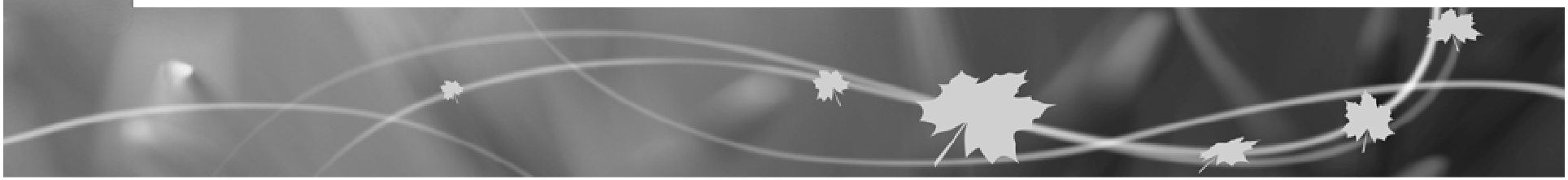
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Analysis and Application of Speciated Atmospheric Mercury

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Outline

- Background information
- Overview of data applications
- Selected example studies

Background information

Atmospheric mercury (Hg) is operationally defined as:

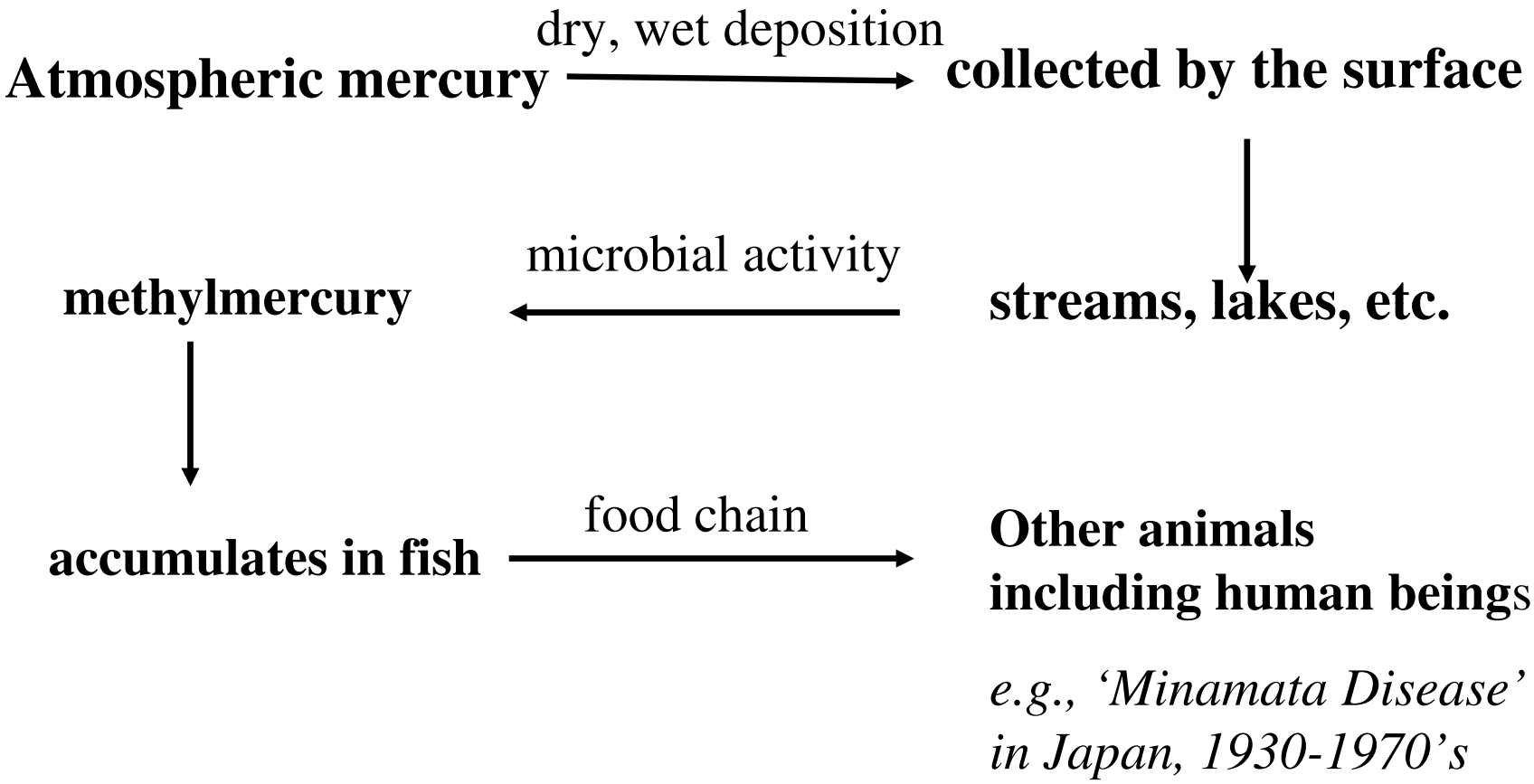
- **Gaseous elemental Hg (GEM)**

typically 1.0-2.0 ng m^{-3}, 0.5-2 years

- **Gaseous oxidized Hg (GOM) or reactive gaseous Hg (RGM)**
- **Particulate-bound Hg (PBM)**

typically 1.0-20.0 pg m^{-3} in North America, could be higher in Asian countries, hours to weeks

Background information



Background information

Potential applications:

(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, 2013)

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

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

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

Overview of data application
- Sour-receptor studies

- Objectives: Identify and quantify the contributions of sources to receptor measurements (e.g., atmospheric Hg, aerosols, ozone, VOCs concentrations in air and deposition)
- Methods: Data analysis and models require receptor measurements to interpret sources and quantify their contributions
  - Multivariate models (e.g., Positive Matrix Factorization, Principal Components Analysis) – input pollutant of interest, other pollutant markers, and meteorological parameters
  - Back trajectory models (e.g. HYSPLIT)
  - Hybrid Receptor Models (combining source contributions or pollutants data with back trajectory data) (e.g., Potential Source Contribution Function, Concentration-weighted trajectory model)
  - Analysis of trends (e.g., seasonal and diurnal patterns, wind direction analysis, analysis of elevated pollution events)

Receptor model	Advantages	Disadvantages
