2005 UPDATES TO THE CARBON BOND MECHANISM: CB05

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Ackowledgements

- EPA: Deborah Luecken and Sarwar Golam
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- ENVIRON: Sunja Rao and Abby Hoats
- Mark Yocke
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Outline

- CB4/CB05 History
- CB05 Objectives
- Mechanism Updates
- Evaluation
- CB05/CB4 Comparison

CB4 (or CB-IV) History

1989	CB4 published (Gery et al. JGR paper, 1989)
1990	**UAM-IV version** of CB4 with updated to PAN reaction rates and explicit methanol/ethanol
1994	updated radical reactions for XO2/XO2N
1996	**OTAG version** with revised isoprene chemistry (Carter "1-product" mechanism). This version is in widespread use (e.g., CAMx M3 and CMAQ)
1999	CB99 developed: $OH + NO_2$ needed correcting
2002	CB2002 developed: not widely used
2005	CB4+ developed by extending the inorganic reactions in the OTAG version of CB4

CB05 Development Objectives

- Update the Carbon Bond Mechanism for use in EPA modeling studies
  - Ozone
  - PM/visibility
  - Air toxics and mercury
- Update science
  - extend range of atmospheric conditions
  - improve linkages from gas-phase chemistry linkage to aqueous and aerosol chemistry
- Understand changes relative to CB4
- Not “change for the sake of change”

CB05 Core Updates (1 of 3)

- Updated rate constants
  - based on recent (2003 – 2005) IUPAC and NASA evaluations
- Extended inorganic reaction set (CB4+)
  - urban to remote tropospheric conditions
    - odd-H reactions, hydrogen (H_2), NO_3 reactions
- NOx recycling reactions
  - represent the fate of NOx over multiple days
    - photolysis and OH-reactions for both nitric acid (HNO_3) and organic nitrates (RNO_3)

CB05 Core Updates (2 of 3)

- Explicit chemistry for methane and ethane
  - clean background atmospheres
- Explicit methylperoxy radical, methyl hydroperoxide and formic acid
  - improved hydrogen peroxide (SO_2 → sulfate)
- Lumped higher organic peroxides, organic acids and peracids
  - improved organic peroxides (SO_2 → sulfate)

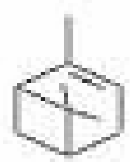
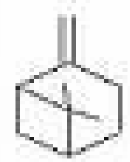
CB05 Core Updates (3 of 3)

- Internal olefin (RHC=CHR) species IOLE
  - higher reactivity at low VOC/NOx
- Higher aldehyde species ALDX
  - higher reactivity at low VOC/NOx
  - acetaldehyde (ALD2) now explicit (air toxics)
- Higher peroxyacyl nitrate species from ALDX called PANX
  - improved nitrogen cycling and transport
- Lumped terpene species TERP
  - biogenic contributions to oxidant and SOA

Summary of CB4 and CB05

	CB4		CB05	
Reactions	**96**		**156**	
Species	**37**		**51**	
Alkanes	2	PAR, CH4	3	+ ETHA
Alkenes	3	ETH, OLE, ISOP	5	+ IOLE, TERP
Aromatics	3	TOL, XYL, CRES	3	
Aldehydes	3	FORM, ALD2, MGLY	4	+ ALDX
Alcohols	2	MEOH, ETOH	2	
Peroxides	1	H2O2	4	+ MEPX, ROOH, PACD
PANs	1	PAN	2	+ PANX

New Organic Precursors in CB05

CB05	Representative Structure	C #	CB4 Equivalent
ETHA	CH_3-CH_3 (explicit species)	2	0.6 PAR + 1.4 NR
IOLE	-CH_2CH=CH-CH_2 -	4	2 ALD2
ALDX	-CH_2-CHO	2	ALD2
TERP	α-pinene and β-pinene  	10	x PAR + y ALD2 + z OLE

- The next few slides show some of the main expansions of the carbon bond mechanism from CB4 to CB05
  - First show CB4
  - Then show changes for CB05

Methane/Formaldehyde in CB4

CH_4

↓ OH

FORM

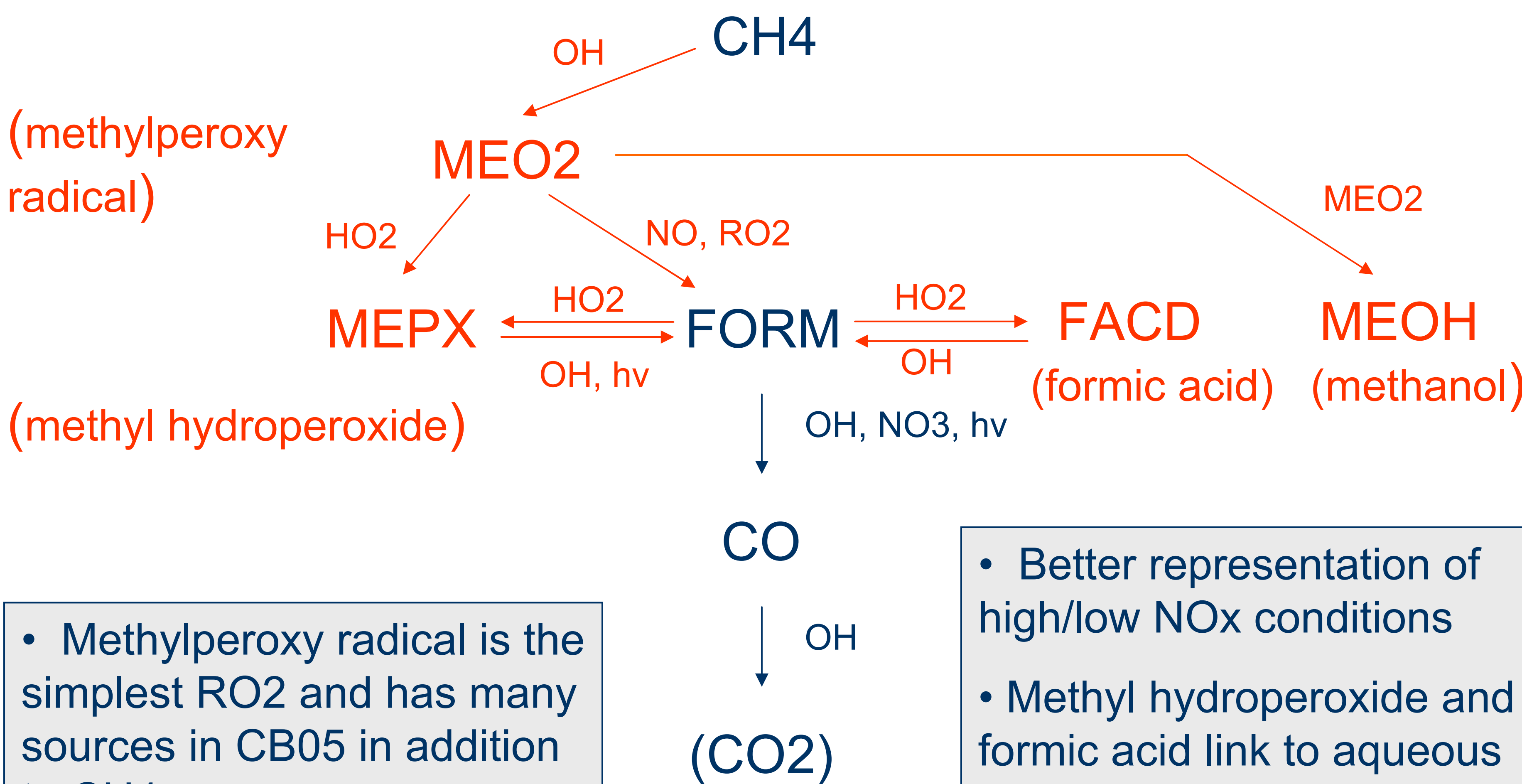
↓ OH, NO_3, hv

CO

↓ OH

(CO_2)

