Accurate estimation of HONO in air quality modeling is important as it affects predictions of HOx as well as ozone concentrations. Also, accurate estimation of emissions of NOx are important since HONO formation depends on nitrogen dioxide (NO2) concentrations and HONO emissions are derived from NOx values. The project will first evaluate NOx emissions from the National Emission Inventory 2008 (NEI2008) and, if necessary, adjust NOx emissions rates to improve predictions of modeled concentrations.

Current air quality models take into account several HONO sources including heterogeneous formation from NO2, but do not account for dependence of this process on humidity, where higher formation is expected with higher humidity. This dependence may be of great importance in the Houston area which is characterized by high humidity, especially in the summer months. Additionally, the current mobile-emission model, the Motor Vehicle Emission Simulator (MOVES), estimates HONO emissions based on the HONO/NOx ratio derived from the tunnel studies done in 2001. However, recent measurement studies in Houston suggest that this ratio is higher. We propose to implement humidity dependence of heterogeneous HONO formation in our air-quality model, as well as use the latest HONO/NOx ratio in estimating emissions of HONO, to evaluate the effect of those changes on HONO predictions as well as on O3 and HOx concentrations, and to perform air quality simulations with the CMAQ model for an episode in summer 2013.
Project Objectives

We propose the following activities:

1. Satellite-derived NO\textsubscript{2} column and EPA AQS NO\textsubscript{x} concentrations will be utilized to evaluate model NO\textsubscript{2} predictions for Southeast Texas. If necessary, NO\textsubscript{2} emissions will be modified and the effect of satellite-adjusted emissions on NO\textsubscript{2} and ozone mixing ratios estimated.
2. Implement humidity dependence of heterogeneous HONO formation in air quality model and evaluate the impact on HONO, O\textsubscript{3}, and HO\textsubscript{x} mixing ratios.
3. Implement new split of NO\textsubscript{x} sources to account for the latest measurements in Houston ratios of HONO/NO\textsubscript{x} and evaluate its impact on HONO, O\textsubscript{3}, and HO\textsubscript{x} mixing ratios.

Methodology

Air quality modeling is performed with the latest version of CMAQ (Byun and Schere, 2006). The WRF model (Skamarock et al. 2008) is employed to simulate meteorological parameters, and the 2008 National Emission Inventory is utilized to estimate emission rates. Simulations are performed for the whole month of September 2013 corresponding to the NASA DISCOVER-AQ Houston campaign during which HONO measurements took place.

The results of Stutz et al. (2004) imply that NO\textsubscript{2} to HONO conversion is dependent on humidity and that the dependence is linear. However, there is no experimental derived equation on humidity dependence that could be directly applied to the 3D model mainly due to difficulties in parameterizing reactive surfaces based on humidity and their corresponding reactive uptake coefficient. Currently CMAQ uses first order conversion of NO\textsubscript{2} to HONO that depends solely on surface to volume ratio (S/V) and NO\textsubscript{2} concentrations. This may either underestimate heterogeneous HONO production during nighttime when usually humidity is high or overestimate HONO during daytime when humidity is low. This work will modify the NO\textsubscript{2} to HONO conversion to make it humidity dependent. Based on the comparison of model to observed data several sensitivities may be performed where the NO\textsubscript{2} to HONO conversion may be scaled to reduce daytime HONO production (for example by the factor (RH/100)) or to increase nighttime production (by the factor (RH/20)).

Recent studies on HONO emissions in Houston (Rappenglueck et al., 2013) show that twice as much HONO is directly emitted from mobile sources compared to widely used value of Kurtenbach et al. (2001). This work will increase HONO emissions from mobile sources and estimate impact on HONO mixing ratios. If the impact is significant recommendation may be given to change estimation of HONO emissions in MOVES model.

