

Aerosol Chemical Speciation Monitor (ACSM) Composition-Dependent Collection Efficiency (CDCE) Value-Added Product Report

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(ACSM) Composition-Dependent Collection
Efficiency (CDCE) Value-Added Product
Report**

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Acronyms and Abbreviations

ACSM	aerosol chemical speciation monitor
ANMF	ammonium nitrate mass fraction
AOS	Aerosol Observing System
ARM	Atmospheric Radiation Measurement
CDCE	composition-dependent collection efficiency
CE	collection efficiency
DAQ	data acquisition
netCDF	Network Common Data Form
SGP	Southern Great Plains
QA	quality assurance
QC	quality control
VAP	value-added product

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1.0 Introduction

Aerosol particles influence the Earth's radiation balance directly by absorbing and scattering light and indirectly by influencing cloud formation, properties, and lifetimes. Measurements of aerosol particle optical properties, mass loading, size distributions, microphysical properties, cloud formation properties, and chemical composition are important for understanding the aerosol life cycle and for validating earth system models that predict these quantities. The U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's Aerosol Observing System (AOS) is a highly instrumented platform that measures many of these aerosol properties in situ. The Aerodyne aerosol chemical speciation monitor (ACSM) is a baseline instrument deployed in the AOS.

The ACSM provides a quantitative measurement of aerosol particle chemical composition for non-refractory (operationally defined as components that evaporate on the 600°C vaporizer) aerosol components in real time. Standard output is the mass concentration of particulate organics, nitrate, sulfate, chloride, and ammonium. One well-known limitation to the accuracy of the ACSM data is in evaluating the fraction of the ambient aerosol particles that are detected by the instrument. This quantity is referred to as the collection efficiency (CE) and is often less than unity. This is attributed to particles rebounding after impaction onto the heated vaporizer rather than being trapped, volatilized rapidly, and detected (Alfarra et al. 2004). Other factors, such as divergence of the aerosol particle beam, may also impact CE, but the particle rebound effect is the dominant factor (Huffman et al. 2005, Alfarra et al. 2004). Scientists will sometimes assume $CE = 0.5$ (i.e., one half of sampled particles are detected) for ambient particles collected during field missions (Allan et al. 2004, Drewnick et al. 2003, Hogrefe et al. 2004). However, parameterizations have been developed that express CE as a function of the measured chemical composition, referred to as the composition-dependent collection efficiency (CDCE) (Middlebrook et al. 2012). The physical explanation for a CDCE, supported by laboratory studies, is that rebound from the vaporizer is a function of the particle phase, with liquid-like particles "sticking" to the vaporizer and solid-like or crystalline particles "bouncing" from the vaporizer (Middlebrook et al. 2012). Thus, particles with compositions are liquids-like under the measurement conditions (e.g., certain organics, acidic particles, particles enriched in nitrate) have CE close to unity while crystalline or solid particles (e.g., deliquesced ammonium sulfate) have lower CE.

This value-added product (VAP) implements the procedure described by Middlebrook et al. (2012) to correct the ACSM data for the composition-dependent collection efficiency. Applying this parameterization improves the accuracy of the ACSM data and brings them into better agreement with other co-located aerosol measurements.

2.0 Algorithm and Methodology

The algorithm reproduces the processing described in Middlebrook et al. (2012), with some modifications to account for the fact that the Middlebrook algorithm was written in Igor while this VAP was written in Python. All input data come from the ACSM b-1 files.

The algorithm steps are:

