QUALITY ASSURANCE PROJECT PLAN (QAPjP) and QA Report for Pacific 2001

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3. Measurement Program

a) Measurement of atmospheric aerosol size distribution
b) And measurement of total particle number concentration

4. Measurement Species and Units

<u>York U Group Instruments</u>

DMA (Differential Mobility Analyzer)	
Particle size distribution (dN/dln(Dp))	particle/cm^3
as a function of diameter	nm
CNC (TSI 3010 Condensation Nucleus Counter)	
Number concentration	particle/cm^3 at ambient temperature and pressure
Temperature and relative humidity sensor inside the DMA	
Temperature	^oC
Relative humidity	%

<u>Richard Leaitch's Group Instrument</u>

CNC (TSI 3022 CNC)	
Particle number concentration	particle/cm^3 at ambient temperature and pressure

5. Representative Size Range (if PM)

3010 CNC: > 9 nm
3022 CNC: > 5 nm

6. Measurement Platform (surface, airborne)

Surface

7. Measurement Sites (surface only)

DMA: Sumas Mountain
CNC: Sumas Mountain

8. Measurement Objective(s)

DMA and 3010 CNC: to measure atmospheric aerosol size distribution from 9.3 nm to 604 nm.
3022 CNC: to measure the total number concentration for atmospheric aerosol bigger than 5 nm.
Temperature and RH sensor: to measure the temperature and relative humidity for the aerosol flows sampled from the inlet line.

9. Measurement Details

9.1. Field Measurements

9.1.1. Measurement Principle

Total atmospheric aerosol number concentration: The condensation of butanol was used to grow particles to a size detectable by light scattering. The 3022 CNC operating in the photometric mode for total concentration excess of 7,000 particle/cm^3 and single particle mode for concentration mode when concentration below 7,000 particle/cm^3.

Atmospheric aerosol size distribution: Particles are charged, size selected by electrical mobility using a differential mobility analyzer (DMA) and counted with a 3010 condensation nucleus counter (CNC). The aerosol flow was not dried.During the period between August 13 to August 15, the 3022 CNC data were recorded using pulse counting mode, which appeared to significantly undercount the particle number concentration when the total concentration exceed 10,000 particle/cm^3. The 3022 analog output was used from August 15 noon till all the way to the end of the study.

The 3022 CNC begin to give disagreement with the 3010 CNC from August 24 afternoon. 3022 CNC was disconnected for repairing on August 26 on noon.

9.1.2. Instrumentation (Manufacturer/Model)

DMA: TSI Incorporated, model 3071
CNC: TSI Incorporated, model 3010, model 3022
Temperature and RH senser inside DMA: Vaisala, model 50Y

9.1.3. Flow System

DMA and CNC: The flow inlet is a 3/8-inch stainless steel tube with an inverted “U” shape at the inlet. The inlet line is located 2 meters above the trailer. Inside the trailer, the inlet line is split among three different systems: 3022 CNC, DMA and the PCASP with 3 independent valves to the upstream of all three systems.

The flow for the 3010 CNC connected to the DMA is maintained by an external pump, which was located outside and under the trailer. The flow system in the 3022 CNC is maintained by its internal pump. All the exhausts are bought outisde by 3/8-inch ID Tygon tubing. The Tygon tubings are then connected to a big common exhaust line with an outlet over 10 meters away from the trailer.

9.1.4. Inlet Height Above Ground (if surface)

DMA and CNC: 2 meters above ground level on top of the trailer.

9.1.5. Nominal Flow Rate

DMA sheath air and excess air: 4.97 alpm (actual liters per minute)
Aerosol sample flow for 3010 CNC: 0.99 alpm
Aerosol sample flow for 3022 CNC: Not recorded, nominally 0.3 alpm

9.1.6. Flow Measurement/Control

3010 CNC flow rate was controlled by critical orifice and measured by means of the pressure drop across a laminar flow element, which was checked at least once daily.

DMA sheath flow was measured with a mass flow meter and recorded continuosly. The DMA aerosol flows were measured by means of the pressure drop across laminar flow elements, which were checked at least once daily.

For 3022 CNC, internal flow control was relied on.

9.1.7. Flow Temperature and Pressure

Temperature: indoor ambient.
Pressure: slightly below ambient (“under pressure” mode).

9.1.8. Sampling Times/Period/Frequency

DMA and 3010 CNC, 3022 CNC: Both systems collect data continuously for 24 hours a day and 7 days a week. Each size distribution is 5 minutes long, and starts on every 5 minutes of an hour, e.g. 1100, 1105, 1110. 288 scans are collected everyday except during the period for instrument checkup. Hourly average data on every hour of each day is provided by averaging all the 5-minute-data within that hour.

