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PAPER

Passive ammonia monitoring in the United States: Comparing three different sampling devices†

Melissa A. Puchalski,*[a] Mark E. Sather,[b] John T. Walker,[c] Christopher M. B. Lehmann,[d] David A. Gay,[d] Johnson Mathew[e] and Wayne P. Robarge[f]

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The need for ambient gaseous ammonia (NH_3) measurements has increased in the last decade as reactive NH_3 concentrations and deposition fluxes show little change even with tightening standards on nitrogen oxides (NO_x) emissions. Currently, there are several networks developing methods for adding NH_3 measurements in the U.S. Gaseous NH_3 measurements will provide scientists and policymakers data which can be used to estimate ecosystem inputs, validate air quality models including trends and regional variability, and evaluate changes to the environment based on additional emission reduction requirements and estimates of critical nitrogen load exceedances. The passive samplers described in this paper were deployed in duplicate or triplicate and collocated with annular denuders or continuous instruments to determine their accuracy. The samplers assessed included the Adapted Low-Cost Passive High Absorption (ALPHA), Radiello®, and Ogawa passive samplers. The median relative percent differences (MRPD) between the reference method and passive samplers for the ALPHA, Radiello® and Ogawa were −2.4%, −37% and −44%, respectively. The precision between duplicate samplers for the ALPHA and Ogawa samplers, was 7% and 6%, respectively. Triplicate Radiello® precision was assessed using the coefficient of variation (CV). The CV for the Radiello® samplers was 10%. This article discusses the statistical results from these studies.

[a]*Clean Air Markets Division, U.S. EPA 1200 Pennsylvania Ave. NW, Washington D.C., U.S.A. E-mail: puchalski.melissa@epa.gov; Tel: +202-343-9882*
[b]*Air Quality Analysis Section, U.S. EPA Region 6 1445 Ross Ave., Dallas, TX, U.S.A*
[c]*National Risk Management Research Laboratory, U.S. EPA 109 T.W. Alexander Dr, Research Triangle Park, NC, U.S.A*
[d]*National Atmospheric Deposition Program, Illinois State Water Survey, University of Illinois at Urbana-Champaign, 2204 Griffith Dr, Champaign, IL, U.S.A*
[e]*Houston Laboratory, U.S. EPA Region 6,10625 Fallstone Rd., Houston, TX, U.S.A*
[f]*North Carolina State University, PO Box 7619, Raleigh, NC, U.S.A*

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Introduction

Gaseous ammonia (NH_3) is the most abundant alkaline gas in the atmosphere.[1] The largest source of NH_3 emissions is agriculture; including animal husbandry and NH_3-based fertilizer application.[2] It is estimated that agricultural emissions make up between 80 to 90 percent of total NH_3 emissions in the United States.[3,4] Other sources of NH_3 include industrial processes, vehicular emissions, and volatilization from soils and oceans. Non-point source emissions, such as those from agricultural sources, are difficult to quantify on a regional level.

While there have been no long-term NH_3 monitoring studies in the U.S., the National Atmospheric Deposition Program/National

Environmental impact

The contribution of nitrogen to ecosystems and $PM_{2.5}$ formation is known to be significant in the US, however, there have been few monitoring efforts to establish baselines, measure trends or regional variability, and deposition rates. To date, only one national network, the NADP's AMoN, routinely measures NH_3 concentrations. This article describes the work from three studies, which used different passive samplers to measure ambient concentrations of NH_3. In each study, passive samplers were deployed in replicates to determine precision and collocated with a reference method to determine the accuracy. Recommendations and lessons learned are included for each passive NH_3 sampler described. In addition, this article provides an assessment which will allow data users to combine data sets from studies using each of the three samplers.

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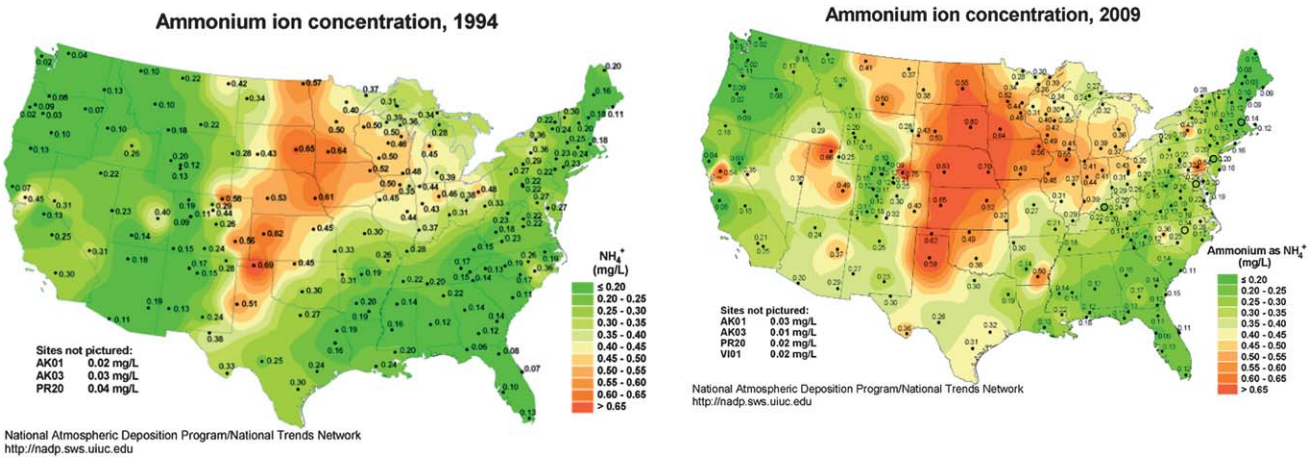

Fig. 1 NADP/NTN NH_4^+ concentrations from 1994 and 2009. Ammonium concentrations are in mg L^{-1} and concentration classifications are consistent between years. Samples are annual precipitation-weighted averages of weekly precipitation concentrations as collected each Tuesday morning.

Trends Network (NADP/NTN) has measured ammonium (NH_4^+) concentrations in precipitation for more than 30 years. The NADP data shows that throughout the central U.S. NH_4^+ concentrations have increased. Increases have also been observed in areas such as eastern North Carolina, where growth in animal production has occurred over the same time period.[5] Fig. 1 shows stark increases in volume-weighted average NH_4^+ concentrations from NADP's NTN measurements between 1994 and 2009.

