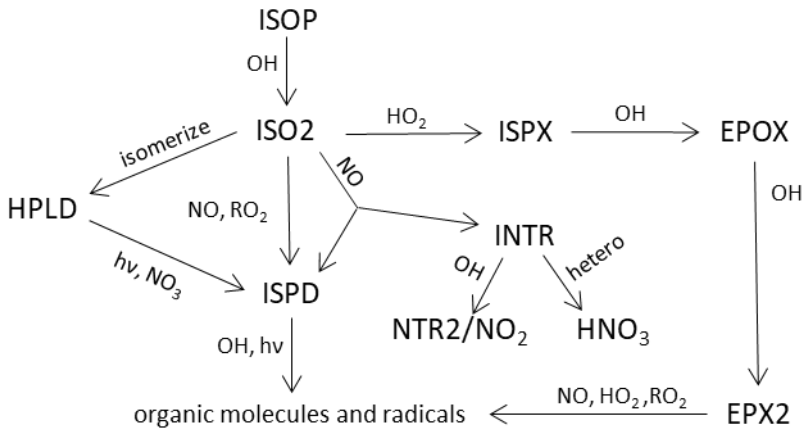
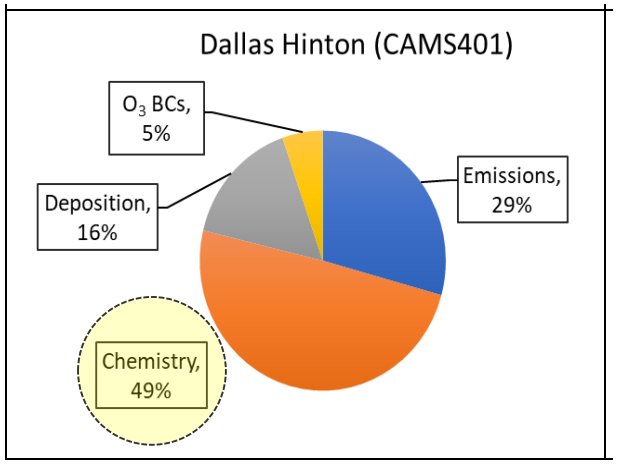
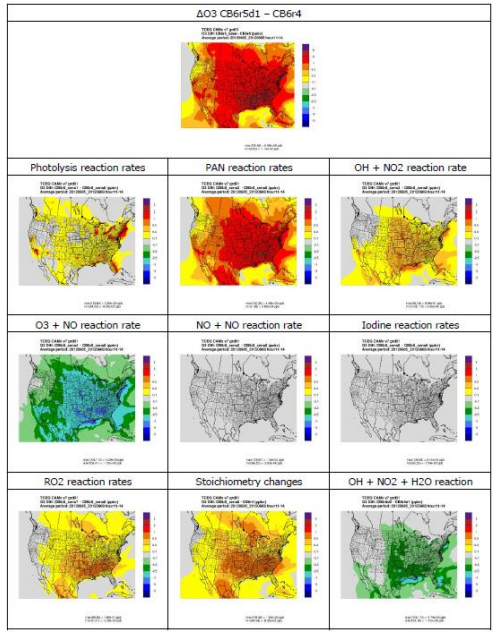
Carbon Bond Mechanism: CB6





Contributions to uncertainty in model O_3



Greg Yarwood

gyarwood@ramboll.com

Atmospheric Chemical Mechanisms Conference
Current Atmospheric Chemical Mechanisms Training
November 5, 2020

RAMBOLL Bright ideas. Sustainable change.

Acknowledgments and Disclaimer

Texas Commission on Environmental Quality

Texas Air Quality Research Program

US Environmental Protection Agency

Electric Power Research Institute

Gary Z. Whitten, Gookyoung Heo, Ross Beardsley, Bonyoung Koo, Tejas Shah, Alan M. Dunker and others

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Topics

- History of CB6 revisions
- Carbon Bond (CB) design
- Maintaining mechanism mappings
- Mechanism uncertainties
- CB6 revision 5 (CB6r5)
- CB7 in 2021

CB6 History

- The first version of **CB6** was completed in **2010** (Yarwood et al., 2010). The primary source for rate constant and photolysis data was the IUPAC panel.
- The first revision of CB6 to be widely used was **CB6r2** (revision 2; Hildebrandt Ruiz and Yarwood, **2013**) was first released in April 2014. CB6r2 introduced uptake of multi-functional organo-nitrates (ONs) by organic aerosol with subsequent hydrolysis to nitric acid. Also, the reaction mechanisms of isoprene and aromatics were updated from CB6.
- **CB6r2h** added reactions of iodine, bromine and chlorine compounds to account for ozone destruction in the marine boundary layer of the Gulf of Mexico (Yarwood et al., 2014).
- **CB6r3** was developed from CB6r2 to better represent wintertime high ozone events in the Rocky Mountains by accounting for temperature (and pressure) effects on alkyl nitrate formation (Emery et al., 2015). This is the latest version in CMAQ.
- **CB6r4** was developed to more efficiently model ozone depletion in the marine boundary by including only the 16 most important reactions of inorganic iodine (Emery et al., 2016). DMS was added in 2018. This is the latest version in CAMx7.
- **CB6r5** update just completed in **2020**

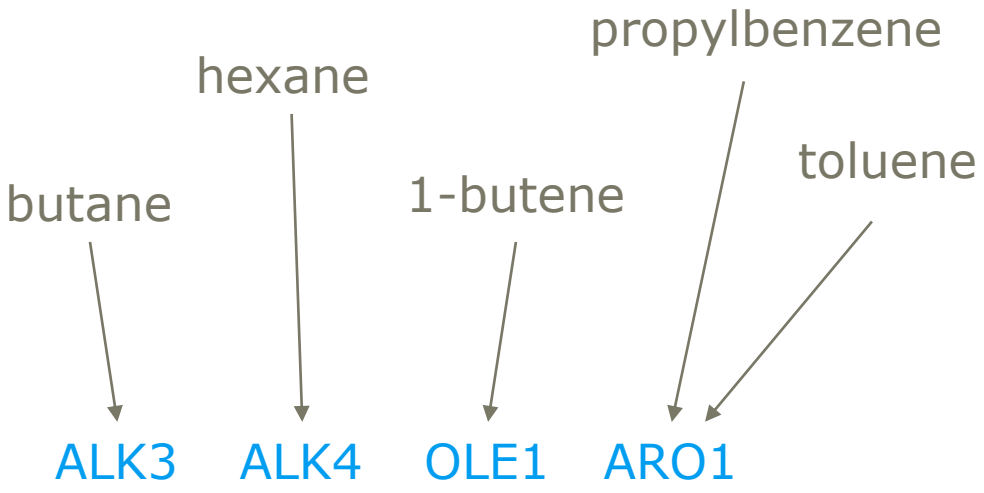
- CB6 mechanism listings are actively updated in the CAMx User's Guide: www.camx.com

