

1 **Inter-annual and decadal changes in tropospheric**
2 **and stratospheric ozone**

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19 **Abstract.** Ozone data beginning October 2004 from the Aura Ozone Monitoring
20 Instrument (OMI) and Aura Microwave Limb Sounder (MLS) are used to evaluate the
21 accuracy of the Cloud Slicing technique in effort to develop long data records of
22 tropospheric and stratospheric ozone and for studying their long-term changes. Using
23 this technique, we have produced a 32-year (1979-2010) long record of tropospheric and
24 stratospheric ozone from the combined Total Ozone Mapping Spectrometer (TOMS) and
25 OMI. The analyses of these time series suggest that the quasi-biennial oscillation (QBO)
26 is the dominant source of inter-annual variability of stratospheric ozone and is clearest in
27 the Southern Hemisphere during the Aura time record with related inter-annual changes
28 of 30-40 Dobson Units. Tropospheric ozone also indicates a QBO signal in the tropics
29 with peak-to-peak changes varying from 2 to 7 DU. Decadal changes in global
30 stratospheric ozone indicate a turnaround in ozone loss around mid-1990's with most of
31 these changes occurring in the Northern Hemisphere from the subtropics to high latitudes.
32 The trend results are generally consistent with the prediction of chemistry-climate models
33 which include the reduction of ozone destroying substances beginning in the late 1980's
34 mandated by the Montreal Protocol.
35

36 **1. Introduction.**
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38 The measurement of tropospheric ozone from satellite remote sensing began with the
39 studies by *Fishman and Larsen* [1987] and *Fishman et al.* [1990]. In those studies
40 tropospheric column ozone (TCO) was derived by subtracting co-located stratospheric
41 column ozone (SCO) from total column ozone. SCO was calculated from Stratospheric
42 Aerosol and Gas Experiment (SAGE) ozone profile measurements while Total Ozone
43 Mapping Spectrometer (TOMS) measurements were used for total column ozone. The
44 method was named the tropospheric ozone residual (TOR) technique and was effective in

45 producing global maps of tropospheric ozone albeit limited primarily to a seasonal
46 climatology because of sparse data sampling for SAGE. *Chandra et al.* [2003] used the
47 greater spatial and temporal coverage of stratospheric ozone from the Upper Atmosphere
48 Research Satellite (UARS) Microwave Limb Sounder (MLS) in combination with TOMS
49 total ozone to improve monthly maps of TOR. More recently *Ziemke et al.* [2006] and
50 *Schoeberl et al.* [2007] used two separate residual algorithms combining Aura Ozone
51 Monitoring Instrument (OMI) and MLS measurements to produce global fields of TOR
52 with improved temporal and spatial coverage beyond previous studies.

53
54 An alternative residual technique is the convective-cloud differential (CCD) method
55 [*Ziemke et al.*, 1998] which uses total column ozone and SCO from the same satellite
56 instrument. The CCD method is the most basic form of “cloud slicing” for measuring
57 tropospheric and stratospheric ozone [e.g., *Ziemke et al.*, 2001, 2009, and references
58 therein]. Gridded measurements from the CCD method are restricted to the tropics;
59 however mid-to-high latitude measurements may be obtained with this method and are
60 given generally as zonal averages over the Pacific. An advantage with the CCD method
61 is that by using a single instrument the potential errors arising from residual differencing
62 are largely alleviated. This is important for deriving a long record of TCO and SCO from
63 several combined instruments.

64
65 The CCD technique takes advantage of the fact that UV-measuring instruments such as
66 Total Ozone Mapping Spectrometer (TOMS), Global Ozone Monitoring Experiment
67 (GOME), and OMI do not measure ozone lying below optically thick clouds. The CCD
68 method assumes that one can make an accurate estimate of SCO using high-reflecting
69 deep convective clouds (reflectivity $R > 0.8$) in the tropical Pacific region. It was shown
70 by *Ziemke et al.* [2009] from combined Aura OMI and MLS measurements that ozone
71 concentrations inside thick clouds in the Pacific are small to within a few ppbv. The
72 CCD method works well for deriving SCO in the Pacific because the above-cloud
73 column ozone measured by OMI for thick clouds is essentially equivalent to SCO to
74 within 1-2 DU. The CCD method of *Ziemke et al.* [1998] further assumes that SCO is
75 invariant along longitude in the tropics. With these assumptions, TCO in tropical
76 latitudes can be calculated at any given location by differencing low reflectivity ($R < 0.2$)
77 total column ozone and high reflectivity ($R > 0.8$) SCO from the Pacific region within the
78 same latitude range. High reflecting clouds generally do not have physical cloud heights
79 reaching tropopause altitude and the column ozone above the cloud may vary
80 considerably even when $R > 0.8$. As a practical solution, SCO in the Pacific is calculated
81 using only minimum values of above-cloud column ozone in each gridded region. These
82 minimum values are then averaged over the eastern and western tropical Pacific to derive
83 a single measurement of SCO.

84
85 The validity of these assumptions has been established by comparing TCO and SCO
86 derived from the CCD method with TCO and SCO derived from ozonesondes and
87 satellite data including TOMS/MLS, TOMS/Halogen Occultation Experiment instrument
88 (HALOE), and TOMS/SAGE combinations [e.g., *Ziemke et al.*, 1998, 2005; *Chandra et al.*,
89 2003]. Application of the CCD method from TOMS data was extended over the

90 Pacific region into the middle and high latitudes between 50°S and 60°N [Ziemke *et al.*,
91 2005] for the time record 1979-2003.

92
93 The objective of this study is to evaluate strengths and weaknesses of the CCD technique
94 by incorporating Aura OMI and MLS ozone and to study inter-annual and decadal
95 changes in tropospheric and stratospheric ozone. The Aura MLS measurements of SCO
96 provide a stringent test of CCD SCO when compared to sparse satellite occultation
97 measurements in previous studies. This is important for establishing a long record (1979-
98 present) of CCD TCO and SCO from combined OMI and TOMS instrument
99 measurements. Long record data products are important for addressing issues including
100 trends in tropospheric ozone and pollution, stratospheric ozone depletion, and decadal
101 changes in the global Brewer Dobson Circulation.

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103 In the following, section 2 discusses the Aura OMI and MLS measurements, section 3
104 describes the CCD and OMI/MLS residual methodologies, section 4 discusses inter-
105 annual variability of tropospheric and stratospheric ozone, section 5 discusses some
106 results from the TOMS+OMI 1979-2010 extended ozone dataset, and finally section 6
107 provides a summary.

108 109 **2. Aura OMI and MLS Ozone Measurements.**

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111 The OMI and MLS are two out of a total of four instruments onboard the Aura spacecraft
112 which is flown in a sun-synchronous polar orbit at 705 km altitude with a 98.2°
113 inclination. Aura was launched in July 2004 and has been providing data measurements
114 since August 2004 to the present. The spacecraft has an equatorial crossing time of 1:45
115 pm (ascending node) with around 98.8 minutes per orbit (14.6 orbits per day on average).
116 Schoeberl *et al.* [2006] provide an overview of the EOS Aura mission and discuss the
117 various measurements from the four Aura instruments.

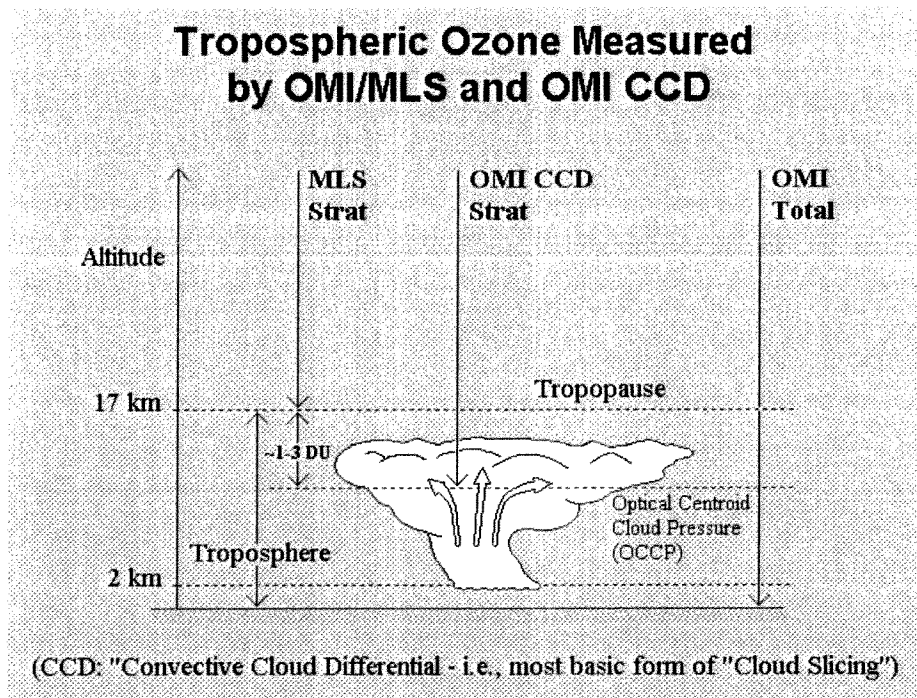
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119 The OMI is a nadir-scanner which at visible (350-500 nm) and UV wavelength channels
120 (UV-1: 270-314 nm; UV-2: 306-380 nm) detects backscattered solar radiance to measure
121 column ozone with near global coverage (aside from polar night latitudes) over the Earth
122 with a resolution of 13 km × 24 km at absolute nadir. Aside from ozone, OMI also
123 measures Optical Centroid Cloud Pressure (OCCP), aerosols, NO₂, SO₂, HCHO, and
124 several other trace gases in the troposphere and stratosphere [Levelt *et al.*, 2006].
125 Measurements of ozone from OMI are determined using the OMTO3 v8.5 algorithm
126 which is an extension of the TOMS v8 algorithm. A description of the TOMS v8
127 algorithm may be obtained from the TOMS V8 CD DVD ROM, or from the OMI
128 Algorithm Theoretical Basis Document (ATBD) from the TOMS web page
129 http://toms.gsfc.nasa.gov/version8/v8toms_atbd.pdf. One difference between the TOMS
130 v8 and the OMTO3 v8.5 algorithms is the treatment of clouds. The TOMS v8 and earlier
131 versions of OMTO3 use a cloud pressure climatology based on thermal infrared cloud-
132 top pressures, whereas OMTO3 v8.5 uses in situ OCCP derived with OMI by the
133 rotational Raman scattering method.

