Ambient Ammonia Monitoring Initiative

NAAMC – 2009 – Nashville, TN
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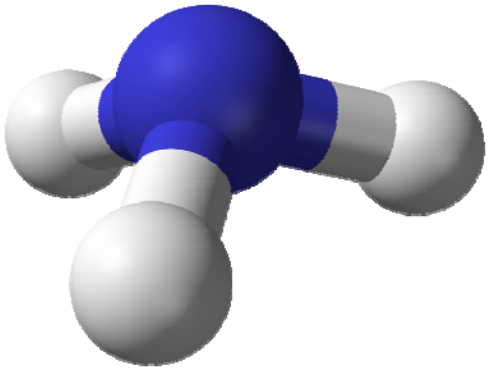
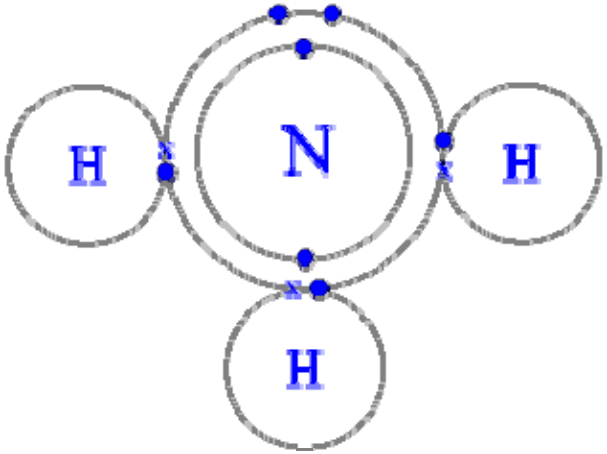




Overview

- Ambient NH_3 concentrations are increasing with limited knowledge of:
  - Trends
  - Regional variability
  - Seasonality
  - Deposition and emission 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 improvement 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 and can be a significant fraction of $PM_{2.5}$ mass
  - Assessment of programs
  - Changes in fine particle composition
- Support for Secondary NOx/SOx NAAQS?
  - EPA presentations to CASAC have indicated that total reactive nitrogen data (which includes NH_3) may be useful in determining atmospheric factors that inform whether a future standard may be met

Need for Ammonia Monitoring (cont.)

- Science Advisory Board (SAB) comments on importance of ammonia
  - NO_Y, NH_X (ammonia + ammonium), and N_2O are all components of reactive nitrogen
  - "…one needs to know both the present reactive nitrogen concentration or loading within a reservoir and the threshold at which negative impacts are manifested."
  - "Monitor NH_3, NH_X, NO_Y, NO_2, NO, and PAN, measure or infer deposition, and support the development of new measurement and monitoring methods."
  - Reference: SAB Discussion of draft report "Reactive Nitrogen in the United States"

