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On the accuracy of Total Ozone Mapping Spectrometer retrievals over tropical cloudy regions

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Abstract. Motivated by the desire to accurately derive tropospheric ozone from Total Ozone Mapping Spectrometer (TOMS) measurements, we investigate several aspects of these observations in the presence of highly reflecting clouds. Using the collocated Temperature Humidity InfraRed (THIR) measurements of cloud-top pressures, we identify three TOMS algorithm errors resulting from the inaccurate assignment of cloud-top pressure. The most significant error results from the inappropriate tropospheric ozone amount added below cloudy scenes to complete the total ozone column. After accounting for the cloud-height errors, we find significant total ozone column excesses of 10-15 Dobson units (DU) (1 DU = 2.6867×10^{16} molecules cm^{-2}) over high-altitude, highly reflecting clouds compared with clear area observations. After accounting for additional algorithm errors involving the tropospheric ozone climatology and considering potential dynamical, photochemical, and NIMBUS-7/Earth Probe calibration errors, approximately 4-9 DU excesses over cloudy scenes remain. We speculate that the TOMS algorithm approximation of clouds as opaque Lambertian reflecting surfaces may account for a significant portion of these unexplained excesses. The excess ozone due to calibration error and unknown sources will affect the tropospheric ozone derived from TOMS measurements using clear/cloudy difference techniques.

1. Introduction

Tropospheric ozone plays a key role in the chemical processes [*Logan et al.*, 1981] and energy budget of the troposphere [*Ramanathan and Dickinson*, 1979; *Fishman et al.*, 1979]. Although tropospheric ozone cannot be routinely retrieved from current space-based measurements, several methods have been developed to derive tropospheric ozone from satellite measurements. These methods include the Tropospheric Ozone Residual (TOR) method [*Fishman and Brackett*, 1997; *Fishman et al.*, 1990] (i.e., compute the difference between Total Ozone Mapping Spectrometer (TOMS) total ozone and Stratospheric Aerosol and Gas Experiment (SAGE) or Solar Backscattered Ultraviolet (SBUV) stratospheric ozone), the Modified Residual method from TOMS measurements [*Kim et al.*, 1996; *Hudson and Thompson*, 1998], and the Convective Cloud Differential (CCD) method [*Ziemke et al.*, 1998]. The first method suffers from poor spatial coverage in SAGE or from the uncertainties in the lower stratospheric ozone amounts in SBUV. The second method suffers from the uncertainties in the assumptions about stratospheric ozone and background tropospheric ozone. The CCD method [*Ziemke et al.*, 1998] derives tropospheric ozone by computing the difference between total ozone in clear areas and ozone above high-reflectivity clouds. The CCD method does not require other satellite ozone measurements as the TOR method; however, the CCD results depend on the accuracy of retrieved ozone above high-reflectivity clouds. Because the tropospheric ozone constitutes only about 10% of the total ozone, small errors associated with clouds might significantly affect the derived tropospheric ozone.

Ozone errors due to inaccurate cloud characterization in version-6 TOMS retrievals [*Hudson et al.*, 1995; *McPeters et al.*, 1996; *Thompson et al.*, 1993], which were addressed in version 7 (v7), concerned mostly low-altitude clouds. While the v7 corrected somewhat the excess ozone reported over these low-altitude clouds [*McPeters and Labow*, 1996], some discrepancies remain. One significant discrepancy involves the difference between the assumed cloud-top pressure and the actual pressure. The v7 uses the monthly International Satellite Cloud Climatology Project (ISCCP) climatology to determine cloud-top pressures, thereby reducing the difference between assumed cloud-top pressures and actual

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compared with previous versions; however, TOMS still does not use the actual value for the altitude of the cloud top. The cloud height error in the TOMS v7 data can be assessed with Temperature Humidity InfraRed (THIR) measurements collocated (temporally and spatially) with the NIMBUS-7 (N7) TOMS instrument. In addition, high-reflectivity clouds (i.e., reflectivity $\geq$ 80%) are treated as opaque Lambertian surfaces in the TOMS v7 algorithm. When cloud reflectivity is less than 80%, the algorithm uses a partial cloud model. This partial cloud model assumes that the reflected radiance results from a cloudy scene of reflectivity 80% with a cloud fraction f and from a clear scene of reflectivity 8% with a fraction of $1-f$ [*McPeters et al.*, 1996]. Becasue the actual clouds are not opaque Lambertian surfaces [*Knibbe et al.*, 2000] and might be extremely variable in the TOMS fields of view (FOV), the assumption of Lambertian surfaces and the partial cloud model might cause errors in the TOMS ozone retrieval.

This paper analyzes the cloud-height-induced errors, reanalyzes the total ozone difference between tropical high-altitude cloudy areas and neighboring clear areas by correcting these errors, and investigates other potential errors associated with TOMS measurements over high-reflectivity clouds. We describe the cloud-height-induced errors and their corrections in section 2. To investigate other potential errors associated with high clouds, we first correct cloud-height-related errors that can be assessed with THIR data. Section 3 reanalyzes the total-ozone difference between cloudy areas and clear areas in the v7 TOMS data after correcting the cloud height induced errors. Correction of cloud-height-related errors leads to excess ozone over cloudy areas, and we investigate the possible reasons for the excess ozone over cloudy areas in section 4. The impacts of cloud-related errors on derived tropospheric ozone are discussed in section 5 with conclusions in section 6.

2. Cloud Height Induced Errors and Their Correction

In the radiance look-up table for the TOMS v7 algorithm, the radiance is computed only at 1013-hPa (1 atm) and 405-hPa (0.4 atm) pressure levels. When the assumed cloud-top pressure is not at these two levels, the TOMS algorithm computes the calculated radiance by linearly interpolating/extrapolating the radiances at these levels, introducing an error in the retrieved ozone. Because the TOMS instrument cannot detect ozone below optically thick clouds, the retrieval strategy is to include a climatological tropospheric ozone amount below clouds according to a simple monthly ISCCP cloud climatology [*McPeters et al.*, 1996]. However, the monthly mean cloud climatology might be significantly different from the actual cloud heights and thereby introduce other ozone retrieval errors. On the one hand, the TOMS algorithm will mistreat the ozone absorption and Rayleigh scattering between the actual and assumed cloud pressure levels, which will affect the retrieved column ozone above clouds. On the other hand, incorrect cloud-top heights will affect the ozone added below clouds. We call the above three errors associated with cloud-top height as radiation interpolation error ($\Delta O_{3,\,rad}$), ozone retrieval error above cloud ($\Delta O_{3,\,above}$), and ozone retrieval error below cloud ($\Delta O_{3,\,below}$). The first error depends only on the assumed cloud height, while the last two errors are related to both the assumed and actual cloud heights. If we know the actual and assumed cloud heights, we can correct the TOMS-retrieved total ozone by the following equation:

$$O_{3,corrected} = O_{3,uncorrected} - \Delta O_{3,rad} - \Delta O_{3,below} - \Delta O_{3,above} \qquad (1)$$

The correction terms (ΔO_3) are defined in the sense that overestimates in total ozone column are positive. Then, these errors are removed by subtracting the overestimated ozone amount from the uncorrected column.

2.1 Radiation Interpolation Error

We obtain the radiation interpolation error using the TOMS version 7 algorithm (TOMSV7) and its forward model: TOMS radiative transfer code (TOMRAD). We calculate the backscattered radiances using TOMRAD, input those radiances into TOMSV7, and then retrieve the total ozone at the same input conditions. The difference between the retrieved total ozone and the input total ozone is defined as the radiation interpolation error in Dobson units (DU), (1 DU = 2.6867×10^{16} molecules cm^{-2}). Figure 1a shows the $\Delta O_{3,\,rad}$ as a function of cloud-top pressure, solar zenith angle ($\theta_\circ$), and satellite zenith angle (θ) for the TOMS standard low-latitude ozone profile L275 (i.e., with a total column ozone of 275 DU), cloud reflectivity of 90%, and latitude of 0°. The radiation interpolation error at 1013 hPa and 405 hPa is nearly