134

135 SCO is calculated for the OMI/MLS residual method using MLS v2.2 ozone. The MLS
136 instrument is a thermal-emission microwave limb sounder that measures vertical profiles
137 of mesospheric, stratospheric, and upper tropospheric temperature, ozone, and several
138 other constituents from limb scans taken in the direction ahead of the Aura satellite
139 orbital track. The MLS profile measurements are made about 7 minutes before OMI
140 views the same location during ascending (daytime) orbital tracks. These we refer to as
141 "co-located" measurements between OMI and MLS. MLS also measures ozone and
142 other atmospheric constituents for descending nighttime orbits which on a given day can
143 be up to ± 12 hours different in time from OMI daytime measurements. With combined
144 ascending and descending nodes MLS makes around 3500 vertical profile measurements
145 over the Earth per day. This study includes only the ascending orbit co-located data from
146 MLS for deriving SCO. Details regarding the instrument including spectrometers,
147 spectral channels, calibration, and other topics are discussed by *Waters et al.* [2006] and
148 in related papers in the same journal. *Froidevaux et al.* [2008; and personal
149 communication, 2011] provides validation results for MLS v2.2 measurements of ozone
150 and other trace gases. At the present time an MLS v3.3 data product is also provided to
151 the science community. While v2.2 retrieval has 37 pressure levels, v3.3 has 55 pressure
152 levels and other improvements; however, v3.3 also has more outliers/missing data in the
153 ozone measurements than with v2.2. Our analysis of SCO derived from MLS shows that
154 there is little difference between using v2.2 or v3.3 other than a small systematic offset
155 (v3.3 minus v2.2) of about 2.5 DU. Information regarding MLS v3.3 ozone
156 measurements is available online from the NASA Data and Information Services Center
157 (http://disc.sci.gsfc.nasa.gov/gesNews/mls_new_data_version_release).
158

159 3. The CCD and OMI/MLS Residual Methodologies.

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161 Two residual methods are used for deriving TCO and SCO from Aura OMI and MLS
162 measurements. The first is the approach of *Ziemke et al.* [2006] and the second is the
163 CCD method of *Ziemke et al.* [1998]. Figure 1 is a schematic diagram illustrating both of
164 these residual techniques in the tropics where the tropopause is typically ~16-17 km
165 altitude year-round.
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169 **Figure 1.** Schematic illustration of the OMI/MLS tropospheric ozone residual method
170 (OMI total column ozone minus MLS stratospheric column ozone) and the convective-
171 cloud differential (CCD) residual method (OMI total column ozone minus OMI above-
172 cloud column ozone).

173

174 3.1. The OMI/MLS Residual Method.

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176 For the OMI/MLS residual method in Figure 1, SCO is derived from vertically integrated
177 MLS ozone profiles which are subtracted from OMI total column ozone to derive TCO.
178 Tropopause pressure, which separates tropospheric from stratospheric column ozone
179 comes from National Centers for Environmental Prediction (NCEP) using the World
180 Meteorological Organization (WMO) $2\text{K}\cdot\text{km}^{-1}$ lapse rate tropopause definition. SCO
181 from MLS is determined by pressure integration of ozone volume mixing ratio profiles
182 from 0.0215 hPa down to the NCEP tropopause. The MLS ozone profile measurements
183 were linearly interpolated in log-pressure to the existing NCEP tropopause pressure to
184 derive SCO. MLS SCO (in Dobson Units, DU; $1\text{ DU} = 2.69 \times 10^{20}\text{ molecules}\cdot\text{m}^{-2}$) was
185 determined by standard log-pressure integration of ozone volume mixing ratio:

186
$$\text{SCO} = 0.79 \int_{0.0215\text{hPa}}^{P_{\text{tropopause}}} X P \cdot d \ln P, \text{ where } X \text{ is ozone volume mixing ratio in units ppbv}$$

187 and P is pressure in units hPa. The recommended range for scientific analysis of MLS
188 v2.2 ozone profiles is 0.0215-215 hPa. As was done by Ziemke *et al.* [2006], nearly
189 global SCO from MLS for each day was achieved by including ozone retrievals down to
190 316 hPa.

191

192 MLS SCO data were binned to 1° latitude \times 1.25° longitude to be compatible with OMI
193 level-3 (L3) gridded total column ozone. Tropopause pressures from NCEP analyses

194 were re-binned to this same resolution from a coarser $2.5^\circ \times 2.5^\circ$ gridding. It is noted for
195 MLS limb measurements that the horizontal optical path is about 300 km which is larger
196 than the horizontal size of OMI L3 gridded data, but is comparable to the size of original
197 NCEP gridded measurements. To derive a high density SCO field we have used the two-
198 step spatial interpolation of *Ziemke et al.* [2006]. The interpolation for SCO includes first
199 a moving 2D (latitude/longitude) Gaussian window along daytime orbit to fill in
200 intermittent gaps along-track for MLS SCO, followed secondly by a linear interpolation
201 along longitude between existing MLS SCO data. This interpolation approach preserves
202 the along-track measurements of SCO from MLS at all latitudes. NCEP measurements of
203 tropopause pressure were re-binned to the same 1° latitude \times 1.25° longitude resolution.
204 Following the determination of SCO and TCO at $1^\circ \times 1.25^\circ$ resolution, the SCO data
205 were averaged in $5^\circ \times 5^\circ$ bins to be compatible with OMI SCO from the CCD method.

206 207 **3.2. The CCD Residual Method.**

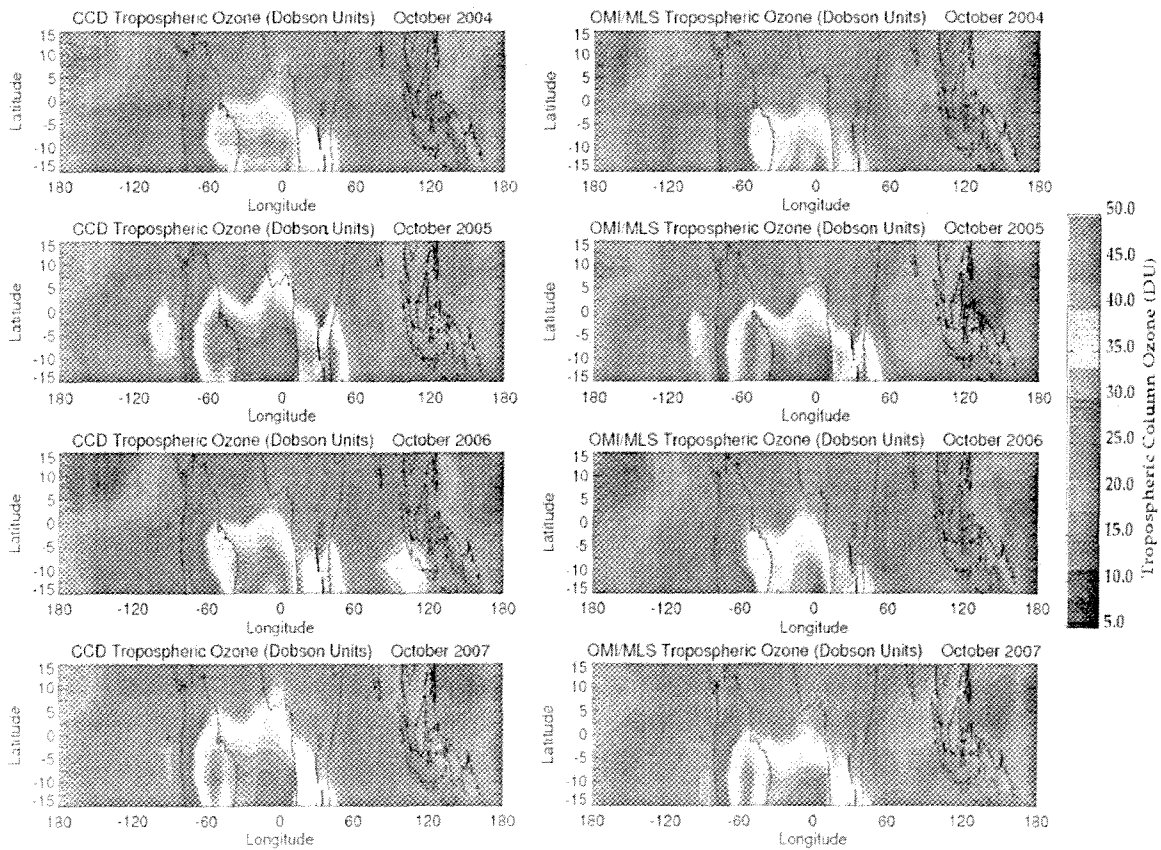
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209 The CCD method illustrated in Figure 1 uses a collective ensemble of high reflectivity
210 (i.e., reflectivity $R > 0.8$) above-cloud column ozone measurements from OMI within
211 specified gridded regions (here 5° latitude \times 5° longitude boxes) to determine SCO.
212 Cloud tops that lie lower in the troposphere will have larger above-cloud column ozone
213 amounts provided that spatial variability of ozone is small over the region. High
214 reflectivity scenes represent generally deep convective cloud systems, however their
215 physical cloud tops may not generally reach tropopause altitude and column ozone above
216 the cloud may vary considerably even with $R > 0.8$. As a practical approach, SCO in the
217 Pacific is estimated statistically within each gridded region using only minimum values
218 of above-cloud column ozone. This is done within each region by subtracting 2σ from
219 the mean value where σ is calculated RMS of the ensemble. All calculations are made
220 each day with an absolute minimum number of $R > 0.8$ level-2 footprint scenes in each
221 $5^\circ \times 5^\circ$ region chosen as 10.

222
223 The minimum ensemble values are associated with deep convective clouds with small
224 ozone concentration lying between the OCCP and the tropopause. Evidence for the latter
225 effect in tropical latitudes was shown by *Kley et al.* [1996] during the Central Equatorial
226 Pacific Experiment (CEPEX). Their study indicated from ozonesondes near-zero ozone
227 concentrations in the upper troposphere with the passing of deep convective cloud
228 systems. Possible mechanisms stated for the exceedingly low ozone measurements in the
229 upper troposphere included chemical destruction of ozone by yet unidentified reactions
230 and vertical transport via convective clouds of very low ozone concentrations from the
231 low troposphere. Low ozonesonde concentration in the upper troposphere is also
232 described in later studies by *Folkins et al.* [2002] and *Solomon et al.* [2005] as an
233 indicator of deep convection and associated vertical injection of low ozone amounts
234 upwards from the boundary layer/low troposphere. *Vomel and Diaz* [2010] in a more
235 recent paper suggest that the near-zero ozone concentrations in the upper troposphere by
236 *Kley et al.* [1996] were biased low because of uncertainties in ozonesonde cell currents.
237 Following a reprocessing of the CEPEX ozonesondes, *Vomel and Diaz* [2010] indicated
238 that lowest ozonesonde concentrations in the upper troposphere in the Pacific may be
239 more typically ~ 10 ppbv. Assuming a constant mixing ratio of 10 ppbv lying between

240 the tropopause and OMI OCCP (~300-500 hPa for minimum above-cloud ozone scenes)
241 this is equivalent to 1-3 DU in column amount. Even with such non-zero ozone
242 concentrations lying between the tropopause and OCCP for thick clouds, the estimate of
243 SCO in the Pacific from the CCD method should still be accurate to about 1-3 DU in
244 absolute numbers.

