

Evaluating the SAPRC and Carbon Bond chemical mechanisms for use in southeast Texas

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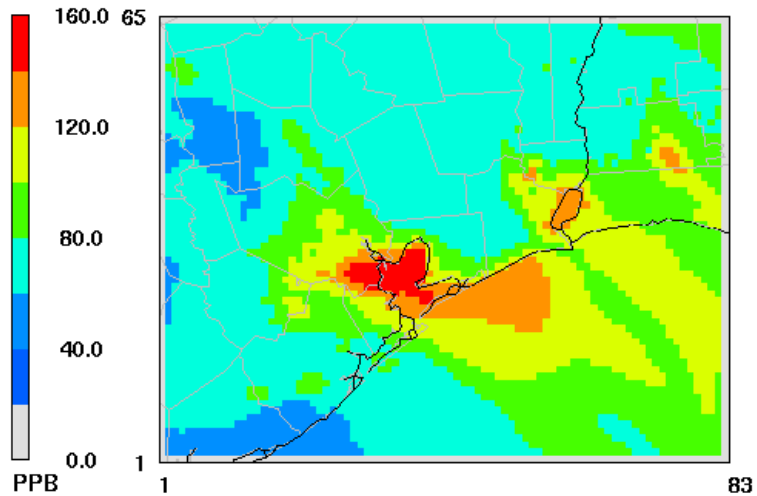
International Conference on
Atmospheric Chemical Mechanisms
December 8, 2006

Distinct ozone formation chemistry in Houston-Galveston

- Industrial source region adjoining urban area.
- Elevated concentrations of reactive VOCs coemitted with NO_x from industrial facilities
- Substantial and rapid O₃ formation (> 50 ppb/hr) relative to slower formation and accumulation in most other urban areas
- Significant variability of O₃ production over spatial scales of ~ 1km.

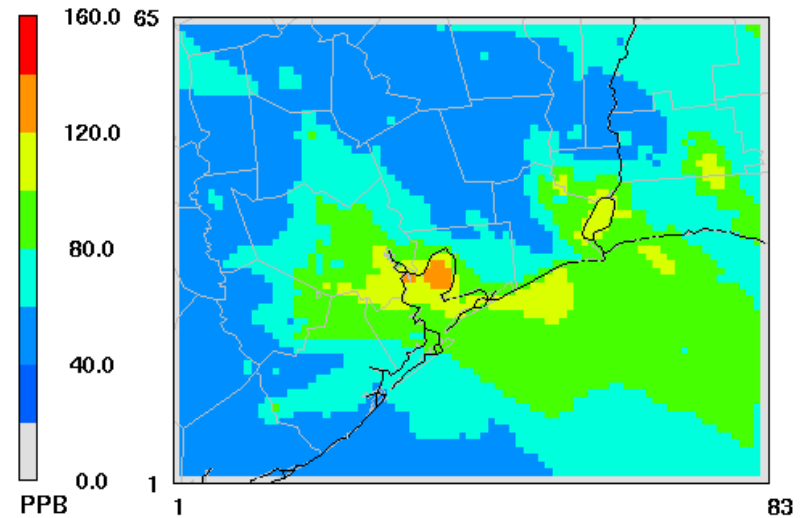
Domain-wide max O₃ concentrations in CAMx

SAPRC-99

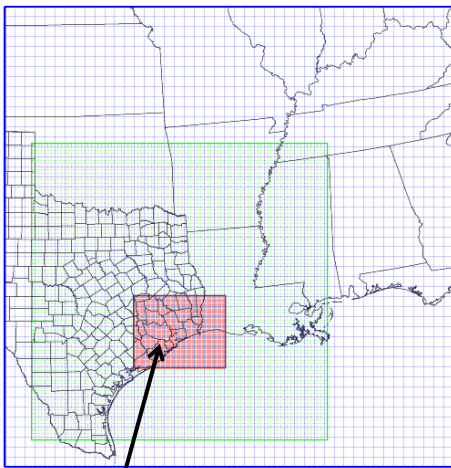


August 30,2000 15:00:00
Min= 0.0 at (1,1), Max= 157.2 at (35,28)

