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This study compared ambient ammonia concentrations measured by the National Atmospheric Deposition Program's Ammonia Monitoring Network (AMoN) with active denuder samplers at five Clean Air Status and Trends Network (CASTNET) sites for 1-year.
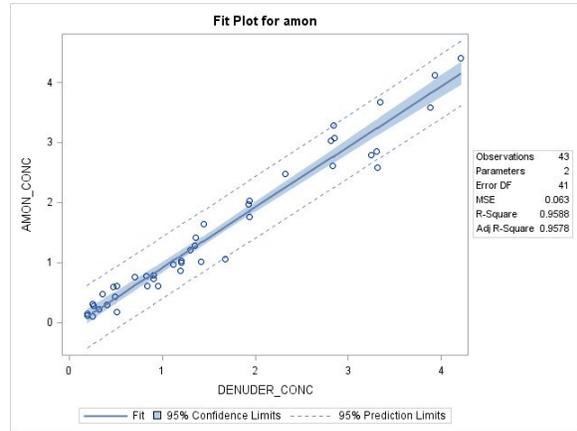
For one year, passive ammonia samplers were co-located with two ammonia active samplers at five CASTNET sites. The passive samplers are used by the National Atmospheric Deposition Program (NADP) Ammonia Monitoring Network (AMoN) at more than 50 monitoring sites. The results of this study demonstrate that the AMoN data may be used with confidence by data users, while additional design modifications should be made before the MPPD are deployed within a network. Dry deposition estimates from routine network measurements of ammonia concentrations, such as AMoN, will improve estimates of total nitrogen loading to sensitive ecosystems and may be used to validate air quality models.

A statistical comparison of active and passive ammonia measurements collected at Clean Air Status and Trends Network (CASTNET) sites

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Abstract

Atmospheric concentrations of ammonia (NH_3) are not well characterized in the United States due to the sparse number of monitors, the relatively short lifetime of NH_3 in the atmosphere, and the difficulty in measuring non-point source emissions such as fertilized agricultural land. In this study, we compare measured weekly concentrations of NH_3 collected by two denuder systems with a bi-weekly passive NH_3 sampler used by the National Atmospheric Deposition Program's (NADP) Ammonia Monitoring Network (AMoN). The purpose of the study was to verify the passive samplers used by AMoN and characterize any uncertainties introduced when using a bi-weekly versus weekly sampling time period. The study was conducted for 1-year at five remote Clean Air Status and Trends Network (CASTNET) sites. Measured ambient NH_3 concentrations ranged from 0.03 µg NH_3 m^{-3} to 4.64 µg NH_3 m^{-3} in upstate New York and northwest Texas, respectively, while dry deposition estimates ranged from 0.003 kg-N ha^{-1} wk^{-1} to 0.47 kg-N ha^{-1} wk^{-1}. Results showed that the bi-weekly passive samplers performed well compared to annular denuder systems (ADS) deployed at each of the five CASTNET sites, while the MetOne Super SASS Mini-Parallel Plate Denuder System (MPPD) was biased low when compared to the ADS. The mean relative percent difference (MRPD) between the ADS and MPPD and the ADS and AMoN sampler was -38% and -9%, respectively. Precision of the ADS and MPPD was 5% and 13%, respectively, while the precision of the passive samplers was 5%. The results of this study demonstrate that the NH_3 concentrations measured by AMoN are comparable to the ADS and may be used to supplement the high-time resolution measurements to gain information on spatial gradients of NH_3, long-term trends and seasonal variations in NH_3 concentrations.

Keywords

Ammonia; Long-term monitoring; Nitrogen budget; Dry deposition; Passive sampling

1. Introduction

United States monitoring networks, such as the U.S. Environmental Protection Agency's (EPA) CASTNET and the NADP's National Trends Network (NADP/NTN), Atmospheric Integrated Research Monitoring Network (NADP/AIRMoN), and AMoN provide measurements that allow data users to evaluate trends in sulfur and nitrogen pollutants. In the United States, total sulfur and nitrogen deposition fluxes have historically been reported using measurements from NADP's wet deposition networks (NTN and AIRMoN) plus estimates of dry deposition from CASTNET or model output, where measurements are not available. Ambient pollutants that are not routinely measured by monitoring networks and areas where there are spatial gaps between monitoring sites create uncertainties in reported deposition estimates. Gaseous NH_3, peroxyacetyl nitrate (PAN), and organic nitrogen contribute to particle formation, critical load exceedances and acid deposition, but the contributions of the individual pollutants to the total nitrogen budget have not been verified across large spatial scales due to the lack of measurements. This paper presents the results from a field inter-comparison study between passive and active NH_3 measurement methods that may be used in routine monitoring networks.

Ammonia is known to be a significant contributor to secondary particle formation, the eutrophication of sensitive ecosystems and the acidification of soils.[1,2,3,4] As the most abundant alkaline gas in the atmosphere, NH_3 will quickly react with acidic aerosols to form fine particulate matter ($PM_{2.5}$).[5,6,7] Gaseous NH_3 reacts with sulfuric acid (H_2SO_4) or nitric acid (HNO_3) to form secondary aerosols such as ammonium bisulfate ($(NH_4)HSO_4$), ammonium sulfate ($(NH_4)_2SO_4$), or ammonium nitrate (NH_4NO_3) which contribute to respiratory illness and premature death.[8,9] Furthermore, the eutrophication of natural water bodies from run-off or deposition of ammonium (NH_4^+) can lead to reductions in water quality, biodiversity loss, and increases in algal blooms.[10,11,12]

The largest sources of NH_3 emissions include agriculture (about 80%), fires (9%) and fossil fuel combustion from mobile and stationary sources (4%).[13,14,15] Emissions from non-point sources, such as agriculture, are difficult to characterize due to the size of the area where emissions occur and seasonal variability. Ammonia concentrations are typically highest in the spring and summer due to agriculture activities, such as fertilizer application, and higher temperatures leading to a shift toward the gas phase in the ammonium nitrate (NH_4NO_3) equilibrium.[16,17,18,19,20,21]

Increases in population and the demands that creates on agricultural systems have led to increases in total reduced nitrogen deposition ($NH_x = NH_4^+ + NH_3$) in the Midwest and Central US.[14,22] Ammonia that is not deposited contributes to secondary particle formation. The US EPA published the final rule for the PM2.5 National Ambient Air Quality Standard (NAAQS) in January 2013. The primary standard for PM2.5 requires an area to not exceed a 3-year average $PM_{2.5}$ concentration of 12 $\mu g\ m^{-3}$. The secondary standard, used to protect public welfare, remained at 15 $\mu g\ m^{-3}$. In general regard for PM, new approaches may be considered for reducing $PM_{2.5}$ in areas that may exceed the standard, including reducing NH_3 emissions. Vayenas et al.[23] showed that in western PA a 50% reduction in NH_3 would lead to a 29% reduction in inorganic $PM_{2.5}$.

