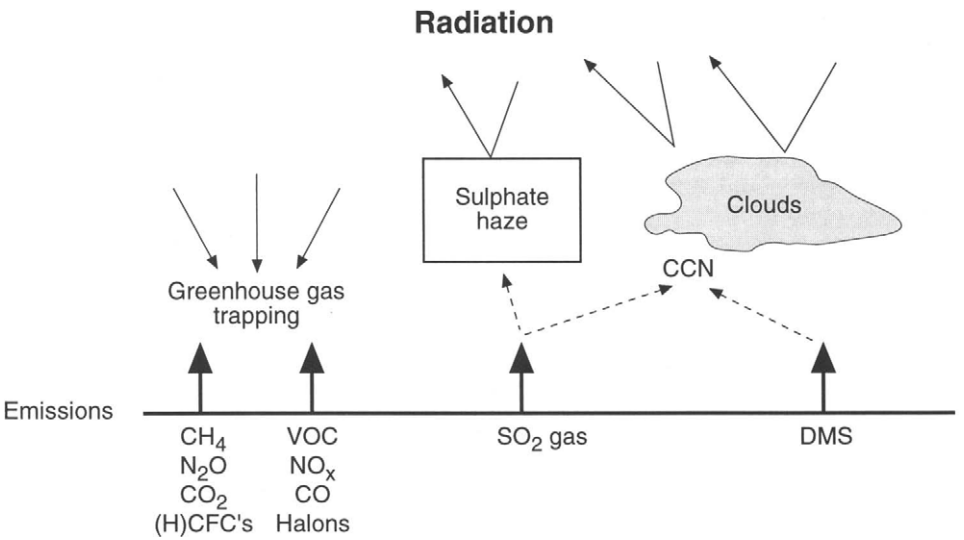

Figure 1.2
Interference of radiation with gases, aerosols and clouds

- The effect of clouds is even more complex. Depending on cloud physics and cloud dynamics, clouds may exert a positive or negative feedback in radiative forcing. It is assumed, and this certainly holds for low level stratos- and stratocumulus clouds over the oceans, that the average net effect is a negative one. Cloud statistics are very sensitive to minor changes in atmospheric circulation patterns and the hydrological cycle. Also the number of condensation nuclei may play a role, especially over the oceanic areas of the Southern Hemisphere and to a lesser extent also over oceanic areas of the Northern Hemisphere. At the moment it is not clear in what way cloud statistics will react to climate change. The uncertainties projected increase in average global temperature (ranging between 2-5 K) for doubling the atmospheric CO_2 concentration is merely due to the way clouds are treated in the climate models.

The role of atmospheric ozone needs special attention in global change. Depletion of stratospheric ozone may alter the UV-B climatology, while an increase in tropospheric ozone may have serious adverse effects on the biosphere. Tropospheric ozone is not emitted, it is formed in the atmosphere by chemical reactions involving compounds such as NO_x, CO and VOC, which are called ozone precursors. The role of tropospheric ozone in climate change is significant. A complicated factor being, that the magnitude of the O_3-forcing effect is height dependent with a maximum around the tropopause and an "opposite" effect above 30 km. Since the effect of precursor emissions and atmospheric chemical processes on tropospheric ozone levels depend on varying regional atmospheric conditions, it is difficult to predict future global changes in tropospheric ozone concentrations accurately. This also holds for changes in stratospheric ozone depletion. Although the ozone depletion substances, due to their long atmospheric residence times, are distributed evenly over the globe, there exists large regional differences in the depletion of the ozone layer, notably in the antarctic and arctic regions, over the tropics and at medium latitudes. One may state that next to the hydrological cycle and the direct and indirect effects of tropospheric aerosol, changes in the ozone column density distribution pose the largest uncertainty in model calculations of climate forcing due to anthropogenic induced changes in the composition of the atmosphere.
Related to stratospheric ozone depletion are, as was mentioned before, possible changes in the UV-B climatology. This needs special attention since UV-B plays an important role in the chemistry of the atmosphere and may enhance urban photochemical smog and UV-B may also exhibit negative effects on the biosphere. The UV-B climatology is dependent on many factors of which the most important are:

- Stratospheric ozone destruction.
- Changes in tropospheric ozone.
- Scattering by aerosols and interaction with clouds.

Insight in these processes is crucial to predict changes in the UV-B climatology to be expected near the surface of the earth.

The NRP subtheme "Atmospheric processes and UV-B radiation" is aimed at studying the aforementioned processes. Changes in the composition of the atmosphere on a global scale and related changes in radiative forcing may have far reaching social-economic consequences especially with regard to preventive and adaptive measures to be taken. For this reason projects belonging to this theme, cannot predominantly be qualified as basic science, but are at the same time policy oriented.
The assessment report will focus on uncertainties in our understanding of 3 priority issues i.e.:

I. Clouds, aerosols and radiation
II. The role of atmospheric ozone in global change
III. Tropospheric budgets of non-CO_2 greenhouse gases

The projects to be assessed and the priority issue they are linked with, are listed Table 1.2.

Table 1.2
List of projects in the NRP subtheme on "Atmospheric processes and UV-B radiation"

Title	Projectleader	Number
Clouds, aerosols and radiation		
Formation and air/sea exchange of dimethylsulphide (DMS) from marine sources	R.Guicherit	850026
The role of aerosols of anthropogenic origin in the radiation balance of the atmosphere	H.M. ten Brink	852066
Clouds-radiation-hydrological interactions in a limited area model	A. van Lammeren	851058
The effect of clouds on ultraviolet radiation and photodissociation rate in the troposphere	H. van Dop	850018
The role of atmospheric ozone in global change		
Dutch participation in the international network for the detection of stratospheric change (NDSC)	D.P.J. Swart	850024
Spectral UV radiation measurements and correlation with atmospheric parameters	H. Kelder	852088
Determination of the UV-B climate in The Netherlands: high resolution spectral measurements, monitoring and modelling from perspective of risk-analysis	H. Slaper	852087
Stratosphere Troposphere Experiment: Study by aircraft measurement	P.J.H. Builtjes	VvA205
Budget studies		
Climate modelling/Global Modelling of Atmospheric Chemistry (GLOMAC)	H. Kelder	851050
Application of 2-D global models	M.G.M. Roemer	852072
Global modelling of atmospheric trace gases "Application of a global three dimensional model"	J.P. Beck	852070
Continental ozone issues: monitoring of trace gases, data analysis and modelling of ozone over Europe "Dutch contribution to the EUROTRAC-TOR project"	J.P. Beck	852094

2. CLOUDS, AEROSOLS AND RADIATION

Aerosol particles play an important role in the radiation budget of the atmosphere because of their direct interaction (absorption and scattering) of solar and terrestrial radiation, as well as through their influence on cloud formation processes. Aerosol particles have a lifetime of a few weeks in the troposphere and occur in highly variable concentrations. A large proportion of the particles, which are of interest for the radiation balance and for cloud processes are derived from natural sources, anthropogenic gaseous sulphur emissions, emissions of carbonaceous and organic particles, and biomass burning.

It is complicated to determine the direct effect of aerosols. This is due to the fact that the effect is dependent on the aerosol absorption to backscattering ratio, surface albedo, total aerosol optical depth and solar elevation. Their is, however, general agreement, that anthropogenically generated sulphate aerosols will reduce solar irradiance, leading to a net negative change in radiative forcing and thus regionally offsetting the effect of warming due to increased concentration of greenhouse gases.

The global radiation (energy) balance is very sensitive to cloud albedo, particularly for marine stratus clouds which cover a substantial part (about 25%) of the earth. Cloud albedo itself is sensitive to changes in droplet number concentration. The droplet number depends on the concentration of cloud condensation nuclei (CCN) which in turn depends on condensation nuclei (CN) or on the aerosol concentration. The ability of an aerosol particle to act as a CCN under low supersaturation found in clouds depends on its size and its chemical composition (notably its water solubility and substances that influence surface tension). There is a significant non-linearity in the effect on cloud formation and cloud microphysics of changes in CCN concentration; depending on the starting CCN concentration. The effect is far more pronounced in areas (such as clean oceanic sites) where low aerosol concentrations prevail, compared to more polluted areas, e.g. areas over the continents which are strongly influenced by anthropogenic emissions.
The hypothesis by Charlson et al (1987) of a connection between climate and phytoplankton activity in ocean surface waters is based on the fact that CCN concentrations in air over oceans far from land are low, that CCN available in clean maritime air are composed almost totally of sulphate particles, and that this sulphate originates almost entirely from emissions of dimethylsulphide (DMS) from the ocean surface (see Figure 2.1).

This subtheme comprises 4 projects.

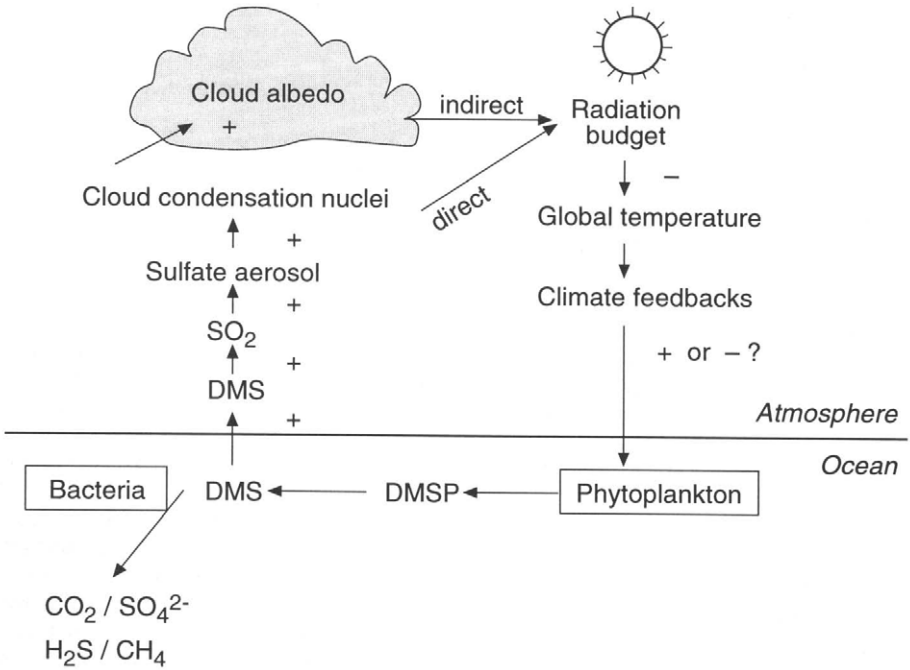

Figure 2.1
Proposed feedback cycle between climate and marine DMS production (adapted from M.O. Andreae, 1990)

2.1 Formation and air/sea exchange of dimethylsulphide (DMS) from marine sources

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Introduction

Global climate and the "greenhouse effect" can be influenced by several feedback mechanisms. The present project focuses on dimethyl sulphide (DMS) as a likely candidate for important negative feedback processes. DMS is the most important biogenic precursor of non-seasalt sulphate (NSS-SO_4) which is a major source of

cloud condensation nuclei (CCN). DMS production in marine environments is linked to phytoplankton and macro-algae; it is formed from the precursor ß-dimethylsulphoniopropionate (DMSP), which is believed to be an osmoregulating or cryoprotecting agent.

It is important to realise, that the ultimate flux of DMS to the atmosphere is dependent on many biological and physical/chemical factors. The production of DMSP by algae is subject to species abundance and composition, which is a function of the environmental conditions. The conversion of DMSP to DMS by algae and microorganisms, the degradation of DMS and DMSP by bacteria, loss of compounds due to sedimentation, photochemical processes or escape to the atmosphere, all processes are intricately linked to each other. The various paths of formation and degradation of DMSP and DMS, and their relative importance are presented in Figure 2.2a, where the state of the art at the start of the project is depicted.
Quantification of the DMS emitted to the atmosphere has been found difficult as large temporal and geographic differences occur. For a better estimation of the fluxes, a proper understanding of the (micro)biological processes in the water column related to the biogeochemical cycle of DMS(P) is essential.

Although the possible effects upon the world climate will to a large extent be a function of open ocean processes, coastal waters (and sediments) may play an important role on a regional scale, not in the last place because of its enhanced algal productivity. If we consider the algal species *Phaeocystis* sp. and *Emiliania huxleyi as* typical and important representatives for coastal and open ocean waters respectively, Figure 2.3 illustrates schematically the DMS(P) cycles that play a role in the various marine compartments.

The objectives of the present project are:
- To assess these processes and rates of biological production.
- To assess the processes of degradation and transformation in the water column and the role of sedimentation therein.
- To estimate the fluxes from water to the atmosphere.

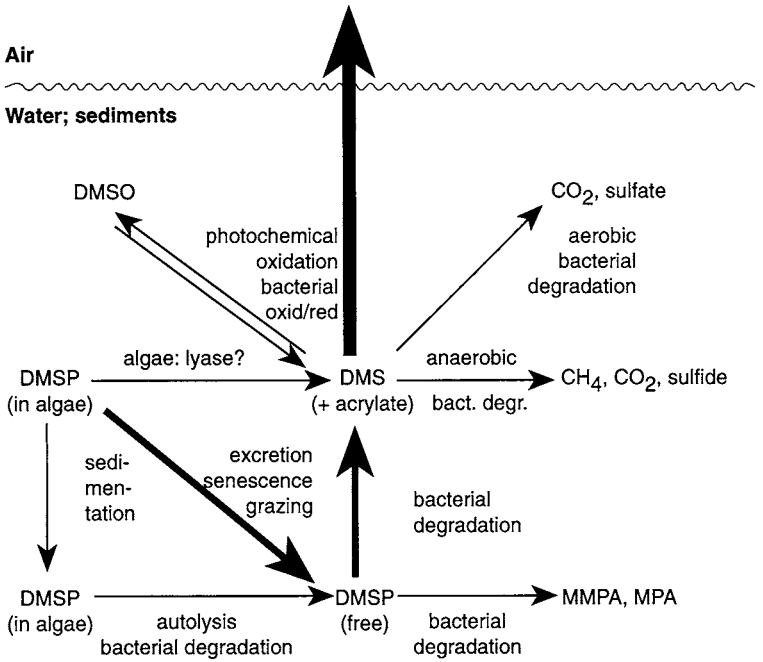

Figure 2.2a
The understanding of major DMS pathways before the start of the NRP/DMS project

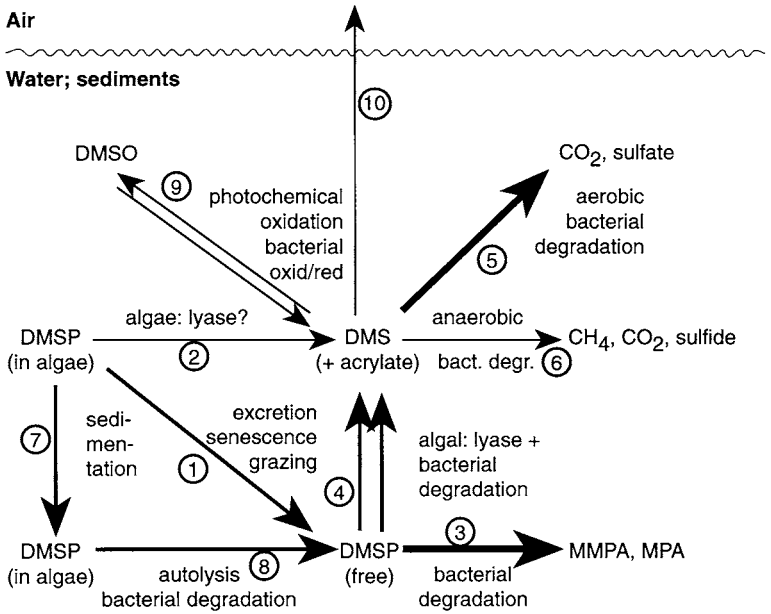

Figure 2.2b
Our understanding of the major DMS pathways including results of the NRP/DMS project

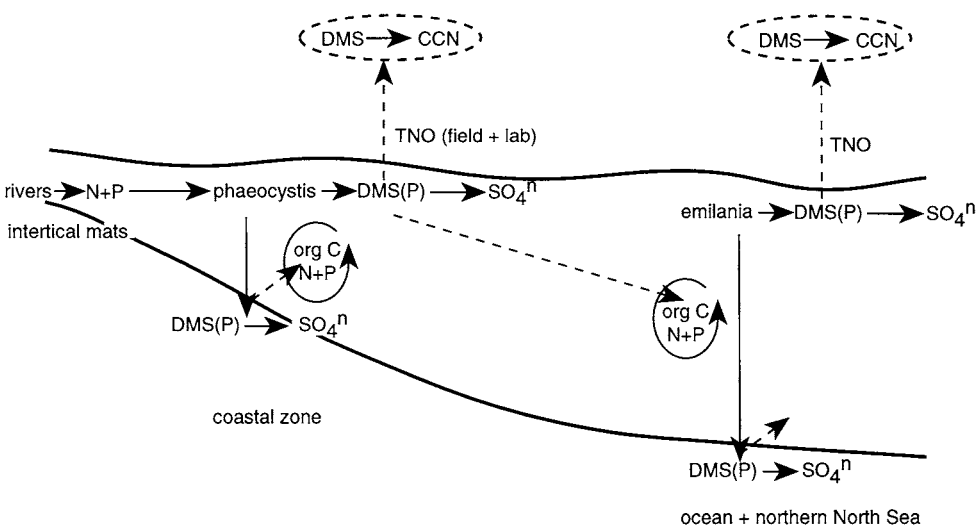

Figure 2.3
The sulphur cycle in different parts of the marine environment

To investigate the different parts of the DMS(P) cycle, experiments were performed under well defined laboratory conditions, in large experimental enclosures (mesocosms) and in the natural environment (Dutch coastal waters). In this project research focussed on species typical for the Dutch coastal environment because it was considered that although the rates may not be comparable to those in oceanic systems, the processes as such will probably be analogous in both systems.
Within the project a close cooperation was established between different marine scientific disciplines, in order to be able to tackle the various routes of production/elimination and the process rates involved.

The project is a combined scientific effort of the:
- University of Groningen, Department of Marine Biology and Department of Microbiology.
- TNO Institute of Environmental Sciences, Department of Biology, and Department of Environmental Chemistry.
- Netherlands Institute for Sea Research, Department of Applied Scientific Research.

In the following sections the DMS(P) production/elimination paths will be discussed in the framework of the activities performed within the present project. References will be made to the numbered routes (paths) in Figure 2.2b, which represents the situation as we understand it now.

Laboratory studies
Phytoplankton. DMSP is produced intracellularly by phytoplankton. Two mechanisms are to be considered for the formation of DMS, either direct (through algal lyase) or via DMSP that is released into solution (by excretion, senescence and/or predation).

Until now, little attention has been paid to the influence of environmental stress factors on the DMSP content of algal cells, and the possible role of algae in the conversion of DMSP to DMS (paths 1 and 2). As it is often suggested that bacteria are most important in this conversion (see below), evidence for an important role of phytoplankton itself was never presented. As *Phaeocystis* sp. is considered an important producer of DMSP in coastal waters, this species was investigated in detail in laboratory studies.

It is often hypothesized that DMSP production in algae is stimulated under nitrogen limited conditions, when DMSP substitutes for other - nitrogen containing - osmolytes. This was tested by inducing osmolyte production in axenic *Phaeocystis* sp. cultures at different salinities (from 25 to 45×10^{-3}) and different N:P ratios. Although DMSP per cell did increase with salinity, indicating its function as an osmolyte, no significant difference was found between the N and P limited cultures.

In *Phaeocystis* sp. cultures, that were free of bacteria (axenic) the transformation of extracelluar DMSP to DMS and acrylate was measured (path 2). It was proven that this conversion could be correlated with an enzymatic (lyase) reaction associated with the cells, which could be inhibited by heating. The lyase activity in

living cultures increased with temperature: at 5 °C activity was 50% of the activity at 20 °C.
During the growth phase of an axenic *Phaeocystis* sp. culture leakage of DMSP or DMS was very low. DMS production started in early stationary phase, when only small amounts of dissolved DMSP appeared to be present, indicating a rapid conversion of DMSP by the algal lyase. In a completely lysed culture, approximately 75 % of total DMSP was found to have been converted to DMS.

In experiments with crude extracts of *Phaeocystis* sp. cells, the DMSP-lyase activity exhibited an alkaline optimum, which is in contrast to results from experiments with other organisms as reported in the literature. This points into the direction of a species specific enzyme.

Bacteria. Once DMSP or DMS are liberated in the water column, bacterial degradation/transformation may occur. Previous studies on the microbial metabolism of DMSP had shown that there are two pathways for degradation of DMSP. The first pathway involves a cleavage to dimethyl sulphide (DMS) and acrylate (path 4). The second pathway involves the demethylation to 3-S-methylmercaptopropionate (MMPA) and subsequently to 3-mercaptopropionate (MPA) (path 3). DMS may be further degraded to CO_2 and SO_4^{2-} (path 5) under aerobic conditions.

From a variety of marine sources (phytoplankton cultures, sediments, macro-algae and mesocosms) bacteria capable of degradation DMS or DMSP in aerobic environments could be isolated and characterized during the present project. Common characteristics of these strains are the ability to utilize a broad substrate spectrum, their motility and their coccoid rod-like morphology.

Apart from aerobic conversion of DMS(P), anaerobic degradation of both DMS and DMSP is possible. With a few exceptions, anaerobic processes are not considered important for the water column. However, anoxic sediments can be abundant in many coastal waters, where they may influence the cycling of DMS(P).
Under anoxic conditions, DMS may be converted by sulphate-reducing bacteria or by methanogens to methane (path 6). The degradation step from DMSP via MMPA and MPA (path 3), can be followed by a conversion to methane by methanogens. Except for DMS-metabolizing methanogens, no anaerobic microorganisms that are responsible for one of the above mentioned conversions had been isolated from anoxic marine sediments.

During this study it was found that demethylation of DMSP to MMPA in anoxic Waddensea sediments is coupled to sulphate reduction. A pure culture of a DMSP-demethylating sulphate-reducing bacterium, which was identified on basis of physiological characteristics and positive hybridisation with genus-specific molecular RNA probes as a *Desulfobacterium* sp, was isolated from the sediment. Certain other *Desulfobacterium* species were also found to demethylate DMSP. It is, however, not yet clear what the ratio of DMSP cleavage over DMSP demethylation is at natural (anoxic) concentrations of DMSP. Recently a DMSP-cleaving anaerobic bacterium was isolated which ferments acrylate to propionate and presumably CO_2 but which is not able to utilize DMS. This strain

showed a high DMSP-lyase activity (approximately 10 μmol/min.mg protein) and a rather high Km value for DMSP (150 μM).

The methanogens *Methanosarcina* sp strain MTP4 and *Methanosarcina acetivorans* were found to be able to convert MMPA to MPA and methane during growth. Methanogenic conversion of MMPA to MPA was only found in anoxic Waddensea sediment when certain antibiotics, acting against bacteria but not methanogens, were used. Under non-inhibited conditions MMPA was rapidly converted to methanethiol, which was subsequently converted to methane.

