Response to Reviewer Comments

Anonymous Referee #1

Comment: In this paper accuracy and precision associated with processing of the MARGA instrument chromatograms was studied. The results of the MARGA automated software were compared with the results of the chromatograms corrected using Chromeleon software (Dionex). A systematic bias was found especially at low concentrations. The authors should take into account: 1. Especially the chromatograms of low concentration samples should always be manually checked and reprocessed. The normal procedure is not (or at least shall not be) just trusting the results of automated integration. Therefore, I can't find the point, why just the "not-so-well" automatically integrated results (without any other manual peak integration adjustment) were compared with the off-line system. My opinion is that you should use (or at least add) the results found after the best possible off-line MargaTools-correction. Especially, for blank-results, it is questionable to use the chromatograms without checking, because depending on the parameters used, baseline noise can be considered as real peaks.

Response: This is a valid point and warrants clarification of our approach. Our analysis of accuracy in section 3.2 was based on comparison of results generated with the offline MARGA tool (single point LiBr internal standard calibration) to the same chromatograms reprocessed with Chromeleon software (multi-point external standard calibration). For this comparison, periods of instrument malfunction, peaks which were misintegrated, and peaks in which the LiBr internal standard concentration was outside $\pm 10\%$ of the nominal target concentration were excluded from the comparison. This filtering procedure would include low concentrations in which there was an obvious problem with the original peak integration. The results presented in section 3.2 therefore do represent the best possible results from the MARGA tool. The first paragraph of Section 3.2.1, beginning at line 315, has been modified to clarify our analysis. "Chromatograms reprocessed by the MARGA tool were individually examined and concentrations were filtered for periods of instrument malfunction, peak misintegration, and LiBr internal standard outside $\pm 10\%$ of the nominal target concentration. This filtering procedure would include low concentrations in which there was an obvious problem with the original peak integration. Filtered data were not included in the comparison between the MARGA tool and Chromeleon. Table S3 presents the percentage of data excluded from the comparison."

We now also clarify that the laboratory comparison of standards and method detection limits also excludes peaks in which obvious misintegration by the MARGA tool was observed. The following sentence has been added to Section 3.1 line 250: "Peaks that were obviously misintegrated by the MARGA tool were not included in this analysis."

Comment: For measuring low concentrations the LiBr internal standard used in this study is quite high (320 _g/l Li and 3680 _g/l Br) and could be at least half of that. The external standards you used should were much lower. You get more bias, if the concentration of the ITSD is much higher than the measured concentrations.

Response: The LiBr internal standard concentrations (320 ug/L Li⁺ and 3680 ug/l Br⁻) are recommended by the MARGA manufacturer. We recommend calibrating with a range of external standards appropriate for ambient concentration levels at a particular sampling site to avoid or reduce the bias that may be introduced by relying solely on the internal LiBr standard.

Comment: For low concentrations it is better to use a concentration column. The loop size used was not mentioned in the text.

Response: The loop size information is now included in the text under section 2.1 line 122.

Comment: p. 6 r. 160 : : : MargaTool: : : peak search sensitivity and peak search smoothing: : : are applied to all chromatograms. – Yes, BUT you can select the chromatograms you want to reprocess and use different parameters to each chromatogram. If you want to use different integrating parameters for the first peaks of one chromatogram and different ones for the last ones, then you have to save them separate files. Like File_A for Chloride and File_B for nitrate and sulphate. That is not so handy and it really is time-consuming, I agree.

Response: We agree. Batch re-integration using the MARGA tool is inflexible and time-consuming.

Comment: p. 9 r. 264 : : : the detection limits: : :evaluated here are large than in Rumsey and Walker (2016): : : I honestly hope that Rumsey and Walker did reanalyze the chromatograms, without doing that the detection limits will be quite high. And the detection limits vary also depending on the purity of the system and the column used.

Response: Yes, the chromatograms were evaluated in Rumsey and Walker (2016) using the MARGA tool with peak search sensitivity and smoothing, similar to what the reviewer described above.

Comment: There would be more benefit of the article for the MARGA community, if you would also tell, what kind of Java script you used for reformatting MARGA raw data.

Response: We now indicate in the acknowledgements that the Java scripts used are available upon request (line 596). We are happy to share them.

Comment: You could also make a list of the changes that could be done to make the MargaTools better.

Response: A list of recommendations for improving MARGA data quality are now included in the conclusions section (from line 577):

"...we make the following recommendations for controlling accuracy:

• Do not rely solely on the LiBr internal standard to ensure accuracy of the chromatographic analysis

- Calibrate with multi-point curves using external liquid standards
- Use a range of external standards appropriate for expected ambient concentration levels and for resolving potential non-linearity in detector response at low concentrations".

Anonymous Referee #2

Review of Chen et al. Chromatography related performance of MARGA. This paper is mainly concerned with showing the improvements in data quality through the use of a software tool as an alternative to the standard MARGA data analysis package provide by Applikon. This paper in within the scope of the journal. The authors report that their analysis using alternative proprietary software improves the accuracy of peak identification and corrects for a low bias in anions reported by the standard MARGA analysis. The comparison is grounded by a series of full system calibrations using standards of ammonium nitrate and sulfate. The two chromatogram analysis methods were also compared in the field.

Comment: Inflexibility of MARGA tools for the analysis and quality control of chromatograms. The main issue that authors highlight is the inflexibility of the software tools supplied with the MARGA system for the post-processing of data. This is especially problematical with field instruments especially those deployed over extended periods in the field. The authors note that this inflexibility is problematic when dealing with changing instrument performance such as when the column begin degrading with age. In addition to the issues regarding the usability and utility of the MARGA software tools the authors report that the MARGA itself is a useful tool for the studying the relationships between the gas a particle phase composition in the atmosphere. I would say that obviously this has been shown before and data sets and validation of the instrument performance have been published by a number of authors.

Response: We agree. MARGA has been utilized widely around the world and its utility in studies investigating atmospheric composition and air-surface exchange are well documented. A number of relevant publications have been cited in our introduction section (line 77-79).

Comment: My major recommendation for this paper is to add an explicit set of recommendations as if they were providing advice to other users or software developers. A number of issues with the data analysis and flexibility or lack of have been identified by the authors (and in my experiences have also noted their existence and the difficulty in post processing of MARGA datasets adequately). I my opinion this instrument could do with far more manufacturer/user group interaction and Applikon may find that if researchers are given permission and the tools to modify and develop the software tools ad far more powerful instrumental technique will be developed.

Response: Following the same comment from reviewer 1, a list of recommendations for improving MARGA data quality are now included in the conclusions section (from line 577):

"...we make the following recommendations for controlling accuracy:

- Do not rely solely on the LiBr internal standard to ensure accuracy of the chromatographic analysis
- Calibrate with multi-point curves using external liquid standards
- Use a range of external standards appropriate for expected ambient concentration levels and for resolving potential non-linearity in detector response at low concentrations"

Changes to manuscript in response to review comments are highlighted in yellow.

Chromatography related performance of the Monitor for Aerosols and Gases in Ambient Air (MARGA): laboratory and field based evaluation

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7 Changes in response to discussion review comments highlighted in yellow.

