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Hugo De Backer

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Abstract

At the Royal Meteorological Institute of Belgium ozone soundings have been performed since 1969. During these 30 years of observation the procedures of handling the sensors have been subject to changes. Some changes had influence on the measured ozone concentrations. Efforts have been made to reduce the errors and to construct a homogeneous time series. This report describes the post-flight procedures applied to calculate the final data set. Finally, the ozone climatology of Uccle is presented as an application of this data set. A linear trend analysis on the data set reveals an ozone decline in the stratosphere (up to -1 % per year), while ozone increases (up to +1.5 % per year) are found near the ground.

Samenvatting

Het Koninklijk Meteorologisch Instituut van België voert sinds 1969 ozonpeilingen uit. Tijdens de 30 jaar van waarnemingen zijn de behandelingsprocedures enkele malen gewijzigd. Sommige wijzigingen hebben invloed op de gemeten ozonconcentraties. Er werden dan ook inspanningen geleverd om de fouten te beperken en een homogene tijdreeks op te bouwen. Dit rapport bevat een beschrijving van de ”post-flight” procedures die toegepast worden bij de berekening van de uiteindelijke data set. Op het einde wordt, bij wijze van toepassing, de ozonklimatologie van Ukkel voorgesteld. Uit een lineaire trend analyse van deze data set blijkt dat ozon in de stratosfeer afgenomen is (tot -1 % per jaar), terwijl een ozontoename (tot +1.5 % per jaar) gevonden wordt bij de grond.

Résumé

Depuis 1969, l’Institut Royal Météorologique de Belgique effectue par sondage des mesures de la distribution verticale de l’ozone. Durant ces 30 ans, plusieurs changements ont été introduits dans les procédures d’observation. Certains de ces changements ont eu des répercussions sur les mesures des concentrations d’ozone. Des efforts ont été entrepris afin de réduire ces erreurs et de construire une base de données homogène dans le temps. Dans ce document, nous décrivons les procédures ”post-flight” appliquées pour le calcul final des données d’ozone. Pour conclure, les valeurs climatologiques de l’ozone à Uccle sont calculées comme exemple de l’utilisation de ces données. Une analyse des tendances linéaires montre que la quantité d’ozone décroît dans la stratosphère (jusqu’á -1 % par an), tandis qu’une hausse (jusqu’à +1.5 % par an) est observée près du sol.

Contents

1 Introduction

Ozone is a minor atmospheric constituent with particular physical and chemical properties. Among these, the strong absorption of UVB (radiation with wavelengths between 280 and 320 nm) is very important for the biosphere. Indeed, ozone in the stratosphere is an effective protective shield against damaging radiation of the sun in this spectral region. After the discovery of the potential influence of human activities on the ozone layer, efforts have been made to understand the dynamical and chemical properties of atmospheric ozone. Better understanding of the behaviour of ozone in the atmosphere may also help to improve the performance of general atmospheric circulation models, used among others for weather prediction and climate modelling. To achieve these aims high quality measurements of the distribution (in space and time) of atmospheric ozone are needed.

Different techniques for the measurement of atmospheric ozone are available. One group of instruments is dedicated mainly to determine the ozone column density, i.e. the total amount of ozone found in a column from the ground to the top of the atmosphere at a certain location. This quantity is measured from the ground by spectroscopy in the UV part of the spectrum with the Dobson [*Dobson*, 1957a,b] and Brewer [*Brewer*, 1973] instruments, in the visible by SAOZ [*Pommereau and Goutail*, 1988] or in the infra red by FTIR instruments [*Brown et al.*, 1992]. It may be noted that the UV technique is considered as a reference [*Komhyr*, 1989]. Also from satellites, total ozone is determined by the measurement of backscattered light at different spectral resolutions and ranges (e.g. the TOMS [*Herman et al.*, 1991] and the TOVS [*Smith et al.*, 1979] techniques in the UV and infra red, respectively).

These measurements give no information on the vertical distribution of ozone in the atmosphere. With the Umkehr technique [*Mateer and Dütch*, 1964] it is possible to retrieve ozone profiles with a limited number of layers (up to 9) with the Dobson and Brewer instruments. With lidar instruments it is possible to get a better height resolution, but their height range is restricted, and meteorological observation constraints may introduce a bias [*De Backer et al.*, 1994]. Measurements of the vertical distribution are also performed from space, either by the limb scanning or occultation techniques (e.g. SAGE [*Cunnold et al.*, 1984]). By the measurement of high resolution backscattered spectra (GOME [*Rozanov et al.*, 1997] and its successor SCIAMACHY) it is hoped to obtain also information on the vertical distribution of trace gases.

These techniques provide good global coverage, but their vertical resolution is limited. Moreover, all these techniques are rather new, and no long-term time series exist for the detection of long term trends, especially in the troposphere [*SPARC*, 1998]. For this purpose only ozone sonde observations are available now. However, ozone sonde stations with long (30 year) records are very sparsely and unevenly spread over the globe. In Uccle (50°48'N, 4°21'E, 100 m), Belgium, an ozone sonde program is running since 1969 with 3 ascents per week. The ozone profile time series since 1966 in Payerne (46°49'N, 6°56E, 491 m, Switzerland), since 1967 in Hohenpeißenberg (47°48'N, 11°01'E, 990 m, Germany) and since 1969 in Uccle are among the longest in the world.

Ozone sondes are carried aloft with a balloon similar to regular meteorological sondes. They provide ozone profiles from the ground to the burst level (generally between 30 and 35 km) with a resolution of a few 100 metres. The major problem with these sondes is the homogeneity of the time series. One reason for this is that each profile is measured with another instrument. Moreover, the performance of the sensor is sensible to the preparation procedure. In a continuous effort to improve quality of individual

results, the homogeneity of the time series may be lost. Care must also be taken at the changeover from one instrument type to another, which occurred in Uccle in April 1997 [*De Backer et al.*, 1998b].

Before any analysis of such a time series for trends, a careful examination of the history of the measurements is necessary [*SPARC*, 1998]. The Hohenpeißenberg time series has already undergone a reevaluation [*Köhler and Claude*, 1998]. At Uccle some steps in that direction have already been undertaken in the past [*De Backer*, 1994]. The present report is intended as a summary and an overview of the different efforts made to produce a homogeneous time series with the Uccle ozone sonde data. More detailed discussions of the applied techniques can be found in the references. First the measurement principle is explained. Afterwards a brief history of the preparation and launch practices of the sensors is given. Then the different post-flight processing steps to improve the quality of the data are documented. Finally a short analysis of the climatology and the trends of the homogenised time series of vertical ozone profiles measurements at Uccle for the 30-year period 1969-1998 is presented.

2 The measurement technique

The sensors used in Uccle are of the wet electrochemical type. They are based on the chemical reaction of ozone with a buffered potassium iodine solution to produce free iodine:

$$2\,KI + O_3 + H_2O \longrightarrow 2\,KOH + I_2 + O_2 \qquad (1)$$

The free iodine then causes an electrical current (of two electrons) when electrodes are immersed in the solution. This current is converted electronically in an interface and telemetered to a receiving system through a standard meteorological radiosonde, which also measures pressure, temperature and humidity. The radiosonde and the ozone sensor are attached to a balloon, filled with hydrogen. This balloon train ascents at a rate of about $6\,m\,s^{-1}$. In about 90 min an altitude of 30 to 35 km is reached, where the balloon bursts and the assembly descents with a parachute. If the ozone sensor is found, it can be used again after cleaning and checking. Since the recorded current is proportional to the number of ozone molecules passed through the solution the ozoneconcentrations can be determined at each moment during the flight. During the years two types of sensors have been used in Uccle.

2.1 The Brewer-Mast ozone sonde

The Uccle ozone profile time series starts in January 1969. At that time the Brewer-Mast (BM) ozone sensor, was considered as the best choice for this kind of measurements. The basics of this type of sensor are described by *Brewer and Milford* [1960]. It consists of a plastic electrochemical cell with a platinum gauze cathode and a silver wire anode immersed in $2\,cm^3$ of a buffered 0.1 % solution of KI, through which the ambient air is continuously blown by means of a miniature pump. An external polarizing source of 0.42 V is connected to the electrodes. If the air contains ozone, iodine is formed by reaction (1). At the cathode the iodine is reduced to iodide:

$$I_2 + 2\,e \longrightarrow 2\,I^- \qquad (2)$$

To prevent a continuous current after the formation of iodide from reaction (2), the iodide is converted at the anode to the insoluble AgI through:

$$2\,(\,I^- - e + Ag \longrightarrow AgI\,) \tag{3}$$

The main disadvantage of this type of sonde is that its pump assembly is made of plastic and contains a metal piston needing some oil for proper functioning. Plastic, metal and especially oil are ozone destroying products. Therefore the gain of the sensor is in general less than theoretically expected. Another problem is that the results obtained with this type of sensors show high variability between sensors, and are even not constant in time for one sensor.

2.2 The ECC ozone sonde

Another type of ozone sonde, the so-called Electrochemical Concentration Cell (ECC) was developed by *Komhyr* [1969]. In this design the electrolytic cell consist of two half cells, each filled with solutions of different concentrations of KI. The two half-cells are separated by an ionbridge, providing an ion pathway, but retarding the mixing of the anode and cathode solutions. Both electrodes are platinum gauzes. At the cathode, with low (0.5 - 2 %) KI concentrations, reaction (2), the same as for the BM, takes place. In the anode side of the cell the solution is saturated and therefore iodide is removed by the following oxidation:

$$3\,I^- - 2\,e \longrightarrow I_3^- \tag{4}$$

At the same time, the different concentrations of the KI solutions provide an electromotive force of about 0.13 V. Thus, an external battery is not needed to drive this cell. Another advantage of this cell, compared to the BM is that it is completely (including the pump) manufactured in Teflon, which does not destroy ozone.

During different intercomparison and testing campaigns it was shown that the ECC sonde results are much more consistent, and that the ECC sondes are easier to handle [e.g. *WMO* 1994 and *Smit et al.* 1998]. On the other hand, no unique relation between the ECC and BM results could be established from the published comparison results. However, it was decided at Uccle to change from BM to the ECC types of sondes. From April 1997 onwards the routine ozone soundings at the station are performed with the latest version of the ECC sondes, namely the Z-ECC sondes [*EN-SCI*, 1996]. As to be pointed out in section 4 this changeover was well prepared so that it is possible to obtain a homogeneous time series without a break at the time of the changeover.

3 History of the time series

With a time series of more than thirty years it is almost inevitable that some changes occurred in the procedures. Many facts, such as changes in the preparation procedure, the availability and the quality of ancillary measurements may affect the final result. Therefore, relevant events, which might have had influence on the quality of the ozone profile measurements, are summarised in Table 1.

