Southeast Texas Photochemical Modeling Technical Committee meeting

Modeling the uncertainty of several VOC and its impact on simulated VOC and ozone in Houston, Texas

Pan, S., Choi, Y. (ychoi6@uh.edu), Roy, A., Li, X., Jeon, W., and Souri, A.H.

Department of Earth and Atmospheric Sciences
University of Houston

October 19, 2015

Introduction

- VOCs can be a significant contributor to ground-level ozone in urban areas, where ozone is typically VOC-sensitive.
- VOCs show significant temporal and spatial variations; the uncertainty of VOC emissions contributes to simulated ozone bias in models.
- Houston is characterized by high population, a large cluster of petrochemical industries and rich biogenic sources. It is classified as a nonattainment area for ozone.
- WRF-SMOKE-CMAQ was used to study uncertainty of the simulated VOC and surface ozone concentrations in southeast Texas during September 2013.

Data and Model

Model set-up:

- WRF v3.5
- SMOKE v3.1 with EPA 2008 NEI
- CMAQ v5.0.1 with CB-05
- Initial and boundary conditions were obtained from real-time Air Quality Forecasting system at UH (http://spock.geosc.uh.edu/)

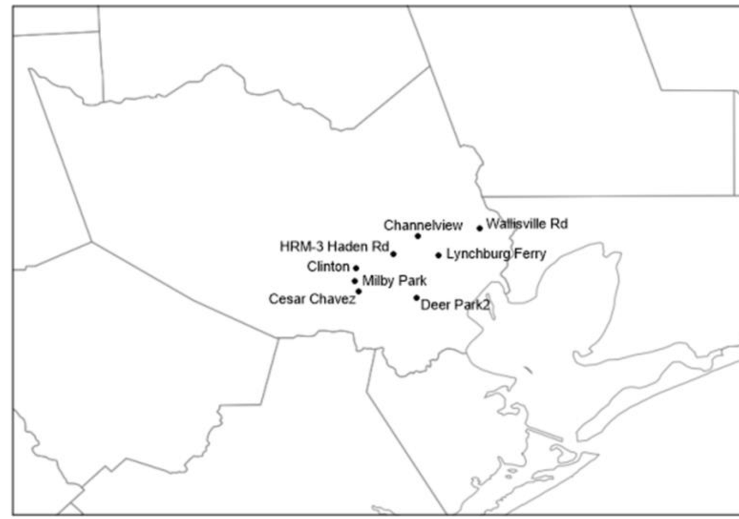


Figure 1. Location of the VOC monitoring sites in Houston industrial regions.

Data

- Model simulations
  - BASE: CMAQ v5.0.1
  - SENS: CMAQ v5.0.1 with adjusted VOC emissions
- TCEQ Auto-GC VOC measurements
- TCEQ CAMS measurements
- OMI HCHO remote sensing data
- DISCOVER-AQ HCHO aircraft data

Methodology

Procedures

- Run BASE model simulation
- Evaluation of Six VOCs between BASE and Auto-GC data
- Modeled-to-observed ratio at each site and a site-average ratio were calculated for each VOC. These ratios adjust emissions
- Run SENS model simulation
- Evaluate simulated VOC and ozone

Evaluation of six VOC species

- BASE simulation over-predicted ethylene, while under-predicting isoprene and ethane.

Table 1a. Evaluation for BASE and Auto-GC

Species	Site name	N	Corr	IOA	RMSE	MAE	MB	OM	MM	MM/OM
Ethylene	ALL	4776	0.25	0.42	4.9	2.2	1.14	1.67	2.81	1.68
	Channelview	526	0.41	0.49	3.2	2.1	1.26	1.72	2.98	1.73
	Deer Park2	512	0.47	0.62	2.5	1.3	0.46	1.14	1.60	1.40
	HRM-3 Haden Rd	576	0.13	0.25	8.5	3.4	1.31	2.68	3.99	1.49
	Milby Park	641	0.60	0.75	1.8	1.2	0.49	1.36	1.85	1.36
	Clinton	625	0.53	0.65	1.8	1.1	0.51	1.28	1.79	1.40
	Wallisville Rd	614	0.30	0.52	3.6	2.0	−0.06	2.11	2.05	0.97
	Lynchburg Ferry	641	0.28	0.35	8.8	5.3	4.59	1.99	6.58	3.31
	Cesar Chavez	641	0.55	0.71	1.5	0.9	0.39	1.10	1.49	1.35
Ethane	ALL	4776	0.40	0.51	9.2	5.1	−4.32	7.83	3.52	0.45
	Channelview	526	0.52	0.55	6.6	4.4	−4.18	7.24	3.06	0.42
	Deer Park2	512	0.38	0.52	5.6	3.2	−1.97	5.23	3.26	0.62
	HRM-3 Haden Rd	576	0.43	0.56	7.7	5.2	−4.45	8.67	4.22	0.49
	Milby Park	641	0.45	0.49	9.1	5.6	−5.39	8.18	2.79	0.34
	Clinton	625	0.33	0.49	7.1	4.7	−4.24	6.87	2.63	0.38
	Wallisville Rd	614	0.32	0.48	15.1	7.8	−6.46	10.82	4.37	0.40
	Lynchburg Ferry	641	0.44	0.56	9.4	5.2	−3.64	8.03	4.39	0.55
	Cesar Chavez	641	0.46	0.51	8.6	4.4	−3.81	7.16	3.35	0.47
Isoprene	ALL	4352	0.23	0.44	0.4	0.2	−0.20	0.31	0.10	0.32
	Channelview	526	0.65	0.58	0.3	0.3	−0.25	0.36	0.11	0.31
	Deer Park2	512	0.32	0.49	0.3	0.2	−0.14	0.22	0.08	0.36
	HRM-3 Haden Rd	576	0.07	0.45	0.9	0.6	−0.58	0.66	0.09	0.14
	Milby Park	217	0.34	0.52	0.2	0.2	−0.13	0.18	0.05	0.28
	Clinton	625	0.21	0.49	0.3	0.2	−0.18	0.24	0.07	0.29
	Wallisville Rd	614	0.55	0.66	0.3	0.2	−0.11	0.27	0.17	0.63
	Lynchburg Ferry	641	0.33	0.54	0.2	0.1	−0.03	0.16	0.12	0.75
	Cesar Chavez	641	0.35	0.53	0.3	0.2	−0.19	0.29	0.10	0.34

