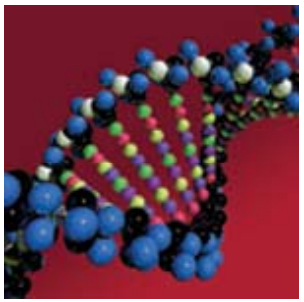
CB6

Version 6 of the Carbon Bond Mechanism


Greg Yarwood, ENVIRON

Gookyoung Heo, UT Austin

Gary Whitten, SmogReyes

Presented by Mark Estes, TCEQ

October 14, 2010

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Outline

- CB6 Objectives
- Project Team
- Mechanism Design
- Preparing Emissions for CB6
- Evaluation with Chamber Data
- CAMx Implementation and Testing
- Conclusions and Recommendations

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CB6 Objectives

- TCEQ-sponsored research suggests mechanism differences (i.e. uncertainties) may influence response to emission reductions
- Carbon Bond mechanism last updated in 2005
  - New data and interpretations emerge
  - Faster computers permit more detailed mechanisms
  - Several updates ready from TCEQ projects in FY08/09
    - Toluene, isoprene, nitryl chloride, NO2*
- CB6 objectives
  - Update mechanism core to 2010
  - Expand mechanism to address emerging needs
  - Combine and integrate available updates from recent TCEQ work
  - Perform complete mechanism evaluation
  - Implement and test in CAMx

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Project Team

- Gary Whitten
  - Consultant in Point Reyes, California
  - Inventor of Carbon Bond approach (CB2, CB4/CBM-X, CB05/CB05-TU)
  - Project Role: Mechanism updates for isoprene, aromatics, alkenes
- Gookyoung Heo
  - Post-doc at UT Austin and soon moving to UC Riverside
  - Project Role: Mechanism evaluation; Critical review of mechanism updates and implementation
- Greg Yarwood
  - Principal at ENVIRON in Novato, California
  - Role: Overall mechanism design/implementation; CAMx

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CB6 Mechanism Design

- Constraints
  - Maintain backwards compatibility with existing databases
    - Can use CB05 (or even CB4) emission with CB6
  - Computational efficiency
    - Limit simulation time increases
- Emerging needs
  - Lower ozone standard emphasizes regional problems
    - Improve long-lived, abundant VOCs such as propane
    - Fate of NOz (e.g., organic nitrates) – recycled back to NOx?
  - Secondary organic aerosol (SOA) often important for fine PM
    - Gas-phase chemistry should support SOA requirements
    - Volatility basis set (VBS) being used for gas/aerosol partitioning
    - Aqueous reactions form SOA from dicarbonyls (e.g., glyoxal)

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CB6 Updates for Oxidants

- Oxidant updates
  - Inorganic reactions to IUPAC 2010
  - Recent photolysis data (IUPAC, NASA/JPL, other)
  - New aromatics chemistry
  - New isoprene chemistry
  - New ketone species (acetone and higher ketones)
  - Explicit propane, benzene, ethyne (acetylene)
- Optional oxidant updates
  - Optional means available and can chose whether/when to use
  - Nitryl chloride (ClNO2) formation and chlorine atom reactions (based upon TexAQS 2000 and TexAQS II results)
  - Photo-excited NO2 (NO2*) which remains controversial – real or artifact?

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CB6 Updates that Support Aerosol Modeling

- Additional SOA precursors

  Added new VOCs that are SOA precursors

  – Benzene

  – Ethyne (acetylene)

- Explicit alpha-dicarbonyls: –C(O)CH(O) also –C(O)CH_2OH

  Aqueous reactions form SOA by polymerizing these compounds

  – Glyoxal (GLY), methylglyoxal (MGLY), glycolaldehyde (GLYD)

  – Precursors are isoprene, aromatics, ethene, propene (etc.), ethyne

  – GLY and GLYD are newly explicit in CB6

- Improved hydrogen peroxide

  Hydrogen peroxide converts SO_2 to sulfate aerosol in clouds

  – Improve how some peroxy radical reactions (RO2 + HO2) are handled

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Preparing Emissions for CB6

- Propane: PRPA
  - In CB05 was 1.5 PAR + 1.5 NR
- Benzene: BENZ
  - In CB05was 1 PAR + 6 NR
- Ethyne (acetylene): ETHY
  - In CB05 was ALDX
- Acetone: ACET
  - In CB05 was 3 PAR
- Higher ketones: KET
  - Methyl ethyl ketone ($CH_3C(O)CH_2CH_3$) is the prototypical example
  - MEK was 4 PAR in CB05, is 3 PAR + KET in CB6
- Other new CB6 species (e.g., GLY, GLYD) have negligible emissions

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Summary of CB6 and CB05

	CB05	CB6	Change
Gas-phase reactions	156	218	+ 40%
Photolysis reactions	23	28	+ 22%
Gas-phase species	51	77	+ 50%
Emissions species for ozone	16	21	+ 31%

Some notable reaction rate changes from CB05 to CB6:

- $OH + NO_2 = HNO_3$ increased by 5% => greater radical sink
- $HCHO + h\nu = 2\ HO_2 + CO$ increased by 23% => greater radical source
- $HO_2 + NO = OH + NO_2$ increased by 5% => more efficient ozone formation
- $NO_2 + h\nu = NO + O$ increased by 7% => more ozone
- $N_2O_5 + H_2O = 2\ HNO_3$ decreased by ~80%
  - Less NOx removal at night
  - Very important to include N_2O_5 reaction on aerosol surfaces

