Use of a global model to understand speciated atmospheric mercury observations at five high-elevation sites

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Objectives

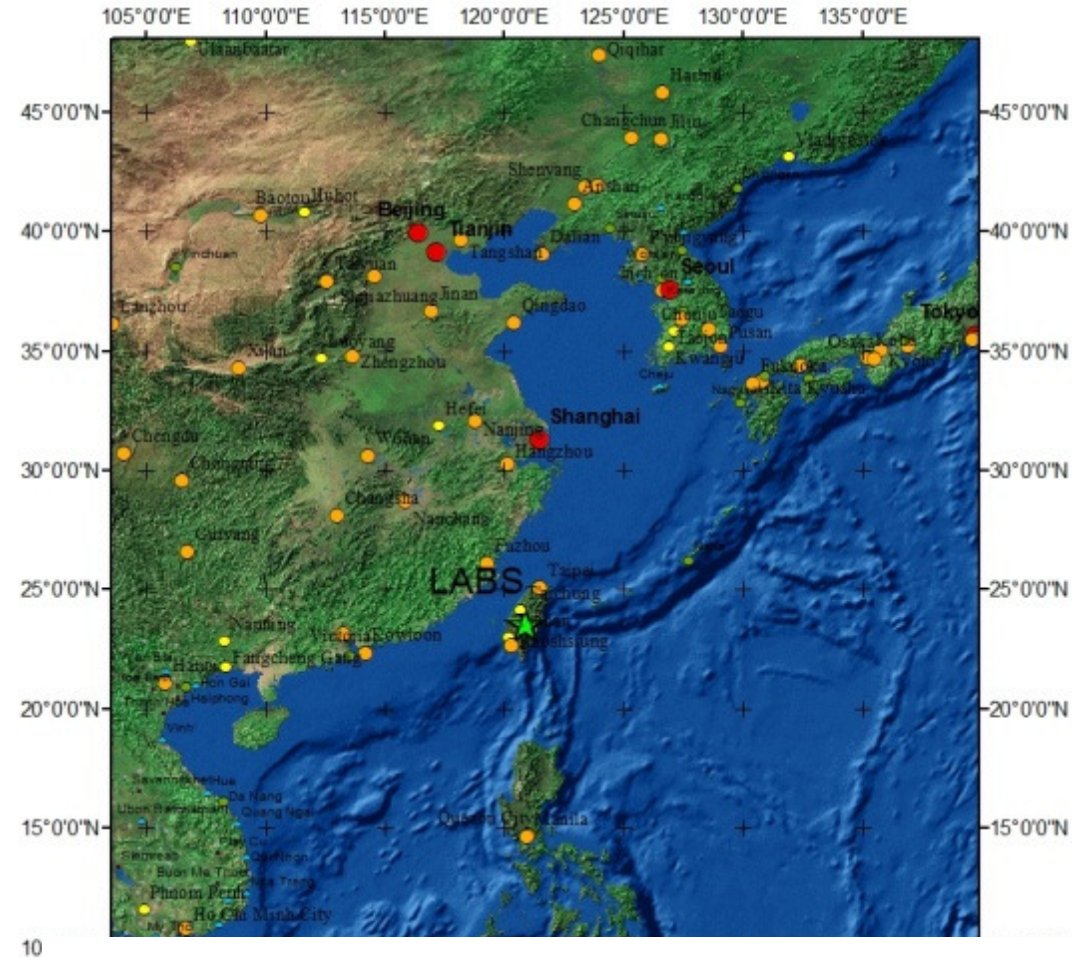
- Compare available Tekran® instrument measurements of GEM/GOM/PBM along with ozone and meteorology from five surface sites that have reported interception of dry free troposphere air, with simulated speciated Hg concentrations from the GEOS-Chem Hg coupled atmosphere-ocean-land model in order to examine spatio-temporal trends and interspecies correlations both in the observations and the model.
  - Look at observations across sites for common features
  - Use the model to constrain the processes important for GOM+PBM=RM.
  - Vary the model chemistry to probe for clues on likely oxidation mechanisms for GEM.

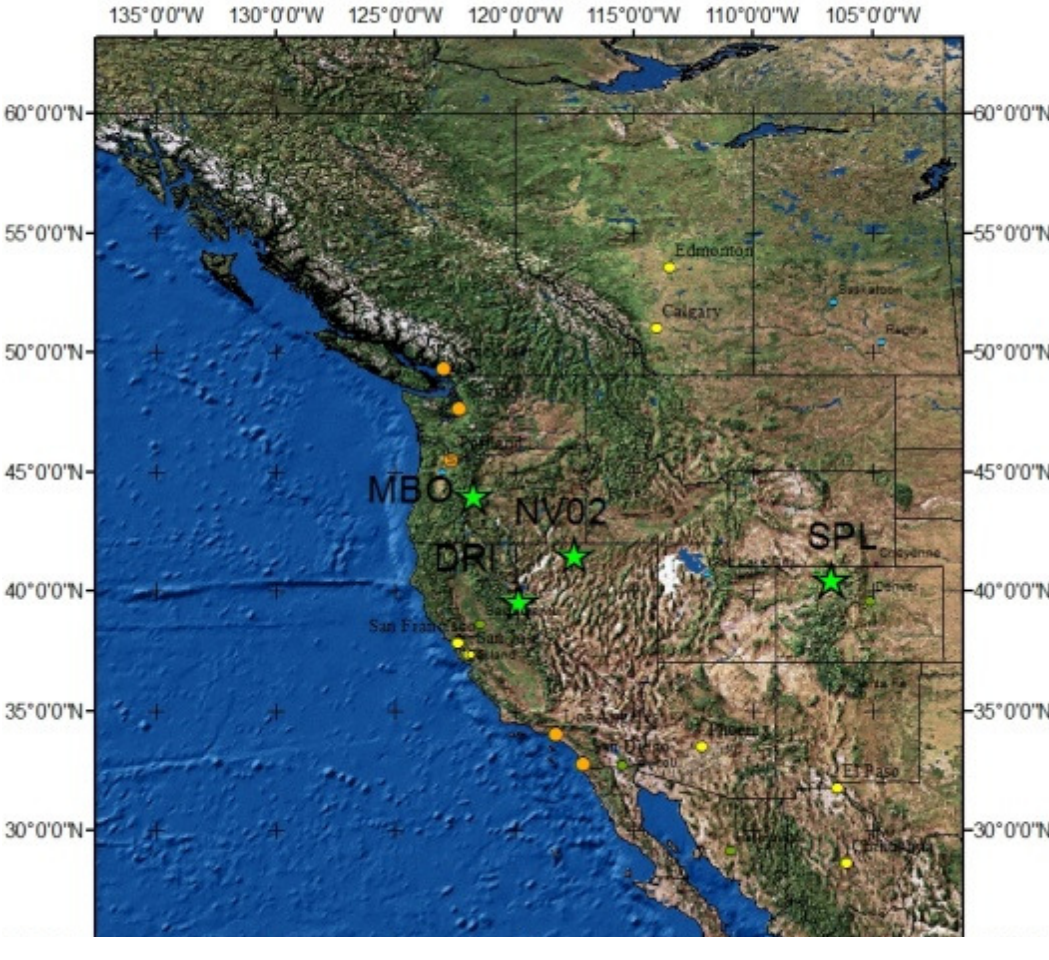
Issues with Observations and Model

- GOM and PBM from Tekran® 1130/1135/2537 system may be biased low due to poor uptake efficiency and interferences (Gustin and Jaffe, 2010; Gustin et al., 2013; Ambrose et al., 2013; Huang et al., 2013; Kos et al., 2013; Huang et al., 2014; Jaffe et al. 2014).
- However, Tekran® 1130/1135/2537 system may perform more accurately in extreme low humidity environments (Moore et al., 2013; 2014).
- GEOS-Chem has been extensively evaluated against MDN data (Amos et al., 2012; Holmes et al., 2010; Selin and Jacob, 2008) as well as surface land-based sites, ship cruises, and plane flight data of GEM and seawater concentrations (Selin et al., 2008; Holmes et al. 2010; Soerensen et al., 2010; Amos et al., 2012).
- However, oxidation chemistry in model may not represent reality
  - e. g. Modeled GEM > observed GEM in UT/LS (ARCTAS) (Holmes et al., 2010)

