

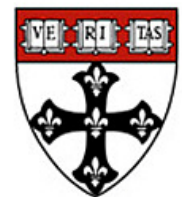
Overview of challenges using speciated Hg measurements to support model evaluation and development

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28 July 2014
Workshop @ Earth Science-2014

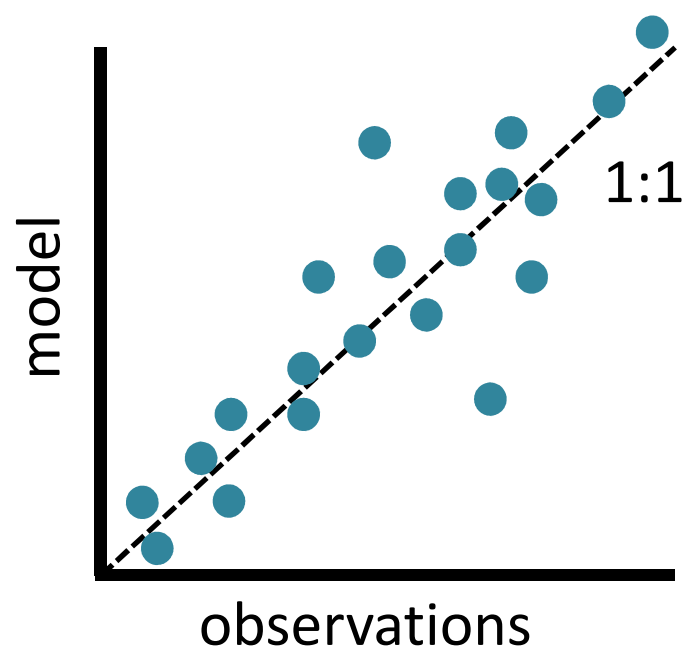


Harvard School of
Public Health

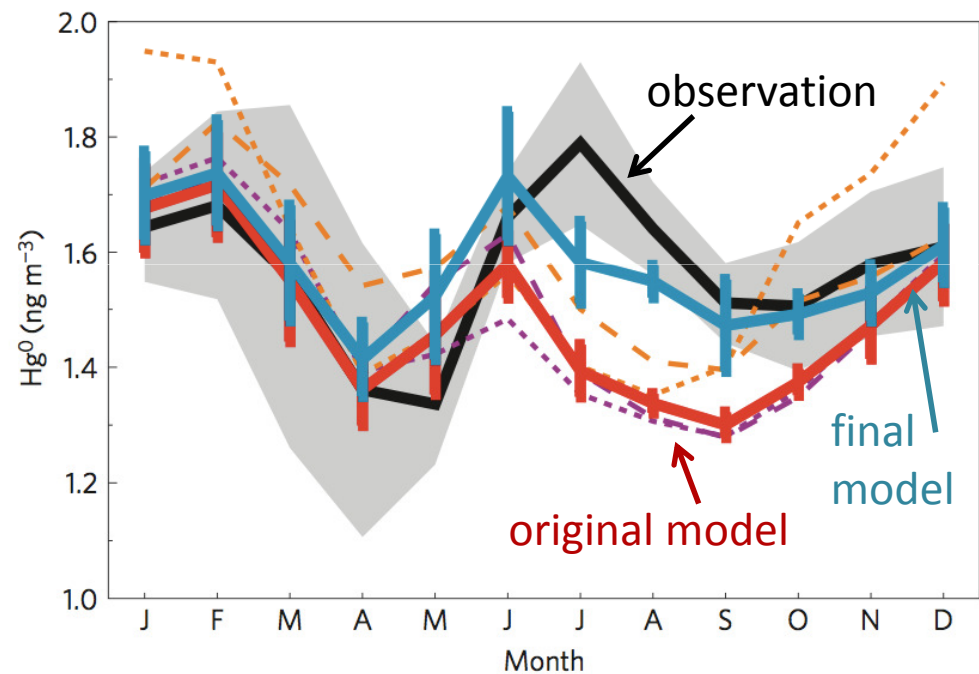


Observations support model evaluation and model development

Evaluation



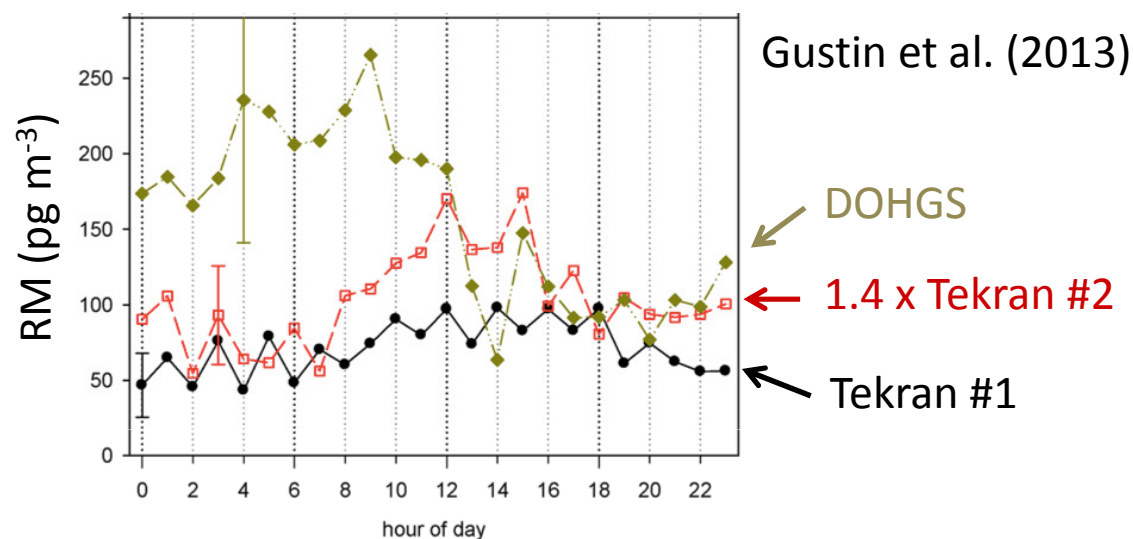
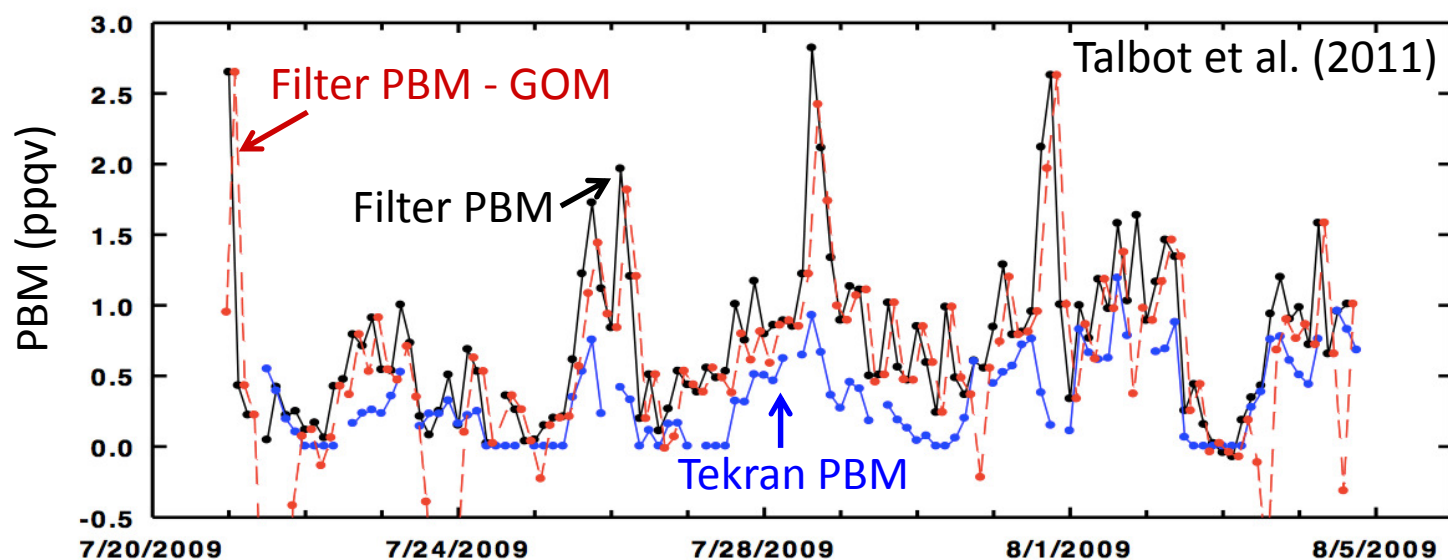
Development



Fisher et al. (2012)

The most interesting science happens when the model and observations don't agree.

