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

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Grant #

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

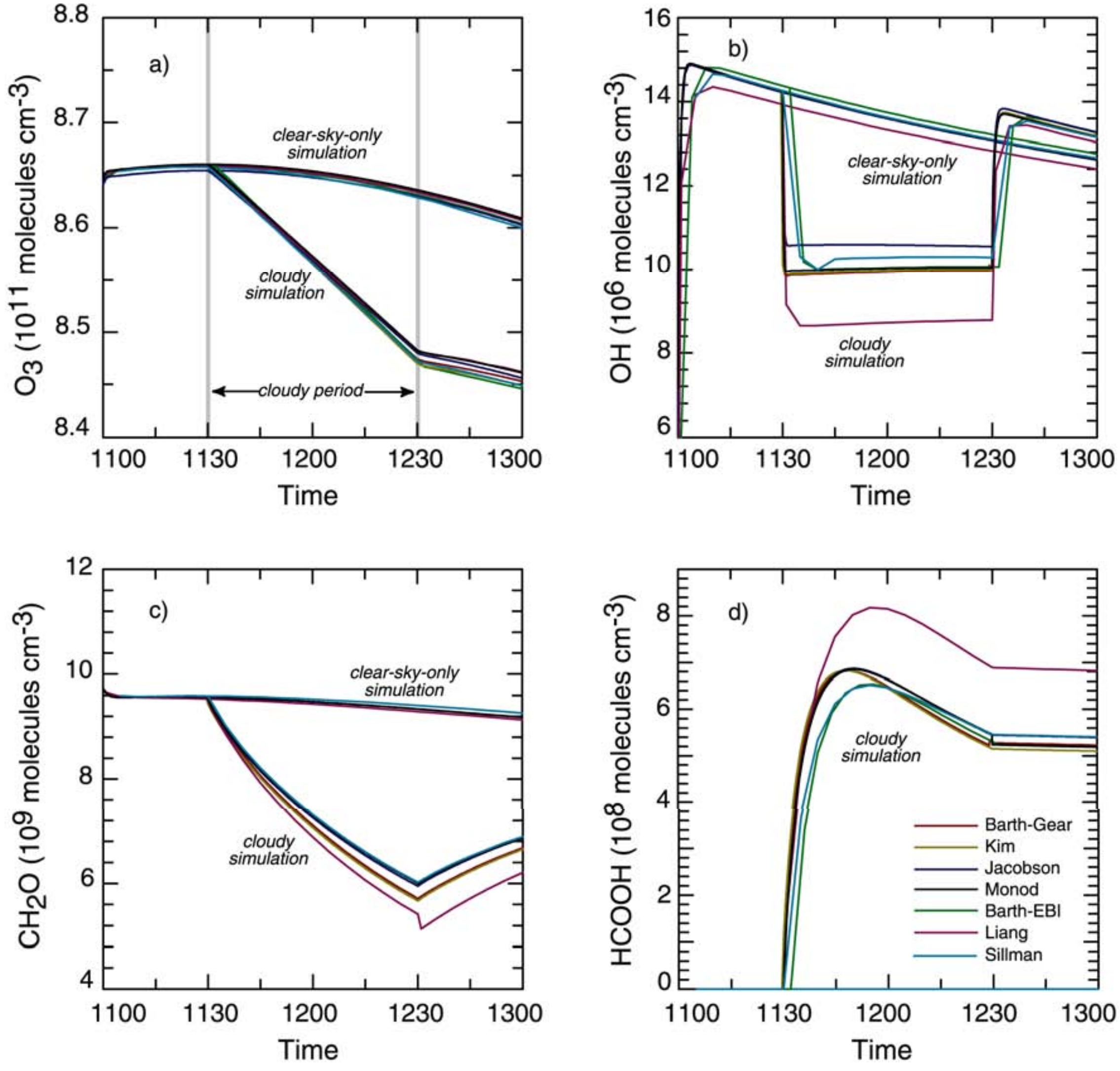
Modifications to CMAQ

- 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

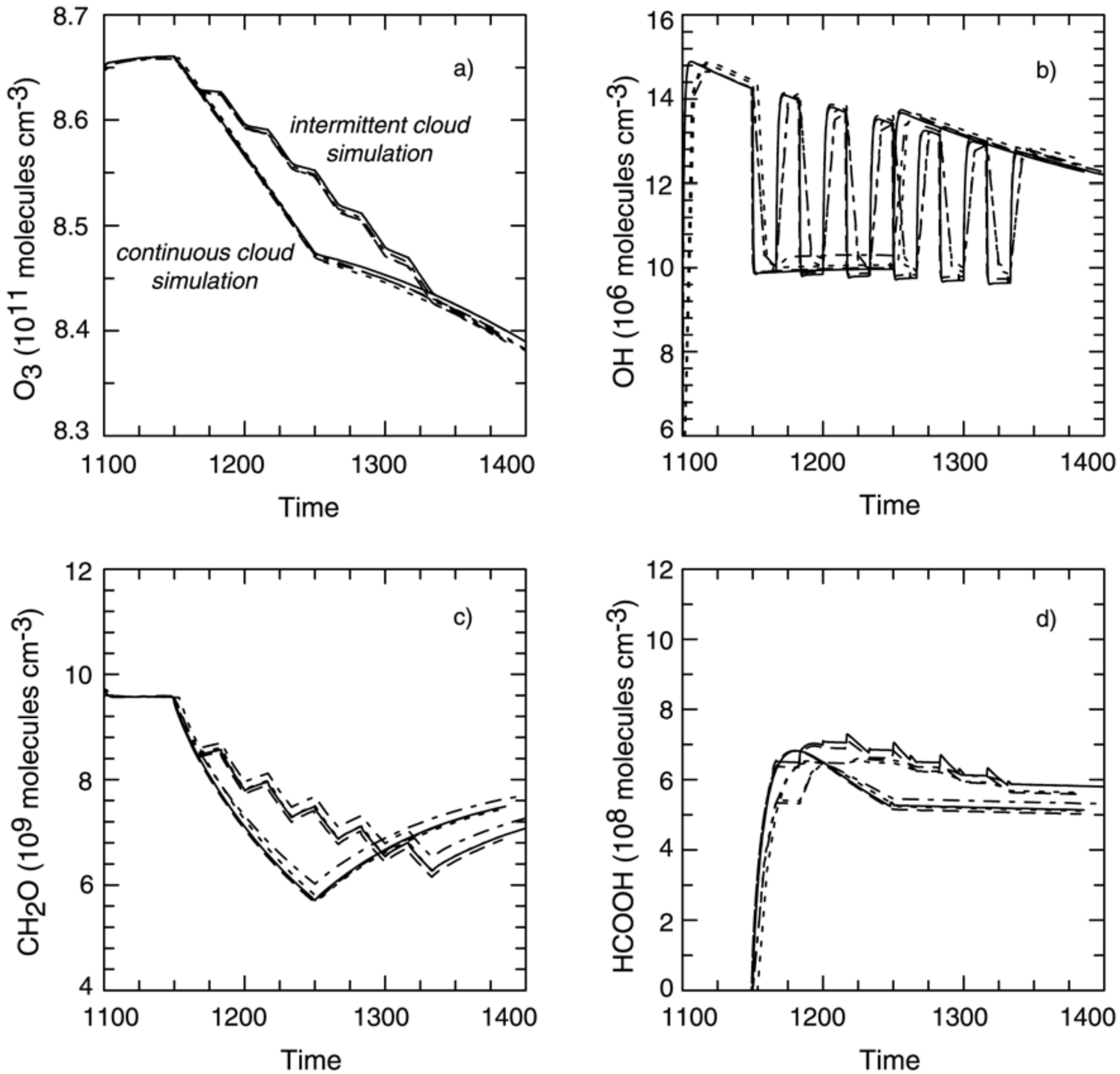
Numerical solution for gas+aqueous photochemistry

- 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)

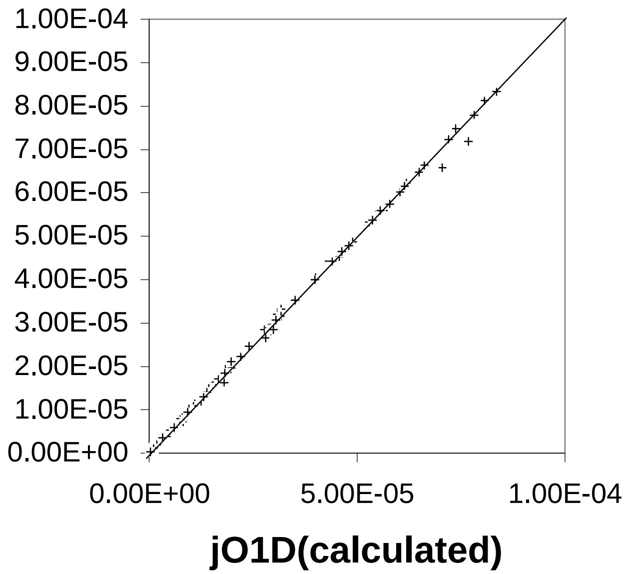


Intermittant clouds
(*Barth et al*., 2003)

