CMAQ modeling and analysis of radicals, radical precursors, and chemical transformations

Beata H. Czader,¹ Xiangshang Li,¹ and Bernhard Rappenglueck¹

Received 7 May 2013; revised 28 July 2013; accepted 30 August 2013; published 4 October 2013.

[1] Air quality simulations were performed for the Houston-Galveston-Brazoria area for springtime conditions in May and June of 2009. Meteorological parameters predicted by Weather Research and Forecasting (WRF) model, for which data assimilation with recursive objective analysis was performed, are well simulated most of the time. The Community Multiscale Air Quality (CMAQ) model driven by meteorology from WRF simulates ozone and many other trace species, including radical precursors such as HCHO and HONO, with a satisfactory agreement with observations. While CMAQ satisfactorily captures the daily variations of the OH radical, it sometimes underestimates its high daytime values. Concentrations of HO₂ are often underpredicted in polluted air masses and persistently severely underpredicted at low NOₓ conditions, when the Houston air is affected by marine air masses. In contrast, concentrations of H₂O₂ and CH₃OOH are almost always overpredicted by the model, the overprediction occurs frequently in the polluted air and occurs always when marine air is encountered. Those mispredictions are consistent despite day-to-day variations in meteorological conditions and emissions and bring into question current representation of radical-related chemistry in the model as radical production and recirculation in the model is overtaken by termination processes and creation of more stable compounds, such as H₂O₂ and CH₃OOH. Smaller model biases of H₂O₂ and peroxides are associated with lower humidity. The relative importance of various photolysis processes as radical sources in the Houston atmosphere was also elucidated. Morning HO₂ formation is dominated by HONO while ozone contributes the most during midday. HONO contribution to HO₂ formation is more pronounced at the surface layer where most of it is formed, radical production from ozone is more important at elevated levels where higher concentrations of ozone are observed. Formaldehyde contributes up to 40% and also peaks during midday, but on days when high morning concentrations of formaldehyde are observed, its contribution to HO₂ in the morning exceeds that of ozone. Photolysis of H₂O₂ is a minor contributor to radical levels.


I. Introduction

[2] Over the last decade, several comprehensive air quality field studies in Houston, Texas, including the Texas Air Quality Study 2000 (TexAQS-2000) [e.g., Ryerson et al., 2003; Daum et al., 2004; Banta et al., 2005, and references therein] in summer 2000, the Second Texas Air Quality Study (TexAQS-II) [Parrish et al., 2009], and the TexAQS-II Radical and Aerosol Measurement Project (TRAMP) [Lefer and Rappenglück, 2010; Olaguer et al., 2009] in summer 2006, and more recently the Study of Houston Atmospheric Radical Precursors (SHARP) [Olaguer et al., 2013] in spring 2009 have focused on this city’s complex air quality.

[3] The significant presence of petrochemical facilities and power plants in southeast Texas (SETX) [Daum et al., 2003; Ryerson et al., 2003; Daum et al., 2004] as well as complex meteorological conditions including large-scale dynamics [Ngan and Byun, 2011], land-sea breeze conditions [e.g., Banta et al., 2005; Day et al., 2010], wind field and boundary layer depth [Darby, 2005; Banta et al., 2011], and frontal passages [Rappenglück et al., 2008; Ngan and Byun, 2011] make it a hotbed for air pollution in the region and a challenge for air quality modeling [Ngan et al., 2012].

[4] Photochemical modeling of ozone formation in the Houston area generally underestimates the concentrations of free radical precursors contributing to ozone formation [Byun et al., 2007; Olaguer et al., 2009; Osthoff et al., 2008; Osthoff et al., 2009; Simon et al., 2009a, 2009b; Mao et al., 2010; Ziemba et al., 2010]. There are unresolved questions about the quantitative contribution of direct emissions and atmospheric reaction products to the formation of compounds...
that contribute to the free radical chemistry [Vogel et al., 2003; Stutz et al., 2004; Volkamer et al., 2007; Li et al., 2008; Elshorbany et al., 2009; Li et al., 2010; Thornton et al., 2010], including producing Houston’s high ozone [Dasgupta et al., 2005; Olaguer et al., 2009; Chen et al., 2010; Rappenglück et al., 2010; Buzzi-Guven and Olaguer, 2011].

