Environmental chamber experiments and CMAQ modeling to improve mechanisms to model ozone formation from HRVOCs

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Outline

- Background
- Overall approach of this project
- Part I: Chamber experiments, mechanism development and evaluation
- Part II: CMAQ simulations
- Conclusions

Background: Ozone and HRVOC emissions

- Emissions of **H**ighly **R**eactive **V**olatile **O**rganic **C**ompounds (HRVOCs) contribute to ozone pollution in Houston.
- Emissions of HRVOCs (ethene, propene, isobutene, 1-butene, cis-2-butene, trans-2-butene, 1,3-butadiene) are regulated in Southeast Texas (Title 30, Texas Administrative Code, Chapter 115; TCEQ, 2013, http://www.tceq.texas.gov/airquality/stationary-rules/voc/hrvoc.html).

(Source: http://maps.google.com)

Background: HRVOC emissions and chemical mechanisms

- **Condensed chemical mechanisms** commonly used for air quality modeling are designed to model O_3 formation from typical urban ambient VOC mixtures.
- **Reliable chamber experimental data for mechanism evaluation** are available only for ethene and propene among the 7 alkenes regulated as HRVOCs.

7 HRVOC alkenes

Ethene ($CH_2=CH_2$)
Propene ($CH_2=CHCH_3$)

1-Butene ($CH_2=CHCH_2CH_3$)
trans-2-Butene ($CH_3CH=CHCH_3$)
cis-2-Butene ($CH_3CH=CHCH_3$)
Isobutene ($CH_2=C(CH_3)_2$)
1,3-Butadiene ($CH_2=CHCH=CH_2$)

Non-HRVOC alkenes in urban emissions

1-Pentene ($CH_2=CHCH_2CH_2CH_3$)
1-Hexene ($CH_2=CHCH_2CH_2CH_2CH_3$)

trans-2-Pentene ($CH_3CH=CHCH_2CH_3$)
cis-2-Pentene ($CH_3CH=CHCH_2CH_3$)

2-Methyl-2-butene ($CH_3CH=C(CH_3)_2$)

Overall approach of this project

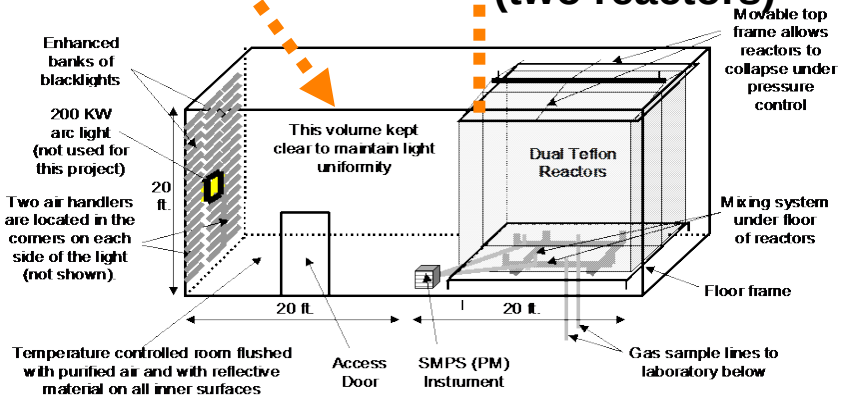
- **Project team**:
  - Gookyoung Heo and William Carter (UCR)
  - Qi Ying (TAMU)
- **Overall objective**: Develop more reliable chemical mechanisms that can be used to simulate ozone formation from both urban emissions and industrial HRVOC emissions.
- **Tasks of this project**:
  - Design and carry out chamber experiments (UCR)
  - Evaluate and develop mechanisms (UCR)
  - Implement mechanisms into CMAQ (TAMU)
  - Carry out CMAQ simulations (TAMU)
- **Project officers**:
  - Elena McDonald-Buller (AQRP project officer)
  - Ron Thomas (TCEQ liaison)

Part I: Experiments carried out at UCR

- 25 experiments (50 reactor runs) for the 10 test alkenes.
- 11 experiments for chamber characterization or quality assurance.
- 36 reactor runs were selected and used for evaluating and improving mechanisms.

UCR's EPA chamber building

Dual reactors (two reactors)



Schematic of the UCR's EPA chamber on the second floor

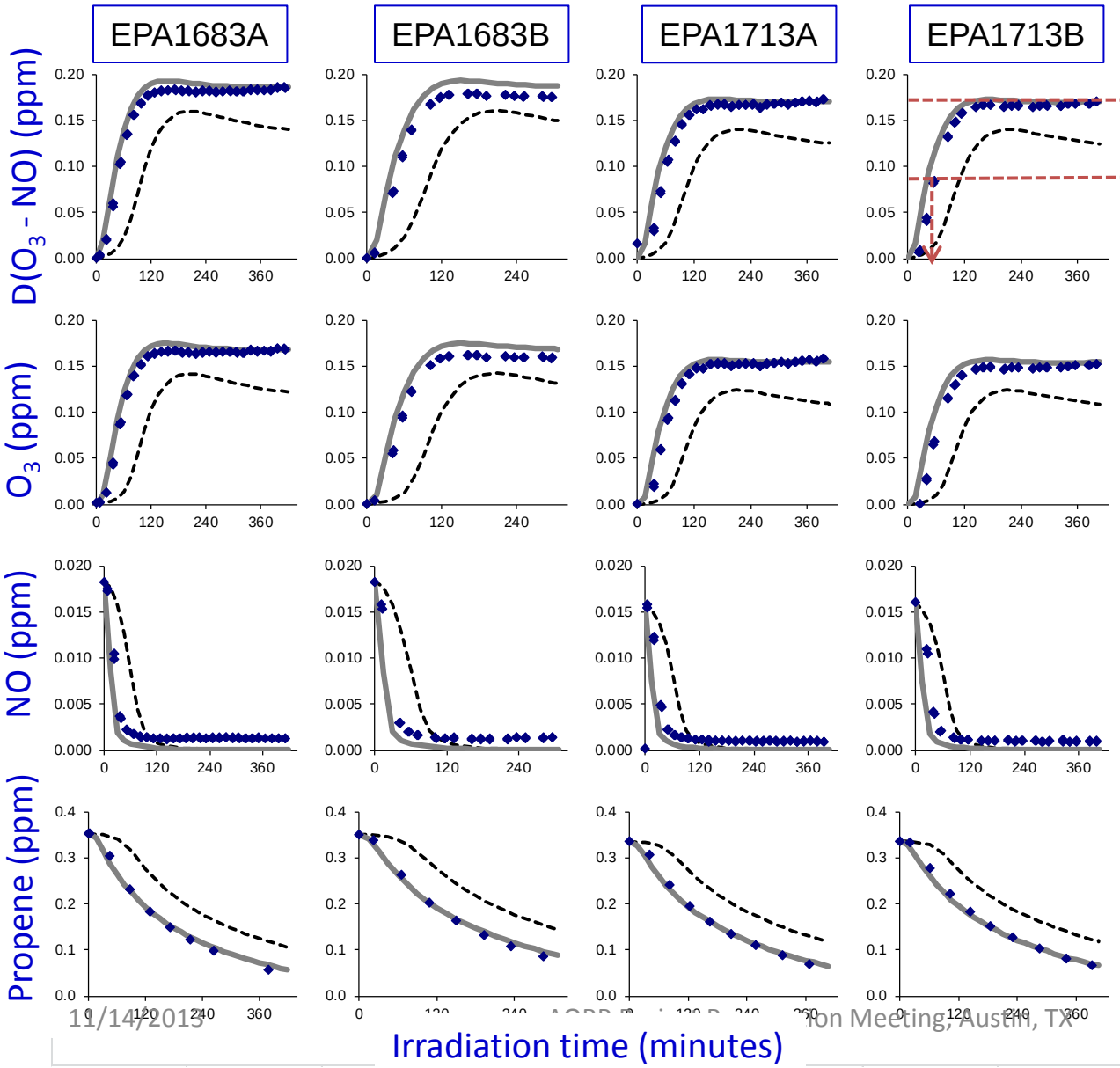
Compound	Planned	Carried out	Used
1-butene	3	4	4
isobutene	3	5	4
trans-2-butene	2	4	3
cis-2-butene	3	6	4
1,3-butadiene	3	4	4
1-pentene	2	4	4
1-hexene	2	5	5
cis-2-pentene	2	4	2
trans-2-pentene	2	4	2
2-methyl-2-butene	2	10	4
[sum]	*24*	*50*	*36*

Mechanisms and performance metrics used

- Mechanisms used:
  - SAPRC-07T (S07T): "toxics" version of SAPRC-07 already implemented and available in CMAQ (Hutzell et al, 2012).
  - SAPRC-11D (S11D): detailed SAPRC-11 which uses updated reactions for aromatic compounds (Carter and Heo, 2013) and ~330 model species to more explicitly represent reactive VOC emissions.
  - SAPRC-11L (S11L): standard-lumped version of SAPRC-11 using the same lumping methods used for the standard-lumped **SAPRC-07L** (Carter, 2010).
- Performance metrics:
  - Maximum O_3: highest O_3 concentration by the end of the experiment if O_3 increases by less than or equal to 5% in the last 30 minutes of the experiment.
  - $D(O_3\text{-}NO)$ Rate: average rate of change of $D(O_3\text{-}NO)$ between the starting time of the irradiation (i.e., t = 0) and the time of $0.5 \cdot Max(D(O_3\text{-}NO))$

$D(O_3\text{-}NO)$ = accumulated O_3 formation and NO oxidation
$= ([O_3]_t - [O_3]_0) + ([NO]_0 - [NO]_t)$

Mechanism evaluation and development: (1) Propene



Max(D(O_3-NO))

0.5·Max(D(O_3-NO))

D(O_3-NO) = accumulated O_3 formation and NO oxidation = $([O_3]_t - [O_3]_0) + ([NO]_0 - [NO]_t)$