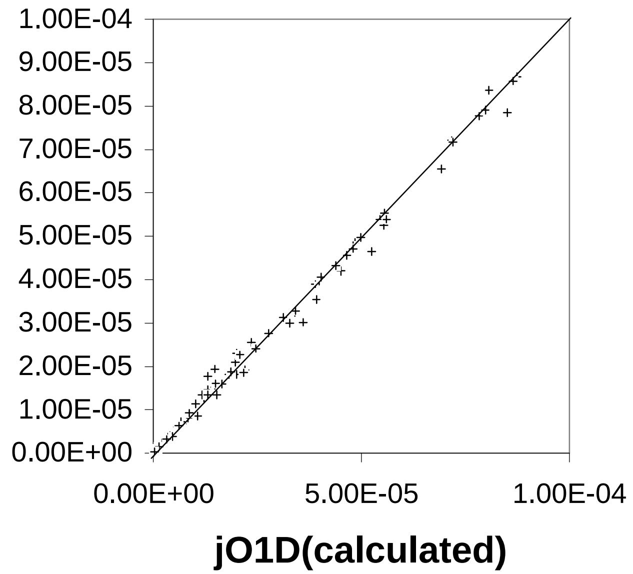


Evaluation of photolysis parameterization (vs. TUV model, Madronich and Flocke)

Single cloud layer



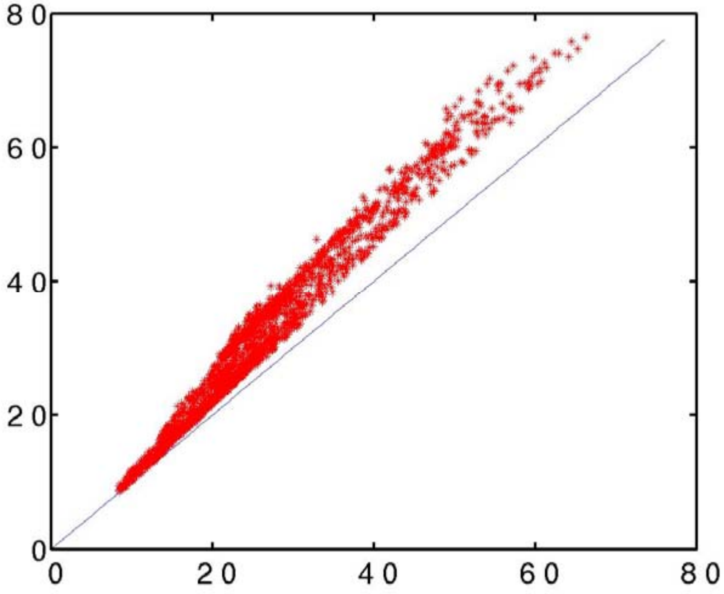
Two cloud layers

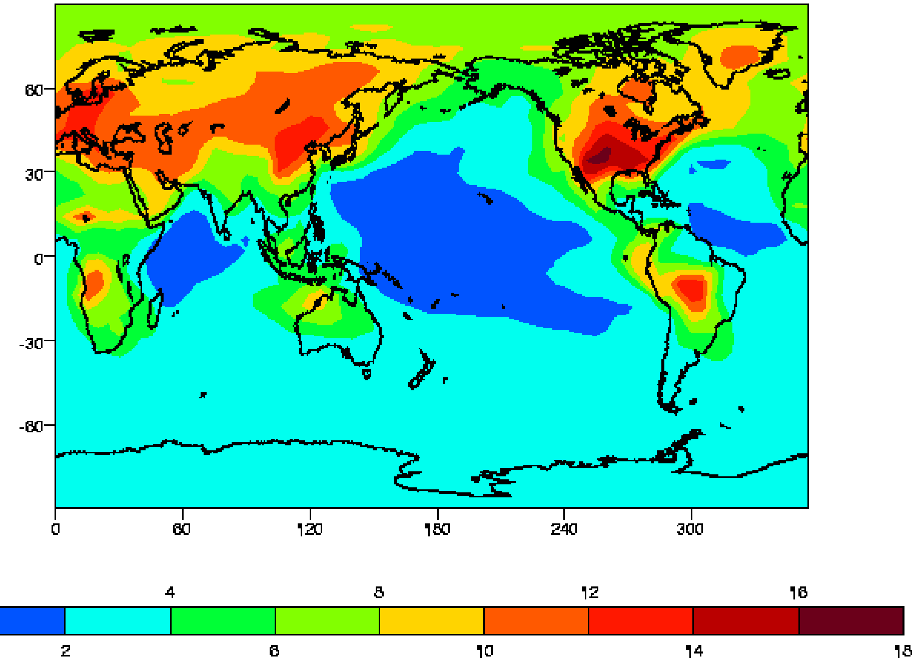


Previous result: global O_3

- 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

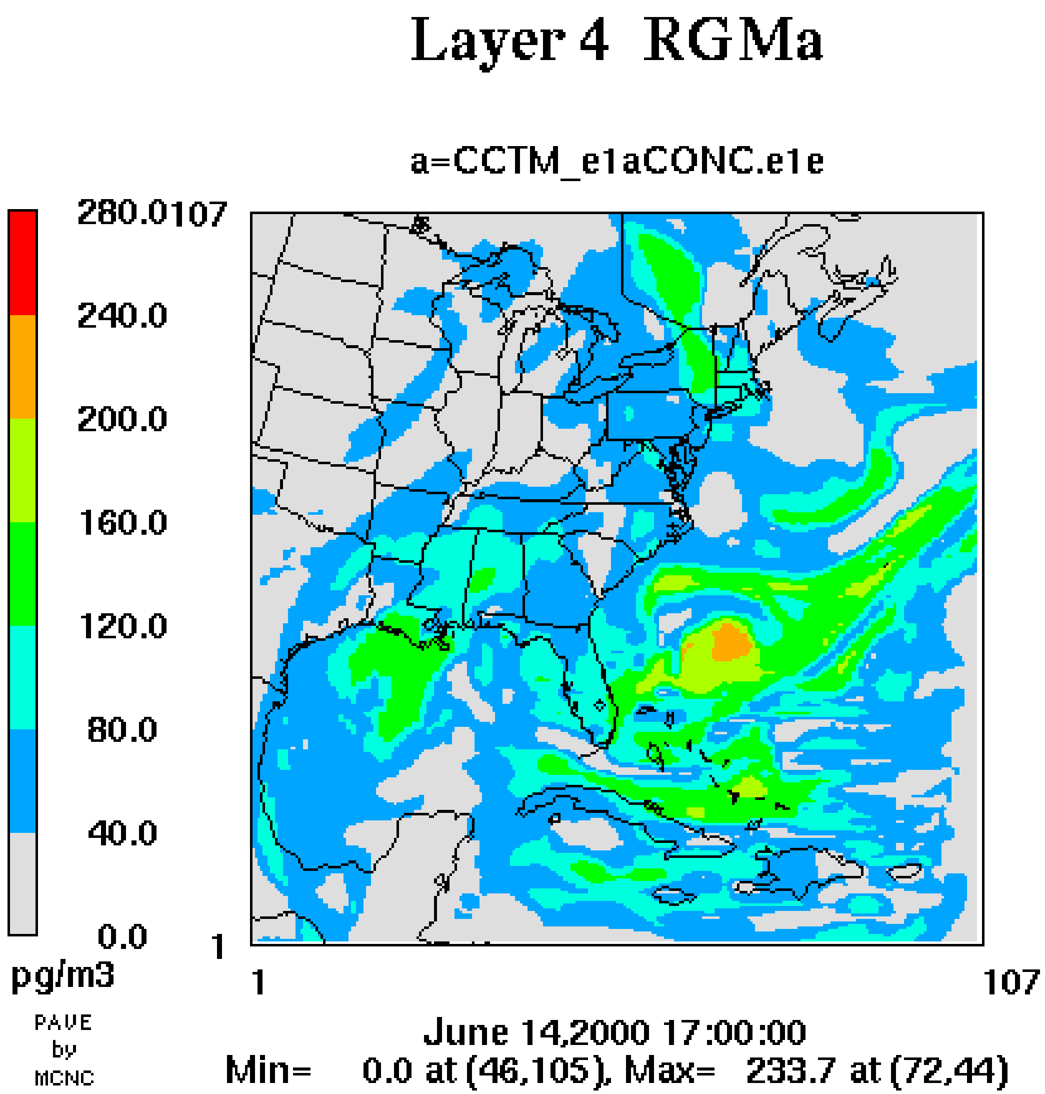
(aqueous phase)