1. Load the b-level data files.

2. Remove bad data. Several of the ACSM species concentrations display anomalous, 1-point “spikes” in both the positive and negative that are not real. The ammonium and organic concentration data are the most affected by these spikes. We remove these spikes by applying a simple filter that identifies spikes as datapoints that are more than 5x different than both the previous and next datapoint. When spikes are found, the data are replaced by simple linear interpolation for the CDCE calculation only.
3. Smooth the organic, ammonium, nitrate, sulfate, and chloride species concentrations. In this VAP we use a five-point, first-order Savitsky-Golay filter from the SciPy package. Middlebrook et al. (2012) implemented a binomial filter in the Igor analysis package.
4. Calculate the mass fraction of ammonium nitrate (ANMF).
5. Calculate the ammonium mass needed to fully neutralize the measured nitrate, sulfate, and chloride (hereafter referred to as NH4_{pred}).
6. Calculate the ratio of the measured ammonium mass to the ammonium mass needed for full neutralization. ($\text{NH4}_{\text{meas}}/\text{NH4}_{\text{pred}}$)
7. The algorithm then enters a decision tree to calculate the CDCE based on the chemical composition according to the following conditions:
 - a. If NH4_{pred} is below the instrument detection limit of 0.2 ug/m^3 :
 - i. CDCE defaults to 0.5
 - b. Elseif the aerosol is largely neutralized (defined as $(\text{NH4}_{\text{meas}}/\text{NH4}_{\text{pred}}) > 0.75$), calculate the CDCE according to equation 4 in Middlebrook et al. (2012).
 - i. $\text{CDCE} = (0.0833 + 0.9167 * \text{ANMF})$
 - c. Else the aerosol is acidic, calculate the CDCE according to equation 6 in Middlebrook et al. (2012).
 - i. $\text{CDCE} = (1 - 0.73 * (\text{NH4}_{\text{meas}}/\text{NH4}_{\text{pred}}))$
8. Record which of the three equations above was used to calculate the CDCE.
9. Clip the CDCE to values of 0.5–1.0 using the NumPy clip function. In other words, values smaller than 0.5 are set to 0.5 and values larger than 1.0 are set to 1.0. Values between 0.5 and 1.0 are left unchanged.
10. Calculate the CDCE-corrected values of each species.
 - a. e.g., $\text{Org_CDCE} = \text{org} * (1/\text{CDCE})$
11. Perform QA/CQ checks. Most of these tests are based on recommendations in Middlebrook et al. (2012). The tests that are used to trigger QC bits are:
 - a. Test for a negative value of $(\text{NH4}_{\text{meas}}/\text{NH4}_{\text{pred}})$. This represents a non-physical value. If true, set QC bit 1.
 - b. Test for a negative value of the ammonium nitrate mass fraction. This represents a non-physical value. If true, set QC bit 2.

- c. Test for a value of the ammonium nitrate mass fraction greater than 1. This represents a non-physical value. If true, set QC bit 3.
- d. Test for values of $\text{NH}_4_{\text{pred}}$ below instrument LOD of 0.2 ug/M^3 . If true, set QC bit 4.

12. Bitpack the QC bits.

3.0 Input Data

The input data for this VAP come entirely from the ARM b-1-level ACSM netCDF files. These b-1-level files apply standard ACSM calibrations described in the literature to the raw data files output natively by the instrument and generate QA/QC fields. The mass loading of the species measured by the ACSM (organics, sulfate, nitrate, ammonium, and chloride) are used in the VAP calculation. All of the b-level data, including the QC variables, are reported in the VAP output unchanged; species concentrations that have been adjusted for the CDCE are renamed by appending “_cdce” to the end of the variable name.

The input file names are named as follows:

XXXaosacsmYY.b1, where XXX is the site code and YY is the facility code. For example, sgpaosacsmE13.b1 represents data from the SGP site and the E13 facility.

Input variables retrieved from the ACSM input datastream and passed through to the output datastream are shown below in Table 1.

Table 1. Variables retrieved from ACSM b-level input files.

Variable Name	Description and Notes
instrument_serial_number	ACSM serial number
new_start	New start acquisition indicator [units: amu]
mz_start	Starting m/z for scan range [units: amu]
mz_delta	Delta m/z for scan mode [units: amu]
mz_scan_width	Scan width for first scan range [units: amu]
mz_resolution	Channel m/z resolution [units: amu]
DAQ_version	Program version number
number_scans_open	Number of open scans
number_scans_closed	Number of closed scans
number_of_sets	Number of sets
saves_per_sample	Number of saves per sample
saves_per_filter	Number of saves per filter
RIE_ORG	Relative ionization efficiency organic
RIE_SO4	Relative ionization efficiency sulfate
RIE_NH4	Relative ionization efficiency ammonium