8 Abstract

Evaluation of the semi-continuous Monitor for Aerosols and Gases in Ambient Air 9 (MARGA, Metrohm Applikon B.V.) was conducted with an emphasis on examination of 10 accuracy and precision associated with processing of chromatograms. Using laboratory standards 11 and atmospheric measurements, analytical accuracy, precision, and method detection limits 12 derived using the commercial MARGA software were compared to an alternative 13 14 chromatography procedure consisting of a custom Java script to reformat raw MARGA conductivity data and Chromeleon (Thermo Scientific Dionex) software for peak integration. 15 Our analysis revealed issues with accuracy and precision resulting from misidentification and 16 misintegration of chromatograph peaks by the MARGA automated software as well as a 17 systematic bias at low concentrations for anions. Reprocessing and calibration of raw MARGA 18 data using the alternative chromatography method lowered method detection limits and reduced 19 variability (precision) between parallel sampler boxes. Instrument performance was further 20 evaluated during a one-month intensive field campaign in the fall of 2014, including analysis of 21 diurnal patterns of gaseous and particulate water soluble species (NH₃, SO₂, HNO₃, NH₄⁺, SO₄²⁻ 22 and NO₃⁻), gas-to-particle partitioning, and particle neutralization state. At ambient 23 concentrations below ~ $1 \mu g/m^3$, concentrations determined using the MARGA software are 24 biased +30% and +10% for NO₃⁻ and SO₄²⁻, respectively, compared to concentrations determined 25 using the alternative chromatography procedure. Differences between the two methods increase 26 at lower concentrations. We demonstrate that positively biased NO_3^{-1} and SO_4^{2-1} measurements 27 result in overestimation of aerosol acidity and introduce non-trivial errors to ion balances of 28 29 inorganic aerosol. Though the source of the bias is uncertain, it is not corrected by the MARGA online single-point internal LiBr standard. Our results show that calibration and verification of 30 31 instrument accuracy by multi-level external standards is required to adequately control analytical

accuracy. During the field intensive, the MARGA was able to capture rapid compositional
 changes in PM_{2.5} due to changes in meteorology and air mass history relative to known source
 regions of PM precursors, including a fine NO₃⁻ aerosol event associated with intrusion of arctic
 air into the southeast U.S.

36

37 1. Introduction

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39 Secondary inorganic aerosols are formed from gaseous precursors including ammonia (NH₃), nitric acid (HNO₃) and sulfur dioxide (SO₂), producing ammonium nitrate 40 (NH_4NO_3) , ammonium bisulfate (NH_4HSO_4) and ammonium sulfate $((NH_4)_2SO_4)$ particles. 41 42 These gaseous precursors and particulate matter, which partition between phases to establish a thermodynamic equilibrium of ammonium-sulfate-nitrate (Finlayson-Pitts and Pitts, 2000; 43 Seinfeld and Pandis, 2006), represent a significant fraction of PM_{2.5} (Seinfeld and Pandis, 2006; 44 Pinder et al., 2007) and contribute to atmospheric deposition of nutrients and acidity. The 45 implementation of National Ambient Air Quality Standards has reduced emissions of NO_x and 46 47 SO_2 ; however, NH₃ is not regulated and has not been routinely monitored until relatively recently (Puchalski et al, 2015). Nevertheless, to further reduce fine particulate matter, 48 controlling NH₃ emissions has been suggested to be more cost-effective than further reductions 49 of NO_x and SO₂ in some cases, (Vayenas et al, 2005; Pinder et al., 2007). Reduction of NH₃ 50 51 emissions may also represent the most effective strategy for reducing atmospheric nitrogen 52 deposition to acceptable levels (Li et al., 2016) in some ecosystems. High-frequency simultaneous measurements of the gas and aerosol components of the ammonium-sulfate-nitrate 53 54 system are required to investigate inorganic aerosol characteristics (e.g., phase partitioning, acidity) and formation processes and to quantify the dry component of nitrogen deposition. 55 56 Traditionally, integrated denuder and/or filter based techniques (i.e., 24 hours or longer) have been used to monitor inorganic aerosols and their precursors (Trebs et al 2004 and 57 58 references therein; Benedict et al., 2013; Chen et al., 2014). The disadvantages of poor temporal resolution and labor intensity as well as positive and negative sampling artifacts make these 59 60 methods difficult to deploy for extended periods of time and of limited use for characterization of rapidly changing atmospheric conditions. Recent development of near real-time semi-61

62 continuous analyzers, including the Particle-Into-Liquid sampler (PILS-IC, Metrohm AG,

63 Herisau, Switzerland), Particle-Collector-Ion Chromatograph (PC-IC), Aerosol Mass

Spectrometer (AMS, Aerodyne Research Inc., USA), Ambient Ion Monitor-Ion Chromatograph 64 (AIM-IC, URG Corp. And Dionex Inc., USA) and the Monitor for Aerosols and Gases in 65 Ambient Air (MARGA, Metrohm Applikon B.V., the Netherlands) facilitate monitoring 66 inorganic atmospheric constituents with much higher time resolution (Jayne et al., 2000; Weber 67 et al., 2001; Al-Horr et al., 2003; Trebs et al., 2004; Schaap et al., 2011; Markovic et al., 2012). 68 A version of the MARGA incorporating two sample boxes (MARGA 2S), similar to the system 69 70 described here, has recently been used to quantify dry deposition using a micrometeorological gradient flux method (Rumsey and Walker, 2016). 71

MARGA's capability of near real-time (hourly) simultaneous measurement of water 72 soluble particulate species as well as their gaseous precursors makes it a state-of-art research 73 74 instrument. Such time-resolved measurements allow investigation of highly time sensitive, rapidly changing pollution episodes as well as aerosol processes such as gas/particle partitioning 75 76 and neutralization state. The MARGA has been deployed in widely varying environments to monitor ambient gaseous and particulate water soluble species including NH₃, SO₂, HNO₃, 77 NH4⁺, SO4²⁻ and NO3⁻ (Schaap et al., 2011; U.S. EPA, 2011; Makkonen et al., 2012; Mensah et 78 79 al., 2012; Khezri et al., 2013; Huang et al., 2013; Rumsey et al., 2014; Shi et al., 2014; Allen et al., 2015; Twigg et al., 2015; Rumsey and Walker, 2016). Although the MARGA denuder and 80 steam jet aerosol collector (SJAC) have been evaluated for collection efficiency of gases and 81 particles (Wyers et al., 1993; Khlystov et al., 1995), there is relatively limited data on accuracy 82 and precision of concentration measurements (Weber et al., 2003; Trebs et al., 2004; Makkonen 83 et al., 2012; Lee et al., 2013; Rumsey et al., 2014; Allen et al., 2015). Phillips et al. (2013) found 84 85 that HNO₃ determined by the MARGA's wet rotating denuder displays a cross-sensitivity to N_2O_5 . The magnitude of the resulting positive bias in HNO₃ is highly dependent on the ambient 86 87 conditions (eg. NO_x, O₃, biogenic VOC concentrations and temperature) responsible for N₂O₅ production. Lee et al. (2013) observed differences in SO_4^{2-} , NH_4^+ and NO_3^- at a suburban site in 88 Hong Kong where an AMS instrument measured only 33-60% of the PM mass measured by a 89 collocated MARGA. Part of the difference was attributed to different particle size cut of the 90 91 inlets used (PM_{1.0} for AMS and PM_{2.5} for MARGA). Rumsey et al. (2014) compared the MARGA to a reference time-integrated denuder/filter pack system. SO₂, SO₄²⁻ and NH₄⁺ agreed 92 within 15% between the two systems; however, HNO₃ and NH₃ comparisons showed an 93 underestimation by MARGA of 30%, mostly likely due to loss to the surface of the long (≈ 4 m) 94

polyethylene sample tubing used. Though differences between the MARGA and other
measurement systems have been observed, the extent to which the differences may be
attributable solely to chromatorgraphy has not been evaluated.

