Experimental Studies of Atmospheric Changes (ESAC)

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SUMMARY

The present report summarizes the original scientific results that have been obtained in 1997 in the frame of the ESAC project, Experimental Studies of Atmospheric Changes. The results contribute to a better understanding of the aeronomic processes that govern the Earth troposphere and stratosphere and of their evolution and variability, on short- and long-term timescales.

Among the scientific results are the evaluation of trends and budgets of the stratospheric chlorine (Cl_y), inorganic fluorine, and of the reactive nitrogen (NO_y) families at the Jungfraujoch (Switzerland): they play a primary role in the control of the stratospheric processes that interact with ozone. As to Cl_y, one observes the consequences of the implementation of the Montreal Protocol: the rate of increase of its tropospheric source gases that are under control (e.g., CFC-12) has dropped drastically, and one observes a slow-down of the increase of stratospheric Cl_y. On the contrary, the inorganic fluorine budget is increasing more rapidly in 1996 than in 1985, in line with the progressive replacement of the phased-out CFCs by HCFCs and FCs. Regarding NO_y, one observes a barely significative positive trend of order 0.3 %/year over the last 12 years, that is commensurate with the one of N_2O, which is the source of stratospheric NO_y; the trend is not uniform for all species within the family. The evolution of one of its main components, NO_2, has been studied in detail because of the pronounced impact of the Mount Pinatubo volcanic eruption of June 1991 and consequent enhanced aerosol load of the stratosphere. The combination of available datasets from infrared and UV-visible observations at the Jungfraujoch which started in 1985 shows a maximum reduction of the NO_2 column by 45% by early January 1992, and a return to normal by January/February 1995 only; the recovery appears to follow closely that of the aerosol load as observed at the closest lidar station at Garmisch-Partenkirchen.

The importance of BrO in the ozone catalytic destruction has been recognized lately. First results have been obtained at Harestua (Norway) as to its variability in and outside the polar vortex. An anti-correlation between the BrO and NO_2 column abundances has been confirmed.

The evolution of SF_6 has been studied, because of its potentially important contribution to the greenhouse effect if the exponential increase by 8.3 %/year observed presently at the Jungfraujoch goes on. That's the reason why SF6 has been added to the gases to be regulated by the "Kyoto Protocol On Climate Change" (1-10 Dec. 1997).

At Ukkel (Belgium) the behaviour of tropospheric ozone has been studied as part of the 'Regional Differences in Tropospheric Ozone' (RIFTOZ) project, and the evolution between 1969 and 1996 of the ozone vertical distribution up to about 30 km altitude has been revised, after correction for measurement artefacts. The ozone trend in the boundary layer is reduced, but still positive (0.5 to 1%/year). The free troposphere trend is smaller than 1%/year, i.e., below the value previously thought. The magnitude of the ozone negative trend in the middle stratosphere (above 25 km) is considerably reduced. On the contrary, below the ozone maximum at about 22 km, the trend has become more negative, up to about -0.5 %/year.

Tropospheric measurements of ozone and additional species like SO_2, NO_2, toluene, benzene, H_2CO and HONO have been performed at the ULB campus in Brussels; the interpretation is ongoing.

UV irradiance monitoring at Ukkel has been continued and the implementation of an operational forecasting of the internationally standardized UV Index has been prepared. This implied, among others, the establishment of a local UV irradiance climatology at noon above Ukkel, based on the data gathered since 1989.

The scientific results are based mainly on experimental ground-based data which are continuously controlled for quality. Validation efforts are still ongoing. Locally, intercomparisons of data series obtained by different instruments and techniques at the same site, (e.g., O_3 and NO_2 at the Jungfraujoch) have been conducted. They resulted in an homogenization of the SAOZ NO_2 time series. Regarding O_3, the appearance of a systematic offset between both time series led to the development of a climatology for the O_3 vertical distribution which improves the FTIR spectra analysis; its impact on the SAOZ data is being tested also, and final results are expected next year. Analogously, intercomparisons between two different ozone sonde types used at Ukkel, Brewer Mast from 1969 to 1997 and Z-ECC since 1997, have been conducted in order to determine and correct for systematic biases as a function of altitude, enabling thus homogenization of the whole time series and therefore the revision of the trends cited above. The O_3 and NO_2 data as part of the international networks with near-global coverage prove very useful for satellite validation purposes, in particular TOMS/Earth Probe and TOMS/ADEOS. The complementarity between the ground-based column data at the Jungfraujoch and ATMOS and HALOE/UARS vertical profile data has been exploited for mutual validation and for deriving additional information such as the tropospheric versus stratospheric part of the columns; this work is in progress. At the same time, upgrades of the ATMOS retrieval algorithms have been implemented and numerous applications of it have been verified.

In addition, new spectroscopic laboratory data that are of interest to the atmospheric remote sensing community have been obtained. They concern O_2 and $(O_2)_2$ absorptions in the infrared and UV-visible, NO_2 absorption cross sections as a function of pressure and temperature, and line position and intensity measurements of various heavier molecules in the infrared.

1 INTRODUCTION: OBJECTIVES & METHODOLOGY

The global objective of ESAC, Experimental Studies of Atmospheric Changes, is to contribute to a better understanding of the photo-chemical and physical processes that govern the Earth troposphere and stratosphere and of their evolution and variability, on the short- to long-term timescale. Four particular research themes are: the ozone variability and changes at mid-latitude and at the polar boundary in Europe and the underlying mechanisms, the chlorine and NO_y budgets and the UV-oxidation capacity of the lower atmosphere.

ESAC addresses these questions mainly through the production and interpretation of experimental ground-based data, obtained from long-term monitoring or dedicated campaign activities. Space borne data, ancillary data (e.g., meteorological) and atmospheric modelling results support the ground-based observations in the geophysical studies. Laboratory experiments provide missing or unsatisfactory spectroscopic data for increasing the accuracy and precision of the geophysical parameters retrieved from the remote sensing data.

