

BELGIAN IMPULSE PROGRAMME  
**GLOBAL CHANGE**  
1990-1996  
CHANGES IN  
THE CHEMICAL COMPOSITION  
OF THE ATMOSPHERE



Federal Office for  
SCIENTIFIC, TECHNICAL  
AND CULTURAL AFFAIRS

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The aim of this report is to provide an overview of the research results of the Belgian Global Change Programme (1990-1996) for policymakers, scientists who are not experts in this field, and anyone else who is interested. This section on atmospheric chemistry also includes the results of the Belgian participation in the EUREKA European Programme on the Transport and Transformation of Trace Gases in the Troposphere over Europe (EUROTRAC). Several environmental issues of societal importance are considered. The report highlights Belgian expertise in this field and Belgium's contributions to international research efforts.

The report also provides background information and recommendations for policymakers, and will help to increase public awareness of the key issues of global change. It is not the aim of the report to be exhaustive in presenting research results, nor to duplicate what has been achieved in other assessments. More detailed information on the results of the Belgian Global Change Programme (1990-1996) can be found in the final reports on each project and in related publications.

The preparation of this document required considerable dialogue between scientists with a different backgrounds. This process of information exchange and cross-fertilisation between scientists is itself of interest, and is the key to successful multi-disciplinary research on global change.

## MEMBERS AND AUTHORS OF THE A&I GROUP

**Chairperson:** M. VANDERSTRAETEN , Head of the Impulse Programme on Global Change, Federal Office for Scientific, Technical and Cultural Affairs, Brussels

**Person consulted:** G. BRASSEUR, Professor, Université Libre de Bruxelles, Faculté des Sciences, Département des Sciences de la Terre, Brussels and Director of the National Center for Atmospheric Research, Boulder, Colorado, USA

ADAMS F., Professor, Micro- en Sporenanalyse Centrum, University of Antwerp

COLIN R., Professor, Laboratory of Molecular Physical Chemistry, Free University of Brussels (ULB)

DE MUER D, Dr., Royal Meteorological Institute, Brussels

GERARD J.C., Professor, Laboratory for Planetary and Atmospheric Physics (LPAP), Institute of Astrophysics, University of Liège

MAENHAUT W., Professor, Institute for Nuclear Sciences, Laboratory of Analytical Chemistry, University of Gent

PEETERS J., Professor, Department of Chemistry, Laboratory of Physical and Analytical Chemistry, KU Leuven

SIMON P.C., Professor, Belgian Institute for Space Aeronomy, Brussels

VAN CLEEMPUT O., Professor, Faculty of Agricultural and Applied Biological Sciences, University of Gent

VANDER AUWERA J., Professor, Laboratory of Molecular Physical Chemistry, Free University of Brussels (ULB)

VAN DER WERF A., Programme Manager Impulse programme on Global Change, Federal Office for Scientific, Technical and Cultural Affairs, Brussels.

VAN GRIEKEN R., Professor, Micro- en sporenanalyse Centrum, University of Antwerp

VINCKIER C., Professor, Department of Chemistry, Laboratory of Physical and Analytical Chemistry, KU Leuven

ZANDER R., Professor, Institute of Astrophysics, University of Liège

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# EXECUTIVE SUMMARY AND RECOMMENDATIONS

The chemical composition of the atmosphere is changing. A large amount of observational data suggests that some of these changes are caused by human activities. Agricultural practices, industry, domestic activities and transport all release in the atmosphere pollutants which may (directly or indirectly) affect our climate, with potentially important economic and social consequences. Pollution may also reduce the protection that the biosphere gives against harmful ultraviolet radiation, and, for example, increase the risk of skin cancer among humans. In severe cases, atmospheric pollution may produce health hazards, damage forests and reduce agricultural productivity. The causes of these societally important effects are beginning to be better understood through programmes such as the Belgian Global Change Programme and the Belgian participation in EUROTRAC (European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents over Europe).

## 1. Chemistry - Climate Interactions

The increasing concentrations in the atmosphere of the so-called "greenhouse gases" such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and halocarbons have a forcing effect on natural atmospheric processes. The consequences for the earth's climate are not well understood, but from numerous studies of atmospheric models we believe that the average surface temperature of the globe will increase by several degrees. An important factor that determines future climate forcing is the ability of the ocean and the terrestrial biosphere to store a fraction of the CO<sub>2</sub> released as a result of burning fossil fuels. Global models of the carbon cycle help to quantify the fluxes and storage of carbon in the earth's atmosphere, ocean and ecosystems.

Another potential cause of climate change is provided by the release in the atmosphere of anthropogenic sulphur compounds, especially SO<sub>2</sub>, produced as a result of coal burning. This gas is converted to aerosols which tend to scatter back into space part of the solar energy intercepted by the earth's atmosphere and consequently tend to cool the earth.

Most greenhouse gases have a long atmospheric lifetime and should produce climate forcing on a global scale. Sulphur compounds, on the other hand, have a much shorter lifetime, so the forcing they produce should affect mostly the industrialized regions of the world. The response of the climate system to such inhomogeneous changes can be studied using complex climate models. Large uncertainties remain, however, in the quantification of these climate changes (see report by the climate group).

The research conducted under the Belgian Global Change Programme and the Belgian participation in EUROTRAC leads us to recommend:

- a. In any *national or international* policy on climate change, the effects of radiatively active gases other than carbon dioxide (i.e. methane, nitrous oxide, halocarbons, tropospheric ozone) should be taken into account.
- b. As a tool for *environmental management*, emission inventories of greenhouse gases, SO<sub>2</sub> and ozone precursors in Belgium should be regularly updated and made accessible to the international scientific Community. The methodologies used to establish these inventories should be improved and harmonized at the national level in accordance with international guidelines.
- c. Without *substantial reductions in the atmospheric concentrations of greenhouse gases*, climate forcing will continue to increase and will most likely produce substantial changes in the earth's climate. Our own latitudes are likely to be affected (see report on climate impacts). Specific measures in relation to the Climate Convention, especially energy savings and the use of alternative sources of energy, should be implemented as soon as possible. Such measures will contribute to sustainable development.



- d. *The fact that some types of aerosols partly counterbalance greenhouse forcing cannot be used as an argument for maintaining high levels of particles in the atmosphere. These aerosols produce health problems, contribute to acidification of lakes and soils, reduce visibility and spoil buildings and materials. They also damage our cultural heritage.*
- e. *In spite of the fact that industrialized countries, including Belgium, have reduced their SO<sub>2</sub> emissions, industrialisation and land use changes in several developing countries (e.g. southeast Asia) could produce regional changes in climate forcing, with global consequences. It is therefore important for Belgium to support international measures addressing this question.*

As large uncertainties remain in our understanding of the processes affecting climate forcing, research in this area should address the following key issues:

- a. *Since changes in the atmospheric abundance of carbon dioxide represent a major contribution to climate forcing, the global carbon cycle should be further studied and related modelling capabilities should be supported.*
- b. *Belgian participation in international programmes using remote sensing techniques to monitor the state of the atmosphere should be maintained.*
- c. *Research should concentrate on the chemical budget of radiatively active gases and aerosols (chemical, physical and radiative properties) and their spatial distribution on local, regional and global scales.*
- d. *The radiative forcing of aerosols remains very uncertain. Research should better quantify the direct -(interactions with incoming solar radiation) as well as the indirect effects (cloud formation) of these aerosols.*

## 2. Stratospheric Ozone

*The observed reduction in the abundance of stratospheric ozone, and specifically the formation (since the late 1970s) of the Antarctic ozone hole each spring, is now unambiguously attributed to increased levels of industrially manufactured chlorofluorocarbons (CFCs) in the atmosphere. As a result of international agreements (e.g. the Montreal Protocol and its amendments), the production of these CFCs has been phased out, and this should restore the "natural" ozone layer in a time frame of several decades.*

Increasing levels of biologically harmful UV-B radiation have also been recorded over the last decade. There is a solid evidence that since 1980 the ozone column abundance over Belgium and other mid-latitude regions of the northern hemisphere has decreased by approximately 4% per decade (6% from January to May). *After the eruption of Mt. Pinatubo in the Philippines (1991), abnormally low ozone concentrations were recorded. These are believed to be due to the simultaneous presence of anthropogenic chlorine and increased aerosol concentrations in the stratosphere.*

The use of alternative halocarbons, such as the hydrogenated chlorofluorocarbons, is acceptable if their ozone depletion potential (ODP) and their *global warming potential (GWP)* is *substantially lower than those of the fully halogenated chlorofluorocarbons.*

For more than 20 years it has been suggested that the release in the atmosphere of nitrogen oxides by a projected fleet of high-altitude aircraft may deplete ozone in the stratosphere. Calculations based on our most up-to-date knowledge of chemical processes suggest that the impact of these aircraft is limited under most circumstances.

The research conducted under the Global Change Programme leads us to recommend:

- a. *The latest amendment to the Montreal Protocol should be strictly respected and implemented in Belgium. Belgium should contribute to the global implementation of the Protocol by transferring appropriate technologies to developing countries.*
- b. *Chlorofluorocarbons (CFCs) are being replaced by alternative compounds including hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Because of their demonstrated contribution to the greenhouse effect, however, these compounds should be limited to essential needs. They should be phased out over a reasonable period of time.*

- c. *Because stratospheric ozone depletion has been more severe than originally predicted, governments should take actions to support new and environmentally clean technologies. In addition, efforts should be made to recover, when possible, halocarbons from fire extinguishers, cooling systems and other CFC containing appliances.*
- d. *Ozone trends and UV-B radiation should be closely monitored in Belgium. Belgian observational capabilities within the framework of international networks, space programmes and coordinated European campaigns should be enhanced.*
- e. *The role of methyl bromide (CH<sub>3</sub>Br), which has various natural and anthropogenic sources, should be further investigated. However, because of the potential danger of this compound to the ozone layer, measures should be taken as soon as possible to reduce the use of methyl bromide as an agricultural fumigant.*
- f. *The government should make the general public more aware (e.g. through organized information campaigns) of the danger to human health of UV-B exposure. This problem is becoming more serious as ozone depletion takes place. It is recommended that daily UV-B forecasts of indices over the European continent be provided to the Belgian public through the news media.*

In addition to these measures, scientific research should focus on the following issues:

- a. *The budget of ozone and the mechanisms responsible for the observed ozone trends in the lower stratosphere and upper troposphere need to be better quantified through more accurate field observations of the relevant chemical constituents, as well as through laboratory and modelling studies.*
- b. *The potential causes of the observed ozone depletion at mid-latitudes need to be further studied. This requires a better understanding of heterogeneous chemical processes related to the presence of aerosols, as well as better quantification of mass exchanges through the dynamic barriers to meridional and vertical transport (the polar vortex, subtropical jet and tropopause).*
- c. *The potential impact of present and future aircraft emissions on atmospheric ozone should be further studied through a close collaboration between the scientific community, industry and governments.*

### **3. Tropospheric Ozone**

The increasing concentration of ozone in the troposphere, particularly in the boundary layer of the industrialized regions, is caused by increasing emissions of ozone precursors such as nitric oxide and

non-methane hydrocarbons. Episodes of photochemical ozone production are now often observed during summertime in Belgium.

*Even on a longer timescale the concentration of tropospheric ozone has been increasing: yearround increases of 1.0-1.5 %/yr have, for example, been recorded in Belgium and in the free troposphere. Model calculations suggest that the abundance of tropospheric ozone may have doubled since the beginning of the pre-industrial era. An important prerequisite for our understanding of the observed changes in tropospheric ozone is to determine the relative contributions of natural versus anthropogenic factors in the photochemical production of ozone.*

The research conducted under the Belgian Global Change Programme and the Belgian participain EUROTRAC leads us to recommend:

- a. *Because ozone and its precursors (hydrocarbons and nitrogen oxides) can be transported over hundreds of kilometres and because of the occurrence of ozone episodes, ozone reduction strategies must be developed on a European scale. To be most effective, the measures should be specific to each region of the European continent.*

- b. *In order to prevent ozone episodes, the authorities should have access to day-to-day model predictions indicating to what degree hydrocarbon and nitrogen oxide emissions should be reduced.*
- c. *A reduction in the anthropogenic emissions of hydrocarbons will not have a substantial effect on the background concentration of tropospheric ozone at the hemispheric scale. To limit the formation of ozone at that scale, the abundance of nitrogen oxides must be reduced.*
- d. *At the regional scale, stricter hydrocarbon emission standards may not lead to the expected improvement in air quality near forested areas, where biogenic (natural) hydrocarbons are abundant. In this case reduction of NO<sub>x</sub> emissions is the appropriate strategy.*
- e. *The monitoring network for tropospheric ozone and related chemical compounds at the surface and in the free troposphere should be maintained and, if possible, expanded. Additional species should be measured.*

*A strong scientific programme must be carried out to address the remaining uncertainties.*

*Important issues are:*

- a. *The global and regional budgets of NO<sub>x</sub> and hydrocarbons should be better quantified. The specific role of agricultural activities in the formation of tropospheric ozone precursors should be addressed. Surface exchanges of chemical compounds over different types of ecosystems need to be better understood.*
- b. *Modelling activities should be further developed, with predictive capabilities for ozone episodes and long-term changes. National and international harmonisation is required for this activity.*
- c. *Laboratory kinetic studies must further investigate the mechanisms leading to the formation of ozone, and specifically the photochemical degradation of hydrocarbons at various NO<sub>x</sub> concentrations. Generic chemical mechanisms for the major classes of hydrocarbons should be developed for use in models.*
- d. *The effects of ozone episodes on human health should be investigated by means of epidemiological and clinical studies. Ozone reduction scenarios based on cost/benefit relationships must be studied. Reliable data on the benefits to public health and crop yields of a substantial reduction in tropospheric ozone should be generated.*
- e. *Uncertainties in the observations of chemical compounds need to be reduced by the development of new and more accurate measurement techniques, instrument inter-comparison and coordinated field campaigns.*
- f. *Catalytic converters in automobiles should be inspected regularly (e.g. once a year) and checked for NO<sub>2</sub>-emissions.*

# 1 INTRODUCTION

Changes in the chemical composition of the atmosphere at the local, regional, and global scales are real and well-documented. The atmospheric abundance of several gases contributing to the greenhouse effect (including carbon dioxide, methane, nitrous oxide and halocarbons) has increased as a result of human activities. At the same time the concentration of sulphate particles, which are believed to cool the earth's surface, has increased in industrialized regions as a result of coal combustion.

Ozone too has been affected by human activities. Ozone absorbs solar ultraviolet radiation, and so protects the earth's biosphere (phytoplankton, crops, humans, etc.) from harmful UV-B radiation. It is now certain that the release of halocarbons, especially chlorofluorocarbons (CFCs), has led to substantial destruction of ozone in the stratosphere, and has caused the formation of a springtime "ozone hole" over Antarctica.

In the troposphere, on the other hand, the concentration of ozone is increasing. This is caused by the release of nitrogen oxides associated with combustion, and hydrocarbons of both natural and anthropogenic origin. Ozone buildup occurs not only in urban areas (where ozone "episodes" are observed in summer under particular meteorological situations), but also in remote regions of the northern hemisphere.

Ozone, which is a strong oxidant, is harmful to human health and can damage plants. It also affects the vertical distribution of temperature, especially

above the tropopause. Finally, ozone is a greenhouse gas, and as such is influencing the earth's climate.

The earth's atmosphere is generally described in terms of several thermal layers (Fig. 1.1) which are vertically stratified. For example, the troposphere, the region in which we live, extends from the surface to a height of approximately 12 km. Its temperature decreases with height at an average rate of about 7 degrees Celcius per km. This layer is characterized by rapid vertical exchanges of mass and energy associated with evolving weather patterns.

The layer above the troposphere extends to a height of around 50 km and is called the stratosphere. The temperature in the stratosphere increases with altitude, so this layer is very stable and resists vertical exchanges of mass and energy driven by convection. This region is also characterized by low concentrations of water vapour and high concentrations of ozone. Other atmospheric regions include the mesosphere (between 50 and 85 km) and the thermosphere (above 85 km).

Dynamic and chemical conditions in the atmosphere vary not only with height but also with latitude. The tropics, for example, are characterized by strong convective activity (tornadoes and hurricanes) and intense solar irradiation. Middle and high latitudes are characterized by meteorological processes at the synoptic scale (e.g. the passage of fronts) and more moderate photochemical activity.

The planetary boundary layer is directly influenced by exchange processes at the earth's surface; urban, rural and remote conditions need to be distinguished. The chemical composition of the earth's

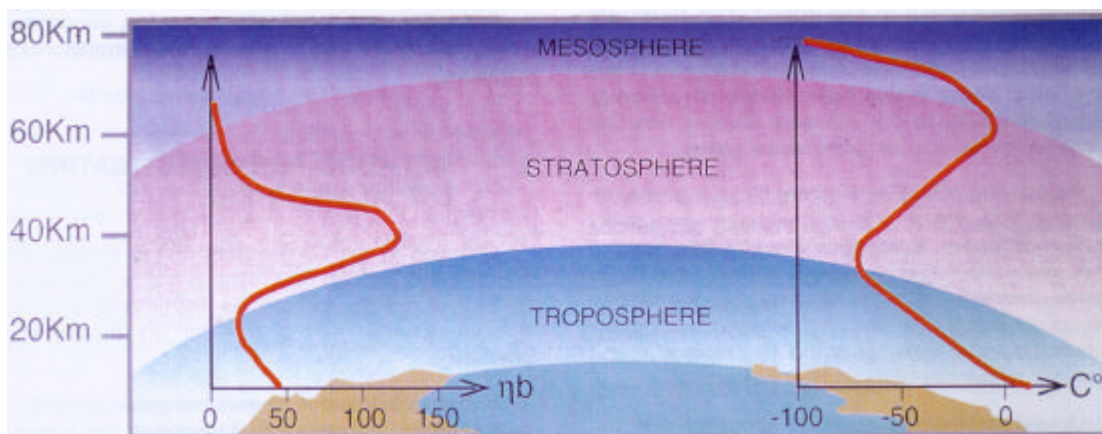


Fig. 1.1. – The earth's atmosphere and its vertical structure (WMO), (1995), The Changing Ozone Layer)

atmosphere is primarily a product of the biosphere. At the same time, through deposition processes, the atmosphere affects the biosphere. In addition, numerous complex chemical and photochemical transformations, as well as transport processes at various spatial and temporal scales, influence the distribution of trace constituents in the atmosphere.

Under natural conditions, the exchange of chemical compounds at the surface depends primarily on biological processes as well as on meteorological conditions in the planetary boundary layer. Perturbations are associated with agricultural practices (e.g. the extensive use of fertilizers, growing numbers of cattle, and the burning of biomass) and industrial and domestic activities (energy production, chemical manufacture, transport). The latter originate mostly in Europe, north America, and south-east Asia, and have substantially affected the atmospheric composition in the northern hemisphere, even far away from the pollution sources.

Observations from ground-based, airborne and spaceborne instruments have provided key information to document the fundamental processes that determine the regional and global distribution of gases and aerosols in the troposphere and stratosphere. The climatic impact of anthropogenic perturbations remains to be estimated, and requires the development of sophisticated models.

Biospheric processes affect the chemical composition of the atmosphere through the surface exchange of several gases:  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$  and a large variety of hydrocarbons. Biospheric sources of  $\text{CO}_2$  are mainly related to deforestation and soil carbon loss by microbial processes. In reduced soil systems such as natural and managed wetland, rice paddies and landfills,  $\text{CH}_4$  is produced by a consortium of anaerobic micro-organisms in the last step of the catabolism of organic carbon. On the other hand wetlands also have a large sequestering capacity for  $\text{CO}_2$ , so it is not clear whether they are a net source or sink for greenhouse gases.

Natural and cultivated soils are a major source of  $\text{NO}$  and  $\text{N}_2\text{O}$ , mainly through bacterial nitrification and denitrification. Nitrification characterizes aerobic soils, while denitrification occurs in soils where  $\text{O}_2$  is limited. Increasing nitrogen input by applying fertilizers, or increasing carbon and nitrogen cycling by converting forest and grassland to cropland, substantially influences  $\text{NO}$  and  $\text{N}_2\text{O}$  production.

Upland soils can also be an important sink for atmospheric methane. However, the same processes which increase  $\text{N}_2\text{O}$  and  $\text{NO}$  production in soils also decrease the  $\text{CH}_4$  uptake capacity of upland

soils. Land use changes, increased fertilizer use and greater nitrogen deposition rates can therefore have a doubly negative impact on the biospheric contribution of aerobic soils to greenhouse gases.

Ammonia volatilization from mineral fertilizers and manure is an important contribution to  $\text{NH}_3$  emission and consequently to acid deposition. This in turn increases the formation and emission of  $\text{NO}$  and  $\text{N}_2\text{O}$ .

This report is part of a more comprehensive document integrating the results of global change research financed by the OSTC (including the research relevant to Belgium's participation in EUROTRAC). It addresses the methodologies used to investigate the important processes occurring in the atmosphere. It discusses the global budget of ozone and other chemical compounds in the stratosphere, and assesses the causes of ozone depletion in the polar and mid-latitude regions. It emphasizes the role of heterogeneous chemistry on polar stratospheric clouds and sulphate aerosols in an atmosphere perturbed by the presence of man-made chlorofluorocarbons (CFCs).

The report also discusses the mechanisms that are believed to determine the formation and destruction of ozone in the troposphere on a global scale, and emphasizes the role of natural and anthropogenic ozone precursors. The role of sulphate aerosols and the related budget of sulphur compounds is also discussed. Finally, it addresses the impacts of several potential changes in the chemical composition of the atmosphere: first, the change in the biologically harmful solar ultraviolet radiation reaching the earth's surface caused by changes in ozone abundance; and second, the changes in climate forcing associated with increasing concentrations of greenhouse gases and tropospheric aerosols.

## 2 METHODS FOR INVESTIGATING THE ATMOSPHERE

Changes in the composition of the atmosphere are detected through field measurements. The development of reliable and precise instruments is therefore an essential part of research on atmospheric chemistry.

Instruments capable of measuring the concentration of minor gaseous constituents in the troposphere and stratosphere have been available for many years. However, the need for faster and more accurate measurements of a widening range of species

- including the measurement of several different gases simultaneously - has required a substantial effort to improve the performance of these instruments.

Instruments can be used on the ground, in aircraft or balloons for studies of a restricted geographical area, or in satellites orbiting the earth for long-term observations over wide areas. Chemical species are not the only components of the atmosphere affecting its evolution. Suspended solid particles (aerosols) and clouds also play an important role and improved instruments to measure these are also needed.

Laboratory work is also important in atmospheric research. Not only are many instruments developed and tested in the laboratory before being used in the field, but fundamental properties of atmospherically important molecules – reaction rates, absorption cross sections, reaction products and quantum yields of photodissociative processes must be carefully measured in the laboratory before we can understand the complex chemistry of the atmosphere. Special computer algorithms must also be developed in the laboratory to allow us to extract meaningful data from raw field measurements.

Field measurements yield a picture of the current state of the atmosphere, whilst accumulated historical data provides information about past trends. We also need to know how the atmosphere will change in the future: reliable short-term and long-term predictions of changes on both regional and global scales are mandatory before decisionmakers can act. These predictions can only be achieved by simulation. Complex computer-based models relating natural and anthropogenic emissions to their environmental consequences are indispensable tools for policymakers.

## 2.1 Instruments

### 2.1.1 Atmospheric gases

Most atmospheric composition measurements use spectroscopic techniques. The principle of spectroscopy is the absorption of electromagnetic radiation at specific wavelengths (from the far infrared to the near ultraviolet) by molecules present in the atmosphere. The technique has been used for many years in the laboratory but has required adaptation to meet the requirements of atmospheric science and to provide the ruggedness necessary for use in the field.

Many species are present in the atmosphere only at very low concentrations; most are measured in parts per billion by volume, but molecules at concentrations as low as 0.1 parts per trillion by volume can have a significant influence on chemical and

physical processes in the atmosphere. Measuring such low concentrations requires long absorption paths - up to several kilometres for ground-based tropospheric measurements - and often large telescopes to direct and collect the light.

The light source used may be the sun (direct or diffused light), the moon, a star or an artificial lamp. When direct observation of the sun is used, the optical path through the whole atmosphere is determined by the solar zenith angle of observation (SZA). When vertically scattered light (zenithal) measurements are undertaken at dawn or dusk, one must take into account the long sunlight path in the stratosphere, followed by the vertical downward path through the troposphere.



Fig. 2.1 - View through the emitting telescope of an 800 m atmospheric absorption set-up installed on the campus of the University of Brussels. The reflecting mirror can be seen on the opposite building  
(Photo P. Hannaert, Journal "Le Soir")

The measurement techniques must be selective so that the measurement of a particular target gas is not affected by the presence of other species. Given the large number of species present in a polluted atmosphere this can be very difficult. Measurements must also be fast enough to eliminate the effects of rapid local variations in concentration, especially near ground level.

One basic difficulty in atmospheric measurements based on spectroscopy is the impossibility of obtaining a blank (the spectrum that would correspond to the complete absence of the species being

investigated). This leads us to the use of sophisticated computer methods for processing the raw spectroscopic data. Finally, spectroscopic measurements are based on precise laboratory studies of the absorption properties of the species investigated.

In the visible-ultraviolet region of the spectrum one highly selective spectroscopic technique is known as differential optical absorption spectroscopy (DOAS). This allows us to study a large number of gases whose typical detection limits are listed in Table 2.1. Fig. 2.2 shows a typical DOAS spectrum.

Table 2.1 - Detection limits for visible and ultraviolet spectroscopic measurements of some important atmospheric molecules (5 km absorption path length)

Species	Wavelength range (nm)	Detection limit (pptv)
SO <sub>2</sub>	290-310	17
CS <sub>2</sub>	320-340	500
NO	200-230	240
NO <sub>2</sub>	330-500	80
NO <sub>3</sub>	600-670	2
HNCO <sub>2</sub>	330-380	40
H <sub>2</sub> CO	300-360	400
O <sub>3</sub>	300-335	1900
NH <sub>3</sub>	200-220	150
Benzene	230-280	4000
Naphthalene	310-320	100
OH	308	0.1
ClO	260-320	20
OCIO	300-450	0.8
BrO	300-370	30
LO	400-470	10

In the near, middle and far infrared the most commonly used instruments are Fourier transform spectrometers (FTS). Their frequency multiplexing and large throughput allow to measure many molecules at once, and provide large signal-to-noise ratios at high recording speed when used with cooled detectors.

Around the mid-1970s, when the depletion of the ozone layer first became a concern (see Section 3.1), researchers sought precise, multi-species measurements throughout the stratosphere and all around the globe. The result was the ATMOS instrument, a

fast, high-resolution FTS specially designed to provide such measurements on repeated missions aboard the NASA Space Shuttles (Fig. 3.1). With the collaboration of Belgian scientists, its optical and cryogenic detection components were optimized for operation in the mid-infrared region where over two dozen atmospheric constituents show characteristic absorption features detectable in solar occultation mode (see Section 3.2). The spectrometer is fed with solar radiation through a hemispherical acquisition and guidance system and a telescope.

### 2.1.2 Atmospheric aerosols

The importance of atmospheric aerosols is emphasized in Chapters 6 and 7. For studies of their chemical composition aerosol particles are generally separated from the air by means of filters, impactors and cyclones, or by samplers based on combinations of these devices. To examine the physico-chemical transformations of particulate species in the atmosphere and model their dry deposition, researchers separate the particles into different size classes.

### 2.1.3 Belgian contributions

Between 1990 and 1996 various Belgian groups contributed to the development of instruments for studying the atmosphere. Typical examples are:

#### Instrumentation

- development and improvement of conventional grating spectrometers using the DOAS method for subsequent operation at permanent observation sites (e.g. International Scientific Station of the Jungfraujoch, ISSJ) and use in several field campaigns;
- the first adaptation of FTS to atmospheric measurements in the UV-VIS region. The instrument's high resolution, wide spectral coverage and laserbased internal frequency calibration make it ideal for multiple-species atmospheric studies;
- construction of PC-controlled guidance systems to feed instruments with solar radiation throughout the day;
- development of specific algorithms to calculate concentrations from spectra taken with the sun or artificial light sources. Although the analysis techniques are basically the same, each instrument requires its own specific algorithm adapted to the type of light source used, the wavelength calibration method, the dispersive properties of the instrument and the type of detector;

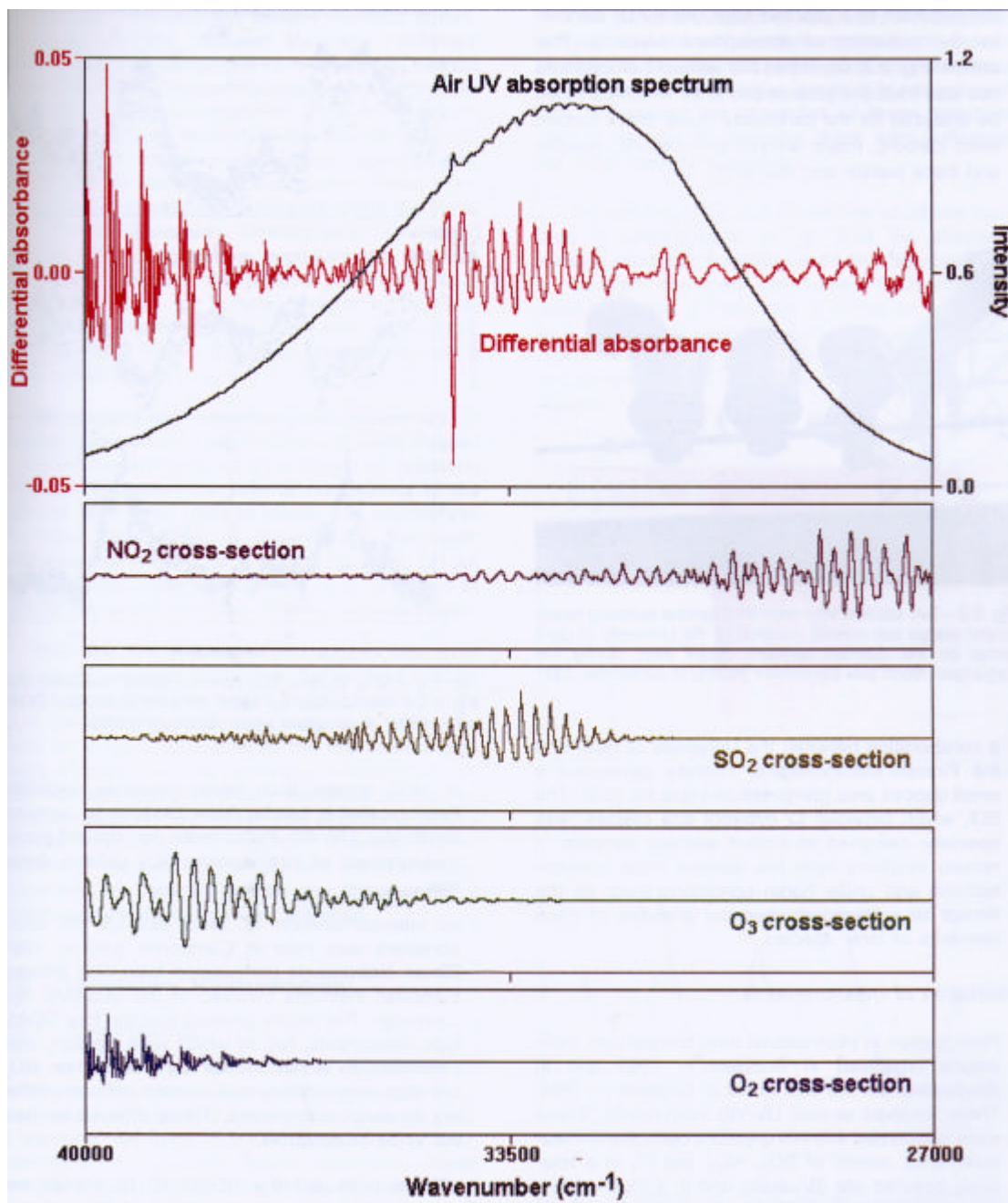


Fig. 2.2. – Typical DOS atmospheric spectrum. The black line is the response of a Fourier transform spectrometer (FTS) to UV-VIS light from a xenon lamp that has travelled 800m through the boundary layer. The absorption of  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$  and  $\text{SO}_2$  are visible as small “wiggles” on the black curve. The red line is the differential spectrum which “amplifies” these absorption. The four lower curves are differential absorption cross-sections for these four molecules, measured in the laboratory.