Approach

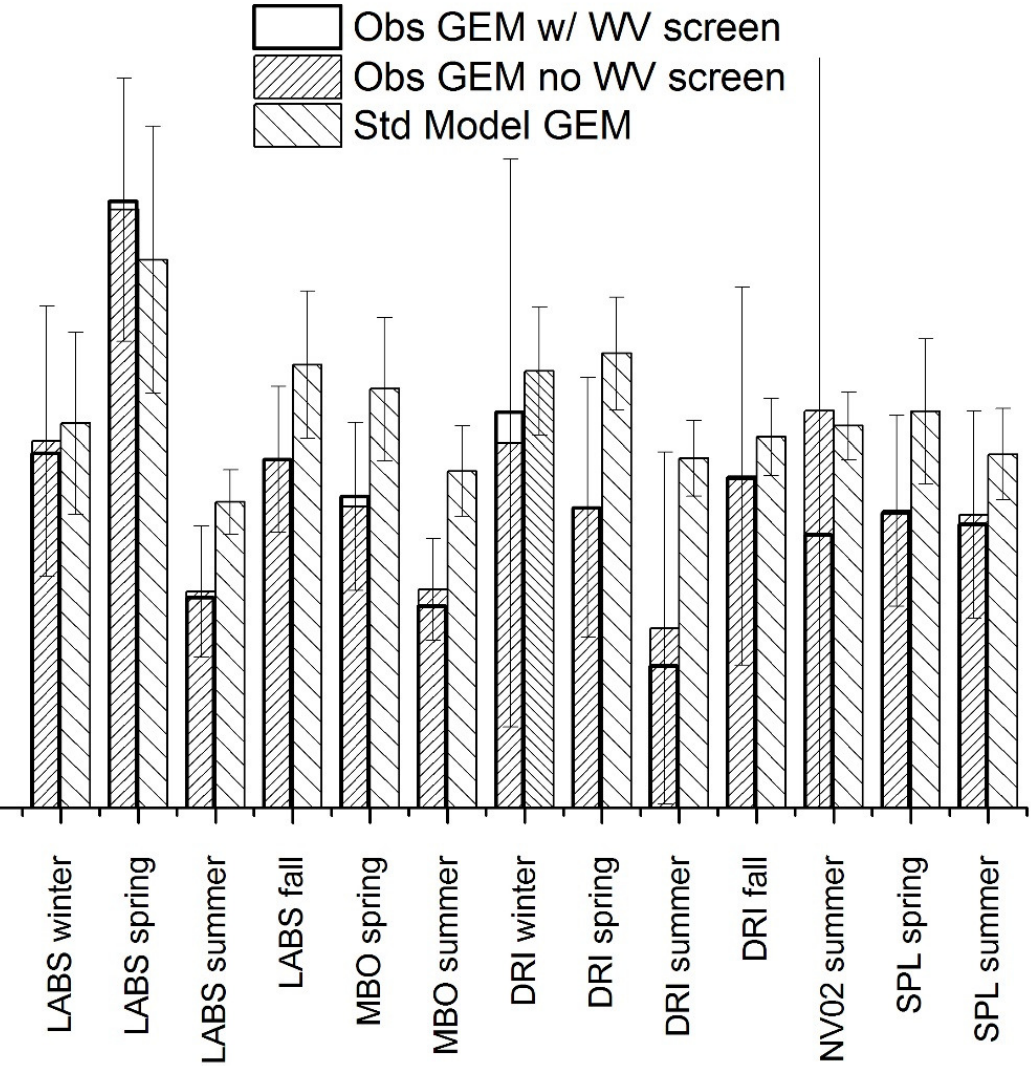
- Filter observations on water vapor mixing ratio (eliminate when WV > 75th percentile). Create “FT” data set for comparison with model.
- Examine interspecies correlations (e. g. RM vs. GEM) within the observations and compare with interspecies correlations in the model.
- Absolute observation-model comparison less important.
- Determine if similar or different trends are evident in both observations and model.





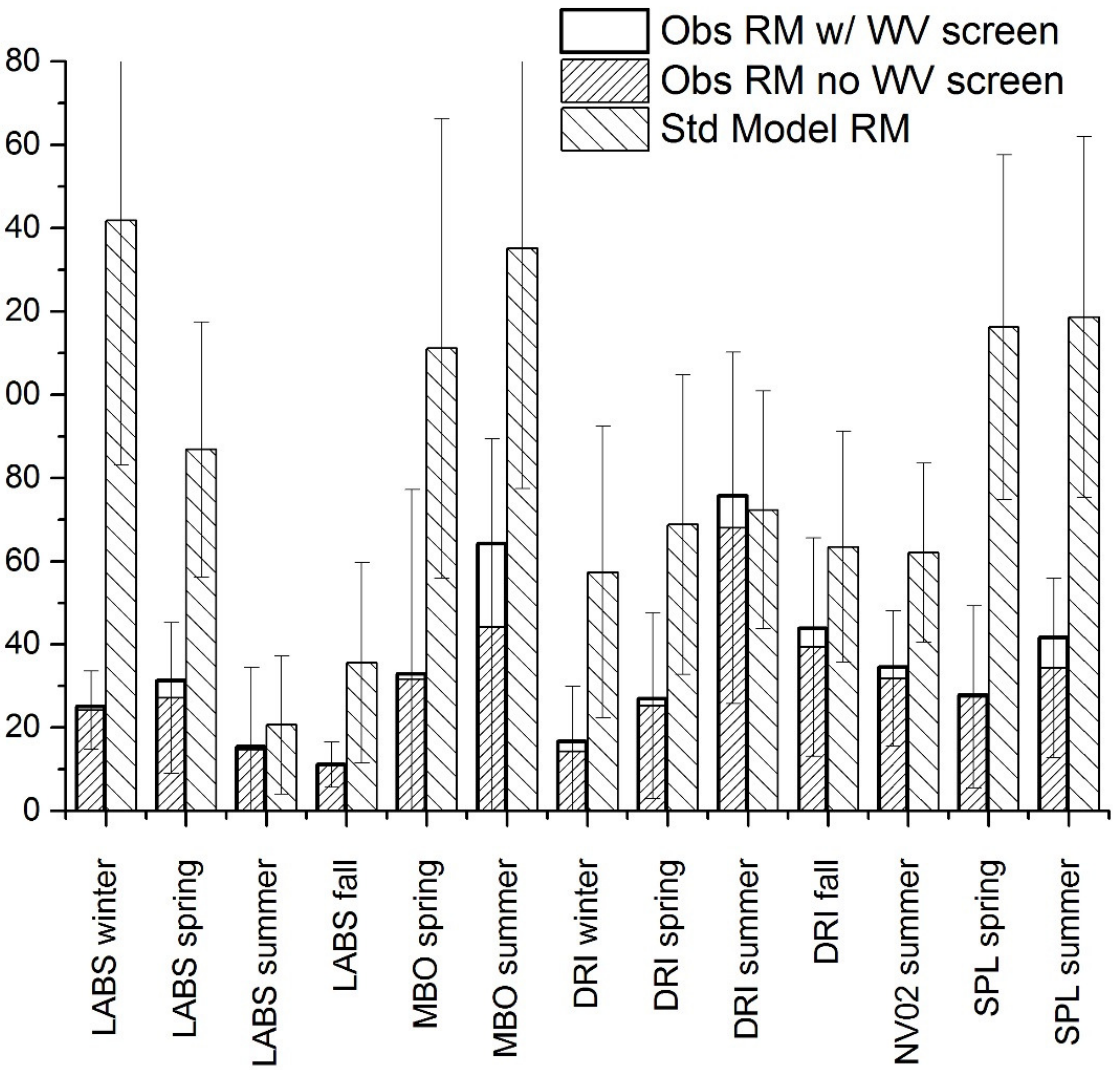
Locations of 5 sites used for this study

