

Passive Diffusion Monitoring for Ammonia in the U.S.

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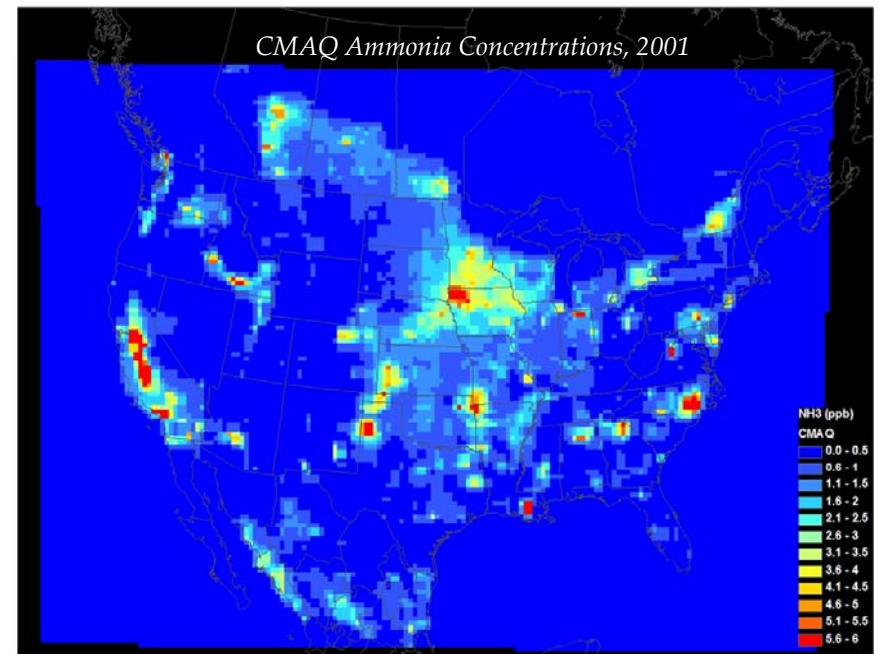
National Atmospheric
Deposition Program



ILLINOIS

Monitoring Goals

- Determining the spatial distribution of ammonia concentrations,
- Determine the seasonality of these concentrations,
- Help in meeting air quality goals, and improve modeling,
- Provide information for other scientific and policy needs.
- Cost efficient Network

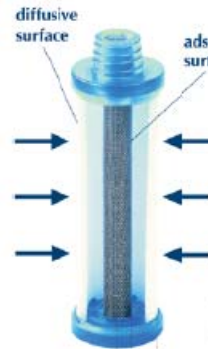


Goals of This Project

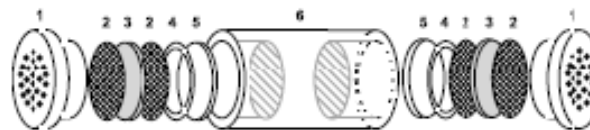
- Test the Passive Samplers for Performance
- Develop a cost efficient Network
 - procedures
 - sites
- Measurement of Ammonia Concentrations

Passive Diffusion Sampler Alternatives

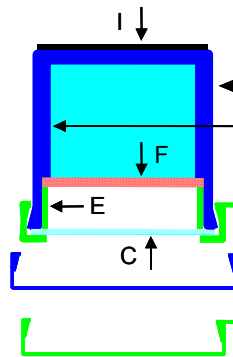
● Radiello



● Ogawa

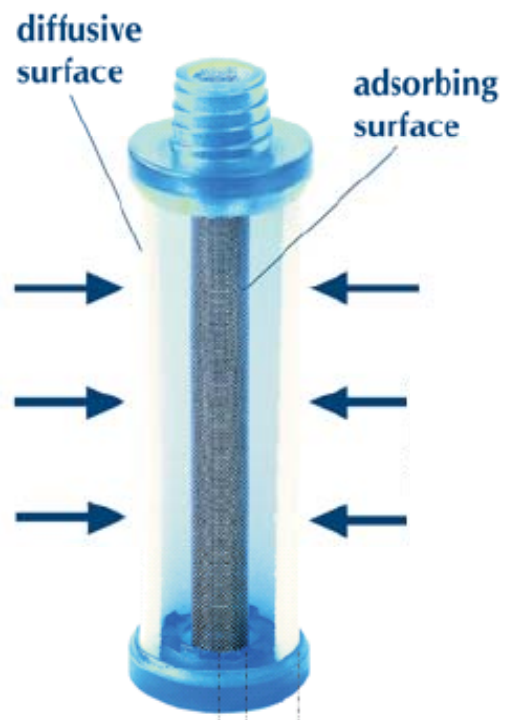
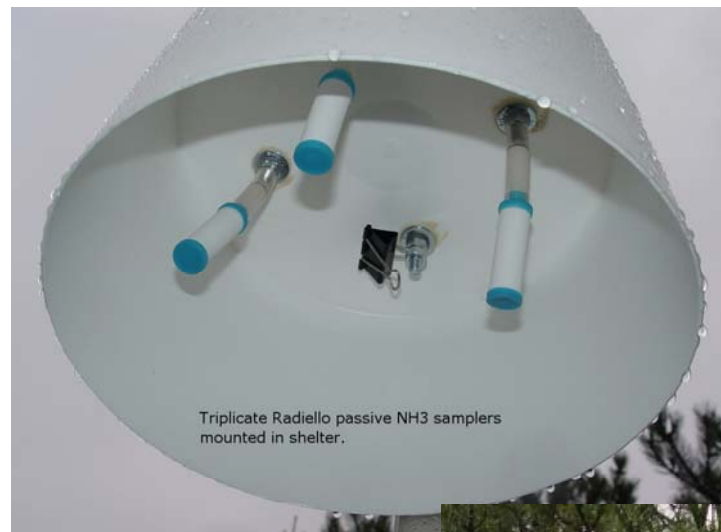


● Alpha



● All vs. Denuders (“standard method”)

