

## **Responses to comments from referees**

### **Anonymous Referee #1**

Received and published: 13 February 2014

In this manuscript Budisulistiorini et al. investigate the performance of an ACSM during a long-term deployment in Atlanta, GA by comparing it to various established online and offline measurement techniques. Although the ACSM is yet around for several years, literature evaluating its performance is still relatively sparse making this manuscript a valuable addition. The manuscript is well structured and written apart from a few missing articles. However, there are very few significant new findings and some of the conclusions could have been investigated more closely. Altogether I second the publication in AMT after the following comments have been addressed.

#### **General comments:**

- For me it is not identifiable from the manuscript if the correct regression model was used. According to the text, slopes and correlations were calculated using the linear regression model. If this means the ordinary linear regression, it is not sufficient for the case shown. In ordinary linear regression, the sum of the squared vertical distances between the y data values and the corresponding y values on the fitted line are minimized, i.e. only the error of the y values is accounted for. In many cases this can yield different (inverse) slopes depending on which dataset is plotted on the y axis. In a comparison of data from two instruments both axes are error-prone, which demands an orthogonal regression. Only the slopes are affected by this, the coefficients of determination remain valid and the same. Please clarify and, if applicable, refit the data.

For the original manuscript, we used ordinary linear regression in the calculation. We agreed that the approach is not appropriate based on the reasons provided by the reviewer; therefore, we have refitted the data as proposed by the reviewer for the revised manuscript.

- More details about the calibrations of both ACSM would be desirable. Were they calibrated on site using the same equipment for both ACSM? Was the calibration system checked for consistency? How often were the calibrations repeated and how much did the RIEs and RFs vary? Were the same calibration values used for all seasons (obviously not for the SO<sub>4</sub> RIE)? An estimate of the uncertainties of the calibration system would be useful since these of course also propagate into the data

In the Experimental Section, we added the following text:

*“We calibrated the ACSM on site. The UNC ACSM was calibrated using a separate calibration system from the GIT ACSM. Different calibration values were used for different seasons. Calibrated RIE and RF values from the two ACSM are summarized in a table in the supplement section (Table S1).”*

The sentence and table below were added to the supplement:

*“The default RIE value for ammonium ( $RIE_{NH_4}$ ) was 3.5; however, the value obtained from ACSM calibrations was approximately 5.8 (Table S1). “*

**Table S1.** Statistics of calibration values obtained from UNC and GIT ACSMs.

Date	UNC ACSM			GIT ACSM		
	$RF_{NO_3}$	$RIE_{NH_4}$	$RIE_{SO_4}$	$RF_{NO_3}$	$RIE_{NH_4}$	$RIE_{SO_4}$
Mean	4.19E-11	5.81	0.67	3.26E-11	4.40	0.59
1-std deviation	1.53E-11	1.01	0.09	1.26E-11	0.38	0.04
% uncertainty	36%	17%	14%	39%	9%	7%

- The author suggests to not only calibrate the ACSM for  $NH_4$  and  $NO_3$  but also for  $SO_4$  and organics. I see that a calibration of  $SO_4$  was performed and deemed useful, but what about the calibration with organics? Why was this not done? If the authors could suggest a set of organic compounds for such a calibration or even show an example and give values for the organic RIE in the ACSM my concerns about the novelty would be greatly reduced.

In this study we focus on intercomparison of ACSM and established air quality monitoring measurements. We would suggest a separate and more in-depth study to look at RIE of organic compounds, as was done for the AMS (Jimenez et al., 2003; Alfarra et al., 2004). Our current hypothesis is that the ionization efficiency (IE) for ambient organic aerosols might vary due to their different precursors. Some laboratory-generated SOA from  $\alpha$ -pinene and isoprene experiments might be a good starting point to estimate the RIE values of SOA, as well as known primary organic aerosol (POA) types.

We added these sentences to the main text of Section 4.2:

*“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 organic 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 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.”*

- Another point which would add something new to the manuscript is an extension of the comparison of the two ACSM from only the concentrations and time series (section 3.1) to mass spectra. How similar are the mass spectra of two ACSMs sampling the same aerosol, i.e. are there observable differences in the organics fragmentation?

As carefully outlined in the abstract and introduction, our research aim was to only conduct an instrument performance comparison, especially against established monitoring data. Suggestion of comparing mass spectra of the two ACSMs is well taken; however, it is not within the scope of this present study and is suggested for future work.

- The author assumes that chloride was mostly below the detection limit. Were the detection limits of both ACSM measured or estimated?

According to Ng et al. (2011), detection limit of ACSM is  $0.02 \mu\text{g m}^{-3}$ . Some of the measurements are lower than the detection limit but some are not.

We revised the sentence as:

*“Weaker correlations of chloride might be due to its low concentration in Atlanta.”*

- An overview about the measured mass loading could be mentioned earlier in the text.

We added an overview about ACSM mass loading as the first paragraph of Result section.