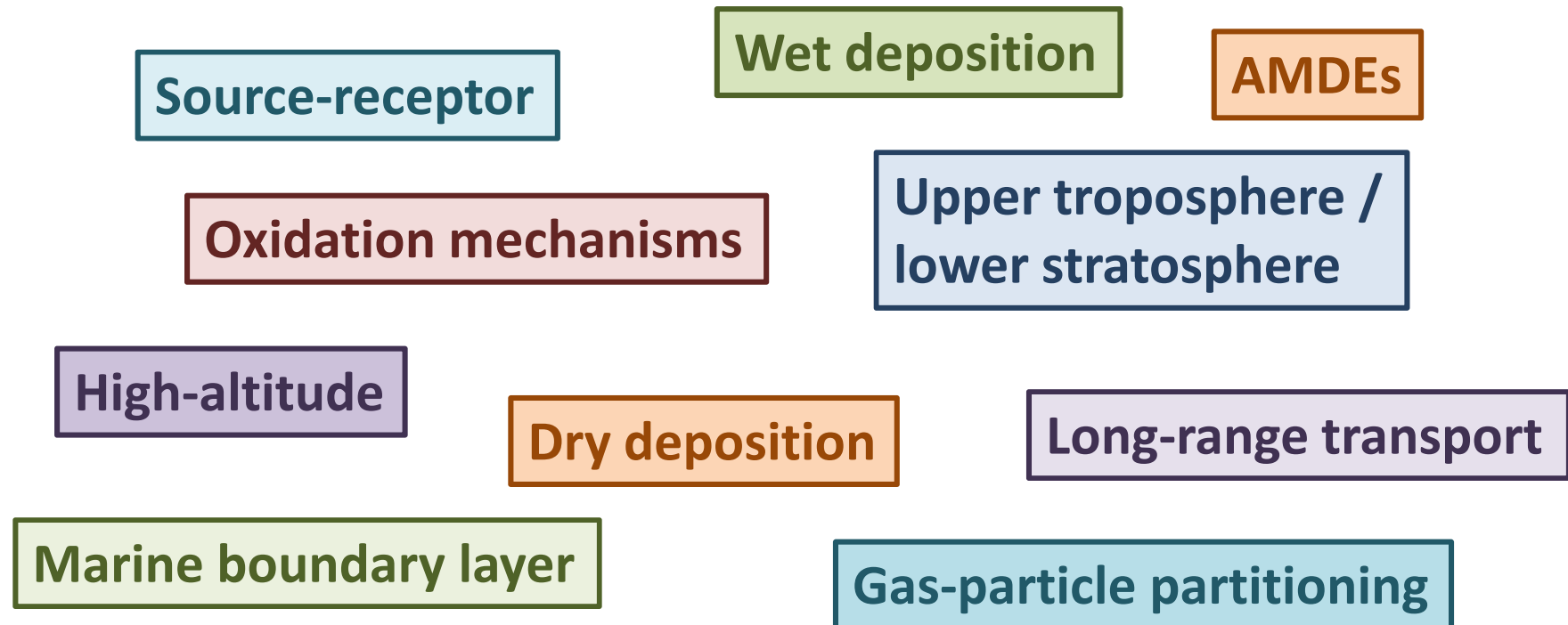
Mounting evidence suggests Tekran GOM and PBM have substantial problems



Numerous models simulate speciated atmospheric mercury

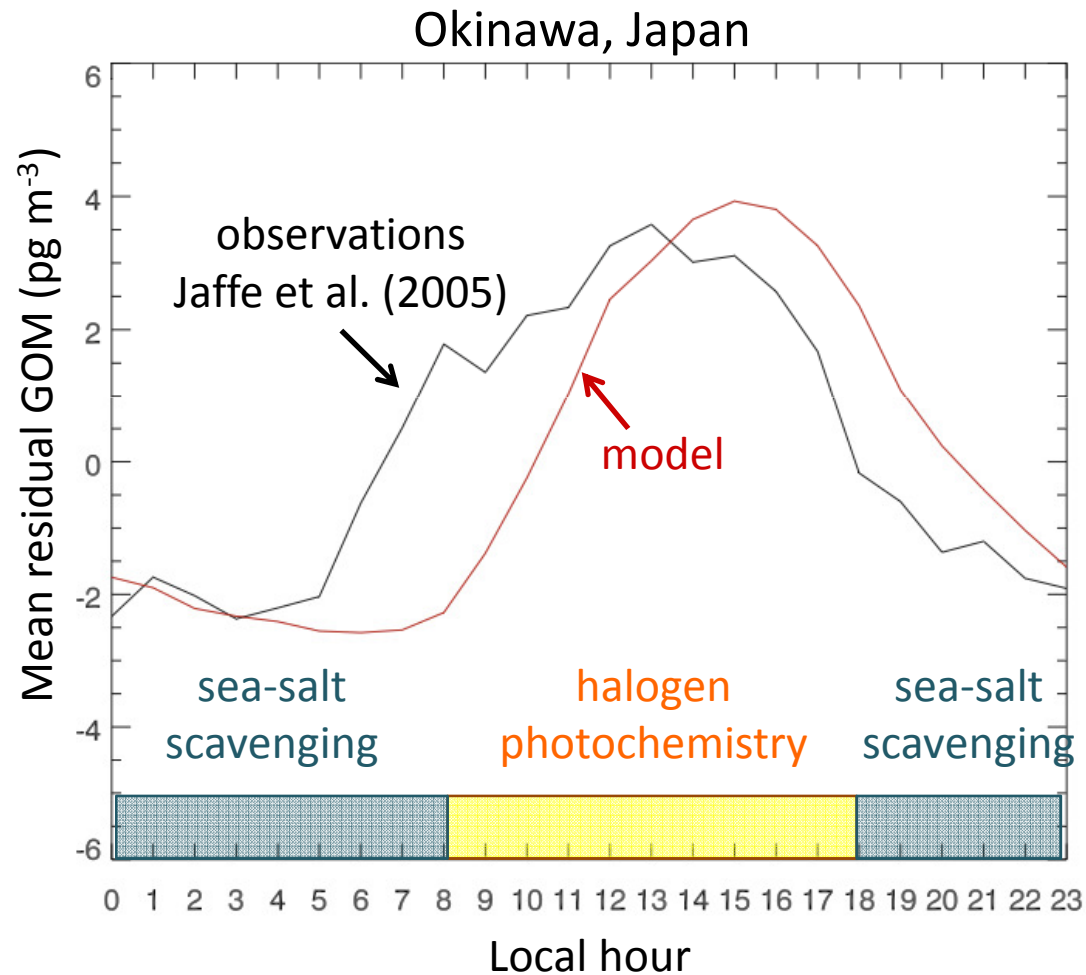


What are the topics being studied with speciated Hg models?



What have we learned from this work?

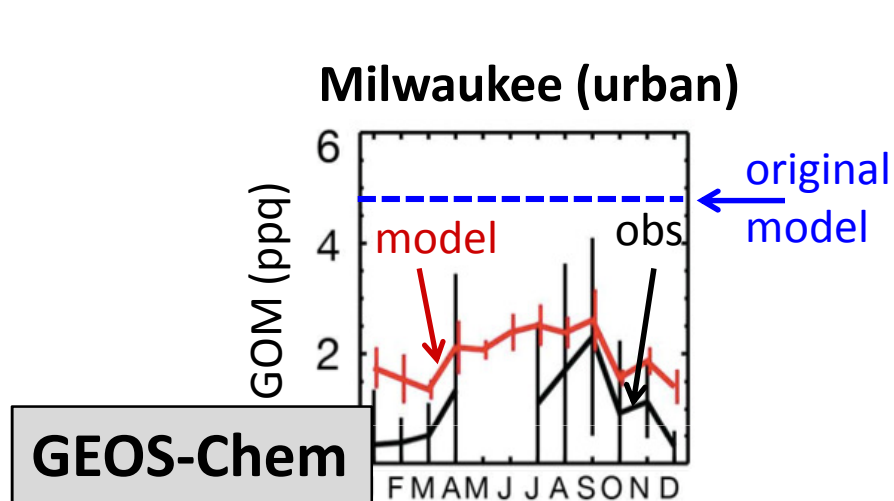
Halogen chemistry and sea-salt drive GOM diurnal variability in the marine boundary layer



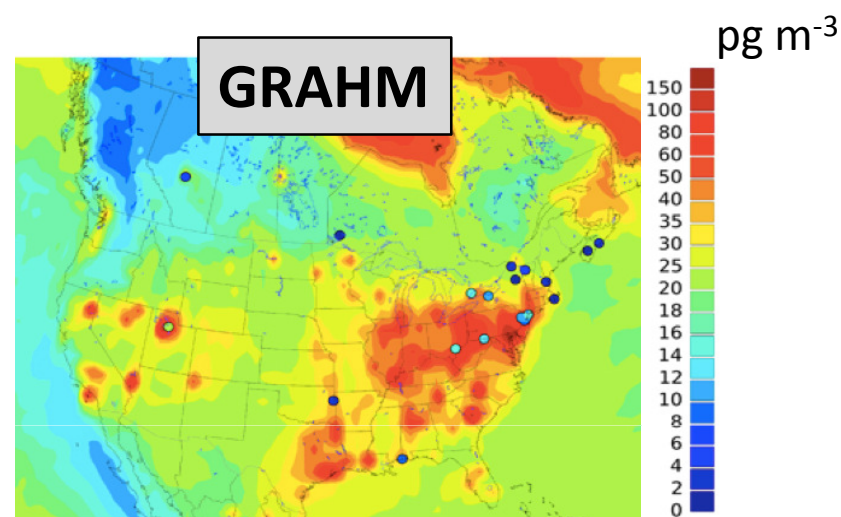
Selin et al. (2007)

Hedgecock & Pironne (2001; 2004); Hedgecock et al. (2003); Holmes et al. (2009)

