A Modeling Study on Ozone Formation in the Upper Troposphere in Relation to Thunderstorms

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ABSTRACT

Tropospheric ozone is important because of its deleterious effects as urban smog at ground level, its role as a greenhouse gas in the upper troposphere (UT), and its control of the oxidizing capacity of the troposphere through its photochemical derivative hydroxide (OH). Thunderstorms can affect ozone in the UT through production of nitrogen oxides (NOx) by lightning and convective transport of carbon monoxide (CO), hydrocarbons, and other volatile organic compounds that produce peroxy radicals. The purpose of this study was to better understand the importance of specific reaction rates in UT ozone chemistry by analyzing data generated by a high-resolution WRF-Chem simulation in which thunderstorms were explicitly represented at a horizontal resolution of 4 km. Our aim was to determine if thunderstorms associated with the annual North American Monsoon influenced the fate of NOx and peroxy radicals in the UT. Using output for a typical summer day, we mapped the most important peroxy radical production reactions and compared these with maps of storms as well as boundary layer and lightning-NOx tracers. The results indicated that the oxidation of CO, methane and short-lived, intermediate species such as formaldehyde and organic peroxides were the most important reactions. Furthermore, higher reaction rates of formation of peroxy radicals were found in areas were the boundary layer tracer was transported by convection. Long term implications of the research include contributing to a growing body of knowledge on ozone formation as ozone has far reaching effects on the quality of life of plant and animal species.

1. Introduction

   The study of tropospheric ozone (O_3) can shed light on various photochemical processes that occur within the atmosphere that can have far reaching effects on the quality of life for humans as well as plant and animal species. Although stratospheric ozone absorbs high frequency ultraviolet light that in large doses poses harm to human beings, ground level or tropospheric ozone is generally viewed in a different way due to its oxidizing properties and its role in subsidiary reactions that produce constituents of urban smog. More specifically, O_3 acts as a greenhouse gas radiatively in the upper troposphere, controls the oxidizing capacity of the troposphere i.e. cleaning capacity of the troposphere through its photochemical derivative OH, and functions as a major environmental and atmospheric pollutant at ground level (Cooper, et al., 2006; 2007).
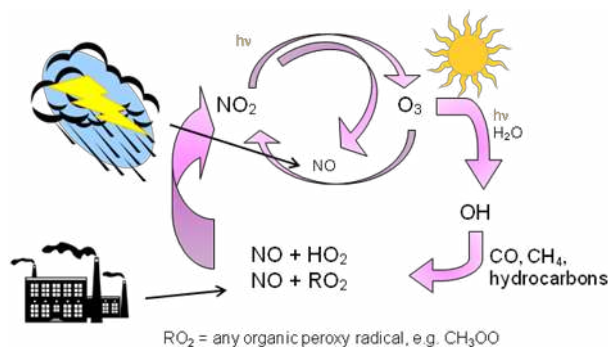
   Tropospheric ozone forms from the oxidation of CO and volatile organic compounds (e.g. methane, isoprene, aldehydes, and peroxides) in the presence of nitrogen oxides and sunlight. In particularly, NOx and VOCs have various anthropogenic, biogenic and natural sources including fossil fuel combustion, isoprene emitted by oak trees, biomass burning and thunderstorms. NO emissions from lightning account for a significantly smaller percentage of total nitrogen oxide emissions as compared to emissions generated by the burning of fossil fuels (Brasseur et al., 1999). Nonetheless, studies show that lightning-NOx emissions may play a larger role in the Earth's NOx budget as lightning within thunderstorms produces nitrogen oxides throughout the entire troposphere (Brasseur et al., 1999).

   Numerous studies have previously explored this area of atmospheric research, providing relevant background and a framework to begin investigation; however, they have been limited in various aspects. One such study in 2006 estimated NOx emissions from lightning using TES and used the GEOS-Chem global chemistry-transport model to illustrate ozone enhancements as well as reproduce patterns of convection on a daily basis. Nonetheless, the study was not able to explicitly represent the relative distributions of lightning intensities using the model configurations and underestimated the ozone enhancement intensities seen by actual data generated by TES (Jourdain, et al., 2010).

   Furthermore, two studies performed by O.R Cooper and Colleagues also provided invaluable background for the present study by analyzing data measurements of tropospheric ozone collected over North America from July-August 2004 and August 2006 from 14 various sites (Cooper, et al., 2006; 2007). Researchers found an average of 15 ppbv more residual ozone in the upper troposphere than in the more polluted ground level, thus highlighting the importance of UT convective transport of ozone precursors to ozone formation. Moreover, the studies found

that only 2 ppbv of the enhancement over eastern North America could be accounted for by vertical mixing of ozone from the boundary layer, thus indicating that the remaining 14 ppbv resulted from in situ production (Cooper, et al., 2006; 2007).

