Intercomparison of an Aerosol Chemical Speciation Monitor (ACSM) with ambient fine aerosol measurements in downtown Atlanta, Georgia

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Abstract. Currently, there are a limited number of field studies that evaluate the long-term performance of the Aerodyne Aerosol Chemical Speciation Monitor (ACSM) against established monitoring networks. In this study, we present seasonal intercomparisons of the ACSM with collocated fine aerosol ($PM_{2.5}$) measurements at the Southeastern Aerosol Research and Characterization (SEARCH) Jefferson Street (JST) site near downtown Atlanta, GA, during 2011–2012. Intercomparison of two collocated ACSMs resulted in strong correlations ($r^2 > 0.8$) for all chemical species, except chloride ($r^2 = 0.21$) indicating that ACSM instruments are capable of stable and reproducible operation. In general, speciated ACSM mass concentrations correlate well ($r^2 > 0.7$) with the filter-adjusted continuous measurements from JST, although the correlation for nitrate is weaker ($r^2 = 0.55$) in summer. Correlations of the ACSM NR-PM_1 (non-refractory particulate matter with aerodynamic diameter less than or equal to 1 μm) plus elemental carbon (EC) with tapered element oscillating microbalance (TEOM) $PM_{2.5}$ and Federal Reference Method (FRM) PM_1 mass are strong with $r^2 > 0.7$ and $r^2 > 0.8$, respectively. Discrepancies might be attributed to evaporative losses of semi-volatile species from the filter measurements used to adjust the collocated continuous measurements. This suggests that adjusting the ambient aerosol continuous measurements with results from filter analysis introduced additional bias to the measurements. We also recommend to calibrate the ambient aerosol monitoring instruments using aerosol standards rather than gas-phase standards. The fitting approach for ACSM relative ionization for sulfate was shown to improve the comparisons between ACSM and collocated measurements in the absence of calibrated values, suggesting the importance of adding sulfate calibration into the ACSM calibration routine.

1 Introduction

Atmospheric fine particulate matter with aerodynamic diameters less than or equal to 2.5 μm ($PM_{2.5}$) have adverse effects on human health (Dockery et al., 1993), reduce visibility, and play a role in Earth's climate (IPCC, 2013). As a result, there has been an ongoing need to resolve the chemical composition of $PM_{2.5}$ in order to identify their exact sources, and thus, develop effective control strategies. Organic matter (OM) contributes a major fraction (25–70 %) of the submicron (PM_1) mass in the troposphere; however, its sources,

composition, and atmospheric chemical transformations remain unclear (Jimenez et al., 2009). Inorganic aerosol constituents, such as sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and chloride (Cl^-) can also be major components of $PM_{2.5}$, depending on location and time of year.

Numerous methods for measuring the mass and chemical composition of PM have been put forward, including integrated filter samplers with subsequent laboratory analysis (e.g., Baumann et al., 2003; Solomon et al., 2003b), semi-continuous methods (e.g., Weber et al., 2003a, b; Lim et al., 2003), and real-time instruments (e.g., Gard et al., 1997; Lee et al., 2002; Jimenez et al., 2003). Differences between sampling techniques may occur for a host of reasons, including design, analysis methods, and assumptions used in data reduction. Hence, comparison of new sampling methods with established techniques allows one to determine its suitability for long-term air quality monitoring.

The Aerodyne Aerosol Chemical Speciation Monitor (ACSM, Ng et al., 2011) is designed for reliable long-term operation with minimal user intervention. The key differences between the ACSM and the aerosol mass spectrometer (AMS, Jayne et al., 2000) is that the former lacks a particle beam chopper and uses a relatively lower sensitivity quadrupole and, therefore, data must be averaged over a longer period to obtain sufficient signal-to-noise for quantification. Recent studies showed that the ACSM data are strongly correlated ($r^2 > 0.8$) with the Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (Ng et al., 2011), time-of-flight ACSM (ToF-ACSM), and compact time-of-flight AMS (Fröhlich et al., 2013). Comparisons of SO_4^{2-} aerosol showed good correlations between the ACSM and the particle-into-liquid sampler coupled to an ion chromatograph (PILS-IC), and the Thermo Scientific Sulfate Particulate Analyzer (model 5020i), where the ACSM measured 31 % lower for SO_4^{2-} than these two instruments. For NO_3^- aerosol, the ACSM measured 25 % lower than the PILS-IC (Ng et al., 2011). A recent deployment of the ACSM in Beijing, China, reported a good correlation between the total non-refractory PM_1 (NR-PM_1) estimated from the sum of all species measured by the ACSM with the $PM_{2.5}$ measured by the tapered element oscillating microbalance (TEOM), where the ACSM NR-PM_1 reported 64 % of the TEOM $PM_{2.5}$ mass (Sun et al., 2012).

The present study compares ambient NR-PM_1 measured by the ACSM with a suite of collocated particle measurements in Atlanta, Georgia. The collocated particle measurements include another ACSM operated by the Georgia Institute of Technology (GIT), continuous SO_4^{2-}, NO_3^-, and NH_4^+ measurements operated by Atmospheric Research & Analysis Inc. (ARA), semi-continuous organic carbon/elemental carbon (OC/EC) measurements, total $PM_{2.5}$ mass measured by TEOM, integrated SO_4^{2-}, NO_3^-, and NH_4^+ by particle composition monitor (PCM) developed by ARA, and

integrated $PM_{2.5}$ and PM_1 mass measurements based on the Federal Reference Method (FRM).

In the discussion that follows, we first compare individual species (i.e., OM, SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-) and total NR-PM_1 mass measured from collocated ACSMs during a short period between January and February 2012. Secondly, we compare species measurements (minus chloride) and total mass from the ACSM with organic carbon (OC), SO_4^{2-}, NO_3^-, NH_4^+, and $PM_{2.5}$ from continuous and filter measurements at the Jefferson Street (JST) site during summer and fall 2011. We compare mass from the ACSM with total mass from integrated FRM measurements in three short periods of January–February, April–May, and July 2012. Lastly, we estimate aerosol density from continuous measurements between 17 October to 20 November 2012. From this intercomparison, we have gained more knowledge on continuous ambient aerosol measurements, including the importance of calibrating the routine monitoring aerosol instruments with true aerosol standards rather than gas-phase standards, as well as sulfate calibration as additional routine calibration for the ACSM.

