

*Biogeochemical cycling of Hg and methyl Hg in
Great Smoky Mountains National Park*

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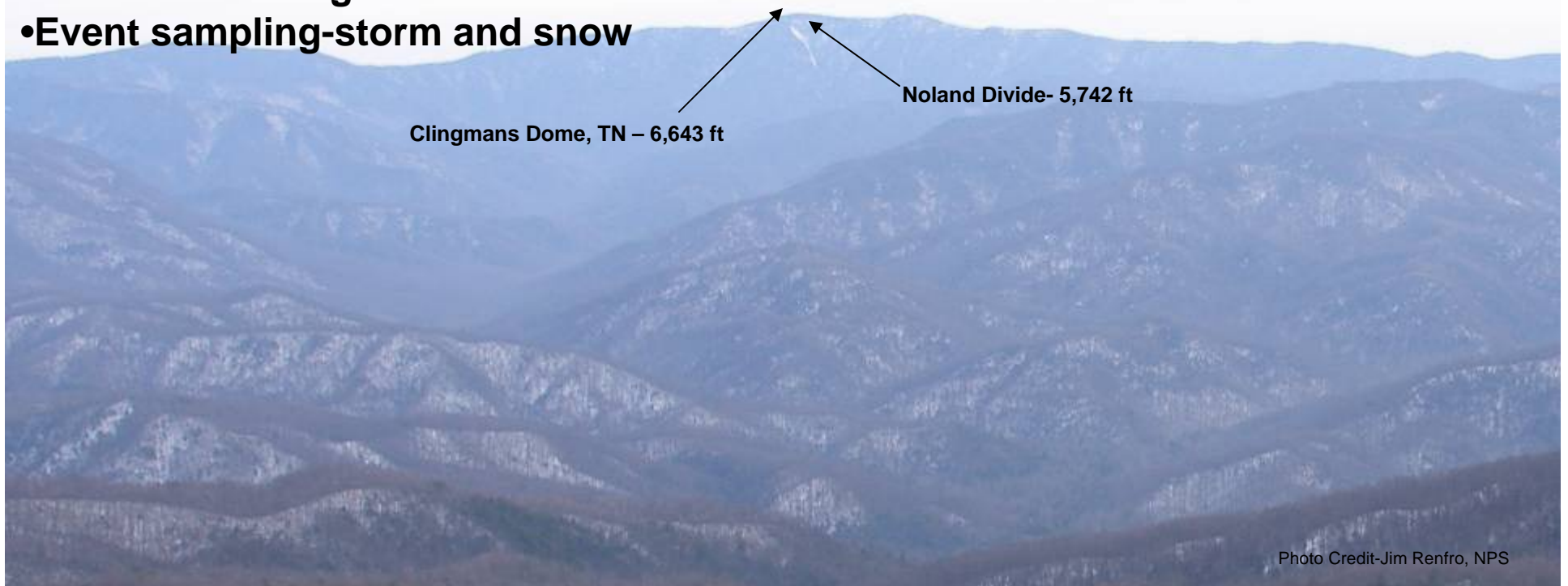
**National Atmospheric Deposition Program
Annual Fall Meeting**