Below are the sentences we added to the first paragraph of Section 3.

*“The ACSM measured about  $11.6 \mu\text{g m}^{-3}$  of OM,  $3.2 \mu\text{g m}^{-3}$  of  $\text{SO}_4^{2-}$ , and  $0.61 \mu\text{g m}^{-3}$  of  $\text{NO}_3^-$  during summer 2011. The numbers decreased in fall 2011, except for nitrate (Table S2). The ACSM measured chloride on average of  $0.02$  to  $0.04 \mu\text{g m}^{-3}$  in summer and fall.”*

- Suggestions for additional references:

AMS: Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an Aerosol Mass Spectrometer for Size and Composition. Analysis of Submicron Particles, Aerosol Science and Technology, 33, 49-70, 2000

CE: A.M. Middlebrook, R. Bahreini, J.L. Jimenez, and M.R. Canagaratna. Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data. Aerosol Science and Technology, DOI:10.1080/02786826.2011.620041, 46, 258–271, 2012.

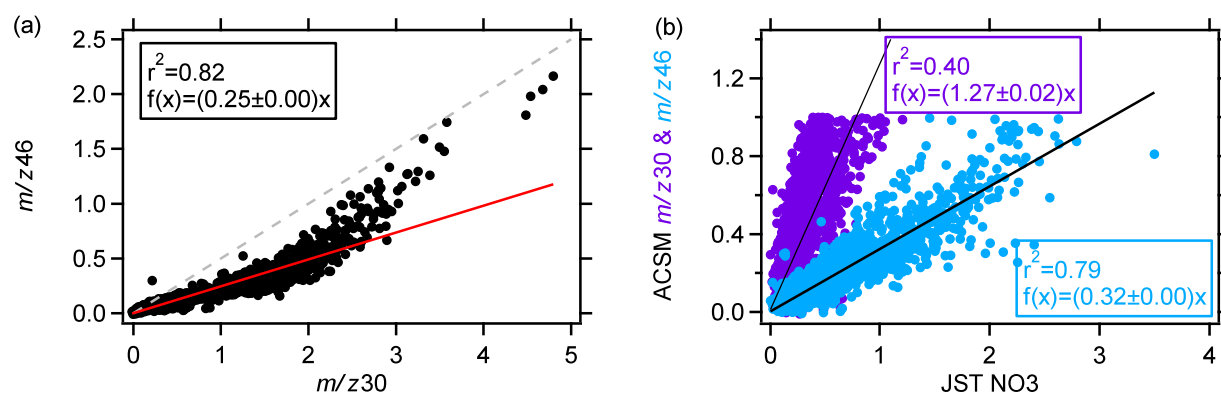
ACSM intercomparisons: Fröhlich, R., Cubison, M. J., Slowik, J. G., Bukowiecki, N., Prévôt, A. S. H., Baltensperger, U., Schneider, J., Kimmel, J. R., Gonin, M., Rohner, U., Worsnop, D. R., and Jayne, J. T.: The ToF-ACSM: a portable aerosol chemical speciation monitor with TOFMS detection, Atmos. Meas. Tech., 6, 3225-3241, doi:10.5194/amt-6-3225-2013, 2013.

We added the additional references as suggested.

- I have doubts about the presented evidence for organic nitrates at  $m/z$  30. The authors plot  $m/z$  30 and  $m/z$  46 against the JST  $\text{NO}_3$  and conclude that the higher signals at  $m/z$  30 in fall suggest that there are additional signals other than  $\text{NO}_3$  in the  $m/z$  30 channel. For me the situation in fall (Fig. S9(b)) looks more to come from a nonconstant nitrate fragmentation which depends on the total nitrate loading. This was a known ACSM issue, originating from the internal detector settings and are resolved since DAQ version 1.4.3.8. It seems as if the  $m/z$  30 decreases at higher loadings while the  $m/z$  46 increases. If this was the case in the examined dataset can be found out by plotting  $m/z$  46 vs  $m/z$  30 and checking for a non-linearity there. In Fig. S8(a) these trends do not show because of the lower loadings. I suggest to re-check the fits in fall after excluding all

points higher than approx.  $1 \mu\text{g}/\text{m}^3$  to look at about the same concentration range as in summer and see if the observed slope difference can still be observed.

Plot of  $m/z$  46 vs  $m/z$  30 from fall dataset suggests that there is some non-linearity in the  $\text{NO}_3$  fragments despite their strong correlation. Also, slope of  $m/z$  30 (1.27) and  $m/z$  46 (0.32) at low loading ( $< 1 \mu\text{g}/\text{m}^3$ ) are close to the original full scale plot, 1.31 and 0.34 for  $m/z$  30 and  $m/z$  46, respectively. Slope of  $m/z$  30 vs JST  $\text{NO}_3$  is lower compared to the one from summer (1.58), which suggests similar trend is observed at low loading. These might suggest influence of organic species on nitrate; however, since the relationship is heteroscedastic, the influence remains uncertain.



