Examining the role of NO_x and acidity on organic aerosol formation through predictions of key isoprene aerosol species in the United States

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Introduction

Isoprene contributes significantly to organic aerosol in the southeastern United States where biogenic hydrocarbons mix with anthropogenic emissions. The Community Multiscale Air Quality (CMAQ) model currently underestimates secondary organic aerosol (SOA), especially in the summer.

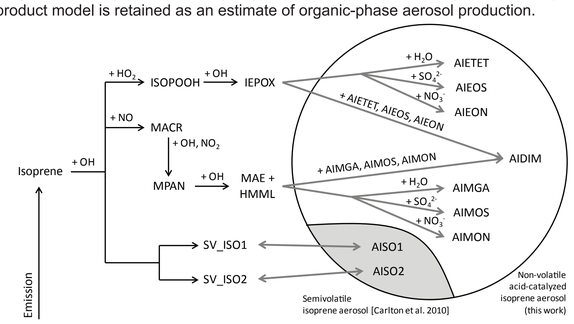
Objectives
- Update the CMAQ isoprene SOA treatment to account for the role of NO_x
- Predict known isoprene-derived aerosol-phase constituents for comparison to observations
- Determine if the new pathways better represent isoprene SOA and how they respond to changes in emissions

Model Description

New Aerosol Species

Two epoxides have been proposed as isoprene SOA precursors:
- IEPOX formed under low-NO_x conditions [Paulot et al. 2008 Science, Surratt et al. 2010 PNAS]
- MAE formed under high-NO_x and high NO_2/NO conditions [Lin et al. 2013 PNAS]

These epoxides have large Henry's law coefficients and can participate in acid-catalyzed particle-phase reactions leading to known isoprene-derived aersosol species. Both IEPOX and MAE+HMML from MPAN are considered precursors to isoprene SOA. Seven new aerosol species, accounting for the role of different nucleophiles, are added to the model. They include 2-methyltetrols (AIETET), 2-methylglyceric acid (AIMGA), organosulfates (AIEOS, AIMOS), organonitrates (AIEON, AIMON), and dimers (AIDIM). The Odum 2-product model is retained as an estimate of organic-phase aerosol production.



Aerosol formation requires particle-phase reaction in which an **ACID** catalyzes the epoxide ring opening and a **NUCLEOPHILE** adds to the ring.

	Aerosol Species	MW [g mol^{-1}]	OM/OC	Parent Hydrocarbon	Nucleophile Added
IEPOX-derived aerosol	2-methyltetrol	136	2.27	IEPOX	water
	IEPOX-derived OS	216	3.60	IEPOX	sulfate
	IEPOX-derived ON	181	3.02	IEPOX	nitrate
MPAN-derived aerosol	2-methylglyceric acid	120	2.50	MAE, HMML	water
	MPAN-derived OS	200	4.17	MAE, HMML	sulfate
	MPAN-derived ON	165	3.44	MAE, HMML	nitrate
	dimers (as tetrol dimer)	248	2.07	IEPOX	2-methyltetrol
				IEPOX	IEPOX-derived OS
				IEPOX	IEPOX-derived ON
				MAE, HMML	2-methylglyceric acid
				MAE, HMML	MPAN-derived OS
				MAE, HMML	MPAN-derived ON

Uptake Process

Aerosol formation is modeled as uptake onto aqueous accumulation-mode aerosols.

$$\gamma = \left(\frac{1}{\alpha} + \frac{v}{4HRT\sqrt{D_a k_{particle}}} \frac{1}{f(q)} \right)^{-1}$$

$$f(q) = coth(q) - \frac{1}{q}$$

$$q = r_p \sqrt{\frac{k_{particle}}{D_a}}$$

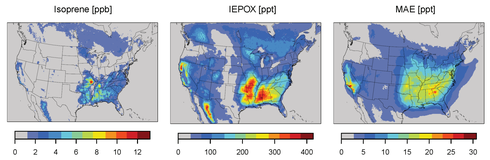
$$k_{particle} = \sum_{i=1}^{N} \sum_{j=1}^{M} k_{i,j} [nuc_i][acid_j]$$

γ	Uptake coefficient
α	Accomodation coefficient (0.02, McNeill et al. 2012 ES&T)
v	Mean molecular speed (gas)
H	Effective Henry's Law Coefficient (2.7x10^6 M atm^{-1} for IEPOX, 1.2x10^5 M atm^{-1} for MAE)
R	Gas constant
D_a	Diffusivity of epoxide in aerosol phase
$k_{particle}$	Pseudo first-order reaction rate constant for each epoxide
q	Diffusoreactive parameter
r_p	Particle radius
$k_{i,j}$	Third-order rate constant for reaction of nuc$_i$ and acid$_j$ in particle
nuc_i	Concentration of nucleophile i (water, sulfate, nitrate, or monomer)
$acid_j$	Concentration of acid j (H^+ or bisulfate)

