Chemical characterization of ozone formation in the Houston-Galveston area: A chemical transport model study

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An episodic simulation is conducted to characterize ozone (O₃) formation and to investigate the dependence of O₃ formation on precursors in the Houston-Galveston (HG) area using a regional chemical transport model (CTM). The simulated net photochemical O₃ production rates, \( P(O₃) \), in the Houston area are higher than those in most other U.S. urban cities, reaching 20–40 ppb hr\(^{-1} \) for the daytime ground NO\(_x\) levels of 5–30 ppb. The NO\(_x\) turnaround value (i.e., the NO\(_x\) concentration at which \( P(O₃) \) reaches a maximum) is also larger than those observed in most other U.S. cities. The large abundance and high reactivity of anthropogenic volatile organic compounds (AVOCs) and the coexistence of abundant AVOCs and NO\(_x\) in this area are responsible for the high O₃ production rates and the NO\(_x\) turnaround value. The simulated O₃ production efficiency is typically 3–8 O₃ molecules per NO\(_x\) molecule oxidized during the midday hours. The simulation reveals a RO₂ peak up to 70 ppt at night, and the reactions of alkene-NO₃ and alkene-O₃ are responsible for more than 80% of the nighttime RO₂ in the residual layer, contributing to over 70% and about 10%, respectively. Isoprene accounts for about 40% of the nighttime RO₂ peak concentration. The nighttime RO₂ level is limited by the availability of alkenes. Hydrolysis of N\(_2\)O₅ on sulfate aerosols leads to an increase of HNO₃ by as much as 30–60% but to a decrease of NO\(_x\) by 20–50% during the night in the lower troposphere. Heterogeneous conversion of NO₂ to HONO on the surfaces of soot aerosol accelerates the O₃ production by about 1 hour in the morning and leads to a noticeable increase of 7 ppb on average in the daytime O₃ level. The sensitivity study suggests that the near-surface chemistry over most of the Houston metropolitan area is in or close to the NO\(_x\)-VOC transition regime on the basis of the current emission inventory. Doubling AVOC emissions leads to the NO\(_x\) sensitive chemistry. Biogenic VOCs contribute about 5% on the average to the total near-surface O₃ in the Houston area.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; KEYWORDS: pollution, ozone, modeling


1. Introduction

Air pollution is a persistent and pervasive environmental problem that imposes serious environmental issues and economic costs on the societies in urban cities around the world. Ozone (O₃) is a major secondary photochemical pollutant and the most abundant tropospheric oxidant. In the lower troposphere, O₃ has detrimental effects on human health and ecosystems. Tropospheric O₃ is a critical constituent in the atmosphere. In addition, as a key precursor for the hydroxyl radical OH, ozone is an oxidant controlling the oxidizing capacity of the atmosphere and hence the lifetime of reactive atmospheric pollutants and many reduced chemical species. O₃ is also an important greenhouse gas with strong absorption in the infrared band near 9.6 µm, significantly affecting climatic changes.

Ozone pollution has emerged as a major environmental problem in Texas. For example, Houston has become a
city with one of the most severe O3 pollution problems in the nation [Environmental Protection Agency (EPA), 2000; Kleinman et al., 2002; Daum et al., 2003; Zhang et al., 2004]. High concentrations of ozone violating the 1-hour or the new 8-hour National Ambient Air Quality Standard (NAAQS) were frequently observed over the Houston-Galveston (HG) area during the summer months. The NAAQS for ozone allows no more than 1 exceedance per year (on an average over 3 years) of a daily maximum 1-hour average ozone concentration of 125 ppb by volume during the summer months. The new standard requires that the third highest 8-hour averaged O3 concentration (averaged over 3 years) does not exceed 85 ppb [Chameides et al., 1997]. The average number of O3 nonattainment days in the decade of 1991–2000 is 38 days in the HG area and has remained steady. A number of unusual chemical and meteorological features distinguish the HG area from other urban areas with similar problems. First, this area contains an unusual mix of precursor sources, in addition to the usual mix typical of this region result in large emissions of biogenic VOCs (BVOCs), and anthropogenic NOx from transportation. Houston is one of the largest metropolitan areas in the United States and hosts one of the world largest petrochemical complexes, emitting a great quantity of NOx and highly reactive VOCs (including alkene and aromatics). In addition, the extensive vegetation and warm temperatures that are important in this region result in large emissions of biogenic VOCs (BVOCs). The coexistence of the abundant reactive anthropogenic VOCs (AVOCs), BVOCs, and anthropogenic NOx leads to distinct air chemical features over this area. For instance, data collected during the Texas Air Quality Study (TexAQS) 2000 suggest that the O3 photochemical formation processes are more rapid and more efficient than in other urban areas [Kleinman et al., 2002]. Also, ozone pollution episodes in the HG area are frequently associated with land/sea breeze flow reversal [Nielsen-Gammon, 2000; Allen et al., 2002].

4] Air quality in the HG area has achieved substantial improvement over the past two decades. However, the trend of the improvement has flattened over the past decade despite of continuous effort in the emissions control measures. A significant issue arises: Do we have sufficient scientific understanding of the physical and chemical processes that determine the ozone concentration in order to formulate effective control strategies? O3 formation is a complicated process in which chemistry (including gas-phase chemistry and heterogeneous chemistry), transport, emissions, and deposition interact. Three-dimensional (3-D) chemical transport models (CTMs) are probably the most powerful tool to gain an understanding of these interacting processes and to predict the spatial and temporal distributions of O3 and primary (emitted directly into the atmosphere) and other secondary pollutants, which are essential for evaluation of cost-effective pollutant control strategies. The model is also an ideal tool to synthesize spatially diverse and sporadic chemical measurements into a coherent picture of the air chemical composition. For the O3 formation and budget issues, although several observational results have been published, to date very few results using scientifically oriented CTMs have appeared in the refereed literature for the HG area. In addition, a significant amount of soot particles (~5% of total fine particles) is emitted into the atmosphere in this region. The soot particles potentially play an important role in modulating nighttime NOx and early morning OH concentrations, hence affecting O3. At present, few regional/urban scale air quality models, if any, include soot particle heterogeneous chemistry.