CB-IV

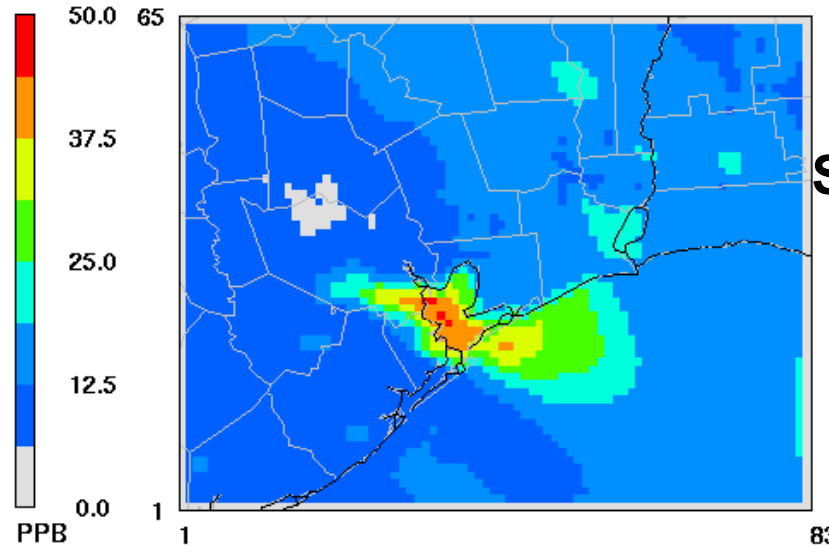


August 30,2000 15:00:00
Min= 0.0 at (1,1), Max= 123.9 at (37,30)



Regional Domain East Texas Subdomain HGBPA Subdomain

Modeling
Domain



August 30,2000 15:00:00
Min= 0.0 at (1,1), Max= 44.4 at (33,28)

SAPRC minus CB-IV

Differences up to 45 ppb

Aug. 30, 2000

Relative reductions in 8-hour O₃ after 75% NO_x cut

Monitor	SAPRC-99	CB-IV	Difference from CB-IV
Aldine	23.2 %	22.3 %	4.0 %
Chnnlview	17.7 %	12.9 %	37.2 %
DeerPk	15.6 %	8.9 %	75.3 %
Seabrook	16.9 %	7.1 %	138.0 %
BaylandPk	16.2 %	13.6 %	19.1 %
Westhollow	17.8 %	12.0 %	48.3 %

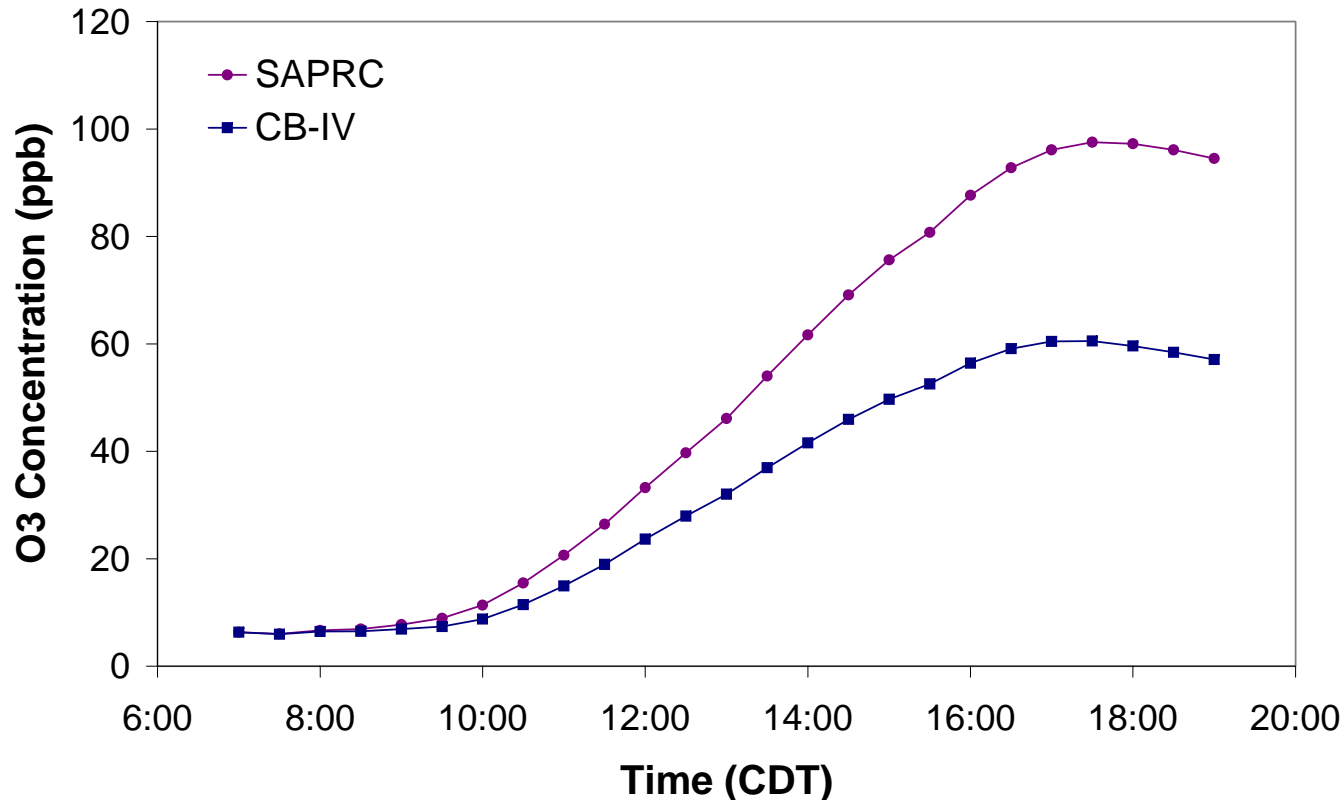
$$\% \text{ relative reduction} = \left(1 - \frac{\text{basecase w/ 75\% NO}_x \text{ cut}}{\text{basecase}} \right) * 100\%$$

