Elevated ozone in the troposphere over the Atlantic and Pacific oceans in the Northern Hemisphere

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Received 23 June 2004; revised 19 October 2004; accepted 28 October 2004; published 1 December 2004.

[1] Tropospheric column ozone (TCO) is derived from differential measurements of total column ozone from Total Ozone Mapping Spectrometer (TOMS), and stratospheric column ozone (SCO) from the Microwave Limb Sounder (MLS) instrument on the Upper Atmosphere Research Satellite (UARS). It is shown that TCO during late spring and summer months over the Atlantic and Pacific oceans at northern mid-latitudes is about 50–60 Dobson Units (DU) which is about the same as over the continents of North America, Europe and Asia (except high altitude mountain regions), where surface emissions of NO_x from industrial sources, biomass and biofuel burning, and biogenic emissions are significantly larger. The zonal characteristics of TCO derived from satellite measurements are generally simulated by a global chemical transport model called MOZART-2, but some discrepancies are also shown. The model results are analyzed to delineate the relative importance of surface NO_x emission, lightning NO_x and stratospheric flux. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 3362 Meteorology and Atmospheric Dynamics: Stratosphere/troposphere interactions; 3367 Meteorology and Atmospheric Dynamics: Theoretical modeling. **Citation:** Chandra, S., J. R. Ziemke, X. Tie, and G. Brasseur (2004), Elevated ozone in the troposphere over the Atlantic and Pacific oceans in the Northern Hemisphere, *Geophys. Res. Lett.*, *31*, L23102, doi:10.1029/2004GL020821.

1. Introduction

[2] Ozone is a precursor molecule of the hydroxyl (OH) radical which is the main oxidizing agent of several pollutants in the troposphere. In the troposphere ozone is produced primarily by photochemical oxidation of hydrocarbons in the presence of NO_x ($NO + NO_2$) with additional contribution from the stratosphere through stratosphere–troposphere exchange (STE). It is generally believed that tropospheric ozone has been increasing since pre-industrial times as a result of increased concentration of ozone-producing pollutants in Europe and North America [e.g., *Lelieveld and Dentener*, 2000; *Hauglustaine and Brasseur*, 2001; *Lelieveld et al.*, 2002]. There is concern that with industrialization of Asian countries tropospheric ozone may be increasing in the Northern Hemisphere (NH) through long-range transport. Global models of chemistry and transport have been used to assess the contribution of Asian pollution over regions of Asia, North America, and Europe [e.g., *Berntsen et al.*, 1999; *Li et al.*, 2001; *Liu et al.*, 2002; *Phadnis et al.*, 2002]. Model results are usually compared with ozonesonde measurements which are few and far between. At NH mid-latitudes, column ozone derived from ozonesonde measurements tends to peak during summer months when anthropogenic emissions resulting from fossil fuel combustion and biomass burning are high [*Logan*, 1999]. It is difficult to assess the global implications of these results particularly over the vast regions of the Atlantic and Pacific oceans where ozone measurements are sparse. Comparisons of satellite measurements of TCO with global models have been limited mostly to tropical regions because of lack of satellite measurements of TCO outside the tropics.

[3] The purpose of this paper is to use TCO data from TOMS/MLS [*Chandra et al.*, 2003] to characterize the zonal properties of TCO at NH mid-latitudes and to study the implications of various processes affecting TCO by using a global 3-D chemical transport model called MOZART version 2 [*Horowitz et al.*, 2003]. The zonal and seasonal characteristics of TOMS/MLS TCO between ±30° was analyzed in detail by *Chandra et al.* [2003] and compared with a global 3-D model of tropospheric chemistry (GEOS-CHEM) for 1996–1997. In this paper a similar comparison of TOMS/MLS TCO is made with the MOZART-2 model to delineate the relative importance of STE, lightning, and anthropogenic NO_x emission. As *Chandra et al.* [2003] showed, TCO is derived using version 7 TOMS measurements with reflectivity <0.2. In addition, the calibration of MLS is adjusted to TOMS by normalizing MLS SCO to TOMS SCO derived from the convective cloud differential method.

