New project:

Impact of climate change on air quality in the U.S.: Global- and regional-scale models for ozone and mercury

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with results from previous EPA-STAR project:

Models and measurements for investigating atmospheric transport and photochemistry of mercury

Gerald J. Keeler and Sanford Sillman

(EPA R-82979901-0)

Critical Issues for modeling

- Predicting future air quality in response to changes in climate+emissions (in coordination with HTAP)
- What measurements can identify the impact of global changes in air quality?
- Impact of global background p'chem versus episodic transport
- Does ozone affect atmospheric mercury?
- Model improvements: integrated gas, aqueous and aerosol chemistry

Models

- Climate:
  NCAR Finite-Volume Community Climate Model (FVCCM)
  w/ IPCC emission scenarios for 2050
  including aerosol-climate coupling
- Global photochemistry/transport:
  IMPACT (LLNL/Michigan)
  including hybrid dynamical representation of nitrate/ammonia aerosols (Feng, 2006)
- Regional: modified CMAQ for eastern USA

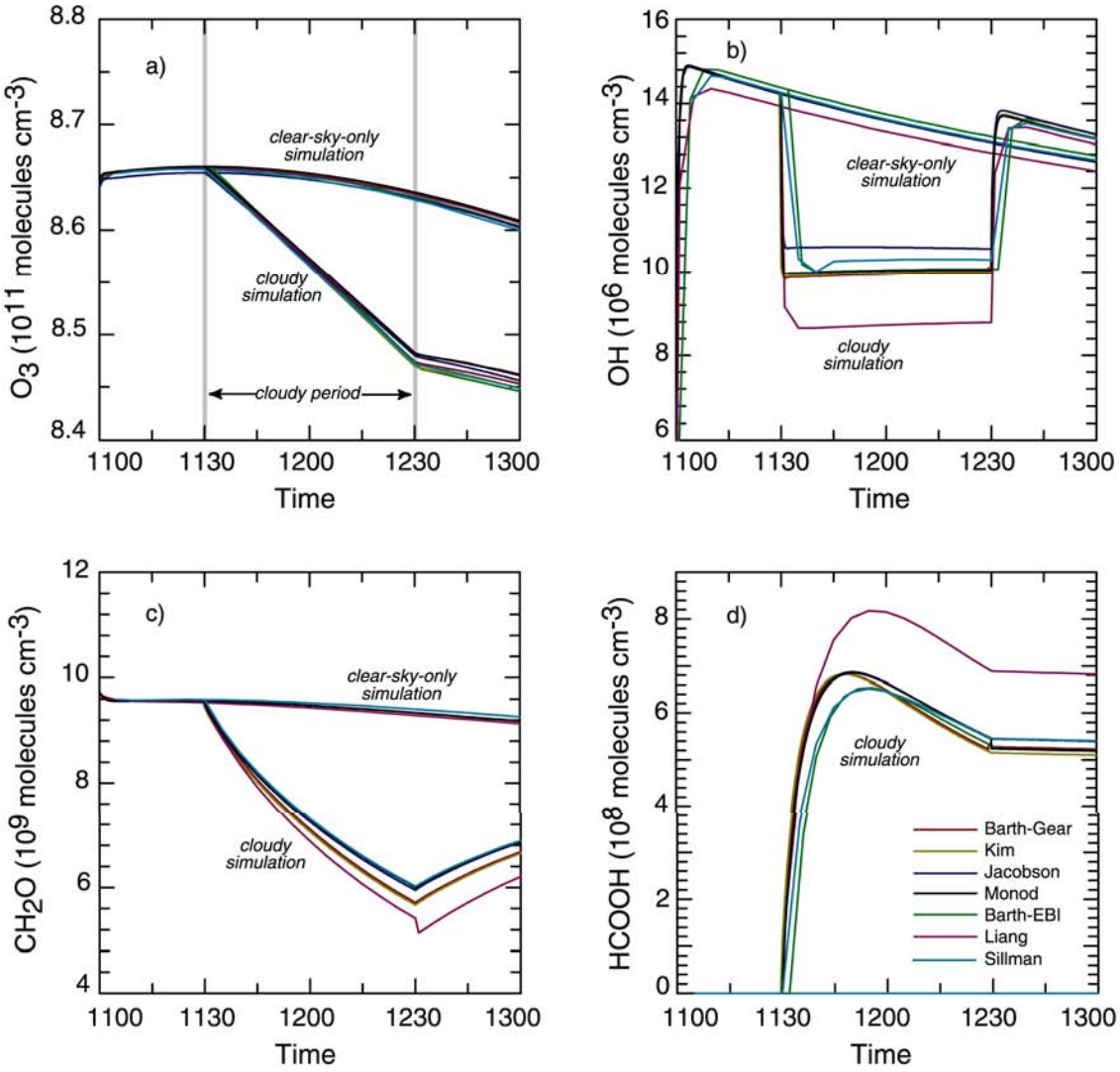
Modifications to CMAQ

- Integrated solver for combined gas+aqueous photochemistry (simultaneous solution)
- 70 aqueous reactions, 26 Hg reactions, 300+ gas-phase reactions (for O_3, NO_x, VOC, SO_4, halogens, etc)
- Aqueous solver tested in model intercomparison (Barth et al., 2003)
- Improved representation of j-values in clouds, replacing approximate format in original CMAQ
- Future: integrate gas+aqueous+aerosol chemistry
- Same gas+aqueous chemistry in global model

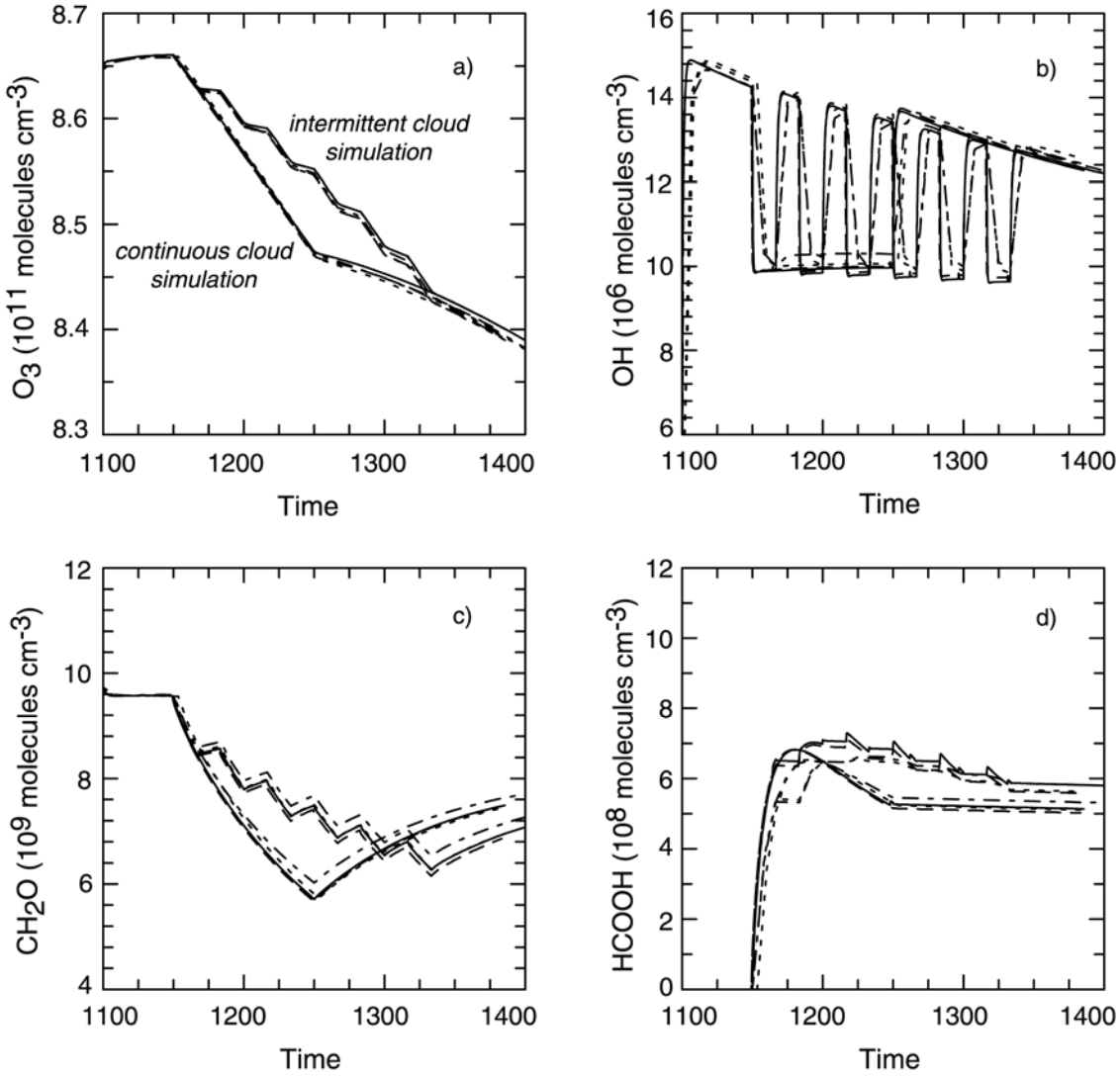
Numerical solution for gas+aqueous photochemistry

- Implicit (reverse Euler) solution
  with extension for exponential decay
  in remote locations
- Calculates gas-aqueous partitioning, gas-phase and aqueous p'chem.
- Fast solver for j-values in clouds
- Direct input of individual reactions
- Integrated into CMAQ
- Tested in model intercomparison (Barth 2003)
  (including effect of intermittent clouds)

Model intercomparison
(*Barth et al*., 2003)

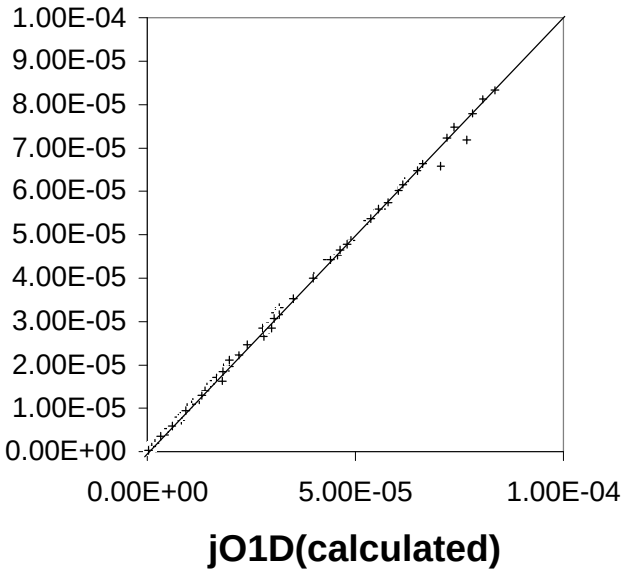


Intermittant clouds
(*Barth et al*., 2003)