[Hanson et al. 1994 JGR; Jacob 2000 AE]

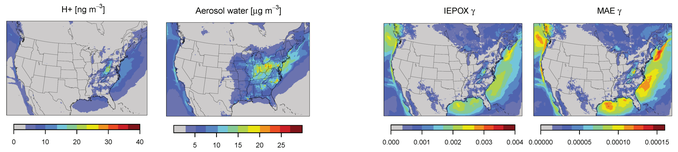
Model Predictions

Gas-phase chemistry provides precursors

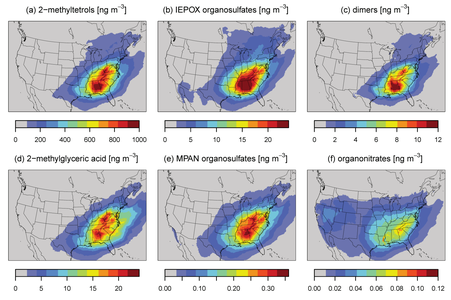


Particle-phase conditions dictate the efficiency of uptake

$k_{i,j}$ x [Acid] x [Nucleophile] $\xrightarrow{H_{itw}}$ Uptake Coefficients



Predicted Concentrations

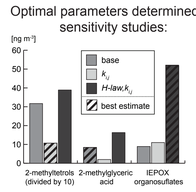


The relative abundance of the aerosol-phase species reflects the parent hydrocarbon concentrations and availability of nucleophiles.
- IEPOX-derived (low-NO_x) aerosol dominates over MPAN-derived (high-NO_x) aerosol due to efficient formation of IEPOX.
- Hydrolysis products (2-methyltetrols, 2-methylglyceric acid) are most abundant due to availability of aerosol water.

Model Evaluation

2-methyltetrol and 2-methylglyceric acid concentrations are better represented by the new pathways than semivolatile absorptive partitioning with laboratory based speciation.

Optimal parameters determined by sensitivity studies:



- Initial hydrolysis rate constant for IEPOX overestimated.
- Organosulfate formation underestimated.

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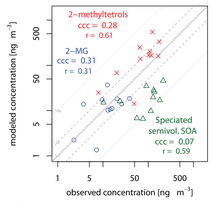
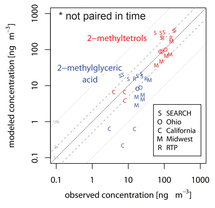
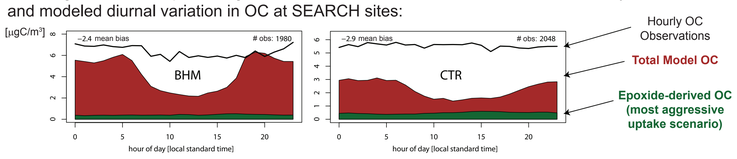


Contiguous United States



- 2-methyltetrols remain overestimated.
- 2-methylglyceric acid well represented with possible exception of CA.

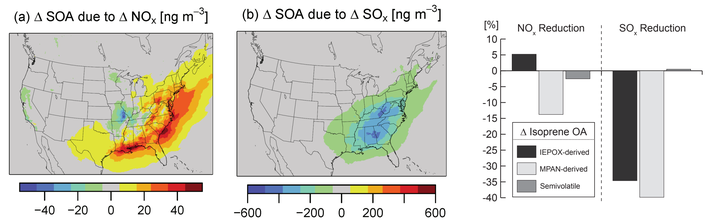
Challenges remain for predicting total OC in the southeast United States as shown by the observed and modeled diurnal variation in OC at SEARCH sites:



Response to Changes in Emissions

The effect of a 25% reduction in anthropogenic and wildfire NO_x and a 25% reduction in SO_x emissions on isoprene SOA was examined.

Change in Isoprene SOA due to a 25% Change in Emissions



- Decreasing NO_x emissions leads to a slight increase in isoprene SOA over most of the eastern US as a result of increased SOA from IEPOX.
- Decreasing SO_x emissions decreases both MPAN-derived and IEPOX-derived aerosol significantly as a result of a reduction in acidity leading to slower rates of particle-phase reaction.
- Traditional Odum 2-product semivolatile isoprene SOA is less sensitive to changes in emissions and generally responds in the opposite direction as the epoxide-derived aerosol.

Summary

- CMAQ has been updated to predict 2-methyltetrols, 2-methylglyceric acid, organosulfates, organonitrates, and dimers from IEPOX and MPAN.
- The new epoxide pathways better represent 2-methyltetrols and 2-methylglyceric acid than traditional Odum 2-product semivolatile SOA with laboratory based speciation.
- The new parameterization is sensitive to changes in SO_x emissions as a result of the dependence on acid-catalyzed particle-phase reactions for aerosol formation.

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