2. TCO From TOMS/MLS

[4] TOMS/MLS measurements overlap for about 20 months (September 1991–April 1993) during the Nimbus-7 TOMS lifetime and for about 2 years (August 1996 to mid-1998) during the Earth Probe (EP) TOMS period. The frequency of MLS measurements also changes from almost daily measurements during the Nimbus-7 period to only a few days per month (5–10 days) during the EP TOMS period. The MLS measurements outside ±34° are available around every alternate month on average because of a 57° inclination of the UARS orbit and planned rotation of the satellite through yaw about every 36 days. Because the MLS instrument does not measure ozone below 100 hPa, zonal maps of TCO are most reliable between ±30°

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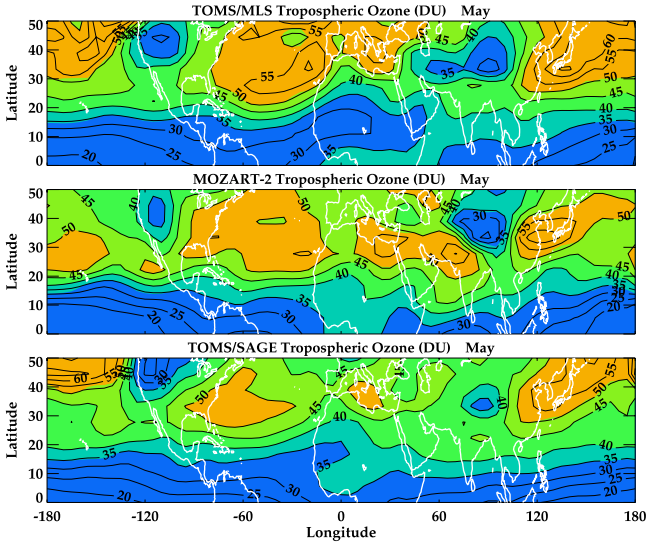

Figure 1. TCO (in DU) in the NH for late spring (May). TCO fields are derived from (top) TOMS/MLS, (middle) MOZART-2 model, and (bottom) TOMS/SAGE as discussed in the paper. A 3-point running average in the zonal direction was applied to accentuate large-scale zonal features.

where tropopause pressure is close to 100 hPa. In this latitude region TOMS/MLS residual can be used to derive TCO with only minor adjustments for tropopause pressure. Outside ±30°, useful estimates of TCO can still be made after making appropriate adjustments for changes in tropopause pressure, particularly for summer months [see *Chandra et al.*, 2003, Figure 8]. For World Ozone and Ultraviolet Radiation Data Centre (WOUDC) sonde sites, between 20°N and 50°N, the relative bias and RMS difference between TOMS/MLS and WOUDC TCO are respectively −5 DU and 9.1 DU. These values are reduced to 0.2 DU and 5.1 DU when only May–August data are used in calculations. Further validation of TOMS/MLS TCO is made by comparing with TCO from the TOMS and Stratospheric Aerosol and Gas Experiment (SAGE) combination as discussed by *Fishman and Brackett* [1997]. We will show that TCO fields derived from the two sets of data are qualitatively similar.

3. MOZART Version 2 Model

[5] MOZART-2 is a global chemical transport model developed at National Center for Atmospheric Research (NCAR), the Geophysical Fluid Dynamics Laboratory (GFDL) at Princeton University, and the Max Planck Institute of Meteorology (Hamburg) to simulate the distribution of tropospheric ozone and its precursors [*Horowitz et al.*, 2003]. It simulates the concentrations of 63 chemical species from the surface to the lower stratosphere. The model can be driven with a variety of meteorological inputs such as data from the NCAR Community Climate Model (CCM) with a horizontal resolution of 2.8° × 2.8° and 34 vertical levels from the surface to about 4 hPa. The model can also be driven using meteorological reanalysis data from National Centers of Environmental Prediction (NCEP) or European Center for Medium-range Weather Forecast (ECMWF). In this paper, we have used both the NCAR CCM and the ECMWF reanalysis data for 1997. The latter allows a direct comparison of model results with TOMS/MLS data for the same period.

