Comparison of the SAPRC and Carbon Bond photochemical mechanisms under conditions relevant to Southeast Texas

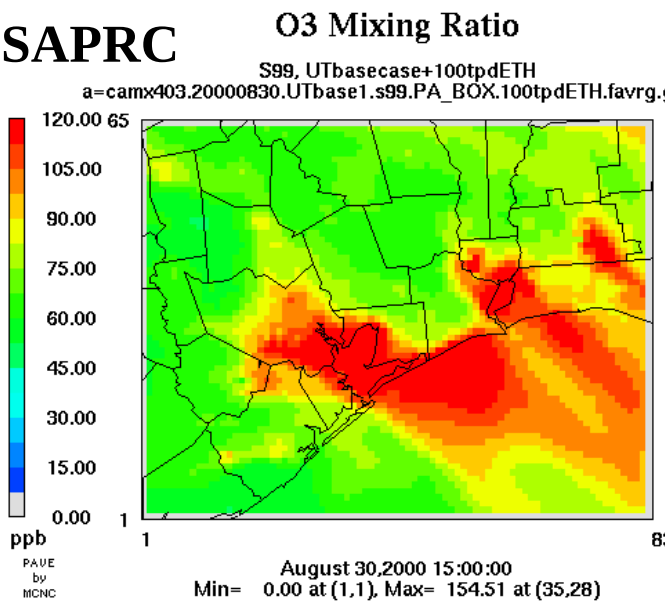
Maedeh Faraji, Yosuke Kimura,
Elena McDonald-Buller, David Allen
University of Texas at Austin

Houston-Galveston versus other Urban Areas

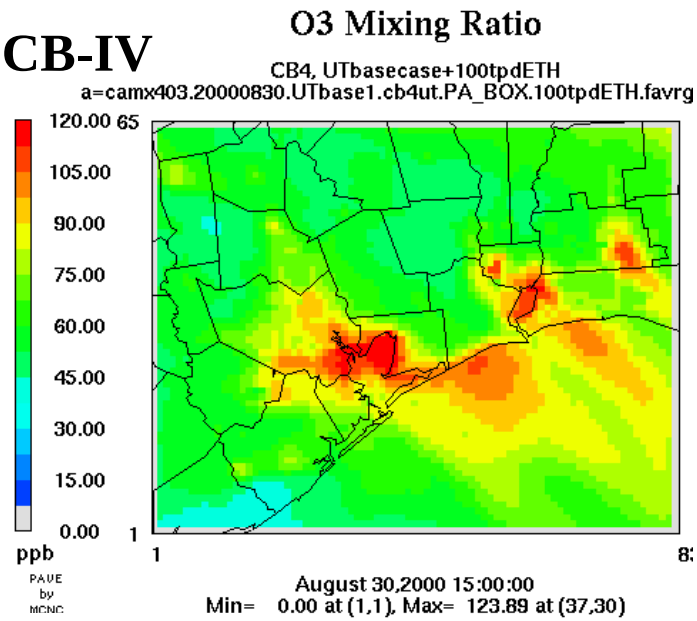
- For NOx sensitive urban areas all versions of SAPRC and CB mechanisms yield similar O_3 predictions (Dodge, 2000)
- For modeling done of summer 2000 in southeast Texas, SAPRC99 predicts concentrations of O_3 that are 30-50 ppb higher than in all versions of CB-IV

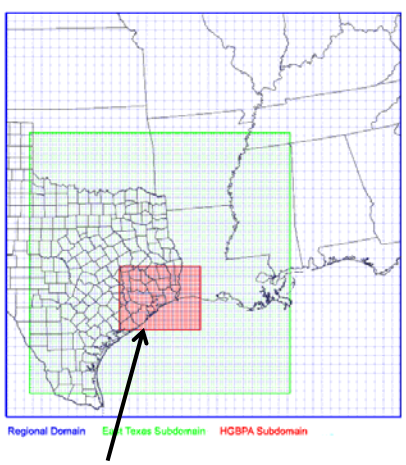
Predictions of domain-wide max O_3 concentrations in CAMx on August 30, 2000

