Atmospheric
Measurement
Techniques
Open Access
Discussions

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

S. H. Budisulistiorini[1], M. R. Canagaratna[2], P. L. Croteau[2], K. Baumann[3], E. S. Edgerton[3], M. S. Kollman[4], N. L. Ng[4,5], V. Verma[5], S. L. Shaw[6], E. M. Knipping[7], D. R. Worsnop[2], J. T. Jayne[2], R. J. Weber[5], and J. D. Surratt[1]

[1]Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA
[2]Aerodyne Research, Inc., Billerica, MA 01821, USA
[3]Atmospheric Research & Analysis, Inc., Cary, NC 27513, USA
[4]School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
[5]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA
[6]Electric Power Research Institute, Palo Alto, CA 94304, USA
[7]Electric Power Research Institute, Washington, D.C. 20036, USA

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

AMTD

6, 11181–11213, 2013

Intercomparison of an Aerosol Chemical Speciation Monitor

S. H. Budisulistiorini et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Intercomparison of an Aerosol Chemical Speciation Monitor

S. H. Budisulistiorini et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

The Aerodyne Aerosol Chemical Speciation Monitor (ACSM) was recently developed to provide long-term real-time continuous measurements of ambient non-refractory (i.e., organic, sulfate, ammonium, nitrate, and chloride) submicron particulate matter (NR-PM$_1$). Currently, there are a limited number of field studies that evaluate the long-term performance of the 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. The collocated measurements included a second ACSM, continuous and integrated sulfate, nitrate, and ammonium measurements, as well as a semi-continuous Sunset organic carbon/elemental carbon (OC/EC) analyzer, continuous tapered element oscillating microbalance (TEOM), 24 h integrated Federal Reference Method (FRM) filters, and continuous scanning electrical mobility system-mixing condensation particle counter (SEMS-MCPC).

Intercomparison of the two collocated ACSMs resulted in strong correlations ($r^2 >$ 0.8) for all chemical species, except chloride ($r^2 = 0.21$); mass concentration for all chemical species agreed within ±27 %, indicating that ACSM instruments are capable of stable and reproducible operation.

Chemical constituents measured by the ACSM are also compared with those obtained from the continuous measurements from JST. Since the continuous measurement concentrations are adjusted to match the integrated filter measurements, these comparisons reflect the combined uncertainties of the ACSM, continuous, and filter measurements. In general, speciated ACSM mass concentrations correlate well ($r^2 > 0.7$) with the continuous measurements from JST, although the correlation for nitrate is weaker ($r^2 = 0.55$) in summer. Differences between ACSM mass concentrations and the filter-adjusted JST continuous data are 5–27 %, 4–25 %, and 34–51 % for sulfate, ammonium, and nitrate, respectively. These comparisons are all close to

the stated ±30 % accuracy of the ACSM except for nitrate. These discrepancies could be due to positive biases in the ACSM nitrate concentrations from interferences at the NO^+ (m/z 30) fragment ion and/or negative artifacts in the nitrate filter measurement (from volatilization of NH_4NO_3) are also possible.

The organic matter (OM)/OC ratios derived from linear regression of ACSM OM vs. Sunset OC/EC analyzer are 4.18 ± 0.04 and 3.59 ± 0.02 for summer and fall, respectively. Linear correlations of the ACSM NR-PM$_1$ plus EC with TEOM PM$_{2.5}$ mass are strong ($r^2 > 0.7$) with percentage difference of 19 % and 80 % during summer and fall, respectively. On the other hand, the ACSM NR-PM$_1$ correlation with FRM PM$_1$ is high ($r^2 > 0.8$) with percentage difference of ±47 % over three seasons. Correlation of ACSM NR-PM$_1$ plus EC mass with SEMS-MCPC PM$_1$ volume concentration results in an estimation of aerosol density of $1.61\,\mathrm{g\,cm^{-3}}$ for fall 2012 period.

ACSM organic concentrations measured during this study were obtained using relative ionization efficiency (RIE) values observed in Aerodyne Aerosol Mass Spectrometer (AMS). Explicit calibration of the ACSM relative ionizations for ammonium, nitrate, and sulfate, during this study was shown to improve the comparisons between ACSM and collocated measurements for these species. The accuracy of the organic and total mass concentrations would likely also be improved if organic relative ionization efficiency values for the ACSM were available during this study. Laboratory calibrations of ACSM relative ionization efficiencies using organic particles of known composition are recommended for future studies.

1 Introduction

Atmospheric fine particulate matter with aerodynamic diameters less than or equal to 2.5 microns (PM$_{2.5}$) have adverse effects on human health (Dockery et al., 1993), reduce visibility, and play a role in Earth's climate (Hallquist et al., 2009). 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, 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.

During the US EPA-sponsored Supersites project at the Southeastern Aerosol Research and Characterization (SEARCH) Jefferson Street (JST) site near downtown Atlanta, Georgia, comparison of continuous measurements showed a good correlation between aerosol mass spectrometry (AMS) and ion-chromatography (IC) techniques. Furthermore, a stronger correlation was found from comparison of the AMS with the semi-continuous methods for SO_4^{2-} and NO_3^- than with the particle analysis by laser mass spectrometry (PALMS) (Solomon et al., 2003a, and references therein). Comparison of integrated samplers showed that mass, SO_4^{2-}, NO_3^-, NH_4^+, and organic carbon (OC) concentration agreed within ±20 %, ±10 %, ±30–35 %, ±10–15 %, and ±35–45 %, respectively (Solomon et al., 2003b). Solomon et al. (2003b) suggested that significant differences between samplers measuring OC and NO_3^- are due to their semi-volatile characteristics and collection issues as well as differences in sampler designs (i.e., inlet efficiency, presence of denuder for semi-volatile species, and evaporation from the filter when placed behind a denuder). In addition, the SEARCH sites also conduct $PM_{2.5}$ monitoring based on Federal Reference Methods (FRM) in order to

compare results of research methods with those relevant for compliance with the National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$. A significant conclusion from the Supersite comparison study is that the semi-continuous methods suffered less from sampling artifacts due to the shorter sampling periods and method of collection than

5   the filter-based methods (Solomon et al., 2003a).

