

Summary Report: Improving characterization of reduced nitrogen at IMPROVE and CSN monitoring sites

Christopher Rogers, Kevin Mishoe, Marcus Stewart, Katherine Barry
Wood Environment & Infrastructure Solutions, Inc.

Joann Rice, Xi (Doris) Chen
U.S. EPA, OAR, OAQPS, AQAD

John T. Walker
U.S. EPA, ORD, CEMM, AESMD

Melissa Puchalski
U.S. EPA, OAR, OAP, CAMD

Ralph Baumgardner
U.S. EPA, ORD, CPHEA, PHESD

Bret Schichtel
NPS, ARD

October 7, 2020

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1.0 Introduction

1.1 Overview

Total reduced nitrogen (NH_x) measurements are not routinely performed in the US and currently no regulatory requirements exist to measure NH_x . However, scientific and policy interest in the increasing trend in NH_x concentrations in many regions of the US has evolved since NH_x can lead to atmospheric fine particulate matter ($\text{PM}_{2.5}$) formation and visibility impairment and, once deposited, can cause eutrophication, loss of species biodiversity and algal blooms. This study, set in the southeastern US, was designed to measure reduced nitrogen and to assess measurement methods for implementation in long-term monitoring networks, specifically the Interagency Monitoring of Protected Visual Environments (IMPROVE) and Chemical Speciation (CSN) networks. The IMPROVE network provides routine measurements of speciated particulate matter (PM) that support the regional haze rule and source apportionment analyses. The CSN provides data that support emission control strategies, health effects research, and model evaluation. Both networks collect a 24-hour integrated sample every 3 days.

The goal of this study was to determine whether acid-coated filters could be deployed at existing sites using existing network equipment to measure reduced nitrogen concentrations in hot, humid environments. Incorporating an NH_x measurement into the CSN and IMPROVE networks would leverage existing infrastructure, reduce costs and provide national coverage. The addition of NH_x also offers the potential for providing NH_x and particulate ammonium (NH_4^+) estimates at sites co-located with the National Atmospheric Deposition Program's (NADP) Ammonia Monitoring Network (AMoN). Hourly measurements are ideal for evaluation of chemical transport models (CTMs) and understanding atmospheric processes that vary diurnally. On the other hand, the use of speciation samplers for 24-hour NH_x samples, collected every 3 days, is a cost-effective way to improve current understanding of the spatial and temporal variability of NH_x and to generate data useful for source apportionment, potential for PM formation, and more general model evaluation. When co-located with AMoN, monthly, seasonal and annual averages of NH_4^+ can be generated which are of direct benefit to PM and oxides of nitrogen and sulfur (NO_x/SO_x) NAAQS reviews and subsequent implementation. Chen *et al.* (2014) performed a similar study in the Western and midwestern US using only the IMPROVE sampler. In that study the acid-impregnated filter data compared well with Annular Denuder Filter Pack System (ADFPS) (URG Corp) measurements.

1.2 Discussion

Over the past two decades, the chemical composition of the atmosphere has changed markedly from one dominated by oxidized secondary particles including nitrate (NO_3^-), sulfate (SO_4^{2-}), and carbonaceous aerosols, and their associated precursor gases (NO_x , SO_x , VOCs, SVOCs), to an

atmospheric mixture that includes a significant amount of reduced inorganic nitrogen ($\text{NH}_x = \text{NH}_4^+ + \text{NH}_3$) (Li *et al.*, 2016; Du *et al.*, 2014). Total atmospheric nitrogen compounds are still primarily in inorganic forms but have significant contributions from organically bound nitrogen (both reduced and oxidized forms) (Jickells *et al.*, 2013). Looking forward, the shift to larger relative contributions of atmospheric NH_x is projected to continue as existing rules and technologies continue to decrease NO_x emissions from the transportation and energy generation sectors (U.S. EPA, 2016) with an expected modest increase in NH_3 emissions (Ellis *et al.*, 2013; Martin *et al.*, 2015). As atmospheric emissions and composition evolve in response to rules, ambient and deposition monitoring networks must evolve to best inform decision makers and address such questions as:

1. Cause of adversity: What atmospheric species and emission sources contribute to PM, regional haze and nitrogen deposition?
2. Mitigate adversity: What options in emissions reductions are available to reduce PM, regional haze and nitrogen deposition?
 - a. How much remaining capacity is available in rules and NAAQS provisions that target emission reductions in oxidized nitrogen species?
 - b. How effective are potential reductions in reduced nitrogen?

To answer these questions, it is necessary to characterize reduced nitrogen emission sources and atmospheric composition. Ammonia is the precursor emission while particulate NH_4^+ is important as the controllable pollutant under the PM NAAQS. Current monitoring networks are relatively well positioned to characterize inorganic oxides of nitrogen (NO_y), but poorly positioned to characterize NH_x , the increasingly dominant reduced component of atmospheric nitrogen. This limitation is affecting our ability to understand and mitigate the causes of excess PM, regional haze and nitrogen deposition. Measurements of NH_x would provide a metric for evaluating emission inventories and validating chemical transport models and provide input into nitrogen deposition estimates. Having the speciated measurements ($\text{NH}_3 + \text{NH}_4^+$) is analogous to the importance of NO_y measurements.

Ammonia and NH_4^+ directly contribute to excess nitrogen deposition through dry and wet deposition and together now dominate the inorganic nitrogen deposition budget across most of the U.S. (Li *et al.*, 2016). Ammonium directly contributes to PM and the resulting haze, while NH_3 indirectly affects PM and haze levels. Ammonia also plays an important role in governing aerosol acidity (Silvern *et al.*, 2017; Pye *et al.*, 2020) which effects its hygroscopicity (water uptake). This in turn influences the aerosol water content and its contributions to haze and formation of secondary organic aerosols from biogenic VOC emissions (Carleton *et al.*, 2010, Carleton and Turpin, 2013). The lack of reduced nitrogen measurements hinders our ability to assess these direct and indirect effects on air quality issues and the ability to develop, test and refine the simulation of important atmospheric processes governing the roles of reduced nitrogen compounds in particle formation and deposition. The importance of understanding

trends and the spatial variability of reduced nitrogen is recognized; NH_4^+ concentrations are measured at more than 150 CSN sites and more than 90 CASTNET sites and NH_3 concentrations are measured at more than 90 sites as part of AMoN. However, the CSN measurements underestimate NH_4^+ concentrations (Yi *et al.*, 2006) while CASTNET measures weekly integrated samples and AMoN collects two-week samples, making these data most suitable for seasonal and annual characterizations.

1.3 Study Objectives

Study objectives from the Southeastern US Reduced Nitrogen Study are:

1. Evaluating the feasibility of deploying acid-impregnated filters to measure NH_x in national networks
2. Characterizing any biases in existing NH_4^+ measurements collected at CSN and CASTNET sites
3. Provide a recommendation to the Office of Air Quality Planning and Standards (OAQPS) who manages the CSN for measuring NH_x using a cost-effective method on a timescale that informs the PM NAAQS review, regional haze policies, and critical loads exceedances linked to reduced nitrogen deposition

2.0 Measurement Locations

In the pilot study by Chen *et al.* (2014), it was shown that NH_x could be measured in the IMPROVE network at several Western and Midwestern sites. Before deploying this technique in national networks, this study expanded the Chen *et al.* (2014) work to the warm, humid eastern U.S. Acid-impregnated filters were deployed in both CSN and IMPROVE samplers in North Carolina and Florida during the summer of 2017 (Figure 1). In this study, a spare module [37 millimeter (mm) filter diameter for IMPROVE, 47 mm filter diameter for CSN] was fitted with a phosphorous acid (H_3PO_3) impregnated cellulose filter to collect and sustain (no volatile losses) both particulate NH_4^+ and NH_3 . A URG annular denuder filter pack system (ADFPS) was used as a reference method. The ADFPS included an NH_3 denuder, followed by a nylon filter to collect particles and a backup denuder to capture any NH_3 volatilized from the nylon filter. The sum of NH_3 from both denuders and NH_4^+ from the nylon filter constituted a reference NH_x sample.

Figure 1. Monitoring Locations in the Southeastern US



The Duke Forest research site in the NC Piedmont area (Figure 2) was managed by John Walker of EPA's Office of Research and Development (ORD).. Measurements were conducted in an unfertilized 15 ha grass field in the Blackwood Division of Duke Forest, Orange County, North Carolina, USA (35.9745 latitude, -79.0990 longitude). A variety of air quality and meteorological measurements (N.C. Forest Service Fire Forecast, National Oceanic and Atmospheric Administration (NOAA) Climate Reference Network, and AMoN) were performed at this site, which is periodically also used for special studies (Rumsey and Walker, 2016). Instruments were operated in the middle of the field adjacent to the NC Forest Service and NOAA meteorological towers and collocated with the AMoN sampler (Figure 3). In addition to the routine measurements conducted in the grass field, weekly CASTNET filter pack measurements (DUK008) and meteorological data were collected at the forest flux tower located immediately adjacent to the grass field.

Figure 2. Duke Forest, NC Monitoring Location

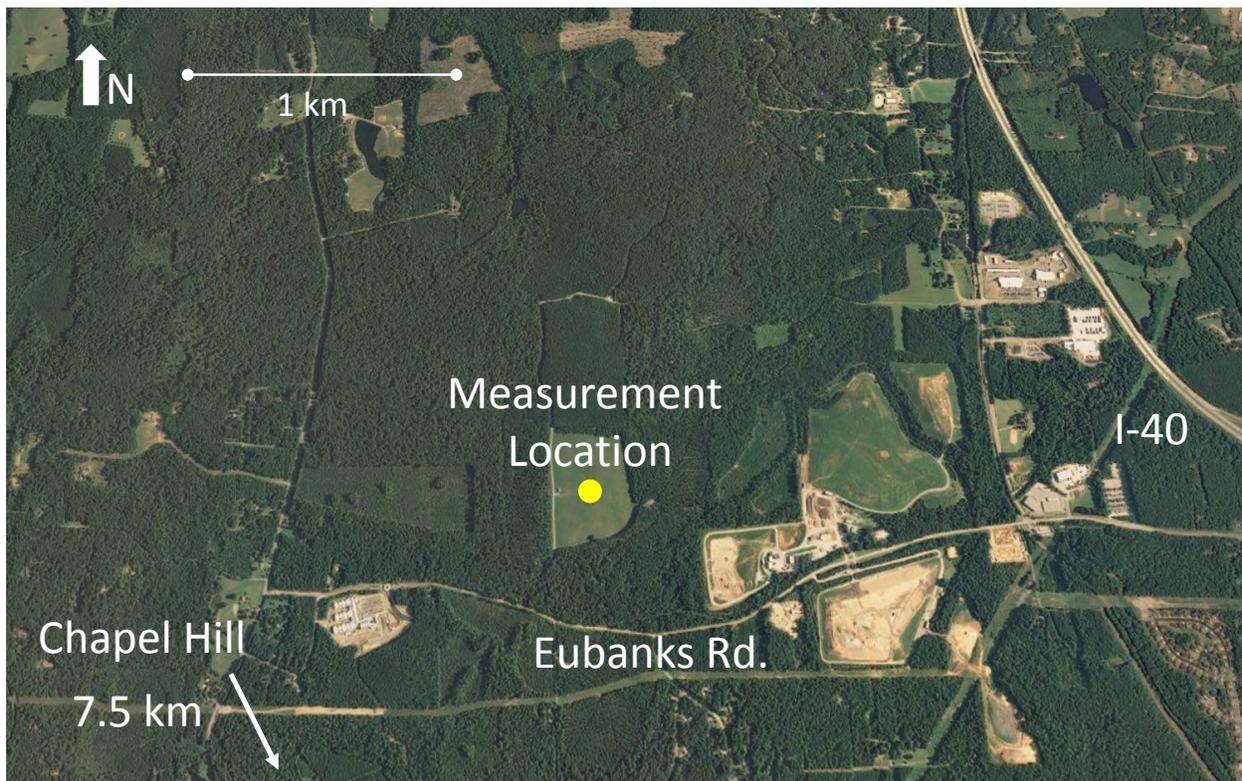
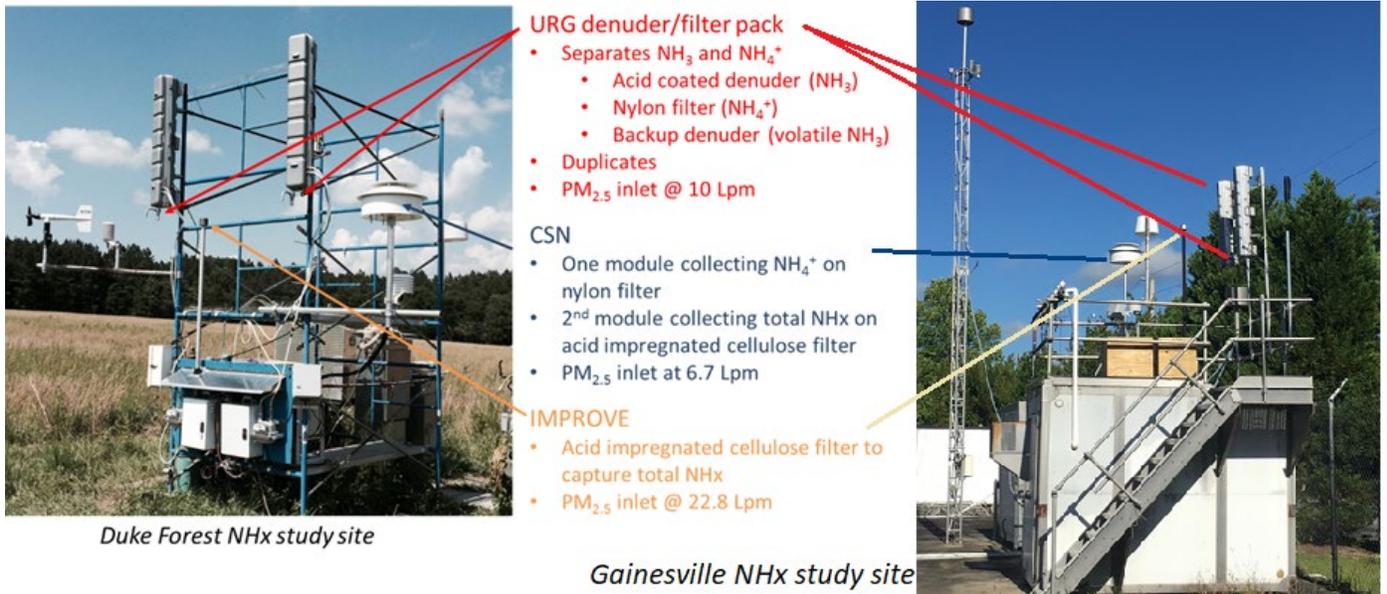


Figure 3. Duke Forest and Gainesville NH_x Sampling Equipment



The Gainesville, FL site was served by Wood Environment & Infrastructure Solutions (Wood), which operates CASTNET and several of the NADP network sites. The Gainesville site (29.6497 latitude, -82.4914 longitude) served as the 2nd study site. Instrumentation was mounted on the roof of the CASTNET shelter used for testing equipment/methods (Figure 3). In addition to the IMPROVE, CSN, and ADFPS measurements, weekly CASTNET filter pack, biweekly AMoN NH₃ samples, and hourly meteorological data were also collected in Gainesville.