Notation: N – Number of data points; Corr – Correlation; IOA – Index of Agreement; RMSE – Root Mean Square Error; MAE – Mean Absolute Error; MB – Mean Bias; OM – Observed Mean; MM – (Base case) Model Mean; MM/OM – (Base case) Model Mean divided by Observed Mean. Units for RMSE/MAE/MB/OM/MM: ppb.

Evaluation of six VOC species

- BASE simulation over-predicted benzene, toluene and xylene.

Table 1b. Evaluation for BASE and Auto-GC

Species	Site name	N	Corr	IOA	RMSE	MAE	MB	OM	MM	MM/OM
Benzene	ALL	4766	0.18	0.34	1.5	0.5	0.17	0.44	0.61	1.39
	Channelview	526	0.21	0.41	0.9	0.6	0.23	0.51	0.74	1.45
	Deer Park2	511	0.27	0.44	0.8	0.2	0.02	0.27	0.29	1.07
	HRM-3 Haden Rd	576	0.29	0.31	1.7	0.9	0.76	0.43	1.19	2.77
	Milby Park	641	0.56	0.73	0.5	0.3	0.00	0.39	0.39	1.00
	Clinton	625	0.29	0.48	0.8	0.4	−0.10	0.48	0.38	0.79
	Wallisville Rd	605	0.52	0.59	0.5	0.3	0.21	0.23	0.43	1.87
	Lynchburg Ferry	641	0.10	0.24	3.3	1.4	0.45	0.79	1.24	1.57
	Cesar Chavez	641	0.59	0.66	0.5	0.3	−0.20	0.43	0.23	0.53
Toluene	ALL	4766	0.32	0.46	1.5	0.8	0.57	0.64	1.22	1.91
	Channelview	526	0.35	0.34	1.2	0.8	0.54	0.65	1.19	1.83
	Deer Park2	511	0.35	0.53	1.0	0.5	0.17	0.53	0.70	1.32
	HRM-3 Haden Rd	576	0.27	0.32	2.5	1.6	1.32	0.68	2.00	2.94
	Milby Park	641	0.51	0.59	1.3	0.8	0.63	0.76	1.38	1.82
	Clinton	625	0.31	0.41	1.4	0.9	0.63	0.72	1.34	1.86
	Wallisville Rd	605	0.60	0.52	0.9	0.5	0.46	0.31	0.77	2.48
	Lynchburg Ferry	641	0.31	0.40	1.8	1.1	0.87	0.46	1.33	2.89
	Cesar Chavez	641	0.50	0.60	1.5	0.6	−0.05	1.01	0.96	0.95
Xylene	ALL	4766	0.34	0.51	0.7	0.4	0.26	0.35	0.61	1.74
	Channelview	526	0.34	0.51	0.5	0.3	0.09	0.42	0.51	1.21
	Deer Park2	511	0.62	0.61	0.4	0.3	0.22	0.20	0.42	2.10
	HRM-3 Haden Rd	576	0.12	0.29	1.3	0.7	0.31	0.48	0.80	1.67
	Milby Park	641	0.52	0.57	0.8	0.5	0.44	0.37	0.81	2.19
	Clinton	625	0.30	0.41	0.8	0.5	0.37	0.42	0.79	1.88
	Wallisville Rd	605	0.63	0.48	0.5	0.3	0.26	0.13	0.39	3.00
	Lynchburg Ferry	641	0.40	0.57	0.7	0.4	0.27	0.30	0.57	1.90
	Cesar Chavez	641	0.60	0.75	0.5	0.3	0.10	0.44	0.54	1.23

Notation: N – Number of data points; Corr – Correlation; IOA – Index of Agreement; RMSE – Root Mean Square Error; MAE – Mean Absolute Error; MB – Mean Bias; OM – Observed Mean; MM – (Base case) Model Mean; MM/OM – (Base case) Model Mean divided by Observed Mean. Units for RMSE/MAE/MB/OM/MM: ppb.