SAPRC

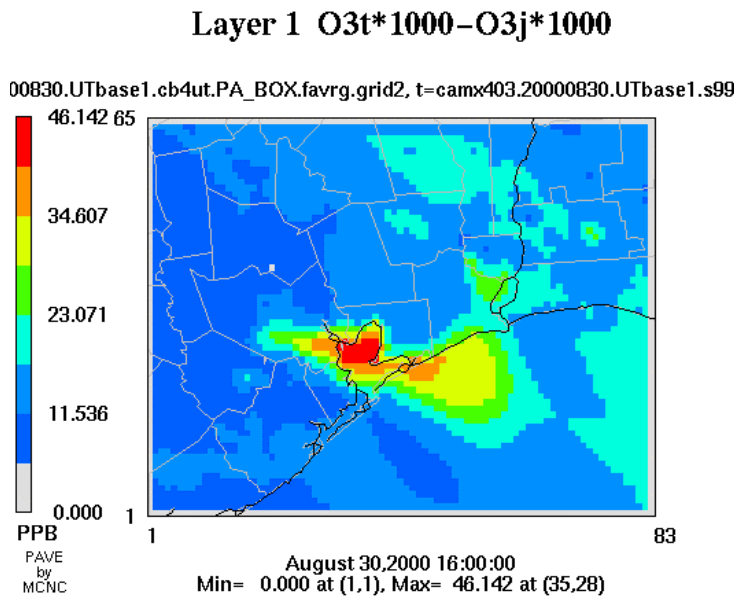


CB-IV



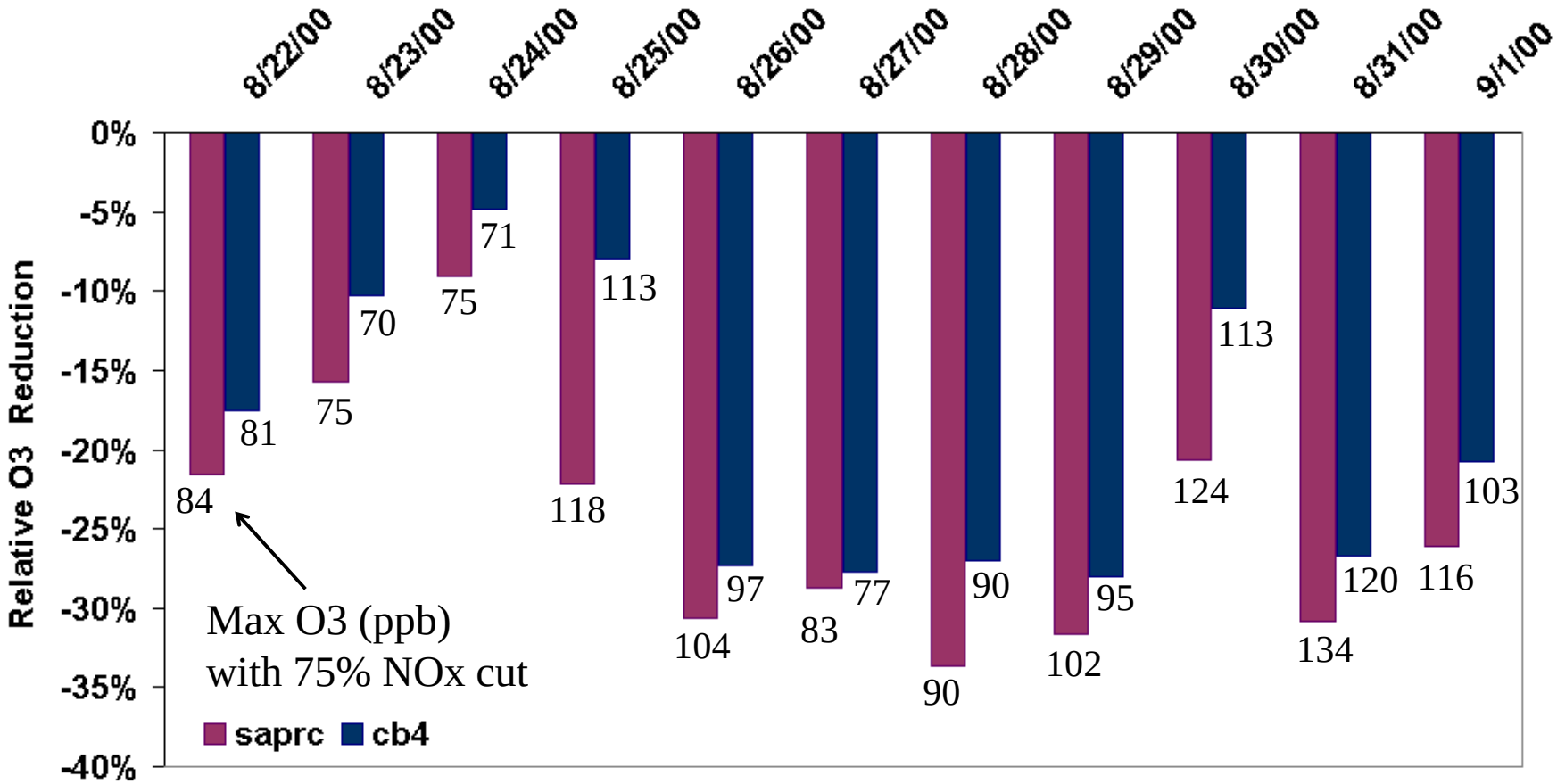


Modeling Domain



Differences can exceed 45 ppb

Percentage reductions to max O_3 concentrations in response to 75% NOx cuts



Domain-wide maxima in O_3 concentrations differ at high NOx emission conditions but largely disappear at low NOx conditions

Policy implications of differences between SAPRC and CB-IV

- SAPRC predicts consistently larger relative reductions in O_3 than CB-IV under significant NOx reductions
- SAPRC is particularly more sensitive to NOx emissions than CB-IV on certain high-O_3 days
- Demonstrating attainment for the 8-hr O_3 standard considers relative reductions in O_3 predicted by the mechanisms
- Differences in mechanism NOx sensitivity important for attaining the 8-hr O_3 standard particularly on high-O_3 days

What are the unique features of atmospheric chemistry in Houston?

- Regions with very high hydrocarbon reactivity near high NOx emission density
- Significant differences in free radical sources between two mechanisms and between the mechanisms and observations
- Not strictly a Houston phenomenon; similar differences in mechanisms reported for LA (Yarwood, *et al*., 2003)