5] Tropospheric radical chemistry is traditionally discussed in terms of the daytime photochemically produced hydroxyl radical. Radicals are also important during nighttime; it is especially true for ozone and the nitrate radical (NO3), which both act as key initiators of the degradation of alkenes, particularly biogenic species, such as isoprene [Suh et al., 2001; Zhang and Zhang, 2002a] and monoterpenes [Götz et al., 2001]. These reactions not only act as the major sink for alkenes in the troposphere at night but also initiate the formation of peroxy radicals (HO2 + RO2) and hydroxyl radicals at night [Zhang et al., 2002a; Zhang and Zhang, 2002b] and represent a major source of these radicals at night [Cantrell et al., 1997; Carslaw et al., 1997; Ariya et al., 2000; Geyer et al., 2003]. Paulson and Orlando [1996] suggested that reactions of ozone with anthropogenic alkenes are the most important source of HO2 (OH + HO2 + RO2) in many urban settings during the day and evening. The nighttime radical chemistry can also increase the atmospheric oxidizing capacity, affecting the ozone-relevant chemistry.

6] Heterogeneous reactions on aerosols have the potential to play a major role in determining the chemical composition of the atmosphere. Recently, it has been recognized that heterogeneous chemistry involving reactions on and within aerosols and cloud droplets may affect tropospheric O3 concentrations through modulating the interconversion of NOx and hydrogen oxides (HO2 + RO2) or direct loss of O3 [Cantrell et al., 1996; Harrison et al., 1996; Jacob, 2000]. For example, there is clear evidence that nighttime hydrolysis of N2O5 on sulfate aerosols corresponds to a major atmospheric sink of NOx [Tie et al., 2001]. Soot particles are produced by incomplete combustion of fossil fuels. Several recent field and laboratory studies have suggested that carbon soot importantly affects NOx and O3 chemistry by providing an effective surface for mediating the interconversion among several NOx members [Calvert et al., 1994; Lammel and Cape, 1996; Lary et al., 1997; Ammann et al., 1998; Aumont et al., 1999; Kotamarthi et al., 2001]. In the urban air, nighttime HONO often accumulates to several parts per billion due to the heterogeneous conversion of NOx on soot particles [Calvert et al., 1994; Harrison et al., 1996]. There is increasing evidence suggesting that the heterogeneous conversion of NO2 to HONO occurring on the soot particle surfaces is solely responsible for the nighttime HONO formation (up to a level of a few parts per billion) in urban air [Reisinger, 2000]. The photolysis of HONO at sunrise provides a major morning source for HO2, affecting the O3 production and atmospheric oxidizing capacity.

[7] In this study a 3-D regional CTM is applied to investigate ozone formation in the HG area and to improve our understanding of the processes controlling ozone formation and distributions for an episode occurring during 7–11 September 1993. The objectives of this study consist of...
(1) assessing the chemical and physical processes that contribute to the high O₃ levels, (2) evaluating the major sources of nighttime RO₂, (3) quantifying the influence of the heterogeneous chemistry of sulfate and soot aerosols on the nighttime NOₓ budgets and the O₃ concentrations, and (4) evaluating the sensitivity of urban O₃ response to anthropogenic NOₓ and VOC emissions and BVOC emissions. A brief description of the methods employed in this study is given in section 2. Section 3 discusses the model performance, the in situ photochemical O₃ production rate and O₃ production efficiency, the responses of O₃ to precursor emissions, the major sources of nighttime RO₂, and the impacts of heterogeneous reactions on sulfate and soot aerosols on the budgets of NOₓ and O₃. A summary of the conclusions is provided in section 4.

2. Methodology

[8] The chemical transport model (CTM) was modified from a 3-D regional CTM, HANK, initially developed at the National Center for Atmospheric Research (NCAR) [Hess et al., 2000; Lei, 2003]. The HANK model has been successfully applied to investigate the episodic chemistry and transport in the Pacific Basin [Hess et al., 2000; Hess, 2001].

[9] The CTM is driven by 1-hour average meteorological output fields from the Penn State University/National Center for Atmospheric Research (PSU/NCAR) Mesoscale Modeling System (MM5) [Grell, 1993]. The MM5 uses initial and boundary conditions from the National Centers for Environmental Prediction (NCEP) reanalysis and is nudged toward the reanalysis data set. The chemical boundary and initial conditions for the CTM are derived from a daily average output of the Model of Ozone and Related Chemical Tracers version 2 (MOZART-v2) [Horowitz et al., 2003]. Both MM5 and CTM use the Grell cumulus scheme [Grell, 1993]) for deep and shallow convective transport and the medium-range forecast (MRF) boundary layer scheme [Hong and Pan, 1996] for vertical diffusion and transport in the planetary boundary layer (PBL).

[10] In this study the CTM is configured to a Lambert conformal grid with Houston located in the domain center (95°W, 30°N). The domain size is 48 × 48 grid cells with the horizontal resolution of 12 km (the outer domain size for the MM5 is 36 × 36 grid cells with the grid size of 36 km in which the one-way nesting is used). There are 38 vertical layers between the surface and 100 mb with 21 layers in the lowest 2 km of the model atmosphere to resolve small-scale structures of meteorology and chemistry in the PBL.