Carbon Bond Design

Condensing gas-phase chemistry is also called “lumping”

Lumped Molecule: most mechanisms

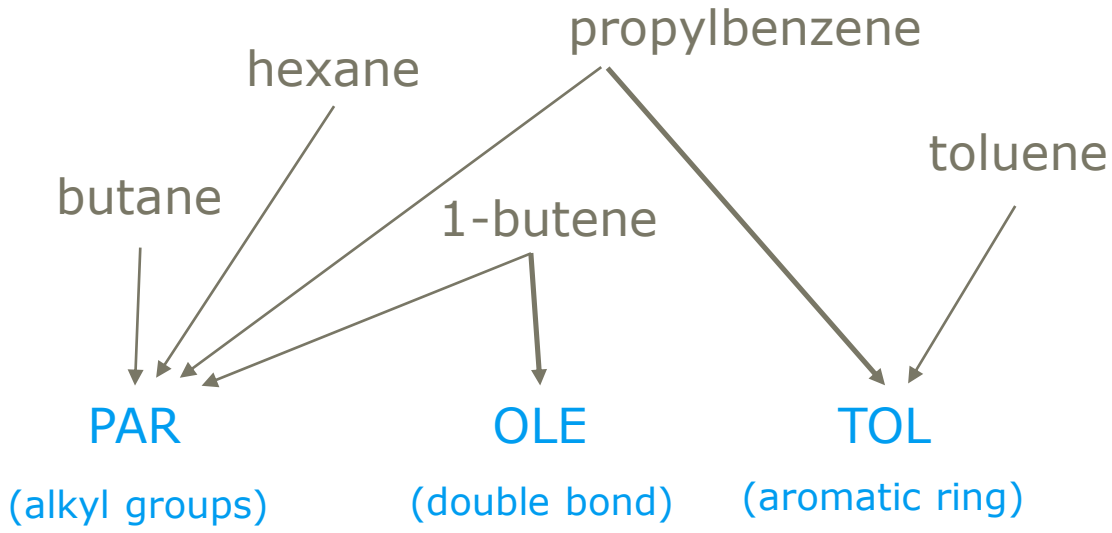
Represent molecules using surrogate molecules



Lumped Structure: Carbon Bond

Represent characteristics using surrogate molecules

Motivation: lumping scheme that conserves carbon



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CB6 Model Species

(Not a complete species list)

Explicit

- Alkanes: methane, ethane, propane
- Alkenes: ethene, isoprene
- Aromatic: benzene
- Alkyne: ethyne
- Aldehydes: formaldehyde, acetaldehyde, glyoxal, glycolaldehyde, methylglyoxal
- Ketones: acetone

Lumped

- Alkanes: PAR
- Alkenes: OLE, IOLE, TERP
- Aromatic: TOL, XYL
- Aldehydes: ALDX
- Ketones: KET

- A large fraction of emissions are treated explicitly in CB6 and other mechanisms
- The conceptual difference between “lumped structure” and “lumped molecule” mechanisms is becoming less applicable

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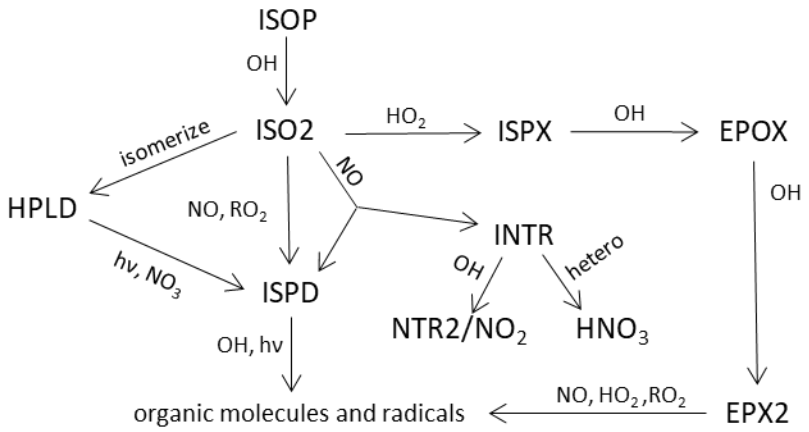
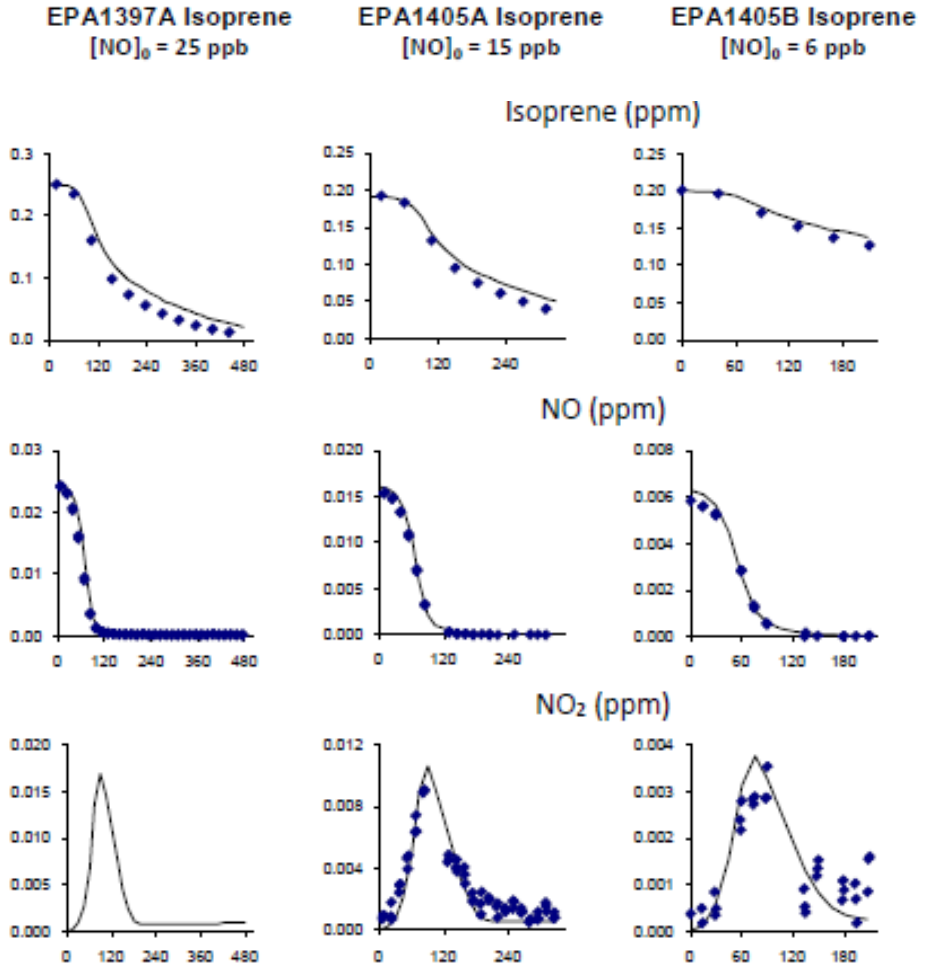
CB6r2 Isoprene Mechanism