Figure 4. Gainesville, FL Monitoring Location



In addition to the two study sites, additional QA testing was performed at the Research Triangle Park ambient air innovation research site (AIRS) located on the EPA campus in late 2017 through early 2018 using the same ADFPS system deployed at Duke Forest. Equipment was operated by staff in EPA ORD/AEMD.

3.0 Sampling Methods & Procedures

A description of the measurements is provided in this study's Quality Assurance Project Plan (QAPP) (U.S. EPA, 2018). Table 1 summarizes the samplers operated at the two sites.

Table 1. Summary of measurement methods from both the Duke Forest and Gainesville monitoring locations

Sampler	Channels (measured)	Cutpoint	Flow Rate	Sample Period
URG denuder/filter pack system (ADFPS) – in duplicate	Na ₂ CO ₃ -coated denuder (HNO ₃ – not analyzed)	Teflon coated cyclone - 2.5 μm	10 lpm	1 in 3 day, 24-hour samples
	H ₃ PO ₃ -coated denuder (NH ₃)			
	Nylon filter (NH ₄ ⁺)			
	H ₃ PO ₃ -coated backup denuder (volatile NH ₄ ⁺)			
CSN MetOne SuperSASS	MgO denuder (not analyzed) + nylon filter (NH ₄ ⁺)	Cyclone - 2.5 μm	6.7 lpm	1 in 3 day, 24-hour samples
	47 mm H ₃ PO ₃ -impregnated cellulose filter (NH _x)	Cyclone - 2.5 μm	6.7 lpm	
IMPROVE PM Sampler	37 mm H ₃ PO ₃ -impregnated cellulose filter (NH _x)	2.5 μm	22.8 lpm	1 in 3 day, 24-hour samples
CASTNET	Teflon filter (NH ₄ ⁺ , SO ₄ ²⁻ , NO ₃ ⁻)	N/A	3 lpm	Weekly
	Nylon filter (HNO ₃ , SO ₂)			
	K ₂ CO ₃ impregnated cellulose filter (SO ₂)			
AMoN	Radiello (NH ₃)	N/A	Passive	Bi-weekly

Notes:

Na₂CO₃: sodium carbonate

H₃PO₃: phosphorous acid

MgO: magnesium oxide

K₂CO₃: potassium carbonate

The acid-impregnated cellulose filters eliminated off-gassing of ammonia that can occur in routine sampling operations when collecting ions on nylon filters with base properties. The nylon and cellulose filters were subsequently analyzed by the Wood laboratory for NH_4^+ by Ion Chromatography (IC). With the exception of preparing the H_3PO_3 -impregnated filters, described in section 10.3 of this report, all sampling and analysis protocols were identical to those in the routine operations of IMPROVE (<http://vista.cira.colostate.edu/Improve/particulate-monitoring-network/>) and CSN (<https://www.epa.gov/amtic/chemical-speciation-network-field-qapps-and-sops>). The ADFPS protocols were adapted from EPA's Inorganic compendium Method IO4.2 (<https://www3.epa.gov/ttn/amtic/inorg.html>).

Filters and denuders were prepared and shipped to Duke Forest by the Wood laboratory. The ORD laboratory extracted the denuders and shipped the extracts to Wood for analysis. Wood prepared and shipped travel blanks to the Duke Forest site. Laboratory blanks were routinely run for each method.

Nylon extracts from CSN and the ADFPS were re-analyzed in 2018 for SO_4^{2-} and NO_3^- following the CASTNET QAPP v9.2 (U.S. EPA, 2019).

4.0 Laboratory Procedures

4.1 Preparation of Sampling Media

Procedures for preparation and extraction of sampling media are summarized in Appendix A.

4.2 Chemical Analysis

Laboratory IC quality control procedures are fully described in section 3.3.2 of the CASTNET QAPP (U.S. EPA, 2019). Details relevant to this study are summarized below. It is noted that while CASTNET routinely analyzes for NH_4^+ using colorimetry, IC analysis was used in this project for consistency with IMPROVE and CSN laboratory methods. The description and methods for IC analysis for the CASTNET anions in the CASTNET QAPP Appendix 4 Laboratory SOP (GLM-3180-001) is the same procedure that was followed here for NH_4^+ .

Denuder and filter extracts were analyzed for NH_4^+ by Wood using a Thermo/Dionex ICS-1600 ion chromatograph (Thermo/Dionex Corporation, 2009) equipped with a Thermo/Dionex CG16 cation guard column, Thermo/Dionex CS16 cation analytical column, and Thermo/Dionex CERS 500 self-generating suppressor. Samples were injected onto the analytical column from a 50 μL loop and eluted in 30 mM methanesulfonic acid at a flow rate of 1 mL min^{-1} .

Procedures for chemical analysis and quality assurance are described below. Details of chemical preparation for chemical analyses are included in Appendix B.

4.2.1 Sample Analysis

The IC analysis follows the procedures described in the CASTNET QAPP Appendix 4 Laboratory SOP (GLM3180-001 section 6.2) with the exception of cation columns and the use of the methanesulfonic acid solution as the eluent.

4.2.2 Data Analysis

1. Data files were processed using algorithms contained in the data collection software (Chromeleon 7.2 from Thermo/Dionex). Parameters were adjusted as dictated by instrument performance.
2. Chromatograms were examined visually. Any anomalies in the data batch were noted in the narrative.
3. Responses were exported to an Excel spreadsheet.
4. Data were assembled in a batch folder, including copies of all extraction worksheets, run logs, certificates of analyses and processing methods, hard copies of each chromatogram, and other necessary documentation.

4.2.3 Quality Control

1. Filter blanks (BLK): If any analyte from an extracted filter exceeded 1 µg/filter, the box that the filter came from was marked "Failed", removed from the lab and not used for sample collection.
2. One BLK was analyzed during each extraction. The BLK for extracted samples was the applicable volume of extraction solution followed by the appropriate extraction procedure. The BLK results were required to be less than or equal to two times the reporting limit for the analytes of concern.
3. A CCV was analyzed at a frequency of 10 percent for every analytical batch, as well as at the beginning and end of each run. The measured value of the CCV was required to be within ± 10 percent of the certified value.
4. An SRM was used for an initial and a final calibration verification. The measured value of the reference sample was required to be within ± 10 percent of the certified value.
5. All calibration curves were required to contain a minimum of five points for quadratic calculations and have a correlation coefficient greater than or equal to 0.995. See Appendix B for a complete description.
6. Approximately 5 percent of samples from each batch were analyzed in duplicate (DUP1, DUP2) to monitor within-run precision. Sample extracts were selected at random and reinjected for analysis. For samples greater than five times the reporting limit (0.02 µg-N mL⁻¹), the relative percent difference (RPD) of the replicate samples was required to be within ± 20 percent. For samples with concentrations less than or equal to five times the reporting limit, the absolute difference between sample and replicate was required to be less than the reporting limit.
7. An internal system monitoring spike (rubidium bromide) was used in the IC analysis to assess shifts in retention time and sample injection volume.
8. All sample responses were within the standard calibration range (0.00 to 5.00 µg mL⁻¹). Any samples with responses above the calibration curve high standard were diluted and reanalyzed.

4.2.4 Corrective Actions

Table 2 summarizes QC procedures and the corrective actions taken when the QC samples were not within acceptance criteria.

Table 2. QC Procedures, Acceptance Criteria, and Corrective Actions for IC Chemical Analyses

Quality Control	Acceptance Criteria	Corrective Action
Calibration curve	Correlation coefficient ≥ 0.995	Rerun calibration standards. If still out of control, prepare new calibration standards and recalibrate the instrument, or document why data were acceptable.
Calibration curve responses	Bracket all samples	Dilute and reanalyze samples exceeding the calibration range, or document why data were acceptable.
Reference standard (SRM) <i>[Accuracy indicator; brackets all samples in run]</i>	$\pm 10\%$ of the certified true value	Rerun standard. If still out of control, recalibrate instrument and reanalyze samples, or document why data were acceptable.
Control standard (CCV) <i>[Accuracy indicator; analyzed every 10 injections]</i>	$\pm 10\%$ of the certified true value	Rerun standard. If still out of control, recalibrate instrument and reanalyze samples since last acceptable CCV, or document why data were acceptable.
MB (BLK)	≤ 2 times the RL	Determine the cause of blank problem.

Notes: RL = Reporting limit
RPD = Replicate percent difference

Source: Wood

Laboratory precision was estimated by analyzing replicate injections of randomly selected extracts. Approximately 5% of the IC samples from each batch were reanalyzed. Differences between the original and replicate concentrations were calculated as relative percent difference (RPD). The data quality indicator (DQI) precision goals are summarized in Table 3. Laboratory accuracy was determined by analyzing reference samples and control standards (CCV). An independent National Institute of Standards and Technology (NIST)-traceable reference standard was analyzed at the beginning and end of each analytical run. One midlevel CCV, produced by an independent laboratory and NIST-traceable, was analyzed every ten IC samples. The responses relative to the CCV and reference samples were required to be within $\pm 10\%$ (the accuracy DQI criterion) of the certified target values.

Table 3. Data Quality Indicators for Laboratory Analyses

Analyte	Acceptance criteria				
	Method	Precision (RPD)	Accuracy (%)	Nominal Reporting Limits	Lower Limit of Detection
Ammonium (NH ₄ ⁺)	IC	20	90-110	0.020 µg-N/mL	0.020 µg-N/mL

4.2.5 Calculations

All calculations were performed with data reduction algorithms that reside in the instrument software. Separate calibration curves were prepared for NH₄⁺ by plotting the response (peak area) of standards against concentration values using quadratic regression in the instrument software. Sample concentrations were calculated using the quadratic equation for the curve. The analyst was allowed to eliminate points to improve accuracy throughout the range of calibration but at least 5 points plus a blank had to remain.

4.3 Field and Laboratory Blanks

Blanks were assessed to characterize contamination on denuders and filters that may have occurred in the laboratory and field. Weekly laboratory blanks were prepared and analyzed on H₃PO₄ denuders, H₃PO₄ filters, and nylon filters. Field or trip blanks for ADFPS, IMPROVE, and CSN were prepared and analyzed biweekly at both field sites. For IMPROVE and CSN, field blanks consisted of filters placed in the normal configuration within the sampler but unexposed. For the ADFPS, field blanks consisted of a standard sample train, including the cyclone inlet, placed in the ADFPS enclosure in the normal sampling configuration but left unexposed. The ADFPS field blank was deployed and collected with the exposed sample for the corresponding sample period. Trip blanks were not unpacked from the shipping container. Note that the ADFPS samplers were changed out two or three times per week, depending on the 1:3 schedule, as opposed to weekly change out of the IMPROVE and CSN samplers.

4.4 Chain of Custody and Field Forms

Chain of custody forms accompanied all samples during shipping from the analytical laboratory through field sampling and until receipt and analysis. Field notes (including sample volume, time and sample module identifiers) were recorded on the forms and archived at the analytical laboratory. Examples of the chain of custody and field forms are included in Appendix C.

4.5 Shipping

All samples and extractions were shipped in insulated coolers with ice blocks to maintain a temperature below 4°C. Filter based samples were shipped to the EPA facility and transported to and from the Duke Forest site each Monday by the site operators, to be installed during the

following week. Upon receipt, the receiver recorded the temperature of the samples, time of receipt, and initials on the Shipping Temperature Log (See Appendix C) included with each cooler and transferred the samples to a refrigerator until deployment. The samples exposed during the previous week, along with denuder extractions, were returned to the analytical laboratory using fresh ice blocks. Upon receipt at the laboratory, the temperature of the samples, time of receipt, and initials were recorded on the Shipping Temperature Log and all samples are transferred to a cold room for storage.

All samples collected at the Gainesville site were stored in the laboratory cold room at $\leq 4^{\circ}\text{C}$ until deployment and immediately following sample collection.

5.0 Data Analysis and Management

5.1 Data Analysis, Interpretation, and Management

Laboratory, flow, concentration, and QC data were managed and reported to EPA by Wood under EP-W-16-015 Task Orders 1012 and 2012.

5.2 Data Reporting Requirements

Laboratory data were stored in Wood's laboratory information management system (LIMS) Element Data System. Element is used to organize and schedule the analyses performed by the CASTNET laboratory. Laboratory procedures, including setting up projects in the Element Data System are described in the CASTNET QAPP (U.S. EPA, 2019). Calculations for converting the mass of an analyte (NH_4^+) in each extract to atmospheric concentrations are described in section 4.4.1 of the CASTNET QAPP. Laboratory data, including mass, extract volumes, and blank results were transferred to SQL Server for calculating atmospheric concentrations. The CASTNET QA Manager verified the concentration data before the results were transferred to EPA as described in the CASTNET QAPP Appendix 6 (Data Operations SOPs).

5.3 Data Analysis

Duplicate URG ADFPS systems were deployed to collect collocated samples to determine precision of the reference method. Precision was calculated by aggregated mean relative percent difference (MRPD):

$$MRPD = \frac{1}{k} \sum_{j=1}^k \left(\frac{S1 - S2}{S1 + S2} \right) \times 200$$

where:

S1 = The value for the primary measurement

S2 = The value for the co-located duplicate measurement

k = The number of pairs of duplicate measurements (approximately 44 for this study)

Accuracy is calculated as percent recovery (%R) between the IMPROVE or CSN NH_x or NH_4^+ measured concentration and the URG ADFPS concentration:

$$\%R = \left(\frac{Y - X}{X} \right) \times 100$$

where:

Y = The measured value (CSN or IMPROVE)

X = The reference value (ADFPS)

Bar charts were created using R, SAS, or Tableau software to compare the 24-hour concentrations between the three measurement systems for each site. Additionally, average concentrations were reported for each measurement system for NH_x and NH_4^+ .

5.4 Data Storage Requirements

Electronic copies of the data are stored by Wood and EPA/Clean Air Markets Division (CAMD) in an Oracle database. Data tables were created to store the CSN, IMPROVE, and URG ADFPS ambient concentration data. QA, flow, and temperature data are stored in a separate table. Wood will maintain the data records in accordance with the CASTNET QAPP. The CASTNET database is maintained by Wood's Data Management Center (DMC) and Data Management, Analysis, Interpretation and Reporting Manager (DMAIRM). The CASTNET database is backed up following the procedures and schedules described in the CASTNET QAPP.

6.0 Quality Metrics (QA/QC Checks)

6.1 Calibration and Auditing of Field Equipment

Continuous data (flow and temperature) were validated according to the validation procedures described in section 4.3 of the CASTNET QAPP (U.S. EPA, 2019), following calibration procedures for the SuperSASS sampler (<https://www.epa.gov/amtic/chemical-speciation-network-quality-assurance>). Flow data are typically flagged as invalid if the value is outside the nominal flow by > 10% (<https://www.epa.gov/amtic/chemical-speciation-network-data-reporting-and-validation>). Ambient temperature data are flagged if the value is < -40 or > 50 ° C. However, for this study, criteria for data review were established based on flow volume criteria, and no samples were invalidated based solely on nominal flow in order to improve data capture. Table 4 summarizes the target flow volumes per sample for each system.

