Response to Anonymous Referee #1:

We thank the reviewer for providing insightful comments and helpful suggestions that have substantially improved the manuscript. Below we have included the review comments followed by our responses in italic. In the revision of this manuscript, we have highlighted those changes accordingly in blue font.

1) Review of “Ozone production and its sensitivity to NO\textsubscript{X} and VOCs: results from the DISCOVER-AQ field experiment, Houston 2013” The authors state several times that these results have important emissions control policy implications but it is not clear what type of program implementation would be needed based on the diurnal ozone production efficiencies presented here.

Response: We are not suggesting a specific implementation program (which is beyond the scope of this work), however, are suggesting that it may be more beneficial at certain locations, during certain times of day, to regulate VOCs based on the diurnal ozone production efficiencies we report. We are providing a scientific basis through which policy makers could develop an emission reduction strategy.

2) Given that this paper is focused on NO\textsubscript{X} and VOC contribution to O\textsubscript{3} production the authors should provide NO\textsubscript{X} and VOC measurements from this study and also compare those with previous Houston field studies to provide more context about how these pollutants are decreasing and for VOC how total VOC and VOC reactivity is decreasing to support conclusions about ozone production efficiency. Also, a comparison with another area like Baltimore would be useful.

Response: Both NO\textsubscript{x} and VOC levels in Houston have been continuously decreasing in the past 15-20 years as shown in Figure 1(S1 in paper), the time series of NO, NO\textsubscript{x}, ethene, and propene at two monitoring sites near the Houston Ship Channel.
Figure 1. Time series of NO, NOx, ethene and propene concentrations at the Deer Park and Clinton sites from 1998 to 2014. The Deer Park site is located southeast of the Ship Channel. The Clinton site is located on the northwestern end of the Ship Channel. Each data point represents an average of hourly samples collected between July 1 and November 30 for each year. Missing data points indicate that too few valid samples (< 70%) were collected during that year. NO and NOx* data collected hourly using chemiluminescence sampler with molybdenum catalyst to convert NOx* (not true NOx because Mo catalyst converts other N species besides NO₂ to NO) to NO. VOC data collected over a 40-minute period each hour using automated gas chromatography with cryogenic pre-concentration.

The NOx levels and OH reactivity in Houston during DAQ2013 and in Maryland during DAQ2011 are quite different, as shown in Figure 2. Houston has much higher NOx levels throughout the day. For OH reactivity, it is greater in Houston than in Maryland in the morning, but is comparable in both locations in the afternoon. Note as shown in Figure 4, due to different emission sources, in Houston anthropogenic VOCs are the main contributor to the OH reactivity from VOCs, while in Maryland, biogenic VOCs (mainly isoprene) dominates the OH reactivity from VOCs. Different NOx levels and different VOC sources in Houston and Maryland are responsible for the different OPE values in the two areas.
3) The authors provide CMAQ simulated ozone production efficiency but provide no information about the emission inventory used for the simulation and how well the model predicted NOx, NO2, VOC, and O3 compared with the aircraft and surface measurements made during the field study. Is it ok that the model predicts a similar OPE to the box model but not capture the magnitudes of the precursors or ozone correctly? The information presented about OPE is useful, but additional work is needed for this to provide a more comprehensive understanding of ozone production in Houston with respect to the models used by regulators for decision support and context from the many previous Houston field studies.

Response: The WRF and CMAQ model options are described in Table 1. In Section 2.3, we also added the following a few sentences to describe the emissions we used in the CMAQ simulations: “The 2012 baseline anthropogenic emissions from the Texas Commission on Environmental Quality (TCEQ) were used as input to CMAQ. These emissions contain the most-up-to-date Texas anthropogenic emissions inventory and a compilation of emissions estimates from Regional Planning Offices throughout the US. Biogenic emissions were calculated online within CMAQ with Biogenic Emission Inventory System (BEIS). Lightning emissions were also calculated online within CMAQ.”

CMAQ simulated a high bias in surface and aloft ozone (Tables 1). CMAQ also simulated a low bias in CO, CH2O, isoprene, NO2, and NO aloft and a high bias in NOy aloft (Table 2). Recent work has shown that oceanic emissions of iodine and bromine result in ozone destruction (Carpenter et al., 2013). The high ozone bias in our results is expected due to the lack of oceanic iodine and bromine emissions and the associated chemistry. Biases in surface ozone are larger near the coastline (i.e., Galveston) than sites inland (i.e., Conroe).
Table 1. Mean bias (MB), normalized mean bias (NMB), normalized mean error (NME), root mean square error (RMSE), and Gross Error (GE) of surface ozone for the 2nd iterative 1 km WRF simulations covering all of September 2013.

<table>
<thead>
<tr>
<th></th>
<th>Surface Ozone (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>9.5</td>
</tr>
<tr>
<td>NMB (%)</td>
<td>39</td>
</tr>
<tr>
<td>NME (%)</td>
<td>51</td>
</tr>
<tr>
<td>RMSE</td>
<td>15</td>
</tr>
<tr>
<td>GE</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 2. Second iterative 1 km CMAQ simulated mean bias (MB), normalized mean bias (NMB), normalized mean error (NME), and root mean square error (RMSE) of O₃, CO, CH₂O, Isoprene (ISO), NO₂, NO, and NOy covering measurements made onboard the NASA P-3B aircraft on all flight days during the DISCOVER-AQ field campaign.

<table>
<thead>
<tr>
<th>Model</th>
<th>O₃</th>
<th>CO</th>
<th>CH₂O</th>
<th>ISO</th>
<th>NO₂</th>
<th>NO</th>
<th>NOy</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>0.8</td>
<td>-5.8</td>
<td>-0.3</td>
<td>-0.02</td>
<td>-0.5</td>
<td>-0.3</td>
<td>0.04</td>
</tr>
<tr>
<td>NMB</td>
<td>1.4</td>
<td>-4.8</td>
<td>-16</td>
<td>-7.7</td>
<td>-39</td>
<td>-66</td>
<td>1.3</td>
</tr>
<tr>
<td>NME</td>
<td>15</td>
<td>17</td>
<td>37</td>
<td>70</td>
<td>70</td>
<td>84</td>
<td>61</td>
</tr>
<tr>
<td>RMSE</td>
<td>12</td>
<td>35</td>
<td>1.4</td>
<td>0.7</td>
<td>3.1</td>
<td>2.2</td>
<td>4.7</td>
</tr>
</tbody>
</table>

4) The last half of the introduction section reads like a white paper on the Houston DISCOVER-AQ field study. Since this paper does not present any information relevant to the mission of that field study which was to validate satellite measurements the discussion of the DISCOVER-AQ campaign could be de-emphasized in favor of more time spent on the multitude of historical field studies in the Houston area. Also, the authors never clearly state in the introduction what they are presenting and why that information is novel.

