https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

Total column ozone measurements by the Dobson spectrophotometer at Belsk (Poland) for the period 1963-2019: homogenization and adjustment to the Brewer spectrophotometer

Janusz W. Krzyścin[1], Bonawentura Rajewska-Więch[1], Janusz Jarosławski[1]
[1]Institute of Geophysics, Polish Academy of Science, Warsaw, 01-452, Poland
Correspondence to: Janusz W. Krzyścin (jkrzys@igf.edu.pl)

Abstract. The total column ozone (TCO_3) measurements by the Dobson spectrophotometer #84 have been carried out at Belsk (51°50', 20°47'), Poland, since March 23, 1963. In total, ~115,000 intra-day manual observations have been taken up to December 31, 2019. These observations were made for various combinations of double wavelength pairs in UV range (AD, CD) and the observation category, i.e., direct Sun, zenith blue, and zenith cloudy depending on the weather conditions. The long-term stability of the instrument was supported by frequent (~almost every 4 yr.) intercomparisons with the world standard spectrophotometers. Trend analyses, based on the monthly and yearly averaged TCO_3, can be carried out without any additional corrections to the intraday values. To adjust this data to the Brewer spectrophotometer observations also performed at Belsk, a procedure is proposed to account for: less accurate Dobson observations under low solar elevation, presence of clouds, and sensitivity of the ozone absorption on temperature. The adjusted time series shows that the Brewer-Dobson monthly averaged differences are in the range of about ±0.5%. The intra-day TCO_3 data base, divided into three periods (1963-1979,1980-1999, and 2000-2019), is freely available at https://doi.pangaea.de/10.1594/PANGAEA.919378 (Rajewska-Więch et al., 2020).

1 Introduction

The monitoring of total column ozone (TCO_3) started in 1924 in Oxford (the United Kingdom) with prototype of the Dobson instrument (DI). Before the Second World War, there existed data records from 2 stations Oxford (DI #1) and Arosa (DI #2) archived in the World Ozone and Ultraviolet Radiation Data Centre (WOUDC). After the international geophysical year in 1958, the total number of the stations with routine TOC_3 increased up to about 50. The ozone observations were triggered in the early 1980s after discovery the ozone hole in the Antarctic spring by Chubachi (1984) and Farman et al. (1985). The variability of the ozone layer was of particular interests since ozone is the only gaseous component of the atmosphere that absorbs shortwave solar radiation in the UVB range (280-315 nm) that is harmful for any organisms living on the Earth. The ozone depletion became a widely debated environmental issue that led to the signing of an international agreement, the Montreal Protocol (MP) 1987, to protect the ozone layer by reducing the production and use of the ozone depleting substances (ODS).

Until, the late 1970 the Dobson spectrophotometer was the only optical instrument for TCO_3 ground-based measurements. Monitoring of TCO_3 required a lot of man-power because the Dobson observations involve many manual steps and the obtained TCO_3 value depended to some extent on individual observers' skill in manipulating the instrument. A need of automatization of TCO_3 measurements resulted in a development of an automated instrument – the Brewer spectrophotometer. It was designed in Canada and after developments during 1970s was available for the ozone monitoring in the early 1980s. However, differences between the Dobson and the Brewer records data were found. Kerr at al. (1988) suggested that this difference was due to temperature dependence of the ozone absorption coefficients (O_3AC). The Bass & Pour coefficients (Bass and Pour, 1985), which replaced the previous ones by Vigroux (1967), have been used operationally in the ground-based network since the early 1990s (Komhyr et al, 1993). Vanicek (2006) found that the difference could reach of ~4% in comparisons of the Brewer and Dobson monthly mean data taken in Hradec Kralove, Czech Republic, because of using the Bass & Paur O_3AC at

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

fixed temperature. There were several attempts to recalculate the O_3AC (Redondas et.al., 2014) and finally the recalculation proposed by Serduchenko et al. (2014) has been recommended for the ground-based TO_3 network. The application of these temperature-dependent absorption coefficients significantly reduced the artificial seasonality in the Dobson-Brewer differences to less than 1% (Redondas et al., 2014). However, the data from the Dobson network has not yet been recalculated with use of the new O_3AC, as knowledge of the stratospheric temperature and the vertical ozone distribution over the observing sites is required to obtain the effective temperature.

The ozone issue is still important as the ozone recovery rate expected from the regulations of the MP 1987, and its further amendments, has also been driven by the recent climate changes (e.g., negative trends in the lower stratospheric ozone in the NH midlatitudes, Ball et al., 2018). Moreover, surprising increases of the CFC11 concentration in the troposphere have been found in some regions linked to ODS leakage from its long-term storing reservoirs (Lickley et al., 2020) and a return of ODS use in industry (Montzka et al., 2018; Dhomse et al., 2019). The ozone hole surprises with its variability from an extreme small extent in 2019 (Krzyścin, 2020) to extreme large one in 2020 (https://public.wmo.int/en/media/news/2020-antarctic-ozone-hole-large-and-deep?). Therefore, a question has to be contemplated as to whether it is still worth performing ozone observations by the Dobson spectrophotometer, which was designed and put into operation almost 100 years ago.

The Central Geophysical Laboratory of the Institute of Geophysics, Polish Academy of Sciences, at Belsk (51.84°N, 20.78°E), Poland, started monitoring of the atmospheric ozone (TCO_3 and the ozone vertical profiles by the Umkehr method) on 23 March 1963. In Europe, there are only two stations with longer time series including Arosa (since 1926, Staehelin et al., 1998) and Hradec Kralove (since 1961, Vaniček et al., 2012). The importance of the Belsk's TCO_3 time series comes from the Dobson's measurements carried out regardless of the weather conditions excluding only the days with continuous rain or snow fall. Various efforts have been made to support the quality of the Belsk's TCO_3 data (e.g., Dziewulska-Łosiowa et al., 1983; Degórska and Rajewska-Więch, 1991) as the less accurate zenith sky TCO_3 observations in cloudy conditions were only available for some of the days, especially in the late autumn and winter. This paper presents further steps in the homogenization of the Belsk's TCO_3 time series for the period 1963-2019 in perspective of the long-term variability of the atmospheric ozone and possibility of a replacement of the Belsk's Dobson with the state-of-the art Brewer spectrophotometer.

