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Large upper tropospheric ozone enhancements above midlatitude North America during summer: In situ evidence from the IONS and MOZAIC ozone measurement network

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[1] The most extensive set of free tropospheric ozone measurements ever compiled across midlatitude North America was measured with daily ozonesondes, commercial aircraft and a lidar at 14 sites during July-August 2004. The model estimated stratospheric ozone was subtracted from all profiles, leaving a tropospheric residual ozone. On average the upper troposphere above midlatitude eastern North America contained 15 ppbv more tropospheric residual ozone than the more polluted layer between the surface and 2 km above sea level. Lowest ozone values in the upper troposphere were found above the two upwind sites in California. The upper troposphere above midlatitude eastern North America contained 16 ppbv more tropospheric residual ozone than the upper troposphere above three upwind sites, with the greatest enhancement above Houston, Texas, at 24 ppbv. Upper tropospheric CO measurements above east Texas show no statistically significant enhancement compared to west coast measurements, arguing against a strong influence from fresh surface anthropogenic emissions to the upper troposphere above Texas where the ozone enhancement is greatest. Vertical mixing of ozone from the boundary layer to the upper troposphere can only account for 2 ppbv of the 16 ppbv ozone enhancement above eastern North America; therefore the remaining 14 ppbv must be the result of in situ ozone production. The transport of NO_x tracers from North American anthropogenic, biogenic, biomass burning, and lightning emissions was simulated for the upper troposphere of North America with a particle dispersion model. Additional box model calculations suggest the 24 ppbv ozone enhancement above Houston can be produced over a 10 day period from oxidation reactions of lightning NO_x and background mixing ratios of CO and CH_4. Overall, we estimate that 69–84% (11–13 ppbv) of the

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16 ppbv ozone enhancement above eastern North America is due to in situ ozone production from lightning NO_x with the remainder due to transport of ozone from the surface or in situ ozone production from other sources of NO_x.

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1. Introduction

[2] Ozone is a key trace gas for both the chemistry and radiative balance of the troposphere [*Intergovernmental Panel on Climate Change*, 2001], and as it is the principal pollutant associated with photochemical smog its presence in the lower troposphere has large implications for issues of air quality. Currently, international research programs such as the SPARC Project (Stratospheric Processes and their Role in Climate) and IGAC (International Global Atmospheric Chemistry) are focusing research on the dynamics and composition of the upper troposphere and lower stratosphere because of this region's influence on global climate change, with ozone once again a trace gas of primary interest.

[3] Chemical transport model (CTM) studies indicate that North American emissions have a major impact on net global tropospheric ozone production [*Li et al.*, 2002]. However, verifying CTM estimates of the North American ozone budget is difficult because of the limited number of profiling sites across the continent. Long-term ozonesonde profiling has been conducted at six locations in Canada, but all are at relatively high latitudes [*Tarasick et al.*, 2005], and at just two sites in the USA: Boulder, Colorado and Wallops Island, Virginia. However, the National Oceanic and Atmospheric Administration (NOAA) initiated the Trinidad Head, California and Huntsville, Alabama sites in the late 1990s [*Newchurch et al.*, 2003]. Data coverage increased in 2004 with the addition of the NOAA site at Narragansett, Rhode Island, and four new Canadian sites along the USA/Canada border. However, large data gaps still exist in the southwestern and south-central USA and the sampling rate of once per week means it will take several years to build a North American ozone climatology.

[4] To finally measure the daily ozone distribution across midlatitude North America during the most photochemically active part of the year, NASA, NOAA, Environment Canada, and several US universities pooled resources during the 1 July to 15 August 2004 ICARTT (International Consortium for Atmospheric Research on Transport and Transformation) study to launch ozonesondes from several sites across the eastern USA and Canada under the IONS (INTEX Ozonesonde Network Study) program (see overview of IONS by A. M. Thompson et al. (IONS-04 (INTEX Ozonesonde Network Study, 2004): Perspective on summertime UT/LS (upper troposphere/lower stratosphere) ozone over northeastern North America, submitted to *Journal of Geophysical Research*, 2006, hereinafter referred to as Thompson et al., submitted manuscript, 2006)). Additional ozone profiles across eastern North America were obtained from five instrumented commercial aircraft that fly between North America and Europe under the European MOZAIC program. To increase the sample size, MOZAIC profiles were combined with ozonesonde profiles from nearby locations to form 14 free-tropospheric measurement sites (Figure 1). An additional upper tropospheric ozone monitoring site was available near Los Angeles from combined lidar and MOZAIC measurements. This data set contains the most extensive set of free tropospheric ozone measurements ever compiled across midlatitude North America. In this study we focus on measurements that were made only in the troposphere and subtract the model-estimated stratospheric ozone from each profile leaving a tropospheric residual ozone. An interesting result was that the overall network showed a greater amount of tropospheric residual ozone in the upper troposphere than in the lower troposphere. Furthermore the upper troposphere above eastern North America contained far greater tropospheric residual ozone mixing ratios than the upwind sites, with the largest values above Houston, Texas. We use a particle dispersion model to demonstrate that the upper tropospheric ozone maximum above eastern North America is largely the result of in situ ozone production from lightning NO_x.

5. Conclusions

[58] This study assembled the most comprehensive set of ozone measurements ever collected in the free troposphere above midlatitude North America during a single season. By focusing on measurements taken only in the troposphere and by calculating and subtracting the influence from aged stratospheric intrusions (up to 20 days old) we produced a data set of tropospheric residual ozone values across the study region. On average the upper troposphere above midlatitude eastern North America contained 15 ppbv more tropospheric residual ozone than the more polluted layer between the surface and 2 km above sea level (Figure 4c). Furthermore the upper troposphere above midlatitude eastern North America contained 16 ppbv more tropospheric residual ozone than the upper troposphere above 3 upwind sites, with the greatest enhancement above Houston at 24 ppbv (Figure 7d). Our detailed simulation of lightning NO_x emissions tied to the exact times and locations of actual cloud-to-ground lightning flashes across North America shows that lightning is the dominant source of NO_x in the upper troposphere. Overall, we estimate that 69–84% (11–13 ppbv) of the 16 ppbv ozone enhancement above eastern North America is due to in situ ozone production from lightning NO_x with the remainder due to transport of ozone from the surface or in situ ozone production from other sources of NO_x.

[59] This study contains several sources of uncertainty, greatest of which are the lightning NO_x emission rate and the lifetime of NO_x in the upper troposphere, and we have been careful to take the variability of these values into account. We have provided some broad estimates of the lightning NO_x contribution to the widespread upper tropospheric ozone enhancement across eastern North America, and additional chemical transport model studies and measurements are required to refine the quantification of the contribution of lightning NO_x to the upper tropospheric ozone enhancement for the individual measurement stations. However, some confirmation of our results is provided by a recent study that showed great foresight into the existence of the upper tropospheric ozone maximum above Texas.