

# Mercury Speciation at a Suburban Site in the Mid-Atlantic US: Seasonal and Diurnal Variations and Source-Receptor Correlationship

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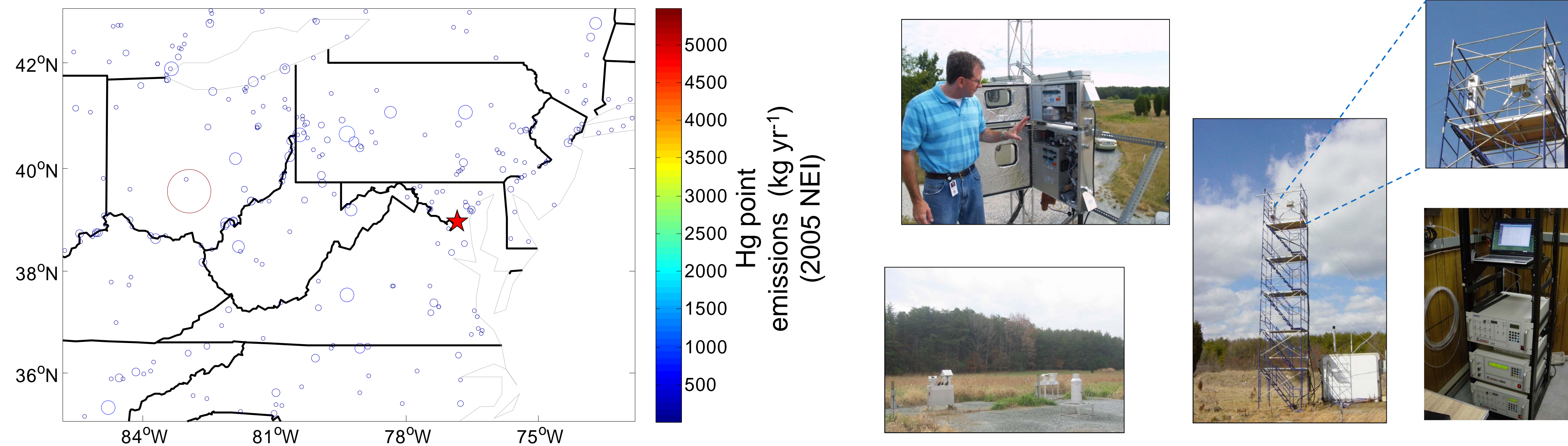
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## Motivation

- To establish long-term data record of ambient concentrations of mercury speciation (GEM, GOM, and PBM).
- To assess the regional budget of atmospheric mercury using long-term measurements with high-time resolution.
- To elucidate source-receptor relationships and examine relative contributions of natural and anthropogenic processes.

