Ozone column retrieval from solar UV measurements at ground level: Effects of clouds and results from six European sites

Colette Brogniez,[1] Mickaël Houët,[1] Anna Maria Siani,[2] Philipp Weihs,[3] Marc Allaart,[4] Jacqueline Lenoble,[1,5] Thierry Cabot,[5] Alain de la Casinière,[5] and Esko Kyrö[6]

Received 18 March 2005; revised 25 July 2005; accepted 26 September 2005; published 17 December 2005.

[1] A differential absorption method, developed by the Laboratoire d'Optique Atmosphérique (LOA), is applied to retrieve the total ozone column from UV global irradiance spectra under clear and cloudy sky conditions. Contrarily to clear sky, cloudy sky generates a high uncertainty in the retrieved ozone column. This study shows that under cloudy conditions the daily ozone mean is a rather good estimation of the true value. The standard deviation allows us to estimate the relative uncertainty of this mean value, i.e., about 7%. Results for all conditions from 3 years at Villeneuve d'Ascq are presented, as well as a comparison with TOMS (Total Ozone Mapping Spectrometer) data. The results are very similar to those obtained for clear days: In 75% of cases both values agree to within 5%; however, some cases present larger relative differences. Over the 3 years considered, there is a bias less than 3% (LOA > TOMS). This method is applied to five other European sites involved in the EDUCE (European Database for UV Climatology and Evaluation) project. Three of them are Brewer stations. The results of the comparison between the LOA-retrieved ozone and TOMS data show that a relative difference smaller than 5% is obtained in 63–80% of the cases, depending on site and year. Biases smaller than 3% are observed (LOA > TOMS). The comparison between the LOA-retrieved ozone and total ozone data from direct sun and zenith sky observations of the Brewer instruments shows better agreement. For more than about 80% of cases, except at one site, the relative difference is smaller than 5%, and the biases are smaller than 1%. The LOA method allows us to obtain a complementary data set and hence to provide time series of reliable measurements of total ozone column under all sky conditions.

Citation: Brogniez, C., M. Houët, A. M. Siani, P. Weihs, M. Allaart, J. Lenoble, T. Cabot, A. de la Casinière, and E. Kyrö (2005), Ozone column retrieval from solar UV measurements at ground level: Effects of clouds and results from six European sites, *J. Geophys. Res.*, *110*, D24202, doi:10.1029/2005JD005992.

1. Introduction

[2] Stratospheric ozone plays a key role in the attenuation of UVB radiation (280–320 nm) and its presence is necessary to allow the existence of life at the Earth surface. The discovery of its decrease above Antarctic continent in the 1980s has motivated the scientific community to perform long-term measurements of the UV radiation in order to investigate the effects of the ozone depletion. In recent years the interest of the scientific community and policy makers regarding the impact of human activities on climate and biosphere has been increasing. Both the rise of global mean surface temperature and the ozone negative trend emerge as possible indicators of such impact [*World Meteorological Organization* (*WMO*), 1994, 1998, 2002; *Solomon*, 1999; *Staehelin et al.*, 2001].

[3] Time series analysis offers a consolidated methodology mainly for assessing the existence of trends and/or changes in geophysical parameters. Concerning atmospheric total ozone, the availability of long time series from ground-based stations, mainly from Dobson and Brewer instruments and from satellite measurements, allowed us to assess ozone variability also in terms of its impact on solar ultraviolet radiation [*WMO*, 1994, 1998, 2002]. As another alternative to the Dobson and Brewer total ozone measurements used worldwide, the ground-based total ozone retrievals based on UV-MultiFilter Rotating Shadowband Radiometer instruments (UV-MFRSR) can be used to monitor the ozone variations over large-scale areas [*Slusser et al.*, 1999; *Gao et al.*, 2001]. Dobson and Brewer instruments measure total ozone with an uncertainty of 1% for air mass values less than 3, in agreement within 1% with TOMS (Total

[1] Laboratoire d'Optique Atmosphérique, CNRS, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France.
[2] Physics Department, University of Rome "La Sapienza," Rome, Italy.
[3] Institut fuer Meteorologie und Physik, Universitaet fuer Bodenkultur, Vienna, Austria.
[4] Royal Netherlands Meteorological Institute, De Bilt, Netherlands.
[5] Interaction Rayonnement Solaire Atmosphère, Université Joseph Fourier, Grenoble, France.
[6] Arctic Research Center, Finnish Meteorological Institute, Sodankylä, Finland.

0148-0227/05/2005JD005992$09.00

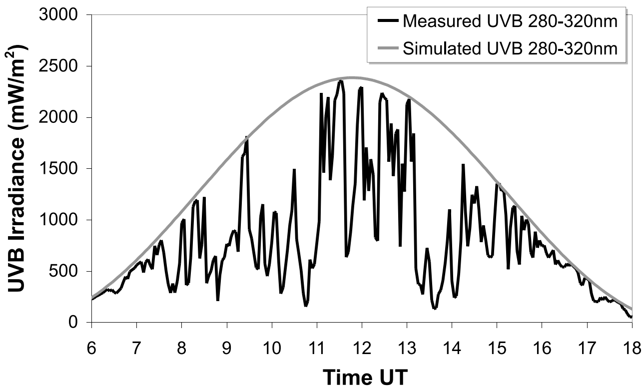

Figure 1. Measured UVB irradiance provided by the broadband instrument on 12 June 2004 at VdA (solid curve) and modeled UVB irradiance under clear sky (shaded curve).

Ozone Mapping Spectrometer) data [*Fiotelov et al.*, 2002]. *Dahlback* [1996] showed a relative difference of 0.3% between the Dobson and the Brewer spectroradiometers in Oslo (Norway). *Slusser et al.* [1999] showed that the mean ratios of column ozone retrieved by the multifilter rotating shadow-band radiometer and that retrieved by the Brewer and Dobson instruments range from 1.10 to 1.037 in all sky conditions. *Bernhard et al.* [2003] found that the ozone column from multichannel UV radiometer at San Diego (USA) agree within 12 DU with TOMS observations.

[4] This work is based on the methodology for retrieving the vertical ozone column from UV global irradiance spectra, already described by *Houët and Brogniez* [2004]. Information on this methodology and its first application to cloudless days is summarized in section 2. The difficulties generated by clouds in the ozone retrieval are explained and a method is proposed to process cloudy days. The ozone column is retrieved from each single spectrum, as for cloud-free days, and daily averages are computed. The sensitivity tests to cloud cover are presented applying the above methodology to the UV irradiances collected at Villeneuve d'Ascq (VdA, France) under all sky conditions. Section 3 presents the results for all clear and cloudy days and the comparison with TOMS data (version 8).

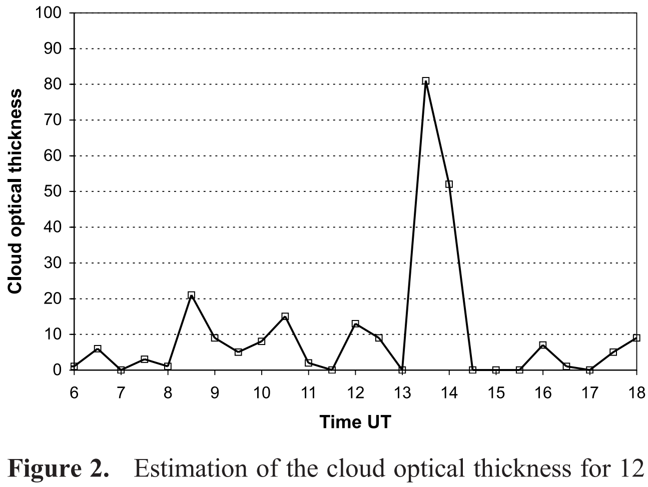

Figure 2. Estimation of the cloud optical thickness for 12 June 2004 at VdA.

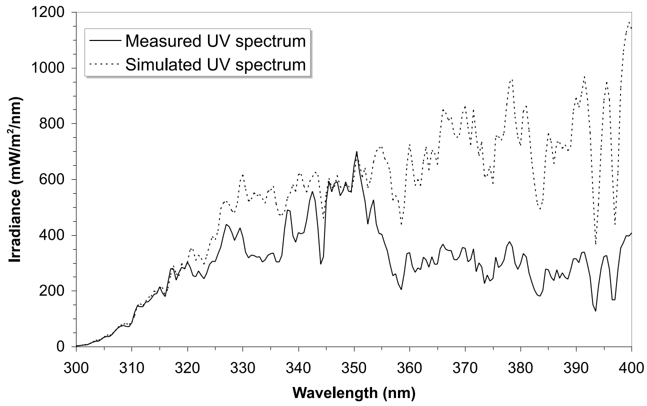

Figure 3. Distorted UV spectrum measured on 12 June 2004, at 1230 UT, and comparison with a UV spectrum simulated for cloudless conditions.

[5] In section 4, total ozone values are also retrieved at five other European stations of Rome (Italy), Sonnblick (Austria), De Bilt (the Netherlands), Briançon (France) and Sodankylä (Finland) that participated in the EDUCE project (European Database for UV Climatology and Evaluation) [*Seckmeyer et al.*, 2002]. Results from the comparison of the total ozone columns retrievals at the EDUCE sites with TOMS data as well as with data inferred from direct sun and zenith sky measurements for three Brewer instruments, are presented. Section 5 reports the conclusions.