September 12, 2007

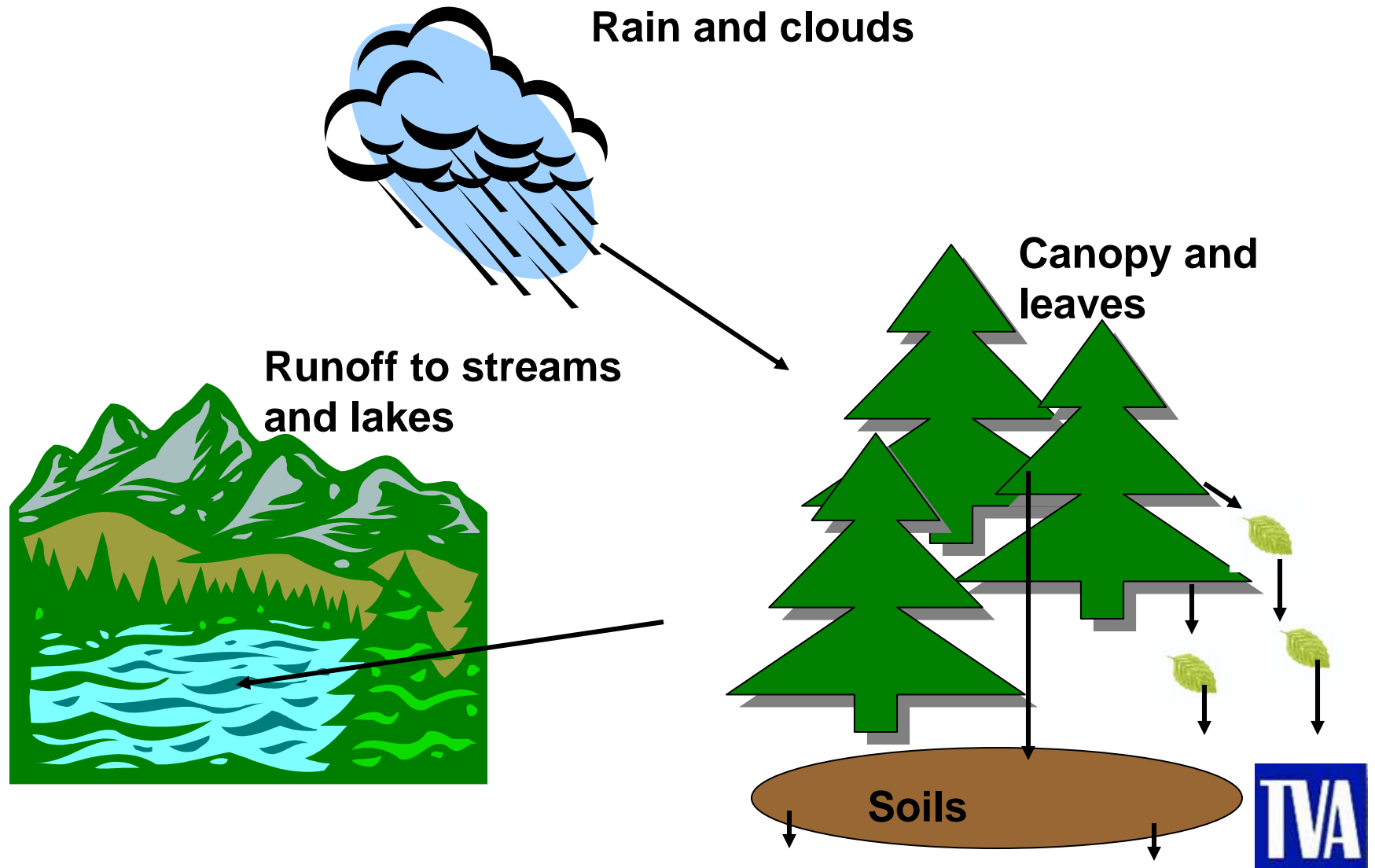
TVA

Approach and Objectives

- **Watershed budget of mercury**
- **Measure total and methyl Hg in throughfall, leaf litter, and soils in conjunction with the current wet deposition sampled by the Mercury Deposition Network**
- **Measure total and methyl Hg and quantify dissolved phase at two elevations**
- **Measure watershed components such as sulfate, total suspended solids, and dissolved organic carbon**
- **Event sampling-storm and snow**



