

Supporting Information for:

Ozone Production and Its Sensitivity to NO_x and VOCs: Results from the DISCOVER-AQ Field Experiment, Houston 2013

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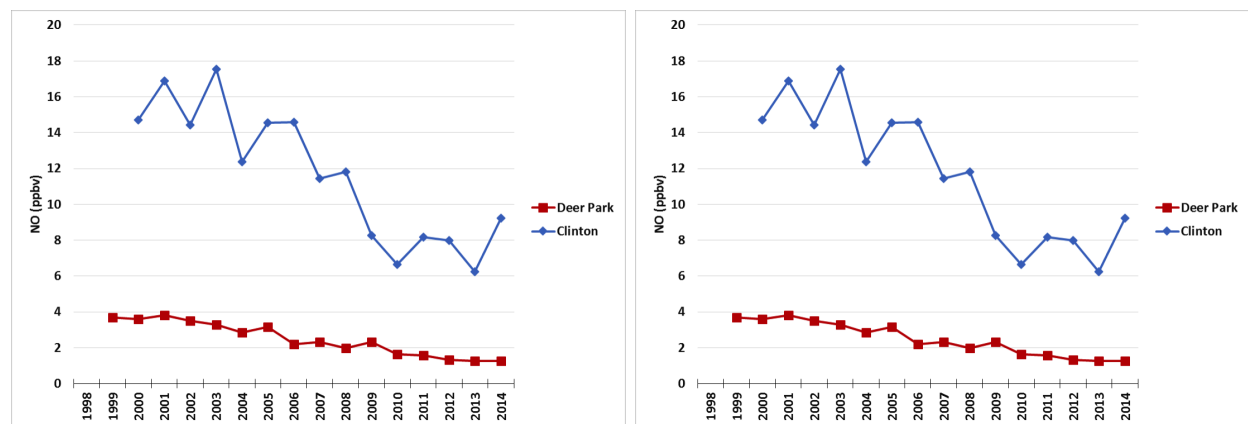
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SI 1.

Both NO_x and VOC levels in Houston have been continuously decreasing in the past 15-20 years as shown in Figure 1, the time series of NO_x, ethane, and propene at two monitoring sites near the Houston Ship Channel.



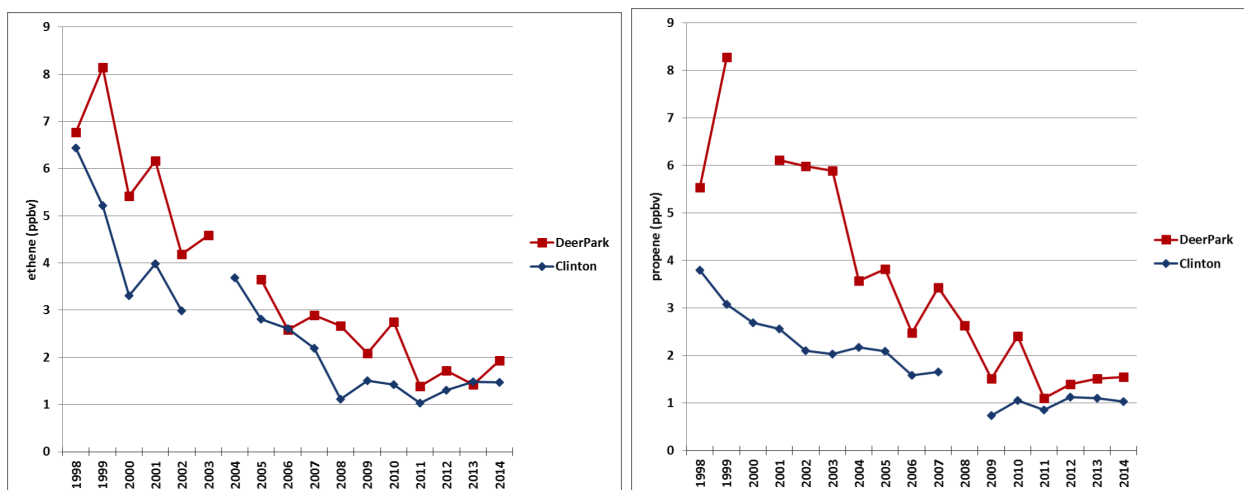


Figure S1. Time series of NO, NO_x, ethane and propene concentrations at the Deer Park and Clinton sites from 1998 to 2014. The Deer Park site is located in southeast of the Ship Channel. The Clinton site is located on the northwestern end of the Ship Channel. Each data point represents an average of 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 NO_x* data collected hourly using chemiluminescence sampler with molybdenum catalyst to convert NO_x* (not true NO_x 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 NO_x 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 NO_x levels throughout the day. For OH reactivity, it is greater in Houston than in Maryland in the morning, but is comparable in both location 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 NO_x levels and different VOC sources in Houston and Maryland are responsible for the different OPE values in the two areas.