2. Total Ozone Retrieval From UV Spectral Measurements

2.1. Methodology

[6] The total ozone column (TOC) is routinely retrieved at the Laboratoire d'Optique Atmosphérique (LOA) by a differential absorption method applied to UV global irradiance spectra measured with a Jobin Yvon scanning spectroradiometer in VdA. This method is based on the comparison between two ratios of irradiances at two selected wavelengths, one ratio simulated beforehand and stored in a look up table (LUT) and one calculated from the UV measurements [*Stamnes et al.*, 1991]. A previous work [*Houët and Brogniez*, 2004] reports the tests performed to

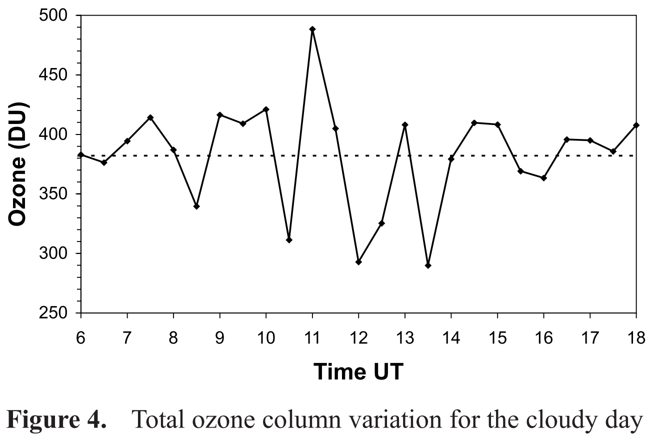

Figure 4. Total ozone column variation for the cloudy day 12 June 2004 at VdA.

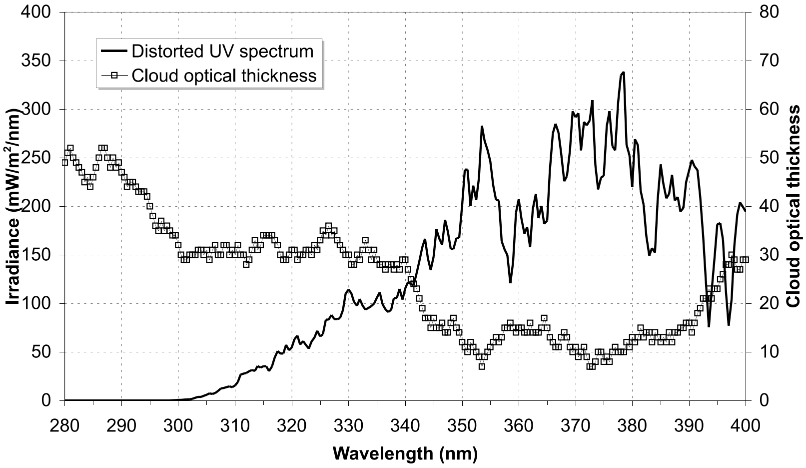

Figure 5. Simulated UV spectrum (left scale) distorted by a random cloud optical thickness and the cloud optical thickness used (right scale).

estimate the sensitivity of several ratios to instrumental, environmental and atmospheric parameters (other than ozone). This work has led to the selection of five irradiance ratios which have a low dependence on either previous parameter:

$$R_1 = \frac{E_{340}}{E_{305.5}},\ R_2 = \frac{E_{339}}{E_{305.5}},\ R_3 = \frac{E_{323.5}}{E_{305.5}},$$
$$R_4 = \frac{E_{339} + E_{339.5} + E_{340}}{E_{304.5} + E_{305.5} + E_{306.5}},\ R_5 = \frac{\overline{E_{340}; E_{345}}}{\overline{E_{305}; E_{310}}}$$

where the bottom index specifies the wavelength in nm at which the irradiance E is taken. R_5 is the ratio of irradiances averaged over small wavelength intervals. The selected ratios are stored in 23 LUTs corresponding to different aerosol parameters and atmospheric profiles of pressure, temperature and ozone. Five values of TOC are thus retrieved from a spectrum by comparing measured ratios to simulated ones. The mean of the five values has been shown to give a good estimate of the true value. Results have been presented for the data collected in VdA under cloud-free conditions for the years 2000, 2002 and 2003. On average the uncertainty of the retrieved total ozone is about 3%, and comparisons of TOC daily averages with ozone data from TOMS show a mean relative difference of 2%, as well as a small bias of about 2%, (LOA > TOMS).

[7] Cloudy days data were excluded from this first analysis because the sensitivity tests performed showed that clouds might cause a high uncertainty in the retrieved ozone [*Houët and Brogniez*, 2004]. These days were identified via two methods. First, using UVB broadband measurements performed with a three minutes time frequency. Figure 1 shows, for a case study, the comparison of the broadband irradiance measured on 12 June 2004 at VdA with a clear sky UVB irradiance modeled using the radiative transfer code DISORT [*Stamnes et al.*, 1988]. The irradiance variability due to clouds appears clearly.

[8] Second, estimating the (aerosol+cloud) optical thickness. It is obtained by comparing the average of measured irradiances in the 330–390 nm range with the average of the irradiances modeled in the same wavelength range with DISORT for various cloudy skies and stored in a LUT. Figure 2 shows the optical thickness retrieved for the case study. When the retrieved optical thickness is higher than 4, the sky is classified as cloudy.

[9] The combination of both methods allows us to determine cloudy and cloudless days and also the temporal variability of the cloud cover.

[10] Since ancillary measurements enabling the selection of clear days are not always available on UV sites, and since the selection, when it is done, is not perfect, in the current work the inference of TOC is carried out for all sky conditions.

2.2. Ozone Retrieval Under Cloudy Conditions

[11] In case of homogeneous cloud cover with constant optical thickness during the day, the sensitivity tests performed in the previous study revealed that the retrieved ozone column is estimated to within 3% [*Houët and Brogniez*, 2004]. This cloud case is, however, unusual and the spatial heterogeneity of the cloud cover as well as the temporal variability of its optical thickness produce high

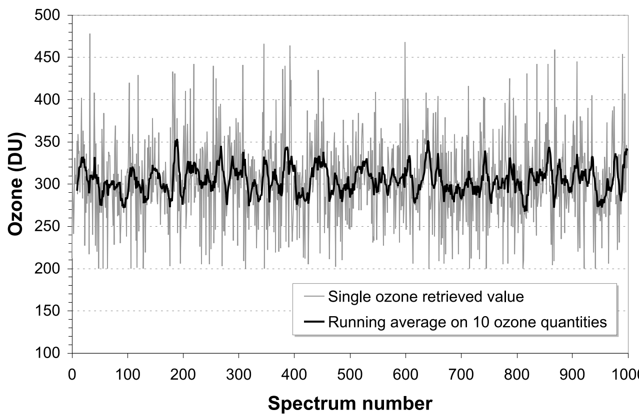

Figure 6. Ozone retrieved for 1000 simulated spectra deformed by a variable cloud optical thickness (shaded curve) and running average over 10 ozone values (solid curve).

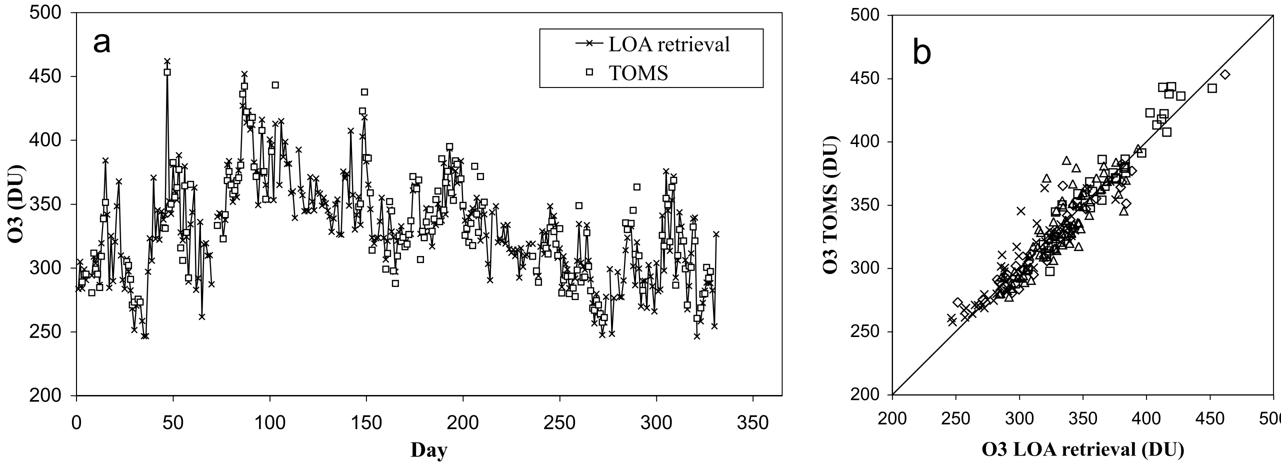

Figure 7. (a) Time evolution of ozone from LOA and from TOMS at VdA in 2000. (b) O_3 from TOMS versus O_3 from LOA retrieval at VdA in 2000. Diamonds are for winter period, squares are for spring, triangles are for summer, and crosses are for autumn.

variation of the retrieved ozone column during the day. Indeed, a variation of the cloud optical thickness during a scan (the Jobin Yvon instrument takes 6 min for each scan) may cause a distortion of the spectrum and perturb the results of the algorithm. However, during a cloudy day, the distortion of the spectra caused by the variation of the optical thickness is relatively random. Thus it may be anticipated that calculating the daily average of the ozone quantities may minimize these distorting effects on ozone retrievals. For example on 12 June 2004 at VdA, distorted spectra were observed during the whole day. Figure 3 presents the spectrum measured at 1230 UT and the spectrum simulated with DISORT for a cloudless sky. The clouds caused distortion, mainly in the 340 nm region where irradiances are used to calculate the irradiance ratios needed for the ozone algorithm.

[12] The TOC quantities retrieved during this day are reported in Figure 4. Fast and large variations of TOC are observed, for example at 1230 UT the retrieved TOC is 325 DU, while at 1300 UT it is 408 DU. These variations are unlikely due to real fluctuations of the total ozone column but are rather due to the cloud cover. TOMS provides an estimate of the actual TOC that can be used to evaluate the quality of our retrieval.

[13] A value rather close to TOMS value is obtained when the daily average of our retrievals is considered: it gives 382 DU to be compared to 405 ± 8 DU from TOMS (2% uncertainty according to *McPeters et al.* [1998]). The relative difference is 6%, which seems reasonable considering the high variability of the cloud cover of that day (there is 22% relative difference between the TOC retrieved at 1230 UT and TOMS value). The standard deviation of the retrieved ozone is quite large, 42 DU, i.e., 11% of the average value, while during a clear day the ozone standard deviation never exceeds 5 DU [*Houët and Brogniez*, 2004].

