Impact of updated traffic emissions on HONO mixing ratios simulated for urban site in Houston, Texas

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Received: 10 July 2014 – Accepted: 5 August 2014 – Published: 20 August 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

Recent measurements in Houston show that HONO traffic emissions are 1.7 % of NO\textsubscript{x} emissions which is about twice the previously estimated value of 0.8 % based on tunnel measurements in 2001. The 0.8 % value is widely used to estimate mobile emissions of HONO for air quality modeling applications. This study applies the newly estimated HONO / NO\textsubscript{x} ratio in the WRF-SMOKE-CMAQ modeling system and estimates the impact of higher HONO traffic emissions on its mixing ratios. Since applied emission inventory resulted in overestimates of NO\textsubscript{x} mixing ratios and because HONO emissions and chemical formation depends on the magnitude of NO\textsubscript{x}, thus, before proceeding with HONO emission modifications emissions of NO\textsubscript{x} were adjusted to reflect current emission trends. The modeled mixing ratios of NO\textsubscript{x} were evaluated against measured data from a number of sites in the Houston area. Overall, the NO\textsubscript{x} mean value dropped from 11.11 ppbv in the base case to 7.59 ppbv in the NO\textsubscript{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\textsubscript{x} case (0.71 vs. 0.75) and the Absolute Mean Error (AME) is lowered from 6.76 to 4.94. The modeled mixing ratios of HONO were evaluated against the actual observed values attained at the Moody Tower in Houston. The model could not reproduce the morning HONO peaks when the low HONO / NO\textsubscript{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 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. This study results sheds light on the underestimated HONO and OH in the morning from global/regional chemical transport models with the typical emission of 0.8 % HONO emission out of the total NO\textsubscript{x} emissions.
Introduction

Photolysis of nitrous acid (HONO) is an important source of hydroxyl radical (OH). OH plays a crucial role in the oxidation of volatile organic compounds (VOCs) leading to the formation of ozone and secondary organic particulate matter. Main sources of OH are photolysis of ozone, formaldehyde, alkenes, and nitrous acid (Elshorbany et al., 2009; Mao et al., 2010; Kim et al., 2014). Photolysis of ozone and formaldehyde are the most important sources of OH during mid-day and afternoon hours; however, the highest contribution to radical production during early morning hours comes from photolysis of HONO (Czader et al., 2012, 2013).

HONO can be either formed through chemical reactions or emitted to the atmosphere from combustion processes. Among the most known chemical sources of HONO is the gas-phase formation from the reaction between OH and nitric oxide (NO) (Pagsberg et al., 1997) and the heterogeneous formation on surfaces from the hydrolysis of nitrogen dioxide (NO$_2$) (Kleffmann et al., 1998; Finlayson-Pitts et al., 2003). Other chemical sources of HONO are described elsewhere (Kleffmann et al., 2005, 2007; George et al., 2005; Stemmler et al., 2006, 2007; Crowley and Carl, 1997; Li et al., 2008, 2009; Carr et al., 2009; Amedro et al., 2011). Emissions of HONO from traffic were estimated by Kirchstetter et al. (1996) and Kurtenbach et al. (2001) who performed tunnel studies and reported exhaust emission ratio of HONO to NO$_x$ in a range of 0.003–0.008. The value of 0.008 is used in the Community Multiscale Air Quality (CMAQ) model to calculate HONO emissions from mobile sources (Foley et al., 2010) as well as in other models, for example, in a box model employed to study HONO sources in Houston (Wong et al., 2013). The relative contribution of HONO emissions from traffic to other sources when using the HONO to NO$_x$ ratio of 0.008 is about 9% based on simulations for eastern US (Sarwar et al., 2008). For high NO$_x$ areas in China Li et al. (2011) calculated as high as 26% contribution of HONO emissions to its total sources but they could not reproduce the high morning peak values of HONO associated with traffic emissions. Czader et al. (2012) studied HONO formation for Houston conditions and...
also applied the 0.008 HONO/NO$_x$ ratio to estimate HONO emissions. In addition to default sources of HONO present in CMAQ they implemented photolytic HONO formation; however, on many occasions the peak morning values continued to be underpredicted by the model. Recent measurements performed in Houston in 2009 show that the observed HONO/NO$_x$ emission ratio is 0.017 (Rappenglueck et al., 2013), which is about twice as high as previously reported and implemented in CMAQ modeling system. The impact of using higher HONO emissions in air quality modeling applications has not been evaluated. Therefore, in this work HONO emissions from mobile sources will be doubled to reflect the newly reported HONO/NO$_x$ emission ratio and the impact of higher HONO traffic emissions on its mixing ratios will be estimated in the WRF-CMAQ modeling system. The impact of increased HONO on the OH and O$_3$ will also be investigated in this study.

