



Tekran Mercury Speciation Intercomparison at Horicon Marsh, Wisconsin

Mark L. Olson¹ and David Grande²

National Atmospheric Deposition Program ¹, Wisconsin Department of Natural Resources²



National Atmospheric Deposition Program



The Horicon site is a rural background site located in central Wisconsin



In-situ study from August 2013 – August 2014

Objectives

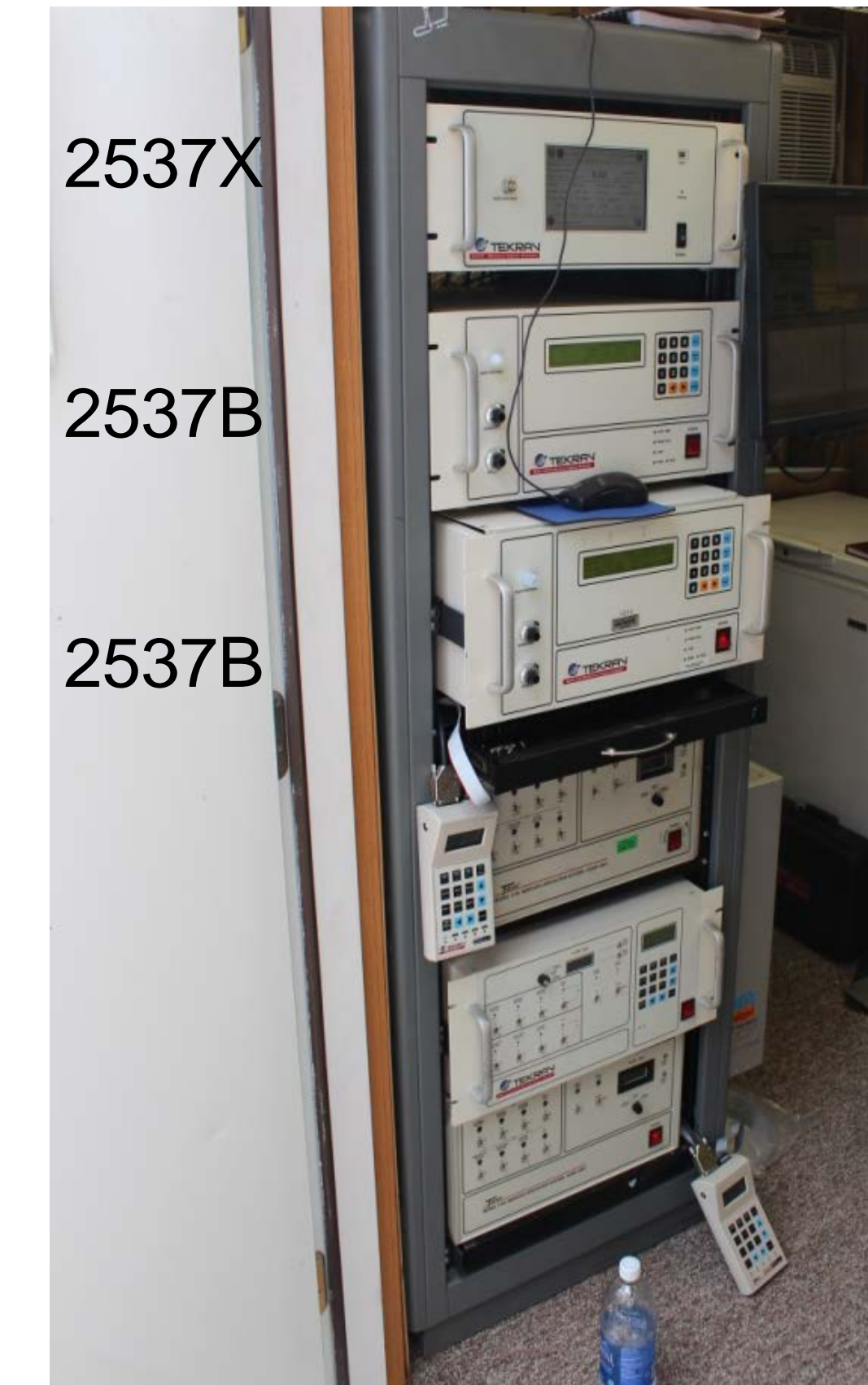
- Compare the Tekran 2537X analyzer to the 2537B
- Evaluate particulate glassware yielding higher concentrations
 - Are the results real? If not, can the glassware be restored?