Table 4. Flow Volume Targets for Each Sampling System

Sample System	Target (m ³)
CSN SuperSASS	9.6
IMPROVE PM Sampler	31.3
URG ADFPS	14.6

Flow calibrations were performed at the start of the sampling period, approximately at the mid-point of the study, and at the end of the study period. Flow rates for the SuperSASS and ADFPS samplers were verified using a NIST-traceable MesaLabs Definer 220 dry piston flow meter (MesaLabs, Lakewood, CO). Calibration of the SuperSASS sampler is described by EPA: (<https://www.epa.gov/amtic/chemical-speciation-network-quality-assurance>). Calibration of the IMPROVE sampler is described in the IMPROVE SOP 226 (http://airquality.crocker.ucdavis.edu/files/6614/5808/2356/TI226H_Calibration_of_Flow_Check_Devices.pdf). A Magnehelic differential pressure meter (Dwyer Instruments, Michigan City, IN) was used to calibrate pressure sensors in the IMPROVE sampler. The flow rate through the sampler was calculated using the pressure drop across a flow restriction and the density of ambient air. The Magnehelic flow check device was calibrated using a Definer 220 NIST-traceable flow meter. Calibration results were used to review the concentration measurements from each sampler-type. During flow audits, temperature sensors in the SuperSASS and IMPROVE samplers were calibrated at one point using a NIST-traceable reference thermometer. The temperature criterion for each system is ± 1 degree C. The SuperSASS and IMPROVE pressure sensor criteria were $\pm 10\%$.

7.0 Results

7.1 Results from the Summer 2017 Monitoring

Field, trip and laboratory blanks were routinely monitored for each sampling system. A summary of the blank results is shown in Table 5. Median concentrations are shown in $\mu\text{g-NH}_4 \text{ mL}^{-1}$ and

trip blanks were only shipped to Duke Forest because the laboratory was located at the Gainesville monitoring site. The number of samples are shown in parentheses.

Table 5. Summary of Blanks Results

Blank	Duke Forest	Gainesville
Field Blanks		
ADFPS Nylon Filter	0.000 (3)	0.0002 (7)
CSN Nylon Filter	0.000 (3)	0.0031 (7)
Acid-Coated Denuder	0.0576 (3)	0.0032 (7)
CSN Acid-Impregnated Filter	0.0152 (3)	0.0048 (7)
IMPROVE Acid-Impregnated Filter	0.0162 (3)	0.002 (7)
Laboratory Blanks		
37 mm Cellulose Filter		0.000 (30)
47 mm Cellulose Filter		0.000 (30)
Nylon Filter		0.000 (30)
Acid-Coated Denuder	0.0046 (13)	0.0054 (15)
Trip Blanks		
ADFPS Nylon Filter	0.00235 (4)	
CSN Nylon Filter	0.00165 (4)	
Acid-Coated Denuder	0.00665 (4)	
CSN Acid-Impregnated Filter	0.0078 (4)	
IMPROVE Acid-Impregnated Filter	0.00715 (4)	

Flow was recorded continuously for the ADFPS, IMPROVE and CSN samplers. Figures 5 and 6 show flow volume from Duke Forest and Gainesville, respectively. Actual flows were used to calculate the ambient concentrations. At Duke Forest the CSN flow rate was stable and the IMPROVE flow rate was stable until 10/1/2017. The ADFPS at Duke Forest performed well. At the Gainesville site all three sampling types experienced high variability in the flow.

Figure 5. Flow Volumes measured at the Duke Forest, NC Site

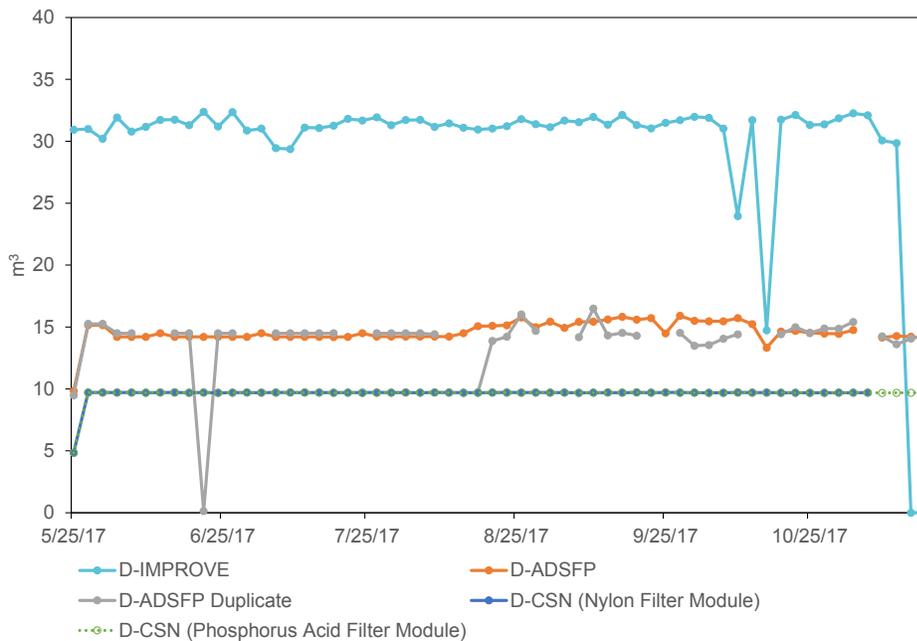
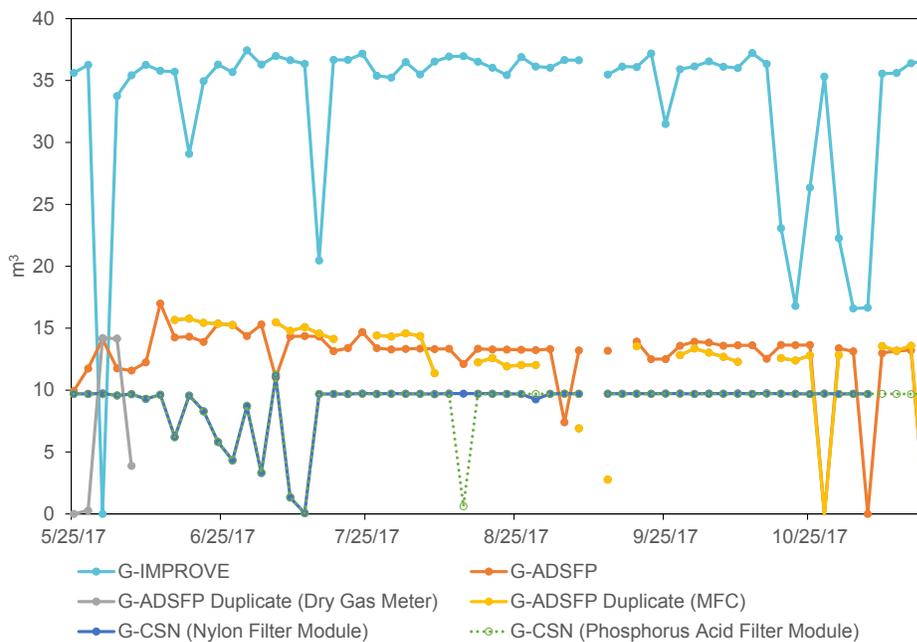


Figure 6. Flow Volumes measured at the Gainesville, FL Site



Ambient concentrations of NH_x from each of the sampling systems are shown in Figure 7 from the Duke Forest site. The ADFPS NH_x value was reported as the nylon NH_4^+ concentration plus the NH_3 collected on the primary denuder and the volatilized NH_4^+ collected on the backup acid-coated denuder. There was good agreement between the primary ADFPS and the duplicate system. The correlation between the two showed a slope of 0.94 and an r^2 of 0.9 (Figure 8).

Figure 7. Comparison of NH_x Concentrations Measured by IMPROVE, CSN, and ADFPS Methods at Duke Forest, NC

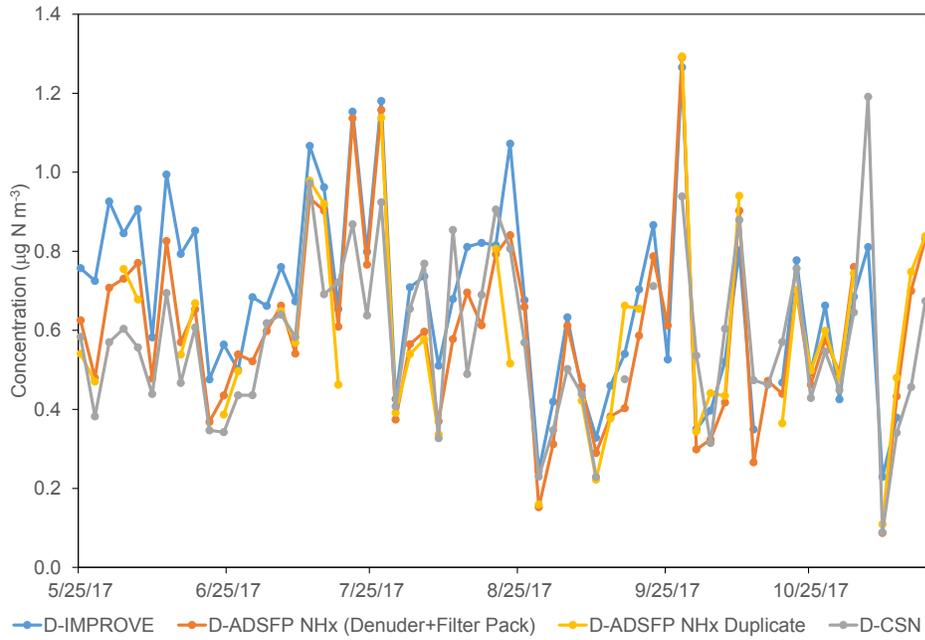
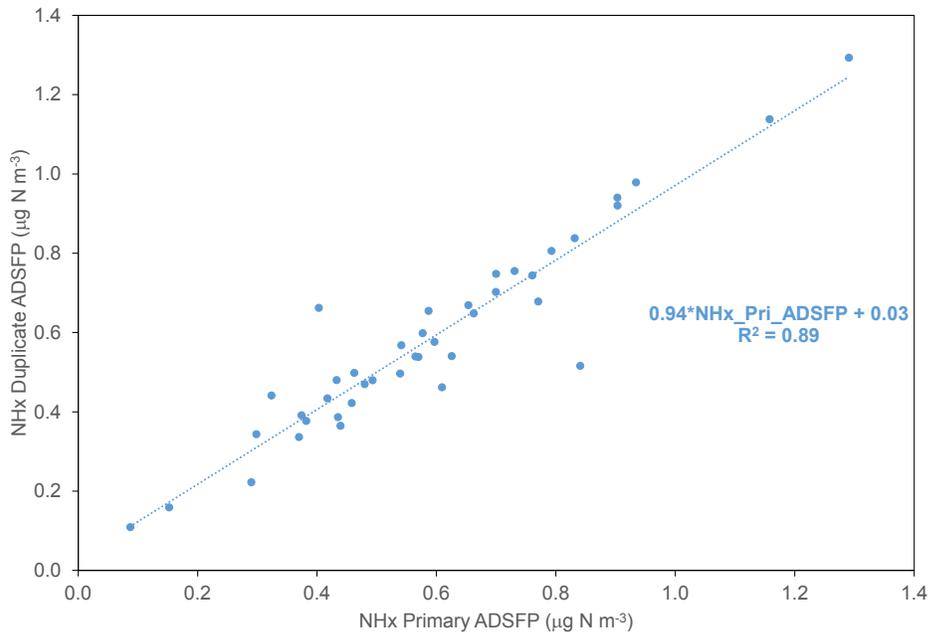


Figure 8. Scatter Plot of Primary ADFPS NH_x Concentration compared with the Duplicate ADFPS at Duke Forest, NC



The linear relationship between the ADFPS and the CSN SuperSASS sampler and the IMPROVE sampler from Duke Forest are shown in Figure 9. There was good agreement between the ADFPS and IMPROVE systems with a slope of 0.95 and r^2 equal to 0.89. These results were similar to results presented in the western US in the NH_x pilot network (Chen *et al.*, 2014). Agreement between the ADFPS and the CSN system was fair with a slope of 0.69 and an r^2 equal to 0.71. The CSN was biased low as compared to the ADFPS. There seems to be less NH_x retained on the acid-impregnated filter in the CSN system at higher concentrations.

Figure 9. Linear relationship between the ADFPS versus CSN NH_x results and ADFPS versus IMPROVE NH_x results at Duke Forest

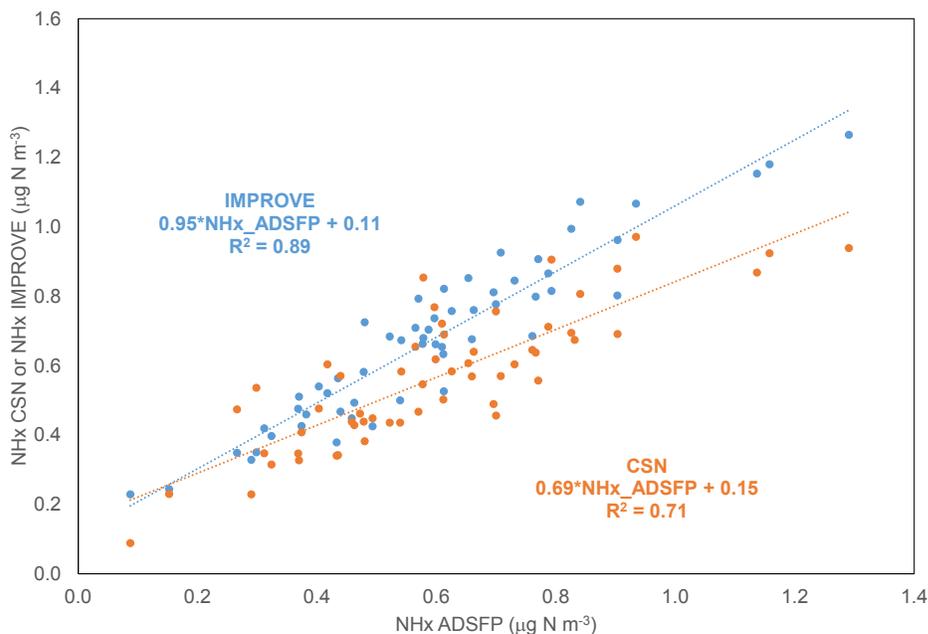
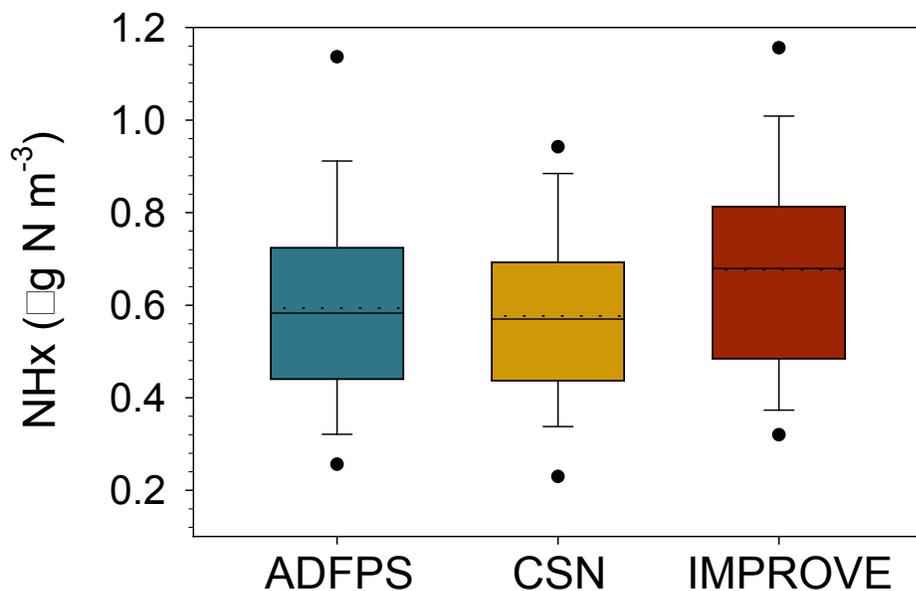


Figure 10 shows the distribution of NH_x concentrations measured during the study at the Duke Forest, NC site. The boxes represent the 25th and 75th percentile, the solid and dashed lines within the box represent the median and mean, respectively, the whiskers represent the 10th and 90th percentiles, and dots represent the 5th and 95th percentiles. Median concentrations over the 6-month period were similar for each sampling method.

