# Passive Diffusion Monitoring for Ammonia in the United States

## The Ammonia Monitoring Network: AMoN


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## Abstract

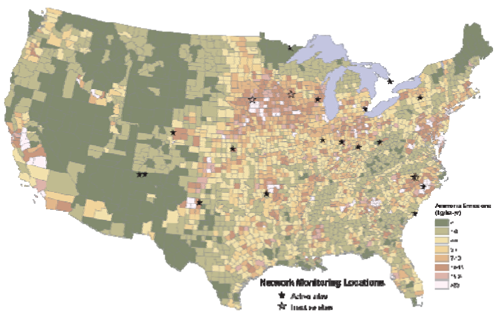

Ammonia ($NH_3$) is the primary basic gas in the atmosphere and is becoming an increasingly important pollutant throughout the United States. The largest sources of $NH_3$ in the United States come from agricultural emissions including $NH_3$-based fertilizers and livestock waste (Seinfeld and Pandis 1998). After $NH_3$ is emitted it can react with acidic particles and gases to form ammonium sulfate and ammonium nitrate particles, a large component of $PM_{2.5}$. As reductions in $SO_2$ and $NO_x$ emissions occur regionally, the need to understand the changing atmospheric process between $NH_3$ and other pollutants increases.

Currently there are no nationwide networks using active samplers to measure $NH_3$ in the United States. Denuders are considered the reference method for $NH_3$ measurements in the field and are the most widely used active $NH_3$ samplers; however they require electricity and a shelter for housing the data logger. CASTNET sites already equipped with a shelter, tower and electricity allow the denuder to be cost effective; however the CASTNET network has sparse coverage especially in the Midwest where ammonia concentrations are known to be increasing. Therefore, passive samplers are being considered for deployment at sites participating in the National Atmospheric Deposition Program (NADP) which will provide better spatial coverage across the US. NADP was also selected as the coordinating body for the passive ammonia monitoring initiative because the program is a collaboration between federal agencies, states, Tribes, universities and organizations.

Currently, EPA/NADP have deployed Radiello passive samplers in triplicate at 18 sites. The network site map is shown in the figure below with the $NH_3$ emissions concentrations from the Carnegie Mellon emissions model (2002). As shown in the figure, most of the sites are located in areas with high $NH_3$ emission fluxes. Most of the sites have been measuring ammonia concentrations for over a year, some sites close to two years. The samplers have been deployed for two week time periods and then shipped back to Illinois State Water Survey's (ISWS) Central Analytical Laboratory (CAL) for analysis. The triplicate samples plus one field blank are analyzed by Flow Injection Analysis.

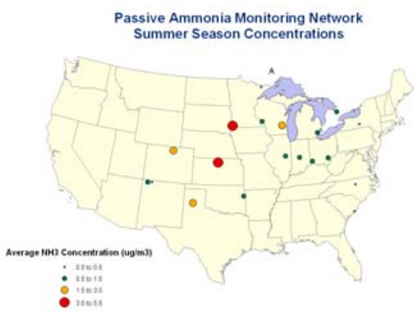
The goal of this initiative is to provide long-term monitoring of ammonia to better understand the trends, regional and seasonal variability and deposition fluxes. Current deposition and air quality model developers lack the ability to verify modeled $NH_3$ concentrations and fluxes, therefore, making it difficult to predict the effects future emission reductions will have on air quality.

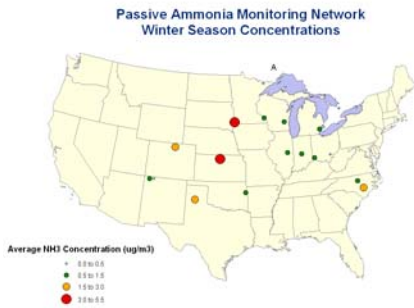

### Modeled Ammonia Emissions and AMoN Site Locations




## Network Results from AMoN

Network results from AMoN from the triplicate Radiello samplers deployed from 2007 through April 2009 are shown in the figures below for the winter and summer seasons. The highest $NH_3$ concentrations measured were in areas known to have high $NH_3$ emission fluxes. An additional site in southeastern Pennsylvania is expected to join the network (CASTNET site: ARE128) within the next month. The area in southeastern PA is known to experience high $NH_3$ emissions due to the large agricultural operations and CASTNET does not currently measure ambient $NH_3$ concentrations, therefore the measurements from this site will benefit not only our understanding of the spatial variability in $NH_3$ concentrations, but also lend some insight into the $NH_3$ source regions in the Eastern US.




