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Application of Monitored Speciated Atmospheric Mercury Data

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Applications in literature

(i) **Identifying Hg source-receptor relationships** (Lynam et al., 2006; Swartzendruber et al., 2006; Choi et al., 2008; Rutter et al., 2009; Weiss-Penzias et al., 2009; Huang et al., 2010; Sprovieri et al., 2010; Cheng et al., 2012, 2013a,b, 2015)

(ii) **Understanding Hg cycling and partitioning** (Engle et al., 2008; Steffen et al., 2008; Amos et al., 2012, Cheng, 2014)

(iii) **Evaluating Hg transport models** (Baker and Bash, 2012; Zhang et al., 2012a)

(iv) **Quantifying Hg deposition budget** (Engle et al., 2010; Lombard et al., 2011; Zhang et al., 2012b; Cheng 2015)

Recent studies in Environment Canada

- ✓ **Chen et al., 2013**
- ✓ **Cheng et al., 2012, 2013a, b; 2014a, b; 2015a, b**
- ✓ **Cheng and Zhang, 2015**
- ✓ **Fang et al., 2012**
- ✓ **Kos et al., 2013**
- ✓ **Wright and Zhang, 2015**
- ✓ **Zhang et al., 2009; 2012a, b**

Five selected studies

1. Speciated and total Hg dry deposition at AMNet

2. Relative contributions of gaseous oxidized mercury and fine and coarse particle-bound mercury to mercury wet deposition

3. Gas-particle partitioning regression modeling

4. Source-receptor study comparing a coastal and inland rural site

5. Impact of measurement uncertainties on receptor modeling

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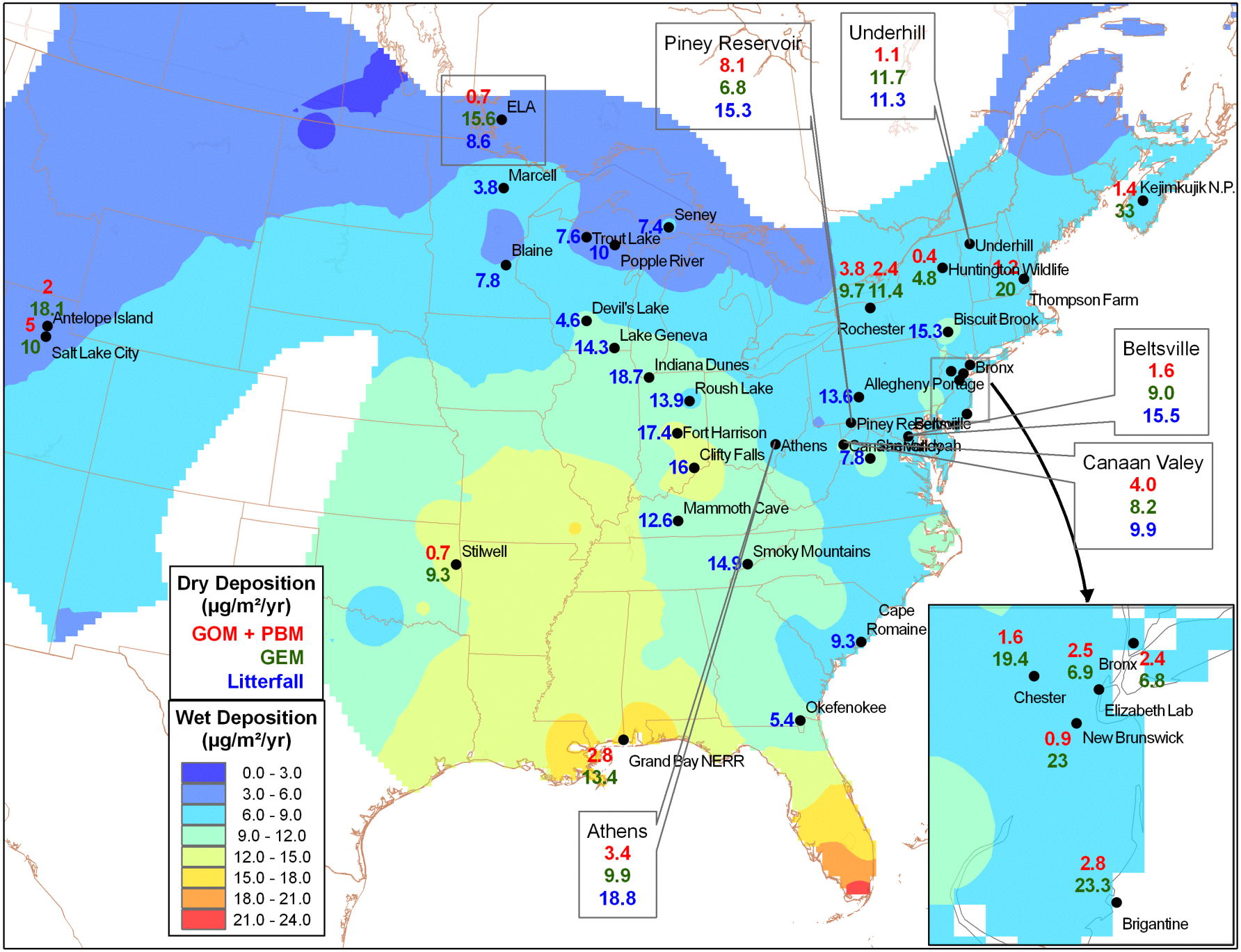
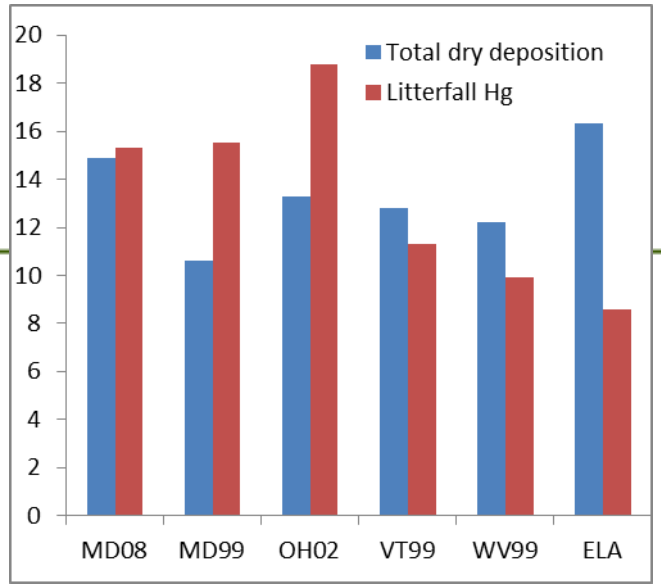
1. Speciated and total Hg dry deposition at AMNeT