Response: We have removed lines 89-96 and combine lines 97 – 100 and took out lines 102-106. We edited lines 81-84 to read: “In the work presented here, we provide investigations of spatial and temporal variations of ozone production and its sensitivity to NOx and VOCs to provide a scientific basis to develop a non-uniform emission reduction strategy for O₃ pollution control in urban areas such as Houston.”
5) The authors do not need to explain why CB05 is used rather than CBIV, but an explanation about why CB05 was used rather than the newer version CB6 is necessary. At several points in the manuscript the authors note that organic nitrate fate can confound OPE interpretation so the choice of an older Carbon Bond mechanism that has a less realistic treatment of organic nitrates is needed. Also, it is not clear why all species have the same two-day deposition lifetime. Species like O3 and HNO3 deposit out of the atmosphere and very different rates.

Response: CB05 is the most up to date Carbon Bond mechanism in CMAQ (i.e., CB6 has not been implemented into CMAQ at the time the analysis was performed). The box model was constrained for all long-lived measured species like ozone and HNO3 and we do not assume a two-day deposition lifetime. An additional two-day lifetime due to deposition and heterogeneous losses is assumed for calculated species in the box model. Most calculated species like OH, HO2 and RO2 are reactive intermediates and have lifetimes on the order of seconds to minutes, much shorter than 2 days. Adding this additional two-day lifetime would not affect the model results at all. There are a few long-lived species (like organic acid and alcohols) calculated in the model that could potentially accumulate to levels much higher than the levels in the ambient air. We have revised this sentence: “An additional lifetime of two days was assumed for some calculated long lived species such as organic acids and alcohols to avoid unexpected accumulation of these species in the model.”

6) Please provide information about the emission inventory and modeling used as input to the CMAQ simulation and the source of the initial and boundary conditions.

Response: The WRF and CMAQ model options have been described in Table 1. In Section 2.3, we also added the following a few sentences for the emissions we used in the CMAQ simulations: “The 2012 baseline anthropogenic emissions from the Texas Commission on Environmental Quality (TCEQ) were used as input to CMAQ. These emissions contain the most-up-to-date Texas anthropogenic emissions inventory and a compilation of emissions estimates from Regional Planning Offices throughout the US Biogenic emissions was calculated online within CMAQ with Biogenic Emission Inventory System (BEIS). Lightning emissions were also calculated online within CMAQ.” It is also listed in Table 1 of this manuscript.

7) In the results section, please provide some comparison of CMAQ estimated VOC, speciated VOC, NO, NO2, HNO3, PANs, HNO3, and O3 with measurements.

Response: An evaluation of the improved WRF and CMAQ model simulations for the entire month of September 2013 was conducted. Statistics used to evaluate WRF and CMAQ are described Tables 3. CMAQ simulated a high bias in surface and aloft ozone (Table 1). CMAQ also simulated a low bias in CO, CH2O, isoprene, NO2, and NO aloft and a high bias in NOy aloft (Table 2). Recent work has shown that oceanic emissions of iodine and bromine result in ozone destruction. The high ozone bias in our results is expected due to the lack of oceanic iodine and bromine emissions and the associated chemistry. Biases in surface ozone are larger near the coastline (i.e., Galveston) than sites inland (i.e., Conroe) as shown in Figure 3.
Table 3. Definition of the statistics used in WRF and CMAQ model evaluations. In these equations M represents the model results, O represents the observations, and N is the number of data points.

<table>
<thead>
<tr>
<th>Mean Bias (MB)</th>
<th>$MB = \frac{1}{N} \sum_{i=1}^{N} (M_i - O_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normalized Mean Bias (NMB)</td>
<td>$NMB = \frac{\sum_{i=1}^{N} (M_i - O_i)}{\sum_{i=1}^{N} O_i} \times 100%$</td>
</tr>
<tr>
<td>Normalized Mean Error (NME)</td>
<td>$NME = \frac{\sum_{i=1}^{N}</td>
</tr>
<tr>
<td>Root Mean-Square Error (RMSE)</td>
<td>$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (M_i - O_i)^2}$</td>
</tr>
<tr>
<td>Gross Error (G)</td>
<td>$GE = \frac{1}{N} \sum_{i=1}^{N}</td>
</tr>
</tbody>
</table>

Table 4. Mean bias (MB), normalized mean bias (NMB), normalized mean error (NME), root mean square error (RMSE), and Gross Error (GE) of 2 m temperature, 10 m wind speed, and 10 m wind direction for the 2nd iterative 1 km WRF simulations covering all of September 2013.

<table>
<thead>
<tr>
<th>2 m Temperature (K)</th>
<th>10 m Wind Speed (m/s)</th>
<th>10 m Wind Direction (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>Model</td>
<td>Model</td>
</tr>
<tr>
<td>MB</td>
<td>0.2</td>
<td>-0.8</td>
</tr>
<tr>
<td>NMB (%)</td>
<td>0.1</td>
<td>-17</td>
</tr>
<tr>
<td>NME (%)</td>
<td>0.4</td>
<td>36</td>
</tr>
<tr>
<td>RMSE</td>
<td>1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>GE</td>
<td>1.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Figure 3. Observed (*) and CMAQ simulated (solid lines) maximum 8 hour average ozone at La Porte Sylvan Beach (red), Conroe (purple), Galveston (blue), and West Houston (green) during September 2013.

8) The authors suggest one difference in OPE between Houston and Baltimore is due to reactivity. Please provide speciated VOC concentrations from each field study by reactivity so this relationship is clearer.

Response: The median OH reactivity due to non-methane hydrocarbons (NMHCs) was 3.3 s\(^{-1}\) observed during DISCOVER-AQ 2013 in Houston and 1.2 s\(^{-1}\) observed during DISCOVER-AQ 2011 in Maryland. As shown in Figure 4, alkanes and alkenes were dominant contributors to the OH reactivity due to NMHCs in Houston in 2013, while isoprene and alkanes were dominant contributors to the OH reactivity due to NMHCs in Maryland in 2011. The differences in overall OH reactivity and its distributions in the two locations are responsible to the different OPEs in the two different environments. We have included this in the Supporting Information.
**Figure 4.** Distributions of OH reactivity due to non-methane hydrocarbons in DISCOVER-AQ 2011 in Maryland (left) and 2013 in Houston (right).

9) The authors make a lot of strong conclusions about trends in OPE when NOX is greater or less than 1 ppb as shown in Figure 14. The points in Figure 14 do not show a distinct relationship above or below any level of the NOX concentrations. Perhaps box plots binned by NOX concentration would be a better way to show this type of relationship (if it really exists).

*Response:* We have updated Figure 13 by adding median OPE values binned by NOx concentration on top of the individual data points and the trend seems more distinct.
Figure 13. Ozone production efficiency (OPE) versus NOx in the box model (blue circles) and the CMAQ model pink dots) results. The linked blue circles show the median OPE values binned by NOx concentration in the box model, while the linked red triangles show the median OPE values binned by NOx concentration in the CMAQ model, OPE is calculated according to its definition as the net ozone formation rate divided by of the formation rate of NOz.
Response to Anonymous Referee #2:

We thank the reviewer for providing insightful comments and helpful suggestions that have substantially improved the manuscript. Below we have included the review comments followed by our responses in italic. In the revision of this manuscript, we have highlighted those changes accordingly in blue font.