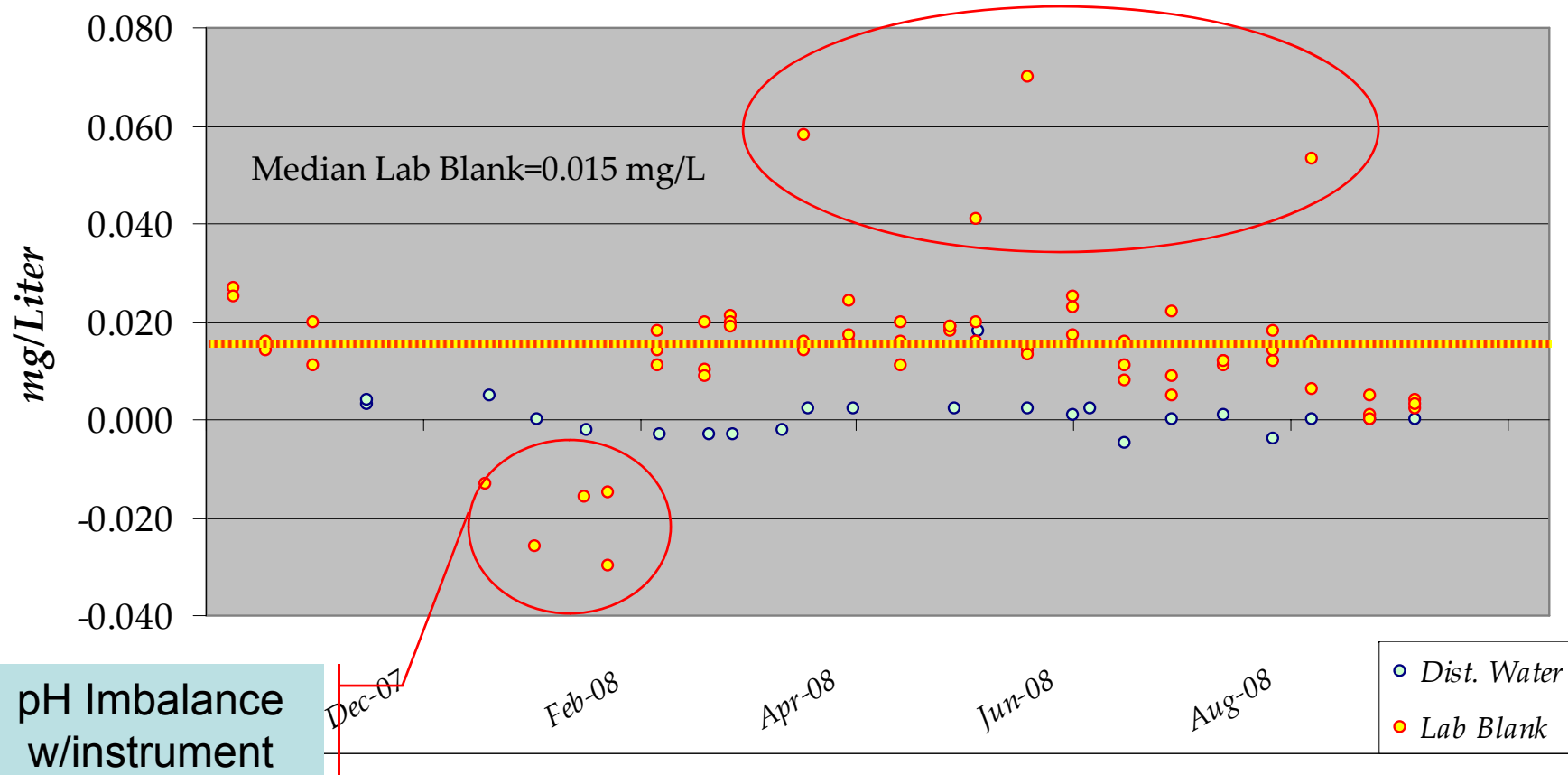
Radiello



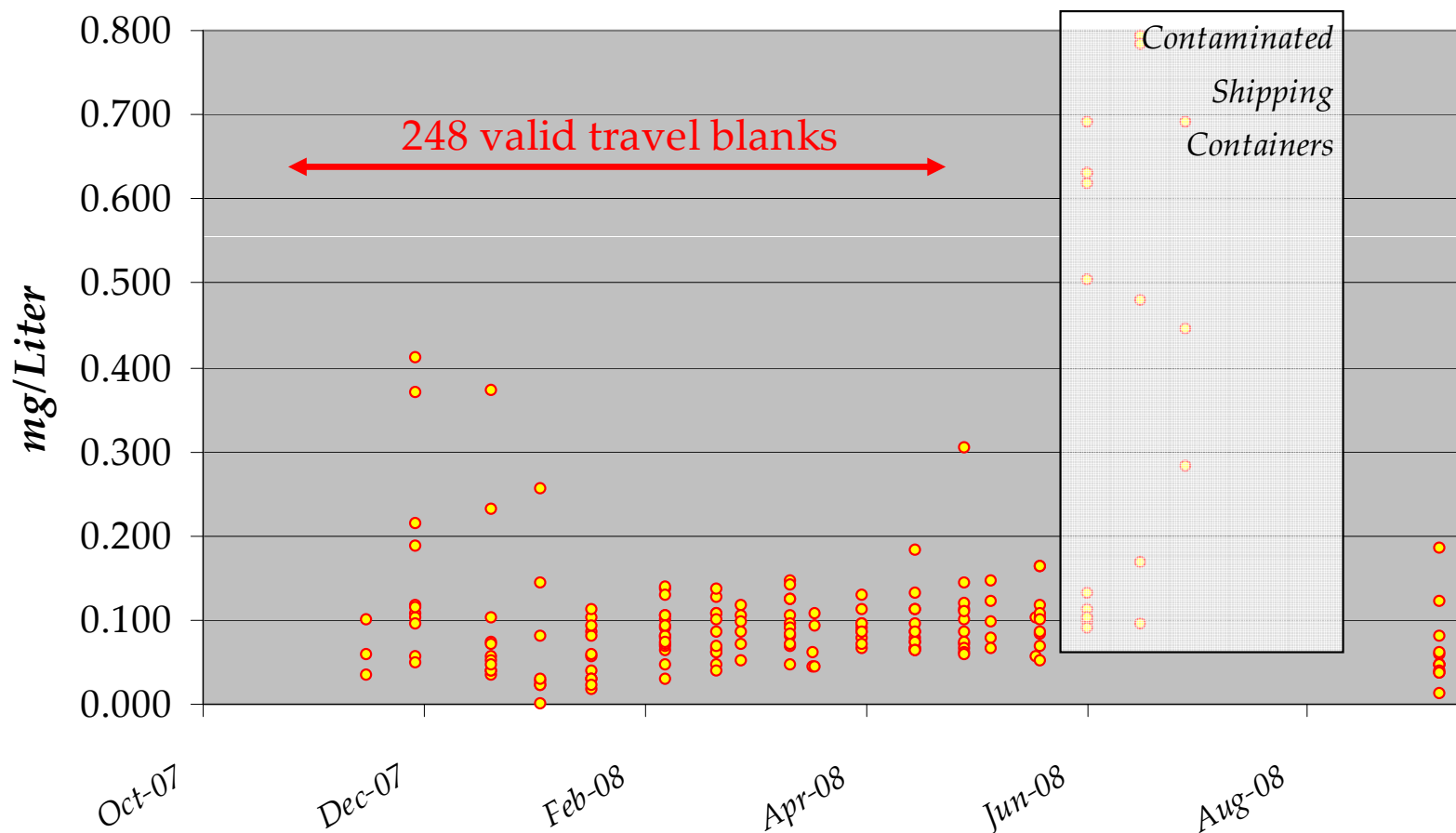
Results of the Diffusive Samplers

- Blanks
 - Laboratory Blanks
 - Travel Blanks
- Accuracy
 - vs. denuder
- Repeatability
 - Triplicate samples
- Reporting limit

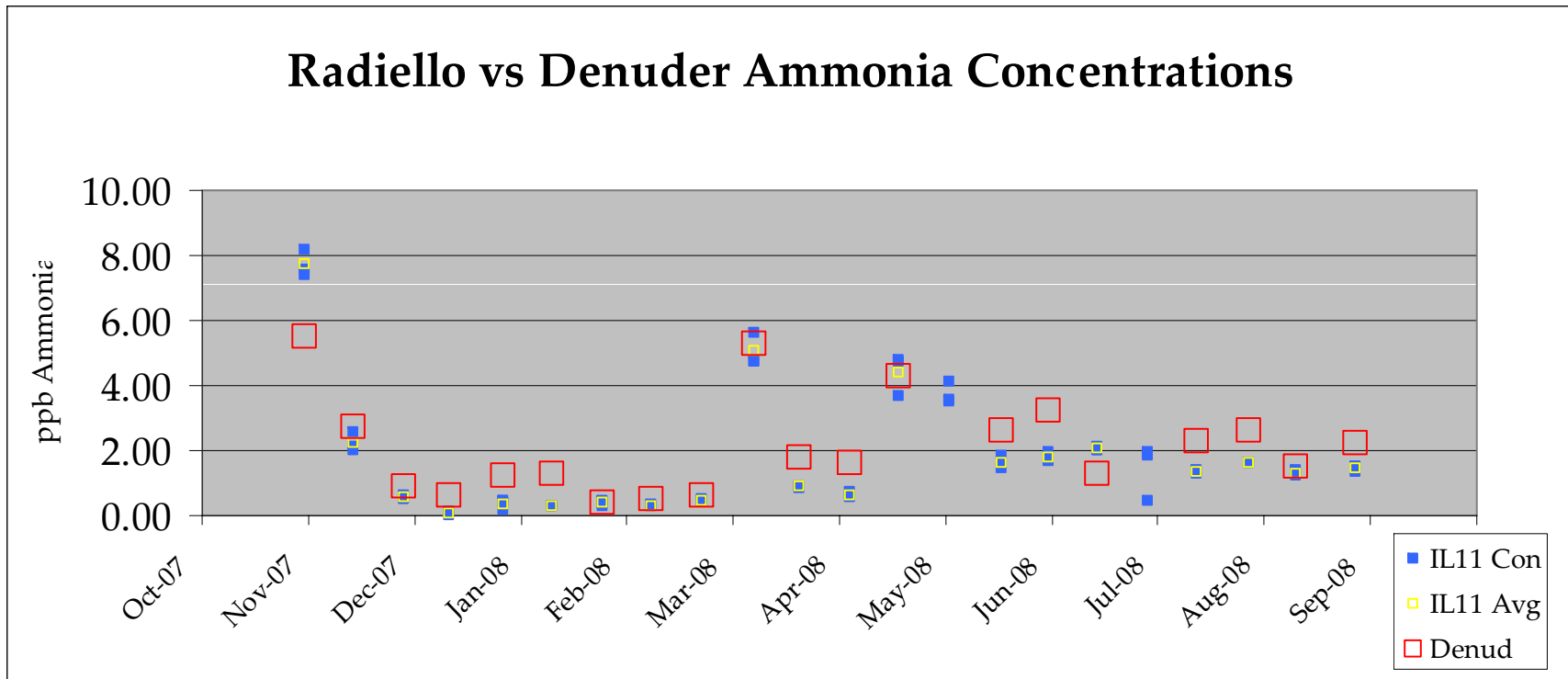
Radiello Ammonium Lab Blanks With Time



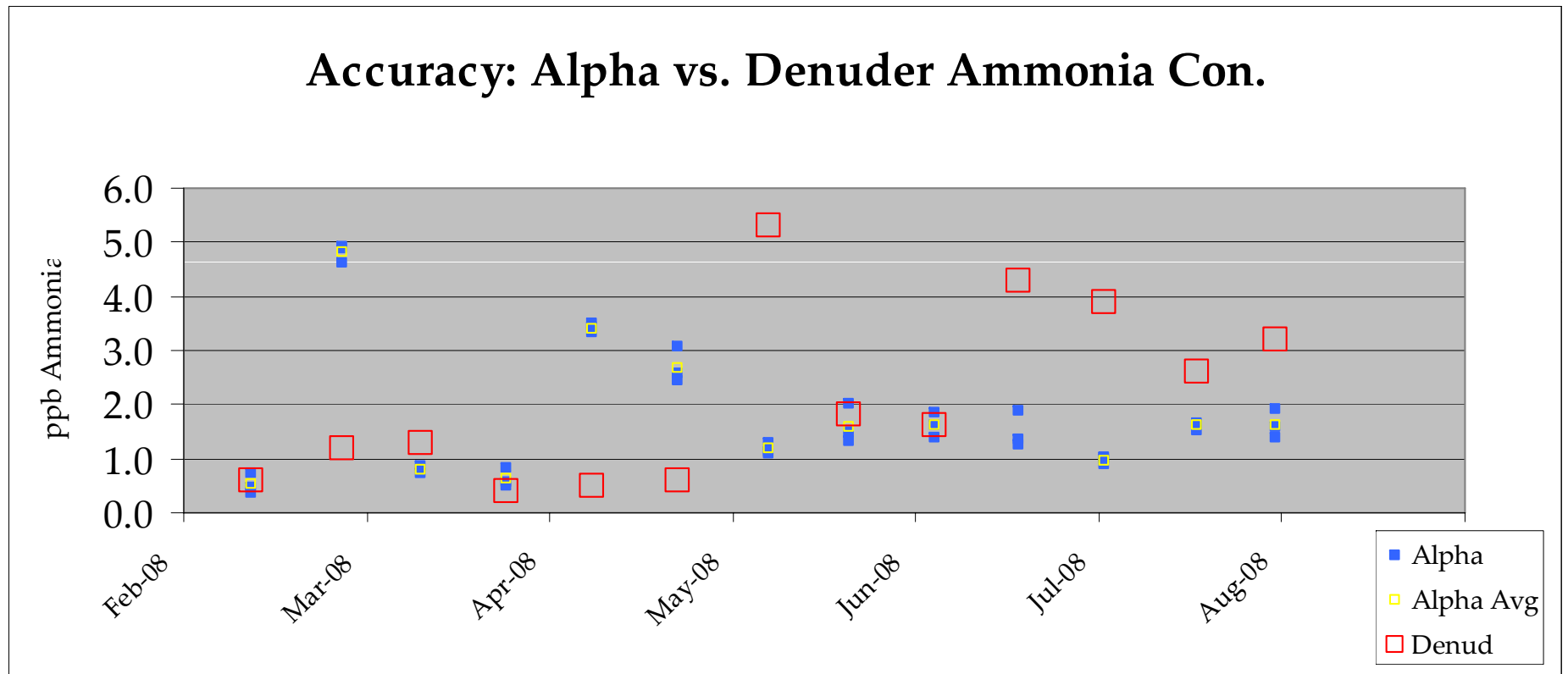
Radiello Ammonium Travel Blanks With Time



