Review of Direct-sun total ozone data from a Bentham spectroradiometer: methodology and comparison with satellite observations

The paper is a good discussion of an alternative to the Brewer spectrometer system. More information is needed concerning the fiber optic connection of the Bentham to the direct-sun viewing capability. From the description, it would appear that the fiber optic cable moves during the day. This would change the radiometric transmission of the fiber and affect the derived amount of O3 and the afternoon Langley calibration. There are methods to minimize this effect, but the authors do not discuss such methods. In the absence of minimizing fiber effects, the observed apparent diurnal O3 variation should not be discussed.

If the authors measured the slit function of the Bentham, this should be discussed. Use of a triangular slit function may be satisfactory, but may not, if the Bentham differs significantly from a triangle.

Use of the Bass and Paur cross sections is now known no to be optimum. Kerr derived a modification to the Bass and Paur cross sections using measurements from a double Brewer at Mauna Loa. These modifictions make the modified Bass and Paur equivalent to the Daumont cross sections and other more recently measured cross sections.

The authors should discuss the omission of effects arising from omitted SO2 and O2:O2 absorption in their derivation of TOC.

A variation of 40 to 50 DU attributed to diurnal O3 variation in the lower troposphere is too large.

There are numerous minor suggestions and corrections embedded in the manuscript that should be addressed.

In its present form the paper rates as Good in Scientific Significance, Fair Scientific Quality. and Good in Presentation Quality. The scientific quality could be improved by the author's response to the above comments.

1.Does the paper address relevant scientific questions within the scope of AMT? YES
2.Does the paper present novel concepts, ideas, tools, or data? YES
3.Are substantial conclusions reached? YES
4.Are the scientific methods and assumptions valid and clearly outlined? NO
5.Are the results sufficient to support the interpretations and conclusions? NO
6.Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? YES
7.Do the authors give proper credit to related work and clearly indicate their own new/original contribution? YES
8.Does the title clearly reflect the contents of the paper? YES
9.Does the abstract provide a concise and complete summary? YES
10.Is the overall presentation well structured and clear? YES WITH MINOR CHANGES
11.Is the language fluent and precise? YES WITH MINOR CHANGES
12.Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? YES
13.Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? NO
14.Are the number and quality of references appropriate? YES
15.Is the amount and quality of supplementary material appropriate? NONE

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Atmospheric Measurement Techniques Discussions

Direct-sun total ozone data from a Bentham spectroradiometer: methodology and comparison with satellite observations

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Abstract

A methodology to obtain the total ozone column (TOC) from the direct-solar spectral measurements of a Bentham spectroradiometer located at Granada (Spain) is presented in this paper. The method relies on the differential absorption technique using two pairs of direct irradiance at adjacent wavelengths between 305 and 340 nm. The extraterrestrial constant was determined from the extrapolation to zero air mass of each wavelength pair (Langley plot method). We checked the strong influence of the cloud cover on the Bentham TOC measurements using simultaneous sky images taken with an All-sky camera. Thus, reliable TOC data are exclusively obtained during cloud-free conditions or partly cloudy conditions without the solar disk obstructed. In this work, the hourly TOC averages retrieved by the Bentham instrument with a standard deviation smaller than 3 % (~ 10 Dobson Unit) are selected as high-quality TOC data. The analysis of the diurnal TOC variations during cloud-free days showed a differential behavior between the morning and afternoon periods. Thus, while the mornings exhibit an almost stable pattern, the afternoons displays a monotonic TOC increase which could be related to photochemical processes in the lower troposphere associated with the formation of surface ozone. Finally, the Bentham TOC measurements were validated against the satellite data derived from three satellite instruments: OMI, GOME and SCIAMACHY. The mean absolute values of the relative differences between satellite and ground-based data were smaller than 3 % which highlight the high reliability of the retrieval method proposed in this paper to derive TOC data.

1 Introduction

It is well known that ozone plays a very important role in the atmospheric chemistry, since it absorbs the most energetic part of the solar ultraviolet (UV) radiation spectrum, protecting life on the Earth's surface from this detrimental radiation. Additionally, acting as a major greenhouse gas, the ozone has a substantial influence over the

AMTD

5, 8131–8160, 2012

weather and climate on regional to global spatial scales (Kiehl et al., 1999; Rex et al., 2004). The ozone layer depletion during the past two decades and the expected ozone recovery after the successful implementation of the Montreal Protocol have a great interest for the human society (Zerefos et al., 2012). Therefore, it remains important to measure the magnitude of the ozone changes and monitor their long- and short-term trends over different regions (World Meteorological Organization (WMO), 2006). For that, well-calibrated and well-maintained ground-based instruments are a crucial tool (Komhyr, 1980; Basher, 1982; Kerr et al., 1984; WMO, 1996, 2008). In addition, these accurate ground-based instruments are also required for assessing the quality of satellite ozone observations (e.g. Fioletov et al., 2002; Balis et al., 2007; Antón et al., 2010a, 2011) and for forecasting tasks in several fields such as the climate change, air pollution, and public information of the UV index (e.g. Long et al., 1996; Schmalwieser and Schauberger, 2000).

The most accurate method for determining the atmospheric ozone is the called differential absorption technique which uses ratios of direct spectral irradiance at few discrete wavelengths between 305 and 340 nm, where ozone presents very different absorption properties. The Brewer and Dobson spectrophotometers rely on this technique and it is generally considered as the standard method for surface remote sensing of the total ozone column (TOC) (Komhyr, 1980; Kerr et al., 1984; WMO, 2008). In addition, TOC data using the same method have been derived from other ground-based instruments such as the M-83 and M-124 filter ozonemeters (Bojkov et al., 1994), the Total Ozone Portable Spectrometer (TOPS) (Flinn et al., 1996), the microprocessor-controlled version of TOPS (MICROTOPS) (Morys et al., 2001), the Ultraviolet Multifilter Rotating Shadow-band Radiometer (UV-MFRSR) (Gao et al., 2001), and the Jobin Yvon spectroradiometer (Kiedron et al., 2007).