One of the major goals of TRAMP and SHARP was to analyze radical sources and sinks (and production and loss rates), in order to evaluate their impact on the formation of secondary products and to validate and refine air quality modeling. These efforts were largely supported by a unique suite of measurements implemented at the Moody Tower site on the campus of the University of Houston [29°43.50′N, −95°20.28.50′W; 65 m above ground level (agl)], which included in situ measurements of hydroxyl radicals (HO•), including producing hydrogen peroxide (H2O2), methyl hydroperoxide (HONO), and formaldehyde (HCHO) as well as compounds and several radical precursors. These include nitrous acid (HNO2), nitric acid (HNO3) [Lefer and Rappenglück, 2010; Olaguer et al., 2013] which, due to their high solubility, will ultimately remove hydrocarbon- and nitrogen-containing compounds from the atmosphere.

Using this data set, a variety of box modeling studies were performed to describe radical chemistry [Chen et al., 2010; Mao et al., 2010; Ren et al., 2013; Wong et al., 2011; Wong et al., 2012]. Czader et al. [2012] applied a three-dimensional air quality model, CMAQ (Community Multiscale Air Quality), coupled to MM5 (Mesoscale Model, version 5) and with an enhanced HONO module to analyze the impact of HONO on ozone and hydroxyl radical and validated the results against TRAMP data.

As air quality is strongly influenced by the day-to-day weather conditions, accurate meteorological simulation is the foundation for reliable air quality modeling [e.g., Ngan et al., 2012]. In this work we show results of meteorological and photochemical grid modeling for the SHARP period, and the performance of the models, with special emphasis upon in situ Moody Tower measurements to assess how well-modeled representations of radical precursors, radicals, and terminal removal compounds are represented in the model. In addition, we quantify OH sources for selected and well-modeled high ozone days during the SHARP period using the Integrated Reaction Rate approach (IRR) in CMAQ. In a sensitivity study, we calculate chemical transformation processes for HCHO along a backward trajectory passing the highly polluted Houston Ship Channel and ending at the Moody Tower site to elucidate potential sources for this radical precursor.

2. Model Setup

The three-dimensional Community Multiscale Air Quality (CMAQ) model [Byun and Schere, 2006] version 4.7.1 and the Weather Research and Forecasting (WRF) model version 3.2.1 [Skamarock et al., 2008] were utilized in this study. For our air quality modeling study targeting the Houston area, we switched the meteorological model from Fifth-Generation PSU/NCAR Mesoscale Model (MM5) used in previous studies [Czader et al., 2012; Ngan et al., 2012] to WRF due to several advantages of WRF, such as better mass conservation and better resolution in numerical schemes. The following modeling configuration is adopted based on our past experiences: the Statewide Air Pollution Research Center-99 (SAPRC-99) chemical mechanism [Carter, 1990, 2000] including aerosols and aqueous chemistry, the Asymmetric Convective Method 2 (ACM2) for vertical diffusion and cloud treatment, 23 vertical layers between the surface and 50 mbar (around 20 km height) model top. The lowest layer near the surface has a thickness around 34 m. This CMAQ version takes into account heterogeneous HONO formation on urban and leaf surfaces [Foley et al., 2010]. Simulations were performed for the 4 May–6 June 2009 period that coincides with the SHARP campaign. Two days spin-up time was used to obtain realistic initial conditions. WRF and CMAQ simulations were carried out for three nested domains with grid resolutions of 36, 12, and 4 km, respectively. The largest 36 km domain spans across the continental United States while the 12 km domain covers the south central region of the U.S. Simulation results from 12 km domain were used to obtain meteorological and chemical boundary conditions for the 4 km domain. The domain of interest for analysis covers Houston-Galveston-Brazoria counties and has a 4 km grid resolution (see Figure 1).

Within CMAQ, the integrated process rate (IPR) analysis was carried out to track contributions of chemical and transport processes to pollutant mixing ratios. In addition, the integrated reaction rate (IRR) analysis was employed to investigate chemical sources and losses of pollutants as well as their impact on radical and ozone formation.

Meteorological data were simulated with WRF v3.2.1. For model input we utilized the North American Mesoscale (NAM) analysis data (DS609.2 GCIP-Eta) from the National Center for Atmospheric Research (NCAR). NAM data have a resolution of 40 km with output every 6 h. For terrain and Land Use/Land Cover (LU/LC), we used the standard USGS (United State Geological Survey) 24 category data. Besides the standard grid nudging for data assimilation with downloaded NAM data, we also utilized the University of Houston-Real Time Data Assimilation System (UH-RTDAS) for objective analysis [Byun et al., 2008]. UH-RTDAS has two prominent features: the adoption of a comprehensive observational data set from the Meteorological Assimilation Data Ingest System (MADIS) and the Continuous Ambient Monitoring Stations (CMS) system, operated by the Texas Commission on Environmental Quality (TCEQ); and a recursive objective analysis process ingesting observations at all nested domains [see also Ngan et al., 2012]. It has been widely accepted that data assimilation is very effective in improving meteorological simulations, and the effectiveness is related to the amount and coverage of the available meteorological observations.