The ACSM is reliable for long-term operation with minimum user intervention, yet it provides similar composition data as from the AMS. The key differences between the ACSM and the AMS is that the ACSM lacks a particle beam chopper for particle sizing measurements and utilizes a lower grade quadrupole that results in reduced sensitivity

10 of the ion signals (Ng et al., 2011). The ACSM performance has been evaluated with collocated measurements during its initial deployment in Queens, New York (Ng et al., 2011). This recent study 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), where all species, except for NO_3^-, were measured 5–24 % lower by the ACSM

15 (Ng et al., 2011). 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). The ACSM measured 31 % lower for SO_4^{2-} than these two instruments (Ng et al., 2011). For NO_3^- aerosol, the ACSM measured 25 % lower than the PILS-IC (Ng et al., 2011). A recent

20 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 tapered element oscillating microbalance (TEOM), where the ACSM NR-PM_1 reported 64 % of the TEOM $PM_{2.5}$ mass (Sun et al., 2012).

25 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 OC/EC measurements, total $PM_{2.5}$

Intercomparison of an Aerosol Chemical Speciation Monitor

S. H. Budisulistiorini et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

mass measured by TEOM, continuous PM_1 volume concentrations obtained by a scanning electrical mobility system (SEMS) coupled to a mixing condensation particle counter (MCPC), 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 OC, SO_4^{2-}, NO_3^-, NH_4^+, and $PM_{2.5}$ from continuous and filter measurements at the JST site during summer and fall 2011. Lastly, 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, and from continuous measurements (i.e., SEMS-MCPC) from 17 October to 20 November 2012.

2 Experimental section

2.1 Site description

Ambient aerosol from Atlanta, Georgia, was collected at the 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 (Solomon et al., 2003a; Hansen et al., 2003). The JST site is one of the research sites of 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) of fragmented ions at a rate of $500\,\text{ms}\,\text{amus}^{-1}$. Particle-laden and particle-free
air were sampled interchangeably and averaged over $\sim 30\,\text{min}$ intervals for each measurement. The ACSMs were calibrated for absolute and relative ionization efficiencies (RIEs) of NO_3^- and NH_4^+, respectively, according to procedures explained in Ng
et al. (2011) and the resulting values for each instrument are reported in Table 1. An
airbeam 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 instead of a diffuse naphthalene source due to low naphthalene emission. 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).

$$C_S = \frac{CE_s}{T_{m/z}} \times \frac{10^{12}}{RIE_S} \times \frac{Q_{cal} \times G_{cal}}{RF_{NO_3}} \times \frac{1}{Q \times G} \sum_{\text{all i}} IC_{S,i} \qquad (1)$$

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. Q and G

are similar to Q_{cal} and G_{cal} during calibration; thus, these parameters cancel each other out.

RIE$_s$ (relative ionization efficiency) 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. Relative ionization efficiency of ammonium (RIE$_{NH_4}$) for both ACSMs is provided in Table 1. Instead of default RIE$_{SO_4}$ = 1.2, fitted RIE$_{SO_4}$ values of 0.95, 0.77, 0.79, 1.1, 0.73, and 0.44 were used for summer and fall 2011, winter, spring, summer, and fall 2012 datasets, respectively. Details on calculation of fitted RIE$_{SO_4}$ values are provided in the supplemental section. Explicit calibration of RIE$_{SO_4}$ during winter 2013 yielded a value of ~ 0.7 indicating that the fitting approach is consistent with the calibrations. 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 collection efficiency (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 suggested that CE is not influenced by highly acidic aerosol or ammonium nitrate 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. Once the combined uncertainties due to the calibrations and assumptions are taken into account, the speciated ACSM mass concentrations are estimated to be accurate to within ±20–35 % based on AMS uncertainty (Bahreini et al., 2009).

S. H. Budisulistiorini et al.

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 a.g.l. The particle measurements consist of 24 h filter sampling conducted every third day (daily for $PM_{2.5}$ and PM_1 mass) and 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 2, 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 SEMS-MCPC as done for the ACSM.

2.3.1 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 semivolatile compounds and with main flow rate of $3\,L\,min^{-1}$. Sample air was pulled through PM_{10} inlet followed by $PM_{2.5}$ very sharp cut cyclone that goes inside the trailer where a multitube nafion drier (Perma Pure) is installed 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). Black carbon (BC) or EC is measured using a Magee Scientific

Model AE-16 single-beam aethalometer that measures EC based on attenuation of light at a wavelength of 880 nm.

Inorganics, OC, and total mass concentrations from the continuous analyzers (hereafter referred as Level_1 data) 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. The resulting filter-adjusted continuous data (hereafter referred as Level_2 data) have been shown to agree well ($r^2 > 0.8$) with the filter-based measurements (Edgerton et al., 2006). 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. Results of intercomparison between ACSM and filter measurements are presented in the supporting information.

2.4 Total particle mass and volume 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 particle composition monitor (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 Rupprecht and Patashnick 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.

Total PM_1 volume measurements were obtained using the Brechtel Manufacturing Incorporated (BMI) SEMS equipped with a cylindrical-geometry DMA and an MCPC. The DMA was set to size particles between 10–1000 nm in diameter for both up and down scans. DMA 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

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 3. Weaker correlations of chloride might be due to its low concentration in Atlanta, and thus, the measurements are likely within the detection limit of both ACSMs.