2.3. Uncertainty Estimation

[14] On clear days, the relative uncertainty of the retrieved ozone quantity was estimated at 3% [*Houët and*

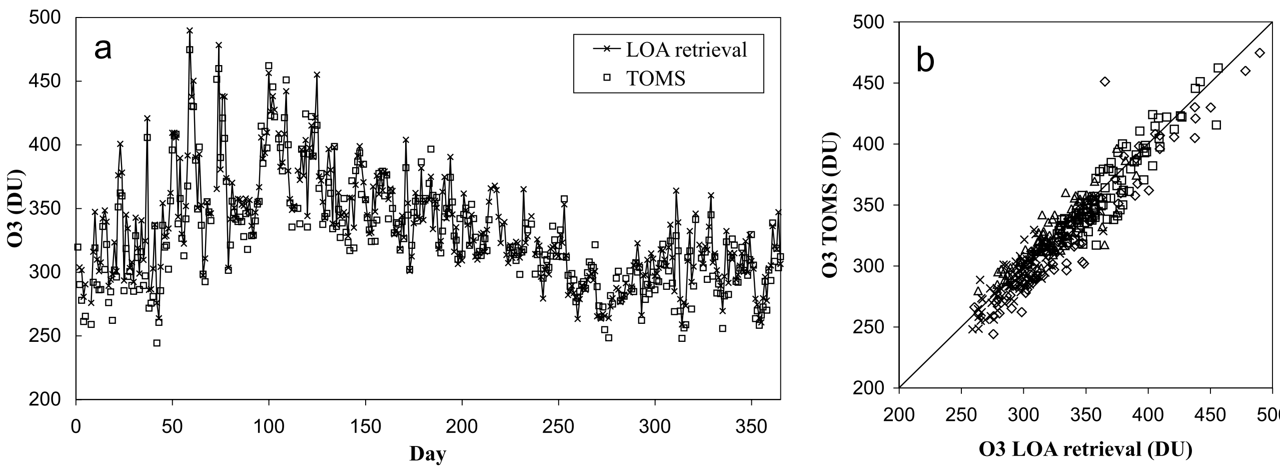

Figure 8. (a) Same as Figure 7a but for 2002. (b) Same as Figure 7b but for 2002.

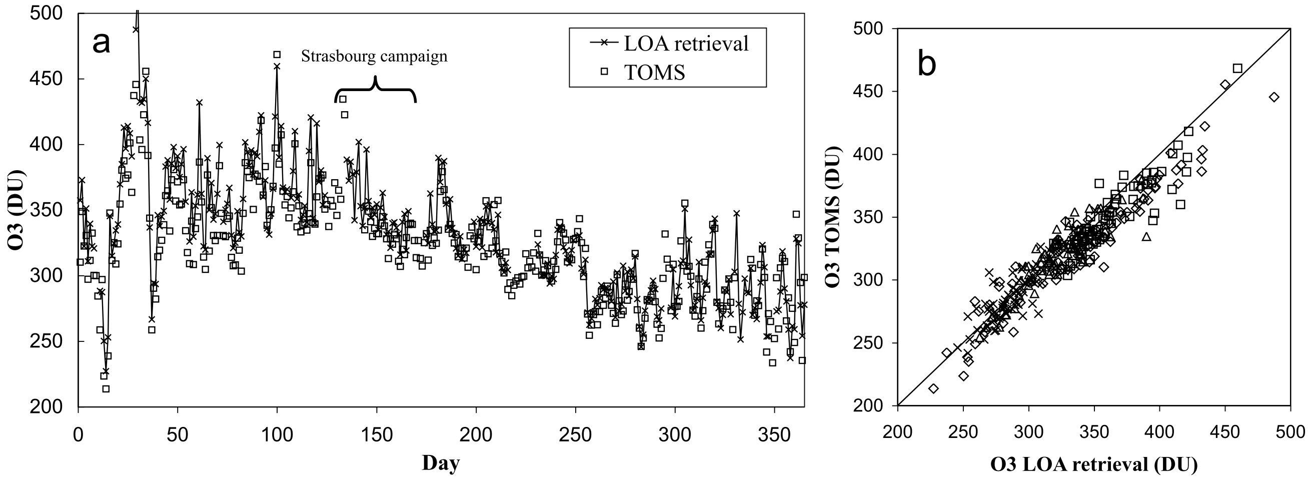

Figure 9. (a) Same as Figure 7a but for 2003. (b) Same as Figure 7b but for 2003.

Brogniez, 2004]. It can be considered inherent to the method. While computing a daily average, the relative uncertainty of the mean value must be accounted for. To estimate the relative uncertainty of a daily average, several distorted UV spectra are simulated with the DISORT code. Realistic variable cloud optical thickness is used to simulate reasonable deformed spectra. The cloud optical thickness cannot be randomly chosen for all wavelengths, some constraints are set. First, a cloud optical thickness chosen randomly between 0 and 70 is applied to the first wavelength (280 nm). Then, at the following wavelength, the cloud optical thickness is randomly chosen within an interval defined by the optical thickness at the previous wavelength ±2. Thus some modeled spectra are highly distorted whereas others are weakly distorted. This allows us to simulate cases that could be encountered during cloudy days, with an exception for particular cases caused by storm clouds where cloud optical thickness can strongly vary from approximately 0 to 100 in a few minutes. Figure 5 presents an example of a UV spectrum simulated with 300 DU, along with the random cloud spectral optical thickness used.

[15] The ozone value inferred from this single spectrum is bad, indeed the algorithm provides an ozone column equal to 347 DU instead of the input value, 300 DU, that is 16% relative error. However, because the cloud effects on several measured spectra are random and could be opposite, the daily average of the ozone quantities is expected to be close to the right value. The computation of 1000 deformed spectra allows a statistical study of the cloud effects. These 1000 spectra are simulated with the same ozone quantity and are randomly distorted by a variable cloud optical thickness. Figure 6 shows the retrieved ozone columns for these 1000 spectra.

[16] The average value is equal to 300 DU, confirming that the cloud effects are randomly opposite. During a day, the number of spectra measured by our instrument and used to determine the TOC varies approximately from only 10 in winter to 30 in summer (one spectrum measured each half hour and for a solar zenith angle smaller than 80°). Calculating an average with 10 ozone values allows us to reduce the unwanted cloud effects, indeed, in the worst case the running average reaches 350 DU.

[17] The standard deviation calculated with 10 spectra allows us to give an overestimation of the uncertainty of the mean value by using Student's law. For 10 ozone values and for a 99% confidence level, the confidence interval of the mean value is

$$I_c = \frac{2.76 \times \sigma_{O3}^{day}}{\sqrt{10}} \quad (1)$$

where σ_{O3}^{day} is the ozone standard deviation.

[18] The total relative uncertainty of the daily ozone quantity is given by:

$$RU = \sqrt{\left(\frac{I_c}{\langle O_3 \rangle_{day}}\right)^2 + 0.03^2} \quad (2)$$

where $\langle O_3 \rangle_{day}$ is the ozone daily average and 0.03 is the relative uncertainty of the method.

[19] By observing the results from the 1000 spectra, one can conclude that the total relative uncertainty on the daily ozone quantity varies from 3% to 20%, with only 10% of the relative uncertainties larger than 10%. The mean uncertainty is about 7%.

[20] To summarize, one can say that while on cloud-free days TOC is well retrieved from a global irradiance spectrum, on cloudy days each TOC retrieved from a single spectrum is often unreliable. Nevertheless there is a simple way to estimate the mean real TOC under cloudy condi-

Table 1. Number of Cases With a Relative Difference Between LOA Daily Means and TOMS Ozone Columns Smaller Than 3% or 5% or Greater Than 10% at VdA[a]

	2000	2002	2003
<3%	53	50	48
<5%	82	74	72
>10%	4	6	5

[a]Number of cases is given in percent.

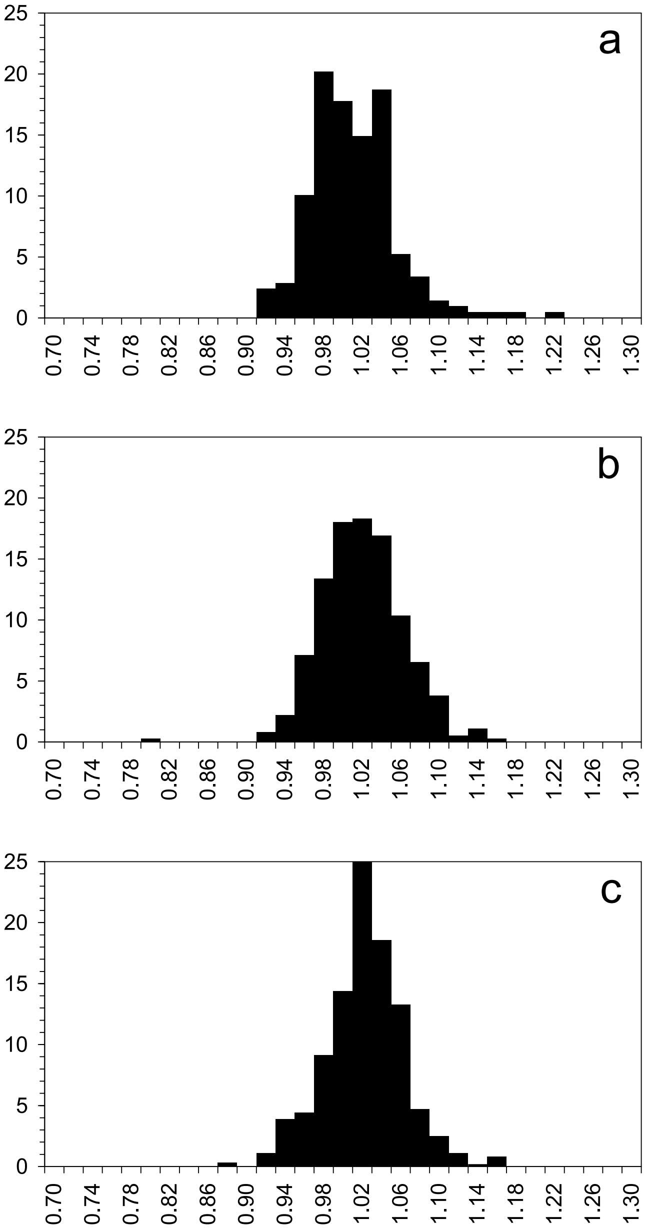

Figure 10. (a) Occurrence frequency of ratios O3(LOA)/O3(TOMS) for 2000 considering all the days (clear and cloudy). (b) Same as Figure 10a but for 2002. (c) Same as Figure 10a but for 2003.

tions: it is by averaging on a daily basis the TOCs retrieved from all global irradiance spectra.