It was concluded that conversion of MMPA in anoxic marine sediments directly or indirectly results in the formation of methane. The anaerobic metabolism of DMS was also studied in anoxic Waddensea sediment. In this sediment DMS appeared to be converted to methane, as had been described for other anoxic marine sediments. The conversions of DMS to methane seems to be restricted to *Methanosarcina* species. The population of DMS-metabolizing methanogens appears to be in the same range as the total population of methylotrophic (i.e. methanol- and trimethylamine-utilizing) methanogens (1-6x10^6 cells per gram dry weight).
Both pathways indicate that methane can be produced under anaerobic conditions; there may thus exist a positive flux of methane to the atmosphere. Thus, in anoxic marine environments, not only the counteractive effect of global warming through DMS may take place, but also the production of the potent greenhouse gas methane.

Mesocosm studies
Apart from the direct production of DMS by algae, DMSP may be introduced into the water column by various other mechanisms (path 1). Living algae may excrete DMSP, the DMSP may be liberated when the algal cells die (senescence), or zooplankton may release DMS(P) during or after digestion of the algal cells (predation, sloppy feeding). Particulate DMSP may be transported out of the surface layers by sedimentation.

In order to study the role of phytoplankton and zooplankton (and their interaction) in the production of DMSP and the release of DMS to the water column (and eventually to the atmosphere), three series of large scale experimental systems (pelagic mesocosms) were used to study the development of phytoplankton blooms as function of the presence of zooplankton, different nutrient regimes, species composition and varying general environmental characteristics. Measurements on densities and activities of aerobic DMS(P) metabolizing bacteria were included. In one mesocosm experiment the deposition of particulate matter (containing $DMSP_{part}$) was quantified.

The first two mesocosm experiments showed that the DMS is generally released in the water column directly after the peak of the phytoplankton bloom, during the senescence phase. This was observed for a diatom bloom. For the bloom of *Phaeocystis* sp. in the last mesocosm experiment, a maximum DMS production was found during the stationary phase; no direct correlation was found with chlorophyll-*a*. The decline of the *Phaeocystis* bloom did not lead to an increased DMS concentration. However, but just before the release of DMS a dramatic drop in cellular $DMSP_{part}$ was observed. The latter species produced substantially

higher amounts of DMS(P) than the diatom species, which confirmed earlier findings reported in the literature.

Due to boundary effects, the duration of the chlorophyll-*a* peak appeared to be compressed in time in our mesocosm studies, as was the peak of $[DMS]_{water}$. It appeared that the change in DMS concentration could occur very fast. In a matter of days the $[DMS]_{water}$ can change by orders of magnitude. Both increase and decrease of $[DMS]_{water}$ showed this dynamic character.

In mesocosm-systems with apparently similar characteristics (both in chlorophyll-*a*, nutrients, plankton assemblages) the production of DMS did not always follow the same pattern. Considering the results of the last mesocosm experiment the role of *Phaeocystis* may have been underestimated in the first two experiments. Another reason could be that the importance of the microbiological activity is not fully understood.
In order to study the potential effect of zooplankton upon the production of DMS, in a number of mesocosm experiments the zooplankton was inhibited or removed. A positive influence of zooplankton *e.g.* of grazing (path 1) upon the release of DMS into the watercolumn could not be found, however. This could indicate that zooplankton does not play an important role in the DMS(P) dynamics. However, as the time axis of the phytoplankton bloom in the mesocosm experiments is compressed, a mismatching of life stages of algae and zooplankton may have biased these experiments to some extent.

During this last experiment, deposition of suspended particulate matter was studied (path 7). At least in the mesocosms, sedimentation is an important sink for biomass of *Phaeocystis* sp. The sedimentation of *Phaeocystis* cells showed a good correlation with *Phaeocystis* cell numbers in the water column, suggesting that the sinking rate of *Phaeocystis* cells was rather constant. The daily sedimentation of living cells being nearly equal to the standing stock at that time.
At the decline of the *Phaeocystis* bloom in the mesocosm, sedimentation accounts for only 50 % to the observed loss in biomass. This strongly suggests that cell lysis in the water column must have been important at this time. Although this cell lysis does increase the $DMSP_{diss}$ concentration, this does not lead to a peak in the DMS concentration: possibly the production and consumption are of a similar magnitude.

The importance of bacteria in the conversion of DMSP and DMS was studied in the same mesocosm experiments.
The DMSP-degrading population consisted of a variety of microorganisms. Bacterial populations are strongly stimulated by the collapse of an algal bloom, as their substrate becomes abundant from the decaying algal cells. The DMS-utilizing bacterial population reacted upon the increase of DMS with a delay of about a week. The DMS assimilating ability seemed to need some induction.

The bacterial activity found in the mesocosm systems, 10-1000 µmol DMS per mg protein per day, was in the range of activities of laboratory cultures.
The biological turnover rate ranged between and 0.2 and 0.6 days, whereas the turnover by DMS efflux ranged between 2 and 5 days. In these experiments, the contribution of the bacteria to the loss of DMS was calculated to be approximately

90% of the total DMS loss. This figure should be taken with some care, as only few observations were made. Nevertheless, the importance of this process should not be underestimated.

Although limited data on the turnover of DMSP exist, they indicate a key role for the demethylation of DMSP via MMPA (path 3) rather than the cleavage of DMSP (path 4). This means that only a fraction of the $DMSP_{water}$ seems to contribute to the formation of DMS.

In benthic mesocosm studies carried out separately, addition to the sediment of fresh algal material (dominated by *Phaeocystis* sp., path 7) resulted in a strong (benthic) microbial response after 2 days, which indicated that freshly deposited algae become subject to rapid bacterial degradation. In shallow waters, benthic processes are therefore likely to have a strong influence on the processes in the water column in the pelagic mesocosms.
Since many *Phaeocystis* cells reach the mesocosm floor intact, there is also a continuous downward transport of considerable amounts of particulate DMSP. Sedimentation of DMSP may significantly contribute to the production of DMS in sheltered, shallow systems like the mesocosms, as a result of autolysis or bacterial degradation on the bottom (path 8). Despite the relatively high downward transport of DMSP, and the potentially fast transformation to DMS, there was no evidence that DMS in the water column correlated with the sedimentation rate. In deep, oceanic systems, path 6 may be a sink for $DMSP_{part.}$

Since the rates of bacterial transformation were not sufficiently well determined, it seems premature to base budget studies on these results.
Another unknown box in such budget studies forms the potential formation of dimethylsulphoxide (DMSO) by photochemical oxidation and/or bacterial activity (path 9). This compound has worldwide received little attention, due to the problematic analysis.

By closing of one mesocosm system, the actual flux of DMS over the water-atmosphere interface could be determined.
The measured flux of DMS to the atmosphere (path 10), under constant wind speed conditions (1.3 m/s) in one mesocosm system, confirmed that the maximum efflux of DMS from the waterphase to the atmosphere took place at the same period of the development of the phytoplankton bloom, linked to the (elevated) water concentrations. The measured flux of DMS (at this low wind speed) agreed well with the calculated flux according to the Liss-Slater model (see next Section).

Field observations
The laboratory observation that the DMSP-lyase activity could result from a species specific enzyme, was confirmed by field experiments.
During the spring bloom of 1993, a DMSP-lyase-assay was applied to natural seawater samples off the Dutch coast. A very good correlation was observed between the DMSP-lyase activity and *Phaeocystis* sp. numbers, the most abundant species found during the cruise ($r^2 = 0.9660$, $n = 23$). No correlation was found with either one of the other species. From these results a potential DMS production via route 2 by *Phaeocystis* sp. cells in the field was calculated. It appeared that DMS production rates were in the same order of magnitude as the

total abiotic loss factors (fluxes of DMS to the atmosphere and photochemical degradation).

In order to try to link the processes in the mesocosms to the natural environment, water samples were collected regularly in the Marsdiep tidal channel over a period of 1.5 years. Measurements of DMS(P) and other organic sulphur compounds in the coastal waters of the Marsdiep tidal inlet, showed that also here only during or shortly after the phytoplankton peak the majority of the DMS was released. In only one week the $[DMS]_{water}$ increased or decreased five to ten fold. Maximum concentrations were up to 20 nM, as compared to 450 nM in the mesocosms in the same period.

Other sulphur compounds, like carbonylsulphide (COS) and dimethyldisulphide (DMDS) were found to change not much with the time of the year, with concentrations substantially lower than those of DMS (for COS and DMDS respectively: 1.2 nM and 0.35 nM in the field, comparable to 1 nM and 0.4 nM found in the mesocosms).

Maximum concentrations of particulate DMSP observed, were about 1500 nM in the Marsdiep, which is substantially less than those found in the mesocosms (7500 nM). The ratio of particulate DMSP/Chl-*a*, however, was 20 nmol/µg in the Marsdiep which compared well with the 10-60 nmol/µg in the mesocosm experiment.
The Marsdiep experiment (and the last mesocosm experiment) showed, that from the total amount of DMSP produced by the phytoplankton, only 5 to 10% can be detected as DMS in the watercolumn.

The sea to air transfer-velocity of DMS has been experimentally determined. This parameter is of major importance in calculating the DMS flux from the DMS concentration in the water (flux = concentration in water x transfer velocity). Liss and Slater showed that the transfer velocity (of CO_2) primarily to be dependant on the wind velocity. Their empirical relations are being applied to DMS as well. To our knowledge there have been no report of the experimental determination of the sea-air transfer velocity of DMS in the open literature.
In this study the transfer velocity of DMS from water to the atmosphere has been determined by two different methods :

- Enclosure (at low, artificial wind velocity of 1.3 m/s).
- Concentration vs. height gradient method (field measurements, wind velocities over a range from nearly 0 up to 11 m/s).

Good agreement was found between the Liss-Slater relations and the experimental data at lower wind velocities (up to 4 m/s). At higher velocities the Liss Slater relations underestimates the transport velocity up to 20 %., assuming, however, that the collected water in the field observations contained a representative amount of DMS for the surface waters that determined the atmospheric concentrations.

Climate modelling
The influence of the sea to air transport of DMS upon the climate has been estimated by mathematical modelling.

In the atmosphere DMS is converted to primarily sulphate and methanesulfonic acid (MSA). The climate effect has been calculated using a global zonal averaged 2D atmospheric chemistry and transport model. This global model has a resolution of 10 x latitude and 20 layers (of 500m and 1km height) in a vertical dimension from 0 to 16 km. Transport is described by using seasonally averaged data for advection and eddy-diffusion and also for DMS emissions (literature data). The data base contained over 130 different chemical compounds and over 200 different chemical reactions.

The climate effect has been calculated from the direct climate effect of sulfate aerosols, and the effect of DMS emissions has been compared to that of anthropogenic SO_2 emissions. The radiative forcing resulting from DMS emissions amounts to a global annual averaged value of -0.4 W/m^2.

It was shown, that at northern hemisphere mid-latitudes, the radiative forcing by sulfate aerosols is governed more by anthropogenic sulfurdioxide (SO_2) emissions than DMS emissions. DMS, however, still accounts for 20 to 30 % of the annual averaged radiative forcing of sulfate aerosols. At the other latitudes and especially on the southern hemisphere, DMS is the major precursor of sulfate aerosols and the relative contribution of DMS emissions to the direct radiative forcing was calculated ranging from 50–99 %.

Conclusion

Many routes of formation/degradation of DMS(P) and related compounds were studied in this project. Figure 2.2a presents the situation as we understood it at the start of the project; Figure 2.2b summarizes our present understanding, based on our experimental results. Bold arrows indicate that these paths are considered important.

It became possible to get a better insight in the production and fate of DMSP and DMS, and the relative importance of the DMS flux to the atmosphere and bacterial turnover as the main loss factors for DMS during an algal bloom.

The strong relation with the development of algal blooms was confirmed. It was found that the efflux of DMS to the atmosphere was definitely episodic in character: closely connected to (only) the occurrence of an algal bloom, fast increases and decreases of DMS in the water column were observed in all experiments. The importance of the processes, as indicated by the arrows in Figure 2.2b, may temporarily be enhanced due to physical effect: wind speed and turbulence. This emphasizes the significance of the processes that may occur over short time periods. Because not all results fit easily into one model, and because the importance of the bacterial compartment could only in a late stage of the project be confirmed, it seems too early to quantify the rates of the various processes.

Based on the availability of $DMSP_{part}$, the DMS_{water}, and the calculated and measured DMS fluxes, it was calculated that only part of the DMSP produced is transformed into DMS, and that only part of this DMS produced actually escapes to the atmosphere. This implies that minor changes in the bacterial and phytoplankton population density or composition, could have pronounced effects on the global S budget, with all of its consequences.

Assessment
This project has given insight in some important processes governing the oceanic S-cycle. A major finding is, that only part of the DMSP produced, is transformed into DMS and that only a small part of this DMS actually escapes to the atmosphere. This implies that minor changes in the bacterial and phytoplankton population density or composition, could have pronounced effects on the global sulphur budget, with all its consequences.
For the transfer of DMS a good agreement was found between the Liss-Slater relations and the experimental data.
It was also found that the global annual radiative forcing due to DMS derived aerosols amounts to -0.4 W/m^2. It was further found that at northern midlatitudes DMS accounts for 20-30% of the radiative forcing due to sulphate aerosols. For the other latitudes and especially over the southern hemisphere DMS is the dominant precursor of sulphate aerosols. The indirect effects due to cloud formation are much harder to deal with, no attempts are made. Although progress in understanding the oceanic S-cycle has been achieved, the state of the art is such, that at his moment no predictions can be made, with respect to expected changes in DMS emissions as a result of expected environmental changes, and the consequence thereof on climate change.

2.2 The role of aerosol of anthropogenic origin in the radiation balance of the atmosphere

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Direct effect
The present study aims at assessing the influence of anthropogenic aerosol particles on the solar radiative flux in Europe. Aerosol particles reflect shortwave radiation and absorb little infrared terrestrial radiation. They thus exert a cooling forcing over surfaces with low albedo, the "direct" forcing effect.
Aerosol particles originate both from natural and anthropogenic sources. The anthropogenic particles form an (extra) forcing factor introduced by mankind. They mostly result from fossil fuel combustion. Estimates for the forcing by the anthropogenic aerosols indicate a regional forcing in the heavily polluted regions of Europe of up to 10 $W.m^{-2}$ with an uncertainty of the same order of magnitude. This means that, after the forcing by clouds, the forcing effect of aerosols is the second largest climatic forcing term.

The forcing by aerosols is a regional effect, because of the limited residence time of the particles in the atmosphere. Better quantification of the "direct" aerosol effect in Europe is studied by ECN in a separate European project, of which the progress report is in press. A main preliminary conclusion is that nitrate and, possibly, carbonaceous aerosol are more important than sulfate in the local "direct" effect. In the above mentioned estimates sulfate was used as the only anthropogenic aerosol component. The actual local forcing is therefore higher due to nitrate and carbonaceous aerosol. These aerosol components are not directly emitted but almost exclusively formed in the atmosphere from gaseous emissions, which makes source apportionment difficult.

Indirect effect
In de indirect effect, anthropogenic aerosols act as a radiative cooling forcing via clouds. Aerosol particles serve as the nuclei on which the clouds in the atmosphere form. In the present study, ECN assesses the influence of anthropogenic aerosol particles on cloud structure. Anthropogenic aerosol particles act as extra cloud nuclei, in addition to the natural nuclei. The extra cloud droplets change the microstructure of the clouds and thus their radiative transfer as well as their lifetime. Simple radiative models show that this leads to an increase in the reflectivity of the clouds. The influence on the infrared absorption is, however, small. Thus anthropogenic aerosol particles exert an "indirect" radiative cooling effect.

Sensitivity studies show that the "indirect" effect is most important in marine stratus near polluted continents.

Cloud chamber
In a first approach to assess the effect of anthropogenic aerosols on clouds the differences in the microphysics of clouds formed in clean and polluted marine air were investigated. This is done by artificial cloud formation using a cloud chamber, drawing in ambient air and comparing the number of cloud droplets formed. The site of the cloud chamber is ideally located to study marine clouds, since it is situated at the coast of the North Sea in The Netherlands. In arctic North-West airflows only natural aerosols occur and extra anthropogenic aerosol is present when the air travels more southerly over the UK.
In the cloud chamber the supersaturation can be controlled in the range of 0.1 to 0.3% supersaturation values, which correspond to the supersaturations in the marine stratus of interest. The particle size and number-concentration of the ingoing aerosol and the unactivated aerosol (particles not grown to droplets) are also compared. First, laboratory generated aerosols were used for testing the performance of the chamber. Aerosol particles with a size larger than approximately 0.07 μm were found to grow into cloud droplets. This "critical" size was in agreement with the calculated size for the supersaturations used. From these tests it was concluded that the chamber has the proper characteristics for simulating marine stratus.

Results
The number of cloud droplets in the polluted air is higher by a factor of three compared to that in the clean air. This is less than the increase in particle number. A substantial fraction of the particles larger than the critical size do not grow, presumably since they are not soluble, see below.
In order to compare results obtained with the cloud chamber with actual clouds, ECN cooperates with one of the leading institutes (Brookhaven National Laboratory) in the ARM program of US-DoE, in the evaluation of the microstructure of clean and polluted marine stratus off the coast of Nova Scotia. ECN has also participated in a recent cloud study near the English west coast.

In special campaigns, droplets and aerosol particles were collected for chemical analysis. Unfortunately these campaigns were on days with continental air. In the polluted continental air, the number concentration of particles is about twenty times higher than that in the clean marine air, but the number of cloud droplets is

not proportionally larger. Droplet concentrations were typically 1100 per cm^{-3}, independent of the aerosol concentration. This is indicative of a saturation effect of the cloud number in continental air. This phenomenon is in part explained by the fact that particles with the proper size are non-soluble and therefore cannot act as cloud nuclei. Measurement of the actual amount of non-soluble particles is very difficult, because most cloud nuclei are small and thus contain very little mass.

Preliminary conclusions[1] [2]

- The local "direct" aerosol effect can be assessed by measurements and is thus easier to quantify than the "indirect" effect.
- Nitrate seems of more importance for the local direct effect than sulfate.
- Non-soluble, presumably carbonaceous, particles form a central factor, both in the direct and the indirect effect.

Assessment

The project is one of the so called "late starters". Progress is questionable. No substantial new results are as yet available. The use of a cloud chamber seems promising. At this moment it cannot be judged if the goals of the project will be met.

2.3 Clouds-radiation-hydrologic interactions in a limited-area model

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Introduction

Clouds play an important role in our climate. Clouds produce precipitation which is an essential ingredient of the hydrological cycle. Clouds modify the earth-radiation budget. Thin cirrus clouds have a warming effect while low clouds have a distinct cooling effect (Ramanathan, 1989). Clouds dominate the vertical transport of energy, momentum and trace gases in the free troposphere. Despite their importance, clouds are represented only rudimentary in climate as well as weather forecast models. It appears that the model representation of clouds in climate models has a major impact on model predictions for climate change. Cess et al. (1989) showed that cloud feedback is a major source of uncertainty in model responses to climate forcing.

There are two main reasons why the uncertainties with respect to clouds are so large. The first reason is that cloud processes are extremely complicated. A proper

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1. In the present summary the comments by the cluster coordinator on the presentation of 19 May 1994 are incorporated. These comments centred on the magnitude and the uncertainty of the aerosol forcing relative to the magnitude/uncertainty of the forcing by clouds and on the values for the anthropogenic forcing in recent literature.

2. In a special investigation, which was not part of the European project, the local "direct" aerosol effect in November 1993 was studied. The data indicate a local daytime radiative forcing by the aerosol in polluted air of 20 $W.m^2$.

representation of clouds requires the parameterization of subgrid processes both on the macroscale (cm - km) and on the microscale (<< cm). Cloud parameterization is still in its infancy.
The second reason is the lack of good quantitative observations of cloud characteristics (cloud cover, cloud structure, optical depth, droplet spectra). This lack of good data hampers the development and validation of models. Satellites begin to provide useful data on global cloud statistics and corresponding radiation budgets (ISCCP, ERBE). However, these data sets still have to be validated.

To validate these global data sets on a regional scale, detailed measurements of the cloud cover and structure are necessary. It is important to measure the variability of the cloud characteristics within one datapoint of the global dataset. High resolution measurements are also crucial for the development and improvement of parameterization schemes for clouds and cloud-radiation interactions.

The aim of the project "Clouds-Radiation-Hydrologic interactions in a limited-area model" is threefold:
- Provide a detailed regional dataset on cloud cover and cloud characteristics.
- Analyze the ISCCP and ERBE datasets with respect to validity and possible applications for climate model verification.
- Create a model environment for the enhancement of regional data analysis and for the improvement of parametrizations of clouds and radiation.

These items will be described below.

Hybrid cloud detection system
A proper description of clouds and cloud-radiation interactions in climate models requires the parametrization of the subgrid processes which determine cloud cover and cloud structure. To develop and improve these parametrizations a set of measurements is required, so results of the model can be validated. At the KNMI a project is ongoing which yields accurate and high resolution cloud measurements over the Netherlands. A hybrid cloud detection system in which both groundbased and satellite remote sensing instruments data are combined has been built. This cloud detection system is described in full detail by Stammes et al. (1994). An outline is given below.
The cloud detection system is used to retrieve the following cloud characteristics: cloud cover fraction, cloud top temperature, cloud base height, cloud base temperature, reflectivity and optical thickness; it provides information on the 3-dimensional structure of cloud ensembles. The cloud detection system consists of a network of stations for groundbased remote sensing and a processing environment for AVHRR and METEOSAT measurements. In the 120x120 km target area a network of stations for groundbased remote sensing has been built. Each station consists of a LIDAR ceilometer, narrowband IR radiometer and a pyranometer. On two stations more extensive radiation measurements are done. This provides data for the analysis of cloud-radiation interactions. In order to obtain a complete description of the geometry and height of the clouds the signals from the various instruments are correlated.
Other available tools for interpretation of the measurements are data on the actual atmospheric conditions from model analysis and radiosonde. Radiative transfer calculations are performed using Lowtran-7 (Kneizys, 1988) for longwave

and DAK (Stammes, 1994) for shortwave radiation. AVHRR data will be analysed using the Apollo retrieval scheme (Saunders and Kriebel, 1988), which has been implemented at the KNMI. The use of state-of-the-art retrieval techniques is guaranteed by the international cooperation with other institutes with a tradition in satellite remote sensing, among others: D.L.R. (Oberpfaffenhofen), L.M.D. (Paris), Universität Berlin.

The following data is archived:

a)	Satellite instruments:	NOAA/AVHRR, Meteosat
b)	13 Groundstations:	LIDAR, IR-radiometer and solar radiation
c)	Radiation stations:	Direct, diffuse and total downward SW flux, downward and upward LW flux
d)	Other datasources:	3-hourly analysis data of the operational HIRLAM (High Resolutional Local Area Model) weather forecast model, 6-hourly rawinsonde data in De Bilt

The aim is to obtain continuous data on clouds and radiation for two years.
The hybrid cloud detection system will also be used to create a dataset which will be compared with the results of the ISCCP algorithm.