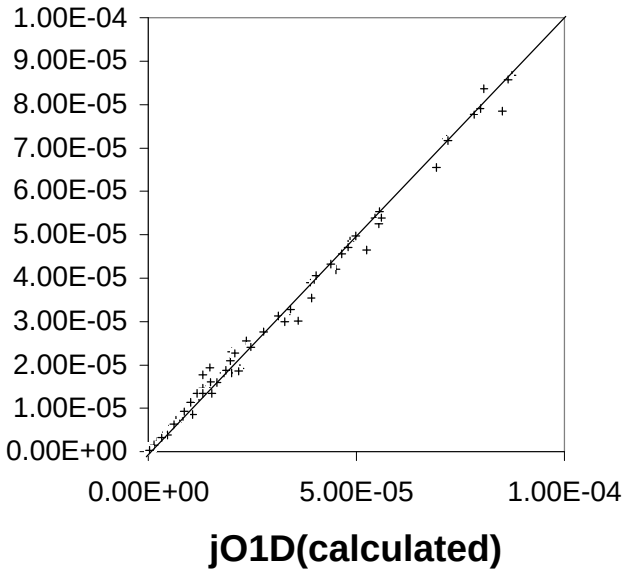


Evaluation of photolysis parameterization (vs. TUV model, Madronich and Flocke)

Single cloud layer



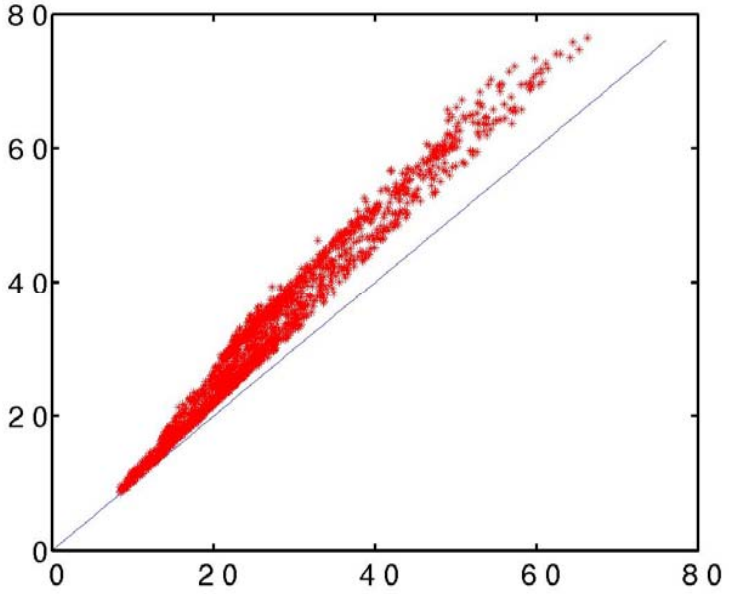
Two cloud layers

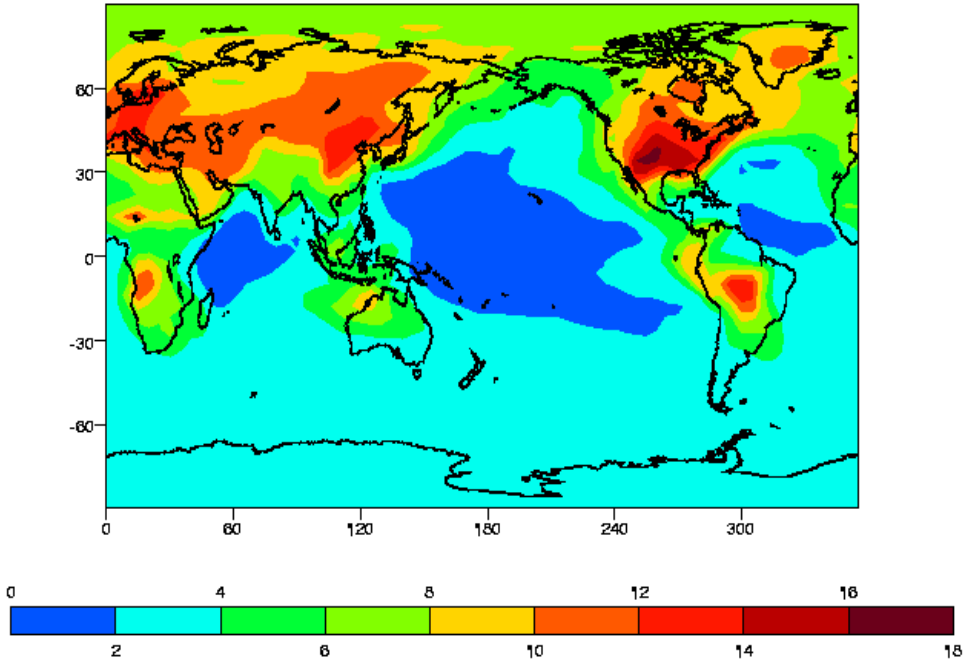


Previous result: global O_3

- Inclusion of aromatics, terpenes and isoprene nitrates affects model O_3:
  20% increased O3
  30% increased PAN
  (*Ito et al*., 2006, consistent with *von Kuhlmann et al*., 2005, etc.)
- Large changes in methyl glyoxal, hydroxyacetone (test vs. measurements from Spaulding et al.,2003) - possible implication for aerosol formation

O_3 (Extended - Base) Chemistry





Measurements vs models w/ base and extended chemistry

Species	**Measured** (Spaulding) (ppb)	**Base model** (ppb)	**Extended model** (ppb)
Glycol-aldehyde	0.63	0.06	0.30
Hydroxy-acetone	0.38	0.16	0.68
Methyl glyoxal	0.12	0.05	0.12

Prior result: mercury

- Photochemical conversion from Hg^0 can result in >200 pg m^{-3} reactive gaseous mercury (RGM) at 3 km, matching measurements in Florida (Sillman et al., 2007, submitted)

Hg chemistry incorporated into CMAQ

(Lin and Pehkonen, 1997, 1998; Val Loon et al., 2000; Sommar et al., 2000, Lindberg, 2002; Khalizof, 2003,

chlorine from JPL 2003, bromine from Sander 1996)

Hg0-to-HgII

(mainly gas-phase)

- Hg0+O3=>HgO
- Hg0+CL2=>HgCL2
- Hg0+OH=>HgOH
- Hg0+OH(aq)=>Hg^{2+} etc.

HgII-to-Hg0

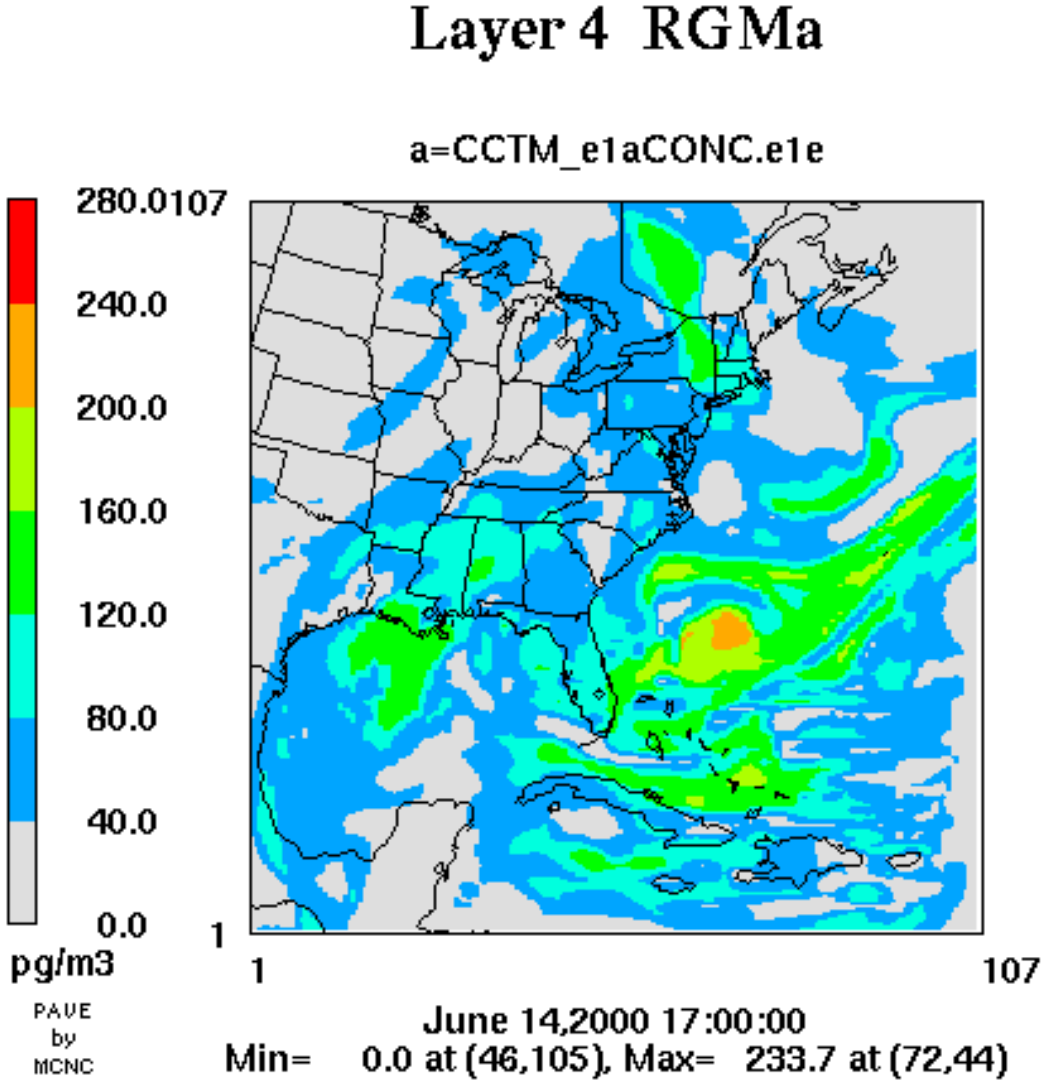
(aqueous phase)

- Hg^{2+}+HO2(aq)=>Hg0 etc.