Variable Name	Description and Notes
RIE_NO3	Relative ionization efficiency nitrate
RIE_CL	Relative ionization efficiency chloride
CE	Effective fraction of particles entering the instrument that are detected. The value here was entered in the ACSM DAQ and is used for the b-level file calculations.
airbeam_normalization_factor	Accounts for changes in system sensitivity by normalizing by the N2 signal in filtered air. Calculated as Ref_N2_signal/N2 signal in filtered air
total_organics	Mass concentration of total organics, ambient aerosol in air [units: ug/m ³]
qc_total_organics	Quality check results on variable: Mass concentration of total organics, ambient aerosol in air
ammonium	Mass concentration of ammonium, ambient aerosol in air [units: ug/m ³]
qc_ammonium	Quality check results on variable: Mass concentration of ammonium, ambient aerosol in air
ammonium_predicted	Mass concentration of ammonium predicted for neutralization. [units: ug/m ³]
sulfate	Mass concentration of sulfate, ambient aerosol in air [units: ug/m ³]
qc_sulfate	Quality check results on variable: Mass concentration of sulfate, ambient aerosol in air
nitrate	Mass concentration of nitrate, ambient aerosol in air [units: ug/m ³]
qc_nitrate	Quality check results on variable: Mass concentration of nitrate, ambient aerosol in air
chloride	Mass concentration of chloride, ambient aerosol in air [units: ug/m ³]
qc_chloride	Quality check results on variable: Mass concentration of chloride, ambient aerosol in air
acsm_vol_conc	ACSM volume concentration. The calculation assumes the following densities (units of g/cm ³); org = 1.2; SO4 = 1.77; NO3 = 1.72; NH4 = 1.77; Chl = 1.53. [units: cm ³ /m ³]
qc_acsm_vol_conc	Quality check results on variable: ACSM volume concentration
lat	North latitude [units: degree_N]
lon	East longitude [units: degree_E]
alt	Altitude above mean sea level [units: m]

4.0 Output Data

The ACSMCDCE VAP produces a single daily file named XXXacsmcdce.YY.c1.YYYYMMDD.HHMMSS.nc where XXX is the site code, YY is the facility code, YYYYMMDD.HHMMSS is the date and time.

Output variables unique to the ACSMCDCE VAP are shown below in Table 2. The rest of the variables are passed through from the b-1 level files.

Table 2. Variables output by the ACSMCDCE VAP.

Variable Name	Description and Notes
acsm_vol_conc_cdce	Total particle volume concentration corrected for the CDCE, measured by the ACSM in units of cm^3/M^3 . The calculation assumes the following densities (units of g/cm^3); org = 1.2; SO_4 = 1.77; NO_3 = 1.72; NH_4 = 1.77; chl = 1.53.
ammonium_cdce	Mass concentration of ammonium, corrected for the CDCE, measured by the ACSM in units of ug/M^3 .
CDCE	the value of the composition-dependent collection efficiency calculated by the VAP and used to correct the data.
CDCE_equation	The equation used to calculate the value of the CDCE following Middlebrook et al. 2012. 1 = predicted NH_4 below instrument LOD. Assume CE = 0.5; 2 = Middlebrook Equation 4; 3 = Middlebrook equation 6.
chloride_CDCE	Mass concentration of chloride, corrected for the CDCE, measured by the ACSM in units of ug/M^3 .
nitrate_CDCE	Mass concentration of ammonium, corrected for the CDCE, measured by the ACSM in units of ug/M^3 .
qc_acsm_vol_conc_cdce	Quality check on ACSM volume concentration corrected for CDCE. Bit 1 - qc_CDCE has indeterminate assessment, bit 2 - qc_acsm_vol_conc has bad assessment, bit 3 - qc_acsm_vol_conc has indeterminate assessment.
qc_ammonium_cdce	Quality check on mass concentration of ammonium corrected for CDCE. Bit 1 - qc_CDCE has indeterminate assessment, bit 2 - qc_ammonium has bad assessment, bit 3 - qc_ammonium has indeterminate assessment.
qc_CDCE	Quality checks on the calculation of CDCE. Bit 1 - measured NH_4 to NH_4 needed for full neutralization < 0, bit 2 - ammonium nitrate mass fraction < 0, bit 3 - ammonium nitrate mass fraction > 1, bit 4 - predicted ammonium below instrument limit of detection. QC bits do not necessarily indicate the CDCE calculation is wrong and instead indicate caution should be used.