3. Results at Villeneuve d'Ascq: Comparison With TOMS

[21] The spectroradiometer working at VdA (50.61°N, 3.15°E) is a Jobin Yvon double monochromator with a full width at half maximum (FWHM) equal to 0.7 nm. The TOC is calculated for each spectrum using the method briefly recalled in 2.1. For the ozone retrieval the LUT used was calculated with an Ångström coefficient equal to 1.5, an aerosol optical thickness at 1 μm equal to 0.05 and a constant single scattering albedo equal to 0.9. Depending

Table 2. Yearly Average and Standard Deviation (in Brackets) of the Ratio O3[LOA]/O3[TOMS] for Clear, Cloudy and All Days, for 3 Years at VdA

	2000	2002	2003
Clear days	0.992 [0.020]	1.037 [0.039]	1.016 [0.037]
Cloudy days	1.002 [0.042]	1.018 [0.044]	1.025 [0.044]
All days	1.001 [0.041]	1.019 [0.044]	1.023 [0.043]

on the season, the LUT used is that obtained with the most relevant atmospheric ozone, pressure and temperature profiles. The daily average of the retrieved ozone columns is then calculated (from at least 10 values) and compared with TOMS value (version 8). Figures 7–9 present these results for the 3 years, 2000, 2002 and 2003.

[22] In Figure 9a the bracket indicates values obtained with the same instrument in Strasbourg (48.3°N, 7.6°E), France, during a measurement campaign. The corresponding TOMS values are those obtained for this site. For the 3 years there is no obvious difference depending on the season.

[23] Table 1 summarizes the results obtained for the comparison with TOMS data for these 3 years. High differences between LOA and TOMS, >10%, are generally not associated to a lower number of daily observations but are generally related to large values of the total relative uncertainty of TOC LOA daily averages.

[24] The results of these comparisons are very similar to those presented by *Houët and Brogniez* [2004] obtained for clear days only. For the 3 years the relative difference between both values does not exceed 5% in approximately 75% of the cases, and it does not exceed 3% in about 50% of the cases.

[25] Figure 10 presents the frequency of occurrence of the ratios O3(LOA)/O3(TOMS). The histograms are almost symmetrical and centered on 1.00 for 2000 and 1.02 for 2002 and 2003. A bias of approximately 2% (LOA > TOMS) is observed for cloudy and clear days for 2002 and 2003 (Table 2). Considering the relative uncertainty of

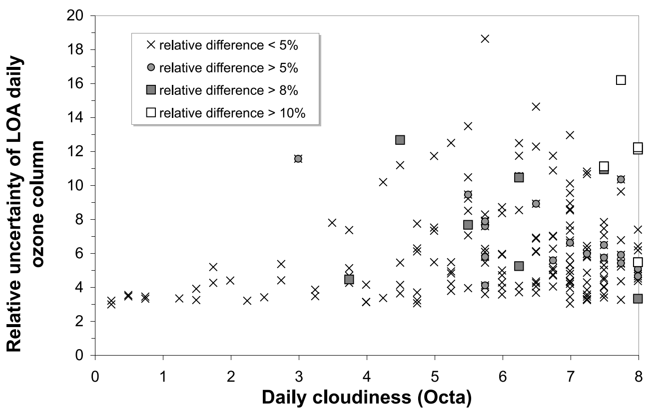

Figure 11. Total relative uncertainty (in percent) of the daily average of the LOA retrieved ozone columns (equation (2)) versus daily cloudiness for 2000. Each symbol represents a day and the different symbols correspond to a relative difference between LOA and TOMS (|LOA − TOMS|/TOMS) as indicated in the upper left corner.

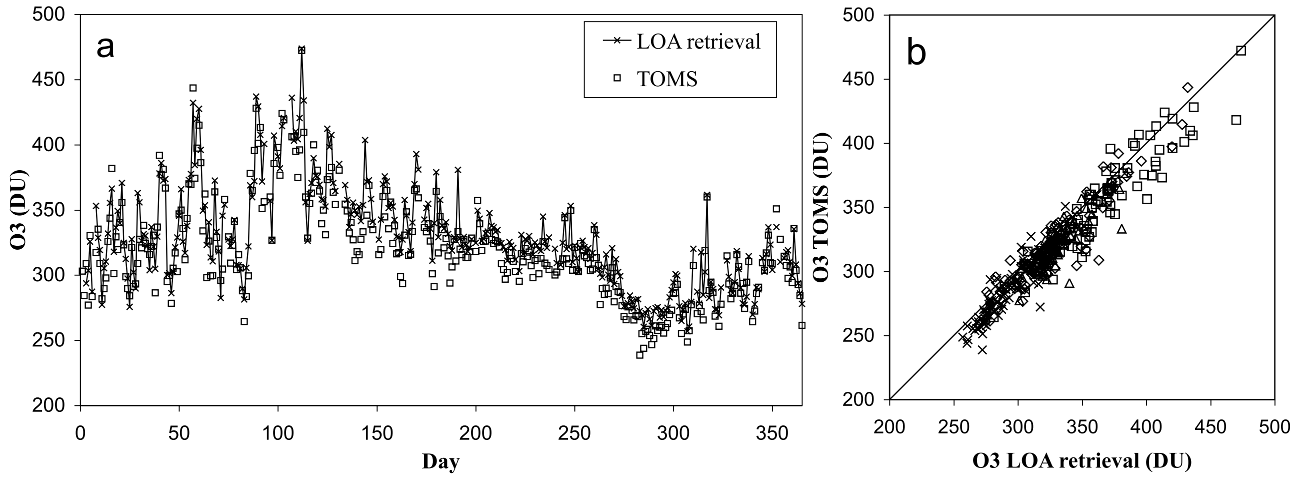

Figure 12. (a) Same as Figure 7a but for Rome in 2001. (b) Same as Figure 7b but for Rome in 2001.

both data sets, 7% for LOA and 2% for TOMS, the agreement is satisfying. Thus calculating the daily average of retrieved ozone values allows us to obtain a TOC consistent with that provided by TOMS.

[26] Table 2 compares the results obtained for clear days [*Houët and Brogniez*, 2004] with the cloudy-day results for the 3 years. It is interesting to note that, except in 2000, the standard deviations obtained from the cloudy days are very similar to those obtained from clear days. Except for few cases, the clouds finally do not affect significantly the ozone comparison, provided that the daily average is used.

[27] For 2000, the cloudiness is available from Météo France. These data, given every 3 hours during the day and expressed in octas, allow us to estimate a daily value and see the impact of the cloudiness on the relative uncertainty of the ozone quantity calculated with equation (2), and the impact on the comparison with TOMS data (Figure 11). As was expected, for the clear days (cloudiness $\leq$2 octas), the comparison between our values and TOMS data is good with relative differences always smaller than 5% (crosses). Moreover, for these cases the relative uncertainty of the daily ozone quantity never exceeds 6%. One can conclude that weak cloud coverage is not a problem for retrieving TOC with this method. The unfavorable agreements between LOA and TOMS ozone quantities (relative difference >10%, white squares) are all found, as could be expected, for cloudiness greater than 7 octas. For the cloudy days (cloudiness larger than 5 octas), the relative uncertainties are sometimes very high, one of them reaching 19%. For this cloudiness ($\geq$5 octas), some relative differences between LOA and TOMS values greater than 8% are found, associated with a moderate uncertainty of the LOA retrieved value (smaller than 6%). This could be due to a relatively constant cloud optical thickness leading to a weak daily variation of the retrieved ozone. On the opposite, the case mentioned previously with 19% relative uncertainty corresponds to an agreement between LOA and TOMS values better than 5% (cross). For high cloudiness again, several days show small relative uncertainties and are in good agreement with TOMS, indicating that finally, the cloud cover has no undesirable impact on the ozone retrieval. Two bad agreements are also found with a moderate cloud cover (3–4 octas) and with a moderate relative uncertainty (7–8%).