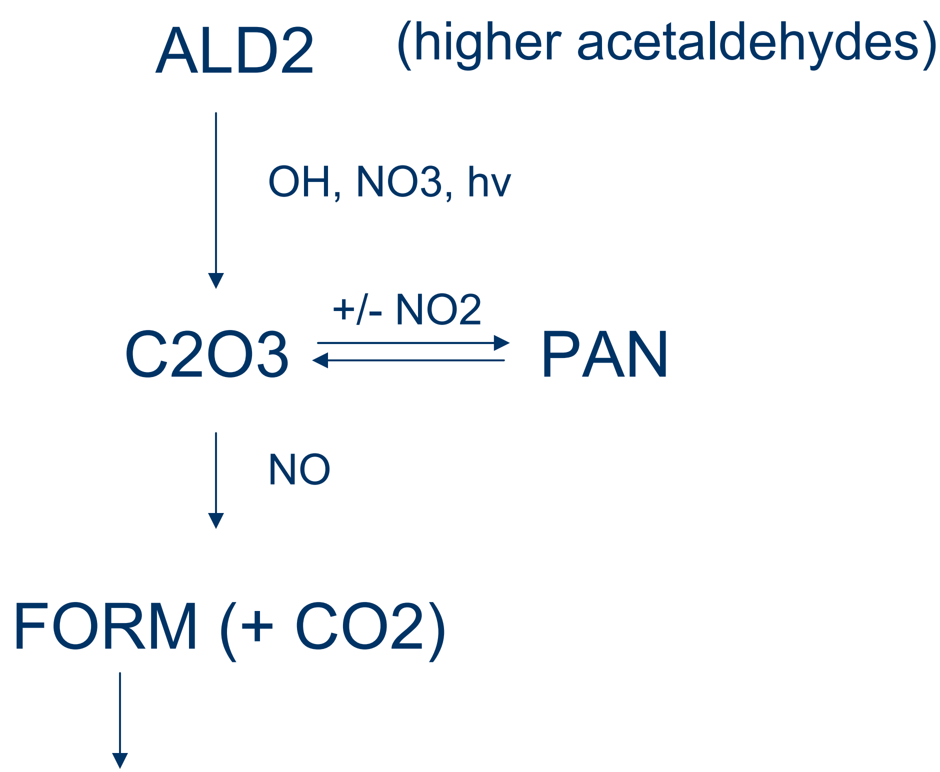
Methane/Formaldehyde in CB05



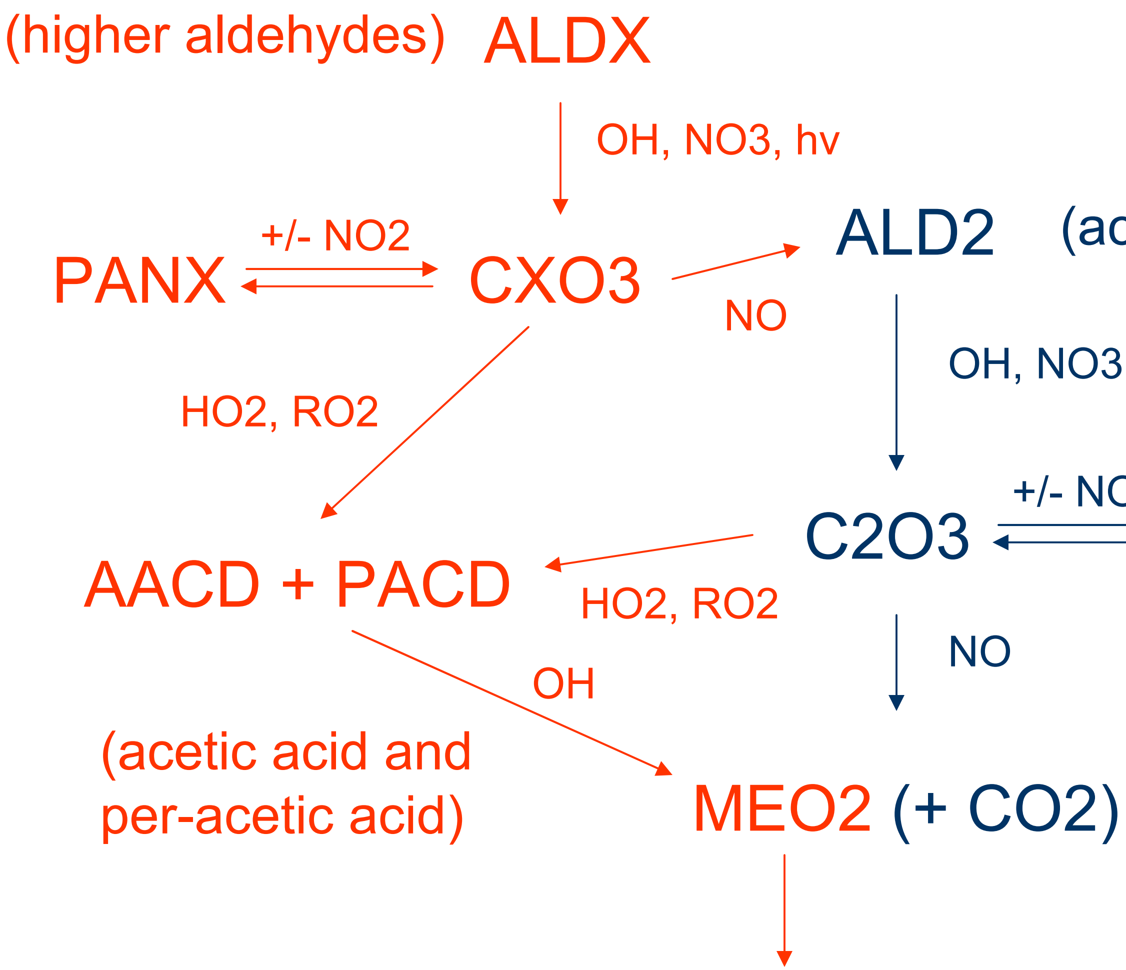
- Methylperoxy radical is the simplest RO2 and has many sources in CB05 in addition to CH4

- Better representation of high/low NOx conditions
- Methyl hydroperoxide and formic acid link to aqueous phase chemistry

Higher Aldehydes in CB4



Higher Aldehydes in CB05



- Better representation of high/low NOx conditions
- More extensive aldehyde and PAN chemistry

Alkanes (PAR) in CB4

PAR (alkanes and paraffinic carbon)

↓ OH

(aldehydes) ALD2 + ROR

↓ ↓

ALD2 + PAR (ketones)

↓ ↓

Alkanes (PAR) in CB05

PAR (alkanes and paraffinic carbon)

↓ OH

(aldehydes) ALDX + ALD2 + ROR

ROR ↓

ALD2 + PAR (ketones)

- Paraffinic chains with 3+ carbons can produce ALDX
- ALDX photolyzes faster than ALD2

- Similar change for terminal olefins (OLE)