The objective of this study is to evaluate MARGA performance with a focus on accuracy 98 and precision characteristics related to automated chromatography analysis. Specifically, we 99 investigate misidentification and misintegration by the MARGA software as well as errors and 100 101 uncertainties resulting from such issues. To aid efficiency and flexibility in the reprocessing of MARGA chromatograms, an alternative chromatography procedure, based on offline analysis of 102 103 raw MARGA data, was employed. Using laboratory standards, analytical accuracy, precision, 104 and method detection limits derived from the two chromatograph processing methods were compared. Field measurements were used to further evaluate instrument performance and to 105 106 demonstrate the ability of the MARGA instrument to resolve important atmospheric processes, including diurnal patterns of observed gaseous (NH₃, SO₂, HNO₃) and particulate water soluble 107 species (NH₄⁺, SO₄²⁻ and NO₃⁻), fine particle neutralization state, and changes in atmospheric 108 109 composition related to synoptic meteorological patterns. Using aerosol neutralization state as a 110 case study, the impact of chromatography errors on measurement accuracy was assessed.

111

112 2. Methods and materials

113 2.1 MARGA system

Details and principles of the MARGA system have been previously described (Rumsey et 114 115 al., 2014; Rumsey and Walker, 2016). Briefly, the MARGA sampler box consists of a wet rotating denuder (WRD) and a steam jet aerosol collector (SJAC), which enables semi-116 117 continuous collection and measurement of gaseous and water soluble inorganic particulate species in the ambient air. When drawn through the WRD, gaseous species are collected by 118 119 diffusion into a liquid film while particles pass through the WRD to the SJAC where super-120 saturation grows the particles by condensation. Liquid samples from the WRD and SJAC are 121 continuously collected in individual syringes and analyzed by Ion Chromatography (IC) on an hourly basis at the detector unit. Cation and anion sample loop volumes are 500 μ l and 250 μ l, 122 123 respectively. By employing two sets of liquid syringes, a set of samples is collected while samples from the previous hour are analyzed. To monitor accuracy and automatically adjust 124 125 concentrations, liquid samples are mixed with an internal lithium bromide (LiBr) standard at a 126 fixed ratio before injection for IC analysis.

128 2.2 Chemical materials

129 DI water (18.2 MΩ·cm, Milli-Q Reference system, Millipore) with 10 ppm H₂O₂ (30% certified ACS grade, Fisher Scientific) was used as absorbance solution for the MARGA WRD 130 and SJAC sample collection. H₂O₂ was added to prevent bacteria growth and subsequent loss of 131 NH4⁺. The MARGA internal standard LiBr (>99%, ACROS Organics) aqueous solution was 132 prepared at concentrations of $320\mu g/L Li^+$ and $3680 \mu g/L Br^-$. Solid chemical standards 133 NH4NO3, NH4Cl, (NH4)2SO4, NaNO3, KCl, CaCl2 · 2H2O and MgSO4·7H2O (≥99% certified 134 ACS grade, Fisher Scientific) were used to prepare stocks and various levels of liquid external 135 standards. Certified aqueous analytical standard solutions purchased from Alltech Associates 136 (Anion Mix 1, Cation Mix B, Alltech Associates, Inc) served as accuracy check standards. We 137 138 note here that "internal" standard refers to the MARGA LiBr standard that is mixed with every MARGA liquid sample immediately upstream of the IC injection loop. "External" standards 139 refer to liquid standards that are introduced at the WRD and SJAC, as described in more detail 140 below. 141

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143 2.3 Chromatography

MARGA proprietary chromatography software consists of an online version used for 144 automated analysis when the instrument is in measurement mode and a "MARGA tool", so 145 named by the manufacturer, used for offline analysis of chromatograms, either individually or in 146 batches, but otherwise identical to the online version. In both cases, liquid analyte concentrations 147 are determined by calculating the total amount of injected sample directly from the conductivity 148 measurement following the method of van Os et al. (1984). As mentioned previously, accuracy 149 150 is controlled by adjusting the measured concentration based on a single point internal LiBr standard, at a working concentration of 320 µg/L of Li⁺ and 3680 µg/L of Br⁻, which is injected 151 152 with each sample. The MARGA software does not employ a multipoint calibration curve. 153 During post processing of field data, it was discovered that peaks integrated by the

MARGA tool showed a certain degree of misidentification and inconsistent integration. Specific integration issues include incorrectly defined baseline due to peak fronting and tailing and shifting between "drop perpendicular" and "valley to valley" integration options among samples (shown in Supplemental Information). As indicated by the examples shown in Supplemental

Information, baseline selection by the MARGA tool could vary from sample run to run, which
could introduce significant errors and uncertainties. Integration issues are particularly
problematic when the IC analytical columns deteriorate due to extended use. Under such
conditions, unresolved peaks occurred more frequently.

In addition to misidentification and misintegration issues with the MARGA software, 162 reintegration of individual peaks with the MARGA tool was found to be inefficient and 163 inflexible. Although the MARGA tool contains adjustable integration parameter settings such as 164 peak search sensitivity and peak search smoothing, the parameters are applied to all 165 chromatograms. For example, the adjusted parameter may achieve the desired integration for a 166 particular misintegrated peak, but other peaks which were deemed as integrated properly prior to 167 any adjustments may subsequently be improperly integrated. The inability to manually adjust 168 169 the integration for individual peaks makes post-processing of chromatograms time consuming. Hence, an alternative chromatography software (Chromeleon V7.2, Thermo Scientific Dionex) 170 171 was tested for reprocessing of MARGA chromatograms.

In order to import MARGA generated chromatograms to the Chromeleon
chromatography data processing system, raw MARGA chromatography data (.dat format) were
converted to time series of conductivity (.txt format) using the MARGA tool. Using the
Chromeleon generated template (.cdf format) file, as well as a custom Java script, a batch of
MARGA conductivity time series (.txt format) files are converted to their corresponding .cdf
format. A folder of conductivity data files in cdf format is then imported to Chromeleon for
chromatogram reprocessing.

179 MARGA and Chromeleon approaches were compared in terms of peak areas and 180 calculated concentrations of internal and external liquid standards, as well as determinations of 181 laboratory blanks, method detection limits, and air concentrations during ambient sampling. To 182 compare integration characteristics between the MARGA tool and Chromeleon software, a series of external liquid standards (Table S1), representing a range of concentrations equivalent to \approx 183 $0.05 - 10.5 \,\mu g/m^3 \,\text{NH}_4^+$, NO_3^- and SO_4^{2-} in air, were run through the MARGA instrument with 184 185 the air pumps and SJAC steam generator disconnected. This configuration allowed liquid 186 standards to pass through the entire sampling (i.e., WRD and SJAC and liquid sampling lines) and analytical (i.e., syringes and ICs) components of the system. The resulting chromatograms 187 were used to generate a calibration curve using Chromeleon, in which peak areas were related to 188

189 liquid standard concentration (μ g/L). These peak areas and concentrations were then compared 190 directly to peak areas and concentrations generated by the MARGA software (without any 191 further manual peak integration adjustment), the latter being adjusted only by the internal LiBr 192 standard. A certified accuracy check standard was used to evaluate the accuracy of the calibration curves generated by Chromeleon and all of the analytes were found to be within the 193 10% accuracy check criteria. System blanks using absorbance solution were evaluated in the 194 195 same manner as the external liquid standards. Finally, both the MARGA internal standard (LiBr) and a subset of the external standards were verified by independent analysis on a Dionex ICS-196 2100 (Thermo Scientific, Waltham, MA) multi-point calibrated with additional certified 197 198 standards. Due to different loop size and corresponding detection limit of the Dionex system, only a subset of the external standards was independently verified. 199

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201 2.4. Field study

202 Field measurements were conducted in a grass field at the Blackwood Division of Duke Forest (35.98°N, 79.09°W) near Chapel Hill, NC. Duplicate MARGA sample boxes (SB1 and 203 204 SB2) were positioned in parallel (i.e., collocated) with inlets ≈ 1.5 m above the ground. Both MARGA sample boxes employed a Teflon coated cyclone-type inlet with an aerodynamic 2.5 205 206 µm cut size at a flow rate of 16.7 LPM (URG-2000-30EH, University Research Glassware Corporation). A short (0.2 m) length of 25.4 mm O.D. Teflon tubing connected the atmospheric 207 inlet to the MARGA denuder. MARGA sampler and detector boxes were equipped with weather 208 209 protection enclosures which were temperature controlled at 25°C.