The ozone soundings started begin 1969 with BM ozone sondes. In 1971 the profile measurements were complemented with concurrent total ozone measurements at the same station. Then in 1981 the sondes were exposed to higher ozone concentrations

Date			Event
03	Jan	1969	Start, BM ozone sensor with VIZ radiosonde; launchtime 8-10 UT
28	Jul	1971	Dobson total ozone available in Uccle
01	Oct	1981	Change in preconditioning procedure (electrostatic ozoniser)
01	Mar	1985	New launchtime 10:30UT
28	Apr	1989	Apparent change in sonde performance
01	Jan	1990	Change to Vaisala radiosonde; new launch time 11:00UT
22	May	1992	Start measuring c_0
01	Apr	1997	Change to Z-ECC sondes
01	Feb	1998	New launch time 11:30UT
01	Dec	1998	Box temperature from pump hole

Table 1: Overview of the history of the ozonesounding program at Uccle. For details, see text.

during the preparation (see section 3.1). Apart from shifts in launchtime (see also section 4.2.1), there were two major changes in equipment. From 1990 onwards, another type of radiosonde was used and in 1997 the type of ozonesonde itself was changed. There also is a change in the sonde performance, which seems to start with the use of a new delivered order of BM sondes. Concerns about the decreasing sensitivity of the BM sensors caused the setup of equipment to measure the efficiency before launch, by the determination of the ground calibration factor c_0 in 1992.

How these events are considered is subject of section 4.2. The quality of the measurements obtained with electrochemical sensors also depends upon the preparations before the launch. The reason for this is that ozone is easily destroyed. Any impurity in the system, as well as the walls themselves can cause ozone losses. The next sections give more detailed information on the preparation procedures. Another problem encountered with the data of the ozone soundings during the 1970's is the interference with SO_2 in the polluted mixing layer of Brussels. The procedure applied to correct for this is explained in section 4.2.5

3.1 Pre-flight preparations for the Brewer-Mast ozone sonde

Since about 1987, the preparation procedure for the BM sondes is based on the recommendations by *WMO* [1987]. This means that all sondes (recovered as well as new ones) are cleaned thoroughly. First, the anode is treated by electrolyse with a small aluminium strip in a 10 % NaCl solution. The silver wire is then cleaned mechanically with a small brush. The platinum gauze is heated in a gas flame. Then all the components (also from the pump) are cleaned in an ultrasonic bath (once with a cleaning agent for laboratory apparatus and twice with pure distilled water). After drying, the sondes are reassembled, and the pump piston is oiled carefully with the special oil delivered with the BM sensors. The pump efficiency is measured with a Brooks volume calibrator which replaces since mid 1990 the classic burette with soap. The sondes are then preconditioned by saturating the walls with ozone, to prevent wall losses. To this end the sensor and pump are run (without solution) with high ozone concentrations. The prepared sonde is then stored in a clean plastic bag until the day of release. Since May 1992, ozone containing air (about 280 μ g/m^3 at room conditions) from a calibrated ozone source is applied before launch to the running sensor for about 10 min. From this measurement a ground calibration factor (c_0) is determined. Afterwards ozone-

free air is applied to the running sensor for at least 20 min to reach a sufficiently low background current (generally below 0.5 μA). Then the sonde is put in its original Styrofoam box, and the batteries are checked (especially the polarizing potential of 0.42 V). With the sensor connected through the interface with the radiosonde, a high ozone concentration (from a UV lamp) is applied to the running sensor for a few seconds. This removes eventual contaminations in the sensor and makes it possible to test the transmission to the receiving system.

In the period before 1987, the main deviation from this procedure is that the newly arrived sensors were not disassembled and cleaned before use. Another, even more important difference occurs in the period before October 1981, when the ozone concentrations applied to the sensor during the preconditioning phase were much lower.

3.2 Pre-flight preparations for the Z-ECC ozone sonde

The Z-ECC sondes are prepared exactly as described in the manufacturer's manual [*EN-SCI*, 1996] (with the buffered 0.5% KI cathode solution). After c_0 is determined as for the BM sensor, also this sensor is packed in the original Styrofoam box. When the sensor is connected via the interface to the radiosonde, the same checking procedure as for the BM is applied.

4 Post-flight processing

From the basic chemistry of the sensors, as described in section 2, it follows that for each ozone molecule entering the solution, a current of two electrons is generated in the external circuit. This current I is telemetered to the groundstation by the radiosonde. On the other hand, the time interval Δt (in seconds) needed to pump 100 cm^3 of ambient air through the solution is measured before launch. Then the number of moles of ozone, n_{O_3}, in 100 cm^3 of air is:

$$n_{O_3} = \frac{I\,\Delta t}{2\,F} \tag{5}$$

where F is Faraday's constant which equals 9.6487 10^4 C mole^{-1}. The partial pressure of ozone is calculated by the application of the ideal gas law to Eq. (5) for a volume V of air at temperature T_{air}:

$$\begin{aligned} p_{O_3} &= \frac{n_{O_3}\,R\,T_{air}}{V} \\ &= \frac{I\,R\,\Delta t\,T_{air}}{2\,V\,F} \end{aligned} \tag{6}$$

For V = 100 cm^3 Eq. (6) becomes:

$$p_{O_3} = k\,I\,\Delta t\,T_{air} \tag{7}$$

with

$$k = 0.43085\ \text{Pa C}^{-1}\,\text{K}^{-1}$$

It should be noted that the temperature T_{air} in Eq. (7) is the temperature inside the pump, since it refers to the volume V (100 cm^3) which passed through the pump during the interval Δt.

4.1 The standard procedure

The calculation of ozone partial pressure in Eq. (7) is based on the knowledge of the air flow generated by the miniature pump. This flow rate is determined before launch, at room conditions of pressure and temperature. It is known that the efficiency of the pumps decreases with decreasing ambient pressure [*Komhyr and Harris*, 1965]. It is a standard practice to correct for this effect by pump efficiency correction profiles. Generally those mentioned in the *WMO* [1987] recommendations are used for the BM sondes, while those in the EN-SCI manual [*EN-SCI*, 1996] are used for the Z-ECC. The temperature T_{air} needed in Eq. (7) is not measured but is set to 300 K [*WMO*, 1987].

If total ozone is available from a Dobson or a Brewer instrument, then this quantity is compared with the integrated amount of ozone from the sonde profile. Above de burst level of the sonde the residual ozone (between 30 and 50 DU, or about 10-15 % of the total column) must be estimated. This is done by assuming a constant mixing ratio, or by using a climatological mean. For profiles, obtained with BM sensors, the whole profile is multiplied with the ratio between the total ozone amount from the spectrophotometer and the integrated amount from the sonde. In this way, agreement between both is forced. The correction factors for Z-ECC are very close to 1, while for BM they are roughly 1.1-1.3. This means that 10 to 30 % of the ozone is not detected by the BM sensor and has to be redistributed over the profile. Since the use of the linear factor causes height dependant differences between data obtained with BM and Z-ECC, it is better to apply a nonlinear correction, as will be explained in section 4.2.7.

4.2 Homogenisation of the Uccle data set

As mentioned in section 3 there have been a lot of changes during the observational period, the most radical being the change of type of sensor in 1997. Before that change from BM to Z-ECC type sondes a study of quasi simultaneous measurements with BM at Uccle and with ECC at De Bilt [*De Backer et al.*, 1996] showed that there were important height dependant differences. From measurements in a vacuum chamber *De Backer et al.* [1998a] suggested that an erroneous compensation for the loss of pump efficiency at reduced pressures may cause this problem. Finally, *De Backer et al.* [1998b] showed that with a new correction for the loss of pump efficiency, it is possible to get close agreement between data sets obtained with BM and Z-ECC. This pump efficiency problem comes besides the elements mentioned in section 3. How all these instrumental effects are treated to produce a homogeneous time series is described in the next sections.

4.2.1 Change in launch time

Up to March 1985 the ozone sondes were launched independently of the routine radio soundings for meteorological purposes. This practice resulted in a large scatter in the launch time (sondes were launched when their preparation was finished). In 1985 the ozone sondes were coupled with the regular soundings for local noon bringing the launch time closer to noon. Stricter requirements on the times of the observations used in weather prediction models caused other shifts in the time of launch.

Figure 1 shows how the launch-time has changed over the years. Major changes happened in March 1985, January 1990 and February 1998. If a diurnal cycle is present, then changes in the launch time may affect trends derived from the time series.

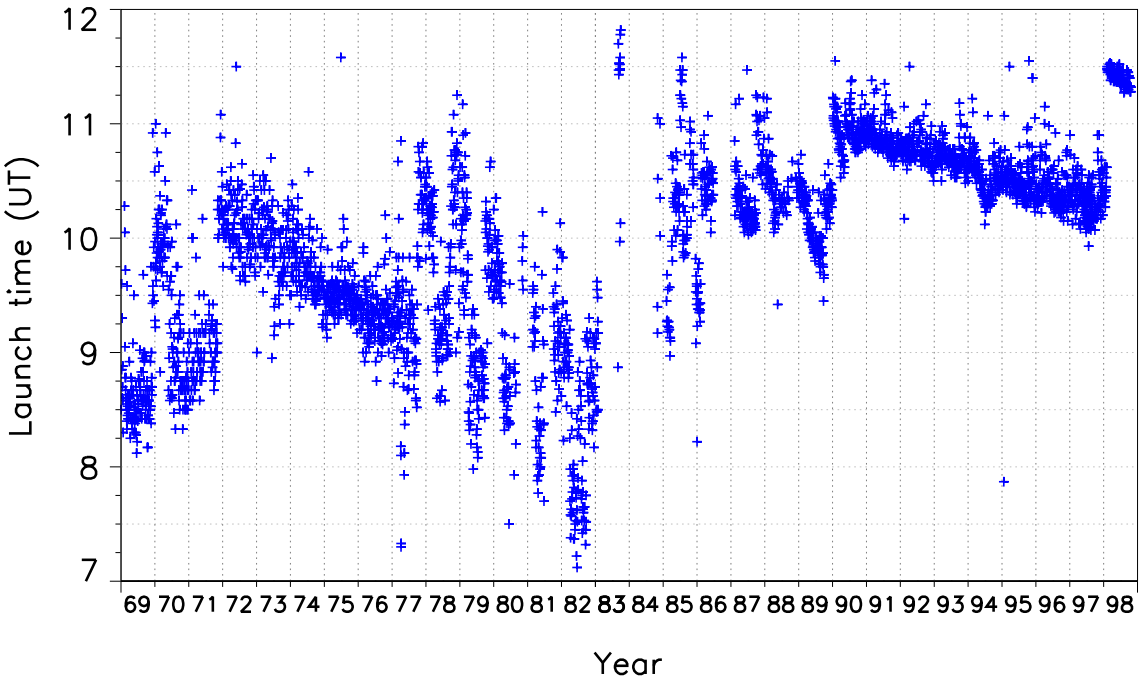

Figure 1: Start times of the ozone sonde ascent at Uccle, launched between 7 and 12 UT.