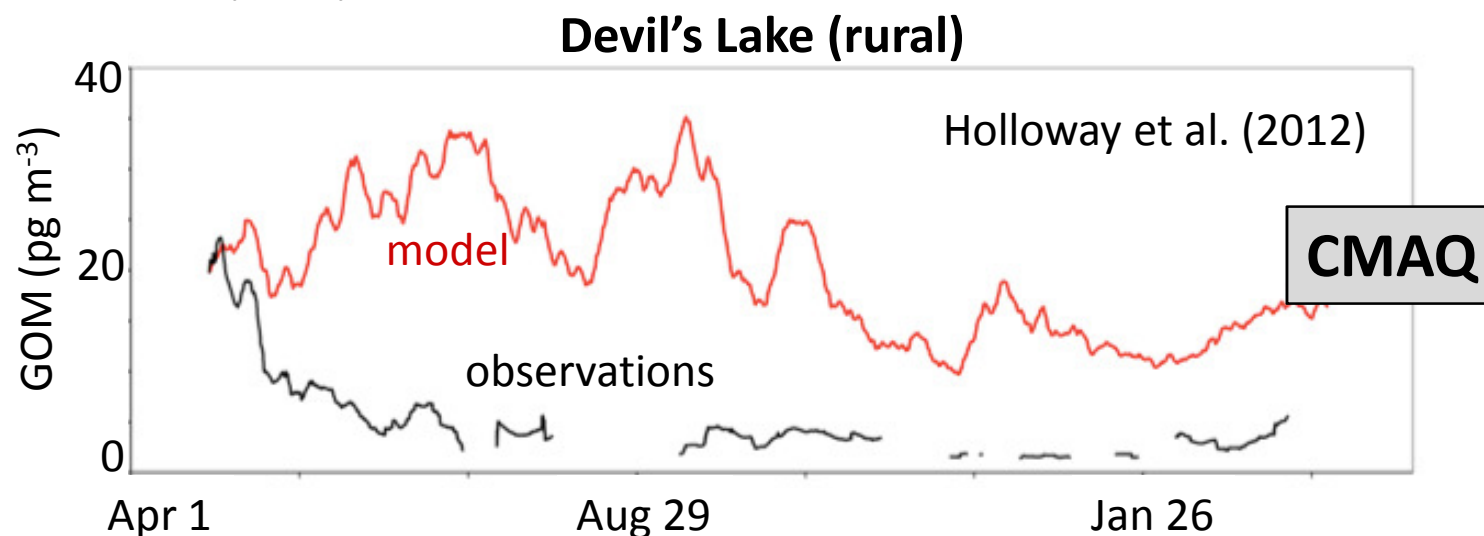
Models are overestimating GOM more than can be explained by instrument bias



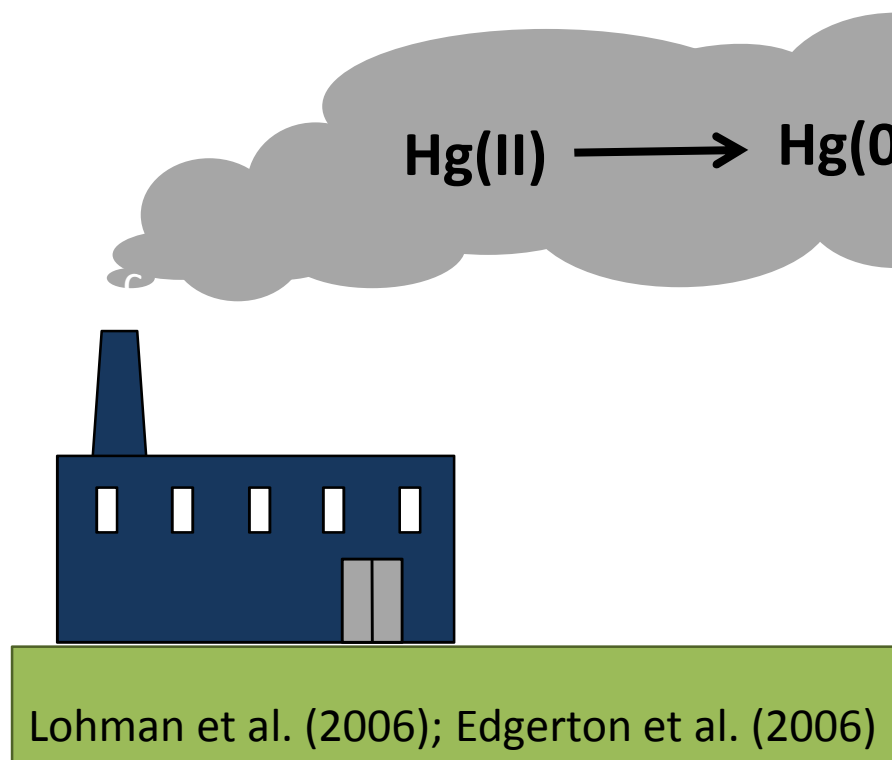
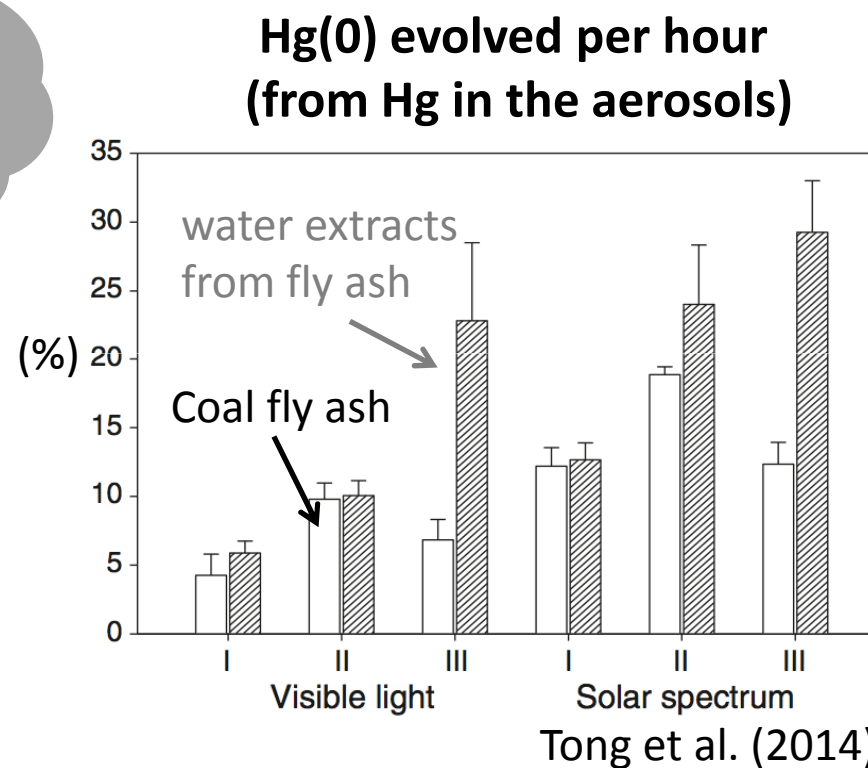
Amos et al. (2012)



Kos et al. (2013)



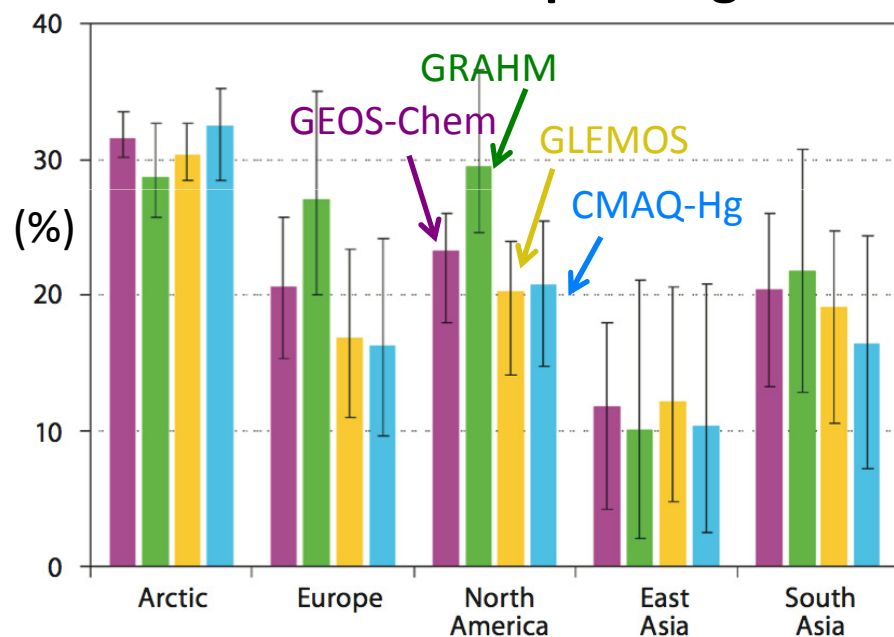
In-plume reduction hypothesized as mechanism to help reconcile model overestimate



Laboratory evidence that in-plume reduction may be happening via heterogeneous chemistry.

