

Global validation of empirically corrected EP-Total Ozone Mapping Spectrometer (TOMS) total ozone columns using Brewer and Dobson ground-based measurements

M. Antón,^{1,2,3} M. E. Koukouli,⁴ M. Kroon,⁵ R. D. McPeters,⁶ G. J. Labow,^{6,7} D. Balis,⁴ and A. Serrano^{2,3}

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[1] This article focuses on the global-scale validation of the empirically corrected Version 8 total ozone column data set acquired by the NASA Total Ozone Mapping Spectrometer (TOMS) during the period 1996–2004 when this instrument was flying aboard the Earth Probe (EP) satellite platform. This analysis is based on the use of spatially co-located, ground-based measurements from Dobson and Brewer spectrophotometers. The original EP-TOMS V8 total ozone column data set was also validated with these ground-based measurements to quantify the improvements made by the empirical correction that was necessary as a result of instrumental degradation issues occurring from the year 2000 onward that were uncorrectable by normal calibration techniques. EP-TOMS V8-corrected total ozone data present a remarkable improvement concerning the significant negative bias of around ~3% detected in the original EP-TOMS V8 observations after the year 2000. Neither the original nor the corrected EP-TOMS satellite total ozone data sets show a significant dependence on latitude. In addition, both EP-TOMS satellite data sets overestimate the Brewer measurements for small solar zenith angles (SZA) and underestimate for large SZA, explaining a significant seasonality (~1.5%) for cloud-free and cloudy conditions. Conversely, relative differences between EP-TOMS and Dobson present almost no dependence on SZA for cloud-free conditions and a strong dependence for cloudy conditions (from +2% for small SZA to -1% for high SZA). The dependence of the satellite ground-based relative differences on total ozone shows good agreement for column values above 250 Dobson units. Our main conclusion is that the upgrade to TOMS V8-corrected total ozone data presents a remarkable improvement. Nevertheless, despite its quality, the EP-TOMS data for the period 2000–2004 should not be used as a source for trend analysis since EP-TOMS ozone trends are empirically corrected using NOAA-16 and NOAA-17 solar backscatter ultraviolet/2 data as external references, and therefore, they are no longer considered as independent observations.

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1. Introduction

[2] The role of atmospheric ozone in protecting all living organisms from the detrimental effects of ultraviolet solar irradiation is quite well known. In addition, ozone layer

changes could be associated with global climate change and vice versa. Ozone is a greenhouse gas, so change in its column abundance may contribute to global climate change. While an increase in tropospheric ozone leads to warming of the troposphere, a decrease in stratospheric ozone leads to cooling in the stratosphere [Steinbrecht *et al.*, 2003]. At the same time, the ozone distribution itself is driven by atmospheric circulation and the atmospheric temperature distribution and is influenced by their variability, and hence potentially affected by climate change [World Meteorological Organization (WMO), 2006]. The work of Newman *et al.* [2009] simulated a future world (“world avoided”) where the ozone depleting substances were never regulated, and its production grew at an annual rate of 3%. They found by means of this “world avoided” simulation that 17% of the globally averaged column ozone would be

¹Departamento de Física Aplicada, Universidad de Granada, Granada, Spain.

²Departamento de Física, Universidad de Extremadura, Badajoz, Spain.

³Geophysics Centre of Evora, University of Evora, Evora, Portugal.

⁴Laboratory of Atmospheric Physics, Physics Department, Aristotle University of Thessaloniki, Thessaloniki, Greece.

⁵Royal Netherlands Meteorological Institute, De Bilt, Netherlands.

⁶NASA Goddard Space Flight Center, Greenbelt, Maryland, USA.

⁷SSAI (Science Systems Applications Inc.), Lanham Md, Maryland, USA.

destroyed by 2020 and 67% by 2065 in comparison to 1980. Therefore, close monitoring of the changes in the ozone layer has become a subject of major concern both by the scientific community and the general public from a wider perspective than only the imperative recovery from chemical ozone loss alone.

[3] Several studies using ground-based and satellite measurements have demonstrated that since the end of the 1970s until the beginning of the 1990s, there have been significant negative trends in total ozone in the middle and high-latitude regions of the two hemispheres (for e.g., *Stolarski et al.* [1992], *Callis et al.* [1997], *Harris et al.* [1997], *Stahelin et al.* [2001]). The successful implementation of the Montreal Protocol on Substances that Deplete the Ozone Layer and its later amendments has created high expectations about the recovery of the total ozone toward pre-1980s levels as a result of the declining halogen loading in the stratosphere. The work of *Newchurch et al.* [2003] reported signs of an ozone turnaround after 1996 from a statistical analysis of observations in the upper stratosphere, where ozone is mainly controlled by gas phase catalytic cycles.

[4] Satellite instruments provide daily images of the global ozone distribution with good spatial resolution that is an important advantage over the local measurements of ground-based ozone from a sparse network. Such global ozone coverage from the satellite vantage point has been available since the late 1970s with observations provided by the Total Ozone Mapping Spectrometer (TOMS) installed on three successive satellites: Nimbus-7 (1978–1993), Meteor-3 (1993–1994), and Earth Probe (EP) (1996–2005) [*McPeters et al.*, 1996a, 1998]. These TOMS global observations have proven to be crucial to the understanding of the geographical and temporal distribution and variability of the total ozone column (TOC) [e.g., *Herman et al.*, 1993; *Herman and Larko*, 1994; *McPeters et al.*, 1996b; *Malanca et al.*, 2005; *Hudson et al.*, 2006; *Antón et al.*, 2008a]. These observations are being continued by the Ozone Monitoring Instrument aboard the NASA EOS-Aura platform [*Levelt et al.*, 2006] since October 2004 onward.

[5] Extensive validation exercises on the Nimbus7-TOMS and Meteor3-TOMS total ozone data have been performed in the past decades [e.g., *Bojkov et al.*, 1988; *Fleig et al.*, 1986; *Kyro*, 1993; *Bojkov and Fioletov*, 1995; *McPeters and Labow*, 1996c; *Fioletov et al.*, 1999]. In addition, recent studies have focused on the comparison of the EP-TOMS TOC data with ground-based measurements recorded by well-calibrated spectrophotometers [e.g., *Masserot et al.*, 2002; *Fioletov et al.*, 2002; *Bramstedt et al.*, 2003; *Labow et al.*, 2004; *Vanicek*, 2006]. All these validation exercises have shown the continuing improvement in the successive versions of the TOMS retrieval algorithm, with a very high quality of the last available version (V8) [*Bhartia and Wellemeier*, 2002], which was released in 2004. In the most recent global-scale validation work of *Balis et al.* [2007a], the average agreement of EP-TOMS V8 ozone data with ground-based and other satellite TOC measurements is at the 1% level. Nevertheless, these satellite observations began to display significant deviations from the ground truth by the middle of the year 2000. This problem is not related to the TOMS algorithm, but it is related to a complex issue involving the inhomogeneous degradation of

the scanning mirror on the EP-TOMS instrument causing a calibration error even after onboard correction methods that leads to the application of algorithmic soft calibration methods. The detected error in the instrument performance appears to depend on latitude, season, lifetime, and wavelength [*Haffner et al.*, 2004]. Thus, NASA Goddard Space Flight Center (GSFC) warned users that EP-TOMS TOC data after the year 2000 are not recommended for the calculation of long-term ozone trends. To correct the influence of this instrument degradation on TOC observations, an empirical calibration technique has been applied to the data [*McPeters et al.*, 2007].

[6] This empirically corrected data (EP-TOMS V8-corrected) has been made available since September 2007. Since then only a handful of validation exercises with these satellite data have been performed and published in the literature [*Labow et al.*, 2006; *McPeters et al.*, 2008; *Antón et al.*, 2010]. In addition, to the best of our knowledge, no global comparisons between the TOC satellite observations derived from the V8-original and V8-corrected EP-TOMS data sets have been published to date. Given the above, an elaborate validation effort of the corrected EP-TOMS data set using reliable ground-based measurements is required to assess its quality and accuracy.

[7] The main objective of this paper is to report on a global-scale validation of the TOC data derived from the latest EP-TOMS retrieval algorithm (V8-corrected), using spatially and temporally co-located ground-based measurements from the well-established networks of Dobson and Brewer spectrophotometers during the period 1996–2004. The original EP-TOMS V8 ozone data covering during the same period were also compared with ground-based measurements to quantify the improvements made by the empirical correction. The observed discrepancies are quantified and their likely origins examined in detail.

[8] The paper is organized as follows. The satellite and ground-based measurements are described in section 2. Section 3 introduces the methodology. The results and discussion are presented in section 4. Finally, section 5 summarizes the main conclusions.

2. Data

2.1. Satellite Observations

[9] The NASA TOMS instrument is a downward nadir viewing spectrometer that measures backscattered Earth radiances at six discrete ultraviolet (UV) wavelengths (312–380 nm for Nimbus-7 and Meteor-3 TOMS or 308–360 nm for EP-TOMS). The set of six discrete 1 nm wavelength bands is measured at each of 35 scan positions at 3° intervals to continuously cover the regions between the orbital paths providing spatial coverage at all latitudes from a Sun-synchronous polar orbit. Depending on orbital altitude, the spatial resolution is about 50 × 50 km for the nadir view and about 75 × 200 km at the extreme cross-track scan positions. TOMS also measures the solar irradiance for each wavelength band once every day to provide radiance normalization. The solar irradiance measurements are recorded using a diffuser plate to scatter sunlight into the instrument. The total ozone data are derived from the backscattered UV reflectance by the TOMS retrieval algorithm. Finally, the total ozone data are averaged in a daily gridded format of

1.00° latitude by 1.25° longitude (level 3 data). This particular instrument was onboard the polar-orbiting Sun-synchronous Earth Probe (EP) satellite between July 1996 and December 2005. The unit used in this paper for the total ozone column is the Dobson Unit ($1 \text{ DU} = 2.69 \times 10^{16}$ molecules cm^{-2}).

