# Data Collection, Analysis and Application of Speciated Atmospheric Mercury

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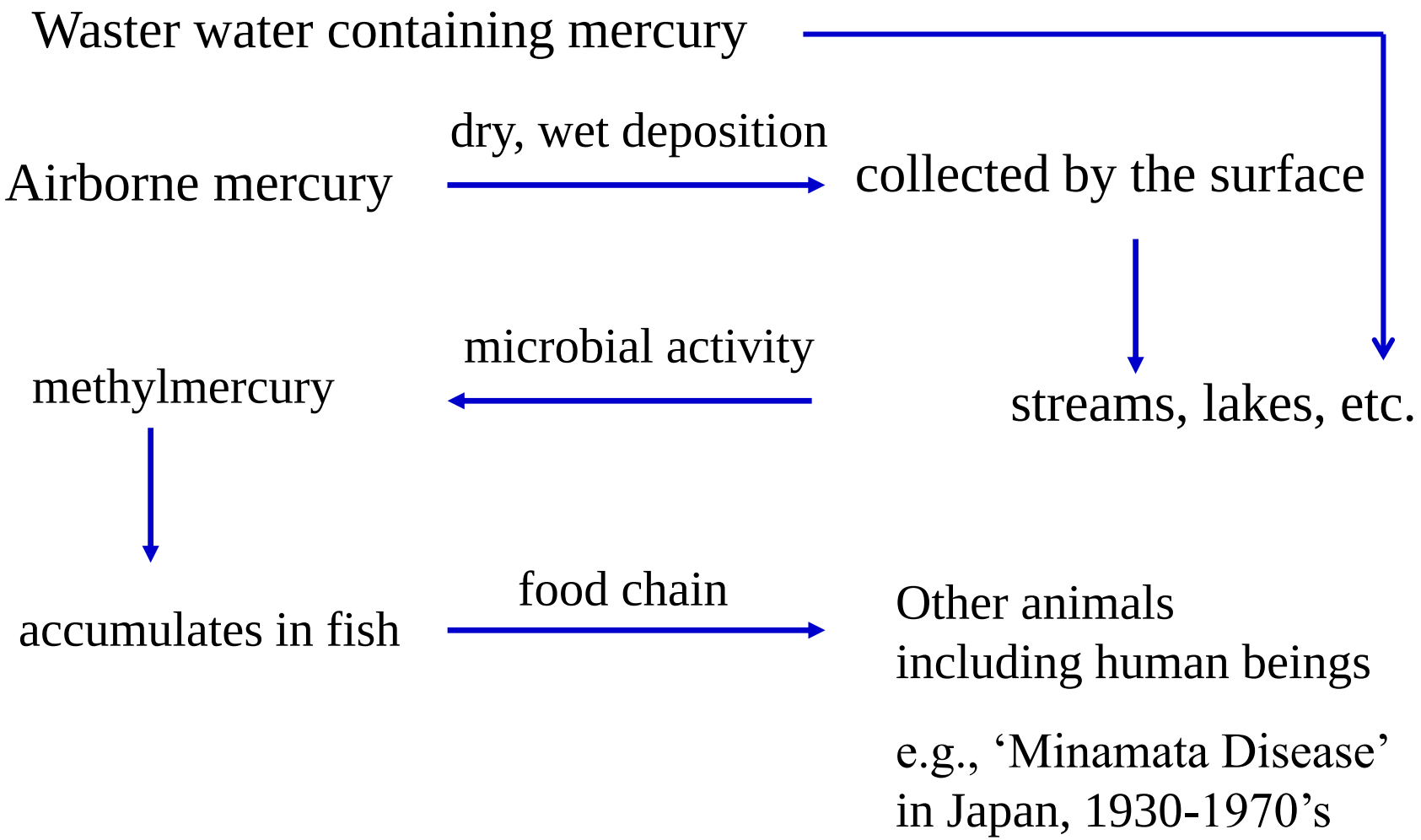
# Why is it important to study mercury cycling?



# Why is it important to study mercury cycling?

## Minamata Convention on Mercury

- **An international treaty designed to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds**

- **Signed by delegates from 140 countries on 19 January 2013**

# Definition of speciated atmospheric mercury

- GEM: gaseous elemental Hg
  - $Hg^0$ (dominant form in air)
  - Volatile, not water soluble
  - Atmos. residence time: ½ - 1 year, capable of long-range transport
  - Typically measure TGM (total gaseous Hg) = GEM + GOM
- GOM: gaseous oxidized Hg
  - $Hg^{2+}$
  - More water soluble, undergo wet deposition
  - Atmos. residence time: ~ days, short-range transport
- PBM: particulate-bound Hg (typically <2.5 µm particles are measured)
  - $Hg^{2+}$
  - Undergo wet deposition, short-range transport

GOM & PBM: operationally defined, exact chemical composition unknown, but likely composed of $HgCl_2$, $HgBr_2$, HgO, and/or $Hg(OH)_2$; enters ecosystems where it can convert to toxic MeHg

# Routine monitoring of speciated mercury

- **NADP's Atmospheric Mercury Network (AMNet) and Global Mercury Observation System (GMOS) are two of the largest networks monitoring atmospheric mercury forms**
- **Both networks measure GEM, GOM and PBM using the Tekran speciation system**

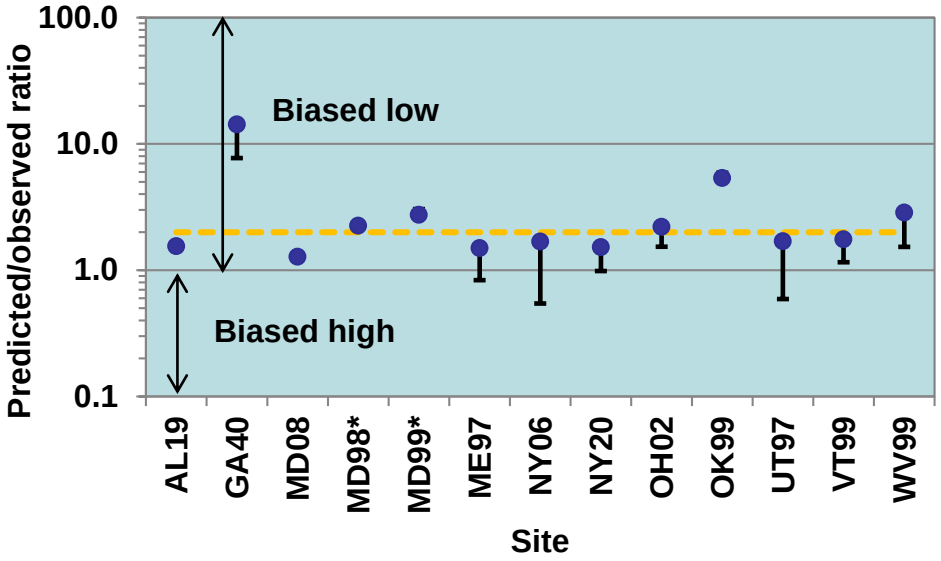
# Measurement challenges for GOM and PBM

- Exact chemical composition of GOM and PBM is unknown
  - Essential for determining the measurement uncertainties and developing calibration systems
- Sampling issues
  - Interferences by elevated ozone and other gases and aerosols (chemical reactions) and by water vapor (decline in collection efficiency)
  - Efficiency of denuders at collecting GOM depends on the form of GOM and not all forms of GOM collected
    - $HgCl_2 > HgBr_2 > HgO$ (**Huang et al. 2013**)

# Measurement uncertainties

- Emerging research suggests GOM and PBM measurements have significant uncertainties (**Jaffe et al. 2014**)
- Intercomparison studies of different instrumentation and measurement methods for atmospheric mercury suggest the Tekran GOM measurements may be biased low by:
  - Factor of 1.3-3.7 (**Huang et al. 2013**)
  - Factor of 2-3 (**Gustin et al. 2013**)
  - Factor of 3-5 (**Ambrose et al. 2013**)
  - Up to factor of 12 (**Gustin et al. 2015**)
- An indirect method suggest a factor of 2 or larger uncertainties at 6 of the 13 sites (**Cheng and Zhang, 2016**)

# Uncertainty assessment – from 13 sites




Bias ratio = $\frac{\sum predicted\ GOM}{\sum observed\ GOM}$

Error bars = scavenging ratio method uncertainties = ratio of weekly to monthly biases

>Factor of 2 uncertainty: six sites **(above orange line)**
Between a factor of 1.5 and 1.8 uncertainty: six sites
<Factor of 1.5 uncertainty: one site

Taking into account the method uncertainties:
Measurements are likely biased low by at least a factor of 2 at four of the thirteen sites (GA40, MD98, MD99, OK99)

**Cheng and Zhang (EST, 2016)**

# Example data applications

- **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; Wang et al., 2013; Cheng et al., 2012, 2013a,b, 2015, 2016, 2017, Xu et al., 2016)
- **Evaluating Hg transport models** (Baker and Bash, 2012; Zhang et al., 2012; Kos et al., 2013; Gustin et al., 2015; Weiss-Penzias et al., 2015; Angot et al., 2016)
- **Quantifying Hg dry deposition budget** (Engle et al., 2010; Lombard et al., 2011; Zhang et al., 2012, 2016)
- **Understanding Hg cycling, gas-particle partitioning, oxidation mechanisms** (Obrist et al., 2 011; Amos et al., 2012; Timonen et al., 2013; Cheng et al., 2014; Shah et al., 2016; Ye et al., 2016, Gabay et al., 2017)
- **Other applications** (Steffen et al., 2005; Chen et al., 2013; Cole et al., 2013, 2014; Cheng et al., 2014, 2015; Brown et al., 2015; Castro and Sherwell, 2015; Martin et al., 2017)

# Receptor-based analysis

**Uses ambient air concentrations to identify and apportion sources; sources are unknown**

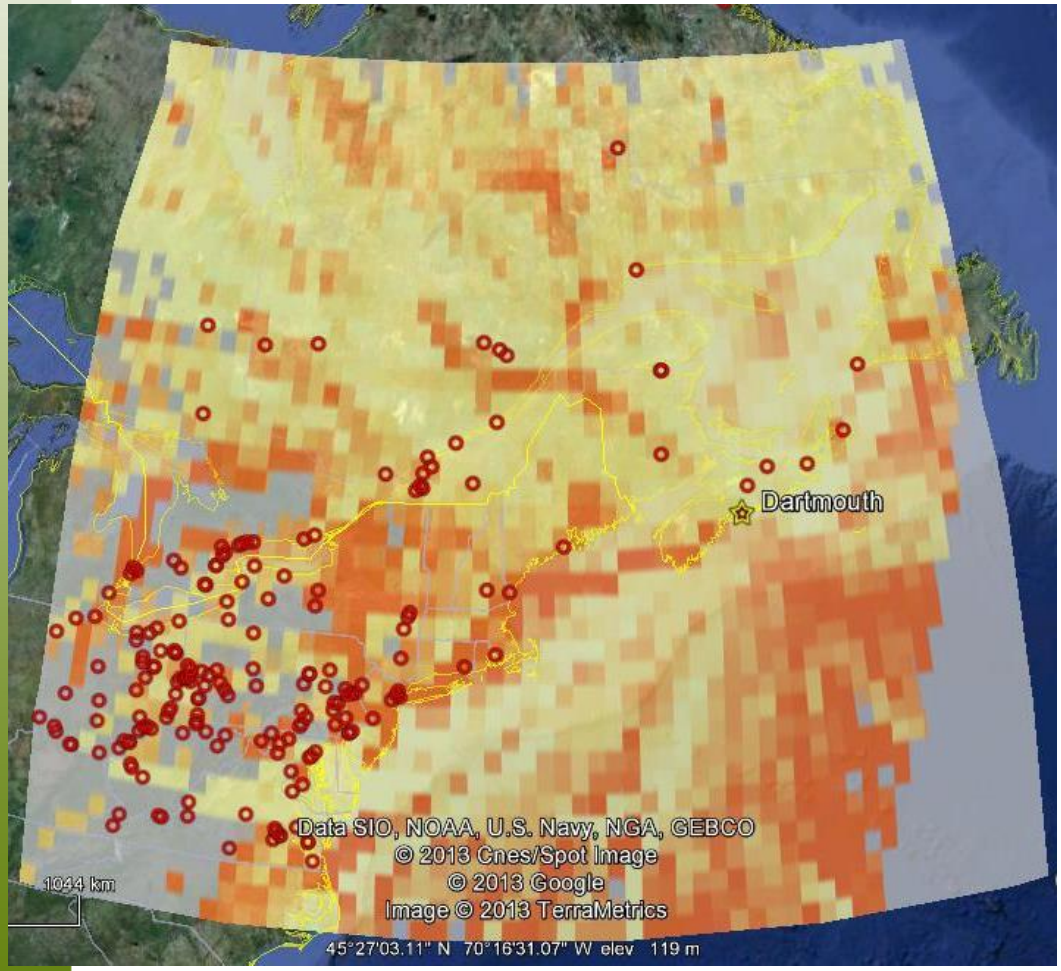
- Multivariate methods:
  - Positive Matrix Factorization (PMF) model
  - Principal Components Analysis (PCA)
  - Cluster analysis
- Hybrid concentration-trajectory methods:
  - Potential Source Contribution Function (PSCF)
  - Concentration-Weighted Trajectory (CWT)
  - Other variations: gridded frequency distribution, residence time weighted concentration, simplified quantitative transport bias analysis

**See a detailed review in Cheng et al. (ACP, 2015)**

# CWT Modeled source regions

**weak regions (10th percentile CWT)**

**major source regions (90th percentile CWT)**




## Source regions impacting atmospheric Hg at Dartmouth, NS

- Compare modeled source regions to known Hg sources (NPRI & TRI emissions data)
- CWT predicted source areas where there Hg point sources (power plant, cement mfg. in Pennsylvania)
- CWT predicted source areas from the Atlantic Ocean (Evasion of Hg?)

**Cheng et al. (ACP, 2013)**

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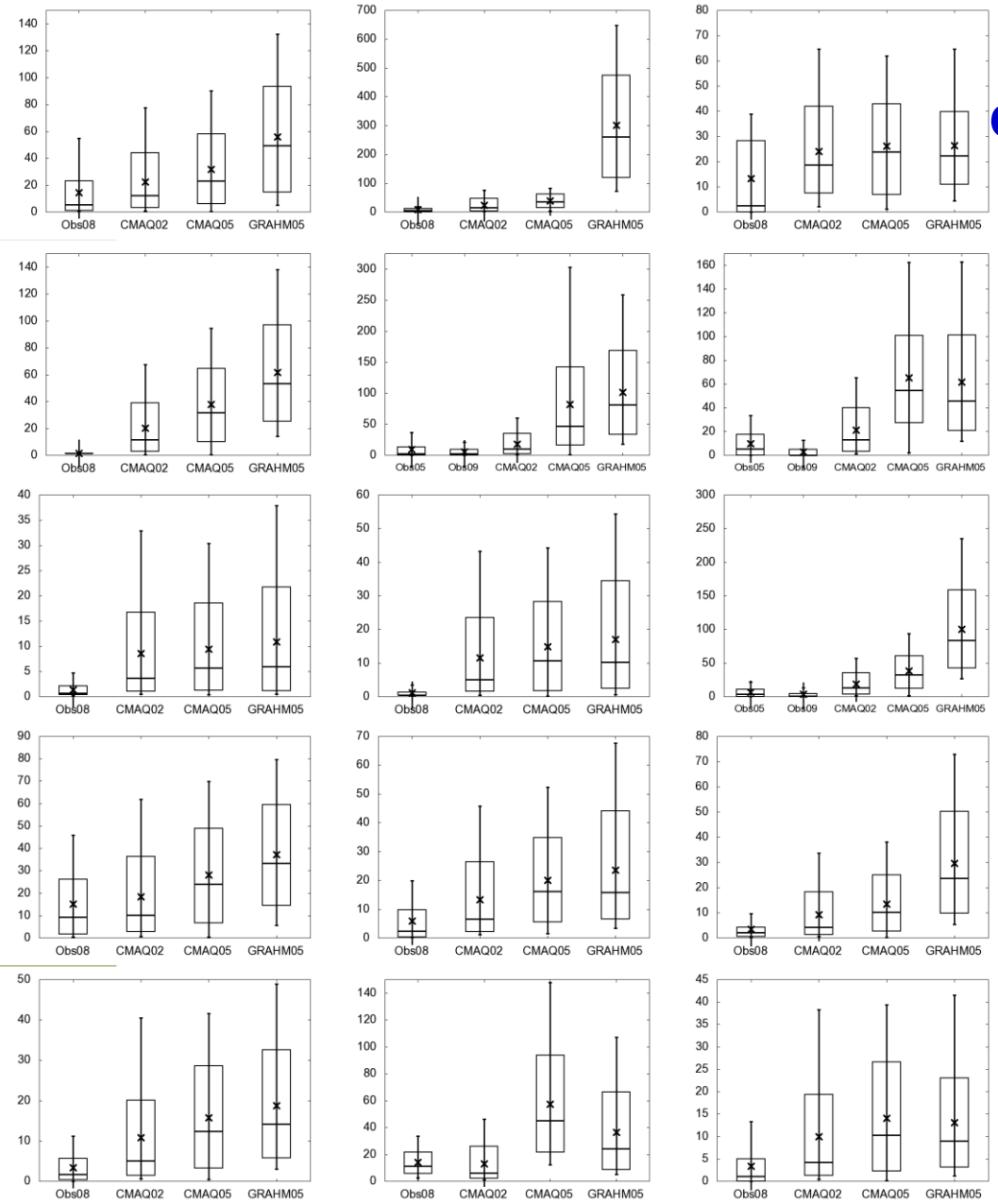
# Results – Comparing the coastal and inland site

| 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 |

Cheng et al. (JGR, 2013)

# CTM Model Evaluation




## Comparison of hourly RGM (pg m$^{-3}$)

CMAQ2002:

Overestimated by a factor of 2-8 at 13 sites

CMAQ2005

Overestimated by a factor of 2-27 at all of the 15 sites

GRAHM2005

Overestimated by a factor of 3.5-40 at all of the sites

**Zhang et al. (EP, 2012)**

Which led to model improvement

**Kos et al. (ACP, 2013)**

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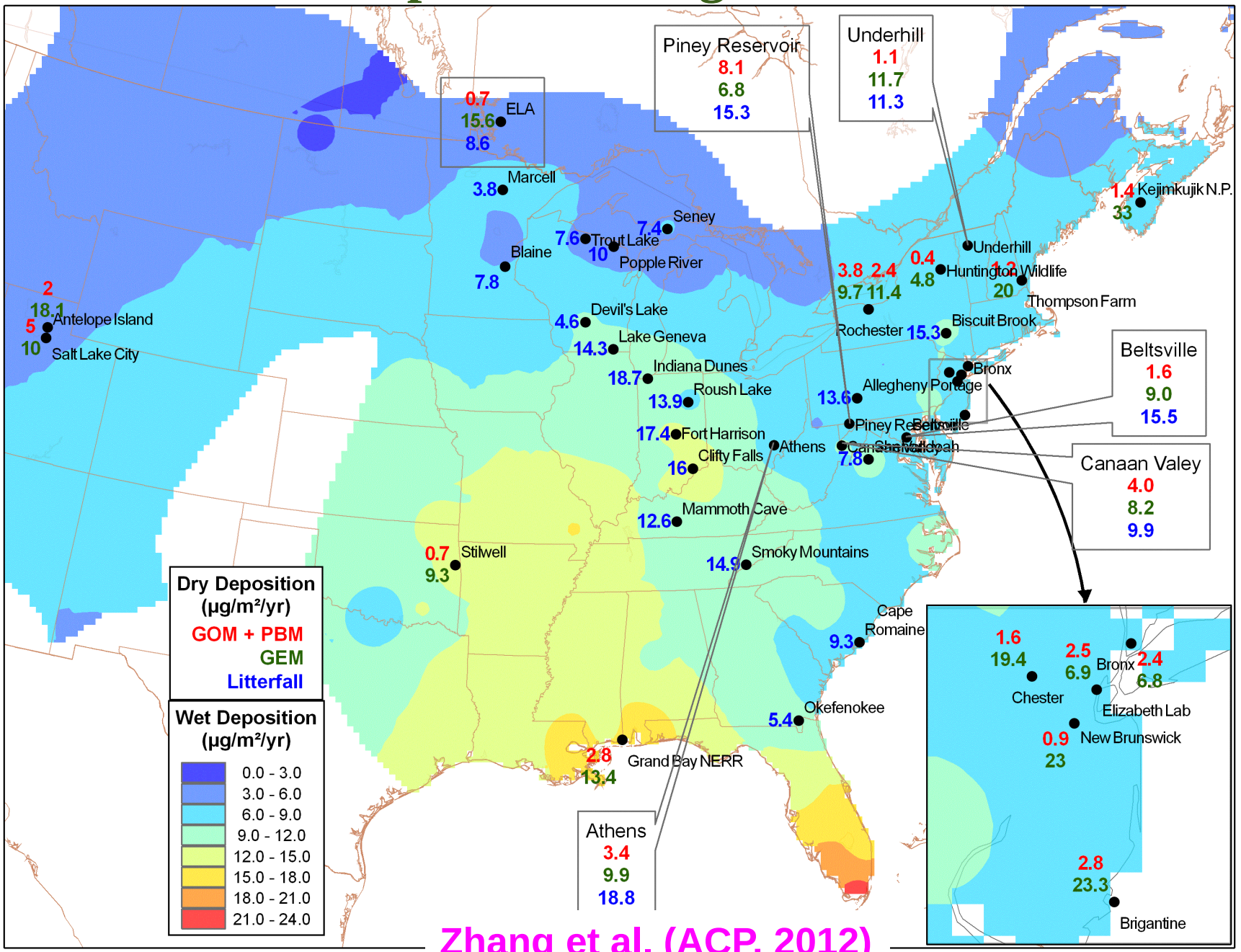
# Deposition Budget




Zhang et al. (ACP, 2012)

# Regression models: gas-particle partitioning

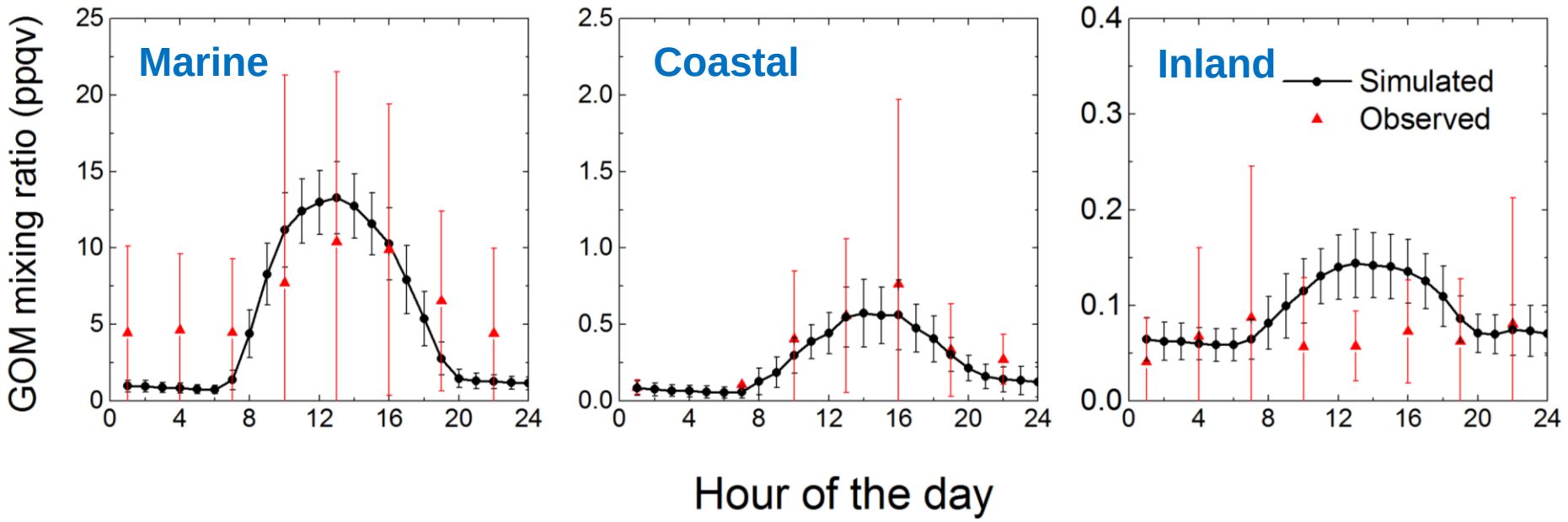
Generalized $K_p$-temperature model:

| Site(s) | Regression Equation | $R^2$ | |
|---|---|---|---|
| NS01 | $Log(1/K_p) = 15.41 – 4285.73(1/T)$ | 0.59 | Cheng et al. (2014) |
| 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 | |

**Most CTMs currently use a constant partitioning**

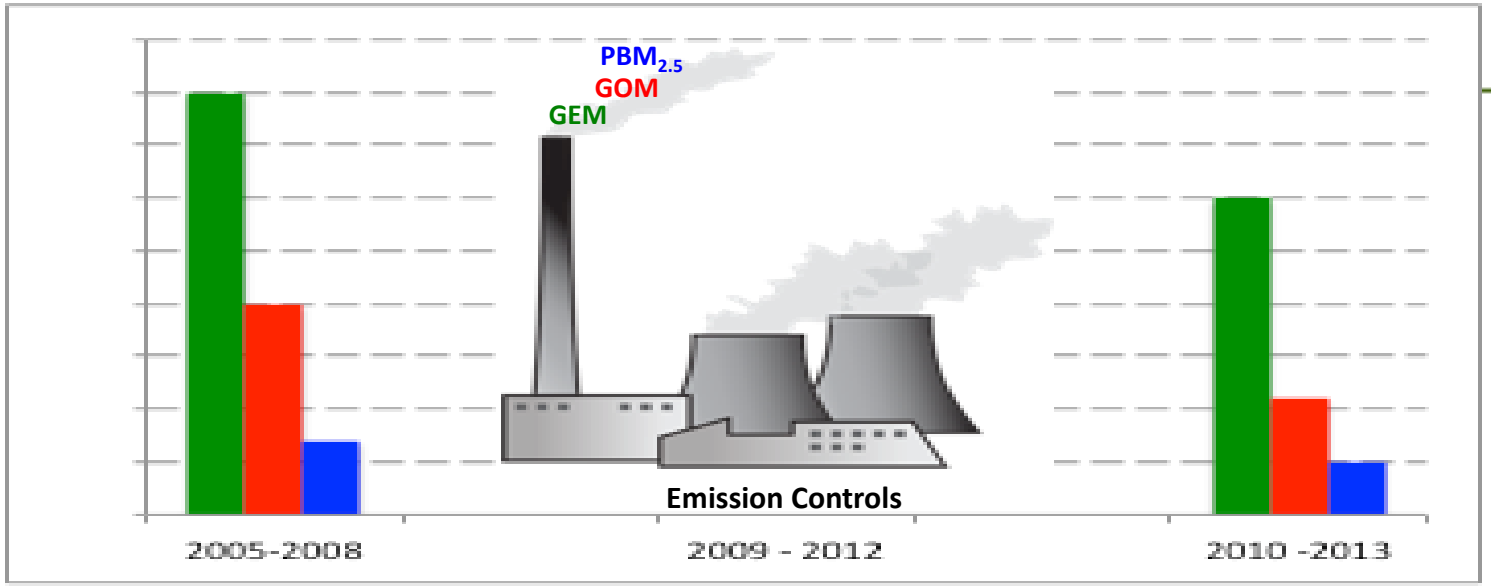
# Investigation of chemical mechanisms

## - State-of-the-Art Hg Box Model Simulations of GOM




- GOM diurnal cycles in various environments were reproduced using a box model with a GEM oxidation mechanism involving $O_3$, OH, $H_2O_2$, Br, BrO, Cl, $Cl_2$, and I radicals
- During daytime Br initiated GEM oxidation dominated Hg oxidation in MBL
- Ozone and OH radicals dominated Hg oxidation at coastal and inland sites
- It was hypothesized that gas-particle partitioning of oxidized Hg in MBL could make an important contribution to atmospheric GOM

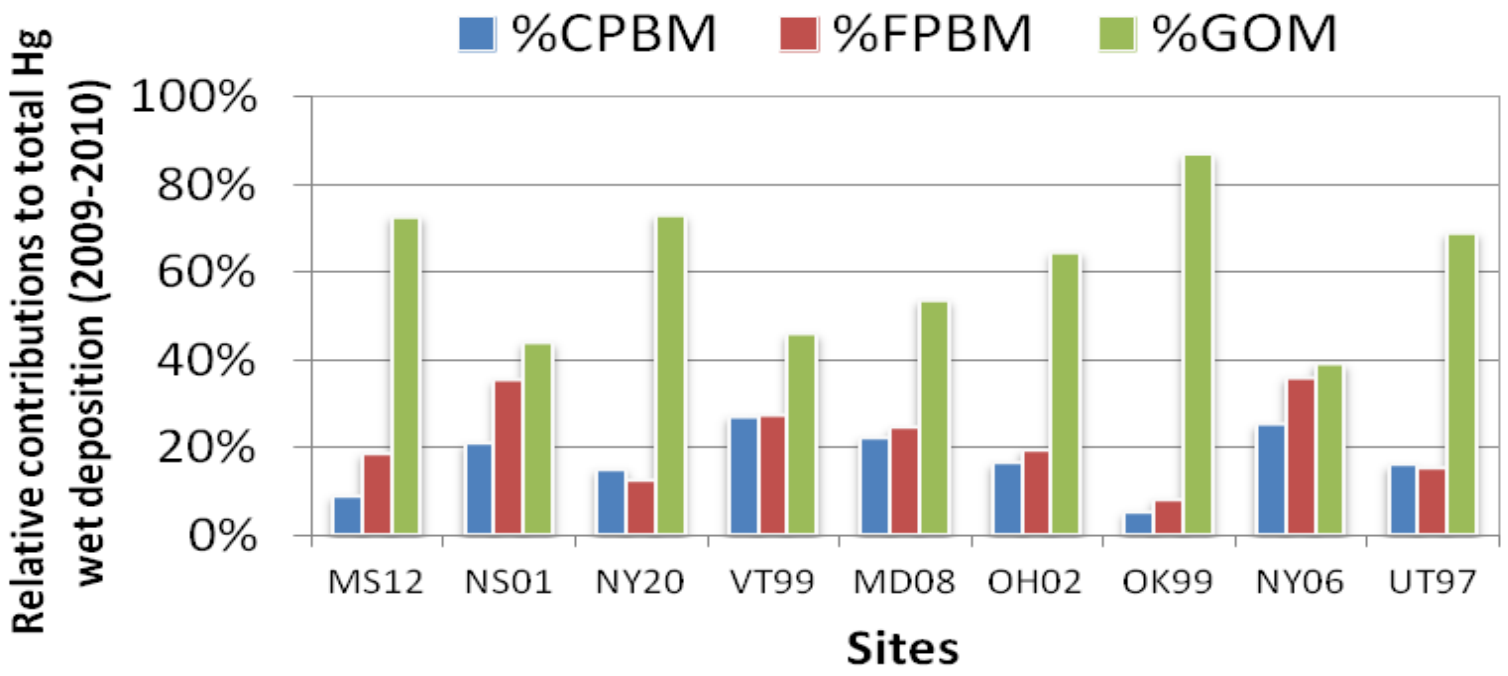
# Investigation of emission-reduction effects and long-term trends




- From 2000 to 2013, United States power plant total mercury emissions decreased from ~40 Mg $yr^{-1}$ to ~20 Mg $yr^{-1}$.
- In 2013, power plant mercury emissions from states upwind and adjacent to MD08 decreased by up to 80% of their 2000 mercury emissions.
- Significant reductions in the atmospheric concentrations of GEM (13%), GOM (75%), PBM2.5 (43%) and SO2 (75%) occurred at MD 08 between 2000 and 2013.
- Global mercury emission reductions are needed for further reductions in the atmospheric concentrations of GEM.

**Castro and Sherwell (EST, 2015)**

# Relative contributions to wet deposition




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

**AMNet and Most CTMs excluded coarse particles**



Cheng et al. (JGR, 2015)

# A synthesis of future research needs

- **Refinement of mercury emission estimations,**
- **Quantification of dry deposition and air-surface exchange**
- **Improvement of the treatment of chemical mechanisms in chemical transport models**
- **Increase in the accuracy of oxidized mercury measurements**
- **Better interpretation of atmospheric mercury chemistry data**
- **Harmonization of network operation**

Zhang L., Lyman S., Mao H., Lin C.-J., Gay D.A., Wang S., Gustin M.S., Feng X., and Wania F.: A synthesis of research needs for improving the understanding of atmospheric mercury cycling. Atmospheric Chemistry Physics Discussion, doi:10.5194/acp-2017-375, 2017.

# A step further

**Coordinated research and linkage between air, water and wildlife community because:**

**– knowledge on atmospheric mercury cycling will be eventually used for assessing mercury impacts on ecosystem and human health**

# Thank you!