[6] MOZART-2 is built on the framework of the transport model MATCH (Model of Atmospheric Transport and Chemistry) [*Rasch et al.*, 1997], and includes representations for advection, convective transport, boundary layer mixing, and wet and dry deposition. Surface emissions of chemical species include those from fossil fuel and industrial activity, biomass burning, biogenic emissions from vegetation and soils, and oceanic emissions. Aircraft emissions of NO_x and CO are included in the model based on *Friedl* [1997]. Biomass burning emissions are calculated by using both climatological inventories such as that of *Hao and Liu* [1994], and from satellite fire observations [*Goloub and Arino*, 2000]. In climatological runs we use climatological inventory of biomass burning combined with climatological CCM dynamical output to study the impact of biomass burning on chemical compounds in the NH. However, satellite observation shows that high degree of spatial and temporal variabilities of biomass emissions of chemical species such as CO exists. For example, in 1997 there are large fires occurring in Indonesia during September–November which results in large emissions of CO and NO_x, leading to significant increases in O_3. In this case we use an inventory based on satellite fire count combined with ECMWF wind to study this event.

4. Zonal Variability in TCO

[7] The Mozart-2 model, based on ECMWF 1997 reanalysis data, allows a direct comparison of model results with TOMS/MLS data for the same year. The data coverage from TOMS/MLS during 1997 is relatively sparse, about 5–6 days per month compared to almost daily measurements in 1992. However, the two years are essentially similar with respect to their zonal characteristics in late spring (May) and summer (July) months and are averaged for comparing with MOZART-2 model based on the 1997 run. This averaging is particularly useful since MLS measurements north of 30° are not always available due to the UARS yaw maneuvering as in May 1997. The main features of TOMS/MLS data are also comparable to zonal characteristics of TCO derived from the tropospheric residual method using several years of collocated data from TOMS and SAGE II. Figures 1 and 2 compare zonal characteristics of TCO for late spring (May) and summer (July) conditions in the NH derived from (top) TOMS/MLS, (middle) MOZART-2 and (bottom) TOMS/SAGE. The SAGE data are based on the version 6.2 algorithm (documentation may be obtained at http://www-sage2.larc.nasa.gov/data/v6_data/) and uses all available data from 1984 to 2003 with the exception of the period from June 1991 to August 1996. This gap includes the Mt. Pinatubo eruption period when SAGE measurements could not be made due to aerosol loading and May 1993–July 1996 when TOMS measurements were not available.

[8] There are several interesting features in TOMS/MLS data which are comparable to MOZART-2 and TOMS/SAGE data: (1) A plume structure emanating from industrial regions such as eastern China and Japan, traversing over the Pacific Ocean to the west coast of North America; (2) A similar plume structure emanating from the eastern coast of North America traversing over the Atlantic Ocean to Europe; (3) TCO values over most of the oceanic regions

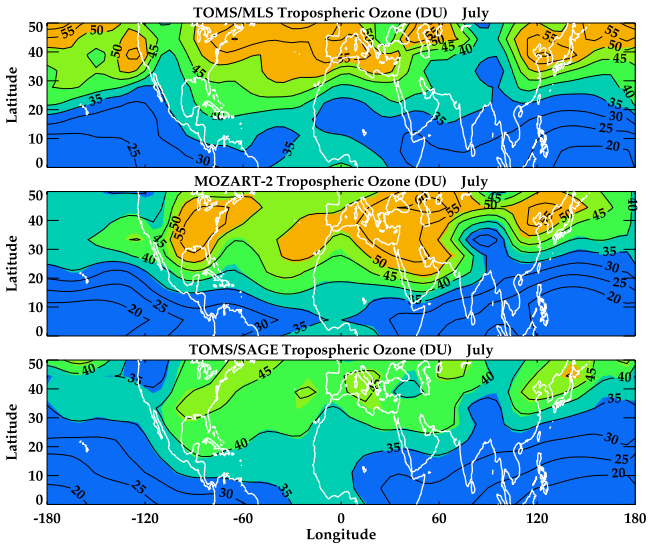

Figure 2. Same as Figure 1 but representing summer (July).

in the Atlantic and Pacific oceans are relatively high (∼50–60 DU) and comparable to industrial regions even though the oceanic regions are pollution free; (4) Lower values of TCO are seen mostly over the regions of Rocky Mountains, Tibetan Plateau and the Himalayas, which are affected by the topography of these regions; (5) The tropical region shows a wave pattern with maximum values (30–35 DU) in the Atlantic and minimum values (20–25 DU) in the Pacific, a feature of this region over most of the year [e.g., *Chandra et al.*, 2003, and references therein]; (6) There is no indication that TCO values are significantly higher over the Middle-East (∼20°N–35°N, ∼40°E–50°E) or over northern India (∼20°N–30°N, ∼70°E–85°E) compared to other regions. The Middle East increase was predicted by *Li et al.* [2001] based on the GEOS-CHEM model and a northern-India increase was reported by *Fishman et al.* [2003] based on TOMS/SBUV data. They attributed this increase to a population effect in India.