Until recently, monitoring networks did not measure ambient NH_3 concentrations and currently there are no networks measuring the flux of gaseous NH_3. Many factors contribute to the difficulty in measuring NH_3. Concentrations and deposition fluxes have high spatial and temporal variability, and, in sulfur-rich areas, NH_3 will quickly react to become $(NH_4)_2SO_4$.[14] In addition, NH_3 dry deposition fluxes are bi-directional, meaning a surface can become a sink or a source.[24] Until recently, the Community Multi-Scale Model (CMAQ) estimated NH_3 flux using a uni-directional algorithm. This typically led to over predicting the flux of NH_3 in areas where there is emission or re-emission of NH_3 from the surface. CMAQ now includes a bi-directional air-surface exchange rate for NH_3.[25] The bi-directional flux option is not included in routine model runs at this time. However, EPA is looking at ways to use measured NH_3 concentrations to estimate the bi-directional flux. There is an increasing need to be able to validate the air quality and deposition models (such as CMAQ) as NAAQS are tightened and secondary standards are considered. It is estimated that in some regions of the US NH_3 accounts for ~20% of dry nitrogen deposition.[26]

To address the need for routine NH_3 measurements at current monitoring locations, the EPA's Clean Air Markets Division (CAMD), EPA's Office of Research and Development (ORD), and EPA's Office of Air Quality Planning and Standards (OAQPS) developed this study to compare passive and active sampling methods for ambient NH_3 measurements. Five CASTNET sites were selected for the study based on site operator capabilities, variability in estimated NH_3 concentrations, participation in AMoN, and site infrastructure.

1.1 Clean Air Status and Trends Network (CASTNET)

An overview of CASTNET can be found in Holland et. al.[27] and Sickles et. al.[28]. Additional information including quality assurance and annual reports is available at: http://www.epa.gov/castnet. Briefly, CASTNET is a 90 site long-term, rural monitoring network that has been operated by the US EPA since 1987. Currently, the National Park Service (NPS) and Wyoming's Bureau of Land Management (BLM) operate 25 and 5 CASTNET monitoring stations, respectively, with EPA operating the balance of sites. CASTNET collects weekly integrated measurements of particles and gases on a 3-stage filter pack mounted on a 10 m tower. The weekly filter packs are analyzed for sulfur dioxide (SO_2), HNO_3, particulate sulfate (SO_4^{2-}), particulate nitrate (NO_3^-), NH_4^+, chloride (Cl^-) and base cations. CASTNET is the only network in the US that estimates dry deposition of sulfur and nitrogen species. Dry deposition fluxes are estimated as the product of modeled deposition velocities and measured pollutant concentrations. Dry deposition velocities are calculated using the Multi-Layer Model (MLM) described by Finkelstein et al.[29] and Myers et al.[30]. The MLM does not currently have the capability to calculate NH_3 deposition velocities; however, CMAQ provides gridded NH_3 deposition velocities, which may be used for estimating NH_3 fluxes.

1.2 Chemical Speciation Network (CSN)

The Chemical Speciation Network (CSN) is funded through the EPA but operated by individual states. The CSN began in 1999 to monitor particulates based on health effects; therefore, most sites are located in urban areas. The goal of the network is to monitor speciated PM2.5 for compliance determinations

with the NAAQS. Twenty-four hour speciation samples are collected at more than 200 CSN sites on a varying frequency depending on the data application requirements of the individual states. CASTNET and CSN collect sulfur and nitrogen species on a filter; however, unlike the CASTNET filter pack, the CSN uses a cyclone with a 2.5 μm size selection cut point.

1.3 Ammonia Monitoring Network (AMoN)

The NADP is comprised of federal, state, local, and tribal organizations as well as universities and private companies. They operate three national wet deposition networks and two ambient concentration networks throughout the US and Canada. The newest network, AMoN, began in 2007 as a pilot network and was initiated as an official NADP network in 2010. There are currently more than 60 AMoN sites operating in the US. Approximately two-thirds of the AMoN sites are collocated with CASTNET. The goal of AMoN is to measure ambient concentrations of NH_3 at as many sites throughout the US as possible in a cost-effective network. Each AMoN site measures a 2-week integrated NH_3 concentration by deploying a Radiello® passive sampler coated with phosphorous acid (H_3PO_3) to absorb NH_3. The Radiello® passive samplers were selected for the network based on their ease of use, reliability, precision, accuracy and relatively low-cost.[31]

2. Experimental

Five CASTNET sites were selected for the CASTNET NH_3 inter-comparison study. The five sites were selected based on location, collocation with an AMoN sampler, site operator and site sponsor interest and regional representation. The CASTNET sites that participated in the study are shown in Table 1. An ADS, a Met One Super SASS using a MPPD and the AMoN sampler were co-located with the CASTNET filter pack. The ADS and MPPD samples were deployed in two consecutive one-week periods to coincide with the AMoN schedule. In addition to the 5 site study, a 4-stage filter pack was designed and tested to determine if the addition of a H_3PO_3 coated filter to the 3-stage CASTNET filter pack would capture NH_3 without interfering with the long-term CASTNET measurements. Detailed information about each method is provided below.

Table 1 Ammonia measurement methods for the five site study.