Global data sets
The Earth Radiation Budget Experiment (ERBE) dataset contains invaluable information about the radiation budget at the top of the atmosphere. The International Satellite Cloud Climatology Project (ISCCP) dataset contains information on clouds, their height, temperature, optical thickness, etc. Both global datasets are derived from satellite measurements and cover many years.

ERBE. During the NPR project the literature on ERBE dataprocessing scheme was studied (Feijt, 1992). The main questions were: Can ERBE data be used for climate model validation and how can the data be used most reliably? Special attention has been given to assumptions about atmospheric and surface conditions, field-of-view homogeneity, spectral variability, time and space variability of cloud cover. It is concluded that the errors in radiative fluxes show much variation related to geographical and atmospheric conditions and the viewing geometry, the positions of the sun and the satellite relative to the area. Nevertheless, monthly mean values data are useful for climate model validation if used properly. Individual values should be used with caution, because the accuracy is highly dependent on the viewing geometry and surface/cloud type observed.
It is advisable to users of the ERBE dataset to spend some time on the merits of the data. Likewise it would be good practise if global datasets which are to be used over a wide range of research areas were accompanied by an indication of the errors involved, written down in a way readable by the non-specialist investigator.

ISCCP. In the course of 1993 parts of the ISCCP-cloud detection algorithm were implemented at the KNMI. Numerous case-studies have been performed on the merits of these modules for North-West Europe. This yielded a feel for the sensitivity of the algorithm for atmospheric conditions and possible related error-sources. Furthermore, the literature on the algorithm was studied in order to obtain insight into the coherent set of thresholds making up the detection algorithm. Recently, Rossow (1993a, b, c) published a validation study on the cloud

detection algorithm. In general his findings agree well with our own investigations (to appear in KNMI technical report in 1994). The algorithm performance decreases with: increasing variability of the surface albedo and temperature, decreasing contrast between clouds and surface and decreasing temporal variability of the cloud fields. As the ISCCP algorithm is based on spatial and temporal coherence tests this is not surprising. In terms of geographic areas: The algorithm performs well over ocean, somewhat worse over landsurfaces and worst over polar regions. Moreover the algorithm is hampered by areas of persistent cloudfields and stormtracks. Two cloud types are missed frequently: low broken cloud fields and high semi-transparent cirrus clouds. Both cause little contrast in albedo and brightness temperature and are hard to identify especially over cold bright surfaces (polar regions) or highly variable land surfaces.
The cloud climatology over the period 1982-1988 shows a global mean annual cloudcover of 63%, which is on the higher end of the range of values which are reported in literature. Rossow (1993c) states that this value is still an underestimation, because the derived cloud fraction is too low about 10% over land and 10-15% in polar regions. The derived cloud fractions are approximately correct over ocean.

The hybrid cloud detection system will provide a dataset which will be intercompared with the results of the ISCCP algorithm. This comparison will yield information on the merits of the basic assumptions and the used thresholds, and hopefully give directions for improvement of the ISCCP cloud detection algorithm.

The model environment
A Regional Atmospheric Climate MOdel (RACMO) has been implemented at KNMI (Christensen and van Meijgaard, 1992). This is a descendant of the High Resolution Limited Area Model (HIRLAM) and the Global Climate Model developed at the Max Planck Institute in Hamburg (ECHAM). HIRLAM is the optional weather forecast model at the KNMI which employs a 50 km grid and 16 layers. RACMO inherited the dynamics and initialization environment from HIRLAM. All physics modules, including the liquid water and radiation modules, stem from the ECHAM model. There is a close cooperation with the research groups involved in the development of HIRLAM and ECHAM. The research environment supports flexible module management, so new versions of cloud and radiation modules can be activated and compared.
The Mocrette radiation scheme is included in the RACMO (Morcrette, 1991). This scheme has been extended to include trace gases and aerosols.
In addition to the Morcrette scheme a radiative transfer code for the shortwave spectrum was developed. This KNMI Doubling-Adding radiative transfer model (DAK, Stammes, 1994) is a line-by-line model which yields so-called exact results provided exact information on the atmospheric conditions and constituents is given. DAK was adapted to calculate the radiative properties of a plan-parallel cloud of which the user can define the cloud droplet size distribution and optical thickness.

Assessment
The cloud detection system has been completed and measurements have been started. It appears that the combination of ground-based and satellite-based

remote sensing provides unique information on clouds, amongst others on the small scale structure of clouds and on cloud bottom and cloud top.
The ground stations may well serve as a prototype for a global cloud detection network. A global network consisting of 13 stations / 120x120 km (as was discussed in the section dealing with the Hybrid cloud detection system) must, however, be precluded in my opinion.
An assessment of ERBE data has been completed. The strong and weak points of ERBE are highlighted.
A similar assessment of ISCCP data will be finished this year. Major conclusions are given in the summary report.
The model environment has been created and is in its testing phase. This environment includes newly developed radiation codes, which account for the important radiatively active trace gases, for aerosols and for plan-parallel clouds (see summary report). In summary it may be stated that this project is highly relevant for understanding the earths' radiation budget. The results seem very promising. International cooperation is an important aspect.

2.4 The effect of clouds on ultraviolet radiation and photodissociation rates in the troposphere

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Introduction

Most chemical transformations in the atmosphere are initiated by the photodissociation of molecules due to UV radiation. The intensity of the UV radiation field at different altitudes in the atmosphere is determined by the incoming solar flux, solar zenith angle, ground albedo and atmospheric composition. In the atmosphere the relevant processes include Rayleigh scattering, aerosol extinction, gaseous absorption (mainly by ozone) and the presence of clouds. Changes in these physical parameters will alter the amount of solar UV radiation available to dissociate of molecules in the atmosphere. Several studies (Tsay and Stamnes, K. 1992; Madronich, 1987; van Weele and Duynkerke 1993) have shown that clouds are the main cause of changes in the radiation field throughout the troposphere.
Since many important chemical species such as ozone, hydrogen peroxide and nitrogen dioxide are photodissociated by ultraviolet radiation, it is of fundamental importance that we should be able to understand and adequately estimate the effect of clouds on the radiation field and as a consequence the effect on tropospheric chemistry, both on a global and regional scale.

Methods

Within the framework of NPR-I, in 1990 IMAU started a study to determine this effect. The strategy of the study was based on a combination of radiometric measurements and radiative transfer modelling. To carry out the measurements, we developed a photo-electric instrument to measure actinic flux (Van der Hage et al., 1994). The actinic flux is defined as the radiative flux incident on a sphere with unit area. With this radiometric quantity one can calculate photodissociation rates

of molecules and also estimate the biological effects. Vertical profiles were taken and surface measurements were made within the framework of the international experimental campaign ASTEX (Vilà-Guerau de Arellano 1994). During this campaign detailed measurements were made of cloud properties (liquid water content, cloud-base height, cloud-top height, effective radius, etc.) by other research institutes. These observations constitute a complete data base for the validation of radiative transfer models and the development of parameterizations. In addition, actinic flux surface measurements were made in Antarctica (to study the effect of surface albedo) and in De Bilt in collaboration with KNMI (Van Weele et al. 1994). The latter experimental campaign include measurements of UV-A and UV-B irradiances and global radiation.

Results

The comparison of these vertical profiles measurements and surface measurements of actinic flux are in very good agreement with the model results calculated with the radiative transfer model based on the delta-Eddington approximation designed at IMAU, see Vilà-Guerau de Arellano et al. (1994). The measurements and model calculations revealed that the key parameters governing the effect of layered clouds on the UV radiation are: cloud optical depth and solar zenith angle. A parameterization based on the experimental and model results concerning the effect of layered clouds on the photodissociation rates is currently being implemented in the regional atmospheric chemistry model LOTOS at TNO (Van Weele et al., 1993).

Assessment

This project aims at the measurement of the influence of clouds on the profiles of the actinic flux. An instrument has been developed and the actinic flux has been measured during field campaigns. The expected enhancement of this flux at the cloud top and reduction below the cloud were reported. A quantitative comparison between observed data and radiative transfer calculations are in very good agreement. Much has been achieved in the project and results have been published in refereed journals. For the troposphere as a whole, the net effect of clouds on tropospheric chemistry, however, is expected to be small. Locally and temporary the production- and destruction rate of chemical species may be altered.

3. THE ROLE OF ATMOSPHERIC OZONE IN GLOBAL CHANGE

3.1 Introduction

Nearly all the earth's atmospheric ozone is found in the stratosphere (about 90%) and the remainder in the troposphere (10%). In the stratosphere ozone levels largely depend on competing (photo)chemical reactions. Ozone in the stratosphere is formed by photolysis of oxygen by short-wavelength solar radiation and destroyed by longer wavelength sunlight. Various trace constituents also react with ozone. Ozone formation and destruction processes are normally in dynamic equilibrium, however, when the concentration of constituents capable of destroying ozone increases, the balance is upset and a new equilibrium is reached which sustains less ozone. In the troposphere, next to transport of ozone-rich air from the stratosphere and destruction of ozone at the earth's surface, ozone is also being formed and destroyed by photochemical reactions in which volatile organic

compounds (mainly methane and nonmethane hydrocarbons), carbonmonoxide and nitogenoxides play a dominant role. Depending on the chemical regime (i.e. the NO_x mixing ratio) there may be a net production or net destruction of ozone. The combined amount of ozone in the stratosphere and troposphere, known as total column ozone, occupies on average 300 Dobson units (or milli-atmospheric centimeters, equivalent to 3 mm of ozone at standard temperature and pressure). The main region of ozone formation is found at heights around 25 km in tropical regions. The level at which the maximum concentration of ozone occurs is much lower nearer the poles than near the equator. For example, highest ozone concentrations are found at about 18 km at 75, N and S, and at 15 km over the Arctic.

The distribution of ozone around the globe is by no means uniform. Ozone at all latitudes other than around the equator shows a marked seasonal variation, with a maximum in spring and a minimum in autumn. The highest concentrations are found in the Arctic region in spring. The lowest concentrations occur at the equator, where there is little change of ozone with latitude or with season. Besides the regular seasonal variations, ozone values exhibit short-term, local variations of equal magnitude which can take place within a few days. These variations are closely associated with meteorological conditions in the upper atmosphere, particularly at higher latitudes. Finally the total ozone column also varies naturally from year to year at any particular location. The natural variability in ozone makes trends in total ozone column difficult to detect.

From the point of view of live on earth, the most important property of ozone is its ability to absorb UV radiation emitted by the sun. UV radiation is harmful to humans and ecosystems, and is classified according to wavelength UV-A (320-400 nm), UV-B (280-320 nm) and UV-C (< 280 nm). The subdivision of the UV waveband into A and B is not unequivocally. Sometimes the division between AV-B and UV-A is set at 315 nm, and the UV-A region is sometimes defined as 315-380 nm. In this document, unless specifically stated otherwise, the aforementioned divisions will be taken. Atmospheric oxygen (and a small fraction of ozone) block all UV-C radiation completely at higher levels in the atmosphere. The ozone layer also absorbs most, but not all, of the UV-B radiation. Ozone absorption of UV-A radiation can be neglected, which means that ozone depletion is of little consequence where UV-A is concerned.
The intensity of the UV-B radiation to which man and the ecosystem is being exposed depends on:

- Sun's angle
- Cloudiness
- Stratospheric ozone column density
- Tropospheric aerosol
- Ozone content in the troposphere and in the PBL
- Surface albedo
- NO_2- and SO_2 total column

The change in ozone column thickness with latitude and the difference in prevailing suns' angles combine to produce a very large gradient in natural solar UV from the tropics to high latitudes. At higher latitudes, at which e.g. The Netherlands is situated, also a large difference between winter and summer UV levels exists. As

shall be discussed later the period of maximum ozone depletion over the Northern Hemisphere, occurring in winter/spring, happens to coincide with the period when absolute UV irradiance values are at their lowest and therefore least harmful. Imposed upon the annual cycle in UV, are long term variations arising from trends in stratospheric and tropospheric ozone, in cloud cover and aerosols (which scatter and diminish UV) and upward trends in tropospheric pollution which absorbs UV.

Ozone absorption is important in both ultraviolet and infrared parts of the spectrum. The radiative forcing due to ozone depends on whether it is in the stratosphere or troposphere. The radiative forcing is greatest near the tropopause and so the ozone trends of most interest are those observed in the upper troposphere and lower stratosphere.
Measurements of atmospheric ozone over the last twenty years has shown a significant decrease of stratospheric ozone as depicted in Figure 3.1. In the northern Hemisphere the losses are most pronounced in winter and spring (6% per decade) and less pronounced in the other seasons (3% per decade).

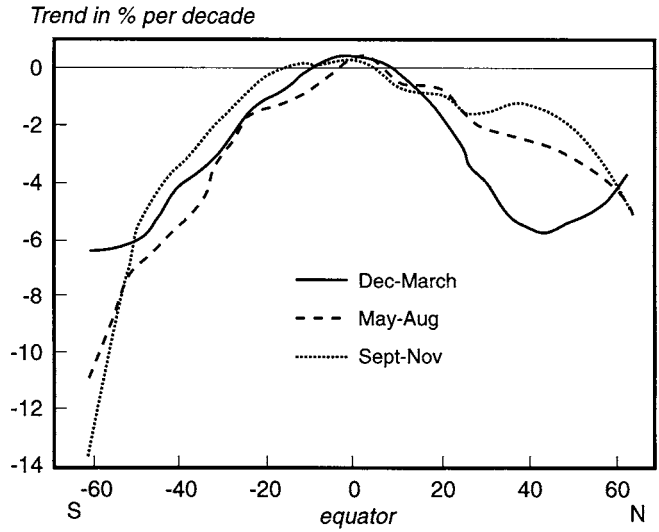

Figure 3.1
Ozone trends in % / decade in dependence of latitude and time of the year. Results are from TOMS-measurements taken in the period 1978-1991

Recently the trends have (temporarily) been increasing, with total ozone in 1992 and 1993 at exceptionally low levels world wide. Chemical and dynamical processes in the tropopause region have an important bearing both on total ozone, the vertical distribution of ozone and on the exchange of other trace gases. Some of the observed decreases in total ozone, especially at mid-latitudes, is simply caused by transfer of air masses containing markedly different amounts of ozone and are not the result of ongoing chemical destruction processes. A major fraction of the ozone

decrease, both long-term and in 1992/1993, has occurred in the lower stratosphere at altitudes starting almost at tropopause level up to 25 km. The reason for this behaviour is the occurrence of aerosols or PSC in this part of the atmosphere. The presence of PSC and aerosols can affect the chemical balance by providing surfaces on which chemical reactions eventually leading to ozone loss can proceed, an effect which is enhanced at lower temperatures. The anomalous behaviour of ozone in 1992/1993 has been attributed to the eruption of Mt Pinatubo in the Philippines in June 1991 which injected large amounts of gaseous SO_2 into the stratosphere which then chemically was transformed into sulphuric acid droplets i.e. aerosols.

The state of knowledge regarding ozone trends in the troposphere is not good as in the stratosphere. There are a limited number of ozonesonde stations with records suitable for long-term trend analysis and even at these sites data quality remains questionable. The stations are located mainly in the Northern Hemisphere. Over the last 20-30 years the largest change in free tropospheric ozone seems to have occurred over Europe with an increase of about 50% since the end of the 1960s. The change over North America seems to be less. i.e. about 10-15%. The change has become less pronounced at the second halve of the 1980s, from whereon no change has been observed over North America and also over Europe the observed trends were smaller than before; actually levels of tropospheric ozone over North America and Europe may now be on the decline. Ground-based measurements both in the boundary layer and at mountain sites have revealed a significant rise in tropospheric ozone since pre-industrial times both in Northern and Southern Hemispheric sites (Figure 3.2).

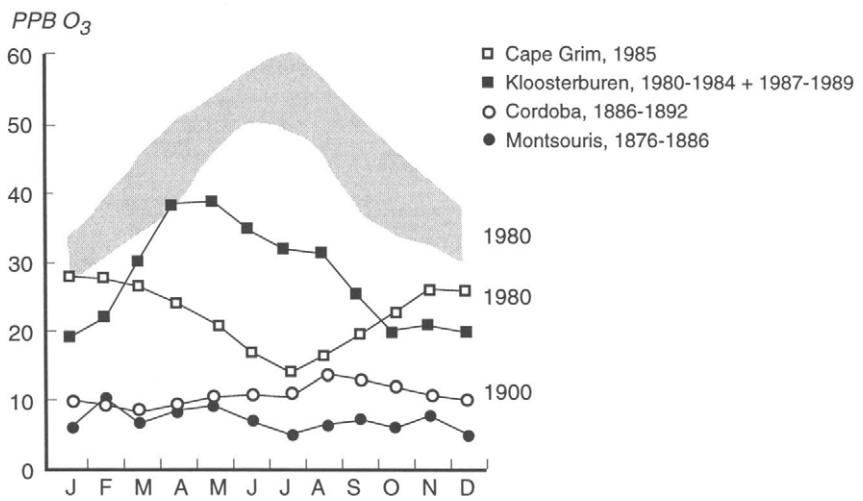

Figure 3.2
Ozone trends in the free troposphere. Also depicted are ozone levels over continental mid-western Europe

Observations conducted in recent years have confirmed that tropospheric ozone has increased at many stations in the Northern Hemisphere. In the Southern Hemisphere tropospheric ozone seems to have remained constant or may have even decreased (Figure 3.3). The latter tendency now also seems to be the case at stations in the Northern Hemisphere.

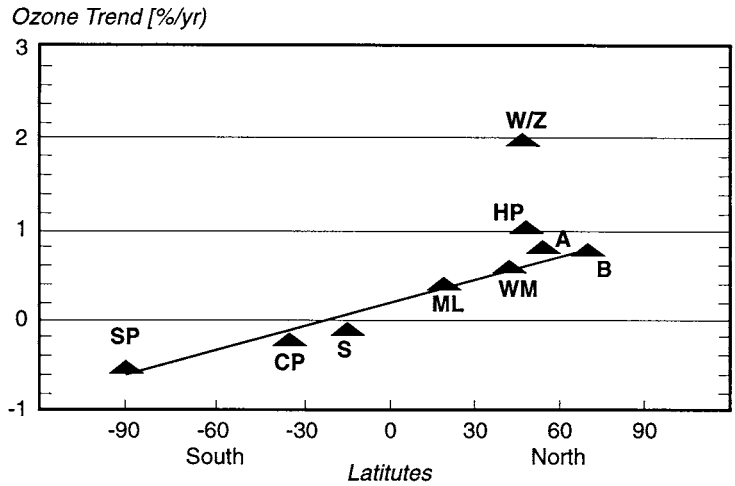

Figure 3.3
Trends in tropospheric ozone observed at different latitudes. Only coastal and high-altitude observatories were included. South Pole 90°S, 2800 m a.s.l., start 1975; CP: Cape Point, 34°S, 1982; S. Samoa, 14°S, 1975; ML: Mauna Loa, 20°N, 3400 m, 1973; WM: Whiteface Mountain, 43°N, 1600 m, 1973 Z: Zugspitze, 47°, 3000 m, 1978; W: Wank, 47°N, 1800 m, 1978; HP: Hohenpeissenberg, 48°N, 1000 m, 1971; A. Arkona, 53°N, 1956; B: Barrow, 70°N, 1973. The solid line is a linear fit through the data, excluding the sites in southern Germany (HP, W and Z). Source: Volz-Thomas (1993)

The role of atmospheric chemistry in the steady state chemical composition of the atmosphere is of great importance in order to assess the associated radiative forcing on climate. The atmospheric abundance of a component is governed by its rate of production and removal. A number of atmospheric feedback mechanisms are known which have the potential to change the atmospheric removal rate, principally through perturbation of the UV radiation field and most notably the global hydroxyl field.
Even an chemical species like CO_2, which is regarded as being "inert" influences atmospheric chemical processes. CO_2 tends to cool the stratosphere. This has an effect on rate constants of chemical reactions, in such a way that stratospheric ozone levels may increase. This will lead to a negative feedback of temperature perturbations in the stratosphere. On the other hand lower stratospheric temperatures potentially favour the formation of PSC. This may worsen lower stratospheric ozone depletion and allowing a deeper penetration of UV radiation into lower altitudes.

For a reactive compound such as CH_4 the relations are far more complex. An increase in CH_4 emissions will lead to a tropospheric ozone increase, notably in northern midlatitudes during summer and in the tropical upper troposphere. The tropospheric OH abundance on the other hand will decrease, leading to a longer residence time of chemically and/or radiatively active trace gases such as CH_4 itself, CO, HCFC's, etc. In the stratosphere, an increase in water vapour abundance and significant perturbations of ozone and chlorine species can be expected. The reason is that H_2O is the source of odd hydrogen (HO_x), which accounts for ozone destruction, notably below 30 km and above 50 km. At other altitudes NO_x is the domant species where ozone loss is concerned. In the presence of HO_x, more NO_x is converted in less reactive HNO_3 and HO_2NO_2; consequently, an ozone increase can be expected at this altitude range. Finally CH_4 reacts efficiently with chlorine atoms to form the less reactive reservoir species HCl, counteracting ozone destruction by CFC's.
An important feedback mechanism that affects the lifetimes of many atmospheric constituents is the change of UV radiation reaching the troposphere due to changes in the stratospheric ozone column density. Reduction in stratospheric ozone leads to enhanced penetration of UV radiation into the troposphere. This in turn will yield increased production of O(1D) and OH and enhance reactions that produce or destroy tropospheric ozone. Whether this results in a net increase or decrease of tropospheric ozone depends on the NO_x mixing ratio.
Chemical and physical processes occurring in clouds and aerosols play a major role in determining the chemical composition and the radiative properties of the atmosphere. Aerosols also affect the earth's heat balance directly by backscattering of shortwave radiation and, indirectly, by their influence on the reflectivity of clouds.
Clouds are considered to be an important removal pathway for some atmospheric trace constituents, and the lifetime of these compounds are determined to a large extend by the frequency of encounters with precipitating clouds. For example in-cloud oxidation of SO_2 accounts for about 50% of the total SO_2 sink on a global scale. In some areas, direct interception of clouds or fogs with the surface of the earth is an important removal pathway.
Moreover, updraughts within clouds are important means of vertical transport of atmospheric constituents, particularly between the PBL and the free troposphere. In strong convective systems, of the cumulus nimbus type, trace constituents may even be transported into the lower stratosphere.

This subtheme comprises 4 projects.

