EPA's Collaborative Efforts for Ammonia Monitoring in the U.S.

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Overview

- Ambient NH_3 concentrations are increasing with limited knowledge of:
  - Trends
  - Regional variability
  - Seasonality
  - Deposition fluxes
- Gaseous (free) NH_3 concentrations may increase with decreasing SO_2 and NO_x emissions (less aerosol to neutralize) but dry deposition of NH_3 is still not accounted for by monitoring networks

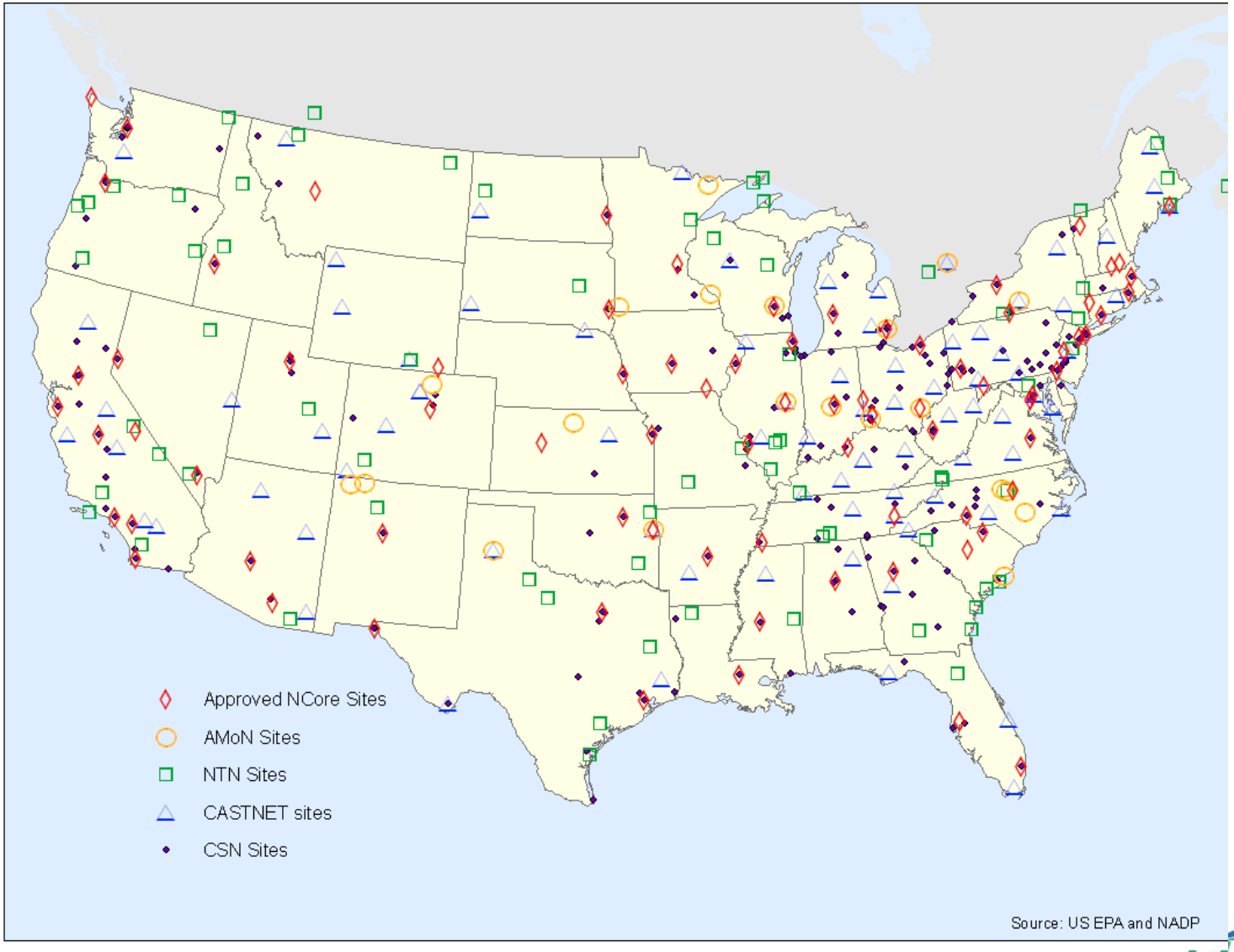
Need for Ammonia Monitoring

- Model development
  - CMAQ development – high temporal and spatial resolution
  - Model validation for ammonia deposition
  - Ecological model development – eutrophication from NH_3 deposition
- $PM_{2.5}$ NAAQS and $PM_{2.5}$ emissions reductions required under new regulation (CAIR replacement rule??)
  - NH_3 is a basic component of particle formation for a significant fraction of $PM_{2.5}$ mass
  - Assessment of programs
  - Changes in fine particle composition