Experimental

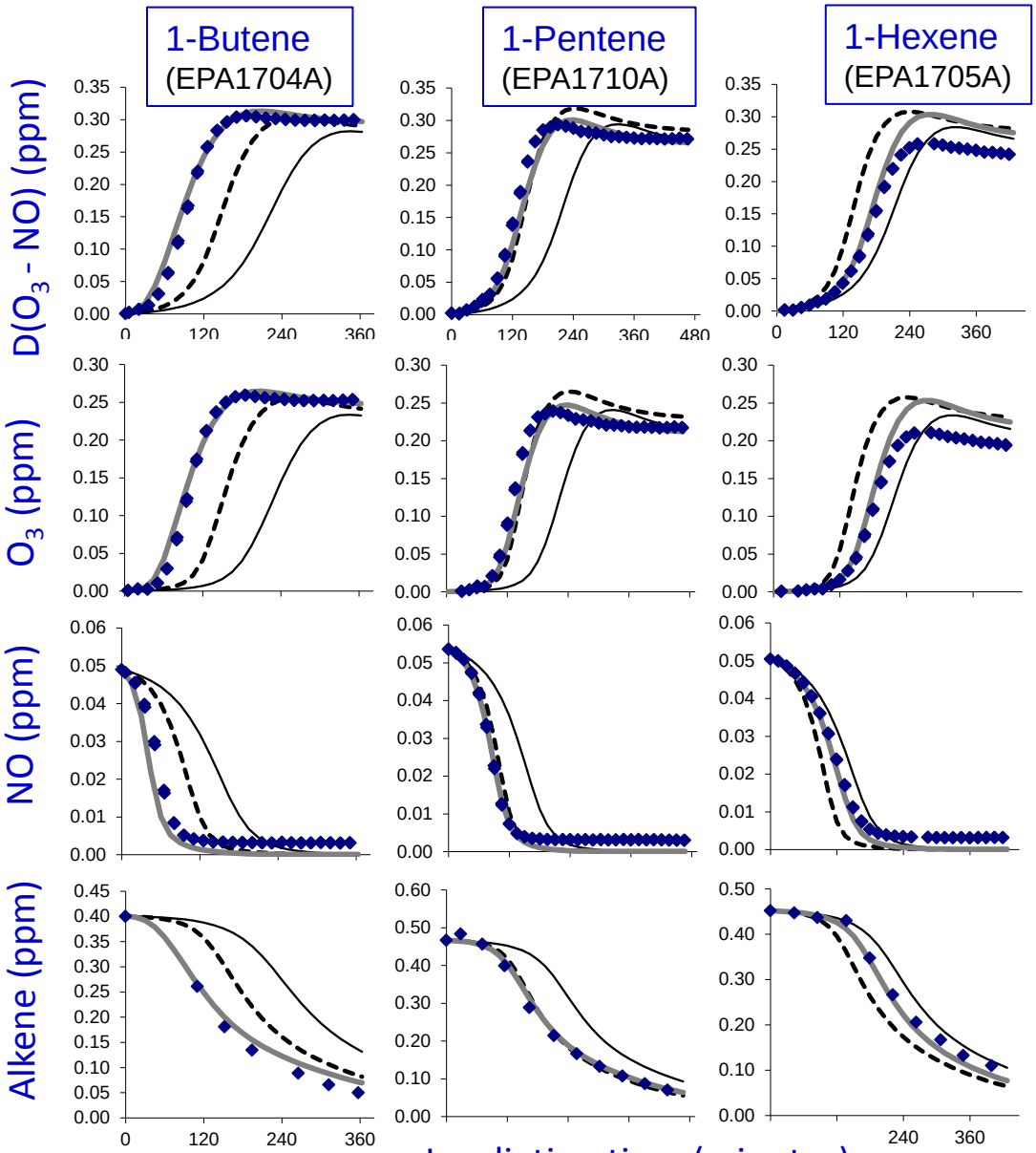
SAPRC-07T

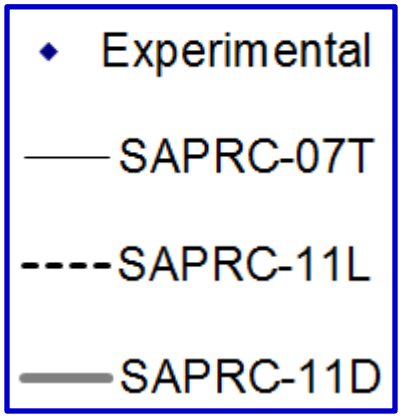
SAPRC-11L

SAPRC-11D

The model performance with SAPRC-11D indicates that the quality of experimental data generated for this project is reasonable for mechanism evaluation.

(2) Unbranched terminal alkenes



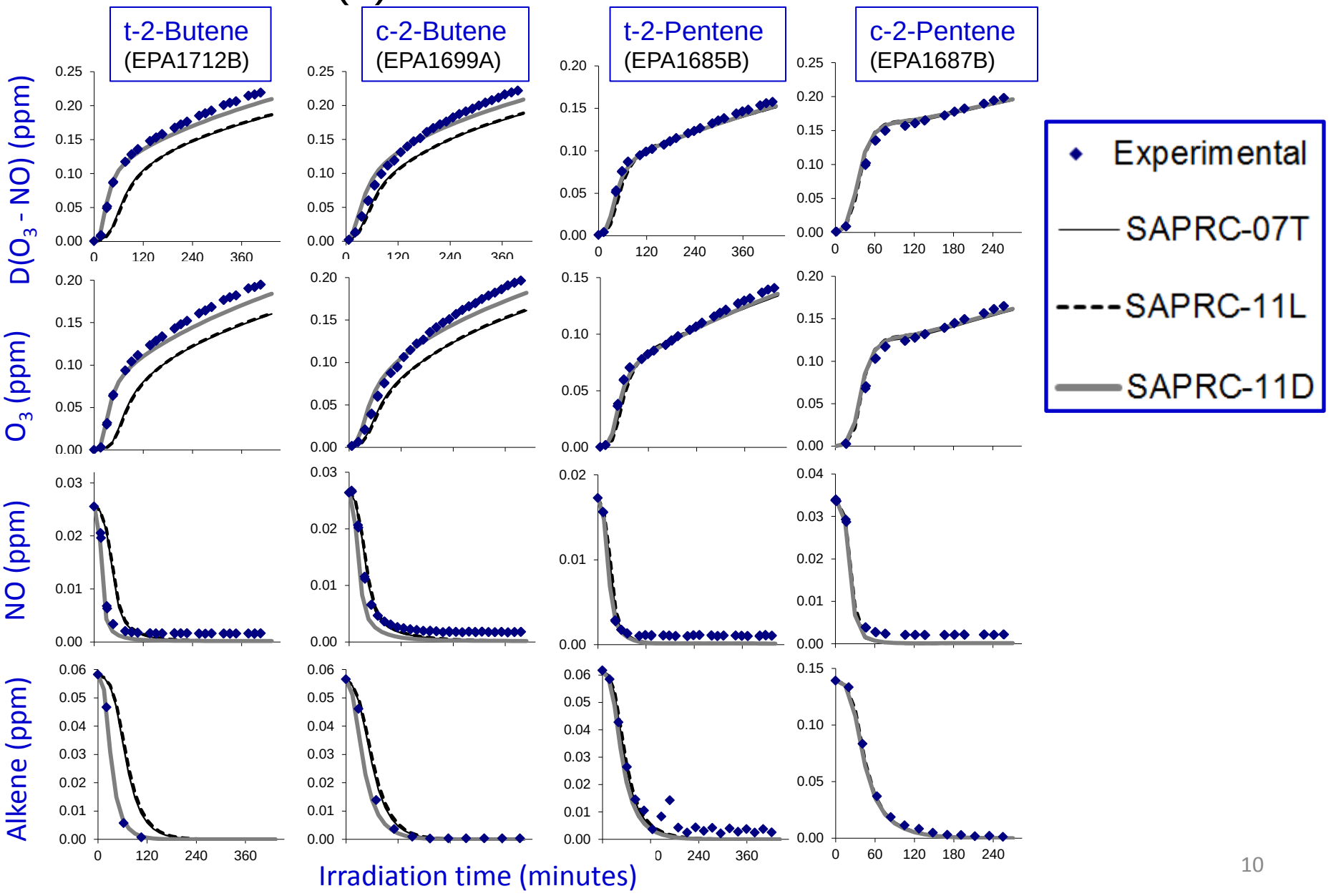


For 1-hexene, even with SAPRC-11D, Max(O_3) was overpredicted, and SAPRC-07T better simulated Max(O_3) than SAPRC-11D.