On the other hand, in the U.S. no long-term, national-scale NH_3 concentration data exist. A lack of NH_3 measurement data has caused a gap in our scientific understanding of the role NH_3 has on the atmospheric reactive nitrogen budget in the U.S. In addition, NH_3 deposition fluxes are not well characterized because they are bi-directional, meaning NH_3 can be deposited to or emitted from vegetation and soils.[6,7,8] Atmospheric NH_3 concentrations and fluxes vary seasonally and regionally. High concentrations are typically observed in the spring and summer due to warmer temperatures and fertilizer application.[9,10,11] Without measured NH_3 gas-phase concentrations, it is difficult to verify model inputs and outputs of the seasonal and regional variations in concentration and deposition. Ammonia plays a significant role in the formation of atmospheric particulate matter, visibility degradation and atmospheric deposition of nitrogen to sensitive ecosystems. Thus, the development of a national monitoring network is relevant to the protection of human and ecosystem health. Ammonia reacts with acidic ions, such as sulfate (SO_4^{2-}) and nitrate (NO_3^-), to form particulate ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3), which are significant contributors to particulate matter mass with a diameter less than 2.5 microns ($PM_{2.5}$). Ground-based measurements of NH_3 will improve air quality models designed to forecast $PM_{2.5}$ concentrations using different emission reduction scenarios. In the U.S., areas may be designated out of attainment for $PM_{2.5}$ even with strict limits on stationary source sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions, due to the formation of ammonia-containing aerosol species. It has been shown that reductions in NH_3 emissions can be a cost-effective strategy for reaching attainment.[12] In addition to contributing to air quality issues, NH_3 deposition can contribute to eutrophication of sensitive ecosystems and loss of biodiversity.[13,14] Several agencies/organizations within the U.S. are evaluating different methods for measuring NH_3 within the constraints of their current monitoring networks. As the U.S. Environmental Protection Agency (EPA) lowers criteria pollutant standards (*i.e.* $PM_{2.5}$) and as secondary standards for ecosystem health evolve, the need to monitor NH_3 in order to quantify temporal trends and seasonal variations in NH_3 concentrations also increases.

At present, passive sampling techniques represent the only cost effective option for establishing a monitoring network with sufficient spatial and temporal coverage (*i.e.*, a 10+ year national network of 100+ sites). In this paper we describe three different NH_3 passive sampler devices (PSDs) which have been deployed in the U.S.: the Adapted Low-Cost Passive High-Absorption (ALPHA), the Radiello® and the Ogawa. The EPA's Office of Research and Development (ORD) has operated a network of ALPHA PSDs in the southeastern agricultural region of North Carolina. Established in November 2007, a pilot passive NH_3 sampling network was operated by the NADP, the Lake Michigan Air Director's Consortium (LADCO) and the EPA's Clean Air Markets Division (CAMD). The pilot network included approximately 20 sites throughout the U.S. using the Radiello® PSDs. EPA's Region 6, located in the south central city of Dallas, TX, has operated several sites with Ogawa PSDs throughout the central U.S.

The ORD tested the performance of the ALPHA sampler in eastern North Carolina as part of the Carolina Ammonia Monitoring Network (CAMNet) to quantify the spatio-temporal variability of NH_3 across a region of widespread animal and crop production. The data set presented here covers the period of May 2007 to May 2008 and comprises 48 sampling periods at 24 sites (Fig. 2). The sampling period was extended from 1 to 2 weeks at four relatively clean sites during the winter and spring to collect sufficient mass at low NH_3 concentrations. These data are supplemented by a comparison between the ALPHA sampler and annular denuder method at an additional site during 2009 as described below.

The NADP, LADCO and CAMD deployed triplicate Radiello® samplers at over 20 sites across the Midwestern U.S. to determine the feasibility of running a national continuous passive NH_3

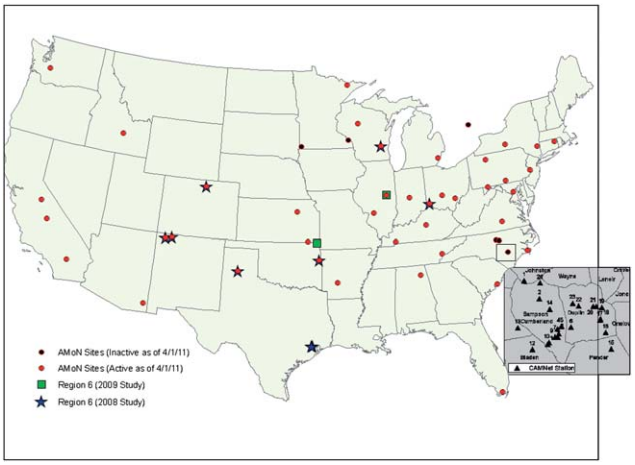

Fig. 2 Map of AMoN sites, Region 6 Ogawa study sites and an insert showing the CAMNet site locations.

network. The study network, the Ammonia Monitoring Network (AMoN), measured NH_3 concentrations between 2007 and 2010 (see http://nadp.isws.illinois.edu/amon). In October, 2010 the AMoN was accepted as an official sub-network within the NADP and as of May 2011 the network has expanded to approximately 40 sites (Fig. 2). The AMoN data through January 2011 are presented here. The Radiello® measurements are supplemented with an intercomparison of all three sampler types and with annular denuders (see Supplemental Material for additional information).

The EPA's Region 6 deployed Ogawa passive sampling devices at seven sites in New Mexico, Colorado, Oklahoma, Texas, Wisconsin and Ohio in 2008, collocated with the NADP Radiello® passive NH_3 monitoring study (Fig. 2). Two additional Ogawa PSD sites were operated in the Houston, TX area, so passive NH_3 data using the Ogawa PSD were analyzed at a total of nine sites. The Ogawa samplers were collocated with a continuous Pranalytica Nitrolux 200 (Nitrolux Model 200; Pranalytica, Inc.; Santa Monica, CA) trace level NH_3 analyzer at the Stilwell, OK site (NADP site OK99). The continuous NH_3 measurements from the Nitrolux were used to assess the accuracy of the Ogawa passive samplers. Additional information about the Pranalytica Nitrolux can be found elsewhere.[15] In 2009, the U.S. EPA Region 6 added collocated Ogawa passive NH_3 samplers at the Bondville, IL site (NADP site IL11). Also in 2009, additional passive NH_3 samples were taken at the Quapaw site in northeastern Oklahoma, a site which had participated earlier in the successful 2007 passive NH_3 monitoring study in the Four Corners area and eastern Oklahoma.[16]

The three studies described, using three different samplers, are summarized in this paper to show the applicability of each. In addition, supplemental information is provided for the special studies. The precision, accuracy and detection limits are presented to allow researchers interested in monitoring NH_3 at a low-cost, to determine which sampler performance would best meet their data quality objectives.

Experimental

Passive samplers use Fick's Law to calculate the rate of diffusion across a surface. The pollutant gas diffuses across the membrane surface of the sampler onto an absorbing substrate at a derived flow rate. Passive air sampling methods have been used for many years for many analytes because they are simple, reliable and inexpensive, and therefore, can be widely deployed.[17] Flow rate through the passive sampler is calculated using eqn (1):

$$m_{NH3} = \frac{D_{NH3}\ x\ A}{\Delta x} \tag{1}$$

where m_{NH3} is the passive sampler flow rate ($cm^3\ min^{-1}$), D_{NH3} is the gas diffusion coefficient at ($cm^2\ min^{-1}$), A is the samplers effective cross-sectional area (cm^2) and Δx is the sampler diffusion distance (cm). D_{NH3} assumes a temperature of 25 °C for the Radiello® and Ogawa samplers, whereas D_{NH3} was adjusted for temperature in the CAMNet ALPHA study.[18]

The ambient concentration of NH_3 determined by the passive sampler depends on the mass of NH_3 adsorbed by the collection filter, exposure duration, and diffusion coefficient. The mass of NH_3 adsorbed by the collection filter (Q_{NH3}) is:

$$Q_{NH3} = (c_e – c_b)v \tag{2}$$

where c_e is the filter extract concentration of NH_4^+ (μg mL^{-1}), c_b is the extract concentration of an unexposed travel blank (μg mL^{-1}), and v is the volume of the extract (mL).