CAMD Participation in Ammonia Monitoring Efforts

- Existing monitoring networks used in ammonia monitoring equipment QA and development
  - CASTNET currently measures NO_3^-, HNO_3, NH_4^+
  - NADP wet deposition measurements (NH_4^+, NO_3^-)
  - CSN/NCore (NH_4^+/NO_3^-, NO_y, NO_x)
- Collaborative efforts between EPA divisions, NADP and Colorado State University (CSU) to develop new tools for ammonia monitoring
  - Passive and active sampling systems being explored

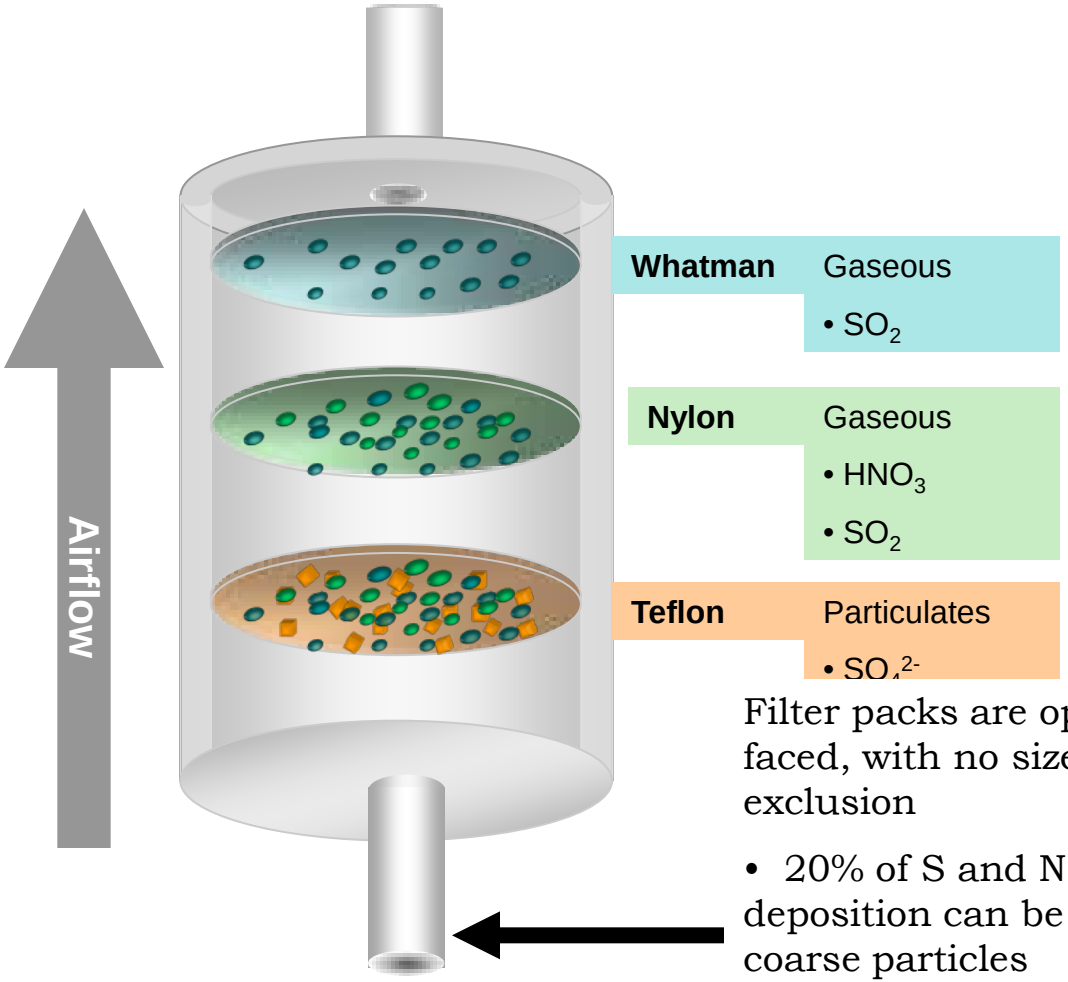
Existing Network Infrastructure



Clean Air Status and Trends Network (CASTNET)

- Long-term monitoring network developed to assess regional trends in pollutant concentrations and dry deposition
- 87 site locations in rural areas including National Parks and Class One areas
- Many sites have been in operation for more than 15 years
- Dry deposition estimates