Monitoring Methods

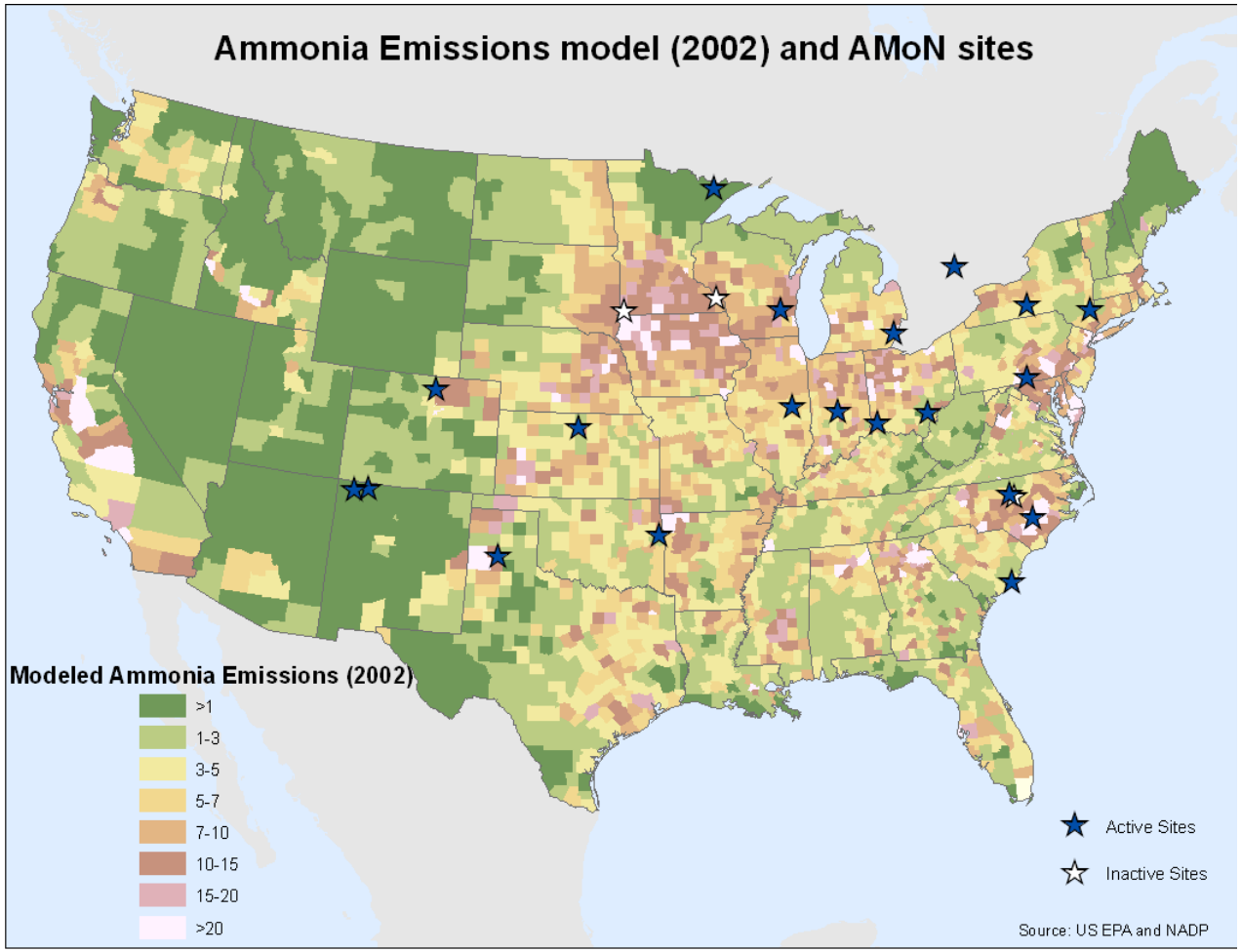
- There are three primary approaches to monitoring ambient NH_3:
  - Passive devices
    - Multiple models in use and evaluated
    - Only provide 1 or 2 week integrated values
  - Integrated methods (Denuders)
    - Annular & new parallel plate versions available
    - Provide shorter integrated period data
  - Continuous methods
    - Multiple methods (photo-acoustic, TDLs, cavity ring-down, on-board IC (wet chemistry), etc)
    - Some methods do not have low enough detection limits
    - Others are not mature enough for routine monitoring
    - Sample train interferences need to be addressed

Who's doing what?

- National Acid Deposition Program (NADP) is operating the Ammonia Monitoring network (AMoN) pilot
  - Utilizes passive methods (currently using Radiello)
- Region 6 – Evaluated Ogawa passive samplers in "Four Corners Study"
- CAMNet – Using ALPHA passive devices, ORD supports validation of Tropospheric Emissions Spectrometer measurement of NH_3
- OAQPS, OAP-CAMD, and ORD are involved with furthering the use or understanding of all three monitoring methods

➢ Low hanging fruit for establishing monitoring in our routine networks is the use of passive or integrated methods