Bentham DMc 150 instrument is a spectroradiometer designed for measuring the spectral irradiance in the range between 280–600 nm. This instrument may record the direct spectral irradiance through a collimator tube mounted in a sun tracker. Thus, the Bentham direct solar measurements allow the determination of the TOC data by means

The method is similar to that used for the double Brewer 83 (see Cede et al. Proc. of SPIE Vol. 5886, doi: 10.1117/12.620167)

of the differential absorption technique. ~~However, to our knowledge, there are not any publications in literature about this specific issue~~. Lenoble et al. (2004) derived TOC data from a Bentham instrument located at Briançon (France) using an estimated direct sun irradiance from the difference between global and diffuse irradiances. Instead of the differential absorption technique, the retrieval method used in that work was based on the slope of the spectrum between 305 and 330 nm, correlated with ozone cross sectsions. On the other hand, Brogniez et al. (2005) applied a TOC retrieval fitting radiative transfer model simulations with global spectral measurements recorded by two Bentham instruments at Sonnblick (Austria) and Briançon (France).

In this framework, the main objective of this paper is to retrieve TOC data from direct sun measurements recorded by a Bentham spectroradiometer located at Granada (Spain), using the differential absorption technique. These TOC measurements are compared with satellite observations from three instruments in order to asses its accuracy. The three satellite instruments are the Ozone Monitoring Instrument (OMI) on board AURA, Global Ozone Monitoring Experiment (GOME) on board ERS-2 and the Scanning Imaging Absorption spectroMeter for Atmospheric CartograpHY (SCIAMACHY) on board ENVISAT.

The paper is organized as follows. The ground-based measurements and satellite observations are described in Sect. 2. Section 3 introduces the methodology used to retrieve the TOC data from the Bentham spectroradiometer. Section 4 focuses on the determination of the extraterrestrial constant. Results and discussion are presented in Sect. 5. Finally, Sect. 6 summarizes the main conclusions of the work.

2 Data

2.1 Ground-based measurements

A Bentham double-monochromator spectroradiometer (DMc150) is installed since 2005 at the Andalusian Center for Environmental Studies (CEAMA), Granada, Spain

(37.2° N, 3.6° W, 680 m a.s.l.), and it is operated by the Physics Atmospheric Group of the University of Granada. This spectroradiometer is programmed to take diurnal measurements of global, direct and diffuse UV spectral irradiance between 280 nm and 400 nm (each 0.5 nm) every 15 min. The spectral ~~resolution~~ sampling of this instrument is 0.48 nm with a wavelength setting uncertainty smaller than 0.1 nm. The full width at half maximum (FWHM) is 1.05 nm, being determined by a laser light at 325 nm. The double-monochromator is connected to two diffusers installed at the CEAMA rooftop by means of two optical fibers; one of them for the ~~measure of the global~~ measurement of global and diffuse irradiances, and the other one has a limited field of view of 1.2° thanks to a collimator tube with three ~~optic~~ optical diaphragms which is mounted in a sun tracker (2AP model from Kipp & Zonen) in order to perform~~s~~ measurements of direct sunlight only. The pointing accuracy of sun tracker is lower than 0.02° due to a sun sensor, which guaranties that collimator tube is always looking into the sun disk. The double-monochromator is installed in a container which temperature is stabilized at 25 °C by a peltier cell air/air system.

The Bentham spectroradiometer used in this study possesses an excellent maintenance record. In this sense, a calibration procedure is ~~monthly performed~~ performed monthly using a mercury lamp (wavelength shift correction) and a pre-calibrated 120 W lamp (NIST standard) following the method of Sperling et al. (1996). The raw signal first is wavelength shift corrected and then is converted in physical units (W m^{-2} nm^{-1}) using the measurements of the calibrated lamp and the convolution of the spectra assuming a triangular slit function of the spectroradiometer with a FWHM of 1.05 nm (Slaper et al., 1995). Bernhard and Seckmeyer (1999) quantified the radiometric uncertainties of a similar UV spectroradiometer finding, for solar zenith angle (SZA) equal to 30°, an expanded ($k = 2$) uncertainty of 9.9 %, 6.3 % and 6.6 % for 300, 350 and 400 nm, respectively. The uncertainties for SZA = 60° are similar, except for 300 nm when it rises up to 12.7 %.

Was the slit function measured? A triangle might not be a good approximation.

AMTD

5, 8131–8160, 2012

Direct-sun total ozone data from a Bentham spectroradiometer

M. Antón et al.

2.2 Satellite observations

Put in the OMI overpass time

The OMI instrument is a nadir viewing wide-swath UV-visible hyperspectral spectrometer which was launched onboard the NASA EOS-Aura satellite platform in July 2004 (Levelt et al., 2006). This satellite instrument measures the solar light backscattered to space by the Earth's atmosphere and surface in the wavelength range from 270 to 500 nm with a spectral resolution of 0.45 nm in the ultraviolet and 0.63 nm in the visible. The instrument has a 2600 km wide viewing swath such that it is capable of daily, global contiguous mapping of total ozone with an unprecedented high spatial resolution of $13 \times 24\,km^2$ at nadir. The OMI retrieval algorithm used in this paper (called OMI-TOMS) works with measurements at four discrete 1 nm wide wavelength bands centered at 313, 318, 331 and 360 nm, and it applies an empirical correction to remove errors due mainly to aerosols and clouds (Bhartia and Wellemeyer, 2002).