210 Sampler air flow rates were measured and verified weekly by connecting a NIST traceable primary standard flow meter (Bios DryCal DC-Lite flowmeter, Mesa Laboratories, 211 212 Inc., Lakewood, CO) to the sampler inlets. Based on the calibration by the flow meter, MARGA reported flow rates were overestimated by 6% and 8% for sample box 1 (SB1) and 2 (SB2), 213 respectively, and air concentrations were adjusted accordingly. Initial data validation was 214 conducted by monitoring the MARGA automated status codes; data with internal standard LiBr 215 216 responses outside of $\pm 10\%$ nominal concentrations were invalidated and excluded from further 217 analysis.

To compare air concentrations derived from MARGA and Chromeleon software, the liquid calibration curves (see above section 2.2) generated by Chromeleon were used to calculate 220 liquid concentrations, and by combining with air and liquid flow rates, corresponding air 221 concentrations were derived. The Chromeleon derived air concentrations were then compared to 222 air concentrations generated by the MARGA software, which used only the internal LiBr 223 standard as a calibration adjustment. For this comparison, the same air and liquid flow rates were 224 used. Both sets of air concentrations were corrected for system blanks and air flow rate calibrations. The MARGA was operated continuously in the field from 15 October to 17 225 226 November 2014. However, due to a failure of the IC degasser unit, no valid data were generated from 31 October to 2 November 2014. 227

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229 2.5. Ancillary field data

A 10 m meteorological station is maintained and managed at Duke Forest by the North 230 Carolina Division of Forest Resources and Bureau of Land management. Verified hourly 231 metrological data were obtained online: (http://mesowest.utah.edu). Concentrations of PM_{2.5} 232 mass (TEOM model 1400ab, R&P Thermo Scientific, Franklin, MA) and organic/elemental 233 carbon (OC/EC, Model 4 Semi-continuous field analyzer, Sunset Laboratory, Inc., Hillsborough, 234 235 NC) were measured adjacent to the MARGA instrument. Backward air mass trajectories were calculated for select periods using the Hybrid Single Particle Lagrangian Integrated Trajectory 236 237 (HYSPLIT) model (Draxler and Rolph, 2003) with NOAA ARL EDAS 40 km meteorological data. Trajectories were run for 168 hour periods at an arriving height of 500 m above the ground 238 level. To aid interpretation of the back trajectories, facility emission inventory data for NO_x, SO₂, 239 and NH₃ were retrieved from the 2011 National Emission Inventory database 240 241 (http://www.epa.gov/ttn/chief/net/2011inventory.html).

242

243 3 Results and discussion

244 3.1. Laboratory study of chromatography characteristics

MARGA chromatograms were systematically examined by running a series of liquid external standards over a range of concentrations listed in Table S1. Each standard level was analyzed for approximately 20 hours, producing N = 80 observations for 4 analytical channels combined (two sample boxes for gas and aerosol channels). The same sets of chromatograms were re-processed by Chromeleon to generate multi-point calibration curves for each analyte. Peaks that were obviously misintegrated by the MARGA tool were not included in this analysis.

Relationships between peak area and standard concentration were linear except for SO_4^{2-} , for 251 which a polynomial fit was adopted to better represent the entire concentration range. All 252 calibration curves had r^2 values > 0.999. A certified check standard was used to evaluate the 253 accuracy of the calibration curves generated by Chromeleon and all analytes were found to be 254 within the 10% accuracy check criteria. Using absorbance solution to assess contamination, 255 blank concentrations of NO_3^- and SO_4^{2-} reported by Chromeleon were 0.002 and 0.080µg/m³. 256 257 respectively, while the corresponding system blanks determined by the MARGA tool were 0.018 and 0.109 μ g/m³. NH₄⁺ was not detectable in the blank solution. 258

Table 1 lists estimated method detection limits for the species of interest calculated using 259 both the MARGA tool and Chromeleon. Method detection limits were calculated as 260 2.58×standard deviation of the lowest detectable external standards, a statistical method 261 described in detail by Currie (1999). Method detection limits calculated using the MARGA 262 software are substantially larger than corresponding detection limits calculated with Chromeleon, 263 indicating more variability in the MARGA integrations from sample to sample. Such 264 inconsistency will translate to larger uncertainties for low concentration samples. This is 265 266 particularly important when attempting to resolve very small differences between two MARGA sample boxes, a requirement for flux gradient applications (Rumsey and Walker, 2016). Error 267 268 propagations inherited from misintegration could be minimized by reexamining the chromatograms. We note that the detection limits of the instrument evaluated here are larger, 269 270 particularly for anions, than those reported by Rumsey and Walker (2016), which used the same MARGA software but a different instrument. This indication of variability demonstrates the 271 272 need to characterize individual measurement systems. The detection limits calculated with Chromeleon are more similar to those reported by Rumsey and Walker (2016). 273

274 Table S2 lists the internal standard peak areas as integrated by the MARGA tool and 275 Chromeleon for each of the corresponding external standard levels. Note that while the 276 concentrations of anions and cations in the external standards vary by level, the actual concentration of the internal standard does not. For both Li⁺ and Br⁻, systematically larger peak 277 278 areas are calculated by the MARGA software. While the systematic difference for Br⁻ is rather consistent (17%), differences in Li⁺ between the two software techniques decrease with 279 increasing external standard concentration. As the peak areas of Na^+ and NH_4^+ increase, the close 280 retention times of Na⁺, NH₄⁺, and Li⁺ cause the peaks to appear more like unresolved lumps (i.e., 281

282 peak merging effect). At these higher standard concentrations, the MARGA software 283 underestimates the Li⁺ peak area relative to Chromeleon integration from sample to sample 284 becomes less consistent. This is likely due to the MARGA software frequently shifting between "drop perpendicular" and "valley to valley" integration options between samples, introducing 285 more variability to the calculated areas (see Supplemental Information Figure S1). For 286 consistency, the "drop perpendicular" integration option was adopted for all Chromeleon 287 reprocessing. We observed that as the concentration levels increase, the errors due to adopting 288 different integration options could be as much as 6% at the highest external standard 289 concentration equivalent to $\approx 10.5 \,\mu\text{g/m}^3$. In summary, the consistent 17% difference in Br⁻ peak 290 areas between software packages is not necessarily a source of error in the final calculation of 291 MARGA liquid concentrations. For Li⁺, the variability in integration and decrease in the 292 293 difference in peak area between the two software packages at higher standard levels would translate to systematic differences in corresponding NH_4^+ liquid concentrations above ≈ 100 294 $\mu g/L$ ($\approx 2.5 \mu g/m^3$ in air). 295

In addition to underestimation of Li⁺, other issues associated with MARGA processing of cation chromatograms include misidentification of NH_4^+ as Na^+ when a negligible Na^+ peak existed and misidentification of NH_4^+ and Na^+ peaks together as a single NH_4^+ peak. For anion chromatograms, NO_3^- peaks were rather frequently discovered as not identified at all; SO_4^{2-} peaks were found to have an incorrectly defined baseline due to peak fronting and tailing (see Supplemental Information Figures S2 - S5). These issues become more prevalent with column age.