Episode: Aug 25-Sept 6, 2000

Policy implications: Required vs. predicted relative reductions in ozone with 75% NOx cut

Monitor	Design Value (2003-2005)	Required for Attainment	Predicted with SAPRC-99	Predicted with CB-IV
BaylandPk	102 ppb	16.0 %	16.2 %	13.6 %
DeerPark	101 ppb	15.0 %	15.6 %	8.9 %

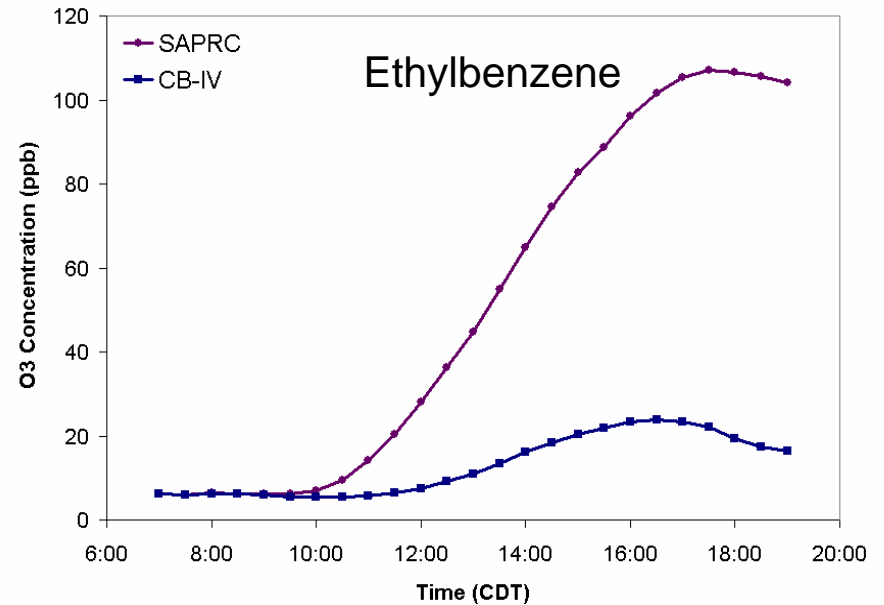
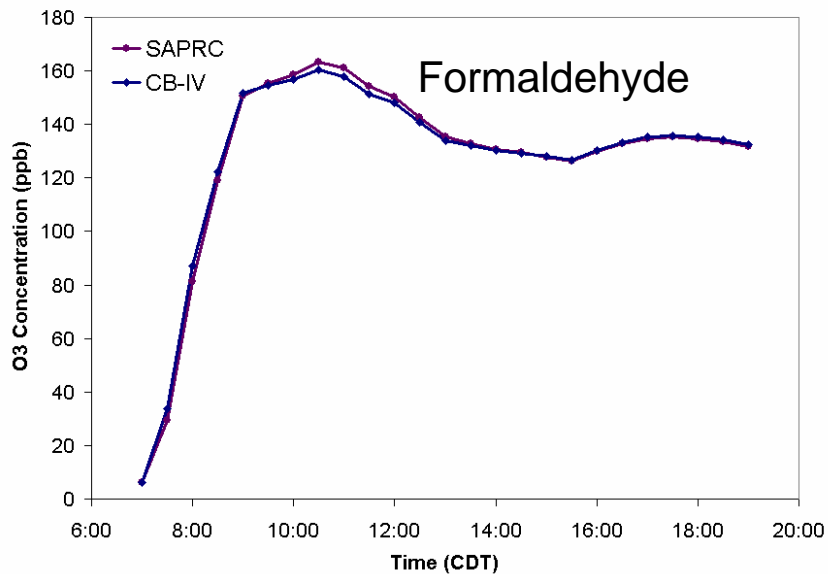
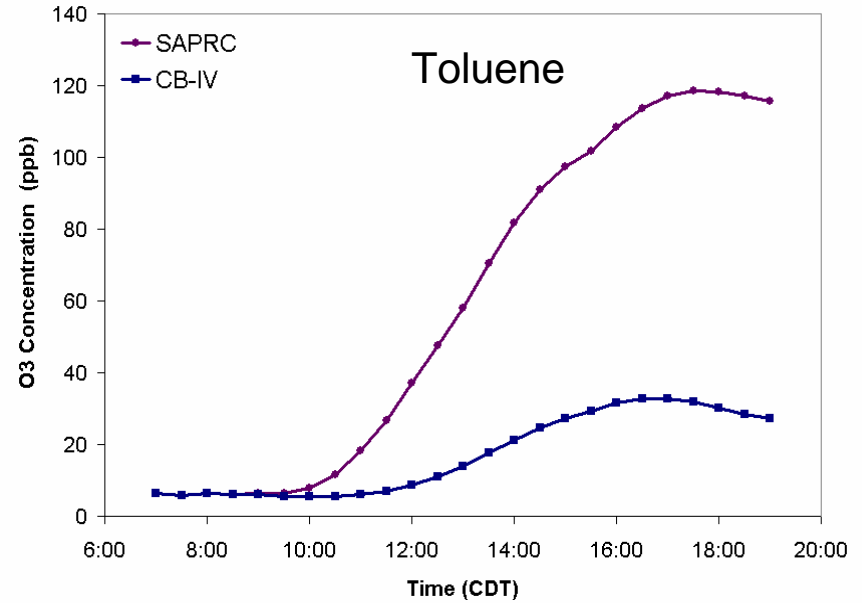
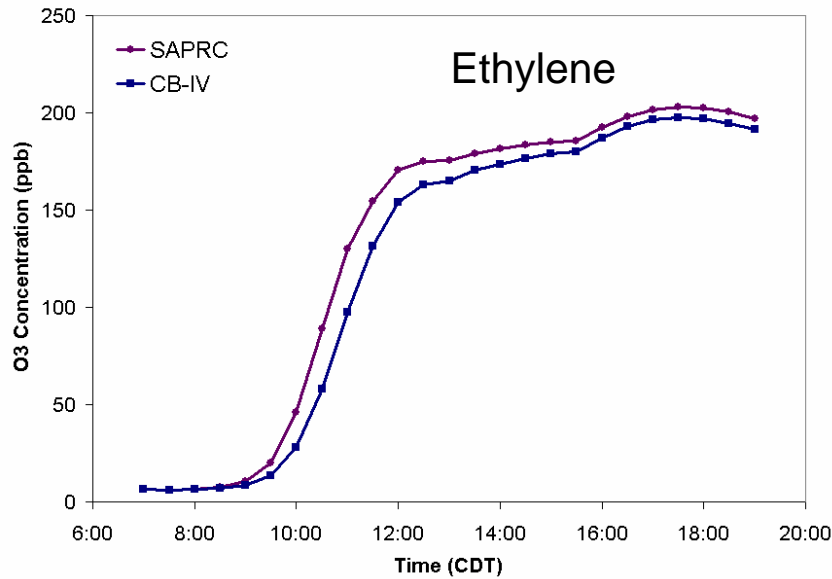
Comparison of SAPRC-99 and CB-IV in box model under conditions of industrial source region



