Quality Assurance Project Plan: Improving characterization of reduced nitrogen at IMPROVE and CSN monitoring sites

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May 23, 2017

Revision: 0
Category: 4

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List of Acronyms and Abbreviations

ADFPS	annular denuder filter pack system
Amec Foster Wheeler	Amec Foster Wheeler Environment & Infrastructure, Inc.
BS	blank spike
°C	degrees Celsius
CASTNET	Clean Air Status and Trends Network
CCV	continuing calibration verification samples
CSN	Chemical Speciation Network
DI	deionized
DQI	Data Quality Indicator
DQO	Data Quality Objective
EPA	U.S. Environmental Protection Agency
H_3PO_3	phosphorous acid
HNO_3	nitric acid
IC	ion chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
K^+	potassium ion
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
mL	milliliter
N	nitrogen
Na^+	sodium ion
Na_2CO_3	sodium carbonate
NADP	National Atmospheric Deposition Program
NH_3	ammonia
NH_4^+	ammonium
NIST	National Institute of Standards and Technology
NOx	nitrogen oxides
NO_3^-	particulate nitrate
NPS	National Park Service
NTN	National Trends Network
$PM_{2.5}$	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
SOP	standard operating procedures
SQL	structured query language
SRM	standard reference material
SVOC	semi-volatile organic carbon
VOC	volatile organic carbon

1   PROJECT DESCRIPTION AND OBJECTIVES

The Interagency Monitoring of Protected Visual Environments (IMPROVE) and Chemical Speciation (CSN) networks provide routine measurements of speciated particulate matter that support regional haze and PM NAAQS programs. The Clean Air Status and Trends Network (CASTNET) and National Atmospheric Deposition Program (NADP) provide routine measurements of speciated particulate, gaseous and wet deposition to support acid deposition programs. Over the past two decades, the chemical composition of the atmosphere has changed markedly from one dominated by nitrate, sulfate and carbonaceous aerosols, and their associated precursor gases (NOx, SOx, VOCs, SVOCs), to an atmospheric mixture that includes a significant amount of reduced inorganic nitrogen – particulate ammonium (NH_4^+) and its precursor gas, ammonia (NH_3).   The magnitude of this change is reflected by a nationwide shift in the atmospheric nitrogen budget from one dominated by inorganic oxidized compounds, to one where reduced inorganic nitrogen species ($NHx = NH_3 + NH_4^+$) now have similar or greater concentrations (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 reduced inorganic nitrogen is projected to continue as existing rules and technologies continue to decrease NOx 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, monitoring networks must evolve to best inform decision makers that 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 becomes necessary to characterize reduced nitrogen emission sources and atmospheric composition. Current monitoring networks are relatively well positioned to characterize inorganic oxides of nitrogen, but poorly positioned to characterize the increasingly dominant reduced component of atmospheric nitrogen. This severe limitation is affecting our ability to understand and mitigate the causes of excess PM, haze and nitrogen deposition, in which reduced nitrogen compounds are playing an increasingly important role.

Ammonia and particulate 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 levels and the resulting haze, while NH_3 indirectly affects PM and haze levels. Ammonia also plays an important role in governing the acidity of sulfate aerosol (Silvern et al., 2017) 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 reduced nitrogen is recognized; NH_4^+ is measured in the CSN program and NH_3 is measured in the NADP's Ammonia Monitoring Network (AMoN) network. However, the CSN measurements underestimate NH_4^+ concentrations (Yi et al., 2006) and AMoN collects two week samples, making these data most suitable for seasonal and annual characterizations.

To address the current monitoring deficiencies we posit, "What is a practical and cost effective approach to improve characterization of reduced inorganic nitrogen that could be deployed into existing national networks?" A spatially rich network of high time-resolved (e.g., hourly) NH_3 and particulate NH_4^+ measurements would be an ideal result, but technological and resource limitations preclude that outcome in the immediate future. Ammonia is important as it is the emission species (natural and anthropogenic processes) and precursor responsible for the majority of reduced nitrogen in the atmosphere. Particulate NH_4^+ is important as it is the "controllable" component of NHx relative to the PM NAAQS and potentially nitrogen deposition. Total NHx is important as it reflects the result of NH_3 emissions in the atmosphere and includes the major transformed species (NH_4^+). It can be reasoned that if we had one new measurement, NHx would be the priority as it provides a metric for evaluating emissions and modeling results, and together contributes to nitrogen deposition. In this regard, measurement of total NHx is somewhat analogous to the importance of measuring total oxidized nitrogen (NOy).