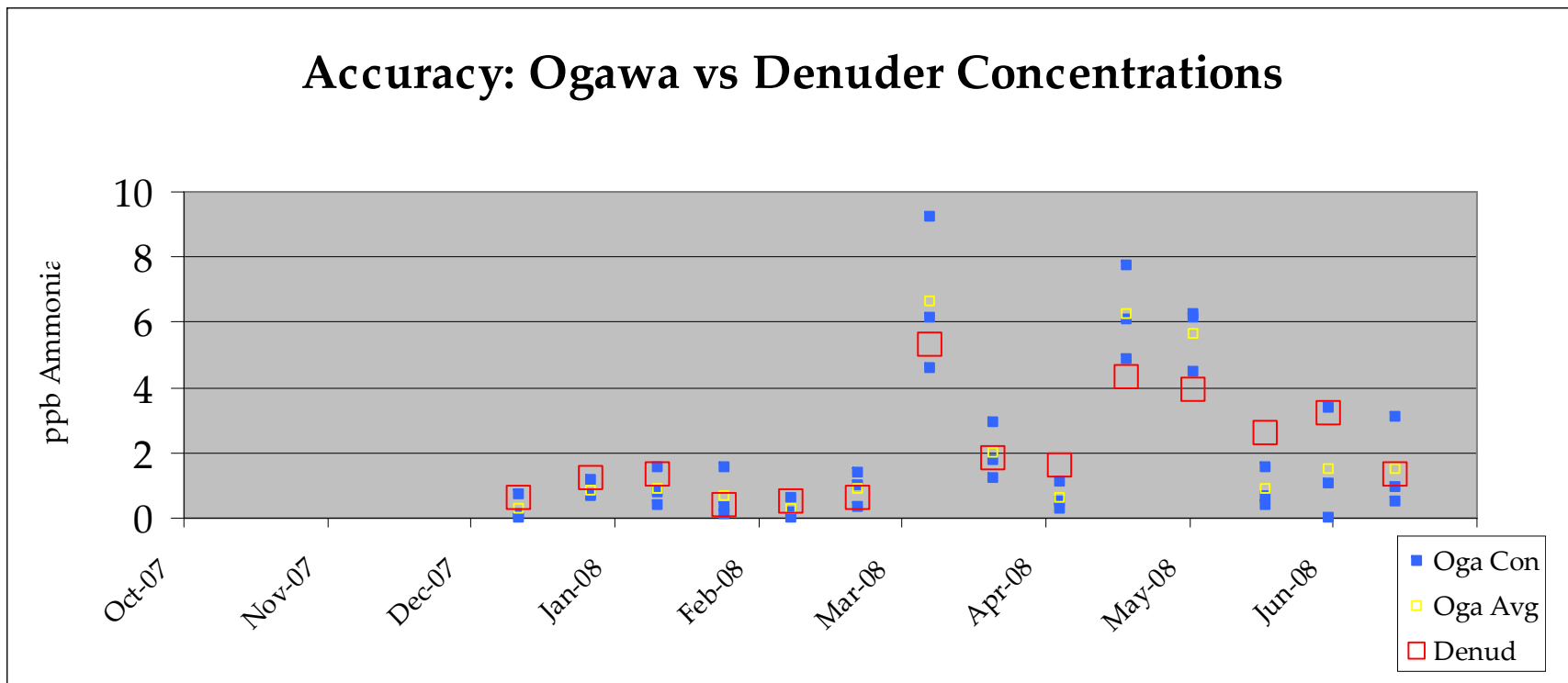
Radiello Accuracy



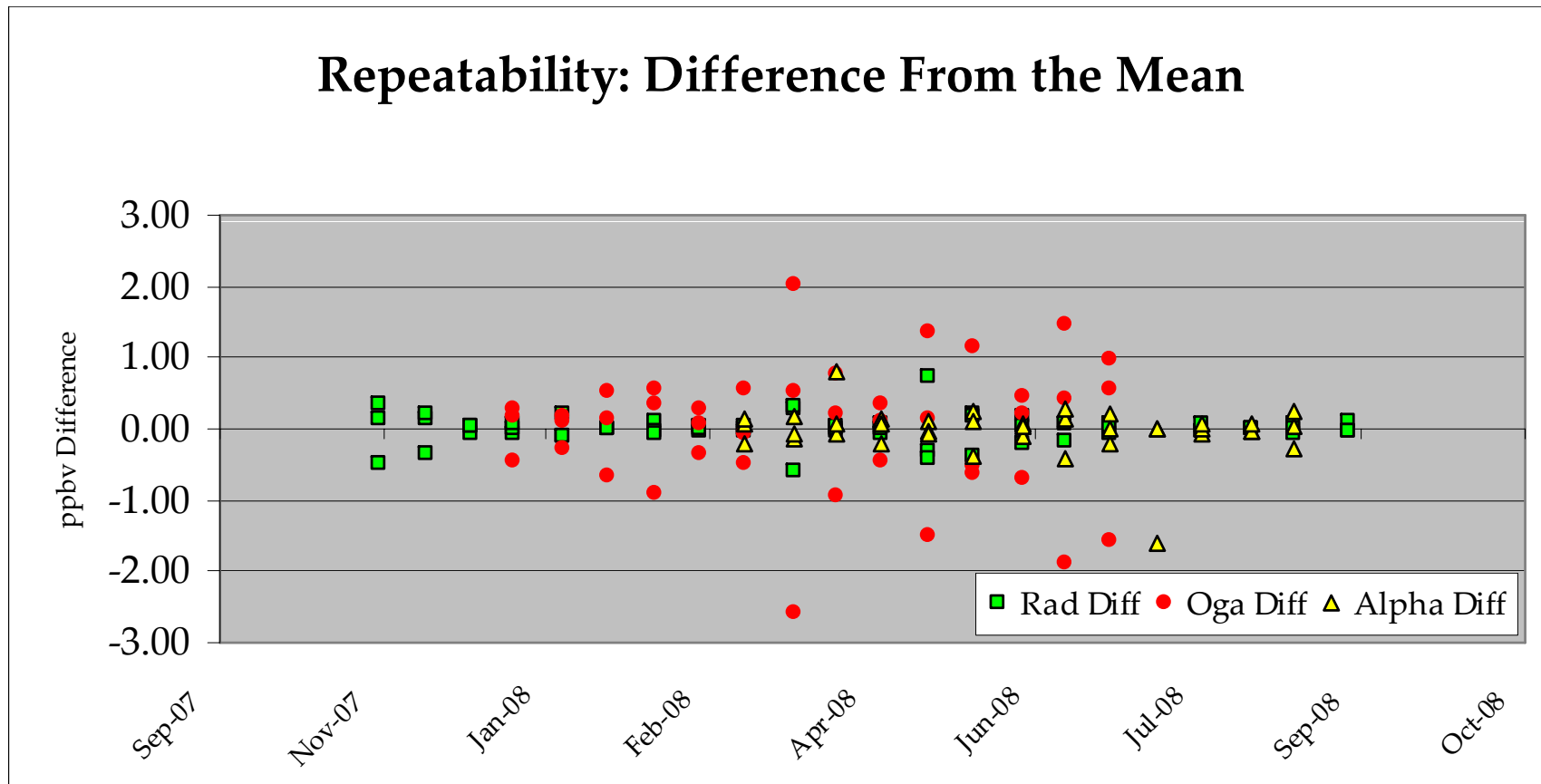
Alpha Accuracy



Ogawa Accuracy



Repeatability of Passives

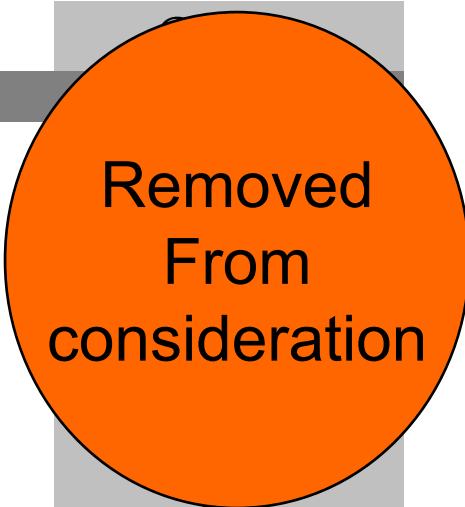


Repeatability Comparison

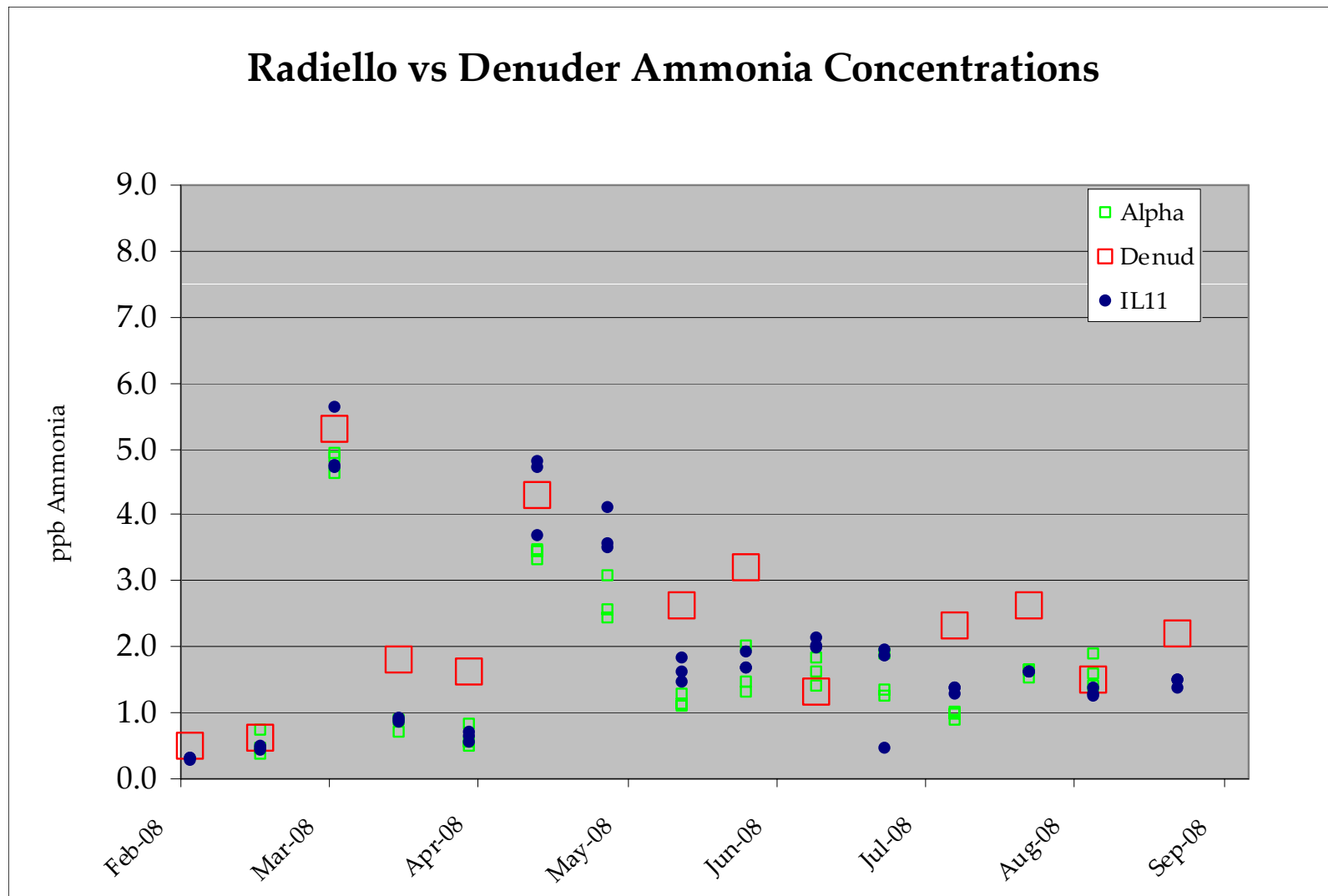
Comparisons

ppbv units

| Measure | <i>Radiello</i> | <i>Alpha</i> | |
|-----------------------------|-----------------|--------------|----|
| Repeatability | | | |
| median difference (vs avg) | 0.00 | 0.01 | |
| maximum difference (vs avg) | 0.73 | 0.79 | |
| Standard Dev. Of difference | 0.19 | 0.33 | |
| 75th perc. Difference | 0.07 | 0.11 | |
| 25th perc. Difference | -0.05 | -0.08 | |
| interquartile range | 0.12 | 0.18 | |
| n | 63 | 39 | 42 |



Radiello x Alpha Accuracy



Radiello x Alpha, Cost

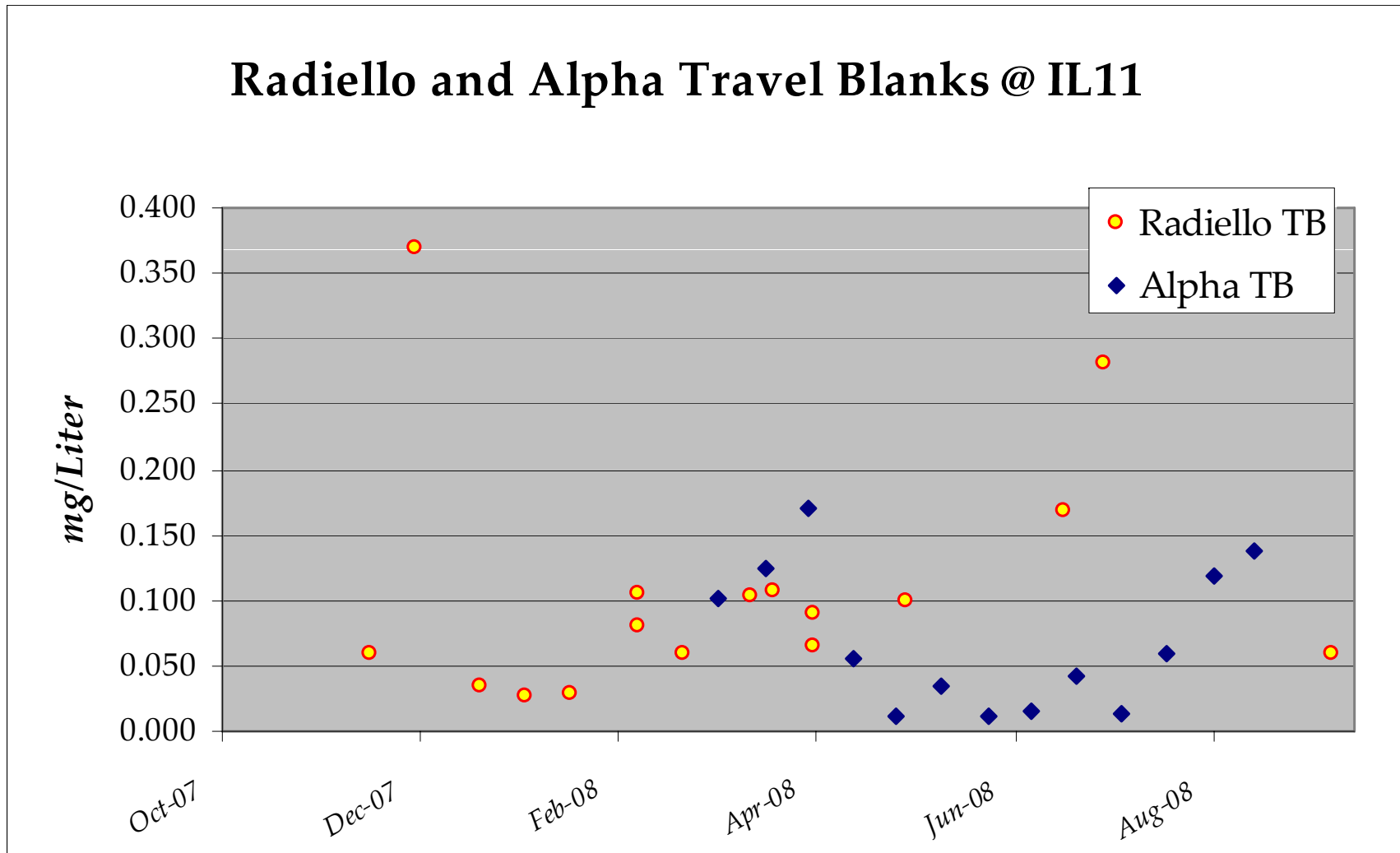
Comparisons

Costs

| Measure | Radiello | Alpha |
|-----------------------------------|--------------|---------------|
| Costs | | |
| Body (\$) | \$8.00 | \$23.00 |
| no. of body uses | 10 | 100 ++ |
| Replaceable "core"/filter (\$) | \$11.00 | 42¢ |
| replaceable membrane | | \$2.10 |
| 1 year, triplicate samples | \$874 | \$60 |
| cleaning (hrs) | minimal | minimal |
| preparation | little | somewhat more |

Alphas are English (£ to \$ conversion)

Radiello vs. Alpha Travel Blanks



Low Bias for Passive Diffusion Samplers

- Consistently below the denuders

| | Average ppbv | ppbv | Median % | Abs % |
|---------------------------|-----------------|-------|-------------|-------|
| Denuder | 2.56 | 2.30 | | |
| Radiello | 2.02 | 1.61 | | |
| Alpha | 1.78 | 1.60 | | |
| Radiello - Den Difference | -0.54 | -0.75 | -34% | 37% |
| Alpha - Den Difference | -0.80 | -0.99 | -35% | 35% |