**Figure For Reply.** ACSM nitrate fragmentation from fall 2011 dataset (a) and comparison of ACSM nitrate fragmentation during low nitrate mass loading ( $< 1 \mu\text{g}/\text{m}^3$ ) and JST nitrate.

- Regressions in suppl. Fig. S10 and S11: since the distributions are heteroskedastic one of the assumptions of the classical regression model is violated and one has to take special care about the confidence intervals. Coefficients of determination and slopes should still be valid, but the given confidence intervals are blurred and likely incorrect.

We thank the referee for this valuable input. We revised the paragraph to reflect the concern of heteroscedasticity of the data distributions.

*“In order to investigate the influence of organic or oxygenated organic species to  $m/z$  30, time series traces of excess of  $m/z$  30 signal ( $\Delta m/z$  30) calculated by formula provided in Bae et al. (2007) in the summer and fall are presented in Figures S10 and S11, respectively. The  $\Delta m/z$  30, which is suggested to be derived from organic-related or organic nitrate-related  $m/z$  30 (Bae et al., 2007), has positive values most of time, but the signal is lower in summer (Figure S10a) than in fall (Figure S11a). Scatterplots of  $\Delta m/z$  30 and HOA factors (Figures S10b and S11b) derived from positive matrix factorization (PMF) (Budisulistiorini et al., 2013) show weak or no correlations ( $r^2 < 0.2$ ), but they are better for correlations with OOA factor (Figures S10c and S11c). The moderate correlation of  $\Delta m/z$  30 with OOA factor ( $r^2 = 0.5$ ) in the fall might indicate that the  $m/z$  30 signals measured by the ACSM are influenced by oxygenated organic species. However, care must be taken for the correlations of  $\Delta m/z$  30 and OOA as the plots suggest that variances are not constant throughout data distributions (heteroscedastic). This resulted in biased standard error leading to bias in statistics and confidence intervals.”*

Specific comments:

The referee is a non-native English speaker. Hence, language comments are merely suggestions.

- “Collocated” or “co-located”? (e.g. P11183 L10)

Both collocated and colocated are acceptable. We keep using collocated for this manuscript.

- P11184 L5: Close bracket after “. . .OC”

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The brackets are for OM. Abbreviations at the beginning of the sentence might not be clear, thus we revised it as follows:

*“The organic matter (OM) to OC ratios ratios derived from linear regression of ACSM OM versus Sunset OC/EC analyzer are  $4.18 \pm 0.04$  and  $3.59 \pm 0.02$  for summer and fall, respectively.”*

- P11184 L27: the instead of their

“their” in the sentence copied below is related to PM<sub>2.5</sub> chemical species. Thus, we keep this as it is.

*“As a result, there has been an ongoing need to resolve the chemical composition of PM<sub>2.5</sub> in order to identify their exact sources, and thus, develop effective control strategies.”*

- P11186 L7: replace “as from” with “like”. Here the authors should add that the ACSM not only has reduced sensitivity but also lower mass resolution than the AMS. Numbers about sensitivity and mass resolution would also be useful

We revised the sentence as suggested:

*“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 sensitivity quadrupole ( $0.5\text{--}1\text{ s amu}^{-1}$ ) compared to Q-AMS ( $1\text{ ms amu}^{-1}$ ) and have a lower mass resolution (200 amu) (Ng et al., 2011).”*

- P11186 L9: “lower grade quadrupole”. Lower than what? Please specify.

This has been addressed together with the comment above.

- P11188 L7: “amu<sup>(-1)</sup>” could be misunderstood as “amu\*s<sup>(-1)</sup>”

We replaced amu<sup>-1</sup> with amu<sup>-1</sup>.

- P11189 L9: The range of SO<sub>4</sub> RIEs used is relatively large (0.44-1.10). Does this represent the uncertainty of the fitting approach or is there a seasonal variation?

The fitting approach statistics show  $0.79 \pm 0.22$  of mean  $\pm$  1-standard deviation. Recent sulfate RIEs from ammonium sulfate calibration suggested  $\text{RIE}_{\text{SO}_4}$  value of  $0.67 \pm 0.09$  with uncertainty of 14%. These suggest that fitting approach has larger uncertainty compared to calibration results.

**Table For Reply:** Statistics of sulfate RIEs from fitting approach and calibration

Date	Fitted RIE_SO4	Calibrated RIE_SO4	
		UNC	GIT
Mean	0.79	0.67	0.59
1-sigma %	0.22	0.09	0.04
uncertainty	28%	14%	7%

The table above is added into the supplement section as Table S1 as mentioned earlier. Also, we added the information into the main text:

*“Instead of default  $\text{RIE}_{\text{SO}_4} = 1.2$ , fitted  $\text{RIE}_{\text{SO}_4}$  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  $\text{RIE}_{\text{SO}_4}$  values are provided in the supplemental section. Explicit calibration of  $\text{RIE}_{\text{SO}_4}$  during winter 2013 yielded a value of  $0.67 \pm 0.09$  indicating that the fitting approach value ( $0.79 \pm 0.22$ ) is consistent with the calibrations, with a larger uncertainty (Table S1).”*

- P11189 L23: which assumptions?