Mean GEM by Site and Season



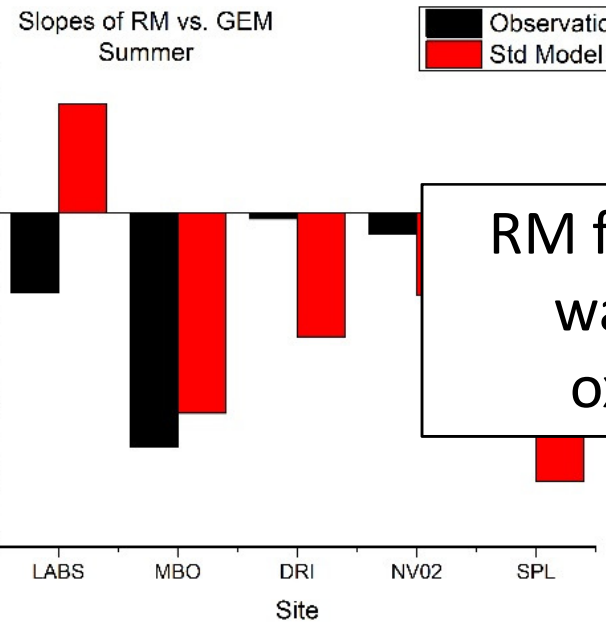
- Observations
  - Highest GEM at LABS during spring.
  - Lowest GEM at DRI during summer.
  - Summer GEM < spring GEM.
  - FT GEM < all GEM (esp. NV02).
- Model
  - Highest GEM at LABS during spring.
  - Summer GEM < spring GEM (matched 11% difference in observations at MBO
  - Did not reproduce low GEM values at D (+32% compared to observations).

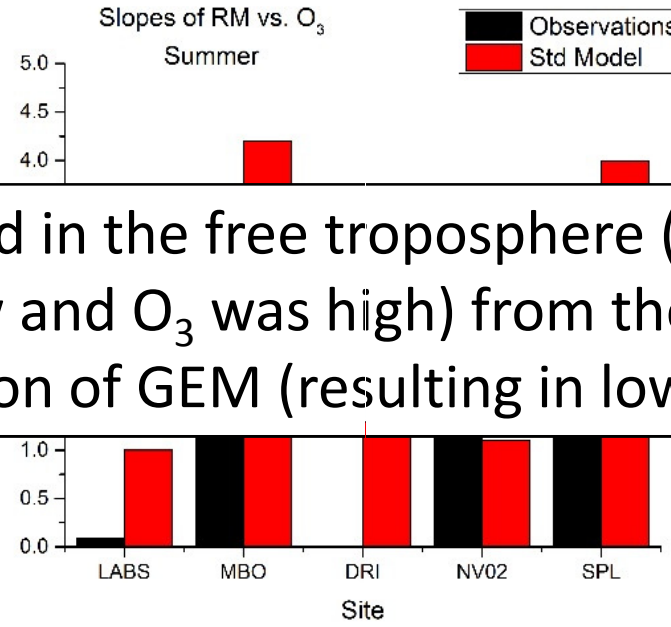
Mean RM by Site and Season

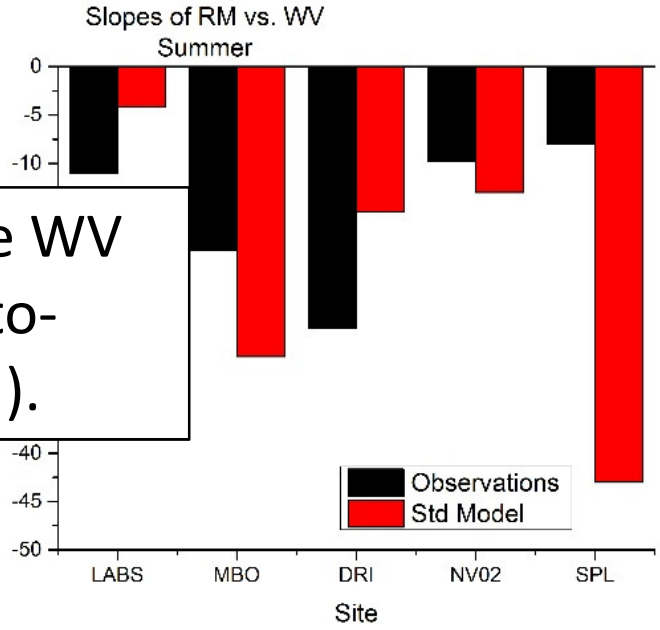


- Observations
  - RM varied by 7x between sites.
  - RM highest in summer, except at LABS.
  - FT RM > all RM (esp. summer MBO, DR SPL).
- Model
  - RM varied by 7x between sites.
  - Spring RM ≈ summer RM at MBO and SPL.
  - Modeled RM > observed RM by 2.5x overall.

Slopes of Interspecies Correlations - Summer







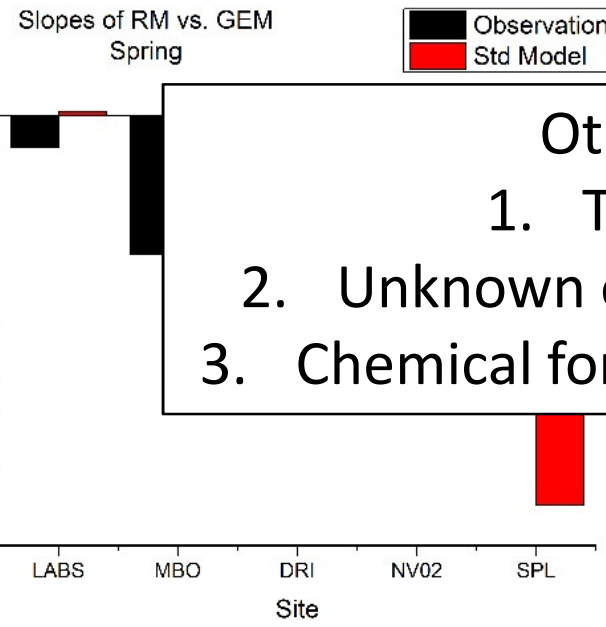
RM formed in the free troposphere (where WV was low and O_3 was high) from the photo-oxidation of GEM (resulting in low GEM).