March to Sept 2008 measurements only

- Denuders
 - flow checks to two separate mass flow devices
 - Lab blanks and travel blanks are clean
 - 2 sequential denuders; no breakthrough to 2nd denuder
 - Agree with monitor (Nitrolux 200)
- Radiellos & Alphas
 - Generally agree
 - Limited observations, particularly for winter

Radiello Method Detection Limit

- With a two-week sample,
- Average lab blank of 0.014 mg/L
- Standard deviation of ± 0.016 mg/L, and
- Method Detection Limit = (L blank +2 std)

Method Detection Limit of 0.15 ppbv NH_3

Summary

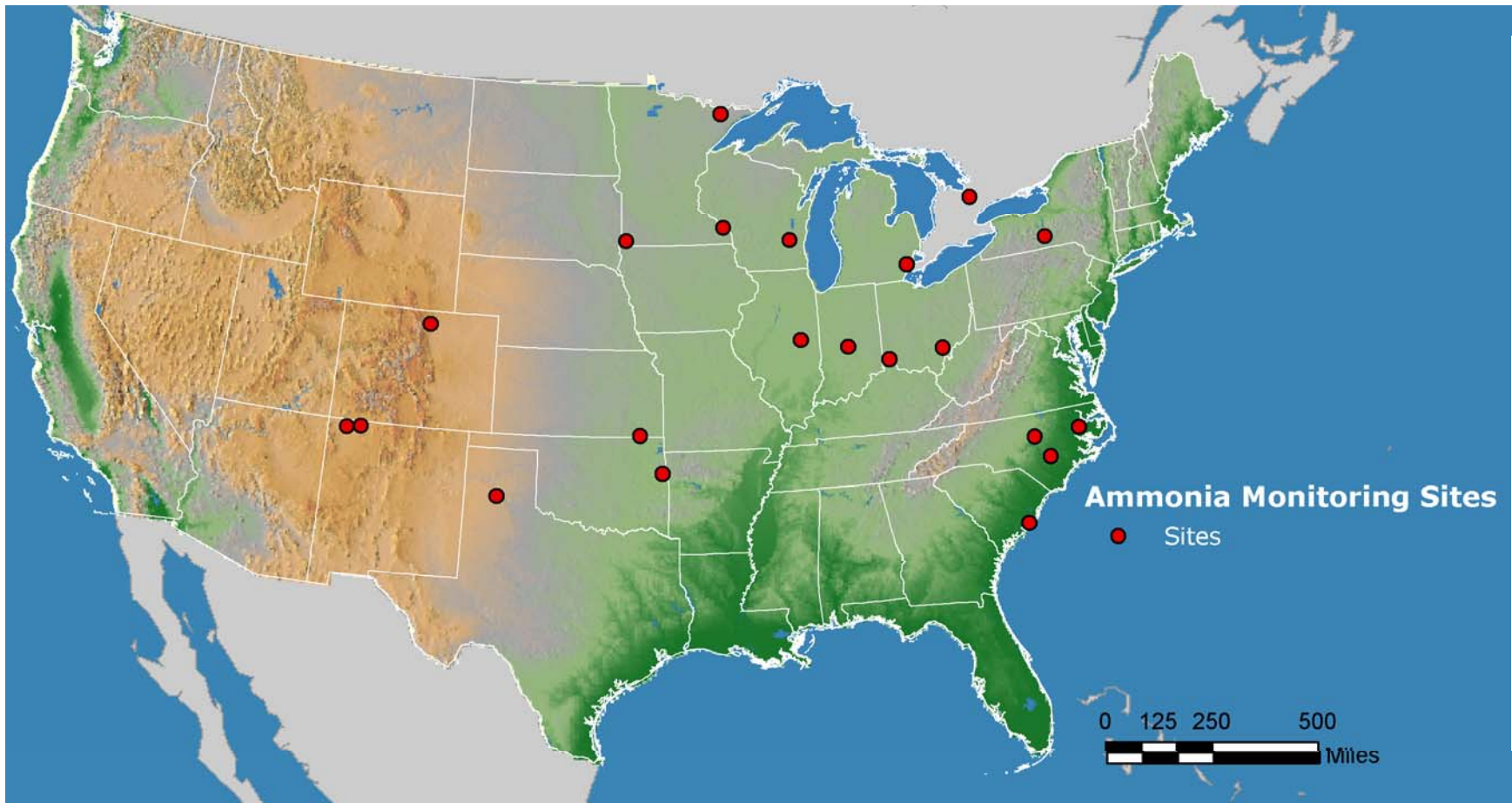
- Ogawa
 - No longer being considered
 - High variation within triplicates (wind orientation likely)
- Radiello
 - Generally good agreement with denuders
 - Relatively low bias
 - Low variation between replicates
 - Good blanks
 - Expensive!
- Alpha
 - Blanks seem to be as good as Radiello
 - Generally good agreement with denuders
 - Relatively low bias
 - Low variation between replicates
 - LOW cost
 - Considering for adoptions

Ammonia Monitoring Network (AMoN)

- 21 Sites operating (as of Sep 2008)
- Two-week samples in triplicate
- Radiello Sampler
- Sampling began Oct 30, 2008
- 393 triplicate measurements (9/2/08)



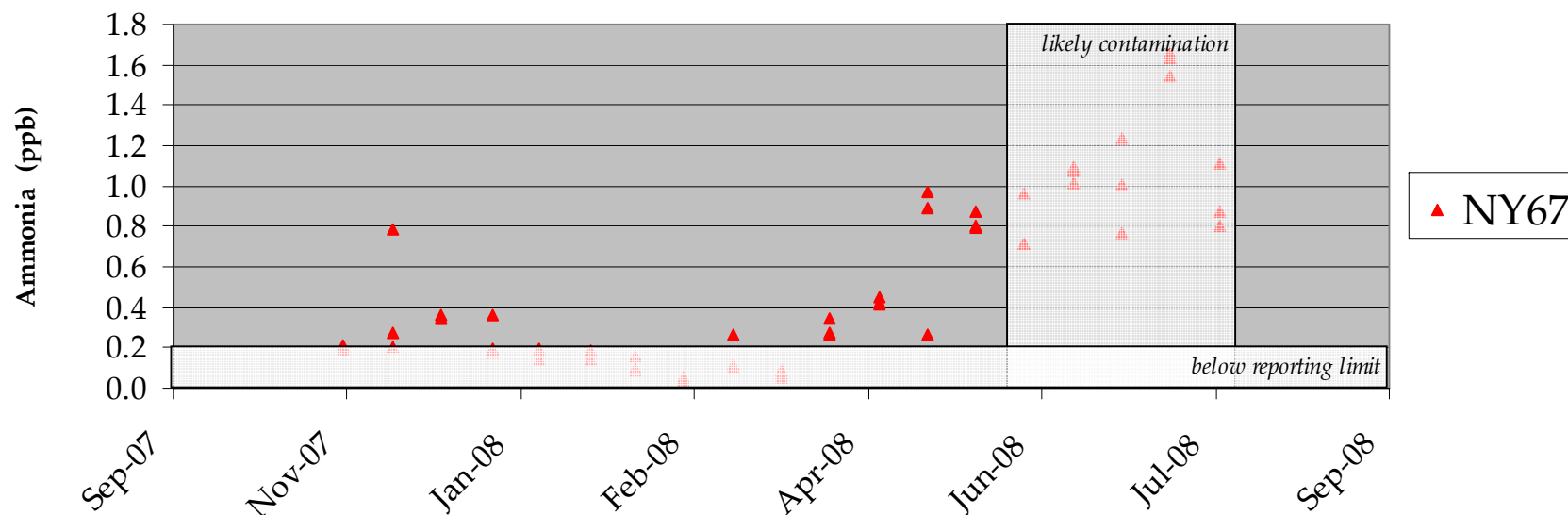
Network Sites



- Measurement Results
 - General stats
 - Max, min, etc overall sites
 - Time lines by site or state or region

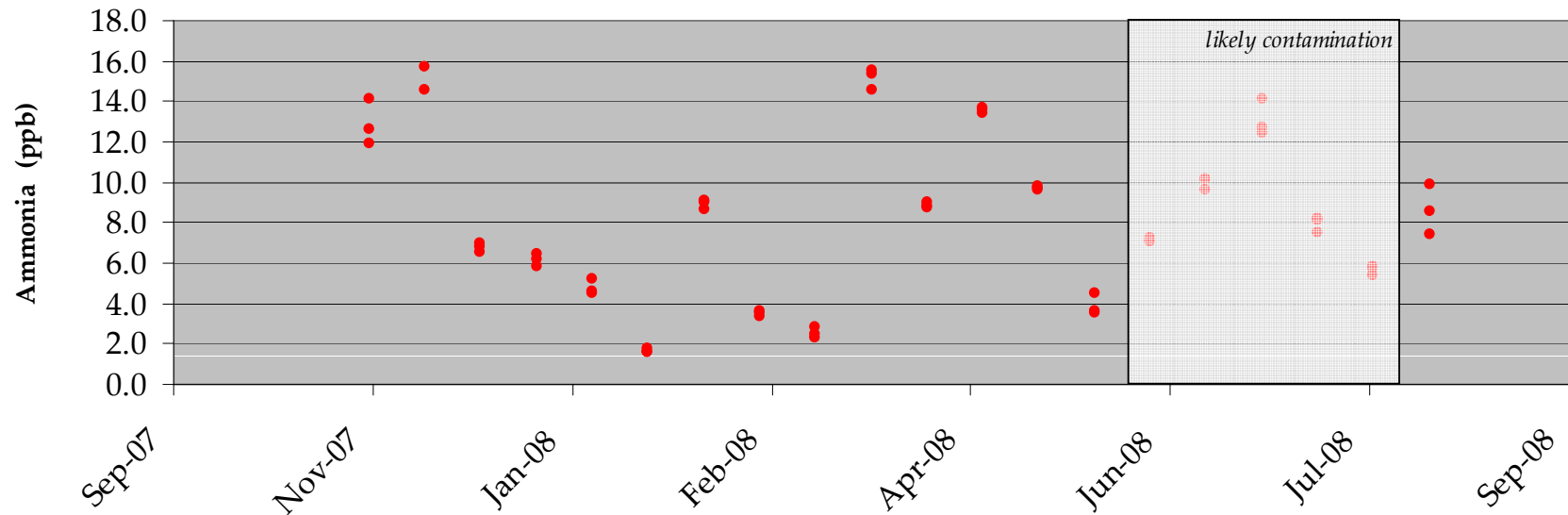
- Median, range max min weekly standev about mean, n=

