MIT ATMOSPHERIC CHEMISTRY

Constraining Hg oxidation and lifetime

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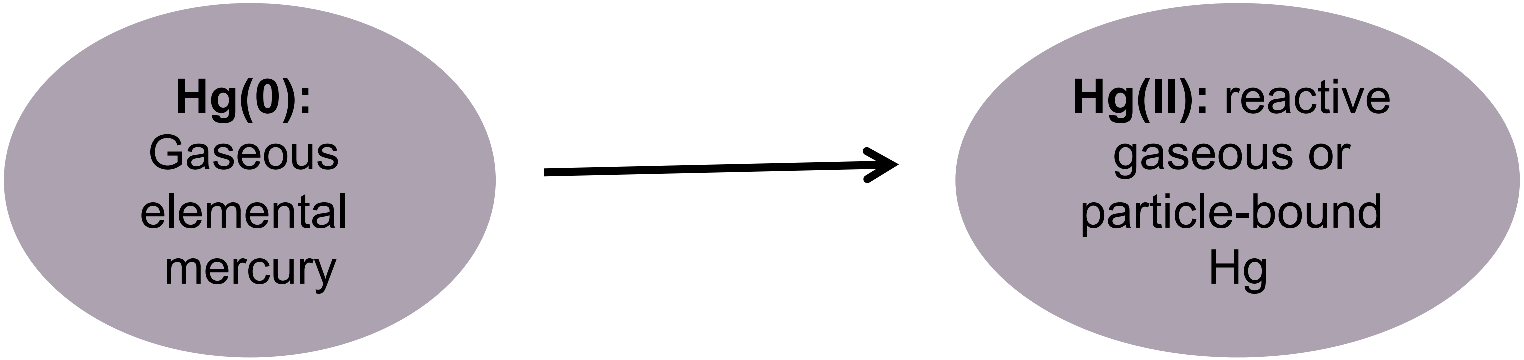
Mercury Oxidation Puzzle



What oxidizes mercury in the atmosphere? Probably involves Br, in a two step oxidation with intermediate HgBr. HgBr then reacts with (OH, Br, others (I?)) to get Hg(II).

Many uncertainties in measured rate constants, as well as Hg(II) measurements with traditional methods (Tekran)

Thus, a challenge to constrain oxidation processes with models like GEOS-Chem.

Mercury *Oxidation Ratio*

- Ratios of hydrocarbons that react with different lifetimes have been used to measure effective oxidation age of air
- For mercury, in background air, Hg(II) is purely an oxidation product.
- Consider a dry air parcel in the free troposphere.

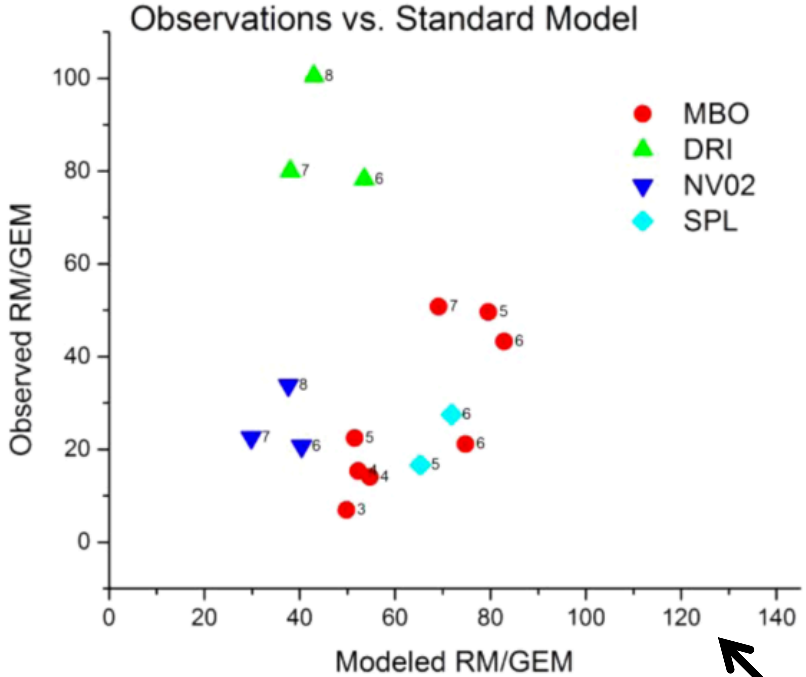
$$\ln(Hg_t^0) = \ln(Hg_0^0) - \int_{t=e}^{m} k_{eff}[oxidant]d\,t$$