The ESA Global Ozone Monitoring Experiment (GOME) on board the Second European Sensing Satellite (ERS-2) has been recording global measurements of total ozone column since July 1995 (Burrows et al., 1999). The ground swath (960 km) is divided into three ground pixels of 320 km (across orbit) × 40 km (along orbit). The operational algorithm for the retrieval of total ozone column from this satellite instrument is the GOME Data Processor (GDP), which has undergone several years of progressive improvement since its first release in 1995 (Van Roozendael et al., 2006; Loyola et al., 2011). The GDP algorithm has two main steps to derive TOC data: the Differential Optical Absorption Spectroscopy (DOAS) least-squares fitting for the ozone slant column, followed by the computation of a suitable Air Mass Factor (AMF) to make the conversion to the vertical column density.

The SCIAMACHY was launched in March 2002 aboard the European platform ENVISAT. This satellite instrument has a total swath width of 960 km with a typical spatial resolution in nadir of 60 km across track by 30 km along track (Bovensmann et al., 1999). The SCIAMACHY Ground Processor (SGP) Version 5.0 is the current operational algorithm for the retrieval of total ozone column from this satellite instrument,

AMTD

5, 8131–8160, 2012

Direct-sun total ozone data from a Bentham spectroradiometer

M. Antón et al.

which is based on the GDP. More details about this algorithm can also be found in the work of Lerot et al. (2009).

3 Total ozone retrieval

Attenuation of direct-solar irradiance through the atmosphere can be described by the Beer-Lambert law (e.g. Iqbal, 1983). This law assumes that the measured intensity of direct-solar spectral irradiance I_λ at the Earth's surface can be approximated as:

$$\ln I_\lambda = \ln I_{0\lambda} - \left[\alpha_\lambda \mu \Omega + \beta_\lambda \frac{p}{p_0} m + \delta_\lambda \sec\theta\right], \quad (1)$$

where:

What is the effect of SO_2 and O_2:O_2 on the measurements?

- $I_{0\lambda}$ is the solar irradiance at the top of the atmosphere (extraterrestrial irradiance) at wavelength λ.
- α_λ is the ozone absorption coefficient at wavelength λ.
- μ is the relative optical air mass of the ozone layer (the ratio of the slant path of the beam through the ozone layer to the vertical path).
- Ω is the total ozone column in the atmosphere expressed in Dobson units (1 DU = 10^{-3} cm pure ozone at standard temperature and pressure).
- β_λ is the Rayleigh molecular scattering coefficient of the air at wavelength λ.
- p and p_0 are the station pressure and the mean sea level pressure at 1013.25 hPa, respectively.
- m is the relative optical air mass of the whole atmosphere (the ratio of the slant path of the beam through the whole atmosphere to the vertical path).

AMTD
5, 8131–8160, 2012

– δ_λ is the aerosol scattering coefficient (optical depth) at wavelength λ.

– θ is the SZA, in degrees.

In general, TOC values are retrieved from the measurements of the direct solar irradiances at more than one wavelength by differential optical absorption techniques. In this study the double-pair wavelengths, 305.5–325.5 nm (A1–A2) and 317.5–340.0 nm (D1–D2), which approximately correspond to the A (305.5–325.4 nm) and the D (317.6–339.8 nm) pairs for the Dobson instrument (WMO, 2003; Basher, 1982; Komhyr, 1980) have been chosen to obtain the TOC from the Bentham spectroradiometer. These two pairs of adjacent wavelengths with different ozone absorption coefficients are selected to minimize the effects of other atmospheric constituents, mainly aerosols, with the absorption by ozone being the major factor affecting the relative intensities of these double-wavelength pairs. Therefore, measurements of irradiances made at those four wavelengths are expressed by four equations of the form given in expression 1 with different values for $I_{0\lambda}$, α_λ, β_λ and δ_λ. These four equations may be linearly combined to obtain the total column ozone as (WMO, 1996; Vanicek, 2006; Scarnato et al., 2009):

$$\Omega = \frac{F_0 - F - \left[\beta \cdot (p/p_0) \cdot m\right]}{\alpha \cdot \mu}. \tag{2}$$

The term F is directly derived from the Bentham measurements:

$$F = \ln \frac{I_\lambda(\mathrm{A1})}{I_\lambda(\mathrm{A2})} - \ln \frac{I_\lambda(\mathrm{D1})}{I_\lambda(\mathrm{D2})}. \tag{3}$$

The term F_0 is the extraterrestrial constant (ETC) for the instrument (F value outside the Earth's atmosphere):

$$F_0 = \ln \frac{I_{0\lambda}(\mathrm{A1})}{I_{0\lambda}(\mathrm{A2})} - \ln \frac{I_{0\lambda}(\mathrm{D1})}{I_{0\lambda}(\mathrm{D2})}. \tag{4}$$

AMTD
5, 8131–8160, 2012

The ETC value is determined in this work from the extrapolation to zero air mass of each wavelength pair (Langley plot method) which is described in detail in Sect. 4.

The terms α is the differential absorption coefficient obtained as:

you shold use O3 x-sect from [Daumont et al., 1992], which are the current ones

$$\alpha = (\alpha_{A1} - \alpha_{A2}) - (\alpha_{D1} - \alpha_{D2}), \tag{5}$$

where α_{A1}, α_{A2}, α_{D1}, α_{D2} are the Bass and Paur (1985) ozone absorption coefficients (the current remote sensing standard for ozone) at a fixed temperature of 227.0 K (Komhyr, 1993). This temperature must be representative of the average column temperature weighted by the ozone concentration (called effective temperature). The real effective temperature changes with the height, latitude, and season. Antón et al. (2008) showed that the effective temperature at Madrid for the period 1995–2002 ranges between 218 K (summer) and 232 K (winter) (see its Fig. 2), with a mean effective temperature of 226.5 K. This value can be also assumed as representative for South Spain.