Quality Assurance

- Site audits were performed by the AMNet Site Liaison in August and November of 2013 and September of 2014. Results from the audit are outlined in the 2013 AMNet QA Report <http://nadp.isws.illinois.edu/amn/>
- Inlet flow rates were checked at least monthly except during winter months. **Inlet flow rates varied by <2% between instruments and <0.5% within instruments**

Syringe Standard Additions

- 2537 Injections were performed each site audit. **Injections never varied by more than 4% with an overall average of 1.5%**
- A preliminary method detection limit test was performed in September of 2014. Ten low level injections of 50 pg were performed in each instrument. **Recovery variability was 2% or less on each instrument. Yielding detection limits of less than 3 pg for GEM** See Future Plans
- Seven sets of injections have been performed by the AMNet Site Liaison. **Accuracy was 3.8% (±1.6%, n=92) for SN 396 and 0.7% (± 1.6%, n=100) for SN 5001.**



Particulate Glassware

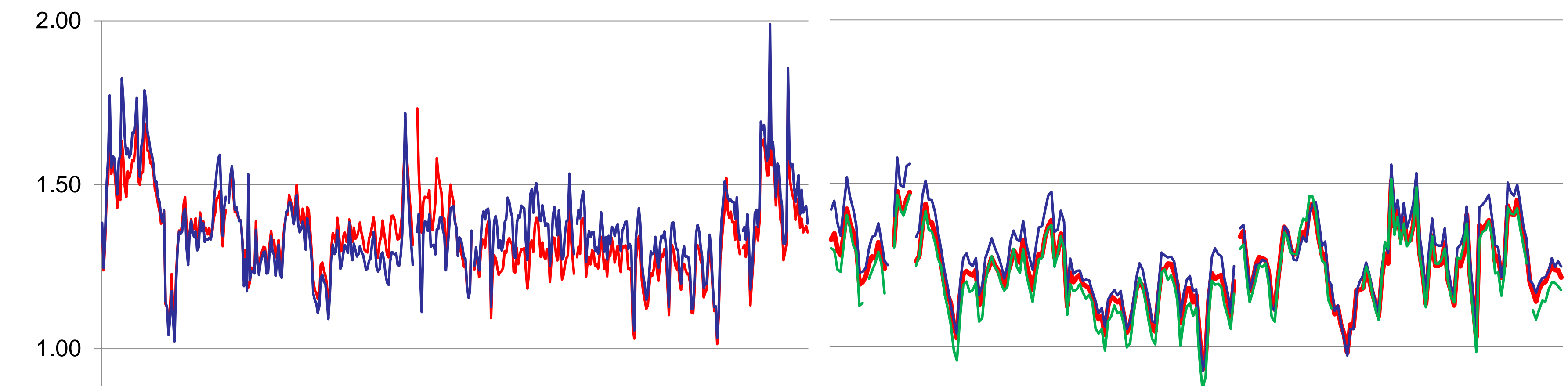
Periodically after a particulate filter (RPF) glassware change a positive step function (PSF) was observed. The PSF RPF produced typical blank and pyrolyzer results, only the particulate values were elevated. Tracing the results to a particular RPF, the PSF RPF was compared to other RPF's determining it was a function of the glassware, not the analyzer. A cleaning procedure matrix was designed to determine if the PSF RPF could be restored to normal operating levels. Additional steps may be added to the AMNet RPF cleaning procedure.

Design Flaws:

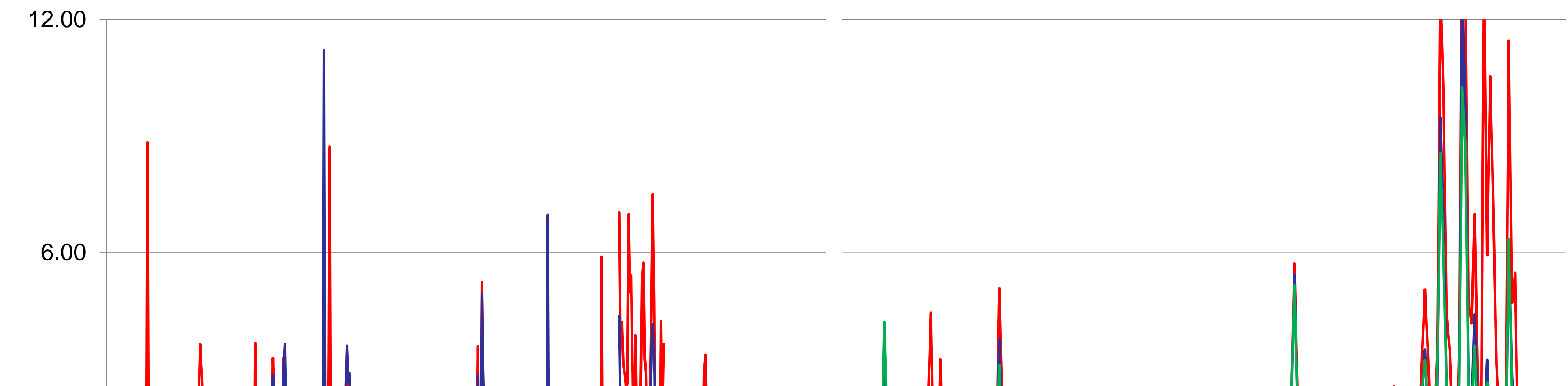
- The MDL study will always be biased high using manual injections
- The MDL estimate was performed using 50pg injections which are >10 times the MDL
- Horicon GOM and PBM concentrations are too low for good estimates for variability
- FUNDING! We have no money

Future Plans:

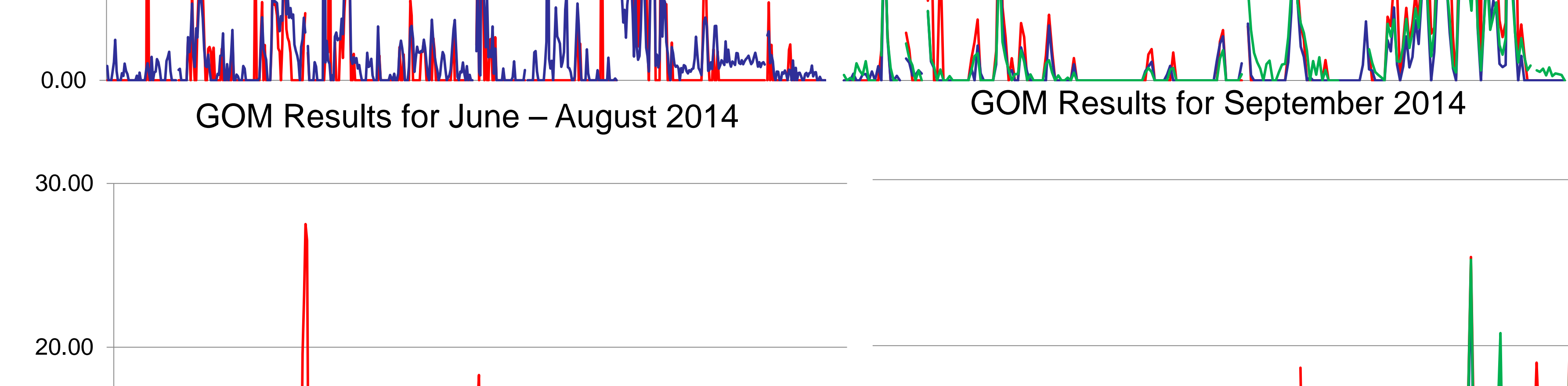
- A third instrument has been installed and the intercomparison will continue through 2014
- Injections have been performed with a 25ul syringe, purchase a 5ul syringe and perform additional MDL studies at lower masses
- Chamber experiments to influence GEM, GOM and PBM concentrations



