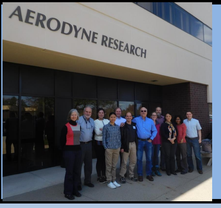

Evaluation of Six Years of Aerosol Chemical Speciation Monitor Data from the ARM Southern Great Plains Site

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Introduction

The first DOE ARM Aerosol Chemical Speciation Monitor (ACSM) users meeting was held on April 11-13, 2017 at Aerodyne Research, Inc., to discuss the Southern Great Plains (SGP) ACSM data quality and establish best practices for data collection and processing. The participants examined six years of calibration and processed data. Specific issues raised by data users were addressed and case studies from two field experiments and the most recent data from the ACSM installed in the newly commissioned SGP Aerosol Mobile Facility 7 (AMF7) were examined. The participants recommended that the SGP ACSM data be reprocessed using calibration values averaged over the history of SGP ACSM calibrations. They also recommended that the data quality be evaluated by comparing (1) observed versus predicted particulate ammonium (NH_4^+) mass loadings, and (2) ACSM mass loadings versus mass loadings calculated from particle size and light scattering data. The contents of the data streams from the ACSM were defined based on ARM requirements and the necessary tasks to implement these recommendations were assigned to the mentor and the instrument manufacturer.

ACSM Concentration Calculation

$$C_s = \left[\left(\frac{1}{CE * T_{m/z} * RIEs * RF_{NO_3}}\right)\sum_{all\ i} IC_{s,i}\right] * \left(\frac{AB_{ref}}{AB_{meas}}\right)$$

Where

C_s ≡ The mass concentration of species s (μg m^{-3})
CE ≡ The ACSM collection efficiency of particulate mass
RIE_s ≡ The relative ionization efficiency of species s $\left(\frac{RF_s}{RF_{NO3}}\right)$
RF_{NO_3} ≡ The response factor to particulate nitrate (amps /$\mu g\ m^{-3}$)
$IC_{s,i}$ ≡ The sum of the ion currents (amps) for each of the molecular fragments formed by species s
$T_{m/z}$ ≡ Mass–dependent transmission efficiency of mass spectrometer
AB_{meas} ≡ Measured air beam (m/z 28) for a given sample flowrate (amps)
AB_{ref} ≡ Reference air beam (m/z 28) for a given sample flowrate (amps)

Table 1: Calibration history of SGP ACSM collected over six years of operation. The missing values on 7/3/2013 and 11/15/2016 are because of documented problems with the calibrations. "Stdev" is standard deviation. "rel stdev" is relative standard deviation

date	RF NO_3	RIE NH_4	RIE SO_4	Ref N_2	Ref NO_3/Ref N_2
4/14/2010	4.40E-11	5.60		9.90E-08	4.44E-04
7/3/2013					
8/1/2014	2.97E-11	6.19	0.82	5.95E-08	4.99E-04
9/3/2014	4.08E-11	7.09	1.07	8.11E-08	5.03E-04
7/7/2015	2.75E-11	7.33	0.70	6.66E-08	4.13E-04
10/6/2015	4.57E-11	5.77	1.03	9.94E-08	4.60E-04
1/14/2016	4.49E-11	6.39	0.91	9.65E-08	4.65E-04
3/22/2016	4.42E-11	7.76	1.05	9.97E-08	4.43E-04
10/25/2016	2.49E-11	4.28	0.65	6.80E-08	3.66E-04
11/15/2016					
8/24/2017	2.81E-11	5.13	0.60	8.86E-08	3.17E-04
2/5/2018	2.27E-11	5.40	0.52	5.74E-08	3.95E-04
average	3.53E-11	6.09	0.82	8.16E-08	4.29E-04
stdev	9.41E-12	1.08	0.21	1.73E-08	5.86E-05
rel stdev	0.27	0.18	0.26	0.21	0.14

The SGP ACSM has been calibrated quarterly starting in July 2015. The stability of the instrument of the instrument over the over a year and half and six calibrations (Table 1).

The data should be reprocessed using the average calibration values measured over the six year history of the ACSM operation at SGP; including the average RF_{NO3}, RIE_{NH4} and RIE_{SO4} and a Ref N_2 calculated from the Ref NO_3/Ref N_2 average.

There are a number of parameters that need to be evaluated to perform a thorough evaluation of the data. Some of these can be implemented by the DMF and DQO.

- Selected m/z should be plotted for evaluation of the air beam, m/z 28; naphthalene, m/z 128; and baseline noise at m/z 140. Generated for each time period that is post-processed by the MENTOR at the time the MENTOR post-processes the data.
- Predicted ammonium vs observed ammonium should be calculated and plotted on a monthly basis.
- SMPS, UHSAS, or TDMA data, when available, should be used to calculate mass loadings. The calculated mass loadings should be plotted versus total ACSM mass.
- Nephelometer scattering coefficient should be used to calculate mass loading and plotted versus ACSM Total Mass.

