

Section 0 Quality Assurance/Quality Control (QA/QC) for SPARTAN project

April 20th 2015

Outline of General Procedures for filter analysis, nephelometer light scatter, and AOD

S1: Pre and post- filter weighing QA/QC

1. Balance should already be on for ~ 24 hours.
2. Filters (both Teflon and Nuclepore) are left equilibrating for ~24 hours
3. Ensure room humidity is $30\% < RH < 40\%$ and temperature is $20^{\circ}\text{C} < T < 25^{\circ}\text{C}$ before weighing. Record actual RH and T values in log next while weighing filters
4. Run internal mass balance calibration program
5. Weigh 1 and 200 mg reference weights in triplicate (external calibration)
6. Take individual filters from labeled petri dish, pass under electrostatic blower, and weigh on balance in triplicate
7. Standard deviation (SD) of triplicate must be $< 10\ \mu\text{g}$ or else filters are re-weighed (discarded in order of weighing)
8. Filter mass (Post-weighed minus preweighed) must be > 0 else discarded
9. Total mass, SD, and associated label number are saved in collective spreadsheet

S2: Site selection

1. Ensure SPARTAN instruments are far from trees and walls
2. Obtain GPS locations accurate to 4 decimal places
3. Establish file sharing method with site operators for nephelometer data and cartridge flow data

S3: Cartridge Flow data QA/QC

1. Assemble together the internal (IN) and external (EX) recorded flows from log sheet filled in by site operators. Define mean $\overline{Flow} = (IN_i + EX_i + IN_f + EX_f)/4$.
2. If we have a record of internal continuous flow via sampler memory card, then take mean continuous flow weighted by external/internal endpoint flows

$$Flow = \overline{Flow}_{cont} \sqrt{\frac{EX_i}{IN_i} \cdot \frac{EX_f}{IN_f}}$$

3. If post-weighted nuclepore (coarse, PM_c) filter mass is $> 160\ \mu\text{g}$ OR if end flows are $< 3.5\ \text{lpn}$, disregard mass of that filter.
4. Harvard Impactor (HI) collocation is used to evaluate but not to calibrate PM_{2.5}
5. Absolute PM_{2.5} masses (μg) are converted to concentrations ($\mu\text{g}/\text{m}^3$) using mean flow rates and duty percentages (e.g. 24 hours at 4 lpm = $5.76\ \text{m}^3\ \text{air} = 100\%$ duty).

S4: Aerosol Optical Depth (AOD) QA/QC

1. Collect sun photometer data from sites within 10 km of SPARTAN location
2. Ensure data is either level 1.5 (cloud-screened) or level 2.0 (hand-inspected). Since AERONET has its own QA/QC (Smirnov et al., 2000), we implicitly trust AOD data at level 1.5 or 2.0
3. Interpolate AOD at 550 nm using AERONET angstrom exponent
4. Define satellite daily AOD₁₀₋₁₄ as mean of AOD values measured between 10:00 and 14:00.
5. Save hourly mean AOD for later use

S5: Nephelometer QA/QC

1. Obtain memory card data from site bi-weekly (shared file or email). Ensure csv files are not corrupted
2. Average 15-second values into hourly bins using program
3. Program skips hourly data whenever mean hourly RH > 80%, or if 535nm scatter exceeds 1300 Mm⁻¹
4. If mean scatter exceeds 1000 Mm⁻¹ for a full week and no known PM episode occurred, instrument is considered dirty and requires cleaning/re-calibration (e.g. contaminated with dirt deposits and/or insects).
5. Instrument is first mailed to Halifax for a general cleaning. If unsuccessful (e.g. possible electronics malfunction), instrument is mailed to AirPhoton
6. Record the sampled date ranges in a spreadsheet
7. Calculate angstrom exponent, backscatter ratio, and scatter at 550 nm
8. Save hourly-mean data for later use

S6: Equivalent Black Carbon (E-BC) QA/QC

1. Switch on Smoke Stain Reflectometer (SSR). Device is ready when reads 100.0 (with single decimal place).
2. Allow 15 minutes to warm up
3. Place reflectometer sensor onto white and grey circular panel to calibrate
4. Measure reflectivity R of filters in triplicate.
5. Reject values such that $R > 90$ or $R < 20$ (below linear sensitivity range or indistinguishable from blanks)
6. Convert R to BC concentration using a mass absorbance cross section representative of polluted urban areas: $\sigma = 10 \text{ m}^2/\text{g}$ (Bond and Bergstrom, 2006)

S7: Ion Chromatography (IC) QA/QC

1. Label extraction containers (pink vials) and storage containers (amber vials)
2. Cut filter in half, and place one half in the triple-washed vials
3. Add isopropyl alcohol (0.12 mL) and water (2.9 mL) sequentially (4% solution) (Gibson et al., 2013)
4. Sonicate filters in water bath for 25 minutes

5. Write extraction data and volume in **IC/ICP log book**
6. Program sampling tray and space with water every 4th sample (anions) or every sample (cations)
7. Prepare fresh IC eluent, check for smooth baseline and air-free lines are, then load all the 0.5 mL samples into the autosampling tray
8. Start autosampler. Run will complete in 20 hours.
9. Check IC next day, and note date of completion in **IC/ICP logbook**
10. Visually adjust peak areas via Chromeleon software tools
11. Check linearity of IC calibration standards; convert concentration ($\mu\text{g/l}$) to mass on filter (μg) via extraction volume
12. Download data to USB stick and save in shared file. Note date in **IC/ICP logbook**
13. Merge raw file data into "IC summary" Excel file (two files, anion/cation, per site)
14. Do not officially report values 2x larger than highest standard (NB: only sulfate is considered an issue here)