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 3 for summer (8 August to 14 September) and fall (17 October to 21 December) 2011 sampling periods. Collocated mass and chemical constituents 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 meteorological variation across seasons and instrumentation differences in aerosol measurements. In summer, the ACSM has a strong correlation ($r^2 > 0.7$) with all continuous measurements from JST, except for NO_3^- which has a moderate correlation ($r^2 = 0.55$). Similarly, the ACSM has strong correlations ($r^2 > 0.7$) with continuous measurements from JST in the fall, except for SO_4^{2-} during periods in December where it has a weak correlation ($r^2 = 0.22$) (Fig. S5).

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) and the resulting ratios (from linear regression slopes in Table 3) of OM/OC are 4.18±0.04 and 3.59±0.02 in summer and fall, respectively. ACSM OM vs. 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. The linear regression slopes are 0.95 and 1.27 with intercepts of −0.38 and −0.30, for summer and fall, respectively. These results are close to previous sulfate intercomparisons between ACSM and collocated measurements (slope = 0.95, 0.69, 0.69, for HR-ToF-AMS, PILS-IC, and sulfate particulate analyzer, respectively) (Ng et al., 2011). The ACSM and filter measurements show a good trend ($r^2 > 0.7$, see Fig. S7) for the December period, suggesting that the large discrepancies observed between the ACSM and JST data might be caused by some unknown issues with the JST continuous measurements during this sampling period.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

For NH_4^+ comparison, correlations are high ($r^2 = \sim 0.8$) and intercepts for both sum-
mer and fall are insignificant. The intercomparison with filter NH_4^+ measurements yields
slopes of 0.67 ($r^2 = 0.69$) for summer and 1.30 ($r^2 = 0.96$) for fall.

Intercomparisons between ACSM NO_3^- and JST continuous NO_3^- result in linear re-
gression slopes of 1.34 ($r^2 = 0.55$) and 1.51 ($r^2 = 0.81$) in the summer and fall, respec-
tively. During both summer and fall, the intercepts are about 0.3, which might indicate
a baseline offset issue. Similarly, intercomparison with filter-derived NO_3^- resulted in
a large slopes of 2.56 with a weak correlation ($r^2 = 0.36$) and insignificant intercept
in summer and 1.27 with a good correlation ($r^2 = 0.74$) and an intercept of 0.38 in
fall. The weaker correlation in the summer might be due to the low NO_3^- loadings and
evaporative losses from filters that will be discussed later.

JST did not measure Cl^- continuously. Intercomparison of Cl^- measurements from
the ACSM and filters resulted in a weak correlation in summer ($r^2 = 0.12$) with a slope
of 0.38, but a stronger association in fall ($r^2 = 0.80$) with a slope of 0.52.

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, re-
spectively, and slopes of 1.19 and 1.80 for summer and fall, respectively (Table 3).
A strong association between the ACSM PM_1 and the filter-derived $PM_{2.5}$ was found,
with r^2 values of 0.96 and 0.96 and slopes of 1.14 and 1.70 in summer and fall, respec-
tively. 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 concentra-
tions, it is also possible that the adjusted TEOM values are lower than the ACSM PM_1
values because of evaporation 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 (Table 3), and the mass concentrations agreed within ±47 %. For the same period, comparison of ACSM NR-PM$_1$ and FRM-PM$_{2.5}$ shows a good correlation > 0.80 and the mass concentration agreed within ±39 % (Fig. 2). The tighter comparisons during summer ($r^2 > 0.8$) compared to winter ($r^2 = \sim 0.6$) might suggest meteorological influence to total mass measurements.

The SEMS 4 min data were averaged to the ACSM sampling time of 30 min and comparison of PM$_1$ is presented in Fig. 3. Comparison of ACSM NR-PM$_1$ mass concentration and SEMS PM$_1$ volume concentration shows a strong association ($r^2 = 0.89$, slope = 1.46 ± 0.01, and intercept = 1.25 ± 0.11).

4 Discussion

4.1 Intercomparison between ACSM instruments

Based on slopes of the linear regression from UNC ACSM vs. GIT ACSM provided in Table 3, UNC ACSM measured 14 % higher OM, 27 % lower SO$_4^{2-}$, 2 % lower NO$_3^-$, 21 % higher NH$_4^+$, and 40 % lower Cl$^-$ than GIT ACSM. This gives an overall ±27 % of percentage difference of speciated mass concentrations, with exception of Cl$^-$ (40 %), between two independent ACSM measurements. The largest difference in these comparisons is observed from SO$_4^{2-}$ which can be attributed to instrument RIE fitting results. The fitting approach yielded SO$_4^{2-}$ RIE values of 0.79 for the UNC ACSM and 0.54 for the GIT ACSM. The calibrated RIE$_{NH_4}$ values for the UNC ACSM and GIT ACSM were 6 and 4.3, respectively. Larger difference of Cl$^-$ measurement 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. Therefore, Cl$^-$ uncertainty might need to be viewed separately from the other species. Taken together, this comparison indicates that the ACSM mass concentrations (speciated and total) lie within the estimated uncertainty of this technique.

4.2 OM/OC ratio

Comparisons of ACSM OM and Sunset OC/EC resulted in OM/OC ratios of 4.18 ± 0.04 for summer and 3.59 ± 0.02 for fall. The large OM/OC ratios might be attributed to evaporation of semi-volatile organic compounds (SVOCs) from the Sunset OC/EC analyzer, or condensation of SVOC or adsorption of VOC on the filter (Couvidat et al., 2013), which is reflected in the JST filter-adjusted continuous data.

