EXECUTIVE SUMMARY

Understanding the non-linear relationship between ozone (O_3) production and its precursors is critical for the development of an effective ozone 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. Sensitivity of ozone production to nitrogen oxides (NO_x) and volatile organic compounds (VOCs) represents a major uncertainty for oxidant photochemistry in urban areas and is expected to vary from location to location and at different times of the day.

The Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) campaign in Houston in August/September 2013 provided rich data sets to examine and improve our understanding of atmospheric photochemical oxidation processes related to the formation of secondary air pollutants like ozone and particulate matter (PM). In this project, an analysis of ozone production and its sensitivity to NO_x and VOCs is conducted. An observation-constrained box model based on the Carbon Bond mechanism, Version 5 (CB05), was used to study the photochemical processes along the NASA P-3B flight track as well as at eight surface sites where the P-3B conducted spiral profiles. Ozone production rates were calculated at different locations and at different times of day and its sensitivity to NO_x and VOCs were investigated. Ozone production efficiency (OPE), defined as the ratio of the ozone production rate to the NOx oxidation rate, was calculated using observations as well as box and CMAQ model results and its correlation with other parameters such as radical sources and NOx mixing ratio was evaluated.

The purpose of this work is to provide scientific information for policy decisions related to ozone control strategies for the State Implementation Plan (SIP) in Texas. This project specifically addresses one of the AQRP priority research areas: Improving the understanding of ozone and particulate matter (PM) formation, and quantifying the characteristics of emissions in Texas through analysis of data collected during the DISCOVER-AQ campaign. The following tasks were performed in this project and results from each task are lasted:

(1) To investigate spatial variations of ozone production and its sensitivity to NO_x and VOCs in Houston during DISCOVER-AQ.

Hotspots of ozone production, $P(O_3)$, over Downtown Houston and the Houston Ship Channel were observed due to significant emission sources in this area. Diurnal variations of ozone production rate at eight individual locations where the P-3B conducted vertical spirals show that the ozone production rate 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.

(2) To investigate temporal variations of ozone production and its sensitivity to NO_x and VOCs in Houston during DISCOVER-AQ.

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. It is noticed that high $P(O_3)$ mainly occurred with L_N/Q, where

L_N is the radical loss via the reactions with NOx and Q is the total primary radical production, is greater than 0.5, i.e., in the VOC sensitive regime.

Ozone production tended to be more VOC sensitive in the morning with high $P(O_3)$ of 30-50 ppbv hr^{-1}. The diurnal variation of L_N/Q indicates that $P(O_3)$ was mainly VOC sensitive in the early morning and then transited 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. Ozone production was generally NOx sensitive in the afternoon with spatial variations, even though there were periods when $P(O_3)$ was VOC sensitive. At Deer Park, $P(O_3)$ was mostly VOC sensitive for the entire day.

(3) To provide scientific information for a non-uniform emission reduction strategy to control O_3 pollution in Houston using spatial and temporal variations of ozone production and its sensitivity to NO_x and VOCs.

Based on the results from this project, a non-uniform emission reduction strategy, i.e., where/when to control what, for an O_3 pollution control plan in Houston was derived to provide scientific information for policy decisions. In general, O_3 production tends to be more VOC sensitive in the morning with high ozone production rates. The diurnal variation of L_N/Q indicates that $P(O_3)$ was mainly VOC sensitive in the early morning and then transited 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. This suggests that control of VOC may be an effective way to control O_3 in Houston. In the afternoon, O_3 production is more NOx sensitive with spatial variabilities. At Deer Park, ozone production was mostly VOC sensitive for the entire day. At Moody Tower and Channelview, ozone production was VOC sensitive or in the transition regime. At Smith Point and Conroe, ozone production was mostly NOx sensitive for the entire day.

(4) To calculate ozone production efficiency (OPE) at different locations using the number of ozone molecules produced per molecule of NOx consumed in the box and CMAQ models.

Ozone production efficiency (OPE) was about 8 during DISCOVER-AQ 2013 in Houston, i.e., 8 molecules of ozone were produced when one molecule of NOx was consumed. This OPE value is greater than the average OPE value (5.9±1.2) obtained during the Texas Air Quality Study in 2006 (TexAQS2006) [Neuman et al., 2009]. One possible reason for this increased OPE is the continuous reduction in NOx emissions in Houston between 2006 and 2013 pushed NOx levels closer to 1 ppbv in 2013, thus OPE increased since OPE increases as NOx decreases when the NOx level is greater than ~1 ppbv (Figure 2-11). This OPE value is about a factor of 1.5 to 2 higher than the OPE obtained in the DISCOVER-AQ 2011 study in Maryland due to higher photochemical reactivity in Houston.

The results from this work strengthen our understanding of O_3 production and development of the State Implementation Plan (SIP), which is essential to meet the primary and secondary National Ambient Air Quality Standards (NAAQS) for ozone.