2   Experimental section

2.1   Site description

Ambient aerosol from Atlanta, Georgia, was collected at the Jefferson Street (JST) site (33.7775° N, 84.4166° W), which is located in a mixed industrial–residential area about 4.2 km northwest of downtown Atlanta (Hansen et al., 2003; Solomon et al., 2003a). The JST site is one of the research sites of Southeastern Aerosol Research and Characterization (SEARCH) network that is equipped with a suite of gas, particle, and meteorological measurements. Details of these measurements are described in subsequent sections. The University of North Carolina at Chapel Hill (UNC) ACSM was operated continuously at JST from 27 July 2011 through 21 September 2012, while the GIT ACSM was deployed at this site from 31 January through 29 February 2012. The period when both ACSMs were collocated at JST is used to evaluate the ACSM performance, and the extended periods in 2011 and 2012 are used to evaluate the accuracy of ACSM measurements against established monitoring network measurements.

2.2   NR-PM_1 and chemical measurements by the ACSM

During February 2012, NR-PM_1 was measured by two ACSMs that belong to UNC and GIT, and placed in an air-conditioned trailer at JST. Sampling conditions for both ACSMs are described in Table 1. Both ACSMs were operated to scan 150 mass-to-charge (m/z) ratios of fragmented ions at a rate of 500 ms amu^{-1}. Vaporizer and heater biases were set at 600 °C and 100.30 V, respectively, with the bias voltage chosen to maximize the N_2 (m/z 28) signal. Particle-laden and

Table 1. UNC and GIT ACSMs sampling setup at the JST site for a short period between January–February 2012.

	UNC	GIT
Sampling inlet	$PM_{2.5}$ cyclone	$PM_{2.5}$ cyclone
Sampling line length	5.00 m	5.00 m
Sampling line diameter	0.64 cm OD and 0.46 cm ID stainless steel tube	1.27 cm ID for 1 m of length 0.95 cm ID for 4 m of length
Sample drying	50-tube Nafion dryer (Perma Pure PD-50T-24SS) with 7.00 L min^{-1} of sheath air coming from dry/zero air system	200-tube Nafion dryer (Perma Pure PD-200T-12 MPS) running with 0.50 L min^{-1} sheath air flow (under vacuum)
ACSM sampling flow rate	3.00 L min^{-1}	3.00 L min^{-1}
RF_{NO_3} calibration	3.79×10^{-11}	3.97×10^{-11}
RIE_{NH_4} calibration	6.00	4.30
RIE_{SO_4} fitting	0.79	0.54
RIE_{NO_3} default	1.10	1.10
RIE_{Cl} default	1.30	1.30
$RIE_{Organic}$ default	1.40	1.40
Reference flow (Q_{cal} in cm^3 s^{-1})	1.39	1.35
Data acquisition software	ACSM DAQ v1.4.2.2	ACSM DAQ v1.4.2.5
Data analysis procedure	ACSM Local v1.5.2.0	ACSM Local v1.5.2.0

particle-free air were sampled interchangeably and averaged over ∼ 30 min intervals for each measurement. We calibrated the ACSM on site. The ACSMs were calibrated for response factor (RF) and relative ionization efficiency (RIE) using a separate calibration system for UNC and GIT. The resulting values for each instrument are reported in Table 1, and for UNC ACSM, different calibration values were used for different seasons.

Data acquisition software provided by ARI was used to process the measurements to obtain total organic and inorganic (i.e., SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-) aerosol mass concentrations. Further details of the concentration calculation are discussed by Ng et al. (2011) and shown in Eq. (1).

$$C_s = \frac{CE_s}{T_{m/z}} \times \frac{10^{12}}{RIE_s} \times \frac{Q_{cal} \times G_{cal}}{RF_{NO_3}} \times \frac{1}{Q \times G} \sum_{all\, i} IC_{s,i} \quad (1)$$

Species mass concentration (C_s) is calculated based on measured ion current (IC in amps) at fragment ion i. CE_s is collection efficiency for species s, and RF_{NO_3} is instrument response factor from calibration. $T_{m/z}$ is correction for the m/z dependent ion transmission efficiency of the quadrupole. Q_{cal} and G_{cal} are the volumetric sample flow rate and multiplier gain, respectively, and were determined from calibration, while Q and G are obtained during the measurements. During data processing, calibrated and measured Q and G cancel each other out as part of air beam correction factor (Eq. 2), and no separate correction is applied for flow rate. The air beam correction is applied as it is uncertain whether air beam signal changes due to gain or flow changes.

$$\text{Air beam correction factor} = \frac{Q_{cal} \times G_{cal}}{Q \times G} \quad (2)$$

An air beam signal (i.e., m/z 28) was used to normalize the measurements with respect to instrument measurement sensitivity (i.e., secondary electron multiplier (SEM) gain decay) and sampling flow rate. The effusive naphthalene source was not used due to lower signal-to-noise compared to m/z 28 and its dependency on effusion flow and/or background contamination. Moreover, the changes in flow rate need to be accounted for by using the filtered air beam. The ACSM uses a filtered air mass spectrum to account for backgrounds (e.g., N_2 and CO). These signals will vary with flow rate or slowly desorbing material. Contribution of the slowly desorbing material, however, is generally small compared to the N_2 signal at m/z 28.

RIE_s for species s was determined from calibrations of laboratory-generated aerosols of each species using Aerodyne AMS (Alfarra et al., 2004; Canagaratna et al., 2007). Since the ACSM particle vaporization and ionization source are similar but not identical in design to that of the AMS, there may be differences in RIE values compared to those referenced above. The vaporizer is identical between ACSM and AMS systems. The ion formation chamber in the ACSM is somewhat smaller than in the AMS. The ion source volume in the ACSM is calculated to be 370 mm^3 and that of the AMS is 580 mm^3. We note, however, that the effective volume is really defined by the electric fields and it is not easily calculated. In both systems the diameter of the extraction into the ion optic lens region is 3 mm. The smaller ion source volume (with tighter spatially distributed electric fields) in the ACSM could result in larger variability of the relative ionization efficiencies with respect to precise particle beam alignment, which is currently being investigated.

