Reactive Plume Modeling to Investigate NO_x Reactions and Transport in Nighttime Plumes and Impact on Next-day Ozone (AQRP-2011-020)

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Acknowledgement

- The Air Quality Research Program is administered by the University of Texas at Austin.
- This project (AQRP-20) was conducted jointly by ENVIRON and the National Oceanic and Atmospheric Administration (NOAA).
- The results of this project have been reviewed by the TCEQ.

Objectives of AQRP Study

- Evaluate nocturnal chemistry and transport of nitrogen oxide species (e.g., NO, NO_2, NO_3, N_2O_5) in coal-fired power plant plumes
- Analyze the vertical profile of ambient pollutant concentrations (e.g., NO_Y, VOC) during the night in the residual daytime and nocturnal boundary layers

Scope of AQRP Study

- Analyze nighttime chemistry and mixing in coal-fired power plant plumes using TexAQS II NOAA P-3 aircraft measurements
- Conduct reactive plume modeling of power plant plumes using SCICHEM
- Conduct photochemical modeling of power plant plumes using CAMx

Nighttime Aircraft Measurement Issues

- Locating and sampling horizontally across a power plant plume center is difficult.
  - Typically at night the lower troposphere becomes stratified (stable conditions) with minimal vertical mixing and dispersion.
  - Power plant plumes tend to have a shallow vertical extent (~100 m).

- Plume transect data is difficult to interpret.
  - Not all the data will be for the plume center.
  - The chemistry differs between plume center and plume edge.

- Plume modeling is compromised.
  - Plume models model the plume center.
  - Validating model results with plume transect data will be less certain.

Nighttime Chemistry of Nitrogen Oxides

- $NO + O_3 \rightarrow NO_2 + O_2$
- $NO_2 + O_3 \rightarrow NO_3 + O_2$
- $NO_3 + NO \rightarrow 2NO_2$
- $NO_3 + NO_2 \leftrightarrows N_2O_5$
- NO_3 + VOC $\rightarrow$ Products
- N_2O_5 + AER-H_2O (het) $\rightarrow$ $2HNO_3$(aq)
- N_2O_5 + AER-Cl (het) $\rightarrow$ HNO_3(aq) + $ClNO_2$(aq)

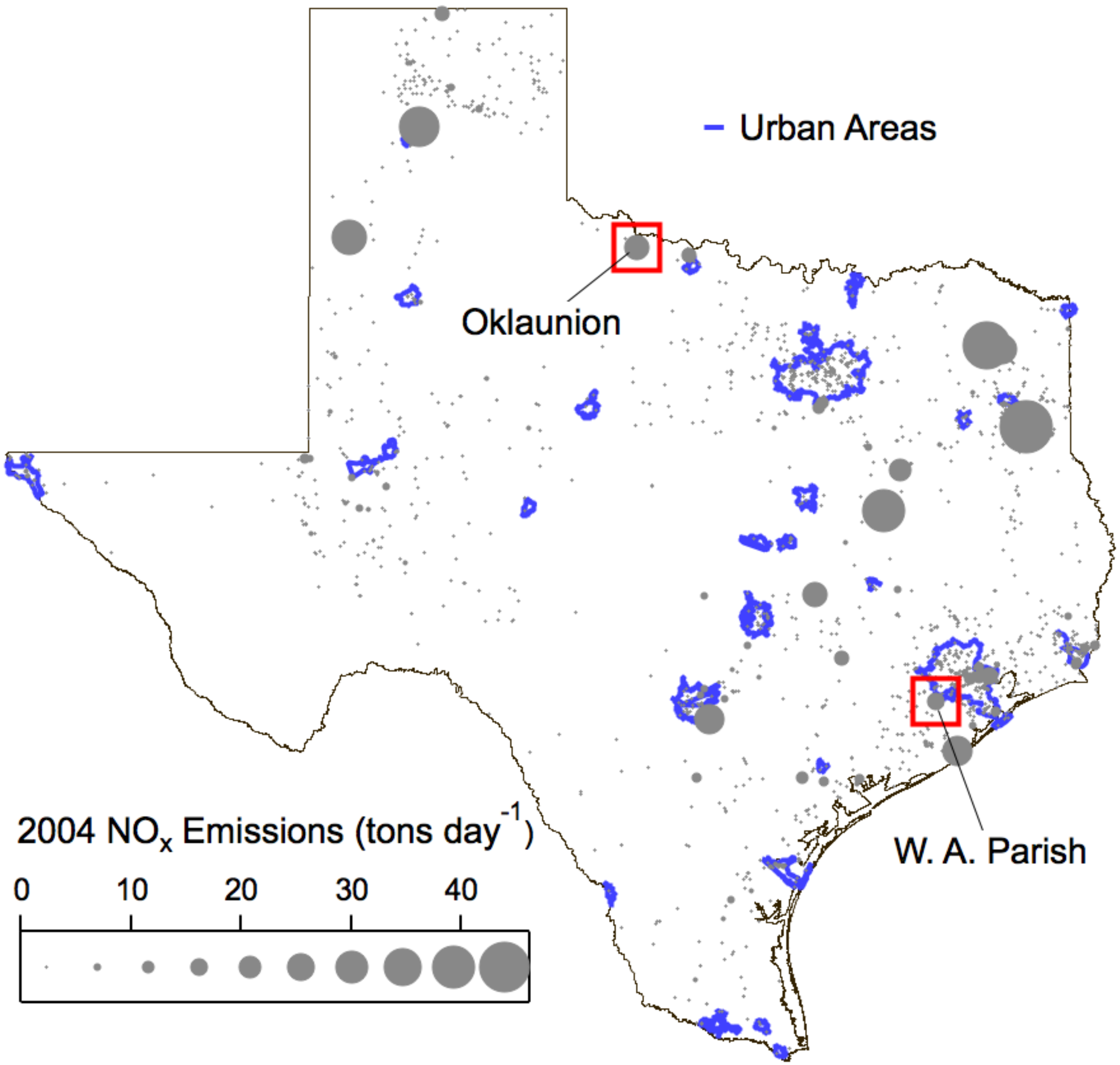
Coal-fired Power Plants

- Nighttime aircraft sampling was collected from two coal-fired power plant plumes: Oklaunion and W.A. Parish.

