Evaluation of Dobson and Brewer total ozone observations from Hradec Králové Czech Republic, 1961-2002

Report of the project CANDIDOZ, Working group WG-1
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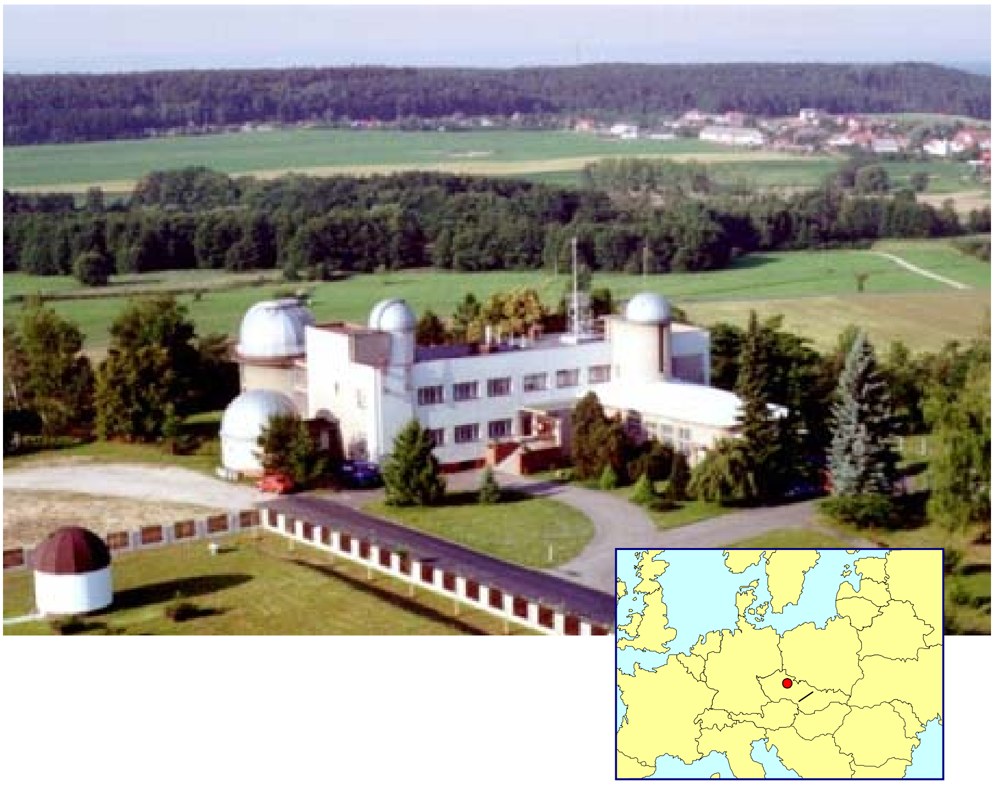

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SUMMARY

1. INTRODUCTION

After a significant reduction of the stratospheric ozone was confirmed in the early eighties the scientific community focused its attention on estimation of trends of ozone reduction in different latitudes and on their prognoses for next decades. In coming years identification of the ozone recovery has become one of the main research tasks that will allow scientists to assess what are the real effects of the Montreal Protocol and its amendments on protection of the ozone layer and whether the atmosphere still has a capacity for natural regeneration of stratospheric ozone. This is also one of the main tasks of the CANDIDOZ project (**C**hemical **and** **D**ynamical **I**nfluences on **D**ecadal Ozone Change) established under the FP-5 of the European Commission in 2002.

The total column of ozone in the atmosphere (total ozone) is one of the most important parameters that characterize condition of the ozone layer over a particular region. In the global scale, monitoring of the total ozone is carried out in ground-based networks and by satellites. Both systems work separately and generate data sets of specific quality, size and geographical coverage. Therefore, a proper application of data series for statistical analyses (e.g. assessment of temporal changes, estimation of trends or prognoses) requires a precise knowledge of technologies used for observations and processing the raw data.

Ground-based measurements of total ozone are mostly performed at stations included in the network of the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO) or in the Network for the Detection of the Stratospheric Change (NDSC) - see: http://www.wmo.ch/web/arep/gaw/measurements.html and http://www.ndsc.ws/ . Though total ozone can be measured by several methods at the ground, the observations made with the Dobson and Brewer ozone spectrophotometers located at about 140 stations (about 60 in Europe) *[WMO, 2001a]* produce the absolute majority of total ozone data used for scientific applications. Both spectrophotometers have become standardized instruments regularly operated and maintained under separate calibration systems. Because of different calibration scales and due to certain differences in technology of measurements total ozone data originated with Dobson and Brewer (D/B) spectrophotometers must be taken as independent data sets for scientific analyses. This is an important aspect if both sorts of data sets are taken from individual or collocated D/B stations, mainly for estimation of long-term trends or for validation of satellite observations.

The Solar and Ozone Observatory (SOO-HK) of the Czech Hydrometeorological Institute (CHMI) in Hradec Kálové, Czech Republic is one of a few D/B collocated stations of the GAW network where both well maintained and regularly calibrated ozone spectrophotometers have been operating for a long-time. Routine and experimental total ozone observations carried out at SOO-HK allow investigation of relation between D/B data series. The analyses of simultaneous measurements taken under various atmospheric and operational conditions can contribute to assessment or explanation of differences between Dobson and Brewer total ozone observations that have been identified at other collocated stations *[Staehelin et al., 2003]*. Moreover, the re-processed D/B data sets from SOO-HK can also contribute to validation of total ozone data from space systems (TOMS, GOME).

The early identification of recovery of the ozone layer requires analyses of reliable observations originated with different instruments. The quality of such data sets must be well evaluated, especially at stations with long-term continuous records. This was the main reason why a complex re-evaluation of total ozone observations from Hradec Králové has been included as a specific task into the WG1 of the CANDIDOZ project. The re-evaluation continues and extends outputs from a previous work done at SOO-HK in the eighties *[Vaníček, 1991, 1994]*.

2. MONITORING OF TOTAL OZONE IN HRADEC KRÁLOVÉ

a) The Solar and Ozone Observatory Hradec Králové - characteristics

The Solar and Ozone Observatory of the Czech Hydrometeorological Institute in Hradec Králové is a specialized branch-section of CHMI dealing with long-term monitoring of solar radiation and condition of the ozone layer over the territory of the Czech Republic (CR). The Observatory is located in the building of the Astronomical Observatory and Planetarium in Hradec Králové - see the picture in the front page. The building stands on a hill in the southern outskirts of the town (100.000 inhabitants), away from local pollution sources and with an open southern horizon. It is surrounded mostly by fields and forests. The nearest buildings are family houses about 100-200 m to the north and east. The Observatory is at the altitude which is 40 m over the town's elevation. Geographical coordinates of the observatory are 50.177 N, 15.839 E, 285 m a.s.l.. The degree of pollution of the air by aerosol and man-made gases is from medium to low; the pollution comes mainly from urban agglomeration. More information about SOO-HK is available at its web site:
http://www.chmi.cz/meteo/ozon/hk-e.html

b) Programme of total ozone observations at SOO-HK

SOO-HK was founded in 1951 as a professional meteorological station. Participation of the Observatory in the International Geophysical Year (1957-1959) initiated implementation of the ozone monitoring programme at SOO-HK. This started in 1961 by regular measurements of total ozone with the Dobson ozone spectrophotometer and was extended by installation of the Brewer spectrophotometer No. 098 in December 1993. Since 1961 the Observatory has been registered as a GAW station No.096 (meteorological index 11649). The observations from SOO-HK represent one of the longest uninterrupted total ozone data series deposited in the World Ozone and UV Data Centre (WOUDC) of WMO in Toronto that are frequently used for national and international ozone related projects and research studies *[Vaníček, 2001]*.

c) Calibration histories of ozone spectrophotometers operated at SOO-HK

Before the complex re-evaluation of total ozone observations from SOO-HK started in 2002 a detailed investigation of calibration histories of the both spectrophotometers D074 and B098 was performed and summarized *[Vaníček, 2002]*. This technical paper was prepared under the project *No.: 205/01/0003 "Development of Technologies for the European Dobson Calibration Center"* supported by the Grant Agency of CR. The report gives detail histories of calibration campaigns, technical tests and maintenance of D074 and B098 since the very beginning of their operation at the Observatory. New sets of updated calibration constants of both spectrophotometers have been re-defined for particular periods of measurements. The new calibration constants are related to the calibration scales represented by the world Dobson and Brewer standard instruments. As the outputs published in the report represent basic input parameters for re-processing and evaluation of the whole observational data base from SOO-HK they were widely used for the CANDIDOZ project and, if necessary, are included also in this report – see the next chapters.

2.1. Observations made with the Dobson spectrophotometer D074

Figure 1. *The Dobson ozone spectrophotometer D074 operated at the Solar and Ozone Observatory in Hradec Králové equipped with the semi-automated facility for data recording and processing of observations*

a) Types and schedules of measurements

The Dobson ozone spectrophotometer No. 074 (D074), see *Figure 1*, was purchased in 1959 and installed at SOO-HK in 1960. Total ozone measurements and processing of data were performed according to instructions and manuals prepared by Prof. G.M.B. Dobson *[Dobson. 1957a, 1957b, 1962]* and with calibration constants of D074 provided by the manufacturer R.&J Beck, Ltd., London *[Vaníček, 2002]*. The first recorded Direct Sun (DS) total ozone observations were taken at SOO-HK in January 1961 and they continued with various frequency by the end of 1961. Since February 1962 regular observations have been made in more than 10 days per month. Measurements on zenith scattered light (blue sky ZB and cloudy sky ZC) started in 1967 and 1969, respectively. The zenith observations significantly contribute to the monitoring program at stations located in regions with cloudy climate condition or in high latitudes. This was the reason why ZB and ZC measurements have been implemented into the monitoring programme in Hradec Králové very soon.

Total ozone is measured with D074 every day (mostly around the noon) if the weather conditions ate suitable for observations (no rain or heavy clouds), preferably when direct solar beams are available (DS direct sun observations). The measurements are made on A,C,D wavelength pairs in 1-minute intervals so that mainly AD double-pair can be used for calculation of total ozone - see Chapter 2.1.b). While in the period 1961-1965 the A-D observations were mostly made, since 1966 the C-D-A readings have been regularly performed as a standard sequence. After 1967/1969 the DS measurements were immediately followed by ZB/ZC observations to get quasi-simultaneous total ozone values for development of zenith polynomials and cloud-correction tables for D074 - see Chapter 3.2.e).

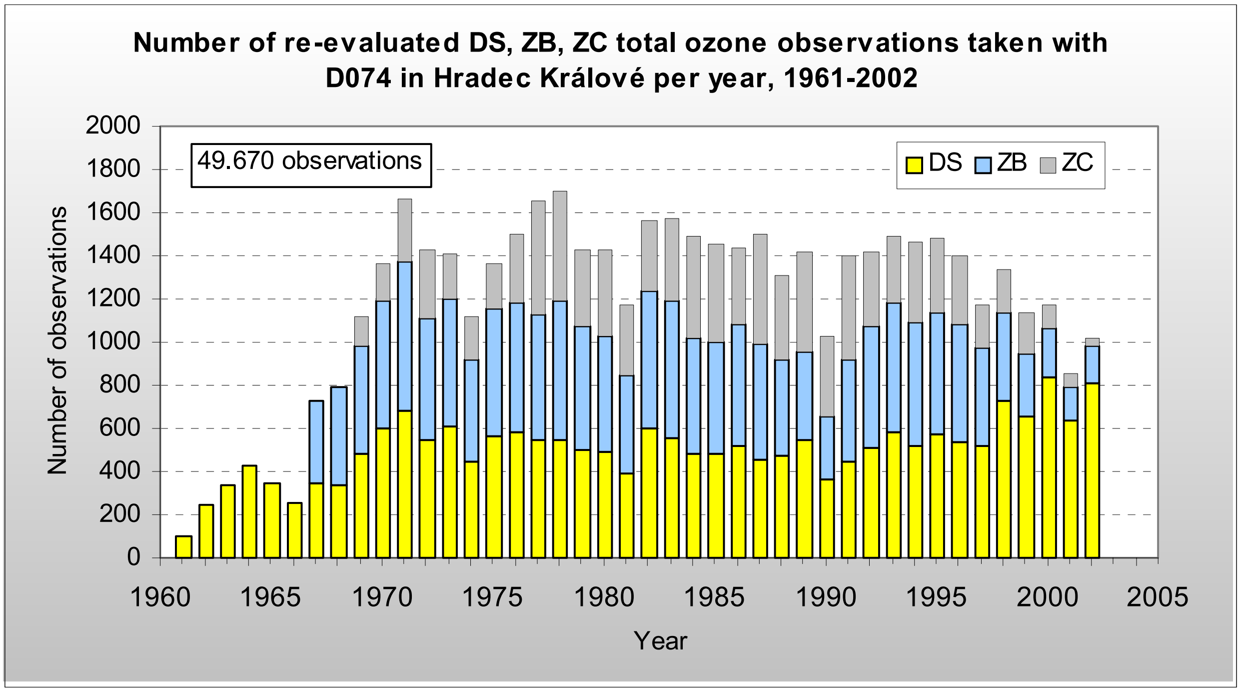

Figure 2. *Numbers of re-evaluated total ozone observations performed with the D074 at SOO-HK in particular years of the period 1961-2002*

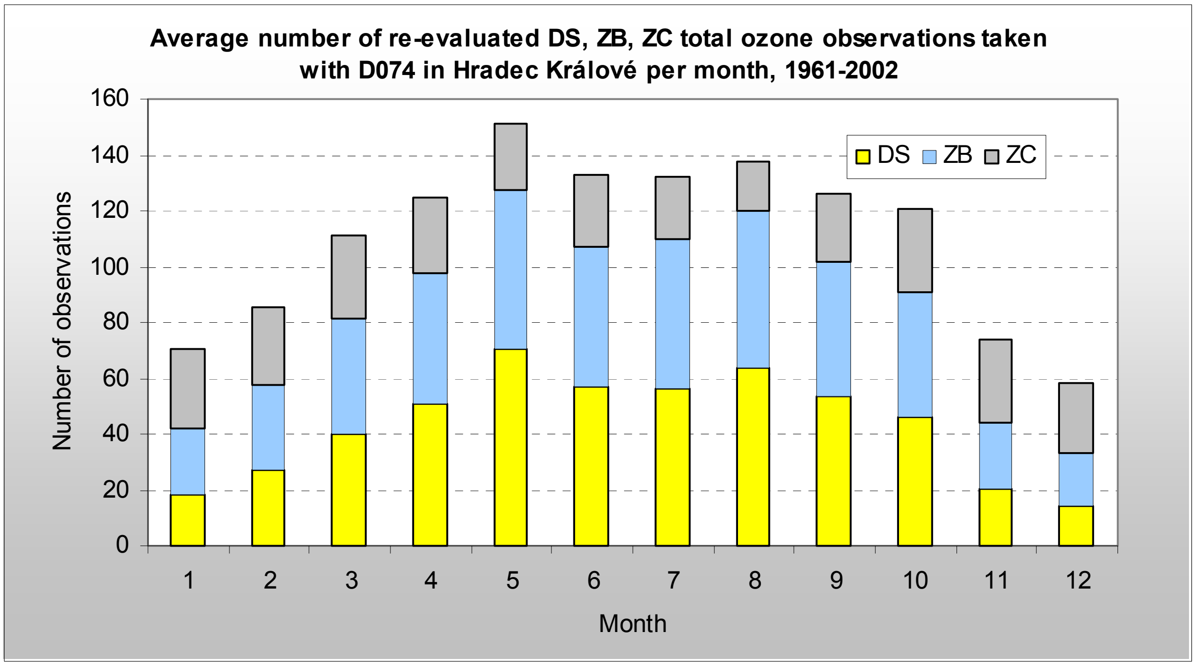

Figure 3. *Average numbers of re-evaluated total ozone observations performed with D074 at SOO-HK in particular months of the period 1961-2002*

Numbers of observations that are available for particular years after a quality check and filtering done under the re-evaluation process in 2002 is viewed in *Figure 2*. The graph shows a rapid increasing of the total amount of measurements up to 1400 per year at the end of the sixties and quite stable distribution of DS, ZB and ZC observations afterwards. After 1999, when D074 was preferably used for reference measurements, the number of DS observations relatively increased while the zenith measurements reduced. The total number of observations (completed sequences) deposited in the historical data base was 52.162 for the period 1961-2002 and it was reduced to 49.670 sequences after the re-evaluation and quality check done under the CANDIDOZ project.

In Figure 3 average annual amounts of particular types of observations are sorted by months to demonstrate differences in yearly distribution of measurements due to astronomical and climate conditions for observations (mainly duration of the sun shine and amount of clouds). The graph shows that in the period March - October DS measurements contribute by 45-50 % while in the period November - February only by 25-35%. The rest are the zenith observations (mainly ZB) that significantly enlarge the database and influence the total ozone statistics.

b) Processing of observational data - theory

The methodology of measurements and calculation of total ozone is defined in the fundamental papers *[Dobson. 1957a]* and *[Komhyr, 1980]* and is also described in many subsequent publications including *[Vaníček, 2002]*. Therefore, only key relations that are important for understanding the data re-processing are included in this report.

Measurement of total column ozone in the atmosphere with the Dobson ozone spectrophotometer comes out from the equation of attenuation of the solar ultraviolet radiation by key atmospheric constituents.

$$\log I = \log I_0 - \alpha \mu O_3 - \beta m p/p_o - \delta \sec ZA \qquad (1)$$

where:

- I_0 ... spectral intensity outside the atmosphere (extraterrestrial)
- I ... spectral intensity of solar radiation at the ground
- O_3 ... total amount of ozone in the atmosphere in Dobson Units (mili-atm-cm)
- ZA ... zenith angle of the Sun
- m ... relative path of the solar radiation through the atmosphere
- p ... observed air pressure at the ground
- p_o ... mean sea level pressure
- α ... spectral absorption coefficient of ozone
- β ... spectral Rayleigh molecular scattering coefficients of the air
- δ ... spectral scattering coefficients of aerosol particles
- μ ... relative path of the solar radiation through the ozone layer

For two wavelengths with a high (λ_1) and low (λ_2) ozone absorption selected in the ultraviolet part of the solar spectrum the total ozone can be calculated from the relation:

$$O_3 = (N - (\beta_1 - \beta_2) m p/p_o - (\delta_1 - \delta_2) \sec ZA) / (\alpha_1 - \alpha_2) \mu \qquad (2)$$

where:

$$N = \log(I_{01}/I_{02}) - \log(I_1/ I_2) = N_0 - \log(I_1/ I_2) \qquad (3)$$

If wavelength pairs A,C,D given in *Table 1* are taken then the influence of aerosol particles can be eliminated by subtraction of their equations (2) and the relation for total ozone adjusted for the pairs AD, CD as:

$$O_{3AD} = (N_A / \mu_A - N_D / \mu_D) / (\alpha_A - \alpha_D) - (\beta_A - \beta_D)\, m\, p / (\alpha_A - \alpha_D)\, \mu_{AD}\, p_o \quad (4)$$
$$O_{3CD} = (N_C / \mu_C - N_D / \mu_D) / (\alpha_C - \alpha_D) - (\beta_C - \beta_D)\, m\, p / (\alpha_C - \alpha_D)\, \mu_{CD}\, p_o \quad (5)$$

where μ_A, μ_C, μ_D are values of μ calculated for times of each observed wavelength pair separately *[Komhyr, 1988]*, *[Staehelin et al., 2003]*.

The parameter N expresses the difference between logarithms of ratios of extraterrestrial and ground intensities of radiation at both wavelengths as it can be measured by a Dobson instrument. Values of N therefore depend on actual properties of the atmosphere (mainly on total amount of ozone) represented by $\log(I_1/ I_2)$ and on technical condition of the instrument given by the ratio $N_0 = \log(I_{01}/I_{02})$ that is called the "extraterrestrial constant - ETC". ETC is defined for a particular spectrophotometer and used for development of N-Tables that convert R-values (position of the dialing ring) onto N-values (3). The N-Tables represent key calibration constants of the instrument *[Vaníček, 2002]*.

Table 1. *Ozone effective absorption and atmospheric scattering coefficients adopted for selected wavelength pairs in January 1992 (the Bass-Paur Scale) [Komhyr et al., 1993].*

Pair	Wavelength nm	Ozone Abs. Coeff. α (atm-cm)-1	Atm. Scatt. Coeff β (atm)-1
A	λ_1 305.5 λ_2 325.4	1.915 0.109	0.489 0.375
C	λ_1 311.5 λ_2 332.4	0.873 0.040	0.450 0.341
D	λ_1 317.5 λ_2 339.9	0.384 0.017	0.414 0.310

c) Maintenance of the Dobson data records

Since the very beginning of total ozone observations made with D074 at SOO-HK all the original "raw data" and calculated total ozone values were recorded in hand-written forms implemented by WMO. The filled-in forms are deposited in the archives of the Observatory. The raw-data sets comprise date, time and type (DS, ZB,ZC) of observations, R-values for wavelength pairs A,C,D and weather conditions during measurements (amount and type of clouds in the zenith, visibility). Since January 1986, when SOO-HK was equipped with a personal computer, the observed data have been routinely recorded onto magnetic media together with calculated total ozone values and re-printed as hard-copies by PC printers, as well. These input/output data files are kept together with calibration records and tests of the instrument D074 in a complex database that allows re-processing of any particular or the entire series of measurements taken with the spectrophotometer in the period 1961 onwards - see Chapter 3.

2.2. Observations made with the Brewer spectrophotometer B098

a) Operation schedules for total ozone and total SO_2 measurements

The Brewer ozone spectrophotometer, type MAR-IV, No. 098 (B098), see *Figure 4*, was installed at SOO-HK by experts of the International Ozone Service Inc., Toronto, Canada in December 1993. Regular observations of total ozone and global UV-B spectral irradiance started officially on January 1, 1994. The calibration constants defined by the producer in the Acceptance Manual *[SCI-TEC, 1993]* were used in the first year of operation of B098 and they were updated in next years - see Chapter 4.1. Measurements of total ozone and technical tests of the instrument are performed in the fully automated mode under the guide-lines defined and recommended in the Maintenance and Users Manuals provided by the producer - the SCI-TEC Instruments company, Canada, now Kipp&Zonen, Delft, the Netherlands: http://www.kippzonen.com/ *[SCI-TEC, 1990, 1992, 1999]*.

Figure 4. *The Brewer MARK-IV spectrophotometer B098 operated at the Solar and Ozone Observatory in Hradec Králové*

Since 1994 both Direct Sun (DS) and Zenith Sky (ZS) total ozone observations and UV-B scans have been performed at SOO-HK every day in schedules created for the fixed zenith angles ZA = 75, 70, … , 30, local apparent noon. The ZA-schedules give enough number of simultaneous total ozone and UV observations for the same positions of the Sun in different seasons (this allows a later development and application of ozone/UV models) and they save the spectrophotometer from fast degradation. Commands for regular Standard Lamp (SL) and Mercury Lamp (HG) tests are also included in daily schedule that has the following basic structure - for details see *[SCI-TEC, 1999]*:

pf b1 sl uv hg ds zs ds zs ds (6)

As the definition of operational schedules of Brewer spectrophotometers is very flexible some other schedules, not mentioned here, are used for specific reasons at SOO-HK, e.g. for experimental or comparative observations or for calibration procedures. The sequence of the schedule (6) includes both Direct Sun (ds) and Zenith Sky (zs) commands for total ozone measurements. If Sun is covered by clouds the instrument makes only zenith observations. The spectrophotometer makes a decision whether to make or not a DS measurement by means of the empirical regression function developed for the location of SOO-HK and included in the operational software package. Numbers of photon counts and actual value of μ are taken as proxies in the regression. It should be pointed out here that the Brewer spectrophotometer does not recognize actual condition of the sky in the zenith. Therefore, it can not distinguish between blue and cloudy zeniths and makes the general Zenith Sky (ZS) type of measurements. This is a difference in comparison with the Dobson spectrophotometer where the operator can always decide what type of observations is to be made - either ZB or ZC. Simultaneous DS and ZS observations performed under the schedule (6) also allow to develop zenith polynomials for B098 like for the D074 instrument - see Chapter 4.2.b).

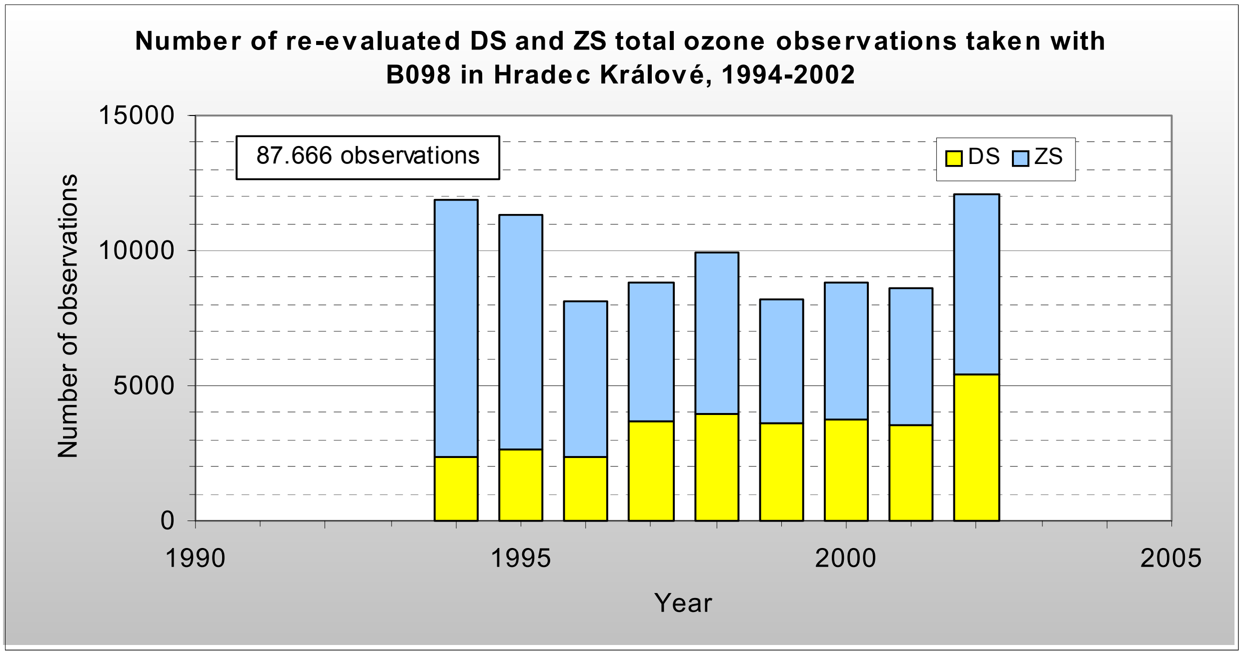

Figure 5. *Number of re-evaluated total ozone observations performed with the Brewer spectrophotometer B098 at SOO-HK in particular years of the period 1994-2002*

Distribution of 87.666 re-evaluated observations performed by B098 at SOO-HK in particular years of 1994-2002 is viewed in *Figure 5*. It is evident, comparing with *Figure 2*, that the automated B098 generated about 7 times more measurements than the manually operated D074. This demonstrates a higher observational capacity of the Brewer spectrophotometer. Almost the same rate appears for monthly average numbers of measurements presented in *Figure 6*. The most favorite conditions for observations are in May, the worst are in November and in December. The graph in *Figure 5* also demonstrates an evident increase of the number of DS observations in 1997 when a subroutine for detection of “clear Sun” has been included into the operational programme of B098 - see the previous paragraph.