9.1.9. Sampling Methods

N/A

9.1.10. Filter Type/Coating Type/Reagent Type

N/A

9.1.11. Planned Changes to Instruments or Methods During Study

Not planned

9.2. Laboratory Measurements (If Applicable)

9.2.1. Laboratory Name and Address

N/A

9.2.2. Analytical Method(s)

N/A

9.2.3. Sample Extraction or Work-up

N/A

9.2.4. Analytical Detection Limits

N/A

10. Quality Assurance/Quality Control

10.1. Field Quality Assurance/Quality Control

10.1.1. Traceability

N/A

10.1.2. Calibration

All flow meters were calibrated before going to the field.
The DMA, 3010 CNC and 3022 CNC were all inter-compared with the DMA and other CNCs from Richard Leaitch's group in MSC before going to the field.

10.1.3. Zeros and spans

N/A

10.1.4. Blanks

N/A

10.1.5. Field Quality Control procedures

N/A

10.1.6. Precision determination

N/A

10.1.7. Comparison with other measurements

The York U size distribution data was compared with the nano DMA size distribution data from Richard Leaitch's group for the period between August 19 to 31 for consistency.

We arrived with a final conclusion that there is no significant difference in size measurement between the two methods. But there is a concentration multiplier fractor between the two sets of measurements. It is found that the concentration measurement from Leaitch's group is higher than the YorkU DMA data by a factor of 1.71. The value of the factor varies from 1.2 to 2.4.The cause of this is not yet identified.

10.1.8. Inspections and Audits

N/A

10.2. Laboratory Quality Assurance/Quality Control

10.2.1. Traceability

N/A

10.2.2. Calibration procedures

All instruments and flow meters were calibrated before going to the field

10.2.3. Blanks

N/A

10.2.4. Other lab QC

N/A

10.2.5. Precision determination

N/A

10.2.6. Comparison with other methods

N/A

10.2.7. Audits

N/A

11. Data Management and Quality Control

11.1. Raw Data Recording

All the size distributions were taken by the computer using Igor Pro with our own custom program. Results were copied and the data were vetted for any obvious problem on the next day.

11.2. Final Data Reporting

5 minutes number distribution data will be recorded and reported. Hourly average will also be provided by averaging the 5 minutes data.

11.3. Data Quality Control and Validation

All the data values will be flagged as either Valid (V) or Missing (M). For the missing data, the values will be reported as “-999”.

11.4. Validity Flags

Based on Narsto flags, assigned as follows:

<u>For the DMA measurements of size distribution:</u>
V0 : valid data
V4 : valid data taken during periods when the DMA voltages or flows were slightly different from the standard conditions.
V6 : as for V4 but when the variation was large enough to cast doubt upon the data.
V7 : a spike in the largest size bin was manually removed and the data were reprocessed. The value in the largest size bin may not be reliable.
M1 : missing data because instrument was not in operation.
M2 : missing data because it was invalidated (zero runs and severe errors in the DMA flows and/or DMA voltages).
Missing data are entered as "-999".

<u>For the 3022 CNC measurements of total number:</u>
V0 : valid data
V6 : the CNC data were recorde in pulse counting mode which is inaccurate at the concentrations encountered.
M1 : missing data because instrument was not in operation.
M2 : missing data because it was invalidated (zero runs and for anormal reading).
Missing data are entered as "-999".

11.5. Below Method Detection Limit Values

11.6. Derived Parameters

11.7. Explanation of Zero or Negative Data

For the data, which are not available, are reported as “-999”. All the missing data can due to either one of the following cases: zero run testing for the instrument, non-operation condition for the instrument, instrument under repairing, instrument operating under conidtion beyond the normial condition which is regarded as invalid data.

12. Data Quality Objectives (Pre-Study)

12.1. Accuracy

12.2. Precision

Base on counting statistics.

12.3. Comparability

12.4. Representativeness

12.5. Completeness

12.6. Other Quality Information

End of Pre-Study QAPjP

Start of Post-Study QA Report

13. Significant Changes to Site, Instruments or Methods During Study

14. Post-study Data Quality Indicators (DQIs)

14.1.1. Accuracy

14.1.2. Precision

Method for estimation of the uncertainty for the size distribution data is given below in 14.3. The uncertainty is calculated combining the uncertainties associate with the counting statistics, DMA sheath air and aerosol flow, maximum and minimum voltage in each scan, the bin width of each size bin, scanning time, CNC counting efficiency and the bipolar charging efficiency.

14.1.3. Comparability

<u>Combined DMA data and the 3022 comparison</u>
Combining the nano DMA data (covers from 3 – 9 nm) from Richard Leaitch with the York long DMA data (covers from 9 – 650 nm) to form a complete size distribution. The particle count from each bin is then multiplied by the counting efficiency of the TSI 3022 CNC (the counting efficiency is obtained from TSI). The sum of counts from all bins is then compared with the total counts recorded from the TSI 3022 CNC.