1. The analyses performed and the approach used are tried and true so technically, there are no major faults with the work (though I question the use of a box model in Houston when the meteorology is so complex - why not just use the 3D model as it can provide answers to some of the questions asked and the ambient data can be used for model evaluation). However, due to a lack of novelty and a lack of truly new findings that warrant an entire manuscript, I am unable to recommend this manuscript for publication in ACP.

Response: The reviewer’s comment prompted us to re-examine the literature, where we found a few more relevant papers (i.e. Thielmann et al., 2002; Zaveri et al., 2003; Ryerson et al., 2003; Griffin et al., 2003, Kommalapati et al., 2016), but none that thoroughly addressed the issues that we cover in this paper.

In response to why we did not just use a 3D model, the box model is constrained to observed meteorological parameters and chemical species such as $O_3$, $NO_x$, $CO$, and some $VOC$s, which we find to be more useful than a 3D model for this kind of analysis since it eliminates some uncertainties, or errors that a 3D model could have. A 3D CTM may have major problems with the emissions inventories as described by Yu et al. (2012) and Travis et al. (in review in ACPD, 2016), who show that modeled NOy was twice as high than observed. Our box model simulation could reduce uncertainties in the ozone production and sensitivity calculations.

We have stated at the end of Section 2.2: “The box model analysis is necessary for ozone production and its sensitivity to $NO_x$ and $VOC$s because the box model was constrained to measured species (e.g., $NO$, $NO_2$, $CO$, HCHO, etc.) and meteorological parameters (e.g., photolysis frequencies) that are essential to calculate ozone production rates. Even though there is good agreement in general between the box model and the 3D model, there are still some differences between the measurements and the output from the 3D model, e.g., NOx, CO, HCHO and photolysis frequencies.”

2. With regard to figures, Figure 1 is not necessary (the ozone isopleth is "classic"), Figure 2 would be better as a map with points/labels as the extraneous stuff is distracting, and Figures 3 and 4 can be combined. In addition, some of the figures are intuitive based on previous work in Houston and other locations (5, 6, 8, and 9).

Response: We would like to keep Figure 1 in the paper. Since Figure 1 is ozone production and not ozone concentration as traditional EKMA $O_3$ isopleth diagrams are, it could provide useful information for the reader about how ozone production changes with regarding to NOx and VOC and NOx and VOC sensitive regimes of ozone production. As suggested, we have changed
Figure 2 to a map with points and labels. Figures 3 and 4 are combined. Figures 5, 6, 8 and 9 are the results from the DISCOVER-AQ Houston campaign showing spatial and temporal variations of ozone production and its sensitivity to NOx and VOCs. To our knowledge, there has not been a single study that covers such a large spatial range on this topic, and the data from this campaign provide us the unique opportunity to do such an analysis.

Figure 2. DISCOVER-AQ ground and spiral sites (yellow dots) during the September 2013 Houston campaign.

3. My largest criticism of this work is that it is known from three previous field campaigns that ozone production rates and sensitivities in Houston are temporally and spatially dependent. It seems to be that the most new information appears on lines 203-205 (line 206 is intuitive) regarding O3 loss and the split between RO2 and HO2 reactions with NO (unless this information is published elsewhere and I am unaware) and on line 255+ where it is noted that OPE has decreased in Houston compared to previous campaigns (due to the decrease in NOx emissions). I do not believe that these warrant a manuscript by themselves.

Response: The reviewer was right that there have been some previous studies, including three previous studies in Houston in 2000, 2006, and 2009 and some others in other locations, on ozone production and its relationships to NOx and VOCs (e.g., Kleinman et al., 2002; Ryerson et al., 2003; Newman et al., 2009; Mao et al., 2010; Chen et al., 2010; Ren et al., 2013), but to our
knowledge, none of them has done systematic analysis on ozone production and its sensitivity to NOx and VOCs and covers such large spatial (urban and suburban) and temporal ranges as the DISCOVER-AQ Houston campaign does in 2013. For example, the SHARP study in 2009 (Ren et al., 2013) and the Texas Air Quality Study Radical and Aerosol Measurement Project (TRAMP) in 2006 (Mao et al., 2010; Chen et al., 2010) did cover ozone production and its sensitivity to NOx and VOCs, but they were focus on the data collected at a single location at Moody Tower at the University of Houston. Kleinman et al. (2002) and Ryerson et al., (2003) from TexAQS I in 2000 and Newman et al. (2009) from TexAQS II in 2006 discussed ozone production efficiencies (OPE), but they did not talk about the dependence of OPE on NOx and did not cover the sensitivity of ozone production to NOx and VOCs. The rich data set collected during the DISCOVER-AQ Houston campaign provides us a unique opportunity to perform this systematic analysis and we believe it is worth to inform the atmospheric chemistry community about the latest findings from this study to reflect the changes in chemical conditions (e.g., emissions) in Houston since previous studies.

4. The authors do not put Houston in the context of other locations. For example, they state on line 68 that "there are a limited number of observation-based studies on ozone production and its sensitivity to NOx and VOCs." There have been such studies made in Houston (SHARP, TexAQS I and II) as well as in other locations across the US (Nashville, New England) and Europe. It would be appropriate to make such comparisons.

Response: We have cited results from other studies in other locations (e.g., Zaveri et al., 2003; Griffin et al., 2004; Thielmann et al., 2002) in the introduction and compared the results from this study to those from other locations. Our study is unique in that it examines the spatial and temporal variations in ozone production and its sensitivity. Other studies are mostly ground-based (i.e., single location like SHARP) or with limited spatial/temporal coverage. We found a higher OPE in this study than what was found in previous studies in Houston, which is probably due to continuous emission control as NOx levels were continuously pushed to ~1ppbv and thus we got a higher OPE.

We have revised this sentence as: “There are some observation-based studies on ozone production and its relationships with NOx and VOCs [e.g., Thielmann et al., 2002; Zaveri et al., 2003; Ryerson et al., 2003; Griffin et al., 2003; Kleinman et al., 2005a; Neuman et al., 2009; Mao et al., 2010; Ren et al., 2013]”

In Section 3.1, we have added one sentence: “Similar instantaneous ozone production rates have been observed in two previous studies in Houston in 2000 and 2006 [Kleinman et al., 2002a; Mao et al., 2010].”

In Section 3.2, we revised a sentence to: “Houston area OPE values range from about a factor of 1.3 to 2 higher than the OPEs calculated from the DISCOVER-AQ 2011 study in Maryland, likely due to higher photochemical reactivity in Houston (Figure S4). The 2011 Maryland OPEs
ranged from 3.4 to 6.1 when all measured data below 1 km are used (Ren, X., unpublished data). An OPE of ~8 was calculated [He et al., 2013] for the 2011 Maryland DISCOVER-AQ campaign for measured data below the 850 hPa level during vertical spirals with a strong linear correlation ($r^2 > 0.8$) between $O_3$ and NO$_2$. Additionally, OPEs of 7.7-9.7 were obtained from a ground site during the New England Air Quality Study (NEAQS) 2002 (Griffin et al., 2004).”

