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Supplemental Material

Additional Detailed Information Regarding the Radiello® Precision at all AMoN Sites

The Radiello® passive samplers have been deployed in triplicate throughout the AMoN network since late 2007. Figure A-1 shows the precision, as the average coefficient of variation (CV), for the triplicate samplers for each site with more than 10 sampling time periods between October 2007 and March 2011. As expected, sites with lower concentrations typically have a higher coefficient of variation (*i.e.* NY67). The overall precision of the triplicate samplers for the network is ~10%, which agrees well with the precision of the URG denuders (approximately 6%).[1] The precision of the triplicate Radiello® samplers has allowed the NADP to confidently deploy one sampler per site per sampling time period, with 5% of the network receiving triplicates. This will lower costs, while still maintaining a quality control check for precision.

Additional Detailed Information Regarding the Passive Ammonia Data collected at the Farmington Airport and Navajo Lake, New Mexico sites for 2007-2010

The close comparison between the Ogawa and Radiello® PSDs at the Farmington Airport and Navajo Lake, NM sites in 2008 enabled a four year trend analysis for passive NH_3 concentrations at these two sites for 2007-2010 (See Table A-1). A review of the summary statistics revealed that passive NH_3 concentrations were unchanged during the period 2007-2010 at both the Farmington Airport and Navajo Lake sites. At the Navajo Lake site the 2010 annual NH_3 mean of 0.4 ppb is significantly greater than the 2008 annual NH_3 mean of 0.2 ppb, but over two months of valid data were missing from the Navajo Lake site in both 2008 and 2010 as indicated in the caption for Table A-1. Figure A-2 displays the time series of the Ogawa PSD and Radiello® PSD ambient NH_3 data at the Farmington Airport and Navajo Lake sites for 2007-2010. Annual maxima ambient NH_3 concentrations occurred in the summer months and annual minima ambient NH_3 concentrations occurred in the winter months at both sites.

Additional Detailed Information Regarding the 2009 Bondville, IL Ogawa Study

In 2009, the U.S. EPA Region 6, the NADP and Illinois State Water Survey (ISWS) met to review some variable passive Ogawa NH_3 results produced from December, 2007-June, 2008 by the ISWS at the Bondville, IL site (Figure A-3). The U.S. EPA Region 6 visited the Bondville site and the ISWS in 2009, and also conducted a follow-up field test with Ogawa PSDs from May 26, 2009 through June 23, 2009 (Table A-2). For the follow-up field test, the Ogawa PSDs were prepared using the U.S. EPA Region 6 Houston Laboratory analytical lab procedures, including prescribed storage of the citric acid impregnated filters in the freezer before field use as per the Ogawa protocol[2]. All

Ogawa PSDs for the 2009 follow-up field test were then analyzed by the Houston Laboratory using ion chromatography (Metrohm-Peak, Riverview, FL).

As seen in Table A-2, good precision results of the Ogawa PSDs were obtained for both the filters deployed under the EPA Region 6 shelters and for the filters deployed under the ISWS shelter for the 2009 follow-up field test. A control site in Houston was also operated and produced similar precision results. In addition, the ISWS results for the Radiello® and ALPHA samplers under the single sample housing are also shown and had similar precision results.

From the 2009 test results and visit to the ISWS and Bondville site the following three observations were noted, all helpful when considering the variability of the ISWS December, 2007 – June, 2008 Ogawa data: (1) The ISWS citric acid Ogawa filters were stored in their original packaging, double bagged and inside a clean bench, but not frozen. The phosphoric acid based ALPHA and Radiello® samplers were stored the same way, but without the same variability; (2) The laboratory analytical methods were different, specifically that the ISWS employed flow injection analysis (FIA)/colorimetry while the EPA Region 6 used IC/conductivity analysis; (3) sampler orientation differed between the methods, specifically that the Region 6 Ogawa PSDs were always oriented horizontal to the ground under their respective rain shelters with no specification on horizontal direction while the ISWS, for their December, 2007 - June, 2008 Ogawa study, placed an "A" triplicate sampler horizontal to the ground and oriented North/South, placed a "B" sampler vertically, and placed a "C" sampler also horizontal but oriented East/West. The "B" triplicate sampler was usually the lowest in concentration (Figure A-3).