Because in air quality applications HONO is derived from the NO$_x$ emission inventory and chemical formation of HONO is directly related to NO and NO$_2$ mixing ratios; therefore, HONO predictions by air quality models depend on how well the model reflects emissions of NO$_x$. Czader et al. (2012) pointed out that the correlation between measured and simulated HONO values increased significantly when data points with wrong NO$_2$ prediction were ignored and only data for which NO$_2$ values were simulated within 70% of the measured value were considered. Therefore, accurate estimation of NO$_x$ in air quality models is crucial to properly simulate HONO mixing ratios. Previous studies used remote sensing and in-situ surface observations to analyze accuracy of NO$_x$ emissions and indicated that the National Emission Inventory (NEI) has large uncertainty in emissions in urban areas (Choi et al., 2012; Choi, 2014). Of particular, Choi (2014) issued that both NEI2005 and NEI2008 have significant NO$_x$ overestimates in Houston. Thus, in this study, before proceeding with modifications of HONO emissions, NO$_x$ emissions will be adjusted using the U.S. Environmental Protection Agency (EPA) annual trend values and the absolute amounts of simulated surface NO$_x$ concentrations will be evaluated.
2 Methodology

Meteorological parameters were derived with the Weather Research and Forecasting (WRF) model version 3.5 (Skamarock et al., 2008). NCEP North American Regional Reanalysis (NARR) data provided by the NOAA/OAR/ESRL PSD (available at: http://www.esrl.noaa.gov/psd/) were utilized to initialize WRF simulations. The 2008 National Emission Inventory (NEI2008) generated by the Environmental Protection Agency (EPA) was processed with the Sparse Matrix Operator Kernel Emissions (SMOKE) system to obtain gridded, chemically and temporally resolved emission files ready to use in an air quality model. The air quality simulations were performed with the three-dimensional Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006) version 5.0.1 with the Carbon Bond 05 chemical mechanism and aerosol 5 module (cb05tucl_ae5_aq).

Simulations were performed for a domain with 4 km grid resolution covering southeast Texas, with 84 grid cells in east-west direction, 66 grid cells in south-north direction, and 27 vertical layers. The boundary conditions were obtained from the University of Houston air quality forecasting system (http://spock.geosc.uh.edu) from a larger domain with 12 km grid resolution, 150 grid cells in east-west direction and 134 grid cells in south-north direction. Initial conditions were also obtained from the air quality forecasting results from the nested southeast Texas domain. Simulations were performed for the month of September 2013 during which the DISCOVER-AQ campaign took place in Houston providing many different meteorological and chemical measurements that can be utilized for model evaluation.

2.1 Adjusting NO\textsubscript{x} and HONO emissions

Previous studies used remote sensing and in-situ surface observations to analyze accuracy of NO\textsubscript{x} emissions and pointed to the fact that the National Emission Inventory (NEI) has large uncertainties in emission for urban areas (Choi et al., 2012; Choi, 2014). Of particular, Choi (2014) issued that both NEI2005 and NEI2008 might have...
significant overestimates of NO\textsubscript{x} emissions in Houston even with the consideration of the uncertainties caused from other chemical and physical processes. Adequate estimation of NO\textsubscript{x} emissions is critical for properly predicting HONO mixing ratios.

Since our simulations employed NEI2008 there was a need of adjusting emissions to reflect conditions of 2013. In this study, instead of relying on the remote-sensing-derived data or surface-measured data to adjust an emission inventory (e.g., Kim et al., 2009, 2011; Choi et al., 2012; Choi, 2014) we use the long-term trends of anthropogenic NO\textsubscript{x} emission reported by U.S. EPA. Then the impact of the adjusted NO\textsubscript{x} emissions on surface NO\textsubscript{x} concentrations is evaluated by comparing the simulated and observed NO\textsubscript{x} concentrations. According to EPA, emission of nitrogen oxides from anthropogenic sources were reduced between 2008 and 2013. Table 1 shows emission values based on the EPA trends (available at: http://www.epa.gov/ttn/chief/trends/index.html#tables) for on-road mobile sources and other anthropogenic sources excluding wildfires. Relatively to values for the year 2008 there was 28\% reduction in on-road mobile NO\textsubscript{x} emissions on a nationwide scale and 20\% reduction in other anthropogenic NO\textsubscript{x} emissions in year 2013. To follow the emissions trends we created a sensitivity case in which on-road NO\textsubscript{x} emissions were reduced by 30\% and anthropogenic point source emissions were reduced by 20\%.

