Spring to summer northward migration of high O_3 over the western North Atlantic

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Received 6 October 2007; revised 3 January 2008; accepted 30 January 2008; published 29 February 2008.

[1] Tropospheric O_3 columns retrieved from OMI and MLS measurements, NO_2 columns from OMI, and upper tropospheric O_3 concentrations from TES over North America and the western North Atlantic from April to August 2005 are analyzed using the Regional chEmical and trAnsport Model (REAM). Large enhancements of column and upper tropospheric O_3 over the western North Atlantic comparable to those over the eastern United States are found in the satellite measurements and REAM simulations. The O_3 enhancement region migrates northward from spring to summer. Model analysis indicates that the northward migration is driven by seasonal shifts of O_3 transported from the stratosphere and that produced through photochemistry from surface emissions and lightning NOx. As their uncertainties improve, satellite measurements of O_3 and its precursors will be able to provide more quantitative constraints on pollutant outflow from the continents.
Citation: Choi, Y., Y. Wang, Q. Yang, D. Cunnold, T. Zeng, C. Shim, M. Luo, A. Eldering, E. Bucsela, and J. Gleason (2008), Spring to summer northward migration of high O_3 over the western North Atlantic, *Geophys. Res. Lett.*, *35*, L04818, doi:10.1029/2007GL032276.

1. Introduction

[2] Major pathways for North American pollution outflow in the free troposphere include cloud convection [e.g., *Pickering et al.*, 1988] and transport by the warm conveyor belt (WCB) [e.g., *Cooper et al.*, 2002; *Li et al.*, 2005]. The large impact of convection with associated lightning on O_3 and its precursors in the upper troposphere (UT) over North America are evident in the in situ measurements in two experiments: the SASS (Subsonic Assessment) Ozone and NO_X Experiment (SONEX) [e.g., *Singh et al.*, 1999] and the Intercontinental Transport Experiment-North America, Phase A (INTEX-A) [e.g., *Singh et al.*, 2006]. The enhanced O_3 and its precursors in the UT can be quickly exported to the western North Atlantic by westerly winds [*Choi et al.*, 2005; also Springtime transition of NO_2, CO and O_3 over North America: Model evaluation and analysis, submitted to *Journal of Geophysical Research*, 2007]. Another mechanism, WCB, associated with mid-latitude cyclones, transfers air pollutants from the boundary layer to the free troposphere.

[3] Many investigators have reported better agreement between the satellite measurements and the model results in tropical regions than at mid and high latitudes partly due to the difficulty in simulating cloud convection and lightning at mid latitudes [e.g., *Chandra et al.*, 2004; *Martin et al.*, 2006; *Ziemke et al.*, 2006; *Hudman et al.*, 2007]. Recent GEOS-CHEM studies have shown that lightning NOx production at higher latitudes in the standard global model needs to be increased by up to a factor of 4 [e.g., *Li et al.*, 2005; *Martin et al.*, 2006; *Hudman et al.*, 2007]. *Choi et al.* [2005] demonstrated that the transient enhancements of lightning NOx and the convective transport of CO have large enough signals for satellites to detect.

[4] In this work, we examine O_3 enhancements over the western North Atlantic during the transition from spring to summer in 2005 using measurements from recent satellite instruments, the Ozone Monitoring Instrument (OMI), the Microwave Limb Sounder (MLS), and the Tropospheric Emission Spectrometer (TES) onboard the NASA Aura satellite. These O_3 enhancements are direct evidence of continental outflow and the ability of models to simulate these features is necessary before applying the models to assess the impacts of pollutant emissions. We investigate how O_3 enhancements in the outflow region over the North Atlantic compare to the source region of its precursors and if the location of large O_3 outflow changes from spring to summer. Further, we apply the Regional chEmical and trAnsport Model (REAM) [*Choi et al.*, 2005; also submitted manuscript, 2007] to investigate the contributions by surface pollutant emissions, lightning NO production, and transport from the stratosphere to the observed spring to summer migration of O_3 enhancements over the western North Atlantic.