The data from 2011 through 2017 from the SGP ACSM was reprocessed using these values. This analysis resulted in conflicting results. Figures 1 through 6 present time series of SGP ACSM for the winter of 2016-2017, the year 2017 through September, and April through September.

The data from the winter of 2016-2017 show high levels of NO_3. This pattern is present in every year of data from SGP. All winter periods are dominated by nitrate. The correlation between total mass loading measured by the ACSM and calculated using the default values of collection efficiency of 0.5 are not in agreement with the total mass calculated from size distribution data and compositionally dependent density collected by either the SMPS or the UHSAS (Figure 3 , SMPS data not shown). UHSAS and SMPS data are in agreement with each other within 1%.

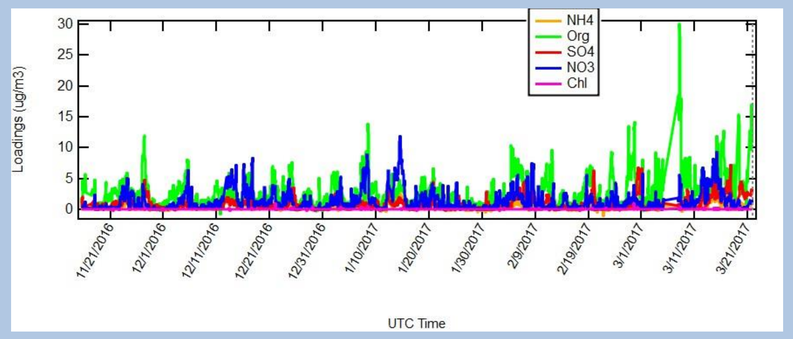

Figure 1: Time series of data from November 15, 2016 through May 31 2017

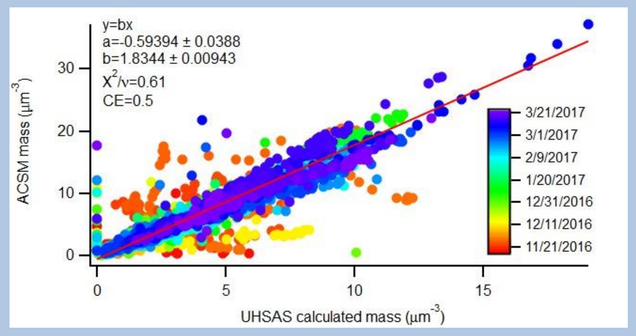

Figure 2: Correlation plot of ACSM measured total mass determined with the collection efficiency at the default value of 0.5 with mass calculated from UHSAS size distribution. The fit is an orthogonal distance regression.

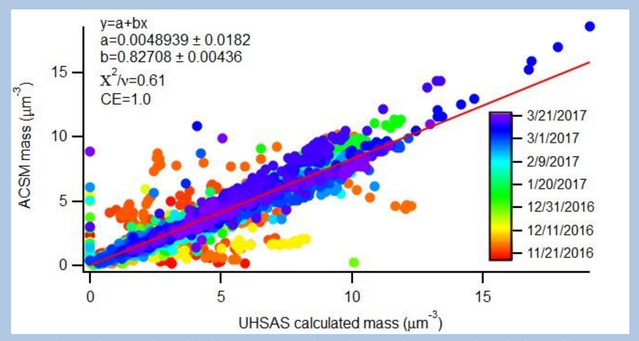

Figure 3: Correlation plot of ACSM measured total mass determined with the collection efficiency (CE) equal to 1.0 with mass calculated from UHSAS size distribution. The fit is an orthogonal distance regression.

Figure 2 is a correlation plot of the ACSM mass determined using a CE of 0.5 versus the mass calculated from the UHSAS size distribution. A linear fit to this data using an orthogonal distance regression has a slope of 1.8. This suggests that the default collection efficiency does not represent the behavior of the nitrate dominated aerosol. The CE can be thought of as a factor used to compensate for the particles which bounce off the vaporizer and therefore are not measured by the mass spectrometer. Ammonium nitrate is hydrated at any RH. Internally mixed particles dominated by ammonium nitrate will have significant water content and as a result will not bounce as much as dry particles.

Figure 3 shows the same correlation plot with the ACSM data processed using a CE of 1.0. The agreement is much better. The slope of the orthogonal distance regression is 0.83. This analysis suggests that a compositionally dependent collection efficiency should be used to calculate ACSM mass loadings when the aerosol is composed of high levels of nitrate. The actual CE is probably closer to 7.5.