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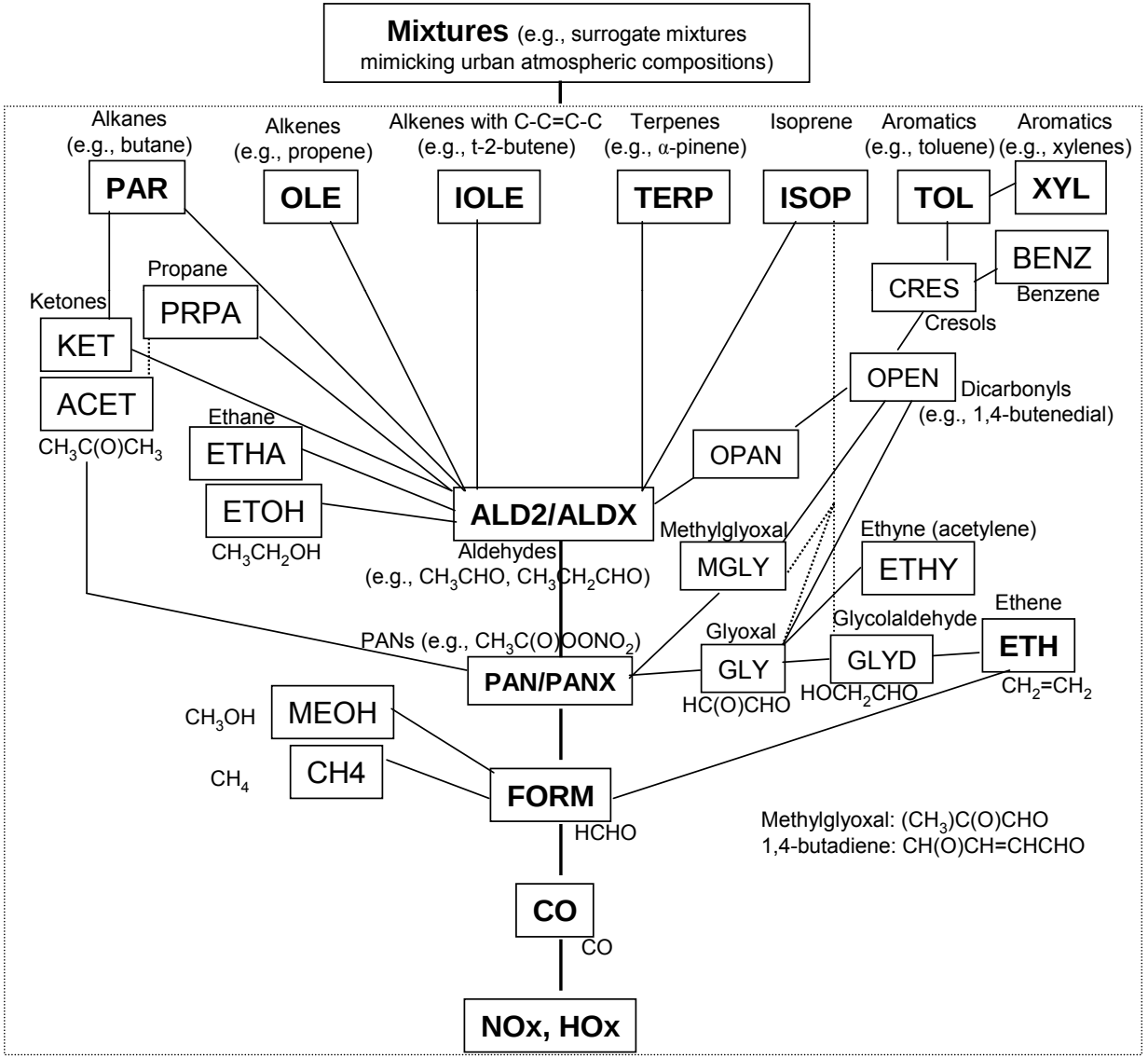
Evaluation with Chamber Data

- Evaluated CB6 using environmental chamber simulations
- Evaluated CB6 using a hierarchical approach (e.g., from CO – NOx system to complex VOCs – NOx system)
- Used ~340 chamber experiments of 8 different smog chambers (7 indoor and 1 outdoor)
  - First, screened available chamber experimental data to select useful data for mechanism evaluation
- Used 3 performance metrics to evaluate CB6:
  - Max(O_3): Maximum O_3 concentration
  - Max(D(O_3-NO)): Maximum $\{([O_3] - [NO])_{t=t} - ([O_3] - [NO])_{t=0}\}$
  - NOx crossover time: Time when NO_2 becomes equal to NO
- Compared CB05, CB05-TU and CB6
  - Also produced chamber simulation results for CB05 and CB05-TU

Hierarchical Approach

- Test each component of CB6, and systematically evaluate the entire CB6 mechanism while minimizing compensating errors



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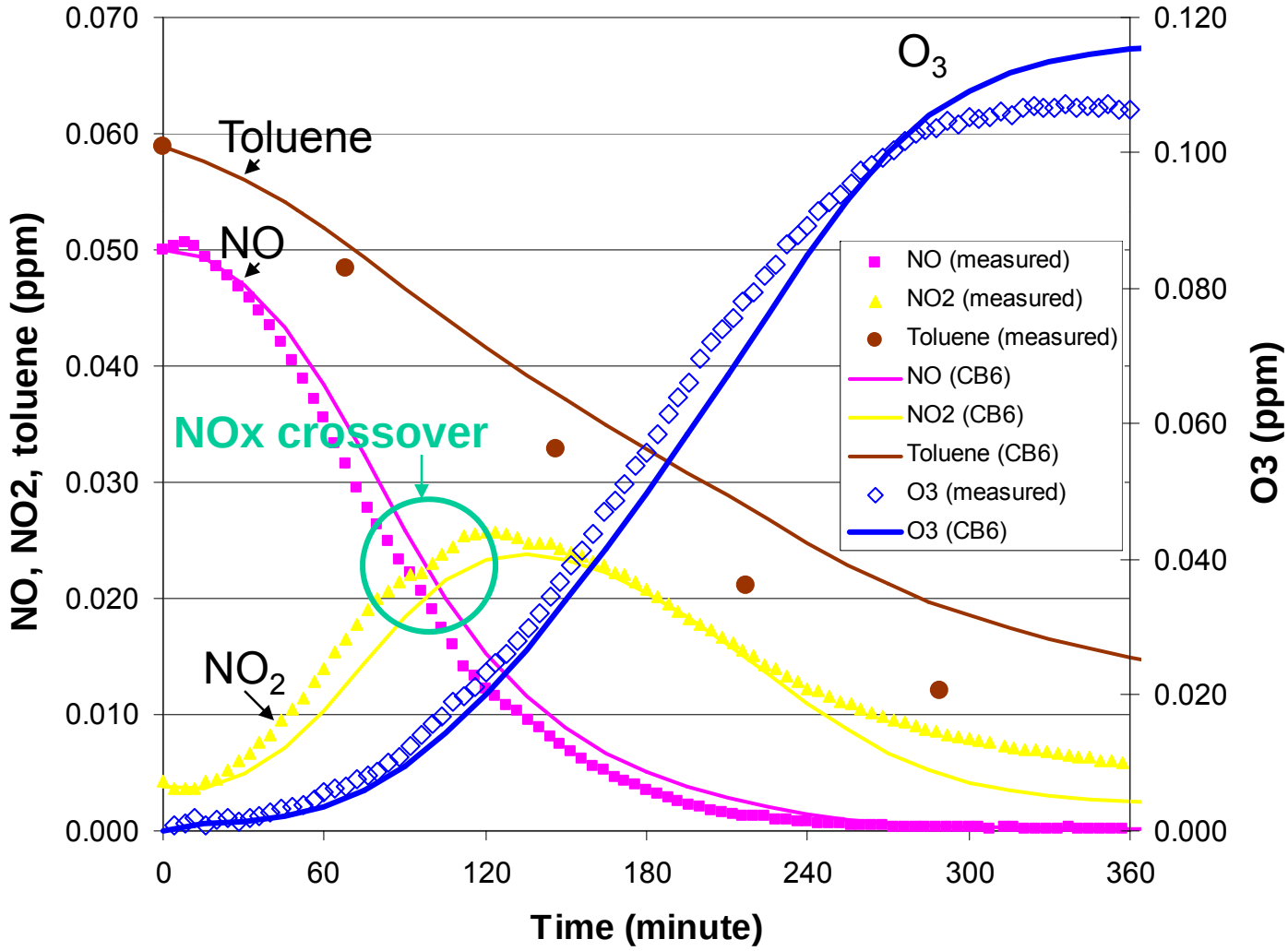
Chamber Data

- UC Riverside chamber database
  - UC Riverside database contains experimental data for thousands of experiments produced at UC Riverside and TVA (Tennessee Valley Authority)
  - Note: UNC chamber data were not used due to the light model issue
- Selecting chamber data useful for CB6 evaluation
  - Excluded blacklight-used experiments whenever possible
  - For most cases, 10 ppb < [NOx]o < 300 ppb
- Evaluating each components of CB6
  - Used ~195 chamber experiments of single test compounds (or special mixtures) (e.g., CO - NOx)
  - For MEOH (methanol), ETOH (ethanol), ETHA (ethane) and PRPA (propane), only blacklight/mixture experiments were available
- Evaluating interactions of CB6 components and CB6 as a whole
  - Used 145 surrogate mixture experiments (e.g., 8-compnent VOC mixture – NOx)