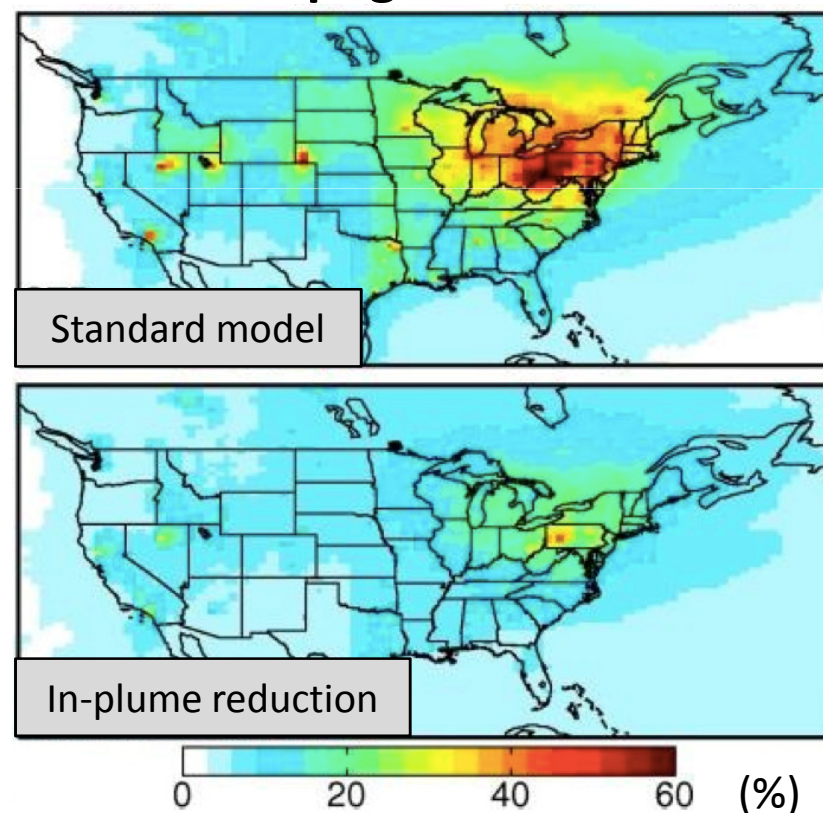
Modeled source-receptor relationships sensitive to emission speciation

Foreign contribution to deposition in different receptor regions



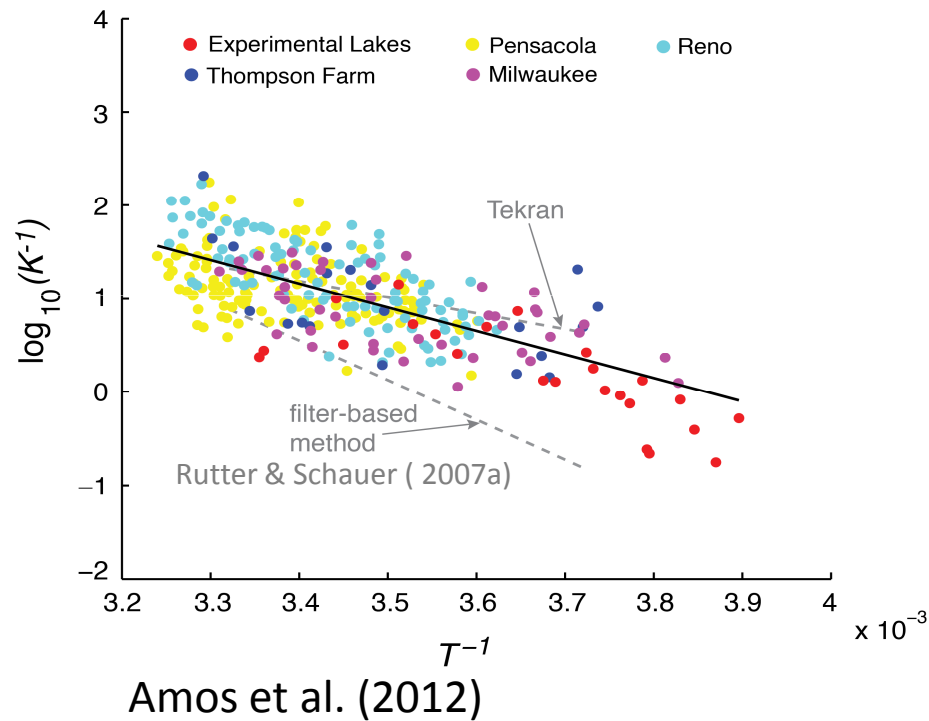
AMAP/UNEP (2013) adapted from
Travnikov et al. (2010)

Contribution to deposition from North American anthropogenic sources

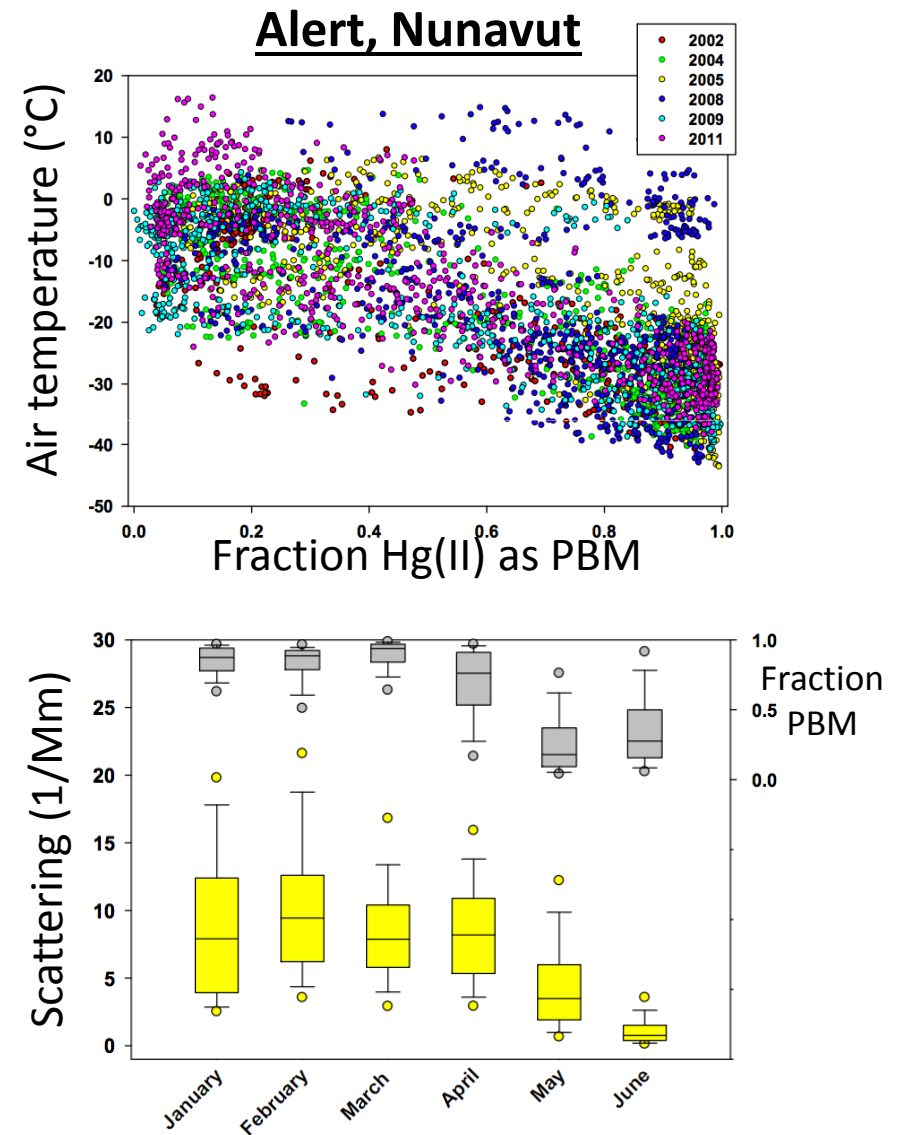


Y. Zhang et al. (2012)

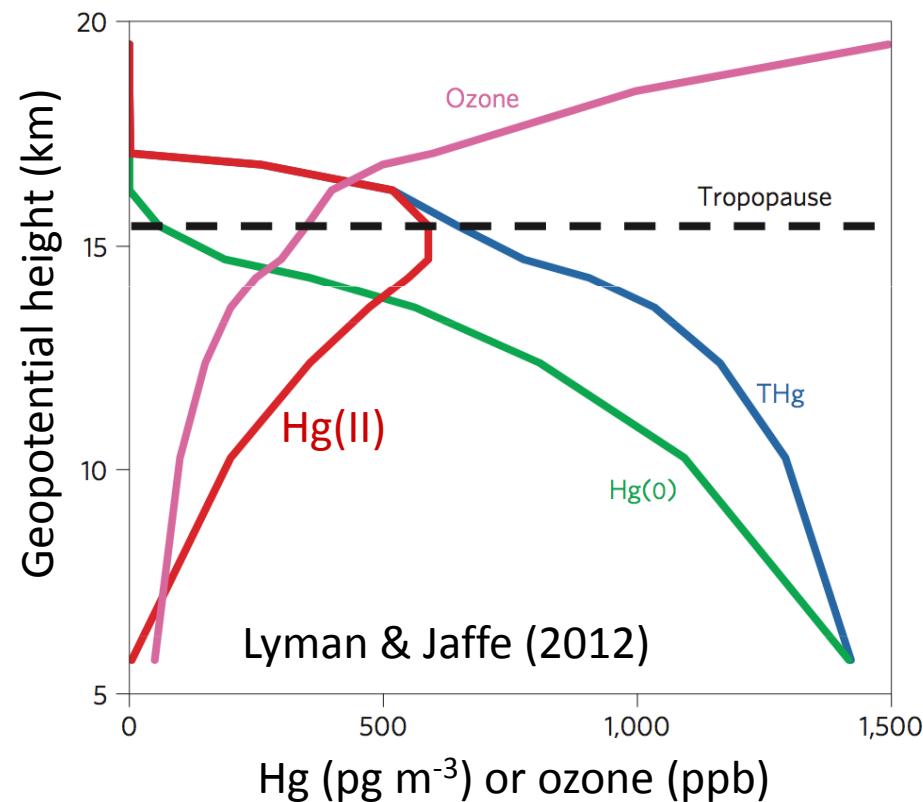
Temperature and aerosol concentration are driving GOM-PBM partitioning



Steffen et al. (2014)



Gas-particle partitioning is a key process controlling Hg profiles near the UTLS



But measured PBM at Mt. Bachelor much less than predicted.