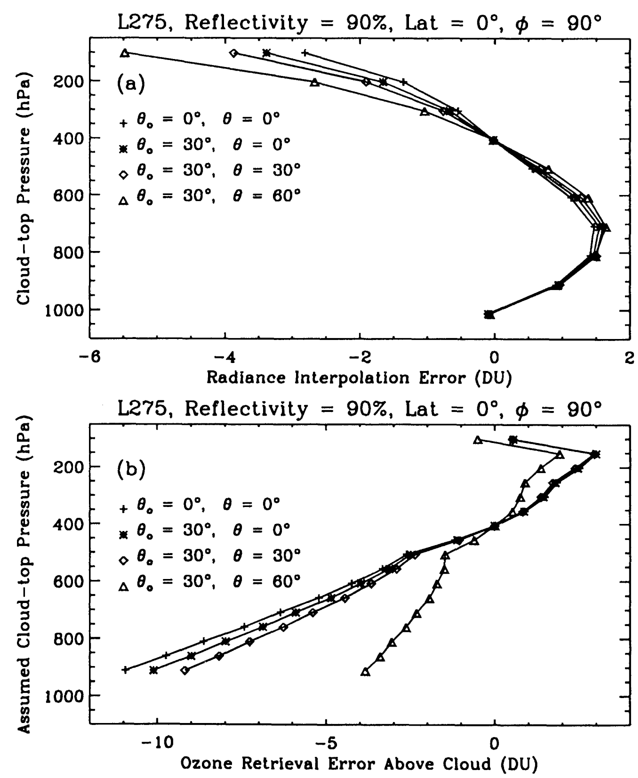

Figure 1. Cloud-height-induced errors for solar zenith angles $\theta_\circ$, satellite zenith angles θ, low-latitude 275 DU ozone profile, 90% cloud reflectivity, and relative azimuthal angle of 90°. (a) Radiation interpolation error. (b) Ozone retrieval error above cloud as a function of assumed (for ozone retrieval in TOMSV7) cloud-top pressures at an actual (for forward calculation in TOMRAD) cloud-top pressure of 405 hPa.

zero, because the look-up table used in the algorithm is computed at these two levels. Because the backscattered radiances are not linearly proportional to the cloud-top pressures, linear interpolation/extrapolation between these two levels causes some errors in the retrieved ozone. When the cloud-top pressure is greater than 405 hPa, $\Delta O_{3,\ rad}$ is positive and peaks at 700 hPa with a magnitude of about 1.7 DU. The viewing geometry has a small effect on $\Delta O_{3,\ rad}$ at pressures greater than 405 hPa. When the cloud-top pressure is less than 405 hPa, $\Delta O_{3,\ rad}$ is negative and increases in magnitude with the increase of cloud-top height. The viewing geometry has larger effects on $\Delta O_{3,\ rad}$ at altitudes above 405 hPa. The $\Delta O_{3,\ rad}$ at 100 hPa is about –2.8 DU at nadir and about –5.5 DU at $\theta_\circ$ = 30° and θ = 60°. The $\Delta O_{3,\ rad}$ varies little with cloud reflectivity. From cloud reflectivity of 80% to 100%, positive errors decrease only 0.2 DU at 700 hPa and negative errors decrease in magnitude by 0.8 DU at 100 hPa. Because the assumed cloud-top pressure in TOMS algorithm is usually greater than 300 hPa, the $\Delta O_{3,\ rad}$ is within ±2 DU in the TOMS v7 data. However, we should be careful when simulating ozone retrieval for high clouds at pressures of less than 300 hPa using TOMSV7 due to the larger $\Delta O_{3,\ rad}$ above such high-altitude clouds.

2.2. Retrieval Error Above Cloud

The ozone retrieval error above cloud, $\Delta O_{3,\ above}$, can also be assessed by using forward calculations in TOMRAD and by retrieving the total ozone in TOMSV7 at cloud-top pressures different from the pressure prescribed in TOMRAD. The $\Delta O_{3,\ above}$ is defined as the difference between the retrieved column ozone above cloud using the assumed (retrieval in TOMSV7) cloud-top pressure and the actual (forward calculation in TOMRAD) cloud-top pressure after the radiation interpolation error at each pressure level has been corrected. Because the $\Delta O_{3,\ above}$ depends on both the retrieval assumed and forward calculated actual cloud-top pressures, we put the actual cloud-top pressure at 405 hPa but assume cloud-top pressure at different pressure levels in the retrievals. Figure 1b shows the ozone retrieval error above cloud as a function of assumed cloud-top pressure. The $\Delta O_{3,\ above}$ is negative below 405 hPa and usually positive above 405 hPa in the upper troposphere. The $\Delta O_{3,\ above}$ peaks at 150 hPa, indicating that the retrieved ozone is the largest at 150 hPa for this set of measured radiances. Below 150 hPa, the $\Delta O_{3,\ above}$ is almost linearly proportional to the cloud-top pressure. The $\Delta O_{3,\ above}$ decreases with the increase of viewing geometry. The $\Delta O_{3,\ above}$ also varies with cloud reflectivity in magnitude because the multiple scattering error is largest for highest reflectivities, but it still maintains a similar shape as a function of cloud heights. From cloud reflectivity of 80% to 100%, positive errors increases by ~1 DU at 150 hPa and negative errors increase in magnitude by ~4 DU at 900 hPa. Atmospheric multiple scattering above the cloud increases for lower-altitude clouds, thus increasing the sensitivity to tropospheric ozone. This behavior results in the curve in Figure 1b, because the TOMS algorithm erroneously corrects for multiple scattering from low-altitude clouds that are actually at 405 hPa. The opposite effect occurs above 405 hPa for the analogous reason.

Although the results in Figure 1b are calculated for clouds at 405 hPa in the forward model, those results can be used to determine $\Delta O_{3,\ above}$ for any pair of actual and assumed cloud pressures to within ±0.4 DU (within ±0.1 DU if none of the two levels is less than 300 hPa) by taking the difference of the abscissa value retrievals (i.e., the value at the assumed pressure minus the value at the actual pressure) between any two pressure levels. Theoretically, the $\Delta O_{3,\ above}$ could be as large as -11 DU (the sum of –9 – 2 for $\theta_\circ$ = 0° and θ = 0°) if the actual cloud-top pressure is 200 hPa but assumed at 800 hPa. However, for tropical high-reflectivity clouds, the assumed cloud-top pressure is usually ~400 hPa, while the actual cloud-top pressure is less than 400 hPa. The $\Delta O_{3,\ above}$ under such conditions is underestimated within 2 DU. For a cloud actually at 100 hPa but assumed at 400 hPa, the $\Delta O_{3,\ above}$ is only -0.5 DU for the first three sets of viewing geometry and +0.5 DU for view zenith angle of 60°.

2.3. Retrieval Error Below Cloud

The ozone retrieval error below cloud is straightforward. This error is simply the amount of climatological ozone between the assumed and actual cloud-top heights. We define $\Delta O_{3,\ below}$, consistent with the other error terms, such that underestimates in the total column due to this error result in negative values. The $\Delta O_{3,\ below}$ depends on the cloud-height errors, the effective cloud fraction, and the actual vertical ozone profile. When the assumed cloud height is lower than the actual height, the total ozone will be underestimated because the algorithm fails to include the tropospheric ozone between the assumed and actual cloud altitudes. Larger differences between assumed and actual cloud height result in larger errors. $\Delta O_{3,\ below}$ is also linearly proportional to the cloud fraction. Therefore, an error of 100 hPa in cloud-top pressure at 40% reflectivity (effective cloud fraction of 0.44) has less effect on the ozone retrieval than a similar error at 80% reflectivity (effective cloud fraction of 1 for reflectivities ≥ 80%). The $\Delta O_{3,\ below}$ also depends on the actual ozone profile. Because TOMS observations provide no direct information about the vertical profile, the ozone below cloud is obtained from the TOMS standard ozone profiles derived from ozonesonde climatologies. The deviation of the TOMS standard profiles from the actual profile will lead to an error in the ozone added below a cloud. This error due to inappropriate climatological ozone profiles will be discussed in section 4. In this paper, we define $\Delta O_{3,\ below}$ based on the TOMS standard ozone profiles. The $\Delta O_{3,\ below}$ can be a significant fraction of the tropospheric column. For example, using the ozone profile L275, the ozone amount is about 8 DU between 200 and 400 hPa, about 16 DU between 100 and 400 hPa, and about 10 DU between 400 and 700 hPa.

