

Revision 5 of the Carbon Bond 6 Mechanism (CB6r5)

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Acknowledgments and Disclaimer

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Overview of the Carbon Bond 6 Mechanism

- The Carbon Bond 6 (CB6) mechanism is a condensed mechanism of tropospheric oxidant chemistry that is suitable for use in 3-D atmospheric models (e.g., CAMx)
- Volatile organic compounds (VOCs) are grouped according to their molecular structure to improve computational efficiency while maintaining accuracy

2010

Carbon Bond 6 released

2013

Revision 2 (CB6r2) – introduced heterogeneous reaction of organic nitrates (ON) and updated reactions of isoprene and aromatics.

2015

CB6r3 – ON improvements for winter ozone (current version in CMAQ)

2016, 2019

CB6r4 – Iodine and dimethylsulfide chemistry for marine environments (current version in CAMx)

Prioritization of Mechanism Review and Updates

- “Top 50” parameters in CB6r4 contributing to uncertainty in O₃ production
 - Dunker et al. (2020) estimated the uncertainty in O₃ predictions due to uncertainty in all CB6r4 parameters as well as emissions, deposition velocities and boundary conditions
 - Estimated uncertainty due to all rate constants and stoichiometric parameters in CB6r4
- Reactions involving nitrogen oxides (NO_x), hydrogen oxide radicals (HO_x) and odd oxygen radicals (O_x)
- Reactions of simpler organic compounds (methane, ethane, propane, ethene, ethyne, formaldehyde, acetaldehyde, acetone, benzene, toluene) with oxidants (OH, NO₃, O₃)

Data Sources for CB6r5

- International Union of Pure and Applied Chemistry (IUPAC) Task Group on Chemical Kinetic Data Evaluation
 - Reviews produced continuously
 - <http://iupac.pole-ether.fr/?cmd=redirect&arubalp=12345#>
- National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL) Panel for Data Evaluation
 - Reviews produced periodically
 - Current evaluation was released in 2015 (Burkholder et al., 2015)
 - <http://jpldataeval.jpl.nasa.gov>

Summary of Updates

- 152 reactions were reviewed
- 47 reaction rates are changed due to new data being available
 - 41 updated rate constants
 - 6 update photolysis reactions: FORM (2), ALD2, ALDX, GLY, GLYD

Largest Rate Increase



5.50E-5 → 5.01E-4

Largest Rate Decrease



2.73E-15 → 4.00E-16

- One new reaction
- No modification to chemical species (**No changes needed for emissions, boundary conditions**)
- Several changes to reaction products

Review of the OH+NO₂ reaction

- Ranked 8th in the “Top 50” from Dunker et al. (2020)
- IUPAC and JPL recommend substantively different rate constants, CB6r4 uses the current JPL recommendation
- Amedro et al. (2020) provides new laboratory measurements
 - Recommend a rate constant in between the JPL and IUPAC recommendations
 - Measurements show that water vapor (H₂O) accelerates the rate of the OH+NO₂ reaction (H₂O more effective as a third body, M) which accelerates the reaction in humid regions
- We retained the current reaction rate until there is more consensus among recommendations
- Added a reaction to account for the acceleration caused by water vapor based on new measurements by Amedro et al. (2020)
 - A simple implementation:



Mechanism Testing with CAMx

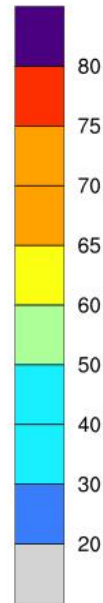
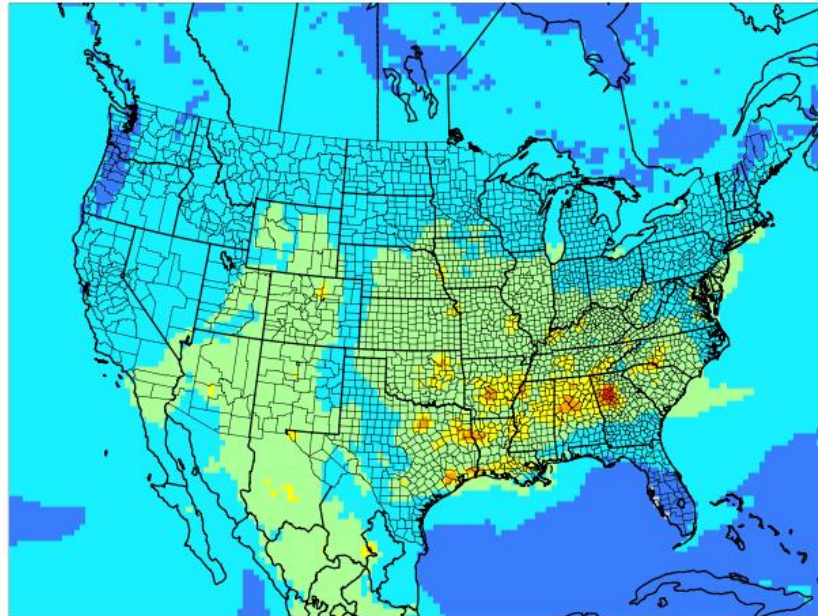
- Performed CAMx simulations with CB6r4 and CB6r5 for a high ozone period in June, 2012 using the TCEQ modeling platform
- 9 simulations to isolate the impacts of the updates for important groups of chemical reactions
- Applied the Chemical Process Analysis probing tool to assess how chemical reactions were influencing model species concentrations during simulations