(Timonen et al., 2014)

What's different in the PBL, free troposphere, and UTLS?

- Aerosol composition?

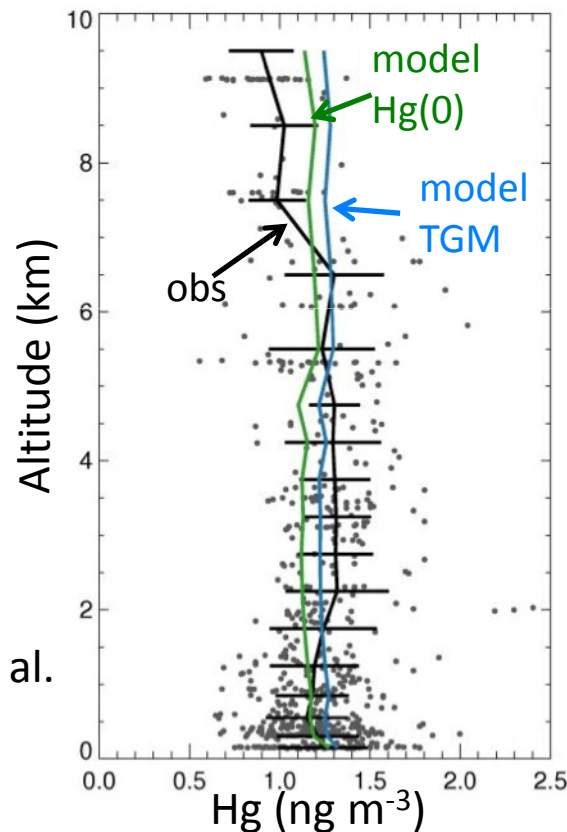
(Rutter & Schauer, 2007b)

- Humidity?

Kim et al. (2012)

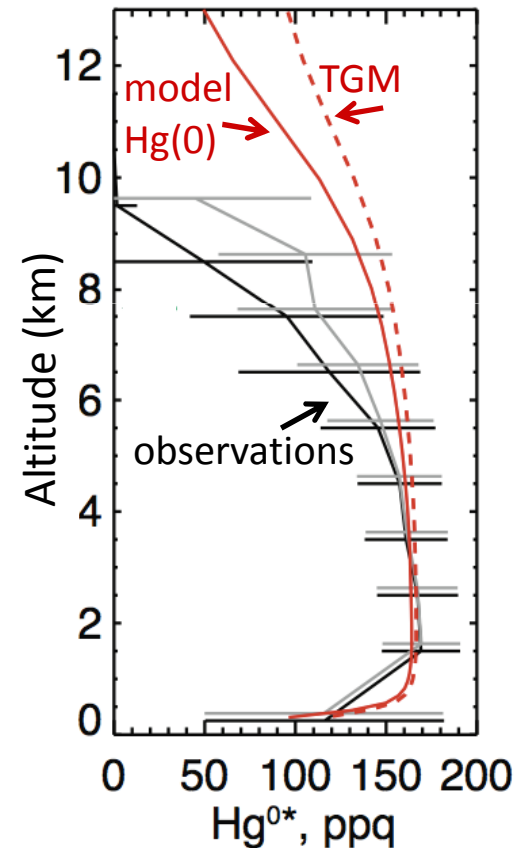
Hg removed from the upper troposphere/lower stratosphere (UTLS) faster than models can explain

California + Nevada (Summer)



Y. Zhang et al.
(2012)

Arctic (Spring)



Holmes et al.
(2010)

ARCTAS
2008

Vertical distribution of speciated Hg is a key issue.

AMAP/UNEP (2013)

Too little oxidation in models in the upper troposphere / lower stratosphere (UTLS)

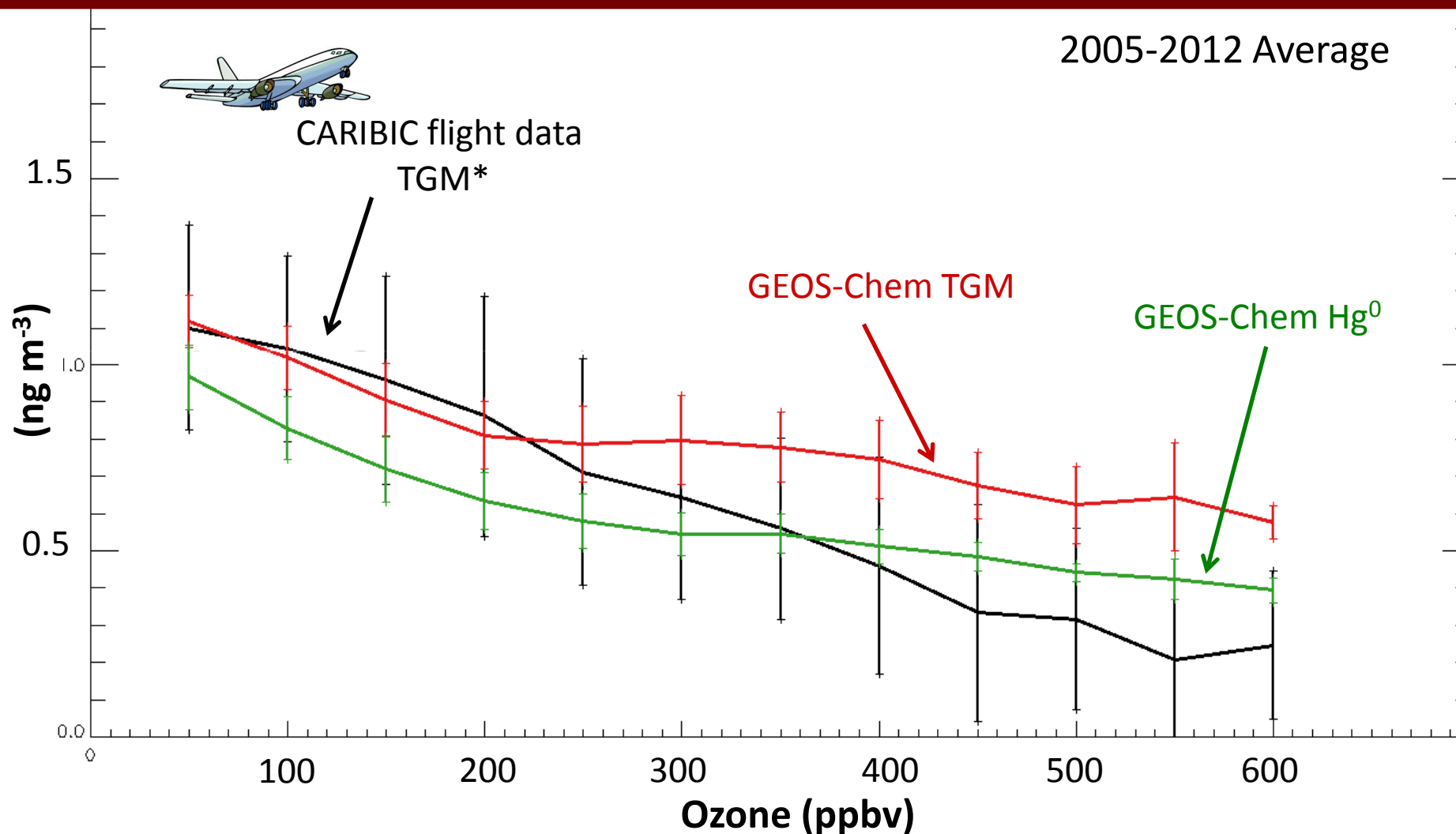
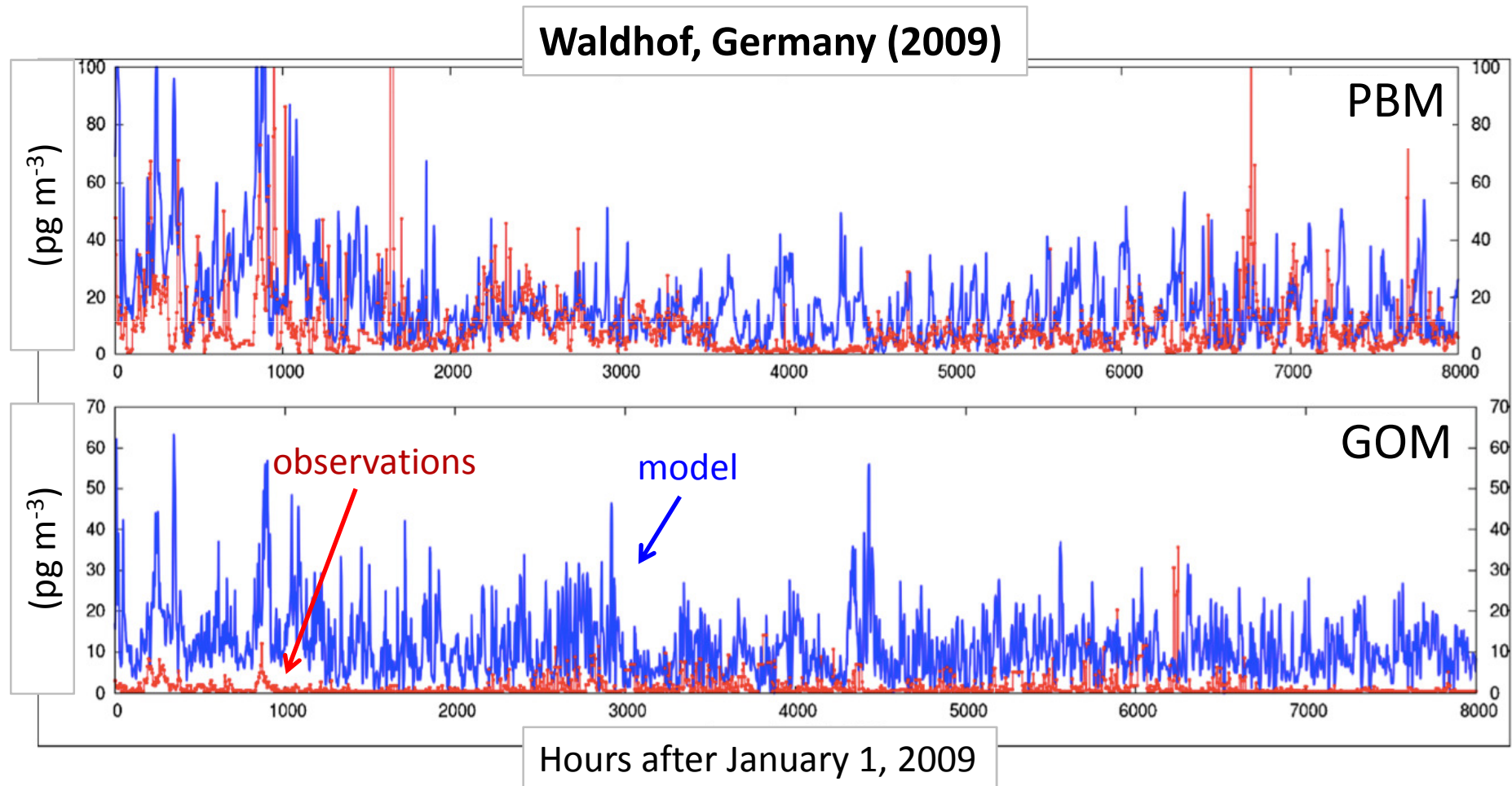