Target molecules are HCl, $ClONO_2$, HF, COF_2, NO, NO_2, HNO_3, O_3, N_2O, CH_4, CO, HCN, OCS, C_2H_2, C_2H_6, CO_2, N_2, SF_6, CFC-12, HCFC-22,.... The first 8 among them are primarily controlling the state of the stratosphere and the photolytic ozone destruction processes via the Cl_x and NO_x catalytic cycles and are to be monitored as routinely as possible. The CFCs and HCFCs are sources for Cl_x, while N_2O (nitrous oxide) is the main source of NO_y. UV irradiance data are fundamental in any study regarding the atmosphere's oxidation capacity.

The observatories involved are: Harestua, at the polar boundary (Norway, 60.1°N, 10.4°E), and Ukkel (Belgium, 50.5°N, 4.5°E) and the International Station of the Jungfraujoch (ISSJ, Swiss Alps, 46.5°N, 8.0°E, 3580m alt., resp.) at mid-latitude; additional sites may be involved for particular campaign activities.

ESAC uses the following instrumentation: high-resolution Fourier-transform spectrometry in the UV-visible and infrared, for direct absorption measurements in the field or in the laboratory, photodiode array spectrometers using the technique of Differential Optical Absorption Spectroscopy (DOAS) for zenith-sky observations in the UV-visible, Dobson and Brewer spectrophotometers, ozone sondes, and UV irradiance spectroradiometers. All of these instruments/techniques have been involved in various types of validation activities, but related updates and efforts to improve are always continuing.

The ESAC project builds on the experience and data that have been acquired in the precedent project SMAC (Spectroscopic Studies of Atmospheric Changes), and in the frame of international programmes, such as NDSC (Network for the Detection of Stratospheric Change), the European ground-based networks (ESMOS, SCUVS,...) and through satellite validation efforts that are still going on, partly within the frame of ESAC.

The long-term monitoring activities at Ukkel, the Jungfraujoch and Harestua represent a continuous effort encompassing observations, instrument maintenance, regular data analysis and submission of validated time series to the NDSC and European archiving centres. The next sections summarize the original (preliminary) scientific results that have been obtained during the first year of the ESAC project (1997).

2 EVALUATION OF LONG-TERM MONITORING DATA

2.1 BUDGET AND TREND STUDIES

2.1.1 Ozone (O_3)

2.1.1.1 Ozone total column data

Validation of the Fourier transform infrared (FTIR) and Système d'Analyse par Observations Zénithales (SAOZ) ozone data

Presently, most column retrieval algorithms for the analysis of Fourier transform infrared spectrometer data use a non-linear least-squares fit procedure of the experimental and the corresponding synthetic spectra (Park J. H., 1983). Two critical parameters herein are (i) the instrument line shape function and its actual parameters at the time of observation, and (ii), the a priori vertical profiles of the target and of the interfering gases. A standard a priori vertical profile is generally adopted for all measurement conditions, and the instrument function is supposed to be known accurately. Often an extra ad-hoc parameter, the so-called effective apodisation (EAP), is added among the parameters to be fitted for optimisation of the resulting column abundance. The present investigation aims at the development and evaluation of a geophysical model for the vertical ozone distribution to replace the standard profile in the data analysis, with the same purpose of optimizing the retrieved ozone column amount without the need for the effective apodisation if possible. The model is based on local meteorological/dynamical parameters, namely the local tropopause height, and on a climatology for its seasonal variation. The development has been conducted for interpretation of the FTIR measurements at Jungfraujoch, but it should be valid for all midlatitude observations.

The Royal Meteorological Institute at Ukkel has one of the longest homogeneous time series of ozone sonde data in Europe. Ten years of ozone vertical profile data, from 1985 to 1995, have been sorted in 9 classes corresponding to tropopause altitudes from (7.0 ± 0.5) km to (15.0 ± 0.5) km, from which an average profile per class has been derived. Above 25 km altitude, these profiles are extended by the seasonally dependent CIRA '86 model (Keating, G. et al., 1986) for the 40° to 50°N latitude band, interpolated to the ISSJ latitude of 46.5°N. As such, the resulting ozone vertical profile model consists of a set of 108 (= 9 x 12) profiles, covering all possible tropopause heights and seasons. It will be called hereafter the O_3-versus-tropopause seasonal profile model. Its agreement with sonde and microwave observations at Payerne and Bern, respectively, which are both within 100 km of ISSJ, has been verified.

For evaluation of the effectiveness of the model, the ISSJ Bruker IR O_3 spectra for 1995 have been analysed with the SFIT algorithm (Rinsland et al., 1984), first using the standard O_3 profile, and then using the O_3-versus-tropopause seasonal profile model. All other parameters have been kept identical in both runs. The resulting O_3 column data have been compared with those obtained at ISSJ by SAOZ. The role of the EAP has been checked at the same time. Hereinafter the first cited run will be referred to as the standard-O_3-model run, the second one as the improved-O_3-model run.

The standard-O_3-model run results in an offset between FTIR and SAOZ O_3 column data of the order of 2%, the FTIR columns being smaller than the SAOZ ones. The magnitude of the negative offset (lower FTIR columns) increases systematically with increasing ozone total column amounts. Both the offset and the slope of the offset's dependence on total ozone amount are reduced by about 25% if one uses the improved-O_3-model. It turns out, however, that the adjustment of the EAP in the fit procedure leads to better results, even in the improved-O_3-model run. Thus one concludes that the O_3-versus-tropopause seasonal profile model indeed addresses most of the atmospheric changes that are otherwise dissimulated by an adjustment of the EAP, but that an additional adjustment of the EAP in the fit procedure is still beneficial to improve the accuracy of the retrieved ozone column amounts.

A standard analysis of the FTIR ozone spectra over the complete period 1990 to1996 that overlaps the SAOZ time series reveals a seasonal variation in the relative difference between both data sets. A peak-to-peak amplitude of order 7.4% around a mean offset of minus 3.8% for the FTIR data with respect to the SAOZ data is observed. Inspection of the results of the improved-O_3-model-run for the single year 1995 shows that the amplitude of this seasonal disagreement is slightly reduced, by about 7%. This is a preliminary result which has to be consolidated after analysis of the whole time series.