The 2006 study furthered confirmed early experiments that found an ozone maximum over the southeastern USA caused by the summer UT anticyclone that traps convectively transported ozone, ozone precursors and lightning-NOx above the area. The North American Monsoon was also found to control the western side of the anticyclone and westernmost extent of ozone maximum (Cooper, et al., 2007). The studies also discussed the previous difficulty in quantifying ozone production due to a lack of data. Nonetheless, the Cooper studies did not parameterize lightning NOx emissions produced by a large scale grid but simulated lightning by FLEXPART calculations using data generated by NLDN. Additionally, the studies identified the importance of lightning-NOx to ozone formation, but failed to account for specific reaction rates and peroxy radicals that lead to NOx formation in the UT (Cooper, et al., 2006; 2007).

A 2007 study performed by Barth and Colleagues served as a basic blueprint and reference for the design and implementation of the present study. Barth & Colleagues used a 3-D convective cloud model to examine the formation and sinks of formaldehyde, formic acid, hydrogen peroxide and methyl hydrogen peroxide in one specific thunderstorm in order to gain a better understanding of the importance of certain ozone precursors in the UT as well as estimate UT ozone production. While exploring O_3-NOx-CH_4 chemistry as affected by cloud microphysics and lightning NOx production, researchers found that it was unlikely that lightning would affect concentrations of HO_X precursors near convective activity and that both types of peroxides contributed equally to O_3 production downwind of convection (Barth, et. al., 2007).

The study also discussed in depth the importance of convective transport in ozone formation moving chemical species from the boundary layer to the UT through a c-shaped vertical profile as influenced by the North American Monsoon (Barth, et. al., 2007). Moreover, the study underlined the greater persistence of transported species in the UT that are more likely to be transported globally and increase ozone mixing ratios. The current study plans to expand upon these findings and generalizations by using the same model created by Barth & Colleagues to determine the ten most important peroxy radical formation reactions that subsequently contribute ors to ozone formation during a UT ozone formation period from July 15th- August 3rd, 2006.

Other studies also show that nitrogen oxides are more widespread within storm anvils than cloud bases, and that ozone has a greater persistence and lifetime in the upper troposphere where it can be carried globally through convection (Dye, et al., 2000). This moreover reveals the importance of research concerning ozone concentrations in the upper versus lower troposphere. However, others suggest that ozone from the stratosphere could also be a large contributor to enhanced ozone in the upper troposphere (Jourdain, et al., 2010). The present study hopes to better understand the formation and distribution of peroxy radicals as well as obtain more accurate results from the model of Barth & Colleagues at a finer resolution (ΔX= 4km), thus highlighting convection on the model grid.

Previous modeling studies have not explicitly represented thunderstorms and could only parameterize convection because individual storms were too small to be characterized by model grids at $\Delta x = 50$km or greater (Barth, et. al., 2007). By representing thunderstorms on the model grid at a finer resolution, the present study should be able to determine explicitly if lightning storms in conjunction with the North American monsoon play a deciding role in the amount of ozone in the upper troposphere. If thunderstorms do play a determining role in the amount of ozone in the upper troposphere, then the present model study should be able to explicitly represent the storms in order to accurately estimate the transport of ozone and lightning-NOx production.

2. Methods

a. Model Description

WRF- Chem, or the Weather Research and Forecasting Model coupled with chemistry, was created through a collaborative agreement amongst NOAA, NCAR, PNNL, EPA and universities. The model allows the user to model chemistry and aerosols from cloud scales to regional scales. Dynamically, WRF-Chem uses a Runge-Kutta time integration method "to solve conservative flux-form nonhydrostatic compressible equations" (Skamarock, et al., 2005). The model predicted meteorology parameters include u, v, w, theta, p, water vapor, cloud water, rain, ice and snow as well as tracer variables and chemical species.

The Regional Atmospheric Chemistry Mechanism (RACM) was used to represent the gas-phase chemistry. The mechanism consisted of 17 stable inorganic species, 4 inorganic intermediates, 32 stable organic species and 24 organic intermediates to generate 77 chemical species and 237 reactions (Stockwell, et al, 1997). The MADE/SORGAM modal approach was used for aerosols and specifically two modes, Aitken and accumulation, were used to determine chemical species including sulfate, nitrate, ammonium, sodium, chloride, sea salt, soil (dust), primary organic carbon and secondary organic carbon (Barth, et al., in preparation). The model also accounted for dry/wet deposition and lightning-NOx emissions. Finally, the NOAH land surface model was included in the model configuration as well as single-moment cloud physics parameterization (Lin, et al., 1983).

The current model entitled the North American Monsoon 2006 WRF-Chem Simulation modeled meteorological, physical, dynamical and chemical processes, specifically peroxy radical reactions in the upper troposphere, over the United States and Mexico from July 10th- August 3rd, 2006. The convective system resolution simulation was designed by the primary investigators to analyze the role played by the North American Monsoon in upper tropospheric ozone formation. The 3-D model configuration consisted of a fine horizontal resolution ($\Delta X = 4$ km) as well as 1200 x 900 x 51 grid points which allowed for the explicit representation of convective transport. The vertical resolution from the surface to top of the domain was p =10 hPa or z ~ 30 km.