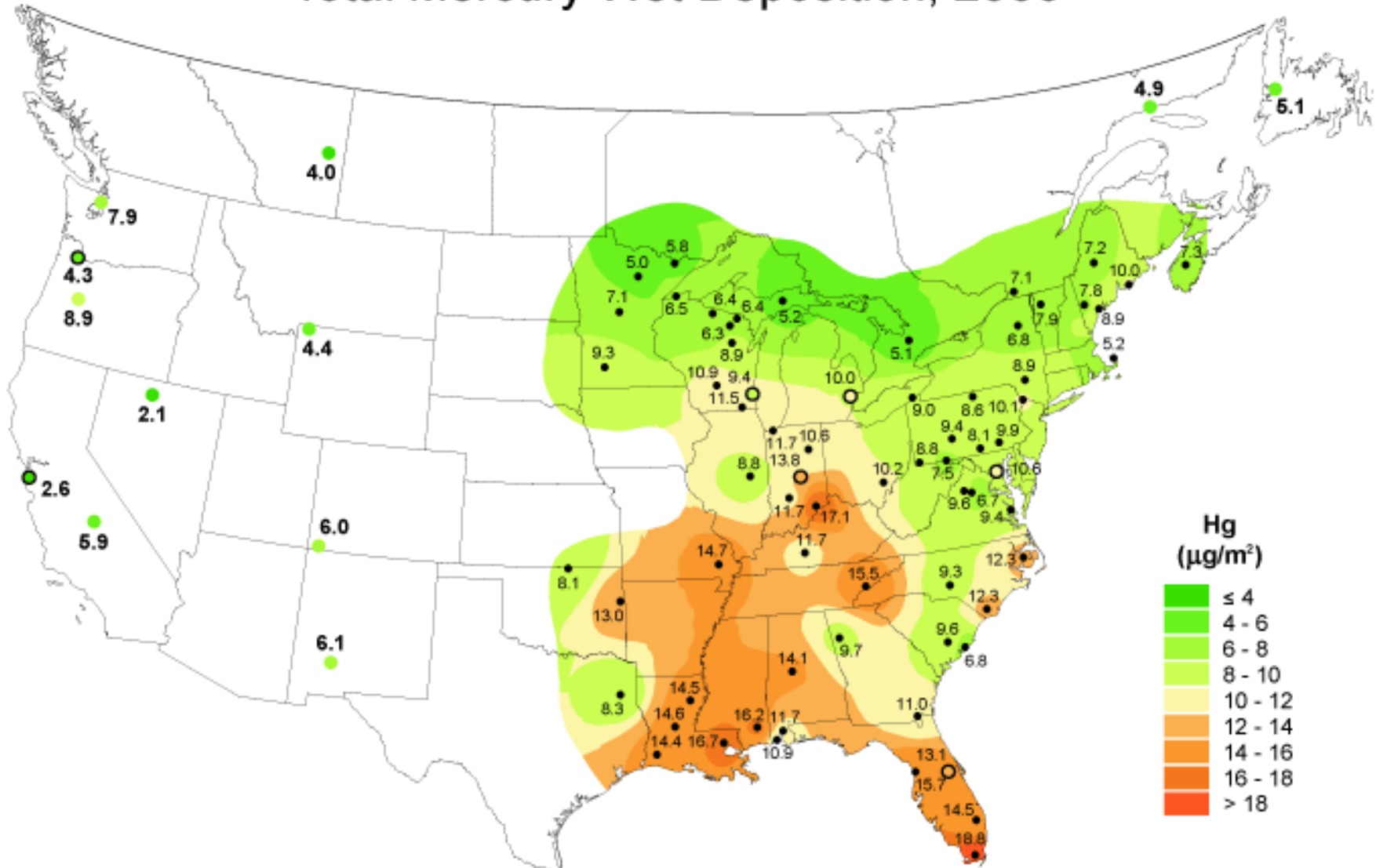
Watershed budget of mercury



Purpose of Study

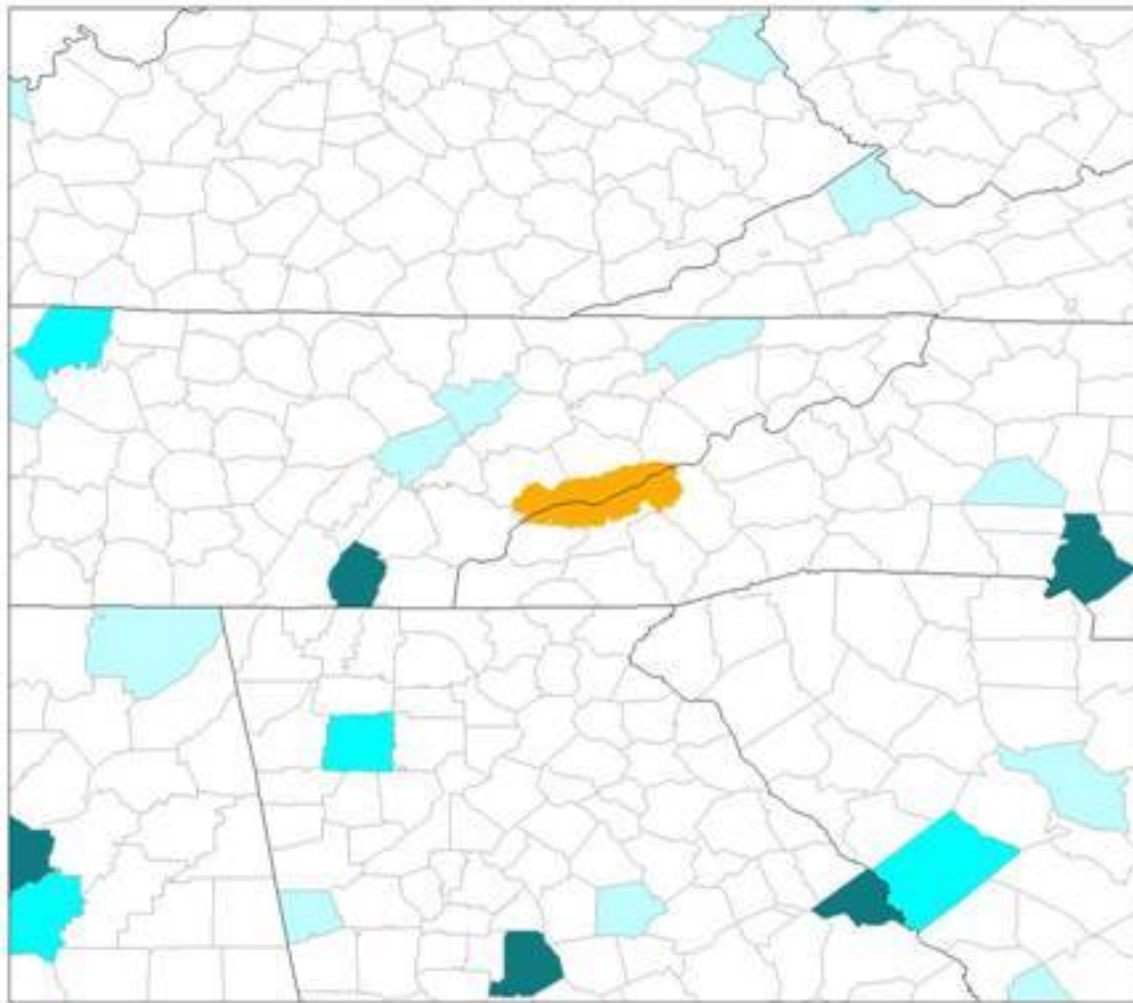
- **Is it really high in the Smokies?**
- **Weekly total mercury in wet deposition at Clingmans Dome since 2002 as part of MDN, known as TN-12.**
- **Since 2002, seasonal (May-October) concentration average of 9.10 ng/L; seasonal deposition average of 4.5 $\mu\text{g}/\text{m}^2$**
- **Weekly methyl mercury (wet deposition) at TN-12 for 2006 and 2007**
- **Dry and cloud deposition of Hg also contributes to the total deposition the ecosystem receives. These aren't being measured...**
- **Understand complex cycling-terrestrial systems (lag time after deposition, organic matter form binding complexes, amount of sulfate and total suspended solids influence).**

Total Mercury Wet Deposition, 2006

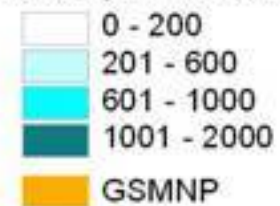


National Atmospheric Deposition Program/Mercury Deposition Network

Nearby Sources of Mercury to Great Smoky Mountains National Park



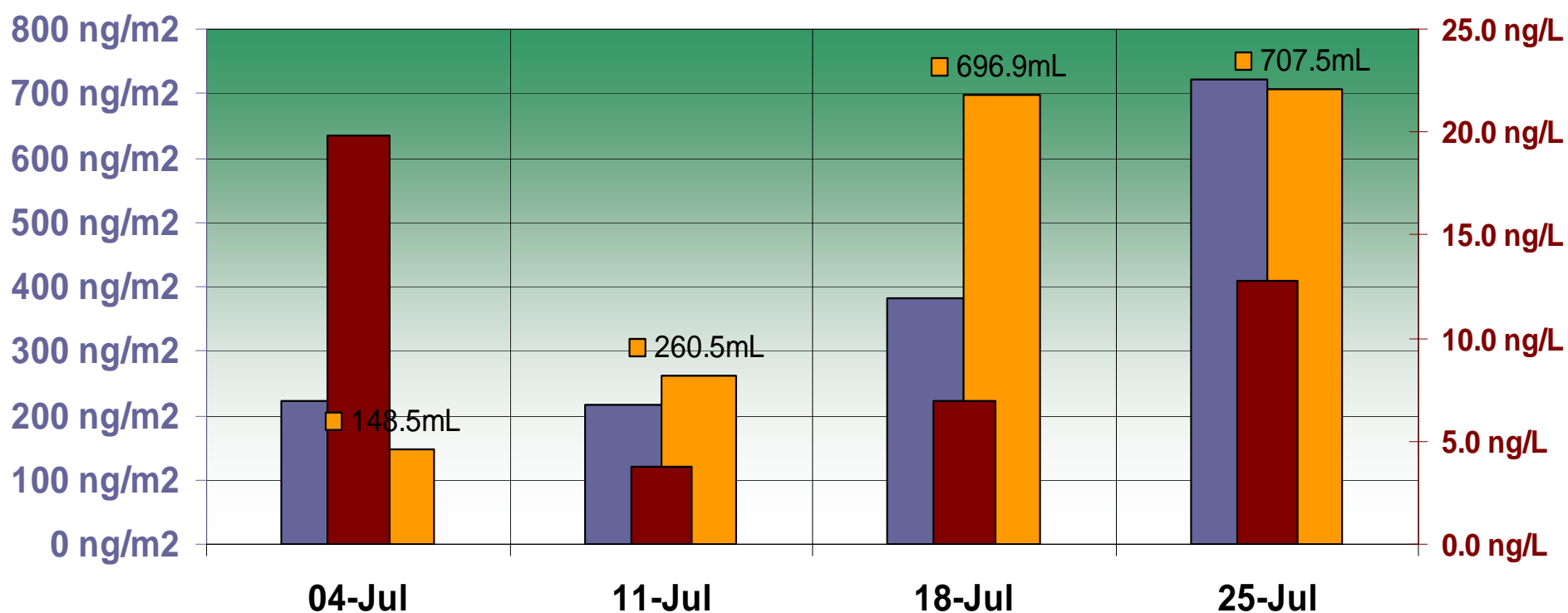
Mercury Emissions (lb)