Ammonia Monitoring Network (AMoN) - Pilot



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

Source:http://nadp.sws.uiuc.edu/nh3net/

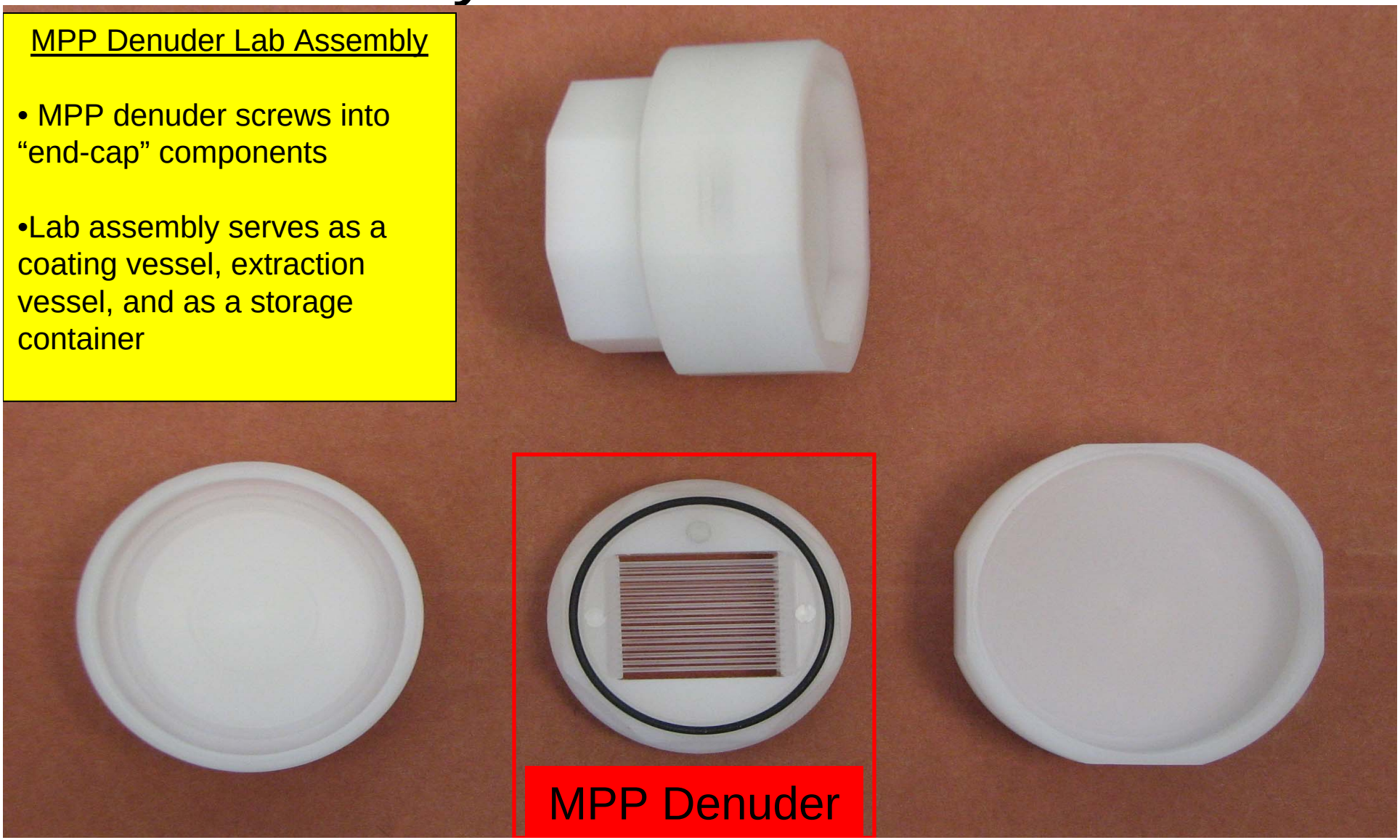
Ambient Ammonia Monitoring Initiative for the CSN