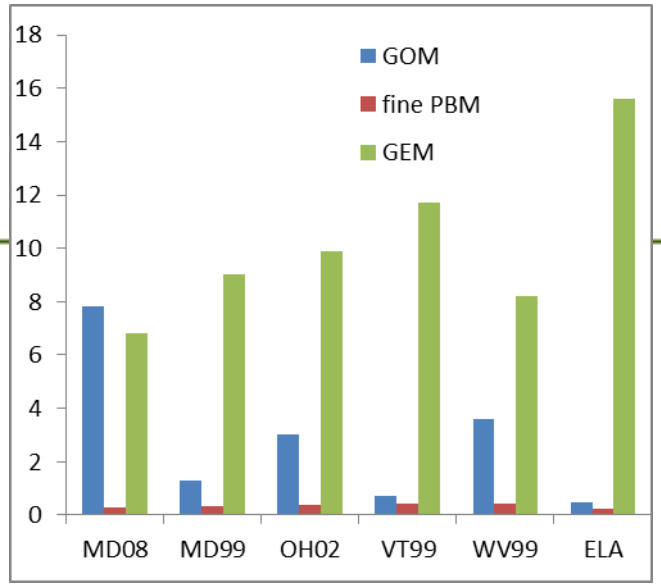
Goals:

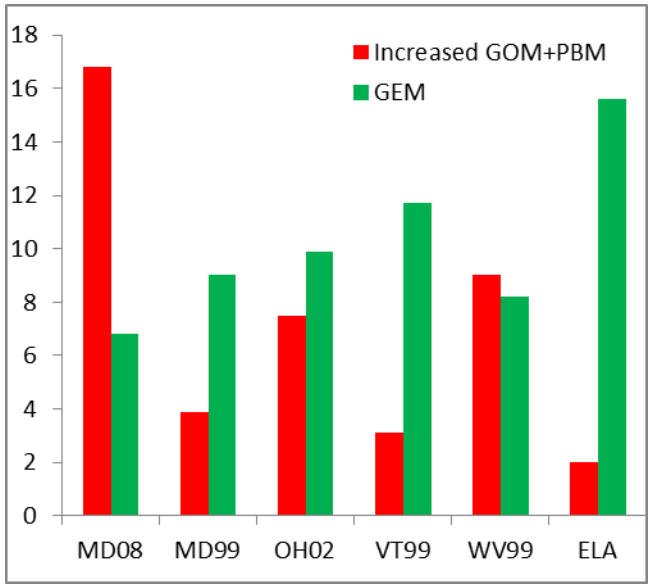
- To get a relatively good estimation of mercury dry deposition at multiple monitoring sites
- **Quantify the relative importance of each Hg species**
- Quantify the relative importance of dry and wet deposition
- Shed some light on litterfall deposition – is it from collecting all three species or mainly from GEM?