245 3.2.1. Comparisons of CCD and OMI/MLS Gridded Tropical TCO measurements

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247 The primary measurement derived from the CCD method of Ziemke *et al.* [1998] is
248 gridded TCO in low tropical latitudes. We have evaluated the CCD TCO data from OMI
249 by comparing with coincident OMI/MLS residual measurements. Figure 2 shows TCO
250 from the CCD method (left panels) with TCO from OMI/MLS (right panels) for four
251 consecutive October months beginning in 2004. It is well known that October (like
252 September and November) coincide each year with large enhancements of tropospheric
253 ozone in the tropical south Atlantic. This zonal wave-one pattern in TCO in the tropics is
254 caused largely by a combination of effects from the dynamical Walker circulation and
255 photochemical sources including biomass burning and lightning [e.g., *Sauvage et al.*,
256 2007, and references therein].
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259
260 **Figure 2.** Tropospheric column ozone (in Dobson Units) derived from the CCD residual
261 method (left panels) and the OMI/MLS residual method (right panels) for four

262 consecutive October months beginning in 2004. Blue to red colors represent smallest to
263 largest values, respectively.

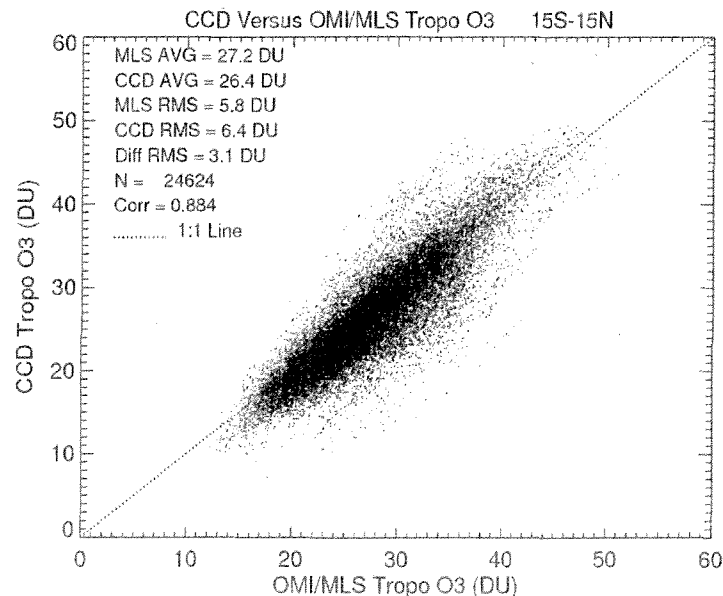
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265 There is substantial inter-annual variability present in Figure 2 in the Atlantic region
266 where year-to-year differences are ~ 10 DU. October 2004 and 2006 coincided with two
267 El Nino events whereas October 2005 was non-ENSO (i.e., neither El Nino nor La Nina
268 conditions) and October 2007 coincided with a strong La Nina event. Although ENSO
269 events are predominantly an Indian Ocean/Pacific Ocean phenomenon, it is possible that
270 ENSO may have contributed in some way to the observed ozone inter-annual variability
271 in the Atlantic where lowest ozone abundance is seen to occur during El Nino events. It
272 is also possible that unrelated year-to-year changes in ozone precursors and/or
273 meteorological conditions is the primary cause for the inter-annual variations in Atlantic
274 TCO. There is also evidence as discussed later in section 5.1 of reduction of tropical
275 tropospheric ozone in years 2004 and 2006 related to the quasi-biennial oscillation
276 (QBO). (The analysis of inter-annual variability of TCO in the Atlantic is beyond the
277 scope of this study.)

278

279 Figure 3 shows a scatter plot comparing the two TCO products accumulated over the
280 entire six years in the tropical domain 15°S - 15°N (as shown in Figure 2). The ensemble
281 averages and RMS values listed in Figure 3 are comparable for the two products with
282 average values of about 27 DU and 6 DU, respectively. The calculated RMS of CCD
283 minus OMI/MLS difference time series is much smaller at around 3 DU with an overall
284 cross-correlation between the two datasets of 0.88. The conclusion from Figures 2 and 3
285 is that these two gridded products are essentially similar with an average of about 3 DU
286 statistical RMS difference and nearly zero offset.

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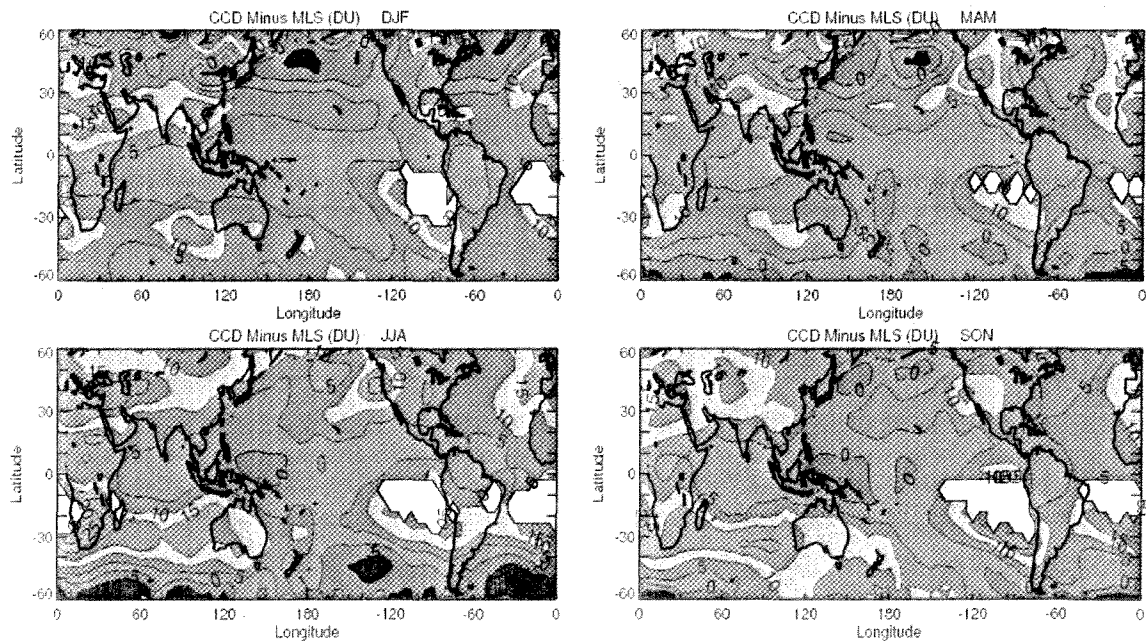
289 **Figure 3.** Scatter plot of CCD versus OMI/MLS monthly mean gridded tropospheric
290 column ozone (in Dobson Units) accumulated over the six-year record in the tropics. The
291 measurements for both products are gridded at $5^{\circ}\times 5^{\circ}$ latitude-longitude resolution and
292 extend from central latitudes 12.5°S to 12.5°N along all longitudes

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3.2.2. Tropospheric Ozone Associated with Deep Convective Clouds.

Key to the CCD method is the abundance of ozone lying inside deep convective clouds. Figure 4 shows seasonal contour plots of the difference of OMI CCD minimum above-cloud column ozone minus MLS SCO averaged over the six years. We refer to these residual differences in Figure 4 as “cloud ozone” which represents tropospheric column ozone lying between the tropopause and OCCP under conditions of deep convective clouds (i.e., scenes where reflectivity exceeds 0.8). It is inferred that much of the column ozone amounts shown in Figure 4 are a manifestation of ozone lying in the boundary layer/lower troposphere that is injected upward into these clouds. Some of the measurements in Figure 4 are negative and even exceed -5 DU in high latitudes, particularly during winter months. The negative column amounts in Figure 4 are obviously not correct and are caused by yet unresolved offset differences between MLS SCO and OMI above-cloud column ozone in wintertime high latitudes where solar zenith angles are highest, often exceeding 75° .

Ideally, wherever the CCD method is working correctly in deriving local measurements of SCO the differences between the two ozone datasets in Figure 4 should be zero. The differences in Figure 4 are generally small in the Pacific extending from the tropics to high latitudes, but there are offset differences as large as 10 DU or even 20 DU in the extra-tropics of both hemispheres in regions away from the Pacific. It will be shown that these offset differences are mostly recurring annual cycle features and that tropospheric and stratospheric ozone from the CCD method are more accurate after these measurements are deseasonalized.



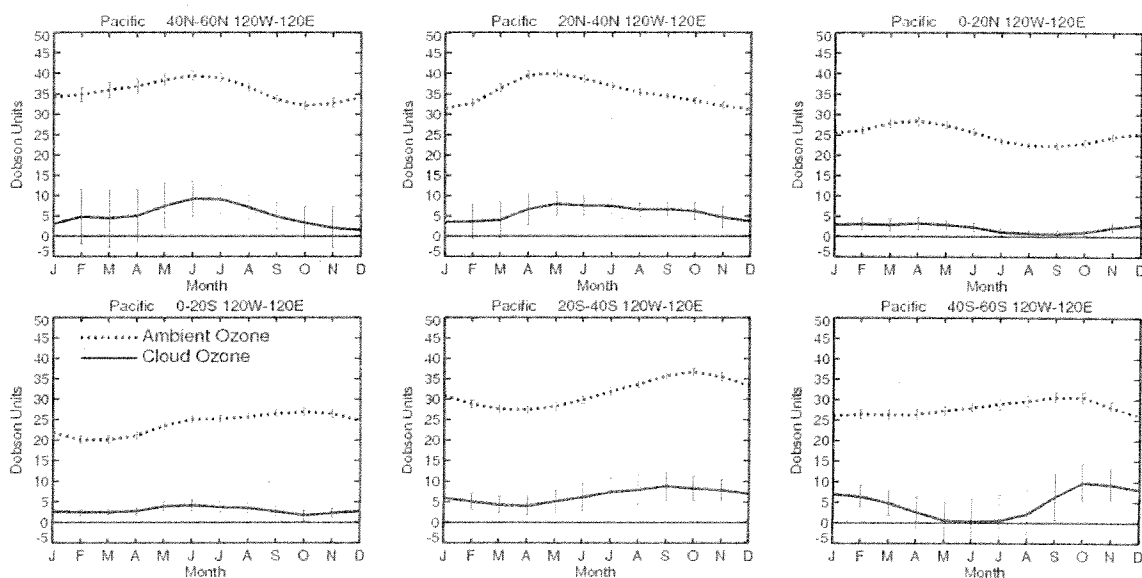
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Figure 4. Three-month seasonal averages (December-February, March-May, June-August, and September-November) of CCD above-cloud column ozone minus MLS stratospheric column ozone over the time record 2004-2010. Contour numbers represent

322 Dobson Units. The colors violet/blue to orange represent negative to positive values,
 323 respectively. We denote these measurements in this figure as “cloud ozone”, the amount
 324 of column ozone lying between the tropopause and cloud OCCP under conditions of deep
 325 convection.