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

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

RGM at 3000m

Sillman et al, JGR, submitted

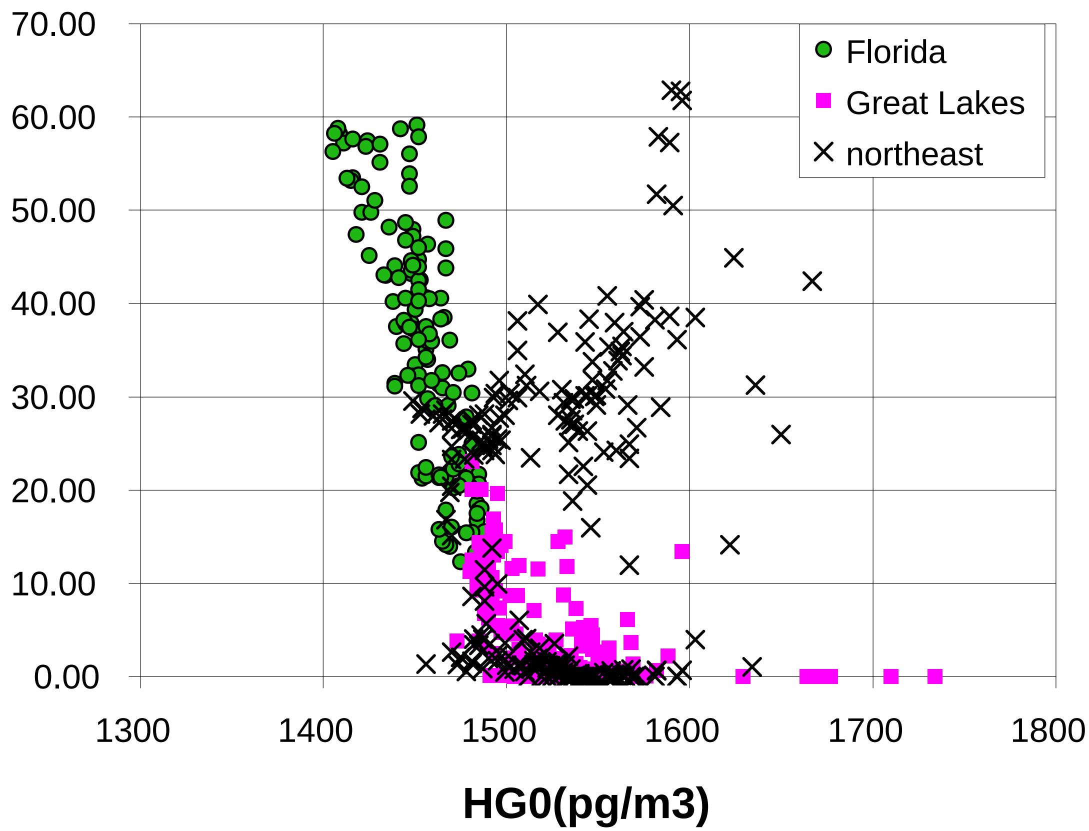


Prior result: mercury

- 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)

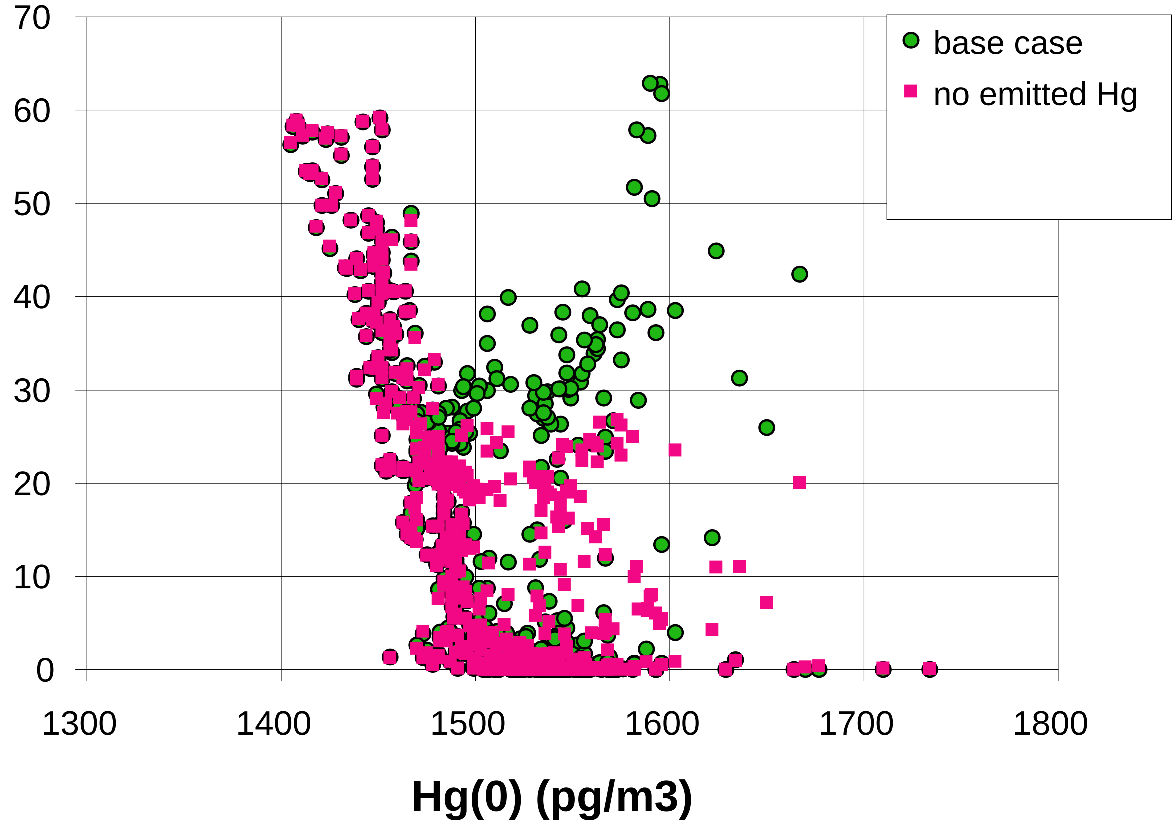
(WARNING: Results do not preclude impact from local Hg in Florida)

RGM vs Hg0

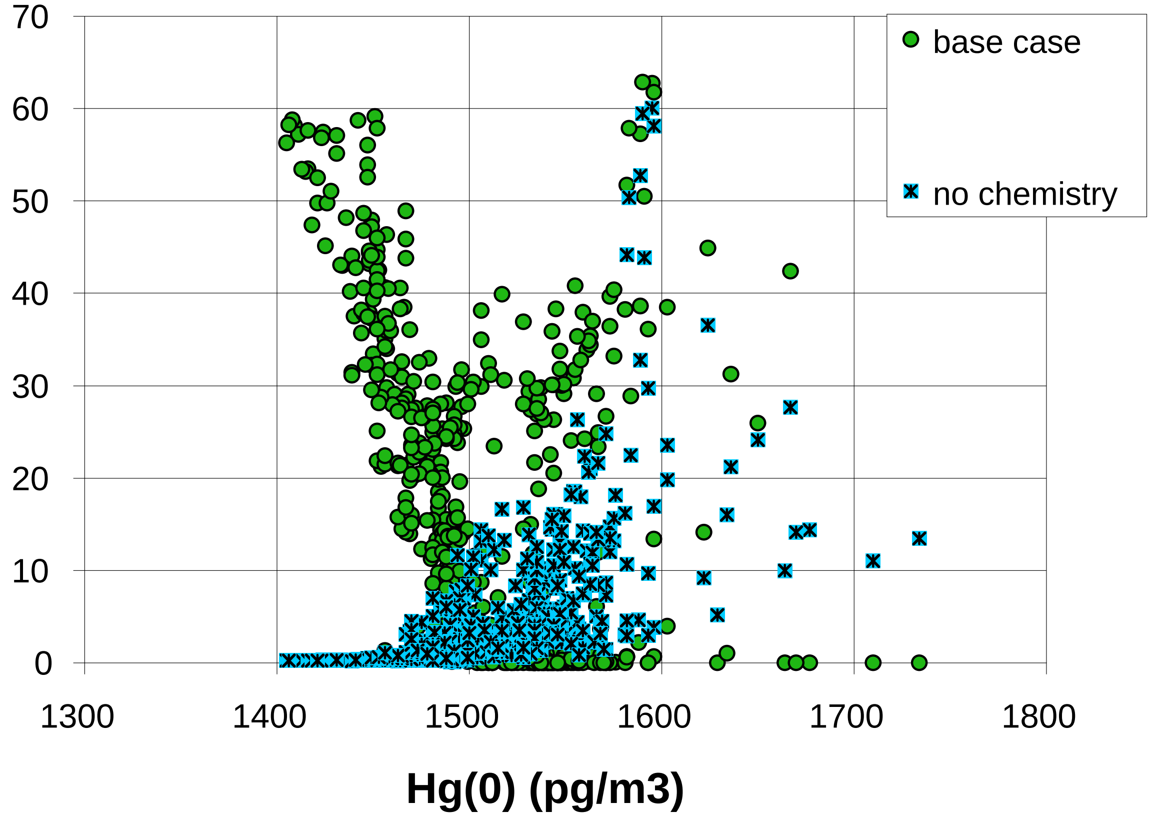


70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
1300
1400
1500
1600
1700
1800
HG0(pg/m3)
Florida
Great Lakes
northeast