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 nonurban aerosol (Turpin, 2001; Lim and Turpin, 2002; Russell, 2003). They are also larger than those found from recent HR-ToF-AMS intercomparisons with 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, 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 or 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.

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 LA (Turpin, 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.

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 using the AMS instrument which is similar but not identical to the ACSM. Thus, there is a need to conduct laboratory calibrations using organic particles of known composition for determination of organic RIE values for the ACSM. The large OM/OC ratios might also be attributed to uncertainties the Sunset OC/EC analyzer. 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 denuder (Grover et al., 2008). Also, Sunset OC was estimated to have about 20 % of uncertainty (Peltier, 2007), which may contribute to the high OM/OC ratio although this uncertainty is still within 30 % of ACSM uncertainty.

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

On average, ACSM measured SO_4^{2-} 5 % lower and 27 % higher than continuous measurements in summer and fall, respectively. For NH_4^+, ACSM measured 6 % and 29 % higher than continuous measurements in summer and fall, respectively.

The fact that SO_4^{2-} is more abundant in summer and NO_3^- is more abundant in fall, is likely indicative of the influence of meteorology on particle transformations in the atmosphere. Previous comparison of SO_4^{2-} measurements from the Thermo Electron 5020 Sulfate Particulate Analyzer with filter-based methods from laboratory and field
5 studies observed good correlations (i.e., slope derived from field study was closer to 1 than that of laboratory study) (Schwab, 2006). It should be noted that Schwab (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 5–27 % compared to that of
10 the continuous modified HSPH sulfate analyzer. 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 filter data, the bias could be due to artifacts from the filter data.

4.4 Discrepancies of NO_3^- measurements

15 On average, ACSM measured NO_3^- about 34 % and 51 % higher than continuous measurements in summer and fall, respectively. 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 possible due to contributions to this ion from NO^+ fragments of organic nitrates and/or contributions from organic CH_2O^+ ions. Further investigation of interference of m/z 30 is
20 provided in the supplemental section.

The continuous NO_3^- data are adjusted to the integrated NO_3^- data and this can impose measurement biases, especially for semi-volatile compounds such as NO_3^-. Hering et al. (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
25 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:

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

one with a Teflon pre-filter 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 favour metathesis of NH_4NO_3. Summer results showed that PCM1 agreed with PCM2 within 5 % and that > 95 % of the NO_3

5 from PCM1 was on the nylon backup filter. Fall results showed agreement within 10 % and > 90 % on the nylon filter (Edgerton et al., 2005). While the use of nylon backup filters likely minimized NO_3^- losses during sampling, additional loss during filter storage and conditioning before off-line chemical analysis cannot be ruled out and could have contributed to the observed discrepancy.

10 Changes in meteorological conditions from summer to fall might influence the equilibrium partitioning behaviour of nitrogenous compounds. Low temperatures and high relative humidity (RH) in the fall could create thermodynamic conditions that favour 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 sum-

15 mer 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

20 possible, the discrepancy may be due to under-estimation of JST NO_3^- due to volatility losses from the filters which are used to scale the JST NO_3^- Level_1 data. 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

25 On average, the ACSM measured 16.8 ± 6.9 and $13.7 \pm 10.0\,\mu g\,m^{-3}$ of PM_1 mass in summer and fall, respectively, while the TEOM measured 13.7 ± 5.1 and $9.1 \pm 5.6\,\mu g\,m^{-3}$ of $PM_{2.5}$ mass during the same periods. ACSM PM_1 was determined by summing

ACSM organic and inorganics plus EC measurements from JST site. This study shows that ACSM PM_1 is 19–80 % higher than TEOM $PM_{2.5}$. Previous intercomparisons of the same instruments in summer at Beijing suggested that ACSM 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 for organic ACSM species, in particular, 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).

Average NR-PM_1 masses measured by the ACSM are on average 47 % higher, 30 % lower, and 7 % higher than PM_1 mass measured by the FRM method for winter 2011 and spring and summer 2012, respectively (see Fig. 2). Comparison of ACSM with FRM $PM_{2.5}$ mass shows percentage differences of 30 %, 39 %, and 12 % in winter, spring and summer 2012, respectively. The discrepancies between the ACSM and FRM methods are larger during winter and spring, compared to that of summer, and the direction of the comparison 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 in over- or under-estimation of ACSM NR-PM_1 mass.

Strong association of ACSM NR-PM_1 mass concentration and SEMS PM_1 volume concentration ($r^2 = 0.89$) suggests ACSM performs well in measuring total mass. Slope resulted from the comparison can be used to estimate aerosol density. Comparison suggests a slope of 1.46; 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 1.61 g cm^{-3} for fall 2012 period.

Using the same approach in Zhang et al. (2005b), we estimated that the typical dry density of NR-PM$_1$ plus EC in Atlanta is 1.61 g cm^{-3}. The estimation is 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 g cm^{-3}, 1.77 g cm^{-3}, and 1.77 g cm^{-3} (Zhang et al., 2005b and references therein). The estimated aerosol density of 1.61 g cm^{-3} is higher than the traditional ambient aerosol density of 1.2 g cm^{-3} (Turpin, 2001); however, it is actually not too far from ambient aerosol density of 1.46 g cm^{-3} estimated in Pasadena (Hayes et al., 2013). This might suggest that aerosol composition in Atlanta during fall season is different from previous studies (Turpin, 2001).