- Texas AQRP project 10-014 performed new chamber experiments and improved mechanisms
- New isoprene mechanism designed based on emerging experiments and theory (in 2011)
- Three new experiments from the EPA chamber at UCR (designed by Bill Carter) constrained the CB6r2 isoprene mechanism in a critical range of NO concentration



CB6r2 Isoprene Mechanism



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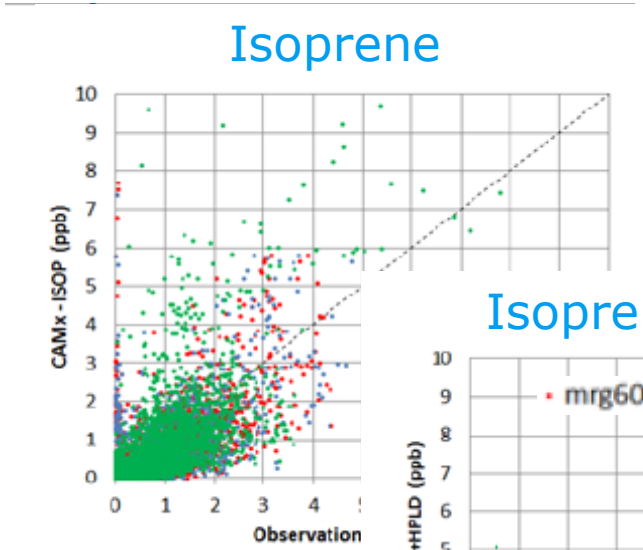
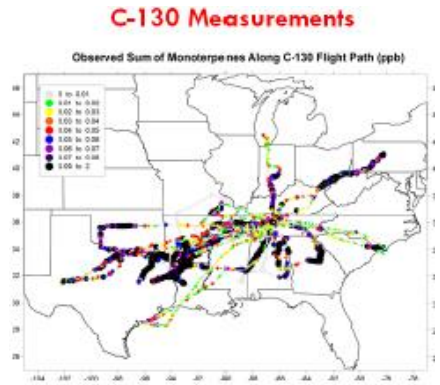
http://aqrp.ceer.utexas.edu/projectinfo%5C10-042%5C10-042%20Final%20Report.pdf

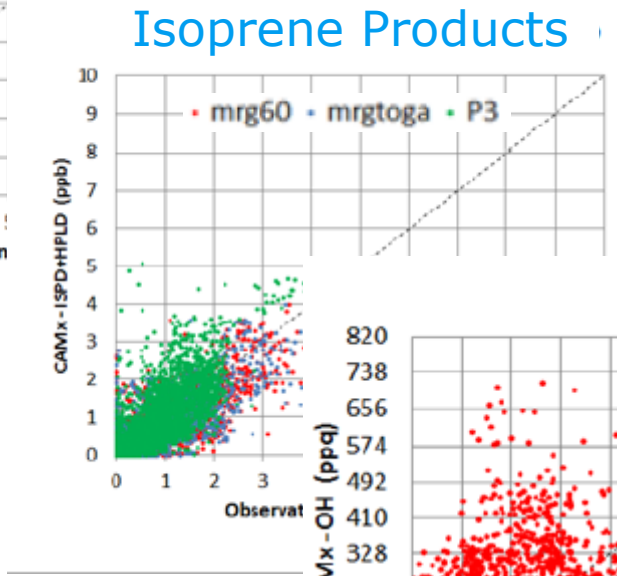
Isoprene: Aircraft Evaluation

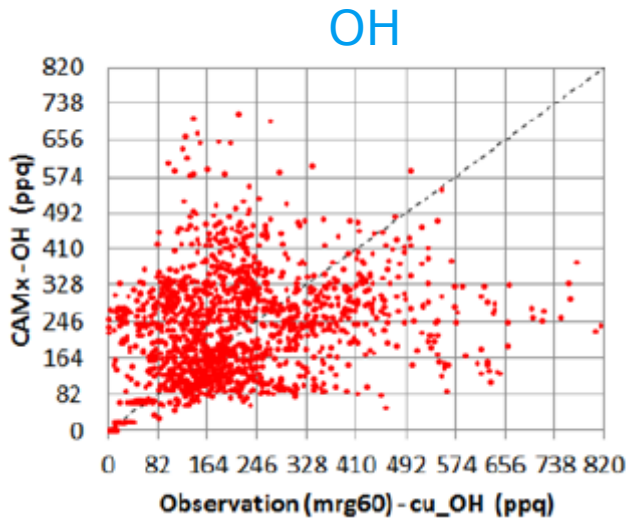
- Texas AQRP Project 14-016 improved biogenic emission inventories (MEGAN model)
  - Also evaluated CAMx model with CB6r2
  - Showing CB6r2 comparisons to NCAR C-130 and NOAA P3 flight data (flight map) from June-July 2013