The terms β, related to the Rayleigh molecular scattering coefficients, is calculated as:

The Brewer uses a modified version of the Bass and Paur that were derived by James Kerr at Mauna Loa. These data closely match Daumont

$$\beta = (\beta_{A1} - \beta_{A2}) - (\beta_{D1} - \beta_{D2}), \tag{6}$$

where β_{A1}, β_{A2}, β_{D1}, β_{D2} are derived from (Komhyr et al., 1989):

$$\beta_\lambda = 1.787 \times 10^{10} \lambda^{-4.25}. \tag{7}$$

The atmospheric pressure needed to adjust the Rayleigh scattering coefficient was measured by an automatic weather station at the study site. Pressure data were recorded as 1 min averages, and subsequently processed to hourly means.

The relative optical air mass of the whole atmosphere is obtained using the expression proposed by Kasten and Young (1989):

$$m = \frac{1}{\left(\cos\theta + 0.050572 \cdot (96.07995 - \theta)^{-1.6364}\right)}. \quad (8)$$

where θ is the SZA.

Finally, the optical air mass of the ozone layer, also called the ozone air mass factor (AMF), can be approximated to the following expression (Komhyr, 1980; Bernhard et al., 2005):

$$\mu = \frac{1}{\sqrt{1 - \frac{(R+r)^2}{(R+h)^2}\sin^2\theta}} \quad , \quad (9)$$

where R is the mean earth radius; r is the height of the station above mean sea level, in kilometers; h is the height of the ozone layer above mean sea level at station location; and θ is the SZA. We obtain this parameter assuming a fixed value of 0.9965 for the ratio $(R+r)/(R+h)$, the same value used by the Brewer and Dobson algorithms (Basher et al., 1982). Using this fixed value together with a mean radius of the Earth of 6370 km and a null altitude for our ground-based station, the ratio assumes an ozone layer 21.99 km above the station. Antón et al. (2009) showed that the relative differences between the operational ozone AMF values considered by Brewer instruments and simulated values using real ozone profiles at Madrid are completely negligible for solar zenith angles smaller than 75°. This good agreement is related to the fact that the fixed altitude of the ozone layer assumed by the Brewer algorithm (∼ 22 km) is very close to the real altitude of the ozone mass centre at Madrid during all seasons (the average altitude of the ozone layer over Madrid is 21.7 ± 1.8 km). We expect very similar results for South Spain since the ozone profile above Madrid can be considered representative of the ozone profile over the Iberian Peninsula.

AMTD
5, 8131–8160, 2012

4 Extraterrestrial constant

According to the Beer-Lambert law, the ratio between the direct-solar irradiance at two wavelengths λ_1 and λ_2 may be expressed as:

$$\ln \frac{I(\lambda_1)}{I(\lambda_2)} = \ln \frac{I_0(\lambda_1)}{I_0(\lambda_2)} - \left(\tau_{\lambda_1} + \tau_{\lambda_2}\right) \cdot m \quad (10)$$

where τ_{λ_1} and τ_{λ_2} are the total atmospheric optical depth for the wavelengths λ_1 and λ_2 taking into account all factors contributing to the solar attenuation.

If a series of direct-solar irradiance measurements is taken over a range of the relative optical air mass during which the total atmospheric optical depth remained constant, the term $\ln \frac{I_0(\lambda_1)}{I_0(\lambda_2)}$ may be determined from the ordinate intercept ($m = 0$, no atmosphere) of a least-squares fit between the term $\ln \frac{I(\lambda_1)}{I(\lambda_2)}$ and m. This procedure is a slight modification of the commonly known as Langley-plot technique (Thomason et al., 1982; 1983; Marenco et al., 2002) which utilizes spectral irradiance and not the ratios like our method. To obtain the ETC (Eq. 4) of the Bentham instrument, this modified Langley method can be applied for the pairs of wavelengths A1–A2 and D1–D2.

We performed Langley-plot analysis for 30 cloud-free half-days, originating from morning measurements in late spring and summer. The selection of cloud-free periods is based on the cloud cover information given by an All-Sky Imager (Cazorla et al., 2008, 2009). This camera provides images of the whole sky dome in daytime every 5 min, being installed over the same sun tracker next to the Bentham collimator tube. The cloud cover is characterized in octas ~~oktas~~ (eighths of sky), taking exclusively those half-days with null octas oktas during the observation period which must cover air-mass values smaller than 3 (SZA smaller than 70°). Additionally, the 30 selected cases satisfied the criterion that more than twenty direct irradiance spectra yielding a correlation in the Langley plots of better than 0.99. However, this restrictive criterion may not guarantee that the data actually contain no optical depth variation. Thus, a slow and monotonic diurnal TOC variation may produce well-aligned data in the Langley plots, but their

AMTD
5, 8131–8160, 2012

ordinate intercepts can differ substantially from the correct extraterrestrial constant (Arola and Koskela, 2004). In contrast, the ratio of the direct-solar irradiance at two very close wavelengths makes the Langley method employed in this work insensitive to changes in the atmospheric aerosol load (the aerosol optical thickness presents no significant dependence in the narrow spectral range employed for the TOC retrieval).