2. Satellite Measurements: OMI-MLS Tropospheric Column O_3, OMI Tropospheric Column NO_2, and TES O_3

[5] The nadir horizontal resolutions of OMI, MLS, and TES are 13×24 km^2, 30×150 km^2, and 5×8 km^2, respectively. The tropospheric O_3 column is derived using a residual method by estimating the stratospheric O_3 column using MLS O_3 profiles above 215 hPa and subtracting that amount from OMI level 2 total column O_3 [*Yang et al.*, 2007]. The mid-latitude stratospheric O_3 columns between 215 hPa and the tropopause are obtained by SAGE II mapping. The detailed validation of the OMI-MLS tropospheric column O_3 products was performed by *Yang et al.* [2007].

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0094-8276/08/2007GL032276$05.00

[6] The retrieved tropospheric NO_2 columns from OMI measurements [*Bucsela et al.*, 2006] and their uncertainties are obtained from the NASA Goddard Earth Sciences Distributed Active Archive Center. We use only OMI tropospheric NO_2 column data with a cloud fraction of <20%. TES O_3 data are obtained from the NASA Langeley Atmospheric Science Data Center. Only upper tropospheric TES O_3 retrieval data with degrees of freedom of >3.5 are used. REAM results for comparison are processed with TES retrieval averaging kernels for O_3 [*Worden et al.*, 2007].

3. Model Description

[7] The REAM model was used previously by *Choi et al.* [2005; also submitted manuscript, 2007], *Jing et al.* [2006], and *Wang et al.* [2006] to simulate chemical transport over North America. We use the same setup here (with a horizontal resolution of 70 km). Spring and summer 2005 GEOS-CHEM global chemical transport model (version 7.2) simulations [*Bey et al.*, 2001] are used to specify initial and boundary conditions for trace gases. Emission inventories for combustion and industrial sources and algorithms for biogenic sources are adopted from GEOS-CHEM, except for the fossil fuel NO_X and CO emissions over the United States, which are taken from the 1999 US Environmental Agency National Emission Inventory (version 2). A production rate of 3.0×10^{26} NO molecules per flash (K. Pickering, personal communication, 2005) is specified for both intracloud and cloud-to-ground flashes. More details of REAM set up and evaluations with surface, ozonesonde, aircraft, and satellite measurements are presented by Choi et al. (submitted manuscript, 2007).

4. Results and Discussion

4.1. OMI-MLS Tropospheric O_3

[8] Figure 1 shows the monthly mean tropospheric column O_3 derived from OMI-MLS measurements and the corresponding model simulations from April to August 2005. REAM-simulated tropospheric O_3 columns are 1–11% lower than those derived by OMI-MLS measurements, and the correlation coefficients improve from 0.59 to 0.77 from April to August. Simulated vertical O_3 profiles compare well with ozonesonde measurements except for the underestimations in the upper troposphere particularly in spring due to a low bias in the specified upper boundary condition (Choi et al., submitted manuscript, 2007). The influence of the upper boundary condition decreases in July and August because the vertical gradient of upper tropospheric O_3 decreases.

[9] The OMI-MLS columns indicate high O_3 over the eastern United States and the western North Atlantic. Over the continent, the activation of photochemistry from spring to summer, driven in part by increasing solar insolation, is evident as high O_3 concentrations move northward. Continental O_3 enhancements are overestimated in July and August in regions affected by lightning (C. Zhao, unpublished results, 2007), implying that its effect is overestimated in the model.

[10] Despite large surface emissions of O_3 precursors over North America, O_3 enhancements over the western North Atlantic are as high as they are over the eastern United States. In fact, O_3 column enhancements over the oceanic regions are higher than they are over land in April and May. As the season progresses from spring to summer, the high O_3 regions over the western North Atlantic move northward from the coast off Florida to the coast off New England.