Total mercury at Clingmans Dome, GSMNP July, 2006

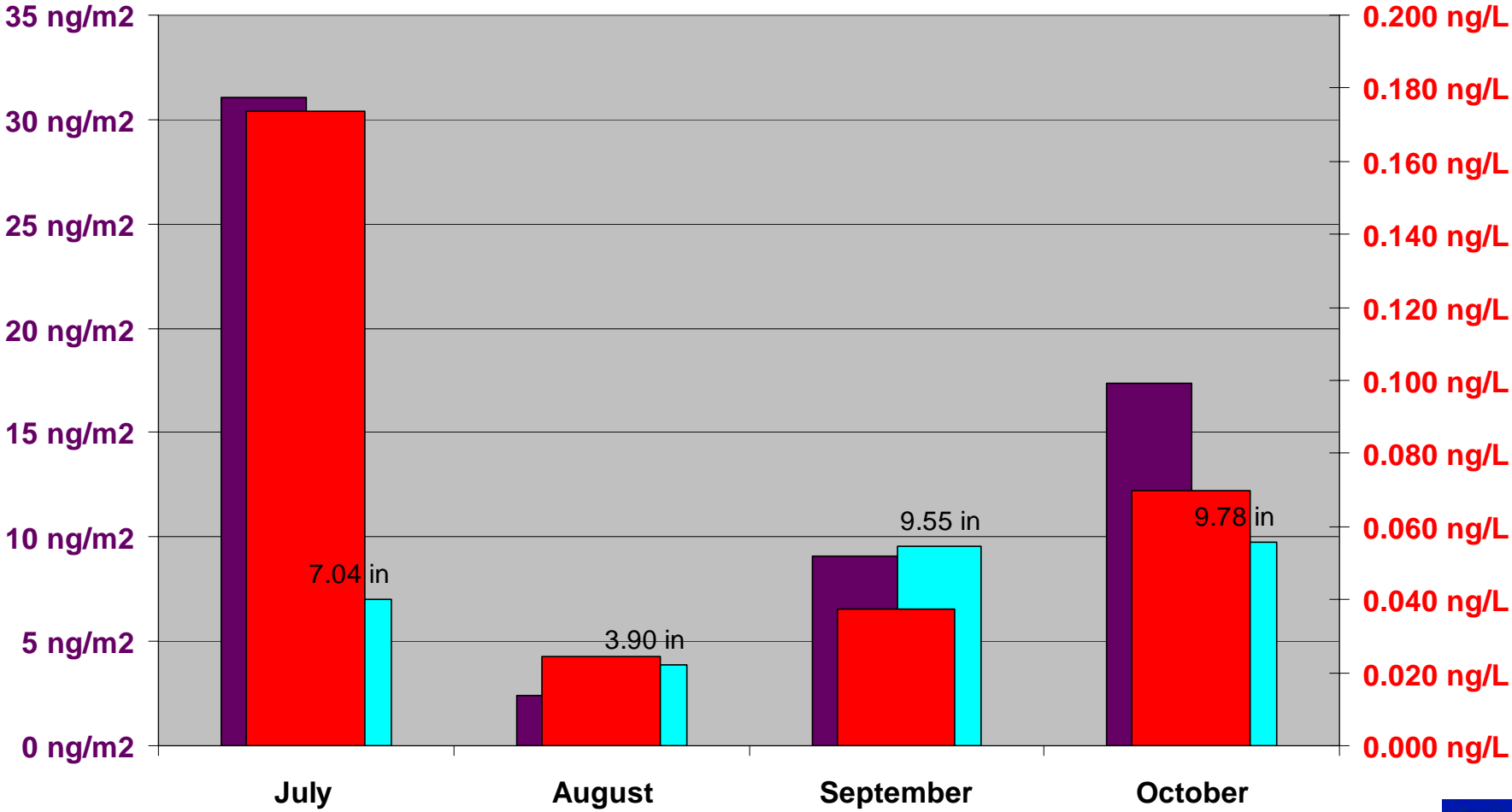
MDN Preliminary Precipitation Summary: TN12

■ Weekly Hg Deposition ■ Precip Vol ■ Precip. Hg Conc.