CASTNET Site ID/NADP Site ID	Site Name	AMoN	Single ADS (NHx only)	Full ADS	Super SASS MPPD	Super SASS Ion Module	CASTNET filter pack
ARE128/PA00	Arendtsville	x		x	x	x	x
CHE185/OK99	Cherokee Nation	x		x	x	x	x
CTH110/NY67	Connecticut Hill	x	x				x
PAL190/TX43	Palo Duro	x	x				x
ROM206/CO88	Rocky Mountain NP – Longs Peak	x		x	x	x	x

Figure 1 Map of ACCS site locations. Green stars indicate the site operated the full suite of measurements while the orange stars show the sites that operated the single denuder systems and did not include a Super SASS ion module. CASTNET sites are shown as light blue circles and AMoN sites are shown as black triangles. *(Created December 2, 2014)*
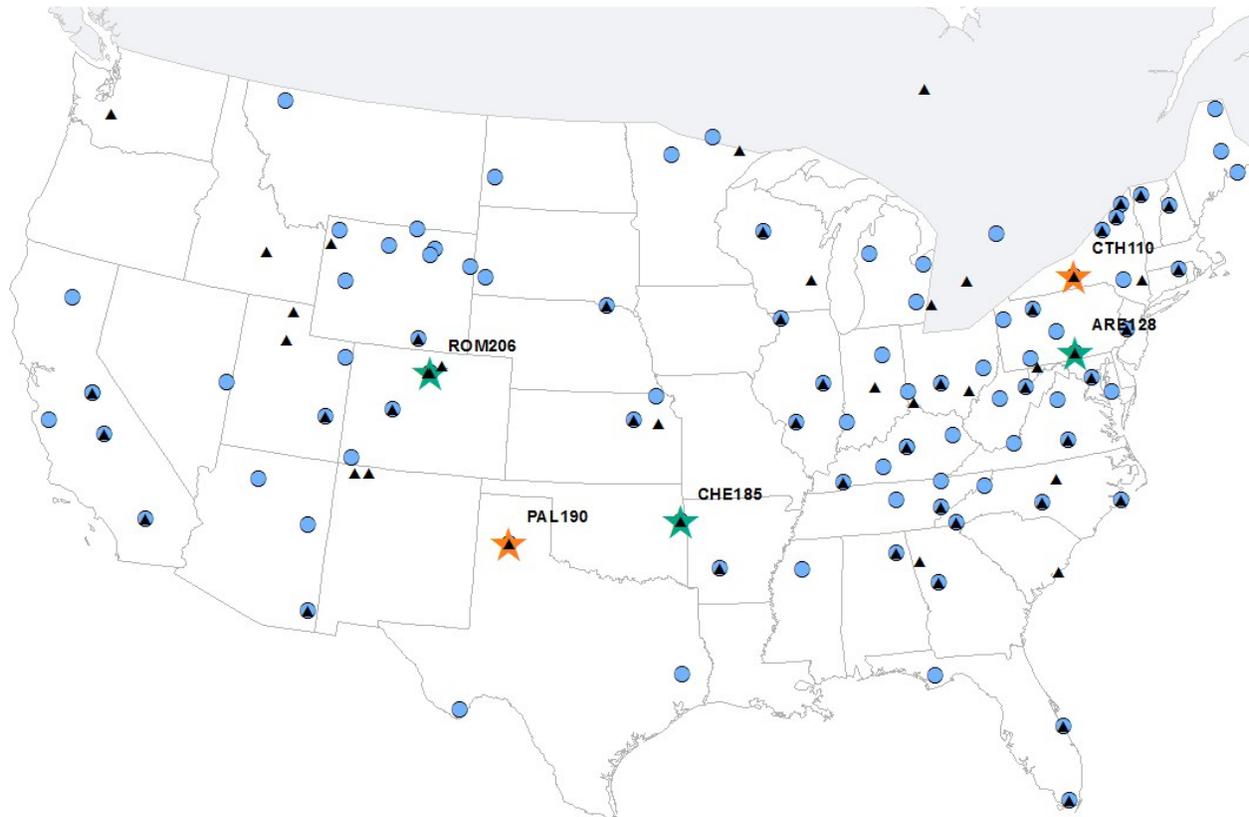
The Arendtsville (ARE128/PA00) CASTNET site began operation in 1988 and is located in the southeast region of Pennsylvania. The site is located between fruit orchards at the Pennsylvania State University Fruit Research and Extension Center. The Cherokee Nation Stilwell CASTNET site (CHE185/OK99) has been operating since 2002. The site is located in an agricultural area in eastern Oklahoma. The tribe also operates an NCore station at this location (http://www.epa.gov/ttnmain1/amtic/ncore/index.html). The Connecticut Hill CASTNET site (CTH110/NY67) is located in upstate New York in a forested area. This site has been operating in the CASTNET program since 1987 and is collocated with an AIRMoN site. The Palo Duro CASTNET site (PAL190/TX43) is located in a prairie region in northwest Texas on land owned by the Texas A&M Agrilife Research and Extension Center. The site has been in operation since 2007. The Rocky Mountain CASTNET site (ROM206/CO88) is situated at just over 2,700 m elevation in Rocky Mountain National Park. This is a co-located site with the NPS-sponsored CASTNET site (ROM406). The EPA-sponsored site (ROM206) started in 2001 while the NPS-sponsored site began in 1994. A map of the site locations is shown in Figure 1.

2.1 CASTNET 4-stage filter pack

Routine CASTNET measurements are made with a three-stage filter pack using a Teflon filter for collecting particulate SO_4^{2-}, NO_3^- and NH_4^+; a nylon filter for collecting HNO_3 and SO_2 (as SO_4^{2-}) and a K_2CO_3-impregnated cellulose filter for collecting the remaining SO_2.[32] For this study, a 4th-stage was added to the current 3-stage design to attempt to capture gaseous NH_3. Several iterations of the design were tested at the AMEC Environment & Infrastructure, Inc. laboratory in Gainesville, FL. The first method included adding a H_3PO_3-impregnated cellulose filter in the 4th spot, which was extracted using dionized water (DIW). Next, a citric acid-impregnated cellulose filter was placed in the 4th spot and extracted using DIW. Finally, the K_2CO_3-impregnated cellulose filter in the 3rd spot was replaced with a H_3PO_3-impregnated cellulose filter. The results were poor for the two 4-stage configurations tested in that no NH_3 was collected on the 4th filter. Replacing the K_2CO_3-impregnated cellulose filter with a H_3PO_3-impregnated cellulose filter allowed for the NH_3 to be collected, but it is not viable to remove longer-term filter pack-based SO_2 measurements from CASTNET in favor of NH_3 measurements. Therefore, a 4-stage filter pack was never deployed during the inter-comparison study at the 5 CASTNET sites. Results from the 4-stage filter pack testing phase can be found in the ACCS summary report here: http://www.epa.gov/castnet.

