

Author's answer to Anonymous Referee #3

The authors greatly acknowledge the anonymous reviewer (Referee #3) for carefully reading the manuscript and providing constructive comments.

Referee GC #1: 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.

Author's response GC #1: If the movement of optical fiber affects the irradiance measurement, then it would affect the calibration lamp measurements. In this sense, we look for calibration files of lamps developed in the same day at different time. We find two spectra taken the 10th March 2009 at 12:13 PM and 16:48 PM. There are 4.5 hours between the two measurements (approximately from noon to sunset). The relative differences between the spectrum at 16:48 PM and the spectrum at 12:13 PM have been calculated for the wavelengths used in this paper. The maximum difference appears at 325 nm, being -1.7%. The differences between the spectra of the same lamp at different times are lower than the uncertainties of the self instrument, and it shows the effect of fibre is negligible and the diurnal O₃ variation can be discussed. In addition the spectral differences between sunset and noon for the calibration lamp are shown in the Figure 1, showing differences lower than 2% for all wavelengths higher than 300 nm.

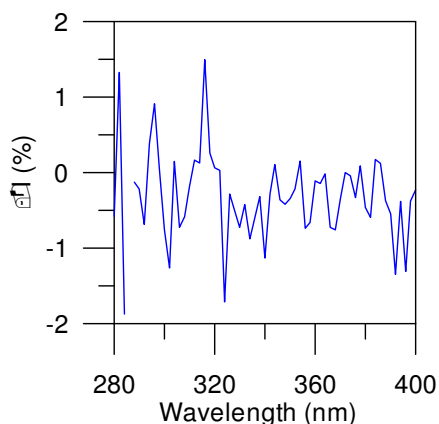


Figure 1: Difference (ΔI) between the irradiance registered at 16:48 PM and the irradiance at 12:13 PM (ΔI) at 10th March 2009, for the same calibration lamp.

Referee GC #2: 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.

Author's response GC #2: The measured slit function is represented in Figure 2. It is not triangular but as a first approximation we consider that, because it makes easier

calculations. In fact, the measured slit function and the triangular function are similar in -1 nm, 0 nm, 0.5 nm and 1 nm, the points that we use in the measurements (every 0.5 nm).

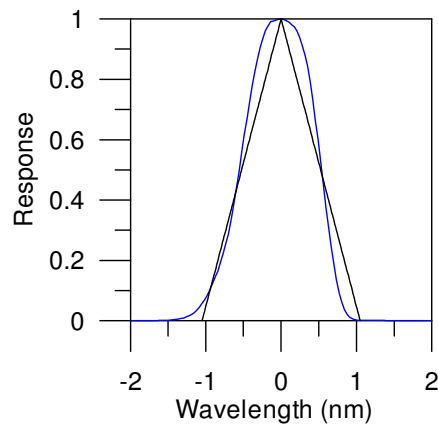


Figure 2: Measured slit function (blue) and 1.05FWHM triangular slit function (black) for the Bentham spectroradiometer.

Referee GC #3: Use of the Bass and Paur cross sections is now known not to be optimum. Kerr derived a modification to the Bass and Paur cross sections using measurements from a double Brewer at Mauna Loa. These modifications make the modified Bass and Paur equivalent to the Daumont cross sections and other more recently measured cross sections.

Author's response GC #3: Literature shows that Brewer systems yield near similar results when its operational retrieval is being performed with either the BDM (Brion, Daumont, Malicet) or standard BP (Bass and Paur) ozone absorption cross section data set (Redondas and Cede, 2006). These authors have also shown that with either cross section data sets there is little to no dependence of the Total Ozone Column (TOC) estimate on the atmospheric temperature at which the ozone resides. This is most likely a fortunate interplay between the temperature dependence of the cross sections, the choice of the central wavelengths and the width of the Brewer wavelength bands around these central wavelengths. Finally, Kerr (2002) has shown that by using 10+ wavelength bands the Brewer can in principle yield an estimate of the effective ozone temperature, that is the ozone profile weighed with the temperature profile. This author also concluded that his more advanced retrieval algorithm yields near similar results to the operational retrieval algorithm using only 4 wavelength bands which supports the quality of the historical Brewer data series continued to date.