3.2 Dutch participation in the international network for the detection of stratospheric change (NDSC)

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Introduction

The Network for Detection of Stratospheric Change is a set of 5 high-quality, remote sounding research stations for observing and understanding the physical and chemical state of the stratosphere. These stations, where ozone and key ozone-related parameters are measured, are complemented by both secondary stations and satellite measurements. Currently, over 65 scientists from 15 countries are involved with NDSC. The NDSC is a major component of the upper atmosphere research effort and has been endorsed by national and international scientific agencies, including the International Ozone Commission, The United Nations Environmental Programme (UNEP), and the World Meteorological Organisation (WMO).
The goals of NDSC are:

- To make observations through which changes in the physical and chemical state of the stratosphere can be determined and understood. In particular to make the earliest possible identification of changes in the ozone vertical distribution and to discern the cause of these changes.
- To provide an independent calibration of satellite sensors of the atmosphere.
- To obtain data that can be used to test and improve multidimensional stratospheric chemical models, thereby enhancing confidence in the predictive and assessment capabilities of these models.

Project description

The NRP project described in this abstract comprises the development of a stratospheric ozone lidar, one of the primary NDSC research instruments, and implementation of this instrument at one of the 5 NDSC primary sites, the station of Lauder in New Zealand. This groundbased instrument is capable of obtaining a vertical concentration distribution in the altitude range of 15 to 45 kilometers. Vertical resolution is 1 kilometer at 20 kilometers altitude, increasing to 5 kilometers at 45 kilometers altitude. Measurement error is typically about 1% at 20 km, increasing to 10-20% at 45 km. These figures hold for a single vertical profile obtained in a measurement time of about 1 hour. Errors are of a statistical nature, and will decrease when a number of profiles is averaged in e.g. a monthly or yearly mean profile. As of this writing, June '94, the development and preliminary validation are nearly completed, and the system will be shipped to New Zealand in August-September. It will be implemented in the network before the project expires at the end of the year. A typical profile obtained by the lidar is given in Figure 3.4. A balloon profile taken in Uccle, Belgium is also shown for intercomparison.

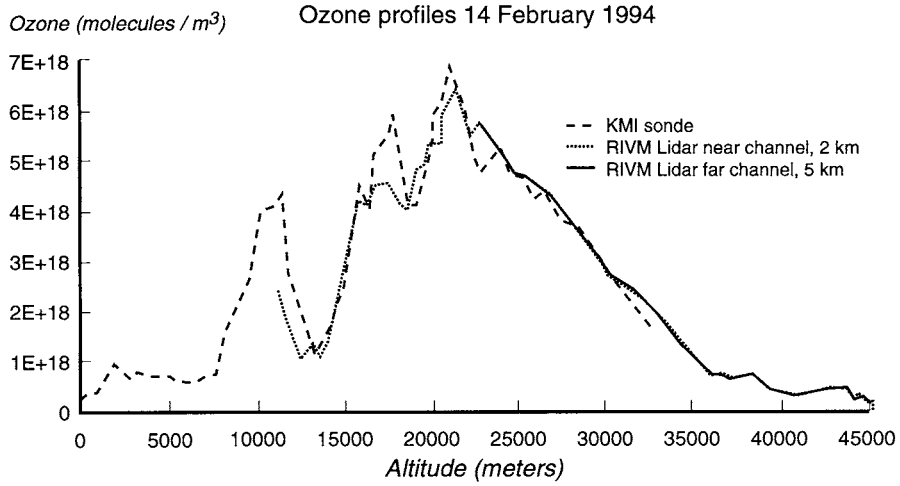

Figure 3.4
Ozone profiles measured at February 14, 1994 with lidar and sonde. Lidar data were taken in Bilthoven, the Netherlands, at 24:00 MET. Sonde data were taken in Uccle, Belgium at 12:00 MET (de Muer and de Backer, private communication). Uccle and Bilthoven are separated by approximately 160 km

International collaboration
This project has provided us an excellent opportunity to enter the international research on stratospheric ozone and related species, a field virtually non-existent in the Netherlands only a few years ago. During the development of the instrument we have established close links with researchers and institutes that have lidarprograms in this field: NASA and NOAA in the United States, NIES and MRI in Japan, York University in Canada, CNRS in France, to mention some. In the framework of the NDSC network, international relations are to numerous to indicate all individually, and range from universities and national environmental research institutes to political bodies like WMO and UNEP. A special set of relationships is generated by the international team of principal investigators with instruments at the Lauder station, with e.g. NIWA from New Zealand, and again different researchers from the US, Australia, Japan and Italy.

Project results and spin-off
By the end of this year, the project will have met the goals we set out for five years ago:

- A state of the art measuring lidar instrument for stratospheric ozone has been developed successfully.
- We have succeeded in obtaining a strong position for this instrument in a (the) most prominent international stratospheric monitoring network. The system will be part of a multicomponent, multiyear daily monitoring scheme.

- We will contribute to the NDSC database, cohosted by NOAA, NILU and Rutherford Appleton Laboratory. We will take part in the establishment of a long term dataset on the status of the stratosphere. As a contributor, we will have early access to all NDSC data worldwide.
- We have established a firm position and good contacts in the international research community in this field.

The future
As the NRP project draws to an end, the work with the developed lidar will enter a new phase. A scientific collaboration has been set between RIVM and the Free University of Amsterdam (VU) and a Dutch PhD student will work in New Zealand on research with this instrument. A rigorous intercomparison and quality assurance program will be conducted using groundbased lidar (NASA), balloon sondes (NIWA) and microwave instruments (NOAA). A routine monitoring scheme will be implemented, and a database will be generated for climatological purposes and trend analyses. The system will take part in the validation of the performance of the GOME instrument on ESA'S ERS-2 satellite to be launched early 1995. Many other scientific uses of the system are foreseen.

Assessment
This project is technologically and scientifically of high quality. A state-of-the-art measuring lidar instrument for stratosphere ozone has successfully been developed. International cooperation via NDSC is ensured. The goals of the project will certainly be met. In order to be a complete success funds for prolonged measurements (10-20 years) should become available.

3.3 Spectral UV radiation measurements and correlation with atmospheric parameters

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Introduction
The goal of the research of the KNMI in the NPR-I project was to develop a UV-monitoring network, to study the relation between UV and meteorological parameters like ozone and clouds, and to analyse trends in the UV-climatology in the Netherlands. For this purpose UV-measuring instruments have been developed.
Theoretical research was performed using a spectral radiative transfer code coupled to an atmosphere model. Both the UV-measurements and the theoretical methods are discussed, and some results are shown.

UV-measurements
The UV-measurements consist of spectral and narrow band measurements. Both types of measurements will be discussed.

Spectral UV-measurements. Are required to determine the relation between ground level UV and various kinds of atmospheric constituents. For example, O_3 and SO_2

exhibit similar wavelength dependent absorption structures in the UVB, although the optical thickness for both species is quite different. Because the absorption structures are roughly 2 nm wide, spectral measurements should be performed with a wavelength step of maximal 0.5 nm with a resolution of 0.1 nm or better. Extinction by aerosol is assumed to be continuous but different in strength in the UVA and the UVB. To distinguish extinction due O_3 and aerosol, measurements should start below 295 nm and reach far into the UVA.

For such spectral measurements a diode array detector coupled to a single monochromator was employed. This instrument took part in the EC-STEP intercomparison of UV measuring instruments in Garmisch-Partenkirchen in July 1993.
Compared to the double monochromators equipped with photomultipliers, the diode array instrument behaved as good as could be expected. The limited dynamical range of approximately 10^3 (cf. a photomultiplier having a dynamical range of 10^6) and the poor straylight rejection make it possible to perform measurements between 300 and 420 nm. For measurements below 300 nm the straylight signal exceeds the instrumental noise.

In Figure 3.5 measurement of the spectral UV taken in Garmisch-Partenkirchen are shown. The curve denoted by AI was recorded with the double monochromator of the group from Austria, Innsbruck. This instrument was considered as 'the standard' together with 2 other instruments. It is seen that the UV spectrum obtained with the KNMI diode array instrument deviates at most approximately 10% from the AI spectrum. Using a better UV filter or an alternative method to substract straylight, this may be improved to a deviation smaller than 5%. This will be tested in an intercomparison to be held in Bilthoven in August 1994, in which KNMI, RIVM and the AI group will take part.

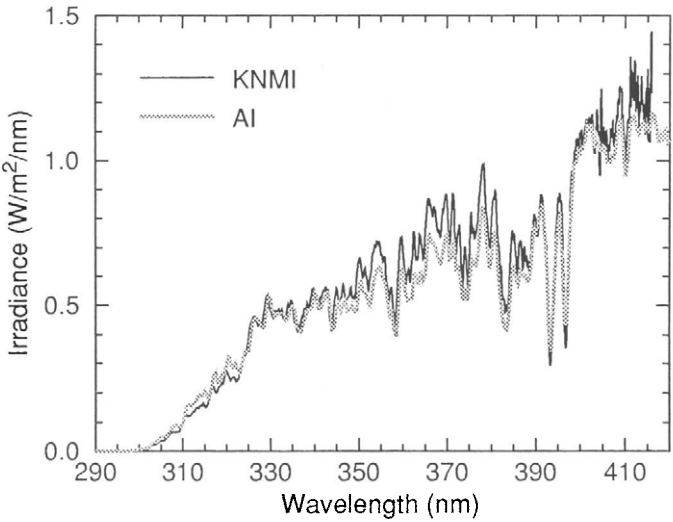

Figure 3.5
UV spectra measured with the KNMI diode array instrument and the AI double monochromator (Garmisch-Partenkirchen, July 24, 1993, 12:48 UT)

In December 1993, Brewer #100 arrived at the KNMI. This is a standard instrument for continuous O_3-column measurements, and since this instrument is the version equipped with a double monochromator, it is particularly suitable for UVB-measurements as well (a similar instrument also took part in the Garmisch-Partenkirchen intercomparison and performed so well that is was considered as one of the three standard instruments. Since January 1994 this instrument is continuously measuring the ozone column in The Bilt. In Figure 3.6 Brewer ozone measurements for 1994 for The Bilt are shown together with TOMS measurements for The Bilt averaged over the period 1980-1992. In between the ozone measurements the spectral UV-irradiance is measured from 286.5 to 365 nm with a 0.5 nm step. This instrument thus provides almost simultaneous measurements of the O_3-column and the UV-irradiance, so that the relation between these two quantities can be ideally correlated. The Brewer #100 is our primary ozone and UV monitoring instrument. It is intended to produce semi-annual KNMI-reports with combined UV and ozone measurements.

In Figure 3.7 measurements of the UV-irradiances of February 19 and 20, taken at 12:05 UT on both days, are shown. There was a large difference in the ozone column on these days: 386 and 431 DU for February 19 and 20, respectively. Also the atmospheric aerosol load on February 20 was much greater than on the 19th. The difference in the UV-irradiances for wavelengths larger than approximately 330 nm is due to the difference in aerosol, whereas for wavelengths below 330 nm it is the combined effect of differences is ozone and aerosol.

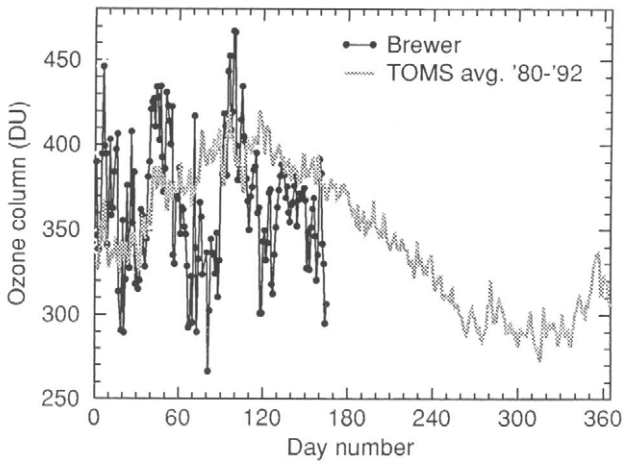

Figure 3.6
Measurements of the ozone column (in Dobson Units) made in The Bilt with Brewer #100 compared with TOMS satellite measurements for The Bilt averaged over the period 1980-1992

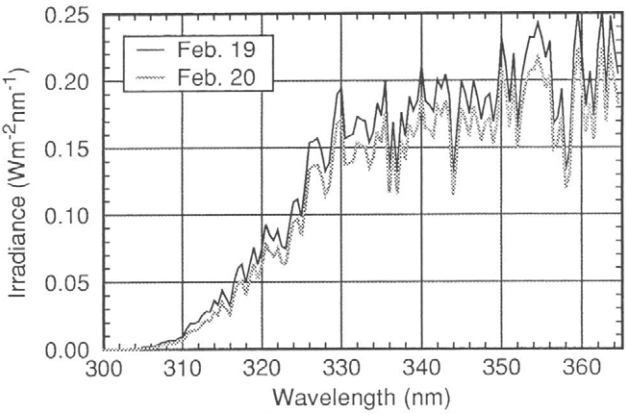

Figure 3.7
Measurements of the UV irradiance for February 19 and 20, 1994, 12:05 UT. The ozone columns were 386 DU and 431 DU for February 19 and 20, respectively, and on February 20 there was much more aerosol in the boundary layer

Narrow band UV instruments. Spectral UV measuring instruments are difficult to operate and expensive. To set up a network of UV instruments in The Netherlands more simple instruments are needed. Therefore narrow band instruments were developed aside the spectral UV instrument. Specifications and requirements for the instruments were formulated by the science department of KNMI, and Kipp & Zonen (Delft, The Netherlands) constructed the prototypes. After testing the instruments extensively for a period of 3 years they will be installed in The Bilt in the middle of 1994 as regular UV-monitoring instruments.

Two types of measuring devices have been chosen: irradiance and direct solar UV meters, one in the UVB and one in the UVA wavelength region. The irradiance meters record the vertical UV-flux, similar to the standard pyranometer. The direct UV meter is mounted on a solar tracker and detects the UV-radiation coming from the direction of the Sun. From a combination of the vertical flux and the direct measurements, the ratio between the amount of scattered and directly transmitted UV is determined. This ratio typically depends on the amount of aerosol in the atmosphere in the UVA, and again in the UVB absorption by ozone, especially for the direct UVB measurements, is important. When these UVB measurements are combined with the ozone measurements of the Brewer, effects due to ozone can be eliminated. This way it will be possible to really distinguish absorption by ozone and scattering by aerosol in the UVB.

The sensors basically exist of a UV-sensitive photodiode, a UV-interference filter, temperature stabilization, and some electronics. The filters can be chosen freely, and for the UVA we use a filter with a central wavelength of 367 nm and a full width half maximum (FWHM) of 10 nm. In the UVB a narrower filter is needed to avoid errors in the measurements because of the steepness of the UV spectrum in this wavelength region. At his moment the UVB instruments contain an

interference filter with a central wavelength of 306 nm and a FWHM of 4 nm. However, Kipp & Zonen recently found filters with the same central wavelength, but with a FWHM of 2 nm. These filters will be installed and tested as soon as possible.

There are several ways of analyzing the measurements of the narrow band instruments. One way is to determine the ratio between the direct and the diffuse (= scattered) UV-radiation in the UVA and UVB. Moreover, combining the data from the narrow band instruments with the spectral UV measurements and the ozone measurements can provide additional information on the aerosol contents of the atmosphere. Combining all measurements also provides the possibility to check the calibration consistency of the instruments. Another simple application of the direct and irradiance measurements is that they immediately show whether or not it was a cloudless day. However, due to lack of time and man power, analysis of the data has to be postponed to a later time.

UV radiative transfer and atmospheric modelling

For UV radiative transfer calculations we use the Doubling/Adding method KNMI (DAK). This is an 'exact' multiple scattering model, which at the moment is coupled to an atmosphere model. In the model approximately 32 layers are used for atmospheric gases for Rayleigh scattering (0 to 100 km altitude). Up to now aerosol optical properties and profiles have been used from the LOWTRAN model atmosphere because better data for The Netherlands is not available at this time. Profiles and columns of the UV-absorbing gases ozone and NO_2 are already taken into account in the model, and gases such as SO_2 and O_2 will be added in the future.

As an example of a comparison of a measurement and calculations, Figure 3.8 shows a measurement of the UV irradiance recorded by the AI-group during the Garmisch Partenkirchen intercomparison (July 1994), together with 2 computed

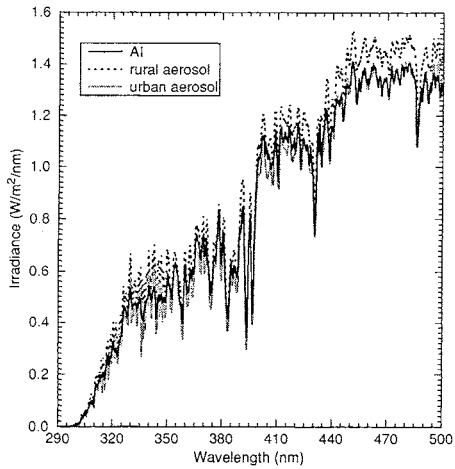

Figure 3.8
Measurements and calculations of the UV irradiance for Garmisch Partenkirchen, July 24, 1994, 12:48 UT. The ozone column was 285 DU and in the calculations only the boundary layer aerosol was varied

curves: one for an urban and one for an rural boundary layer aerosol. From comparing such model calculations with measurements we learned that especially variations in boundary layer aerosol can have effects on the UVB irradiance similar in magnitude to those due to the daily variation in the ozone column.

KNMI UV-calibration laboratory

It is a well known fact in the UV-measuring world that calibration of the instruments is a difficult task and requires special equipment. Because the KNMI has planned to continue the UV-research, and calibration is so important, an investment has been made by the institute to realize a high quality UV calibration laboratory.
The design of the lab is flexible so that several types of UV instruments can be calibrated. It measures 5x6 m, is divided into a lamp room and an instrument room (both separately airconditioned), and will be completely painted with a special absorbing black paint. Also a special high accuracy lamp power supply together with calibration lamps will be installed, and the calibrations will be performed and registered by a computer. According to the plans this facility should also become available for calibrations for non-KNMI work.

Assessment

During NPR-I facilities of a technologically high level have been created to monitor ground level UV in The Bilt in various ways, producing a fairly complete data set. At the end of NPR-I all measuring equipment will be beyond the experimental phase and become operational. Also facilities for proper UV-calibrations and experiments will then be available.

The KNMI radiative transfer code (DAK) has been adapted for use in the UV-region and various parameters such as profiles and columns of O_3, NO_2, aerosols and aerosol optical properties, that affect the UV transfer in the atmosphere have been investigated. However, the model needs improvement, and also a better characterization of the atmosphere is needed to compare local measurements with computed UV-spectra. This work is still in an initial stage.

Monitoring of UV irradiances and ozone, combining measurements with computations, etc., is long term work and requires a lot of time in the near future. The main result of NPR-I thus can be summarized by stating that the required measuring facilities have been realized, and now the phase of measuring and data analysis has arrived.
International cooperation is an important aspect. Cooperation on a national level with RIVM (see next project) should be strengthened. With respect to radiative transfer modelling in general, it must be recommended that groups in The Netherlands who use and/or develop these models (IMAU, KNMI, RIVM) should closely cooperate.

3.4 Determination of the UVB climate in The Netherlands: high resolution spectral measurements, monitoring and modelling from the perspective of risk analysis

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Introduction

Increased levels of biologically effective UV could lead to a variety of harmful effects for man and the environment, among which: skin cancer, impairment of the immune system, reduced biomass production by phytoplankton, and changes in aquatic and terrestrial ecosystems and food chains (UNEP 1991, Gezondheidsraad 1993). Furthermore tropospheric photochemistry could be influenced by changes in UV-irradiances. Therefore knowledge of the UV-climate and changes caused by human activities is highly relevant.

Risk assessment

Research at RIVM is focussed on integrated risk assessment of environmental changes. An integrated source risk model was developed for the effects of ozone depletion, the UV-chainmodel, which was applied for the evaluation of skin cancer risks in relation to various halocarbon production scenarios (Slaper et al 1992, RIVM 1993). Skin cancer is already one of the most common cancers among the Caucasian population, with 15-20 thousand cases each year in The Netherlands (around 1200 cases per million year). The model predicts an increased level of yearly effective UV doses in The Netherlands due to decreases in ozone. Around the year 2000 the increase in yearly effective UV at ground level is estimated to amount to approximately 15% (Slaper et al 1992). After the year 2000 a slow recovery could occur if all countries in the world fully comply with the Copenhagen Amendments of the Montreal protocol for a reduction in production and emission of ozone depleting substances. The consequences of the increased levels of UV can, at present only be estimated quantitatively for skin cancer. Elevated risklevels are expected to peak approximately 40 years after the peak exposures, thus reflecting the delay between exposure and the occurrence of tumours. The additional number of cases of skin cancer in The Netherlands associated with the increased UV-levels amount to around 200 new cases per million per year for the Copenhagen scenario (Slaper et al 1994, Slaper 1994). In terms of increased mortality an additional 2-3 per million per year is estimated for the Copenhagen scenario (RIVM 1993). An excess death risk of one per million per year is often referred to as the Maximum Permissible risk level for chemical substances and (ionizing) radiation sources by policymakers in The Netherlands. Such a risk level is associated with an increase in surface effective UV of 5% (3-6%, depending on the different estimates for the melanoma risks). It should be noted that it is not a priori clear that skin cancer is the primary adverse effect. Nevertheless, changes in effective UV-exposure of no more than 5% are relevant from the perspective of skin cancer risks.

Relevance and objectives of UV-measurements

Integrated models are by definition simplifications and extrapolations, and therefore need to be verified and updated by means of monitoring and detailed analysis of UV-transfer in relation to atmospheric changes. When aiming at risk

assessments for the UV-related effects of man made changes in atmospheric composition it is highly relevant to investigate the biologically relevant UV irradiances and the relation between the UV irradiance and atmospheric parameters. Ozone measurements and monitoring has been established at many sites and by satellites, however, a worldwide network of spectral UV-monitoring is lacking (UNEP, 1991). This lack of UV-monitoring data, especially the lack of spectral data, is generally recognized as a gap in the present scientific knowledge. During the past five years several (inter)national initiatives have emerged to improve the situation. RIVM and KNMI participate in a project from the EC STEP and Environment program. That project focuses on international standardisation of calibrations and intercomparisons of measurement systems, since at present no standardized measurement technique is established. The UV-monitoring project at RIVM, which is supported by the National Research Program, contributes to the specification of systems for future UV-monitoring networks and provides high quality spectral monitoring data. The main objectives of the RIVM-project are:

- Design and building of a spectral monitoring system capable of measuring the biologically and photochemically relevant solar UV at groundlevel in the wavelength range: 295-450 nm.
- High resolution spectral measurement of present UV-irradiances in The Netherlands.
- Validation of UV-transfermodels and determination of primary important atmospheric parameters.

Measurement system

The RIVM UV-monitoring system is designed to obtain data that could be used (both now and in the future) for effect evaluations and model validation. Specifications of the system are directly derived from these goals in a definition study (van Sonderen, et al, 1991). In order to be able to evaluate a variety of effects, and in view of the strong wavelength dependence of biological effectiveness and atmospheric UV-absorption, knowledge of the spectral distribution of the UV is required. The biological effectiveness of sunlight is primarily determined by the UVB. The solar irradiance in the UVB range changes over more than 6 orders of magnitude due to the strong wavelength dependence of the ozone absorption. This puts high demands on measurement systems with respect to dynamic range, linearity, stray light rejection and spectral resolution. From the monitoring perspective long term stability and reliability are important, and in order to reduce effects of changing atmospheric conditions during a recording of the spectrum the duration of a measurement must be minimized.