[10] The satellite total ozone data used in this work have been processed using two versions of the TOMS algorithm: Version 8 (denoted “original” in this study) [Bhartia and Wellemeyer, 2002; Wellemeyer et al., 2004] and Version 8-corrected [McPeters et al., 2007]. These algorithms use only two wavelengths (317.5 and 331.2 nm) to derive total ozone data, whereas the other four wavelengths are used to identify aerosols and clouds and for error correction. The algorithm uses the measured directional albedo at each cross-track position as input, and a modeled lookup table based on climatologies for surface albedo, cloud albedo, cloud top height, ozone profile, and temperature profile.

[11] The V8-corrected version was released in 2007 and answers to problems in the quality of the EP-TOMS total ozone data occurring since the middle of the year 2000. These problems were believed to be related to changes in the front optical properties of the satellite instrument, most likely due to a nonuniform degradation of the scanning mirror [Haffner et al., 2004]. The empirical correction applied to the EP-TOMS data is based on multiple validation techniques using geophysical data, such as retrieved tropical total ozone and minimum surface reflectivity, to detect errors in the satellite observations [McPeters et al., 2007]. Furthermore, the data have been adjusted to agree with zonal means of the total ozone column data from NOAA-16 and NOAA-17 solar backscatter ultraviolet (SBUV)/2 instruments. The two versions of the TOMS algorithm use the 331.2 nm wavelength to derive surface reflectivity at small solar zenith angles but switch to 360 nm when the ozone absorption at 331.2 nm becomes significant because of long atmospheric path length. This surface reflectivity is used to retrieve the TOMS Lambertian Equivalent Reflectivity (LER) at 360 nm by means of a Lambertian cloud model with a cloud albedo of 0.80. This satellite LER is strongly correlated with clouds and surface albedo, allowing the characterization of the fractional cloud cover over the TOMS pixel with sufficiently small surface albedo. This variable plays no role in the TOMS ozone retrieval.

2.2. Ground-Based Measurements

[12] The well-established, worldwide network of Brewer and Dobson spectrophotometers is generally considered as the standard for surface remote sounding of the TOC. Both types of instrument rely on the method of differential absorption in the Huggins band where ozone exhibits strong absorption features in the ultraviolet part of the solar spectrum. This technique has been described in detail by several reference papers, e.g., Dobson [1957], Komhyr [1980], Basher [1982], and Kerr [2002].

[13] Most Dobson instruments are manually operated. Its measurement principle relies on the ratio of the direct sunlight (DS) intensities at two standard wavelengths. The most common combination, used for more than 98% of instruments, is the double pair (305.5/325.4; 317.6/339.8 nm) [Komhyr et al., 1993]. The world standard instrument,

Dobson 83, is normally located in Boulder, CO, but it is taken to Mauna Loa, HI, for regular calibrations using the Langley plot method [Komhyr et al., 1989].

[14] The Brewer spectrophotometer works with principles similar to the Dobson instrument but has an improved optical design and is fully automated. TOC values are obtained taking the ratio of sunlight intensities at four wavelengths between 306 and 320 nm with a resolution of 0.6 nm overcoming the spectral interference of sulfur dioxide with ozone [Kerr et al., 1984; Kerr, 2002]. The Brewer network calibration is based on a triad of reference Brewer spectrophotometers maintained by Meteorological Service of Canada at Toronto, Canada [Fioletov et al., 2005].

[15] When Brewer spectrophotometers are properly calibrated and regularly maintained, the TOC records obtained through DS measurements can potentially maintain a precision of 1% over long time intervals [Basher, 1982; WMO, 1996]. The Dobson spectrophotometer measures TOC values with an accuracy of 2%–3% for solar zenith angles smaller than 75° [Komhyr et al., 1989]. Staehelin et al. [2003] summarizes the results of the comparisons between the simultaneous total ozone data recorded by collocated Dobson and Brewer spectrophotometers at 19 locations of the two hemispheres. This work showed different approaches of Dobson-Brewer ozone comparison (monthly or daily averages, quasi-simultaneous data), reporting small but consistent characteristics in the differences between the total ozone data derived from both instruments. The use of different wavelengths in Dobson and Brewer spectrophotometer and the different temperature dependence for the ozone absorption coefficients introduced in the two retrievals may cause small differences in the measurements made by these instruments (within $\pm 1\%$) [Kerr et al., 1988; Van Roozendaal et al., 1998; De Backer and De Muer, 1991]. Different stray light properties between the two types of spectrophotometers and the sensitivity of the Dobson instrument to sulfur dioxide are possible additional contributing factors to the differences between the Brewer and Dobson total ozone measurements.

3. Methodology

[16] Daily mean values of TOC measurements recorded from Dobson and Brewer spectrophotometers are available from the World Ozone and Ultraviolet Data Centre archive (<http://www.woudc.org>). The ground-based TOC data selected for the comparisons are only based on records of DS measurements that are the most accurate TOC data measured from ground-based spectrophotometers. Tables 1 and 2 list the locations of the Brewer and Dobson instruments used in this work, respectively. The use of daily averaged, ground-based data instead of, for example, hourly averaged data centered around the EP-TOMS overpass is feasible owing to the well-known, long-term chemical stability of stratospheric ozone over most ground-based stations. Nevertheless, some stations underneath the edge of the polar stratospheric vortex may experience strong variations in ozone over the course of the day as a result of the movements of the vortex.

[17] The study presented in this paper uses EP-TOMS total ozone data retrieved by the TOMS algorithm version V8-original and version V8-corrected. The two overpass satellite data sets are produced by the NASA/GSFC TOMS

Table 1. List of Brewer Stations Used in the Comparisons^a

WMO ID	Station Name	Lat	Lon	Elevation	Country
322b	Petaling Jaya	3.1	101.65	46	Malaysia
10b	New Delhi	28.6	77.22	216	India
287b	Funchal	32.7	-17.05	59	Portugal
332b	Pohang	36	129.38	0	Korea
295b	Mount Waliguan	36.2	100.53	3816	China
213b	El Arenosillo	37.1	-6.73	41	Spain
346b	Murcia	38	-1.17	69	Spain
82b	Lisbon	38.8	-9.13	105	Portugal
308b	Madrid	40.5	-3.55	0	Spain
261b	Thessaloniki	40.5	22.97	4	Greece
305b	Rome University	41.9	12.52	0	Italy
282b	Kislovodsk	43.7	42.66	2070	Russia
65b	Toronto	43.8	-79.47	198	Canada
326b	Longfenshan	44.8	127.6	0	China
321b	Halifax	44.9	-63.5	0	Canada
319b	Montreal	45.5	-73.75	0	Canada
301b	Ispra	45.8	8.63	0	Italy
35b	Arosa	46.8	9.67	1860	Switzerland
100b	Budapest	47.4	19.18	140	Hungary
99b	Hohenpeissenberg	47.8	11.02	975	Germany
290b	Saturna	48.8	-123.1	0	Canada
331b	Poprad-Ganovce	49	20.32	0	Slovakia
320b	Winnipeg	49.9	-97.24	0	Canada
96b	Hradec Kralove	50.2	15.83	285	Czech Republic
338b	Regina	50.2	-104.7	0	Canada
53b	Uccle	50.8	4.35	100	Belgium
318b	Valentia	51.9	-10.25	0	Ireland
316b	Debilt	52	5.18	0	Netherlands
241b	Saskatoon	52.1	-105.3	550	Canada
174b	Lindenberg	52.2	14.12	98	Germany
50b	Potsdam	52.4	13.05	89	Germany
76b	Goose	53.3	-60.38	44	Canada
21b	Edmonton	53.6	-113.5	668	Canada
279b	Norkoping	58.6	16.12	0	Sweden
77b	Churchill	58.8	-94.07	35	Canada
123b	Yakutsk	62.1	129.75	98	Russia
284b	Vindeln	64.3	19.77	0	Sweden
267b	Sondrestrom	67	-50.98	150	Greenland
262b	Sodankyla	67.4	26.65	179	Finland
24b	Resolute	74.7	-94.98	64	Canada
315b	Eureka	79.9	-85.93	10	Canada

^aFirst column denotes WMO station number.

team (<http://toms.gsfc.nasa.gov/>). Overpass means in this paper that the distance between the center of the satellite pixel and the location of the ground-based stations is always smaller than 150 km. Time series of both satellite and ground-based TOC data used in this work extend from July 1996 to December 2004.