- OAQPS wanted to move forward in an effort to identify a method that was efficient, economical, and easy to insert into the existing CSN logistical infrastructure
- We considered:
  - Passives: Because they don't require much infrastructure,
    - However, they have long averaging periods
  - Annular denuders: Are well characterized
    - However, implementation would require new sampling hardware and there are concerns with denuder breakage in shipment
  - SASS honeycomb denuders
    - However, their aluminum alloy composition posed too many unknowns: phosphorous (or other) acid coating interactions, sample extraction, and subsequent IC results
- Therefore, we moved forward on developing a novel denuder designed to fit in existing CSN infrastructure

Mini Parallel Plate (MPP) Denuder

- OAQPS, OAP-CAMD, and ORD collaborated with Colorado State Univ. (CSU), Aerosol Dynamics, and MetOne to create a novel denuder to fit in the CSN's SASS units
- New design is compact, using etched quartz as substrate, fitting in existing SASS filter modules
- Substrate coating: Phosphorous Acid (5%)
- Will be coupled with a PTFE (Teflon) coated $PM_{2.5}$ cyclone

Anatomy of the MPP Denuder



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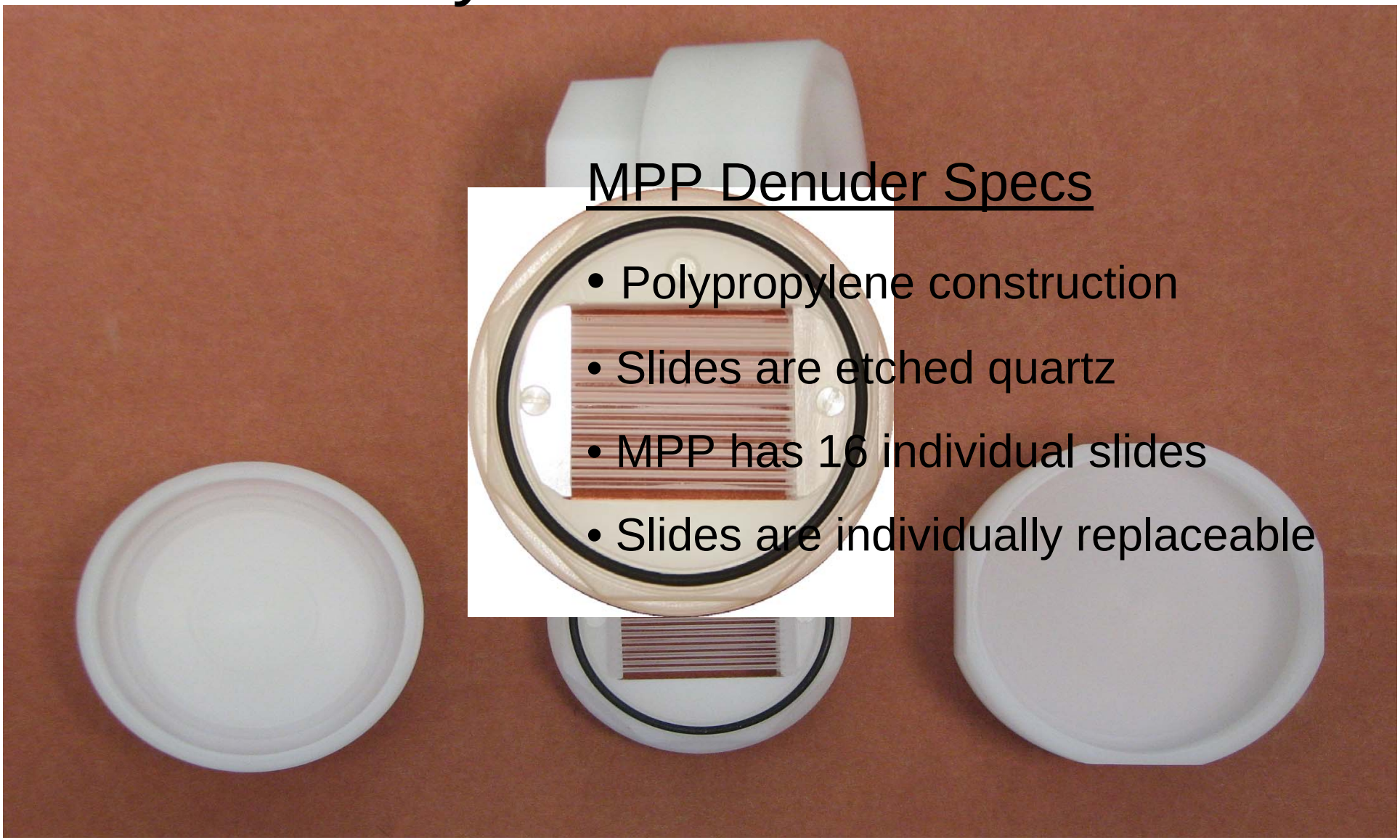