1. What are the reasons for the differences in O_3 predictions between SAPRC and CB-IV?

2. Which mechanism is a more accurate representation of Houston's O_3 formation chemistry?

Reasons for Differences in O_3 predictions between SAPRC and CB-IV

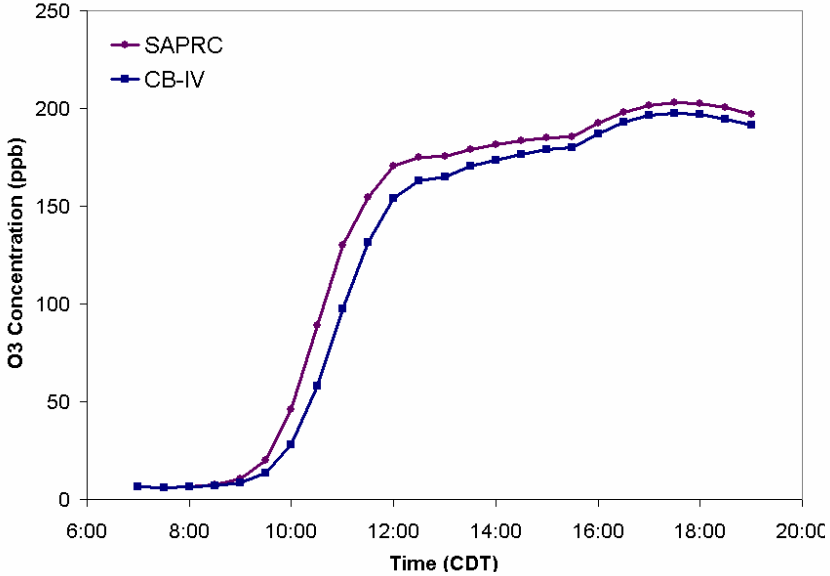
- **Aromatics Chemistry**
- Free Radical Sources and Sinks

Sensitivity studies in Box Model

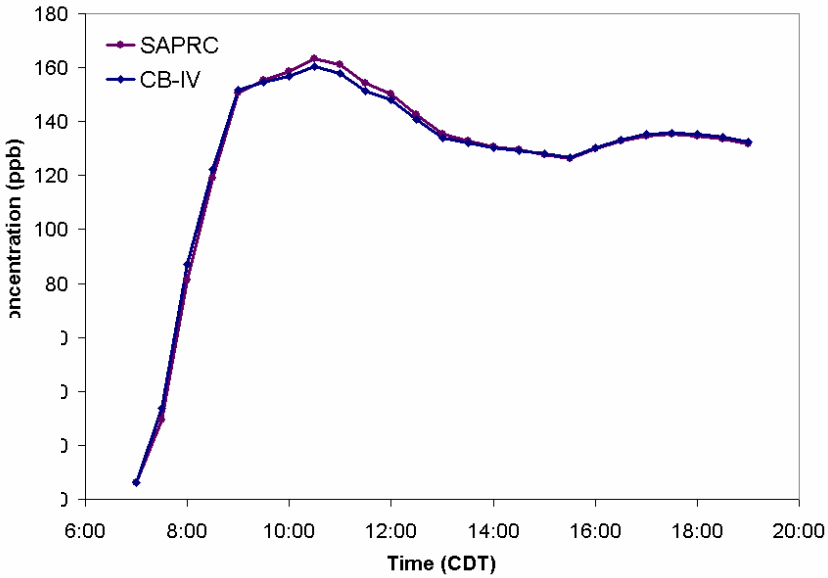
- Simplifies transport and diffusion but represents chemical transformations in detail
- Re-created differences in SAPRC and CB-IV in box model
- Representative of Houston conditions, particularly locations with high O_3 concentrations

Ozone Predictions in Box Model under high-O3 Houston conditions when VOC emissions are assumed to be single explicitly-modeled species