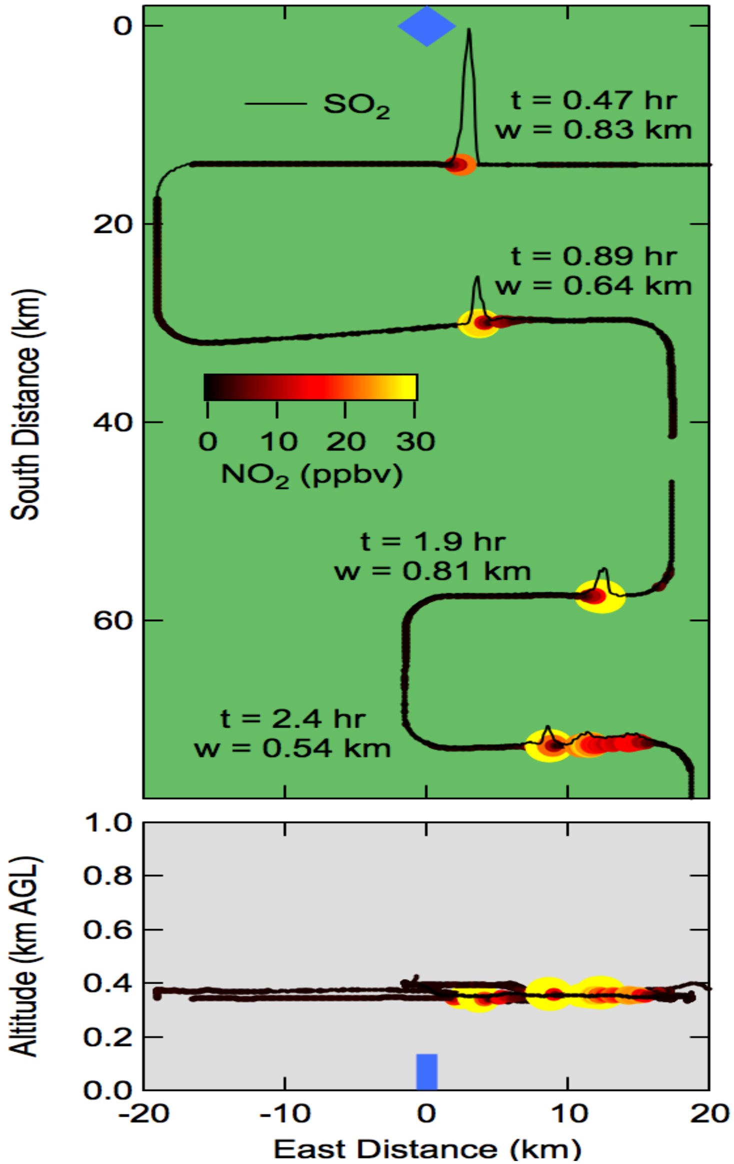
- Oklaunion (near Wichita Falls), a 670 MW plant with low NO_X burners and a single stack (~ 4 lbs NO_X /hr per MW), was sampled during the night of October 10-11, 2006.

- W.A. Parish (near Houston), a 2470 MW plant with low NO_X burners, selective catalytic reduction (SCR) and multiple stacks (~ 0.4 lbs NO_X /hr per MW), was sampled during the night of October 11-12, 2006.

Location of Oklaunion and W.A. Parish

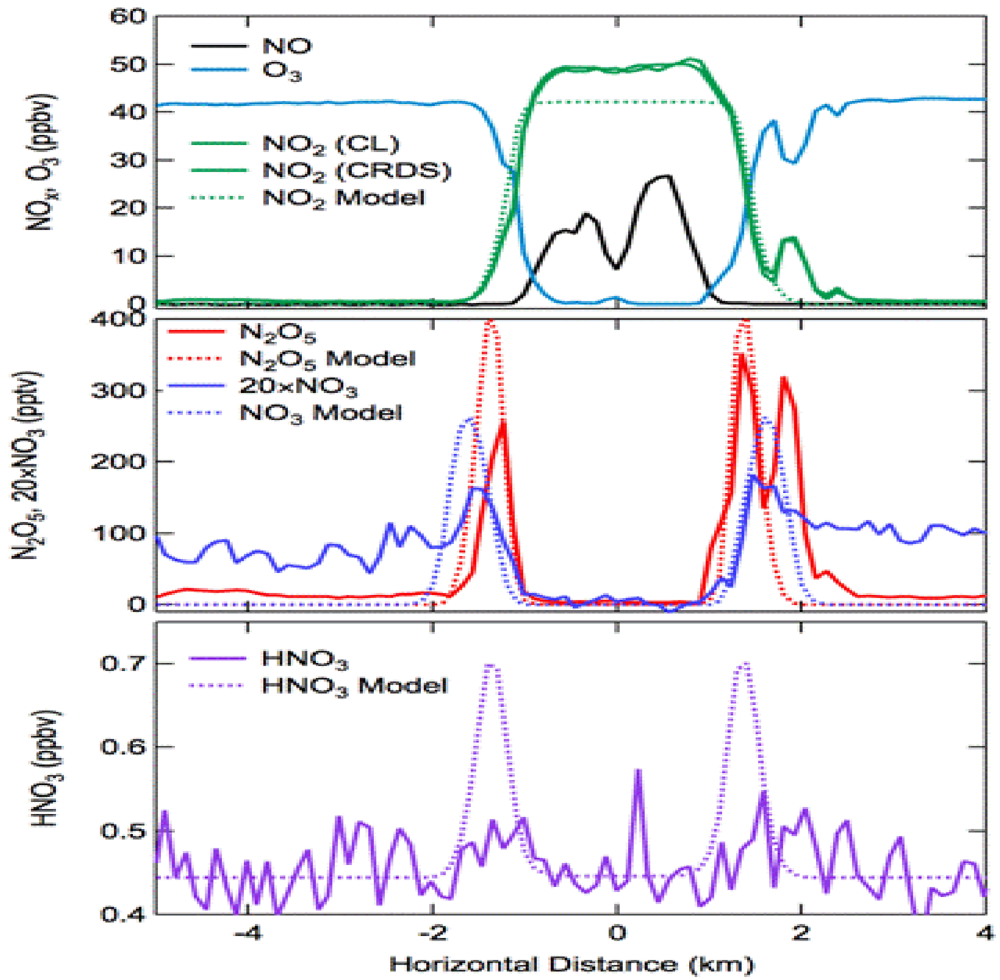


Oklaunion



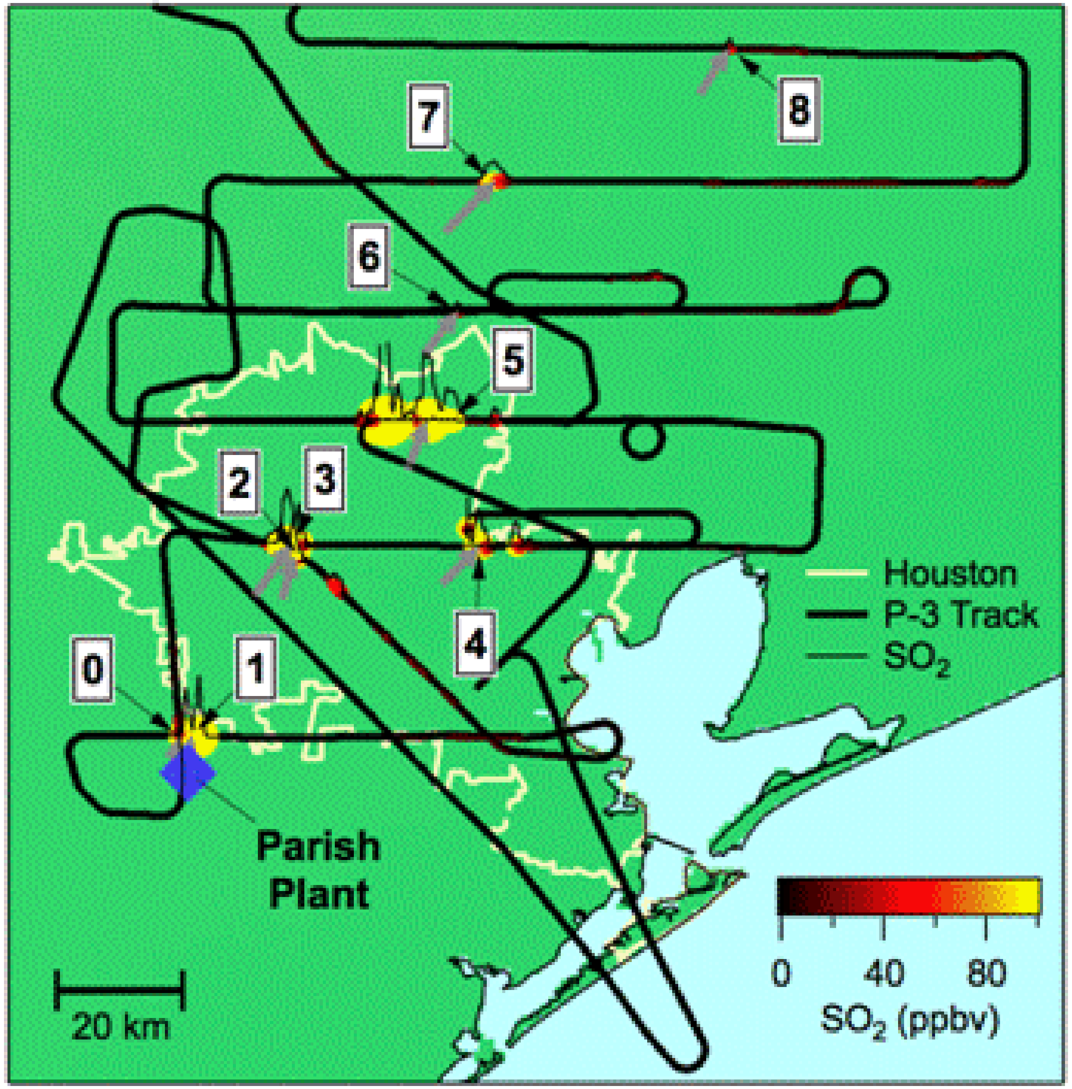
- This segment of the NOAA P-3 flight track shows a series of four downwind plume intercepts at an average altitude 345 m above ground level.
- The black trace superimposed on the track in the upper panel shows SO_2, which gives a measure of the plume width as it advects downwind.
- Numbers next to each intercept indicate the transport time based on the local wind speed and direction, distance from the source, as well as the plume width (Gaussian full width at half maximum, FWHM).

