Evaluating Isoprene Oxidation Mechanisms in Regional Models Using In Situ Observations of Formaldehyde

23

mmarvin@umd.edu

Margaret R. Marvin[1], G. M. Wolfe[2,3], R. J. Salawitch[1,4,5], T. P. Canty[4], A. Ring[4], D. L. Goldberg[6,7], A. Fried[8]

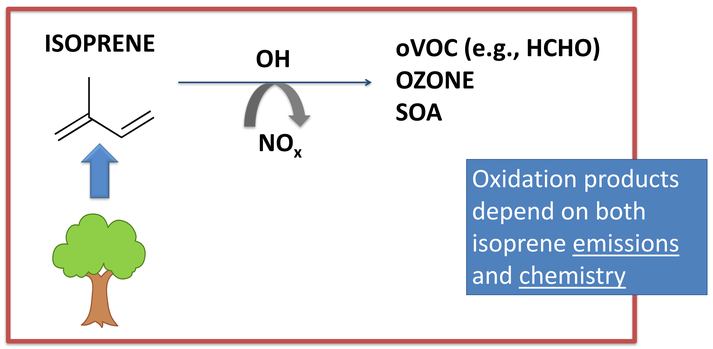
[1]Department of Chemistry and Biochemistry, UMCP; [2]JCET, UMBC; [3]Atmospheric Chemistry and Dynamics Laboratory, NASA GSFC;
[4]Department of Atmospheric and Oceanic Science, UMCP; [5]ESSIC, UMCP; [6]Energy Systems Division, ANL; [7]Computation Institute, UChicago; [8]Institute of Arctic and Alpine Research, CU Boulder

Summary

- We use *in situ* observations of HCHO from DISCOVER-AQ to test different isoprene mechanisms within the CAMx model framework
- Simulated HCHO is highest in isoprene-rich areas, and averages 4-5 ppb in the Baltimore-Washington Region (BWR) throughout July of 2011
- The CB6r2 and CB6r2-UMD mechanisms demonstrate cancelling effects on simulated HCHO relative to CB05
- All simulations underestimate HCHO with respect to observations
- The HCHO/NO_2 column ratio from CB6r2-UMD suggests that urban areas of the BWR are in transition between ozone production regimes

Background and Motivation

- Isoprene (C_5H_8) comprises ~30% of global non-methane VOC emissions, and is highly reactive to oxidation by OH ($\tau \approx 1$ h)



- Formaldehyde (HCHO) is a high-yield product of isoprene oxidation as well as a precursor of tropospheric ozone production
- Uncertainties in isoprene chemistry and emissions impact modeled HCHO mixing ratios, by at least 12% and up to a factor of 2, respectively

Research Questions

1. How do regional models respond to different isoprene mechanisms?
2. How well do regional models simulate isoprene oxidation products?
3. What are the implications for modeled ozone?

Gas-Phase Chemical Mechanisms

Mechanism	Species	Reactions	Reference
CB05	53	156	Yarwood et al., 2005
CB6r2	77	216	Ruiz and Yarwood, 2013
CB6r2-UMD	77	216	Marvin et al., 2017

CB: Carbon Bond Mechanism

CB6r2-UMD increases HCHO production relative to CB6r2:

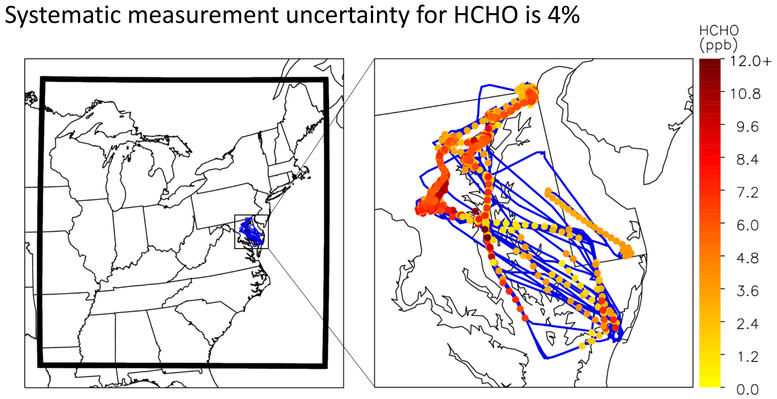
1. Adds HCHO as a product of HPALD + hv
2. Adds HCHO as a product of MVK + OH and MACR + OH
3. Adds HCHO as a product of GLYD + OH
4. Increases product fraction of HCHO in $IEPOXO_2$ + HO_2 and $IEPOXO_2$ + NO
5. Updates PAN equilibrium rate constants to IUPAC 2014

In Situ Observations

Aircraft Campaign: DISCOVER-AQ (Phase 1)

DISCOVER-AQ (or D-AQ): Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality

- Flights were conducted over the BWR in July of 2011
- *In situ* HCHO observations were collected by the NCAR DFGAS instrument (Lancaster et al., 2000) aboard the NASA P-3B research aircraft
- Systematic measurement uncertainty for HCHO is 4%