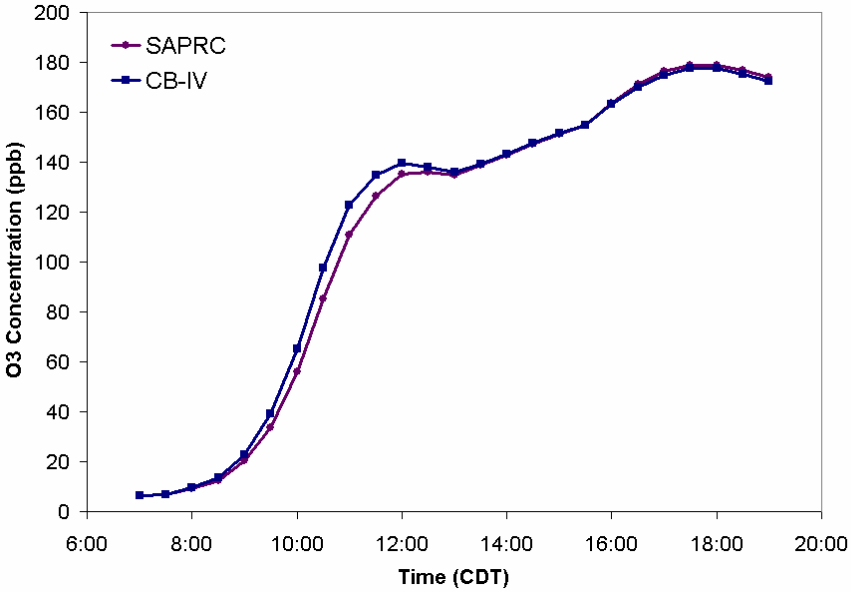
Ethylene



Formaldehyde

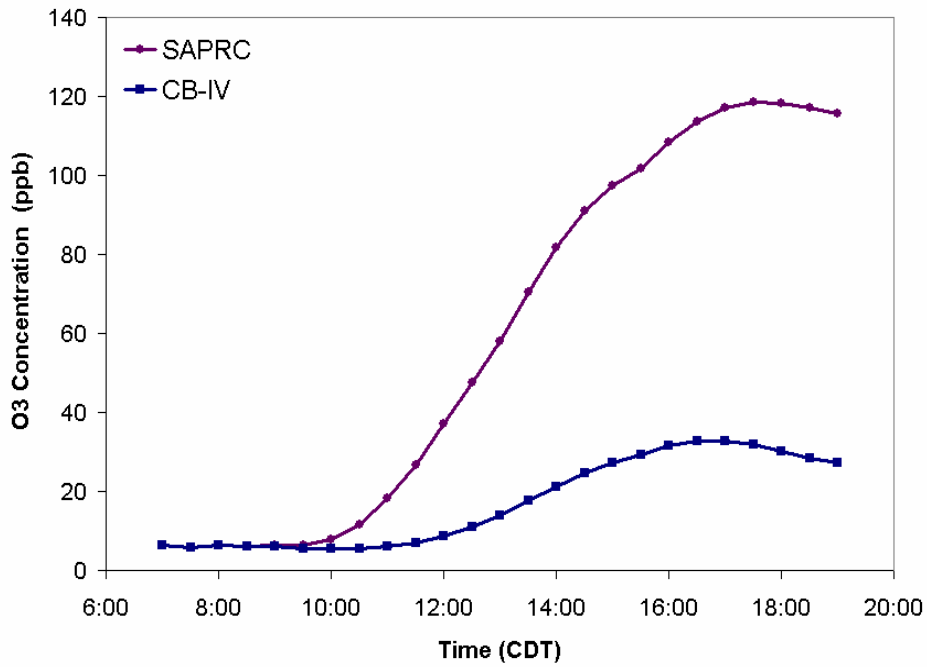


Isoprene

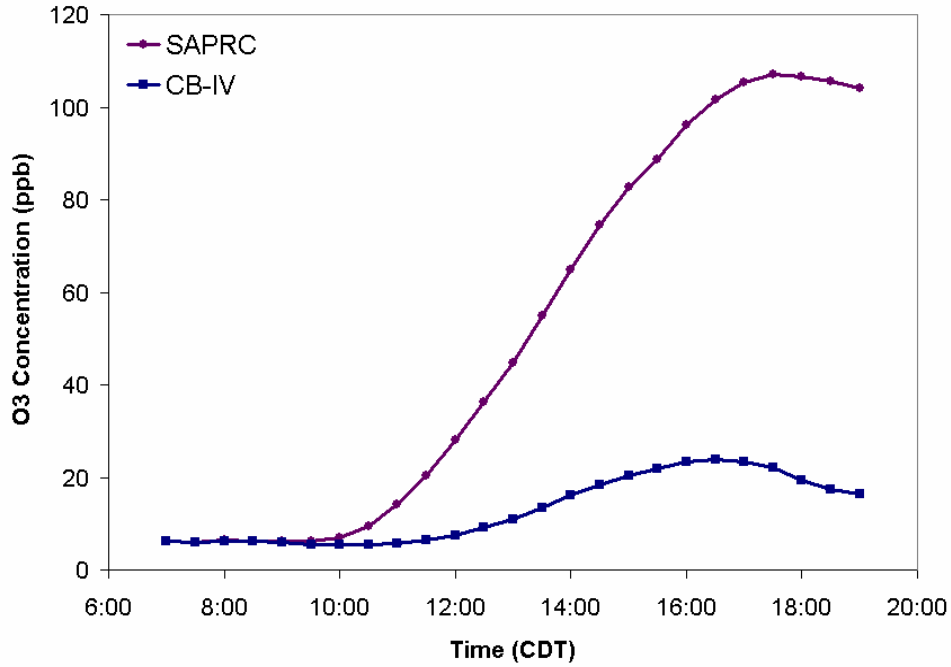


Ozone Predictions in Box Model under high-O_3 Houston conditions when VOC emissions are assumed to be single Mono-substituted Aromatics