Positive Matrix Factorization (Keeler et al., 2006)	• Multivariate • Down-weight variables based on signal to noise ratio	• Requires knowledge of source profiles • Chemical reactions and transformation not included
Principal Components Analysis (Huang et al., 2010)	• Multivariate • Available in most statistical software	• Similar to PMF model
HYSPLIT back trajectories (Lyman and Gustin, 2008)	• Identify potential locations of sources • Models air mass transport	• Uncertainties in the distance travelled • Applies more to regional than local airflows
Potential Source Contribution Function (Fu et al., 2011)	• Mapping of probable source areas based on trajectory residence time	• Applies to concentrations above an arbitrary threshold only
Gridded Frequency Distribution (Gustin et al., 2012)	• Use of multiple trajectory start heights and locations	• Applies to elevated pollution events only
Concentration-weighted trajectory model (Cheng et al., 2013)	• Concentration is the weighting factor for the trajectory residence time	• Model evaluation requires comprehensive emissions inventory

Watson et al., 2008

Example major findings from source-receptor studies

- Positive Matrix Factorization and UNMIX models both identified coal combustion as the dominant contributor (70%) to Hg wet deposition in eastern Ohio (Keeler et al., 2006)
- Analysis of seasonal and diurnal patterns and Gridded Frequency Distribution identified local electricity power plants, long-range transport from U.S. Northeast, and vehicular emissions as potential sources contributing to Hg dry deposition in Florida (Gustin et al., 2012)
- Principal Components Analysis identified 6 factors affecting speciated atmospheric Hg in Rochester, New York: snow melt, coal combustion, Hg oxidation, wet deposition, traffic, other combustion (Huang et al., 2010)
- Concentration-weighted trajectory model identified industrial sources and fossil fuel power plants in southern Ontario and Quebec and eastern U.S. affecting speciated atmospheric Hg in Dartmouth, Nova Scotia (Cheng et al., 2013)