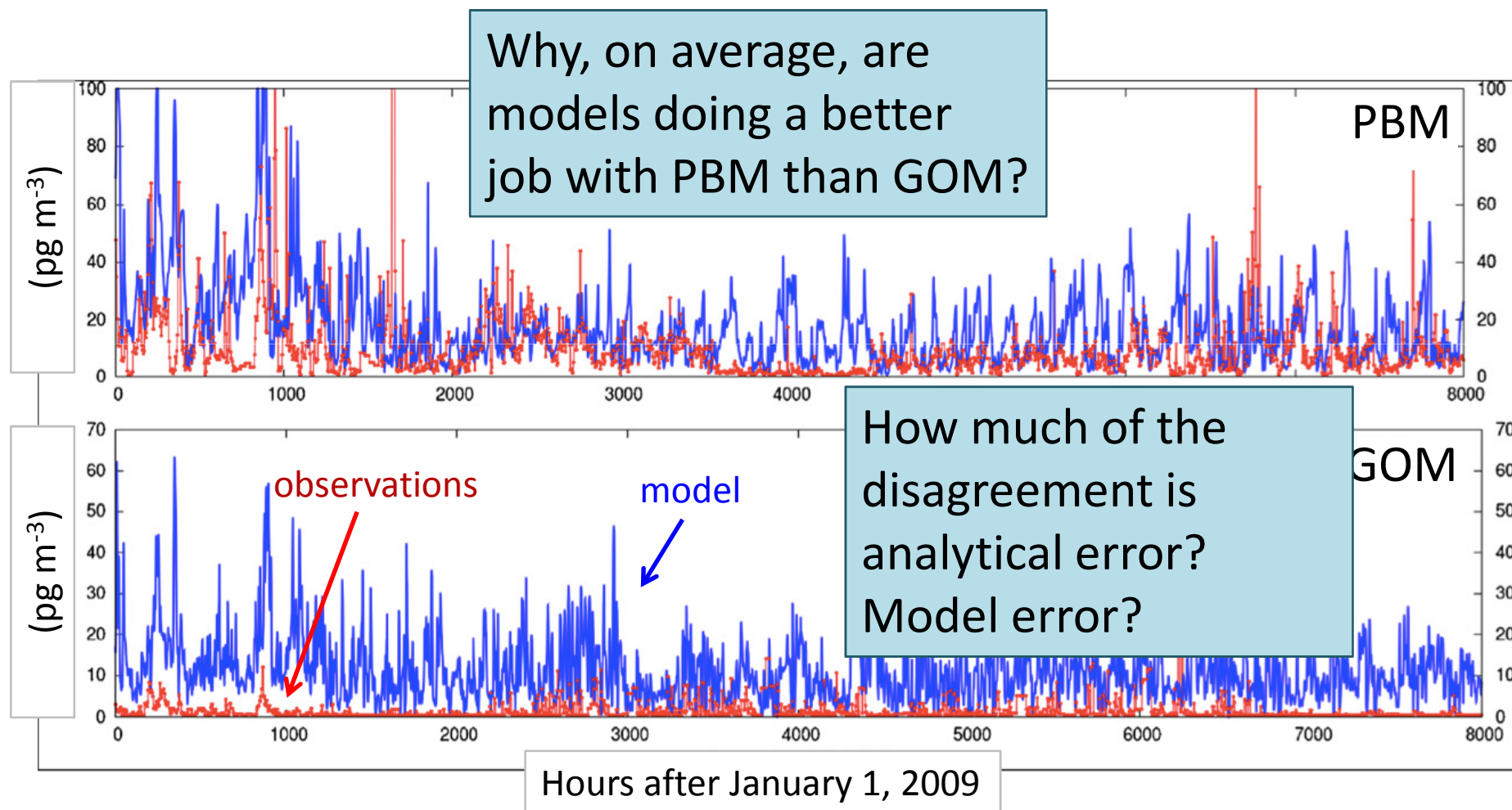
Figure courtesy of Hannah Horowitz (hmhorow@fas.harvard.edu)

Some questions can't be answered right now
because of measurement uncertainty



Bieser et al. (2014)

Some questions can't be answered right now because of measurement uncertainty



Bieser et al. (2014)

Moving forward



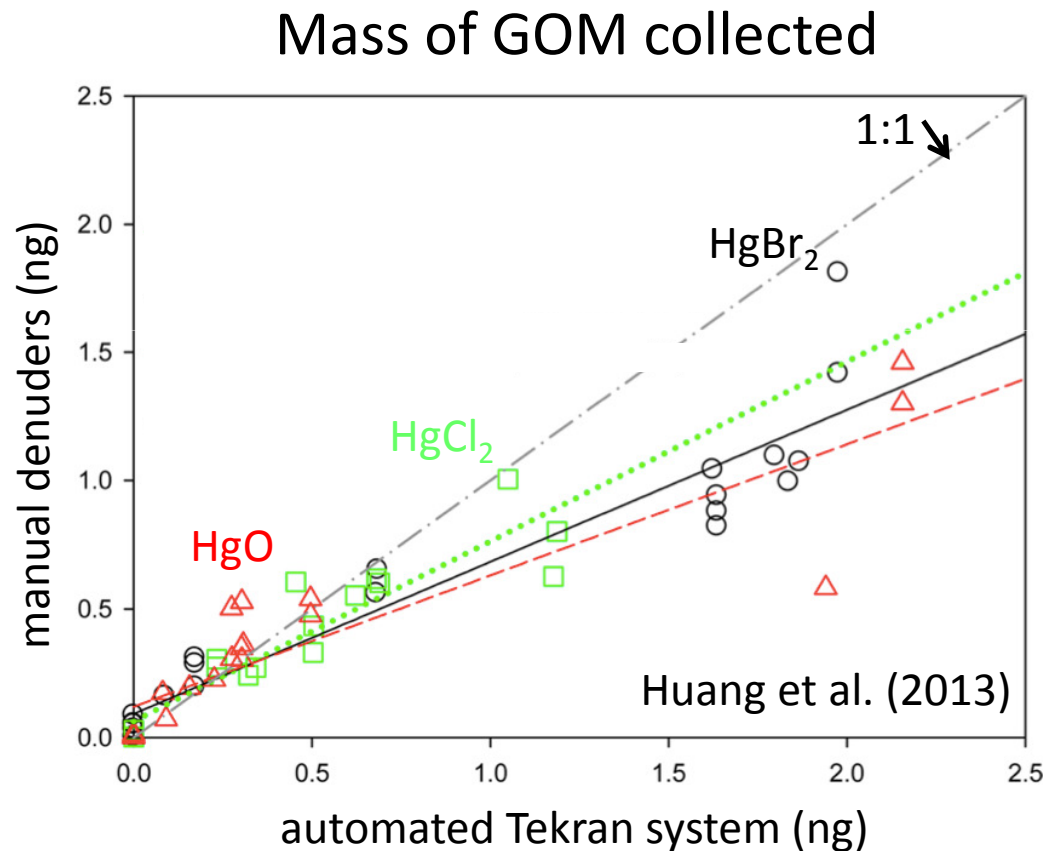
Develop new instrumentation

- UW DOhGS (U. Washington)
- GC-MS (U. Utah)
- LIF (U. Miami)
- Nylon filters (U. Nevada)
- U. Houston system

Continue using Tekran units

- Calibration
- Characterize interferences (O_3 , RH)
- Correction factors
- Reconfigure inlet?