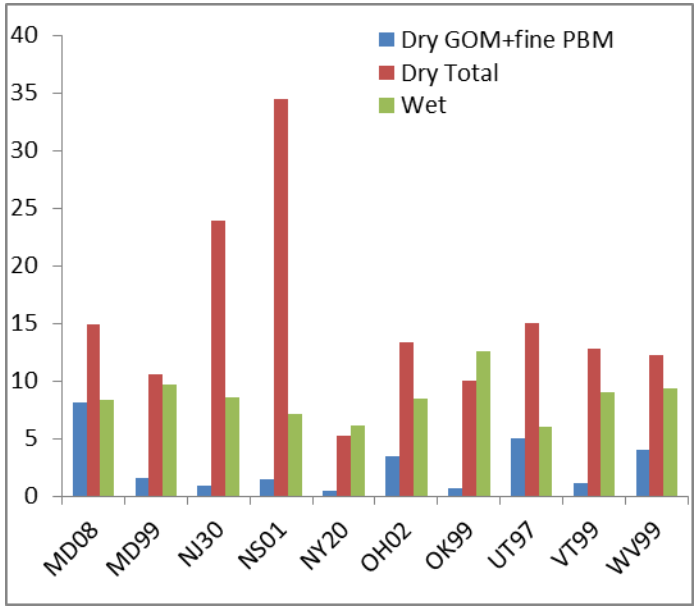
Zhang L., Blanchard P., Gay D.A., Prestbo E.M., Risch M.R., Johnson D., Narayan J., Zsolway R., Holsen T.M., Miller E.K., Castro M.S., Graydon J.A., St. Louis V.L., and Dalziel J., 2012. Estimation of speciated and total mercury dry deposition at monitoring locations in eastern and central North America. Atmos. Chem. Phys. 12, 4327-4340.


Piney Reservoir
8.1
6.8
15.3
Underhill
1.1
11.7
11.3
0.7
15.6
8.6
ELA
Marcell
3.8
Seney
7.4
7.6
Trout Lake
10
Popple River
Blaine
7.8
1.4
33
Kejimkujik N.P.
Underhill
3.8
2.4
9.7
11.4
0.4
4.8
Huntington Wildlife
1.2
20
Thompson Farm
Biscuit Brook
15.3
Rochester
2
18.1
5
10
Antelope Island
Salt Lake City
Devil's Lake
4.6
Lake Geneva
14.3
Indiana Dunes
18.7
Roush Lake
13.9
Beltsville
1.6
9.0
15.5
Bronx
Allegheny Portage
13.6
17.4
Fort Harrison
Athens
Clifty Falls
16
7.8
Canaan Valey
4.0
8.2
9.9
Mammoth Cave
12.6
0.7
9.3
Stilwell
14.9
Smoky Mountains
Cape
Romaine
9.3
Okefenokee
5.4
2.8
13.4
Grand Bay NERR
Athens
3.4
9.9
18.8
1.6
19.4
2.5
6.9
Bronx
2.4
6.8
Chester
Elizabeth Lab
0.9
23
New Brunswick
2.8
23.3
Brigantine
Dry Deposition
(µg/m²/yr)
GOM + PBM
GEM
Litterfall
Wet Deposition
(µg/m²/yr)
0.0 - 3.0
3.0 - 6.0
6.0 - 9.0
9.0 - 12.0
12.0 - 15.0
15.0 - 18.0
18.0 - 21.0
21.0 - 24.0


Total dry deposition
Litterfall Hg
20
18
16
14
12
10
8
6
4
2
0
MD08
MD99
OH02
VT99
WV99
ELA


GOM
fine PBM
GEM
18
16
14
12
10
8
6
4
2
0
MD08
MD99
OH02
VT99
WV99
ELA


Increased GOM+PBM
GEM
18
16
14
12
10
8
6
4
2
0
MD08
MD99
OH02
VT99
WV99
ELA


Dry GOM+fine PBM
Dry Total
Wet
40
35
30
25
20
15
10
5
0
MD08
MD99
NJ30
NS01
NY20
OH02
OK99
UT97
VT99
WV99

Conclusions

- Estimated dry deposition amount is supported by litterfall measurements
- **GEM deposition is as important as or more important than RGM+Hgp**
- **A large portion of litterfall is from GEM deposition**
- Dry deposition is in a similar magnitude to wet deposition
- Significant seasonal and spatial pattern have been identified
- **Known uncertainties should not change the major conclusions (e.g., doubling GOM+PBM dry deposition)**

Five selected studies

1. Speciated and total Hg dry deposition at AMNeT

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5. Impact of measurement uncertainties on receptor modeling

2. Relative contribution of oxidized mercury to mercury wet deposition

Motivation

- Coarse fraction of PBM is not negligible (~30%), but not monitored by AMNet
- Coarse particles are scavenged (~10 times) faster by precipitation than fine ones (Wang et al., 2014)
- Most mercury CTMs do not simulate coarse PBM, but are frequently evaluated using monitored wet deposition data
- Most CTMs overpredict surface GOM and PBM by a factor of 2-10.