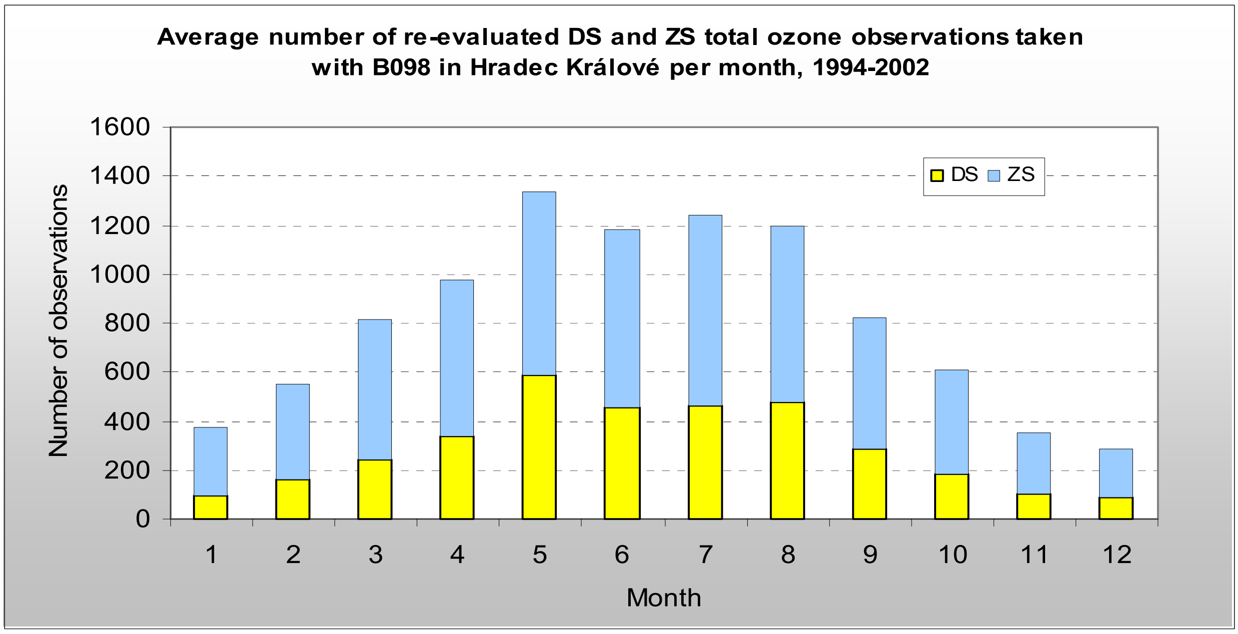

***Figure 6**. Average number of re-evaluated total ozone observations performed with the Brewer spectrophotometer B098 at SOO-HK in particular months of the period 1994-2002*

b) Processing of observational data - theory

The principle of measurements of total ozone and SO_2 column in the atmosphere with the Brewer spectrophotometer is similar to the method used for the Dobson spectrophotometer. The Brewer instrument measures spectral irradiances I_i of the solar radiation at 5 wavelengths $\lambda_1 \ldots \lambda_5$ selected by rotating slit mask - see *Table 2*. The irradiances are registered as photon counts F2 … F6 generated in the photo tube.

***Table 2.** Positions of the slitmask and the selected wavelengths defined for technical tests and total ozone, SO_2 and NO_2 measurements with the Brewer MARK-IV spectrophotometer*

Slitmask position	**Photon counts**	**Intensities**	**Selected wavelengths λ (nm) for O3 and SO_2**	**for NO_2**
0			λ = 303.2	HG Tests
1	F1		Dark Count	
2	F2	I_1	$\lambda_1 =$ 306.3	431.4
3	F3	I_2	$\lambda_2 =$ 310.0	437.3
4	F4	I_3	$\lambda_3 =$ 313.5	442.8
5	F5	I_4	$\lambda_4 =$ 316.8	448.1
6	F6	I_5	$\lambda_5 =$ 320.0	453.2
7			Dead Time λ_2 & λ_4	

If sulphur dioxide is taken into account as a selective absorber then the equation (1) can be re-written using linear combinations F, F_0 $\Delta\alpha$, $\Delta\beta$, $\Delta\delta$ of logarithms of extraterrestrial and measured intensities I_i , I_{0i} , ozone and SO_2 differential absorption coefficients α_i, α_i', Rayleight molecular scattering coefficients β_i and scattering coefficients of aerosol particles δ_i as:

$$F = F_0 - \Delta\beta\, m\, p/p_o - \Delta\delta \sec Z - \Delta\alpha\, O_3\, \mu - \Delta\alpha'\, SO_2\, \mu' \quad (7)$$

By means of linear combinations of photon counts F(i) specified in *Table 2* and measured with the instrument the values of total ozone and total sulphur dioxide can be calculated by relations (see e.g. *[Josefsson, 1986]*, *[Wardle et al., 1987]*, or *[SCI-TEC, 1988]*) :

$$O_3 = (M(9) - F_0) / \Delta\alpha\, \mu \quad (8)$$

$$SO_2 = (M(8) - S_0) / \Delta^*\alpha'\, \mu' - \Delta^*\alpha\, O_3\, \mu / \Delta^*\alpha'\, \mu' \quad (9)$$

where M(i) are ratios defined by F(i) as:

M(4) = F(5) - F(2)
M(5) = F(5) - F(3)
M(6) = F(5) - F(4))
M(7) = F(6) - F(5))
M(8) = M(4) - 3.2 M(7)
M(9) = M(5) - 0.5 M(6) - 1.7 M(7)

The linear combinations F_0 and S_0 are called the ozone and SO_2 "extraterrestrial constants" of the Brewer spectrophotometer (like N_0 in the relation (3) for the Dobson spectrophotometer). F_0 and S_0 are important instrument-dependent calibration constants which significantly influence accuracy of ozone and SO_2 measurements - see. Chapter 4.1.c).

c) Maintenance of the Brewer data files

On the contrary to the Dobson spectrophotometer (if it is not equipped with a special auxiliary PC-controlled system) the Brewer observations and data processing are fully automated. The instrument is controlled by a connected PC equipped with an operating software package that allows standardized performance of pre-defined working schedules, reading signals from the instrument, processing the data and recording all input/output data in the instrument´s database. The data are saved in free-accessible files and they are maintained and updated automatically during operation of the instrument.. Therefore, the database is flexible for external utilizations by means of any compatible software tools applied by users. This makes fast re-processing, statistical operations or data transfers possible. At SOO-HK a very powerful auxiliary software package called O3BREWER has been created and installed in 2000. The software has been installed at some other Brewer stations of the GAW network and it is free-available at: http://www.chmi.cz/meteo/ozon/brewerweb/main.htm.

2.3. Application of the total ozone data from SOO-HK - a need of re-evaluation

a) Scientific and operational applications of data

As mentioned in Chapter 2.b), the outputs of total ozone measurements (daily and monthly averages) from SOO-HK are regularly deposited in WMO/WOUDC Toronto since the observations started in 1961 and 1994, respectively. The data files are free-accessible to users there. The more detailed data like individual observations sorted by type, time and SZA are not available in WOUDC. They are used for specific analyses carried out at SOO-HK or by external partners. The D/B measurements taken at satellite overpass or ozone sounding times are typical examples. Samples of individual measurements created for investigation general technical characteristics of both instruments (μ or temperature dependence, D/B data relations, etc.) represent specific applications of the data. Moreover, total ozone observations from SOO-HK are operationally presented together with UV-Index values in Czech mass media in daily reports that inform the public about actual condition of the ozone layer over CR. The observations are also submitted every day to the World Ozone Mapping Center of WOUDC where they are used with assimilate satellite observations for mapping of global distribution of total ozone in the northern hemisphere.

b) Reasons for re-evaluation

Total ozone data series from SOO-HK have been generated by D074 and B098 under different technical condition of both instruments in particular time periods of their operation defined by individual intercomparisons or technical adjustments. A complex analysis of calibration histories and re-definition of calibration constants of the spectrophotometers using all available historical records including regular lamp tests was completed in 2002 *[Vaníček, 2002]*. This study and special software tools created at SOO-HK *[Staněk, 1998]* allow a fast re-calculation of all total ozone observations performed in Hradec Králové by means of compatible instruments´ constants related to the Dobson and Brewer world standards and using the same set of the Bass-Paur ozone absorption coefficients *[Komhyr et al., 1993]* implemented by the International Ozone Commission (IOC) in January 1992. In this way it is possible to create updated D/B total ozone data sets homogenized according to calibration and operational constants and by means of unified technology of data processing. Thus, the re-evaluated observations would represent the data sets of the highest achievable quality which can contribute to precise investigation of long-term trends of total ozone in the northern mid latitudes as well as to an assessment of relation between total ozone data originated by different instruments.

3. RE-EVALUATION OF THE DOBSON TOTAL OZONE OBSERVATIONS, 1961-2002

3.1. Calibration history of the Dobson spectrophotometer D074

a) Dobson reference spectrophotometers, international comparisons

Dobson ozone spectrophotometers are operated and observations are processed by means of sets of calibration constants which guarantee required accuracy of total ozone measurements. The constants are defined towards reference Dobson instruments recognized as the standards for the network. Since the end of the seventies the Dobsons operated in the GAW network have been maintained in the calibration scale represented by the World Primary Dobson Spectrophotometer (WPDS) D083 established by the Climate Monitoring and Diagnostic Laboratory (CMDL) of NOAA, Boulder, Colorado, USA - the World Dobson Calibration Center (WDCC) *[Komhyr et al., 1989]*. Either WPDS or the traveling standard instrument D065 (implemented and regularly compared towards D083 at CMDL) are used for calibration campaigns organized under co-operation of NOAA/CMDL and WMO/GAW

[Evans, 1994, 2001]. Since 1999 the spectrophotometer D064 has been used as a regional reference instrument at ICs organized by the Meteorological Observatory Hohenpeissenberg (MOHp) of the German Meteorological Service designated as the WMO Regional Dobson Calibration Center - Europe *[Koehler, 2002]*. Regular calibrations/intercomparisons of instruments from the network are scheduled in about four-year periods to update calibration constants periodically and to keep the accuracy of instruments on the required level *[WMO, 2001b]*.

b) Intercomparisons of D074 - relation towards reference instruments

The spectrophotometer D074 from Hradec Králové was originally calibrated by the producer in 1959 and in the next decades at several intercomparisons (ICs) listed in *Table 3*. In 1986, at IC-86 Arosa, the instrument was first directly compared towards the world standard WPDS. Since that time D074 was permanently kept in the WPDS´s calibration scale. Due to the regular calibrations its offset was less than 1 % comparing to reference instruments after 1986 - see *Figure 7*. For the period 1961-1986 there were three ICs of D074 performed (*Table 3*) - at IC-59 towards an unknown reference of the producer, at IC-69 towards D084 (not being officially recognized as a reference), at IC-79 towards D071 (for several years an official regional reference, but with unstable condition *[Grasnick et al., 1991]*). Therefore, these ICs do not represent reliable and reference points in the calibration history of D074 (see offsets higher that 1% at IC-79 viewed in *Figure 7*). They can be only taken as auxiliary sources of information for validation of re-constructed sets of calibration constants, as described in detail in *[Vaníček, 2002]* and briefly commented in the next paragraph.

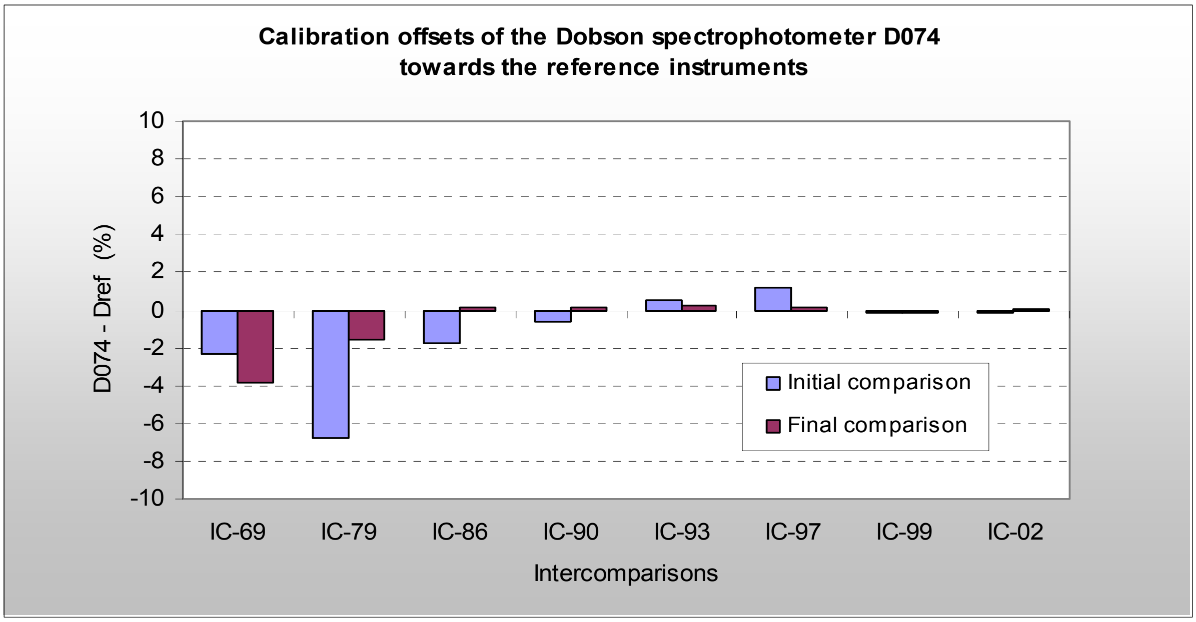

Figure 7. *Calibration offsets of the Dobson spectrophotometer D074 towards the reference instruments at intercomparisons performed in the period 1969-2002*

Table 3. *International comparisons and calibrations of the Dobson spectrophotometer D074 and periods of use of the calibration constants*

Year	**Place**	**Acronym**	**Reference instrument**	**Calibration constants defined (see Appendices A and B) - period in use**	
1959	London	IC-59	Not known, Beck-London	QT-59	01.01.1962 - 12.06.1979
				NT-59	01.01.1962 - 31.12.1969
				RR-59	01.01.1962 - 25.06.1979
1969	Siofok	IC-69	D084, Belsk, Poland	NT-69	01.01.1970 - 12.06.1979
1979	Potsdam	IC-79	D071, Potsdam, Germany	QT-79	13.06.1979 - 15.07.1990
				NT-79	13.06.1979 - 14.08.1986
				RR-79	09.06.1979 - 13.07.1986
1986	Arosa	IC-86	D083, NOAA, Boulder, USA	NT-86	15.08.1986 - 25.07.1990
				RR-86	15.08.1986 - 26.07.1990
1990	Arosa	IC-90	D065, NOAA, Boulder, USA	QT-90	17.07.1990 - 27.07.1997
				NT-90	26.07.1990 - 21.07.1997
				RR-90	02.08.1990 - 21.07.1997
1993	Hradec Králové	IC-93	D065, NOAA, Boulder, USA	No changes of calibration constants	
1997	Kalavryta	IC-97	D065, NOAA, Boulder, USA	QT-97	22.08.1997 - 31.12.2002
				NT-97	22.07.1997 - 16.07.1999
				RR-97	22.07.1997 - 16.07.1999
1999	Arosa	IC-99	D065, NOAA, Boulder, USA	NT-99	17.07.1999 - 23.07.2002
				RR-99	17.07.1999 - 23.07.2002
2002	Hohenpeissenberg	IC-02	D064, MOHP, Germany	NT-02	24.07.2002 - 31.12.2002
				RR-02	24.07.2002 - 31.12.2002

c) Re-definition of calibration constants of D074 for the period 1961-2002

There are three basic sets of calibration constants necessary for operation of a Dobson spectrophotometer and processing of total ozone observations *[Dobson,1957a]*, *[Komhyr, 1980]*. These are:

- Q-Setting Tables (QT)
  The tables for a correct selection of standard wavelengths according to the actual temperature of the instrument

- N-Tables (NT)
  The tables allow conversion of R-readings (positions of the dialing ring) onto N-values used for calculation of total ozone by equations (4) or (5). The N-Tables are defined by the instrument´s "Extraterrestrial Constant" $N_0 = \log(I_{01}/I_{02})$ and by logarithms of spectral intensities $\log(I_1/I_2)$ derived from calibration of wedges - se the relation (3).

- Reference R-Readings (RR)
  The values of Standard Lamp Tests performed with the instrument´s standard lamps at ICs when new Q-Tables and/or N-Tables are implemented. The Reference R-Readings are used for routine corrections of N-Tables based on regular (monthly) lamp tests performed at a station in time periods between particular ICs *[Komhyr, 1980]*.

It is evident from *Figure 7* that calibration constants defined at intercomparisons of D074 (*Table 3*) perfectly represented the calibration scale of WPDS after IC-86 while for the period before August 1986 they need to be re-defined. The first backward corrections of D074 calibration constants were done in 1991 after the spectrophotometer passed through ICs-79,86,90 in an attempt to re-calculate historical total ozone observations from SOO-HK *[Vaníček, 1991]*. But this work was not complex as some technical records, calibration protocols and information about stability of technical parameters of D074 were not known to the author at that time.

The historical pieces of information on D074 and its operation gathered at SOO-HK (mainly old protocols of Standard Lamp Tests) and from external sources in the last decade allowed a detailed re-construction of its calibration history *[Vaníček, 2002]*. These calibration constants specified in *Table 4* were used together with monthly routine or approximated Standard Lamp Tests for re-calculation of the entire series of Dobson observations from Hradec Králové, as described in Chapter 3.2.

Table 4. *Calibration constants of the Dobson spectrophotometer D074 recommended for a re-processing of the total ozone observations taken with the instrument in the period 1961-2002 [Vaníček, 2002].*

Period of application	**Q-Tables**	**N-Tables**	**Ref. R-Readings**	**SL-Corrections**
01.01.1961 - 12.06.1979	QT-59	NT-79/86	RR-79/RR-86	Monthly approx. of SL-Tests
13.06.1979 - 14.08.1986	QT-79	NT-79/86	RR-86	Monthly approx. of SL-Tests
15.08.1986 - 18.07.1990	QT-79	NT-86	RR-86	Regular monthly SL-Tests
19.07.1990 - 21.071997	QT-90	NT-90	RR-90	Regular monthly SL-Tests
22.07.1997 - 16.07.1999	QT-97	NT-97	RR-97	Regular monthly SL-Tests
17.07.1999 - 31.12.2002	QT-97	NT-99	RR-99	Regular monthly SL-Tests

3.2. Re-calculation of D074 total ozone observations

The re-defined calibration constants of D074 allowed re-processing of the total ozone data series created with the spectrophotometer at SOO-HK in 1961-2002 on the highest achievable level of accuracy related to the WPDS´s. The re-calculation was performed with respect to general recommendations and procedures summarized in [Bojkov et al.,1993]. Results of re-evaluations of Dobson data sets at other GAW stations were also taken into account, e.g. *[Degorska M. and B. Rajewska-Wiech, 1991]*, *[Bjarnason et al., 1992]*, *[De Muer and De Backer, 1992]*, *[Koehler, 1995]*, *[Staehelin et al., 1998]*, *[Josefsson, 2000]*. The key technological steps of the re-calculation of observations from Hradec Králové are specified in the following paragraphs.

a) Ozone absorption and Rayleigh scattering coefficients

The ozone absorption and Rayleigh scattering coefficients are important parameters in the equations (4) and (5) for total ozone calculations. Values of the coefficients were changed in the last decades several times as the knowledge of atmospheric spectroscopy and laboratory technologies were improved. Those sets of coefficients used in the Dobson network are listed in *Table 5 [IOC, 1991]*. Application of different sets of coefficients for routine processing of Dobson total ozone observations have several impacts that should be taken into account if the observations are re-evaluated and the data files are taken by users for scientific analyses. These can be specified as follows.

− The Dobson stations with long-term records used different sets of coefficients in the past- see *Table 5*. If the observations have not been re-processed or corrected with respect to one reference set of coefficients (usually the latest Bass-Paur) the data series are not homogeneous in quality during a certain time period. Then breaks in trends can appear not due to atmospheric processes but as a result of changes of coefficients used for calculation of total ozone.

− Total ozone observations deposited in central data bases like in WOUDC were submitted from stations as final data (daily or monthly averages of total ozone) calculated by means of coefficients valid in actual period of time. Though the data files in WOUDC have been corrected for the Bass-Paur scale *[WMO/WOUDC]* in some local/national databases the total ozone values may still be kept in different scales. This should be investigated by data users station by station before the data sets are used for scientific applications.

− The Dobson total ozone data stored in WOUDC have been converted into the Bass-Paur scale by means of multiplication factors recommended by IOC *[Megie et al., 1991]* with errors less than 0.3% for AD pair and $1< \mu <3$ and $220 < O_3 < 550$ DU. Nevertheless, if Dobson data sets are re-evaluated at a station where original raw records are available, an exact re-processing of measurements by means of homogenized calibration constants of spectrophotometer (s) and the latest set of ozone absorption coefficients is recommended. The re-evaluated observations should be re-deposited into WOUDC as a new data set equipped with proper comments and description of the re-evaluation technology applied.

− The ozone absorption coefficients are temperature-dependant. The Bass-Paur set of coefficients actually used in the GAW network is defined for the mean stratospheric temperature (effective ozone temperature) -46.3 ^{o}C weighted by standard ozone and temperature profiles (US Standard Atmosphere 1962) for 45 ^{o}N, $\mu = 2$ and 325 DU total ozone. These facts should be reflected if the Dobson observations are compared with total ozone measurements performed with other instruments using different wavelengths (e.g. Brewer spectrophotometers) or with total ozone data determined with ozone absorption coefficients/scales not mentioned in Table 5 (e.g. ozone cross sections used in satellite systems).

The total ozone measurements originated with D074 in 1962-2002 were processed and deposited into WOUDC in particular years and months in both Vigroux and the Bass-Paur scales according to currently valid set of absorption coefficients. In 1991 all observations of 1962-1990 were converted into Vigroux 1968 scale *[Vaníček, 1991]* and re-submitted to WOUDC. Later, the entire data series from SOO-HK were adjusted by the staff of WOUDC for the Bass-Paur scale using the correction factors recommended by IOC. This is the latest version of the data set available at WOUDC in 2002 - marked as **D074-V1991** in this paper. For a complex re-processing of the Dobson observations taken at SOO-HK, which is a subject of this Report, the set of Bass-Paur ozone effective absorption and Rayleigh coefficients was used, as defined in *[Komhyr et al., 1993]* and given in *Table 1*.

Table 5. *Sets of ozone absorption and Rayleigh coefficients which have been officially implemented and applied at Dobson stations since the thirties [IOC, 1991]*

Version of the coefficients	**Reference**	**Period of application**
The original set	[Ny and Choong, 19333]	before 01.06.1956
The first Vigroux set (IGY)	[Dobson, 1957]	01.06.1956 - 31.12.1967
The second Vigroux set	[Vigroux, 1967]	01.01.1968 - 31.12.1991
The Bass-Paur set	[IMegie et al., 1991]	01.01-1992 onwards

b) Calculation of the relative optical air mass of the ozone layer - μ

The relative optical path length of the UV solar beam through the ozone layer μ is a parameter calculated for the exact date and time of a total ozone observation. Therefore, μ needs to be determined as precisely as possible because its value influences accuracy of total ozone calculation by equations (4) or (5). Calculation of μ (described e.g. in *[Komhyr, 1980]*) is mostly affected by the accuracy of determination of the solar zenith angle through relevant astronomical parameters ("time equation" and declination of the Sun) for the time when Dobson observations are taken at individual pairs A,C,D - see Chapter 2.1.b). At present the astronomical tables recommended for calculation of SZA e.g. in can be replaced by exact calculations by computers. In the updated version of the software package DOBSON-4.0 developed at SOO-HK *[Staněk, 1998]*, which was used for re-processing of the Dobson observations of 1961-2002, the altitude of the ozone layer was approximated for Hradec Králové from *[Komhyr, 1980]* and calculations of μ_A, μ_C and μ_D were done by means of algorithms and subroutines presented in *[Meeus, 1991]* - more details are available at : http://www.srrb.noaa.gov/highlights/sunrise/calcdetails.html.

c) Input raw-data sets

Since the very beginning of operation of D074 the original readings of total ozone observations (the raw data) have been carefully filed and archived at SOO-HK. Therefore there are no periods with missing records at the Observatory. The raw data were written into standard forms recommended by WMO till 1984. Since 1985, after SOO-HK was equipped with personal computers, the readings have been recorded by operators into a modified version of the form and they are automatically saved in electronic files.

Altogether 52.162 total ozone observations were taken with D074 in the period 1961-2002. A complex re-processing of these measurements and evaluation of outputs was done by means of the software package DOBSON-4.0 that works with electronic input data files. Therefore, the raw data of 28.671 observations taken in the period 1961-1984 and archived in hand-written paper forms had to be converted onto CDs before re-calculations were performed (the input data of the years 1985-2002 were available on CDs from routine processing at the PC). All 52.162 total ozone measurements were re-calculated without a preceding quality check. The raw data of DS and ZB/ZC measurements were selected into input files and processed separately in two steps, as described in the next paragraphs.

d) Re-processing of direct sun DS observations

In the first step the D074 Direct Sun observations were processed for AD and CD double-pairs by the equations (4) and (5). The re-defined calibration constants specified in *Table 4* and the Bass-Paur set of the ozone absorption and the Rayleigh molecular scattering coefficients were used for the entire period 1961-2002. The relative optical path lengths μ_A, μ_C, μ_D were calculated for the times of R_A, R_C, R_D readings taken in the C-D-A sequence.

e) Re-processing of zenith observations (ZB.ZC) - updating of the zenith polynomials

The Zenith Blue and Zenith Cloudy total ozone measurements are not calculated by relations that exactly describe physical processes in the atmosphere. These types of observations are processed by means of empirical relations between $R_{A,C,D}$-readings ($N_{A,C,D}$-values) and $\mu_{A,C,D}$ values determined from a ZB measurement and a DS O_{3AD} total ozone measured quasi-simultaneously. For the ZC observations empirical cloud-corrections are also applied. The relations were originally represented by manual graphs (zenith charts) that were typical for an instrument and a place of its operation *[Dobson. 1957a]*, *[Komhyr, 1980]*. In the recent years the charts have been replaced and empirical relations are mostly expressed by polynomial regressions calculated on computers *[Asbridge et al., 1996]*, *[De Backer, 1998]*.

The ZB and ZC measurements taken with D0074 at SOO-HK have been processed by the DOBSON-4.0 software that includes also a statistical supporting package DOBSTOOL for development or updating of zenith polynomials and cloud-corrections CCs *[Staněk, 1998]*. The polynomial is defined as a multi-regression function:

$$O_{3ZB} = a_0 + a_1\mu + a_2y + a_3\mu^2 + a_4y^2 + a_5\mu y + a_6\mu^2 y + a_7\mu y^2 + a_8\mu^3 + a_9y^3 \quad (10)$$

where $a_0 \ldots a_9$ are regression coefficients and $y = N_A - N_D$ or $y = N_C - N_D$.