Chamber Simulation Results: Time series plots

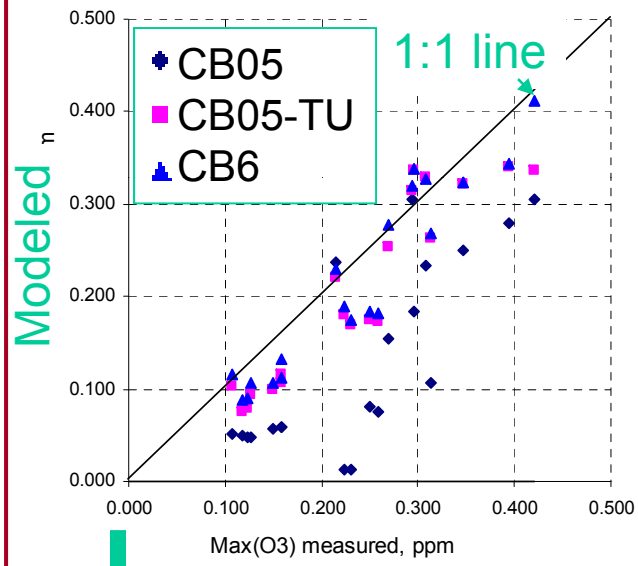
- Example: experiment TVA080 (toluene – NOx experiment in the TVA chamber)
- As NO and toluene are oxidized, O_3 increases



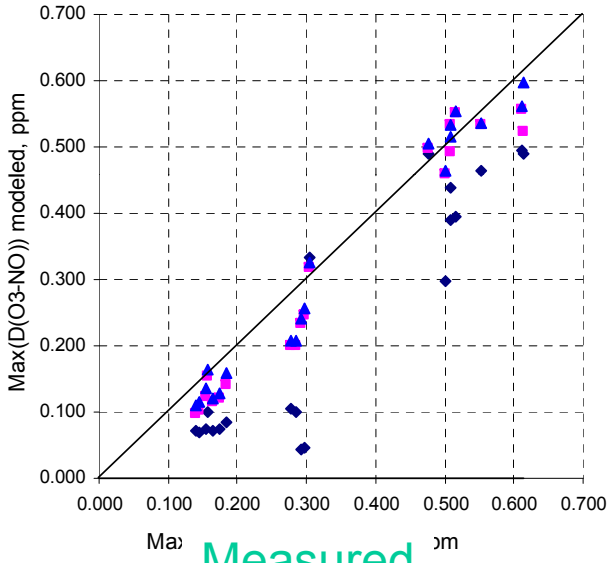
Chamber Simulation Results: Results for TOL

- 20 TOL – NOx experiments (18 with toluene and 2 with ethyl benzene)
- Performance metrics were used to quantify mechanism performance.

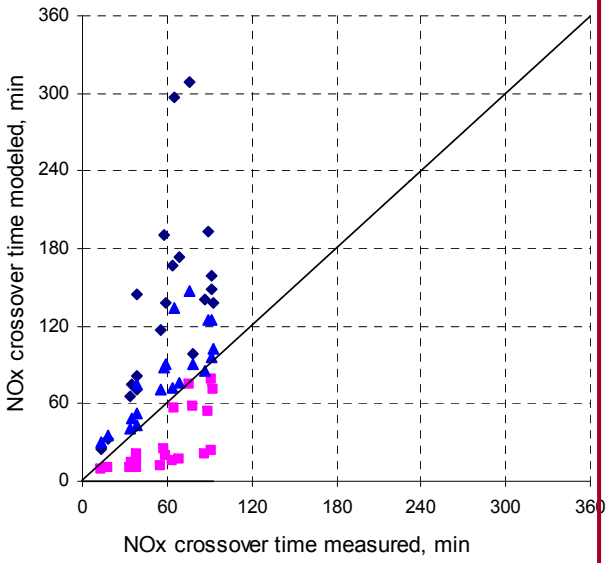
Max(O_3)



Max(D(O_3-NO))