Cheng I., Zhang L., and Mao H., 2013. Relative contributions of gaseous oxidized mercury and fine and coarse particle-bound mercury to mercury wet deposition at nine monitoring sites in North America. JGR-Atmospheres, in press.

Methodology - concept of scavenging ratio

Scavenging ratio: $W = C_{prec}/C_{air}$

Wet deposition: $F = C_{prec}P = WC_{air}P$

$F_{total} = F_{GOM} + F_{FPBM} + F_{CPBM} = C_{prec}P$ **(Total Hg wet dep.)**

Need to assume coarse PBM concentration (or mass fraction),

and W values

Methodology – coarse PBM

Assume coarse PBM formed by gas-particle partitioning and

the partition coefficient normalized by PM mass,

$$C_{CPBM} = C_{FPBM} \times \%PM_{2.5\text{-}10} / \%PM_{2.5}$$

Note: This assumption is valid for most locations; however sources and formation of CPBM remain uncertain and location-dependent.

Constrain the Hg coarse fraction to ≤ *0.3 of the total PBM mass to avoid overprediction*

Methodology – W

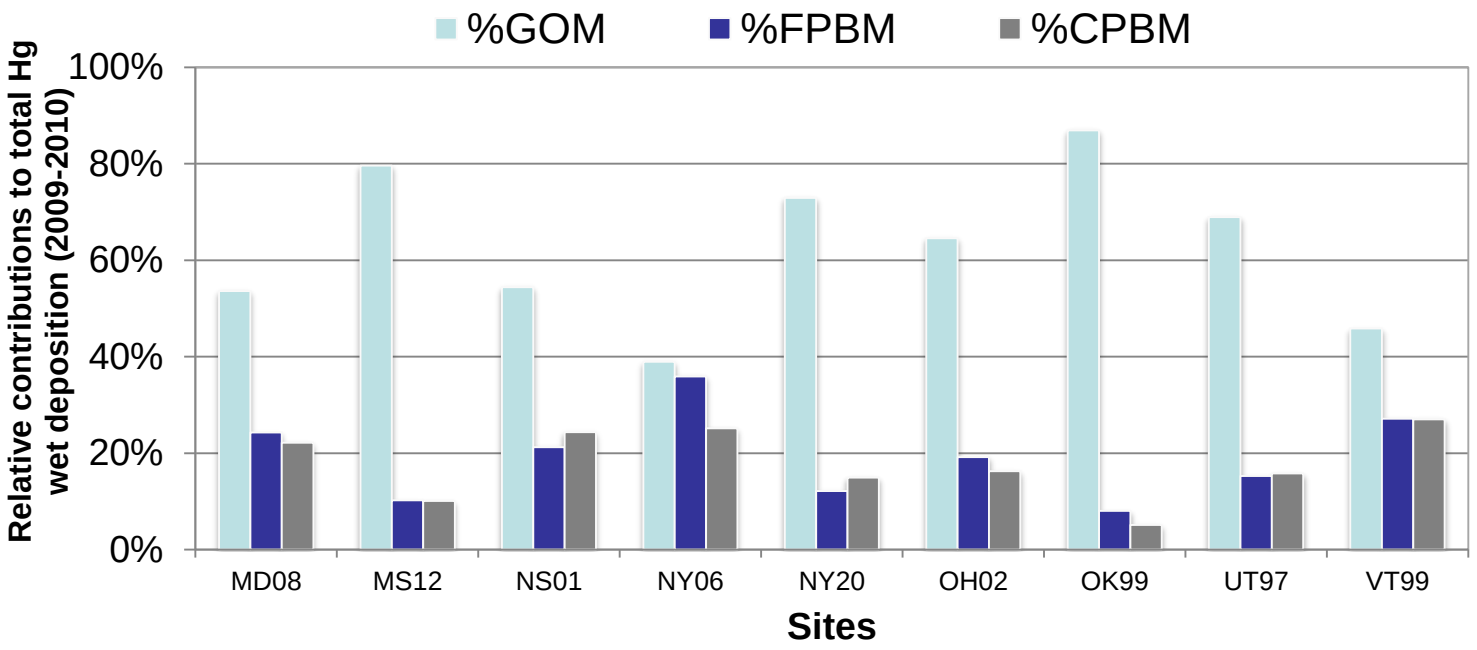
W for K^+ to determine *W* of fine particles, then F_{FPBM}

- **Note: at coastal sites, K^+ has a bimodal particle size distribution and is predominantly associated with coarse sea salt. Thus, W for fine particles was reduced by a factor of 2 for coastal locations, to be consistent with the ratio of fine/coarse particle W's at other site categories.**