***Table 6**. Regression coefficients of the zenith polynomials (10) of the instrument D074 and the location of SOO-HK, AD, CD double-pairs, summer and winter months, developed for 1967-2002*

Regression Coefficients	**Summer M,A,M,J,J,A,S,O**		**Winter N,D,J,F**	
	AD	CD	AD	CD
a_0	274.34956	313.32672	312.51712	60.40558
a_1	-460.00467	-454.84292	-426.49899	-273.33932
a_2	10.51474	26.78874	8.909783	35.749038
a_3	238.91454	242.49975	169.74567	156.41758
a_4	-0.00372	0.17229	-0.01418	-0.11383
a_5	-5.24900	-16.59829	-2.91408	-15.09512
a_6	-0.00369	-0.02528	0.34615	1.21073
a_7	0.01778	0.16737	0.00068	0.07282
a_8	-24.80584	-24.89736	-21.25218	-20.30799
a_9	-0.00009	-0.00485	0.00006	-0.00041

Tests of zenith polynomials defined at different stations showed their geographical and seasonal dependency *[Asbridge et al., 1996]*. Therefore, specific winter (N,D,J,F,) and summer (M,A,M,J,J,A,S,O) polynomials have been developed for D074 and the location of SOO-HK. The polynomials, which are represented by coefficients given in *Table 6*, have been applied for recalculations of zenith observations in this study. The coefficients were determined by the statistical least-square-fit method using 13.553 simultaneous (less than 5-

minute time-shift) DS and ZB observations performed at SOO-HK in the period 1967-2002. Also a table of cloud-corrections CC (given in DU) and opacity multiplication factors OF (*Table 7*) has been prepared by the DOBSTOOL program for the climate condition of SOO-HK and applied for processing of ZC measurements by the relation:

$$O_{3ZC} = O_{3ZB} + CC * OF \quad (11)$$

The quality and accuracy of the re-processed ZB and ZC observations are assessed in the next Chapter 3.3.

Table 7. *Cloud-corrections CC in DU and opacity factors (11) determined for the instrument D074 and the location of SOO-HK, AD, CD double-pairs, 1967-2002*

Mu X	**1.0**	**1.2**	**1.4**	**1.6**	**1.8**	**2.0**	**2.2**	**2.4**	**2.6**	**2.8**	**3.0**	**3.2**
AD double pair												
250	8	8	8	10	10	9	7	7	8	8	9	10
275	8	8	8	10	10	9	7	7	8	8	9	10
300	10	10	9	9	9	9	8	8	9	9	9	10
325	11	11	10	9	9	9	9	9	10	10	10	11
350	11	11	10	9	9	10	10	10	10	10	11	12
375	11	11	10	9	9	11	11	11	10	10	11	12
400	10	10	10	9	9	11	11	11	11	11	11	11
425	9	9	9	9	9	10	11	11	11	11	11	11
450	9	9	9	9	9	10	11	11	11	11	11	11
475	9	9	9	9	9	10	11	11	11	11	11	11
500	9	9	9	9	9	10	11	11	11	11	11	11
525	9	9	9	9	9	10	11	11	11	11	11	11
550	9	9	9	9	9	10	11	11	11	11	11	11
CD double pair												
250	18	18	18	19	19	18	17	16	14	13	13	13
275	18	18	18	19	19	18	17	16	14	13	13	13
300	17	17	17	17	18	19	20	18	16	13	13	13
325	16	16	16	15	16	20	22	20	18	13	13	13
350	16	16	16	14	15	18	20	18	16	13	13	13
375	15	15	15	13	14	15	17	16	14	13	13	13
400	15	15	15	13	14	14	15	14	13	13	13	13
425	14	14	14	13	13	13	13	13	13	13	13	13
450	14	14	14	13	13	13	13	13	13	13	13	13
475	14	14	14	13	13	13	13	13	13	13	13	13
500	14	14	14	13	13	13	13	13	13	13	13	13
525	14	14	14	13	13	13	13	13	13	13	13	13
550	14	14	14	13	13	13	13	13	13	13	13	13
Opacity Factor: OF = 0.3 (small), 0.7 (medium), 1.0 (large), 1.2 (fog)												

3.3. Evaluation of outputs

The re-calculated total ozone observations represent a new data set created with D074, hereafter marked as **D074-V2003**, which will replace the previous version D074-V1991. Before D074-V2003 measurements are officially implemented and used for scientific applications the quality of the new data needs to be evaluated with respect to accuracy of the instrument D074 and methodology of the re-processing described in the previous chapters. Impacts of statistical sampling of the measurements according to type and number of the data and relation between D074-V1990 and D074-V2003 need to be investigated, as well.

a) Quality assessment of the re-calculated observations

Direct Sun observations

- An instrumental accuracy of DS-AD total ozone measurements up to 1% can be achieved with a well adjusted, regularly calibrated and properly operated Dobson instrument *[Basher, 1982]*. This conclusion has been confirmed by results of many ICs performed in the recent decades *[Basher, 1994]*, *[Evans, 1994]*, *[Evans, 2001]*, *[Koehler, 2002]*.

- The D074 instrument operated at SOO-HK is regularly calibrated and keeps its accuracy towards the WPDS below 1% since VII/1986, as documented in *Figure 7*. The same accuracy can be reached in the period VI/1979-VIII/1986 if re-defined calibration constants, mainly NT-79/86, are used *[Evans, 2002]*.

- For the period I/1961-VI/1979 the calibration constants were re-constructed by means of the Standard Lamp tests *[Vaníček, 2002]*. These can be verified by IC-69 taken at Siofok, May 1969 (*Table 3*). The corrections of NT-79/86 for May 1969 give -2.0 % average corrections towards the WPDS level which is in a very good agreement with the -2.3 % offset defined in *[Basher, 1994]*.Taking into account the range of SL corrections derived for D074 from 1961 to 1979 a shift towards the calibration scale of WPDS can be estimated to be in the limits 1-2% for the whole period 1961-1979.

- Dobson spectrophotometers are calibrated at ICs for DS measurements and the range of μ = 1.15-3.2. Primary aim is to define calibration constants for the standard wavelength double pair AD. For some instruments, depending on their technical parameters, the μ-range can be extended even for $\mu > 3.2$ if DS-CD observations with the focused image of Sun are taken *[Komhyr, 1980]*. At SOO-HK the instrument D074 is operated for μ = 1.12 - 3.4. Because of geographical location of the observatory these limits allow the whole-year period of DS-AD measurements. A certain amount of reliable measurements is available up to μ = 3.6.

- If DS-CD observations are performed for low positions of Sun ($\mu > 3.0$) the values of O_{3CD} should be corrected for the standard AD values O_{3AD}. The corrections can be determined from simultaneous DS-AD and DS-CD measurements as they are instrument and site dependant *[Komhyr, 1980]*. For SOO-HK and D074 the differences were calculated from 18.267 AD and CD measurements taken in 3-minute intervals of the period 1967-2002 see *Figure 8*. The graph shows that till the mid of eighties the differences were almost stable (smoothed averages from 0 to -1%). Then offsets has increased up to +4% by the end of the nineties. As a detailed investigation has shown that the differences are not μ or O_3 dependant, this phenomenon could be either of an instrumental origin or it appears due to changes of the local environment (e.g. by decreasing of SO_2 and aerosol pollution in the last two decades). In any case, *Figure 8* confirms that corrections of O_{3CD} need to be determined for each instrument and station separately before they are applied, as concluded in *[Komhyr, 1980]*. Thus, for D074 and SOO-HK the accuracy of corrected DS O_{3CD} values is estimated to be about 2-3 % for individual observations and 1- 2 % for long-term averages.

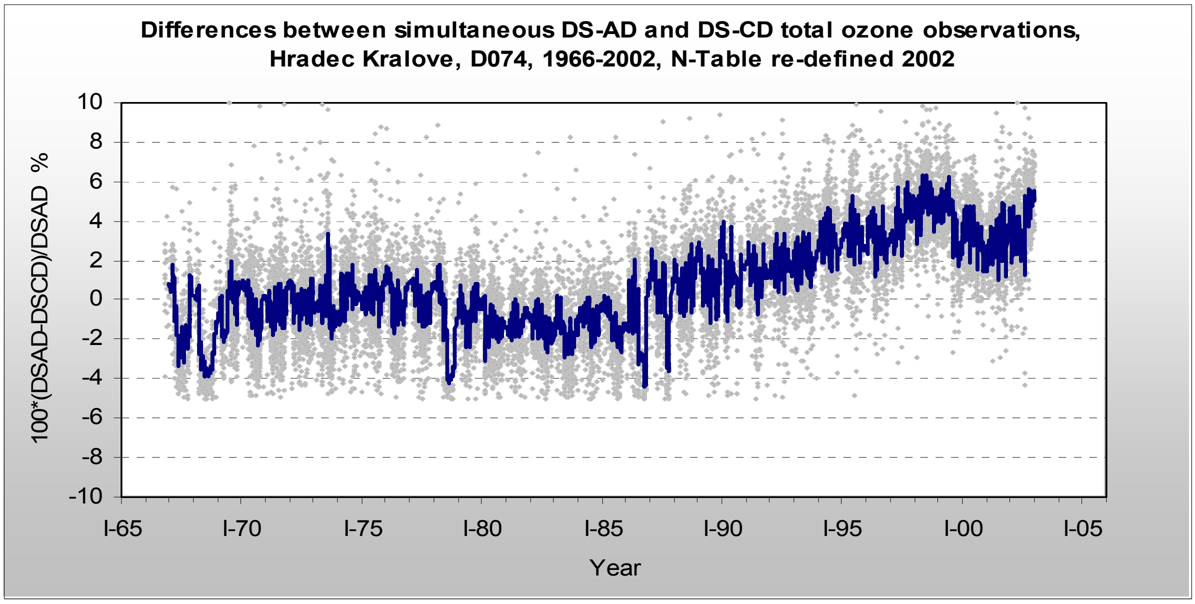

Figure 8. *Differences between simultaneous DS-AD and DS-CD total ozone observations, Hradec Královė, D074, 1966-2002, re-calculated* D074-V2003 *data*

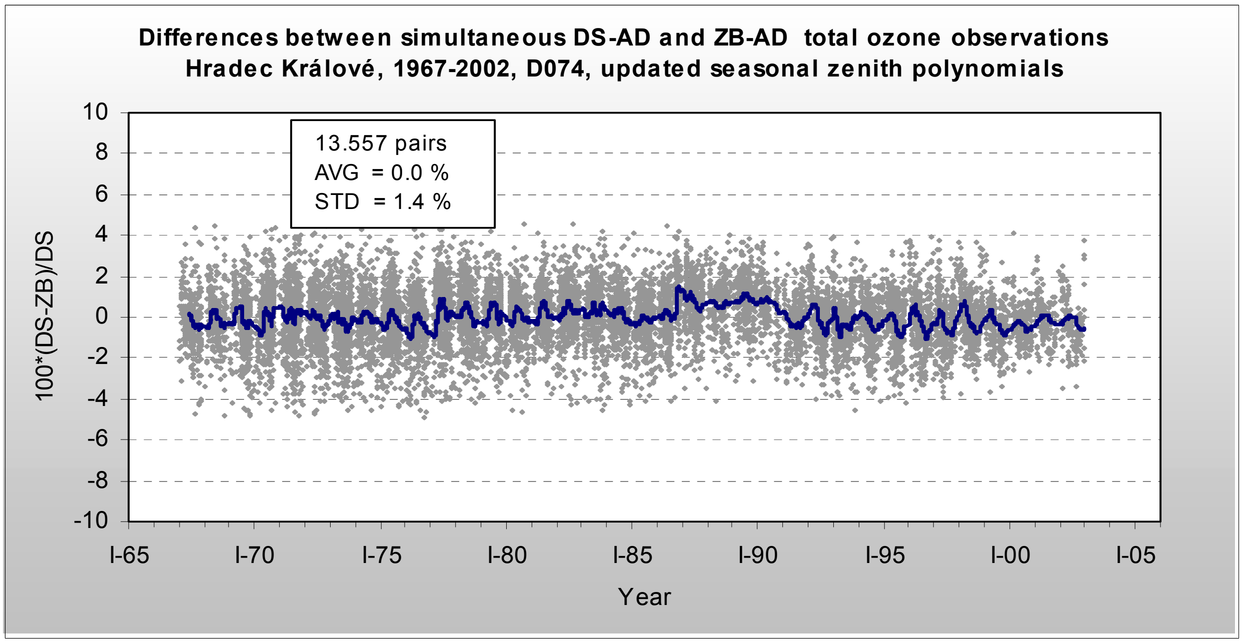

Figure 9*.* *Differences between simultaneous DS-AD and ZB-AD total ozone observations, Hradec Královė, D074, 1967-2002, updated seasonal zenith polynomials, re-calculated* D074-V2003 *data set*

Zenith observations

- Zenith observations (both ZB and ZC) have been processed by means of the seasonal zenith polynomials and cloud correction tables as described in Chapter 3.2.e). The re-calculated zenith measurements were validated by simultaneous (+-5 min) DS-AD total ozone observations.

- Differences of total ozone were calculated for 13.557 DS and ZB pairs of the period 1967-2002 and viewed in *Figure 9*. The graph shows that the differences are consistent for the whole period. The average difference and standard deviation are 0.0 and 1.4 %, respectively. 87 percents of differences are within 2% limits. These statistical parameters confirm that accuracy of ZB-AD observations can be generally estimated up to 2 percents for D074 and location of SOO-HK.

- Though a certain seasonal variation of differences appears in *Figure 9*, application of summer and winter zenith polynomials significantly eliminated a seasonal dependence as documented by graphs in *Figure 10*. The standard deviation of difference is below 2% even for winter months when total ozone reaches the highest variability.

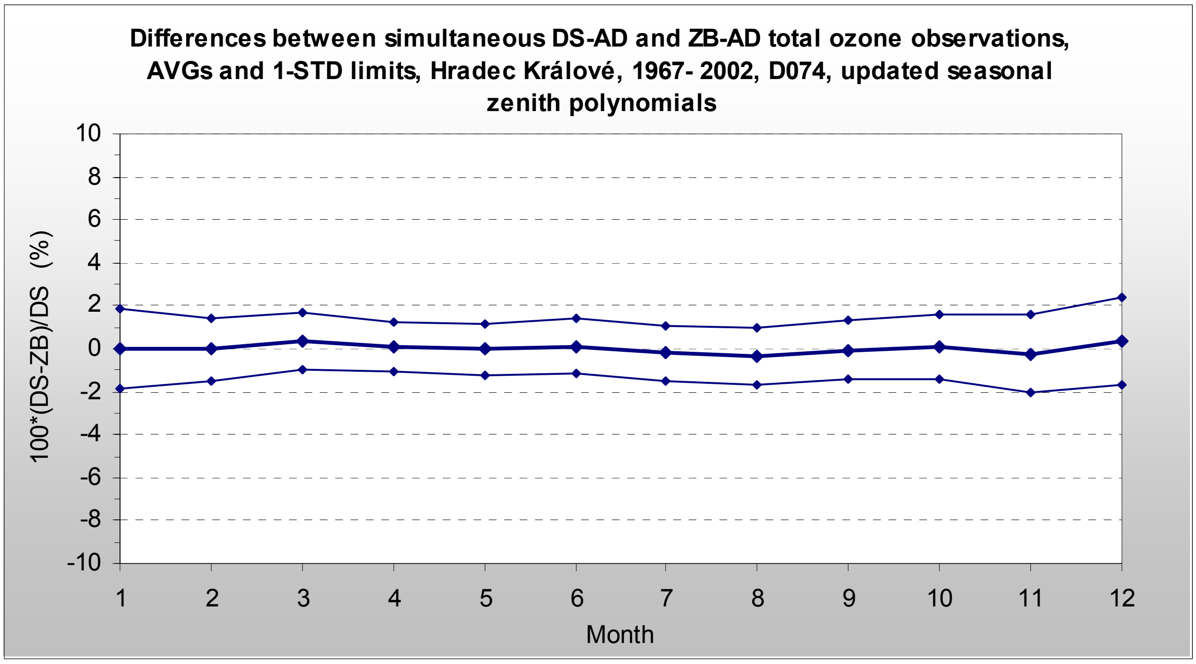

***Figure 10**. Differences between simultaneous DS-AD and ZB-AD total ozone observations, AVGs and 1-STD limits, Hradec Králové, D074, 1967-2002, updated seasonalzenith polynomials, re-calculated* D074-V2003 *data set*

- Application of zenith polynomials and cloud correction tables was validated for the AD double pair by 941 simultaneous (+- 5 min.) DS-AD and ZC-AD total ozone observations taken for low (OF=1.0), middle (OF=0.7) and high (OF=0.3) type of clouds. The outputs, which are displayed in *Figure 11,* show that though the average differences are below 1-percent limit for all types of clouds, the standard deviations reach 3% for low clouds (the highest values and variation of the opacity factor OF). Therefore, the general level of accuracy of the ZC measurements can be estimated to be about 3 percent lower than DS measurements. This conclusion is in a good agreement with results obtained for another mid latitude station Uccle, Belgium *[De Backer, 1998]*. Nevertheless, the low monthly averages of differences (less than 1%) indicate that good ZC observations should not introduce significant uncertainty into analyses of long-term trends of total ozone at stations located in cloudy climate condition.

− Validation of zenith polynomials and cloud correction tables for CD double-pair was also performed by means of the D074-V2003 data set. The analysis gave similar results as for ZB-AD and ZC-AD observations up to μ = 3.6. If corrections of O_{3CD} for O_{3AD} are applied (see comments to *Figure 8* in the section "Direct Sun") averages of differences towards simultaneous DS-AD values are less than 1% and STD = 2.6%.. This confirms that even that ZB-CD observations are more variable (almost twice higher than for ZB-AD) the monthly averages of zenith O_{3CD} can contribute to reliable estimation of long-term trends of total ozone. It should be pointed out, that these conclusions are related to the instrument D074 and condition of SOO-HK. Nevertheless, similar results can be expected for other well calibrated Dobson spectrophotometers and different locations.

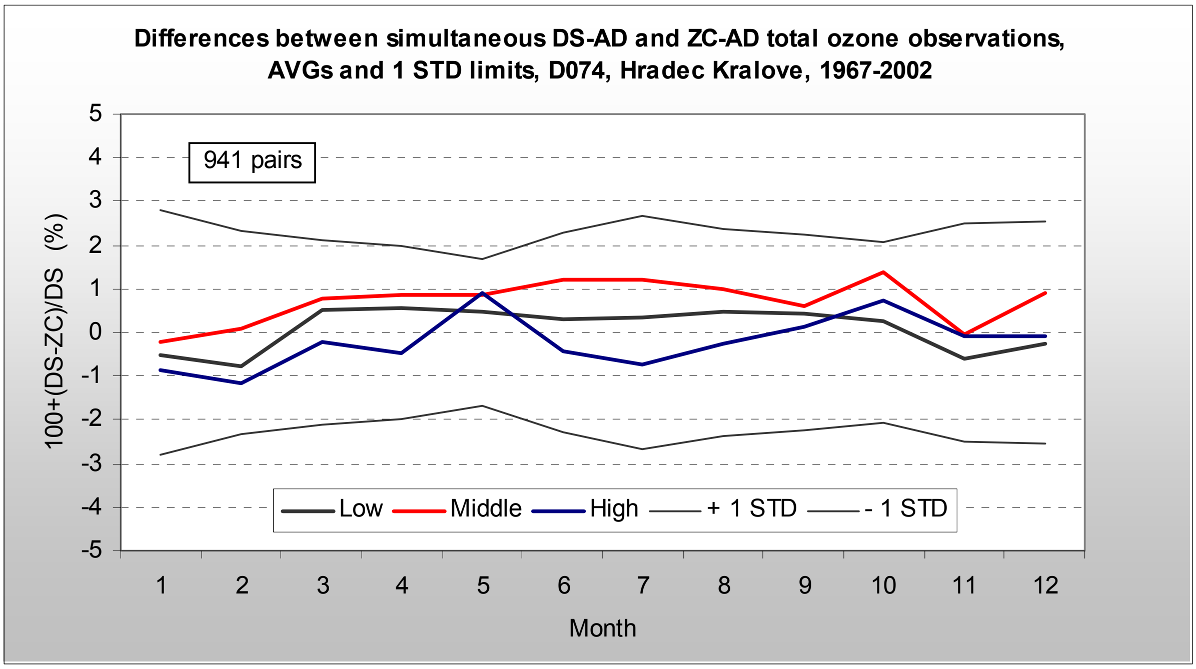

Figure 11. *Differences between simultaneous DS-AD and ZC-AD total ozone observations, AVGs and 1-STD limits (of Low Clouds), Hradec Králové, D074, 1967-2002, updated seasonal zenith polynomials, re-calculated* D074-V2003 *data*

b) Differences between the original and re-calculated total ozone data series

The total ozone data series D074-V2003 replaces the previous version D074-V1991 deposited into WOUDC in 1991 and later extended by December 2002. The comparison of both data sets is essential for assessment of data quality improvement and impacts on long-term statistics. In this Report the relation between data series is demonstrated by differences of monthly averages of total ozone in particular years of 1961-2002 because these are the basic data taken by users from WOUDC for trend analyses and other scientific applications. Differences between the original and new monthly averages calculated from all reliable observations are plotted in *Figure 12* and *Figure 13*. The graphs lead to the following conclusions:

– In the period 08/1986-12/2002 (after IC-86) the instrument D074 was regularly calibrated and its calibration constants updated. Therefore, minor differences (up to +-1%) have appeared in this period, mainly due to application of new zenith polynomials and because of excluding a certain number of non-reliable measurements originally included in D074-V1991. Only in several months (mostly D,J,F) the differences are higher even up to +5% because a major number of observations taken for μ > 3.4 have not been included into D074-V2003 (see Chapter 3.3.a). This lower the winter total ozone averages in the old data set D074-V1991.

– In the period 1/1970-7/1986 the re-defined calibration constants were used (introduction of IC-69 at Siofok and application of NT-79/86, see *Table 3* and *Table 4*) and high-μ observations were cut off. This generated higher monthly averages (generally by +2% and in winter up to +5%) for all years of the new data set.

– In the period 1/1961-12/1969 the differences between D074-V1991 and D074-V2003 are small (about +-2%). Only in several months they reach even -30% (January 1966) due to reduction of non-reliable DS observations in winter months before ZB/ZC measurements started in 1967. This resulted in significant differences between data samples for calculation of monthly averages (different number of days with observations) from D074-V1991 and D074-V2003 in the sixties. Provided that only the months with more than 10 days with observations are taken the extreme differences disappear- see the lines for "Selected months" in *Figure12* and *Figure 13*.

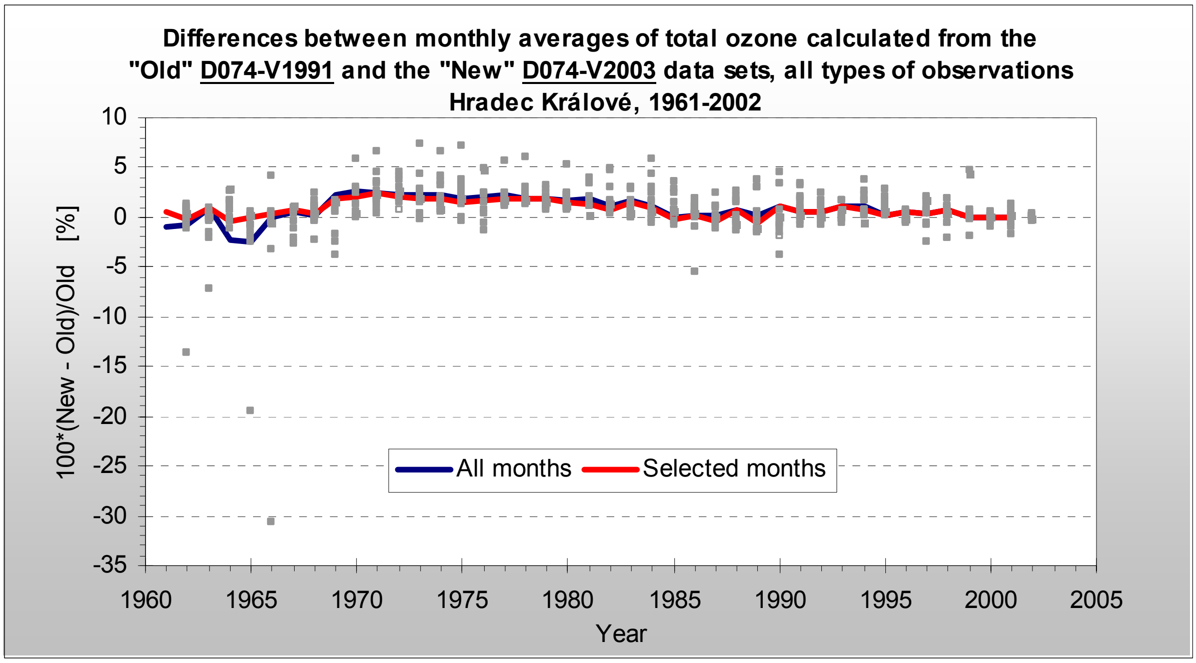

***Figure 12**. Differences between monthly averages of total ozone calculated from the "Old" D074-V1991 and the "New" D074-V2003 data sets, all types of observations are included, Hradec Králové, 1961-2002. The smoothed curves are for "All months" and the "Selected months" (more than 10 days with observations).*

− Average differences are positive, do not exceed +2.0% and they reach the highest values in the main part of the pre-ozone-hole period. Therefore, it might be expected that the new D074-V2003 data set gives the long-term depletion of the ozone layer in Hradec Králové somewhat more pronounced (by the magnitude of 1 % in winter-spring months) comparing to recent trends estimated from the D074-V1991 data set.

− The average differences in *Figure 13* show that there are not significant shifts in the annual course of total ozone between D074-V1991 and D074-V2003 data.