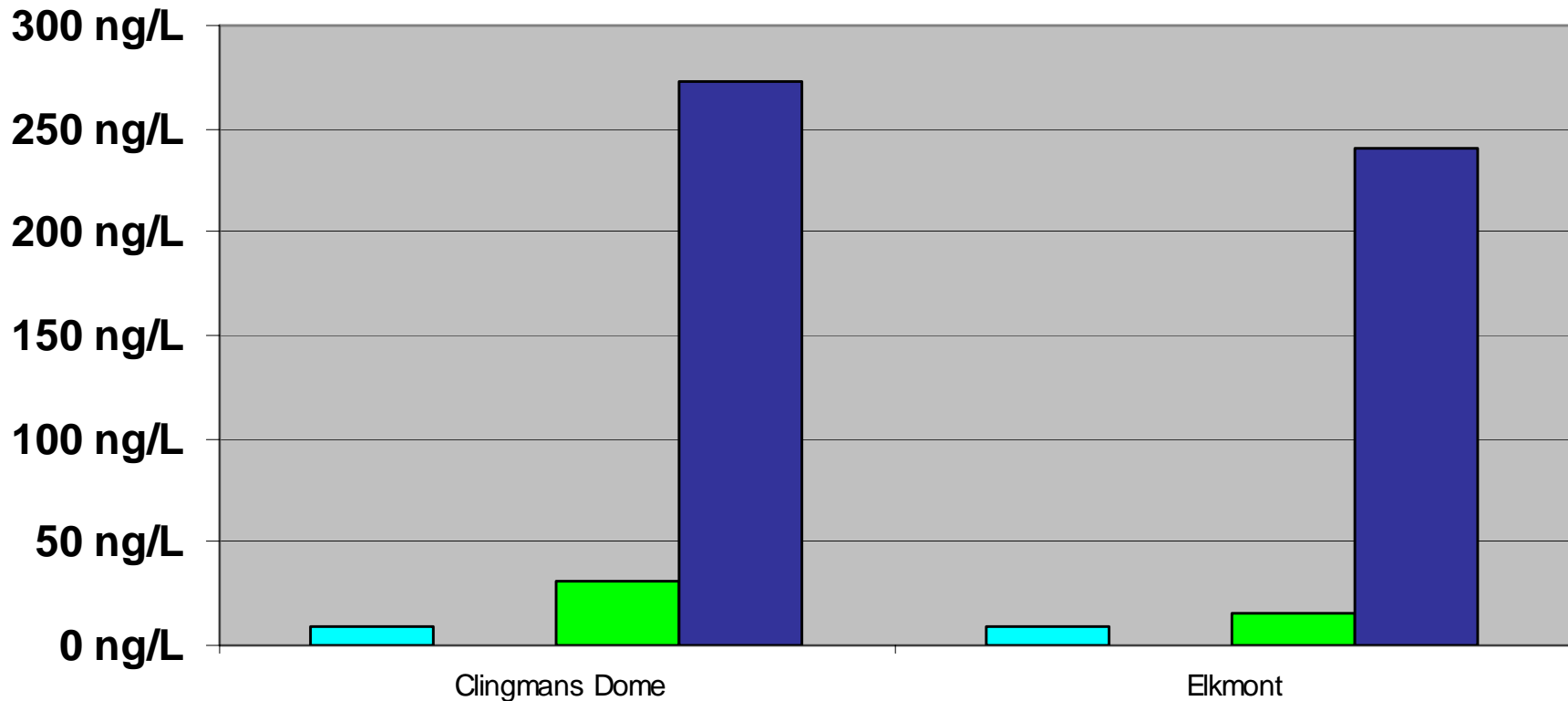
Clingmans Dome TN-12 Methyl Mercury Concentration 2006

■ MHg Deposition
 ■ Precip final
 ■ Precip MHg Conc

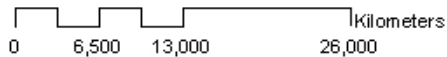


Total versus Methyl Mercury in GSMNP July, 2006

■ Precip. Hg Conc. (Vol Wght) ■ Precip. MHg Conc. ■ MHg Deposition ■ THg Deposition



Sampling sites for mercury analysis in Great Smoky Mountains National Park



- ▲ Proposed study sites for measuring throughfall, litterfall, soil, and streams.