W for Ca^{2+}, Mg^{2+}, Na^+ to determine *W* of coarse particles, then F_{CPBM}

$$F_{GOM} = F_{total} - F_{FPBM} - F_{CPBM}$$

Results - Relative contributions



GOM: 39-87%; FPBM: 8-36%; CPBM: 5-27%

Conclusions

- **Total Hg wet deposition is predominantly from GOM**
- **FPBM and CPBM wet deposition important:**
  - During winter because of snow scavenging
  - At urban sites because of higher FPBM in air
- **Major factors that affect the relative contributions: Site characteristics, gas-particle partitioning, snow scavenging**
- **Despite the model uncertainties, the study shows that CPBM contributions to total Hg wet deposition should be considered when Hg transport models are evaluated with Hg wet deposition measurements**

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3. Regression modeling of GOM and PBM partitioning

- Understanding processes affecting GOM and PBM concentrations in air
- Improving mercury deposition estimates and assessing impacts to ecosystems
  - Majority of chemical transport models assume Hg(II) is distributed at fixed ratios between the gas and particulate phases regardless of the location – not supported by scientific theory
  - Need to develop Hg(II) gas-particle partitioning model with a stronger theoretical basis, e.g. a surface adsorption model that parameterizes gas-particle partitioning using a partition coefficient (K_p)

Cheng I., Zhang L., and Blanchard P., 2014. Regression modeling of gas-particle partitioning of atmospheric oxidized mercury from temperature data. Journal of Geophysical Research – Atmospheres, 119, 11,864–11,876.

Methodology

- Hg(II) partition coefficient:
  - K_p = *f*(temperature)

$$Kp = \frac{PBM}{(PM_{2.5})(GOM)}$$

- Hg(II) fraction in particles:
  - Alternative gas-particle partitioning parameter used in literature

$$f_{PBM} = \frac{PBM}{GOM + PBM}$$

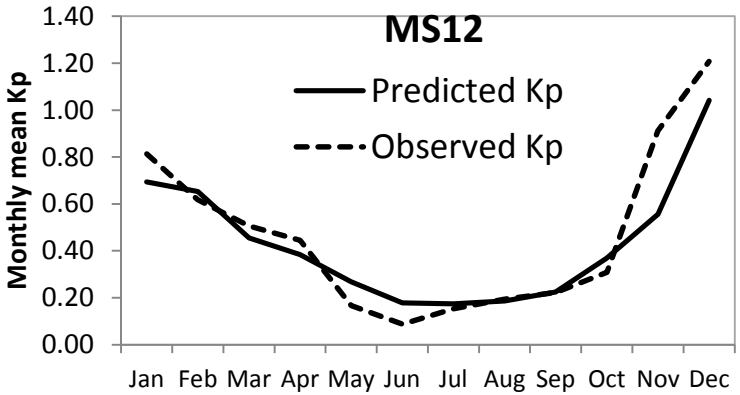
- Apply regression analysis to develop models for K_p and f_{PBM} as a function of temperature
- Generalized model using 10 sites data: $Log(1/K_p) = 12.69 – 3485.30(1/T)$
- Site specific model for each of the 10 sites

  $Log(1/K_{pavg}) = a + b/T$ (exponential)

  $f_{PBMavg} = c + d/T$ (linear)

Site-specific model results

- Model evaluation of site-specific models:
  - Model fit of data improved: R^2 = 0.5-0.96 at 9/10 sites
  - Good agreement with average observed K_p and f_{PBM}
  - Good agreement with monthly average observed K_p and f_{PBM}



Overall, results show strong temperature dependence of Hg(II) particle partitioning

- Weak correlation between predictions and observations (2-4 hr): r = 0.11-0.43
  - 2-4 hr K_p and f_{PBM} may be influenced by other factors (source effects, wind direction changes?)
  - Exact chemical composition of Hg(II) unknown – potentially affect aerosol water uptake and Hg(II) aqueous-phase reactions