[18] The relative differences (RD) between the daily ground-based (GB) TOC measurements and the satellite TOC observations (TOMS) were calculated for spatiotemporal collocation by each station by the following expression:

$$RD_i = (100) \frac{TOMS_i - GB_i}{TOMS_i} \quad (1)$$

[19] Comparisons between satellite and ground-based TOC data were done separately using the Brewer and Dobson data sets. This procedure is more reliable for validation than the use of selected “good” stations from both ground-based networks [McPeters *et al.*, 2008] as the Brewer and Dobson systems may have counterbalancing errors. Thus, the dependence of these relative differences as

a function of the latitude, satellite solar zenith angle (SZA), satellite cloud fraction cover (LER), and satellite TOC observations are analyzed for each data set. In addition, from these relative differences, monthly mean values are pro-

Table 2. List of Dobson Stations Used in the Comparisons^a

WMO ID	Station Name	Lat	Lon	Elevation	Country
111d	Amundsen-Scott	-90	-24.8	2835	Antarctica
268d	Arrival Heights	-77.8	166.4	250	Antarctica
57d	Halley Bay	-75.5	-26.73	31	Antarctica
101d	Syowa	-69	39.58	21	Antarctica
339d	Ushuaia	-54.9	-68.31	7	Argentina
29d	Macquarie Island	-54.5	158.97	6	Australia
342d	Comodoro Rivadavia	-45.8	-67.5	43	Argentina
256d	Lauder	-45	169.68	3701	New Zealand
253d	Melbourne	-37.5	144.58	125	Australia
91d	Buenos Aires	-34.6	-58.48	25	Argentina
159d	Perth	-32	115.85	2	Australia
343d	Salto	-31.6	-57.95	31	Uruguay
340d	Springbok	-29.7	17.9	1	South
27d	Brisbane	-27.5	153.03	5	Australia
265d	Irene	-25.3	28.22	1524	South Africa
200d	Cachoeira-Paulista	-22.7	-45	573	Brazil
191d	Samoa	-14.3	-170.6	82	USA
84d	Darwin	-12.5	130.83	0	Australia
219d	Natal	-5.83	-35.2	32	Brazil
175d	Nairobi	-1.27	36.8	1710	Kenya
214d	Singapore	1.33	103.88	14	Singapore
216d	Bangkok	13.7	100.57	2	Thailand
31d	Mauna Loa	19.5	-155.6	3397	USA
2d	Tamanrasset	22.8	5.52	1395	Algeria
245d	Aswan	24	32.45	193	Egypt
209d	Kunming	25	102.68	1917	China
190d	Naha	26.2	127.67	29	Japan
152d	Cairo	30.1	31.28	35	Egypt
11d	Quetta	30.2	66.95	1799	Pakistan
7d	Kagoshima	31.6	130.6	283	Japan
14d	Tateno	36.1	140.13	31	Japan
106d	Nashville	36.3	-86.57	182	USA
341d	Hanford	36.3	-119.6	73	USA
213d	El Arenosillo	37.1	-6.73	41	Spain
252d	Seoul	37.6	126.95	84	Korea
107d	Wallops Island	37.9	-75.52	4	USA
293d	Athens	38	23.7	15	Greece
82d	Lisbon	38.8	-9.13	105	Portugal
208d	Shianghai	39.8	117	13	China
67d	Boulder	40	-105.3	1634	USA
12d	Sapporo	43.1	141.33	19	Japan
40d	Haute Province	43.9	5.75	580	France
201d	Sestola	44.2	10.77	1030	Italy
226d	Bucharest	44.5	26.13	92	Romania
19d	Bismarck	46.8	-100.8	511	USA
35d	Arosa	46.8	9.67	1860	Switzerland
20d	Caribou	46.9	-68.02	192	USA
100d	Budapest	47.4	19.18	140	Hungary
99d	Hohenpeissenberg	47.8	11.02	975	Germany
96d	Hradec Kralove	50.2	15.83	285	Czech Republic
36d	Camborne	50.2	-5.32	88	UK
53d	Uccle	50.8	4.35	100	Belgium
68d	Belsk	51.8	20.78	180	Poland
50d	Potsdam	52.4	13.05	89	Germany
116d	Moscow	55.8	37.57	187	Russia
165d	Oslo	59.9	10.72	50	Norway
43d	Lerwick	60.2	-1.15	90	UK
51d	Reykjavik	64.1	-21.9	60	Iceland
284d	Vindeln	64.3	19.77	0	Sweden
105d	Fairbanks	64.8	-147.9	138	USA
199d	Barrow	71.3	-156.6	11	USA
89d	Ny-Alesund	78.9	11.88	0	Norway

^aFirst column denotes WMO station number.

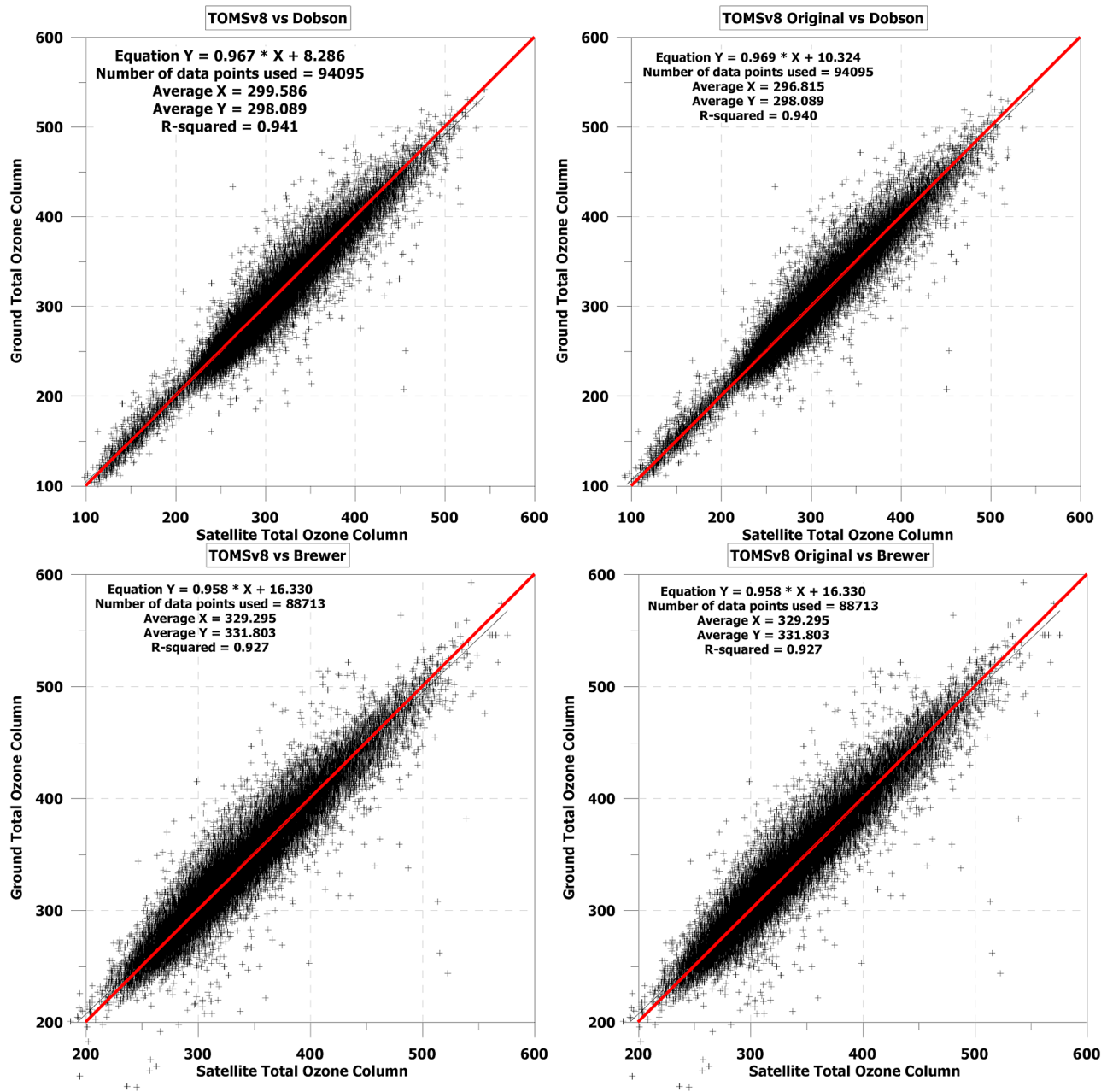


Figure 1. Scatterplot between satellite- and ground-based observations for the whole period 1996–2004, plotted separately for (top) Dobson and (bottom) Brewer instruments. In the left and right column, the corrected TOMS V8 and original TOMS V8 data are displayed, respectively.

duced to obtain time series of the satellite-ground-based differences. For this analysis of the time series, we averaged the individual station comparisons separately over the Northern and Southern hemispheres. On the other hand, for the analysis of the dependence on latitude, the relative differences from all ground-based stations within the selected latitudinal belt were binned together to calculate its average value. This global study of latitudinal dependence can only be analyzed from the Dobson spectrophotometers, since there are no quality-assured data from Brewer instruments in the Southern Hemisphere.

[20] From the relative differences derived from expression 1, the mean bias error (MBE) parameter was also calculated for each data set as

$$MBE = \frac{1}{N} \sum_{i=1}^N RD_i, \quad (2)$$

where N is the number of data pairs TOMS-Brewer (or TOMS-Dobson).

[21] In addition, a lineal regression analysis is performed between the TOC values recorded by ground-based spec-

Table 3. Statistical Parameters Obtained in the Regression Analyses Between TOMS V8-Corrected and Dobson Total Ozone Data for the Three Different Periods: 1996–2000 (data set 1), 2001–2004 (data set 2), and 1996–2004 (data set 3)^a

	<i>N</i>	Slope	<i>R</i> ²	RMSE (%)	MBE (%)
Data set 1	59,475 (59,475)	0.973 (0.970)	0.946 (0.946)	0.48 (0.59)	+0.229 ± 0.036 (−0.215 ± 0.036)
Data set 2	34,620 (34,620)	0.960 (0.967)	0.933 (0.932)	0.93 (1.22)	+0.793 ± 0.038 (−1.019 ± 0.040)
Data set 3	94,095 (94,095)	0.967 (0.969)	0.941 (0.939)	0.64 (0.79)	+0.437 ± 0.037 (−0.511 ± 0.038)

^aResults for the TOMS V8 original correlation are shown in parentheses. The parameters shown are the number of correlative data points (*N*), the slope of the regression, the coefficients of correlation (*R*²), the root-mean-square errors (RMSE), and the mean bias error (MBE).

trophotometers and the TOMS V8 instrument. Regression coefficients, coefficients of correlation (*R*²) and the root-mean-square errors (RMSEs) are evaluated in this analysis.