We want model output to be comparable to measurements (and vice versa)



Models

HgCl₂, HgBr₂, HgBrCl, HgO,...

Bulk Hg(II)

Tekran

Hg(II) compounds collected on a KCl denuder

Moving forward



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Continue using Tekran units

- Calibration
- Characterize artifacts (O_3 , RH)
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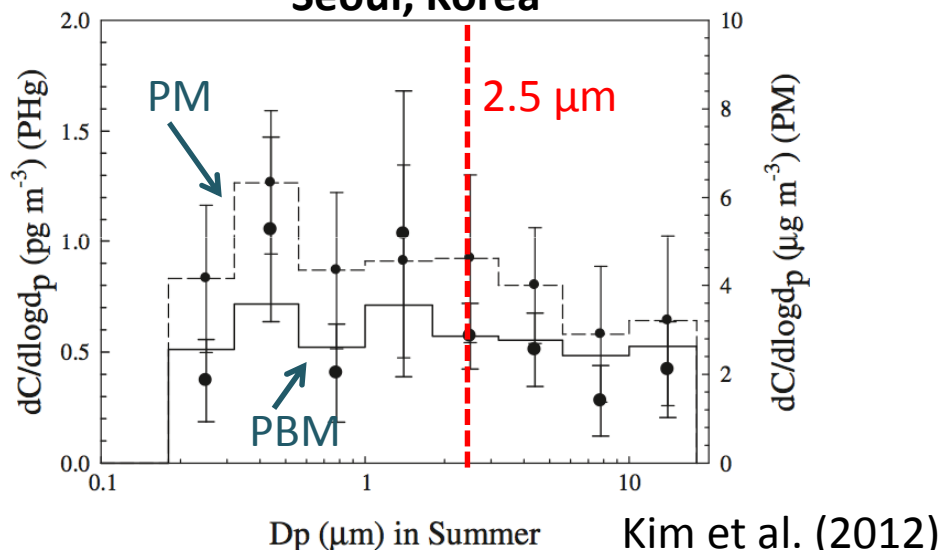
My wish list

1. Gaseous Hg(II) – total or individual compounds
2. Size fractionated particulate Hg(II)

Reliable Hg(II) measurements are the key to pinning down the oxidation-reduction mechanism(s)

Particle size distribution

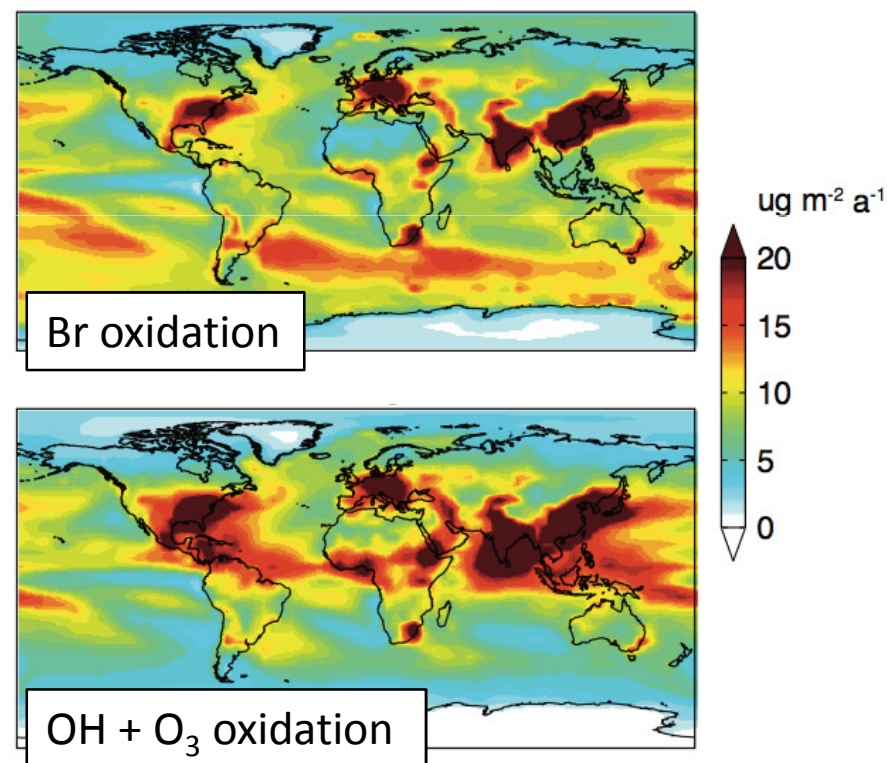
Seoul, Korea



We're missing PBM with a $2.5 \mu\text{m}$ cutoff.

Talbot et al. (2011); Malcom et al. (2008); Keeler et al. (1995)

No wet deposition data where model difference is largest



Holmes et al. (2010)

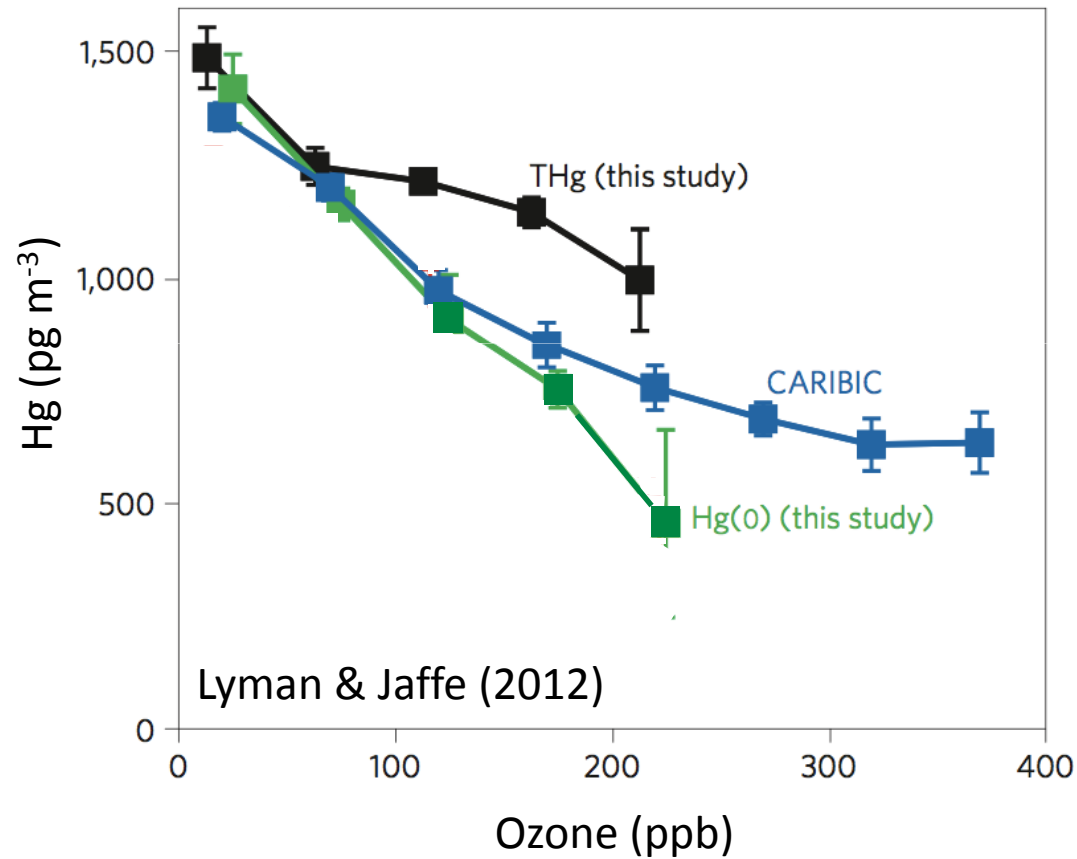
Closing thoughts

- Models cannot be evaluated against GOM and PBM.
- Although limited, we've made progress understanding Hg(II) cycling:
 - Halogens + sea salt in the MBL
 - Gas-particle partitioning
 - Emission speciation
 - Vertical profile & UTLS
- Moving forward, focus on gaseous Hg(II) measurement.
- **Broader Implications:** Better constraining the atmosphere improves understanding of soil and ocean cycling.