(integrated gas/aqueous/aerosol chem. is crucial)

RGM at 3000m

Sillman et al, JGR, submitted

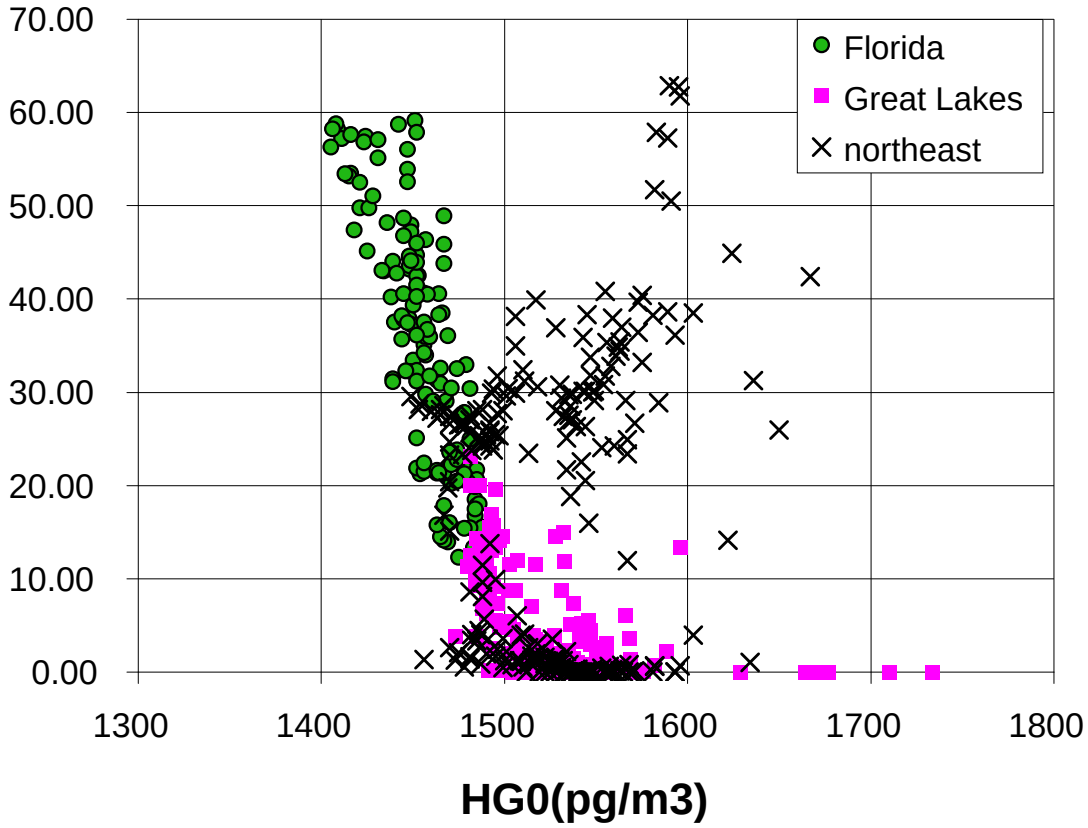


Prior result: mercury

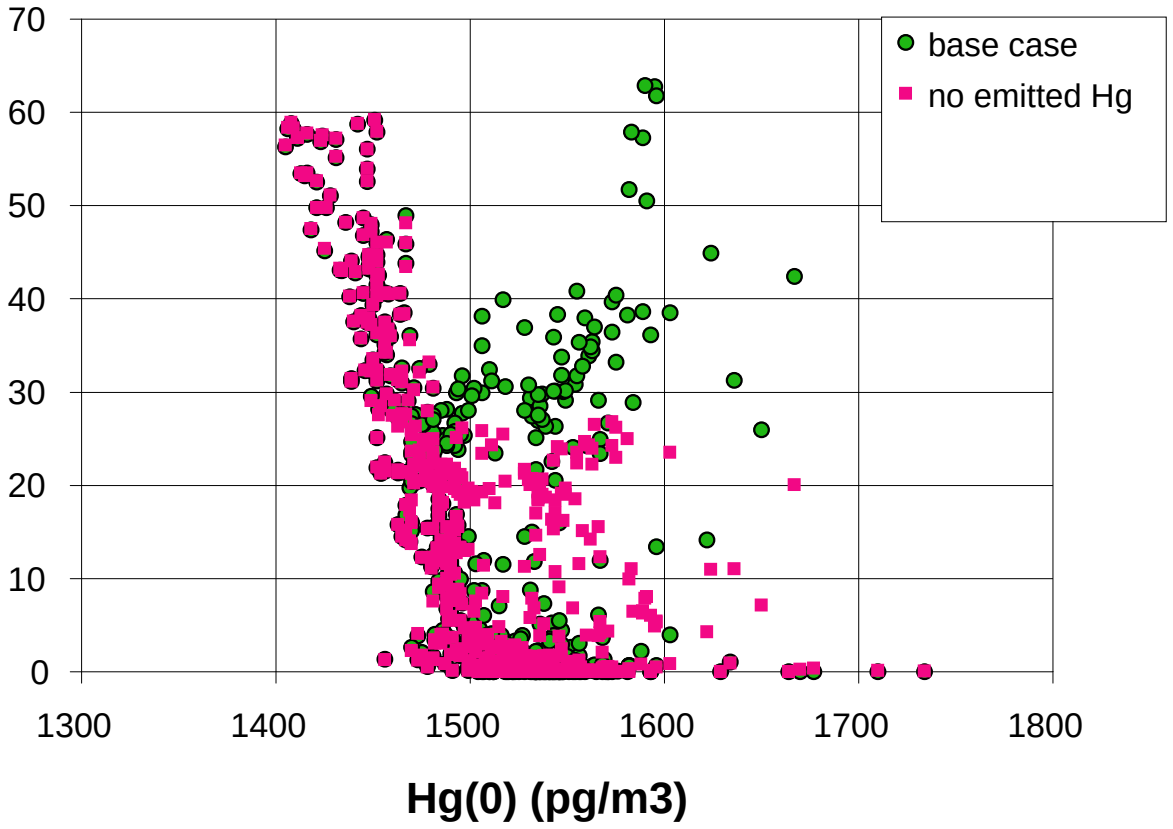
- Correlation between ambient RGM and Hg^0
  can identify global background RGM
  (negative correlation, model for Florida)
  versus RGM from emissions
  (positive correlation, model for northeast)

(WARNING: Results do not preclude impact from local Hg in Florida)