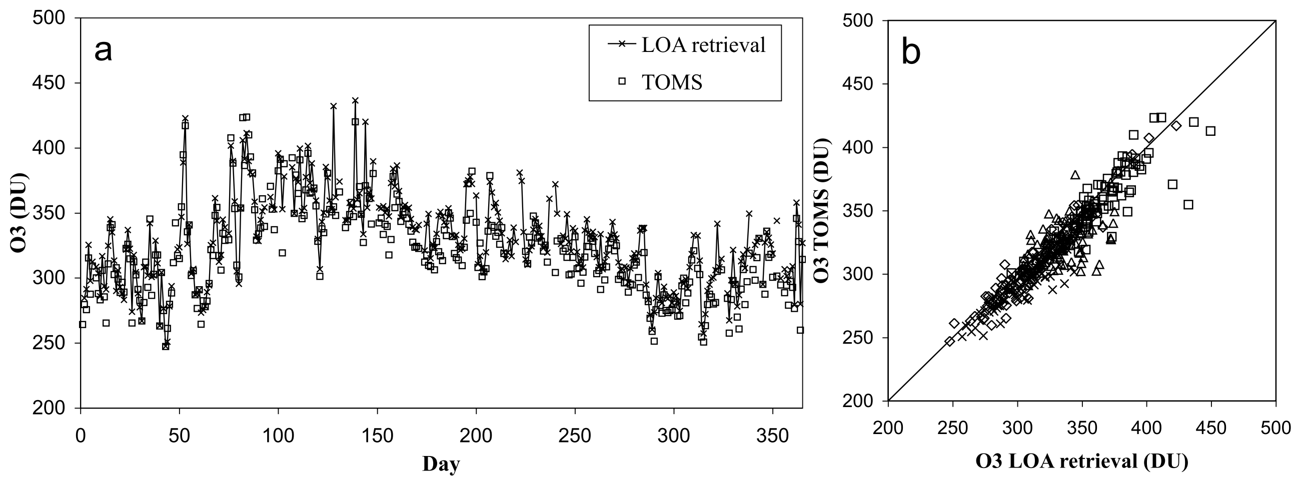

Figure 13. (a) Same as Figure 7a but for Rome in 2002. (b) Same as Figure 7b but for Rome in 2002.

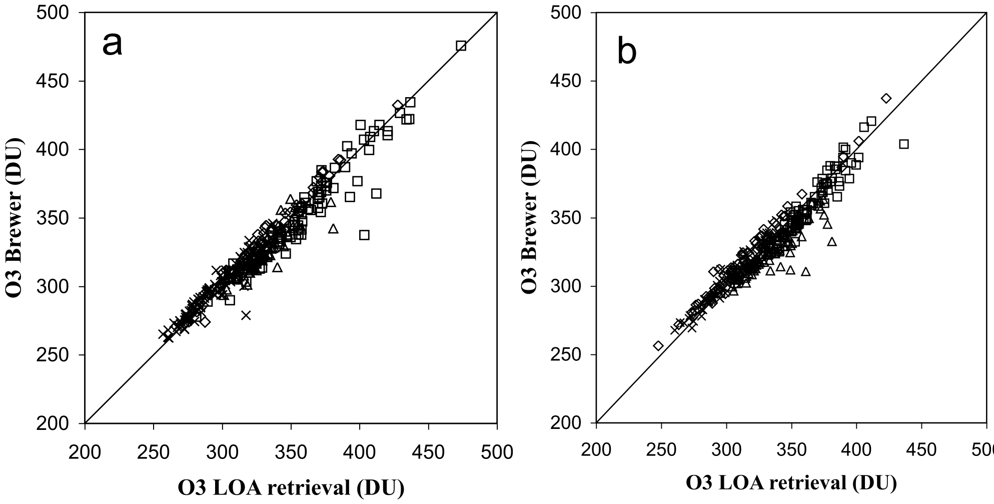

Figure 14. (a) O_3 from Brewer versus O_3 from LOA retrieval at Rome in 2001. The symbols have the same meaning as in Figure 7b. (b) Same as Figure 14a but for Rome in 2002.

[28] To summarize, during clear and weakly cloudy days, the relative uncertainty is small (<5%) and the agreement with TOMS is good (relative difference <5%). During cloudy days, the agreement with TOMS is good (relative difference <5%) in most cases and the relative uncertainty remains acceptable (<10%). However, approximately 5% of the cases show a large relative difference with TOMS data.

4. Results at EDUCE Sites: Comparison With TOMS

[29] The method is applied to other instruments participating in the EDUCE program [*Seckmeyer et al.*, 2002]. The instruments are selected on the basis their FWHM is in the range allowing a good ozone retrieval by using our LUTs [*Houët and Brogniez*, 2004]. The appropriate LUT is selected according to the season and to the actual ground albedo, and it is computed with the standard aerosol parameters: the Angström coefficient is 1.5, the aerosol optical thickness at 1 μm is 0.05 and the single scattering albedo is 0.9. As for VdA, to calculate the daily ozone values all spectra measured with a solar zenith angle smaller than 80° are considered.

4.1. Rome (41.90°N, 12.52°E, Italy)

[30] A Brewer spectrophotometer is used to perform direct sun ozone column and global irradiance measurements. The irradiances are measured in the 290 to 325 nm spectral range at 0.5 nm step, with a FWHM of 0.6 nm. The error for a typical TOC inferred from direct sun measurements is estimated at 1% [*Fioletov et al.*, 1999]. The analysis of Rome Brewer ozone column from direct sun observations (called further "O3 Brewer") and the most recent version of TOMS satellite data (version 8) indicated that the ground-based observations are systematically larger than the satellite data. For the years considered in this study, the bias is 3.6% in 2001 and 1.5% in 2002 (G. R. Casale and A. M. Siani, personal communication, 2004).

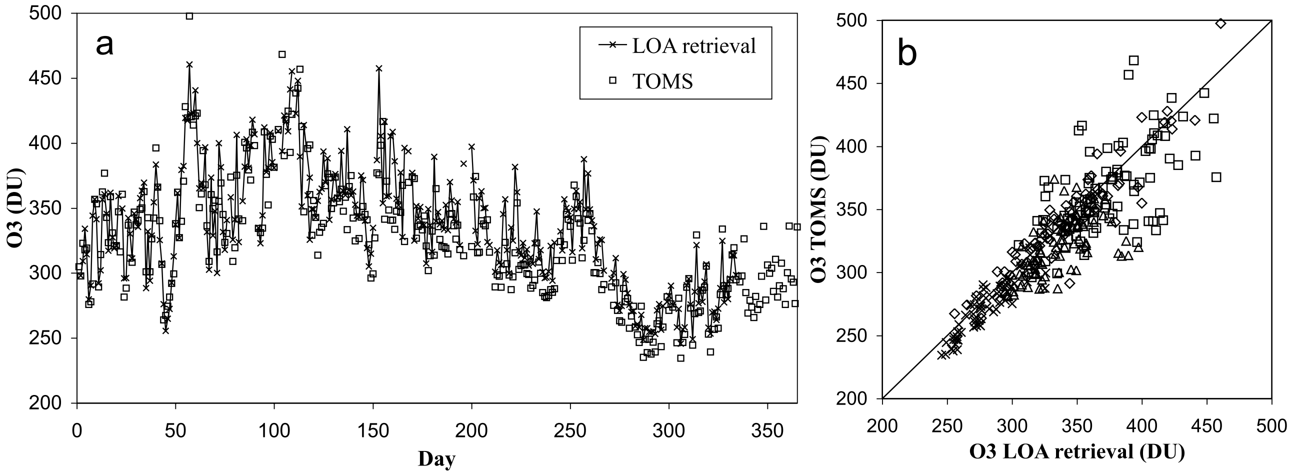

Figure 15. (a) Same as Figure 7a but for Sonnblick in 2001. (b) Same as Figure 7b but for Sonnblick in 2001.

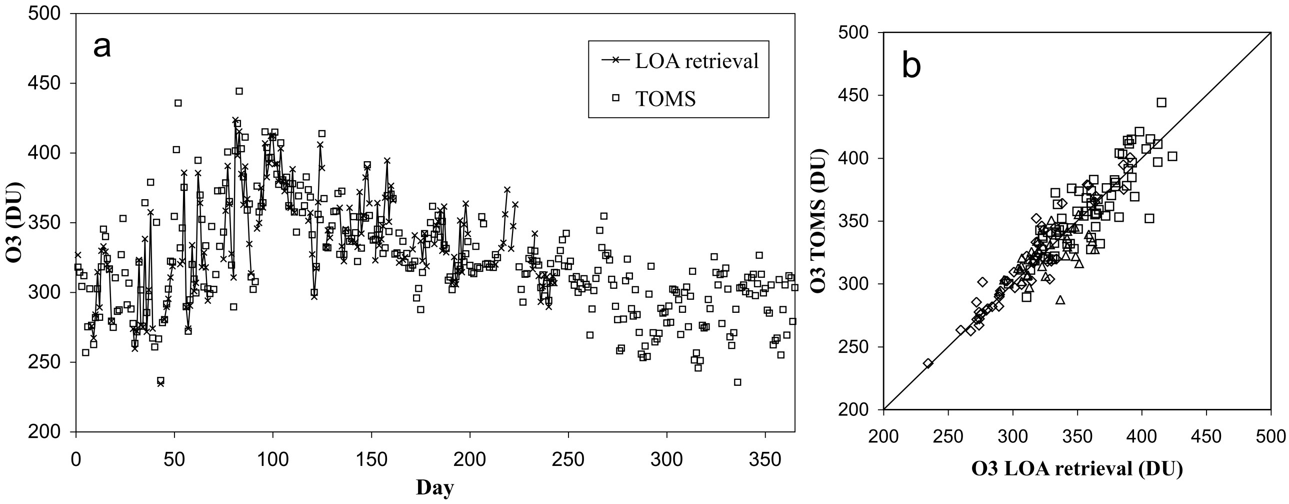

Figure 16. (a) Same as Figure 7a but for Sonnblick in 2002. (b) Same as Figure 7b but for Sonnblick in 2002.

[31] Following the LOA method only one ratio (R_3) can be used for retrieving ozone for the Rome instrument. The results for the years 2001 and 2002 are presented in Figures 12 and 13 respectively.

[32] The mean percentage difference between both data sets does not exceed 5% in 75% of the cases for the whole period considered. The result is similar to those obtained with VdA for 2002 and 2003. A mean bias of 3% is observed between the LOA retrieved TOC and TOMS values (LOA > TOMS), that is consistent with G. R. Casale and A. M. Siani (personal communication, 2004) study. During the summer it reaches 6%. Data on aerosol parameters from the Aeronet database [*Holben et al.*, 1998] are missing in summer, so we cannot compare them to the input values of the used LUT. Therefore the observed bias cannot be attributed to the aerosol loadings. The standard deviation of the ratio O3 LOA/O3 TOMS is about 0.037 for both years.