Use of the O_3-versus-tropopause seasonal profile model will impact the quantitative evaluation of the evolution of the ozone amount above Jungfraujoch during the last decade, in particular its seasonal variation. This topic will be addressed again when the final validation of the model is completed.

The benefits of the implementation of the same O_3 climatology in the calculation of the air mass factors which are important in the SAOZ data analysis are investigated in parallel.

2.1.1.2 Ozone tropospheric column data

The Riftoz (Regional Differences in Tropospheric Ozone) project aims at explaining the differences observed in the tropospheric ozone behavior in different European regions. As part in this project, the RMI had to carry out ozone soundings each day during June, July and August 1997 by means of ECC ozonesondes. This resulted in a very valuable time series of ozone soundings which will be used in creating a coherent and complete 3-D tropospheric ozone data set over Europe for the summer of 1997. Additional information such as general meteorological situation, vertical air mass stability and horizontal extent to which the ozone soundings can be extrapolated, has also been provided.

In the time series of the integrated ozone amount in the troposphere a very high value was noticeable on the 1st of June. This is due to a difference between the thermal tropopause (WMO definition) and the ozone tropopause. During the periods from 12 to 13 July and from 6 to 13 August there is a clear signature of photochemical ozone production in the boundary layer (sunny weather, high temperatures, and high integrated ozone amounts in the boundary layer). It is interesting to see that during the latter period the integrated ozone amount in the free troposphere also shows a cumulative effect, which points to an overflow of ozone from the boundary layer to the free troposphere during episodes of high ozone. On August 14 the ozone amount in the boundary layer and in the free troposphere dropped by about 60 and 40 percent respectively, due to a change of air mass from a continental to a marine one.

Several cases of stratospheric intrusions were found from the soundings, which could sometimes be followed over several days. A very pronounced intrusion was seen from 14 to 16 July, with signatures of stratospheric air to levels as low as the 700 hPa pressure level.

2.1.1.3 Ozone vertical profile data

Ozone sonde intercomparison

The vertical distribution of ozone has been measured at RMI since 1969 with the Brewer-Mast (BM) ozonesondes. For various reasons it was decided to change to the Z-ECC type of ozonesonde in 1997. To assure the homogeneity of the long-term data series it was necessary to have good information on possible systematic differences between data obtained with both types of ozone sensors. Results of international intercomparisons found in the literature were not conclusive, and not applicable to our station. Therefore a campaign of double soundings, with both types of sonde on the same balloon was started in October 1996. By the end of 1997, 23 successful pairs were available for intercomparison.

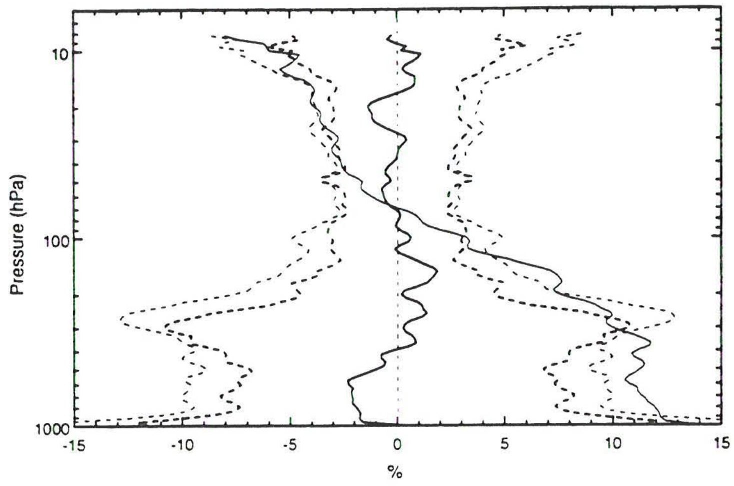

Fig. 1. Mean percentage differences between ozone profiles obtained from simultaneous measurements with Brewer-Mast and Z-ECC sondes with the standard (thin solid line) and the newly proposed (thick solid line) correction procedures in Ukkel. The thin and thick dashed lines give the standard deviation of the differences, with the standard and new correction procedures respectively.

Figure 1 shows that with the standard operational procedures there is a systematic, altitude dependent difference between both types of profiles. Near the ground the BM sondes measure on average up to 15% more ozone than the Z-ECC sondes. Around the 40 hPa level (which is near the mean level of the ozone maximum at 22 km) the agreement is excellent, but at higher levels the BM sondes underestimate the ozone amounts, ending at about -5 % at the highest level of the soundings. The differences are statistically significant in the whole troposphere and above the ozone maximum. An earlier intercomparison of the Brewer-Mast ozone profiles in Ukkel with ECC profiles measured in De Bilt (Nl) showed similar deviations. From those results, it is suspected that an underestimation of the decrease of the pump efficiency with decreasing pressure of the BM sondes causes these discrepancies. In addition to the double soundings the efficiency of the pumps of both types of sondes was tested in a vacuum chamber at different pressures and temperatures before launch. From the results of these extensive measurements, a new altitude dependent correction profile was proposed. When it is applied, the two types of ozonesondes agree within 3 % (see thick line in Figure 1), while the differences are statistically insignificant over nearly the whole altitude range (0-32 km). The standard deviation of the differences is also lower, suggesting that part of the instrumental noise has been removed.

Re-evaluation of trends in the ozone vertical distribution

The re-evaluated data set of ozone soundings at Ukkel from 1969 to 1996 was used for a sensitivity study of instrumental effects on calculated ozone trends. The results are shown in Figure 2. All the calculated trends are based on a least squares analysis of deseasonalized data.

With the standard algorithm and the usual corrections for calculation of ozone profiles from soundings with sondes of the Brewer type, the ozone trends in the middle troposphere amount to 1.2 to 1.4 %/yr. In the boundary layer the calculated trends are even larger than 2.5 %/yr (dashed line in Figure 2). In the middle stratosphere the magnitude of the negative trends shows a pronounced increase with altitude, to values of about -1.4% near mean burst level.