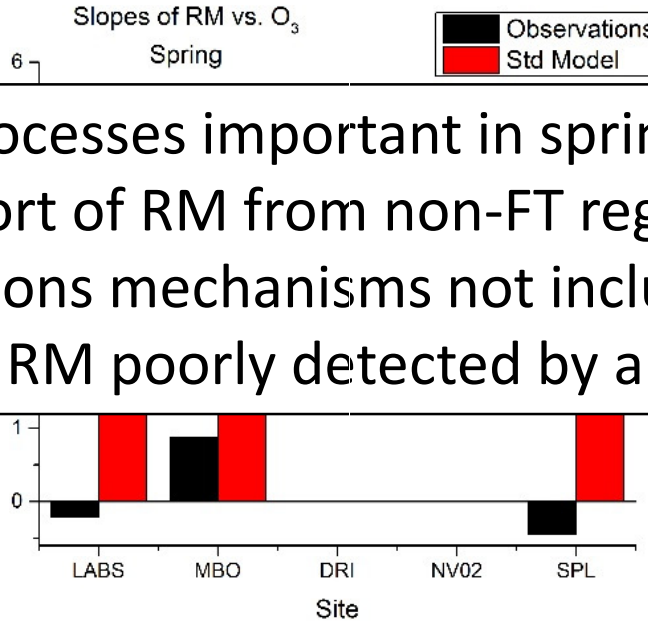
RM:GEM relationship is negative in Obs. and Model (except LABS)

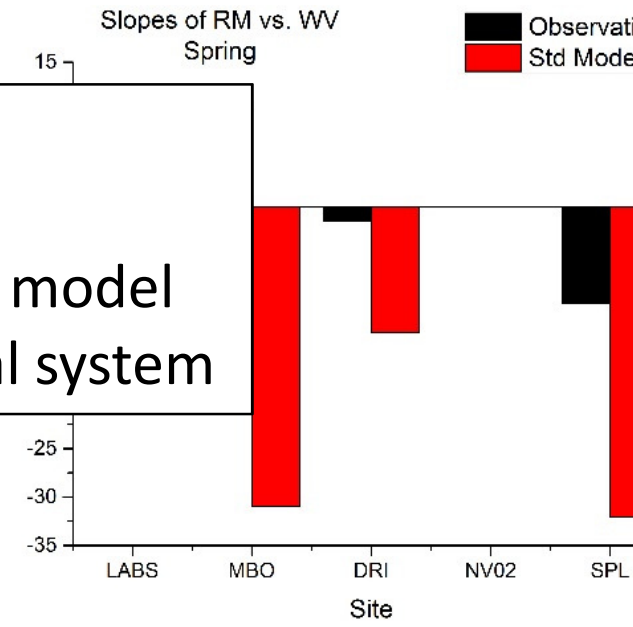
RM:O_3 relationship is positive in Obs. and Model (weak at LABS and DRI)

RM:WV relationship is negative in Obs. and Model

Slopes of Interspecies Correlations - Spring







Other processes important in spring:

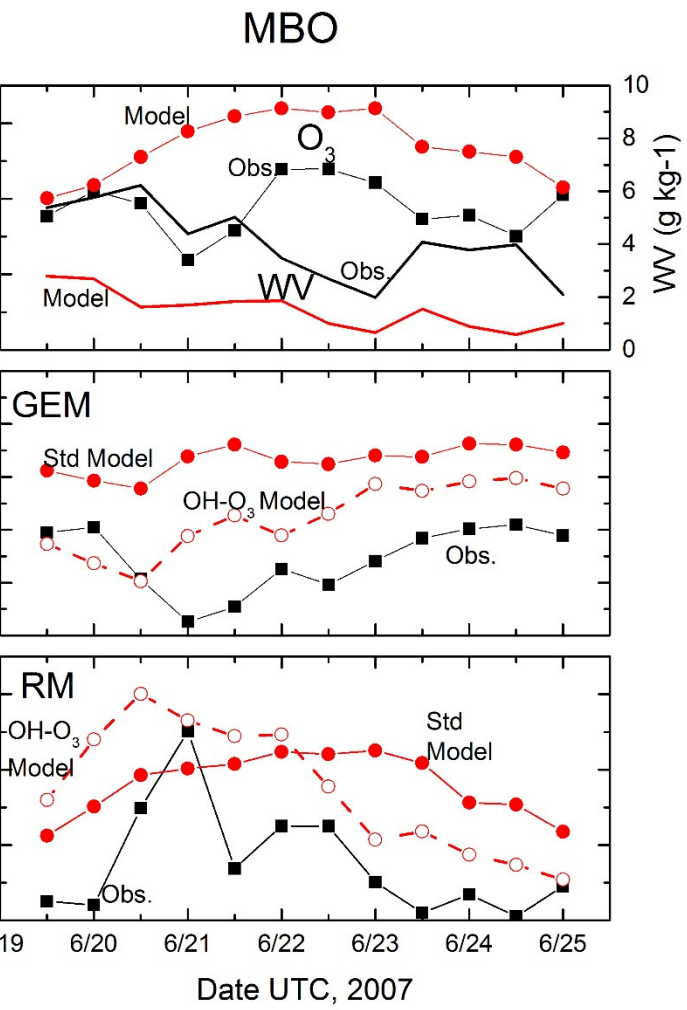
1. Transport of RM from non-FT regions
2. Unknown oxidations mechanisms not included in model
3. Chemical forms of RM poorly detected by analytical system