Assumptions used in estimating collection efficiency (CE) as explained in Bahreini et al. (2009). We revised the sentence as follow:

*“The speciated ACSM mass concentrations are estimated to be accurate to within  $\pm 20$ –35% based on AMS uncertainty (Bahreini et al., 2009).”*

- P11191 L3ff: At first look this seems to be circular, the continuous measurements are adjusted to the filters and then correlate well with the filters. The names “Level\_1” and “Level\_2” are obsolete, they are only used at one more instance in the manuscript.

We deleted the names “Level\_1” and “Level\_2”.

- P11193 L2: The authors supposedly do not mean to find meteorological variations across seasons as stated in the text but variations of aerosol parameters

We revised the text as follows.

*“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.”*

- P11193 L3-L8: I suggest dropping this paragraph. Repetition of content from Sect. 3.2.1

We followed the suggestion to drop the sentences.

- P11194 L3: Please recheck the slope of 0.67 from the summer intercomparison of NH4. After having a look at Fig. S6(d) it seems too low.

We have re-calculated the slope and got the same value.

- P11194 L7: Please clarify the baseline comment. I am not aware of a baseline calculation in the ACSM software.

We revised the text as follows.

*“During both summer and fall, the intercepts are about 0.3, which might indicate differences in limit of detection between the instruments.”*

- P11194 L8: “slope” instead of “slopes”

We have revised accordingly.

- P11195 L4: how is the +/-47% variation calculated?

We reported percentage difference between measurements. 47% difference was based on the largest difference between ACSM NR-PM<sub>1</sub> and PM<sub>1</sub> which is from winter 2011 data. To clarify the meaning, we revised the sentence as follows.

*“Comparison between the ACSM NR-PM<sub>1</sub> and FRM PM<sub>1</sub> in winter, spring, and summer 2012 shows a good correlation, with  $r^2$  values of  $> 0.80$  (Table 3), and the mass concentrations differences are 7–47%.”*

- P11195 L8: please specify meteorological influence

As requested, we added explanation the following in Section 3.2.2:

*“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 as positive bias could be expected from filter measurement during colder seasons (Solomon et al., 2003b, Solomon et al., 2003a).”*

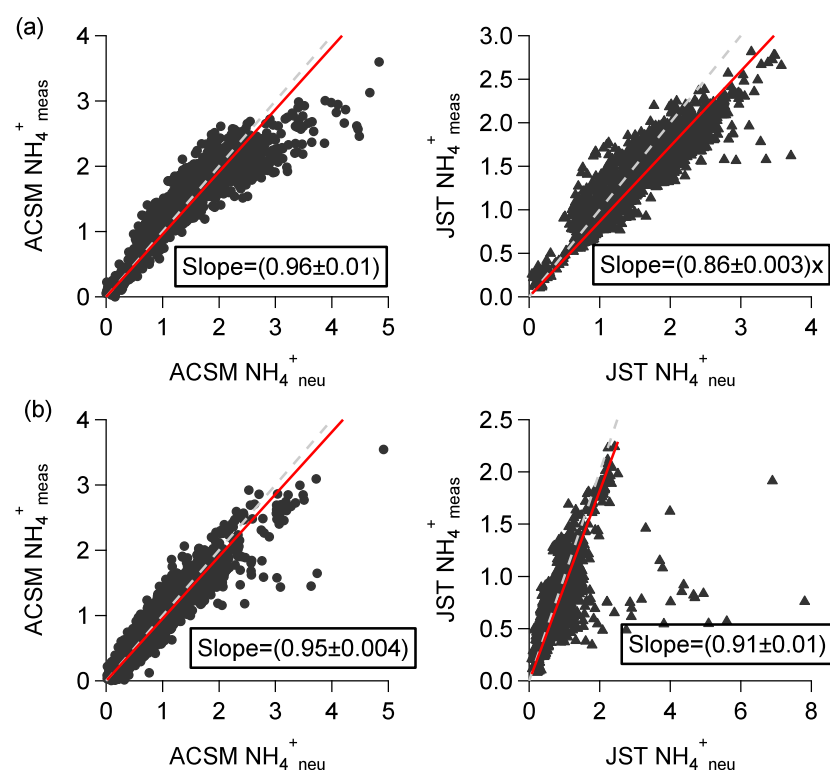
- P11197 L22: Where does this 30% uncertainty estimation come from?

ACSM uncertainty is assumed to be similar with AMS uncertainty as reported in Bahreini et al. (2009).