Table 2. Statistics of calibration values obtained from UNC and GIT ACSMs since mid 2011 to early 2013.

Date	UNC ACSM			GIT ACSM		
	RF_{NO_3}	RIE_{NH_4}	$RIE^*_{SO_4}$	RF_{NO_3}	RIE_{NH_4}	$RIE^*_{SO_4}$
Mean	4.17×10^{-11}	5.71	0.67	3.26×10^{-11}	4.40	0.59
1-std deviation	1.53×10^{-11}	1.01	0.09	1.26×10^{-11}	0.38	0.04
% uncertainty	37 %	18 %	14 %	39 %	9 %	7 %

* Sulfate aerosol calibrations were not conducted until early 2013.

The default RIE value for ammonium (RIE_{NH_4}) was 3.5; the value obtained from ACSM calibrations was approximately 5.71 (Table 2). The default RIE of sulfate was 1.2, which the real value could be estimated by fitting measured sulfate and predicted sulfate values, derived from $NH_{4,pred}$ equation (Eq. 3). Measured sulfate ($SO_{4,meas}$) is sulfate that is measured by the ACSM, while predicted sulfate ($SO_{4,pred}$) is the estimated value of sulfate from ion balance approach (Eq. 4).

$$NH_{4,pred} = 2 \left(\frac{MW\ NH_4}{MW\ SO_4} \right) SO_{4,meas} \tag{3}$$
$$+ \left(\frac{MW\ NH_4}{MW\ NO_3} \right) NO_{3,meas} + \left(\frac{MW\ NH_4}{MW\ Chl} \right) Cl_{meas}$$

$$SO_{4,pred} = \tag{4}$$
$$\frac{NH_{4,meas} - \left(\frac{MW\ NH_4}{MW\ NO_3} \right) NO_{3,meas} - \left(\frac{MW\ NH_4}{MW\ Chl} \right) Cl_{meas}}{2 \left(\frac{MW\ NH_4}{MW\ SO_4} \right)}$$

The previous value of RIE_{SO_4} 1.2 is then multiplied by slope obtained from fitting $SO_{4,pred}$ versus $SO_{4,meas}$ and used as the RIE_{SO_4} value of this study. UNC ACSM applied fitted RIE_{SO_4} values of 0.95, 0.77, 0.79, 1.1, 0.73, and 0.44 for summer and fall 2011, winter, spring, summer, and fall 2012 data sets, respectively. Explicit calibration of RIE_{SO_4} by atomizing $(NH_4)2SO_4$ using the same calibration system from UNC during winter 2013 yielded a value of 0.67 ± 0.09 indicating that the fitting approach value (0.79 ± 0.22) is consistent with the calibrations, with a larger uncertainty (Table 2). We found that SO_4^{2-} percent difference between ACSM and collocated measurement at JST was improved from about 50 % to less than 30 %. Therefore, in addition to regular calibration using NH_4NO_3, we recommend additional calibration using $(NH_4)_2SO_4$ to obtain an RIE_{SO_4} value specific for the ACSM.

A CE of 0.5 was used to calculate mass concentration. We used a Nafion dryer to dry ambient air samples; investigation of species-dependent CE (Middlebrook et al., 2012) suggested that CE is not influenced by highly acidic aerosol (Fig. S1 in the Supplement) or ammonium nitrate (Fig. S2 in the Supplement) as provided in the supplemental information. Some measurement periods were excluded from the data analysis due to operational and maintenance issues, such as shutdown during calibrations. Aerosol mass spectrometer uncertainty was estimated 20–35 % (Bahreini et al., 2009) which included CE uncertainty of 30 %. A recent study of composition dependent CE parameterization (Middlebrook et al., 2012) has substantially contributed to narrow the uncertainty of AMS, which could be used as a guideline for ACSM accuracy (~ 30 %).

2.3 Chemical constituents measured by integrated and continuous particle measurements at JST site

Details of the JST site measurements are provided elsewhere (Hansen et al., 2003; Edgerton et al., 2005, 2006). Inlets for particle samplers are mounted on the rooftop of the sampling trailer about 5 m above ground level. The particle measurements consist of 24 h filter sampling conducted every third day (daily for $PM_{2.5}$ and PM_1 mass), and of continuous and semi-continuous measurements by instruments placed in an air-conditioned trailer. Integrated, semi-continuous, and continuous $PM_{2.5}$ measurements are listed in Table 3, and described briefly below. Field blank loadings of JST site measurements are generally insignificant for SO_4^{2-}, NH_4^+ and OC, but can be significant for NO_3^- and EC mostly due to loadings at or below detection limit of those components (Edgerton et al., 2005). We emphasize here that the JST site aerosol instruments are based on gas phase detection of aerosol conversion products (e.g., SO_2 from SO_4^{2-} and NO from NO_3^-), therefore, are calibrated with standard gases instead of directly by particle mass generated from an atomizer combined with scanning electrical mobility sizer (SEMS) mixing condensation particle counter (MCPC) as done for the ACSM.

Particle components measurements

Details of the semi-continuous and continuous $PM_{2.5}$ sampling and analysis are provided in Edgerton et al. (2006) and in the supporting information. Briefly, $PM_{2.5}$ mass is measured continuously using an R & P Model 1400a/b TEOM operated at 30 °C to reduce losses of semi-volatile compounds and with main flow rate of 3 L min⁻¹. Sample air was pulled through a PM_{10} inlet followed by a $PM_{2.5}$ Very Sharp Cut Cyclone (BGI Incorpored) that goes inside the trailer where a multi-tube Nafion drier (Perma Pure) is installed

Table 3. Summary of integrated, semi-continuous, and continuous $PM_{2.5}$ analyses at JST.