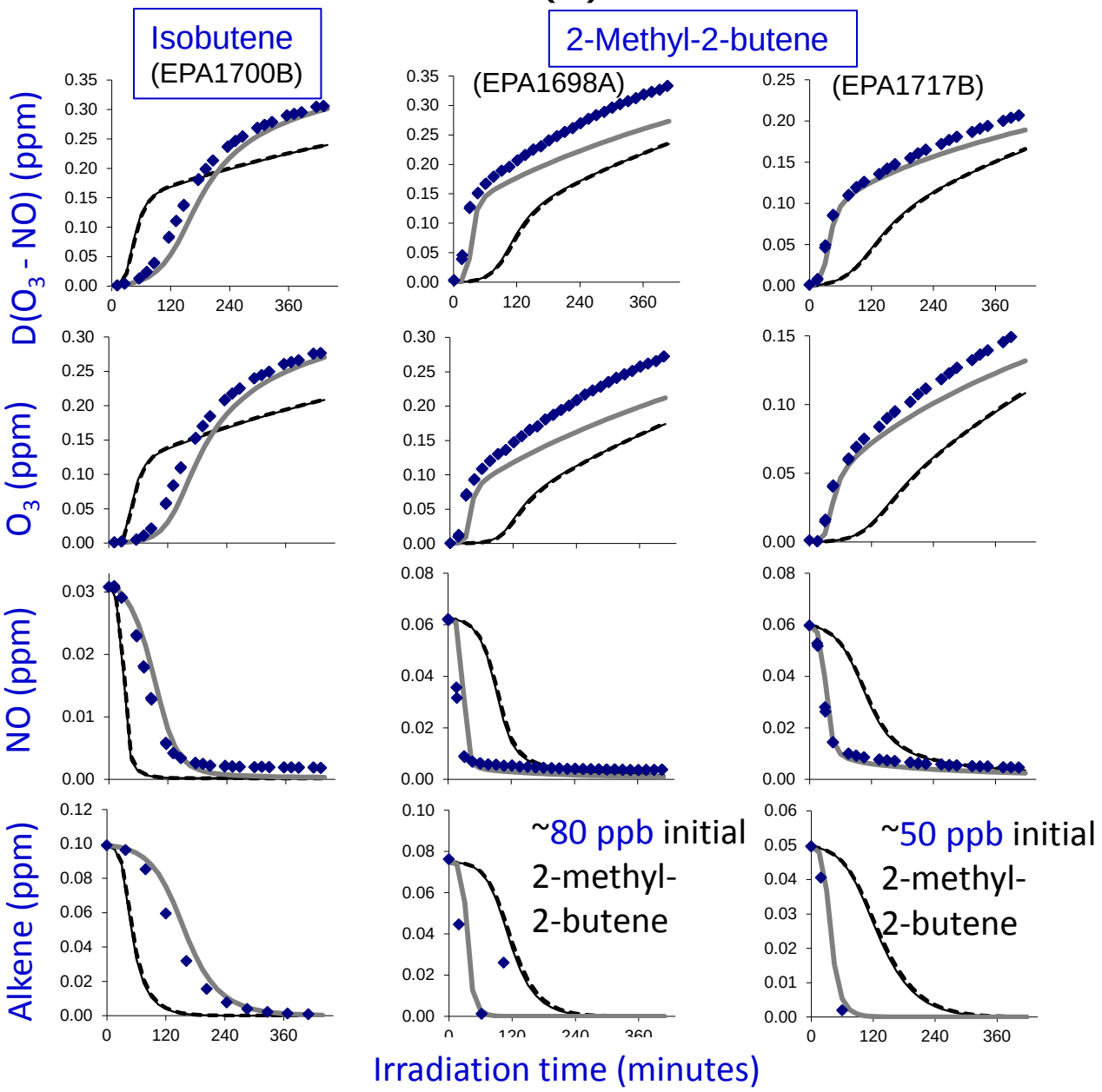
In a test version of SAPRC-11D, increasing the NOx sink resulted in improving the Max(O_3) performance.

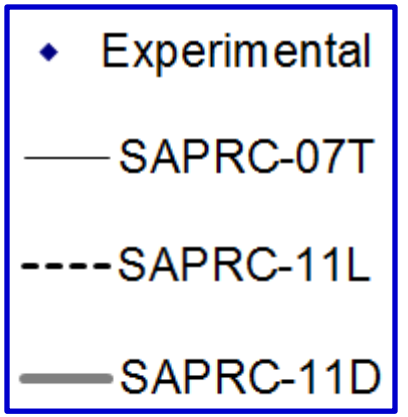
Note: 1-hexene behaves differently from 1-butene and 1-pentene due to a major role of H-shift isomerization of alkoxy radicals ($RO^{\cdot}$) formed from reaction with OH.

(3) Unbranched internal alkenes



(4) Branched alkenes





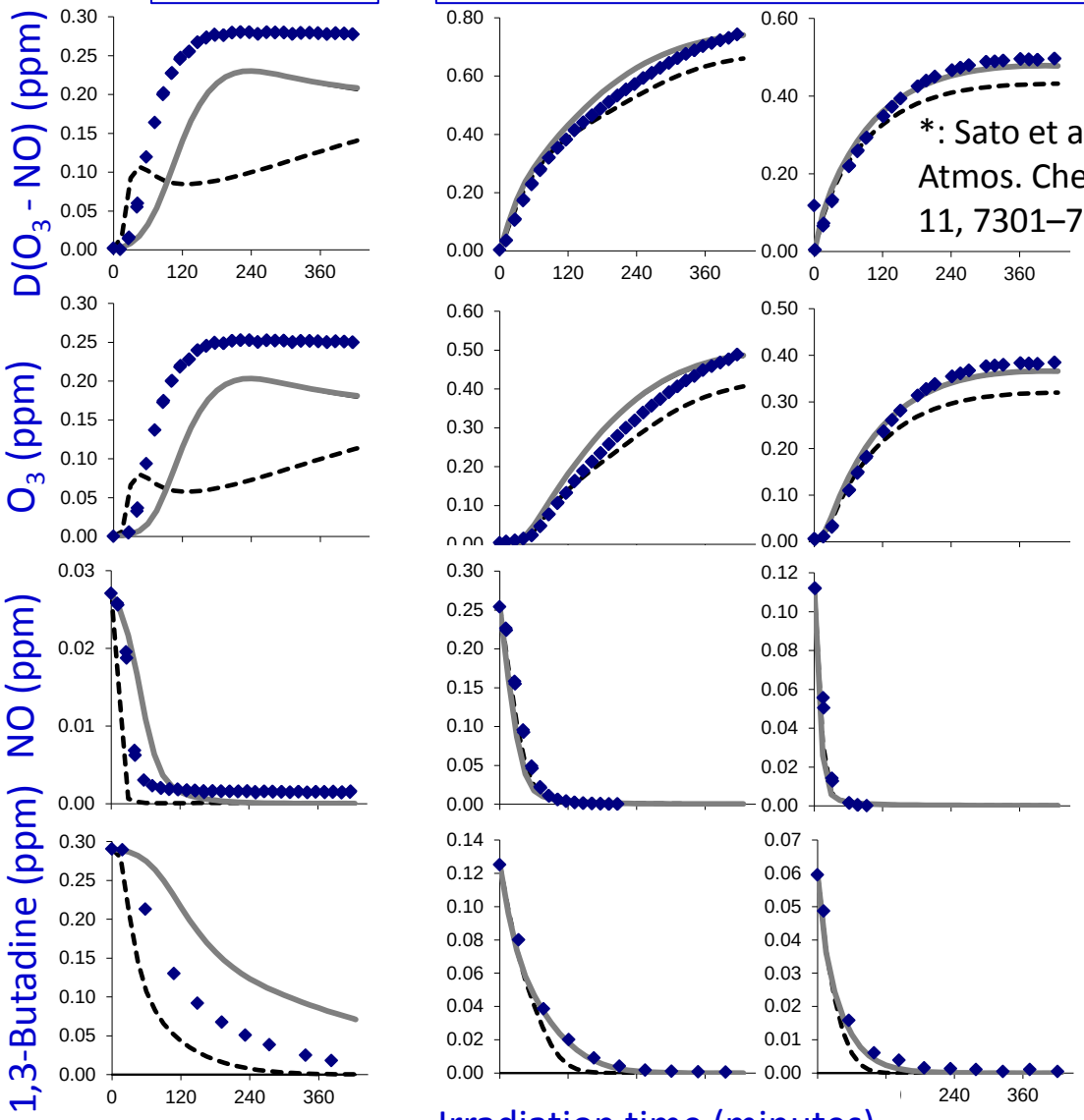
Isobutene and 2-methyl-2-butene are difficult to model with the lumped OLE2 reactions (which work reasonably for cis/trans 2-butene and 2-pentene).

Even with SAPRC-11D, Max(O_3) for 2-methyl-2-butene was underpredicted.

(5) 1,3-Butadiene

EPA1700B

Previous expts* with added H_2O_2: EPA1702A and EPA1072B



*: Sato et al (2011, Atmos. Chem. Phys., 11, 7301–7317)

Experimental

SAPRC-07T

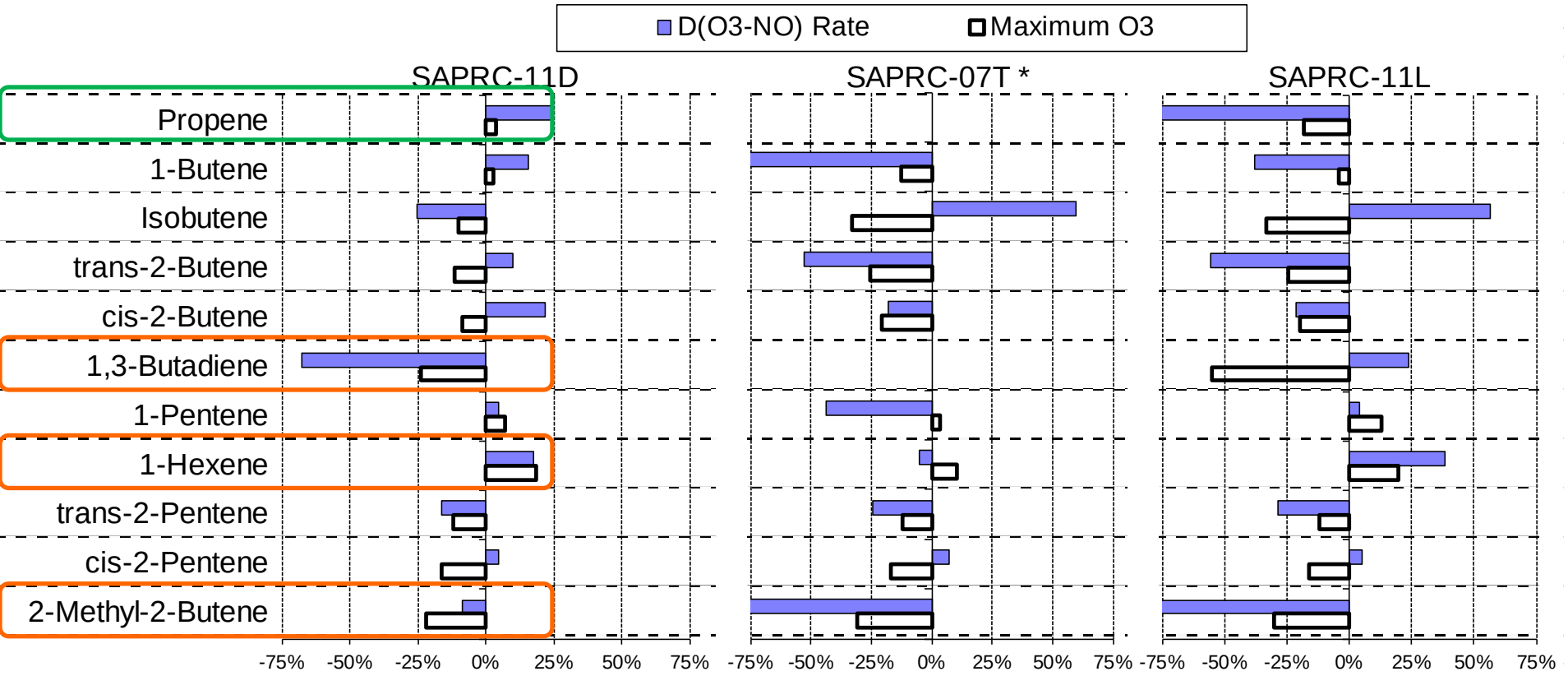
SAPRC-11L

SAPRC-11D

For 1,3-butadiene experiments carried out for this project, all mechanisms showed poor performance. This problem was not detected by previous experiments with added H_2O_2 by Sato et al (2011).

