

ATMOSPHERIC RESEARCH RELATED TO GLOBAL CHANGE AT THE BELGIAN INSTITUTE FOR SPACE AERONOMY

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It is evident that within a programme such as Global Change, which aims at "the understanding of the interactive physical, chemical and biological processes that regulate the total Earth system", the study of the atmosphere should be of primary importance.

Therefore and in response to the need for a study of global-scale changes in the atmospheric composition a special core project of the International Geosphere Biosphere Programme (IGBP) was started, called IGAC (International Global Atmospheric Chemistry).

The Belgian Institute for Space Aeronomy (BISA) was founded in 1964 under the impulse of Prof. M. Nicolet and has since then contributed significantly to our knowledge of the physics and chemistry of our atmosphere. One of its major study objects is the stratosphere, through modeling, observations and laboratory work. It is the purpose of this paper to give an overview of the work of BISA related to Global Change.

Although strictly speaking IGAC is only concerned with tropospheric research and although stratospheric studies are treated within the SPARC (Stratospheric Processes and their Role in Climate) project of the World Climate Research Programme (WCRP), we have also summarized in this paper the work of BISA concerning the stratosphere.

Most of this work is directly related to the ozone problem. The latter has been the focal point of many international research efforts, especially since the discovery of the ozone hole and the results of an international ozone trend study. This study provided evidence for a worldwide ozone decrease in the stratosphere of the order of a few percent in 20 years and at the same time an ozone increase in the troposphere.

It is worthwhile noting that these findings were actually the very first real quantifications of global changes and that the atmosphere is one of the regions where the impact of man is unambiguously shown. In this context the decision of the Royal Swedish Academy of Sciences to award the 1995 Nobel Prize in Chemistry to P. Crutzen,

M. Molina and F.S. Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone" can be considered as a confirmation of the importance of atmospheric research.

To give an overview of the global change related research in BISA in the paragraphs hereafter, we have subdivided the work into the field measurements or observations, laboratory work and modeling.

The field measurements include ground based remote sensing, in-situ measurements with balloon borne instruments and sounding of the atmosphere from space. They mainly provide data concerning the composition of the stratosphere or information about solar radiation driving the chemical processes in the atmosphere.

The objectives of the laboratory work are twofold. From one side experiments are set up to measure fundamental data required for photochemical models, such as absorption cross sections of atmospheric constituents. On the other hand laboratory experiments also provide data needed to interpret field measurements, such as for instance rate coefficients of ion-molecule reactions involved in chemical ionization experiments.

Finally the modeling efforts use experimental and observational data to describe atmospheric processes within a mathematical framework. The comparison of model results and observations leads to a continuous improvement of our understanding of atmospheric processes.

It should also be mentioned that most of the scientific studies of BISA related to the IGBP Global Change programme, also contribute to several international programmes, such as :

- the Environment Programme of the European Commission (DG XII);
- the Earth Observation Programme of ESA and other agencies (NASA, NASDA,....);
- the Network for the Detection of Stratospheric Change (NDSC);

- SPARC, a project of WCRP;
- the correlative measurement programmes of several satellite-borne experiments (UARS, GOME and in future ADEOS, ODIN and ENVISAT-1 with the atmospheric instruments GOMOS, SCIAMACHY and MIPAS);
- EUROTRAC, a project of EUREKA.

Field measurements

Ground based observations

Ground-based remote sensing measurements of stratospheric species have been extensively used to increase the scientific understanding of stratospheric processes at high and mid-latitudes. The first European Arctic Stratospheric Ozone Experiment (EASOE) coordinated by the European Commission (EC) during the winter 1991/1992 has demonstrated the need for a complementary approach between high quality ground-based observations, aircraft and balloon measurements, combined with satellite data and model calculations.

Since the 1950s, the International Scientific Station of the Jungfraujoch (ISSJ) has been equipped with infrared spectrometric instruments for solar and atmospheric observations, in particular by the Institut d'Astrophysique of the Université de Liège. The actual instrumentation for remote sensing in the infrared consists of two Fourier-Transform Infrared (FTIR) spectrometers with a spectral resolution of the order of 0.0025 cm^{-1} . Additional techniques have been implemented as, e.g., microwave radiometers (Univ. of Bern), a SAOZ UV/Visible spectrometer (BISA, (1)), and others. The continuing effort of combined observations with a guarantee for high quality makes that the ISSJ, the Observatoire de Haute Provence (OHP), and Plateau de Bure together have been designated as the alpine station at northern mid-latitude of the international Network for Detection of Stratospheric Change (NDSC).

Since 1990, the Belgian Institute for Space Aeronomy has been participating in the observations of tropospheric and stratospheric constituents with the FTIR instruments and in their interpretation. *HCl*, *ClONO₂*, *NO*, *NO₂*, *HNO₃*, *HF*, *COF₂*, and *O₃* total column amounts are monitored continuously; also some CFC and HCFC compounds are observed regularly. Up to now, BISA essentially focused on the development of its own algorithm for inversion of the FTIR spectra, called SFSP (SynthSpec & FitSPec), and on the interpretation of the ozone and *NO₂* observations at ISSJ. This latter work has been done in collaboration with P. Demoulin and R. Zander of the Institut d'Astrophysique of the Université de Liège.

In the SFSP method a synthetic spectrum is calculated with high precision. In the Synthspec module the earth

curvature and refraction, the spectroscopic parameters of all interfering gases, actually taken from HITRAN92, and the instrument characteristics if desired, are taken into account. The retrieval part (Fitspec) is based on an iterative procedure, searching for a minimum weighted rms difference between experimental and synthetic spectra, the weight being proportional to the absorption depth. Recently, the procedure has been adapted to permit a quasi-automatic retrieval of a target species in a large series of spectra, and the speed has been increased by about a factor 30. Some preparatory work has been done with the purpose of including solar lines in the synthetic spectrum calculation. SFSP has been validated in the ESMOSII/NDSC Infrared spectral fitting algorithms intercomparison exercise (1993-1994) (2). BISA has also some experience with an alternative, public-domain code SFIT (C.P. Rinsland), that was validated in the same exercise.

The actual long-term database of ozone at ISSJ started in 1984, based on FTIR data, and has been complemented with SAOZ data from mid-1990 on. In order to benefit fully from the combined dataset, their mutual agreement has to be checked. It should be noted that FTIR data are available only for clear-sky days, whereas SAOZ data are taken daily, at twilight; therefore both databases are complementary. The intercomparison of the FTIR and SAOZ datasets, up to now limited to 1993 and the first half of 1995, resulted in the following findings (1) :

(i) Spectroscopic laboratory work (3) has identified the least temperature dependent ozone absorption lines in the bands $3\nu_3$ ($\sim 3040 \text{ cm}^{-1}$), $\nu_1+\nu_2-\nu_3$ ($\sim 2850 \text{ cm}^{-1}$) and $\nu_1+\nu_3$ ($\sim 2150 \text{ cm}^{-1}$), taking into account the combined effect of the lower energy level of the transition and the temperature dependence of the Lorentz halfwidth. The intercomparison demonstrated that the most stable FTIR results and the smallest FTIR-SAOZ differences are obtained using several lines simultaneously in the $(3039.18 - 3040.05 \text{ cm}^{-1})$ μ window in the $3\nu_3$ band.

(ii) The intercomparison should take into account the fact that both instruments possibly probe different air masses, depending on the measurement time and season (1). If dynamic effects of small spatial scale are dominating the ozone behaviour, they show up as an apparent random mutual disagreement between both datasets. Such effects have been observed in the winter-spring of 1993, and could be identified by using additional data from nearby stations (Arosa, Payerne).

