Box modeling in support of SEAC^{4}RS: variations in the dependence of CH_2O on isoprene, MVK+MACR and NO_x

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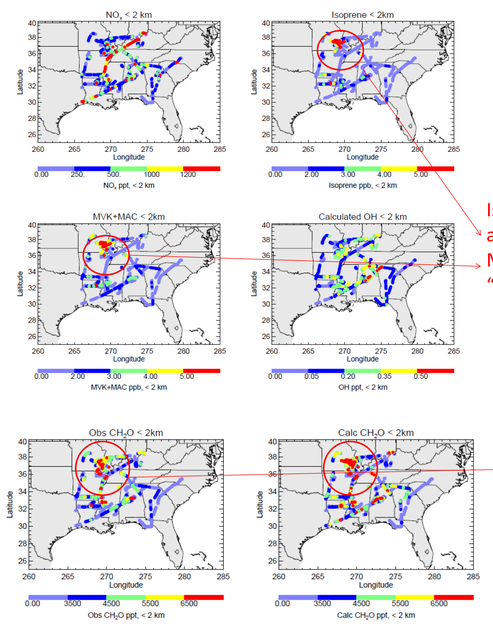
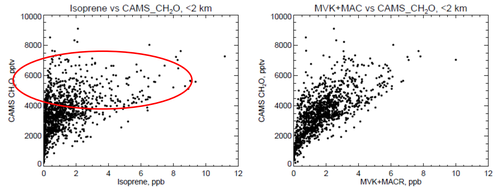
A look at SE US Isoprene chemistry…



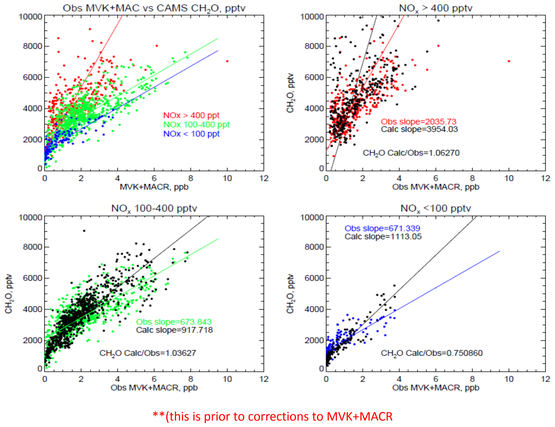
Isoprene and MVK+MACR "hot spot"

"Hot spot" also seen in observed and calculated CH_2O, but relationship is messy



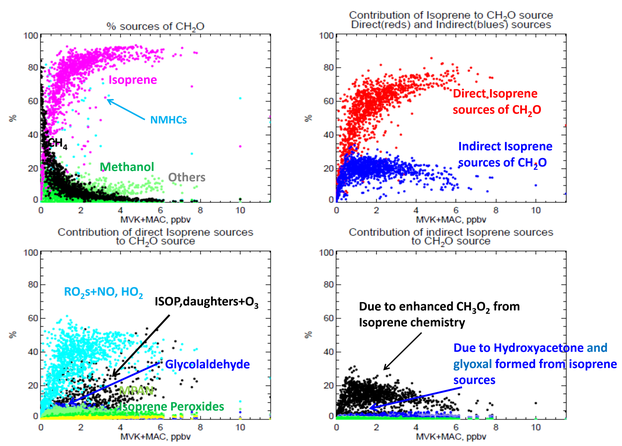
CH_2O > 5 ppbv seen for all concentrations of Isoprene. Somewhat better relationship for the longer-lived MVK+MACR

CH_2O/MVK+MACR relationship as a function of NO_x: Observed and Diagnosed (Observations in colors, Model calculations in black)



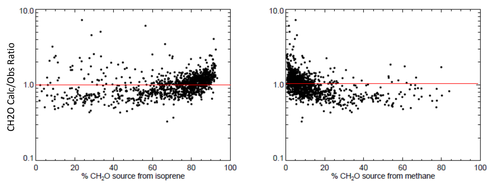
**(this is prior to corrections to MVK+MACR as announced at science team meeting)

CH_2O BUDGET FOR <2 km SE U.S. (shown as function of MVK+MAC):



CH_2O Budget calculated using an assumed steady state source allocation method. All sources traced back to: CH_4, Isoprene, Alcohols, Ketones, NMHCs, Mixed source. Additional sources are assigned to the following categories (Acetic Acid, CH_3OOH, MCO_3/PAN, Acetaldehyde) if the model was constrained to observation (i.e., if transported precursors impact formation). If model-calculated, then these sources are reassigned according to their own source allocations:

CH_2O Calc/Obs ratio as function of % source from Isoprene and methane

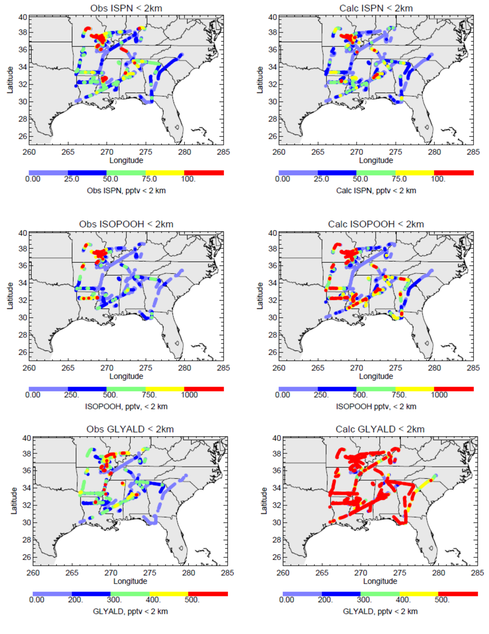


CH_2O predictions within 10% for NO_x> 100 ppt. CH_2O underpredicted at lower NO_x. Underpredictions correlate with decline in percentage contribution from isoprene. Background photochemical source of CH_2O slightly underpredicted??

Selected other comparisons

Slopes indicate NET production of CH_2O per molecule of MVK+MACR of
~2 for higher NO_x (>400 ppt)
~4 calculated
~.7 for lower NO_x.
~.7-1.1 calculated

For isoprene (plots not shown), slopes indicate NET production of CH_2O per molecule of isoprene of
2.6 for high NO_x (>400 pptv)
5 calculated
.4-.6 for lower NO_x
.7-1.4 calculated



NASA Langley Time-dependent, observationally constrained photochemical box model

Diurnal steady state approach using a detailed HO_x-NO_x-CH_4-NMHC mechanism
(model is integrated to find converging diurnal profiles of predicted species converge to within a given tolerance)
Reactions and rates are taken from recommendations in *JPL (2011)* and *IUPAC (2006)*
Diurnal variation of clear-sky photolysis rates is calculated using TUV (DISORT 8 streams) *(Madronich and Flocke, 1998)*
Clear-sky photolysis rates are then normalized to give observed value of photolysis rate at time of measurement.

ISOPRENE mechanism: Updated based on MIM2 *(Taraborelli et al., 2009),*
and isoprene nitrate/peroxide/epoxide chemistry from *Paulot et al. 2009a* and *2009b*
Isomerization of isoprene peroxy radicals *(Crounse et al. 2011)* are estimated as in GEOS-Chem chemical mechanism

For base calculations, model is run FULLY CONSTRAINED, using observations of location, physical parameters,
And the standard constraints for NO, O_3, CO, H_2O, photolysis, NMHCs, and Methanol.

ADDITIONAL CONSTRAINTS are included for MVK+MACR, PAN, HNO_3. (*Note, Isoprene is included in order to properly diagnose OH concentrations and additional isoprene oxidation products, but MVK+MACR is held to observations.*)
During computation, Isoprene set to zero at night, and constraint of MVK+MACR to observations is removed at night.

Ethanol assumed to = 3% Methanol (median from INTEX-NA)
Calculated radicals include OH, HO_2, RO_2, Glyoxal, Methylglyoxal, etc…
Calculated radicals for comparison to observations include: CH_2O, HNO_4, CH3OOH, ISOPOOH, ISOPN, Glycolaldehyde, Hydroxyacetone, etc…

Data used here are from the DC8 Preliminary RN version of the merge (April 3)

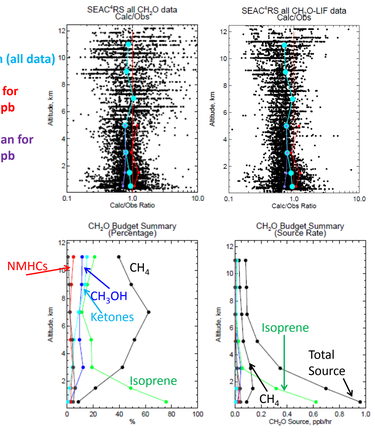
Full SEAC4RS data set:
Generally good representation of CH_2O but slightly underpredicted.
Median Calc/Obs for CH_2O-CAMS=0.88 (.99 when MVK+MAC > 100 ppt, n=2325)
Median Calc/Obs for CH_2O-LIF=0.70 (.98 when MVK+MAC > 100 ppt, n=2369)

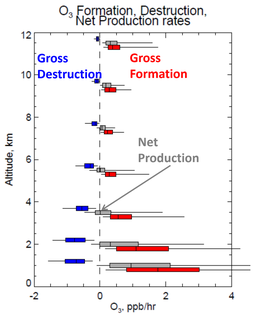
In boundary layer, CH_2O source strength is a median of ~1 ppb/hour

Blue line: median (all data)

Red line: median for MVK_MAC>0.5 ppb

Purple line: median for MVK_MAC<0.1 ppb





Unconstrained Mode:

Good representation of MVK+MAC
**(this is prior to corrections to MVK+MACR as announced at science team meeting)

Overpredictions for PAN, HNO_3