## Statistical Inter-comparison Studies

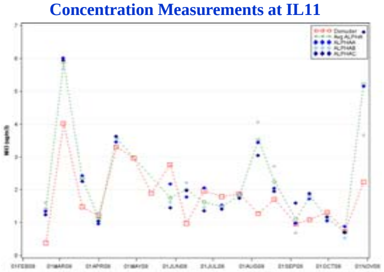
### Accuracy, Precision and Bias

Triplicate Radiello, Adapted Low-Cost Passive High Absorption (ALPHA) and Ogawa samplers were collocated with an annular denuder system (ADS) in Bondville, IL (IL11) to compare the accuracy, precision and bias of each passive sampler type. The results from the initial study are presented here. A second inter-comparison study is nearly complete between three sets of triplicate Radiello and ALPHA samplers and collocated duplicated denuders at IL11 and Cherokee Nation, OK (OK99). A third study looking at the precision of Radiello and ALPHA samplers at five sites is complete but the data has not yet been analyzed.

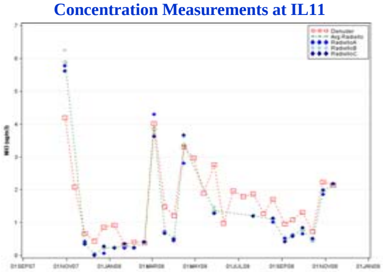
The figure (a) below shows the accuracy and precision of the Radiello sampler versus the ADS while figure (b) shows the results from the ALPHA sampler versus the ADS at IL11. The results from the inter-comparison at Bondville show that the Radiello and ALPHA passive samplers have fairly high precision at the varying $NH_3$ concentrations. The Radiello sampler shows slightly better precision than the ALPHA. The Ogawa results are not shown, but there was consistently a very high and a very low measurement with each sampling time period.

The accuracy of the measurement for both passive samplers when compared with the denuder measurements is high. At higher $NH_3$ concentrations, the ALPHA sampler appears to be biased high against the denuder, while the Radiello, excluding the first sampling time period, shows a small negative bias.

**(a) Triplicate Radiello versus Denuder $NH_3$ Concentration Measurements at IL11**



**(b) Triplicate ALPHA versus Denuder $NH_3$ Concentration Measurements at IL11**



## Theoretical Uncertainty versus Cost

The theoretical uncertainty was estimated by calculating the standard error of the mean (SEM) for one to ten samplers (Equation 1) and then using the SEM to calculate the coefficient of variance (CV) for each n (Equation 2). To look at how the uncertainty varied with cost, the ratio of uncertainty per dollar was calculated for the Radiello and ALPHA samplers. The results are shown in the table below.

**Cost Analysis**

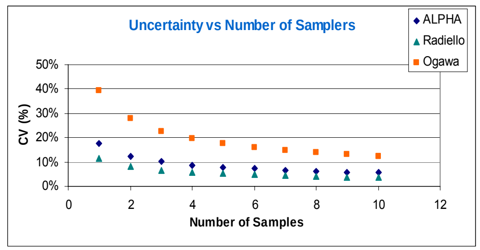
| No. of Samplers | 1 | 2 | 3 |
|---|---|---|---|
| **Radiello** | | | |
| CV (%) | 11.6% | 8.2% | 6.7% |
| Cost/Site/2wk ($) | $110 | $132.50 | $155 |
| Uncertainty/Cost | **0.11** | 0.06 | 0.04 |
| **ALPHA** | | | |
| CV (%) | 17.6% | 12.4% | 10.2% |
| Cost/Site/2wk ($) | $90 | $100.00 | $110 |
| Uncertainty/Cost | 0.20 | 0.12 | **0.09** |

Equation 1: $SEM = \frac{\sqrt{2}*\sigma}{\sqrt{n}}$

Equation 2: $CV(\%) = \frac{SEM}{X} *100$

*Where*:
SEM = standard error of the mean
σ = average standard deviation
n = number of theoretical samples
X = average $NH_3$ concentration

The goal of the analysis was to not only see how the number of samplers affected the uncertainty in the measurement, but also to see how the uncertainty compared with the expected precision of an active sampler (ADS). From the literature, ADS precision is ~5%. As shown in the figure below, the theoretical precision for the Ogawa sampler does not reach 5% with 10 samplers, however the Radiello is expected to have < 5% CV value when four or more samplers are deployed. The ALPHA samplers have ~10% variance with triplicate samplers.




## Next Steps

1. Finalize the statistical results from the inter-comparison studies
   a) Three sets of triplicate ALPHA and Radiello samplers and one $NH_3$ denuder at IL11 (to be completed Sept. 15th 2009)
   b) Triplicate Radiello and ALPHA samplers at IL11, OK99, Connecticut Hill, NY (NY67), Palo Duro, TX (TX43) and Clinton Crops Research Station, NC (NC35) (Sampling completed July 2009)
2. Present results from studies
   a) At the NADP Fall Meeting in October 2009
   b) Publish in a peer-reviewed journal article
3. Update SOPs to reflect any changes in sampler, laboratory or data handling protocols based on feedback from NADP and peer-reviewed article
4. Propose AMoN receive NADP network status at the Spring 2010 NADP meeting