2 Data and Methods

2.1 The Dobson Spectrophotometer

The Dobson spectrophotometer is a double monochromator deigned to measure TCO_3 by the technique of the Differential Optical Absorption Spectroscopy (Dobson, 1957). The TCO_3 values from Direct Sun (DS) observations are calculated based on the Beer's Law applied to spectral irradiances of solar radiation for selected wavelengths with strong and weak absorption by the ozone layer. These wavelengths are denoted as A (305.5/325.0 nm), C (311.5 /332.4 nm), and D (317.5/339.9 nm). The TCO_3 values are determined from linear combination of the logarithm of the ratios between A pair and D pair irradiances that is called the double AD wavelengths pair algorithm to reduce the effects of the aerosols scattering on calculated ozone. It is also possible to use C pair irradiances instead of the A pair, i.e., the so-called double CD pair, to obtain TCO_3 if the solar irradiance at the shorter wavelength of A pair is too weak because of a large ozone absorption under high air masses ($\mu > 3$) and/or during cloudy conditions.

Another option to calculate TCO_3 by the Dobson spectrophotometer is to use scattered sunlight from the zenith sky (ZS) at the same wavelengths as in the DS observations. In this case, the same algorithm is implemented but the result needs to be reduced by empirical charts. The charts after Rindert (1973) have been used throughout the whole period of the Belsk's observations for AD and CD double wavelength pairs. The operational data archived in the PANGAEA data base was obtained using the

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

Earth System Science Data
Open Access
Discussions

Bass and Paur ozone absorption coefficient at fixed temperature of -46.3 °C according the recommendation of Komhyr et al. (1993).

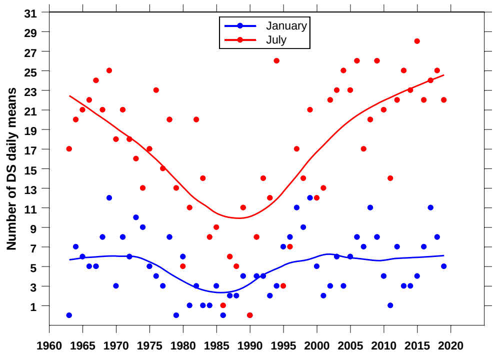

Figure 1: Number of TCO_3 daily means for January and July in the period 1964-2019.

Figure 1 shows time series of the number of daily TCO_3 means obtained from DS intraday observations with AD and/or CD wavelength pairs in January and July for the 1963-2019 period. Number of the DS daily means per month is larger in June because of the usually less cloudy conditions in this month compared to January and the longer day length during the summer (i.e., greater chance for cloudless conditions). The monthly mean TCO_3 for January is mostly based on ZS observations. It is worth mentioning that reduced number of DS observations (less than 15 per month) were possible in July for the period 1985-1995. In this period, ZS observations under almost cloudless conditions, i.e., the so-called zenith blue (ZB) observations, replaced DS observations, as the solar disc was not clear due to the large contamination of Belsk's atmosphere by industrial aerosols. At that time, the Belsk's observers were recommended to choose ZB type of the observations in clear-sky conditions.

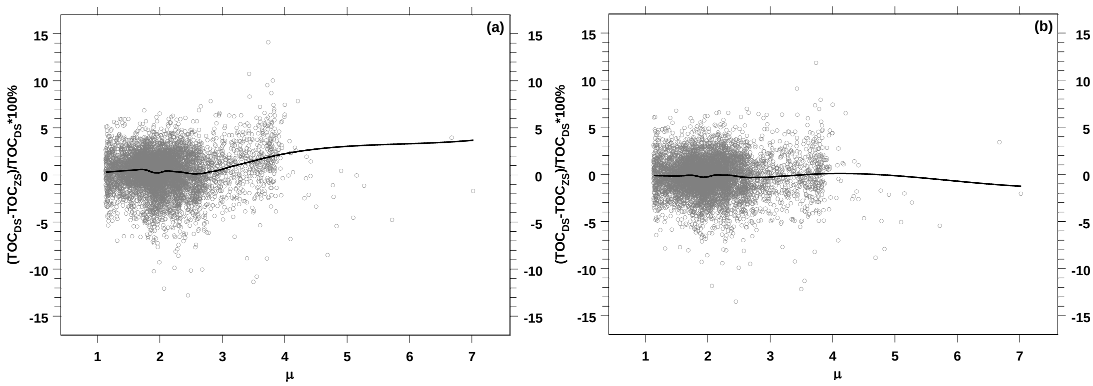

Figure 2: Air mass dependence of differences between daily mean TCO_3 values by DS and ZS measurements as a percentage of the DS TCO_3 values: original data (a), ZS TCO_3 after the correction using the transfer function (1) (b).

The TCO_3 values by ZS observations could be calculated for almost all-weather conditions (excluding cases with heavy and variable cloudiness) but they are reliable, i.e., close to the DS values, for the air masses up to 2.8 (Fig.2a). However, the empirical reduction curves (proposed by Rindert, 1973), which have been applied for the whole period of the Belsk's observations to convert ZS values to equivalent DS values, did not reflect all of the possible combinations of cloud types and their configuration in the sky. Therefore, the DS-ZS differences can sometimes exceed 5%. To eliminate a drift of the DS-ZS differences, the following transfer function is used for large air masses:

$$
\begin{aligned}
TCO_{3,\,ZS}^{*} &= (1 + 0.0125(\mu - 2.8)) \times TCO_{3,\,ZS} \quad \text{, for mi } \mu \subset [2.8, 4.0] \\
TCO_{3,\,ZS}^{*} &= 1.015 \times TCO_{3,\,ZS} \quad \text{, for } \mu > 4.0
\end{aligned}
\qquad (1)
$$

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

Earth System Science Data Discussions

where $TCO_{3,\,ZS}$ is the TCO_3 value derived from ZS observations, μ is air mass during the Dobson observation, and $TCO_{3,\,ZS}*$ is pertaining the corrected value for μ >2.8. The smoothed pattern of the DS-ZS differences (Fig.2b) is close to zero after the application of the transfer function.

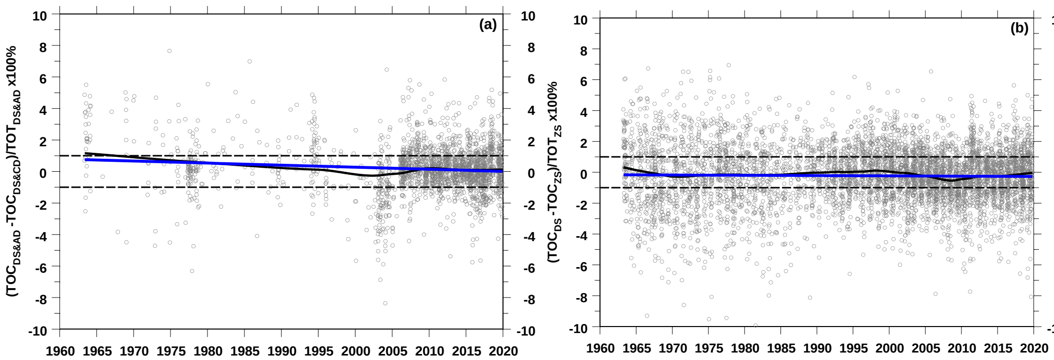

Figure 3: Time series of relative differences between daily means of TCO_3: DS&AD versus DS&CD measurements (a), DS versus ZS measurements (b). Black curve shows the smoothed pattern of the data. The blue line is the linear regression line.