Conducted sensitivity studies in box model to identify specific hydrocarbons contributing to differences in the industrial source region.

➤ Sensitivity studies are not representative of actual atmospheric conditions

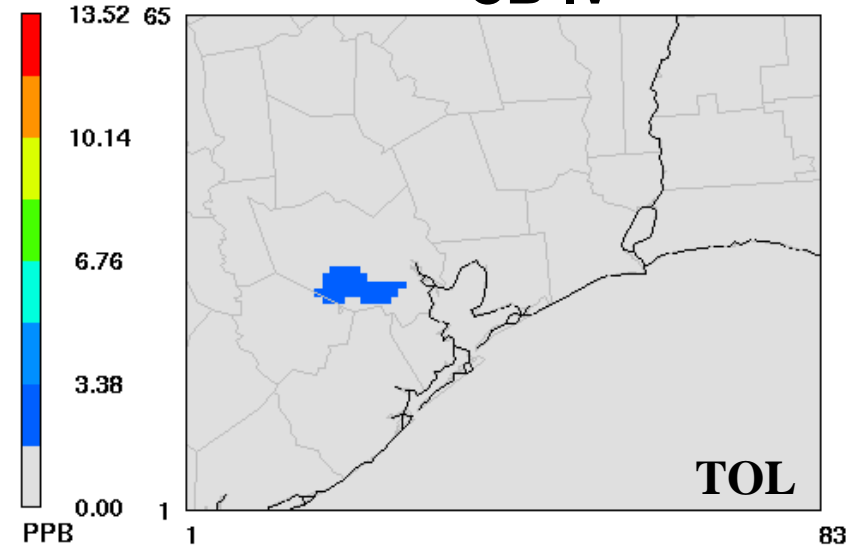
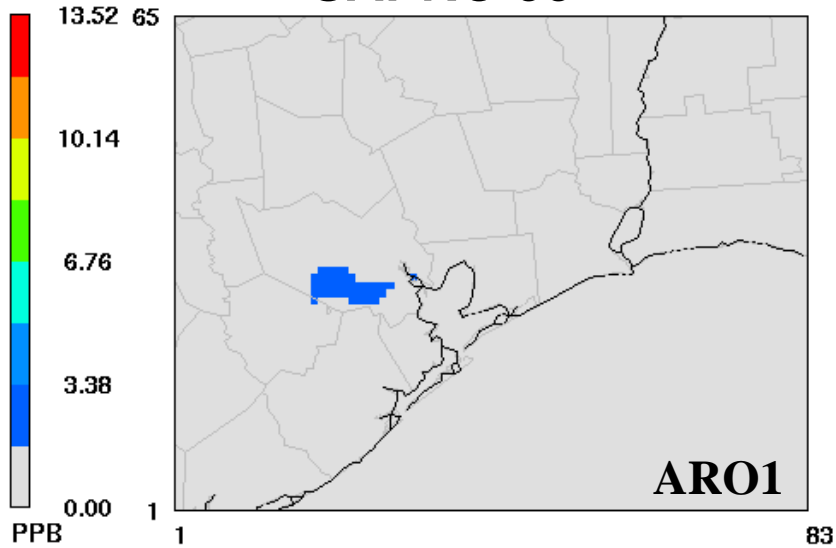
O₃ predictions in box model: VOC emissions assumed to be single explicitly-modeled species vs. mono-substituted aromatics



Different predictions of cresols for consistent mono-substituted aromatics inventories

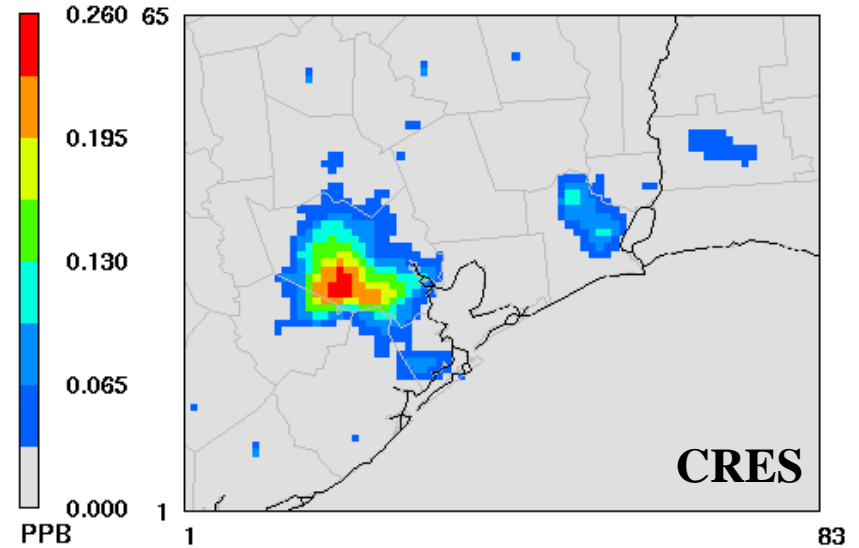
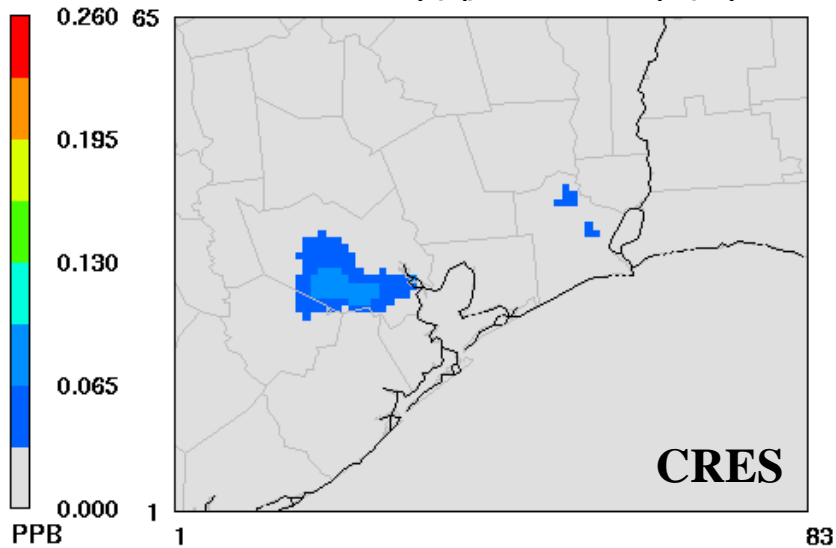
SAPRC-99