Anthropogenic, aircraft, biogenic and wildfire plus NO produced from lightning emissions were included in the model. Anthropogenic emissions were obtained from both the US EPA National Emission Inventory (NEI) that estimated typical emissions during the 2005 summer weekday as well as from the Mexico 2006 NEI representative. The MEGAN model

(Guenther, et el., 2006) was used to calculate online biogenic emissions for isoprene, a-pinene and limonene and fires were estimated from observations from the MODUS sensor (Wiedinmyer, et el., 2006). Aircraft emissions of CO, NO and SO_2 were obtained from the 1999 1x1° resolution provided by Baughcum, Boeing (Barth, et al., in preparation).

Two types of scalars were included in the model, one being passive or transported, and the other having first-order decay with a time scale of one day. The scalars always maintained a value of one throughout simulation within its specified region. Eight scalars tracked boundary layer air, stratospheric air and air from horizontal boundaries as well as a wildfire tracer. The boundary layer tracer and lightning-NO_X were the only tracers used in the current analysis (Barth, et al., in preparation).

b. Technical Analysis

The present simulation was run using data generated from July 10th-August 3rd, 2006 during the North American Monsoon 2006 WRF-Chem Simulation. Using WRF-Chem output for a typical summer day, the 27th of July, 40 rates of reaction at different times of the day were mapped in molecules/cm3/s to calculate different rates of reactions focusing on hydrocarbon reactions that produce peroxy radicals. The plots of these reaction rates were produced by the post script *HC-RXNRates_10km_07-27_megan.ps* from the NCL script *hc_rxnrates_10km.ncl*. Spatial analysis was then performed to determine the 12 top reactions with highest rates (Figure 1).

Figure 1. Reaction Rates, 7-27-2006, 21 UTC
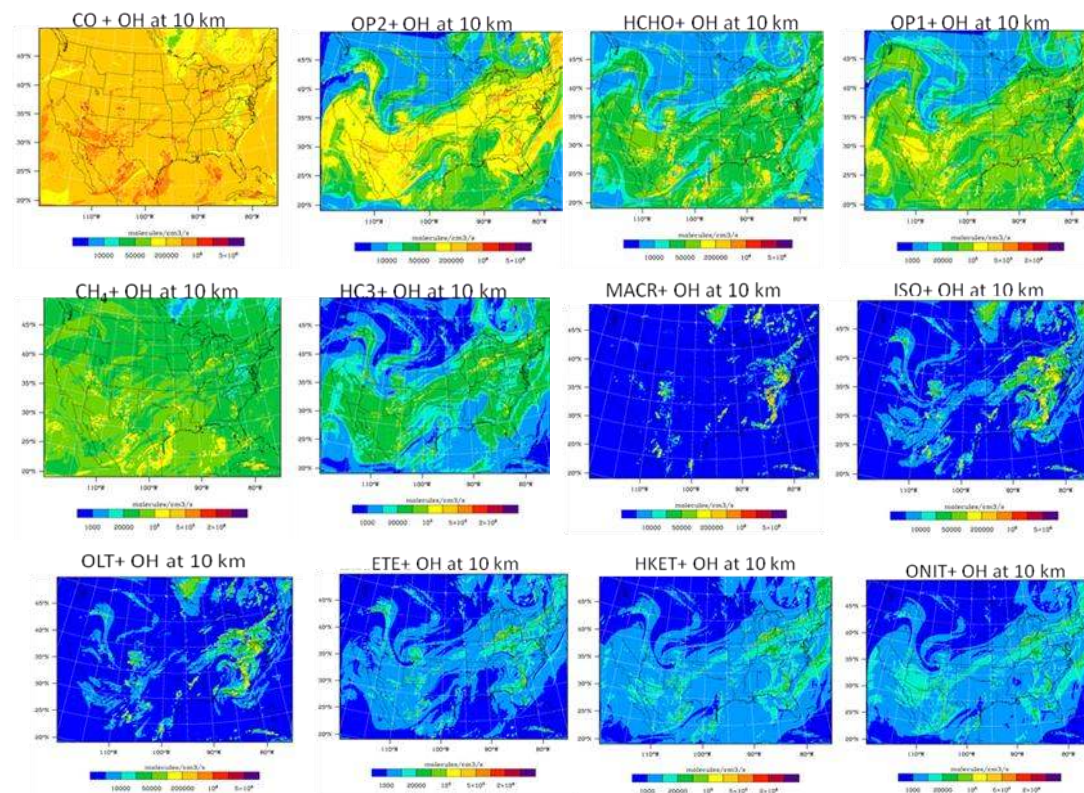
After ranking the reactions approximately by highest rates, the NCL script was rewritten to look at only those top twelve reactions. It was then run for several days of output to determine a day with good convective outflow specifically from July 15th to August 3rd starting at 0 UTC and ending at 21 UTC. These plots were then compared with a LNOx tracer to track the NO produced by lightning as well as radar reflectivity, boundary layer and CO tracers to determine how well these parameters correlated (Figure 2). The dBZ or radar reflectivity was used to detect the location of thunderstorms while the BL tracer was used to mark the location of convective transport in the UT.

