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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozone Production and Its Sensitivity to NO_X and VOCs: Results from the DISCOVER-AQ Field Experiment, Houston 2013" *by* Gina M. Mazzuca et al.

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Response to Anonymous Referee #1: 02 June 2016

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 with track change.

1) Review of "Ozone production and its sensitivity to NOX 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

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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 NOX and VOC contribution to O3 production the authors should provide NOX 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 NOx 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 NOx, ethane, and propene at two monitoring sites near the Houston Ship Channel.

Figure 1 caption: Time series of NO, NOx, ethane and propene concentrations at the Deer Park and Clinton sites from 1998 to 2014. The Deer Park site is located in 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.

Figure 2 caption: Diurnal variations of NOx (left) and OH reactivity (Right) in Houston (linked blue circles) during DAQ2013 and in Maryland (linked red triangles) during DAQ2011.

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, NOZ, 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 caption. 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 2 caption. 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.

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 than 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 (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. 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 7-3.

Table 3 caption. 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 4 caption. 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.

Figure 3 caption. 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 2, 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 caption. 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 14 (now 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 5 (13) caption. 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.

Please also note the supplement to this comment:

http://www.atmos-chem-phys-discuss.net/acp-2016-215/acp-2016-215-AC1-supplement.pdf

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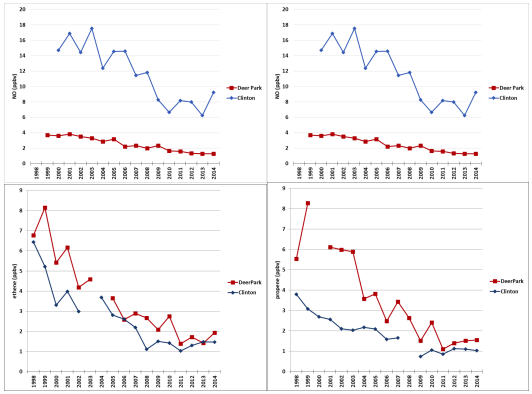

Fig. 1. Fig1:Time series of NO, NOx, ethane and propene concentrations at the Deer Park and Clinton sites from 1998 to 2014.

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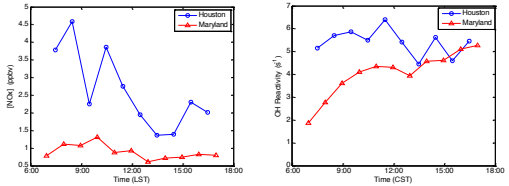

Fig. 2. Fig2:Diurnal variations of NOx (left) and OH reactivity (Right) in Houston (linked blue circles) during DAQ2013 and in Maryland (linked red triangles) during DAQ2011.

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	Surface Ozone (ppbv)
MB	9.5
NMB (%)	39
NME (%)	51
RMSE	15
GE	12

Fig. 3. 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

		O_3	CO	CH_2O	ISO	NO2	NO	NOy
Model	MB	0.8	-5.8	-0.3	-0.02	-0.5	-0.3	0.04
	NMB	1.4	-4.8	-16	-7.7	-39	-66	1.3
	NME	15	17	37	70	70	84	61
	RMSE	12	35	1.4	0.7	3.1	2.2	4.7

Fig. 4. 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, etc.

Mean Bias (MB)	$MB = \frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)$
Normalized Mean Bias (NMB)	$NMB = \frac{\sum_{i=1}^{N}(M_i - O_i)}{\sum_{i=1}^{N} O_i} \times 100\%$
Normalized Mean Error (NME)	$NME = \frac{\sum_{i=1}^{N}\lvert M_i - O_i\rvert}{\sum_{i=1}^{N} O_i} \times 100\%$
Root Mean-Square Error (RMSE)	$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(M_i - O_i)^2}$
Gross Error (G)	$GE = \frac{1}{N}\sum_{i=1}^{N}\lvert M_i - O_i\rvert$

Fig. 5. 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.

	2 m Temperature (K)		10 m Wind Speed (m/s)		10 m Wind Direction (deg)	
		Model		Model		Model
MB		0.2		-0.8		32
NMB (%)		0.1		-17		26
NME (%)		0.4		36		26
RMSE		1.6		2.3		51
GE		1.2		1.7		32

Fig. 6. 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

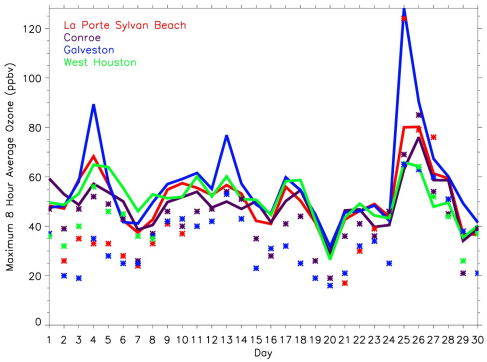

Fig. 7. Fig3:Observed (*) and CMAQ simulated (solid lines) maximum 8 hour average ozone at La Porte Sylvan Beach (red), Conroe (purple), Galveston (blue), and West Houston (green) during September 2013.

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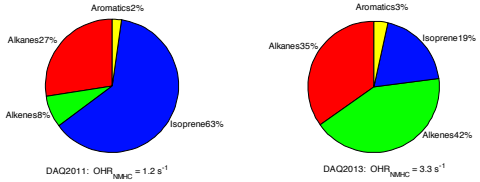

Fig. 8. Fig4:Distributions of OH reactivity due to non-methane hydrocarbons in DISCOVER-AQ 2011 in Maryland (left) and 2013 in Houston (right).

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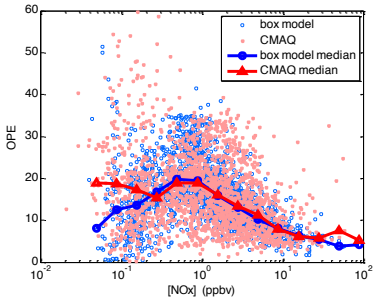

Fig. 9. Fig5:Ozone production efficiency (OPE) versus NOx in the box model (blue circles) and the CMAQ model pink dots) results.

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