Toluene



Ethylbenzene

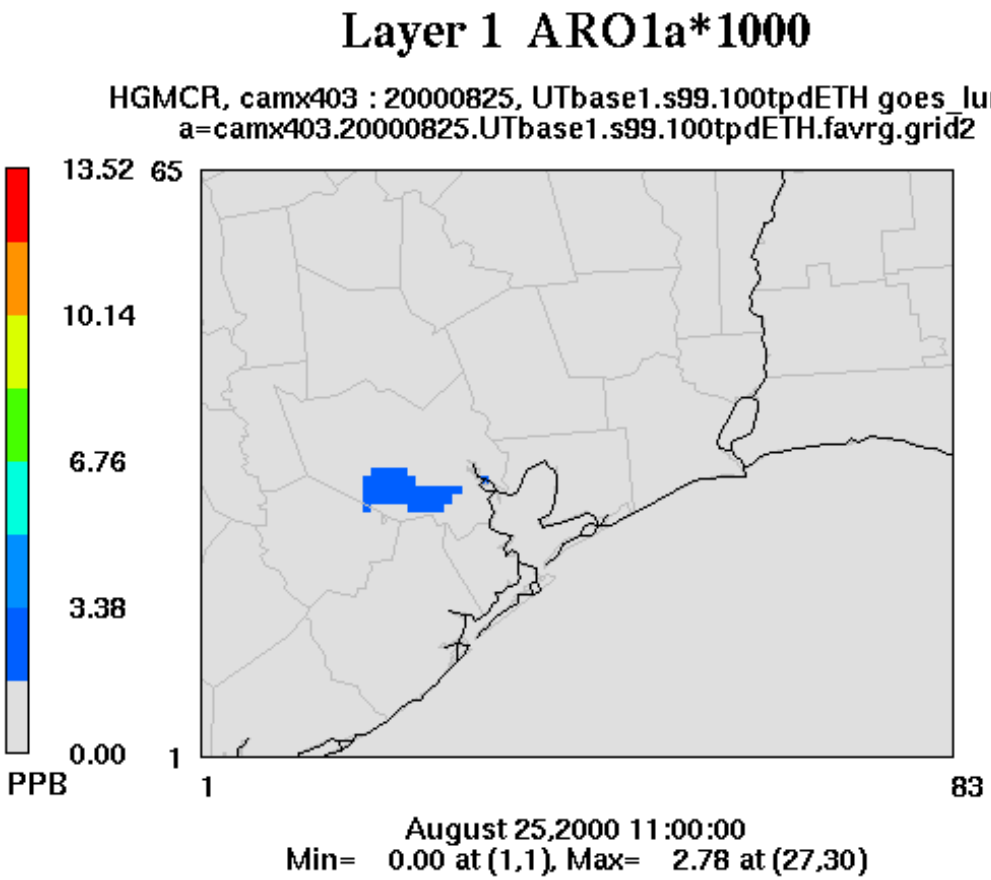


Aromatics Chemistry in SAPRC vs. CB-IV

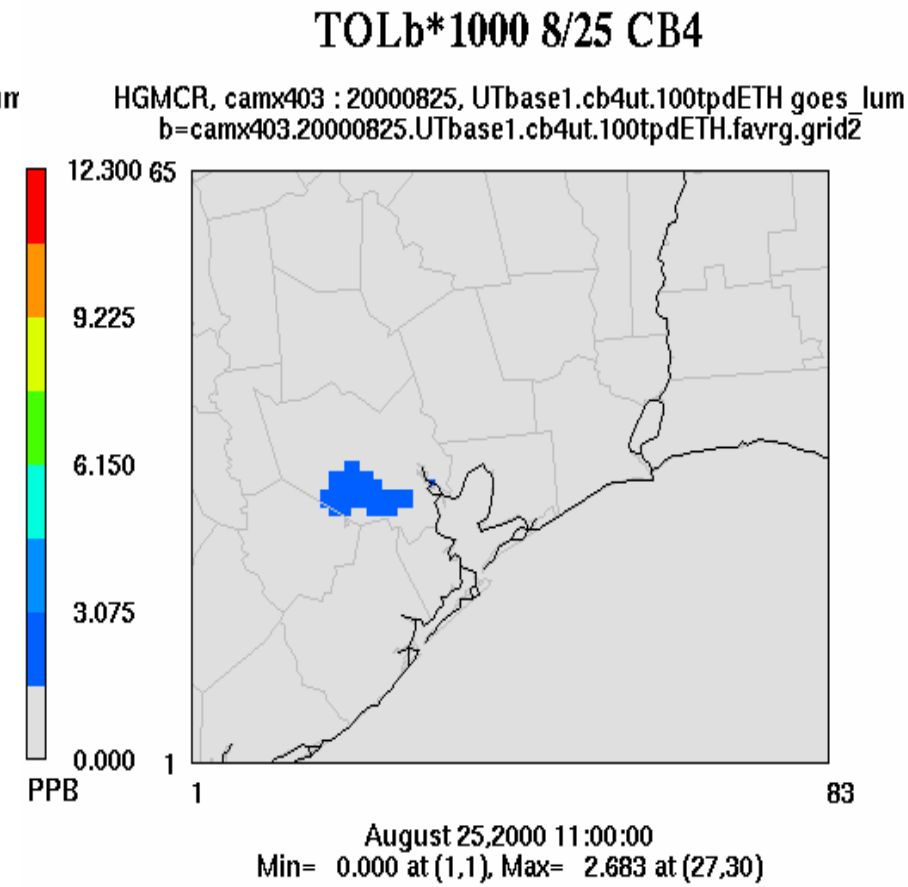
- OH-initiated reactions of aromatics yield ring-retaining and ring-opening products
  - Ring-retaining products include stable cresols
  - Ring-opening products include reactive dicarbonyl species (e.g., methyl glyoxal)
- Different branching ratios of ring-retaining vs. ring-opening products in SAPRC and CB-IV
- SAPRC predicts much higher ring-opening products which lead to more free radicals
- In isolation, does not explain the entire difference between SAPRC and CB-IV

Consistent Toluene inventories between SAPRC and CB-IV on August 25, 2000 at hour 11:00

