Elevated ozone in the troposphere over the Atlantic and Pacific Oceans in the northern hemisphere

S. Chandra[1,2], J. R Ziemke[1,2], and Xuexi Tie[3]

[1]University of Maryland Baltimore County (UMBC) Goddard Earth Sciences and Technology (GEST), Baltimore, Maryland

[2]Also at NASA Goddard Space Flight Center, Code 916, Greenbelt, Maryland

[3]National Center of Atmospheric Research, Boulder, Colorado

Abstract. Tropospheric column ozone (TCO) is derived from differential measurements of total column ozone from Nimus-7 and Earth Probe TOMS, and stratospheric column ozone from the Microwave Limb Sounder instrument on the Upper Atmospheric Research Satellite. It is shown that TCO during summer months over the Atlantic and Pacific Oceans at northern mid-latitudes is about the same (50-60 Dobson Units) as over the continents of North America, Europe and Asia, where surface emissions of nitrogen oxides from industrial sources, biomass and biofuel burning and biogenic emissions are significantly larger. This nearly uniform zonal variation in TCO is modulated by surface topography of the Rocky and Himalayan mountains and Tibetan Plateau where TOC is reduced by 20-30 Dobson Units. The zonal characteristics of TCO derived from satellite measurements are well simulated by a global chemical transport model called MOZART-2 (Model of Ozone and Related Chemical Tracers, version 2). The model results are analyzed to delineate the relative importance of various processes contributing to observed zonal characteristics of TCO, and they are shown that the surface emission of NOx contributes about 50% of the TCO at northern mid-latitudes, especially over the continents of North America, Europe and Asia. The result of TOC derived from TOMS and the analysis from MOZART-2 indicate that TOC is a very usefull tool to study tropospheric O_3 pollution resulting from surface emissions of pollutants.

1. Introduction.

Ozone is a precursor molecule of the hydroxyl (OH) radical which is the main oxidizing agent of several pollutants in the atmosphere. 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 the tropospheric ozone concentration has been increasing since the pre-industrial time as a result of increased concentration of ozone producing pollutants in Europe and North America [e.g., *Leliveld and Dentener*, 2000; *Hauglustaine and Brasseur*, 2001]. There is a concern that with the industrialization of Asian countries, tropospheric ozone may be increasing in the northern hemisphere through long-range transport. *Lelieveld et al.*, [2002] have suggested that the Mediterranean region is a crossroad of global pollution, where polluted air from different regions of the world converge. 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, Zhang et al., 2003]. Model results are usually compared with ozonesonde measurements, which are few and far in-between. At mid-latitudes in the northern hemisphere, column ozone derived from ozonesonde measurements tends to peak during summer months when the rate of photochemical production of ozone and anthropogenic emissions resulting from fossil fuel combustion, and biomass burning are high [*Brasseur et al.*, 1998; *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 generally sparse. Evidence of enhancement in upper tropospheric ozone over the north Atlantic region was shown by *Thouret et al.* [1998] from aircraft measurements. Unfortunately they could not investigate the broad Pacific Ocean region due to lack of aircraft flights.

The purpose of this paper is to use recently derived satellite data [*Chandra et al.*, 2003] to

characterize the zonal properties of TCO at mid-latitudes in the northern hemisphere and to study the implications of anthropogenic NO_x emissions using a global three dimensional chemical transport model called MOZART version 2 [*Horowitz et al.*, 2003]. The zonal characteristics of TCO is derived from differential measurements of total column ozone from Nimbus-7 Earth Probe TOMS and stratospheric column ozone from the MLS instrument on UARS and compared with modeled TCO with and without anthropogenic NO_x contribution.

2. TCO From TOMS/MLS.

TOMS/MLS measurements overlap only 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 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 cover a latitude range from 34° to 80° every 36 days because of a 57° inclination of the UARS orbit and planned rotation of the satellite through yaw every 36 days. As a result, TCO measurements outside ±34° are available every alternate month on average.

