Evaluating Isoprene Oxidation Chemistry in Gas-Phase Chemical Mechanisms Using In Situ Observations of Formaldehyde

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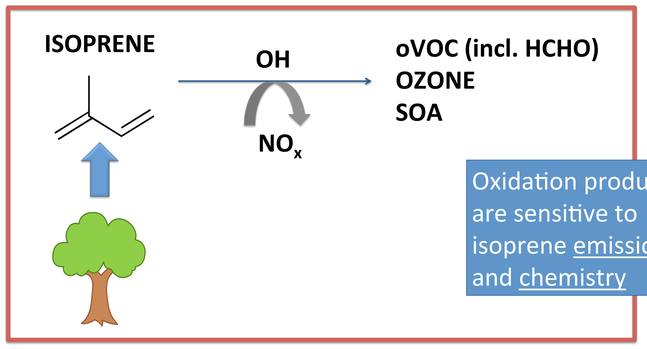
Summary

- We use *in situ* observations of HCHO from the summertime Southeast US to test isoprene chemistry in gas-phase mechanisms
- Mechanisms containing more developed isoprene oxidation chemistry tend to simulate HCHO more accurately
- Most mechanisms reproduce the NO_x-dependence of observed HCHO, but underestimate the magnitude of measured HCHO mixing ratios
- Differences in modeled HCHO are traced to late-gen isoprene chemistry
- Simulated HCHO directly impacts modeled ozone production rates

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)



Oxidation products are sensitive to isoprene emissions and chemistry

- Isoprene chemistry is inconsistent among the gas-phase chemical mechanisms used in chemical transport models
- Formaldehyde (HCHO) is a high-yield product of isoprene oxidation that can be used to evaluate and compare mechanisms

Research Questions

1. How well do gas-phase mechanisms reproduce isoprene chemistry?
2. Which mechanistic differences impact isoprene oxidation products?
3. What are the implications for modeled ozone and SOA?

Gas-Phase Mechanisms

Mechanism	Species	Reactions	Reference
CB05	53	156	Yarwood et al., 2005
CB6r2	77	216	Ruiz and Yarwood, 2013
GEOS-Chem (v9-2+)	171	505	Mao et al., 2013[a]
MCMv3.2[b]	455	1476	Saunders et al., 2003
MCMv3.3.1[b]	610	1974	Jenkin et al., 2015

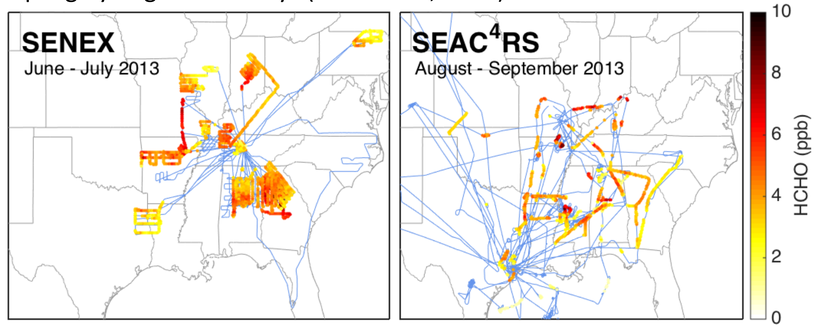
[a]With updates from Kim et al., 2015; Fisher et al., 2016; Marais et al., 2016; and Travis et al., 2016
[b]Isoprene subset

CB: Carbon Bond Mechanism
MCM: Master Chemical Mechanism

Methods

Aircraft Campaigns: SENEX 2013 and SEAC[4]RS 2013

SENEX: SouthEast NEXus (Warneke et al., 2016)
SEAC[4]RS: Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (Toon et al., 2016)



Daytime, boundary-layer HCHO observations were collected by the ISAF-LIF instrument (Cazorla et al., 2015)

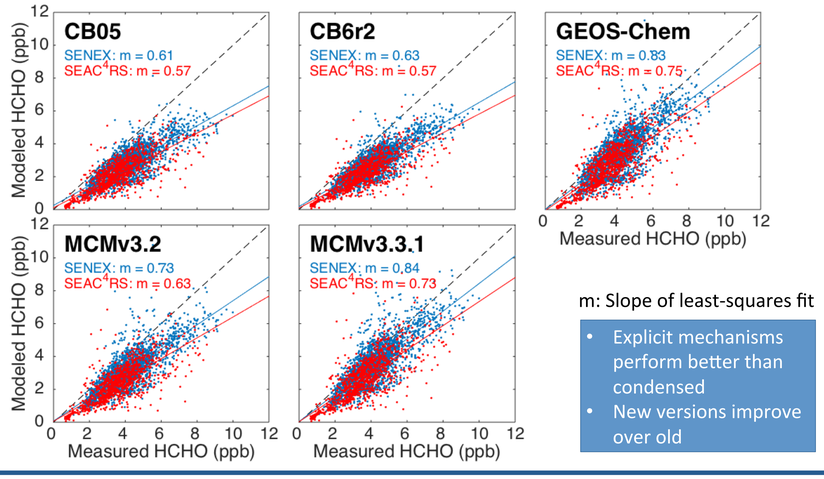
Box Model: F0AMv3

F0AM: Framework for 0-D Atmospheric Modeling (Wolfe et al., 2016)