**Clingmans
Dome, 6,643 ft**



Noland Divide, 5,742 ft

Photo credit-Jim Renfro, NPS

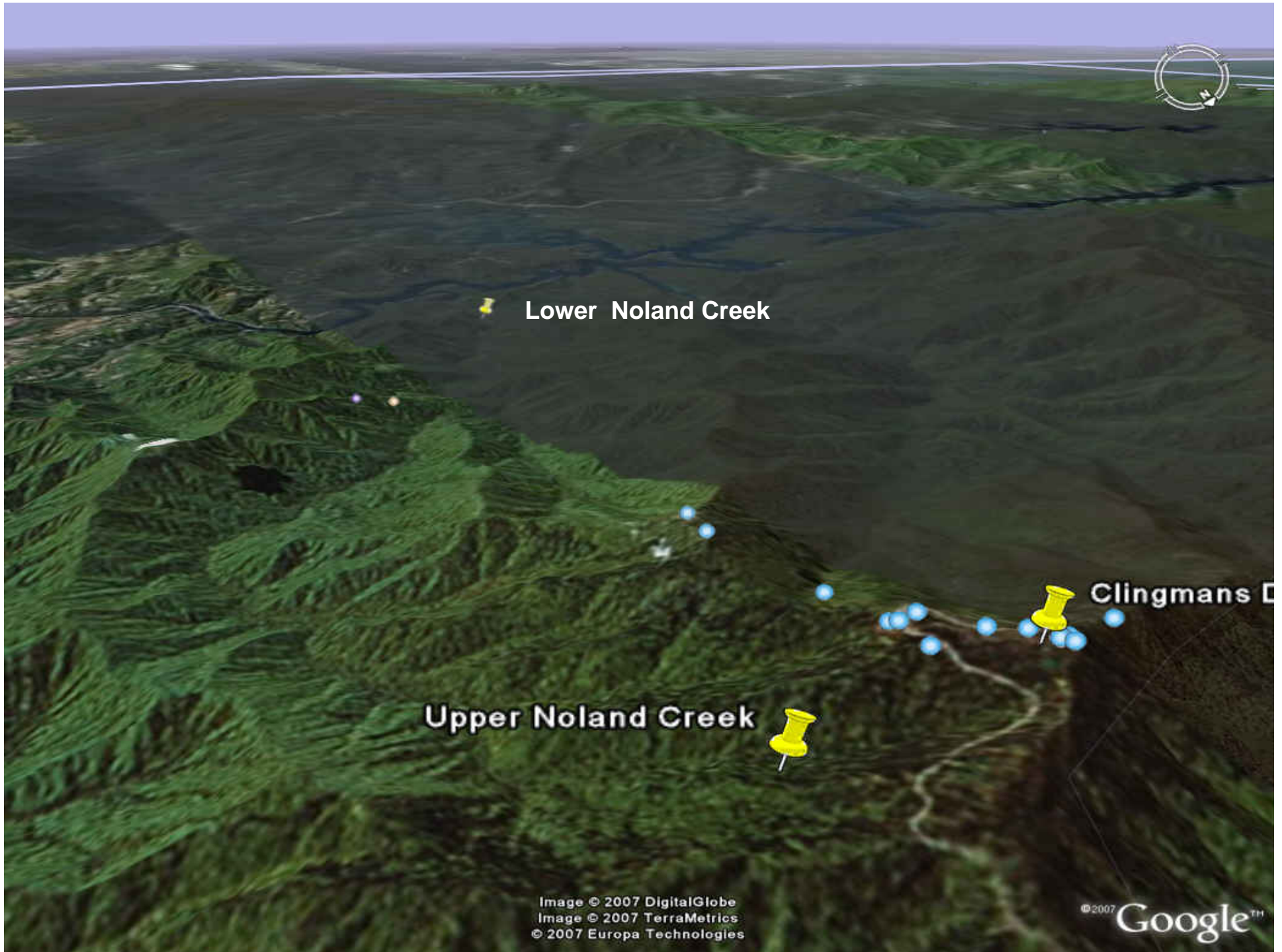


**Bryson City,
2,704 ft**

- Clingmans Dome and upper portion of Noland Creek are dominated by spruce-fir and have rich, organic soils and receive a high amount of cloud deposition.


- Lower portion in Bryson City is in mixed hardwood.





 Lower Noland Creek

Upper Noland Creek 

Clingmans D 

Deposition Collection

- Monthly analysis (May-October)
- Total and methyl mercury
- Sulfate
- Throughfall and 3 rain gauges dispersed per site to capture variability
- Surface soil (organic horizon) and soil solution (6", 12", and 24")
- Litterfall traps (two at each site)



Soil lysimeters



Litterfall



Canopy throughfall



Open-site throughfall



Wet deposition MDN, TN-12

Stream Sampling-Noland Creek

- **Monthly analysis (May-October)**
- **Storm event sampling (seasonal)**
- **Total and methyl mercury**
- **Dissolved organic carbon**
- **Dissolved mercury**
- **Sulfate**
- **Total suspended solids**
- **pH, temperature**
- **Stream flow and height**



Methodology

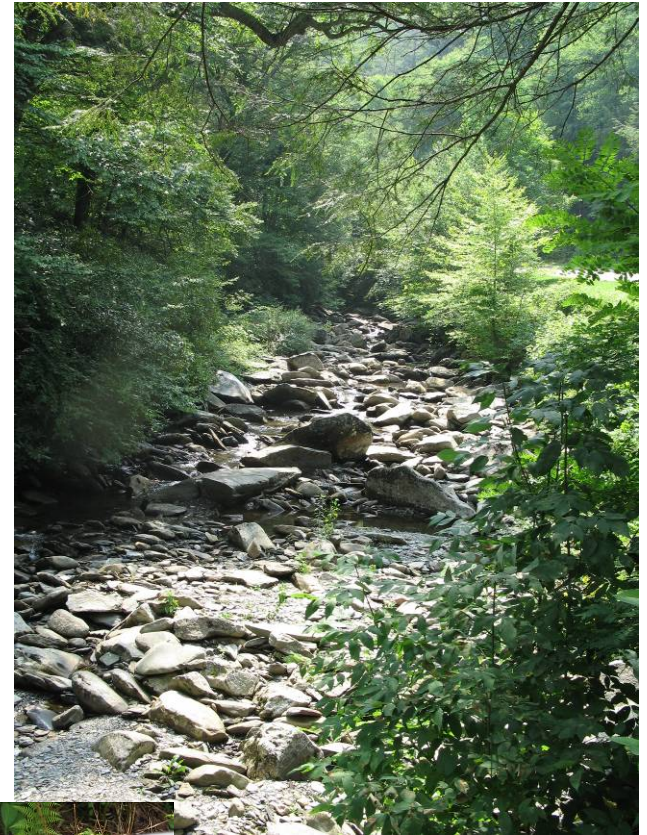
- Clean hands/dirty hands for sampling
- Double-bagged material
- Throughfall-acid washed glass funnels with teflon tubing and amber acid washed collection bottles, ~10ml of dilute HCl added as preservative
- Stream collection-laboratory prepares bottles, triple rinsed with stream water, shipped overnight on ice to laboratory
- Field blanks, spikes, duplicates/triplicates, use laboratory DI water