Figure 10. Box plot of Duke Forest, NC NH_x concentrations



The time series from Gainesville, FL for each of the sampling systems is shown in Figure 11. The CSN pump began to fail following removal of the sample installed on 6/6/2017. Performance slowly degraded, and it was repaired prior to the sample installed on 7/15/2017. This issue, along with several other operational problems with the SuperSASS, resulted in a loss of almost 2 months of concentration data during June and July. The NH_x results from the IMPROVE and CSN samplers showed a negative bias. There was good agreement between the primary and duplicate denuder systems with a slope of 0.81 and an r^2 equal to 0.69 (Figure 12), although precision was not as good compared with results from Duke Forest.

Figure 11. Comparison of NH_x Concentrations Measured by IMPROVE, CSN, and ADFPS Methods at Gainesville, FL

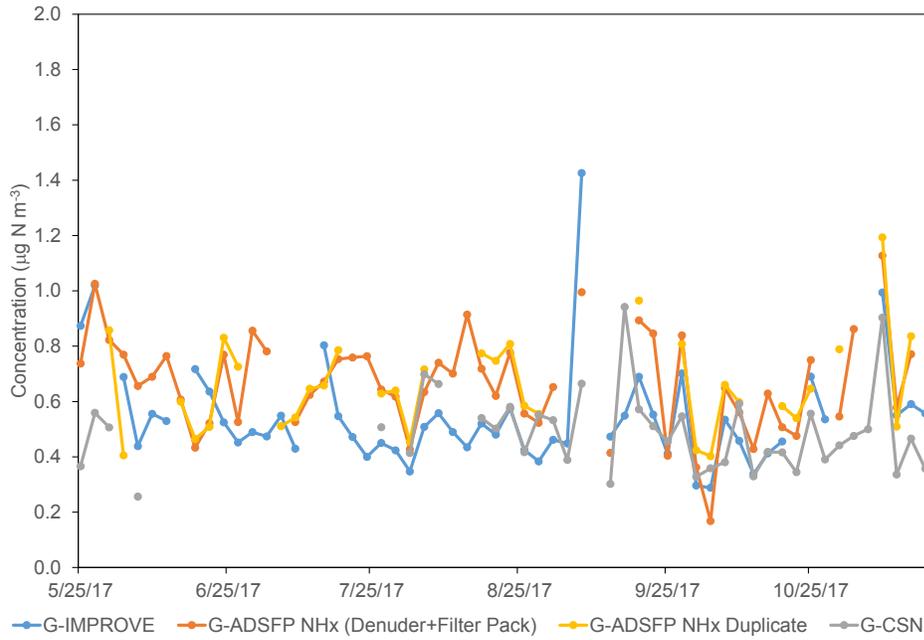
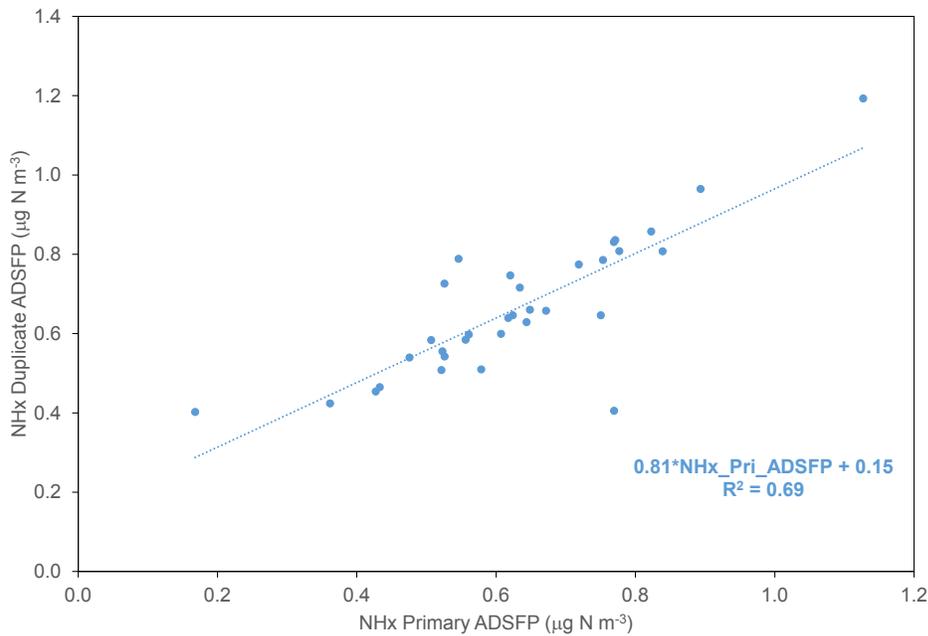


Figure 12. Scatter Plot of Primary ADFPS NH_x Concentration compared with the Duplicate ADFPS at Gainesville, FL



Agreement between the ADFPS and the CSN SuperSASS sampler and the IMPROVE sampler from Gainesville are shown in Figure 13. At Gainesville the range of concentrations as measured by the ADFPS was narrower (0.17-1.13 $\mu\text{g m}^{-3}$) than the NH_x concentrations measured in Duke Forest (0.087-1.29 $\mu\text{g m}^{-3}$). The agreement in NH_x concentrations was relatively poor compared to Duke Forest for both CSN and IMPROVE with a slope = 0.43 and $r^2 = 0.44$ and slope = 0.72 and $r^2 = 0.42$, respectively. While the cause of the poor performance is not obvious, differences in meteorology between the two sites may be a factor.

Figure 13. Linear relationship between the ADFPS versus CSN NH_x results and ADFPS versus IMPROVE NH_x results at Gainesville, FL

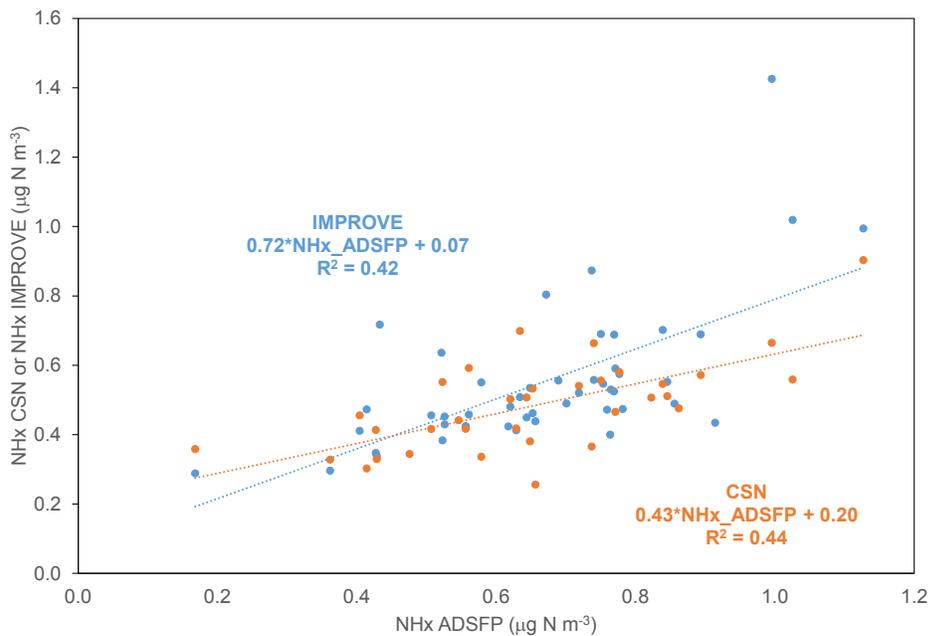
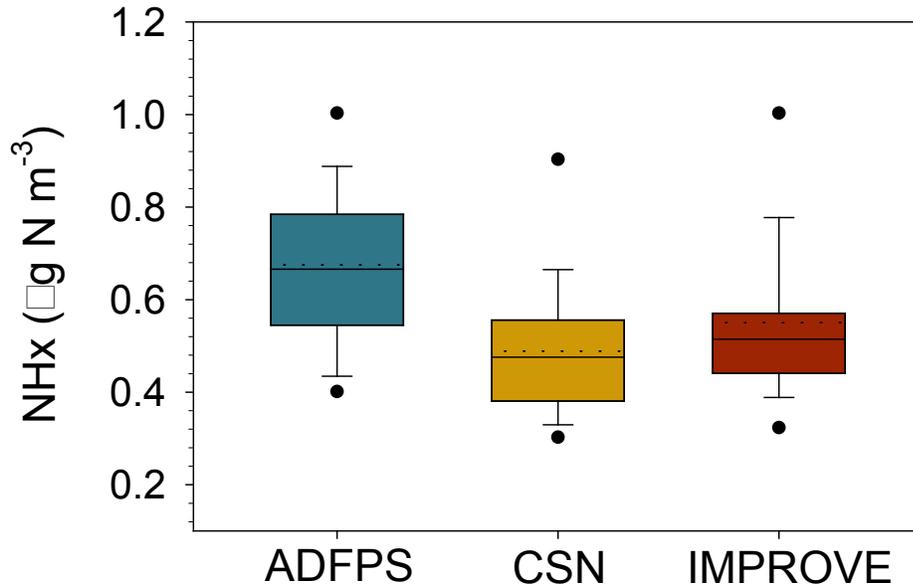


Figure 14 shows the distribution of NH_x concentrations measured during the study at the Gainesville, FL site. As in Figure 10, boxes represent the 25th and 75th percentile, the solid and dashed lines within the box represent the median and mean, respectively, the whiskers represent the 10th and 90th percentiles, and dots represent the 5th and 95th percentiles. Both the CSN and IMPROVE samplers collected less NH_x than the ADFPS.

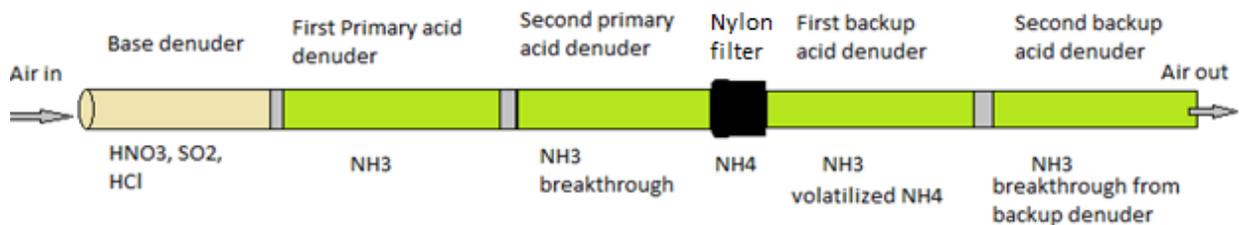
Figure 14. Box plot of Gainesville, FL NH_x concentrations



7.2 Results from the Supplemental Study Conducted at EPA Research Triangle Park Facility

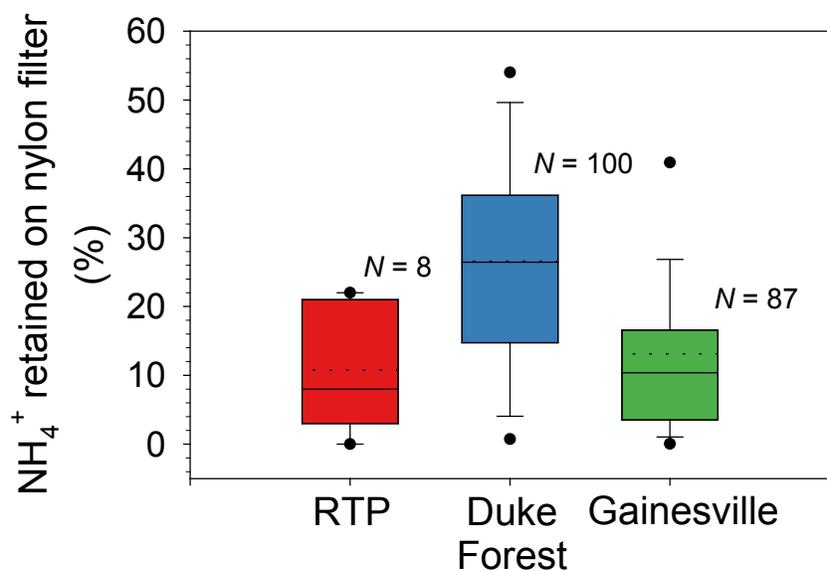
It was noted during the 6-month study period that there was a significant fraction of NH_x being collected on the backup acid coated denuder. The performance of the ADFPS was challenged by collecting 24-hour samples with a second primary denuder as well as a second backup denuder (Figure 15). The additional breakthrough denuders were deployed three times each at Duke Forest and Gainesville. For more information about the field set up during the supplemental study refer to Appendix D. The results indicated there was breakthrough of NH_3 on the primary denuder (the second primary denuder was collecting NH_3). Additional sampling was performed by EPA/ORD at the EPA Research Triangle Park (RTP) campus following the 6-month study to further test the capture efficiency of the primary acid denuder.

Figure 15. ADFPS with additional breakthrough denuders for determining if NH_3 collected on the backup denuder was a result of NH_3 capture efficiency on the primary acid denuder or volatilization of NH_4^+ from the nylon filter



Testing at RTP showed that the collection efficiency of NH_3 on the primary acid coated denuder was $> 95\%$ ($N=32$), in contrast to the more limited assessment during the 6-month field study. The NH_4^+ collected on the nylon filter versus the total NH_4^+ collected from the nylon filter and backup denuder was also assessed. The NH_4^+ retained on the nylon filter was $< 30\%$ of the total NH_4^+ retained by the nylon filter plus the NH_3 captured by the backup denuder. The backup denuder captured NH_3 breakthrough from the primary denuder and NH_4^+ volatilized from the nylon filter. Figure 16 shows the variability in the amount of NH_4^+ retained on the nylon filter (as a % of the filter NH_4^+ plus NH_3 on backup denuder) at the three sites. Similar losses of NH_4^+ from nylon filters have been reported in the literature (Solomon *et al.*, 2000; Yu *et al.*, 2006).

Figure 16. Ammonium retained on the nylon filter as percent of total (nylon filter plus NH_3 captured on the backup denuder from volatilized NH_4^+). Boxes represent the 25th and 75th percentile, the solid and dashed lines within the box represent the median and mean, respectively, the whiskers represent the 10th and 90th percentiles, and dots represent the 5th and 95th percentiles.



The nylon filter had poor capture efficiency of NH_4^+ . On the other hand, the total NH_4^+ was represented by the particulate fraction of NH_x and that value was used to compare to the NH_4^+ concentrations measured by CASTNET. For the NH_x comparisons described in section 7.1 the ADSFP NH_x concentration was calculated using the concentration of NH_3 from the primary denuder and the volatilized NH_4^+ captured as NH_3 on the breakthrough denuder plus particulate NH_4^+ that was retained on the nylon filter. This value should be an accurate representation of total NH_x concentration measured by the ADSFP, given the results of this breakthrough study.