4. Results and Discussion

[22] To analyze the proportionality and similarity of the ground-based and satellite-based observations, several linear regression analyses were performed between the TOC values measured from the TOMS V8 instrument and the ground-based data from Brewer and Dobson spectrophotometers. These data are fitted for three different periods: 1996–2000 (data set 1), 2001–2004 (data set 2), and 1996–2004 (data set 3). The slopes and statistical parameters obtained for the different regression analyses are presented in Tables 3 and 4 for the TOMS-Dobson correlation and TOMS-Brewer correlation, respectively. The agreement between ground-based and TOMS V8 total ozone data is excellent for the three data sets (*R*² higher than 0.92). In addition, the scatterplots presented in Figure 1 for data set 3 reveal a high degree of proportionality with a notably small spread (RMSE smaller than 3%). It can be seen that TOMS V8-corrected data present a more reduced spread compared with respect to the TOMS V8 original data. Tables 3 and 4 also show the MBE parameters obtained for the three data sets. The MBE values for the TOMS V8-corrected data range between −0.5% and −1.0%, indicating a very slight underestimation of the ground-based TOC measurements. The TOMS V8 original data present a more negative MBE (∼−2% for data set 3), showing that these satellite data clearly underestimate the ground-based data. In addition, the statistical parameters shown in Tables 3 and 4 indicate that the agreement between the satellite and ground-based data is slightly better for Dobson than for Brewer spectrophotometer. This result is associated with the small differences between the measurements recorded by the two ground-based instruments that were noted in subsection 2.2.

[23] The variation of the relative differences between the two satellite TOC data sets and ground-based measurements as a function of latitude is shown in Figure 2. It can be

observed that the V8-corrected TOC data are larger in value than the V8 original TOC data for all latitudes. Over the global latitudinal coverage of the Dobson comparison, there is no significant meridional dependence of these differences discernible for the two TOMS algorithms, which vary within 2%. Large positive relative differences (∼4%) were found over the equator both for the Dobson as well as for the Brewer comparisons, which are most likely related to quality issues of a single ground-based station. In addition, the higher values of the relative differences over the tropics could possibly be related to the cloudiness interfering with the satellite retrieval. The EP-TOMS retrieval was using an IR-based cloud height climatology that, based on recent experience with OMI retrievals, are likely in error [Newchurch *et al.*, 2001]. This shows up in regions where the cloud height is actually lower than it was expected by the climatology. Over midlatitudes the behavior of the differences is slightly different between the two hemispheres. While the relative differences for the Southern Hemisphere shows significant changes between neighboring latitudinal belts, the values for the Northern Hemisphere present a smoother behavior, most likely due to better statistics for the Northern Hemisphere. Finally, comparison results from high-latitude stations show large spreads as the analysis is based on fewer observational points for these latitudinal belts.

[24] To analyze the long-term stability of the EP-TOMS V8 total ozone data, the time series of the monthly mean differences between satellite and ground-based data for the V8-corrected (left column) and the V8-original (right column) data sets are shown in Figure 3. Comparison results were separated for the Northern and Southern hemispheres. The time series of the two data sets show no significant drift until mid-2001. After that date, the satellite-ground-based differences for the original TOMS V8 data show an increasing bias for the two hemispheres, with a drop of satellite total ozone observations of around 3%. Although this bias is evident in both the Dobson and Brewer comparisons, it is clearly larger in the comparison against Brewer data. This satellite drift can be largely attributed to the degradation issues of the TOMS instrument explained in

Table 4. Statistical Parameters Obtained in the Regression Analyses Between TOMS V8 and Brewer Total Ozone Data for the Three Different Periods: 1996–2000 (data set 1), 2001–2004 (data set 2), and 1996–2004 (data set 3)^a

	<i>N</i>	Slope	<i>R</i> ²	RMSE (%)	MBE (%)
Data set 1	52,809 (52,809)	0.965 (0.957)	0.925 (0.925)	1.24 (1.71)	−1.081 ± 0.037 (−1.525 ± 0.038)
Data set 2	35,904 (35,904)	0.944 (0.958)	0.931 (0.924)	0.89 (2.49)	−0.516 ± 0.038 (−2.328 ± 0.041)
Data set 3	88,713 (88,713)	0.958 (0.958)	0.926 (0.924)	1.09 (2.02)	−0.852 ± 0.038 (−1.850 ± 0.039)

^aResults for the TOMS V8 original correlation are shown in parentheses. The parameters shown are the number of correlative data points (*N*), the slope of the regression, the coefficients of correlation (*R*²), the root-mean-square errors (RMSE), and the mean bias error (MBE).

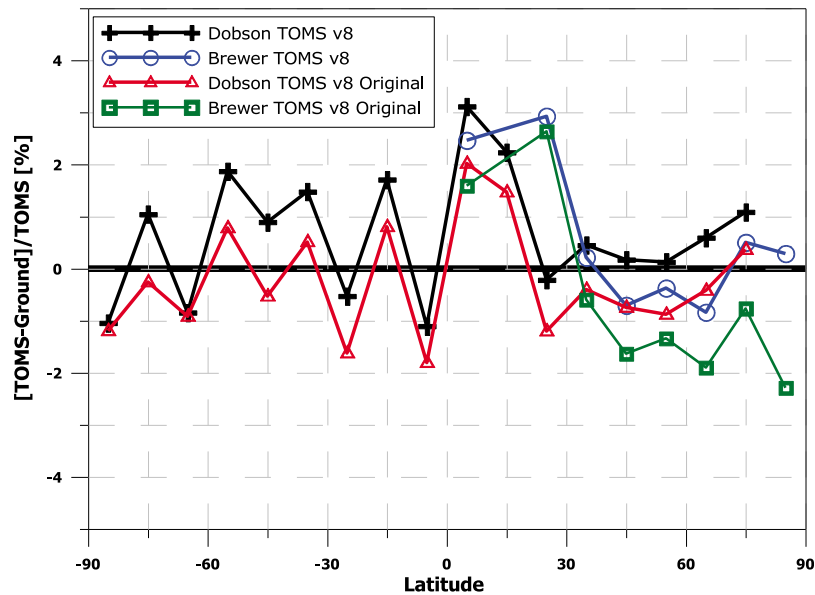


Figure 2. Mean relative differences between TOMS V8 measurements (both original and corrected) and ground-based total ozone data as a function of the ground pixel/station latitude grouped in 10° latitude bins.

section 2.2, and this feature of the TOMS V8 total ozone data was also observed by other authors [Bramstedt *et al.*, 2003; Balis *et al.*, 2007a]. After attempts to correct the basic calibration failed, an empirical correction derived from comparisons with NOAA 16 and 17 SBUV/2s was applied to correct for this drift. The TOMS V8-corrected data were released in 2007. Figure 3 shows that the time series of this corrected data set improves notably with respect to the original data set after the year 2000. We thus performed a comparative analysis between satellite and ground-based data for two separate periods, 1996–2000 and 2001–2004 to highlight the improvement of the new data set. Table 5 shows the mean relative differences between TOMS V8 (original and corrected) and ground-based (Brewer and Dobson) total ozone data and its standard deviation for these two periods. These mean relative differences were calculated from monthly averages of both satellite and ground-based data. It can be seen that the TOMS ground-based differences presents a significant improvement for the Brewer comparison, mainly in the period 2001–2004. Thus, the mean value of these differences change from -1.98% (original data set) to -0.16% (corrected data set). In contrast, the results show that there is no improvement for TOMS-Dobson comparison since the relative differences change from -0.94% (original data set) to $+0.94\%$ (corrected data set). Nevertheless, Table 5 shows that the standard deviations for the relative differences derived from the corrected

data set as for Dobson as for Brewer instruments are smaller than the standard deviations obtained by the original data.

[25] The time series in Figure 3 show that there is a clear seasonality for TOMS-Brewer comparisons with an amplitude of $\sim 1.5\%$ but that there is little seasonality for TOMS-Dobson comparisons in either hemisphere. The work of Balis *et al.* [2007a] indicated that TOMS V8 and Dobson total ozone data have similar dependence on the lower stratospheric temperature because the wavelengths used by the TOMS algorithm are closer to those for the Dobson spectrophotometer than for the Brewer instruments. As a consequence, the TOMS-Dobson errors associated with the stratospheric temperature variability possibly cancel out when calculating their differences. Thus, the different seasonality between Brewer and Dobson comparisons may be partially attributed to the different temperature dependence of the ozone absorption cross sections in the wavelength ranges used in the retrievals of the two spectrophotometers [Van Roozendaal *et al.*, 1998]. In addition, the seasonality in TOMS-Brewer comparison could be also caused by errors in the instrument extraterrestrial constant of Brewer spectrophotometers that are determined during the calibration of these types of instruments. However, these constants can change with time, making it necessary to introduce a correction based on regular standard lamp test results, but this is not always done at some stations. Finally, the seasonality in satellite-ground-based differences could be partially asso-

Table 5. Mean Relative Differences Between TOMS V8 and Ground-Based Total Ozone Data and Its Standard Deviation for Two Different Periods (1996–2000 and 2001–2004)

	Mean \pm Standard Deviation (1996–2000)		Mean \pm Standard Deviation (2001–2004)	
	Original	Corrected	Original	Corrected
Brewers	$-1.11\% \pm 0.74\%$	$-0.70\% \pm 0.68\%$	$-1.98\% \pm 1.37\%$	$-0.16\% \pm 0.89\%$
Dobsons	$-0.09\% \pm 0.52\%$	$0.37\% \pm 0.49\%$	$-0.94\% \pm 1.07\%$	$0.94\% \pm 0.68\%$