VOC emissions adjustment

Increase:
Isoprene
Ethane

Decrease:
Ethylene
Benzene
Toluene
Xylene

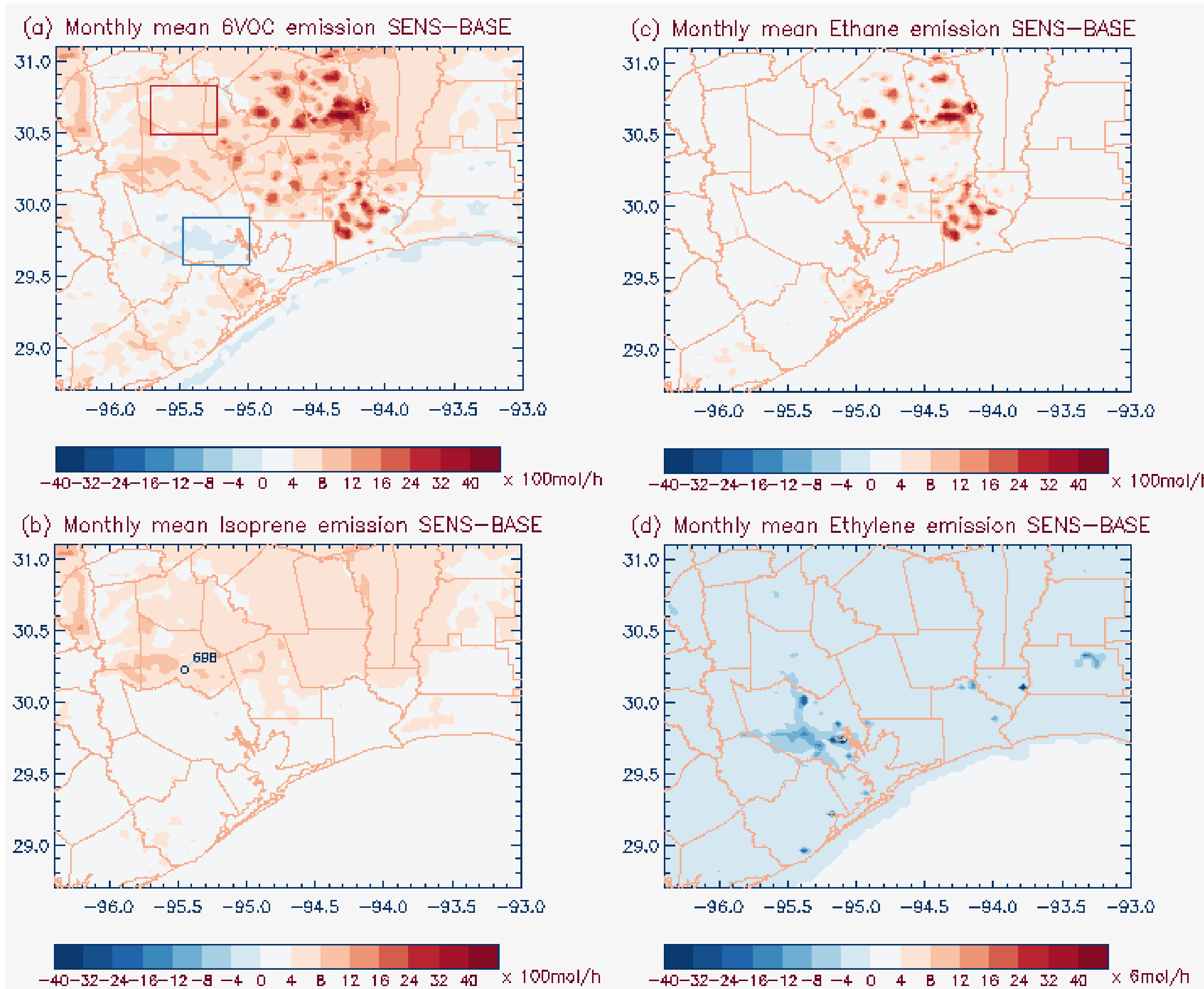


Figure 2. The difference between monthly mean surface adjusting emissions (SENS) and baseline emissions (BASE) for September 2013 for (a) sum of six VOC species; (b) Isoprene; (c) Ethane and (d) Ethylene (Note the different color-bar scales for Ethylene).

Improvement of VOC simulation after emission adjustment (1)

Adjusted model better reproduced variability in OMI HCHO columns, and also slightly better reproduced aircraft HCHO concentrations.

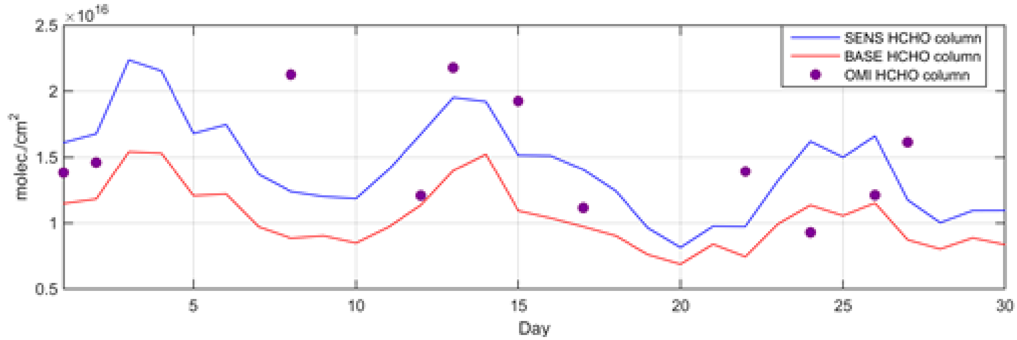


Figure 3a. Time series of averaged HCHO column between OMI measurements, BASE and SENS simulation. Only HCHO columns over the land part of research domain were considered.

