Speciation Measurements: Wisconsin QA Study and What We Know About AMNet Data Quality

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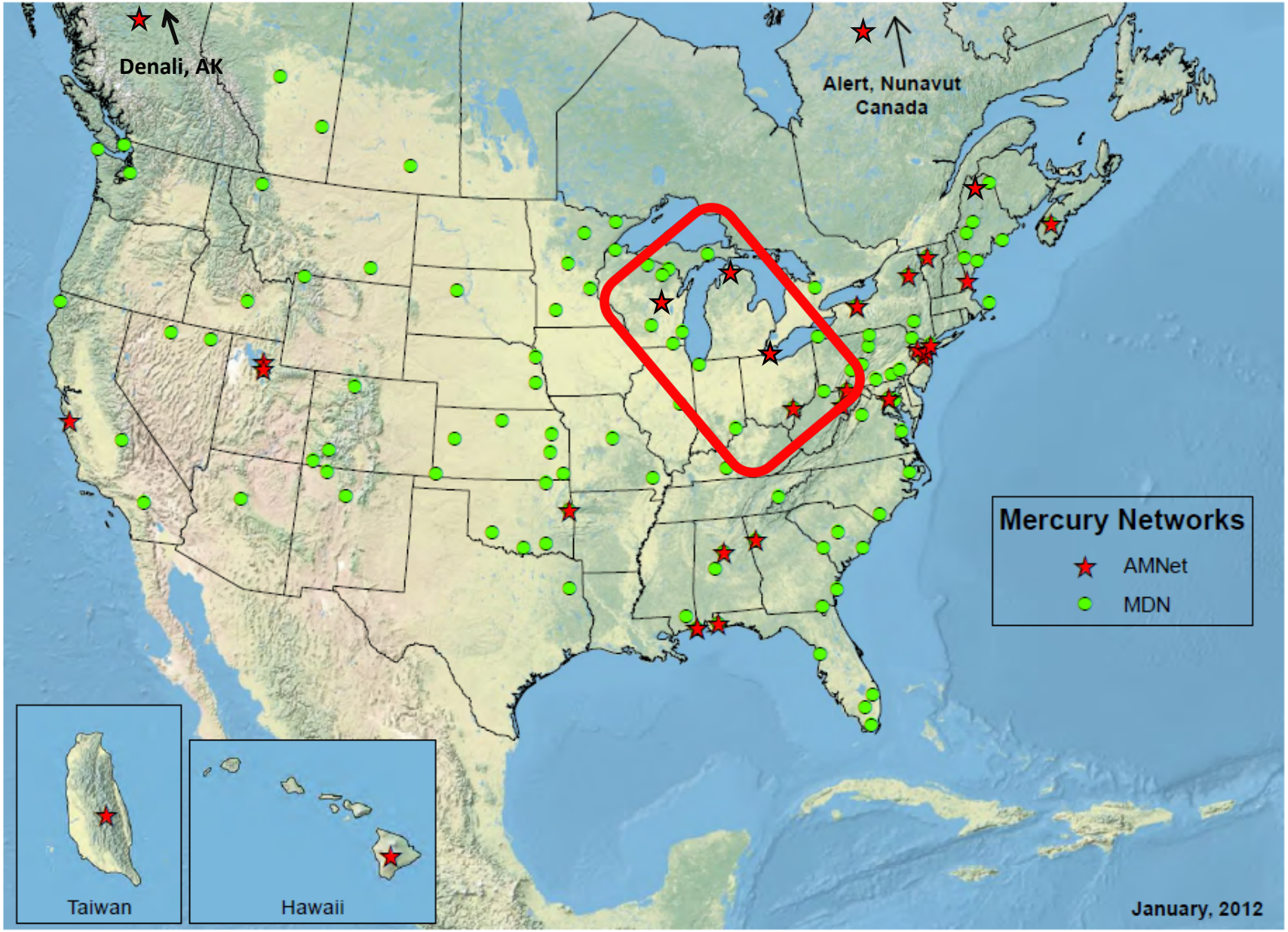
Speciation Measurements

- Gaseous Elemental Mercury (GEM)
  - Low water solubility, ng/m3
- Gaseous Oxidized Mercury (GOM)
  - Water soluble, pg/m3
- Particulate Bound Mercury (PBM)
  - Water soluble, pg/m3