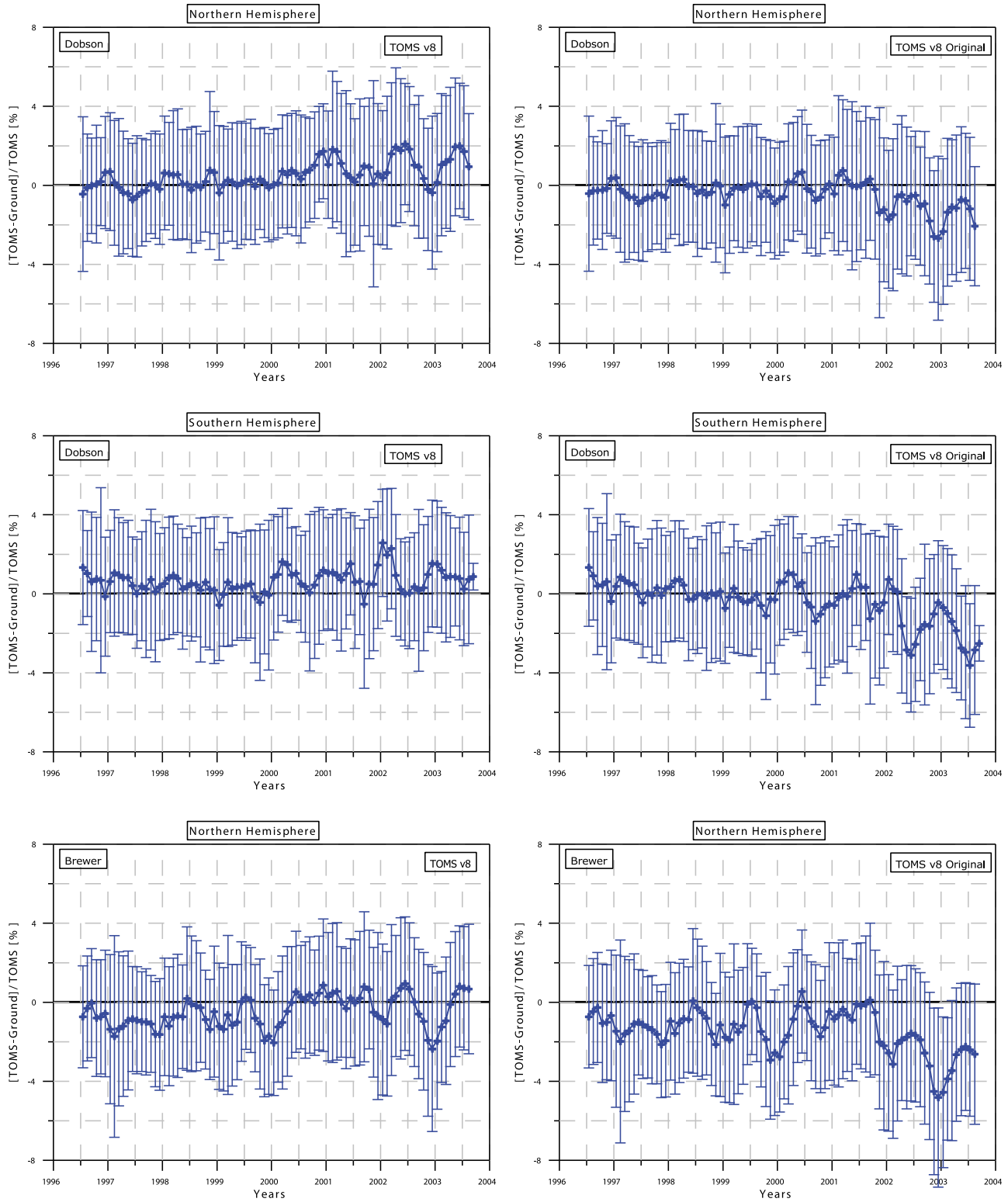


Figure 3. Time series of the monthly mean differences by hemisphere for the TOMS (left) V8-corrected and the (right) V8-original data sets. (top) Northern Hemisphere for the Dobson comparisons, (middle) Southern Hemisphere for the Dobson comparisons, and (bottom) Northern Hemisphere for the Brewer comparisons. A marked improvement in the new data set after year 2001 for all of the above is notable.

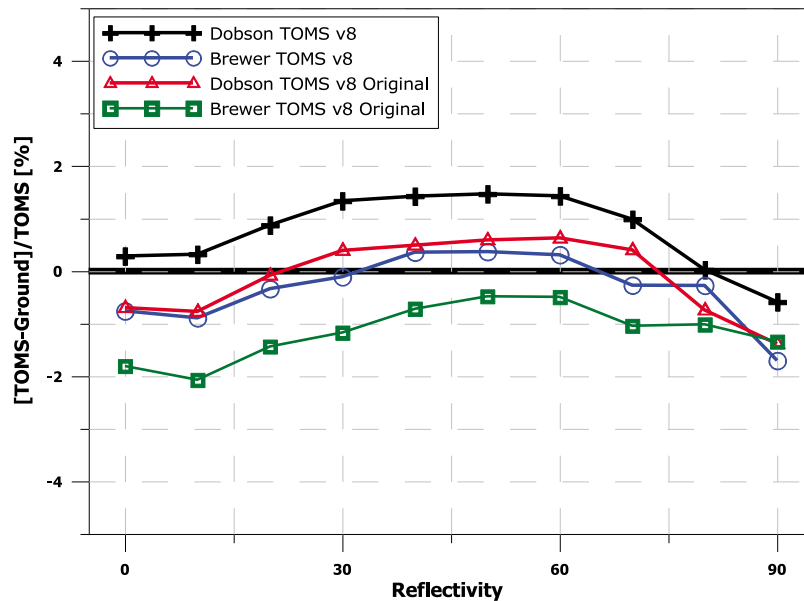


Figure 4. Investigating the possible effect of the reflectivity on the differences between the TOMS V8 time series and the ground-based measurements.

ciated with instrument effects in the TOMS satellite platform. The two plots of Figure 3 (top) show a strong seasonality in the time series after year 2001. This effect is mainly due to the influence of several Dobson stations located between 0°N and 30°N. This issue is currently under investigation.

[26] Under cloudy conditions the satellite is only sensitive to the ozone column above the cloud top and the TOMS ozone retrieval must estimate the amount of ozone below the cloud top [McPeters *et al.*, 1998]. The current TOMS algorithm obtains this ghost column amount from the TOMS V8 ozone profile climatology and a satellite-based cloud pressure climatology derived from IR observations, generating significant uncertainties in the retrieval of the total ozone column [Lamsal *et al.*, 2007]. Thus, it is interesting to study the influence of clouds on the satellite measurement and satellite-ground-based comparison exercises. Figure 4 shows the evolution of the relative differences between satellite and ground-based total ozone data as a function of the LER, the Lambert Equivalent Reflectivity. The LER variable is a function of the geometric cloud fraction and the albedo of the cloud and surface and represents the fraction of measured Earth radiance originating from the cloudy part of the ground pixel. A high value of the LER variable indicates that the satellite observation is performed with a significant amount of cloudiness in the instrument's field of view. In contrast, the Dobson and Brewer ground-based instruments derive the corresponding measurements from direct sun measurements under cloud-free conditions that occur during sufficiently long periods in between clouds. From Figure 4 the remarkable stability of the TOMS algorithm under cloudy conditions can be inferred even when the satellite LER values become very high, revealing that neither Brewer nor Dobson comparisons present a significant dependence on the effective cloud fraction. Thus, the cloud-dependent error of TOMS total ozone observations (corrected and original)

presents only a weak positive dependence on LER values as for Dobson as for Brewer data up to LER values around 60%. For higher LER values, the relative differences present a smooth negative dependence, suggesting that the TOMS ozone profile and cloud pressure climatologies are relatively accurate, which is to be expected when a sufficient amount of averaging towards the climatological values has taken place. One should also appreciate the substantial statistical spread indicating situations where large deviations from the climatology occur. Antón *et al.* [2009a] compared the a priori TOMS V8 partial columns with true ozone profiles from ozone sonde measurements in Madrid (Spain), showing that the lowest two layers present relative differences of about 15% between the measurements and the satellite climatology. This result could partially explain the behavior of the deviation of the relative differences (2σ spread), which increases as a function of LER (not shown), in agreement with previous results of the OMI total ozone data retrieved from TOMS V8 algorithm (OMI-TOMS ozone data) [Balis *et al.*, 2007b; Antón *et al.*, 2009b]. This increased scatter is also partially associated with the choice of cloud pressure under cloudy conditions. Figure 4 also shows that there is no significant change in cloud fraction dependence between TOMS V8 original and corrected total ozone observations, indicating that the difference between the two satellite data sets is not related to the LER variable.