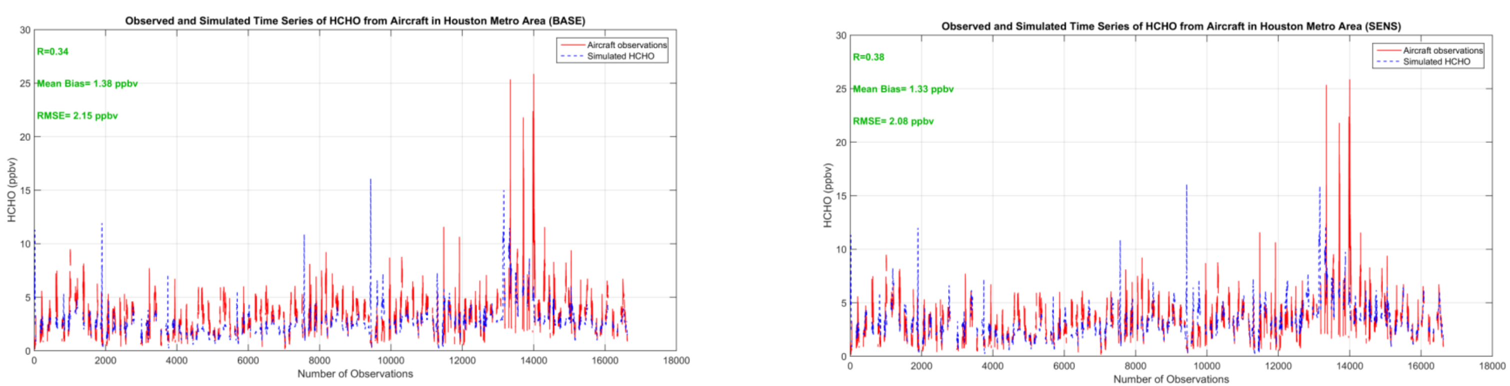
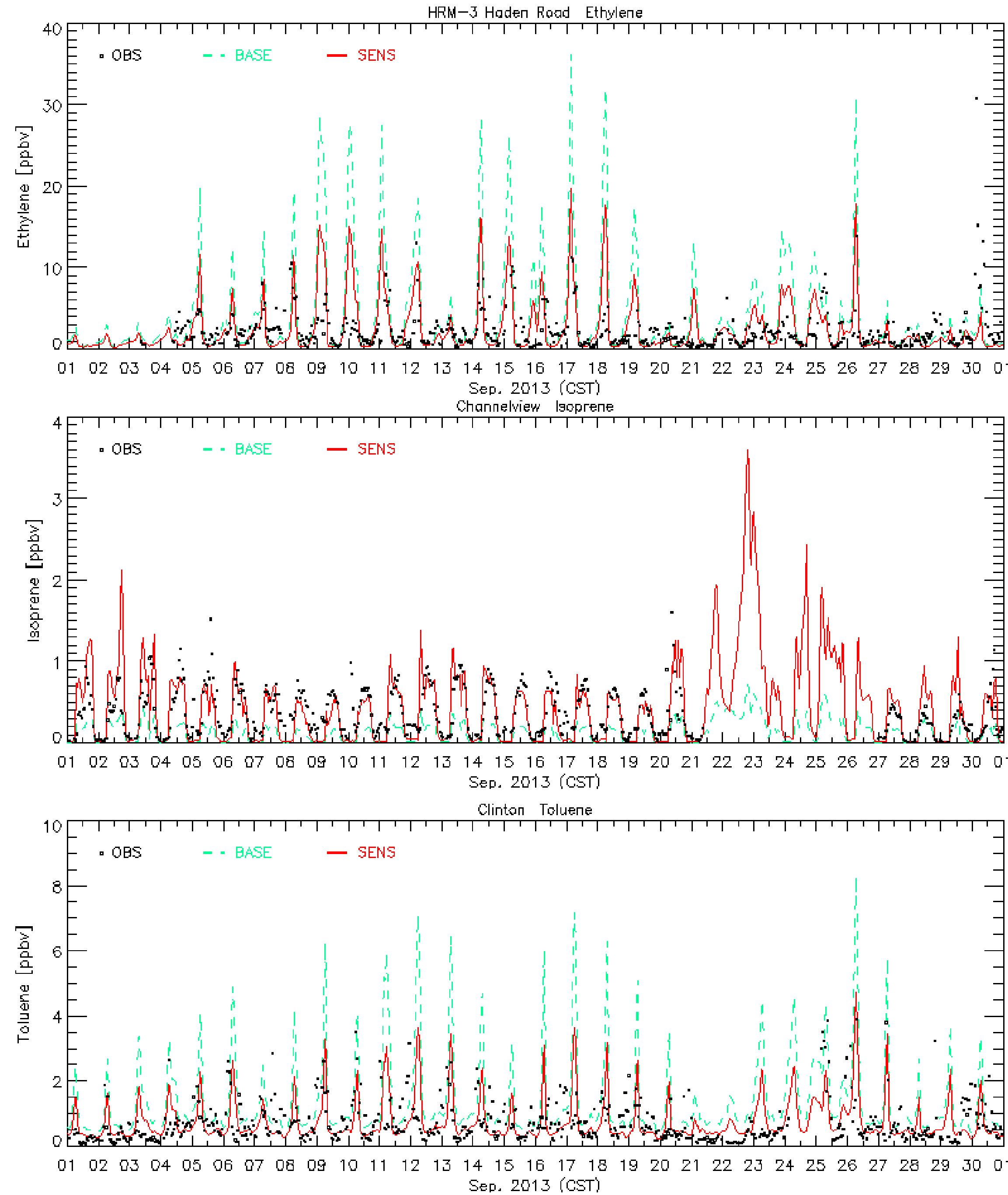