NADP's Mercury Networks



Four LADCO Sites

- Athens, Ohio
  - Long Term Data Set, 2004 to Present
- Horicon, Wisconsin
  - 2010 to Present
- South Bass Island, Ohio
  - 2012 to Present
- Pellston, Michigan
  - Installed last week
  - Previous U Michigan Site

    - *Data through 2014 is available on the web*

WI07 Horicon, Wisconsin

- 17 month Tekran collocation experiment
- 12 months with 2 speciation systems (2537X:2537B)
  - GEM hourly average, 4% difference. T=3.43 P=<0.00
- 5 months with 3 speciation systems (2537X:B:B)
  - GEM 3.3% difference
  - 2.9% of time one was > 10%
  - > 90% data completeness
  - T-stat at 0.05
    - 2 passed, 1 failed (t=0.23, p=0.41)

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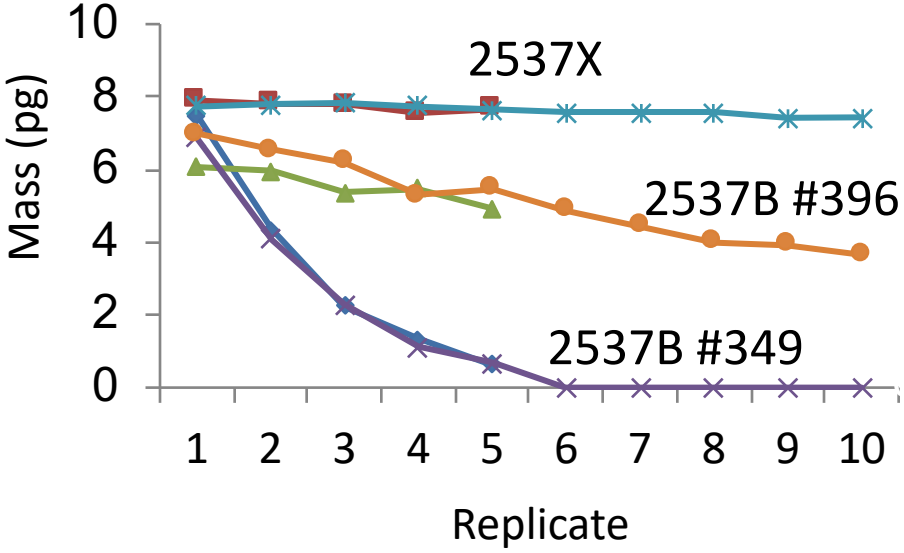
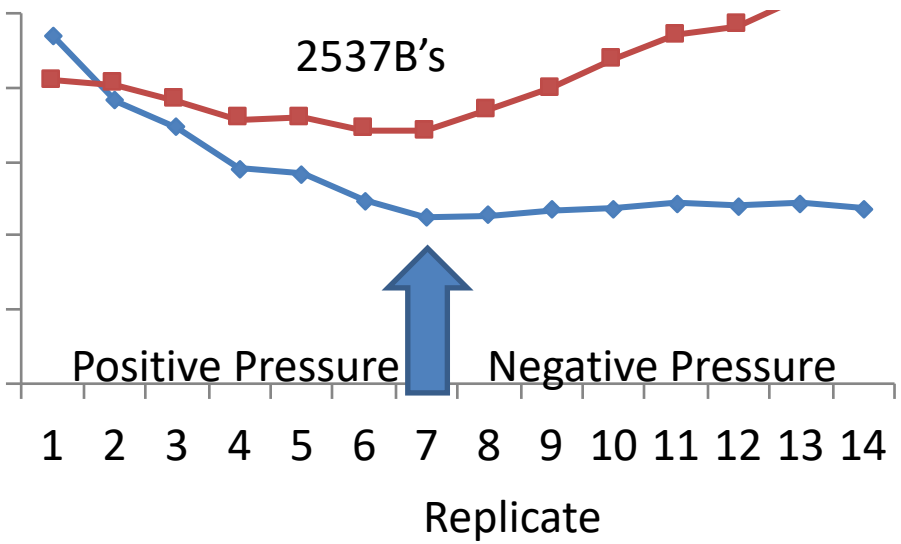
Instrument Detection Limit

- Route cell vent into sample train
- Supplement sample volume with zero air
- Add 7 pg of Hg to injection port
- Goal: daisy chain all 3 together for between instrument comparison, *this did not work*