CB-IV



August 25,2000 11:00:00
Min= 0.00 at (1,1), Max= 2.78 at (27,30)

August 25,2000 11:00:00
Min= 0.00 at (1,1), Max= 2.68 at (27,30)



August 25,2000 11:00:00
Min= 0.000 at (1,1), Max= 0.096 at (26,30)

August 25,2000 11:00:00
Min= 0.000 at (1,1), Max= 0.245 at (21,30)

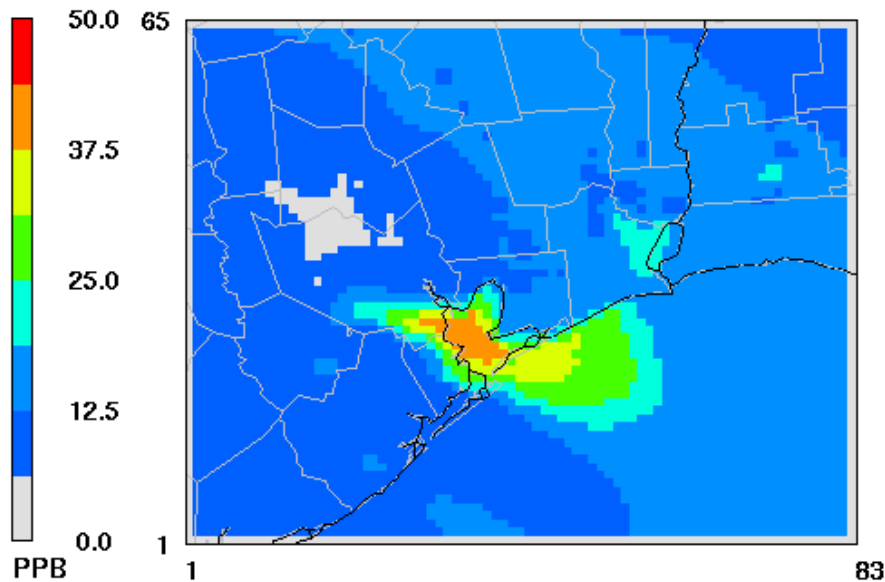
Eliminating aromatics:

Large differences in ozone persist

Hypothesis: If aromatics chemistry explains entire difference, eliminating aromatics should cause mechanisms to converge.