[11] REAM captures the observed O_3 enhancements over the eastern United States and the western North Atlantic and the northward migration of high O_3 outflow over the oceanic region. To examine the reasons for the migration from spring to summer, we conduct sensitivity simulations. O_3 concentrations without lightning and surface NOx emissions are subtracted from the standard simulation to compute the effects of these sources. In a third sensitivity study, we first run tagged tracer simulations using GEOS-CHEM to compute the fractions of O_3 transported from the stratosphere. The Synoz method is used in GEOS-CHEM to simulate cross-tropopause transport [*Bey et al.*, 2001]. We remove the stratospheric contributions in the REAM sensitivity simulation by using only the tropospheric portions of initial conditions and lateral and upper boundary conditions for O_3. We estimate the stratospheric contribution by subtracting O_3 in the third sensitivity simulation from the standard one. The results are shown in Figure 1. Over the United States, the contributions of surface NOx emissions, stratospheric transport, and lightning during the summertime in this study are 41–52%, 31–36%, and 15–22%, respectively, comparable to those (45–50%, 35–40%, and 15–20%) by *Chandra et al.* [2004].

[12] In April and May, the largest contribution to high column O_3 is due to transport from the stratosphere. The resulting O_3 enhancements are over the southeastern United States, adjacent Gulf of Mexico, and western North Atlantic regions. Transport of O_3 from the stratosphere decreases from spring to summer as wave propagation from the troposphere to stratosphere weakens in summer [e.g., *Wang et al.*, 1998, and references therein]. Photochemical contribution from surface NOx emissions is small in April but becomes comparable to the stratospheric contribution in May as photochemical activity increases with larger solar insolation and more abundant water vapor [e.g., *Wang et al.*, 2003; Choi et al., submitted manuscript, 2007]. The contribution from lightning NOx remains small during this period in 2005.

[13] In June, July, and August, the stratospheric contribution becomes much smaller (>a factor of 2 decreases over the western North Atlantic). At 300 hPa, for example, stratospheric contributions decrease from 20–40% in April to <20% in June. The contribution from surface NOx emissions is similar to that in May and the outflow region of high O_3 moves toward the coast of the northeastern United States. The contributions from lightning NOx are much larger than in May. The outflow region of high O_3 produced from lightning NOx is similar to that of surface NOx-produced O_3, reflecting increasing convective activities in summer.

[14] *Yang et al.* [2007] has conducted comprehensive comparisons of the OMI-MLS tropospheric O_3 columns with ozonesonde measurements. As an illustration, we show the comparison of OMI-MLS tropospheric O_3 columns with ozonesonde measurements at Wallops Island (38°N, 75°W),

