Using SEAC⁴RS observations to improve modeling of isoprene chemistry in GEOS-Chem

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SUMMARY

We evaluate model representation of isoprene sources and chemistry in the Southeast U.S. using SEAC⁴RS observations and a high-resolution version of the GEOS-Chem model with biogenic emissions from MEGAN v2.1.

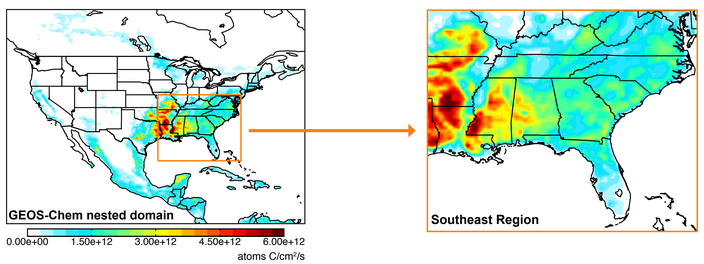
Campaign-averaged statistics for isoprene and its oxidation products show model high biases above 1 km, likely due to errors in boundary layer heights and mixing. Below 1 km, GEOS-Chem provides a reasonable simulation of several species, including in particular isoprene peroxides and HCHO. Isoprene shows a mean low bias but with significant variability.

Large model overestimates are seen for organic nitrates formed from isoprene oxidation under high-NO_x conditions. Ongoing work will identify the sources of these biases, with initial emphasis on organic nitrate sinks including photolysis, deposition, and loss to aerosols.

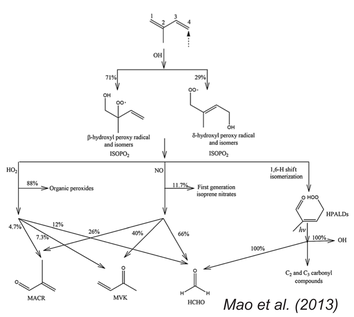
Over the low-NO_x Ozarks region, GEOS-Chem shows large positive biases in isoprene and isoprene peroxides. Although coincident with a temperature bias of up to +3K, a sensitivity simulation indicates that temperature alone cannot explain the model isoprene overestimates.

1. GEOS-Chem SEAC⁴RS simulation

The GEOS-Chem full chemistry simulation was run with GEOS-FP meteorology for August-September 2013. The model was run at high horizontal resolution (0.25°x0.3125°) over North America, nested within the global GEOS-Chem simulation, with boundary conditions from a 4°x5° run. Results shown here are preliminary output, revision RB. Anthropogenic emissions are from NEI 2008 and biomass burning emissions are from FINN. Biogenic emissions are from MEGAN v2.1. Mean biogenic isoprene emissions for the SEAC⁴RS period (1 Aug - 22 Sep 2014) are shown below for the full high-resolution domain (left), and for the Southeast U.S. (right), defined here by the orange box.



Isoprene oxidation chemistry is based on Mao et al. (2013). The first steps of the oxidation process are shown in the figure to the right. The mechanism also includes explicit treatment of second generation nitrates, as well as nighttime oxidation of isoprene by nitrate radicals. Isoprene nitrates are subject to removal via photolysis, deposition, and oxidation by OH, with lifetimes of hours to days.



Mao et al. (2013)

Acknowledgments:
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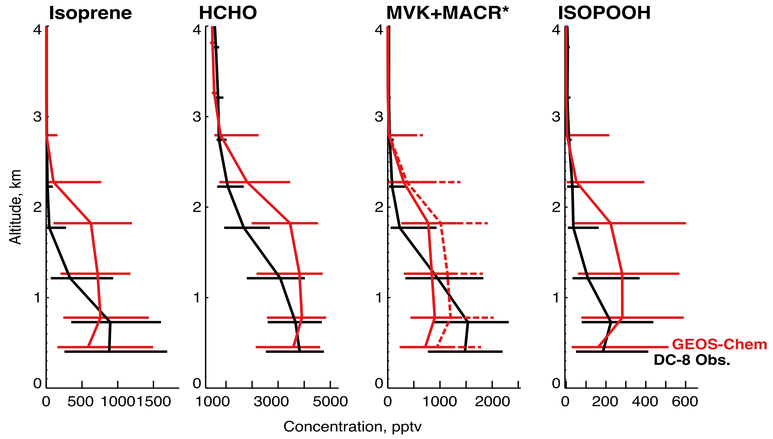
References:
Mao, J., F. Paulot, D.J. Jacob, R.C. Cohen, J.D. Crounse, P.O. Wennberg, C.A. Keller, R.C. Hudman, M.P. Barkley, and L.W. Horowitz. (2013), Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry, J. Geophys. Res., 118, doi:10.1002/jgrd.50817.

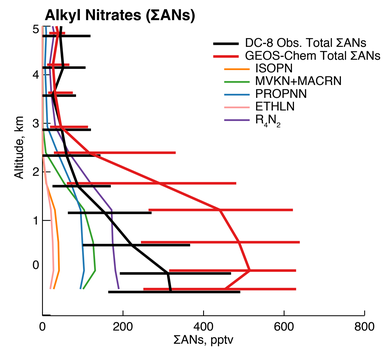
2. Isoprene and its oxidation products in the Southeast U.S.



Data: Wisthaler, Hanisco, Wennberg (PIs)

The figure above compares median profiles from GEOS-Chem sampled along the flight track to DC-8 observations over the Southeast U.S. for isoprene, formaldehyde (HCHO), methyl vinyl ketone (MVK) + methacrolein (MACR) and isoprene peroxides (ISOPOOH). For MVK+MACR, the dotted line shows the model concentrations of MVK+MACR+ISOPOOH to bracket the uncertainty in the measurement.