CB05 Development and Evaluation

- Developed first, evaluated second: No mechanism ~~tuning~~ refinement stage

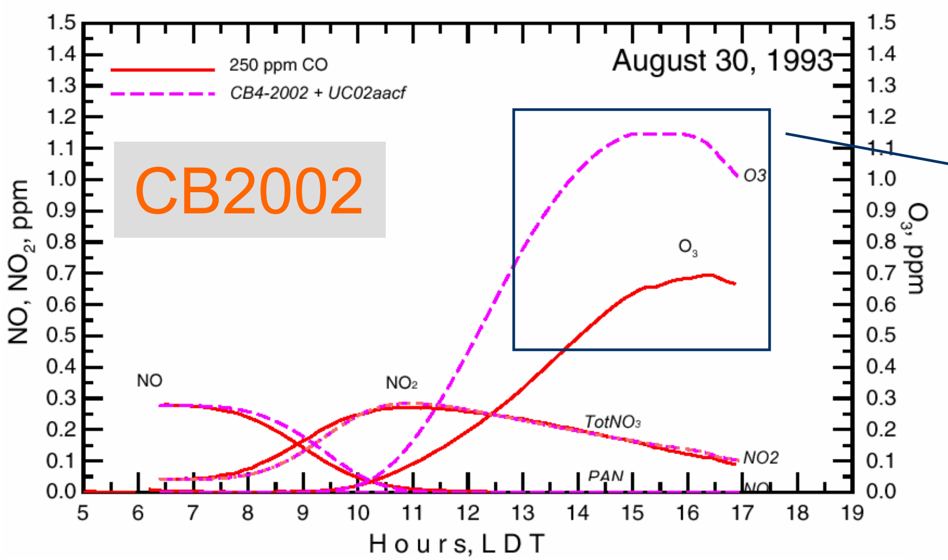
- UNC chamber data
  - Implemented CB05 in “Morpho”
  - Updated chamber mechanism
  - Compared to CB2002 – similar to CB4

- UCR chamber data
  - CB05 implemented and tested by Bill Carter
  - Chamber mechanism re-adjusted for CB05 by Carter
  - Evaluated both CB05 and fixed-parameter SAPRC99 used in CMAQ

UNC Experiments

- Show results related to CB05 mechanism updates
  - Chamber mechanism: CO
  - Higher aldehydes: ALDX
  - Terminal olefins: OLE (benefit of ALDX)
  - Internal olefins: IOLE
- Other species
  - Aromatics: TOL and XYL

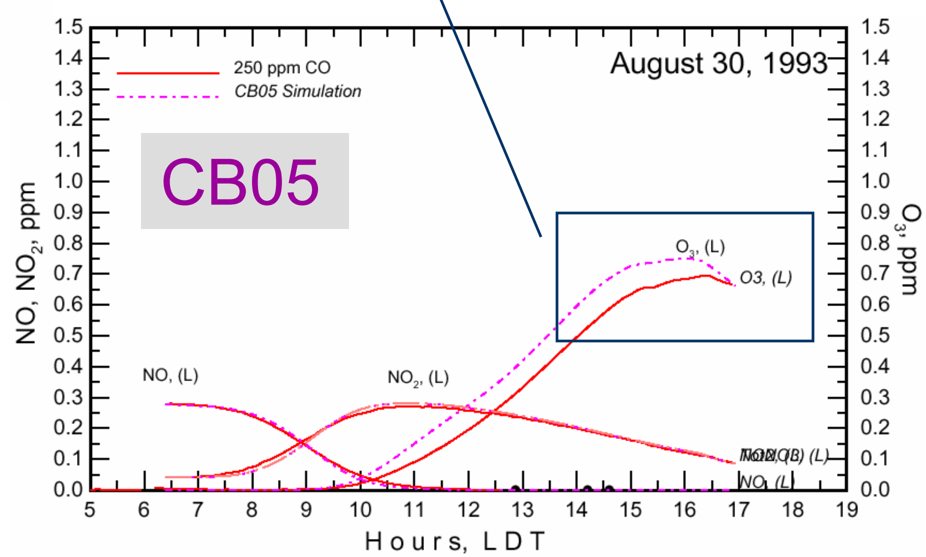
UNC Chamber: CO



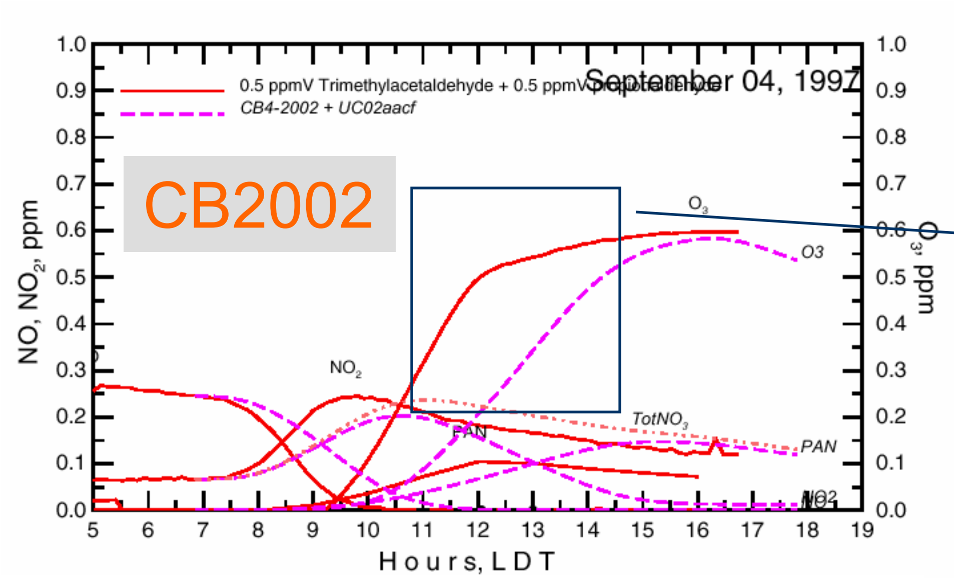
Updated chamber mechanism improves NO →NO_2 conversion and O_3 yield in characterization experiments with CO