The seasonal and zonal characteristics of TCO derived from the TOMS/MLS residual is discussed by *Chandra et al.* [2003] for latitudes between ± 30°. Because the MLS instrument on UARS does not measure ozone below 100 hPa, zonal maps of TCO are most reliable between ± 30° 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. We have extended our data coverage to ± 50° after making appropriate adjustments for changes in tropopause pressure as discussed in *Chandra et al.* [2003]. In this paper, however, we use only summertime measurements between 20°N and 50°N when pollution level in the northern hemisphere is expected to be high. For WOUDC sonde sites between these latitudes, the relative bias and rms difference between TOMS/MLS and WOUDC TCO are respectively 3.7 DU and 6.2 DU.

3. MOZART Version 2 Model.

MOZART-2 is a global chemical transport model developed at 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]. (This manuscript is available on the web at http://www.gfdl.noaa.gov/~lwh/mozart/moz2_paper.pdf.) In its standard configuration, MOZART-2 simulates the concentrations of 63 chemical species from the surface up to the lower stratosphere. The model can use meteorological inputs derived from either a general circulation model (GCM) or from a meteorological reanalysis. It includes an extensive evaluation of MOZART-2 via comparison with CMDL surface measurements of CO and O_3, global O_3 sonde data, and multiple species (including O_3, CO, NO_x, PAN, HNO_3, various NMHC, CH_2O, etc.) from a large number of aircraft field campaigns.

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]. The chemical scheme used in MOZART-2 includes oxidation schemes for the non-methane hydrocarbons ethane, propane, ethane, propene, isoprene, α-pinene (as a surrogate for all terpenes), and n-butane (as a surrogate for all hydrocarbons with 4 or more carbons, excluding isoprene and terpenes). Heterogeneous reactions of N_2O_5 and NO_3 on sulfate aerosols are included in MOZART-2 using prescribed sulfate aerosol distribution [*Tie et al.*, 2001]. Photolysis frequencies are calculated using a pre-calculated "lookup" table [*Brasseur et al.*, 1998]. The model sources of NO_x consist of 4 TgN/y from lightning and 40.79 TgN/y from surface emissions. The latter consists of emissions from 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).

4. Zonal Variability in TCO.

Figure 1 compares the zonal variability in TCO derived from TOMS/MLS (upper panel) with the MOZART-2 model (lower panel) for latitudes between 20°N and 50°N. It is based on the average of May and July months and represents summer condition in the northern hemisphere. TOMS/MLS values are based on 1992 measurements when TCO values were obtained on almost a daily basis. In Figure 1, June values are not included since TOMS/MLS values for this month were not available north of 34° due to the UARS yaw maneuver.

There are several interesting features in TOMS/MLS data. (1) TCO values over most of the oceanic regions in the Atlantic and Pacific Oceans and Mediterranean Sea (especially in the downwind regions of the continents of North America, Europe and Asia) are relatively high (~50-65 DU) even though these regions are not locally polluted.

They are comparable to those over the Eastern and Western United States, Europe, Western China and Japan, which are main sources of industrial pollution. (2) Lower values (~25-30 DU) of TCO are mostly seen over the regions of Rocky Mountains, Tibetan Plateau and the Himalayas, which are affected by the topography of these regions. The high summer values of TCO over the continents are comparable to TCO values measured from ozonesondes at several locations in the USA, Europe, and Japan [e.g., *Logan,* 1999; *Newchurch et al.*, 2003].

A TCO field derived from the MOZART model (Figure 1, lower panel) is remarkably similar to TOMS/MLS field over most of the regions north of 30°N. There are few noticeable differences between model and observation. For example, model values of TCO tend to be higher by about 10 DU over eastern USA and the Mediterranean regions. The regions of ozone deficiency over both the Rocky Mountains and Tibet are wider in TOMS/MLS data than in the model. This difference extends farther south in the

Himalayan region encompassing northern India, Middle East and northern Africa.(Figure 1) and may be related to differences in meteorological conditions of the model and observations. The TOMS/MLS TCO field is based on 1992 data whereas the model represents an average present climatological condition.