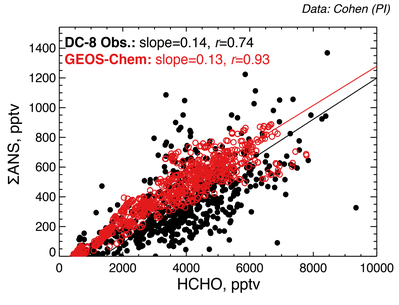
GEOS-Chem provides a reasonable estimate of isoprene and its standard oxidation products in the boundary layer. There is on average a small bias in surface-level isoprene, although there is large variability in the structure of the bias. Model overestimates above the boundary layer likely reflect problems with boundary layer height and mixing driven by the underlying meteorological fields.



Data: Cohen (PI)

Alkyl nitrates (ΣANs, left) are significantly overestimated in GEOS-Chem at altitudes <3 km. The lumped alkyl nitrate $\mathbf{R_4N_2}$ **dominates the simulated ΣANs budget.** Approximately 60% of simulated R_4N_2 comes from nighttime isoprene oxidation.

The ΣANs overestimate is driven by second generation oxidation products; first generation isoprene nitrates (ISOPN) are unbiased in the lowest 1 km. Propanone nitrate (**PROPNN**), responsible for on average 20% of modeled ΣANs in surface air, is **a factor of 5 too high.**



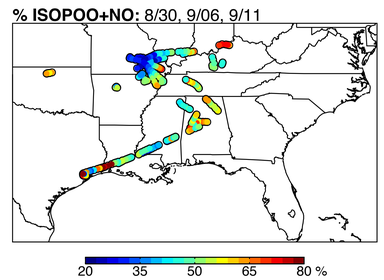
Data: Cohen, Hanisco (PIs)

There is a **strong observed correlation between HCHO and ΣANs**. The slope of the relationship (0.14) is slightly lower than during ICARTT (0.17, Mao et al., 2013) and SENEX (0.25, Mao, pers. comm.)

Despite model biases in the ΣANs simulation, **the HCHO-ΣANs relationship is well represented in GEOS-Chem**, with a modeled slope of 0.13.

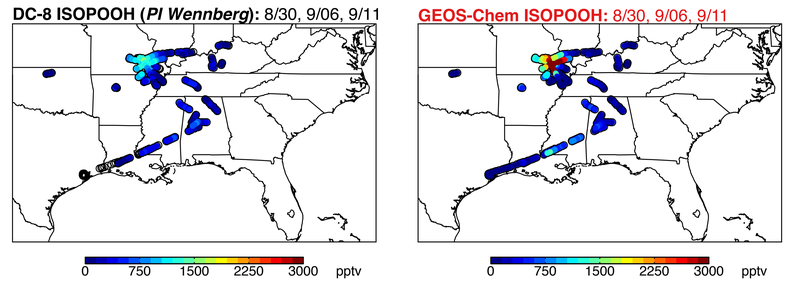
3. Large model biases in the low-NO_x Ozarks region

High- vs. low-NO_x regimes can be distinguished in the GEOS-Chem simulation based on model chemistry. The map below shows the simulated percentage of isoprene peroxy radicals (ISOPOO) reacting with NO along the DC-8 tracks for altitudes < 1 km during flights on 8/30, 9/06, and 9/11, 2013.

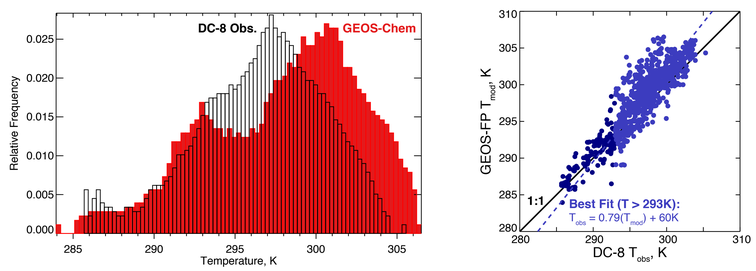


High values (e.g., near Houston) imply most ISOPOO is reacting with NO, indicating high-NO_x environments, whereas low values indicate low-NO_x environments.

The lowest values during the campaign were observed in the boundary layer over the Ozarks during these three flights, indicating **very low NO_x conditions**. In this region GEOS-Chem displays **significant ISOPOOH overestimates**, shown below.



The ISOPOOH bias over the Ozarks is coincident with a **high bias in isoprene of ~3 ppbv and in boundary layer air temperature of ~3K**. The temperature bias is pervasive throughout the Southeast, with GEOS-FP temperatures up to 9K too high, and may help explain the isoprene and ISOPOOH biases in the Ozarks. Distributions of observed and modeled boundary layer air temperature in the Southeast region are shown below.



We use the best fit line between DC-8 and GEOS-FP 0-1 km temperatures (for T_{obs} > 293 K) to correct surface air temperature for use in computing MEGAN isoprene emissions. We find that this correction decreases isoprene over the Ozarks by <1 ppbv and ISOPOOH by <200 pptv, but is **insufficient to entirely correct the Ozarks biases**.

Comparisons between the SEAC⁴RS observations and the nested GEOS-Chem simulation highlight problems with current model representation of isoprene sources and chemistry in both low- and high-NO_x environments. Isoprene and ISOPOOH are overestimated in the low-NO_x Ozarks region, while isoprene-derived nitrates are overestimated across the Southeast U.S. Ongoing work will focus on identifying the causes of these discrepancies.