326
 327 Line plots of 12-month annual cycles of CCD cloud ozone in the Pacific in 20° latitude
 328 bands from 60°S to 60°N are shown as solid curves in Figure 5. Plotted also as dotted
 329 curves in Figure 5 are corresponding TCO time series from OMI/MLS. We refer to these
 330 measurements as background “ambient” ozone. Included in Figure 5 for all time series
 331 are calculated standard error of mean numbers which provide a measurement
 332 proportional to inter-annual variability; as example, inter-annual variability for cloud
 333 ozone in high latitudes in Figure 5 is around 3-4 time larger than in the tropics.

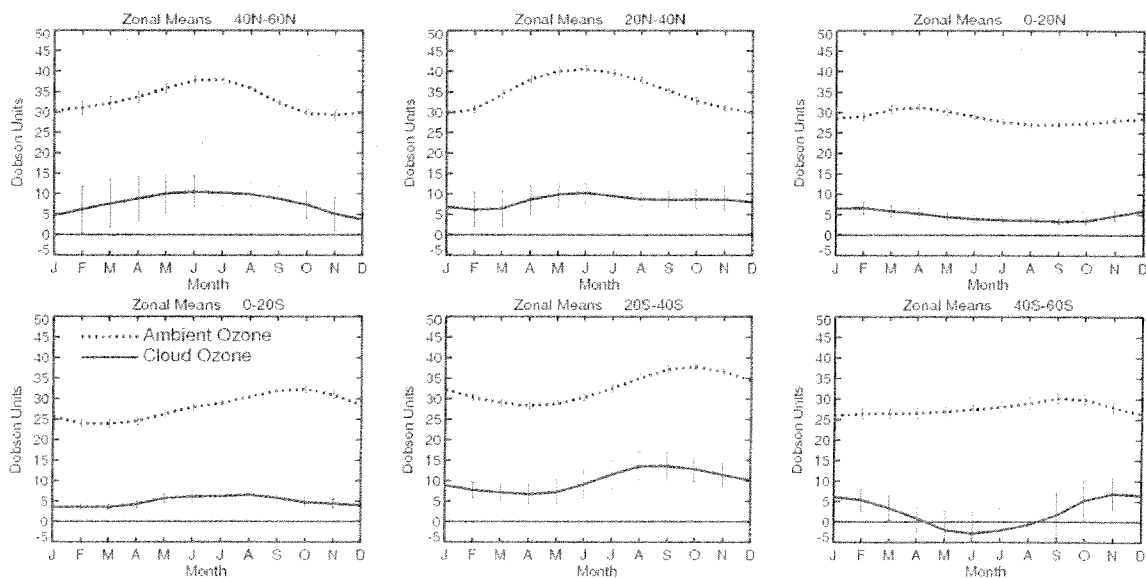
334
 335 The annual cycles and annual mean values for cloud ozone measurements in the tropics
 336 in Figure 5 are small at only about 1-3 DU, however annual cycles and annual means can
 337 exceed 5 DU in the extra-tropics. Ambient ozone in Figure 5 maximizes in spring-
 338 summer months (March-July) in the Northern Hemisphere and the spring months
 339 (September-November) in the Southern Hemisphere. The cloud ozone in Figure 5 is
 340 always substantially smaller than ambient ozone at all latitude ranges, yet within the
 341 RMS uncertainties the annual cycles are generally similar for both column amounts.
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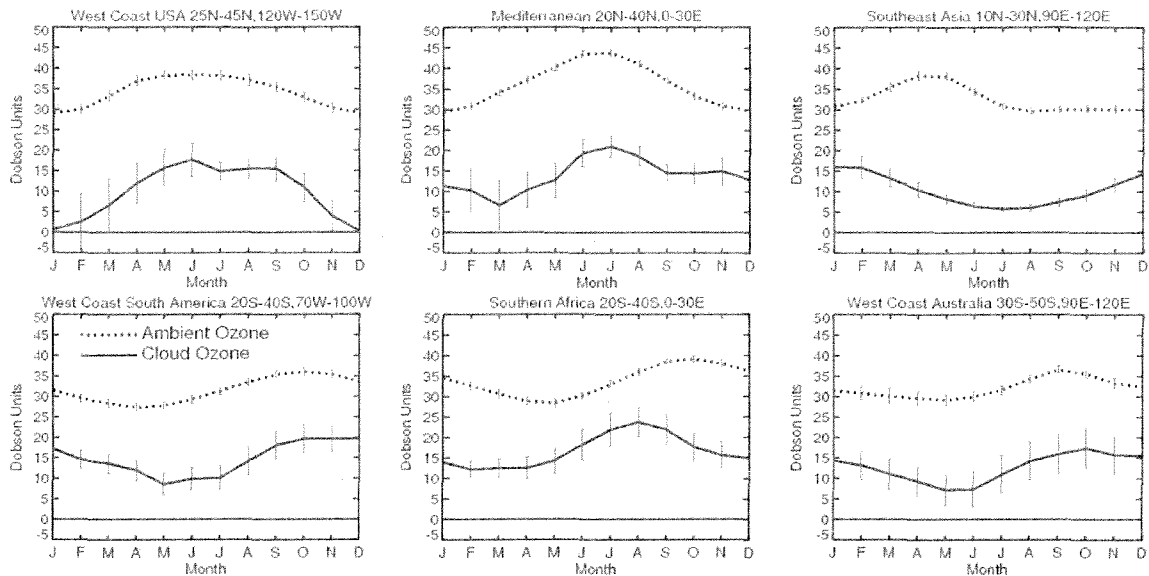
343
 344 **Figure 5.** Solid curves: Line plots of CCD 12-month annual cycles of cloud ozone
 345 averaged within six non-overlapping 20° latitude bands in the Pacific. The latitude bands
 346 are (from upper left to lower right): 40°N-60°N, 20°N-40°N, 0°-20°N, 0°-20°S, 20°S-40°S,
 347 and 40°S-60°S. The Pacific averaging is for the longitude domain 120°W-120°E about
 348 the dateline. Dotted curves: Same as solid curves but for background ambient column
 349 ozone from OMI/MLS residual. These annual cycle time series are all derived by
 350 averaging together data for similar months over the six years. The vertical bars represent
 351 calculated $\pm 1\sigma$ RMS standard error of mean.
 352

353 Figure 6 is the same as Figure 5 except that the time series were derived for zonal means
 354 rather than Pacific means. The conclusions for zonal means are similar to those
 355 discussed for Pacific means except that cloud ozone annual means are larger at most
 356 latitudes for zonal mean measurements. Figure 7 shows more annual cycle line plot
 357 comparisons, but instead for six extra-tropical regions where cloud ozone often exceeds
 358 5-20 DU (i.e., exceeding 50% of ambient ozone in some months). It is interpreted that
 359 these extra-tropical regions are more polluted with boundary layer/lower tropospheric
 360 ozone. The annual cycles for cloud ozone and ambient ozone are not correlated for
 361 Southeast Asia and southern Africa in Figure 7. For southern Africa, ambient ozone
 362 maximizes in September-October (same as the other two Southern Hemisphere regions in
 363 the figure), whereas cloud ozone maximizes much earlier around August; August is a
 364 peak month for biomass burning in the southern Africa region.
 365

366 The conclusions from Figures 4-7 are that Pacific means and zonal means have nearly the
 367 same geophysical signatures in annual cycles for both the cloud ozone and ambient ozone,
 368 and also that most of the offset differences in Figure 4 (which represent ozone measured
 369 in deep convective clouds) are recurring annual cycle features. Later in section 4 we will
 370 show that after removing annual cycles from the data that inter-annual variability for the
 371 Pacific mean and zonal mean data products of both TCO and SCO from the CCD method
 372 are precise measurements to within a few DU relative to OMI/MLS residual ozone, not
 373 just in the tropics but extending to high latitudes.
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 377 Figure 6. Similar to Figure 5 but for zonal mean measurements.
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 381 **Figure 7.** Similar to Figures 5 and 6 but instead for six broad regions of the globe where
 382 measured CCD cloud ozone is large with peak abundances of ~15-20 DU. These six
 383 regions are from upper left to lower right (compare these regions with Figure 4): West
 384 Coast of the USA, Mediterranean, Southeast Asia, West Coast of South America,
 385 Southern Africa, and West Coast of Australia.

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 387 **4. Inter-annual Variability of Tropospheric and Stratospheric Ozone.**

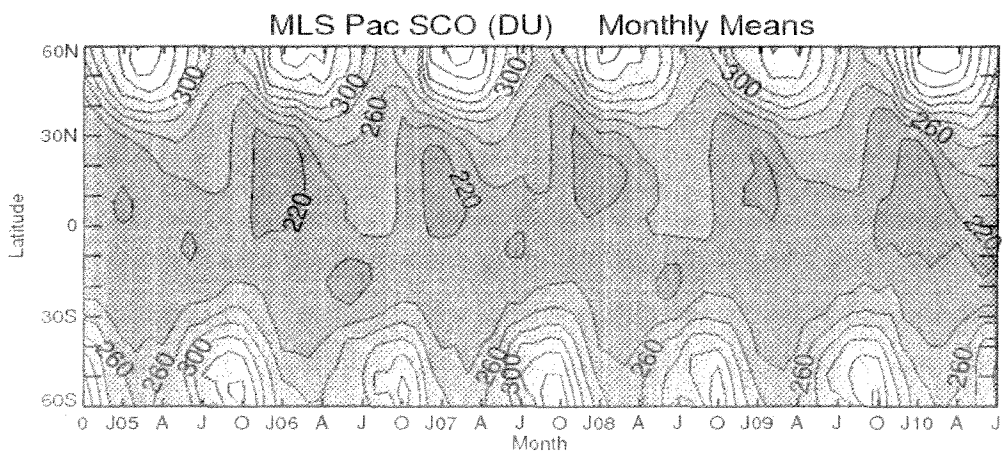
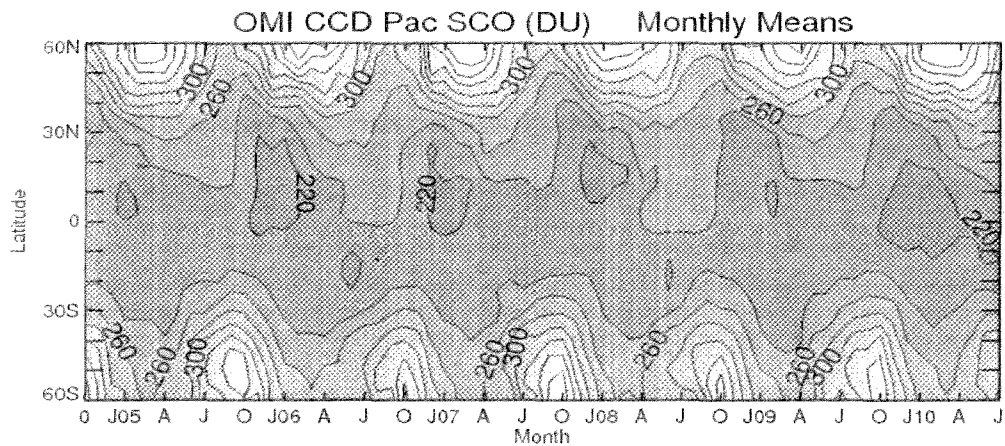
388
 389 In the study by Ziemke *et al.* [2005] the CCD measurements of TCO and SCO from
 390 combined Nimbus 7 and Earth Probe TOMS were extended to middle and high latitudes
 391 in the Pacific under the assumption that deep convective clouds with low boundary layer
 392 ozone conditions persist outside the tropics just as they do in the tropics. The CCD
 393 measurements of SCO were tested against SAGE II SCO for the time period 1984-2003.
 394 Despite sparse SAGE measurements those comparisons showed that SAGE and CCD
 395 SCO in the extra-tropics compared well in annual means and even better (to 2-4 DU
 396 differences) from the tropics to high latitudes when comparisons were made for summer
 397 months only.