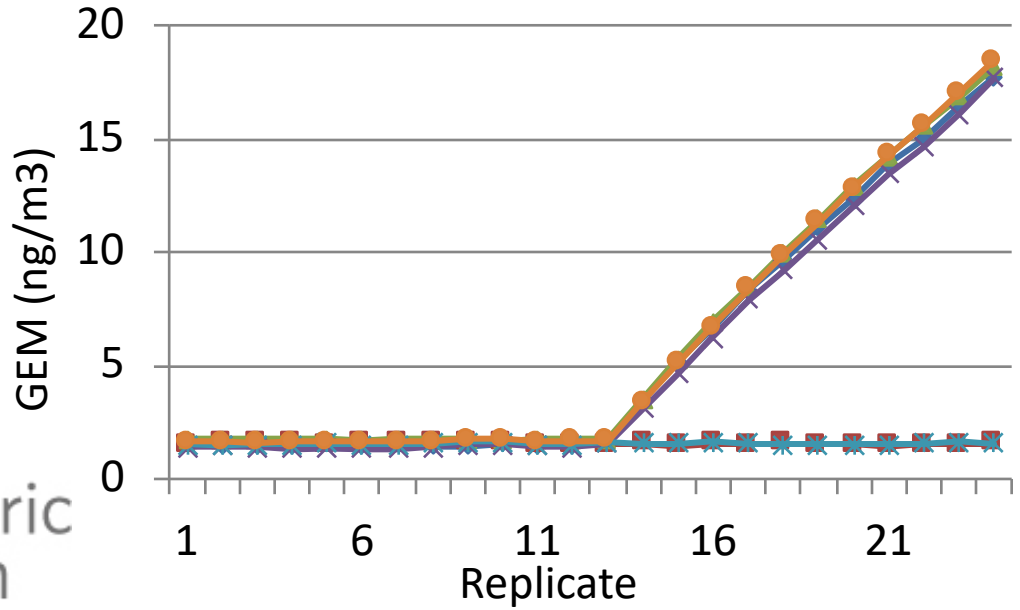
IDL 2537X = 0.51 pg





Method Detection Limit

- Cell vent into ambient air sample stream
- Two instruments evaluated, one left to monitor ambient air
- Repeated 3 times, similar results
- 2537X = 1.85 pg
- 2537B = 2.16 pg



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Detection Limit Concentrations

Instrument Detection Limit

Parameter	Sample Size	IDL
GEM	5 L	0.102 ng/m3
GEM	7.5 L	0.068 ng/m3
GOM and PBM2.5	1 hr*	0.851 pg/m3
GOM and PBM2.5	2 hr*	0.426 pg/m3

* 10 lpm

GEM Method Detection Limit

Parameter	Sample Size	MDL 2537B	MDL 2537X
GEM	5 L	0.432 ng/m3	0.369 ng/m3
GEM	7.5 L	0.288 ng/m3	0.246 ng/m3

Hot Topic - Denuder Bias

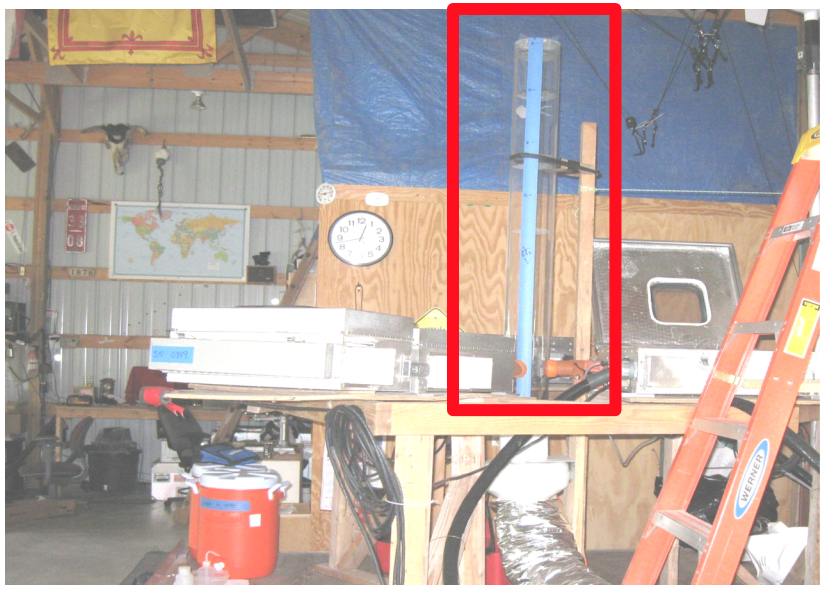
- Appears to be a negative GOM bias
- Depends on form of GOM
- Concentration of Ozone
- Relative Humidity
- McClure et.al. SEARCH site BHM, AMNet AL19
  - $HgBr_2$ efficiency 20-54%, inverse with O_3 and RH