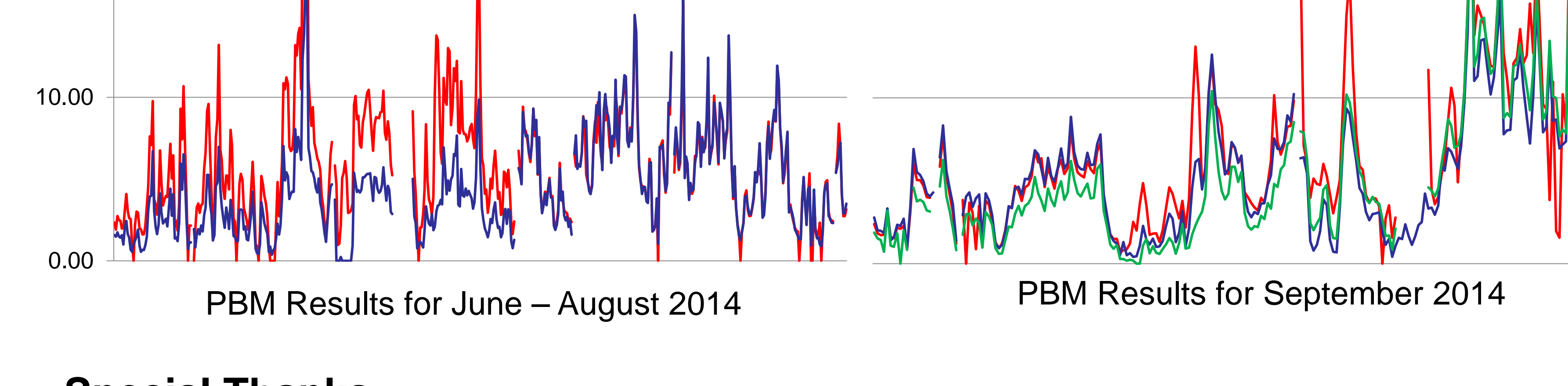
GEM Results for June – August 2014



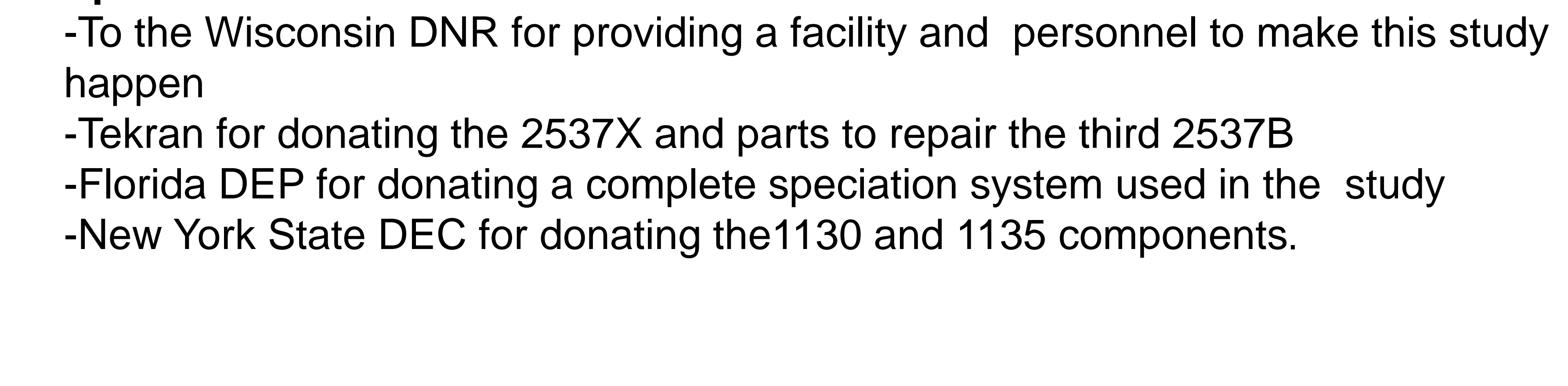
GEM Results for September 2014



GOM Results for June – August 2014



GOM Results for September 2014



PBM Results for June – August 2014



PBM Results for September 2014



Equal Inlet heights

Instrument performance

Hourly averages of GEM were compared after AMNet screening. Of the possible 3059 averages, 2585 (85%) were valid and used in the comparison

Contact Information:

Mark L Olson, molson@illinois.edu

608-335-4232

David Grande, david.grande@wisconsin.gov

Special Thanks:

- To the Wisconsin DNR for providing a facility and personnel to make this study happen
- Tekran for donating the 2537X and parts to repair the third 2537B
- Florida DEP for donating a complete speciation system used in the study
- New York State DEC for donating the 1130 and 1135 components.