NEI provides emission rates for nitrogen oxides, during the processing with SMOKE NO\textsubscript{x} emissions for mobile sources are separated into 90\% NO, 9.2\% NO\textsubscript{2}, and 0.8\% HONO. However, Rappenglueck et al. (2013) reports much higher HONO contribution from mobile sources in Houston; based on all measurements HONO traffic emissions are 1.7\% of NO\textsubscript{x} emissions which is about twice the previously estimated value of 0.8\% based on tunnel measurements in 2001. To reflect the latest observations in air quality modeling additional sensitivity case was created in which contribution of HONO from mobile sources was doubled at the cost of NO\textsubscript{2}. The following speciation was used for the sensitivity case: 90\% NO, 8.4\% NO\textsubscript{2}, and 1.6\% HONO.

The following three simulations cases are performed and analyzed in this study: B – base case, with NO\textsubscript{x} emissions rates obtained from NEI2008 and
HONO / NO\textsubscript{x} = 0.008; N – reduced emissions of NO\textsubscript{x} case: mobile sources × 0.7, point sources × 0.8; NH – similar as N but with doubled HONO emissions from mobile sources, this is HONO / NO\textsubscript{x} = 0.016.

### 2.2 Measurements

Measured values from the Continuous Ambient Monitoring Stations (CAMS) system, operated by the Texas Commission on Environmental Quality (TCEQ), were utilized for evaluating NO\textsubscript{x} emission inventory. During the time period of interest 30 stations inside our 4 km modeling domain reported NO\textsubscript{x} measurements. Figure 1 shows location of sites in the Houston-Galveston metropolitan areas where color of the symbol indicates the measured mean NO\textsubscript{x} mixing ratios during the month of September 2013. Several sites, such as 78, 84, 618, 619, and 1016 have low mean values; those sites reflect regional and/or suburban conditions. Couple sites, such as 26 and 53, have medium range NO\textsubscript{x} values reflecting urban air mixture dominated by traffic emissions. Many sites close to highways or in downtown Houston are exposed to heavy traffic as well as a combination of traffic and industrial emissions. They have very high NO\textsubscript{x} mean values; those are CAMS sites 1, 8, 114, 403, 408, 411 and the Moody Tower (MT) site described below.

The Moody Tower, located east of downtown, was designated as a “super” site during air quality study campaigns in Houston in years 2006 (Lefer and Rappenglück, 2010) and 2009 (Olaguer et al., 2013) during which many chemical and meteorological measurements were taken. During September 2013 measurements at the Moody Tower complimented the DISCOVER-AQ campaign. The measurements were taken at 60 m a.g.l. In addition to NO\textsubscript{x} and ozone, HONO was also measured on several days during the month of September 2013.
3 Results

3.1 Evaluation of NO\textsubscript{x} modeling

Table 2 shows summary of statistical parameters for modeling NO\textsubscript{x} mixing ratios for the base case (B) and the reduced NO\textsubscript{x} case (N) as compared to measured values at CAMS sites, where $R$ is the Pearson coefficient, AME – absolute mean error calculated as:

\[
\text{AME} = \left( \frac{1}{n} \right) \sum_{1}^{n} |C_{m} - C_{o}|
\]  

(1)

"n" is the number of data points, "m" corresponds to modeled values and "o" to observed ones;

IOA – index of agreement, calculated according the following equation:

\[
\text{IOA} = 1 - \frac{\sum_{1}^{n} (C_{m} - C_{o})^2}{\sum_{1}^{n} (|C_{o} - \bar{O}| + |C_{m} - \bar{O}|)^2}
\]  

(2)

"\bar{O}" corresponds to observed mean value. Compared to a Pearson coefficient the index of agreement is a more comprehensive measure of how well the concentrations are predicted since it takes into account not only scattering of data but also biases (Willmott, 1981).