(iii) Although a small negative systematic offset not exceeding 5% may still exist, with the FTIR *O₃* values being lower than the SAOZ ones, the agreement between FTIR and SAOZ data comes very close to the one obtained in the most recent intercomparison among various UV/Vis spectrometers including SAOZ (4), of the order of 5% also.

(iv) For each technique, the analysis of the spectra requires an atmosphere model. The 1993 data clearly reveal a correlation between the tropopause pressure and the O_3 column especially as to the short-term fluctuations: the degree of linear correlation r increases from .49 to .58 after removal of slow (seasonal) variations. Actually ongoing work studies the tropopause characteristics and other auxiliary data of meteorological nature (potential vorticity, stratospheric temperatures, etc.) at ISSJ, in order to see whether from these parameters a model of the atmosphere can be built that provides a better representation of the real day-to-day variations of the atmospheric conditions (instead of the standard models adopted up to now), for improving the mutual agreement between both datasets.

trend has been derived over 10 years, (i) using data all-year round, and (ii) excluding the first trimester of each year (data points represented by open circles), in which larger O_3 variations occur. The values obtained for the sinusoidal variation are quite similar in both cases: 22.3% pp in case (ii) as compared to 25.6% pp in case (i). However the derived rate of O_3 decrease changes from (-0.76 ± 0.12) % per year with the 1990 reference value equal to 3.23×10^{13} mol/cm² in case (i) (dashed line), to (-0.38 ± 0.11) % per year in (ii) with the 1990 value equal to 8.06×10^{15} mol/cm² (solid line). The difference between both trend-values is indicative of the fact that the maxima in the seasonal variation were more pronounced in the first 5 years of the considered period. These results are close to the ones published in WMO (5) under similar conditions.

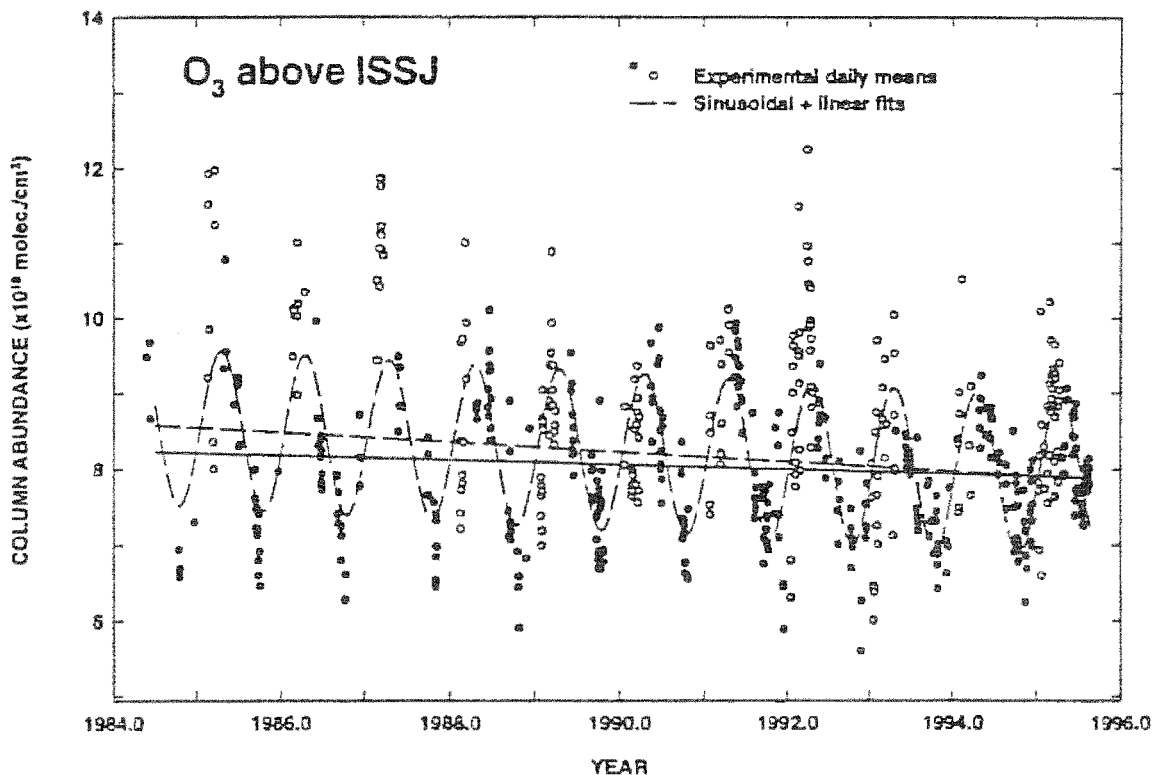


Figure 1 : Evolution of the ozone column above ISSJ (1984-1995) as obtained in a collaboration between BISA and the "Institut d'Astrophysique" of the "Université de Liège". The open circles indicate data within the first trimester of each year; they are included in the trend estimate represented by the dashed line (see text).

The above results have permitted an evaluation of the long-term O_3 trend covering the 1984-1995 period at ISSJ, the reference value taken at the beginning of 1990 (Figure 1). The fit superimposes a sinusoid for representing the seasonal variation, and a linear trend. The

it should be noted that these trends include the perturbed post-Pinatubo period in which O_3 values were particularly low.

Analogous to ozone, we dispose of two databases for NO_2 at ISSJ, one derived from FTIR measurements from 1985 on, the other one derived from SAOZ observations since mid-1990. Again, their mutual agreement is of the utmost importance for exploiting the data for the study of the NO_2 column and diurnal variation and its long-term evolution. Some preliminary results for the 1992-1995 data show a mutual agreement within 5% if the SAOZ data are restricted to the usually adopted observation interval of 87° to 91° solar zenith angle, thus of the same order of magnitude as the agreement obtained between various UV-Vis instruments (4); the SAOZ results appear systematically lower than the FTIR ones. In this comparison, the diurnal variation has been considered. This work is still in progress.

Beside the series of stratospheric gases monitored by IR solar observations, further measurements of O_3 and NO_2 vertical columns have been performed at ISSJ since 1990. These trace gases are measured at twilight, in the 300-600 nm spectral region, based on the DOAS (Differential Optical Absorption Spectroscopy) technique.

The role of heterogeneous chemistry on stratospheric aerosols has been confirmed by the monitoring of the stratosphere during the last six years. More specifically, the nitrogen compounds partitioning has been strongly modified due to the huge volcanic eruption of Mt. Pinatubo in June 1991 which injected up to 30 millions of tons of sulphur dioxide into the stratosphere.

Ground-based measurements of NO_2 abundance covering one year before and five years after the Mt. Pinatubo eruption have been carried out at the International Scientific Station at the Jungfrauoch (Switzerland, 46°N , 8°E) and at Sodankyla (Finland, 64°N , 27°E) (6). The NO_2 vertical column abundance is measured during the morning and evening twilight by application of the differential absorption method using the sunlight scattered at zenith in the visible range. The available time series shows a significant reduction of NO_2 starting in winter 1991-1992, after the eruption of the Mt. Pinatubo volcano, as is visible in Figure 2.

A maximum decrease of about 35% is observed in January 1992 at both stations. The continued time series of observations show a similar behaviour at both latitudes, i.e. the recovery of the NO_2 column until August 1994. These results are compared with 2-D chemical model calculations including the effect of heterogeneous reactions using Mt. Pinatubo aerosols parameters as observed by lidar in the Alps (Figure 3). In general the modeled NO_2 columns agree qualitatively with the observations although the amplitude of the seasonal variation is underestimated, possibly due to internal limitations of the model which e.g. does not include diurnal changes. The observed and calculated NO_2 percent changes are in good agreement which confirms quantitatively the impact of the heterogeneous chemistry on stratospheric NO_2 .