CASTNET 3-Stage Filter pack



Filter packs are open-faced, with no size exclusion

- 20% of S and N deposition can be from coarse particles
- HNO_3 reacts with inlets

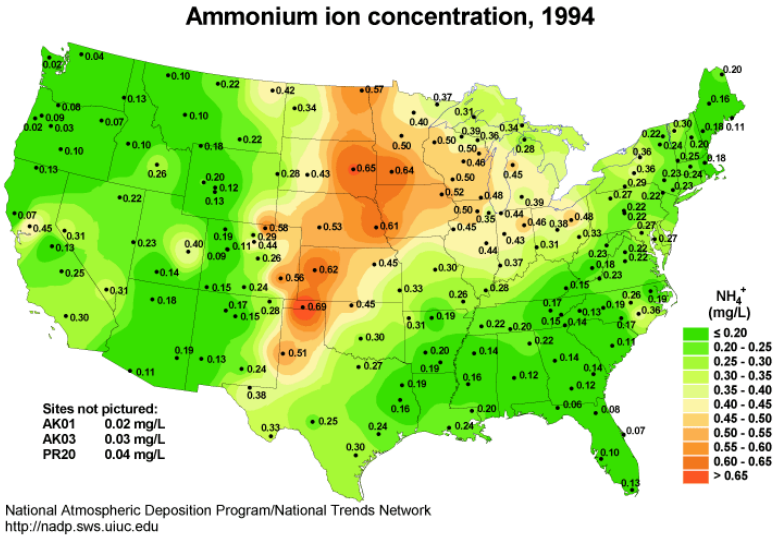
Gas and particle concentrations in air are measured by filter packs and then used to estimate daily dry deposition

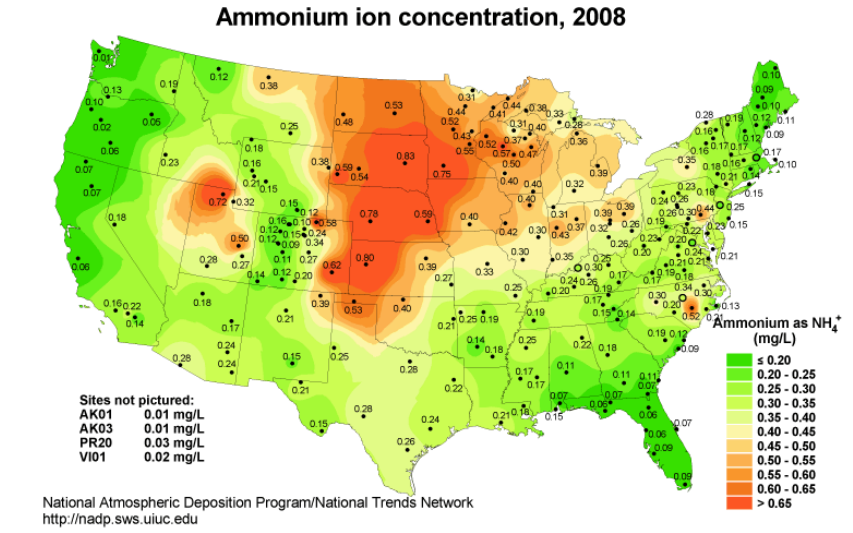
CASTNET 4-Stage Filter pack

- CASTNET workshop held in RTP, NC in August to utilize the current infrastructure to meet future monitoring needs
- One consensus recommendation from the workshop – add a phosphorous acid coated cellulose filter to capture volatilized NH_3 from NH_4NO_3 captured on the Teflon filter

National Atmospheric Deposition Network (NADP)

- Long-term wet deposition monitoring since 1978
- Weekly precipitation samples from over 250 sites analyzed for pH, SO_4^{2-}, NO_3^-, NH_4^+, Cl^- and base cations
- Increasing NH_4^+ measured in precipitation especially in the Midwest





Chemical Speciation Network (CSN)

- 192 Sites
- The Met One Super SASS™ has 8 channels allowing for varied combinations and sequential sampling
- $PM_{2.5}$ gravimetric mass
- $PM_{2.5}$ speciation
- New NH_3 denuder of the Super SASS™ would fit into existing structure

CAMD's collaborative efforts to develop NH_3 monitoring methods

- MARGA
  - Speciated multi-pollutant hourly measurements at RTP (CAMD/ORD) in the testing/development phase
- Met One Super SASS™
  - Daily denuder measurements in the testing phase. Jeff Collett (CSU) is working with OAQPS and CAMD to meet the requirements needed to deploy the denuders in the CSN network
- AMoN
  - NADP's passive ammonia monitoring network pilot project. Collaboration between NADP, CAMD, ORD, states, LADCO, etc.