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Extra slides

TGM becomes more ambiguous with height



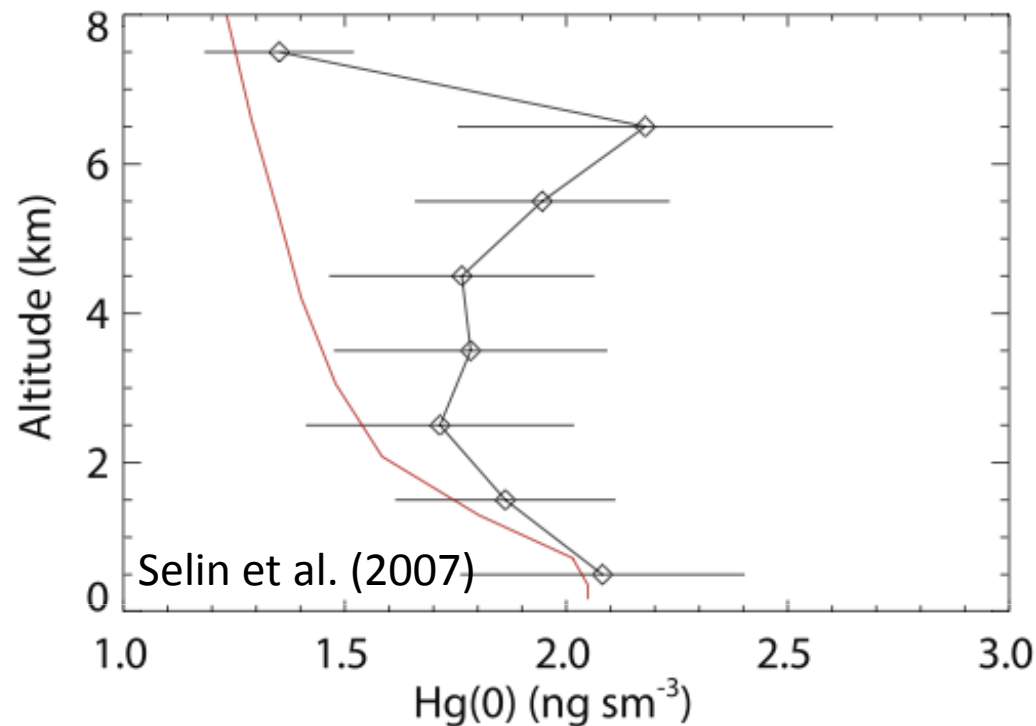
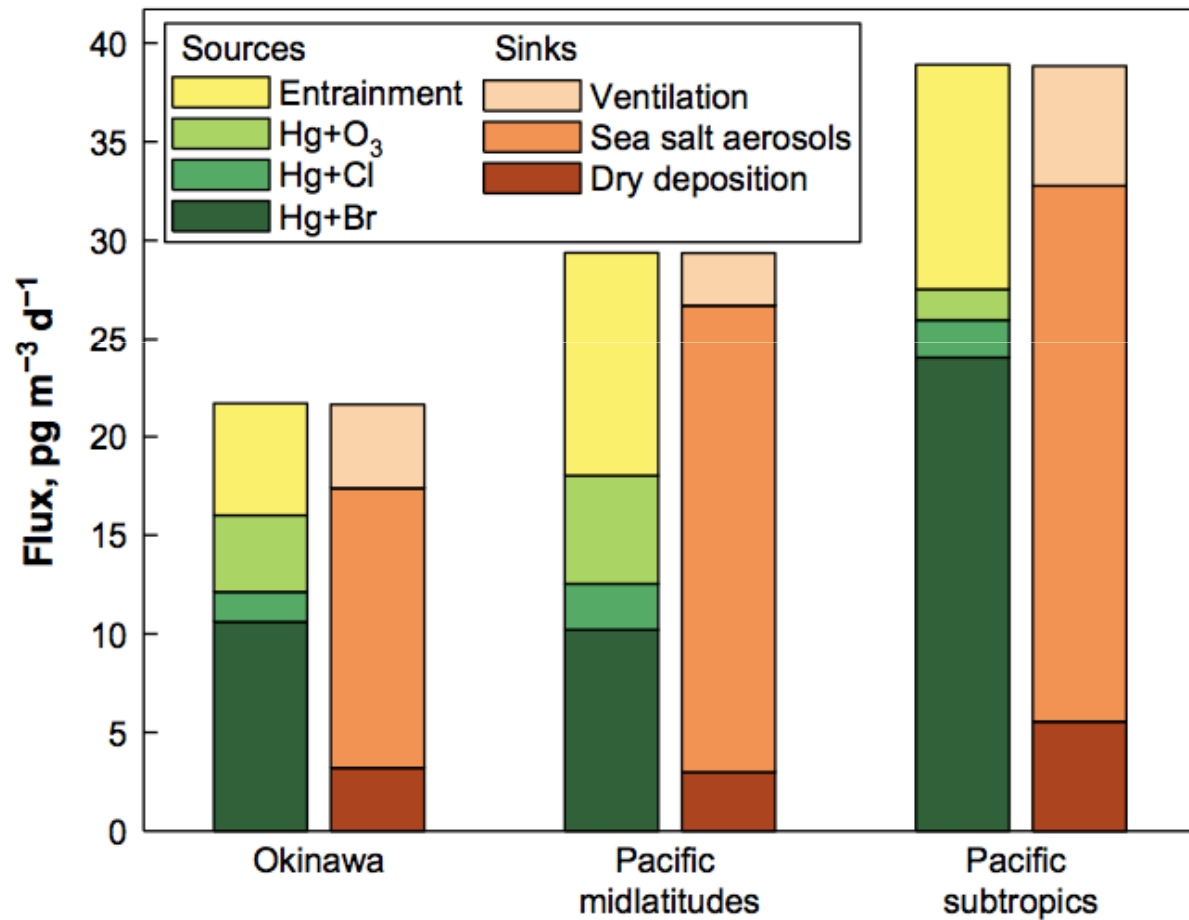


Figure 5. Vertical distribution of Hg(0) mixing ratios near southern Japan. Observations from the ACE-Asia aircraft campaign in April–May 2001 [*Friedli et al.*, 2004] (in black) are compared to monthly mean model results for April over the same domain (in red). The observations are averaged in 1 km bins, and error bars indicate 1 standard deviation. “sm³” refers to a cubic meter under standard conditions of temperature and pressure, so that “ng sm⁻³” is a mixing ratio unit.

Hg budget in the marine boundary layer



Holmes et al. (2010)

References: Source-receptor studies

- Wright et al. (2014), Investigation of mercury deposition and potential sources at six sites from the Pacific Coast to the Great basin, USA. *STOTEN*
- I. Cheng et al. (2012), ACP – Experimental Lakes region
- Corbitt et al. 2011
- Sunderland et al. (2008), Environmental Pollution

What kind of problems are people working on with speciated Hg models?

- Source-receptor
- Wet and dry deposition (Myers et al., 2013, ACP; Leiming Zhang's group + Chen; Yanxu Zhang 2012/3 in ACP and Atmosphere)
- Gas-particle partitioning
- High altitude (Peter; Lyman and Jaffe; Hannah Horowitz)
- Marine boundary layer cycling
- Oxidation mechanisms (De Simone et al., 2014)
- Inverse analysis

In-plume reduction

- Edgerton et al. 2006
- Lohman et al. 2006
- Arnot ter Schure's blimp work
- Tong et al. 2014, *Atmospheric Research* – Hg(II) reduction on fly ash and aerosols in power plant plumes. Isotopic measurements from Rollison et al. 2013 *Chemical Geology* support reduction on aerosols – note, I don't think Rollison measured in plumes, or at least not deliberately

In a perfect world, I would ask for an instrument that...

- Could distinguish between individual Hg(II) compounds
- Size fractionated particle-bound Hg(II), not just a 2.5 μm cutoff (G. C. Fang et al., 2012, Atmospheric Environment)

Better obs will support these specific model things

- Inverse analysis (you need as much information as possible to beat down the error)
- Diagnosing chemical mechanisms / chemical regimes, including aqueous reduction (Bash et al., 2014, *Atmosphere*)
- Predicting GOM and PBM concentrations from wet deposition data (Chen et al., 2013, ACP – Leiming Zhang's group)

What models need in order to use Tekran GOM/RGM and PBM data

- Quantification of error
- Characterization of artifacts
- Correction factor (Huang et al., 2013)

Other Hg modeling talks

- Frank Marsik: An overview of measurement and modeling approaches for the estimate of temporal and spatial variations in mercury dry deposition.
- Xiaohong Xu: An overview on the use of trajectory models to investigate potential sources of atmospheric mercury
- Peter Weiss-Penzias: Use of global model results to understand airborne oxidized mercury observations at five sites

Papers w/ speciated Hg modeling

- Lyman and Jaffe (2011?) – Science or Nature
- Timonen et al. (2012?) - ACP

Modelers to look up on Web of Science

- Noelle Selin
- Chris Holmes
- Krish Vijayaraghavan
- Jesse Bash
- Tracey Holloway
- Mark Cohen
- Frank Marsik
- Xiaohong Xu
- Yanxu Zhang
- Long Chen
- Lyatt Jaegle
- Oleg
- Ian Hedgecock
- Bieser
- Ashu Dastoor