Statistical parameters were calculated for all available data pairs from CAMS sites inside the modeling domain. The measured mean value from all sites is 7.76 ppbv, the simulated mean value dropped from 11.11 ppbv in the base case to 7.59 ppbv in the reduced NO\textsubscript{x} case becoming closer to the observed mean. Both, $R$ and IOA are improved in the reduced NO\textsubscript{x} case ($R = 0.58$, IOA = 0.71 in the base case, $R = 0.59$, IOA = 0.75 in the reduced NO\textsubscript{x} case) and AME is lowered from 6.76 to 4.94 ppbv. Overall, the reduced NO\textsubscript{x} simulation case gives better NO\textsubscript{x} prediction in comparison to the base case.
When looking at individual stations affected by emissions from different sources, the improvement from NO\textsubscript{x} reductions is beneficial for most of sites, but leads to underpredictions at several sites. Many stations with medium range NO\textsubscript{x} mixing ratios, such as CAMS 35 and 53 show improvement from NO\textsubscript{x} reduction. There are also cases when NO\textsubscript{x} continue to be too high even after reduction of emissions. This is the case for CAMS sites 26 and 78 that represent sub-urban conditions with low measured NO\textsubscript{x} mixing ratios (usually below 10 ppb) and low mean values of 5.61 and 3.29, respectively. The model represents them as urban sites with significant traffic signature and therefore with much higher than measured mixing ratios. Very high NO\textsubscript{x} mixing ratios are recorded in areas with heavy traffic and close to industrial facilities in the eastern part of Houston; these are 1, 403, 411, and 416. NO\textsubscript{x} mixing ratios at those stations were heavily overpredicted and consequently those stations benefit the most from NO\textsubscript{x} reductions as presented in Fig. 2. Our results are similar to the previous study by Choi (2014) who issued that NO\textsubscript{x} mixing ratios at urban regions are overpredicted by air quality models, but NO\textsubscript{x} at the rural regions are underpredicted.

The Moody Tower site served as a super site for couple of measurements campaigns in Houston and many different chemical and meteorological parameters were measured there, including NO, NO\textsubscript{2}, and HONO. It is located in close proximity to downtown and major highways and is affected by quite high NO\textsubscript{x} emissions. Figure 3 shows comparison of measured at the Moody Tower and simulated mixing ratios of NO (top) and NO\textsubscript{2} (bottom). Again, two simulation cases are compared: the case with regular emissions as included in NEI2008 (B) and the reduced NO\textsubscript{x} emissions case (N). It can be seen that for both compounds the peak values were overpredicted by the base case while reduced NO\textsubscript{x} case resulted in lower mixing ratios making them closer to the observed values. In particular, NO mixing ratios are much better predicted by reduced NO\textsubscript{x} emissions case. Both, NO\textsubscript{2} morning peaks and low range day and nighttime values, although lowered, continue to be overpredicted most of the time.
3.2 HONO modeling

Since reduction of NO\textsubscript{x} emissions resulted in better prediction of NO\textsubscript{x} mixing ratios at the Moody Tower and nearby areas this case was used as a base for testing impact of increased HONO emissions. Figure 4 shows changes in HONO emissions rates between the sensitivity case in which HONO / NO\textsubscript{x} = 0.016 (indicated as NH) and the base case that used HONO / NO\textsubscript{x} = 0.008 (indicated as N). Doubling HONO emissions resulted in up to 0.01 mol s\textsuperscript{-1} increase in emission rates from mobile sources along highways. Figure 5 shows differences in simulated mixing ratios of HONO for morning conditions at 7 a.m. LT that corresponds to the time of the highest HONO emissions from traffic and the highest HONO mixing ratios. The left panel shows results for the surface layer. It can be seen that changes of mixing ratio at the surface occur along highways following the pattern of emission changes presented in Fig. 4. Differences of HONO mixing ratios at the second modeled layer, which corresponds to measurements taken at the Moody Tower, are shown in the right panel of Fig. 5. At this level the air is mixed and the spatial signature of mobile emissions diminishes.