- development of a stacked filter unit (SFU) sampler for the collection of atmospheric aerosols. This device (Fig. 2.3) separates the aerosol particles into two size fractions (coarse and fine), which can then be analyzed for the particulate mass, black carbon (soot carbon), major anionic and cationic species and trace metals and elements.



Fig. 2.3 - Two stacked filter unit (SFU) aerosol sampling heads (under orange rain covers), installed by the University of Gent group on the German research vessel Alkor during the Lagrangian North Sea Experiment (NOSE) in September 1991

- a collaboration between the University of Gent and the Finnish Meteorological Institute developed a small deposit area low-pressure impactor (SDI). The SDI, which provides 12 different size classes, was specially designed to collect aerosol samples in remote locations (with low aerosol mass concentrations) and under harsh conditions (such as the Arctic) for subsequent chemical analyses of trace elements or ionic species.

#### Validation of measurements

- Participation in international inter-comparison campaigns organized in Brussels in 1992 and in Weybourne (on the east coast of England) in 1994. These involved several UV-VIS instruments. These were concerned with long-path tropospheric measurements, mainly of  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{O}_3$  in a relatively polluted site (Brussels) and in a much cleaner area (Weybourne). During the latter campaign, results from the spectrometers were compared with those from more conventional commercial instruments. Fig. 2.4 shows the variations in concentrations of  $\text{NO}_2$ ,  $\text{O}_3$ , and  $\text{SO}_2$  observed over a 24-hour period during the Brussels urban campaign (1992) by eight different DOAS instruments;

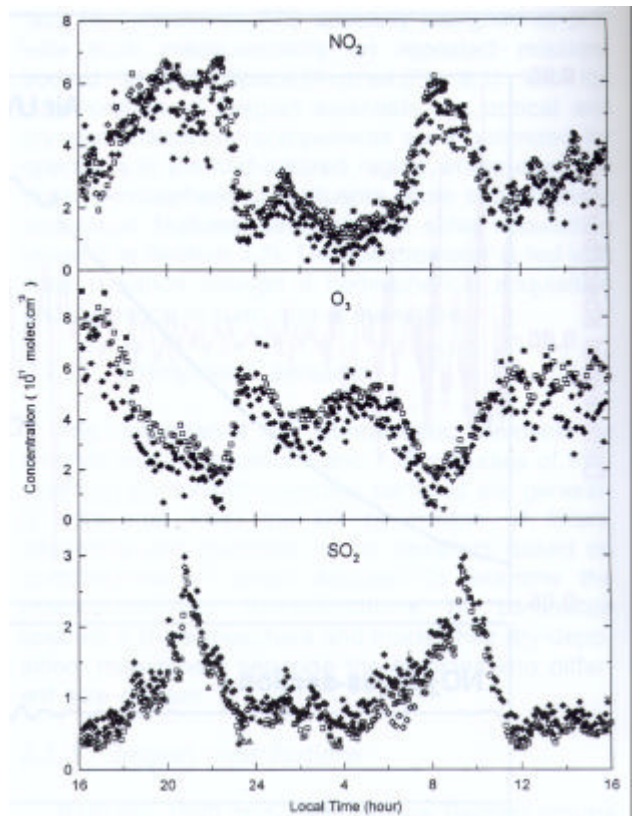


Fig. 2.4 -  $\text{NO}_2$ ,  $\text{O}_3$  and  $\text{SO}_2$  concentrations measured during a 24-hour period by eight different European DOAS instruments at an urban site in Brussels (1992)

- in 1992 groups from seven countries, including Belgium, met in Lauder (New Zealand) to compare zenith-sky UV-VIS instruments for ground-based measurement of stratospheric  $\text{NO}_2$  column densities;
- an inter-comparison of zenith-sky UV-VIS spectrometers was held in Camborne (UK) in 1994. Eleven instruments participated from nine different European institutes involved in the SESAME field campaign. The results showed that the four DOAS type instruments, two of which were Belgian, were consistent to within 3% for  $\text{O}_3$  and 5% for  $\text{NO}_2$ , but that larger differences existed between different types of instruments. These differences have yet to be investigated.

These trials led the NDSC-SC to accept two Belgian UV-VIS instruments as part of the Network, one to be operated at ISSJ and the second now permanently installed at the Harestua Observatory (Norway). These instruments took part in the EASOE and SESAME international field campaigns. The results of these campaigns are described in Chapter 3.

Between 1990 and the present the ISSJ laboratory has been the "nucleus" for many instrument inter-comparison campaigns co-ordinated by Belgian scientists. These involved various remote techniques including very high-resolution Fourier transform spectrometry, laser heterodyne spectrometry, UV-VIS spectroscopy, microwave emission spectrometry, and in situ air sampling at the station. These campaigns, more specifically developed within the frame of ESMOS (European Stratospheric Monitoring stations)/NDSC programmes, represented a substantial effort to assess the relative performances of these techniques for remote, long-term, multiplespecies investigations. They concluded that, overall, high-resolution Fourier transform spectrometry is the most suitable technique.

Recognizing the important role played by IR remote observations in atmospheric studies, Belgian scientists co-ordinated a further series of validation exercises to assess the internal consistency of the retrieval algorithms used to derive the abundances of telluric gases from IR observations. Two such exercises, developed in 1992-94 as part of the ESMOS/NDSC activities, involved 16 groups from all around the world and nine different retrieval codes.

While the first exercise demonstrated first-order agreement between the codes, the second indicated the great care that needs to be taken if results from the different codes are to agree to  $\pm 2\%$ . The need for ways to characterize the instruments precisely (in particular their apparatus functions at various wavelengths) was clearly identified as the key to future improvements in retrieval algorithms. Within the frame of NDSC, it is important to ensure that all stations of the network comply with retrieval procedures that are carefully defined and documented, if optimum consistency is to be achieved.

## 2.2 Laboratory Measurements

### 2.2.1 Spectroscopy

In order to use spectroscopic techniques to determine the composition of the atmosphere or evaluate the influence of minor constituents on global warming, we need to know the absorption characteristics of important telluric molecules. These provide a spectral signature for each species that allows us to detect it and measure its concentration in the atmosphere. Some of the existing absorption data is unsatisfactory, especially for species such as CFCs, HCFCs and HCFs that have only recently become of interest. More information is also needed in the promising far-infrared (FIR) region used by satellites.

One important aspect of laboratory investigations is their close link with fundamental research. Indeed, in order to be able to predict accurately the spectral characteristics of trace gases, it is necessary to fully understand the properties of these molecules and to be able to describe them with sufficiently accurate theoretical models.

The spectra in Fig. 2.5 shows two situations common in spectroscopy. In Fig. 2.5a the absorbing species produces spectral bands that are completely resolved (rotational structures). Each observed absorption line is fitted, using computer programs, to a model that describes very precisely its shape, position and intensity. This situation is mostly encountered in the infrared and far-infrared spectral regions.

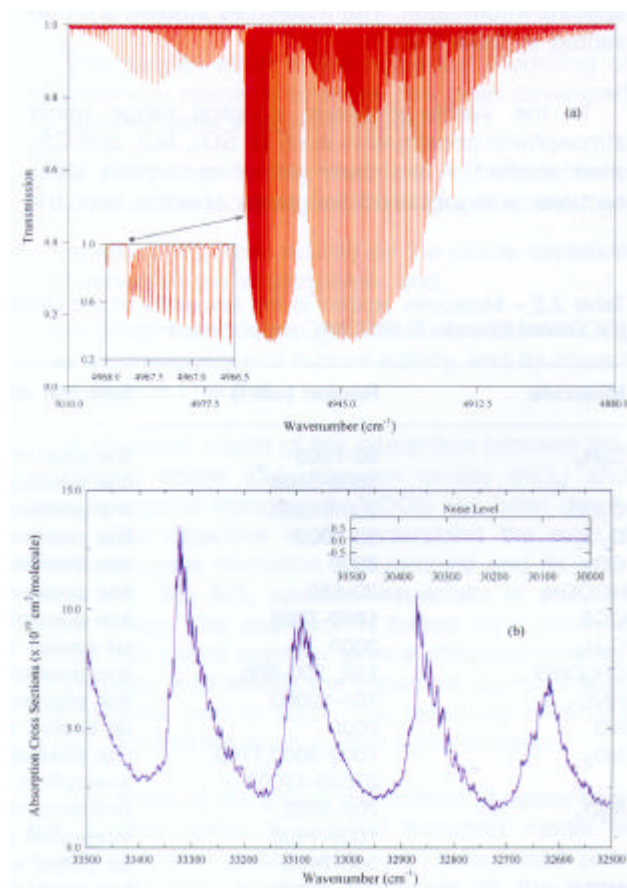


Fig. 2.5 - Examples of typical laboratory absorption spectra in two different ranges recorded using Fourier transform spectroscopy. (a) High-resolution spectrum of carbon oxysulphide (OCS) in the infrared region around 2 Nm. Almost every line of the bands observed is well resolved, as shown in the inset. (b) Absorption cross-section of sulphur dioxide (SO<sub>2</sub>) in the ultraviolet region around 0.3 Nm. Only broad features are observed as a result of line broadening and overlapping of the individual rotational lines

In the visible-ultraviolet region (Fig. 2.5b) the individual lines, even for lighter molecules, are generally not resolved. This is due to broadening caused by intra-molecular (pre-dissociation) or intermolecular (pressure and Doppler broadening) phenomena. The information that can be gained from the spectrum is limited to details of the absorption cross section as a function of the wave number.

Between 1990 and 1996 the University of Brussels conducted numerous spectroscopic studies of atmospheric constituents. All the work was carried out using two high-performance Fourier transform spectrometers. It involved the development of hardware including absorption cells, a supersonic jet apparatus (described below) and gas handling systems. Computer programs were also written to handle these spectra and retrieve the sought spectral information. The molecules studied are presented in Table 2.2.

In the visible-ultraviolet spectral range minor atmospheric constituents such as SO<sub>2</sub>, NO<sub>2</sub> and CS<sub>2</sub> were studied. A complete set of absorption cross sections was obtained for these species over the

Temperature range important for atmospheric studies (20° C down to -70°C).

In the infrared and far-infrared regions more than of only 25 different minor atmospheric constituents were studied. These include acetylene (C<sub>2</sub>H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), nitrous acid (HNO<sub>2</sub>) and formic acid (HCOOH). The work carried out led altogether to the identification of some 50 000 absorption features.

The data consists mainly of the precise position of the absorption lines and in some cases their intensities. Heavier species such as nitrogen hemitetroxide (N<sub>2</sub>O<sub>4</sub>), CFCs, HCFCs and HFCs were also studied, yielding absorption cross sections and integrated absorption cross sections at various temperatures (see Chapter 7.2).

A new experimental technique was developed for heavier species whose individual line structures cannot be resolved under normal laboratory conditions. Its basic idea is to reduce the number of absorption lines by cooling the gas to a very low temperature, leading to a much sparser spectrum that can be analyzed. This is achieved by using a supersonic jet instead of a standard absorption cell. The gas, mixed with a high-pressure inert gas, is injected through a

Table 2.2 - Molecules studied in the laboratory at the University of Brussels and at the IASBIBIRA within the framework of the Global Change/EUROTRAC programmes

Molecule	Region (cm <sup>-1</sup> )	Spectral data
C <sub>2</sub> H <sub>2</sub>	50-1300	line positions
	2500-3500	line positions and absolute intensities
C <sub>2</sub> HD	200-15000	line positions and absolute intensities
C <sub>2</sub> D <sub>2</sub>	50-1000	line positions
CO <sub>2</sub>	3000	line intensities and jet cooled spectra reference measurements
HCOOH	20-130	line positions and absolute intensities
OCS	1850-7800	line positions and absolute intensities
C <sub>2</sub> H <sub>6</sub>	3000	jet cooled spectra-line positions
XH <sub>3</sub> CHO	150, 700-900	line positions
HNO <sub>2</sub>	700-12000	line positions
NO	2000	jet cooled spectra-line positions
NO <sub>2</sub>	1000-3000, 1700	line positions – jet cooled spectra
	27000-42000	absorption cross sections
N <sub>2</sub> O <sub>4</sub>	700-3500	positions of vibrational bands
	1000-1900	integrated absorption cross sections
	300-7000	jet cooled spectra – line positions
N <sub>2</sub> O	700-12000	line positions and absolute intensities
H <sub>X</sub> N <sub>Y</sub> O <sub>Z</sub>	IR	compilation of literature data
B <sub>R</sub> NO	1800	line positions
HCFC HFC	600-1500	absorption cross sections and Global Warming Potentials for 12 HCFCs and HFCs (see Chapter 7)
HOCl	1200-1300	absolute line intensities
CS <sub>2</sub>	27000-42000	absorption cross sections
O <sub>2</sub>	27000-42000	absorption cross sections
SO <sub>2</sub>	27000-42000	absorption cross sections

small hole into a chamber that is held at low pressure by large vacuum pumps. Under such conditions the gas forms a supersonic jet with a temperature of only a few degrees Kelvin, and its spectrum is recorded with a Fourier transform spectrometer. So far this technique has been used to study gases including methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>) and ammonia (NH<sub>3</sub>).

### 2.2.2 Chemical Kinetics

Knowledge of the rate coefficients and product distributions for key elementary reactions involved in tropospheric ozone formation from volatile organic compounds, both biogenic and anthropogenic, is of the utmost importance. As illustrated by Fig. 4.1, all the reactions involve very reactive free radicals, both as reactants and products. Examples are OH, (hydroxy)alkyl, (hydroxy)alkylperoxy and (hydroxy)alkoxy radicals.

A method developed at the KULeuven for investigating radical reactions of atmospheric interest uses a combination of two techniques: dischargeflow (D-F) and molecular beam sampling mass spectrometry. Multi-stage flow reactors offer the unique advantage of spatially separated reaction regions, each with reaction times down to a few milliseconds. In such a multi-stage reactor, a specific radical is first prepared, usually starting out from H or F atoms and sometimes in successive stages. The radical is subsequently reacted, downstream, with a molecular compound added via one of a set of coaxial, movable, inlet tubes.

If necessary, the product radical(s) of this first reaction can be reacted with another compound added further downstream. The gas at the exit of the flow reactor is sampled through a small opening in a hollow quartz cone, which leads to the first of two or three differentially-pumped vacuum stages. Once the gas enters the sampling system its density drops sharply, so that no further collisions occur and the gas composition is "frozen". The core of the resulting molecular jet finally traverses the electron-impact ion source of a quadrupole mass spectrometer housed in the last vacuum stage.

To avoid interference by ionized fragments from other (molecular) compounds, radicals are often monitored at an ionizing electron energy only a few tenths of an eV above the ionization potential. In other instances, however, electron energies have to be increased up to 20 or 30 eV. This is the case, for example, when measuring the quantitative product distribution of the various isomeric hydroxyalkyl or hydroxyalkenyl adducts formed in the primary reaction of OH with (poly)alkenes; here the various isomeric radicals are distinguished from one another by

their different fragmentation mass spectra. The fragmentation spectra of the pure, single radical isomers were characterized in separate studies.

## 2.3 Models

Field measurements are essential in identifying key global environmental issues and monitoring trends in the atmosphere's composition, but they are restricted to specific locations or periods of time. A true understanding of global atmospheric change must also rely on numerical simulations. We can use these to check our understanding of the key processes which control the observed perturbations. Even more importantly, models are the only way to project into the future what is observed today. Their ability to simulate scenarios, including socio-economic changes, make them an essential tool to guide decisions at national and international levels.

The Belgian effort in the numerical modelling of atmospheric chemical changes has been developed to address three important issues:

- the factors controlling the level of tropospheric ozone at the local, regional and global scales;
- the effect of human activity on the ozone depletion observed in the stratosphere; and
- the present and future growth of atmospheric CO<sub>2</sub> as a consequence of human activity, and its impact on climate changes.

A chemical model of the interaction between tropospheric ozone (O<sub>3</sub>), nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs) has been developed. The objective is to understand the role of VOCs in ozone formation and removal and its coupling with the NO<sub>x</sub> species, especially in polluted urban areas. The approach is based on a reduced model that lumps together several chemical species. Its purpose is to assess the impact of chemical submechanisms and to study the sensitivity of ozone levels to variables such as the light intensity.

The study of the global distribution of ozone near the surface needs a detailed transport model in which chemical constituents are transported over large distances, reacting chemically at the same time. The Intermediate Model for the Annual and Global Evolution of Species (IMAGES) has been developed to study the global distribution of chemical compounds in the troposphere, as well as their global budget. The model accounts for natural and anthropogenic emission at the surface, long-range transport, convective exchanges, chemical transformations, and surface wet and dry deposition.

The horizontal resolution of this model is 5° in longitude and latitude, with a vertical range that extends from the earth's surface to a height at which the pressure has fallen to 20 mb. Transport is driven by wind data taken from the analysis performed by the European Centre for Middle Range Weather Forecasting. Cloud details and lightning frequency are taken from satellite observations. IMAGES focuses on ozone and its precursors as well as on sulphur compounds in the free troposphere.

The study of the depletion of stratospheric ozone by natural routes (such as aerosols injected into the stratosphere by volcanic eruptions) or to human activities (halocarbons) requires sophisticated models combining a detailed treatment of the photochemistry with atmospheric transport processes. A model of this kind in which quantities are averaged along the parallels (a 2-D model) was used in the Belgian Global Change Programme (1990-1996) to evaluate the relative role of natural and anthropogenic perturbations to the ozone layer.

The model extends from the earth's surface to a height of 85 km in 1 km steps, and from the north to the south pole in 5° steps. Approximately 50 species and 110 chemical reactions are taken into account to describe the behaviour of the oxygen, hydrogen, nitrogen, chlorine, bromine, fluorine and sulphur compounds. Heterogeneous reactions on the surface of sulphate aerosols and polar stratospheric cloud particles are also included.

The study of the accumulation of CO<sub>2</sub> in the atmosphere and the prediction of CO<sub>2</sub> concentrations during the coming decades requires a detailed model of the redistribution of anthropogenic CO<sub>2</sub> between the three main carbon reservoirs: the atmosphere, the biosphere and the ocean. For this purpose two numerical models have been built: one evaluates the net CO<sub>2</sub> ocean-atmosphere sink, and the other calculates the CO<sub>2</sub> exchange by photosynthesis and respiration between the atmosphere and the biosphere.

The ocean carbon model calculates the worldwide horizontal and vertical distribution of total (organic and inorganic) carbon, alkalinity, phosphate and oxygen. Dynamic (transport) data is provided by off-line ocean general circulation models (OGCMs); at present the model can use hydrodynamic data from either the Hamburg MPI model or the Louvain-la-Neuve model. The ocean carbon model calculates the productivity of the marine biosphere, the settling to depth of organic carbon and carbonate shells, and their dissolution or decay as they move from the upper to the deeper ocean. This model will be used to locate the sources and sinks of CO<sub>2</sub> in the global ocean

and to evaluate the net atmosphere-ocean flux, a necessary step towards a solution of the famous "missing sink" problem (see Section 7.1).

Similarly, a detailed model is needed to quantify regions the CO<sub>2</sub> exchange between the atmosphere and the biosphere and to determine whether the biosphere acts as a net sink of CO<sub>2</sub>. A new model named CARAIB (Carbon Assimilation in the Biosphere) has been developed and validated. It has a 1° x 1° spatial resolution and calculates the rates of photosynthesis and dark respiration for various vegetation types, driven by climatic (temperature, precipitation, insolation) and soil variables. The difference between the net primary productivity and the soil microbial respiration (two fluxes of nearly equal value but in opposite directions) provides the net CO<sub>2</sub> flux to or from the atmosphere.

### 3. STRATOSPHERIC OZONE AND RELATED GASES

Ozone has been recognized as a permanent constituent of the atmosphere for more than a century, but the mechanisms leading to its production and destruction in the stratosphere and the troposphere have been identified only relatively recently.

25 years ago the Nobel Prize Winner, Paul Crutzen discovered that the largest ozone loss in the stratosphere was due to the catalytic effect of nitrogen oxides, and Harold Johnston indicated that a fleet of supersonic aircraft in the lower stratosphere could cause substantial ozone depletion. It was only 20 years ago that Ralph Cicerone and Richard Stolarski suggested that ozone could also be destroyed catalytically by atmospheric chlorine, and that Nobel Prize Winner Mario Molina and Sherry Rowland indicated that ozone could be depleted by man-made chlorofluorocarbons. These theories complemented our earlier understanding of the ozone budget, based on the work of Nobel Prize Winner Mario Sydney Chapman and of David Bates and Marcel Nicolet.

One of the key findings of the early 1980s was the drastic decrease in springtime ozone abundance over the south pole that has happened since the late 1970s. The formation of an ozone "hole" covering an area as large as the Antarctic continent (more than 20,000 km<sup>2</sup> during the four last austral springs) has been shown to result from the release of chlorofluorocarbons into the atmosphere and the presence of polar stratospheric clouds (PSCs).

Several of the processes involved in the Antarctic ozone loss (see Section 3.1) seem also to operate in the Arctic, where significant ozone depletion has

already been observed, especially during the European Sesame campaign in the winter of 1994/1996. What is less well understood is the cause of the ozone depletion observed over populated regions at midlatitudes in the northern hemisphere.

Before CFCs and other artificial halogenated substances were produced and released on a large scale, methyl chloride (CH<sub>3</sub>Cl) and methyl bromide (CH<sub>3</sub>Br) were the dominant natural sources of halogenated compounds in the atmosphere. Studies at the University of Gent show the importance of savanna fires as a source of these compounds.

An understanding of the processes affecting the budget of stratospheric ozone requires an accurate measurement of the key nitrogen- and chlorine-containing species. The Belgian contribution to the ATMOS mission (see Section 3.2 and Fig. 3.1.) has been crucial in this regard. Ground-based observations made by Belgian scientists with state-of-the-art instruments (often improved "in-house") at various European sites have also provided the key to assessing long-term changes in stratospheric ozone



Fig. 3.1 - View from the Space Shuttle in orbit. The shuttle bay contains the ATMOS Fourier transform spectrometer which studies the atmosphere remotely during solar occultations. Also embarked as core payloads of the ATLAS programme were the Belgian SOLCON and the French/Belgian SOLSPEC instruments, both of which measure characteristics of solar radiation that interacts with our environment

and ozone-related species, especially after large volcanic eruptions such as that of Mt. Pinatubo (Philippines) in 1991.

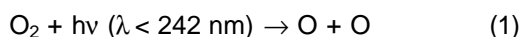
The use by Belgian scientists of sophisticated chemical transport models to interpret the observed data and simulate the past and future evolution of ozone has also been an important contribution from the Belgian Global Change Programme.

### 3.1 Global Budget of Stratospheric Ozone

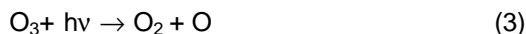
Atmospheric processes are characterised by strong interactions between chemical composition, dynamics and radiative budget. Ozone is a key minor constituent influencing the troposphere, the stratosphere and the mesosphere. It provides the main stratospheric heat source through the absorption of solar ultraviolet radiation, and thus is important in determining the temperature profile in the stratosphere and the general circulation. Ozone therefore couples the stratospheric and the tropospheric climates through complex processes involving radiative, chemical and dynamic effects.

Atmospheric processes are of major concern in the study of global atmospheric change experienced since the industrial revolution and more recently in stratospheric ozone depletion. The following section provides a brief review of our current knowledge of stratospheric ozone chemistry.

Ozone, which protects the biosphere from harmful solar ultraviolet radiation, is produced in the upper stratosphere by photo-dissociation of molecular oxygen by solar radiation of wavelengths shorter than 242 nm (Chapman, 1929)



The ozone itself photo-dissociates to form atomic oxygen:



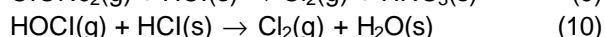
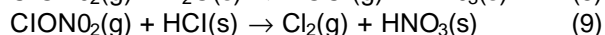
Later it was realised that this reaction is catalysed by various radicals, mainly according to the scheme:



The radical catalyst X can be H, OH, NO, Cl or Br.

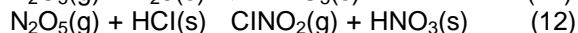
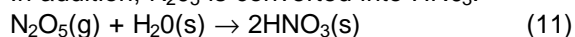
Most radicals are produced through the oxidation and/or photo-dissociation of tropospheric species such as H<sub>2</sub>O, CH<sub>4</sub>, H<sub>2</sub>, N<sub>2</sub>O and halocarbons. Nitrogen oxides can also be supplied by downward transport from the lower thermosphere during the polar night. The gas-phase chlorine catalytic cycle is predominant in the upper stratosphere, with a maximum efficiency at altitudes around 40 km. Fig. 3.1 illustrates the complexity of the main processes that determine the structure of the stratosphere.

Different ozone destruction processes predominate in the lower stratosphere. Since the discovery of the dramatic springtime depletion of ozone over Antarctica, additional processes besides Reactions 3 to 7 are needed to explain the rapid reduction in ozone concentration observed at altitudes between 15 km and 20 km. They involve heterogeneous reactions of reservoir (inactive) species at the surface of solid particles, the so-called polar stratospheric clouds (PSCs). These particles are mixtures of nitric acid and water vapour, or pure water, depending on the temperature prevailing inside the Antarctic polar vortex during the polar night. Under such conditions, laboratory studies have shown that chlorine reservoirs such as ClONO<sub>2</sub> and HOCl are converted into active chlorine:

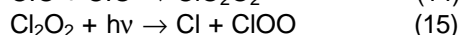
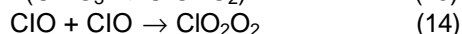
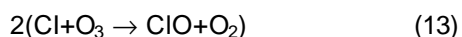


(g) denotes the gas phase and (s) the solid phase.

In addition, N<sub>2</sub>O<sub>5</sub> is converted into HNO<sub>3</sub>:

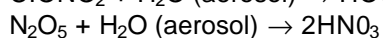
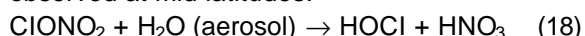


When sunlight returns to the polar regions in late winter, Cl<sub>2</sub>, HOCl and ClONO<sub>2</sub> are photolysed to produce Cl and ClO radicals. Since the concentration of NO<sub>2</sub> is lower than usual due to N<sub>2</sub>O<sub>5</sub> conversion into HNO<sub>3</sub> (Reactions 11 and 12), a large amount of ClO remains available to destroy ozone, mainly through the cycle:



These photolytic processes are initiated by solar ultraviolet radiation of wavelengths longer than 300 nm.

Similar heterogeneous reactions on the surface of the sulphuric acid aerosol droplets present at all latitudes play an important role in the ozone reduction observed at mid-latitudes:



The roles of these two reactions increase after major volcanic eruptions like Mt. Pinatubo in June 1991, when they lead to significant NO<sub>x</sub> reductions at all latitudes.

### 3.2 Observations of Stratospheric Constituent

Ground-based remote sensing measurements of stratospheric species have been extensively used to increase our scientific understanding of stratospheric processes at high and middle latitudes. Several campaigns within the European Arctic Stratospheric Ozone Experiment (EASOE), co-ordinated by the EC during the winter 1991-1992, have demonstrated the need for an approach that combines high-quality observations from ground stations, aircraft and balloons with satellite data and model calculations.

In response to concern about the destruction of the protective ozone layer and the need to understand the causes of this, scientists made many observations from the ground, aircraft, balloons and spacecraft. The Belgian contribution to this work was original and important.

Crucial in this respect was the work of the University of Liège on the Atmospheric Trace Molecule Spectroscopy (ATMOS) project, a US-developed and co-ordinated effort involving very high quality remote measurements of the chemical composition of the atmosphere from aboard Space Shuttles. The project used a fast, high-resolution FTIR spectrometer which is briefly described in Section 2.1. From each of the four ATMOS flights so far (in 1985, 1992, 1993 and 1994), concentration profiles of more than 30 telluric gases were measured at altitudes between 10 km and 150 km over extensive areas of the globe, and their changes over time were studied.

The large number of gases (see Table 3.1) measured almost simultaneously allowed scientists to study complete "families" of gases such as the nitrogen oxides, and to evaluate the total budgets of chlorine (Cl) and fluorine (F) - sources, sinks and reservoirs - which play an important role in determining the levels of stratospheric ozone.

A unique feature of the ATMOS work is its self-consistency. The instrument's wide spectral coverage means that it can also provide details of phys-





ical conditions such as temperature and pressure profiles. This is made possible by measuring the spectra of "reference" gases such as CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>, whose concentrations in the atmosphere are relatively uniform and well known.