The zonal similarities/differences between model and observations are further illustrated in Figure 2 for the latitude band 35°N-40°N as an example. Figure 2 also shows the estimated changes in TCO due to topography alone. These values are calculated using National Centers for Environmental Prediction (NCEP) surface terrain pressure and WOUDC ozonesonde profile climatologies from several stations over North America and Europe. Figure 2 shows high values of TCO (50-60 DU) over land and oceans inferred from both TOMS/MLS and the MOZART-2 model as in Figure 1, followed by large decreases over regions of high elevation encompassing the mid-western part of USA (~20 DU) and Tibet (~30 DU).). The decrease in TCO over these regions are comparable to ozone deficiency inferred from total column ozone measurements [*Zou*, 1996] and suggest that the latter is of tropospheric origin. *Zou* [1996] has attributed the ozone deficiency in these regions to changes in circulation pattern caused by changes in heat flux from the surface to the air over the mountains. It may be noted that TCO changes due to topography for these regions are relatively smaller (~10-15 DU) as shown in Figure 2.

5. Implications of Elevated Ozone Over the Oceans.

The nearly uniform distribution of TCO over land and ocean at mid-latitudes, inferred from both the model and the data, suggests that surface ozone and its chemical precursors are transported over long distances from the places of their origins. To estimate these effects, the MOZART-2 model was run for 13 months (use the first month for spin out) by turning off sources of surface NO_x emissions (40.79 TgN/y) but retaining the NO_x emissions from lightning (4 TgN/y) and stratospheric input of O_3 (342 Tg/y). The result of this run for the summer condition is shown in the upper panel of

Figure 3. Shown in Figure 3 (lower panel) is also the difference of the model runs with and without surface NO_x emissions. The latter provides an estimate of TCO related to surface emissions of NO_x only. As seen in Figure 3, the TCO field without surface emission is relatively uniform with a mean value of about 30-35 DU over both land and ocean. This field is largely determined by ozone flux from the stratosphere, which has a significantly large component in the northern hemisphere. . The stratospheric influx of O_3 in the model in the northern hemisphere is 256 TgO_3 /y compared to 87 TgO_3/y in the southern hemisphere. The NOx emission from lightning can also contribute to the TCO, with a significant seasonal and vertical varibilities. For example, the study by Zhang et al. [2003] suggests that over the US, the lightning provides about 20 to 30% O_3 concentrations above 500 hPa in summer.

The TCO values related to surface emissions of NO_x are higher by 10-15 DU over the land compared to ocean which has a mean value of about 20 DU. The latter corresponds to about 40% of TCO values in these regions and suggests that the large scale transport plays a major role in transporting the manmade pollution from the industrial regions of USA, Europe, China, and Japan to the pristine oceanic regions of the Atlantic and Pacific Oceans. Analyses of tropospheric ozone profiles from MOZART-2 model suggests that the NO_x related changes are mostly in regions below 500 hPa whereas STE related changes are in the regions above 500 hPa.

6. Summary and Conclusions.

In this paper we have studied the implications of industrial pollution at northern mid-latitudes from the industrialized countries in this region. Our study is based on TCO derived from TOMS/MLS measurements and the MOZART-2 model. Satellite data (TOMS/MLS) show that during summer months, TCO is almost uniformly distributed over most of the land and oceans. Over the remote regions of the Atlantic and Pacific oceans, TCO values are in the range of 50-60 DU which are the same as over the continents of North America, Europe, and Asia where surface emissions of NO_x from

industrial sources are significantly high. The MOZART-2 model, which captures most of the zonal features of the observed TCO, suggests a 40-50% increase in TCO from industrial sources, biomass and biofuel burning, and biogenic emissions. The TCO produced from the surface emissions of NOx are located over the continents of North America, Europe and Asia, and transported into Atlantic and Pacific oceans, producing an increase in TCO of 20-25 DU in the source regions and 15-20 DU in the remote oceans. This study suggests that the result of TOC derived from TOMS and coupled with the analysis from MOZART-2 provide a very usefull tool to study the tropospheric O_3.

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.

References

Berntsen, T. K., S. Karlsdottir, and D. A. Jaffe, Influence of Asian emissions on the composition of air reaching the North Western United States, *Geophys. Res. Lett., 26*, 2171-2174, 1999.