Measured = Solid Line

Simulated = Dashed Line



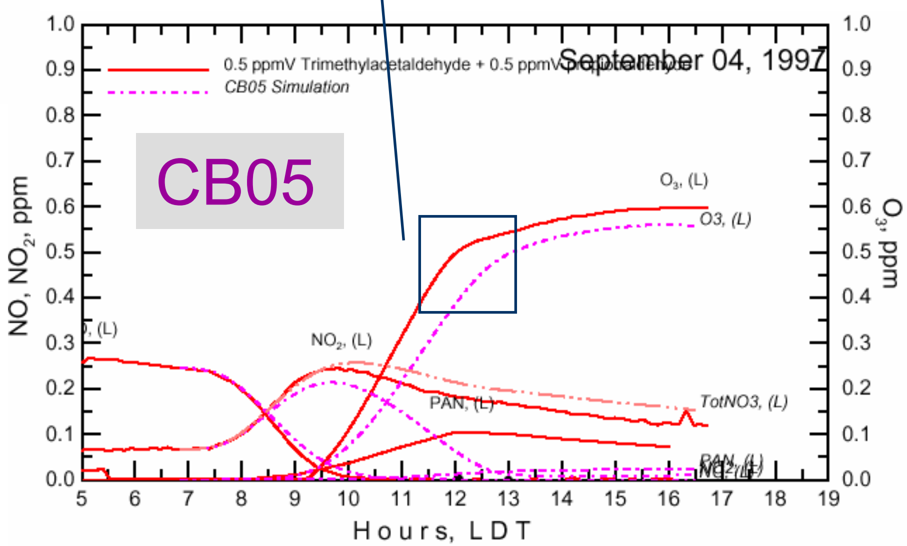
UNC Chamber: ALDX



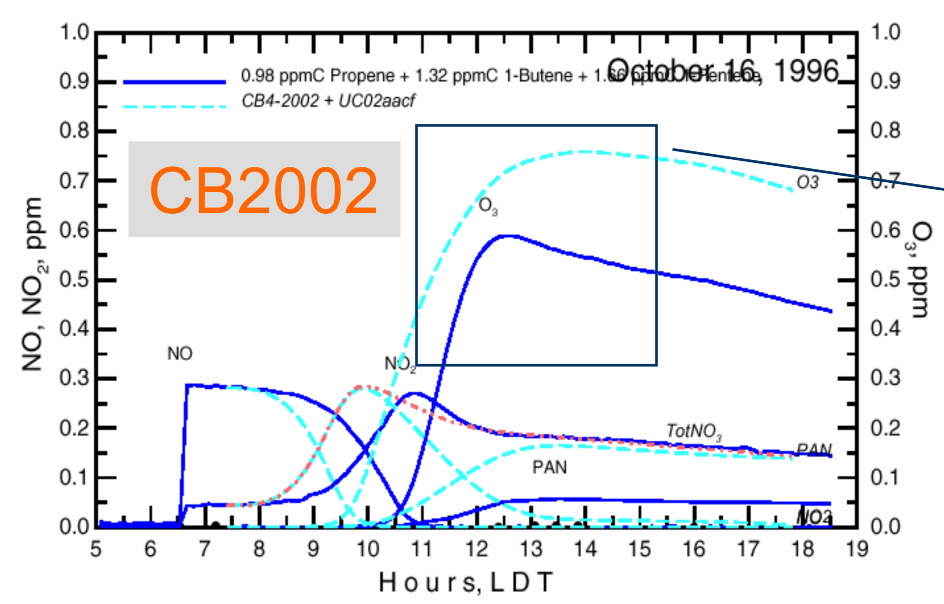
ALDX photolysis improves NO →NO_2 conversion and O_3 timing in experiments with trimethylacetaldehyde and propionaldehyde

Measured = Solid Line

Simulated = Dashed Line



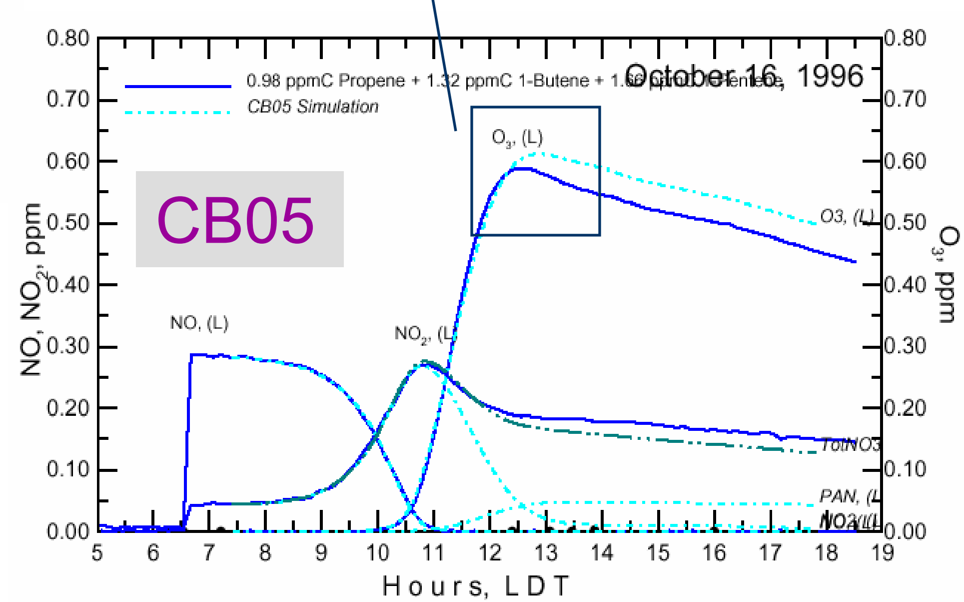
UNC Chamber: OLE



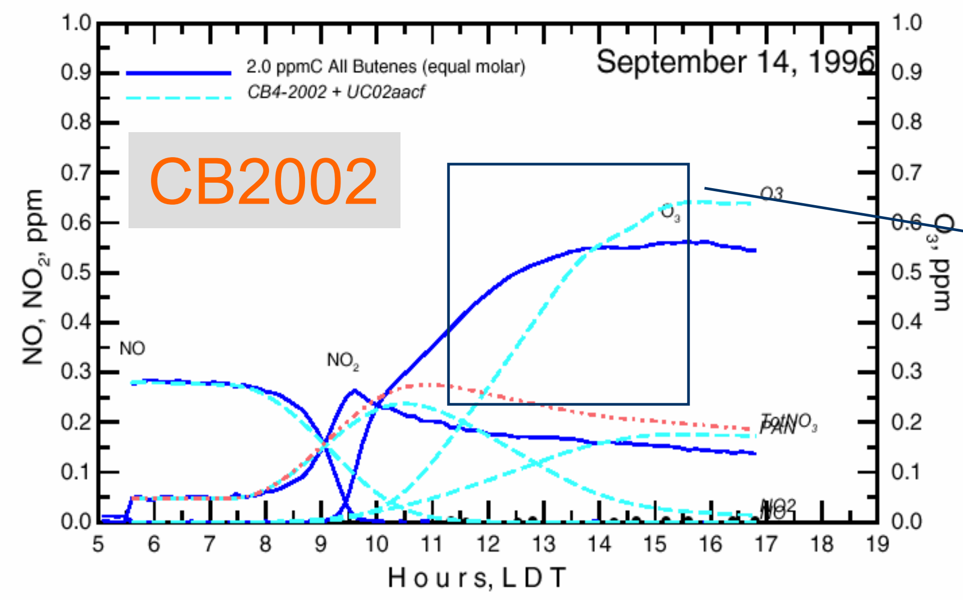
ALDX product improves NO → NO_2 conversion and O_3 timing in experiments with propene, 1-butene and 1-pentene

Measured = Solid Line

Simulated = Dashed Line



UNC Chamber: IOLE

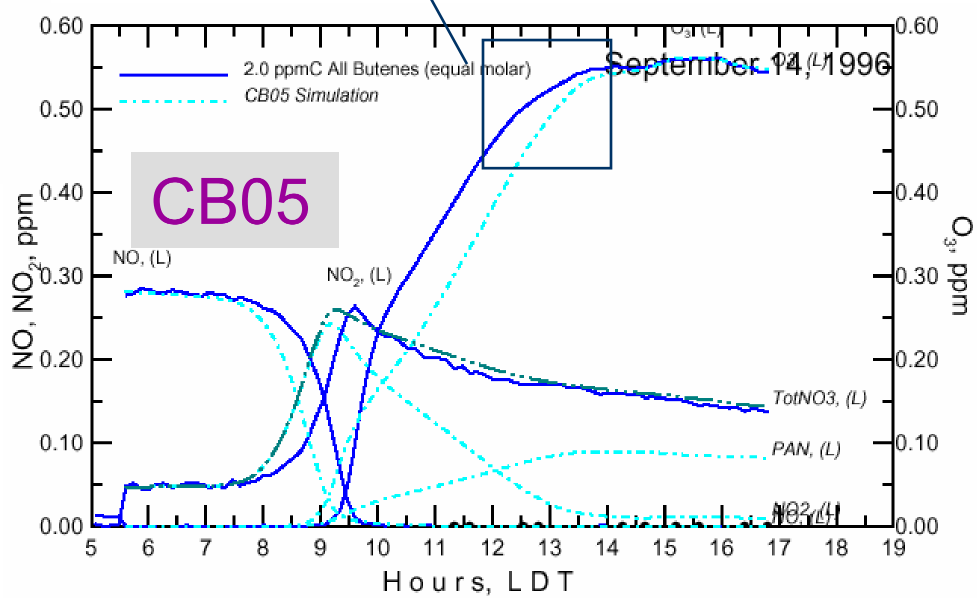


IOLE reactions and ALDX product improve NO, NO_2 and O_3 timing and peaks in experiments with equimolar mixture of 1-butene, cis-2-butene, trans-2-butene, and isobutene.