Variable Name	Description and Notes
qc_chloride_cdce	Quality check on mass concentration of chloride corrected for CDCE. Bit 1 - qc_CDCE has indeterminate assessment, bit 2 - qc_chloride has bad assessment, bit 3 - qc_chloride has indeterminate assessment.
qc_nitrate_cdce	Quality check on mass concentration of nitrate corrected for CDCE. Bit 1 - qc_CDCE has indeterminate assessment, bit 2 - qc_nitrate has bad assessment, bit 3 - qc_nitrate has indeterminate assessment.
qc_sulfate_cdce	Quality check on mass concentration of sulfate corrected for CDCE. Bit 1 - qc_CDCE has indeterminate assessment, bit 2 - qc_sulfate has bad assessment, bit 3 - qc_sulfate has indeterminate assessment.
qc_total_organics_cdce	Quality check on mass concentration of organics corrected for CDCE. Bit 1 - qc_CDCE has indeterminate assessment, bit 2 - qc_total_organics has bad assessment, bit 3 - qc_total_organics has indeterminate assessment.
sulfate_CDCE	Mass concentration of sulfate, corrected for the CDCE, measured by the ACSM in units of ug/M ³ .
total_organics_CDCE	Mass concentration of organics, corrected for the CDCE, measured by the ACSM in units of ug/M ³ .

4.1 Plots

In addition to producing daily netCDF files, the ACSMCDCE VAP also produces two daily plots that show the data and a selection of diagnostic information related to help characterize the data produced. Sample plots from June 26, 2020 are shown below.