[11] To better represent the chemistry of a polluted urban troposphere and to accommodate the chemical species in the emission inventory, a hybrid chemical mechanism is used in this study. The inorganic chemistry part is similar to that in the work of Hess et al. [2000], except with the addition of the HONO gas chemistry, and the organic gas chemistry is based on the CB4 mechanism [Gery et al., 1989; Simonaitis et al., 1997] used in the Comprehensive Air Quality Model with extensions, version 3.1 (see http://www.camx.com). The CB4 mechanism is modified to represent the chemistry in both the polluted and remote troposphere [Lei, 2003]. Briefly, the modifications include an explicit representation of organic peroxy radical CH₃O₂, an updated isoprene oxidation mechanism [Lei et al., 2000, 2001; Zhang et al., 2000; Lei and Zhang, 2001; Zhang et al., 2002b, Zhao et al., 2003, 2004] following Paulson and Seinfeld [1992], an updated C₂H₄ oxidation chemistry following that in the work of Klonecki et al. [2003], and updated rate constants following Sander et al. [2000]. In addition, the heterogeneous removal of N₂O₅ on the surface of sulfate aerosols and the conversion of NO₂ to HONO on the surface of soot aerosols are included in the chemical mechanism (see section 3.5) as a part of the standard simulation.

[12] Emissions data in this study are provided by Texas Commission on Environmental Quality (TCEQ). This emission data set is denoted as the Coastal Oxidant Study for Southeast Texas (COAST) emissions inventory (EI) herein. The chemical compounds are specified using the CB4 mechanism, and the data are temporally resolved at hourly average intervals and spatially resolved at a 16 × 16 km² resolution. For other non-CB4 species and/or emissions outside the COAST EI domain (global emissions), the emission data are taken from the MOZART emissions database and are interpolated onto the CTM domain and grid size. In the interpolation the MOZART model species are converted to CB4 species on the basis of the CB4 and MOZART speciation principle. All emissions (except the aircraft emissions) are assumed to be released at the surface (the model’s lowest layer) and assumed instantaneously diluted over the entire grid box. Kore et al. [1995] pointed out that the measured ratios of VOC/NOₓ are consistently 4–12 times larger than those from the COAST EI within the industrial plumes. Recent field measurements from the TexAQS 2000 campaign also indicate that the measured ratios of industrial alkenes/NOₓ are a factor of 3–10 higher than those estimated from the emission inventory. As a result, we increase the point source emission of alkenes (OLE and C₂H₄) by a factor of 5 in this study.

[13] A 5-day stagnant ozone pollution period occurring during 7–11 September 1993 is chosen for this study. This period represents a NAAQS ozone exceedance episode along the coastal region near the Galveston Bay and the Gulf of Mexico shoreline. An extensive ground-based observation of O₃, NOₓ, and other pollutants was conducted during the same time period associated with the COAST field project [Koroc et al., 1995]. The chemical measurements provide data for our model validation. Figure 1 depicts the geographic distributions of the surface air quality monitoring stations in the HG area that collected pollutant data during the episode. Also shown in Figure 1 is a region with a dense monitoring network that is encompassed by a thick rectangle, which is designated as the South Harris (SH) region in this paper, representing the Houston area.

[14] Meteorologically, this episode was characterized by no significant weather systems passing through Texas [Lei, 2003]. During this period the overall temperature distribution did not change significantly from day to day. The large-scale winds were northerly and weak over southeast Texas. No strong cold fronts or warm fronts influenced the general weather regime in the southeast Texas coastal area, which featured a morning northerly component due to the land breeze, an afternoon wind varying between a southerly component due to the sea breeze influence, and a northerly
component due to the synoptic scale forcing. The HG area was cloud-free for most of the episode except on 9 September, which was predominantly overcast (J. W. Nielsen-Gammon, private communication, 2000).

The simulation (both MM5 and CTM) is initiated at 1200 UTC, 6 September 1993, allowing 17 hours for spinning-up to damp the influences of initial conditions. Note that in the MRF scheme the vertical eddy diffusion coefficient ($K_c$) in the PBL is determined by a Richardson number–dependent first-order closure. At night, when mixing is driven by wind shear and mechanical turbulence, the Richardson number–bounded $K_c$ values are generally too small ($\sim 10^{-2}$ m$^2$ s$^{-1}$ in this simulation) to adequately represent the vertical turbulent diffusion. Therefore the nighttime (1900–0700 LT) $K_c$ values in the PBL are adjusted according to a procedure described as following. If a $K_c$ value in the lowest seven model layers ($\sim 430$ m above ground level (AGL)) during a nighttime period is smaller than 1 m$^2$ s$^{-1}$, the $K_c$ value is set to 1 m$^2$ s$^{-1}$ and then scaled by a factor of 1–3. The day-varying scaling factor is selected such that the modeled NO$_x$ concentrations at the lowest model layer are close to the observations at night. The adjustment of the nighttime $K_c$ value in the low atmosphere also likely compensates other uncertainties caused by meteorological and emission factors, such as placing stack emissions in the model bottom layer.

Owing to the relatively coarse model resolution used in the present simulation, some detailed features of meteorological and chemical processes may not be sufficiently resolved, such as the subgrid chemical processes in the industrial plumes from the petrochemical complexes. The results and conclusions obtained from this study likely represent the urban-scale average aspects of O$_3$, its precursors, its formation, and its response to O$_3$ precursors. They may not be entirely applicable to small regions characterized with highly localized distinct meteorological and chemical features. Modeling with a higher model resolution (e.g., 4 km) will likely better characterize the highly localized features, and this effort is currently in progress.