5. What is the basis for assuming a two-day lifetime for all calculated species to avoid build up?

Response: We do not provide a citation because we chose this value somewhat arbitrarily. By decreasing or increasing two days to one or ten days, it would not have much affect on the simulation results. This is because the box model already constrained all measured long-lived measured species. The additional lifetime of two days for the calculated species is to account for losses due to dry and wet deposition, vertical and horizontal diffusion, and to prevent accumulation of long-lived species in the box model. Most calculated species like OH, HO$_2$ and RO$_2$ are reactive intermediates and have lifetimes on the order of seconds to minutes, much shorter than 2 days. By adding this additional two-day lifetime would not affect the model results at all. There are a few long-lived species (like organic acid and alcohols) calculated in the model that could potentially accumulate to levels much higher than the levels in the ambient air.

We have revised this sentence: “An additional lifetime of two days was assumed for some calculated long lived species such as organic acids and alcohols to avoid unexpected accumulation of these species in the model.”

**Additional References**


Thielmann, A., A. S. H. Pre’vo’t, and J. Staehelin, Sensitivity of ozone production derived from

Yu, S. C., et al. (2012), Comparative evaluation of the impact of WRF-NMM and WRF-ARW meteorology on CMAQ simulations for O3 and related species during the 2006 TexAQS/GoMACCS campaign, Atmospheric Pollution Research, 3(2), 149-162.


List of changes in revised, marked up manuscript below: (line numbers may be slightly off on unmarked up version)

1) We revised the sentences on lines 68-70 to read:

“There are some observation-based studies on ozone production and its relationships with NOx and VOCs [e.g., Thielmann et al., 2002; Zaveri et al., 2003; Ryerson et al., 2003; Griffin et al., 2003; Kleinman et al., 2005a; Neuman et al., 2009; Mao et al., 2010; Ren et al., 2013]”

2) We have removed lines 91-98 and combine lines 99 – 102 and took out lines 104-108. We edited lines 83-86 to read:

“In the work presented here, we provide investigations of spatial and temporal variations of ozone production and its sensitivity to NOx and VOCs to provide a scientific basis to develop a non-uniform emission reduction strategy for O3 pollution control in urban areas such as Houston.”

3) We have revised the sentence on lines 144-146 to read:

“An additional lifetime of two days was assumed for some calculated long-lived species such as organic acids and alcohols to avoid unexpected accumulation of these species in the model.”

4) We added the following on lines 153-159:

“The box model analysis is necessary for ozone production and its sensitivity to NOx and VOCs because the box model was constrained to measured species (e.g., NO, NO2, CO, HCHO, etc.) and meteorological parameters (e.g., photolysis frequencies) that are essential to calculate ozone production rates. Even though there is good agreement in general between the box model and the 3D model, there are still some differences between the measurements and the output from the 3D model, e.g., NOx, CO, HCHO and photolysis frequencies.”
5) We added the following on lines: 170-176

“The 2012 baseline anthropogenic emissions from the Texas Commission on Environmental Quality (TCEQ) were used as input to CMAQ. These emissions contain the most-up-to-date Texas anthropogenic emissions inventory and a compilation of emissions estimates from Regional Planning Offices throughout the US. Biogenic emissions were calculated online within CMAQ with Biogenic Emission Inventory System (BEIS). Lightning emissions were also calculated online within CMAQ.”

6) On lines 189-190 in Section 3.1, we have added one sentence:

“Similar instantaneous ozone production rates have been observed in two previous studies in Houston in 2000 and 2006 [Kleinman et al., 2002a; Mao et al., 2010].”

7) On lines 257-264 in Section 3.2, we revised a sentence to read:

“Houston area OPE values range from about a factor of 1.3 to 2 higher than the OPEs calculated from the DISCOVER-AQ 2011 study in Maryland, likely due to higher photochemical reactivity in Houston (Figure S4). The 2011 Maryland OPEs ranged from 3.4 to 6.1 when all measured data below 1 km are used (Ren, X., unpublished data). An OPE of ~8 was calculated [He et al., 2013] for the 2011 Maryland DISCOVER-AQ campaign for measured data below the 850 hPa level during vertical spirals with a strong linear correlation ($r^2 > 0.8$) between $O_3$ and NO$_x$. Additionally, OPEs of 7.7-9.7 were obtained from a ground site during the New England Air Quality Study (NEAQS) 2002 (Griffin et al., 2004).”

8) We updated figure 2 (line 466)

9) We combined originally separate figures into Figure 3 (line 471)

10) We updated figure 8 (line 494)

11) We have updated Figure 13 by adding median OPE values binned by NOx concentration on top of the individual data points and the trend seems more distinct (line 530)
Ozone Production and Its Sensitivity to NOx and VOCs: Results from the DISCOVER-AQ Field Experiment, Houston 2013

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Abstract An observation-constrained box model based on the Carbon Bond mechanism, Version 5 (CB05), was used to study photochemical processes along the NASA P-3B flight track and spirals over eight surface sites during the September 2013 Houston, Texas deployment of the NASA DISCOVER-AQ campaign. Data from this campaign provided an opportunity to examine and improve our understanding of atmospheric photochemical oxidation processes related to the formation of secondary air pollutants such as ozone (O3). O3 production and its sensitivity to NOx and VOCs were calculated at different locations and times of day. Ozone production efficiency (OPE), defined as the ratio of the ozone production rate to the NOx oxidation rate, was calculated using the observations and the simulation results of the box and Community Multiscale Air Quality (CMAQ) models. Correlations of these results with other parameters, such as radical sources and NOx mixing ratio, were also evaluated. It was generally found that O3 production tends to be more VOC sensitive in the morning along with high ozone production rates, suggesting that control of VOCs may be an effective way to control O3 in Houston. In the
afternoon, O₃ production was found to be mainly NOₓ sensitive with some exceptions. O₃ production near major emissions sources such as Deer Park was mostly VOC sensitive for the entire day, other urban areas near Moody Tower and Channelview were VOC sensitive or in the transition regime, and areas farther from downtown Houston such as Smith Point and Conroe were mostly NOₓ sensitive for the entire day. It was also found that the control of NOₓ emissions has reduced O₃ concentrations over Houston, but has led to larger OPE values. The results from this work strengthen our understanding of O₃ production; they indicate that controlling NOₓ emissions will provide air quality benefits over the greater Houston metropolitan area in the long run, but in selected areas controlling VOC emissions will also be beneficial.

Keywords Ozone production; Ozone Production Efficiency; Houston; DISCOVER-AQ

1. Introduction

Understanding the non-linear relationship between ozone production and its precursors is critical for the development of an effective ozone (O₃) control strategy. Despite great efforts undertaken in the past decades to address the problem of high ozone concentrations, our understanding of the key precursors that control tropospheric ozone production remains incomplete and uncertain [Molina and Molina, 2004; Xue et al., 2013]. Atmospheric ozone levels are determined by emissions of ozone precursors, atmospheric photochemistry, and transport [Jacob, 1999; Xue et al., 2013]. A major challenge in regulating ozone pollution lies in comprehending its complex and non-linear chemistry with respect to ozone precursors, i.e., nitrogen oxides (NOₓ) and volatile organic compounds (VOCs) that varies with time and location (Figure 1). Understanding the non-linear relationship between ozone production and its precursors is critical for the development of an effective ozone control strategy.