DS&AD observations provide the most accurate TCO_3 values (Dobson, 1957) when the air mass is below 2.5. However, these observations are not possible for northern sites like Belsk when the noon air mases above 2.5 appear in the period from 3rd November up to 9th February with the maximum air mass equal to 3.75 on 23th December. Therefore, DS&CD observations are recommended for these periods (Dobson, 1957). Additional intraday TCO_3 values, especially after 2005, were calculated using both DS&AD and DS&CD type of the Dobson's observations to find out a relationship between these TCO_3 values. Figure 3a shows that the relationship is quite stable in the 1963-2019 period, i.e., the smoothed differences (black curve) are within [0 %, 1 %] range and the linear regression line (blue line) is trendless. The similar comparison between DS and ZS observations, after application of the transfer function (1), provides that the smoothed differences are close to the zero line in the whole period of the observations (Fig. 3b).

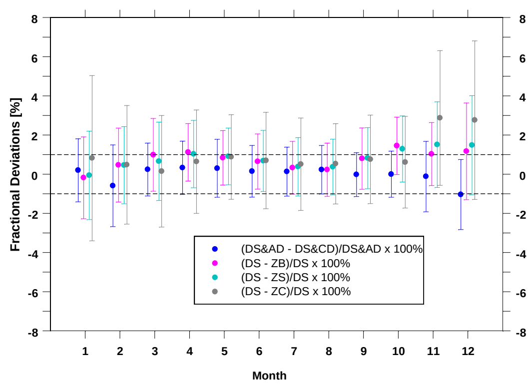

Figure 4: The monthly mean relative differences between daily TCO_3 means derived from various types of the Dobson measurements. Bar denotes the range: mean ± standard deviation.

The monthly mean TCO_3 differences between various subsets of the TCO_3 data are calculated from the whole period of the Belsk's observations are presented in Fig. 4. The differences are from the monthly averaging of the daily mean TCO_3 values for the following classes: DS&AD, DS&CD, ZB, ZS, and for less reliable ZS observations when the sky was covered by clouds i.e., the so-called zenith cloudy (ZC) observations. For all ZS intraday values when $\mu \geq 2.8$, the correction function (1) was applied. The TCO_3 differences relative to the DS&AD values are within the ± 1% range almost throughout the whole year excluding autumn/early winter months (November-December) where the AD observations are not recommended because of low solar elevation at noon. For each selected month, from January to September, the range between the monthly mean

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

differences is about ~1% for the all considered subsets of the Dobson observations. The maximum range of the difference is 4% in December, i.e., -1% for DS&AD versus DS&CD, and 3% DS versus ZC.

2.2 Calibrations of the Dobson spectrophotometer

The Dobson spectrophotometer #84 at Belsk has been operated continuously since 23 March 1963 at the same place with only a few breaks of the observations (lasting up to a few weeks) due to the international calibration campaigns with other Dobson instruments. Frequent intercomparisons of the Belsk's Dobson with the world standard instrument combined with the recalibration of the optical wedge of the instrument and the calculation of the resulting R/N tables were crucial in maintaining quality of the Belsk's Dobson.

The first DI intercomparison was held at Belsk in June/July 1974. The participating Dobsons were compared against the World Primary Standard (WPS) Dobson Spectrophotometer #83 and the optical wedge of the Belsk's Dobson was recalibrated (Dziewulska-Łosiowa and Walshaw, 1975). The next DI intercomparison was held in Potsdam (Germany) in June 1979 also with attendance of the same WPS. During the comparison the new R/N tables were obtained that differed only slightly from those calculated in the Belsk's inter-comparison (Dziewulska-Łosiowa et al. 1983). The subsequent campaigns were in Arosa (1986, 1990, and 1995) with the WPS Dobson #83. Next intercalibrations (2000, 2005, 2009, 2014) were organized at the European regional Dobson calibration center, the Meteorological Observatory Hohenpeissenberg, Germany. The local European sub-standard, DI #64, was used as the reference instrument during inter-comparisons at the center. After the intercomparisons, the new R/N tables were obtained and used immediately, i.e., after the instrument arrival to the observing site, as input to TCO_3 calculation algorithm. The retrieval software has not been changed since its first operational use in 1981 (Degórska et al., 1978).

The first homogenization of the Belsk's TCO_3 data for the period 1963-1981 by Dziewulska-Łosiowa et al., (1983) was based on the Potsdam's R/N tables, extraterrestrial constants determined at Belsk in 1974 during the first DI intercomparison, the O_3AC by Vigroux (1967), and zenith sky irradiances (for AD and CD observations) were reduced to the DS equivalent values by means of the empirical charts after Rindert (1973). The next homogenization was in 1991 by Degórska and Rajewska-Więch (1991). All data collected before 1992 was re-evaluated on the reading-by-reading basis using the O_3ACs (at fixed temperature at -46.3 °C) after Bass and Paur (1985) that were recommended for processing Dobson TCO_3 measurements since 1 January 1992.

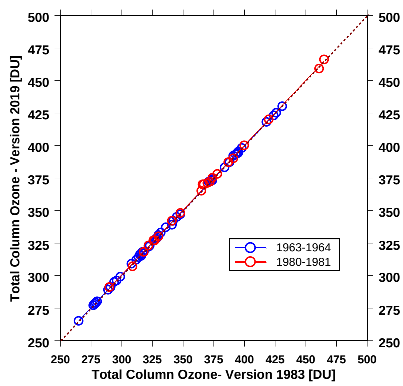

Figure 5: TCO_3 daily means by AD&DS measurements in the period 1963-1964 and 1980-1981 calculated with present (2019) calculation algorithm (R/N based on the 2014 intercomparison) versus those by the same algorithm using old (1979) R/N tables.