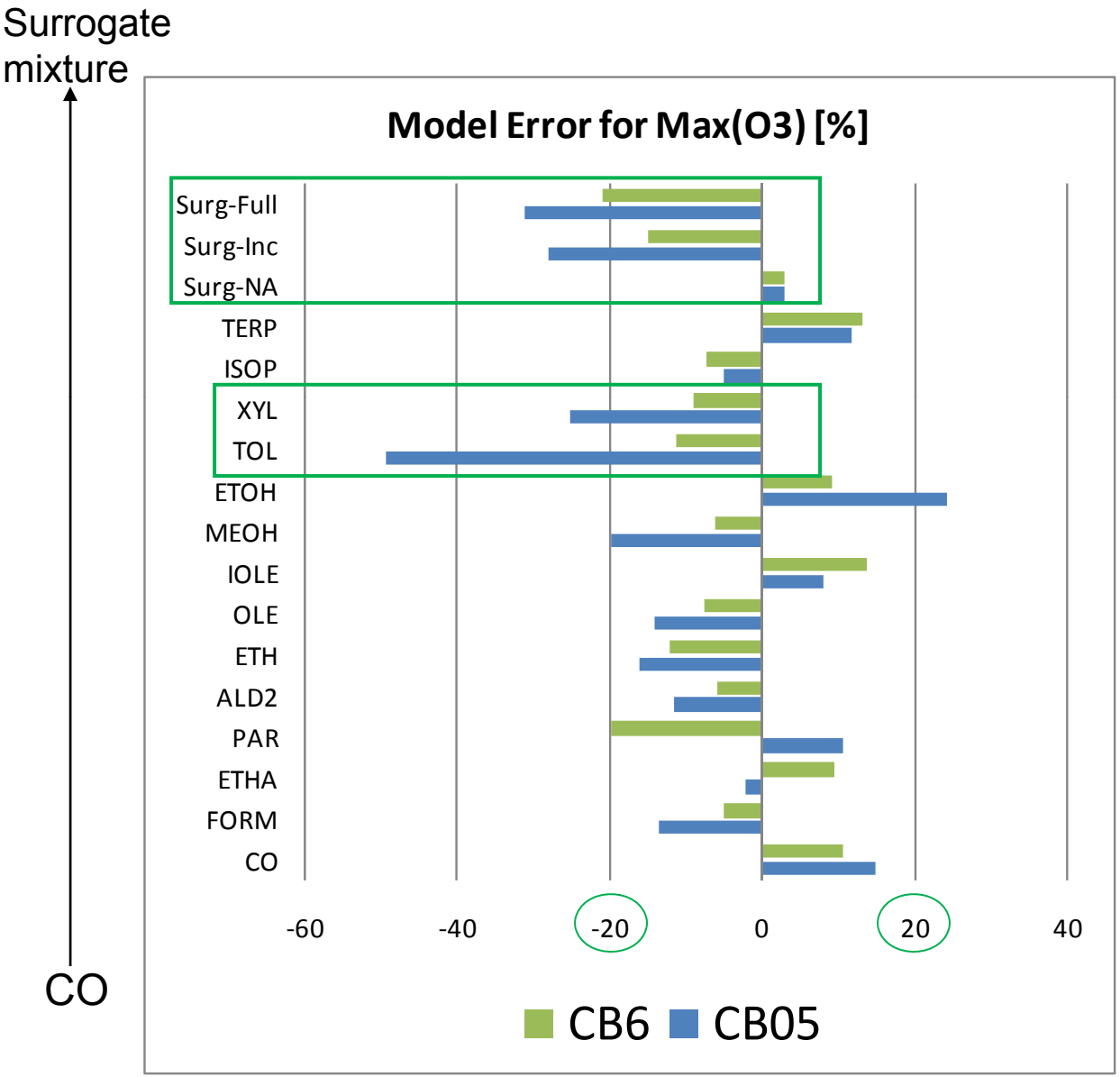
NOx crossover time



Summary of mechanism performance using model errors of metrics

	Max(O_3) [%]			Max(D(O_3-NO) [%]			NOx crossover time [min]		
	CB05	CB05-TU	**CB6**	CB05	CB05-TU	**CB6**	CB05	CB05-TU	**CB6**
Average model error	-49	-17	**-11**	-40	-14	**-10**	79	-29	**22**
Standard deviation	28	16	**15**	26	14	**12**	63	19	**20**

Performance of CB6: Max(O_3)



Model errors [units: %]:

(model – measured)/measured

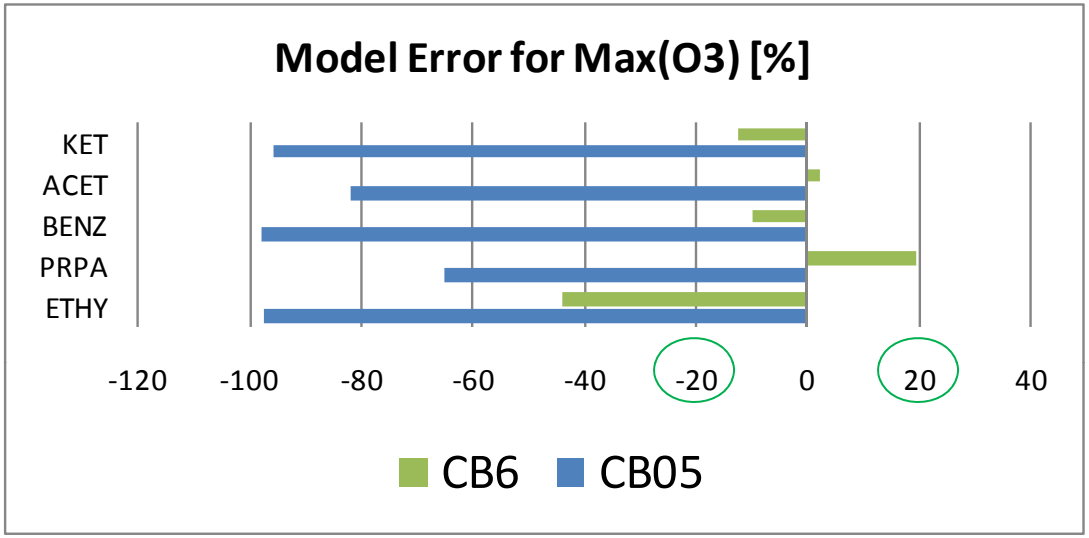
Surg-Full experiments: full surrogate VOC mixtures

Surg-NA experiments: no aromatics

CB6 generally improved and within +/- 20% bias

Note: Only blacklight/mixture experiments were available for MEOH (methanol), ETOH (ethanol), ETHA (ethane).

New Species in CB6: Max(O_3)



Model errors [units: %]:

(model – measured)/measured

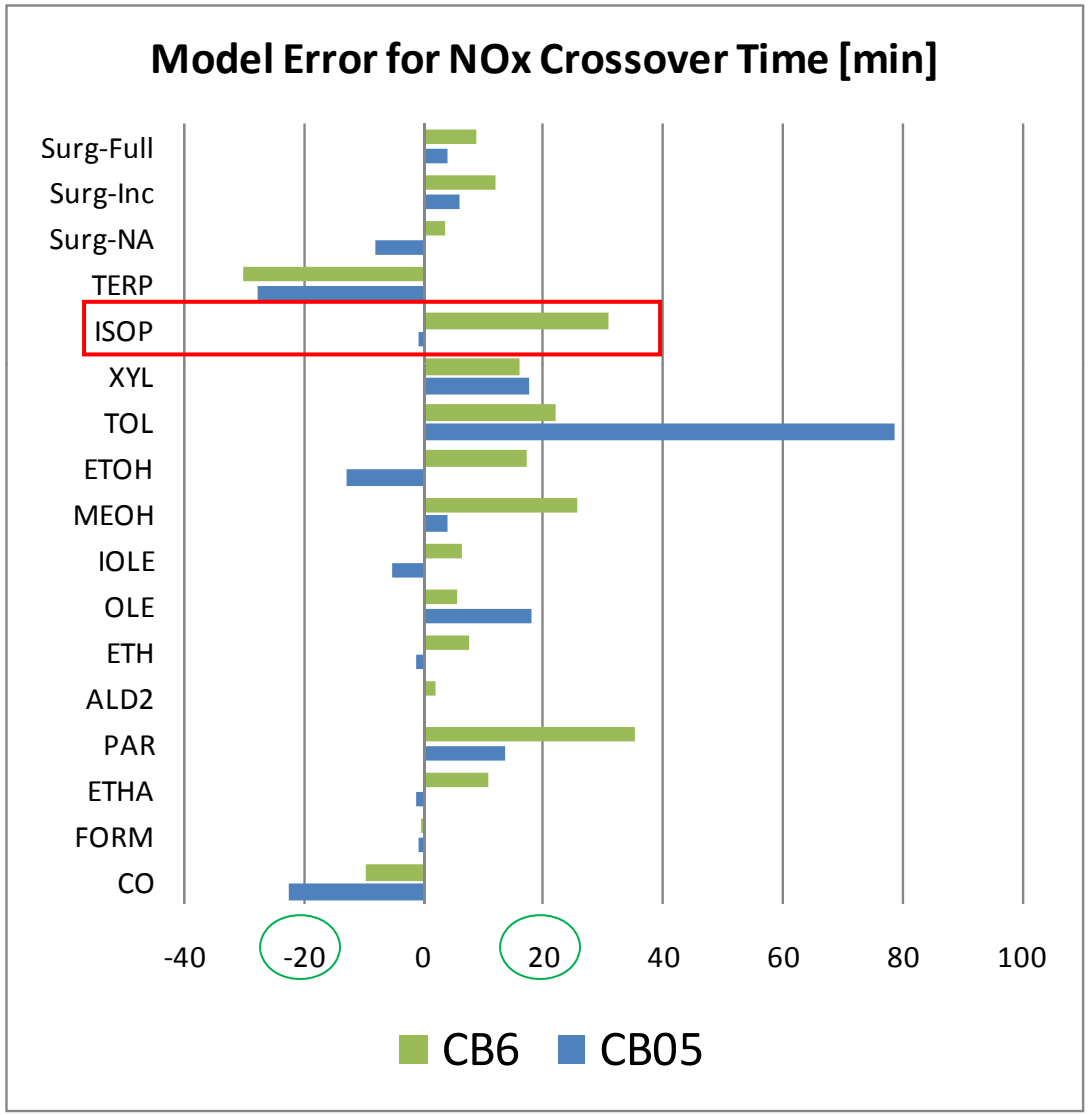
CB6 much improved and within +/- 20% bias