In a test version of SAPRC-11D, increasing the radical yield in the reaction of 1,3-butadiene with O_3 resulted in improving the model performance.

Mechanism performance summary



Model bias = (model-experiment)/average(model, experiment)

*Results are not shown for SAPRC-07T simulations of propene and 1,3-butadiene because these compounds are represented explicitly so the results are essentially the same as for SAPRC-11D.

The average model biases of D(O_3-NO) Rate by SAPRC-07T for 1-butene and 2-methyl-2-butene were -76% and -106%, respectively. The average model biases of D(O_3-NO) Rate by SAPRC-11L for propene and 2-methyl-2-butene were -75% and -107%, respectively.

Part I - Summary

- This project generated experimental data useful to evaluate mechanisms for the 10 alkenes (5 HROVCs and 5 non-HRVOCs).
- The detailed SAPRC-11 (SAPRC-11D) modeled ozone formation from the tested alkenes generally better than the condensed versions.
- SAPRC-11D also showed limitations:

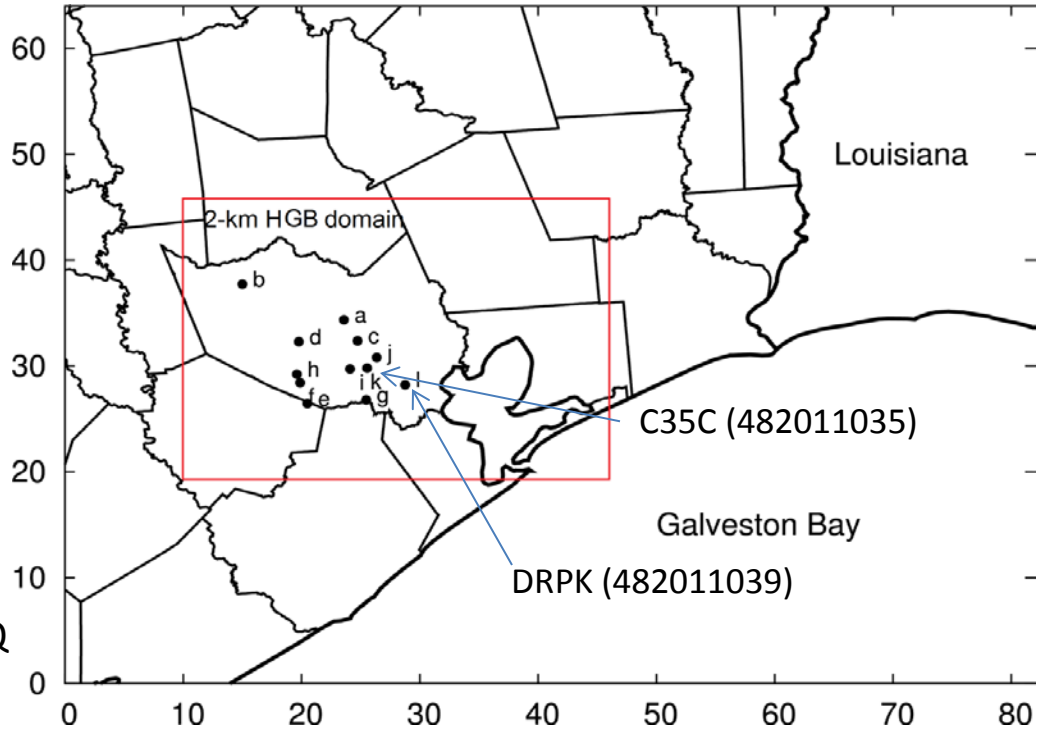
  (1) overpredicted Max(O_3) for 1-hexene by ~20%.

  (2) underpredicted Max(O_3) for 2-methyl-2-butene by ~20%.

  (3) underpreicted the ozone formation and NO oxidation rate by ~65% and underpredicted Max(O_3) for 1,3-butadiene by ~25%.
- The results for propene, 1-butene, 1-pentene and 1-hexene indicate that C_{3+} 1-alkenes share similar O_3 formation chemistries but also have differences among those 1-alkenes.
- The results for cis/trans 2-butene and 2-pentene indicate that unbranched internal alkenes share similar ozone formation chemistries.
- Isobutene and 2-methyl-2-butene behave differently from unbranched internal alkenes in regard to ozone formation.

Part II – CMAQ simulations: Model set-up

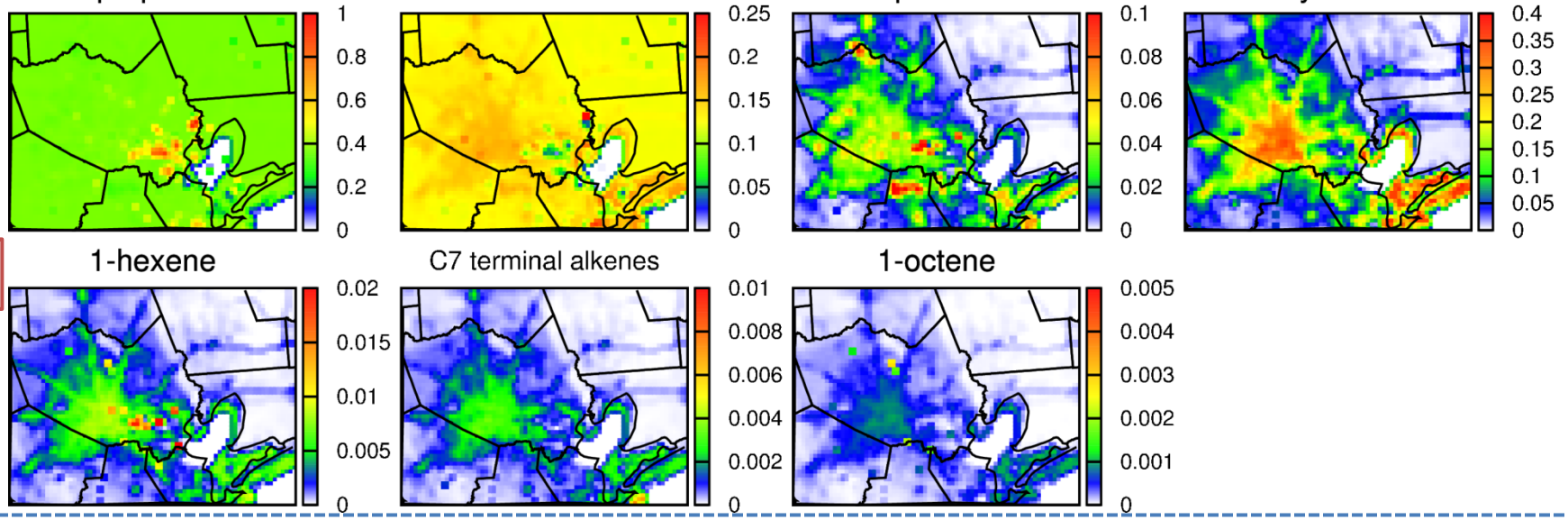
- SMOKE2.6/CMAQ v5.01
- Episode: 8/28 – 9/15/2006
- Meteorology: TCEQ MM5
- Domain: TCEQ 8-h SIP
  - ❑ 36, 12, 4 and 2-km grids
- Emissions
  - ❑ 2005 NEI v4.2 + TCEQ point sources
  - ❑ Biogenic emissions: BEIS v3.14
  - ❑ VOC speciation: SPECIATE 4.3 + TCEQ
  - ❑ Wildfire: FINN (NCAR)
- Chemical Mechanisms
  - ❑ S11D (422 spcs, 1127 rxns)
  - ❑ S11L (126 spcs, 354 rxns)
  - ❑ S07L* (133 spcs, 609 rxns)
  - ❑ S07T* (150 spcs, 689 rxns) * "C" version



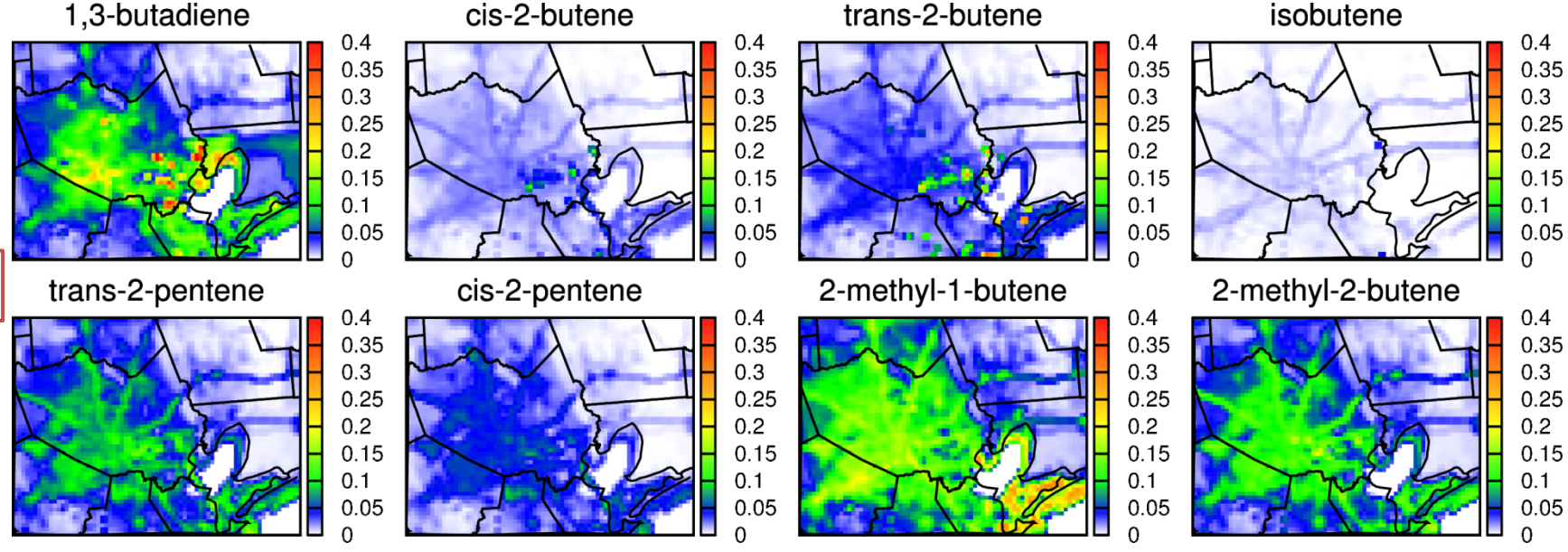
The Continuous Ambient Monitoring Stations (CAMS) are: (a) HALC, (b) HNWA, (c) HWAA, (d) HLAA, (e) HCQA, (f) BAYP, (g) HSWA, (h) SHWH, (i) HROC, (j) HOEA, (k) C35C, and (l) DRPK.

