Atmos. Meas. Tech. Discuss., 8, C3728–C3738, 2015
www.atmos-meas-tech-discuss.net/8/C3728/2015/

Atmospheric Measurement Techniques
Discussions

# *Interactive comment on* "ACTRIS ACSM intercomparison – Part I: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with Time-of-Flight ACSM (ToF-ACSM), High Resolution ToF Aerosol Mass Spectrometer (HR-ToF-AMS) and other co-located instruments" *by* V. Crenn et al.

**V. Crenn et al.**

crenn.vincent@gmail.com

Received and published: 5 November 2015

Dear Editor

Thank you very much for your attention to our manuscript. Please find below our responses to both Referee Comments. We have taken all comments into consideration, and revised our manuscript accordingly. With our Best Regards

Response to Referee #1

We thank Referee#1 for the review and for his specific comments, which have all been considered as follows:

1. The title is too long and not good for readers to catch the point.

Author's response: Based on your suggestion, the title was changed to: "ACTRIS ACSM Intercomparison - Part I: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments".

2. Page 7259, the second paragraph, it's not necessary to show the number of ACSM, e.g., ACSM # 3, when describing the range of the values. If use, "ACSM" and "QACSM" need to be consistent.

Author's response: The number of ACSM was deleted in the second paragraph when describing the range of the values (L496-L501). "Q-ACSM" and "ToF-ACSM" was used in the manuscript to cite Quadripole and Time-of-Flight Aerosol Mass Spectrometer, respectively, whereas "ACSM" was used as a general term to cite both Q-ACSM and ToF-ACSM. Modifications have been made in the manuscript.

3. This manuscript didn't discuss much about relative ion transmission efficiency, which might vary significantly between different instruments. Have the authors checked the fitting curves of ion transmission efficiency between m/z 50 – 150 for different ACSMs. Would it be an important factor contributing to the measuring uncertainties?

Author's response: We agree that Relative Ion Transmission (RIT) efficiency is a key parameter in the ACSM data treatment as well as the Airbeam correction. The RIT, through the variable Tm/z, is taken into account in the calculation of the chemical mass concentrations and associated uncertainties. Due to the use of a lower grade of quadrupole mass spectrometer, the RIT of ACSM depends on m/z. Therefore a correction must be applied to compensate the rapid decrease of ion transmission at high m/z. An internal naphthalene standard, continuously emitted, is used to correct the ion transmission by following the signal at m/z 128, which allows the determination of the type of correction to be applied: exponential, linear, power or quadratic. In this study, different RIT fitting curves were used depending on ACSMs. Power law fitting curves were chosen for ACSMs #6, 8, 9, and 11 to explain the variation of ion transmission whereas exponential RIT fitting curves were used for the others. Sensitivity tests were performed to check the importance of the fitting curves of ion transmission efficiency between m/z 50 – 150 for different ACSMs. The Figure 1 shows the slopes of mass concentrations of NR-PM1 major components obtained with the four different RIT fitting curves proposed in the data treatment for two ACSMs using different RIT fitting curves (#8: power law fit and #12: exponential fit). NO3, Chl and NH4 have fragments at m/z below 50 and are not sensitive to different RIT fitting curves. Only Org and SO4 mass concentrations could be affected by the corrections used with fragments between m/z 50 – 150. However, the slopes of mass concentrations obtained between the two different fitting curves used in this work (exponential and power law) are very close to 1. Based on these results, the type of RIT correction was not considered as a major issue in the calculation of mass concentrations and, for that reason, was not taken into account here for the ACSM measurement uncertainties. However, the authors agree that this parameter must be chosen with caution during the ACSM data treatment. In this respect, one paragraph was added in the revised manuscript (Sect. 3.1.3.) to provide such explanations regarding the influence of RIT corrections on concentration measurements.

4. With nitrate, sulfate, and ammonium measurements, aerosol particle acidity can be estimated. I suggest the authors adding some discussions on the uncertainties in

estimating particle acidity using ACSM data, which is an important parameter widely used in the AMS community.