Ethyne (ETHY) could be improved

Note: Only blacklight/mixture experiments were available for PRPA (propane)

Performance of CB6: NOx crossover time

Surrogate mixture



CO

Model errors [units: minute]:

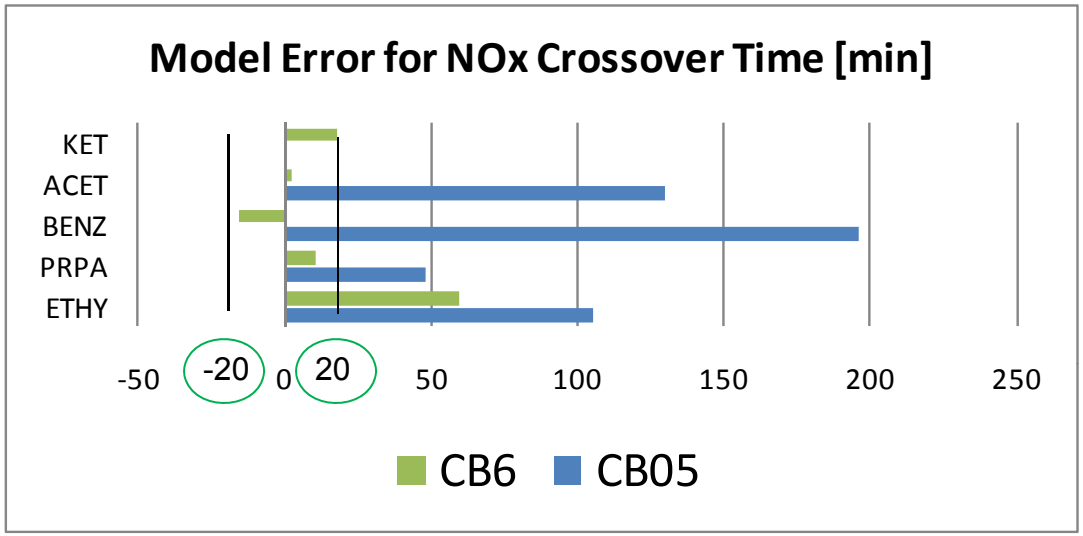
(model – measured)

Delayed crossover time for isoprene with CB6:
- Need for further work?
- Only 6 experiments

CB6 comparable to CB05 and mostly within +/- 20 min

Note: Only blacklight/mixture experiments were available for MEOH (methanol), ETOH (ethanol), ETHA (ethane).

Ne Species in CB6: NOx crossover time



Model errors [units: minute]:

(model – measured)

CB6 much improved and within +/- 20 min except for ethyne (ETHY)

Note: Only blacklight/mixture experiments were available for PRPA (propane)

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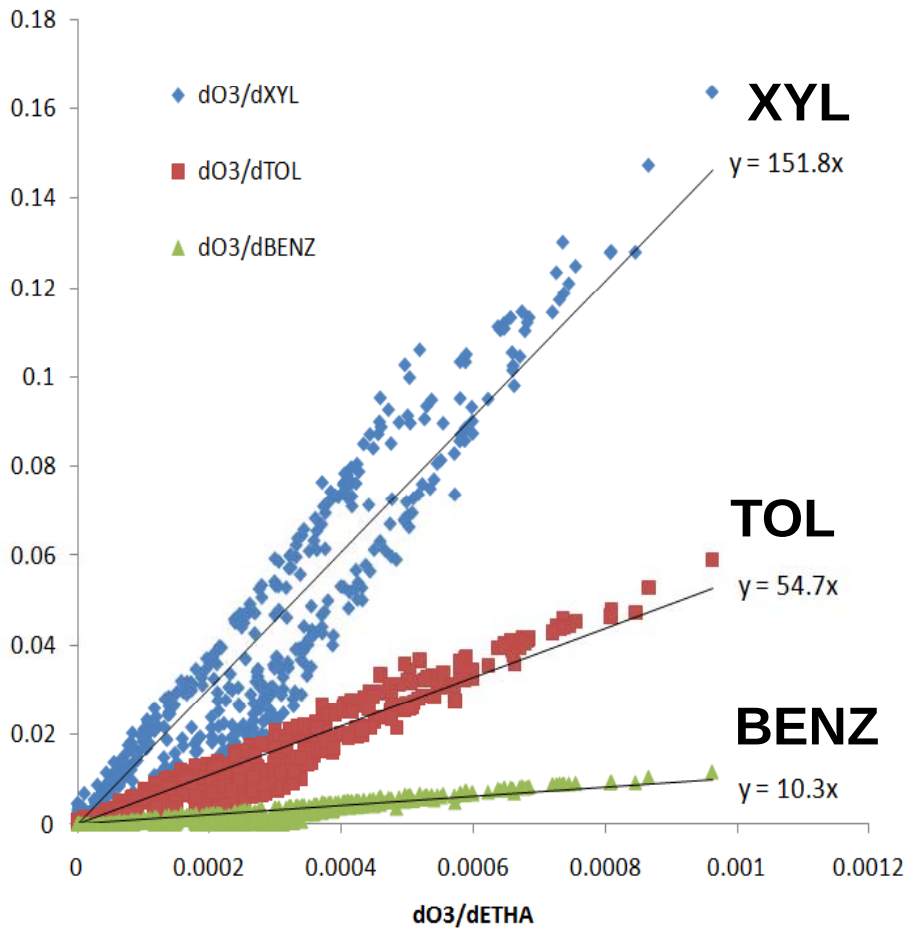
Summary of CB6 Performance