Super SASS™ Design for Measuring NH_3

- Miniature-parallel plate denuders to capture sample with enough room for filter cassettes under the bucket
- Comparison with ADS in CSU laboratory showed a 95% collection efficiency for NH_3

(Development/Initial Analysis by Dr. Susanne Herring (Aerosol Dynamics, Inc.) & Professor Jeffrey L. Collett, Jr. (CSU)

Super SASS™ NH_3 Denuder Deployment

- Following acceptance testing, OAQPS will deploy Super SASS in the CSN
- CSN sites will be selected based on:
  - Collocation with other networks – CASTNET, NADP, or IMPROVE
  - Collocation with other passive, continuous or active NH_3 monitoring
  - Future NCore site
  - Willing state, Tribe or local agency

Passive Ammonia Monitoring

- US Canada workshop (Chicago, 2007) on ammonia: participants came to a consensus on:
  - The need for ammonia monitoring
  - NADP should be the coordinating body
  - Passives should be explored
  - Long-term network is preferred
  - Widespread participation between agencies, states, Tribes and organizations is necessary

Pros and Cons of Passive Samplers

- Pros
  - No pumps required
  - No power source required
  - Inexpensive
  - Not prone to breakage during shipping and handling
  - Ease of operation and set-up
- Cons
  - Annular denuders provide 24-hour samples while passives need to be exposed for 1-2 weeks or longer