Wood re-analyzed the nylon extracts for NO_3^- and SO_4^{2-} to determine if the nylon filter was ineffective at capturing particles in general or if the poor retention was specific to NH_4^+ . The ratio

of NH_4^+ : SO_4^{2-} from the ADFPS extracts were compared to CASTNET and CSN. CASTNET measures NH_4^+ and SO_4^{2-} using a Teflon filter. Results from Duke Forest and Gainesville supported the Research Triangle Park results that the NH_4^+ was not being retained on the nylon filter. The results are summarized in Table 6.

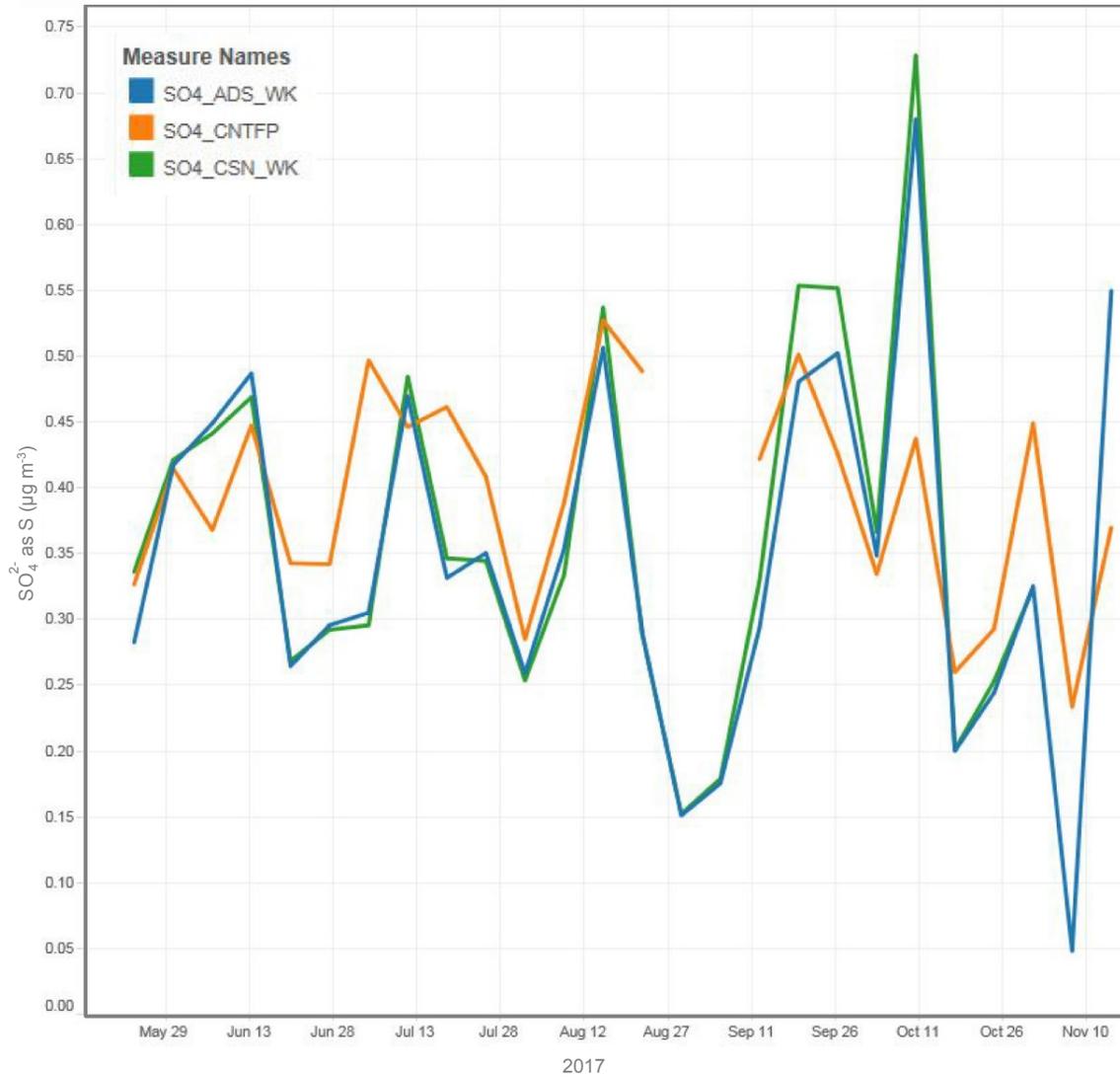
Figure 17 shows the comparison between CASTNET, ADFPS and CSN for SO_4^{2-} and NH_4^+ . Notably, SO_4^{2-} compared very well among the three methods but CSN was biased low for NH_4^+ indicating the bias was not due to the overall nylon filter particle capture efficiency but rather the ability of the filter to retain NH_4^+ after initial collection. Similar results were noted at existing co-located CASTNET/CSN sites in Arendtsville, PA and Perkinstown, WI. The median ratio of NH_4^+ / SO_4^{2-} from CASTNET (Teflon/Teflon) was approximately twice that of CSN (nylon/nylon) indicating lower capture efficiency of NH_4^+ on the nylon filter with good correlation for SO_4^{2-} from the Teflon and nylon filters.

Table 6. Ratio of NH_4^+ : SO_4^{2-} mass concentrations from filter extracts during the NH_x sample period

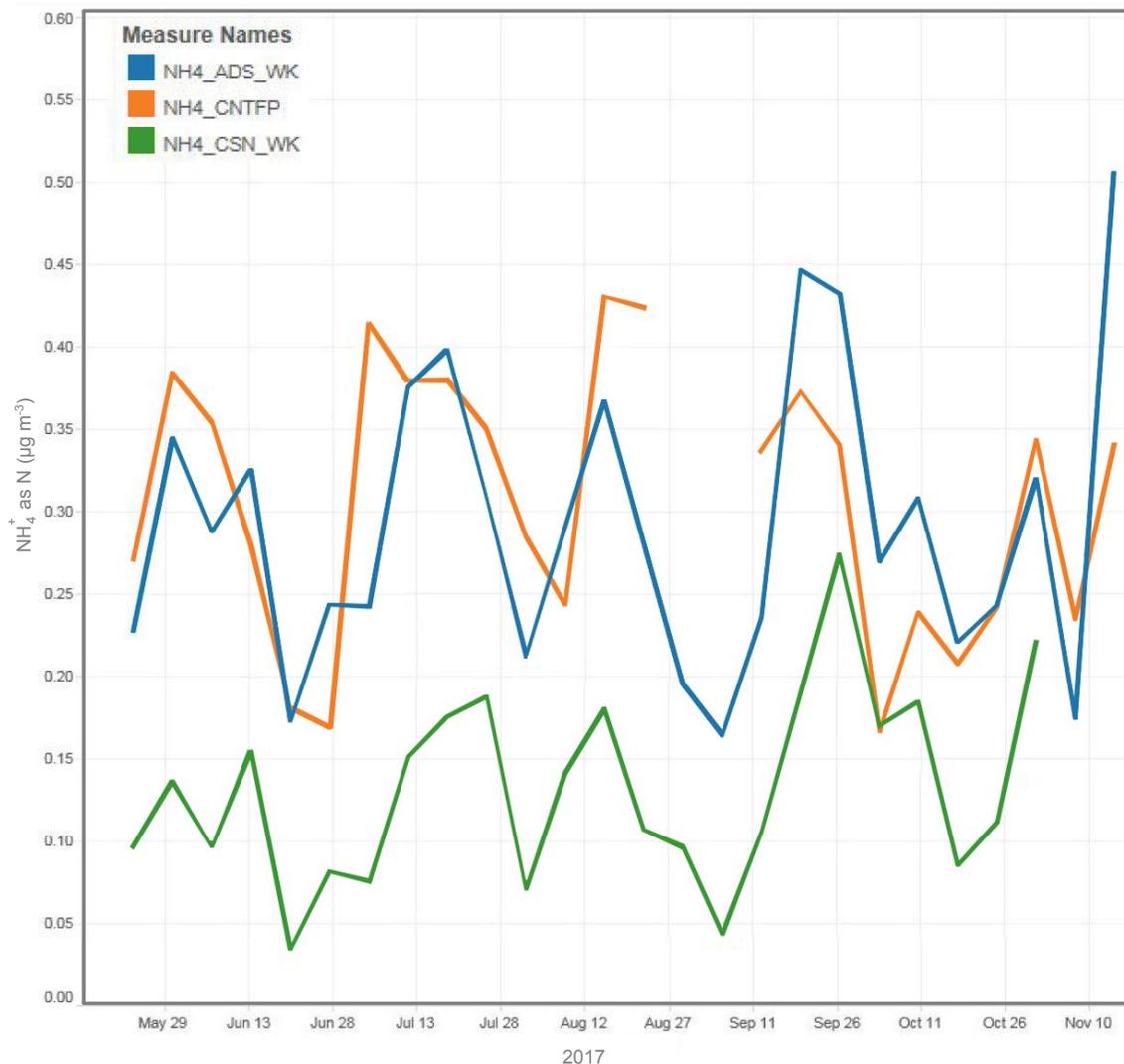
Method	Duke Forest	Gainesville
CASTNET (Teflon)	0.35	
ADFPS (nylon + backup denuder)	0.35	0.35
CSN (nylon)	0.14	0.10

Figure 17. Time series from Duke Forest of (a) SO_4^{2-} concentrations and (b) NH_4^+ concentrations from ADFPS (green), CASTNET (orange - Teflon), and CSN (green - nylon). ADFPS and CSN concentrations are weekly averages matching the CASTNET sampling period.

(a)

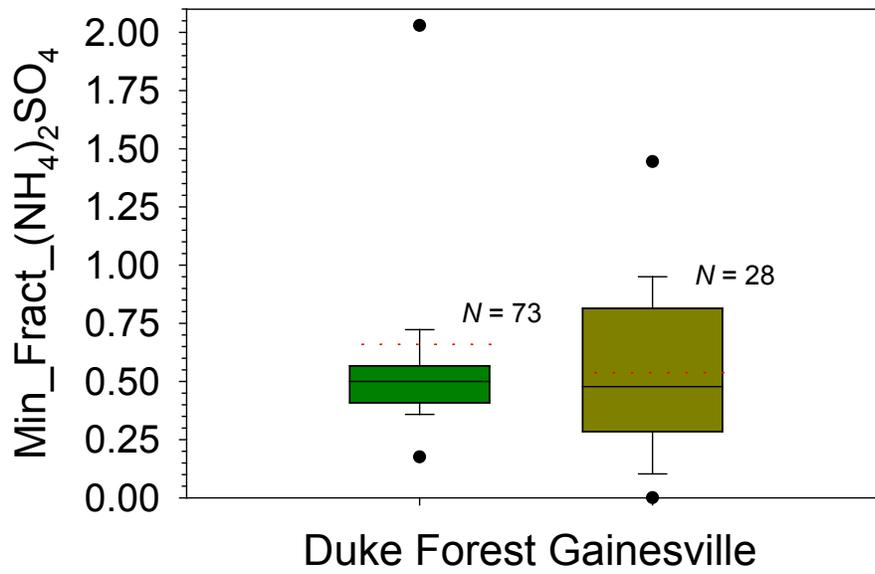
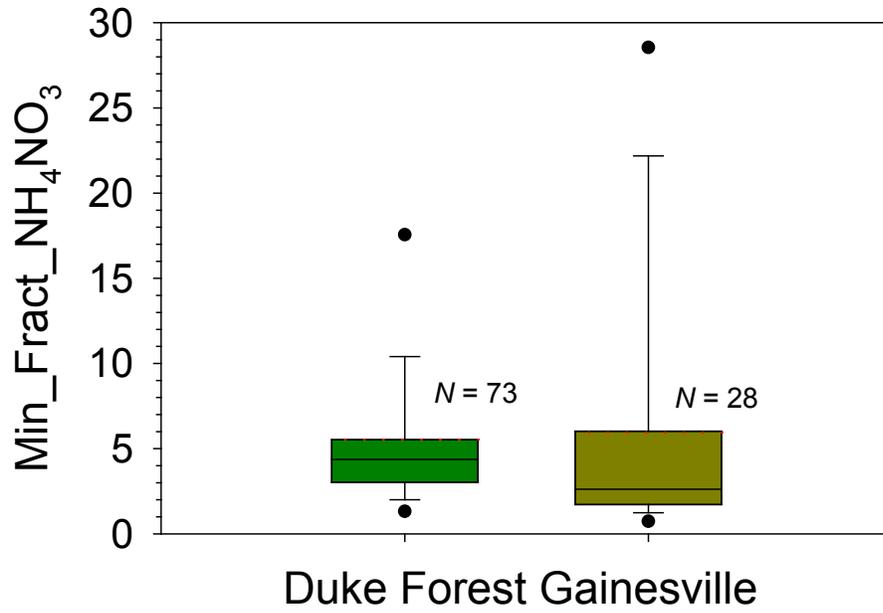


(b)



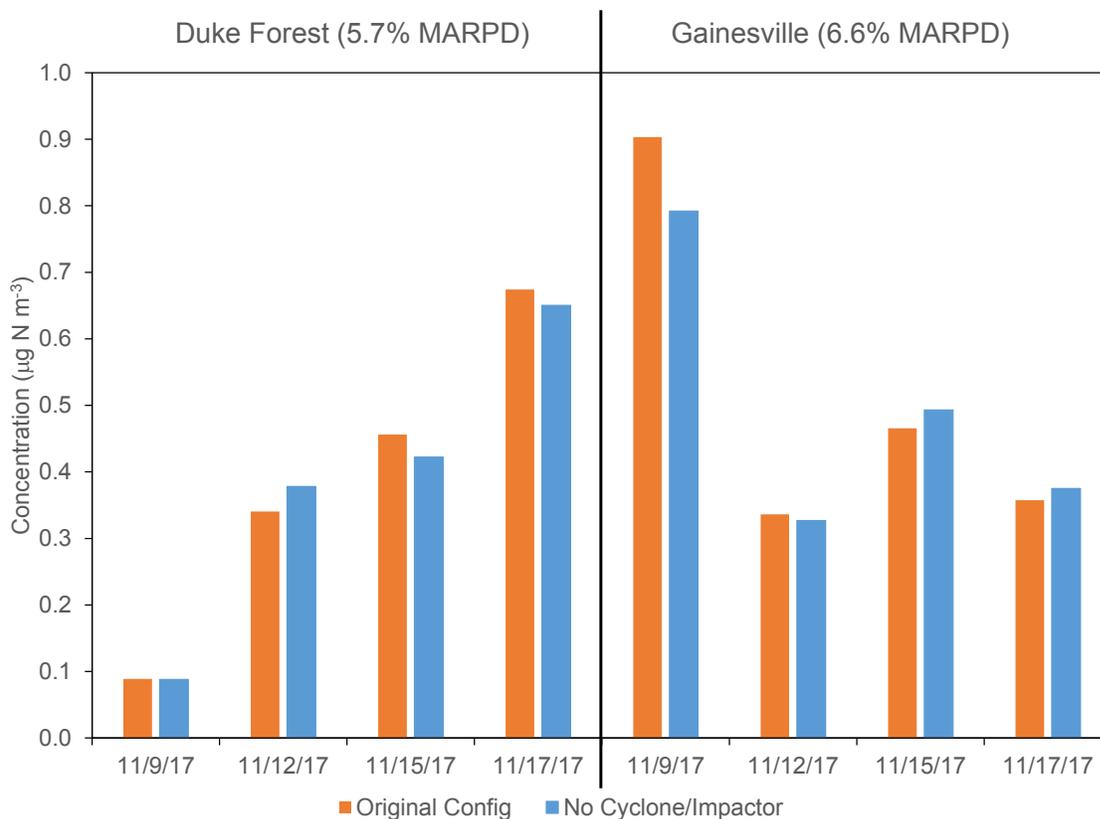
The nylon filter captured SO_4^{2-} but showed losses of NH_4^+ . To verify that the loss of NH_4 from the nylon filter was not due only to volatilization of NH_4NO_3 , the maximum amount of NH_4 from the nylon filter that could be associated with NH_4NO_3 was calculated. The remaining NH_4 that could be associated with $(\text{NH}_4)_2\text{SO}_4$ was then calculated. Those results were used to determine the minimum fraction of NH_4 loss from both NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$. The results are summarized in boxplots as the ratio of NH_4 as measured on the breakthrough denuder/maximum amount of NH_4 associated with NO_3 or SO_4^{2-} . The mean and median minimum fraction of NH_4 lost from NH_4NO_3 was greater than 1 at both sites indicating there was more NH_4 lost from the nylon filter than could be explained by 100% volatilization of NH_4NO_3 . The mean and median minimum fraction of NH_4 lost from $(\text{NH}_4)_2\text{SO}_4$ was approximately 0.5 at both sites, indicating a substantial amount of loss associated with $(\text{NH}_4)_2\text{SO}_4$.