RAMIX, multi instrument comparison

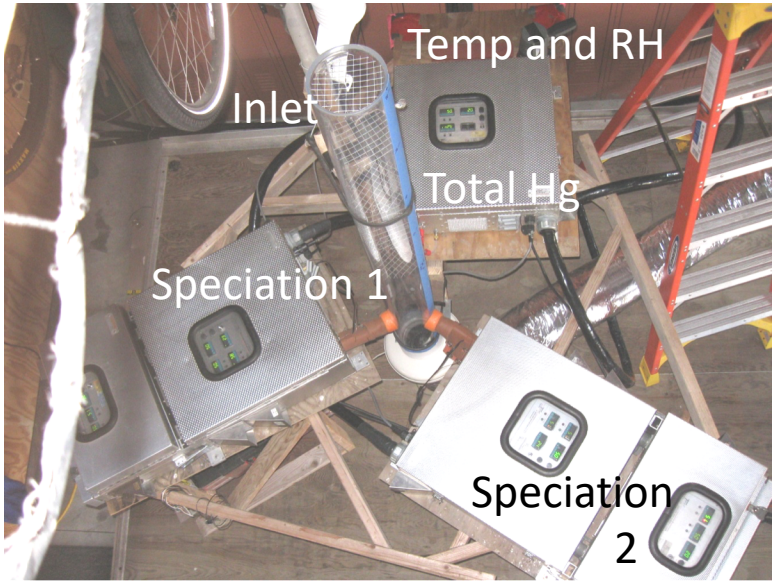
- Manifold study
- GOM capture efficiency in presence of Ozone and or moisture
- “GOM production in manifold”
- Seven instruments, two Tekran Speciation
- Results need to be replicated

NADP CEEPAMS

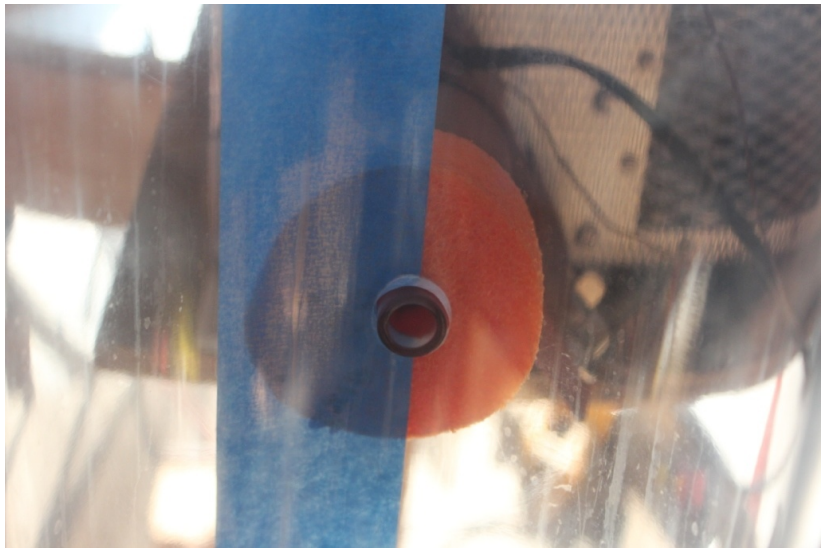
- Chimney Experiment to Establish Precision and Accuracy for Mercury Species
- 3 instrument manifold experiment
  - 2 Tekran speciation systems
  - 1 modified DOHGS system for total Hg
- Vertical Manifold with inlets are same location
- $HgCl_2$ and $HgBr_2$ permeation tubes
- Speciation systems set to AMNet protocols
- Record temperature and relative humidity