Measured = Solid Line

Simulated = Dashed Line

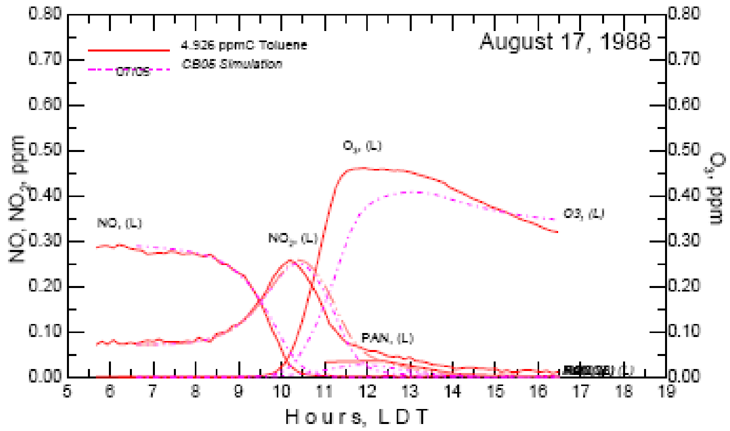
(Vertical Scales Differ)

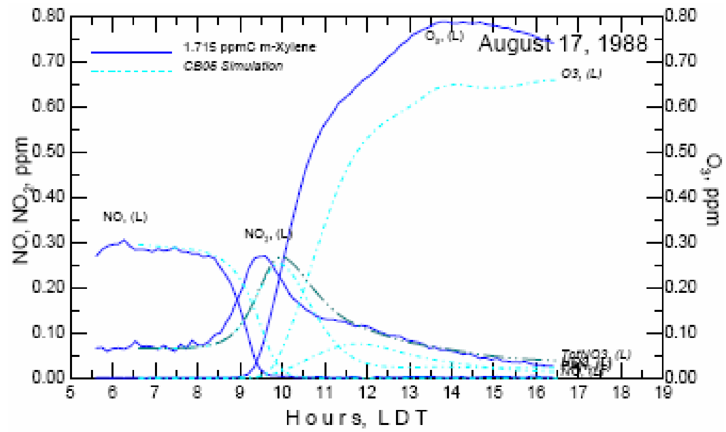


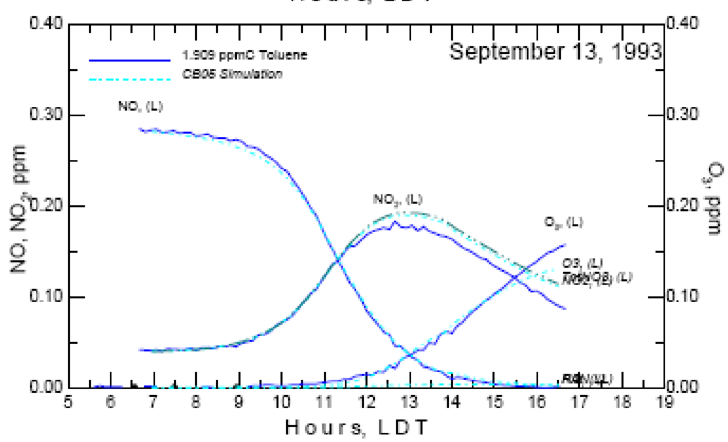
UNC Chamber: Aromatics

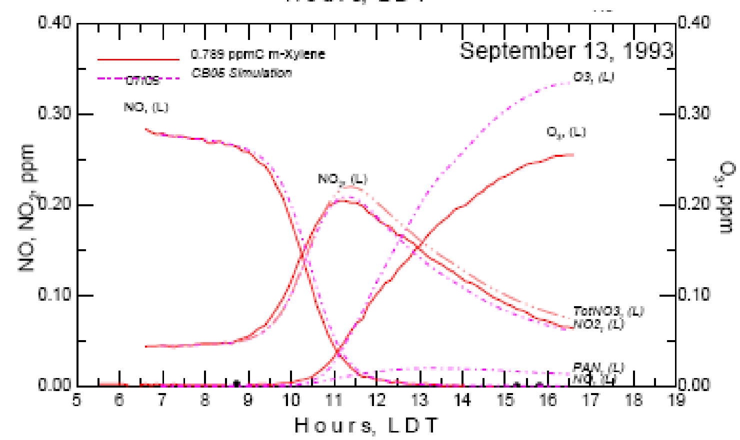
TOL CB05 tends to be slow, but have correct final ozone

XYL CB05 has mix of ozone under and over-prediction









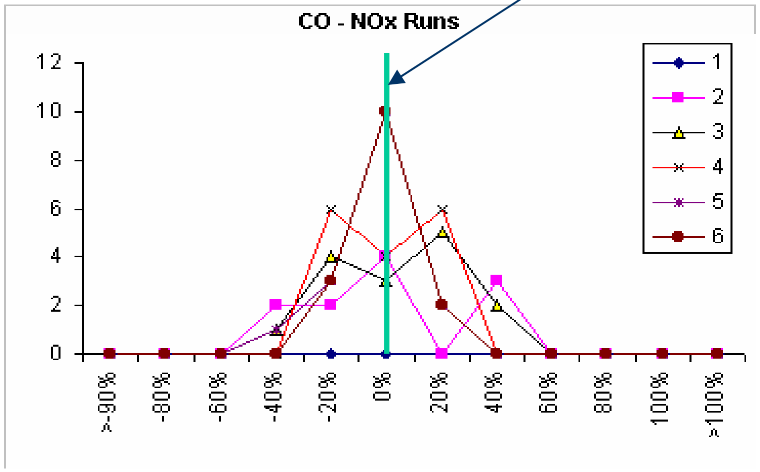
UCR Experiments

Compound	Number of Experiments
Carbon monoxide	18
Formaldehyde	24
Acetaldehyde	12
Ethene	39
Propene	89
t-2-Butene	12
Isoprene	18
Butane	10
Octane	5
Toluene	28
m-Xylene	27
o-Xylene	13
123-trimethylbenzene	9
Alpha-Pinene	11
Beta-Pinene	9
EPA surrogate mixture	25
Full surrogate mixture	18

- Over 350 experiments
  - Several chambers
  - Individual compounds
  - Mixtures of compounds

- Charts to summarize many experiments
- Ozone bias by hour
  - Lines show 6 hours
  - Bias binned and counted