[9] In general, TOMS/MLS values are within 5 DU of climatological values derived from TOMS/SAGE both in May and July. In July, however, there are few locations north of 30°N in the Pacific and Atlantic regions where TOMS/MLS and TOMS/SAGE differences are in the range of 10–15 DU and may reflect real changes in TOMS/MLS values with respect to climatology. The difference between model and TOMS/MLS is shown in Figure 3 (top) for May and (bottom) July. Because of the difficulty in evaluating model uncertainty, it is difficult to assess the statistical significance of the difference of modeled and observed values of TCO shown in Figure 3. Recognizing an RMS uncertainty of about 5 DU in TOMSMLS measurements based on ozonesonde comparison, a difference of 10 DU or greater is probably significant. Using this criterion, Figure 3 suggests that the observed and model differences both in May and July are not significant over the tropical region and over a vast area at mid-latitudes. Their differences are however, significant in the eastern half of the Pacific region between 25°N and 50°N. Observed values in this region are 10–15 DU higher than model values. In (bottom) July the observed values are lower by 10–15 DU than model values over the Middle East, Eastern Europe, southern USA, and Mexico. In (top) May some of the differences over land are reduced to statistically insignificant values. However, model values seem to be significantly higher than observed values over the Sahara and northwest region of India. Though error in TOMS/MLS measurements cannot be ruled out, a possible explanation for TOMS/MLS and model differences may be attributed to underestimation and overestimation of TCO from MOZART-2. For example, in Figures 1 and 2 there is a TCO plume zone starting from east China (a highly polluted region) to the USA west coast. It is possible that MOZART-2 underestimates the outflow of China pollution to the west coast of USA. Similarly, Sahara and northwest India are away from industrially polluted regions. The model may overestimate effects such as long-range transport and biomass burning. In general, the TCO differences between TOMS/MLS and ozonesondes over most of the mid-latitude regions during the summer of 1997 are ∼3 DU. For example, TOMS/MLS minus sonde is −2.6 DU over Wallops Island (38°N, 75°W), and +2.2 DU over Tateno, Japan (36°N, 140°E).

[10] Both TOMS/MLS and MOZART-2 show significant decrease in TCO from late spring to summer over vast areas of the Pacific Ocean and Southeast Asia as shown in Figure 4. Figure 4 (top) shows a decrease of 5–10 DU from late spring to summer over most of the Pacific region and Southeast Asia. In comparison most of the regions north of 30°N encompassing North America, Europe, and Asia show slight increase or no change from May to July. With some minor exceptions these features are well produced by MOZART-2 as shown in Figure 4 (bottom). *Liu*

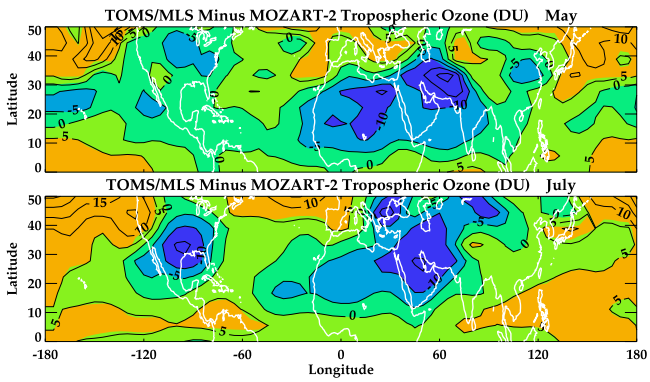

Figure 3. Difference (TOMS/MLS minus MOZART-2) of middle and top panels in (Figures top 1) and (bottom 2).