- Sect. 4.3: I suggest to include information about the “neutralization balance (NH<sub>4</sub> measured vs NH<sub>4</sub> predicted)” for both ACSM and continuous measurements

We added the figure below to the supplemental information and the following text to Section 4.3 in the main text:

*“Sulfate measurements from ACSM and filter show a good trend ( $r^2 > 0.7$ , see Figure 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 either the JST continuous measurements or ACSM during this sampling period. Both ACSM and continuous measurements show that slopes of NH<sub>4</sub><sup>+</sup> measured versus NH<sub>4</sub><sup>+</sup> predicted (neutralized) are slightly less than 1 (Figure S8). This suggests during both summer and fall 2011, the aerosol was slightly acidic.”*



*Figure S8. Comparison of NH<sub>4</sub> measured and predicted (neutralized) during (a) summer, and (b) fall 2011.*

- P11200 L24: remove “in”. An incorrect RIE of organics would produce a constant offset, this could be pointed out more precisely.

We have revised the text as suggested.

- P11201 L10: why is this the “traditional ambient aerosol density”? The cited 1.2 gcm<sup>-3</sup> is an organic aerosol density according to Turpin et al. Published overall densities of ambient aerosol are usually higher. E.g. a similar density of 1.61 gcm<sup>-3</sup> was reported from Beijing. Cf.: Hu,



Min, et al. "Estimation of Size-Resolved Ambient Particle Density Based on the Measurement of Aerosol Number, Mass, and Chemical Size Distributions in the Winter in Beijing." *Environmental Science & Technology* 46.18 (2012): 9941-9947.

We thank the referee for pointing this out. We were mistakenly referring to organic aerosol density as opposed to ambient aerosol density. The text has been revised accordingly.

*"The estimated PM<sub>1</sub> aerosol density of 1.61 g cm<sup>-3</sup> is consistent with recent ambient aerosol density estimations, such as 1.61 g cm<sup>-3</sup> in Beijing (Hu et al., 2012) and 1.46 g cm<sup>-3</sup> in Pasadena (Hayes et al., 2013)."*

- P11201 L13: This last sentence is very general.

We deleted this sentence as part of changing the prior sentence to follow above comment.

- P11202 L5: The AMS is not really the predecessor of the ACSM. The instruments are related, but both have different fields of application and reasons of existence.

We omitted the word "predecessor" from this sentence:

*"Discrepancies found in the intercomparisons of the ACSM and the collocated measurements might be explained by the following: (1) RIE value of organic 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<sub>3</sub><sup>-</sup> signal; and (3) evaporative losses of semi-volatile species from the filter measurements used in the collocated continuous measurement adjustment."*

- Missing authors in the following citations: Jimenez 2009, Peltier 2007, Polidoro 2008, Schwab 2003, Takegawa 2005 and Turpin 2001

We thank the referee for pointing the missing authors. Citations have been fixed accordingly.

- Suppl P4 L2: The standard RIE of SO<sub>4</sub> which should be used for the fitting is 1.2 not 1.5, is it?

We thank the referee for catching this mistake. The standard value of RIE<sub>SO<sub>4</sub></sub> is 1.2. We have corrected the text.

*"Previous value of RIE<sub>SO<sub>4</sub></sub> 1.2 is then multiplied by slope obtained from fitting SO<sub>4,pred</sub> versus SO<sub>4,meas</sub> and used as the RIE<sub>SO<sub>4</sub></sub> value of this study."*

- Suppl Fig. S4 (a): Do the authors have a hypothesis why the sunset OC seems to have such a large offset?

The large offset might be due to condensation of SVOC or adsorption of VOC on the filter. The Sunset OC/EC was a semi-continuous. It collects particles on filter. Once collection is complete (after ~50 minutes), the oven is purged with 10% O<sub>2</sub> in He, and then ramped up to a set point of

850 °C according to the NIOSH 5040 analysis protocol. Much of this information is already in the main text under Section 4.2.

- Suppl Fig. S7 and S6: In my opinion these figures could also go into the main document.

In the main text, we focus on inter-comparison of the ACSM measurements and the final JST measurements data, which is the filter-adjusted continuous. JST filter measurements serve as adjustment to the JST continuous measurements, and thus any discrepancies are already included in the final output. Adding these figures might create redundancy in the discussion.

## **Anonymous Referee #2**

Received and published: 12 February 2014

This paper reports on an intercomparison exercise between the ACSM and a variety of other measurements over a long time period. Given that this is a new instrument suited to monitoring, thorough evaluation work such as this is important. While this work is important in principle, I didn't really get a feel for what the outcomes contribute in terms of understanding the instrument or development of best practice. In some instances, such as the investigation of interferences with nitrate, I do not feel the problem was investigated in as great a depth as possible. In others, such as the poor quantification of sulphate, this only serves to highlight a problem that has already been identified and rectified by the manufacturers (sulphate calibrations are now standard practice). This is not to say that this is not publishable, but I think that in some places, a deeper analysis of various issues could be performed. The paper also needs to be clearer in its conclusions about the outcomes and recommendations of this work. It should also be very clear to identify which issues (e.g. the need for routine sulphate calibrations) have since been addressed; given that the paper features a number of coauthors from Aerodyne, one might be forgiven for thinking that these issues are still outstanding and would reflect badly on the instrument.