These three errors can reinforce or cancel each other when added up. For example, an actual cloud height of 500 hPa, which is assumed to be at 200 hPa, results in a $\Delta O_{3,\ rad}$ of about -2 DU, a $\Delta O_{3,\ above}$ of about +4 DU, and a $\Delta O_{3,\ below}$ of about +11 DU, resulting in a corrected column +13 DU higher than the uncorrected column. An actual cloud at 200 hPa, assumed to be at 500 hPa, incurs a $\Delta O_{3,\ rad}$ of +1 DU, a $\Delta O_{3,\ above}$ of -4 DU, and a $\Delta O_{3,\ below}$ of –11 DU, resulting in a total error of -14 DU. For tropical high-reflectivity clouds, because the assumed cloud-top pressure is about 400 hPa and larger than the actual pressure, the $\Delta O_{3,\ rad}$ and $\Delta O_{3,\ above}$ are small and the total ozone error is dominated by the $\Delta O_{3,\ below}$, resulting in underestimating the actual ozone columns for these scenes. For high-altitude tropical clouds the total error can be quite significant.

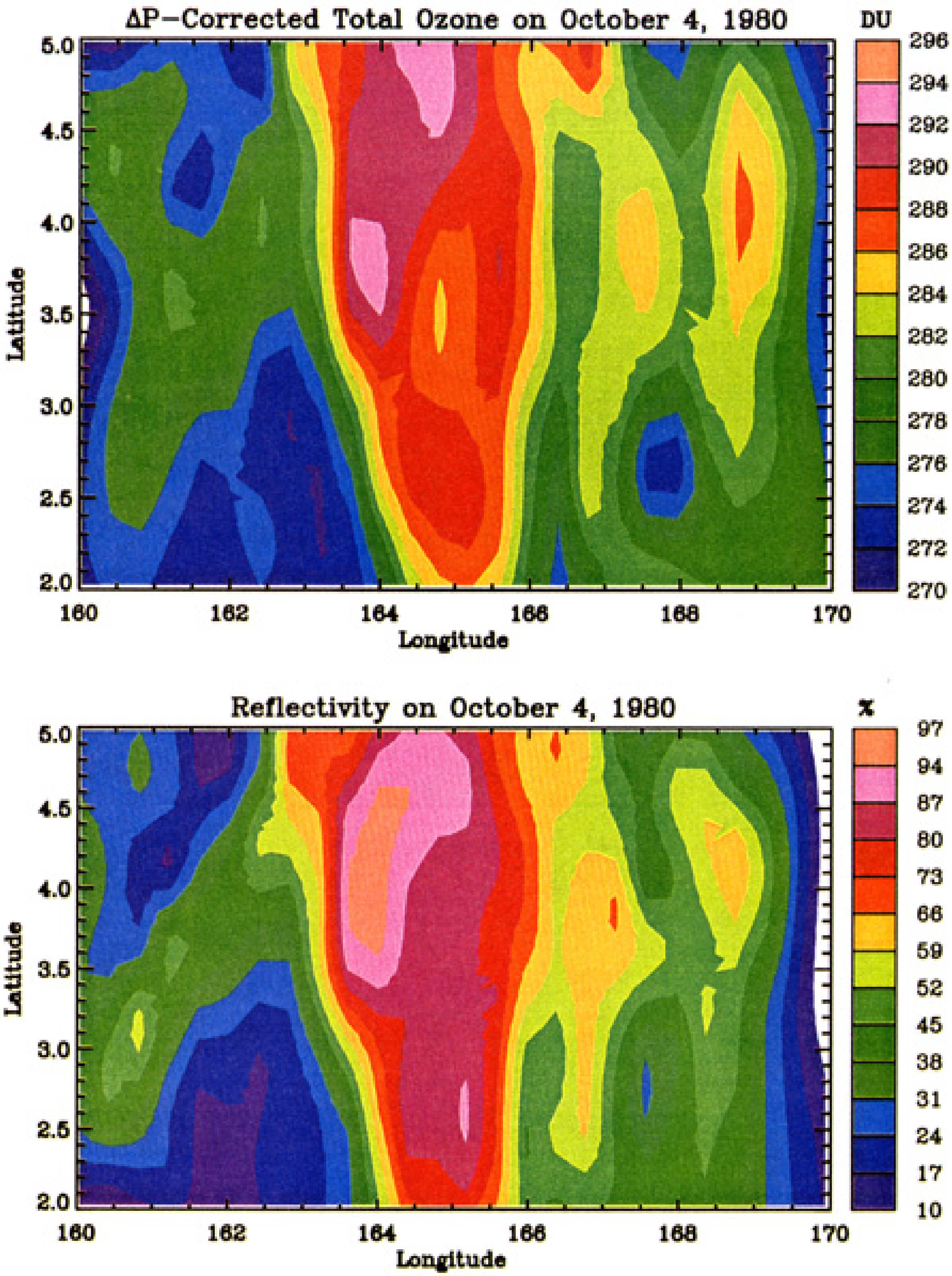

Plate 1. Spatial distribution of (top) total column ozone after ΔP correction and (bottom) reflectivity for the case in Figure 2.

2.4. Correction of Cloud-Height-Induced Errors

Correcting the cloud-height-induced errors described above requires knowledge of the actual cloud height. We use THIR cloud-top pressures to assess the cloud-height-induced errors. The THIR measurements are available from the beginning of the TOMS record in 1979 until the end of 1984 in the current TOMS v7 level 2 data. For high clouds, currently archived THIR data often report cloud-top pressures between 60 and 80 hPa and sometimes lower. These pressures correspond to altitudes significantly higher than the typical tropical tropopause pressure of ~100 hPa, indicating some errors in the derived cloud heights. The THIR data are currently being reprocessed at the NASA Goddard Space Flight Center (GSFC). In this new version THIR data, cloud-top temperatures are converted from THIR-measured radiances at 11.5 μm and cloud-top pressures are derived from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) 2.5° by 2.5° 6-hourly analyzed grids of temperature profiles. Because THIR pixels have higher spatial resolution than TOMS pixels, the THIR pixels (about 50 THIR pixels at low and middle latitudes) were averaged together with collocated TOMS fields of view (FOV). In this THIR cloud-height determination, the most significant source of potential error would be in the accuracy of the analyzed grids of the global NCEP/NCAR temperature data. In addition, the average of THIR 11.5-μm radiances over the collocated TOMS FOV could present a problem in cases of extremely variable cloud cover over the TOMS FOV (e.g., broken clouds) (D. Larko, personal communication, 2000). Cloud top pressures in the new version THIR data are seldom smaller than 100 hPa and are about 80 hPa larger than the old version THIR data for those high clouds above 200 hPa, with smaller differences for clouds between 200 and 600 hPa. Unfortunately, the new THIR data are available for only a few months in 1982, 1983, and 1984. We adjust all the archived THIR data for high clouds above 400 hPa based on the differences seen in the few months of the new THIR data. This approximate correction essentially applies correction bias between the new THIR cloud pressures and the archived THIR cloud pressures to the entire data set [*Newchurch et al.*, 2001]. The THIR cloud data are also less accurate when cloud reflectivity is less than 40%. However, owing to the smaller effective cloud fraction at low reflectivity, this effect of inaccuracy in THIR is commensurately smaller.

We designate the correction of the above three cloud-height-induced errors as the ΔP correction. For $\Delta O_{3,\ above}$ and $\Delta O_{3,\ rad}$, we use TOMRAD and TOMSV7 to build look-up tables of these errors as a function of cloud height, total ozone (using low-latitude ozone profiles L225, L275, and L325), cloud reflectivity, solar zenith angle ($\theta_\circ$ = 0°, 15°, 30°), and satellite zenith angle (θ = 0°, 15°, 30°, 45°, 60°). We then linearly interpolate these parameters (cosine of the solar zenith angle and the cosine of the satellite zenith angle) to obtain these errors for all conditions. For $\Delta O_{3,\ below}$, we compute the ozone amounts between any given two pressure levels using the two profiles that bracket the given total ozone and then linearly interpolate to get the ozone amount between these levels for the given total ozone. The $\Delta O_{3,\ below}$ is simply this ozone amount multiplied by the effective cloud fraction. The current TOMSV7 algorithm interpolates/extrapolates the climatological ozone below clouds from the first two Umkehr layer amounts of ozone (1013-506 hPa, 506-253 hPa). Because the ISCCP cloud-top pressures are usually greater than 250 hPa, this extrapolation does not incur errors. However, when using the TOMSV7 algorithm to simulate ozone retrieval for high clouds above 250 hPa, additional care should be taken to avoid this interpolation error by using the first four Umkehr layer amounts of ozone.