In a pilot study by Chen et al. (2014), it was shown that NHx could be measured in the IMPROVE particle monitoring network at several western and Midwestern sites. However, the monitoring performance in humid environments has not been demonstrated. Incorporating an NHx measurement into the CSN and IMPROVE networks would leverage the existing network's infrastructure, reducing cost and allowing for national coverage. The addition of NHx also offers the potential of providing NHx and NH_4^+ estimates at sites co-located with AMoN NH_3 passive samplers. The use of speciation samplers results in 24-hour NHx samples, collected every 3 days, which greatly increases the ability to evaluate chemical transport models and emissions relative to the biweekly AMoN observations. When co-located with AMoN, monthly, seasonal and annual averages of particulate NH_4^+ can be generated which are of direct benefit to PM and NOx/SOx NAAQS reviews and subsequent implementation.

Why is NHx a value added measurement?

1. Reflects contributions to the atmosphere and deposition resulting from NH_3 emissions.
2. Though limited by differences in aggregation periods, an estimate of particulate NH_4^+ can be generated when combining NHx with a collocated NH_3 measurement, such as AMoN.
3. With available cations and anions from the nylon filter module, temperature and relative humidity data, and estimates of total oxidized reactive nitrogen, an estimate of both NH_3 and NH_4^+ can be approximated from an NHx value using thermodynamic models.

4. NHx integrated over 24 hours is advantageous for atmospheric model and emissions evaluation, emissions strategy development and NAAQS reviews and implementation. One can reason that NHx by itself is a more valued observation than ammonia or ammonium for those purposes.
5. Complements the existing NH_4^+ and NH_3 measurements in CSN and AMoN respectively.

In this study, a spare module (37 mm IMPROVE, 47 mm CSN) will be 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. The method has been tested successfully in several western and midwestern locations (Chen et al., 2014) using the URG annular denuder/filter pack system (ADFPS) as a reference sampler. The ADFPS includes 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 constitutes a reference NHx sample. Before deploying this technique in national networks, the proposed study will extend the Chen et al. (2014) work to warmer, more humid eastern U.S. environments. The Duke Forest research site in the NC piedmont area is led by John Walker of EPA's ORD and a Gainesville, FL location served by Amec Foster Wheeler, which operates CASTNET and several of the NADP network sites, will provide two warm weather humid sites of moderate (Duke Forest) and low (Gainesville) NHx levels for testing. Both sites will be outfitted with CSN, IMPROVE and a URG reference sampler collecting a 24-hr sample every third day and AMoN (consecutive 2 week sampling periods) for six months starting in the May - June 2017 time period. In addition, each CSN sampler will run a second module with the standard nylon filter and MgO denuder for NH_4^+ analysis to characterize NH_4^+ measurement uncertainties in ongoing speciation monitoring networks.

Objectives of the study, e.g.:
- Test the NHx monitoring method in hot and humid environments with low to moderate NH_3 concentrations.
- Assess sources of uncertainty in the measurement
- Develop standard sampling protocols that can be employed in a routine network.

2   ORGANIZATION AND RESPONSIBILITIES

This project will be carried out by staff from EPA (ORD/NRMRL, OAR/OAQPS, and OAP/CAMD), NPS and Amec, Foster, Wheeler Environment and Infrastructure, Inc.. Dr. John Walker, ORD, and Amec, Foster, Wheeler will oversee daily activities at the Duke Forest and Gainesville sites, respectively. These onsite activities include set-up and calibration of the IMPROVE and CSN samplers and the URG reference samplers and sample changeouts, packaging and mailing of filters and denuders for analysis. Denuder preparation and extraction for the Duke Forest site will be conducted by John Walker's laboratory. All other filter and denuder preparation and extractions and all laboratory analyses will be conducted by Amec Foster Wheeler at the Gainesville, FL laboratory. Melissa Puchalski (OAP) will provide direction to Amec Foster Wheeler as the work assignment manager. Joann Rice (OAQPS) and Dr. Bret Schichtel (NPS) will provide direction for operation of the CSN and IMPROVE

samplers to ensure compliance with established protocols for the CSN and IMPROVE networks, respectively. John Walker will provide direction for operation of the URG Annular Denuder Filter Pack System (ADFPS) reference sampler. Dr. Xi Chen (ORD/NRMRL/APPCD) will provide direction regarding preparation and analysis of filter and denuder samples. Dr. Richard Scheffe will serve as the overall technical lead be responsible for analyzing results and developing and providing overall project direction, preparation of the QAPP, QA/QC activities, analysis of data, report generation, and preparation of a journal manuscript.