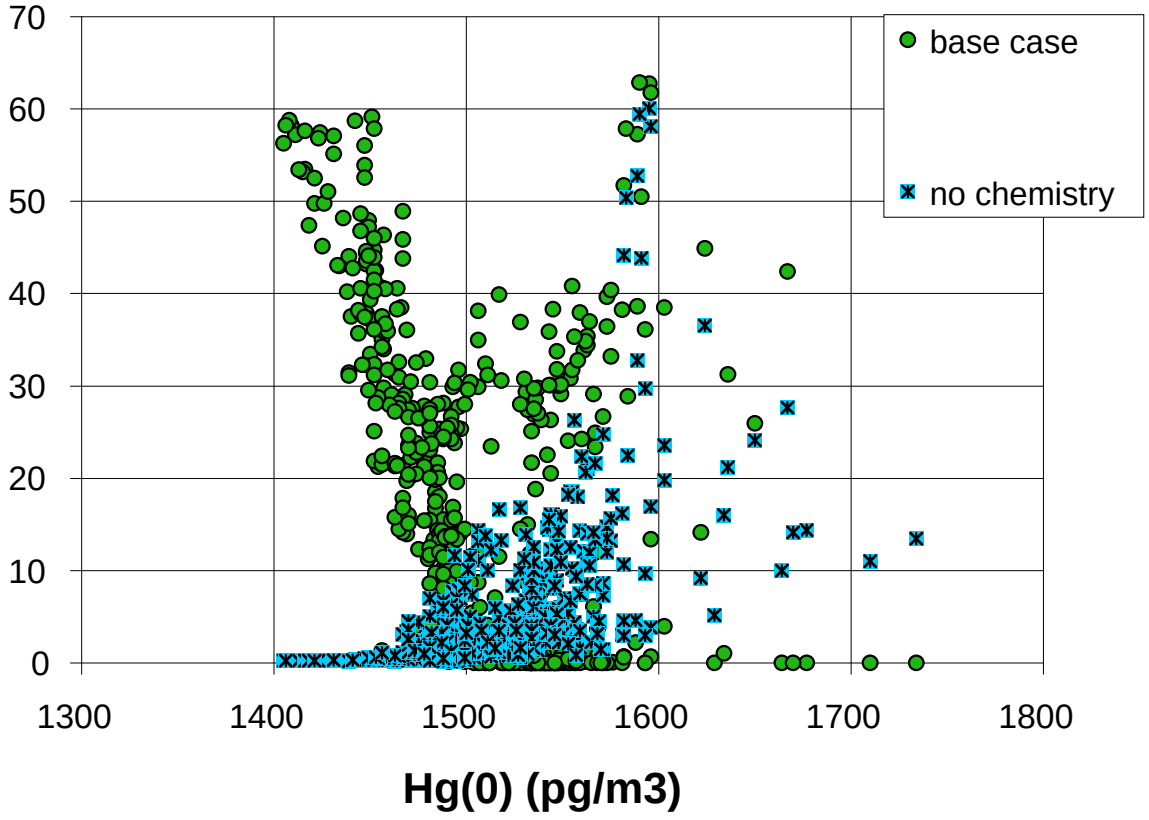
RGM vs Hg0



RGM vs Hg0: zero emissions



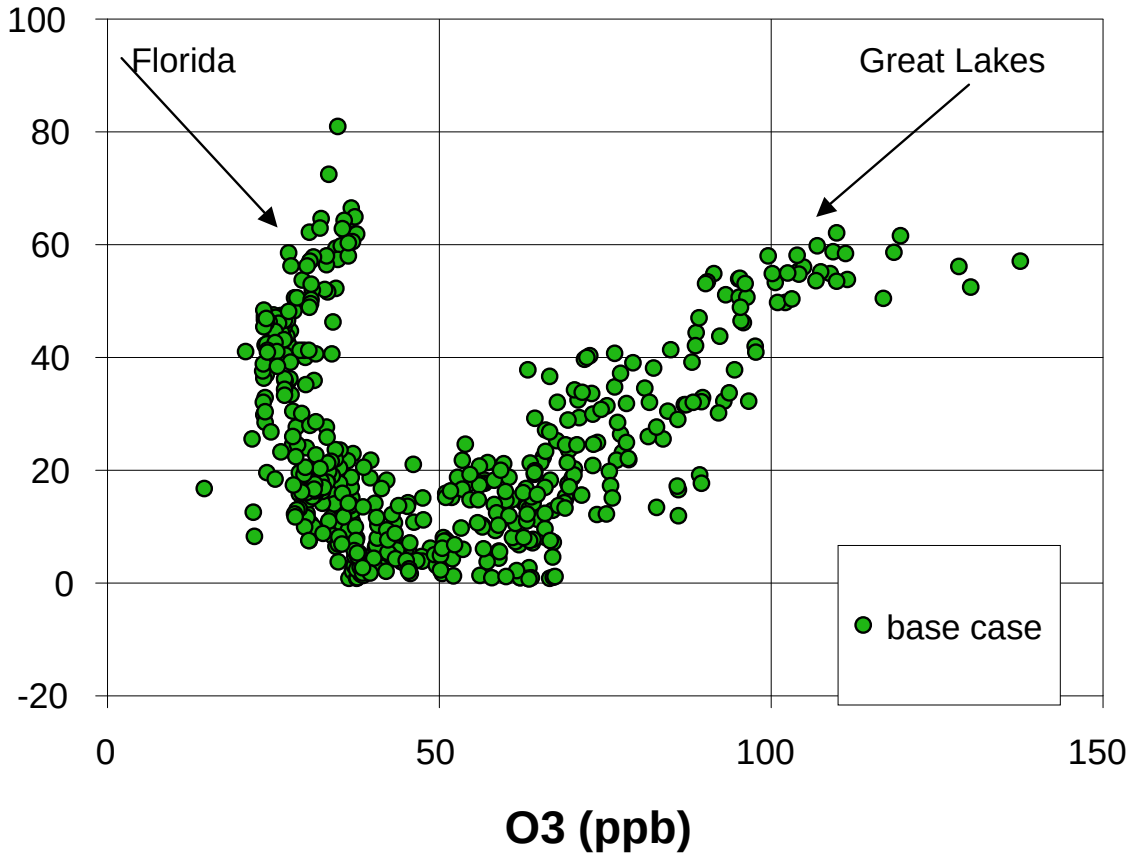
RGM vs Hg0: zero background Hg



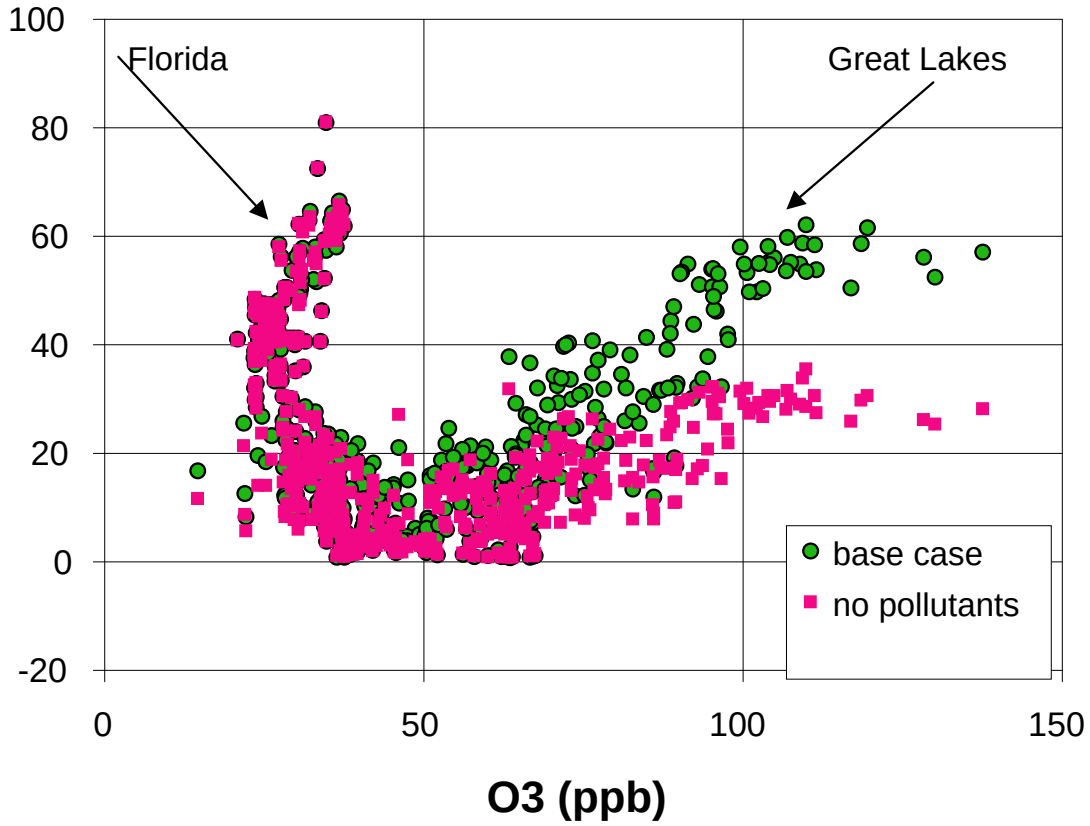
Prior result: O_3 and mercury

- Models predict a correlation between ambient O_3 and RGM during region-wide pollution events
- The correlation is largely due to simultaneous photochemical production of O_3 and RGM, both resulting from anthropogenic precursors of O_3

Model ambient RGM vs O3 (June 14, 2000)



Model RGM vs O3 -with influence of anthropogenic O3 on RGM removed



Prior result: Hybrid dynamic aerosol model (Feng and Penner, 2007)

- Hybrid dynamic model for nitrate-ammonium aerosols (in place of standard gas-aerosol equilibrium)
- Used in global IMPACT model
- Result: 25% higher fine-mode NO_3^- aerosols, reduced coarse mode, higher gas-phase HNO_3.
  (mainly in remote locations)

Hybrid dynamic model for aerosol NO_3^-

Fine NO_3^-, coase NO_3^-, HNO_3g
(TgN global)
Equilibrium vs H. dyn. model

Fine mode nitrate aerosol
(pptv)

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

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are needed to see this picture.

For future investigation:

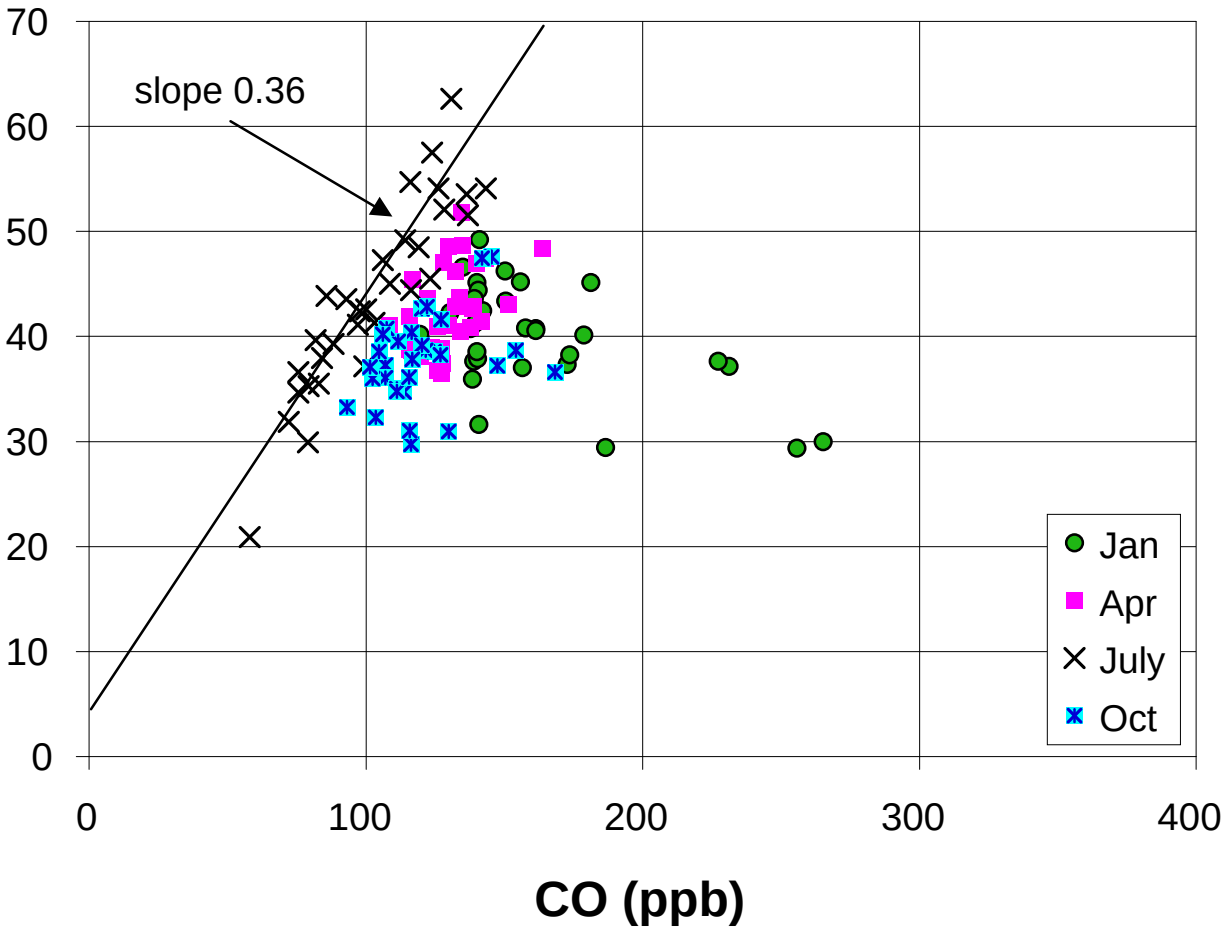
Can species correlations provide a measurement-based signal for the impact of global-scale processes on local O_3?