Sensitivity of ozone production to NOₓ and VOCs represents a major uncertainty for oxidant photochemistry in urban areas [Sillman et al., 1995; 2003]. In urban environments, ozone is formed through photochemical processes when its precursors NOₓ and VOCs are emitted into the atmosphere from many sources. Depending on physical and chemical conditions, the production of ozone can be either NOₓ-sensitive or VOC-sensitive due to the complexity of these photochemical processes. Therefore, effective ozone control strategies rely heavily on the accurate understanding of how ozone responds to reduction of NOₓ and VOC emissions, usually
simulated by photochemical air quality models [e.g., Sillman et al., 2003; Lei et al., 2004; Mallet and Sportisse, 2005; Li et al., 2007; Chen et al., 2010; Tang et al., 2010; Xue et al., 2013; Goldberg et al., 2016]. However, those model-based studies have inputs or parameters subject to large uncertainties that can affect not only the simulated levels of ozone but also the ozone dependence on its precursors.

There are some observation-based studies of ozone production and its relationships with NO\textsubscript{x} and VOCs [e.g., Thielmann et al., 2002; Zaveri et al., 2003; Ryerson et al., 2003; Griffin et al., 2003; Kleinman et al., 2005a; Neuman et al., 2009; Mao et al., 2010; Ren et al., 2013]. Using in-situ aircraft observations, Kleinman et al. [2005a] studied five U.S. cities and found that ozone production rates vary from nearly zero to 155 ppb hr\textsuperscript{-1} with differences depending on precursor concentrations NO\textsubscript{x}, and VOCs. They also found that in Houston, NO\textsubscript{x} and light olefins are co-emitted from petrochemical facilities leading to the highest ozone production of the five cities [Kleinman et al., 2005a]. Using the data collected at a single surface location during the Study of Houston Atmospheric Radical Precursors (SHARP) in spring 2009, the temporal variation of O\textsubscript{3} production was observed: VOC-sensitive in the early morning and NO\textsubscript{x}-sensitive for most of the afternoon [Ren et al., 2013]. This is similar to the behavior observed in two previous summertime studies in Houston: the Texas Air Quality Study in 2000 (TexAQS 2000) and the TexAQS II Radical and Aerosol Measurement Project in 2006 (TRAMP 2006) [Mao et al., 2010; Chen et al., 2010]. In a more recent study using measurements in four cities in China, ozone production was found to be in a VOC-sensitive regime in both Shanghai and Guangzhou, but in a mixed regime in Lanzhou [Xue et al., 2013]. In the work presented here, we provide investigations of spatial and temporal variations of ozone production and its sensitivity to NO\textsubscript{x} and VOCs to provide a scientific basis to develop a non-uniform emission reduction strategy for O\textsubscript{3} pollution control in urban and suburban areas such as the greater Houston metropolitan area.

This work utilized observations made during the Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) campaign in Houston in September 2013. This field campaign is unique due to the comprehensive air sampling performed over a large spatial (urban and suburban areas in and around Houston) and temporal (entire month of September 2013) range. Measurements were collected from various platforms including the National Aeronautics and Space Administration (NASA) P-3B and B-200 aircraft, ground surface sites, and mobile laboratories. Eight surface
monitoring stations (Smith Point, Galveston, Manvel Croix, Deer Park, Channelview, Conroe, West Houston, and Moody Tower) were selected where the P-3B conducted vertical spirals (Figure 2) [DISCOVER-AQ whitepaper].

2. Methods

2.1 Ozone production Scenarios and Sensitivity

During the day, the photochemical O$_3$ production rate is essentially the production rate of NO$_2$ molecules from HO$_2$ + NO and RO$_2$ + NO reactions [Finlayson-Pitts and Pitts, 2000]. The net instantaneous photochemical O$_3$ production rate, P(O$_3$), can be written approximately as the following equation:

\[
P(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum k_{RO_2i+NO}[RO_{2i}][NO] - k_{OH+NO_2}[OH][NO_2][M] - P(\text{RONO}_2) - k_{HO_2+O_3}[HO_2][O_3] - k_{OH+O_3}[OH][O_3] - k_{O(1D)+H_2O}[O(1D)][H_2O] - \sum L(O_3 + \text{alkenes})
\]  

(1)

where, \( k \) terms are the reaction rate coefficients; RO$_{2i}$ is the individual organic peroxy radicals. The negative terms in Eq. (1) correspond to the reaction of OH and NO$_2$ to form nitric acid, the formation of organic nitrates, P(\text{RONO}_2), the reactions of OH and HO$_2$ with O$_3$, the photolysis of O$_3$ followed by the reaction of O(\(^1\)D) with H$_2$O, and O$_3$ reactions with alkenes. Ozone is additionally destroyed by dry deposition.

The dependence of O$_3$ production on NO$_x$ and VOCs can be categorized into two typical scenarios: NO$_x$ sensitive and VOC sensitive. The method proposed by Kleinman [2005b] was used to evaluate the O$_3$ production sensitivity using the ratio of L$_N$/Q, where L$_N$ is the radical loss via the reactions with NO$_x$ and Q is the total primary radical production. Because the radical production rate is approximately equal to the radical loss rate, this L$_N$/Q ratio represents the fraction of radical loss due to NO$_x$. It was found that when L$_N$/Q is significantly less than 0.5, the atmosphere is in a NO$_x$-sensitive regime, and when L$_N$/Q is significantly greater than 0.5, the atmosphere is in a more VOC-sensitive regime [Kleinman et al., 2001; Kleinman, 2005b]. Note that the contribution of organic nitrates impacts the cut-off value for L$_N$/Q to determine the ozone production sensitivity to NO$_x$ or VOCs and this value may vary slightly around 0.5 in different environments [Kleinman, 2005b].
2.2 Box Model Simulations

An observation-constrained box model with the Carbon Bond Mechanism Version 2005 (CB05) was used to simulate the oxidation processes in Houston during DISCOVER-AQ. Measurements made on the P-3B were used as input to constrain the box model. From the box model results, the ozone production rate and its sensitivity to NO\textsubscript{x} and VOCs were calculated allowing us to calculate ozone production efficiency at different locations and at different times of day.

CB05 is a well-known chemical mechanism that has been actively used in research and regulatory applications [Yarwood et al., 2005]. Organic species are lumped according to the carbon bond approach, that is, bond type, e.g., carbon single bond and double bond. Reactions are aggregated based on the similarity of carbon bond structure so that fewer surrogate species are needed in the model. Some organics (e.g., organic nitrates and aromatics) are lumped. The lifetime of alkyl nitrates is too long in CB05 and has been corrected in CB6r2 [Canty et al., 2015], but this should have minimal impact on our findings because the model is constrained to observations as indicated below.