303

304 3.2 Field study

In order to assess the potential impact of chromatography related analytical errors observed during the laboratory evaluation, MARGA performance was further investigated during a one-month field campaign. Air concentrations generated by the MARGA tool and Chromeleon are compared over a range of chemical and meteorological conditions, using particle neutralization state as a case study. Intrusion of artic air into the southeast U.S. provided an opportunity to observe rapidly changing and distinct patterns of gas-to-particle partitioning within the ammonium-nitrate-sulfate system. In the following sections, air concentrations presented in time series and summary statistics describing ambient measurements were generatedby Chromeleon unless otherwise indicated.

314 3.2.1 MARGA accuracy

Chromatograms reprocessed by the MARGA tool were individually examined and
concentrations were filtered for periods of instrument malfunction, peak misintegration, and LiBr
internal standard outside ±10% of the nominal target concentration. This filtering procedure
would include low concentrations in which there was an obvious problem with the original peak
integration. Filtered data were not included in the comparison between the MARGA tool and
Chromeleon. Table S3 presents the percentage of data excluded from the comparison. NO₃⁻

peaks appeared to be the analyte most affected, especially in the case of HNO_3 (up to 6.2% of the

data). At sampling sites where HNO₃ concentrations are typically below $1\mu g/m^3$, data rejection

323 may be more extensive.

Air concentrations derived from the MARGA and Chromeleon software approaches were 324 compared by ordinary least squares regression using Chromeleon as the reference (Figure 1). 325 Over the entire range of conditions, concentrations calculated using the MARGA tool were 326 within 5% (slopes, Figure 1), on average, of those reported by Chromeleon for SO_4^{2-} , SO_2 , NH_4^+ 327 and NH₃. Very good agreement is observed for NH₄⁺ and NH₃, with slopes close to unity and 328 intercepts near zero. As concentrations were below 2.5 μ g/m³, potential disagreement resulting 329 from differences in cation integration at higher concentrations (section 3.1) was not observed. 330 Although the accuracy of NO_3^- was poorer, it was within 10%, overall. By contrast, HNO₃ 331 concentrations, which were mostly below 1.0 μ g/m³, showed a positive bias of approximately 332 30%. Correlation of HNO₃ between the MARGA tool and Chromeleon also revealed a more 333 scattered pattern compared to other analytes. The 30% positive bias in MARGA HNO₃ results is 334 also observed for NO₃⁻ concentrations below $\approx 1.0 \,\mu\text{g/m}^3$ (Supplemental Information Figure S6). 335 Restricting the NO₃⁻ regression comparison to lower concentrations results in slopes of ≈ 1.4 and 336 1.5 over concentration ranges of $0 - 0.5 \text{ µg/m}^3$ and $0 - 0.25 \text{ µg/m}^3$, respectively, with intercepts 337 near zero; the disagreement increases at concentrations below $0.25 \,\mu g/m^3$. SO₂ and SO₄²⁻ results 338 339 also show positive bias in the MARGA results at lower concentrations, though not as large as 340 observed for HNO₃ and NO₃. For SO₂, slopes of $\approx 1.1, 1.15$, and 1.2 are observed over concentration ranges of $0 - 1.0 \,\mu g/m^3$, $0 - 0.5 \,\mu g/m^3$, and $0 - 0.25 \,\mu g/m^3$, respectively, with 341 intercepts near zero. Agreement improves at concentrations above $1.0 \,\mu g/m^3$ as the slope 342

approaches unity. Over the entire range of conditions, SO_4^{2-} also shows good agreement, on average, though with a significant offset (0.14 µg/m³, Figure 1). At lower concentrations (Supplemental Information Figure S6), a pattern of disagreement similar to SO_2 emerges; over the range 0 – 1.0 µg/m³, a slope and intercept of 1.09 and 0.09 are observed, respectively. Similar discrepancy patterns were observed for SO_4^{2-} and NO_3^{-} when lower level external standards were tested. In contrast to anions, cation results showed consistently good agreement even at low concentrations.

350 The source of bias between the MARGA and Chromeleon results may result from several factors: 1) MARGA overestimation from incorrectly defined peak start and end points due to 351 peak fronting and tailing; 2) incorrect baseline definition for smaller peaks (i.e., low observed 352 HNO₃ and NO₃⁻ concentrations) as compared to larger peaks; or perhaps the most likely 353 explanation, 3) inability of the van Os method used by the MARGA software to fully linearize 354 the relationship between peak area and liquid concentration at low concentrations. As noted 355 above, the method of van Os et al. (1984) for anion analysis with chemical suppression allows 356 calculation of the sample concentration directly from the conductivity measurement. van Os et 357 358 al. concluded that relationships between the amount of sample injected and total peak area were linear over the range 2.0 - 40.0 mg/L. It was noted, however, that calculated concentrations at 359 the 1.0 mg/L standard level, the lowest concentration tested, were slightly low for NO₃⁻ and Cl⁻ 360 and slightly high for SO_4^{2-} . Subsequently, the 1.0 mg/L standard level was not used in the final 361 362 regression analysis used to test the linearity of the method. Accounting for differences in injection loop size between studies, the 1.0 mg/L level used by van Os et al. (1984) is a factor of 363 364 2 to 2.5 larger than the highest standard concentration tested in our study (Table S1) and a factor of 25 (SO₂) to 125 (HNO₃) larger than the corresponding average observed air concentrations 365 366 (Table 2). It is possible that the method of van Os et al. (1984) systematically over-predicts anion concentrations at the lower concentrations observed in our study. This accuracy issue 367 368 would not be controlled by the single point Br⁻ internal standard (3680 μ g/L), which is within the 369 linear response range of anion concentrations tested by van Os et al. (1984).

The NO_3^- bias observed here may help to explain the results of previous studies. Five semi-continuous analyzers, which included an earlier version of a Wet-Annular Denuder/Steam-Jet Aerosol Collector (Trebs et al., 2004, 2008) that predates the commercialized MARGA, were evaluated and inter-compared by Weber et al. (2003) for measurements of NO_3^- and SO_4^{2-} in 374 PM₂₅ at the Atlanta EPA supersite. The earlier version MARGA analyzer showed a range of 25% to 34% significantly higher NO_3^- concentration as compared to a group mean of the five 375 semi-continuous monitors evaluated while measured SO_4^{2-} agreed well (within 10%). This 376 discrepancy was suspected to be a sampling artifact of NO₃⁻ formed from NO_x in the MARGA 377 particle steam collector, though there was a lack of correlation with measured NO_x. Four 378 instruments including a MARGA, an AMS, a denuder difference analyzer as well as an 379 380 integrated nylon filter based IMPROVE sampler were evaluated by Allen et al. (2015) during the 2013 Southern Oxidant and Aerosol Study (SOAS) campaign for particulate NO₃. The 381 MARGA measured much higher NO_3^- concentrations than the other three analyzers at this 382 southeastern US site where NO_3^- was mostly below 1.0 μ g/m³ during the sampling period. 383 Differences in inlet cyclone size cuts and cyclone efficiencies for supermicron particles may be 384 385 partly responsible. However, these examples of significantly higher MARGA NO₃⁻ relative to other methods, as well as the results of this study, warrant further investigation of potential 386 chromatography related biases. 387