- (O_3-CO-PAN-HNO_3-H_2O_2)
- (Including episodic transport and the changing global background)

Model O_3 vs CO

Sable Island: 4 seasons

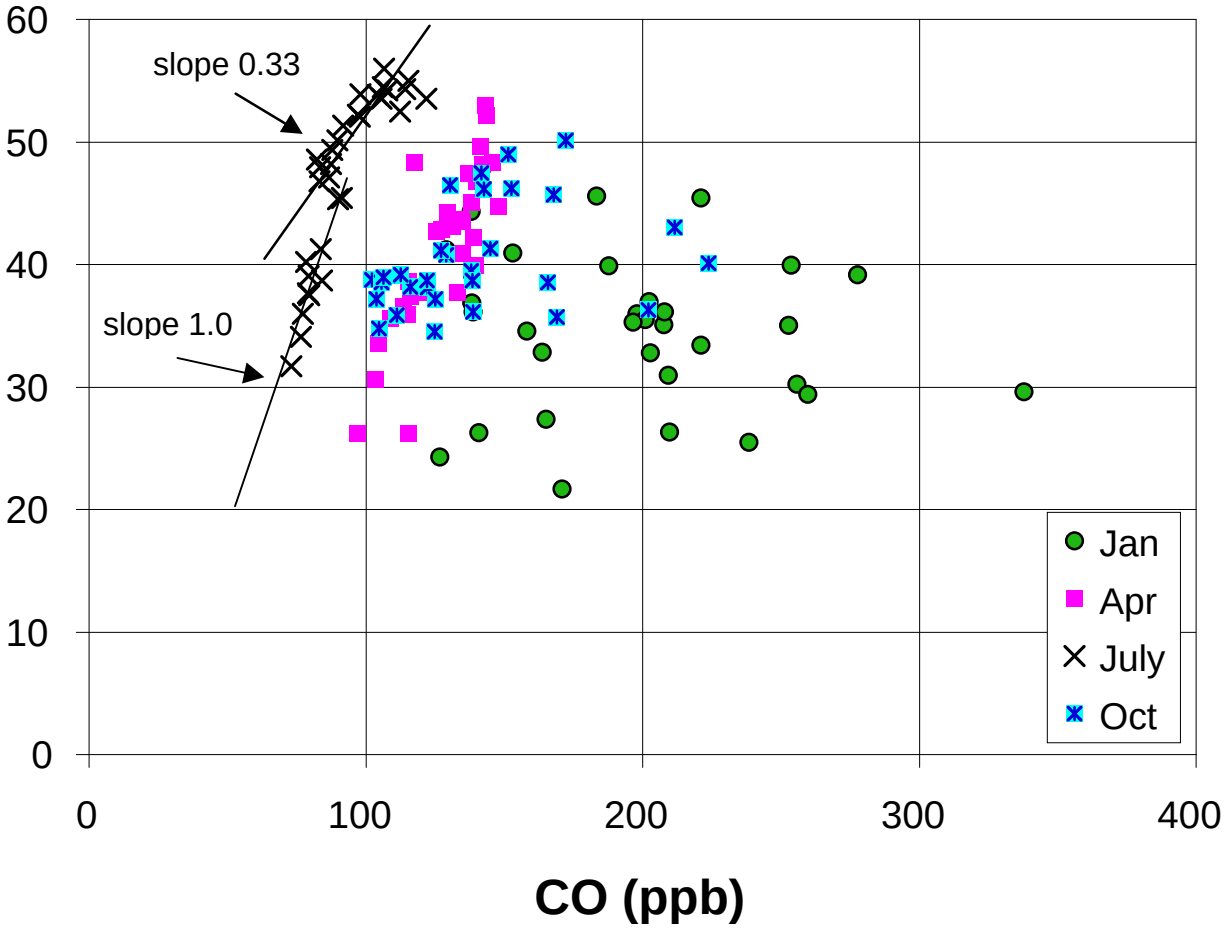
summer slope 0.36: Episodic transport?



Model O_3 vs CO

California/Sierra Nevada

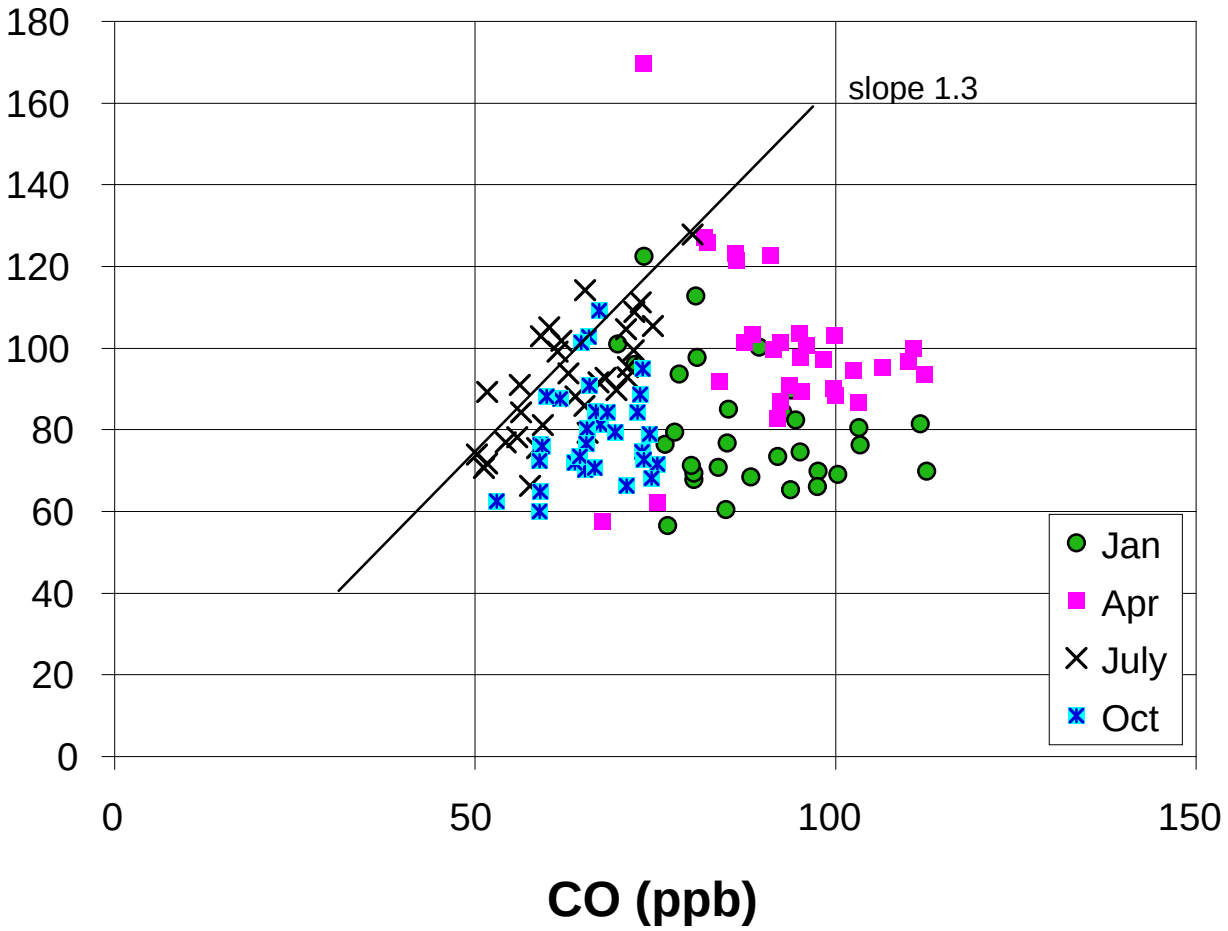
slope >1.0 = global background?