It is well known that diurnal variations are present in the mixing layer [e.g. *De Muer et al.* 1997]. However, it is difficult to account for the differences in launch time, since the magnitude of the diurnal cycle strongly depends on the prevailing weather conditions. Therefore, no correction for the different launch times is available. For studies of stratospheric ozone and ozone in the free troposphere this will not cause any problems. If analyses of the data in the boundary layer are undertaken, care should be taken for the launch times. It could, for example, be considered to select only those soundings launched within a well-defined time window. Such a routine will at once exclude the few soundings performed in the afternoon or overnight for special campaigns. Another possiblity is to try to combine the profile measurements with, whenever available, groundlevel observations.

4.2.2 Response time

When a varying quantity is measured using a sensor with a certain finite response time, errors are expected, of which the smoothing of peaks is the most eyecatching. The response function of the BM has been analysed by *De Muer and Malcorps* [1984]. They also proposed a deconvolution method to correct for the distortion. Software is available to apply this method to the Uccle data set but generally this is not done. The reason is that with the normal ascent velocity, the resolution of the data is sufficient, and the deconvolution often generates spurious peaks, due to noise in the data. For certain studies, however, also the data obtained during the much faster descent are used. If profiles gathered during ascent and descent are compared, there is generally a shift in altitude between the profiles, and the descent data are smoothed. In such cases, the deconvolution brings both profiles in better agreement and real differences (e.g. due to photochemical production in the boundary layer) become visible.

4.2.3 Box temperature

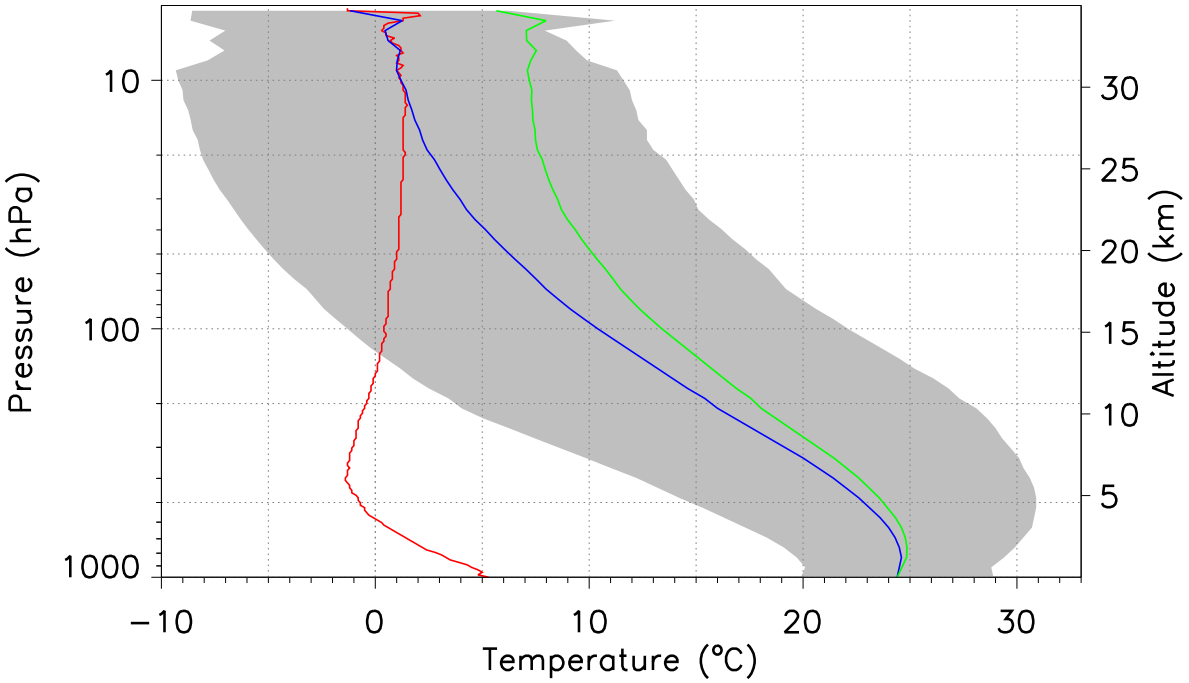

Figure 2: Mean box temperature during ascent (blue line) and descent (red line) from the BM soundings during 1990 and 1991. The grey zone indicates the 2σ limits corresponding with the variations of the box temperature during ascent. The green line represents the adjusted mean box temperature applied before 28 April 1989

The temperature T_{air} in Eq. (7) is the temperature of the air inside the pump [*De Muer*, 1984]. This temperature was not measured routinely until the end of 1989. With the new Vaisala radiosonde system, used since 1 January 1990, the temperature inside the ozone box is measured, and this one is used as an approximation of T_{air}. For the period before 1990 the mean box temperature as derived from the soundings during 1990 and 1991 (Fig. 2) is used. It was observed that the quality of the isolating box had changed over the years. The observers remarked that the Styrofoam was much looser and both halfs fitted not so well after 28 April 1989. Therefore it is expected that the box temperature was higher before April 1989. From some occasional measurements by *De Muer and Malcorps* [1984] and *De Muer* [1984] it is estimated that the box temperature before April 1989 was about 7° C at the 10 hPa level. The following adjusted box temperature (T_e) tries to account for this and is used before 28 April 1989:

$$T_e = T_m + (3 - \log_{10}(p))\, k_T \tag{8}$$

where T_m is the average box temperature over the period 1990-1991 (Fig. 2), p the pressure (in hPa) and k_T is set to 3° C to obtain about 7° C at 10 hPa. From the actual values of the box temperature it is seen that the default standard value of 300 K mentioned in section 4.1 produces an overestimation of the ozone partial pressure of about 8 % near the top of the soundings. Of course the use of the mean box temperature and Eq. (8) does not remove this error completely, since the individual box temperatures may deviate largely from the mean (2σ zone in Fig. 2). It should also be noted that the box temperature also has an effect on the correction for the pump efficiency

(section 4.2.7) working in the other direction. As will be shown, the combined effect of decreasing temperature is an increase of calculated ozone partial pressure.

Since December 1998 the box temperature is measured with the thermistor in the pump hole, as recommended by the quality control team of THESEO. The temperature differences between a free thermistor and one in the pump hole are 3-4 % at the highest [*O'Connor*, 1998]. The combined result of these small temperature differences on Eq. (7) and on the effect described in section 4.2.7 is even lower.

4.2.4 Altitude measurement

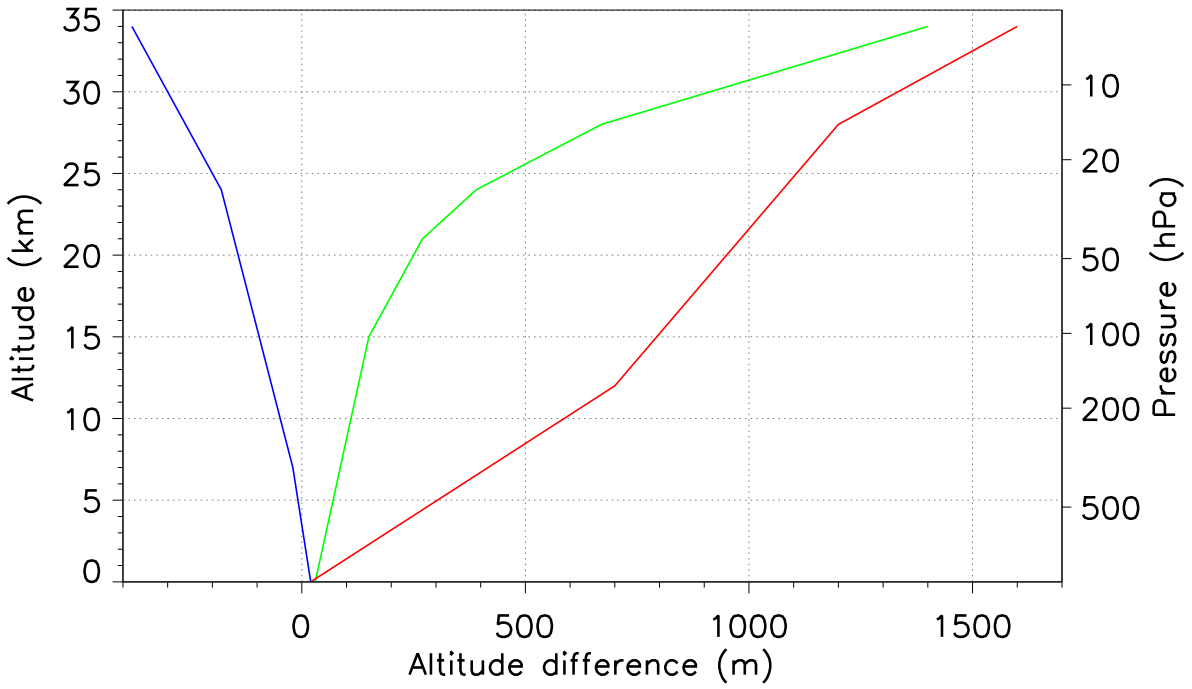

Figure 3: Mean differences between altitudes measured by radar and by VIZ sondes 1988-1989 (green line), by VIZ sondes 1985-1988 (red line) and by Vaisala sondes after 1990 (blue line).

It has already been shown earlier [*De Muer and De Backer*, 1992a] that changes in the accuracy of the pressure sensor have repercussions to the ozone profiles. Figure 3 displays the altitude differences between the altitudes obtained from radar and from radiosondes measurements. As discussed by *De Muer and De Backer* [1992a], the deviations originate in a slow response of the pressure detection system. It was also shown that the differences have changed during the observation period, probably due to an additional calibration error in the period 1985-1988. Consequently, different corrections of the altitude and pressure values are made for different periods. This means that for the period January 1988 until December 1989, a correction corresponding to the green line in Fig. 3 is made. For the period March 1985 until December 1987 the correction is done according to the red line in the figure. Before 1985 no radar information is available, but as a save guess the correction corresponding to the green line in Fig. 3 is made. *De Muer and De Backer* [1992a] showed that for average ozone profiles the application of this altitude correction lowers the ozone concentrations by about 5 % from the ground to 20 km. Between 20 and 25 km the correction changes sign. At

higher altitudes the altitude correction increases the ozone concentrations gradually up to about 15 % above 30 km.