Analyte	Instrument	Analytical method	Detection Limit ($mg\,m^{-3}$)	Frequency/Time Resolution
Integrated samples				
Mass	FRM (Teflon, 47 mm)	Gravimetry	0.2	daily
SO_4^{2-}	PCM1 (Teflon, 47 mm)	IC	0.05	3-day
NO_3^-	PCM1 (Teflon, 47 mm)	IC	0.01	3-day
NH_4^+	PCM1 (Teflon, 47 mm)	AC	0.03	3-day
Volatile-NO_3^-	PCM1 (Nylon, 47 mm)	IC	0.02	3-day
Volatile-NH_4^+	PCM1 (Citric acid-coated cellulose, 47 mm)	AC	0.04	3-day
OC	PCM3 (Quartz, 37 mm)	TOR	0.08	3-day
Continuous samples				
Mass	R & P 1400a/b TEOM (modified)	Oscillating microbalance	2.0	5 min
SO_4^{2-}	HSPH (modified)	Reduction to SO_2/PF	0.4	1 min
NO_3^-	Thermo Scientific	Reduction to NO/CL	0.25	1 min
NH_4^+	Thermo Scientific	Oxidation to NO/CL	0.07	1 min
OC / TC	Sunset OC/EC Analyzer	Combustion to CO_2/NDIR	0.5	60 min

Notes: Volatile-NO_3^- and Volatile-NH_4^+ are collected on back filters as HNO_3 and NH_3 dissociation on the front filter; IC represents ion chromatography technique; AC represents automated colorimetry method; TOR indicates thermal/optical reflectance method; PF represents pulsed fluorescence technique; CL indicates ozone-NO chemiluminescence method; HSPH stands for Harvard School of Public Health.

to dry the sample. SO_4^{2-} is measured continuously using a modified Harvard School of Public Health (HSPH) Sulfate Particulate Analyzer. NH_4^+ and NO_3^- were measured using a three-channel continuous differencing method developed by ARA, Inc. (Edgerton et al., 2006). Total carbon (TC) was semi-continuously measured by a Sunset OC/EC instrument (model 3), which collects particles on a filter. Once collection is complete (after ~ 50 min), the oven is purged with 10 % O_2 in He, and then ramped up to a set point of 850 °C according to the NIOSH 5040 analysis protocol.

Inorganics, OC, and total mass concentrations from the continuous analyzers were adjusted to match the filter-based data via linear regression since the continuous analyzers have been shown to drift over time. New adjustments are applied every 1–2 months, depending on the stability of the individual analyzer. With respect to carbon measurements, OC is calculated as the difference between filter-adjusted TC and filter-adjusted EC, and OM is estimated from applying an OM/OC ratio of 1.4 (Edgerton et al., 2006).

The component mass loadings from each filter were blank-corrected using SEARCH network-wide average loadings from field blanks, then the corrected loading was normalized by sampling volume. Details of the integrated measurements at the JST site are provided in Edgerton et al. (2005). This study will focus on comparison between ACSM and JST filter-adjusted continuous measurements (Figs. S3, S4 and S5 in the Supplement). Results of intercomparison between ACSM and filter measurements are presented in the supporting information (Figs. S6 and S7 in the Supplement).

2.4 Total particle mass measurements

$PM_{2.5}$ mass concentrations were obtained by several methods during this campaign. Continuous total mass concentrations were obtained with the TEOM (after adjustment to match the integrated PCM-based $PM_{2.5}$). The JST-integrated

$PM_{2.5}$ values were obtained by adding blank-corrected PCM measurements together with volatile NO_3^- from PCM nylon, volatile NH_4^+ and volatile OM from PCM back filter.

FRM filter samples were collected for 24 h using dual R & P Model 2025 sequential FRM monitors to determine both $PM_{2.5}$ and PM_1 mass. 47 mm diameter Teflon filters (2 μm pore size) were used for these measurements, and the collection, processing, and analysis of these filters followed FRM protocol (Code of Federal Regulations, 2001). PM_1 filters were sampled during three separate sampling periods: January to February, April, and July 2012, representing winter, spring, and summer seasons, respectively.

2.5 Aerosol density estimation

Total PM_1 volume measurements were obtained using the Brechtel Manufacturing Incorporated (BMI) SEMS equipped with a cylindrical-geometry differential mobility analyzer (DMA) and coupled to an MCPC (Sorooshian et al., 2008). The DMA was set to size particles between 10–1000 nm in diameter for both up and down scans. Differential mobility analyzer sheath airflow rate was set to $5\,L\,min^{-1}$ and particles were sampled at $0.5\,L\,min^{-1}$. Particle volume concentration from each scan was collected every 120 s, and both up and down scans were averaged to get one data point every 4 min and 30 s, which includes the scanning delay time.

3 Results

The ACSM measured about $11.6\,\mu g\,m^{-3}$ of OM, $3.2\,\mu g\,m^{-3}$ of SO_4^{2-}, and $0.61\,\mu g\,m^{-3}$ of NO_3^- during summer 2011. The numbers decreased in the fall 2011, except for nitrate (Table S1 in the Supplement). The ACSM measured chloride on average of 0.02 to $0.04\,\mu g\,m^{-3}$ in summer and fall, respectively.

3.1 Intercomparison between the UNC and GIT ACSMs

The UNC and GIT ACSMs were collocated from 10 January to 23 February 2012. Intercomparisons of chemical species between the two ACSMs shown in Fig. 1 indicate strong correlations ($r^2 > 0.8$), except for chloride ($r^2 = 0.21$). Slopes and intercepts of the linear regression are provided in Table 4. Weaker correlations of chloride might be due to its low concentration in Atlanta.