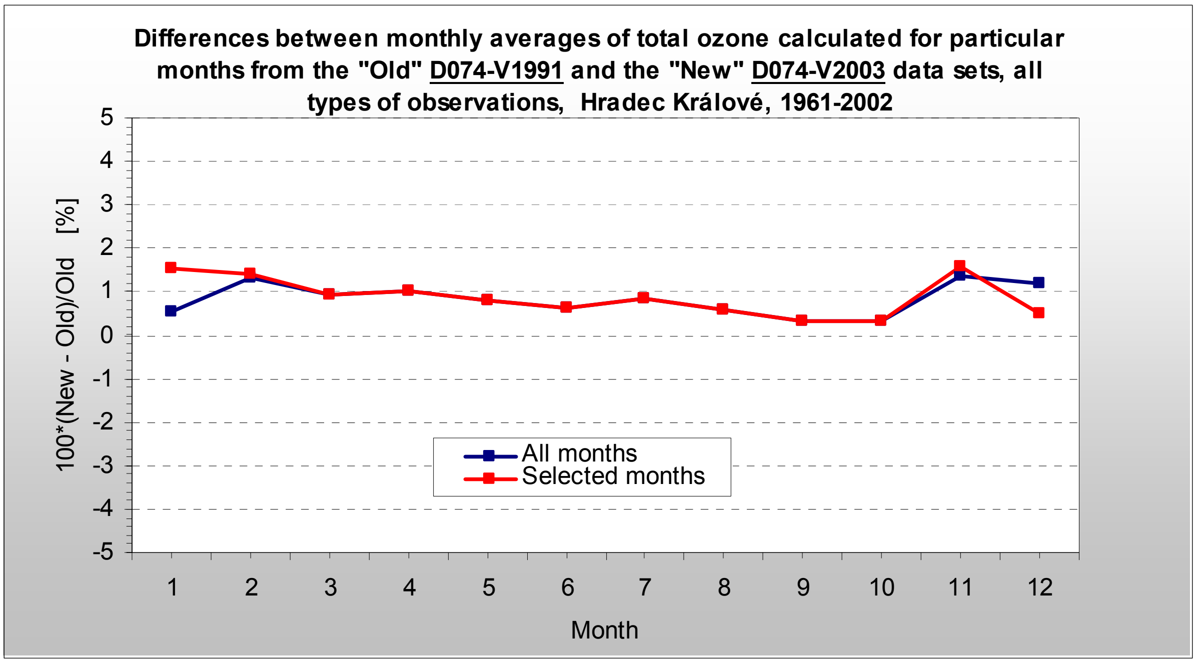

Figure 13. *As Figure 12 but averaged for particular months of the year.*

c) Sampling data for type of observation

Total ozone observations are carried out in different time-schedules at Dobson stations. Some stations take only DS measurements while the others perform also ZB/ZC observations, either daily (if weather condition allows) or on selected (e.g. working) days. Therefore, frequency and type of observations might be different from station to station, from season to season or even from year to year. In this way calculation of daily, monthly and yearly statistics can be influenced by selection (sampling) of available data.

Measurements performed with D074 at SOO-HK in the period 1961-2002 are described in Chapter. 2.1.a). Values of total ozone from individual DS-AD observations are the basic recorded outputs. As climate condition of the observatory is rather cloudy both DS and ZB/ZC measurements have been routinely done and O_{3AD} and O_{3CD} calculated since 1967. Therefore, there are sets of mixed DS and zenith observations available for many days that are used for calculation of daily/monthly averages. Though the DS-AD data take priority *[Komhyr, 1980]* it has been documented in Chapter 3.3.a) that well performed and correctly processed ZB and ZC measurements can be taken as a reliable source of data which do not degrade the quality of statistical parameters.

A high variety (by type and time) of observations at SOO-HK allows to investigate how the basic statistics will change for different sampling of the data. This was done for calculation of monthly averages from the D074-V2003 data set sorted with respect to the type and the number of observations in a month. The same analysis can be prepared for any other time periods (decades, seasons etc.)

Monthly averages of total ozone were calculated for “ALL” (DS+ZB+ZC) and DS only observations separately. Their differences (points) are plotted together with 12-month running means (corresponding to yearly averages) in *Figure 14* and *Figure 15*. The graphs allow the following conclusions.

- For the majority of months the differences (points) are within limits from +2% to -5%. For several very cloudy winter months (D,J,F), when only a few days with DS measurements are available, the offsets reach extreme values (e.g. -25% in December 1985).
- If months with insufficient number of days with DS observations (less than 10 days in a month) are excluded then except of December average monthly and yearly differences do not exceed -2.0% limit (see the “Selected months” line in *Figure15*). Also, offsets in particular months and years are long-term consistent and mostly within +- 3% limits, as *Figure 14* documents.
- It is evident that DS measurements generally originate smaller monthly and annual averages of total ozone than “ALL” data, though *Figures 9,10,11* do not show any significant and persistent shifts between DS and ZB/ZC observations. The explanation is that zenith measurements introduce higher total ozone values due to the fact that they are frequently taken under cloudy weather conditions connected with penetrations of cold and ozone-rich air masses into Northern mid-latitudes.
- If the frequency of zenith measurements is changed at a mid-latitude station like the one in Hradec Králové, then increasing of average total ozone is very probable due to higher percentage of days with high ozone air masses included. This conclusion is documented at SOO-HK by smaller differences in *Figure 14* after 2000 when frequency of zenith observations has been reduced (see *Figure 2*).

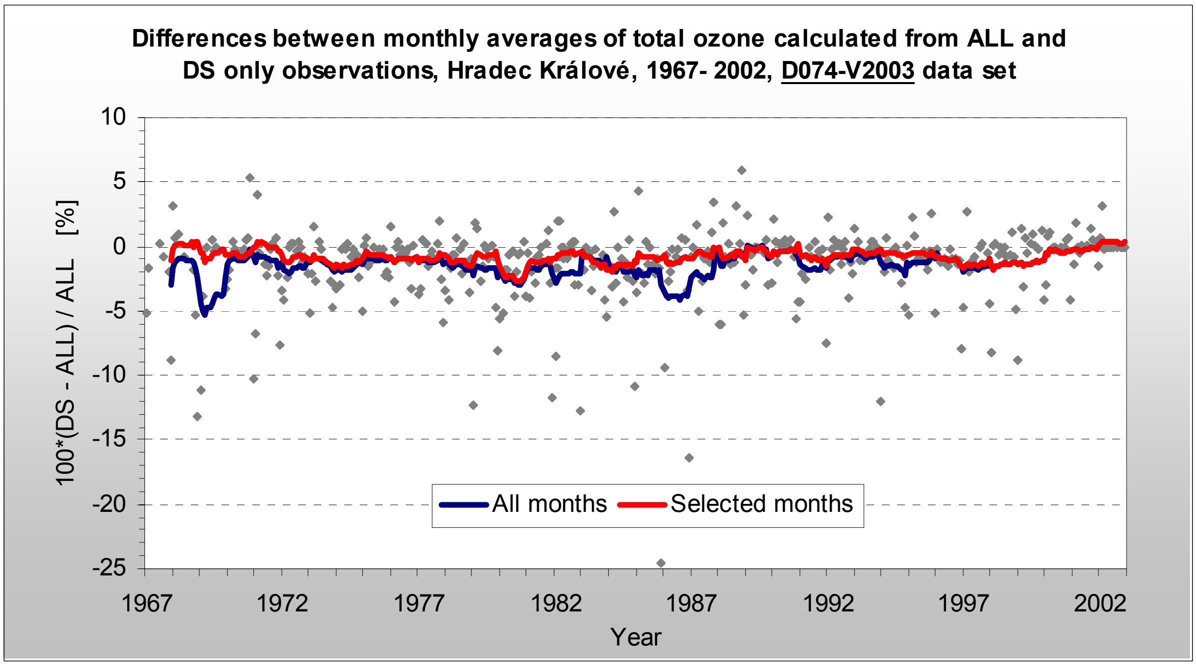

***Figure 14**. Differences between monthly averages of total ozone calculated from ALL and from DS only observations, Hradec Králové, 1967-2002, D074-V2003 data set. Smoothed curves are 12-running means for “All months” and for “Selected months” (more than 10 days with DS observations).*

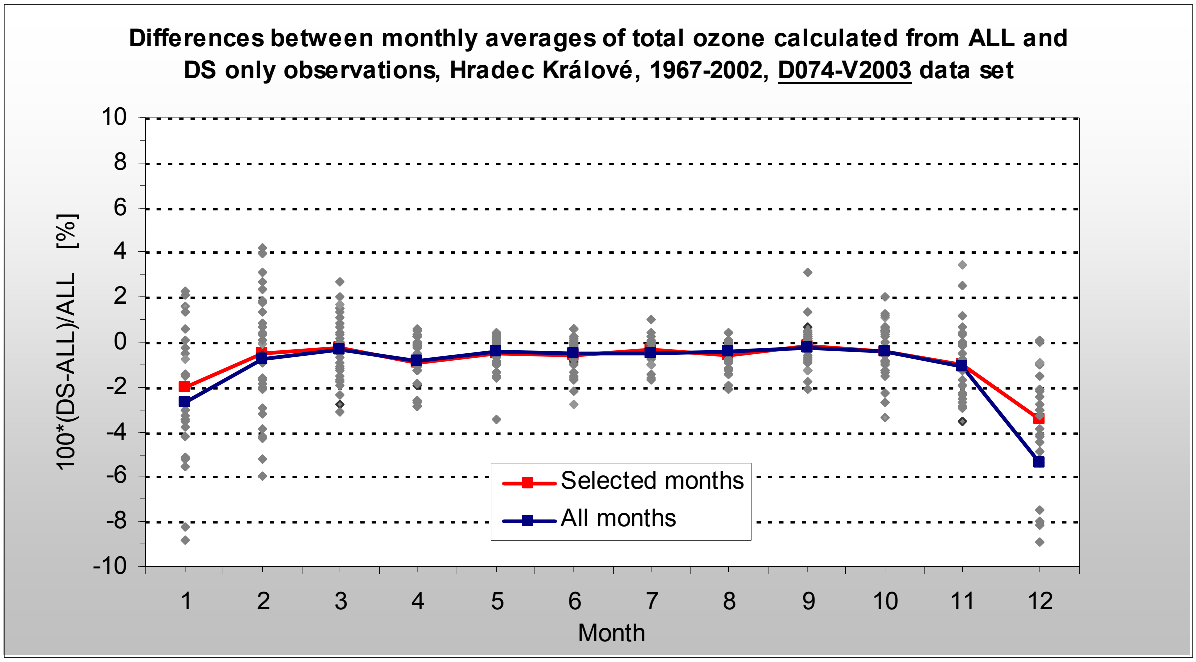

***Figure 15**. Differences as in Figure 14 averaged for each month of the year over the period 1967-2002*

d) *Impact of number of days with observations on the accuracy of calculation of monthly mean total ozone*

Monthly total ozone statistics deposited in WOUDC are calculated from daily averages or from daily representative values which strongly depend on the number of days with observations in a month. If the number is too low (e.g. because of bad weather conditions or due to interrupted operation of the instrument) then statistical parameters are not representative and can lead to incorrect conclusions. A typical and extreme example is documented in *Figure 14* by the -25% difference between DS and ALL monthly averages for December 1985 when total number of days without any observation was 24 (AVG = 325 DU) while DS measurements were taken only on 2 days (AVG = 245 DU).

To assess the accuracy of monthly averages calculated from an incomplete set of daily values, we used the Monte Carlo technique. The accuracy of the monthly means estimated from incomplete daily data sets was expressed for individual months of the year in dependence on the number of days with daily total ozone available. The experiment is described in Appendix A. Its basic results (numbers of days in particular months needed to reach 1 to 5 percent accuracy of estimation of monthly means at the 95% confidence level) are given in *Table 8* (Table A1 in Appendix A). The table shows strong annual dependence of the numbers of days being the highest in winter and the lowest in summer. Generally, if a monthly average of total ozone is to be estimated with better than 3 percent accuracy then at least 10 days in summer months and up to 20 days in winter months are needed. It has to be pointed out that *Table 8* is based on total ozone data observed in Hradec Králové and therefore, it is relevant to the northern mid-latitudes where high ozone variations appear in winter season. For other regions the values of the days needed to achieve a given accuracy will be different - the highest in the equatorial zone.

Table 8. *Numbers of days in particular months needed to reach 1 to 5 percent accuracy in estimating monthly means of total ozone on the 95% confidence level. The data are based on Dobson observations taken in Hradec Králové, 1961-2002.*

	Month											
Accuracy	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1%	29	26	29	27	25	24	24	23	24	26	27	29
2%	24	22	24	20	16	15	14	13	16	17	21	24
3%	19	17	18	14	10	9	9	8	10	11	15	18
5%	11	10	10	7	5	4	4	3	5	5	8	11

e) Creation of new D074-V2003 data files for WOUDC

The new D074-V2003 data set created under the project CANDIDOZ is available for the partners. After the Project is completed the new data will be re-deposited into WOUDC, Toronto with the following specifications.

- D074-V2003 data are given in the 1992 Bass-Paur Scale for the whole period 1961-2002.

- The total ozone values at WOUDC are only the AD “All-type” (DS, ZB, ZC) observations. To avoid misunderstanding due to correction/conversion from CD to AD values by users the CD measurements have not been included into the new files at WOUDC. The CD data are available on request at SOO-HK.

- The D074-V2003 data will be submitted into WOUDC as files coded in the new extCSV format *[WMO/WOUDC, 2001]*. The data and instructions about coding can be downloaded from the web site: http://www.woudc.org. This Report will be deposited at the WOUDC web site as an auxiliary metadata information source in the section “Data - Data Summaries and Reports”.

- Monthly averages of total ozone calculated from ALL and DS only observations of the period 1961-2002 are given as a sample of D074-V2003 outputs in *Table B1* and *Table B2* in Appendix B. The values are marked by shading according to their accuracy of estimation of monthly means related to number of days with observations - see *Table 8*.

4. RE-EVALUATION OF THE BREWER TOTAL OZONE OBSERVATIONS, 1994-2002

4.1. Calibration history of the Brewer spectrophotometer B098

a) Brewer reference spectrophotometers, international comparisons

Brewer spectrophotometers are operated and total ozone observations are processed in a routine automated regime controlled by the PC as described in Chapter 2.2.a). Original calibration constants are defined for each instrument by the manufacturer in the “Acceptance Manual”. The constants are corrected or re-defined by calibrations towards a group of instruments called the World Primary Brewer Spectrophotometer Triad (WPBST). The triad is maintained by the Meteorological Service of Canada (MSC), Toronto designated as the World Brewer Calibration Center (WBCC) *[Kerr et.al., 1998]*. WPBST is comprised of three instruments (B008, B014, B015) which together define an independent calibration scale for the whole Brewer network - in the same way like WPDS (D083) for the Dobson network. Unlike the Dobson spectrophotometers that are calibrated at ICs organized as WMO/GAW actions the calibrations of Brewer instruments are performed at stations by the traveling reference Brewer spectrophotometer B017 that is maintained and operated by a commercial company - the International Ozone Service Inc., Toronto (IOS). Calibrations/intercomparisons are done on a request of instruments owners, usually every two years. List and results of Brewer ICs have not been summarized and published yet. Calibration constants are available at IOS and at individual Brewer stations.

b) Intercomparisons of B098 - relation towards reference instruments

The Brewer spectrophotometer B098 operated in Hradec Králové was originally calibrated by the producer (SCI-TEC) in 1993 and then regularly in two-year periods by specialists from IOS. A list of all ICs is given in *Table 9*. Relative differences towards reference instruments are viewed in *Figure 16*. It is evident from the graph that offsets of the instrument B098 were always less than 1.2% in total ozone at all intercomparisons. This confirms a very good maintenance and calibration stability of B098 in the considered period. If the reference instrument B017 operated by IOS is supposed to be a stable tracer of the calibration scale defined by WPBST then a conclusion can be made that the spectrophotometer B098 was operated at SOO-HK on the world calibration level with the accuracy better than 1 percent during the whole period of 1994-2002.

Table 9. *Calibrations / intercomparisons of the Brewer spectrophotometer B098, performed in the period 1993-2002*

Date	Place	Acronym	Company	Reference	Cal. const. changed
July 1993	Saskatoon, Canada	IC-93	SCI-TEC	B011	The original set implemented
07.09.1995	Hradec Kralove, CR	IC-95	SCI-TEC	B017	F_0, S_0, MR8, MR9, $\Delta^*\alpha$
20.06.1997	Hradec Kralove, CR	IC-97	IOS	B017	F_0, S_0, MR8, $\Delta\alpha$, $\Delta^*\alpha$, CSN
27.05.1999	Poprad, Slovakia	IC-99	IOS	B017	none
29.05.2001	Budapest, Hungary	IC-01	IOS	B017	PDT, F_0, S_0, MR8, MR9

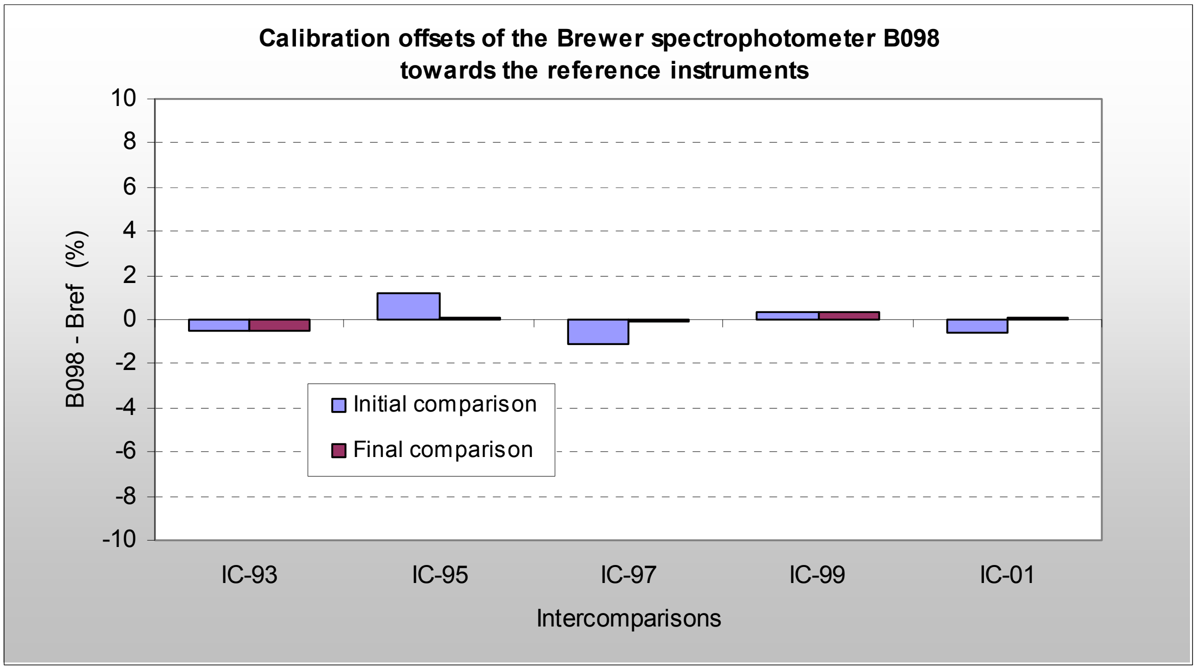

***Figure 16**. Calibration offsets of the Brewer spectrophotometer B098 towards the reference instruments at intercomparisons performed in the period 1993-2002*

c) Validity of calibration constants of B098 in the period 1994-2002

Basic calibration constants (see Chapter 2.2.b)) that were defined for the spectrophotometer B098 and used in particular periods of 1994 - 2002 are given in *Table 10*. From January 1994 to July 1997 the constants were determined at intercomparisons IC-93, IC-94, IC-95 and IC-97. Some constants (F_0, S_0, MR8, MR9) were also changed between these ICs if regular SLTs showed significant changes of the ratios M8 or M9, respectively. In 1999 automated operational corrections of ETCs by smoothed SL outputs were implemented. Therefore, since that year the reference values of F_0, S_0, MR8, MR9 have been changed only at ICs. Outputs from IC-99 are not included in *Table 10* because no changes of calibration constants were made at this intercomparison. Before this Report was completed another IC-03 of B098 towards B017 was done in Warsaw, Poland, May 2003. Results of IC-03 showed that the offset between D098 and the traveling reference D017 was below 0.5 %. This confirmed a very good calibration stability of B098 in 2003.

Important changes of constants came from the Scan Test and the Dispersion Test performed at IC-97 when both new ozone ETC and ozone absorption coefficients were defined and implemented for calculation of total ozone and SO_2. Stability of the calibration level of B098 is documented by graphs of long-term changes of some key calibration constants during the entire operation of the instrument at SOO-HK this is commented in detail in *[Vaníček, 2002]*. It can be said that the calibration history of the instrument B098 is perfectly documented and all relevant parameters needed for re-processing of total ozone and total sulphur dioxide observations are available in log-files at SOO-HK. The spectrophotometer B098 has never been out of operation except of short interruptions of measurements due to servicing or participation at ICs held out of Hradec Králové.

Table 10. *Calibration constants defined for the Brewer spectrophotometer B098 and used in particular periods of its operation till 31.12.2002 (Date = date of a change of the previous constants) [Vaníček, 2002].*

Date **Calibr. constant**	**01.01. 1994**	**01.06. 1994**	**01.10. 1994**	**21.04. 1995**	**07.09. 1995**	**01.01. 1997**	**20.07. 1997**	**24.05. 2001**
Dead Time PDT	4.4E-8	4.4E-8	4.4E-8	4.4E-8	4.4E-8	4.4E-8	4.4E-8	3.8E-8
Ozone ETC F_0	3107.0	3103.0	3101.0	3097.0	3090.5	3090.5	3125.5	3100.0
SO_2 ETC S_0	3168.0	3163.0	3156.0	3153.0	3353.0	3336.0	3331.0	3280.0
O_3 abs. coef. $\Delta\alpha$.	0.3443	0.3443	0.3443	0.3443	0.3443	0.3443	0.3347	0.3447
O_3 abs. coef. $\Delta^*\alpha$.	1.1559	1.1559	1.1559	1.1559	1.1224	1.1224	1.1214	1.1214
SO_2 abs. coef. $\Delta^*\alpha'$.	2.3500	2.3500	2.3500	2.3500	2.3500	2.3500	2.3500	2.3500
Reference Ratio MR8	3632	3600	3620	3617	3615	3593	3600	3570
Reference Ratio MR9	1932	1910	1926	1922	1916	1910	1910	1892
Calibr. Step No. CSN	290	290	290	294	294	294	294	294

4.2. Re-calculation of B098 total ozone and SO_2 observations

It has already been concluded in the previous chapter that there were not significant changes of calibration constants of B098 at ICs. Unlike the first decades of D074 spectrophotometer the constants of B098 are well documented and were regularly updated for the whole period of its operation. Therefore, total ozone data files created with B098 and deposited into WOUDC in the period 1994-2002 do not need urgent corrections. Nevertheless, a certain improvement of the original total ozone and SO_2 data can be achieved by re-evaluation of calibration constants by backward smoothing (applying Gauss smoothing filter) of the routine tests (mainly SL) and by updating of the original zenith polynomials provided by the producer.

a) Re-processing of direct sun (DS) total ozone observations

In the period 1994-1999 the total ozone and SO_2 observations were routinely processed by the extraterrestrial constants F_0 and S_0 given by date and values in *Table 10*. The ETCs were kept unchanged for reduction of measurements in particular sub-periods. After IC-99 the ETCs were continuously corrected by SL tests. Under a complex re-evaluation within the project CANDIDOZ altogether 31.202 DS total ozone measurements made with B098 from 01.01.1994 to 31.12.2002 have been re-calculated by means of ETCs adjusted for every day smoothed SL corrections. Because SL tests did not identify any significant changes in technical condition of B098 *[Vaníček, 2002]* the corrections reflected only slow long term changes of optical components and SL due to their natural aging. It can by concluded, that for the whole period 1994-2002 the DS total ozone measurements were with the accuracy +- 1% related to the calibration level of the traveling reference B017. Due to regular comparisons of B017 with the reference triad WPBST this accuracy should be representative also towards the world standard triad *[Lamb, 2003]*.

b) Re-processing of direct sun (DS) total SO_2 observations

As it has been mentioned in the previous paragraph, DS total SO_2 measurements were re-processed with ETCs given in *Table 10*. The results are viewed in *Figure 17*. It is evident from the graph that total amount of SO_2 in Hradec Králové decreased by about 2 DU in the second half of the nineties when brown coal power stations (the main SO_2 sources in the country) were equipped with filter facilities. Nevertheless, there were some episodes when sulphur dioxide reached high values even after 1997, mostly during winter atmospheric inversions. It is a common feature for Brewer stations that negative values appear in results. This is caused by the technique which is used and the way in which the observational data are processed. A question how to interpret or correct the negative values still needs to be answered by Brewer experts. Generally, total SO_2 contributed by less than 2 DU (~0.5%) to atmospheric compounds in Hradec Králové in recent years. This was below the precision threshold of the instrument [*McElroy and Sevastiouk, 2003*]. In this paper all the values (including the negative ones) were used for data analyses.

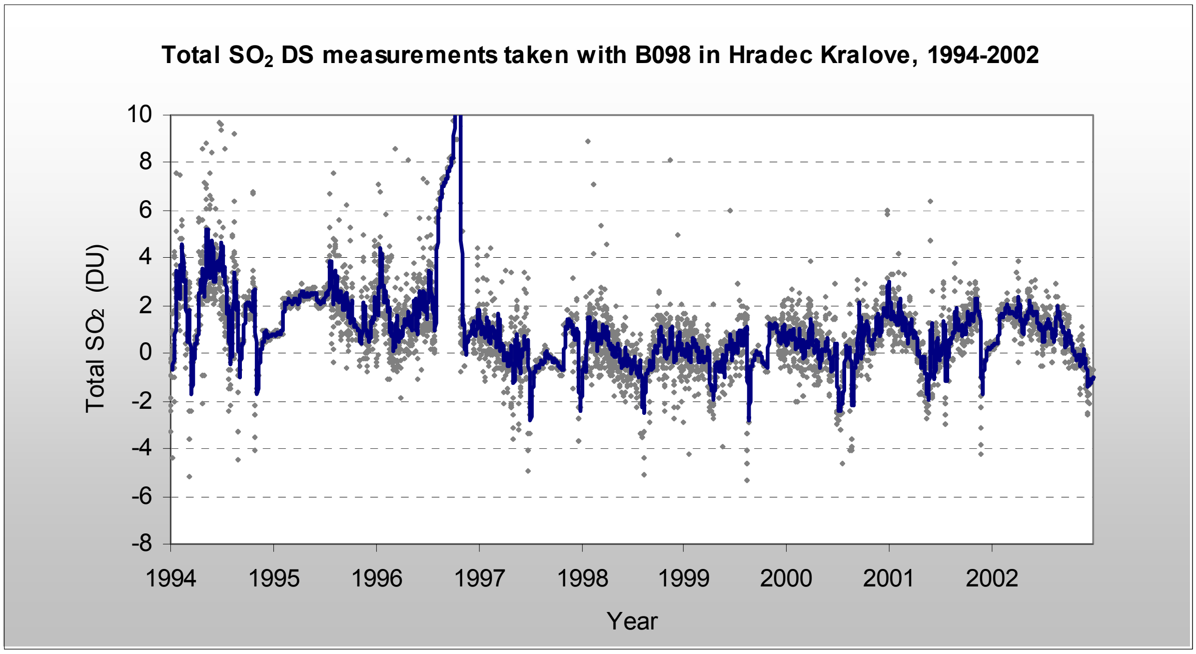

***Figure 17**. Re-processed DS measurements of total SO_2 taken with the Brewer spectrophotometer B098, Hradec Králové, 1994-2002*

c) Re-processing of zenith sky (ZS) total ozone observations - updating of the zenith polynomials

The Brewer spectrophotometer allows measurement of total ozone from zenith observations in a similar way like the Dobson spectrophotometer. The only difference is that the Brewer instrument can not distinguish zenith blue and zenith cloudy condition and takes observations for all skies marked as ZS (Zenith Sky). The ZS observations are processed by means of zenith polynomials as described in Chapter 3.2.e). The polynomial is characterized by nine multi-regression coefficients defined in the Constants File of the instrument. The parameters M(9)-sky, μ , F_0 are the input proxies [*SCI-TEC, 1988*]. As the polynomial is instrument and location dependent, it is recommended to adjust it for each spectrophotometer and station (local climate and geographical conditions) separately so that the highest accuracy of data reduction is achieved - see e.g. [*Muthama et al., 1995*] or [*De Backer, 1998*]. Altogether 17.672 simultaneous (+- 10-minute) DS and ZS measurements made with B098 in Hradec Králové were used for development and validation of several zenith polynomials defined by regression coefficients given in *Table 11* and discussed in the next chapter.