Additional Detailed Information on the NADP Passive Ammonia Inter-comparison Study

The NADP ran a passive NH_3 inter-comparison study between annular denuders and the ALPHA, Radiello® and Ogawa samplers.[3] An illustration showing the three sampler types is provided in Figure A-4. The inter-comparison study was run at IL11 and OK99 (ALPHA and Radiello® samplers only) during several weeks in 2008 and 2009. The purpose of the study was to determine which sampler was the most accurate, had the least variablity and could be deployed easily for use in the AMoN. The results, shown in Figure A-5, assisted the NADP community in concluding the Radiello® samplers were the best option for network-wide deployment. Figure A-5 shows the triplicate average concentration for each passive versus the measured denuder concentration with the equation for the best fit line and R^2 value. The Ogawa samplers produced better results when the Region 6 group deployed and analyzed the results.

As mentioned in the article, network-wide deployment requires that the sampler be accurate for varying concentrations (high concentrations near agricultural sources versus low concentrations in forests). Factory-prepared supply batches are verified through documented Quality Assurance procedures by the NADP, ensuring consistency of measurements. It was found that Radiello® samplers were faster to assemble and require

no coating in the laboratory, saving the network money on time and labor as compared to other sampler types.

References

[1]Bash, J.O.; Walker, J.T.; Katul, G.G.; Jones, M.R.; Nemitz, E.; Robarge, W. Estimation of in-canopy ammonia sources and sinks in a fertilized *Zea Mays* field; *Environ. Sci. & Technol.* **2010**, 44, 1683-1689.

[2]*NH_3 Sampling Protocol Using the Ogawa Sampler*, Yokohama City Research Institute for Environmental Science, Yokohama Japan, 2nd edition, October 2010.

[3]National Atmospheric Deposition Program, Central Analytical Laboratory: Standard Definitions for Ammonia Monitoring Network (AMoN) Special Study Intercomparison Calculations. Illinois State Water Survey; SOP Number: DA-4065.0, Champaign, IL, **2009.**

Electronic Supplementary Material (ESI) for Journal of Environmental Monitoring

Supplemental Tables

Table A-1 Summary statistics for Farmington Airport and Navajo Lake, NM passive ammonia sites; 2007 data 3-week integrated samples using Ogawa PSDs; 2008-2010 data 2-week integrated samples using Radiello®; no valid Radiello® data from 6/10/08-8/19/08; no valid data from Navajo Lake site from 1/5/2010-3/18/2010.

Site	Year	Sampler	N	Mean (ppb)	Min. (ppb)	Max. (ppb)	Standard deviation (ppb)	95% confidence interval around mean (ppb)
Farmington Airport	2007	Ogawa	18	1.5	0.5	2.9	0.5	1.2-1.7
	2008	Radiello	18	1.0	0.6	1.6	0.3	0.9-1.2
	2009	Radiello	25	1.2	0.5	1.7	0.3	1-1.3
	2010	Radiello	26	1.5	0.4	4.9	0.9	1.1-1.8
Navajo Lake	2007	Ogawa	18	0.2	No detection	0.5	0.1	0.1-0.3
	2008	Radiello	19	0.2	No detection	0.5	0.1	0.1-0.2
	2009	Radiello	26	0.3	No detection	2.2*	0.4	0.1-0.5
	2010	Radiello	20	0.4	No detection	1.0	0.3	0.3-0.5

*7-day sample

Table A-2. Special passive NH_3 study at Bondville, IL site and the Houston, TX control site.