The box model was run using measurements, including long-lived inorganic and organic compounds and meteorological parameters (temperature, pressure, humidity, and photolysis frequencies), from the NASA P-3B. One-minute archived data were used as model input (available at http://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html). The model ran for 24 hours for each data point to allow most calculated reactive intermediates to reach steady state, but short enough to prevent the buildup of secondary products. An additional lifetime of two days was assumed for some calculated long-lived species such as organic acids and alcohols to avoid unexpected accumulation of these species in the model. At the end of 24 hours, the model generated time series of OH, HO\textsubscript{2}, RO\textsubscript{2}, and other reactive intermediates. The box model covered the entire P-3B flight track during DISCOVER-AQ, including the eight science sites where the P-3B conducted spirals. Note that unlike a three-dimensional chemical transport model, the zero-dimensional box model simulations did not include advection and emissions. Although advection and emissions are certainly important factors for the air pollution formation, they can be omitted in the box model since all of the long-lived radical and O\textsubscript{3} precursors were measured and used to constrain the box model calculations. The box model analysis is necessary for ozone production and its sensitivity to NO\textsubscript{x} and VOCs because the box
model was constrained to measured species (e.g., NO, NO₂, CO, HCHO, etc.) and meteorological parameters (e.g., photolysis frequencies) that are essential to calculate ozone production rates. Even though there is good agreement in general between the box model and the 3D model, there are still some differences between the measurements and the output from the 3D model that are shown below, e.g., NOx, CO, HCHO and photolysis frequencies.

2.3 WRF-CMAQ Model Simulations

The WRF model was run from 18 August 2013 to 1 October 2013 with nested domains with horizontal resolutions of 36, 12, 4, and 1 km and 45 vertical levels. This work utilized results from the 4 km domain. The modeling domains are shown in Figure 3. WRF was run straight through (i.e., was not re-initialized at all) using an iterative technique developed at the EPA and described in Appel et al. (2014). Observational and analysis nudging were performed on all domains. Model output was saved hourly for the 36 and 12 km domains, every 20 minutes for the 4 km domain, and every 5 minutes for the 1 km domain. WRF and CMAQ configuration options and inputs are shown in Table 1.

WRF model results were used to drive the CMAQ model offline. The 2012 baseline anthropogenic emissions from the Texas Commission on Environmental Quality (TCEQ) were used as input to CMAQ. These emissions contain the most-up-to-date Texas anthropogenic emissions inventory and a compilation of emissions estimates from Regional Planning Offices throughout the US. Biogenic emissions were calculated online within CMAQ with Biogenic Emission Inventory System (BEIS). Lightning emissions were also calculated online within CMAQ. CMAQ was run with the process analysis tool to output ozone production rate (P(O₃)), ozone loss rate (L(O₃)), and net ozone production rate (net P(O₃)) as well as ozone production efficiency (OPE).

3. RESULTS

3.1 Photochemical O₃ Production Rate, Sensitivity, and Diurnal Variations

Figure 4 shows the net ozone production rate, net P(O₃), calculated using the box model results along the P-3B flight track for all flight days during the Houston deployment. There are several P(O₃) hotspots over the Houston Ship Channel located to the east/southeast of downtown Houston as well as downwind, over Galveston Bay. This is expected because of large emissions
of NOx and VOCs from the Houston Ship Channel, where the highest P(O3) was observed – up to ~140 ppbv hr\(^{-1}\). P(O3) values up to ~80-90 ppbv hr\(^{-1}\) were observed over Galveston Bay, mainly on September 25, 2013, consistent with high ozone levels observed across the Houston area on that day. Similar instantaneous ozone production rates have been observed in two previous studies in Houston in 2000 and 2006 [Kleinman et al., 2002a; Mao et al., 2010].

Figure 5 shows the indicator L\(_{\text{NO}}\)/Q of ozone production sensitivity along the P-3B flight track for all flight days during the Houston deployment. P(O3) was mainly VOC-sensitive over the Houston Ship Channel and its surrounding urban areas due to large NOx emissions. Over areas away from the center of the city with relatively low NOx emissions, P(O3) was usually NOx-sensitive. Vertical profiles of P(O3), L(O3), and net ozone production calculated using the box model results (Figure 6) show that:

1. RO\(_2\) + NO makes about the same amount of O\(_3\) as HO\(_2\) + NO in the model;
2. O\(_3\) photolysis followed by O(\(^{1}\)D)+H\(_2\)O is a dominant process for the photochemical ozone loss;
3. the maximum net P(O3) appeared near the surface below 1 km.

In the diurnal variations of P(O3), a broad peak in the morning with significant P(O3) in the afternoon was obtained on ten flight days during DISCOVER-AQ in Houston (Figure 7). High P(O3) mainly occurred with L\(_{\text{NO}}\)/Q > 0.5 (i.e., in the VOC sensitive regime). The diurnal variation of L\(_{\text{NO}}\)/Q indicates that P(O3) was mainly VOC sensitive in the early morning and then transitioned towards the NOx sensitive regime later in the day (Figure 8). High P(O3) in the morning was mainly associated with VOC sensitivity due to high NOx levels in the morning (points in the red circle in Figure 8). Although P(O3) was mainly NOx sensitive in the afternoon between 12:00 and 17:00 Central Standard Time, CST (UTC-6 hours), there were also periods and locations when P(O3) was VOC sensitive, e.g., the points with LN/Q > 0.5 between 12:00 and 17:00 (CST) in Figure 8.

Diurnal variations of ozone production rate at eight individual locations where the P-3B conducted vertical spirals show that the ozone production is greater than 10 ppb hr\(^{-1}\) on average at locations with high NOx and VOC emissions, such as Deer Park, Moody Tower and Channelview, while at locations away from the urban center with lower emissions, such as Galveston, Smith Point, and Conroe, the ozone production usually averaged less than 10 ppb hr\(^{-1}\) (Figure 9). The dependence of P(O3) on the NO mixing ratio ([NO]) shows that when [NO] is
less than ~1 ppbv, ozone production increases as the [NO] increases, i.e., P(\(O_3\)) is in NOx sensitive regime. When the NO mixing ratio is greater than ~1 ppbv, ozone production levels off, i.e., P(\(O_3\)) is in a NOx saturated regime (Figure 10). It was also found that at a given NO mixing ratio, a higher production rate of HOx results in a higher ozone production rate. Diurnal variations of the indicator of ozone production sensitivity to NOx and VOCs, L\(_{N/Q}\), at eight individual locations where the P-3B conducted vertical spirals show that (1) at Deer Park, P(\(O_3\)) was mostly VOC sensitive for the entire day; (2) at Moody Tower and Channelview, P(\(O_3\)) was VOC sensitive or in the transition regime; and (3) at Smith Point and Conroe, P(\(O_3\)) was mostly NOx sensitive for the entire day; and Galveston, West Houston, and Manvel Croix P(\(O_3\)) was VOC sensitive only in the early morning (Figure 11).

### 3.2 Ozone Production Efficiency

Ozone production efficiency (OPE) is defined as the number of molecules of oxidant Ox (= \(O_3 + NO_2\)) produced photochemically when a molecule of NOx (= NO + NO\(_2\)) is oxidized. It conveys information about the conditions under which \(O_3\) is formed and is an important parameter to consider when evaluating impacts from NOx emission sources [Kleinman et al., 2002]. The OPE can be deduced from atmospheric observations as the slope of a graph of Ox concentration versus the concentration of NOx oxidation products. The latter quantity is denoted as NO\(_x\) and is commonly measured as the difference between NO\(_y\) (sum of all odd-nitrogen compounds) and NOx, i.e. NO\(_z\) = NO\(_y\) - NOx.