3. Total Ozone Differences Between Cloudy and Clear Areas

We investigate ozone retrieval errors over high-reflectivity cloudy areas by analyzing the total column ozone difference between cloudy areas and clear areas. An assumption used in this analysis of the total ozone difference is that the ozone amount above the cloud-top altitude is the same for both clear and cloudy areas. This assumption is also invoked in the CCD method. The retrieved ozone in clear areas could contain errors because of the lower sensitivity of TOMS to lower tropospheric ozone [*Klenk et al.*, 1982; *Hudson et al.*, 1995], which will be discussed in section 4.1. We first corrected the cloud-height induced errors using the adjusted THIR data for subsequent investigation of other ozone retrieval errors.

Figure 2a shows a scatterplot of the TOMS total ozone versus TOMS-measured 380-nm reflectivity in a region with a range of scenes from high convective clouds to clear areas. Ozone columns over the high clouds are about 5 DU larger

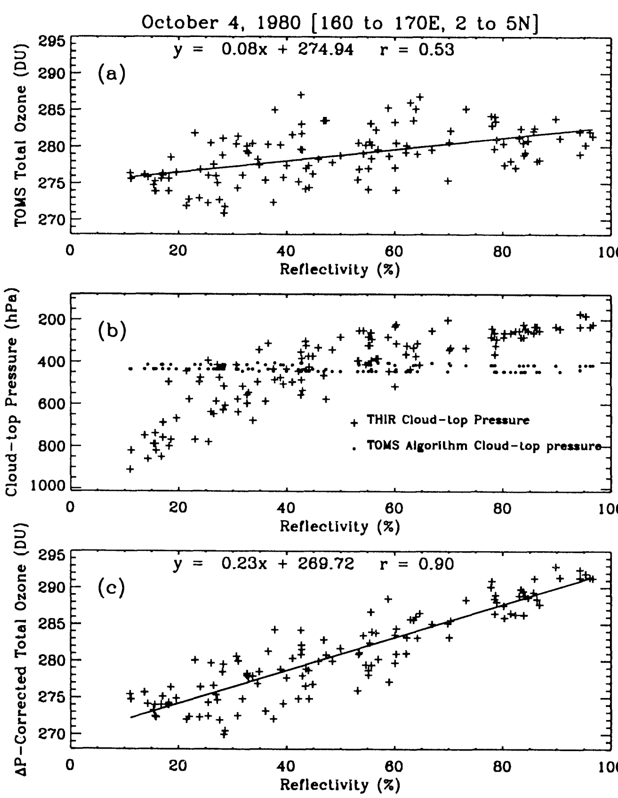

Figure 2. Example of total ozone distribution in the western Pacific Ocean (160°-170°E, 2°-5°N) on October 4, 1980. (a) TOMS-retrieved total ozone versus TOMS-measured 380-nm reflectivity. (b) TOMS-assumed and THIR-measured cloud-top pressure versus reflectivity. (c) Total ozone after ΔP correction versus reflectivity.

than columns over the adjacent clear areas. The cloud-top pressure difference between the TOMS-assumed and the THIR-measured, seen in Figure 2b, shows the TOMS-assumed cloud-top pressure is about 420 hPa, but the THIR pressure varies directly with the reflectivity. Compared with the THIR-measured pressure, the TOMS-assumed pressure is usually overestimated at reflectivity greater than 40% and underestimated at reflectivity less than 40%. The result of applying the ΔP correction to this case appears in Figure 2c. The ΔP correction typically increases the magnitude of the slope by 15 DU/100%-reflectivity and shows a much stronger correlation between ozone and reflectivity. The spatial correlation for this case is clearly shown in the high spatial coherence between the total ozone and reflectivity seen in Plate 1. The correction is most remarkable for high-reflectivity pixels (greater than 80%), increasing the total ozone by about 9 DU. Although the cloud-top-pressure difference between the THIR pressure and the assumed pressure is also very large for low-reflectivity clouds, the correction is very small. The corrected slope drops by only 2 DU/100% when excluding the partially cloudy pixels. Owing to the smaller effective cloud fraction at lower reflectivity, the ΔP correction diminishes with lower reflectivity cases. Of the 15 DU/100% slope increase, 12 DU/100% is contributed by $\Delta O_{3,\ below}$. $O_{3,\ above}$ and $\Delta O_{3,\ rad}$ together account for the other 3 DU/100% increase. After correction, the total ozone difference between the cloudy locations (reflectivity greater than 80%) and adjacent clear locations (reflectivity less than 20%) is ~15 DU.

The above case, which shows a strong correlation between ozone and reflectivity after ΔP correction, is not occasional, but rather is frequent in tropical high-reflectivity cloudy areas. To demonstrate this result, we select two regions in the western Pacific Ocean (160°-170°E, 2°-5°S and 160°-170°E, 2°-5°N) and two regions in equatorial Africa (10°-20°E, 2°-5°S and 10°-20°E, 2°-5°N) to analyze the total ozone differences between cloudy and clear areas. We chose these regions because indirect satellite measurements [*Fishman and Brackett*, 1997; *Fishman et al.*, 1990; *Kim et al.*, 1996; *Ziemke et al.*, 1998] indicate that tropical tropospheric ozone is usually lowest in the western Pacific Ocean, except in El Niño years, and highest in the Atlantic Ocean and Africa. Errors in the locations of maximum and minimum total ozone might give the range of errors in tropical areas. Figures 3a and 3b show the time series of the uncorrected total column-ozone differences (cloudy/clear total ozone) between cloudy areas (scenes with reflectivity ≥80%) and clear areas (scenes with reflectivity ≤20%) in 1980. The restriction on cloud reflectivity excludes the effects of partial clouds on the following results. The uncorrected column ozone differences throughout 1980 range from approximately −10 to +10 DU. The ΔP correction is applied to only cloudy measurements. The ΔP-corrected column ozone differences (Figures 3c and 3d), however, are all positive and significantly larger than the uncorrected results. The average total ozone difference increases from 2 ± 3 DU to 15 ± 3 DU in the two western Pacific Ocean regions and from 1 ± 5 DU to 11 ± 3 DU in the two equatorial Africa regions. The mean assumed cloud-top pressure, taken from the monthly ISCCP, is 435 ± 21hPa for the two western Pacific Ocean regions and 431 ± 54 hPa for the two equatorial Africa regions, while the actual cloud-top pressure from the THIR instrument is 182 ± 20 hPa and 253 ± 55 hPa, respectively. Because the cloud-top pressure is overestimated by ~200 hPa and the cloud-height-induced errors are dominated by $\Delta O_{3,\ below}$, the ΔP correction, therefore, leads to much larger total ozone differences between cloudy areas and clear areas. The change in the cloudy/clear total column-ozone difference due to corrections of $\Delta O_{3,\ rad}$ and $\Delta O_{3,\ above}$ is only ~2 DU, consistent with the results shown in Figure 1.

Figure 4 indicates the time series of uncorrected total column ozone differences in the same regions in 1999 using Earth Probe (EP) TOMS v7 data. Compared with N7 TOMS data (Figures 3a and 3b), the slopes are shifted toward more negative values. The average total column ozone differences are −4 ± 2 DU and −6 ± 6 DU for western Pacific Ocean regions and equatorial Africa regions, respectively. The total ozone difference between cloudy and clear areas in EP is about 6 DU less than that in N7. During the EP TOMS period, THIR cloud data are not available for correcting cloud-height-induced errors. However, we expect the magnitude of ΔP correction should be similar to the magnitudes in Figure 3, because the assumed cloud-top pressure is the same in 1980 and 1999 and the actual-top pressure is expected to be similar. Therefore if we have the actual cloud-top pressure for ΔP correction, the total ozone differences between high-reflectivity cloudy and clear areas in 1999 will still be positive but about 6 DU less than those in 1980. This bias in the total ozone difference between high-reflectivity and low-

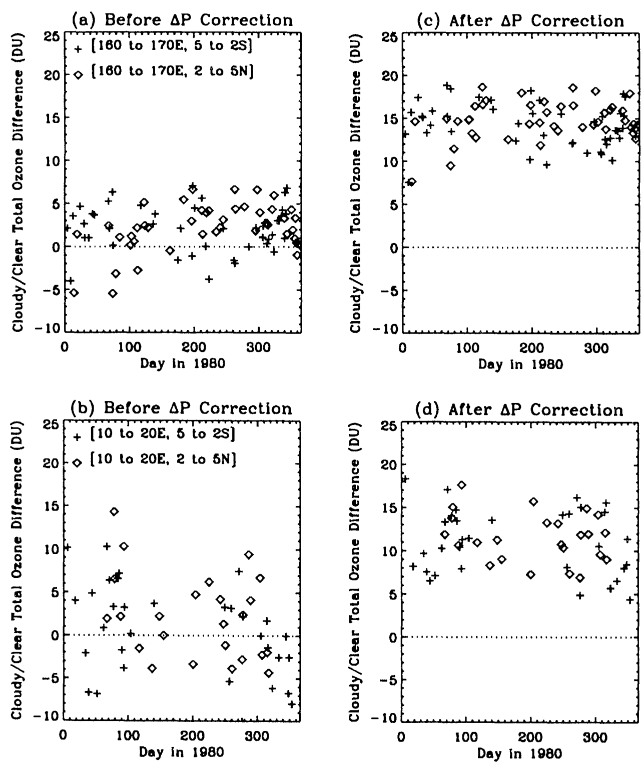

Figure 3. Time series of the total ozone difference between clear areas (reflectivity ≤20%) and cloudy areas (reflectivity ≥80%) for (a) two regions in the tropical western Pacific Ocean and (b) two regions in equatorial Africa in 1980. (c) Results after ΔP correction to the data in Figure 3a. (d) Results after ΔP correction to the data in Figure 3b.