3. Results and Discussions

3.1. Model Performance

Since a major uncertainty in regional photochemical modeling lies in the meteorological inputs [Seaman, 2000; Solomon et al., 2000], it is critical to accurately simulate the
meteorological fields. Among the meteorological parameters the wind field, temperature, and cloud cover are the determining factors in influencing air quality. The model reproduces the weak synoptic-scale surface flow and sea breeze flow reversal in the HG area during the period of 8–11 September 1993, although the onset timing and the duration of the sea breeze do not always match exactly with the measurements [Lei, 2003]. The simulated surface wind speeds agree with the observations within 2 m s\(^{-1}\), and the predicted surface temperatures are in agreement with the observations within 4°C. The model also captures the evolution of the PBL height and the response of the PBL height to different underlying land use characteristics in the HG area [Lei, 2003].

[18] The modeled concentrations of O\(_3\) in the lowest model layer (0 to ~30 m above ground level) are compared with available ground measurements. The model values are instantaneous, while the observation data are averaged over a 1-hour interval. Figure 2 displays the comparison of model versus observed near-surface O\(_3\) concentrations at six stations (cf. Figure 1) in the HG area over the episode. On a site-to-site basis the agreement between the simulations and observations is reasonably good. For most of the stations the model reproduces the diurnal variation and daily peak of O\(_3\) concentrations. Figure 3 depicts the spatial distributions of calculated (in colored contours) and observed (in colored dots) near-surface concentrations of O\(_3\) at 1500 LT. Here 1500 LT corresponds to the average time when the peak O\(_3\) levels occur during this episode, although the exact timing varied geographically. The spatial patterns of predicted and observed O\(_3\) are generally well matched. For example, on 8–9 September, the model

Figure 2. Site-by-site comparisons of simulated and observed surface O\(_3\) during the 7–11 September 1993 episode (starting at 0000 LT, 7 September). The dot points denote observation and the solid line represents simulation. Refer to Figure 1 for the site information.
correctly predicts that high levels of O$_3$ are located in the Galveston Bay region and in south Houston. It appears in the figure that a daytime O$_3$ minimum zone exists along the west coastline of the Galveston Bay, which is exemplified on 8 and 10 September. This O$_3$ minimum is likely due to the persistent high levels of NO$_x$ level in this zone that inhibits the O$_3$ photochemical formation and/or titrates O$_3$. Several factors may be responsible for the high concentrations of NO$_x$ in this area. First, there are substantial amounts of NO$_x$ emissions from petrochemical plants and ships on either side of this region. Second, the stable boundary layer over the ocean surface refrains the vertical mixing and traps the emitted NO$_x$. Third, the relatively coarse model horizontal resolution may place some inland emissions over adjacent ocean surface grids. Finally, a possible underestimate of VOC emissions in the emission data may also contribute to the O$_3$ minimum, as revealed by the results from the sensitivity study (section 3.3). Because of the lack of observations in this region, it is not affirmative whether this O$_3$ minimum zone represents an artifact. The model also reproduces reasonably well the observed daytime surface NO$_x$ in the HG area (not shown in this paper) within about 15% overall [Lei, 2003; Zhang et al., 2004].

3.2. O$_3$ Formation Rates and Production Efficiencies

In order to understand the photochemical behavior of O$_3$ formation with respect to ambient NO$_x$ levels, we examine the net photochemical O$_3$ production rates $P(O_3)$, the difference between the gross photochemical O$_3$ production rate $P(O_3^+)$, and the photochemical loss rate $P(O_3^-)$ during a particular time window. Figure 4 shows the calculated $P(O_3)$ as a function of NO$_x$ at 1300–1500 LT in the SH region during the 5-day episode. The time interval of 1300–1500 LT is selected because it is believed that the photochemical processes in urban plumes are most active during this period, and therefore the photochemical characteristics are most representative. The model values at the bottom model layer from all model grids within the SH region are chosen since there exists the most intense monitoring network and the model results for O$_3$ (and NO$_x$ as well) have been verified. Note also that almost all modeled chemical characteristics discussed below are obtained in this region. The net photochemical O$_3$ produc-

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Comparisons of simulated versus observed surface O$_3$ at 1500 LT during the episode: the colored dots are from observations, and the colored contour corresponds to simulations. The time shown is in MMDDHH (MM, month; DD, day; HH hour).
tion generally increases as NOx increases from 0.6 to 20 ppb. The \( P(O_3) \) appears to decrease as NOx further increases above 30 ppb. Owing to the scarcity of high NOx values, however, the decreasing trend of \( P(O_3) \) at high NOx is not affirmative. The NOx turnaround value, defined as the NOx level at which \( P(O_3) \) reaches a maximum, is higher than 15 ppb. We also examined the \( P(O_3) \)-NOx relationship at higher altitudes up to 500 m; it remains the same (except that the average \( P(O_3) \) decreases quickly within the lowest 200 m owing to sharply reduced NOx levels). There are fewer data points with NOx above 10 ppb. There are two important features for \( P(O_3) \) in the SH region as revealed in this figure. First, \( P(O_3) \) increases as NOx increases up to 20 ppb. In most other urban areas the ozone production generally decreases as NOx reaches above 10 ppb, e.g., in New York, Philadelphia, Phoenix, and Nashville [Daum et al., 2000; Kleinman et al., 1997, 2002]. Second, for the NOx values of 5–30 ppb, which correspond to the most frequently observed NOx levels near the surface during the midday in Houston, the \( O_3 \) production rates are 20–40 ppb hr\(^{-1}\). Those values are much higher than in most other U.S. cities (10–20 ppb hr\(^{-1}\)) [Stallman et al. 1990, Kleinman et al. 1995, 1997, and Daum et al. 2003] have demonstrated that at low NOx the gross chemical \( O_3 \) production rate (\( P(O_3^{+}) \)) is nearly a linear function of the NO concentration, while at high NOx, \( P(O_3^{+}) \) is proportional to the VOC reactivity and inversely proportional to the NOx concentration. Although the \( O_3 \) photochemical loss term (\( P(O_3^{-}) \)) contributes to the scatter in the \( P(O_3) \)-NOx relationship under urban conditions, in general it does not qualitatively affect the relationship [McKeen et al., 1991]. The frequently measured summertime ground NOx concentrations of 5–30 ppb in Houston are similar to those in other urban cities in the United States. The much higher values of the \( P(O_3) \) and NOx turnaround in the Houston metropolitan area are likely explained by the high abundance and reactivity of VOCs coexisting with abundant NOx in this area. Further diagnoses indicate that a majority of the abundant and reactive VOCs are from anthropogenic sources [Lei, 2003; Zhang et al., 2004]. These results are consistent with those revealed by the aircraft observations conducted during the recent TexAQS 2000 Study [Kleinman et al., 2002].