Table 3.1 - Molecules observed by ATMOS

Reference gases:	CO <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub>
Minor constituents:	N <sub>2</sub> O, CH <sub>4</sub> , CO, H <sub>2</sub> O, O <sub>3</sub>
Nitrogen compounds:	NO, NO <sub>2</sub> , HNO <sub>3</sub> , HNO <sub>4</sub> , N <sub>2</sub> O <sub>5</sub> , ClONO <sub>2</sub>
Halogenated species:	HCl, HF, CH <sub>3</sub> Cl, CCl <sub>4</sub> , CFCI <sub>3</sub> , CF <sub>2</sub> Cl <sub>2</sub> , CHClF <sub>2</sub> , COF <sub>2</sub> , CF <sub>4</sub> , SF <sub>6</sub>
Others:	C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , HCN, OCS, SO <sub>2</sub> , secondary isotopes of O <sub>3</sub> , H <sub>2</sub> O and CH <sub>4</sub>

As an example of the benefit of measuring many species simultaneously, Fig. 3.3 shows the chlorine inventory throughout the stratosphere. The data was derived primarily from ATMOS observations during the third Atmospheric Laboratory for Applications and Science mission (ATLAS-3) of 3-14 November 1994. The diagram shows the excellent conservation of chlorine at altitudes above 16 km; when compared to that derived from the first ATMOS mission in 1985 it indicates an increase of 36% in the loading of stratospheric Cl over the 9.5 year time interval separating the two missions. This increase precisely mirrors the change in the amount of organic Cl con-

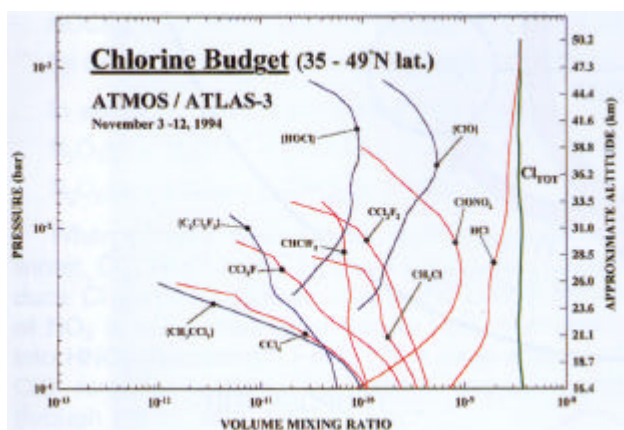


Fig. 3.3 - An original example of the advantages of multispecies measurement as performed by the ATMOS instrument from aboard the Space Shuttle during the ATLAS-3 mission in November 3-12, 1994. The chlorine budget (ClTOT green line) can be established through the entire stratosphere by combining seven volume mixing ratio profiles measured by ATMOS (red profiles) with four additional profiles provided by other instruments. The constancy of ClTOT versus altitude demonstrates the conservation of the Cl budget throughout the earth's atmosphere, sources, sinks, and reservoirs combined

tained in the main chlorine-bearing source gases (the CFCs) released at ground level, thus indicating that the Cl loading in the stratosphere is primarily of anthropogenic origin.

Internally-consistent multiple-species measurements such as those from ATMOS are also valuable for testing and validating multi-dimensional models of the atmosphere.

Belgian observational activities at the International Scientific Station of the Jungfrauoch (ISSJ, Switzerland; 46°N, 8°E) have also contributed significantly to the characterization and understanding of the stratosphere above Europe (Fig. 3.4). Using state-of-the-art grating and Fourier transform spectrometers the scientists involved have studied and monitored the chemical composition of the earth's atmosphere, troposphere and stratosphere combined.



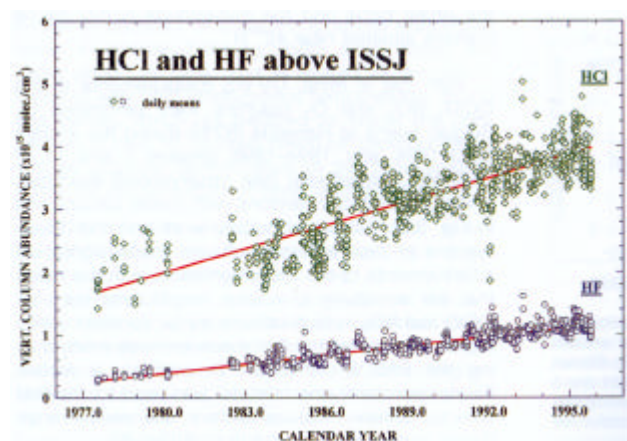
Fig. 3.4 - A view of the international Scientific Station of the Jungfrauoch (ISSJ), located in the Swiss Alps, at an altitude of 3580 m. This facility is regularly visited by Belgian scientists to monitor the mean state, variability and secular trend of the earth's atmosphere through high-quality solar observations in the infrared (University of Liège group) and UV-VIS regions (Belgian Institute for Space Aeronomy). With the Observatoire de Haute Provence and the Plateau de Bure in France, the Jungfrauoch is part of the Alpine Station selected as a primary site by the international NDSC to monitor the evolution of the stratosphere at northern mid-latitudes

The latter project was part of the international Network for the Detection of Stratospheric Change (NDSC), in which ISSJ formed part of the northern mid-latitude Primary NDSC Alpine Station, along with the Observatoire de Haute Provence and Plateau de Bure, France. Despite local interference caused by tropospheric gases, the high spectral resolution of the ISSJ instruments allows precise measurements of many key stratospheric constituents, including HCl, ClONO<sub>2</sub>, NO, NO<sub>2</sub>, HNO<sub>3</sub>, HF, COF<sub>2</sub> and O<sub>3</sub> all being monitored routinely using the infrared remote technique.

As an example of the long-term studies performed at ISSJ, Fig. 3.5 shows the vertical column abundances of HCl and HF observed since 1977. The increase of these halogenated inorganic molecules in the stratosphere reflects the growing release of their parent source gases at ground level during the 1970s and 1980s, in particular the widely used CFC 11 (CCl<sub>3</sub>F), CFC 12 (CCl<sub>2</sub>F<sub>2</sub>) and HCFC 22 (CHClF<sub>2</sub>).

The 1987 Montreal Protocol and its London (1980) and Copenhagen (1992) amendments aim at a progressive phase-out of the most widely used and ozone-damaging CFCs. The CFCs targeted in particular are those that have sufficiently long lifetimes to be transported into the stratosphere and to be photo-dissociated there by solar UV radiation.

Despite these agreements, however, the total inorganic chlorine load in the stratosphere has continued to rise and will probably continue to do so for several years to come. As a consequence, ozone losses are expected to increase for the remainder of this decade, with a gradual recovery throughout the 21st century.



Identifying the point at which the stratospheric Cl load starts to drop is critical. This turning point will validate the decision to phase out CFCs and set a historical milestone from which to calculate how soon the ozone layer will return to its normal thickness.

Further measurements performed at ISSJ since 1990 have used the DOAS technique in the UV-VIS spectral region at twilight to measure vertical column amounts of O<sub>3</sub> and NO<sub>2</sub>.

The role of heterogeneous chemistry on the surface stratospheric aerosols has been confirmed by stratospheric monitoring during the last six years. More specifically, the partitioning of nitrogen compounds was seen to be strongly modified by the eruption of Mt. Pinatubo in June 1991, which injected up to 30 million tonnes of sulphur dioxide aerosol into the stratosphere.

Measurements of NO<sub>2</sub> abundance over the period from one year before the Mt. Pinatubo eruption to five years afterwards were carried out at the ISSJ and at Sodankyla (Finland, 67°N, 27°E). Both showed a significant reduction of NO<sub>2</sub> after the eruption, starting in winter 1991-1992. Both stations showed a maximum decrease in NO<sub>2</sub> levels of about 35% in January 1992, followed by similar recovery trends up to August 1994 (Fig. 3.6)

These results have been compared with 2-D radiative dynamic chemical model calculations which include the effect of heterogeneous reactions. The models use aerosol data from the Mt. Pinatubo eruption, as observed in the Alps using LIDAR techniques (Fig. 3.7). In general, the models agree qualitatively with the observed data, though they under-estimate

Fig. 3.5 - The evolution of the vertical column abundances of hydrogen chloride (HCl) and hydrogen fluoride (HF) measured above ISSJ by ULg researchers. This long-term data indicates that the burdens of HCl and HF above the European continent have increased during the last two decades by factors of 2.5 and 3.5 respectively. The increases convincingly reflect the rates of change in the release of Cl- and F- bearing anthropogenic source gases (mainly CFCs) at ground level during the same period. The seasonal variations and relative anomalies observed in the two data sets (i.e. at the beginning of 1992 and 1993) are primarily associated with latitudinal transport and allow us to identify masses of air which have undergone heterogeneous processing at high latitudes before their transport to lower latitudes. The HCl and HF measurements reported here form the longest and most consistent data available to date from around the world

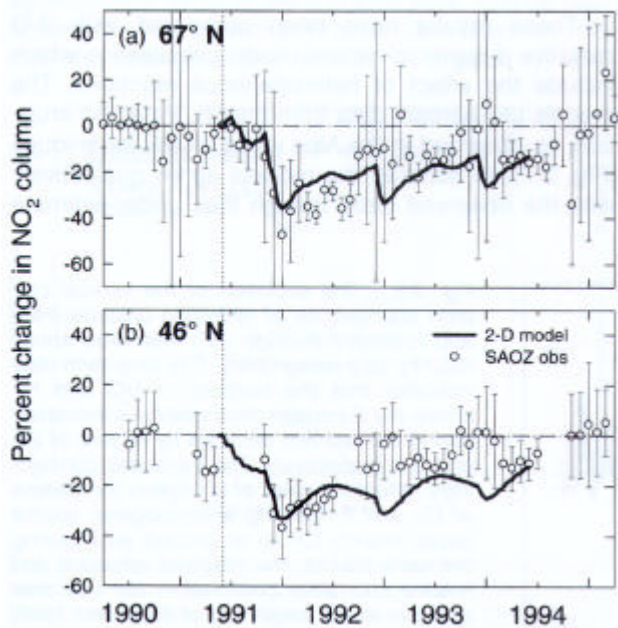


Fig. 3.6 - Relative changes in the monthly average morning and evening NO<sub>2</sub> total amounts relative to the respective unperturbed (pre-Pinatubo) reference value observed at (a) Sodankyla and (b) the International Scientific Station of the Jungfrauoch. The vertical dotted line indicates the day of the Mt. Pinatubo eruption

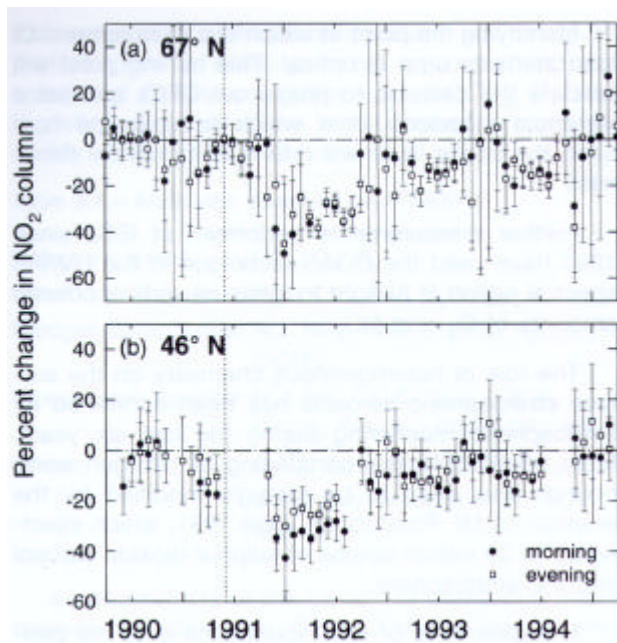


Fig. 3.7 - Comparison of experimental and calculated results for the daily in monthly average NO<sub>2</sub> total amount at (a) Sodankyla and (b) the International Scientific Station of the Jungfrauoch. These daily monthly averages are a mean between the corresponding morning and evening values given in Fig. 3.6. The vertical dotted line indicates the day of the Mt. Pinatubo eruption

the seasonal variation - possibly because of internal limitations in the models which, for instance, do not include diurnal changes. The observed and calculated relative changes in NO<sub>2</sub> levels agree well, quantitatively confirming the impact of heterogeneous aerosol chemistry on stratospheric NO<sub>2</sub>.

Perturbations in stratospheric chemistry caused by chlorine activation through heterogeneous processes can be observed at middle and high latitudes when stratospheric temperatures are low. These low temperatures are associated with the displacement of the polar vortex during winter and early spring in the northern hemisphere. The very lowest stratospheric temperatures observed so far in the Arctic occurred in January 1996, leading to chlorine activation by processes similar to those responsible for the ozone hole in Antarctica. Ozone depletion rates comparable to those observed during the austral spring were observed, but, because of the instability of the polar vortex over the Arctic, these conditions did not persist for long enough to allow an ozone hole to develop.

Despite the international effort and the important results obtained during the first Arctic and Antarctic campaigns, several scientific issues, mainly related to ozone depletion outside the polar regions, remain controversial. This is because of the complex coupling between chemistry and dynamics, especially in the northern hemisphere.

In order to study the connection between the Arctic and middle latitudes the EC set up a Second European Stratospheric Arctic and Midlatitude Experiment (SESAME). Ground-based monitoring was extended to around 60°N in order to fill the geographical gap between observations taken north of the Arctic circle and the mid-latitude NDSC alpine stations situated near 45° N.

With this in mind, UV-VIS measurements of the OCIO, NO<sub>2</sub> and O<sub>3</sub> columns were performed by Belgian teams at Harestua (60°N) during the winters 1993-1994 and 1994-1996 (phases I and III of SESAME, respectively) (see observational examples in Fig. 3.8 and comparisons with model calculations in Fig. 3.9). Careful laboratory work and the development of new analysis software made significant improvements to the instrumentation, with the result that the sensitivity to scarce constituents such as OCIO and NO<sub>2</sub> in high-latitude winter conditions was higher than during the first measurements made during the EASOE campaign. In addition, a mobile Fourier transform spectrometer was used for the first time for similar measurements in the visible range during winter 1996 (phase III of SESAME).

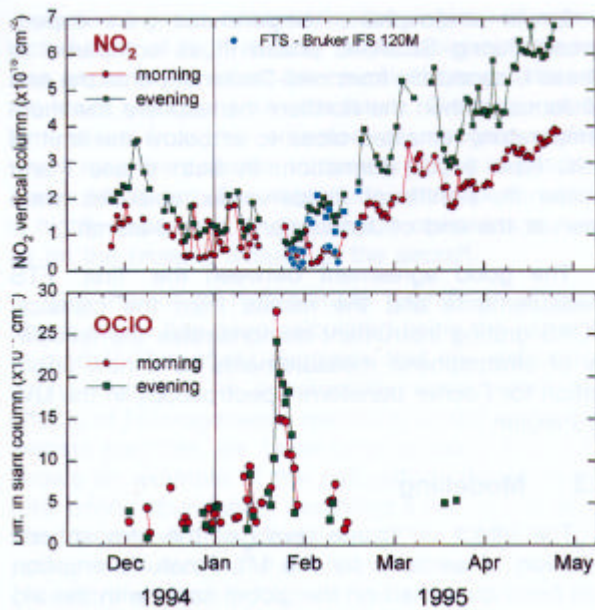


Fig. 3.8 - Time series of  $\text{NO}_2$  and OCIO observations performed at the Harestua station ( $60^\circ\text{N}$ ) during SESAME phase III

The morning and evening  $\text{NO}_2$  measurements are averages of observations taken between  $87^\circ$  and  $91^\circ$  SZA. In the case of the direct sun data obtained from January to March 1995 with the FTS instrument, the average was usually taken between  $83^\circ$  and  $88^\circ$  SZA. Despite this zenith-angle difference, which could introduce some difference due to the diurnal variation of  $\text{NO}_2$ , the agreement between the direct sun and zenith-sky results is quite satisfactory.

The  $\text{NO}_2$  time series show the well-known seasonal variation primarily due to the change in illumination. In addition,  $\text{NO}_2$  column amounts were much lower in January-February 1995 than during the same period in 1994. This is related to the occurrence of very cold stratospheric temperatures during this period, which are believed to favour the conversion of  $\text{NO}_x$  to nitrogen reservoir compounds as well as possible denitrification of the polar stratosphere by condensation of nitric acid on PSCs.

OCIO amounts measured inside the polar vortex during January 1995, on the other hand, are larger than the corresponding figures from January 1994. This indicates higher chlorine activation in January 1995. Most OCIO observations are obtained inside or at the edge of the polar vortex, showing that the activation is essentially limited to the vortex region. However, significant OCIO amounts were also detected outside the vortex, for example at the beginning of January 1995.

The ozone column amounts determined during SESAME phases I and III from zenith-sky and direct sun observations (daily averages) are shown in Fig. 3.10 and 3.11. Low  $\text{O}_3$  column amounts (as compared to the long-term climatology derived from TOMS data) were measured in March during both phase I and phase III of SESAME, when the polar vortex was moving above Harestua (as compared to the 12-year TOMS climatology). These measurements are consistent with episodes of  $\text{O}_3$  chemical destruction inside the polar vortex in March 1994 and 1995, reported from other SESAME observing sites. However, the influence of tropospheric heights should be investigated before drawing conclusions.

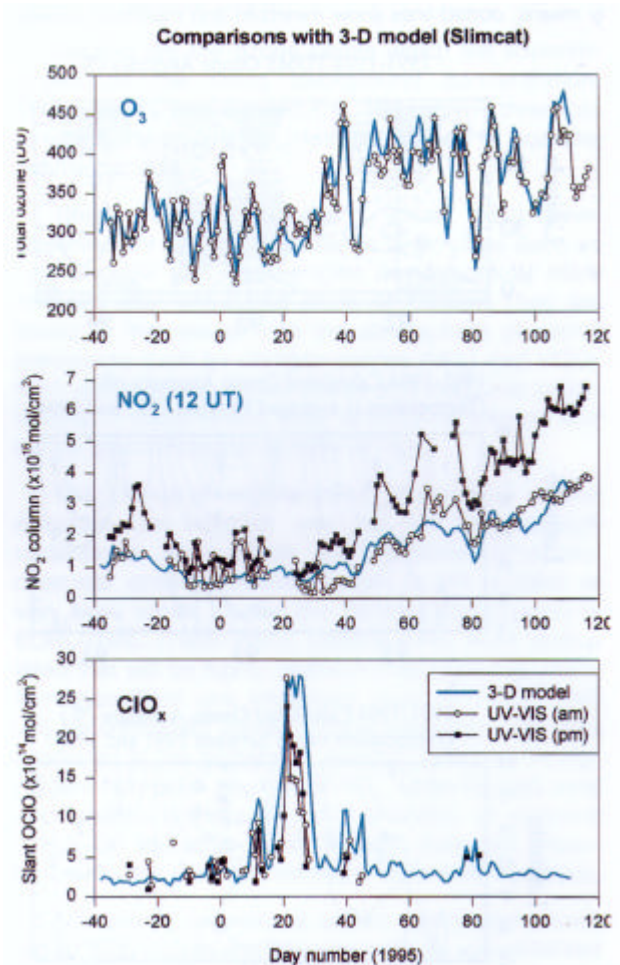


Fig. 3.9 - Time series of  $\text{NO}_2$ , OCIO and  $\text{O}_3$  column amounts obtained during SESAME phase III, compared with the three-dimensional model calculations performed by the Cambridge group. These calculations used real dynamic parameters derived by the European Centre for Medium Term Weather Forecasting (ECMWF) from meteorological observations

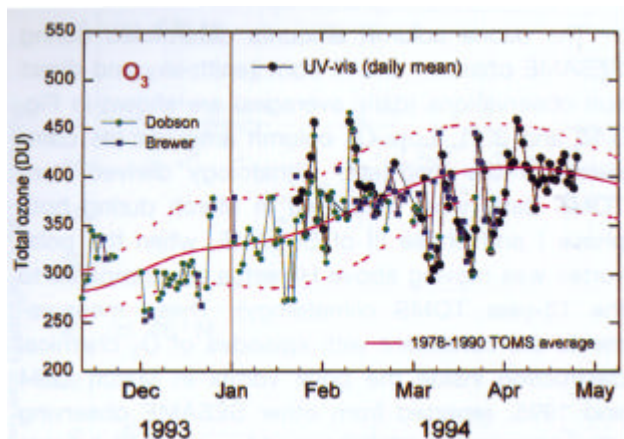


Fig. 3.10 - Comparison of the  $O_3$  time series obtained at Harestua ( $60^\circ N$ ) with the long-term (1978-1990) TOMS climatology above Oslo (solid line shows the average of monthly means, dotted lines show minimum and maximum values)

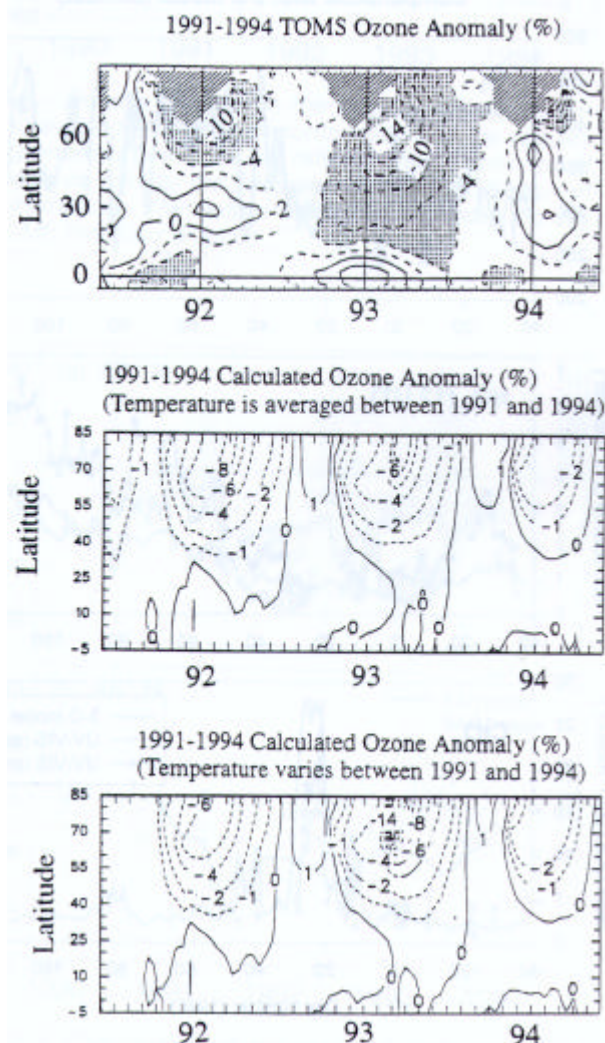


Fig. 3.11 - The anomaly in the ozone column after the eruption of Mt. Pinatubo, represented as a function of latitude and time (in %). (a) Values resulting from an analysis of ozone measurements by the TOMS instrument. (b) Values calculated from a 2-D model with seasonally varying temperature. (c) As (b) but taking into account inter-annual temperature changes

Lower stratospheric temperatures were experienced during SESAME phase III as compared to phase I, especially from mid-December until the end of January when the northern hemisphere minimum temperature remained close to or below the limit of PSC type II (ice) formation. In both phase I and phase III, significant inside-vortex episodes were seen at the end of January and in mid-March.

The good agreement between the "first" FTS measurements and the results from the classical DOAS grating instrument demonstrates the feasibility of stratospheric measurements as a new application for Fourier transform spectroscopy in the UVVIS region.

### 3.3 Modelling

The effect on ozone levels of the atmospheric injection of aerosols by the Mt. Pinatubo eruption has been quantified on the global scale with the aid of the two-dimensional (2-D) model presented in Section 2.3. The model suggests that the ozone changes observed during the first year after the eruption were caused primarily by changes in the meridional circulation (associated with stratospheric heating by the clouds in the tropics) and the photolysis rate of molecules such as ozone (associated with the backscattering of light by clouds).

It is only one year after the eruption, after the volcanic material has been transported to the polar regions, that chemical destruction of ozone becomes important. At that time, the model suggests an anomaly of 10-20% in the middle- and high-latitude ozone column in late winter (Fig. 3.11). This is due to the heterogeneous conversion of nitric oxides into nitric acid, and the related activation of chlorine compounds in the lower stratosphere.

This anomaly lasts for only 2-3 years because volcanic aerosol particles are progressively removed from the stratosphere. Its magnitude is only partly influenced by the intensity of the eruption (provided that sufficiently large amounts of sulphur dioxide penetrate the stratosphere) because at high aerosol loads the conversion of nitrogen oxides into nitric acid, a key step in the activation of chlorine, becomes insensitive to the aerosol surface area density.

On the other hand, the magnitude of the ozone change following a volcanic eruption depends very much on the chlorine load in the stratosphere (and hence on the amount of man-made chlorofluorocarbons released into the atmosphere). Model calculations show that, for chlorine loads representative of the pre-industrial era, the ozone abundance in the stratosphere should increase, not decrease, after a large volcanic eruption.

Exhaust gases released by the engines of a projected fleet of high-altitude (supersonic) aircraft are also expected to affect the chemical composition of the lower stratosphere in the future. The major problem arises from the emission of nitrogen oxides, which have the potential to destroy ozone at altitudes above 15-20 km. The magnitude of the perturbation is highly dependent on the engine emissions as well as on the cruising altitude of the aircraft.

The impact of high-altitude aircraft on stratospheric ozone has been calculated using the same 2D model. This study suggests that the calculated ozone depletion is substantially lower when the effects of heterogeneous reactions on the surface of aerosol particles are taken into account. Fig. 3.12 shows an example of the calculated change in the total ozone abundance, assuming a fleet of 500 highaltitude aircraft flying between 17 and 20 km, and taking into account the effects of heterogeneous chemistry on background sulfate aerosols.

The model suggests that, for aircraft emitting 15 g of NO<sub>2</sub> per kg of fuel burned, the global average reduction in the ozone column should be of the order of 1.0-1.5% for flight altitudes of 17-20 km. However, the injection of nitrogen oxides and water vapour by the aircraft engines tends to favour the formation of polar stratospheric clouds in polar regions during wintertime, and hence a reduction in the ozone abundance at high latitudes. The exact magnitude is difficult to estimate because the chemical processes involved are extremely sensitive to temperature. The model, however, suggests an ozone depletion over the Arctic of up to 5-10%.

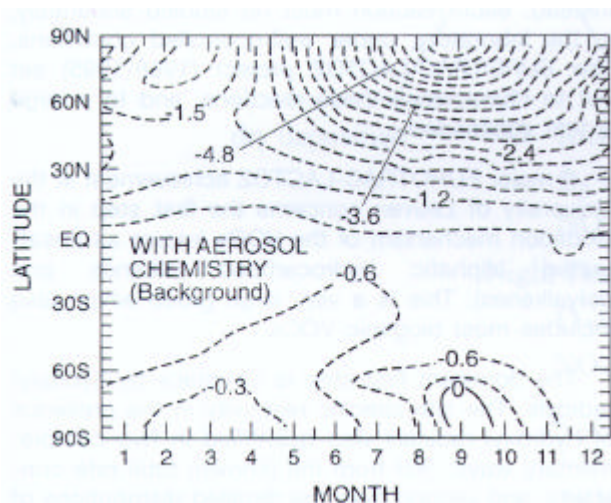


Fig. 3.12 - Change in the ozone column abundance (%) caused by a fleet of 500 supersonic aircraft flying at altitudes of 17-20 km. The calculation, as a function of latitude and season, was made using a 2-D model

#### 4 TROPOSPHERIC OZONE AND ITS PRECURSORS

The tropospheric ozone problem has two major facets. First we must consider the background ozone concentration in rural and remote areas. It appears that during the last decade this concentration has increased at 0.5-1 % /yr and has doubled during the past century. If this trend continues, ozone will soon become a greenhouse gas as important as carbon dioxide (its role as a greenhouse gas will be discussed in Section 7.2). In addition, the current levels of 40-60 mg/m<sup>3</sup> are approaching the value of 65 mg/m<sup>3</sup> recommended by the E.U. as the threshold for vegetation damage during the growing season. This could lead to a substantial decrease in the yields of various crops.

Second are the ozone peaks which are superimposed on the rising background concentration. These peaks can exceed the 180 mg/m<sup>3</sup> threshold at which the population must be notified of possible health hazards.

These "ozone episodes", which have been observed for several decades in large cities such as Los Angeles and Mexico City, are becoming more frequent over populated areas of Europe. They are linked to the release into the atmosphere of ozone precursors such as nitrogen oxides (NO<sub>x</sub>) and VOCs from automobiles, power plants and industrial installations, in areas where solar radiation is intense and hence photochemical activity is high.

The chemical mechanisms involved in ozone episodes are complex and not yet well enough understood. As a result, the prediction of photochemical ozone production rates is still subject to very large errors. During the Belgian participation in EUROTRAC (1989-1995), general rules were formulated that will be highly useful in characterizing ozone formation from one important class of VOCs. This will be discussed below. Ozone precursors are also produced in the biosphere. Aerobic soils can be significant non-point sources of NO, while flooded soils and landfills contribute to the emission of methane (CH<sub>4</sub>). On the other hand, aerobic soils are important sinks for CH<sub>4</sub> and perhaps other hydrocarbons.

Also poorly understood are the mechanisms leading to high ozone abundances outside industrialized regions, at regional and even hemispheric scales. To address this question we have to estimate to what extent ozone and its precursors are exported from urban source regions and to what extent ozone is locally produced in rural regions. Biogenic hydrocarbons (isoprene, terpenes, etc.) and their degradation products can give rise to significant amounts of

ozone in high-NO<sub>x</sub> environments. As part of the Belgian Global Change Programme (1990-1996) the oxidation mechanisms of one of these hydrocarbons ( $\alpha$ -pinene) were simulated in a laboratory experiment, which will be discussed in this section.

It should be clear that the chemistry underlying tropospheric ozone formation is universal and that its unravelling requires an effort that vastly exceeds the scientific resources of one (small) country. Only studies on a global scale - EUROTRAC, the E.U. programmes and similar north American work, and the IGBP/IGAC programme - can meet a challenge of such complexity in a reasonable time span.

The role of ozone in the free troposphere, specifically near the tropopause, is also important, since this gas affects the oxidizing capacity of the atmosphere and contributes to radiative climate forcing. Ozone represents the photochemical source of electronically excited oxygen atoms, which efficiently oxidize water vapour and hence lead to the formation of hydroxyl radicals (OH). These radicals react at different rates with a large number of atmospheric constituents (including greenhouse gases like methane and other pollutants such as hydrocarbons, sulphur and nitrogen compounds), determining their atmospheric lifetimes as well as their abundances.

Ozone concentrations in the northern hemisphere may have changed in response to human activities, including anthropogenic surface emissions (NO<sub>x</sub> and hydrocarbons) associated with combustion processes, and emissions at high latitudes from commercial and military aircraft. The magnitude of ozone trends, however, has not been established with certainty, especially in the upper troposphere.

Ozone soundings taken at the Meteorological Institute of Belgium extend to an altitude of about 35 km, covering both the biosphere and the lower and middle stratosphere. This dataset has not only been used to deduce profiles of ozone trends as a function of season but also gives information about ozone exchange between the lower stratosphere and the free troposphere.

Global chemical transport models have also been used to quantify the global budget of tropospheric ozone and to assess the potential causes of past and future trends.

## 4.1 Global Budget of Tropospheric Ozone

### 4.1.1 Chemical scheme governing the formation and fate of tropospheric ozone

#### *Qualitative and quantitative characterisation of oxidation mechanisms of unsaturated VOCs*

In industrialised and urbanised areas, tropospheric ozone is produced by the photochemical oxidation of volatile organic compounds (VOCs), with nitrogen oxides (NO<sub>x</sub>) acting as catalysts. The process is driven by sunlight (Fig. 4.1).