Although also the Vaisala sondes, used from 1990 onwards, show a difference (in opposite direction, blue line in Fig. 3), no altitude correction is made for this type of sondes, since the differences are much smaller, and the results were based on a smaller number of comparisons.

4.2.5 SO_2 interference

The electrochemical sensors used to measure ozone are also sensible to other atmospheric trace species, such as SO_2. *Schenkel and Broder* [1982] showed that the decrease in ozone readings of BM sondes is proportional to the SO_2 concentration, the proportionality factor being equal to 1, within the limits of uncertainty of their measurements. On the other hand *De Muer and De Backer* [1992b], showed that there was an important decrease in SO_2 concentrations during the 1970's. Therefore a method was developed to estimate the vertical distribution of SO_2 from measurements of ρ_g, the SO_2 density at the ground level [*De Muer and De Backer*, 1993]. The method is based on two assumptions: (1) the SO_2 mixing ratio is constant from the ground to the mixing height, and (2) the SO_2 mixing ratio above the mixed layer decreases exponentially with the logarithm of the air pressure, such that the integrated SO_2 amount equals the reduced thickness of the SO_2 layer.

The height of the mixing layer is determined as the crossing point of the adiabate, starting from the ground at a temperature of 1 K above the measured surface temperature (T_g), and the actual measured temperature profile. From the first assumption, the SO_2 partial pressure (p_{SO_2}) in the mixed layer can be derived:

$$p_{SO_2}(p) \;=\; \frac{\rho_g\, T_g\, R}{m_{SO_2}}\,\frac{p}{p_g} \qquad \text{for } p_m \;\leq\; p \;\leq\; p_g \tag{9}$$

where:

R represents the gas constant (8.31436 J mole^{-1} K^{-1});
m_{SO_2} molecular weight of SO_2;
p_g air pressure at the surface; and
p_m air pressure at the top of the mixing layer.

From the second assumption the SO_2 partial pressure above the mixing ratio is calculated:

$$p_{SO_2}(p) \;=\; \frac{\rho_g\, T_g\, R}{m_{SO_2}}\,\frac{p}{p_g}\,\left(\frac{p}{p_m}\right)^{a} \qquad \text{for } p \;<\; p_p \tag{10}$$

An empirical expression for a derived by *De Muer and De Backer* [1993]

$$a \;=\; \left(\frac{1}{1.74 \;-\; 0.98\,\frac{p_g}{p_m}} \;-\; 1\right)^{-1} \tag{11}$$

is used to define the exponential decrease in the free troposphere.

Equation (11) only requires the pressure at the ground (p_g) and at the top of the mixing layer (p_g), which are derived from the meteorological radiosonde data, obtained together with the ozonedata.

Equations (9) and (10) additionally need ρ_g, the SO_2 density at the ground at the time of the sounding. For these data several sources are at our disposal. Basically we

use the long term data series of daily mean values of SO_2 measured at Uccle, a station making part of an SO_2-soot network, installed by the Belgian Institute of Hygiene and Epidemiology in cooperation with the Royal Meteorological Institute of Belgium. The results of these measurements are reported in *Institut Royal Météorologique de Belgique* [1968-1974] and *Institut d'Hygiène et d'Epidémiologie* [1975-1990]. This data set covers the most important period, but has no information on the diurnal variation of SO_2. Another network, operational since 1977 in the Belgian urban areas, measures every half hour. From these measurements the mean diurnal variation of SO_2 for each calendar month, relative to the daily mean was calculated for the urban area of Brussels. Then with the whole time series of daily mean values, an estimate can be made for the SO_2 concentration at launch time by multiplying the mean value for Uccle from the SO_2-soot network with the appropriate ratio for the time of the ozone sounding. Uccle is at the southern, more residential, outskirts of the city. The prevailing wind direction at the site is from South-West. Therefore it is possible that, although the ground level measurements are in the polluted air belt of the city, the SO_2 concentrations are not equally distributed over the whole mixing layer at the sounding site. It may also be noted [*De Backer*, 1994] that the measuring technique in the network is not specific for SO_2. Therefore the measurements are an upper limit for the real SO_2 concentrations. For these reasons, the SO_2 concentrations are divided by a factor of three, which brings the ozone concentration at the same level as those from other European ground observations. After September 1993 the SO_2-soot network data are not available. From that time onwards a more crude estimate of the daily SO_2 concentration is made from the exponential decay functions determined by *De Muer and De Backer* [1992b]. It should be noted at this point that the SO_2 concentrations in Brussels have diminished dramatically from 1969 to about 1985, and that they have stabilized at low values afterwards, making their influence on ozone soundings negligible. During the late 60s and early 70s, SO_2 concentrations occasionnaly peaked to more than 100 μg m^{-3} (corresponding to about 4 mPa). In such cases the correction for SO_2 is about 100 % and sometimes negative currents are present, indicating that the impact of SO_2 was even higher. Ascents during which currents lower than or equal to zero were registered, are not corrected, and are omitted from time series analysis.

Since the Z-ECC sondes were not used in Uccle before 1996, no correction for SO_2 is applied to ozone profiles obtained with this type of sensor.

4.2.6 Background current

As part of the recent (after May 1992) pre-flight preparation procedure the signal of the sensor, when ozone free air is pumped through the cell, is recorded. Special attention is drawn not only to the background current (I_b) before exposure to ozone but also to the decay of the current after ozone has been given to the sensor for its calibration. If this current is not sufficiently low (i.e. below .1 μA for Z-ECC) after 15-30 min the sonde is rejected.

4.2.6.1 The Brewer-Mast sonde The background current of the BM sondes has a mean value ($\pm 1\sigma$) of .1 $\pm$ .05 μA for the period November 1995 to March 1997. Although a current of .1 μA represents about .3 mPa ozone partial pressure in the troposphere (Eq. (7) with ΔT = 30 s and T_{air} = 300 K), no correction is recommended for the background current of BM sondes [*WMO*, 1987]. Further investigations are required before

a correction for the background current (if it is available for the older soundings) can be made for BM.

Change of the BM preparation procedure As mentioned in section 3 there has been a change in the preconditionning of the sondes in October 1981, which influenced the performance of the sondes at the beginning of the flight. From the comparison of ascent to descent ratios of ozone profiles before and after that date *De Backer* [1994] found that the lower tropospheric part was too low for the ascent of the soundings before October 1981. Without correction this will introduce an erroneous positive trend in the lower layers of the data set. Therefore the following correction is made between the ground and 70 hPa to the ascent part of ozone profiles obtained before October 1981:

$$\Delta p_{O_3}(p) \;=\; 0.7\,\frac{\log_{10} p - \log_{10} 70}{\log_{10} p_g - \log_{10} 70}\;\mathsf{mPa} \qquad \text{for } p \;>\; 70\,\mathsf{hPa} \tag{12}$$

where:

p represents the ambient pressure in hPa; and
p_g surface pressure in hPa.

Equation (12) can also be interpreted to be a correction for a negative background current caused by impurities in the sensor.

4.2.6.2 The Z-ECC sonde For 217 Z-ECC sensors prepared between October 1996 and March 1998 the mean background current ($\pm 1\sigma$) is $.019 \pm .016\,\mu$A. In the Z-ECC manual [*EN-SCI*, 1996], the question which type of background correction to use is left open. Therefore, we follow the recommendation of *Reid et al.* [1996], and we subtract the background current (I_b), obtained before the ground calibration, from the measured cell current over the whole altitude range.

4.2.7 Pump efficiency and total ozone

As explained in section 4.1, it is a common practice to calculate the ratio between the total ozone amount, obtained from total ozone measurents with a co-located Dobson or Brewer spectrophotometer, and the integrated ozone amount from the sonde profile. This ratio is then commonly called the correction factor of the profile. For BM profiles it is part of the standard procedure to multiply the whole profile with this correction factor [*WMO*, 1987]. Very often this correction factor is considered as a quality control: if it is close to unity the measurement was good, large deviations from unity may indicate problems. For ECC type of sondes the correction factor is generally close to 1, but for BM it is usually in the range 1.1 to 1.3, and even higher values are found (see, e.g., [*WMO*, 1994]). *De Backer et al.* [1996], suspected that the standard correction for the decrease of the pump efficiency [*WMO*, 1987] caused this discrepancy. The following describes the application to the Uccle sounding data series of the method proposed by *De Backer et al.* [1998b] to solve this problem.

For our time series we use for total ozone ($O_{3,t}$) the daily mean value of total ozone measured with the co-located Brewer n°16. When no Brewer data are available (before January 1984, and during some short interruptions) the re-evaluated and SO_2 corrected data of Dobson n°40 [*De Muer and De Backer*, 1992b], also at the same station, are used. Since both instruments compare very well [*De Backer and De Muer*,

1991], the use of both sources for total ozone will have no influence on the homogeneity of the series. Prior to the introduction of the Dobson instrument in July 1971, $O_{3,t}$ was estimated from measurements of total ozone at surrounding stations in Germany and Great Britain. Although also these measurements have been rescaled to the Bass-Paur ozone absorption coefficients [*Bass and Paur*, 1984] adapted by *WMO* [1992], it must be admitted that the use of these estimates introduces an unknown error.

Each ozone profile is calculated following Eq. (7), with the corrections for the box temperature, the altitude error, the SO_2 interference and the background current as described above. However, no pump correction profile is applied. Then the profile is integrated yielding the amount $O_{3,i}$ between the ground and the top of the sounding.

If the pressure, p_b, at the burst level of the sounding is below 16 hPa, then the residual amount of ozone, $O_{3,r}$, is estimated assuming a constant mixing ratio above the burst level. To reduce possible errors of the last point of the sounding the mean mixing ratio between 16 hPa and the top of the sounding is used. Then an initial correction factor c_1 is calculated:

$$c_1 = \frac{O_{3,t}}{O_{3,i} + O_{3,r}} \qquad \text{for } p_b < 16\,\text{hPa} \tag{13}$$

If the burst level is between 16 and 30 hPa then the residual ozone $O_{3,R}$ is estimated from the climatological mean from the TOMS satellite [*McPeters et al.*, 1997] and the initial correction factor is determined as follows:

$$c_1 = \frac{O_{3,t} - O_{3,R}}{O_{3,i}} \qquad \text{for } 16\,\text{hPa} \leq p_b < 30\,\text{hPa} \tag{14}$$

If the ozone profile ends before 30 hPa is reached, no reasonable estimate of the residual ozone can be made, and no further correction is possible. These soundings should be treated with caution. For analysis of the long term series it is best to exclude these profiles.

The values of c_1 from Eqs. (13) and (14) are necessarily higher than the traditional correction factors since no correction for the pump efficiency is applied at this stage.