Table 11. *Regression coefficients of zenith polynomials developed for the Brewer spectrophotometer B098 in Hradec Králové and particular periods of their application*

Regression Coefficients	In use from 01-01-1994	In use from 01-10-1994	In use from 20-07-1997	In use from 01-01-2000
a_1	-0.25248	-0.00640	-0.00640	0.06669
a_2	0.23591	-0.01968	-0.01968	-0.09405
a_3	-0.04802	0.01654	0.01654	0.01495
a_4	2.22230	0.17077	0.17358	-0.14279
a_5	-1.77109	0.28053	0.27670	0.65989
a_6	0.40909	-0.06126	-0.06223	-0.05121
a_7	-4.44317	-0.49136	-0.44364	-0.11405
a_8	4.34310	0.45626	0.44903	-0.10363
a_9	-0.88220	-0.04506	-0.04676	-0.04678

4.3. Evaluation of outputs

The re-calculated total ozone and total SO_2 observations create a new data set hereafter marked as **B098-V2003** in this paper which replaces the previous version B098-ORIG continuously deposited into WOUDC during the period 1994-2002. In this chapter an assessment of quality and impacts of data sampling are given like for the D074-V2003 data set originated with D074 - see Chapter 3.3.

a) Quality assessment of re-calculated observations

Procedures of the Brewer data controlling programme are used to do the first QA checks of calculated total ozone values. It is important to note that each total ozone value (observation) is determined from a series of "readings" (usually 5). Each reading is calculated from photon count ratios coming from several (usually 20) revolutions of the slit mask - see equation 8) and Chapter 2.2.b). Total ozone is then calculated as an average of readings and is accepted as a reliable value if Standard Deviation of readings is less than 2.5 DU. It is possible to define numbers of revolutions and readings in the Brewer controlling programme. It should be pointed out that the higher numbers are the more precisely total ozone value is determined but the longer period is needed to make the observation. The B098 instrument was operated and total ozone calculated from 5 readings and 20 revolutions at SOO-HK, as recommended in [*SCI-TEC, 1993*]. A new requirement for B098 saying that only observations with more than 2 successful readings shall be taken for calculation of total ozone appeared in April 2000 and was immediately implemented. The same restriction was applied for re-processing of the entire B098 total ozone data series under the project CANDIDOZ. Thus, the number of DS measurements has been somewhat reduced in B098-V2003 comparing to B098-ORIG data sets but quality of the data has been improved.

Direct Sun observations

- Results of calibrations at ICs listed in *Table 9* and viewed in *Figure 16* show that calibration offsets of the spectrophotometer B098 were less than 1% during its operation. As the traveling standard B017 represents the world Brewer calibration scale with a better than 1 % precision [*Lamb, 2003*] it can be expected that the same calibration fit of B098 has been achieved also towards WPBST at ICs.

- Comparative DS measurements were carried out under the standard automated operational schedule of B098 at all ICs. Therefore, DS total ozone observations routinely made with B098 in Hradec Králové in 1994-2002 should not permanently exceed 1% limit of accuracy for the range of μ = 1.12 - 3.5 if proper operational adjustments of calibration constants (mainly SLT corrections of ETCs) are made.

- With regard to the conclusions above, the accuracy of re-calculated DS total ozone observations included into the B098-V2003 data set is estimated to be generally below 1.5 % of the calibration scale represented by WPBST.

Zenith observations

- In the first step one general zenith polynomial (one set of regression coefficients) was developed for the instrument B098, location Hradec Králové and period 1994 - 2002 by means of 17.972 simultaneous (+- 10 min.) DS and ZS observations (mostly blue or partially cloudy sky). Zenith total ozone values were recalculated by the polynomial and compared with DS observations - see *Figure 18*.

- It is evident from *Figure 18* that the differences between DS and ZS values do not have concordant behavior within the whole period 1994 - 2002. A detailed investigation led to definition of break points dated 01.01.1994, 01.10.1994, 20.07.1997, 01.01.2000. For particular sub-periods defined by those dates specific polynomials have been developed - see *Table 11*.

- In the second step the updated polynomials given in *Table 11* were used for re-calculation of 32.340 all-type (including cloudy skies) zenith measurements. These were finally compared with quasi-simultaneous (up to +-3 hours) DS observations - see *Figure 19*.

- Differences viewed in *Figure 19* are more consistent during 1994 - 2002. But the average (0.9 %) and the standard deviation (2.6 %) are higher than for Dobson zenith observations (see *Figure 11*). This is due to missing cloud corrections which are not applicable for Brewer measurements.

- Generally, the accuracy of zenith total ozone measurements carried out with the Brewer spectrophotometer in Hradec Králové is estimated to be about +- 3 % for blue skies and +- 5 % for cloudy skies.

- Unlike Dobson observations the tests of seasonal Brewer polynomials do not give improvement of accuracy of total ozone measurements.

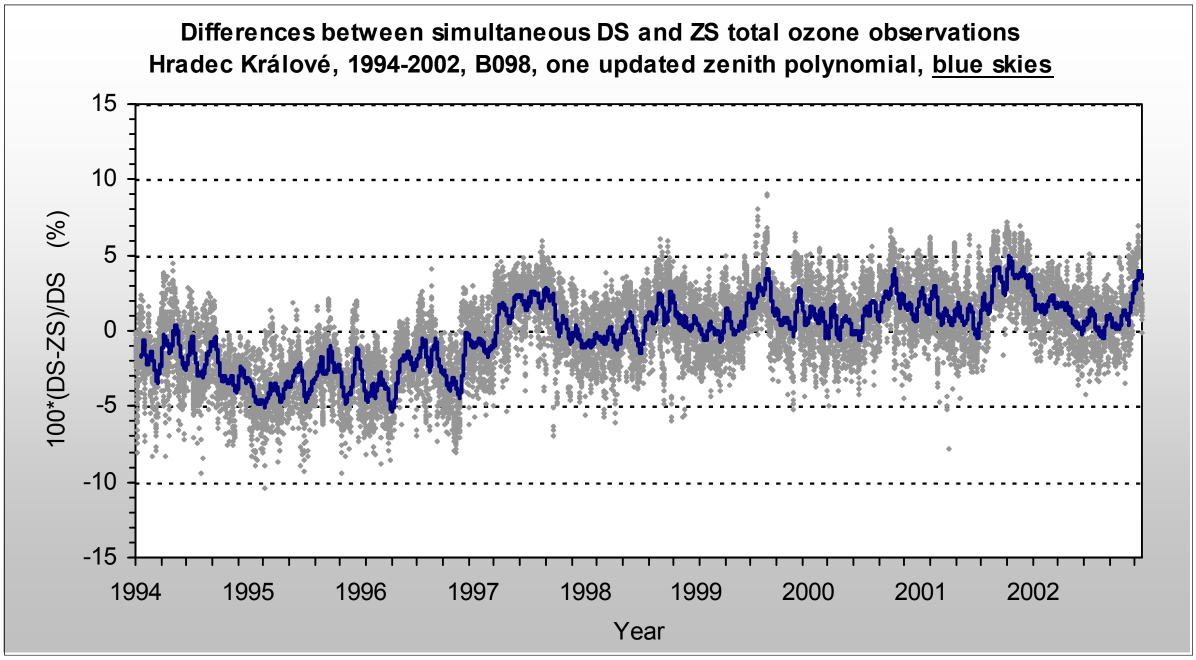

Figure 18. *Differences between simultaneous DS and ZS total ozone observations taken with the spectrophotometer B098 in Hradec Králové in the period 1994-2002 (one updated zenith polynomial, blue skies only)*

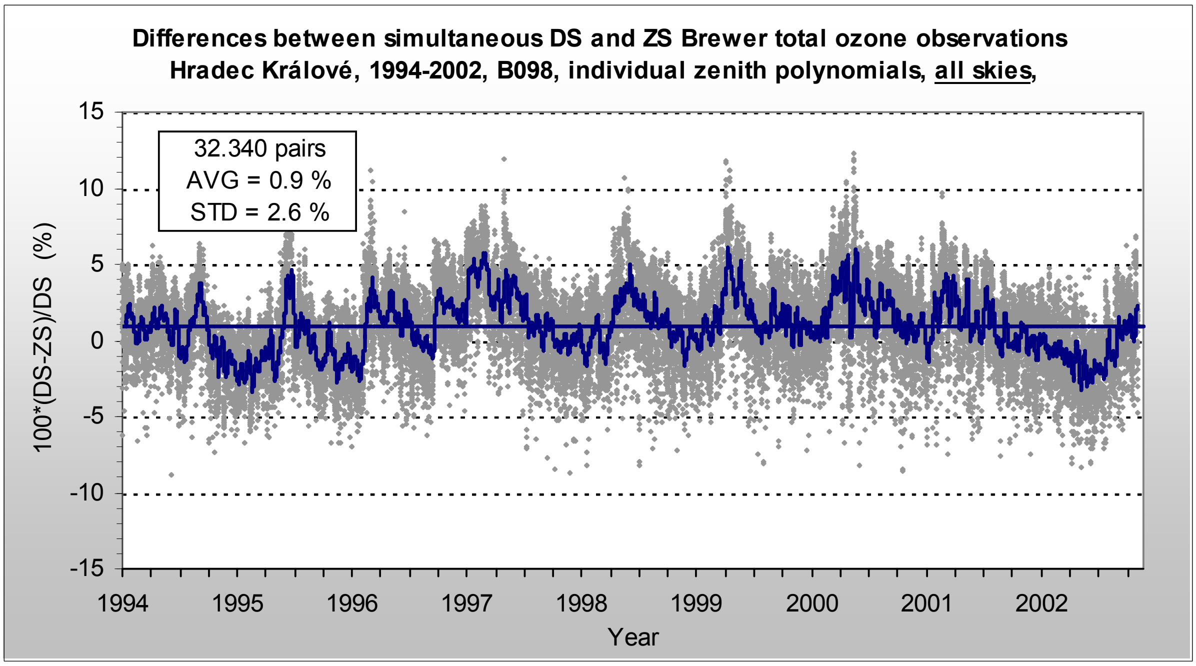

***Figure 19**. Differences between simultaneous DS and ZS total ozone observations taken with the spectrophotometer B098 in Hradec Králové in the period 1994-2002. The zenith polynomials were updated for particular sub-periods (see Table 11), all skies*

b) Differences between original and re-calculated total ozone data series

Original total ozone observations performed with B098 and deposited in WOUDC as B098-ORIG data have been re-processed and filed in the new B098-V2003 data set. As the calibration level of the B098 instrument was fairly stable during 1994-2002 (see previous chapters) differences between both data series could arise either from backward daily corrections of ETCs by SL tests in 1994-1999, from application of updated zenith polynomials or from the newly applied restriction on the number of readings for calculation of total ozone - Chapter 4.3.a). Comparison of monthly averages of total ozone from "old" B098-ORIG and "new" B098-V2003 data sets which are presented in *Figure 20* and *Figure 21* allow the following conclusions.

- In the first years of observations a higher variability of differences was caused by the influence of original zenith measurements due to the less representative zenith polynomial. Also lower number of DS observations (and therefore days with DS measurements) in B098-V2003 contributed to higher differences in this period.

- After the zenith polynomials were updated in 1997 and 2000 (*Table 11*) the differences have become lower and stable.

- Generally, the new data set B098-V2003 gives somewhat higher total ozone values (+ 0.8 % for 1994-1997 and + 0.6% for 1998-2002). This is supposed to be due to corrections gained from SL tests and applied on the ozone ETC.

- After 2000 when daily corrections of ETCs, updated zenith polynomials and restriction for the number of readings are routinely applied the differences are almost negligible.

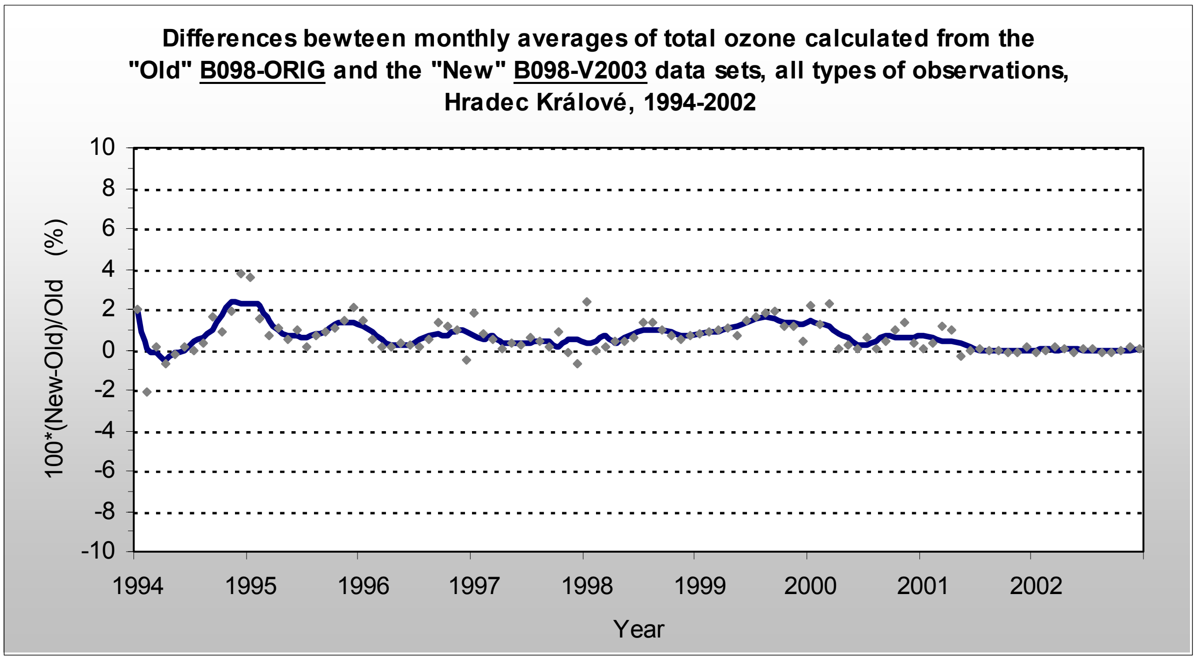

Figure 20. *Differences between monthly averages of total ozone calculated from the "Old" B098-ORIG and the "New" B098-V2003 data sets, all types of observations are included, Hradec Králové, 1994-2002*

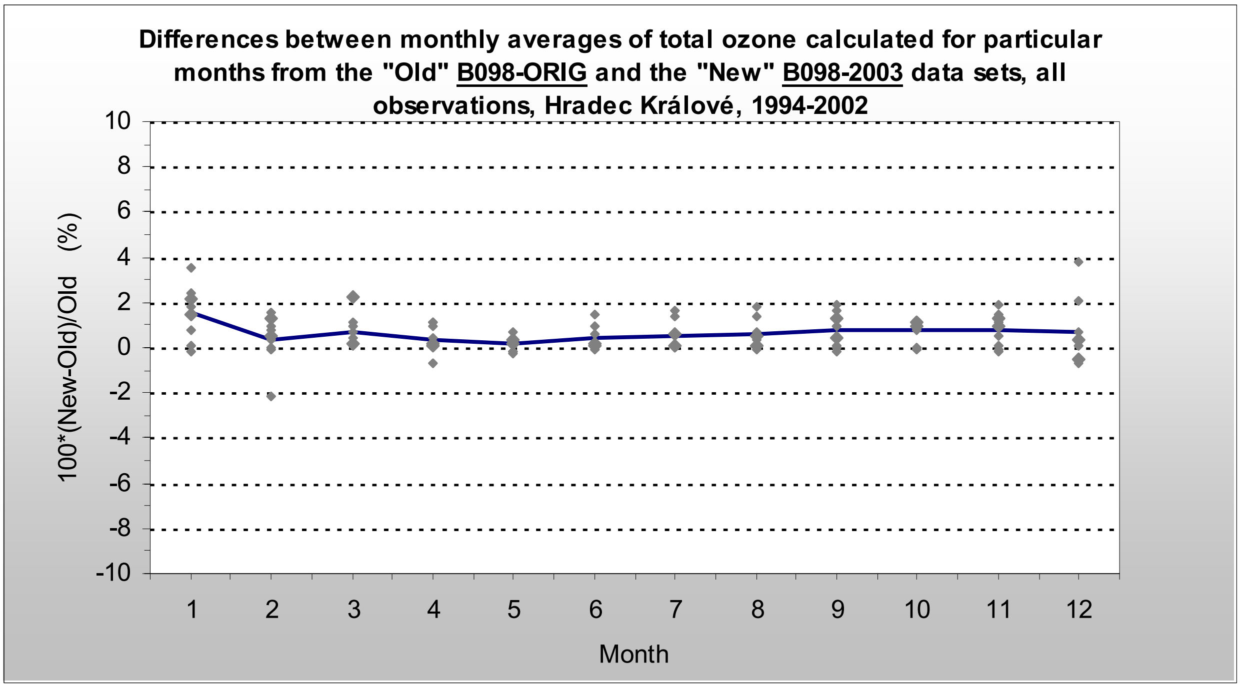

***Figure 21**. As Figure 20 but averaged for particular months of the year*

c) Sampling data for daily and monthly averages

Effects of sampling daily averages of total ozone with regard to number of days with DS measurements have been analyzed for the B098-V2003 data set in a similar way like for the Dobson observations in Chapter 3.3.c). Results that are documented by *Figure 22* and *Figure 23* can be summarized as follows.

- Comparing with Dobson observations the Brewer measurements show generally lower differences between ALL and DS monthly means including winter months. Extreme values (> 5 %) occur only rarely. In the major number of months the differences are in limits of +2 % and - 3 %. This is due to higher number of DS observations made by B098 under its automated schedules up to $\mu = 3.5$ than by the manually operated D074 instrument.

- If only "Selected" months (more than 10 days with DS observations, red curves) are taken then smoothed differences estimate a general offset between ALL and DS monthly averages below 2 % and only in some periods of 1994-2002.

- Somewhat higher monthly averages calculated from "All" observations are likely to come from zenith measurements taken in the automated regime on heavy clouds in the summer season. In winter months the agreement between ALL and DS monthly averages is better for B098 observations than for D074 measurements (compare *Figure 23* and *Figure 15*).

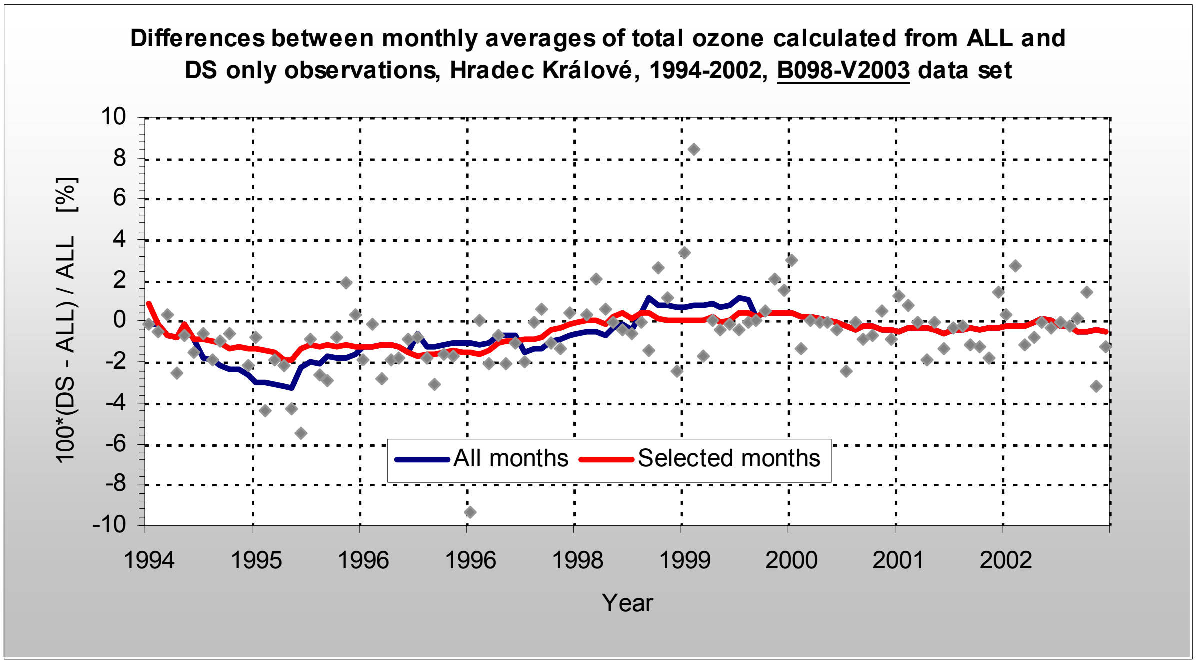

Figure 22. *Differences between monthly averages of total ozone calculated from ALL and with DS only observations, Hradec Králové, 1994-2002, B098-V2003 data set. Smoothed curves are polynomial regressions for All months and Selected months (more than 10 days with DS observations).*

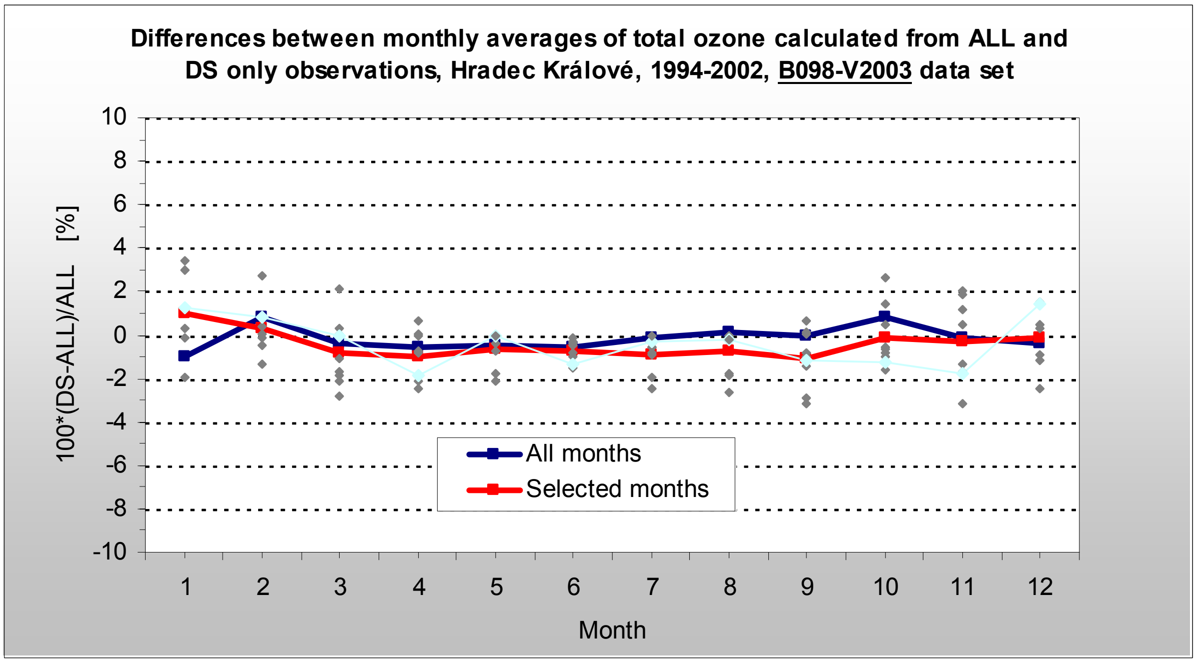

Figure 23. *Differences as in Figure 22 but averaged for each month of the year over the period 1994-2002*

d) Creation of new <u>B098-V2003</u> data files for WOUDC

As the Brewer spectrophotometer B098 was operated with well defined calibration constants in the whole period 1994 - 2002 the new <u>B098-V2003</u> data set does not differ too much from the original data series <u>B098-ORIG</u> (see Chapter 4.3.b)). Nevertheless, application of daily corrections of ETC by HGL tests before 1999 and re-definition of zenith polynomials have introduced certain changes that should be reflected in the world data base. This is a reason why monthly data files of <u>B098-V2003</u> coded in the extCSV format will be re-deposited into WOUDC after the CANDIDOZ Project is completed.

Similarly like for the new Dobson data in Appendix B there are given *Table B3* and *Table B4* with monthly averages of total ozone calculated from ALL and DS only observations of the period 19994-2002 included in the <u>B098-V2003</u> data set.