Concentrations: New York 67 (Connecticut Hill)



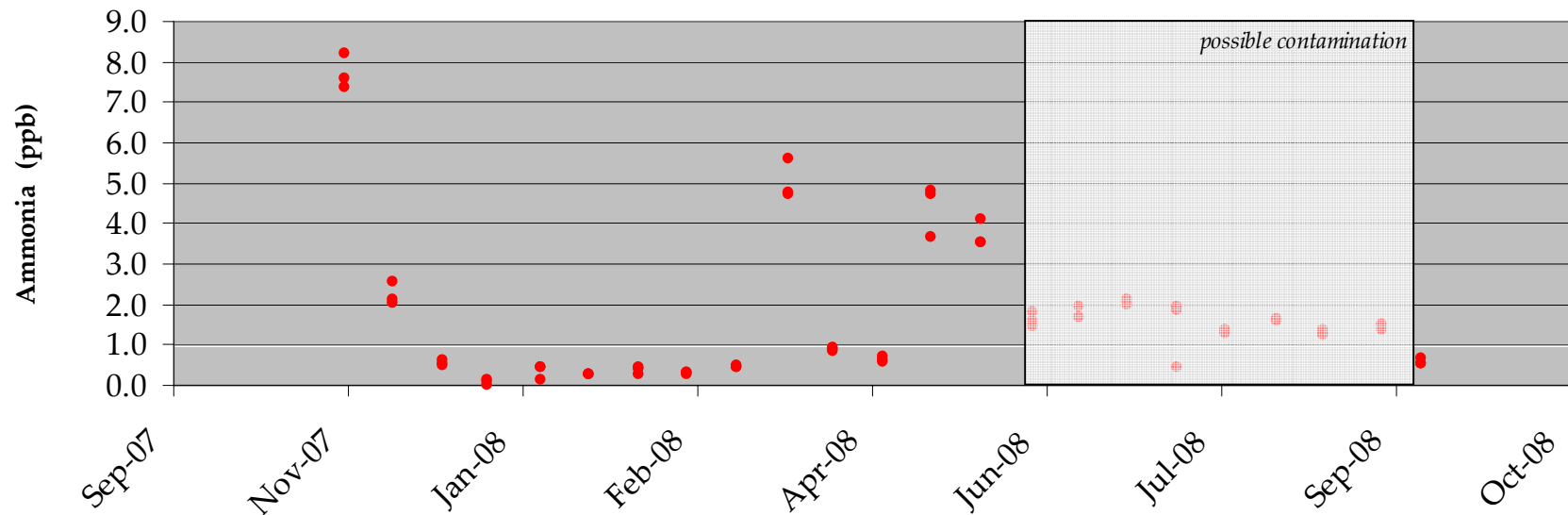
| | |
|---------------|------|
| Median | 0.34 |
| 95 Perc | 1.30 |
| 5th Perc | 0.06 |
| Maximum | 1.66 |
| Minimum | 0.03 |
| Average | 0.50 |
| St. Deviation | 0.44 |

Concentrations: Kansas 24 (Coffeeville)



| | |
|---------------|-------|
| Median | 8.12 |
| 95 Perc | 14.68 |
| 5th Perc | 2.24 |
| Maximum | 15.68 |
| Minimum | 1.57 |
| Average | 8.18 |
| St. Deviation | 3.98 |

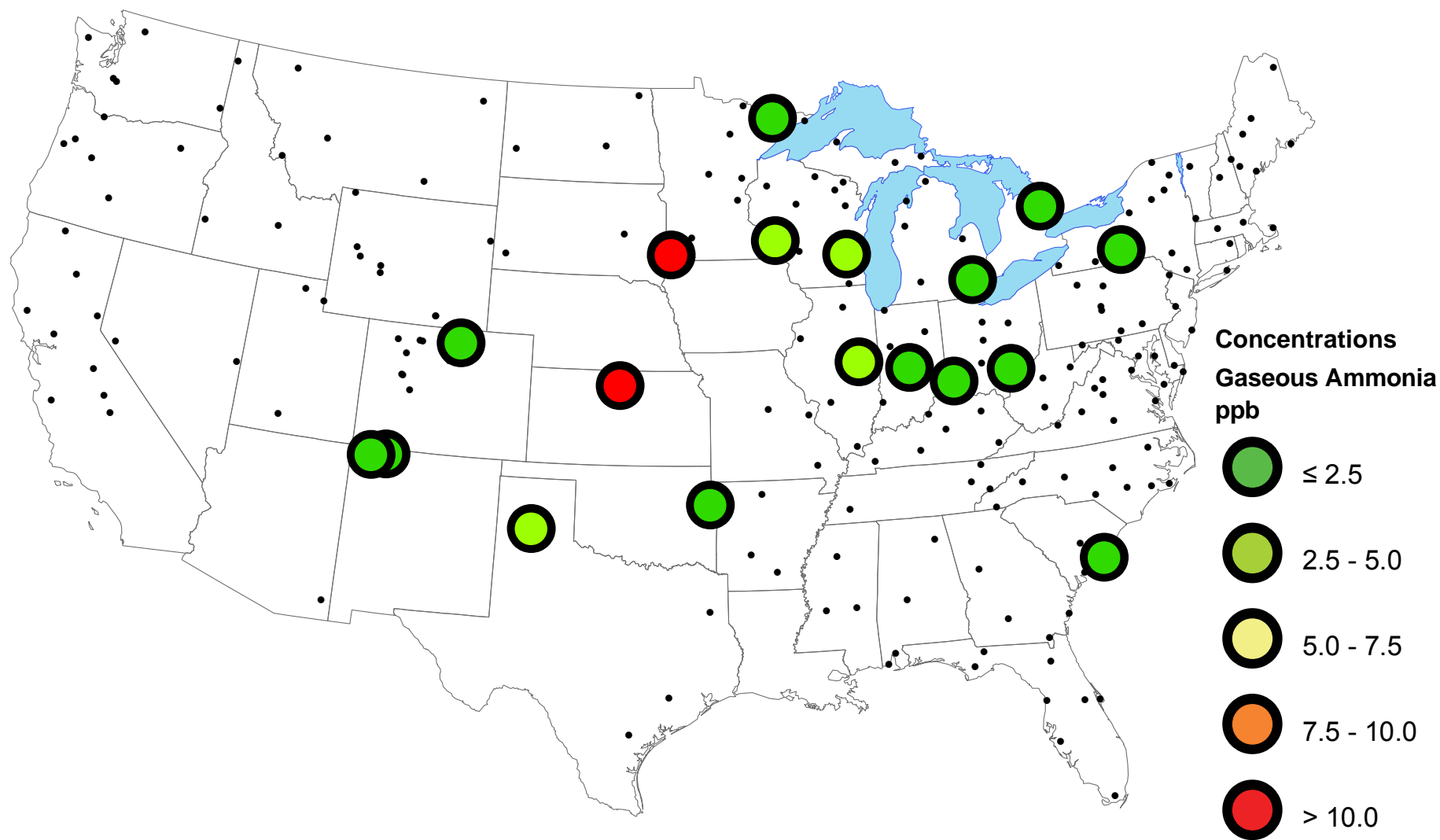
Concentrations: Illinois 11 (Bondville)



| | |
|---------------|------|
| Median | 1.35 |
| 95 Perc | 5.29 |
| 5th Perc | 0.19 |
| Maximum | 8.19 |
| Minimum | 0.00 |
| Average | 1.74 |
| St. Deviation | 1.84 |