388

389 3.2.2 MARGA precision

Precision statistics (Table 2) were derived from orthogonal least squares regression (Wolff 390 et al., 2010) of concentrations from the two MARGA sample boxes operated in parallel (i.e., 391 collocated). Orthogonal least squares acknowledges uncertainty in both the X and Y variables 392 393 (i.e. measurements from both sample boxes) and the standard deviation of the residuals of the regression is therefore a measure of the overall precision of the MARGA system. Concentrations 394 of particulate NO_3^- , SO_4^{2-} , NH_4^+ , gaseous SO_2 and NH_3 agree well between the sample boxes, 395 with slopes within 5% of unity and negligible intercepts (Table 2), indicating no significant 396 397 systematic differences between the two sample boxes. The standard deviations (precision) and relative standard deviations (RSD, expressed as a percentage of the average air concentrations) 398 of the regression residuals reported here ($\mu g/m^3$) for NO₃⁻, SO₄²⁻, NH₄⁺, and NH₃ are similar (< 399 10% RSD) to those reported by Rumsey and Walker (2016). The lower precision for SO₂ 400 401 reported here is most likely related to larger differences in concentration between sample boxes during periods of rapid concentration changes associated with the arctic air episode (Figures 2 402 and 3). 403

404 Relative to the other analytes, HNO₃ showed a much more significant difference between the two sampler boxes (regression slope of 0.83). Additionally, HNO₃ precision (15.8% RSD) 405 406 was much lower than observed for NO₃⁻ aerosol (4.8% RSD) at nearly identical average 407 concentrations. These findings, in combination with the excellent agreement between sample boxes for NO_3^{-} , suggest that the HNO₃ measurements were influenced by inlet, rather than 408 analytical, issues. As indicated by the much higher Henry's law coefficient of HNO₃ relative to 409 410 NH₃ and SO₂, HNO₃ is "sticky" and therefore more prone to inlet losses as well as re-evaporation from inlet/tubing surfaces. Although the inlet cyclones used were Teflon coated, and the Teflon 411 tubing connecting the cyclone to the WRD was very short (0.2 m), our results suggest 412 differences in transmission efficiencies of the two inlets. Similar difficulties in sampling HNO₃ 413 have been reported previously for studies in which size selective inlets and/or significant lengths 414 of sample tubing were used for MARGA sampling (Trebs et al., 2004; Rumsey et al., 2014; 415 Allen et al., 2015). In our study, the length of inlet tubing between the cyclone and WRD was 416 similar to the length of tubing (0.3 m) used by Rumsey and Walker (2016), the difference being 417 that no size selective inlet was used by Rumsey and Walker. In their study, multiple collocation 418 419 experiments showed much better agreement, on average, between the two sample boxes and better precision (5.8% RSD), suggesting that the cyclone may be the primary source of 420 421 disagreement between sample boxes in the current study. It is important to note, however, that concentrations of HNO₃ observed in the current study were generally very low, averaging 0.19 422 $\mu g/m^3$ over the study period. Such low concentrations contribute to greater relative variability 423 424 between sample boxes. Our results re-emphasize the requirement of low affinity tubing and inlets 425 with respect to both materials and surfaces/lengths for HNO₃ sampling.

426

427 3.2.3 Temporal patterns of gas and particle concentrations

Figure 2 shows time series of hourly gas phase concentrations of HNO₃, SO₂ and NH₃, and particle phase NO₃⁻, SO₄²⁻ and NH₄⁺ (as local time (EDT)). From mid-October to mid-November, meteorological conditions were mild and humid (Figure 3), which is typical of fall in the southeast U.S. However, an arctic outbreak of cold air impacted the site from 13 to 17 November, accompanied by much lower temperature and relative humidity. Wind speed was typical of the site, averaging 2 m/s. The prevailing wind directions were northwest and southwest before the cold air period and northerly during the dry and cold period. 435 Figure 4 shows the diurnal pattern of gas and particle concentrations. Only days with hourly data coverage greater than 65% were used for calculating diurnal profiles (N = 26). NH₄⁺ 436 and SO_4^{2-} exhibited a single mode pattern with a peak around 9-11 am local time. NO_3^{-} showed a 437 similar peak in the morning and a smaller peak at 9-11 pm. Morning peaks most likely represent 438 439 the downward mixing of aerosols from aloft when the nocturnal boundary layer breaks down. The second peak of NO_3^- at night may be related to night time NO_3^- radical chemistry 440 (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006) leading to formation of particulate 441 NO₃⁻. The mid-afternoon (2-3pm) peak in gas phase HNO₃ results from photochemical 442 processing of NO_x. NH₃ showed a much broader afternoon peak, which may reflect local 443 emissions from natural sources during warmer afternoon periods. The diurnal pattern of SO₂ 444 showed a pronounced peak around 10-11 am, and two less pronounced peaks at 8 pm and 1 am, 445 respectively. This pattern may reflect the competition between emission and dry deposition, as 446 well as boundary layer dynamics: higher emissions during the day versus slower dry deposition 447 rates and shallower boundary layer at night. The diurnal pattern is also affected by the large SO_2 448 spikes observed during the arctic air mass period, presumably associated with increased 449 emissions resulting from greater energy demand. 450

Gas/particle partitioning presented as fraction in the particle phase is shown in Figure 5.
In order to examine the aerosol neutralization state, chemical composition ratios were calculated
as:

454
$$R1 = \frac{NH_4^+}{SO_4^{2-}}$$
 (1)

455

456
$$R2 = \frac{NH_4^+}{NO_3^- + 2 \times SO_4^{2-}}$$
 (2)

457

where ratios R1 and R2 are molar concentration based. R1 = 2 reflects an aerosol entirely composed of $(NH_4)_2SO_4$, which is the fully neutralized state of $SO_4^{2^-}$. R1 > 2 indicates the presence of NH_4NO_3 in addition to $(NH_4)_2SO_4$, while R1 < 2 signifies a state of NH_4^+ deficit indicative of an acidic aerosol. Moreover, a ratio of R2 = 1 indicates a fully neutralized aerosol containing NH_4NO_3 and $(NH_4)_2SO_4$, while R2 > 1 represents as condition of excess NH_4^+ . A value of R2 < 1 suggests acidic aerosol comprising NH_4NO_3 and a combination of NH_4HSO_4 and 464 $(NH_4)_2SO_4$ or, alternatively, NO_3^- associated with supermicron particles from aged sea salt or 465 crustal materials (Allen et al., 2015).