RGM vs Hg0: zero emissions



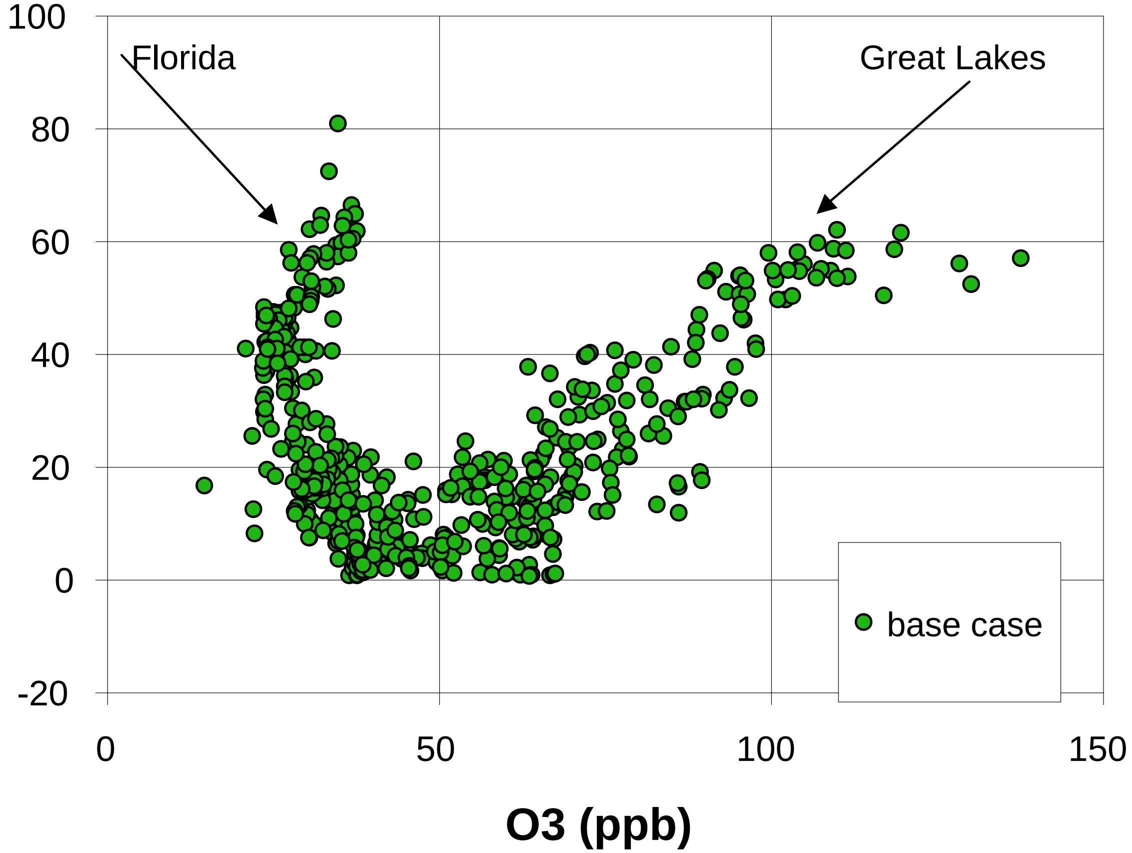
RGM vs Hg0: zero background Hg



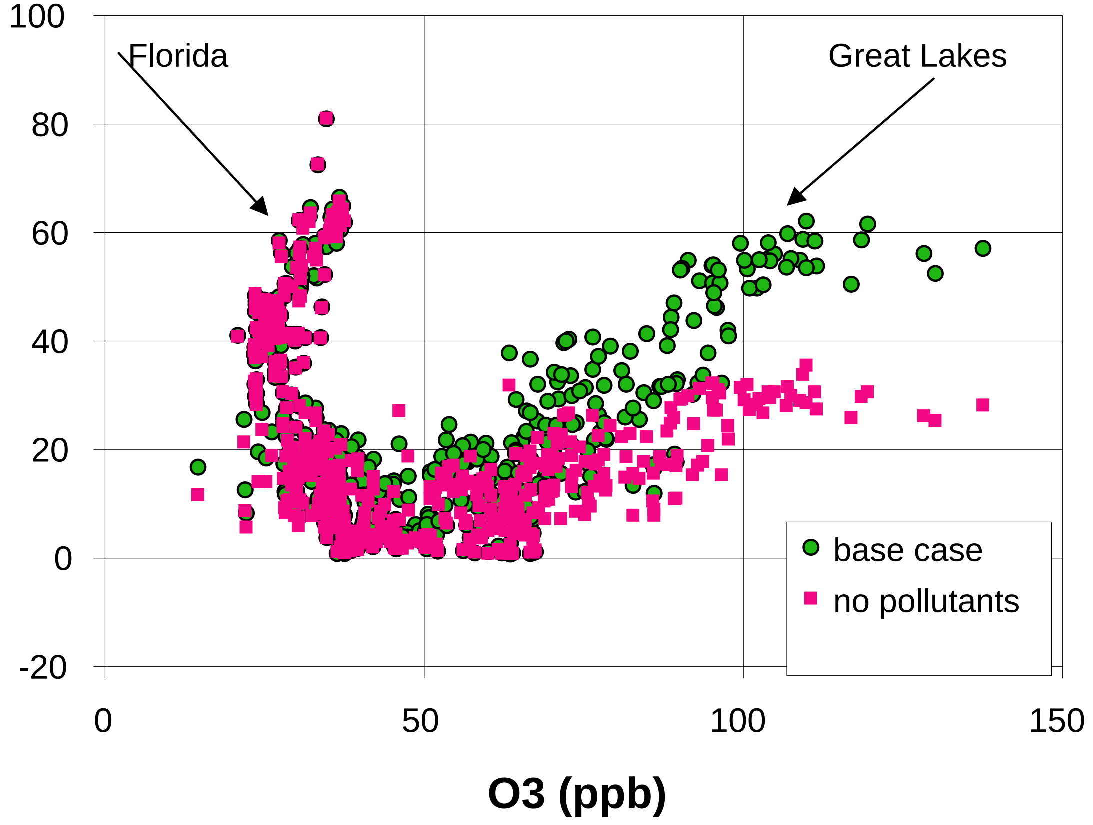
Prior result: O_3 and mercury

- 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:

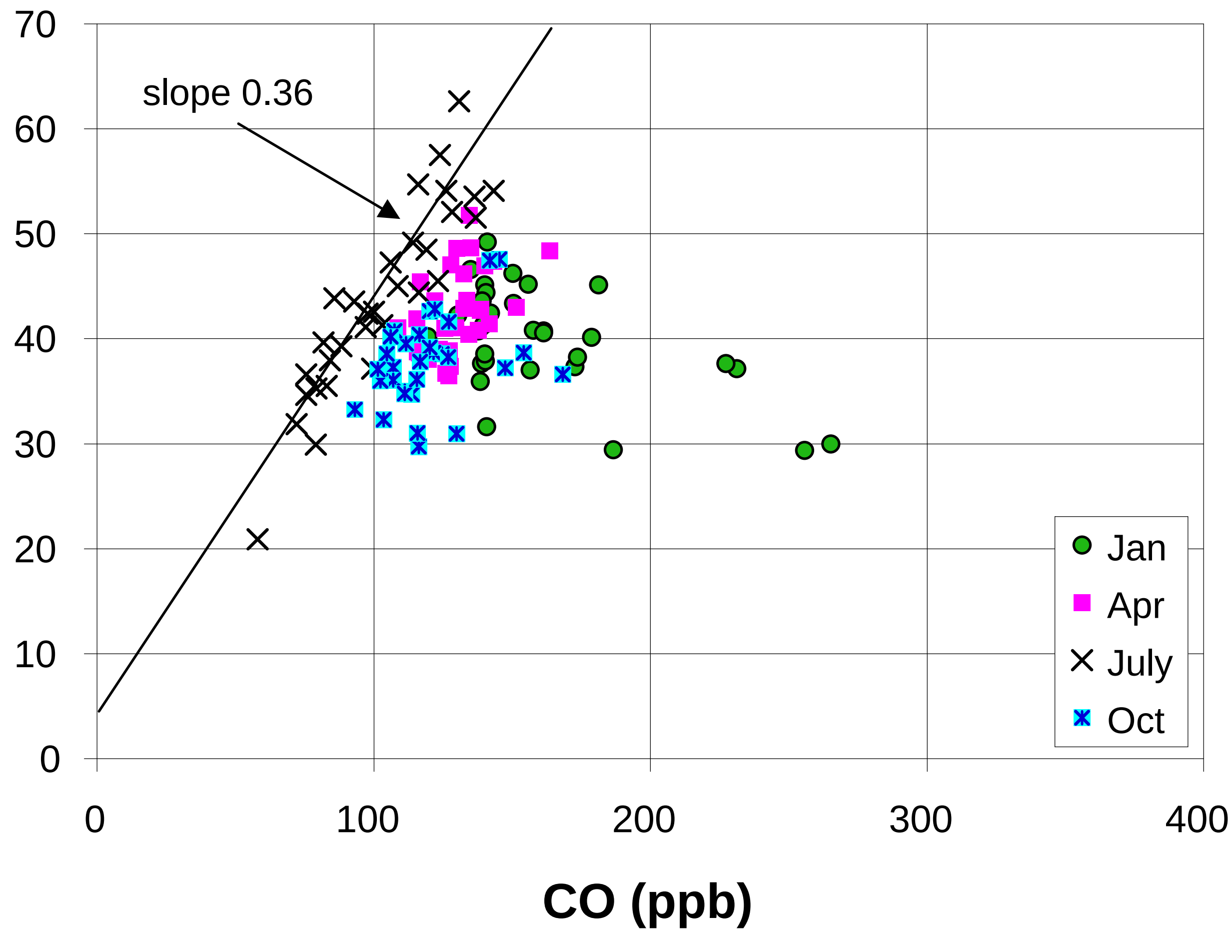
Can species correlations provide a measurement-based signal for the impact of global-scale processes on local O_3?