Accomplishments

The National Emission Inventory 2008 was evaluated for NO\textsubscript{x} values. Two approaches have been tested and were published in two papers: (1) adjusting NO\textsubscript{x} emissions using the remote sensing data from the Global Ozone Monitoring Experiment-2 (GOME-2) (Choi et al., 2014) and (2) adjusting NO\textsubscript{x} emissions using EPA National emission trends (Czader et al., 2014).
For the first approach, we analyzed the simulation results from a CMAQ model and GOME-2 NO$_2$ retrievals over the United States for August 2009 to estimate model-simulated biases of NO$_x$ concentrations. By comparing GOME-2 NO$_2$ columns to corresponding CMAQ NO$_2$ columns, we produced satellite-adjusted NO$_x$ emission and compared baseline emission CMAQ simulations with GOME-2 adjusted emissions. We found that the latter exhibited decreases of -21.3% emissions over the Lower Middle region. In addition, we found that changes in NO$_x$ emissions generally mitigate discrepancies between the surface NO$_x$ concentrations of baseline CMAQ and those of AQS at EPA AQS stations (mean bias of +149% to -7.8%). The relatively high simulated NO$_x$ biases from baseline CMAQ over LM (+149%) are likely the results of over-predictions of simulated NO$_x$ emissions, which could shed light on those from global/regional Chemical Transport Models (Choi et al., 2014). We also perform more detailed investigations on surface NO$_x$ and O$_3$ concentrations in the urban and outflow region, LM (e.g., Houston, Beaumont and Sulphur). From this case study, we found that the GOME-2 adjusted emission decreased surface NO$_x$ concentrations significantly in the urban area of LM (up to 10 ppbv) during the daytime and that simulated NO$_x$ concentrations from CMAQ with GOME-2 emissions compare well to those of in-situ EPA AQS observations. Over Houston, Beaumont, and Sulphur, large reductions in NO$_x$ emissions from CMAQ with GOME-2 adjusted emission coincides with large reduced concentrations of simulated NO$_x$. These concentrations are similar to those of the EPA AQS NO$_x$ observations. However, the resulting simulated increase in surface O$_3$ at the urban stations in Houston and Sulphur exacerbated preexisting high O$_3$ over-predictions of the baseline CMAQ. This study implies that the high O$_3$ biases in the urban areas of LM cannot be explained by simulated high NO$_x$ biases over the region. This study also suggests that both in-situ surface NO$_x$ and O$_3$ observations should be used simultaneously to resolve issues pertaining to simulated high/low O$_3$ bias and that remote-sensing data could be used as a constraint for bottom-up emissions. In addition, we also found that day-time O$_3$ reductions over the outflow regions of LM following large reductions in NO$_x$ emissions in the urban areas are significantly large. These findings provide policymakers in the region with information critical to establishing strategies for mitigating air pollution.

For the second approach, we observed overestimates of NO$_x$ mixing ratios and adjusted emissions of NO$_x$ to reflect current anthropogenic emission trends reported by U.S. EPA. Relatively to values for the year 2008 there was 28% reduction in on-road mobile NO$_x$ emissions on a nationwide scale and 20% reduction in other anthropogenic NO$_x$ emissions in year 2013. To follow the emissions trends we created a sensitivity case in which on-road NO$_x$ emissions were reduced by 30% and anthropogenic point source emissions were reduced by 20%. The modeled mixing ratios of NO$_x$ were evaluated against measured data from a number of sites in the Houston area. Overall, the NO$_x$ mean value dropped from 11.11 ppbv in the base case to 7.59 ppbv in the NO$_x$ adjusted case becoming much closer to the observed mean of 7.76 ppbv. The Index of Agreement (IOA) is improved in the reduced NO$_x$ case (0.71 vs. 0.75) and the Absolute Mean Error (AME) is lowered from 6.76 to 4.94 (Czader et al., 2014).

The modeled mixing ratios of HONO were evaluated against the actual observed values attained at the Moody Tower in Houston and are presented in Figure 1. The model could not reproduce the morning HONO peaks when the low HONO/NO$_x$ ratio of 0.008 was used to estimate HONO emissions. Doubling HONO emissions from mobile sources resulted in higher mixing ratios, the mean value increased from 0.30 ppbv to 0.41 ppbv becoming closer to the observed mean concentrations of 0.69 but still low; AME was slightly reduced from 0.46 to 0.43.
IOA for simulation that used the 2001 emission values is 0.63 while for simulation with higher HONO emission it increased to 0.70. Increased HONO emissions impacted OH mixing ratio, up to about 6% increase was found during morning and mid-day hours. The impact on ozone is marginal.