3.2 Intercomparison of ACSM with collocated JST measurements

Intercomparisons of species and total mass measurements by the ACSM, continuous particle measurements from JST, Sunset OC analyzer (model 3), and TEOM $PM_{2.5}$ (model 1400a/b) at the JST site are given in Table 4 for summer (8 August to 14 September) and fall (17 October to 21 December) 2011 sampling periods. Collocated mass and chemical constituent measurements were averaged to the ACSM sampling times to allow for a direct intercomparison. Previous intercomparison studies conducted at the same site have been limited to the summer season (Solomon et al., 2003a); therefore, results from this study could reveal possible aerosol measurements variation across seasons and instrumentation differences in aerosol measurements.

3.2.1 Species comparison

ACSM OM is strongly correlated with OC from the Sunset OC/EC analyzer (r^2 values are 0.86 and 0.92 for summer and fall, respectively); the resulting ratios (from the linear regression slopes in Table 4) of OM/OC are 4.85 ± 0.05 and 3.85 ± 0.02 in summer and fall, respectively. Aerosol Chemical Speciation Monitor OM versus Sunset OC correlations are likely higher since they are both real-time and not affected by storage related losses, such as that from the filter measurements.

ACSM SO_4^{2-} is strongly correlated with that from JST continuous measurements in the summer ($r^2 = 0.84$) and for some periods in the fall ($r^2 = 0.83$; September–November); however, the correlation is weaker for some periods in December ($r^2 = 0.22$) when JST measured several instances of very high SO_4^{2-} aerosol. Percent differences between the measurements are 4 and 44 % for summer and fall, respectively. These results are close to previous sulfate intercomparisons between ACSM and collocated measurements (slope = 0.95, 0.69, and 0.69, for HR-ToF-AMS, PILS-IC, and sulfate particulate analyzer, respectively) (Ng et al., 2011).

For NH_4^+ comparison, correlations are high ($r^2 = \sim 0.8$) and intercepts for both summer and fall are insignificant. Differences between ACSM and JST measurements are 20 % ($r^2 = 0.79$) for summer and 51 % ($r^2 = 0.76$) for fall.

Table 4. Correlations between the ACSM and the collocated measurements at JST site. Slope and intercept ± 1 standard deviation from each linear regression correlations are presented.

	JST Continuous[c]	
	Summer 2011	Fall 2011
Mass[a]		
r^2	0.71	0.83
Slope	1.50 ± 0.02	2.10 ± 0.02
Intercept	-2.89 ± 0.31	-4.36 ± 0.20
OM vs. OC[b]		
r^2	0.86	0.93
Slope	4.85 ± 0.05	3.85 ± 0.02
Intercept	-7.34 ± 0.19	-2.99 ± 0.09
SO_4^{2-}		
r^2	0.84	0.83
Slope	1.04 ± 0.01	1.44 ± 0.02
Intercept	-0.73 ± 0.04	-0.54 ± 0.03
NO_3^-		
r^2	0.55	0.81
Slope	2.14 ± 0.04	1.77 ± 0.02
Intercept	0.06 ± 0.01	0.08 ± 0.02
NH_4^+		
r^2	0.79	0.76
Slope	1.20 ± 0.02	1.51 ± 0.02
Intercept	-0.19 ± 0.02	-0.61 ± 0.01

[a] ACSM PM_1 is calculated from sum of ACSM species and Sunset EC. [b] For ACSM-to-ACSM comparison, it is OM vs. OM. [c] JST measures $PM_{2.5}$ mass and chemical constituents.

Intercomparisons between ACSM NO_3^- and JST continuous NO_3^- result in percent differences of 114 % ($r^2 = 0.55$) and 77 % ($r^2 = 0.81$) in the summer and fall, respectively. The weaker correlation and larger discrepancy in the summer might be due to the low NO_3^- loadings and evaporative losses from filters that will be discussed later.

3.2.2 Total mass comparison

ACSM PM_1 mass was determined from the sum of ACSM OM, SO_4^{2-}, NO_3^-, NH_4^+, and Cl^- as well as EC from the Sunset OC/EC analyzer. The intercomparison of the ACSM PM_1 and TEOM $PM_{2.5}$ shows a good correlation, with r^2 values of 0.71 and 0.83, respectively, and discrepancies of 50 and 110 % for summer and fall, respectively (Table 4). As in the speciated ACSM and PCM measurement comparisons, discrepancies in the fall might have resulted from positive biases of species measurements by the ACSM. Since the TEOM measurements are adjusted to match filter mass concentrations, it is also possible that the adjusted TEOM values are lower than the ACSM PM_1 values because of evaporation
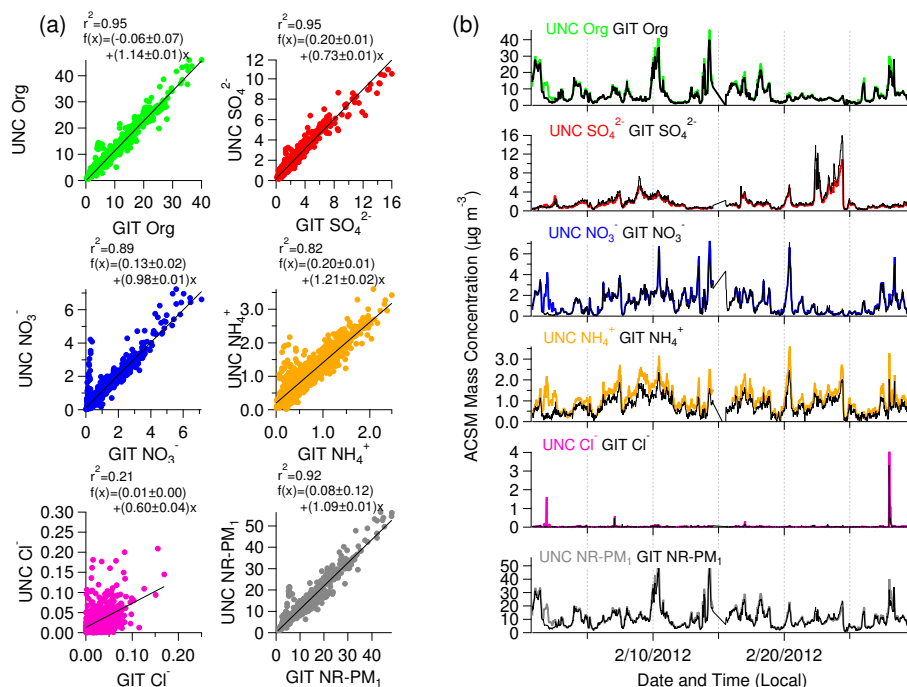
Figure 1. (a) Linear regression correlation and **(b)** time series plots of organic and inorganic constituents measured by the UNC and GIT ACSMs. ACSM measurements from UNC are colored by species while those from GIT are colored in black.

of semi-volatile organics and nitrates from the filters during storage.