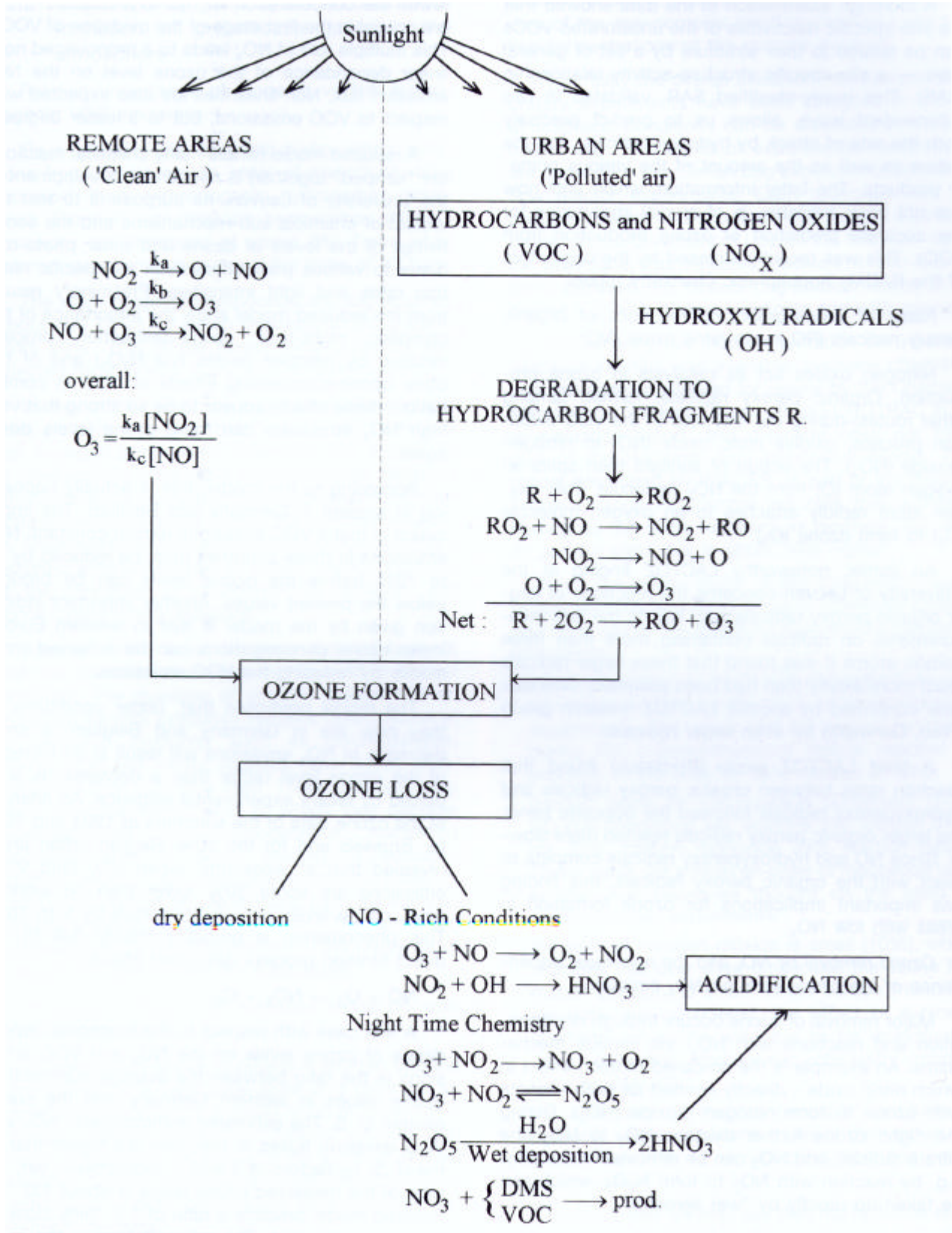
There are three main chemical classes of VOCs, each of which has up to a hundred members. Released into the atmosphere, each class reacts chemically in a different way, and each individual substance in a class reacts at a specific rate, forms specific intermediate degradation products and has a specific "total ozone formation potential" (OFP). The OFP is the maximum number of ozone molecules that can be created from the oxidation of a single VOC molecule.

The formation of ozone from VOCs, in the presence of NO<sub>x</sub> and sunlight, involves a long sequence of individual chemical reactions. Generally, organic radicals formed from VOCs combine rapidly with oxygen molecules to form organic peroxy radicals. These subsequently oxidise nitric oxide (NO) to nitrogen dioxide (NO<sub>2</sub>), which then forms ozone.

As a result, in order to be able to predict ozone production in the ambient air we must first study many hundreds of different chemical reactions. These studies cannot be done in "normal" air; instead, each reaction must be studied separately, in the laboratory, under well-controlled conditions. The EUROTRAC-LACTOZ project (1988-1995) set out to characterise these reactions, and to a large extent succeeded.

A major EUROTRAC-LACTOZ achievement at the University of Leuven concerns the first step in the oxidation mechanism of the VOCs known as unsaturated aliphatic hydrocarbons (alkenes and polyalkenes). This is a very large group which also includes most biogenic VOCs.

The dominant first step is an attack by hydroxyl radicals. The site-specific reactivity in the presence of hydroxyl radicals was quantified in two complementary ways: first from the (known) total rate constants, and second from the detailed distributions of the primary products. The latter were measured in the laboratory by mass spectrometry specially adapted for the qualitative and quantitative analysis of the complex organic radicals involved.





A thorough examination of the data showed that the site-specific reactivities of the unsaturated VOCs can be related to their structure by a set of general rules - a site-specific structure-activity relationship (SAR). This newly-identified SAR, validated in two independent ways, allows us to predict precisely both the rate of attack by hydroxyl radicals, and the nature as well as the amount of the various primary products. The latter information, which until now has not been available, is of crucial importance for the accurate prediction of ozone production from VOCs. This was recently stressed by the originators of the RADM2 tropospheric chemistry model.

*Rates of ozone-producing reactions of organic peroxy radicals (ROB with nitric oxide (NO)*

Nitrogen oxides act as catalysts in ozone production. Organic peroxy radicals, formed (among other routes) during the first step in the VOC oxidation process, oxidise nitric oxide (NO) to nitrogen dioxide (NO<sub>2</sub>). The action of sunlight then splits an oxygen atom (O) from the NO<sub>2</sub> molecule. This oxygen atom rapidly attaches to an oxygen molecule (O<sub>2</sub>) to form ozone (O<sub>3</sub>).

An earlier, noteworthy LACTOZ finding at the University of Leuven concerns the reactions of larger organic peroxy radicals with NO. In the first measurements on radicals containing more than three carbon atoms it was found that these larger radicals react more slowly than had been assumed. This was later confirmed by another LACTOZ research group (Riso, Denmark) for even larger radicals.

A third LACTOZ group (Bordeaux) found that reaction rates between organic peroxy radicals and hydroperoxy radicals followed the opposite trend: the larger organic peroxy radicals reacted more slowly. Since NO and hydroperoxy radicals compete to react with the organic peroxy radicals, this finding has important implications for ozone formation in areas with low NO. *Ozone removal by NO<sub>x</sub> and the non-linear dependence of the ozone level on NO<sub>x</sub> emissions*

Major removal of ozone occurs through dry deposition and reactions with NO<sub>x</sub>, via various mechanisms. An example is the so-called titration effect in which nitric oxide - directly emitted as such - reacts with ozone to form nitrogen dioxide (NO<sub>2</sub>). During the night, ozone further oxidises NO<sub>2</sub> to NO<sub>3</sub> (the nitrate radical), and NO<sub>3</sub> can be removed irreversibly, e.g. by reaction with N<sub>2</sub>O to form N<sub>2</sub>O<sub>5</sub>, which can be taken up rapidly by "wet aerosols". Thus NO<sub>x</sub> has a multiple role in ozone chemistry: it is essential for ozone formation, but it also destroys ozone. Furthermore, very high NO<sub>x</sub> levels

lower the concentration of hydroxyl radicals which are crucial in the first stage of the oxidation of VOCs. This multiple role of NO<sub>x</sub> leads to a pronounced nonlinear dependence of the ozone level on the NO<sub>x</sub> emission flux. Non-linearities are also expected with respect to VOC emissions, but to a lesser degree.

A reduced model (where many chemical reactions are "lumped" together) is now under development at the University of Leuven. Its purpose is to test the impact of chemical sub-mechanisms and the sensitivities of the levels of ozone and other photo-oxidants to various parameters such as specific reaction rates and light intensities. Preliminary results from the reduced model show the importance of the complex, night-time ozone-destruction process induced by nitrogen oxides (via N<sub>2</sub>O<sub>5</sub>) and of the other ozone-suppressing effects of NO. In combination, these effects appear to be so strong that very high NO<sub>x</sub> emissions can force ozone levels down again.

According to the model, this is actually happening at present in Germany and Belgium. The implication is that if VOC emissions remain constant, NO<sub>x</sub> emissions in these countries must be reduced by up to 70% before the ozone levels can be brought below the present values. Another important indication given by the model is that in western Europe lower ozone concentrations can be achieved more readily by reducing the VOC emissions.

The model prediction that, under conditions as they now are in Germany and Belgium, a small decrease of NO<sub>x</sub> emissions will result in an increase of the ozone level rather than a decrease, is supported by recent experimental evidence. An analysis of the ozone data of the summers of 1994 and 1995 for Brussels and for the other Belgian urban areas revealed that at weekends, when NO<sub>x</sub> (and VOC) emissions are some 30% lower than on working days, ozone levels actually increased by 5 to 10%. This phenomenon is probably mainly due to the direct titration process described above:  
$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$

A test case with respect to the functional dependence of ozone levels on the NO<sub>x</sub> and VOC emissions is the ratio between the average summertime ozone values in western Germany and the northeastern U. S. The estimated anthropogenic NO<sub>x</sub> and VOC emission fluxes in Germany are higher than in the U. S. by factors of 3 and 2, respectively; yet, the ratio of the measured ozone levels is about 1.0. The reduced model predicts a ratio of 1.2, fairly close to the measured value. The rationalization is the combined ozone-suppressing effect of NO<sub>x</sub> at the very high NO<sub>x</sub> emission fluxes of Germany.

#### 4.1.2 *The role of biogenic hydrocarbons in the formation of greenhouse gases in the atmosphere*

Relative importance of biogenic versus anthropogenic VOC-emissions

On a global scale, biogenic hydrocarbon emissions from forests are an order of magnitude more important than anthropogenic hydrocarbon emissions. Biogenic non-methane hydrocarbon (NMHC) emissions are estimated at about 830 Tg/yr, while anthropogenic emissions are of the order of 90 Tg/yr.

The main biogenic compounds are the terpenes (about 400 Tg/yr), of which  $\alpha$ -pinene ( $C_{10}H_{16}$ ) represents 40%. This is the reason why  $\alpha$ -pinene was selected for a kinetic study at laboratory scale.

In view of their reactivity and the enormous quantities emitted, it is clear that NMHCs play a crucial role in global atmospheric chemistry. On a regional or local scale in urban and industrial areas, biogenic emissions on a yearly basis are less important than anthropogenic sources. During the summer, however, when temperatures and light intensities are high, biogenic emissions even in urban areas contribute to the formation of photochemical oxidants and hence ozone smog episodes.

Another point about biogenic hydrocarbons is that their emission above forests may lead to aerosol formation. The question of whether  $\alpha$ -pinene is an important aerosol precursor remains open. Some of its oxidation products, such as pinonaldehyde, pinonic acid and nitrate adducts, have higher melting points than  $\alpha$ -pinene itself. These products may reach a concentration level at which they become super-saturated and homogeneous nucleation processes start to occur, leading to aerosols. Another route for heterogeneous reactions is through adsorption on pre-existing particles such as sodium chloride, fly ash or sand. The adsorbed hydrocarbons can be transformed in the presence of sunlight and photo-catalytic substances.

Reaction products of  $\alpha$ -pinene oxidation with hydroxyl radicals

As mentioned above,  $\alpha$ -pinene is emitted into the atmosphere on a very large scale and must be an important source of trace gases such as aldehydes, ketones, carbon monoxide, carbon dioxide and ozone. In addition it is known to be a strong aerosol precursor. In this way  $\alpha$ -pinene will affect the concentrations of both greenhouse gases and photochemical oxidants.

Very little, however, is known about the transformation mechanisms of  $\alpha$ -pinene in the atmosphere.

A study in situ in the atmosphere is unthinkable in view of the very complex reaction chemistry and the low concentrations of the radicals involved.

To simplify the overall oxidation mechanism, laboratory experiments have been designed in which atmospheric conditions can be simulated in a controlled way. Two types of experimental techniques are currently in use: Teflon bag experiments and fastflow reactor experiments. Each technique has its own advantages and shortcomings. For the  $\alpha$ -pinene project at the University of Leuven the fast-flow reactor technique was selected because it can distinguish between the various degradation routes of  $\alpha$ -pinene, i.e. with hydroxyl radicals and with ozone.

Until recently not much information on  $\alpha$ -pinene oxidation kinetics was available.  $\alpha$ -pinene chemistry was not even considered for review by the Chemical Mechanisms Working Group within EUROTRAC in its re-evaluation report, and  $\alpha$ -pinene does not form part of the Regional Acid Deposition Model. The model developed by IMAGES as part of the Belgian Global Change Programme assumes that  $\alpha$ -pinene undergoes the same reactions as isoprene, but with an aerosol yield that is about 50% higher.

From the kinetic study of the  $\alpha$ -pinene/hydroxyl radical reaction in the presence of molecular oxygen and nitric oxide, we can learn several new pieces of information:

- aerosol formation is much less important than was previously thought on the basis of smog-chamber experiments. The upper limit for aerosol formation during the  $\alpha$ -pinene/hydroxyl radical reaction is probably of the order of 25% instead of 50%;

- product yields for the  $\alpha$ -pinene conversion under NO-rich conditions are: acetone 3%, carbon dioxide 23%, carbon monoxide 39% (carbon basis). These yields are at least an order of magnitude larger than was previously thought on the basis of smog-chamber experiments;

- the yield of nitrogen dioxide is small (10%), which indicates that over short timescales the ozone formation capacity is small. When carbon monoxide reactions are considered, the effect of  $\alpha$ -pinene chemistry on ozone will have to be re-evaluated using elaborate atmospheric chemistry models such as IMAGES;

- the chemistry of the "condensable" products is probably not as important in view of their rather low yields. Their role as aerosol precursors has yet to be checked.

In conclusion we may say that the fast-flow reactor study of the  $\alpha$ -pinene/hydroxyl radical reaction system yields valuable quantitative information on the atmospheric degradation of  $\alpha$ -pinene. In order to

increase our confidence in the data when it is extrapolated to atmospheric conditions, the effect of reactor pressure and NO<sub>x</sub> concentration on the various product yields must be checked. Another important question still to be resolved is why the product yields derived from smog-chamber experiments are very different from our fast-flow reactor results.

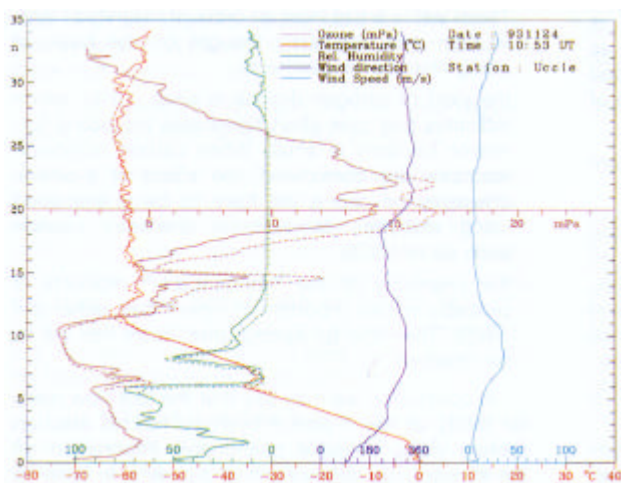
#### 4.1.3 Stratospheric ozone intrusions in the troposphere

The tropospheric ozone budget is governed not only by in situ photochemical production of ozone and ozone deposition at the surface, but also by the exchange of air masses between the stratosphere and the troposphere.

In particular, "tropopause folds", which occur in connection with upper tropospheric fronts in the polar jet stream region, are thought to be responsible for much of the mass exchange across the tropopause. Evidence for such events may be found in vertical profiles of ozone and meteorological parameters, when the following criteria - all of which point to air of stratospheric origin - are met simultaneously (see an example in Fig. 4.2):

- a pronounced ozone maximum in the free troposphere;
- very low relative humidity at the height of the ozone peak;
- a thermally stable layer in the vicinity of the ozone peak;
- a pronounced wind speed maximum between the tropospheric ozone maximum and the tropopause.

Using these criteria, the extensive time series of ozone soundings at Uccle (see Section 5.2) was



analysed to identify weather situations showing clear evidence of stratospheric ozone intrusions into the troposphere. This study was performed within the framework of the TOR (Tropospheric Ozone Research) sub-project of EUROTRAC, in co-operation with the "Service d'Aéronomie" of CNRS.

On average, 4.8% of the ozone profiles at Uccle show the presence of folds, and the frequency of tropopause folds is, within the limits of uncertainty, similar for all seasons. Intense stratospheric ozone intrusions related to tropopause folds are thus not confined to winter and early spring, as was commonly assumed; in fact the highest ozone concentrations in the folds (an important factor determining the amount of stratospheric ozone which intrudes the troposphere) occur in spring and early summer, suggesting a maximum exchange across the tropopause at this time of the year.

This is confirmed by the fact that the gross wet and dry deposition of artificial beta radioactivity, measured at Uccle in the 1960s and early 1970s, also show a maximum in June. This implies that if tropopause folds are the major agent for stratosphere-troposphere exchange, these events should be more efficient in spring and early summer. This hypothesis may be substantiated in future through case studies.

In contrast to the Uccle observations, only 2% of Ozone profiles measured at the Observatoire de Haute Provence show the presence of tropopause Folds. Although this difference has a considerable Statistical uncertainty, it may reflect the fact that the More northerly Uccle station is nearer to the average position of the polar jet stream.

Fig. 4.2 - Ozone sounding performed on 24 November 1993 at Uccle, showing an example of an intrusion of stratospheric air into the troposphere. The intrusion, which occurred at around the 7 km level, was caused by an upper tropospheric front in the polar jet stream region. The solid lines show data collected during the ascent of the sonde, and the dashed lines represent the descent. Differences between the ascent and descent data highlight the variability in time and space of ozone and meteorological data

## 4.2 Changes in Tropospheric Ozone

### 4.2.1 Episodes of photochemical ozone production in the boundary layer

Over western Europe, episodes of photochemical ozone formation in the boundary layer occur mostly during the summer months under specific weather conditions: an anticyclone centred over western or central Europe, sunny weather, high temperatures and weak winds.

Soundings showing higher ozone concentrations in the lowest few kilometres of the atmosphere than in the lower free troposphere are taken as evidence of photochemical ozone production. In a series of balloon soundings performed at Uccle, almost all the ozone profiles that fulfilled this condition took place between April and September; the maximum number of cases was found in August. There is also some indication from this data that episodes of photochemical ozone production over Belgium have been more frequent in recent years than in the 1970s.

The processes which influence ozone episodes take place in the lowest few kilometres of the atmosphere, where intense turbulent mixing occurs (the so-called convective mixed layer) and where the largest concentrations of ozone precursors are found. The intensity of ozone episodes is mainly determined by the strength of the net ozone production rate in the convective mixed layer during daylight hours. Knowledge of this rate is therefore crucial to predicting ozone episodes.

The scientific literature provides some indirect estimates of the ozone production rate near the surface under anticyclonic conditions. One example is based on simultaneous surface measurements of O<sub>3</sub>, NO, NO<sub>2</sub> and the NO<sub>2</sub> photolysis rate. However, these calculations cannot take into account the important influence of vertical ozone transport during the morning rise of the convective mixed layer, since no data at higher levels was available.

So far no studies have yielded a direct calculation of the integrated ozone production rate in the convective mixed layer. To study the quantitative daily variation of this variable, the Meteorological Institute performed a number of measuring campaigns with a tethered balloon sounding system (comprising an ozone sonde and a special radio sonde) at Tombeek (a semi-rural area at about 18 km SE of Brussels), during the summer months under stable anticyclonic conditions. During these campaigns (which were mostly part of the TOR subproject of EUROTRAC), detailed profiles of ozone and meteorological parameters up to an altitude of

about 1200 m were measured continuously between sunrise and sunset.

An electric winch released and then retrieved the tethered balloon at a speed of 0.5 m/s. The variation of the ozone profiles depends upon a number of factors: net local ozone formation rate, horizontal transport, the daily variation in the height of the mixed layer, and the ozone deposition rate at the surface. By taking all these processes into account, the researchers were able for the first time not only to calculate the vertically integrated ozone production rate in the convective mixed layer, but also to quantify this as a function of solar radiation intensity. The main results (which are also important for the modelling of tropospheric ozone) are:

- the vertically integrated ozone production rate  $P_i$  in the convective mixed layer over a semi-rural area ranges between 0 and 9  $\mu\text{g m}^{-2} \text{s}^{-1}$ . These values show a daily variation between sunrise and sunset: peak values occur during the first significant increase of direct solar radiation (at least when this increase occurs after the morning rush-hour). This phenomenon may be explained by the assumption that VOCs which accumulate near the surface during the morning hours are taken up in the ozone formation process from the moment the solar radiation is intense enough;

- the maximum values of  $P_i$  are proportional to the direct solar radiation  $I$  in the normal plane:

$$P_i = I/C \quad (1)$$

$$C = 65 \text{ W s } \mu\text{g}^{-1} \text{ up to } I = 650 \text{ W m}^{-2}$$

- at solar radiation intensities above 650  $\text{W m}^{-2}$  the maximum ozone production rate shows no further increase with  $I$  (see Fig. 4.3). In this case the lifetime of NO<sub>2</sub> before its destruction by photolysis is too short to make NO<sub>2</sub> concentration a rate-limiting factor in photochemical ozone production in the boundary layer. Instead, the ozone production rate is mainly limited by the rate of supply of hydrocarbons. The value of  $C$  in equation (1) might be different for other regions, depending upon the mean concentration of hydrocarbons.

### 4.2.2 Modelling of long-term changes in global tropospheric ozone

Industrial and domestic combustion, and human burning of biomass, have released into the atmosphere large quantities of ozone precursors. This has occurred mainly in the northern hemisphere, and the substances involved include nitrogen oxides, hydrocarbons and carbon monoxide.

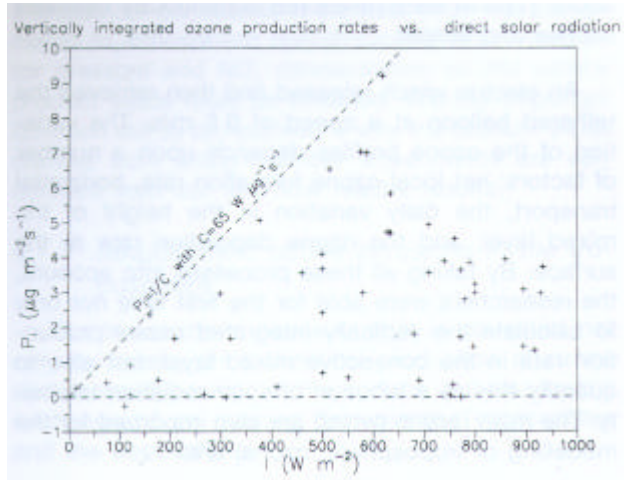


Fig. 4.3 - Scatter diagram of all the vertically-integrated ozone production rates calculated from a number of measuring campaigns with a tethered balloon sounding system, as a function of the direct solar radiation in the normal plane

One of the consequences of these anthropogenic emissions is the pollution events (photochemical smog) frequently reported in large urban areas during summertime. An important question is to what extent these regional events also affect the climate on the hemispheric and even global scales. Here it is interesting to note that at the beginning of the 20th century, ozone levels in continental Europe were 15-20 ppbv, compared to today's ozone concentrations of the order of 40 ppbv even in some remote areas (e.g. the north Atlantic and the subtropical Pacific Oceans). Simulations performed with the IMAGES model show the calculated present-day distribution of NO<sub>x</sub> (Fig. 4.4a) and O<sub>3</sub> (Fig. 4.4.b). They suggest that, on average, since pre-industrial times the concentration of tropospheric ozone in the northern hemisphere has approximately doubled during the summer (Fig. 4.4c), when photochemical processes are operating most efficiently. The corresponding increase in wintertime is smaller.

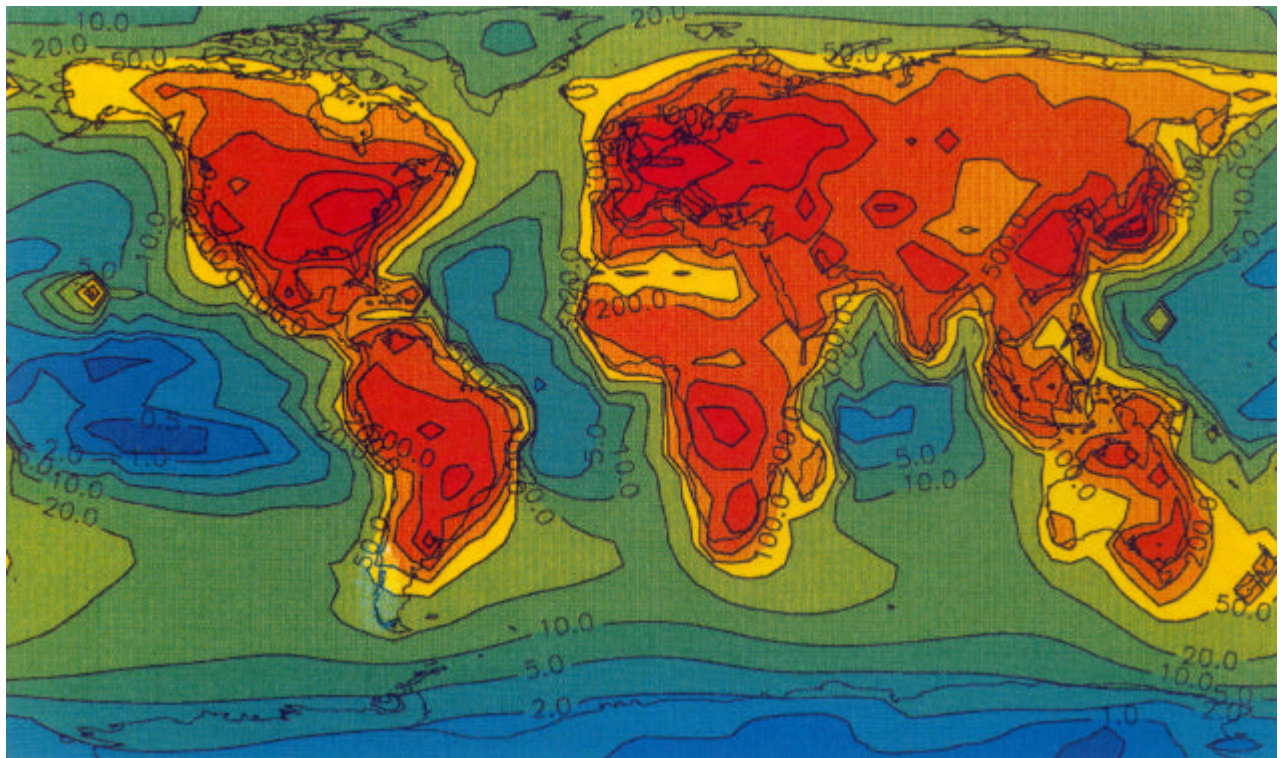


Fig. 4.4 - (a) Global distribution in July, near the earth's surface of the mixing ratio of NO<sub>x</sub> (pptv). ( $\sigma = 0,995$ ). All the data was calculated using the IMAGES Model

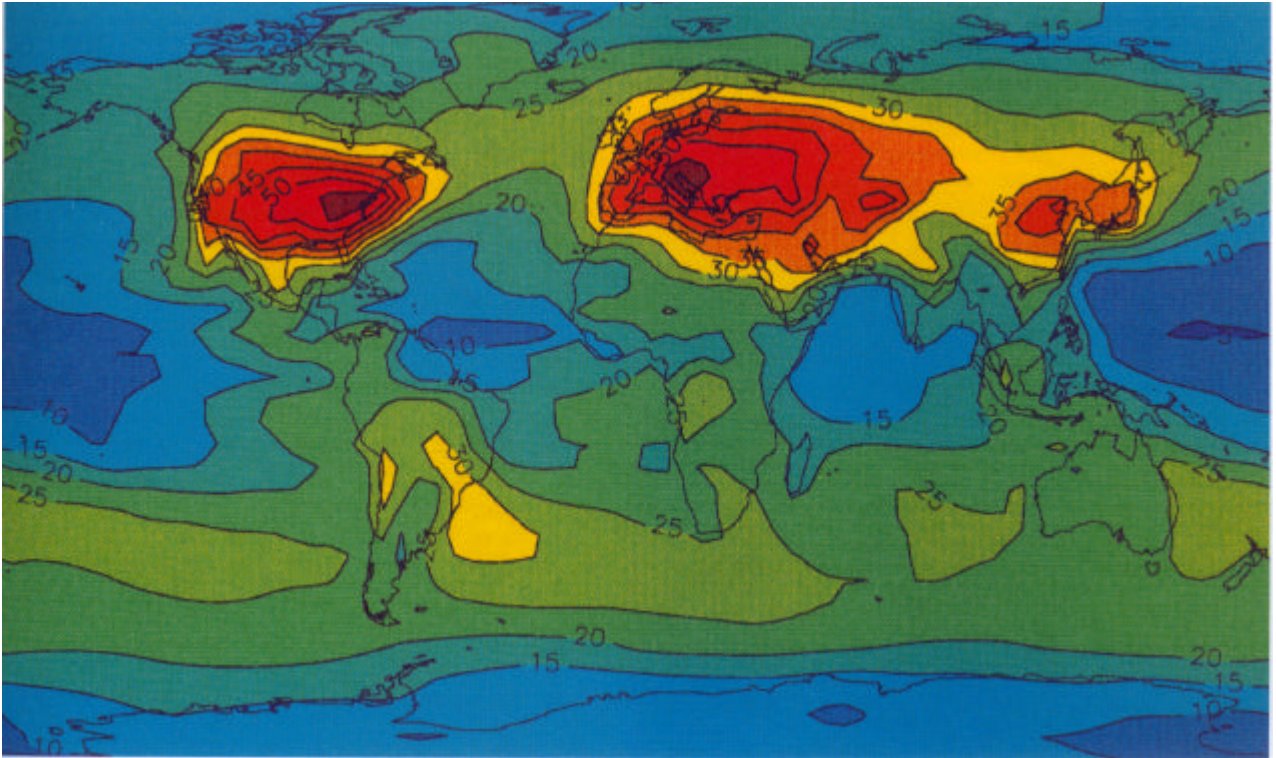


Fig. 4.4. – (b) Global distribution in July, near the earth's surface of the mixing ratio of  $O_3$  (ppbv). ( $\sigma = 0,995$ ). All the data was calculated using the IMAGES Model

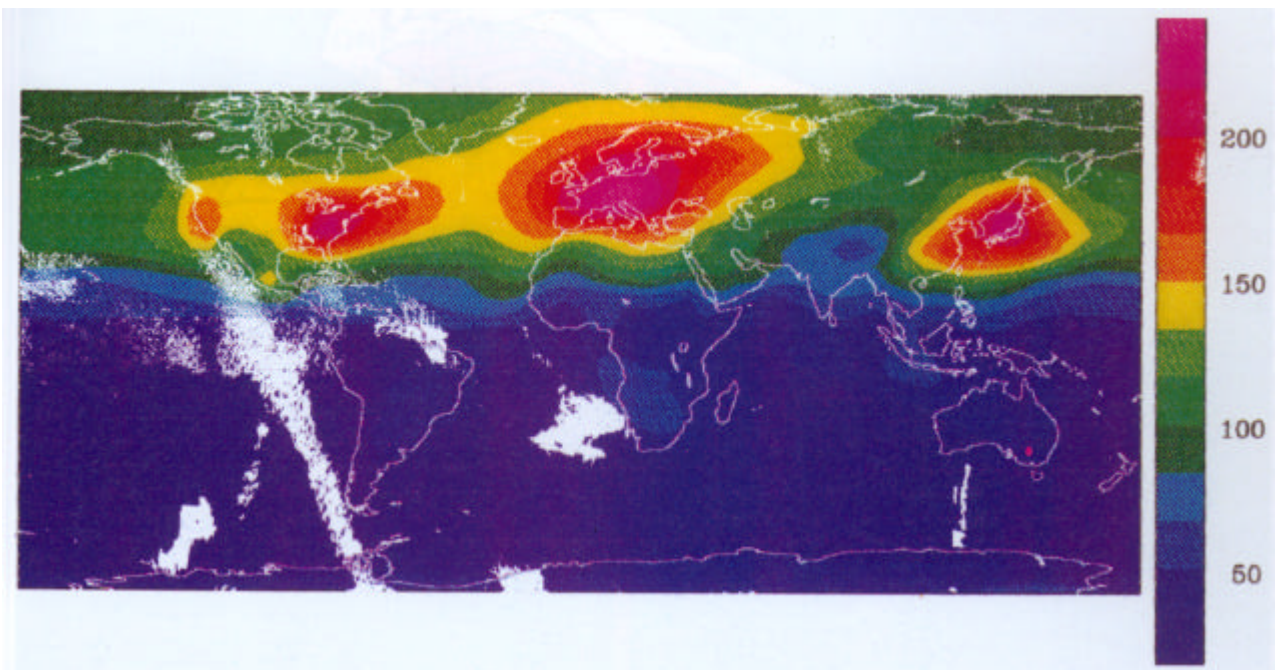


Fig. 4.4 – (c) Relative change (%) in the ozone concentration from pré-industrial times to present day. All the data was calculated using the IMAGES model. (day 182 at  $\sigma = 0,995$ )

The abundance of greenhouse gases and pollutants in the atmosphere is strongly affected by the oxidizing capacity of the atmosphere, and hence by the tropospheric abundance of radicals whose concentration is directly affected by the presence of ozone. This is the case, for example, for the hydroxyl radical (OH), whose concentration is directly affected by the emissions of several pollutants.

