Ozone production and its sensitivity to NO\textsubscript{x} and VOCs: results from the DISCOVER-AQ field experiment, Houston 2013

Gina M. Mazzuca\textsuperscript{1}, Xinrong Ren\textsuperscript{1,2}, Christopher P. Loughner\textsuperscript{2,3}, Mark Estes\textsuperscript{4}, James H. Crawford\textsuperscript{5}, Kenneth E. Pickering\textsuperscript{1,6}, Andrew J. Weinheimer\textsuperscript{7}, and Russell R. Dickerson\textsuperscript{1}

\textsuperscript{1}Department of Atmospheric and Oceanic Science, University of Maryland, College Park, MD 20742, USA  
\textsuperscript{2}Air Resources Laboratory, National Oceanic and Atmospheric Administration, College Park, MD 20740, USA  
\textsuperscript{3}Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20740, USA  
\textsuperscript{4}Texas Commission on Environmental Quality, Austin, TX 78711, USA  
\textsuperscript{5}NASA Langley Research Center, Hampton, VA 23681, USA  
\textsuperscript{6}NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA  
\textsuperscript{7}National Center for Atmospheric Research, Boulder, CO 80307, USA

Correspondence to: Xinrong Ren (ren@umd.edu)

Received: 11 March 2016 – Published in Atmos. Chem. Phys. Discuss.: 13 May 2016
Revised: 22 August 2016 – Accepted: 11 October 2016 – Published: 22 November 2016

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 Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality (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 (O\textsubscript{3}). O\textsubscript{3} production and its sensitivity to NO\textsubscript{x} and volatile organic compounds (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 NO\textsubscript{x} 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 NO\textsubscript{x} mixing ratio, were also evaluated. It was generally found that O\textsubscript{3} 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 O\textsubscript{3} in Houston. In the afternoon, O\textsubscript{3} production was found to be mainly NO\textsubscript{x}-sensitive with some exceptions. O\textsubscript{3} 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 NO\textsubscript{x}-sensitive for the entire day. It was also found that the control of NO\textsubscript{x} emissions has reduced O\textsubscript{3} concentrations over Houston but has led to larger OPE values. The results from this work strengthen our understanding of O\textsubscript{3} production; they indicate that controlling NO\textsubscript{x} 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.

1 Introduction

Understanding the nonlinear relationship between ozone production and its precursors is critical for the development of an effective ozone (O\textsubscript{3}) 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 nonlinear chemistry with respect to ozone precursors, i.e., nitrogen oxides (NO\textsubscript{x}) and volatile organic compounds (VOCs), that varies with time and location (Fig. 1). Understanding the nonlinear relationship between ozone production and its precursors is critical for the development of an effective ozone control strategy.

Sensitivity of ozone production to NO\textsubscript{x} 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 NO\textsubscript{x} and VOCs are emitted into the atmosphere from many sources. Depending on physical and chemical conditions, the production of ozone can be either NO\textsubscript{x}-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 NO\textsubscript{x} 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 US cities and found that ozone production rates vary from nearly 0 to 155 ppbv h\textsuperscript{-1}, with differences depending on the concentration of ozone precursors 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 (Fig. 2) (DISCOVER-AQ whitepaper, 2009).

2 Methods

2.1 Ozone production scenarios and sensitivity

During the day, the photochemical O\textsubscript{3} production rate is essentially the production rate of NO\textsubscript{2} molecules from HO\textsubscript{2}+NO and RO\textsubscript{2}+NO reactions (Finlayson-Pitts and Pitts, 2000). The net instantaneous photochemical O\textsubscript{3} production rate, \(P(O_3)\), can be written approximately as the following equation:

\[
P(O_3) = \text{net } P(O_3) (\text{ppb h}^{-1})\]

Figure 1. Ozone production empirical kinetic modeling approach (EKMA) diagram using box model results with NOx levels varying from 0 to 20 ppbv and VOC levels from 0 to 200 ppbv. The mean concentrations of other species and the speciation of NO\textsubscript{x} 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 NO\textsubscript{x} and VOCs in Houston.
\[
P(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum k_{RO_2+NO}[RO_2][NO] \\
- k_{OH+NO_2+M}[OH][NO_2][M] - P(RONO_2) \\
- k_{HO_2+O_3}[HO_2][O_3] - k_{OH+O_3}[OH][O_3] \\
- k_{O(1D)+H_2O}[O(1D)][H_2O] - L(O_3 + alkenes),
\]