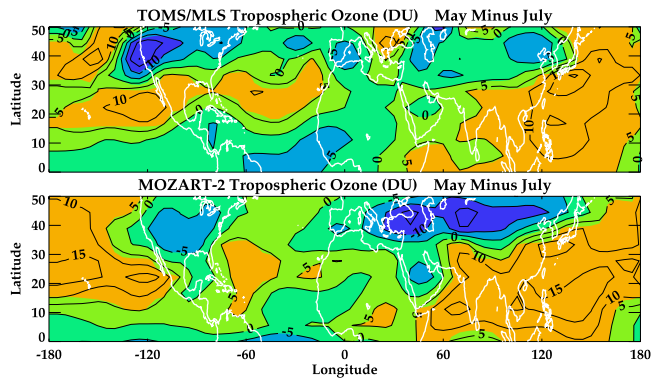

Figure 4. May minus July TCO (in DU) for (top) TOMS/MLS and (bottom) MOZART-2 model.

et al. [2002] have inferred similar changes from ozonesondes along the Asian Pacific Rim and have used the GEOS-CHEM model to analyze sonde results. Figure 4 gives a much broader perspective of changes in TCO than one can get from sonde measurements alone.

5. Implications of Elevated Ozone Over the Oceans

[11] In spite of significant differences between observed and modeled values in certain regions, the MOZART-2 model captures most of the zonal features of observed TCO including changes from late spring to summer in the NH. The model provides a valuable tool for analyzing the relative importance of various processes (e.g., surface NO_x emissions, lightning NO_x, and STE) which contribute to observed characteristics of TCO. The MOZART-2 model sources of NO_x consist of 4 TgN/y from lightning and 40.79 TgN/y from surface emissions, and 0.6 TgN/y from aircraft emissions. Surface emissions consist of industry/fossil fuel (23.11 TgN/y), biomass burning (9.81 TgN/y), biogenic/soil (6.62 TgN/y), and biofuel combustion (1.25 TgN/y). We have evaluated the model sensitivity by turning on and off the emission sources in each category. First, we turn off the NO_x emission from lightning (4 TgN/yr) to study the impact of the lightning NOx emission on TCO. Next, we turn off surface emission (40 TgN/yr) and lightning (4 TgN/y) but retain the aircraft component (0.6 TgN/yr). In the latter case the tropospheric ''residual ozone'' is largely, but not entirely due to stratospheric flux of ozone because of non-linearities in tropospheric ozone production, and a relatively small contribution from the aircraft emission. Our preliminary analysis suggests that the contributions from surface emission of NO_x and STE (''residual ozone'') appears relatively large over oceans and may be responsible for the nearly uniform distribution of TCO over northern mid-latitudes. For example, in July the contributions to TCO due to STE, surface NO_x emissions, and lightning over the USA are respectively 35–40%, 45–50% and 15–20%. The corresponding values over the Atlantic and Pacific oceans at mid-latitudes are 50–55%, 30–35% and 10–15%. In general, the STE contribution tends to be higher than surface NO_x emissions in the ''high'' middle latitudes (30°N to 50°N). The contribution from surface NO_x emissions is higher than STE over tropical and ''low'' middle latitudes (20°N to 30°N). The significant contribution from lightning (25–30%) is mostly limited to tropical latitudes. These conclusions are in general agreement with *Lelieveld and Dentener* [2000].

6. Summary and Conclusions

[12] In this paper we have studied the zonal characteristics of TCO during summer and late spring in the NH based on TOMS/MLS and TOMS/SAGE data, and the MOZART-2 model. At tropical latitudes TOMS/MLS TCO indicates lower values in the Pacific (20–25 DU) and higher values in the Atlantic (30–35 DU). At mid-latitudes north of 25°N, the zonal pattern changes significantly with nearly uniform values over both ocean and land. The TCO values over surface emission-free regions of the Atlantic and Pacific oceans are relatively high (50–60 DU) and are comparable to industrial regions of North America, Europe, and Asia where surface emissions of NO_x from industrial sources are significantly high. Some of these features are of climatological nature as inferred from several years of TOMS and SAGE measurements. The sensitivity study of the MOZART-2 model suggests that although ozone and its chemical precursors are transported over long distances from the places of their origin, the contribution from the stratosphere appears relatively large over oceans and may be responsible for nearly uniform distribution of TCO over northern mid-latitudes. With improvements in our measuring capability of tropospheric ozone on future satellite missions, the relative importance of these processes can be better quantified with global models such as MOZART-2.

[13] **Acknowledgments.** We wish to thank P. K. Bhartia for helpful discussions. Funding for this research was provided by Goddard Earth Science Technology (GEST) grant NCC5-494. NCAR is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation.

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