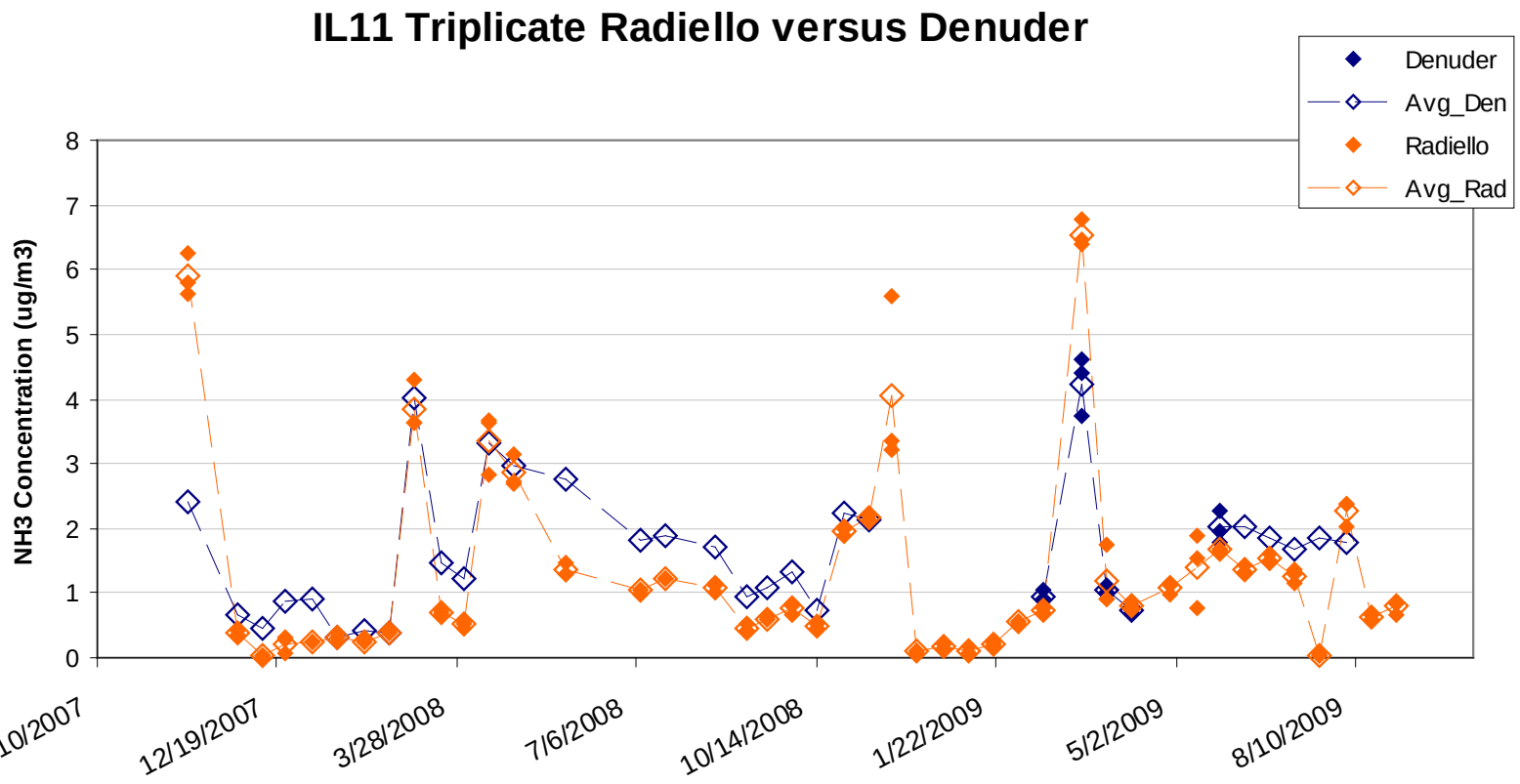
Precision and Accuracy

The good, the bad and the ugly….

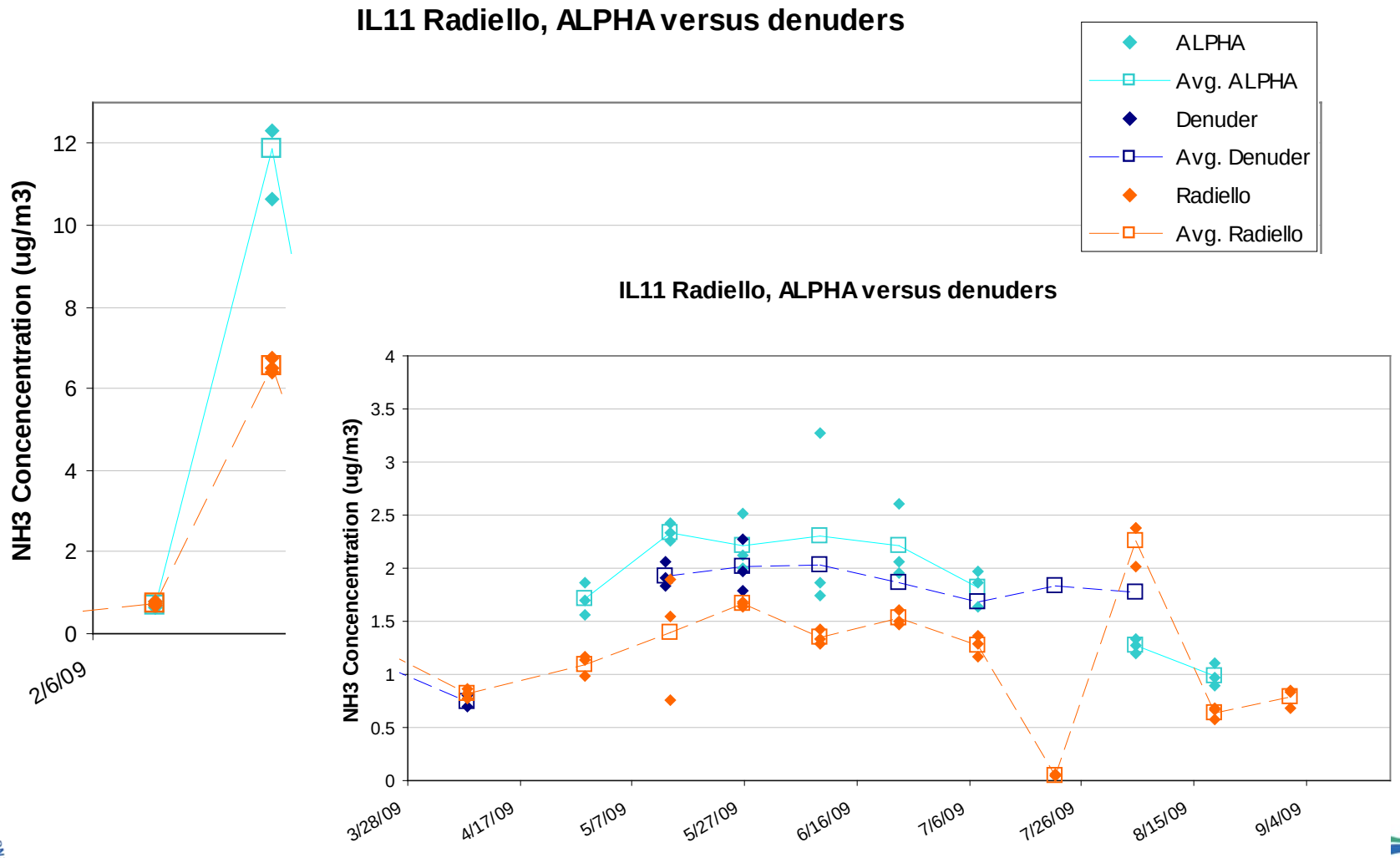
Sampler	Radiello	Adapted Low-cost Passive High-Absorption (ALPHA)**	Denuder***
Accuracy (Median ARPD)*	20.8%	17.4%	-
Precision (CV)**	6.8%	10.0%	8.8%

*Accuracy from IL11 & OK99.
**Results from 5 site inter-comparison study (5/09-7/09) at IL11, OK99, NC35, NY67 and TX43.
***Denuders were run in triplicate at IL11 to compare precision of ADS to passive samplers.