The Langley-plots for the two pairs of wavelengths corresponding to a particular day (2 July 2005) are shown in Fig. 1. The two regression lines for the morning values have been added to the figure, being their ordinate intercepts (-0.410 ± 0.011 and -0.36 ± 0.06) the two terms (left and right) of the Eq. (4) which allow the determination of the ETC (-0.054 ± 0.017). The error corresponds with the sum of the standard errors associated with the two ordinate intercepts. Additionally, the afternoon values for the two pairs of wavelengths have also been added to the plot. It can be seen that the data are well-aligned which could be confused with correct Langley plots. For these afternoon cases, the ordinate intercepts are -0.109 ± 0.005 and -0.27 ± 0.004, which lead to an erroneous ETC value of $+0.166 \pm 0.009$. This large difference between the morning and the afternoon ETC is related to the differential behavior of the TOC changes during these two periods which is analyzed in the next section for this particular day.

Table 1 shows the main statistical parameters for the daily ETC obtained for the selected days. The ETC presents a coefficient of variation (SD/Mean) of 19 % which indicate a significant day-to-day variability of the calibration constant. This variability in the ETC values may be mainly associated with the diurnal TOC fluctuations commented above. Marenco et al. (2002) showed that the atmospheric disturbances during Langley plots act as random processes, and thus their influence on ETC may be minimized by averaging over a sufficiently large number of days. Therefore, the mean ETC value (-0.071) obtained from the 30 daily values is assumed as representative of the extraterrestrial constant in Eq. (2). The error of this mean ETC value is 0.019 which is derived from the average of the daily standard errors. Thus, the relative uncertainty of the ETC can be estimated around 27 %.

AMTD
5, 8131–8160, 2012

To analyze the effects of the large ETC uncertainty on TOC retrieved from the Bentham spectroradiometer, we have derived the experimental TOC data using the mean ETC (−0.071), and the estimated TOC values using the following four ETC values: −0.044 (maximum), −0.060 (percentile 75), −0.081 (percentile 25), −0.089 (minimum). The relative changes with respect to the mean ETC value are 38 %, 15 %, 14 % and 25 %, respectively. The ratio of the estimated and the experimental TOC values is calculated for each Bentham spectrum recorded during the 30 selected half-days. Figure 2 shows all these ratios as a function of SZA. It can be seen that the influence of the ETC variability on TOC data is quite limited. Thus, the variations of the modeled TOC values with respect to the experimental data are smaller than 3 %, appreciating a decrease of the experimental-modeled TOC differences when the SZA increases (differences smaller than 1 % for SZA of 70°). Therefore, the use of the mean ETC in Eq. (2) to obtain the Bentham TOC data introduce a reduce uncertainty in these experimental values.

5 Results and discussion

5.1 Bentham total ozone data

one TOC measurement was retreived every 15 minutes between April 2005 and May 2006.

From each Bentham direct-sun spectrum ~~recorded every 15 min one TOC measurement was retrieved between April 2005 and May 2006~~. Hourly TOC data were determined by the average of the four TOC measurements recorded every hour. The success of the TOC retrieval by Bentham spectroradiometer is highly dependent on the stability of the atmosphere during the direct-sun measurements at each specific wavelength. In this sense, the variability of the cloud cover may produce strong changes on direct-sun measurements, making the TOC retrieval unreliable.

Figure 3 shows three plots with the diurnal evolution of the hourly TOC retrievals for several days. The errors bars represent the standard deviation (SD) of the hourly averages. The three plots also include the diurnal evolution of the cloud cover, characterized

AMTD
5, 8131–8160, 2012

in oktas octas from the All-Sky Imager described in Sect. 4. Additionally, the punctual daily TOC data given by the satellite OMI instrument over the study site have been added to the plots in order to have a reference value.

Figure 3 (top) shows the TOC evolution for the day 12 October 2005. It can be seen that the day presents cloud-free conditions (null oktas octas) until 14:00 GMT and then a substantial increase of the cloudiness with a maximum value of 7 oktas octas around 16:00 GMT. The Bentham TOC retrieval exhibits a great stability during the clear sky period with TOC values between 266 and 275 DU. The TOC value derived from OMI instrument during the satellite overpass was 269 DU, indicating the good agreement between ground-based and satellite-based TOC measurements. In addition, for this clear sky period, the SD presents values smaller than 3 DU (~ 1 %) which point out the significance of the Bentham TOC data retrieved during cloud-free conditions. In contrast, the presence of clouds in the afternoon clearly makes the hourly TOC data unreliable, showing large error bars (SD higher than 28 DU) and a strong variability in the averages. Therefore, the SD parameter may be used for selecting high-quality TOC data retrieved by the Bentham spectroradiometer.

The diurnal evolution of TOC retrievals for three completely cloud-free days (null oktas octas) is shown in Fig. 3 (middle). This plot exhibits the typical pattern of the diurnal variability of TOC data over Granada. Thus, it can be observed that TOC remains almost constant until midday, suffering then a monotonous monotonic increase toward sunset that can reach up to 40–50 DU. For instance, the day 2 July 2005, the TOC is nearly stable in the morning (time < 12 h) with values in the range 280–293 DU and a small coefficient of variation of 1.5 %. This first part of the TOC evolution corresponds to the two Langley extrapolations (black lines) shown in Fig. 1. A high TOC stability is found most of the cloudless ~~in the most of cloudless~~ mornings at Granada since, for example, the coefficient of variation is always lower than 2 % for the 30 cloud-free mornings used to obtain the extraterrestrial constant. In the afternoon of 2 July 2005, the TOC shows a substantial linear increase from 292 DU at 12:00 GMT to 336 DU at 16:00 GMT, corresponding to the grey points in Fig. 1. This monotonic TOC variation is the response from the ~~responsible of~~ the large