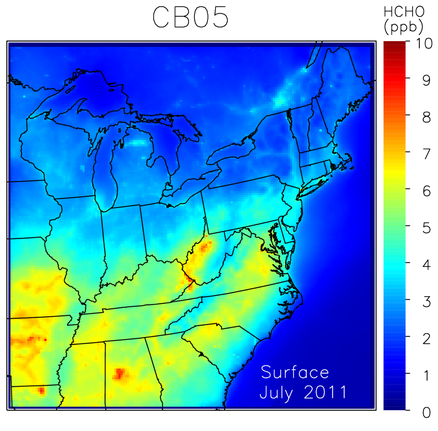


Model Analysis

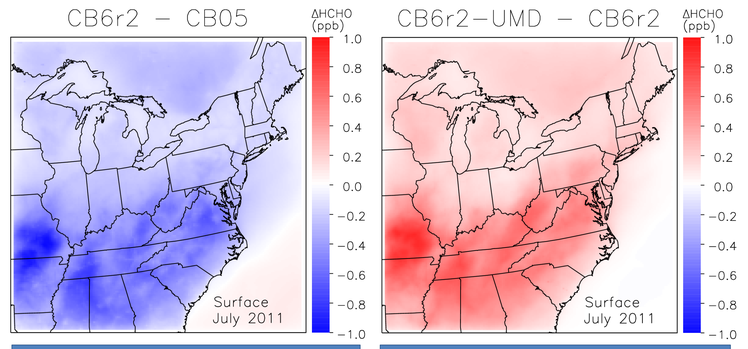
Regional Model: CAMx v6.40

CAMx: Comprehensive Air Quality Model with Extensions (www.camx.com)

- Model domain comprises the Eastern United States in July of 2011
- Resolution is 12 km x 12 km with 35 vertical layers
- All inputs are processed for 2011
  - Meteorology: WRF v3.4 (EPA, 2014a)
  - Anthropogenic emissions: NEI v2 (EPA, 2014b)
  - Mobile emissions: MOVES 2014 (EPA, 2014b)
  - Biogenic emissions: BEIS v3.6.1 (Bash et al., 2016)
  - Boundary conditions: GEOS-Chem v8.3.2 (Henderson et al., 2014)
- Modeled species mixing ratios are output hourly
- Simulations differ only with respect to the chemical mechanism used



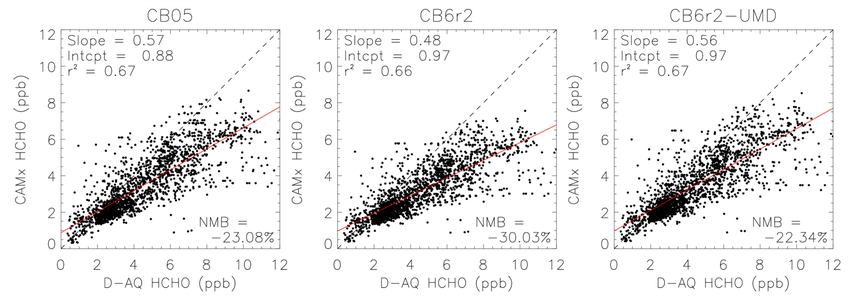
- Average simulated HCHO mixing ratios in the BWR for July 2011 are ~5 ppb
- The highest simulated HCHO mixing ratios occur over the Southeast United States, which is rich in isoprene



Preliminary results suggest that HCHO decreases due to an underestimation of PAN in CB6r2

Increased HCHO reflects the changes made in CB6r2-UMD to increase HCHO production from isoprene oxidation

Comparison to Observations



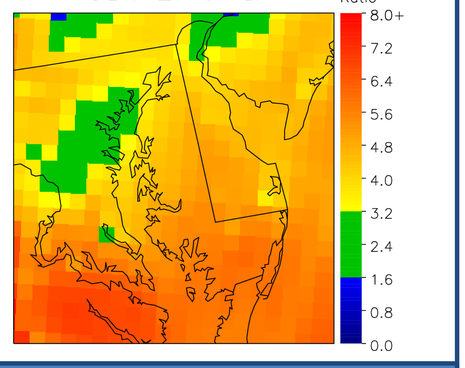
All simulations underestimate HCHO observations by 20-30%, which indicates remaining model deficiencies (perhaps in chemistry, emissions, meteorology, etc.)

Implications for Modeled Ozone

- The HCHO/NO_2 tropospheric column ratio is used to characterize ozone production regimes

For DISCOVER-AQ:
VOC-limited: <1.6
NO_x-limited: >3.2
Transition: 1.6-3.2
(Roberts et al., in prep.)

Most of the BWR is in the NO_x-limited regime, except for urban areas, which are in transition



Next Steps

- Repeat analysis for the Southeast United States in June and July of 2013 for comparison with data from the SENEX mission
- Test sensitivity of simulated HCHO to isoprene emissions

Acknowledgements

We appreciate support from NASA ESSF, ACCDAM, ACMAP, and MAP, as well as EPA STAR.