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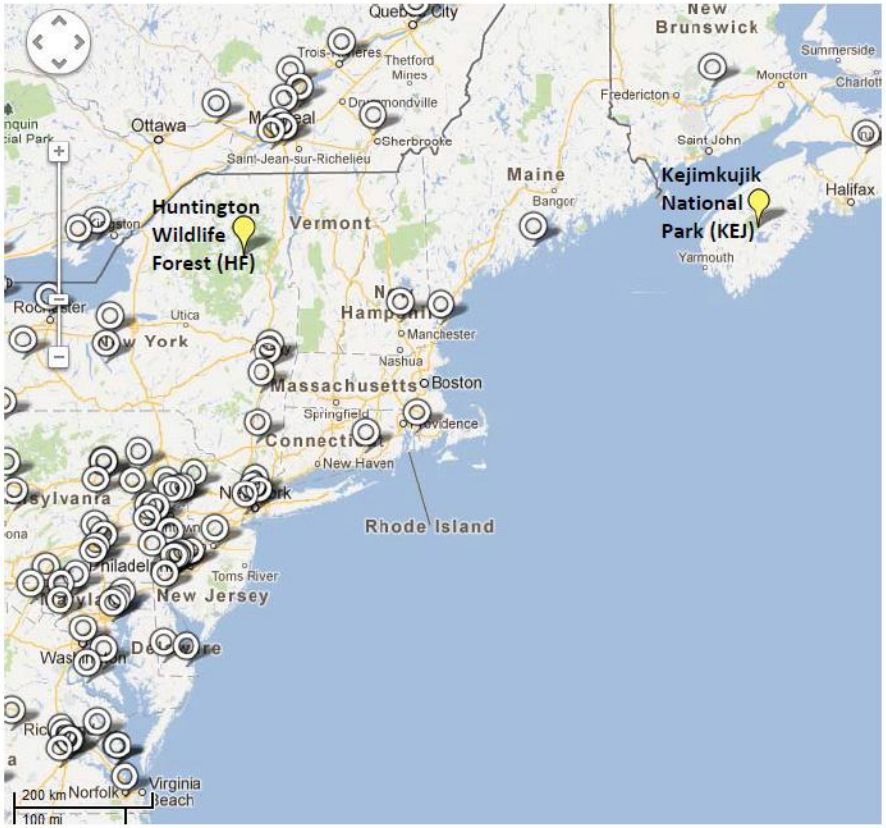
4. Source-receptor study comparing a coastal and inland rural site

Goal: **Compare sources and atmospheric processes** affecting GEM, GOM, and PBM at a coastal (Kejimkujik National Park, Nova Scotia) and inland site (Huntington Wildlife Forest, New York)



Cheng I, Zhang L., Blanchard P., Dalziel J., Tordon R., Huang J., Holsen T.M., 2013. Comparing mercury sources and atmospheric mercury processes at a coastal and inland site. JGR - Atmpsheres, 118, 2434-2443