The SO_2 levels in the lower troposphere above the urban area of Brussels decreased rapidly in the 1970s and to a lesser extend in the 1980s. After applying a correction for the SO_2 interference on the ozone soundings at Ukkel, as described by *De Muer et al.* (1994), the calculated ozone trends in the boundary layer are reduced by about half of the value without SO_2 correction; in the lower free troposphere trends of about 1%/yr are found (see curve with solid triangles in Figure 2). Upper tropospheric and stratospheric trends are hardly affected by this additional correction.

Before re-evaluation of the Ukkel time series of ozone soundings, a jump was observed in 1989, which resulted in too high ozone values in the troposphere and too low

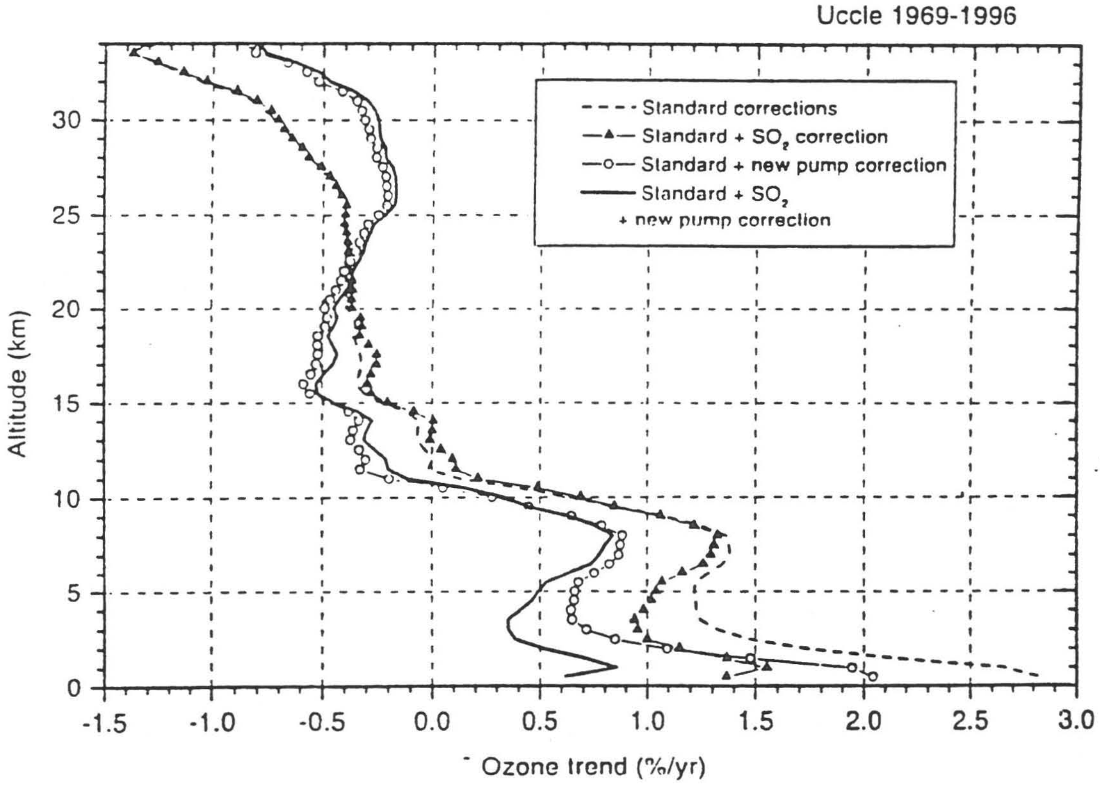

Fig. 2 Profiles of calculated ozone trends at Ukkel for the period 1969-1996. The different curves are obtained with different combinations of corrections applied to the sounding data.

values above the ozone maximum. After application of the pump efficiency profile which was measured in the lab (and which shows much higher pump corrections than adopted in the standard profile) this anomaly was largely removed. This new pump correction has also a pronounced effect on the calculated ozone trends, the magnitude of the calculated negative trends in the middle stratosphere being considerably reduced. As a consequence of the normalization of the ozone profiles, the calculated ozone trends below the ozone maximum are also affected: the ozone trend profile below the ozone maximum (which is at about 22 km) is lowered, resulting in more pronounced year-round negative trends up to about -0.5%/yr in the lower stratosphere. With all corrections applied, the positive trend in the troposphere is considerably reduced and varies between 0.35 and 0.85 %/yr (see solid line in Figure 2).

2.1.2 Nitrogen dioxide (NO_2) and reactive nitrogen (NO_y)

2.1.2.1 Stratospheric budgets and trends

The stratospheric budget of reactive nitrogen (NO_y), due mainly to NO, NO_2, NO_3, HNO_3, N_2O_5, HO_2NO_2, $ClONO_2$ and $BrONO_2$, is obtained by summing the individual columns of these compounds, with N_2O_5 being counted twice. As NO_3, N_2O_5, HO_2NO_2 and $BrONO_2$ cannot be measured from the ground, NO_y above ISSJ is defined here as: :

$$\{NO_y\} = \{NO\} + \{NO_2\} + \{HNO_3\} + \{ClONO_2\} \qquad (1)$$

where the braces indicate vertical column abundances. The species omitted represent less than 5% of the total NO_y under typical conditions expected at mid-latitudes. Recent trend evaluations derived over the 1985 to 1997.3 period for the individual species considered in equation (1) are statistically insignificant for NO and HNO_3, but significant and positive for NO_2 (+0.7 ± 0.3) %/yr and $ClONO_2$ (+3.8 ± 0.8) %/yr. Their combination according to (1) leads to an NO_y growth rate equal to (+0.3 ± 0.3) %/yr, which is barely indicative of a slight increase which prevailed since the mid-1980s, but it is commensurate with the trend of (0.35 ± 0.04) %/yr for the N_2O source gas of NO_y over the same period.

Remark: with respect to the growth rates of N_2O volume mixing ratios at the ground derived globally by the in situ networks mentioned above (typically 0.25 %/yr), the Jungfraujoch increase in the N_2O vertical column has consistently been higher. We believe that the difference is indicative of the heightening of the tropopause by some 150 m over the period 1985 to the present. This can result from some warming of the troposphere or/and cooling of the stratosphere and is in line with similar findings in the long-term ozone and temperature data bases gathered at Hohenpeissenberg, Germany (Claude and Steinbrecht, 1996).