Science Options	CAMx Base Case setup
Version	Version 7.0
Vertical Grid Mesh	29 Layers (TCEQ's CAMx vertical structure)
Time Zone	CST
Chemistry mechanism	CB6r4 or CB6r5 gas-phase mechanism
Horizontal Grids	4 km nested within 12 km and 36 km
Meteorology	TCEQ's 2012 WRF meteorology
Photolysis mechanism	TUV version 4.8 with TOMS ozone column data
Advection Scheme	Piecewise Parabolic Method (PPM)
Cloud convection scheme	On / Relaxed Arakawa-Schubert
Planetary Boundary Layer mixing	K-theory/ KV100 patch
In-line IX emissions	Oceanic iodine (Ix) emissions computed from saltwater masks
Chemistry Solver	EBI
Parallelization	MPI and OMP

Impact on Ozone Concentrations

CB6r5

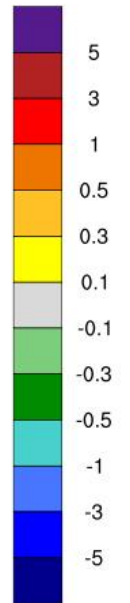
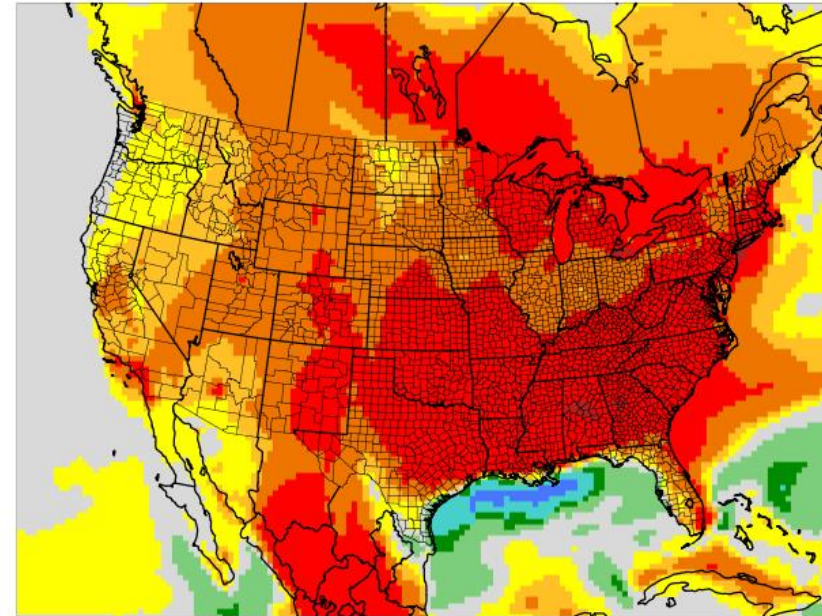
TCEQ CAMx v7 grd01
Hourly O3 Concentration (ppbv)
Average period: 20120605_20120608 hour11-14



max(107,41) = 76.7 ppb
min(23,89) = 17.6 ppb

CB6r5 – CB6r4

TCEQ CAMx v7 grd01
O3 Diff: CB6r5d3 - CB6r4 (ppbv)
Average period: 20120605_20120608 hour11-14