Oklaunion



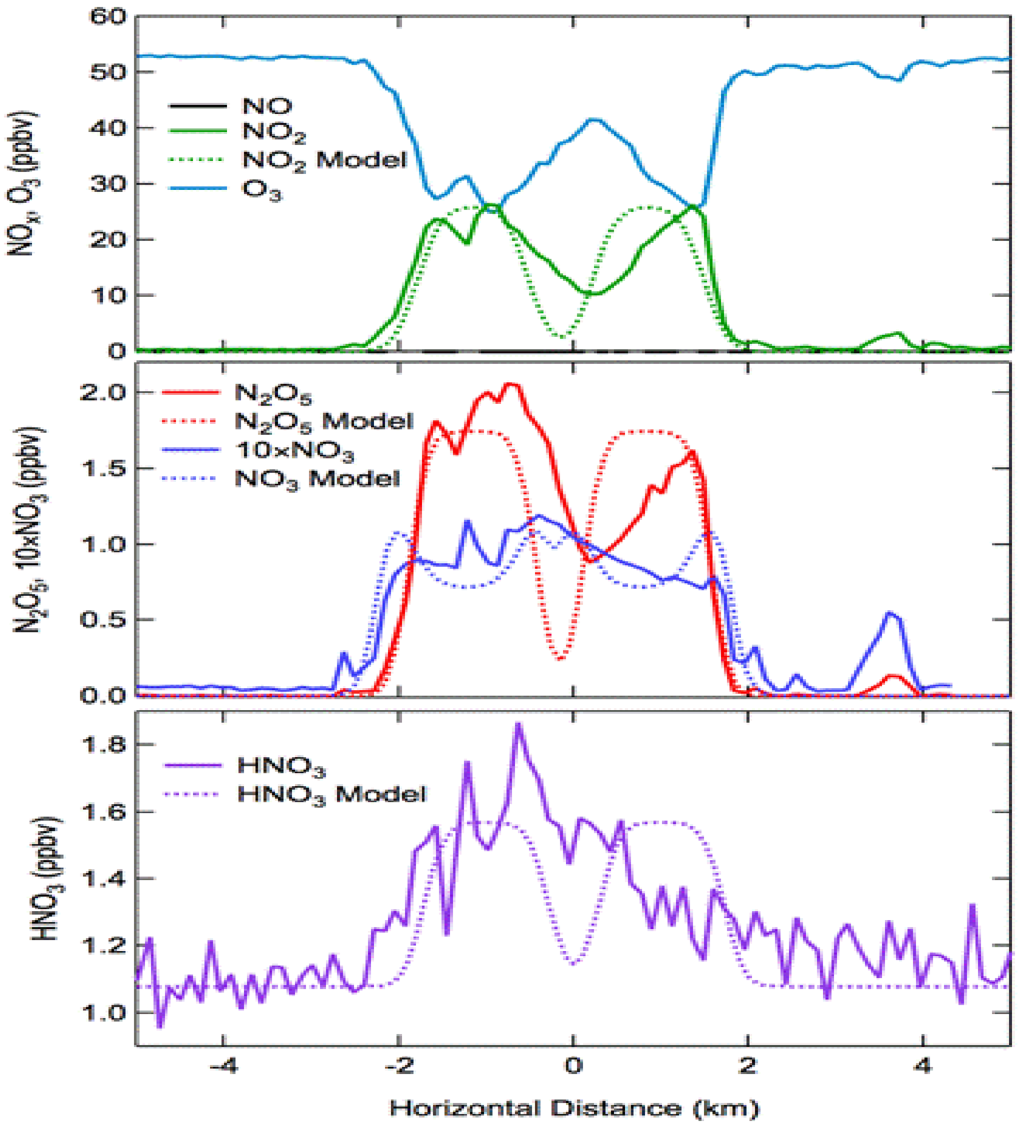
- This expanded view of a single nighttime Oklaunion power plant intercept shows:
  - NO, NO_2 and O_3 (top);
  - NO_3 and N_2O_5 (middle); and
  - HNO_3 (bottom).
- Two separate NO_2 measurements, chemiluminescence (CL) and cavity ring down (CRDS) are shown in the top plot.
- Dashed lines in each plot are the results of a simplified reactive plume model that incorporates mixing and chemistry.
- Within the plume, O_3 is titrated to zero and excess NO exists.

W.A. Parish



- The NOAA P-3 flight track on October 11-12, 2006, shows a series of downwind intersects of the plume from the Parish power plant at altitudes between 550 m and 800 m above ground level.
- Numbers identify the location of specific transects, which are ordered by distance from plant but are not chronologic in time.
- The color and size are coded by the SO_2 concentration (color shown in bar).

W.A. Parish



- The expanded view of a single nighttime W.A. Parish power plant intercept shows:
  - NO, NO_2 and O_3 (top);
  - NO_3 and N_2O_5 (middle); and
  - HNO_3 (bottom).
- Two separate NO_2 measurements, chemiluminescence (CL) and cavity ring down (CRDS), are shown in the top plot.
- Dashed lines in each plot are the results of a simplified reactive plume model that incorporates mixing and chemistry.
- Within the plume, NO is reacted to NO_2 and excess O_3 exists.