$$Hg_0^0 = Hg_t^0 + Hg_t^{II}$$ ← In free trop with no loss

$$t_a\langle[oxidant]\rangle = \int_{t=e}^{m}[oxidant]d\,t = -\frac{1}{k_{eff}}\ln\left(\frac{Hg_t^0}{Hg_0^0}\right)$$

$$= -\frac{1}{k_{eff}}\ln\left(\frac{Hg_t^0}{Hg_t^0 + Hg_t^{II}}\right)$$

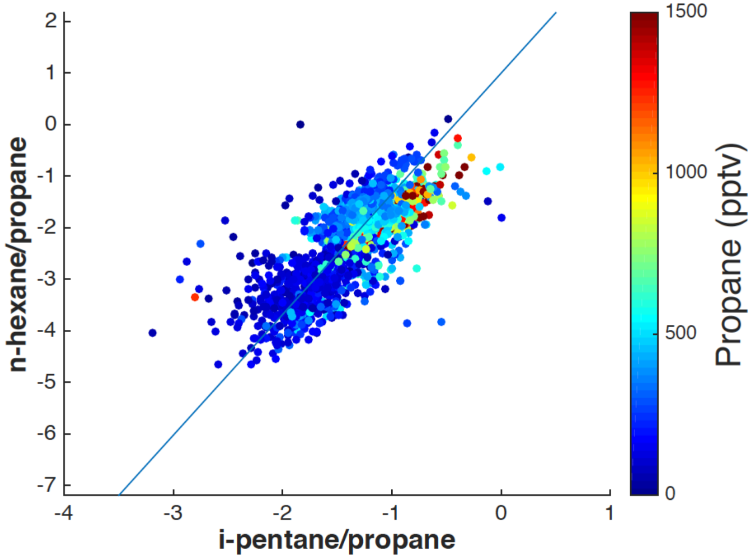
Hypothesis: Hg oxidation ratio can be used to 1) better understand chemistry, and 2) maybe eventually as a useful time clock?

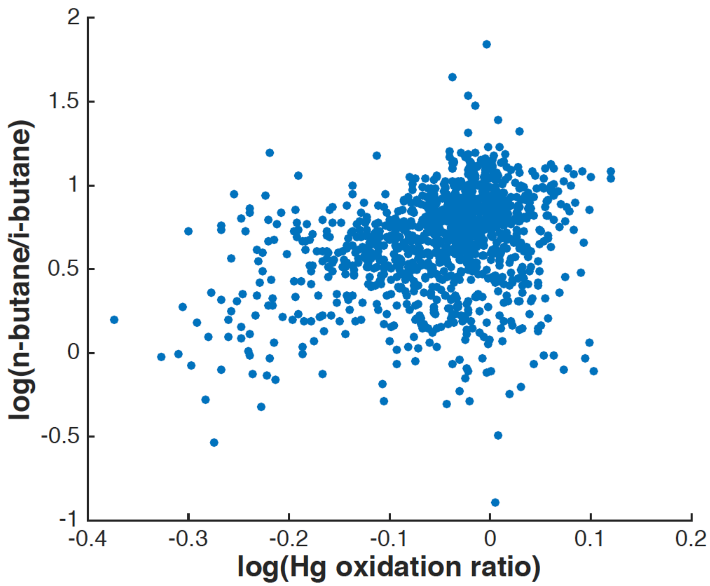


Weiss-Penzias et al., ACP, 2015

Testing oxidation hypotheses (NOMADSS)

If [oxidant] is OH, lifetime associated with the mercury oxidation ratio should correlate with other OH-based lifetimes….