\( O_3 \) production efficiency (OPE), which is generally defined as the number of \( O_3 \) molecules generated per NOx molecule oxidized (\( NO_x = NO_x - NO_x^2 \)), determines the efficiency of NOx in the \( O_3 \) production. The OPE is related to \( P(O_3) \) by

\[
OPE = P(O_3)/P(NO_x),
\]

where \( P(NO_x) \) is the net NOx production rate. Figure 5 presents the OPE values as a function of NOx at 1300–1500 LT during the episode within the model bottom layer in the SH region. In Figure 5, \( P(NO_x) \) does not include the contributions from dry and wet deposition and particulate NOx heterogeneous removal because of their minor importance compared to the contributions from the gas-phase reaction of NOx with OH and the production of organic nitrates in this study. The calculated OPE values in Houston are 3–8 molecules of \( O_3 \) per molecule of NOx oxidized for the simulated daytime NOx levels of 5–30 ppb. Figure 5 illustrates the nonlinear relationship between the \( O_3 \) production efficiency and NOx, as suggested by Liu et al. [1987]. We also analyze the partition of NOx and its production rate \( P(NO_x) \). At the bottom model layer in the SH region, HNO3 produced from the gaseous reactions of NOx with OH accounts for 75% of NOx, and \( P(HNO_3) \) (production rate of HNO3 from the gaseous reaction) accounts for 84% of \( P(NO_x) \). Although the gross production rate of peroxyacetyl nitrate (PAN) is a factor of 3 higher than \( P(HNO_3) \), PAN is in equilibrium and thus its net contribution to \( P(NO_x) \) is very small.

### 3.3. Sensitivity of \( O_3 \) Formation to Precursors

[21] High \( O_3 \) levels formed in the urban centers and over rural areas are due to precursors of anthropogenically emitted VOCs and NOx. In addition, natural VOCs also play an important role in \( O_3 \) formation in urban and rural areas [Trainor et al., 1987; Chameides et al., 1988]. A large amount of effort has been devoted to developing an effective \( O_3 \) control strategy by reducing the emissions of \( O_3 \).
precursors. The key issue in developing an effective O$_3$ control strategy is to understand the nonlinear relationship between O$_3$ and its precursors. In this section we evaluate the response of O$_3$ levels to the O$_3$ precursor emissions in the HG area by varying the emission rates and comparing the results to a reference run. The reference run represents the episodic simulation presented above. Considering the probable underestimating of VOCs in the emission inventory in the reference case, we also explore the sensitivity of the model results by varying the emissions of AVOC and biogenic VOCs (mainly isoprene).

### 3.3.1. Sensitivity to Emission Changes

[22] The sensitivity of O$_3$ formation to reductions in anthropogenic NO$_x$ or AVOC emissions is studied. Results are presented for a 50% reduction in the emissions of NO$_x$ and AVOC separately. Since an uncertainty in the VOC EI can lead to a corresponding uncertainty in the representativeness of the reference case, we also examine the effects of a perturbation to the reference case on the responses of O$_3$ to the precursor emission reductions. Here the perturbation corresponds to doubling AVOC emissions.

![Figure 6](image)

**Figure 6.** The percentage change of O$_3$ in the bottom model layer, averaged from 1300 to 1500 LT over the episode, due to a 50% reduction in (a) NO$_x$ emissions, (b) AVOC emissions, and (c) doubling of AVOC emissions.

[23] Since the crucial factor in determining the O$_3$ levels is the net photochemical O$_3$ production rate, $P(O_3)$, the sensitivity of O$_3$ change to its precursor reductions is largely determined by the response of $P(O_3)$ to the precursor reductions. Figure 7a shows the percentage changes in $P(O_3)$ at 1300–1500 LT during the episode as a function of the reference run NO$_x$ for the two emission reduction cases (i.e., a 50% reduction in both the NO$_x$ and AVOC emissions). For NO$_x$ < 5 ppb the NO$_x$ control case is significantly more effective than the AVOC control in reducing O$_3$ production, while the AVOC control run is of little effectiveness in reducing O$_3$ production. For NO$_x$ > 15 ppb, however, the AVOC control is more effective than the NO$_x$ control. As NO$_x$ continues to increase, the NO$_x$ control strategy may lead to an increase in the O$_3$ production. The NO$_x$ turnaround value is about 15 ppb (where the $P(O_3)$ difference switches sign). The different responses to the two control strategies can be explained by the dependence of O$_3$ production on the precursor levels as discussed in the previous section; that is, at low NO$_x$, $P(O_3)$ is proportional to NO and only weakly dependent on VOC, but at high NO$_x$ and at the reference run VOC levels, $P(O_3)$ is proportional to VOC but inversely to NO$_x$. For the NO$_x$ level of 8–12 ppb, both emission controls have equal sensitivities. Considering that the frequently measured ambient midday ground NO$_x$ levels are in the range of 5–30 ppb in Houston, in which most O$_3$ violations occur during this episode, Figure 7a suggests that Houston is in or close to the transition regime. Since this episode is representative of the summertime ozone pollution situation in the HG area,
the results may partially explain the problem described in the introduction: The O₃ level remained constant over the past decade despite of the emission reduction efforts.

