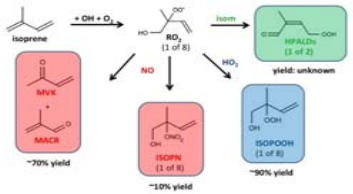
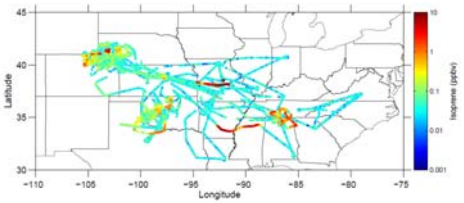
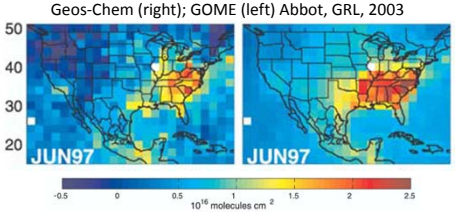
Isoprene Photo-oxidation During DC3

John Crounse, Jason St. Clair, Alex Teng, Paul Wennberg,
with contributions from Bill Brune, Ron Cohen, Tom Ryerson, Armin Wisthaler





Geos-Chem (right); GOME (left) Abbot, GRL, 2003

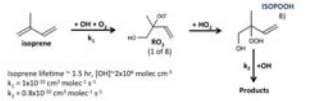


DC3 offered the first opportunity to systematically observe the suite of oxidation products of isoprene made possible by Caltech's chemical ionization mass spectrometer. These data reveal that 1) even in this heavily NOx impacted region, a large fraction of isoprene oxidation proceeds via NO-independent chemistry; 2) that the formation of alkyl nitrates during oxidation of isoprene is a significant mechanism for sequestration (ouch!) of NOx and 3) newly discovered oxidation products are a substantial fraction of the carbon contributed to the atmosphere by isoprene (hydroperoxides, C5 hydroperoxy aldehydes, and epoxides).

The fate of isoprene hydroxy peroxy radicals

There is significant controversy surrounding the fate the first generation hydroxyperoxy radicals formed from isoprene oxidation by OH. Some modeling efforts have suggested that unimolecular isomerization may dominate the chemistry of isoprene with profound implications for oxidant levels and ozone formation.

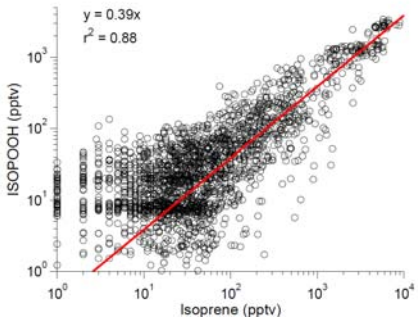
Isoprene peroxy + HO_2



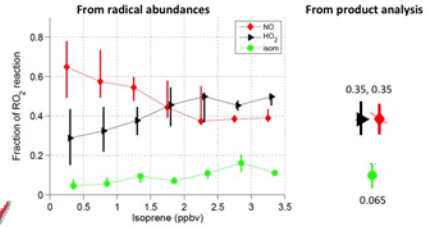
Steady State Approximation: $P_{ISOPOOH} = L_{ISOPOOH}$

$k_1[isoprene][OH]F_{HO2}Y_{ISOPOOH} = k_2[ISOPOOH][OH]$

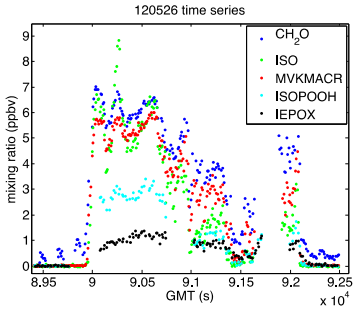
$[ISOPOOH]/[isoprene] = k_1/k_2F_{HO2}Y_{ISOPOOH}=1.1F_{HO2}$



We use similar correlation analysis (e.g. isoprene nitrates vs isoprene hydroperoxides and HPALD vs isoprene hydroperoxides to estimate the fraction of the peroxy radicals reacting with NO and via isomerization.

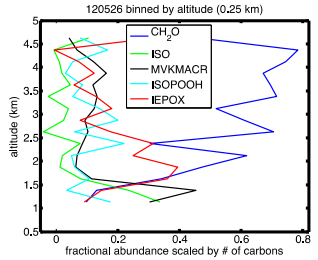


Formaldehyde column and inference of isoprene emissions

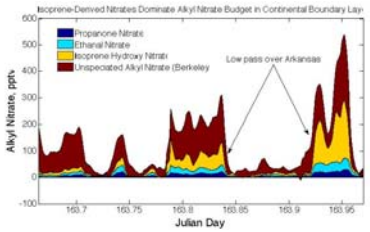


Formaldehyde column observations have been inverted to estimate emissions of isoprene. The relationship between the two is rather straight forward when the peroxy radical chemistry is dominated by NO: Each isoprene oxidized yields prompt formation of (1-alpha)*isoprene formaldehyde molecules where alpha is the sum of the nitrate and hydroxyaldehyde yields (~30%).

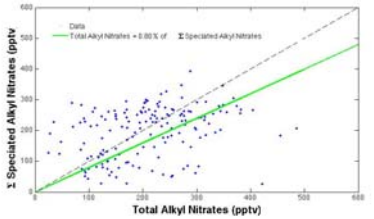
However, only ~1/2 of the peroxy radicals react with NO in the DC3 region. Thus, estimation of the isoprene emissions from formaldehyde requires accurate estimate of the yield (and timescale of the yield) of formaldehyde from the non-NO channels. DC3 offers the first systematic observations of the concentrations of these major products (hydroxyhydroperoxides, epoxides, and hydroperoxyaldehydes).



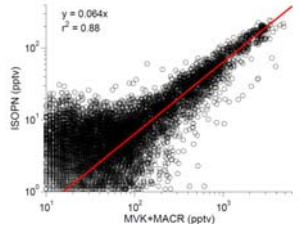
Alkyl Nitrate Budget in Biogenically-Impacted Regions



Isoprene-derived alkyl nitrates comprise a large fraction of the total alkyl nitrates in the boundary layer across the DC3 region. Here the three largest contributors are plotted along with the observations from Berkeley of the total of all alkyl nitrates.



Adding in other more minor contributors from 2nd and 3rd generation isoprene alkyl nitrates nearly closes the alkyl nitrate budget of the boundary layer.



Isoprene hydroxynitrates and the sum of MVK and MACR are highly correlated. The observed slope, 6.4%, is however nearly twice that simulated by Xie et al. suggesting either the source is larger or the lifetime longer than simulated.