[33] The comparisons between LOA TOC retrievals and daily means of Brewer ozone columns shown in Figure 14a and 14b indicate very small biases, 0.4% in 2001 and 0.7% in 2002 (LOA > O3 Brewer), and standard deviations equal to 0.029 for both years, which confirms confidence in the LOA retrieval. Few large differences are also observed during the summer in 2002.

4.2. Sonnblick (47.05°N, 12.95°E, Austria)

[34] This site is located in the Alps, at 3100 m altitude. The spectroradiometer operating at this site is a Bentham. Its FWHM is equal to 0.78 nm. The spectral irradiances are provided from 288.5 nm to approximately 402 nm. For these data all ratios can be used. According to *Houët and Brogniez* [2004] we account for the site altitude effect. The results for the years 2001 and 2002 (Bentham measurements available up to the end of August) are presented in Figures 15 and 16 respectively.

[35] The relative difference between both values does not exceed 5% in 63% of cases in 2001 and 73% in 2002. There is a bias observed between our quantities and TOMS quantities equal to 2.9% in 2001 (LOA > TOMS) and there

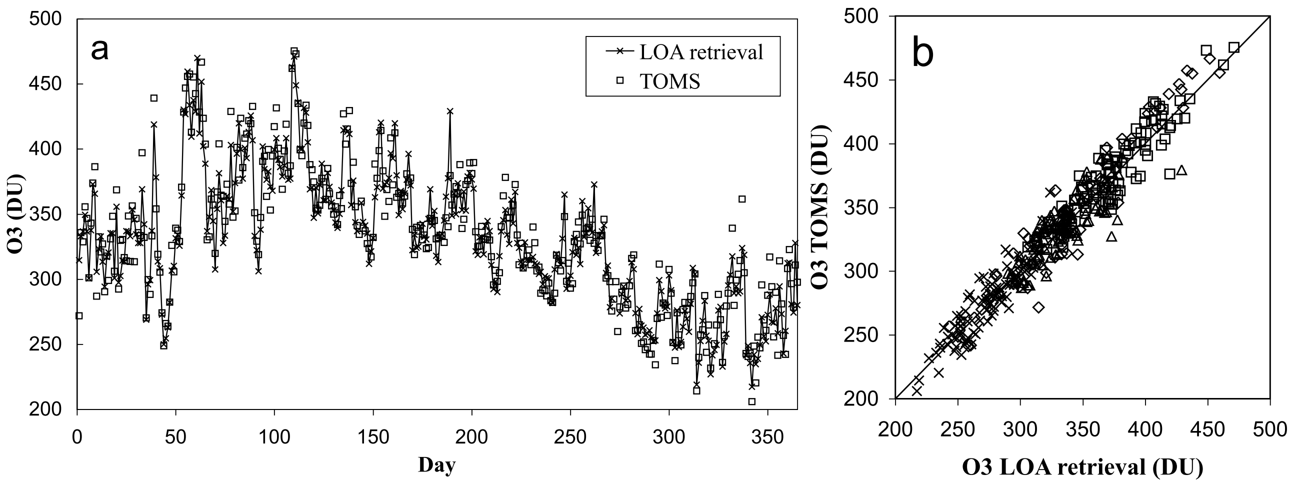

Figure 17. (a) Same as Figure 7a but for De Bilt in 2001. (b) Same as Figure 7b but for De Bilt in 2001.

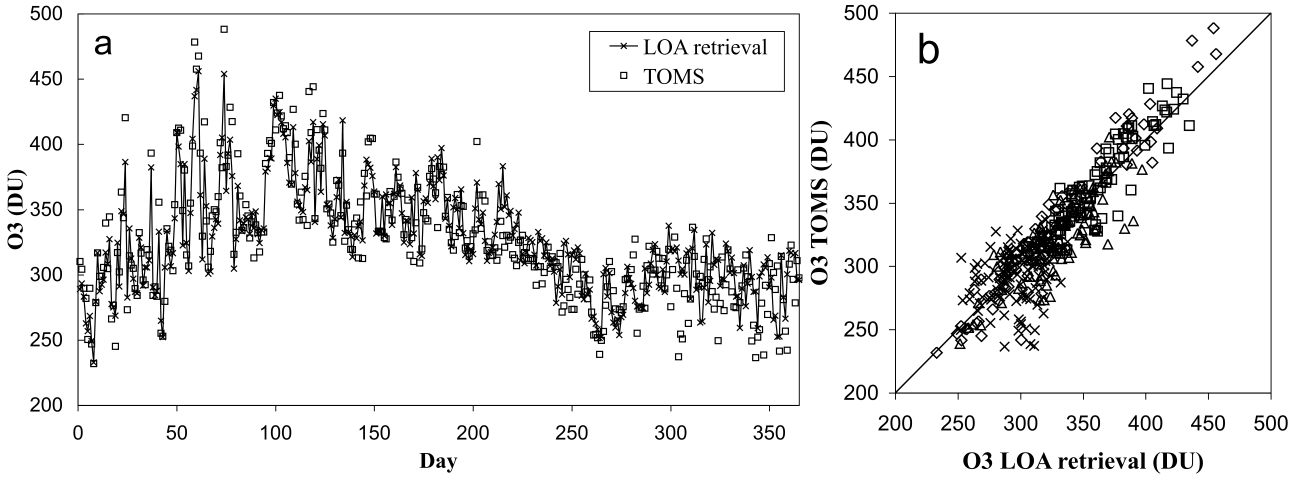

Figure 18. (a) Same as Figure 7a but for De Bilt in 2002. (b) Same as Figure 7b but for De Bilt in 2002.

is no bias in 2002. The standard deviation of the ratio O3 LOA/O3 TOMS is large in 2001, it is 0.062 and in 2002 it is 0.046. The agreement looks slightly better in autumn (crosses).

4.3. Debilt (52.10°N, 5.18°E, the Netherlands)

[36] The spectroradiometer operating at this site is also a Brewer with a FWHM equal to 0.55 nm. The spectral irradiances are provided from 280 to 363 nm. For these data all ratios can be used. The results for the years 2001 and 2002 are presented in Figures 17 and 18 respectively.

[37] The relative difference between both values does not exceed 5% in 77% of cases in 2001 and in 63% of cases in 2002. For 2002 large relative differences appear mainly in the second part of the year, especially in autumn (crosses). For this site, no significant bias is observed between LOA and TOMS quantities (biases smaller than 1% for both years). The standard deviation of the ratio O3 LOA/O3 TOMS is equal to 0.041 in 2001 and in 2002 it is equal to 0.068, that is rather large.

[38] TOC is also retrieved from direct sun and zenith sky measurements. The comparison with LOA retrievals is shown in Figures 19a and 19b. It is satisfying with biases also very small (1% in 2001 (O3 Brewer > LOA) and smaller than 1% in 2002) and standard deviations about 0.040 for both years. There is no differences between the seasons.

[39] All these comparisons show that the results from the three data sets are quite consistent.

4.4. Briançon (44.90°N, 6.65°E, France)

[40] This site is located in the French Alps, at 1300 m altitude. Two spectroradiometers operate on this site: a Jobin Yvon (JY) and a Bentham. The FWHM of the JY is equal to 0.7 nm, that of the Bentham is equal to 0.9 nm. The spectral irradiances are provided from 280 nm to 450 nm for the JY and from 294 nm to 400 nm for the Bentham. We have accounted for the altitude effect for the TOC retrieval. Figures 20 and 21 present the results for 2002 for the JY and the Bentham respectively.

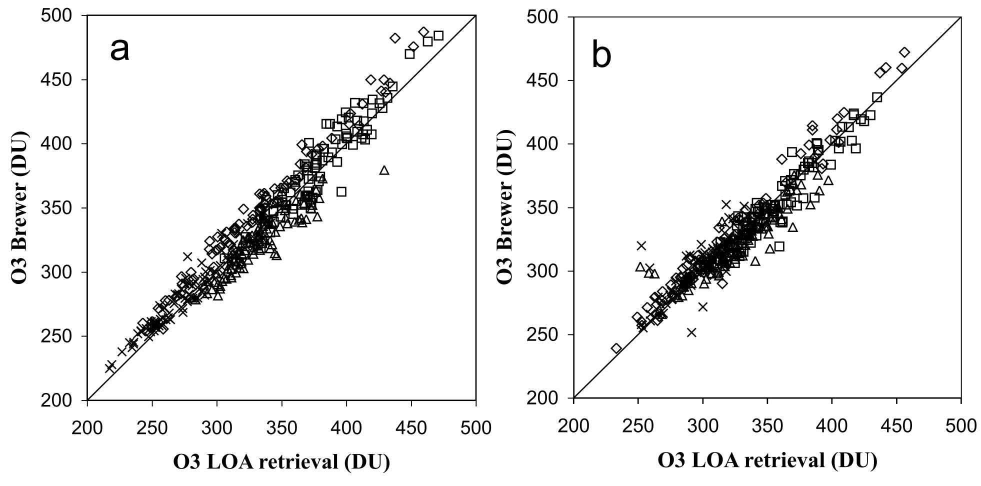

Figure 19. (a) Same as Figure 14a but for De Bilt in 2001. (b) Same as Figure 14a but for De Bilt in 2002.