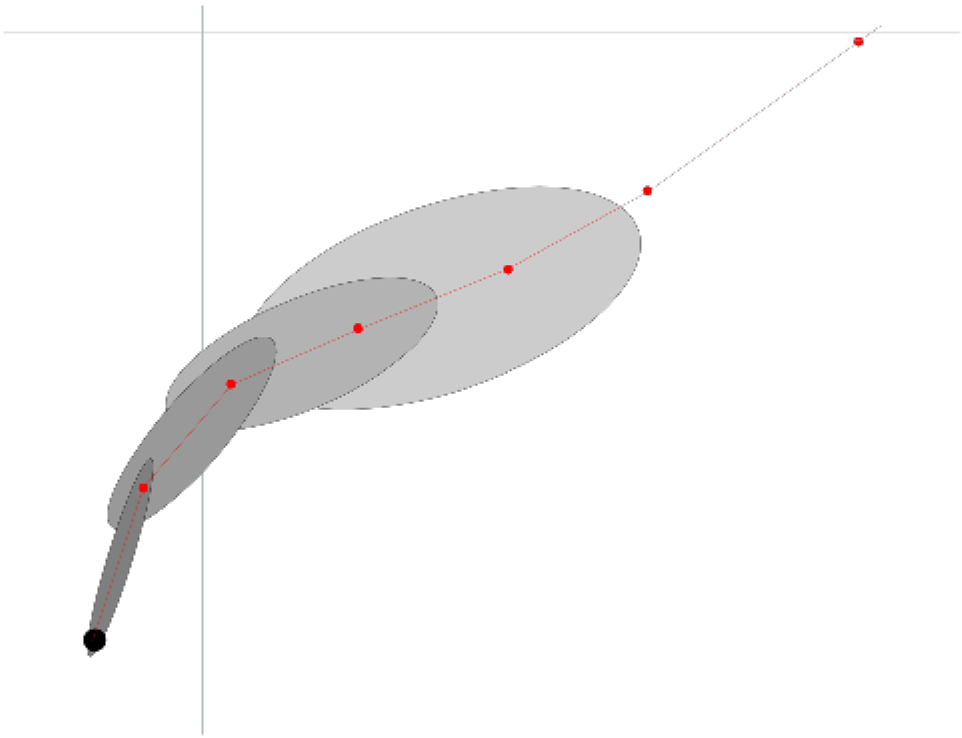
Implications

- Since N_2O_5 and NO_3 undergo heterogeneous reactions, some can be removed from the gas phase and would not be available as ozone precursors the next morning.
- When the NO concentration in the plume is higher than the ambient ozone concentration, such as for the Oklaunion plume, the formation of N_2O_5 and NO_3 is minimal and occurs at the edges of the plume. Therefore, minimal NO_X can be lost via removal of N_2O_5 or NO_3.
- When the NO concentration in the plume is lower than the ambient ozone concentration, such as for the Parish plume, appreciable N_2O_5 and NO_3 are formed within the plume center. Therefore, appreciable NO_X could be lost from the plume via removal of N_2O_5 or NO_3.
- Lower NO_X emissions from EGUs not only reduce these ozone precursors during the day but also allow removal of NO_X at night. This is due to loss of N_2O_5 and NO_3 due to the formation of appreciable HNO_3, when the NO concentrations in the plume are less than the ambient ozone concentration.

SCICHEM Modeling of Power Plant Plumes

- Overview of SCICHEM
- Initial Modeling Results
- Model Refinements
- Implications

Overview of SCICHEM



This planview shows a series of puffs emitted from a stack.
The red line represents the puff centerline.

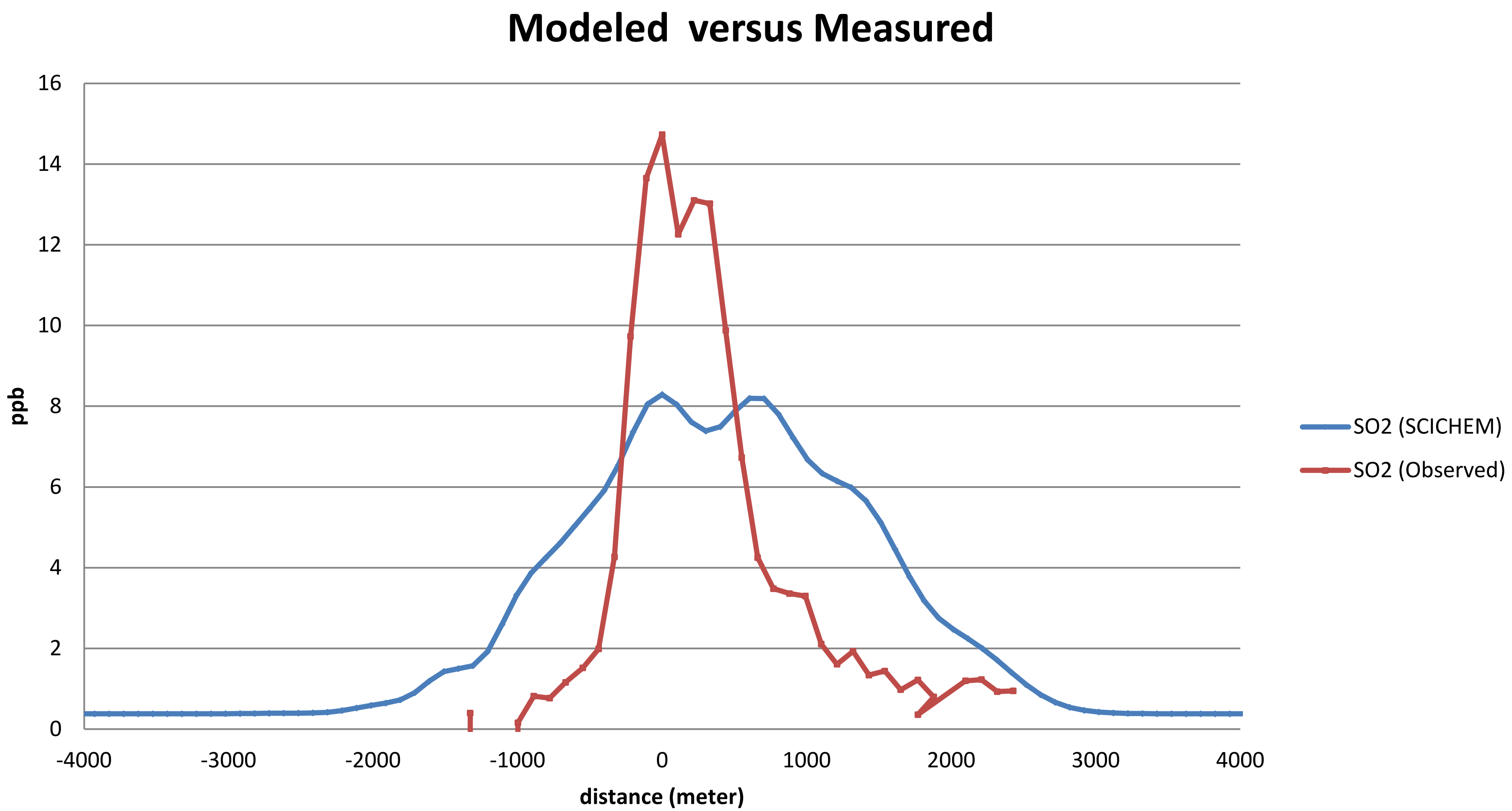
Overview of SCICHEM

- SCICHEM is based on the SCIPUFF lagrangian air parcel transport and diffusion model with an added chemical module.
- Emission plumes are represented by a series of three-dimensional puffs that are assumed to have Gaussian concentration distributions in each of the three planes (i.e., X-Y, Y-Z and X-Z).
- Local meteorology (observed or modeled winds) affects the downwind transport and dispersion of the puffs.
- The chemical module includes the CB05 gas-phase, aerosol (SO_4, NO_3, NH_3, SOA) and aqueous-phase chemistry.
- Chemical reactions occur between the plume constituents (e.g., nitrogen oxides) and the constituents in the ambient air (e.g., ozone).