The optical wedge calibrations taken during the whole period of the ozone observations at Belsk only slightly influenced the TCO_3 values. Figure 5 shows the comparison of TCO_3 calculated for the first 2-year period (1963-1964) and last 2-year period (1980-1981) of the time series after the first homogenization in 1983. The original TCO_3 values from DS&AD observations presented by Dziewulska- Łosiowa et al. (1983), which were based on Vigroux O3AC, are converted to the values derived by

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

means of the Bass and Paur O_3AC (i.e., multiplied by 0.9743, as recommended by the International Ozone Commission in 1992) and compared to the pertaining values obtained with presently used retrieval including the Bass and Paur O_3AC and R/N tables derived during the very recent inter-comparison in 2014. There is almost 1-1 correspondence between both TCO_3 data i.e., the slope of linear fit is 0.9999 and 0.9962 for the period 1963-1964 and 1980-1981, respectively. The maximum difference between TCO_3 by the 1979 Potsdam R/N tables and presently used the 2014 Hohenpeissenberg R/N tables is below 1 %. The small differences, less than 1% between TCO_3 values are also found after comparison of DS&AD TCO_3 in August 2020 derived using various R/N tables that were operationally used in the 1990s and 2020s (Fig.6).

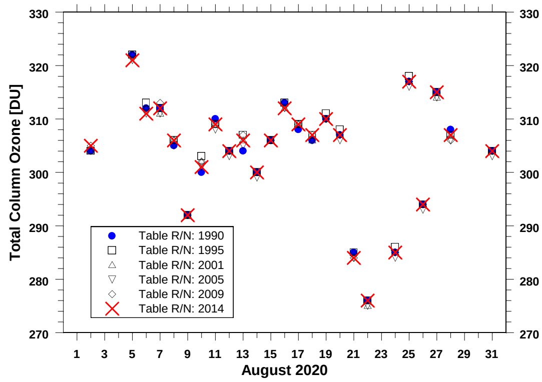

Figure 6: Daily means of TCO_3 in August 2020 from DS&AD measurements as calculated with different R/N tables obtained during intercomparisons in the 1990s and 2000s.

Therefore, it can be concluded from these comparisons of the DS&AD measurements that the Belsk's Dobson showed a stable performance over the whole period of the measurements. A linear approximation of TCO_3 values in periods between the calibration campaigns was not necessary to account for changes of R/N values and instrument's aging.

2.3 Adjustment to the Brewer spectrophotometer

The complementary monitoring of TCO_3 and vertical profiles by the Brewer spectrophotometer #64 (BS64) Mark II (with single monochromator) has been started at Belsk in 1991. Like other Brewers, the BS64 is a fully automated, self-testing, PC-controlled instrument designed for continuous long-term observations in all weather conditions. The quality of BS64 measurements has been supported by regular (yearly or at least every two years) comparisons with the international travelling reference instrument provided by the International Ozone Services Inc. (https://www.io3.ca/index.php). The BS64 instrument's constants re-defined after each comparison were immediately included to the operational software.

The Brewer TCO_3 is derived from the weighted linear combination of the solar irradiances at five wavelengths (306.3, 310.0, 313.5, 316.8, and 320.0 nm) to eliminate noise caused by SO_2 absorption in the UV range (Kerr et al., 1988). The operational Brewer algorithm uses the Bass and Paur O_3AC at -45 C° for two categories (DS and ZS) of the observations. There are many BS observations throughout the day regardless of weather conditions. Cycles of 5 observations, which are taken within about 3-4 minutes, are repeated every 5 to 20 minutes throughout the day depending on the instrument schedule. The mean TCO_3 value, averaging 5 observations, is calculated if the scatter of these TCO_3 values is small. i.e., standard deviation is less than 2.5 Dobson unit (DU). This makes it difficult to directly compare the TCO_3 values with the spectrophotometers.

2.3.1 Correction for the effective temperature

Figure 7a shows the time series of the difference between Brewer and Dobson TCO_3 daily means (Brewer minus Dobson TCO_3 as % of the Dobson TCO3 value) based on the DS observations at Belsk for the period 2002-2019. This period has been selected as more intraday DS&AD and DS&CD observations were performed (see Fig.3a) due to the increased interest in the Dobson data intended for constructing a transfer function to the Brewer equivalent TCO_3 values prior to the anticipated change

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

of the monitoring policy to less frequent intraday Dobson measurements carried out only near the noon during perfect weather conditions. The well-known seasonality of the Brewer-Dobson differences, i.e., underestimation of the Dobson TCO_3 in the cold period of the year, could be observed after the smoothing by the locally weighted scatterplot smoothing (LOWESS, Cleveland, 1979) applied to time series of Brewer-Dobson differences.

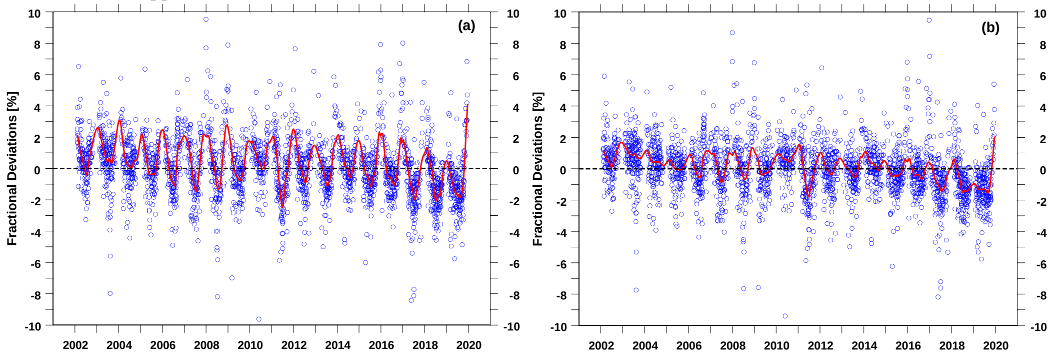

Figure 7: The differences between the Brewer and Dobson TCO_3 daily means as percentage of the Dobson TCO_3 value: original data after application of the correction function (1) to the Dobson ZS data (a), the Dobson and Brewer TCO_3 corrected for the effective temperature (b). Red curve represents the smoothed pattern by LOWESS filter.