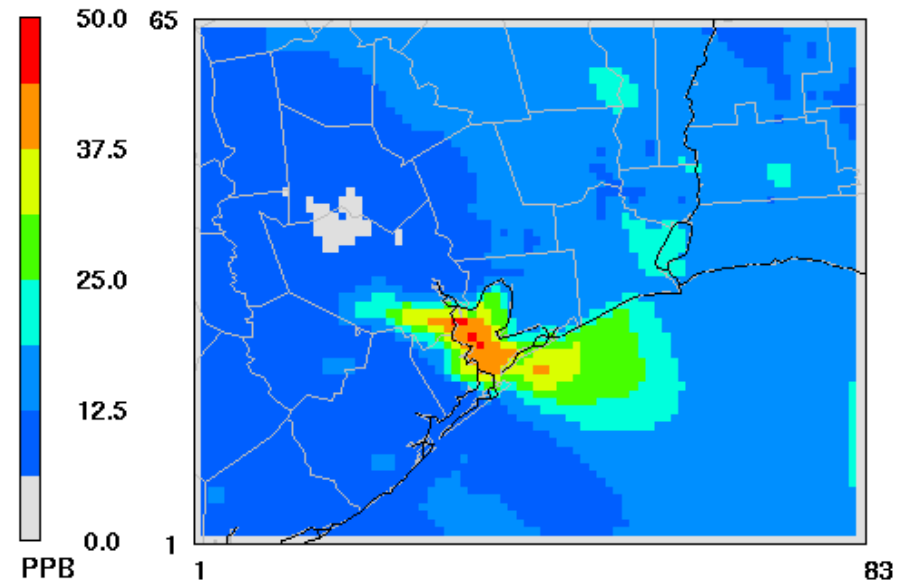
SAPRC-99 minus CB-IV

without aromatics emissions



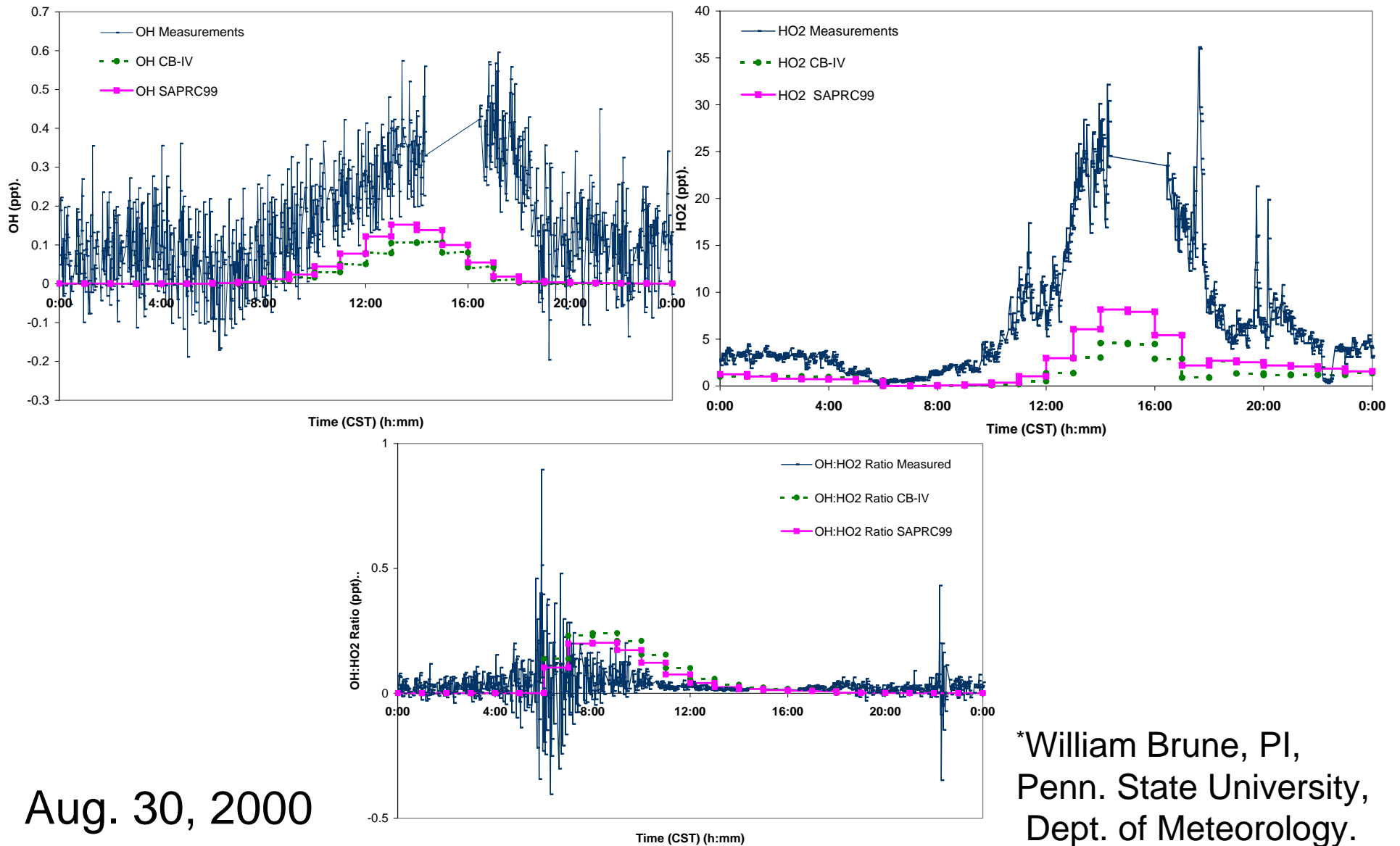
August 30, 2000 15:00:00
Min= 0.0 at (1,1), Max= 43.3 at (34,28)

basecase



August 30, 2000 15:00:00
Min= 0.0 at (1,1), Max= 44.4 at (33,28)

Predictions of HO_x with SAPRC-99 and CB-IV in CAM_x relative to measurements* in industrial source region