It was concluded that the optimal spectral system consists of two complementary instruments:

- A scanning spectroradiometer with a double monochromator and photon counting detection for the UVB region of the spectrum.
- A spectrograph with photodiode array detection for the longer wavelengths in the UVB and the UVA.

In addition to these two spectral instruments two broad band detectors were added: a pyranometer that records integrated irradiances from 300-3000 nm, and a Roberson Berger biometer which records the erythemally (sunburn) weighted UV

dose. These integrated measurements are used to determine changes during a scan and to fill in gaps in the monitoring data set.

Measurement protocol
The monitoring system is operational since april 1993. The first year is used to improve and establish the system and operational procedures. The RIVM monitoring system participated in a European intercomparison in July 1993 in Garmisch Partenkirchen. Daily sequences of measurements are taken since October 1993. The measurements are collected fully automatic each twelve minutes during day time (Reinen et al, 1993).
The spectral structures of the measurements with the RIVM-monitoring system reproduce the Fraunhofer structures found in the extraterrestrial spectrum (see Figure 3.9a). A technique was developed to use the Fraunhofer structures for an internal wavelength calibration. This technique is applied to all measured spectra and serves as a validation criterium. It was found that the stability of the wavelength calibration is generally within 0.1 nm. For irradiance calibration NIST-calibrated 1000 W lamps are used.

Results and data analysis
Evaluation of effects requires the calculation of effective UV-irradiances. Effective irradiances are obtained by multiplication of spectral irradiances with the proper action spectra, and a subsequent integration over the effective wavelength region. Action spectra are sets of weighting factors reflecting the effectivity of various wavelengths. Many action spectra have a shape similar to the one shown in Figure 3.9b. It should be realized, however, that effective doses/irradiances are strongly dependent on the exact shape of the action spectra, and can therefore be different for different effects.

Figure 3.10 shows the diurnal variation of effective UV (weighted with the STESLA-action spectrum (Slaper 1987)) for two days in October. October 29 (1993) was a cloudless day and the measurements compare very well with modelcalculations for clear day situations, applying ozone values as measured by KMI in Uccle for that day. October 21 (1993) had some variation in cloud cover, as is clearly shown by the reduction in UV during parts of the day.

The spectral measurements are used to study the influence of various atmospheric parameters. Factors of primary importance for the effective UV-irradiance are: solar height, ozone, cloud cover and aerosol content. It was found that on average cloud cover and aerosol load reduced clear sky effective UV irradiances by 20-30%.

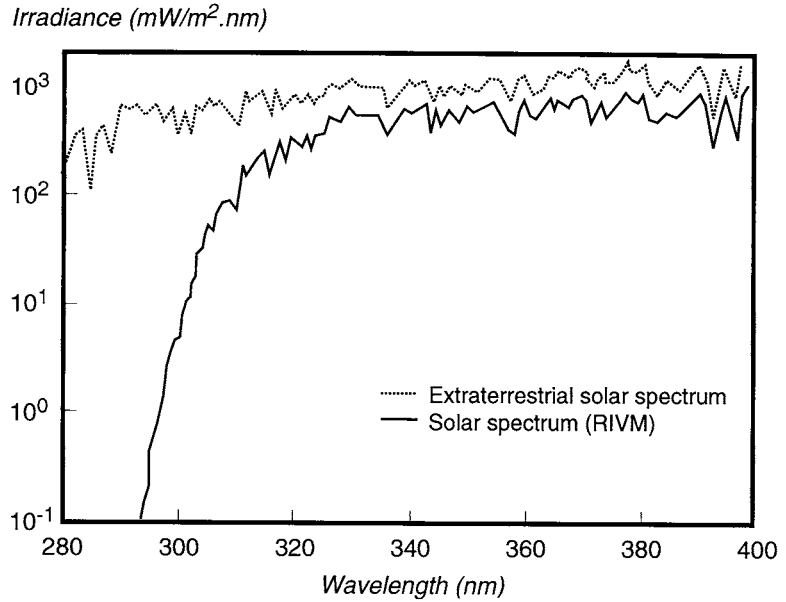

Figure 3.9a
Extraterrestrial and surface solar UV-spectrum, and effective UV

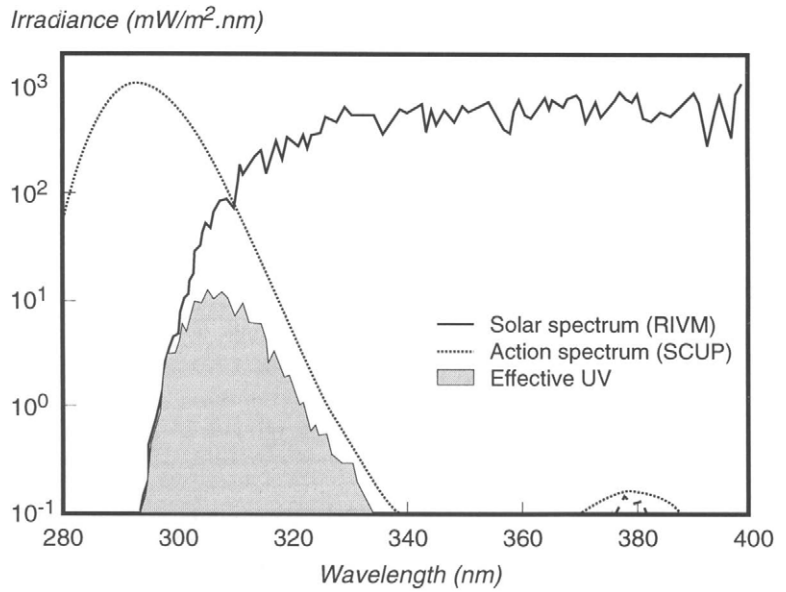

Figure 3.9b
Sample solar UV-spectrum and effective UV

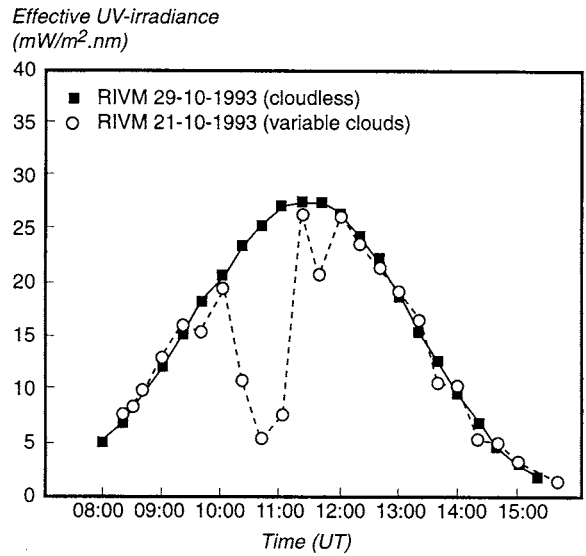

Figure 3.10
Diurnal variation in effective UV

Clouds and aerosols reduce both effective UV and visible light. Therefore, we expected a correlation between a cloud/aerosol induced reduction of ground level irradiances of the pyranometer and spectral UV-measurements. This relationship could be used to add an empirical correction to model calculations for cloudless conditions, in order to estimate the effective UV. The first analysis shows some promising results (Reinen et al,, 1994, Bordewijk et al, 1994). Further analysis is needed to substantiate these findings. The observed relationships provide an opportunity to estimate effective UV-irradiances on the basis of model calculations in combination with ozone values and pyranometer measurements. At present uncertainties in the method are in the order of 10-20%. Figure 3.11 shows a comparison between daily sums of effective UV doses obtained from measurements, as compared to the modelled effective UV, applying the empirical correction for cloud and aerosol reduction to a clear sky model calculation (De Leeuw, 1988). Daily sums were based on at least 10 spectral measurements, and the ozone values obtained from KMI in Uccle (Belgium) were applied in the clear sky model calculations. Applying the method UV-doses could be estimated in periods and places where UV-measurements are lacking. It should be noted that further long term measurements are needed to establish the findings. Further analysis is also aimed at revealing similar relationships between spectral measurements and a broad band Robertson Berger biometer.
Such methods could contribute to a reduction in the number and complexity of measurement systems required in a UV-monitoring network. Furthermore the methods can be applied to estimate UV-irradiances/doses over time periods where detailed UV-monitoring is lacking. High quality and resolution spectral monitoring remains necessary at a number of sites in order to establish the longterm stability of the empirical relationships and serve as reference instruments.

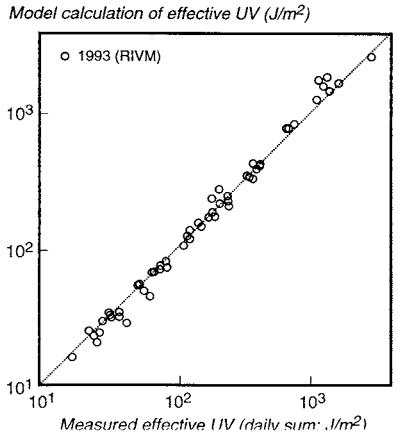

Figure 3.11
Daily effective UV-sums: model versus measurements

The method described above is applied to estimate the total yearround effective UV received in the past year in The Netherlands. Figure 3.12 shows monthly totals of effective UV-doses at ground level in Bilthoven for the year 1993. The open bars on top show the reduction in effective UV by clouds and aerosols. Applying the method for the year 1991 to 1993, we see that 1992 was estimated to have 14% higher doses than 1991 and 1993 11% higher doses (Figure 3.13). The main reason for the increases in 1992 and 1993 are differences in the thickness of the ozone layer, explaining a 9% increase in 1992, and a 15% increase in 1993. Compared to 1991 the reduction by clouds was estimated to be smaller in 1992 and larger in 1993. Thus the real UV-burden was higher in 1992 than in 1993, although based upon ozone measurements higher doses were expected in 1993. A preliminary evaluation of the first months of 1994 showed lower doses than the calculated doses in the same periods in 1993 and 1992. Both ozone levels and cloud reduction are responsible for the lower irradiances.

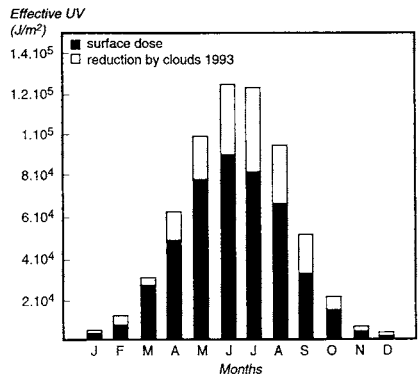

Figure 3.12
Monthly totals of effective UV in Bilthoven

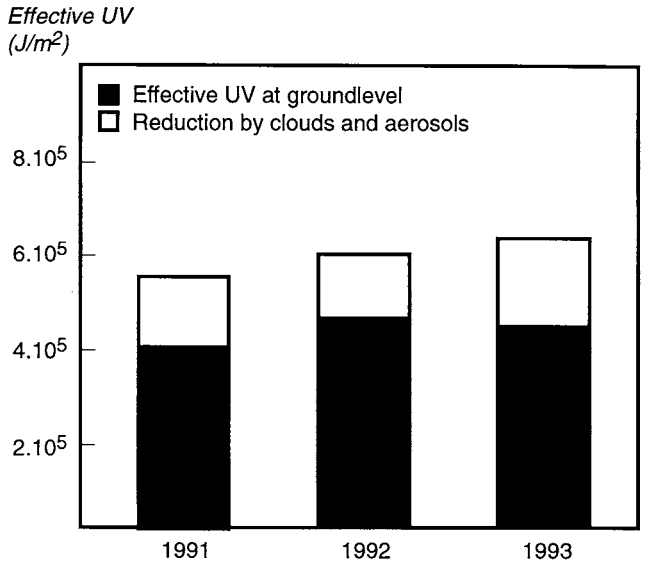

Figure 3.13
Yearly total effective UV

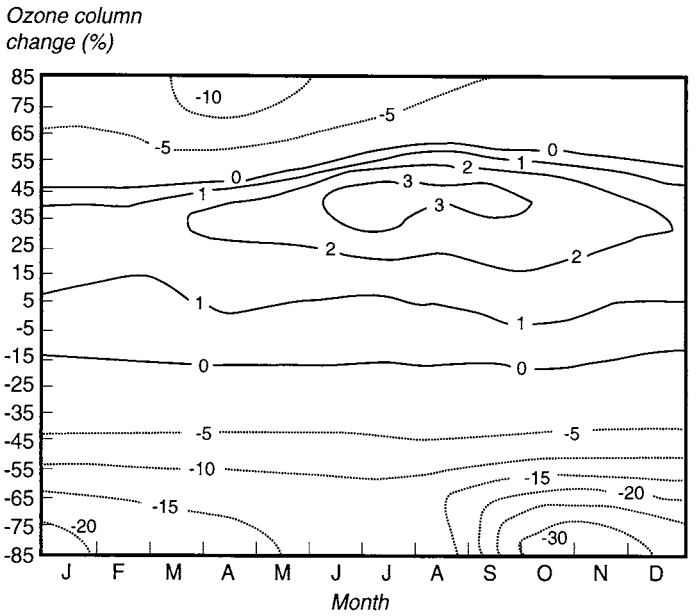

Figure 3.14
Ozone column change (%). Preindustrial / present. (Hauglustaine et al., 1994)

Assessment
A spectral monitoring system was designed, built and applied to obtain information on the effective UV-irradiances in The Netherlands. An analysis of spectral measurements has shown an empirical relationship between the reduction of UV by clouds and aerosols and a reduction of global radiation as measured with a pyranometer. This relationship is applied to estimate the UV-burden in the previous years. Compared to 1991 the effective UV dose received at ground level was 14% higher in 1992 and 11% higher in 1993. The increase is caused by decreased ozone levels, and is also influenced by variations in cloud cover and aerosol loads. A preliminary evaluation of data from the first months in 1994 shows that effective UV doses are lower than in the same period for the previous two years. The goals of the project are met. From a technological and scientific point of view the results are of high quality. International cooperation is envisioned. Interaction with Project No. 85/20/88 should be strengthened. The role of aerosols and tropospheric pollution in the UVB radiation transfer model should be dealt with in more detail.

Note by the subtheme coordinator R. Guicherit
Calculated, measured and future projections of increased UVB levels should be regarded in perspective. A maximum increase in yearly effective UV of 15% at groundlevel around 2,000 is comparable with moving about 400 km nearer to the equator (e.g. Groningen - Maastricht) or moving to an altitude of 500 m compared to sealevel. The consequences of this, in terms of effects and risks are beyond the scope of this part of the national research programme and shall be dealt with elsewhere. Of great importance in my view are effects of increased UV on atmospheric chemistry notably at middle and upper tropospheric levels, leading to changes in chemical reactivity, lifetimes of pollutant etc. Furthermore local and regional scale tropospheric pollution and cloudcover also affect UV levels and their trends. Although tropospheric O_3 accounts only for about one tenth of the total ozone column, it is a more effective absorber of UV radiation than stratospheric ozone (on a molecule by molecule basis) under high sun conditions (see e.g. Brühl and Crutzen, 1989). Model calculations (see e.g. Hauglustaine et al., 1994) have shown, that despite stratospheric O_3 loss, due to tropospheric O_3 increase, the ozone column density may have increased since the industrial revolution over a large part of the globe, i.e. from 15°S to 55°N (Figure 3.14). This suggests that changes in tropospheric ozone alone (i.e. at constant stratospheric ozone, aerosols and cloud cover) must have had considerably reduced UV radiation over large areas of the globe. Other factors such as changes in cloud cover, cloud optical properties, and troposphere aerosol load may also have affected trends in UV radiation. Although there are indications that cloudiness over both hemispheres are on the increase since the turn of the century and emissions of aerosols and precursors of aerosols have dramatically changed since the turn of the century and may either increase or decrease in the near future, there are at the present insufficient data to assess whether these changes will offset predicted UV trends. My impression is that major parts over the N-Hemisphere are still experiencing UV irradiances below preindustrial levels due to troposphere pollutants and possibly changes in cloud cover. Although UVB levels may be on the increase in the future, preindustrial levels will not be reached for many part of the globe.

3.5 STREAM; Stratosphere Troposphere Experiment, study by Aircraft Measurements

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Introduction

A total of three flights were carried out at 16, 17 and 18 February 1993 with a two engine jet, a Cessna Citation II, which operated from Kiruna airport in Northern Sweden. In situ measurements were performed of different trace gases in the free troposphere and lower stratosphere. The measurements were performed in the afternoon, at different levels between 6 and 12.3 km altitude; one flight level in the troposphere and three in the stratosphere. The aircraft maintained for 10 minutes at every level, except at the maximum level were it was maintained for 45 minutes. The flights were carried out North and North-East of Kiruna to 73 N.

Data analysis have been carried out for preliminary HNO_3 data, O_3 and N_2O. O_3 was measured by a chemiluminescence monitor, with ethylene as reaction gas. Optimalization of the technique, including pressure independence down to 300 mb has been described by Gregory et al. (1983). N_2O was measured using a tunable diode laser (TDLAS) spectrometer which is described in detail by Wienhold et al. (1994). HNO_3 was measured with a Ne cooled quadruple mass spectrometer. The air was sampled through a 4 cm diameter inlet tube. The technique is described in detail by Arnold and Knopp (1987).

O_3 concentrations ranged from 60 ppbv in the free troposphere to 700 ppbv in the stratosphere at maximum altitude. HNO_3 concentrations were 4-5 ppbv at maximum altitude, decreasing with altitude to less than 100 pptv at the tropopause level. N_2O concentrations varied between 240-290 ppbv in the stratosphere and were occasionally less than 220 ppbv. Tropospheric concentrations were 300-310 ppbv. Low O_3/N_2O ratios have been found in the lower stratosphere for N_2O concentrations down to 200 ppbv.

The air parcels with the lowest ratios were measured during the flight on 17-02-93, accompanied by relatively low HNO_3/N_2O ratios. The 10 days back trajectories of these air parcels follow the inner vortex structure, suggesting that the air has descended to the lower stratosphere. The "shift" in the O_3/N_2O ratio on the 17th extends to theta=315 K, implying that descending vortex air has reached the tropopause. Further, the low O_3/N_2O ratios on the 17th suggest that O_3 loss has occurred. Based on comparison of the O_3/N_2O ratio on the 17th with that on the other days, 36% O_3 loss is calculated. Although there are no previous simultaneously measured in situ data of HNO_3, N_2O and O_3 available, the HNO_3 data is compared with estimated HNO_3 from measured NO_y from the AASE I and II missions, assuming that NO_y contains 80% HNO_3. Our results show significantly higher HNO_3 concentrations relatively to O_3 and to N_2O compared to the results of the AASE I and AASE II campaigns. The ratio NO_y/O_3 measured during AASE I is constant with altitude in the stratosphere, while our HNO_3/O_3

ratio shows much more variability in the stratosphere with increasing ratios with altitude.

The measurements during AASE I were performed before the eruption of Mt. Pinatubo, so that the higher ratio values measured during STREAM could be caused by enhanced sulphuric acid aerosol abundance in the lower stratosphere, leading to enhanced HNO_3 concentrations by heterogeneous reactions on the aerosols. However, the STREAM data also show significant higher HNO_3/O_3 ratios relatively to N_2O compared to the results of AASE II, which was performed after the eruption of Mt. Pinatubo. These differences could partly be explained by the suggested O_3 loss, since the ratio HNO_3/O_3 relatively to N_2O is lower for the 17th compared to the other days. However, different meteorological conditions during the period of the measurements, e.g. less influences by vortex air of mixing of air from lower latitudes, affecting the ratios of the trace gases, should be taken into account.

Our higher HNO_3/O_3 and HNO_3/N_2O ratios may also indicate enhanced heterogeneous chemistry on sulphate aerosols compared to 1993, due to enhanced sulphuric aerosol abundance in the lower stratosphere by gravitational settling of the aerosols. An alternative explanation of the enhanced HNO_3 concentrations may be sedimentation of earlier formed PSC's, which evaporated in the lower stratosphere, releasing HNO_3. The vortex was relatively cold and stable during the winter, allowing particles to sedimentate into the lower stratosphere.
Also low HNO_3 concentrations relatively to N_2O were found on 17-02-93, which were lower than previous measurements during AASE I and AASE II in the Arctic vortex (Loewenstein et al., 1993; Kawa et al., 1990). These low HNO_3 concentrations, corresponding to low N_2O concentrations suggest that denitrification has occurred during descent of air in the vortex. This suggestion is supported by the fact that the 10-days back trajectories of all concerned air parcels follow the inner vortex structure, preventing mixing with HNO_3 rich air.

Model calculations
10 Days back trajectories, ending at the flight track have been used as input for a lagrangian chemical box model to simulate the STREAM data. The model is based on a chemical scheme originally developed by Müller et al. (1993). Numerical calculations were carried out using the FACSIMILE code (Curthis and Sweetenham, 1987). The chemical scheme is coupled to a radiative transfer model, developed for stratospheric conditions, including multiple scattering at low zenith angles. Detailed description of the model can be found in Lary and Pyle (1991). Heterogeneous reactions on sulphuric aerosols have been included (Tolbert et al., 1988).
Initial concentrations were derived by a 2-D photochemical stratospheric model (Bruhl and Crutzen, 1988), originally developed by Gidel et al. (1983) and Crutzen and Gidel (1983). Also HALOE data have been used as initial data for calculations at mid northern latitudes and EASOE data (Crewell, pers. comm., 1994; Von Clarmann, 1993). Aerosol concentrations were taken from Deshler et al. (1993).
Preliminary results indicate discrepancies between model results and measurements. The model shows higher O_3 relatively to N_2O and lower HNO_3 relatively to O_3. Recent measurements during the AASE I and II missions show

that the ratio O_3/N_2O, NO_y/N_2O and NO_y/O_3 are constant in the lower stratosphere with small latitudinal variation. Therefore these discrepancies may not be an input problem and the chemical description of the model will further be investigated.

Assessment
The objective of the project is to measure trace gas concentrations in the Arctic lower stratospheric vortex. However, because only 3 components were measured, the information obtained is scarce, making the interpretation of the results difficult.
In future experiments, therefore more attention should be paid to measuring strategy with regard to the minimal number of parameters to be measured.
Finally one should reflect upon how the results can optimally be used in other modelling studies.