Project schedule and milestones are as follows: 1) deploy CSN/IMPROVE and URG reference samplers by May 23, 2017, 2) complete data collection in the late fall/early winter of 2016/2017, 3) a data analysis report within 30 days after completion of the six month sampling period, 4) an EPA report based on the data analysis report with recommendations for next steps and distribution to the broader SLT community, and 5) a peer reviewed published paper incorporating project results in mid-2018.

3   SCIENTIFIC APPROACH

We propose to sample for ambient NHx (sum of ammonia gas and particulate ammonium) using phosphorous acid coated cellulose filters in IMPROVE and CSN samplers following methodology established by Chen et al. (2014), and URG ADFPS samplers with 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 will constitute a reference NHx sample, the results of which will be compared to the results obtained using both the IMPROVE and CSN samplers containing acid treated filters.

The acid treated filters will eliminate off gassing of ammonia which occurs in routine sampling operations collecting ions on nylon filters with base properties. Filters subsequently are analyzed for NH_4^+ by IC. Other than the preparation of phosphorous acid coated filters, described in section 9 of this QAPP, all sampling and analysis protocols are identical to those in the routine operations of IMPROVE and CSN. Relevant standard operating procedures (SOPs) are referenced in the text. The NHx sampling and analysis methodology has been demonstrated to perform well in western and Midwestern U.S. locations; the objective of this study is to extend previous work to warmer and more humid environments to ascertain potential applicability of the technique at a national scale.

Approximately 6 months of sampling conducted every 3 days will provide 60 or more samples per sampling channel per site covering the warmest and most humid periods in relatively extreme high dew point conditions associated with the NC and FL locations. The 60 samples will enable calculation of measurement accuracy of each CSN and IMPROVE sampler relative to the URG ADFPS which is considered the reference sampler in this study.

4   MEASUREMENT PROCEDURES

4.1   Field Sites

Duke Forest, Chapel Hill, NC

Measurements will be 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 routine measurements (N.C. Forest Service Fire Forecast, NOAA Climate Reference Network, NADP AMoN NH_3) are performed at this site, which is periodically also used for special studies (Rumsey and Walker, 2016). Instruments will be operated in the middle of the field adjacent to the N.C. Forest Service and NOAA meteorological towers and collocated with the NADP AMoN sampler. In addition to the routine measurements conducted in the grass field, weekly CASTNET filter pack measurements (DUK008) are conducted at the forest flux tower located immediately adjacent to the grass field.