Fractions of alkenes in OLE1 and OLE2

OLE1

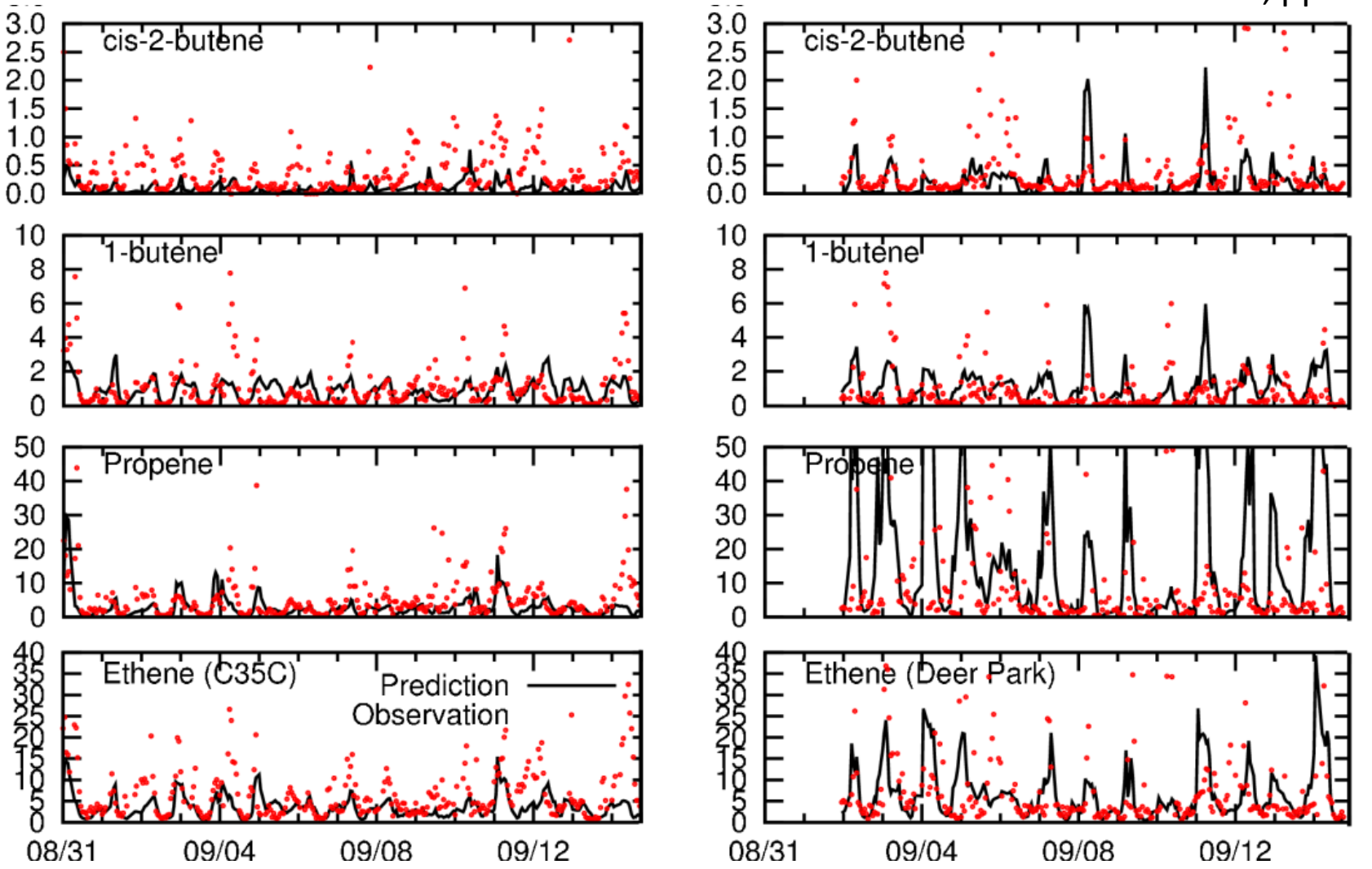


OLE2



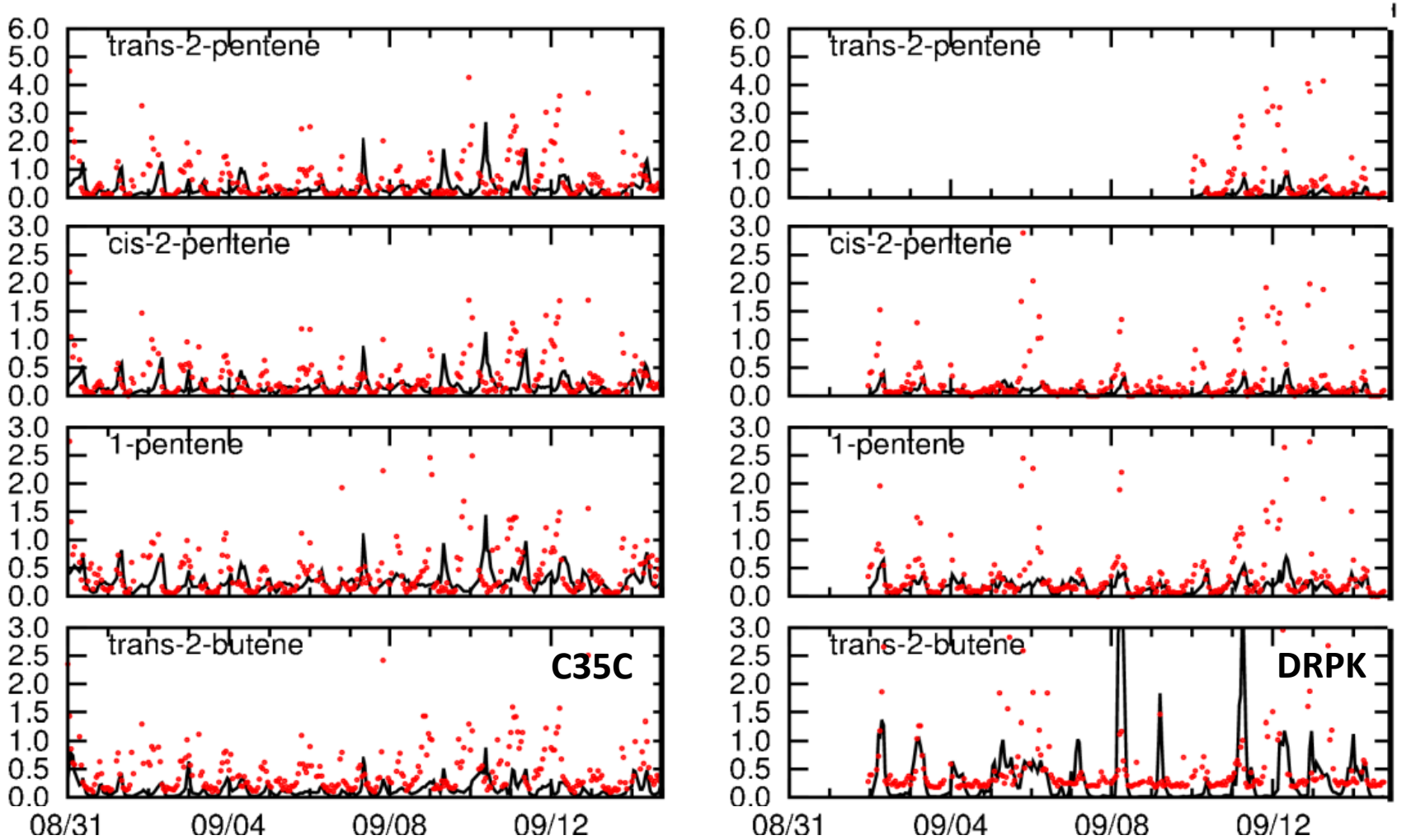
Results – Alkenes (1)