Model O_3 vs CO

California/Sierra Nevada, 50 kPa

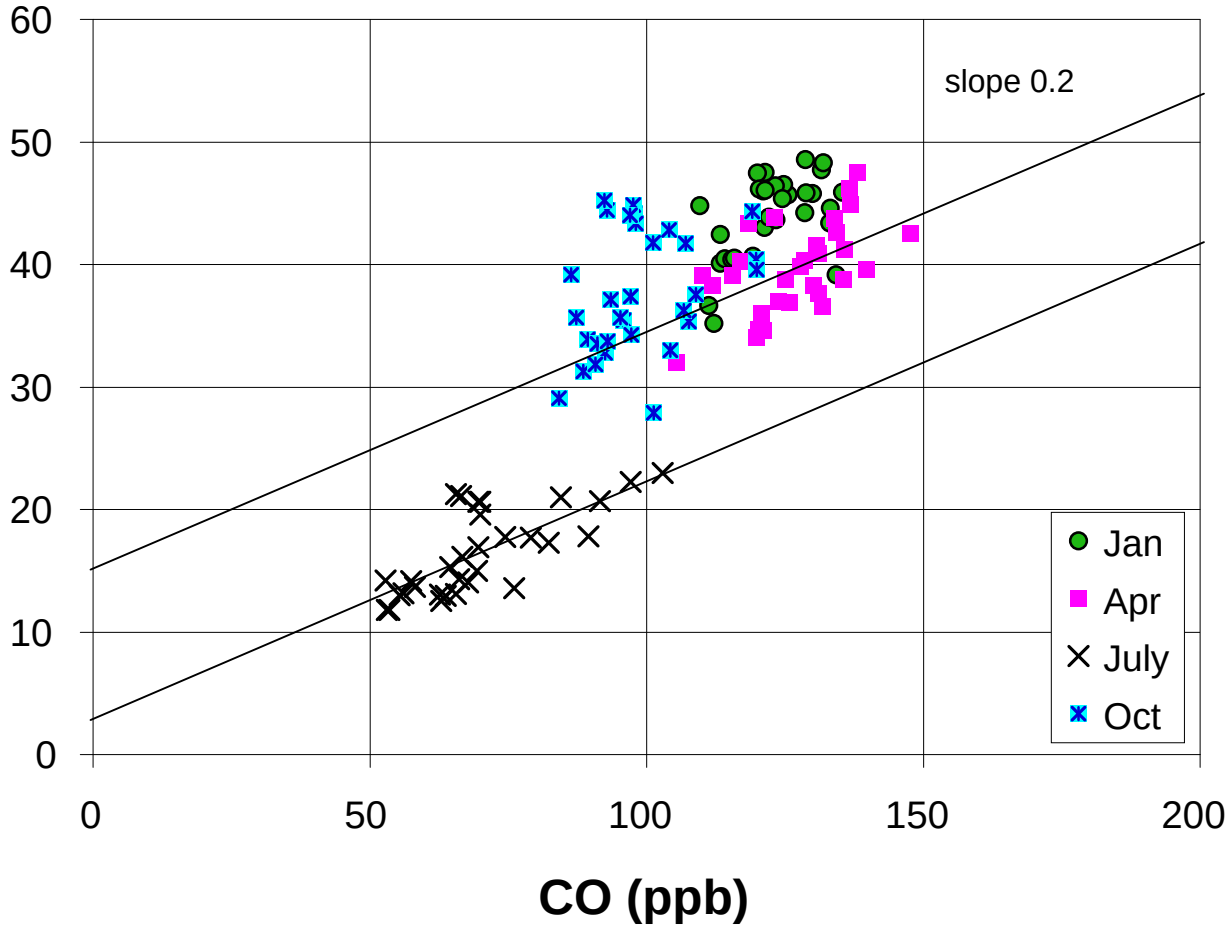
slope >1 is common at 50 kPa



Model O_3 vs CO

Aleutians

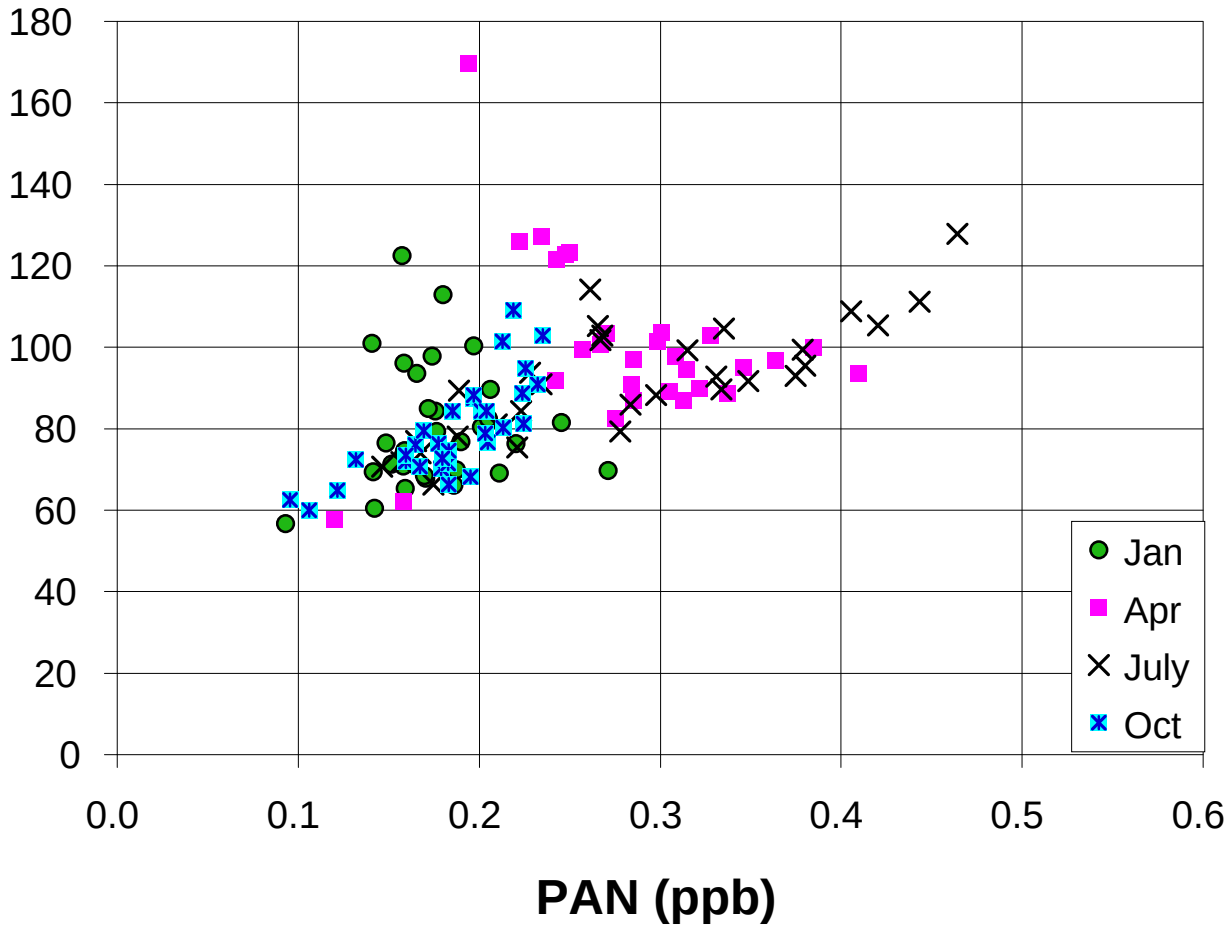
slope 0.2=episodic transport w/O_3 loss?



Model O_3 vs PAN

California/Sierra Nevada, 50 kPa

(+ vs - correlation = different origin?)



Tasks

- CMAQ: link gas, aqueous and aerosols
- Global model: add aqueous/Hg chem.
- Present-day global scenario
- Present day CMAQ - episodes in eastern US.
- Model evaluation vs. measured O_3, CO, NO_y, aerosols and Hg (Keeler)
- Global pattern of Hg wet deposition
- Regional/global simulations for 2050.
- Identify changes in O_3, CO, PAN, HNO_3, H_2O_2 as identifiers of changed global conditions

Expected results and benefits

- Forecast for global impact on regional air quality (from this and other models)
- Methods to identify local versus global impacts on O_3 and mercury from measurements
- Methods to identify global change impact.
- Investigation of new phenomena:
  relation between O_3 and RGM;
  effect of aqueous photochemistry
- Improved model capability (CMAQ)

Partial list of references

Barth, M., S. Sillman, R. Hudman, M. Z. Jacobson, C.-H. Kim, A. Monod, J. Liang, Summary of the cloud chemistry modeling intercomparison: Photochemical box model calculation. *J. Geophys. Res.*, 108(D7), 4214, doi:10.1029/2002JD002673, 2003.

Feng Y., J. E. Penner (2007), Global modeling of nitrate and ammonium: Interaction of aerosols and tropospheric chemistry, J. Geophys. Res., 112, D01304, doi:10.1029/2005JD006404.

Fiore A. M., L. W. Horowitz, D. W. Purves, H. Levy II, M. J. Evans, Y. Wang, Q. Li, R. M. Yantosca (2005), Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, J. Geophys. Res., 110, D12303, doi:10.1029/2004JD005485.

Fiore, A. M., D. J. Jacob, I. Bey, R. M. Yantosca, B. D. Field, A. C. Fusco, and J. G. Wilkinson (2002), Background ozone over the United States in summer: Origin, trend, and contribution to pollution episodes, *J. Geophys. Res.*, *107*(D15), 4275, doi:10.1029/2001JD000982.

Ito, A., S. Sillman and J. E. Penner, Effects of additional non-methane volatile organic compounds, organic nitrates and direct emissions of oxygenated organic species on global tropospheric chemistry, *J. Geophys. Res.*, in press, 2006.

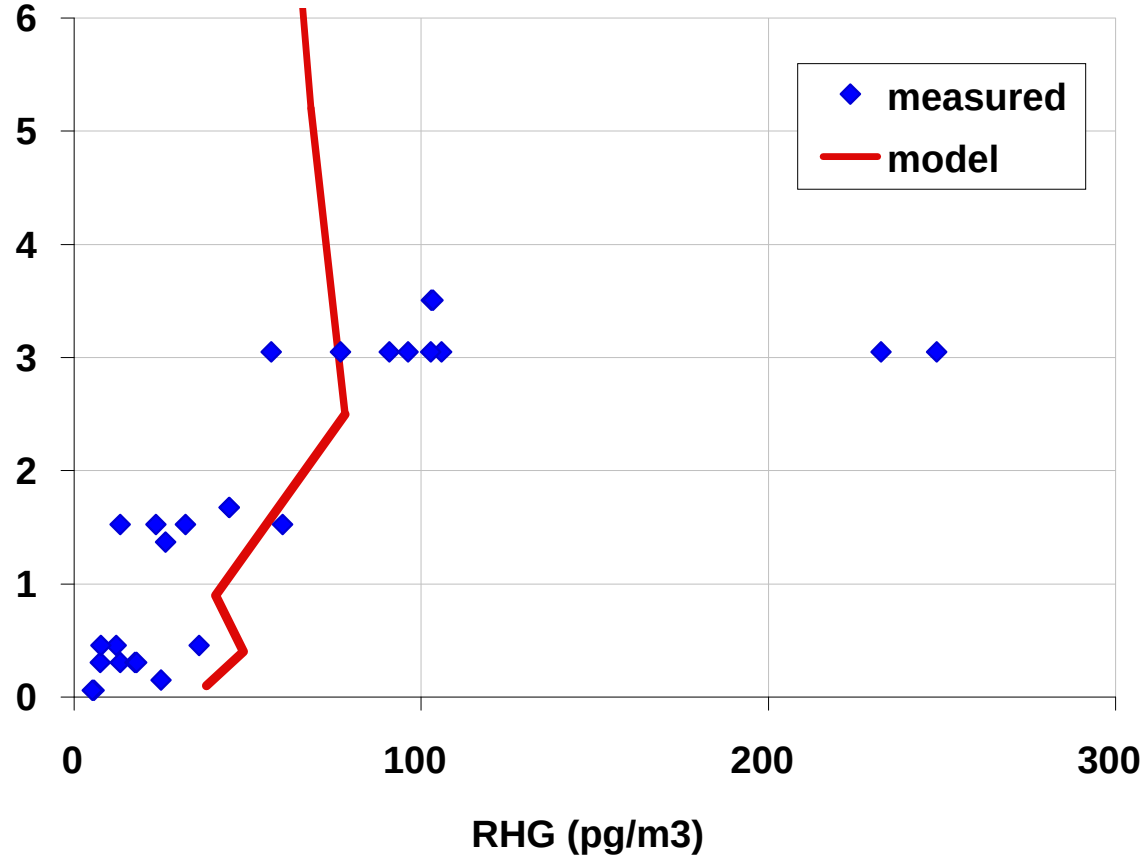
Madronich, S. and S. Flocke, *The role of solar radiation in atmospheric chemistry, in Handbook of Environmental Chemistry (P. Boule, ed.),* Springer_Verlag, Heidelberg, pp. 1-26, 1998.