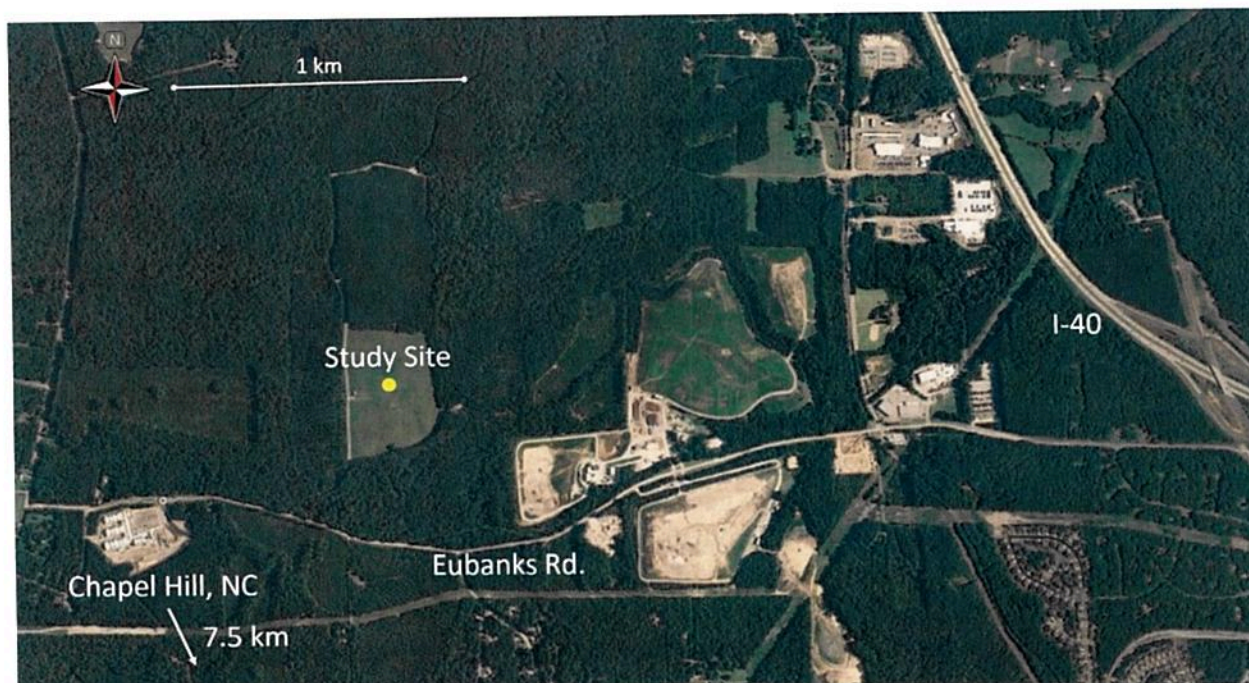Figure 1. Duke Forest study site

Gainesville, Florida

The Amec, Foster, Wheeler laboratory (29.6497 latitude, -82.4914 longitude) near Gainesville, Fl will serve as the 2nd study site. Instrumentation will be mounted on the roof of the site shelter. In addition to the IMPROVE, CSN, and ADFPS measurements, weekly CASTNET filter pack and biweekly AMoN NH_3 samples will also be collected.

Figure 2. Gainesville, FL study site

4.2   Annular Denuder/Filter Pack System

The reference measurement (Inorganic Compendium method IO-4.2 modified) for this study ueses a URG (URG Corporation, Chapel Hill, NC) annular denuder/filter pack system (ADFPS) consisting of the following components in series (Chen et al., 2014):

- A sodium carbonate (Na_2CO_3)-coated annular denuder for scrubbing gaseous HNO_3

- A H_3PO_3-coated annular denuder for collection of gaseous NH_3

- A 2-stage filter pack containing a nylon filter for collection of particulate NH_4^+

- A backup H_3PO_3-coated annular denuder for collecting gaseous NH_3 that may volatilize from the nylon filter

Denuders and filters are extracted with deionized water and analyzed for NH_4^+ by ion chromatography (Section 5.3).

Like the IMPROVE and CSN systems described below, the ADFPS will sample for 24 hour periods, every 3 days, on a midnight to midnight schedule yielding 24-hour average concentrations. Air flow through the samplers is mass flow controlled at a rate of 10 Lpm using a computerized pump (URG Corporation, Chapel Hill, NC). The inlet is a Teflon coated cyclone (URG Corporation, Chapel Hill, NC) with a particle cutoff of 2.5 μm aerodynamic diameter.

Out of approximately 60 total ADFPS samples per site collected over the duration of the study, 44 will be collocated at both the Duke Forest and Gainesville sites. ADFPS samples are changed

out two or three times per week, depending on the 1:3 day sampling schedule, as opposed to weekly change out of the IMPROVE and CSN samplers.

4.3   Met One SuperSASS CSN Sampler

The Met One SuperSASS (www.metone.com) sampler (also used for the CSN) contains parallel metal sample canisters; each with its own inlet, PM2.5 sharp-cut cyclone, denuder (if applicable), and 47-mm filter holder. The canisters are mounted in a sampling head with a radiation shield. The canister cyclone inlets point downward. The sampling head has independent sampling channels, each operated with a mass flow controller and a sample flow rate of about 6.7 liters per minute. The Met One sampler will sample for 24 hour periods, every 3rd day, on a midnight to midnight schedule yielding 24-hour average concentrations.

For this study, two channels of the Met One will be operated. About 60 samples will be collected on each channel. One channel will be configured with a magnesium oxide (MgO) coated aluminum denuder followed by a nylon filter. The nylon filter will be extracted and analyzed (Section 5.3) for particulate NH_4^+. The denuder is a multi-cell (honeycomb) configuration. The denuder removes interfering acid gases, but will not be extracted for analysis. The second channel will be configured with a H_3PO_3-impregnated cellulose filter. The cellulose filter will be extracted and analyzed (Section 5.3) for total NHx ($NH_3 + NH_4^+$) as NH_4^+. See section 5.4 for the frequency of field and lab blank collection. For reference, the routine CSN SOP used for sampling is located at: https://www3.epa.gov/ttn/amtic/files/spectraining/MetOneSASSSOP.pdf

4.3   IMPROVE Sampler

The Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler is a suit of modules to collect PM2.5 and PM10 samples on different filter media. Each module has its own inlet; a PM2.5 sharp-cut cyclone or PM10 inlet; an optional denuder; and 37-mm filter holder. Each module also has a critical orifice to control the air flow. The PM2.5 and PM10 modules are configured to sample with a constant flow rate of 22.8 liters per minute and 16.9 liter per minute respectively. In the standard configuration, the IMPROVE sampler collects samples for 24 hour periods, every 3rd day, on a midnight to midnight schedule yielding 24-hour average concentrations.