Initial Modeling Results

- SCICHEM was applied to the Oklaunion power plant plume monitored during the night of October 10-11, 2006.
- Cross-sectional measurements of the plume along the downwind transport indicate insignificant horizontal spreading due to either a lack of dispersion or the aircraft not positioned to measure the center of the plume.
- Using typical settings for SCICHEM modeling features, such as plume rise and puff growth, the model over-estimated measured plume widths especially at the more downwind locations.
- In addition, the SCICHEM model did not replicate the concentration of N_2O_5 and NO_3 observed at the edges of the plume.

Initial Modeling Results

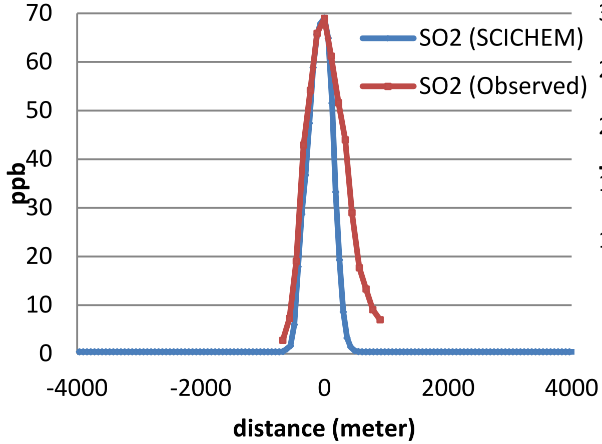


Model Refinements

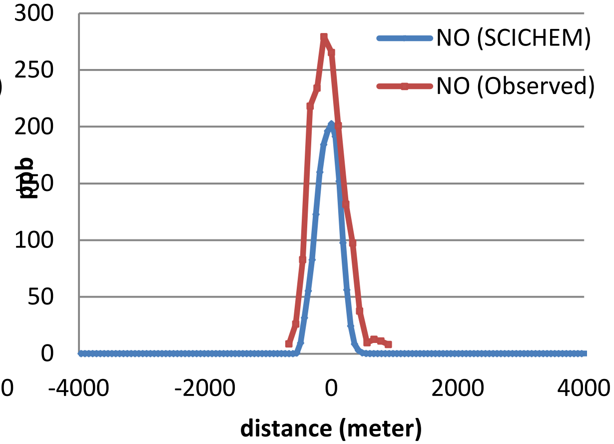
- Several sensitivity analyses were conducted testing various SCICHEM modeling features.
- Horizontal and vertical puff growth parameters were modified to reduce the growth rate and limit the plume dispersion.
- The number of puffs used to define the plume was increased from a few hundred to several thousand to enhance the chemistry at the edges of the plume.
- The plume center was specified at 400 meters (i.e., plume rise was not used).

Model Refinements

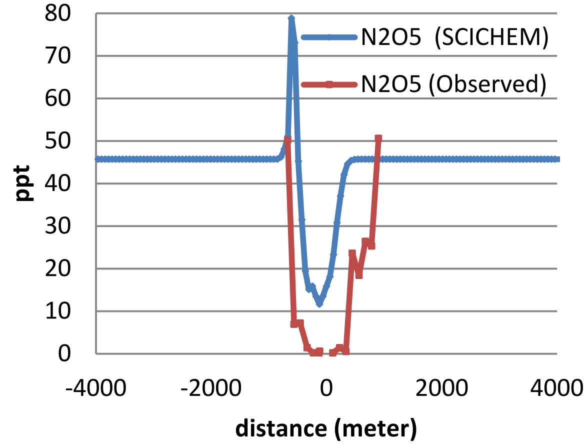
Plume Intercept 13



Plume Intercept 13

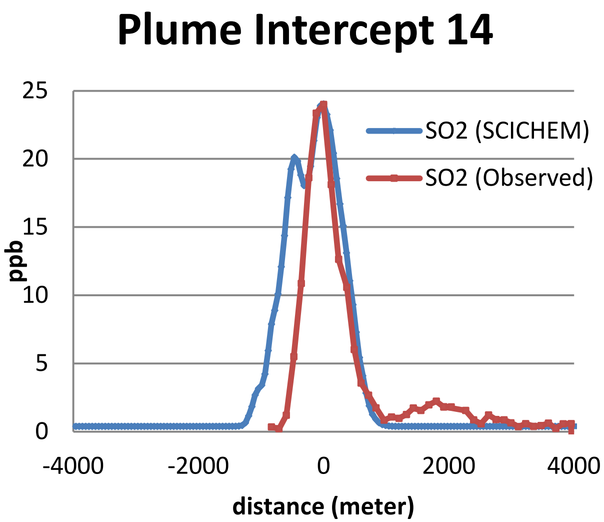


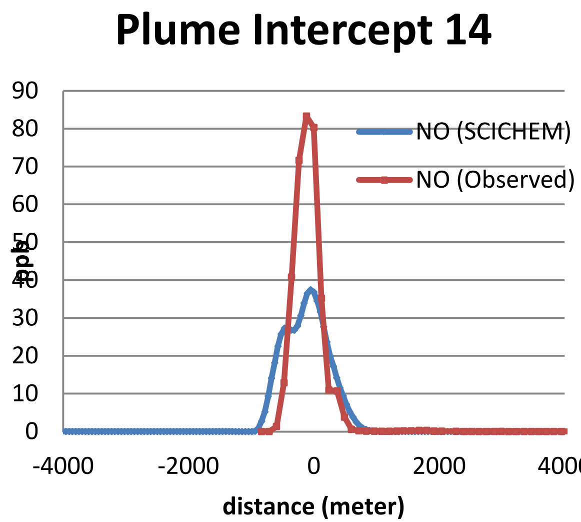
Plume Intercept 13

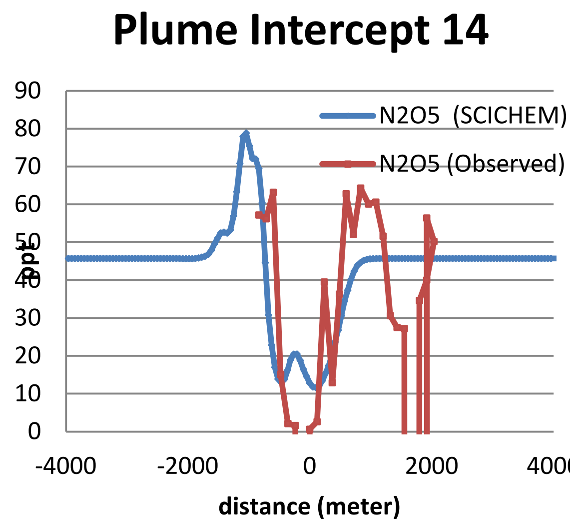


Transect 13: 0925 hours, 14 km downwind of Oklaunion, at 347 m above ground level

Model Refinements







Transect 14: 0933 hours, 30 km downwind of Oklaunion, at 343 m above ground level