466 Two distinct periods of contrasting aerosol composition were observed (Figure 5d). With R1 mostly less than 2 and R2 less than or close to 1, aerosol measured during October primarily 467 comprised NH₄HSO₄ and (NH₄)₂SO₄. When R1 approached 1 for three short episodes in October, 468 particles most likely existed solely as NH₄HSO₄. The observed acidity most likely suppressed 469 470 NO₃⁻ partitioning and formation, which is reflected by a significant decrease in the molar ratio of NO_3^{-1} in aerosol phase to as low as 0.1-0.2 (Figure 5a). Limited aerosol NO_3^{-1} formation was also 471 reported by Allen et al. (2015) at a southeastern US (SOAS) site where aerosol was acidic. By 472 473 contrast, R1 was mostly above 2 in November, indicating the presence of NO₃⁻. From 13 to 17 November, R1 reached as high as 4. Nevertheless, R2 was generally close to 1 during November, 474 indicating an aerosol comprised of NH₄NO₃ and (NH₄)₂SO₄. In contrast to the SO₄²⁻ dominated 475 October period, NO₃⁻ was a much greater contributor to inorganic aerosol in November; molar 476 concentrations of NH₄NO₃ even surpassed (NH₄)₂SO₄ when R1 reached 4 during the cold air 477 event. It should be noted that only acidity from inorganic species was examined in this study and 478 479 the ion balance could be further affected if organic acids were present and taken into account. As noted above and illustrated in Figure S6, a positive bias in NO_3^- and SO_4^{2-} resulting 480 from peak integration and processing with the MARGA tool is observed for air concentrations 481 below ~ $1.0 \,\mu\text{g/m}^3$. Our field study provides an opportunity to quantify the impact of these errors 482 483 over a range of chemical and meteorological conditions. For this analysis, the difference between hourly concentrations determined by the MARGA versus Chromeleon software was 484 calculated as a percent relative to the Chromeleon result (i.e., 100% (MARGA-485 Chromeleon)/Chromeleon). Overall statistics of the hourly relative differences are summarized 486 in Figure 5e, including differences in phase partitioning (i.e., molar ratios calculated as 487 particle/(particle+gas)) and neutralization state (R1 and R2). As expected, differences in the 488 NH₄⁺/NH₃ partitioning ratio are near zero because no bias was observed between Chromeleon 489 490 and MARGA derived concentrations of NH₃ and NH₄⁺. Average and median differences in the SO_4^{2-}/SO_2 partitioning ratio were similarly small, which is expected given that average SO_4^{2-} 491 and SO₂ concentrations were 1.41 and 0.98 μ g/m³, respectively (Table 2). These concentrations 492 493 are above the level at which biases between MARGA and Chromeleon become significant. Mean

494 and median differences in the NO₃⁻/HNO₃ partitioning ratio were \approx -10% and -1.5%,

495 respectively, indicating a smaller ratio calculated with the MARGA software. As shown in 496 Figure 5e, the NO_3^-/HNO_3 partitioning ratio exhibits much larger hourly variability relative to 497 the other analytes, reflecting a combination of larger concentration bias and random error associated with integration of very small peaks. The average relative difference in R1 was \approx -498 499 13%, resulting from the combination of a constant offset and concentration dependent difference between MARGA versus Chromeleon SO₄²⁻ results (section 3.2.1). Differences in R1 increase 500 non-linearly with decreasing SO₄²⁻ concentration, reaching $\approx -25\%$ at 0.5 µg SO₄²⁻ /m³. The 501 average relative difference in R2 was \approx -14%, also exhibiting larger differences at lower 502 concentrations. Following the propagation of error in R2, differences are primarily driven by 503 much higher absolute concentrations of SO_4^{2-} relative to NO_3^{-} . Though absolute differences are 504 larger for NO_3^- concentrations, low concentrations result in a lesser contribution to the overall 505 506 difference in R2 between the MARGA and Chromeleon methods.

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508 3.2.4 Arctic event

As noted above, an arctic outbreak of cold air impacted the site from 13 to 17 November. 509 The average temperature dropped from 12.9°C to 4.5 °C during this period, with a minimum of -510 3.9°C, which is well below normal for this site. RH ranged from 21 to 77% during the cold air 511 event. Total concentrations of gases plus particles were $\approx 2X$ higher during the cold arctic event 512 for NH₃ and NH₄⁺, SO₄²⁻ and SO₂; while for NO₃⁻ and HNO₃, a factor of 5 difference was 513 observed (summary shown in Table 3). Though air was drier during the arctic event, 514 temperatures were cold enough to drive partitioning of gas phase inorganic compounds towards 515 the particle phase. In addition to elevated NO_3^- concentrations, three distinct episodes of SO_2 516 occurred, with a maximum concentration of $32.56 \,\mu g/m^3$ (Figure 2). Back trajectory analysis 517 (see Supplemental Information Figure S7) suggests that these SO₂ events reflect transport of 518 emissions from power plants and other point sources in the mid-west (see facility SO₂ emission 519 520 inventories Figure S8 in Supplemental Information). SO₂ from more local sources during the 521 extremely dry and cold arctic air conditions might also have contributed to the observed SO_2 spikes. 522 Gas and particle chemistry during the 13 to17 November period, including TEOM PM_{2.5}

Gas and particle chemistry during the 13 to17 November period, including TEOM PM_{2.5} mass and elemental/organic (EC/OC) carbon concentrations, are examined in more detail in Figure 6. This four-day period represents the highest concentrations of SO_4^{2-} , NH_4^+ , NO_3^- and OC 526 concentrations, as well as lowest temperature, observed during the study. However, total $PM_{2.5}$ 527 mass showed less variability than the other species. Summaries of concentrations of gaseous and 528 particulate species are presented in Table 3 during and outside of the cold air event. In order to 529 better examine the arctic air mass intrusion, three sub-periods were selected, featuring a high 530 SO_4^{2-} episode; high NH₄⁺ and NO₃⁻ episode; and a high OC episode (individual periods are marked and color coded in Figure 6). Inorganic components in particles demonstrated a pattern 531 532 of high concentrations for periods1 and 2, while less so during period 3. Particulate organic composition as represented by OC showed an opposite pattern, peaking in period 3. Differences 533 in time resolved concentrations of inorganic and organic species illustrate different emission 534 sources for inorganic and organic particulate pollutants. Back trajectories associated with the 535 three episodes are presented in Figure 6. For inorganic episodes 1 and 2, air masses originated 536 from the arctic and passed through the U.S. mid-west and Ohio River valley where emissions of 537 inorganic aerosol precursors, SO₂ and NO_x, from power plants and heavy industries were 538 539 encountered. Gas phase NH₃ concentrations are very low during these episodes, with the majority of NHx in the particle phase. By contrast, trajectories associated with the high OC 540 541 episode (period 3) suggest more of a northeastern origin and perhaps a greater influence of residential wood burning associated with cold temperatures. During periods 1 and 2, inorganic 542 543 compounds contributed the majority of PM_{2.5} mass. The estimated sum of inorganics including SO_4^{2-} , NO_3^{-} and NH_4^{+} accounted for 61±31% and 83±24%, respectively of the PM_{2.5} mass for 544 545 period 1 and 2. In contrast, inorganic compounds only accounted for 22±11% of PM_{2.5} mass during period 3. 546

547

548 4 Summary and conclusions

549 The MARGA is a state-of-art instrument that measures near real-time water soluble 550 particulate species as well as their gaseous precursors. The current commercial version of the 551 MARGA incorporates a continuous internal standard (LiBr) to verify and calibrate instrument response for automated data generation and reporting. Close examination of MARGA 552 553 chromatograms revealed a number of issues, including misidentification and misintegration of 554 analyte peaks. Peak integration across similar chromatograms was found to be inconsistent with the MARGA software shifting between integration options "drop perpendicular" and "valley to 555 556 valley" among samples. In addition, NO_3^- peaks were rather frequently discovered as not

integrated or identified; SO₄²⁻ peaks were found to have an incorrectly defined baseline due to
peak fronting and tailing. Adjustment of individual peak integrations was found to be difficult
and inefficient with features provided by MARGA tool software. Hence, an alternative
integration software, Chromeleon by Thermo Scientific Dionex, was used to reprocess the raw
chromatograms. A custom Java script was developed to incorporate MARGA raw conductivity
data into Chromeleon for reprocessing.