4. TROPOSPHERIC BUDGET OF NON-CO_2 GREENHOUSE GASE

4.1 Introduction
The non CO_2 greenhouse gases, excluding water vapour, currently have concentration levels in the troposphere well above their natural background. The concentration of CH_4 is about a factor 2.5 above its natural background, tropospheric ozone also about a factor 2.5. The N_2O-concentrations is about 10% above its natural value, and the CFC-concentrations are nearly completely anthropogenic in origin.
The aim of the study of the tropospheric budget of non CO_2 greenhouse gases is to understand and determine in a quantitative way the processes which govern these budgets.
An overall understanding leads to a model with which in a reliable manner the relation is given between anthropogenic and biogenic emissions and the concentrations of these non CO_2 greenhouse gases. Ambient measurements are required to investigate the relevant processes, for evaluation of the results of the modelsimulations and for trend measurements.
Models, if they have proven to be reliable, can be used to investigate the causes of historical trends, and to calculate future trends as a result from emission scenarios and abatement policies. These type of models can be used both scientifically and for policy making.

Budget studies combine different elements. In the first place, and often of primary importance, is accurate knowledge concerning anthropogenic and biogenic emissions. The overall tropospheric models contain meteorological and chemical submodels, as well as dry and wet deposition and radiation models.
The overall models are directed to budget studies of CH_4, N_2O, O_3 and CFC, but consequently also address CO, NO_x, VOC, HCFC and include clouds and aerosols.
Both global and regional modelling are essential, regional modelling is important for the greenhouse gases with a relative short residence time like O_3, and also aerosols.
And last but not least, an essential element of budget studies is the evaluation of modelresults versus reliable and representative ambient measurements.

Global and regional tropospheric models are directed to the simulation of the troposphere as a whole, and consequently integrate all available knowledge in a consistent and coherent way. Tropospheric models have considerable prognostic capabilities, because they are based on the solution of the in principle 'complete' diffusion equation.
In this cluster of budget studies, the main focus was on the development and improvement of tropospheric models, and the creation of a reliable and representative ambient measurement data base.

Work has been directed to the improvement and development of both 2-D and 3-D global models, and 3-D regional models the driving concept was the setup of a hierarchy of models with different balances between chemistry and meteorology.

The outcome of this cluster of budget studies is a hierarchy of models capable of addressing a range of questions concerning the relationship between emissions and the concentrations of non CO_2 greenhouse gases.

A key element, also for the future, remains the evaluation of the models against ambient data, and the reliability of the models in their evaluation of abatement strategies and future trends.

This subtheme comprises 4 projects.

4.2 GLOMAC; Subproject of EUROTRAC related to climate modelling of KNMI

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Stratosphere / troposphere exchange
The goal of this research is to quantify the amount of ozone reaching the troposphere from the ozone layer.
This research is motivated by the fact that ozone is a very reactive gas that plays an important part in the chemistry of the troposphere. Most of the ozone in the troposphere is (today) created in the troposphere itself, as a result of the oxidation of hydrocarbons. Human activities are important sources of these hydrocarbons.

A part of the ozone in the troposphere is of stratospheric origin. It is brought there from the ozone layer by a process that is called stratosphere/troposphere exchange.

It is currently thought that the stratosphere/troposphere exchange is driven by the global scale circulation cell in the stratosphere. In the equatorial zone, or more precise over Indonesia, tropospheric air can pass through the tropopause and so enter the stratosphere. A large circulation cell through the stratosphere, and possible the mesosphere brings the air towards the poles. In the winter season this air can pass the tropopause again in the polar and mid-latitude zones.

The process currently dominating the discussion over mid-latitude stratosphere/troposphere exchange is the so called tropopause folding. It is essential to realize that the height of the tropopause over the mid-latitudes is not a fixed property, but has strong fluctuations with a typical timescale of one day. The actual heights vary between 5 and 12 kilometres. These variations are closely linked to the tropospheric weather; a well developed ridge of high pressure will cause the tropopause to be relatively high, a developing low can cause the tropopause to sink to very low values. In the last case, a new tropopause can form above the old one, isolating a blob of stratospheric (ozone rich) air in the troposphere. This air will eventually dissolve into the troposphere.

The very changeable height of the tropopause is also responsible for day to day fluctuation in the total ozone values over the mid-latitudes. With 'total ozone' the column integrated amount of ozone above a certain point of the globe is meant. This quantity is in the order of 5 to 12 grams per square meter.

The best way to estimate the stratosphere/troposphere exchange is probably to quantify the mass-flux in the stratospheric circulation cell mentioned before. Direct measurements are not possible. An indirect method has been used in the past by Holton.
One can also look at the details of the process of tropopause foldings. One must realize, however, that the tropopause foldings are not the driving force behind the circulation cell in the stratosphere, nor are the tropopause foldings directly caused by this cell.

One can study the details of stratosphere/troposphere exchange with observations. Here we must make use of the fact that the stratospheric and tropospheric air have slightly different properties, and so one can distinguish between the two. The most important are the mixing ratios of ozone and water vapour.

The ozone mixing-ratio is 10 to 100 times higher in the stratosphere than in the troposphere. Near the tropopause it is a reasonably well conserved property, so it can be used as a tracer for stratospheric air. Unfortunately it is not possible to get a good three dimensional field of the ozone distribution near the tropopause from a satellite.

The only measurements with sufficient resolution are in situ measurements, for example from balloon or aircraft based instruments, or lidar measurements. In either case measurements are far too infrequent to obtain a total hemispheric mass flux without extensive extrapolations.

We do have the possibility to study stratosphere/troposphere exchange in the global weather prediction models (GCM). These models, however, do not (yet) contain ozone as a trace gas. So we will have to parametrize the ozone mixing ratio in some way.

In the current study we have looked at a quantity called the potential vorticity (PV). PV is relatively easy to compute, and behaves a lot like ozone. It is high in the stratosphere and low in the troposphere, and a conserved quantity. It has been

observed that PV can be used to identify intrusions of stratospheric air in the troposphere.

It would seem logical that, if there is a linear relation between ozone mixing ratio and PV, then there must also be a relation between column integrated ozone (total ozone) and column integrated PV. To investigate this we did a multiple variable regression analysis between TOVS total ozone maps and the PV on 15 pressure levels computed from ECMWF forecast fields. It was found that the results were indeed consistent with a linear relation between ozone mixing ration and PV, between levels of 400 and 50 hPa. The regression coefficient of this linear relation proved to have a seasonal cycle, and a large inter annual variability (Allaart et al., 1993).

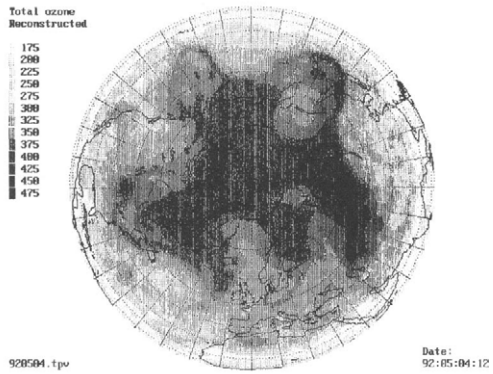

Figure 3.15
Synoptic map of NOAA-TOVS total ozone data valid for May 4, 1992, 12 UT. Notice the extended structure of high ozone values from the North-East to South-West over central Europe

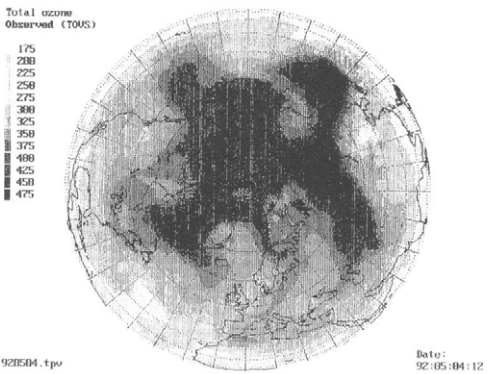

Figure 3.16
Column integrated potential vorticity scaled linearly to show the remarkable resemblance to the Ozone values in Figure 4.1. Data computed from ECMWF global vorticity and temperature fields

This result has been very fruitful; it enabled us to distinguish between dynamical and other (possible chemical) effects on a regional scale on the ozone layer. For example we could prove that the very low ozone values recorded in January 1992 over Europe were caused for 50% by dynamical effects on a regional scale.

Also this method enables us to forecast total ozone amounts for a few days ahead, based on the weather forecasts from the ECMWF. This method is now the basis for the daily predictions of damaging UV radiation made at the KNMI.

In order to compute the mass flux through the tropopause, first a practical definition of the tropopause is needed. The official WMO definition, which defines the tropopause in terms of the temperature gradient is only one of the possible definitions. It is generally assumed that for atmospheric chemistry, the dynamical tropopause, defined in terms of constant PV, is a more suitable definition. We have investigated this and found that there is a very poor agreement between the two definitions of the tropopause.

We also started an observational programme. At least once a week we launch balloon borne ozone sondes which can, with a very high vertical resolution, detect ozone rich, and dry air in the troposphere. We assume these are the signatures of tropopause foldings. Again we found that there is only a very poor agreement between the observed structures and the folding events found in the ECMWF forecasts.

Meteorological aspects of global modelling of atmospheric chemistry

Introduction. The work of Allaart, described in the previous section was supported by NPR. In the following sections we will describe the general progress of GLOMAC related work at KNMI.

*Boundary-layer parametrization (G.H.L. Verver).*In current transport and chemistry models the parametrization of turbulent transport of chemical reactive gases is the same as for inert gases. Most models use a down gradient description similar to molecular diffusion. The turbulent exchange coefficient then depends on stability. However, for reactive gases, this will introduce errors for two reasons. The first is that it is assumed that each horizontal layer is well mixed. This will not be the case for all species. Correlated or anti correlated concentration fluctuations on a subgrid scale will enhance or diminish the effective reaction rates. The second reason is that turbulent fluxes of one species will depend on the flux of the others. This is not incorporated in the usual K-diffusion description. Both effects depend on the ratio of the chemistry timescale and the turbulent timescale.

It was found that a second order model is able to describe these phenomena, and that in the case of non-neutral boundary-layers the concentration and temperature covariance must be taken into account (Verver, 1994). A second order model that explicitly describes fluxes and (co-)variances is now being developed. The aim is to deduce simpler parametrizations for use in global transport models, that take into account the effects mentioned above.

Deep Convection (P. Siebesma). Pieter Siebesma studied the different convection parametrizations and constructed a new one.

Vertical diffusion by dynamic instabilities (H. Kelder). Vertical diffusion by instabilities was studied with a theoretical model. We found a new type of propagating instabilities (Lott et al., 1992). Observations of small scale transport of ozone was studied in the framework if the AESOE campaign (Teitelbaum et al., 1994).

Unresolved non-turbulent transport (M.A.F. Allaart, H. Kelder, L.C. Heijboer, G.J.M. Velders, P.J.F. Velthoven). At KNMI a global atmospheric circulation and chemistry model ("TMK") was implemented. This is an off line transport model coupled to the ECMWF (European Centre for Medium-Range Weather Forecasts) analyzed windfields. TMK is one of the models used within GLOMAC. As KNMI is responsible for the meteorological part, much effort has been put into upgrading the meteorological input of the model.

With this model we have done studies of the transport of passive traces (Velders et al., 1994). A number of chemical reactions has also been added in collaboration with other members of GLOMAC: P. Crutzen and J. Lelieveld. We have used the upgraded model to study the transport of aircraft emissions (Van Velthoven et al., 1994).

The model was also used to study the exchange between troposphere and the stratosphere. For this purpose we increased the number of vertical levels near the tropopause. We studied the influence of the horizontal resolution on the cross-tropopause mass-fluxes in the model (Kelder et. al., 1994). In order to compute the cross-tropopause ozone fluxes a new ozone climatology is being constructed (Fortuin et al., 1994).

Assessment

Potential Vorticity (PV) can be used to identify intrusions of stratospheric air into the troposphere. This has been published before and was reconfirmed by this project. By using this method one may hope to discriminate between transport and chemistry as the cause of changes in ozone column density in the future. To be able to do so is a long way to go and it is not sure if it can be done at all. The correlation between PV and O_3 column after all is an empirically one of which the validity is limited. The author does not discuss how the stratosphere/troposphere flux is determined and how it should be dealt with in models, which is one of the objectives of the project. Finally this method can be used to forecast total O_3 for a few days ahead and its consequences for the UVB radiation climatology. From the abstract it seems that also progress has been made for those parts of the project not funded by NPR i.e. the meteorological aspects of global modelling.
The project as a whole is relevant in perspective of global change and scientifically of good quality.

4.3 Application of 2-D global models

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This abstract summarizes the main findings obtained in this project so far. A global two dimensional model, the TNO version of the Isaksen model, was used to study the following issues:

1 the relation between emissions and concentrations of CO and CH_4 on a global scale. ;
2 the tropospheric oxidising capacity of the troposphere (O_3, OH);
3 analysis of differences between results of the 2-D model and other models;
4 scenario calculations using the EDGAR/GEIA data base.

Due to the fact that the EDGAR/GEIA data base is not yet accessible the last item has not been addressed until now.

Introduction

The last 10-15 years global scale models have been developed to describe the emissions, transport, degradation and removal processes of gases in the troposphere. These models vary in dimensionality (0-D Æ 3-D), in the way the chemistry is represented, the climatological fields, photodissociation rates, basic emissions, etc. The performance of models is usually validated against observations. However, on a global scale there are not enough measurements to have sufficient knowledge of the distributions of most of the gases, except for methane and to some extent ozone and carbon monoxide. Consequently, the validation of tropospheric global scale models is poor and primarily based upon the comparison for the three above mentioned species.
A striking example of the fact that agreement between observations and model results on just a few species and measurements is insufficient as validation test is given in Figure 4.3 (Guthrie and Yarwood, 1991). The five different models predict a wide range of methane levels in the year 2100 based on the same emission scenarios.

Model intercomparisons

In 1992 and 1993 two intercomparison workshop were organised to identify the causes in the diversity of model responses. TNO's 2-D model was one of the models which were compared in these workshops. An overview of some of the characteristics of these models is given in Figure 4.4 and Tables 4.1 and 4.2. Table 4.1 shows that the emissions are within about 40 percent of each other which is consistent with the generally accepted uncertainty ranges of the global scale emissions. Figure 4.4a and 23b show a wide range of photodissociation rates used by the different models under the same conditions. A closer inspection indicated that some of the discrepancies in the photodissociation rates are due to the way clouds are treated. Given these differences (and many others) it is not surprising that the global averages of some key species differ in the order of a factor of two (CO and O_3) or more (NO_x). Only for methane there is hardly any difference.

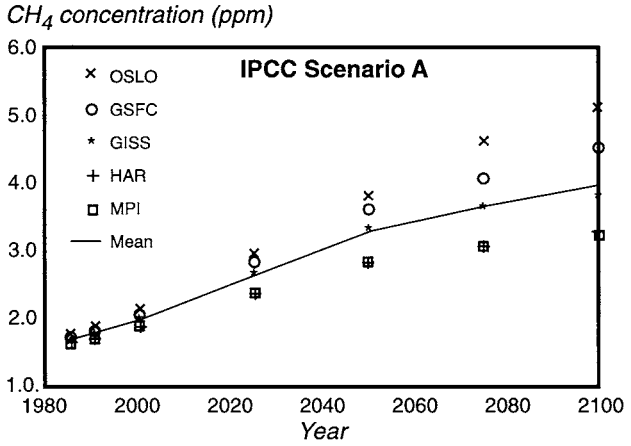

Figure 4.3
Calculated CH_4 concentrations 1985-2100. Source Guthrie&Yarwood, 1991

Table 4.1
Base case emissions used in the models

Model	CH_4 $TgCH_4/yr$	CO (Tg C/yr)	NO_x (surface) (Tg N/yr)
Cambridge	405	828	36
Harwell	485	675	34
TNO	550	616	32
MPI-CNRS-3D	fixed m.r.	729	30
MPI-1D	540.5	537	34
FSFC	400	785	29
LLNL	453	fixed m.r.	39.4

Table 4.2
Average tropospheric mixing ratios calculated by the models for the base case

Model	CH_4 (ppm)	CO (ppb)	OH (E5 cm^{-3})	O_3 (ppb)	NO_x (ppt)
Cambridge	1.71	131	7.1	51	143
Harwell	1.63	88	8.5	77	40
TNO	1.66	75	10.5	49	66
MPI-CNRS-3D	1.97	97	8.7	36	55
MPI-1D	1.75	84	10.8	44	114
FSFC	1.75	90	7.5[a]	54	56
LLNL	1.59	67	8.3	67	53

[a] approximate value derived from mixing ratio

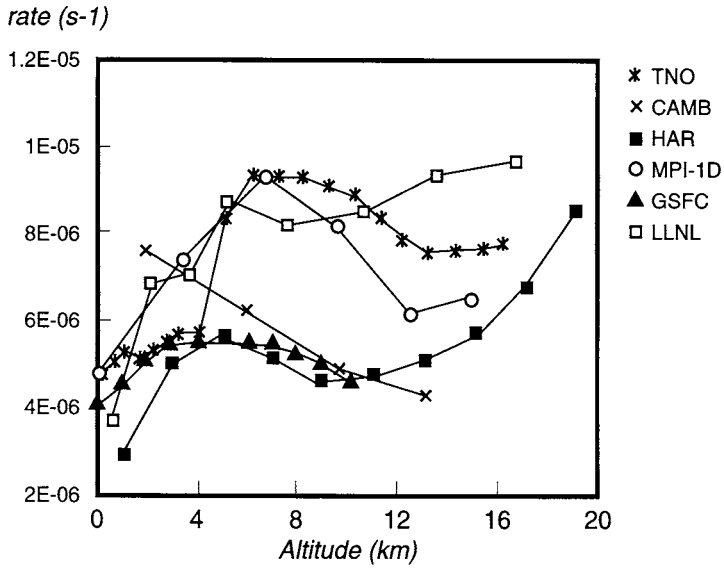

Figure 4.4a
Photodissociation rate (s^{-1}) as a function of altitude (km); 50°N; 21 June. $J(O_3$ n $O(^1D))$

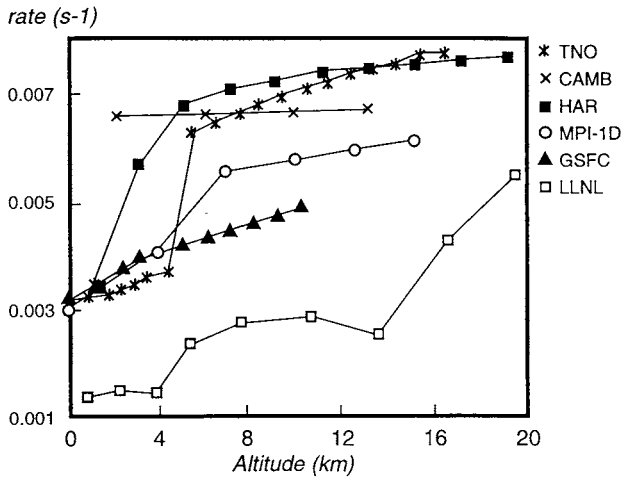

Figure 4.4b
Photodissociation rate (s^{-1}) as a function of altitude (km); 50°N; 21 June. $J(NO_2 \rightarrow NO+O(^3P))$

Also the chemistry behaves quite differently. Under fixed conditions four chemical schemes were tested (Fig. 3.19 and 3.20). This illustrates furthermore the variety in model responses. Unfortunately for most of the parameters no yardsticks exist to identify which parameter values or chemical schemes are acceptable and which ones are flawed.
In the future more intercomparison activities for tropospheric models are foreseen and needed to narrow uncertainties in model input and output.

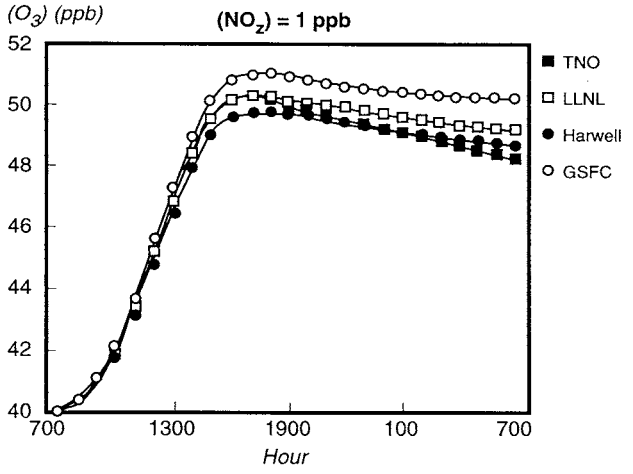

Figure 4.5
Daily trend of the O_3 concentration; $NO_z = 1$ ppb ($NO_{z\,=\,NO\,+\,NO2}$ + $NO_3 + 2N_2O_5$)

O_3 and OH

Since preindustrial times the tropospheric ozone content has increased substantially. Comparing the Montsouris series (1876-1910) with current ozone records, a doubling to tripling of ground level ozone concentrations at northern mid-latitudes is found. The indication is that the role of tropospheric chemistry in the formation of ozone has changed from a small net sink in the preindustrial era to a source comparable in size with the influx of ozone from the stratosphere (Table 4.3). The net chemical ozone production (or destruction) is the small difference between two large terms: ozone production and ozone destruction. The third term in the budget is dry deposition. Also calculations are presented in this table for scenarios in which NO_x and NMHC emissions are doubled. It should be noted that the assumed influx from the stratosphere is now regarded as being somewhat too high; demonstrating once more the importance of a net free troposphere source.

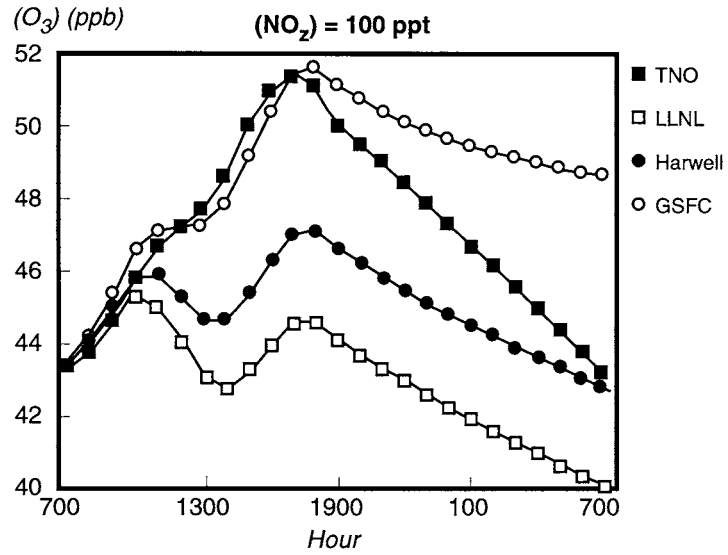

Figure 4.6
Daily trend of the O_3 concentration; NO_z = 100 ppb.

Table 4.3
Global average ozone budget (10^{10} molec. $cm^{-2}.s^{-1}$)

Runs	Chemical production	Chemical destruction	Net. Ch. Prod./Destr.	Deposition	Flux from stratosphere
Preindustrial	20.0	21.5	- 1.5	5.9	7.4
1990	44.8	39.2	5.6	13.0	7.4
2.0 * NO_x	55.0	47.5	7.5	15.9	7.4
2.0 * NMHC	49.9	42.8	7.1	14.5	7.4

A more detailed analysis of these processes reveal large regional differences (Figure 4.7)

The tropical middle troposphere is a large sink region to ozone due to:
1 the photodissociation of ozone into $O(^1D)$ followed by the reaction with H_2O to produce OH, and
2 the reaction of ozone with HO_2.
The lowest levels of the northern mid-latitudes is a chemical source region because of the oxidation of VOCs in a NO_x-rich environment.