Figure 12 shows the photochemical oxidant Ox as a function of NO\(_z\) during DISCOVER-AQ in Houston in 2013. The two data sets plotted here were collected on September 25 and 26, when high ambient ozone concentrations were observed, and for the data collected during all other flights. Note that the slopes obtained from these two data sets are essentially the same and an average OPE of ~8 is derived from the observations, meaning that 8 molecules of ozone were produced when one molecule of NOx was consumed. Even though higher ozone concentrations were observed on September 25 and 26, the OPE on these two days are not different from those in other flights, indicating the ozone event on these two days was not caused by a higher OPE, but mainly, by higher concentrations of ozone precursors (and thus higher ozone production rates) and background ozone as indicated by the intercepts in the regression of the two data sets in Figure 12. The high ozone observed on those days could also be due to slower ventilation and
different meteorological conditions such as a lower boundary layer height, northerly transport from inland air pollution source regions, stagnant conditions from the high-pressure system, and the bay and gulf breezes.

The OPE value of ~8 during DISCOVER-AQ in Houston in 2013 is greater than the average OPE value obtained during the Texas Air Quality Study in 2006 (TexAQS2006; OPE=5.9±1.2) [Neuman et al., 2009] and TexAQS2000 (OPE=5.4) [Ryerson et al., 2003]. One possible reason for this increased OPE is the continuous reduction in NO\textsubscript{x} emissions in Houston from 2000 to 2013 pushed NO\textsubscript{x} levels closer to 1 ppbv in 2013 (Figure S1), thus OPE increased since OPE increases as NO\textsubscript{x} decreases when the NO\textsubscript{x} level is greater than ~1 ppbv (Figure 13).

Houston area OPE values range from about a factor of 1.3 to 2 higher than the OPEs calculated from the DISCOVER-AQ 2011 study in Maryland, likely due to higher photochemical reactivity in Houston (Figure S4). The 2011 Maryland OPEs ranged from 3.4 to 6.1 when all measured data below 1 km are used (Ren, X., unpublished data). An OPE of ~8 was calculated [He et al., 2013] for the 2011 Maryland DISCOVER-AQ campaign for measured data below the 850 hPa level during vertical spirals with a strong linear correlation ($r^2> 0.8$) between \textit{O}_\textsubscript{3} and NO\textsubscript{z}. Additionally, OPEs of 7.7-9.7 were obtained from a ground site during the New England Air Quality Study (NEAQS) 2002 (Griffin et al., 2004).

When calculating ozone production efficiency using observed \textit{O}_\textsubscript{3} and NO\textsubscript{z}, it is important to know whether there is substantial loss of nitric acid (HNO\textsubscript{3}), because it can affect the OPE by reducing the NO\textsubscript{z} [Trainer et al., 1993; 2000; Neuman et al., 2009] and thus bias the OPE high. The derived OPE in Figure 12 is only valid when there is minimum loss of NO\textsubscript{z} (especially HNO\textsubscript{3}) from the source region to the point of observations. Neuman et al. [2009] found that $\Delta$CO/$\Delta$NO\textsubscript{y}, i.e., the slope in a CO versus NO\textsubscript{y} plot, is an indicator for distinguishing plumes with efficient \textit{O}_\textsubscript{3} formation from plumes with similarly high \textit{O}_\textsubscript{3} to NO\textsubscript{x} oxidation products correlation slopes caused by variable mixing of aged polluted air depleted in HNO\textsubscript{3}. A typical $\Delta$CO/$\Delta$NO\textsubscript{y} ranges from ~40 in background air to ~4-7 in fresh emission plumes in Houston [Neuman et al., 2009]. The $\Delta$CO/$\Delta$NO\textsubscript{y} was examined at different times of the day on September 25 and 26. The results indicate that the $\Delta$CO/$\Delta$NO\textsubscript{y} was about 6.2 (Figure 14a) throughout the day with variation between 6.0 and 7.0 (Figure 14). This demonstrates that the observed \textit{O}_\textsubscript{3} formation was from fresh plumes and was not caused by variable mixing of aged polluted air depleted in HNO\textsubscript{3}.
Using both the box model and CMAQ model results, OPE can also be calculated according to its definition, i.e., the net ozone formation rate divided by the formation rate of NO\textsubscript{2}. Net \(P(O_3)\) was calculated using Eq. (1), while the NO\textsubscript{2} formation rate is the sum of HNO\textsubscript{3} and organic nitrate formation rates. The agreement between the box model-derived and the CMAQ-derived OPEs is very good, with the mean OPEs of 14.8±7.4 in the box model and 16.6±8.1 in the CMAQ model. The dependence of OPE on NO\textsubscript{x} is also similar for both the box and CMAQ models (Figure 13). On average, the maximum of OPE appears at a NO\textsubscript{x} level around 1 ppbv. In general, if the NO\textsubscript{x} level is below 1 ppbv, OPE increases as the NO\textsubscript{x} level increases, while if the NO\textsubscript{x} level is above 1 ppbv, OPE decreases as the NO\textsubscript{x} level increases (Figure 13).

The OPE values calculated using the CMAQ and box model are greater than the values derived from the observations using the slope in the scatter plot of Ox versus NO\textsubscript{2} in Figure 12. This is expected because in the calculation of OPE using the box and CMAQ model results, a few ozone loss processes, such as ozone dry deposition and horizontal/vertical dispersion, were not considered. This could result in higher calculated ozone production rates using the model results.

Spatial variations of OPE demonstrate that except for a few hotspots over Downtown Houston and the Houston Ship Channel, most large OPEs appear away from the urban center, e.g., the northwest and southeast of the area, while in areas with high NO\textsubscript{x} emissions close to the urban center lower OPEs were generally observed (Figure 15). This is again consistent with the results in Figure 13 that the maximum of OPE appears at a NO\textsubscript{x} level around 1 ppbv.

### 4. Discussion and Conclusions

On average, ozone production \(P(O_3)\), was about 20-30 ppbv hr\(^{-1}\) in the morning and 5-10 ppbv hr\(^{-1}\) in the afternoon during DISCOVER-AQ in Houston in 2013. The diurnal variation of \(P(O_3)\) shows a broad peak in the morning with significant \(P(O_3)\) in the afternoon obtained on ten flight days in September 2013. High \(P(O_3)\) mainly occurred with \(L_{N/Q}\) greater than 0.5, i.e., in the VOC sensitive regime. Since \(P(O_3)\) depends on NO\textsubscript{x} levels and radical production rate, it increases as [NO] increases up to ~1 ppbv and then levels off with further increases of [NO]. At a given [NO], a higher production rate of HO\textsubscript{x} results in a higher ozone production rate. This has implications for the NO\textsubscript{x} control strategies in order to achieve the ozone control goal.
The DISCOVER-AQ campaign in Houston is unique because of its large spatial coverage and thus spatial variations of ozone production and its sensitivity to NOx and VOCs. Diurnal variations of \( P(O_3) \) at eight individual locations where the P-3B conducted vertical spirals show that the \( P(O_3) \) is on average more than 10 ppbv hr\(^{-1} \) at locations with high NOx and VOC emissions, such as Deer Park, Moody Tower, and Channelview, while at locations away from the urban center with lower emissions of ozone precursors such as Galveston, Smith Point, and Conroe, the ozone production rate is usually less than 10 ppbv hr\(^{-1} \) on average. Hotspots of \( P(O_3) \) were observed over Downtown Houston and the Houston Ship Channel due to significant emissions in these areas.