The ACSM data were averaged to the FRM filter sampling times, which was 24 h (midnight to midnight) during each sampling period. Comparison between the ACSM NR-PM$_1$ and FRM PM$_1$ in winter, spring, and summer 2012 shows a good correlation, with r^2 values of > 0.80 (Fig. 2), and the mass concentrations differences vary from 10 % in summer to 73 % in winter. For the same period, comparison of ACSM NR-PM$_1$ and FRM-PM$_{2.5}$ shows a good correlation $r^2 > 0.80$). The tighter comparisons during summer ($r^2 > 0.8$) compared to winter ($r^2 = \sim 0.6$) might suggest meteorological influence on total mass measurements due to positive bias from filter measurement during colder seasons (Solomon et al., 2003a, b).

4   Discussion

4.1   Intercomparison between ACSM instruments

Slopes of the linear regression from UNC ACSM vs. GIT ACSM (Table 4) suggest percentage differences of speciated mass concentrations are 4 to 38 % between two independent ACSM measurements. The SO$_4^{2-}$ difference of 25 % can be attributed to uncertainty in the instrument RIE fitting results. The percent uncertainty of the fitting approach is larger (28 %) than calibration results (7–14 %) recently conducted at both ACSMs. Larger differences of Cl$^-$ measurements

(79 %) are due to its significantly lower concentration in Atlanta during the entire sampling period. This resulted in weaker correlation between the two instruments although both instruments capture similar large peaks of Cl$^-$ for some periods.

4.2   OM/OC ratio

The OM/OC ratios derived from the regression linear slopes are larger than most OM/OC ratios previously reported in the literature. These values are significantly higher than the traditionally used values of 1.6 for urban aerosol and 2.1 for non-urban aerosol (Turpin and Lim, 2001; Lim and Turpin, 2002; Russell, 2003). They are also larger than those found from recent HR-ToF-AMS intercomparisons with the Sunset OC/EC analyzer that report ~ 1.8 from September in Pittsburgh (Zhang et al., 2005a), 1.8 and 1.6 from summer and fall in Tokyo (Takegawa et al., 2005), 1.41–2.15 from March in Mexico (Aiken et al., 2008), 2.59 from August in New York City (Sun et al., 2011) and 3.3 from summer in Pasadena (Hayes et al., 2013). Studies in Atlanta also reported a high variability of OM/OC ratio, from 1.23–3.44 in August 1999 (Baumann et al., 2003) and 1.77 in December 1999 to 2.39 in July 1999 (El-Zanan et al., 2009). These suggest variability in OM/OC ratios based on location, time and meteorological conditions, and/or that the ACSM is measuring organic mass much higher than it should since it is using AMS-based RIE values for organic (i.e., RIE = 1.4) rather than those that have been explicitly measured for ACSM instruments.
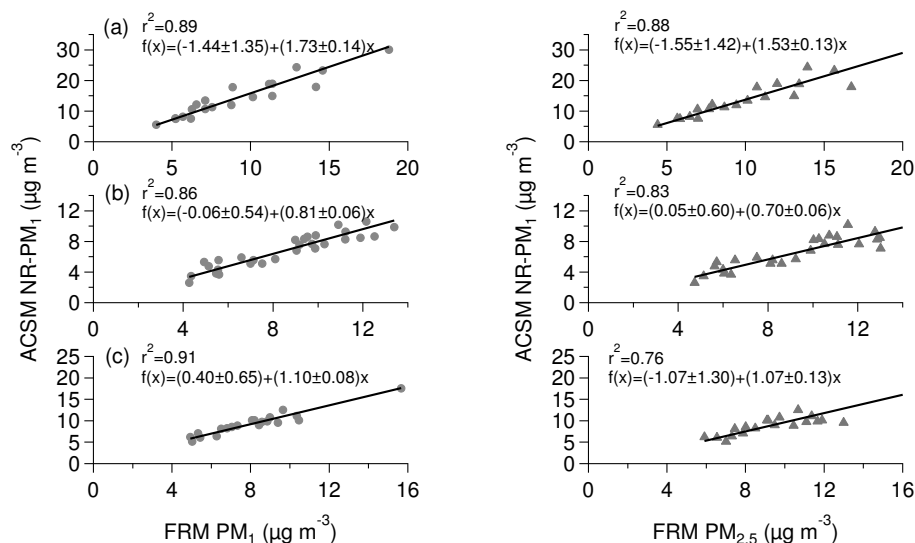
Figure 2. Correlation of ACSM NR-PM1 measurements with those of FRM PM_1 and $PM_{2.5}$ methods during **(a)** winter, **(b)** spring, and **(c)** summer 2012, respectively.

The large OM/OC ratios might also be attributed to under-estimation of OC due to evaporation of semi-volatile organic compounds (SVOCs) from the Sunset OC analyzer, and/or overestimation of OC due to condensation of SVOC or adsorption of VOC on the filter (Couvidat et al., 2013). This is reflected in a large offset at the Sunset OC (Figs. S4 and S5 in the Supplement). The presence of a denuder on the inlet of Sunset OC/EC analyzer, for example, might cause evaporation of particulate OC from the collection filter due to re-partitioning of SVOC after removal of gaseous organics by the denuder (Grover et al., 2008). Also, 20 % of Sunset OC uncertainty (Peltier et al., 2007) together with ACSM uncertainty might propagate the OM/OC ratio.