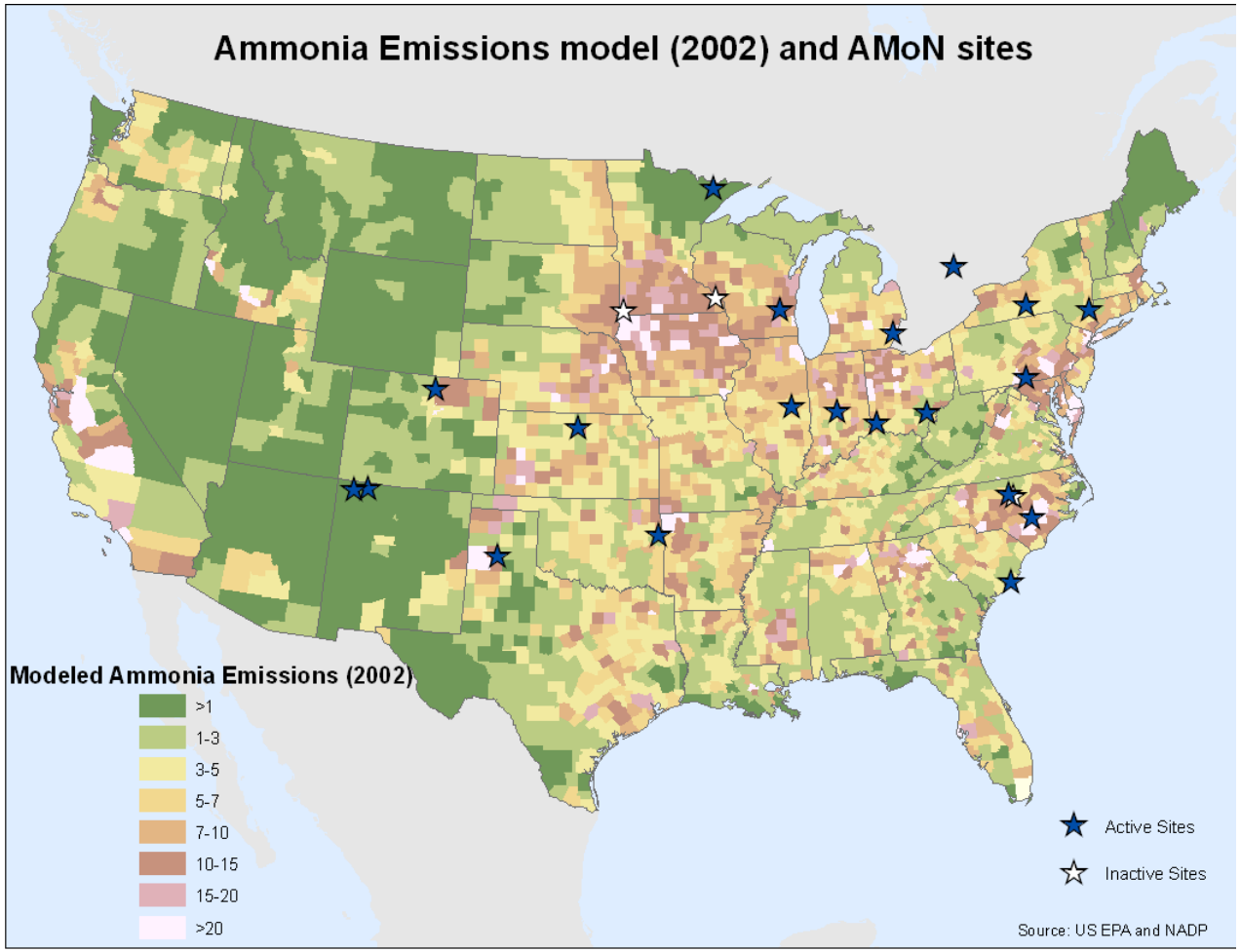
Accuracy & Precision: Radiellos



Accuracy & Precision: ALPHAs



Ammonia Monitoring Network (AMoN)