5   Conclusions

This study aimed 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, FRM filters, and the SEMS-MCPC) over different seasons. Mass concentrations obtained from the two ACSMs agree within ±27 %, except for Cl$^-$. Overall, the percentage differences of ACSM speciated mass concentrations are less than ±30 % from the SEARCH network measurements, except for NO$_3^-$. Comparison of ACSM OM to JST Sunset OC yielded OM/OC ratios of 4.18±0.04 and 3.59±0.02 for summer and fall periods, respectively. ACSM NO$_3^-$ concentrations are about 34–51 % higher than those measured by the SEARCH network instrumentation. For summer and fall 2011; ACSM PM$_1$ was 19–80 % higher than TEOM PM$_{2.5}$. For winter, spring, and summer 2012; ACSM NR-PM$_1$ discrepancies are on average ±47 % and ±39 % to that of FRM PM$_1$ and FRM PM$_{2.5}$, respectively. Estimated aerosol density in Atlanta is 1.61 g cm^{-3},

and estimation using ACSM speciated mass contributions and density gave the same value.

Discrepancies found in the intercomparisons of the ACSM and the collocated measurements might be explained by the following: (1) RIE values (especially for organic) might be higher than the predecessor AMS instrument and have dependencies on location and meteorological conditions; (2) 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. 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.

Supplementary material related to this article is available online at http://www.atmos-meas-tech-discuss.net/6/11181/2013/ amtd-6-11181-2013-supplement.pdf.

References

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ul-
brich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., North-
way, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H.,
Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC
ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight
Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478–4485, doi:10.1021/es703009q,
2008.
Alfarra, M. R., Coe, H., Allan, J. D., Bower, K. N., Boudries, H., Canagaratna, M. R.,
Jimenez, J. L., Jayne, J. T., Garforth, A. A., Li, S., and Worsnop, D. R.: Char-
acterization of urban and rural organic particulate in the Lower Fraser Valley us-
ing two Aerodyne Aerosol Mass Spectrometers, Atmos. Environ., 38, 5745–5758,
doi:10.1016/j.atmosenv.2004.01.054, 2004.
Bahreini, R., Ervens, B., Middlebrook, A. M., Warneke, C., de Gouw, J. A., DeCarlo, P. F.,
Jimenez, J. L., Brock, C. A., Neuman, J. A., Ryerson, T. B., Stark, H., Atlas, E., Brioude, J.,
Fried, A., Holloway, J. S., Peischl, J., Richter, D., Walega, J., Weibring, P., Wollny, A. G., and
Fehsenfeld, F. C.: Organic aerosol formation in urban and industrial plumes near Houston
and Dallas, Texas, J. Geophys. Res., 114, D00F16, doi:10.1029/2008JD011493, 2009.
Baumann, K., Ift, F., Zhao, J. Z., and Chameides, W. L.: Discrete measurements of reactive
gases and fine particle mass and composition during the 1999 Atlanta Supersite Experiment,
J. Geophys. Res., 108, 8416, doi:10.1029/2001JD001210, 2003.
Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q.,
Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trim-
born, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.:
Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol
mass spectrometer, Mass Spectrom. Rev., 26, 185–222, doi:10.1002/mas.20115, 2007.
Code of Federal Regulations: 40 CFR 50, Appendix L to Part 50-Reference Method for the
Determination of Fine Particulate Matter as $PM_{2.5}$ in the Atmosphere, Washington D.C., USA,
2001.
Couvidat, F., Kim, Y., Sartelet, K., Seigneur, C., Marchand, N., and Sciare, J.: Modeling sec-
ondary organic aerosol in an urban area: application to Paris, France, Atmos. Chem. Phys.,
13, 983–996, doi:10.5194/acp-13-983-2013, 2013.

**Intercomparison of
an Aerosol Chemical
Speciation Monitor**

S. H. Budisulistiorini et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G., and Speizer, F. E.: An association between air pollution and mortality in six US cities, N. Engl. J. Med., 329, 1753–1759, doi:10.1056/NEJM199312093292401, 1993.

Edgerton, E. S., Hartsell, B. E., Saylor, R. D., Jansen, J. J., Hansen, D. A., and Hidy, G. M.: The Southeastern Aerosol Research and Characterization Study: Part II. Filter-based measurements of fine and coarse particulate matter mass and composition, J. Air Waste Manage., 55, 1527–1542, 2005.

Edgerton, E. S., Hartsell, B. E., Saylor, R. D., Jansen, J. J., Hansen, D. A., and Hidy, G. M.: The Southeastern Aerosol Research and Characterization Study, Part 3: Continuous measurements of fine particulate matter mass and composition, J. Air Waste Manage., 56, 1325–1341, 2006.

El-Zanan, H., Hansen, D. A., Mazzoleni, L. R., and Zielinska, B.: Analytical determination of the aerosol organic mass-to-organic carbon ratio, J. Air Waste Manage., 59, 58–69, doi:10.3155/1047-3289.59.1.58, 2009.

Gard, E., Mayer, J. E., Morrical, B. D., Dienes, T., Fergenson, D. P., and Prather, K. A.: Real-time analysis of individual atmospheric aerosol particles: design and performance of a portable ATOFMS, Anal. Chem., 69, 4083–4091, doi:10.1021/ac970540n, 1997.

Grover, B. D., Kleinman, M., Eatough, N. L., Eatough, D. J., Cary, R. A., Hopke, P. K., and Wilson, W. E.: Measurement of fine particulate matter nonvolatile and semi-volatile organic material with the Sunset Laboratory Carbon Aerosol Monitor, J. Air Waste Manage., 58, 72–77, doi:10.3155/1047-3289.58.1.72, 2008.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Hansen, D. A., Edgerton, E. S., Hartsell, B. E., Jansen, J. J., Kandasamy, N., Hidy, G. M., and Blanchard, C. L.: The Southeastern Aerosol Research and Characterization Study: Part 1. Overview, J. Air Waste Manage., 53, 1460–1471, doi:10.1080/10473289.2003.10466318, 2003.