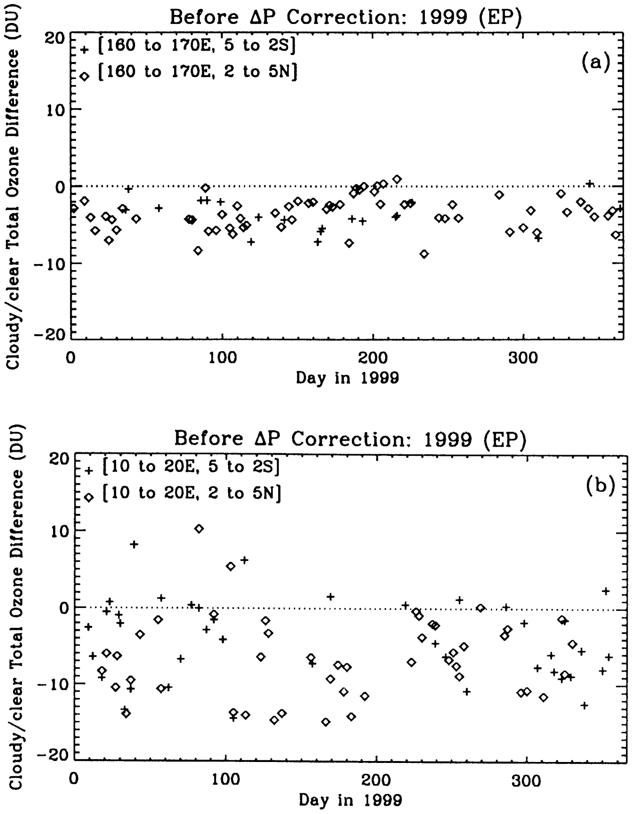

Figure 4. Same as Figures 3a and 3b except for EP TOMS data in 1999.

reflectivity pixels could be due to some nonlinearity calibration errors in EP or N7 or both. The EP instrument is the most recent, and probably best calibrated [*Stolarski et al.*, 2000] (S. Taylor, personal communication, 1999; G. Jaross, personal communication, 2000), but we cannot resolve this difference currently.

After ΔP correction, a strong positive relationship between total ozone and reflectivity remains in N7 TOMS data (and is expected in ΔP-corrected EP TOMS) over tropical high-reflectivity cloudy and neighboring clear areas. If the nonlinearity calibration error is in only the N7 TOMS instrument, excess amounts of at least 9 DU and 4 DU remain unexplained in western Pacific Ocean regions and equatorial African regions, respectively. If EP TOMS still has a residual nonlinearity, the amount of unexplained excess ozone could be either increased or decreased. This excess ozone over cloudy areas must be due to either geophysical phenomena (dynamical redistribution or chemical production) or to some other ozone retrieval errors or both. The sources that lead to cloudy and clear differences in the total ozone will be discussed in section 4.

4. Sources of Excess Ozone Over Cloudy Areas

4.1. Incorrect Tropospheric Ozone Profile

In the two western Pacific Ocean regions, the average THIR cloud-top pressure is 182 hPa, and the TOMS algorithm uses an average of 26 DU climatological tropospheric ozone to add below clouds. However, the average tropospheric ozone (tropopause is ~100 hPa) derived by *Fishman et al.* [1990] and *Ziemke et al.* [2000] is about 20-25 DU. The average tropospheric ozone (1000-100 hPa) of Southern Hemisphere Additional Ozonesonde (SHADOZ) measurements (http://hyperion.gsfc.nasa.gov/Data_services/shadoz/) in 1998-1999 is 20.6 DU (75 profiles) at Fiji (18°S, 178°E) and 24.5 DU (43 profiles) at Java (7°S, 113°E) [*Thompson and Witte*, 1999]. In the two equatorial Africa regions, the average THIR cloud-top pressure is 253 hPa, and the TOMS algorithm adds 24 DU climatological tropospheric ozone below clouds. This climatological tropospheric ozone can be assessed by using ozonesonde measurements at Brazzaville, Congo (4°S, 15°E), during the 1990-1992 TRACE-A period [*Olson et al.*, 1996], which is located in one of the equatorial Africa regions we defined. The annual average tropospheric ozone measured at Brazzaville is 40 DU and the ozone below 250 hPa is 31 DU (82 profiles), greater than the TOMS climatological ozone. Therefore, on average, the actual tropospheric ozone is smaller in the western Pacific Ocean and larger in equatorial Africa compared with the TOMS climatological tropospheric ozone. The effect of overestimating the tropospheric climatology is to overestimate the total column and vice versa. In regions of high-altitude clouds the column overestimate or underestimate is exactly the same as the climatology error. In clear regions, however, the overestimate (underestimate) is smaller in relation to cloudy regions because of the TOMS efficiency factor [*Hudson et al.*, 1995; *Klenk et al.*, 1982], which characterizes the less-than-perfect response to lower-tropospheric ozone amounts.

In order to quantify the effect of deviations from the climatology, we modified the TOMS standard low-latitude ozone profile with a total column ozone of 275 DU (called L275). The stratospheric ozone above 100 hPa is the same as L275 (i.e., 241 DU). For the western Pacific Ocean, the tropospheric ozone is replaced by the annual mean tropospheric ozone profile at Fiji and Java with a tropospheric ozone amount of 22 DU (10.5 DU in 1000-500 hPa, 7 DU in 500-250 hPa, 1.5 DU in 250-180 hPa, 180-125 hPa, and 125-100 hPa). The modified ozone profile has a total column ozone of 263 DU (called L263). For equatorial Africa, the tropospheric ozone is replaced by the annual mean tropospheric ozone profile at Brazzaville with a tropospheric ozone amount of 40 DU (18 DU in 1000-500 hPa, 13 DU in 500-250 hPa, 4 DU in 250-180 hPa, 3 DU in 180-125 hPa, and 2 DU in 125-100 hPa). The modified ozone profile has a total column ozone of 281 DU (called L281). With these ozone profiles, we calculate the radiances at top of the atmosphere under clear-sky condition (reflectivity 8%, surface pressure 1013 hPa, θ_o = 15°, θ = 30°) using TOMRAD and then input these radiances into TOMSV7 to retrieve the total ozone. TOMS overestimates the total ozone by ~2 DU for L263 and underestimates by ~2 DU for L281. Under cloudy conditions with reflectivities ≥80%, the retrieved ozone is overestimated by 7 DU for L263 (the cloud-top pressure is 180 hPa, 26 – 19 = 7 DU) and underestimated by 7 DU for L281 (the cloud-top pressure is 250 hPa, 31 – 24 = 7 DU). Accounting for overestimates due to incorrect climatology in the western Pacific Ocean (e.g., L263) results in a total cloudy/clear difference of ~5 DU (7 – 2) and leaves 4 DU (9 – 5) DU excess ozone over cloudy areas unexplained. In equatorial Africa, however, accounting for the underestimates due to incorrect climatology actually exacerbates the cloudy/clear differences by ~5 DU (7 – 2) and results in 9 DU (4 + 5) DU excess amount of ozone over cloudy areas unexplained.