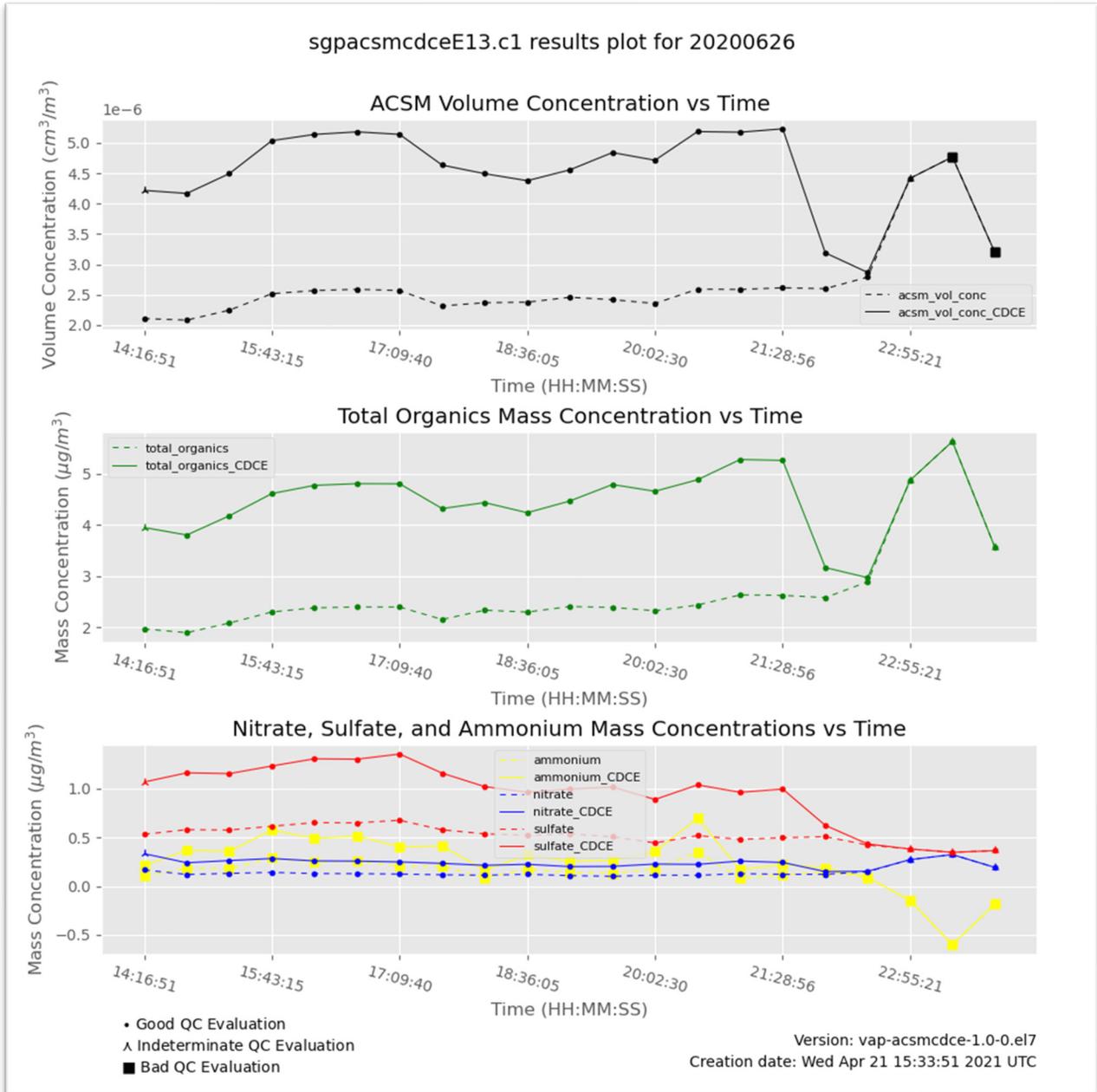


Figure 1. Results quicklook for 2020-06-26.