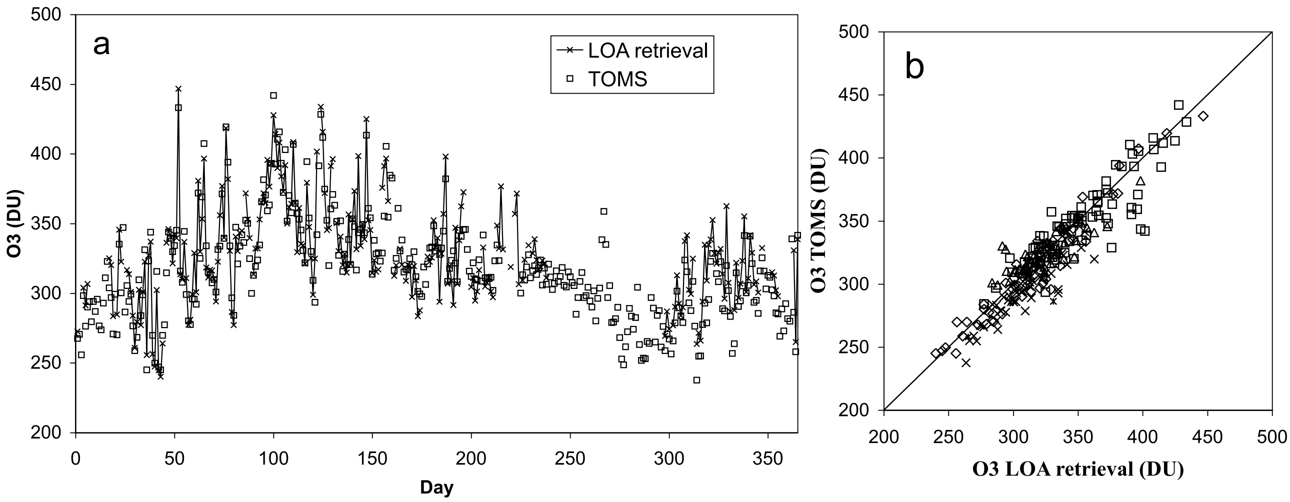

Figure 20. (a) Same as Figure 7a but for Briançon in 2002 – Jobin Yvon instrument. (b) Same as Figure 7b but for Briançon in 2002 – Jobin Yvon instrument.

[41] For the JY instrument the results are close to those obtained for the site of VdA with 84% of our ozone retrievals closer than 5% to TOMS data. A similar bias is observed (1.6%, LOA > TOMS) and the standard deviation of the ratio O3 LOA/O3 TOMS is equal to 0.044. For the Bentham instrument, the bias is larger (4.4%, LOA > TOMS) and the standard deviation is 0.047. Despite the fact that the two instruments are located in the same site, the results on average over the same year differ. The larger bias observed with the Bentham is certainly not due to environmental effects (ground albedo, aerosol parameters, cloud cover, etc.) since these parameters are identical for both instruments. According to *Houët and Brogniez* [2004] the Bentham FWHM (0.9 nm) is not be a problem. The differences could be due to an instrumental parameter that has not been taken into account during the sensitivity tests. Figure 22 presents a comparison between retrievals obtained with both instruments. TOC retrieved with the Bentham instrument are in average 3% larger than those retrieved with the JY instrument. The disagreement is much larger in spring and summer with TOC from Bentham up to 15–20% larger than JY values. Because of technical problems that occurred with both instruments, the comparison cannot be carried out in autumn and during a large period in winter. So there are not enough simultaneous measurements to allow a more detailed analysis of the differences.

[42] A similar study had been previously done at this site for both instruments for 2000, it is detailed by *Masserot et al.* [2002]. In this paper, for all days it was found on a yearly average a 4% positive bias between TOC retrieved with the spectral data and those provided by TOMS. These results are consistent with the 2002 current results obtained for the Bentham, but are worse than those for the JY instrument.

4.5. Sodankylä (67.37°N, 26.63°E, Finland)

[43] The spectroradiometer operating at this site is also a Brewer. Its FWHM is equal to 0.56 nm. The spectral

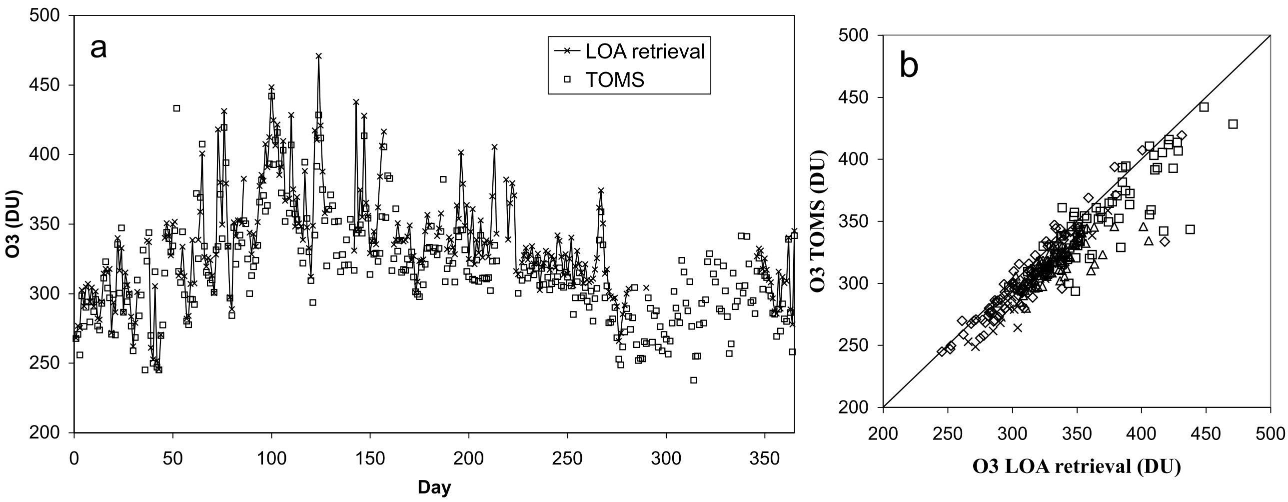

Figure 21. (a) Same as Figure 7a but for Briançon in 2002 – Bentham instrument. (b) Same as Figure 7b but for Briançon in 2002 – Bentham instrument.

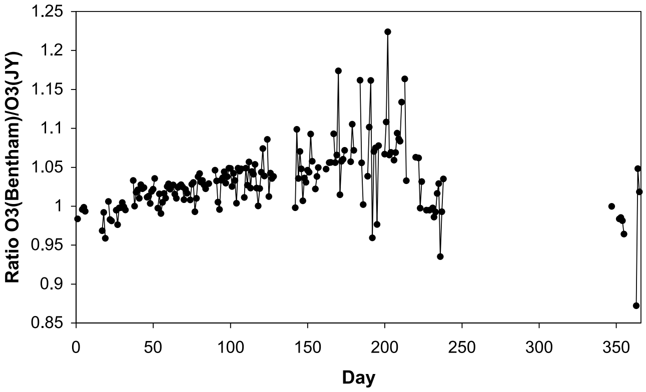

Figure 22. Ratio of TOC from Bentham and from JY for Briançon in 2002.

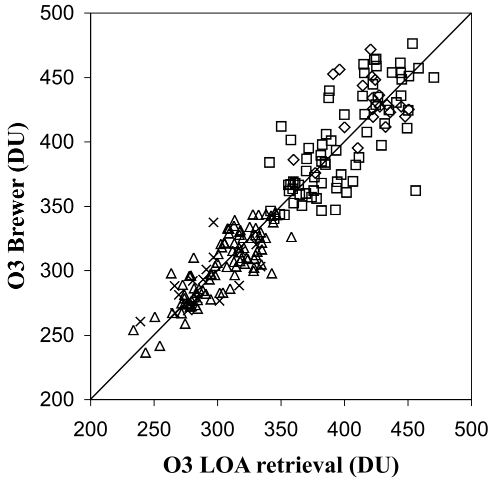

Figure 24. Same as Figure 14a but for Sodankylä in 2001.

irradiances are provided from 280 nm to 325 nm, so, as with Rome's data, only one ratio (R_3) can be used for retrieving ozone. The results for 2001 are presented in Figure 23.

[44] The relative difference between both values does not exceed 5% in 88% of cases. Almost no bias is observed between LOA values and TOMS values and the standard deviation is equal to 0.037. No seasonal effect is observed. For this site, the results seem to be very good, despite the utilization of only one ratio.

[45] TOC is also retrieved from direct sun and zenith sky measurements. Figure 24 shows the comparison between LOA TOC retrievals and Brewer TOC. There is no bias but the standard deviation is rather large, it is equal to 0.058. Spring data (squares) show larger differences. Similar results are found for the comparison between TOMS and Brewer TOC (not shown) with a small bias (1.6%, Brewer > TOMS) and a large standard deviation (0.069). For this location the agreement between LOA retrieved TOC and TOMS data is better than the agreement between LOA retrieved TOC and Brewer TOC.

[46] Tables 3 and 4 summarize these results obtained with these EDUCE sites.

5. Conclusion

[47] In a previous paper [*Houët and Brogniez*, 2004], a method to retrieve total ozone column from UV global spectra measured by scanning spectroradiometers was described. This method allows us to obtain one ozone value for each spectrum and then its diurnal variation. However, this method is highly uncertain if the spectra are measured under cloudy skies with rapidly changing cloud optical depths. A method to estimate the ozone quantity and its relative uncertainty for all skies has been investigated in this paper. For cloudy days, the ozone daily average is calculated and the standard deviation gives an estimate of the relative uncertainty. Even though the diurnal variation is no longer available when calculating a daily average, this method allows us to estimate a local ozone quantity for all clear and cloudy days with a 7% mean uncertainty, allowing us to study the time ozone variations.