SAPRC

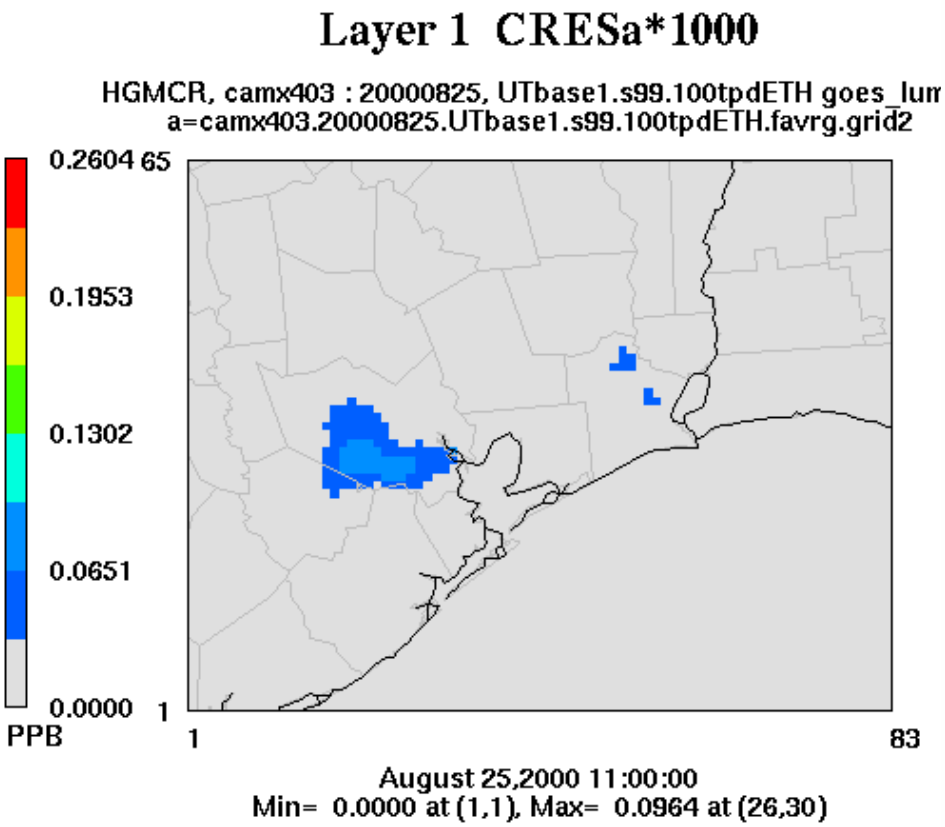


CB-IV

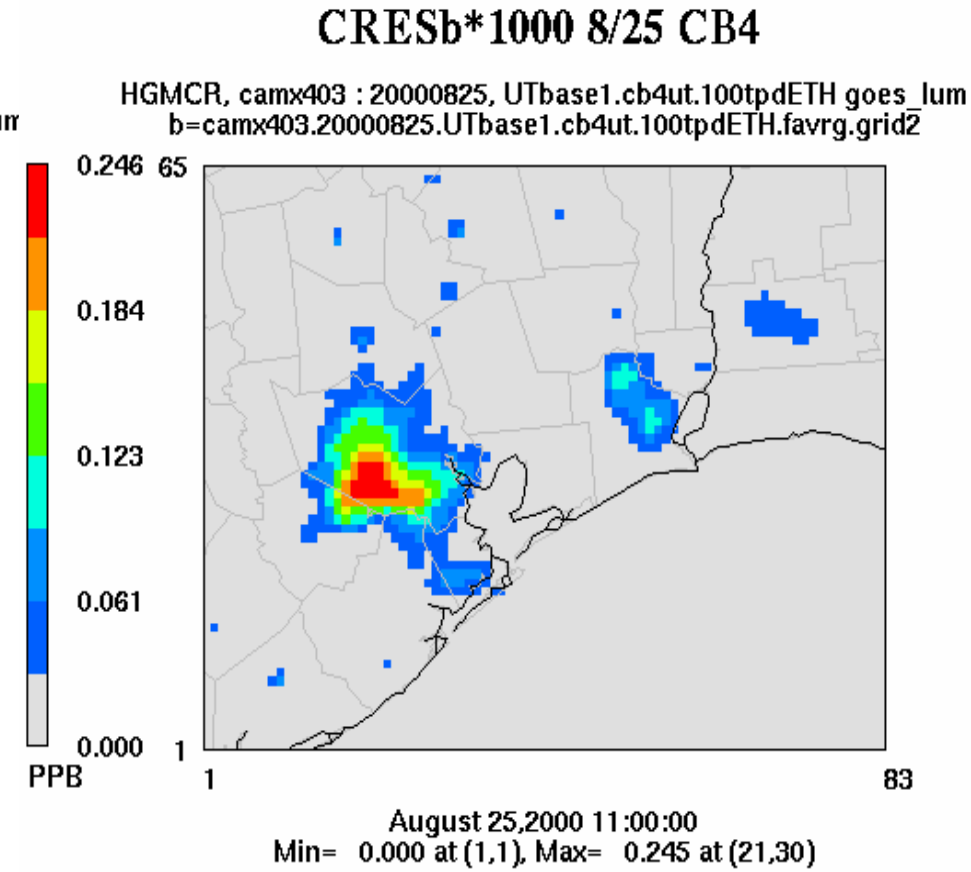


Prediction of Cresols (lumped) in SAPRC versus CB-IV on August 25, 2000 at hour 11:00