Perturbed stratospheric chemistry by chlorine activation through heterogeneous processes can be observed at mid- and high latitudes when low stratospheric temperatures are encountered, associated with the displacement of the polar vortex during winter and early spring in the northern hemisphere. During the winter 1994-1995, the lowest stratospheric temperatures observed so far were experienced in the Arctic in January 1995, 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 have been observed but because of the instability of the polar vortex in the Arctic, the conditions to develop an ozone hole in the northern hemisphere are not met during a sufficiently long time.

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 due to the complex coupling between chemistry and dynamics, specifically in the northern hemisphere. In order to study the connection between the Arctic and the mid-latitude ranges and to improve our knowledge on these issues, a Second European Stratospheric Arctic and Mid-Latitude Experiment (SESAME) was implemented by the EC. It was decided to expand the ground-based measurements for stratospheric monitoring around 60°N to fill in the geographical gap between the observing sites situated beyond the Arctic circle and the mid-latitude Alpine stations situated around 45°N and that contribute to the Network for the Detection of Stratospheric Changes (NDSC). The selected observing sites could be at or near the edge of the polar vortex during winter in order to determine the extent of chemically-induced loss of stratospheric ozone and to investigate transport from high latitude, mainly during late winter-early spring. The observations were based on two main techniques, the Fourier transform spectroscopy in the infrared (FTIR) and the UV-visible differential absorption spectroscopy (UV-Vis). These measurements include total amounts of several reservoir species (FTIR) with ozone, nitrogen dioxide and ClO (UV-Vis). In total, ground-based instruments were operated at about 35 sites, mainly in Europe.

BISA performed UV-visible measurements of ClO , NO_2 and O_3 column amounts at Harestua, 60°N during the winters 1993/1994 and 1994/1995 corresponding respectively to the phases I and III of SESAME (7). A careful laboratory characterization as well as the development of a new analysis software significantly improved the instrumentation. Its sensitivity for the detection of poorly abundant constituents like ClO and NO_2 in high latitude winter conditions was increased as compared to the first measurements made during the EASOE campaign (8). In addition, a mobile Fourier transform spectrometer was used for the first time for similar measurements in the visible range during the 1995 winter (phase III of SESAME).

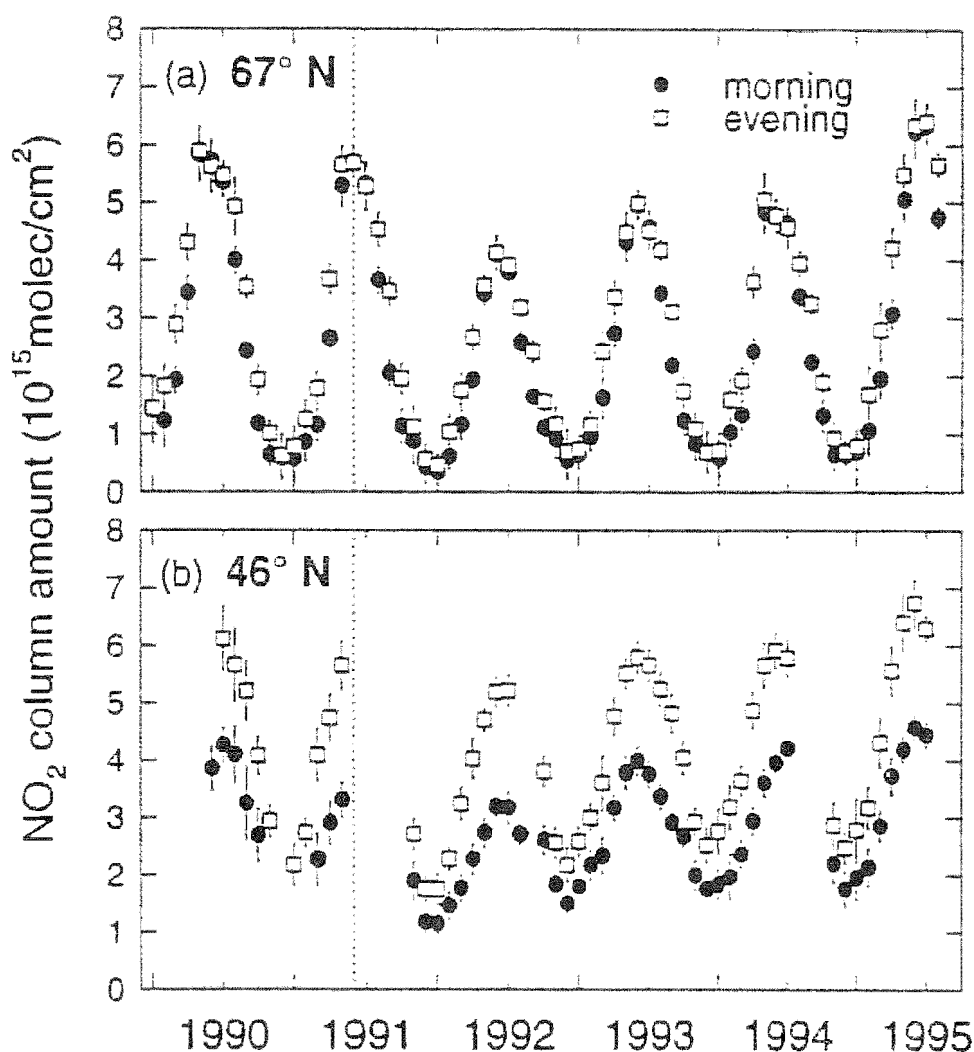


Figure 2 Time series of monthly average NO_2 data available at (a) Sodankylä and (b) at the International Scientific Station at the Jungfraujoch. For each month, an average morning and evening twilight value is plotted. The vertical dotted line indicates the day of the Mt. Pinatubo eruption.

Morning and evening NO_2 amounts are averages of measurements between 87° and 91° SZA (Solar Zenith Angle). In the case of the direct Sun data obtained from January to March 1995 with the FTS instrument the average is usually made between 83° and 89° SZA. Despite this zenith-angle difference which might have some impact on the comparison due to the diurnal variation of NO_2 , the agreement between the direct Sun and zenith-sky results is quite satisfactory.

The NO_2 time series shows the well-known seasonal variation primarily due to the change in illumination. In addition, NO_2 column amounts are 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 NO_x conversion to their reservoirs as well as

possible denitrification of the polar stratosphere by condensation of nitric acid on polar stratospheric clouds (PSCs). Corollary, the OCiO contents inside the polar vortex during January 1995 are quite large as compared to January 1994 indicating larger chlorine activation in January 1995. Most OCiO observations are obtained inside or at the edge of the polar vortex which indicates that the activation is essentially limited to the vortex region.