![Figure 1](image_url)

Figure 1. Measured and modeled HONO mixing ratios at the Moody Tower. Red line corresponds to the base case simulation, for which HONO/NOx=0.008, blue line to the simulation with increased HONO emissions for which HONO/NOx = 0.016

In order to simulate better meteorological conditions for these proposed works, we performed some sensitivity tests by constraining the meteorological data using in-situ measured meteorological data. This work is done by Li et al. (2014). Three WRF-CMAQ simulations for the DISCOVER-AQ 2013 Texas campaign period (30 days in September) are performed to characterize the impact of observation nudging and domain nesting on the simulated meteorological conditions. We found that there are around 7% index of agreement (IOA) gain in temperature and 9-12% boost in u-wind and v-wind when the observation nudging is employed in the simulation. Further performance gain from nested domains over single domain is marginal. The CMAQ simulations based on the above WRF setups showed that the ozone performance slightly improved in the simulation for which nudging is carried out, although not matching up to the improvements in temperature and winds. Further IOA gain achieved with nested domains is quite limited. The results suggest that other factors, such as emission uncertainties, may have contributed to the discrepancies in the performance gain in meteorology and chemistry. Comparing to nudging, domain nesting significantly increased simulation time yet did little to boost ozone predictions. This can be at least partly explained by the fact that our focus area is located away from the boundaries. This study shows that the high ozone episodes during the analyzed time periods were associated with post-front conditions, especially the shifting winds near industry zone. All runs missed the observed high ozone values which reached above 150 ppb in La Porte on September 25, the only day with hourly ozone over 120 ppb. Model’s inability to catch small-scale wind shifts near the industrial zone is likely the main cause of the misses. Despite better wind directions in the simulations with nudging and nested domains, the key feature of wind shift is not present in all runs. This study also shows that overestimated background ozone from the southerly chemical boundary is a critical source for the model’s
general overpredictions of the ozone concentrations from CMAQ during September of 2013. The results of this study shed a light on the necessity of (1) capturing the small-scale wind such as the onsets of bay-breeze or sea-breeze and (2) implementing more accurate chemical boundary conditions to reduce the simulated high-biased ozone concentrations. One promising remedy for (1) is reading observation nudging data at hourly time step instead of the standard one which is done every three hours.

Further, this TARC funding has supported Dr. Beata Czader during the project time period who is a critical person to maintain UH Air Quality Forecasting system (UH-AQF) and many different applications using forecasting system were applied and the details are below.

Future work

Over the remaining project time period, we will perform simulation studies to satisfy the second objective of this project: Implementing humidity dependence of heterogeneous HONO formation in air quality model and evaluate the impact on HONO, O₃, and HOₓ mixing ratios. Our goal for the remaining time period is implementation of the HONO parameterization into the CMAQ, analysis of the results, and preparing another publication.

List of Publications

- Choi, Y., The impact of satellite-adjusted NOₓ emissions on simulated NOₓ and O₃ discrepancies in the urban and outflow areas of the Pacific and Lower Middle US, Atmos. Chem. Phys., 14, 675-690, 2014.

Invited Presentations and list of presentations

- Choi, Y., The impact of observational nudging and nesting on the simulated meteorology and ozone concentrations from WRF-CMAQ during the DISCOVER-AQ 2013 Texas campaign, July 21, 2014, Southeast Texas Photochemical Modeling Technical Committee meeting, Houston-Galveston Area Council, Houston, TX
- Czader, B., Choi, Y., Li, X., Diao, L., Lefer, B., Alvarez, S., and Jull, L., Modeling nitrous acid (HONO) for Houston, NASA Air Quality Applied Science team meeting, January 2014, Houston, TX
• Diao, L., Choi, Y., Czader, B., Choi, S., Joiner, J., and Kim, H., The evaluation of air quality forecasting system based on WRF-CMAQ and WRF-Chem over Houston during the DISCOVER-AQ Houston: surface O\textsubscript{3}, PM2.5 and tropospheric NO\textsubscript{2}, NASA Air Quality Applied science team meeting, January 2014, Houston, TX

• Diao, L., Choi, Y. and Czader, B., Lightning and anthropogenic NO\textsubscript{x} sources over the United States during the Deep Convective Clouds & Chemistry (DC3) field campaign: impact on tropospheric NO\textsubscript{x}, O\textsubscript{3} and outgoing longwave radiation, December 2013, American Geophysical Union meeting, San Francisco, CA

• Czader, B., Choi, Y., and Diao, L, Sensitivity to changes in HONO emissions from mobile sources simulated for Houston area, October 2013, CMAS meeting, Chapel Hill, NC