[27] The seasonal dependence shown in Figure 3 for the TOMS-Brewer relative differences suggests that this comparison depends on the ground pixel solar zenith angle (SZA). In addition, the null seasonality for the TOMS-Dobson relative differences seen in the same figure indicates that the TOMS-Dobson comparisons have no significant dependence on SZA. This analysis may be highly affected by the compensation of cases with opposite sky conditions, i. e., cloud-free and fully cloudy [Antón *et al.*, 2008b, 2009a, 2009b]. We have therefore calculated the relative differences as function of the SZA for cloud-free cases ($R < 10\%$), cloudy

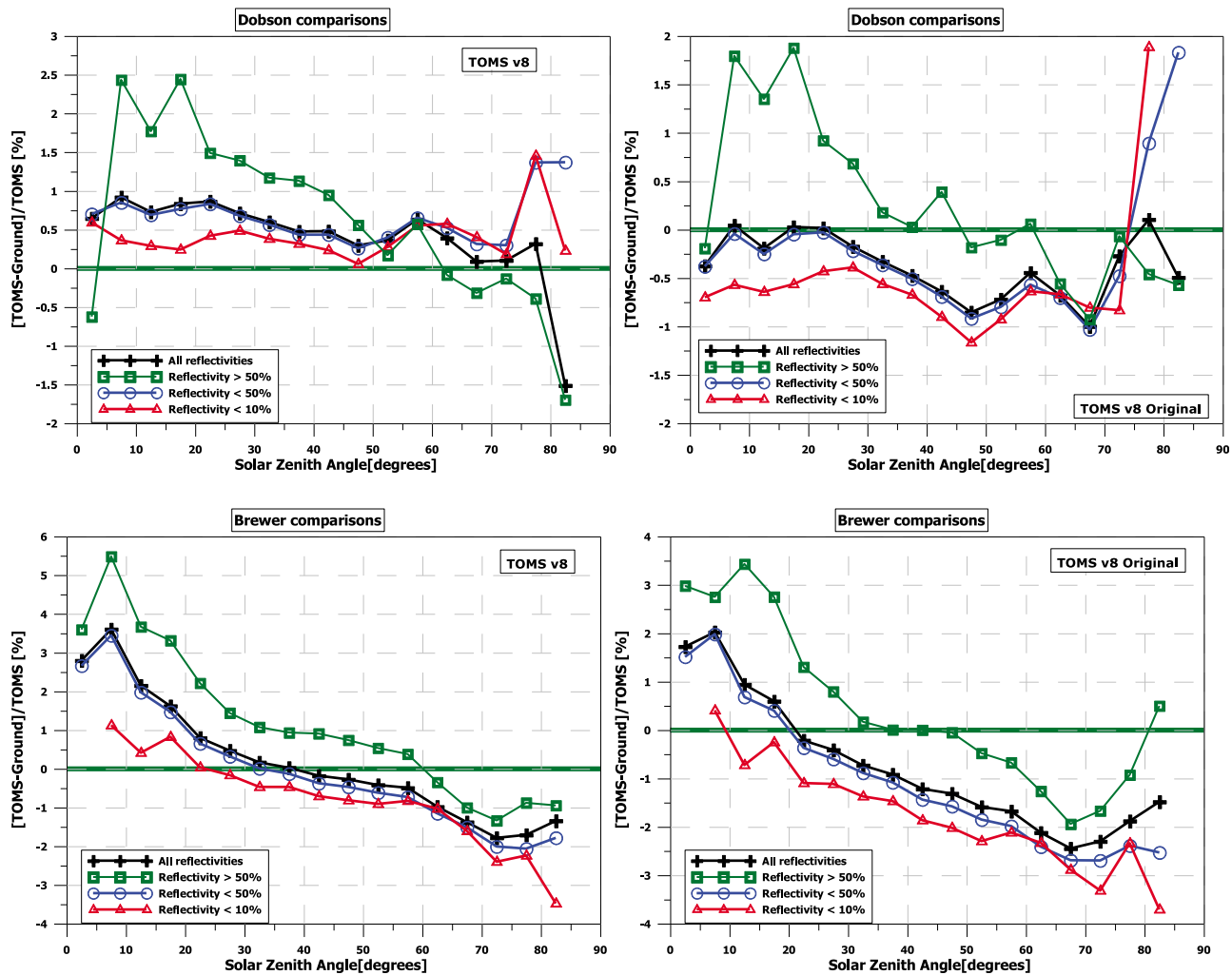


Figure 5. Investigating the possible effect of the cloudy scenes on (left) the TMS V8-corrected time series and (right) the TMSv8 original time series. Four data sets were considered: one with all measurements included irrespective of the associated reflectivity, two where the reflectivity was constrained to be higher and lower than 50%, and one for lower than 10% (cloud-free scenes). The dependency on the solar zenith angle on the cloud conditions is examined here. The Dobson comparisons are shown in the upper graph and the Brewer comparisons in the lower graph.

cases ($R > 50\%$), and all conditions. We note that for the corrected TMS data set, 43% of the cases are for cloud-free conditions and 27% are for cloudy conditions. Figure 5 shows the mean relative differences between TMS V8 measurements (both original and corrected) plotted separately for Brewer (bottom frames) and Dobson (top frames) instruments, as a function of the satellite ground pixel SZA for the three data sets using 5° bins of SZA. It can be seen that the TMS-Brewer relative differences for V8-corrected as for the V8 original data experience a notable decrease with increasing SZA, explaining and confirming the seasonal dependence observed in Figure 3. The evolution of the curve corresponding to all conditions shows that the TMS-Brewer differences for V8-corrected (original) vary from almost +3% (+2%) for small SZA to -1% (-2%) for large SZA. The result agrees with the work of *Balis et al.* [2007a] that showed that EP-TOMS overestimates Brewer measurements by 2% for small SZA and underestimates by -2%

for large SZA. *McPeters et al.* [2008] also showed that the EP-TOMS SZA dependent difference with respect to ground-based measurements from 74 Northern Hemisphere ground stations increases to almost -3% by 70° solar zenith angle. The relative differences corresponding to the two opposite data sets (cloud-free in red and fully cloudy conditions in green) shows a dependence on SZA similar to the curve corresponding to all cases. Nevertheless, it can be seen that the amplitude of the differences is clearly reduced when cloud-free cases are selected.

[28] Figure 5 shows that the differences between the Dobson measurements and the EP-TOMS observations (both corrected and original data) present a remarkably constant behavior with SZA for all cases, in agreement with and confirming the null-seasonal behavior shown in Figure 3. However, from Figure 5, one can infer that when $LER > 50\%$, there is a significant influence of cloudiness in the dependence on SZA of the relative differences between

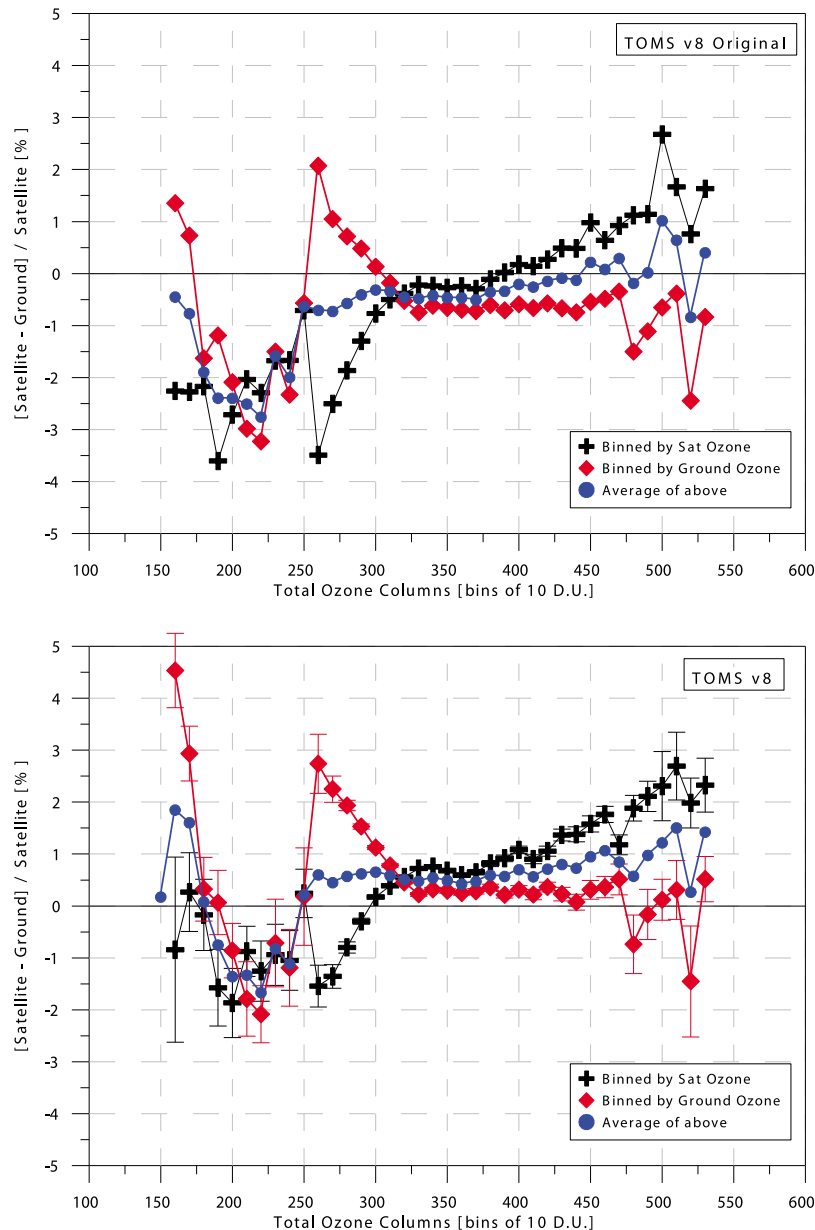


Figure 6. The relative difference of TOMS V8 and ground-based observations as a function of the total ozone column: (bottom) TOMS V8-corrected data set and (top) TOMS V8-original data set.

TOMS-Dobson total ozone data (from +2% for small SZA to -1% for high SZA). This dependence is quite similar to the behavior shown by the TOMS-Brewer comparison for similar sky conditions. Thus, when there is a high amount of cloudiness in the EP-TOMS instrument's field of view, the relative differences between satellite and ground-based total ozone data present a strong dependence on SZA. Under these conditions, the ground-based instruments do not record direct Sun measurement while the satellite makes the corresponding observation on a partially cloudy pixel. The ground-based measurements are recorded before or after these conditions, only during cloud-free cases. Antón *et al.* [2009b] showed a small dependence on SZA of the relative differences between the Brewer total ozone measurements and the OMI-TOMS ozone data for cloud-free and

cloudy conditions. Balis *et al.* [2007b] also showed no significant dependence on SZA for the comparison between ground-based total ozone data and the OMI-TOMS ozone observations for all sky conditions. Therefore, the SZA dependence observed in the EP-TOMS ozone data almost certainly is related to an instrumental effect rather than to the retrieval algorithm.