Overestimation of OM by the ACSM could arise from underestimation of the RIE value of organic species. The RIE values used in this study are based on experiments examining a suite of organic standards using the AMS instrument (Jimenez et al., 2003; Alfarra et al., 2004). Since the two instruments rely on the same vaporizer and ionization conditions (i.e., electron ionization), it was assumed that the RIE values for organics should be similar. However, based on the high OM/OC ratios observed from our intercomparison study, sets of authentic organic standards covering a wide range of chemical classes as well as secondary organic aerosol generated from laboratory experiments, such as isoprene-derived secondary organic aerosol (SOA) (Kleindienst et al., 2006; Lin et al., 2012), need to be systematically analyzed in future work in order to determine the RIE value for organics in the ACSM.

The large OM/OC ratios might also suggest photochemically, well-aged, and well-mixed air masses contain particle-phase organics that are more oxygenated and less-volatile compared to more stagnant air masses where less polar and more volatile organics can be found possibly due to

incomplete photochemical oxidation leading to more labile functional groups and intermediates. An offline polarity-based analysis suggested values of 1.9 to 2.1 for OM/OC ratios due to aging and oligomerization processes in the atmosphere (Polidori, 2008). In addition, water-soluble organic aerosol was observed to have higher OM/OC ratios than that of less water-soluble organics, ranging from 2.1–2.3 in the Great Smoky Mountains to 3.3 in downtown Los Angeles (Turpin and Lim, 2001). Furthermore, ratios of 2–3.12 were observed from organic fractions that could not be extracted using organic solvent (Polidori, 2008), indicating that compound-specific polarity might be related to sources of organic aerosol. Therefore, besides overestimation of OM by ACSM as noted above, high OM/OC ratios might indicate that the organic aerosol is more water-soluble in nature.

4.3 SO_4^{2-} and NH_4^+ measurements variations

Sulfate measurements from ACSM and the filter show a good trend ($r^2 > 0.7$, see Fig. S7 in the Supplement) for the December period, suggesting that the large discrepancies observed between the ACSM and JST data might be caused by some unknown issues with either the JST continuous measurements or ACSM during this sampling period. Both ACSM and continuous measurements show that the slopes of NH_4^+ measured versus NH_4^+ predicted (neutralized) are slightly less than 1 (Fig. S8 in the Supplement). This suggests during both summer and fall 2011, the aerosol was slightly acidic. Investigation of the period where correlation between ACSM and collocated measurement is low in fall season suggest some organic interferences (hydrocarbon-like organic aerosol/HOA) in sulfate fragments, in particular m/z 81 (Fig. S9 in the Supplement).
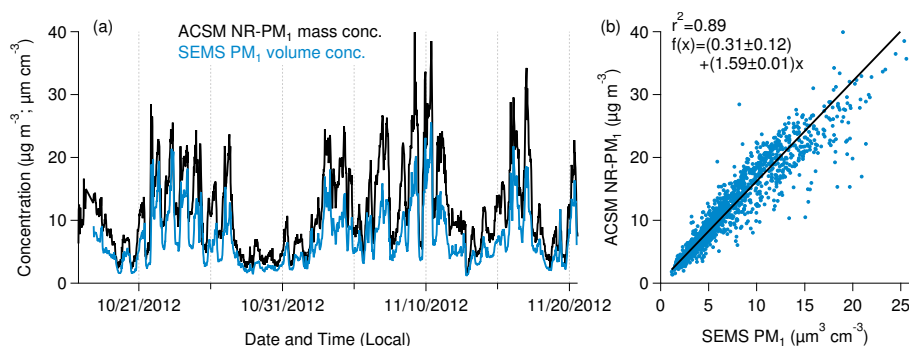
Figure 3. (a) Time series and **(b)** correlation of total aerosol mass measured by ACSM (NR-PM$_1$) and SEMS DMA/MCPC during period of 17 October to 20 November, 2012. Aerosol density was estimated from the linear regression slope of 1.59 multiplied by 1.10 to account for the 10 % of elemental carbon (EC) component that is not measured by ACSM. This results in estimated aerosol density of 1.75 g cm^{-3}.

Previous comparison of SO_4^{2-} measurements from the Thermo Electron 5020 Sulfate Particulate Analyzer with filter-based methods from laboratory and field studies observed good correlations (i.e., slope derived from field study was closer to 1 than that of laboratory study) (Schwab et al., 2006). It should be noted that Schwab et al. (2006) suggested that the slope differences are due to ambient SO_4^{2-} from the field study being catalytically converted to SO_2 faster than the laboratory-generated SO_4^{2-}. During this study, the ACSM SO_4^{2-} measurements discrepancies are 4–44 % compared to that of the continuous modified HSPH sulfate analyzer, with the largest difference occurring during colder months (fall season). This difference is within the expected accuracy of the ACSM measurements, but since the JST continuous SO_4^{2-} values are obtained after adjusting to the filter data, the bias could be due to artifacts from the filter data.

4.4 Discrepancies of NO_3^- measurements

ACSM NO_3^- measurements are based on the measured m/z 30 and m/z 46 ion signals. Positive biases at m/z 30 are possibly due to contributions to this ion from NO^+ fragments of organic nitrates and/or contributions from organic CH_2O^+ ions. A detailed investigation of the interference of m/z 30 is provided in the supplemental section. The relationship of estimated excess signal of m/z 30 linked to organic and oxygenated organic aerosol is found to be heteroscedastic. Thus, oxygenated organic species could not be suggested to directly influence nitrate fragments.

The continuous NO_3^- data are adjusted to the integrated NO_3^- data, which can impose measurement biases, especially for semi-volatile compounds such as NO_3^-. Hering and Cass (1999) reported lower aerosol NO_3^- mass from Teflon filters compared to that from denuded nylon filters. For this study, the PCM filter samples utilized both Teflon and nylon filters downstream of a denuder in order to account for NO_3^- losses. Previous SEARCH results have compared NO_3^- measurements with parallel systems: one with a Teflon prefilter and nylon backup filter (PCM1) and the other with just

a nylon filter (PCM2) (Edgerton et al., 2005). Both systems were denuded to remove artifacts of HNO_3 and NH_3, thus thermodynamics should favor metathesis of NH_4NO_3. Summer results showed that PCM1 agreed with PCM2 within 5 % and that > 95 % of the NO_3 from PCM1 was on the nylon backup filter. Fall results showed agreement within 10 % and with > 90 % on the nylon filter (Edgerton et al., 2005). While the use of nylon backup filters likely minimized NO_3^- losses during sampling, additional losses during filter storage and conditioning before off-line chemical analysis cannot be ruled out and could have contributed to the observed discrepancy.