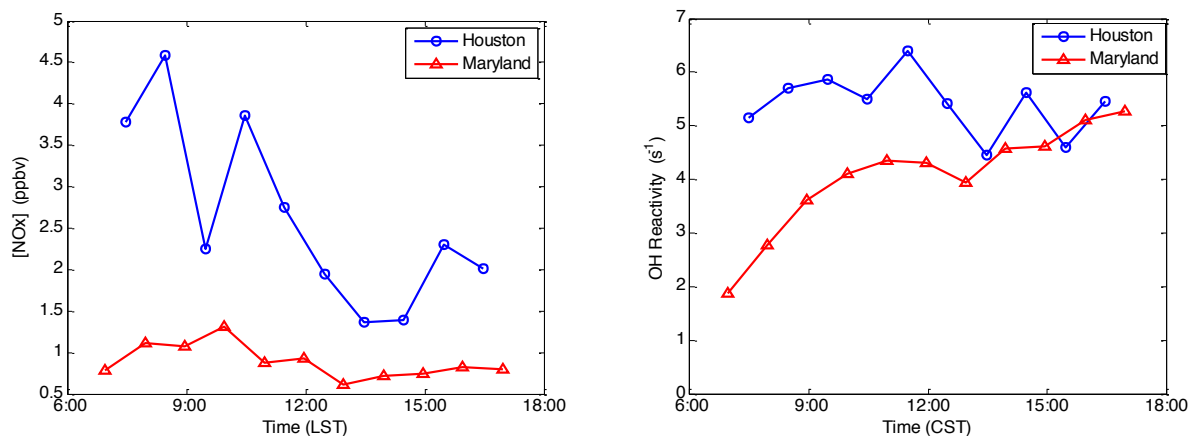


Figure S2. Diurnal variations of NO_x (left) and OH reactivity (Right) in Houston (linked blue circles) during DAQ2013 and in Maryland (linked red triangles) during DAQ2011.

SI 2.

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 NO_y 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 S1. 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.

	Surface Ozone (ppbv)
MB	9.5
NMB (%)	39
NME (%)	51

RMSE	15
GE	12

Table S2. 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 NO_y covering measurements made onboard the NASA P-3B aircraft on all flight days during the DISCOVER-AQ field campaign

		O ₃	CO	CH ₂ O	ISO	NO ₂	NO	NO _y
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

SI 3.

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 Table S3. CMAQ simulated a high bias in surface and aloft ozone (Table S1). CMAQ also simulated a low bias in CO, CH₂O, isoprene, NO₂, and NO aloft and a high bias in NO_y aloft (Table S2). 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 S3.

Table S3. 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.

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)	$NME = \frac{\sum_{i=1}^N M_i - O_i }{\sum_{i=1}^N O_i} \times 100\%$
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 M_i - O_i $
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Table S4. 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.