Figure 3b. Time series comparisons of HCHO mixing ratios between Aircraft measurements, BASE and SENS simulation.

Improvement of VOC simulation after emission adjustment (2)



mitigating mean bias substantially

Figure 4. Time series of several VOC mixing ratios between Auto-GC measurements (OBS), BASE and SENS simulations.

Improvement of VOC simulation after emission adjustment (3)

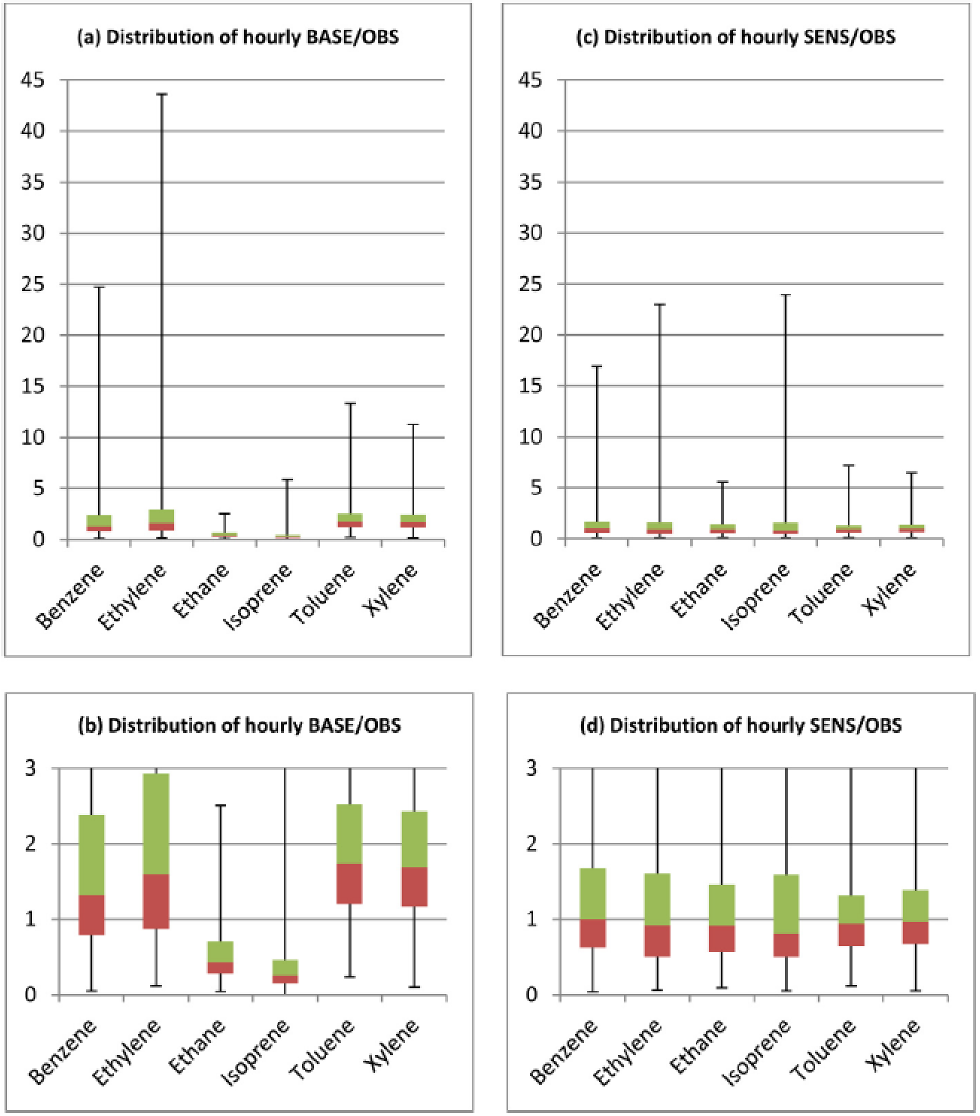


Figure 5. Distribution of the hourly ratios of 8 sites averaged model simulated values to Auto-GC measurements (OBS).

(a) BASE to OBS;
(b) same as (a), with zoomed;
(c) SENS to OBS;
(d) same as (c), with zoomed.

Box tops, middles and bottoms for 75^{th}, 50^{th} and 25^{th} percentile.

The distribution ranges of emission-reduced species became significantly smaller. Also, the medians became to 1 for six VOCs.