Ozone production tended more towards VOC sensitive in the morning with high \( P(O_3) \) and in general, NOx sensitive in the afternoon with some exceptions. It was found that during some afternoon time periods and locations, \( P(O_3) \) was VOC sensitive. The diurnal variation of \( L_{N/Q} \) indicates that \( P(O_3) \) was mainly VOC sensitive in the early morning and then transitioned towards the NOx sensitive regime later in the day. High \( P(O_3) \) in the morning was mainly associated with VOC sensitivity due to high NOx levels in the morning. Specifically, Deer Park was mostly VOC sensitive for the entire day, Moody Tower and Channelview were VOC sensitive or in the transition regime, and Smith Point and Conroe were mostly NOx sensitive for the entire day.

Based on the measurements on the P-3B, ozone production efficiency (OPE) was about 8 during DISCOVER-AQ 2013 in Houston. This OPE value is greater than the average OPE value (5.9±1.2) obtained during the Texas Air Quality Study in 2006 (TexAQS2006), likely due to the reduction in NOx emissions in Houston between 2006 and 2013 that pushed NOx levels closer to 1 ppbv in 2013 from higher NOx levels in previous years. The results from this work strengthen our understanding of \( O_3 \) production; they indicate that controlling NOx emissions will provide air quality benefits over the greater Houston metropolitan area in the long run, but in selected areas controlling VOC emissions will also be beneficial.

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2004.

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Table 1. WRF and CMAQ model options that were used in both the original and improved modeling scenarios.

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<thead>
<tr>
<th>Weather Research and Forecasting (WRF) Version 3.6.1 Model Options</th>
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<td><strong>Radiation</strong></td>
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<td><strong>Microphysics</strong></td>
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<td><strong>Nudging</strong></td>
<td>Observational and analysis nudging</td>
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<td><strong>Damping</strong></td>
<td>Vertical velocity and gravity waves damped at top of modeling domain</td>
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<td><strong>SSTs</strong></td>
<td>Multi-scale Ultra-high Resolution (MUR) SST analysis (~1 km resolution)</td>
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<td><strong>Meteorological Initial and Boundary Conditions and Analysis Nudging Inputs</strong></td>
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<td><strong>Observational Nudging Inputs</strong></td>
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<td><strong>Chemical Initial and Boundary Conditions</strong></td>
<td>Model for OZone and Related chemical Tracers (MOZART) Chemical Transport Model (CTM)</td>
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Figures:

Figure 1. Ozone production empirical kinetic modeling approach (EKMA) diagram using a box model results with NOx levels varying from 0-20 ppbv and VOC levels from 0-200 ppbv while the mean concentrations of other species and the speciation of NOx and VOCs observed during DISCOVER-AQ in Houston in 2013 were used to constrain the box model. This diagram clearly shows the sensitivity of ozone production to NOx and VOCs in Houston.
Figure 2. DISCOVER-AQ ground and spiral sites (yellow dots) during the September 2013 Houston campaign.

Figure 3. 36, 12, and 4 km CMAQ modeling domains (top); 4 and 1 km CMAQ modeling domains. The red dots show the NASA P-3B aircraft spiral locations (bottom).
Figure 4. Net ozone production rate, $\text{net } P(O_3)$ calculated using the box model results along the P-3B flight track during DISCOVER-AQ in Houston in 2013. The size of dots is proportional to $P(O_3)$. 
Figure 5. Ozone production sensitivity indicator, $L_N/Q$, along the P-3B flight track during DISCOVER-AQ in Houston in 2013. $P(O_3)$ is VOC-sensitive when $L_N/Q > 0.5$, and NOx-sensitive when $L_N/Q < 0.5$.

Figure 6. Vertical profiles of ozone production rate (left), ozone loss rate (middle), and net ozone production rate (right) during DISCOVER-AQ in Houston in 2013.
Figure 7. Diurnal variation of ozone production rate colored with the indicator $L_N/Q$ on ten flight days during DISCOVER-AQ in Houston in 2013. The solid red circles represent the median values in hourly bins of $P(O_3)$. Data are limited with the pressure altitude less than 1000 m to represent the lowest layer of the atmosphere.

Figure 8. Diurnal variations of the indicator $L_N/Q$ of ozone production rate sensitivity colored with ozone production rate and median hourly bins of $L_N/Q$ shown in solid red circles (left) and median hourly NO and NO$_2$ concentrations (right) below 1000 m during DISCOVER-AQ in Houston in 2013.
Figure 9. Diurnal variations of ozone production rate at eight individual spiral locations. Individual points are 1-min data colored with $L_N/Q$ and the linked red circles represent the median values in hourly bins of $P(O_3)$. Data are limited with the pressure altitude less than 1000 m to represent the lowest layer of the atmosphere.
Figure 10. Ozone production as a function of NO mixing ratio. Individual data points are the 1-minute averages and are colored with the production rate of HOx (= OH + HO_2) during DISCOVER-AQ in Houston in 2013. The linked solid red circles represent the median values in [NO] bins. Note a log scale is used for the x-axis.
**Figure 11.** Diurnal variations of the indicator of ozone production sensitivity to NOx and VOCs, $L_{N/Q}$, at eight individual spiral locations during DISCOVER-AQ in Houston in 2013. Individual points are 1-min data colored by $P(O_3)$ and the linked red circles represent the median values in hourly bins of $P(O_3)$. Data are limited with the pressure altitude less than 1000 m to represent the lowest layer of the atmosphere.
Figure 12. Photochemical oxidant, Ox (=O$_3$+NO$_2$) as a function of NOz (=NOy-NOx) during DISCOVER-AQ in Houston in 2013. Red dots are the data collected on September 25 and 26, 2013 when high ambient ozone concentrations were observed. Blue circles are the data collected during other flights. Data are limited with the pressure altitude less than 1000 m to represent the lowest layer of the atmosphere.
Figure 13. Ozone production efficiency (OPE) versus NOx in the box model (blue circles) and CMAQ model (pink dots) results. The linked blue circles show the median OPE values binned by NOx concentration in the box model, while the linked red triangles show the median OPE values binned by NOx concentration in the CMAQ model, OPE is calculated according to its definition as the net ozone formation rate divided by of the formation rate of NOz.
**Figure 14.** CO versus NOy and linear regression on September 25 and 26 at different times of the day: (a) 07:00-17:00 (all data), (b) 07:00-09:00, (c) 09:00-11:00, (d) 11:00-13:00, (e) 13:00-15:00, and (f) 15:00-17:00 (CST).

**Figure 15.** Ozone production efficiency (OPE) along the P-3B flight track during DISCOVER-AQ in Houston in 2013. OPE was calculated using the box model results as the ratio of net ozone formation rate to the formation rate of NOz.