Brasseur, G. P., D. A. Hauglustaine, S. Walter, J. F. Muller, P. Rasch, C. Granier, and X. Tie, MOZART: A global three-dimensional Chemical-Transport-Model of the atmosphere, *J. Geophys. Res., 103*, 28,265-28,289, 1998.

Chandra, S., J. R. Ziemke, and R. V. Martin, Tropospheric ozone at tropical and middle latitudes derived from TOMS/MLS residual: Comparison with a global model, *J. Geophys. Res., 108* (D9), 4291, doi: 10.1029/2002JD002912, 2003.

Friedl, R., Atmospheric effects of subsonic aircraft: Interim assessment report of the advanced subsonic technology program, NASA Ref. Publ. 2400, 143pp, 1997.

Haughlustaine, D. A., and G. P. Brasseur, Evolution of tropospheric ozone under anthropogenic activities and associated radiative forcing of climate, *J. Geophys. Res., 106*, 32,337-32,360, 2001.

Horowitz, L.W., S. Walters, D. Mauzerall, L. Emmons, P. Rasch, C. Granier, X. Tie, J.F. Lamarque, M. Schultz, and G. Brasseur, A global simulation of tropospheric ozone

and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res.*, in press, 2003.

Li, Q., et al., A tropospheric ozone maximum over the Middle East, *Geophys. Res. Lett., 28*, 3235-3238, 2001.

Liu, H., et al., Sources of tropospheric ozone along the Asian Pacific Rim: An analysis of ozonesonde observations, J. *Geophys. Res., 107*(D21), 4573, doi: 10.1029/2001JD002005, 2002.

Leliveld, J., and F. J. Dentener, What controls tropospheric ozone?, *J. Geophys. Res., 105*, 3531-3551, 2000.

Leliveld, et al., Global air pollution crossroads over the Mediterranean, *Science, 298*, 794-799, 2002.

Logan, J. A., An analysis of ozonesonde data for the troposphere: Recommendations for testing 3-D models and development of a gridded climatology for tropospheric ozone *J. Geophys. Res., 104*, 16,115-16,149, 1999.

Newchurch, M. J., M. A. Ayoub, S. Oltmans, B. Johnson, and F. J. Schmidlin, Vertical distribution of tropospheric ozone at four sites in the United States, *J. Geophys. Res., 108*(D1), 4031, doi: 1029/2002JD001059, 2003.

Phadnis, M. J., H. Levy II, and W. J. Moxim, On the evolution of pollution from South and Southeast Asia during the winter-spring monsoon, *J. Geophys. Res., 107*(D24), 4790, doi: 10.1029/2002JD002190, 2002.

Price, C., Penner, J., and Prather, M., 1997: NOx from lightning. 1. Global distribution based on lightning physics, *J. Geophys. Res. 102*, 5929-5941, 1997

Rasch, P.J., N.M. Mahowald, B.E. Eaton, Representations of transport, convection, and the hydrologic cycle in chemical transport models: Implications for the modeling of short-lived and soluble species, *J. Geophys. Res., 102*, 28,127-28,138. 1997.

Tie, X, G. Brasseur, L. Emmons, L. Horowitz, and D. Kinnison, Effects of aerosols on tropospheric oxidants: A global model study, *J. Geophys. Res., 106*, 22931-22964, 2001.

Thouret, V., A. Marenco, P. Nedelec, and C. Grouhel, Ozone climatologies at 9-12 km altitude as seen by the MOZAIC airborne program between September 1994 and August 1996, *J. Geophys. Res., 103*, 25,653-25,679, 1998.

Zou, H., Seasonal variation and trends of TOMS ozone over Tibet, *Geophys. Res. Lett.*, *23*, 1029-1032, 1996.