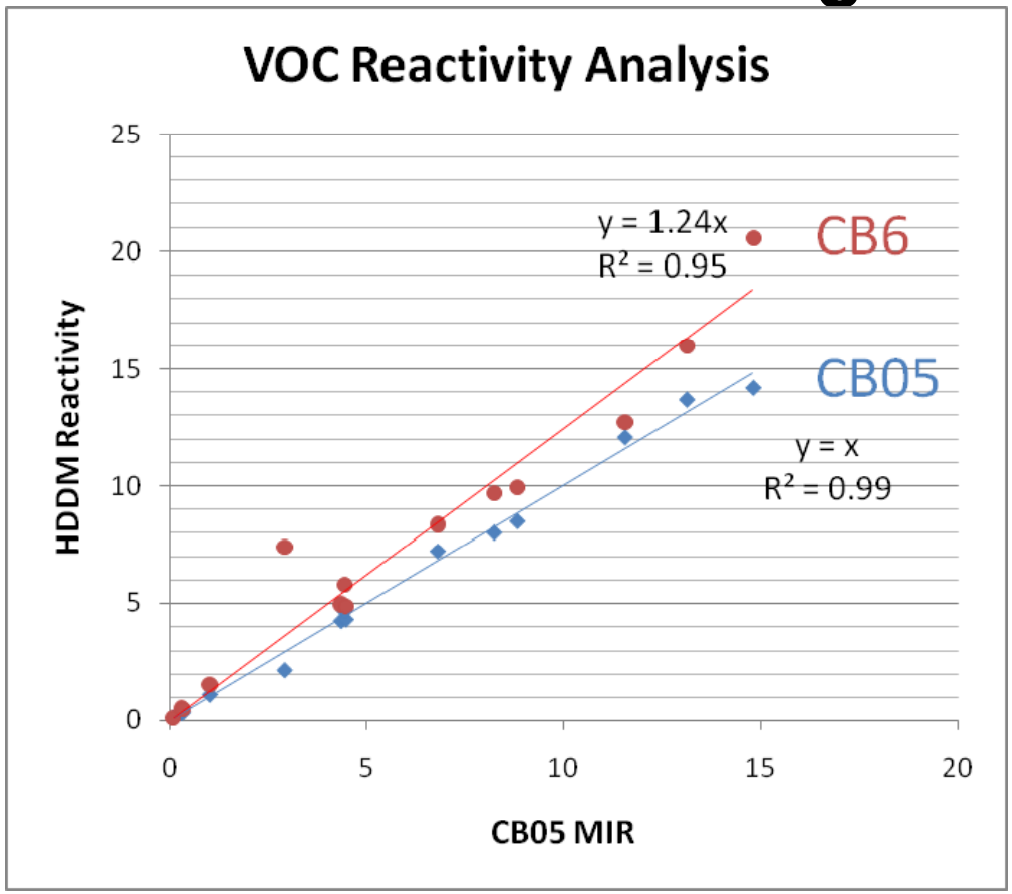
- Overall summary: CB6 performed better in simulating O_3 than CB05 and CB05-TU
- CB6 Performance for major components existing both in CB05 and CB6
  - Inorganics (CO and other inorganics): similar
  - Aldehydes (FORM, ALD2, ADLX): similar or better
  - Alcohols (MEOH, ETOH): not clear due to experiment uncertainties
  - Alkanes (ETHA, PAR): not clear due to experiment uncertainties
  - Olefins (ETH, OLE, IOLE): similar
  - Aromatics (TOL, XYL): far better than CB05 especially for TOL
  - Isoprene (ISOP): worse performance in simulating NOx crossover times
  - Terpenes (TERP): similar
- Performance for newly added explicit species
  - CB05 performed better than CB05 for ACET (acetone), KET (higher ketones), PRPA (propane), BENZ (benzene) and ETHY (ethyne)
- Performance for surrogate VOCs-NOx mixtures: Similar or better
- Further studies: (1) GLY (glyoxal), TOL and XYL, ISOP and ETHY; (2) using experimental data of blacklight-used experiments and UNC chamber experiments.

Use HDDM to Assess VOC Reactivity

- Use HDDM with Los Angeles episode
- Use dO3/dVOC and dO3/dNOx to identify VOC limited grid cells
- Calculate dO3/dVOC for individual VOC species
  - Assume each has same spatial/temporal emissions distribution as total VOC
- Relative reactivity for each VOC is like an MIR factor



VOC Reactivity Analysis for Los Angeles modeling evaluation



CB6 and CB05 reactivity factors calculated from an LA simulation using HDDM and calibrated to CB05 MIRs

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VOC Reactivity Analysis

CB6 Species	CB05	CB6	Change
ETHA	0.135 (a)	0.135 (a)	0%
PRPA	0.504 (b)	0.541	7%
PAR	0.336	0.509	51%
ACET	1.01 (b)	0.564	−44%
KET	0.336 (b)	1.39	314%
ETHY	7.22	0.487	−93%
ETH	4.26	4.95	16%
OLE	8.02	9.66	20%
IOLE	13.7	16	17%
ISOP	12.1	12.7	5%
TERP	8.5	9.91	17%
BENZ	0.336 (b)	1.39	314%
TOL	2.15	7.39	244%
XYL	14.2	20.5	44%
FORM	4.32	4.87	13%
ALD2	4.68	5.8	24%
ALDX	7.22	8.35	16%
MEOH	0.354	0.48	36%
ETOH	1.11	1.53	38%

- CB6 and CB05 reactivity factors calculated relative to ethane using CAMx-HDDM for Los Angeles

- Increased reactivity with CB6 for many species, especially aromatics, C4+ alkanes (PAR), alcohols

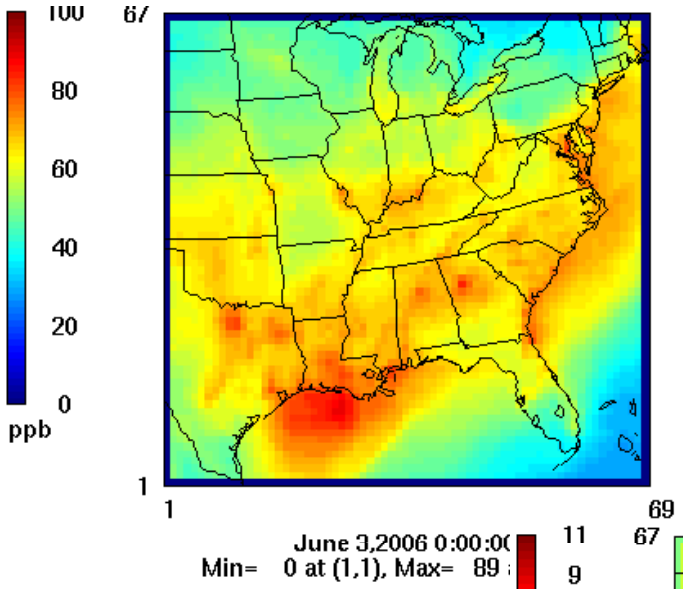
- Changes expected for species that are newly added in CB6 (see note b)

(a) The reactivity of ethane (ETHA) was held constant at 0.135

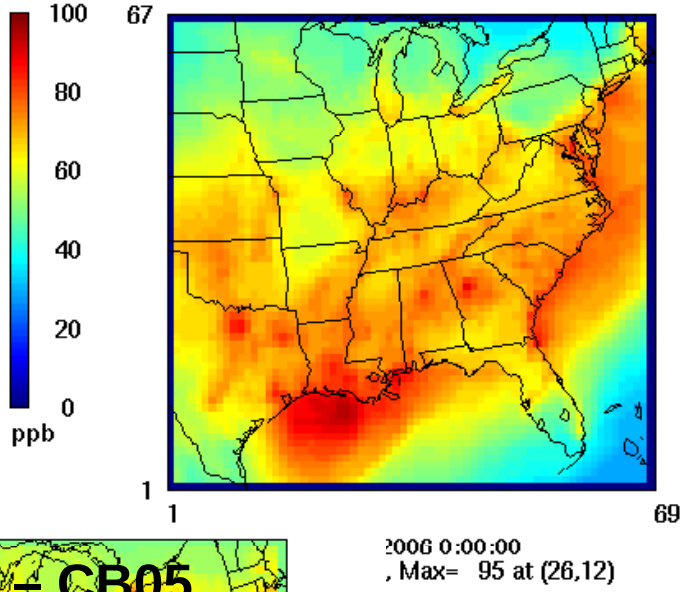
(b) PRPA, ACET, KET, ETHY and BENZ are not model species in CB05 and therefore are represented by surrogate species