Because the actual tropospheric ozone exhibits seasonality in these regions, the effect of incorrect TOMS standard climatology on total cloudy/clear difference also exhibits monthly variation. Similar calculation using the monthly mean ozonesonde profiles at these two regions indicates that the resulting cloudy/clear difference due to the incorrect TOMS tropospheric climatology ranges from –1 to 10 DU in the western Pacific Ocean and from –2 to –10 DU in equatorial Africa. However, averaging of monthly total cloudy/clear differences gives almost the same result as using annual mean profiles to represent the actual tropospheric ozone. The deviation (7 DU) of the actual tropospheric ozone from the climatological amount cannot fully account for the total ozone difference of 9 DU in the western Pacific Ocean.

4.2. Dynamical Influence of Deep Convection on Total Ozone Distribution

Deep convection that penetrates the mid-latitude tropopause will have two potential effects on the column ozone. First, the top of the convective complex will push the lower stratosphere up, resulting in a reduced stratospheric column ozone [*Poulida et al.*, 1996; *World Meterological Organization*, 1985; *Mattingly*, 1977]. However, the work of *Folkins et al.* [1999] and *Kley et al.* [1996] show that tropical convection rarely reaches the tropopause. Second, boundary layer and free tropospheric air raised in the convective columns will be deposited into the upper troposphere [*Poulida et al.*, 1996]. Over relatively clean marine areas, this convection effect will distribute low-ozone air throughout the troposphere. Although there is a seasonal cycle in the tropopause height at tropical locations [*Randel et al.*, 2000] and a seasonal cycle in the stratospheric ozone column in the tropics, with lowest values in January-April [*Logan*, 1999], which could be due to convection, the Brewer Dobson circulation being strongest in the northern winter, etc., this seasonal cycle cancels out in the cloudy/clear pair used here.

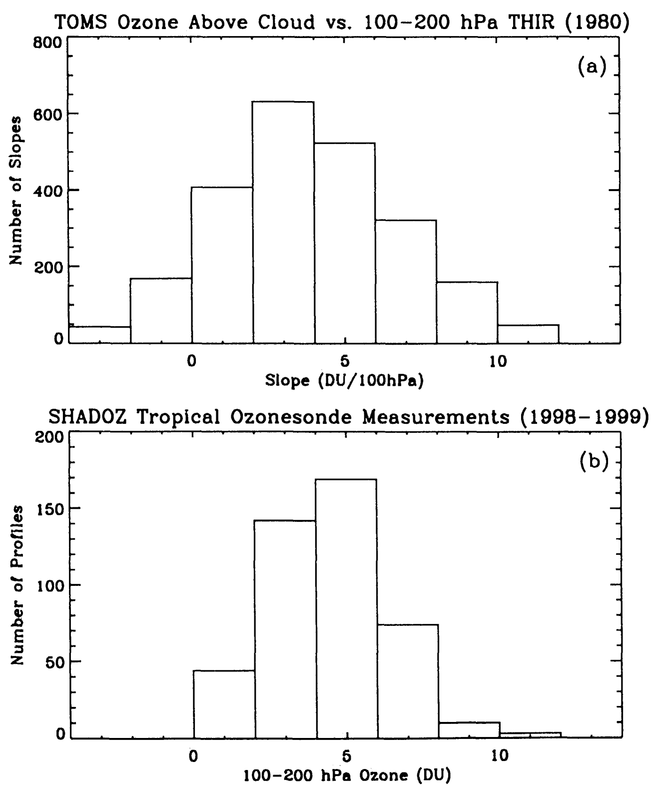

Figure 5. Histograms of ozone between 100 and 200 hPa. (a) Linear regression slope between TOMS ozone above cloud and THIR cloud-top pressure for measurements with reflectivity greater than 80% and THIR cloud-top pressure between 100 and 200 hPa. (b) SHADOZ ozonesonde measurements between 100 and 200 hPa at eight tropical stations in 1998-1999.

Seeking evidence for these effects, we inspect the tropical (10°S-10°N) TOMS data in 1980 for reflectivities greater than 80% and THIR cloud-top pressure between 100 and 200 hPa based on the linear regression slopes between TOMS-measured ozone above cloud and THIR. The slopes are calculated from accumulating individual daily data in 10° longitude × 5° latitude areas where there are more than 10 such individual measurements. The histogram of these slopes is shown in Figure 5a, in which we have omitted slopes not significant at the 2-sigma level. The mean slope is 4.0 ± 3.5 DU/100 hPa. By comparison, the tropospheric ozone between 100 and 200 hPa for all meteorological conditions from eight tropical SHADOZ ozonesonde measurements in 1998-1999 [*Thompson and Witte*, 1999] (Figure 5b) is 4.4 ± 1.9 DU, consistent with the mean TOMS slope. Because we see no significant statistical difference between TOMS columns between 100 and 200 hPa over cloudy conditions and ozonesonde measurements between 100 and 200 hPa over all conditions, we conclude that either the TOMS field of view is too large to see this localized effect or the effect actually does not occur.

4.3. Photochemical Production Over Convective Clouds

In polluted regions, deep convection can transport boundary layer ozone precursors such as NO_x and Volatile Organic Compounds (VOC) into the upper troposphere and lower stratosphere. Lightening associated with deep convective clouds would also produce a large amount of NO_x to participate in ozone generation. Photolysis frequencies are strongly coupled with the cloud field; high-reflectivity clouds largely increase the actinic flux and therefore increase the j values to produce ozone [*Madronich*, 1987]. Therefore one might expect some ozone production from these factors. However, using a photochemical model, *Pickering et al.* [1990] estimated that the diurnally averaged net ozone production rate is only 16 ppb d^{-1} at 7 km for convective cloudy conditions. The time periods associated with the formation and dissipation of these clouds, usually of the order of a few hours, are too short for chemical ozone production to explain the excess ozone over cloudy areas.

4.4. Treatment of Clouds as Opaque Lambertian Surfaces

The TOMS algorithm treats high-reflectivity clouds (reflectivity greater than 80%) as opaque Lambertian surfaces [*McPeters et al.*, 1996]. However, the actual clouds are not opaque surfaces; photons penetrate into the clouds. Under cloudy conditions, the multiple scattering in clouds enhances the ozone absorption path length. This effect can produce errors as large as 300 DU [*Mayer et al.*, 1998] in the retrieved ozone from ground global radiance measurements under very thick cloudy conditions without taking the effects of multiple scattering into account. Satellite-based remote sensing methods, which employ the backscattered radiation, are much less sensitive to this effect because the path length enhancement of reflected radiation is typically about 2 [*Kurosu et al.*, 1997], but still probably enough to produce an error of approximately 4-9 DU ozone depending on the photon penetration depth and the actual ozone in clouds. Because the cloud particles are much larger than the TOMS wavelengths, the photo pathlength enhancements should be very similar at all six TOMS wavelengths. However, the ozone absorption enhancement is wavelength dependent, stronger in the ozone absorptive wavelengths. The triplet method in the TOMSV7 algorithm cannot eliminate this effect and therefore will retrieve more ozone above clouds. The ozone absorption is also dependent on the actual ozone amount in clouds where photons reach. The ozone retrieval error due to treating clouds as opaque clouds is expected to be larger in the equatorial Africa region than the western Pacific Ocean region because there is usually more tropospheric ozone in the equatorial Africa region. In addition, high-altitude clouds near the tropopause consist of ice crystals. Neglecting the scattering properties by treating clouds as Lambertian surfaces might produce additional effects on ozone retrieval. From our reanalysis of the TOMS data over high tropical cloudy areas, there is still about approximately 4-9 DU excess amount of ozone remaining unexplained by geophysical phenomena or known retrieval errors. The treatment of the clouds as Lambertian surface, which does not account for in-cloud multiple scattering and the scattering properties of ice crystals, is potentially responsible for the excess retrieved ozone seen in our analysis.