Author's response: We agree that aerosol acidity is an important parameter widely used in the AMS community notably because aerosol pH influences the determination of the collection efficiency (CE), with the nitrate content and the relative humidity (Middlebrook et al., 2012). For ACSMs (and also AMS), the particle acidity is usually calculated by doing the ion balance with nitrate, sulfate (and eventually chloride) and ammonium measurements. However, Hennigan et al. (2015) have recently shown that the ion balance or molar ratios of cations and anions may not be a good proxy for aerosol pH and thus for particle acidity. That is an important point why we didn't discuss the particle acidity here. Furthermore, in our study, a constant RIE of 1.2 was taken for SO4 for all Q-ACSMs due to lack of a proper calibration made for (NH4)2SO4. High uncertainties may be then associated with the calculation of acidity preventing for a thorough discussion on this parameter. Based on your suggestion, the following sentences were then added within Appendix C in the Supporting Material: "For ACSMs (and also AMS), the particle acidity has commonly been estimated based on the ion balance between nitrate, sulfate (and possibly chloride) and ammonium measurements. Due to issues related to RIENH4 and RIESO4 calibrations, highlighted in the present study, such calculations should then be performed and interpreted circumspectly. Moreover, Hennigan et al. (2015) have recently shown that the ion balance or molar ratios of cations and anions may not be a good proxy for aerosol pH, reinforcing the need to handle such calculations with caution.". Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15, 2775-2790, doi:10.5194/acp-15-2775-2015, 2015.

5. Fig. 11, PIL-IC should be PILS-IC.

Author's response: Legend of Figure 11 modified.

Response to Referee #2

We thank Referee #2 for the review and for his specific and minor comments, which have all been considered as follows:

1. Page 7270, Lines 20-24: The authors should realize that ACSM users in other parts of the world may not have more than 1 SMPS system in their labs as these are not cheap instruments. I would argue that this conclusion of validating the size of ammonium nitrate or ammonium sulfate particles downstream of a DMA (part of 1 SMPS system) used to generate the calibrant aerosol with another SMPS system shouldn't be taken as required by all future users who may not have access to two of these expensive systems. I think the authors should say that if possible this type of check should be done.

Author's response: The authors fully agree with the reviewer. Therefore, we added in the conclusions: "This type of check should be done if users have a second SMPS".

2. Related to # 1 above, it remains unclear to me why the authors of this paper didn't use RIE sulfate values specific to each ACSM. Why is this? Is this due to the study being done before the Budisulistiorini et al. (2014, AMT) paper was published that indicated the need for RIE sulfate calibrations? This is understandable if this is the case, but it was unclear.

Author's response: As explained in section 3.1.2., in this study, a default RIESO4 value of 1.2 was applied to calculate sulfate mass concentrations for each ACSM due to the lack of a proper specific RIESO4 calibration and to a higher dispersion of SO4 measurements obtained when using different RIESO4 values for each instrument. In Budisulistiorini et al. (2014), the RIESO4 value needed to obtain full neutralization of secondary inorganic aerosols was estimated by fitting ACSM measured and predicted SO4 values (SO4,meas and SO4,pred, respectively) for each instrument, where SO4,pred is the estimated value of SO4. Such a methodology was also tested here but didn't lead to any improvement for ACSM measurement reproducibility, as detailed

in the supporting material (Appendix B).

3. In an ideal world, the authors would have captured other seasons to see how the 13 ACSMs intercompared. Budisulistiorini et al. (2014, AMT) found that different seasons yielded different results between ACSM and collocated datasets. Of particular concern in this prior study was that the OM-to-OC ratios became VERY VERY high during more photochemically active seasons, such as summer. OM-to-OC values, where as in winter the OM-to-OC ratios were similar to what was observed here in the present study! This suggested that RIE for organics may not be the same as the AMS instruments and should also be calibrated like ammonium, nitrate, and sulfate. At minimum, the authors should acknowledge the need to do such intercomparison studies in the future that cover other seasons (especially more photochemically active seasons). The OM-to-OC ratios observed in the warmer seasons is a bit concerning and does suggest the need for laboratory studies to more thoroughly examine what the RIE is for organics depending upon how oxidized the organic material is within the aerosol sampled by the ACSM. Wouldn't you all agree this is a concerning issue that remains for the ACSM?