Ozone column amounts were determined during SESAME phases I and III from zenith-sky and direct Sun observations. Low O_3 column amounts (as compared to the long term climatology derived from TOMS data) are measured in March both during SESAME phase I and phase III when the polar vortex was moving above Harestua (as compared to the 12-year TOMS climatology). These measurements are consistent with episodes of O_3

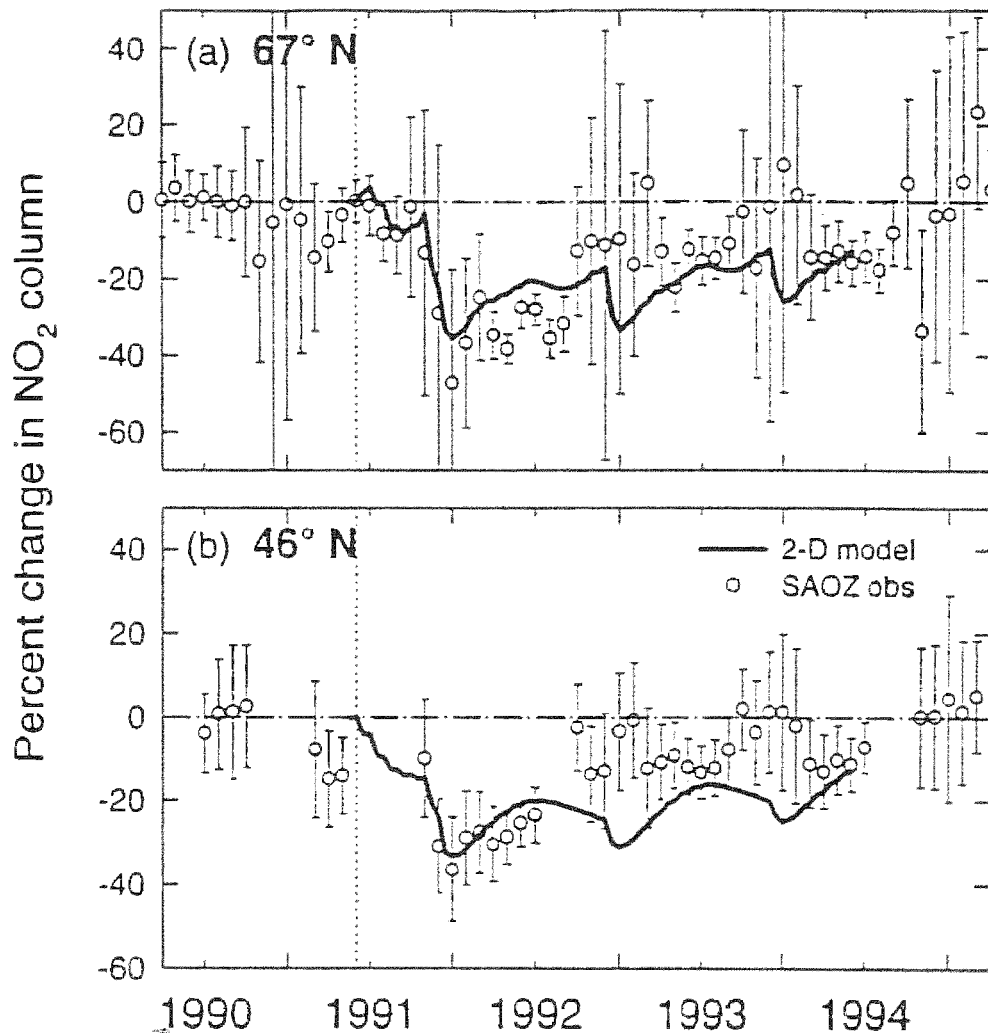


Figure 3 : Comparison between experimental and modelled results for the monthly average NO_2 total amount change at (a) Sodankyla and (b) at the International Scientific Station at the Jungfraujoon. The experimental results are based on those presented in figure 2. The vertical dotted line indicates the day of the Mt. Pinatubo eruption.

chemical destruction inside the polar vortex in March 1994 and 1995, reported from other SESAME observing sites.

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. Two significant inside-vortex episodes were monitored during phase I and phase III, both years at the end of January and mid-March.

The good agreement of the first FTS measurements with the classical DOAS grating instrument results demonstrates the feasibility of the stratospheric UV-visible

measurements as a new application of the Fourier transform spectroscopy in that spectral range.

Balloon borne measurements

Although a long term global study of the structure and composition of the Earth's atmosphere requires regular and long term observations with satellite borne instruments, stratospheric balloons still play an important role in experimental aeronomy. They are not only appropriate for the study of localized phenomena but are a necessary tool for experiments requiring an in situ sampling of atmospheric species such as ion mass spectrometry. Stratospheric balloons are also excellent platforms for the development of space instruments.

The Belgian Institute for Space Aeronomy has a long experience in ballooning and has performed numerous experiments with balloons with a volume ranging from 30,000 m³ to 1,000,000 m³.

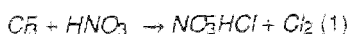
Presently the balloon experiments of BISA are focused on active chemical ionization mass spectrometry (ACIMS) aiming at the detection of trace gases such as *HNO*₃ and *N*₂*O*₅, which play a major role in the ozone depletion. This method, developed by Arnold and co-workers (9) of the Max-Planck-Institut für Kernphysik in Heidelberg (MPIH), relies upon the reactions of atmospheric trace gases with ions produced by an external ion source, mounted in front of a balloon borne mass spectrometer. This leads to specific product ions. From the relative abundance of the signals of the precursor and product ions in the obtained mass spectra, the mixing ratios of the reactive trace gases can be determined.

In the MACSIMS (Measurement of Atmospheric Constituents through Selective Ionization Mass Spectrometry) project, which is a collaboration between the Belgian Institute for Space Aeronomy (Brussels, Belgium), the "Laboratoire de Physique et Chimie de l'Environnement du CNRS" (Orléans, France) and the "Physikalisches Institut" of the University of Bern (Switzerland) and which is partially financed by the European Commission, a new balloon borne instrument has been developed for the measurement of stratospheric trace gases such as *HNO*₃, *N*₂*O*₅ and *ClONO*₂.

The ACIMS method developed by the MPIH group is based upon the ionization of the ambient air by a high frequency high voltage discharge. This method produces mainly *CO*₃⁻ ions and its clusters as precursor ions, which react with *HNO*₃ to produce *NO*₃⁻ ions. The innovation of our method lies in the fact that in the MACSIMS instrument a selective ionization is used, obtained through a DC discharge in gases, which are normally not present in the stratosphere. These gases are integrated in the payload in small steel bottles. Through the use of gas mixtures such as *Ar/Cl*₂ and *Ar/CH*₃*I*, *Cl*₂⁻ and *I*⁻ source ions can be produced. The selective reactions of these ions can then be used for the derivation of trace gas concentrations.

Furthermore the use of a new balloon borne Mattauch-Herzog mass spectrometer with simultaneous ion detection capabilities (10) should allow a high altitude resolution in the balloon measurements.

Recently nitric acid profiles have been determined in the stratosphere in the altitude range 30 to 20 km, from results of balloon flights with the MACSIMS instrument (11), using the reaction



Where it was originally thought that through the use of *I*⁻ ions (produced by a DC discharge in *Ar/CH*₃*I*) and the reaction *I*⁻ + *N*₂*O*₅, the mixing ratio of dinitrogen pentoxide could be determined, recent laboratory studies (12) have shown that with this method no distinction can be made between *N*₂*O*₅ and *ClONO*₂.

Therefore new developments, such as the addition of a third source ion, or the choice of a new ion parent gas will be required. The laboratory studies and new instrumental developments required for this purpose will be performed within the MACSIMS II and SIMULION projects.

Observations from space

The grille spectrometer experiment on board the ATLAS1 mission

Space-borne experiments on board the NASA Shuttle have the advantage of large spatial coverage of the Earth, but have a limited time duration per mission. The latter disadvantage has been overcome by the concept of regularly spaced re-flights of the same experiments on board successive missions. ATLAS, Atmospheric Laboratory for Applications and Science, has been conceived along the same ideas: the mission's objective is the investigation of the Earth's atmosphere, climate and solar relationships, and effects on them of the products of industrial complexes and agricultural activities, through a series of 11 flights lasting about 10 days each that are distributed over a period of one solar cycle. Moreover, they succeed the Spacelab missions starting in 1983 up to 1985 that already carried on board some of the ATLAS experiments, thereby allowing to extend the long-term monitoring even further backwards.