4.5. Error Summary

Table 1 summarizes the cloud-related errors in 1980 from N7 TOMS v7 data over tropical high-reflectivity cloudy areas, including cloud-height-induced errors, incorrect tropospheric climatology, nonlinearity calibration errors, and unknown sources (e.g., treatment of clouds as non-Lambertian surfaces). After correcting for known algorithm errors (ΔP correction), TOMS reports 15 DU more ozone over cloudy regions than over clear regions in the Pacific Ocean and 11 DU more over cloudy observations in equatorial Africa. Assuming the actual annual mean tropospheric ozone is represented by 22 DU in the western Pacific Ocean and 40 DU in equatorial Africa, we can confidently ascribe about 5 DU of the Pacific difference and approximately –5 DU of the Africa difference to known incorrect tropospheric ozone climatology in the algorithm. Approximately 6-7 DU could be ascribed to a calibration error if all the N7-EP difference is allotted to N7 calibration error. Then, ~4 DU in the Pacific and ~9 DU in equatorial Africa remains unexplained with a 1σ uncertainty of 3 DU taken from the Table 1 standard deviations. The adjustment of THIR data reduces the ΔO_3 after ΔP correction by ~5 DU and decreases the unknown sources by only ~2 DU. The ozone differences due to unknown sources will change if the assumptions about the actual tropospheric ozone and calibration errors are inappropriate. The cloud-top pressure for high clouds is usually overestimated by ~200 hPa, causing an underestimate in the total ozone over cloudy areas by approximately 10-15 DU. The negative cloud-height-induced errors, however, tend to cancel the positive errors. Therefore the overall error is small in the current TOMSV7 total column ozone data. Although we discussed ozone retrieval errors only in tropical high-reflectivity cloudy areas, the errors are not confined to tropical cloudy areas but also apply to midlatitude and high-latitude regions.

5. Impacts of Ozone Retrieval Errors on Derived Tropospheric Ozone

Ozone retrieval errors associated with clouds can affect the derived tropospheric ozone from TOMS data. For the TOR method [*Fishman and Brackett*, 1997; *Fishman et al.*, 1990] that uses only the TOMS total column ozone over all-sky conditions, the ozone retrieval errors associated with clouds have almost no effect on the derived tropospheric ozone because the overall error in the total ozone is small. For the clear/cloudy difference method, which assumes that the difference between clear total ozone and ozone above clouds from TOMS is equal to the tropospheric column ozone; its accuracy depends on the retrieved total ozone both over clear areas and above clouds. Having accounted for the incorrect tropospheric climatology below clouds, the unexplained cloudy/clear difference is actually the ozone difference above the cloud level between cloudy areas and clear areas plus the calibration error. According to Table 1, the excess ozone above clouds is ~8 DU (calibration errors plus unknown sources, i.e., the sum of column 4 and column 6 in Table 1 minus $\Delta O_{3,\ rad}$ and $\Delta O_{3,\ above}$ errors of about 2 DU) in the western Pacific Ocean and ~14 DU in equatorial Africa. Regardless of whether the excess ozone over cloudy areas

Table 1. Contribution of Different Types of Errors to Annual Mean Total Ozone Cloudy/Clear Difference, ΔO_3 (DU), Over Tropical High Convective Clouds and Neighboring Clear Areas in 1980 NIMBUS-7 TOMSV7 Measurements[a]

Region	ΔO_3 Before ΔP correction	ΔO_3 After ΔP Correction	Calibration error[b]	Incorrect Climatology	Unknown Sources
Western Pacific Ocean	2(3)	15(3)	~ 6	~ 5[c]	~ 4
Equatorial Africa	1(5)	11(3)	~ 7	~-5[d]	~ 9

[a]Values in parentheses indicate 1 standard deviation. The ΔP correction is defined in section 2.4 as the sum of the radiation interpolation error and retrieval error above clouds and below clouds.
[b]Assume the calibration error is in only the N7 TOMS instrument.
[c]The annual average tropospheric ozone is assumed to be 22 DU in the western Pacific Ocean.
[d]The annual average tropospheric ozone is assumed to be 40 DU in equatorial Africa.

Table 2. Average Cloud-Top Pressure of Tropical High-Reflectivity (>80%) Clouds (P_{cld}), Ozone Over Those Clouds ($O_{3,\,ab}$), Ozone Below Clouds ($O_{3,\,bl}$) Derived by Using the Clear/Cloudy Difference From 1980 NIMBUS-7 TOMSV7 Measurements, Their Corresponding Values After Correcting Ozone Retrieval Errors Associated With Clouds, and the Stratospheric Ozone ($O_{3,\,strat}$) and Tropospheric Ozone ($O_{3,\,trop}$) Derived by Subtracting or Adding Ozone Between Clouds and the Tropopause (Assumed at 100 hPa) According to Ozonesonde Measurements[a]

Region	P_{cld}, hPa	$O_{3,ab}$, DU	$O_{3,bl}$, DU	Corrected $O_{3,ab}$, DU	Corrected $O_{3,bl}$, DU	$O_{3,strat}$, DU	$O_{3,trop}$, DU
Western Pacific Ocean	182(20)	248(9)	14(2)	240(9)	20(2)	237 (9)	23(2)
Equatorial Africa	253(55)	264(10)	14(5)	250(10)	30(5)	241(10)	39(5)

[a]Values in parentheses indicate 1 standard deviation.

results from ozone retrieval errors or geophysical phenomena, it will affect the basic assumption of the clear/cloudy difference method, tending to underestimate the tropospheric ozone. In addition, the insensitivity to lower tropospheric ozone will affect the retrieved ozone under clear conditions. On annual average, the clear-sky total ozone is overestimated by ~2 DU in the western Pacific Ocean and underestimated by ~2 DU in equatorial Africa due to the deviation from the TOMS standard climatological tropospheric ozone. Therefore the derived tropospheric ozone using the clear/cloudy difference method will be underestimated by ~6 DU (2 DU clear-sky overestimate – 8 DU cloudy-sky excess = -6 DU) in the western Pacific Ocean and ~16 DU (-2 DU underestimate – 14 DU excess = -16 DU) in equatorial Africa. In EP TOMS data, due to the bias of approximately 6-7 DU in the clear/cloudy difference, the derived tropospheric ozone is expected to be about correct in the western Pacific Ocean and underestimated by 9 DU in equatorial Africa. In the above analysis, the effects of ozone retrieval errors on derived tropospheric ozone are based on annual mean values and are subject to the accuracy of THIR cloud-top pressure and to the actual tropospheric ozone. However, the assignment of non-linearity calibration error to N7 TOMS does not affect the derived tropospheric ozone because both calibration errors and unknown sources contribute to the cloudy/clear ozone difference above cloud level.

Table 2 lists the average ozone above clouds (column 3) and the average retrieved tropospheric ozone below clouds (column 4) using the clear/cloudy difference (clear total ozone minus ozone above high reflectivity clouds) in the two western Pacific Ocean regions and the two equatorial Africa regions. The average values are derived from the daily values corresponding to Figures 3c and 3d, respectively. The derived tropospheric ozone is lower than the ozonesonde measurements at Brazzaville, Fiji, and Java, supporting the fact that the derived tropospheric ozone is underestimated. After correcting for the excess ozone over cloudy areas (6 DU for Pacific and 16 DU for equatorial Africa) and adding ozone between cloud tops and tropopause based on ozonesonde measurements (3 DU between 180 and 100 hPa for Pacific and 9 DU between 250 and 100 hPa for equatorial Africa), the tropospheric ozone is 23 DU in the western Pacific Ocean and 39 DU in equatorial Africa, consistent with the annual mean tropospheric ozone measured at Brazzaville, Java, and Fiji. The stratospheric ozone, after correction of the overestimation above clouds and subtracting ozone between cloud tops and tropopause, is 237 DU in the western Pacific Ocean and 241 DU in equatorial Africa. On average, the stratospheric ozone in equatorial Africa is 4 DU larger than that in the western Pacific Ocean, consistent with the observed stratospheric ozone wave 1 pattern of *Newchurch et al.* [2001].

The above analysis implies that the derived tropospheric ozone would be underestimated by using the clear/cloudy difference techniques. However, in the CCD method [*Ziemke et al.*, 1998], a clear/cloudy difference method, the particular stratospheric ozone sampling actually accounts, at least partly, for the discrepancy described above. The CCD method derives the assumed zonally invariant stratospheric ozone from the minimum ozone measurements in scenes with reflectivities greater than 90% in 5° longitude × 5° latitude areas in the western Pacific Ocean regions. The measurements with the monthly minimum ozone above clouds are probably over those clouds with tops up to the tropopause. But the monthly minimum ozone could cancel the erroneous overestimation of ozone over high clouds (~6 DU in the western Pacific Ocean) because the monthly minimum ozone is usually approximately 5-10 DU smaller than the average ozone above high clouds. The derivation of tropospheric ozone in equatorial Africa is more difficult because of the relatively lower and less frequent high-reflectivity clouds and larger excess ozone above clouds. The assumption of zonally invariant stratospheric ozone avoids this difficulty, but the derived ozone will be subject to this assumption. For example, the derived ozone in equatorial Africa will be overestimated by 4 DU if assuming the same stratospheric ozone as in the western Pacific Ocean. The total ozone difference between cloudy and clear areas from EP is about 6 DU less than that from N7. Because the excess ozone over high-reflectivity cloudy areas is smaller in EP, subtracting the smaller cloudy ozone from the total clear ozone results in about 6 DU more tropospheric ozone in EP. This result is consistent with the 5 DU bias of derived tropospheric ozone from EP and N7 TOMS data [*Ziemke et al.*, 2000].