Figure 2. Radar Reflectivity, LNOx, BL and CO Tracers for Sample Day, 7-28-06, 0 UTC
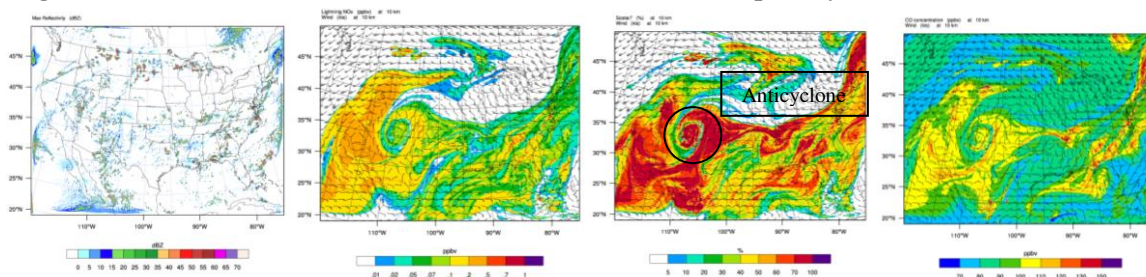
Ultimately, July 23rd, 2006 was chosen as a day that represented good convective outflow on the model grid as well as good correlation with location of thunderstorms and NO produced by lightning (Figure 3).

Figure 3. Radar Reflectivity, LNOx, BL and CO tracers for Sample Day, 7-23-06, 0 UTC
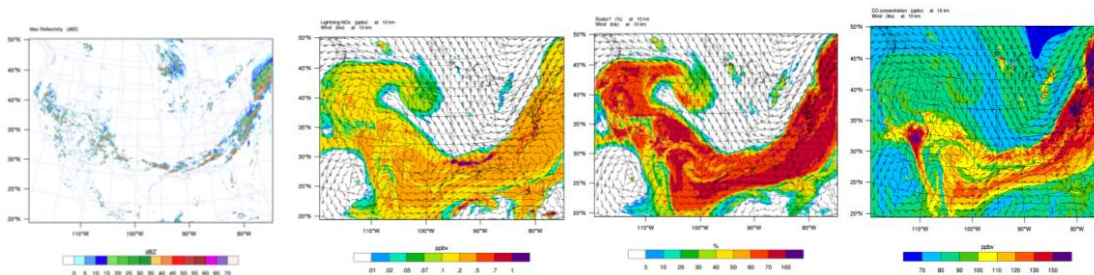
Finally, these plots were utilized to compare and calculate rates of reactions in regions with new air from convection i.e. deep convection versus regions with less new air from convection. Since the transported original air from the boundary layer can be visualized with the use of the BL tracer, new scripts (*frg_constBL-2.ncl* and *frg_constBL-1.ncl*) were utilized to calculate whether or not convective transport influenced composition of species as well as rates of reaction. In order to compare rates of reactions and species concentration in air influenced by convection and in air less influenced by convection, an appropriate boundary layer threshold was empirically obtained.

Ultimately, the final threshold value used was one in which at a maximum 70-100% of the BL tracer was transported and at a minimum only 60-70% of the BL tracer was transported. Moreover, the average concentration was calculated in each region between 9.5 and 12.5 km of altitude from 0 UTC to 12 UTC. Data was obtained from July 20th -23rd in order to view the chemistry over a few days time in order to create a composite picture.

3. Results

After plotting the 40 rates of reactions from 0 UTC to 21 UTC on July 27th, 2006, the top 12 species that are oxidized to form peroxy radicals were determined and analyzed (Table 1). The results indicated that the oxidation of CO, methane and short-lived, intermediate species such as formaldehyde and organic peroxides were the most important to peroxy radical formation. The oxidation of CO was found to have the highest average reaction rate ranging from 200000 - 10^6 molecules/cm^3/s, while the oxidation of organic nitrates had the lowest average reaction rate ranging from $1000 – 10^5$ molecules/cm^3/s.

Table 1. Species Concentration Rank
(Ranks are approximate and vary slightly by time of day)

| Rank	Species	Name
1	CO	Carbon monoxide
2	OP2	Higher organic peroxides
3	HCHO	Formaldehyde
4	OP1	Methyl hydrogen peroxide
5	CH_4	Methane
6	HC3	Alkanes
7	MACR	Methacrolein
8	ISO	Isoprene
9	OLT	Terminal alkenes
10	ETE	Ethene
11	HKET	Hydroxyl ketone
12	ONIT	Organic nitrate

Additionally, those chemical species such as CO, formaldehyde, methane and organic peroxides formed in part from anthropogenic and natural sources such as combustion reactions involving exhaust fumes, natural gas and oil, decomposition of organic material, rubber and plastic industries and finally building and household products were found to exhibit the highest reaction rates in the upper troposphere. Furthermore, after testing various BL tracer thresholds that allowed for a sufficient view of species concentration, a boundary layer threshold minimum in which 50-100% of the BL tracer was transported was discarded as too large (Figure 4).