De Backer et al. [1998b] showed that the efficiency of the miniature pumps is dependant on the temperature of the pump (especially for BM type of sonde). The following temperature correction was derived:

$$k(T) = a_{0,0} + a_{0,1}\,T + a_{1,0}\,\log_{10}(p) + a_{1,1}\,T\,\log_{10}(p) \tag{15}$$

where:

$k(T)$ represents the factor by which the time to pump 100 ml at 20°C must be multiplied to obtain the time at temperature T in °C; and

$a_{i,j}$ regression coefficients.

	BM	Z-ECC
$a_{0,0}$	1.17749	1.08912
$a_{0,1}$	-0.00842671	-0.00482722
$a_{1,0}$	-0.0446558	-0.0240274
$a_{1,1}$	0.00194705	0.00134294

Table 2: Coefficients of Eq. (15) for BM and Z-ECC sondes.

Table 2 lists the coefficients $a_{i,j}$ for BM and Z-ECC as they are obtained from measurements in a vacuum chamber at different temperatures. Figures 4 and 5 show the resulting corrections for BM and Z-ECC, respectively. It is clear from these figures that the correction is much more important for BM than for Z-ECC sondes, also due to the larger variations of the box temperature of the BM. In contrast with the direct effect of the temperature in Eq. (7), discussed in section 4.2.3, the effect of a lower temperature is to increase the calculated ozone partial pressure. It may be noted that at high altitudes, the effect of the temperature dependence is larger than the direct effect.

After correcting for the temperature effect on the pump efficiency, also a correction for the pressure dependence is made. If the ground calibration factor, c_0, valid for the measurements at ground level pressure is known, we can use the following correction for the decrease of the pump efficiency [*De Backer et al.*, 1998b]:

$$c(p) = c_0 \frac{1 + \sqrt{\frac{b}{p}}}{1 + \sqrt{\frac{b}{p_0}}} \tag{16}$$

where:

$c(p)$	represents the correction factor at pressure p;	
p_0		pressure at the ground; and
b		parameter depending on the performance of the sensor.

The parameter b is then determined in such a way that the integrated amount of ozone (increased by the residual amount of ozone) corresponds with the concurrent measurement of total ozone with a spectrophotometer. The range of values of b was confirmed

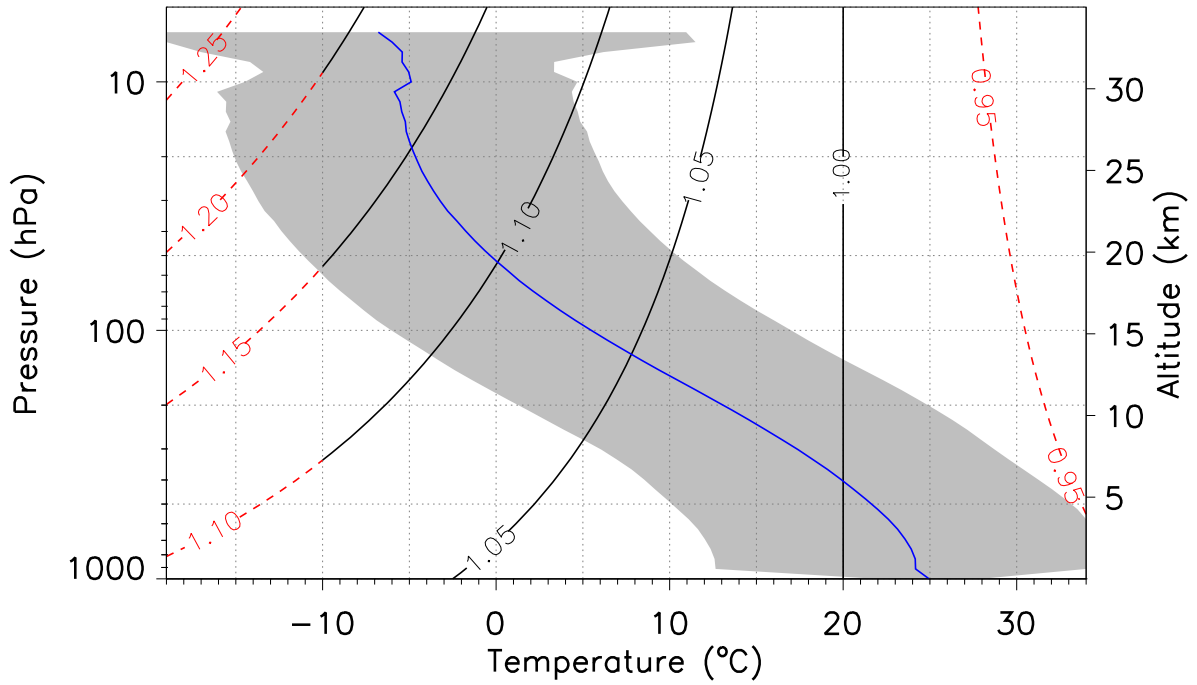

Figure 4: Mean ratios between the time needed to pump 100 ml at temperature t and pressure p and the time at 20°C with BM pumps. The solid black lines result from interpolation between the measured points with a polynomial (Eq. (15)); the dashed red lines indicate extrapolation. The blue line and shaded area show the mean and 2σ of the box temperatures for BM observed between 1990 and 1998.

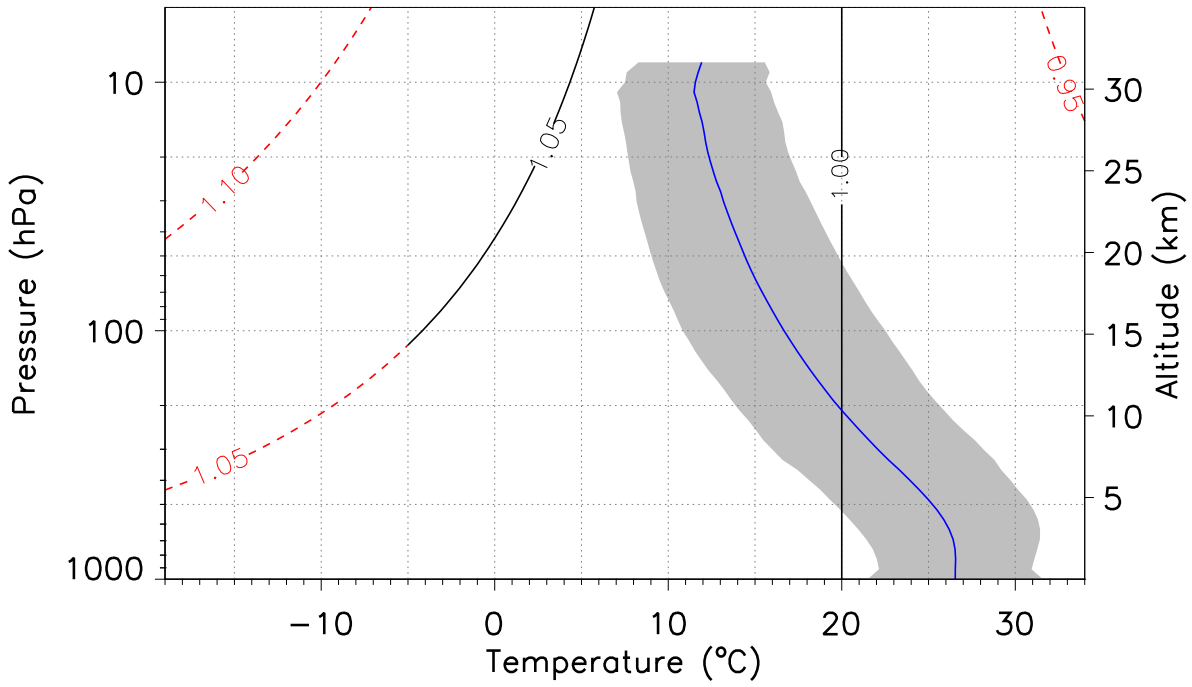

Figure 5: As Figure 4 but for Z-ECC (mean box temperature over period Oct 1996 until March 1998).

by measurements of the pump efficiencies in a vacuum chamber. It was shown by *De Backer et al.* [1998b] that this method reduces the systematic differences between ozone profiles obtained with BM and Z-ECC to values below the statistical 95 % significance level.

4.2.7.1 Correction for data after 1992 As part of the preparation procedure we measure since 22 May 1992 the response of the sonde to a calibrated ozone source. Then b is the only unknown parameter in Eq. (16), and we can apply the method described above directly. The only restriction is that a minimum value for b of 0.35 and 0.07 is imposed for BM and Z-ECC, respectively. The corresponding correction curves have almost the same values at 10 hPa as the standard pump corrections for the different types of sondes. If these minimum values are applied, a new linear correction factor is calculated similar to Eq. (13) or (14). In the following c_l will refer to this correction factor that is equal to c_0 if the value of b is higher than the minimum.

The reason for the limitation of the values of b at the lower edge is that we never measured lower pump corrections in the vacuum chamber. If the calculations from the ozone profile and c_0 result in lower values of b, this is probably due to the fact that the c_0 was not valid at the moment of the launch. This is possible when the calibration was erroneous for some reason, or when there has been a change in the sonde performance.

The effect of the new pump efficiency correction is shown in Fig. 6 for Z-ECC sondes (black line) and BM sondes (blue line). It is clear that the effect on the BM is more important than on the Z-ECC sondes.