Emissions were derived with Sparse Matrix Operator Kernel Emissions (SMOKE) system [Houyoux et al., 2000] using the National Emission Inventory (NEI) and the Texas inventory (TEI). NEI for the year 2002 was applied for the largest domain (36 km resolution). It was also used for 12 and 4 km resolution nested domains for areas not covered by the Texas inventory. In addition, NEI provided emissions of particulate matter for all three domains. The Texas inventory utilized in this work included: Ozone Season Day (OSD) and hourly emissions for 2006 baseline point source inventory, the Base5b 2007 area and nonroad emissions, 2006 biogenic emissions normalized to 2009 meteorological conditions, and mobile emissions derived from “linked based” and the High Performance Monitoring System (HPMS) data (available at:
ftp://ftp.tceq.state.tx.us/pub/OEPAA/TAD/Modeling/HGB8H2/ ei06). In addition, HONO emissions were derived from on-road and off-road NO\textsubscript{x} sources based on the emission ratio HONO/NO\textsubscript{x} = 8 \times 10^{-3} by Kurtenbach et al. [2001].

### 3. WRF Simulation Results and Comparison With Observations

[12] Overall the 4 May–6 June 2009 period was characterized by dry weather conditions and predominantly southerly winds. There were four fronts, with cooler temperatures and rain passing through the Houston area on the following dates: 3, 16, 28 May, and 4 June.

[13] The comparison of regional average daily surface temperature for the entire simulation period resulted in a Pearson correlation coefficient of \( r = 0.91 \) based on about 38,000 hourly data points. The model has an overall bias of \(-0.3^\circ\text{C}\) with all of the days less than \(1^\circ\text{C}\). The low bias indicated excellent energy budget in the model. The overall and daily model standard deviations are also very close to the observed ones—meaning the model well captures the temperature variation magnitude in the region. Hourly winds at the local scale are hard to predict by meteorological models,
including WRF. The performance of the model also greatly depends on the quality of input analysis data. The evaluation of simulated parameters in the 4 km domain is based on observed data obtained from the CAMS system. This system comprises 55 stations reporting wind and temperature data during the evaluation period. As a reference, the 4 km CMAQ domain has a grid size of 83 × 65, totaling 5395 cells, which would result in about one station per 100 cells. All the evaluations are based on “exact match” comparison in which the observation is compared to the model value of the grid cell that exactly matches the observation location. Overall, the model performed well in simulating the winds with a Pearson correlation coefficient of 0.71 and 0.9, for the horizontal wind components U and V, respectively. Additional evaluation was performed for the Moody Tower super site where meteorological as well as chemical parameters were also measured. Figure 2 shows time series comparison of modeled and observed wind direction (WD), wind speed (WS), at the Moody Tower location, and the planetary boundary layer (PBL) height measured from the surface about 500 m North of the Moody Tower using remote sensing techniques [Haman et al., 2012]. The objective analysis significantly improved WRF model performance for days when the simulated wind fields are notably different from the observations. Overall, wind speed and directions are properly predicted. For most of the days, for which measured PBL data are available, WRF predicted the PBL height well. There are 3 days when the PBL height is underpredicted, such as on pre- and post-frontal days on 16 and 18 May, respectively, and on 21 May. Also, on several occasions, modeled PBL rises a couple of hours earlier compared to measured PBL. Temperature time series are very well predicted by WRF. There were a couple of