8-hr Ozone: Eastern US episodes

CB05

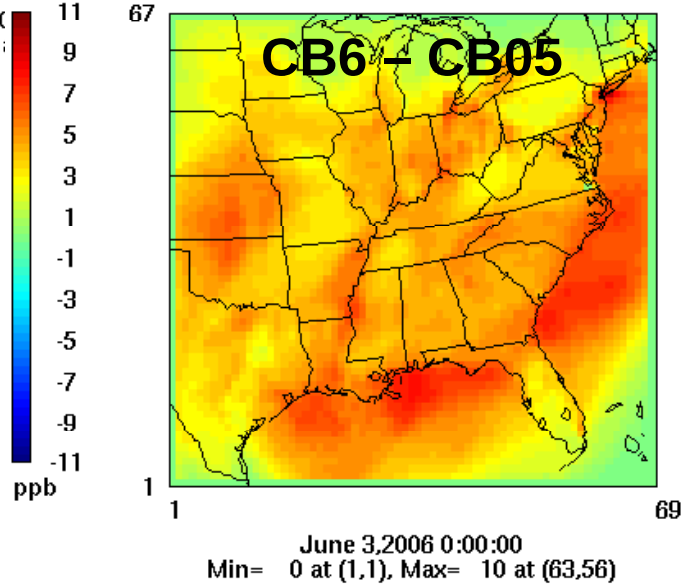


CB6



Episode Daily
Max 8-Hr Ozone

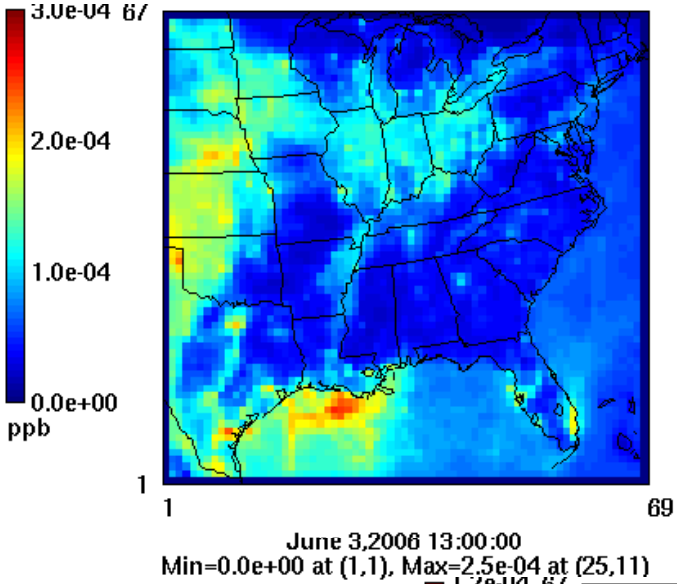
CB6 – CB05



Ozone increases

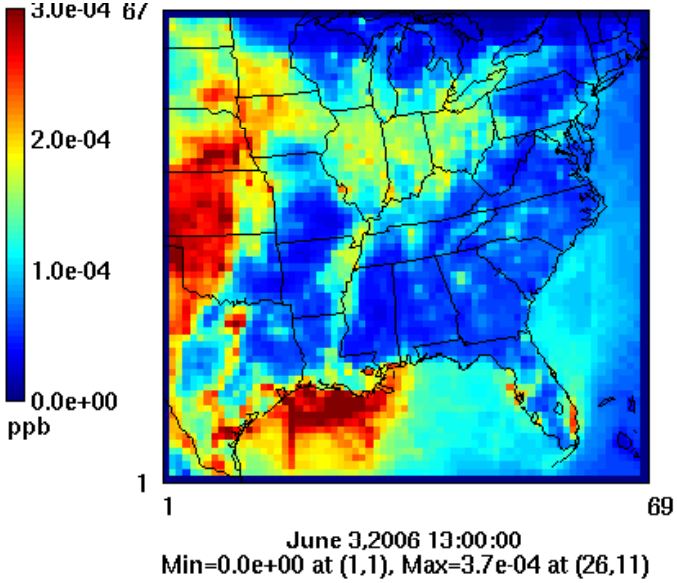
Hydroxyl radical (OH) at 1 pm

CB05



June 3,2006 13:00:00
Min=0.0e+00 at (1,1), Max=2.5e-04 at (25,11)

CB6



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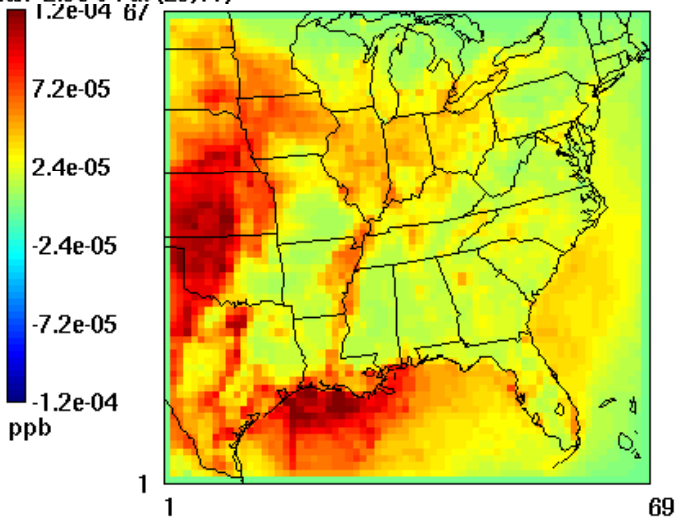
Episode Average 1-Hr OH at 1 pm



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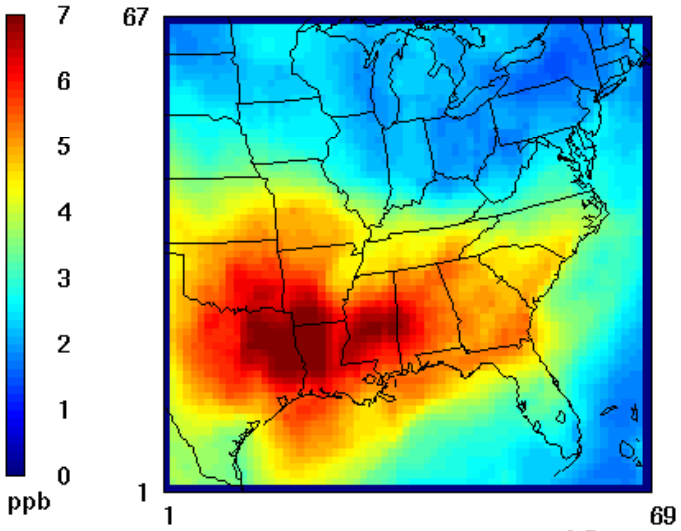
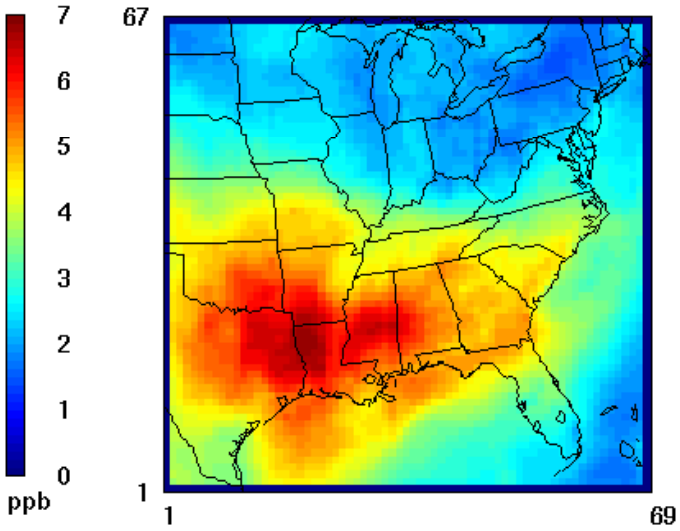
Hydrogen Peroxide (H_2O_2)