- (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

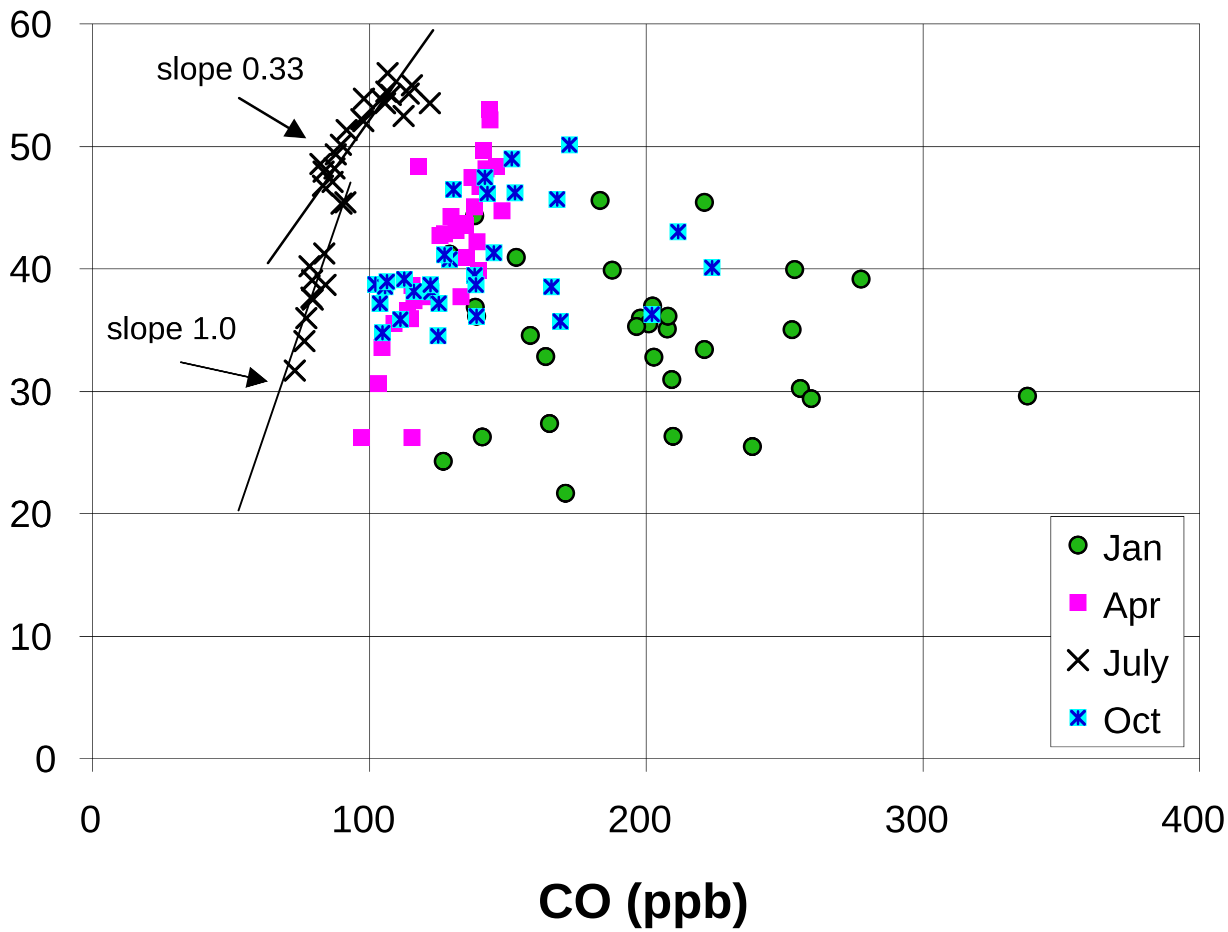
summer slope 0.36: Episodic transport?



Model O_3 vs CO

California/Sierra Nevada

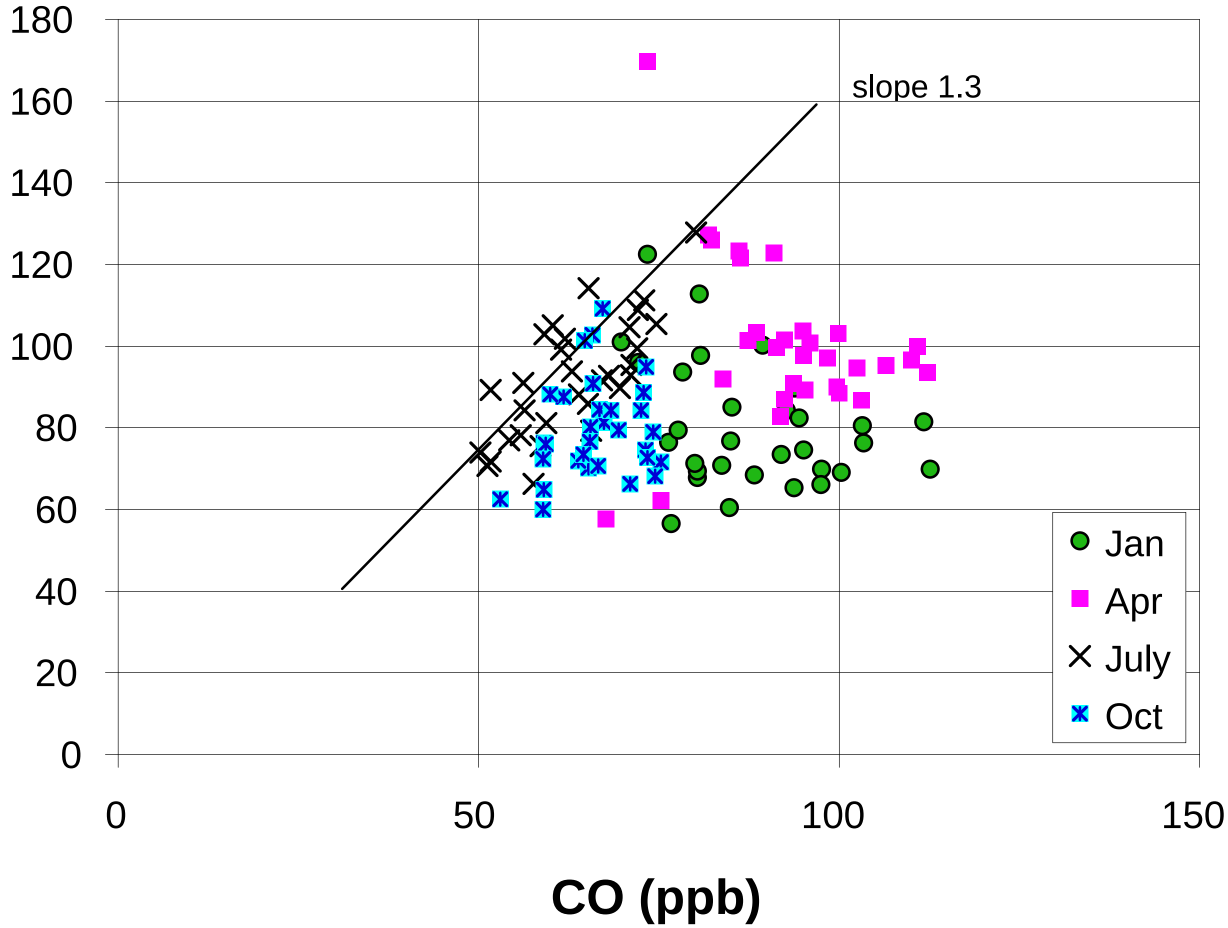
slope >1.0 = global background?