Change in simulated ozone (1)

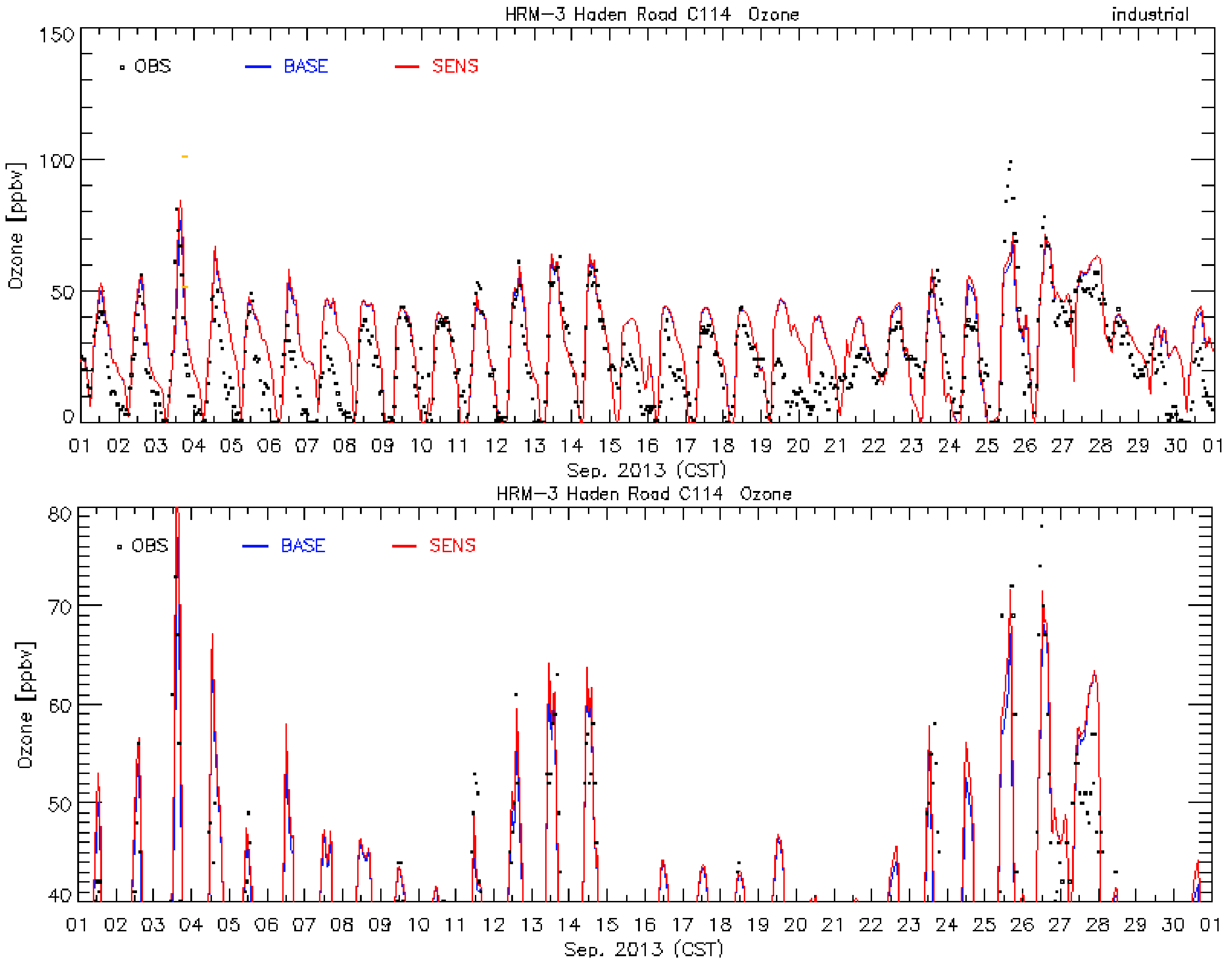
Table 2. Ozone statistics between observation, BASE and SENS simulations

Site name	N	B Corr	B IOA	B MB	OM	BM	SM	Corr D	IOA D	MB D
ALL	33,308	0.73	0.80	8.3	24.4	32.7	33.2	0	0	0.4
Channelview	656	0.74	0.81	8.1	21.7	29.8	30.2	0.01	0	0.4
Deer Park2	656	0.76	0.84	5.9	25.5	31.5	31.9	0	0	0.4
HRM-3 Haden Rd	713	0.77	0.85	5.8	23.3	29.0	29.5	0.01	0.01	0.4
Clinton	708	0.70	0.81	5.1	22.3	27.3	27.8	0.01	0.01	0.5
Wallisville Rd	714	0.78	0.87	3.3	26.1	29.4	29.8	0	0	0.4
Lynchburg Ferry	707	0.74	0.84	5.3	23.8	29.1	29.5	0	−0.01	0.3
UH WG Jones Forest	652	0.72	0.84	−0.7	29.3	28.5	29.5	0	0	0.9
Conroe Relocated	714	0.77	0.87	3.0	28.2	31.2	32.0	0	0	0.8
Northwest Harris Co.	704	0.80	0.85	7.8	22.6	30.5	31.3	0	0	0.9

Notation: N – Number of data points; B Corr, B IOA, B MB – Base case Correlation, Index of Agreement, Mean Bias; OM – Observed Mean; BM – Base case model Mean; SM – Sensitivity case model Mean; Corr D, IOA D, MB D – Differences of Correlation, Index of Agreement, Mean Bias between Sensitivity case and Base case; Units for B MB/OM/BM/SM/MB D: ppb.