	SH									NH					
June*	-80.0	-70.0	-60.0	-50.0	-40.0	-30.0	-20.0	-10.0	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0
16.250	+++	+++	++++	++++	++++	+++	+++	++	++	++	+++	++++	+++++	+++++	++++	++++	++++
15.250	0	0	0	+	+	+	+	+	+	+	+	+	+	+	0	+	+
14.250	0	0	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+
13.250	0	0	0	+	+	+	+	++	++	++	++	+	+	+	+	+	+
12.250	0	0	0	+	+	+	++	++	++	++	++	++	++	++	+	++	++
11.250	0	0	0	+	+	++	++	++	++	++	++	++	++	++	++	++	++
10.250	0	0	0	+	+	++	++	++	++	++	++	++	++	++	++	++	++
9.250	0	0	0	+	+	++	++	++	++	++	-	+	+	++	++	++	++
8.250	0	0	0	+	+	+	+	+	++	-	--	--	-	+	++	++	++
7.250	0	0	0	+	+	+	-	-	-	--	--	--	--	0	+	+	++
6.250	0	0	0	0	+	-	--	--	--	--	---	---	--	-	+	+	+
5.250	0	0	0	0	+	--	--	--	--	---	---	---	--	0	+	+	+
4.250	0	0	0	0	+	--	---	--	--	---	----	---	--	-	++	+	++
3.250	0	0	0	0	+	--	---	---	---	---	----	----	--	++	++	+	++
2.750	0	0	0	0	+	--	---	---	---	---	----	----	--	++	++	+	++
2.250	0	0	0	0	+	--	---	---	---	---	----	----	++	+++	+++	+	++
1.750	0	0	0	0	+	--	---	---	---	---	----	---	+++	++++	++++	+	++
1.250	0	0	0	0	++	--	--	--	--	--	---	--	++++	++++	++++	+	++
0.750	0	0	-	0	++	++	+++	+++	+++	+++	++	++++	+++++	+++++	++++	+++	++
0.250	----	----	----	----	----	----	----	---	--	--	----	---	-----	-----	-----	-----	-----

* altitude (km)

The classification is as follows (NP: net production; ND: net destruction).

+++++	:	5.10^{12}	<NP	
++++	:	1.10^{12}	<NP	< 5.10^{12}
+++	:	5.10^{11}	<NP	< 1.10^{12}
++	:	1.10^{11}	<NP	< 5.10^{11}
+	:	1.10^{10}	<NP	< 1.10^{11}
0	:	-1.10^{10}	<NP/ND	<$+1.10^{10}$
-	:	-5.10^{10}	<ND	< -1.10^{10}
--	:	-1.10^{11}	<ND	< -1.10^{11}
---	:	-5.10^{11}	<ND	< -1.10^{11}
----	:	-1.10^{12}	<ND	< -5.10^{11}
-----	:		ND	< -1.10^{12}

Figure 4.7
Production and destruction regimes for ozone in the troposphere.
Unit: molec.cm^3/month

Assessment
This study clearly demonstrates the uncertainties in scenario modelcalculations, even when state of the art models are being used. E.g. CH_4 concentrations in 2100 for the IPCC scenario "A" may range between 3 and >5 ppm. Consequently the atmospheric residence time may vary from 8.5 to over 13 years. The international community of modellers should agree which 'standard' model to be adopted for policy issues of a supranational nature, more or less the way it was decided for the ECE-EMEP-project on transboundary pollution over Europe. For tropospheric ozone, it is now accepted that a major part is produced in the troposphere itself. The net production is of the same order of magnitude as the influx from the stratosphere[3]. Depending on the future emission scenario used, tropospheric ozone production will further increase with serious consequences for man and the ecosystem and furthermore for the radiation budget of the atmosphere.
This project is highly relevant for policy making; the model seems to perform well, especially for components with atmospheric residence times of a few weeks or more, when compared to other state of the art models.

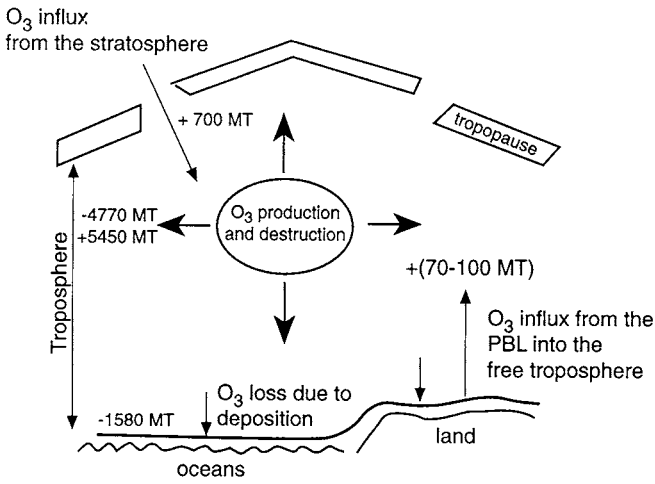

Figure 4.8

4.4 Global modelling of atmosphere trace gases "application of a global three dimensional model"

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Introduction
The research in this project is performed in collaboration with TNO-MW. The broad objective of this project is the production of the 'base-document CH_4' and a

3. From discussion with PIs cooperating in this priority issue the O_3 budget, at present, most probably is as being depicted in Figure 4.8.

document on aircraft and air pollution, both also by order of the Ministry of the Environment. To be able to make the necessary scenario runs and assessments we had to put into operation a global three-dimensional model (the MOGUNTIA model) at RIVM. With this MOGUNTIA model the relations between emissions and concentrations of trace gases relevant to ozone and its relates species on a global scale are studied.
In this extended abstract the focus will be on the study on effects of aircraft emissions. The CH_4 study will be reported in our final NPR report.

Considerations
Aircraft emissions affect the chemical composition of the atmosphere in several different ways, depending on flying altitude and location. The conventional subsonic fleet grew extensively in the 1970s and 1980s and is expected to growth by a further 100% during the next two decades. This has led to several model studies focusing on effects of aircraft emissions on ozone in the upper troposphere (Hidalgo and Crutzen, 1977; Isaksen, 1980; Derwent, 1982; Ehhalt et al., 1992; Beck et al., 1992). These studies have predicted an increase in upper tropospheric ozone levels due to emissions of NO_x varying between 5 and 12%. The aircraft-induced changing ozone profile could have implications for the atmospheric radiative balance.
The previous modelled estimates of the ozone increases probably suffer from considerable errors due to uncertainties in the magnitude and distribution of emissions and differences between models. Furthermore, a number of simplifications were made in the representation of aircraft emissions in atmospheric chemistry models.
Firstly, in these studies it was assumed that the present subsonic fleet emits all exhaust gases below the tropopause. However, new estimates predict that a considerable part (25 to 50%) of the emissions from the subsonic fleet are deposited directly into the lower stratosphere. Residence times in the lower stratosphere are expected to be longer than those in the upper troposphere due to less efficient vertical overturning. So, the mixing and chemistry in the lower stratosphere are different from that in the upper troposphere. Obviously, the effects of emissions in the lower stratosphere will also be different from those in the upper troposphere.
Secondly, in the previous work it was assumed that immediate large scale mixing of all emissions occurs. For this reason, the impact of flight corridor effects on the predictions has not been assessed. Again, in the previous work, the chemical composition of the source gases during largescale mixing is considered identical to that of the emission at the tail pipe. Initially, the exhaust plume from an aircraft is isolated and highly turbulent. The exhaust entrains ambient air and expands to dimensions of several hundred metres. Finally, it is subject to dispersion and mesoscale transport before it becomes zonally mixed. This is illustrated by the estimate that in the upper troposphere over the North Atlantic, emissions of a single aircraft are mixed in about a day in a volume of 5000 km along the flight path, 1000 km wide and 2 km in altitude. However, about 500 aircrafts per day use this corridor and burn 100 tonnes of fuel each. This implies that the emissions may be highly concentrated in heavily travelled flight corridors, causing zonal differences and local impacts of aircraft emissions separate from global perturbations due to long-range transport of emissions.
Thirdly, another process omitted is the possible involvement of nonlinear reactions involving NO_y species and heterogeneous chemistry occurring on ice particles in

the contrail. Soot and sulphur particles in the exhaust favour formation of ice crystals. The response to emitted NO_x is expected to change if heterogeneous chemistry occurs. The $NO_x - O_3$ chemistry is very nonlinear and results in a greater ozone production per unit of NO_x for lower NO_x concentrations (Liu et al., 1987). In most models immediate largescale mixing of aircraft emissions is assumed. However, a part of the NO_x had probably already been converted to NO_y before the plume reached grid dimensions. Therefore the ozone production caused by the NO_x emissions is overestimated. For this reason, the role of chemical plume processes in aircraft emissions need to be assessed.
The aim of our present work is to determine the effects of emissions of NO_x and other exhaust components from aircraft with the MOGUNTIA model, in particular with respect to changes in the upper troposphere and lower stratosphere. Focusing on the considerations mentioned above, we take into account the chemical processes in an aircraft plume in the upper troposphere before largescale mixing occurs. Therefore an exhaust plume model is being developed and the plume model study is expected to result in a parametrization of the sub-grid, in particular $NO_x - NO_y$. chemistry of the plume. Using this parametrization the global NO_x emission fields of aircraft can be translated into new processed fields, in which the sub-grid effects have been taken into account. These new emission fields will be used as input for a MOGUNTIA study on the effects of aircraft emissions at cruising altitudes on the global atmosphere.

The aircraft exhaust plume model

In the aircraft exhaust plume model the kinetics and diffusion of an exhaust plume are simulated from almost immediately after the 'tailpipe' until the concentrations in the plume are equal to the background concentrations, or until the plume has grown to 3D-model grid dimensions.
The model consists of two sets of differential equations representing the mass balance equations in and outside the exhaust plume. The FACSIMILE package (Curtis and Sweetenham, 1985), which applies a version of Gears' method, has been used to calculate the arithmetic solutions of the chemical equations.
The chemistry of the plume is calculated using a set of reactions given by Beck et al. (1992). This set consists of 42 species, 73 gas-phase reactions and 16 photolytic reactions. Six primary NMHCs represent the emitted species and their degradation pathways. The concentrations in the ambient air are also calculated using this set of reactions. The photolysis constants are calculated from the intensity of the sun, the absorption cross-section and the quantum yields of the compounds. Background concentrations are based on the measurements of the STRATOZ III campaign (Drummond et al., 1988). Currently, the set of reactions does not contain any heterogeneous reactions, but it will be extended with heterogeneous chemistry in a short while. Also, for extension to the lower stratosphere the tropospheric chemistry will be replaced with a stratospheric reaction set. The diffusion part of the model was based on the theory of Gelinas and Walton (1974), which states that the kinetics and chemistry of an exhaust plume can be described separately. In this approach, the plume is described by a box of variable volume, which always encompasses the exhaust species. So, the explicit spatial dependence is suppressed, and the resultant time dependent equations can be readily solved using standard kinetic methods. The dimensions of an exhaust plume are about 3 km high and about 100 km wide after 24 hours expansion. The

simulation of only one exhaust plume will be extended to the simulation of several plumes later.
The exhaust plume model was shown to be a good instrument to study plume chemistry. Generally speaking, maximum perturbations (caused by the emission of an aircraft) of the plume concentrations exist only in the first few hours after injection and disappear after about a day. We found that these perturbations strongly depend on the amount of emission, hour of the day and the season when injection takes place, as well as the background concentrations.
The O_3 concentration in the plume rapidly decreases after the injection of emissions, in particular caused by the reaction of emitted NO with O_3. The O_3 concentration is reestablished to a level similar to the background concentration in about an hour due to mixing with background air. Subsequently, some production of ozone occurs and the resulting concentration in the plume is somewhat higher than the background level for a few hours.
The high NO_x concentration occurring immediately after injection decreases rapidly due to mixing with background air. Subsequently, some production of ozone occurs and the resulting concentration in the plume is somewhat higher than the background level for a few hours.
The high NO_x concentration occurring immediately after injection decreases rapidly due to mixing with background air. However, a part of the NO_x is also converted to NO_y components. At first, HONO is formed; this then undergoes rapid photolytical decomposition. Subsequently, HNO_3 is formed and after some hours also HO_2NO_2, from which formation was initially inhibited through a lack of HO_2 (caused by the reaction of NO with HO_2).
The calculated NO and NO_2 concentrations in the plume are quite similar to measured amounts in a young plume (Arnold et al., 1992). But the measured perturbations of HONO and HNO_3 are 10 to 20 times greater than calculated in the exhaust plume model. A reason for this discrepancy may be our limited set of reactions. The formation of HONO and HNO_3 in our exhaust plume model is only by reaction of respectively NO and NO_2 with OH. However, the concentration of OH in the plume is too low for a very rapid transformation. For this reason, it seems that there must be another reaction pathway for the formation of HONO and HNO_3. Heterogeneous reactions are a possibility for this pathway.

Translation of aircraft emission fields
The parametrization of sub-grid chemistry was initially in the form of a simple conversion factor: an emission of x molecules of NO_x is converted after expansion to grid-dimension into y molecules of NO_x and z molecules of NO_y (HNO_3, HONO, HO_2NO_2, N_2O_5, PAN), with x = y+z. The transformation of NO_x into NO_y components depends strongly on the altitude of emission and background concentration (e.g. NO_y, OH and HO_2) components, and less on the time of injection (time of day, season) and amount of emission. The higher the altitude of aircraft emissions the slower the conversion of NO_x into NO_y. Here the lower temperatures are the primary reason, followed by the lower OH and HO_2 concentrations.

As a first parametrization, it is assumed that after one day the exhaust plume has reached grid dimensions and the plume model predicts:

$f(NO_y) = 0.7$
$f(NO_x) = 0.3$

So, in the new emission fields the NO_x emissions will be differentiated into NO_x (30%) and NO_y (70%) components, the latter group divided in specific components contributing to NO_y.

MOGUNTIA-model runs

The processed emission fields are used as input for the MOGUNTIA model. MOGUNTIA is a global tropospheric 3D-model incorporating transport and chemistry and it was originally developed at the Max Planck Institute in Mainz (Zimmermann, 1988). It has grid dimensions of 10° x 10° x 100 hPa, starting at the surface and extending to the 100 hPa level. The dynamics of the model are calculated with ECMWF fields, assuming turbulent mixing. The reaction set used for the chemistry is from Dentener (1993).
The calculations are performed with aircraft emission fields and corresponding anthropogenic NO_x emission fields based upon data of McInnes and Walker (1992) and Müller (1992), processed by Olivier (1994). Preliminary results of unprocessed 1990 emission fields show an increase in the ozone concentration at the location of the North-Atlantic flight corridor at the cruising altitude of 8%. The processed emission fields show an increase of about 6% at the similar location.

Assessment

The exhaust plume model was shown to be a good instrument to study plume chemistry. A comparison of the calculations with measurements shows a discrepancy for HONO and HNO_3 concentrations in the plume caused perhaps by missing (heterogeneous) reactions in the reaction set. A parametrization of the sub-grid chemistry has been developed to take into account sub-grid effects (found in the study using the exhaust plume model) in a study of the global effects of NO_x emissions from aircraft. This parametrization is, at first, a conversion factor. As a first estimate, it is assumed that after one day the exhaust plume has reached grid dimensions. After this, a 70% conversion of NO_x into NO_y is calculated. Preliminary results with the MOGUNTIA model show that this conversion results in a lower ozone production than due to unconverted emission fields. It is not clear which organic components are used to calculate ozone production. Usually the reaction set is limited to avoid excessive long computer calculation time. This may lead either to over- or underestimation of chemical species mixing ratios. The PI has furthermore clearly indicated what the main problems are when dealing with the effects of aircraft emissions on atmospheric chemistry i.e.:

- The assumption by modellers that emissions by subsonic aircraft mainly occur in the upper troposphere while in fact may be up to 50% occurs in the lower stratosphere, where the effects should be different.
- The assumption by many modellers, that large scale mixing of emissions immediately occur.
- The negligence of nonlinear reactions involving NO_y species and heterogeneous chemistry occurring on (ice)particles in the contrail.

For these reasons the calculated effects given in recent literature of aircraft emissions on e.g. the O_3 column density distribution are questionable.

The CH_4 study has not been dealt with in this summary but will be reported at a later stage in the final report.
An assessment of this part of the project has therefore been omitted.

4.5 Continental ozone issues; monitoring of trace gases,data analysis and modelling of ozone over Europe "Dutch contribution to the EUROTRAC-TOR project"

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Introduction
The Dutch part of the EUROTRAC-TOR project consists of contributions from TNO, KEMA and RIVM. The research activities concentrate on measurements at the high quality observatory 'Kollumerwaard', interpretation of the data, hosting the international TOR data base and chemistry and transport modelling. The interpretation activities centre around four basic tasks as they were posed in the NRP-TOR project proposal:

1. How much higher is the mean ozone concentration in the boundary layer over Europe than that averaged over northern mid-latitudes, and what is the seasonal, latitudinal and vertical variation of ozone within the adjacent free troposphere? Is there a secular trend in the concentrations of ozone and precursor molecules in the boundary layer or in the background atmosphere ?
2. What are the emissions and distribution of the precursors responsible for the particular excess of ozone ?
3. Can we measure how much of the excess ozone in the boundary layer spills over into the background atmosphere ? Is it possible to quantify by co-measurements of ozone and other tracers the proportion of ozone produced in the troposphere to that transferred from the stratosphere to the troposphere at our location ?
4. How much ozone and how many precursors are transported across regional boundaries ?

A full assessment of all the questions raised in the four tasks is beyond the scope of this extended abstract. In the following sections we discuss the Kollumerwaard observatory, the internal production of ozone in Europe, the exceedance of critical levels of ozone in Europe and exchange processes between the boundary layer and the free troposphere. A more elaborate evaluation of the above mentioned questions is expected to be given in our final NRP report.

The Kollumerwaard observatory

The Kollumerwaard observatory is one of the main sites within the EUROTRAC-TOR network. Partly due to the funding from the current NRP project the site is now equipped with instruments measuring O_3, NO, NO_2, PAN, VOCs, CO, CO_2, CH_4, j(NO_2), and meteorological parameters. Observations are generally performed on an hourly basis. In order to establish a coherent network and homogeneous observations several intercalibration experiments were carried out. The Dutch groups participated in round robins on VOCs, PAN, CO, CO_2, CH_4, NO_x and O_3. The data are reported regularly to the TOR data base which is hosted by RIVM. Furthermore the data are reported to the EMEP programme and the WMO climate data archive. The spatial distribution of the sites in the TOR network allows the observation of the chemical processing of polluted air typical of the European continent. The Kollumerwaard site, bordering the North Sea, is one of the sites representing the 'European boundary layer background'.

The Kollumerwaard data

(Abstract from a TOR report by M.G.M. Roemer, J.P. Beck, P. Esser and L.S. de Waal).

The ozone and oxidant (=NO_2 + O_3) concentrations measured at Kollumerwaard and averaged over the period March 1989 - February 1993 were analyzed as a function of wind direction. The wind sectors are taken at intervals of 10 degrees. The analysis demonstrates that for most wind directions the ozone concentrations at Kollumerwaard are strongly influenced by ambient NO_x concentrations. The ozone concentrations in the sector 090°-240° (European continent) are 10-20 ppb lower than the oxidant concentrations reflecting a shift in the photostationary state reaction due to elevated NO_x concentrations.

The lowest (daily averaged) oxidant concentrations are observed in the continental sector 090°-240°. The ozone and oxidant concentrations at ground level are determined by a number of processes; influx from the free troposphere, advection from other regions, chemical production and destruction, and deposition. It will be clear that air coming from the continent is more polluted with ozone precursors (VOC, CO, NO_x) than marine air and that therefore the ozone forming potential is higher. However, this does not necessarily have to lead to higher ozone/oxidant concentrations. The minimum in oxidant concentrations coming from the continent can be a result of:

1. lower ozone background concentrations (in the free troposphere) over the continent than over the Atlantic Ocean;
2. continental air being so rich of NO_x that it suppresses the OH concentrations and consequently blocks ozone production and/or
3. dry deposition.

The O_3 and O_x concentrations were also evaluated as a function of wind speed. Except for the summer season the ozone and oxidant concentrations tend to converge to some upper value with increasing wind speed. Stronger wind implies more turbulent mixing and consequently a better exchange of air with the free troposphere. Since from these measurements alone we cannot establish whether at high wind speeds the observations represent truly free tropospheric air we call it pseudo free tropospheric air. In the northern wind sector the free tropospheric oxidant concentrations are 30-33 ppb in winter. During the summer months a different behaviour is observed. Ozone and oxidant concentrations increase at low

wind speeds until a maximum and decrease thereafter. A possible explanation may be found in the factor that bad weather and associated full cloud cover during the passage of depressions considerably lowers the ozone production.
The ozone data from the former Kloosterburen site and the Kollumerwaard site were analyzed on trends. The trend in the ozone concentration from all data is -1.2% per year (1979-1993) and of oxidant it is -1.2% per year. The same downward feature is observed from the dataset from the clean sector in the north. However, the annual trend in this sector is less downward (-0.6 and -0.9%.year for ozone and O_x respectively) then the trend averaged over all wind directions.

The internal production of ozone within Europe
(Summary from Beck and Grennfelt, 1994).
The internal production of ozone within Europe was estimated by selecting monitoring stations from the TOR network which were found to be very little affected by local sinks as well as by European ozone production and destruction. Emission of NO_x from traffic in the vicinity of a monitoring station is an important sink for ozone, in particular during inversions when high NO concentrations may consume a substantial part of the ozone. Another sink is the deposition to vegetation during nighttime inversions. Both sinks may cause systematic diurnal variation in the concentration of O_3. In this evaluation the ratio maximum to minimum (O_3max / O_3min) hourly concentrations from the mean diurnal variation for the summer and winter half year respectively were used. The ratios varied considerably; from 5 to 8 in the areas most influenced by local sinks to 1.04 - 1.40 in the areas with the smallest influence from local sinks. The second criterion was that the stations should very seldom experience ozone episodes. Only four lowland (<500 m a.s.l.) monitoring stations were found fulfilling these criteria. These were Jelöy and Svanvik in Norway, Mace Head in Ireland and Strath Vaich in Scotland. At these stations ozone episodes very seldom occurred.
The mean diurnal variation from the four background stations were assumed to represent the background ozone concentration in Europe. The summertime mean concentration at the four background sites was 32 ppb. The internal ozone production was then calculated as the difference between the diurnal curves from the actual monitoring station and the mean for the four background sites. At most sites this approach gives a production of ozone during daytime (mainly between 9:00 and 21:00h) and a destruction of ozone during the night. Since most vegetation effects are caused by stomatal uptake of ozone, it may be more appropriate to look only at daytime differences. Based on these assumptions the internal ozone production in Europe has been calculated to be of the order of 10-30 ppb at remote lowland sites in central Europe. In the south of Scandinavia the internal ozone production is of the order of 5-8 ppb. In the south of the UK, as well as at sites on the continent more influenced by local and mesoscale pollution, several sites show a mean ozone destruction, which at some sites may exceed 10 ppb. Table 4.5 summarizes the analysis on internal ozone production in Europe.