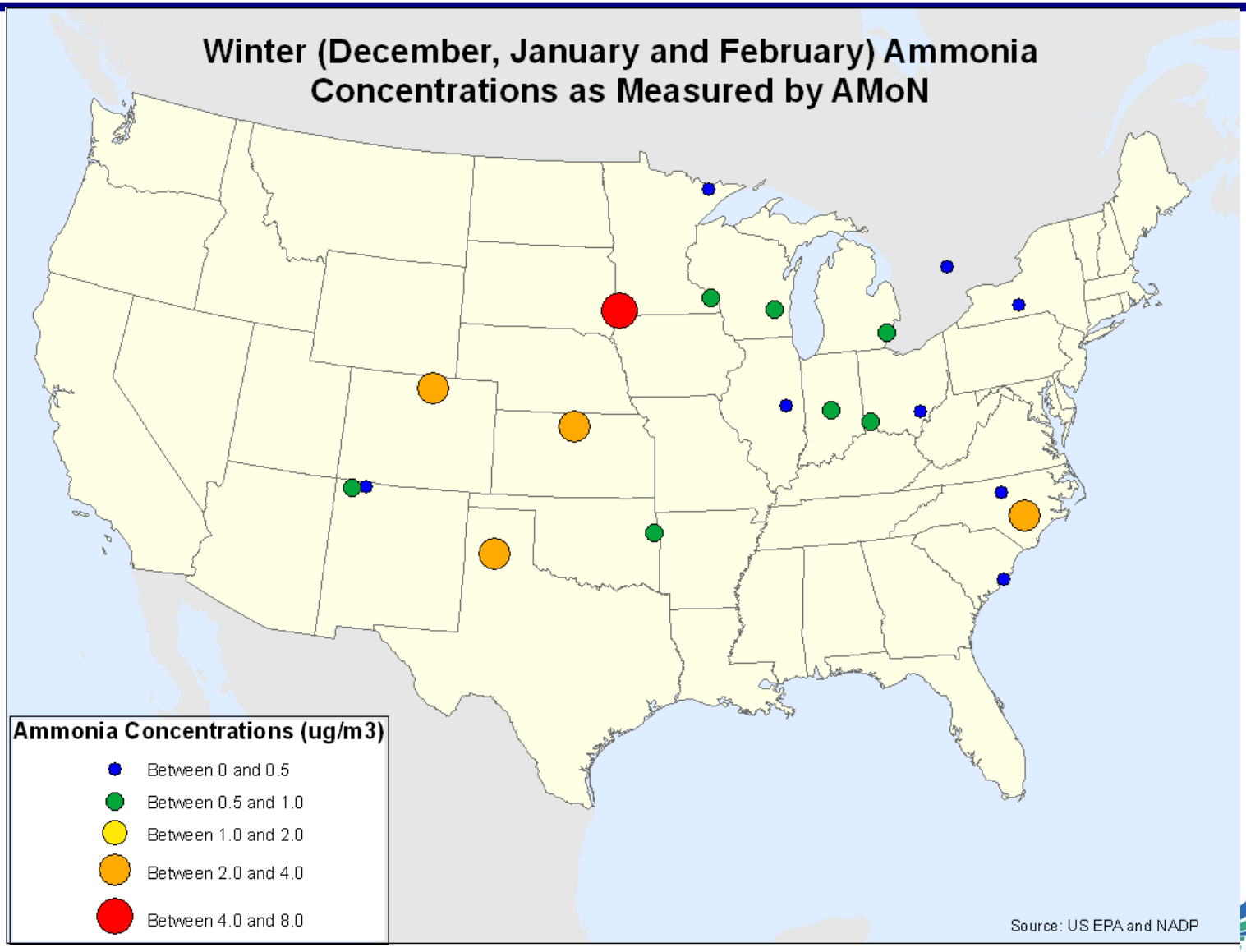


20 NADP sites across the US located in regions with high NH_3 emissions (modeled)

AMoN Network Operation

- Radiello passive samplers run in triplicate for precision measurements
- Two-week samples (and travel blank) are sent to ISWS CAL for analysis
- Concentration data is posted on the NADP AMoN website for users to download (http://nadp.sws.uiuc.edu/nh3net/)

Seasonal NH_3 Concentrations



AMoN Participation

- Additional partners can enter cooperative agreement with NADP Program Office
- NADP's Central Analytical Laboratory will ship samplers every two weeks and analyze samples
- Program Office will QA and post the data on the NADP website