[29] Finally, the variation of the relative difference between the TOMS V8 and ground-based total ozone measurements as a function of the ground-based data is shown in Figure 6 (bottom, corrected data set; top, original data set). Because of statistical sampling issues, the blue line (the average of the red and black curves) should be seen as the proper curve showing the total ozone dependent differences. Either ground-based or satellite-based binning runs

into numerical problems. The divergence of values at ~ 250 DU occurs because the satellite and ground-based instruments are not sampling the same air mass in a region of rapid ozone change (the presence of the polar vortex). The differences at very low total column ozone (< 240 DU) are not fully understood at the moment but similar analysis of ozone values from the Ozone Monitoring Instrument (OMI) on EOS-AURA do not show such a dependence so it should be assumed that this is an instrument response problem specific to Earth Probe TOMS. Under very low ozone conditions, e.g., the ozone hole, Earth radiances contain much more UV light than under normal conditions. This could lead to EP-TOMS receiving intensities where the data may not have been corrected properly because the number of measurements used to correct the radiances under these conditions were relatively small and the detector characterization may not have been as robust [Labow *et al.*, 2006]. On the other hand, high TOC conditions may push the signal-to-noise limits of the EP-TOMS instrument. In addition, under very high ozone conditions, both Dobson and Brewer Mark 1 systems are known to fail [Redondas and Cede, 2005]. The UV signals received on the ground become so small that other signals start to dominate the recorded data, for example, detector dark current and stray light from longer wavelengths that still hold an appreciable intensity. Figure 6 also shows that the variation of the relative differences for the TOMS V8-corrected and original observations is very similar, indicating that the corrected version is not an improvement with respect to the dependence on the total ozone column.

5. Conclusions

[30] The main conclusion drawn from this global-scale validation exercise is that the upgrade to EP-TOMS V8-corrected total ozone data represents a marked improvement with respect to the significant negative bias shown by the original EP-TOMS V8 satellite observations after year 2000 due to instrumental degradation issues. EP-TOMS reports systematically lower total ozone values about 1% of average from this year onward (Tables 3–5), reaching values higher than 3% in 2003 (Figure 3). This work has also shown that the two total ozone data sets (original and corrected) have a very similar behavior with respect to latitude (zonal means), solar elevation (seasonality), and ozone column dependence. In this sense, neither shows any significant dependence on latitude. In reference to seasonality, TOMS satellite data overestimate the Brewer measurements for small SZA and underestimate for large SZA. In contrast, there is almost no seasonality for TOMS–Dobson comparisons when all cases were used. This study shows that the cloudiness of the satellite ground pixel has a strong effect on the dependence on SZA of the relative differences of satellite to ground-based. Finally, the dependence of the satellite–ground-based relative differences on total ozone shows good agreement for column values above 250 DU.

[31] Overall we conclude that the empirical correction of the EP-TOMS data record provides a reprocessed set of improved quality. We emphasize the remarkable success of the “internal calibration and empirical correction” effort performed by the NASA TOMS team to salvage EP-TOMS data. Nevertheless, the empirically corrected EP-TOMS

total ozone data should not be used for global ozone trending due to remaining issues in the data set and because it is no longer an independent data set but tied to the NOAA 16 and 17 SBUV data trends. However, the corrected V8 EP TOMS data can be used to study the day-to-day and seasonal variability of the total ozone column. In addition, these satellite ozone data can be used as input in radiative transfer models to the estimation of the ultraviolet radiation.

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References

- Antón, M., A. Serrano, M. L. Cancillo, and J. A. García (2008a), Total ozone and solar erythemal irradiance in southwestern Spain: Day-to-day variability and extreme episodes, *Geophys. Res. Lett.*, *35*, L20804, doi:10.1029/2008GL035290.
- Antón, M., D. Loyola, B. Navascués, and P. Valk (2008b), Comparison of GOME total ozone data with ground data from the Spanish Brewer spectroradiometers, *Ann. Geophys.*, *26*, 401–412.
- Antón, M., D. Loyola, M. López, J. M. Vilaplana, M. Bañón, W. Zimmer, and A. Serrano (2009a), Comparison of GOME-2/MetOp total ozone data with Brewer spectroradiometer data over the Iberian Peninsula, *Ann. Geophys.*, *27*, 1377–1386.
- Antón, M., M. López, J. M. Vilaplana, M. Kroon, R. McPeters, M. Bañón, and A. Serrano (2009b), Validation of OMI-TOMS and OMI-DOAS total ozone column using five Brewer spectroradiometers at the Iberian Peninsula, *J. Geophys. Res.*, *114*, D14307, doi:10.1029/2009JD012003.
- Antón, M., J. M. Vilaplana, M. Kroon, A. Serrano, M. Parias, M. L. Cancillo, and B. A. de la Morena (2010), The empirically corrected EP-TOMS total ozone data against Brewer measurements at El Arenosillo (Southwestern Spain), *IEEE Trans. Geosci. Remote Sens.*, *48*(7), 3039–3045, doi:10.1109/TGRS.2010.2043257.
- Balis, D., J. C. Lambert, M. Van Roozendaal, R. Spurr, D. Loyola, Y. Livshitz, P. Valks, V. Amiridis, P. Gerard, J. Granville, and C. Zehner (2007a), Ten years of GOME/ERS2 total ozone data: the new GOME Data Processor (GDP) Version 4: II. Ground-based validation and comparisons with TOMS V7/V8, *J. Geophys. Res.*, *112*, D07307, doi:10.1029/2005JD006376.
- Balis, D., M. Kroon, M. E. Koukoulis, E. J. Brinksma, G. Labow, J. P. Veefkind, and R. D. McPeters (2007b), Validation of Ozone Monitoring Instrument total ozone column measurements using Brewer and Dobson spectrophotometer ground-based observations, *J. Geophys. Res.*, *112*, D24S46, doi:10.1029/2007JD008796.
- Basher, R. E. (1982), Review of the Dobson spectrophotometer and its accuracy, *Global Ozone Res. Monit. Proj., Rep. 13*, World Meteorol. Organ., Geneva, Switzerland, Dec. (Available at <http://www.esrl.noaa.gov/gmd/ozwv/dobson/papers/report13/report13.html>).
- Bhartia, P. K., and C. Wellemeyer (2002), TOMS-V8 total O₃ algorithm, in *OMI Algorithm Theoretical Basis Document, vol. II, OMI Ozone Products*, edited by P. K. Bhartia, pp. 15–31, NASA Goddard Space Flight Cent., Greenbelt, Md. (Available at http://eosps.gsf.nasa.gov/eos_homepage/for_scientists/atbd/index.php).
- Bojkov, R. D., C. Mateer, and A. Hanson (1988), Comparison of ground-based and total ozone mapping spectrometer measurements used in assessing the performance of the global ozone observing system, *J. Geophys. Res.*, *93*, 9525–9533, doi:10.1029/JD093iD08p09525.
- Bojkov, R. D., and V. E. Fioletov (1995), Estimating the global ozone characteristics during the last 30 years, *J. Geophys. Res.*, *100*, 16,537–16,551, doi:10.1029/95JD00692.
- Bramstedt, K., J. Gleason, D. Loyola, W. Thomas, A. Bracher, M. Weber, and J. P. Burrows (2003), Comparison of total ozone from the satellite instruments GOME and TOMS with measurements from the Dobson network 1996–2000, *Atmos. Chem. Phys.*, *3*(5), 1409–1419.
- De Backer, H., and D. De Muer (1991), Intercomparison of total ozone data measured with Dobson and Brewer Ozone Spectrophotometers at Uccle (Belgium) from January 1984 to March 1991, including zenith sky observations, *J. Geophys. Res.*, *96*, 20,711–20,719, doi:10.1029/91JD02159.
- Dobson, G. M. B. (1957), Observers’ handbook for the ozone spectrophotometer, in *Annals of the International Geophysical Year, V, Part 1*, pp. 46–89, Pergamon Press, New York.