Spaulding, R.S., G.W. Schade, A.H. Goldstein, and M.J. Charles, Characterization of Secondary Atmospheric Photooxidation Products: Evidence for Biogenic and Anthropogenic Sources, *J. Geophys. Res.*, 108, D8, 4247, doi:10.1029/2002JD002478, 2003.

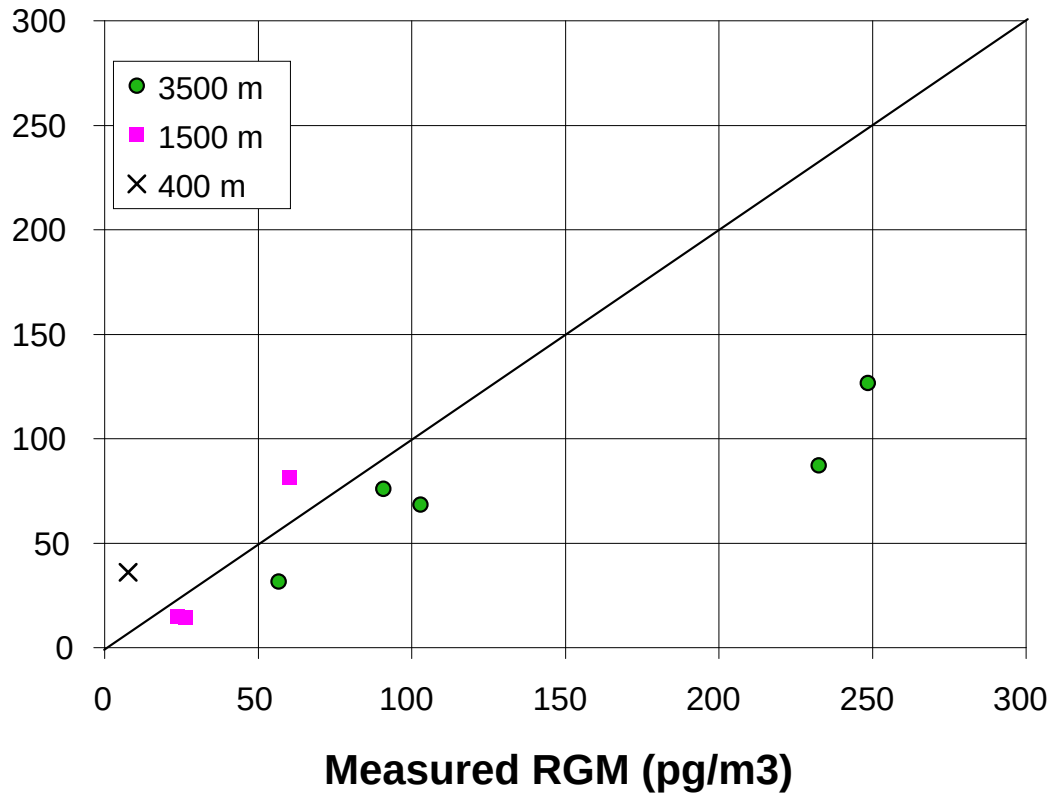
von Kuhlmann, R., M. G. Lawrence, U. Pöschl, and P. J. Crutzen (2004), Sensitivities in global scale modeling of isoprene, *Atmos. Chem. Phys.*, *4*, 1-17.

Additional slides

RGM vs altitude: Model and measurements (Landis)

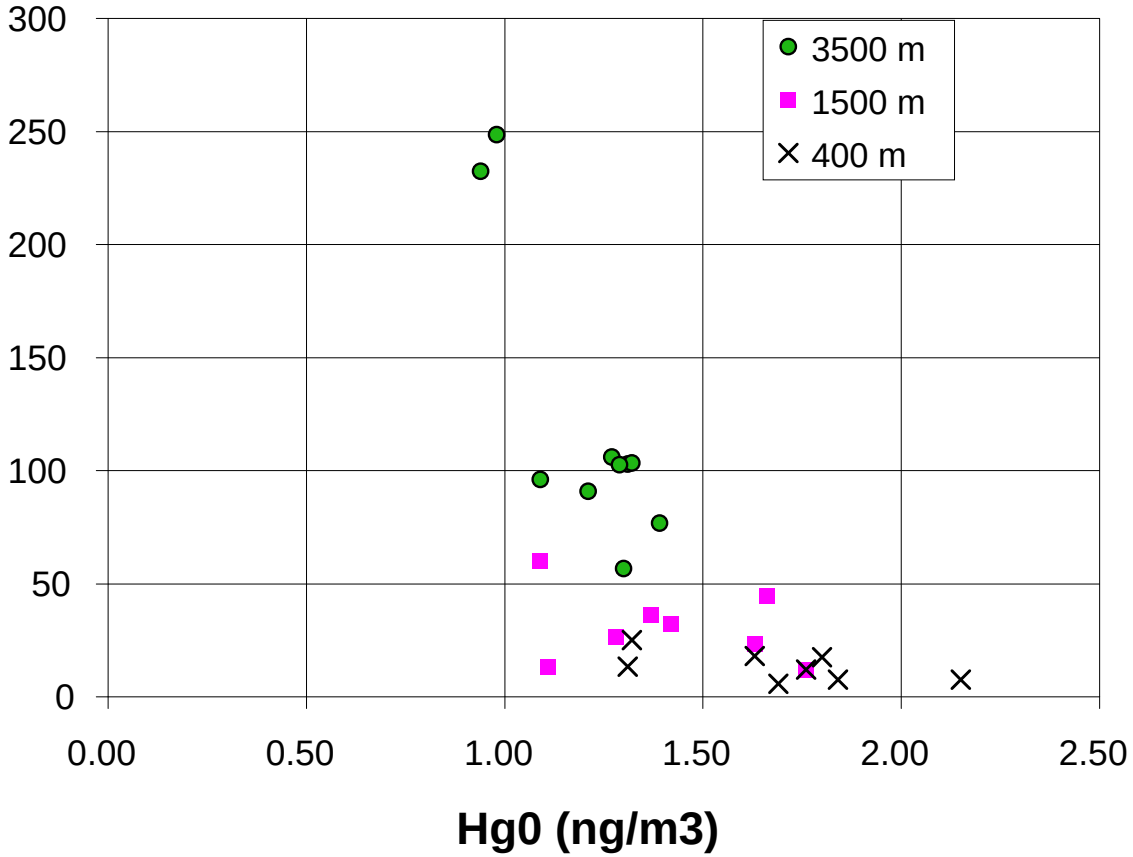


Model vs measured RGM in Florida



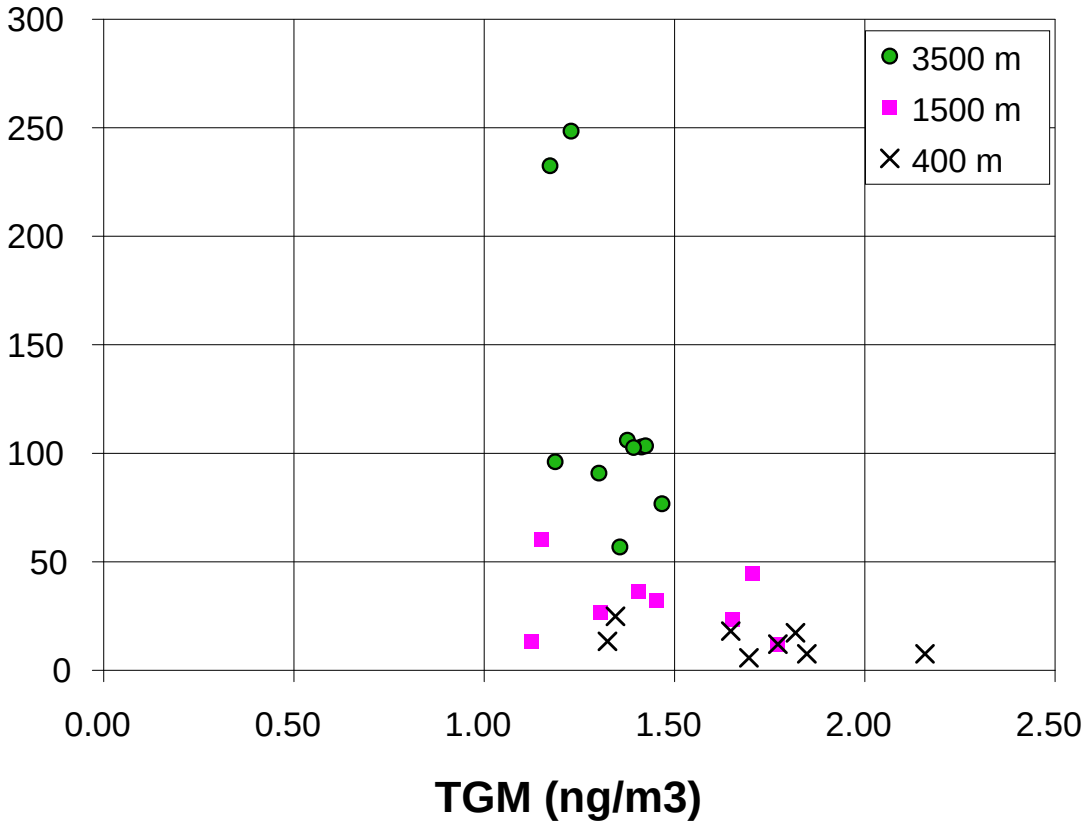
RGM v Hg0: Florida June measurements

(Landis)