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, \( P(RONO_2) \), the reactions of \( OH \) and \( HO_2 \) with \( O_3 \), the photolysis of \( O_3 \) followed by the reaction of \( O(1D) \) with \( H_2O \), 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 that, when \( L_N/Q \) is significantly greater than 0.5, the atmosphere is in a more \( VOC \)-sensitive regime (Kleinman et al., 2001, 2005b). Note that the contribution of organic nitrates impacts the cutoff 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 5 (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 \( NO_x \) 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 together. 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 h 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 2 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 h, the model generated time series of OH, HO$_2$, RO$_2$, and other reactive intermediates. The box model simulations 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$_3$ 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$_x$ and VOCs because the box model was constrained to measured species (e.g., NO, NO$_2$, CO, HCHO) 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 3-D model, there are still some differences between the measurements and the output from the 3-D model that are shown below, e.g., NO$_x$, CO, HCHO, and photolysis frequencies.

### 2.3 WRF–CMAQ model simulations

The Weather Research and Forecasting (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 Fig. 3. WRF was run straight through (i.e., was not re-initialized at all) using an iterative technique developed at the EPA and de-

---

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

<table>
<thead>
<tr>
<th>WRF Version Options</th>
<th>CMAQ Version Options</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Radiation</strong></td>
<td>Longwave: Rapid Radiative Transfer Model (RRTM)</td>
</tr>
<tr>
<td></td>
<td>Shortwave: Goddard</td>
</tr>
<tr>
<td><strong>Surface layer</strong></td>
<td>Pleim-Xiu</td>
</tr>
<tr>
<td><strong>Land surface model</strong></td>
<td>Pleim-Xiu</td>
</tr>
<tr>
<td><strong>Boundary layer</strong></td>
<td>Asymmetric Convective Model (ACM2)</td>
</tr>
<tr>
<td><strong>Microphysics</strong></td>
<td>WRF Single-Moment 6 (WSM-6)</td>
</tr>
<tr>
<td><strong>Nudging</strong></td>
<td>Observational and analysis nudging</td>
</tr>
<tr>
<td><strong>Damping</strong></td>
<td>Vertical velocity and gravity waves damped at top of modeling domain</td>
</tr>
<tr>
<td><strong>SSTs</strong></td>
<td>Multi-scale Ultra-high Resolution (MUR) SST analysis (~1 km resolution)</td>
</tr>
<tr>
<td><strong>Meteorological initial and boundary conditions and analysis nudging inputs</strong></td>
<td>NAM 12 km</td>
</tr>
<tr>
<td><strong>Observational nudging inputs</strong></td>
<td>NCEP ADP Global Surface and Upper Air Observational Weather Data</td>
</tr>
<tr>
<td><strong>Chemical mechanism</strong></td>
<td>Carbon Bond mechanism (CB05)</td>
</tr>
<tr>
<td><strong>Aerosol module</strong></td>
<td>Aerosols with aqueous extensions version 5 (AE5)</td>
</tr>
<tr>
<td><strong>Dry deposition</strong></td>
<td>M3DRY</td>
</tr>
<tr>
<td><strong>Vertical diffusion</strong></td>
<td>Asymmetric Convective Model 2 (ACM2)</td>
</tr>
<tr>
<td><strong>Emissions</strong></td>
<td>2012 TCEQ anthropogenic emissions Biogenic Emission Inventory System (BEIS) calculated within CMAQ</td>
</tr>
<tr>
<td><strong>Chemical initial and boundary conditions</strong></td>
<td>Model for Ozone and Related chemical Tracers (MOZART) chemical transport model (CTM)</td>
</tr>
</tbody>
</table>
VOCs from the Houston Ship Channel, where the highest
emissions are located to the east/southeast of downtown Houston as well as downwind, over Galveston Bay. This is expected because of large emissions of NOx from industrial offices throughout the US. Biogenic emissions were calculated online within CMAQ with the 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 \( P(O_3) \), ozone loss rate \( L(O_3) \), and net ozone production rate (net \( P(O_3) \)) as well as OPE.