398
 399 We use the Aura MLS measurements of SCO which have greater spatial and temporal
 400 coverage than SAGE to evaluate how well the CCD method works outside tropical
 401 latitudes. Figure 8 compares latitude versus month contour diagrams of SCO averaged
 402 over the Pacific (120°W-120°E) from OMI CCD (top) and MLS (bottom). SCO in
 403 middle and high latitudes for either OMI or MLS in Figure 8 is largest in both
 404 hemispheres from winter into spring with large 80-100 DU peak-to-peak annual-cycle
 405 changes. There is indication of large inter-annual variability in both data sets from the
 406 tropics to high latitudes which includes an apparent QBO signal in the tropics with a
 407 period of about two years.

408
 409 The SCO data in Figure 8 were further deseasonalized to evaluate inter-annual changes
 410 (Figure 9). Deseasonalization was accomplished by subtracting for each month a global
 411 monthly mean climatology value (determined by averaging similar months over the six-

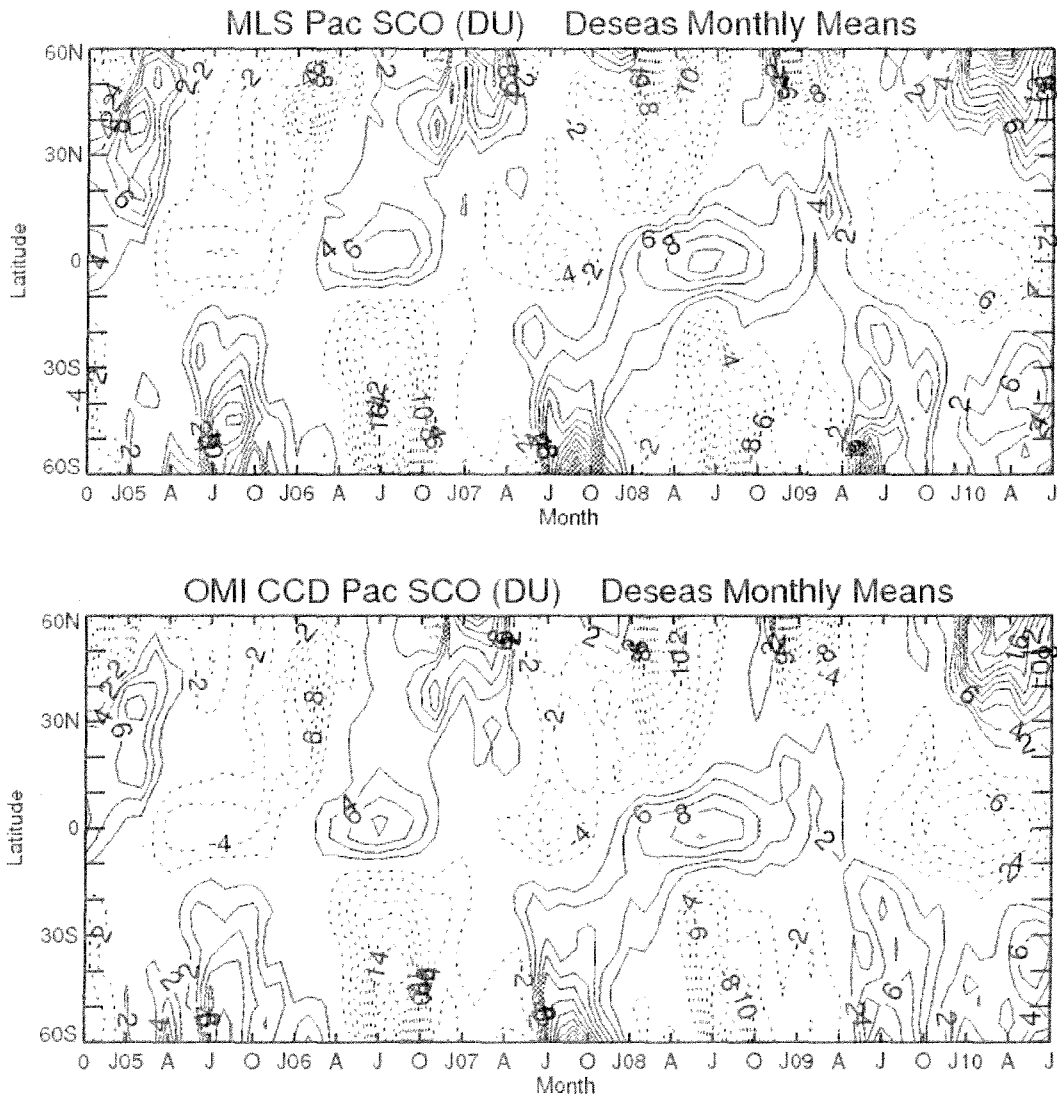
412 year record). The dominant inter-annual signature in Figure 9 is the QBO which during
413 the Aura record shown has about a 24-month period and is characteristically centered
414 about the equator extending to high latitudes of both hemispheres.
415

416 The tropically driven QBO induces a global secondary circulation with opposite vertical
417 wind fields between the tropics and extra-tropics [e.g., *Andrews et al.*, 1987]. Subsidence
418 (ascent) of stratospheric air mass in equatorial latitudes associated with the QBO-induced
419 circulation coincides with ascent (subsidence) of stratospheric air mass in the extra-
420 tropics. In the tropics the subsidence of air mass driven by the QBO during the
421 descending westerly phase (i.e., descending eastward zonal winds in the low-mid
422 stratosphere) is seen in Figure 9 as anomalous increases in tropical SCO that maximize
423 around the months May-October for years 2006 and 2008. The QBO-induced down-
424 welling circulation in the tropics coincides with opposite upwelling in the extra-tropics
425 which is seen in Figure 9 as anomalous reductions in SCO of 10-20 DU in high latitudes
426 of both hemispheres in winter-spring months. The extra-tropical QBO variability appears
427 clearer in the Southern Hemisphere because of a synchronous phase coupling between the
428 Brewer Dobson Circulation annual component and the QBO which during the Aura
429 record had about a 24-month cycle.
430
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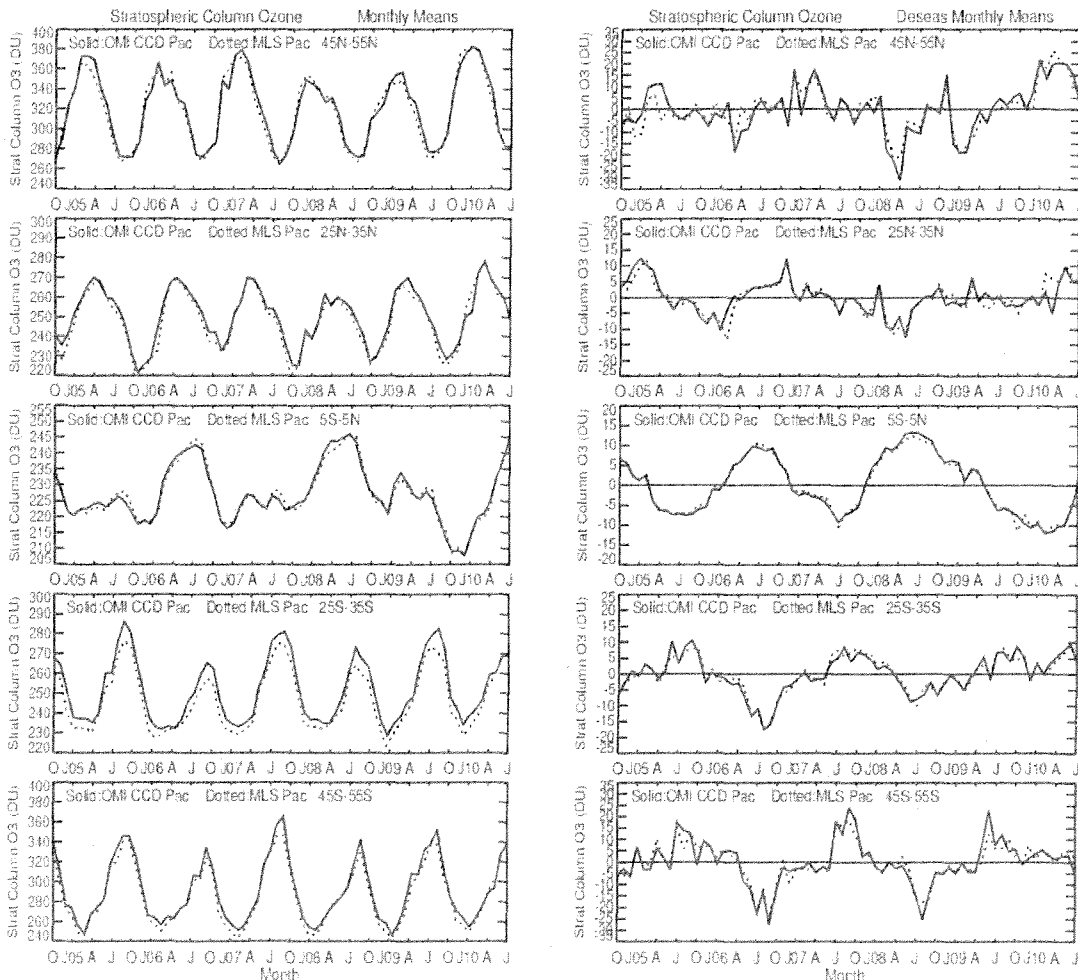
433 Figure 8. Latitude versus month contour diagrams of monthly mean stratospheric
 434 column ozone (in Dobson Units) averaged over the Pacific (120°W-120°E) from OMI
 435 CCD (top) and MLS (bottom). Dark to light shading designates smaller to higher column
 436 amounts, respectively. The contour values for both diagrams begin at 200 Dobson units
 437 and increment by 20 Dobson Units.
 438
 439
 440