Simulated monthly mean ozone showed a minor change: a 0.4 ppb or 1.2% increase.

Change in simulated ozone (2)



A change of more than 5 ppb was seen in hourly peaked ozone, moving predictions closer to observations.

Figure 6. Time series of ozone concentrations between CAMS measurements (OBS), BASE and SENS simulations.

Process Analysis of Ozone

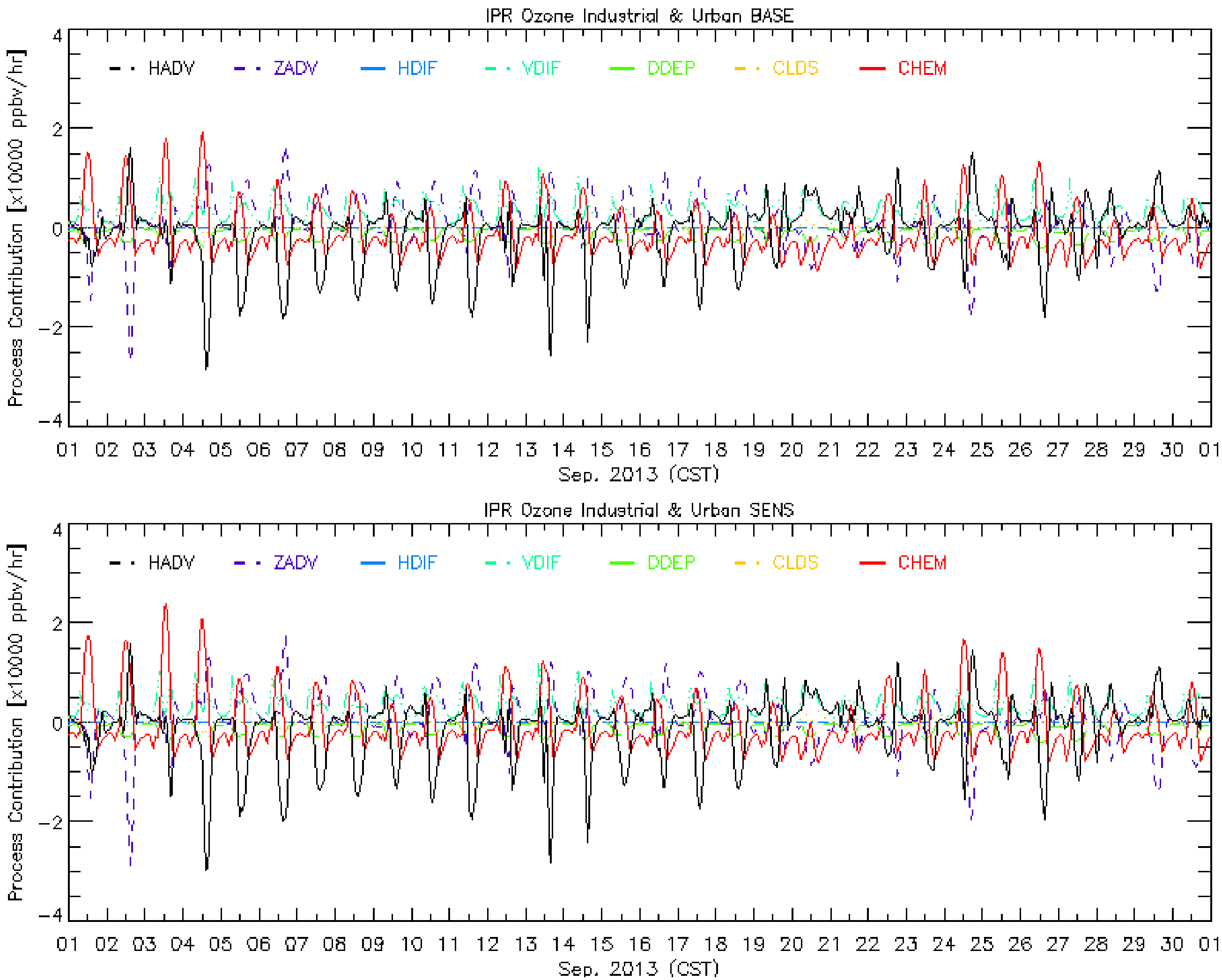


Figure 7. Contributions of atmospheric processes to ozone concentrations from surface to PBL height at industrial and urban area during Sept. 2013 for BASE and SENS simulations (HADV – horizontal advection, ZADV – vertical advection, HDIF – horizontal diffusion, VDIF – vertical diffusion, DDEP – dry deposition, CLDS – cloud process, CHEM – chemistry reaction).

Chemistry is the main process contributing to ozone production; positive chemistry contribution increased in sensitivity simulation due to the emission increase.

