Ambient Ammonia Monitoring Initiative

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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
  - $\text{NO}_Y$, $\text{NH}_X$ (ammonia + ammonium), and $\text{N}_2\text{O}$ 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 $\text{NH}_3$, $\text{NH}_X$, $\text{NO}_Y$, $\text{NO}_2$, 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
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

MPP Denuder Lab Assembly

• MPP denuder screws into “end-cap” components

• Lab assembly serves as a coating vessel, extraction vessel, and as a storage container
Anatomy of the MPP Denuder

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 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

CSU collection efficiency tests:

MPP prototype vs. URG

Source: J. Collett & M. Schurman, CSU
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 two 1-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 NH₃ 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 NH₃ levels

- The pilot would allow EPA to fully understand the reality of running NH₃ 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 NH₃ might become a routine analyte in the CSN
Questions?