Figure 18. Minimum fraction of NH_4^+ loss association with NO_3^- and SO_4^{2-}



During the supplemental study in Research Triangle Park, NC the inlet was removed from the SuperSASS to verify that the CSN inlet wasn't scrubbing NH₃. There were very small differences between the sampling systems with and without the inlet. The results are shown in Figure 19. The mean absolute relative percent difference (MARPD) was < 7% for the 8 co-located samples.

Figure 19. Mean absolute relative percent difference (MARPD) between CSN samplers with (orange) and without (blue) a cyclone at the inlet



8.0 Conclusions

Even though final results of the study are presented in this report, there are several outstanding questions that should be explored to understand the poor NH_4^+ capture efficiency of the nylon filter (Yu *et al.*, 2006). Answering these questions will reduce uncertainty in the reported CSN NH_4^+ concentrations. Also, analyzing meteorological data may help in determining why the retention of NH_4^+ was not consistent over the sample period or across the sites.

In addition, different types of cellulose filters were used for the CSN and IMPROVE samplers. The CSN 47 mm cellulose filters were procured from Whatman and listed as Type 41, which is rated for coarse particle retention. The Whatman 47mm cellulose filter is also used by CASTNET, where it is impregnated with potassium carbonate (K_2CO_3) for SO_2 sample collection. The IMPROVE 37 mm filters used were procured from SKC Omega Specialty Division and listed as Type 40, which is rated as “medium.” During the procurement process, a 37 mm Type 41 cellulose filter was not available for use in the IMPROVE system. The ratings for Type 40 and 41 indicate there is a 98% retention of 8 μm and 20 μm particles, respectively. Acid-impregnation procedures were identical. It is recommended that the two types of cellulose filters be investigated further in a laboratory setting (chamber study) to determine if the different ratings have any effect on the NH_4^+ collection efficiency.

Overall, the acid-impregnated filters performed well for NH_x in the SuperSASS and IMPROVE PM sampler at the Duke Forest site. The median NH_x concentrations from the ADSFPS, CSN, and IMPROVE from Duke Forest were reasonably close (0.59, 0.57, 0.68 $\mu\text{g m}^{-3}$, respectively). The performance of the acid-impregnated filters at the Gainesville site was poor, with the filters significantly underestimating the NH_x concentrations. The median NH_x concentrations from the reference method (ADSFPS) and the CSN and IMPROVE samplers from the Gainesville site were 0.66, 0.48, 0.51 $\mu\text{g m}^{-3}$, respectively. Besides the CSN pump failure, the cause of the poor performance from the Gainesville site is unclear. Gainesville does have high humidity and morning dew which could have impacted the sampling. We conclude that the acid-impregnated filter method is not suitable for measuring NH_x in environments similar to Gainesville and an additional evaluation is needed to fully understand the negative biases and potential resolutions. It is recommended that air quality and meteorological modeling results (i.e. CMAQ, WRF) be used to determine if biases are greater during specific meteorological conditions to help characterize the uncertainty and identify potential sampling locations for future studies. If further evaluation can satisfy questions about the meteorological impacts to sample retention and resolve the differences in pore size and associated particle retention, a next step could be to deploy the acid-impregnated cellulose filters at a small subset of both CSN and IMPROVE sites to determine if adding NH_x as a measured parameter is feasible across a national network. This would provide a better assessment across different regions, land use types, and climates. If a small pilot is successful, deploying across existing networks would provide a novel, cost-

effective method for measuring NH_x with little burden to the monitoring agencies while filling a significant gap in our understanding of the nitrogen budget.

9.0 References

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10.0 List of Acronyms and Abbreviations

ADFPS	annular denuder filter pack system
AESMD	Atmospheric and Environmental Systems Modeling Division
AQAD	Air Quality Assessment Division
ARD	Air Resources Division
BLK	blank
BS	blank spike
°C	degrees Celsius
CAMD	Clean Air Markets Division
CASTNET	Clean Air Status and Trends Network
CCV	continuing calibration verification samples
CEMM	Center for Environmental Measurement and Modeling
CMAQ	Community Multiscale Air Quality Model
CPHEA	Center for Public Health and Environmental Assessment
CSN	Chemical Speciation Network
DI	deionized
DQI	Data Quality Indicator
DQO	Data Quality Objective
EPA	U.S. Environmental Protection Agency
H ₃ PO ₃	phosphorous acid
HNO ₃	nitric acid
IC	ion chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
K ⁺	potassium ion
K ₂ CO ₃	potassium carbonate
km	kilometer
L	liter
LIMS	laboratory information management system
Lpm	liters per minute
m	meter
MAD	mean absolute difference
MARPD	mean absolute relative percent difference
MFC	mass flow controller
µg	microgram
µg/m ³	micrograms per cubic meter
mg	milligram
MgO	magnesium oxide
mL	milliliter
N	nitrogen
Na ⁺	sodium ion

Na ₂ CO ₃	sodium carbonate
NADP	National Atmospheric Deposition Program
NH ₃	ammonia
NH ₄ ⁺	ammonium
NIST	National Institute of Standards and Technology
NO _x	nitrogen oxides
NO ₃ ⁻	particulate nitrate
NPS	National Park Service
NTN	National Trends Network
OAP	Office of Atmospheric Programs
OAQPS	Office of Air Quality Planning and Standards
OAR	Office of Air and Radiation
ORD	Office of Research and Development
PHESD	Public Health and Environmental Systems Division
PM _{2.5}	mass of particles with a mean diameter of less than 2.5 μm
ppb	parts per billion
ppm	parts per million
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RL	reporting limit
RPD	relative percent difference
SO _x	oxides of sulfur
SO ₂	sulfur dioxide
SO ₄ ²⁻	particulate sulfate
SOP	standard operating procedures
SQL	structured query language
SRM	standard reference material
SVOC	semi-volatile organic compounds
VOC	volatile organic compounds
Wood	Wood Environment & Infrastructure Solutions, Inc.
WRF	Weather Research and Forecasting Model

11.0 Appendix A: Preparation and Extraction of Sampling Media

11.1 ADFPS Phosphorous Acid Coated Denuder

Denuders are coated with 2% phosphorous acid (H_3PO_3), extracted with 10 mL deionized water, and extracts are analyzed for NH_4^+ by ion chromatography. ADFPS H_3PO_3 denuders are prepared and extracted as described below.

Preparation of H_3PO_3 (PA) Solution (2%):

1. Add 10 grams of H_3PO_3 to a 500 volumetric flask and use 50 mL of DI to rinse weigh boat into the flask.
2. Dilute to volume with methanol.
3. Wear a face mask and work quickly to avoid adsorption of ammonia from the air.

Washing:

1. This procedure is performed in the washroom where all required components are available.
2. Rinse each cap with deionized water (DI), filling, swishing, and dumping three times.
3. Using a properly labeled squeeze bottle, rinse the denuder with methanol (MeOH) over the labeled denuder waste container.
4. Rinse the denuder, running DI through the channels for ~10 seconds on each side. Rinse the outside threads of both ends.
5. Put the denuder into a large wash tub and fill with DI.
6. Soak for ~30 minutes.
7. Repeat steps 4 through 6 two times, for a total of three soaking periods.
8. Shake water out of the denuder and caps and allow drying in an aluminum foil lined heat resistant tray covered with aluminum foil in the drying oven about two hours at 60° C.

Coating and Drying:

1. This procedure is performed in the washroom where all required components are available. Wear a face mask and gloves.
2. Place a Pyrex dish containing about ¼ inch citric acid next to where you will be working in the hood.
3. Pipette 10mL of 2% phosphorous acid coating solution into the denuder with bottom cap attached. The bottom of the denuder is the end that the inner quartz tube is recessed about ⅛ inch from the end of the aluminum denuder tube.
4. Secure top cap of the denuder and invert 20 times. The top of the denuder is the end that the inner quartz tube is recessed about one inch from the end of the aluminum denuder tube.
5. Remove the top cap and pour excess coating solution into the labeled denuder waste container.

-
6. Screw the denuder securely into the URG drying manifold so the direction of drying flow is downward; this will allow gravity to remove excess solution from the denuder.
 7. Dry for approximately 20 minutes with 5 liters per minute nitrogen purge. The 'honeycomb' quartz inside the URG denuder will cloud when dry.
 8. Remove the denuders from the drying manifold and install both caps. A blank red label should be attached near the top end to signify H_3PO_3 coating. Write the logbook/page ID on the label and place the denuder in a resealable plastic bag. Refrigerate until needed.
 9. Two lab blanks should be pulled for extraction each coating session and/or each batch of coating solution made.

Extraction:

1. This procedure is performed in the washroom where all required components are available. Wear a face mask and gloves.
2. Place a Pyrex dish containing $\frac{1}{4}$ inch of citric acid in the hood where you are working.
3. Ensure the bottom cap of the denuder is attached firmly and remove the top cap.
4. Pipette 10 mL DI water into the denuder and cap tightly. Invert the denuder 20 times.
5. Tap the top cap a couple times. Unscrew the top cap and set aside.
6. Decant the extract carefully from top end of the denuder into the sample extract bottle.
7. Remove the red Lab ID label from the denuder and attach to the sample extract bottle.
8. Refrigerate until analysis.

11.2 ADFPS Sodium Carbonate Coated Denuder

Denuders are coated with 1% sodium carbonate (Na_2CO_3). In this study, the Na_2CO_3 denuder serves only to remove HNO_3 from the sample stream. For that reason, the Na_2CO_3 denuder is not quantitatively extracted and analyzed.

Na_2CO_3 Coating Solution (1%):

1. Dissolve 5 g of Na_2CO_3 and 5 g of glycerol in 250 mL of DI in a 500mL volumetric flask.
2. Dilute to volume with MeOH.

Washing the Denuder:

1. This procedure is performed in the washroom where all required components are available.
2. Rinse each cap using deionized water (DI), filling, swishing, and dumping three times.
3. Using a squeeze bottle rinse the denuder with methanol (MeOH) over a labeled denuder waste container.
4. Rinse the denuder, running DI through the channels for ~10 seconds on each end. Rinse the outside threads as well.
5. Put the denuder into a large wash tub and fill with DI.
6. Allow to soak for ~30 minutes.

-
7. Repeat steps 4-6 two times, for a total of three soaking periods.
 8. Shake water out of the denuder and caps and allow drying in an aluminum foil lined heat resistant tray, covered with aluminum foil in the drying oven, for about two hours at 60° C.

Coating and Drying URG Na₂CO₃ Denuder:

1. This procedure is performed in the washroom where all required components are available.
2. Pipette 10mL of 1% Na₂CO₃ coating solution into the denuder with bottom cap attached. The bottom of the denuder is the end that the inner quartz tube is recessed about 1/8 inch from the end of the aluminum denuder tube.
3. Secure top cap of the denuder and invert 20 times. The top of the denuder is the end that the inner quartz tube is recessed about one inch from the end of the aluminum denuder tube.
4. Remove the top cap and pour excess coating solution into a labeled denuder waste container.
5. Remove the bottom cap and place the denuder and caps in a desiccator to dry overnight. The desiccant should be fresh.
6. Remove the denuders from the drying manifold and install both caps. A blank green label should be attached near the top end to signify Na₂CO₃ coating. Write the logbook/page ID on the label. Place the denuder in a clean resealable plastic bag and refrigerate until needed.

11.3 Phosphorous Acid Impregnated Cellulose Filters

Improve (37 mm, SKC cellulose type 40, #225-18A) and CSN (47 mm, Whatman cellulose type 41, #1441-047) filters are coated with 3% phosphorous acid (H₃PO₃), extracted with 20 mL deionized water, and extracts are analyzed for NH₄⁺ by ion chromatography. H₃PO₃ impregnated filters are prepared and extracted as described below.

H₃PO₃ (PA) Solutions:

1. 3% PA – Dissolve 30 g of H₃PO₃ in 100 mL of DI in a 1L volumetric flask. Bring to volume with methanol.

Impregnating Cellulose Filters with Phosphorous Acid:

1. Gloves and a face mask must be worn whenever working with the filters and the filters handled in a hood. In addition, a Pyrex dish containing about 1/4 inch of citric acid should be placed near the area where you are working with the filters.
2. Place filters into a wide-mouth polypropylene bottle and cover with 3% PA solution and seal.
3. Sonicate for 30 minutes. Drain the PA solution into an appropriate waste receptacle.

-
4. Add DI to the bottle to cover the filters and sonicate again for 30 minutes. Drain the DI. Repeat this procedure two more time for a total of 3 DI rinses.
 5. Cover the filters with 3% PA and sonicate again for 30 minutes. Drain the PA solution.
 6. Cover the hood work area with aluminum foil and wipe with a towel soaked with the 5% PA solution.
 7. Tear another piece of foil and fold to fit inside the modified nitrogen desiccator. Wipe the foil with a fresh towel soaked with the 5% PA solution. Also wipe the inside top of the desiccator. Clean gloved fingertips, forceps and petri slide bottoms with the 5% PA solution.
 8. Place each filter in a cleaned petri slide (do not cover) and place the slide in a desiccator.
 9. When all of the filters are in the desiccator, attach the nitrogen gas source to the modified desiccator with flow control. Turn on nitrogen gas flow to ~5 LPM. Close hood sash completely.
 10. Check for dryness in 6 hours; continue the nitrogen purge overnight (if necessary) until the filters are visibly dry.
 11. When the filters are dry, clean the tops of the petri slides with a paper towel soaked in the 5% PA solution. Working quickly, place the tops on the slides. Arrange the slides on the plastic tray and place in a marked sealable bag.
 12. Place a paper towel soaked in 5% PA solution in the bottom of the plastic storage container. Put the bag containing the tray of impregnated filters on top of the soaked paper towel and seal the container.
 13. Refrigerate the container.
 14. Two impregnated filters should be acceptance tested with each impregnating procedure.