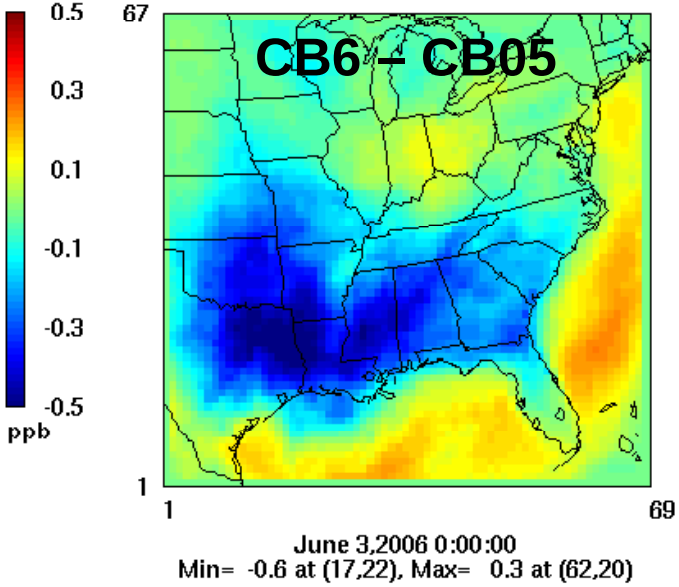
CB05



CB6



CB6 – CB05

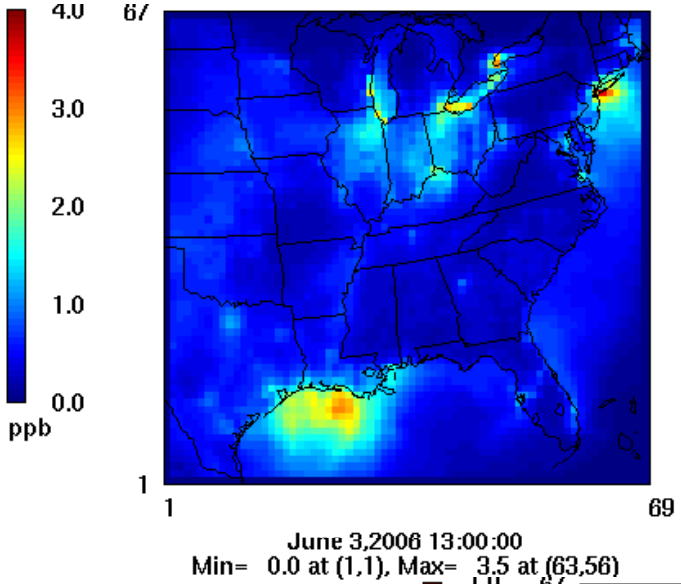


Episode Daily Max 8-Hr H_2O_2

Lower H_2O_2 in areas with high biogenic VOC

Nitric Acid (HNO3) at 1 pm

CB05



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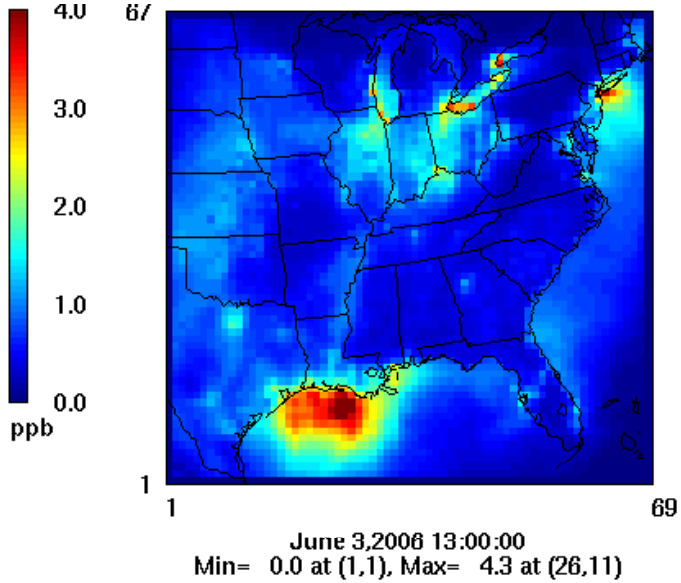
CB6



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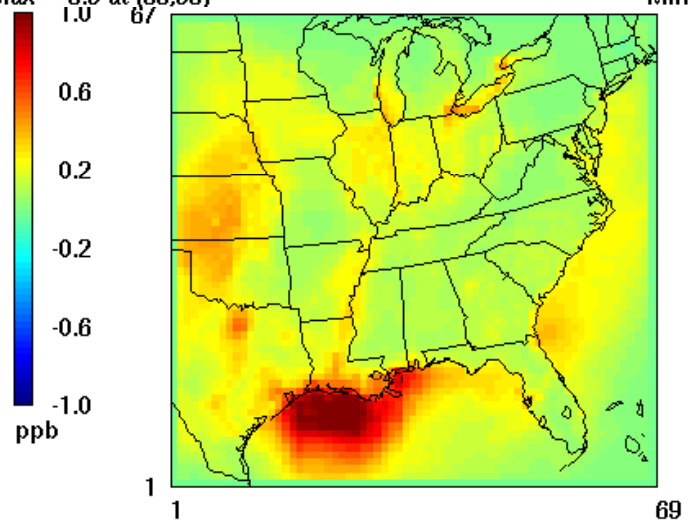
Episode Average 1-Hr HNO3 at 1 pm



June 3,2006 13:00:00
Min= -0.0 at (65,63), Max= 1.3 at (26,11)

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- $HO_2 + NO = OH + NO_2$ increased by 5% => more efficient ozone formation
- $NO_2 + h\nu = NO + O$ increased by 7% => more ozone
- $N_2O_5 + H_2O = 2\ HNO_3$ decreased by ~80%
  - Less NOx removal at night
  - Very important to include N_2O_5 reaction on aerosol surfaces

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Conclusions and Recommendations

- CB6 mechanism agrees better with chamber data than CB05
- Mechanism issues remain, including
  - Aromatics
    - Nature and magnitude of the NOx sinks
      - Experiments proposed to the AQRP
    - Uncertainties for dicarbonyl products
      - Acetylene experiments suggest glyoxal is uncertain
      - Obtain and analyze European data (EUPHORE chamber)
  - Isoprene
    - Performance could be improved
    - Only 6 experiments, none from the UCR EPA chamber
  - NOx recycling from organic nitrates
      - Experiments proposed to the AQRP
  - Relationship between pure compound and mixture experiments

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Conclusions and Recommendations

- CAMx implementation complete, but more testing recommended
  - Simulation times greater than expected
    - Mechanism sensitivity tests
  - Los Angeles results for VOC-limited conditions as expected
  - TCEQ domain results for NOx-limited conditions need to be explained
    - Mechanism sensitivity tests
    - Make use of HDDM, including sensitivity output for radicals
  - Compare CB6 and CB05 emissions sensitivity
- Test OSAT/PSAT implementation
- Implement chemical process analysis (CPA)