2.2 URG annular denuder system

ADS based on a modified EPA Compendium Method IO-4.2[33] were used as the reference method for this inter-comparison study. Duplicate URG annular denuders (URG Corp., Chapel Hill, NC) with Savillex filter packs outfitted with Teflon-coated cyclones with a 2.5 µm size selection cut-point were prepared, shipped and analyzed at the AMEC laboratory. Three sites were selected to deploy a full system with 2 denuders (acidic and basic) and a 2-stage filter pack while the two additional sites deployed a modified system with one denuder and a 2-stage filter pack for analysis of NHx-only.

The dual denuder system included an acidic (H_3PO_3-coated) denuder for capturing NH_3 behind a basic denuder coated with sodium carbonate (Na_2CO_3) for capturing HNO_3 and SO_2 with a 2-stage filter pack

consisting of a nylon filter for collecting particulate SO_4^{2-} and particulate NO_3^- and a H_3PO_3 impregnated cellulose filter for collecting NHx. The single denuder system included a H_3PO_3-coated denuder and a two-stage filter pack (nylon filter for collecting NH_4^+ and a H_3PO_3 impregnated cellulose filter for collecting NHx). The acidic denuders were analyzed by Automated Colorimetry (AC) using DIW as the extraction fluid (EPA method 350.1).[34] The basic denuders were extracted using DIW and analyzed by ion chromatography (IC). The nylon filter was extracted with DIW and analyzed by IC for the dual denuder systems or analyzed by AC for all filters. The H_3PO_3 impregnated filter was extracted using DIW and analyzed by AC.

All five sites deployed the ADS for two consecutive 1-week periods to coincide with the AMoN schedule. The ADS was placed within a modified CASTNET rain shield at 10 m. Air flow through the ADS was set at 3 lpm with a mass flow controller. Flow was logged with CR3000 Mircologgers (Campbell Scientific, Logan, UT) already present at the CASTNET sites. The site operators removed the ADS after each sampling period, capped the ends, and shipped the denuders and filters back to the AMEC laboratory.

2.3 Radiello® passive sampler

The passive samplers were deployed by the NADP as part of the AMoN network.

The Radiello® passive samplers are commercially available through Sigma Aldrich and manufactured by Fondazione Salvatore Maugeri (http://www.radiello.com). Each sampler is comprised of a diffusive body (60 mm height x 16mm diameter, 1.7 mm thickness, 25 ± 5 µm average porosity) and a cylindrical sampling cartridge (60 mm length x 4.8 mm) impregnated with H_3PO_3 by the manufacturer. Additional information about the Radiello® samplers used in the AMoN can be found in Puchalski et. al.[31].

Radiello® samplers are prepared, shipped, and analyzed by the NADP Central Analytical Laboratory at the Illinois State Water Survey (ISWS). The samplers are shipped in clean glass jars with Teflon-lined lids. A single travel blank is placed in a separate jar and is never opened by the site operator. Both jars are shipped in a sealed bag with a scavenging filter coated with 10% citric acid in methanol. After the Radiello® samplers are returned to the lab from the site operator, they are analyzed by Flow Injection Analysis (Hach/Lachat Analytics, Inc. Quik Chem 8000 Milwaukee, WI) following EPA Method 350.1.[34] The NADP reports an instrument detection limit of 6 µg $NH_4^+L^{-1}$.

2.4 Super SASS system

Mini-parallel plate denuders (MPPDs) were manufactured by Met One and designed to fit inside the standard canister used by the Met One Super SASS system, a system used at CSN sites for 24-hour measurements. The Super SASS speciation sampler is an 8-channel sampler which allows for varied combinations of pollutants and sequential sampling. A Teflon-coated cyclone with a 2.5 µm size selection cut-point was used for the Super SASS system. The MPPD's were coated with H_3PO_3 at the AMEC laboratory. A H_3PO_3-impregnated cellulose filter followed the MPPD to collect particulate NH_4^+ and any remaining NH_3. The MPPD and filter were analyzed by AC using DIW for extraction. For this study, the MPPDs were deployed for two consecutive 1-week periods to match the AMoN schedule.

The Super SASS system was placed on a second 10 m tilt down tower at the 3 sites selected for MPPD sampling. The Super SASS flow system was calibrated prior to deployment. The target flow rate was 6.7 lpm and verified to within 5%.

2.5 Sample Schedule

The ADS and Super SASS modules were deployed for 2 consecutive one-week periods every 6 weeks beginning on August 31st 2010 to coincide with the AMoN sample schedule (deployed every two weeks). CASTNET filter packs were also deployed on their routine 1-week schedule. The full ACCS schedule is shown in Figure 2. The AMoN site at Rocky Mountain National Park (CO88) did not begin until May 11, 2011 so there were only 4 sampling periods when the ADS and Super SASS were co-located with AMoN. There were a total of 10 sampling periods for the other four sites.

Figure 2 Sample schedule for the inter-comparison study. CASTNET and AMoN samplers were deployed on a one-week and two-week schedule, respectively. This table shows the weeks when the ADS and Super SASS were deployed.
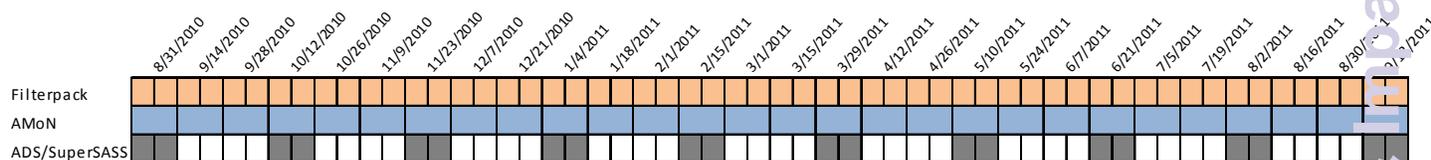
3. Results

Two week ambient ammonia concentrations measured by the passive samplers ranged from 0.03 µg NH_3 m^{-3} to 4.64 µg NH_3 m^{-3}. The concentrations were typically high in the spring and low during the winter months which is consistent with results from other ammonia measurement studies.[35,36]

3.1 Laboratory and Field Blanks

Method blanks were run during each sample batch for each two week sampling period (N=40). The method blanks were analyzed by AMEC by running the reagents for each laboratory analysis. The median method blank was 0.0041 µg N for the ADS and 0.00405 µg N for the MPPD (N=24).