The Grille spectrometer has been developed and operated as a joint French-Belgian experiment (ONERA/LPMA and BISA)¹. First deployed from stratospheric balloons in the seventies, it participated in the Spacelab-1 mission in December 1983 and the first ATLAS mission in 1992. Its objectives are the study of the vertical composition of the Earth's lower stratosphere up to the lower thermosphere by means of infrared solar occultation absorption spectroscopy, with focus on measurements of the following 10 molecules, in the 2.5 to 10 μm spectral range: *CO*, *CO*₂, *NO*, *NO*₂, *N*₂*O*, *H*₂*O*, *CH*₄, *O*₃, *HCl*, and *HF* (13). The retrieval of the Grille/ATLAS1 data has been performed independently by at least two different inversion algorithms, one being a least-squares global fit method, the other one an optimized Mill's inversion algorithm (20): as such, the quality of the results has been assessed reliably. Whenever possible, the results have been compared to correlative data from ATMOS on board the same mission or from HALOE on board UARS.

Global results of the Spacelab-1 flight, including a presentation of the instrument and the occultation technique, are summarized by Girard et al. (14). During the ATLAS1

mission (March 24 to April 2, 1992), results have been obtained in the latitudinal belt ranging from the equator up to 55°S, especially for H_2O , CH_4 , CO and NO (15,16,17,18). In addition, an important conclusion as to the long-term trend of the stratospheric chlorine content could be drawn from a comparison of the vertical profiles of HCl measured by Grille in 1992, shown in Figure 4, with those determined by ATMOS in 1985, shown in Figure 4, with those determined by ATMOS on board Spacelab-3 in 1985 (19,20). The HCl mixing ratio above 50 km is a prime measurement of the effective stratospheric chlorine loading. According to the Grille spectrometer observations at 55 km, it amounts to (3.6 ± 0.2) ppbv, in good agreement with the mean asymptotic value of (3.4 ± 0.3) ppbv estimated from averaged HCl spectra from ATMOS on board the same mission (21). In comparison with the mean 1985 HCl volume mixing ratio above 50 km of (2.55 ± 0.28) ppbv, measured by ATMOS during the Spacelab-3 mission (22), the present value demonstrates an increase of (0.15 ± 0.05) ppbv/yr (alias somewhat less than 6%/yr), only slightly higher than model predictions

that evaluate to 0.11 to 0.13 ppbv/yr (WMO, 1995, and references therein (5)). The dataset presented here is too limited to derive any significant latitudinal variations.

ORA on EURECA

The ORA project is a collaboration between the Belgian Institute of Space Aeronomy and the Department for Atmospheric, Oceanic and Planetary Physics of the University of Oxford. It has a twofold objective. The first one is a simultaneous measurement of aerosols, ozone and NO_2 in the middle atmosphere in order to contribute to our understanding of the role of aerosols in atmospheric chemistry (23,24), which became obvious since the discovery of the Antarctic ozone hole (25,26,27).

The second objective of the ORA experiment is to measure the water vapour concentration in the mesosphere with the aim of investigating the detailed balance of upper atmospheric water vapour, which is still not fully understood (28).

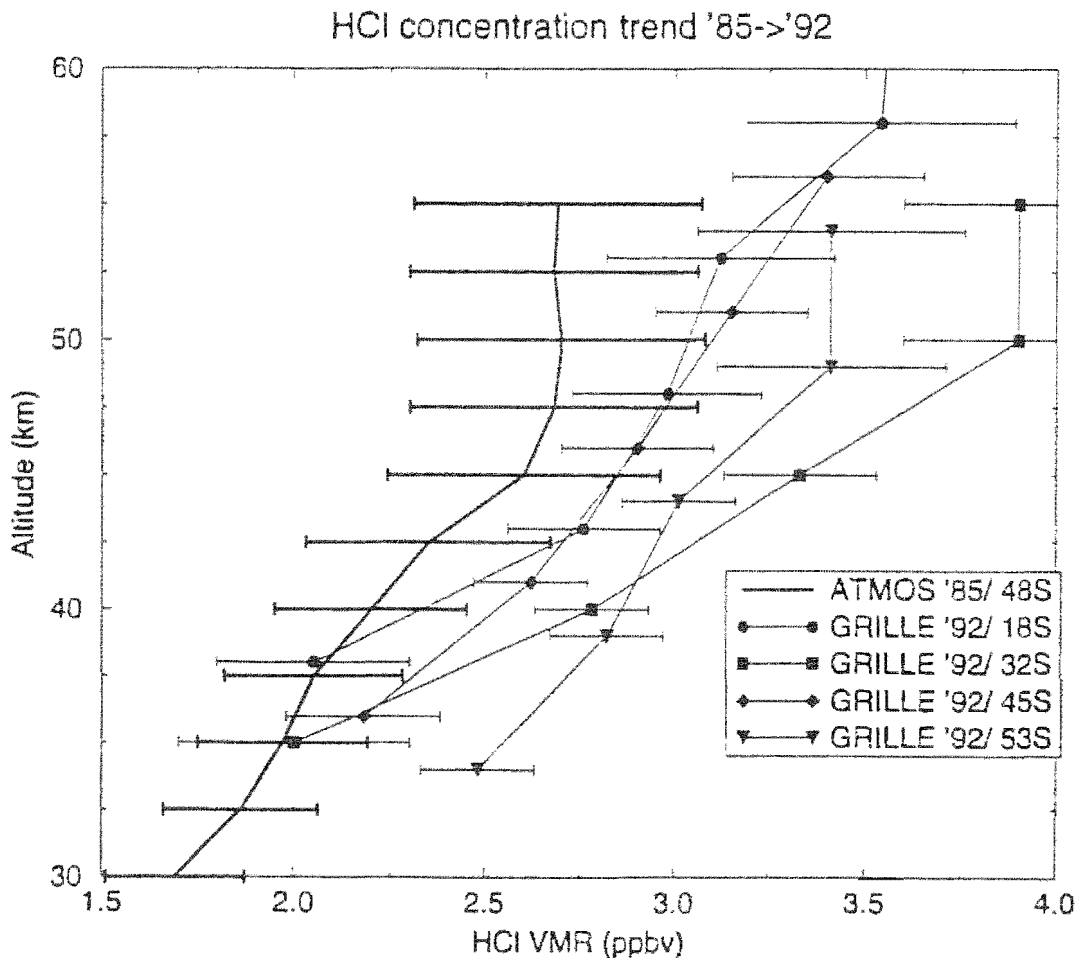


Figure 4. The ensemble of vertical profiles of HCl determined by the Grille experiment during the ATLAS1 mission, in comparison with a profile observed by ATMOS in May 1985 at 43°S.

The ORA (Occultation Radiometer), which has been developed for the EURECA (EUropean REtrievable CArrier) and which is described in more detail elsewhere (29,30,31), contains two major parts. The infrared unit, designed to measure water vapour and carbon dioxide (which was used for total density determinations) was delivered by the Oxford team (32).

The UV-visible unit, delivered by BISA, was designed to measure ozone, NO_2 , water vapour and aerosols, through absorption measurements in discrete wavelengths in the region of the solar spectrum from 250 to 1020 nm. It consists of 8 modules of similar design, each containing: a quartz window, an interference filter to isolate the appropriate wavelength domain, a simple optics to limit the field of view to $\pm 2^\circ$ and a detector (either a Silicon photodiode or a Gallium-Phosphide diode, depending on the wavelength). The wavelength of the different UV-visible channels together with the major light absorbers is given in Table 1.

can be converted into curves of signal versus grazing height. These signals, which result from an integration over the optical path across the atmosphere and another integration over the apparent solar disc are highly non linear functions of the local extinction profiles.

To retrieve total absorption profiles from these signals at the used wavelengths, a new method referred to as NOPE (Natural Orthogonal Profile Expansion) has been developed in BISA (33).