3 Results

3.1 Photochemical \( O_3 \) production rate, sensitivity, and diurnal variations

Figure 4 shows the net \( P(O_3) \) calculated using the box model results along the P-3B flight track for all flight days during the Houston deployment. There are several \( P(O_3) \) hot spots 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 \( P(O_3) \) was observed – up to \( \sim 140 \) ppbv h\(^{-1}\). \( P(O_3) \) values up to \( \sim 80-90 \) ppbv h\(^{-1}\) were observed over Galveston Bay, mainly on 25 September 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., 2002; Mao et al., 2010).

Figure 5 shows the indicator \( L_N/Q \) of ozone production sensitivity along the P-3B flight track for all flight days during the Houston deployment. \( P(O_3) \) 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, \( P(O_3) \) was usually NOx-sensitive. Vertical profiles of \( P(O_3), L(O_3) \), and net ozone production calculated using the box model results (Fig. 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 \( O(D) + H_2O \) is a dominant process for the photochemical ozone loss,
3. the maximum net \( P(O_3) \) appeared near the surface below 1 km.

In the diurnal variations of \( P(O_3) \), a broad peak in the morning with significant \( P(O_3) \) in the afternoon was obtained on 10 flight days during DISCOVER-AQ in Houston (Fig. 7). High \( P(O_3) \) mainly occurred with \( L_N/Q > 0.5 \) (i.e., in the VOC-sensitive regime). 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 (Fig. 8). High \( P(O_3) \) in the morning was mainly associated with VOC sensitivity due to high NOx levels in the morning (points in the red circle in Fig. 8). Although \( P(O_3) \) was mainly NOx-sensitive in the
afternoon between 12:00 and 17:00 Central Standard Time (CST: UTC−6 h), there were also periods and locations when $P(O_3)$ was VOC-sensitive, e.g., the points with $L_N/Q > 0.5$ between 12:00 and 17:00 CST in Fig. 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 ppbv h$^{-1}$ on average at locations with high NO$\textsubscript{x}$ 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 ppbv h$^{-1}$ (Fig. 9). The dependence of $P(O_3)$ 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 a NO$_x$-sensitive regime. When the NO mixing ratio is greater than ~1 ppbv, ozone production levels off; i.e., $P(O_3)$ is in a NO$_x$-saturated regime (Fig. 10). It was also found that at a given NO mixing ratio a higher production rate of HO$_x$ results in a higher ozone production rate. Diurnal variations of the indicator of ozone production sensitivity to NO$_x$ 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 in the transition regime; (3) at Smith Point and Conroe $P(O_3)$ was mostly NO$_x$-sensitive for the entire day; and (4) at Galveston, West Houston, and Manvel Croix $P(O_3)$ was VOC sensitive only in the early morning (Fig. 11).

### 3.2 Ozone production efficiency

OPE is defined as the number of molecules of oxidant O$_3$ (= O$_3$ + NO$_2$) produced photochemically when a molecule of NO$_x$ (= 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 NO$_x$ emission sources (Kleinman et al., 2002). The OPE can be deduced from atmospheric observations as the slope of a graph of O$_3$ concentration vs. the concentration of NO$_x$ oxidation products. The latter quantity is denoted as NO$_x$, and is commonly measured as the difference between NO$_x$ (sum of all reactive-nitrogen compounds) and NO$_y$, i.e., NO$_x = NO_y - NO_x$. 