Intercomparison of an Aerosol Chemical Speciation Monitor

S. H. Budisulistiorini et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., Hu, W. W., Toohey, D. W., Flynn, J. H., Lefer, B. L., Grossberg, N., Alvarez, S., Rappenglück, B., Taylor, J. W., Allan, J. D., Holloway, J. S., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Massoli, P., Zhang, X., Liu, J., Weber, R. J., Corrigan, A. L., Russell, L. M., Isaacman, G., Worton, D. R., Kreisberg, N. M., Goldstein, A. H., Thalman, R., Waxman, E. M., Volkamer, R., Lin, Y. H., Surratt, J. D., Kleindienst, T. E., Offenberg, J. H., Dusanter, S., Griffith, S., Stevens, P. S., Brioude, J., Angevine, W. M., and Jimenez, J. L.: Organic aerosol composition and sources in Pasadena, California during the 2010 CalNex campaign, J. Geophys. Res.-Atmos., 118, 9233–9257, doi:10.1002/jgrd.50530, 2013.

Hennigan, C. J., Sullivan, A. P., Fountoukis, C. I., Nenes, A., Hecobian, A., Vargas, O., Peltier, R. E., Case Hanks, A. T., Huey, L. G., Lefer, B. L., Russell, A. G., and Weber, R. J.: On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City, Atmos. Chem. Phys., 8, 3761–3768, doi:10.5194/acp-8-3761-2008, 2008.

Hering, S. and Cass, G.: The magnitude of bias in the measurement of PM_{25} arising from volatilization of particulate nitrate from teflon filters, J. Air Waste Manage., 49, 725–733, doi:10.1080/10473289.1999.10463843, 1999.

Jimenez, J. L.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525–1529, doi:10.1126/science.1180353, 2009.

Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, J. Geophys. Res., 108, 8425, doi:10.1029/2001JD001213, 2003.

Lee, S., Murphy, D. M., Thomson, D. S., and Middlebrook, A. M.: Chemical components of single particles measured with Particle Analysis by Laser Mass Spectrometry (PALMS) during the Atlanta SuperSite Project: focus on organic/sulfate, lead, soot, and mineral particles, J. Geophys. Res., 107, 4003, doi:10.1029/2000JD000011, 2002.

Lim, H. and Turpin, B. J.: Origins of primary and secondary organic aerosol in Atlanta: results of time-resolved measurements during the Atlanta Supersite Experiment, Environ. Sci. Technol., 36, 4489–4496, doi:10.1021/es0206487, 2002.

Lim, H., Turpin, B. J., Edgerton, E., Hering, S. V., Allen, G., Maring, H., and Solomon, P.: Semicontinuous aerosol carbon measurements: comparison of Atlanta Supersite measurements, J. Geophys. Res., 108, 8419, doi:10.1029/2001JD001214, 2003.

Intercomparison of an Aerosol Chemical Speciation Monitor

S. H. Budisulistiorini et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol, Aerosol Sci. Technol., 45, 780–794, 2011.

5 Peltier, R. E.: Investigating a liquid-based method for online organic carbon detection in atmospheric particles, Aerosol Sci. Technol., 41, 1117–1127, 2007.

Polidori, A.: Organic $PM_{2.5}$: fractionation by polarity, FTIR spectroscopy, and OM/OC ratio for the Pittsburgh aerosol, Aerosol Sci. Technol., 42, 233–246, doi:10.1080/02786820801958767, 2008.

10 Rastogi, N., Zhang, X., Edgerton, E. S., Ingall, E., and Weber, R. J.: Filterable water-soluble organic nitrogen in fine particles over the southeastern USA during summer, Atmos. Environ., 45, 6040–6047, doi:10.1016/j.atmosenv.2011.07.045, 2011.

Russell, L. M.: Aerosol organic-mass-to-organic-carbon ratio measurements, Environ. Sci. Technol., 37, 2982–2987, doi:10.1021/es026123w, 2003.

15 Schwab, J. J.: Field and laboratory evaluation of the Thermo Electron 5020 Sulfate Particulate Analyzer, Aerosol Sci. Technol., 40, 744–752, 2006.

Solomon, P. A., Chameides, W., Weber, R., Middlebrook, A., Kiang, C. S., Russell, A. G., Butler, A., Turpin, B., Mikel, D., Scheffe, R., Cowling, E., Edgerton, E., St. John, J., Jansen, J., McMurry, P., Hering, S., and Bahadori, T.: Overview of the 1999 Atlanta Supersite Project, J.

20 Geophys. Res., 108, 8413, doi:10.1029/2001JD001458, 2003a.

Solomon, P., Baumann, K., Edgerton, E., Tanner, R., Eatough, D., Modey, W., Maring, H., Savoie, D., Natarajan, S., Meyer, M. B., and Norris, G.: Comparison of integrated samplers for mass and composition during the 1999 Atlanta Supersites project, J. Geophys. Res., 108, 8423, doi:10.1029/2001JD001218, 2003b.

25 Sun, Y.-L., Zhang, Q., Schwab, J. J., Demerjian, K. L., Chen, W.-N., Bae, M.-S., Hung, H.-M., Hogrefe, O., Frank, B., Rattigan, O. V., and Lin, Y.-C.: Characterization of the sources and processes of organic and inorganic aerosols in New York city with a high-resolution time-of-flight aerosol mass apectrometer, Atmos. Chem. Phys., 11, 1581–1602, doi:10.5194/acp-11-1581-2011, 2011.

30 Sun, Y., Wang, Z., Dong, H., Yang, T., Li, J., Pan, X., Chen, P., and Jayne, J. T.: Characterization of summer organic and inorganic aerosols in Beijing, China with an Aerosol Chemical Speciation Monitor, Atmos. Environ., 51, 250–259, doi:10.1016/j.atmosenv.2012.01.013, 2012.