Auto GC measurements, ppbC

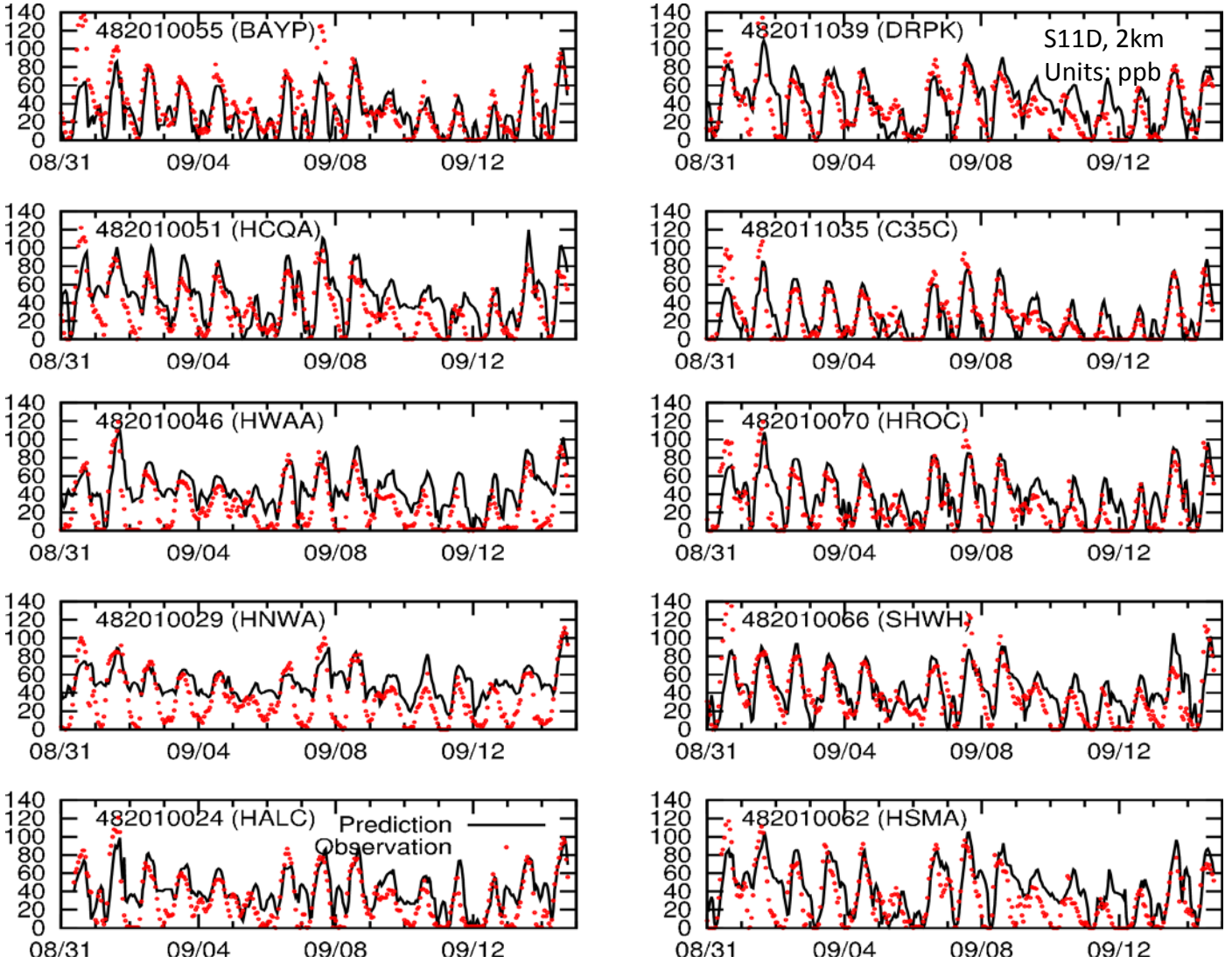


Results – Alkenes (2)

Auto GC measurements, ppbC



Results – Ozone time series



Results – Ozone statistics

	MNB				MNE				AUP			
	S11D		S11L		S11D		S11L		S11D		S11L	
	4km	2km	4km	2km	4km	2km	4km	2km	4km	2km	4km	2km
HALC	-0.08	-0.06	-0.11	-0.09	0.15	0.15	0.17	0.17	-0.05	0.00	-0.08	-0.03
HNWA	-0.07	-0.07	-0.10	-0.10	0.12	0.13	0.14	0.14	-0.06	-0.04	-0.09	-0.06
HWAA	0.02	0.03	-0.02	-0.01	0.16	0.15	0.15	0.15	0.05	0.06	0.02	0.03
HLAA	0.04	0.00	0.00	-0.04	0.17	0.16	0.15	0.16	0.10	0.07	0.04	0.03
HCQA	0.06	0.08	0.02	0.04	0.26	0.26	0.24	0.25	0.14	0.16	0.13	0.12
BAYP	-0.21	-0.22	-0.24	-0.25	0.24	0.25	0.26	0.27	-0.20	-0.20	-0.21	-0.23
HSMA	-0.03	-0.02	-0.06	-0.05	0.23	0.23	0.23	0.23	0.04	0.04	0.00	-0.01
SHWH	-0.10	-0.08	-0.14	-0.12	0.23	0.23	0.23	0.23	-0.02	0.01	-0.06	-0.03
HROC	-0.12	-0.08	-0.15	-0.13	0.22	0.22	0.23	0.21	-0.06	-0.03	-0.08	-0.07
HOEA	-0.11	-0.15	-0.15	-0.18	0.20	0.21	0.21	0.22	-0.12	-0.15	-0.15	-0.18
C35C	-0.17	-0.24	-0.18	-0.28	0.22	0.27	0.23	0.30	-0.06	-0.14	-0.03	-0.18
DRPK	-0.08	-0.04	-0.11	-0.07	0.17	0.17	0.18	0.18	-0.04	-0.02	-0.06	-0.05
Avg	**-0.07**	**-0.07**	-0.10	-0.11	**0.20**	0.20	0.20	0.21	-0.02	**-0.02**	-0.05	-0.05

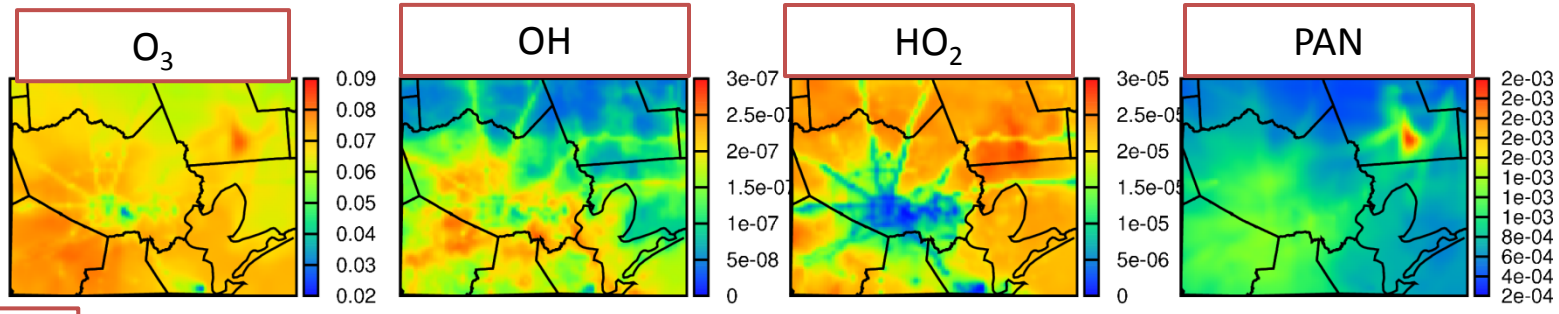
$$\mathrm{MNB} = \frac{1}{N}\sum_{i=1}^{N}\frac{C_{m,i} - C_{o,i}}{C_{o,i}} \qquad MNE = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|C_{m,i} - C_{o,i}\right|}{C_{o,i}} \qquad AUP = \frac{C_{p,ppeak} - C_{o,opeak}}{C_{o,opeak}}$$