The IMAGES model suggests that since the preindustrial era the change in the oxidizing capacity of the atmosphere has been small, although the chemical lifetime of a gas like methane may have increased by 15% during the 20th century. Based on certain assumptions on future population growth and energy consumption (including new emission controls), the model predicts substantial global perturbations, including changes in the deposition of nitrates and sulphates on the earth's surface. The changes in ozone are expected to be largest over Asia.

Model calculations made by IMAGES also suggest that subsonic aircraft have increased the abundance of nitrogen oxides in the upper troposphere

(10-12 km) by 30-80 %, depending on the emission inventory adopted (currently uncertain by a factor of two) and the season. The corresponding increase in the concentration of ozone near the tropopause is of the order of 5-10% in the summer and 1-3% in the winter. The perturbation is not limited to flight corridors, but, as Fig. 4.5 shows, affects the entire northern hemisphere. The magnitude of the effect depends on the levels of water vapour, hydrocarbons, and nitrogen oxides in the upper troposphere - all quantities that are not well quantified on a global scale.

A major uncertainty in these predictions is associated with our poor estimates of  $\text{NO}_x$  sources (lightning, combustion at the surface, intrusion from the stratosphere, emissions from soils) and sinks (e.g. conversion to nitric acid), and their effects on the concentration of nitrogen compounds near the tropopause. For example, the uncertainty in the amount of  $\text{NO}_x$  produced by lightning is at least a factor of 10.

Growing commercial aircraft traffic will further affect ozone in the future.

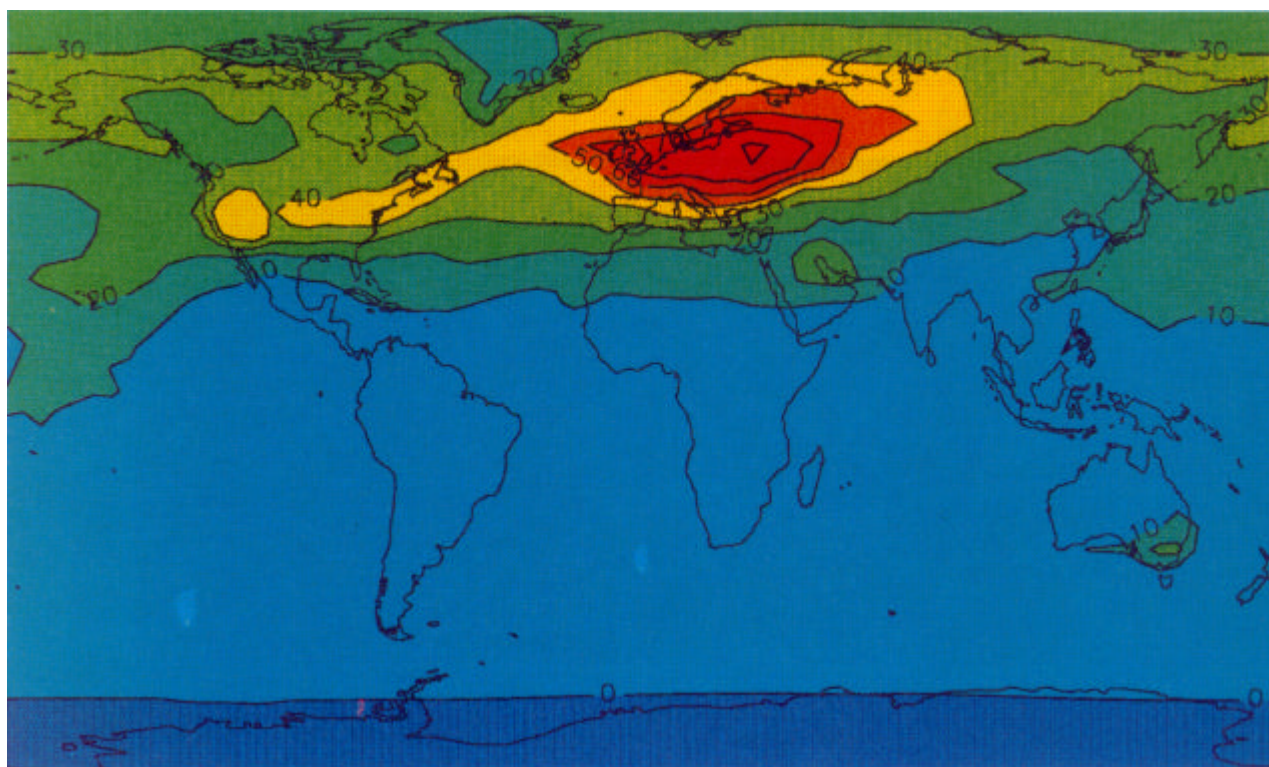


Fig. 4.5 (a) -  $\text{NO} + \text{NO}_2$  change (%) due to aircraft - July, 250 mb baseline.

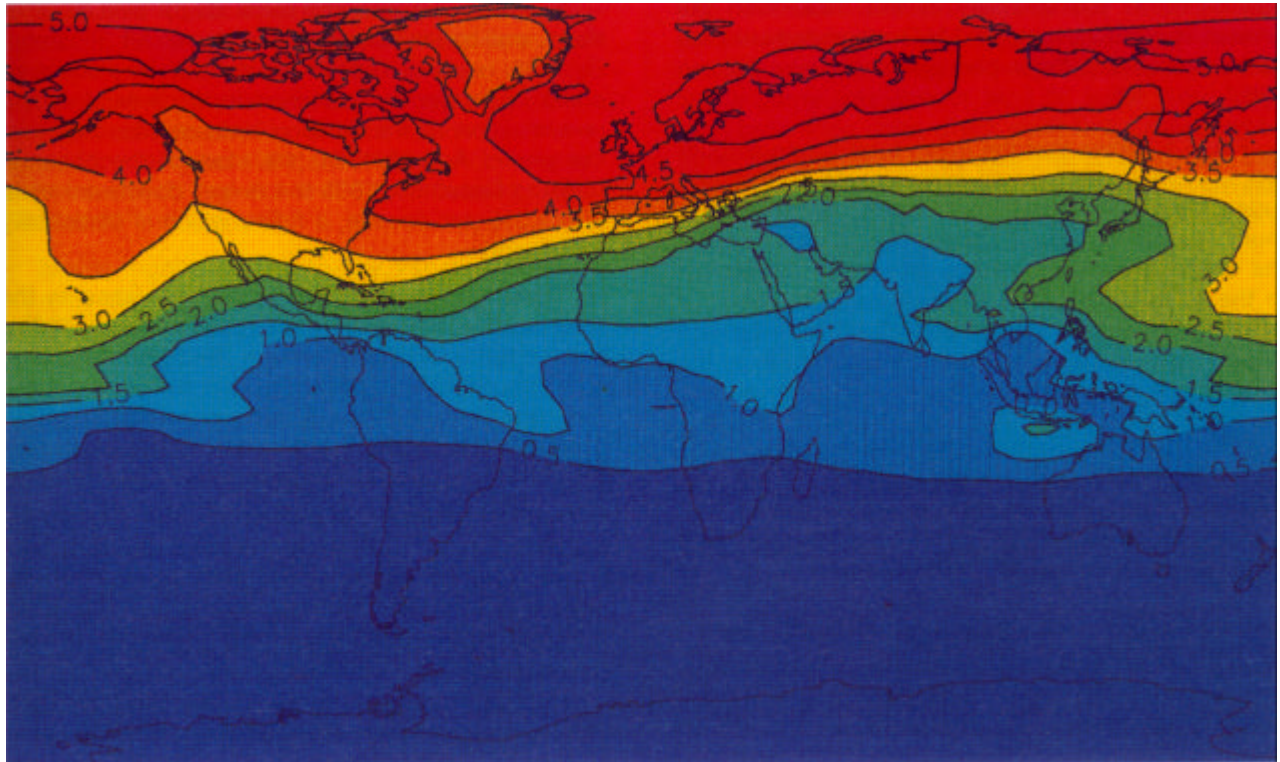


Fig. 4.5 (b) – O<sub>3</sub> change (%) due to aircraft – July, 250 mb baseline.

## 5. OBSERVED OZONE TRENDS AND CHANGES IN UV-B

### 5.1 Observed Total Ozone Trends

The total ozone amount is defined as the total thickness of the ozone layer, from the earth's surface to the top of the atmosphere, under standard conditions of pressure (1012.25 hPa) and temperature (0°C). Since 1971, daily measurements of the total ozone amount have been performed at the Meteorological Institute of Belgium (KMI/IRM) using a Dobson spectrophotometer. World-wide there are about 50 instruments of this type, forming a basic network for long-term ozone monitoring. With this type of instrument the total ozone amount is calculated from the quasi-simultaneous measurement of the relative intensity of sunlight at four different wavelengths in the UV spectral region between 305 and 340 nm.

Since 1983 ozone measurements have also been taken at KMI/IRM using a Brewer spectrophotometer. This instrument is similar to the Dobson spec-

trophotometer, but it is based on state-of-the-art technology and is completely automated. Five wavelengths are used in the UV region between 306 and 321 nm, allowing the Brewer spectrophotometer to calculate the total amounts of both SO<sub>2</sub> and ozone.

Over the whole period of observations a considerable effort has been made to preserve the quality and long-term stability of the data. The calibration of the two types of instrument is kept completely independent to allow the detection of any systematic drift. During the 1970s and 1980s the SO<sub>2</sub> amount in the boundary layer at Uccle fell significantly (as it did over most urban areas in western Europe and north America). This induced a spurious trend in the Dobson total ozone data, but the ozone data has now been corrected for this effect.

In the 1994 WMO Scientific Assessment Report of Ozone Depletion it was recognised that work still needs to be done to assess the impact of SO<sub>2</sub> on ozone measurements at many individual stations. Since the start of the Brewer observations at Uccle the agreement with the Dobson results - after correction for changes in SO<sub>2</sub> - is excellent, giving



confidence in the reliability of the data. With the Brewer spectrophotometer, UV-B measurements are performed several times per day as well (see Section 5.4).

Fig. 5.1 shows that the mean total ozone amount has a pronounced annual variation. At middle latitudes the maximum occurs in spring and the minimum in autumn. This is primarily a consequence of the seasonal variation of the general air circulation in the stratosphere. The total ozone amount has a large day-to-day variability, especially from January to April. This is mainly related to the variability of the origin of air masses in the lower stratosphere over the measuring station. If we also consider the fact that the mean total ozone amount seems to vary over the course of a solar cycle (about 11 years), it is clear that total ozone trends only make sense if they are calculated over sufficiently long periods of time (at least one solar cycle).

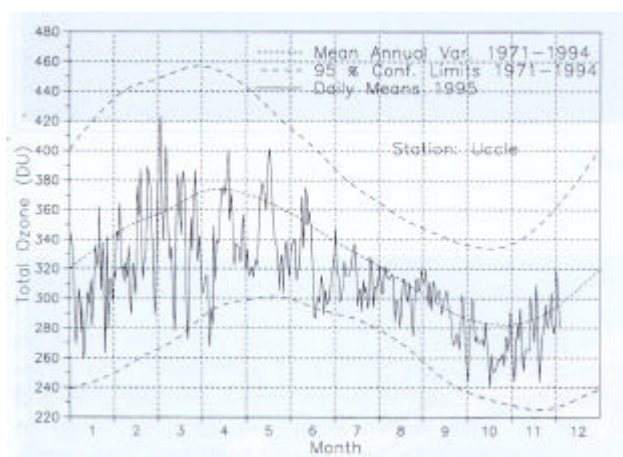


Fig. 5.1 - Mean annual variation in the total ozone amount measured at Uccle over the period 1971 through 1995, and variation of the daily means in 1995. The total ozone amounts are expressed in Dobson units ( $1 \text{ DU} = 10^{-3} \text{ cm at } 1013.25 \text{ hPa and } 0^\circ\text{C}$ ). By definition, 95% of all total ozone values over the period 1971-1994 were within the 95% confidence limits

It is important to note that the observed total ozone trends over Belgium, and everywhere else in the northern mid-latitudes, are highly dependent upon the period chosen. Up to November 1991 the total ozone trend at Uccle as calculated from the Dobson data (corrected for S02) showed virtually no overall trend. During the winters 1991-1992 and 1992-1993 very low total ozone values were measured, and this is widely believed to be at least partly related to the eruption of Mt. Pinatubo in June 1991 (see Section 3.2).

In 1994 there was still some doubt over whether the overall ozone decrease was due to Mt. Pinatubo. By 1995, however, the low values that were observed could no longer be explained in this way. A recent re-evaluation of the Dobson data reveals that over the period August 1971 (the start of the observations) to December 1995 the overall downward trend was 1.5% per decade, a figure which is statistically significant.

This trend is due to a strong decrease in the mean ozone level since the beginning of the 1980s. Over the period from Januari 1980 to December 1995, the total ozone decrease at Uccle was 4.1

per decade (see Fig. 5.2). The downward trend is observed throughout the year but is largest in winter and spring (-6% per decade from Januari to May).

Fig. 5.1 shows that the daily mean total ozone values in 1995 were mostly below the long-term mean value. On the other hand the number of daily mean values below the 95% confidence limit is not unusual. This simply means that only relatively high ozone values (which are mostly associated with polar air masses in the lower stratosphere) were affected. This is in agreement with observations of chemically-induced ozone depletion over the Arctic (see Chapter 3).

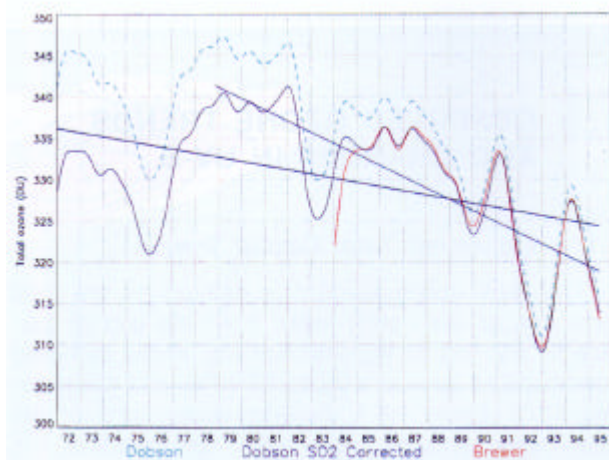


Fig. 5.2 - Running mean of the total ozone amount measured at Uccle with a Dobson spectrophotometer before (dashed blue line) and after (solid blue line) SO<sub>2</sub> correction, and measured with an automated Brewer spectrophotometer (solid red line). The straight lines indicate the linear trend (after SO<sub>2</sub> correction) over the whole time period and the period after Januari 1980, respectively. The agreement between the Brewer and Dobson instruments (after SO<sub>2</sub> correction) is excellent. The difference between the two curves in 1984 is an artifact due to the method by which running means are calculated at the beginning and end of a time series. Since the calibrations of the two instruments are kept completely independent, this good agreement gives confidence in the reliability of the results

In addition to the total ozone measurements performed at Uccle, infrared solar observations made by Liège scientists at the ISSJ have been analyzed for changes in ozone vertical column abundance over the last decade. Fig. 5.3 shows the O<sub>3</sub> column abundance between 1984 and 1995 (for comparison of the scales in Fig. 5.2 and 5.3, 1 Dobson Unit = 2.687 x 10<sup>16</sup> molec/cm<sup>2</sup>).

Beside significant day-to-day variations, the O<sub>3</sub> columns display a seasonal variation superimposed on a longer-term decrease. Over the 12-year period covered by Fig. 5.3, the ensemble of all daily mean columns (red and black points combined) shows a decrease of 7.6% per decade (at Uccle the decrease over the same period is 6.0% per decade). However, if we exclude those measurements made during the first 100 days of the year (red points), the remaining data (black points only) gives a mean decrease of only 3.9% per decade. This difference shows that over the last decade the decrease in ozone was substantially larger during the first part of each year than during the remaining months, which agrees with the Uccle data.

It is encouraging that the ozone data from both Uccle and the ISSJ, derived independently and using two different techniques, lead to very similar conclusions about both long-term rates of change and seasonal variations in the total ozone column above

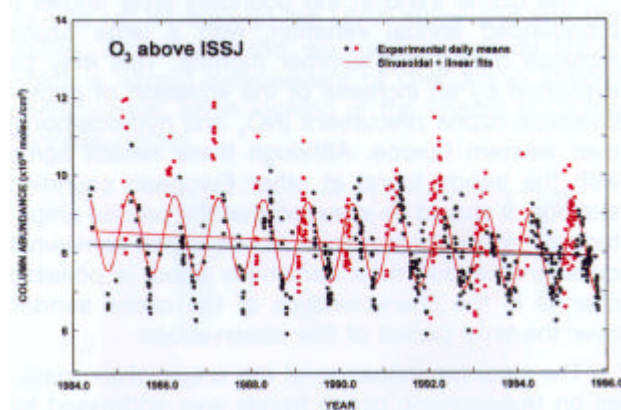


Fig. 5.3 - Vertical column abundances of ozone measured above the ISSJ over the last 12 years. The data reflects significant day-to-day, seasonal, and long-term variations. The entire set of measurements (red and black points combined) reflects a rate of O<sub>3</sub> decrease of 0.76%/yr. Excluding those columns measured during the first 100 days of each year (red values) results in a decrease of only 0.39%/yr. This shows that over the last decade the ozone decrease was substantially larger during winter and early spring than during the rest of the year. To date, chemical and dynamic model calculations have been able to reproduce neither the magnitude of the ozone decrease observed at northern mid-latitudes since the mid-1980s, nor its differential change over various periods of the year

two different northern mid-latitude sites. These results also confirm findings from satellite measurements; as such they are very important because space-borne instruments tend to suffer from longterm calibration drifts which need to be assessed by other observational methods. Researchers are currently using mathematical models to try to explain the small differences which do exist between the ISSJ and Uccle ozone data.

## 5.2 Observed Trends in Stratospheric Ozone

Since 1969 regular balloon soundings with ozone sondes have been performed at KMI/IRM. Ozone concentration as a function of altitude is measured using a small electrolytic cell through which ambient air is pumped. Each balloon also carries a radiosonde to measure temperature, humidity and wind speed.

These soundings, which normally reach an altitude of about 34 km, are performed three times a week. This has produced one of the longest and most complete time series of ozone measurements in the world. In any month the mean vertical distribution of ozone partial pressure over Uccle shows a maximum at around 11 km above the tropopause. From February to May a secondary ozone maximum is often found in the lower stratosphere, with a very steep gradient which extends through the levels just below the tropopause.

Over the past few years (within the framework of the TOR sub-project of EUROTRAC) a great deal of effort has been put into the homogenisation of the whole data set to remove all known instrument errors. Recently the time series of all reliable ozone profiles over the period from 1969 through 1995 was analysed at relative altitude levels determined with respect to the tropopause. The results clearly reveal the different behaviour of ozone trends in the stratosphere and the free troposphere as a function of the season. The main conclusions about stratospheric ozone are (Fig. 5.4):

- between 7 and 14 km above the tropopause (which is around the level of the main ozone maximum) the trend is about -0.5%/yr and is negative throughout the year. From 16 km above the tropopause to the top of the soundings, the trend is weak and not statistically significant;
- from February to June the boundary between negative trends in the stratosphere and positive trends in the troposphere coincides with the tropopause, highlighting the different processes that determine ozone concentration in the two layers of the atmosphere. At this time of the year the largest negative

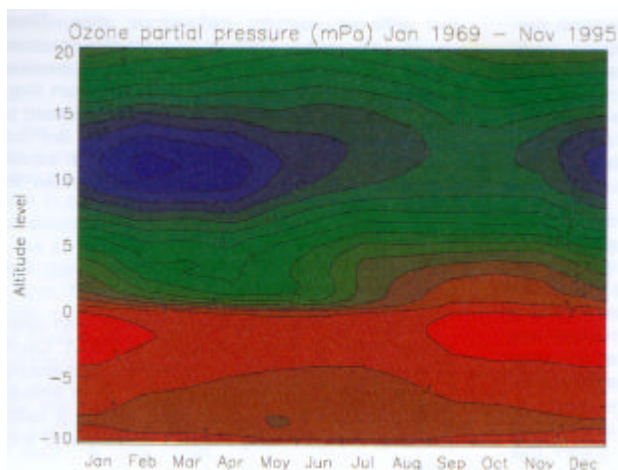


Fig. 5.4 - Cross-section of the vertical distribution of ozone trends (in %/yr) at Uccle over the time period 1969 through 1995. Vertical scale: negative values are relative altitude levels between the tropopause (level 0) and the ground (level -10); positive values are kilometres above tropopause level. In the green (red) area the positive (negative) trends are statistically significant at the 5% level

trends (up to about -1 %/yr) are found below the ozone maximum, which coincides in season and altitude with the occurrence of the secondary ozone maximum. Since this secondary ozone maximum is mostly found in air masses coming from the Arctic, it is tempting to assume that this pronounced downward trend comes from losses of ozone through heterogeneous chemistry;

- from July to January the positive ozone trend in the free troposphere extends to an altitude of about 1-6 km above the tropopause.

During the winters of 1991-1992 and 1992-1993 the stratospheric ozone values observed at Uccle were about 15-35% lower than the long-term mean (as in most mid-latitude stations in the northern hemisphere). This is widely believed to be at least partly related to the eruption of Mt. Pinatubo in June 1991. This effect is also attributed to ozone losses through heterogeneous chemistry (see Section 3.2)

### 5.3 Observed Trends in Tropospheric Ozone

In the discussion of tropospheric ozone we must consider two different layers. In the boundary layer (which extends from the surface up to about 2 km above mean sea level), the chemical and dynamic behaviour of ozone is determined by a number of specific processes such as dry deposition at the surface, intense vertical mixing in the convective mixed layer and the fact that most of the precursors for photochemical ozone production are emitted near the surface. In the free troposphere (which extends from the top of the boundary layer up to the

tropopause) the ozone concentration is much less influenced by local or regional processes.

The Uccle ozone soundings show a year-round ozone increase in the free troposphere over the period from 1969 to December 1995 (see Fig. 5.4), with the largest values in the upper troposphere (up to 1.5% during September and October) and the lowest values above the top of the boundary layer.

The ozone trend in the boundary layer shows a pronounced annual variation, with a large ozone increase during the summer months. This may be explained by an increase of the emission of photochemical ozone precursors ( $\text{NO}_x$  and hydrocarbons) over western Europe. Although these results agree with the trends found at other European sounding stations, it should be stressed that the precise amplitude of tropospheric ozone trends is still somewhat questionable due to uncertainties about a possible change in the characteristics of the ozone sondes over the time period of the observations.

The possible influence of the origin of air masses on tropospheric ozone trends was addressed by analysing wind directions. During the winter months the ozone concentration in both the boundary layer and the free troposphere are virtually independent of the wind sector. During the summer months the ozone concentrations in the boundary layer at Uccle are highest when the wind is easterly. It also appears that this produces the largest ozone increases (about 2%/yr.). This is readily explained by the fact that easterly winds over Belgium during the summer are mostly associated with warm and sunny weather, which favours photochemical ozone production in the boundary layer (see Section 4.2.1).

The possibility of a link between stratospheric and tropospheric ozone trends was studied. Variations within individual months of integrated stratospheric ozone amounts show a strong negative correlation with variations of ozone concentrations in the lower troposphere. This points to a radiative effect: lower concentrations of stratospheric ozone cause increased penetration of UV radiation into the troposphere. This in turn may lead to increased net ozone production in the free troposphere at relatively high NO<sub>x</sub> concentrations.

#### 5.4 Changes in UV-B

Significant ozone reduction has been observed on a global scale at mid- and high latitudes in both hemisphere since the end of the 1970s. Because solar UV-B radiation (280-315 nm) (and, to a much lesser extent, UV-A at 315-400 nm) is strongly absorbed by stratospheric ozone, the global climatology of UV irradiance at the earth's surface will be affected by changes in the amount of ozone. In turn, these two wavelength bands are responsible for many important photo-reactions in biological systems.

Each biological process is characterised by a specific "action spectrum". Most have a maximum at wavelengths shorter than 300 nm or even below 280 nm (UV-C). They decrease sharply - by several orders of magnitude - in the UV-B region, where the UV irradiance itself increases steeply with wavelength. Some processes, however, have action spectra that tail off through the UV-A range and into the visible. Because of this we need to include UV-A, which is almost independent of changes in atmospheric ozone, when looking at the impact of ozone changes on life.

The convolution of the biological action spectrum with the UV solar irradiance at the earth's surface gives the instantaneous biological dose rate for each specific biological effect. The effects of UV-B on people - skin cancer, cataracts and immune response decrease - need to be adequately studied. It is therefore important to quantify future stratospheric ozone trends and to relate these to biological changes caused by UV-B, on both global and regional scales.

From the well-known absorption by ozone of sunlight in the UV-B spectral region (290 to 315 nm), it follows that the UV-B irradiance (direct and diffuse components) at the earth's surface should increase as the total ozone amount decreases. A study of Brewer spectrophotometer data (see Section 5.1) shows a strong negative correlation between total ozone amounts and UV-B radiation intensities under clear sky conditions. The negative correlation is most pronounced at wavelengths below 305 nm. Fig. 5.5 shows that at these wavelengths a 1 % decrease in total ozone gives an increase of about 4% in UV-B irradiance.

The anti correlation between the total ozone amount and the UV-B radiation dose has also been demonstrated by data acquired since 1993 using an automatic station operated by IASB/BIRA (see Fig. 5.6). This has two double monochromators with two different fields of view (global and 10°), and covers the full UV and visible ranges from 280 to 680 nm. This instrument has been calibrated against the Brewer spectrophotometer described above.

The main difficulty in measuring UV irradiance comes from the need for very accurate radiometric absolute calibration and long-term stability in the

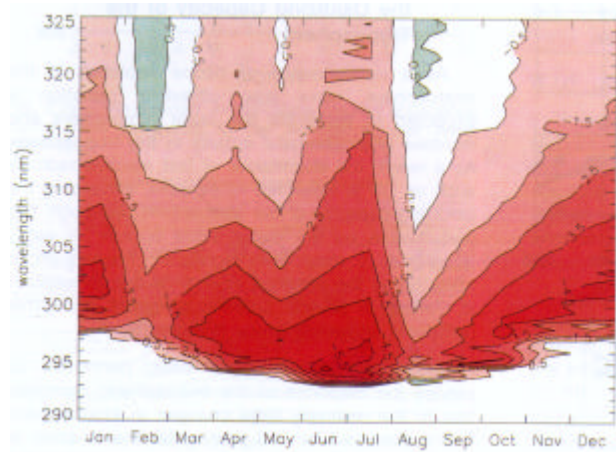


Fig. 5.5 - Percentage change in UV-B at different wavelengths for 1 % total ozone change at noon and clear sky conditions, as calculated from quasi-simultaneous measurements of total ozone and UV-B at Uccle with a Brewer spectrophotometer. The UV-B changes are largest at wavelengths shorter than 303 nm. The lower border of the isolines indicate the shortest wavelengths reaching the surface at Uccle, as a function of the season. The apparent decrease in the change in UV-B near the lower border is an artifact caused by a signal-to-noise ratio that is too low for reliable statistical calculations

**INFLUENCE OF TOTAL OZONE COLUMN ON THE UV-B IRRADIANCE FOR SIMILAR METEOROLOGICAL CONDITIONS.**

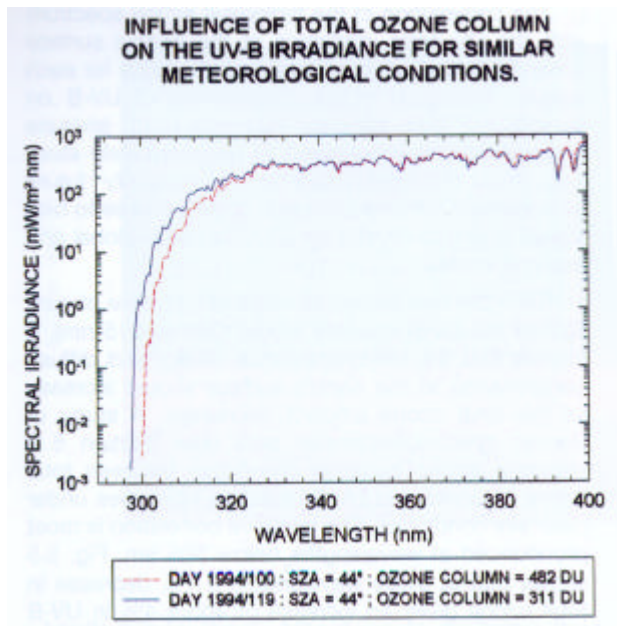


Fig. 5.6(a) - Influence of total ozone column on the UV-B irradiance for similar meteorological conditions

**ANTICORRELATION BETWEEN UV-B IRRADIANCES (NORMALISED FOR SZA AND CLOUD EFFECT) AND TOTAL OZONE COLUMN.**

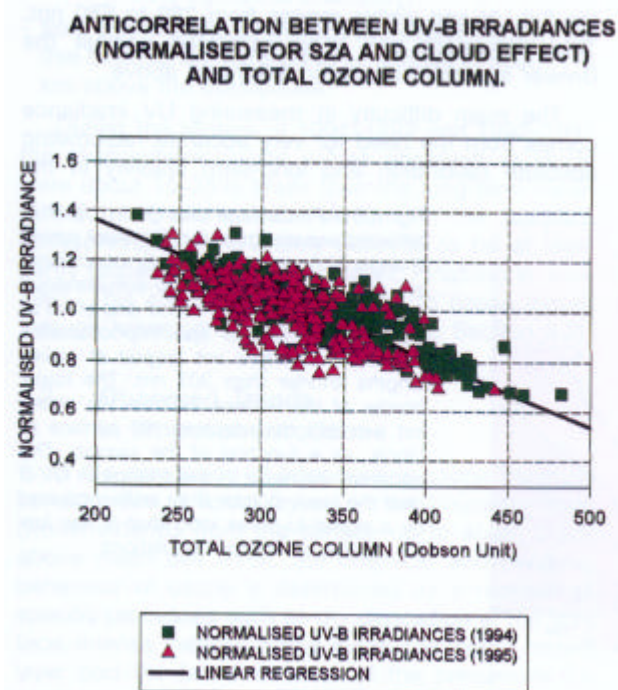


Fig. 5.6(b) - Anticorrelation between UV-B irradiances (normalised for SZA and cloud effect) and total ozone column

measuring instruments. Several European monitoring stations have failed to detect the long-term increase in UV-B intensity which should accompany the decrease in total ozone. The main reason is the larger errors in UV-B measurements as compared to total ozone measurements, but there are other factors influencing the UV transmission in the troposphere. These include trends in the density of aerosols observed over Europe.