4.2.7.2 Correction for data between 1989 and 1992 For soundings prior to 22 May 1992 we do not have c_0 measurements. Therefore we make an estimate of c_0 from the

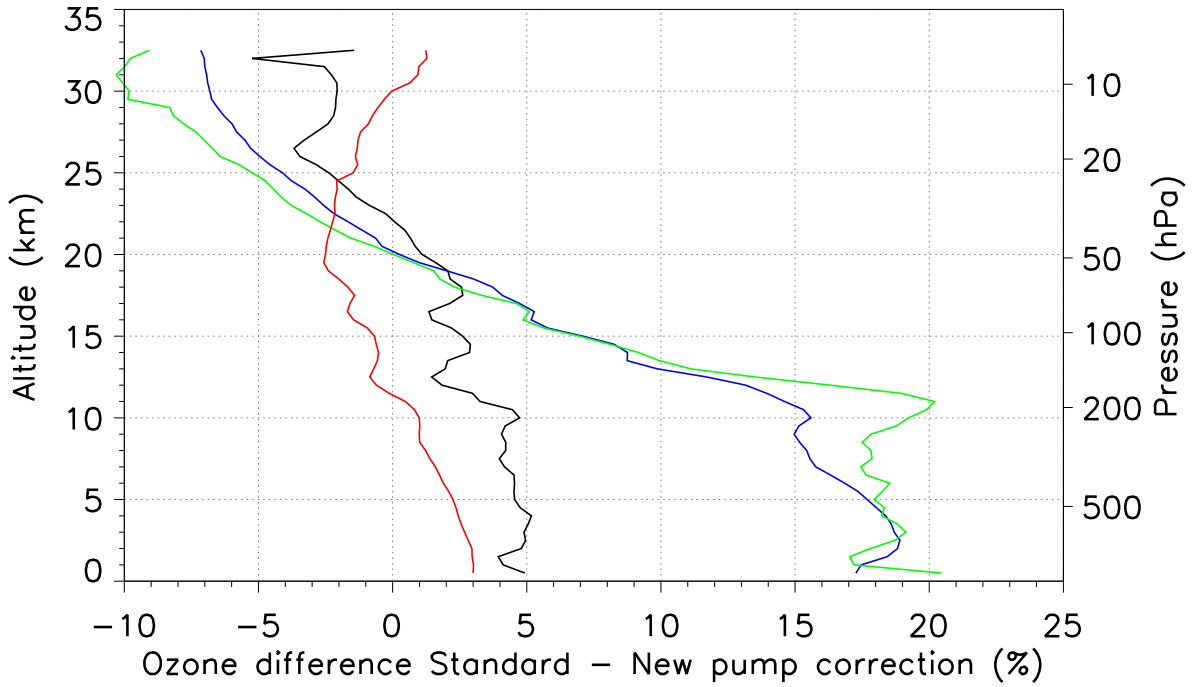

Figure 6: Percentage ozone differences between one year averaged ozone profiles calculated with the standard pump correction, and with the new pump correction explained in section 4.2.7 for the different periods: for BM sondes, over the period March 85 - Feb 86 (red line); for BM, over the period Jan - Dec 91 (green line); for BM, over the period Jan - Dec 93 (blue line); and Z-ECC sonde, over the period March 97 - Feb 98 (black line).

relation between c_0 with c_1. Figure 7 shows this relation for the soundings where both c_0 and c_1 were determined. The correlation coefficient between both parameters is 0.68 for 521 observations. From a least squares fit of a polynomial of the 2^{nd} order in c_1 we find:

$$c_0 \;=\; 0.616875 \;+\; 0.382277\, c_1 \;-\; 0.000969106\, c_1^2 \qquad (17)$$

This enables us to estimate the value of c_0 for the soundings where it is not measured. This result is however only used for the period 28 April 1989 until 22 May 1992, for reasons explained in the next section. As seen if Fig. 6 the effect this correction (green line) is on the average nearly the same as the correction with the measured values of c_0 (blue line).

4.2.7.3 Correction for data before 1989 As already mentioned earlier in this report there was an abrupt change in the data in April 1989. This is illustrated in Fig. 8 showing the evolution of ozone at the 10 hPa level (where no big changes over the years are expected) when no attempt is made to change anything around that time (no correction for temperature change). A jump of more than 15 % is seen around 1989. In section 4.2.3 it was already mentioned that the quality of the isolating box changed at the time the sondes were delivered after the movement of the manufacturing company. Not only the quality of the isolation but also the quality of the sondes seem to have changed at that time. It appears to us that the quality of the pumps was better before than after that date. This means that Eq. (17) is not valid for the period before 1989.

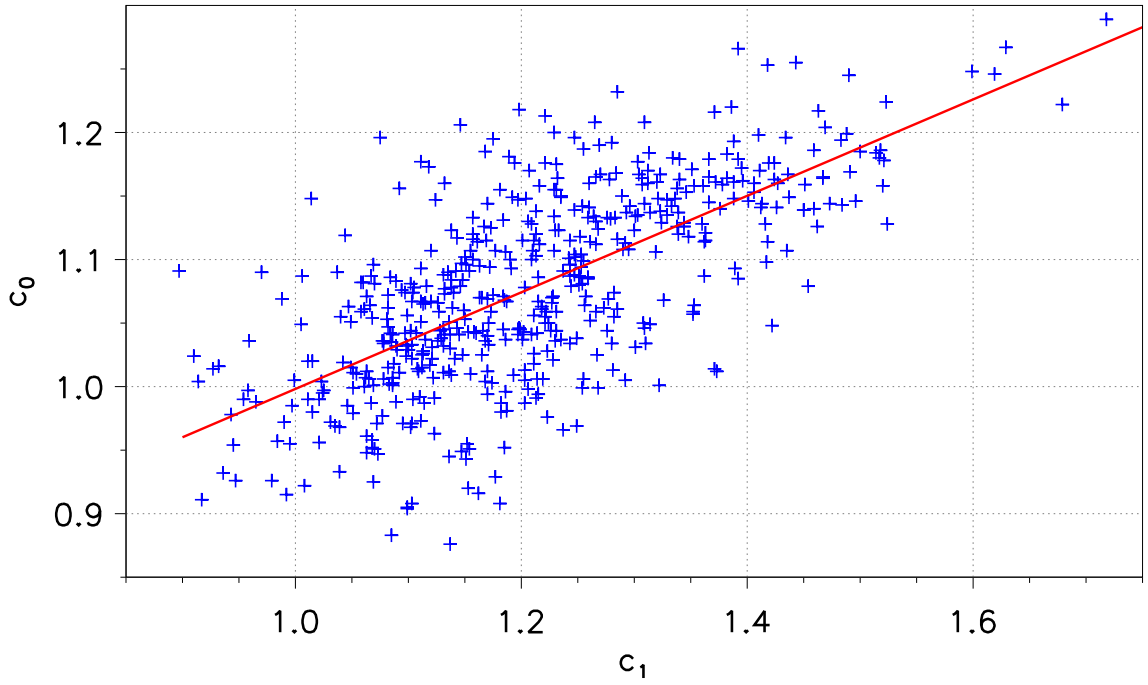

Figure 7: Approximation of c_0 as function of c_1 for BM. The red curve is the result of a least squares fit (see text).

Instead we use a corrected estimate c_0':

$$c_0' = c_0 + \alpha\,(c_1 - c_0) \tag{18}$$

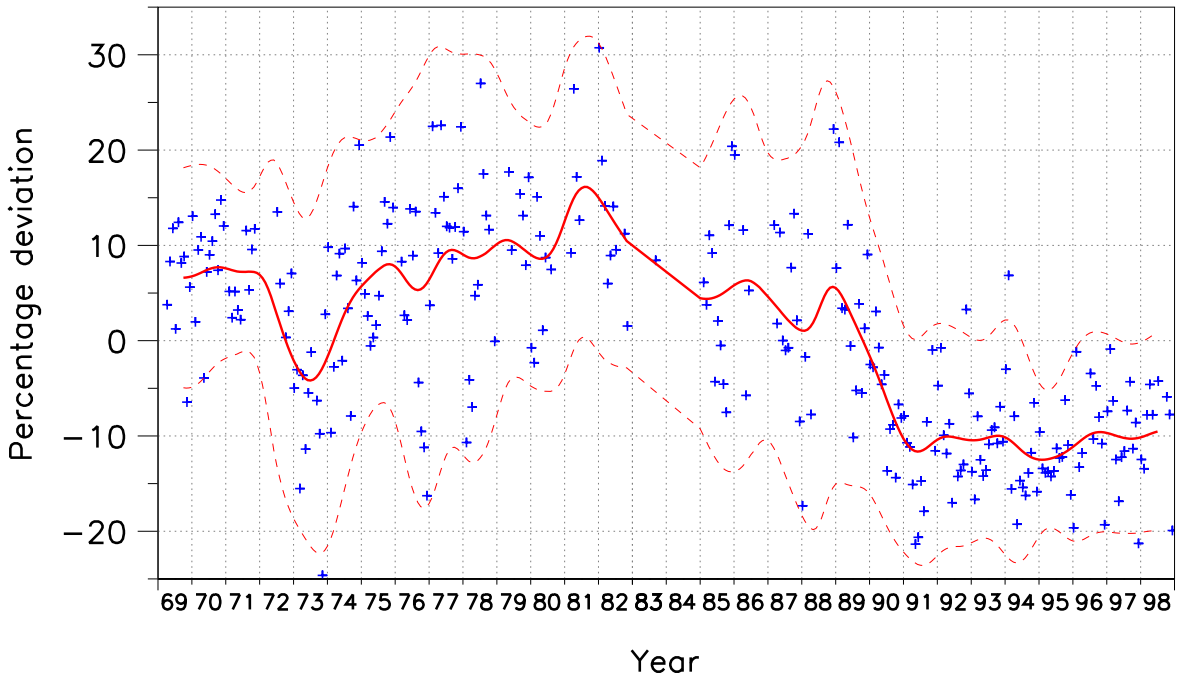

Figure 8: Percentage deviations of the monthly mean ozone partial pressures at the 10 hPa level from the long term mean. The thick red line is the result of filtering the data with a Gaussian filter with 2σ of one year, The thin red lines give the 2σ variability within the years. Results obtained without adjustment for the change in April 1989.

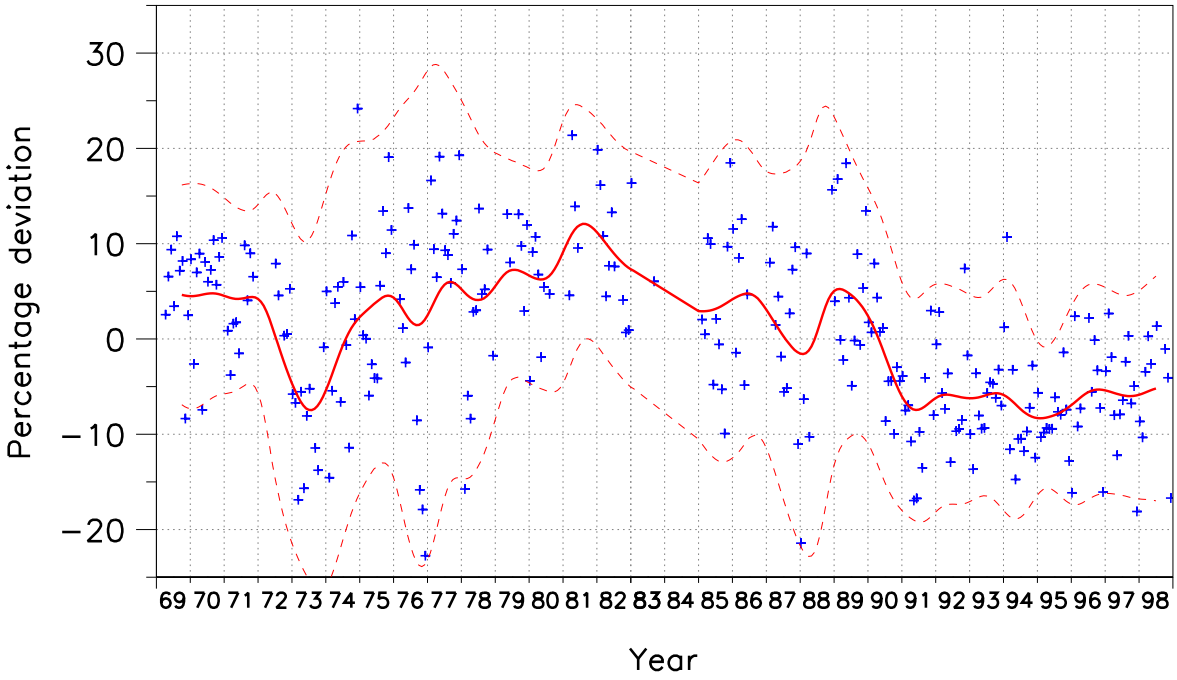

Figure 9: As Fig. 8 but after adjustment for the change in April 1989 as described in the text.