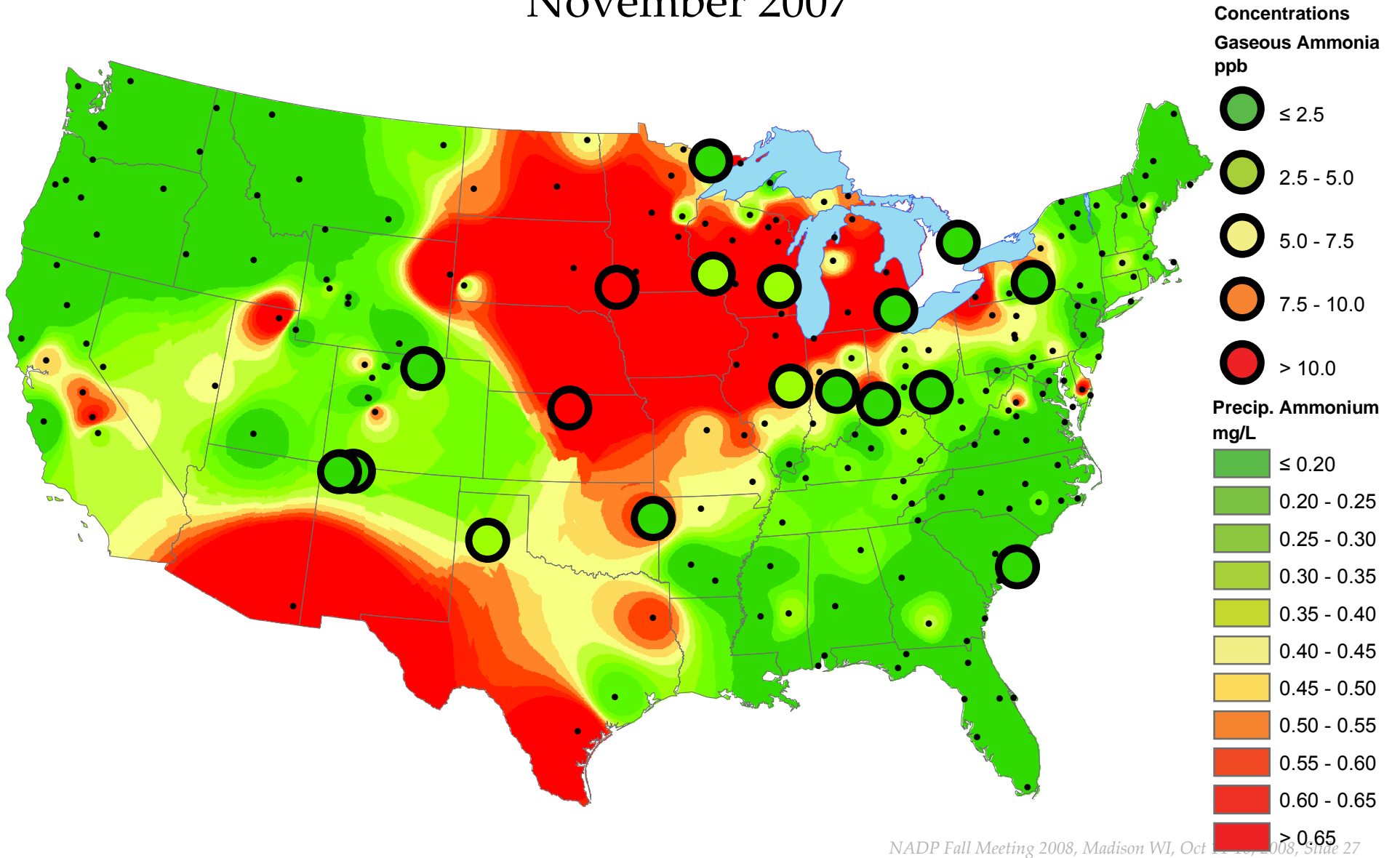
Fall Concentrations

November 2007



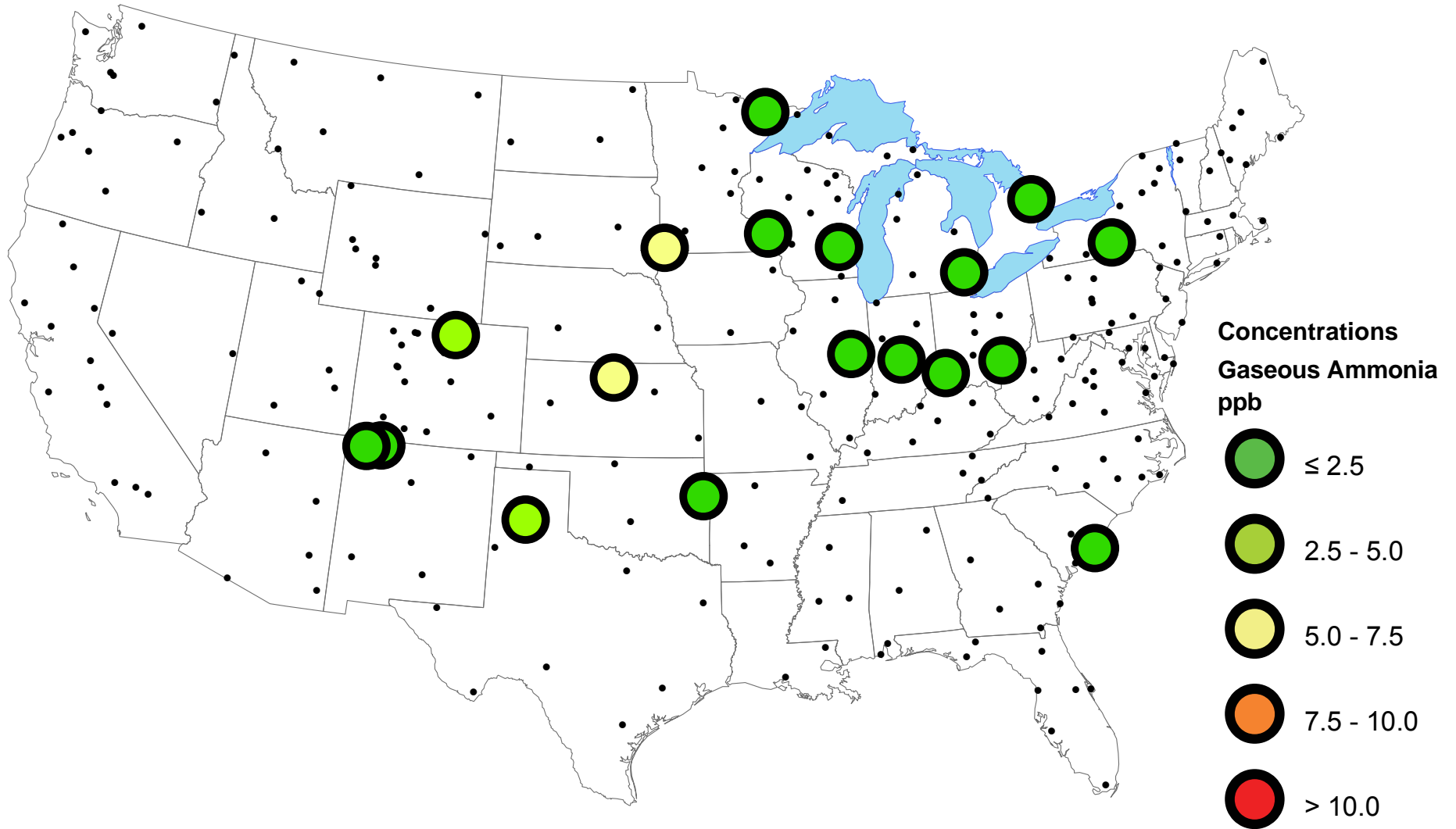
Fall Concentrations

November 2007



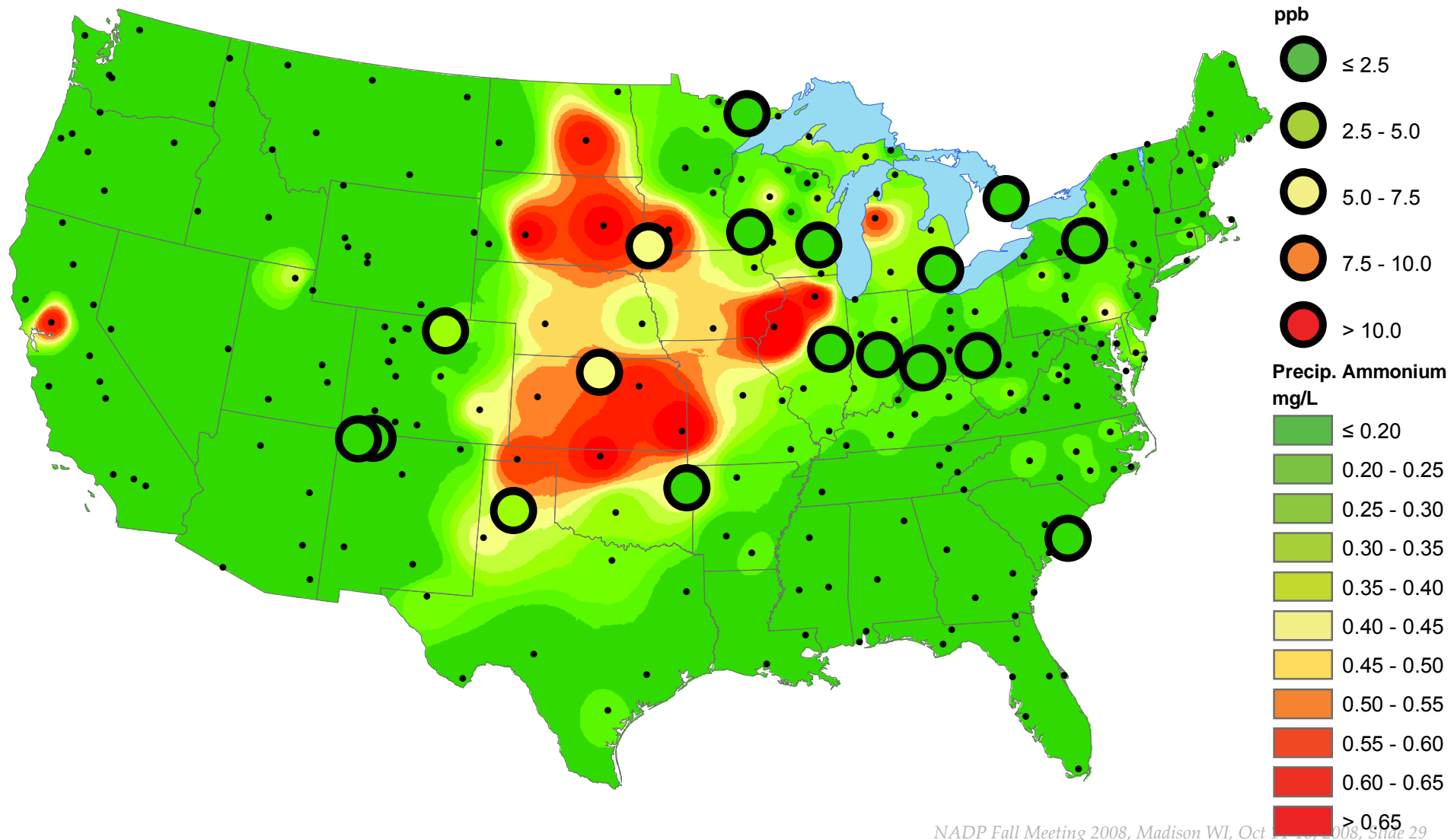
Winter Concentrations

December 2007 – February 2008



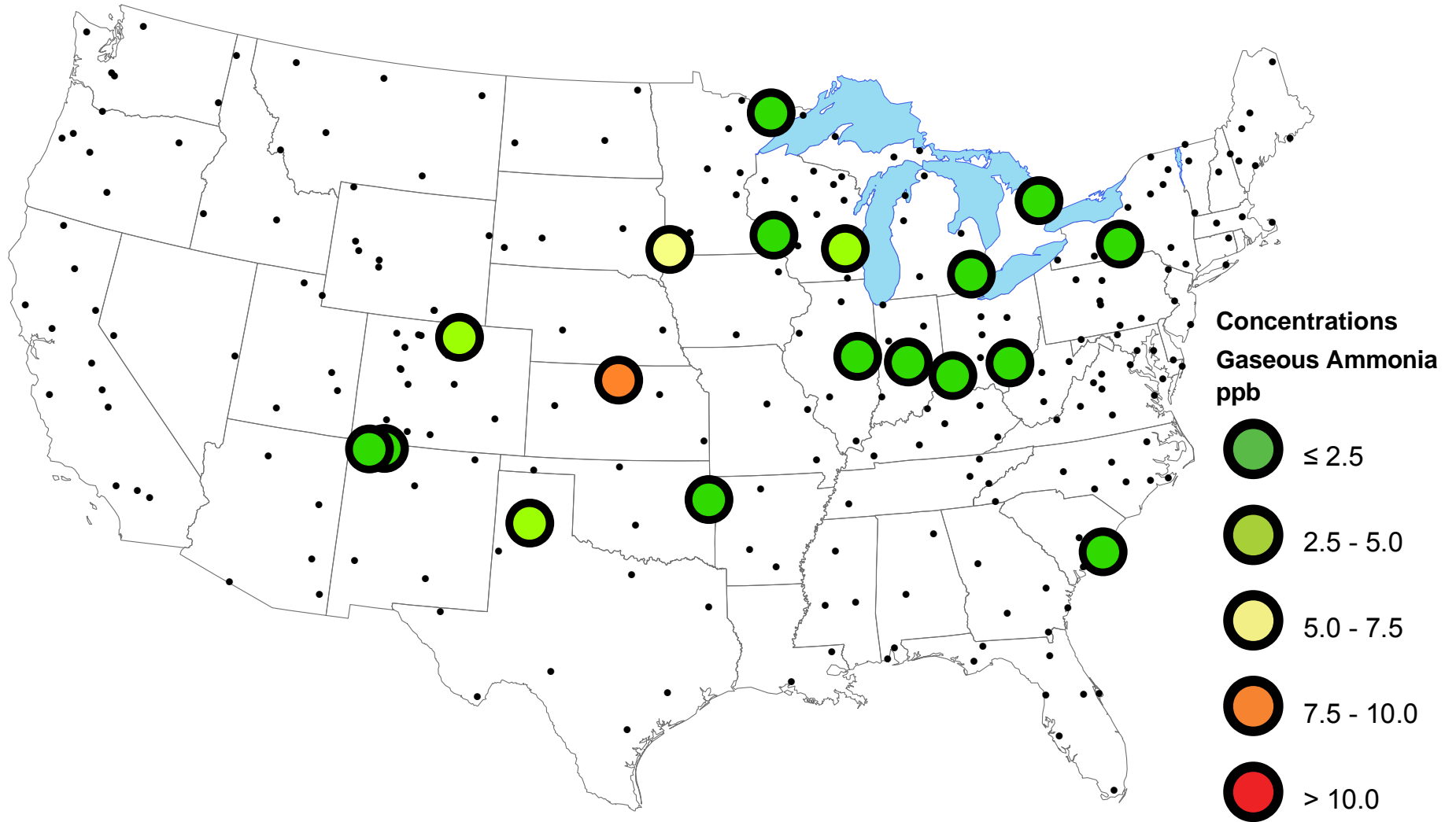
Winter Concentrations

December 2007 – February 2008



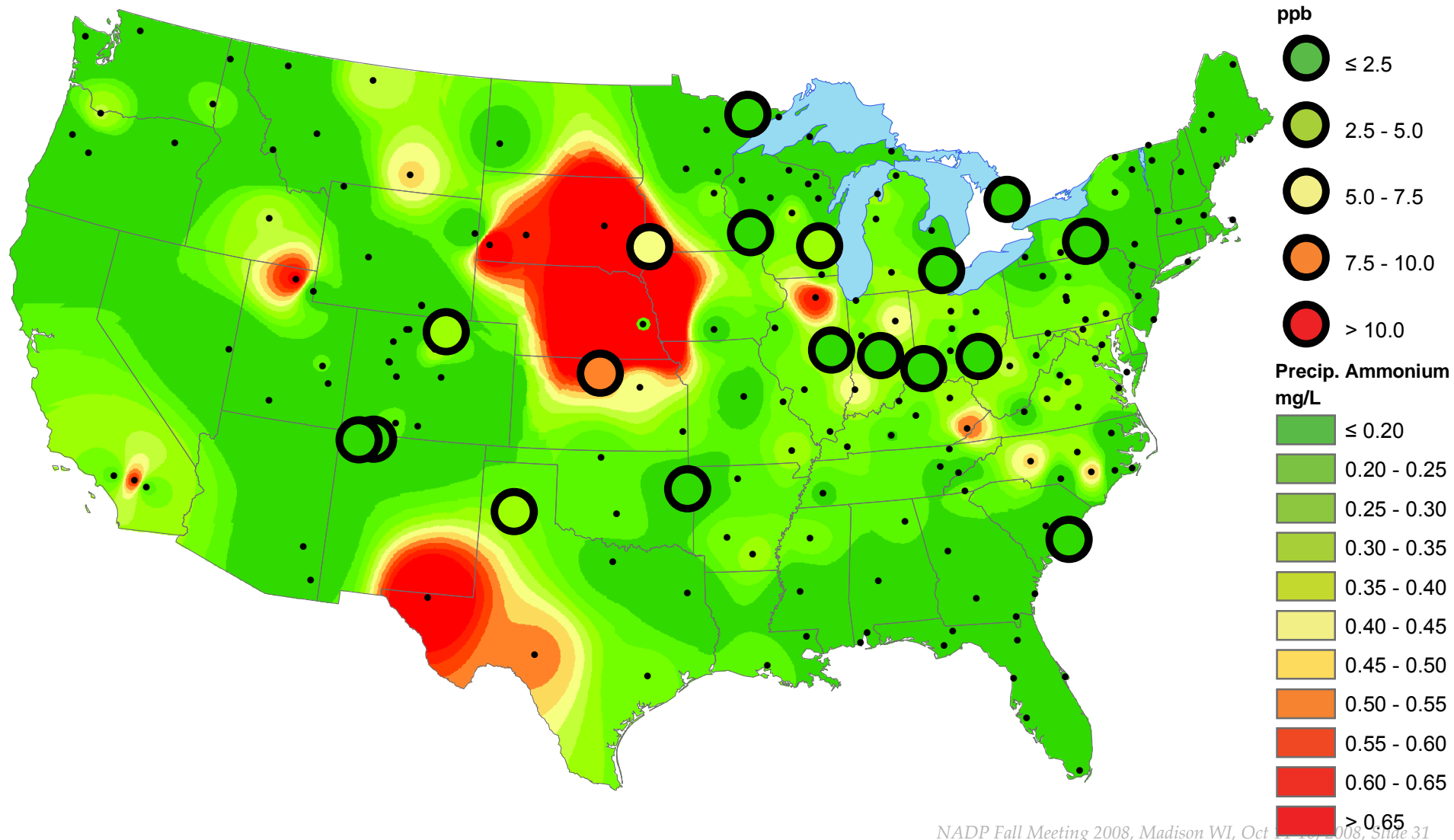
Spring Concentrations

March 2008 – May 2008



Spring Concentrations

March 2008 – May 2008



Next Steps

- Funding through October 2009
 - Seek additional sponsors
 - Reduce costs of Radiellos
 - Determine optimum number of replicates
 - Decision on elimination by January 2009
- Field blank corrections
 - Still too much contamination
 - Goal: 0.2 ppbv correction (limit)
 - Prep, removal, analysis all in one hood
 - New glass shipping tubes (into ISWS next week)

Next Steps

- Additional denuder comparisons
 - NC sites
 - Environment Canada
- Additional alphas at CO and TX sites
- Make preliminary data available by January 2009
- Meeting of interested parties
 - Thursday afternoon
 - NADP Spring 2009

Acknowledgements

- Additional financial support from the Lake Michigan Air Directors Consortium (LADCO), Chicago IL