## Measurements

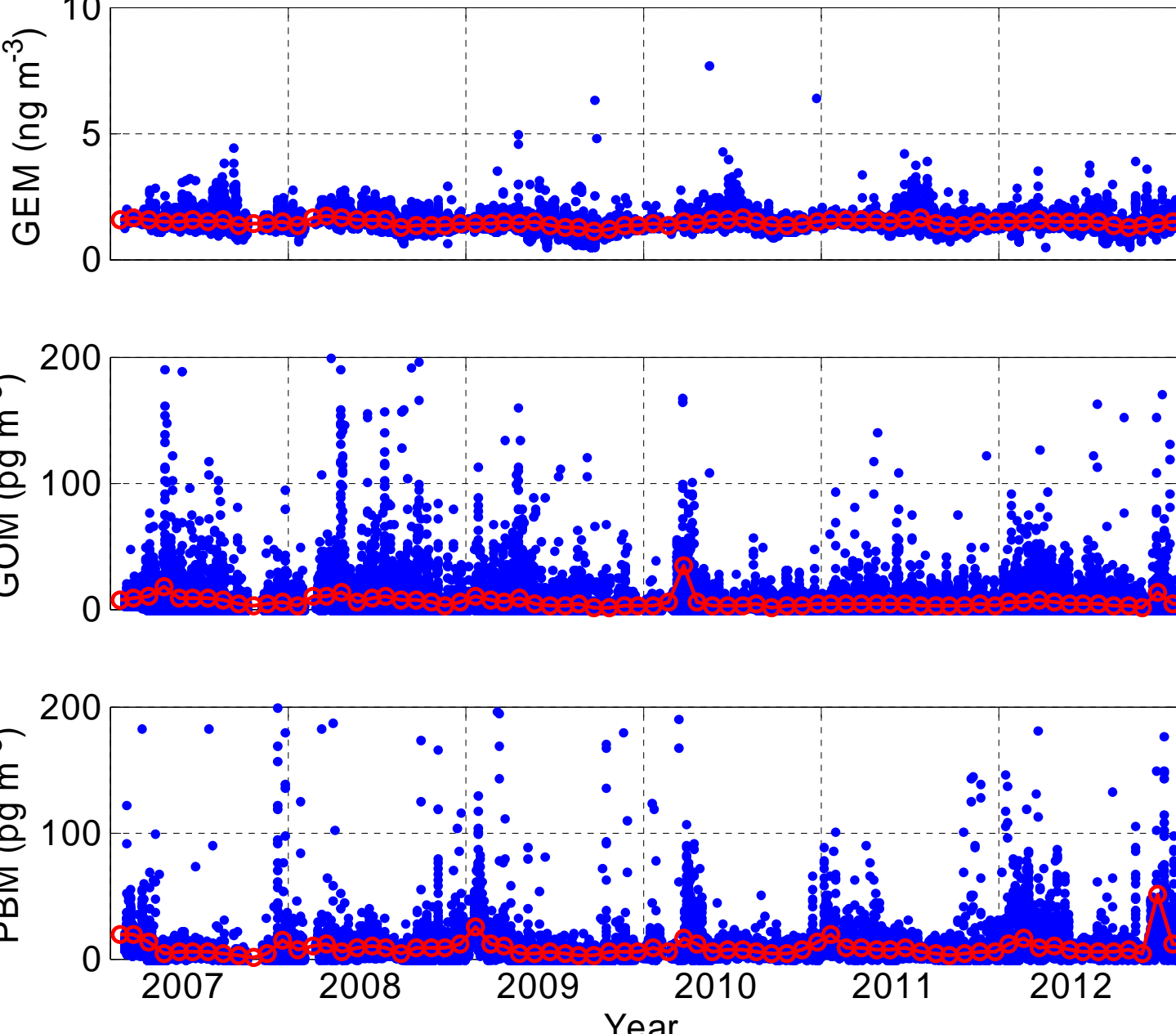
- **when:** Jan. 2007 – Dec. 2012 (still on-going)
- **where:** MD99 in Beltsville, MD, (39.0282°N, 76.8172°W), a suburban portion of the Washington, DC metropolitan area.
- **what:** Hg speciation (GEM, GOM, and PBM), CASTNet measurements (O<sub>3</sub>, SO<sub>2</sub>, CO, NO, NO<sub>y</sub>, wind, T, RH, and precipitation), and weekly NADP/NTN measurements (major ions in precipitation) and MDN (mercury wet deposition).



**Fig.1** Left: the location of the site and regional Hg point sources (color-coated circles with circle area proportional to emissions) near Beltsville, MD based on the EPA 2005 NEI. Right: pictures showing the instrumentation at the Beltsville site.

## Results

### Inter-annual Variations



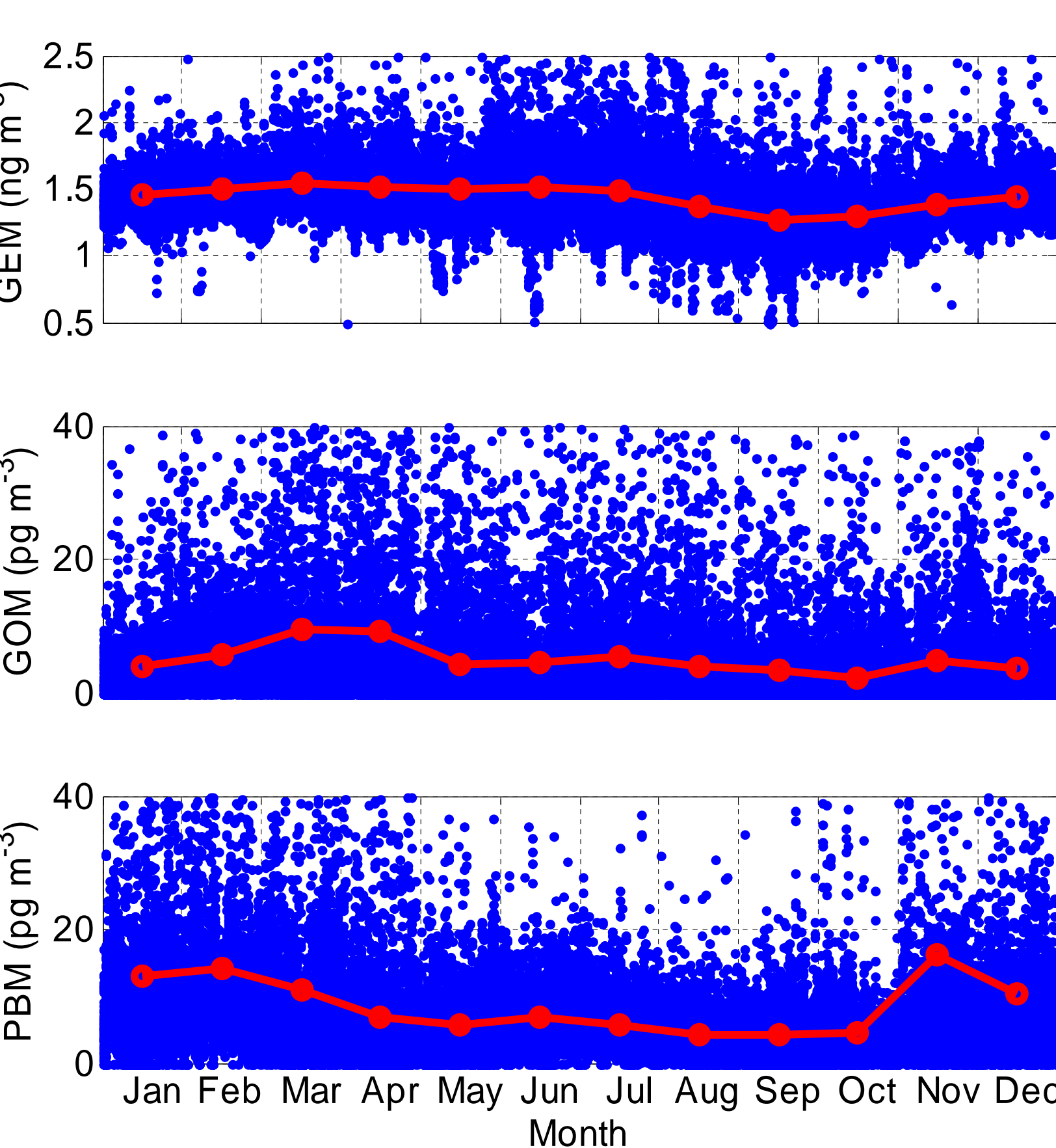
**Fig. 2** Time series of mercury speciation measured at the Beltsville site in Maryland from 2007 to 2012.

**Table 1.** Statistics of measured hourly concentrations of GEM, GOM, and PBM at the Beltsville site in Maryland. Minimum concentrations for GOM and PBM were zero (not shown).

Year	[GEM] (ng m <sup>-3</sup> )				[GOM] (pg m <sup>-3</sup> )			[PBM] (pg m <sup>-3</sup> )		
	min	max	median	mean±std	max	median	mean±std	max	median	mean±std
2007	0.76	4.47	1.46	1.49±0.29	254	3.1	8.0±15.8	809	3.7	7.7±24.6
2008	0.64	2.94	1.44	1.46±0.24	430	1.9	7.2±17.7	1009	5.7	7.8±19.4
2009	0.47	18.1	1.32	1.33±0.42	239	0.95	4.5±10.7	438	3.7	6.7±14.3
2010	0.88	21.1	1.41	1.45±0.39	6848	1.3	5.3±10.3	553	5.4	7.7±17.1
2011	0.70	4.20	1.47	1.48±0.21	140	1.0	3.0±6.5	1677	4.7	7.1±25.0
2012	0.49	3.94	1.43	1.43±0.20	888	1.3	4.6±18.0	7312	5.3	11.9±136
All	0.47	21.1	1.42	1.43±0.31	6848	1.4	5.0±39.7	7312	4.9	8.5±66.7

- No significant year-to-year trends for GEM and PBM.
- Maybe slight reduction in GOM after 2009 (also seen in Fig. 5).
- Extremely high GEM, GOM, and PBM levels were observed occasionally.

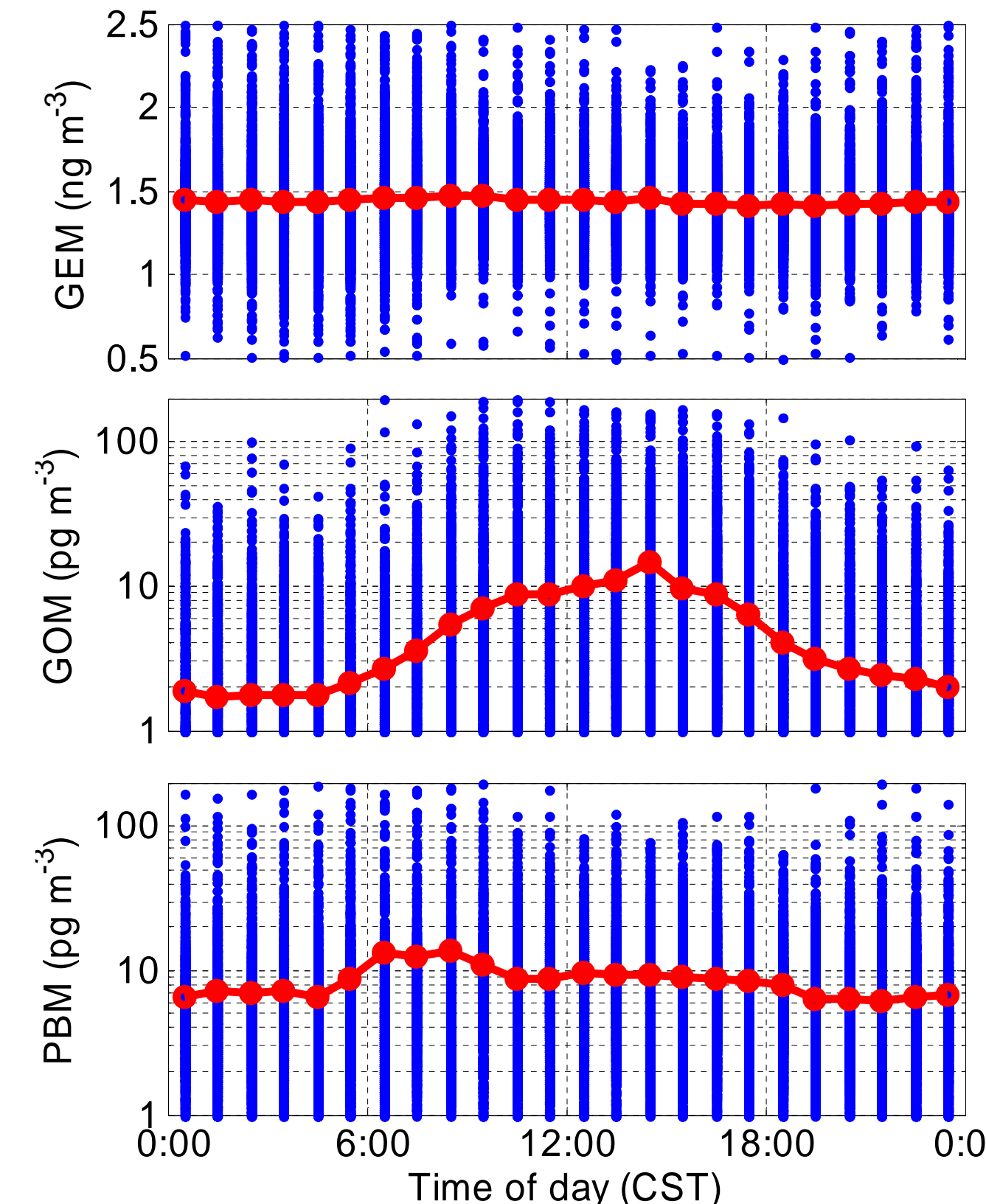
### Seasonal Variations



**Fig.3** Seasonal (left) and average diurnal variations (right) of mercury speciation measured at the Beltsville site from 2007 to 2012. The individual dots represent 1-hour data and the linked circles are composite monthly (left) or hourly (right) mean values.

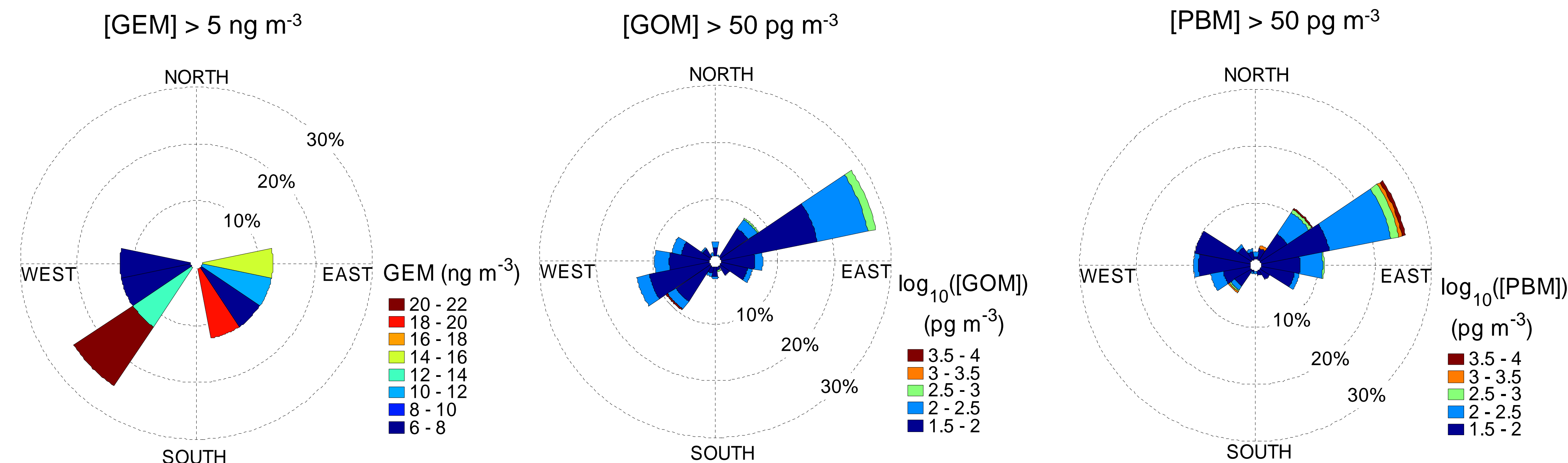
- Seasonal:
  - GEM: higher in spring/summer, min. in fall
  - GOM: peak in spring, low in summer/fall
  - PBM: higher in spring
- Diurnal:
  - GEM: max. in AM and min. in late PM/early evening
  - GOM: max in mid-day/afternoon, low at night
  - PBM: max. in the morning and low at night

### Diurnal Variations



## Results (cont'd)

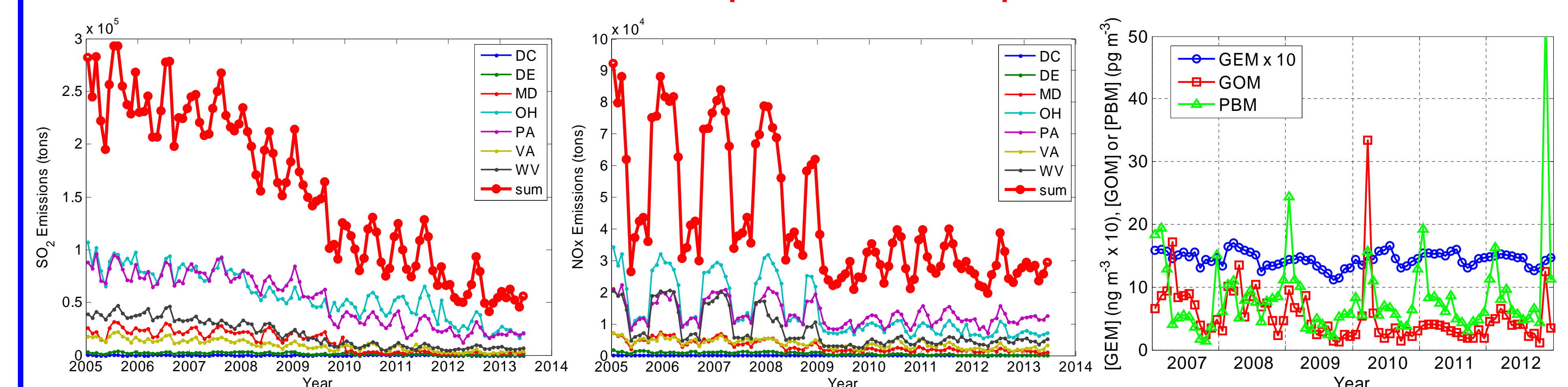
### Wind Rose of Elevated Hg Species



**Fig.4** Wind rose plots of elevated levels of Hg species with [GEM]>5 ng m<sup>-3</sup>, [GOM]>50 pg m<sup>-3</sup>, and [PBM] > 50 pg m<sup>-3</sup> measured at the Beltsville site.

- Elevated GEM events occurred with southerly winds, especially with winds from SW and SSE.
- Elevated GOM and PBM events occurred with E/NE and W/SW winds.
- Extremely high [GEM] (up to 21 ng m<sup>-3</sup>), [GOM] (up to 6.8 ng m<sup>-3</sup>) and [PBM] (up to 7.3 ng m<sup>-3</sup>) were observed at this site. These extreme events might be associated with localized emissions of mercury species.

### Source-receptor Correlationship



**Fig.5** Monthly SO<sub>2</sub> (left) and NO<sub>x</sub> (middle) emissions from the sates near the Beltsville site from 2005 to 2013 as well as monthly averaged concentrations of mercury species measured at the Beltsville site.

- Significant emission reduction in both SO<sub>2</sub> and NO<sub>x</sub> in the areas near the Beltsville site from 2005 to 2013, especially the significant reduction during 2009/2010.
- No significant reduction in GEM or PBM, maybe slight reduction in GOM after 2009.
- Either speciated mercury concentrations are not significantly affected by power plants or the reduction of mercury emissions is not as much as the reduction of SO<sub>2</sub> and NO<sub>x</sub> emissions.

## Summary

- Six years of continuous measurements of mercury speciation with current measurements still on-going.
- GEM: no significant inter-annual variation, minimum in fall, peak in the morning and low in the early evening.
- GOM: slight reduction after 2009 which might be due to emission reduction, high in spring and peak in mid-day.
- PBM: no significant inter-annual variation, peak in the early morning probably due to morning rush hour.
- Significant emissions in SO<sub>2</sub> and NO<sub>x</sub> esp. after 2009, but only slight reduction in GOM with no decrease trends in GEM and PBM, indicating the reduction of Hg emissions is not as much as the reduction of SO<sub>2</sub> and NO<sub>x</sub> emissions.

### On-going and Future Work

- Use of high-resolution meteorological and up-to-date mercury emission data for HYSPLIT trajectory analysis and Hg model simulations as well as the correlation between atmospheric Hg and Hg in wet deposition.

### Acknowledgements

- US EPA for funding
- CASTNet for trace gas and meteorological measurements