2.1.2.2 Evolution of the NO_2 amount above Jungfraujoch since 1985.

As a consequence of the eruption of Mount Pinatubo in June 1991 in the Philippines (15°N, 120°E) and the corresponding globally enhanced aerosol load in the stratosphere, a reduction of the NO_2 amount was observed at ISSJ. Part of this was attributed to enhanced conversion of N_2O_5 to HNO_3 due to heterogeneous processing on the aerosol particles surfaces (e.g., Hofmann and Solomon, 1989; Brasseur and Granier, 1992; Rinsland et al., 1994). A precise quantification of the reduction requires the establishment of a reliable pre-Pinatubo NO_2 climatology. To this end the FTIR time series of NO_2 columns at the Jungfraujoch observatory, which starts as early as 1985, has been combined with the SAOZ series which only starts in mid-1990, but which has the advantage of providing morning and evening twilight data each day. Before combining SAOZ and FTIR time series, a mutual validation has been performed which leads to the following two conclusions. First, the SAOZ time series must be homogenized: a correction factor equal to 1.17 must be applied to the initial operational period (mid-1990 to mid-1991). The origin of this correction has been identified recently (see section 2.2). Secondly, the FTIR data need to be offset by -5% to be in agreement with the SAOZ data. However, because of the NO_2 diurnal variation and the different sampling times of the FTIR and SAOZ instruments, a direct intercomparison and/or combination with the SAOZ data is impossible. Therefore, a photochemical model (Nevison et al., 1996) must be used for evaluating the morning and evening twilight values corresponding to FTIR measurements which are spread throughout the day. The model uses actual temperature data, locally measured ozone column values and a mean monthly NO_2 vertical profiles at midlatitude derived from SAGE II observations. The resulting combined time series of the NO_2 abundance at Jungfraujoch and its evolution during the last decade, in terms of monthly mean percentage differences relative to the pre-Mount Pinatubo climatology established over the 1988 to mid-1991 period, are displayed in Figure 3 and discussed next.

The reduction of the NO_2 amount peaks at the turnover between 1991 and 1992 and amounts to 45% with respect to the pre-Mount Pinatubo 1988 to mid-1991 mean level; no distinct behaviour between morning and evening columns is observed. The recovery can be modeled reasonably well by a sum of two exponentials, an initial fast one with an *e*-folding

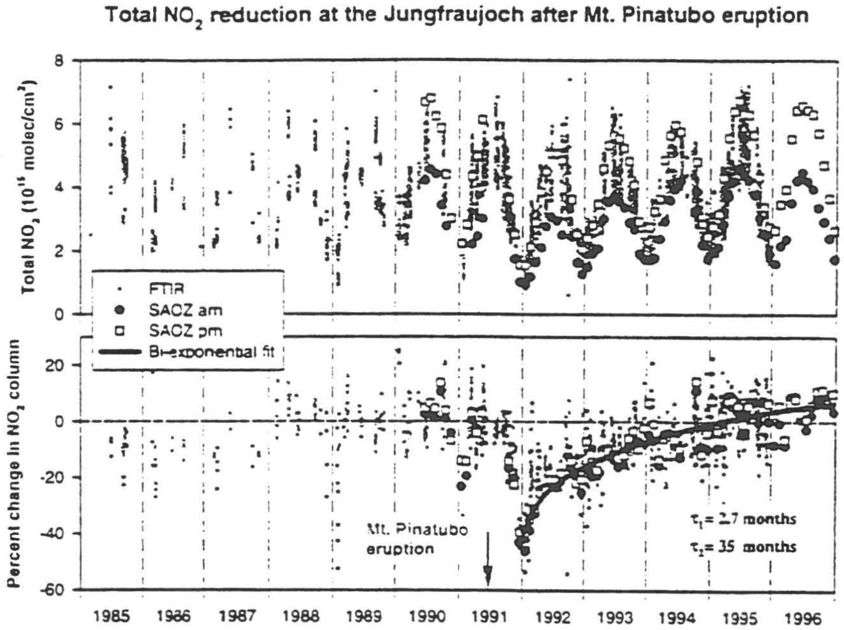

Fig. 3. Top: Superposition of FTIR (small open circles) and SAOZ (solid circles and open squares) time series of NO_2 columns at the Jungfraujoch. Bottom: Percentage monthly mean NO_2 vertical column reductions observed at the Jungfraujoch by the SAOZ and FTIR instruments. Reductions are evaluated relative to the 1988 to mid-1991 monthly mean reference values derived from the FTIR observations. SAOZ data are monthly means for morning and evening vertical column amounts; FTIR data are daily values.

time of 2.7 months, followed by a slower one with an *e*-folding time of 35 months (solid line in Figure 3). If we limit the fit to the 24-month period following the maximum impact for comparison with the decay of the aerosol load measured above the closest lidar station of Garmisch-Partenkirchen (Jäger *et al.,* 1995), we find approximately the same 10-month *e*-folding time, as represented by the dashed line in Figure 3. By mid-1994, both the aerosol load and the NO_2 reduction had decreased to about 10% of their maximum value. The NO_2 amount came to complete recovery only by January/February 1995. The NO_2 abundance observed at the end of 1996 appears to be higher by about 7% than the reference level, which might be related to the fact that the actual aerosol load came down approximately to the 1978/1979 background level, at least below the 1988/1991 one (H. Jäger, private communication, 1997). Further observations in 1997 and 1998 are needed to confirm the latter NO_2 value and the long-lasting recovery time.