Time Period	Site samples	Concentration (ppb)	Average concentration of triplicates or duplicates (ppb)
5/26/09-6/9/09	**Bondville (ISWS shelter)**		
Ogawa (EPA Region 6)	Sample 1	2.3	
	Sample 2	2.2	
	Sample 3	2.2	2.2
	Sample (travel)	0.5	
ALPHA (ISWS)	Sample 1	3.1	
	Sample 2	2.9	
	Sample 3	3.6	3.2
	Sample (travel)	0.8	
Radiello (ISWS)	Sample 1	2.4	
	Sample 2	2.4	
	Sample 3	2.3	2.4
	Sample (travel)	0.3	
Denuder (ISWS)	Sample 1	3.3	
	Sample 2	2.6	
	Sample 3	2.8	2.9
	Bondville (EPA Region 6 shelters)		
Ogawa (EPA Region 6)	Sample 1	2.3	
	Sample 2	2.3	
	Sample 3	2.1	2.2
	Sample (travel)	0.5	
	Houston Control Site (Clinton Drive)		
Ogawa (EPA Region 6)	Sample 1	2.0	
	Sample 2	2.1	2.0
	Sample (travel)	0.5	
6/9/09-6/23/09	**Bondville (ISWS shelter)**		
Ogawa (EPA Region 6)	Sample 1	1.3	
	Sample 2	1.5	
	Sample 3	1.4	1.4
	Sample (travel)	0.5	
ALPHA (ISWS)	Sample 1	4.7	
	Sample 2	2.7	
	Sample 3	2.5	3.3
	Sample (travel)	0.3	
Radiello (ISWS)	Sample 1	1.9	
	Sample 2	2.0	
	Sample 3	1.9	1.9
	Sample (travel)	0.2	
Denuder (ISWS)	Sample 1	2.9	2.9
	Bondville (EPA Region 6 shelters)		
Ogawa (EPA Region 6)	Sample 1	1.3	
	Sample 2	1.4	
	Sample 3	1.3	1.4
	Sample (travel)	0.5	
	Houston Control Site (Clinton Drive)		
Ogawa (EPA Region 6)	Sample 1	1.4	
	Sample 2	1.5	1.5
	Sample (travel)	0.5	

Supplemental Figures

Figure A-1. Average Coefficient of Variation (%) versus Radiello® NH_3 concentration (µg m^{-3}) for all AMoN sites with more than 10 sampling periods. The average CV for all sites is 10.3%.