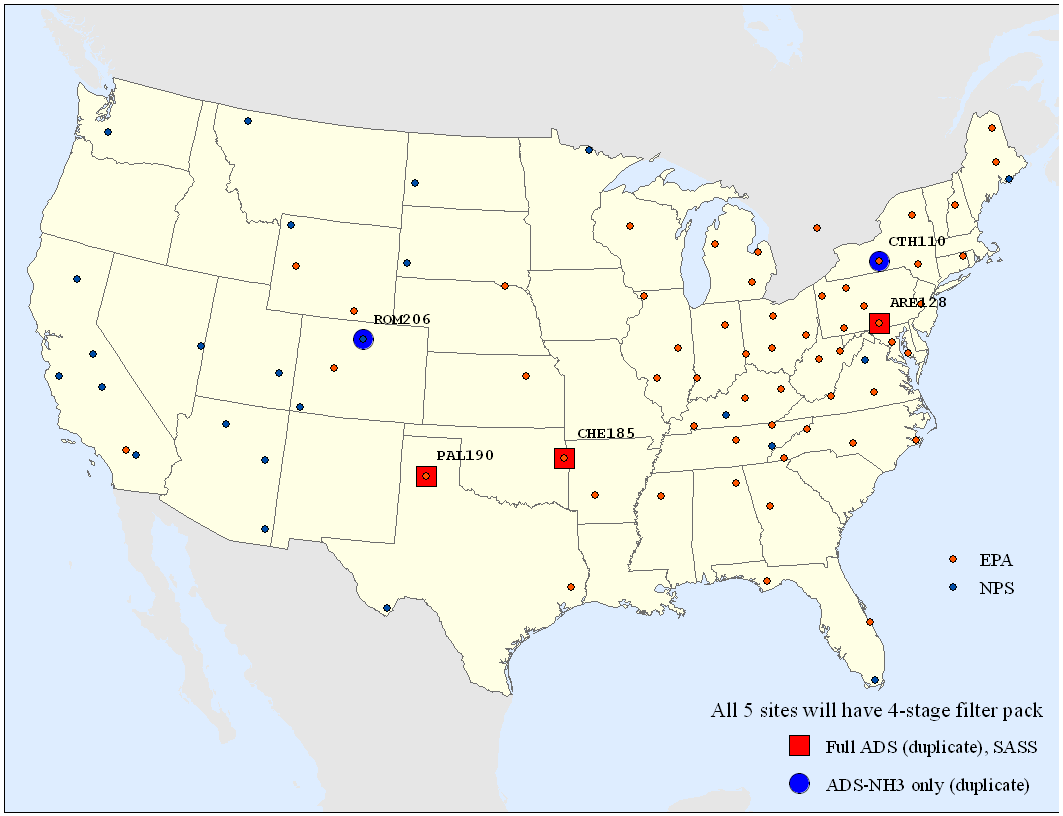
Conclusion

- What do we know now? Not much.
- Will the Super SASS™ NH_3 denuders have a 95% collection efficiency in the field?
- Can we add a 4^{th} filter to the CASTNET filter pack without creating a bias in other pollutants we currently capture?
- Travel blanks?
- Elevation sites?

NH_3 Monitor Inter-comparison Study

- Support from EPA (OAQPS, ORD, CAMD) w/ Mactec as contractor
- 5 sites with triplicate Radiello samplers (AMoN sites)
- 3 sites with Super SASS™ + NH_3 denuders
- Annular denuders with 2-stage filter pack
  - NH_3-only
  - NH_3, HNO_3, NO_3^-, NH_4^+
- 4th filter on CASTNET filter pack
- CASTNET 3-stage filter pack

Map and schedule



- CASTNET 3-stage filter will run on normal weekly schedule
- Passive samplers will run on normal 2 week schedule
- CASTNET 4-stage filter pack, ADS and SASS™ will run for 2 1 week samples every 6 weeks
- 1 year, nine 2-week sampling time periods

NH_3 Monitor Inter-comparison Study

- Final report to characterize:
  - CASTNET filter pack NH_3/NH_4^+
  - OAQPS will use results to look at Super SASS™ NH_3 mini parallel plate denuder
    - Precision
    - Accuracy
    - Adaptability in network
  - Elevated travel blanks or contaminations for phosphorous acid coated filters or denuders
  - Any NH_3 loss due to 1-week sample time for the Super SASS NH_3 denuders

Final thoughts

- Possibly have 3 networks providing ammonia concentration measurements in the future –
  - AMoN
  - CASTNET
  - CSN/NCore
- Not possible without collaborating with other EPA divisions, NADP, other organizations, States, Tribes and universities to support ambient ammonia monitoring development

Acknowledgements

- State of Pennsylvania
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