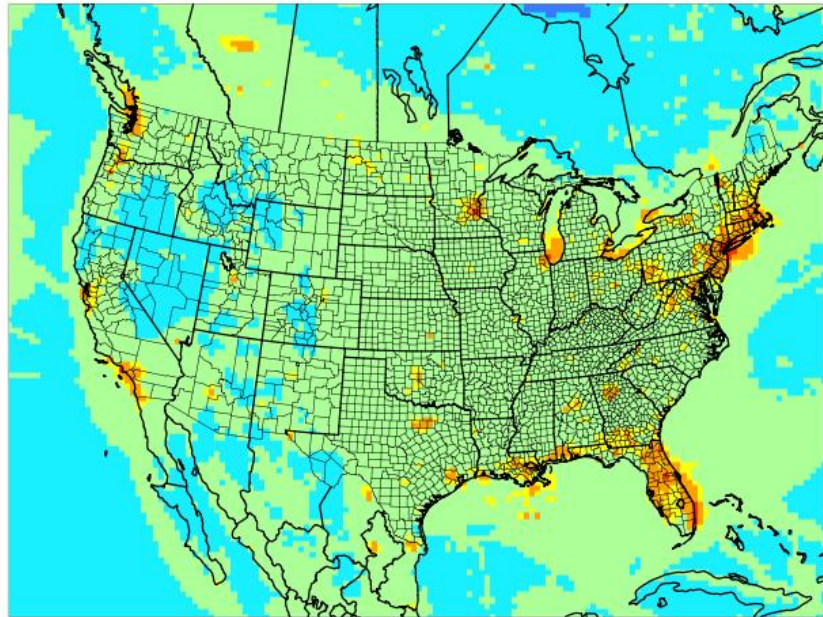


max(130,68) = 4.60e+00 ppb
min(96,24) = -1.43e+00 ppb

Impact on Nitrogen Dioxide Concentrations

CB6r5

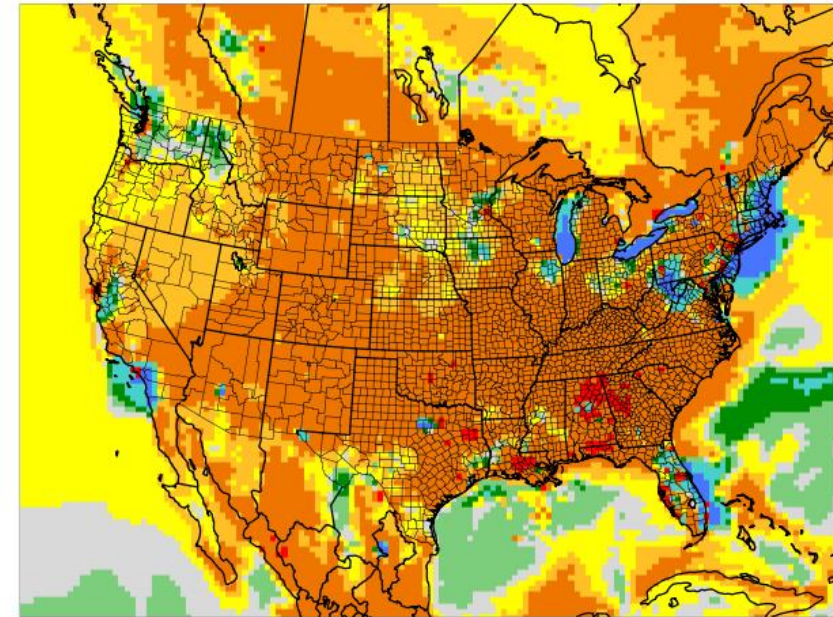
TCEQ CAMx v7 grd01
Hourly NO2 Concentration (ppmv)
Average period: 20120605_20120608 hour11-14



max(129,67) = 4.4e-02 ppmv
min(103,110) = 8.1e-06 ppmv

CB6r5 – CB6r4

TCEQ CAMx v7 grd01
NO2 Diff: CB6r5d3 - CB6r4 (ppmv)
Average period: 20120605_20120608 hour11-14

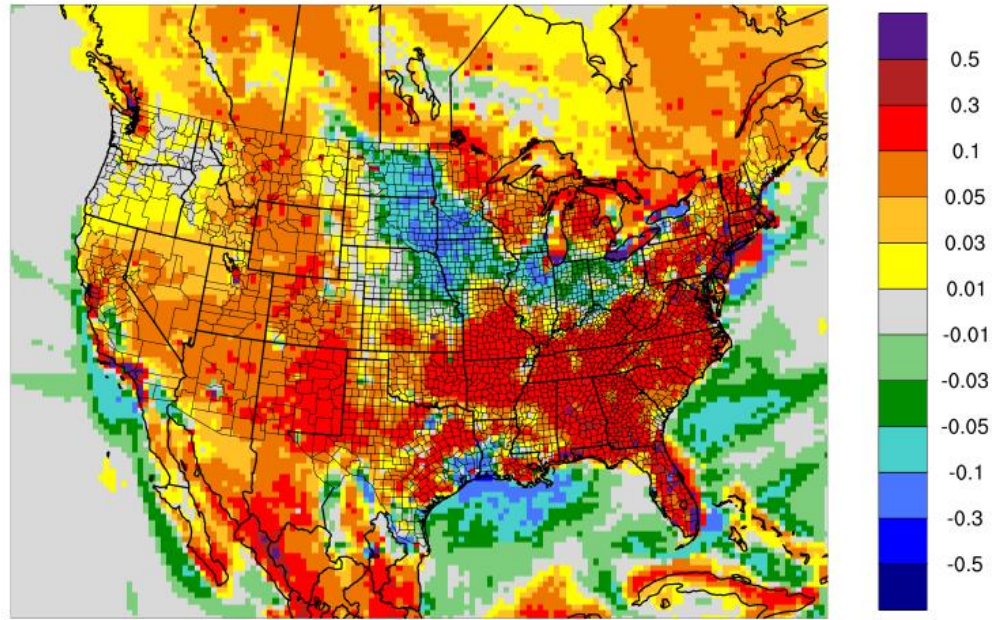


max(129,67) = 2.30e-03 ppmv
min(133,68) = -4.95e-04 ppmv

Impact on Ozone Production and Destruction

ΔO_3 Production (CB6r5 – CB6r4)