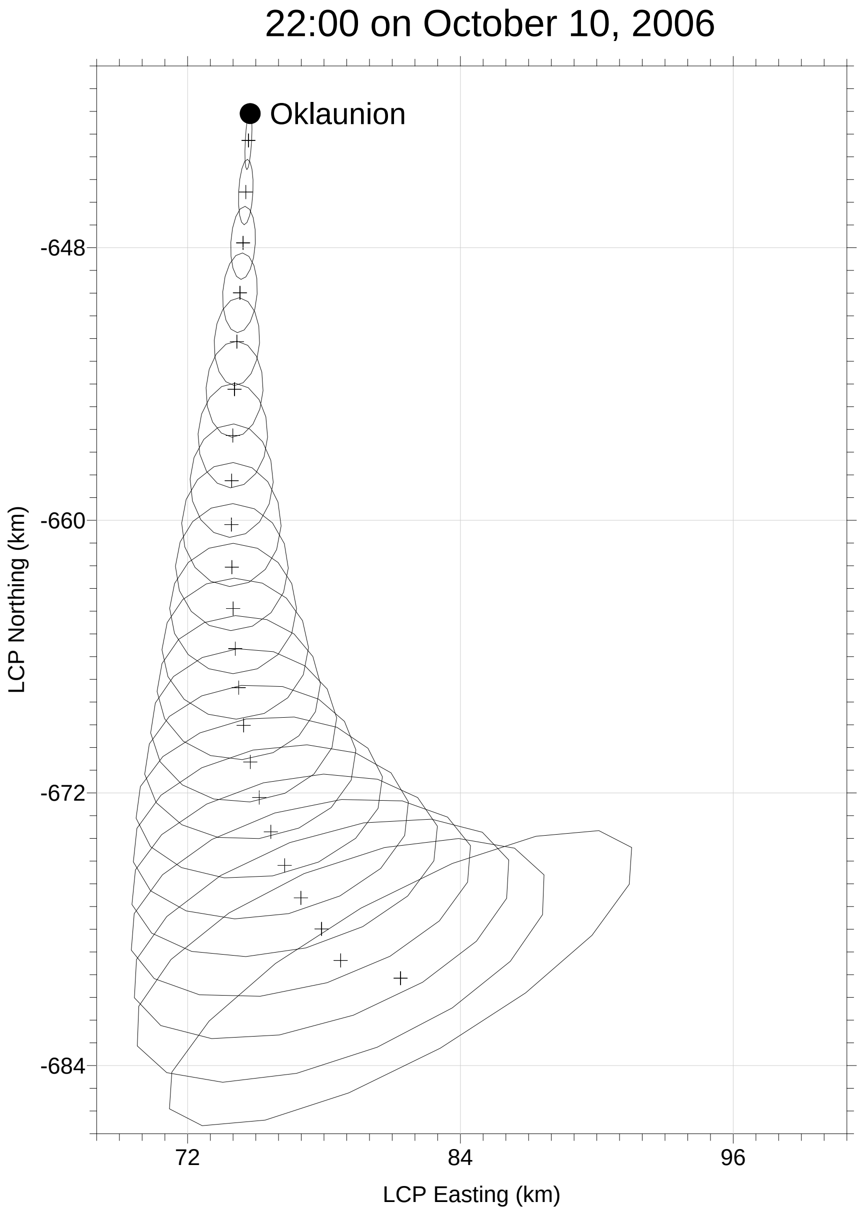
Implications

- To replicate the plume transects, the typical SCICHEM model configuration was modified to a rather large degree (e.g., from hundreds to thousands of puffs), which greatly increases computer simulation time and may not be practical for regulatory use.

CAMx Modeling of Power Plant Plumes

- Overview of CAMx Plume-in-Grid
- Initial Modeling Results
- Model Refinements
- Implications

Overview of CAMx Plume-in-Grid



This is a depiction of the train of CAMx PiG puffs (ellipses) emitted from the Oklaunion power plant at 2200 LST, October 10, 2006, projected on a 12 km gridded modeling domain.

Overview of CAMx Plume-in-Grid (PiG)

- CAMx PiG uses an algorithm very similar to the SCICHEM model to represent a point source emission plume as a series of three-dimensional puffs nested within the CAMx gridded modeling domain.
- The sequence of ellipses with center points represents the perimeter and centroid, respectively, of the horizontal depiction of overlapping puffs.
- Near the source, the ellipses represent overlapping puffs, with minimal horizontal dispersion, and the ellipse is elongated in the downwind direction.
- At extended distances downwind, there are many overlapping puffs with notable dispersion in the horizontal plane, and the ellipses representing the perimeter of the puffs become elongated perpendicular to the wind direction.

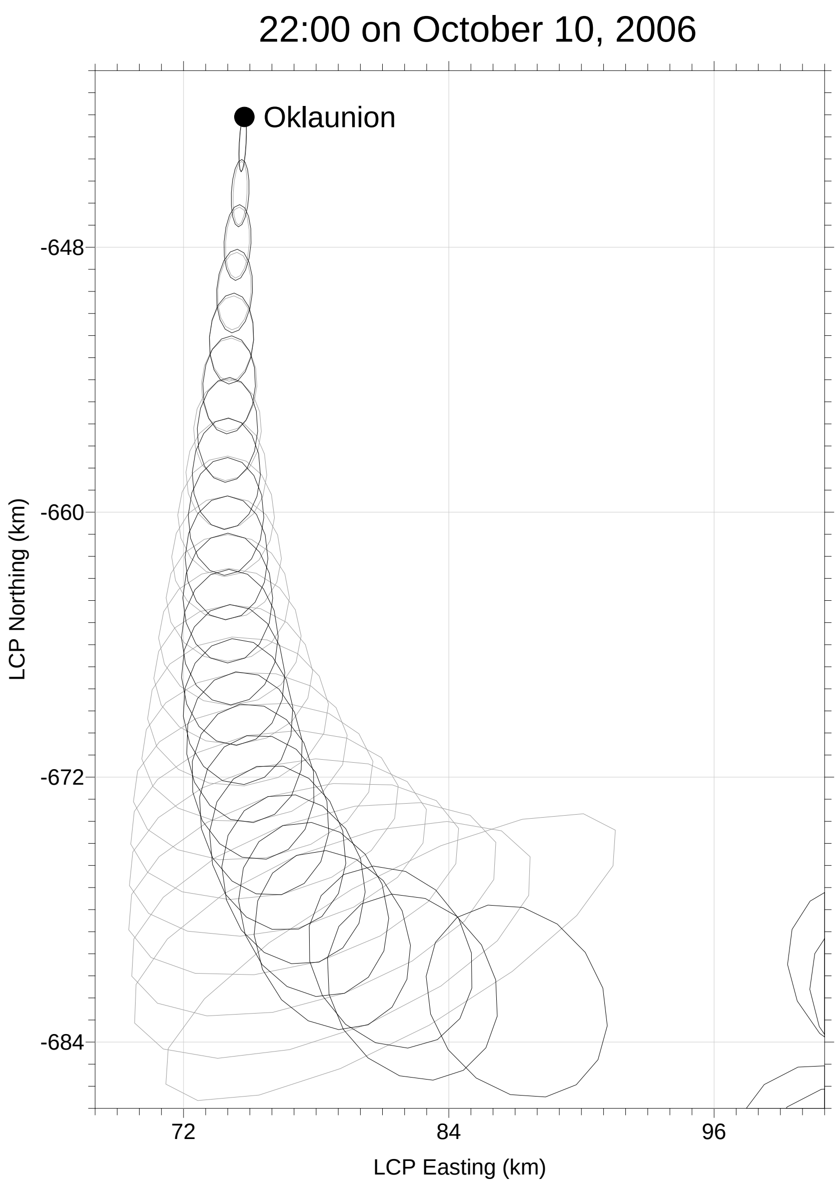
Initial Modeling Results

- CAMx with PiG was applied to the Oklaunion power plant plume monitored during the night of October 10-11, 2006.
- Cross-sectional measurements of the plume along the downwind transport indicate insignificant horizontal spreading, due to either a lack of dispersion or the aircraft not positioned to measure the center of the plume.
- Using typical settings for CAMx with PiG modeling features, such as plume rise and puff growth, the model over-estimated measured plume widths especially at the more downwind locations.
- In addition, the CAMx with PiG model did not replicate the concentrations of N_2O_5 and NO_3 observed at the edges of the plume.