For the time being special attention has been given to the analysis of the extinction profiles at 1013 nm, which are mainly caused by aerosols. The present data set clearly shows important differences between the retrieved total extinctions and the ones for standard atmosphere conditions, due to the presence of volcanic aerosols injected into the stratosphere by the Pinatubo eruption. The aerosol loading resulting from the Mt. Pinatubo eruption is clearly recognized in Figure 5.

Table 1: Wavelength of the different UV-vis channels and major light absorbers

λ (nm)	259	340	385	435	442	600	943	1013
Predominant constituents	O_3 neutrals	neutrals aerosol	aerosol NO_2	aerosol NO_2	aerosol NO_2	O_3 aerosol	aerosol H_2O	aerosol

BISA was also responsible for the mechanical structure, electronics hard- and software, qualification of the instrument and management with ESA.

The ORA instrument, was flown on the EURECA mission (31 July 1992-1 July 1993) and performed its measurements through the occultation technique or limb tomography method, which allows to derive an absolute quantity, namely the slant path optical thickness from a relative transmission measurement.

From the EURECA carrier, which had an orbit of 508 km altitude and 28° inclination, and which was a sun pointing satellite, measurements of the attenuation of solar radiation through the atmosphere over a period of about 9 months were obtained.

The data of the infrared unit being analyzed by the Oxford group, we will limit ourselves here to the results obtained with the UV-visible unit.

During 9 months (from August 1992 until May 1993) of continuous operations more than 6000 sunsets and sunrises were recorded in the wavelength channels shown in Table 1.

The raw data as obtained from the instrument are curves representing the light intensity as a function of time, which

Before analyzing global fields of total absorptions due to aerosols as obtained with our data between about 40°N and 40°S a validation of the data set should be performed. This validation, which consists in comparing the ORA results with the geo-synchronous results of SAGE II (Stratospheric Aerosol and Gas Experiment) is now in process and shows a good agreement between the data of both satellite experiments and confirms the promising nature of the huge data set obtained by the ORA instrument.

Laboratory measurements

Halocarbon radiative forcing

The "Laboratoire de Chimie Physique Moléculaire" from the ULB made a very important contribution, with the collaboration of BISA, to the knowledge of IR absorption cross sections of man-made halocarbons, with an original and comprehensive study of a variety of so-called alternative halocarbons to be used mainly in replacement of the current CFCs which will be phased-out in 1996, according to the Montreal protocol and its amendments. The IR cross section measurements were performed using a Fourier transform IR spectrometer (FTIR), with a resolution of 0.03 cm^{-1} between 600 and 1500 cm^{-1} and

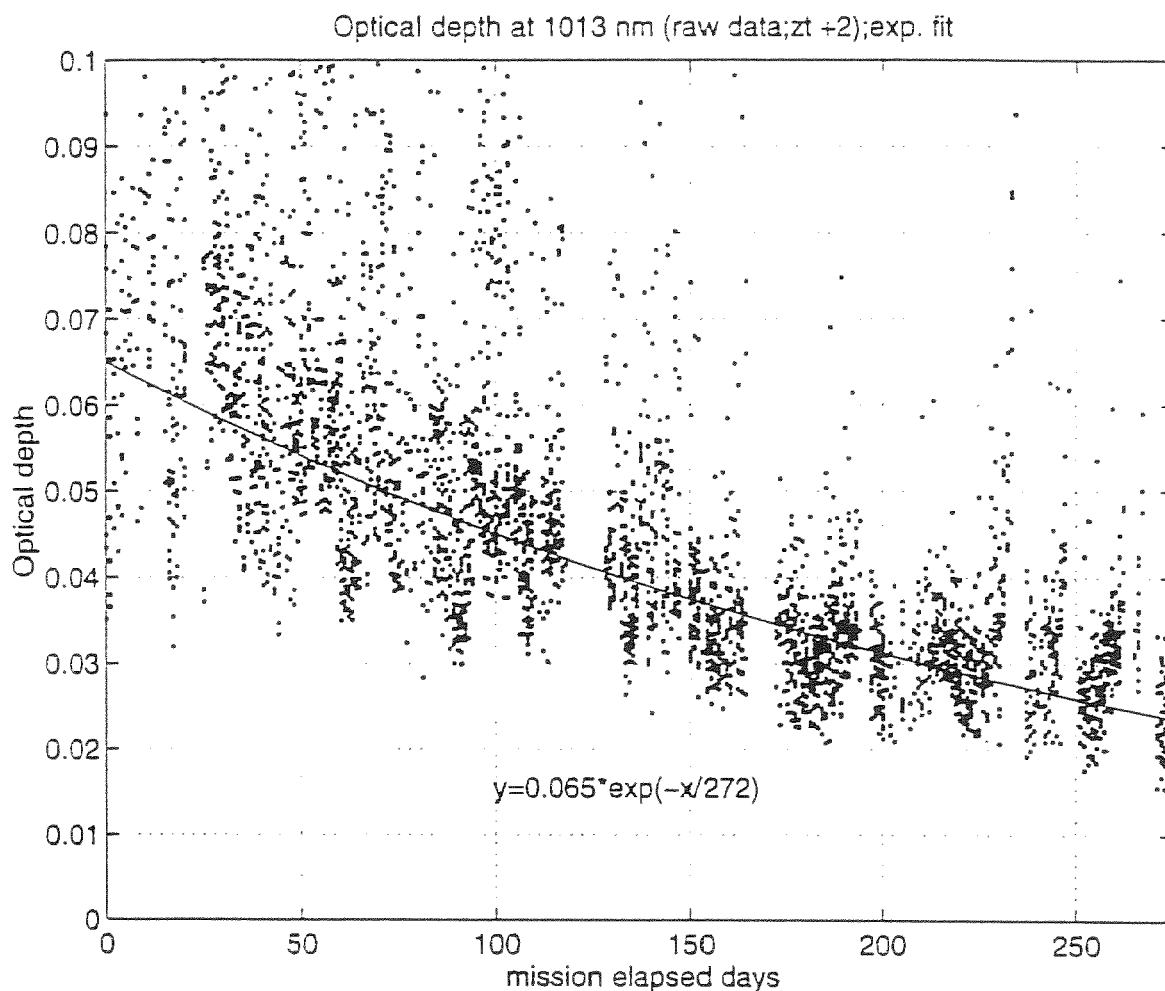


Figure 5 : Optical depth measured by ORA at 1013 nm from 2 km above the tropopause to space. The aerosol loading of Mt Pinatou is clearly relaxing with a time constant of about 270 days.

at three temperatures, namely 287, 270 and 253K. Integrated cross sections have been introduced into a two-dimensional radiative-chemical-dynamic model from NCAR (USA) in order to calculate the Global Warming Potentials (GWPs) of each gas. These calculations show that for three compounds (HCFC22, HCFC142b, HFC125) the GWPs (relative to CFC11) are higher than unity for a 5- to 10- year period. Moreover, these compounds maintain a relatively strong GWP for a very long time. Therefore, taking into account the fact that for some industrial applications larger quantities of CFC alternatives are sometimes needed to replace the current CFCs in order to obtain an equivalent efficiency, their contribution to the GWP may remain important. These results will help in the definition of future regulation, considering the current estimate of radiative forcing by halocarbons. They were included in the last WMO-UNEP Assessment of Ozone Depletion, 1994 published in 1995 (chapters 8 and 13 of reference 5).

Ion-molecule reaction measurements

In order to study some of the ion-molecule reactions which are used in balloon borne active chemical ionizations instrument MACSIMS, a flow tube of the classical design (34) coupled to a quadrupole mass spectrometer was built in BISA. With this instrument the reactions of HNO_3 with C_n^+ and I_n^+ ($n = 2,3$) have been studied at room temperature (35).