Overview of data application
Hg cycling and partitioning

- Some studies focused on the understanding of Hg cycling and partitioning (Engle et al., 2008; Steffen et al., 2008; Rutter and Schauer, 2007)
- Wang (2010), Zhang (2012) conducted studies of gas-particle partitioning at emission sources
- Amos et al. (2012) developed a regression model for the partitioning coefficient
- Cheng et al. (2014) further developed partitioning regression models

Overview of data application
- Evaluating Hg transport models

- Zhang et al. (2012) first evaluated CMAQ and AURAMS using AMNet data, and identified a factor of 2-10 over prediction of surface concentrations of GOM and PBM from Hg transport models
- Baker and Bash (2012) found similar conclusions using a later version of CMAQ
- Two other studies evaluated GEO-CHEM
- Kos et al. (2013) explored causes of the discrepancies between measured and modelled GOM and PBM

Overview of data application
- Estimating Hg dry deposition

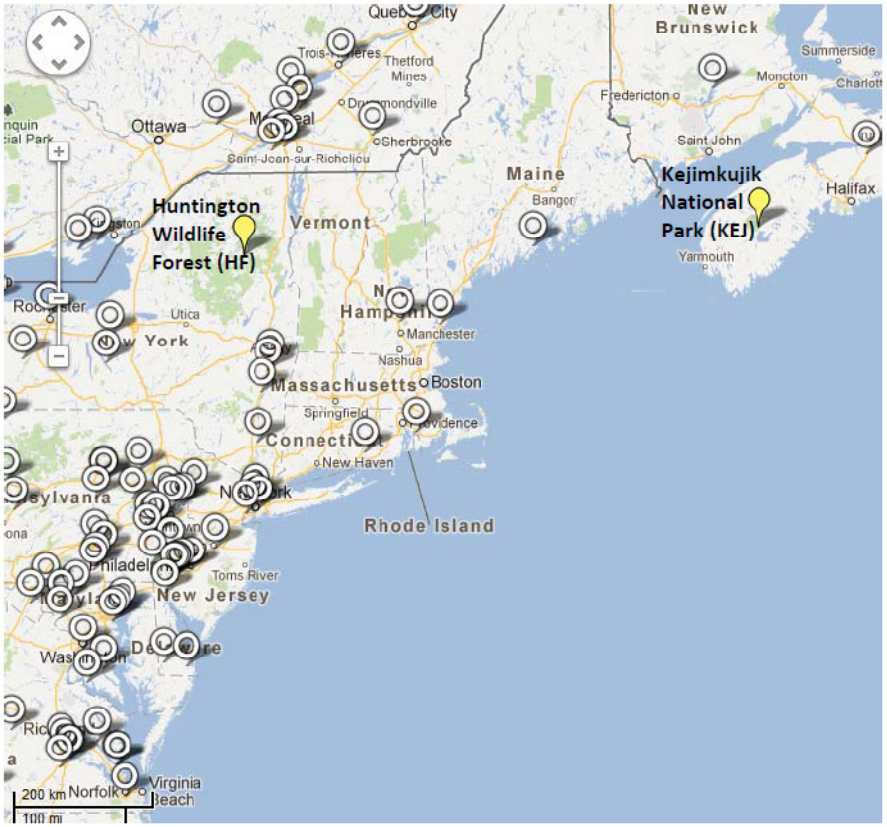
- Most studies only included GOM and PBM in the dry deposition budget (Engle et al., 2010; Lombard et al., 2011; Amos et al., 2012)
- Zhang et al. (2012) estimated speciated dry deposition and using litterfall Hg as constrain, and identified GEM is as important as or more important than GOM+PBM over vegetated surfaces.
- Sakata, M., and K. Asakura (2007), Cheng et al. (2014) estimated speciated Hg to Hg wet deposition

