Overview of measurement approaches for the estimation of temporal and spatial variations in mercury dry-deposition

Frank J. Marsik
University of Michigan, Ann Arbor, Michigan, USA

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Outline

- Value of the measure
- Factors which influence mercury dry-deposition
- Measurement approaches (Surrogate)
- Measurement approaches (Vegetation sampling)
- Conclusions/Future directions

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Value of the Measure

- Quantification of magnitude
  - Total Maximum Daily Load
  - Relative importance of wet- vs. dry-deposition
- Characterization of spatial trends
  - Local, Regional, National
- Characterization of temporal trends
  - Short-term studies
    - Days to weeks (monitor synoptic meteorological or local source impacts)
  - Long-term studies
    - Seasonal
    - Multi-year (monitor changes in deposition following changes in emissions)

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Quantification of Magnitude

- Wet-deposition of mercury is relatively well quantified, while measurements of dry-deposition of mercury are limited.

- Various studies have suggested that annual dry-deposition of mercury can be equivalent to wet-deposition in some locations

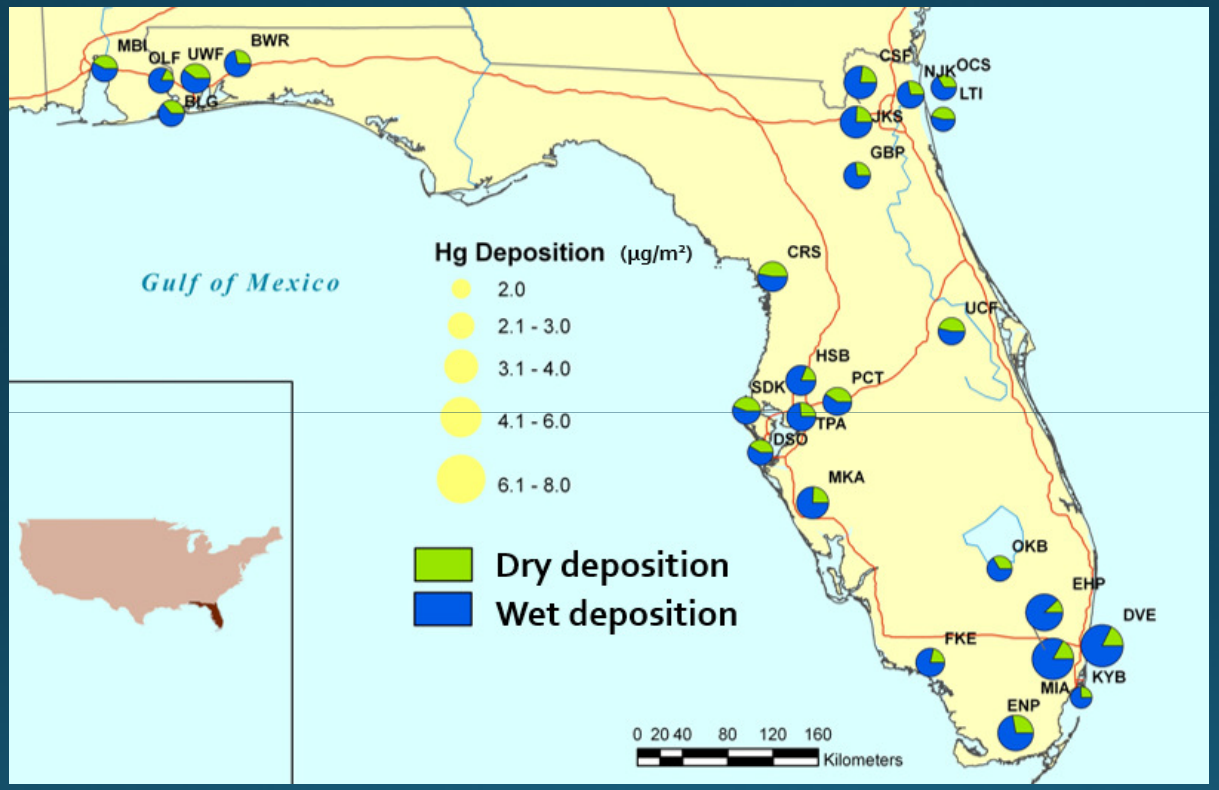
Detroit, Michigan			
Year	Wet (ug/m^2)	Dry (ug/m^2)	Total (ug/m^2)
2003	10.6	16.8	27.4
2004	10.4	13.6	24.0
2005	12.0	11.7	23.7
2006	9.2	8.1	17.3

*Wet deposition (measured); Dry deposition (inferential model)
Keeler et al. (Final Report to Michigan Great Lakes Protection Fund, 2009)

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Quantification of Spatial Trends

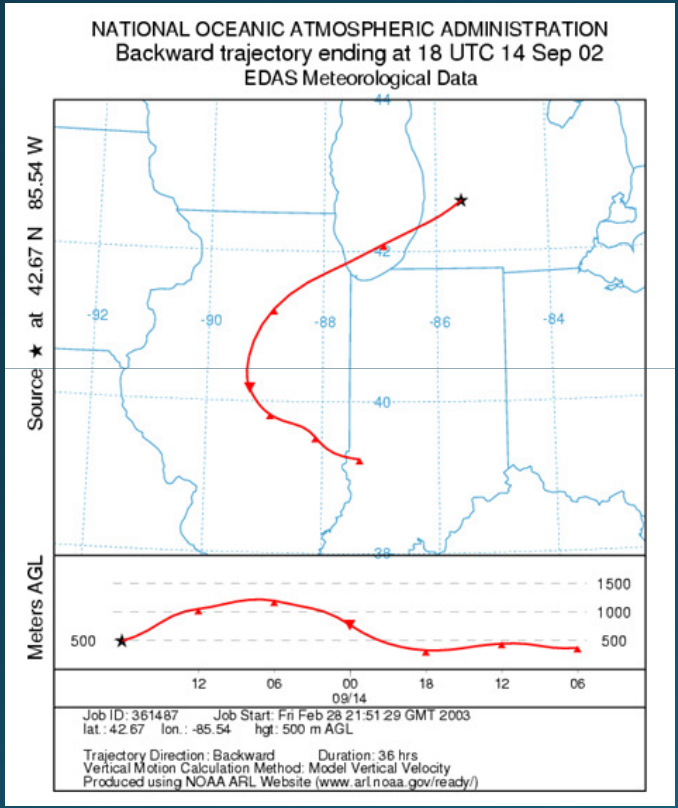
July 2009 (South) and July 2010 (north)



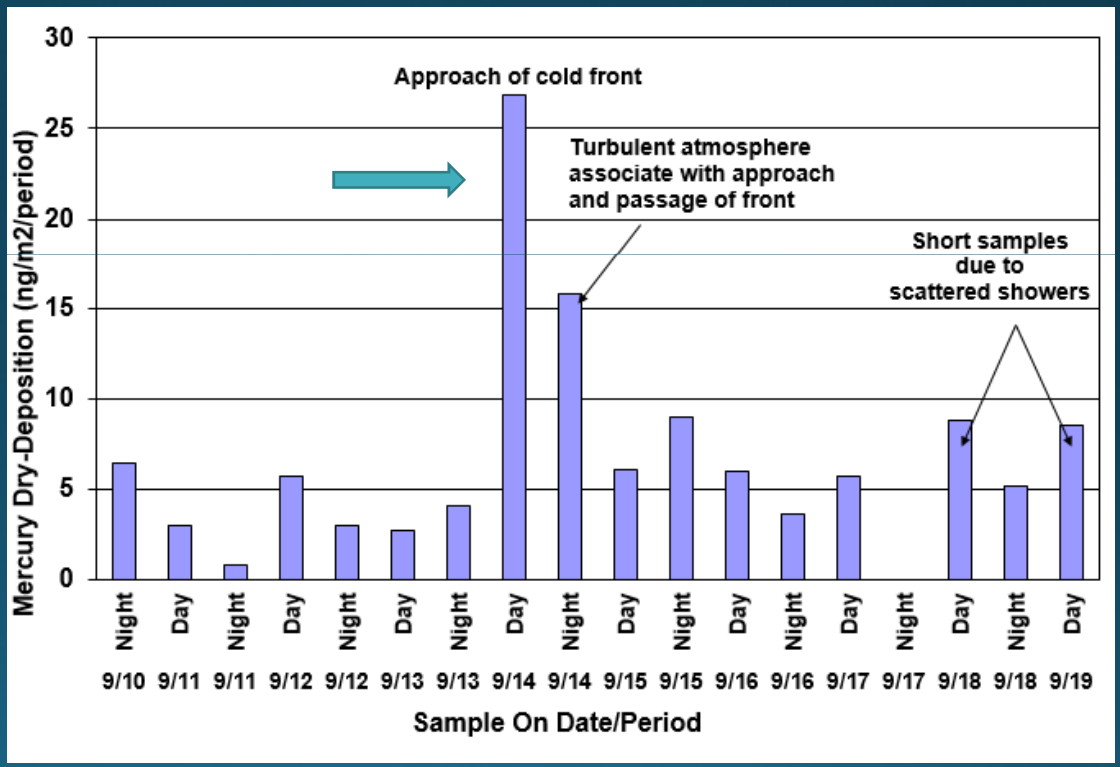
Source: Preliminary data, Naima Hall (University of Michigan Air Quality Laboratory)

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Quantification of Temporal Trends

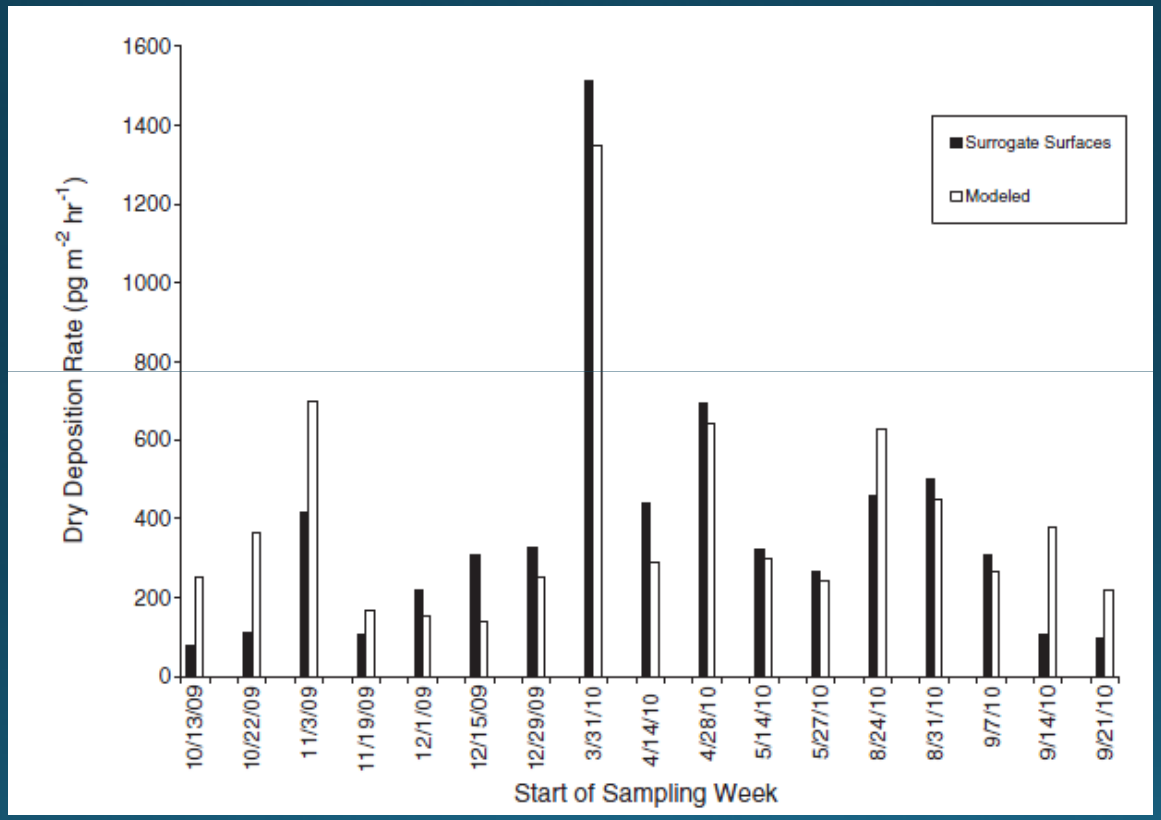


Mercury Dry-Deposition over Soybean Canopy
Clarksville, MI (Surrogate Water Surface)
(RGM + pHg, ng/m2/period)



Source: Marsik and Keeler
(Project Final Report to the Michigan Great Lakes Protection Fund, 2008)

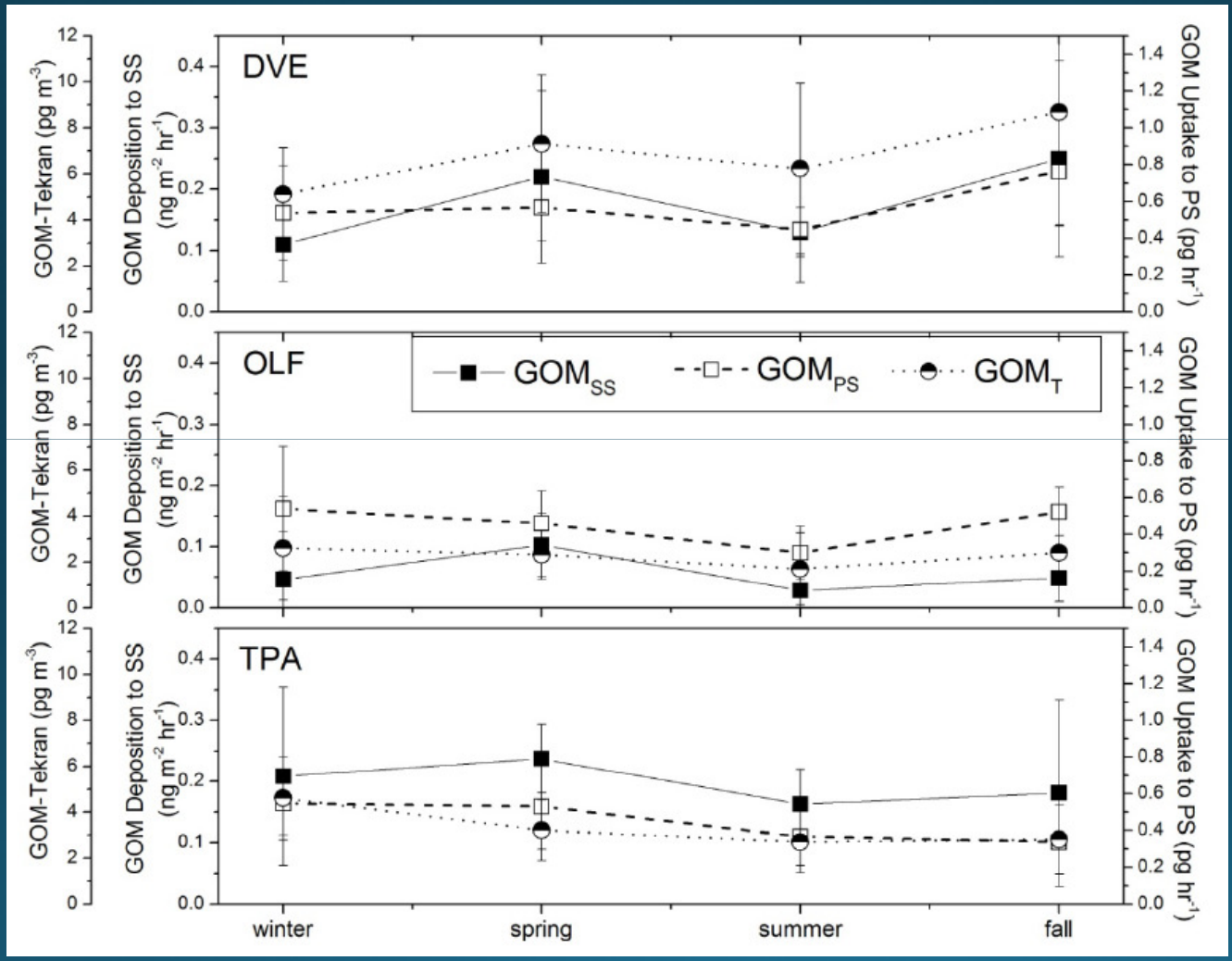
Quantification of Temporal Trends



Castro et al. (STOTEN, 2012) – Garrett County, MD, USA

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Quantification of Temporal Trends



Source: Gustin et al. (Atmospheric Chemistry and Physics, 2012)

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Factors which influence mercury dry-deposition

- Atmospheric characteristics
  - Temperature
  - Winds



Turbulence

- Chemical characteristics of depositing species
  - Solubility
  - Reactivity
  - Diffusivity
  - Physical state (gas or particle)
- Chemical and physical characteristics of deposition surface

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Factors which influence mercury dry-deposition

- Physical influences of deposition surface



Source: Audubon Society



Source: imgisland.com











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Factors which influence mercury dry-deposition

- Physical influences of deposition surface



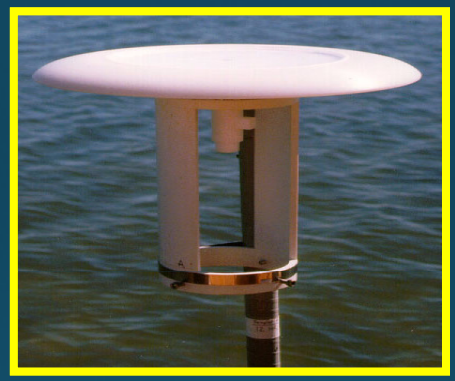


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Mercury Dry Deposition Measurement Intercomparison

University of Michigan - Ann Arbor, MI - 04 to 13 August 2008







Frank Marsik, Naima Hall (University of Michigan)
Steve Brooks,Chris Moore (NOAA)
Mae Gustin, Seth Lyman (University of Nevada –Reno)
Tom Holsen, Jiaoyan Huang, H-D. Choi (Clarkson University)
Matt Landis (U.S. EPA)
Laurier Poissant, Martin Pilote (Environment Canada)
Eric Prestbo, Mark Olson (NADP/USGS/Tekran)

Project Funded by the Great Lakes Air Deposition Program

Study Participants and Approaches

- **University of Nevada-Reno**
  - Cation-exchange surrogate surface
  - Passive samplers ambient concentration
  - Lyman et al., 2009 (*Environmental Science and Technology, 43, 6235–6241*)

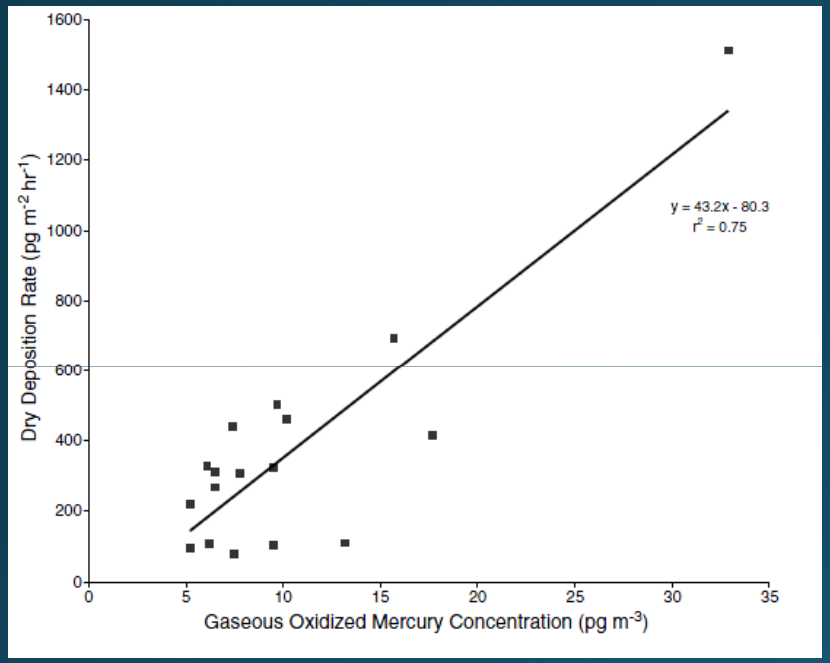


- **University of Michigan**
  - Water surrogate surface
  - Turf surrogate surface
  - Dew sampling
  - Marsik et al., 2006 (*Environmental Science and Technology, 41,136-149*)

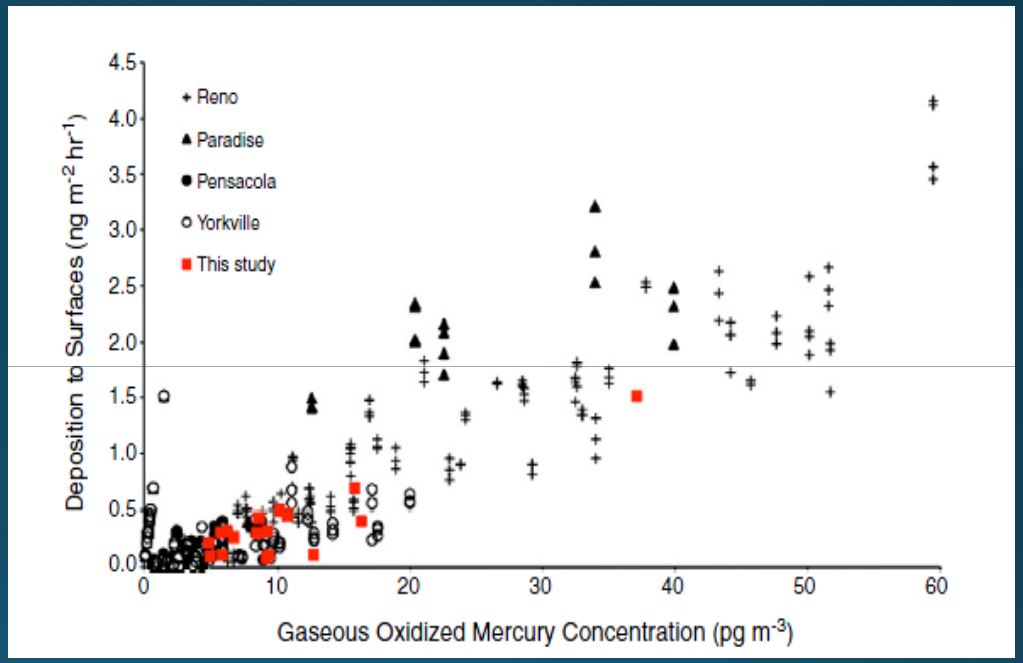


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Cation Exchange Membranes (CEM)



Castro et al. (STOTEN, 2012)
Garrett County, MD, USA

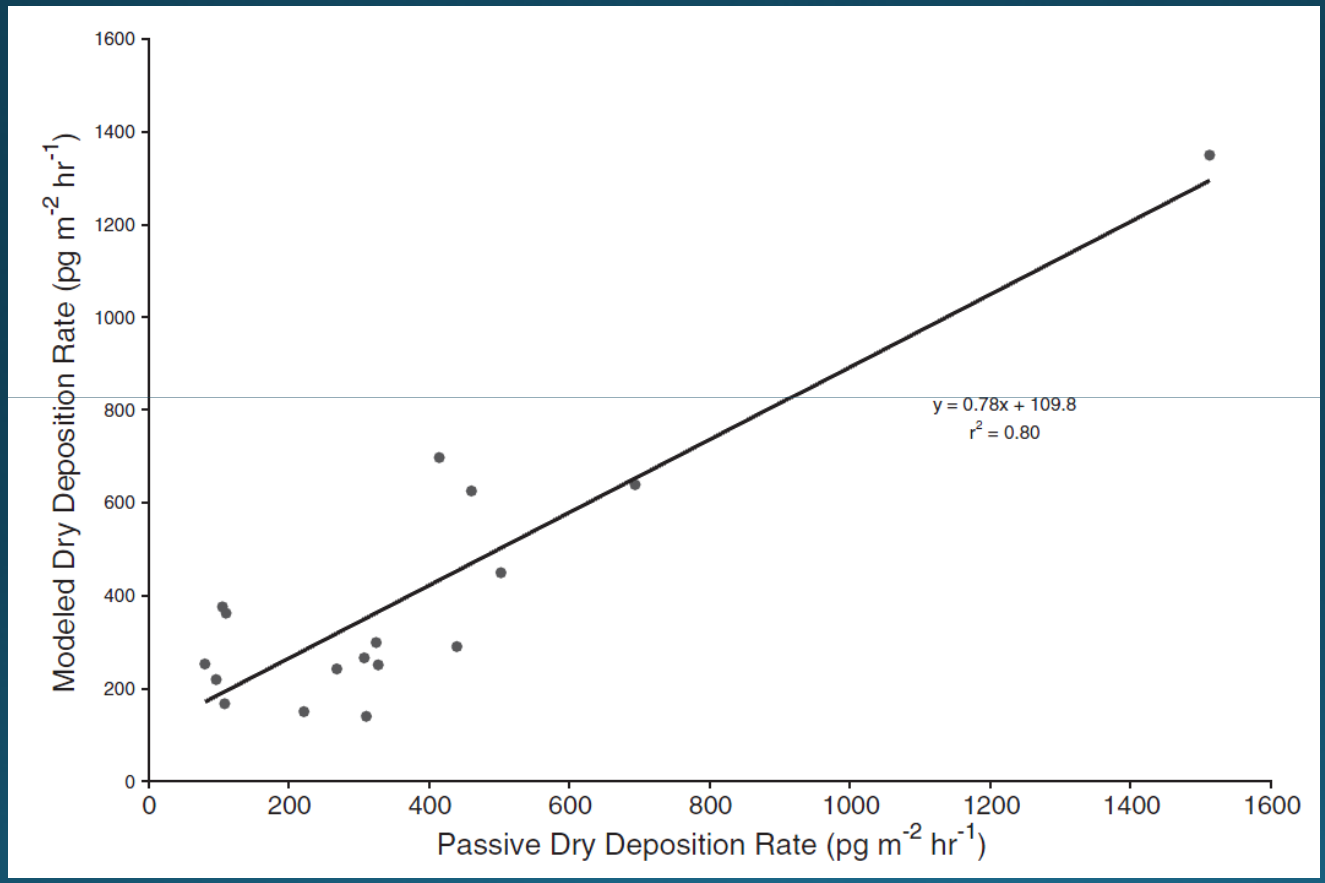


Data provided to Castro et al. (STOTEN, 2012)
By S. Lyman and M. Gustin

Fang et al. (Environmental Forensics, 2013) -
Knife-edged surrogate surface/Ion Exchange Membrane for Taiwan traffic study

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Cation Exchange Membranes (CEM)

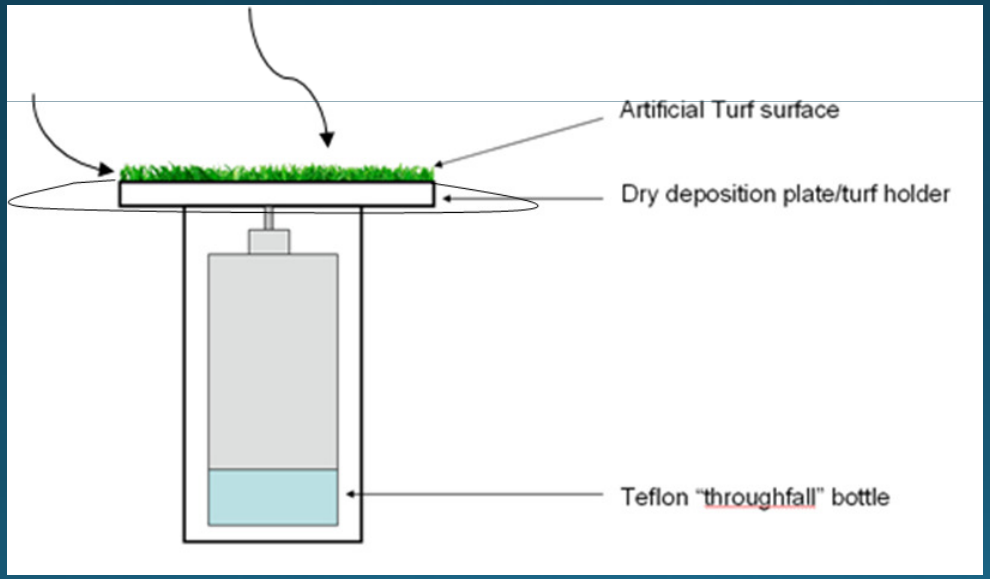


Castro et al. (STOTEN, 2012) – Garrett County, MD, USA

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Turf Surrogate Surface (TSS)

- Avoids contamination by rainfall
- Not all particle deposition is downward, thus horizontal impaction potentially important



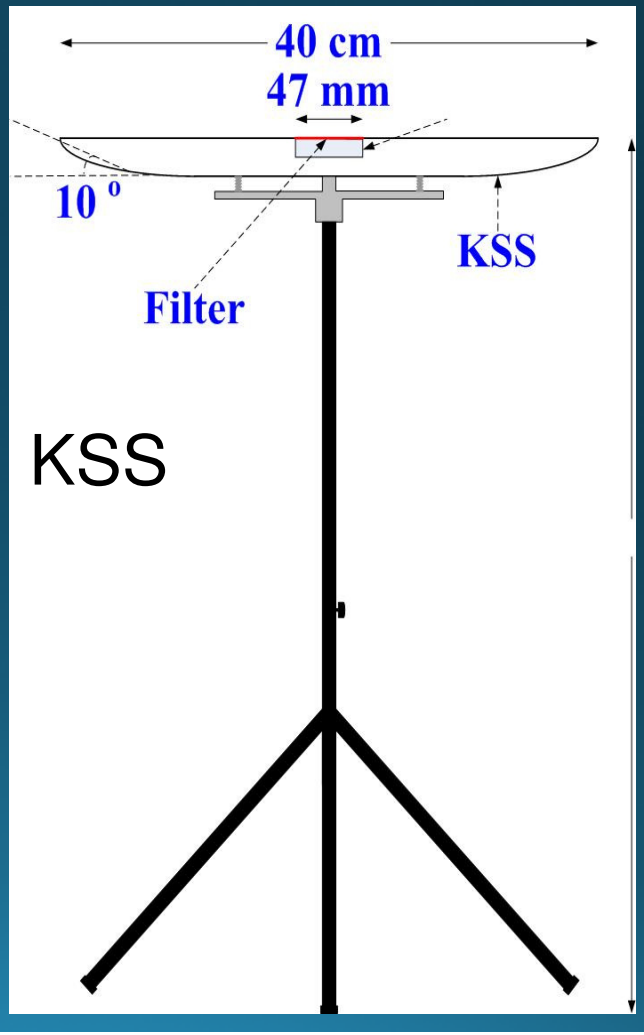
Mercury (RGM + pHg) Dry Deposition = $(Hg_{turf} + Hg_{throughfall}) - Hg_{rain\ only}$

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Study Participants and Approaches

- **Clarkson University**
  - Water surrogate surface
  - Filter surrogate surface
  - Gold foil surrogate surface
  - *Tasdemir and Holsen (2005) Atmospheric Environment, 39, 1845-1854)*





Study Participants and Approaches

USEPA Dry Deposition Monitoring

Automated Water Surface Surrogate Dry Deposition Collector

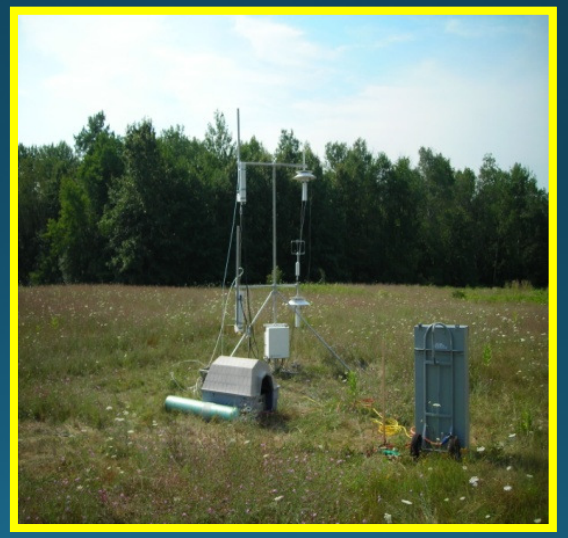


Similar to approach of Sakata and Marumoto (Atmospheric Environment, 2005)

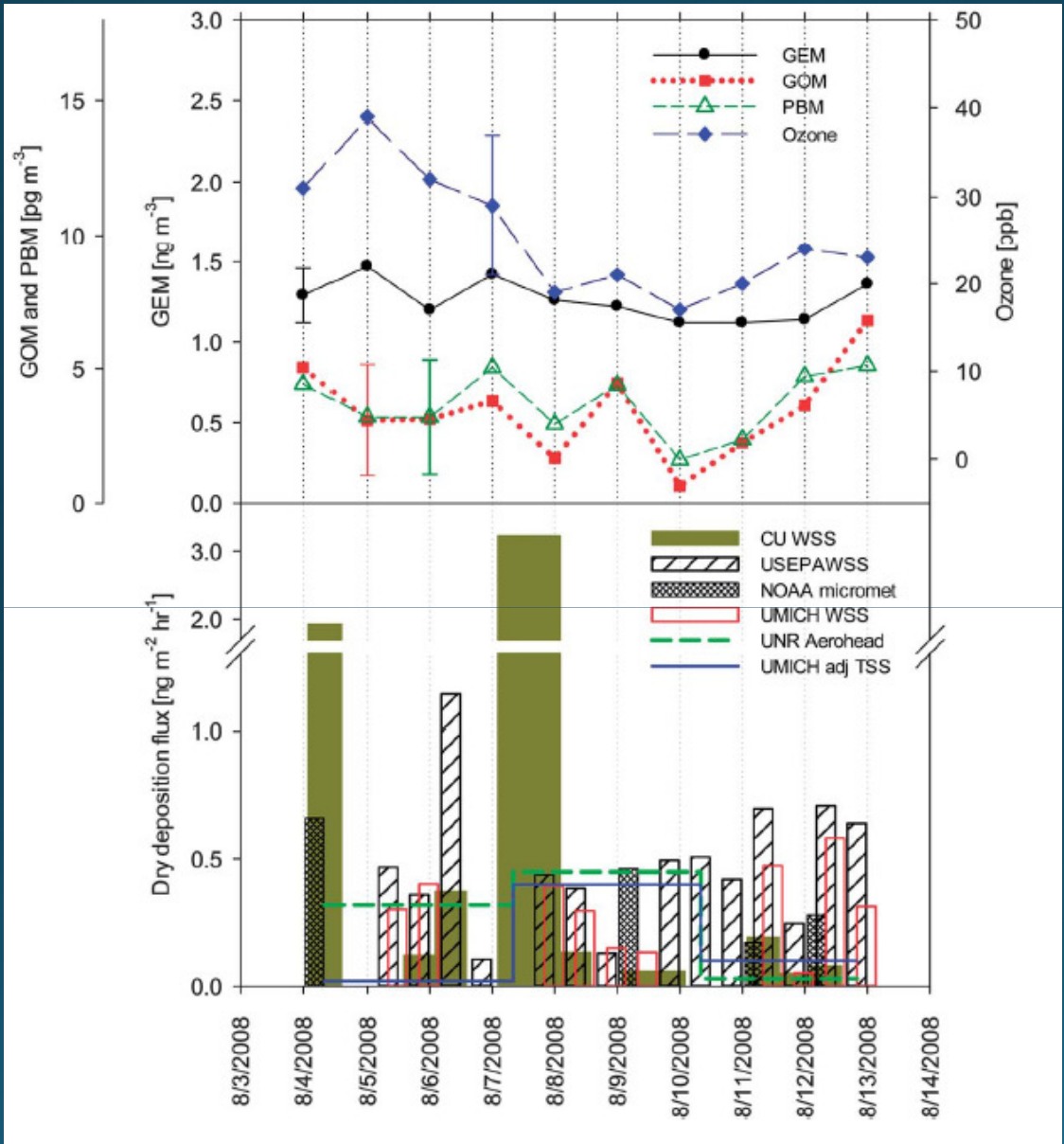
Study Participants and Approaches

- **Environment Canada**
  - Micrometeorological flux-gradient approach
  - Poissant *et al.*, 2004 (*Atmospheric Environment. 38, 4205-4214*)

- **NOAA-ATDD**
  - Micrometeorological flux-gradient approach
  - Brooks *et al.*, 2008 (*Atmospheric Environment, 42, 2877-2884*)



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Huang et al. (Environmental Science: Processes and Impacts, 2014)

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Supplemental Intercomparison
TSS and Cation Exchange Membranes

Mercury Dry-Deposition ($ng/m^2/hr$)

Sampling Periods	UMAQL TSS	UMAQL Adjusted TSS	UNR CEM
13 August to 20 August	1.64	0.18	0.27
20 August to 27 August	1.71	0.19	0.00
27 August to 03 September	2.11	0.23	0.45
03 September to 10 September	0.69	0.08	0.03
Average Deposition (ng/m2/hr)	1.54	0.17	0.19

Should we be adjusting surrogate surface estimates by leaf area index in vegetated ecosystems?

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Uptake by vegetation

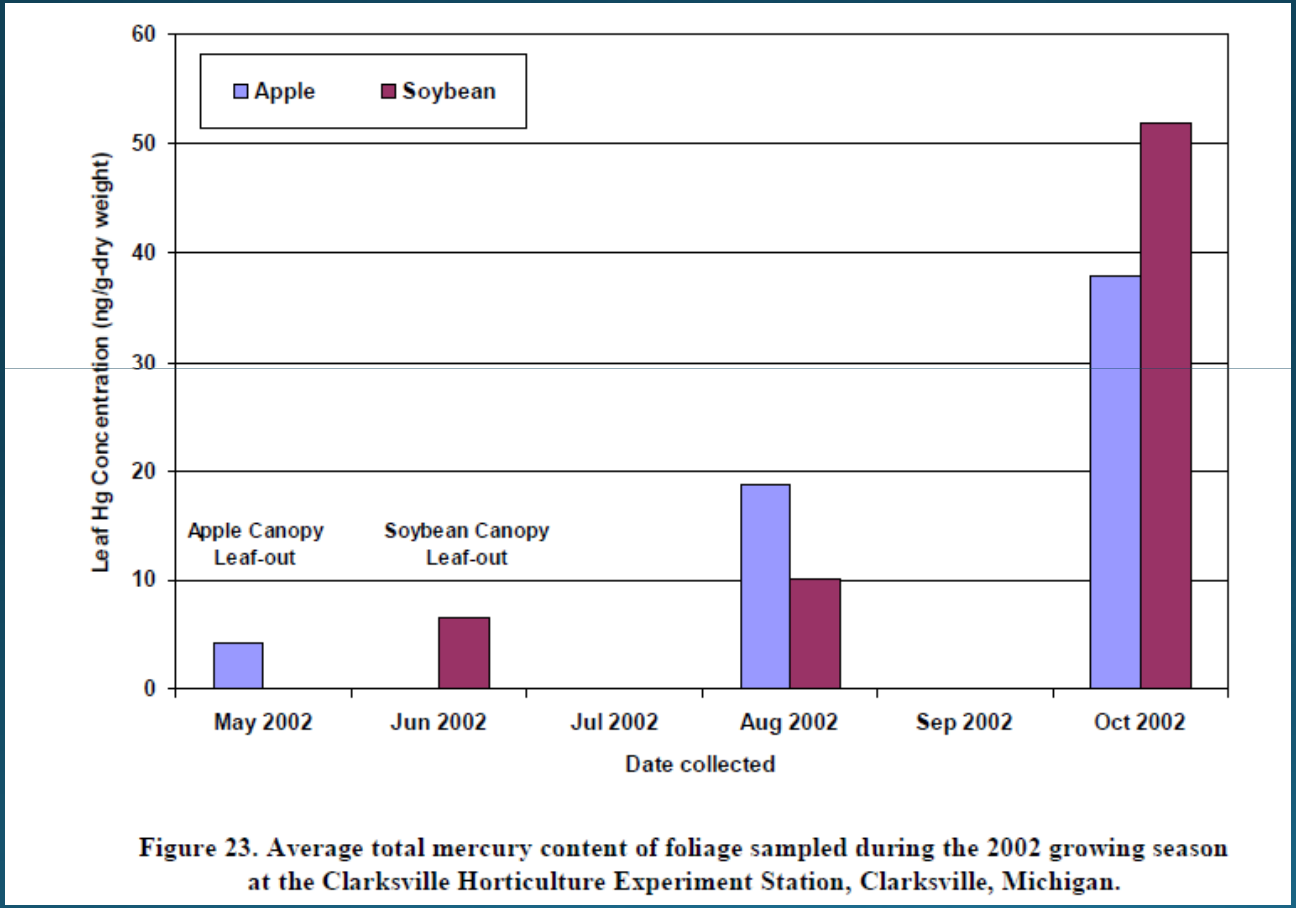


Figure 23. Average total mercury content of foliage sampled during the 2002 growing season at the Clarksville Horticulture Experiment Station, Clarksville, Michigan.

Source: Marsik and Keeler (Project Final Report to the Michigan Great Lakes Protection Fund, 2003)

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Atmospheric Deposition: Litterfall

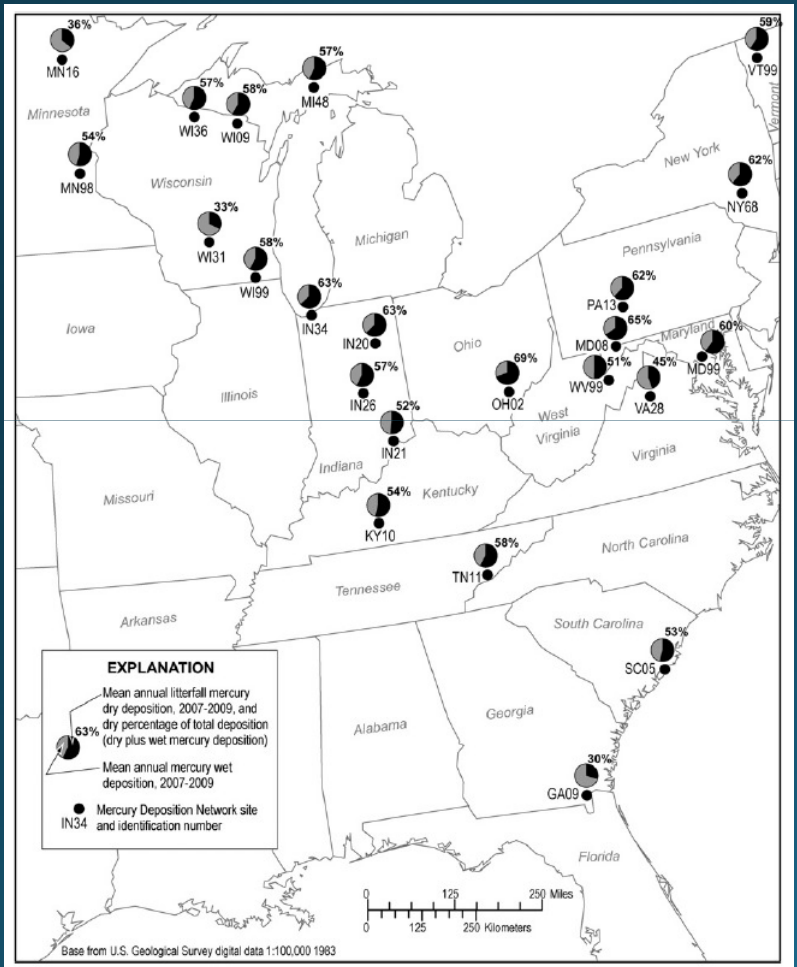


Fig. 2. Mean annual litterfall Hg dry and Hg wet deposition at litterfall Hg study sites, 2007–2009.

Table 1
Mean annual litterfall Hg deposition and Hg wet deposition at litterfall study sites, 2007–2009. [MDN, Mercury Deposition Network (sites on Fig. 2); $(\mu g/m^2)/yr$, microgram per square meter per year, ± one standard deviation of the mean].

MDN site number	Litterfall Hg dry deposition $[(\mu g/m^2)/yr]$	Total dry plus wet Hg deposition[a] $[(\mu g/m^2)/yr]$	Percent Hg dry deposition[b]
GA09	5.4 ± 0.1	18.3	30
IN20	13.9 ± 5.2	22.2	63
IN21	16.0 ± 1.2	31.0	52
IN26	17.4 ± 5.5	30.4	57
IN34	18.7 ± 5.7	29.6	63
KY10	12.6 ± 0.1	23.4	54
MD08	15.3 ± 2.1	23.6	65
MD99	15.5 ± 1.0	25.8	60
MI48	7.4 ± 0.4	13.1	57
MN16	3.8 ± 0.4	10.5	36
MN98	7.8 ± 0.3	14.3	54
NY68	15.3 ± 1.0	24.9	62
OH02	18.8 ± 2.8	27.3	69
PA13	13.6 ± 4.0	22.0	62
SC05	9.3 ± 0.2	17.5	53
WI09	10.0 ± 1.1	17.1	58
WI31	4.6 ± 1.0	14.1	33
WI36	7.6 ± 1.4	13.3	57

Modified from Risch et al. (Environmental Pollution, 161, 2012)

Uptake by "Vegetation"

- Anne Rea (1998)
  - Three sets of ten acid-cleaned, TEFLON leaves
  - Suspended from 16 to 20 September 1996

Element	dry dep. Foliage pg cm^{-2} hr^{-1}	dry dep. Teflon pg cm^{-2} hr^{-1}
Hg	0.023 ± 0.025	0.019 ± 0.025

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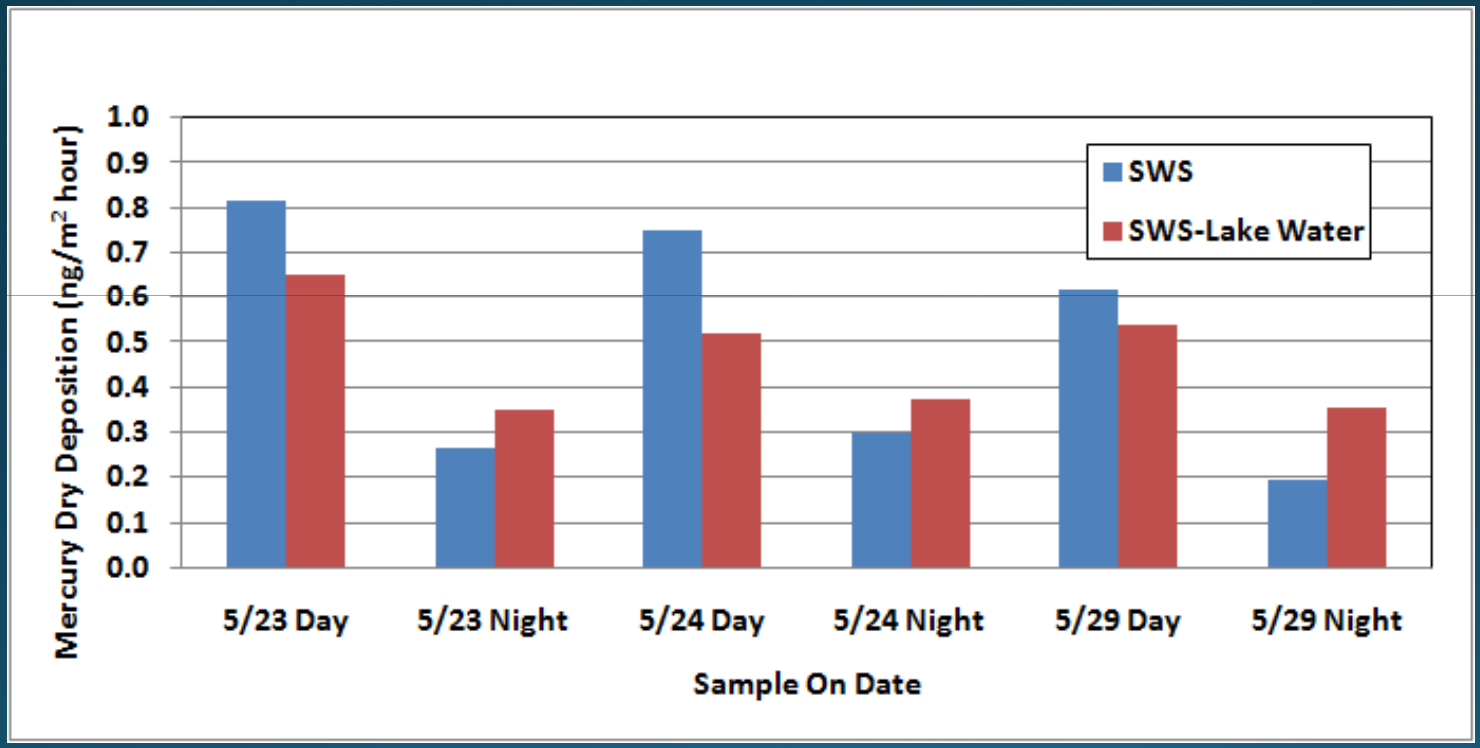
Conclusions

- Surrogate surface and litterfall measures of mercury dry-deposition:
  - Can provide measures of temporal variability
  - Can provide measures of spatial variability
  - Are providing increasing confidence in ability to provide reasonably accurate measures of magnitude

- Next steps
  - Continued integration with models to narrow uncertainties in both measures
  - Comparison of methodologies over greater range of conditions
    - Lai et al. (2008); Huang et al (2014)
  - Development of sensors that more closely mimic natural structures
  - Obtain better understanding of fate of mercury deposited onto surrogate surfaces

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Surrogate Water Surfaces
Ultra-pure water vs natural lake water
(~12 hour samples)



Source: Marsik and Keeler (Project Final Report to the Michigan Great Lakes Protection Fund, 2003)

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