The NH_3 concentration in air is calculated using the diffusional flow rate and the mass of NH_4^+ absorbed on the collection filter. For the Radiello® and Ogawa samplers, the NH_3 concentration is calculated as:

$$C_{NH3} = \frac{Q_{NH3}}{V} = \frac{0.9442\ x\ Q_{NH3} x\ 10^3}{\beta_{NH3}\ x\ m_{NH3}\ xt} \tag{3}$$

where C_{NH3} is the NH_3 concentration in ambient air in μg m^{-3}, Q_{NH3} is described above, V is volume of air sampled in m^3, β_{NH3} is the mass transfer correction factor (unitless), m_{NH3} is defined above, t is the duration of exposure in minutes. The mass transfer correction factors (β_{NH3}) for the Radiello® and Ogawa are 1.19 and 1, respectively.[20] The flow rates (*i.e.* $\beta_{NH3} \times m_{NH3}$) used for the Radiello® and Ogawa samplers (based on filters from both sides of the sampler) are 235 and 31.19 mL min^{-1}, respectively.[20]

For the ALPHA sampler, the NH_3 concentration was calculated according to eqn (3) with the exception that a temperature dependent diffusion coefficient was used.[18] The mass transfer correction factor for the ALPHA is described below.

The three samplers, ALPHA, Radiello® and Ogawa are described individually below. Differences in extraction methods and analytical instrumentation are detailed for each sampler. Comparisons between sampling studies and sampling methods are shown in Table 1. Figure A-4 in the Supplemental Material includes a diagram of each passive sampler described in this paper.

ALPHA

The ALPHA passive sampler (Center for Ecology and Hydrology, Edinburgh) consists of a 26 mm long, 27 mm outer diameter polyethylene tube.[19,21] One end contains a 5μm PTFE membrane, through which NH_3 gas diffuses and is adsorbed onto a phosphorous acid-coated collection filter located at the

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Table 1 Summary of the ALPHA, Radiello® and Ogawa studies. The number of 2-week exposure periods used to estimate the detection limits are shown in parenthesis in the last row

	ALPHA	Radiello®	Ogawa
Deployment Schedule	1 week & 2 week	2 week	2 week & 3 week
Time period	May 2007–May 2008	October 2007–January 2011	2007–2009 (various sampling periods)
Number of sites	25	20	9
Laboratory analysis	Ion Chromatography	Flow Injection Analysis	Ion Chromatography
Field blanks	2 sets of N = 6/deployment	N = 1/site	N = 2/site
Field blank corrected?	Y	N, but reported	Y
Est. Detection Limit, 2-week samples (μg m^{-3})	0.12 (48)	0.16 (108)	0.28 (293)

other end of the diffusion path. The membrane prevents particle collection and thus the NH_3 concentration is not biased high by collection of ammonium aerosol. The membrane also serves to establish a turbulence-free diffusion path between the membrane and the collection filter, thus avoiding "wind-shortening" of the diffusion path. Within CAMNet, samplers were deployed as two replicates for 1 to 2 weeks at each measurement location in an open bottom rain shelter fixed at a height of 1.5 m above ground.

For the CAMNet study, each batch (weekly or biweekly) of samples is accompanied by two sets of six travel blanks (*i.e.* 12 travel blanks per sample period), which account for contamination during transport to and from the field site. In this case, c_b in eqn (2) represents the median of these two sets of travel blanks.

The detection limit, or minimum detectable concentration (L_D), was calculated (eqn (4)) as a function of the standard deviation of field blanks (σ_o) as outlined by Currie[22]

$$L_D = 2t_{1-\alpha,\upsilon}\sigma_o \quad (4)$$

where t is the Student's t-statistic with υ degrees of freedom at the 95th percentile confidence level ($\alpha = 0.05$). Because the batchwise variance of the travel blank is not constant over time, L_D is determined for each batch of six travel blanks.

Laboratory preparation and analysis

Collection filters (25 mm, Swiftlab, UK) were coated with a solution of 5% (w/w) phosphorous acid in methanol. Exposed collection filters were extracted in 2.5 mL deionized water and stored at 4 °C prior to analysis by ion chromatograph (Dionex model DX-120, Dionex, Sunnyvale, CA), which has a typical method detection limit of 0.5 μg NH_4^+-N L^{-1}. The instrument is configured with a CS12A cation separation column, CG12A guard column, 100 μL sample loop and a self-regenerating suppressor (CSRS-300). The eluent is 18 mM methane-sulfonic acid (1 mL min^{-1}). Laboratory and field (travel) blanks were analyzed along with field-exposed samples. Six laboratory blanks were processed for each batch (defined by weekly or biweekly sampler deployment period) of field exposed samples and represent extracts from samplers that are prepared in the laboratory using standard procedures then extracted immediately and stored at 4 °C until analysis. Twelve field blanks were processed for each batch of field exposed samples and represent extracts from unexposed samplers that are transported to and from the field sites with field exposed samplers. The travel blank characterizes all sources of contamination and variability related to laboratory procedures and transport to and from the field site. Capped samplers were transported in 250 mL Nalgene® jars.

Calibration of sampler flow rate

Previous studies with passive devices have shown that the effective sampler flow rate (m_{NH3}) is lower than the theoretical value calculated from eqn (1) due to additional resistance to diffusion by the PTFE membrane at the sampler entrance.[21] The sampling rate must therefore be characterized and calibrated over the range of sampling conditions (*i.e.* NH_3 concentration, duration of exposure, *etc.*) either by field comparison to an independent reference method[23] or exposure to a known concentration of NH_3 under controlled conditions. By quantifying the mass (Q_{NH3}) collected by the sampler at a known air concentration (C_{NH3}) and exposure period (t), the sampler flow rate (m_{NH3}) in eqn (3) may be measured directly. By comparing the measured and theoretical values of m_{NH3}, a correction factor (β_{NH3}, eqn (3)) may be derived.

Similar to the approach of Walker *et al.*,[24] we characterized m_{NH3} by exposing the ALPHA sampler to a range of NH_3 concentrations (1 to 100 μg m^{-3}) in a well-mixed Teflon-lined 61 cm (L) × 30.5 cm (W) × 19 cm (H) acrylic chamber over exposure periods ranging from 1–7 days. Ammonia concentrations were generated by mixing NH_3 (10 ppm ± 5% or 100 ppm ± 5%; Airgas; Durham, NC) with clean air *via* calibrated mass flow controllers or critical orifice. Cylinder concentrations were verified by extractive FTIR and found to be within the reported uncertainty. The concentration of NH_3 in air entering and exiting the chamber was monitored using a dual-cell Pranalytica photoacoustic NH_3 detector (Nitrolux Model 200; Pranalytica, Inc.; Santa Monica, CA).[15]

During the first experiment, batches of five samplers were exposed to 100 μg NH_3 m^{-3} for 1, 2, 4, and 7 days to test potential saturation effects, which may be an issue for samplers located in close proximity to animal production facilities or fertilized fields. Results showed that the mass collection rate (slope) is constant over a 1 week exposure to 100 μg NH_3 m^{-3}, which is on the upper end of the range of concentrations expected within the CAMNet domain. A second study was conducted in which batches of five samplers were exposed to concentrations of 1.8, 9.0, 25.0, and 52.0 μg NH_3 m^{-3} for 2–4 days to further characterize m_{NH3} over a range of concentrations. Combining data from both experiments yielded mean and median ($N = 40$) correction factors of 0.75 and 0.74, respectively, which is consistent with the value of 0.746 obtained by Tang *et al.*[19] *via* field comparison to the DELTA denuder system.[25]

Radiello®

The Radiello® samplers are commercially available through Sigma Aldrich and manufactured by the Fondazione Salvatore Maugeri (http://www.radiello.com). The Radiello® samplers are comprised of the cartridge and the diffusive body (60 × 16mm diam., 1.7 mm thickness, 25 ± 5 μm average porosity). The cylindrical sampling cartridge (60 × 4.8 mm) is made of microporous polyethylene and manufacturers filters impregnated with phosphoric acid. The manufacturer provides a theoretical flow rate of 235 mL min^{-1}, which will be verified through ongoing field and laboratory experiments. The Radiello® samplers are shipped to the AMoN sites directly from the NADP at the Illinois State Water Survey (ISWS).