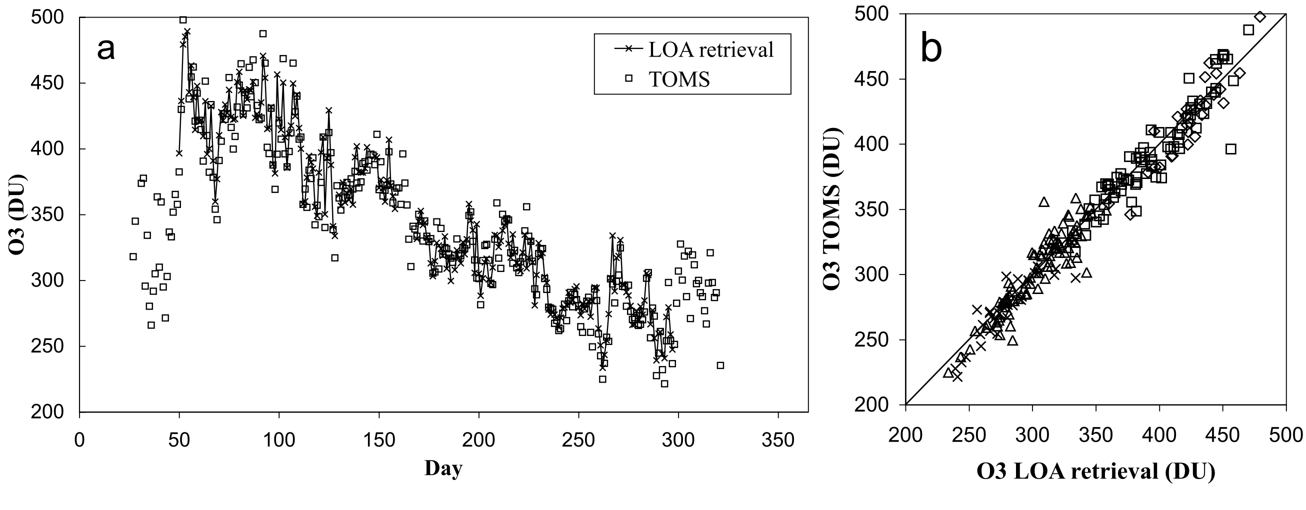

Figure 23. (a) Same as Figure 7a but for Sodankylä in 2001. (b) Same as Figure 7b but for Sodankylä in 2001.

Table 3. Results of the Comparison Between TOC Retrieved by LOA Method and TOMS Values for Five EDUCE Sites in 2001 and/or 2002[a]

	Rome	Sonnblick	Debilt	Briançon JY	Briançon Bentham	Sodankylä
FWHM, nm	0.6	0.78	0.55	0.7	0.9	0.56
2001						
Number of cases <5%	74	63	77	...	...	88
Average [standard deviation]	1.030 [0.037]	1.029 [0.062]	0.996 [0.041]	...	...	1.008 [0.037]
2002						
Number of cases <5%	75	73	63	84	63	...
Average [standard deviation]	1.027 [0.036]	0.999 [0.046]	1.009 [0.068]	1.016 [0.044]	1.044 [0.046]	...

[a]First line under each year is the number of cases (in percent) with a relative difference between LOA and TOMS ozone values smaller than 5%. Second line under each year is the yearly average and standard deviation (in brackets) of the ratio O3[LOA]/O3[TOMS].

[48] The determination of daily TOC is carried out at Villeneuve d'Ascq for all days during 2000, 2002 and 2003. To estimate the effectiveness of the method, comparisons are carried out with data from TOMS. The comparison for all days is quite satisfactory and similar to that obtained for clear days only, with approximately 3/4 of data agreeing within 5%. Of the remaining data approximately 5% disagree by more than 10%. These results are satisfying, considering the large number of cloudy days occurring in Villeneuve d'Ascq and the corresponding numerous distorted spectra.

[49] The LUTs are computed in order to be used with a large variety of instruments [*Houët and Brogniez*, 2004]. Thus the method was applied to the spectra measured at five other EDUCE sites. The agreement with TOMS data is not always as good as the one found for Villeneuve d'Ascq, but it is satisfactory considering the uncertainties associated to each data set. The large differences encountered for some sites during a few periods are very difficult to explain. Considering the method proposed, it is unlikely that the width of the slit function used entails these differences. Indeed, no bias is observed with the De Bilt and Sodankylä instruments, spectroradiometers with a FWHM very different from the Villeneuve d'Ascq FWHM, which is in agreement with the sensitivity test performed in the previous paper [*Houët and Brogniez*, 2004]. The differences could result from local mean aerosol parameters inconsistent with the LUT used, to local atmospheric effects like pollution or to other instrumental parameters that have not been taken into account, such as the shape of the slit function. Considering TOMS data, they are averages over a large pixel (100×100 km^2) so the differences could arise from heterogeneities, due for example to broken clouds. The understanding of differences between the two instruments located at Briançon needs further investigation. At three sites equipped with Brewer instruments, the TOC derived with the proposed method from global spectra have been compared with the TOC derived from direct sun and zenith sky measurements. In four cases among five it was found better agreement than for the comparison with TOMS, more than 80% (even up to 95%) of data agreeing within 5%.

[50] Few large disagreements are observed but there is generally a good consistency between the three data sets. This allows us to conclude that TOC can be retrieved with the proposed LOA method from global irradiance measurements performed at any site even under cloudy conditions.

[51] **Acknowledgments.** The French sites were supported by the French "Ministère de l'Aménagement du Territoire et de l'Environnement." This work was performed in the frame of the EDUCE project supported by the European Commission. The CEMBREU (Centre Européen Médical et Bioclimatique de Recherche et d'Enseignement Universitaire), which hosts the Briançon instruments, is acknowledged for its financial and technical support. The LOA team thanks C. Deroo for her efficient help in handling data.

References

Bernhard, G., C. R. Booth, and J. C. Ehramjian (2003), Real time UV and column ozone from multi-channel UV radiometers deployed in the National Science Foundation's UV monitoring network, *Proc. SPIE Int. Soc. Opt. Eng.*, *5156*, 167–178.

Dahlback, A. (1996), Measurements of biologically effective UV doses, total ozone abundances, and cloud effects with multichannel, moderate bandwidth filter instruments, *Appl. Opt.*, *35*, 6514–6521.

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 data, *J. Geophys. Res.*, *104*, 1737–1747.

Table 4. Results of the Comparison Between TOC Retrieved by LOA Method and Brewer Values (See Text) for Three EDUCE Sites in 2001 and/or 2002[a]

	Rome	Debilt	Sodankylä
FWHM, nm	0.6	0.55	0.56
2001			
Number of cases <5%	95	79	65
Average [standard deviation]	1.004 [0.029]	0.990 [0.039]	1.001 [0.058]
2002			
Number of cases <5%	94	85	...
Average [standard deviation]	1.007 [0.029]	0.998 [0.040]	...

[a]First line under each year is the number of cases (in percent) with a relative difference between LOA and O3 Brewer values smaller than 5%. Second line under each year is the yearly average and standard deviation (in brackets) of the ratio O3[LOA]/O3[Brewer].

Fioletov, V. E., G. E. Bodeker, A. J. Miller, R. D. McPeters, and R. Stolarski (2002), Global ozone and zonal total ozone variations estimated from ground-based and satellite measurements: 1964–2000, *J. Geophys. Res.*, *107*(D22), 4647, doi:10.1029/2001JD001350.

Gao, W., J. Slusser, J. Gibson, G. Scott, D. Bigelow, J. Kerr, and B. McArthur (2001), Direct-Sun column ozone retrieval multifilter rotating shadow-band radiometer and comparison with those from Brewer and Dobson spectrophotometers, *Appl. Opt.*, *40*, 1511–1543.

Holben, B. N., et al. (1998), AERONET—A federated instrument network and data archive for aerosol characterization, *Remote Sens. Environ.*, *66*, 1–16.

Houët, M., and C. Brogniez (2004), Ozone column retrieval from solar UV irradiance measurements at ground level: Sensitivity tests and uncertainty estimation, *J. Geophys. Res.*, *109*, D15302, doi:10.1029/2004JD004703.

Masserot, D., J. Lenoble, C. Brogniez, M. Houët, 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., et al. (1998), Earth Probe Total Ozone Mapping Spectrometer (TOMS) data products user's guide, *NASA Tech. Publ., 1998-206895*, 64 pp.

Seckmeyer, G., et al. (2002), The European Database for Ultraviolet Climatology and Evaluation (EDUCE), paper presented at 6th European Symposium on Stratospheric Ozone, Environ. and Sustainable Dev. Programme, Eur. Comm., Göteborg, Sweden, 2–6 Sept.

Slusser, J. R., J. H. Gibson, D. S. Bigelow, D. Kolinski, M. Wanfeng, G. Koenig, and A. Beaubien (1999), Comparison of column ozone retrievals by use of an UV multi-filter rotating shadow-band radiometer with those from Brewer and Dobson spectrophotometers, *Appl. Opt.*, *38*, 1543–1551.

Solomon, S. (1999), Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, *37*(3), 275–316.

Staehelin, J., N. R. P. Harris, C. Appenzeller, and J. Eberhard (2001), Ozone trends: A review, *Rev. Geophys.*, *39*(3), 231–290.

Stamnes, K., S. C. Tsay, W. J. Wiscombe, and K. Jayaweera (1988), Numerically stable algorithm for discrete ordinate method radiative transfer in multiple scattering and emitting layered media, *Appl. Opt.*, *27*, 2502–2509.

Stamnes, K., J. Slusser, and M. Bowen (1991), Derivation of total ozone abundance and cloud effects from spectral irradiance measurements, *Appl. Opt.*, *30*(30), 4418–4426.

World Meteorological Organization (WMO) (1994), *Scientific Assessment of Ozone Depletion: 1994*, Geneva, Switzerland.

WMO (1998), *Scientific Assessment of Ozone Depletion: 1998*, Geneva, Switzerland.

WMO (2002), *Scientific Assessment of Ozone Depletion: 2002*, Geneva, Switzerland.

M. Allaart, Royal Netherlands Meteorological Institute, NL-3730 De Bilt, Netherlands.

C. Brogniez, M. Houët, and J. Lenoble, Laboratoire d'Optique Atmosphérique, CNRS, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq, France. (colette.brogniez@univ-lille1.fr)

T. Cabot and A. de la Casinière, Interaction Rayonnement Solaire Atmosphère, Université Joseph Fourier, F-38000 Grenoble, France.

E. Kyrö, Arctic Research Center, Finnish Meteorological Institute, FIN-99600 Sodankylä, Finland.

A. M. Siani, Physics Department, University of Rome "La Sapienza," I-00185 Rome, Italy.

P. Weihs, Institut fuer Meteorologie und Physik, Universitaet fuer Bodenkultur, A-1190 Vienna, Austria.