Selected example studies

- **Source-receptor study comparing a coastal and inland rural site**
- **Gas-particle partitioning regression modeling**
- **Speciated and total Hg dry deposition at AMNet**

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 - Atmosheres, 118, 2434-2443

Motivation

- 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**

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**

Conclusions

Factor representing combustion and industrial source was found only in 2009 and not in 2010 for the two sites

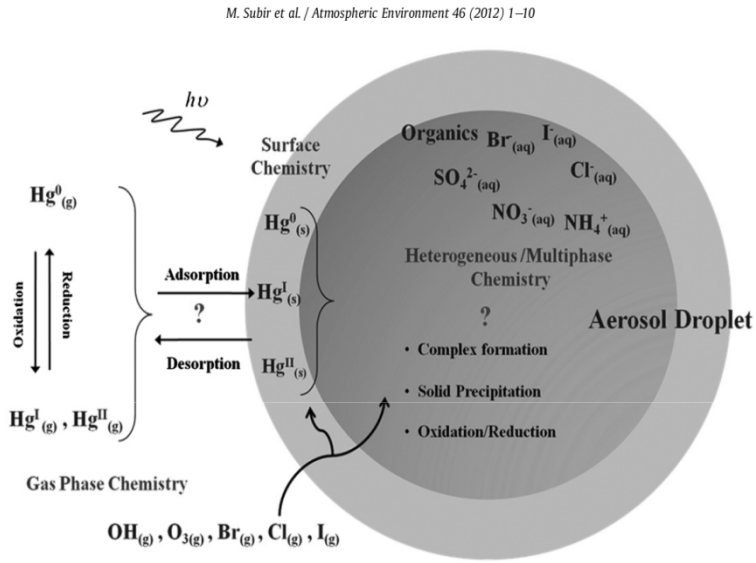
- Possible explanation is large SO_2 and NO_x emission reductions from coal utilities in U.S. over the same time frame

Influence of marine airflow is the key difference in sources and processes affecting speciated atmospheric Hg concentrations at a coastal and inland site

- Evasion of GEM from ocean
- GOM production by GEM-Br reaction is potentially occurring at low O_3 concentrations (<40 ppb) – however there are still many uncertainties on the reactions that produce GOM

Regression modeling of GOM and PBM partitioning

- Hg(II) can distribute between the gas (GOM) and particulate phases (PBM)
- Theories on how Hg(II) partitions: condensation of GOM, adsorption, heterogeneous and aqueous phase chemical reactions
- Potential factors affecting partitioning of semi-volatile pollutants: Air temperature, Aerosol water uptake and relative humidity, Aerosol chemical composition – also affects the 2nd factor



Subir et al., 2012, Atmos. Environ., 46
Figure illustrates the number of ways Hg(II) may interact with aerosols

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. Revised.

Motivation

- 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)

Methodology

- Hg(II) partition coefficient:
  - K_p = *f*(temperature)
- Hg(II) fraction in particles:
  - Alternative gas-particle partitioning parameter used in literature

- Apply regression analysis to develop models for K_p and f_{PBM} as a function of temperature
- Collect ambient air data from 10 Atmospheric Mercury Network sites in U.S. and Canada:
  - PBM and GOM – AMNet uses Tekran Hg speciation system
  - $PM_{2.5}$ – USEPA AirData and Environment Canada NAPS network
  - Air temperature – USEPA CASTNET

Regression model results

- Generalized K_p-temperature model:
  - Daytime data points included, low GOM and PBM excluded in regression model – remove data with large uncertainties data
  - Applied linear and nonlinear models – exponential function provided best data fit for K_p vs. 1/T in terms of R^2

Site(s)	Regression Equation	R^2	
NS01	$Log(1/K_p) = 15.41 – 4285.73(1/T)$	0.59	This study Strong R^2 at only 2/10 sites
VT99	$Log(1/K_p) = 11.93 – 3258.75(1/T)$	0.54	
NS01 and VT99 (combined data)	$Log(1/K_p) = 12.69 – 3485.30(1/T)$	0.55	
5 sites combined	$Log(1/K_p) = 10 – 2500(1/T)$	0.49	Amos et al. (2012)
Urban site	$Log(1/K_p) = 15 – 4250(1/T)$	0.77	Rutter and Schauer (2007)
Urban site	$Log(1/K_p) = 7 – 1710(1/T)$	0.49	