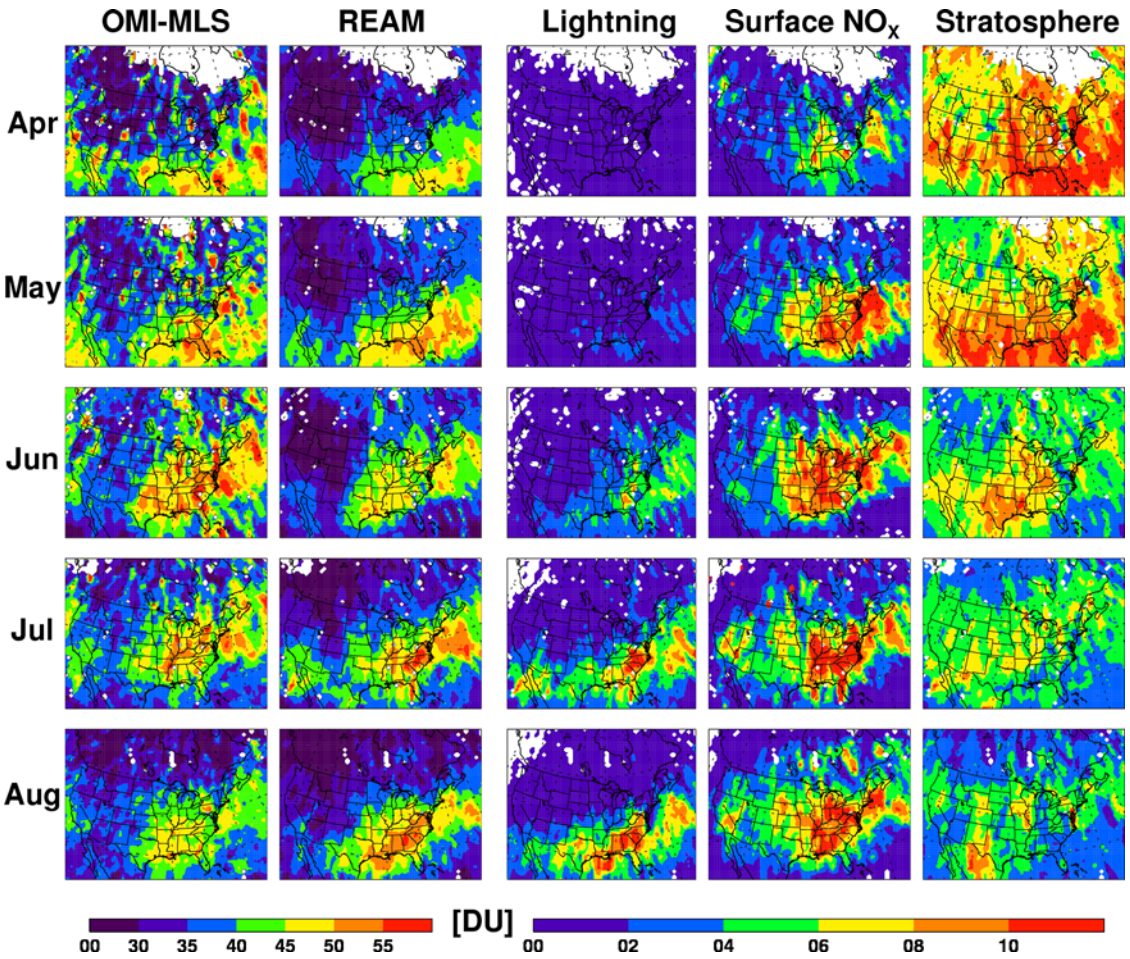

Figure 1. Monthly mean tropospheric O_3 columns from April to August 2005 derived from OMI-MLS satellite measurements (first column), REAM simulations (second column), produced due to lightning NOx (third column), produced due to surface emissions, and transported from the stratosphere (last column).

Goosebay (53.3°N, 60.4°W), Kelowna (49.9°N, 119.4°W), and Yarmouth (43.9°N, 66.1°W) from April to August 2005 (Figure 2). We also show the corresponding REAM simulation results. Compared with ozonesondes, both OMI-MLS and REAM underestimate tropospheric O_3 columns, with mean biases of −2.3 and −4.5 DU for OMI-MLS and REAM, respectively. The correlation coefficients are 0.78 and 0.82, respectively. The model-simulated tropospheric O_3 column is lower than the OMI-MLS because REAM-simulated upper tropospheric O_3 concentrations tend to be low. REAM bias is propagated from GEOS-CHEM through the specified upper boundary condition (Choi et al., submitted manuscript, 2007). The bias in the upper boundary condition likely leads to some underestimates of the stratospheric contribution to the tropospheric O_3 column shown in Figure 1.

4.2. OMI Tropospheric Column NO_2

[15] NOx is a major precursor for tropospheric O_3 production. Figure 3 shows the average tropospheric NO_2 columns retrieved from OMI and simulated by REAM in May–August 2005. Overall, the model results are in reasonably good agreement with OMI retrievals. Compared with the OMI tropospheric NO_2 columns, REAM overestimates NO_2 columns by $\sim 1 \times 10^{15}$ molecules cm^{-2} over