**Figure 4. CO Concentration at 10 km, 7-23-06, BL Threshold Min= 50%**
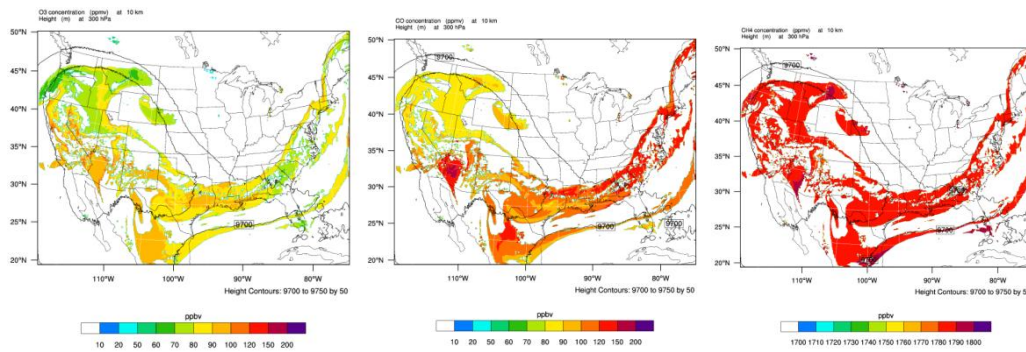
A boundary layer maximum in which 60-100% of the BL tracer was transported was also found to be too large. Conversely, a BL threshold maximum in which 80-100% of the BL tracer was transported was found to be insufficient and too small (Figure 5 & 6).

**Figure 5. CO Concentration at 10 km, 7-23-06, BL Threshold Max =60%**
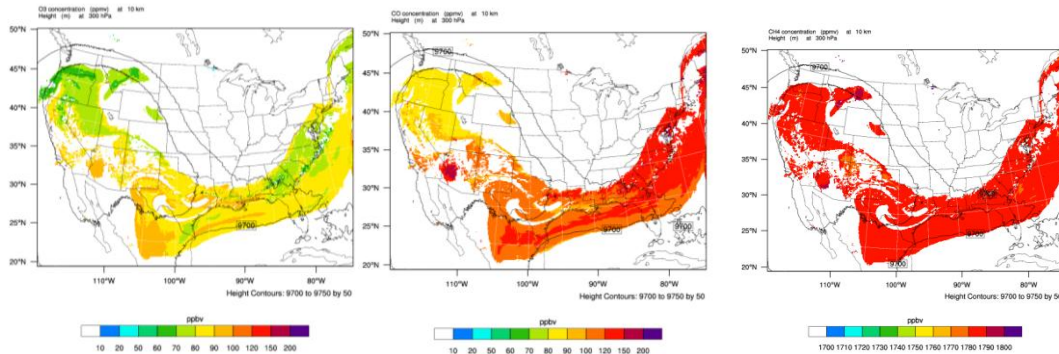
Figure 6. CO Concentration at 10 km, 7-23-06, BL Threshold Max =80%
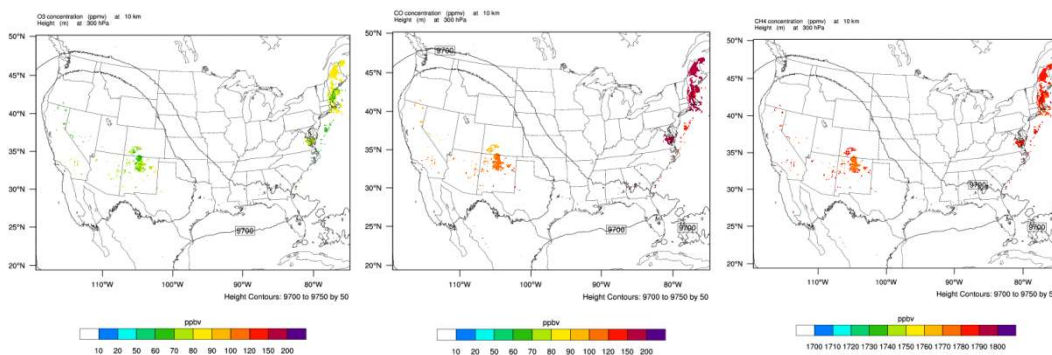
A threshold in which at a minimum 60-70% of the BL tracer was transported throughout the domain and at a maximum 70-100% of the BL tracer was transported throughout the domain was ultimately chosen for the analysis of comparing reactant concentrations and oxidation rates in air less influenced by convection to air recently influenced by convection (Figure 7).

Figure 7. CO Concentration at 10 km, 7-23-06, BL Threshold Min =60% and BL Threshold Max =70%
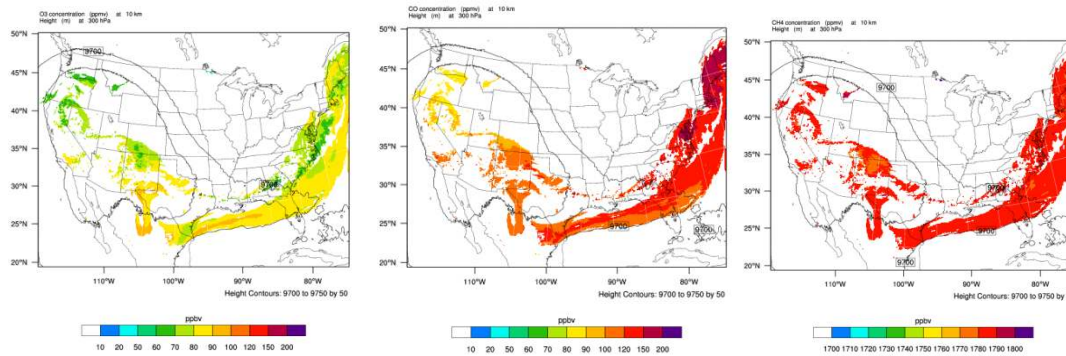
The threshold utilized allowed us to plot species concentrations and reaction rates over a time span of five days from July 20th-July 24th, 2006. In general, species concentration was found to be greater in areas more directly impacted by convective outflow than in areas less affected by convective outflow (See Figures 9). In particular, a peak in concentration is observed during the middle of the day on July 22nd, 2006 extending on to July 23rd, 2006, the day observed to have good convective outflow. Amongst the top 6 species (CO, CH_4, HC3, HCHO and organic peroxides), a definite peak in concentration was found in regions in which 70-100% of BL tracer was transported as compared to regions in which only 60-70% of BL tracer was transported, with the exception of CH_4 concentration which remained constant. Due to its relatively high atmospheric presence of 10 years, CH_4 concentrations tend to remain relatively constant throughout the upper troposphere.