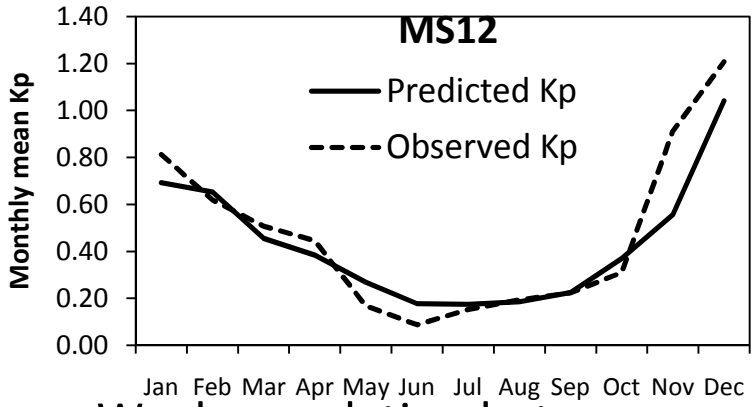
Regression model results

- Model evaluation of **$Log(1/K_p) = 12.69 – 3485.30(1/T)$**:
  - Applied the single K_p equation to all 10 sites
  - Average predicted and observed K_p were more comparable than previous models at 7/10 sites
    - Larger discrepancies for 3 near-source sites may be due to different % of speciated Hg emitted from nearby sources
  - Model K_p in this study have a wider range and higher values than in previous models
  - Predicted and observed K_p correlations: r = 0.12-0.46

- Site-specific Hg(II) gas-particle partitioning models:
  - $Log(1/K_{pavg}) = a + b/T$ (exponential) and $f_{PBMavg} = c + d/T$ (linear) developed for each of the 10 sites
  - K_{pavg} and f_{PBMavg} is the average corresponding to each 2^oC temperature interval
    - 2-4 hr K_p and f_{PBM} have large variability; averaging could reduce the variability and may improve the model R^2