2.1.3 Inorganic Chlorine (Cl)

The combination of HCl and $ClONO_2$ column abundance measurements above ISSJ, combined with ClO background burdens evaluated by model calculations, leads to the conclusion that the inorganic Cl-atom rate of increase in the stratosphere has significantly slowed down during the last decade, from about $3x10^{14}$ atoms/cm^2/yr during the mid-1980s to $1x10^{14}$ atoms/cm^2/yr during 1996 (chlorinated compounds such as HOCl and COClF, not included here in the Cl-atom budget evaluation, account for at most 2% of the total loading; Zander et al., 1992). This results from the implementation of the Montreal Protocol and its Amendments since the late 1980s, calling for substantial and sustained reductions in the production and emission of chlorinated source gases (primarily the anthropogenic CFCs) which contribute to the erosion of the ozone layer. For example, the rate of change of the CFC-12 column abundance above ISSJ dropped from about 4.5 %/yr in 1985 to nearly 1 %/yr in 1996, while that of HCFC-22 maintained an average exponential increase of about 6 %/yr. The significant slowing of the former results from its phase-out by the Montreal Protocol, while the latter remains unregulated. The above rates of change of inorganic Cl and of CFC-12 have been found to agree very well with those derived by ground-based in situ networks such as NOAA-CMDL and GAGE/AGAGE (Montzka et al., 1996; Cunnold et al., 1997). The HCFC-22 rates of change determined above ISSJ have been compared to those derived over the NDSC sites of Lauder (New Zealand), Kitt Peak and Table Mountain (USA) and found to be in very good agreement (Sherlock et al., 1997).

2.1.4 Inorganic Fluorine (F)

The inorganic fluorine budget above ISSJ, which is defined as the sum of the HF column, plus twice that of COF_2, has increased at a quasi-exponential rate of 5.5 %/yr between 1983 and 1997; its increase was equal to $6.2x10^{13}$ atoms/cm^2/yr at time 1985.0, reaching $7.0x10^{13}$ atoms/cm^2/yr during 1996. These values indicate that, in opposition to the slowing of the Cl-atom loading, the F-atom deposition in the stratosphere has continued to increase over the past decade, which is qualitatively in line with the earlier increase of the main CFC-source gases, followed more recently with the progressive replacement of the phased-out CFCs by HCFCs and FCs. The total fluor loading above ISSJ increased by a factor 1.8 between April 1985 and November 1994, which are the dates of the extreme ATMOS missions (Gunson et al., 1996). From the latter, it was found that HF volume mixing ratios above 50 km altitude, which are surrogates of the mean F loading throughout the stratosphere (Zander et al., 1992), increased by nearly a factor 2.0 (from 0.76 ppbv in 1985 to 1.50 ppbv in 1994), thus in line with the inorganic F-atom increase above ISSJ. Notice that during the time period covered here, missing compounds in our inventory (e.g., COClF, CFC-113) account for less than 2 % of the F-budget. The F-atom budget derived at the Lauder site between April 1993 and January 1994 is in good agreement with the ISSJ values for that time.

2.1.5 Bromine Oxide (BrO)

Re-analysis of the UV-visible DOAS measurements performed at Harestua from 1994 to 1996 with an improved analysis code (improvements as to operational efficiency and accuracy of the fit results) confirm the existence of an anti-correlation between BrO and NO_2 column amounts, and show a modulation of the BrO amount with overpasses of the polar vortex (Van Roozendael et al., 1997). The latest upgrade of the UV-vis DOAS instrument at Harestua (improved optical alignment, enhanced signal-to-noise ratio) will provide more precise BrO data from 1998 onward, allowing further geophysical studies regarding BrO and its role in the ozone loss processes.

2.1.6 Sulphur Hexafluoride (SF_6)

Sulphur hexafluoride, SF_6, has been given much attention over recent years (Zander et al., 1991; Maiss et al., 1994), because it is a very long lived gas (many thousand years) with a per molecule-greenhouse effect among the highest of any atmospheric trace gas (Rinsland et al., 1990), and having accumulated in the Earth's atmosphere at a mean exponential growth rate of 8 to 9 %/yr since the mid-1970s. Because of its current low concentration, its contribution to the greenhouse effect remains negligible, but this may no longer be the case if the growth persists for many decades, at which time the achieved loading and the climatic impact will remain "forever", because of the long lifetime. This is the main reason why SF_6 was included by "The Kyoto Protocol On Climate Change" (1-10 Dec. 1997) in a new list of gases that need regulation, along with a number of long-lived perfluorinated compounds (such as CF_4 and C_2F_6), because they threat climate in the long term.

The vertical column abundance of SF_6 above ISSJ has more than doubled since its first monitoring in 1986, and its exponential rate of increase is currently equal to (8.3 ± 0.5) %/yr, which is in excellent agreement with in situ background measurements at various sites around the globe (Maiss et al., 1996). It should be emphasized that measurements of vertical column abundances are convenient for evaluating the total atmospheric content of a gas and its temporal evolution.

2.2 REVISION OF THE SAOZ O_3 AND NO_2 TIME SERIES.

It has been discovered that the SAOZ slit function, and therefore also its effective spectral resolution, depends on the ambient temperature, and that this dependence is wavelength dependent. This dependence has been quantified, and a method has been developed for determining the actual spectrum resolution by non-linear least-squares fitting of the measured zenith-sky spectra to an accurate high-resolution solar Fraunhofer reference. Implementation of this method in the SAOZ spectra analysis algorithm has led to an improved precision and accuracy of the NO_2 measurements, and to a lesser extent, of those of O_3.

Additional improvements resuult from the validation efforts, in particular regarding the air mass factor calculations (Sections 2.1.1.1 and 2.3). An even higher accuracy of the NO_2 time series is to be expected when the pressure- and temperature dependence of the NO_2 absorption cross-sections, determined in the laboratory (Section 5), will be taken into account in the spectra analysis.

Trend studies regarding ozone and NO_2 mentioned above which are based on DOAS data (at least partially) will be repeated after finalisation of these improvements.

2.3 SATELLITE VALIDATION: TOMS/EARTH PROBE AND TOMS/ADEOS

The UV/Visible SAOZ/DOAS spectrometers at the Jungfraujoch and at Harestua are part of a ground-based network of seventeen UV/Visible spectrometers and about twelve Dobson and Brewer spectrophotometers operating at selected NDSC sites. The network stretches from the Arctic to the Antarctic, covering all latitudes and longitudes. The whole set of ozone total column data obtained by this network between summer 1996 and April 1997 has proven very useful for investigating the solar zenith angle dependence, the dispersion, the time dependent drift, and the sensitivity of the TOMS/Earth Probe and TOMS/ADEOS space-borne sensors. At the same time, the validation effort has resulted in improvements of the analysis algorithms of the ground-based data, as mentioned in the previous section (2.2).