Figure 9. Species Concentration in Air Recently Influenced by Convection (red line) and Less Influenced by Convection (blue line) over Time
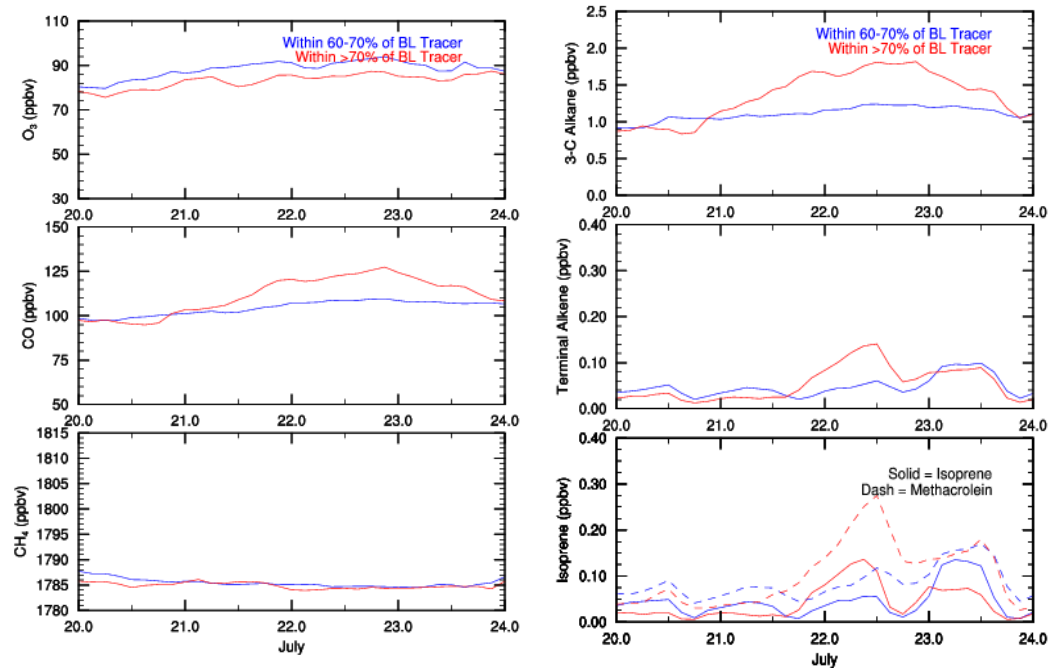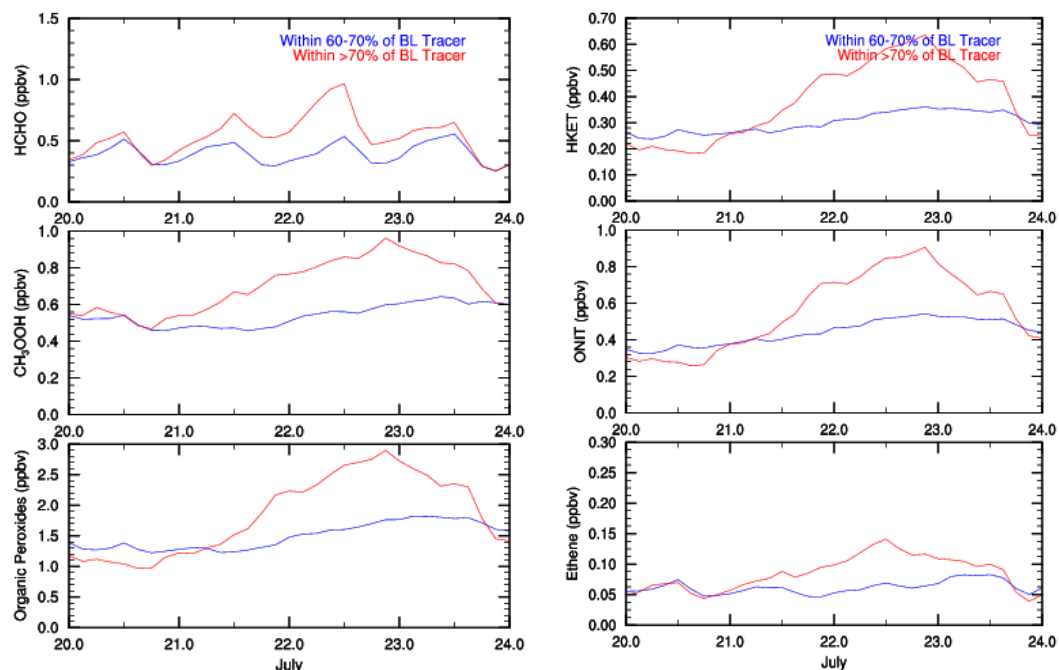
The plots also highlight an inverse trend in ozone concentration from July 20th- 24th, 2006 in which ozone concentration is shown to be greater in areas less impacted by convection in which only 60-70% of the BL tracer was transported by convection. However, this trend is caused by the actual smaller concentration of ozone within the lower troposphere which is convectively transported to the UT.