This effect has been observed by other investigators (Middlebrook et al. 2012). They used a compositionally dependent CE calculated from by parameterizing the CE ACSM mass to the mass calculated from UHSAS using:

$CE_{dry} = 0.083 + 0.92(ANMF)$.

Where:

ANMF is the ammonium nitrate mass fraction.

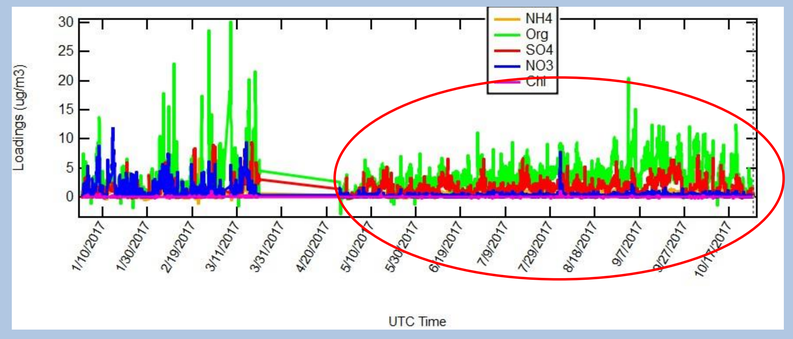

Figure 4: Time series SGP ACSM 2017-01-01 to 2017-09-31. Data gap from 3/21 to 4/26 is because of turbo pump failure.

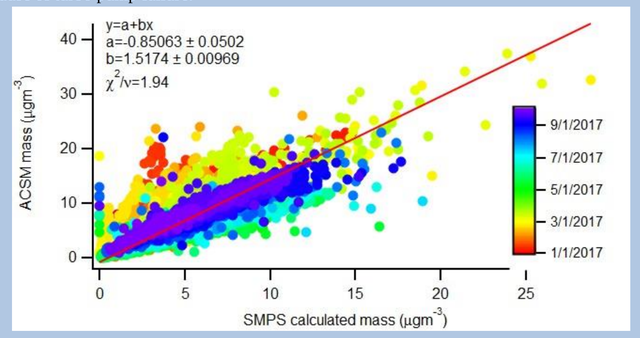

Figure 5: Correlation plot of ACSM measured total mass determined with a collection efficiency (CE) of 0.5 with mass calculated from SMPS data. Data are from 2017-01-01 through 2017-10-31. The fit is an orthogonal distance regression.

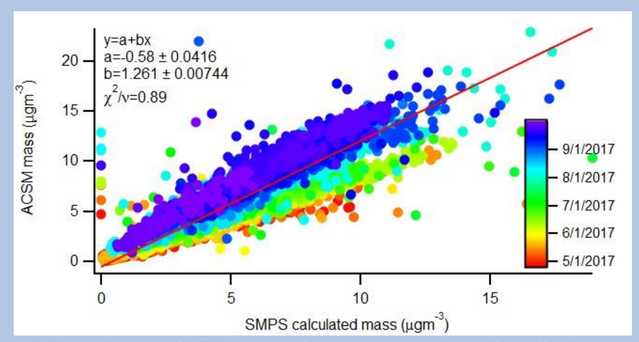

Figure 6: Correlation plot of ACSM measured total mass determined with a collection efficiency (CE) of 0.5 with mass calculated from SMPS data. Data are from 2017-04-24 through 2017-10-31 (Figure 4 red oval). The fit is an orthogonal distance regression.

Figure 4 is a time series of ACSM data from 2017-01-01 through 2017-10-31. The gap in the data is a result of a turbo pump failure. Figure 5 is a correlation plot of the ACSM mass determined using a CE of 0.5 versus the mass calculated from the SMPS size distribution. A linear fit to this data using an orthogonal distance regression has a slope of 1.52. The same correlation plot for the ACSM data collected from 2017-04-24 through 2017-10-31 has a slope of 1.3 showing much better agreement between the mass loading calculated using a CE of 0.5 for the time periods when the aerosol is not dominated by nitrate.

Conclusions:

- The average NO_3 RF, RIE NH_4, and RIE SO_4 are relatively constant over time. Use of the values in Table 1 should be applied across all data collected with this instrument. The average reference air beam was determined using the average ratio of average RF NO_3 divided by the average Ref N_2 or 8.2e-8.
- The default collection efficiency gives good results when compared with mass loadings calculated using UHSAS or SMPS data when the aerosol is neutralized or contains only a small fraction of ammonium nitrate.
- The use of a composition dependent collection efficiency (CDCE) requires more study.

Action Items:

The second DOE ARM Aerosol Chemical Speciation Monitor (ACSM) Users meeting will be held in the spring 2018 to address these and other issues.