The meaning of Eq. (18) is that the contribution of the loss of pump efficiency to the correction factor c_1 becomes smaller, while the overall gain of the cell is less. Tests with different values showed that the lowest standard deviations at the 10 hPa level were obtained with α=0.85. The lower limit of b is set to 0.09 for soundings prior to April 1989 to account for the better performance of the pumps. This also implies that for the period before 28 April 1989 in general lower pump correction profiles are used.

Figure 9 shows the time series of the monthly deviations at the 10 hPa level after the application of the boxtemperature adjustment (section 4.2.3) and Eq. (18). Obviously the size of the jump in 1989 is reduced but not completely removed by this procedure. To determine whether this jump is real or an artifact further study is required.

The amplitude of the correction can be compared to those for the other periods in Fig. 6 (red line).

4.3 Summary of the homogenisation procedures

Figure 10 gives an overview of the correction procedures used for the homogenisation of the Uccle ozonesonde time series as a function of time. The lowermost bars represent the type of radio- and ozone sonde used. The bar T_{box} indicates what is used for the box temperature, a corrected average, the average (A) or the measured value (see section 4.2.3). Then the altitude corrections (section 4.2.4) are represented. For which period SO_2 correction (section 4.2.5) is applied or estimated (E) can be seen in the corresponding bar. The treatment of the background current I_b is illustrated in the next bar. Here "correction" means the correction for the low ozone preconditioning at the beginning of the time series, and Z the Z-ECC method. Total ozone ($O_{3,t}$) is estimated before July 1971, but available afterwards. Finally the pump correction is done in different ways, depending on the available information as described in section 4.2.7.

From Fig. 10 it can be seen that, as we go further back in time, the uncertainties in-

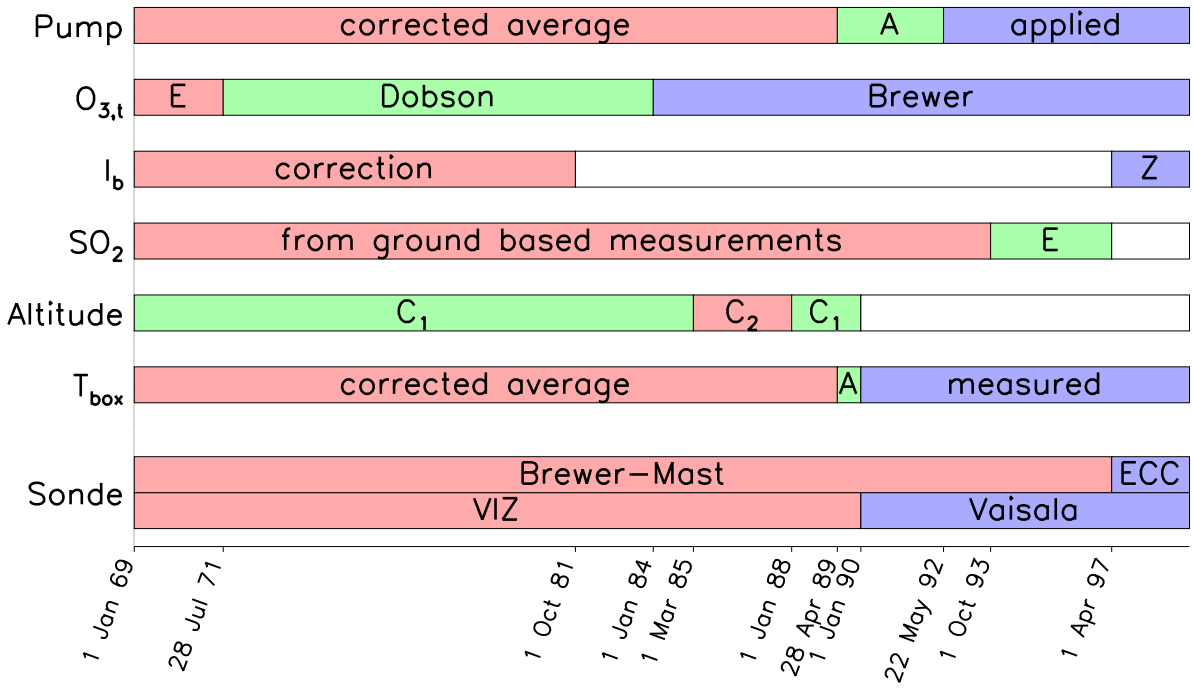

Figure 10: Overview of the corrections applied to the ozone profiles at Uccle. For details, see text.

crease due to the lack of information. Especially the lack of knowledge of c_0 causes an important problem. The changeover from BM to Z-ECC sondes was well documented and therefore causes no artificial break in the time series. The average of c_0 for the period 1989-1992 seems to work quite well. The not well known changes in 1989, however, can still have their influence on the data: it is not clear whether the remaining changes in that period are real ozone changes, or whether they are artifacts due to changes in instrument performance, insufficiently corrected for. The earlier changes had, after the proposed corrections, smaller effects on the ozone partial pressure at the 10 hPa level.

5 Data analysis

Since the data are now of the highest possible quality, we can start using them for analysis. This is illustrated with some examples in the next sections.

5.1 Ozone climatology at Uccle

Since we have enough data, it is possible to calculate a season-height cross section of the mean ozone partial pressure over the station. Figure 11 shows such a plot. It is known that stratospheric and tropospheric circulations are not directly linked. On the other hand the level of the tropopause is not at a fixed geometric height. Analysis of ozone data on fixed pressure or altitude levels would mix stratospheric and tropospheric measurements at levels around the tropopause, where the ozone gradient is large. To avoid this problem the following height scale is used. For levels above the tropopause the height is expressed in km above the tropopause. Between the tropopause and the ground a relative height scale is used ranging from 0 (tropopause)

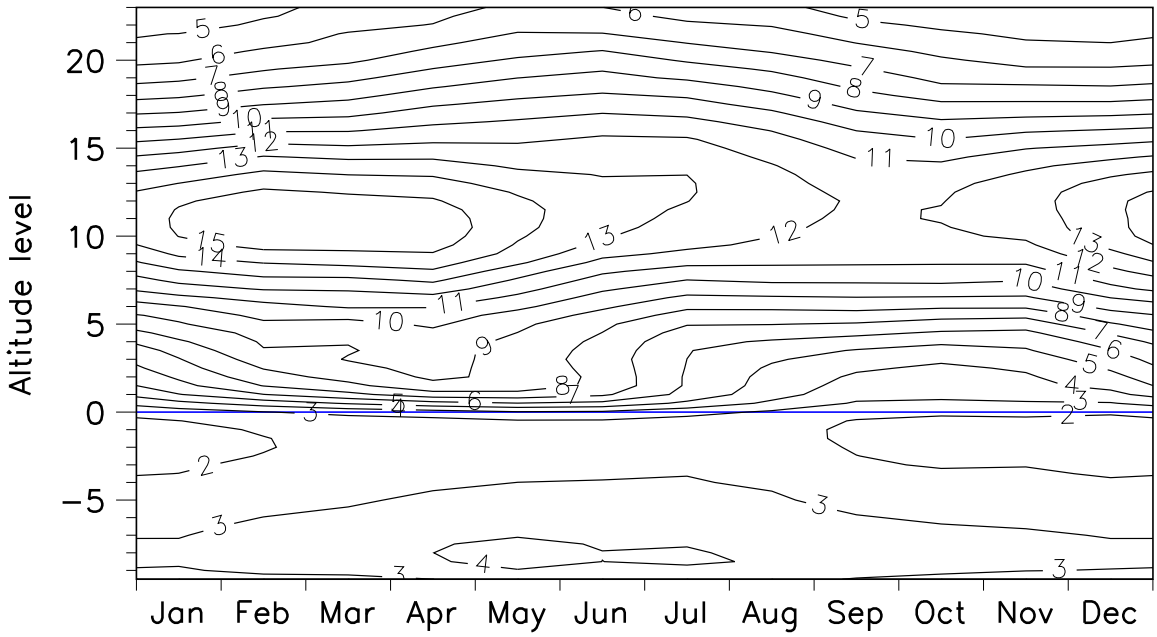

Figure 11: Season-height cross-section of mean ozone partial pressure (in mPa) at Uccle for the period January 1969 to December 1998. The height scale is relative to the tropopause (blue line). Positive values are in km above the tropopause; the negative values are relative heights between the tropopause (0) and the ground level (-10).

to -10 (ground). Since the tropopause at our station has a mean height of 9-10 km, the tropospheric height scale is approximately km below the tropopause.

The mean feature of Fig. 11 is an ozone maximum in the stratosphere, at about 11 km above the tropopause ($\pm$21 km above the ground). The intensity of the maximum changes during the year, reaching its highest values (more than 15 mPa) during late winter and early spring. This maximum is related to the general circulation pattern in the stratosphere. Below this main maximum there is a secondary maximum just above the tropopause during spring. In the troposphere the dominant feature is the summer maximum, which is probably caused by photochemical production in the free troposphere.

Not only the mean values themselves, but also the variability is interesting to get an idea of the seasonal behaviour of atmospheric ozone. Figures 12 and 13 show the percentage standard deviations, within and between months, of the ozone partial pressure at Uccle. They represent the fast day-to-day changes and the long-term year-to-year variability, respectively.

The percentage standard deviation within months (Fig. 12) is highest just below the tropopause. This is caused by the large day-to-day changes that occur during intrusion events. High day-to-day variability is also noticed in the lower stratosphere below the ozone maximum during winter and early spring. In the troposphere the variability is lowest in the mid-troposphere, but increases again near the ground, especially during summer. This may be related to the fast buildup of photochemical ozone episodes.