Laboratory preparation and analysis

The standardized extraction and preparation procedures for the Radiello® are posted on the AMoN website (http://nadp.isws.illinois.edu/amon). The NADP assembles the Radiello® samplers one day before shipment. They are assembled in a laminar flow hood (Air Science, Fort Myers, FL) with impregnated carbon to remove ambient NH_3. Each sampling body is individually tracked and is cleaned prior to assembly using a heated sonicator.

Triplicate samplers are placed in a cleaned glass jar with a Teflon-lined lid. The single travel blank is placed in a second jar. The sampler sets are placed inside a sealed bag with a scavenging filter. The scavenging filter is soaked in a 10% citric acid in methanol coating solution and dried for 5 min in the hood. Travel blanks are not opened by the site operator. All samplers are stored frozen to help mitigate contamination until they are deployed.

The samplers are shipped back (maximum of 3 days shipping) to the CAL in the same bags and jars. Upon receipt, the samples are frozen in their jars, and are extracted within one week. After extraction with 10 mL dionized water, samples are analyzed by Flow Injection Analysis (Lachat Analytics, Inc., Quik Chem 8000 Milwaukee, WI) following EPA Method 350.1. This is a colorometric determination using indophenol as an indicator. The NADP reports an analytical method detection limit of 3 μg $NH_4^+L^{-1}$ for the period of study. All network data is reported in the AMoN database and posted online.

Field sampling

Each AMoN site is set up with a rain shelter placed approximately 2 m above the ground. The site operators clip the Radiello® samplers into the shelter every other Tuesday for a two week sample, and ship the used samplers back to the CAL with a field form which includes the date and time the sample was deployed and removed, any new activities around the site (fertilizer applied, *etc.*) and any problems the site operator had (lost or compromised sample, *etc.*). This information is documented in the NADP database and used for sample validation and quality assurance (QA). Additional information about the field operations can be found on the AMoN website.

Ogawa

The Ogawa PSD is made up of a solid cylindrical polymeric body (2 cm × 3 cm) with a diffusion barrier and two stainless steel screens on each side. For all studies, the Ogawa PSDs, obtained from Ogawa & Co., Inc., Pompano Beach, Florida, used filters coated with citric acid by the manufacturer. Details of site set up, sample preparation and handling, chemical analyses using the ion chromatograph (IC), and concentration calculations, are found in the 2007 study publication.[16]

Laboratory preparation and analysis

For the 2008 and 2009 studies the Metrohm IC, which has a detection limit of 10 μg NH_4^+-N L^{-1}, had a 4 mm column and a 10 μL sample loop size equipped with a C2 guard column and a C2-150 (4 mm × 150 mm) separation column for cations. The IC was used in conductivity detection mode. To elute the ammonium ion, a mixture of 1.75 millimoles (mM) oxalic acid plus 0.75 mM dipicolinic acid at a flow rate of 1 mL min^{-1} was used.

Field sampling

Ogawa PSDs were typically mounted on an aluminum pole approximately 1.5 meters above the ground, while a few sites mounted the samplers at approximately 5 meters atop existing monitoring trailers. Unlike the ALPHA and Radiello® samplers, each Ogawa sampler was placed under its own separate rain shelter. Samplers were replaced on a 2-week or 3-week sampling schedule. Additional information on the Ogawa field sampling campaign can be found in Sather *et al.*[16]

Results

Accuracy

This section presents detailed accuracy statistics for each of the three samplers as used in recent U.S. studies. Statistical methods used include regression, relative percent difference (RPD) and 95% confidence interval analyses. Annular denuders (URG Corp., Chapel Hill, NC) and the Nitrolux (Pranalytica Inc., Santa Monica, CA) were used to assess the accuracy of the passive samplers here. Denuders are commonly used as the reference method for NH_3 and the Nitrolux showed reasonably comparable results to active NH_3 sampling methods in von Bobrutzki *et al.*[15] Ideally, accuracy of the individual samplers would be compared over the same range of observed concentrations. Because the results presented here represent three studies conducted in different areas, the ranges of concentrations measured by the individual PSDs are different. For the accuracy assessment, concentrations measured with the Ogawa and Radiello® samplers ranged from ≈ 0.0–2.5 μg m^{-3} and ≈ 0.25–6.5 μg m^{-3}, respectively. Concentrations measured with the ALPHA sampler covered a larger range of concentrations from ≈ 0.0–8.5 μg m^{-3}. As described below, the ALPHA site location in Clinton, NC is influenced by local agricultural sources and thus experiences higher concentrations than are measured at the Ogawa and Radiello® sites. For example, 36% of the ALPHA concentrations are >2 μg m^{-3}, compared to 22% and 4% for the Radiello® and Ogawa samplers, respectively. These differences in concentration distributions should be considered when comparing the accuracy results presented below.

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ALPHA. Accuracy of the ALPHA sampler, with the flow rate correction applied, was assessed by comparison to phosphorous acid coated glass annular denuders.[26,27] Denuders were operated for 24 h at a mass flow controlled air sampling rate of 10 Lpm. Denuders were extracted with 10 mL deonized water and analyzed for NH_4^+ by ion chromatography. ALPHA *versus* denuder comparisons took place at Duke Forest, near Chapel Hill, NC, and the Clinton Horticultural Crops Research Station, near Clinton, NC (Fig. 2), from January to November, 2009. The Duke Forest site is a suburban site characterized by relatively low NH_3 concentrations[28] while the Clinton site is in an area of widespread animal and crop production and therefore experiences much higher NH_3 concentrations.[29] For this comparison, the mean and median daily denuder NH_3 concentrations during a weekly period containing seven observations (*i.e.*, denuders were not operated in replicate) were compared to the mean and median of four replicate ALPHA weekly measurements. Denuder precision during previous studies was <10% expressed as coefficient of variation of replicates.[29,30]

Agreement between the two methods was assessed by calculating the absolute relative percent difference between concentrations and by reduced major axis (RMA) regression. Ayers demonstrated in an analysis of air quality data that RMA regression was superior to ordinary least squares regression, which tends to underestimate the slope parameter and overestimate the intercept when both X and Y variables contain error.[31]

Regression analysis comparing weekly mean and median ALPHA and denuder samples (N = 72 observations) showed good agreement between the two methods. Slopes (±standard error) were 0.85 ± 0.034 and 0.91 ± 0.042 for mean and median weekly concentrations, respectively, and corresponding R^2 values were 0.89 and 0.85. Intercepts of 0.07 and 0.08 for mean and median concentrations, respectively, were not statistically significant ($P < 0.1$). It is important to note that the regression results were significantly influenced by a single observation corresponding to the highest reported denuder concentration (Fig. 3). The influence of this observation on the regression results was quantified using the DFBETAS statistic produced by the SAS Proc Reg procedure, which is a scaled measure of the change in a regression parameter estimate (slope or intercept) calculated by deleting the ith observation. A threshold value of '2' is commonly used to identify influential observations (DFBETA > 2). The single outlier identified in Fig. 3 exceeded a value of 3 for the slope term when comparing both mean and median concentrations. If this observation, which may be indicative of contamination in the denuder sampling manifold, is removed, the slope terms for mean and median concentrations increase to 0.90 ± 0.027 and 0.99 ± 0.034, respectively, with corresponding increases in R^2 values to 0.94 and 0.92. Intercepts were reduced to 0.02 and −0.01, respectively, and were not statistically different from zero ($P < 0.1$). For comparison, the least squares regression results for each of the reference methods (URG annular denuders or Nitrolux) and passive samplers are shown in Fig. 4. While there is considerable variability about the regression lines when comparing weekly periods, overall the methods agree well.