Laboratory blanks were analyzed after the ADS and MPPD were prepared, but before shipping. Laboratory blanks were analyzed each sampling period for the ADS and MPPD. The median laboratory blank was 0.0264 µg N for the ADS (N=10) and 0.0068 µg N for the MPPD (N=9).

In addition to the method and laboratory blanks, one field blank was shipped to each site for each method for 2-weeks during the 12-month study. ADS field blanks ranged from 0.017 µg NH_3 m^{-3} on 3/29/2011 to 0.080 µg NH_3 m^{-3} on 5/10/2011 at ARE128, PA and CHE185, OK, respectively. The median ADS field blank concentration was 0.047 µg $NH_3 m^{-3}$ (N=5). The median MPPD field blank concentration was 0.0037 µg NH_3 m^{-3}. The MPPD field blank concentrations from CHE185/OK99 and ROM206/CO88 were below the detection limit.

AMoN sites received one travel blank during each sampling time period (1 travel blank for each 2-week sample period). Radiello® field blank concentrations were between 0.04 and 0.39 μg NH_3 m^{-3} with a median concentration of 0.15 μg NH_3 m^{-3} (N = 44) during the study sampling period. The median travel blank concentration for all AMoN sampling periods for the 5 sites was 0.15 μg NH_3 m^{-3} (N=121) indicating the 10 sampling periods selected for the study was a good representation of the whole dataset.

Field blanks were higher for the AMoN samplers than each of the denuder methods. The AMoN field blanks are not used to blank correct the ambient concentrations by the NADP, but the field blank concentrations are available in the public dataset. In 2013, the NADP modified the AMoN protocol by reducing the number of travel blanks from one per site per sampling period to one per site every fourth sampling period. The AMoN field blanks are used for network-wide quality control. The NADP assigns a quality rating code of 'd' to any samples exceeding 0.2 mg-N L^{-1}, which is the AMoN reporting limit. During this study, the field blanks were all below the reporting limit and approximately 20% of the ambient samples were below 0.2 mg-N L^{-1}.

While NADP does not blank correct the AMoN dataset, a comparison between uncorrected AMoN samplers versus the ADS and field blank corrected passive samplers versus the ADS is shown below. There is greater uncertainty in the field blank corrected values due to the uncertainty in the concentrations reported below the detection limit.

Table 2 shows the field blank concentrations from the 5 sites for the Radiello® samplers. The highest field blank concentrations were measured at PAL190/TX43.

Table 2 Field blank NH_3 concentrations (μg NH_3 m^{-3}) from the 5 sites as measured by the passive samplers from the bi-weekly sample periods. Results include the minimum, 10th percentile, median, 90th percentile and maximum concentrations measured. N is the number of field blanks from the 10 sampling weeks. The ADS and MPPD results are from a single field blank shipped to each site during the sample period (N=1).

	AMoN						ADS	MPPD
Site	Minimum	P10	P50	P90	Maximum	N Blanks	Field Blank	Field Blank
ROM206/CO88	0.07	0.091	0.15	0.17	0.18	4	0.028	>0.0037
CTH110/NY67	0.04	0.067	0.10	0.15	0.17	10	0.047	
CHE185/OK99	0.09	0.09	0.14	0.20	0.24	10	0.080	>0.0037
ARE128/PA00	0.09	0.09	0.17	0.23	0.23	10	0.017	0.0097
PAL190/TX43	0.07	0.12	0.21	0.31	0.39	10	0.054	

3.2 Precision of NH_3 sampling methods

The precision of the NH_3 samplers is reported here as the median coefficient of variation (CV) between the duplicate ADS and duplicate Super SASS MPPD and triplicate passive samplers for each site. The average concentration, standard deviation, and precision is shown for each site in Table 3 for the sampling time period. AMoN precision is not shown for sample times outside of the inter-comparison

study period (ie. CV was calculated for weeks 1-2, but not for weeks 3-6 when the ADS and MPPD were not deployed).

The average ADS precision (median CV) for the five sites was 5%. Ammonia concentrations, as measured by the ADS, ranged from 0.02 to 5 µg NH_3 m^{-3} during the measurement period at CHE185, OK and ARE128, PA, respectively. The average concentration as measured by the ADS was 1.40 µg NH_3 m^{-3}.

The average precision of the triplicate AMoN passive samplers was 5% and the average concentration was measured as 1.35 µg NH_3 m^{-3}. This is slightly better than the overall AMoN network precision during the same time period (August 2010 – September 2011), where the average concentration for the network was 1.1 µg NH_3 m^{-3} and the average CV was 9%. The increase in triplicate sampler variability across the network is expected due to lower ambient concentrations.

Table 3 Precision values calculated from duplicate and triplicate samplers at the sampling sites during the inter-comparison study.

NADP ID	CASTNET ID	AMoN			ADS			MPPD		
		Concentration (µg/m³)	Standard Deviation	Precision (%)	Concentration (µg/m³)	Standard Deviation	Precision (%)	Concentration (µg/m³)	Standard Deviation	Precision (%)
NY67	CTH110	0.35	0.07	13	0.46	0.056	4			
PA00	ARE128	1. 25	0.062	3	1.37	0.10	5	0.79	0.048	6
OK99	CHE185	1.38	0.12	4	1.46	0.11	3	0.88	0.17	15
TX43	PAL190	3.23	0.14	4	3.34	0.14	2			
CO88	ROM206	0.53	0.02	2	0.344	0.049	13	0.19	0.041	18
Averages		**1.35**	**0.08**	**5**	**1.40**	**0.090**	**5**	**0.61**	**0.084**	**13**

The average NH_3 concentration measured by the ADS was approximately double the concentration measured by the MPPD at the 3 sites. Precision of the duplicate Super SASS MPPD was 13%, approximately double the variability of the ADS. The average precision of ADS from the same three sites was 7%. The average NH_3 concentration as measured by the MPPDs ranged from 0.20 µg NH_3 m^{-3} at ROM206 to 0.81 µg NH_3 m^{-3} at CHE185.