- After improving the isoprene simulation to near-neutral bias we found
  - Good correlation and low bias for isoprene products (MVK+MACR+HPALD)
  - OH in comparable range with fair correlation









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http://aqrp.ceer.utexas.edu/projectinfoFY14_15/14-016/14-016%20Final%20Report.zip

Maintaining Mechanism Mappings

Mapping "chemical compounds" to "model species"

Here are mappings from EPA SPECIATE v5 compounds to CB6, CB05, SAPRC, RACM2, CRI model species:

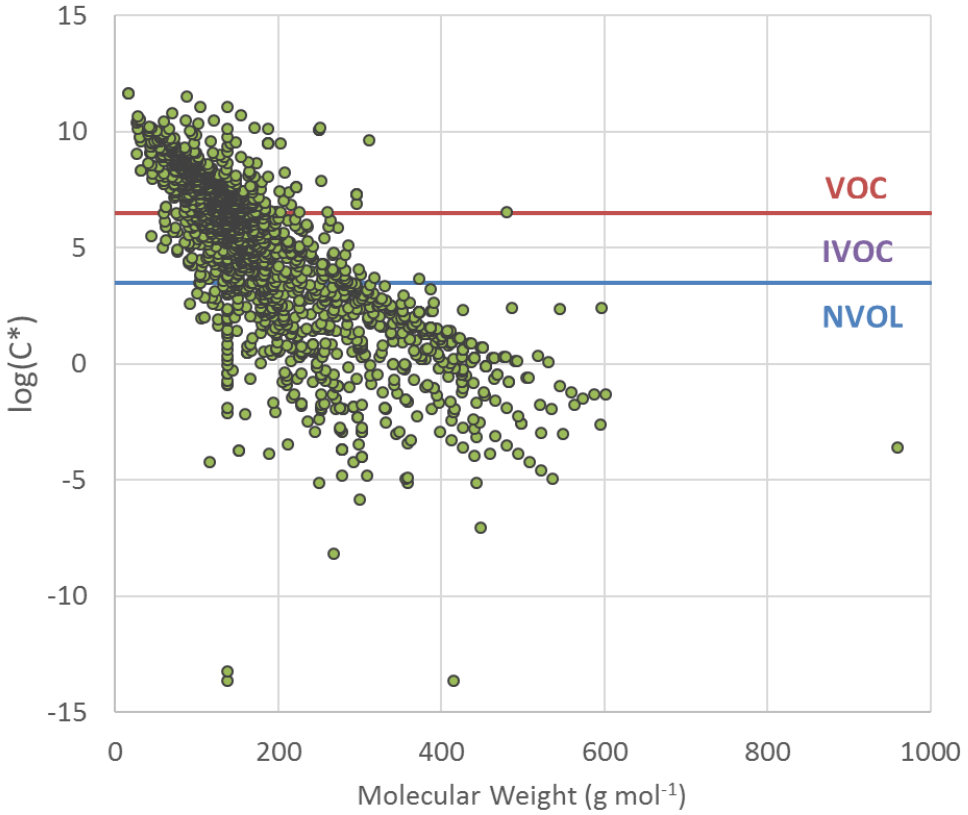
https://github.com/CMASCenter/Speciation-Tool

Maintenance is needed when new speciation profiles are added to SPECIATE that contain new compounds

Supported by US EPA

Issue: low volatility compounds

Strategies: map to IVOC and NVOL *or* CMAQ VBS



Estimated saturation concentration (C*) of compounds in SPECIATE 5.0 at 298 K as a function of molecular weight using EPA's EPI Suite

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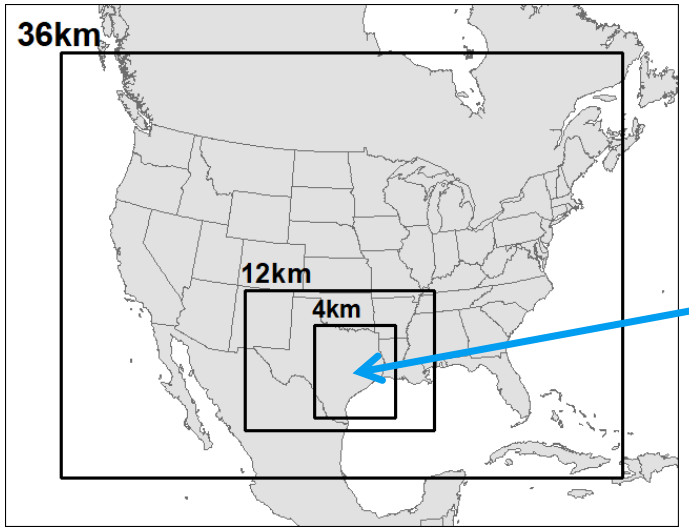
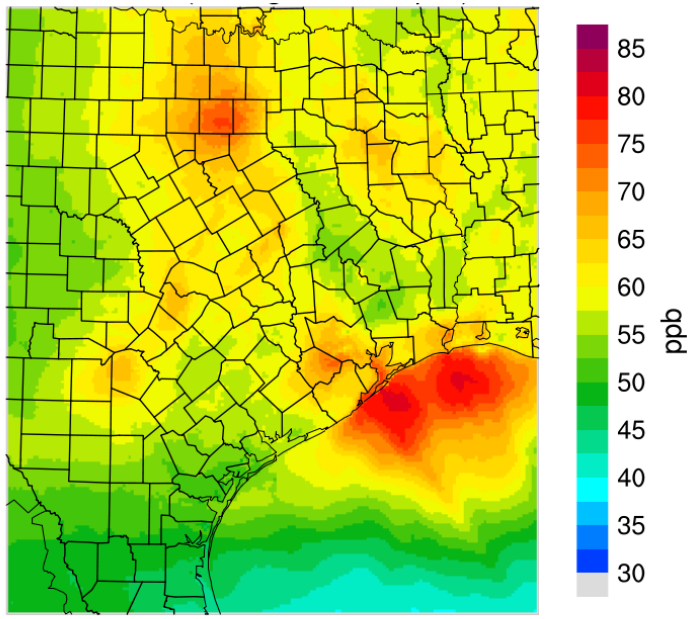
How does Mechanism Uncertainty Influence 3-D Model Results?