5. COMPARISON OF DOBSON AND BREWER DATA SERIES

5.1. Comparison of monthly and daily averages (WOUDC files)

a) Monthly averages - all observations

Monthly averages of total ozone deposited in WOUDC are predominantly used for long-term trend analyses by the scientific community. They are calculated from daily means submitted from stations. Data originators usually decide which observations (sorted by type, time, μ , etc.) are taken for daily statistics. This fact is frequently not considered by data users and it could happen that the values are not sorted in consistent samples, as discussed in Chapter 3.3.b) and Chapter 4.3.c). In this paragraph the monthly <u>D074-V2003</u> and <u>B098-V2003</u> averages are compared to assess differences between both data series if no sampling of WOUDC files is done. The differences are drawn in *Figure 24* and *Figure 25* (blue dots and lines). The graphs show a slow but evident trend that marks a change of relation between both data series at the beginning and in the end of the period considered. In several months of substantially different numbers of days with observations the differences exceed 5 % limits. Generally, Brewer values are higher, mainly in last five years. The average annual course of differences viewed in *Figure 25* has about 2-percent amplitude.

b) Monthly averages - DS observations

If monthly averages calculated only from DS observations are compared (red smoothed lines and dots in *Figure 24* and *Figure 25*) the trend of differences becomes more pronounced prior 1998 and then the shift is almost stable (around -2 %) till 2002. The DS averages more sharply indicate the years 1997 and 1998 as periods when relation between D074 and B098 data series has evidently changed. Large offsets in several months come again from different numbers of DS measurements in those months. Annual course of differences is nearly the same like for ALL data in summer months. In winter average DS offsets drop down even below -5 % due to extremes in several moths. For example, in December 1996 when only 17 Dobson and 77 Brewer DS observations were made, the difference reached even -21 %. Therefore, it can be concluded, that:

- Monthly averages calculated just from DS observations follow the same long-term changes like those derived from ALL measurements

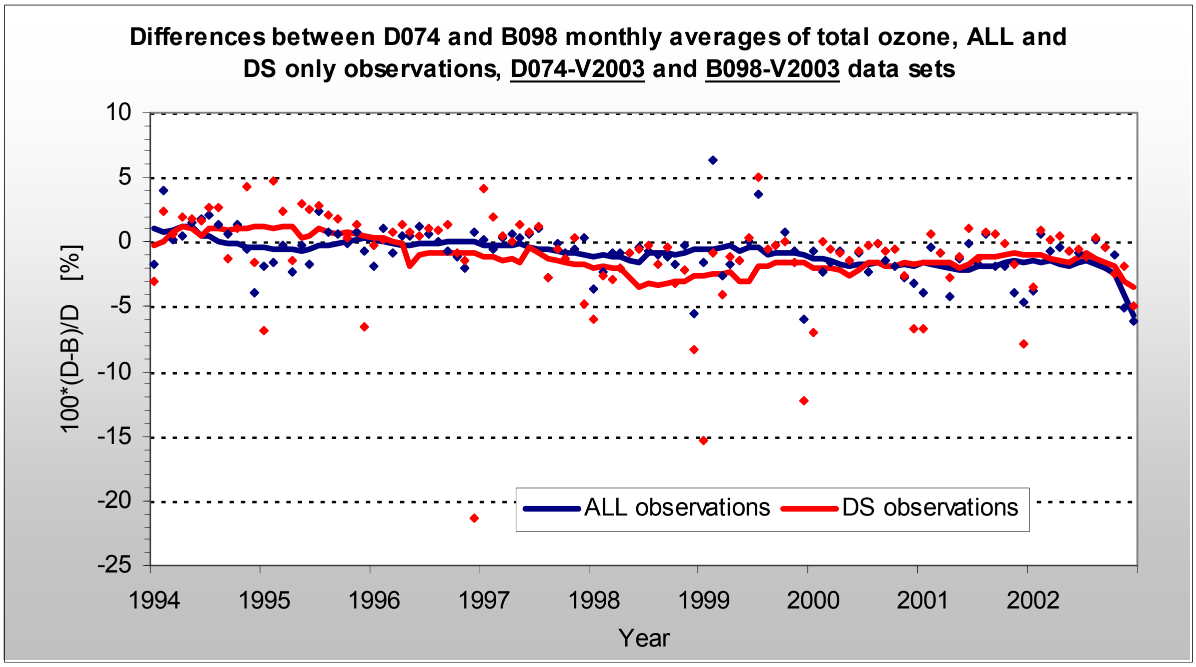

Figure 24. *Differences between monthly averages of total ozone measured with D074 and B098. ALL (DS + zenith) and DS only observations, Hradec Králové, 1994-2002, D074-V2003 and B098-V2003 data sets*

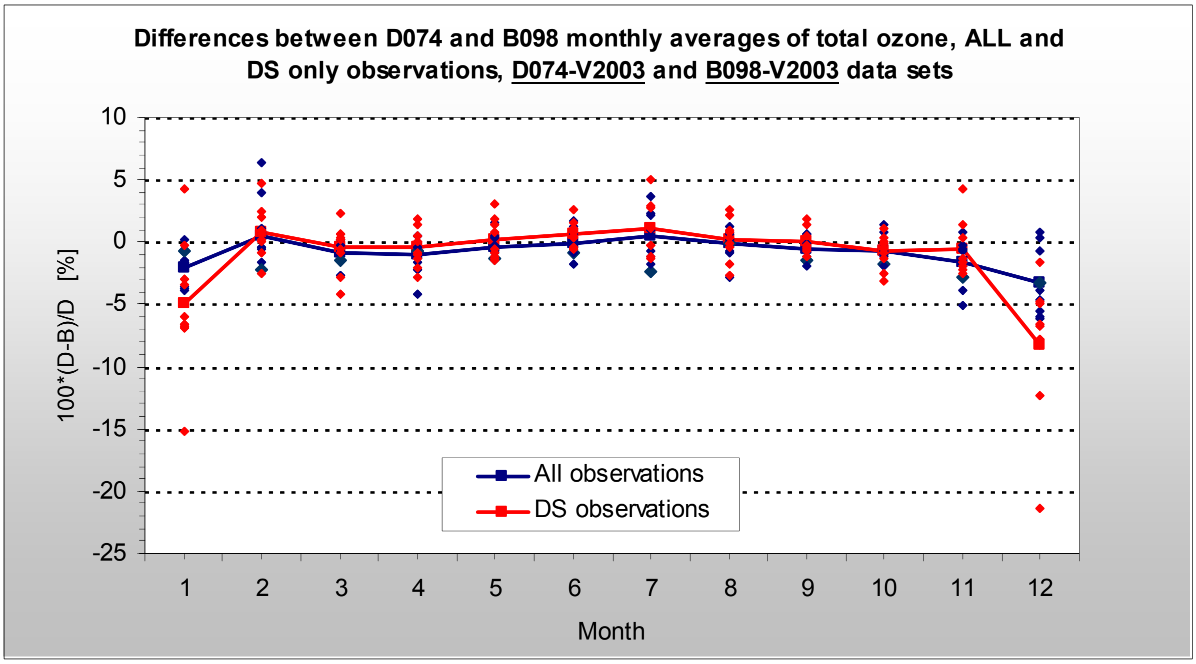

Figure 25. *As Figure 24 but for particular months of the year*

- If only DS monthly averages are taken for statistical analyses, input data samples can be substantially influenced by months with small numbers of DS measurements. This concerns winter months in Hradec Králové, above all.

- DS monthly averages better indicate a long-term concordance of calibration levels of D074 and B098 ozone spectrophotometers than averages derived from ALL measurements. But detailed investigation of relation of both data series needs more sophisticated data sets to be used, mainly DS daily averages or DS simultaneous observations.

c) Daily averages - DS observations

Daily averages of total ozone from each station are deposited in WOUDC for Dobson and Brewer observations in separate files. If the daily values are compared without sorting data for type of observations then DS and zenith measurements are mixed and a higher variation of differences appears. It depends on data users whether all observations or only DS values are taken for statistical analyses. To investigate consistency of D074 and B098 the data series altogether 1.674 pairs of Dobson and Brewer daily averages calculated only from DS measurements of the period 1994-2002 were compared and their differences viewed in *Figure 26*. Zenith cloud observations were excluded to avoid influence of the cloudiness. The differences show an evident annual course with a maximum to minimum range of 3-4 % (maximum in summer and minimum in winter seasons) and a well pronounced shift of the smoothed curve in June/July 1997.

It can be concluded that annual oscillations evidently originate in quasi-periodical seasonal influences of atmospheric parameters or in μ-dependant technical features of D074 and B098 instruments. All these factors can affect the precision of operation of both spectrophotometers and the accuracy of processing of observations, as it has been found at other Dobson/Brewer mid-latitude stations [*Staehelin et al., 2003]*. But the persistent difference that has been identified after July 1997 more probably comes from a shift of calibration levels of D074 and B098. This phenomenon was investigated more precisely by means of simultaneous observations - see the next chapter.

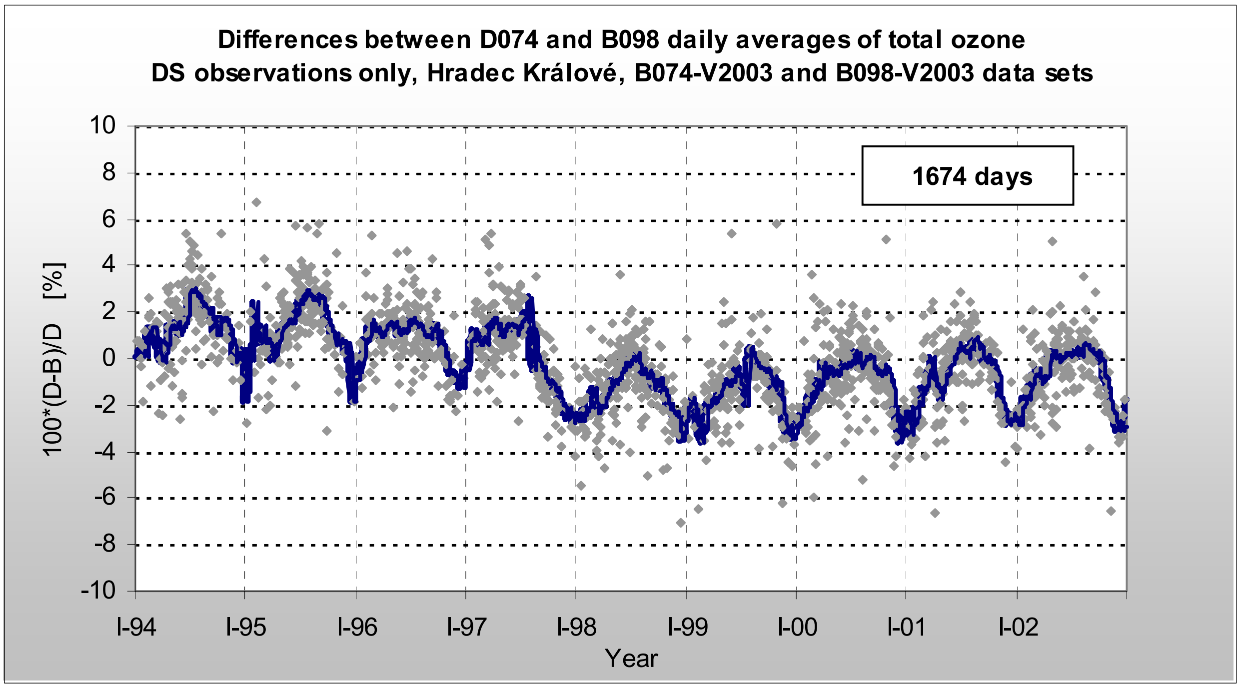

Figure 26. *Differences between daily averages of total ozone measured with D074 and B098. DS observations, Hradec Králové, 1994-2002, D074-V2003 and B098-V2003 data sets.*

5.2. Comparison of individual simultaneous DS observations

a) Data sets

Comparison of simultaneous observations can give the most accurate information about relation between total ozone measurements performed with Dobson and Brewer spectrophotometers and about calibration stability of instruments operated at a particular station. The term “simultaneous measurements” means observations taken in such short time-intervals which eliminate all substantial influences on accuracy of measurements, mainly due to diurnal variation of ozone, atmospheric parameters and operational condition of instruments.

Individual total ozone observations are usually not deposited in WOUDC though the new extCSV format allows it. These data are available at stations or in databases of institutions which operate the spectrophotometers but they are often restricted to external users. For this study which is prepared under the CANDIDOZ project special high-quality data series of individual total ozone measurements performed in Hradec Králové were created from the D074-V2003 and B098-V2003 data sets. Only parallel QA-checked routine D074 DS-AD and B098 DS observations shifted in time by less than 10 minutes have been taken. In this way 5.132 D/B pairs have been selected from the period 01.01.1994 - 31.12.2002 and used for the analysis.

The data were in further steps corrected for the key known parameters that in different ways influence the Dobson and Brewer observations *[Staehelin et al., 2003]*. These were:

- ozone absorption coefficients adjusted for the actual temperature of the ozone layer
- total Sulphur Dioxide in the atmosphere
- optical air mass of the ozone layer

Some other parameters like temperature of the instruments and the aerosol optical depth were not considered as they are expected to be well compensated by standard operational and data processing procedures defined for both types of spectrophotometers - see Chapters 2.1.b) and 2.2.b).

b) Corrections for ozone effective temperature and ozone absorption coefficients

The Dobson and Brewer spectrophotometers measure total ozone at different UV wavelengths (*Table 1* and *Table 2*). Therefore, different spectral ozone absorption coefficients and Rayleigh scattering coefficients are used for calculation of total ozone by relations (2) and (8). As the coefficients are generally defined for stratospheric temperature -46.3 °C *[Komhyr et al., 1993]* their values are not adjusted for actual temperature of stratospheric ozone during observation. Thus, the annual course of temperature of the ozone layer above a station affects accuracy of calculation of total ozone and contributes to seasonal variations of differences between D/B observations. Corrections of total ozone values for real ozone temperature have been determined by Kerr as 1.3% per 10 °K for the Dobson and 0.7 % per 10 °K for the Brewer measurements (0.6 % per 10 °K for the differences*) [Kerr et al., 1988]*.

The corrections mentioned above were applied to simultaneous observations from Hradec Králové using effective temperatures of the ozone layer TO3 calculated for particular days with D/B measurements. Values of TO3 were established by weighting of the ozone vertical distribution by vertical profiles of temperature measured by ozone sounds in Prague (100 km from SOO-HK) and at Hohenpeissenberg (correlated, 450 km from SOO-HK). Finally, only 2.434 simultaneous pairs of D/B observations from SOO-HK taken on days with available TO3 were used for the comparison. Their differences are drawn in *Figure 27* where the black line represents original uncorrected and the red line TO3 corrected smoothed differences. The curves show that a certain effect on decrease of amplitudes has been achieved in winter seasons (by about 0.8 %) while in summer the differences are almost the same (TO3 agrees better with standard temperature -46.3 °C). The shift in 1997 remains unaffected.

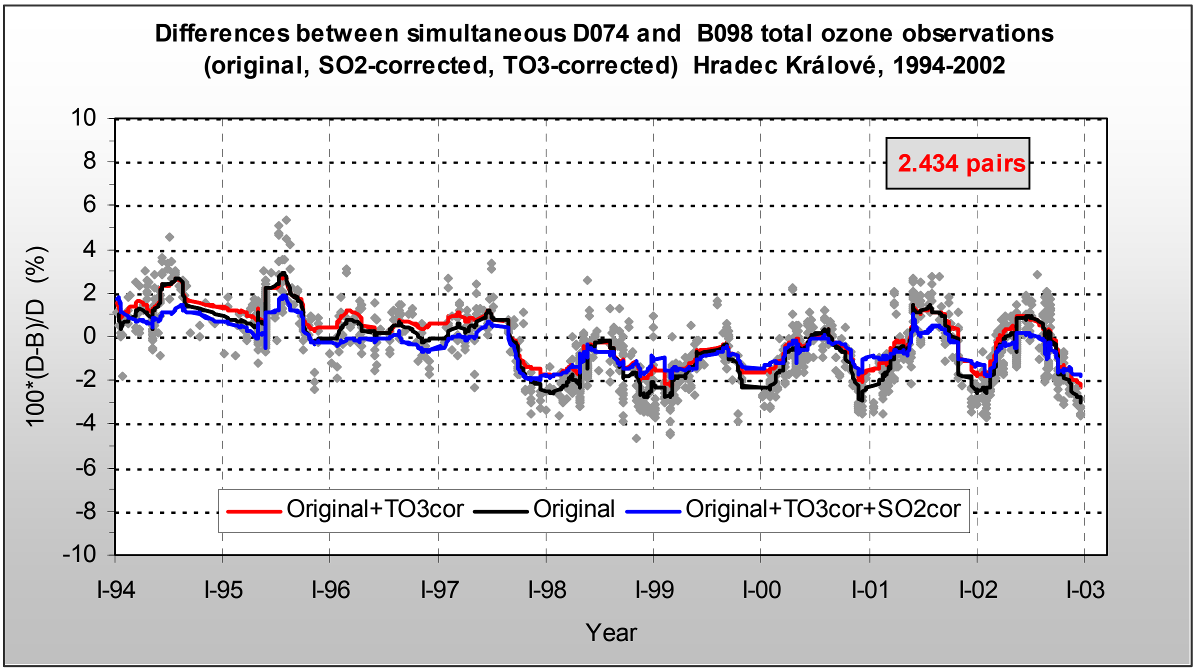

***Figure 27**. Differences between individual simultaneous (+- 10 min) DS total ozone observations measured with D074 and B098. Original, SO_2 and TO3 corrected values. Hradec Králové, 1994-2002, D074-V2003 and B098-V2003 data sets.*

c) *Corrections for total SO_2*

Total ozone values measured by the Dobson spectrophotometer are not corrected for total SO_2 present in the atmosphere while the Brewer observations allow calculation of both total ozone and SO_2 separately - see relations (8) and (9). At stations located in clean conditions (e.g. high-altitude or remote places) contribution of SO_2 to Dobson total ozone can be neglected. But at stations located near significant sources of air pollution SO_2 can affect Dobson observations substantially *[De Muer and De Backer, 1992]*. At SOO-HK Brewer DS total SO_2 usually does not exceed 2-3 DU that is within an estimated range of accuracy of SO_2 measurements. Nevertheless, some episodes with higher values appeared in the recent years, mainly prior 1997 - see *Figure 17*. This was a reason why also Dobson total ozone values from the simultaneous observations have been corrected using Brewer SO_2 multiplied by the factor 1.40 (a factor of conversion of SO_2 values onto equivalent total ozone changes derived at SOO-HK from simultaneous D074 and B098 measurements). The differences are viewed in *Figure 27* (blue line).

Generally, the SO_2 corrections have somewhat reduced amplitudes of annual variation of differences. For positive SO_2 values this corresponds with the physical background. But application of negative SO_2 for corrections is not realistic and according to recommendation of experts *[McElroy and Fioletov, 2003]* these should not be taken into account. This is a reason why offsets between the red and blue lines in winter months of 1998-2000 (the highest number of negative SO_2) should be taken as not fully representative.

d) Corrections for μ - dependence

The Dobson and Brewer spectrophotometers show a certain dependency of their precision on the ozone air mass μ that corresponds to the zenith angle of Sun. If calibration constants are well defined then the dependency mostly comes from different sensitivity of particular instrument (usually Dobson) to low intensity of DS UV radiation (high μ-values) and from an additional signal originated by the UV stray light inside the spectrophotometer. The μ-dependency could be partially caused by the different design of optical systems of spectrophotometers (single or double monochromators, different inlet view angles, different selection of operational UV wavelengths). But also specific features of each instrument can contribute to the μ-dependency, e.g. shifted slit functions or a high reflectivity of internal surfaces. Because of these aspects and to guarantee required accuracy of calibration constants the Dobson and Brewer spectrophotometers are routinely calibrated towards reference instruments for the range of the relative air mass up to μ = 3.2 *[Evans, 1996, 2001]*, *[Lamb and Sevastiouk, 2003]*.

The D074 and B098 spectrophotometers are operated at SOO-HK with calibration constants established for the range of μ = 1.15-3.2 at intercomparisons with the accuracy below 1 % that also compensates their μ-dependency *[Vaníček, 2003]*. Therefore, it can be expected that a μ-dependency of differences between D/B simultaneous observations should remain below the same limit. To investigate this assumption the differences corrected for TO3 and SO_2 of the whole period I.1994-XII.2002 (blue line in *Figure 27*) were plotted against μ and approximated by the linear regression- see *Figure 28.a)*. The slope of the line indicates a certain μ-dependency that is less than 1% for μ from 1.15 up to 3.5 and that is practically equivalent to the annual amplitudes in *Figure 27*. Thus, the curve could be applied on the final correction of differences. But if the same graphs are constructed for the periods I.1994-VI.1997 and VI.1997-XII.2002 of consistent D/B relations separately, then no μ-dependencies appear, see *Figure 28.b)* and *Figure 28.c)*. The explanation is that the slope of the linear regression in *Figure 28. a)* is only due to formal statistical processing of data samples of different features (shift in calibration levels) and corrections of the D/B differences using one linear regression from *Figure 28.a)* would not have a physical reason.

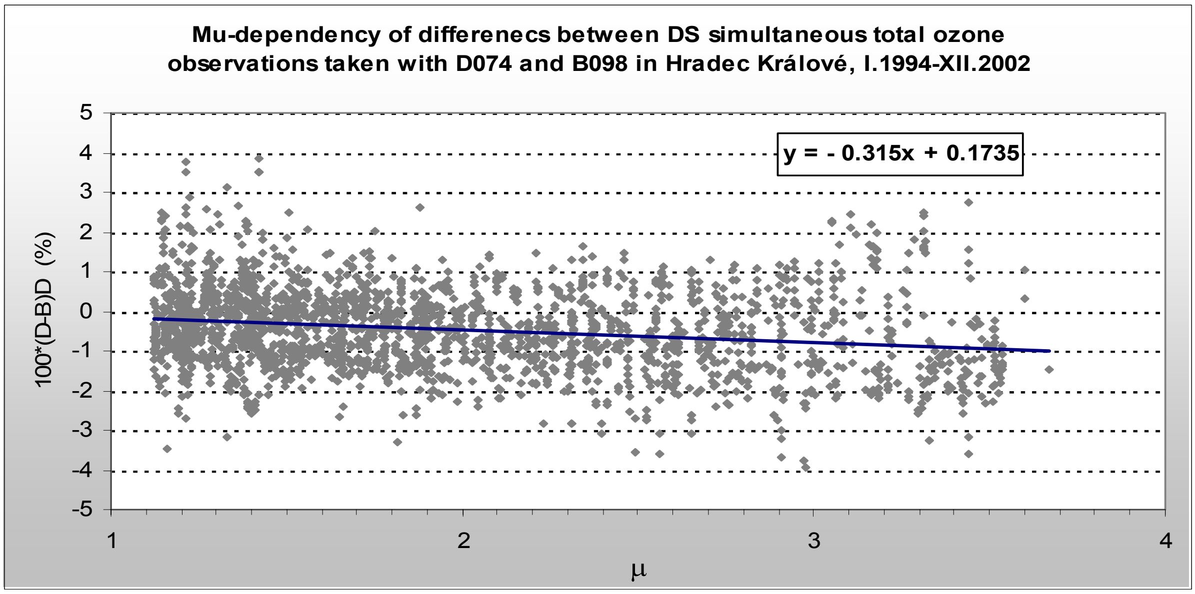

Figure 28. a) μ - dependency of d*ifferences between individual simultaneous DS total ozone observations measured with D074 and B098. TO3 and SO_2 corrected values. Hradec Králové,* D074-V2003 *and* B098-V2003 *data sets, different periods of 1994-2002*

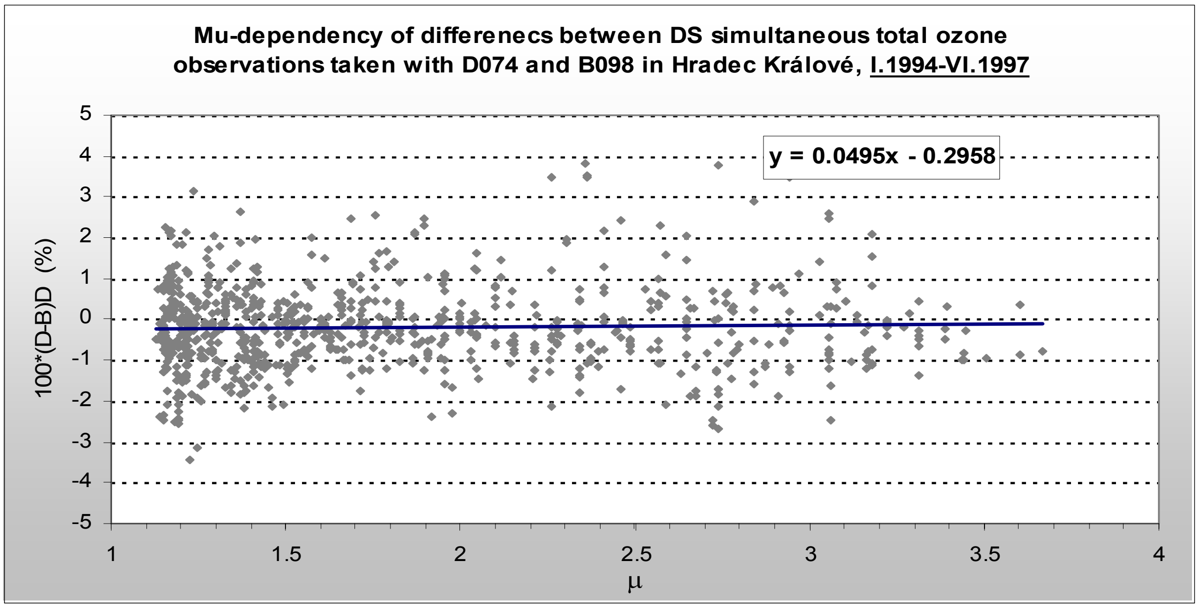

Figure 28. b) *As Figure 28 a) but for the period I/1994-VI/1997*

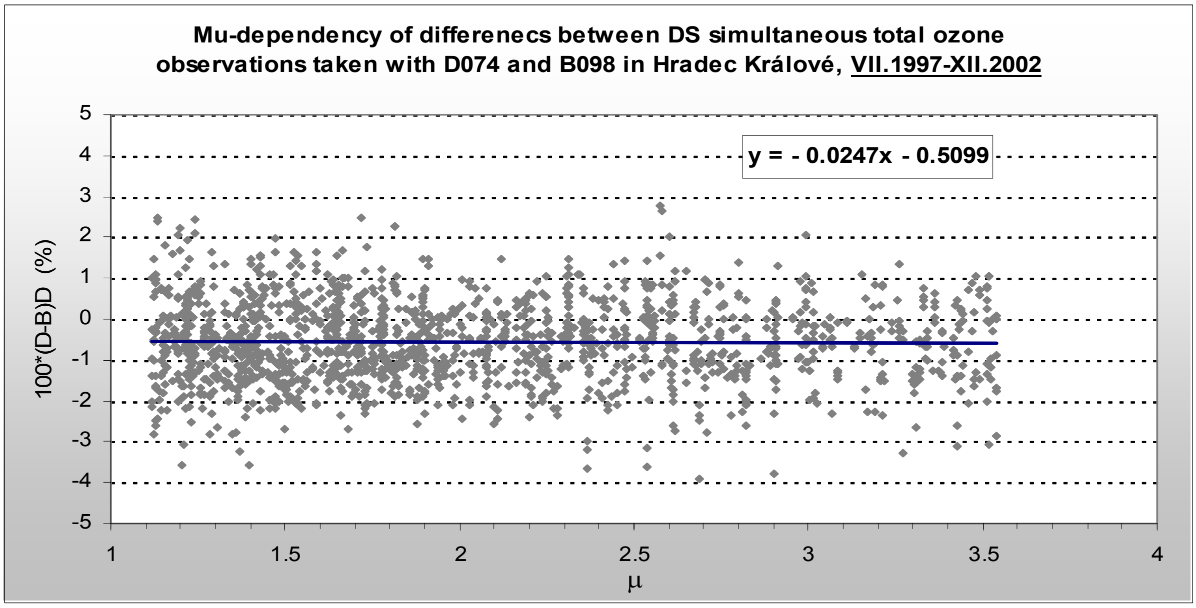

Figure 28. c) *As Figure 28 a) but for the period VII/1997-XII/2002*

e) Other possible factors

The selection of simultaneous Dobson and Brewer observations and their corrections for ozone efficient temperature and partially for total SO_2 have reduced amplitudes of the D/B differences by about 50 percent. The remaining residual annual variations can hardly be explained by a μ-dependency due to the internal stray light in the case of D074 and B098 instruments. It seems that some other factors still cause the differences.

If an assumption is accepted that annual changes of temperature of instruments are well compensated by their calibration constants then a stronger influence of seasonal variation of ozone temperature can be expected to be the reason of residual amplitudes. This may happen if the real ozone cross sections differ remarkably from those predefined for the UV operational wavelengths (*Table 1* and *Table 2*).