Chemical Analyses

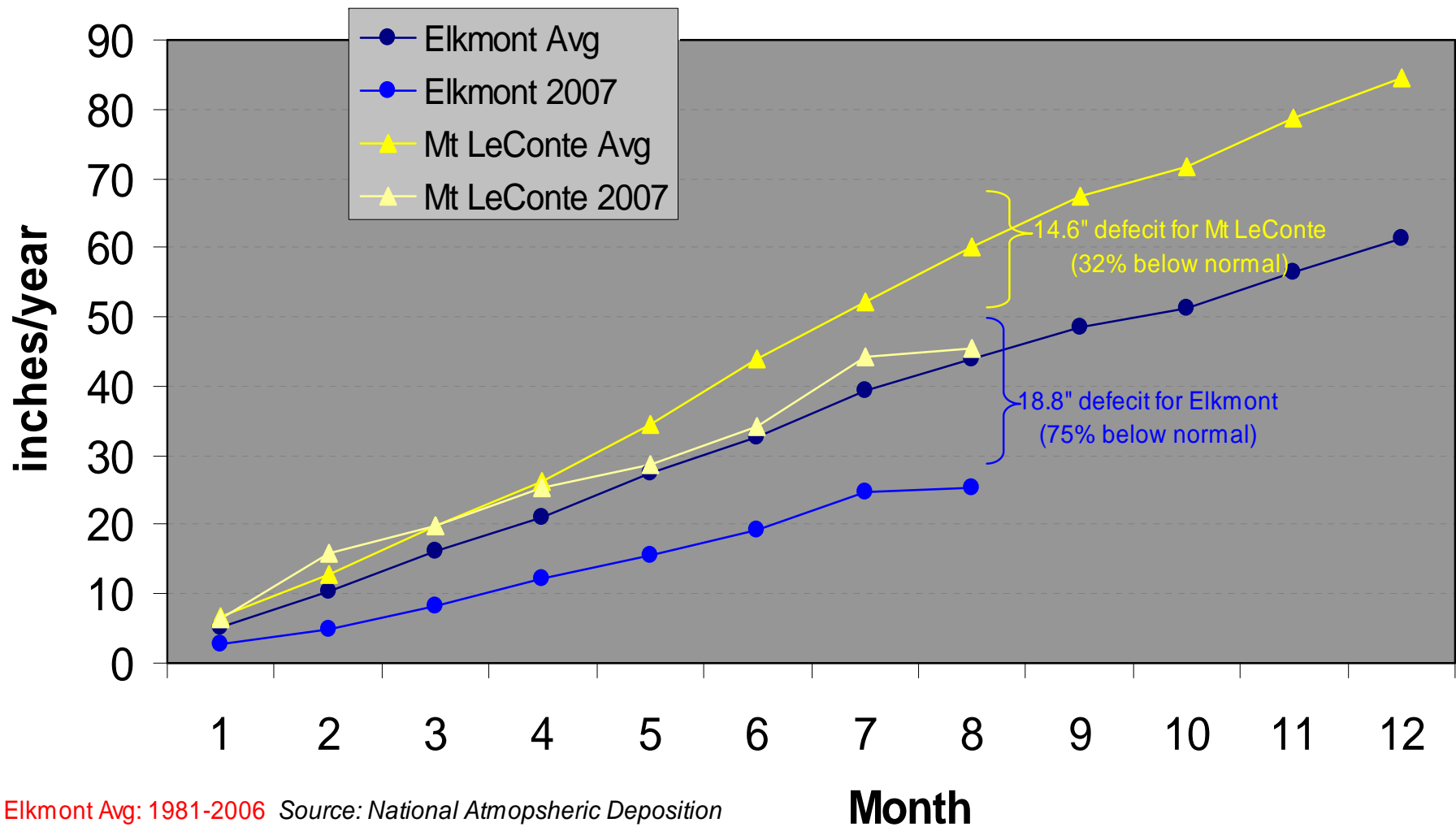
- Total Hg-oxidize with BrCl overnight and analyzed with CVAFS
- Methyl Hg-preserved with 0.4% HCl, distilled, and analyzed with CVAFS
- Sulfate-ion chromatography (EPA 300)
- Dissolved organic carbon (EPA 415.1)

Preliminary Results

- **Massive drought in Tennessee!
Difficulty in catching storms**
- **Very few soil solution samples**
- **Not enough sample volume from
throughfall sample for both total and
methyl Hg measures!**
- **Minor bear attacks-lost one litterfall trap
and replaced throughfall**



Long-Term Average* Monthly Cumulative Precipitation vs 2007 Precipitation at Elkmont (2,100 ft) and Mt LeConte (6,491 ft)



* Elkmont Avg: 1981-2006 Source: National Atmospheric Deposition

* Mt LeConte Avg: 1987-2006 Source: National Weather Service



Throughfall Samples

Site	Collector	Total Hg Dep ng/m ²	Ratio of TF to open
CD	TF1	1900	38
	TF2	145	2.9
	TFOP	50	
ND	TF1	240	2.4
	TFOP	180	
BYS	TF1	690	
	TF2	403	
	TF3	2050	

- Variability in throughfall collectors
- Ratio of inputs of throughfall to open precipitation is 2.65, slightly higher than in literature ~1.8
- Rainfall amounts were higher at lower elevation-this could influence differences between the sites
- Total wet deposition for June 2007=1248 ng/m²

Methyl Hg in throughfall

		Total Hg (ng/L)	MeHg (ng/L)	Methyl Hg contribution
ND	TF1	31	0.132	0.004%
BYS	TF2	85.5	0.253	0.003%

Litterfall



Data for June:

<i>Litterfall</i>	Date	Sample 1 (ng/g)	Sample 2 (ng/g)	Avg (ng/g)	Stn Dev
CD	06/14/07	20	29.4	24.7	6.6
ND	06/21/07	38.4	37.2	37.8	0.8
BYS	07/11/07	11.7	216	113.85	144.5

Comparison of throughfall and litter

	open precip (ng/l)	Avg. TF (ng/l)	Avg. litter (ng/g)
Clingmans	8.23	23.7	24.7
Noland	13	31	37.8
Bryson		115	113.85

- Studies have shown higher inputs of Hg in litterfall than precipitation or throughfall



Surface soils

Soil	Date	Tot. Hg (ng/g)	Sulfate (mg/kg)	Methyl Hg (ng/g)
Clingmans	06/14/07	387	337	.
Noland	06/21/07	318	483	.
Bryson	07/11/07	64.8	.	1.38

- Soil is the greatest pool of Hg
- Higher elevation soils contain higher amounts of total mercury



Soil Solution

<i>Solution</i>	Date	Tot Hg (ng/L)		
		6"	12"	24"
Clingmans	06/14/07	22.1	33	19.4
Noland	06/21/07	20.6	0	.
Bryson	07/11/07	.	.	4.68