The combined data set of the SAOZ/UV-visible network together with 3-dimensional CTM (Chemistry-Transport Model) modelling by Meteo-France has enabled the determination of the winter-spring ozone loss in the Arctic in 1993/1994 and 1994/1995 (Goutail et al., 1997).

2.4 ATMOS RELATED STUDIES

The main task envisaged in this part of the research is to contribute to the production of an "ATMOS-Version 3" set of volume mixing ratio profiles which extend reliably to lower altitudes down into the free troposphere (which is not the case for the current Version 2). This effort is being performed jointly with colleagues from the NASA-Langley Research Center (LaRC), and the Jet Propulsion Laboratory (JPL), the latter remaining the cordinator of the ATMOS-related activities.

Two important actions have been initiated during the past year, towards the production of such a Version 3 data base:

a.- the implementation of a new algorithm which fits multiple gases simultaneously, and applies a statistical averaging on results derived from multiple microwindows attached to the same target gas;

b.- the choice of improved sets of microwindows, taking into account the implementation mentioned in point a.-, and allowing to retrieve, automatically, concentrations down to the lowest possible altitude. Because of the difficulty to find a sufficiently large number of good temperature-dependent and –independent CO_2 microwindows in the lowermost altitude region, we may opt for the use, in that region, of tropospheric temperature profiles provided by the NCEP (National Centers for Environmental Prediction, Washington, D.C.; formerly the National Meteorological Center). The reason for this is that too few CO_2 features will not allow to derive T profiles for each occultation that are more reliable than the NCEP ones.

Numerous applications incorporating the above features have been run in an automatic mode to test the performances of the approach. Volume mixing ratio profiles have been retrieved successfully for CH_4, N_2O, O_3 and HNO_3, down to 6 km, and for H_2O, C_2H_6, HOCl, $ClONO_2$, HNO_4, N_2O_5 and H_2O_2, down to 14 km. It was noted with satisfaction that the profiles retrieved with the new algorithm were in very good agreement with those archived as Version 2, over the altitude domain where they overlap.

A further task undertaken recently has dealt with the consistency evaluation among column abundances of various atmospheric gases measured above the Jungfraujoch and integrated volume mixing ratio profiles obtained with ATMOS in 1994 and with HALOE (Halogen Occultation Experiment) aboard UARS (Upper Atmospheric Research Satellite) from October 1991 to present. All ATMOS Version 2 stratospheric volume mixing ratio profiles are currently available. The HALOE "Version 18" data base which has just been released at LaRC, is being transferred progressively, and will be used to (i) intercompare it with the ATMOS Version 2 base above 20 km for consistency assessment, (ii) integrate its profiles over the 15 to 50 km altitude range for comparison with ISSJ columns, and (iii) derive information on tropospheric versus stratospheric contents from the HALOE-ISSJ column differences. The above investigation is in progress for HCl and HF; it can be noted here that the HALOE-Version 18 appears to have improved significantly the HCl content in the upper stratosphere, which previously was generally rated too low with respect to ATMOS and other investigations (Liu et al., 1997; Achard et al., 1997). The above type of intercomparison is planned for all molecules measured concurrently by ATMOS, HALOE, and at ISSJ, i.e., HCl, HF, O_3, NO, NO_2 and CH_4.

3 TROPOSPHERIC CAMPAIGN MEASUREMENTS

Measurements of the atmospheric composition were performed at the ULB site during August, September, October and November 1997. They involved the FTS instrument of the ULB and the grating spectrometers of the IASB. Using simultaneously two detectors, the FTS was able to cover the whole UV-visible region from 15000 to 42000 cm^{-1}, allowing the detection of SO_2, NO_2, O_3, toluene, benzene, H_2CO and HONO. Some experiments were also performed to detect NO_3 during the night. A large quantity of spectra were recorded during this campaign and the interpretation of the results is under way.

In preparation to the Jungfraujoch campaign to be held in May and June 1998, spectra were also recorded with the FTS in the IR region. A new software was developed to help with the identification and simulation of absorption structures found in the IR atmospheric spectra.

A more detailed analysis of these spectra is under way. The first tests of the new suntracker adapted to the BRUKER 120M FTS have been successfully performed.

4 UV RADIATION MEASUREMENTS

4.1 MONITORING

Monitoring of UV spectral radiation has continued at KMI-IRM and at BIRA-IASB on the local site at Ukkel. In the frame of the EC project SUVDAMA, the implemenatation of a relational data base that includes these and all other European spectral UV irradiance measurements and all their ancillary data, is ongoing.

4.2 FORECASTING OF EFFECTIVE UV IRRADIANCE AND UV INDEX

The spectrum of UV radiation at ground level is measured several times per day since 1989 at RMI with a Brewer spectrophotometer. Each spectrum was convoluted with the erythemal action spectrum of the CIE (Commission Internationale de l'éclairage). The resulting UV erythemally weighted irradiances can be converted to the international standardized UV Index, which is an indication for the sunburn risk. From the daily observations of UV spectra, a climatology of effective UV-irradiance at local noon was extracted. Subsequently, it was checked how this effective irradiance depends on the degree of cloudiness. From the results the influence of the mean annual variation of the thickness of the ozone layer was observed: in mid April (when the mean total ozone amount is largest) the intensity of the effective UV irradiance is about 20 % larger than at the end of August (when the elevation of the sun at solar noon is the same as in mid April).

In a next phase, the Tropospheric Ultraviolet Visible (TUV) model developed by *Madronich* (1993) was installed and adapted to the local situation. TUV is a freely distributed FORTRAN coded multiple scattering radiative transfer model. Based on several input parameters, such as solar zenith angle and total ozone column, it calculates the corresponding spectrum. A good agreement with the observed spectra is obtained. Therefore, TUV is a valuable tool for making clear-sky UV Index forecasts, of which the accuracy now mainly depends on that of the total ozone forecast. At the moment, a stepwise multilinear regression of both analyzed and forecasted meteorological parameters together with the last observed total ozone value appears to be the most adequate ozone forecasting method. The resulting clear-sky UV Index forecast for July is in very good agreement with the analyzed values, the standard deviation of the difference between forecasted and observed values being of the order of 0.5.