CAMx model input data provided by the TCEQ

Top10 O_3 days
June 7-9 and 22-28, 2012



Min= 39.7, Max= 81.7

Texas AQRP project 18-007 assessed contributions to uncertainty from:

- Chemistry
- Emissions
- Deposition
- Boundary concentrations

- The analysis of chemistry uncertainty provides useful and unique information

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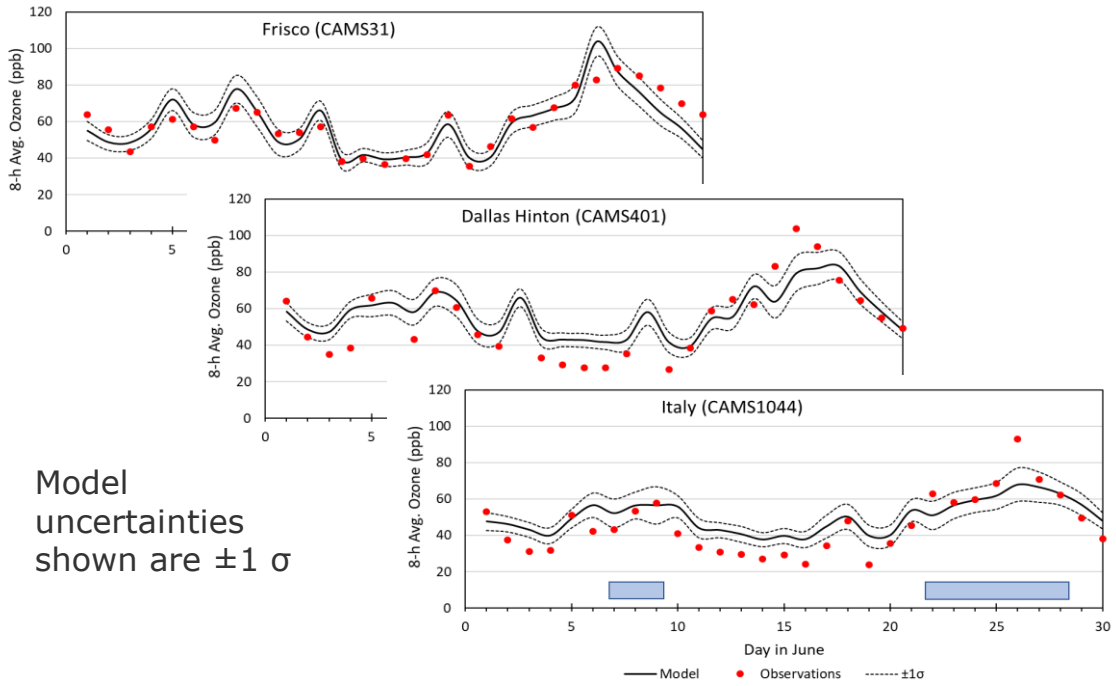
http://aqrp.ceer.utexas.edu/projectinfoFY18_19/18-007/18-007%20QAPP.pdf

Contributions to Model Ozone Uncertainty

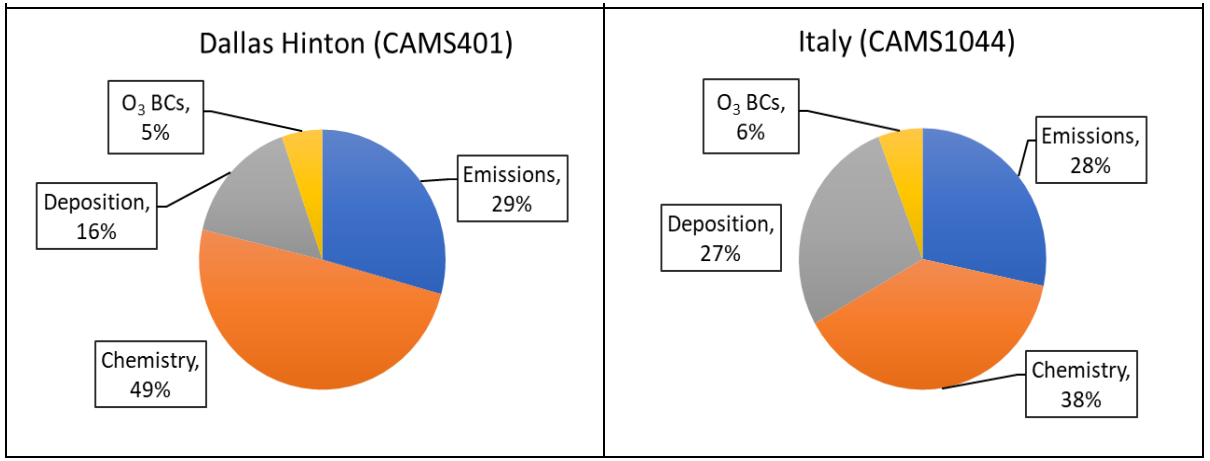
Time-series of MDA8 O_3 with error-bars



Model uncertainties shown are ±1 σ

Included model uncertainties can account for much but not all of the difference from observations

Contributions (%) to total uncertainty in model O_3



Chemistry consistently the largest contributor to model uncertainty – but we didn't investigate meteorology

Emissions or deposition the second largest contributor depending upon location

Chemical Sensitivity Analysis

CAMx DDM can compute

- 1st order sensitivity to rate constant
- 1st order sensitivity to stoichiometric coefficient
- 2nd order sensitivity to rate constant

How many parameters in CB6r4?

- 230 rate constants
- 764 product coefficients
- 452 uncertain product coefficients
- 230 + 452 = too many to evaluate in 3D

Chemical Sensitivity Analysis (CSA)

- Apply DDM to subdomains for parameters in the chemistry
- Local sensitivity, i.e., no communication between grid cells
- Like running many constrained box models
- Implemented as a CAMx "probing tool" and configured at run-time
- Simpler to apply than running many box models

Dunker, A.M., Wilson, G., Bates, J.T. and Yarwood, G., 2020. Chemical Sensitivity Analysis and Uncertainty Analysis of Ozone Production in the Comprehensive Air Quality Model with Extensions Applied to Eastern Texas. Environmental Science & Technology, 54(9), pp.5391-5399.