### **General comments:**

While it is unfortunate that there is a lack of calibration data for sulphate, I regard the method used to retrospectively estimate the RIE to be deeply unsatisfactory, especially seeing as it relies on a reliable nitrate measurement, which elsewhere is deemed to be suffering from interferences. I would be interested to know whether better statistics could be obtained by using different combinations of parameters, such as a single value of the RIE.

Before we attempted to retrospectively estimate sulfate RIE, we used a single value of 1.2 that resulted in poor statistics. This value was based on what is typically assumed for the AMS instruments. From ammonium sulfate calibrations we conducted, we revealed that sulfate RIE value is not constant (as previously assumed). Therefore, we would suggest to use RIE values specific to each dataset. At the time this instrument was deployed in Atlanta, the AMS/ACSM community did not recognize routine calibration using ammonium sulfate as being necessary. The gold standard in the past has been routine calibration for ammonium nitrate in all Aerodyne instruments, especially since all remaining RIE values are adjusted from its value. Thus, the reviewer should be careful in assuming this is done for all instruments (as this is user specific issue), and thus, we found it was incredibly important to conduct both ammonium nitrate and ammonium sulfate calibrations for ACSM instruments. Part of our work motivated Aerodyne to suggest to all AMS/ACSM users to conduct routine calibrations with ammonium sulfate. This is the first time we are publishing this result, so it may be common knowledge to users who attend AMS/ACSM users' meetings, but not in the published literature.

No information is given as to how the vaporiser temperature and heater bias were set. Given that these are known to affect data, this should be covered.

This information has now been added to the experimental section, as follows:

*“Vaporizer and heater bias were set at 600 °C and 100.30 V.”*

Specific comments:

Abstract: I would consider the abstract to be too long. Consider making more concise and reducing the length.

We revised the abstract to be more concise as suggested.

*“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<sub>2.5</sub>) measurements at the Southeastern Aerosol Research and Characterization (SEARCH) Jefferson Street (JST) site near downtown Atlanta, GA, during 2011–2012. Intercomparison of the 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<sub>1</sub> plus EC with TEOM PM<sub>2.5</sub> and FRM PM<sub>1</sub> mass are strong with  $r^2 > 0.7$  and  $r^2 > 0.8$ , respectively. Aerosol density was  $1.75 \mu\text{g m}^{-3}$  estimated from total mass loading from ACSM NR-PM<sub>1</sub> plus EC and volume concentration from scanning electrical mobility system-mixing condensation particle counter (SEMS-MCPC). Discrepancies might be attributed to evaporative losses of semi-volatile species from the filter measurements used to adjust the collocated continuous measurements. Fitting approach for ACSM relative ionization for sulfate was shown to improve the comparisons between ACSM and collocated measurement in the absence of calibrated values.”*

P1185: The focus on the 1999 SEARCH campaign in the introduction is an odd choice. While this was historically highly important in establishing the AMS as a credible technique, this was merely the first of many systematic comparisons between the AMS and IC-based techniques. It would be more informative if the authors were to give other examples of previous comparisons, including more contemporary studies.

We deleted this paragraph and added references to newer studies.

P1188, L14: The reason for not using the naphthalene data should be given here. More information is also needed on how the  $m/z=28$  signal was used because the ACSM does not have an ‘airbeam’ in the same sense as the AMS (not using a chopper). If the background signal was used, diagnostic data should be given, because this will receive significant interference from CO.

The  $m/z$  28 signal was used to adjust measurements over time because it reflects decay in measurement sensitivity (gain decay) as well as drift in sampling flow rate. While, naphthalene effusion only reflects sensitivity degradation over time.

P1191, L7: Perhaps I've missed something, but it should come as no surprise to learn that the filter-corrected data correlates so well with the filter data itself.

We agreed that the two data should compare well and excluded the statement from the text.

P1195, L20: I would regard this discrepancy to be an indictment of the method used to estimate sulphate RIE. Agreement for sulphate in previous literature comparisons has generally been quite good.

We agreed that the sulfate RIE fitting contributed to the discrepancy; however, we would like to emphasize that this approach has helped sulfate intercomparisons. Sulfate comparisons in prior studies have been good since these are AMS instruments and not the ACSM presented here.

P1196, L4: What is the estimated uncertainty of this technique? Personally, I would regard a 27% discrepancy in sulphate to not be acceptable.

ACSM uncertainty is assumed and measured to be similar to AMS uncertainty  $\pm 20\text{--}35\%$  (Bahreini et al., 2009).