zero bias

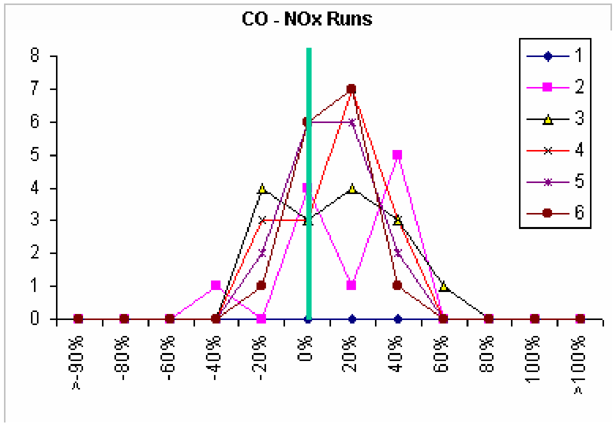


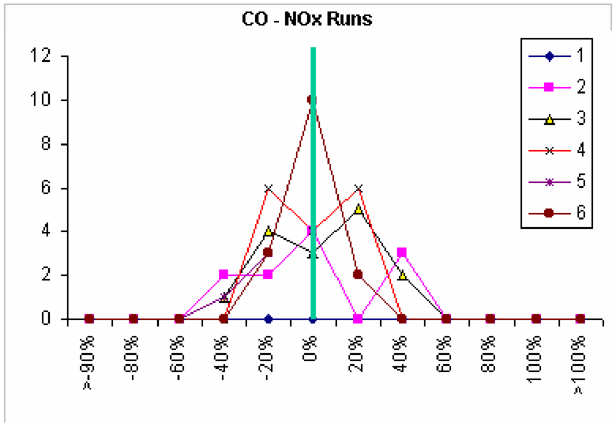
UCR: CO/FORM

CB05

SAPRC99

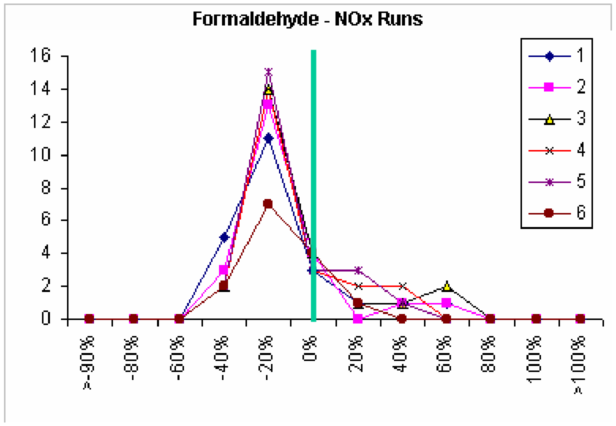
CO

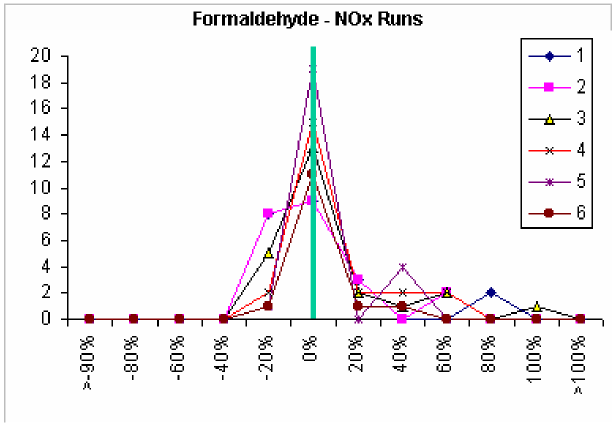




Chamber mechanism better calibrated for SAPRC99 than CB05

Formaldehyde





HCHO photolysis the same: why is the performance different?