We have included the following comment in the text (Section 3 “Total ozone retrieval”):

“Literature shows that spectrophotometers (e.g., Brewer) yield near similar results when its operational retrieval is being performed with either the BP (Bass and Paur) or BDM (Brion, Daumont, Malicet) ozone absorption cross section data set (Redondas and Cede, 2006). These authors have also shown that with either cross section data sets there is little to no dependence of the TOC estimate on the atmospheric temperature at which the ozone resides.”

---- Redondas, A. and Cede, A.: Brewer algorithm sensitivity analysis, SAUNA workshop, Puerto de la Cruz, Tenerife, November, 2006.

---- Kerr, J. B.: New methodology for deriving total ozone and other atmospheric variables from Brewer spectrophotometer direct sun spectra, J. Geophys. Res., 107(D23), 4731, doi:10.1029/2001JD001227, 2002.

Referee GC #4: The authors should discuss the omission of effects arising from omitted SO₂ and O₂:O₂ absorption in their derivation of TOC.

Author's response GC #4: According to the reviewer's suggestion, the following comment has been included in the text (Section 3 "Total ozone retrieval"):

"In the development of the above retrieval technique, it has been assumed that ozone is the most dominant absorption in the 310-340 nm spectral region, and so the effect of other UV absorbers is negligible. However, it is known that the accuracy of TOC measurements can be affected by the UV absorption from other atmospheric gases. In this sense, sulphur dioxide has been found to be the most relevant gas contributor to uncertainties in Dobson data at specific sites under particular atmospheric conditions. Thus, the errors in TOC data measured by Dobson instruments are less than 1% in unpolluted locations, but it can reach up to 10% in areas with high local sulphur dioxide emissions during inversion situations (WMO, 2008b)."

Referee GC #5: A variation of 40 to 50 DU attributed to diurnal O₃ variation in the lower troposphere is too large.

Author's response GC #5: Yes, we agree with this comment. In order to clarify this issue, we have re-phased the information given as:

"The daytime pattern observed in Figure 3 (middle) can be partially 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. It is known that tropospheric ozone column represents about 10% of total column (between 30 and 40 DU), with up to 10 DU in the boundary layer over major middle latitude cities (Zbinden et al., 2006). Thus, surface ozone has a small contribution to total column but due to its marked daytime pattern (e.g., Ribas and Peñuelas, 2004; Adame et al., 2010) present a non-negligible effect on diurnal TOC variations. In this sense, Antón et al. (2010b) analyzed the simultaneous diurnal evolution of both surface and total column ozone data at Madrid. They showed diurnal TOC variations up to 20 DU of which surface ozone changes could explain between 20% and 70%, depending on the mixing layer height. The strong diurnal TOC variations (up to 40-50 DU) found on certain days at Granada cannot be exclusively explained by photochemical processes near the surface, therefore, other factors like transport processes in the upper troposphere and lower stratosphere could also present a significant contribution."

--- Antón, M., López, M., Serrano, A., Bañón, M., García, J.A.: Diurnal variability of total ozone column over Madrid (Spain), Atmospheric Environment, 44, 2793–2798, 2010b.

--- Zbinden, R.M., Cammas, J.-P., Thouret, V., Nédélec, P., Karcher, F., and Simon, P.: Mid-latitude tropospheric ozone columns from the MOZAIC program: climatology and interannual variability, Atmos. Chem. Phys., 6, 1053–1073, 2006.

Specific Comments

Referee SC #1: There are numerous minor suggestions and corrections embedded in the manuscript that should be addressed.

Author's response SC #1: Thanks. All minor suggestions and corrections have been addressed.