P1196, L7: The values of OM/OC are not just high, but unphysically so. CO<sub>2</sub>, the most oxidised form of carbon, has an effective ratio of 3.67.

The reviewer's point is well taken that it is odd to see very high OM/OC ratios. We argue, however, using CO<sub>2</sub> as the upper limit of OM/OC ratio might not be appropriate since some known organic compounds have larger ratios. For example, oxalic acid is 3.75, and methanesulfonic acid (MSA, CH<sub>3</sub>SO<sub>3</sub>H) has an OM/OC ratio of 8.

The possible explanation about the extremely high OM/OC ratio is the large offset of the Sunset OC measurement, and thus, underestimation of OC and overestimation of OM by the ACSM due to inappropriate RIE organic. We added this explanation in the text in Section 4.2:

*"The large OM/OC ratios might be attributed to underestimation of OC due to evaporation of semi-volatile organic compounds (SVOCs) from the Sunset OC/EC 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 (Figures S4 and S5). 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, 20% of Sunset OC uncertainty (Peltier, Weber and Sullivan, 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 organic 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 SOA (Kleindienst et al., 2006; Lin et al., 2012), need to be systematically analyzed in future work in order to determine the exact RIE value for organics in the ACSM.”*

P1198: The issue of nitrate interferences is very important and should really be covered in the main manuscript rather than the supplementary material.

In this study, we focus on performance comparison between ACSM and air quality monitoring network measurements. Nitrate interferences were investigated to help describe discrepancy between measurements. Thus, it is provided in the supplement.

P1200, L26: Comparing mass with volume will never yield a perfect correlation because density is variable. That being the case, why not compare SEMS volume with an ACSM-derived volume, using known densities of the components? A volume contribution from black carbon can be added based on the Aethalometer data.

We compared mass concentration from ACSM to volume concentration from SEMS to estimate ambient aerosol density. We agreed that the correlation would not be appropriate here; therefore, we omitted statement about correlation and directly focused on aerosol density estimation.

Figure S5: It would seem obvious to me that the sulphate events captured by JST but not ACSM coincide with events seen in the organic time series. Has the mass spectra of these events been inspected? Is there any deviation in the sulphate ion ratios during these events?

During period where ACSM sulfate weakly correlated with JST sulfate (Figure 4b), ratios of sulfate fragments were enhanced, particularly for ratio of  $\text{HSO}_3$ :SO. The figure below has been added to the supplemental information and referred in the main text.

*“Investigation of the period where correlation between ACSM and collocated measurement is low in fall season suggests some organic interferences in sulphate fragments, in particular  $m/z$  81 (Figure S9).”*

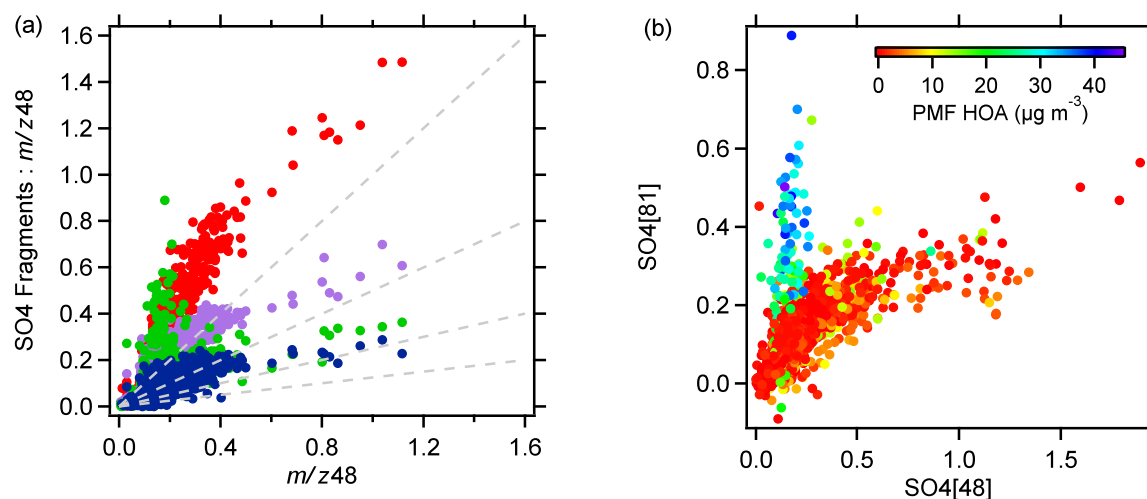
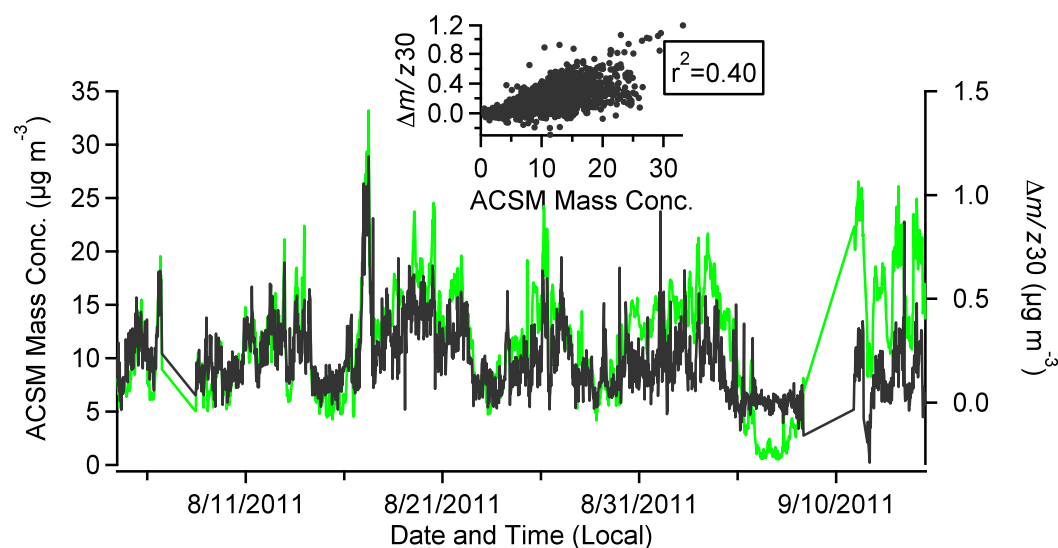