The CB05 and SAPRC99 inorganic mechanisms differ slightly, e.g., OH + NO_2

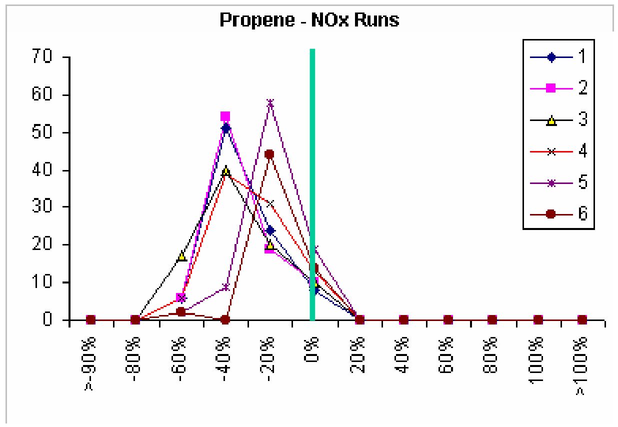
UCR: Olefins

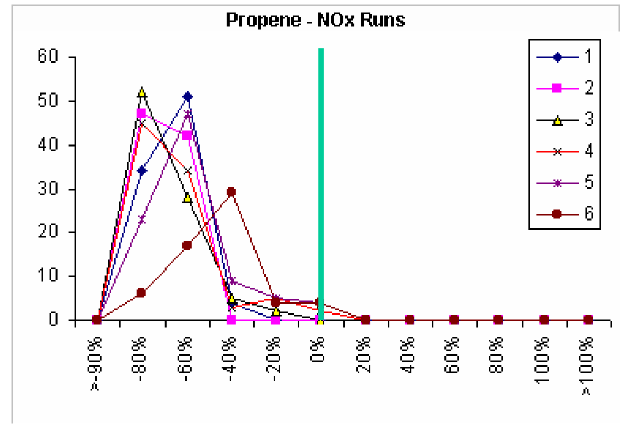
CB05

SAPRC99

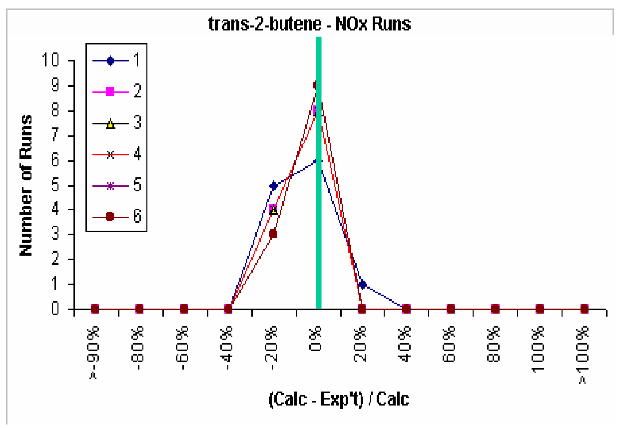
propene

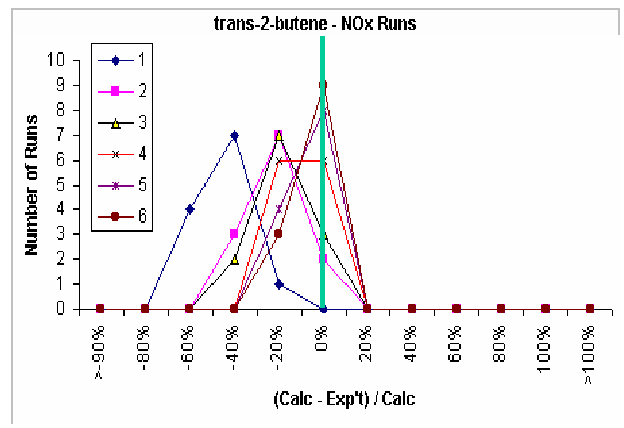
SAPRC99 under-predicts ozone





trans-2-butene





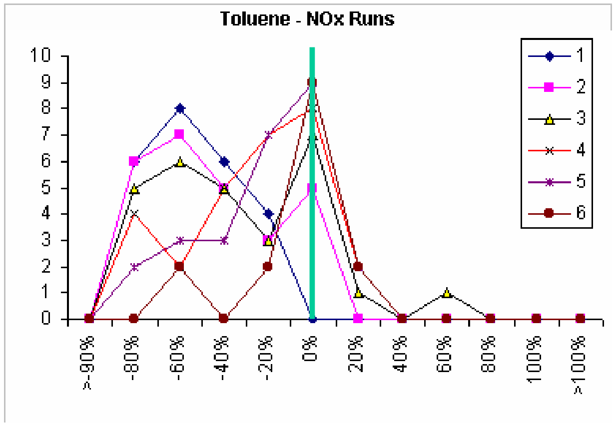
UCR: Aromatics

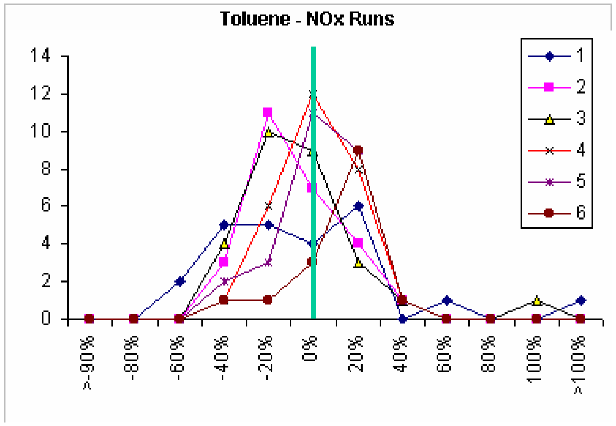
CB05

SAPRC99

toluene

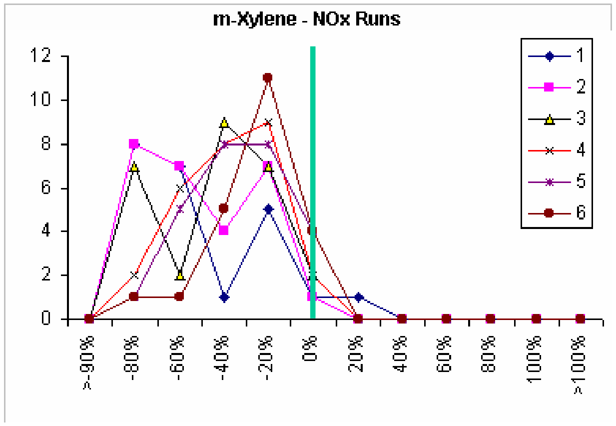
CB05 forms ozone too slowly

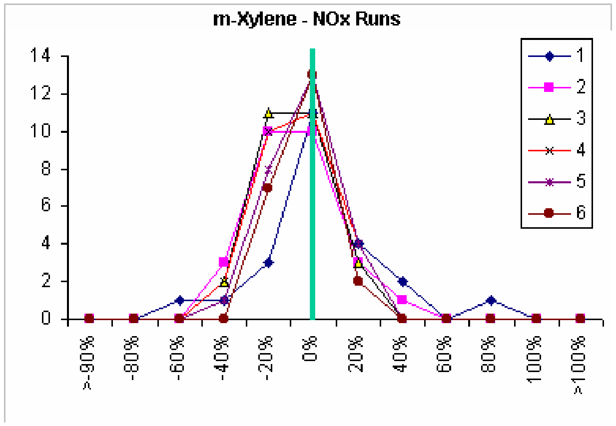




m-xylene

CB05 ozone scattered and too low





ENVIRON

Smog Reyes

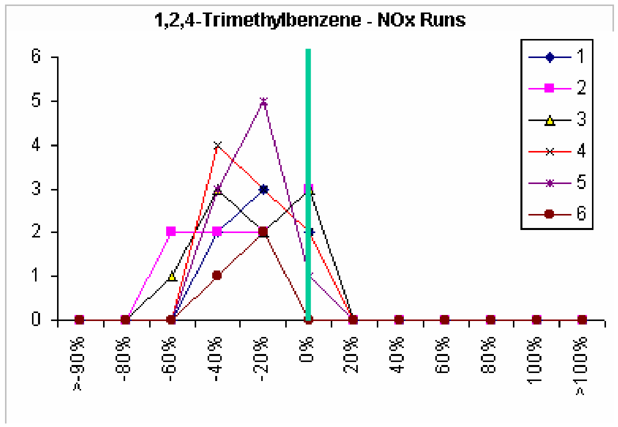
UCR: XYL/TERP

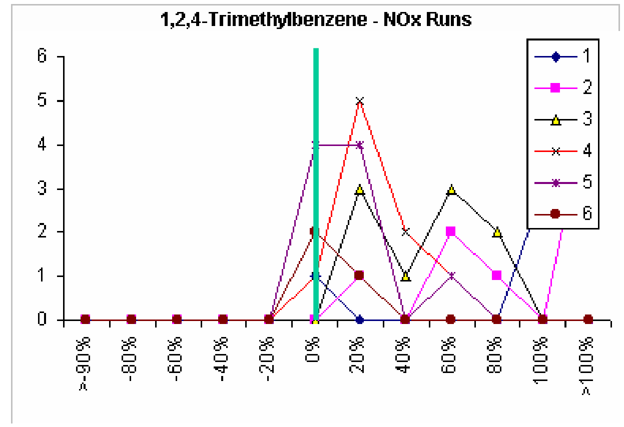
CB05

SAPRC99

1,2,4-trimethylbenzene

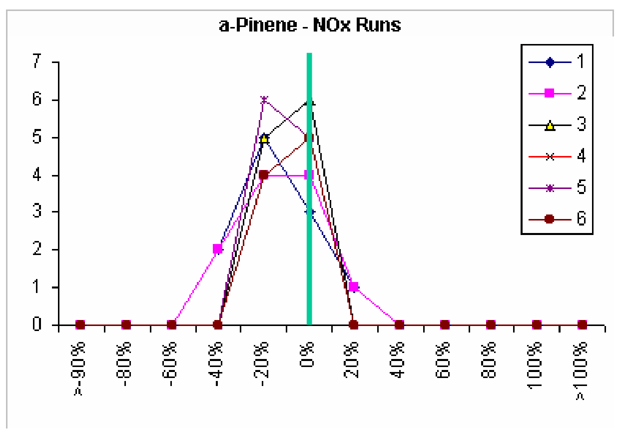
CB05 low
SAPRC99 high

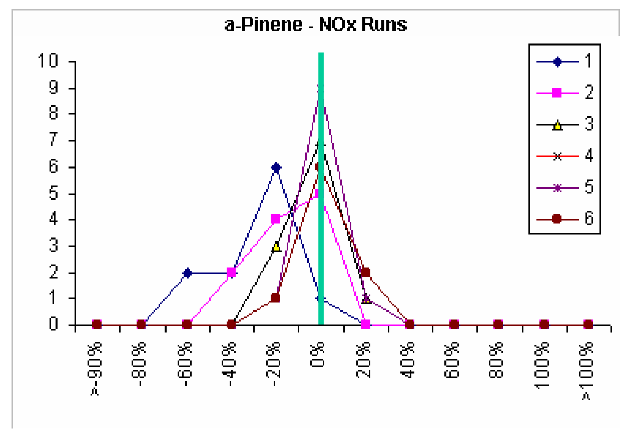




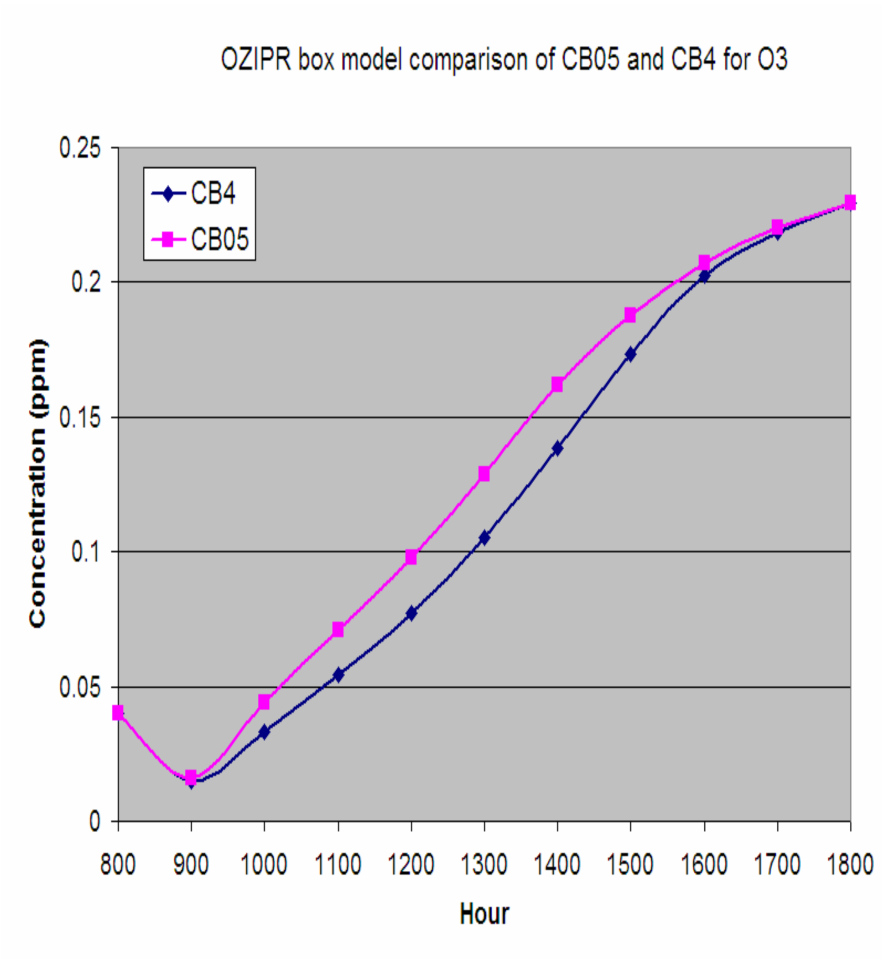
α-pinene