<table>
<thead>
<tr>
<th>Date</th>
<th>N</th>
<th>R</th>
<th>IOA</th>
<th>RMSE</th>
<th>MAE</th>
<th>MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>All days</td>
<td>38,413</td>
<td>0.81</td>
<td>0.88</td>
<td>12.9</td>
<td>10</td>
<td>5.8</td>
</tr>
<tr>
<td>5/19/2009</td>
<td>1,126</td>
<td>0.83</td>
<td>0.91</td>
<td>10.9</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>5/20/2009</td>
<td>1,086</td>
<td>0.85</td>
<td>0.92</td>
<td>12.7</td>
<td>9.4</td>
<td>1.9</td>
</tr>
<tr>
<td>5/30/2009</td>
<td>1,094</td>
<td>0.83</td>
<td>0.91</td>
<td>16.5</td>
<td>13</td>
<td>2.9</td>
</tr>
<tr>
<td>5/31/2009</td>
<td>1,128</td>
<td>0.77</td>
<td>0.74</td>
<td>20.8</td>
<td>17.5</td>
<td>16</td>
</tr>
<tr>
<td>6/5/2009</td>
<td>1,170</td>
<td>0.83</td>
<td>0.87</td>
<td>13.8</td>
<td>11.4</td>
<td>8.2</td>
</tr>
<tr>
<td>6/6/2009</td>
<td>1,131</td>
<td>0.84</td>
<td>0.87</td>
<td>18.5</td>
<td>14.8</td>
<td>11.6</td>
</tr>
</tbody>
</table>

N – number of data points; R – Pearson correlation coefficient; IOA – index of agreement; RMSE – root mean square error; MAE – mean absolute error; MB – mean bias. Dates are formatted as month/day/year.

Table 1. Model Performance Evaluation for Ozone Against CAMS Data

Figure 3. (left) Spatial distribution of ozone from 4 km resolution model output overlaid with measured values (dots) for 20, 30 May, and 6 June; (right) Wind comparison between modeled (blue) and measured (red) values.
4.1. Ozone, CO, and NOx

With Observations

4. CMAQ Simulation Results and Comparison With Observations

4.1. Ozone, CO, and NOx

The model performance for predicting ozone was evaluated by comparing modeled concentrations with observations at several surface CAMS sites in the Houston-Galveston-Brazoria area. In addition, we have utilized the measurements taken at the Moody Tower super site and evaluated the model for a suite of primary and secondary trace gases, including radicals and radical precursors.

Table 1 lists statistical parameters calculated from hourly observed and modeled ozone concentrations at CAMS locations in the Houston-Galveston-Brazoria area for all modeling days as well as separately for each day for which detailed analysis of results was performed and presented below. Overall, the simulated ozone values are in a good agreement with the observed ones. The average correlation coefficient \( r \) for all days is 0.81, and ranges for individual days from 0.61 to 0.91, with the exception of 8 and 17 May for which the correlation coefficient is 0.46 and 0.48, respectively. The mean bias ranges from −4.7 to 16.4. The mean bias is high on 1, 2, and 6 June and much lower on all other simulated days.

Figure 3 shows snapshots of simulated and measured ozone and winds on high ozone days, i.e., 20, 30 May, and 6 June 2009. Figure 3, left shows spatial distribution of simulated ozone concentrations overlaid with ozone measured values (dots) at the time of maximum measured ozone concentration. Figure 3, right shows modeled and measured wind. Ozone plumes on those high ozone days are properly predicted in the region by the CMAQ model. On all of these three high ozone days, prevailing light east wind occurred in the early morning hours. However, slight differences in wind speed and direction, along with different wind shift in noon to afternoon hours on these 3 days resulted in the difference in the locations with high ozone. This phenomenon is typical for the formation of high ozone in Houston as the east winds in the morning bring highly reactive hydrocarbons from the Houston Ship Channel area, located east of Houston, to the Houston downtown area, where these air masses will mix with NOx emissions from mobile sources.

Figure 4 shows time series of several trace gases, including CO, O3, and NO2 at the Moody Tower. The data measured at the Moody Tower are 10 min averages; therefore, for the purpose of comparison of modeled and measured values, CMAQ concentrations were interpolated from hourly values to 10 min intervals, with the exception of ethene that already had 1 h resolution. Two dominant periods can be specified based on the prevailing winds and correspondingly different background levels for many pollutants. The first period spans from 5 to 16 May and is characterized by southerly winds that brought air from the Gulf of Mexico to the Houston area. This time period is characterized by low values of CO, O3, and NOx. After a cold front passage on 16 May, the wind direction changes (see Figure 2), and during the second time period, the dominant winds are north-easterly bringing continental air to Houston and causing air masses to pass through the industrial area with its high emissions before reaching the Moody Tower. Much higher mixing ratios of CO, NOx, and consequently O3 were observed during that period. The modeling results for CO, NOx, and O3 reflect the observed low values during the first time period and the higher values during the second time period, respectively.