Intercomparison of an Aerosol Chemical Speciation Monitor

S. H. Budisulistiorini et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Takegawa, N.: Characterization of an Aerodyne Aerosol Mass Spectrometer (AMS): intercomparison with other aerosol instruments, Aerosol Sci. Technol., 39, 760–770, doi:10.1080/02786820500243404, 2005.

Turpin, B. J.: Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 602–610, 2001.

Weber, R., Bergin, M., Kiang, C. S., Chameides, W., Orsini, D., St, J. J., Chang, M., Bergin, M., Carrico, C., Lee, Y. N., Dasgupta, P., Slanina, J., Turpin, B., Edgerton, E., Hering, S., Allen, G., and Solomon, P.: Short-term temporal variation in $PM_{2.5}$ mass and chemical composition during the Atlanta Supersite Experiment, 1999, J. Air Waste Manage., 53, 84–91, 2003a.

Weber, R., Orsini, D., Duan, Y., Baumann, K., Kiang, C. S., Chameides, W., Lee, Y. N., Brechtel, F., Klotz, P., Jongejan, P., ten Brink, H., Slanina, J., Boring, C. B., Genfa, Z., Dasgupta, P., Hering, S., Stolzenburg, M., Dutcher, D. D., Edgerton, E., Hartsell, B., Solomon, P., and Tanner, R.: Intercomparison of near real time monitors of $PM_{2.5}$ nitrate and sulfate at the US Environmental Protection Agency Atlanta Supersite, J. Geophys. Res., 108, 8421, doi:10.1029/2001JD001220, 2003b.

Zhang, Q., Worsnop, D. R., Canagaratna, M. R., and Jimenez, J. L.: Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols, Atmos. Chem. Phys., 5, 3289–3311, doi:10.5194/acp-5-3289-2005, 2005a.

Zhang, Q., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J.: Time- and size-resolved chemical composition of submicron particles in Pittsburgh: implications for aerosol sources and processes, J. Geophys. Res., 110, D07S09, doi:10.1029/2004JD004649, 2005b.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

AMTD

6, 11181–11213, 2013

Intercomparison of an Aerosol Chemical Speciation Monitor

S. H. Budisulistiorini et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀◀ | ▶▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Sampling setup at the JST site for the UNC and GIT ACSMs.

	UNC	GIT
Sampling inlet	$PM_{2.5}$ cyclone	$PM_{2.5}$ cyclone
Sampling line length	5 m	5 m
Sampling line diameter	0.635 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 L min-1 of sheath air coming from dry/zero air system	200 tube nafion dryer (Perma Pure PD-200T-12 MPS) running with 0.5 L min^{-1} sheath air flow (under vacuum).
ACSM sampling flow rate	3 L min^{-1}	3 L min^{-1}
IE_{NO_3} calibration	3.79×10^{-11}	3.97×10^{-11}
RIE_{NH_4} calibration	6	4.3
RIE_{SO_4} fitting	0.79	0.54
RIE_{NO_3} default	1.1	1.1
RIE_{Cl} default	1.3	1.3
$RIE_{Organic}$ default	1.4	1.4
Reference flow (Q_{cal} in $cm^3 s^{-1}$)	1.39	1.35
Data acquisition software	ACSM_DAQ_v1422	ACSM_DAQ_v1425
Data analysis procedure	acsm_local_1520	acsm_local_1520

Table 2. Summary of integrated, semi-continuous, and continuous $PM_{2.5}$ samples 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.

Table 3. Correlations between the ACSM and the collocated measurements at JST site. Slope and intercept ± 1 standard deviation from each linear regression correlations are presented.

	ACSM – GIT	JST Continuous[c]		FRM PM_1[d]		
		Summer 2011	Fall 2011	Winter 2011	Spring 2012	Summer 2012
Mass[a]						
r^2	0.92	0.71	0.83	0.89	0.87	0.93
Slope	1.09 ± 0.01	1.19 ± 0.02	1.80 ± 0.02	1.47 ± 0.12	0.70 ± 0.05	1.07 ± 0.06
Intercept	0.08 ± 0.12	1.41 ± 0.27	-1.71 ± 0.18	-0.13 ± 1.19	0.17 ± 0.46	0.12 ± 0.54
OM vs. OC[b]						
r^2	0.95	0.86	0.93	–	–	–
Slope	1.14 ± 0.01	4.18 ± 0.04	3.59 ± 0.02	–	–	–
Intercept	-0.06 ± 0.07	-4.72 ± 0.17	-2.12 ± 0.08	–	–	–
SO_4^{2-}						
r^2	0.95	0.84	0.83	–	–	–
Slope	0.73 ± 0.01	0.95 ± 0.01	1.27 ± 0.02	–	–	–
Intercept	0.20 ± 0.01	-0.38 ± 0.04	-0.30 ± 0.02	–	–	–
NO_3^-						
r^2	0.89	0.55	0.81	–	–	–
Slope	0.98 ± 0.01	1.34 ± 0.03	1.51 ± 0.02	–	–	–
Intercept	0.13 ± 0.02	0.27 ± 0.01	0.25 ± 0.01	–	–	–
NH_4^+						
r^2	0.82	0.79	0.76	–	–	–
Slope	1.21 ± 0.02	1.04 ± 0.01	1.25 ± 0.01	–	–	–
Intercept	0.20 ± 0.01	0.02 ± 0.02	0.01 ± 0.01	–	–	–
Cl^- r						
r^2	0.21	–	–	–	–	–
Slope	0.60 ± 0.04	–	–	–	–	–
Intercept	0.01 ± 0.00	–	–	–	–	–