CB05 translation of SAPRC99 TERP works well for α-pinene



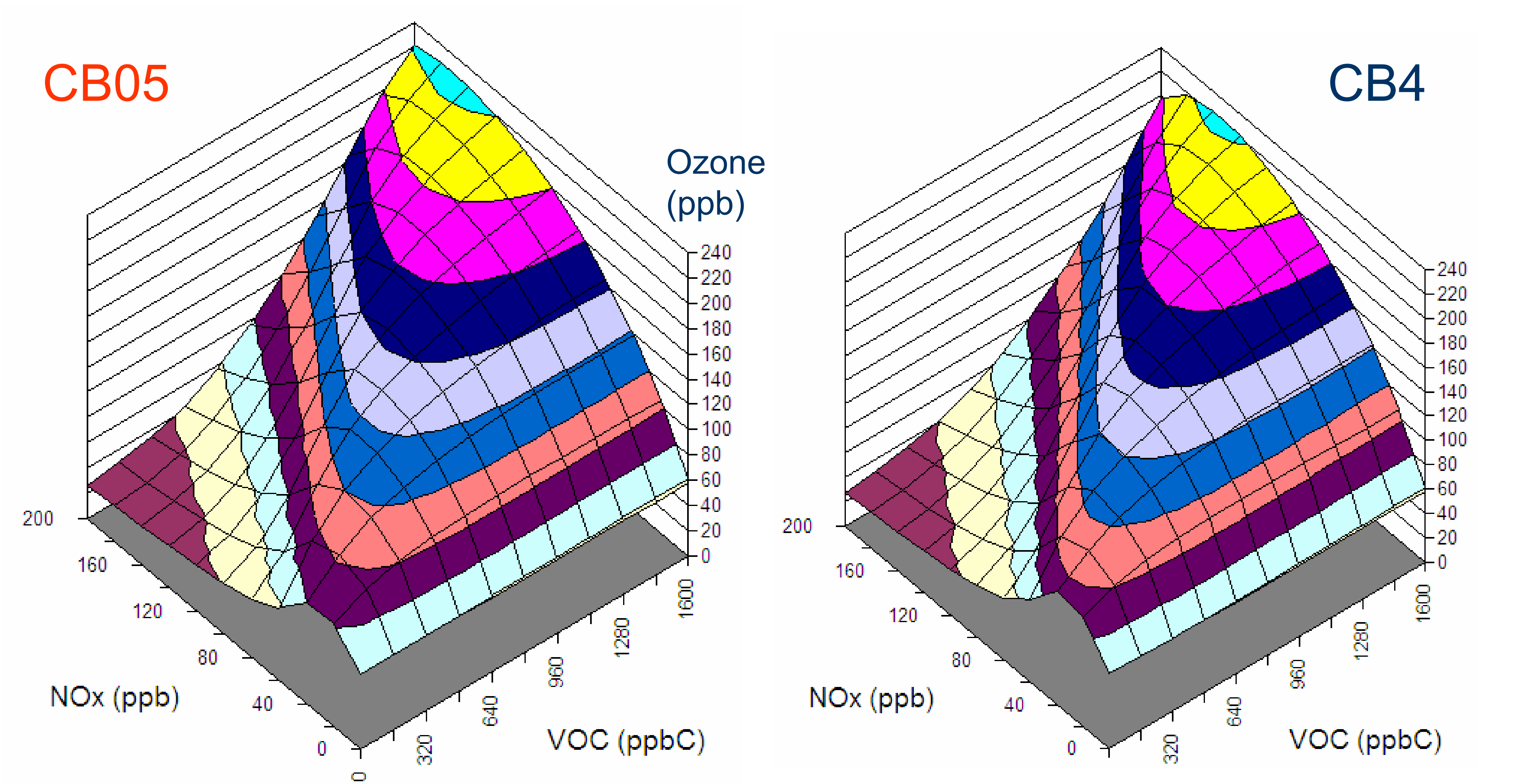


Comparing CB05 and CB4 - Ozone

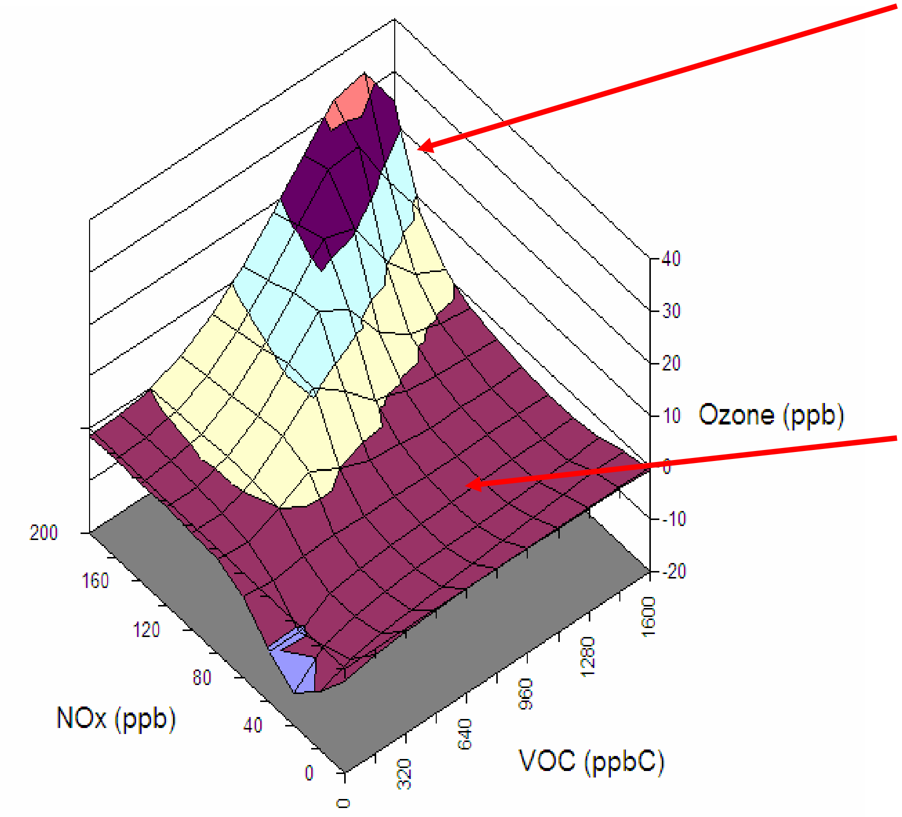


- Urban scenario VOC/NOx = 10
- CB05 has faster ozone production
  - radical production from IOLE and ALDX
- CB05 has same final ozone
  - nitrogen sinks (PANX and PAN) curtail ozone

CB05 and CB4 EKMA Diagrams



Ozone Difference: CB05 minus CB4



- CB05 has higher ozone in VOC-limited conditions
  - radicals from IOLE and ALDX
- CB05 has slightly lower ozone in NOx-limited conditions
  - PANX formation
  - this scenario does not see opposing impact of NOx-recycling reactions

Recommendations

- There should be a comparative study of UCR and UNC chamber experiments, especially for aromatics, to understand apparent chamber differences
- Aromatics mechanism should be updated using new data – after evaluating chamber differences
- Experimental studies of NOx recycling from organic nitrates

Questions?