563 Though a number of chromatography issues with the MARGA commercial software were identified, a relatively small percentage (6.2%) of data, overall, were invalidated due to peak 564 misintegration issues during the one-month field study described here. NO₃⁻ peaks appeared to be 565 the analyte most affected and higher rates of data invalidation may be expected where NO_3^{-1} 566 concentrations are typically low. The additional flexibility and consistency of Chromeleon in 567 568 integrating small peaks results in lower method detection limits relative to the MARGA chromatography software. Very good agreement between the two chromatography methods was 569 observed for cations across the range of observed ambient concentrations and for anions at 570 concentrations above ~ $1\mu g/m^3$. At ambient concentrations below ~ $1\mu g/m^3$, however, 571 572 concentrations determined using the MARGA software are biased +30% and +10% for NO₃⁻ and SO₄²⁻, respectively, compared to concentrations determined using the alternative chromatography 573 574 procedure. Differences between the two methods increase at lower concentrations. Over the range of conditions observed in our field study, the bias in NO₃⁻ produces non-trivial errors in 575 average NO₃⁻ concentrations and metrics of particle acidity. While the cause of this bias is 576 unclear, we make the following recommendations for controlling accuracy: 577 • Do not rely solely on the LiBr internal standard to ensure accuracy of the 578 chromatographic analysis 579 • Calibrate with multi-point curves using external liquid standards 580 • Use a range of external standards appropriate for expected ambient concentration levels 581 and for resolving potential non-linearity in detector response at low concentrations 582 583 During the field campaign, the MARGA captured rapid compositional changes in 584 PM_{2.5}, including changes in neutralization state. A particularly high NO₃⁻ episode associated with 585 arctic air mass intrusion and transport of pollutants from sources in the mid-west U.S. was 586 observed. Our field study further demonstrates the usefulness of the MARGA system for 587 characterizing the temporal characteristics of the sulfate-nitrate-ammonium system associated 588

- with changes in local (i.e., diurnal) and synoptic scale interactions between meteorology,
- 590 emissions, and aerosol processing.
- 591

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593

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600

601 Description of Supplemental Information

Table of multi-level external standards and certified standard; table of peak areas of internal LiBr

standard as integrated by MARGA tool and Chromeleon for different external standard levels;

table of fraction of data points invalidated due to misidentification and misintegration by

605 MARGA tool; figures showing examples of misidentification and misintegration by MARGA

tool; figure showing comparison of Chromeleon and MARGA tool in field samples at low

607 concentrations of SO_4^{2-} and NO_3^{-} ; figure of corresponding back trajectories of three SO_2

- episodes; figure of SO_2 point source emission inventory map (2011) covering middle and eastern
- 609 US.

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758 Tables

Table 1. Method detection limits for chromatograms processed by MARGA tool and re-

760 integrated by Chromeleon.

	Chro	omeleon	MARGA tool			
	MDL(µg/m ³)	# of sample	$MDL(\mu g/m^3)$	# of sample		
$\mathrm{NH_4}^+$	0.02	78	0.04	78		
NH ₃	0.02	78	0.04	78		
SO4 ²⁻	0.08	80	0.13	76		
SO_2	0.05	80	0.08	76		
NO ₃ -	0.08	80	0.14	76		
HNO ₃	0.08	80	0.14	76		

Table 2. Comparison between MARGA sample boxes 1 and 2 for particulate NO_3^- , SO_4^{2-} and

NH₄⁺, gas phase HNO₃, SO₂ and NH₃ by orthogonal least squares regression. N is number of

observations, $C_{average}$ is average air concentration, $\sigma_{\Delta C}$ is the standard deviation of the orthogonal

⁷⁸⁰ least squares residuals (i.e., detection limit (DL)), $\sigma_{\Delta C}/C_{avg}$ is the precision estimate, C_{max} and

781 C_{min} are the maximum and minimum air concentrations, respectively. Percentage of observations 782 below the detection limit (DL) is also included.

	Slope	Intercept	σΔC	Ν	Caverage	C _{max}	C_{min}	$\sigma_{\Delta C}/C_{avg}$	<dl%< th=""></dl%<>
			$\mu g/m^3$		µg/m ³	μg/m ³	μg/m ³	%	
$\mathrm{NH_{4}^{+}}$	0.98	0.01	0.02	616	0.52	2.20	0.10	4	0
NH ₃	1.02	-0.03	0.03	614	0.33	1.62	0	9	5
SO_4^{2-}	0.99	0.01	0.05	602	1.41	4.39	0.17	4	0
SO_2	0.96	0.02	0.15	603	0.98	23.26	-0.01	15	27
NO ₃ -	1.00	0.00	0.01	602	0.21	3.18	0	5	17
HNO ₃	0.83	0.01	0.03	603	0.19	0.97	0	16	20

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	Cold Event			Non-Cold event		
	Average	Median	Max	Average	Median	Max
NH ₃	0.12	0.09	0.29	0.35	0.24	1.62
HNO ₃	0.35	0.30	0.82	0.17	0.13	0.97
SO_2	3.22	1.32	32.56	0.73	0.42	8.09
$\mathrm{NH_{4}^{+}}$	0.99	0.88	2.20	0.48	0.45	1.21
NO ₃ -	1.07	0.72	3.18	0.13	0.09	0.98
SO_4^{2-}	1.93	1.66	4.39	1.33	1.29	3.58
Temperature	4.54	5.00	13.9	12.88	12.20	29.40
RH	50	51	77	70	71	100

Table 3. Summary of concentrations (μ g/m³) of aerosol and precursor gases during and outside of cold air mass periods.

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Concentration by Chromeleon($\mu g/m^3$)



as reported by MARGA tool and Chromeleon. Data points with misintegration issues by

794 MARGA tool were excluded from this comparison. Data for individual sample boxes (SB1 and

SB2) are shown.

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Figure 2. Time series of concentrations of particulate NO_3^- , SO_4^{2-} and NH_4^+ , gas phase HNO₃,

801 SO₂ and NH₃ by collocated MARGA sample boxes 1 (SB1) and 2 (SB2).



Figure 3. Hourly temperature, relative humidity, wind speed and wind direction during the fall2014 field intensive.





- bars represent 1 standard deviation.



- Figure 5. Partitioning molar ratios of a) NO_3^- , b) SO_4^{2-} and c) NH_4^+ in particle phase, calculated
- as particle/(particle+gas); d) molar ratios (R1 and R2) of particulate NO_3^- , SO_4^{2-} and NH_4^+ to
- determine particle neutralization state and acidity; e) relative difference of partitioning molar
- ratios of NO_3^- , SO_4^{2-} and NH_4^+ in particle phase as well as particle neutralization state indicators
- 835 R1 and R2 by Chromeleon and MARGA tool. Negative values indicate a lower ratio calculated
- by the MARGA tool (i.e., positive bias in concentrations calculated by MARGA tool). Solid and
- 837 dash lines inside box represent median and mean, respectively. Top and bottom box represent
- 838 75th and 25th percentiles. Whiskers represent 90th and 10th percentiles. Dots represent 95th and 5th
- percentiles. SB1 and SB2 indicate collocated MARGA sample boxes 1 and 2, respectively.



841 842 843	Figure 6. High concentration periods observed during mid-November 2014. Period 1: highest SO_4^{2-} ; Period 2: highest NH_4^+ and NO_3^- ; Period 3: highest OC. Corresponding back trajectories (arrival at 500AGL, backwards for 168hrs) of individual period peaks (±2hrs) are also presented.
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