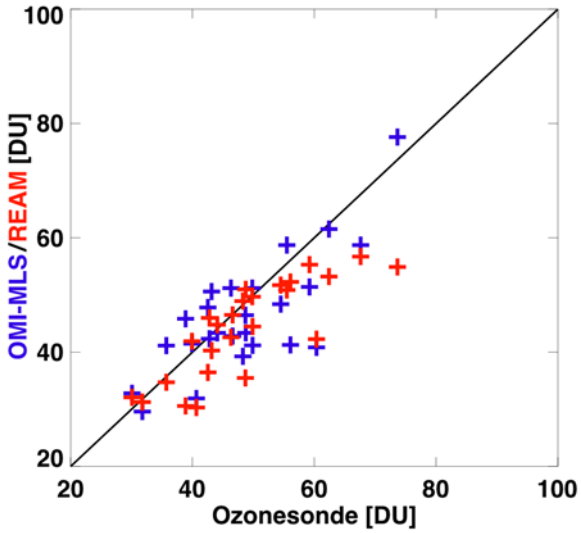

Figure 2. Tropospheric O_3 columns measured by ozonesondes, derived from OMI-MLS and simulated by REAM at Wallops Island, Goosebay, Kelowna, and Yarmouth from April to August 2005. Coincidence criteria for OMI-MLS-derived column ozone are within ±3° by longitude, ±2.5° by latitude on the same day as the ozonesonde measurements.

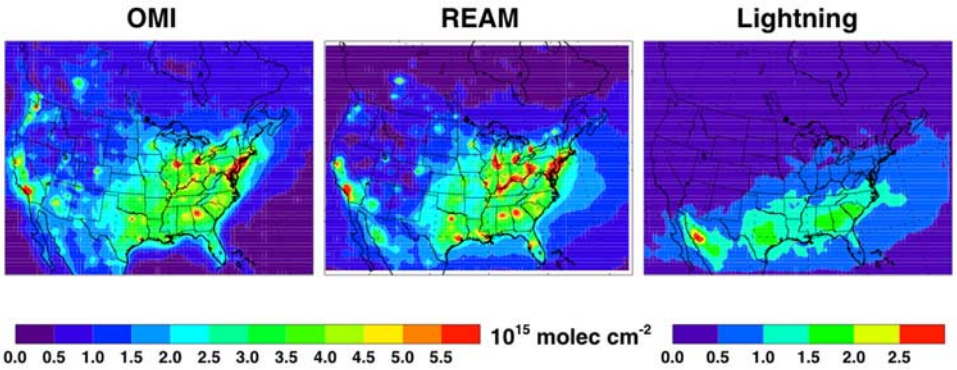

Figure 3. Mean tropospheric NO_2 columns in May–August 2005 from OMI satellite measurements (first column), those from REAM simulations (second column), and those contributed by lightning production in the model (third column). Only OMI data with cloud fractions of <20% are used. Corresponding model results are taken at the same time and locations as the OMI measurements. Lightning contribution is estimated by subtracting simulated NO_2 without lightning production from the standard simulation.

the Ohio Valley, where power plant NO_x emissions are large. *Frost et al.* [2006] found that NO_x emissions from power plants in 2004 were 50% of those in 1999 over the region. This reduction was not taken into account in our simulations. Model results indicate that lightning NO_2 contributions are largest over the southern part of the US. Simulated direct outflow enhancements of NO_2 are off the coast of northeastern US. REAM also simulates higher NO_2 columns over the ocean than OMI. Compared to GOME [*Choi et al.*, 2005; also submitted manuscript, 2007] and SCIAMACHY [*Martin et al.*, 2006], the NO_2 columns retrieved from OMI over the western North Atlantic are lower. The reason for this difference is unclear; detailed studies of OMI and SCIAMACHY NO_2 retrievals are needed. Simulated O_3 enhancements due to lightning (Figure 1) are downwind from the NO_x enhancements because of time needed for photochemical production of O_3.