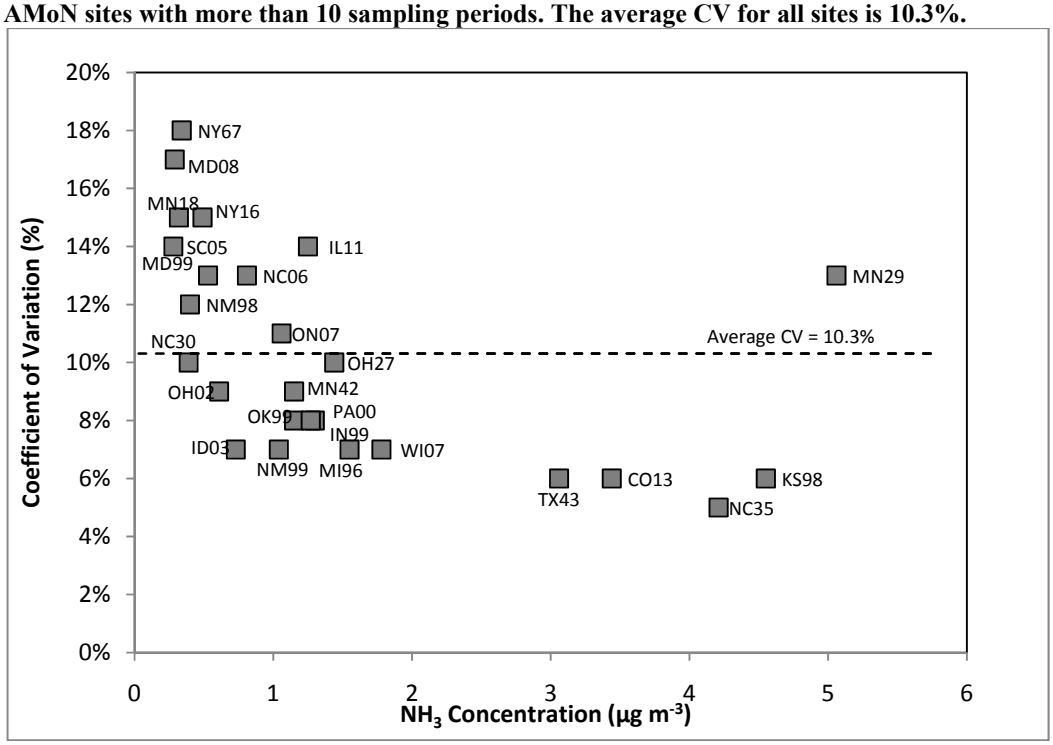

Figure A-2 Passive NH_3 data time series for two sites in San Juan County, New Mexico; 2007-2010; Ogawa PSDs used for 2007 data (3-week integrated samples) and Radiello® PSDs used for 2008-2010 data (2-week integrated samples); 2008-2010 Radiello® PSD data from NADP; Najavo Lake site peak value of 2.2 ppb was a 7-day sample.

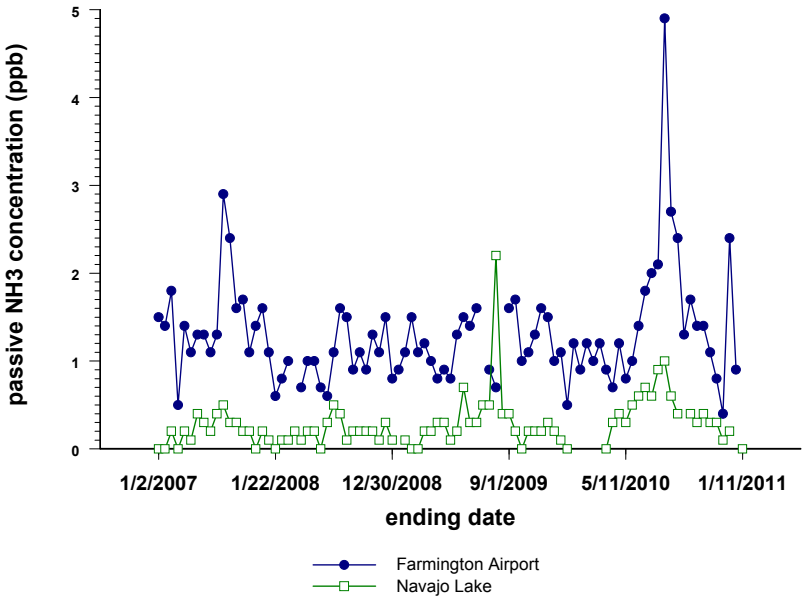

Figure A-3 The NADP Ogawa triplicate samplers versus date off. Triplicate A samplers were oriented horizontally in the North-South direction; Triplicate B samplers were oriented vertically; Triplicate C samplers were oriented horizontally in the East-West direction. This suggests there is a directional bias, as Triplicate B is typically the lowest concentration, and always faced up/down.