Analyzing Mechanism Uncertainty using CSA in CAMx

- Define an uncertainty for each mechanism parameter (rate constant and stoichiometric coefficient)
  - Published for CB6r4
- Compute O_3 sensitivity to each uncertain parameter
  - Species other than O_3 also obtained simultaneously
- Analyze which parameter contribute the most to total mechanism uncertainty
  - Parameters that are influential, or uncertain, or both

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Top 20 CB6r4 Parameters Contributing to Ozone Uncertainty

Parameter	Reaction	Cumulative Variance (%)
k1	NO2 = NO + O	26.5
k55	PAN = NO2 + C2O3	41.3
k3	O3 + NO = NO2	55.6
k63	PANX = NO2 + CXO3	63.7
k25	HO2 + NO = OH + NO2	71.0
k54	C2O3 + NO2 = PAN	77.3
k53	C2O3 + NO = NO2 + MEO2 + RO2	81.9
k45	NO2 + OH = HNO3	84.5
k62	CXO3 + NO2 = PANX	87.2
ROR-228	XPAR = 0.874 ROR +0.874 XO2 + 4 others	89.4
k89	ROOH + OH = 0.540 XO2H + 3 others	90.3
k61	CXO3 + NO = NO2 + ALD2 + XO2H + RO2	91.1
k129	PAR + OH = XPAR	91.8
XO2H-130	ROR = 0.940 XO2H + 8 others	92.5
XO2-228	XPAR = 0.874 ROR +0.874 XO2 + 4 others	93.2
k13	O3 + HO2 = OH	93.6
k76	XO2H + HO2 = ROOH	94.1
k72	MEO2 + HO2 = 0.9 MEPX + 0.1 FORM	94.4
k201	OPAN = OPO3 + NO2	94.8
k223	INO3 = I + NO3	95.1

- Influential uncertain parameters related to:
  - NO-NO_2-O_3 photo-stationary state
  - NO_2 availability (NOx recycling)
  - Radical production
  - Iodine availability
- Top10 account for 89% of variance and Top20 for 95%
- 17 of the Top20 are reaction rates and 3 are stoichiometric coefficients
- NO_2 photolysis ranked top even with small uncertainty (factor 1.1)
- Remaining uncertainties contribute <5% of variance in ozone production

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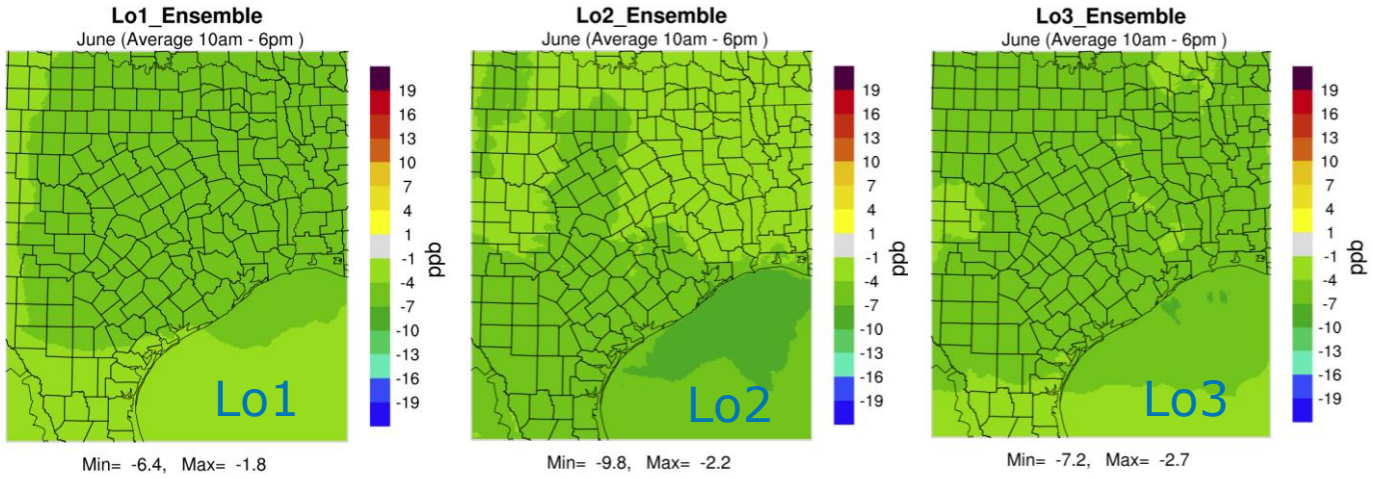
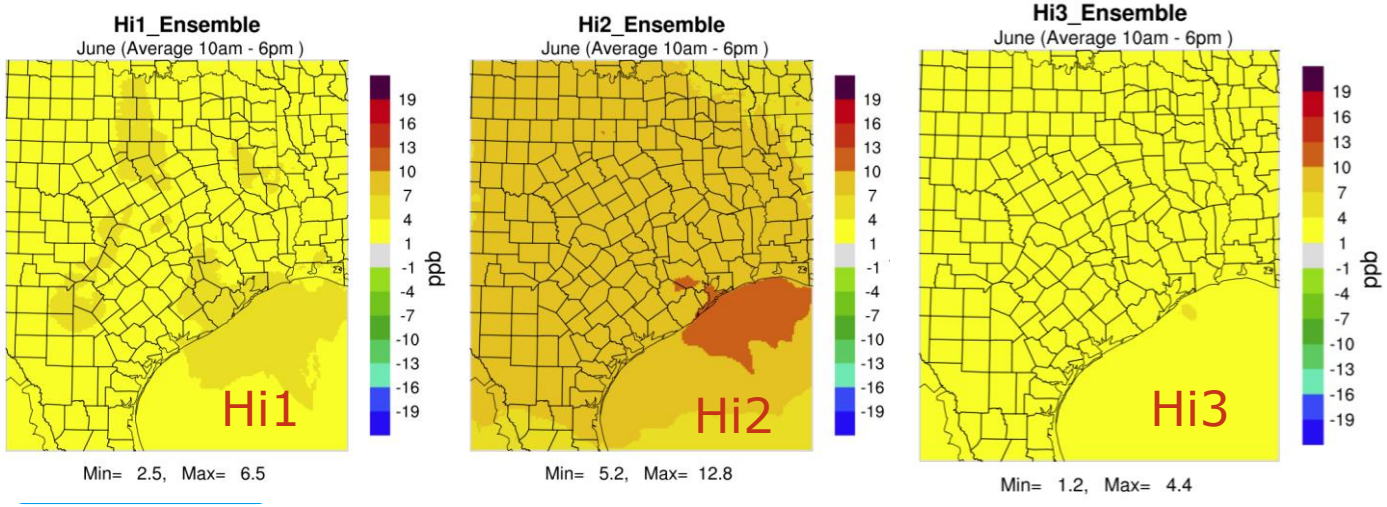
CB6r4 Hi & Lo Mechanisms