4.3. TES UT O_3 Measurements

[16] Due to insufficient spatial coverage of TES O_3 measurements over North America from April to June 2005, we use only TES observations in July and August. TES O_3 distributions are patchy due in part to measurement uncertainties. Figure 4 shows the comparison of TES retrieved and model simulated O_3 mixing ratios at 325 hPa (300–350 hPa). Simulated mean REAM O_3 concentrations are ~5% lower. Comparisons with in situ measurements such as ozonesondes show that the UT TES O_3 measurements tend to be overestimated [*Worden et al.*, 2007]. TES O_3 enhancements are over similar regions of tropospheric O_3 column enhancements shown in Figure 1, although the details of the spatial patterns are different. Different sampling frequencies and more importantly the measurement uncertainties of TES are contributors to the difference. The correlation between TES measurements and REAM simulations ($R \cong 0.5$) is lower than those for tropospheric O_3 column due likely to more patchy measurements from TES. The large enhancements of TES O_3 in southern Canada are not simulated in the model. More analysis is needed to confirm the validity of these enhancements. Simulated UT O_3 enhancements due to lightning are >20 ppbv over the southeastern United States and the western North Atlantic.

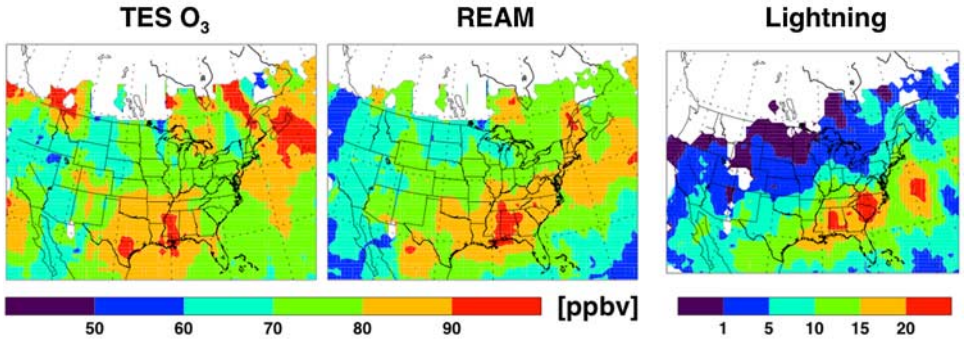

Figure 4. Mean tropospheric O_3 mixing ratios at 325 hPa (300–350 hPa) for July and August 2005 from the TES satellite measurements (first column), those from REAM (second column), and REAM estimated lighting contribution (third column). 27 global survey and 4 special observation products are used. Lightning contribution is estimated by subtracting simulated O_3 without lightning NO_x from the standard simulation. Only TES O_3 data with a degree of freedom of >3.5 are used. Corresponding model results are processed using TES O_3 retrieval averaging kernel and sampled at the same time and locations as the TES measurements.

These enhancements are generally larger than the mean uncertainties of TES O_3 retrievals of 5–20 ppbv.

5. Conclusions

[17] Tropospheric O_3 columns by OMI and MLS, tropospheric NO_2 columns by OMI, and upper tropospheric O_3 by TES from April to August 2005 are analyzed with REAM. Large enhancements of column O_3 over the western North Atlantic, comparable to those over the eastern United States, are found in the OMI-MLS satellite measurements and are simulated by the model. Both OMI-MLS measurements and REAM simulations show a northward migration of high O_3 outflow region from spring to summer. Model results indicate that springtime outflow is mainly driven by transport from the stratosphere and O_3 production from surface emissions, while summertime outflow is mainly driven by O_3 production from surface and lightning NO_x emissions. The northward migration of the outflow over the western North Atlantic primarily reflect the location change from the region with large O_3 transport from the stratosphere to the region with large production by lightning NOx. Upper tropospheric O_3 enhancements due to lightning NOx enhancements are analyzed using TES measurements. While qualitative agreement is found, quantitative analysis is hindered by measurement and simulation uncertainties. Reducing the uncertainties and improving the temporal coverage of satellite measurements are needed to further constrain the factors controlling the continental pollution outflow identified in the model study.

[18] **Acknowledgments.** We thank Kevin Bowman and Qinbin Li for helpful comments on TES data, and Daniel Jacob and Robert Yantosca for providing the GEOS-CHEM model and data. This work was supported by the National Science Foundation Atmospheric Chemistry Program.

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