Table 4.5
Internal ozone production in Europe calculated from the TOR network as the difference in daytime ozone concentration between the actual monitoring station and the mean of the concentrations at four 'boundary layer background' sites

Monitoring area	Number of stations	Internal ozone production (ppb)
Continental Europe; remote sites	6	5 – 30
Continental Europe; urban sites	8	- 5 – + 10
British Isles - south of 54°N	9	- 13 – + 8
British Isles - north of 54°N	6	0 – 3
Scandinavia - south of 62°N	12	5 – 8
Scandinavia - north of 62°N	6	- 3 – + 3

Ozone concentrations in Europe in relation to the critical level concept
(The following section is a summary from a paper by Grennfelt and Beck presented at a UN-ECE meeting in Geneva, 1993).
In order to develop effect oriented control strategies for regional air pollution the concept of critical loads and levels was developed. The concept was accepted in Europe for the assessment of the effects of acidic deposition and it will probably be the basis for the development of control strategies for ozone as well. It is now based on the exceedance of ozone concentrations over a threshold concentration and it is expressed in ppb.hours units. One important issue is to what extent episodic ozone and background ozone contribute to the exceedance of the proposed 40 ppb base concentration. If episodes make the largest contribution, it seems reasonable to concentrate control strategies to eliminate episodic ozone but if the background ozone makes an important contribution it may be necessary to direct strategies to the free tropospheric background.
The importance of episodes for a selected number of TOR sites was evaluated. If we define episodes as hours when the ozone concentration exceeds 60 ppb, episodes contribute to the exceedances by more than 50% at most sites, where the exceedance of less than 2000 ppb.hours per growing season, the contribution from episodes is at most sites less than 50% and at remote sites less than 30%. So the central European oxidant problem is mostly an episode problem while episodes play a minor role for the exceedance of the critical levels at the outskirts of Europe. It is obvious that the ways the critical levels are formulated may influence the control strategies for photochemical ozone in Europe. If critical levels are set to an exceedance of 50 ppb, the control of ozone will almost entirely be directed towards central Europe and one may assume that the exceedance may disappear at the outskirts by controlling the central European problem. If, on the other hand, the base level is set to 30 ppb, ozone becomes an all - European problem and control strategies may be directed towards all Europe. Since non-episodic conditions play an important role for the exceedance of the 30 ppb level it may be necessary to direct control measures to sources outside Europe and also to longer lived components like CH_4 and CO.

Exchange of ozone between the atmospheric boundary layer and the free troposphere

(This section summarizes a presentation by J.P. Beck at the EUROTRAC symposium in Garmisch Partenkirchen, April 1994).

The ozone budget in the troposphere is composed of transport from the stratosphere, photochemical production, deposition at the earth's surface and photochemical destruction. The net photochemical production includes ozone formation both in the free troposphere (FT) and in the atmospheric boundary layer (ABL). There is transfer of air between the FT and the ABL; therefore a separate ozone budget of both layers may be drawn up. Despite the fact that the importance of transport processes on the FT and ABL ozone budgets has been known for long, there is still a large quantitative uncertainty about the fluxes involved.

Except for transfer of ozone between the ABL and the FT, the transport of VOC and NO_x is also of importance because vertical mixing of these components may, due to the non-linearity in ozone formation, cause more efficient ozone production from the same emissions in the FT than would occur directly in the ABL.

The influence of the diurnal cycle in the ABL depth, caused by convective activity, on exchange between the ABL and the FT was studied using a combination of the ground based TOR network, vertical profiles of ozone and meteorological parameters, synoptical information over landcover data. These 'ingredients' were integrated with parametrizations of atmospheric processes in a data analysis model. The convective exchange processes and their influence on the ozone budget at the TOR station Uccle (B) were evaluated with this data analysis model for every hour covering the full year of 1989.

The analysis revealed a flux directed from the ABL to the FT at the Uccle (B) location averaged over June, July and August 1989 of 0.77 x 10^{-3} mole.m^{-2} .day. The downward FT to ABL flux was 0.33 x 10^{-3} mole.m^{-2}.day in the same period. So the net flux is directed upward from the ABL to the FT and has a magnitude of 0.43 x 10^{-3} mole.m^{-2}.day. If we multiply this number with the surface of the countries in northwestern Europe (2,442,510 x 10^6 m^2) it results in a net ABL to FT transport of 1.0 Gmole.day^{-1}. This corresponds to 4 – 6% of the daily cross tropopause flux of ozone in the northern hemisphere in summer[4].

Besides convective growth of the ABL depth, the exchange of air between the ABL and the FT takes place through several meteorological phenomena like clouds, frontal systems, heat island phenomena etc. The influence of these processes is not assessed in the present analysis.

Continental modelling

The ozone budget over Europe consists of three terms:

1) transport in and from other areas including the free troposphere;
2) chemical production and destruction of ozone in the European boundary layer
3) loss of ozone due to dry deposition.

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4 Footnote added by the coordinator (R. Guicherit).
Roemer (1990, report R 90/223) has calculated by means of a 2D-model a yearly net ABL to FT flux of 70 Mton O_3 (0.25 Gmole.day^{-1}) for an zonal area covering 30-55 N.

The LOTOS (LOng Term Ozone Simulation) model is one of the few models covering the whole of Europe and describing the major transport and chemical processes important to photochemistry.
Model simulations show that in Western Europe the influence of transport of ozone from elsewhere, i.c. The Atlantic Ocean plays an important role for the plant growing season ozone concentrations in this part of Europe. A reduction of 20% of the ozone values advected from over the Atlantic Ocean resulted in 5-10T reduction of growing season ozone concentrations over Western Europe. This reduction is somewhat larger than reduction achieved by a 30% reduction of anthropogenic European VOC and NO_x emissions and much more than the effect of a 30% CO emission reduction. The effect of Atlantic inflow of course becomes less over the more continental parts of Europe.

Model intercomparisons
Three Eulerian models [EURAD (Univ. of Cologne), REM (Univ. of Berlin) and LOTOS (TNO) and one Lagrangian model (EMEP) have been used and are being used in an intercomparison of European models. If the model results are evaluated on a rather general level, for instance daily or weekly averages and tendencies, the four models behave in quite a similar fashion with respect to the calculated ozone values. However, if the comparison is carried out in more detail (time specific values, wind roses) the discrepancies can become rather large. It appears that this also holds for the comparison with observations. Time series of observations and model results are found to be in a band of 20-30 ppb width. Agreement or disagreement with observations are evenly distributed among the models. None of the models appear to be of better or even superior quality than the others. Given the differences among the models it seems that they have features in common that limits their success in simulating ozone time series at specific sites. The coarseness in resolution, spatially as well as temporal, and the lack of detailed input information (emissions) seems likely candidates in creating discrepancies between models and observations.

Assessment
In this project amongst other, the fluxes into and out of the European free troposphere are studied and determined. In this way the contribution of Europe to the global or hemispherical budget of O_3, CO_2, CH_4 and NO_x can be determined. The regional aspect of O_3 as a greenhouse gas will also be evaluated at a later stage. Although continental in nature this project is of extreme importance to understand production and destruction processes of one of the important greenhouse gases i.e. O_3. (As a matter of fact O_3 next to CO_2 may become, within a few decades, the most important tropospheric greenhouse gas over the Northern Hemisphere at our latitudes). Moreover "photosmog" has now become an environmental issue of global dimensions of which adverse effects are worse than for e.g. CO_2. Finally, O_3 impacts on the lifetimes and, consequently on the troposphere concentrations of most atmospheric trace gases, including CH_4 and hydrogen containing replacements of the CFC's, which are themselves greenhouse gases. For this reason results obtained by this project are of importance for the consistency of environmental policy making. The project has already given some insight in the processes mentioned before; the O_3 trends in the lower (free) troposphere and the O_3 budget in the free troposphere. Interesting to note that for

some wind sectors there seem to be a decrease in O_3 levels for the period (1979-1993) while in others a slight increase? This is a peculiar situation because other European stations show O_3 levels which are still on the increase. However, the percentage increase seem to have slowed down in recent years.

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6. REFERENCES

Allaart, M.A.F., Helder, H., Heijboer, L.C. 1993. On the relation between ozone and potential vorticity. Geophysical Research Letters 9: 811-814.

Allaart, M.A.F., Heijboer, L.C. Kelder, H., 1994. On the transport of trace gases by extra-tropical cyclones. Proceedings of the Quadrennial Ozone Symposium 1992, p. 82-84.

Andreae M.O., 1990. Proposed feedback cycle between climate and marine DMS production. Marine chemistry 30: 1-29.

Arnold, F. and G. Knop, 1987. Stratospheric trace gas detection using a new balloon-borne ACIMS method. Int. Journ. of Mass and Ion Processes 81: 33-44.

Arnold, F., J. Scheid, Th. Stilp, H. Schlager, M.E. Reinhardt, 1992. Measurements of jet aircraft emissions at cruise altitude I: the odd-nitrogen gases NO, NO_2, HNO_2 and HNO_3. Geophys. Res. Lett. 12: 2421-2424.

Beck, J.P. and Grennfelt, 1994. The internal production of ozone within Europe. Atm. Env. Vol. 28: 129-140.

Beck, J.P., C.E. Reeves, F.A.A.M. de Leeuw, S.A. Pencket, 1992. The effect of aircraft emissions on tropospheric ozone in the northern hemisphere. Atm. Env. 25A: 17-29.

Bernhard, G., 1993. Einfluß von Diffusor-Eigenschaften auf die Bestimmung von Bestrahlungsstärken im UV-Bereich: Versuchsaufbau, Messung und Korreckturverfahren, IFU Schriftenreihe, Bd. 22, Garmisch-Partenkirchen.

Bordewijk, J.A., Slaper, H., Reinen, H.A.J.M., Schlamann, E., 1994. Reduction factors of effective-UV and global radiation; a method to calculate effective-UV daily doses from measurements of global radiation (In press).

Bruhl, C., and P.J. Crutzen, 1988. Scenarios of possible change in atmospheric temperatures and ozone concentration, due to man's activities, estimated with a one-dimensional coupled photochemical climate model. Climate Dynamics 2: 173-203.

Brühl, C. and P.J. Crutzen, 1989. High sun conditions, Geoph. Res. Lett. 16: 703-706.

Cess, R.D. et al., 1989. Interpretation of cloud-climate feedback as produced by 14 atmospheric General Circulation Models, Science 245: 513-516.

Charlson, R.J., J.E. Lovelock, M.D. Andreae and S.G. Warren. 1987. Nature 326: 655-661;

Christensen, J.H. and E. van Meijgaard, 1992. On the construction of a regional atmospheric climate model, KNMI TR-147.

Crutzen, P.J. and L.T. Gidel, J., 1983. A two dimensional photochemical model of the admonsphere. 2: the tropospheric budgets of the anthropogenic chlorocarbons, CO, CH_4, CH_3CL and the effects of various NO_x sources on tropospheric ozone. Geoph. Res. 88: 6641-6661.

Curtis, A.R., W.P. Sweetenham, 1985. FACSIMILE Release H User's Manual. Report AERE R 11771.

Curtis, A.R., and W.P. Sweetenham, 1987. Facsimile/checkmat., Harwell Lab. Report No. AERE R 12805.

De Leeuw, F.A.A.M., 1988. Modelmatige berekening van fotolyse snelheden relevant voor troposferische chemie. RIVM report 228603003 (in Dutch).

Dentener, F., 1993. Heterogeneous chemistry in the troposphere. Ph.D. Thesis, Universiteit Utrecht.

Derwent, R.G. 1982. Two-dimensional model studies of the impact of aircraft exhaust emissions on tropospheric ozone. Atm. Env. 16: 1997-2007.

Deshler, T., B.J. Johnson and W.R. Rozier, 1993. Balloon-borne measurements of Pinatubo aerosol during 1991 at 45^0 vertical profiles, size distributions and volatility. Geoph. Res. Lett. 20, 14: 1435-1438.

Drummond, J.W., D.H. Ehhalt, A. Volz, 1988. Measurements of Nitric Oxide Between 0-12 km Altitude and 67 N to 60 S Latitude Obtained During STRATOZ III. J. Geophys. Res. 93, 15: 831-849.

Ehhalt, D.H., F. Rohrer, A. Wahner, 1992. Sources and distribution of NO_x in the upper troposphere at Northern Mid-Latitudes. J. Geophys. Res. 97: 3725-3738.

Feijt, A.J., 1992. The earth radiation budget experiment: overview of data-processing and error sources, KNMI TR-146.

Fortuin, P., Langematz, U., Dorland, R. van, Kelder, H., 1994. Concurrent ozone and temperature trends derived from sonde measurements, submitted to the proceedings of "NATO-ASI atmospheric ozone as a climate gas".

Gardiner, B.G., and Kirsch, P.J., 1993. Setting Standards for European Ultraviolet Spectroradiometers, Draft report, Cambridge.

Gelinas, R.J., J.J. Walton, 1974. Dynamic-kinetic evolution of a single plume of interacting species. J. Atm. Sciences p. 1807-1813.

Gezondheidsraad 1993. UV straling uit zonlicht; Advies van een commissie van de Gezondheidsraad.

Gidel, L.T., P.J. Crutzen and J. Fishman, 1983. A two dimensional photochemical model of the atmosphere. 1: chlorocarbon emissions and their effect on stratospheric ozone. Geoph. Res. 88: 6622-6640.

Gillotay, D., The 'Transportable Lamp System', a relative reference for the future. Final Report EC-STEP 076, Brussels.

Gregory, G.L., Hudgins, C.H. and R.A. Edahl, 1994. Laboratory evaluation of an airborne ozone instrument that compensates for altitude/sensitivity effects.Env. Sci. Technol. 17: 100-103, 1983.

Hauglustaine et al., 1994. Model calculations. J. of Geoph. Res. 99: 1173-1186.

Heijboer, L.C. and Kelder, H. A nonlinear analytical model of developing extra-tropical cyclones with the associated flow regimes and transport of trace gases. Submitted to Quarterly Journal of the Royal Meteorological Society.

Hidalgo, H. and P.J. Crutzen, 1977. The tropospheric and stratospheric composition perturbed by NO_y emissions of high-altitude aircraft. J. Geophys. Res. 82: 5833-5866.

Hübler, P.C. Murphy, 1987. Ozone production in the rural troposphere and the implications for regional and global ozone distributions. J. Geophys. Res. 92: 4191-4207.

Isaksen, I.S.A., 1980. The tropospheric ozone budget and possible man made effects. Proc. of the Quadrennial Ozone Symposium. WMO, Boulder, 4-9 August.

Kawa, R.S. et al., 1990. Measurements of total reactive nitrogen during the airborne arctic stratosphere expedition. Geoph. Res. Lett. 17, no. 4: 485-488.

Kelder, H. and Teitelbaum, H., 1992. A note on instabilities of as Kelvin-Heimholtz velocity profile in different approximations. Il Nuovo Climento 14: 107-118.

Kelder, H., Velthoven, P. van, Allaart, M., 1994. Exchange between the troposphere and the stratosphere. Accepted for publication in the proceedings of the EUROTRACK symposium 1994.

Kneizys, F.X. et al., 1988. Users' guide to Lowtran-7, Air Force Geophysics Laboratory, Hanscom AFB(MA, AFGL-TR-88-0177.

Lary, D.J. and J.A. Pyle, 1991. Diffuse radiation, twilight and photochemistry. Journ. of Atm. Chem. 13: 373-392.

Liu, S.C., M. Trainer, F.C. Fehsenfeld, D.D. Parrish, E.J. Williams, D.W. Fahey, G. Loewenstein, M. et al., 1993. New obervations of the NO_y/N_2O correlation in the lower stratosphere. Geoph. Res. Lett. 20, (22): 2531-2534.

Lott, F., Kelder, H., Teitelbaum, H., 1992. A transition from Kelvin-Helmholtz instabilities to propagating wave instabilities, Physics of Fluids 4: 1990-1997.

Madronich, S. 1987. Photodissociation in the atmosphere: 1. Actinic flux and the effects of ground reflections and clouds. J. Geophys. Res. 92: 9740-9752.

McInnex, G., and C.T. Walker, 1992. The global distribution of aircraft air pollutant emissions. Warren Spring Laboratory, LR 872 (AP).

Morcrette, J., 1991. Radiation and cloud radiative properties in the European Centre for Medium Range Weather Forecasting system, J. Geophys. Res. 96: 9121-9132.

Müller, R., and P.J. Crutzen. Chlorine activiation mechanisms during polar night. J. Geoph. Res. 98: 20483-20490.

Müller, J.F., 1992. Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases. J. Geophys. Res. 97: 3787-3804.

Ramanathan, V. et al., 1989. Cloud radiative forcing and climate: Results from the earth radiation experiment, Science 243: 57-63.

Reinen, H.A.J.M., Schlamann, Ec., van Sonderen, J.F., Slaper, H., 1993. A new solar UV radiation monitoring station in The Netherlands. Stamnes, K.H. (ed.): In Atmospheric Radiation, Proc. SPIE 2049: 340-349.

Reinen, H.A.J.M., Schlamann, E., Bordewijk, J.A., Slaper, H. 1994. Monitoring UV radiation in The Netherlands set-up and preliminary results. In press in proceedings of the European symposium on effects of environmental UV radiation Munich 27-29 okt. 1993.

RIVM 1993. Nationale Milieuverkenning 3: 1993-2015; ISBN 90 6092 679 X.

Rossow, W.B. and L.C. Garder. 1993. Validation of ISCCP cloud detections. J. Climate 6: 2370-2393.

Saunders, R.W. and K.T. Kriebel. 1988. An improved method for detecting clear sky and cloudy radiances from AVHRR data, Int. J. Remote Sensing 9: 123-150.

Siebesma, A.P. and Cuijpers, J.W.M.: Evaluation of parametric assumptions for shallow cumulus convection. Submitted to Journal of atmospheric sciences 1993.

Slaper, H., den Elzen, M.G.J., van der Woerd, H., de Greef, J., 1992. Ozone depletion and skin cancer incidence: an integrated modelling approach; June 1992; RIVM report 749202001.

Slaper, H., den Elzen, M.G.J., van der Woerd, H.J., 1994. Ozone depletion and skin cancer risks: a scenario study. (In press). In proceedings of the European symposium on effects of environmental UV radiation Munich 27-29 okt. 1993.

Slaper, H., 1993. Ozone depletion and skin cancer incidence: science and policy implications of risk-oriented approaches: in press in proceedings of the US-Dutch symposium: Comparative Risk Analysis and Priority Setting of Air Pollution Issues, June 7-11, Keystone, USA.

Slaper, H., 1987. Skin cancer and UV-exposure: investigations on the estimation of risks, Thesis, University of Utrecht.

Sonderen, J.F. van, Slaper, H., Swart, D.P.J., Smetsers, R.C.G.M., 1991. Definitiestudie spectrometrische UV-meetopstelling. RIVM report 249104001.

Stammes, P. et al. 1994. TEBEX observations of clouds and radiation - potential and limitations. KNMI TR-162.

Teitelbaum, H., Ovarlez, J., Kelderman H, Lott, F., 1994. Some observations of gravity-wave-induced structure in ozone and water vapour during EASOE. Geophysical Research Letters 21: 1483-1486.

Tolbert, M.A., M. Rossi and D.M. Golden, 1988. Hetrogeneous reactions of $CIONO_2$, HCL and HNO_3 with sulfuric acid surfaces at stratospheric temperatures. Geoph. Res. Lett. 15. No. 8 847-850.

Tsay S.Ch. and Stamnes K., 1992. Ultraviolet radiation in the Arctic: the impact of potential ozone depletion and cloud effects. J. Geophys. Res. 97: 7829-7840.

UNEP 1991. Environmental effects of ozone depletion. Panel Report Pursuant to article 6 of the Montreal Protocol on Substances that deplete the ozone layer under Auspices of the UNEP.

Von Clarmann, T. et al., 1993. Retrieval of stratospheric O_3, HNO_3, and $CLOnO_2$ profiles form 1992 MIPAS-B limb emission spectra, results and error analysis. Journ. of Geoph. Res. 98: No. D11.

Van der Hage, J., Boot W., van Dop, H., Duynkerke, P.G. and Vilà-Guerau de Arella, J., 1994. A photo-electric detector suspended under a balloon for actinic flux measurements. Journal of Atmospheric and Oceanic Technology 11: 674-679.

Van Weele, M. and Duynkerke, P.G., 1993. Effect of clouds on the photodissociation of NO_2: observations and modelling. Journal of Atmospheric Chemistry 16: 231-255.

Van Weele, M., Vilà-Guerau de Arellano, J. and Kuik, F., 1994. Combined measurements of UV-A actinic flux, UV-A irradiances and global radiation in relation to photodissociation rates. Submitted to Tellus.

Van Weele, M., Vilà-Guerau de Arellano, J. and Duynkerke, P.G., 1993. A parameterization of the effects of clouds on photodissociation rates; comparisonwith observations. Proceedings XX ITM on Air Pollution Modelling and its Application, Valencia, Spain.

Velders, G.J.M., Heijboer, L.C., Kelder, H., 1994. The simulation of the transport of aircraft emissions by a three-dimensional global model. Annales Geophysicae 12: 385-393.

Velthoven, P.F.J. van, Wauben, W.M.F., Kelder, H. 1994. A comparative study of global 3-D transport of NO_x emitted by aircraft. Proceedings of "Impact of Emissions from aircraft and spacecraft upon the atmosphere", 174178.

Verver, G.H.L., 1994. Comments on: "A modified K-model for chemically reactive species in the planetary boundary layer" by Fujihiro Hamba. Accepted for publication in Journal of Geophysical Research Letters.

Vilà-Guerau de Arellana, J., Duynkerke, P.G. and van Weele, M., 1994. Tethered-balloon measurements of actinic flux in a cloud-capped marine boundary layer. J. Geophys. Res. 99: 3699-3705.

Volz-Thomas, A., 1992. Proceedings of the EUROTRAC Symposium '92. In Borrell P.M. et al. (eds). Ac. Publ. B.V. The Hague.

Wienhold, F.G., T. Zenker, and G.W. Harris, 1994. A dual channel two tone modulation tunable diode laser spectrometer for ground bases and airborne trace gas measurements, to be submitted to Appl. Opt.

Zimmermann, P.H. 1988. Moguntia: a handy global tracer model. In: Van Dop, H. Air Pollution Modelling and its applications VI. NATO/CCMS, Plenum, New-York.