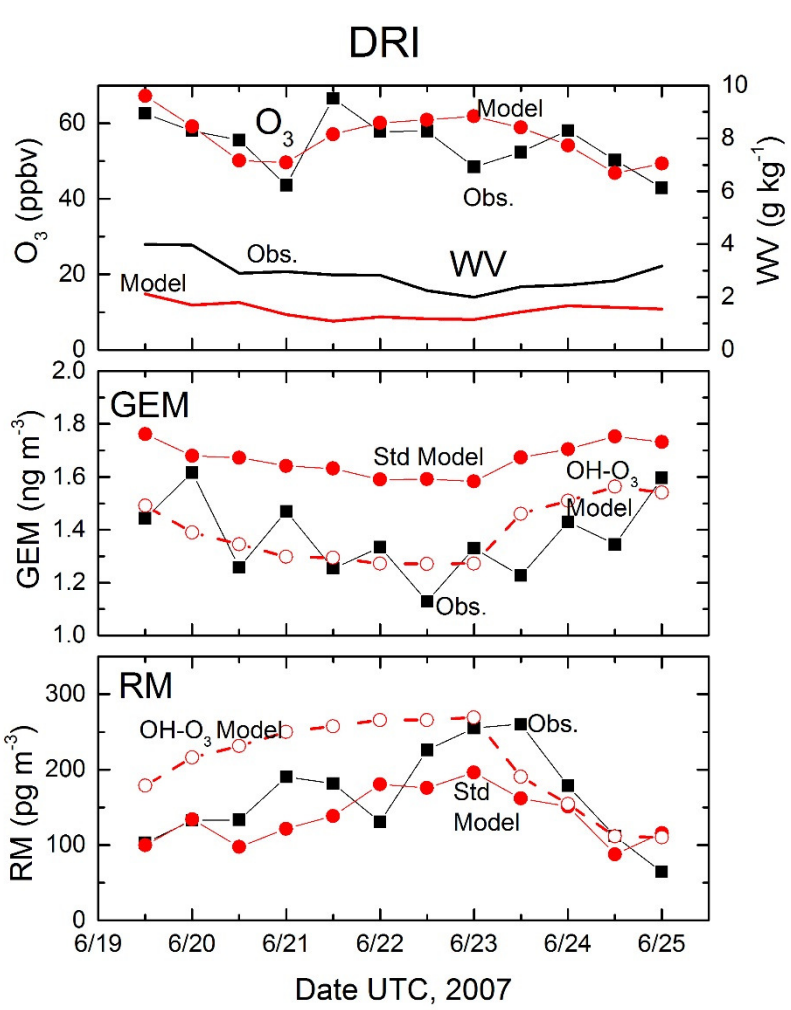
RM:GEM relationship is more negative in Model compared to Obs.

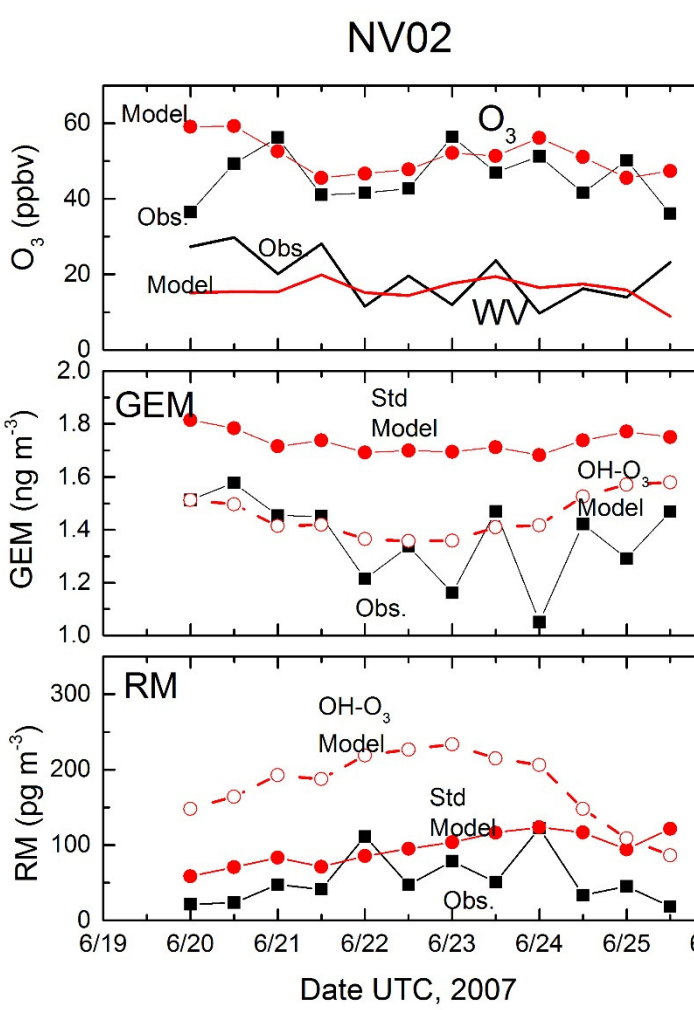
RM:O_3 relationship is more positive in Model compared to Obs.

RM:WV relationship is more negative in Model compared to Obs.

High GOM Event Observed at 3 Sites Sequentially in Time







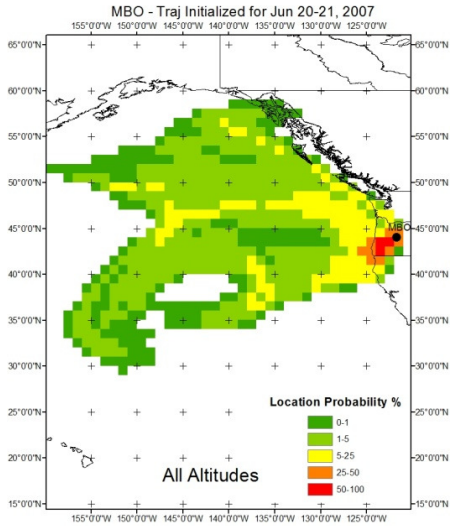
EM
ratio
g^{-1})

-1020, -864
Obs., Std. Model

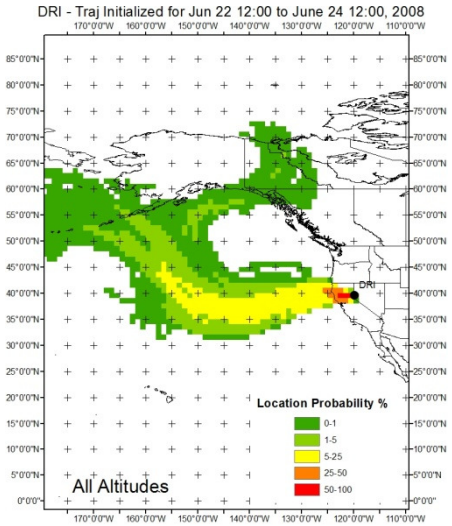
-576, -575
Obs., Std. Model

-181, -417
Obs., Std. Model

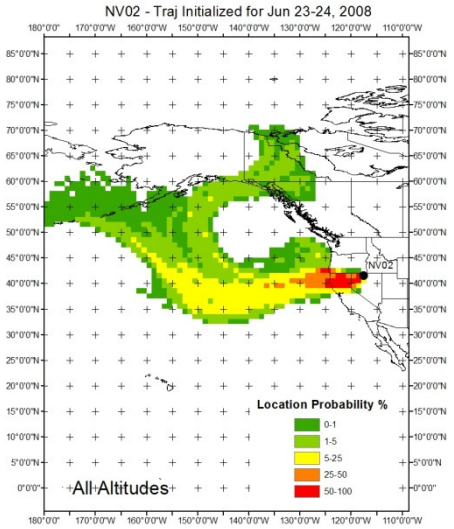
Hysplit Back Trajectories Initialized at Each Site at the Time of GOM Peak Concentration