3.3 Accuracy and comparability of passive and MPPD measurements

Accuracy of the passive samplers was assessed by comparing the 2-week measurement to the two 1-week average annular denuder concentrations and the two 1-week MPPD measurements were compared to the two 1-week ADS measurements (Table 4). The accuracy of the AMoN samplers as compared to the annular denuders was similar across the five study sites with no bias. There was a consistent low bias in the MPPDs as compared to the annular denuders at each site.

Figure 3 shows the time series results from each site for the annular denuders, passives and MPPDs (where they were deployed). The ADS and MPPD measurements were averaged to two-week concentrations for comparison to the AMoN passive samplers. The accuracy of the passive samplers was consistent across all measured NH_3 concentrations.

Figure 4 shows the reduced major axis (RMA) regression results, combining data from all five sites. RMA regression was used to estimate accuracy of each sampler at each site to account for errors in the reference method (ADS).[37] The slope and intercept for the AMoN sampler versus the ADS across the five sites was 1.03 and -0.13, respectively. The best fit line had an r-squared of 0.95 and a Mean Square Error (MSE) of 0.063 for the AMoN versus ADS regression. For comparison (not shown), the slope and intercept for the travel blank corrected passive sampler versus the ADS was 1.00 and -0.25, respectively. The ARE128, PA MPPD measurement from the May 10th 2011 sample deployment period was identified as an outlier with a Cook's D statistic > 2, and as a result that value was removed from the MPPD dataset prior to the regression analysis. The slope and intercept for the MPPD versus the annular denuder across the three sites was 0.56 and 0.0054, respectively. The r-squared for the MPPD versus annular denuder was 0.53 and the MSE was 0.056

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Figure 3 Time series of denuder and passive samplers during inter-comparison study. The black lines represent the AMoN concentrations, the green lines represent the ADS concentrations and the blue lines represent the MPPD concentrations.
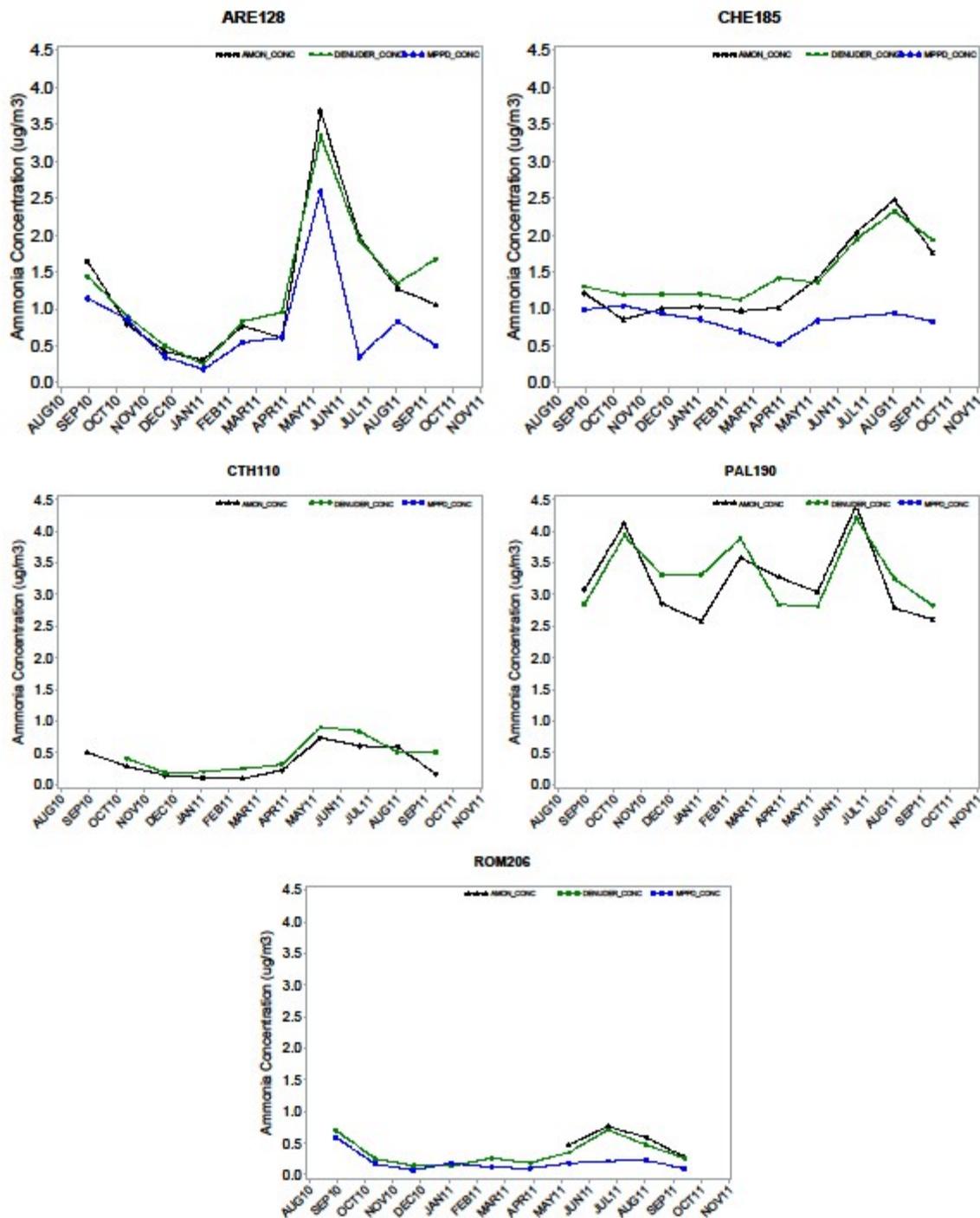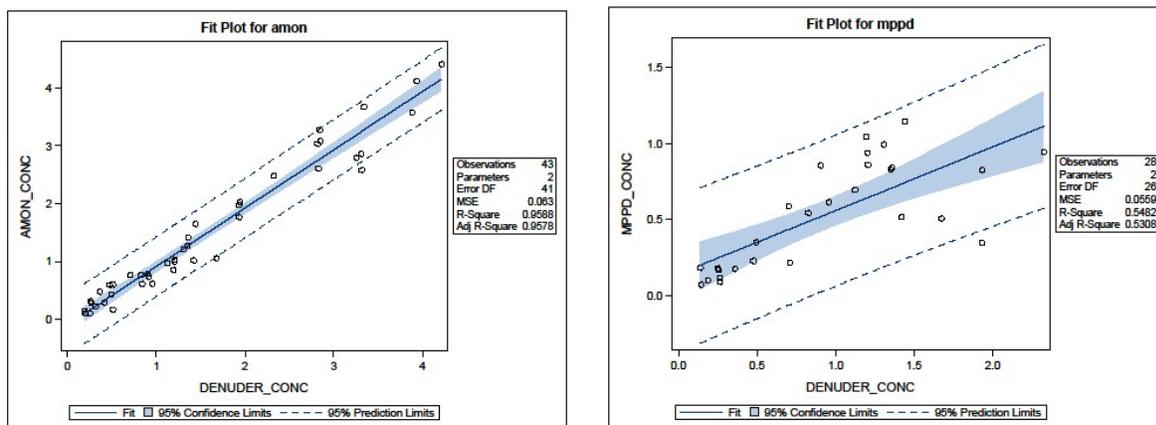
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Figure 4 Reduced major axis regression results showing results from AMoN versus ADS and MPPD versus ADS measurements. Note the axis is not the same in left and right panel. Concentrations are reported as µg m^{-3}.