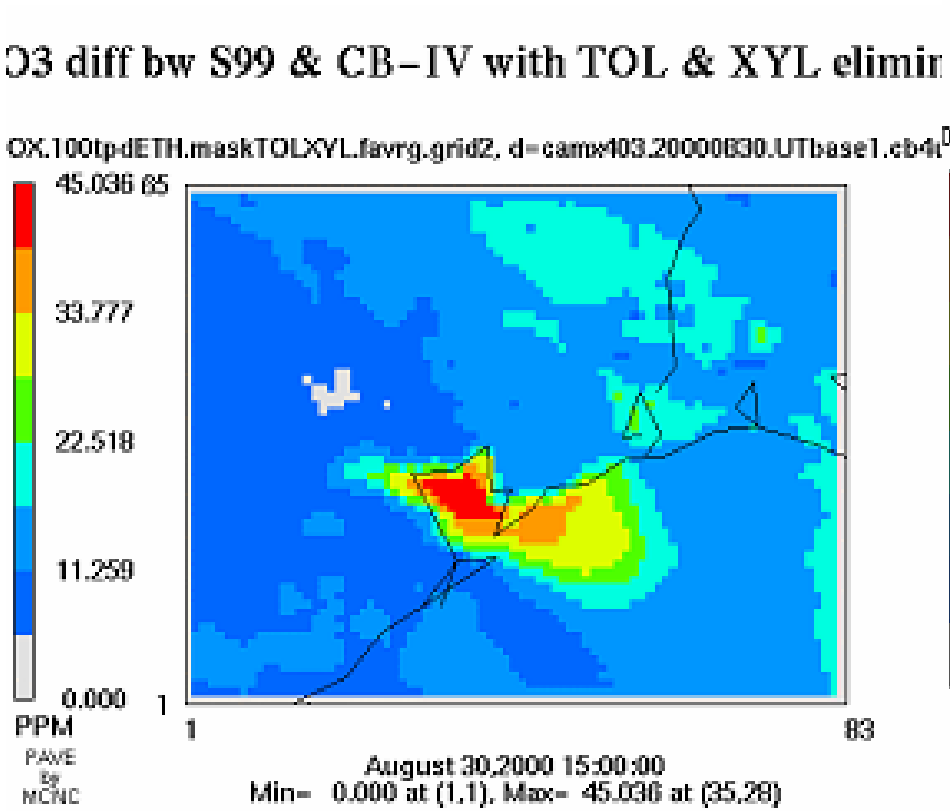
SAPRC



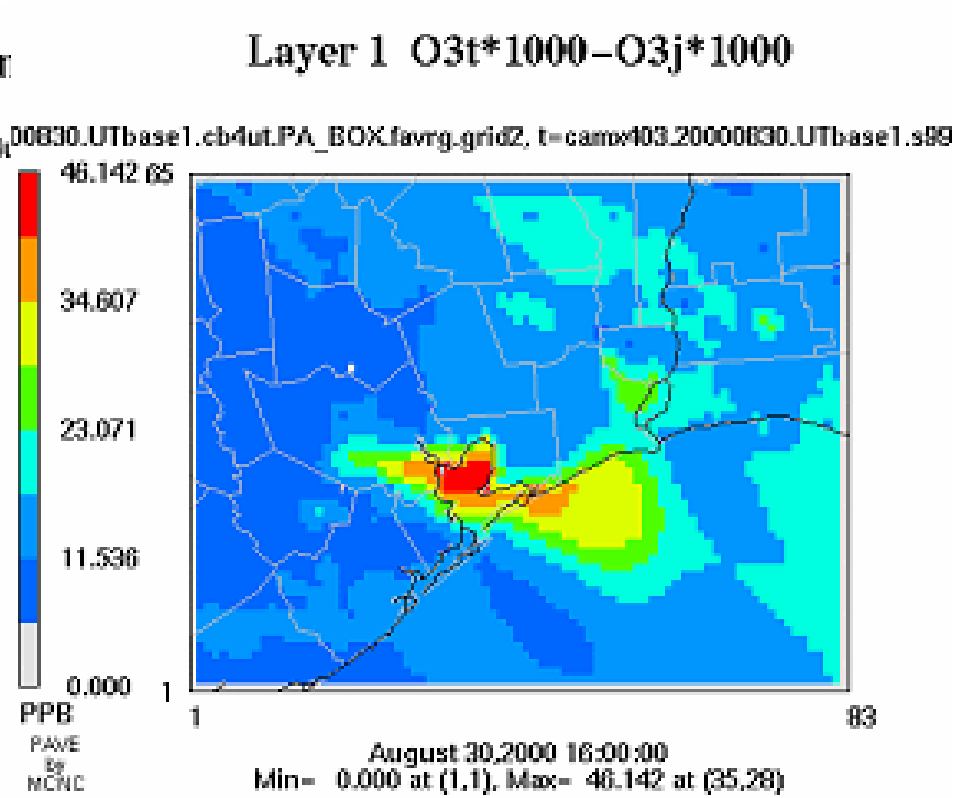
CB-IV



Differences in O_3 predictions on August 30th, 2000 eliminating Aromatic emissions versus basecase



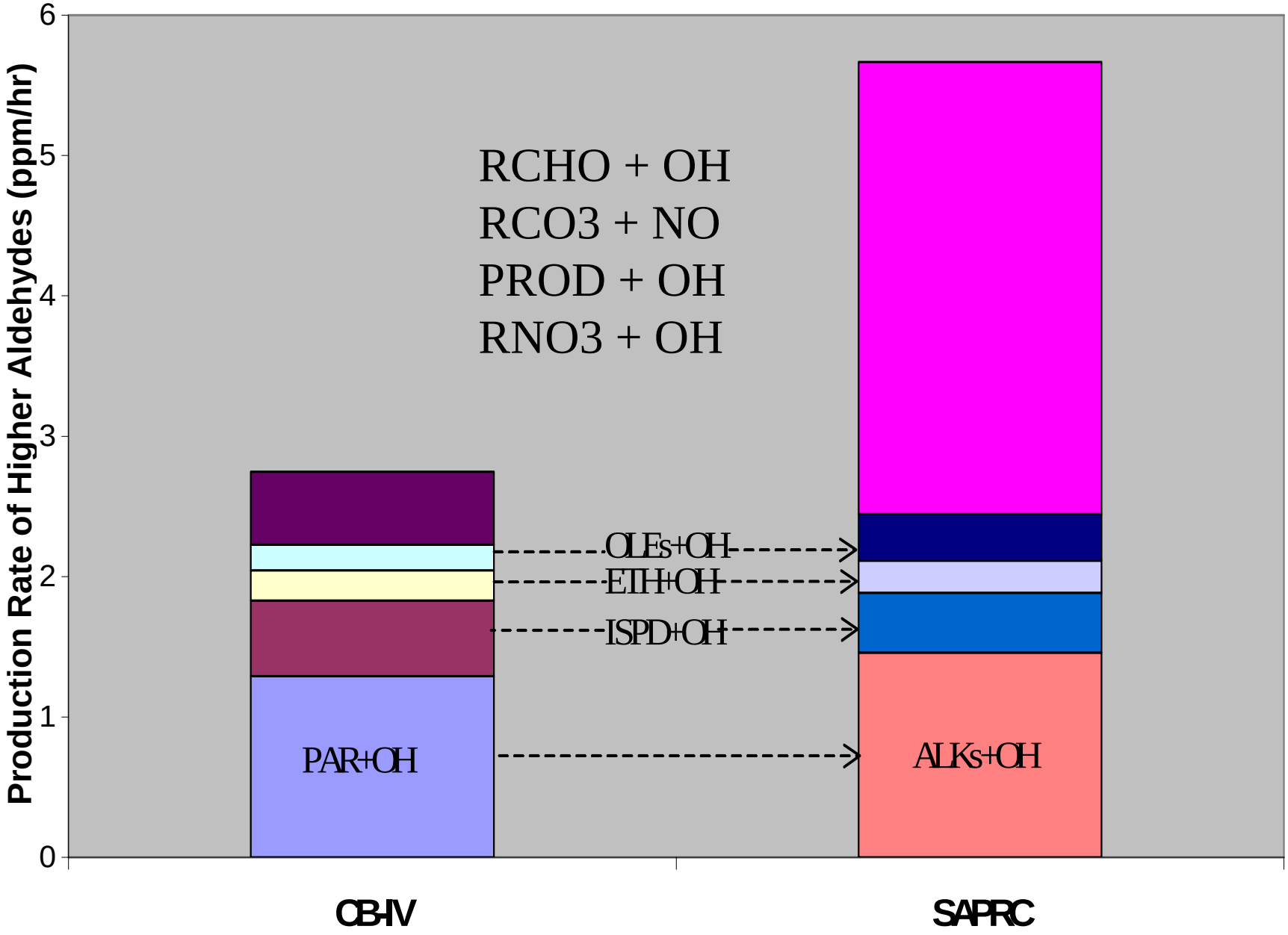
Basecase



Reasons for Differences in O_3 predictions between SAPRC and CB-IV

- Aromatics Chemistry
- **Free Radical Sources and Sinks**

Relative production of higher aldehydes by SAPRC and CB-IV at hour 13:00 on August 25th at location of max difference in O_3