Figure 10. Reaction Rate in Air Recently Influenced by Convection (red line) and Less Influenced by Convection (blue line) over Time
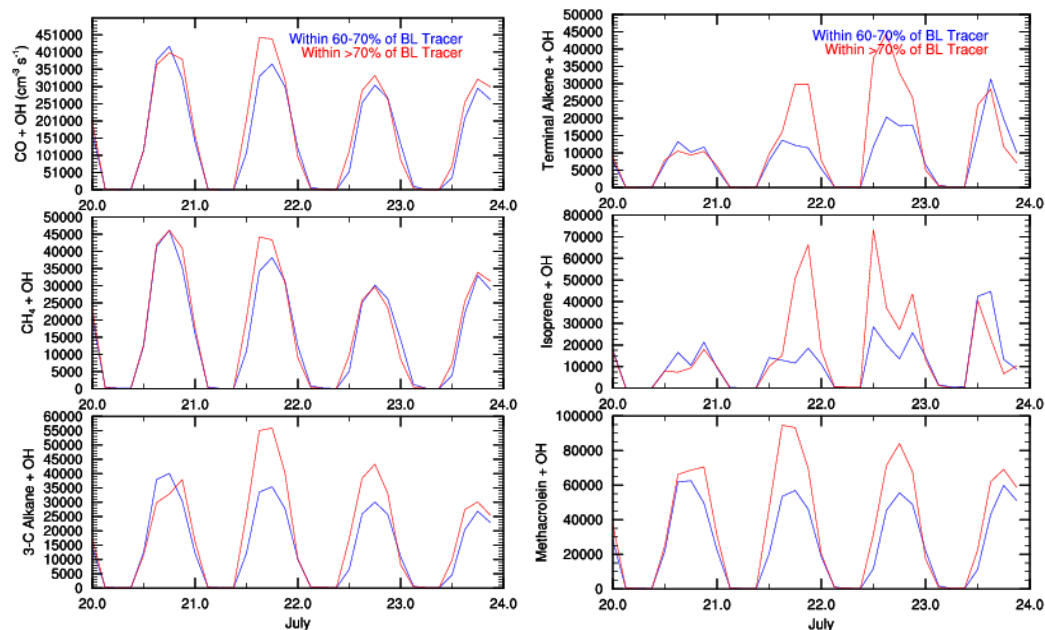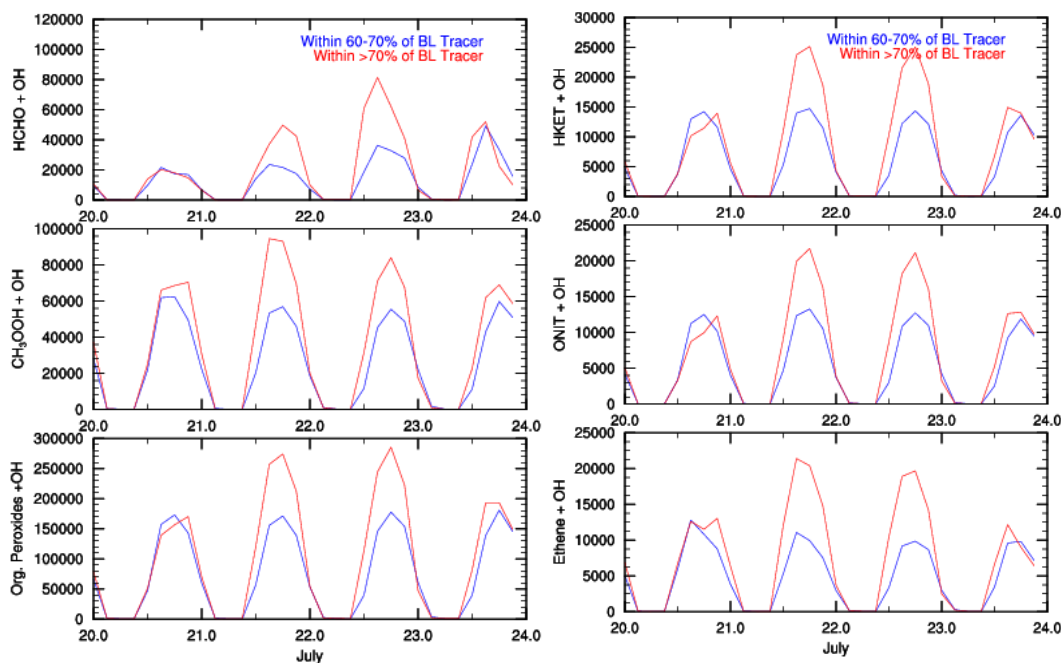
Similar results were obtained when reaction rates were plotted over time (See Figure 10). The peaks and valleys shown on the plots highlight the cyclical nature of the reactions in which photochemical activity stops during nightfall in the absence of sunlight. Thus, the valleys actually represent the nighttime hours in which reactions producing OH radicals were unable to occur.