The mean relative percent difference (RPD) between the AMoN samplers and annular denuders and MPPDs and annular denuders for each site is shown in Table 4. The standard deviation of the differences and the mean RPD between the AMoN samplers and the annular denuders were lower than the standard deviation of the difference and the mean RPD between the MPPD and the annular denuders. The mean RPD for the five sites with AMoN samplers and three sites with MPPD was -9.4 and -38.4%, respectively.

For this study, the field blank corrected passive sampler concentrations (ambient concentration minus field blank concentration) were also compared to the ADS results. The mean RPD between the blank corrected passive samplers and the ADS was -28%. Connecticut Hill (CTH110/NY67) had the greatest mean RPD (-60%). The field blank concentrations ranged from 11% to 110% of the bi-weekly ambient concentrations at CTH110/NY67.

Table 4 Mean relative percent difference (MRPD) between the MPPD results and ADS from the 3 sites and the AMoN versus ADS results from the 5 CASTNET sites. The AMoN measurements resulted in a negative bias when compared to the ADS at each site, but it was small compared with the bias from the MPPD measurements.

NADP ID	CASTNET ID	AMoN		MPPD	
		Standard Deviation of Difference	Mean Relative Percent Difference (%)	Standard Deviation of Difference	Mean Relative Percent Difference (%)
NY67	CTH110	0.12	-31.9		
PA00	ARE128	0.27	-6.4	0.51	-36.6
OK99	CHE185	0.18	-10.3	0.43	-38.2
TX43	PAL190	0.39	-2.5		
CO88	ROM206	0.049	18.0	0.14	-40.3
Averages		**0.25**	**-9.4**	**0.42**	**-38.4**

Bland-Altman plots show agreement between the AMoN passive samplers and ADS and the MPPD and ADS. Bland-Altman is an alternative method for comparing two sample types, without the use of a correlation coefficient, which can be misleading.[38] The bi-weekly difference between the measured ADS and AMoN 2-week NH_3 concentrations are shown in Figure 5 below (left panel). The 95% confidence limits are shown and the dashed line is the mean difference. The x-axis is the average concentration as measured by the two sample methods. There is no apparent bias in differences across the measured AMoN and ADS concentrations. All differences in 2-week concentrations were less than 1 µg NH_3 m^{-3}. In the right panel, Figure 5 shows the difference between the weekly NH_3 concentrations as measured by the MPPD and ADS at the 3 CASTNET sites where the MPPD were deployed. There is a negative bias in the MPPD measurements as compared to the ADS measurements. The comparison results between the MPPD and ADS also show as the NH_3 concentrations increase the comparability between the methods decreases. The bias and trend in lower accuracy at higher concentrations indicate there could be capture inefficiencies during the 1-week field deployment.

Figure 5 Bland Altman plots show correlation in the bias versus the measured concentrations of NH_3. The MPPD measured concentrations were consistently lower the NH_3 concentration measured by the ADS at all sites. The AMoN measurements were comparable to the ADS results over the range of NH_3 concentrations measured during the study.
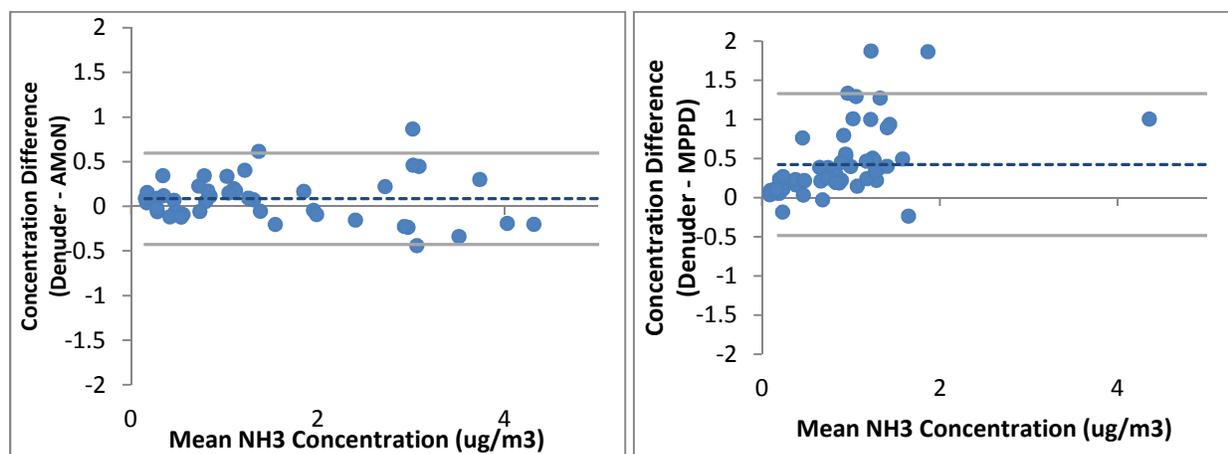
3.4 Flux Estimates

Schwede and Lear[39] have developed a hybrid method for creating interpolated maps of dry and total deposition fluxes using measured concentrations, where available, and gridded modeled deposition velocities or fluxes. The hybrid method developed by Schwede and Lear uses modeled results from the Community Multiscale Air Quality (CMAQ) model for the years 2000-2012. The approach uses measured concentrations from CASTNET, AMoN, NTN and the SouthEastern Aerosol Research and Characterization (SEARCH) network (http://www.atmospheric-research.com/studies/SEARCH/) combined with modeled concentrations and fluxes from CMAQ for areas lacking routine or consistent measurements. Where available, measured concentrations are combined with average estimates of deposition velocities from CMAQ model runs to calculate an estimated flux for each grid cell.