Model O_3 vs CO

California/Sierra Nevada, 50 kPa

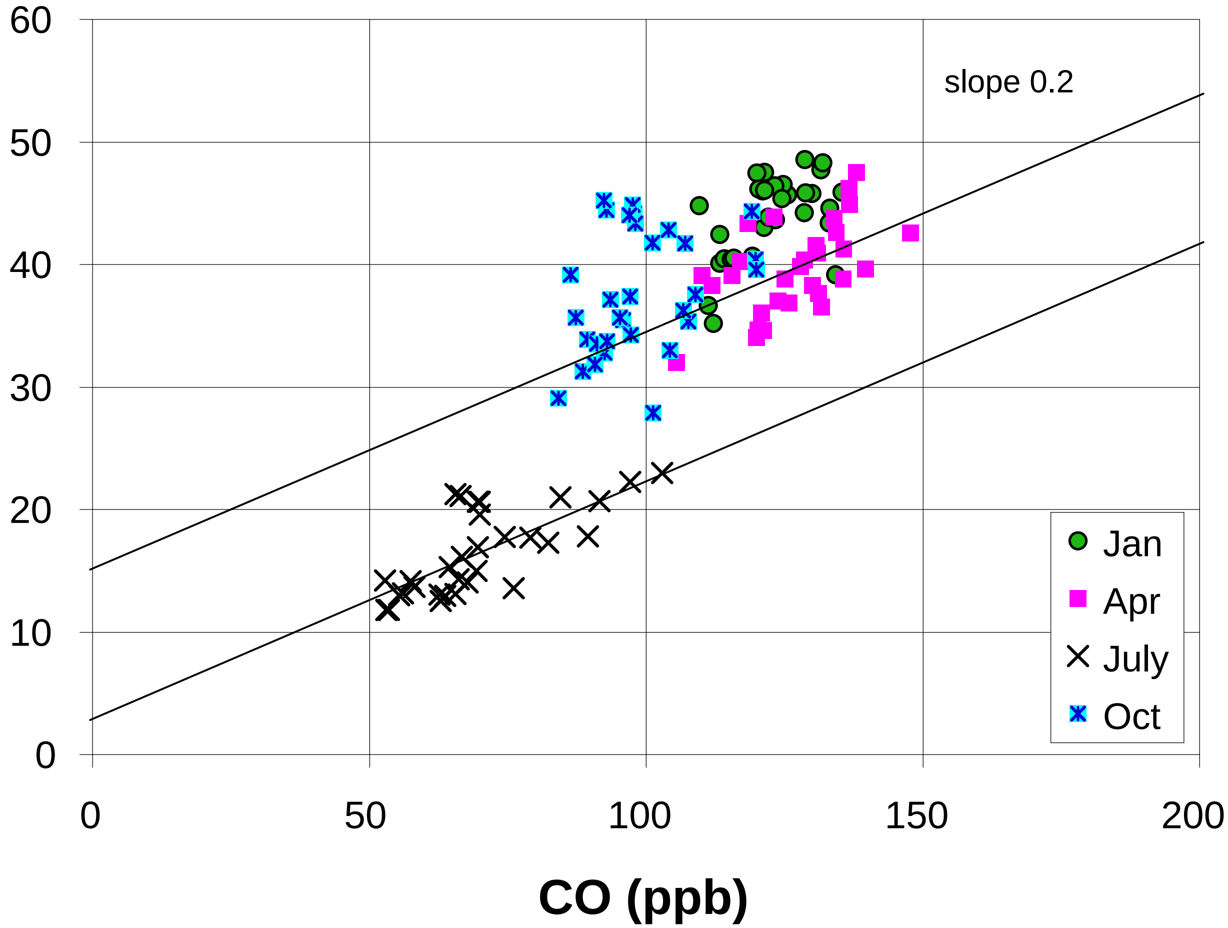
slope >1 is common at 50 kPa



Model O_3 vs CO

Aleutians

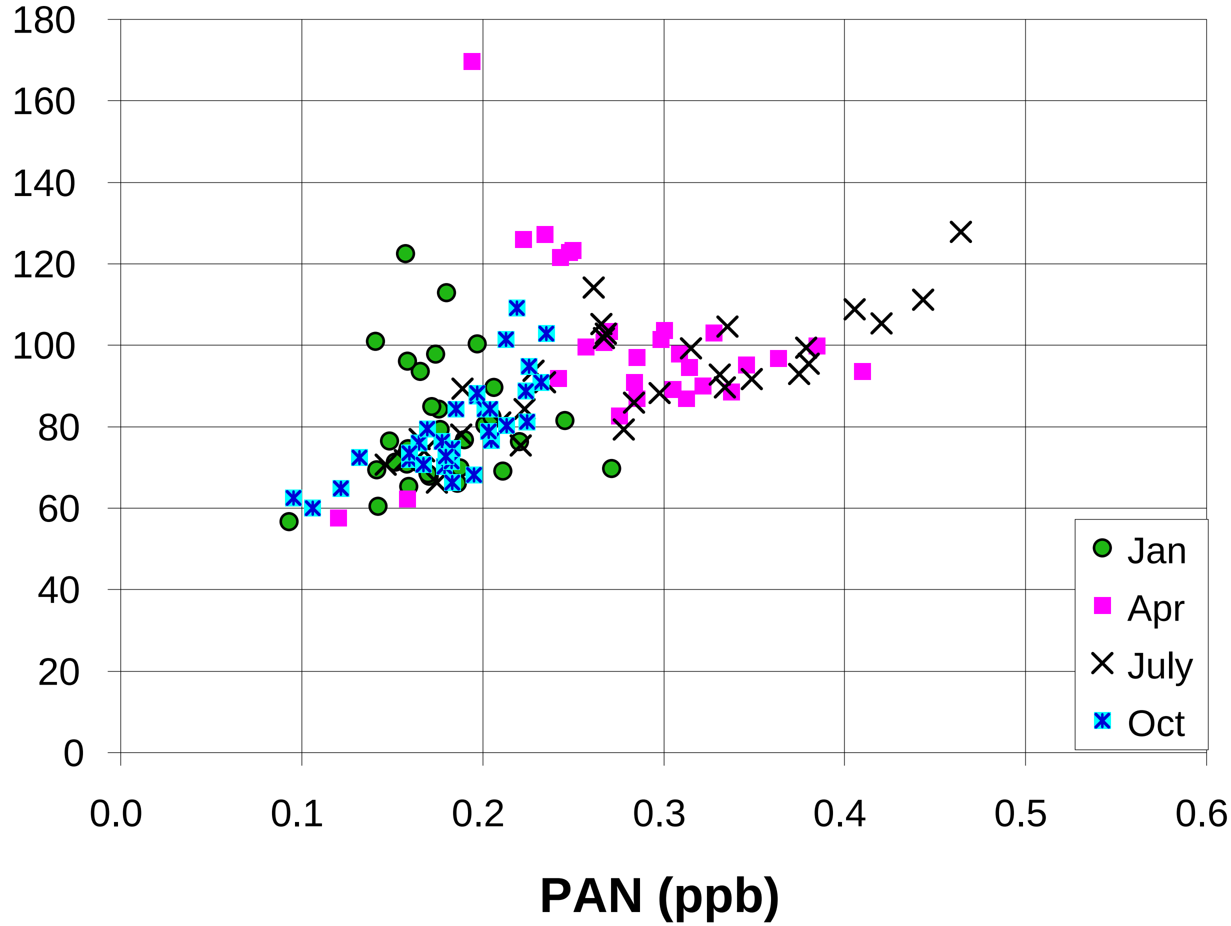
slope 0.2=episodic transport w/O_3 loss?



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)

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Partial list of references

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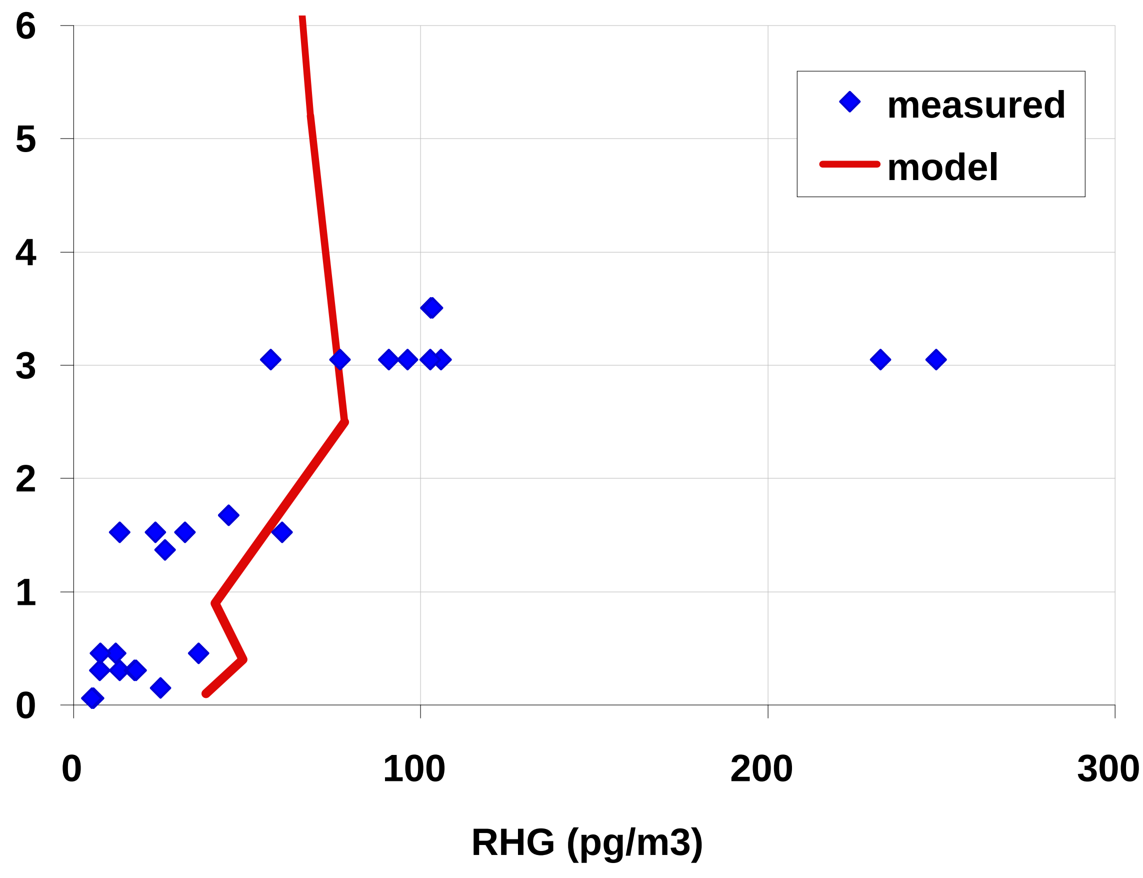
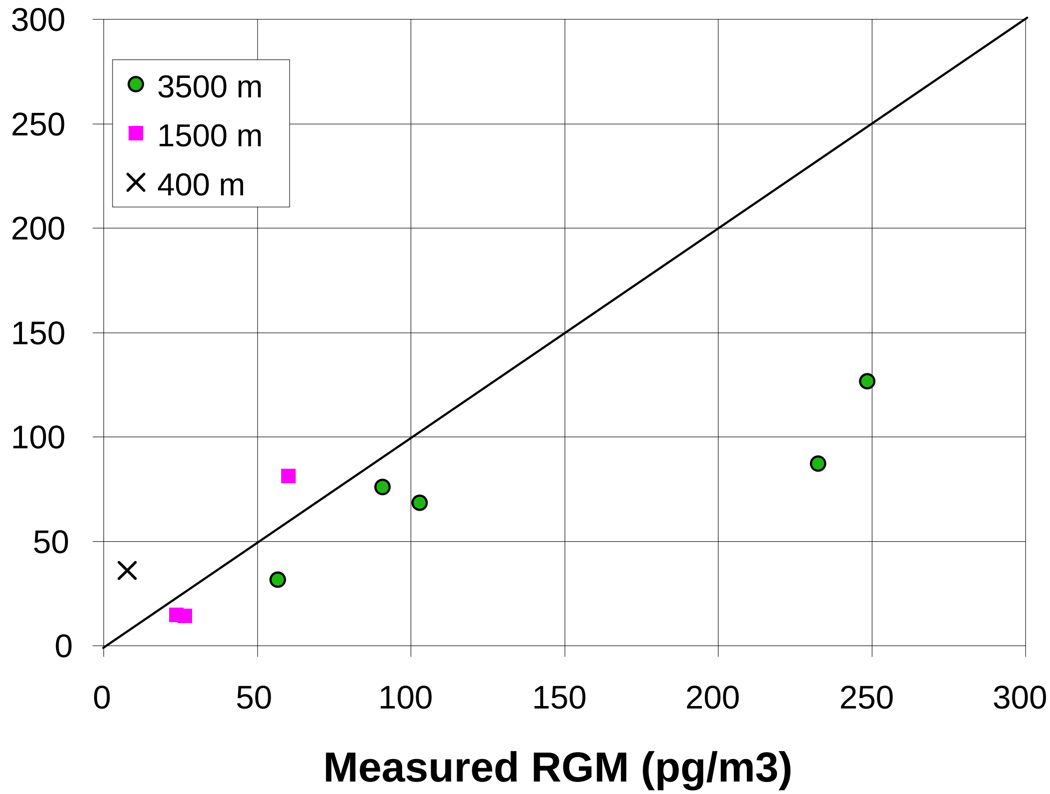
von Kuhlmann, R., M. G. Lawrence, U. Pöschl, and P. J. Crutzen (2004), Sensitivities in global scale modeling of isoprene, *Atmos. Chem. Phys.*, *4*, 1-17.