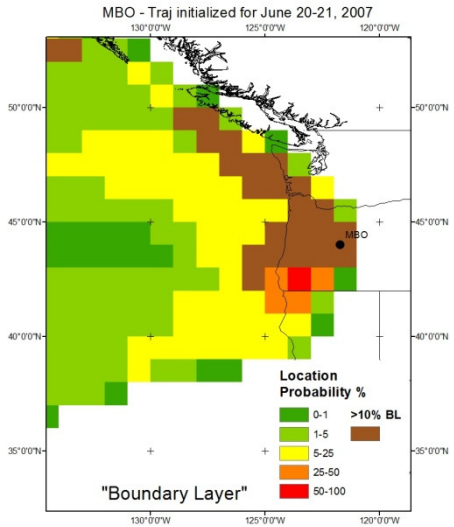
MBO

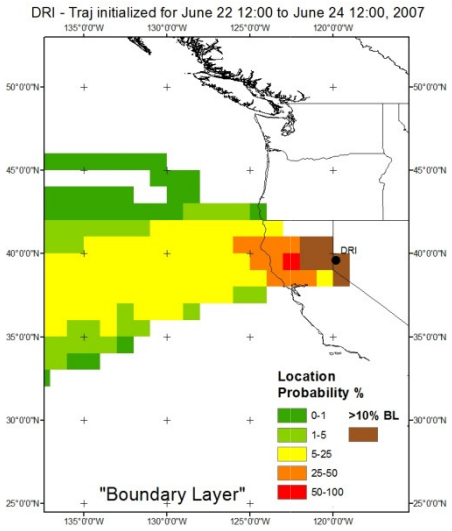


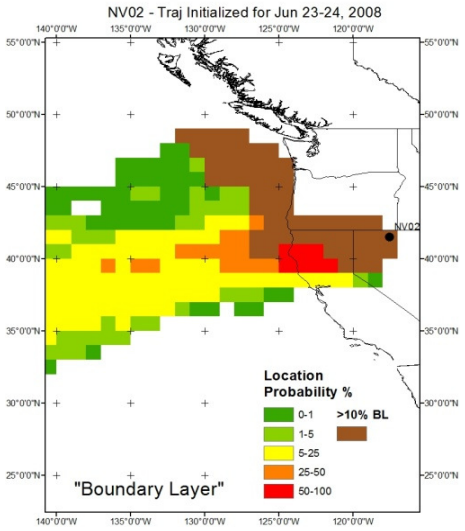
DRI



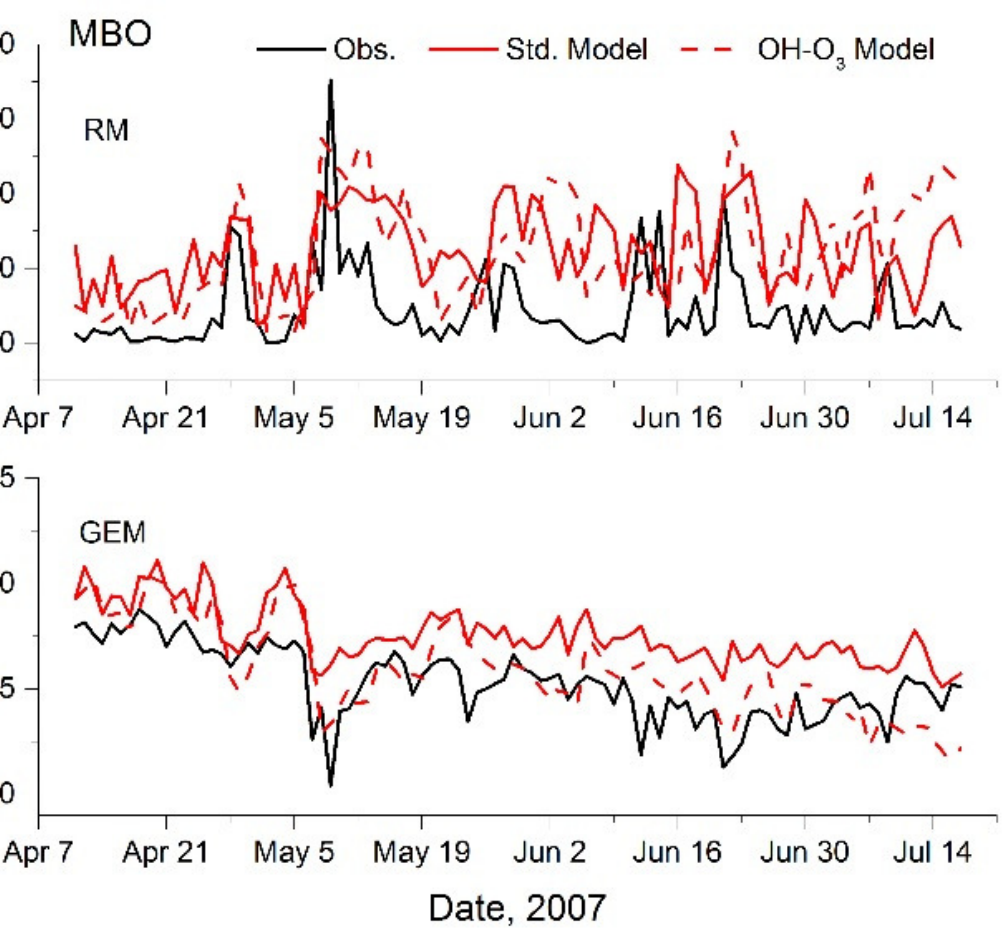
NV02

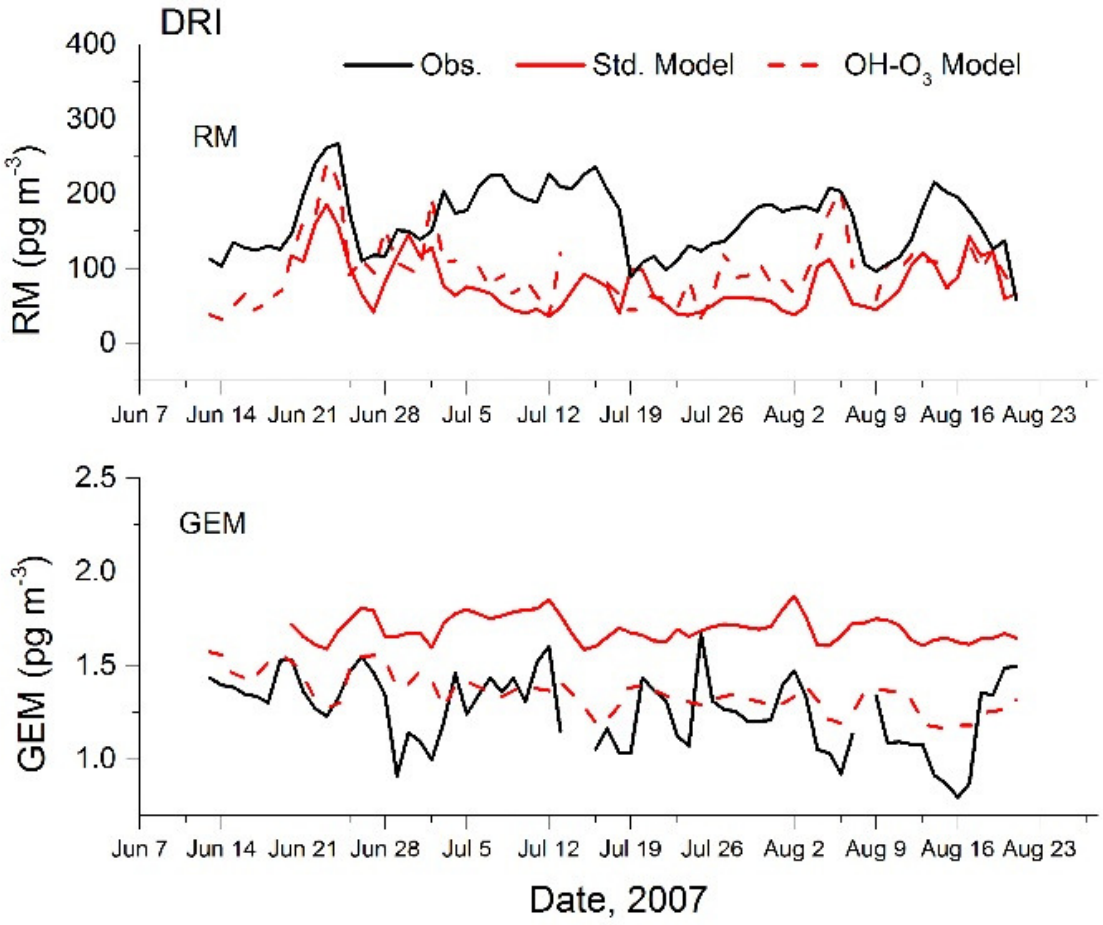