5 LABORATORY SPECTROSCOPIC MEASUREMENTS IN SUPPORT OF ATMOSPHERIC OBSERVATIONS

The use of spectroscopic techniques for the determination of the composition of the atmosphere requires that the absorption features of the atmospheric molecules be known (e.g. their absorption cross-sections). They provide a spectral signature of the species which allows their unambiguous detection in the atmosphere. The Université Libre de Bruxelles is involved in several spectroscopic studies of atmospheric constituents. All the work was carried out using two high performance Fourier transform spectrometers (FTS) and involved the development of the necessary hardware (cells, supersonic jet set-up, gas handling systems) required for the recording of the absorption spectra. Computer programs were also written to handle these spectra and retrieve the needed spectral information.

In the UV-visible range, the atmospheric minor constituents such as NO_2 and O_2 with its $(O_2)_2$ dimer have been studied. Absorption cross-sections have been obtained for these species at different temperature conditions and at various pressures and resolutions. These measurements were performed in collaboration with the Laboratoire de Spectrométrie Moléculaire Atmospherique of the Université de Reims (France), which has developped two multipasscells. The first one, 5 m long, is temperature controlled and can cover optical lengths up to 300 m. The second cell is 50 m long and paths up to 2 km can be used. With these cells, it is possible to operate under low pressure conditions and to study the temperature dependence of the cross-sections.

NO_2

NO_2 absorption cross-sections have been measured at two temperatures (220 K and 294 K) at the resolution of 2 cm^{-1} in the UV-visible range (10000-42000 cm^{-1}). The temperature dependence, already observed by other laboratories, has been confirmed. Moreover, a pressure dependence has been observed for the first time. These two effects have important implications for field measurements, especially for stratospheric NO_2 measurements. The results have been published in the open literature (Vandaele et al., 1997).

O_2 / $(O_2)_2$

The study of the O_2 absorption in the near IR and the UV-visible regions has been continued (Carleer et al., 1997). New results concern the $(O_2)_2$ molecule in the 7000-20000 cm^{-1} range,

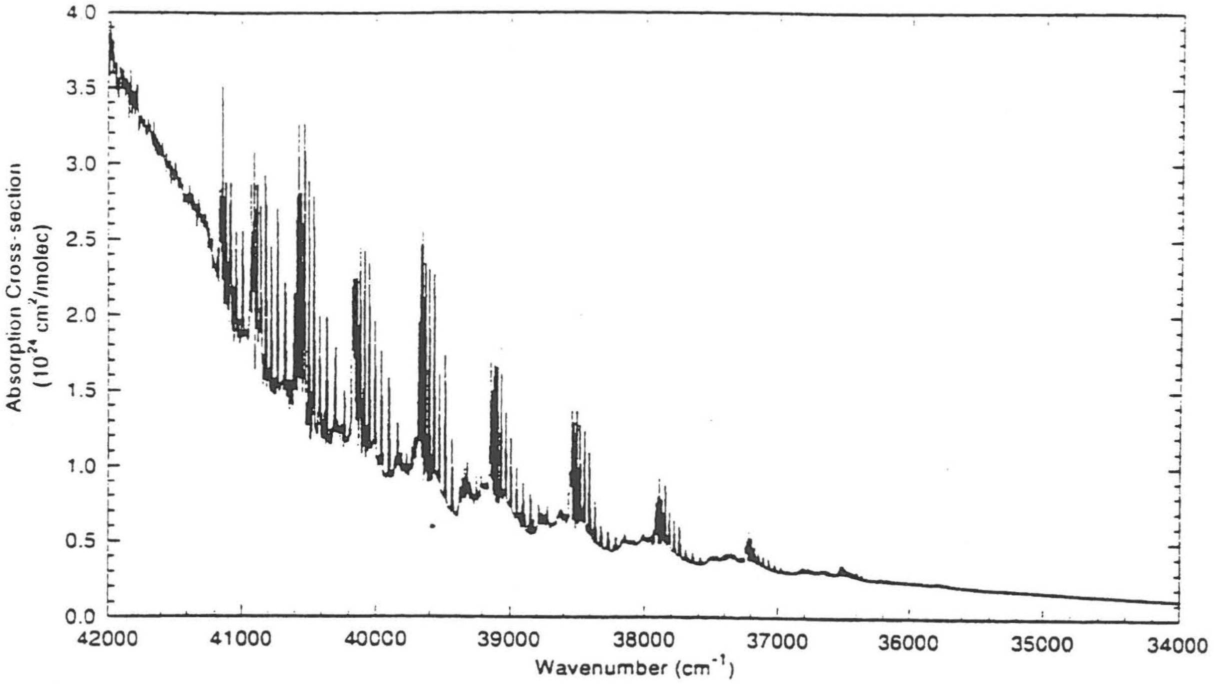

Fig. 4 Absorption cross-section of O_2 in tropospheric conditions (760 torr and room temperature

and the forbidden transitions of O_2 (Herzberg atmospheric bands) between 34000 and 42000 cm^{-1}. In this region, pressure effects due to O_2, N_2 and Ar have been measured in order to separate the contribution of the O_2 absorption from that of the structured underlying continuum, which so far has been assigned to the $(O_2)_2$ dimer. Our experiments however indicate that the latter could be entirely due to collisional effects. Figure 4 presents a spectrum measured in tropospheric conditions (760 torr at room temperature) and clearly shows the two contributions : Well defined absorption lines of the O_2 molecule superposed on the structured continuum.

Intensity measurements have also been performed in the IR and far IR regions. They concern acetylene, C_2H_2, HOCl (Vander Auwera et al., 1997) and COS (Rbaihi et al., 1997) molecules. The information provided is mainly the precise position of the absorption lines and for some the absolute intensities. Heavier species such the HFCs (Vander Auwera, 1997) have also been studied in this context, leading to the determination of absorption cross-sections and integrated absorption cross-sections at various temperatures.

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