4. Discussion and Conclusion

The present study was able to determine the most important oxidation of hydrocarbon reactions forming peroxy radicals using a WRF-Chem simulation in which thunderstorms were represented at a fine resolution ($\Delta X = 4$km) on the model grid. In addition, the results obtained were able to explicitly show that species concentration and reaction rate were influenced by convection. Furthermore, analysis of the WRF-Chem data revealed a definite correlation between locations of thunderstorms, regions where LNOx was transported, peroxy radical formation, CO concentration and regions exhibiting convection on a typical summer day, July 23rd, 2006.

The results highlighted higher rates of peroxy radical formation reactions in regions in which the BL tracer was transported, thus indicating the role of convection in transporting ozone precursor species to the upper troposphere. CO, organic peroxides and formaldehyde in the upper troposphere exhibited the highest reaction rates in convective outflow regions, and methane had a relatively high, yet constant reaction rate and species concentration in regions of convective outflow. Although ozone concentration in air influenced by convection was inversed, this trend was attributed to the lower concentration of ozone at the ground level that is transported through convection. The difference between convectively-influenced O_3 and O_3 in regions less influenced by convection in the UT could also be caused by the production of O_3 once CO and the other hydrocarbons are oxidized. The results also revealed a relationship between peaks in methacrolein, terminal alkene and isoprene as these prior species are formed as intermediates by

the oxidation of isoprene (See Appendix). Reactions involving short-lived species like isoprene and methacrolein also appeared to be more sensitive to convective outflow as indicated by the higher peaks seen on both the 22nd and 23rd of July, 2006.

In the future, the current analysis should be extended to the entire simulation period to better generalize the results obtained, as well as gain a better understanding of the short and long term causes of the upper tropospheric ozone maximum over the southeastern United States. Additionally, future research could attempt to differentiate between anthropogenic versus biogenic production of the most important hydrocarbons reactions forming peroxy radicals. The ozone maximum over Huntsville, Alabama and Houston, Texas, as indicated by previous studies, could also be further explored. Finally, the model results should be tested and compared to actual field observations of ozone, NO_X, hydrocarbon and peroxy radical concentrations. As more data becomes available to scientists to test present model data, more accurate and detailed analysis can be performed to further qualify ozone chemistry and quantify peroxy radical formation in the upper troposphere.

5. Acknowledgements

6. Appendix

Table 2. Species from RACM that are relevant to the current study

No.	Species	Definition	Classification
1	O_3	Ozone	oxidants
2	CO	carbon monoxide	carbon oxides
3	CH_4	Methane	alkanes
4	HC3	alkanes, alcohols, esters, and alkynes with HO rate constant (298 K, 1 atm) less than 3.4 X 10 -12 cm3 s-1	alkanes
5	OLT	terminal alkenes	alkenes
6	ISO	Isoprene	stable biogenic alkenes
7	HCHO	Formaldehyde	carbonyls
8	MACR	methacrolein and other unsaturated monoaldehydes	carbonyls
9	OP1	methyl hydrogen peroxide	organic peroxides
10	OP2	higher organic peroxides	organic peroxides
11	HO	hydroxy radical	odd hydrogen
12	HKET	Hydroxyl ketone	carbonyls
13	ONIT	organic nitrate	organic nitrogen
14	ETE	Ethene	alkenes

Table 3. RACM Reactions that are relevant to the current study

Reaction No.	Reaction
1	$CO + OH \rightarrow HO_2 + CO_2$
2	$CH_4 + OH \rightarrow MO_2 + H_2O$
3	$HC3 + OH \rightarrow HC3P + HO_2 + ALD + ORA1 + CO + GLY + HO + HCHO + H_2O$
4	$OLT + OH \rightarrow OLTP$
5	$ISO + OH \rightarrow ISOP$
6	$HCHO + OH \rightarrow HO_2 + CO + H_2O$
7	$MACR + OH \rightarrow TCO_3 + HKET + MGLY + CO + HCHO + HO_2 + XO_2$
8	$OP1 + OH \rightarrow MO_2 + HCHO + HO$
9	$OP2 + OH \rightarrow HC3P + ALD + KET + HO + XO_2$
10	$HKET + OH \rightarrow HO_2 + MGLY + H_2O$
11	$ONIT + OH \rightarrow HC3P + NO_2 + H_2O$
12	$ETE + OH \rightarrow ETEP$
13	$ISOP + MO_2 \rightarrow MACR + OLT + HO_2 + OLI + HCHO$

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