[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.
[d] Intercomparison with FRM $PM_{2.5}$ is presented in Fig. 2.
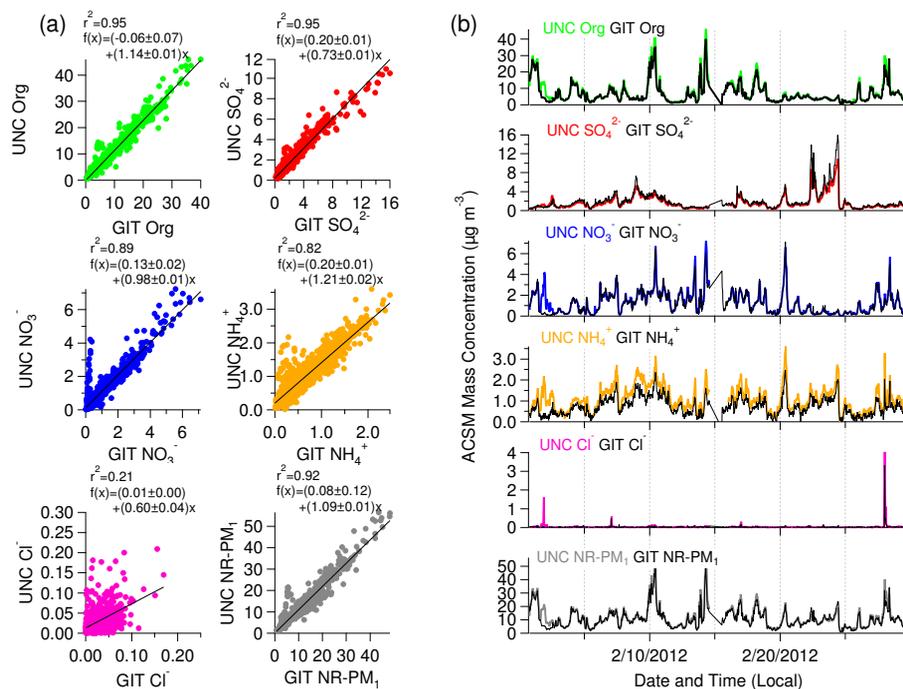
Fig. 1. (a) Linear regression correlation and **(b)** time series plots of organic and inorganic constituents measured by the UNC and GIT ACSMs. ACSM measurements from UNC are colored by species while those from GIT are colored in black.
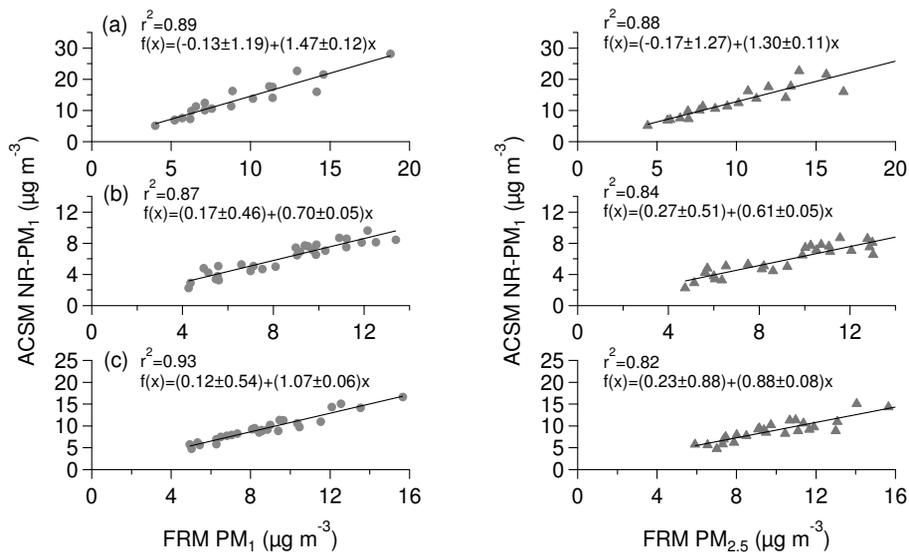
Fig. 2. Correlation scatterplots of PM_1 mass concentrations measured by the ACSM and FRM PM_1 and $PM_{2.5}$ method during **(a)** winter, **(b)** spring, and **(c)** summer 2012, respectively.
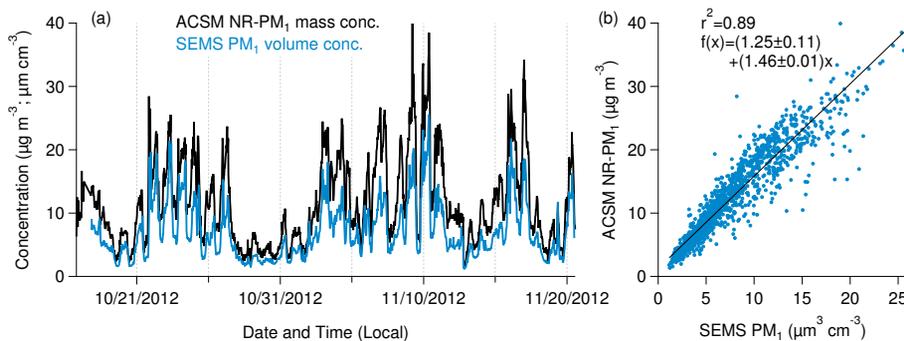
Fig. 3. (a) Time series and **(b)** correlation of total aerosol mass measured by ACSM (NR-PM$_1$) and SEMS DMA/MCPC during period of 17 October to 20 November 2012. Aerosol density was estimated from linear regression slope of 1.46 multiplied by 1.10 to account for 10 % of elemental carbon (EC) component that is not measured by ACSM. This results in estimated aerosol density of 1.61 g cm^{-3}.