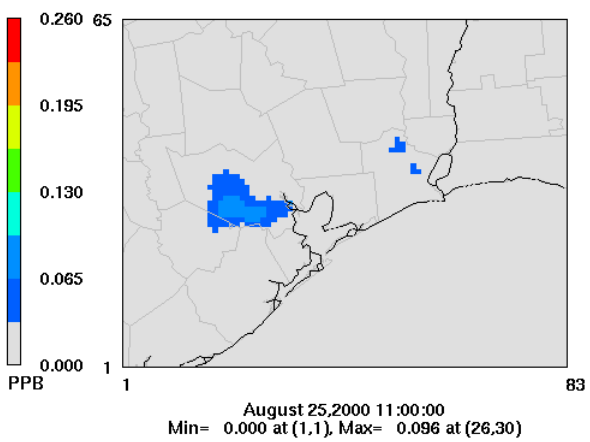
1. What are the reasons for the differences in O_3 predictions between SAPRC and CB-IV?

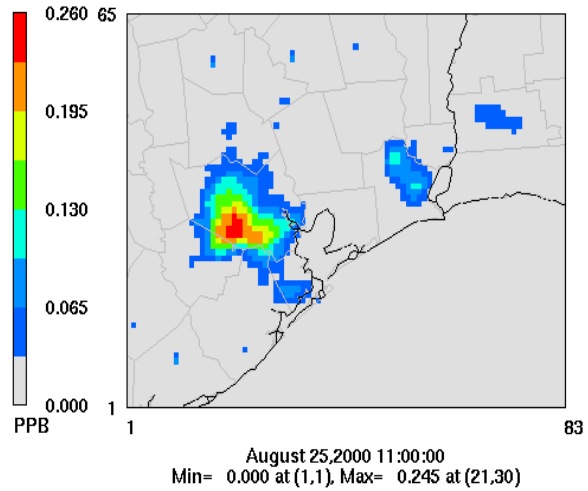
2. Which mechanism is a more accurate representation of Houston's O_3 formation chemistry?

Designing Experiments as part of a large air quality field program, TexAQSII

- Potential observable for evaluating aromatics chemistry: $\frac{\sum \text{Cresols}}{\sum \text{Toluene}}$
- Nitric acid, OH, and NO_2 concentrations can be measured in evaluating free radical termination
- Higher Aldehydes concentrations can be markers for radical sources

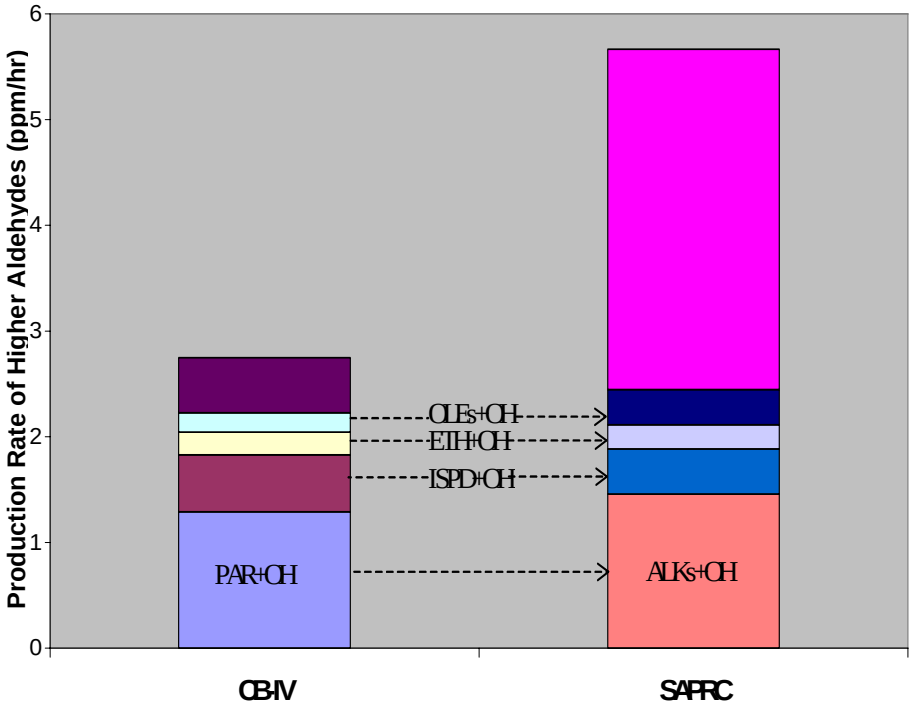
Designing Experiments as part of a large air quality field program, TexAQSII





- Potential observable for evaluating aromatics chemistry: cresol to benzaldehyde ratio or $\frac{\sum \text{Cresols}}{\sum \text{Toluene}}$

Designing Experiments as part of a large air quality field program, TexAQSII



- RCHO + OH
- RCO3 + NO
- PROD + OH
- RNO3 + OH

Higher aldehydes concentrations, organonitrates