The median absolute relative difference between average ALPHA and denuder concentrations was ±28% (Table 2), with highest values observed at concentrations below 0.25 μg NH_3 m^{-3}. The mean absolute relative difference, ±64%, is strongly influenced by a small number (N = 6) of observations in which the blank corrected ALPHA concentration was slightly negative. In this case, the median is a more appropriate statistic. At such low concentrations, the ALPHA concentration becomes increasingly sensitive to the blank correction, a problem that would be reduced to some degree for longer exposures (*i.e.*, increasing ratio of exposed *vs.* blank concentration in sample extract).

Radiello®. Two-week mean triplicate Radiello® concentrations were compared to concentrations from collocated URG annular denuders at IL11 and OK99. There were a total of 36 sampling periods (N) used for the regression analysis between October 2007 and August 2009. Thirty one comparisons are from IL11 and the other five are from OK99. The denuders were deployed for two 1-week time intervals, which differs from the 24-hour deployment schedule used in the ALPHA study. The RMA regression results showing the comparability between the mean and median triplicate Radiello® and denuder NH_3 concentrations are shown in Fig. 5. The DFBETAS statistic was used to determine if there were outliers, but there were no values >2. Therefore, all available data points were used. Slopes (±standard error) for mean and median 2-week concentrations were 1.39 ±

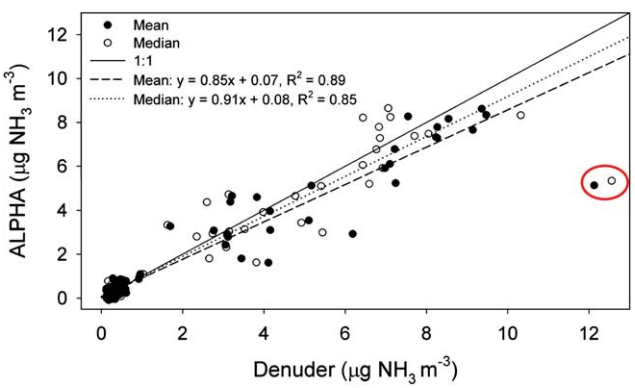

Fig. 3 Comparison of weekly mean and median ALPHA and denuder samples using reduced major axis regression (N = 72). Outlier is circled in red.

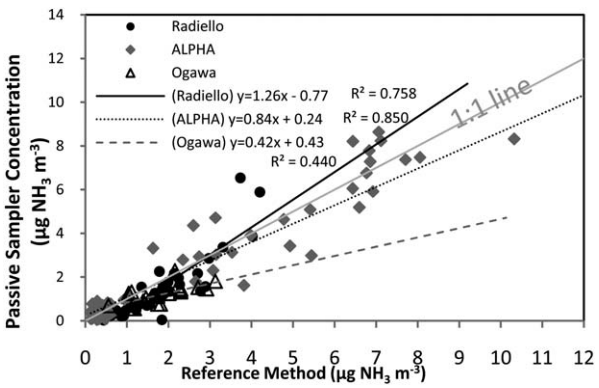

Fig. 4 Linear regression of reference method concentrations (URG denuders for the ALPHA and Radiello® analysis) or Nitrolux (Ogawa analysis) *versus* the passive samplers. The equations for each of the best-fit line are shown with the R^2 value. The 1 : 1 line is shown for reference.

Table 2 Absolute Relative Percent Difference (RPD) of the ALPHA and Radiello® sampler as compared to collocated annular denuder concentrations and the Ogawa sampler as compared to the continuous Nitrolux analyzer. The mean RPD is also shown for each sampler. The ALPHA samplers are compared to 24-hour denuder concentrations while the 2-week Radiello® samplers are compared with consecutive 1-week denuder concentrations. The Radiello® values were calculated from IL11 (Bondville) and OK99 (Stilwell). The Ogawa *versus* Nitrolux values are from the OK99 site

Absolute RPD	ALPHA	Radiello®	Ogawa
N	72	36	23
Max	605%	189%	81%
P_{90}	136%	100%	71%
P_{75}	80%	58%	54%
P_{50} (median)	28%	41%	44%
P_{25}	10%	18%	35%
P_{10}	5%	3%	19%
Min	0%	0%	6%
Mean	64%	47%	45%
Mean RPD	−29%	−40%	−39%
Median RPD	−2.4%	−37%	−44%

0.11 and 1.36 ± 0.10, respectively. The intercepts for the mean and median were −0.96 and −0.92, respectively and significantly different from zero ($P < 0.05$). The R^2 for the mean and median were 0.81 and 0.82, respectively, showing a fairly good linear fit between the reference method and the Radiello® concentrations measured.

The Radiello® passive samplers were found to be consistently biased low. The mean relative percent difference (MRPD) between the Radiello® and phosphorous acid coated denuders at IL11 and OK99 was −40% while the median RPD was −37%. The absolute RPD is shown in Table 2. The highest RPDs occurred at measured NH_3 concentrations below 0.75 μg m^{-3}. Similarly to the ALPHA samplers, the effective sampling rate provided by the manufacturer of the Radiello® is being evaluated in ongoing field and laboratory testing.

Ogawa. Ogawa PSD data were compared to data from both a continuous NH_3 analyzer and another PSD (*i.e.* the Radiello® PSD). For the 2008 study, the Stilwell, Oklahoma site continued to operate a continuous Pranalytica Nitrolux 200 trace level NH_3 analyzer which provided continuous estimates of ambient NH_3 concentrations to compare to the 2-week integrated passive estimates of ambient NH_3 concentrations. Similar comparison statistics between the passive and continuous instruments at the Stilwell, Oklahoma site were obtained in both 2007 and 2008. As previously reported for 2007 for 12 paired observations (3-week integrated), the correlation coefficient, R, was 0.74, with the Nitrolux study mean concentration (2.6 ppb or 1.8 μg m^{-3}) higher than the passive sampler study mean concentration (1.9 ppb or 1.3 μg m^{-3}).[16] In 2008, for 11 paired observations (2-week integrated), the correlation coefficient, R, was 0.55, with the Nitrolux study mean concentration (2.6 ppb or 1.8 μg m^{-3}) again higher than the passive sampler study mean concentration (1.6 ppb or 1.1 μg m^{-3}). Fig. 6 displays RMA regression for the 2007 and 2008 Ogawa passive data (3-week and 2-week integrated values) and the continuous Nitrolux data (3-week and 2-week means). The slope is 0.64 and the R^2 value is 0.44. Table 2 shows the relative percent difference (RPD) summary statistics for all 23 paired observations between the Ogawa PSDs and the continuous Nitrolux analyzer. The Ogawa samplers were found to be consistently biased low.