In general, CMAQ captures daily variations of CO and its background concentrations well. The correlation coefficient \( r \) based on all values from the simulated days is 0.63. As CO
is reacting slowly in the atmosphere, it is well suited to be used as a tracer in transport studies, which has also been shown for the Houston case [e.g., McMillan et al., 2010]; it can also be used in tracking variations of the PBL height [e.g., Newman et al., 2013], reasonable performance of CMAQ predictions of CO gives us additional confidence that transport mechanisms are sufficiently well described in our modeling study for SHARP. In a few cases, though, CMAQ overpredicts maximum CO values. The largest overprediction occurs during nighttimes on 24, 25 May and 29, 30 May and can be linked to an underestimation of the nighttime PBL height (see Figure 2). A possible reason of overprediction of morning CO peaks on 14–16 May may also be misprediction of the PBL. However, since PBL measurements at these times are not available, this hypothesis cannot be verified. The modeled low CO values on 5–12 May may be linked to low CO background values at the southern boundary as average CO concentration at southern boundary is 70 ppb. Ozone and NO$_2$ are well simulated at the Moody Tower, both in terms of magnitude and diurnal variations, with correlation coefficient ($r$) of 0.80 for ozone and 0.64 for NO$_2$. Since the measurements at the Moody Tower were taken at 60 m height above ground level, which corresponds to the second model layer, the effect of direct surface emissions and their uncertainties is less important as pollutants are subject to vertical mixing at this height and the horizontal footprint becomes larger. A similar CMAQ modeling for the same period for the Clinton Drive site, which is surface site close to mobile and industrial emission sources, showed somewhat poorer performance ($r=0.60$ for carbon monoxide, $r=0.81$ for ozone, and $r=0.50$ for NO$_x$) as some major excursions in ambient concentration levels could not be resolved properly by the model any longer (see Figure S1 in the supporting information).

Based on good CMAQ results for the major primary (NO$_x$) and the most important secondary species (O$_3$), the Moody Tower could be regarded as an ideal test bed for modeling radicals, radical precursors, and also loss mechanisms in photochemical processes.

### 4.2. Radical Precursors

While in the past air quality models used to underpredict HONO concentrations, incorporation of formation of HONO from surface hydrolysis of NO$_2$ into CMAQ resulted in significant improvement of CMAQ predictions of HONO [Sarwar et al., 2008; Czader et al., 2012]. HONO modeling results for the 2009 episode shows that not only morning peaks are well predicted by the model but also its daytime values (Figure 5).

![Figure 5](image5.png)

**Figure 5.** Time series of measured and CMAQ-simulated mixing ratios of HONO and NO$_2$ at the Moody Tower for 4 May–6 June 2009. Black dots correspond to measured values, and the red solid line to simulated ones.

![Figure 6](image6.png)

**Figure 6.** Time series of measured and CMAQ-simulated concentrations of HCHO and ethene at the Moody Tower for 4 May–6 June 2009. Black dots correspond to measured values, and the red solid line to simulated ones.
Slight overprediction of HONO morning peak concentrations on several days, such as on 20 and 22 May, can be linked to the overprediction of NO2 as it is the most significant HONO precursor [Czader et al., 2012].

Among many volatile organic compounds (VOCs) included in SAPRC99 chemical mechanism in CMAQ, only several are represented explicitly and their concentrations can be directly compared with measured values. Among them are formaldehyde and ethene as presented in Figure 6. Most of the time, formaldehyde is well predicted at the Moody Tower. Similarly, ethene diurnal variations and magnitude are also well predicted at the Moody Tower, except on 20, 22 May, and 4 June when its concentrations are underpredicted. In addition, at the Clinton Drive site that is in close proximity to industrial facilities and directly exposed to their emissions, CMAQ predicted ethene and formaldehyde concentrations are in good agreement with the observed values (see Figure S2 in the supporting information). Only on several occasions, CMAQ slightly underestimated morning peaks of formaldehyde. Comparing to CMAQ studies for earlier years, e.g., for the TexAQS 2000 campaign [Byun et al., 2007; Czader et al., 2008], no extra olefin emissions were employed to achieve those results.

4.3. Radicals

Among radicals, we compared modeling results with measured values for the hydroxyl radical (OH) and the hydroperoxy radical (HO2) (see Figure 7). Contrary to other species like CO, O3, and NO_x (Figure 4) radicals do not necessarily follow the pattern of low values during the first half of the month of May and higher values during the last part of the study period. For example, HO2 mixing ratios are higher in the low NO_x marine air mixture at the beginning of the month, when midday maxima reach 40 ppt, than at high NO_x conditions occurring in the second half of the month, when daytime HO2 peaks are in the range of 10–45 ppt. While daily variations of OH are well predicted by CMAQ, on several occasions, CMAQ slightly underestimated morning peaks of formaldehyde. Comparing to CMAQ studies for earlier years, e.g., for the TexAQS 2000 campaign [Byun et al., 2007; Czader et al., 2008], no extra olefin emissions were employed to achieve those results.

Figure 7. Time series of measured and CMAQ-simulated mixing ratios of radicals at the Moody Tower for 4 May–6 June 2009. Black dots correspond to measured values, and the red solid line to simulated ones.
occasions, high daytime OH peaks are underpredicted. For example, on 20 May, the measured peak of OH is 0.91 ppt while the modeled one is 0.57 ppt. That underprediction can be linked to underestimation of ethene and formaldehyde concentrations on that day. Nighttime values are underpredicted most of the time, similar to results obtained by Chen et al. [2010] for summer 2006. This may hint to some underrepresented nighttime OH sources in the model. Likely chemical processes include reactions of NO3 with alkanes and O3 with alkenes. The observed-to-modeled ratio for OH is 1.15 for the 5–16 May time period and 1.36 for 17–31 May. The model severely underpredicts HO2 midday maxima during the first half of May when humid and clean marine air was brought to Houston. The HO2 observed-to-model ratio for this time period is 2.66. HO2 values are much better predicted during the second half of the month in polluted continental air with the observed-to-model ratio of 1.52. The observed-to-model ratio of HO2/NO is 2.32 for low NO3 conditions on 5–16 May and 1.11 for high NO3 conditions on 17–31 May. Large discrepancies between modeled and measured HO2/NO ratios during the first time period suggest uncertainties in the model chemistry representation at low NO3 concentrations in marine air masses.

4.4. Loss Mechanisms

[21] Important terminal loss mechanisms in the NO3-VOC system is the formation of hydrogen peroxide (H2O2) and methyl hydroperoxide (CH3OOH) for the VOC compartment and the formation of nitric acid (HNO3) for the NO3 compartment. These compounds are soluble and will eventually be removed from the atmosphere by wet deposition. Figure 8 shows comparison of modeled concentrations of these compounds with observed values at the Moody Tower. Both hydrogen peroxide and methyl hydroperoxide are overpredicted most of the time by CMAQ. This overprediction is severe during the first half of the month when marine air is encountered and NOx sources are limited. Under limited NOx conditions, HO2 + NO2 reaction leads to H2O2 formation as opposite to high NOx regime when HO2 reacts with NO to form HNO3. The fact that the model overpredicts H2O2 and at the same time underpredicts HO2 suggests that radical production and recirculation in the model may be terminated too early in favor of creation of more stable H2O2. The modeled concentrations of H2O2 seem to correlate with water mixing ratios. For example, on 17 and 18 May, the modeled concentrations of H2O2 are lower than at any other simulated day and become much closer to the observed values. On those 2 days, water mixing ratios (not shown) are lower (0.006–0.008) than on most other days (0.014–0.018). Also, the cloud fraction and consequently liquid water content of cloud is zero on 18–20 May indicating clear sky conditions. Smaller model biases for H2O2 associated with no cloud conditions suggest that loss process related to H2O2 scavenging in cloud and precipitation may not be properly accounted for in the model and need to be reevaluated.

[24] HONO, on the other hand, is overall well predicted in unpolluted marine air mass conditions; however, this compound is underpredicted under more polluted conditions in the later period of the field campaign. The results show that CMAQ generally overpredicts significantly loss mechanisms in the VOC compartment, whereas underpredicts loss mechanisms for the NO3 compartment under polluted conditions only.

5. Photolytic Radical Sources

[25] An Integrated Reaction Rate (IRR) analysis was employed to obtain details on chemical transformations in CMAQ including photolysis reactions leading to a production of new radicals. Based on the model performance and high ozone peak events on 19–20 May (weekday), 30–31 May (weekend), and 5–6 June 2009 (Friday/Saturday), a detailed analysis of radical formed from photolytic reactions was performed for those days. The modeled OH matches observed values on 19 and 29 May, and is lower than observed on 20 May. HO2 is well predicted on 19 May, and slightly underpredicted on 20 and 30 May. No measured values are available for 31 May and 5 and 6 June.

[26] Figure 9 shows relative contributions of O3, HONO, HCHO, and H2O2 to HOx (HOx = OH + HO2) production (ppb/h) at the Moody Tower (nighttime sources from reactions of O3 and NO3 are not considered). The data were vertically averaged (accounting for the layer height) from surface up to the modeled PBL height; therefore, different number of layers was taken for averaging at different hours following the growth of PBL. The modeled PBL height nicely followed measured height on 19, 20, 30, and 31 May (see Figure 2), but no PBL measurements are available for 5 and 6 June. Horizontally, data were averaged from nine model grid cells with a cell corresponding to the location of the Moody Tower being in the middle.