It has already been mentioned in the Chapter 4.1.c) of this Report that the best fit of Brewer spectrophotometers with the reference instruments at ICs is achieved not only by adjustment of ETCs but also by re-definition of the ozone absorption coefficients by means of the Dispersion Test. But it is almost impossible to measure slit functions and to establish real operational wavelengths (and ozone cross sections) of particular spectrophotometers at Dobson ICs. Therefore, the best fit towards the reference instruments is achieved only by the adjustment of ETCs. As mainly the A wavelength pair is very sensitive to a perfect definition of ozone coefficients even small shifts of the slits (slit functions) can introduce a stronger temperature dependency of ozone cross sections of the reference double pair AD and thus the D/B differences can become higher than it was theoretically calculated for the ideal wavelengths in Chapter 5.2.b). This effect may be of different magnitude at particular stations because of different technical condition of their instruments. This is the reason why a coordinated investigation of this phenomenon at more stations is needed *[Staehelin et al., 2003].*

f) Shift of the calibration levels of D074 and B098 instruments

The sudden shift of the smoothed curves in June/July 1997 that was identified in *Figure 26* and persists after all corrections in *Figure 27* has been confirmed by all ICs of D074 and B098 intercomparisons held prior and after this date - see *Figure 29*. To asses this change the simultaneous observations of the whole period 1994-2002 were re-processed by means of the calibration constants of D074 and B098 used prior July 1997 (the ICs after June 1997 were not considered). Differences were plotted in *Figure 29* (red line). The graph shows that the <u>Prior 1997</u> constants keep the D/B differences consistent even after 1997 and better diminish their annual variations comparing to the <u>Actual</u> constants (routinely updated after each IC). The total shift of the curves is estimated to be about -1.3 %. This exceeds the instrumental precision of the spectrophotometers and it has to be taken as a serious change of the consistency of both data series.

As the offset of the curves has been confirmed by ICs after 1997, it can be expected, that this phenomenon could come from differences between calibration levels of the reference instruments (B017 and D065) routinely used for calibration of spectrophotometers within the network. Because analyses of maintenance of the references during the second half of the nineties have not been published yet, personal consultations with experts from CMDL and IOS were held in September/October 2004. These discussions lead to conclusions that:

- B017 is regularly calibrated by the Langley plot method at Mauna Loa and cross-checked towards WPBST. No significant shift of calibration constants of B017 has been identified in the last decade.
- D065 is regularly compared towards the WPDS D083 that is absolutely calibrated at Mauna Loa as well. Relation of D065 and D083 will be analyzed and results presented at the Quadrennial Ozone Symposium in 2004
- Side-by-side comparisons of B017 and D065 are not available for a direct assessment of their relation.

From the facts given above it is evident, that a definite conclusion on a calibration shift of the reference instruments based only on the Hradec Králové data cannot be made at present. But the results obtained in this Report challenge the Dobson and Brewer community to investigate the problem at other stations and the calibration centres and to present analyses of maintenance of their reference instruments.

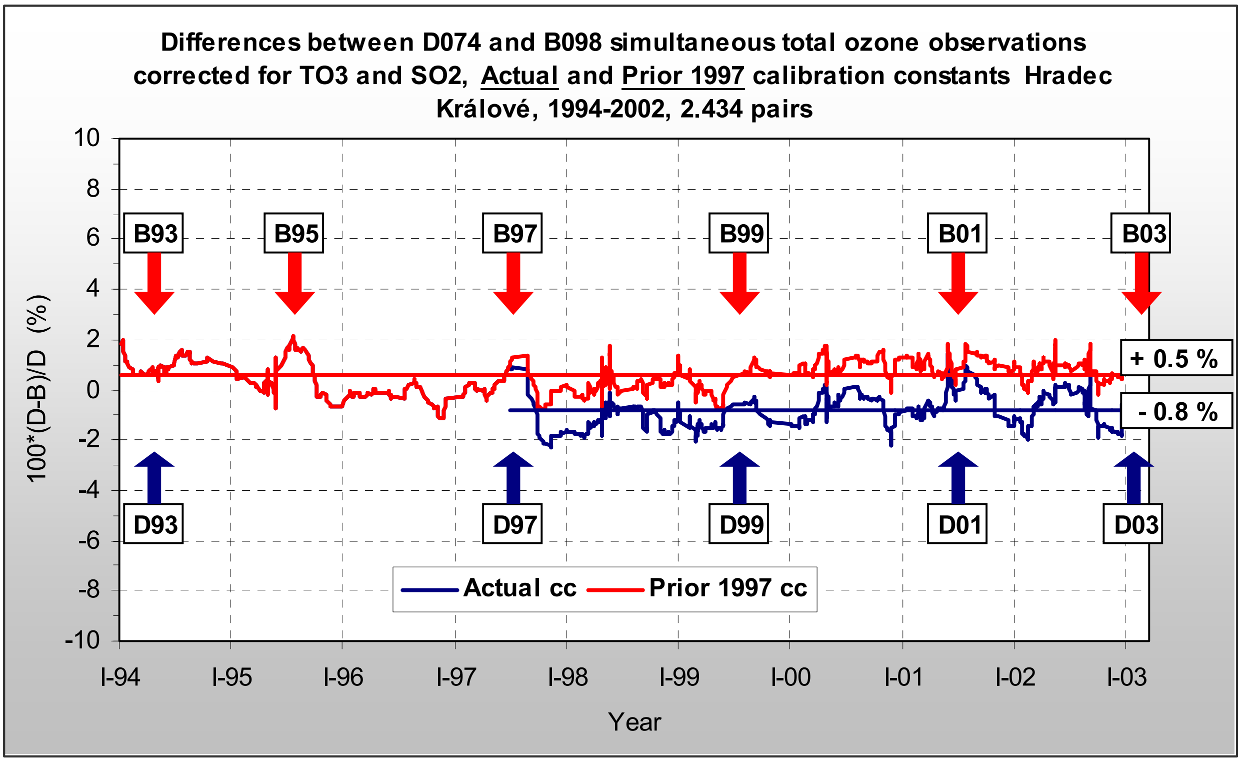

***Figure 29**. Differences between D074 and B098 simultaneous total ozone observations corrected for TO3 and SO_2, re-calculated by means of the Actual and the Prior 1997 calibration constants, Hradec Králové, 1994-2002, D074-V2003 and B098-V2003 data sets, Dobson(D) and Brewer(B) intercomparisons are indicated by arrows*

5.3. Comparison of D074-V2003 and B098-V2003 data with satellite observations

c) Comparison with TOMS data

The re-calculated data sets D074-V2003 and B098-V2003 were compared towards total ozone observations taken with TOMS and GOME satellite instruments. The first comparison was made between D074 measurements and the TOMS Version-7 observations taken with the Total Ozone Mapping Spectrometer (TOMS) onboard of the NIMBUS-7 satellite. This data set is free-available for the period XI/1978-IV/1993 at the NASA/TOMS web site and its accuracy has been estimated to be better that 1% *[McPeters and Labow, 1996]*. The main goal of the comparison was to assess the consistency of the new D074-V2003 data set in the period 1979-1986 that is important for adjustment of the D074 instrument towards the WPDS´s calibration scale - see *Figure 7*. Differences between D074 DS and TOMS-7 overpass observations are drawn in *Figure 30*. The graph shows a small change (- 0.6 %) of the tendency of differences in 1986 after the final adjustment of D074 towards D083 that is still in 1 % limit of precision of both instruments. Generally, the average offset of the differences is +0.2 with STD = 1.9 for the whole period. This confirms a stable quality of the updated calibration constants of D074 and the consistency the new D074-V2003 data series.

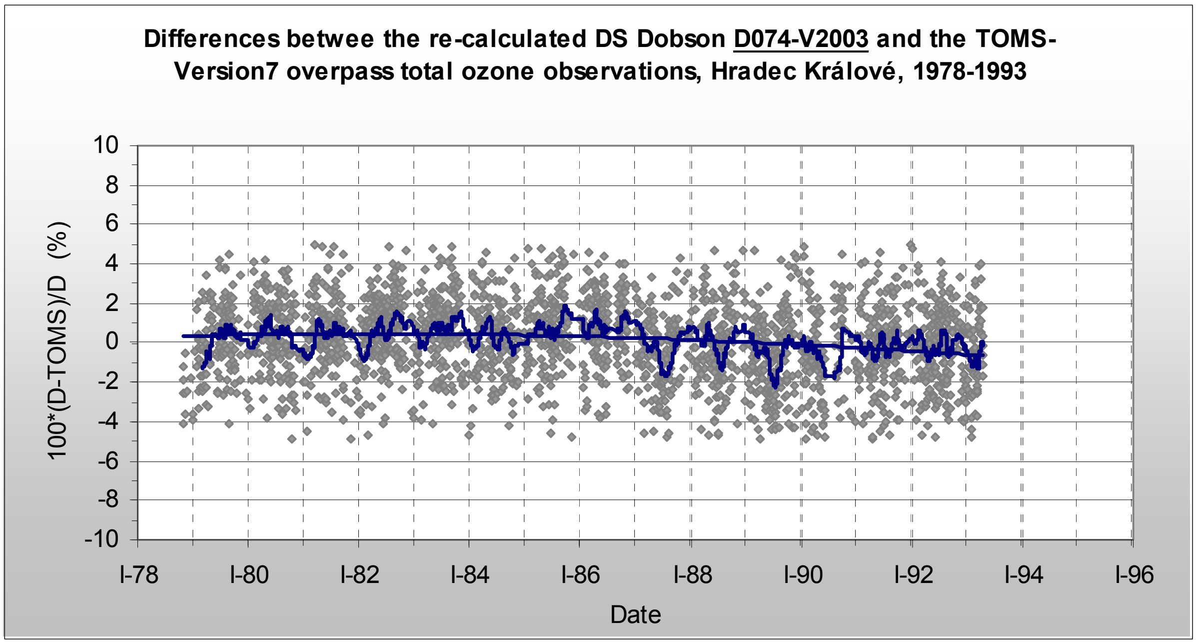

Figure 30. *Differences between re-calculated DS D074-V2003 and TOMS-Version7 overpass total ozone observations, no corrections for SO_2 and TO3 applied, Hradec Králové, period XI/1978-IV/1993*

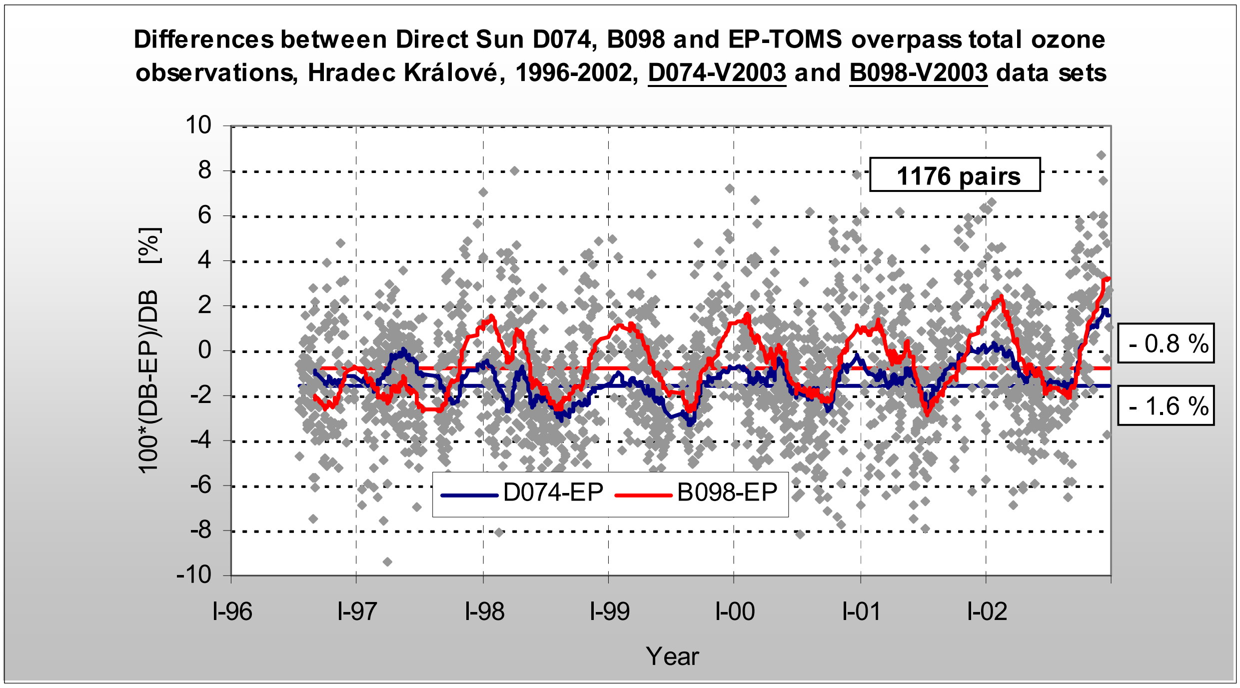

Figure 31. *Differences (smoothed and average) between re-calculated DS D074-V2003, B098-V2003 and the EP-TOMS overpass total ozone observations, no corrections for SO_2 and TO3 applied, Hradec Králové, period VII/1996-XI/2002*

In the second step total ozone observations taken with the TOMS system carried by the Earth Probe (EP-TOMS) satellite *[McPeters et al., 1998]* were used to assess the relation towards Dobson and Brewer measurements performed in Hradec Králové after the change of the calibration states of the spectrophotometers appeared in 1997. EP-TOMS overpass measurements were compared with D074 and B098 DS observations not corrected for SO_2 and TO3. The differences are approximated by smoothed curves and average lines in *Figure 31*. The graph shows evident features of annual oscillations that are more pronounced for the Brewer instrument (red line). As the EP-TOMS facility has certain problems with stability of its precision due technical problems *[WMO, 2003]* the seasonal oscillations are not discussed here but more attention is devoted to an absolute bias between average differences viewed by straight lines. The offset has been found to be - 1.6 % for Dobson values (blue line) while for Brewer observations it is - 0.8 %, finally being -0.8% between both data series. This fact supports the conclusion made in Chapter 5.2.f) that since 1997 the D074 and B098 instruments have been operated in Hradec Králové at calibration levels that differ with each other by about 1 %.

d) Comparison with GOME data

In the Work Package WP1 of the CANDIDOZ Project the scientific group from the University Bremen (UB) works on development of a new algorithm for processing the satellite ozone measurements performed with the Global Ozone Monitoring Experiment (GOME) facility onboard of the ERS-2 satellite. The new technology includes the effective albedo, improved cloud algorithm, improved wavelength fitting by referencing to a solar reference spectrum and inclusion of molecular (ozone) filling-in in the ring effect. The UB group has been provided on request with re-evaluated DS observations from the D074-V2003 and B098-V2003 data sets of the period 1996-1999 for validation of their newest GOME-V4

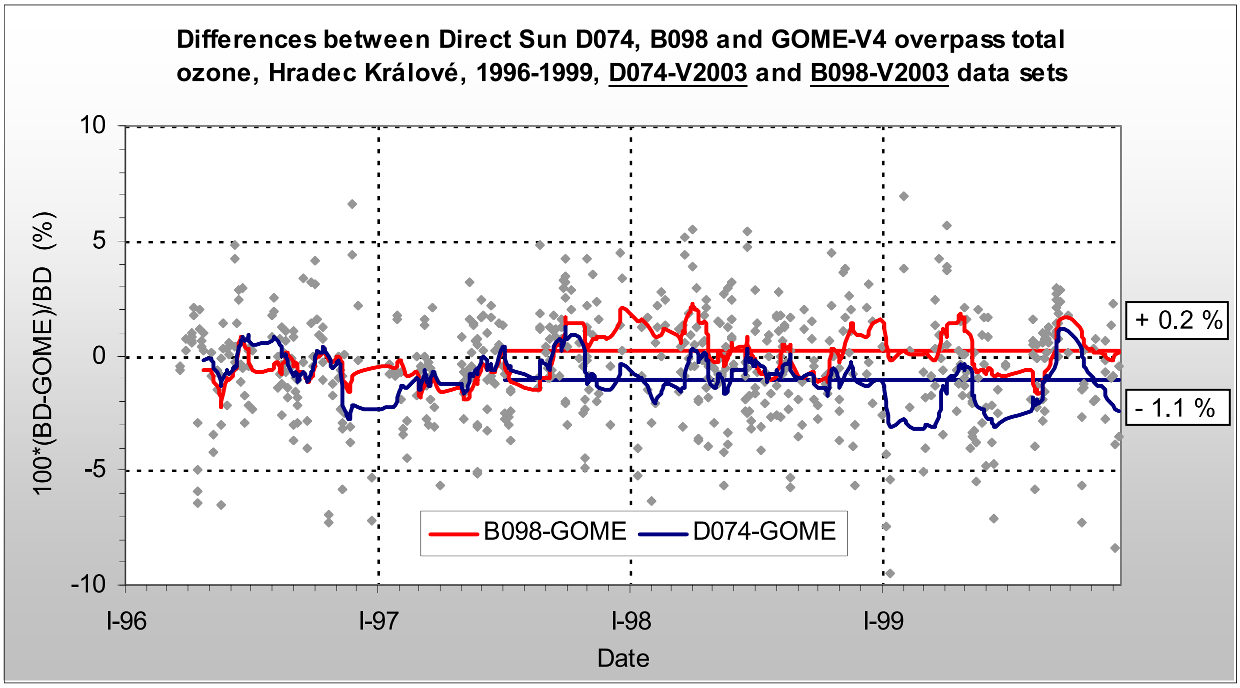

Figure 32. *Differences (smoothed and average) between re-calculated DS D074-V2003, B098-V2003 and the GOME-V4 overpass total ozone observations, no corrections for SO_2 and TO3 applied, Hradec Králové, period 1996-1999. GOME-V4 data provided by University of Bremen [Weber, 2003]*

observations processed by the new algorithm mentioned above. The following preliminary results have been achieved. “For Hradec Králové the comparison gives the bias - 0.1% with +- 2.4% 1sigma for the B098 and - 0.9% with +- 2.5% 1sigma for the D074 instruments. The differences to Dobson show a seasonal cycle of about 2% (+- 1%) throughout the year. The same comparison using operational GOME-V3 data shows the stronger seasonal cycle with the Brewer instrument and to a lesser extent with the Dobson spectrophotometer” *[Weber, 2003]*.

If a graph of average differences is drawn up then biases between D074, B098 and GOME-V4 observations after June 1997 are -1.1 % and +0.2 % respectively - see *Figure 32*. Therefore, almost identical offsets have been found between D074 and B098 for GOME-V4 and for the EP-TOMS observations in the second half of the nineties. In this way approximately 1 % shift between D074 and B098 data series have been confirmed by the GOME independent data source, as well.

6. CONCLUSIONS AND RECOMMENDATIONS

- The D074-V2003 and B098-V2003 data sets represent the latest versions of long-term observations of total ozone performed in Hradec Králové. The re-evaluation of both data series has been done strictly with respect to calibration scales of the world standard instruments WPDS (D083) and WPBST (the reference triad). Both new data sets will be re-deposited into WOUDC and used for the updating total ozone statistics of SOO-HK.

- The average accuracy of individual total ozone observations included in D074-V2003 is estimated to be about 1% for DS, 2% for ZB and 3% for ZC measurements respectively of the period 1979-2002. For years period prior 1979 the accuracy should not be significantly lower.

- The average accuracy of individual total ozone observations included in B098-V2003 is estimated to be about 1% for DS and 3% for ZS measurements respectively of the whole period of 1994-2002

- The accuracy of mean values calculated from both data sets strongly depends on the number of days taken for statistics – see Appendix A and *Table 8* as an example for monthly averages.

- Parallel total ozone observations of the overlapping period 1994-2002 show an evident seasonal course of differences between D074-V2003 and B098-V2003 data series. Amplitudes of the differences are more pronounced for DS daily overages and they have a similar magnitude like differences from other mid-latitude stations operating collocated Dobson and Brewer spectrophotometers.

- If strictly simultaneous observations were selected and corrected for total SO_2 and for ozone efficient temperature then the amplitudes of differences have been reduced by about a half but certain residual seasonal oscillations still persist. These are expected to be originated by the uncertainty in definition of temperature dependency of ozone cross sections related to UV wavelengths really selected by spectrophotometers during routine measurements.

- Uncorrected differences can introduce an additional statistical signal into long-term seasonal trends of total ozone if Dobson observations are replaced/continued by Brewer measurements at a particular station. Therefore, combined D074 and B098 data series are recommended to be used for investigation of this problem that could imply a general impact in the global GAW network.

- The comparison of D074 and B098 observations also shows a sudden shift between both data series in June/July 1997 after intercomparisons of the spectrophotometers towards traveling references. The offset has been confirmed by next ICs realized in later years. The most probable explanation is that this change has appeared due to a shift between calibration levels of the traveling references in the second half of the nineties. Therefore, this phenomenon needs to be investigated by means of parallel Dobson and Brewer observations at more stations.

- The re-evaluated total ozone measurements from SOO-HK were compared with satellite overpass observations. TOMS-V7 data gave a very good (below 1 %) agreement and consistency with D074-V2003. Thus a high quality of the re-calculated Dobson measurements taken in the period 1978-1993 has been validated .Comparison of D074-V2003 and B098-V2003 towards EP-TOMS and GOME-V4 data sets confirmed the systematic bias between D074 and B098 observations after July 1997 that was mentioned in the previous paragraph.

- Though the results presented in this Report are based on the evaluation of total ozone observations from one particular station the key outputs are focused on the goals of the project CANDIDOZ. An assessment of relation between Dobson and Brewer calibration scales and investigation of the consistency of long-term total ozone observations performed by both spectrophotometers in Hradec Králové have general aspects related to the global ozone monitoring system. Regarding to the CANDIDOZ Project it has been documented that a certain part of decadal ozone changes could become of an instrumental origin if the transfer calibration scales into ground-based networks is not permanently controlled and strictly checked. This concerns also satellite observations as algorithms for their processing and validation of the final output data strongly depend on the quality of the ground segment of the integrated ozone monitoring system.

Appendix A

Uncertainty in the monthly mean total ozone estimated from an incomplete set of daily values

Ground-based measurements of total ozone are not available for all days in a month as they are taken (mainly with the Dobson spectrophotometer) only at suitable weather condition. The question stands, what is the error of the monthly mean total ozone estimated from incomplete set of daily values? This error will is estimated here with use of the Monte Carlo method.

Let m is a number of days in a given running month, n is a number of available daily total ozone values within that particular month, $n < m$, Y_n is an average of daily values of these available days, and Y is a real monthly mean total ozone. Y_n is then considered to be an estimate of Y. Further, we assume that the month has 30 days (m = 30) and that daily total ozone values in the particular month follow a normal distribution $N(TO, s^2)$, where TO is a long-term monthly mean and $\boldsymbol{s}$ is the mean standard deviation of daily total ozone within the running month. Note, that s is the standard deviation calculated from 28-31 days in a single month not over the long-term time series. Values of s (rectangles in Figure A1) are lower than standard deviations of the daily total ozone calculated from all days in individual months from a long-term series (circles in Figure A1).

Uncertainty in estimating Y may be estimated by the following numerical experiment:

1. 30 daily values are randomly sampled from normal $N(0,1)$ distribution: $\{x_1, .. , x_{30}\}$. These values represent the standardised daily total ozone values during a month.
2. n values (n < 30) are selected from $\{x_i\}$: $\{x_{i1}, ... , x_{in}\}$. This subset represents the available values of standardised daily total ozone.
3. Averages of the two sets and their difference are calculated: $X = \text{avg}\{x_1, .. , x_{30}\}$, $X_n = \text{avg}\{x_{i1}, ... , x_{in}\}$, $D = X_n - X$. The difference multiplied by s then represents the error of the monthly mean estimated from a limited set of the daily ozone values.
4. Steps 1-3 are repeated many times (e.g.: N = 10000) and the mean, μ_n (should be insignificantly different from zero), and standard deviation, σ_n, of D are calculated.

The value of product $s.\sigma_n$ represents the uncertainty (expressed in terms of the standard error) in estimating the monthly mean total ozone. As s is different for individual months (Figure A1) and σ_n depends on n (Figure A2; notice that σ_n decreases with n increasing and diminishes to zero for n = 30), this uncertainty differs for individual months and number of available daily ozone values.

Assuming that D has approximately a normal distribution, the quantiles of the normal distribution $N(0,\sigma_n^2)$ may be used to estimate bounds of the (1−α)-confidence interval for the monthly mean (interval, in which the monthly mean lies with 100(1−α)% probability:

$$\Pr\left(Y_n - s.\varepsilon(\alpha,\sigma_n) \le Y \le \; Y_n + s.\varepsilon(\alpha,\sigma_n)\right) \;=\; 1-\alpha$$

where

$$\varepsilon(\alpha,\sigma_n) = F^{-1}(1-\alpha/2 \,|\, 0,\sigma_n^2) \quad ,$$

is a (1−α/2)-quantile of the normal distribution. The product $s.\varepsilon(\alpha,\sigma_n)$ is then the half-width of interval in which the value of e_n will lie with probability 1-α. The half-width of the 95% confidence interval for various values of n is displayed in Figure A3 in terms of the absolute errors (in Dobson Units) and in Figure A4 in terms of the relative error. The latter figure shows a value of the relative error, which is exceeded with only 5% probability.

Figure A4. shows that the number of daily values needed for the half-width of the 95% confidence interval for the monthly mean total ozone to fall below a given threshold (e.g. 2%) varies during a year. This is due to the annual cycle of STD(TO)/AVG(TO) ratio (Figure A5). The lowest required number of days is in August (n_{min} = 13), the highest required number is in February (n_{min} = 24). The numbers of days with daily total ozone required to achieve the given relative accuracy in determining the monthly mean total ozone are given in Table AI.

Table I. Number of days with daily total ozone required for a half-width of 95% confidence interval being lower then 1%, 2%, 3% and 5% of a monthly average total ozone value.