To reduce the Brewer-Dobson seasonal difference, it is necessary to apply the temperature dependent O_3ACs instead of the operational ones at T_0= -46.3 °C (Dobson) and T_0= -45.0 °C (Brewer) as was assumed in the TCO_3 retrieval algorithm of these spectrophotometers. Here we use the temperature correction factor, α, calculated by Redondas et al. (2014), i.e., α=0.104 % K^{-1} (for Dobson) and α=0.009 % K^{-1} (for Brewer). These values are based on the O_3AC dependence on temperature obtained by the Institute of Experimental Physics (IUP), University of Bremen, Serdyuchenko et al. (2014). The correction function to account for the actual effective temperature is as follows:

$$TCO_{3,\,\mathrm{NEW}} = (1 + \alpha\,(T_0 - T_{eff})) \times TCO_{3,\mathrm{OLD}} \qquad (2)$$

where T_{eff} is the effective (weighted by the ozone vertical profile) temperature, $TCO_{3,\mathrm{OLD}}$ is the TCO_3 value at the fixed temperature, and $TCO_{3,\,\mathrm{NEW}}$ is the temperature corrected value. Prior application formula (2), TCO_3 values by ZS Dobson observations need to be converted to the DS TCO_3 equivalent using transfer function (1). The effective temperature at noon is taken after the Tropospheric Emission Monitoring Internet Service (TEMIS) overpass data (http://www.temis.nl/climate/efftemp/overpass.html) based on the European Centre for Medium-Range Weather Forecasts (ECMWF) model estimates. Koukouli et al. (2016) found that the ECMWF effective temperature was in good agreement with that from the ozone sounding in northern hemisphere midlatitudes.

Figure 7b shows the time series of the Brewer-Dobson differences after application of the correction function (2). The apparent seasonality seen in Fig.7a disappears but reduced seasonal oscillations still exist. To find out the range of these oscillations, the monthly mean Brewer-Dobson differences are calculated averaging the daily differences and the results are shown in Fig. 8a (DS subset) and Fig. 8b (ZS subset). Comparisons of original DS and ZS data (not accounting for T_{eff} seasonal variability) provides that the seasonal difference is of ~4.5% as calculated from the monthly mean difference value of ~3.5% and -1% in January and July (or August for ZS data), respectively. After application formula (2), the difference is smaller, i.e., ~ 2.5% (DS) and 3% (ZS).

It is worth mentioning that the monthly Brewer-Dobson differences for the temperature corrected data are out of ± 1 % range only in January and December (DS subset) and in addition in November for the ZS subset. To the authors knowledge, the Brewer-Dobson differences for less accurate ZS subset have not yet been discussed by other authors. It seems that a stray light effect, which may be different in the Dobson and Brewer instruments (Belsk's BS64 is a single monochromator unit), is responsible for larger differences between these spectrophotometers in periods with low solar elevation at noon.

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

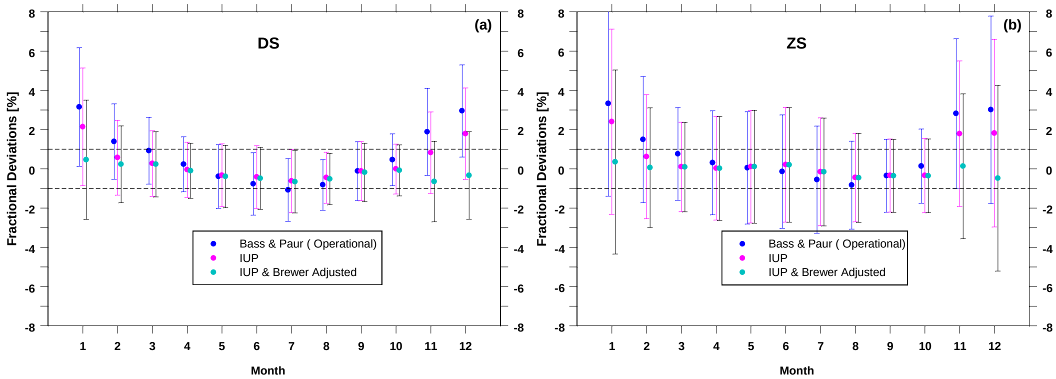

Figure 8. The monthly means of the Brewer-Dobson differences between daily TCO_3 means using operational data (Bass&Paur at fixed temperature), after application of the correction (2) for the dependence of ozone absorption coefficient on temperature based on the ozone absorption coefficients by IUP, and after adjustment of the Dobson TCO_3 to the Brewer equivalent by formula (3) accounting for the stray light effect differences between the spectrophotometers. The results are for: DS measurements (a), ZS measurements (b). Bars denote the range: mean ± standard deviation.

2.3.2 Correction for the stray light effect

The stray light within the instrument causes underestimation of the Dobson TCO_3 of about few percent when slant TCO_3, $\sim\mu\times TCO_3$ (in DU), is over 800-900 (Evans et al., 2009). This observation also concerns the single monochromator Brewer spectrophotometer (e.g., Karppinen et al., 2015). Here, it is decided to construct a simple correction function (i.e., linear function of μ) that will move all-monthly means Brewer-Dobson differences for DS and ZS subset (Figs. 8) to the smallest possible range of the differences being in vicinity of the zero line. The following the Brewer-Dobson adjustment (BDA) function is proposed to transform $TCO_{3,\,\mathrm{NEW}}$ (Dobson TCO_3 after application the transfer function (1) and the temperature correction by formula (2)) to its Brewer equivalent value $TCO_{3,\,\mathrm{DOB\rightarrow BRE}}$:

$$\begin{aligned} TCO_{3,\,\mathrm{DOB\rightarrow BRE}} &= (1+\gamma\mu)\times TCO_{3,\,\mathrm{NEW}} \quad, \mu > \mu_0 \\ TCO_{3,\,\mathrm{DOB\rightarrow BRE}} &= TCO_{3,\,\mathrm{NEW}} \quad, \mu \le \mu_0 \end{aligned} \tag{3}$$

where constant values γ and μ_0 can be different for the ZS and DS subsets. The best pair of γ and μ_0 was experimentally derived examining many combinations of γ and μ_0, taking values from the range of [0, 0.02] and [2.5, 3.5], respectively. Finally, the following constants are derived: $\gamma_{DS} = 0.5625\ 10^{-2}$ and $\mu_{0,DS} = 2.95$ (for DS subset], and $\gamma_{ZS} = 0.6250\ 10^{-2}$ and $\mu_{0,ZS} = 2.8$ (for ZS subset). The corresponding ranges of the monthly mean Brewer-Dobson differences are: [-0.66 % (July), 0.46 % (January)], and [-0.48 % (December), 0.35 % (January)], for the DS and ZS respectively. After application of the BDA function, the Brewer-Dobson monthly mean differences are almost in ± 0.5 % range (see Figs. 8.for the subset IUP & Brewer Adjusted)

3 Results and Discussion

The following subjects were considered to construct the Brewer adjusted record of the Belsk's Dobson measurements for the whole period of the observations (1963-2019): the focus during the inter-calibration Dobson campaigns was on DS&AD type of observations, DS&AD observations have been well calibrated during the whole period of observations (within 1%), the inter-comparisons were carried out in the warm period of the year (usually in summer), there was the seasonal difference between the Dobson and Brewer spectrophotometers depending in some extent on the effective temperature and individual instrument stray light sensitivity. It is worth mentioning that BS64 will ultimately be the primary instrument for the ozone monitoring at Belsk.