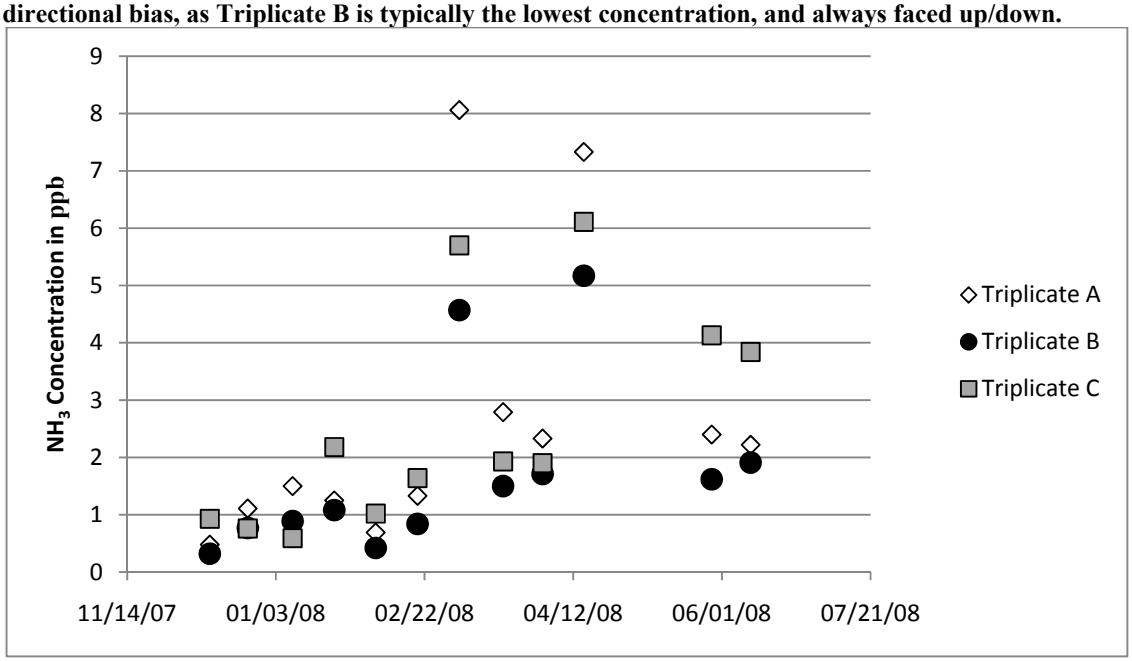

Figure A-4. Diagram of the (a) ALPHA (b) Radiello® and (c) Ogawa passive samplers. Note, the ALPHA and Ogawa samplers are bi-directional while the Radiello® sampler is radial.

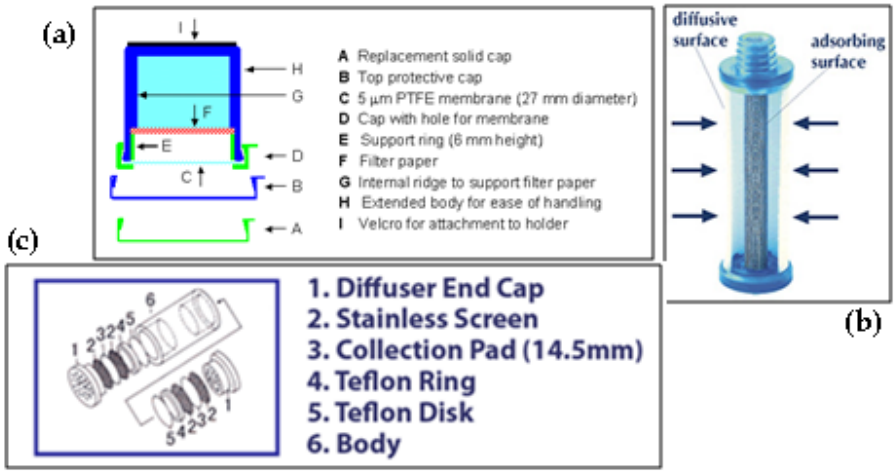

Figure A-5. ALPHA, Ogawa and Radiello® concentrations measured at IL11 and OK99 with collocated URG denuder measurements as a reference. The equations for the best-fit lines are shown. All passive samplers and denuders were deployed and analyzed as part of the NADP inter-comparison study.