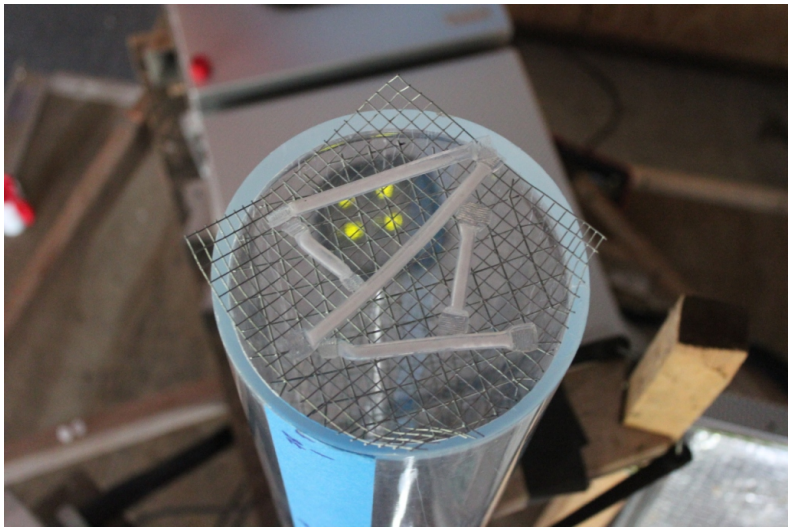
Vertical manifold



Inlets at 120^{o} around manifold



Inlets sealed and protrude into manifold



Permeation tubes on inlet screen

Tekran Systems

- Speciation 1 and 2 are set to AMNet Protocols
  - 10 lpm, inlet 50°C, 2 hour sampling, zero air flush
- Modified Total Hg system
  - 4 lpm, inlet at 50°C, 2 hour sampling, zero air flush
  - Denuder held at 550°C while sampling
- Add varying amounts of $HgBr_2$ or $HgCl_2$

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GOM and PBM Comparison

- GOM and PBM from two speciation systems
- May 29, - June 4, 2015
- 29 collection periods, none were excluded
- 10 periods had GOM additions

Precision Estimates

Parameter	RSD	Mean	Median	F-pseudo
GOM	15%	27.7	3.8	0.772
PBM*	44%	5.7	5.1	2.771

* Focus of study has been on GOM

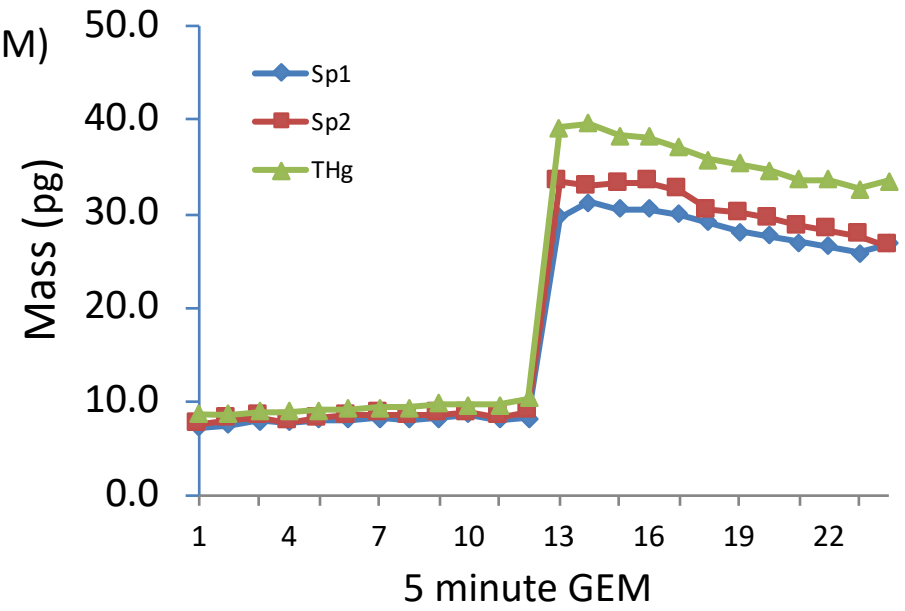
GOM Recoveries

- GEM increased with GOM addition
- GOM added 1 hour into 2 hour sampling
- Calculate Mass and area under curve
- Calc GOM = difference

$GOM = THg_{(GEM)} - Sp1\ (or\ Sp2)_{(GEM)}$

Percent Recovery

- Denuder GOM/Calc GOM



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Quality Assurance

- GEM from speciation one and two were compared using paired t-tests at 0.05
- Comparisons were determined for the first and second hour sampling periods
- Of the 10 June experiments, 5 passed both the first and/or second hour
- Of the 7 August experiments, 5 passed both the first and second hour