Figure S9. ACSM SO4 fragmentation during weak correlation period in fall 2011 (a) which likely due to organic interferences (b).

Figure S10: It would seem obvious to me to try comparing delta30 with the organic mass loading, if an organic interference is suspected. I find similarity between this trace and the OM trace in figure S4 to be quite striking.

We did not see a strong correlation between  $\Delta m/z$  30 and ACSM OM. We added the figure and paragraph below to the supplemental information:

*“On Figure S12 (b and c),  $\Delta m/z$  30 is compared with HOA and OOA factor, respectively, which are resolved from organic fraction using PMF. Thus, we can expect to see similar distribution from comparison with organic mass loading, as illustrated in Figure S14. The correlation between  $\Delta m/z$  30 and organic mass loading is moderate, which suggests that there might be some interference of organic on  $\Delta m/z$  30 fragment of nitrate. Since their distribution is heteroscedastic, which make the confidence interval invalid, relationship between the  $\Delta m/z$  30 and total organic matter should be interpreted more carefully. “*



*Figure S14. Comparison of  $\Delta m/z$  30 with organic mass loading during summer 2011.*

Technical:

P1184, L25: Hallquist et al. (2009) is an odd choice of reference here. Consider using the recent IPCC report instead.

We replaced the reference to IPCC 2013 Summary of Policy Makers.

P1185, L18: The AMS should be qualified as the Aerodyne AMS, as ‘aerosol mass spectrometry’ can also be used as a generic term

We have revised the text accordingly.

P1186, L6: The acronym ‘ACSM’ needs defining

We have added the definition as suggested.

P1186: Ng et al. (2011) needs only to be cited once; the fact the subsequent statistics are from the same paper is self-evident.

We have revised the paragraph as suggested.

P1188, L14: The naphthalene source is effusive, not diffusive.

We have revised the text accordingly.

P1189, L21: Recommend citing Middlebrook et al. (2012) regarding the effect of acidity on CE.

We have added the citation as suggested.



P1190, L27: Was the Sunset instrument online or offline? Also, which temperature protocol was used?

The Sunset OC/EC was a semi-continuous. It collects particles on filter. Once collection is complete (after ~50 minutes), the oven is purged with 10% O<sub>2</sub> in He, and then ramped up to a set point of 850 °C according to the NIOSH 5040 analysis protocol. This information has been clarified and added in the experimental section.

P1191, L1: Were any corrections for shadowing or scattering performed on the Aethalometer data?

We didn't mean to include the description for the Aethalometer since it was not used in the intercomparison here. We will exclude this description from the revised manuscript.

P1192, L5: A reference for the DMA design used should be given, as some DMAs struggle to transmit particles of sizes nearing 1000 nm, even at low flow rates.

We added reference below for the design of BMI-DMA used in this study.

Sorooshian, A., S. Hersey, F.J. Brechtel, A. Corless, R.C. Flagan, and J.H. Seinfeld (2008). Rapid, size-resolved aerosol hygroscopic growth measurements: Differential aerosol sizing and hygroscopicity spectrometer probe (DASH-SP). *Aerosol Science and Technology*, 42(6): 445-464.

P1192, L17: Surely this should be 'below detection limits'?

We have revised the text as suggested.

S7, L20: Being an optical measurement, the Aethalometer strictly measures 'black' carbon, not 'elemental' carbon. The latter implies some form of chemical analysis.

We will exclude this description from the revised manuscript.