For this study, one channel of the IMPROVE PM2.5 module will be operated following the IMPROVE SOP 226 (http://airquality.crocker.ucdavis.edu/files/6614/5808/2356/TI226H_Calibration_of_Flow_Check_Devices.pdf), without the denuder, and collect about 60 samples on a H_3PO_3-impregnated cellulose filter. The cellulose filter will be extracted and analyzed (Section 5.3) for total NHx ($NH_3 + NH_4^+$) as NH_4^+. The sampling will follow the standard IMPROVE schedule. See section 5.4 for the frequency of field and lab blank collection. For reference, the routine SOP used for the sampler in the IMPROVE monitoring program is located at: http://vista.cira.colostate.edu/Improve/particulate-monitoring-network/

5   QUALITY METRICS (QA/QC CHECKS)

5.1   Calibration and Auditing of Field Equipment

Continuous data (flow and temperature) is validated according to the validation procedures described in section 4.3 of the CASTNET QAPP (U.S. EPA, 2016), following calibration procedures for the Super SASS sampler (https://www3.epa.gov/ttn/amtic/files/ambient/pm25/spec/metone.pdf)
 Flow data are flagged as invalid if the value is outside the nominal flow by > 10% (https://www3.epa.gov/ttn/amtic/specguid.html). Ambient temperature data are flagged if the value is below -40 or > 50 degrees C. Flags for data validation are included in Table 4-7 of the CASTNET QAPP. Table 1 summaries the calibration criterion for flow for each measurement system.

Table 1 Calibration criteria for each sampling system

| | Flow criteria | |
	Flagged as Suspect	Flagged as Invalid
CSN SuperSASS	Flow between 6.0 and 6.4; flow between 7.0 and 7.4 lpm	Flow < 6.0 or > 7.4 lpm
IMPROVE PM Sampler	Flow between 15.2 and 16.1; Flow between 17.7 and 18.6 lpm	Flow < 15.2 or > 18.6 lpm
URG ADFPS	Flow between 9.0 and 9.5; flow between 10.5 and 11.0 lpm	Flow < 9.0 or > 11.0 lpm

Flow calibrations will be performed at the start of the sampling period, after 3-months and at the end of the study period. Flow rates for the SuperSASS and ADFPS samplers will be verified using a NIST-traceable MesaLabs Definer 220 dry piston flow meter (MesaLabs, Lakewood, CO). Calibration of the SuperSASS sampler is described here: https://www3.epa.gov/ttn/amtic/files/ambient/pm25/spec/metone.pdf. 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) is used to calibrate pressure sensors in the IMPROVE sampler. The flow rate through the sampler is calculated using the pressure drop across a flow restriction and the density of ambient air. The Magnehelic flow check device is calibrated using a Definer 220 NIST-traceable flow meter. Calibration results will be used to validate the concentration measurements from each sampler-type. The flow rate criterion for each system is ± 10% . During flow audits, temperature sensors in the SuperSASS and IMPROVE samplers are calibrated at one point using a NIST-traceable reference thermometer. The temperature criterion for each system is ± 1 degree C Temperature sensors will be replaced if outside ± 10 degrees C during calibration. The SuperSASS and IMPROVE pressure sensor criteria are ± 10%. If the sensors exceed 10% during the calibration the data would be flagged as invalid.

5.2   Laboratory Procedures

5.2.1   Preparation of Sampling Media

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

5.3   Chemical Analysis

Laboratory IC quality control procedures are fully described in section 3.3.2 of the CASTNET QAPP (U.S. EPA, 2016). Details relevant to this QAPP are summarized below. It is noted that while CASTNET routinely analyzes for NH_4^+ using colorimetry, IC analysis will be used in this project to maintain 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 will be followed here for NH_4^+.

Denuder and filter extracts are analyzed for NH_4^+ by Amec Foster Wheeler 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 are injected onto the analytical column from a 50 uL loop and eluted in 30 mM methanesulfonic acid at a flow rate of 1 mL/min.

Interferences can be caused by substances with retention times that are similar to and overlap with those of the cation(s) of interest. Column overloading can lead to peak tailing, poor peak resolution, and/or carryover into an adjacent downfield peak. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, or other sample processing accessories that lead to discrete artifacts or an elevated baseline in ion chromatograms.