Half-width Month	1%	2%	3%	5%
1	29	24	19	11
2	26	22	17	10
3	29	24	18	10
4	27	20	14	7
5	25	16	10	5
6	24	15	9	4
7	24	14	9	4
8	23	13	8	3
9	24	16	10	5
10	26	17	11	5
11	27	21	15	8
12	29	24	18	11

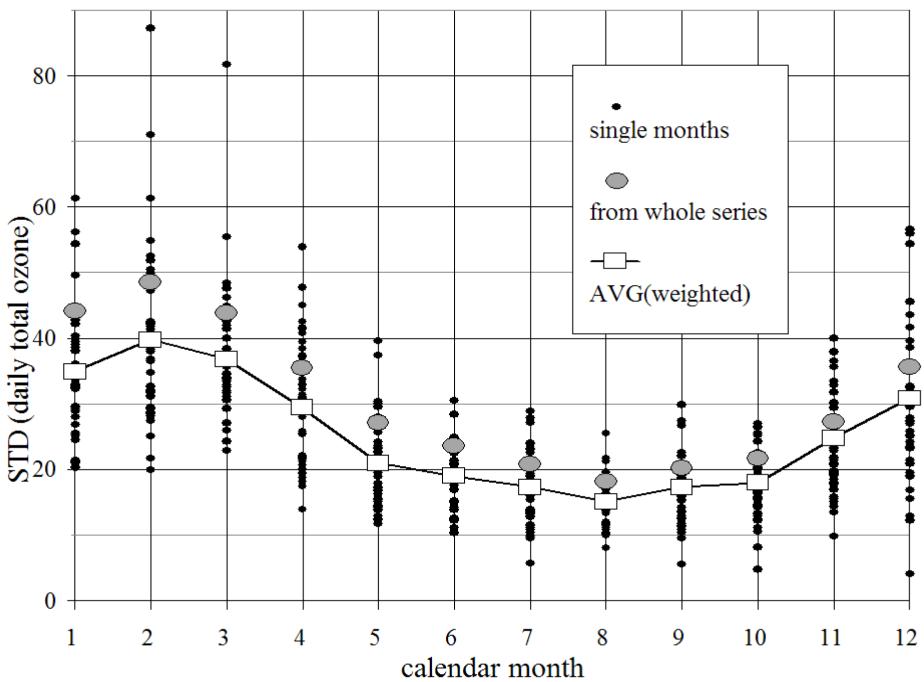

Figure A1. *Standard deviations of daily total ozone values in Hradec Králové (1961-2002). Black dots: standard deviations in individual running months of the 1961-2002 time series. Grey circles: standard deviations calculated from all daily values in a given calendar month. Rectangles: weighted average from the black dots (weight = number of values from which the respective black dot was calculated). The values marked by the rectangles were used to establish the confidence intervals displayed in Figs. 3-4.*

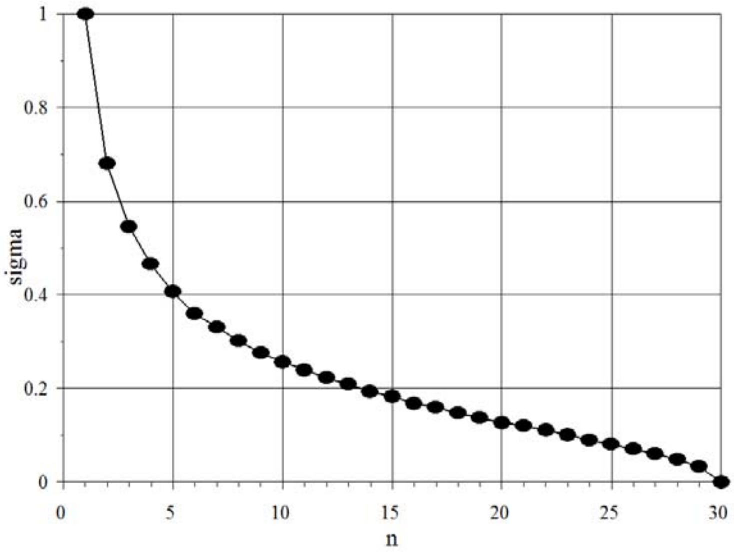

Figure A2. *The dependence of σ_n parameter on n. n is the number of days selected from the 30-days month, and σ_n is the standard deviation of the average of n values sampled from N(0,1) distribution. The values of σ_n were determined by the Monte Carlo method.*

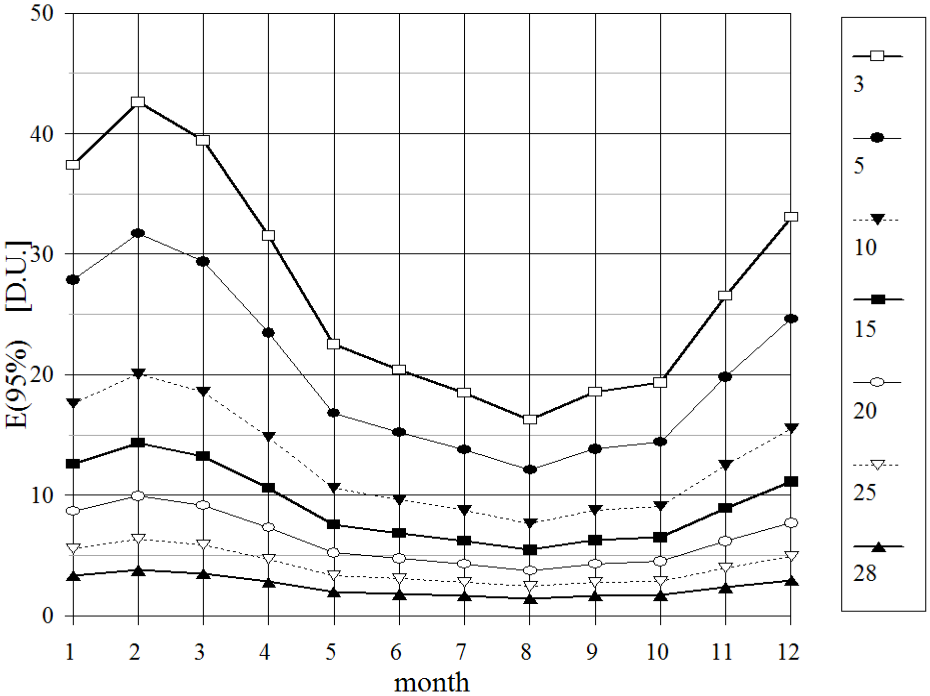

Figure A3. *E(95%) is the half-width of the 95% confidence interval in which the monthly mean of total column ozone lies with 95% probability. The values of the half-width are displayed for various numbers of days from which the monthly mean is estimated. These numbers are given in the legend box. (Note that number of days in all months was considered to be 30 in the model calculations!)*

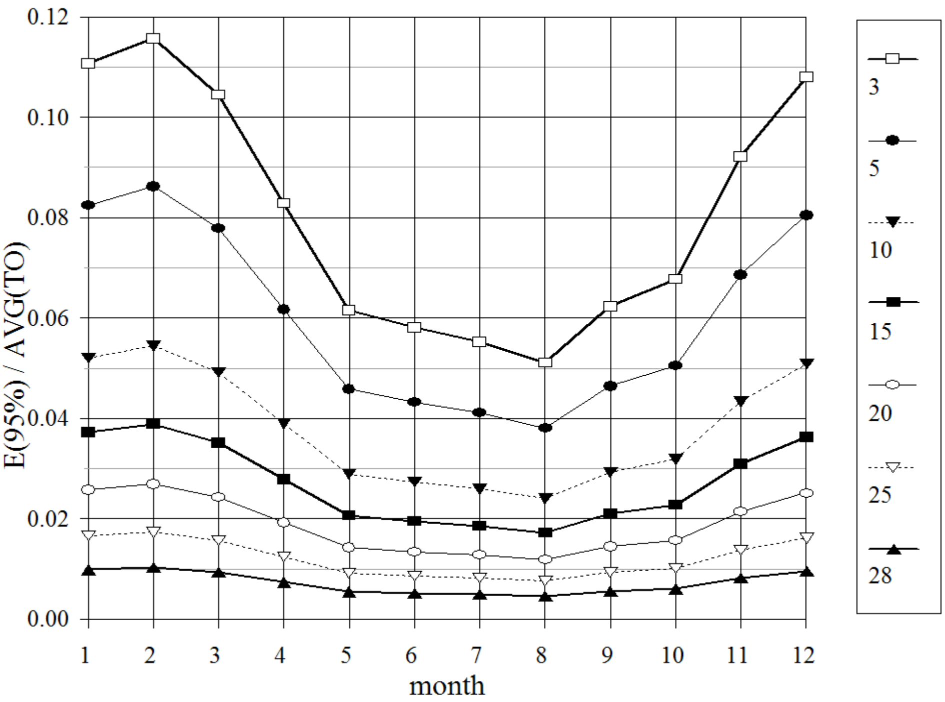

Figure A4. *The same as Figure A3 but the half-width is given in terms of the relative error.*

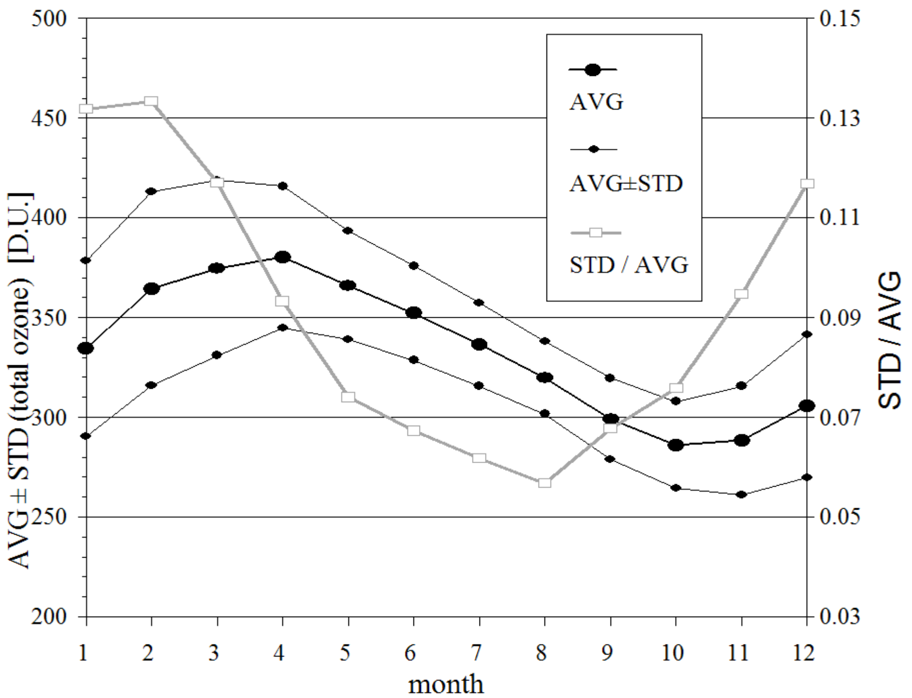

Figure A5. *The annual cycle of total ozone in Hradec Králové. AVG and STD are the average and standard deviation of daily total ozone calculated from all days in a given calendar momth*

Appendix B

Monthly averages of total ozone calculated from the re-evaluated D074-V2003 and B098-V2003 data sets for ALL and DS only observations

Shaded cells represent monthly averages calculated from different numbers of days with observations in particular months and therefore with different accuracy of estimation of daily means. The shading is defined according to limits of accuracy given in Table 8 as follows

White cells	…..	accuracy	=	0-3 %
White-gray	…..	accuracy	=	3-5 %
Dark-gray	…..	accuracy	=	aver 5 %

***Table B1** Monthly averages of Dobson total ozone, Hradec Králové, 1961-2002, D074-V2003 data set, ALL observations.*

Month / Year	1	2	3	4	5	6	7	8	9	10	11	12	Average
1961	348.8		312.4	355.3			326.5	307.8	288.1	269.9	302.9	293.5	311.7
1962	319.7	388.6	428.8	367.9	370.4	344.2	326.3	309.4	293.4	261.5	272.6	286.7	330.8
1963	345.0	405.8	390.6	389.5	381.2	368.4	328.7	310.5	292.5	285.6	277.6	296.0	339.3
1964	315.5	359.7	365.7	394.8	379.1	332.4	325.1	312.1	291.7	283.0	266.3	291.4	326.4
1965	338.7	382.6	404.5	394.8	393.5	347.7	336.6	323.5	295.7	275.0	325.5	280.4	341.5
1966	309.0	358.1	423.7	389.4	378.7	357.7	342.9	315.7	288.8	308.0	305.1	329.8	342.2
1967	370.4	376.7	403.2	367.9	351.0	350.7	332.4	318.8	287.7	273.6	276.3	326.4	336.3
1968	411.2	386.5	405.6	380.4	355.4	346.1	332.3	333.8	303.8	286.8	268.4	358.5	347.4
1969	370.2	428.0	385.3	414.5	374.8	375.0	342.8	341.0	300.2	286.1	298.5	328.7	353.8
1970	335.6	435.3	440.9	429.3	400.9	374.2	346.4	331.6	313.0	292.0	296.0	322.2	359.8
1971	355.0	387.8	412.8	390.6	371.4	368.4	340.6	319.4	319.0	285.1	295.5	312.6	346.5
1972	359.9	371.8	392.5	381.4	377.5	367.1	343.8	320.9	322.7	309.0	299.9	310.9	346.5
1973	328.3	425.1	380.5	445.5	378.2	362.6	355.6	329.2	295.3	304.9	304.4	317.5	352.3
1974	343.0	371.4	351.1	394.6	388.8	377.0	339.6	323.7	296.3	331.4	306.0	316.0	344.9
1975	330.6	346.3	386.1	394.6	365.5	363.8	339.6	326.0	295.0	290.0	302.7	303.7	337.0
1976	336.2	362.8	388.6	384.9	377.0	355.7	353.4	336.0	316.4	282.2	291.9	320.4	342.1
1977	366.0	402.4	371.0	400.1	376.9	368.6	356.3	331.2	307.6	279.3	297.2	311.7	347.4
1978	361.7	377.6	371.1	400.2	390.7	374.1	353.7	334.1	304.8	283.0	286.2	294.1	344.3
1979	372.1	386.2	396.1	415.1	382.5	361.0	363.5	331.7	302.9	298.0	292.5	336.4	353.2
1980	361.2	355.5	401.9	425.3	399.5	377.3	371.4	332.2	303.7	296.4	304.1	321.1	354.1
1981	366.6	383.7	380.2	392.3	399.9	351.9	348.6	333.3	309.6	310.4	314.7	347.0	353.2
1982	367.3	403.1	411.5	397.4	382.7	373.4	346.2	337.5	299.3	296.5	279.5	301.8	349.7
1983	313.0	353.6	358.0	376.6	358.1	351.4	329.9	328.1	300.6	278.1	286.9	312.6	328.9
1984	371.0	373.5	388.5	406.6	383.5	374.7	350.6	331.1	314.3	294.6	283.7	318.0	349.2
1985	376.5	389.0	374.4	369.2	361.7	364.9	331.0	307.0	295.4	279.0	304.7	324.9	339.8
1986	378.1	398.6	363.4	386.8	363.0	349.4	343.3		279.4	283.4	292.3	325.1	342.1
1987	328.7	352.8	419.5	375.9	382.2	352.8	336.9	334.7	300.5	290.4	308.1	298.6	340.1
1988	318.1	354.2	413.9	380.2	362.2	359.8	332.5	319.0	294.8	273.5	273.0	326.6	334.0
1989	315.6	382.8	367.5	370.8	362.8	345.5	334.3	324.3	296.1	281.7	296.1	303.4	331.7
1990	316.8	324.5	334.3	371.0	358.4	342.5		317.0	314.9	277.9	306.1	316.4	325.4
1991	355.3	387.2	368.1	395.4	395.2	373.9	334.8	325.1	299.6	297.2	298.5	287.4	343.1
1992	282.9	340.2	356.4	369.4	351.9	339.9	324.0	295.5	279.6	288.7	277.9	286.0	316.0
1993	293.8	304.2	337.1	334.7	335.5	332.1	323.1	306.3	302.1	273.2	299.3	301.9	311.9
1994	348.3	401.4	344.5	371.2	371.8	339.3	327.9	320.3	306.0	291.4	287.8	302.7	334.4
1995	323.1	335.9	369.5	352.0	343.6	329.4	317.8	318.7	301.8	270.5	289.4	311.1	321.9
1996	307.8	372.7	354.4	355.2	351.7	339.9	334.3	309.8	304.8	280.1	283.1	301.0	324.6
1997	334.7	349.8	343.5	357.2	343.3	345.8	339.5	305.7	280.0	283.4	283.3	294.0	321.7
1998	336.0	324.4	379.2	388.5	369.4	343.6	340.2	320.4	309.3	297.3	310.6	298.8	334.8
1999	330.6	429.1	372.8	369.0	353.7	336.0	336.7	313.7	286.7	290.7	290.3	300.5	334.2
2000	324.7	344.8	351.6	355.7	345.0	323.6	332.2	305.0	291.0	274.6	284.9	322.8	321.3
2001	327.7	363.0	380.0	377.0	349.6	351.4	325.5	306.9	316.8	268.6	276.8	296.5	328.3
2002	303.0	347.1	357.7	376.9	334.4	336.4	320.5	317.2	306.3	294.9	295.2	291.2	323.4

Table B2 *Monthly averages of Dobson total ozone, Hradec Králové, 1961-2002, D074-V2003 data set, only DS observations*

Month / Year	1	2	3	4	5	6	7	8	9	10	11	12	Average
1961	348.8		312.4	355.3			326.5	307.8	288.1	269.9	302.9	293.5	311.7
1962	319.7	388.6	428.8	367.9	370.4	344.2	326.3	309.4	293.4	261.5	272.6	286.7	330.8
1963	345.0	405.8	390.6	389.5	381.2	368.4	328.7	310.5	292.5	285.6	277.6	296.0	339.3
1964	315.5	359.7	365.7	394.8	379.1	332.4	325.1	312.1	291.7	283.0	266.3	291.4	326.4
1965	338.7	382.6	404.5	394.8	393.5	347.7	336.6	323.5	295.7	275.0	325.5	280.4	341.5
1966	309.0	358.1	423.7	389.4	378.7	357.7	342.9	315.7	288.8	308.0	305.1	329.8	342.2
1967	351.5	370.3	403.2	367.9	351.0	350.7	333.2	318.8	285.3	273.6	270.9	297.4	331.2
1968	423.9	388.9	409.4	380.4	355.4	343.6	332.3	333.8	303.8	281.5	254.0	311.1	343.2
1969	328.7	411.3	381.7	414.0	374.8	377.2	341.7	340.8	300.2	286.1	298.5	317.8	347.7
1970	327.1	427.2	442.5	428.3	396.9	372.3	344.9	331.1	314.7	293.9	311.6	289.3	356.7
1971	330.8	403.2	410.8	391.7	366.4	360.3	335.3	318.6	319.9	287.0	288.7	288.6	341.8
1972	347.6	356.3	383.1	380.9	378.5	368.0	342.5	322.2	322.5	305.2	297.6	304.4	342.4
1973	311.2	416.4	386.2	433.8	379.7	362.1	352.0	329.2	295.3	296.8	289.9	307.9	346.7
1974	331.9	360.4	350.6	394.1	387.8	377.9	337.1	323.2	294.0	329.5	298.8	300.2	340.5
1975	330.8	348.7	380.3	389.5	365.2	360.7	337.4	325.1	294.5	283.3	296.8	296.3	334.1
1976	341.5	347.1	388.5	386.3	374.8	355.0	351.8	335.2	312.3	272.8	292.0	317.3	339.6
1977	352.3	389.5	372.7	401.1	371.0	365.9	355.1	328.2	308.5	285.0	289.7	293.5	342.7
1978	349.3	361.8	364.8	397.4	388.1	376.4	353.2	327.1	305.6	279.5	276.2	291.3	339.2
1979	326.5	393.0	401.5	404.0	376.6	361.2	362.8	328.8	303.1	295.6	278.5	309.0	345.1
1980	341.2	337.0	394.9	417.3	396.8	376.1	357.1	325.8	301.6	295.0	305.1	308.6	346.4
1981	364.6	368.4	372.8	381.0	396.5	349.4	348.2	328.5	310.2	314.3	305.7	306.4	345.5
1982	336.2	396.6	419.7	394.0	382.2	370.1	344.0	337.0	300.2	297.6	271.3	263.5	342.7
1983	345.4	347.2	358.0	374.5	345.8	346.2	329.2	323.5	296.8	276.4	274.8	295.7	326.1
1984	365.5	361.6	399.1	395.0	383.1	371.1	335.3	327.2	306.8	296.2	276.0	283.5	341.7
1985	363.1	405.5	366.3	358.8	363.0	359.9	330.7	302.6	289.1	276.4	299.6	245.0	330.0
1986	342.8	396.3	353.4	379.2	362.1	346.6	342.8		281.2	284.9	282.1	272.0	331.2
1987	326.2	352.4	426.5	356.8	380.2	343.1	333.6	333.4	296.6	293.6	318.8	295.8	338.1
1988	299.1	333.0	421.2	377.3	363.2	354.9	330.5	315.3	304.0	274.2	289.1	309.2	330.9
1989	306.1	391.8	365.0	363.9	362.8	345.1	333.5	323.7	294.8	283.0	287.4	295.0	329.3
1990	323.4	325.6	330.0	371.9	359.0	344.4		317.0	316.6	275.6	288.8	302.7	323.2
1991	340.3	379.1	358.5	392.4	395.1	371.1	336.2	322.0	298.7	294.3	297.9	266.0	337.6
1992	289.2	334.1	355.9	371.2	352.1	340.7	319.5	294.9	280.8	277.1	274.3	279.8	314.1
1993	297.7	305.5	333.5	331.5	332.0	329.6	322.2	307.5	303.1	271.7	299.0	265.4	308.2
1994	343.4	393.4	346.7	367.3	370.4	333.7	327.9	318.6	297.5	288.9	274.1	303.0	330.4
1995	305.8	343.3	372.6	347.7	340.5	326.1	316.7	314.8	296.5	269.6	296.7	295.0	318.8
1996	307.0	369.1	350.2	352.0	346.9	334.5	333.5	306.9	301.9	276.3	280.1	277.0	319.6
1997	318.8	359.2	336.9	352.8	339.7	343.1	333.7	305.7	280.5	279.2	281.9	280.9	317.7
1998	308.4	324.6	379.8	386.1	369.4	341.9	339.8	317.9	307.4	300.7	308.3	284.2	330.7
1999	301.4	435.0	361.3	371.2	351.9	336.6	340.1	314.0	286.7	289.9	293.8	287.9	330.8
2000	315.0	347.7	355.3	355.3	344.7	322.9	331.0	305.0	290.9	276.2	286.9	309.5	320.0
2001	323.0	369.7	380.0	375.0	350.1	351.0	325.9	306.9	321.0	269.9	277.9	291.9	328.5
2002	304.9	357.8	357.1	376.9	334.4	336.4	320.5	317.2	306.7	294.9	295.2	291.2	324.4

Table B3 *Monthly averages of Brewer total ozone, Hradec Králové, 1994-2002, B098-V2003 data set, ALL observations.*

Month Year	1	2	3	4	5	6	7	8	9	10	11	12	Average
1994	354.1	385.6	343.6	369.4	366.3	333.4	320.9	316.1	304.0	287.4	289.3	314.5	332.1
1995	329.3	341.2	370.6	359.9	344.6	335.2	310.4	316.2	299.7	270.8	287.1	313.4	323.2
1996	313.5	368.8	357.5	353.6	350.1	335.7	332.4	309.7	307.0	283.2	288.7	298.5	324.9
1997	334.0	351.8	342.6	355.2	342.1	343.7	336.1	314.3	280.3	285.6	284.7	293.0	322.0
1998	348.2	331.7	382.6	391.7	372.4	345.1	342.6	323.4	312.9	302.2	311.5	315.2	340.0
1999	335.6	401.7	382.7	375.1	358.5	335.9	324.2	315.7	287.4	288.4	292.3	318.4	334.7
2000	326.9	352.5	356.9	358.3	349.7	326.3	339.9	305.2	295.3	279.6	292.8	333.2	326.4
2001	340.3	364.3	383.4	392.8	354.0	351.7	331.2	305.0	322.9	273.7	287.6	310.3	334.8
2002	314.5	344.9	360.4	378.2	336.5	339.1	324.2	316.7	307.5	297.9	310.3	309.2	328.3

Table B4 *Monthly averages of Brewer total ozone, Hradec Králové, 1994-2002, B098-V2003 data set, only DS observations*

Month Year	1	2	3	4	5	6	7	8	9	10	11	12	Average
1994	353.7	383.8	344.6	360.4	363.7	328.4	319.0	310.3	301.1	285.7	262.2	307.7	326.7
1995	326.6	327.0	363.8	352.4	330.3	317.7	307.6	308.0	291.2	268.7	292.5	314.3	316.7
1996	307.6	368.4	347.7	347.0	344.0	332.9	329.7	304.2	297.7	278.8	283.9	336.2	323.2
1997	305.4	352.0	335.5	352.7	335.0	340.2	329.6	314.1	282.1	282.7	281.0	294.3	317.1
1998	326.7	332.9	390.8	394.1	372.4	343.6	340.6	323.4	308.4	310.3	315.1	307.6	338.8
1999	347.4	438.6	376.2	375.2	357.0	335.5	323.0	315.5	287.5	289.8	298.5	323.4	339.0
2000	336.9	347.7	357.1	358.2	349.4	324.9	331.7	305.2	292.8	277.7	294.3	330.3	325.5
2001	344.5	367.3	383.4	385.5	354.0	347.1	330.2	304.3	319.2	270.3	282.5	314.8	333.6
2002	315.5	354.5	356.4	375.1	336.5	338.0	324.2	316.0	307.8	302.2	300.8	305.5	327.7

ACRONYMS

B098	Brewer ozone spectrophotometer No. 098
B098-ORIG	original total ozone data set created with B098 and continuously deposited into WOUDC in the period 1994-2002
B098-V2003	re-processed version of total ozone data series created with B098 at SOO-HK and re-deposited into WOUDC in 2003
CANDIDOZ	**C**hemical **an**d **D**ynamical **I**nfluences on **D**ecadal Ozone Change
CC	cloud-correction in DU
CHMI	Czech Hydrometeorological Institute
CMDL	Climate Monitoring and Diagnostic Laboratory of NOAA
CR	Czech Republic
D/B	Dobson versus Brewer
D074	Dobson ozone spectrophotometer No. 074
DU	Dobson Unit (mili-atm-cm)
D074-V1991	re-processed version of total ozone data series created with D074 at SOO-HK and re-deposited into WOUDC in 1991
D074-V2003	re-processed version of total ozone data series created with D074 at SOO-HK and re-deposited into WOUDC in 2003
FP-5	Fifth Framework Programme of the European Commission
F(i)	photon count rates of the Brewer spectrophotometer
F_0	ozone extraterrestrial constant of the Brewer spectrophotometer (ETC)
GAW	Global Atmosphere Watch programme
HGL	Mercury Lamp
I	spectral intensity of solar radiation at the ground
I_0	spectral intensity outside the atmosphere (extraterrestrial)
IC	intercomparison of ozone spectrophotometer(s)
IOC	International Ozone Commission
IOS	International Ozone Service Inc., Toronto
MSC	Meteorological Service of Canada
M(i)	ratios of photon count rates F(i) of the Brewer spectrophotometer
N	N-value, it equals to R-value converted by the N-Table
NDSC	Network for Detection of Stratospheric Change
N_0	ozone extraterrestrial constant of the Dobson spectrophotometer (ETC)
OF	multiplication (opacity) factor for cloud corrections
O_3	total amount of ozone in the atmosphere in Dobson Units
R	R-value, it is a position of the dial ring of the Dobson spectrophotometer
SL	Standard Lamp
SOO-HK	Solar and Ozone Observatory Hradec Králové
SO_2	total amount of sulphur dioxide in the atmosphere in Dobson Units
TO3	effective (weighted) temperature of the ozone layer
WBCC	World Brewer Calibration Center
WDCC	World Dobson Calibration Center
WMO	World Meteorological Organization
WOUDC	World Ozone and UV Data Center, Toronto
WPBST	World Primary Brewer Spectrophotometer Triad
WPDS	World Primary Dobson Spectrophotometer D083
ZA	zenith angle of the Sun

a_i	regression coefficients
m	relative path of the solar radiation through the atmosphere
p	observed air pressure at the ground
p_o	mean sea level pressure
par.	paragraph
α_i	spectral absorption coefficient of ozone
α'_i	spectral absorption coefficients of sulphur dioxide
β_i	spectral Rayleigh molecular scattering coefficient of the air).
δ_i	spectral scattering coefficients of aerosol particles
λ_i	wavelength of the solar radiation
μ	relative optical path length through the ozone layer (at 22 km)
μ'	relative optical path length through the sulphur dioxide layer (at 5 km)
$\Delta\alpha$, $\Delta^*\alpha$	linear combinations of α_i
$\Delta\alpha'$, $\Delta^*\alpha'$	linear combinations of α'_i
$\Delta\beta$, $\Delta^*\beta$	linear combinations of β_i
$\Delta\delta$	linear combination of δ_i
α .	spectral absorption coefficient of ozone
β	spectral Rayleigh molecular scattering coefficients of the air
δ	spectral scattering coefficients of aerosol particles
μ	relative path of the solar radiation through the ozone layer for a particular time of total ozone observation (ozone air mass)

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