We also constructed perturbed versions of CB6r4 (using Monte Carlo) to represent +/- 1 sigma of uncertainty in O_3 production

- 3 "cold" mechanisms: Lo 1,2 3
- 3 "hot" mechanisms: Hi 1,2 3

Figures show O_3 differences (ppb) from the mean of 6 simulations (ensemble mean)

- Each simulation is unique showing the need for an ensemble
- Avg Hi – Avg Lo provided our estimate of uncertainty due to chemistry

Chemical Sensitivity Analysis (CSA) is available in CAMx7

For this analysis, CSA simultaneously computed sensitivity to 697 chemical mechanism parameters (1 model run)

- 230 1st order rate constant sensitivities,
- 15 2nd order rate constants sensitivities
- 452 1st order sensitivities to a product stoichiometric coefficient.
- 59,942 individual sensitivities, i.e., the sensitivity of 86 CB6r4 species to 697 parameters
- 630 grid cells were used for the analysis

CAMx simulation times

- without CSA required 1.3 hours/day using 12 CPU cores
- with CSA required 2.5 hours/day (factor 1.9 longer)

Feasible for a mechanism the size of CB6r4

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CB6 revision 5 (CB6r5)

- Mechanism updates focused on
  - "Top 50" uncertain parameters identified by Dunker et al. (2020)
  - Inorganic reactions
  - Simpler organic reactions
- Considered 152 of the 233 reactions in CB6r4
  - Revised reaction rates for 47 reactions
  - Added one new reaction
  - Most rate constant updates used IUPAC
- Tested in CAMx and will be released in v7.1
  - No significant change in ozone found
  - There are important updates and uncertainties
- Supported by the TCEQ and completed July 2020

Table 2. The CB6r5 mechanism with changes from CB6r4 marked.

No.	Reaction	Rate Constant Expression	k_{298} [a,b]
1	NO2 = NO + O	Photolysis	6.30E-3
2	O + O2 + M = O3 + M	k = ~~5.68E~~6.00E-34 (T/300)^-2.6	~~5.78E~~6.11E-34
3	O3 + NO = NO2	k = ~~1.40E~~2.07E-12 exp(-~~1310~~1400/T)	1.~~73E~~89E-14
4	O + NO ~~+ M~~ = NO2~~+ M~~	Falloff: F=0.85; n=0.84 k(0) = 1.00E-31 (T/300)^-1.6 k(inf) = 5.00E-11 (T/300)^-0.3	~~1.01E-31~~2.26E-12
5	O + NO2 = NO	k = 5.~~50E~~10E-12 exp(~~188~~198/T)	~~1.03E-11~~9.91E-12
6	O + NO2 = NO3	Falloff: F=0.6; n=1.03 k(0) = 1.30E-31 (T/300)^-1.5 k(inf) = 2.30E-11 (T/300)^0.24	2.~~11E~~09E-12
7	O + O3 =	k = 8.00E-12 exp(-2060/T)	7.96E-15
8	O3 = O	Photolysis	3.33E-4
9	O3 = O1D	Photolysis	8.78E-6
10	O1D + M = O + M	k = 2.23E-11 exp(115/T)	3.28E-11

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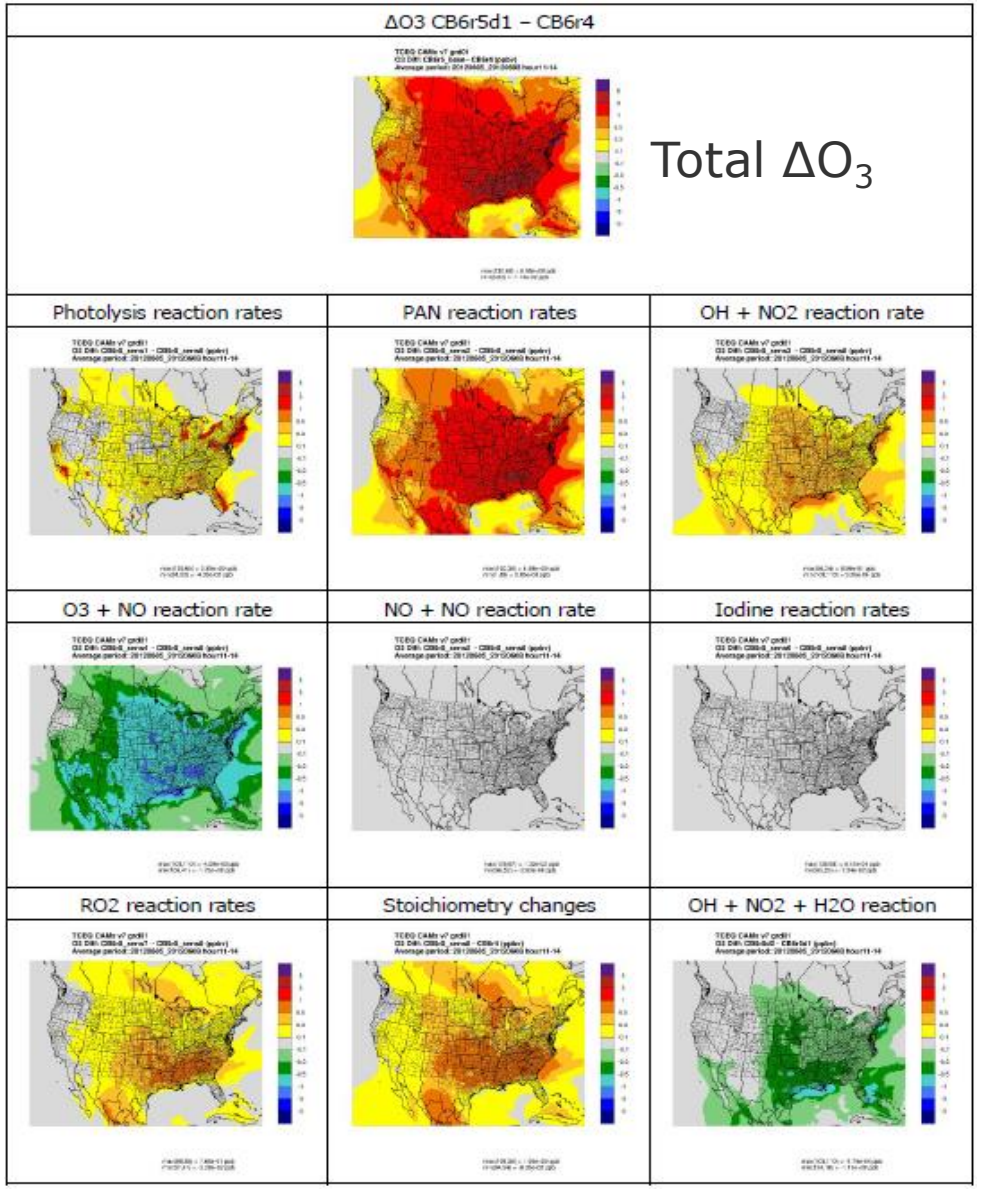
Which CB6r5 Updates are Influential?