HONO is not routinely measured in Houston; in spite of that, during September 2013 HONO was measured at the Moody Tower to compliment measurements during DISCOVER-AQ campaign. However, the measurements were not continuous and the data are limited to several days. Figure 6 shows timeseries of measured and simulated HONO mixing ratios at the Moody Tower. The mixing ratios obtained from the reduced NO\textsubscript{x} simulation case (N), for which the HONO / NO\textsubscript{x} emission ratio of 0.008 was used, are much lower than observed HONO values. The values from the increased HONO case (NH), with the HONO / NO\textsubscript{x} emission ratio of 0.016, are higher, especially the morning peaks, and closer to the observations. The statistical parameters for HONO modeling at the Moody Tower are presented in Table 3. The mean value increased from 0.30 in the base case to 0.41 ppbv in the increased HONO emissions case but continue to be lower than the observed mean of 0.69 ppbv. The index of agreement increased from 0.63 to 0.70 indicating benefits of increased HONO emissions. Clearly,
improvement in HONO peak values can be seen on 12, 18, 23, 24, 25 and 30 September, especially on 12 September the model with increased HONO emissions nicely follow HONO peak while the case with low HONO/NO\textsubscript{x} emission rates resulted in underprediction of the peak value. However; as pointed by Czader et al. (2012) HONO predictions depends on how well the model captures NO\textsubscript{x} concentrations, especially NO\textsubscript{2}, since heterogeneous HONO formation is directly related to NO\textsubscript{2} concentrations and greatly influences morning HONO mixing ratios. It can be seen that overprediction of NO and NO\textsubscript{2} on 11, 19, and 24 September leads to overprediction of HONO. We can conclude that misprediction of precursors is responsible for HONO misprediction and expect that if NO\textsubscript{x} mixing ratios for those days are accurately simulated also HONO values would be close to observation. This is not a case on 18 September when, despite the fact that NO is well predicted and NO\textsubscript{2} overpredicted, HONO peak is underpredicted. The reasoning for that is unknown, but it is probably due to the uncertainties in other HONO sources.

The photolysis of HONO is a source of hydroxyl radical. Figure 7 shows OH mixing ratios (left) and differences in OH mixing ratios (right) between simulation with increased HONO emissions (NH) and regular emissions with 0.008 HONO/NO\textsubscript{x} emissions ratio (N) for 13 September, which is a day with nicely predicted HONO mixing ratios. An increase in OH occurs along highways corresponding to increased HONO mobile emissions. Doubling HONO emissions resulted in up to 6\% of OH increase. The impact of increasing HONO emissions on ozone mixing ratios is smaller. For example, for 13 September, the maximum change in ozone is 0.45 ppbv at 11 a.m. LT, the impact of increased HONO emissions on the afternoon peak ozone value is even smaller, at the 1 ppt level (not shown). Since NO\textsubscript{x} and HONO mixing ratios peak in the morning; therefore, it is understandable that the impact of HONO on ozone is higher during morning time than afternoon hours.
4 Summary

The WRF-SMOKE-CMAQ modeling system was used for evaluation and adjustment of NO\textsubscript{x} emissions. In particular, effects of applying increased HONO/NO\textsubscript{x} emission ratio from mobile sources on HONO mixing ratios were evaluated.

First, NO\textsubscript{x} emissions were adjusted to reflect emission trends. Simulations with adjusted NO\textsubscript{x} emissions resulted in overall better NO\textsubscript{x} prediction as mixing ratios become closer to measured values. The average NO\textsubscript{x} mean value from all analyzed sites dropped from 11.11 to 7.59 ppbv and is much closer to the observed mean of 7.76 ppbv, IOA is improved in the reduced NO\textsubscript{x} case (0.71 vs. 0.75) and the AME is lowered from 6.76 to 4.94. Therefore, the reduced NO\textsubscript{x} case was taken as a base for adjusting HONO emissions according to values measured in Houston.

Doubling HONO emission from mobile sources and therefore making them closer to the newly reported HONO/NO\textsubscript{x} ratio of 0.017 resulted in increased HONO mixing ratios especially during morning peak values. Simulated HONO mixing ratios were compared to values measured at the Moody Tower. The mean value increased from 0.30 ppbv in the base HONO emission case to 0.41 ppbv in the increased HONO emission case and become closer to the observed mean of 0.69, but still low. The index of agreement for simulation that used the 2001 HONO/NO\textsubscript{x} emission ratio of 0.008 is 0.63 while for the simulation with doubled HONO emissions IOA increased to 0.70. Increased HONO emissions from mobile sources resulted in up to 6\% increase in OH. The impact on ozone is marginal.