Model Refinements

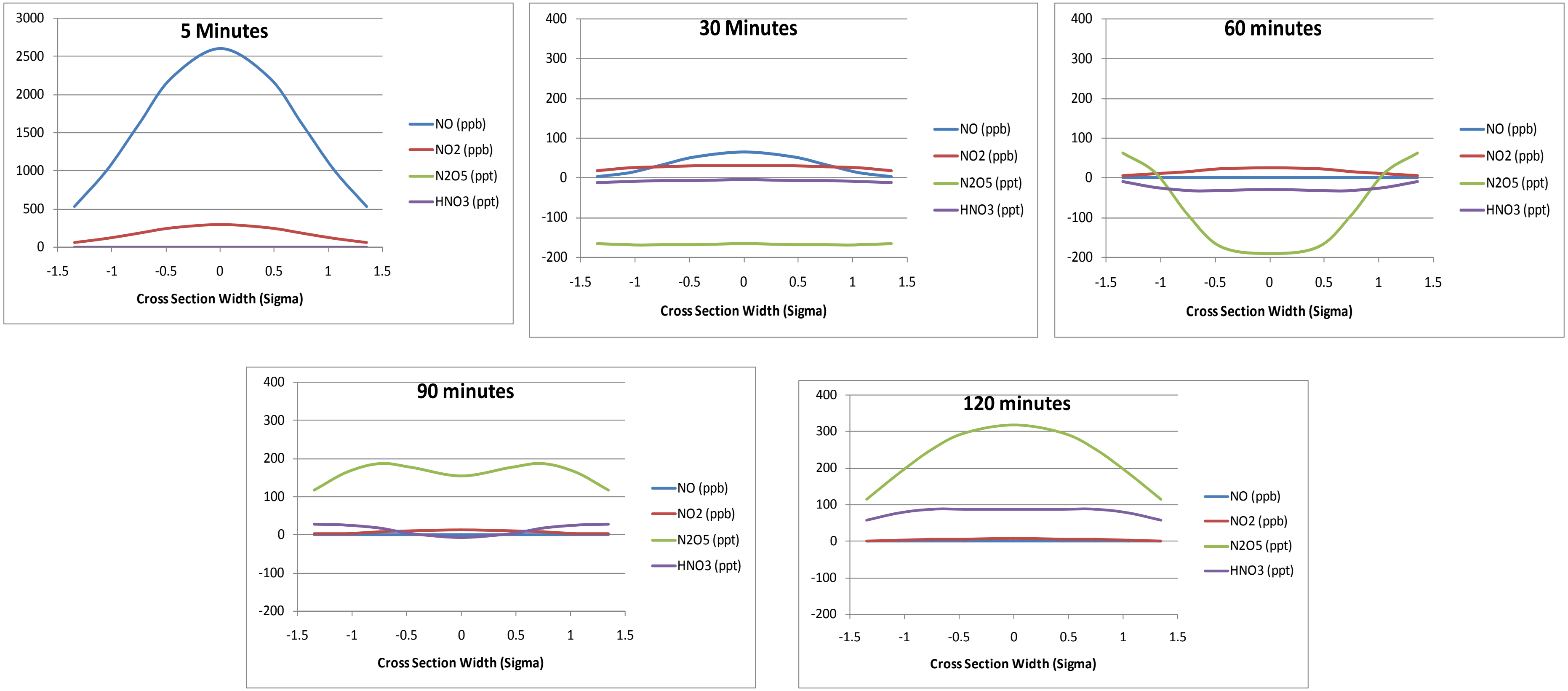
- Modification of PiG Puffs
  - Each PiG puff was divided into five equal volume segments (reactors) with the emitted pollutant mass distributed to each segment according to a normal (Gaussian) distribution.
  - PiG puff growth rates are determined from the surrounding wind field turbulent and shear components. The PiG puff growth rates were modified by removing the contribution from wind shear.
- Flexi-nesting to a High Resolution grid
  - A flexi-nested domain with 200 meter grid spacing was defined for a 6x9 12 km grid cell area including the Oklaunion power plant and a downwind distance sufficient to include approximately three hours of transport.
  - CAMx was run with this high resolution grid for only six hours (1800 – 2400) during the night of October 10, 2006, which took approximately 14 hours to complete.

Model Refinements: PiG Puffs



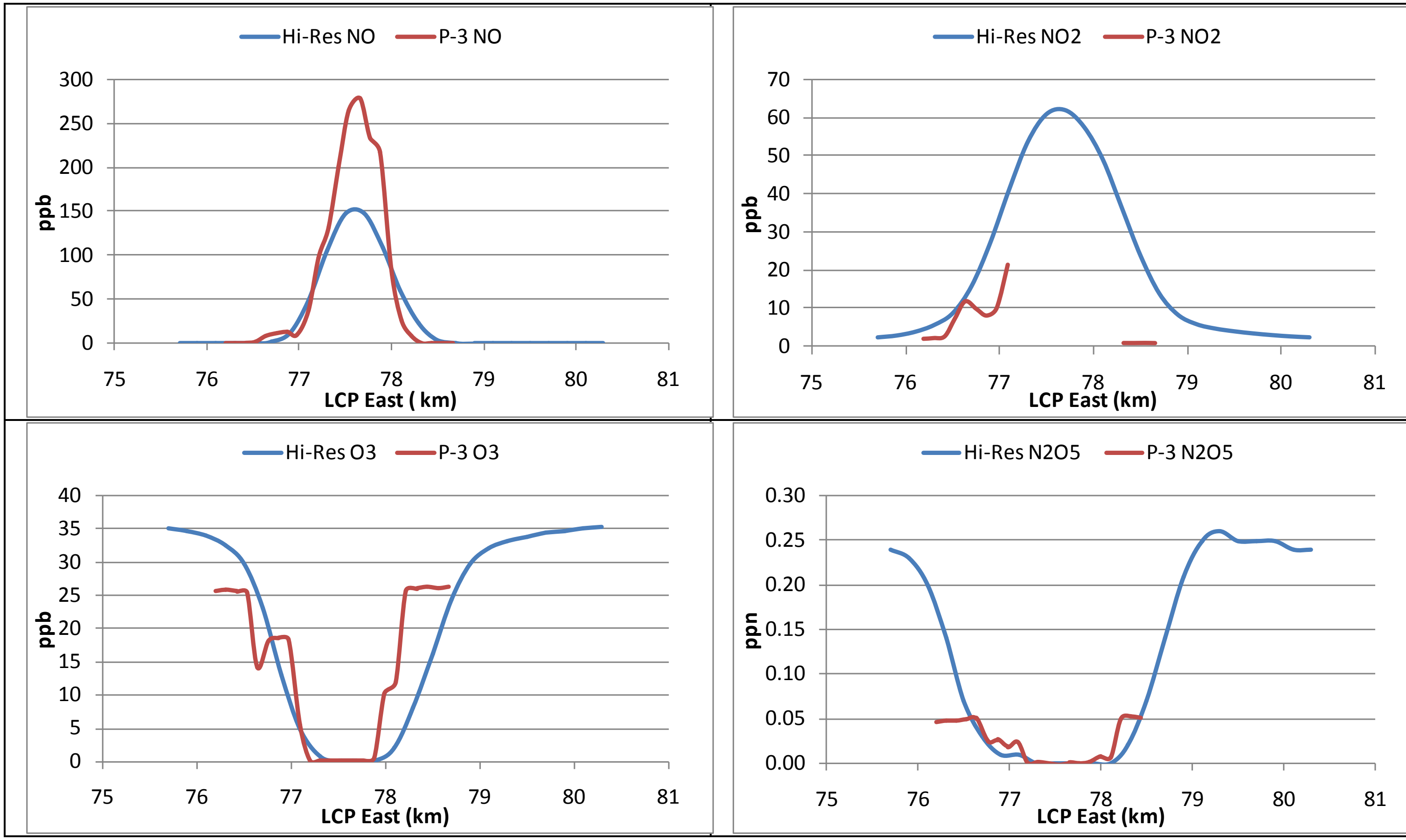
- This is a depiction of the train of CAMx PiG puff (ellipses) emitted from the Oklaunion power plant at 2200 LST, October 10, 2006, projected on a 12 km gridded modeling domain.
- The smaller black puffs are the result of removing wind shear contributions from the puff growth.