From the analysis, it is found that when nano particle is negligible, during the single particle mode, the DMA reading agrees with the 3022 CNC within 2 – 3%.

During the photometric mode, it is usually found that the DMA integrated total does not usually agree with the 3022 total. It is suspected that the cause could due to the photometric calibration of the 3022 CNC.

14.1.4. Representativeness

14.1.5. Completeness

<u>DMA size distribution data</u>
Total number of size distribution: 5380
M1: Missing value because no value is available: 86 (1.6%)
M2: Missing value because invalidated by data originator: 9 (0.2%)
V0: Valid value: 5012 (93.2%)
V4: Valid value despite failing to meet some QC or statistical criteria: 14 (0.3%)
V6: Valid value but qualified due to non-standard sampling conditions (e.g., instrument malfunction, sample handling): 259 (4.8%)

<u>Relative humidity and temperature data</u>
Total number of data point: 5380
M1: 277 (5.1%)
V0: 5103 (94.9%)

<u>CNC 3022 total number concentration data</u>
Total number of data point: 5380
M1: 114 (2.1%)
M2: 21 (0.4%)

V0: 4769 (88.6%)
V6: 476 (8.8%)

14.2. Blank correction (describe whether done and method used):

14.3. Other Quality Information

<u>Uncertainties for the size distribution:</u>
Random uncertainties in dN/dln(Dp)are due to counting statistics. These are not reported but may be calculated from the reported values of dN/dln(Dp). One sigma uncertaintites, s(Dp), for a given bin at a given time may be computed as:

s(Dp) = sqrt(dN/dln(Dp)*ln(Vmax/Vmin)/(ln(W)*tS*Q*fE*beta))

For each size bin, the minimum and maximum sizes are reported in the metadata file. If the reported bin size is within the measured size range of the instruments (which is included in the metadata file as ScanMin and ScanMax), ln(W) will be the ln of the ratio between the measured maximum and minimum size for each specific size bin, which will be a constant. Therefore, taking all the constants out of the above equation will lead to:

s(Dp) = 2.30e-5*sqrt(dN/dln(Dp))/fE

For the first and the last bins, which do not fall within the measured size range, data must be treated cautiously, and ln(W) should be calculated in a different way. Please refer to the notes for more detail on how to calculate the correct ln(W) for the uncertainty calculation.

At sizes for which the effects of multiple charging are significant, the above formula will slightly underestimate the uncertaintites.

All the constants or variables given in the original equation are given as below:

dN/dln(Dp) = reported concentration (particles/cc) for the size bin
ln(W) = ln((maximum size)/(minimum size)) = 0.143912
tS = 270 seconds = time to complete the DMA scan from Vmin to Vmax
ln(Vmax/Vmin) = 6.91 = ln(9999.1 volts /10 volts)
Q = sample flow rate = 16.7 cc/s
beta = 0.201 = (DMA aerosol flow) /(DMA sheath flow)
fE = size dependent detection efficiency = fq*fC
fq = charging efficiency for single charge
fC = 3020 CNC counting efficiency

For distributions that were run under the same conditions (which is the case for the Pacific 2001 field study), the uncertainty expression can be simplified as

s(Dp) = sqrt(dN/dln(Dp)*C)

dN/dln(Dp) = reported concentration (particles/cc) for the size bin
C = one count uncertainty (see metadata table: Estimated Distribution Uncertainty)

To estimate the uncertainty for each data point in the distribution, multiply the distribution for a particular size by the one count uncertainty corresponding to that given size (values are given in the metadata table: Estimated Distribution Uncertainty). After that, a square root of such product will be the estimated uncertainty for that particular size bin.

Note:
The data for the first and last bins that actually contain data must be treated cautiously especially when those bins were not fully covered by the scans. The minimum and maximum diameters of the scan are given as ScanMin and ScanMax. These can be used to assess the effect on the first and last bins containing data as follows:

First bin. The effect depends on the extent to which ScanMin is greater than BinMin where BinMin is the minimum diameter of the first bin containing data.
If BinMin < ScanMin then:
(i) The midpoint diameter should be replaced by (BinMax+ScanMin)/2 where BinMax is the maximum diameter of the bin.
(ii) In computing uncertainties, the width factor, ln(W), should be replaced by ln(BinMax/ScanMin).

Last bin. The effect depends on the extent to which ScanMax is less than BinMax where BinMax is the maximum diameter of the last bin containing data.
If BinMax > ScanMax then:
(i) The midpoint diameter should be replaced by (BinMin+ScanMax)/2 where BinMin is the minimum diameter of the bin.
(ii) In computing uncertainties, the width factor, ln(W), should be replaced by ln(ScanMax/BinMin).

Uncertainties in the particle sizes were calculated from estimated uncertainties in the sheath flow ($\pm$ 4.2 %) and the DMA voltage ($\pm$ 3 volts). The uncertainty for each bin is included in the metadata.

15. References: