

USGS Pilot Study of Mercury in Litterfall at MDN sites, 2007



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Acknowledgements

- **Mark Nilles, USGS Atmospheric Deposition Program**
- **Dave Krabbenhoft, USGS Mercury Research Program**
- **NADP 2007 Executive Committee**
- **MDN site operators and supervisors in Wisconsin, Ohio, Maryland, Tennessee, Kentucky, and Indiana**
- **National Park Service**



Overview

- **Why collect mercury in litterfall data?**
- **Methods for pilot study in 2007**
- **Findings from 2007 data collection**
- **Pilot study in 2008 and future plans**



Mercury Dry Deposition

- Hg dry deposition is highest in forests
- Mercury accumulation in forest canopies is predominantly from the air, not the soil
- Mercury in deciduous foliage increases during the growing season
- Mercury is attached to the leaf surfaces and incorporated into leaf tissue

(Grigal, 2002; Eriksen and others, 2003; Rea and others, 2002; Hintelmann and others, 2002; Miller and others, 2005; Madison Declaration, 2007)

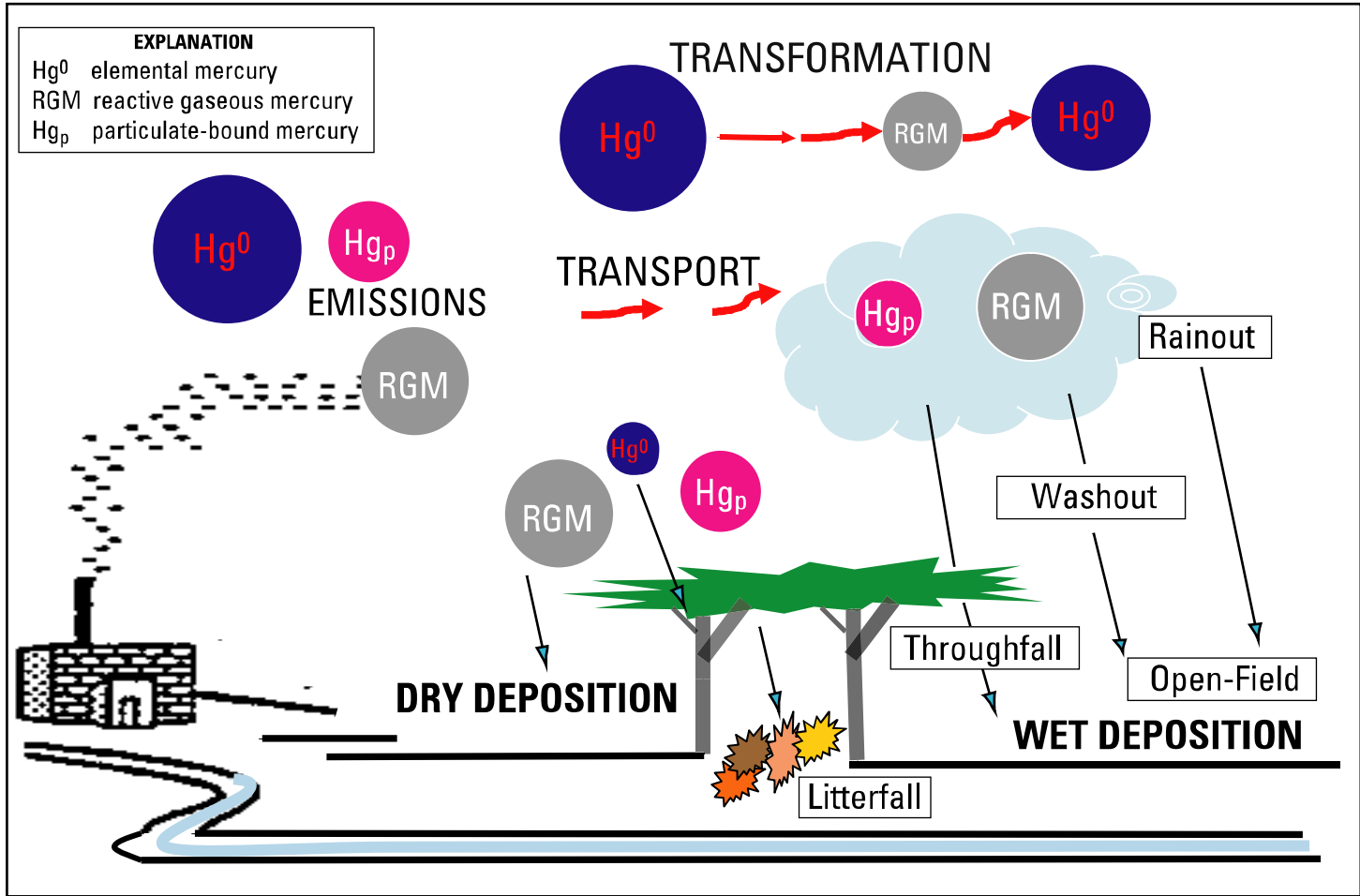


Mercury in Litterfall

- New mercury added to the forest floor is from litterfall
- Mercury deposition from dry deposition in litterfall is greater than from throughfall or from precipitation
- A significant proportion of mercury in the forest canopy and litterfall is atmospheric elemental mercury
- Mercury flux to the soil dominated by litterfall in deciduous forests; by throughfall in coniferous forests

(Sheehan and others, 2006; St. Louis and others, 2001; Demers and others, 2007; Karl and Nelson, 2007)

Atmospheric Mercury Species and Fate



Objectives of Litterfall Pilot Study

- Develop, test, and refine field and office procedures
- Assemble a multi-year set of autumn litterfall data
- Accomplish broad geographic coverage in eastern US
- Sample different forest types, emphasizing deciduous
- Interpret and communicate results of pilot study
- Examine viability of long-term litterfall monitoring



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Methods for Litterfall Pilot Study

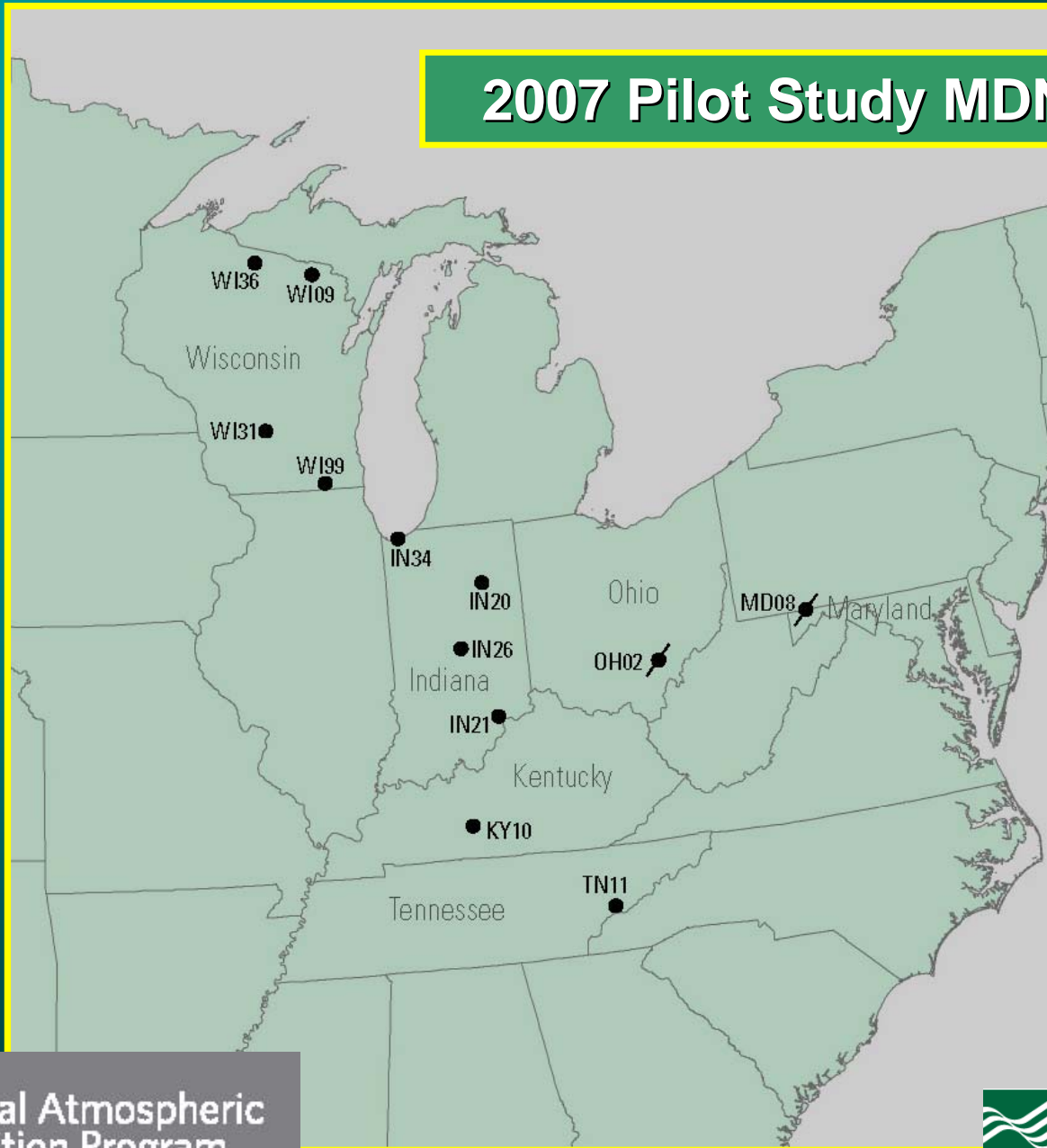
- 12 sites in eastern North America
- Two sets of samples October – December 2007
- 4 passive samplers in sample plot near MDN site
- Samplers deployed and retrieved by MDN operators
- Individual samples analyzed for total mercury
- Estimate mercury litterfall deposition



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2007 Pilot Study MDN Sites

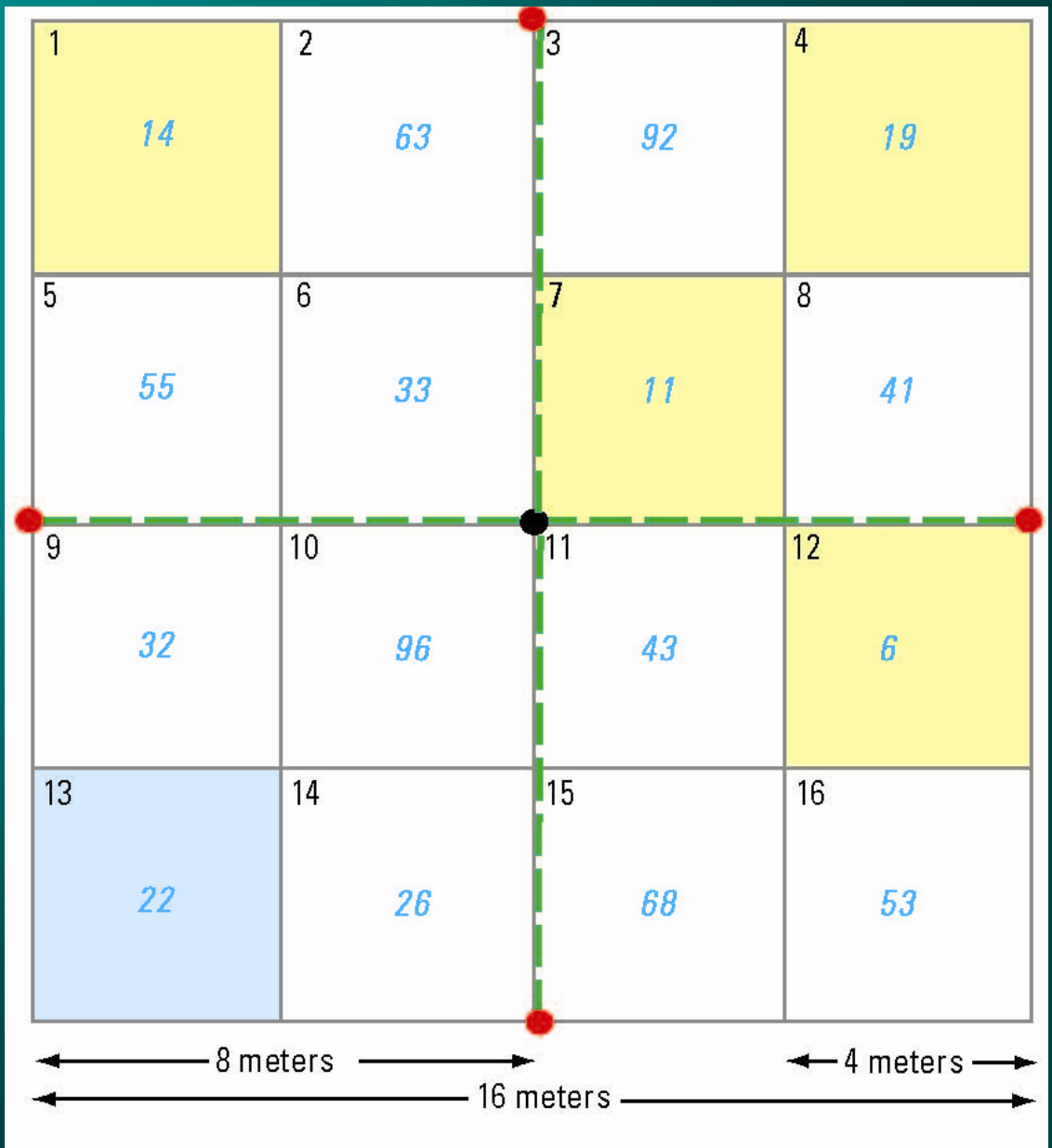


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16 m x 16 m
forest sample plot
with randomly-
selected locations for
passive samplers

Sample plot < 300 m
from MDN collector



Sample Processing & Analysis



- Samplers to USGS
- Samples were bagged, freeze-dried, ground, homogenized, weighed
- Analysis by acid digestion and EPA7470A manual CVAA

Passive sampler (4 per site)



**Hg Concentration (ng/g) X Dry weight litterfall (g) =
Litterfall Hg mass (ng) per 0.25 m²
Sum of 4 samples per site =
Litterfall Hg deposition (ug/m²)**

**Variability among 4 passive samplers per MDN site
(Standard deviation as a percent of total for site)
Summary for 12 sites, Oct-Dec 2007 (n=80)**

Measure	Minimum	Maximum	Median
Litterfall dry weight (g)	1.4 %	6.3 %	2.3 %
Hg mass (ng)	1.6 %	10.5 %	5.4 %

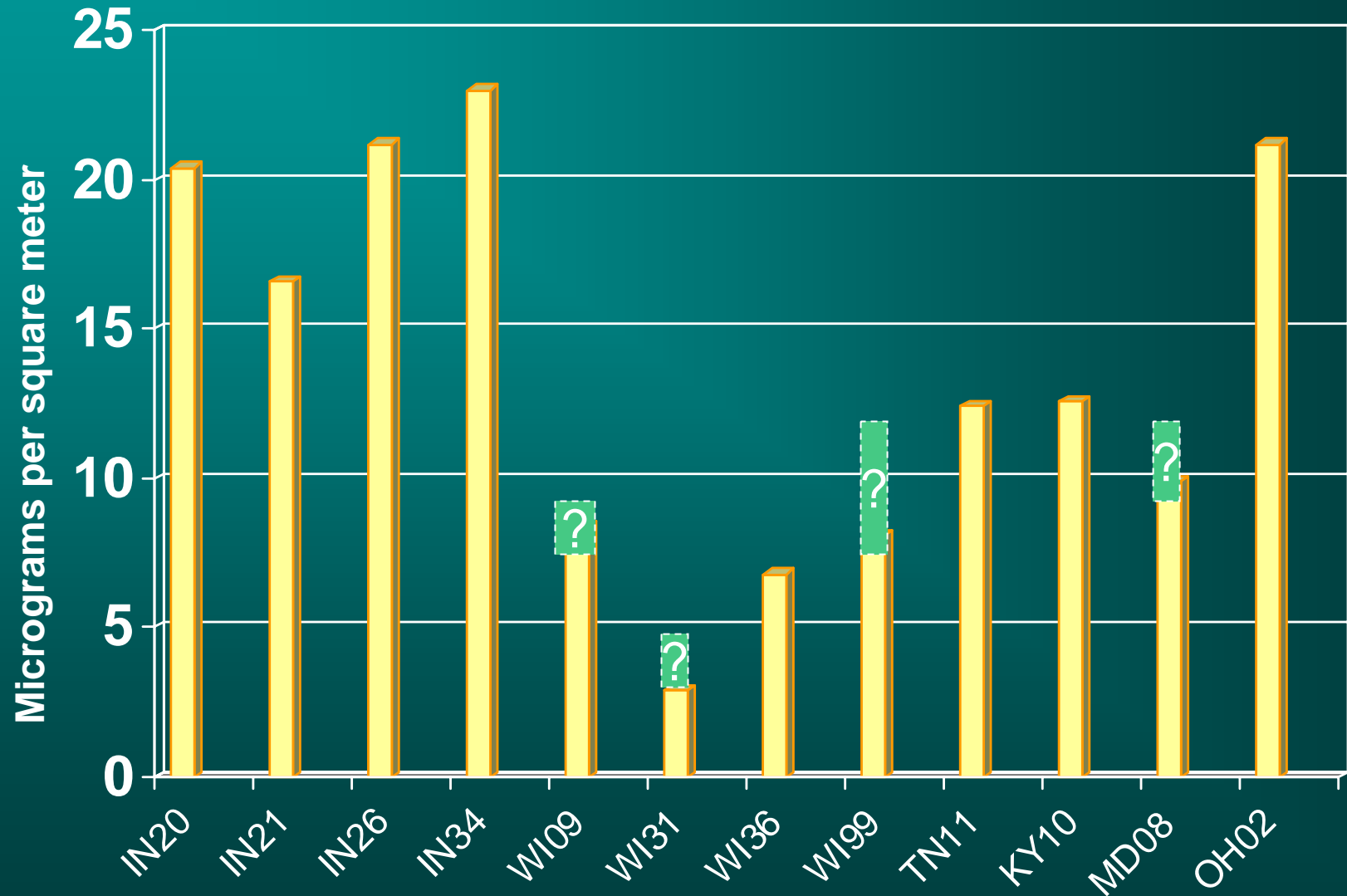
Hg Concentrations in 2007 Litterfall Samples (ng/g)

Time (n)	Minimum	Maximum	Median
Oct – Nov (12)	27.4	75.3	50.7
Nov – Dec (9)	10.8	70.6	25.4
Oct – Dec (21)	31.4	62.7	40.0

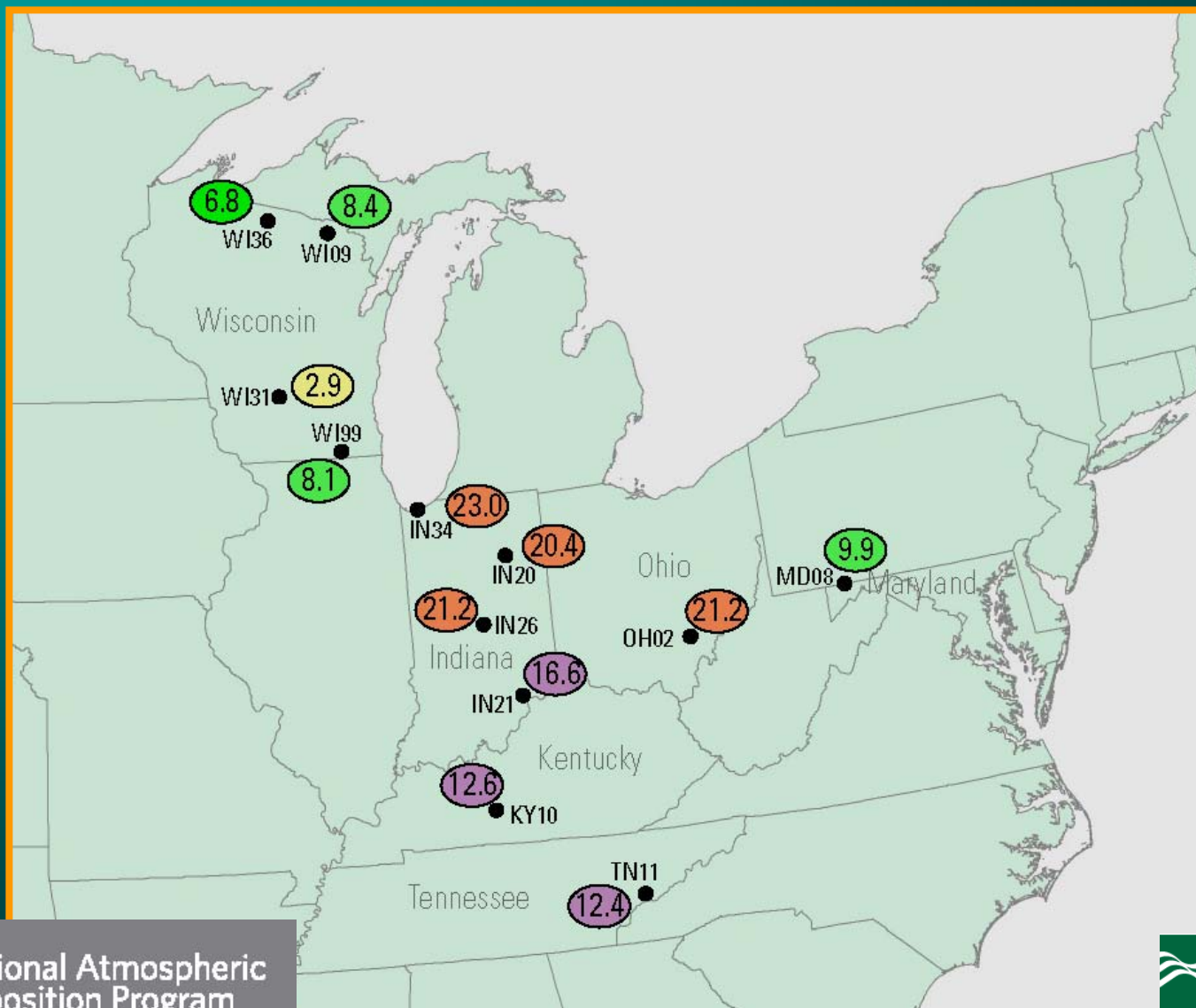
Litterfall Hg Deposition in 2007 Samples ($\mu\text{g}/\text{m}^2$)

Time (n)	Minimum	Maximum	Median
Oct – Nov (12)	2.9	15.0	9.3
Nov – Dec (9)	2.6	10.5	5.0
Oct – Dec (21)	2.9	23.0	12.5

Litterfall Hg Deposition at 12 MDN Sites, Oct-Dec 2007



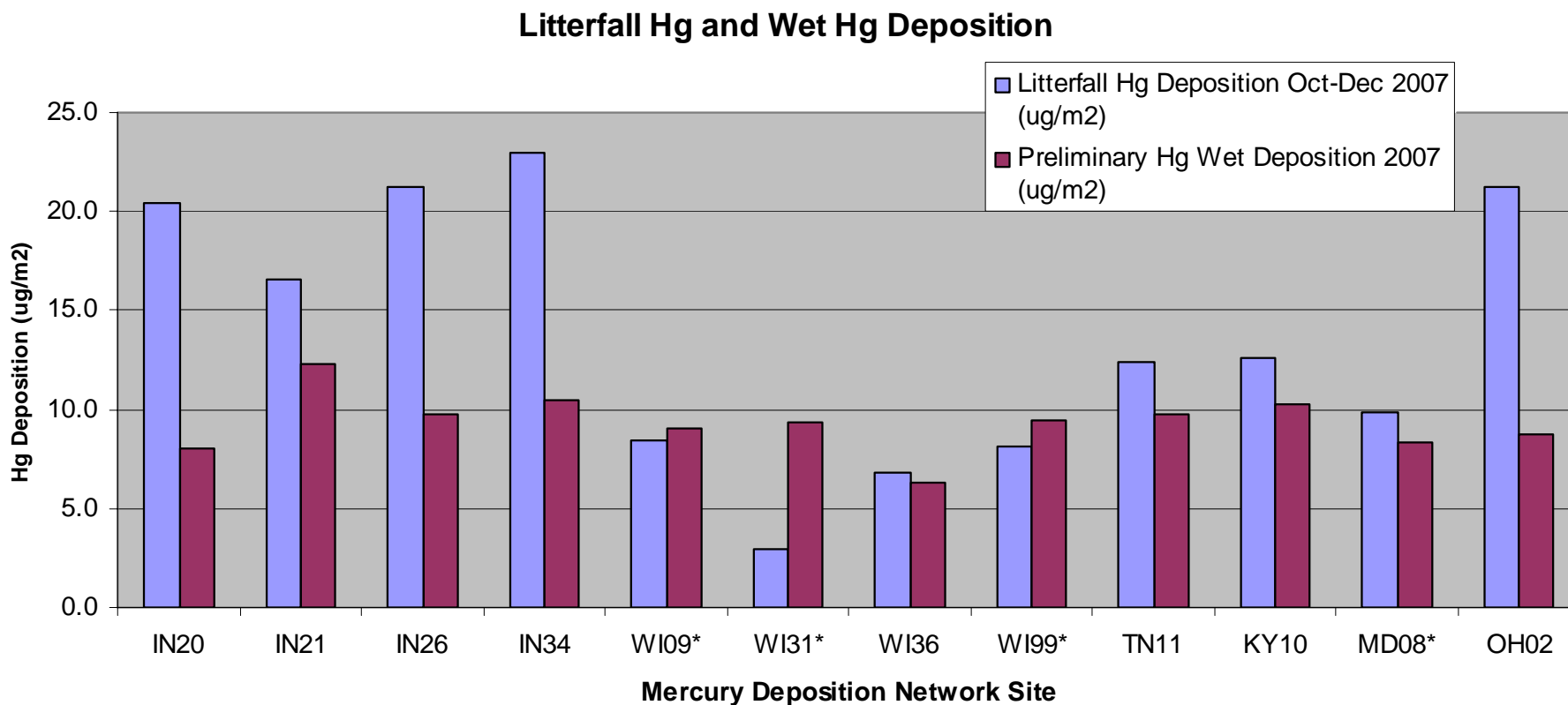
Litterfall Hg Deposition at 12 MDN Sites, Oct-Dec 2007



Litterfall Hg Deposition by Forest Type at MDN Sites, Oct-Dec 2007

Forest type	Tree species	MDN sites	Litterfall deposition (ug/m ²)
Deciduous	oak, maple	IN26, IN34, OH02, KY10	21.2, 23.0, 21.2, 12.6
Deciduous	poplar, maple	IN20, IN21	16.6, 20.4
Mixed	poplar, maple, hemlock	TN11	12.4
Mixed	birch, maple, fir	WI09	8.4
Coniferous	pine, spruce, fir	WI36	6.8

2007 Litterfall Hg Deposition compared with 2007 Hg Wet Deposition



*sample may not include complete autumn litterfall

Ratios of Litterfall Hg Deposition to Hg Wet Deposition 2007

Ratio of Litterfall Hg Deposition to Hg Wet Deposition	MDN sites
2.55 - 2.25 : 1	IN20, OH02
2.25 – 2.0 : 1	IN34, IN26
1.50 – 1.25 : 1	IN21, TN11
1.25 – 1.0 : 1	KY10, MD08*, WI36
< 1 : 1	WI09*, WI99*, WI31*

*sample may not include complete autumn litterfall

Throughfall Hg Deposition and Litterfall Hg Deposition



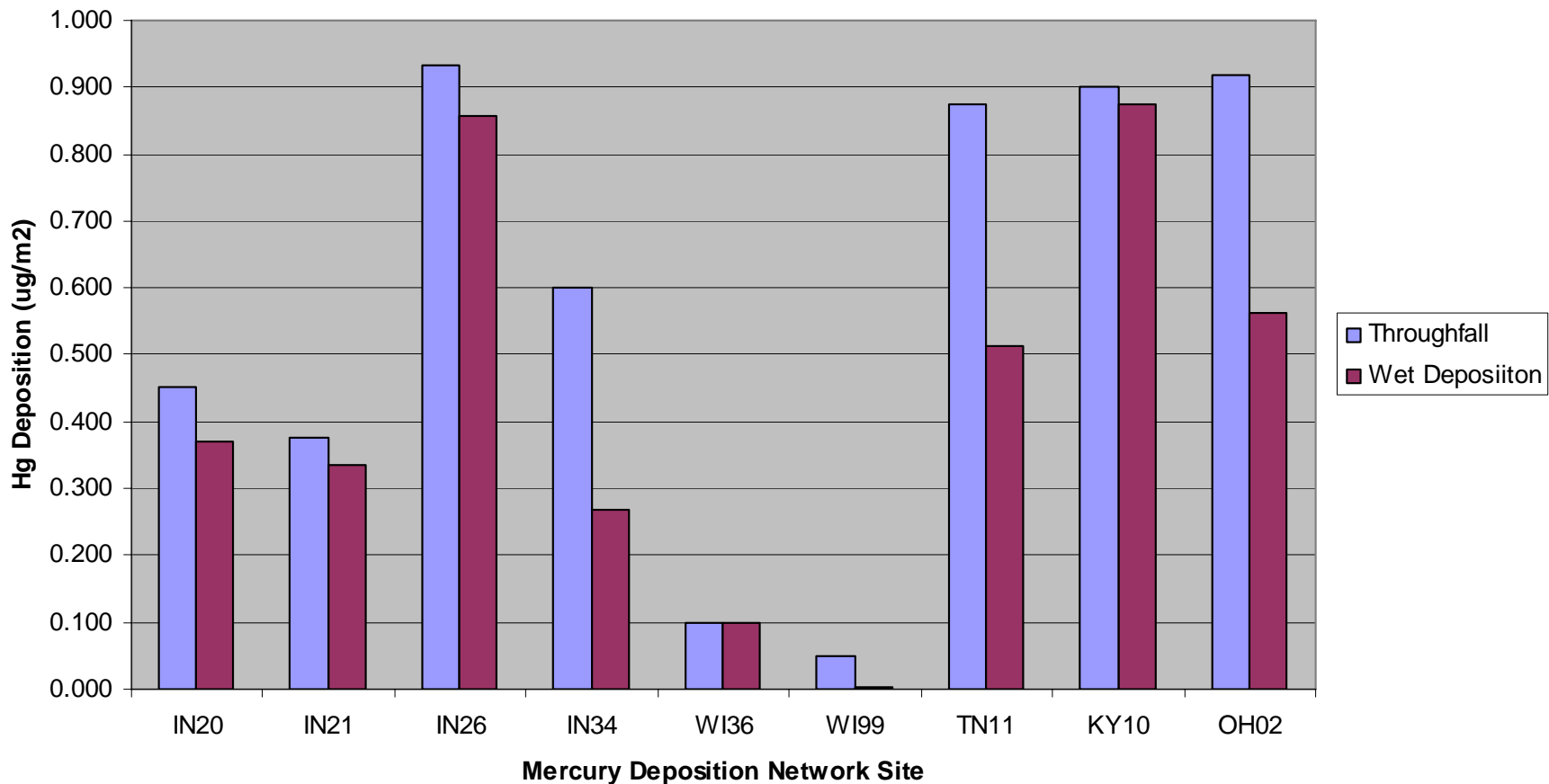
Bulk throughfall sampler
with MDN sampling train

Analysis for Total Hg by
Frontier Geosciences

QA for intra-site
throughfall deposition
variability Oct–Nov (3%)
Nov-Dec (21%)

Bulk Throughfall Hg Deposition*

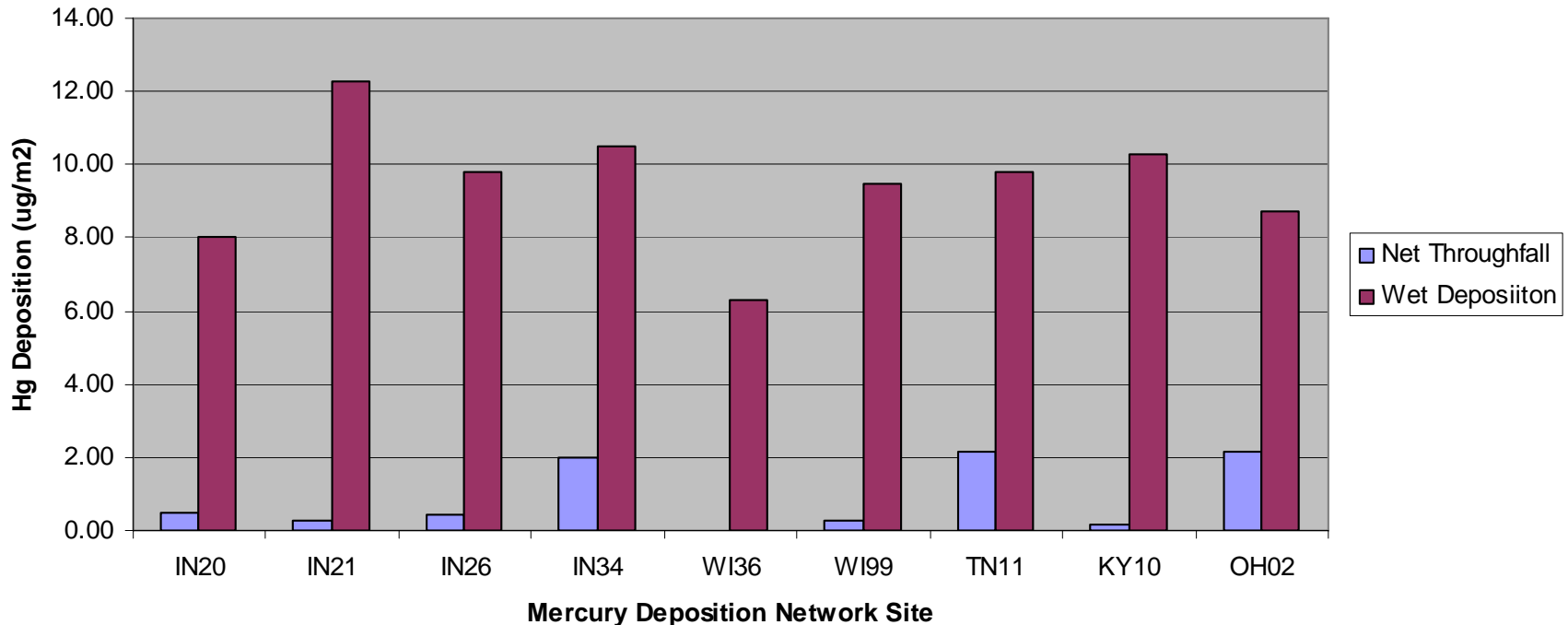
Bulk Throughfall Hg & Open-Field Hg Deposition, Oct-Nov 2007



*sample volume X concentration

Net Throughfall Hg Deposition*

6-Month Deciduous-Leaf-Growth Season Estimated Net Throughfall

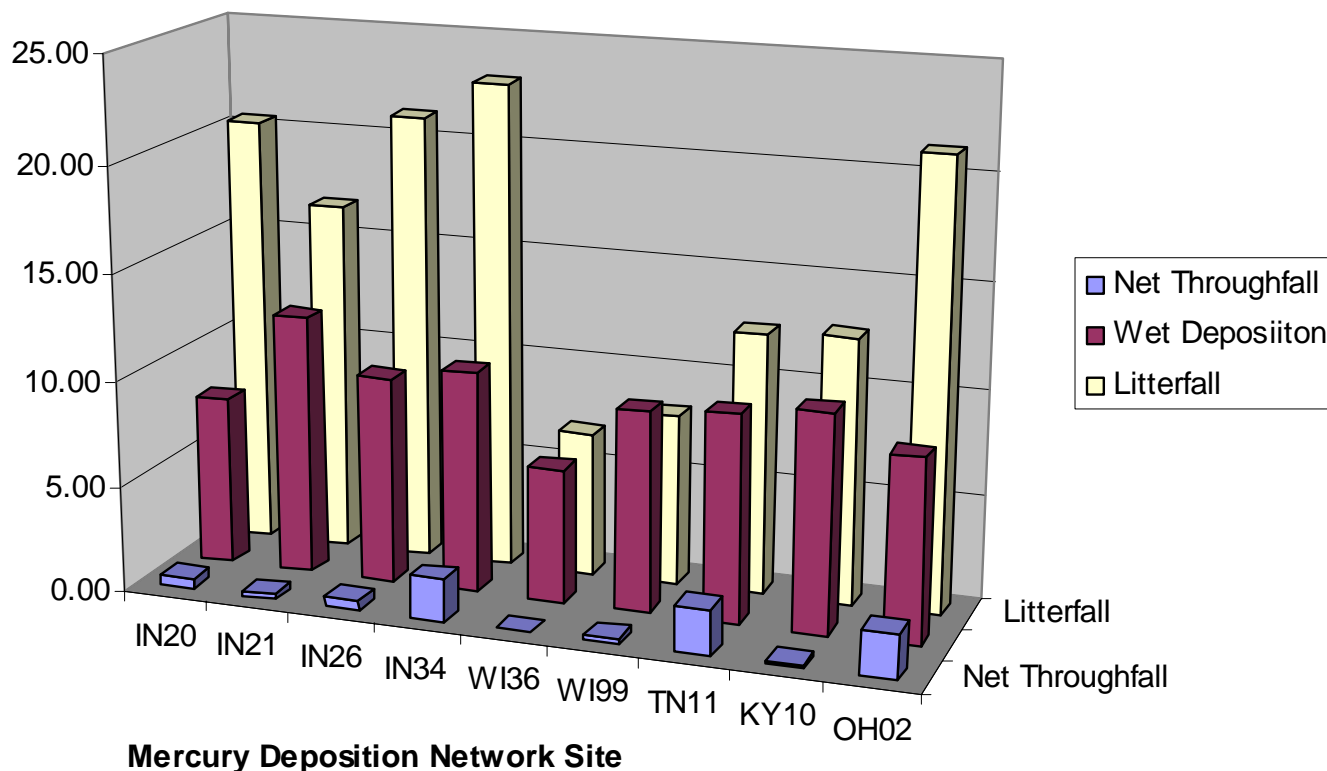


*Bulk throughfall - wet deposition extrapolated to 6 month growing season for deciduous forest canopy.

Estimated to add 2% to 24% to Hg wet deposition.

Total Atmospheric Hg Deposition

Total Annual Atmospheric Mercury Deposition, 2007 (ug/m²)



Litterfall is $\frac{1}{2}$ to $\frac{3}{4}$ of the annual atmospheric Hg deposition.

2008 Hg Litterfall Pilot Study Sites



Summary and Conclusion

- Field and office procedures for litterfall sample collection were successfully tested.
- Litterfall mass and Hg mass varied less than 5 percent among the 4 samplers at a site.
- Litterfall Hg deposition varied by forest type and tree species, highest in oak-maple deciduous forest.
- Mercury in litterfall was at least equal to and often more than double the Hg in wet deposition and was $\frac{1}{2}$ to $\frac{3}{4}$ of the 2007 total atmospheric Hg deposition.
- Multi-year pilot study with broad geographic coverage needed.