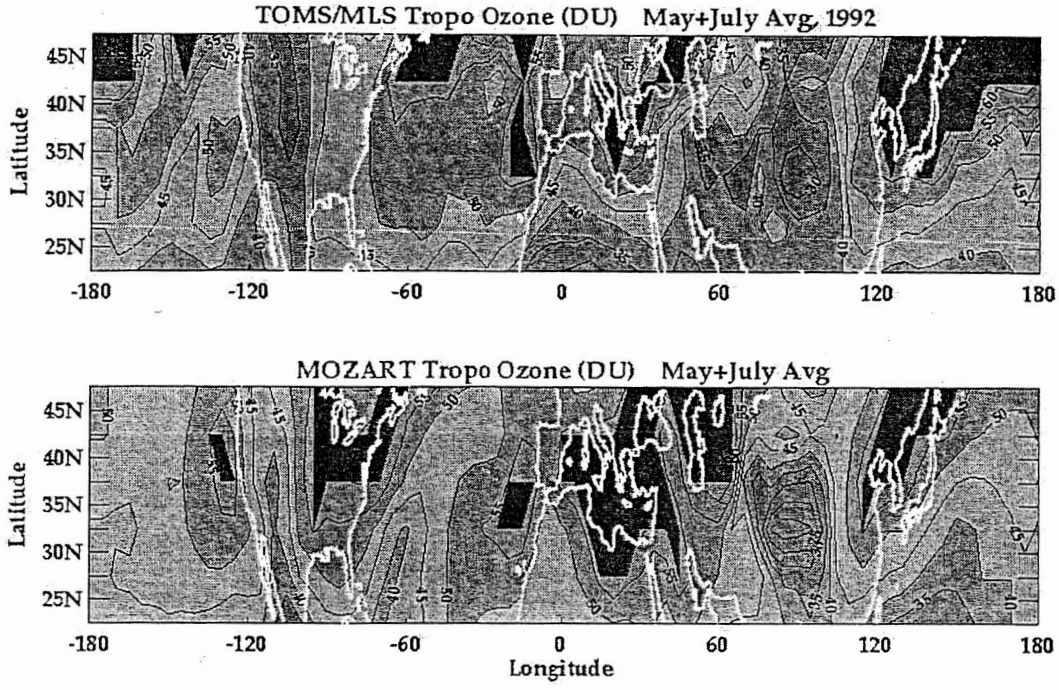

Figure 1. (top) Contour plot of TOMS/MLS tropospheric column ozone (Dobson Units) in the northern hemisphere averaged over May and July 1992 measurements. (bottom) Similar to (top) but for the MOZART model.