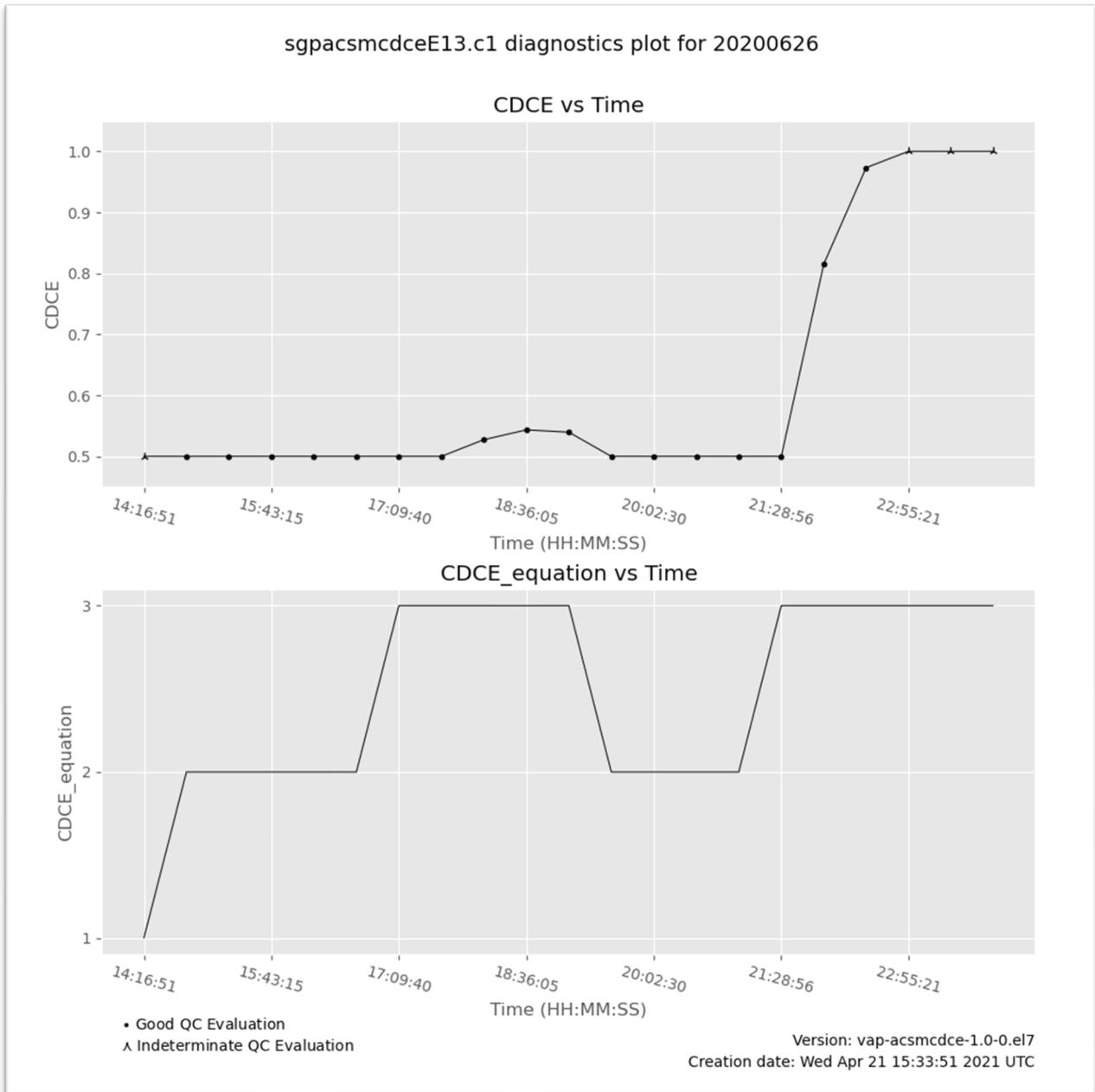


Figure 2. Diagnostics quicklook for 2020-06-26.

5.0 Summary

The ACSM composition-dependent collection efficiency (CDCE) VAP adjusts the ACSM b-1-level files for non-unity detection of particle mass by the instrument. This VAP calculated the necessary correction based on the ACSM-measured chemical composition using the procedure described by Middlebrook et al. (2012), with minor modifications to convert the algorithm from Igor- to Python-based programming. Application of this CDCE improves the mass closure between the ACSM and co-located particle-sizing instruments, such as the scanning mobility particle sizer or the ultra-high-sensitivity aerosol spectrometer.

Because of the improved accuracy, these VAP files should be preferentially used over the b-1-level ARM files whenever available. The VAP is expected to run daily and generate one file each day. Production of the VAP files require data from the preceding and following day to perform the smoothing properly; therefore, production of the VAP files will lag the availability of the b-1 files by at least one day.

6.0 References

- Alfarra, MR, H Coe, JD Allan, KN Bower, H Boudries, MR Canagaratna, JL Jimenez, JT Jayne, AA Garforth, S-M Li, and DR Worsnop. 2004. “Characterization of urban and rural organic particulate in the Lower Fraser Valley using two Aerodyne aerosol mass spectrometers.” *Atmospheric Environment* 38(34): 5745–5758, <https://doi.org/10.1016/j.atmosenv.2004.01.054>
- Allan, JD, KN Bower, H Coe, H Boudries, JT Jayne, MR Canagaratna, DB Millet, AH Goldstein, PK Quinn, RJ Weber, and DR Worsnop. 2004. “Submicron aerosol composition at Trinidad Head, California, during ITCT 2K2: Its relationship with gas phase volatile organic carbon and assessment of instrument performance.” *Journal of Geophysical Research – Atmospheres* 109(D23): D23S24, <https://doi.org/10.1029/2003JD0042808>
- Drewnick, F, JJ Schwab, O Hogrefe, S Peters, L Husain, D Diamond, R Weber, and KL Demerjian. 2003. “Intercomparison and evaluation of four semi-continuous PM_{2.5} sulfate instruments.” *Atmospheric Environment* 37(24): 3335–3350, [https://doi.org/10.1016/S1352-2310\(03\)00351-0](https://doi.org/10.1016/S1352-2310(03)00351-0)
- Hogrefe, O, JJ Schwab, F Drewnick, GG Lala, SB Peters, KL Demerjian, K Rhoads, HD Felton, OV Rattigan, L Husain, and VA Dutkiewicz. 2004. “Semicontinuous PM_{2.5} Sulfate and Nitrate Measurements at an Urban and a Rural Location in New York: PMTACS-NY Summer 2001 and 2002 Campaigns.” *Journal of the Air & Waste Management Association* 54(9): 1040–1060, <https://doi.org/10.1080/10473289.2004.10470972>
- Huffman, JA, JT Jayne, F Drewnick, AC Aiken, TB Onasch, DR Worsnop, and JL Jimenez. 2005. “Design, Modeling, Optimization and Experimental Tests of a Particle Beam Width Probe for the Aerodyne Aerosol Mass Spectrometer.” *Aerosol Science and Technology* 39(12): 1143–1163, <https://doi.org/10.1080/02786826.2011.620041>
- Middlebrook, AM, R Bahreini, JL Jimenez, and MR Canagaratna. 2012. “Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data.” *Aerosol Science and Technology* 46(3): 258–271, <https://doi.org/10.1080/02786826.2011.620041>



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