Because the regenerant is chemically produced in the self-regenerating suppressor, changes in flow or electrical spikes may cause interfering peaks to appear in the sample chromatograms. These peaks are typically relatively small, asymmetrical, and extremely sharp. Broader, more rounded asymmetrical peaks may appear as a result of a change in operating conditions that is isolated to the suppressor itself.

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

5.3.1   Sample Analysis

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

1. Establish a stable baseline by pumping the working eluent through the instrument for at least 30 minutes. The operator's manuals provided by the manufacturer contain detailed

information regarding optimization of instrument performance and optimum operating criteria.

2. Load the auto-sampler vials beginning with the calibration curve followed by the extracted method blank (BLK1), the initial control standard (CCV1), the initial reference sample (SRM1), and extracted samples. Additional control standards (CCV2 through CCV9, CCVA, and CCVB) should be run every 10 samples and at the end of the analytical run. A second RF (SRM2) should also be run preceding the end-of-run CCVx.

3. Each auto-sampler vial cap is scored with a razor knife prior to being placed on the vial. This additional step prevents the auto-sampler needle from getting bent causing a bad injection/replacement.

5.3.2 Data Analysis

1. Data files are processed using algorithms contained in the data collection software. Chromeleon 7.2 from Thermo/Dionex is currently in use. Parameters are adjusted as dictated by instrument performance.

2. Examine all chromatograms visually. Note any anomalies in the data batch narrative.

3. Export the responses to an Excel spreadsheet.

4. Assemble the data batch folder, including copies of all extraction worksheets, run logs, certificates of analyses and processing methods, hard copies of each chromatogram, and any other necessary documentation.

5.3.3 Quality Control

1. If any analyte from an extracted filter exceeds 1 ug/filter, the box that the filter came from must be marked "Failed", removed from the lab and not used for sample collection.

2. One BLK is analyzed with each extraction. The BLK for extracted samples is the applicable volume of extraction solution followed by the appropriate extraction procedure. The BLK results must be less than or equal to two times the reporting limit for the analytes of concern.

3. A CCV is analyzed at a frequency of 10 percent for every analytical batch, as well as at the beginning and end of the run. The measured value of the CCV must be within ±10 percent of the certified value.

4. A SRM is used for an initial and a final calibration verification. The measured value of the reference sample must be within ± 10 percent of the certified value.

5. All calibration curves must contain a minimum of five points for quadratic calculations and have a correlation coefficient greater than or equal to 0.955. See Appendix B for a complete description.

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6. Approximately 5 percent of samples from each batch are analyzed in duplicate (DUP1, DUP2) to monitor within-run precision. Sample extracts are 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 must be with ± 20 percent. For samples with concentrations less than or equal to five times the reporting limit, the absolute difference between sample and replicate must be less than the reporting limit.

7. An internal system monitoring spike (rubidium bromide) is used in IC analyses to assess shifts in retention time and sample injection volume.

8. All sample responses are within the standard calibration range (0.00 to 5.00 µg mL^{-1}). Samples with responses above the calibration curve high standard are diluted and reanalyzed.

5.3.4   Corrective Actions

Table 2 summarizes QC procedures and the corrective actions taken when the QC samples are 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 are acceptable.
Calibration curve responses	Bracket all samples	Dilute and reanalyze samples exceeding the calibration range, or document why data are acceptable.
Reference standard (SRM) (Accuracy indicator; brackets all samples in run)	± 10% of the certified true value	Rerun standard. If still out of control, recalibrate instrument and reanalyze samples, or document why data are acceptable.
Control standard (CCV) (Accuracy indicator; analyzed every 10 injections)	± 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 are acceptable.
MB (BLK)	≤ 2 times the RL	Determine the cause of blank problem. Reanalyze the sample, if necessary, or document why data are acceptable.

Blank Spike (BS)	± 20% of target	Not established
Sample Replicate (DUP) (Analytical precision indicator)	± 20% RPD if the sample is greater than 5 times the RL	Determine the cause of the problem. Reanalyze the sample, if necessary, or document why data are acceptable.

Notes: RL = Reporting
limit
RPD = Replicate percent difference
Source: Amec Foster
Wheeler

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

Table 3. Data Quality Indicators for Laboratory Analyses

Analyte	Method	Acceptance Criteria			
		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

5.3.5 Calculations

All calculations are performed with data reduction algorithms that reside in the instrument software. Separate calibration curves are prepared for NH_4^+ by plotting the response (peak area) of standards against concentration values using quadratic regression in the instrument software. Sample concentrations are calculated using the quadratic equation for the curve. The analyst may eliminate points to improve accuracy throughout the range of calibration but at least 5 points plus a blank must remain.