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

First step of the recalculation was to correct ZS Dobson's observations taking into account a drift relative to DS&AD values (Figs.2). Application of the correction function (1) removed this shift (Fig.2b). Moreover, Fig.3a and Fig. 3b provided that further correction to other types of the measurements was not necessary to eliminate a long-term drift relative to the quality-controlled DS&AD subset. Thus, ZS-DS conversion charts proposed by Rindert (1973) were valid throughout the whole period of the observations suggesting small changes in cloud characteristics in the period 1963-2019.

Next step of the Dobson recalculation was to account for the temperature dependence of O_3AC using the correction function (2) based on very recent O_3AC derived by Serdyuchenko et al. (2014). Application of this formula removed part of the bias between the Brewer and Dobson spectrophotometers both for DS and ZS subset of the observations (Figs.7-8). The agreement within ± 1% range exists in almost all months but not in months with low solar elevation at noon (November-December-January). The last step of the homogenization is to eliminate the difference between the spectrophotometers that has been found in periods of low solar elevation. This is probably related to a technical problem of stray light contamination of TCO_3 observations for large air masses.

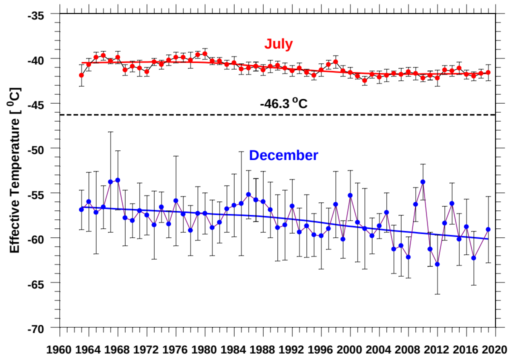

Figure 9: Yearly means of the effective temperature at Belsk in December and July in the period 1963-2019.

Table 1 provides the monthly mean values of the differences between the final and original TCO_3 values. The larger differences of about a few percentages are found in the late autumn and early winter months due to: the TCO_3 underestimation found for ZS observations, increase of O_3AC with decreasing effective temperature, and the stray light effect. For warm part of the year (April-September) and corresponding higher solar elevation, the differences are only in the range of ± 0.5 % range. Figure 9 show that there was an apparent decline in the effective temperature in December for the period 1963-2019 of ~ -4 °C and slight decline in July of ~ -1 °C. This changed only slightly (i.e., 0.4% in December, and ~0.1% in June) TCO_3 values at the end of time series comparing to the TCO_3 values at the start.

Table 1. The monthly and yearly statistics (mean, standard deviation, median, and the 5^{th}-95^{th} percentile range) of the differences between the Brewer adjusted Dobson TCO_3 and operational (at fixed temperature) TCO_3 for the period 1963-2019.

Month/Year	No.	Mean ± SD (%)	Median [5^{th}, 95^{th}] (%)
January	1255	3.61 ± 0.81	3.68 [2.08, 4.78]
February	1287	1.51 ± 0.82	1.39 [0.35, 3.15]
March	1515	0.67 ± 0.34	0.63 [0.18, 1.26]
April	1497	0.27 ± 0.23	0.25 [-0.07, 0.69]
May	1577	-0.09 ± 0.19	-0.10 [-0.36, 0.21]
June	1460	-0.40 ± 0.16	-0.42 [-0.61, -0.15]
July	1594	-0.53 ± 0.15	-0.54 [-0.73, -0.33]
August	1548	-0.41 ± 0.18	-0.44 [-0.67, -0.07]
September	1520	-0.03 ± 0.23	-0.05 [-0.35, 0.35]
October	1546	0.51 ± 0.31	0.47 [0.10, 1.02]
November	1339	3.13 ± 1.16	3.40 [1.05, 4.71]
December	1251	4.48 ± 0.53	4.54 [3.44, 5.24]
Year	17389	0.93 ± 1.68	0.25 [-0.59, 4.55]

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

Open Access Earth System Science Data Discussions

Figure 10a and 10b show the long-term variability of the monthly mean TCO_3 for December and July, respectively, derived from the original data (archived in the PANGAEA data base) and the data after application of all correction functions (i.e., the Brewer adjusted Dobson data). The monthly means were calculated averaging the daily means from DS observations. If there were no such observations within the day, the daily means based only on ZS measurements were considered. The decline in the effective temperature (Fig.9) does not change the variability of the long-term pattern of the smoothed TCO_3 time series. A constant upward shift is found in the colder months (e.g., Fig.10a) and a slight downward shift in the warmer months (e.g., Fig.10b). A constant shift (upward) is also seen in the yearly mean values calculated as the average of all monthly means for each year (Fig.10c). Therefore, the trend estimates in DU will be almost the same if the differences in DU relative to the reference TCO_3 value (e.g., the TCO_3 monthly means before 1980) are considered.

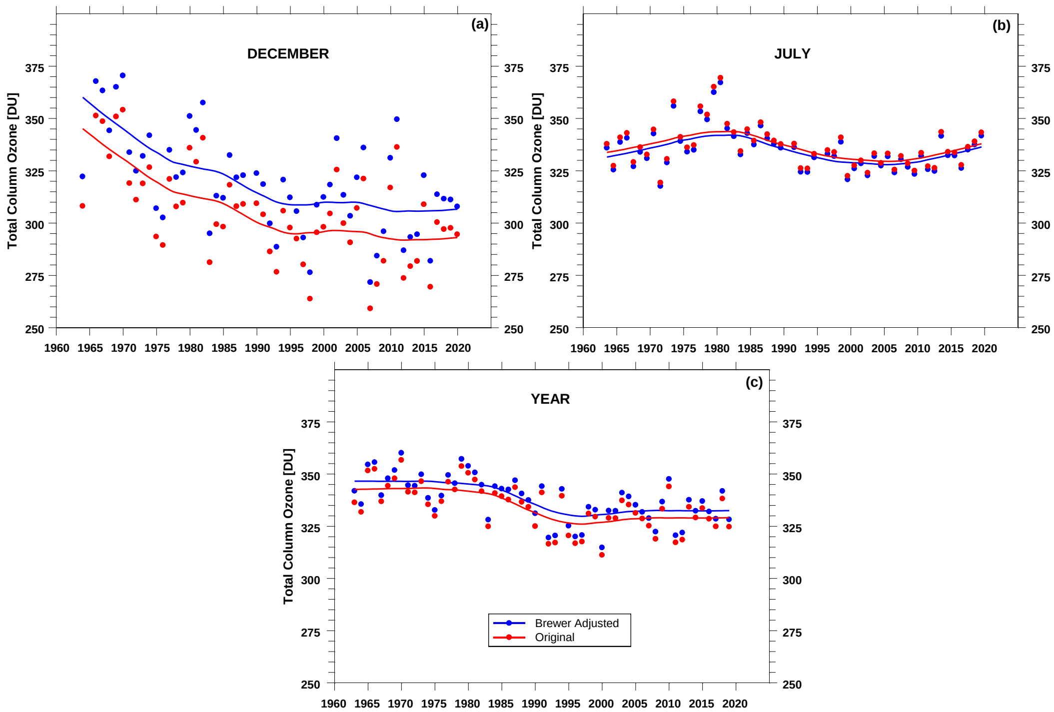

Figure 10: Time series of the averaged daily TCO_3 means for Belsk in the period 1963-2019 using the original data (Bass&Paur at fixed temperature) and the Brewer adjusted Dobson data: monthly means in December (a), monthly means in July (b), yearly means (c). The red and blue curves show smoothed pattern for the original data and the Brewer adjusted Dobson data, respectively.

4 Data availability

The dataset used in this article is available on the PANGAEA repository at https://doi.org/10.1594/PANGAEA.919378 (Rajewska-Więch et al., 2020)

5 Conclusions

The TCO_3 observations by the Dobson spectrophotometer in higher latitude sites, like Belsk, with frequent non ideal conditions for the ozone observations, i.e., numerous cloudy days and low solar elevation at noon in the cold subperiod of the year, should be quality controlled prior to searching for the long-term trends and comparisons with the satellite data. Frequent intercomparisons of the Belsk's Dobson spectrophotometer, which were carried out in perfect weather conditions, showed the stability of the instrument for the whole period for the most reliable DS & AD observations. However, such observations are not possible for numerous days especially during the colder period of the year. The data correction procedure is proposed to account for: less accurate observations under low solar elevation, presence of clouds, and sensitivity of the ozone absorption on temperature.

The results of all intraday measurements for the period 1963-2019 have been previously stored at the PANGAEA data base with additional information including: time of observation, cloudiness type, air mass, and description of the wavelength pair and observation type selected for each individual measurement (Rajewska-Więch et al., 2020). The corrections described by formula (1) and (3) are linear function of air mass, so it can be easily calculated by any user. The effective temperature can be taken from the TEMIS data base and the correction for the ozone absorption dependence on temperature given by formula (2) also requires simple calculations. Thus, it will be possible to use the homogenized Dobson data for comparative studies with other TCO_3 data sources.

The present analysis shows that the original data (archived in PANGAEA data base) can be used in trend analyses based on the TCO_3 monthly and yearly means. Application of all described corrections to the original data provides that the resulting smoothed time series exhibits a constant shift (upward for the cold season and much less downward for the warm season) relative to the original long-term pattern. This finding supports the validity of previous trend analyses of the Belsk's Dobson data (e.g., Krzyścin and Rajewska, 2009; Krzyścin et al., 2013; Krzyścin et al., 2014). The resulting Brewer adjusted Dobson TCO_3 values are found in good agreement with the Brewer data. This will allow for constructing the Dobson-Brewer merged time series as the Brewer observations will soon replace the Dobson measurements at Belsk.

Author contributions. JK wrote the paper and did statistical analysis, BR carried out the data processing, and JJ provided the Brewer data.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. This research was financed by a subsidy of the Ministry of Education and Science in Poland for the Institute of Geophysics of the Polish Academy of Sciences. The authors would like to thank the observing staff from the Main Geophysical Observatory, Polish Academy of Sciences, at Belsk (listed in the paper by Krzyścin et al., 2014) for their commitment to collect the data.

References

Ball, W. T., Alsing, J., Mortlock, D. J., Staehelin, J., Haigh, J. D., Peter, T., Tummon, F., Stübi, R., Stenke, A., Anderson, J., Bourassa, A., Davis, S. M., Degenstein, D., Frith, S., Froidevaux, L., Roth, C., Sofieva, V., Wang, R., Wild, J., Yu, P., Ziemke, J. R., and Rozanov, E. V.: Evidence for a continuous decline in lower stratospheric ozone offsetting ozone layer recovery, Atmos. Chem. Phys., 18, 1379-1394, doi:10.5194/acp-18-1379-2018, 2018.

Bass, A. M., Paur, R. J.: The ultraviolet cross–section of ozone, I, The measurements. In C. S. Zerefos & A. Ghazi (Eds.), Proceedings of the Quadrennial Ozone Symposium (pp. 606–610). Norwell, MA: D.Reidel, 1985.

Chubachi, S.: Preliminary result of ozone observations at Syowa from February 1982 to January 1983, Mem. Natl Inst. Polar Res., 34, 13–19, 1984.

Cleveland, W.S.: Robust weighted regression and smoothing scatterplots, J. Am. Stat. Assoc., 74, 368, 829-836, doi:10.1080/01621459.1979.10481038, 1979.

Dobson, G. M. B.: Observer's handbook for the ozone spectrophotometer, Ann. Int. Geophys. Year, 5, 46–89, 1957.

Degórska, M., Rajewska-Więch, B., and Kowalczyk, R.: A program for computing routine total ozone measurements and lamp tests for a Dobson spectrophotometer, Publ. Inst. Geophys. Pol. Acad. Sc., D-7 (126), 67-75, 1978.

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

Degórska, M., and Rajewska-Więch, B., Retrospective reevaluation of total ozone and Umkehr profile data from Belsk, Poland, Publs. Inst. Geophys. Pol. Acad. Sc., D-36(246), 71-76, 1991.

Dhomse S.S., Feng W., Montzka S.A., Hossaini R., Keeble J., Pyle J.A., Daniel J.S., and Chipperfield M.P.: Delay in recovery of the Antarctic ozone hole from unexpected CFC-11 emissions, Nature Communication., 10, 5781, doi:10.1038/s41467-019-13717-x, 2019.

Dziewulska-Łosiowa, A., and Walshaw, C.D.: The international comparisons of ozone spectrophotometers at Belsk, 24 June-6 July 1974, Publ. Inst. Geophys. Pol. Acad. Sc., 89, 3-38, 1975.

Dziewulska-Łosiowa, A., Degórska, M., and Rajewska-Więch, B.: The normalized total ozone record Belsk, 1963-1981, Publ. Inst. Geophys. Pol. Acad. Sc., D-18(169), 23-73, 1983.