	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

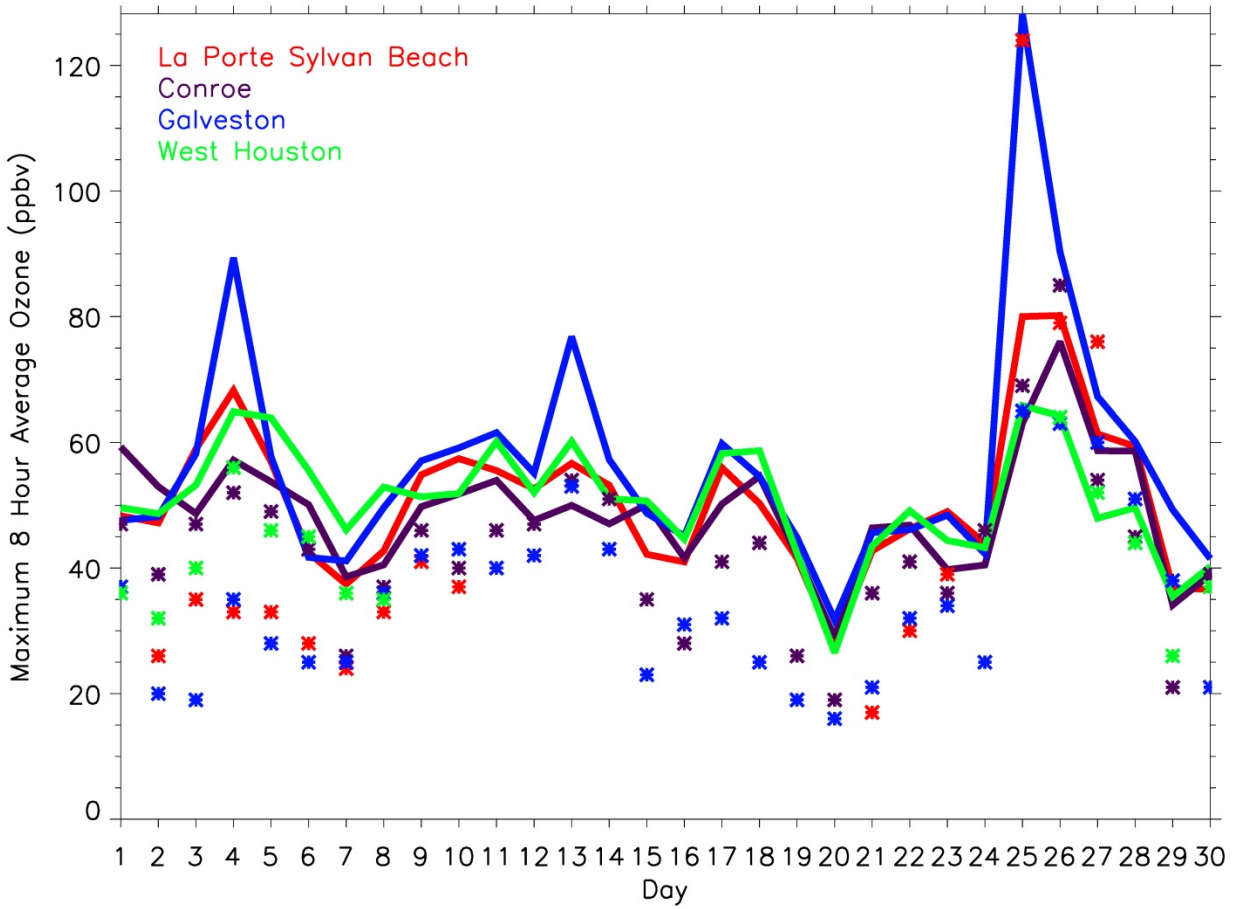


Figure S3. Observed (*) and CMAQ simulated (solid lines) maximum 8 hour average ozone at La Porte Sylvan Beach (red), Conroe (purple), Galveston (blue), and West Houston (green) during September 2013.

SI 4.

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.

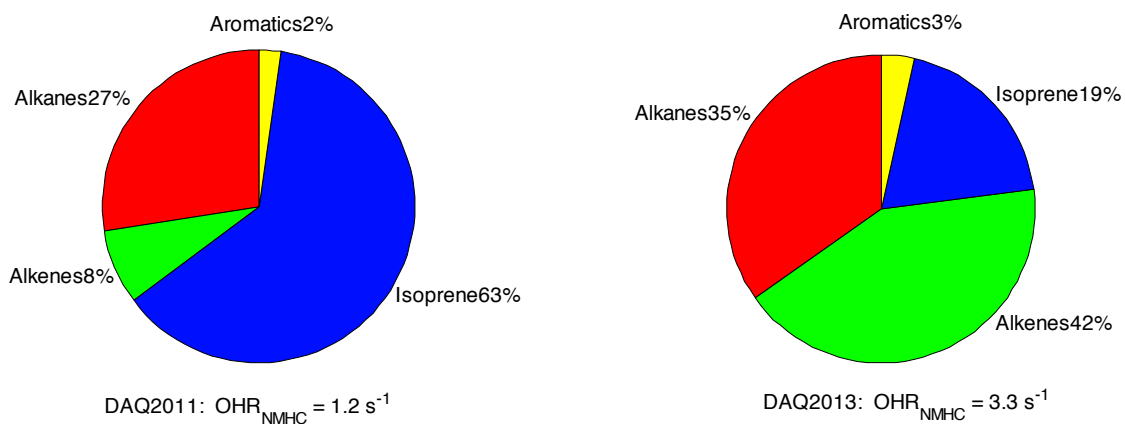


Figure S4. Distributions of OH reactivity due to non-methane hydrocarbons in DISCOVER-AQ 2011 in Maryland (left) and 2013 in Houston (right).