5.4   Field and Laboratory Blanks

Blanks will be assessed to characterize contamination on denuders and filters that may occur in the laboratory and field. Weekly laboratory blanks will be conducted on H_3PO_4 denuders, H_3PO_4 filters, and nylon filters. Field or trip blanks for ADFPS, IMPROVE, and CSN will be conducted biweekly at both field sites. For IMPROVE and CSN, field blanks consist of filters

placed in the normal configuration within the sampler but unexposed. Filters are deployed and retrieved with the exposed samples collected during the corresponding week. For the ADFPS, field blanks consist 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 is deployed and collected with the exposed sample for the corresponding sample period. Trip blanks will not be unpacked from the shipping container. Note that the ADFPS samplers are 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.

5.5   Chain of Custody and Field Forms

Chain of custody forms accompany 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) are recorded on the forms and archived at the analytical laboratory. Examples of the chain of custody and field forms are attached in Appendix C.

5.6   Shipping

All samples and extractions are shipped in insulated coolers with ice blocks to maintain a temperature below 4 degrees C. Filter based samples are 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 records the temperature of the samples, time of receipt, and initials on the Shipping Temperature Log (See Appendix C) included with each cooler and transfers the samples to a refrigerator until deployment. The samples exposed during the previous week, along with denuder extractions, are returned to the analytical laboratory using fresh ice blocks. Upon receipt at the laboratory, the temperature of the samples, time of receipt, and initials are recorded on the Shipping Temperature Log and all samples are transferred to a cold room for storage.

All samples collected at the Gainesville site are stored in the laboratory cold room at $\leq 4\ °C$ until deployment and immediately following sample collection.

6   DATA ANALYSIS AND MANAGEMENT

6.1   Data Analysis, Interpretation, and Management

Laboratory, flow, concentration, and QC data is managed and reported to EPA by Amec Foster Wheeler under EP-W-16-015 Task Order 0012, Characterization of Reduced Nitrogen at IMPROVE and CSN Monitoring Sites.

6.2   Data Reporting Requirements

Laboratory data is stored in Amec Foster Wheeler'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 Quality Assurance Project Plan v.9

(QAPP) (U.S. EPA, 2016). 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 are transferred to SQL Server for calculating atmospheric concentrations. The CASTNET QA Manager will verify the concentration data before the results are transferred to EPA through Oracle 11g as described in the CASTNET QAPP Appendix 6 (Data Operations SOPs).

6.3   Data Analysis

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

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

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 NHx or NH_4^+ measured concentration and the URG ADFPS concentration:

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

where:

      Y = The measured value (CSN or IMPROVE)
      X = The reference value (ADFPS)

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

6.4   Data Storage Requirements

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

7   REPORTING

7.1   Deliverables

Amec Foster Wheeler will submit a Monthly Progress Report by the 15th of each month summarizing field operations, maintenance activities, significant events or changes to the sampling, any problems or issues expected, QA results and work planned for the next reporting period. The reports will also provide EPA with the current costs and expected cost for the next reporting period. The Monthly Progress Reports will be submitted to EPA/CAMD, EPA/ORD and EPA/OAQPS.

Amec Foster Wheeler will deliver an electronic database submittal with valid data and all QA/QC data reported during the field campaign. Data will include:
   (a) 24-hour phosphorous acid coated filter NHx ambient concentrations
   (b) 24-hour nylon filter NH_4^+ ambient concentrations
   (c) 24-hour URG ADFPS NH_3 ambient concentrations (phosphorous acid coated denuder and breakthrough denuder)
   (d) Weekly laboratory blanks
   (e) Monthly field blanks
   (f) Monthly trip blanks
   (g) Flow calibration results

All validated level 3 data will be flagged based on the QA/QC requirements described in section (5). Results from the previous 30-day period will be submitted no later than 30 days after the last sample of the month was removed. The database will be delivered to EPA/CAMD through Oracle on the last day of each month. The CASTNET QA Manager will review all data before it is delivered to EPA/CAMD by the DMAIRM. EPA/CAMD will provide an export database to EPA/ORD and EPA/OAQPS in a .txt file format.