Figure 7b shows the percentage change of \( P(O_3) \) when the 50% emission reductions in NO\(_x\) and AVOC are applied to the doubling AVOC emission case. Note that the NO\(_x\) values used in the x axis correspond to different cases.

3.3.2. Vertical Distributions of O₃ Response to Emission Changes

So far we have restricted our discussion to the horizontal variability of O₃ formation sensitivity near the surface (the bottom model layer). In fact, the O₃ levels in the surface layer are coupled to O₃ concentrations and O₃ production rates at high elevations through rapid vertical mixing in the convective PBL. Therefore it is instructive to examine the O₃ change at different attitudes due to the emission change. Figure 9 illustrates the O₃ percent changes as a function of altitude in the SH region for five emission control cases (a 50% reduction in NO\(_x\) and AVOC emissions, doubling AVOC emissions, the exclusion of isoprene emissions and the exclusion of CO emissions). For the NO\(_x\) control case the percentage change within the PBL is quite uniform, except near the surface where NO\(_x\) decreases sharply with height. The influence of AVOC control drops off more quickly with altitude than that of NO\(_x\) control. The vertical profiles of NO\(_x\) and AVOC (represented by OLE) indicate that at 1300–1500 LT, both NO\(_x\) and AVOC decrease sharply with altitude in the lowest 100 m at a similar rate (decrease about 60%) and remain rather uniform throughout the rest of the mixing layer. This suggests that the greater sensitivity to AVOC in the low altitudes (\( \sim 0–100 \) m) is due to the different chemistry in the near-surface

Figure 8. The percentage change in O₃ as a function of the reference H₂O₂/HNO₃ at 1300–1500 LT during the episode within the bottom model layer over the South Harris region when NO\(_x\) and AVOC emissions are each reduced by 50%.
layer. When integrated throughout the PBL, the NO\textsubscript{x} control is more effective than the AVOC control.

[27] The effect of AVOC doubling on O\textsubscript{3} is nearly symmetrical to the 50\% AVOC reduction case. In the near-surface layer the influence of isoprene on the O\textsubscript{3} concentration (4–5\% in average) is not as significant as AVOCs in the SH region, although isoprene accounts for a significant fraction of VOC emissions in the HG area [Allen and Durrenberger, 2001]. The impact of CO on O\textsubscript{3} is negligible (~1.5\%), contrary to its role in the O\textsubscript{3} formation in the background and global troposphere [Brasseur et al., 1999; Crutzen et al., 1999].

3.4. Nighttime Organic Peroxy Radical Anomaly

[28] In this section we evaluate the nighttime RO\textsubscript{2} sources in the HG area as revealed by the 3-D modeling study. Figure 10a shows simulated temporal and spatial variations of RO\textsubscript{2} averaged in the SH region. A peak RO\textsubscript{2} concentration (up to 90 ppt) occurs in the upper PBL (or the residual layer) at night (around 2100 LT). Nighttime RO\textsubscript{2} levels near the surface are very low because of the small RO\textsubscript{2} source as the result of the depletion of near-surface O\textsubscript{3}. Low O\textsubscript{3} leads to the lack of NO\textsubscript{3}, whose reactions with VOCs (mainly alkenes) are the major source of nighttime RO\textsubscript{2} as we will demonstrate below.

[29] In the CB4 mechanism the major reactions that lead to the production of peroxy radicals at the nighttime are listed in Table 1. Note that high RO\textsubscript{2} yields (>0.9) from the NO\textsubscript{3}-alkene reactions and low RO\textsubscript{2} yields (<0.22) from the O\textsubscript{3}-isoprene reaction are assumed in the CB4 mechanism. In particular, RO\textsubscript{2} is not directly produced from the O\textsubscript{3}-isoprene reaction, and the indirect RO\textsubscript{2} yields are even smaller. We estimate the contributions of these two sources to the nighttime RO\textsubscript{2} production in the SH region. The contribution from the NO\textsubscript{3}-alkene reactions is estimated by taking the difference in the RO\textsubscript{2} concentrations between the reference run (REF case) and the run excluding the NO\textsubscript{3}-alkene reactions (noNO\textsubscript{3} case; no reactions in Table 1 are included). The contributions from the alkene-O\textsubscript{3} reactions are much smaller during the nights of 6, 7, and 10 September, no more than 10 ppt. This is because of the much lower RO\textsubscript{2} yields from the alkene-O\textsubscript{3} reactions as represented in the CB4 mechanism, although the ozonolysis reactions are comparable to the nighttime NO\textsubscript{3} reactions as a sink for alkenes in the troposphere in this study. We also estimated the RO\textsubscript{2} contribution from the ozonolysis reactions by taking the difference in the RO\textsubscript{2} concentrations between the REF case and a case same as the REF case except turning
off the ozonolysis reactions (noO3 case, R4–R6 in Table 1 not included). The resulting nighttime RO2 levels in the noO3 case were higher than those in the REF case (and RO2 from isoprene accounted for a majority). As is the case of daytime RO2 discussed above, this suggests that the nighttime RO2 production is limited by the alkene availability over Houston (and probably in polluted troposphere with abundant NOx and limited VOCs). Under different ambient conditions (VOC abundance, VOC composition, and NOx as well as O3 levels), the nighttime RO2 production may vary significantly.