To address the issue of UV trend monitoring in Europe the EC has funded a co-ordinated project for terrestrial UV measurements. The objective was to produce recommendations for an integrated network throughout Europe giving reliable and accurate spectral measurements from different instruments, either existing or in development. In addition, a travelling calibration system that can be used for all instruments was developed and tested (the Transportable Lamp System, TLS) as well as a computational system for normalizing the results from instruments with different characteristics (optical input geometries, bandpasses, etc.).

Four intercomparison campaigns were carried out between 1991 and 1995 under the auspices of the EC. These allowed significant improvements in instrument characterisation, radiometric calibration and measurement accuracy. A group of UV spectrometers has been identified as a potential core for the future European network which will play a pivotal role in the WMO UV monitoring programme. This is co-ordinated by the newly-appointed Scientific Steering Committee, which is chaired by a Belgian scientist.

**5.5 Depletion of Stratospheric Ozone and the Oxidizing Capacity of the Troposphere**

As a consequence of ozone depletion in the stratosphere, more solar ultraviolet radiation is expected to penetrate the lower atmosphere and increase photochemical activity in the troposphere. As a result, the abundance of fast reactive radicals such as OH is expected to increase, enhancing the oxidizing capacity of the atmosphere. Although this perturbation on the global scale cannot be easily quantified, it may have significant consequences since it has the potential to change the atmospheric lifetime of several greenhouse gases and other pollutants (including ozone precursors).

Model calculations have been performed to assess the response of the tropospheric composition to the relatively large changes in stratospheric ozone observed for 2-3 years after the eruption of Mt. Pinatubo. Fig. 5.6a shows the anomaly in the

ozone column abundance during 1993 compared to the average for year 1989-1990. Fig. 5.7b shows the resulting change in the OH concentration near the surface as calculated by the IMAGES model. The OH abundance increases by approximately 1 % at the equator, and by more than 5% north of 30°N or south of 60°S. This increase is caused by the increased photolysis of ozone, which produces more of the electronically-excited oxygen atom O(1 D) and hence more OH by the  $H_2O + O(1 D)$  reaction.

The gradual decrease in the ozone column associated with human activities has probably somewhat modified the oxidizing capacity of the atmosphere. It is therefore likely to have caused limited changes in the trends of gases such as methane or carbon monoxide in the troposphere. The exact magnitude of this effect remains, however, to be quantified.

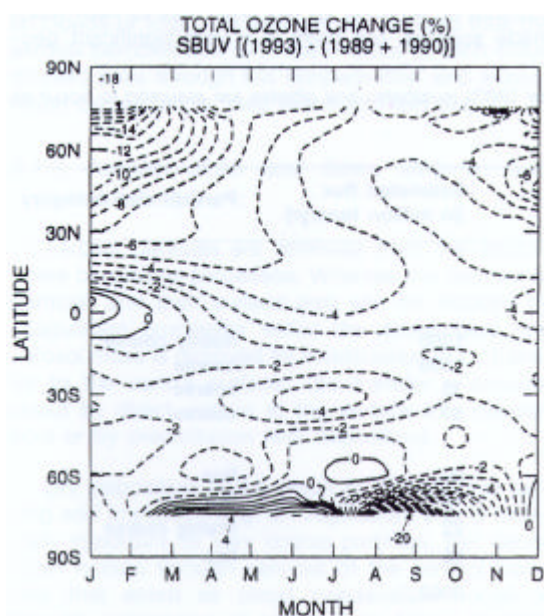


Fig. 5.7a - The anomaly in the ozone column abundance during 1993 compared to the average for the years 1989-1990

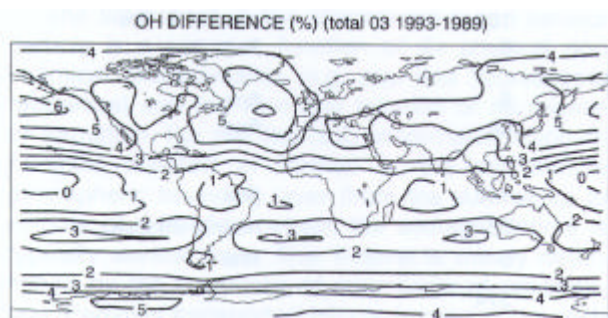


Fig. 5.7b - The resulting change in OH concentration near the surface, as calculated by the IMAGES model

## 6

## ATMOSPHERIC AEROSOLS

Aerosols are tiny liquid or solid particles that are present in the atmosphere. They have diameters ranging from 0.001  $\mu m$  to over 10  $\mu m$ , but the size range 0.1-10  $\mu m$  accounts for most of the mass of aerosols in the atmosphere. Although aerosols form only a small part of the total mass of the atmosphere (about 1 part in 10<sup>9</sup>), they play an important role in atmospheric chemistry. They also affect human and animal health, and they influence climate, either directly by reflecting and absorbing solar radiation or indirectly by modifying the optical properties of clouds.

Tropospheric aerosols are produced by the surface emission or dispersion of material such as smoke or dust, or by the chemical conversion of gases such as sulphur dioxide. These sources can be natural or anthropogenic. It is believed that sources of human origin have increased substantially during the 20th century and are significantly affecting the earth's climate. For example, coal and oil combustion releases large amounts of  $SO_2$  into the atmosphere, whilst deforestation, savanna fires and other biomass burning in the tropics inject large amounts of organic and elemental carbon.

Stratospheric aerosol particles originate mainly from the oxidation of  $SO_2$  injected into the stratosphere by large volcanic eruptions, such as that of Mt. Pinatubo in 1991. Besides this sulphate from volcanic origin there is also a background sulphate concentration. This is believed to be formed primarily by the oxidation of long-lived sulphur compounds (mainly carbonyl sulphide).

### 6.1 Formation, Properties, Transformation and Fate of Tropospheric Aerosols

#### 6.1.1 Sources

Atmospheric aerosols can be produced by two distinct mechanisms: direct injection of particles into the atmosphere, mostly by dispersion processes, resulting in so-called primary aerosols; and transformation of gaseous precursors (through nucleation and condensation processes) into liquid or solid secondary aerosol particles.

Primary aerosols tend to make up the coarse aerosol fraction, with diameters greater than 1  $\mu m$ . They do not travel very far because they settle under the influence of gravity, and they do not penetrate far into the respiratory systems of people or animals. Secondary particles constitute most of the fine particle fraction, with diameters below 1  $\mu m$ ; these have the greatest effect on climate.

Table 6.1 shows the present-day best estimates for the releases of aerosols from the various natural and anthropogenic sources. The flux values for soil dust and sea salt in Table 6.1 are rather arbitrary, as they depend on the minimum transport distance and hence the maximum particle size - chosen.

### 6.1.2 Physical and chemical transformation and size distribution of aerosols

Once emitted into the atmosphere, airborne particulate matter is transported by the winds until it eventually returns to the earth surface. During this atmospheric transport, new very fine particles (with diameters well below 0.1  $\mu\text{m}$ ) are formed by nucleation from gaseous precursors. These "nucleation-mode" particles then grow into "accumulation-mode" particles (with diameters between 0.1 and 1  $\mu\text{m}$ ) by Brownian coagulation. Existing accumulation-mode particles grow as products of gas-phase or multi

phase reactions condense onto them. On the other hand "coarse-mode" aerosol fraction will lose particles at its upper end because of gravitational settling.

Because Brownian motion becomes unimportant for particle sizes above about 0.1  $\mu\text{m}$  diameter, accumulation-mode particles do not readily become attached to coarse-mode particles. As a consequence, distinct fine and coarse particle modes are normally seen in the aerosol number and mass size distributions (Fig. 6.1).

Fig. 6.1 further shows that while the nucleation mode may account for a very large fraction of the total number of particles, it represents a very small fraction of the total mass. In general, most of the mass in the coarse mode is derived from natural sources, while most of the fine mass is from manmade sources, but there is a very significant geo

Table 6.1 - Global emission estimates for major aerosol types in the 1980s (sulphates and nitrates are assumed to occur as ammonium salts)

Source	Estimated flux (in million tons/yr)	Particle size category
<b>Natural</b>		
<i>Primary</i>		
Soil dust (mineral aerosol)	1500	mainly coarse
Sea salt	1300	coarse
Volcanic dust	33	coarse
Primary organic aerosols (marine and continental)	50	coarse
<i>Secondary</i>		
Sulphates from biogenic gases (mainly DMS)	90	fine
Sulphates from volcanic SO <sub>2</sub>	12	fine
Nitrates from N <sub>x</sub> , (lightning, soil microbes)	22	mainly coarse
Organic matter from biogenic gases	55	fine
Subtotal for natural sources	3062	
<b>Anthropogenic</b>		
<i>Primary</i>		
Dust from fossil fuel burning, cement manufacturing, metallurgy, waste incineration etc.	100	coarse & fine
Soot (black carbon) from fossil fuels (coal, oil)	8	fine
Soot from biomass combustion (forest and savanna fires, agricultural burning, fuelwood)	5	fine
Biomass burning (without soot)	80	fine
<i>Secondary</i>		
Sulphates from SO <sub>2</sub> (mainly from coal and oil burning)	140	fine
Nitrates from NO <sub>x</sub> (fossil fuel and biomass combustion)	36	mainly coarse
Organic matter from anthropogenic gases	5	fine
Subtotal for anthropogenic sources	374	
TOTAL	3436	

graphical variability in the relative contributions of the two source types. The bulk of the coarse mass is often made up of sea salt or mineral dust, while most of the fine mass consists of sulphates, organics and soot (Fig. 6.1).

The various chemical transformation processes that take place in the atmosphere may significantly alter the chemical composition of the aerosol. For example, elements that are present in mineral dust particles may be converted into more soluble form (aluminium is an example) or a different oxidation state (transition metals such as Fe). This atmospheric processing may lead to chemical species that harm the environment (as for Al) and to significant changes of the bioavailability of the elements. Much of the atmospheric processing of particles takes place when they are incorporated into liquid water droplets (in clouds or fogs). On average, clouds (and thus the aerosol particles that form the nucleus of each cloud droplet) pass through ten condensation and evaporation cycles before they eventually rain out.

### 6.1.3 Aerosol sinks and fates, lifetimes and variability

Aerosol particles are removed from the atmosphere by various processes. Whereas the number of particles and their surface area can be reduced by coagulation processes within the atmosphere, the aerosol mass is removed by volatilization or by transfer to the earth's surface. The transfer is brought about by direct uptake at the surface (dry deposition) or by precipitation (wet deposition).

Dry deposition is the result of gravitational settling and impaction (e.g. on vegetation) and is especially important for very coarse particles. Wet deposition occurs through rain-out of the aerosol particles that acted as cloud condensation nuclei or through scavenging of particles by falling droplets (wash-out). For particles in the accumulation mode, wet deposition is the major removal process.

The time spent in the atmosphere by an aerosol particle is a complex function of its physical and chemical characteristics (e.g. size and hygroscopic properties) and the time and location of its release or formation. For the fine (sub-micrometer) sulphate particles released or formed in the mid-latitude atmospheric boundary layer (from the surface up to heights of a few kilometres), the average lifetime is typically several days. This lifetime is mainly determined by the frequency of recurrence of precipitation. Particles transported into or formed in the middle or upper troposphere are likely to have longer lifetimes (weeks to months) because of less efficient

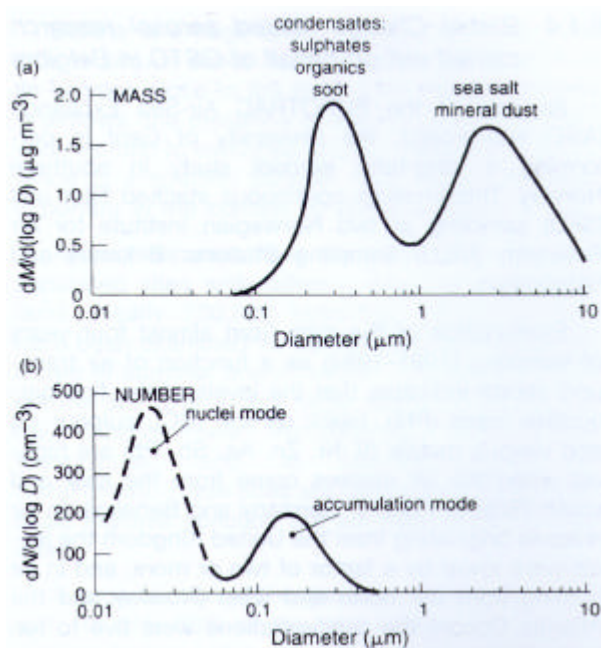


Fig. 6.1 - Aerosol size distribution as a function of (a) mass and (b) number. The distributions are based on large amounts of data from both continental and marine locations. The data is displayed so that the area under the curve corresponds to the total mass and number concentrations, respectively. Very fine (nuclei-mode) particles may account for a very large fraction of the total number of particles, but they contribute very little to the aerosol mass. Conversely, coarse-mode particles (with diameters of 1-10  $\mu\text{m}$ ) are major contributors to the aerosol mass, but make up only a very small fraction of the total number of particles

precipitation scavenging at these altitudes. Lifetimes in the stratosphere are of the order of one year.

The comparatively short lifetimes of aerosols, their limited vertical transport and the uneven distribution of aerosol sources over the globe mean that the atmospheric mass concentration, size distribution, chemical composition and hygroscopic and optical (radiative) properties of aerosols show great variability in time and space. For example, the total aerosol mass concentration is a few  $\mu\text{g}/\text{m}^3$  in clean areas, but can be as high as several  $\mu\text{g}/\text{m}^3$  in dusty cities.

At any single site, within a time of hours or days the concentration can vary by an order of magnitude or more. There can also be large seasonal changes. Concentrations are generally much higher in the atmospheric boundary layer than at higher altitudes. The variability in time and space is also seen in the relative contributions from natural and anthropogenic sources. There can be large variations from region to region in the extent of the anthropogenic perturbation, and within each region the perturbation may vary substantially with time (e.g. with the seasons).



6.1.4 *Global Change related aerosol research carried out on behalf of OSTC in Belgium*

As part of the EUROTRAC Air-Sea Exchange (ASE) sub-project, the University of Gent is performing a long-term aerosol study in southern Norway. This involves continuous stacked filter unit (SFU) sampling at two Norwegian Institute for Air Research (NILU) Sampling Stations: Birkenes and Skreådalen.

Examination of the data from almost four years of sampling (1991-1994) as a function of air transport sector indicates that the levels of the fine particulate mass (PM), black carbon (BC), sulphur (S) and various metals (V, Ni, Zn, As, Sb, Pb) are highest when the air masses come from the east and south (Russia, Poland, Germany and Benelux). In air masses originating from the United Kingdom the levels were lower by a factor of two or more, and in air coming from the north and west (Norway and the Atlantic Ocean) the concentrations were five to ten times lower.

Similar findings were observed in a study of much shorter duration, conducted in September 1992 at the German Nordsee research platform. Simultaneously with this study, the University of Brussels performed research on the atmospheric transport and speciation of mercury (Hg). Total gaseous Hg ranged from 0.7 to 3 ng/m<sup>3</sup> and showed a good correlation with particulate Hg (9-300 pg/m<sup>3</sup>). Organomercury compounds were below the detection limit of 5 pg/m<sup>3</sup> in the atmosphere, but they were detectable in rainwater (0.1-0.2 ng/l), in contrast to rainwater collected above the open oceans. This reveals the importance of the wet deposition of methylmercury in coastal regions.

A Lagrangian transport experiment, the North Sea Experiment (NOSE), was organized within the EUROTRAC ASE sub-project in September 1991. The objectives of NOSE were to examine the changes in concentrations and size distributions of atmospheric particulate species in air masses as they move over the **North Sea**, and to derive from these changes the deposition from the atmosphere into the sea.

Aerosol samples were collected with SFU samplers and cascade impactors aboard two research vessels (Alkor and Belgica) in the **North Sea**, and at several coastal sites. The two ships were aligned so that the Alkor was always directly upwind of the Belgica and about 200 km away.

It was found that the size distributions of mineral dust and anthropogenic elements remained virtually unchanged during the 200 km journey. There was

no change in the total aerosol mass nor in the concentration of sea salt elements. For the mineral dust and anthropogenic elements, on the other hand, levels at the Belgica were only 60-70% of those at the Alkor (Fig. 6.2). This change corresponds to an average total deposition velocity (wet plus dry) of 2 cm/s. This is a very high value, particularly when we consider that there was little rain during the NOSE experiment.

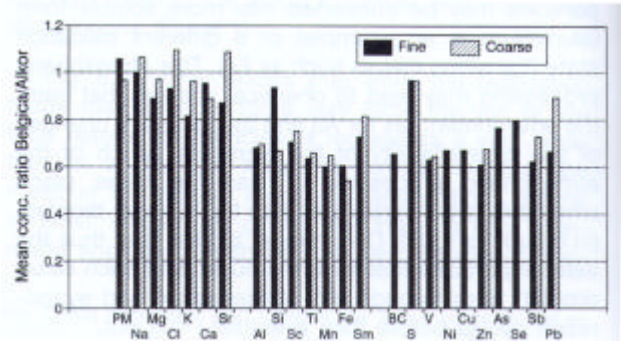


Fig. 6.2 - North Sea Experiment (NOSE), September 1991: average concentration ratios Alkor/Belgica in fine and coarse size fractions for particulate mass (PM), sea salt, mineral dust and anthropogenic elements (based on 13 sample pairs). Although potassium (K) is grouped with the sea salt elements, its fine fraction is to a large extent anthropogenic. Similarly sulphur (S) is grouped with the anthropogenic elements, but this is only correct for its fine fraction; coarse sulphur (S) comes mainly from sea salt. For the mineral dust and anthropogenic elements, levels measured at the Belgica are only 60-70% of those at the Alkor. This change corresponds to an average total deposition velocity (wet plus dry) of 2 cm/s, which is very high. It is quite likely that dilution and mixing processes (entrainment from the marine boundary layer to the free troposphere), as well as deposition, contributed to the large concentration differences observed.

Similar concentration changes were found for gaseous species of continental origin. For example, gaseous Hg showed an average decrease of 20% from the Alkor to the Belgica. It is quite likely that dilution and mixing processes (entrainment from the marine boundary layer to the free troposphere), as well as deposition, caused these large concentration differences.

In addition to these trace-level studies of the chemical composition of bulk and size-fractionated aerosols, much work has been done on characterising individual aerosol particles. When we can see particular chemical species in the same particle we can draw firmer conclusions about their common origin, and hence about their sources. Furthermore, by using techniques that yield surface information about single particles, we can infer the chemical reactions that the particles have undergone in the environment.

Within EUROTRAC ASE, the University of Antwerp collected aerosols for subsequent singleparticle investigations aboard ship (e.g. during NOSE) and on the German research platform. In earlier work, an aircraft was also used to sample aerosols above the southern bight of the North Sea. In addition to these campaign-type measurements, long-term measurements were done at a site near the Belgian coast. The individual particle research lead to the following conclusions:

- in purely maritime air masses coming from the north-west, nearly all the aerosol particles are sea salt. They are generated by gas bubbles breaking at the sea surface. There is a minor sulphate excess due to reaction with natural or anthropogenic sulphur compounds;
- in air masses coming from over the UK, sea salt particles are numerically unimportant relative to the abundant fly-ash particles, which are rich in sulphur;
- air masses that pass over Germany pick up a significant number of gypsum particles from desulphurization processes in power plants;
- air masses that have passed over the western part of Belgium or France contain iron-rich particles from metal processing plants;
- when trace elements are considered at the single particle level, most aerosol particles are a complex admixture of pollutants and natural compounds;
- a large fraction of the large particles are agglomerates of sea salt and pollution particles, particularly under stormy conditions when sea salt particles are more abundant.

In order to quantify the concentrations and deposition fluxes of various elements over the North Sea, the individual particle analyses were complemented by analyses using bulk techniques. This work revealed that:

- for heavy metals like Cd and Pb, atmospheric deposition (mostly due to large particles) equals or exceeds the supply from other sources such as rivers and dumping activities;
- the results of modelling based on emission inventories match the experimental results fairly well;
- the airborne concentrations of Pb and Zn over the North Sea have decreased significantly in recent years.

Another area where aerosols are being studied using single-particle techniques is Siberia. The University of Antwerp is doing this work with OSTC support (within the framework of the bilateral cooperation with Russia and INTAS) and in co-operation with the Russian Academy of Sciences.

Siberia is a huge area (1 million km<sup>2</sup>), and very little is known about its atmosphere. From its size, its location close to the Arctic, the frequent northerly airflows, the presence of enormous local pollution sources next to extended pristine areas and the existence of a specific Siberian haze, Siberia is highly important in the context of global change.

Aerosol samples have been collected at widely separated sites with differing environmental conditions. Nearly 100,000 individual aerosol particles have been examined so far. Aerosols have been collected in summer and in winter -when snow covers the soil over a very large area - in south central Siberia, near Novosibirsk, Krasnoyarsk and Krasnoyarsk, and in Ust-Kamenogorsk (in Kazakhstan). These sites are typical sources of largescale regional pollution but are more than 1000 km apart.

A large fraction of the aerosol is composed of flyash. Roughly 50% of the total sulphur was present in these particles, the rest occurring as pure sulphate particles, as the modellers had predicted. The results show evidence of anthropogenic aerosol transport over distances of more than 1000 km.

Other active sampling sites are near Tiksi, in the extreme central north of Siberia, near the Northern Ocean, in a highly industrialised area. Clean sampling stations are near Lake Baikal and in the mountains on the borders between Siberia and Mongolia and between Kazakhstan and Kirgizia.

In collaboration with research groups from France and the United States, the University of Gent is studying the mass size distributions of atmospheric trace elements at Summit (73°N, 38°W; 3200 m asl), Greenland. The collections are done in field campaigns during the spring and summer, and use two types of cascade impactors. Specific objectives are to provide data to estimate the scavenging probability and dry deposition velocities of the various elements and to examine the importance of fogs as a deposition process.

For the accumulation-mode species sulphate (and S) the average dry deposition velocity is 0.021 cm/s, whereas for coarse-mode elements such as Ca it is of the order of 0.1 cm/s. From separate cascade impactor samplings during the day (in clear weather) and night (with radiative fog), it was found that the levels of both fine sulphur and the coarsemode elements (e.g. Fe) are greatly reduced during fog events. This indicates that at Summit fog is an efficient scavenging process for particles in the 0.1 to 10 μm size range. Measurements with laser particle and condensation nuclei (CN) counters indicated that the very fine (nucleation-mode) particles are

much less efficiently removed by fog. Finally, the relative contributions of snow, fog and dry deposition to the spring-summer flux of several particulate species were calculated.

In a parallel research effort, the University of Antwerp made a comprehensive survey of the concentrations of ionic alkyl lead species in Greenland snow and ice. This work involved ultra-clean sampling, high-resolution separation of individual species, and ultra-sensitive determination procedures. The samples analyzed consisted of fresh or slightly aged surface snow collected on a precipitation event basis at Dye 3 (south Greenland) and Summit, and of deep (up to 20 m) ancient snow and ice obtained by drilling at the Summit site.

Organolead concentrations in the Dye 3 fresh snow varied considerably with the season. By relating the data to the air mass trajectories, the researchers have suggested that the variations are due to changes in the source regions.

The organolead levels in precisely-dated deep ice layers from Summit showed an increasing trend, slightly blurred by seasonal variations, since the early 1970s. The figure were matched to historical data on the distribution of organolead species in gasoline and on the consumption levels of leaded gasoline in Europe and the USA, and also to the concentrations and isotopic composition of total lead in snow and

ice. The research showed that organolead compounds in Greenland are valuable indicators of the global character of lead pollution from leaded gasoline. The residence time of organolead compounds in the polar atmosphere proved to be much longer than in European mid-latitudes, where lead persists for only a few days. The study provided the ultimate proof that the lead in Greenland snow and ice from the past 40 years originated from leaded gasoline.

To examine whether the organolead pattern detected in Greenland could also be seen in vintage wines from Europe, organolead compounds were measured in 22 wines from the French Côtes du Rhône and Rhône Valley regions. Wines from Australia, California and Argentina were included for comparison. Methyl lead species were ubiquitous in the French wines, whereas they were generally not detected in the American samples. The concentration pattern of lead in the French wines matched the increase and subsequent decrease in the historical use of leaded gasoline.

The possibility that the lead contamination could have been introduced by the bio-methylation of mineral lead was examined. The researchers measured the organolead speciation pattern at various stages of alcoholic and malolactic fermentation, both in natural grape must and in a synthetic matrix enriched with a lead salt. No methylation of lead was observed, while there was a slow degradation of tri

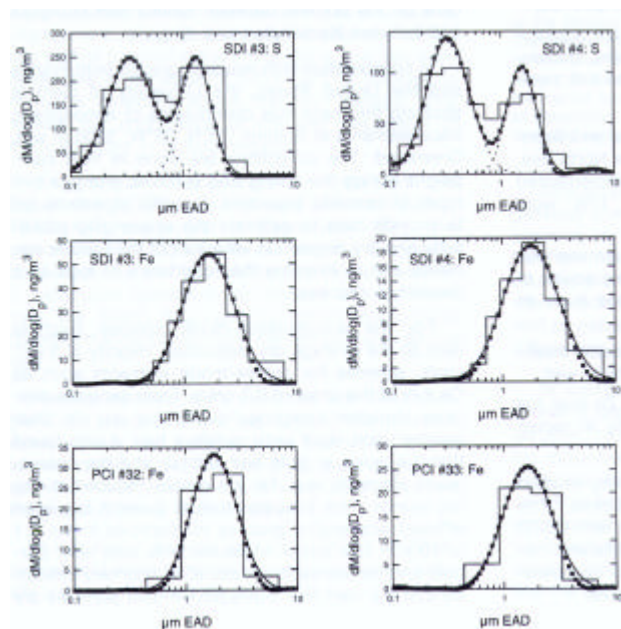


Fig. 6.3 - Mass size distributions for S and Fe in two small deposit area low-pressure impactor (SDI) samples collected at Summit, on the Greenland ice sheet, in June 1993. The histogram gives the raw size distribution (the original data). The filled square symbols show the smoothed size distribution obtained after data inversion, the dashed lines show the log-normal fits to the different modes of the inverted size distribution, and the solid line represents the sum of these fits. Also shown are the size distributions for Fe in two PIXE Int. cascade impactor samples. By conducting separate impactor samplings during day (in clear weather) and night (with radiative fog), the importance of fog as a deposition process can be studied for individual species and as a function of particle size. The size distribution data is also used to calculate the dry deposition velocity of the species

ethyl lead with progressing fermentation. The conclusion is that the organolead compounds observed in wine come from atmospheric pollution.

There is a growing awareness that large-scale biomass burning in tropical and equatorial areas may have a significant impact on the regional and global composition of the troposphere. Biomass burning affects levels of fine aerosols, carbonaceous species and many other particulate species and elements. The University of Gent contributes to the study of that impact by participating in intensive international field campaigns (such as the 1992 Southern Africa Fire-Atmosphere Research Initiative (SAFARI-92)) and by long-term collections at fixed ground-based sites. SAFARI-92 took place from late August to mid-October, the dry season in which most biomass is burned.

From aerosol collections near savanna fires (Fig. 6.4), source profiles were deduced for both the flaming and smouldering phases of these fires. It was found that both phases of savanna fires are major sources of the following species in the coarse size fraction: particulate mass (PM), black carbon (BC), P, K, Ca, Mn, Zn, Sr and I. In the fine fraction both fire phases are major sources of PM, BC, Cl, Br, I, K, Cu, Zn, Rb, Sb, Cs and Pb, and the flaming phase is also a prominent source of Na and S.



Fig. 6.4 - Southern Africa Fire-Atmosphere Research Initiative (SAFARI-92), August-October 1992: a prescribed savanna fire in the Kruger National Park, South Africa. During such fires gases and aerosols were collected with ground-based samplers and from airborne platforms (e.g. helicopters) in order to study the emissions from savanna fires and their effects on regional and global atmospheric chemistry

Aerosols sampled at three "background" sites in the eastern Transvaal, South Africa, were examined with receptor modelling techniques (Fig. 6.5). It was found that on average 40% of the regional fine particulate mass originated from biomass burning, and that sulphates made up a further one-third. The particles from biomass burning were advected with air which came in from the north, whereas the sulphates seemed to originate from fossil fuel burning and industrial activities on the Transvaal Highveld. Natural aerosols (mineral dust and sea salt) were on average responsible for only about 25% of the fine mass.

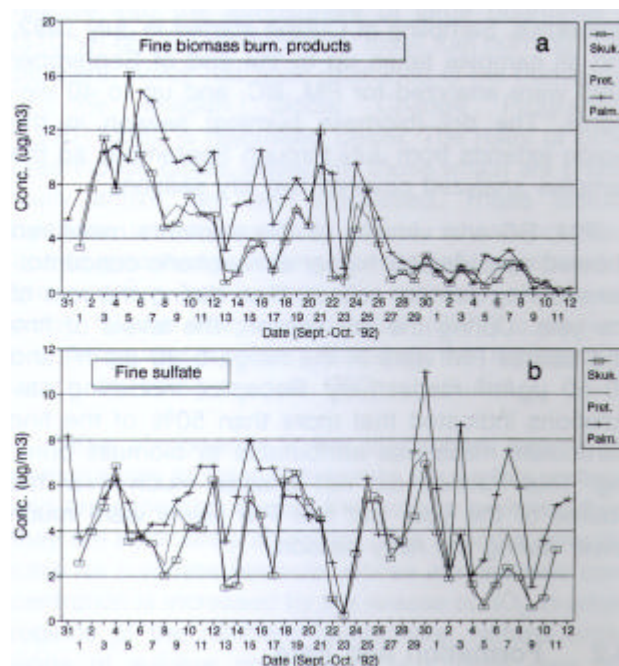


Fig. 6.5 - Southern Africa Fire-Atmosphere Research Initiative (SAFARI-92), August-October 1992: time trends (concentration in  $\mu\text{g}/\text{m}^3$  against date) for the fine particulate mass apportioned to (a) biomass burning and (b) sulphates in 24-hour samples collected at three sites (Skukuza, Pretoriuskop and Palmer) in the eastern Transvaal, South Africa. On average, biomass burning was responsible for about 40% of the total fine aerosol mass, and the sulphates for about one-third

Selected samples from the fires and from a "background" site were analyzed using electron probe X-ray microanalysis (EPMA) at the University of Antwerp. About ten particle types were identified in each sample. At the "background" site, aluminosilicates and sea salts were the major particle types in the coarse fraction, while K-S and S-only particles prevailed in the fine fraction. The results were consistent with those from the bulk analyses on a sample-by-sample basis.