Loading, Unloading and Extracting Exposed Filters:

1. Gloves and a face mask must be worn whenever working with the filters. In addition, a Pyrex dish or large weigh boat containing about ¼ inch of citric acid should be placed near the area where you are working with the filters.
2. Loading PA filters:
 - a. Cover the lab bench with aluminum foil and wipe with a fresh towel soaked with a 5% PA solution. Clean gloved fingertips, forceps and the inside of the sample bottles and tops with the 5% PA solution.
 - b. Use clean forceps to remove the filter from the petri slide and place in the filter holder or filter pack. Attach corresponding Lab ID sample labels.
 - c. A pair of lab blanks should be pulled weekly for extraction.
3. Unloading exposed filters:
 - a. Cover the lab bench with aluminum foil for cleanliness and wipe with a fresh towel soaked with a 5% PA solution. Clean gloved fingertips, forceps and the inside of the sample bottles and tops with the 5% PA solution.

-
- b. Use clean forceps to remove the filter from the filter holder or filter pack by the edges; fold using only the forceps so that the sampled side is inward and place in a 30mL Nalgene bottle. Cap tightly. This will serve as the extraction bottle. Attach corresponding Lab ID sample extract labels.
 - c. Place the sample bottles in sealable bag and store in a freezer until extraction.
4. Extracting exposed filters:
 - a. Remove the sample bottles from the freezer and allow to equilibrate to room temperature.
 - b. Using the Teflon extraction solution, pipette 20 mL into each filter extraction bottle. Cap tightly.
 - c. Sonicate for 45 minutes.
 - d. Prepare a method blank and cation blank spike with each extraction.

11.4 Nylon Filters

ADFPS and CSN (Channel 2) samplers employ 47 mm nylon filters (Pall Nylasorb #66509, 1 μm) for collection of NH_4^+ aerosol. Filters are extracted with 20 mL deionized water and extracts are analyzed for NH_4^+ by ion chromatography. Filters are prepared and extracted as described below.

Loading, Unloading and Extracting Exposed Filters:

Before assembling modules with clean filters, examine filters for tears, holes, etc. If any are damaged, discard the filter. Wear gloves when handling filters and modules. Use forceps when handling the filters.

1. Loading nylon filters:
 - a. Use clean forceps to place in the sampling module. Attach corresponding Lab ID sample labels.
 - b. A pair of lab blanks should be pulled weekly for extraction.
2. Unloading exposed filters:
 - a. Use clean forceps to remove the filter from the sampling module and place in a 30mL Nalgene bottle. Cap tightly. This will serve as the extraction bottle. Attach corresponding Lab ID sample extract labels.
 - b. Store the sample bottles in the cold room until extraction.
3. Extracting exposed filters:
 - a. Remove the sample bottles from the freezer and allow to equilibrate to room temperature.
 - b. Using the nylon extraction solution, pipette 20 mL into each filter extraction bottle. Cap tightly.
 - c. Sonicate for 60 minutes at 23-27°C. Monitor the temperature and add ice to the sonicator to keep the temperature from exceeding 27°C and then overnight on a shaker table at 1 Hz and 4°C.
 - d. Prepare a method blank and cation blank spike with each extraction.

12.0 Appendix B: Chemicals for IC Analysis

Reagent water: deionized (DI) water of resistivity of 15 mega ohms ($M\Omega$) or greater derived from mixed bed ion exchangers, activated carbon filters, and polishing exchangers. Water should contain particles no larger than 0.20 μm .

Methanesulfonic acid (MSA), >99%, ACS reagent grade or better.

Cation concentrated eluent for CS16 (1.0 N MSA): Dissolve 48.05 g of 99% MSA in a final volume of 500 mL with DI.

Cation working eluent solution (30mM MSA): Dilute 120 mL of 1.0 N MSA concentrate to 4.0 L with deionized water.

Blank spike solutions (BS). Cation blank spike solution purchased from High Purity Standards (HPS). A Certificate of Analysis and an expiration date is provided with each lot. The BS is used to verify the accuracy of the extraction.

Individual Cation Calibration stock solutions (1000 $\mu\text{g/mL}$) are purchased as NIST traceable solutions. A Certificate of Analysis and an expiration date will be provided with each stock.

Lithium stock solution (100 $\mu\text{g/mL}$) is purchased as NIST-traceable solution. A Certificate of Analysis and an expiration date will be provided with each stock.

10 $\mu\text{g/mL}$ intermediate cation calibration solution. 5 mLs of each 1000 $\mu\text{g/mL}$ stock standard are added to a 500 mL volumetric flask and diluted to volume with DI. The intermediate solution will have an expiration date 6 months from preparation (or the expiration date of an individual stock if sooner).

100 $\mu\text{g/mL}$ intermediate cation calibration solution. 20 mLs of each 1000 $\mu\text{g/mL}$ stock standard are added to a 200 mL volumetric flask and diluted to volume with DI. The intermediate solution will have an expiration date 6 months from preparation (or the expiration date of an individual stock if sooner).

The working curve will be prepared by adding the volumes listed in Table 7 below to separate 500 mL volumetric flasks. The working curve will have an expiration date one month after preparation.

Table 7. Cation concentration curves (µg/mL)

Cation Standard	Volume of Intermediate Calibration Solutions (mL)			Working Curve Concentrations (µg/mL)	
	10 µg/mL	100 µg/mL	100 µg/mL Li	Li ⁺	Na ⁺ , NH ₄ ⁺ , K ⁺
STD 1			5.0	1.0	0.0
STD 2	1.0		5.0	1.0	0.02
STD 3	2.0		5.0	1.0	0.04
STD 4	5.0		5.0	1.0	0.10
STD 5	25.0		5.0	1.0	0.50
STD 6		5.0	5.0	1.0	1.0
STD 7		25.0	5.0	1.0	5.0

A minimum of five points shall be used for each calibration curve. The concentrations of the daily curve are listed in Table 7 in units of micrograms (µg) per mL.

Thermo Cation I Standard. A Certificate of Analysis and an expiration date is provided with each lot.

Cation Control standards used as continuing calibration verification (CCV) solutions are prepared by diluting 5 mL of the Thermo Cation I stock to a 500 mL final volume with DI. The working CCV will have an expiration of 6 months from preparation (or the expiration date of an individual stock if sooner). A CCV is used to verify accuracy.

Cation Standard Reference Material (SRM) reference solution is purchased as a ready-to-use NIST-traceable standard solution containing analytes of interest with a Certificate of Analysis and an expiration date.

13.0 Appendix C: Chain of Custody Forms

Annular Denuder System	
ADS Channel 1	ADS Channel 2
Installed: Date: ___/___/___ Time: _____ Initials: _____	Installed: Date: ___/___/___ Time: _____ Initials: _____
Removed: Date: ___/___/___ Time: _____ Initials: _____	Removed: Date: ___/___/___ Time: _____ Initials: _____
Total Flow Volume: _____ m ³	Total Flow Volume: _____ m ³
2x4 Blank area for label	2x4 Blank area for label
2x4 Blank area for label	2x4 Blank area for label
2x4 Blank area for label	2x4 Blank area for label

COMMENTS: _____

LAB USE ONLY: LAB TECH RECEIPT _____ DATE: ___/___/___
--

IMPROVE

Date: ___/___/___ Time: ___:___

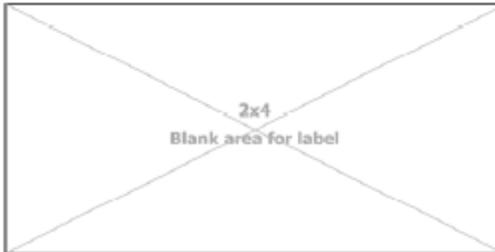
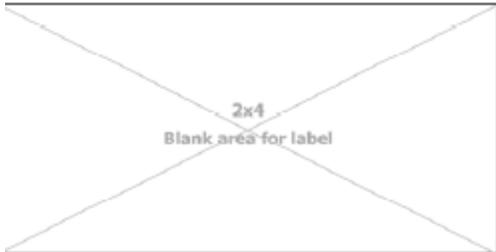
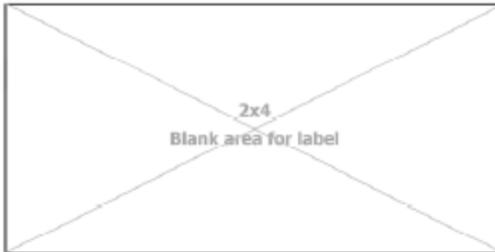
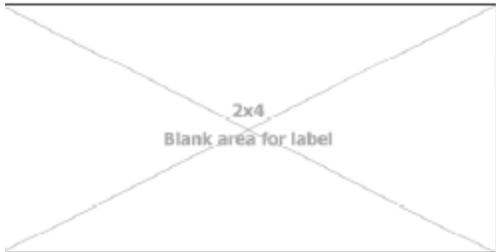
Operator Initials _____

Date: ___/___/___ Time: ___:___

Operator Initials _____

		INITIAL READINGS				FINAL READINGS		
Sample	MaxOri	Cassette	Cyc	Ori	Cyc	Ori	ET	

Date								
5/25/2017		1	---	---	---	---	---	
5/28/2017	Mod B	2	---	---	---	---	---	
		3	---	---	---	---	---	
		4	---	---	---	---	---	



COMMENTS:

LAB USE ONLY:
LAB TECH RECEIPT _____

DATE ___/___/___

CSN SuperSASS

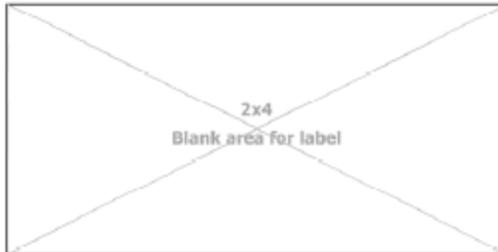
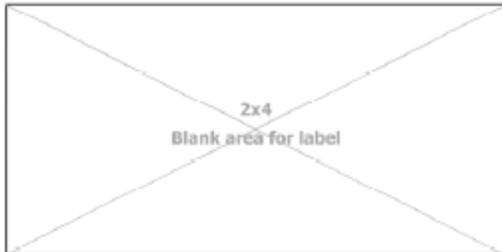
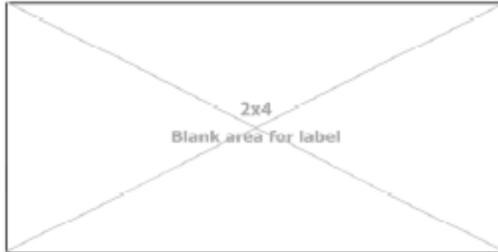
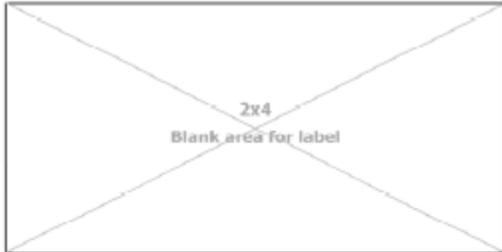
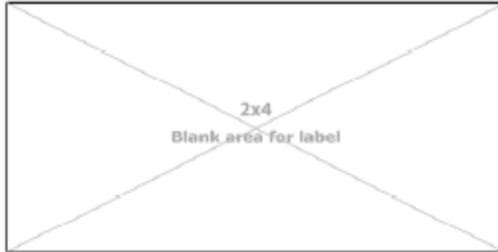
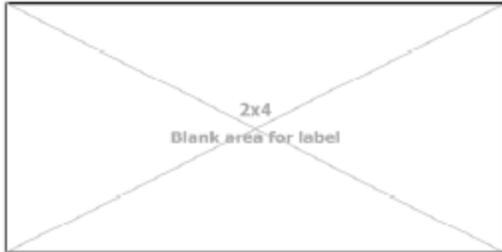
Installed:

Date: ___/___/___ Time: _____ Initials: _____

Removed:

Date: ___/___/___ Time: _____ Initials: _____

Channel Number	Run Time	Sample Volume
1		m ³
2		m ³
3		m ³
4		m ³
5		m ³
6		m ³
7 FB	0	0 m ³
8 FB	0	0 m ³



COMMENTS: _____

<p>LAB USE ONLY: LAB TECH RECEIPT _____ DATE ___/___/___</p>	<p>_____</p> <p>_____</p> <p>_____</p>
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14.0 Appendix D: Characterization of NH₃ Breakthrough on Phosphorous Acid Coated Annular Denuders

14.1 Project description and objectives

This effort builds on the primary project described above to assess the performance of NH_x collection by IMPROVE and CSN samplers in humid environments by comparison to a reference ADFPS sampler. During that study, the ADFPS system was discovered to have a certain degree of NH₃ breakthrough from its primary acid coated denuders for samples collected at both sites. Given the objective and purpose of the previous project, only limited extra sampling was conducted to address such suspected breakthrough issues with the ADFPS. In order to fully evaluate and address the potential impaired NH₃ collection efficiency by the annular denuders under humid conditions, additional sampling is proposed to address such issues. The objective of this study is to extend previous work to further evaluate the performance and NH₃ collection efficiency by ADFPS denuders under warmer and more humid environments across seasons.

Scientific approach

The proposed work deviates from the parent QAPP in three ways:

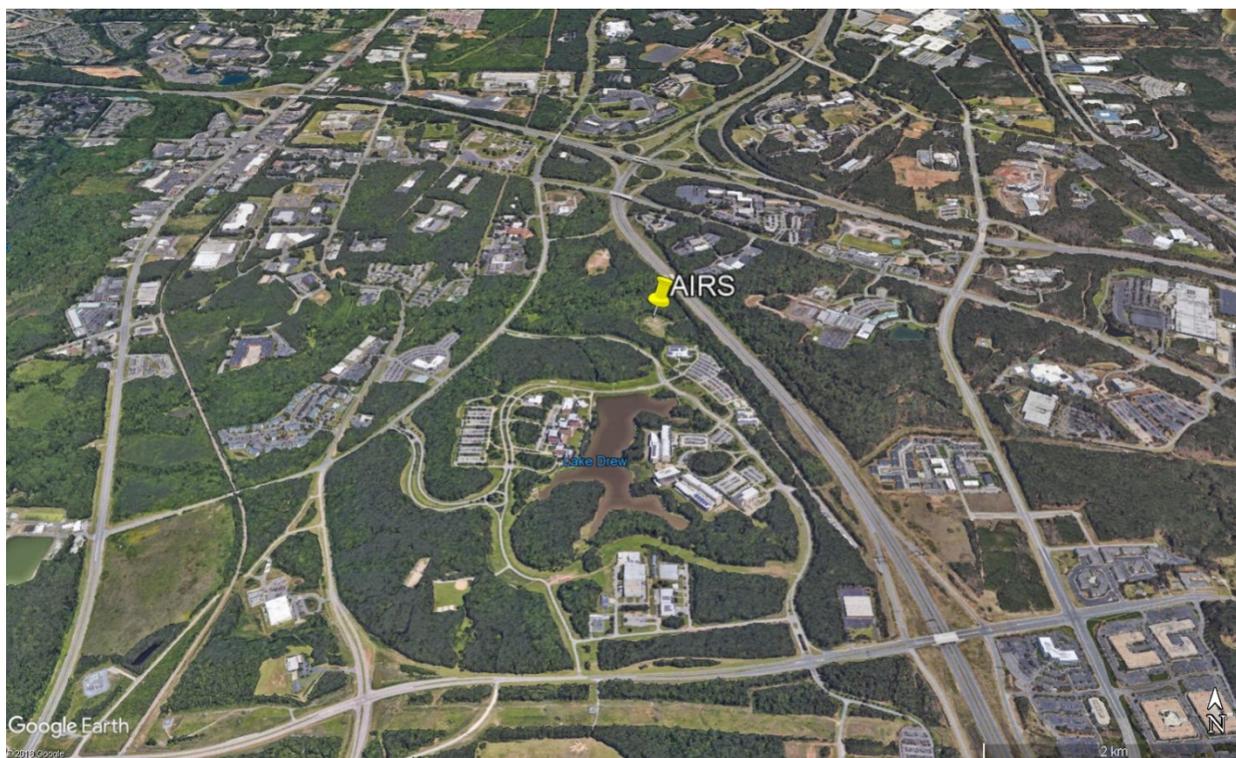
- Measurements will be conducted at the AIRS site adjacent to the EPA campus rather than at Duke Forest, NC or Gainesville, FL.
- An additional acid coated denuder will be added to the ADFPS sampling train to quantify NH₃ breakthrough on the primary acid coated denuder.
- Samples will be analyzed at EPA rather than the AMEC laboratory.