6. Conclusions

Investigating the cloud-related retrieval errors in the TOMS version 7 (v7) data with collocated Temperature Humidity InfraRed (THIR) observations over tropical high-reflectivity cloudy areas, we find significant errors in the TOMS v7 data. These errors result primarily from the inaccurate ozone contribution below the clouds due to the misplaced cloud altitude and partially from radiance interpolation errors and ozone retrieval errors above the misplaced clouds. After applying the correct cloud-top pressure (obtained from THIR), using the appropriate amount of ozone below the cloud, and correcting the radiance interpolation error, we find total column ozone excesses in cloudy regions (reflectivity ≥80%) of 10-15 DU over neighboring clear regions (reflectivity ≤20%) in four representative tropical areas, two in the Pacific Ocean and two in equatorial Africa. Because of compensating errors, the current v7 TOMS total ozone contains much smaller cloudy/clear biases.

We investigated the following sources for those ozone excesses over clouds: incorrect tropospheric ozone climatology, dynamical and chemical influences, instrument calibration error, and the algorithm assumption of an opaque Lambertian scattering surface for cloudy scenes. Correcting the tropospheric ozone climatology reduces the excesses in the western Pacific Ocean but exacerbates the excesses in the equatorial Africa region. We see no evidence for either a dynamical or a chemical mechanism producing a real, geophysical ozone excess over cloudy regions. Minimizing the clear/cloudy discrepancy by ascribing all of a total ozone bias of approximately 6-7 DU between NIMBUS-7 (N7) and Earth Probe (EP) TOMS measurements to a N7 calibration error results in a tropical average cloudy excess of approximately 4-9 DU remaining unexplained.

Although the overall cloud-related error in the current TOMS v7 total ozone is rather small, the excess ozone above clouds is critical to the tropospheric ozone derivation using clear/cloudy difference techniques. Calibration errors and probably the treatment of clouds as Lambertian surfaces overestimate the ozone above high clouds, tending to underestimate the derived tropospheric ozone by approximately 6-16 DU from N7 TOMS data or approximately 0-9 DU from EP TOMS data by using the clear/cloudy difference techniques. The Convective Cloud Differential [*Ziemke et al.*, 1998] method, which derives the assumed zonally invariant stratospheric ozone from the monthly minimum ozone above high clouds in the western Pacific Ocean, cancels or partly cancels the excess ozone above high clouds because the monthly minimum ozone is significantly smaller than the average.

We speculate that a significant amount of this excess could be due to inaccurate treatment of clouds in the TOMS algorithm as opaque Lambertian surfaces rather than a multiple-scattering medium. Further detailed radiative transfer calculations using a non-Lambertian model compared with TOMS radiative transfer code and TOMS v7 algorithm will be performed to analyze the effects of both wavelength-dependent ozone absorption enhancement by in-cloud multiple scattering and scattering properties of ice crystals on ozone retrieval.

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References

Fishman, J., and V.G. Brackett, The climatological distribution of tropospheric ozone derived from satellite measurements using version 7 Total Ozone Mapping Spectrometer and Stratospheric Aerosol and Gas Experiment data sets, *J. Geophys. Res.*, *102,* 19,275-19,278, 1997.

Fishman, J., V. Ramanathan, P.J. Crutzen, and S.C. Liu, Tropospheric ozone and climate, *Nature*, *282,* 818-820, 1979.

Fishman, J., C.E. Watson, J.C. Larsen, and J.A. Logan, Distribution of tropospheric ozone determined from satellite data, *J. Geophys. Res.*, *95,* 3599-3617, 1990.

Hudson, R.D., J.-H. Kim, and A.M. Thompson, On the derivation of tropospheric column from radiances measured by the Total Ozone Mapping Spectrometer, *J. Geophys. Res.*, *100,* 11,137-11,145, 1995.

Hudson, R.D., and A.M. Thompson, Tropical tropospheric ozone from Total Ozone Mapping Spectrometer by a modified residual method, *J. Geophys. Res.*, *103,* 22,129-22,145, 1998.

Kim, J.H., R.D. Hudson, and A.M. Thompson, A new method of deriving time-averaged tropospheric column ozone over the tropics using Total Ozone Mapping Spectrometer (TOMS) radiances: Intercomparison and analysis using TRACE-A data, *J. Geophys. Res.*, *101,* 24,317-24,330, 1996.

Klenk, K.F., P.K. Bhartia, A.J. Fleig, V.G. Kaveeshwar, R.D. McPeters, and P.M. Smith, Total ozone determination from the Backscattered Ultraviolet (BUV) experiment, *J. Appl. Meteorol.*, *21,* 1672-1684, 1982.

Kurosu, T., V.V. Rozanov, and J.P. Burrows, Parameterization schemes for terrestrial water clouds in the radiative transfer model GOMETRAN, *J. Geophys. Res.*, *102,* 21,809-21,823, 1997.

Logan, J.A., M.J. Prather, S.C. Wofsy, and M.B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, *86,* 7210-7254, 1981.

Madronich, S., Photodissociation in the atmosphere 1. Actinic flux and the effects of ground reflections and clouds, *J. Geophys. Res.*, *92,* 9740-9752, 1987.

Mattingly, S.R., The contribution of extratropical severe storms to the stratospheric water vapor budget, *Meteorol. Mag.*, *106,* 256-262, 1977.

Mayer, B., A. Kylling, S. Madronich, and G. Seckmeyer, Enhanced absorption of UV radiation due to multiple scattering in clouds: Experimental evidence and theoretical explanation, *J. Geophys. Res.*, *103,* 31,241-31,254, 1998.

McPeters, R.D., et al., *Nimbus-7 Total Ozone Mapping Spectrometer (TOMS) Data Products User's Guide*, 67 pp., NASA, Washington, D.C., 1996.

McPeters, R.D., and G.J. Labow, 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, 1996.

Newchurch, M.J., D. Sun, and J.H. Kim, Zonal wave-1 structure in TOMS tropical stratospheric ozone, *Geophys. Res. Lett.*, *28,* 3151-3154, 2001.

Olson, J.R., J. Fishman, V.W.J.H. Kirchhoff, D. Nganga, and B. Cros, Analysis of the distribution of ozone over the southern Atlantic region, *J. Geophys. Res.*, *101,* 24,083-24,093, 1996.

Poulida, O., R.R. Dickerson, and A. Heymsfield, Stratosphere-troposphere exchange in a midlatitude mesoscale convective complex 1. Observations, *J. Geophys. Res.*, *101,* 6823-6836, 1996.

Ramanathan, V., and R.E. Dickinson, The role of stratospheric ozone in the zonal and seasonal radiation energy balance of the earth tropospheric system, *J. Atmos. Sci.*, *36,* 1084-1104, 1979.

Stolarski, R.S., R.D. McPeters, G.J. Labow, S.H. Frith, and L. Flynn, On the long-term calibration of the TOMS total ozone record, *Journal* , 2000.

Thompson, A.M., D.P. McNamara, K.E. Pickering, and R.D. McPeters, Effect of marine stratocumulus on TOMS ozone, *J. Geophys. Res.*, *98,* 23,051-23,057, 1993.

Thompson, A.M., and J.C. Witte, SHADOZ (Southern Hemisphere ADditional OZonesondes): A new data set for the Earth science community, *Earth Obs.*, *11,* 27-30, 1999.

World Meteorological Organization, *Global Ozone Research and Monitoring Project*, *Rep. 16*, *Atmospheric Ozone 1985*, vol. I, 478 pp., Geneva, 1985.

Ziemke, J.R., S. Chandra, and P.K. Bhartia, Two new methods for deriving tropospheric column ozone from TOMS measurements: Assimilated UARS MLS/HALOE and convective-cloud differential techniques, *J. Geophys. Res.*, *103,* 22,115-22,127, 1998.

Ziemke, J.R., S. Chandra, and P.K. Bhartia, A new NASA data product: Tropospheric and stratospheric column ozone in the tropics derived from TOMS measurements, *Bull. Am. Meteorol. Soc.*, *81,* 580-583, 2000.

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