- Hg in soil solution has been shown in studies to decrease in depth. Our results are inconclusive thus far.
- Soil solution concentrations are lower than surface soils here
- Lack of rainfall from drought has made it hard to compare depth
Clingman/Noland samples are higher than Hg in solution than those at Walker Branch, TN at 5 ng/L at 2" (Lindberg, 1996)



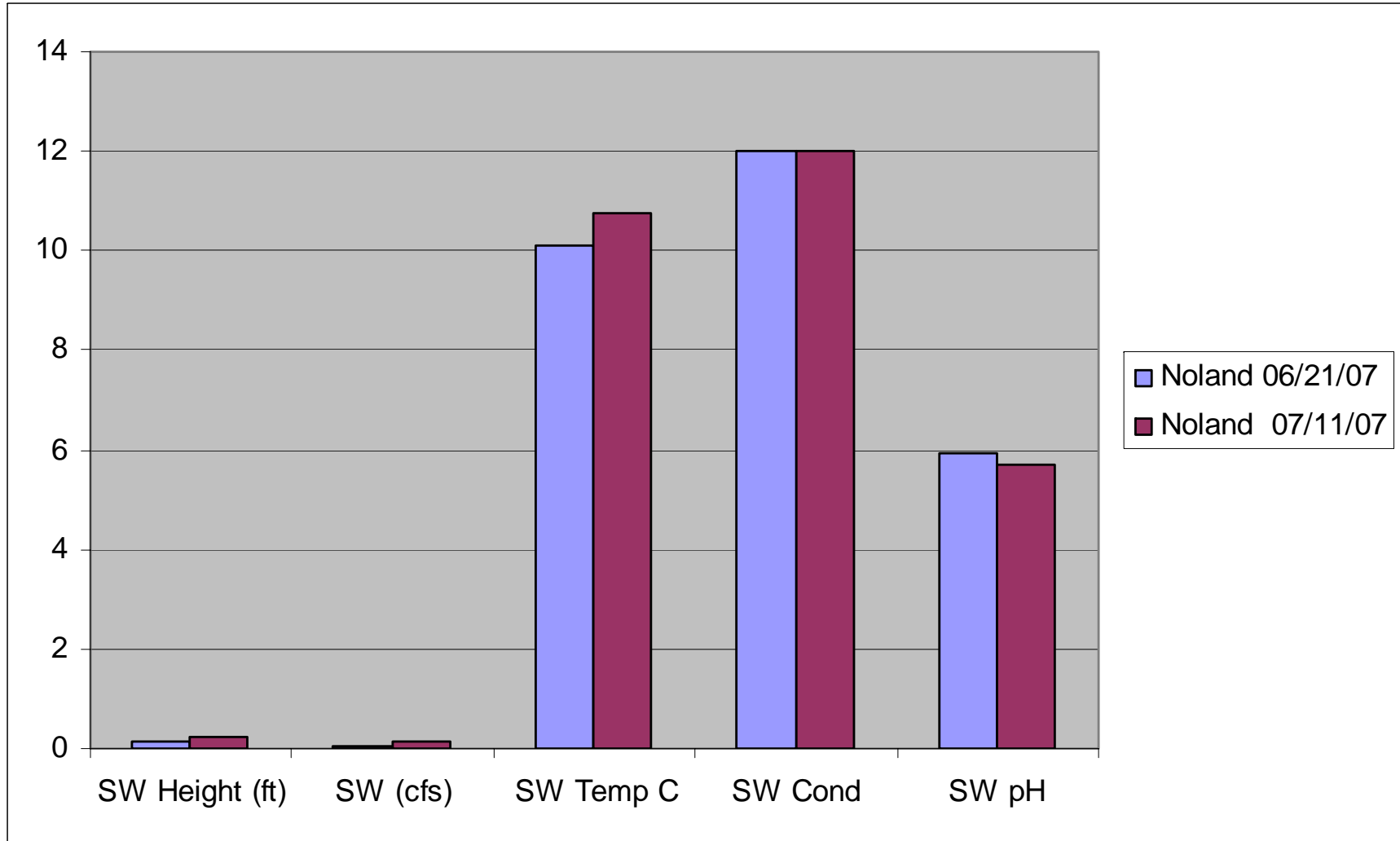
Stream chemistry

		Tot Hg (ng/L)	Dissolved (ng/g)	Sulfate (mg/L)	DOC (mg/L)
ND	06/21/2007	1.4	.	.	.
BYS	07/11/2007	6.5	1.67	0.08	2.04
BYS	07/11/2007	7.16	1.66		

- **Contracts not set up in time to run sulfate or DOC for Noland in June...**
- **Lower elevation sites= higher concentrations**
- **Lower Noland Creek (Bryson) is mostly particulate-bound**
- **Collected small amount of storm sample from lower Noland Creek, concentration =38 ng/L**



Stream flow and height



“Frozen Precipitation” in bulk collectors



Sample ID	Collection Date	Overnight Temp (F)	Air Temp (F)	Total Hg Conc (ng/g)	Total Deposition (ng/m ²)
CD1	04/03/2007	36	61.8	35.8	4686.22
CD2	04/03/2007	36	61.8	22.3	3331.62
ND2	04/03/2007	23	64.9	5.16	689
ND1	05/02/2007	46	61.8	5.64	981.4
ND2	05/02/2007	46	50	8.96	1639.7
ELK	03/08/2007	27	50	3.64	543.8*
*weekly amount					

- Little snow, mostly ice/snow that thawed during the day
- Clingmans Dome has higher concentrations in frozen precipitation

Summary

- Throughfall concentrations are higher than open precipitation.
- Litterfall concentrations are only slightly higher than throughfall concentrations.
- Highest elevation site has the highest concentration of total Hg in soil, but not enough data available to determine vertical profile of Hg in soil solution.
- Only one sample shows that particulate phase of mercury is greater than dissolved.
- Need more data to run correlations
- Still collecting data throughout September/October with plans to continue next year.
- Pray for rain!!

Acknowledgments

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