Additional slides

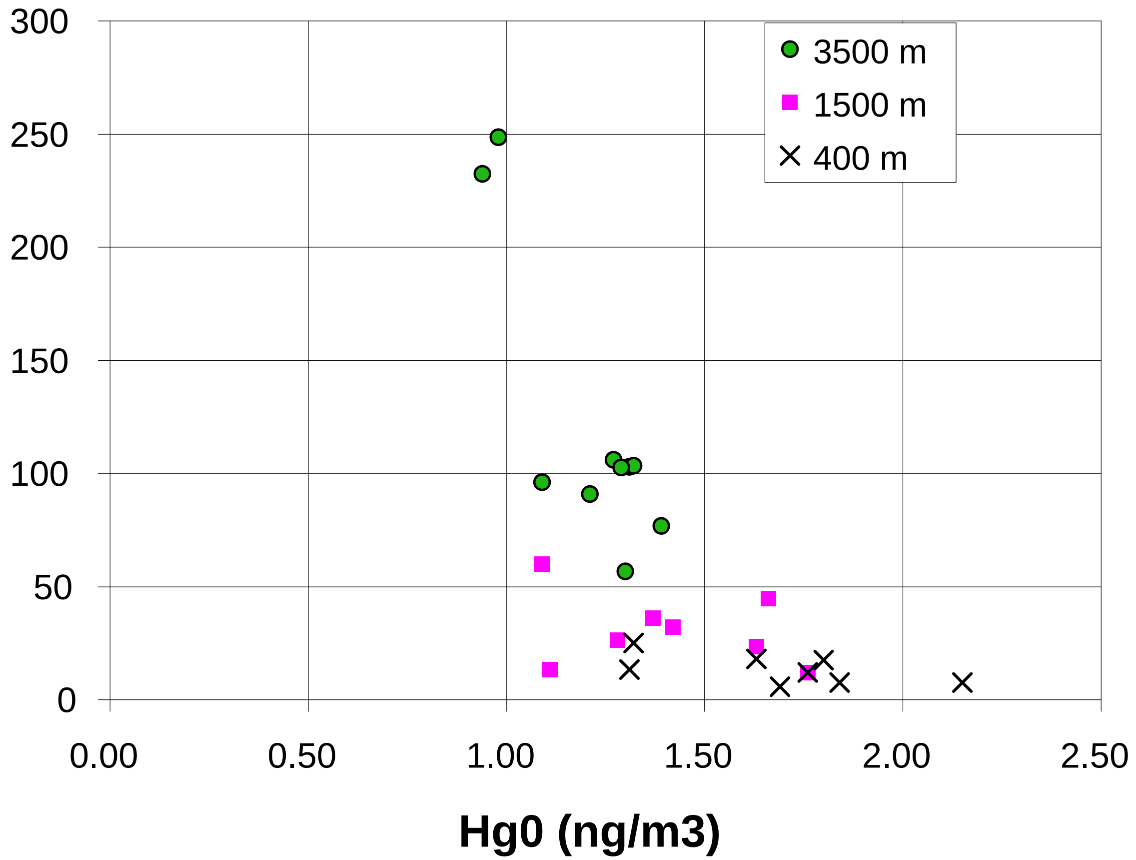
RGM vs altitude: Model and measurements (Landis)



Model vs measured RGM in Florida

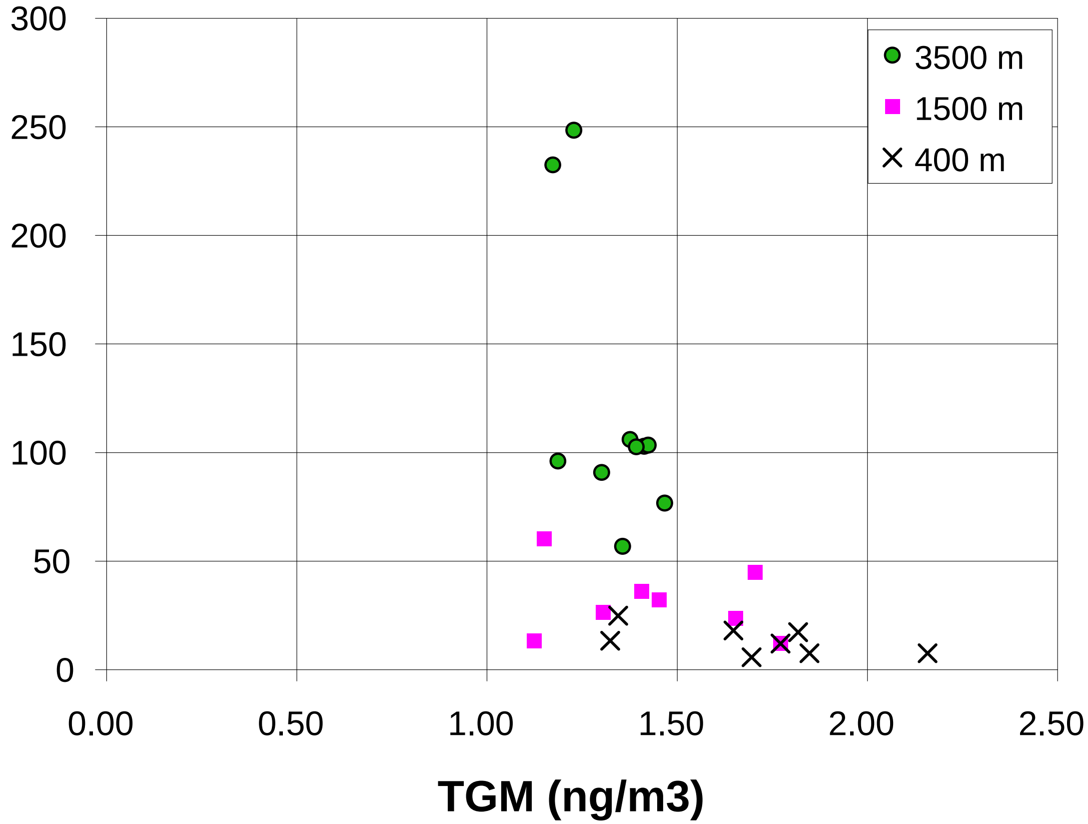


RGM v Hg0: Florida June measurements
(Landis)