The reaction rates for $C_n^+ + HNO_3$ for $n=2$ and 3 have been determined relative to the known reaction rate for $CF^+ + HNO_3$. It was found that nitric acid reacts fast with C_3^+ , resulting mainly in the product ion $NC_3^+ \cdot HCl$. The product ions of the slower two body reaction of C_2^+ could not be determined unambiguously, but most probably NC_2^+ as well as $NC_2^+ \cdot HCl$ are formed. For the study of

$\bar{r}_n + \text{HNO}_3$, the known reaction $\text{CO}_3^- + \text{HNO}_3$ was used as a reference. No reaction has been observed for HNO_3 with \bar{r}_n -ions ($n = 2, 3$).

In addition rate constants or upper limits for rate constants were determined for the reactions of nitric acid with CO_2 , O_2 , HNO_3 , O_2 , HNO_3 and NO_2 , HCl .

The reaction rates obtained in these laboratory studies were used to derive the nitric acid concentration in the stratosphere with the previously mentioned MACSIMS instrument (11).

UV irradiance monitoring at the Earth's surface

An UV irradiance monitoring station is fully operational in Brussels, at BISA since the end of March 1993. This automatic station consists of two double monochromators based on the commercially available Jobin-Yvon model H10D, significantly improved to meet the requirements necessary for such a difficult measurement. It provides spectral measurements of the total solar irradiance (direct and diffuse components) in absolute radiometric units, with a field of view of 2π steradians, and the diffuse irradiance of the zenith sky with a field of view of 10° . The wavelength range covered by these spectrometers is starting well below the atmospheric ozone cut-off around 290-300nm and expands to the visible range up to 680nm. Spectra are measured every 15 minutes, for solar zenith angle smaller than 100° . These instruments have been fully characterized and are periodically calibrated with absolute transfer standards in the BISA laboratory and their stability is frequently checked by means of a Transportable Lamp System (TLS) specially developed at BISA for quality control of UV monitoring instruments deployed in Europe.

The station is completed by three broad-band radiometers : an UV-B meter (280-315 nm), an UV-A meter (315-400 nm) and a total pyrometer (300 nm - 3.5 μm), providing integrated irradiance measurements.

A 10-channel filter radiometer has recently been installed to measure the direct solar irradiance between 300 nm and 1 μm and to determine the ozone column and atmospheric turbidity. Direct measurements of solar spectral irradiance are planned in a near future.

The uncertainties of the measurements performed in Brussels are less than 5%. The current analysis of the data has clearly demonstrated the anti-correlation between the ozone total amount and the UV-B (280-315nm) radiation dose. Higher values have been measured in average in Brussels when significant ozone decreases have been observed. Further work is needed to make a

more detailed assessment on the effect of ozone total amount reduction on UV doses.

Modeling

Tropospheric modeling

Tropospheric chemistry modeling is a relatively recent activity at BISA, since it started in 1988, in close collaboration with scientists of the National Center for Atmospheric Research (NCAR, United-States). The goal of this research is to provide and use state-of-the-art modeling tools that can help us to understand the very intricate relationship between chemistry, climate, and human activities. The emphasis is on global scale modeling, since localized perturbations can affect even the most remote parts of the atmosphere, owing to the wind transport of pollutants. The central component of tropospheric chemistry modeling at BISA is a three-dimensional chemical transport model, named IMAGES (Intermediate Model for the Annual and Global Evolution of Species) (36,37).

The role of man is demonstrated by its important contributions to the emissions of trace gases : e.g., between 50 and 80% of the sources of atmospheric pollutants such as the nitrogen oxides, sulfur dioxide, carbon monoxide and methane are due to or at least controlled by human activities, namely : fossil fuel and wood burning, industrial activities, waste disposal, agricultural activities, deforestation, etc. A detailed inventory of anthropogenic and biogenic emissions has been developed at the institute (38). It is currently used by many modeling groups in Europe and in the United States.

Once emitted, these pollutants undergo complex transformation and transport processes. Typical lifetimes range between hours and years. When a species lifetime is long enough, it can be transported over very long distances and reach almost any part of the troposphere. The representation of the transport of trace gases is one of the key parts of any atmospheric model. The atmosphere is divided by the model into many boxes. Their typical size is 500 km in the horizontal and 1 km in the vertical. We use the analyzed winds from the European Centre for Medium-Range Weather Forecast (ECMWF) to drive the long-range transport of trace gases. As the wind values are monthly averages, the effect of wind variability at time scales smaller than a month must be represented as a diffusion (mixing) process. The diffusion coefficients are calculated from the ECMWF wind variances. Other important transport components that are not taken into account when using large-scale, monthly averaged winds are the rapid turbulent mixing in the atmospheric layer lying just above the surface and the rapid vertical transport associated with cumulus clouds.

These components are treated separately in the IMAGES model.

In order to test the model performance with respect to transport, we simulated the distribution of simple radioactive nuclei (Rn-222 and Kr-85), which have well known emissions and radioactive lifetime, and are measured in many parts of the world. The agreement of model results with the observations is very good.

Fortunately for us, pollutants such as nitrogen and sulfur oxides, carbon monoxide, etc. (which are toxic at high levels) do not accumulate indefinitely in the atmosphere. They are removed by photochemical reactions initiated by the action of sunlight. Solar radiation has indeed the ability to break a large number of molecules, especially in the UV spectrum. Photodissociation gives rise to a production of the so-called radicals (very fast-reacting molecules) which can then attack other molecules. The most important radical in tropospheric chemistry is the hydroxyl radical (OH). Its typical concentration is very low (of the order of 10^5 molecules cm^{-3}), but, thanks to its high and versatile reactivity, OH is responsible for the chemical degradation of a large number of pollutants. The OH chemistry is very complex and its calculations in models requires the inclusion of tens of species and hundreds of reactions. OH is basically produced as a consequence of ozone photolysis in the presence of water vapour. IMAGES takes into account most photochemical processes that are relevant to OH and ozone chemistry.

The oxidation of carbon monoxide and hydrocarbons by OH is the starting point of a complex mechanism which can either produce ozone (at sufficiently high nitrogen oxide levels) or destroy ozone. Human activities tend to increase the potential of the atmosphere to produce ozone. This species is now considered as a key pollutant, because of its toxicity (demonstrated during the well-known "smog episodes" over industrialized areas) and because ozone is radiatively active. It also contributes to the so-called "greenhouse effect", i.e. the warming of the Earth due to the trapping of terrestrial radiation by infrared absorbing molecules. Methane is another example of chemistry-controlled greenhouse gases: its lifetime of about 10 years is controlled by the abundance of the hydroxyl radical. This means that any perturbation of the OH source/sink balance is susceptible to modify the abundance of atmospheric methane.

The degradation of pollutants by reaction with radicals and photodissociation ultimately produce species that can be removed to the Earth's surface, either by wet deposition (i.e., absorption in cloud or rain droplets followed by precipitation) or dry deposition (direct sticking of the gas to the surface). This process explains, for example, the increased acidity of precipitation at our latitudes, as rain is the major process responsible for the removal of sulfuric and nitric acid. Nitrogen deposition

has also beneficial effect to the biosphere, because it is an important nutrient for plants.

The IMAGES model is now operational and is being used for many different kinds of studies. The model results are compared with available observations in order to check the validity of its assumptions and parameterizations. This allows the modelers to find new directions for future research. Heterogeneous processes (i.e., gas-liquid or gas to particle conversion and reaction in the condensed phase), cloud transport, biogenic emissions fluxes are a few among many processes which will require more attention in the future.