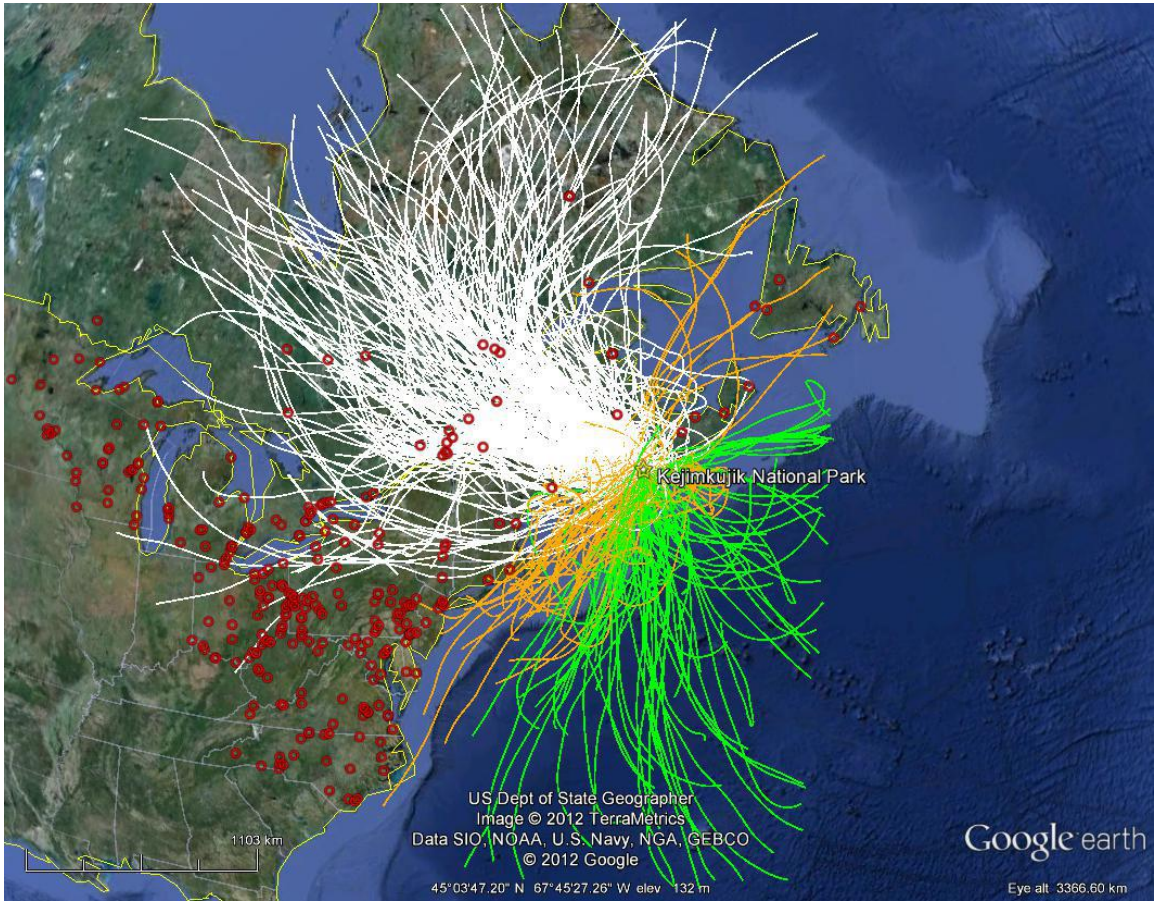
Canada

Background knowledge

- Both sites were identified as biological Hg hotspots in NE North America
- Potential difference in sources and atmospheric processes between coastal and inland sites: influence of the marine boundary layer
  - **Evasion of GEM from the ocean – largest source of natural and re-emitted Hg globally**
  - **Adsorption of GOM by sea-salt aerosols**
  - **Photochemical production of GOM from GEM-bromine reactions – the ocean is a major source of Br**

Method

- Mercury measurements: both sites belong to AMNet; GEM, GOM, PBM measured using an automated speciation system (Tekran)
- Additional ambient air data: Particulate inorganic ions, SO_2, HNO_3, O_3, met data
- Receptor-based methods: PCA, Absolute Principal Components Scores (APCS) with HYSPLIT back trajectory data
- APCS provide details about source contributions to each sampling day - categorize each sampling day to a trajectory pattern (land, coastal, ocean, or mixed airflows)


Kejimkujik National Park
US Dept of State Geographer
Image © 2012 TerraMetrics
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
© 2012 Google
1103 km
45°03'47.20" N 67°45'27.26" W elev 132 m
Eye alt 3366.60 km
Google earth

Results – Comparing the coastal and inland site

Potential Sources or processes (from PCA factors)	Coastal site	Inland site	APCS for the coastal site
Combustion and industrial sources	☑	☑	Coastal > land airflows (Shipping port source)
Wildfires	☑	☑	
Hg condensation on particles in winter	☑	☑	Land and coastal > oceanic airflows
GEM evasion from ocean	☑		Oceanic > land and coastal airflows
Urban emissions		☑	N/A
Hg wet deposition		☑	N/A
Photochemical production of GOM or transport from free troposphere	☑	☑	Not statistically different between airflow patterns

Further analysis examined effects of O_3 bins and water vapor mixing ratio (WVMR) on %GOM/TGM (a measure of GEM oxidation)

- Potential GOM production by GEM-Br reaction at the coastal site at low O_3 bins (<40 ppb) (presence of Br)
- Lack of evidence for free troposphere transport as a GOM source: low WVMR did not coincide with high O_3 and high %GOM/TGM

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5. **Impact of measurement uncertainties on receptor modeling**

5. Impact of measurement uncertainties on receptor modeling

Motivation

- GOM and PBM measurements have large uncertainties and inter-comparison of various Hg measurement methods finds GOM might be underestimated
- Major sources of measurement uncertainties:
  - Challenges of measuring trace concentrations (pg/m^3)
  - Exact chemical forms unknown; thus no calibration methods available
  - O_3 and water vapor interferences, chemical reactions, and variable collection efficiencies depending on form of GOM
  - Difficulty separating GOM from PBM due to gas-particle partitioning, which is temperature dependent

Cheng I., Zhang L., 2015. Impact of measurement uncertainties on receptor modeling of atmospheric Hg. To be submitted soon.

Receptor modeling – Goals

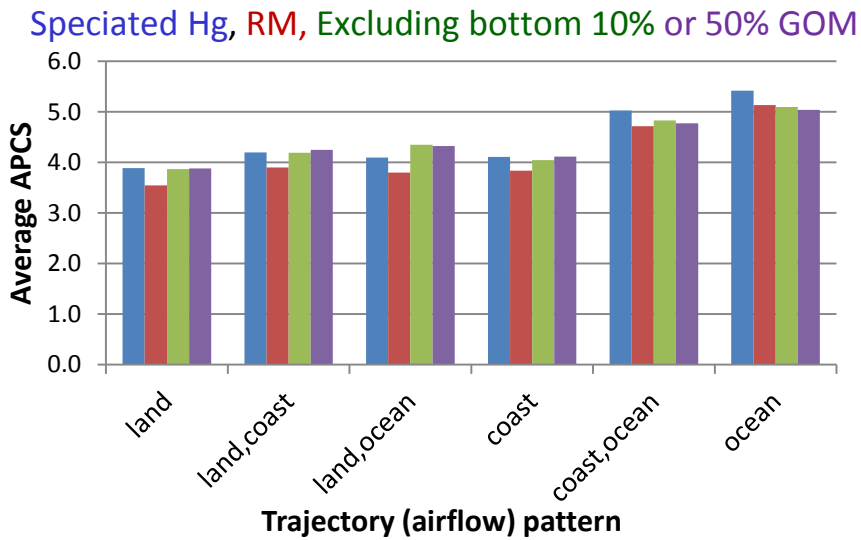
- To investigate the impact of GOM measurement uncertainties on Principal Components Analysis, Absolute Principal Component Scores, and Concentration-Weighted Trajectory receptor models
- Applied the same receptor models as in previous studies, but modified the atmospheric Hg data in two ways:

1. Summed GOM and PBM into reactive mercury (RM)
2. Exclude low GOM measurements (e.g. ≤10th and ≤50th percentile concentrations)

- Compare the receptor model results from this study to previous studies – determine which approach reduces receptor model uncertainties and assess the uncertainties of previous receptor model results

Results – PCA and APCS

Example: GEM evasion from the ocean

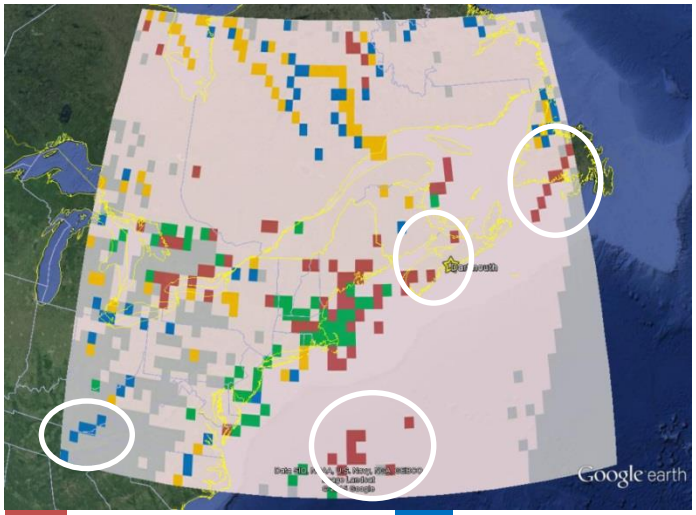


Most results from this study using either the RM or excluding low GOM measurements approach were in agreement with a previous study

- **The GOM photochemical production component was not easily extracted from the RM dataset because the component contained some parameters that could also be assigned to Hg condensation on particles during winter. A non-unique component was extracted.**
- **There was also an additional component generated from the RM dataset that was representative of biomass and soil emissions.**

Results – CWT model

Analysis	Estimated uncertainties of previous source regions
GOM vs. RM	29-56% (source regions identified by GOM, but not by RM), dependent on season
GOM vs. GOM excluding low measurements	Up to 0.5% (source regions identified by GOM, but not by GOM excluding low measurements), dependent on season



- **Isolated source regions identified by GOM or PBM only are circled – considered uncertain source regions**
- **Strong agreement between RM and PBM, less agreement between RM and GOM because PBM > GOM in air most of the time**
- **No improvement to correlation between CWT results and total Hg point source emissions when RM or GOM excluding low measurements were used**

A NADP/AMNet dry deposition project

- **One of the major goals of NADP/AMNet is to provide estimates of mercury dry deposition with reasonable accuracy**
- **TDEP sub-committee approved Zhang and Gay (2014) proposal in 2014 NADP fall meeting**

A NADP/AMNet dry deposition project

Data

- 2-hourly concentration data from AMNet
- Hourly meteorological data archived from Canadian weather forecast model
- Land use data need to be generated

Expected output

- Deposition fluxes of GOM, PBM and GEM at all AMNet sites (usually covering a 1 to 3 km circle)
- Fluxes to each existing LUC within a 3 km circle of each site
- Deposition velocities at weekly temporal resolution
- Missed flux from coarse PBM (not monitored)

A special issue in Atmos. Chem. Phys.

Data collection, analysis and application of speciated atmospheric mercury

Editor(s): R. Ebinghaus and L. Zhang

http://www.atmos-chem-phys-discuss.net/special_issue246.html

- **Designed 10+ overview topics (January-March 2014)**
- **Identified leader authors (March-May 2014)**
- **Organized a workshop and finalized topics (July 2014, San Francisco)**
- **Special issue open date (January – December 2015)**
- **Also accept regularly research papers on the same topics**

A special issue in Atmos. Chem. Phys.

- Overview of measurement uncertainties in speciated mercury and the status of model simulations of speciated mercury
- Overview of uncertainties in Techkran instruments
- Overview of quantifying the air-surface exchange of elemental mercury vapor using enclosure and micrometeorological methods
- Overview of mercury dry deposition measurements
- Overview of Mercury Measurements in East Asia and over the North Pacific
- Overview of mercury measurements in China
- Overview of diurnal and seasonal patterns of speciated mercury at various locations
- Overview of source-receptor studies of speciated atmospheric mercury
- Overview of theoretical estimation of sepciated mercury dry deposition
- Overview of sepciated mercury at emission sources
- Overview of sepciated mercury measurement in Europe
- Overview of litterfall and through fall studies and their relations with dry and wet deposition

Thank you!