Further model analyses indicate that isoprene is surprisingly responsible for about 40% of the nighttime peak RO2 in Houston in this study (15 versus 36 ppt averaged over 1900–2300 LT) in the RO2 peak layer (about 300–400 m AGL) reaches about 60 ppt. This value is much lower than the average simulated isoprene concentration at night (at 1900–2300 LT). Although there are near-zero nighttime emissions of isoprene in the Houston area, the average simulated isoprene concentration at night (at 1900–2300 LT) in the RO2 peak layer (about 300–400 m AGL) reaches about 60 ppt. This value is much lower than the corresponding value of OLE (~2 ppb), but it is sufficient to make a significant contribution to nighttime RO2 owing to its much faster reaction with NO3 than OLE (by a factor of ~80). The nighttime HO2 concentrations in Houston during this episode are typically very low (a few parts per trillion), and therefore no discussion of HO2 is presented in this paper.

3.5. Heterogeneous Impacts

In this model, two heterogeneous reactions are included in the chemical mechanism. One is the removal of N2O3 on the surface of sulfate aerosols

\[ \text{N}_2\text{O}_3 + \text{H}_2\text{O(aerosol)} \rightarrow 2\text{HNO}_3, \quad \text{(2)} \]

and the other is the conversion of NO2 to HONO on the surface of soot particles

\[ \text{NO}_2 + \text{soot} \rightarrow \text{HONO}. \quad \text{(3)} \]

Parameterizations for the heterogeneous chemistry of sulfates and soot particles are discussed below.

3.5.1. Reaction of N2O3 on Sulfate Aerosols

The reaction rate for both reactions is given by \( \gamma \cdot S \cdot \nu/4 \), where \( \gamma \) is the reaction probability, \( S \) is the surface area of the aerosols calculated from the equilibrium size distribution, and \( \nu \) is the molecular thermal velocity of the reactant species. In this simulation, \( \gamma \) is set to 0.1 for N2O3 hydrolysis on sulfate aerosols [Zhang et al., 1995], and the distribution of the sulfate aerosol mixing ratio is derived from the monthly average in the work of Barth et al. [2000]. The surface area of sulfate aerosols is calculated assuming a monodisperse size distribution of dry aerosols with a mean radius of 0.05 \( \mu \text{m} \) and mass density of 1.15 g cm\(^{-3}\). Note that the derived sulfate aerosol mixing ratios from a global model are probably underestimated in the urban regions.

Figure 11a shows the calculated percentage changes in HNO3 due to hydrolysis of N2O3 on sulfate aerosols in the SH region (normalized by HNO3 concentrations in which the hydrolysis reaction is excluded). Evidently,
HNO₃ increases occur during night in the lower troposphere. The increases reach 30–60% during the nights of 6, 7, and 10 September, while the increases become smaller during the nights of 8 and 9 September (10–20%), but occur in a deeper layer, probably due to relatively more active vertical mixing for the latter. The heterogeneous reaction (2) also provides a chemical destruction pathway for NO, for NO₂ + N₂O₅ reaction (2) also provides a chemical destruction pathway for NO₃ through the removal of N₂O₅ which is produced from the NO₂ + NO₃ → N₂O₅ reaction). Figure 11b presents the calculated percentage changes in NO₃ due to hydrolysis of N₂O₅ on sulfate aerosols in the SH region. Like HNO₃, the evident changes in NO₃ occur at night, ranging from 20 to 50%, and the reductions in NO₃ are more homogeneous (compared to HNO₃) in the troposphere.

3.5.2. Reaction of NO₂ on Soot Particles

[35] Ammann et al. [1998] measure the reaction probability (γ) for reaction (3) ranging from 1.1 × 10⁻² to 3.3 × 10⁻⁴, decreasing with the aging of soot particles. There are still arguments about the nature of the surface chemistry of soot. Ravishankara and Longfellow [1999] conclude that HONO formation on soot surfaces is catalytic, while Kleffmann et al. [1999] argue that it is not catalytic and soot will deactivate after long time exposure (a timescale of 10 hours). In this case study, soot nondeactivation is assumed, and the γ value of 5 × 10⁻⁴ is used, corresponding to a low limit of the experimental value. The geographical and temporal distributions of soot particles are assumed to be similar to those of sulfate aerosols in the work of Barth et al. [2000]. The concentrations of soot particles are scaled such that the concentrations are close to reality within the PBL in the HG area (D. Collins, private communication, 2000). Since the emphasis for this case study is to examine the heterogeneous impacts of soot particles on O₃ concentration within the PBL with the scaling as the precondition, the assumption should not cast serious doubts on the outcome of our primary interests. Mass concentrations of soot carbon measured in urban areas are in the range of 1.5–20 μg m⁻³ [Seinfeld and Pandis, 1998]. In Los Angeles, they are ~8 μg m⁻³ in the fall [Chow et al., 1994]. In this case study, soot concentrations in PBL in the HG area are scaled to ~6 μg m⁻³. The soot particle density and mean radius are assumed to be 1.85 g cm⁻³ and 0.012 μm, respectively [D’Almeida et al., 1991], leading to a soot surface area of 7.5 × 10⁻⁶ cm⁻² cm⁻³ and a reaction rate of 3.2 × 10⁻⁵ s⁻¹ (with a mass density of 6 μg m⁻³).