This study results could shed light on the underestimated HONO and OH in the morning from global/regional chemical transport model with the typical emission ratio of 0.8\% HONO emission out of the total NO\textsubscript{x} emissions.

Acknowledgements. The authors would like to thank the Texas Air Research Center (TARC) for supporting this work. They are also thankful to Lijun Diao for help in setting up WRF and to Hyuncheol Kim for helping with CAMS dataset.
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Impact of updated traffic emissions on HONO mixing ratios

B. H. Czader et al.

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Table 1. EPA emission trends for NO\textsubscript{x}.

| NO\textsubscript{x} | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 |
|---------------------|------|------|------|------|------|------|
| mobile              | 6941 | 6241 | 5734 | 5786 | 5398 | 5010 |
| other               | 9872 | 9540 | 9144 | 8594 | 8114 | 7914 |
| total               | 16 813 | 15 781 | 14 878 | 14 380 | 13 512 | 12 924 |
**Table 2.** Summary of statistical parameters for the base case simulation (B) and the reduced NO\textsubscript{x} case (N).

| Site | No. of points | Obs. | Sim. B | Sim. N | Mean | R | AME | Sim. B | Sim. N | IOA | Sim. B | Sim. N |
|------|---------------|------|--------|--------|------|---|-----|--------|--------|-----|--------|--------|
| 1    | 700           | 15.60| 18.95  | 12.41  | 0.44 | 0.45 | 10.52| 8.18   | 0.62 | 0.58 |
| 2    | 695           | 6.34 | 9.13   | 5.42   | 0.49 | 0.54 | 5.39 | 3.62   | 0.54 | 0.70 |
| 8    | 699           | 9.93 | 11.89  | 8.24   | 0.73 | 0.76 | 5.45 | 4.53   | 0.83 | 0.84 |
| 9    | 699           | 5.50 | 10.02  | 6.54   | 0.60 | 0.59 | 5.66 | 3.74   | 0.66 | 0.74 |
| 15   | 668           | 10.48| 12.98  | 7.92   | 0.42 | 0.44 | 8.20 | 6.26   | 0.61 | 0.56 |
| 26   | 697           | 5.61 | 12.58  | 9.58   | 0.52 | 0.56 | 7.96 | 5.45   | 0.47 | 0.61 |
| 35   | 649           | 6.63 | 10.33  | 6.95   | 0.67 | 0.64 | 5.87 | 3.93   | 0.72 | 0.79 |
| 45   | 699           | 3.83 | 4.87   | 3.45   | 0.60 | 0.52 | 2.94 | 2.42   | 0.72 | 0.70 |
| 53   | 684           | 7.69 | 11.56  | 8.80   | 0.76 | 0.77 | 5.74 | 4.28   | 0.82 | 0.87 |
| 64   | 690           | 4.01 | 2.51   | 1.91   | 0.44 | 0.54 | 2.72 | 2.57   | 0.61 | 0.57 |
| 78   | 617           | 3.29 | 10.45  | 7.56   | 0.54 | 0.55 | 7.66 | 5.01   | 0.41 | 0.54 |
| 84   | 533           | 4.34 | 9.08   | 6.88   | 0.69 | 0.70 | 5.57 | 3.82   | 0.68 | 0.78 |
| 114  | 708           | 13.94| 20.87  | 13.79  | 0.48 | 0.50 | 11.44| 7.54   | 0.62 | 0.68 |
| 311  | 635           | 4.58 | 6.75   | 4.92   | 0.52 | 0.58 | 3.74 | 2.70   | 0.66 | 0.75 |
| 403  | 696           | 14.87| 27.20  | 20.08  | 0.40 | 0.42 | 16.40| 11.83  | 0.54 | 0.61 |
| 408  | 703           | 15.17| 12.01  | 8.90   | 0.55 | 0.59 | 7.08 | 7.74   | 0.67 | 0.61 |
| 411  | 692           | 16.57| 22.24  | 15.81  | 0.59 | 0.60 | 10.59| 7.87   | 0.69 | 0.76 |
| 416  | 702           | 13.95| 28.35  | 19.43  | 0.71 | 0.71 | 16.39| 9.29   | 0.69 | 0.81 |
| 617  | 705           | 6.20 | 7.42   | 4.93   | 0.50 | 0.48 | 4.50 | 3.61   | 0.64 | 0.68 |
| 618  | 697           | 2.90 | 3.15   | 1.80   | 0.58 | 0.61 | 1.62 | 1.42   | 0.71 | 0.71 |
| 619  | 559           | 3.04 | 2.38   | 1.67   | 0.38 | 0.48 | 2.34 | 2.01   | 0.58 | 0.58 |
| 620  | 399           | 7.05 | 7.66   | 4.86   | 0.37 | 0.36 | 6.74 | 5.67   | 0.57 | 0.49 |
| 640  | 675           | 2.14 | 1.57   | 1.10   | 0.26 | 0.30 | 1.50 | 1.36   | 0.47 | 0.47 |
| 643  | 671           | 6.30 | 1.82   | 1.35   | 0.21 | 0.24 | 4.97 | 5.15   | 0.46 | 0.44 |
| 1015 | 703           | 13.44| 12.33  | 8.75   | 0.43 | 0.44 | 8.95 | 8.65   | 0.62 | 0.56 |
| 1016 | 608           | 2.25 | 5.18   | 3.73   | 0.40 | 0.40 | 3.55 | 2.50   | 0.48 | 0.57 |
| 1034 | 641           | 2.23 | 1.58   | 1.38   | 0.45 | 0.47 | 1.43 | 1.39   | 0.63 | 0.60 |
| 1035 | 692           | 4.45 | 7.91   | 5.12   | 0.53 | 0.55 | 4.49 | 2.96   | 0.64 | 0.74 |
| 1628 | 630           | 5.91 | 13.64  | 5.09   | 0.43 | 0.50 | 8.39 | 2.98   | 0.42 | 0.69 |
| MT   | 703           | 9.93 | 20.53  | 14.59  | 0.64 | 0.64 | 12.46| 8.02   | 0.63 | 0.74 |