Other than these details, sampling and analytical methods, SOPs, and QA/QC procedures described in the parent QAPP will be followed.

14.2 Field site

The sampling will be conducted at the AIRS site located on the EPA campus in Research Triangle Park, North Carolina (35.8897 latitude, -78.8747 longitude).

Figure 20. EPA campus study site AIRS



14.3 Annular Denuder/Filter Pack System

We propose to evaluate the ADFPS NH_3 denuder collection efficiency by using the URG ADFPS samplers with two NH_3 denuders in series. The configuration of the sampling train is as follow:

- A 1% sodium carbonate (Na_2CO_3)-coated annular denuder for scrubbing gaseous HNO_3
- Two 1% H_3PO_3 -coated annular denuders in series for collection of gaseous NH_3
- A 2-stage filter pack containing a nylon filter for collection of particulate NH_4^+
- A backup 1% H_3PO_3 -coated annular denuder for collecting gaseous NH_3 that may volatilize from the nylon filter

Three weeks of 24hr (from 9am to 9am EST) samples will be collected each season covering different meteorological conditions at the NC EPA site to provide insight into NH_3 denuder performance under warm and humid conditions. Approximately 60 or more samples will be collected starting summer 2018 through winter covering three seasons, which include warmest and humid summer periods as well as relatively dry and cold winter conditions.

14.4 Chemical analysis

Denuder and filter extracts are analyzed for NH_4^+ , NO_3^- and SO_4^{2-} by ORD NRMRL lab using ion chromatography (IC, Dionex model ICS-2100, Thermo Scientific, Waltham, MA). The IC is equipped with guard (IonPac 2mm AG23) and analytical columns (AS23) for anions. The samples are analyzed using an isocratic eluent mix carbonate/bicarbonate (4.5/0.8mM) at a flow rate of 0.25mL/min. Cations are analyzed by Dionex IonPac 2mm CG12 guard and CS12 analytical columns; separations are conducted using 20mM methanesulfonic acid (MSA) as eluent at a flow rate of 0.25mL/min. Multi-point (≥ 5) calibration is conducted using a mixture prepared from individual inorganic standards (Inorganic Ventures, Christiansburg, VA). A mid-level accuracy check standard is prepared from certified standards mix (AccuStandard, New Haven, CT) for quality assurance/quality control purposes.

14.5 Collection efficiency calculations

NH_3 collection efficiency calculations are based on the assumption that any breakthrough or NH_3 not captured by first primary denuder will be secured by second primary denuder in line; hence, the collection efficiency is calculated by following equation:

$$\eta = \frac{N_1}{N_1 + N_2} \times 100\%$$

Where η is NH_3 collection efficiency, N_1 is the NH_3 captured by first primary denuder and N_2 is the NH_3 captured by second primary denuder.

15.0 Appendix E: Validation Log for Study Samples

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
1722040-01	D	ADFPS	5/31/17	I3	concentration determined as outlier during data review	10/23/18
1725049-01	D	ADFPS	6/21/17	I1	quick connect fitting not completely sealed, no air flow	8/29/17
1725049-02	D	ADFPS	6/21/17	I1	quick connect fitting not completely sealed, no air flow	8/29/17
1725034-01	D	ADFPS	6/21/17	I1	quick connect fitting not completely sealed, no air flow	8/29/17
1733034-01	D	ADFPS	8/17/17	I5	temperature thermocouple maxed out, pushed flow rate down, reported it was ~10 lpm but was actually ~7 lpm	9/20/17
1733035-01	D	ADFPS	8/17/17	I5	temperature thermocouple maxed out, pushed flow rate down, reported it was ~10 lpm but was actually ~7 lpm	9/20/17
1733035-02	D	ADFPS	8/17/17	I5	temperature thermocouple maxed out, pushed flow rate down, reported it was ~10 lpm but was actually ~7 lpm	9/20/17
1734066-01	D	ADFPS	8/26/17	I5	MFC readout on pump box 8.9 lpm, previous week 10.1 lpm, likely blockage, pressure low, gas meter high, actual flow likely normal	9/20/17
1734067-01	D	ADFPS	8/26/17	I5	MFC readout on pump box 8.9 lpm, previous week 10.1 lpm, likely blockage, pressure low, gas meter high, actual flow likely normal	9/20/17
1734067-02	D	ADFPS	8/26/17	I5	MFC readout on pump box 8.9 lpm, previous week 10.1 lpm, likely blockage, pressure low, gas meter high, actual flow likely normal	9/20/17
1737034-01	D	CSN	9/13/17	I3	concentration determined as outlier during data review	10/23/18
1738020-01	D	CSN	9/19/17	I3	concentration determined as outlier during data review	10/23/18
1739014-01	D	CSN	9/25/17	I3	concentration determined as outlier during data review	10/23/18
1742016-01	D	IMPROVE	10/16/17	I3	flow volume not nominal, concentration determined as outlier during data review	10/23/18

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
1745059-01	D	CSN	11/9/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18
1746078-01	D	CSN	11/12/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18
1746080-01	D	CSN	11/15/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18
1746035-01	D	IMPROVE	11/15/17	I1	no flow	2/22/18
1746082-01	D	CSN	11/18/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18
1746059-01	D	IMPROVE	11/18/17	I1	no flow	2/22/18
1721041-01	G	ADFPS	5/25/17	I1	pump filter old, clogged	8/29/17
1721042-01	G	ADFPS	5/25/17	I1	pump filter old, clogged	8/29/17
1721042-02	G	ADFPS	5/25/17	I1	pump filter old, clogged	8/29/17
1722030-01	G	ADFPS	5/28/17	I1	pump filter old, clogged	8/29/17
1722031-01	G	ADFPS	5/28/17	I1	pump filter old, clogged	8/29/17
1722031-02	G	ADFPS	5/28/17	I1	pump filter old, clogged	8/29/17
1722049-01	G	IMPROVE	5/31/17	I1	pump controller in standby	8/29/17
1722066-01	G	CSN	6/3/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17
1722067-01	G	CSN	6/3/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17
1723031-01	G	ADFPS	6/6/17	I1	pump filter old, clogged	9/1/17
1723032-01	G	ADFPS	6/6/17	I1	pump filter old, clogged	9/1/17
1723032-02	G	ADFPS	6/6/17	I1	pump filter old, clogged	9/1/17
1723026-01	G	CSN	6/6/17	I3	concentration determined as outlier during data review	10/23/18
1723038-01	G	CSN	6/9/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17
1723039-01	G	CSN	6/9/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17
1724018-01	G	CSN	6/12/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
1724019-01	G	CSN	6/12/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17
1724035-01	G	CSN	6/15/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1724036-01	G	CSN	6/15/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1724037-01	G	IMPROVE	6/15/17	I4	possible switch with 6/18	8/29/17
1725024-01	G	CSN	6/18/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17
1725025-01	G	CSN	6/18/17	I2	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume nominal	11/17/17
1725026-01	G	IMPROVE	6/18/17	S1	possible switch with 6/15	8/29/17
1725037-01	G	CSN	6/21/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1725053-01	G	CSN	6/21/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1725063-01	G	CSN	6/24/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1725070-01	G	CSN	6/24/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1726018-01	G	CSN	6/27/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	9/1/17
1726029-01	G	CSN	6/27/17	I3	ambient temperature sensor inoperative, controlled flow rates to	9/1/17

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
					be extremely inaccurate, flow volume not nominal	
1726035-01	G	CSN	6/30/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1726040-01	G	CSN	6/30/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1727015-01	G	CSN	7/3/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1727020-01	G	CSN	7/3/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	11/17/17
1727043-01	G	ADFPS	7/6/17	I5	pressure at MFC much lower than nominal indicating pump working harder than expected, flow steady but low throughout run, possible obstruction	9/20/17
1727044-01	G	ADFPS	7/6/17	I5	pressure at MFC much lower than nominal indicating pump working harder than expected, flow steady but low throughout run, possible obstruction	9/20/17
1727044-02	G	ADFPS	7/6/17	I5	pressure at MFC much lower than nominal indicating pump working harder than expected, flow steady but low throughout run, possible obstruction	9/20/17
1727040-01	G	CSN	7/6/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	8/29/17
1727041-01	G	CSN	7/6/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	8/29/17
1728024-01	G	CSN	7/9/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	8/29/17

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
1728025-01	G	CSN	7/9/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	8/29/17
1728043-01	G	CSN	7/12/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	8/29/17
1728044-01	G	CSN	7/12/17	I3	ambient temperature sensor inoperative, controlled flow rates to be extremely inaccurate, flow volume not nominal	8/29/17
1728045-01	G	IMPROVE	7/12/17	I4	possible switch with 7/15	8/29/17
1728057-01	G	CSN	7/15/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	8/29/17
1728058-01	G	CSN	7/15/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	8/29/17
1728059-01	G	IMPROVE	7/15/17	S1	possible switch with 7/12	8/29/17
1729026-01	G	CSN	7/18/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	8/29/17
1729027-01	G	CSN	7/18/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	8/29/17
1729038-01	G	CSN	7/21/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	8/29/17
1729039-01	G	CSN	7/21/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	8/29/17
1730019-01	G	CSN	7/24/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	9/20/17
1730020-01	G	CSN	7/24/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	9/20/17
1731027-01	G	CSN	7/30/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	9/20/17
1731028-01	G	CSN	7/30/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	9/20/17

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
1732033-01	G	ADFPS	8/8/17	I5	flow initially low and unsteady through 1200, climbs to nominal levels by 1800	9/20/17
1732034-01	G	ADFPS	8/8/17	I5	flow initially low and unsteady through 1200, climbs to nominal levels by 1800	9/20/17
1732034-02	G	ADFPS	8/8/17	I5	flow initially low and unsteady through 1200, climbs to nominal levels by 1800	9/20/17
1732040-01	G	CSN	8/11/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	9/20/17
1732041-01	G	CSN	8/11/17	I4	outlier, suspect contamination possibly from insect activity, invalidated pending anion analysis	9/20/17
1733022-01	G	ADFPS	8/14/17	S1	flow volume slightly low, concentration high	11/17/17
1733023-01	G	ADFPS	8/14/17	S1	flow volume slightly low, concentration high	11/17/17
1733023-02	G	ADFPS	8/14/17	S1	flow volume slightly low, concentration high	11/17/17
1733020-01	G	CSN	8/14/17	I5	outlier, likely contamination, suspected flow blockage possibly from insect activity, nylon filter not invalidated	9/22/17
1736020-01	G	ADFPS	9/4/17	I5	low flow volume, suspected flow blockage possibly from insect activity	9/22/17
1736021-01	G	ADFPS	9/4/17	I5	low flow volume, suspected flow blockage possibly from insect activity	9/22/17
1736021-02	G	ADFPS	9/4/17	I5	low flow volume, suspected flow blockage possibly from insect activity	9/22/17
1736044-01	G	ADFPS	9/7/17	I5	low flow volume, suspected flow blockage possibly from insect activity	11/17/17
1736045-01	G	ADFPS	9/7/17	I5	low flow volume, suspected flow blockage possibly from insect activity	11/17/17
1736045-02	G	ADFPS	9/7/17	I5	low flow volume, suspected flow blockage possibly from insect activity	11/17/17
1736041-01	G	IMPROVE	9/7/17	S2	concentration is outlier, other methods also go up but do not match	11/17/17
1737045-01	G	ADFPS	9/13/17	I5	low flow volume, suspected flow blockage possibly from insect activity	11/17/17
1737046-01	G	ADFPS	9/13/17	I5	low flow volume, suspected flow blockage possibly from insect activity	11/17/17

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
1737046-02	G	ADFPS	9/13/17	I5	low flow volume, suspected flow blockage possibly from insect activity	11/17/17
1738028-01	G	IMPROVE	9/19/17	S1	flow problem at sample removal but 15-minute flow looks OK	11/17/17
1738040-01	G	IMPROVE	9/22/17	S1	flow problem at sample removal but 15-minute flow looks OK	11/17/17
1739020-01	G	IMPROVE	9/25/17	S1	flow problem at sample removal but 15-minute flow looks OK	11/17/17
1740046-01	G	IMPROVE	10/4/17	S1	flow problem at sample removal but 15-minute flow looks OK	11/17/17
1740065-01	G	IMPROVE	10/7/17	S1	flow problem at sample removal but 15-minute flow looks OK	11/17/17
1743023-01	G	IMPROVE	10/22/17	I1	pump failure	11/17/17
1743057-01	G	ADFPS	10/28/17	I1	no flow, pump programmed incorrectly	11/17/17
1743058-01	G	ADFPS	10/28/17	I1	no flow, pump programmed incorrectly	11/17/17
1743058-02	G	ADFPS	10/28/17	I1	no flow, pump programmed incorrectly	11/17/17
1743059-01	G	ADFPS	10/28/17	I1	cap left on cyclone	11/17/17
1743060-01	G	ADFPS	10/28/17	I1	cap left on cyclone	11/17/17
1743060-02	G	ADFPS	10/28/17	I1	cap left on cyclone	11/17/17
1744027-01	G	IMPROVE	10/31/17	I1	pump failure	11/17/17
1744039-01	G	IMPROVE	11/3/17	I1	pump failure	11/17/17
1745021-01	G	ADFPS	11/6/17	I1	cap left on cyclone	11/17/17
1745022-01	G	ADFPS	11/6/17	I1	cap left on cyclone	11/17/17
1745022-02	G	ADFPS	11/6/17	I1	cap left on cyclone	11/17/17
1745020-01	G	IMPROVE	11/6/17	I1	pump failure	11/17/17
1745060-01	G	CSN	11/9/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18
1745042-01	G	IMPROVE	11/9/17	S1	auxiliary flow source used for first half of sample runtime, then replacement pump installed	11/17/17
1746079-01	G	CSN	11/12/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18
1746081-01	G	CSN	11/15/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18
1746067-01	G	ADFPS	11/18/17	I1	no flow, pump programmed incorrectly	2/22/18
1746068-01	G	ADFPS	11/18/17	I1	no flow, pump programmed incorrectly	2/22/18

Sample ID	Site	Method	Sample Date	Flag	Comment	Date Applied
1746068-02	G	ADFPS	11/18/17	I1	no flow, pump programmed incorrectly	2/22/18
1746069-01	G	ADFPS	11/18/17	I1	no flow, pump programmed incorrectly	2/22/18
1746070-01	G	ADFPS	11/18/17	I1	no flow, pump programmed incorrectly	2/22/18
1746070-02	G	ADFPS	11/18/17	I1	no flow, pump programmed incorrectly	2/22/18
1746083-01	G	CSN	11/18/17	Q1	duplicate CSN H3PO3-impregnated filter sampled without cyclone	1/15/18

16.0 Disclaimer: Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the U.S. EPA.