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

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Observations support model evaluation and model development

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

Fisher et al. (2012)
Mounting evidence suggests Tekran GOM and PBM have substantial problems

Gustin et al. (2013)

DOHGS

1.4 x Tekran #2

Tekran #1

Gustinet al. (2013)

Filter PBM - GOM

Filter PBM

Talbot et al. (2011)

Tekran PBM
Numerous models simulate speciated atmospheric mercury

- PHANTAS
- GRAHM
- GLEMOS
- MSCE-HM
- CMAQ
- TEAM
- ECHMERIT
- ADOM
- DEHM
- WRF-Chem
- GEOS-Chem
- Hg-CTM
- WorM³
- STEM
- Plus a few more...
What are the topics being studied with speciated Hg models?

- Source-receptor
- Wet deposition
- AMDEs
- Oxidation mechanisms
- Upper troposphere / lower stratosphere
- High-altitude
- Dry deposition
- Long-range transport
- Marine boundary layer
- Gas-particle partitioning

What have we learned from this work?
Halogen chemistry and sea-salt drive GOM diurnal variability in the marine boundary layer

Mean residual GOM (pg m\(^{-3}\))

Okinawa, Japan

observations
Jaffe et al. (2005)

model

sea-salt scavenging
halogen photochemistry
sea-salt scavenging

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.

**Milwaukee (urban)**

The graph shows a comparison between observed (obs) and model (model) GOM concentrations in parts per quadrillion (ppq) over the months of January to December. The model predictions are consistently higher than the observations. The model is labeled as "original model." The data is from Amos et al. (2012).

**Devil’s Lake (rural)**

The graph displays the model (model) and observed (observations) GOM concentrations in parts per billion (pg m⁻³) from April 1 to January 26. The model shows significant fluctuations that correspond to changes in observed data. The model is labeled as "CMAQ." The data is from Holloway et al. (2012).

**Map**

The map indicates geographic regions with color-coded GOM concentrations ranging from 0 to 150 pg m⁻³. The concentration levels vary across different areas, suggesting spatial variations in GOM emissions. The map is labeled "GRAHM."
In-plume reduction hypothesized as mechanism to help reconcile model overestimate

Hg(II) $\rightarrow$ Hg(0)

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

Lohman et al. (2006); Edgerton et al. (2006)

Tong et al. (2014)
Modeled source-receptor relationships sensitive to emission speciation

Foreign contribution to deposition in different receptor regions

Contribution to deposition from North American anthropogenic sources

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

Y. Zhang et al. (2012)
Temperature and aerosol concentration are driving GOM-PBM partitioning.

Alert, Nunavut

Amos et al. (2012)

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

Vertical distribution of speciated Hg is a key issue.
AMAP/UNEP (2013)
Too little oxidation in models in the upper troposphere / lower stratosphere (UTLS)

Comparison with standard model indicates oxidation is too low in UT/LS.

Figure courtesy of Hannah Horowitz (hmhorow@fas.harvard.edu)
Some questions can’t be answered right now because of measurement uncertainty.
Some questions can’t be answered right now because of measurement uncertainty.

Why, on average, are models doing a better job with PBM than GOM?

How much of the disagreement is analytical error? Model error?

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)

Mass of GOM collected

Models

HgCl$_2$, HgBr$_2$, HgBrCl, HgO,…

Bulk Hg(II)

Tekran

Hg(II) compounds collected on a KCl denuder
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- 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**

![Graph showing particle size distribution in Seoul, Korea](image1)

- PM
- PBM

We’re missing PBM with a 2.5 μm cutoff.

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

**No wet deposition data where model difference is largest**

- Br oxidation
- OH + O₃ oxidation

![Maps showing global distribution of Br oxidation and OH + O₃ oxidation](image2)

- Holmes et al. (2010)
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

Lyman & Jaffe (2012)
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. “sm$^3$” 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 um 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