| ALL  | 19849         | 7.76 | 11.11  | 7.59   | 0.58 | 0.59 | 6.76 | 4.94   | 0.71 | 0.75 |
Table 3. Statistical parameters for modeling HONO mixing ratios for the Moody Tower site.

| Statistics                        | HONO          |
|-----------------------------------|---------------|
| Number of points                  | 200           |
| Mean                              |               |
| Observed                          | 0.69          |
| Sim. Red. NO\textsubscript{x}     | 0.30          |
| Sim. H                            | 0.41          |
| Max. value                        |               |
| Observed                          | 3.15          |
| Sim. Red. NO\textsubscript{x}     | 2.62          |
| Sim. H                            | 2.93          |
| Correlation coefficient           |               |
| Sim. Red. NO\textsubscript{x}     | 0.58          |
| Sim. H                            | 0.57          |
| Mean Bias                         |               |
| Sim. Red. NO\textsubscript{x}     | −0.39         |
| Sim. H                            | −0.28         |
| Absolute Mean Error               |               |
| Sim. Red. NO\textsubscript{x}     | 0.46          |
| Sim. H                            | 0.43          |
| Index of agreement                |               |
| Sim. Red. NO\textsubscript{x}     | 0.63          |
| Sim. H                            | 0.70          |
Figure 1. Locations of stations performing NO\textsubscript{x} measurements in the Houston-Galveston-Brazoria area during September 2013.
Figure 2. Timeseries comparing measured NO\textsubscript{x} against values simulated with the base case and the reduced NO\textsubscript{x} case at CAMS sites 1 and 411.
Figure 3. NO and NO$_2$ mixing ratio measured at the Moody Tower site and modeled with the base case emissions as well as with reduced NO$_x$ emissions.
Figure 4. Difference in HONO emissions between increased HONO case (NH) and default HONO emissions (N).
Figure 5. Differences in HONO mixing ratios between the increased HONO emission case (NH) and the base HONO emissions (N) for the surface (left) and the second model layer (right).
Figure 6. HONO mixing ratios measured at the Moody Tower site and modeled with regular HONO emissions (N), for which the HONO/NO$_x$ emission ratio of 0.008 was used, and the increased HONO case (NH), for which the HONO/NO$_x$ emission ratio of 0.016 was used.
Figure 7. OH mixing ratios (left) and differences in OH mixing ratios between the base case and increased HONO emission case (right).