MPP Denuder Specs

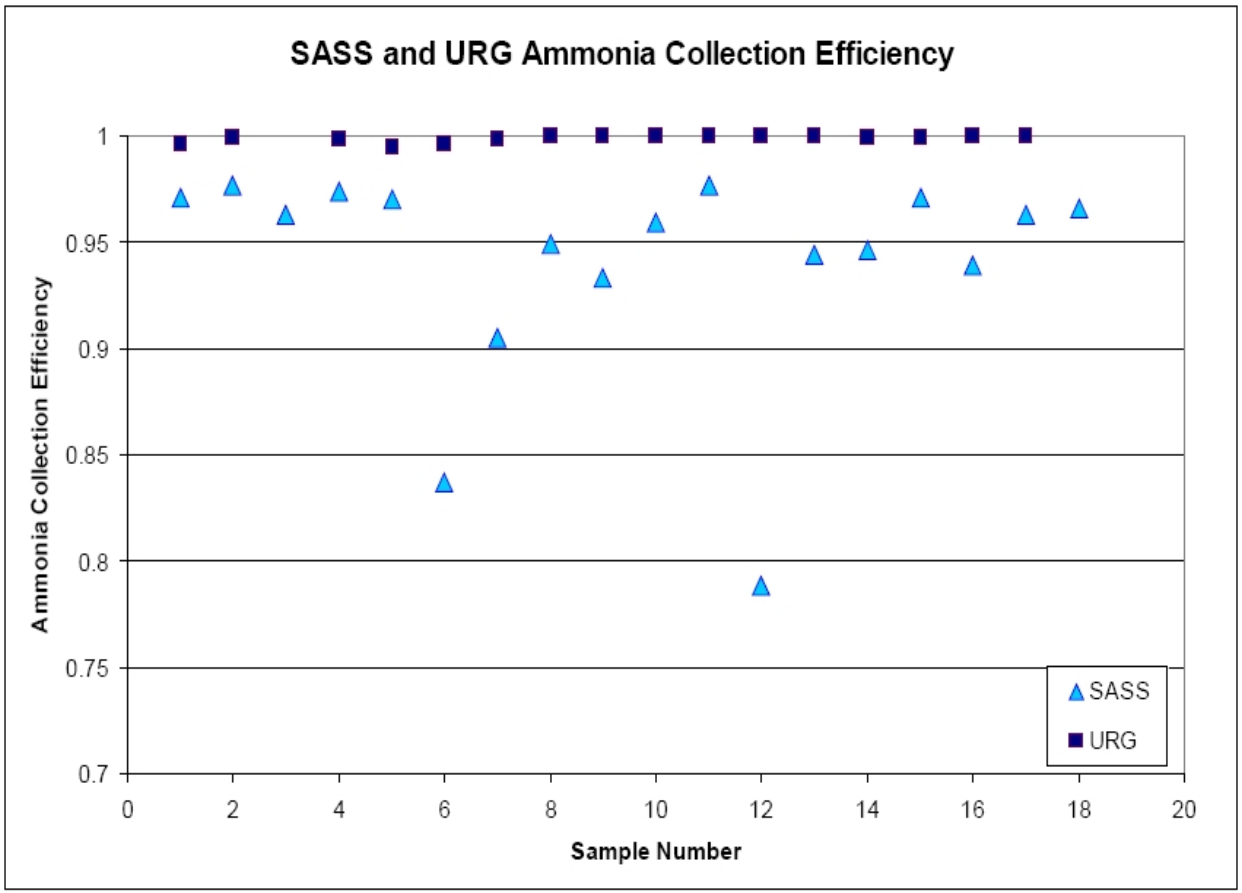
- Polypropylene construction
- Slides are etched quartz
- MPP has 16 individual slides
- Slides are individually replaceable