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Results are presented from the measured concentrations of NH_3 from AMoN and the flux estimates from the hybrid model for the sampling time period of this study (August 2011 through September 2012). As shown in Figure 6, the highest flux estimates were estimated in the summer at the Arendtsville, PA (0.5 kg-N ha^{-1} wk^{-1}) and Palo Duro, TX (0.3 kg-N ha^{-1} wk^{-1}).

Figure 6 Measured NH$_3$ concentrations from AMoN at the 5 sites included in the inter-comparison study and the estimated weekly dry deposition flux. Fluxes were estimated using a hybrid approach described in Schwede and Lear.[39]

4. Discussion

Passive samplers provide a cost-effective method for measuring NH_3 at many sites throughout the US. Passive samplers will provide a tool for evaluating seasonal and annual trends of NH_3 concentrations. Passive samplers and denuders do not provide high temporal resolution concentrations (i.e. hourly measurements), which is important for model development and validation. The ADS data quality was assessed by data completeness criteria. The overall data completeness for the study was 98% for the ADS. While the ADS can be operated on a 24-hour time scale, weekly or daily ADS measurements would be a challenge for network wide deployment because the glass denuders are fragile and break easily during shipping and operator and laboratory handling, making this method expensive for routine use in a nationwide network. With additional development the MPPD could be a viable method for use in the current CSN network, or any site operating a MetOne Super SASS. The loss and capture efficiency of NH_3 should be evaluated by operating 24-hour MPPD samples co-located with seven day MPPD samples to evaluate if there is any NH_3 loss during the weekly deployment. Supplemental high time resolution measurements are necessary to evaluate how well models are predicting NH_3 concentrations and deposition, but these measurements are expensive and typically labor intensive. The Monitor for AeRosols and Gases (MARGA) system (Metrohm Applikon, 3125 AE Schiedam, Netherlands) measures semi-continuous ambient NH_3 concentrations, as well as other gases and aerosols. The AMoN samplers are currently being compared to duplicate MARGA systems at the Beltsville, MD CASTNET site.

CASTNET sites routinely measure total-NO_3 (particulate NO_3^- + HNO_3) and NH_4^+ ion concentrations to estimate dry deposition of nitrogen. Nearly half of the CASTNET sites are now co-located with AMoN therefore estimates of NH_3 deposition at these sites may significantly increase the dry and total nitrogen deposition estimates. The AMoN NH_3 concentrations are being utilized to create gridded estimates of total and dry nitrogen deposition in the hybrid total deposition modeling approach developed by Schwede and Lear.[39] The measured NH_3 concentrations have made significant differences in areas where models were under-predicting the contribution of NH_3 to the total nitrogen loading.

Understanding the role that inorganic reactive nitrogen plays in deposition and NAAQS exceedances is critical to improving air and water quality in sensitive ecosystems. The US EPA, other federal partners, research scientists, and policymakers are evaluating existing monitoring data as part of the review process for the NOx/SOx secondary standard. The concept presented in the 2012 NOx SOx secondary standard actions (http://epa.gov/ttn/naaqs/standards/no2so2sec/cr_fr.html) provided an AAI equation for meeting the required standard in sensitive ecosystems throughout the US. Within comments received on these actions, the Clean Air Scientific Advisory Committee (CASAC) recommended that ambient NH_3 measurements be included in the pilot program. The CASAC felt that with additional validation of AMoN, the passive samplers would be adequate to fulfill the requirements.

Ambient measurements of NH_3 concentrations will provide input data to ecosystems exceeding their nitrogen critical load and areas not meeting NAAQS attainment level for $PM_{2.5}$. In addition, measured NH_3 concentrations will be used to evaluate air quality and deposition models by providing data on the spatial and temporal variability throughout the US. The seasonal patterns of NH_3 measured during this study was consistent with similar studies showing increasing NH_3 concentrations in the spring and

summer due to agricultural emissions.[35] The concentrations at Rocky Mountain National Park were fairly consistent across all seasons, which is similar to the results found in Chen et. al.[40].

The recent addition of the bi-directional flux module to the CMAQ model integrates the resistance-based flux model described by Nemitz et. al.[41] and the US Department of Agriculture (USDA) Environmental Policy Integrated Climate (EPIC) model[42]. The CMAQ model provides a 12-km or 36-km horizontal grid of concentrations or deposition by simulating emissions, atmospheric chemistry processes and wet and dry deposition provide a gridded layer of estimated air concentrations or deposition. In the future, the gridded estimates from the hybrid approach will incorporate the bi-directional CMAQ runs and will be used to estimate the ammonia flux at each AMoN site.[43,44] Comparisons of the current method to the results using the bi-directional model will be performed to better understand how much the current method under- or over-predicts the dry deposition of ammonia.

5. Conclusion

Long-term monitoring networks, such as CASTNET, NTN, and AIRMoN face increasing pressure from reductions in annual budgets combined with increased spatial and temporal requirements to more accurately characterize changes in air quality and evaluate transport and deposition models. Passive samplers are a low-cost method for measuring additional species at remote sites and may supplement more labor intensive and expensive analyzers that provide high temporal resolution measurements, such as the MARGA. AMoN samplers were demonstrated to be well suited to help support these measurement needs as they were comparable to ADS results at all five sites (MRPD = -9%) for a range of NH_3 concentrations, elevations, and climates. Additional work should be considered to improve the performance of the MPPD for use in the Super SASS. Adding NH_3 concentrations to the current suite of measurements collected by the Super SASS would provide daily estimates in areas where NH_3 concentrations are currently not well characterized (e.g. urban areas).

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