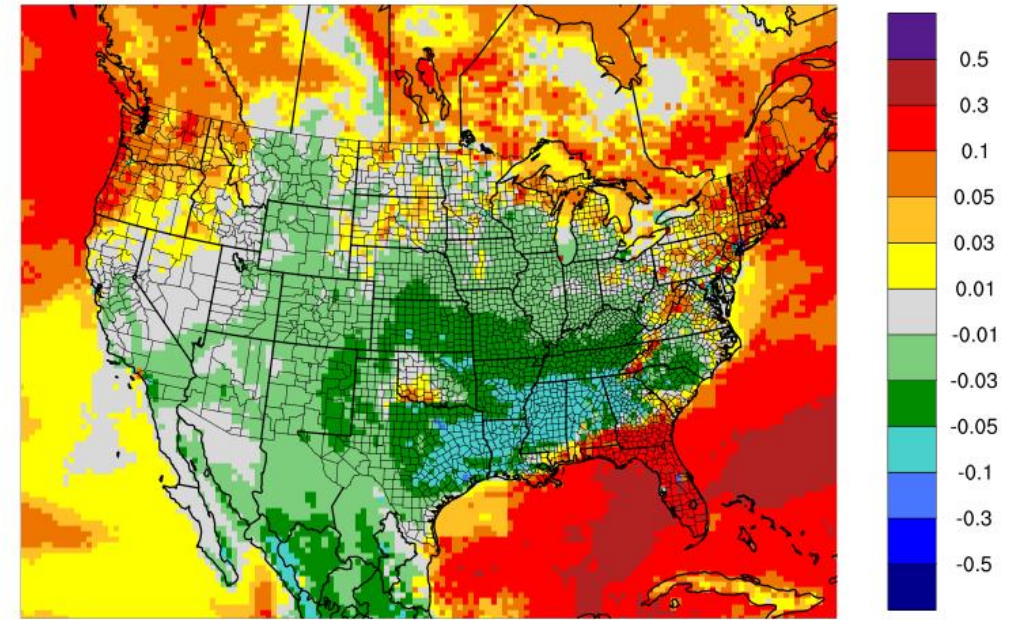
TCEQ CAMx v7 grd01
CB6r5d3 - CB6r4: PO3_net (Avg of PBL)
Average period: 20120605_20120608 hour11-14



max(127,78) = 2.06e+00 ppb/h
min(65,12) = -5.03e-01 ppb/h

ΔO_3 Destruction (CB6r5 – CB6r4)

TCEQ CAMx v7 grd01
CB6r5d3 - CB6r4: O3_dest (Avg of PBL)
Average period: 20120605_20120608 hour11-14



max(15,60) = 6.94e-01 ppb/h
min(129,66) = -5.53e-01 ppb/h

Impact on Model Performance (June 2012)

Statistical Metric	CB6r4	CB6r5
Number of Observations	3012	3012
Average Concentration - Observations (ppb)	46.1	46.1
Average Concentration - Model (ppb)	51.5	51.9
r^2	0.83	0.83
Mean Bias (ppb)	5.4	5.8
Mean Error (ppb)	8.0	8.1
Normalized Mean Bias (%)	11.8	12.6
Normalized Mean Error (%)	17.3	17.5

CB6r5 performed similarly to CB6r4 with statistical metrics (NMB, NME, and r) with both mechanisms meeting the criteria recommended by Emery et al. (2017)

Full Documentation and Release of CB6r5

The full report on CB6r5 can be accessed on the TCEQ website:

<https://www.tceq.texas.gov/assets/public/implementation/air/am/contracts/reports/pm/5822011221014-20200730-Ramboll-CB6r5MechanismChanges.pdf>

CB6r5 will be implemented in CAMx v7.1 which will be released soon!

(see Chris Emery's presentation for more details)

References

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>.

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Emery, C., Z. Liu, A.G. Russell, M.T. Odman, G. Yarwood, and N. Kumar. 2017. Recommendations on statistics and benchmarks to assess photochemical model performance. *J. Air Waste Manage. Assoc.*, 67(5), 582-598.

Thank You!

Questions?