40-50 DU is too large for tropospheric change near the surface. 40 DU is almost the entire troposphere

difference between the morning and afternoon ETC values pointed out in the previous section for this specific day. ~~This behavior can be associated with the diurnal photochemical processes in the lower troposphere related to the formation of ozone near the Earth's surface at populated urban locations.~~ The daytime patterns of the surface ozone present a monotonic increase with minimum values in the morning and maximum in the afternoon which is related to the diurnal solar cycle and the formation of anthropogenic precursors, mainly due to the road traffic in urban sites (Gimeno et al., 1999; Ribas and Peñuelas, 2004; Adame et al., 2010). Antón et al. (2010b) showed a similar diurnal pattern for the TOC data recorded in Madrid, reporting that the surface ozone changes could explain up to 70 % of the diurnal TOC variability. These authors indicated that this percentage strongly depends on the height of the uniformly mixed layer above the surface. Additionally, they also stated that the transport processes in the medium and upper troposphere could also have a significant contribution in the diurnal TOC variability.

Finally, Fig. 3 (bottom) shows the TOC evolution for a cloudy day (23 March 2006) with a strong decrease of cloudiness around solar noon. It can be seen the large bar errors for the most hourly Bentham averages, except the TOC value retrieved between 12:00 and 13:00 GMT with a value of 303 ± 2 DU. This experimental data is very close to the satellite TOC value given by OMI (297 DU). For this one hour period, we observe that the cloud cover varies between 0 and 2 octas oktas. Therefore, partly cloudy conditions with the solar disk not obstructed by clouds throughout one hour can lead to obtain low SD values and thus, reliable hourly TOC data.

5.2 Comparison against satellite observations

To check the reliability of the TOC data retrieved by the Bentham spectroradiometer, we compare these ground-based data with independent high-quality observations inferred from three satellite instruments covering the ultraviolet spectral range: OMI, GOME and SCIAMACHY. The accuracy of these satellite TOC data is very high as they compare to well-established ground-truth reference data within a few percent (Fioletov et al., 2002;

AMTD
5, 8131–8160, 2012
Direct-sun total ozone data from a Bentham spectroradiometer
M. Antón et al.

Bramstedt et al., 2003; Balis et al., 2007; Lerot et al., 2009; Antón et al., 2010a, 2011; Loyola et al., 2011). In this work, the satellite pixel most closely collocated with the ground-based station is selected as the best match every day. In addition, the hourly Bentham TOC data measured each day between 11 and 13 h are averaged, allowing thus the comparison with the punctual daily satellite observations recorded around solar noon. Only those hourly TOC averages with a SD smaller than 10 DU (∼ 3 %) are assumed as valid and, therefore, utilized for intercomparison purposes. This restrictive threshold guarantees an unobstructed solar disk during the four direct solar spectrums measured within one hour.

A linear regression analysis is performed between the TOC values recorded by the Bentham spectroradiometer and the three satellite instruments in order to analyze their proportionality and similarity. Table 2 shows the number of pairs of ground-based and satellite-based data analyzed in this work, in addition to the slope of regression lines, coefficients of correlation (R^2) and the root mean square errors (RMSE). It can be seen that the correlation between the satellite-based and ground-based TOC data is significantly high for the three satellite instruments showing an excellent agreement for OMI ($R^2 \sim 0.95$) and a fairly good agreement for GOME ($R^2 \sim 0.85$) and SCIAMACHY ($R^2 \sim 0.83$), with a significantly small spread for the three correlations (RMSE lower than 3.5 %). Moreover, the statistical analysis renders slopes very close to unity, indicative of their proportionality. Additionally, the three scatterplots shown in Fig. 4 reveal the high degree of agreement between satellite-based and ground-based TOC data. The solid line is the unit slope line with zero bias.

Table 2 also shows the mean bias (MB) and the mean absolute bias (MAB) parameters calculated from the relative differences between the daily Bentham (Ben) TOC data and the satellite TOC data (Sat) using the following expressions:

$$\mathrm{MB} = \frac{1}{N}\sum_{i=1}^{N}\frac{\mathrm{Sat}_i - \mathrm{Ben}_i}{\mathrm{Ben}_i} \tag{11}$$

AMTD
5, 8131–8160, 2012

$$\mathrm{MAB} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\mathrm{Sat}_i - \mathrm{Ben}_i}{\mathrm{Ben}_i}\right| \tag{12}$$

where N is the number of data pairs Satellite-Bentham recorded in the study site.

The MB values close to zero indicate that there is no significant underestimation or overestimation of the TOC data retrieved from the Bentham instrument with respect to the satellite measurements. On average, the underestimation is only 0.6 % with ±2.6 % one standard deviation for OMI and (0.3 ± 3.4) % for SCIAMACHY, while GOME slightly overestimates the Bentham data in (0.2 ± 3.2) %. A value of the standard deviation around 3 % suggests that the random and systematic errors of TOC data inferred from both ground-based and satellite-based instruments are relatively small. In addition, MAB parameters are 2.1 % (OMI), 2.6 % (GOME) and 2.7 % (SCIAMACHY) with standard deviations smaller than 2 %, indicating the statistical significance of the reported values. All these results underline both the consistency and high reliability of the TOC measurements retrieved by the Bentham spectroradiometer located at Granada.

6 Conclusions

The method presented in this work to derive the total ozone column from direct-sun measurements is very promising and could be applied to any of the Bentham spectroradiometer available at many locations around the world.