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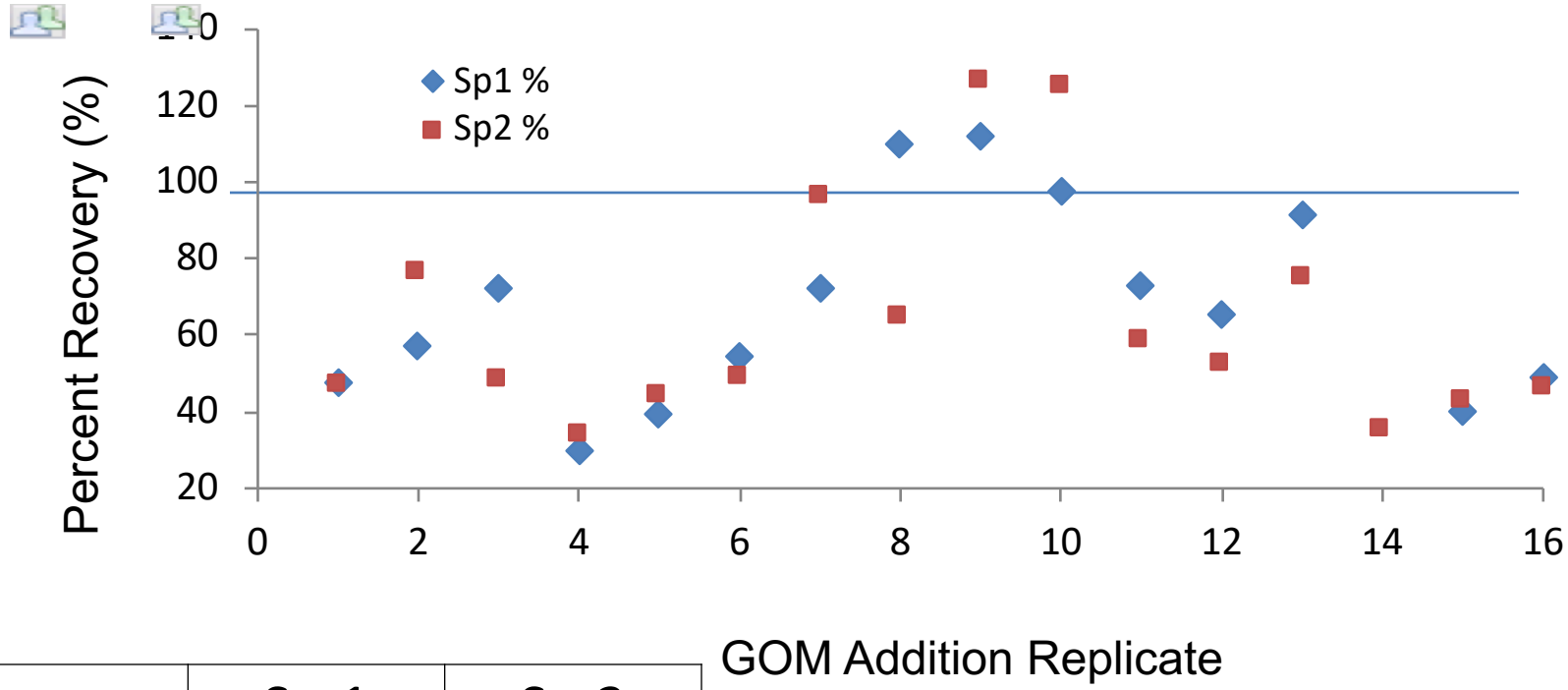
Preliminary Recovery Results



	Sp 1	Sp 2
Avg	64.4%	63.9%
Max	112.2%	126.2%
Min	30.0%	34.1%
stdev	27.6%	29.1%

What's next?

- Decrease uncertainty in results
  - Do we have good mixing?
  - Do the instruments behave differently?
  - Something else that we have not identified?
- Perform experiments in zero air
- Increase inlet temperature to 100^{o}C
- Test different denuder coatings
- Incorporate PBM into study(?)
- Work with others to improve data quality
- Make changes to AMNet Std Operating Practices

Tekran User Group Meeting

- Tekran User Workshop
- September 21-24, 2015
- Washington DC
- Remote access
- Over 50 international experts invited
- Interested?
  - mlolson@illinois.edu
- Currently about 25 attendees

Special Thanks

- Equipment
  - New York State Department of Environmental Conservation
  - Florida Department of Environmental Protection,
  - National Oceanic and Atmospheric Administration,
  - Tekran
- Advice and support
  - David, Bob and Mark from NADP, Vid, Dave, Eric, Mae, Sandy, Winston, XinRong, PK…


Questions?