[36] Figure 12 shows the influence of reaction (3) on the diurnal cycle of near-surface O₃ concentrations averaged over the 5-day episode in the SH region. All stations within the SH domain outlined by the rectangle in Figure 1 are used in the comparison. Reaction (3) accelerates the accumulation of morning O₃ by about 1 hour and leads to a noticeable increase of O₃ concentration over the course of the day (4–12 ppb and about 7 ppb for the midday average). Allen and Durrenberger [2002] found that CTMs were not able to replicate rapid and efficient O₃ formation in Houston industrial plumes, and they attributed the model inability to the underestimate of VOC emissions and the inaccurate representation of mixing in the meteorological input. This case study suggests that heterogeneous conversion of NO₂ to HONO at night potentially enhances the morning O₃ accumulation in Houston industrial plumes. The increase in the morning O₃ by reaction (3) is obvious. Reaction (3) converts NO₂ to HONO and leads to HONO buildup during the night due to high NO₂ concentrations (up to 100 ppb). In the following morning after sunrise, HONO quickly photolyzes to produce OH, which results in enhancing VOC-NOₓ-O₃ chemistry and thus O₃ production rates. Figure 13 substantiates the morning OH increase due to the soot heterogeneous chemistry. The largest O₃ increase occurs in the areas where NOₓ is highest and VOCs are rich. Hence soot particles have appreciable impacts on O₃ in the ship channel area where abundant emissions of both VOCs and NOₓ coexist.

[37] In this case study, only reaction (3) has been considered. Other heterogeneous processes on soot particle surfaces might also have significant roles in NOₓ partitioning and HOₓ and O₃ chemistry, and the understanding on the soot heterogeneous chemistry is far from conclusive. In
addition, soot aerosols can also affect atmospheric radiation due their absorptive property, and thus affect the photochemical processes, resulting in reduction of tropospheric photolysis rates and inhibiting smog production [Dickerson et al., 1997; Liao et al., 1999]. A comprehensive consideration of the chemistry of soot particles is beyond the scope of this study.

4. Conclusions

[38] This paper evaluates the photochemical processes controlling urban ozone pollution in the HG area. A three-dimensional regional chemical transport model (CTM) is applied to investigate ozone formation and its response to precursors in the HG area during a 5-day ozone episode of 7–11 September 1993. The model performance is evaluated by comparing simulated O3 and NOx concentrations to those observed by the TCEQ surface-monitoring network. In general, the magnitude, location, diurnal variation, and peak of the O3 concentrations are well reproduced, and the temporal and geographical variation of O3 is well simulated in the HG area.

[39] The model shows that the simulated net photochemical O3 production rates are 20–40 ppbv hr$^{-1}$ for summer time ground NOx levels of 5–30 ppbv in this area, which are much higher than those in most other urban cities nationwide. Furthermore, the production rate increases with NOx up to 20 ppbv. The NOx turnaround value (the NOx concentration at which the O3 production rate reaches its maximum) is also higher than those in most other urban regions in the United States. The high O3 production and NOx turnover values are attributed to the large abundance and high reactivity of AVOCs and the coexistence of abundant AVOCs and NOx in this area. The model estimates an ozone production efficiency near the surface in the range of 3–8 for the NOx levels of 5–30 ppbv in the early afternoon in the Houston area.

[40] The simulation indicates that a peak concentration of organic peroxy radicals occurs at night in the HG area. The reactions of alkene-NOx and alkene-O3 are responsible for more than 80% of the nighttime RO2 within the residual layer, contributing to over 70% and about 10%, respectively. Isoprene accounts for about 40% of the nighttime RO2 production on average (overwhelmingly through the isoprene-NOx reaction). The RO2 production in Houston is limited by the availability of alkenes.

[41] The model quantifies the impacts of hydrolysis of NO2 on sulfate aerosols and heterogeneous conversion of NOx to HONO on the soot particle surfaces. The hydrolysis reaction leads to an increase of HNO3 by as much as 30–60% during the night in the lower troposphere, while a decrease of nighttime NOx by 20–50% in the troposphere. Soot particles accelerate the production of morning O3 by about 1 hour and lead to an appreciable increase of O3 concentration over the course of the day with a midday average of about 7 ppbv. The soot aerosols affect the O3 formation by modulating the morning OH concentration.

[42] The sensitivity of O3 formation to the precursor emissions is investigated in the Houston area. A 50% reduction in NOx emissions leads to a decrease by about 11% (ranging from 5 to 15%) in the ground O3 level, with the least decrease occurring in the downtown region. A 50% reduction in AVOC emissions results in an O3 decrease by about 8% (ranging from 2 to 10%). The sensitivity analysis of the H2O2/HNO3 ratio suggests that for the transitional regime this ratio is between 0.3 and 0.6.

[43] Considering the probable underestimating for AVOCs in the emission inventory, the effects of doubling AVOC emissions on O3 concentrations and the effectiveness of the precursor emission reductions are examined. The results show that the peak O3 increases 5–15% in the Houston area. The response of O3 production to the 50% reduction in AVOC emissions case, however, is significantly different; there is no O3 increase at any NOx levels. As a result, the NOx control is more effective than the VOC control to mitigate the O3 levels.

[44] The sensitivity test excluding the isoprene emission shows that isoprene does not contribute significantly to the O3 levels in the Houston area (about 5% in average). CO contributes to less than 2% to the total surface O3 concentrations in the HG area.

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