The extraterrestrial constant of the Bentham instrument was obtained by the Langley extrapolation method. This technique is extremely sensitive to TOC fluctuations during the measurement ~~measured~~ period. Thus, a strong difference between the ETC derived from morning (nearly stable TOC values) and afternoon data (monotonic increase TOC values) during the ~~a~~ same day may be observed at the study location. This behavior may be likely associated with the diurnal evolution of the surface ozone at populated urban locations. We chose 30 cloud-free half-days (morning period) to obtain the ETC of

part of this variation in TOC may be instrumental. TOC is usally "flat" during the day unless the stratosphere changes. 40-50 DU (13-16%) is too large a change for the troposphere.

AMTD
5, 8131–8160, 2012

the Bentham spectroradiometer. The TOC presented a diurnal variability smaller than 2 % for each one of the 30 selected half-days. These low fluctuations were enough to produce a large day-to-day ETC variability (coefficient of variation around 19 %). However, the influence of these changes on Bentham TOC retrieval was reduced. Thus, the use of an averaged ETC value as fixed calibration constant introduces a maximum uncertainty smaller than 3 % in the TOC data.

A standard deviation of the hourly TOC values of 3 % (∼ 10 DU) was assumed as the upper threshold to select high-quality Bentham data. This restrictive limit guarantees direct-sun measurements performed during cloud-free conditions or partly cloudy conditions without the solar disk obstructed.

The TOC data provided by the Bentham spectroradiometer were checked by comparisons with the satellite TOC data inferred from the OMI, GOME and SCIAMACHY instruments. The Bentham instrument showed a good agreement with the three satellite instruments being the mean absolute bias lower than 3 % and the standard deviations smaller than 2 %.

Overall the Bentham spectroradiometer has a high potential for the retrieval of reliable direct-sun TOC data, being a viable alternative to the widely utilized Brewer and Dobson spectrophotometers.

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AMTD
5, 8131–8160, 2012

Direct-sun total ozone data from a Bentham spectroradiometer

M. Antón et al.

Table 1. Statistical parameters derived from the determination of the daily extraterrestrial constant of the Bentham spectroradiometer by the Langley technique for the 30 selected cloud-free half-days. The parameters are the following: the mean, the median, the standard deviation, percentiles 25 and 75, maximum and minimum.

	Mean	Median	Stand. Dev.	Perc. 25	Perc. 75	Max.	Min.
ETC	−0.071	−0.074	0.014	−0.081	−0.060	−0.044	−0.089

AMTD
5, 8131–8160, 2012

Table 2. Parameters obtained in the correlation analysis between satellite TOC data (OMI, GOME and SCIAMACHY) and Bentham measurements as gathered over Granada during the period the period between April 2005 and May 2006. The parameters are the following: the number of data (N), the slope of the regression, the correlation coefficients (R^2), the root mean square errors (RMSE), the mean bias (MB) and the mean absolute bias (MAB).

	N	Slope	R^2	RMSE (%)	MB (%)	MAB (%)
OMI	183	1.02 ± 0.02	0.95	2.58	-0.6 ± 2.6	2.1 ± 1.6
GOME	81	0.94 ± 0.04	0.85	3.21	$+0.2 \pm 3.2$	2.6 ± 2.0
SCIAMACHY	95	0.99 ± 0.04	0.83	3.44	-0.3 ± 3.4	2.7 ± 2.0

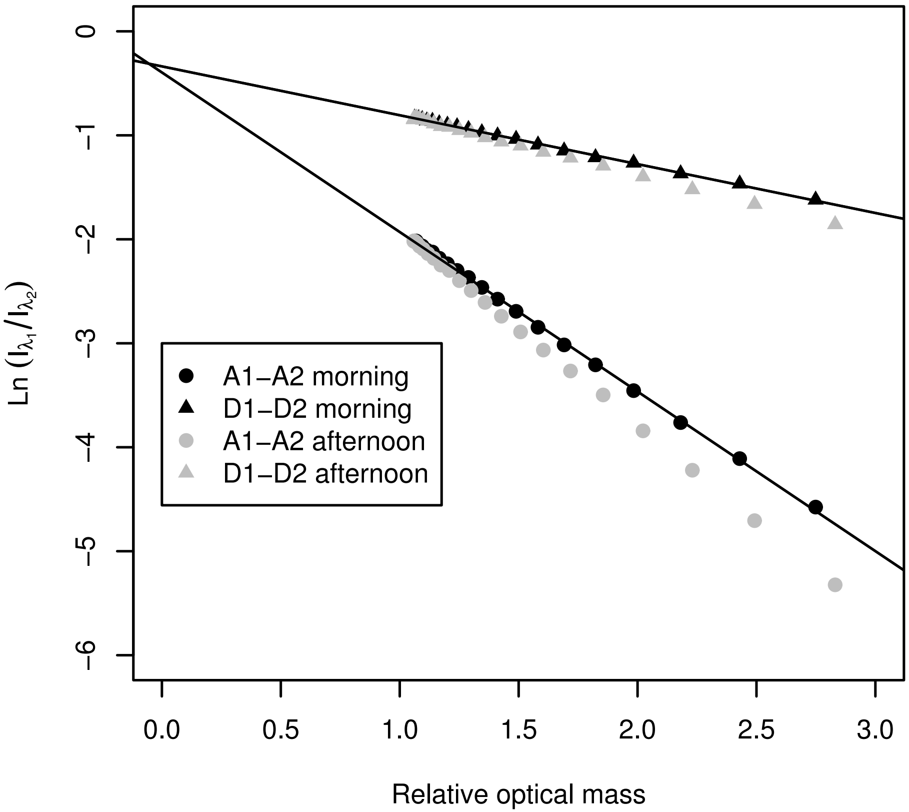

Fig. 1. Langley-plots for the two pairs of wavelengths (A1–A2, D1–D2) corresponding to 2 July 2005. Morning values (time < 12) are shown in black while afternoon values are displayed in grey. The two regression lines for the morning values have been added to the figure.