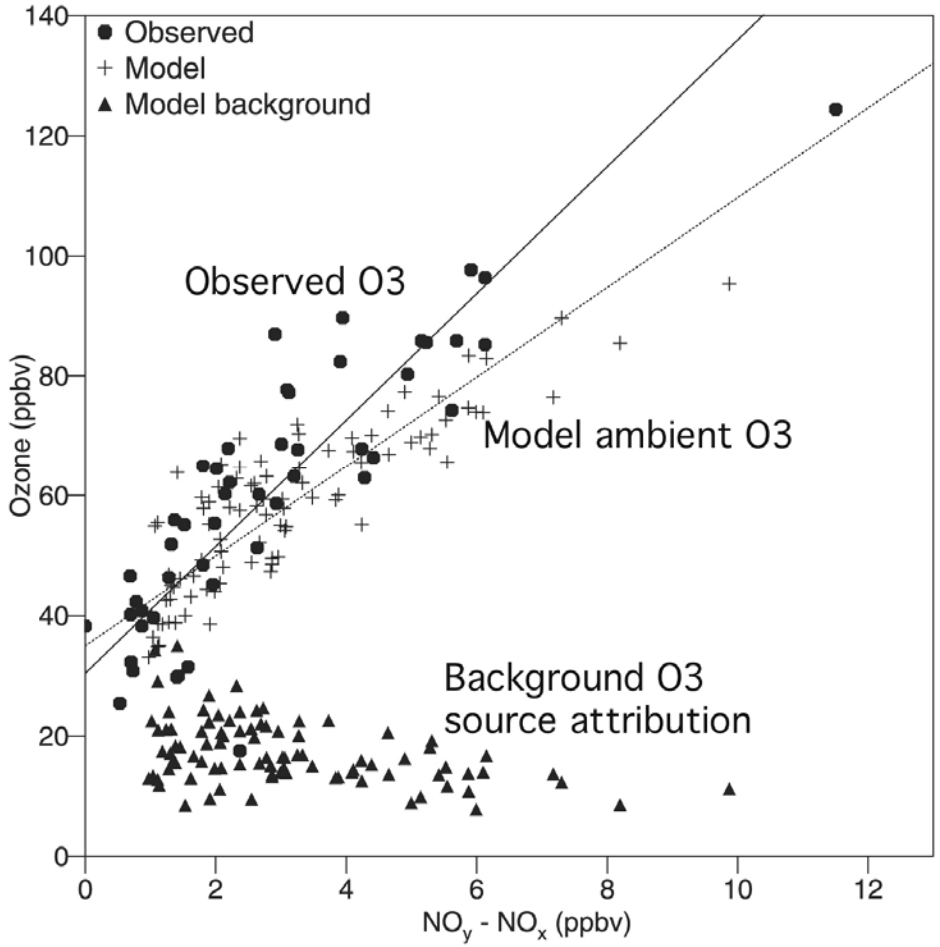
RGM vs Total Hg: June measurements

(Landis)



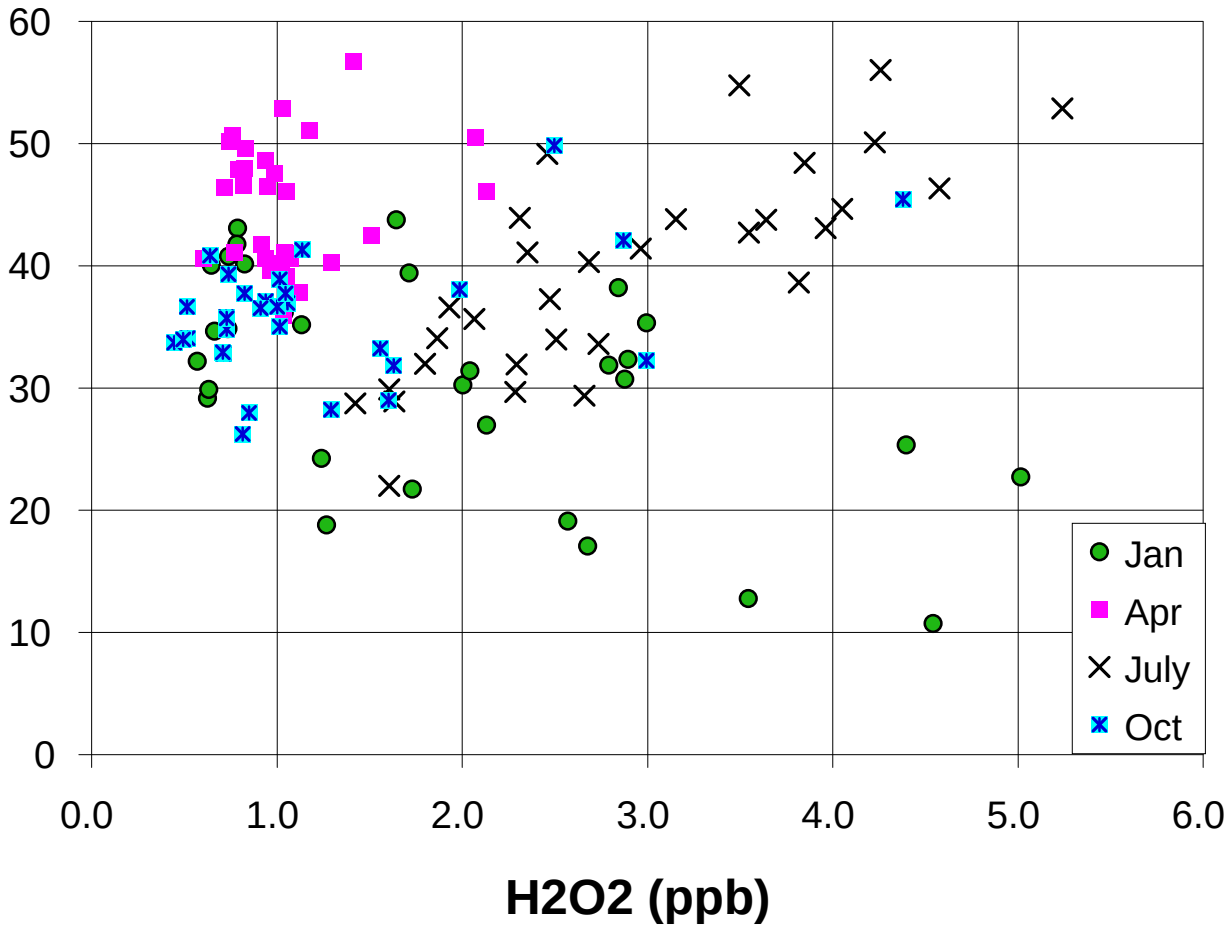
Transported O3 and source attribution: O3 vs NOy (*Fiore et al*., 2002)

Impact is smaller than inferred global background!



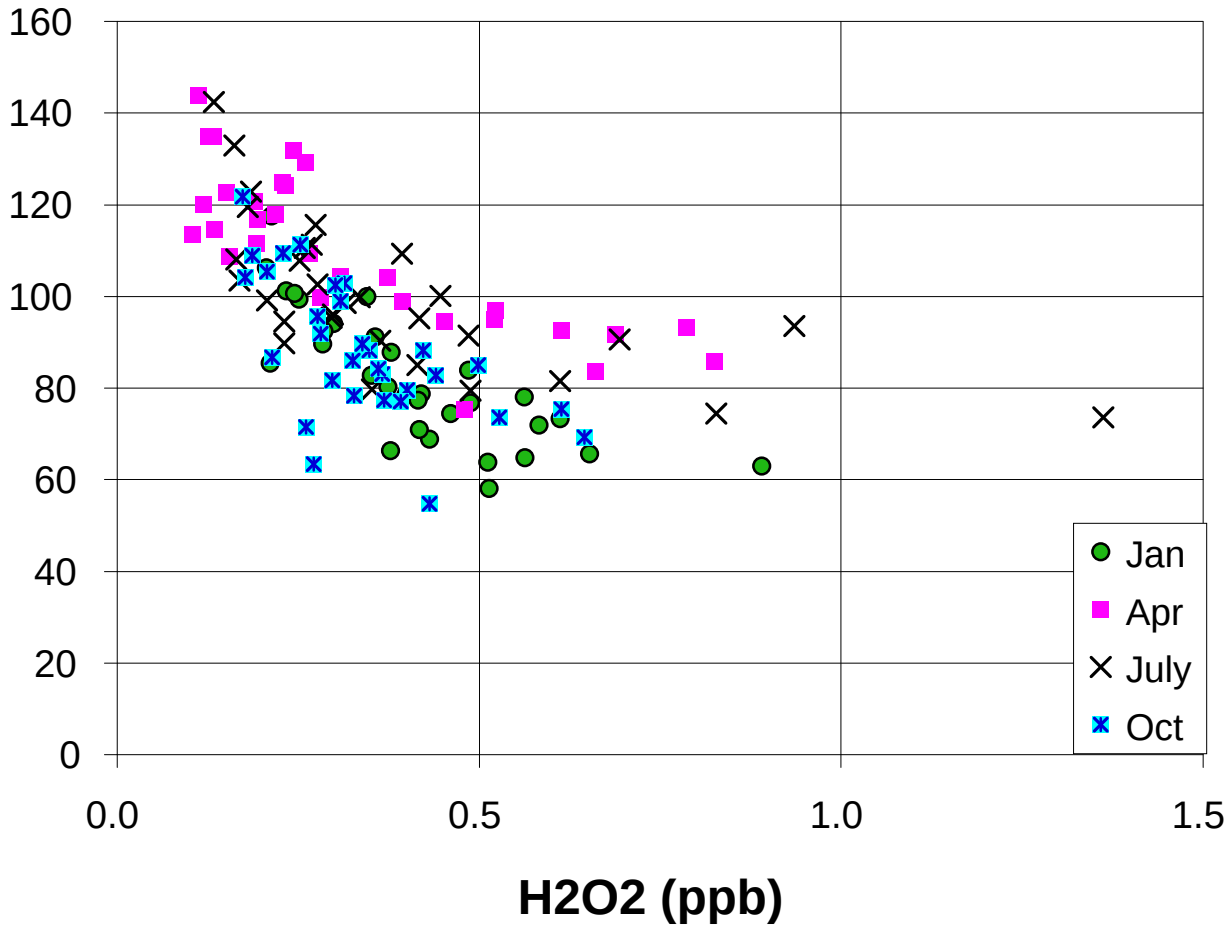
Model O_3 vs H_2O_2

New York/Adirondacks, 99 kPa



Model O_3 vs H_2O_2

New York/Adirondacks, 50 kPa



Conclusions

- Mercury: clear signal for local vs global. (RGM - Hg^0 correlation)
- O_3 - CO slopes:
  - 0.36 for regional production of O_3
  - 0.20 for episodic transport
  - 1.0 for global background p'chem
- O_3-HNO_3 at 50 kPa: signal for background p'chem
- Is there an ambient signal for future changes in background O_3? (O_3-NO_y, O_3-H_2O_2?)
- Next: Evaluate with tracers; measurements