441
 442 Figure 9. Contour diagrams of the same stratospheric column ozone (in Dobson Units)
 443 plotted in Figure 8, but instead with all of the data deseasonalized.
 444
 445 Toward the end of the record in Figure 9 there is anomalously large SCO in the northern
 446 higher latitudes beginning around January 2010 for both OMI and MLS. These increases
 447 coincide with ozone decreases in the tropics associated with the descending easterly
 448 phase of the QBO. A recent study by *Steinbrecht et al.* [2011] combined ozonesondes
 449 from Hohenpeissenberg (48°N, 11°E) and SCIAMACHY total ozone to conclude that

450 these high values of ozone in 2010 were among the largest on record in northern latitudes
 451 during the last 20-25 years. Their study attributes these large ozone enhancements to a
 452 coupling between the QBO and the Arctic Oscillation and North Atlantic Oscillation with
 453 the latter two oscillations being in an unusually persistent negative phase.
 454

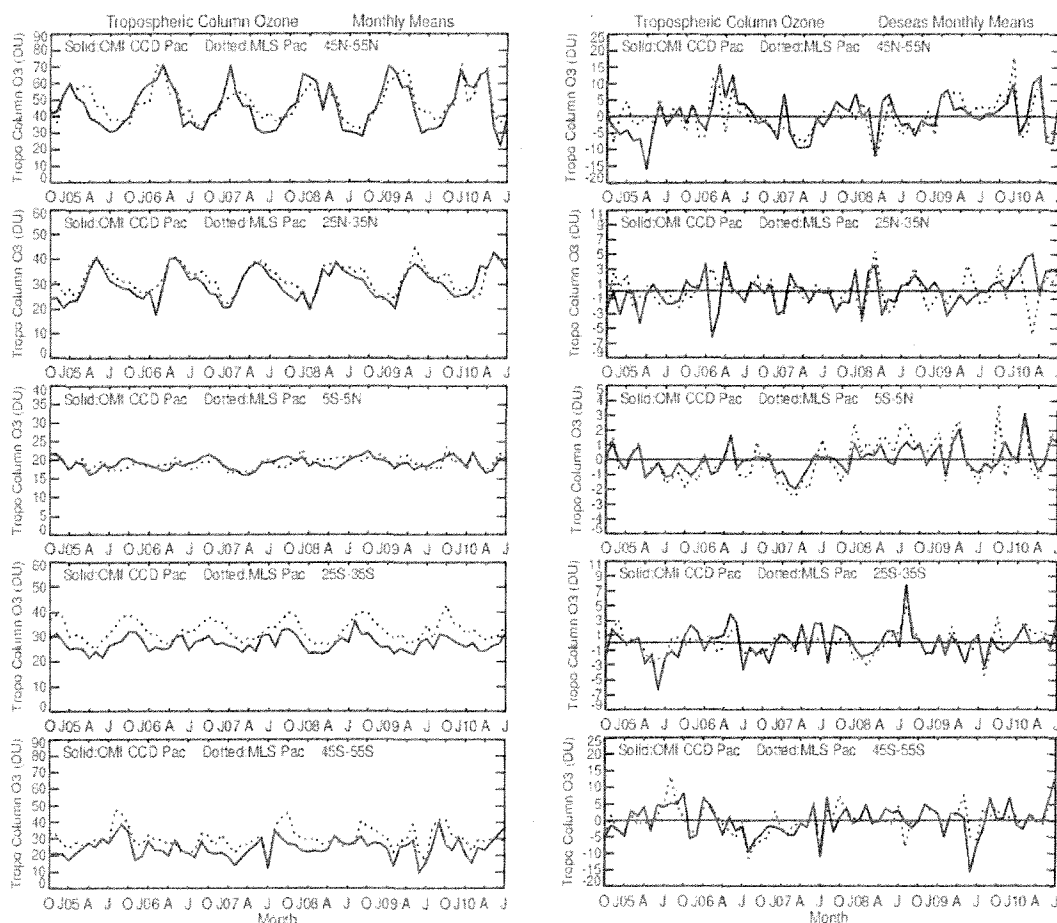
455 Time series of SCO corresponding to the data in Figures 8 and 9 are plotted in Figure 10
 456 in 10° latitude bands (indicated) for monthly means (left panels) and deseasonalized
 457 monthly means (right panels). Shown in all panels in Figure 10 are Pacific averages for
 458 CCD (solid curves) and MLS (dotted curves). Despite seasonally varying offsets up to 5-
 459 10 DU between CCD and MLS in the left panels in Figure 10, when the data are
 460 deseasonalized the month-to-month differences between the two ozone datasets is
 461 reduced for all latitude ranges. The deseasonalized time series in Figure 10 for both
 462 residual methods show that the QBO-related signal in the Southern Hemisphere high
 463 latitudes is associated with inter-annual changes of ~ 30 DU or greater.
 464



465 **Figure 10.** (Left panels) Monthly averaged Pacific mean measurements of CCD SCO
 466 from OMI (solid curve) and MLS SCO (dotted curve) averaged over five indicated 10°
 467 latitude bands. The Pacific mean represents data averaged over the combined eastern and
 468 western Pacific (i.e., longitude range 120°W to 120°E about the dateline). All
 469

470 measurements are in Dobson Units. (Right panels) Same as left panels but with the data
 471 deseasonalized.

472
 473 Pacific mean tropospheric ozone derived from the two residual methods is shown in
 474 Figure 11. Figure 11 is the same as Figure 10 but with TCO plotted rather than SCO.
 475 Shown in Figure 11 are the original time series (left panels) and deseasonalized time
 476 series (right panels) for the same five latitude bands. There are obvious offset differences
 477 between the two methods in the left panels in Figure 11 which are up to ~10 DU in some
 478 months. The deseasonalized TCO time series in the right panels do not have these offsets
 479 and track each other reasonably well.
 480



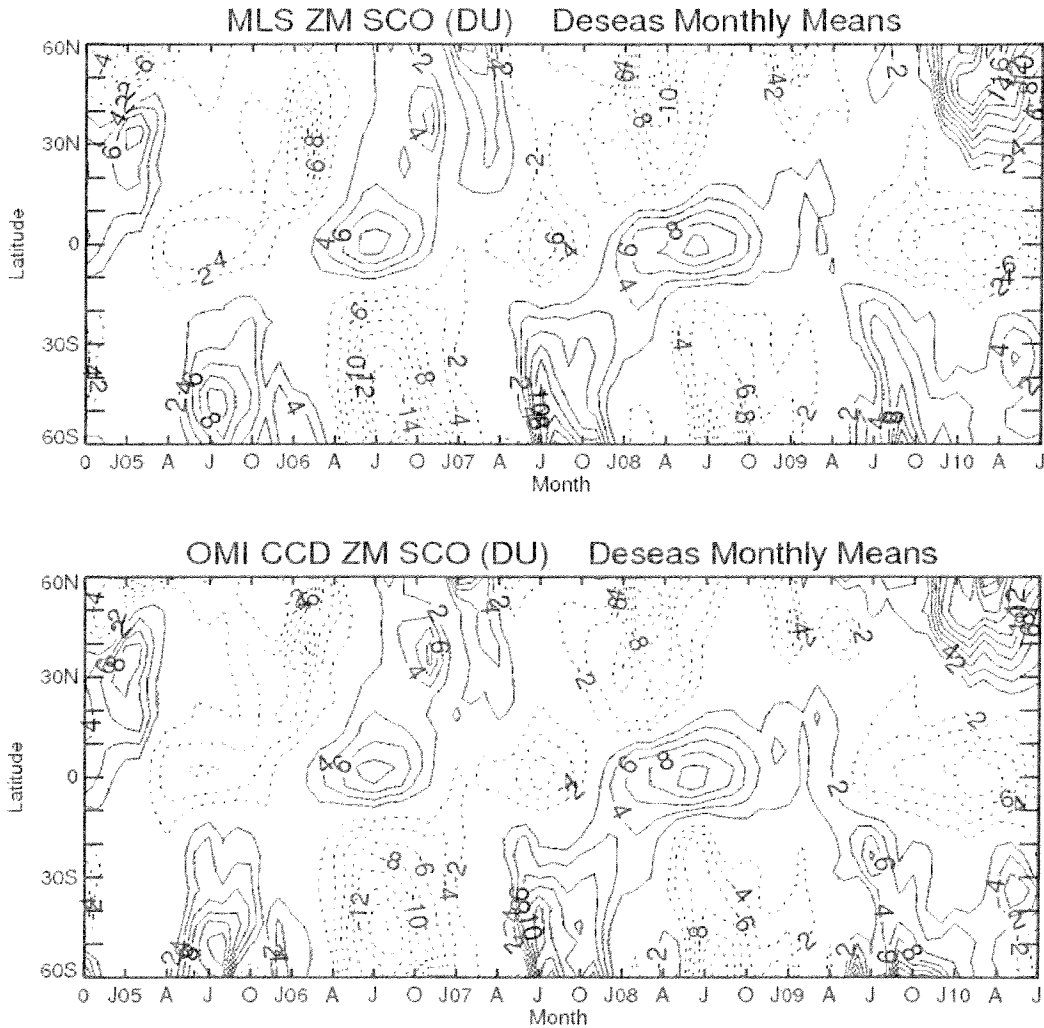
481
 482 **Figure 11.** (Left panels) Monthly averaged Pacific mean measurements of CCD TCO
 483 from OMI (solid curves) and OMI/MLS TCO (dotted curves) averaged over five
 484 indicated 10° latitude bands. The Pacific mean represents data averaged over the
 485 combined eastern and western Pacific (i.e., longitude range 120°W to 120°E about the
 486 dateline). All measurements are in Dobson Units. (Right panels) Same as left panels but
 487 with the data deseasonalized.

488
 489 Figures 9-11 suggest that inter-annual variability of Pacific mean SCO and TCO from the
 490 CCD method from the tropics to high latitudes compares closely to within a few DU with
 491 corresponding measurements from the OMI/MLS residual method. We will show that

492 zonally averaged CCD above-cloud column ozone also compares close to zonal mean
493 SCO from MLS.

494

495 Figure 12 shows contour diagrams of deseasonalized zonal mean SCO from MLS (top
496 panel) and OMI CCD above-cloud column ozone (bottom panel). Comparison with
497 Figure 9 suggests that SCO from the two methods are closer for zonal means than for
498 Pacific means.
499



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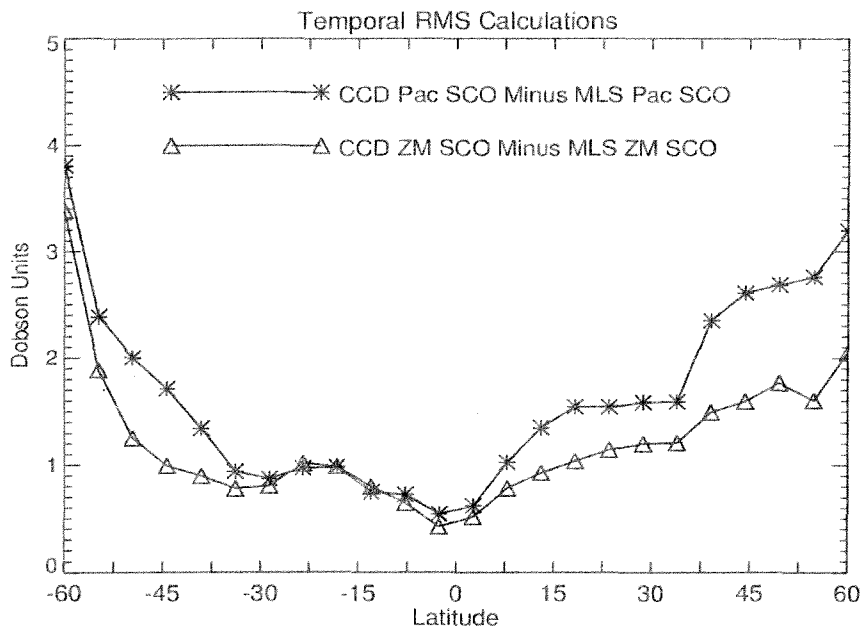
501 **Figure 12.** Same as Figure 9, but instead for zonal means rather than Pacific means.