AMTD

5, 8131–8160, 2012

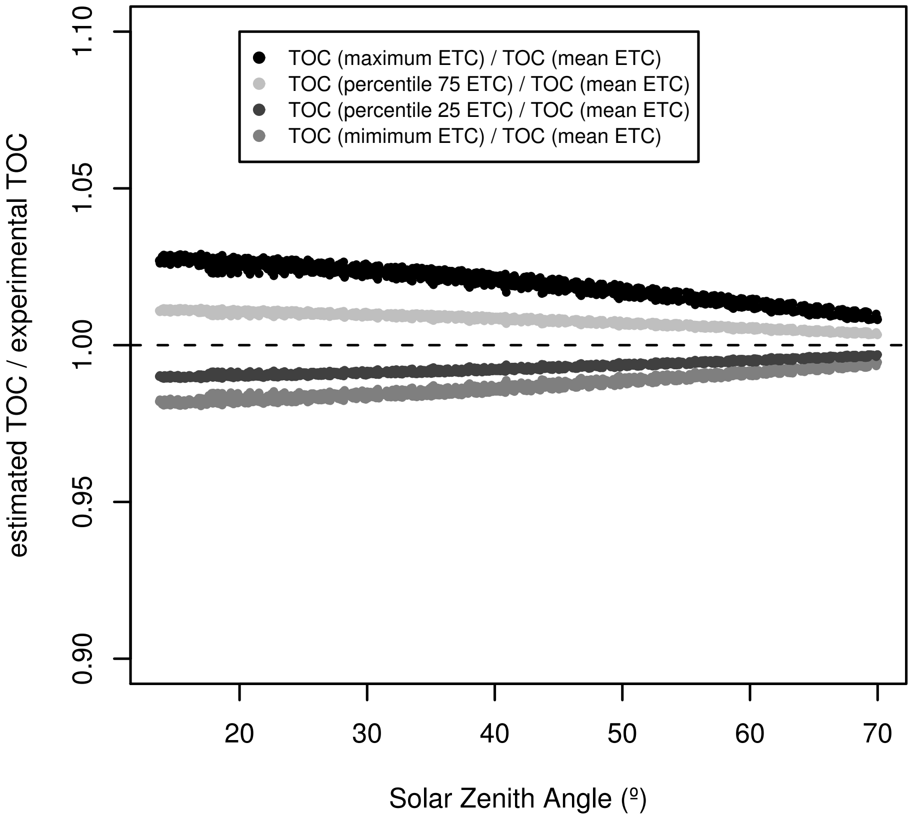

Fig. 2. The ratio of the estimated and the experimental total ozone column as a function of the solar zenith angle for the 30 selected cloud-free half-days. The experimental total ozone data have been derived using the mean ETC value while the estimated data using the maximum, minimum, percentile 75 and 25 ETC values.

AMTD
5, 8131–8160, 2012

Direct-sun total ozone data from a Bentham spectroradiometer

M. Antón et al.

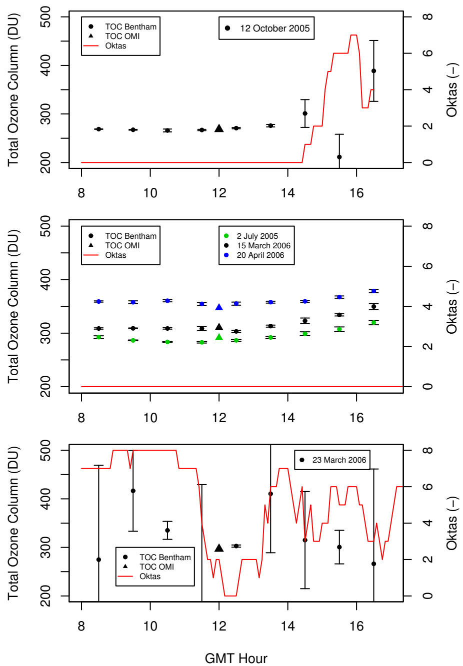

Fig. 3. Diurnal evolution of the total ozone column and the cloud cover characterized in oktas (eighths of sky) for the days: 12 October 2005 (top), 2 July 2005, 15 March 2006 and 20 April 2006 (middle), and 23 March 2006 (bottom). The errors bars represent the standard deviation (SD) of the hourly total ozone averages. The punctual daily total ozone data derived from the satellite Ozone Monitoring Instrument have been also included in the plots. DU, Dobson units.

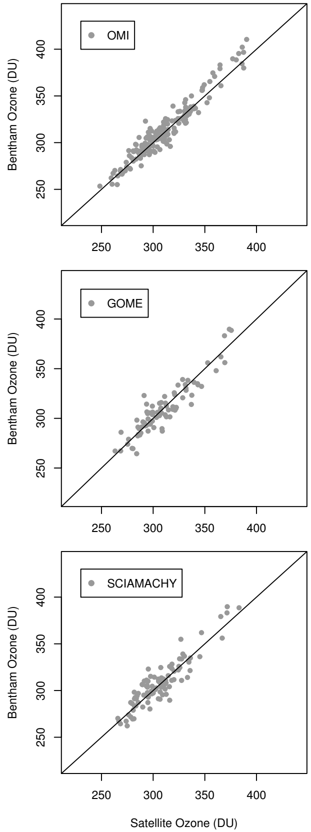

Fig. 4. Correlation between satellite and ground-based TOC data gathered over the Granada for the period between April 2005 and May 2006. (top) OMI versus Bentham. (middle) GOME versus Bentham. (bottom) SCIAMACHY versus Bentham. The solid line represents the unit slope with which the data almost agree. DU, Dobson units.