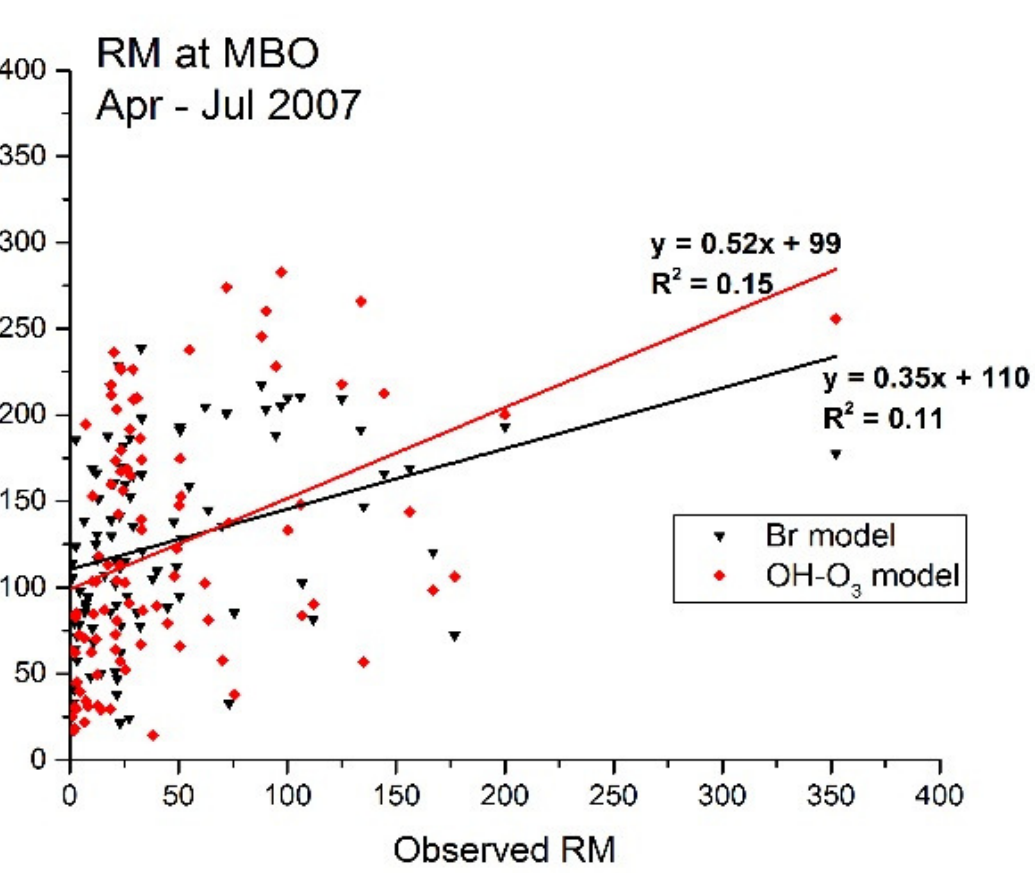


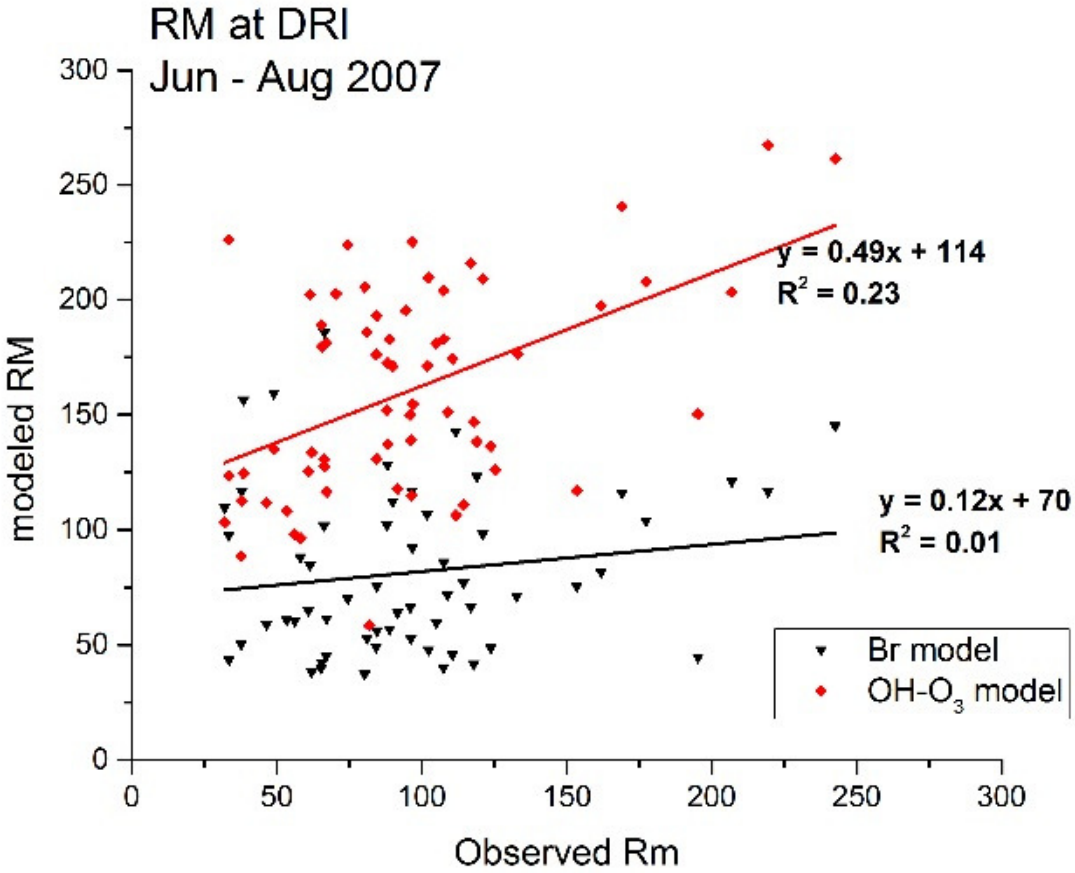
Comparison of observed, standard-modeled, and OH-O_3-modeled RM and GEM daily mean concentrations for spring/summer 2007 at MBO and summer 2007 at DRI.