Evans, R., McConville, G., Oltmans, S., Petropavlovskikh, I., and Quincy, D.: Measurement of internal stray light within Dobson ozone spectrophotometers, Int. J. Remote Sens., 30(15-16), 4247–4258, doi:10.1080/01431160902825057, 2009.

Farman, J. C., Gardiner, B.G., and Shanklin, J.D.: Large losses of total ozone in Antarctica reveal seasonal ClOx /NOx interaction, Nature, 315, 207–210, doi:org/10.1038/315207a0, 1985.

Karppinen, T., Redondas, A., Garcia, R.D., Lakkala, K., McElroy, and C.T., Kyrö, E.: Compensating for the effects of stray light in single-monochromator Brewer spectrophotometer Ozone Retrieval, Atmos.-Ocean, 53(1), 66–73, doi:10.1080/07055900.2013.871499, 2015.

Kerr, J.B., Asbridge, I.A., and Evans, W.F.J.: Intercomparison of total ozone measured by the Brewer and Dobson spectrophotometers at Toronto, J. Geophys. Res-Atmos., 93, 11129-11140, doi:10.1029/JD093iD09p11129, 1988.

Komhyr, W.D., Mateer, C.L, and Hudson, R. D.: Effective Bass-Paur 1985 ozone absorption coefficients for use with Dobson ozone spectrophotometers, J. Geophys. Res., 98(D11), 20451-20465, doi:10.1029/93JD00602, 1993.

Koukouli, M.Z., Zara, M., Lerot, C., Fragkos, K., Balis, D., Van Roozendael, M., Allart, M., and van der A, R.: The impact of the ozone effective temperature on satellite validation using the Dobson spectrophotometer network, Atmos. Meas. Tech., 9(5), 2055-2065, doi:10.5194/amt-9-2055-2016, 2016.

Krzyścin, J.W., and Rajewska-Więch, B.: Ozone recovery as seen in perspective of the Dobson spectrophotometer measurements at Belsk (52°N, 21°E) in the period 1963–2008, Atmos. Environ., 43(40), 6369-6375, doi:10.1016/j.atmosenv.2009.09.018, 2009.

Krzyścin, J.W., Rajewska-Więch, B., and Jarosławski, J.: The long-term variability of atmospheric ozone from the 50-yr observations carried out at Belsk (51.84°N, 20.78°E), Poland, Tellus B., 65(1), 21779, doi:10.3402/tellusb.v65i0.21779, 2013.

Krzyścin, J.W., Borkowski, J., Głowacka, A., Jarosławski, J., Podgórski, J., Pietruczuk, A., Rajewska-Więch, B., Sawicka, A., Sobolewski, P., Wink, J., and Zawisza, W.: Half century of the ozone observation at the Central geophysical Laboratory, IGF, PAS, Belsk, Poland, Achievements, History and Challenges in Geophysics, R. Bialik, M. Majdański, M. Moskalik (Eds.), GeoPlanet: Earth and Planetary Sciences, Springer, Cham, Switzerland, 85-107, doi:10.1007/978-3-319-07599-0_5, 2014.

Krzyścin, J.: Is the Antarctic ozone hole recovering faster than changing the stratospheric halogen loading?, J. Meteor. Soc. Japan, 98, 1083-1091, doi:10.2151/jmsj.2020-055, 2020.

Lickley M., Solomon S., Fletcher S., Velders G.J.M., Daniel J., Rigby M., Montzka S.A., Kuijpers L.J.M., and Stone K.: Quantifying contributions of chlorofluorocarbon banks to emissions and impacts on the ozone layer and climate, Nature Communication, 11, 1380, doi:10.1038/s41467-020-15162-7, 2020.

Montzka S.A., Dutton G.S., Yu P., Ray E., Portmann R.W., Daniel J.S., Kuijpers L., Hall B.D., Mondeel D., Siso C., Nance J.D., Rigby M., Manning A.J., Hu L., Moore F., Miller B.R., and Elkins J.W.: An unexpected and persistent increase in global emissions of ozone-depleting CFC-11, Nature, 557, 413-417, doi:10.1038/s41586-018-0106-2, 2018.

https://doi.org/10.5194/essd-2021-39
Preprint. Discussion started: 22 February 2021

Open Access Earth System Science Data Discussions

Rajewska-Więch, B., Krzyścin, J.W, Sobolewski, P., and Wink, J.: Intraday total column ozone measurements at Belsk, Poland, with the Dobson spectrophotometer no.84 since March 23, 1963 up to December 31, 2019, Institute of Geophysics of the Polish Academy of Sciences, Warsaw, Poland, PANGAEA, doi:10.1594/PANGAEA.919378, 2020

Redondas, A., Evans, R., Stuebi, R., Köhler, U., and Weber, M.: Evaluation of the use of five laboratory-determined ozone absorption cross sections in Brewer and Dobson retrieval algorithms, Atmos. Chem. Phys., 14, 1635–1648, doi:10.5194/acp-14-1635-2014, 2014.

Rindert, S. B.: Constructing empirical blue-sky ozone charts. Dept. of Earth Sciences, Meteorology, Uppsala University Rep. No. 36, 37 pp., 1973.

Serdyuchenko, A., Gorshelev, V., Weber, M., Chehade, W., and Burrows, J. P.: High spectral resolution ozone absorption crosssections – Part 2: Temperature dependence, Atmos. Meas. Tech., 7, 625–636, doi:10.5194/amt-7-625-2014, 2014.

Staehelin, J., Renaud, A., Bader, J., McPeters, R., Viatte, P., Hoegger, B., Bugnion, V., Giroud, M., and Schill, H.: Total ozone series at Arosa (Switzerland): Homogenization and data comparison, J. Geophys. Res-Atmos., 103(D5), 5827-5841, doi:10.1029/97JD02402, 1998.

Vanicek, K.: Differences between ground Dobson, Brewer and satellite TOMS-8, GOME-WFDOAS total ozone observations at Hradec Kralove, Czech, Atmos. Chem. Phys., 6, 5163–5171, doi:10.5194/acp-6-5163-2006, 2006.

Vaníček, K., Metelka, L., Skrivankova, P., and Staněk, M.: Dobson, Brewer, ERA-40 and ERA-Interim original and merged total ozone data sets-evaluation of differences: A case study, Hradec Králové (Czech), 1961-2010, Earth Syst. Sci. Data, 4, 91-100, doi:10.5194/essd-4-91-2012, 2012.

Vigroux, E.: Détermination des coefficients moyens d'absorption de l'ozone en vue des observations concernant l'ozone atmosphérique a l'aide due spectromètre Dobson, Ann. Phys., 2, 209-215, 1967.