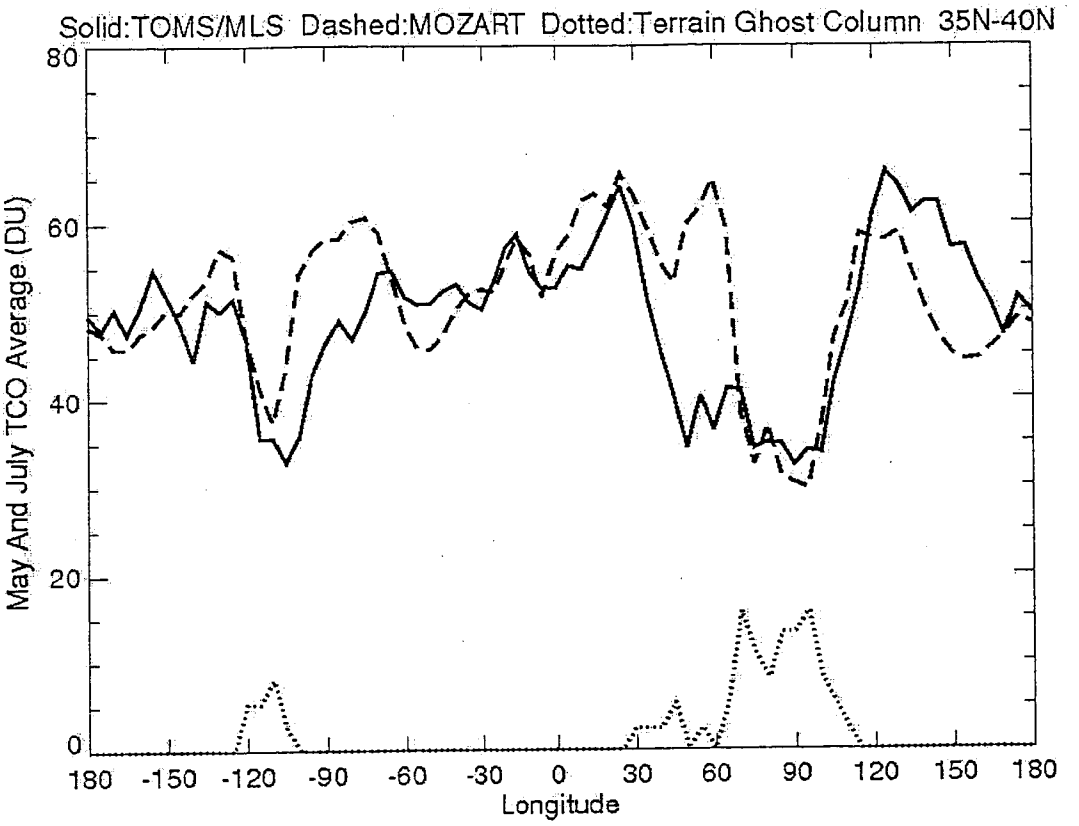

Figure 2. Line plots of tropospheric column ozone averaged over May and July 1992 within latitude band 35N-40N for TOMS/MLS (solid), MOZART (dashed), and Terrain Ghost Column (dotted).

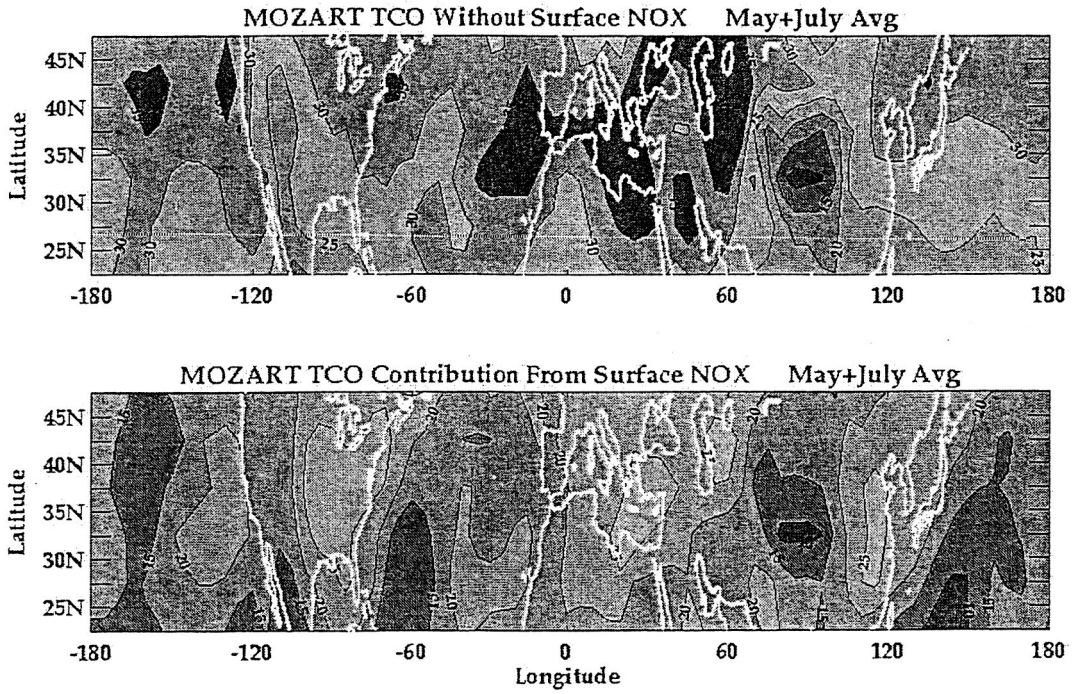

Figure 3. (top) MOZART TCO (in Dobson Units) for model run without surface NO_x emissions. (bottom) Contribution to TCO from NO_x emissions. (This latter field is derived by subtracting the zero surface emission NO_x MOZART TCO field from the MOZART TCO field in Figure 1.)