Line: kinetic slope (m=2.3)

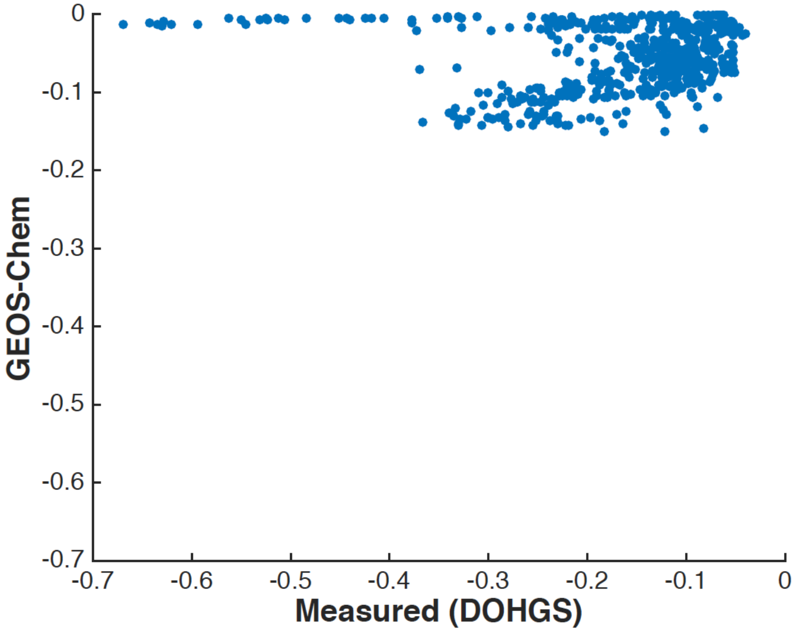
NOMADSS hydrocarbon data do show different degrees of OH oxidation (even at low time resolution mercury timestep). Plot follows Parrish et al. (2007)

Hg oxidation ratios have some correlation with "halogen" [Cl] clocks (r=0.49) …better than "OH" clocks…but high uncertainty

What about Br? Possibility of future analysis with alkenes?

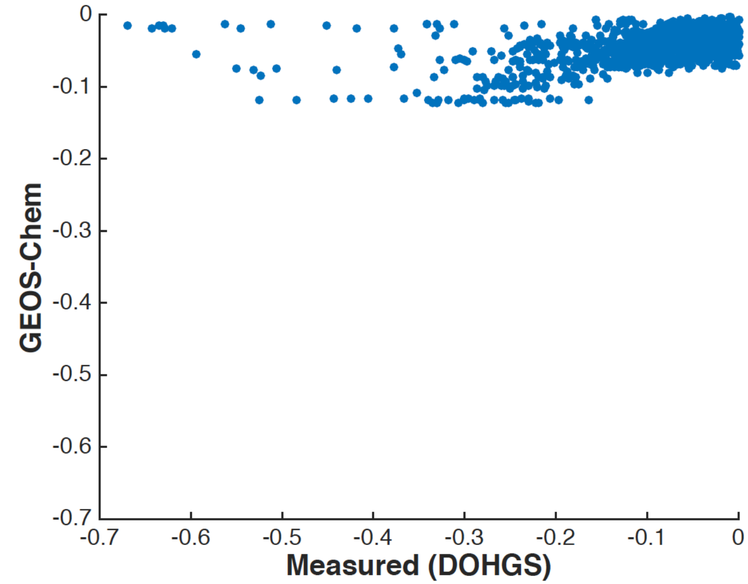
What about in GEOS-Chem?