Though not considered formal deliverables under this QAPP, collocated NADP AMoN and CASTNET filter pack data represent additional datasets that may be useful for interpreting differences between the ADFPS, IMPROVE, and CSN methods. NADP will provide AMoN bi-weekly concentrations on the AMoN website for NC30 and FL94 approximately 60 days after the sample is deployed. These samples are analyzed, validated, and reported as described in the NADP Quality Assurance Plan. CASTNET filter pack data will be analyzed, validated, and reported as described in the CASTNET QAPP. CASTNET filter pack data will be delivered to CAMD no later than 60 days after the last sample of the month was removed. Filter pack data will be delivered through the Oracle database on the last day of each month. CASTNET data is reported on the CASTNET website.

7.2   Products

OAQPS will summarize the results of the study in an EPA report. The results will be presented at external meetings to stakeholders (i.e. NACAA, APCAA, EPA Regions). The report will define the methods, accuracy of the PA-coated filters for the NHx samples, and options for implementing the tested filter designs in CSN and IMPROVE networks. We also anticipate

development of a journal article to document the study results in the peer reviewed literature.

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9   APPENDIX A: PREPARATION AND EXTRACTION OF SAMPLING MEDIA

9.1   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 Ziploc 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 ¼ 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.

9.2   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 HNO3 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 SC (Na_2CO_3) Denuder:

1. This procedure is performed in the washroom where all required components are available.
2. Pipette 10mL of 1% sodium carbonate 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.
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 Na_2CO_3 coating. Write the logbook/page ID on the label. Place the denuder in a clean Ziploc bag and refrigerate until needed.

9.3   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 (H_3PO_3), extracted with 20 mL deionized water, and extracts are analyzed for NH_4^+ by ion chromatography. H_3PO_3 impregnated filters are prepared and extracted as described below.

H$_3$PO$_3$ (PA) Solutions:
1. 3% PA – Dissolve 30 g of H_3PO_3 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 ¼ 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 dessicator. Wipe the foil with a fresh towel soaked with the 5% PA solution. Also wipe the inside top of the dessicator. Clean gloved finger tips, 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 dessicator, 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 finger tips, 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 filterpack. 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 finger tips, 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 filterpack 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.

9.4   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.

<u>Loading, Unloading and Extracting Exposed Filters:</u>
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.

10   APPENDIX B: CHEMICALS FOR IC ANALYSIS

Reagent water: deionized (DI) water of resistivity of 15 mega ohms (MΩ) 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 ug/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 ug/mL) is purchased as NIST-traceable solution. A Certificate of Analysis and an expiration date will be provided with each stock.

10 ug/mL intermediate cation calibration solution. 5 mLs of each 1000 ug/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 ug/mL intermediate cation calibration solution. 20 mLs of each 1000 ug/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 AA1 below to separate 500 mL volumetric flasks. The working curve will have an expiration date one month after preparation.

Table AA1. Cation concentration curves (μg/mL)

Cation Standard	Volume of Intermediate Calibration Solutions (mL)			Working Curve Concentrations (ug/mL)	
	10 ug/mL	100 ug/mL	100 ug/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 AA1 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-touse NIST-traceable standard solution containing analytes of interest with a Certificate of Analysis and an expiration date.

11   APPENDIX C: CHAIN OF CUSTODY FORMS

Annular Denuder System

ADS Channel 1	ADS Channel 2

Installed:

Date: ____/____/____ Time: _____ Initials: _____

Removed:

Date: ____/____/____ Time: _____ Initials: _____

Total Flow Volume: _____ m^3

Installed:

Date: ____/____/____ Time: _____ Initials: _____

Removed:

Date: ____/____/____ Time: _____ Initials: _____

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 _____/_____/_____

_____

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_____

_____

		IMPROVE		

Date: _____/_____/_____ Time: _____   Date: _____/_____/_____ Time: _____

Operator Initials _____   Operator Initials _____

Sample				INITIAL READINGS			FINAL READINGS		
Date		MaxOri	Cassette	Cyc	Ori		Cyc	Ori	ET
**********	**********	**********	**********	**********	**********		**********	**********	**********
5/25/2017			1	__ __	__ __		__ __	__ __	__ __ __
5/28/2017	Mod B	__ __ __	2	__ __	__ __		__ __	__ __	__ __ __
			3	__ __	__ __		__ __	__ __	__ __ __
			4	__ __	__ __		__ __	__ __	__ __ __
**********	**********	**********	**********	**********	**********	**********	**********	**********	**********

2x4 Blank area for label	2x4 Blank area for label
2x4 Blank area for label	2x4 Blank area for label

COMMENTS:

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_____

_____

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

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Blank area for label
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COMMENTS: _____

LAB USE ONLY:
LAB TECH RECEIPT _____

DATE _____/_____/_____

Shipping Temperature Log			
Date	Temperature	Initials	Notes
	°C		
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