[27] In the morning, HONO is a major source of HOx radicals. The magnitude of HONO contribution to HOx depends on its morning concentrations with the highest contribution obtained on 30 May, when the highest HONO concentration
occurred during the SHARP campaign. On that day, very stagnant conditions in the morning caused accumulation of HONO. On other days of interest, even though the HO\textsubscript{x} formation from HONO is lower, HONO continues to be a major HO\textsubscript{x} source during morning hours (between 7:00 and 9:00 Central Standard Time, CST). This is even more pronounced when considering surface layer only (not shown) since HONO is produced and emitted mainly at the surface, and its concentration shows vertical gradient with high values occurring at the lowest layer. Also, midday contributions of HONO to HO\textsubscript{x} formation are more pronounced when considering the whole mixing layer as opposed to the analysis of the surface layer only. Ozone dominates radical production during a day. Its contribution to HO\textsubscript{x} formation peaks in the afternoon hours when ozone concentrations are high. Ozone contribution is slightly higher when considering the whole mixing layer as opposed to the analysis of the surface layer only. This can be explained by higher concentrations of ozone at elevated altitudes. Formaldehyde contribution steadily increases during morning hours and peaks between noon and 13:00 CST; however, its contribution is lower than contribution from ozone. On 19 and 20 May, CMAQ underpredicted morning formaldehyde concentrations (see Figure 6 for time series of measured and modeled formaldehyde concentrations at the Moody Tower). However, on 30 May, CMAQ accurately predicted morning peak concentration of formaldehyde. On that day, formaldehyde dominates HO\textsubscript{x} production at 9:00 CST, and contributes as much as ozone at 10:00 CST. Even though CMAQ predicts much higher concentrations of H\textsubscript{2}O\textsubscript{2} compared to measured values (see Figure 8 for time series of modeled and measured H\textsubscript{2}O\textsubscript{2} concentrations), photolysis of H\textsubscript{2}O\textsubscript{2} is only a minor contributor to radical budget.

6. Sensitivity to Additional Ethene and Propene

An unusually high ethene peak of 16 ppbv was registered on 20 May at the Moody Tower. High concentrations of propene (6 ppb) and formaldehyde (11 ppb) were also measured. CMAQ underpredicted morning peak of these pollutants on 20 May; therefore, a sensitivity study was performed in which additional emissions were added and their impact on radical sources estimated.

On 20 May, east-northeast (ENE) winds occurred early in the morning, advecting pollutants from the Ship Channel area to the Moody Tower (see Figure 10 for backward trajectories). The high ethene peak observed could have resulted by additional emission releases during nighttime and/or early morning. According to the air emission event report database (available at: http://www11.tceq.texas.gov/oce/eer/index.cfm) an emission event occurred in the Houston region. During that event, propene and other VOC were released from 00:20 to 5:00 A.M. CST in the Channel View area, but no ethene emissions were reported.

To locate a possible additional emission release of ethene, a backward trajectory ending at the Moody Tower was overlaid on ethene emissions as presented in Figure 10. The trajectory starts northeast of Houston on 19 May at 21:00 CST and ends at the Moody Tower at 7:00 CST on the following day. There are several points when the trajectory...
7. Conclusion

We performed a sensitivity study and increased emission rates at the point indicated as “A.” Emission rates of ethene at this cell were increased by adding 4 moles/sec to the third model layer, between 1:00 and 7:00 CST. Murphy and Allen [2005] analyzed the emission event database for the Houston area and pointed to an individual emission event in which up to 12,239 lb/h of ethene was released, while the annual average of ethene event emissions was 740 lb/h. Therefore, 4 moles/s, which is approximately 889 lb/h of ethene is a reasonable magnitude for an emission event. In a separate run, we increased emissions of both ethene and propene (surrogate “OLE1” is used in the model to represent propene) by adding 4 mole/s of each compound.