In the fine fraction of the samples from near the fires, many particles had homogeneous composition

tions such as pure KCl or pure  $K_2SO_4$ . At the "background" site virtually no fine KCl particles were present, and the fine K-S particles had lower and much more variable K/S ratios than was the case for the fire samples. This all points to substantial processing of the pyrogenic particles during atmospheric transport, with loss of Cl into the gas phase and conversion of  $SO_2$  into particulate form on existing fine particles.

Long-term collections of aerosols are being made at Cuiaba, in the cerrado (savanna) region of Brazil, to the south of the Amazon basin rain forest, and at Rukomechi, 70 km east-north-east of lake Kariba in Zimbabwe. Sampling at Cuiaba started in July 1992, and all samples taken up to the end of September 1993 were analyzed for PM, BC, and up to 40 elements. The dry (biomass burning) season in the region extends from July through September, so the samples analyzed covered two dry seasons.

PM, BC and virtually all the elements measured showed considerably higher atmospheric concentrations during the dry season than during the rest of the year. During the dry season, the levels of fine and coarse PM were in the range 5-30  $Ng/m^3$  and 10-50  $\mu g/m^3$  respectively. Receptor modelling calculations indicated that more than 50% of the fine particulate mass was attributable to biomass burning. This fraction did not change much over the course of the year, but fine PM levels were much lower during the rainy season.

## 6.2 Formation and Fate of Stratospheric Aerosols

Stratospheric aerosols originate primarily from volcanic eruptions that are strong enough to inject  $SO_2$  (sometimes  $H_2S$ ) into the stratosphere. The  $SO_2$  or  $H_2S$  is first converted into gaseous  $H_2SO_4$  and subsequently into sulphate aerosols. These probably consist of supercooled droplets of  $H_2SO_4 \cdot H_2O$ , with an acid weight fraction of 55-80%.

The concentration of sulphate aerosol decreases with a half-life of 6-9 months, though this appears to vary considerably with altitude and latitude. The decay is most likely due to a combination of sedimentation, subsidence and exchange through tropopause folds.

Besides this sulphate from violent volcanic eruptions, a background concentration of sulphuric acid also appears to be present. Potential sources include carbonyl sulphide from the oceans, low-level  $SO_2$  emissions from volcanoes, and various anthropogenic sources including industrial and aircraft emissions.

The sizes of the stratospheric sulphate particles range from hundredths of a micrometer to several micrometer. Although there is some variability, especially after a volcanic eruption, two log-normal size distributions of spherical, sub-micrometer particles appear to provide a good description of the aerosol. The distribution is originally monomodal with a geometric mean diameter by number of about 0.1  $\mu m$ . Just after an eruption the distribution becomes bimodal, the larger mode being characterized by a mean diameter of about 1  $\mu m$ . Some of the large particles are non-spherical because of the addition of crustal material (volcanic ash).

The stratospheric aerosol loading in 1979 was about 0.5 million tons of sulphate, which was considered to be representative of background conditions. As a consequence of the June 1991 eruption of Mt. Pinatubo in the Philippines, about 30 million tonnes of new aerosol was formed in the stratosphere. The Mt. Pinatubo perturbation appears to be the largest of the century, perhaps the largest since the 1883 eruption of Krakatoa near Java.

Stratospheric sulphate droplets are an excellent substrate for heterogeneous (multi-phase) chemical reactions that involve  $O_3$ ,  $NO_2$  and other gaseous species. As discussed in Chapter 3, the aerosol particles from Mt. Pinatubo led to a significant decrease in the total vertical column abundance of  $NO_2$  above the Jungfrauoch. The volcanic material also gave rise to chemical destruction of  $O_3$  in the polar stratosphere about a year after the eruption, when the sulphate particles had been transported to the polar regions.

Clouds, especially polar stratospheric clouds (PSCs), are another important type of stratospheric aerosol. PSCs consist of solid (ice) particles and are formed in the middle stratosphere over the polar regions during the winter and early spring. These clouds often contain an equal mixture, by weight, of nitric acid and water and form at temperatures 5-10  $^{\circ}C$  warmer than pure ice would form. PSCs play a very important role in stratospheric ozone depletion. In fact, the Antarctic ozone hole was shown to be caused by chemical reactions that occur on nitric acid-ice or pure ice particles. The reactions involved in this ozone destruction are discussed in detail in Chapter 3.

## 7 ATMOSPHERIC CONSTITUENTS AND CLIMATE CHANGES

The sun radiates energy onto the earth as a spectrum extending from the ultraviolet to the infrared. Part of this radiative energy is reflected by the sur

face and by clouds. The remainder is absorbed by the atmosphere as well as by the earth's surface, which is thus heated. Without the presence of the atmosphere, the earth would re-emit as infrared radiation most of the energy it receives (Fig. 7.1) . The resulting equilibrium temperature of the planet would be -18°C.

Much of this re-emission is prevented by the presence of the atmosphere which is transparent to most of the incoming visible and near ultraviolet radiation, but which absorbs a large part of the outgoing infrared radiation. The absorption is due to molecules naturally present in the atmosphere: mainly H<sub>2</sub>O but also CO<sub>2</sub>, O<sub>3</sub>, and CH<sub>4</sub>. This "greenhouse effect" keeps the lower part of the earth's atmosphere at an average temperature of +15°C.

Any factor that alters the radiation received from the sun or emitted by the earth can affect the climate. A change in this energy budget is called radiative forcing. The destruction of the O<sub>3</sub> layer at an altitude of 25 km by man-made compounds such as CFCs will cause positive radiative forcing by letting more energy reach the surface. Similarly, a change

in the infrared absorption properties of the lower atmosphere, caused by the addition of man-made molecules such as CO<sub>2</sub>, CFCs, HCFCs and HFCs, will also cause positive radiative forcing. An increase in the concentrations of man-made "greenhouse gases" will therefore reduce the efficiency with which the earth loses heat to space, and result in a general warming of the lower atmosphere and the earth's surface. These phenomena are collectively known as global warming.

A particularly important question is to what extent the global carbon cycle has been altered by the release into the atmosphere of large quantities (5 GTC/yr) of CO<sub>2</sub> produced by fossil fuel burning. This problem, which has been examined in the framework of the Belgian Global Change Programme (1990-1996), is discussed below. The roles of other greenhouse gases, especially those which are chemically active, are also discussed. These include methane and tropospheric ozone, whose contribution to greenhouse forcing is especially significant in the northern hemisphere. An estimate of the so-called "Global Warming Potential" (GWP) is presented for several species, including the halocarbons which are being used as CFC substitutes.

Other compounds in the atmosphere reduce the transmission of solar radiation to the earth's surface, and are expected to cool the earth in regions where they are sufficiently abundant. This is particularly the case for sulphate aerosols, whose atmospheric concentration is increased by the release of SO<sub>2</sub> in urban regions of the northern hemisphere. Natural emissions of sulphur compounds (e.g. DMS over the ocean) also contribute to the formation of sulphate aerosols. Aerosols affect climate forcing either directly, by reflecting back into space a fraction of the incoming solar radiation, or indirectly, by altering microphysical processes associated with the formation of clouds. A detailed study of these processes performed under the Belgian Global Change Programme (1990-1996) is further summarized below.

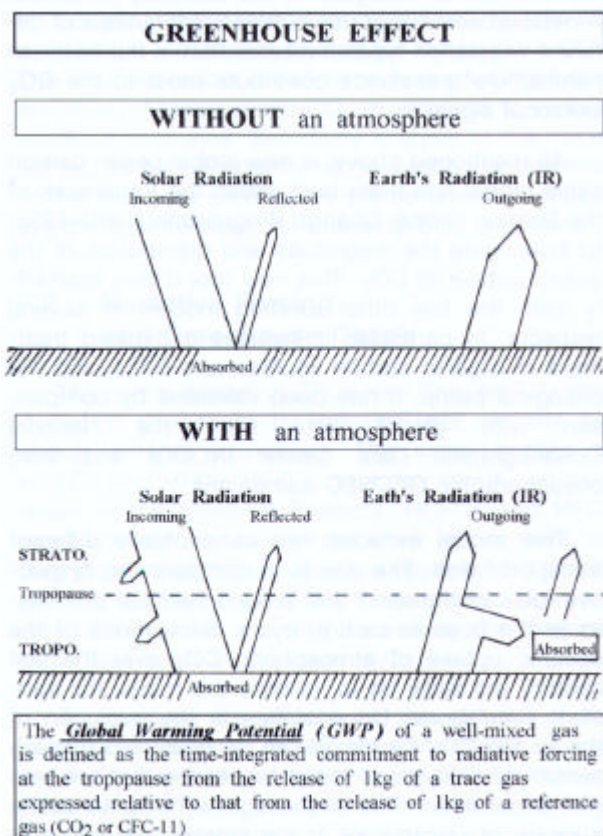


Fig. 7.1 – Greenhouse Effect and Global Warming Potential

## 7.1 The Global Carbon Cycle

The increase of atmospheric CO<sub>2</sub> during the industrial era (from 280 to 360 ppmv) has produced the largest individual perturbation (- 1.6W/m<sup>2</sup>) to radiative forcing. It accounts for over 60% of the sum of all radiatively active greenhouse gases from anthropogenic origin (total forcing - 2.5 W/m<sup>2</sup>). This increase in CO<sub>2</sub> concentration causes part of the outgoing infrared radiation to be trapped within the atmosphere and re-emitted towards the earth's surface.

This additional heating is expected to generate higher surface temperatures (the "greenhouse effect"). For example, an increase in the CO<sub>2</sub> concentration to twice the pre-industrial level would lead to an average radiative forcing of  $\sim 4 \text{ W/m}^2$ , producing a direct average increase of  $\sim 1.2^\circ\text{C}$  in the surface temperature.

It is estimated that internal climatic feedback mechanisms would amplify this global warming to  $1.5\text{--}4.5^\circ\text{C}$ . If CO<sub>2</sub> emissions were maintained at the present level the carbon dioxide concentration would reach  $\sim 500 \text{ ppm}$  (approximately twice its preindustrial value) by the end of the next century.

The CO<sub>2</sub> increase observed since the pre-industrial era is due to fossil fuel combustion, land use conversion and cement production. Out of the annual anthropogenic emission of  $7.1 \text{ GtC}$ , it is estimated that  $2 \text{ GtC}$  is taken up by the oceans and  $3.3 \text{ GtC}$  remains in the atmosphere. Considering that the uptake by forest regrowth is estimated at  $0.5 \text{ GtC}$ , a flux of  $\sim 2.3 \text{ GtC/yr}$  is unaccounted for. This imbalance is usually referred to as the "missing carbon sink". There is now growing evidence that CO<sub>2</sub> uptake by the terrestrial biosphere (the CO<sub>2</sub> fertilisation effect and nitrogen fertilisation) may provide an important additional sink for atmospheric CO<sub>2</sub>.

It is important to note that the global net CO<sub>2</sub> flux from the atmosphere to the ocean can only be determined through the use of ocean carbon cycle models (OCCIVs). Currently the global ocean uptake is thought to be known to within 40%. The main uncertainties stem from differences in the treatment of biogeochemical processes between the two or three different OCCIVs currently being used.

For various reasons there is also much uncertainty over the role of the biosphere in the carbon budget. First, the biospheric carbon sink's natural year-to-year variability due to changing climatic conditions is still largely unknown. This variability may contribute in part to the variations in the CO<sub>2</sub> growth rate observed over the last 35 years. Second, factors such as increased photosynthesis in the presence of increased levels of CO<sub>2</sub> (the fertilization effect) are still not fully understood at the ecosystem and global levels.

As a consequence the University of Liège, supported by the EC Environment Programme, has devoted much effort to developing a coupled atmosphere-ocean-biosphere global carbon cycle model. In the current phase models of the biosphere and the oceans have been developed as separate, autonomous modules. It is expected that in a second phase these will be coupled and adapted to calculate the future levels of atmospheric CO<sub>2</sub> using

emission scenarios such as those from the IPCC studies.

The new CARAIB biospheric model, one of the most advanced predictive tools, calculates the amount of carbon removed by photosynthesis at  $65 \text{ GtC/yr}$ . This important quantity is not measurable on a global scale and is not directly accessible from remote sensing.

CARAIB also predicts the geographical and sea sonal distribution of the net CO<sub>2</sub> flux exchanged between the atmosphere and the biosphere – that is, the difference between the amount of carbon used up by photosynthesis and that released by soil microbial respiration. When coupled to an atmospheric transport model, this vegetation model is able to predict the seasonal variation in the atmospheric CO<sub>2</sub> signal measured at various stations around the world (Fig. 7.2).

Between  $30^\circ\text{N}$  and  $80^\circ\text{N}$ , a region where the seasonal variations are clearly of biospheric origin, CARAIB reproduces the observed amplitude of CO<sub>2</sub> changes to within 5% accuracy. This is the best agreement achieved so far from a predictive biosphere model, and implies that the northern temperate and boreal ecosystems are correctly modelled. A detailed analysis of the relative contributions of different vegetation types indicates that in the northern hemisphere grasslands contribute most to the CO<sub>2</sub> seasonal signal.

As mentioned above, a new global ocean carbon cycle model has been built within the framework of the Belgian Global Change Programme (1990-1996) to investigate the magnitude and distribution of the ocean uptake of CO<sub>2</sub>. This new tool differs markedly from the few other existing models in several respects. In particular, it includes a detailed treatment of organic carbon sources and sinks, and the biological pump. It has been validated by comparison with global data from the National Oceanographic Data Center (NODC) and from oceanographic GEOSEC campaigns.

This model includes two conceptually different transport fields. The aim is to compare the respective roles of transport and biogeochemical processes in the oceanic carbon cycle. Simulations of the oceanic uptake of atmospheric CO<sub>2</sub> over the last century will allow us to validate the model for transient simulations. Uncertainties in the evolution of the air-sea CO<sub>2</sub> exchange can be quantified through sensitivity analysis of those processes that are less well understood. This knowledge will help to define a range of uncertainty in the oceanic response to future CO<sub>2</sub> emission scenarios.

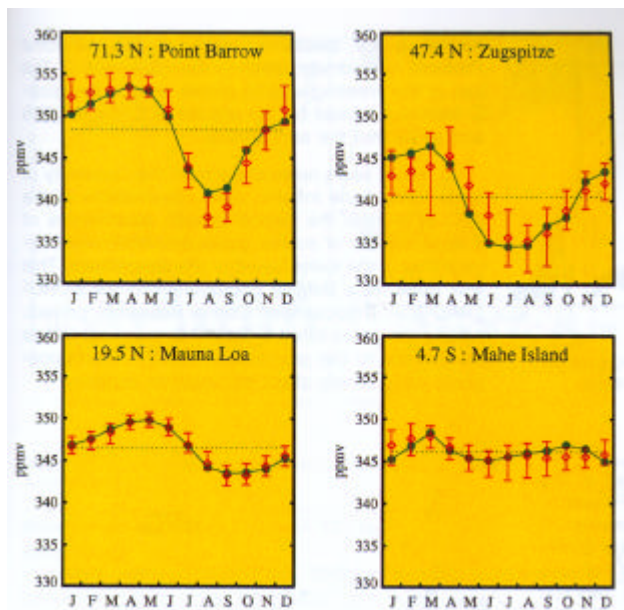


Fig. 7.2 - Seasonal atmospheric CO<sub>2</sub> cycle level at four monitoring stations. The units are volume ratios in ppmv. The green curve shows the results of a simulation in which the CO<sub>2</sub> released by the continental biosphere under average climatic conditions is transported by atmospheric winds. For comparison, the average seasonal cycle observed between 1980 and 1992 at the same stations is shown (red diamonds), with bars indicating the level of variability during the same period. The result illustrates the quality of the **CARAI** model developed at the University of Liege. It also provides a test of the model's predictive capacity necessary to guarantee the reliability of calculations of future atmospheric changes.

Coupling the ocean and biosphere models will establish a complete budget for atmospheric CO<sub>2</sub>. This coupled model will allow us to predict the future evolution of atmospheric CO<sub>2</sub> in response to various emission scenarios. Sensitivity analysis of the model will tell us the uncertainty range, whilst the extremes of the response predictions will be useful in choosing the best strategy for reducing CO<sub>2</sub> emissions.

## 7.2 Radiative Forcing and Greenhouse Gases

The ozone-depleting CFCs (see Chapter 3.1), produced in abundance by industry until recently, are strong infrared absorbers. The same applies to HCFCs and HFCs, CFC substitutes introduced as a result of the Montreal Protocol. HCFCs and HFCs react with OH radicals in the lower atmosphere, so they do not reach the upper atmosphere and do not destroy the ozone layer. All three groups, however, add to the global warming caused by the "natural" molecules such as CO<sub>2</sub> and H<sub>2</sub>O.

To compare the effects on the climate of the emission of different radiatively active gases, a relative index has been introduced: The Global Warming Potential (GWP). Its exact definition can be found in Fig. 7.1. The reference gas for these GWPs is either CO<sub>2</sub> or CFC 11.

Measuring the GWP of a given gas is not a simple matter and relies on a complex model of the atmosphere. The latter includes experimental data such as the earth's averaged solar flux, cloud coverage, surface diffusion and vertical distribution profiles, the chemical and photochemical lifetimes of a large number of species present in the atmosphere and the infrared absorption cross-sections for these species.

In order to determine the GWPs of 12 HCFCs and HFCs, researchers at the Université Libre de Bruxelles used a high-resolution Fourier transform spectrometer to measure the absorption cross-sections of these compounds. Measurements were made in the infrared region from 600 to 1500 cm<sup>-1</sup>. This region corresponds to a so-called "atmospheric window", i.e. a region for which, in the absence of CFCs, HCFCs and HFCs, the atmosphere is largely transparent to infrared radiation.

Fig. 7.3 is a typical example of a very small portion of the high-resolution (0.03 cm<sup>-1</sup>) absorption spectrum of one of the HCFCs (HCFC 142b) studied. The experimental setup used to obtain this spectrum is similar to that briefly described in Section 2.2. The high-purity HCFCs and HFCs were provided by the chemical companies Solvay S.A., Belgium; E.I. du Pont de Nemours, USA; and Asahi Glass Co. Japan.



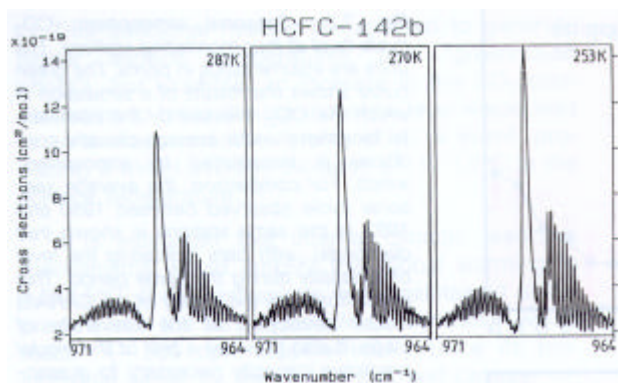


Fig. 7.3 - Portion of the infrared absorption spectrum (crosssection) of HCFC 142b at three different temperatures

This spectroscopic data was then used in the NCAR (National Center for Atmospheric Research, Boulder, Colorado) radiative-chemical-dynamic-2D interactive model to yield GWP values. The GWPs were calculated relative to CFC 11 for time horizons corresponding to 5, 10, 20, 50, 100, 200 and 500 years from now. Table 7.1 shows the results. Fig. 7.4 shows the GWPs as a function of time for five different HFCs.

The main result is clear: all the HFCs shown are environmentally preferable to CFC 11 ( $GWP < 1.0$ ), but some are better (lower GWP) than others. In addition, the results show that for short time horizons (<25 years) some HFCs have GWP values comparable to CFC 11. These results, published in 1993, were of some importance in world-wide environ

mental policy decisions taken at the Montreal Protocol Amendment Meeting (Bangkok, 1993). The aim of the meeting was to further reduce the global warming caused by the release of CFCs, HCFCs and HFCs into the atmosphere.

In recent years researchers from the University of Liege have made infrared solar observations at the ISSJ to monitor the vertical column abundances of a large number of source gases predominantly concentrated in the lower layers of the atmosphere. This was done as a Belgian contribution to the EUROTRAC-TOR (Tropospheric Ozone Research) project. Among the gases listed in Table 7.2, many contribute significantly to the greenhouse effect in the troposphere while others affect its oxidation capacity.

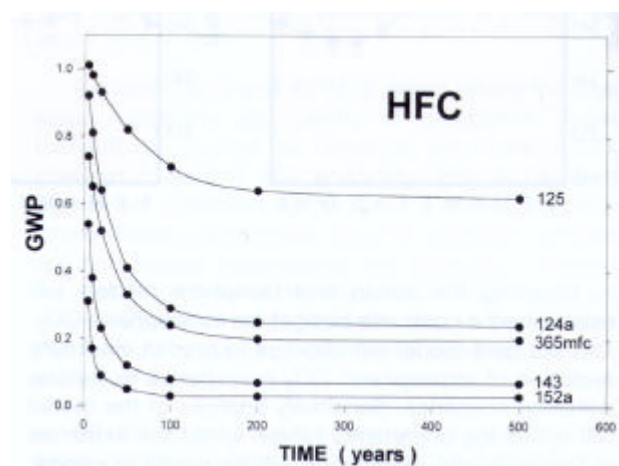


Fig. 7.4 - Time-dependence of the GWPs for five HFCs, relative to CFC 11

Table 7.1 - Radiative forcing values and GWPs of 12 halocarbons, relative to CFC 11

Halocarbon	Lifetime Radiative Forcing/kg		Global Warming Potential						
	years		5 yr	10 yr	20 yr	50 yr	100 yr	200 yr	500 yr
CFC 11 *	57.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HCFC 22	14.3	1.35	1.19	1.06	0.86	0.56	0.41	0.35	0.34
HCFC 12	1.5	0.81	0.25	0.13	0.07	0.04	0.03	0.02	0.02
HCFC 124	6.0	0.95	0.67	0.50	0.32	0.17	0.12	0.10	0.10
HCFC 14b	9.7	0.77	0.63	0.53	0.39	0.22	0.16	0.14	0.13
HCFC 142b	21.1	1.12	1.04	0.97	0.86	0.64	0.50	0.43	0.41
HCFC 225ca	2.4	0.73	0.32	0.19	0.10	0.05	0.04	0.03	0.03
HCFC225cb	6.8	0.88	0.65	0.50	0.34	0.18	0.13	0.11	0.11
HFC 125	33.9	1.04	1.01	0.98	0.93	0.82	0.71	0.64	0.62
HFC 134a	13.1	1.06	0.92	0.81	0.64	0.41	0.29	0.25	0.24
HFC 143	4.3	0.85	0.52	0.36	0.21	0.11	0.08	0.07	0.06
HFC 152a	1.5	1.03	0.31	0.17	0.09	0.05	0.03	0.03	0.03
HFC 365mfc	12.1	0.92	0.74	0.65	0.51	0.32	0.24	0.21	0.21

\*used as a reference gas.

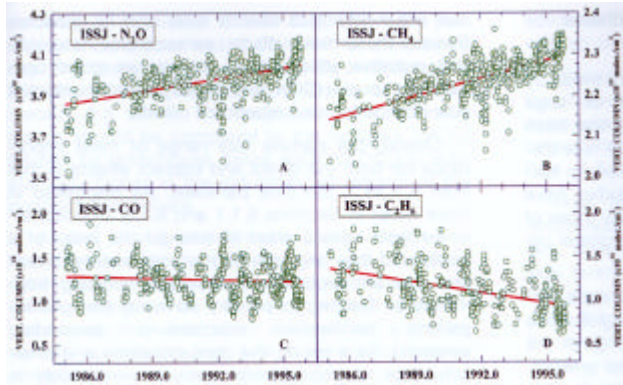


Fig. 7.5 - Graphical representation of the rates of change observed during the last decade in the vertical column abundances of N<sub>2</sub>O (nitrous oxide), CH<sub>4</sub> (methane), CO (carbon monoxide) and C<sub>2</sub>H<sub>6</sub> (ethane) above the ISSJ. The mean rates of increase of N<sub>2</sub>O (0.39%/yr) and CH<sub>4</sub> (0.65%/yr) are of concern as these gases contribute substantially to the greenhouse effect. While CO increased at a rate of about 0.7%/yr before 1985, the data in Frame C suggests a stabilization in the CO burden during the last decade. The C<sub>2</sub>H<sub>6</sub> column abundance above the ISSJ is definitely decreasing (-3.5%/yr). Data such as that reported here is indispensable in quantifying the changes occurring in our environment and in providing explanations through modelling

Table 7.2 - Tropospheric constituents monitored at the Jungfraujoch

- Minor constituents: CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO, H<sub>2</sub>O
- Halogenated source gases: CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub>, CHClF<sub>2</sub>, SF<sub>6</sub>, CCl<sub>4</sub>
- Others: C<sub>2</sub>H<sub>6</sub>, CA, HCN, OCS, H<sub>2</sub>CO, SO<sub>2</sub>

The data reveals occasionally rapid changes which can be attributed to dynamic effects and abnormal meteorological conditions. These include the mixing of masses of air from different latitudes, and local subsidence of the kind observed during vortex conditions over high-latitude polar regions. Many tropospheric gases also undergo seasonal variations associated with modulations in source strengths, sink reactions, or both. Because of such short-term variations, the study of the secular evolution of the atmosphere requires long-term measurements. Fig. 7.5 shows examples of changes in column abundances above the ISSJ for four key gases affecting the greenhouse potential and oxidizing capacity of the troposphere.

Until very recently both CH<sub>4</sub> and CO levels increased regularly. In the last few years, for reasons that are as yet unclear, these increases have slowed significantly. The monitoring of the largest possible number of tropospheric gases, combined with specific simulations, is likely to shed some light on these changes.

To follow the impact of chlorine on the stratospheric ozone layer discussed in Section 3.2, important chlorine sources such as the CFCs CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub> and CHClF<sub>2</sub> have been monitored above the ISSJ during the last decade. Fig. 7.6 shows the results for CCl<sub>2</sub>F<sub>2</sub> and CHClF<sub>2</sub>. The slower rate of increase of CCl<sub>2</sub>F<sub>2</sub> during the last few years reflects the fact that the Montreal Protocol (1987) introduced a progressive phase-out of this compound (Fig. 7.6, top).

CHClF<sub>2</sub> was not included in the Montreal Protocol and continues to increase steadily (Fig. 7.6, bottom).

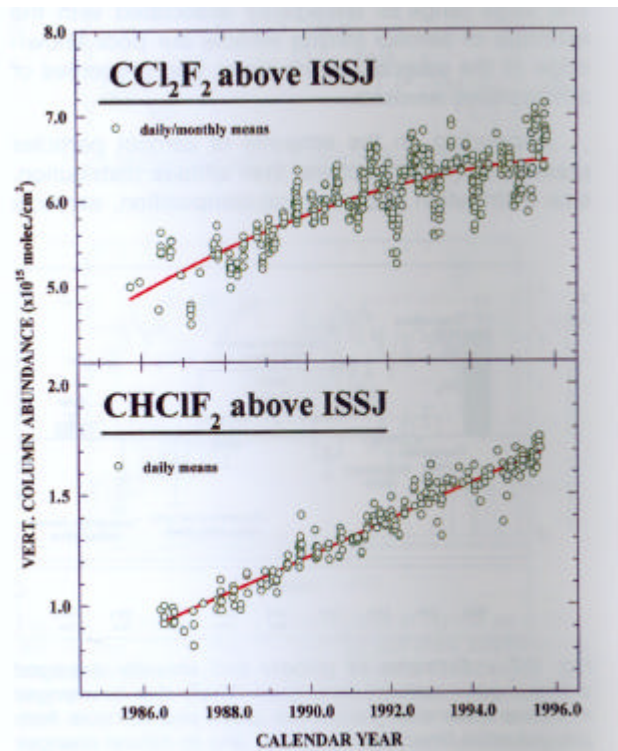


Fig. 7.6 - Two examples of chlorine- (Cl) and fluorine- (F) containing source gases observed above the ISSJ over the last decade. The observed rate of increase of CCl<sub>2</sub>F<sub>2</sub> (CFC 12) has significantly slowed during recent years as a consequence of its regulated phase-out by the Montreal Protocol. This is not the case for the unregulated CHClF<sub>2</sub> (HCFC 22), which continues to increase at a mean exponential rate of 6.1 %/yr Both gases contribute to the greenhouse effect in the troposphere and potentially influence the erosion of the ozone layer by freeing Cl atoms in the stratosphere when photodissociated by solar UV radiation at altitudes above 20 km

### 7.3 Direct and Indirect Climate Effects of Aerosols

The human perturbation of the earth's climate by the introduction into the atmosphere of large amounts of infrared-absorbing gases has now been well studied, and the world's politicians are now discussing this "greenhouse effect" with a view to taking corrective action. However, recent studies have shown that atmospheric aerosols, especially those of sub-micrometer sizes, may also influence global climate.

The climatic effect of aerosols is in most circumstances to cool the earth, and its magnitude is comparable to that of greenhouse warming. In the latest IPCC estimate, for example, the total presentday radiative forcing by greenhouse gases is estimated to be in the range  $+(2.1-2.8) \text{ W/m}^2$ . In contrast, the global mean radiative forcing by anthropogenic aerosols is estimated to be  $-(0.3-3.0) \text{ W/m}^2$ . The large range of uncertainty associated with the estimate of aerosol forcing reflects our poor knowledge of the sources, distributions, and properties of atmospheric aerosols.