502

503 Figure 13 plots temporal RMS values of the difference between CCD and MLS
504 deseasonalized SCO time series for Pacific means (asterisks) and zonal means (triangles)
505 as a function of latitude. (The RMS amplitudes for Pacific means and zonal means in
506 Figure 13 were calculated from OMI minus MLS differences of the data plotted in
507 Figures 9 and 12, respectively.) The RMS values in Figure 13 for most latitudes are
508 generally about 1-2 DU and up to ~2-3 DU at higher latitudes. For zonal means RMS
509 differences are about 0.5-1 DU in the tropics to ~1.5 DU at mid-to-high latitudes. The
510 RMS values in Figure 13 for SCO are equivalent to RMS amplitudes calculated for TCO.

511 This is because the same OMI total column ozone measurements are used for both
512 residual methods.

513
514 These Aura comparisons have given us greater confidence in the CCD measurements of
515 tropospheric and stratospheric ozone derived from previous TOMS measurements. In the
516 next section we discuss a long record of stratospheric and tropospheric ozone determined
517 from combined TOMS and OMI records beginning 1979.
518



519
520 **Figure 13.** Calculated temporal RMS values (in Dobson Units) of the difference between
521 CCD and MLS deseasonalized SCO time series for Pacific means (asterisks) and zonal
522 means (triangles) as a function of latitude. These RMS amplitudes were calculated from
523 the difference between the data plotted in Figures 9 and 12, respectively.

524
525 **5. The TOMS+OMI Ozone Dataset.**

526
527 We have developed an extended record of tropospheric and stratospheric column ozone
528 spanning 1979-2010 by combining TOMS and OMI Pacific mean CCD measurements. It
529 was noted in the data description section that the TOMS ozone uses the version 8
530 algorithm while OMI ozone uses the version 8.5 algorithm. Although there may be
531 retrieval offsets existing between TOMS and OMI measurements because of different
532 algorithms for the separate instruments, our analyses suggest that these offsets are not
533 large and cannot be more than a few DU at most at any latitude. Offsets of only a few
534 DU will adversely affect evaluation of inter-annual variability and calculated trends in
535 tropospheric ozone, but such offsets have less relative impact for stratospheric ozone. In
536 the near future we plan to combine the TOMS and OMI stratospheric and tropospheric
537 ozone data using only the single version 9 processed retrievals. We provide only a brief
538 discussion of ozone trends and inter-annual (QBO) variability in tropospheric ozone for
539 the 1979-2010 data record.
540

541 5.1. Quasi-Biennial Oscillation Signals in Tropical Ozone.

542

543 Although it is well known that there exists a large QBO variability in stratospheric ozone,
544 there is also evidence of a QBO in tropospheric ozone. *Ziemke and Chandra* [1999] first
545 detected a possible QBO in tropospheric ozone using Nimbus-7 TOMS measurements for
546 the 1979-1993 record. A later study by *Chandra et al.* [2002] combined Nimbus-7
547 TOMS with Earth Probe TOMS and found a consistent QBO in tropospheric ozone over
548 a longer record of 1979-2000. The QBO in tropospheric ozone for these studies was
549 clearer to detect in the Atlantic region as opposed to the Pacific as there is additional
550 inter-annual variability in the Pacific related to ENSO events. It was postulated by
551 *Ziemke and Chandra* [1999] that a possible source for the QBO signal could be an upper
552 tropospheric ozone photochemistry response from the QBO in stratospheric ozone.
553 However, the measured tropospheric signal was larger than predicted by photochemical
554 models and it was concluded by *Ziemke and Chandra* [1999] that the source for the QBO
555 signal in tropospheric ozone was most likely of dynamical origin. *Lee et al.* [2010] have
556 reached these same conclusions based upon balloon sonde data from the Southern
557 Hemisphere Additional Ozonesondes (SHADOZ) network. Their analyses of the sonde
558 temperature and ozone measurements suggest that the QBO signal in tropospheric ozone
559 extends down to about mid-troposphere and is of dynamical origin.

560

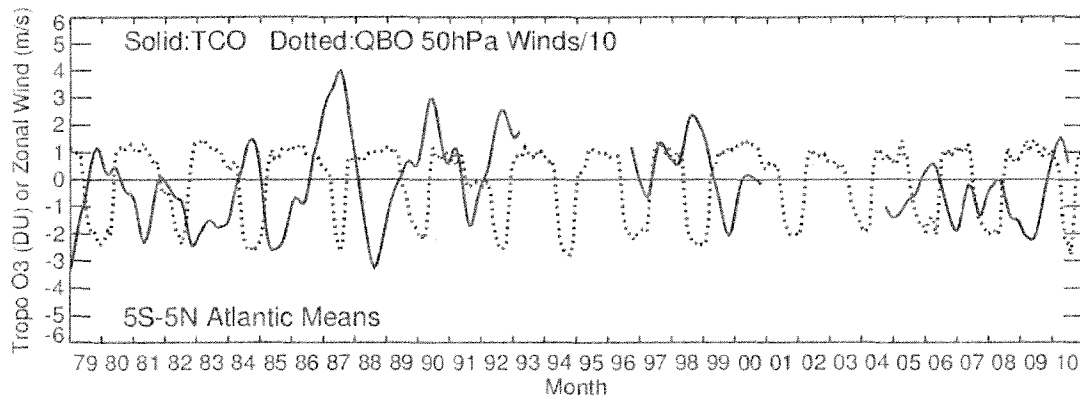
561 Figure 14 plots 50 hPa monthly zonal winds from Singapore (1°N, 104°E) (dotted curve)
562 and deseasonalized tropospheric ozone (solid curve) averaged in the equatorial Atlantic
563 (5°S-5°N, 60°W-60°E). There are two data gaps present in the time series in Figure 14.
564 The first gap is several years of non-existing measurements between Nimbus 7 and Earth
565 Probe TOMS periods. The second gap in Figure 14 represents Earth Probe CCD
566 measurements which have been conservatively flagged as missing after year 2000 for
567 questionable data quality. Tropospheric ozone in Figure 14 was additionally smoothed
568 using a low-pass digital filter as described in the figure caption.

569

570 Comparison of the 50 hPa zonal winds and tropospheric ozone in Figure 14 indicates a
571 persistent negative correlative relationship over the long 32-year multi-instrument record.
572 The QBO signal in tropospheric ozone for the 1979-1993 Nimbus-7 TOMS period in
573 Figure 14 is larger than during the latter EP TOMS and OMI periods. Peak-to-peak
574 differences in ozone for the Nimbus-7 record are ~4-7 DU compared to ~2-4 DU for the
575 latter years. There are some years in Figure 14 where the wind/ozone negative
576 correlation relation is not evident. One case occurs around 1990-1991 (coinciding with
577 the July 1991 Mt. Pinatubo eruption), and another case is in 1997-1998 during an intense
578 tropical El Nino event.

579

580 We conclude from the TOMS+OMI 32-year record that there appears to be a persistent
581 QBO signal in tropospheric ozone with peak-to-peak amplitudes varying from about 2
582 DU up to 7 DU. This evidence further strengthens claims from previous studies of a
583 QBO in tropospheric ozone. We note that *Lee et al.* [2010] from ozonesonde analyses
584 found maximum QBO signal in tropospheric ozone profile measurements of about 8 ppbv
585 (equivalent to ~2-3 DU in upper troposphere) which is not inconsistent with the signal
586 amplitudes that we find from the TOMS+OMI combined record.



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Figure 14. Tropospheric column ozone from the CCD method in Dobson Units (solid curve) plotted versus 50 hPa zonal winds from Singapore (1°N , 104°E) in units $\text{m}\cdot\text{s}^{-1}$ but divided by 10 for scaling (dotted curve). The ozone time series was averaged over the equatorial Atlantic region (5°S - 5°N , 60°W - 60°E). The ozone time series was deseasonalized and detrended, and then smoothed using a recursive low-pass digital filter with one-half filter response at 12-month period (filter response of about 0.8-0.9 for 24-36 month QBO time periods).

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5.2. Ozone Trends.

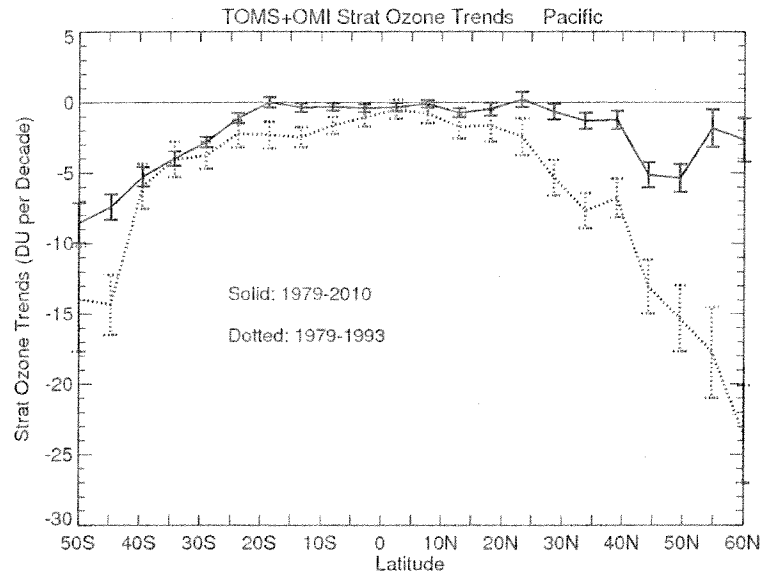
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Trends in tropospheric and stratospheric ozone were calculated by *Ziemke et al.* [2005] for a 25-year record (1979-2003) of TOMS CCD measurements in the Pacific. It was shown that stratospheric ozone trends for the Pacific are nearly identical to trends calculated for zonal means. *Ziemke et al.* [2005] found that trends in tropospheric ozone were near zero most everywhere but marginally positive ($\sim +2$ DU to $+3$ DU decade $^{-1}$) in mid-latitudes of both hemispheres. Trends in stratospheric column ozone were also near zero in the tropics but large and negative (~ -10 to -14 DU decade $^{-1}$) in the mid-high latitudes of both hemispheres. We have made similar calculations of trends using the extended TOMS+OMI 32-year record. The results presented are limited to stratospheric ozone trends; tropospheric ozone trends for the 32-year record are not substantially different from trends shown by *Ziemke et al.* [2005] based on 25 years of data.