Also in 2008, the U.S. EPA Region 6 collocated Ogawa PSDs with Radiello® PSDs at seven sites as part of the national NADP study coordinated by CAMD. The Radiello® PSDs were deployed and run as network samples. Overall, good comparisons were achieved with the collocated Ogawa and Radiello® PSDs (Fig. 7).

All study means were not statistically significantly different at the 95% confidence level, and the lower NH_3 concentration Farmington Airport and Navajo Lake 2008 study means were identical between the Ogawa and Radiello® PSDs. Please reference the Supplemental Material for additional detailed information regarding the passive NH_3 data collected at the Farmington Airport and Navajo Lake sites for 2007–2010.

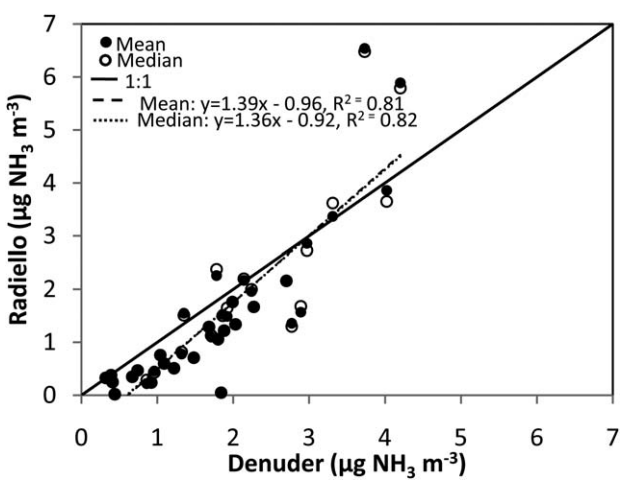

Fig. 5 Comparison of 2-week mean and median Radiello® samplers and denuder concentrations using reduced major axis regression (N = 36).

Precision results

This section presents detailed precision statistics for each of the three samplers as used in recent U.S. studies. Statistical methods used include relative difference, median absolute difference and coefficient of variation analyses.

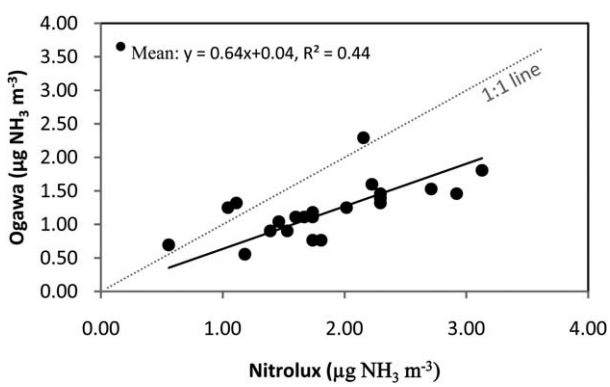

Fig. 6 Comparison of 2-week/3-week Ogawa *versus* Nitrolux NH_3 concentrations using reduced major axis regression (N = 23); 2007 and 2008 data.

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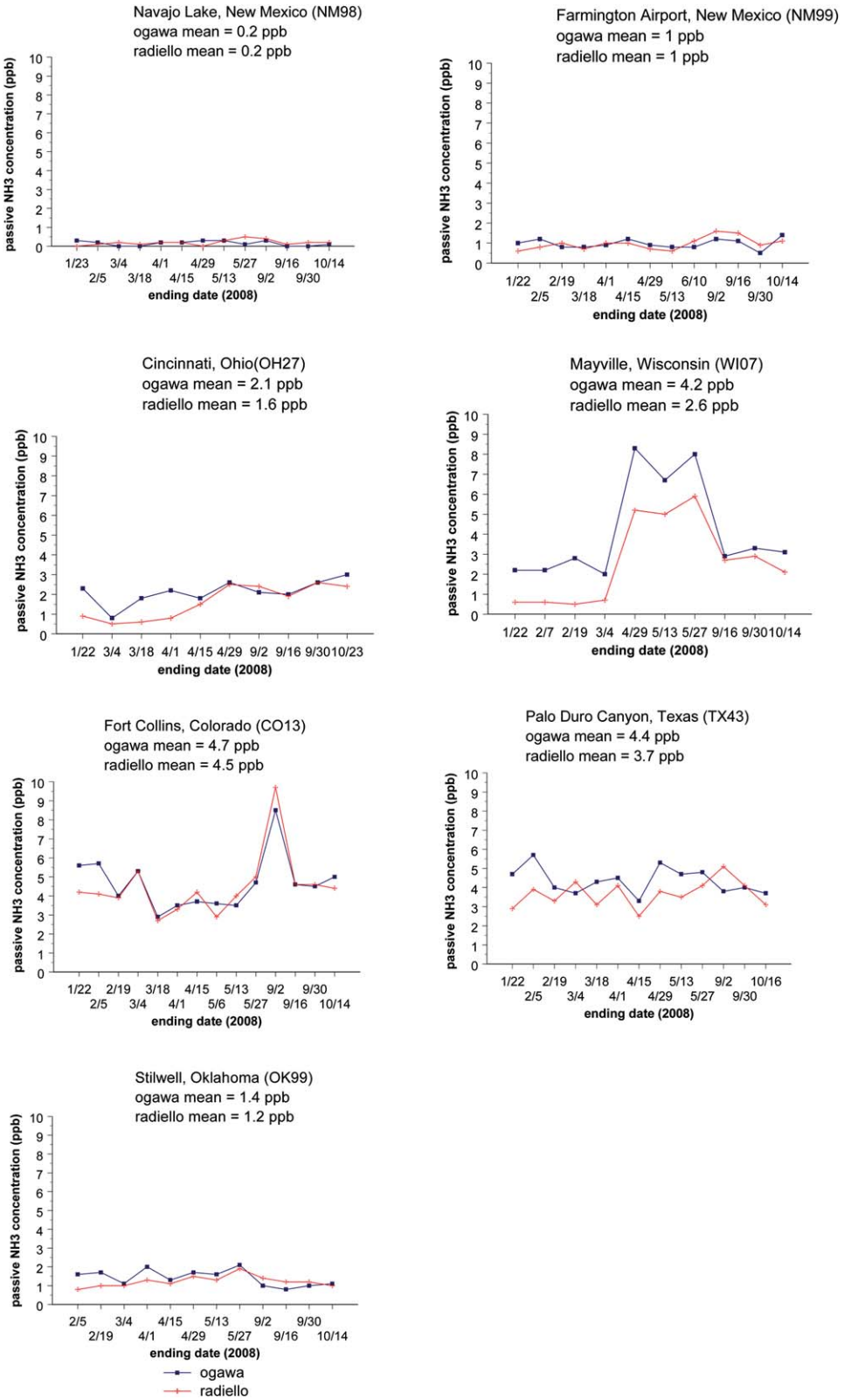

Fig. 7 Passive NH_3 data time series for the seven collocated Ogawa/Radiello® PSD sites in the 2008 U.S. EPA national study; 2-week integrated samples.

ALPHA. The ALPHA results presented in Tables 1 and 3 are calculated from year one of the CAMNet study. ALPHA field blanks were approximately double the laboratory blank, indicating that transport to and from the field sites contributed the same degree of contamination as laboratory procedures.