Site-specific model results

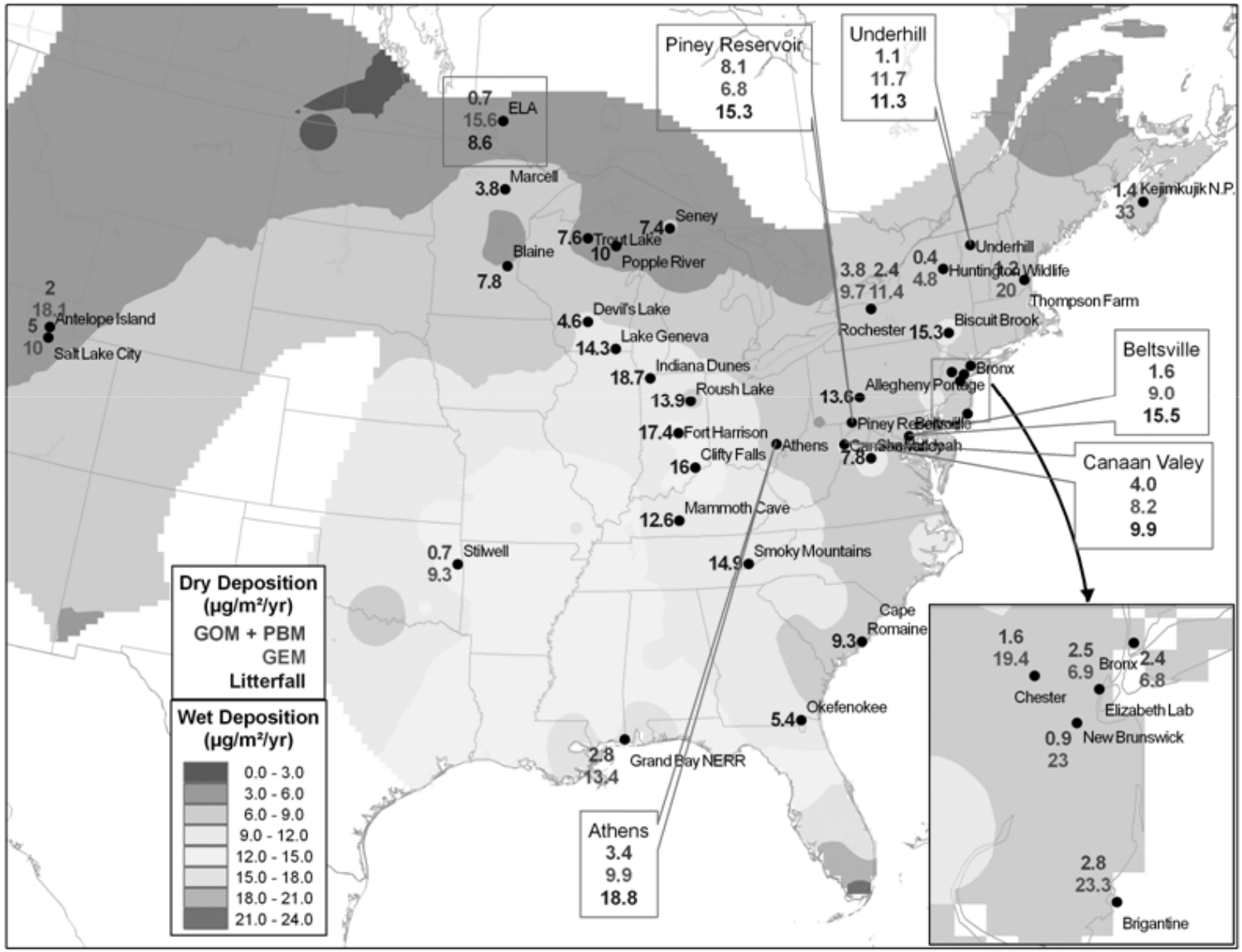
- Model evaluation of site-specific models:
  - Model fit of data improved: R^2 = 0.5-0.96 at 9/10 sites
  - Good agreement with average observed K_p and f_{PBM}
  - Good agreement with monthly average observed K_p and f_{PBM}