The model is also one of the best tools available in order to estimate the impact of human activities or climate change on atmospheric composition. Ecosystem modeling for the present-day climate and for conditions of the Last Glacial Maximum allowed us to estimate the changes in ecosystem distribution and biogenic emissions that are associated to large climatic variations (39).

The impact of industrialization since the last century has been estimated with the model, and agrees with observations in the estimation of surface ozone increase over Western Europe (about a factor of three).

More recently, the model is also being used in the framework of an American assessment of the impact of subsonic aircrafts on the atmosphere. IMAGES has been chosen by NASA in order to determine the major scientific issues and uncertainties in the context of the aircraft problem. Although the effect of aircrafts is relatively small compared with the contributions of the other transportation vehicles, the flight frequencies increase more rapidly in time and could become a problem in the next century. Figure 6 shows an example of model output for this study: it represents the change (in %) in nitrogen oxides concentration at an isobaric level of 250 mb (about 10 km altitude). It appears that aircrafts are major sources of nitrogen oxides in the upper troposphere at our temperate latitudes. The ozone changes, however, peak at only about +5%. These estimates are, however, still preliminary, as they suffer from many important uncertainties. These uncertainties will be the subject of our future work.

Stratospheric modeling

The main objective of this modeling study was to resolve inconsistencies between theory and observations about the ozone depletion at global level and in the polar regions. Models of the composition of the stratosphere including only gas phase chemistry do not explain the trend in summer but underpredict it in winter. Heterogeneous effects are saturated with respect to aerosol surface (either sulfate or Polar Stratospheric Clouds) in the sense that a large increase in the latter is not accompanied by a proportional effect on the chemistry.

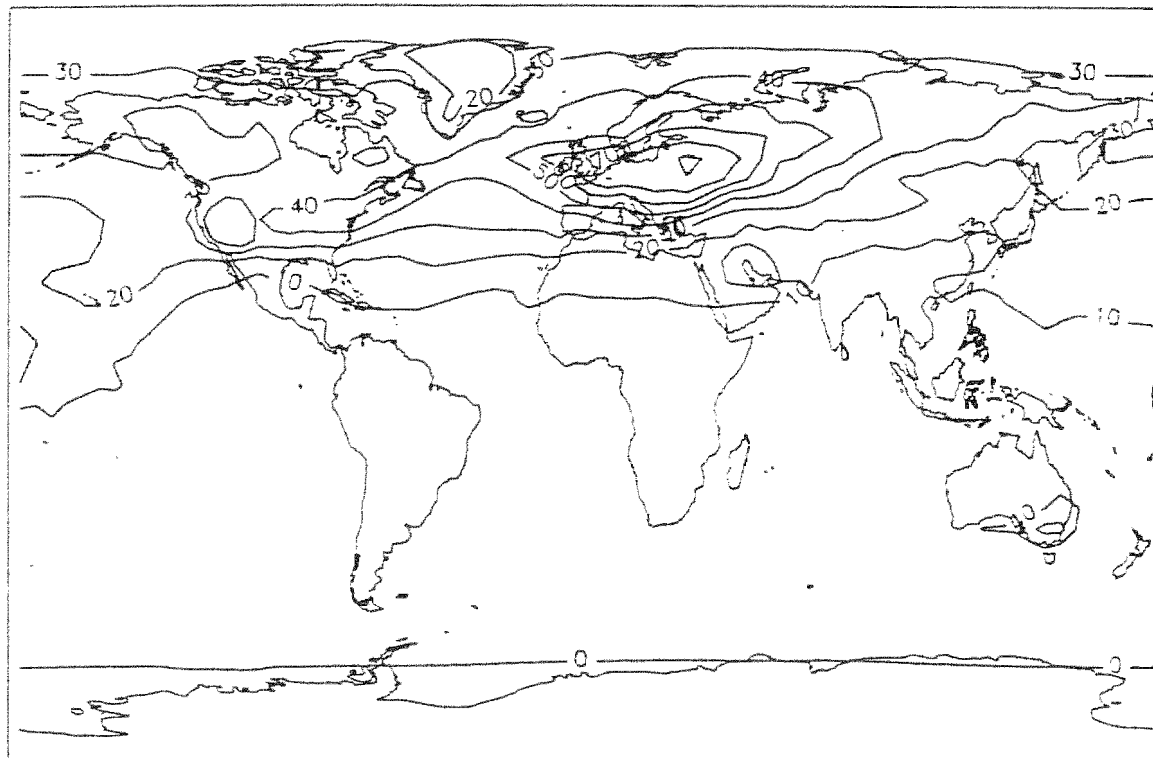
NO_x Change (%) due to aircraft (July, 250 mb)

Figure 6 : Calculated change in nitrogen oxides concentration (in percentage) at an isobaric level of 250 mb (about 10 km altitude) due to aircraft emissions.

This non-linearity also shows as an hysteresis effect when a decrease in the aerosol load is not followed by a return to conditions existing before the aerosol increase.

The mathematical tools developed for these studies consist of a two dimensional model of the composition of the stratosphere (altitude versus latitude), a three dimensional model of the lower stratosphere, and a model of the formation of Polar Stratospheric Clouds (40).

The 2-D model allows climatological studies to be performed. This model is based on a zonally and monthly averaged temperature climatology of the atmosphere, in an isentropic framework. The model includes all relevant chemical reactions. All relevant processes taking place on aerosols (either sulfate or Polar Stratospheric Clouds) are also taken into account. A detailed model of the formation of PSCs is included in the model, thus having a PSC climatology consistent with model climatology including effects such as denitrification and dehydration. This model with PSCs coupled represents very well the PSC climatology as observed by SAM-II (41). The

source gases can have surface concentrations to reflect specific conditions.

The model simulates well the Antarctic ozone hole. Very low ozone values are found from mid-September until mid-October in the lower stratosphere, from 15 to 25 km. The ozone column content has values as low as 150 Dobson units, which is in very good agreement with observations.

With the eruption of Mount Pinatubo, other heterogeneous processes have been studied and found to be important as well. These heterogeneous processes on sulfate aerosol particles have a less efficient ozone-destruction capacity, but due to volcanic eruptions their effect can be enhanced. The low ozone values in the Northern Hemisphere 1992 and 1993 winter can be attributed to heterogeneous processes on sulfate particles as a result from the 1991 Mt. Pinatubo volcanic eruption. Taking all these effects into account, our model studies simulate the observed global ozone decline for the last decade (42) very well.

Since the model is a 2-D climatological model, observed interannual differences, longitudinal effects and thus polar stratospheric clouds during Northern Hemisphere winters can not be simulated. In the Northern Hemisphere, there is evidence for a 5-8% decrease for the last decade in total ozone, with the largest depletion at the highest latitudes during winter and spring. There is abundant direct evidence for perturbed chemistry in the Arctic similar to that of Antarctica (43), but the cold temperatures, necessary for polar stratospheric cloud formation, are generally neither as widespread nor as long lasting as in the spring season in Antarctica. This greater meteorological variability has important consequences for the PSC formation. A 2-D model study is not adequate for simulating PSC and consequently a 2-D model study of Northern Hemisphere polar chemistry is very difficult to interpret. Therefore, we developed a three dimensional model of the lower stratosphere that takes into account a realistic meteorological variability. As of today this model only calculates aerosol evolution (either sulfate or Polar Stratospheric Clouds). It is a part of the ongoing modeling efforts to derive a N.H. PSC climatology from the 3-D model calculations as input into the 2-D model.

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Note

1 ONERA : Office National d'Etudes et de Recherches Aérospatiales, Paris; LPMA : Laboratoire de Physique Moléculaire et Applications, Univ. P. et M. Curie, Paris; BISA : Belgian Institute for Space Aeronomy.

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