Author's response: Yes, we fully agree. The need to better estimate RIE Org was also pointed out during the last AMS-ACSM users meeting in Milano following the European Aerosol Conference (EAC) 2015. A focus will be given on organics during the 2nd ACTRIS intercomparison study at ACMCC (Paris, France). In order to cover a different season, this study will take place in early spring when high levels of long range transported PM generally occur. The OM-to-OC values will be calculated as it has been done for the first ACSM intercomparison and be compared to the winter (late fall) ones obtained in this work. However, such OM-to-OC values approaching 4 during warm months as found in Budisulistiorini et al. (2014, AMT) have never been observed at the SIRTA station. Based on your suggestion, the following sentences were added within section 5.2.2.: "It is also to note that recent studies observed significant seasonal variations of the OM-to-OC ratio, with values up to about 4 during summer (Budisulistiorini et al., 2014), suggesting that the ACSM organic RIE may actually not be constant over time. Future works are still needed to better understand this specific issue. In order to cover different ambient air conditions, a focus will notably be given on organics during the 2nd ACTRIS ACSM intercomparison study at ACMCC, which will take place early spring 2016, a period of the year generally experiencing high levels of long range transported PM.“.

4. Page 7244, Line 19-25: The authors probably should cite Budisulistiorini et al. (2015, ACPD), as they have published 12 months of data from both Atlanta, GA and from Look Rock, TN in the US. Citation information can be found here: http://www.atmos-chem-physdiscuss.net/15/22379/2015/acpd-15-22379-2015.html.

Author’s response: This reference is now cited in the revised manuscript (in the introduction in reference to the 12 months ACSM measurements in the southeastern United States: Atlanta, Georgia and Look Rock, Tennessee).

5. Page 7247, Line 18: Shouldn’t "Chapel Hill, UK" be "Chapel Hill, NC = North Carolina, USA"? I’m pretty sure that is where URG is located.

Author’s response: The URG location was modified in the revised manuscript.

6. "Organic" was changed to "organic" in the new version of the manuscript.

Author’s response: Page 7248, Line 20: Change "Organic" to "organic"

List of all changes made in the manuscript

In the manuscript: “Q-ACSM” and “ToF-ACSM” was used in the manuscript to cite Quadripole and Time-of-Flight Aerosol Mass Spectrometer, respectively, whereas “ACSM” was used as a general term to cite both Q-ACSM and ToF-ACSM.

L1-L7: Title changed to: “ACTRIS ACSM Intercomparison - Part I: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments”.

L113: Reference to Budisulistiorini et al., 2015a added.

L114: Reference to Budisulistiorini et al., 2015 changed to Budisulistiorini et al., 2015a and reference to Budisulistiorini et al., 2015b added.

L119-L121: “, in the southeastern United States: Atlanta, Georgia and Look Rock, Tennessee (Budisulistiorini et al., 2015a)” added.

L199: “Chapel Hill, UK” replaced by “Chapel Hill, NC, USA”.

L228: “Organic” replaced by “organic”.

L361-L371: “Due to the use of a lower grade of quadrupole mass spectrometer, the RIT of ACSM depends on m/z. Therefore a correction must be applied to compensate the rapid decrease of ion transmission at high m/z. An internal naphthalene standard, continuously emitted, is used to correct the ion transmission by following the signal at m/z 128, which allows the determination of the type of correction to be applied: exponential, linear, power or quadratic. In this study, power law and exponential RIT fitting curves were used depending on ACSMs. Sensitivity tests performed showed that the slopes of mass concentrations obtained between the two different fitting curves are very close to 1. Based on these results, the type of RIT correction was not considered as a major issue in the calculation of mass concentrations and, for that reason, was not taken into account in Sect. 5.1.1 for the ACSM measurement uncertainties.” added.