Model Refinements: PiG Puffs



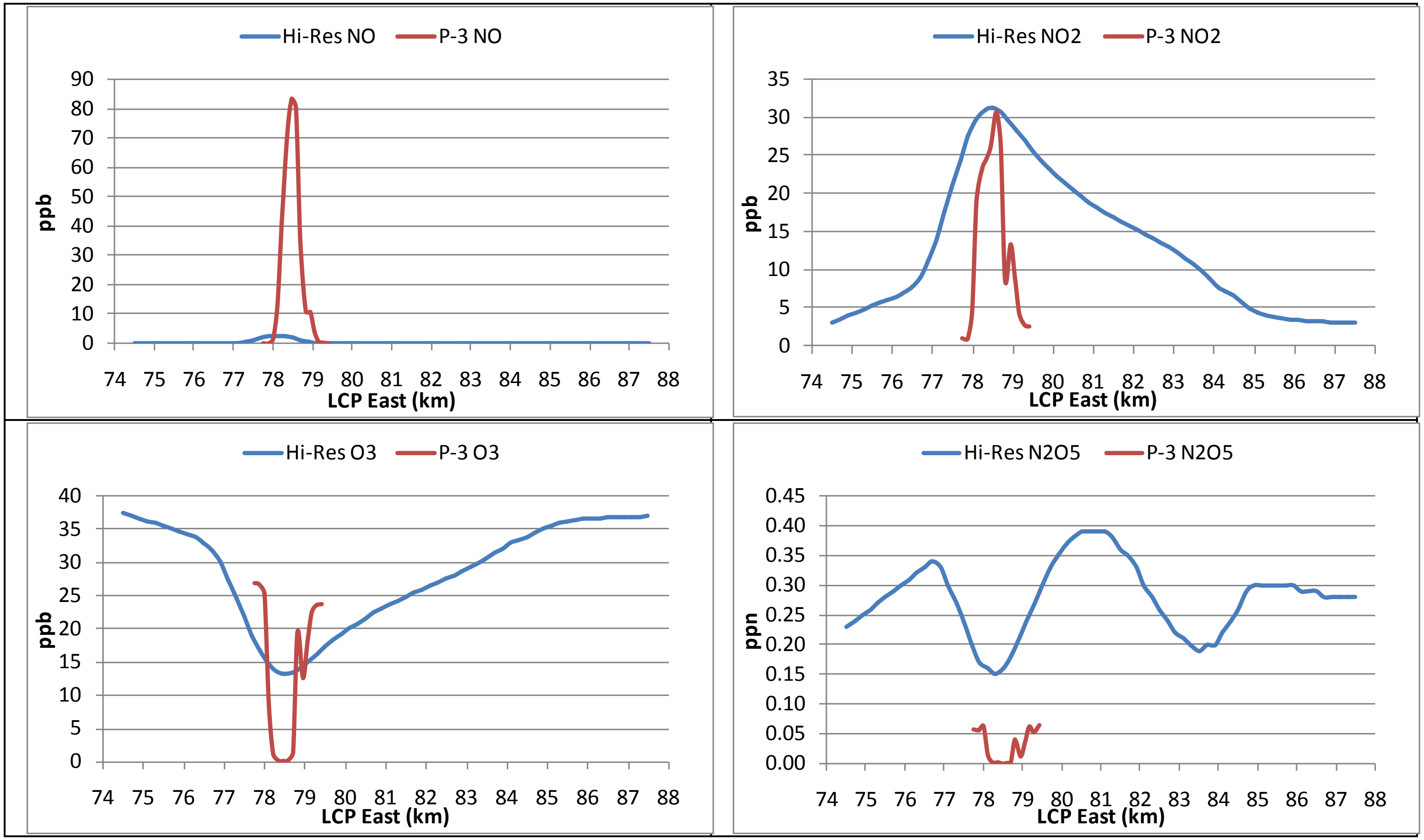
These are graphics of PiG puff cross-sections showing NO_Y species concentrations at 2200 CST for puff ages of 5, 30, 60, 90, and 120 minutes. Puff width is given by multiples of the Gaussian sigma. The zero (0) baseline is the background concentration.

Model Refinements: Flexi-nest



Aligned modeled (layer 5, blue) and measured (red) plume cross-sections of NO (upper left), NO_2 (upper right), ozone (lower left) and N_2O_5 (lower right) at transect 13 for 2130 CST, October 10, 2006.

Model Refinements: Flexi-nest



Aligned modeled (layer 5, blue) and measured (red) plume cross-sections of NO (upper left), NO_2 (upper right), ozone (lower left) and N_2O_5 (lower right) at transect 14 for 2130 CST, October 10, 2006.

Implications

- Modification to the CAMx PiG configuration was unsuccessful in replicating the monitored plume. Although the modifications reduced the simulated plume width and depth, they were still over-estimated resulting in improper characterization of the plume NO_Y species concentrations.
- High resolution flexi-nesting was better able to replicate the plume width close to the source (e.g. transect 13) , but higher modeled background ozone concentrations contributed to poor quantification of the plume NO_Y species concentrations. Further downwind (e.g., transect 14), the simulated plume width and depth were over-estimated, which, coupled with the higher modeled ozone background, resulted in even poorer estimations of the plume NO_Y species concentrations.

Conclusions and Recommendations

- The relative concentrations of the plume NO and ambient ozone are crucial in determining whether there is sufficient ozone to generate an appreciable concentration of NO_3 that will result in overnight losses due to the formation of HNO_3.
- The modifications to the SCICHEM model did result in a better replication of the growth in the plume width during transport downwind. However, the NO_Y species (e.g., NO_2, N_2O_5) were not well replicated. In addition, the modified SCICHEM may not be practical for regulatory use.
- It was not possible to adequately replicate the plume with either the CAMx PiG or flexi-nesting. Neither application was able to replicate the lack of appreciable plume growth measured by the aircraft, which may have been due to sampling the plume edges instead of the plume center. In addition, the modeled ambient ozone was notably over-predicted, which resulted in poor quantification of the plume NO_Y species concentrations.
- These results are intriguing; however, the majority of the study is based on measurements from a single power plant plume for one night, which is not enough to conclude that additional NO_X reduction occurs in a controlled power plant plume due to formation and loss of NO_3 and N_2O_5.