---

**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 10 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 12 shows the photochemical oxidant $O_x$ as a function of NO$_x$ during DISCOVER-AQ in Houston in 2013. The two data sets plotted here were collected on 25 and 26 September, 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 $\sim 8$ is derived from the observations, meaning that 8 molecules of ozone were produced when one molecule of NO$_x$ was consumed. Even though higher ozone concentrations were observed on 25 and 26 September, the OPEs on these 2 days are not different from those on other flights, indicating the ozone event on these 2 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 Fig. 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 $\sim 8$ during DISCOVER-AQ in Houston in 2013 is greater than the average OPE value obtained during the Texas Air Quality Study in 2006 (TexAQS 2006; $OPE = 5.9 \pm 1.2$) (Neuman et al., 2009) and TexAQS 2000.
was examined at different times of the day on September 25 and 26. The results indicate that the \( \Delta CO / \Delta NO_x \) was about 6.2 (Fig. 14a) throughout the day with variation between 6.0 and 7.0 (Fig. 14). This demonstrates that the observed \( O_3 \) formation was from fresh plumes and was not caused by variable mixing of aged polluted air depleted in HNO_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_2. Net \( P(O_3) \) was calculated using Eq. (1), while the NO_2 formation rate is the sum of HNO_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 \pm 7.4 in the box model and 16.6 \pm 8.1 in the CMAQ model. The dependence of OPE on NO_3 is also similar for both the box and CMAQ models (Fig. 13). On average, the maximum of OPE appears at a NO_3 level around 1 ppbv. In general, if the NO_3 level is below 1 ppbv, OPE increases as the NO_3 level increases, while if the NO_3 level is above 1 ppbv, OPE decreases as the NO_3 level increases (Fig. 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 scatterplot of \( O_3 \) vs. NO_2 in Fig. 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 when using the model results.

Spatial variations of OPE demonstrate that, except for a few hot spots 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_3 emissions close to the urban center lower OPEs were generally observed (Fig. 15). This is again consistent with the results in Fig. 13 that the maximum of OPE appears at a NO_3 level around 1 ppbv.

4 Discussion and conclusions

On average, \( P(O_3) \) was about 20–30 ppbv h\(^{-1}\) in the morning and 5–10 ppbv h\(^{-1}\) 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 10 flight days in September 2013. High \( P(O_3) \) mainly occurred with \( L_S/Q \) greater than 0.5, i.e., in the VOC-sensitive regime. Since \( P(O_3) \) depends on NO_3 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 \( H_2O \) results in a higher ozone production rate. This has implications for the NO_3 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 NO\textsubscript{x} 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 h\textsuperscript{-1} at locations with high NO\textsubscript{x} 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 h\textsuperscript{-1} on average. Hot spots 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, NO$_x$-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 NO$_x$-sensitive regime later in the day. High $P(O_3)$ in the morning was mainly associated with VOC sensitivity due to high NO$_x$ 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 NO$_x$-sensitive for the entire day.

Based on the measurements on the P-3B, OPE was about 8 during DISCOVER-AQ 2013 in Houston. This OPE value is greater than the average OPE value ($5.9 \pm 1.2$) obtained during TexAQS 2006, likely due to the reduction in NO$_x$ emissions in Houston between 2006 and 2013 that pushed NO$_x$ levels closer to 1 ppbv in 2013 from higher NO$_x$ levels in previous years. The results from this work strengthen our understanding of O$_3$ production; they indicate that controlling NO$_x$ emissions will provide air quality benefits over the greater Houston metropolitan area in the long run, and in selected areas controlling VOC emissions will also be beneficial.

5 Data availability

One-minute averaged aircraft data during DISCOVER-AQ in Houston in 2013 that were used to constrained the box model were obtained from the NASA DISCOVER-AQ data archive at http://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html. The box and CMAQ model output data are available upon request; please contact X. Ren (ren@umd.edu).
The Supplement related to this article is available online at doi:10.5194/acp-16-14463-2016-supplement.

Acknowledgements. The authors acknowledge the entire DISCOVER-AQ science team for the use of the P-3B measurement data in this work as well as Winston Luke and Paul Kelley at NOAA Air Resources Laboratory for helpful discussion. This work was funded by the Texas Commission on Environmental Quality (TCEQ) through the Air Quality Research Program (AQuRP) at University of Texas Austin (contract no. 14-020) and a NASA ACMAP grant (grant no. NNX15AE31G). The contents, findings, opinions, and conclusions are the work of the authors and do not necessarily represent the findings, opinions, or conclusions of the TCEQ or AQuRP. NASA AQAST supported Russell R. Dickerson.

Edited by: A. Carlton
Reviewed by: two anonymous referees

References


Stillman, S.: The use of \( \text{NO}_2 \), \( \text{H}_2\text{O}_2 \), and \( \text{HNO}_3 \) as indicators for \( \text{O}_3\text{--NO}_x \)-hydrocarbon sensitivity in urban locations, J. Geophys. Res., 100, 14175–14188, 1995.