ALPHA field blanks (Table 3) were generally low with batchwise variability yielding a limit of detection (L_D) ~ 50.0 μg NH_4^+-N L^{-1}. The median L_D is equivalent to 0.24 and 0.12 (μg NH_3 m^{-3}) in air for 1 and 2 week exposures, respectively, at 25 °C. Sampler precision, defined as the median absolute relative difference between duplicate samples, was 7%. As shown in Fig. 8a, RPD tends to increase with decreasing concentration below ≈ 1 μg NH_3 m^{-3}, reaching a median value of 30% for the 20 observations surrounding (10 above/10 below) the weekly detection limit of 0.24 μg NH_3 m^{-3}. It should be noted that a number of the ALPHA sites within CAMNet were located in relatively close proximity to animal production facilities and fertilized crops. For this reason, the distribution of concentrations measured by the ALPHA sampler includes higher concentrations than measured by the Radiello® and Ogawa samplers. Because the RPD varies with concentration, this should be noted when comparing precision results among the three PSDs.

Radiello®. The detection limit for the Radiello® samplers was calculated using eqn (4). The Radiello® median detection limit is 81.3 μg NH_4^+-N L^{-1}, which is approximately 0.16 μg NH_3 m^{-3} over a 2-week exposure. Only one field blank was shipped to each site, therefore the calculation was based on the standard deviation of each blank concentration for each site per sampling period. The Radiello® concentrations are not blank corrected for AMoN. Several sites within the network measure very low concentrations, at or below field blank concentrations, thus correcting for the field blank would result in a negative concentration. In addition, compared to the denuder concentrations, the uncorrected Radiello® is more accurate (RPDs for uncorrected and corrected are −29% and −44%, respectively). However, the NADP does provide the field blank concentration in their online database, should data users wish to blank-correct field data.

Field blanks were very low for the Radiello® samplers, typically less than 0.2 μg NH_3 m^{-3}. Fig. 9 shows the measured field blank concentrations. During the summer of 2008, the first summer of the AMoN special study, there was a spike in blank concentrations. It was determined that during shipment the plastic vials that held the samplers during transport would heat up and release NH_3. The NADP switched to glass vials with Teflon-lined lids for shipping all samplers and the field blank concentrations have remained low.

Table 3 Summary of field blank (FB) concentrations (μg NH_4^+-N L^{-1}) for each of the passive samplers. The ALPHA concentrations were measured during year 1 of CAMNet. The Radiello® field blank concentrations are for samples shipped between October 2007 and January 2011. The FB for the Radiello® and Ogawa concentrations do not include the contamination period during the summer of 2008

	ALPHA	Radiello®	Ogawa
n	288	1429	293
Max	329	156	111
P_{90}	116	109	51
P_{75}	81	86	38
P_{50}	47	62	30
P_{25}	25	39	26
P_{10}	12	31	25
Min	0	0	25

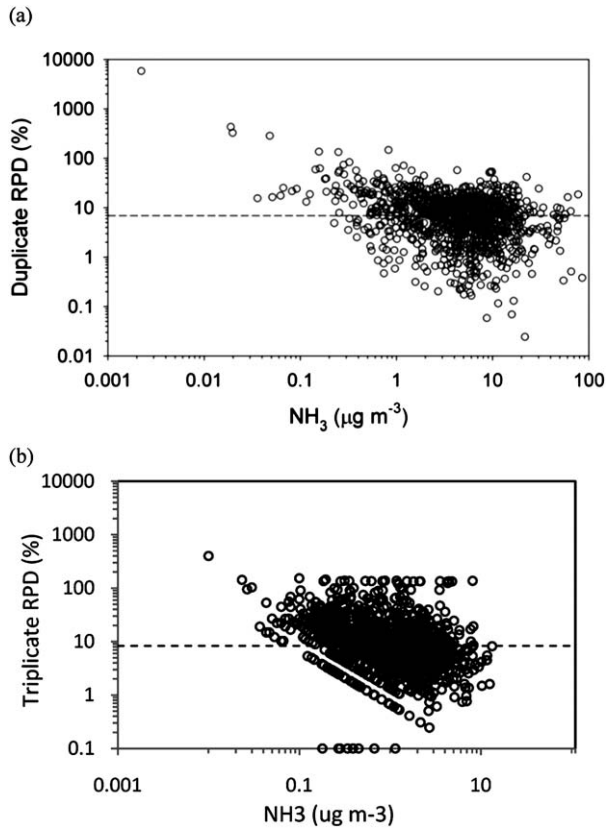

Fig. 8 Relative percent difference (RPD) of (a) duplicate collocated ALPHA samplers *versus* measured concentration (N = 1081) (b) triplicate Radiello® *versus* measured concentration (N = 1384). Dashed line represents median.

Precision of the Radiello® samplers was compared to the precision of duplicate denuders in Bondville. The duplicate denuders had a coefficient of variation (CV) of 6.0% which is similar to results presented elsewhere.[30] Radiello® precision was calculated as the mean CV(%) between the triplicate samplers for each sampling time period at each AMoN site. The average CV for all sites with more than 10 sampling time periods is approximately 10%. Additional discussion on the precision of each individual AMoN site is included in the supplemental information. Figure A-1 shows the CV for each site.

Ogawa. The detection limit of the Ogawa NH_3 PSD in the 2008 study, defined as twice the standard deviation of all valid field blank values, was 0.28 μg m^{-3} for 2-week integrated deployments which compared favorably with the 2007 study (0.18 μg m^{-3} for 3-week integrated deployments) and other passive NH_3 field studies.[32–34] Table 3 displays the complete summary statistics for all field blanks from the 2008 study without June-August as explained in the Discussion section below. The precision for the 2007–2009 Ogawa studies (Table 4) was reviewed by analysis of the absolute differences of data pairs from all sites, using the median absolute difference and 90th percentile of all of the absolute difference values per Sirois and Vet.[35] As seen in Table 4, similar precision statistics were

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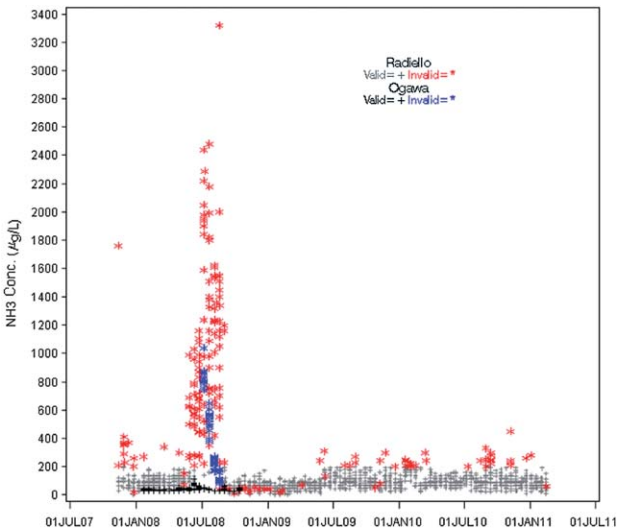

Fig. 9 Field blank concentrations (as liquid extracts) from AMoN Radiello® and Ogawa samplers. Between May 2008 and September 2008 blank concentrations spiked for both sampler types. Shipping the passive samplers in plastic vials during the warm months caused an increase in the blanks. Sample vials have been switched to glass with Teflon-lined lids and blank concentrations have been stable and low since September 2008.