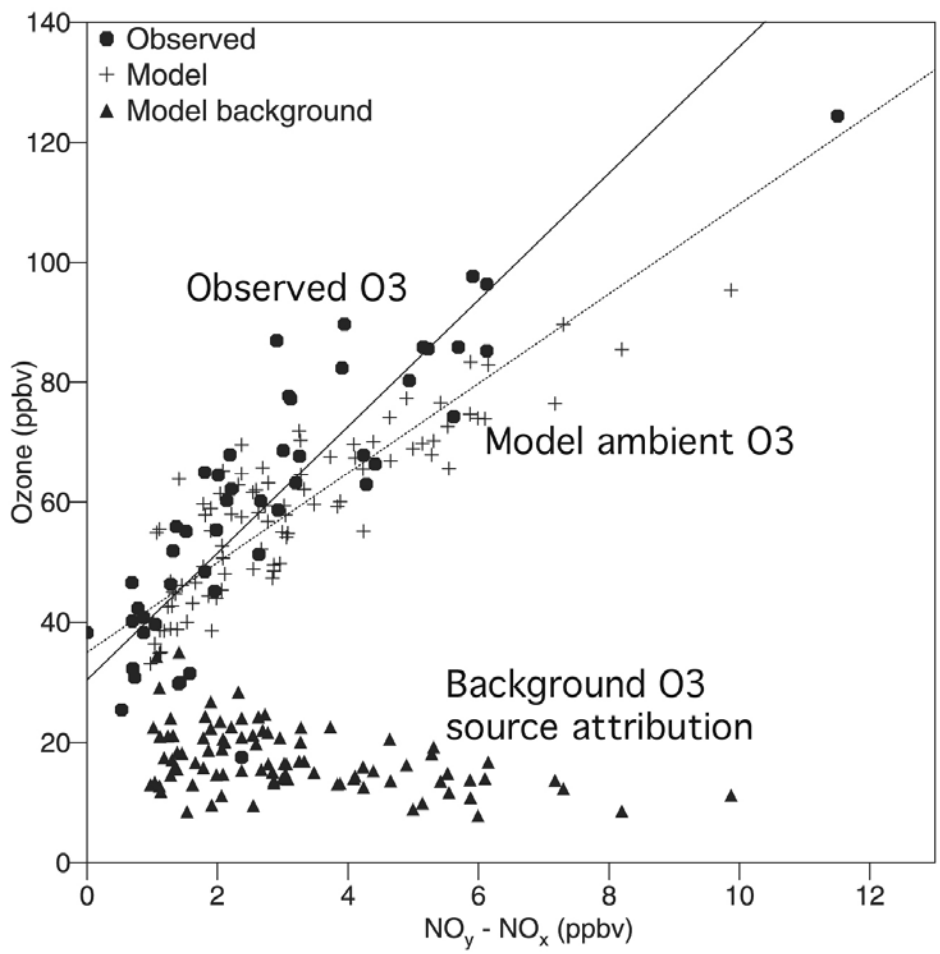
RGM vs Total Hg: June measurements

(Landis)



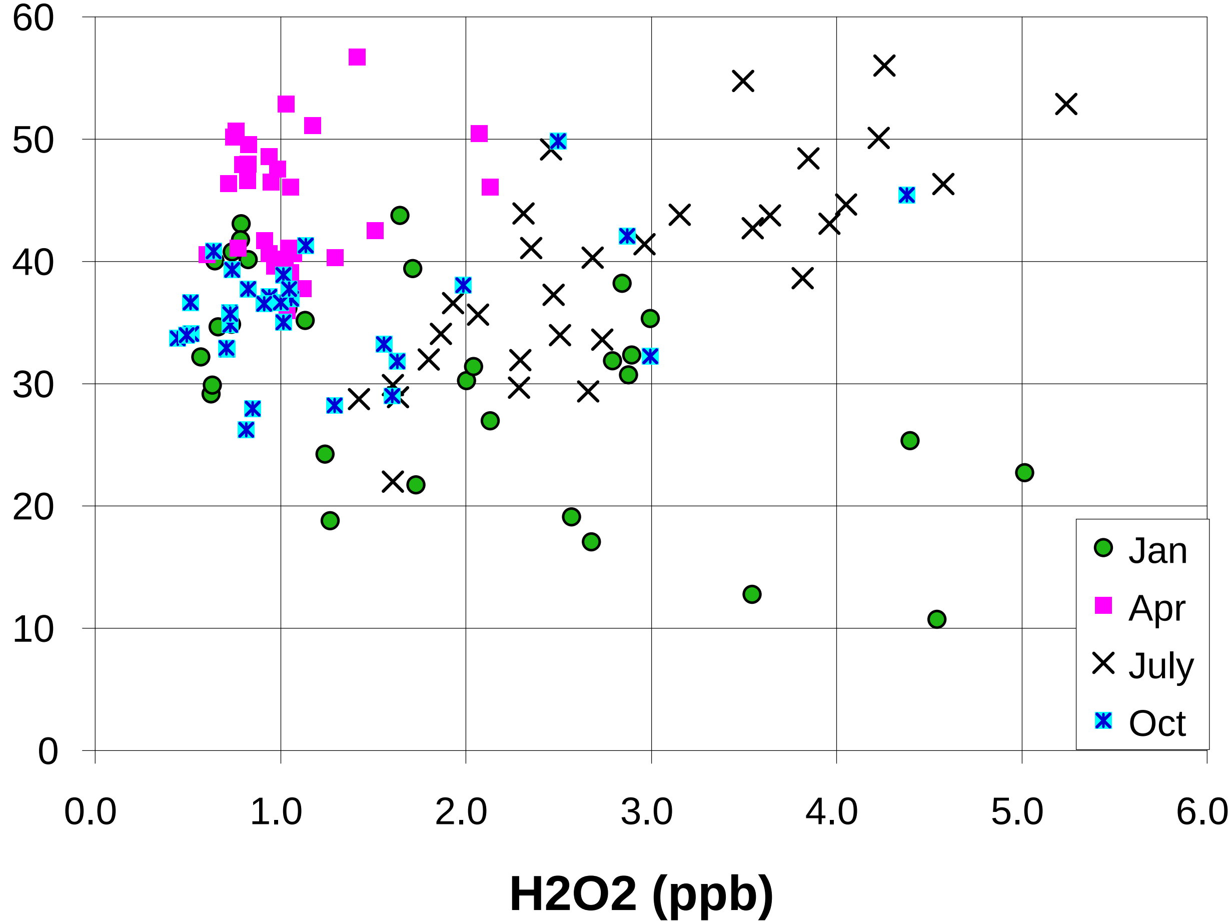
Transported O3 and source attribution:
O3 vs NOy (*Fiore et al*., 2002)

Impact is smaller than inferred global background!



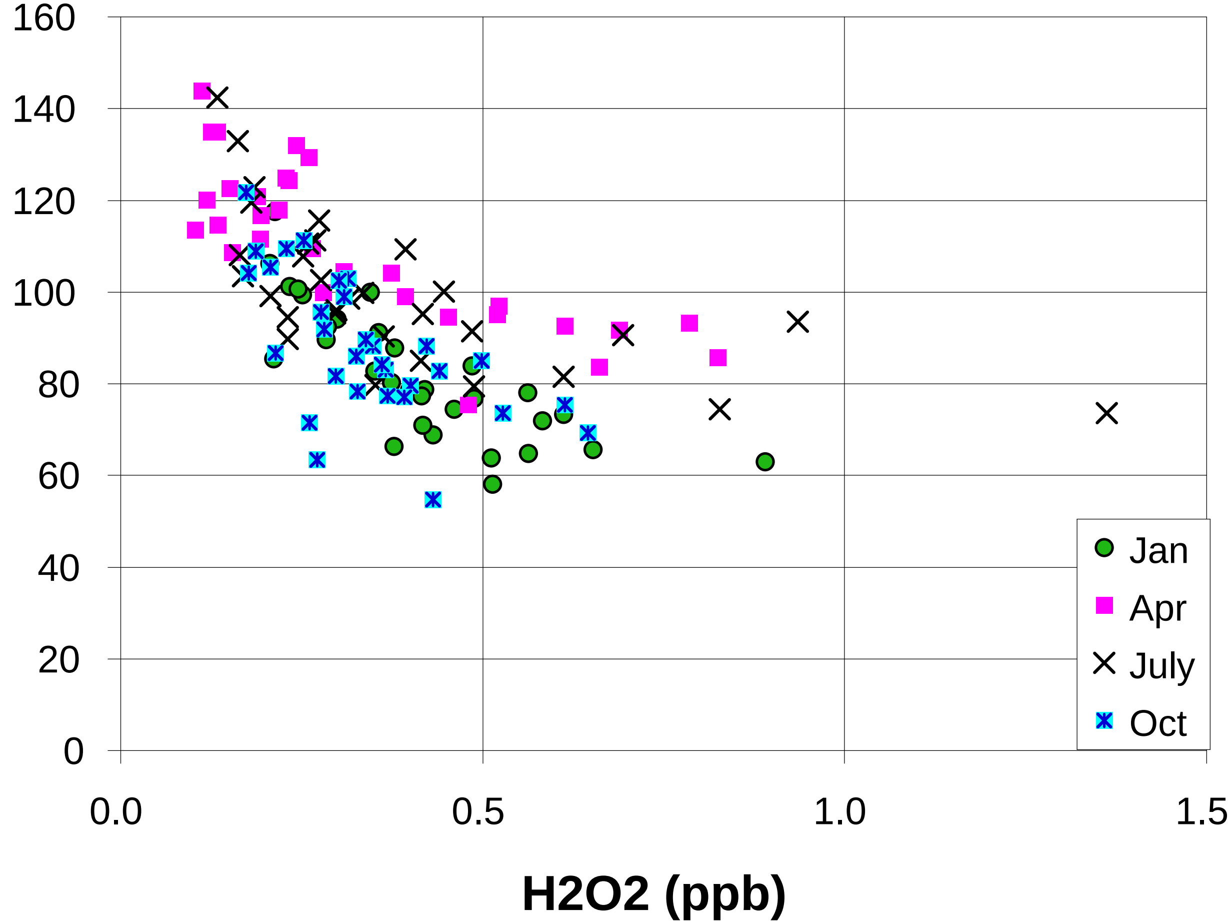
Model O_3 vs H_2O_2

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