Figure 11 compares time series of measured concentrations of ethene, OLE1, and formaldehyde with those obtained from the base case simulations and sensitivity cases. Also, measured and modeled PBL height is plotted in each graph. Ethene and propene concentrations at the Moody Tower increased when additional emissions were added (about 10 ppb increase in ethene mixing ratios and about 8 ppb increase in OLE1 mixing ratios). But there was only little effect on formaldehyde concentrations from additional ethene emissions as about 0.5 ppb of additional formaldehyde was obtained. A larger impact on formaldehyde concentrations (2 ppb increase) was obtained from the case when both ethene and propene emissions were added. However, even though ethene and propene concentrations were increased in the model resulting in a closer match with observations, modeled formaldehyde continued to be underpredicted by about 5 ppb. This suggests that additional release of formaldehyde itself might have occurred that is not accounted for in the model. Another reason for model underprediction is related to the PBL height.

Modeled PBL sharply increases between 8:00 and 9:00 CST on 20 May, which is about 2 h earlier than measured values. At this time simulated formaldehyde concentrations drop while measurements show a peak value at 9:00 CST (see Figure 11).

7. Conclusion

We have used WRF-SMOKE-CMAQ system to simulate air quality in the Houston-Galveston-Brazoria area during springtime conditions in May and beginning of June 2009. Meteorological parameters predicted by WRF, for which data assimilation with recursive objective analysis was performed, are well simulated most of the time. CMAQ driven by meteorology from WRF simulates ambient concentrations of ozone and many other trace species well. No extra olefin emissions had to be employed to achieve those results. This is opposite to the simulations for the year 2000 for which a special imputed inventory with additional emissions of highly reactive VOCs had to be employed in order for the model to capture high ozone peaks. A comparison of modeled and observed CO, which has low reactivity toward OH and can be used as a tracer for transport processes, showed good agreement on most simulated days, so that we have sufficient confidence in model prediction of dynamic processes. Misprediction of CO is associated with misprediction of meteorological parameters like wind direction and/or PBL height as well as with low CO values at the southern boundary. Modeled concentrations of radical precursors, such as HCHO and HONO, yield quite satisfactory agreement with observed values. HONO morning peaks are no longer underpredicted, on some occasions, they are slightly overpredicted, which can be linked to overprediction of its direct precursor NO2. While CMAQ satisfactorily captures the daily variations of the OH radical, it sometimes underestimates its high daytime values. Also, it continuously underpredicts nighttime OH values, which may hint to some understated nighttime OH sources in the model. Likely chemical processes include reactions of NO3 with alkanes and O3 with alkenes. However, there still remain significant uncertainties in predicting other radicals and their removal processes. Concentrations of HO2 are often underpredicted in polluted air masses and persistently severely underpredicted at low NOx conditions, when the Houston air is affected by cleaner, marine air masses. In contrast, concentrations of H2O2 and CH3OOH are almost always overpredicted by the model. The overprediction occurs frequently in the polluted air but is severe and persistent when marine air is encountered. Those mispredictions are consistent despite day-to-day variations in meteorological conditions and emissions and bring into question current representation of radical-related chemistry in the model as radical production and recirculation in the model is overtaken by termination processes and creation of more stable compounds, such as H2O2 and CH3OOH. Smaller model biases of H2O2 and peroxides are associated with lower humidity. Even though some of the radicals are significantly underpredicted by the model, the calculated concentration of ozone compares well with observed values. This may as well point to the need of evaluation of chemical mechanism employed for atmospheric simulations.

The WRF-SMOKE-CMAQ system was also used to elucidate the relative importance of various photolysis processes as radical sources in the Houston atmosphere. Morning HOx formation is dominated by HONO while ozone contributes the most during midday. HONO contribution to HOx formation is more pronounced at the surface layer where most of it is formed. On the other hand, radical production from ozone is more important at elevated levels where higher concentrations of ozone are observed. Formaldehyde contributes up to 40% and also peaks during midday, but on days when high morning concentrations of formaldehyde are observed, its contribution to HOx in the morning exceeds that of ozone. Photolysis of H2O2 is a minor contributor to radical levels.

Simulations were performed focusing on high HCHO peak (11 ppb) observed during morning hours at the Moody Tower. While additional ethene and OLE1 emissions were added to match the corresponding observations at the Moody Tower, these additions were only able to produce small increase of about 2 ppb in the HCHO peak. Other, yet unknown, processes may contribute to the morning hour HCHO peak.

Acknowledgments. The authors would like to express their gratitude to Bill Brune (Penn State University), Jack Dibb (University of New Hampshire), Barry Lefer (University of Houston), Tom Jobson (Washington State University), and the Texas Commission on Environmental Quality (TCEQ) for sharing observational data. Support by the Houston Advanced Research Center (HARC) and the TCEQ for supporting and funding this research under grants H100 and 582-S-64594-FY10-15 is greatly appreciated.

References