Results – Regional differences

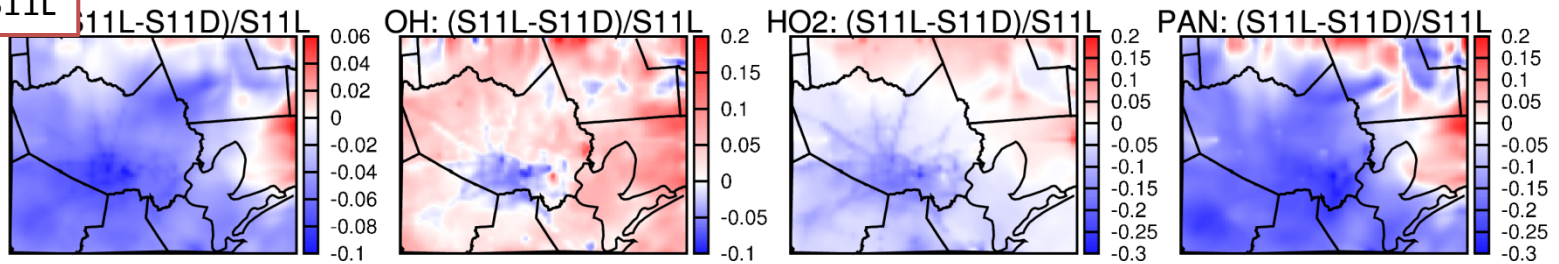
Units: ppm

1300-1400 CDT

S11D

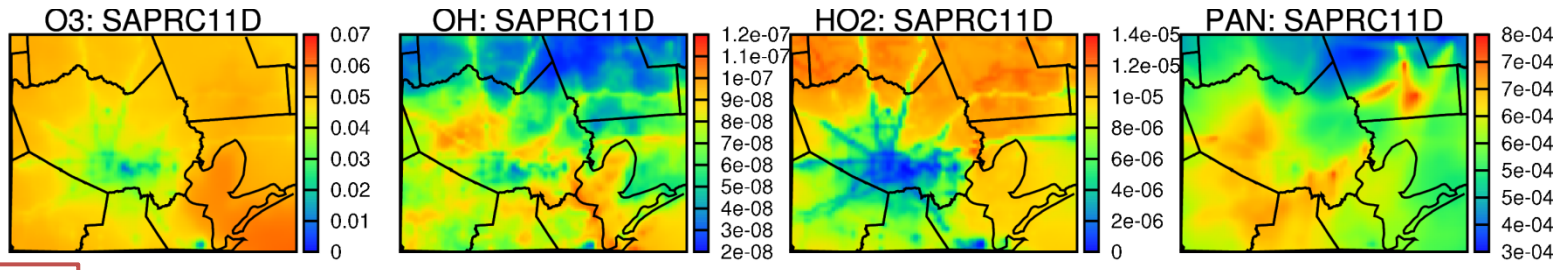


(S11L – S11D)/S11L

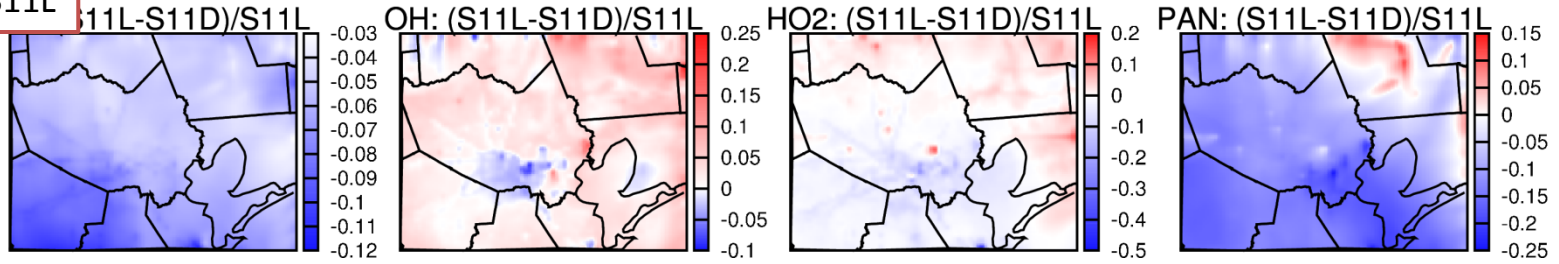


24-HR Average

S11D

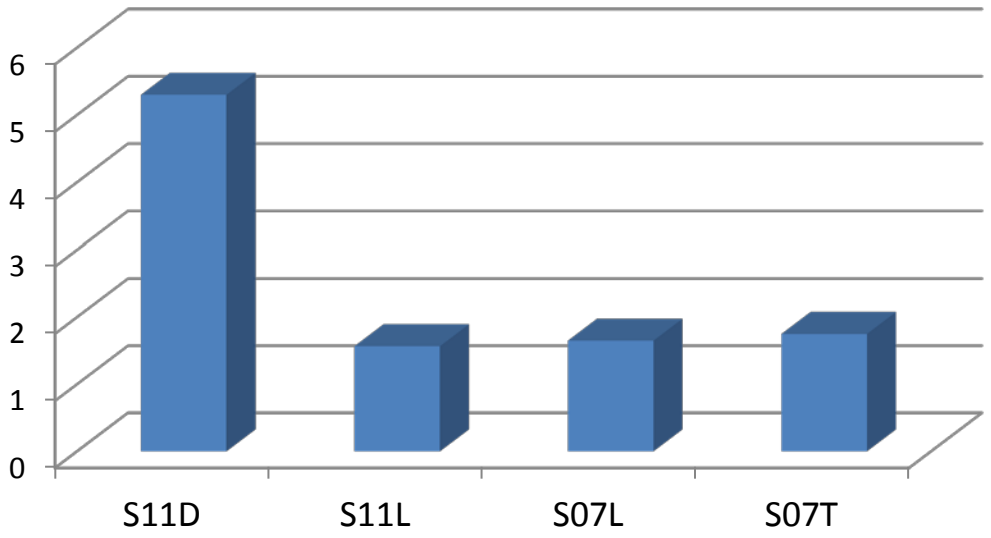


(S11L – S11D)/S11L



Timing results

Time (hours per/day)



- All runs using 8 physical cores (each core is from an Intel Q6600 2.4GHz CPU node with 2G of DDR2 RAM)
- Gigabit Ethernet connection. Results write to an NFS mount.
- MPI: MPICH2 v2.1.4
- Program compiled using the Intel Fortran Compiler (ifort) v11.1 with the following compiler options:

```
-O3 -xSSSE3 -override-limits -fno-alias -mp1 -fp-model precise
```

- Chemistry Solver: SMVGEAR solver in CMAQ

Part II - Summary

- Predicted cis-2-butene, trans-2-butene, 1-pentene, cis-2-pentene and trans-2-pentene are lower than AutoGC measurements at C35C and DRPK (more significant at DRPK).
- S11D gives slightly better ozone model performance than S11L. 2-km and 4-km results are similar in terms of ozone model performance – 4 km is adequate for ozone modeling.
- S11D predicts higher O_3 and PAN throughout the domain than S11L. S11D predicts higher OH and HO_2 in urban Houston areas and lower OH and HO_2 in areas with less anthropogenic emissions than S11L.
- S11D is approximately 3 times more computationally intensive than other lumped mechanisms.

Conclusions (1)

- This project has provided experimental data to evaluate mechanisms for the 10 studied compounds that will eventually contribute to increasing the accuracy of ozone predictions in Texas.
- The detailed SAPRC-11 (SAPRC-11D) reasonably simulated ozone formation from 7 of the 10 alkenes while the performance for 1,3-butadiene, 1-hexene and 2-methyl-2-butene was not satisfactory.
- Isoprene and 1,3-butadiene have many similar mechanistic features. Thus, knowledge gained during updating the isoprene chemistry should be used to update the 1,3-butadiene chemistry, and vice-versa.
- In re-deriving lumping methods for the tested 10 alkenes for the Houston area, reliable emissions data as well as the mechanism evaluation results of this project should be considered.

Conclusions (2)

- Chemically detailed emissions data were useful in inspecting consistency between the compositions of the lumped alkene species (OLE1 and OLE2) used during deriving the mechanism and the emissions inventory data that air quality simulations heavily rely on.
- Explicitly modeling propene and 1,3-butadiene is potentially useful to improve the accuracy of ozone predictions based on the spatial variability of propene and 1,3-butadiene emissions in the Houston area.
- Detailed chemical mechanisms were able to yield better model performance than lumped mechanisms although at a cost of more computation time. A mechanism with a small number of important explicit VOC species should be developed to improve model performance without much penalty for computation time.
- Additional analysis (e.g., process analysis) is needed to explain differences in modeled O_3, PAN, OH and HO_2 between SAPRC-11D and SAPRC-11L.
- Further work is needed to limit the impact of uncertainties in emissions on mechanism comparison under ambient conditions.

Acknowledgements

- This presentation is based on work (AQRP Project 12-006) supported by the State of Texas through the Air Quality Research Program administered by The University of Texas at Austin by means of a grant from the Texas Commission on Environmental Quality.
- Elena McDonald-Buller (AQRP) and Ron Thomas (TCEQ)
- Ajith Kaduwela (CARB) and Deborah Luecken (U.S. EPA) for providing VOC emissions data.

Extra slides

Lumping methods for the 10 alkenes

Tested alkenes	Lumping method		
	SAPRC-07T	SAPRC-11L	SAPRC-11D
1-Butene	OLE1	OLE1	BUTENE1[a]
Isobutene	OLE2	OLE2	ISOBUTEN[a]
trans-2-Butene	OLE2	OLE2	T2BUTE[a]
cis-2-Butene	OLE2	OLE2	C2BUTE[a]
1,3-Butadiene	13-BUTDE[a]	OLE2	BUTDE13[a]
1-Pentene	OLE1	OLE1	PENTEN1[a]
1-Hexene	OLE1	OLE1	HEXENE1[a]
trans-2-Pentene	OLE2	OLE2	T2PENT[a]
cis-2-Pentene	OLE2	OLE2	C2PENT[a]
2-Methyl-2-butene	OLE2	OLE2	M2BUT2[a]

[a]Explicit model species is used instead of OLE1 or OLE2.

Compounds and weighting factors used to derive the mechanisms for the OLE1 and OLE2 lumped model species in the SAPRC-11L and SAPRC-07T mechanisms

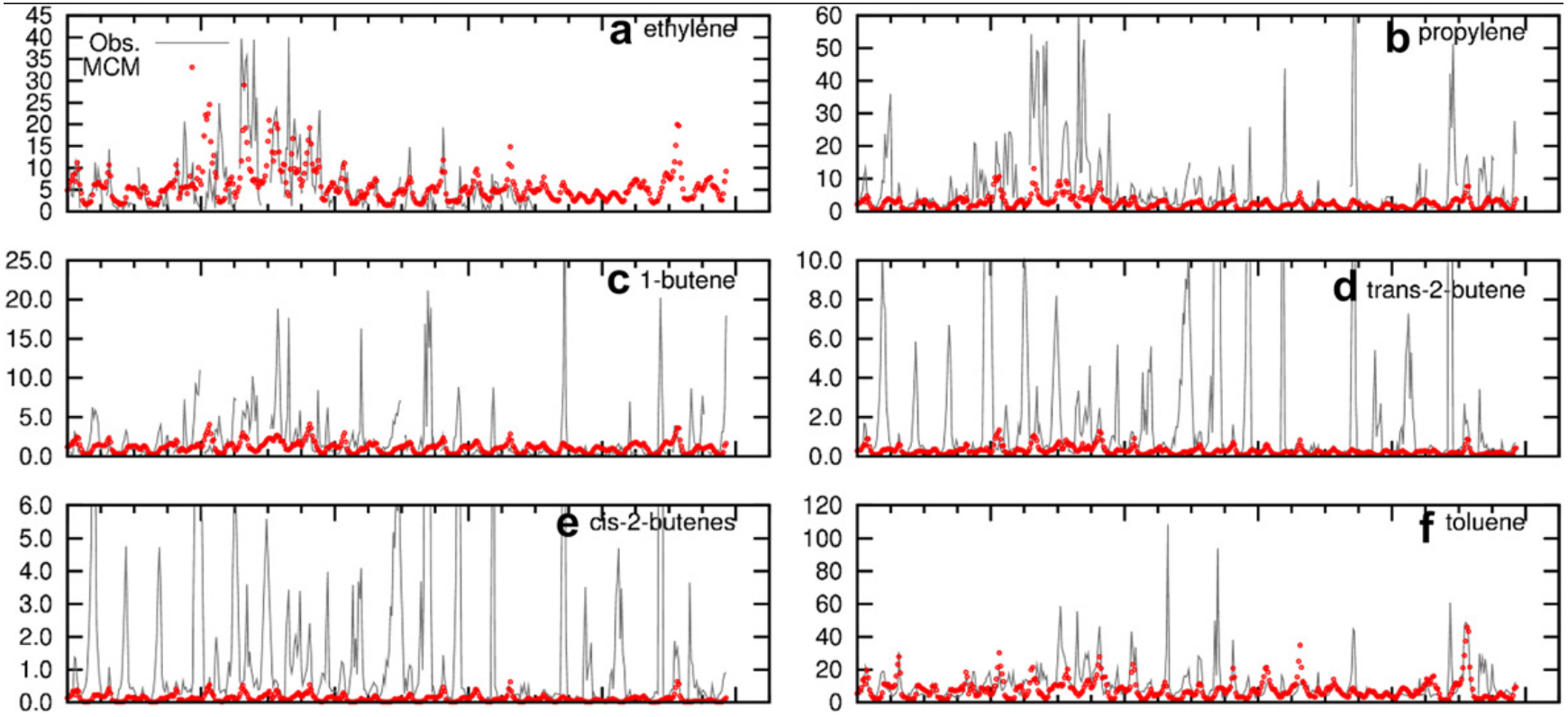
Compounds and weight factors for OLE1		
Compound	SAPRC-11L	SAPRC-07T
propene	29.4%	[a]
1-butene	11.9%	16.9%
1-pentene	11.5%	16.2%
1-hexene	23.7%	33.5%
1-heptene	11.0%	15.5%
1-nonene	4.8%	6.8%
1-octene	2.2%	3.1%
1-undecene	1.8%	2.5%
1-decene	0.9%	1.2%
3-methyl-1-butene	3.0%	4.2%