recorded in all three years, including the statistics for three sites (Farmington Airport, Navajo Lake, and Stilwell) which participated in both the 2007 and 2008 studies. The Quapaw site also recorded similar precision statistics between two non-contiguous years (2007 and 2009). The passive NH_3 data in the 2007–2009 Ogawa studies had a median absolute difference between duplicate field samples of 0.1 ppb or 0.07 µg m^{-3} (0.2 ppb or 0.14 µg m^{-3} for the 2007 Quapaw study). Fig. 10 graphically displays the precision of the Ogawa NH_3 PSDs for the 2008 data, which compared favorably to the precision results reported earlier for the 2007 data.[16]

Discussion

The NADP has recently adapted the passive NH_3 monitoring network into the program, making the network an official subnetwork of the program. The goal of the NADP is to continue to increase the number of sites to improve the spatial coverage of the network. The network will provide the scientific community a baseline for NH_3 concentrations in several regions of the U.S. This will allow policy makers to analyze the effect regulatory emission reductions of NO_x and SO_x have on NH_3 concentrations and $PM_{2.5}$ mass in areas with large NH_3 emissions sources.

The accuracy of the ALPHA, Radiello® and Ogawa samplers, quantified as the median absolute relative percent difference compared to reference methods is 28%, 41%, 44%, respectively and the precision between duplicate samplers is 7%, 10% (triplicates), and 6%, respectively. These results assume that the NH_3 concentrations measured by the annular denuders were accurate for the ALPHA and Radiello® PSD's and the Nitrolux NH_3 concentrations were correct for the comparison with Ogawa PSD's. Lower NH_3 concentrations measured during the Radiello® and Ogawa studies may have caused the results to be less precise and result in lower accuracy than the ALPHA samplers. The ALPHA and Ogawa samplers were tested by the NADP and EPA's CAMD for their applicability in the AMoN, but were not able to produce the same results as EPA's ORD and Region 6 found in their respective passive NH_3 studies.

However, Region 6 ran additional Ogawa samplers in 2009 at the Bondville, IL site and found the Ogawa and Radiello® samplers produced similar results. Please reference the Supplemental Material for detailed information regarding the 2009 Bondville, IL study.

The three passive samplers provided reasonably precise and accurate ambient NH_3 data for each study area. While the

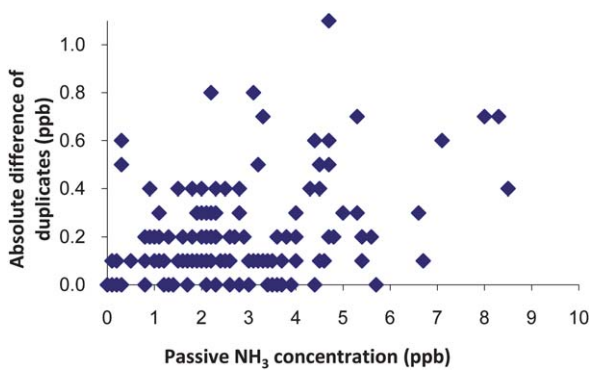

Fig. 10 Precision of the Ogawa NH_3 PSDs for the U.S. EPA Region 6 2008 passive NH_3 study.

Table 4 Precision statistics for EPA Region 6 passive NH_3 studies using Ogawa PSDs; analysis of absolute difference data pairs

# sites/areas	Year	N (data pairs)	Min. (ppb)	Max. (ppb)	Med. (ppb)	90th percentile (ppb)
7/Four Corners, Eastern Oklahoma[16]	2007; 3-week integrated samples	124	0	1	0.1	0.3
9/New Mexico, Colorado, Oklahoma, Texas, Wisconsin, Ohio	2008; 2-week integrated samples	145	0	1.1	0.1	0.46
3/Farmington Airport, Navajo Lake, Stilwell[16]	2007; 3-week integrated samples	54	0	0.4	0.1	0.2
3/Farmington Airport, Navajo Lake, Stilwell	2008; 2-week integrated samples	46	0	0.6	0.1	0.4
1/Quapaw[16]	2007; 3-week integrated samples July-December	16	0.1	1	0.2	0.75
1/Quapaw	2009; 3-week integrated samples July-December	15	0	0.7	0.1	0.26

ALPHA and Ogawa samplers are less expensive to purchase, the NADP has chosen the Radiello® for the national network in part due to their ease of preparation and extraction making them less labor intensive, and thus more cost effective, for a network-wide deployment. In addition, the sampler variation between triplicates was approximately 10%, providing confidence in moving to a single sampler deployed at each site. To ensure the precision remains consistent, the NAPD will continue to deploy triplicates at 5% of the network sites. The ALPHA and Ogawa samplers have shown acceptable precision and accuracy during the regional studies where NH_3 concentrations were typically higher. For any new study, it is recommended that any passive sampler be deployed in triplicate with travel blanks for several sampling periods to measure the error in precision and method technique. Inter-comparison studies between the three samplers promote the use of data from all samplers corrected for any biases in an integrated network-type dataset. In this study, even though the samplers were not compared directly to each other, the samplers were individually compared to a reference method and their respective biases can therefore be quantified. The ORD found the ALPHA samplers to be biased low (median RPD) by 2.4%, while the Radiello® samplers were 37% lower than the denuders and the Ogawa samplers were 44% lower than the Nitrolux.

An important lesson learned from the 2008 NADP study was to not allow plastic shipping vials for PSDs to get too warm. The NADP national study and the EPA Region 6 regional study both used the plastic vials, and the NADP used multi-day ground shipping rather than overnight or second day air shipping, resulting in the warm containers during shipping and therefore, elevated travel blank concentrations. This resulted in several months of invalidated data during the warmer summer months (*i.e.* late June-late August 2008) due to the plastic vial emission of ammonia (from the heated plastic) into the PSDs. The laboratory switched to all glass vials with Teflon-lined lids and immediately saw an improvement (Fig. 9). The U.S. EPA Region 6 Houston Laboratory has also begun using glass vials as an alternative to plastic vials, and removed the contamination issue also (again, Fig. 9). The glass vials can also be reused by washing the vials with deionized water at least three times followed by drying in an ammonia-free environment.

Conclusions

Passive sampling of ambient NH_3 should continue to be explored in the United States. These three studies using three different passive sampling devices show they are reliable, fairly accurate even at lower concentrations, and easy to use. The inter-comparison studies between passive samplers described in this article allow data users to merge datasets, accounting for biases between sampler types, with some confidence that the quality of the data is comparable.

In October, 2010 the NADP approved the AMoN as an official sub-network within NADP. Though this study shows that all three samplers performed adequately for their respective applications, the Radiello® has been chosen for use in the AMoN. While each study showed the passive samplers can provide reliable results, there were some factors to consider when anticipating a deployment at over 100 sites. The network will operate with one Radiello® deployed at each site for 2 weeks and 5% of the network will receive triplicate Radiello® samplers for quality control (QC), each bi-monthly sampling period. The NADP AMoN study shows that the passive samplers can be used in a national network. The goal of the initiative is to expand the passive network into 100+ sites within 3–5 years with support from other federal agencies, states, universities and Native American tribes.

Finally, plastic vials should not be used for packaging or shipping passive NH_3 samplers. This study verified shipment in glass vials with Teflon-lined lids results in very low travel blank concentrations.

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