Depending on the amounts of aerosol particles present in the atmosphere, their altitude distribution, size distribution and chemical composition, aerosols

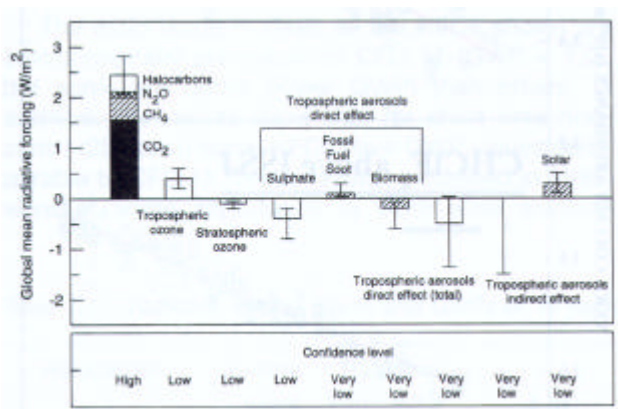


Fig. 7.7 - Estimates of globally and annually averaged anthropogenic radiative forcing (in  $\text{W/m}^2$ ) due to changes in concentrations of greenhouse gases and aerosols from pre-industrial times to the present, and to natural changes in solar output from 1850 to the present. The height of the rectangular bar indicates a mid-range estimate of the forcing, while the error bars show an estimate of the uncertainty range, based largely on the spread of published values. The subjective confidence that the actual forcing lies within this error bar is indicated by the "confidence level". The direct forcing from aerosols comes from the fact that they can reflect or absorb solar radiation and IR radiation. Indirect aerosol forcing arises from the induced change in cloud properties; our quantitative understanding of this latter forcing is very limited at present and hence no bar representing a mid-range estimate is shown. (adapted from IPCC (1994))

can either reflect or absorb solar and IR radiation. Besides these direct effects, aerosols also have indirect radiative effects: they can act as cloud condensation nuclei (CCN) and thereby affect the droplet size distribution and albedo of clouds.

Overall, the particle size range of most importance for both the direct and indirect effects is that from  $0.1$  to  $1 \mu\text{m}$  (fine particles). As discussed in more detail in Sections 6.1.1 and 6.1.3, tropospheric aerosols have a short lifetime (of the order of a week) and they originate from a wide variety of natural and anthropogenic processes, including fragmentation (leading to primary aerosols) and gas-to-particle conversion mechanisms (secondary aerosols). As a result, the concentrations and characteristics of tropospheric aerosols vary widely in space and time. The effect of this is that negative climate forcing by aerosols has a strong regional character, and that the climatic response to aerosol forcing is regionally heterogeneous. Studies of the regional characteristics of aerosols and of their effects are urgently needed to reduce the uncertainty range in the global mean radiative and climatic impact of aerosols.

Sulphate particles are the most commonly observed types of aerosol, and it has been suggested that they are the most important in cloud formation and radiative effects. The sources of sulphur for these particles are both man-made and natural. The natural sources, predominantly DMS and other reduced sulphur gases from marine and terrestrial plants, are relatively evenly distributed worldwide and produce a global background sulphate distribution.

The sources of man-made sulphur emissions, on the other hand, are concentrated in Europe, north America and Asia. According to recent model calculations, the global and annual mean direct forcing due to sulphate aerosols is  $-0.66 \text{ W/m}^2$ , but during July this rises to a maximum of  $-11 \text{ W/m}^2$  in Central Europe and  $-7.2 \text{ W/m}^2$  over eastern China. However, there is still a large uncertainty associated with these model calculations. The latest IPCC report suggests a central value of  $-0.4 \text{ W/m}^2$  for the global annual mean direct forcing due to sulphates, with an uncertainty of a factor of two (and thus a range from  $-0.2$  to  $-0.8 \text{ W/m}^2$ ).

Calculations with the IMAGES model, which accounts for chemical transformations of sulphur compounds in the troposphere, give similar results. The model shows a large increase in the concentration of  $\text{SO}_2$  and sulphates since pre-industrial times (a global average factor of 2-3, and more than two orders of magnitude in some areas of the northern hemisphere). Using a simple radiative model, the global radiative forcing produced by these sulphate

aerosols is estimated to be  $-0.48 \text{ W/m}^2$  for preindustrial conditions and  $-1.28 \text{ W/m}^2$  for the present day. The global cooling produced by anthropogenic aerosols thus corresponds to a forcing of approximately  $-0.8 \text{ W/m}^2$ . The magnitude of this forcing (which should be compared to the radiative forcing caused by greenhouse gases such as  $\text{CO}_2$ ) is substantially higher in the industrialized regions of the northern hemisphere.

As well as sulphate aerosols, carbonaceous particles are produced both naturally and by human activities. The carbonaceous particles include soot (black carbon), which is formed as a result of incomplete combustion and which is essentially a primary aerosol constituent and a wide variety of organic compounds which, are normally referred to by the generic term "organic carbon" and may be emitted as primary particles or produced by gas-to-particle conversion.

The most important anthropogenic sources of atmospheric carbonaceous particles are fossil fuel use and biomass burning. Of the two sources, fossil fuels (especially coal, oil and automotive emissions) dominate in Europe and in the continental mid-latitudes of the northern hemisphere in general. But in tropical and equatorial regions, most of the anthropogenic carbonaceous aerosol is produced by various forms of biomass burning: deforestation, shifting cultivation, savanna fires and the use of wood as fuel. In many areas the mass loading of carbonaceous aerosols is comparable to that of the sulphate particles.

The organic carbon (OC) and black carbon (BC) carbonaceous aerosols have different chemical and radiative properties. OC aerosols primarily scatter radiation, whereas BC aerosols absorb it. Both combustion OC and BC particles have proved to be potential CCN due to the presence of organic or mineral hydrophilic functional groups in the carbonaceous matrix or on the surface of the particles.

Recent calculations have indicated that the global radiative effect of OC particles is a net cooling of the same order as that inferred for industrial sulphates. For the global mean direct radiative forcing for OC aerosols from biomass burning, the latest IPCC estimate is  $-0.2 \text{ W/m}^2$ , but with an uncertainty of a factor of three. BC particles form by far the most effective absorbing component of the aerosol phase. However, the optical absorption properties of BC particles are very dependent on their size and on the chemical nature of their coating, and are thus expected to vary with the origin and age of the particles.

As a result, the direct radiative forcing of soot aerosols is highly uncertain. The most recent IPCC

estimate used a global mean figure of  $+0.1 \text{ W/m}^2$  with an uncertainty of at least a factor of three.

While the uncertainties in the direct radiative forcing of aerosols on climate are very substantial, those associated with indirect radiative forcing are even larger. The latest IPCC report gives only a range of  $-1.5 \text{ W/m}^2$ , with no midrange estimate.

How large is the anthropogenic contribution (world-wide, and on the scale of continents, regions: [e.g. western Europe], individual countries or emission inventory grid points) to the climatically important aerosol types such as fine sulphate? And how does this anthropogenic contribution compare with the contribution from natural sources? (for example

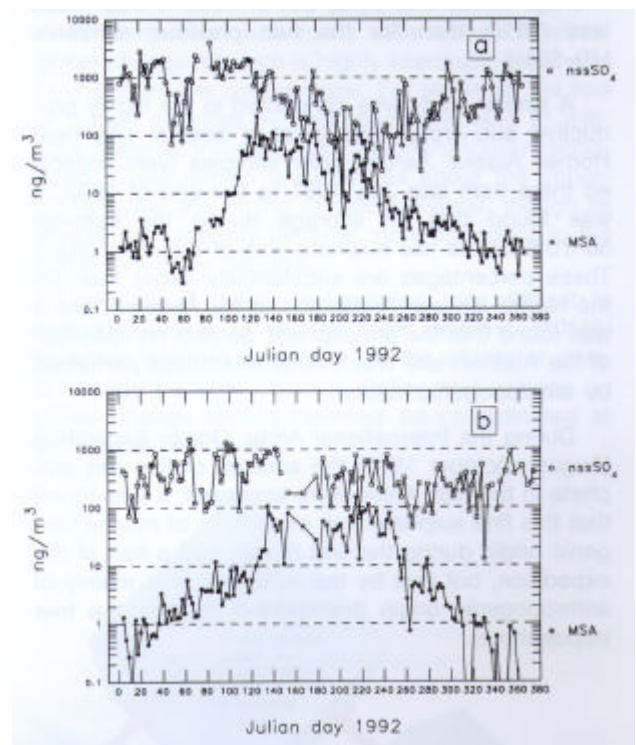


Fig. 7.8 - Time trends (concentrations in  $\text{ng/m}^3$  as a function of day of the year) for non-sea salt (nss) sulphate and methanesulphonate (MSA) at Ny Alesund, Spitsbergen (top) and at Homer, Alaska (bottom) during 1992. Nss sulphate (the most important aerosol type for both direct and indirect climate forcing by aerosols) has both anthropogenic and natural sources, whilst MSA has only natural source (the oxidation of biogenic DMS). MSA serves as an indicator for the natural sulphate derived from the oxidation of DMS. Clearly, the biogenic DMS source varies very significantly over the year (by two to three orders of magnitude and is strongest in spring and summer). Source apportionment calculations for the summer period (June through August) indicate that a very substantial fraction of the nss sulphate can be attributed to the DMS source during the season (about one-third at Ny Alesund, and over 50% at Homer). During winter, early spring, and late autumn, on the other hand, the nss sulphate is almost entirely of anthropogenic origin.

the major natural source of fine sulphate is oceanic emissions of DMS by phytoplankton)

Since early 1991 the University of Gent has been conducting a long-term aerosol study at the Zeppelin background station in Ny Alesund, Spitsbergen. From the results obtained for the years 1991 through 1993 it was concluded that in late autumn, winter and early spring the fine non-sea salt (nss) sulphate is virtually entirely of anthropogenic origin. Between May and September, however, there is a substantial contribution from natural sources, mainly the oxidation of gaseous DMS emitted by marine phytoplankton. In the summer (June-August) of the three years 1991-1993, the natural contribution was on average about one third, but in 1993 it was much less (20%) than for the two previous summers (40-50%).

A similar study was conducted in the highly productive sub-Arctic Pacific, at a coastal site near Homer, Alaska. Aerosol filter samples were collected there from late July 1991 to the end of 1992. It was found that on average during the summer 50-70% of the nss sulphate was of biogenic origin. These percentages are substantially larger than for the higher latitude Arctic site of Ny Alesund, but it was found that the atmospheric aerosol composition at the Alaskan site was overall much less perturbed by anthropogenic inputs.

During the International Arctic Ocean Expedition (August-October 1991) the sources of fine nss sulphate in the high Arctic were assessed. It was found that this fine sulphate was essentially of marine biogenic origin during the first month and a half of the expedition, but that by the autumn it was mainly of anthropogenic origin (transported through the free troposphere).

## APPENDIX 1

### 1. GLOBAL CHANGE RESEARCH IN BELGIUM

#### 1.1 What is Global Change ?

The evolution of the earth system is the result of complex interactions between physical, chemical and biological processes. These involve the atmosphere, the biosphere, the hydrosphere and the cryosphere, as well as the socio-economic system (Fig. 1.1).

Since the industrial revolution man's impact on the earth has become global. High demographic growth rates (especially in developing countries), non-sustainable patterns of production and consumption, and changes in land use associated with agricultural practices have all contributed to the scarcity of natural resources and the earth's carrying capacity is limited.

It has now been established that the increasing concentration of greenhouse gases has led to changes in the radiative balance of the atmosphere. The response of the earth to such forcing (enhanced greenhouse effect) and the related environmental consequences are difficult to predict, but may well include rising sea levels, more frequent floods and changing distributions of climate and vegetation. This will clearly have socio-economic consequences.

During springtime an ozone hole has been observed in the stratosphere above the Antarctic since the late 1970s. In the Arctic and at mid-latitudes the ozone layer has become thinner. More UVB radiation is expected to reach the biosphere, potentially causing increases in glaucoma (cataract) and skin cancer, changes to DNA and deficiencies in the immune system, and decreasing yields from

both agriculture and phytoplankton. The exact effects of the UV-B radiation on the biosphere are not yet well known.

The increase in pollutants (nitrogen and carbon compounds) in the atmosphere is expected to change the self cleaning capacity of the atmosphere (oxidation capacity) and hence the lifetime of some climatically important gases such as methane and HCFCs. Even though measures have been taken to reduce emissions of nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs), the ozone (O<sub>3</sub>) concentration in the lower troposphere has increased considerably during the last decades. Tropospheric ozone is a greenhouse gas and a pollutant causing damage to human health, crop yields and materials.

In comparison with many other research areas, global change research is highly interdisciplinary, and its importance is controversial. For example, the role of human activities - and hence the need to mitigate these activities - is not unanimously recognized. There remain uncertainties about the importance, scale and timing of global change, though its effects will probably become more important in the future than they are now.

Because of these uncertainties, it is difficult to motivate people to change their patterns of consumption and production before the effects of global change become obvious. Policy and science on global change should therefore be co-ordinated at an international level.

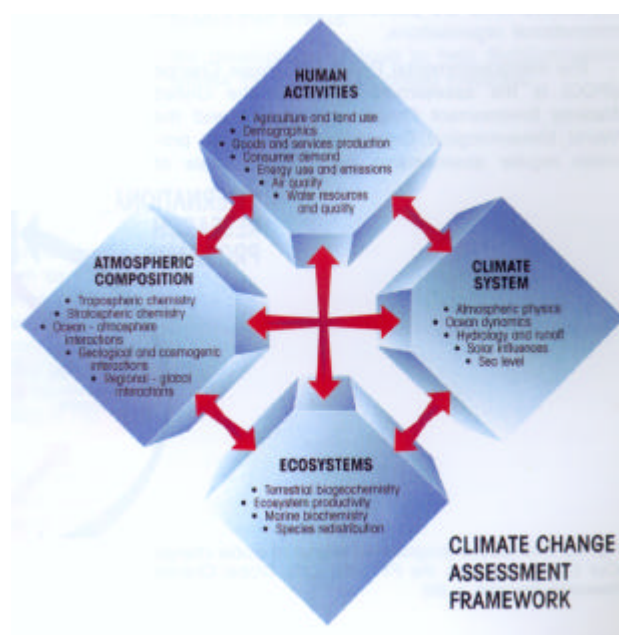


Fig. 1.1 - Schematic diagram of global interactions (Our Changing Planet, the FY 1995, U.S. Global Change Research Program, p 25)

## 1.2 Global Change Research: The International Scene and the Belgian Programme

### Research:

The scientific consensus on global changes in the earth's physical, chemical, biological and socio-economic systems has led to the establishment of three international scientific programmes (Fig. 1.2): the World Climate Research Programme (WCRP), the International Geosphere and Biosphere Programme (IGBP) and the International Human Dimensions of Global Environmental Change Programme (IHDP). On a European level the European Commission (EC) is involved in global change research, in particular through the Environment And Climate Programme (4th Framework programme) including the ENRICH (European Network of Research in Global Change) initiative.

The aim of these programmes is to enhance knowledge and provide policymakers with a sound basis for decision-making on the road towards sustainable development. Taking part in these international programmes gives an added value to national initiatives and allows direct access to research results and other information.

### Assessment:

In order to provide the most up-to-date scientific information to government, industry and the public, assessments are published periodically by the international organisations.

The Intergovernmental Panel on Climate Change (**IPCC**) is the assessment forum of the United Nations Environment Programme (UNEP) and the World Meteorological Organization (WMO). It provides regular assessments on a world scale of

research relating to the climate system, the effects of climate change and climate change mitigation and remediation.

Within the framework of the Vienna Convention, the Ozone Depletion Panel and the Scientific Steering Committee on UV Monitoring of the World Health Organisation (WHO) and Global Atmosphere Watch (GAW) provide decision-makers with the most recent scientific information on stratospheric ozone depletion and its consequences.

### Research in Belgium:

Through the Belgian Global Change Programme, Belgium invested about 542,2 million Belgian francs in global change research between 1990 and 1996.

This multi-disciplinary programme was organised into 27 projects, involving 36 research teams and covering six different areas:

- atmospheric processes relevant to climate change;
- biogeochemical cycles on land and at sea;
- global modelling of climate and environment;
- past climate and environmental changes;
- effects of global change on terrestrial ecosystems, soil, hydrological cycles, sea level etc; and
- socio-economic aspects

The main goal was to contribute to international research efforts dedicated to global environmental and climate change.

The national programme allowed several teams to participate actively in international programmes. These included the International Geosphere and Biosphere Programme (IGBP) core projects: International Global Atmospheric Chemistry (IGAC); Global Change of Terrestrial Ecosystems (GCTE); PAST Global Environmental changes (PAGES); the

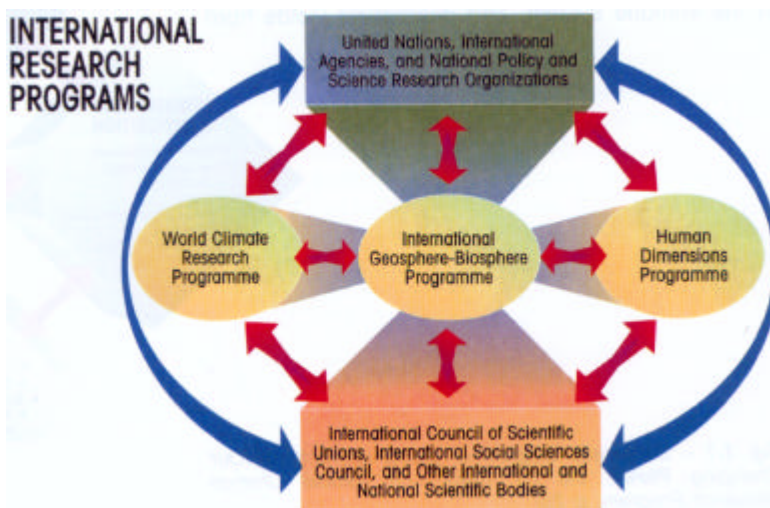


Fig. 1.2 International programmes related to global change (*Our Changing Planet, the FY 1995, U.S. Global Change Research Program, p 90*)

project on Stratospheric Processes and their Role in Climate (SPARC) of the World Climate Research Programme (WCRP); the EC Environment and Climate programme (several projects, including the SESAME, EASOE and TESOE campaigns); and MAST (MARine Science and Technology), including the Ocean Margin EXperiment (OMEX).

In these programmes several Belgian scientists played influential roles as members or chairs of scientific committees.

Other teams participated in space programmes such as the Global Ozone Monitoring Experiment (GOME) launched in April 1995 on board of the second Earth Remote Sensing Satellite (ERS-2), Satellite Pour l' Observation de la Terre (SPOT) VEGETATION, the Advanced Earth Observing Satellite (ADEOS) (NASDA, Japan), and the European Environmental Satellite (ENVISAT), which carried the instruments GOME, SCHIAMACHY and MIPAS. These projects helped to justify Belgium's investment in space programmes as well as in global change research.

Several scientists were active within the framework of the IPCC assessments (1992, 1994, 1995) as authors, reviewers or participants in workshops, and in the scientific assessment of the Ozone Depletion Panel (reports 25:1991 and 37:1994) of the World Meteorological Organisation (WMO).

Through this national programme and the work of the CO<sub>2</sub> working group, the Federal office for scientific, technical and cultural affairs (OSTC) contributed to the negotiation process in the framework of the climate convention, nationally as well as internationally.

### **1.3 Global Change and Sustainable Development**

The 1987 report of the World Commission for the Environment and Development, better known as the Brundtland report, considered global change (with climate change as one of the key issues) as an important threat to the sustainable development of the world. Global change was also at the top of the political agenda during the UNCED (United Nations Conference on Environment and Development) in Rio de Janeiro in 1992.

Achieving sustainable development requires a thorough understanding of the complex forces leading to environmental problems and hindering sustainable socio-economic development. Integrating the concept of sustainable development into practical policymaking affects not only the prioritisation

of research items but also the way research is organised. A multi-disciplinary, holistic approach is needed.

If we are not to mortgage the future of our planet and the lives of future generations, we will have to strive for sustainable development. This in turn requires the best scientific and technical knowledge - so global change research is not simply a matter of scientific curiosity.

Awareness of the global scale of environmental problems has led to the establishment of agreements and action plans at both global and European scales. They include AGENDA 21, the Framework Convention on Climate Change (FCCC), the Vienna convention and the UN-ECE Convention on the Long Range Transport of Air Pollution (LRTAP), the EU Framework Directive for Ozone, and the Fifth Action Programme: Towards Sustainability. It is important that Belgium, which is active in the preparation of these international agreements, has a background of sound science from which to implement them at the federal and regional levels.

The Belgian Global Change Programme (1990-1996) has contributed to:

- a better understanding of the causes and consequences of global change;
- the development of methods and tools that allow to observe, document and predict changes, and to assess their effects;
- the development of tools to help decisionmakers assess the effect of proposed measures.



## APPENDIX 2

The ten best scientific papers resulting from the Belgian Global Change Programme (1990-1996) and the Belgian participation in EUROTRAC for each research team.

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### GC/35/002 - Prof. P.C. Simon (IASB/BIRA)

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## APPENDIX 3

### 3 ACRONYMS AND ABBREVIATIONS

ADEOS	Advanced Earth Observing Satellite (NASDA, Japan)	IBM	Improved bucket model
ASE	Air-sea exchange	IGAC	International Global Atmospheric Chemistry Programme (IGBP)
asl	Above sea level		
ATLAS	Atmospheric Laboratories for Applications and Science	IGBP	International Geosphere-Biosphere Programme (ICSU)
ATMOS	Atmospheric trace molecule spectroscopy	IHDP	International Human Dimensions of Global Environmental Change Programme
BC	Black carbon	IMAGES	Intermediate Model for the Annual and Global Evolution of Species
BIATEX	Biosphere ATMosphere EXchange	IPCC	Intergovernmental Panel on Climate Change (WMO/UNEP)
BIRA/IASB	Belgian Institute for Space Aeronomy	IR	Infrared
CARAT B	Carbon Assimilation in the Biosphere	ISSJ	International Scientific Station of the Jungfraujoeh
CCN	Cloud condensation nuclei		
CN	Condensation nuclei	KMI/IRM	Royal Meteorological Institute (Belgium)
CNRS	National Centre for Scientific Research (France)	LACTOZ	Laboratory studies of chemistry related to tropospheric ozone
DNA	Desoxyribo Nucleic Acid	LRTAP	UN-ECE Convention on Long-Range Tranboundary Air Pollution
DMS	Dimethyl sulphide	MAST	Marine Science and Technology
DOAS	Differential optical absorption spectrometry	MIPAS	Michelson Interferometer for Atmospheric Spectroscopy
EASOE	European Arctic Stratospheric Ozone Experiment (EC)	MSA	Methanesulphonate
EC	European Commission	NASA	National Aeronautics and Space
EU	European Union	NASDA	National Space Development Agency
ECMWF	European Centre for Medium-Term Weather Forecasting	(Japan)	
ENRICH	European Network of Research in Global Change (EC)	NCAR	National Center for Atmospheric Research
ENVISAT	European Environmental Satellite (ESA)	NDSC	Network for the Detection of Stratosphere Change
EPMA	Electron probe X-ray microanalysis	NMHC	Non-methane hydrocarbons
ESA	European Space Agency	NMVOG	Non-methane volatile organic compound
ESMOS	European Stratospheric Monitoring Stations	NODC	National Oceanographic Data Center
		NOSE	North Sea Experiment
EUROTRAC	European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents in the Troposphere over Europe	nss	non-sea salt
FCCC	Framework Convention on Climate Change	OC	Organic carbon
FIR	Far infrared	OCCMs	Ocean carbon cycle models
FTIR	Fourier transform infrared (spectrometer)	ODP	Ozone depletion potential
FTS	Fourier transform spectrometer	OFFP	Ozone formation potential
GAW	Global Atmospheric Watch	OMEX	Ocean Margin EXperiment (EC)
GCTE	Global Change and Terrestrial Ecosystems (IGBP)	OSTC	Federal Office for Scientific, Technical and Cultural Affairs
GMAD	Geometric mean aerodynamic diameter	PAGES	PAst Global changES (IGBP)
GOME	Global Ozone Monitoring Experiment	PAN	Peroxy acetyl nitrate
GOMOS	Global Ozone Monitoring by Occulation of Stars	PIXE	Proton-induced X-ray emission
		PM	Particulate mass
GWP	Global warming potential	PSC	Polar stratospheric cloud
		RZADM	Regional acid deposition model
		SAFARI	Southern Africa Fire-Atmosphere Research Initiative
		SAOZ	Système d'Analyse par Observations Zenithales
		SARs	Structure-activity relationships

SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Cartography
SDI	Small deposit area low-pressure impactor
SESAME	Second European Stratospheric Arctic and Mid-Latitude Experiment
SFU	Stacked filter unit
SOLCON	Solar Constant
SOLSPEC	Solar Spectrum
SPARC	Stratospheric Processes and Their Role in Climate (WCRP)
SPOT	Satellite Pour l'Observation de la Terre
SZA	Solar zenith angle
TLS	Transportable lamp system
TOMS	Total Ozone Mapping Spectrometer
ULg	University of Liege
UNCED	United Nations Conference on Environment and Development (Rio de Janeiro, June `92)
UNEP	United Nations Environment Programme
US	United States
UV	Ultraviolet
VOC	Volatile organic compound
WCRP	World Climate Research Programme (WMO/ICSU)
WHO	World Health Organisation
WMO	World Meteorological Organisation
yr	Year

## APPENDIX 4

### 4 CHEMICAL FORMULAS

Al	aluminium	N <sub>2</sub>	molecular nitrogen
As	arsenic	N <sub>2</sub> O	nitrogen pentoxide
Br	bromine	N <sub>2</sub> O <sub>4</sub>	nitrogen hemitetroxide
BrNO	nitrosyl bromide	N <sub>2</sub> O <sub>5</sub>	nitrogen pentoxide
C	carbon	NH <sub>3</sub>	ammonia
C <sub>10</sub> H <sub>1</sub>	a-pinene	Ni	nickel
C <sub>2</sub> H <sub>2</sub>	acetylene (ethyne)	NO <sub>2</sub>	nitrogen dioxide
C <sub>2</sub> H <sub>6</sub>	ethane	NO <sub>3</sub>	nitrate radical
Ca	calcium	NO <sub>x</sub>	nitrogen oxide
CCl <sub>2</sub> F <sub>2</sub>	CFC 12 (dichlorodifluoromethane)	O	Atomic oxygen
CCl <sub>3</sub> F	CFC 11 (trichlorofluoromethane)	O <sub>2</sub>	molecular oxygen
CCl <sub>4</sub>	carbon tetrachloride	O <sub>3</sub>	ozone
Cd	cadmium	OCS	carbon oxysulphide, carbonyl sulphide
CF <sub>4</sub>	carbon tetrafluoride	OH	hydroxyl radical
CFC	chlorofluorocarbon	Pb	lead
CH <sub>3</sub> CHO	acetaldehyde	S	sulphur
CH <sub>3</sub> Cl	methyl chloride	Sb	antimony
CH <sub>4</sub>	methane	SF <sub>6</sub>	sulphur hexafluoride
CHClF <sub>2</sub>	HCFC 22 (chlorodifluoromethane)	SO <sub>2</sub>	sulphur dioxide
Cl	chlorine	Zn	zinc
ClONO <sub>2</sub>	chlorine nitrate		
CO	carbon monoxide		
CO <sub>2</sub>	carbon dioxide		
COF <sub>2</sub>	carbonyl fluoride		
CS <sub>2</sub>	carbon disulphide		
F	fluorine		
Fe	iron		
H	atomic hydrogen		
H <sub>2</sub> CO	formaldehyde		
H <sub>2</sub> O	water vapour		
HCFC	hydrochlorofluorocarbon		
HCl	hydrochloric acid		
HCN	hydrogen cyanide		
HCOH	formic acid		
HCOOH	formic acid		
HF	hydrofluoric acid		
HFC	hydrofluorocarbon		
Hg	mercury		
HNO <sub>2</sub>	nitrous acid		
HNO <sub>3</sub>	nitric acid		
HNO <sub>4</sub>	peroxynitric acid		
HOCl	hypochlorous acid		
K	potassium		
N	atomic nitrogen		

## APPENDIX 5

### 5 UNITS

Dobson Unit	2 687 x 10 <sup>6</sup> molecules/cm <sup>2</sup>
eV	electron Volt
Gt	gigatonne (10 <sup>9</sup> tonnes)
hPa	hectopascal (equivalent to 1 millibar)
µg	microgramme(10 <sup>-6</sup> grammes)
ng	nanogramme(10 <sup>-9</sup> gramme)
pg	picogramme(10 <sup>-12</sup> gramme)
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
Tg	teragramme (10 <sup>12</sup> grammes)

## APPENDIX 6

## **6 GLOBAL CHANGE PROJECTS (1990-1996) IN THE FIELD OF ATMOSPHERIC CHEMISTRY**

Promotor: W. Maenhaut

Scientists: K. Beyaert, G. Koppen

Composition and origin of the regional atmospheric aerosol at great distance from anthropogenic source areas. Assessment of the extent of the anthropogenic perturbation

Promotor: PC. Simon (coordinator), L. Delbouille, R. Zander, R. Colin

Scientists: M. Van Roozendael, C. Hermans, J.-C. Lambert, C. Servais, G. Roland, F. Melen, J. Bosseloirs, J.-M. Guilmot

SMAC: Spectroscopic Measurements of Atmospheric Changes

Promotor: R. Zander Scientist: E. Mahieu ATMOS Antenna - Belgian contribution to the global study of the chemical composition and physical characteristics of the terrestrial atmosphere through the analysis of infrared solar spectra recorded with the ATMOS (Atmospheric Trace MOlecule Spectroscopy) instrument

Promotor: F. Adams

Scientists: Cl. Witte, F Laturus

Organolead compounds in snow and ice from Greenland

Promotor: C. Vinckier

Scientists: N. van Hoof, F. Compernelle, S. Asthy, S. Aerts Role of apinene in the formation process of greenhouse gases in the atmosphere

Promotor: J.C. Gerard (Coordinator), G. Brasseur

Scientists: G. Colinet; L. François, P Warnant, A. Mouchet, Y. Godderies, B. Nemry, P Ginoux

Global modelling of the coupled chemical-climatic changes due to human activities

## APPENDIX 7

### 7 BELGIAN PARTICIPATION IN EUROTRAC (1988-1995)

Promotor: L. Delbouille, R. Zander  
Scientists: Ph. Demoulin, C. Servais, G. Roland

TOR: Determination of vertical column abundances  
and distribution of atmospheric constituents

Promotor: D. De Muer  
Scientists: ph. Van Haver

TOR: Vertical profiles of ozone and meteorological  
parameters at Uccle, measured with free balloons  
and a tethered balloon.

Promotor: J. Peeters  
Scientists: W. Boullart & J. Vertommen

LACTOZ: Description and Modelling of Chemical  
Processes in Relation with the Tropospheric Ozone  
Budget

Promotor: W. Maenhaut Scientists: F. François

ASE: Elementaire samenstelling en bronnen van  
atmosferische aërosolen boven en rond de  
Noordzee

Promotor: W. Baeyens

Scientists: M. Leermakers, C. Meelman, Q.  
Xianren & P. Lansen

ASE: Air-sea exchanges fluxes of mercury and  
atmospheric inputs to the sea

Promotor: R. Van Grieken Scientists: Injuk Jasna

ASE: Chemische transformatieprocessen en  
depositieprocessen van aërosolen boven de  
Noordzee

Promotor: O. Van Cleemput  
Scientists: A. Vermoesen, P Boeckx

BIATEX: Emissie van gasvormige koolwaterstoffen  
en ammoniak uit de bodem

Promotor: M. Herman Scientists:

JETDLAG: Spectroscopie de la phase gazeuse à  
haute résolution et aspects dynamiques

Promotor: R. Colin  
Scientists: PC. Simon & P Dufour  
TOPAS: Tropospheric OPTical Absorption  
Spectroscopy

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Martine Vanderstraeten