We evaluated sensitivity to groups of reaction updates (hot, cold, neutral ΔO_3)

- Photolysis reaction rates
- PAN reaction rates
- OH + NO2 reaction rate – not updated from NASA
- O3 + NO reaction rate
- NO + NO reaction rate
- Iodine reaction rates
- RO2 reaction rates
- Stoichiometry changes – e.g. RO2 + HO2
- OH + NO2 + H2O reaction – new reaction added

The figure color scale emphasizes difference



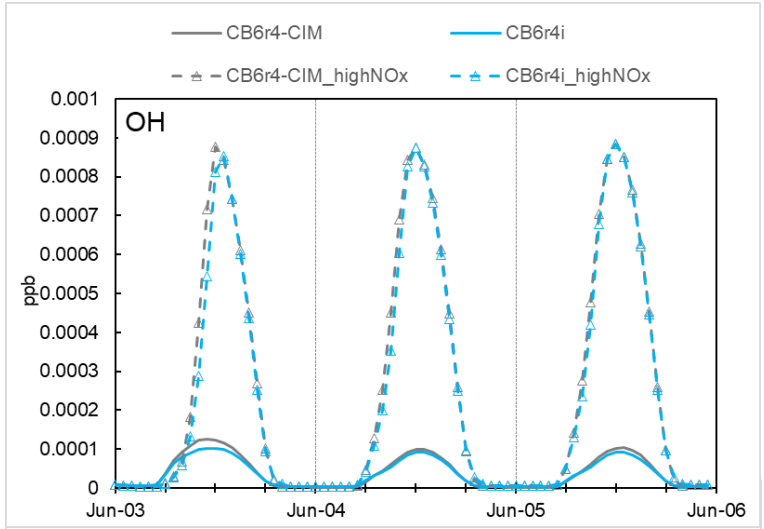
Comments from Developing CB6r5

- PAN
  - The equilibrium constant obtained from the forward/reverse reaction rates disagrees with the discussion notes, for both NASA and IUPAC, and this difference matters
- OH + NO2
  - The difference between the NASA and IUPAC recommendations matters
  - The recent evaluation by Amedro et al. is between NASA and IUPAC
  - Amedro et al. report that water is an effective third body (M) which is important (should be confirmed)
- Aldehyde photolysis quantum yields
  - Differences for similar compounds make it difficult to define a lumped higher aldehyde with confidence

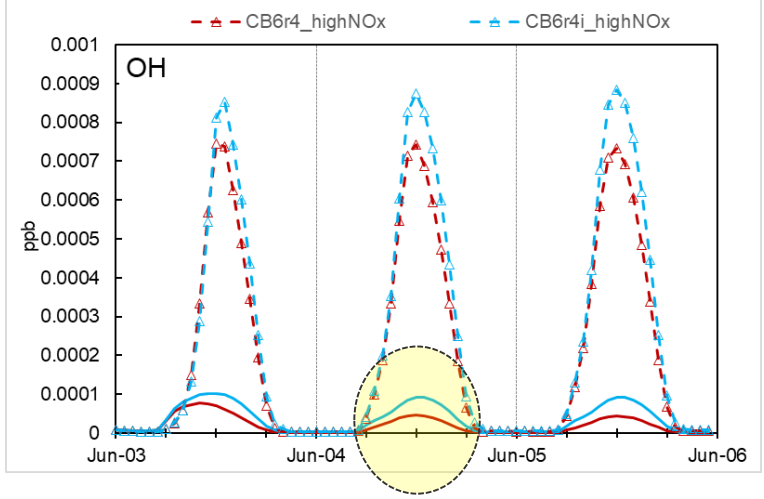
Amedro, D., Berasategui, M., Bunkan, A. J. C., Pozzer, A., Lelieveld, J., and Crowley, J. N., 2020. Kinetics of the OH + NO2 reaction: effect of water vapour and new parameterization for global modelling, Atmos. Chem. Phys., 20, 3091–3105, https://doi.org/10.5194/acp-20-3091-2020

CB7 in 2021

- Start from CB6r5
- Isoprene update
  - Retain CB6 mechanism structure
  - Update parameters to emulate Caltech Isoprene Mechanism (CIM) – CB6r4i
    - Higher OH at low NOx
  - Supported by Electric Power Research Institute (EPRI)
- Suggestions for other changes?
- CB7 supported by TCEQ



CB6r4i compared to CIM



CB6r4i compared to CB6r4

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Closing Remarks

- Uncertainties in gas-phase chemistry are a major contributor to uncertainty in ozone model results (Dunker et al., 2020)
  - 20 parameters in CB6r4 contribute 95% of the uncertainty in ozone production
  - The remaining parameters contribute only 5%
  - Rate constants for PAN and OH + NO_2 remain uncertain to significant degrees
  - Quantum yields for larger aldehyde photolysis are needed
  - What other quantum yields are needed?
- Coupling mechanisms with emission inventories requires regular maintenance
- Methods for condensing detailed mechanisms down to efficient size are needed
- Providing uncertainty estimates for parameters in chemical mechanism enables global uncertainty analysis of models

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Thanks for Attending ACM!