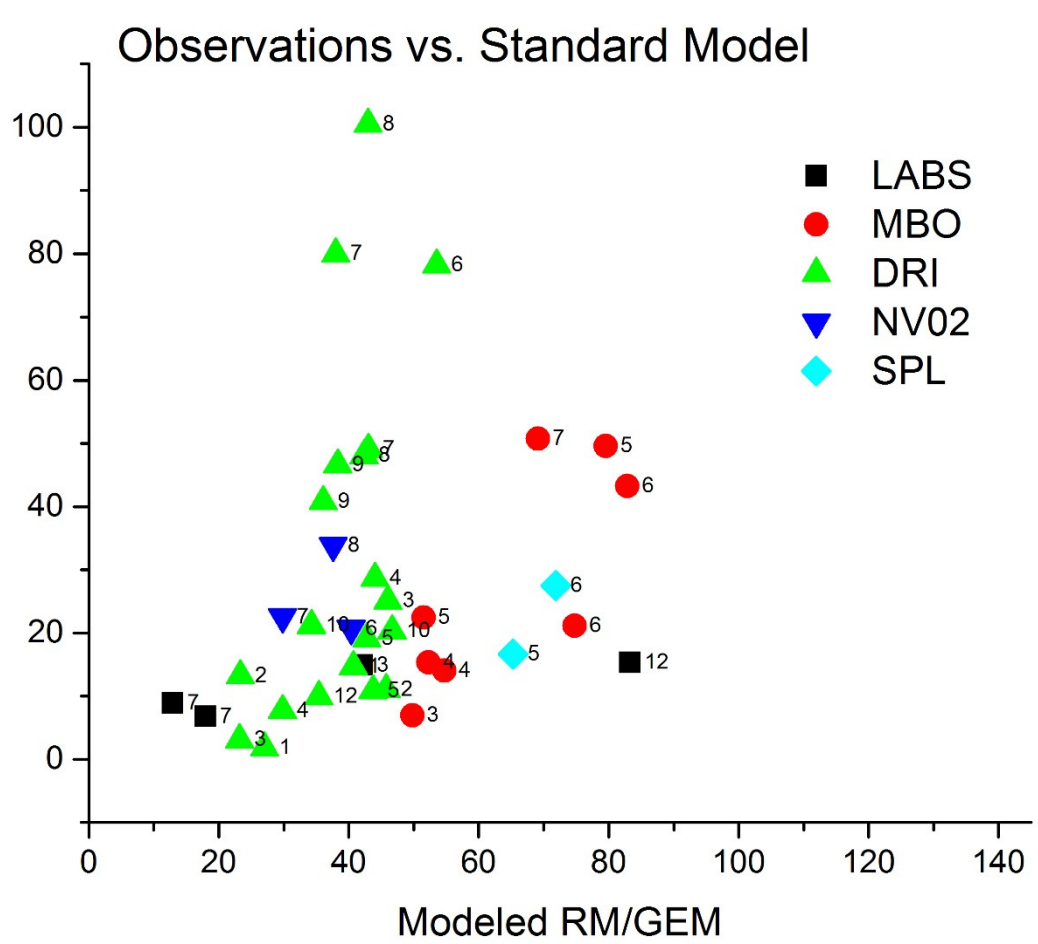


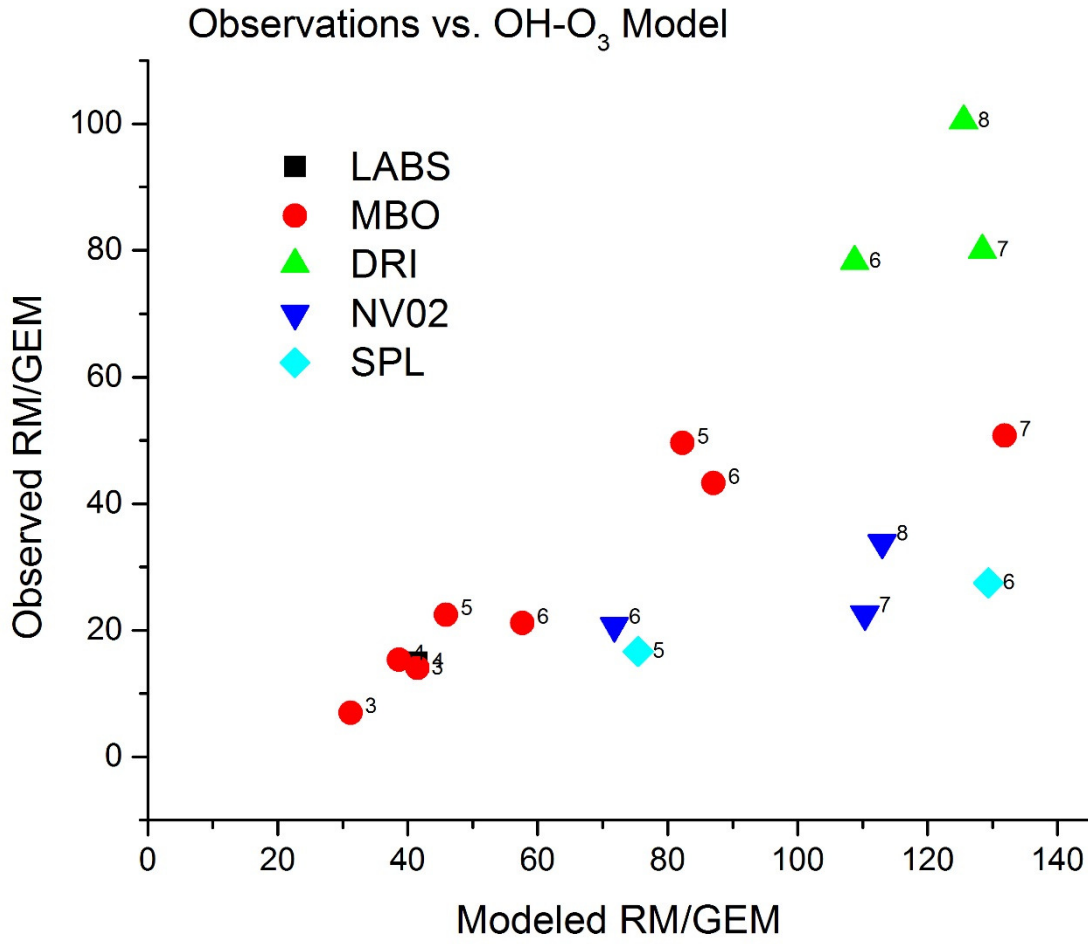
Scatter Plots of Observed vs. Modeled RM at MBO and DRI





Monthly mean RM/GEM from the observations vs. monthly mean RM/GEM in the models





Conclusions

- Observations and standard model agree during the summer over the spring that RM is formed in dry air with high O_3 from photo-oxidation of GEM.
- Modeled and observed RM varied by factor of 7 between sites.
- Modeled RM > observed RM by factor of 2.5 overall.
- Modeled GEM > observed GEM by 10% overall.
- Model reproduced observed trend in RM/GEM ratio at 3 sites during high RM events.

Conclusions

- Model with OH-O_3 oxidation scheme produced RM/GEM ratios that were in closer agreement with observations at DRI compared to model with Br oxidation scheme.
- Varying oxidation scheme for modeled MBO data did not change comparison with observations as much.
- This suggests that OH as an oxidant via the HgBr+OH pathway could be more important in the summer at desert sites.

Scatter Plots of daily mean RM vs. GEM – all sites, spring/summer only