- Callis, L. B., M. Natarajan, J. D. Lambeth, and R. E. Boughner (1997), On the origin of midlatitude ozone changes: Data analysis and simulations for 1979–1993, *J. Geophys. Res.*, *102*, 1215–1228, doi:10.1029/96JD03058.
- Fioletov, V. E., J. B. Kerr, E. W. Hare, G. J. Labow, and R. D. McPeters (1999), An assessment of the world ground-based total ozone network performance from the comparison with satellite, *J. Geophys. Res.*, *104*, 1737–1747, doi:10.1029/1998JD100046.
- Fioletov, V. E., J. B. Kerr, D. I. Wardle, N. I. Krotkov, and J. R. Herman (2002), Comparison of Brewer ultraviolet irradiance measurements with total ozone mapping spectrometer satellite retrievals, *Opt. Eng.*, *41*(12), 3051–3061.
- Fioletov, V. E., J. B. Kerr, C. T. McElroy, D. I. Wardle, V. Savastiouk, and T. S. Grajnar (2005), The Brewer reference triad, *Geophys. Res. Lett.*, *32*, L20805, doi:10.1029/2005GL024244.
- Fleig, A. J., P. K. Bhartia, C. G. Wellemeyer, and D. S. Silberstein (1986), An assessment of the long-term drift in SBUV total ozone data, based on comparison with the Dobson network, *Geophys. Res. Lett.*, *13*, 1359–1362, doi:10.1029/GL013i012p01359.
- Haffner, D. P., S. L. Taylor, C. G. Wellemeyer, G. Jaross, R. D. McPeters, and P. K. Bhartia (2004), EarthProbe TOMS optical degradation and calibration corrections, presented at Quadrennial Ozone Symposium, Eur. Comm., Kos, Greece.
- Harris, N. R. P., et al. (1997), Trends in stratospheric and free tropospheric ozone, *J. Geophys. Res.*, *102*, 1571–1590, doi:10.1029/96JD02440.
- Herman, J. R., R. D. McPeters, and D. Larko (1993), Ozone depletion at Northern and Southern latitudes derived from January 1979 to December 1991 Total Ozone Mapping Spectrometer Data, *J. Geophys. Res.*, *98*, 12,783–12,793, doi:10.1029/93JD00601.
- Herman, J. R., and D. Larko (1994), Low ozone amounts during 1992–1993 from Nimbus 7 and Meteor 3 total ozone mapping spectrometers, *J. Geophys. Res.*, *99*, 3483–3496, doi:10.1029/93JD02594.
- Hudson, R. D., M. F. Andrade, M. B. Follette, and A. D. Frolov (2006), The total ozone field separated into meteorological regimes. Part II: Northern Hemisphere midlatitude total ozone trends, *Atmos. Chem. Phys.*, *6*, 5183–5191.
- Kerr, J. B., C. McElroy, and W. F. J. Evans (1984), The automated Brewer spectrophotometer, in *Proceedings of the Quadrennial Ozone Symposium*, edited by C. S. Zerefos and A. Ghazi, pp. 396–401, Am. Meteorol. Soc., Boston, Mass.
- Kerr, J. B., I. A. Asbridge, and W. F. J. Evans (1988), Intercomparison of total ozone measured by the Dobson spectrophotometers at Toronto, *J. Geophys. Res.*, *93*, 11,129–11,140, doi:10.1029/JD093iD09p11129.
- Kerr, J. B. (2002), 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.
- Komhyr, W. D. (1980), *Operations Handbook—Ozone Observations with Dobson Spectrophotometer*, WMO Global Ozone Research and Monitoring Project, No. 6., Geneva.
- Komhyr, W. D., R. D. Grass, and R. K. Leonhard (1989), Dobson spectrophotometer 83: A standard for total ozone measurements, 1962–1987, *J. Geophys. Res.*, *94*, 9847–9861, doi:10.1029/JD094iD07p09847.
- Komhyr, W. D., C. L. Mateer, and R. D. Hudson (1993), Effective Bass-Paur 1985 ozone absorption coefficients for use with Dobson ozone spectrophotometers, *J. Geophys. Res.*, *98*, 20,451–20,465, doi:10.1029/93JD00602.
- Kyro, E. (1993), Intercomparison of total ozone data from Nimbus 7 TOMS, the Brewer UV spectrophotometer and SAOZ UV-visible spectrophotometer at high latitudes observatory, Sodankyla, *Geophys. Res. Lett.*, *20*, 571–574, doi:10.1029/93GL00806.
- Labow, G. J., R. D. McPeters, and P. K. Bhartia (2004), A comparison of TOMS & SBUV Version 8 total column ozone data with data from ground stations, paper presented at Quadrennial Ozone Symposium, Eur. Comm., Kos, Greece.
- Labow, G. J., R. D. McPeters, and S. Taylor (2006), Recalibrated Earth-Probe TOMS total column ozone data compared to an ensemble of ground stations and OMI, *Eos Trans. AGU*, *87*(52), Fall Meet. Suppl., Abstract A31B-0905.
- Lamsal, L. N., M. Weber, G. Labow, and J. P. Burrows (2007), Influence of ozone and temperature climatology on the accuracy of satellite total ozone retrieval, *J. Geophys. Res.*, *112*, D02302, doi:10.1029/2005JD006865.
- Levelt, P. F., E. Hilsenrath, G. W. Leppelmeier, G. H. J. Van den Oord, P. K. Bhartia, J. Tamminen, J. F. De Haan, and J. P. Veefkind (2006), The Ozone Monitoring Instrument, *IEEE Trans. Geosci. Remote Sens.*, *44*, 1093–1101.
- Malanca, F. E., P. O. Canziani, and G. A. Argüello (2005), Trends evolution of ozone between 1980 and 2000 at midlatitudes over the Southern Hemisphere: Decadal differences in trends, *J. Geophys. Res.*, *110*, D05102, doi:10.1029/2004JD004977.
- Masserot, D., J. Lenoble, C. Brogniez, M. Houet, N. Krotkov, and R. McPeters (2002), Retrieval of ozone column from global irradiance measurements and comparison with TOMS data. A year of data in the Alps, *Geophys. Res. Lett.*, *29*(9), 1309, doi:10.1029/2002GL014823.
- McPeters, R. D., S. M. Hollandsworth, L. E. Flynn, J. R. Herman, and C. J. Seftor (1996a), Long-term ozone trends derived from the 16 year combined Nimbus 7/Meteor 3 TOMS version 7 record, *Geophys. Res. Lett.*, *23*, 3699–3702, doi:10.1029/96GL03540.
- McPeters, R. D., P. K. Bhartia, and A. J. Krueger (1996b), *Nimbus-7 Total Ozone Mapping Spectrometer (TOMS) data products user's guide*, NASA Reference Publication 1384.
- McPeters, R. D., and G. J. Labow (1996c), An assessment of the accuracy of 14.5 years of Nimbus 7 TOMS Version 7 ozone data by comparison with the Dobson Network, *Geophys. Res. Lett.*, *23*, 3695–3698, doi:10.1029/96GL03539.
- McPeters, R. D., et al. (1998), *Earth Probe Total Ozone Mapping Spectrometer (TOMS) Data Products User's Guide*, NASA Reference Publication, NASA, Greenbelt, Md.
- McPeters, R., S. Taylor, and G. Jaross (2007), Empirically corrected TOMS Earth Probe data set, personal communication. (Available at http://toms.gsfc.nasa.gov/news/Corrected_EP_TOMS_README.pdf).
- McPeters, R., M. Kroon, G. Labow, E. Brinksma, D. Balis, I. Petropavlovskikh, J. P. Veefkind, P. K. Bhartia, and P. F. Levelt (2008), Validation of the Aura Ozone Monitoring Instrument total column ozone product, *J. Geophys. Res.*, *113*, D15S14, doi:10.1029/2007JD008802.
- Newchurch, M. J., X. Liu, J. H. Kim, and P. K. Bhartia (2001), On the accuracy of Total Ozone Mapping Spectrometer retrievals over tropical cloudy regions, *J. Geophys. Res.*, *106*, 32,315–32,326, doi:10.1029/2000JD000151.
- Newchurch, M., E.-S. Yang, D. M. Cunnold, G. C. Reinsel, J. M. Zawodny, and J. M. Russell III (2003), Evidence for slowdown in stratospheric ozone loss: First stage of ozone recovery, *J. Geophys. Res.*, *108*(D16), 4507, doi:10.1029/2003JD003471.
- Newman, P. A., et al. (2009), What would have happened to the ozone layer if chlorofluorocarbons (CFCs) had not been regulated?, *Atmos. Chem. Phys.*, *9*, 2113–2128.
- Redondas, A., and A. Cede (2005), Brewer algorithm analysis sensitivity, paper presented at the SAUNA Workshop, Puerto de la Cruz, Spain.
- Staehelin, J. N., R. P. Harris, C. Appenzeller, and J. Eberhard (2001), Ozone trends: A review, *Rev. Geophys.*, *39*, 231–290.
- Staehelin, J., J. Kerr, R. Evans, and K. Vanicek (2003), Comparison of total ozone measurements of Dobson and Brewer spectrophotometers and recommended transfer functions, GAW/WMO report No. 149, TD: 1147.
- Steinbrecht, W., B. Hassler, H. Claude, P. Winkler, and R. S. Stolarski (2003), Global distribution of total ozone and lower stratospheric temperature variations, *Atmos. Chem. Phys.*, *3*(5), 1421–1438.
- Stolarski, R., R. Bojkov, L. Bishop, C. Zerefos, J. Staehelin, and J. Zawodny (1992), Measured trends in stratospheric ozone, *Science*, *256*, 343–349.
- Van Roozendaal, M., et al. (1998), Validation of ground-based UV-visible measurements of total ozone by comparison with Dobson and Brewer spectrophotometers, *J. Atmos. Chem.*, *29*, 55–83.
- Vanicek, K. (2006), Differences between ground Dobson, Brewer and satellite TOMS-8, GOME-WFDOAS total ozone observations at Hradec Kralove, Czech, *Atmos. Chem. Phys.*, *6*, 5163–5171.
- Wellemeyer, C. G., P. K. Bhartia, S. L. Taylor, W. Qin, and C. Ahn (2004), Version 8 Total Ozone Mapping Spectrometer (TOMS) Algorithm, paper presented at Quadrennial Ozone Symposium, Eur. Comm., Kos, Greece.
- World Meteorological Organization (WMO) (1996), *Guide to meteorological instruments and methods of observation*, 6th ed., WMO Publication #8, Geneva, Switzerland.
- World Meteorological Organization (WMO) (2006), *Scientific assessment of ozone depletion: Global ozone research and monitoring project, Tech. Rep. 50*, Geneva, Switzerland.

M. Antón, Departamento de Física Aplicada, Universidad de Granada, Granada, Spain. (mananton@unex.es)

D. Balis and M. E. Koukoulis, Laboratory of Atmospheric Physics, Physics Department, Aristotle University of Thessaloniki, Thessaloniki, Greece.

M. Kroon, Royal Netherlands Meteorological Institute, De Bilt, Netherlands.

G. J. Labow and R. D. McPeters, NASA Goddard Space Flight Center, Greenbelt, MD, USA.

A. Serrano, Departamento de Física, Universidad de Extremadura, Badajoz, Spain.