Compounds and weight factors for OLE2		
Compound	SAPRC-11L	SAPRC-07T
isobutene	10.3%	10.9%
cis-2-butene	8.8%	9.3%
trans-2-butene	11.0%	11.6%
cis-2-pentene	14.3%	15.1%
trans-2-pentene	14.3%	15.1%
cis-2-hexene	4.5%	4.8%
trans-2-hexene	4.5%	4.8%
trans-2-heptene	1.7%	1.8%
trans-3-heptene	3.9%	4.2%
trans-4-nonene	2.2%	2.3%
trans-4-octene	1.9%	2.0%
trans-4-decene	0.7%	0.7%
trans-5-undecene	1.7%	1.8%
2-methyl-1-butene	8.2%	8.7%
3,4-diethyl-2-hexene	0.2%	0.2%
2-methyl-2-butene	4.6%	4.9%
cyclohexene	1.6%	1.7%
1,3-butadiene	5.6%	[a]

[a]Explicit in SAPRC-07T.

Alkenes from TexAQS 2000

- Simulated using CMAQ-MCM at C35C

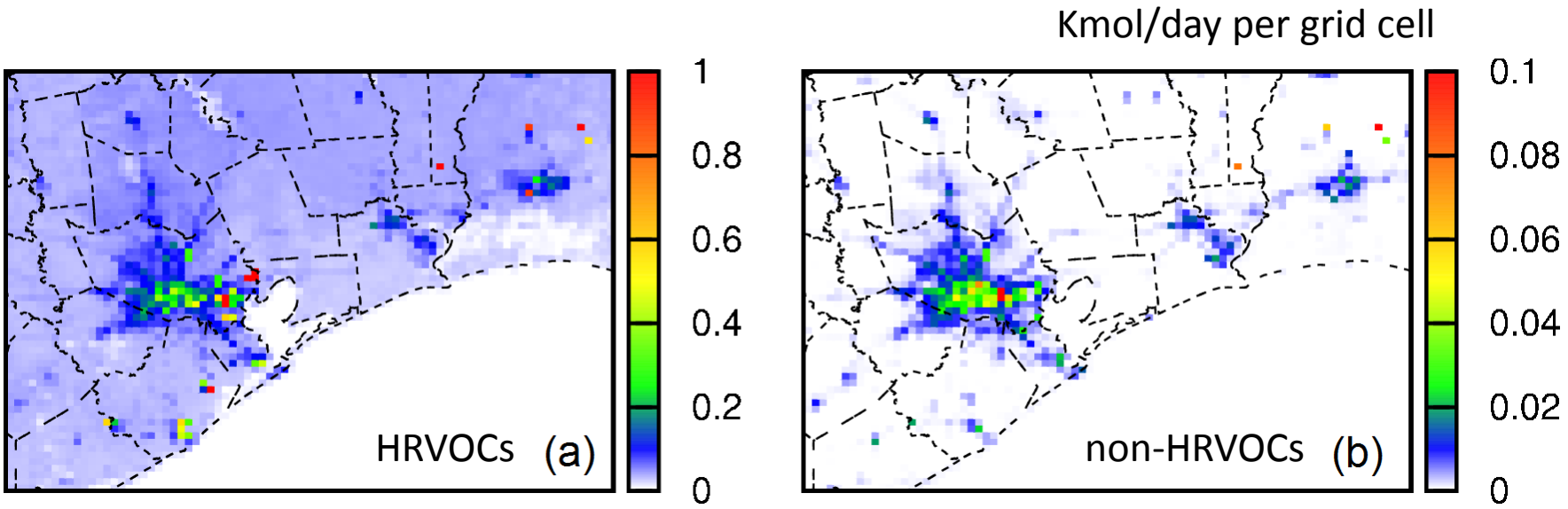


Ying and Li, Atmospheric Environment 45, 2011, 3244-3256

S07 model performance

	MNB				MNE				AUP			
	S07T-4km	S07T-2km	S07L-4km	S07L-2km	S07T-4km	S07T-2km	S07L-4km	S07L-2km	S07T-4km	S07T-2km	S07L-4km	S11L-2km
HALC	-0.088	-0.066	-0.113	-0.091	0.175	0.178	0.173	0.174	-0.03	0.01	-0.06	-0.02
HNWA	-0.069	-0.067	-0.093	-0.091	0.132	0.135	0.132	0.136	-0.02	0.00	-0.04	-0.03
HWAA	-0.006	0.006	-0.023	-0.011	0.145	0.152	0.130	0.134	0.04	0.05	0.01	0.03
HLAA	0.013	-0.027	-0.004	-0.043	0.152	0.165	0.140	0.154	0.05	0.03	0.03	0.01
HCQA	-0.065	-0.043	-0.066	-0.046	0.267	0.265	0.253	0.252	0.07	0.11	0.07	0.10
BAYP	-0.164	-0.132	-0.170	-0.138	0.279	0.275	0.272	0.268	-0.08	-0.05	-0.09	-0.07
HSMA	-0.151	-0.143	-0.155	-0.150	0.273	0.276	0.263	0.265	-0.09	-0.08	-0.10	-0.10
SHWH	-0.128	-0.109	-0.134	-0.114	0.239	0.240	0.229	0.230	-0.01	0.01	-0.02	0.00
HROC	-0.381	-0.388	-0.382	-0.397	0.391	0.403	0.389	0.404	-0.23	-0.22	-0.24	-0.23
HOEA	-0.223	-0.187	-0.244	-0.210	0.261	0.231	0.266	0.233	-0.11	-0.10	-0.14	-0.13
C35C	-0.480	-0.532	-0.466	-0.539	0.480	0.532	0.466	0.539	-0.34	-0.41	-0.33	-0.43
DRPK	-0.180	-0.130	-0.195	-0.145	0.245	0.230	0.240	0.226	-0.09	-0.06	-0.11	-0.07
Avg.	-0.160	-0.151	-0.170	-0.164	0.253	0.257	0.246	0.251	-0.071	-0.060	-0.086	-0.077

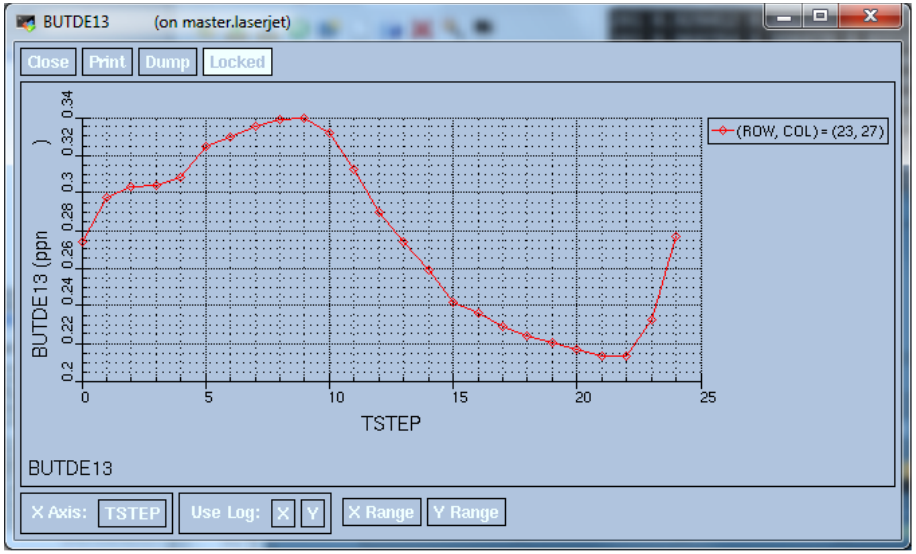
Emission rates of 7 HRVOCs and 5 non-HRVOCs



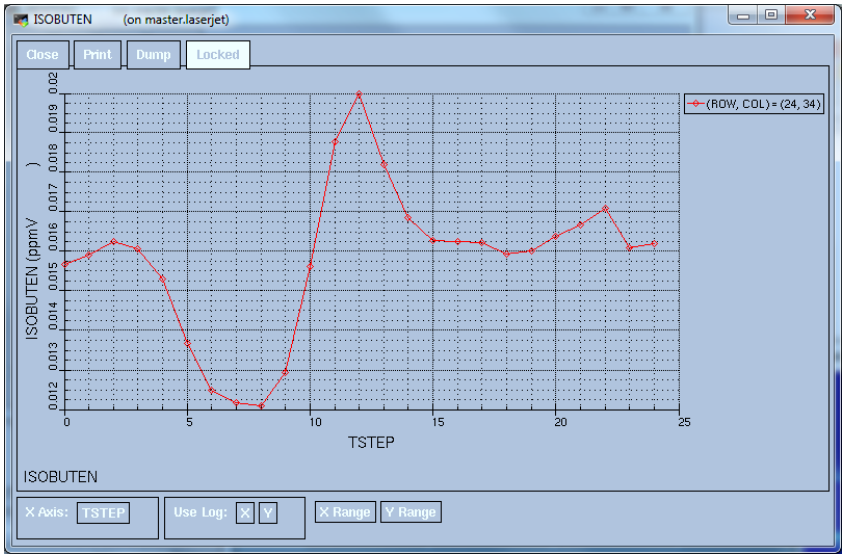
Grid size: 4x4 km

Diurnal variation in alkene fractions

1,3-butadiene (0.2-0.34)



isobutene (0.12-0.20)



* Arbitrary picked grid cell in urban Houston area