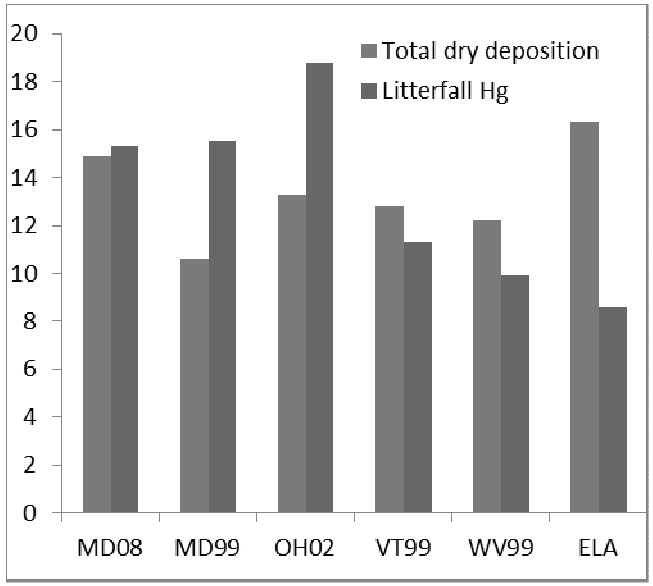


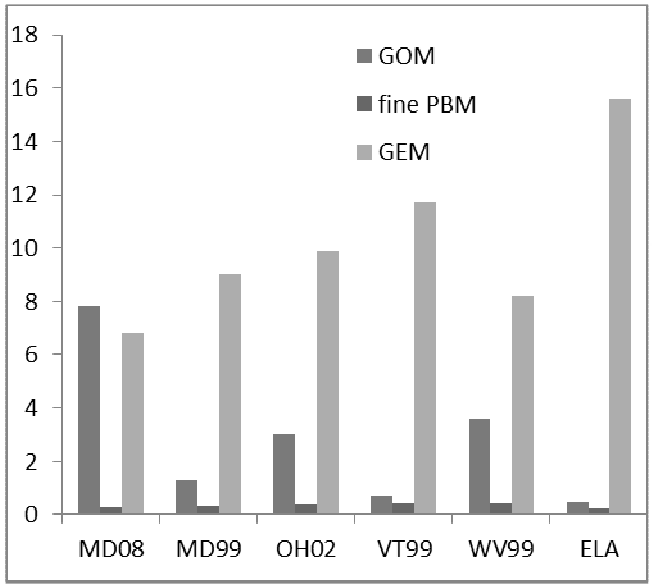
Overall, results show strong temperature dependence of Hg(II) particle partitioning

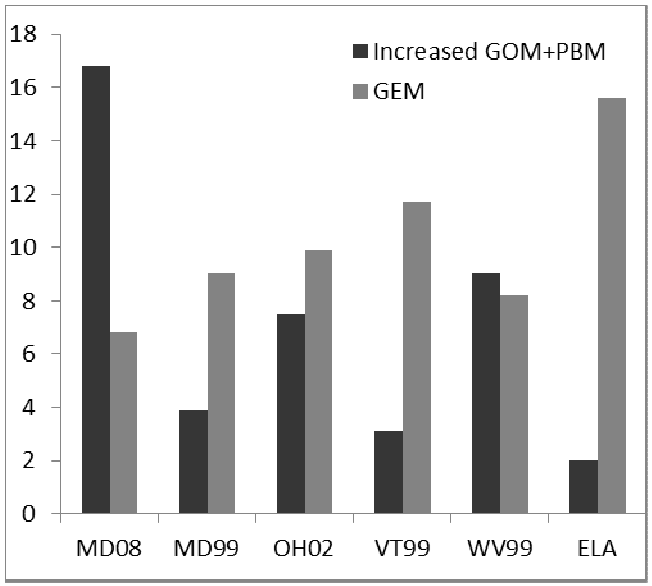
- Weak correlation between predictions and observations (2-4 hr): r = 0.11-0.43
  - 2-4 hr K_p and f_{PBM} may be influenced by other factors (source effects, wind direction changes?)
  - Exact chemical composition of Hg(II) unknown – potentially affect aerosol water uptake and Hg(II) aqueous-phase reactions

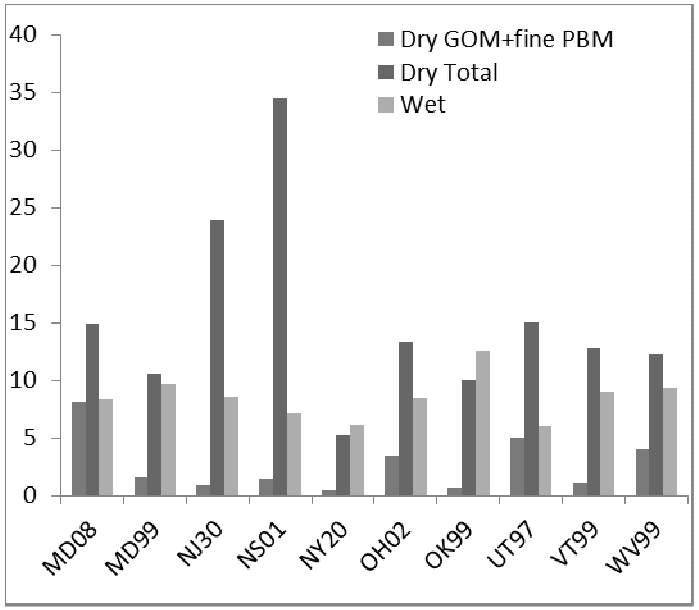
Speciated and total Hg dry deposition at AMNeT




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)**