Spatial change of ozone and precursors

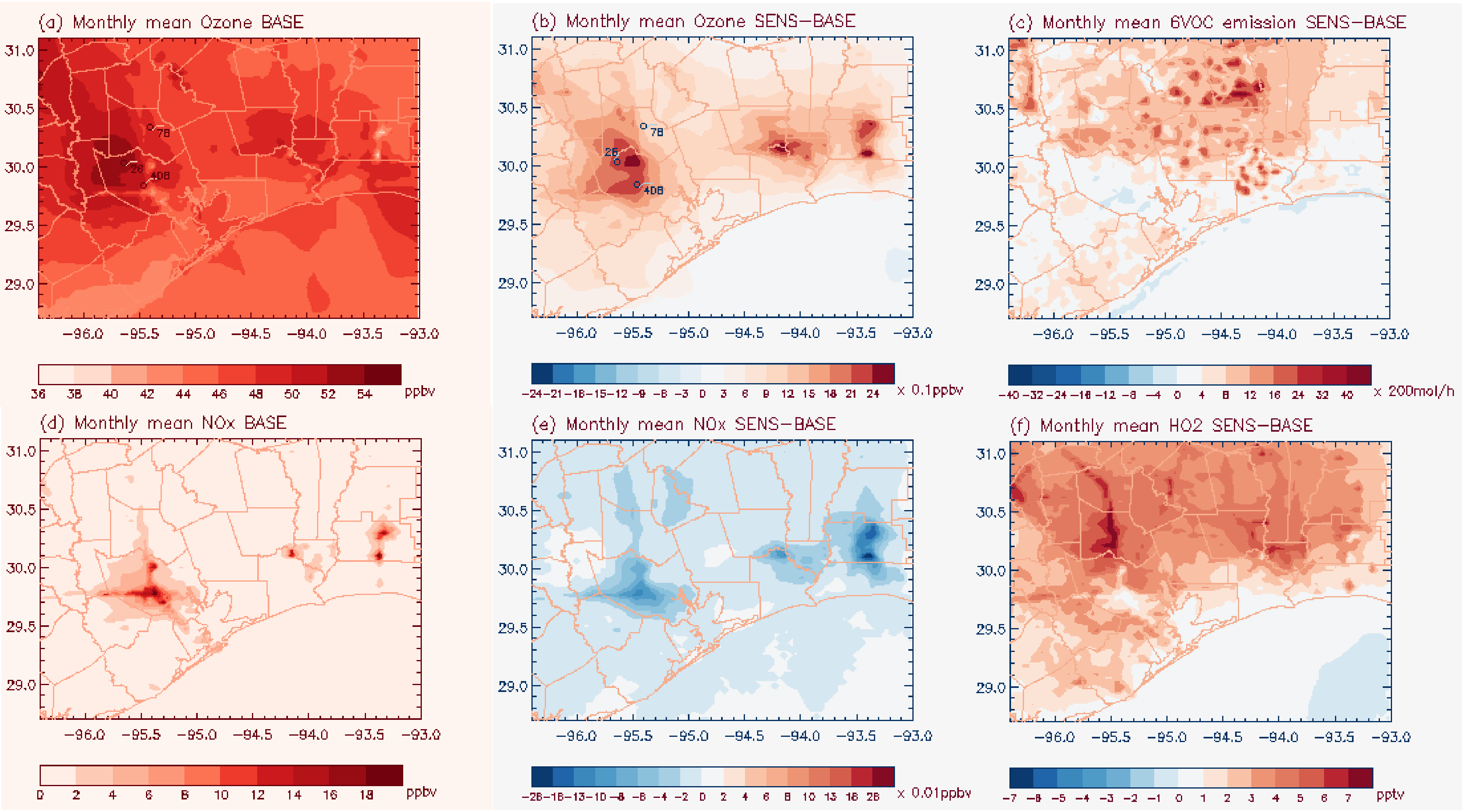


Figure 8. (a) BASE simulated monthly mean of ozone mixing ratio; (b) the difference of monthly mean of ozone mixing ratio between two simulations (SENS - BASE); (c) SENS - BASE monthly mean of sum of six VOC species emissions; (d) BASE simulated monthly mean of NO_x mixing ratio; (e) SENS - BASE monthly mean of NO_x mixing ratio; (f) SENS - BASE monthly mean of HO_2 mixing ratio. Note: the monthly mean values were calculated only for the daytime (13:00-17:00 LT) of September of 2013.

Conclusion

- WRF-SMOKE-CAMQ over-predicted benzene, ethylene, toluene and xylene, while under-predicting isoprene and ethane.
- Adjusting VOC emissions using simulated/observed ratios improved model performance of each VOC species.
- Simulated monthly mean ozone showed a minor change: a 0.4 ppb or 1.2% increase; while a change of more than 5 ppb was seen in hourly peaked ozone, moving model predictions closer to observations.
- Adjusting VOC emissions to observed concentrations shifted ozone hotspots outside industrial/urban region and enhanced peaked ozone in the outflow region during the afternoon. The results indicate that formation of ozone in the outflow could complicate attainment status in neighboring counties.

Acknowledgments

- Authors acknowledge the free use of the TCEQ Auto-GC VOC measurements and CAMS system ozone measurements, NASA OMI and NASA DISCOVER-AQ aircraft campaign HCHO measurements data. This work is supported by Air Quality Research Program 14-014.

Reference

- Pan, S., Choi, Y., Roy, A., Li, X., Jeon, W., Souri, A.H., Modeling the uncertainty of several VOC and its impact on simulated VOC and ozone in Houston, Texas, Atmospheric Environment (2015), doi: 10.1016/j.atmosenv.2015.09.029.

Thank you!

Questions?