S8: Inductively coupled mass spectrometry (ICP-MS) QA/QC

1. Triple wash acid tubes and pre-soak overnight in 10% HNO_3
2. Discard soaking acid water and label tubes
3. Add other half of cut filters to labeled tube
4. Add water and acid sequentially (5% HNO_3)
5. Heat to 97°C for two hours (EPA, 2007)
6. Compensate evaporated water by adding more dropwise (3 mL total), and submit for ICP-MS analysis
7. 25 metals are calibrated with 5 standards from 25 to 500 $\mu\text{g/l}$, three reference metals (^{45}Sc , ^{115}In , ^{159}Tb) and a wash between each batch of 16 samples
8. Convert solution concentrations to airborne via total flow volume and liquid extraction volume (normally 3 mL for a half filter)
9. Note completion and date of filters in IC/ICP logbook
10. Remove suspiciously high metal values (contamination).
11. Retain negative concentrations values
12. If none, copy ICP data to metal summary file (one excel file per SPARTAN site)

S9: Reconstructing $\text{PM}_{2.5}$ mass by chemical and EBC data

1. Convert raw (quality-checked) ion species and metals to ammonium sulfate, ammonium nitrate, sea salt (NaCl), soil, and trace metal oxides using published equations
2. Estimate water retention by species via species-specific κ Kohler values: $\kappa_{v,i}$
3. Calculate residue composition (analogous to organic content) from total mass - reconstructed mass.
4. Negative residue masses RM are retained, unless larger than 10% of inorganic IN_{tot} reconstructed mass, i.e. $[\text{RM}] < -0.1[\text{IN}_{\text{tot}}]$. If more negative, we manually inspect determine on a case-by-case basis.

S10-11: Merging PM_{2.5} mass, composition, AOD, and optical scatter QA/QC

1. Merged non-negative AOD, nephelometer 550 nm (green) scatter, PM_{2.5} mass, water-soluble ion masses, and trace metal masses into one file
2. Calculate water uptake coefficients $\kappa_{v,tot}$ (volume growth coefficients) from partitioned hygroscopic growth of individual species
3. Manually inspect species concentrations growth values where $\kappa_{v,tot} > 0.6$
4. Seasonally smooth $\kappa_{v,tot}$ growth factors (± 45 days)
5. Estimate particle-bound water at variable humidity on hourly basis and dry optical scatter component (using volume growth factors)
6. Relate dry nephelometer scatter at 550 nm relative to PM_{2.5}, variable hourly using equation (2) in original SPARTAN paper
7. Calculate daily mean PM_{2.5} (based on 24-hour mean PM_{2.5}; from 0:00 to 23:00)
8. Calculate daily mean PM_{2.5}/AOD₁₀₋₁₄ ratios.
9. Scan output for suspiciously low/high growth factors (< 0.1 or > 0.5), absolute PM_{2.5} (< 5 and $> 500 \mu\text{g}/\text{m}^3$), and PM_{2.5}/AOD ratios (< 50 or > 500)
10. If data appears satisfactory and self-consistent, upload to website Spartan-network.org

S12: Harvard Impactor (HI) QA/QC

1. Sample 37 mm quartz and Teflon filters at 10 lpm for 24 hours (09:00 to 8:59), collocated with 24-hour AirPhoton/SPARTAN 24-hour samples
2. Use same % duty cycle as normal operation (for 24h instead of 9 days)
3. Externally measure start and end flows of HI and AirPhoton with rotameter
4. Collect minimum 14 samples at given site (ideally 21)
5. Post-weigh Teflon HI, (but not quartz); create scatter plot of PM_{2.5} data
6. Measure carbon content on Quartz HI via OC/EC analyzer

References

- Bond, T. C. and Bergstrom, R. W.: Light Absorption by Carbonaceous Particles: An Investigative Review, *Aerosol Sci. Technol.*, 40(1), 27–67, doi:10.1080/02786820500421521, 2006.
- EPA: Standard Operating Procedure for Trace Metal Analysis of Ambient Air Particulate Samples using ICP-MS. SOP MLD 061., 2007.
- Gibson, M. D., Pierce, J. R., Waugh, D., Kuchta, J. S., Chisholm, L., Duck, T. J., Hopper, J. T., Beauchamp, S., King, G. H., Franklin, J. E., Leaitch, W. R., Wheeler, A. J., Li, Z., Gagnon, G. A. and Palmer, P. I.: Identifying the sources driving observed PM_{2.5} temporal variability over Halifax, Nova Scotia, during BORTAS-B, *Atmos. Chem. Phys.*, 13(14), 7199–7213, doi:10.5194/acp-13-7199-2013, 2013.
- Smirnov, A., Holben, B. N., Eck, T. F., Dubovik, O. and Slutsker, I.: Cloud-Screening and Quality Control Algorithms for the AERONET Database, *Remote Sens. Environ.*, 73(3), 337–349, doi:10.1016/S0034-4257(00)00109-7, 2000.