- Constrained to aircraft observations
  - Meteorology: P, T, and RH
  - Chemistry: NO, NO_2, O_3, CO, PAN, methane, methanol, and isoprene
  - Photolysis: $j(O^1D)$ and $j(NO_2)$
  - Other: Time and location
- J-values adjusted for cloud cover
- Physical losses represented by a 24-hour lifetime
- Integrated 3 days forward in time to reach diel steady state

Results

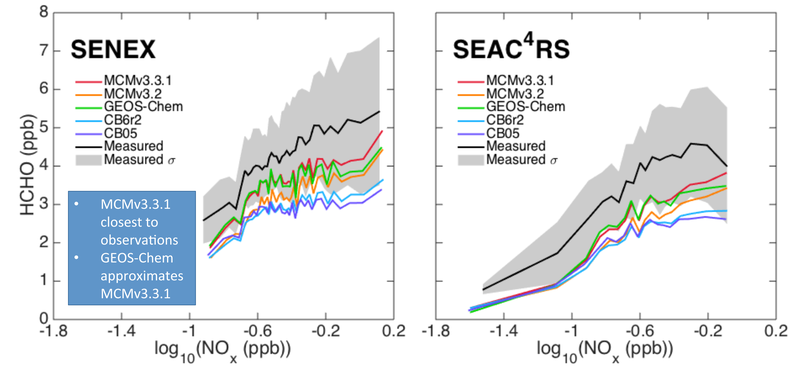
Comparison to Observations



m: Slope of least-squares fit

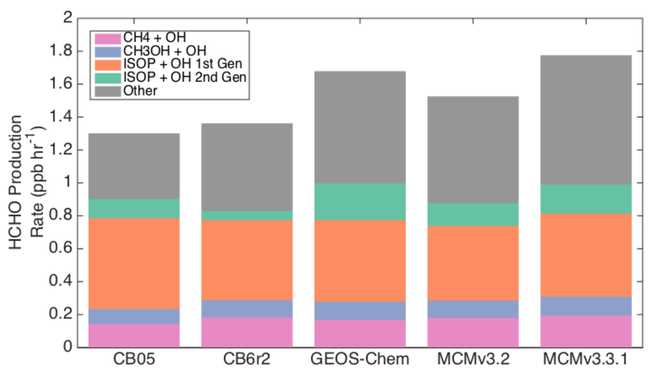
- Explicit mechanisms perform better than condensed
- New versions improve over old

All mechanisms underestimate measured HCHO by at least 0.5 – 1 ppb



- MCMv3.3.1 closest to observations
- GEOS-Chem approximates MCMv3.3.1

Reaction Rate Analysis



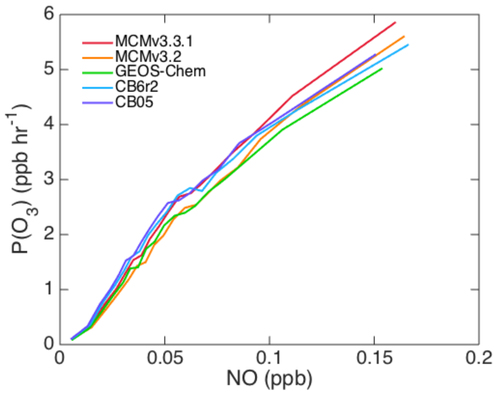
Shown for **SENEX**:
- Inter-model differences due to second- and later-generation isoprene chemistry
- Similar for SEAC[4]RS, but total HCHO production rates are 35 – 40% lower

Implications for Modeled Ozone

$$P(O_3) = k_{HO2+NO}[HO_2][NO] + \sum k_{RO2+NO}[RO_2][NO]$$

k: Reaction rate constant (cm^3 $molecule^{-1}$ s^{-1})
[X]: Species concentration (molecule cm^{-3})
$P(O_3)$: Ozone production rate (molecule cm^{-3} s^{-1}) ⇨ (ppb hr^{-1})

Shown for **SEAC[4]RS**:
- HCHO impacts HO_2 term
- $P(O_3)$ differs between mechanisms up to 1 ppb hr^{-1}
- Similar for SENEX, but larger NO range results in $P(O_3)$ values up to 10 ppb hr^{-1}



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