Log (Hg oxidation ratio)



GEOS-Chem Br simulation shows little skill at reproducing Hg oxidation ratio (process errors?)

Log (Hg oxidation ratio)



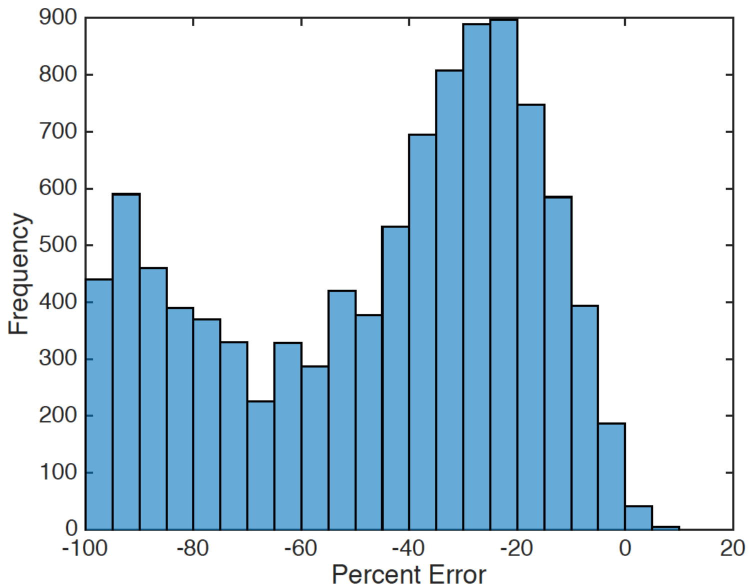
GEOS-Chem with OH chemistry doesn't do much better…

Neither simulation has any relationship with ethane/propane ratio (??).

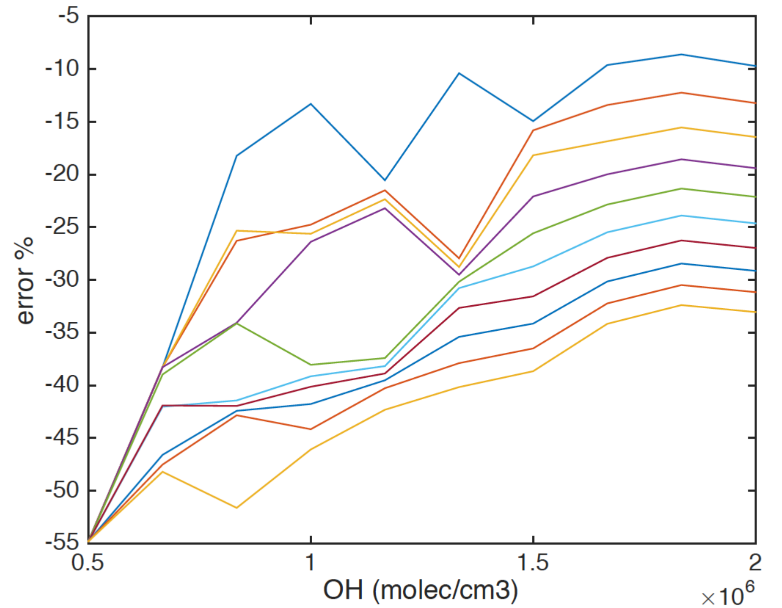
Oxidation rate analysis with GEOS-Chem

GEOS-Chem calculates an effective first-order rate constant based on the rates of the equations at right (several choices), plus concentrations of Br, OH. This is an approximation.

$Hg + Br + M \rightarrow HgBr + M$	k1
$HgBr \rightarrow Hg(0) + Br$	k(-1)
$HgBr + OH, Br \rightarrow Hg(II)$	k2



Overall error vs. ode solver for lifetime given different OH, Br, temperature, pressure (low bias)



Error correlates with e.g. [OH]

Different sensitivity to k2

Warning: *Previous assumptions may not be appropriate for new analyses!*

Acknowledgments

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NSF Atmospheric chemistry program

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