Changes in meteorological conditions from summer to fall might influence the equilibrium partitioning behavior of nitrogenous compounds. Low temperatures and high relative humidity (RH) in the fall could create thermodynamic conditions that favor the partitioning of gaseous NO_3^- to the aerosol phase (Hennigan et al., 2008; Rastogi et al., 2011). The fact that the observed NO_3^- discrepancies are larger in the fall than the summer is consistent with evaporative loss of NO_3^- from the filter samples and reflected in the filter-adjusted continuous data.

In summary, it is unclear if the higher ACSM NO_3^- loadings reflect true NO_3^- levels which include contributions from organic nitrate not captured by JST NO_3^-, or if it is from inaccurate subtraction of m/z 30 originating from oxidized organic aerosol. Also, it is possible the discrepancy may be due to the underestimation of JST NO_3^- due to volatility losses from the filters which are used to scale the JST NO_3^- data. It is likely some combination of all of the above, which cannot be clearly determined from this data set, explains the differences between NO_3^- measurements.

4.5 Total mass measurements variations

ACSM PM$_1$ is sum of ACSM NR-PM$_1$ (i.e., organic and inorganics) plus EC measurements from JST site. This study shows that total mass differences between ACSM PM$_1$ and TEOM PM$_{2.5}$ are 50–110 %. Previous intercomparisons of

the same instruments in summer in Beijing suggested that ACSM NR-PM$_1$ measured $\sim 30\%$ less than TEOM PM$_{2.5}$ (Sun et al., 2012). Since the ACSM PM$_1$ mass is a sum of species concentrations, the discrepancies in species specific intercomparisons described above result in high discrepancies of PM$_1$ mass. Uncertainties in RIE values, particularly for organic species, may be partly responsible for overestimation of certain species resulting in overestimation of NR-PM$_1$ mass. On the other hand, loss of semi-volatile species from the filters (which are used together to adjust TEOM loadings) could also result in lower TEOM PM$_{2.5}$ concentration. This is supported by the fact that in fall, when the meteorological conditions favor semi-volatile organic aerosol enhancement, the slope of the ACSM PM$_1$ to TEOM PM$_{2.5}$ is much higher than that in summer (i.e., slope of 1.80 in fall to 1.19 in summer).

Differences between NR-PM$_1$ masses measured by the ACSM and PM$_1$ mass measured by the FRM method are about 10–73 %, with the lowest difference observed in the summer data set (Fig. 2; Table S2 in the Supplement). Discrepancies between the ACSM and FRM methods are larger during winter and spring compared to that of summer, and the direction of the discrepancy is different in spring (ACSM < FRM) as compared to winter and summer (ACSM > FRM). This might be due to positive artifacts of the filter sampling method, which are likely enhanced in colder months (Solomon et al., 2003a, b). On the other hand, uncertainties in RIE values may also result in inaccurate ACSM chemical constituent measurements leading to over- or underestimation of ACSM NR-PM$_1$ mass.

The slope resulting from the intercomparison of ACSM NR-PM$_1$ mass concentration and SEMS PM$_1$ volume concentration can be used to estimate aerosol density. Comparison suggests a slope of 1.59 (Fig. 3); however, this number will be larger when the refractory components (i.e., EC) are added to NR-PM$_1$. Since the EC measurement for this period (October–November 2012) are not available, we estimated that EC contributes about 10 % to total PM based on available data (i.e., October–November 2011). Hence, the estimated aerosol density in Atlanta is 1.75 g cm^{-3} for fall 2012. In addition, we estimated typical dry aerosol density based on average particle composition of 60.1 % of organics, 30.8 % of inorganics, plus 10 % of EC, and the assumption of organic, inorganics, and EC densities are 1.2, 1.77, and 1.77 g cm^{-3} (Zhang et al., 2005b, and references therein). This approached resulted in typical dry density of 1.61 g cm^{-3}. These numbers are consistent with recent ambient aerosol density estimations, such as 1.61 g cm^{-3} in Beijing (Hu et al., 2012) and 1.46 g cm^{-3} in Pasadena (Hayes et al., 2013).

5 Conclusions

This study aims to compare species and total mass measurements from the ACSM to the collocated measurements at the JST site (i.e., ACSM, JST continuous and filter samplers, and FRM filters) over different seasons. Mass concentrations obtained from the two ACSMs agree within 4–38 %, except for Cl$^-$. Overall, the percentage differences of ACSM speciated mass concentrations agree within 4–51 % from the SEARCH network measurements, except for NO$_3^-$ (77–114 %). Comparison of ACSM OM to JST Sunset OC yielded OM/OC ratios of 4.85 and 3.85 for summer and fall periods, respectively. Discrepancies between ACSM PM$_1$ and TEOM PM$_{2.5}$ are 50–110 %, while discrepancies between ACSM PM1 and FRM PM$_1$ are 10–73 %. Estimated aerosol density based on ratio of mass to volume concentration is 1.75 g cm^{-3}.

Discrepancies found in the intercomparisons of the ACSM and the collocated measurements might be explained by the following: (1) RIE values of organics might have dependencies on sources of organic aerosol; (2) possible interferences from organic and organic-nitrate-specific fragments to the m/z 30 ion signal that constitute ACSM inorganic NO$_3^-$ signal; and (3) evaporative losses of semi-volatile species from the filter measurements used in the collocated continuous measurement adjustment. Future work should systematically examine all of the possibilities. Additionally, calibration of the continuous instruments used at monitoring sites should also be routinely checked with a standard aerosol in addition to the standard gas calibration that is typically performed.

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