The year-to-year variability (Fig. 13) is lower and has a maximum near the ground during summer. This points to the fact that the important ozone episodes during summer are clustered during warm summers. The extreme high day-to-day variability be-

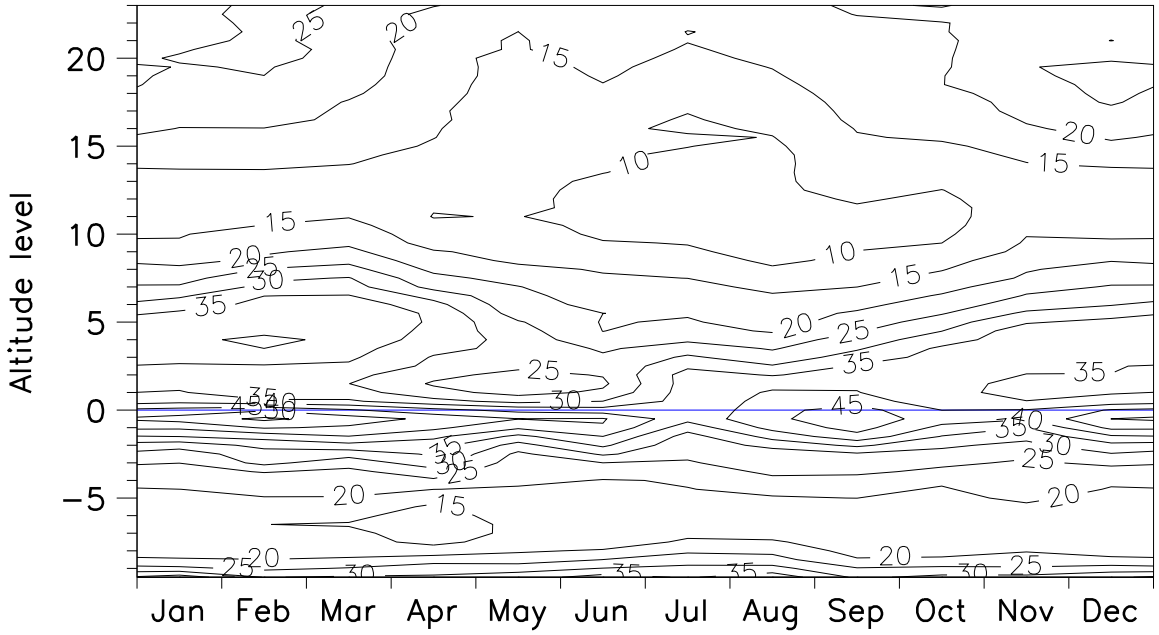

Figure 12: Season-height cross-section of percentage standard deviation within months at Uccle for the period January 1969 to December 1998. The height scale is as for Fig. 11.

low the tropopause is not seen here, which means that the monthly mean values differ not very much for the different years. Quite interesting is that during winter the lower stratosphere shows high variability. There is also a remarkable maximum during fall at

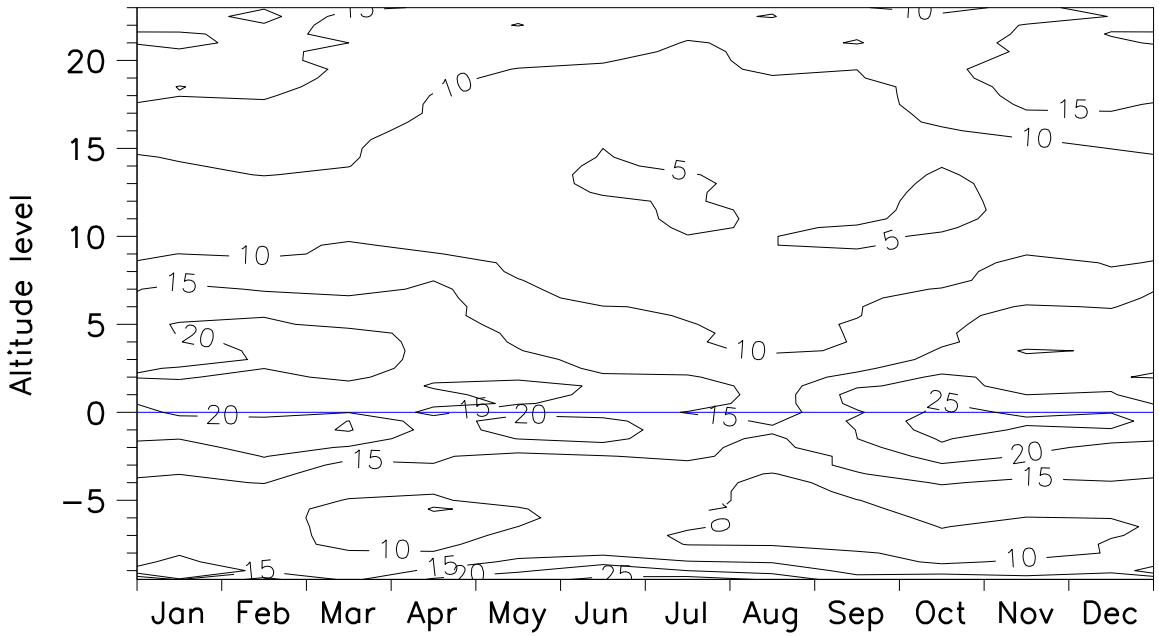

Figure 13: Season-height cross-section of percentage standard deviation between years at Uccle for the period January 1969 to December 1998. The height scale is as for Fig. 11.

the tropopause level. Further study is required to see what are the causes for this.

5.2 Ozone trends at Uccle

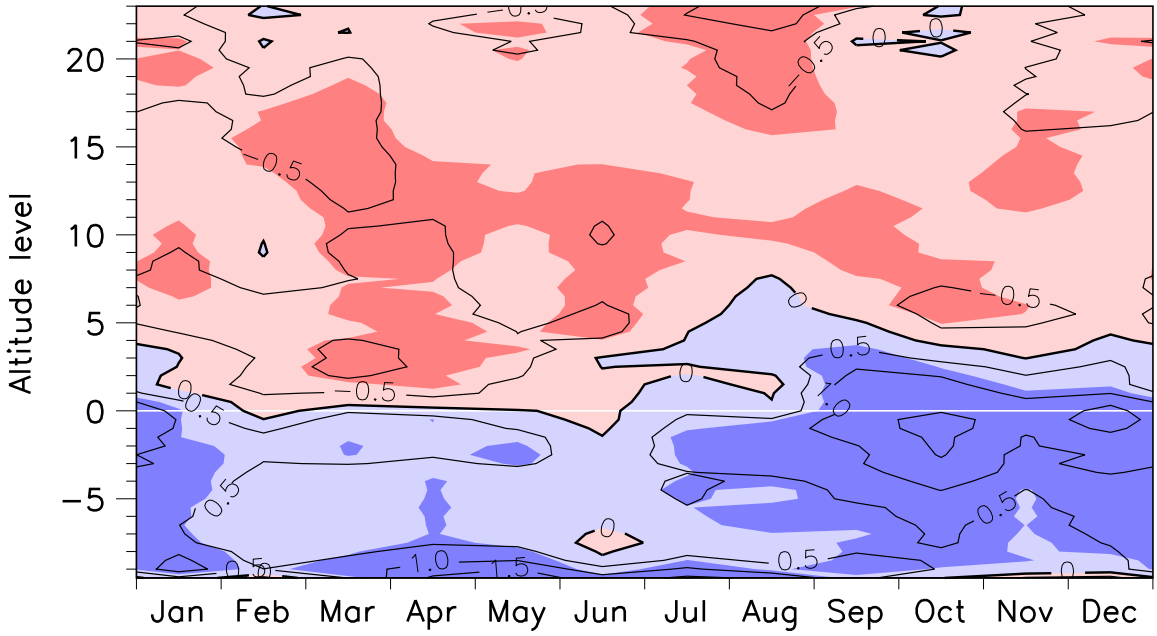

Figure 14: Season-height cross-section of ozone trends in percent per year at Uccle for the period January 1969 to December 1998. The height scale is as for Fig. 11. Areas where the trend is statistically significant at the 95 % level are coloured darker (red for negative and blue for positive trends).

The trends in Fig. 14 are the result of a least square linear regression on the monthly mean ozone partial pressures obtained during the 30 years of observations. Only profiles of sondes reaching the 30 hPa level or higher are included. In general the trends are positive in the troposphere and negative in the stratosphere. During late winter and early spring, the changeover from negative to positive trends is very sharp and located at the tropopause. In the same period the largest negative trends (up to more than -1 % per year) are observed in the stratosphere at the level of the secondary ozone maximum. This learns us that the downward trends in total ozone during this part of the year is caused by processes in the lower stratosphere and that there is no link between the ozone depleting processes in the stratosphere and tropospheric ozone. The highest positive trends (more than +1.5 % per year) are found near the ground during spring and summer, pointing to an increasing occurrence of high ozone episodes over the period 1969-1998. As mentioned in section 4.2.1 this result must be treated with caution, since no correction for the change in launch time has been made.

The positive trends in the whole troposphere during fall and winter, which even extend into the stratosphere are unexplained at this moment. Further studies are needed for complete interpretation of these phenomena, but this is beyond the scope of this report, concentrating on the homogenisation of the data set.

6 Conclusion

The data set of ozone soundings, carried out in Uccle since January 1969, has been carefully examined for instrumental changes and artificial effects. Where possible corrections have been worked out to improve the quality and the homogeneity of the time series. Figure 10 gives an overview of all the corrections applied to the data set. For some corrections estimates had to be made due to the lack of complete information (such as the change of the quality of the sondes). When a planned change was made from BM to Z-ECC sondes, a thorough comparison was carried out. Therefore, this change could be carried out without the introduction of an artificial break.

Using this data set in a simple linear trend analysis shows that the maximum downward trend in ozone, is found in the lower stratosphere in the period March-April, where it reaches locally -1 % per year. Positive trends are found in the troposphere, with a maximum of more than +1.5 % per year near the ground during summer. Positive trends are also found throughout the tropospehere during fall and winter.

The data set can now be used for further investigations of the dynamical and chemical behaviour of the atmosphere.

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A List of Acronyms

FTIR	Fourier Transform Infra Red spectroscopy
GOME	Global Ozone Monitoring Experiment
SAGE	Stratospheric Aerosol and Gas Experiment
SAOZ	Système d'Analyse par Observations Zénithales
SCIAMACHY	SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY
THESEO	THird European Stratospheric Experiment on Ozone
TOMS	Total Ozone Mapping Spectrometer
TOVS	Tiros-n Operational Vertical Sounder

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