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Figure 15 shows calculated trends in Pacific-averaged stratospheric ozone for the TOMS+OMI 32-year record (solid curve) and also, as comparison, stratospheric ozone trends for the Nimbus-7 15-year record beginning from 1979 (dotted curve). The trends in Figure 15 were calculated using the seasonally varying multivariate regression model of *Ziemke et al.* [2005] which included regression fits for combined linear trend, seasonal cycle, QBO, Solar cycle, and ENSO. It is apparent in Figure 15 that the negative trends in stratospheric ozone outside the tropics have reduced in magnitude markedly over the long record compared to the early 15-year record. The largest reduction in trends lies in the Northern Hemisphere extending from the subtropics to high latitudes. Area weighting of the trend differences in Figure 15 for latitudes 50°S to 50°N indicates that 66% of trend reduction lies in the Northern Hemisphere. Trends of 10 to 20 DU decade $^{-1}$

622 in the mid-high latitudes in Figure 15 correspond to trends of approximately 3 to 6%
623 decade⁻¹, respectively.
624



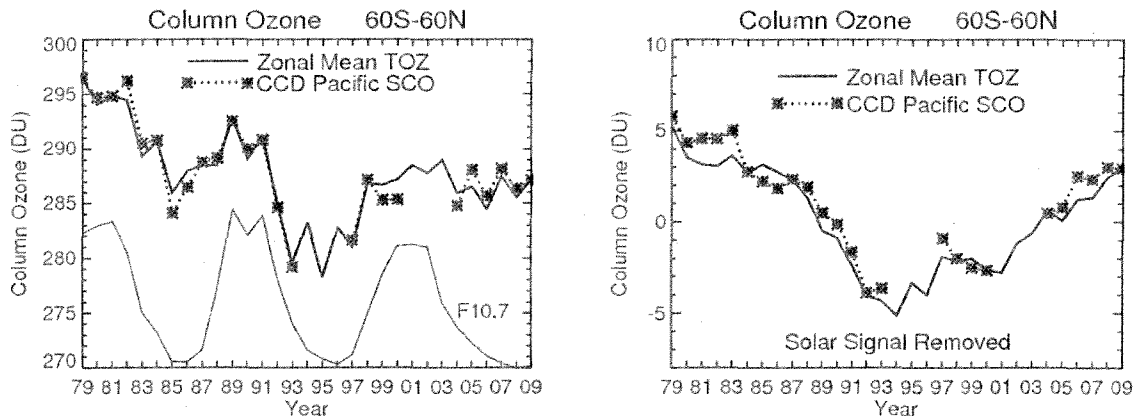
625
626 **Figure 15.** Trends (units DU decade⁻¹) in stratospheric column ozone for the extended
627 TOMS 1979-1993 CCD measurements derived from a linear multivariate regression
628 model (see text). (right) Same as left panel except for 1979-2010 extended TOMS+OMI
629 record. All data were averaged over the Pacific (120°W to 120°E about dateline) within
630 5° latitude bands. Vertical bars indicate ±2σ annual mean trend uncertainties calculated
631 from the regression model. The trend units and latitude range in this figure were chosen
632 to coincide with the trend figures shown by Ziemke *et al.* [2005] in which there were too
633 few Nimbus 7 CCD monthly measurements poleward of 50°S for seasonal trend analysis.
634

635 A complicating factor in assessing global stratospheric ozone recovery and turnaround
636 period of stratospheric ozone loss is solar cycle variability. Figure 16 (left panel) shows
637 annual mean time series of CCD stratospheric ozone (stars) plotted with merged total
638 column ozone from the NASA merged ozone webpage http://acdb-ext.gsfc.nasa.gov/Data_services/merged/. The two time series represent column ozone
639 area averaged between 60°S and 60°N. For stratospheric ozone a constant 31 DU was
640 added to the time series for plotting with total column ozone. This 31 DU represents
641 mean global abundance of tropospheric ozone. Along the bottom in Figure 16 as a proxy
642 of solar UV variability is solar F10.7 cm radio flux time series [e.g., Jackman *et al.*, 1996,
643 and references therein].
644

645
646 One cannot readily identify a turnaround period in the ozone time records in the left panel
647 of Figure 16 because of a dominant solar cycle present. In the right panel of Figure 16
648 we have removed solar cycle variability in both ozone time series using regression
649 (discussed in figure caption). With solar variability removed we identify a turnaround
650 period occurring in the mid-1990's for stratospheric and total column ozone. We can
651 also conclude from the right panel in Figure 16 that tropospheric ozone does not indicate
652 substantial decadal changes.
653

654 The first paper to evaluate global ozone trends and recovery turnaround in models and
 655 satellite measurements was by *Jackman et al.* [1996] which used a 2D chemical transport
 656 model. Interestingly, their model predicted a turnaround in the mid-1990's and recovery
 657 of ozone by 2010 similar to the amounts present in the mid-1980's. These features are
 658 both present in the measurements in the right panel of Figure 16. Similar figures
 659 comparing total column ozone from models and measurements have been shown recently
 660 in the 2010 WMO report and by *Oman et al.* [2010, and references therein]. Most of
 661 these recent models predict a turnaround occurring around year 2000 with largely varying
 662 recovery time periods. Several of these models predict a longer ozone recovery to mid-
 663 1980's levels by year 2020 or later.

664
 665 The Montreal Protocol was an international treaty initiated in 1987 to reduce worldwide
 666 ozone destroying substances such as chlorofluorocarbons and Bromine compounds. As a
 667 result of this treaty, since 1989 there has been a dramatic global reduction in these
 668 substances and a turnaround in ozone trends. Our 32-year ozone record indicates a
 669 turnaround in stratospheric ozone loss in the mid-1990's with recent ozone levels
 670 comparable to amounts present in the mid-1980's. These measurements seem to suggest
 671 a faster stratospheric ozone recovery occurring than predicted by many of the recent
 672 models.
 673



674
 675 **Figure 16.** (Left) Annual mean time series of TOMS/SBUV/OMI merged total column
 676 ozone (thick solid curve along top), TOMS+OMI CCD measurements of stratospheric
 677 column ozone (thick dotted curve along top), and solar F10.7 cm radio flux (thin solid
 678 curve along bottom) which has been rescaled for plotting. Stratospheric column ozone
 679 has had 31 Dobson Units added for visualization in plotting with total column ozone.
 680 Both ozone time series represent area-weighted measurements lying between latitudes
 681 60°S and 60°N. (Right) Similar to ozone plotted in the left panel except that time
 682 averages have been removed and the 11-year solar-cycle signals in the two ozone time
 683 series have been extracted by linear regression. The regression model used to remove 11-
 684 year solar cycle variability in the two ozone time series is $Ozone(t) = C \cdot Solar(t) + \epsilon(t)$ where C
 685 and is a constant, $Solar$ is solar F10.7 cm annual mean time series (with time average
 686 removed) and $\epsilon =$ model residual error. (The two derived residual series $\epsilon(t)$ are plotted in the right panel.) A 3-year
 687 running average was applied to both time series in the right panel for smoothing.
 688
 689

690 6. Summary and Conclusions.

691

692 The convective-cloud differential (CCD) method is the most basic form of the “cloud
693 slicing” technique. This method generates gridded measurements of TCO and SCO in
694 the tropics and also Pacific mean and zonal mean TCO and SCO extending to high
695 latitudes. The CCD method is assessed using Aura OMI and MLS ozone measurements
696 for the period October 2004 through July 2010. TCO and SCO from the CCD method
697 are compared with corresponding OMI/MLS residual measurements in which MLS ozone
698 profiles are used to calculate SCO. The Aura OMI/MLS data provide greatly improved
699 temporal and spatial coverage for evaluating the CCD measurements as previous
700 validation efforts involved sparse data from SAGE and HALOE (for SCO) and
701 ozonesondes (for TCO).

702

703 The analyses indicate that the CCD and OMI/MLS gridded TCO products in the tropics
704 agree to within one DU offset with a mean RMS difference of about 3 DU. RMS
705 differences between these two datasets for inter-annual variations in the Pacific are about
706 0.5-2.5 DU for either TCO or SCO over most latitudes ranging from the tropics to high
707 latitudes. (RMS differences for TCO are the same as for SCO since total column ozone
708 from OMI is used for both residual methods.) RMS differences for either zonal mean
709 TCO or zonal mean SCO vary from about 0.5-1 DU in the tropics to ~1.5 DU at mid-to-
710 high latitudes.

711

712 The Aura OMI/MLS ozone data have given us greater confidence in the CCD
713 measurements of tropospheric and stratospheric ozone derived from previous TOMS
714 measurements. This is important for extending the TOMS data with more recent OMI
715 data to develop a long record of tropospheric and stratospheric ozone for evaluating
716 decadal changes. We have developed from TOMS and OMI measurements a long 32-
717 year (1979-2010) dataset of tropospheric and stratospheric ozone. The analyses of these
718 time series show that the quasi-biennial oscillation (QBO) is the dominant source of
719 inter-annual variability of stratospheric ozone. During the Aura record the QBO
720 variability in stratospheric ozone was of a 24-month periodicity and was clearest
721 throughout the Southern Hemisphere extending to high latitudes. Both CCD and MLS
722 measurements show QBO-related inter-annual variability of stratospheric ozone in the
723 Southern Hemisphere of 30-40 DU. The 32-year dataset also indicates a QBO signal in
724 tropospheric ozone with peak-to-peak amplitudes varying from about 2 DU up to 7 DU.
725 These results further strengthen evidence of a QBO signal in tropospheric ozone as
726 suggested in previous studies based upon much shorter time record measurements from
727 SHADOZ ozonesondes and TOMS satellite ozone.

728

729 Trend analysis of the 32-year record dataset suggests a turnaround in global stratospheric
730 column ozone loss in the mid-1990's with current ozone levels comparable to the mid-
731 1980's. The analysis suggests that most of this turnaround occurred in the Northern
732 Hemisphere extending from the subtropics to high latitudes. The trend results are
733 generally consistent with the prediction of past and recent chemistry-climate models
734 which include the reduction of ozone destroying substances beginning in the late 1980's
735 mandated by the Montreal Protocol.

736

737

738 **Acknowledgments.** The authors thank the Aura MLS and OMI instrument and
739 algorithm teams for the extensive satellite measurements used in this study. We also
740 want to thank S. M. Frith and R. D. Stolarski for providing the merged total ozone data
741 set used in our analyses. OMI is a Dutch-Finnish contribution to the Aura mission.
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743

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