L507-L511: ACSM number deleted when describing the range of the values.

L778-L784: “It is also to note that recent studies observed significant seasonal variations of the OM-to-OC ratio, with values up to about 4 during summer (Budisulistiorini et al., 2014), suggesting that the ACSM organic RIE may actually not be constant over time. Future works are still needed to better understand this specific issue. In order to cover different ambient air conditions, a focus will notably be given on organics during the 2nd ACTRIS ACSM intercomparison study at ACMCC, which will take place early spring 2016, a period of the year generally experiencing high levels of long range transported PM.” added.

L813 “This type of check should be done if users have a second SMPS.” added.

L906-L910: reference “Budisulistiorini, S. H., Baumann, K., Edgerton, E. S., Bairai, S. T., Mueller, S., Shaw, S. L., Knipping, E. M., Gold, A., and Surratt, J. D.: Seasonal characterization of submicron aerosol chemical composition and organic aerosol sources in the southeastern United States: Atlanta, Georgia and Look Rock, Tennessee, Atmos. Chem. Phys. Discuss., 15, 22379-22417, doi:10.5194/acpd-15-22379-2015, 2015a.” added.

L916: reference modified.

L1259: “PIL-IC” changed to “PILS-IC”.

List of all changes made in the Supporting Material

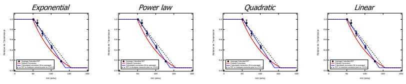
In the Supporting Material: “Q-ACSM” and “ToF-ACSM” was used in the manuscript to cite Quadripole and Time-of-Flight Aerosol Mass Spectrometer, respectively, whereas “ACSM” was used as a general term to cite both Q-ACSM and ToF-ACSM.

L149-L155: “For ACSMs (and also AMS), the particle acidity has commonly been estimated based on the ion balance between nitrate, sulfate (and possibly chloride) and ammonium measurements. Due to issues related to RIENH4 and RIESO4 calibrations, highlighted in the present study, such calculations should then be performed and interpreted circumspectly. Moreover, Hennigan et al. (2015) have recently shown that the ion balance or molar ratios of cations and anions may not be a good proxy for aerosol pH, reinforcing the need to handle such calculations with caution.” added. L196: “ToF-AMS” changed to “ToF-ACSM”.

L224-L226: reference “Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15, 2775-2790, doi:10.5194/acp-15-2775-2015, 2015.” added.

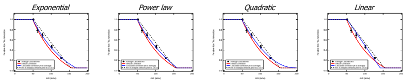
Interactive comment on Atmos. Meas. Tech. Discuss., 8, 7239, 2015.

**a) ACSM #8:**



| | Power law | Quadratic | Linear |
|---|---|---|---|
| Chl | 1.0000 | 1.0000 | 1.0000 |
| NH4 | 1.0000 | 1.0000 | 1.0000 |
| NO3 | 1.0000 | 1.0000 | 1.0000 |
| Org | 1.0004 | 1.0000 | 1.0023 |
| SO4 | 1.0080 | 1.0000 | 1.0073 |

**b) ACSM #12:**



| | Power law | Quadratic | Linear |
|---|---|---|---|
| Chl | 1.0000 | 1.0000 | 1.0000 |
| NH4 | 1.0000 | 1.0000 | 1.0000 |
| NO3 | 1.0000 | 1.0000 | 1.0000 |
| Org | 0.9987 | 0.9997 | 0.9825 |
| SO4 | 0.9995 | 0.9973 | 0.9562 |

**Figure 1.** Diagrams of the RIT corrections obtained with the different RIT fitting curves and correlations with zero intercept fits between Power law, Linear and Quadratic $T_{m/z}$ vs. exponential $T_{m/z}$ for the major NR-$PM_1$ chemical components measured by ACSM a) #8 and b) #12.

**Fig. 1.**