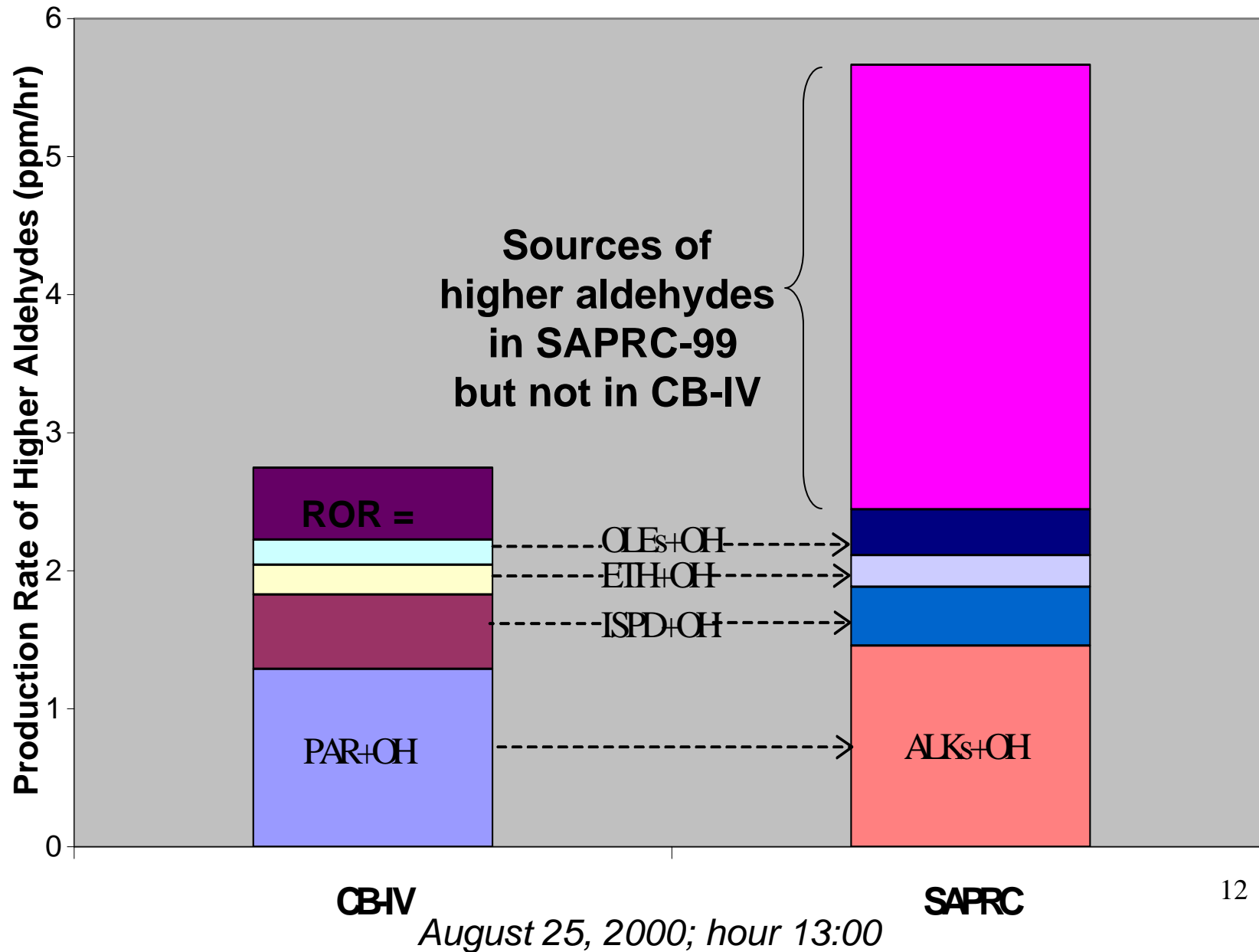
Aug. 30, 2000

*William Brune, PI,
Penn. State University,
Dept. of Meteorology.

Predictions of radicals in Houston-Galveston

- Overall underprediction of radicals in mechanisms relative to measurements
 - Group at UNC postulates additional radical generating emission sources
- Differences in radicals between SAPRC-99 and CB-IV
 - Our focus

Relative production of higher aldehydes in SAPRC-99 and CB-IV at location of max difference in O₃



Dominant sources of higher aldehydes in SAPRC-99 but not in CB-IV

- higher aldehydes + OH
- higher peroxyacyl radicals + NO
- higher reactivity non-aldehyde oxygenates + OH
- organic nitrates + OH
- methyl vinyl ketone + OH
- aromatic ring-opening products + OH

Summary

- Significant differences in predictions between SAPRC-99 and CB-IV under Houston-Galveston conditions
- Significant policy implications
- Differences due to complex and interacting phenomena
 - Aromatics chemistry
 - Free radical chemistry
- Mechansims' predictions will be evaluated against observables from TexAQSII*
- Similar differences reported for LA (Yarwood* *et al.*, 2003)

*Texas Air Quality Study, II: <http://www.utexas.edu/research/ceer/texaqsII/>

*Yarwood, G.; Stoeckenius, T.E.; Heiken, J.G.; Dunker, A.M.; Modeling of weekday/weekend ozone differences in the Los Angeles region for 1997; *J. Air & Waste Manage. Assoc.* **2003.**, 53, 864-875.

Acknowledgements

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- Dr. William Carter
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