SASS Module Assembly

Teflon coated SSC

- Necessary to reduce NH3 loss while removing PM

Initial Evaluation of the MPP Denuder



CSU collection efficiency tests:
MPP prototype vs. URG
Source: J. Collett & M. Schurman, CSU

- CSU did initial evaluations to determine feasibility and characterization
- Collection efficiencies were good, vs. URG: 94.08% vs 99.89%
- Outliers are suspected to be due to handling
- Lab handling will be optimized and standardized

Next Steps

- Ammonia methods inter-comparison study
- In-house EPA chamber characterization
- Laboratory handling and procedure (SOP) and/or best practices development
- CSN Pilot

Ammonia Inter-Comparison Study

- ORD & OAP-CAMD managing, OAQPS supporting, MACTEC contracted support
- Year long evaluation, beginning winter 2009, with nine 2-week sampling periods
- 5 AMoN sites with: Radiellos, Annular denuders, traditional 3-stage CASTNET filter packs, and special 4-stage CASTNET filter pack
- 3 of the 5 sites will have Super SASS with MPP denuders
  - Passive samplers will run on a 2 week exposure schedule
  - Annular denuders and SASS will run for two 1-week exposures
  - CASTNET 3-stage filter will run on normal weekly schedule
  - CASTNET 4-stage filter pack will run for two1-week exposures, matching the annular and SASS denuders

Ammonia Inter-Comparison Study Goals

- Final report to characterize:
  - CASTNET filter pack NH_3/NH_4^+ (NH_X) capacity
  - 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

EPA Chamber Characterization of MPP Denuder

- OAQPS, OAP-CAMD, & ORD collaboration
- Utilize controlled exposure chamber for characterizing:
  - Collection efficiency
  - Maximum loading capacity
  - Effects of short-term (24-hour) and long-term (multi-day) exposure on performance
- EPA may also utilize several labs for extraction to inter-compare lab results for co-located lab exposed samples (RTI, NC State Labs, others?)

Laboratory SOPs/Best Practices

- CSU provided training to both MACTEC and RTI staff
- MACTEC will perform extractions for the Inter-comparison study
- RTI will likely perform extractions for chamber tests and subsequent CSN related operations
- RTI has begun developing its SOPs in anticipation of our studies and pilot
- In limited tests to date, RTI has indicated that they have improved upon lab blank values found in the initial characterization of the MPP denuder at CSU

CSN NH_3 Pilot

- With successful testing of the MPP denuder, EPA will engage State, Local, and Tribal partners to pilot ammonia monitoring at a small set of CSN sites

- EPA is hopeful to begin talks with SLTs by the end of 2010
- EPA would prefer any one of the following sites for the pilot:
  - NCore sites
  - Co-located NCore – CASTNET sites
  - Co-located CSN – CASTNET sites
  - CSN sites in areas known to have higher NH_3 levels
- The pilot would allow EPA to fully understand the reality of running NH_3 denuders in the CSN
  - Laboratory Issues
  - Shipping Issues
  - Integration with existing CSN analytes
  - Costs
  - Unforeseen operational issues
- The lessons learned in the pilot will allow for well-informed decisions to be made in the future on how, where, and when NH_3 might become a routine analyte in the CSN

Questions?