Technical Challenges in Air Quality Monitoring

Quality Control/Quality Assurance

Judith C. Chow (judith.chow@dri.edu)
John G. Watson
Richard J. Tropp
Desert Research Institute
Reno, Nevada, USA

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Quality Control (QC)

- The internal system for estimating and maintaining the precision, accuracy, and validity of air quality measurements.
- QC elements
  - Standard Operating Procedures (SOPs), revised periodically
  - Periodic instrument calibrations with transfer standards
  - Periodic zeros and spans with performance standards
  - Replicate analyses
  - Cross-instrument comparisons
  - Internal consistency tests

Watson et al., 2001

Quality Assurance (QA)

- The external system that verifies the precision, accuracy, and validity of air quality measurements
- QA elements
  - System audits to assure that procedures are being followed or modified to reflect current practice
  - Performance audits that evaluate outputs for external standards
  - Interlaboratory comparisons and collocated sampling
  - Interference evaluation with reference materials

Watson et al., 2001

QC and QA quantify the four attributes of each air quality measurement

- Value (C_m): Measured value of observables
- Accuracy (A): $A(\%) = \frac{100(C_m - C_t)}{C_t}$ The degree of correctness with which a measurement system yields the true value of observables
- Precision (S_m): $S_m = \sqrt{\frac{[\sum_i (C_i - AvgC_i)^2]}{(n-1)}}$ The standard deviation of repeated measurements of the same observable with the same measurement method
- Validity: Evaluation of the extent to which procedures were followed, application of internal/external consistency tests, assignment of validity flags, and removal of invalid measurements

*C_i is the ith measurement of observable C
Avg C_i is the average concentration of the measurement of Cx

Watson et al., 2001

SOPs should prescribe and describe the measurement process

- Brief summary of the measurement method, its principles of operation, expected accuracy and precision, and the assumptions which must be met
- List materials, equipment, reagents, and suppliers. Specifications are given for each expendable item
- Designation of the individual responsible for each part of the procedure
- General traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification
- Start-up, routine, and shut-down operating procedures and an abbreviated checklist
- Copies of data forms with examples of filled-out forms
- Routine maintenance schedules, maintenance procedures, and troubleshooting tips
- Internal calibration and performance testing procedures and schedules
- External performance auditing schedules
- References to relevant literature and related standard operating procedures

Watson et al., 2001

Example of 75 SOPs used for the Fresno Supersite

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Table 2-1. Summary of SOPs Applied to Fresno Supersite Field Measurements

SOP No.	Measurement(s)	Instrument	SOP Title	Date of Last Revision	Primary Source(s)	Status
I. Gases						
FGAS001	Nitrogen Oxides (NO/NO_y)	(TECO) 42 w. internal TEI converter	TECO 42 Oxides of Nitrogen Analyzer	08/01/94	ARB SOP #W.1, W.2, and W.3	Follow ARB procedure
FGAS002	Ozone (O_3)	API 400	API Model 400 Ozone Analyzer	10/02/00		Follow STI procedure
IV. Organic Gases and Particles						
FORG001	Particle-bound PAH	EcoChem Analytics PAS2000	Operation of EcoChem Analytics PAS 2000 Analyzer	03/16/00	DRI SOP #1-410.0	Revision 0 of Fresno Supersite format
FORG002	Toxic hydrocarbons	Xontec 910A canister sampler	Gaseous Toxic Sample Xontech Model 910A	03/01/96	ARB	follow ARB procedure
VIII. Data Base Management						
FDBM001	Meteorological and continuous gaseous data processing		Meteorological and Continuous Gaseous Data Processing and Validation	12/31/94	DRI SOP #3-109.2	Follow DRI procedure
FDBM002	Data processing and validation		Data Processing and Validation	12/31/94	DRI SOP #3-003.4	Follow DRI procedure

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Table 2-3. Summary of Laboratory-related SOPs

DRI SOP No.	Observable/Method	Title	Date of Last Revision
2-101.1	TSP and PM_{10} mass	Gravimetric Analysis, Processing, and Documentation of 8"X10" Glass Fiber Filters for Hi-Vol Sampling	
2-102.3	PM mass	Gravimetric Analysis Procedures	8/30/94
2-114.1	$PM_{2.5}$ FRM mass	$PM_{2.5}$ FRM Gravimetric Analysis	3/1/99
2-107.2	Light transmission	Light Transmission Analysis Procedure	8/3/90
2-105.3	Nylon filter pretreatment	Preparation of Nylon Filters for Nitric acid or Total Nitrate Sampling	4th qtr 94
2-106.3	Quartz-fiber filter pretreatment	Pre-firing of Quartz Fiber filters for Carbonaceous Material Sampling	12/23/94
2-108.3	Sectioning of filters	Sectioning of Teflon and Quartz Filter Samples	2nd qtr 94
2-109.4	Ionic species filter extraction	Extraction of Ionic Species from Filter Samples	8/8/96
2-110.4	Filter pack processing	Filter Pack Assembling, Disassembling, and Cleaning Procedure	11/24/98
2-111.4	Filter pack shipping and receiving	Sample Shipping, Receiving, and Chain-of-Custody	11/24/98
2-112.1	$PM_{2.5}$ FRM filter pack processing	$PM_{2.5}$ FRM Filter Pack Assembly, Disassembly, and Cleaning	3/1/99
2-113.1	$PM_{2.5}$ FRM shipping and receiving	$PM_{2.5}$ FRM Sample Shipping, Receiving, and Chain-of-Custody	3/1/99
2-203.4	Cl^-, NO_3^-, $SO_4^=$	Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography	4th qtr 94
2-204.4	OC and EC in seven fractions	Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples	6/1/00
2-205.2	40 elements from Na to U	X-ray Fluorescence (XRF) Analysis of Aerosol Filter Samples	9/22/90
2-206.4	Na^+, K^+	Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy	4th qtr 94
2-207.5	NH_4^+ or NH_3 as NH_4^+	Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetric Analysis	11/20/98
2-703.1	Volatile organic compounds (C_2-C_{12})	Analysis of VOC in Ambient Air by Gas Chromatography with Cryogenic Concentration	7/2/98
2-704.1	Volatile organic compounds (C_2-C_{12})	Analysis of VOC in Ambient Air by Gas Chromatography and Mass Spectrometry	7/2/98
2-710.1	Carbonyls	Analysis of Carbonyl Compounds by High Pressure Liquid Chromatography	7/9/98
2-720.1	Heavy hydrocarbons (C_8-C_{20})	Analysis of C_8 to C_{20} Volatile Organic Compounds on Tenax by Gas Chromatography with FID or MSD/FTIR Detection	9/21/95
2-750.1	Semi-volatile organic compounds	Analysis of Semi-Volatile Organic Compounds by Gas Chromatography and Mass Spectrometry	6/24/98

Watson et al., 2000

Systems Audit

- Conducted annually by independent/external personnel.
- Review measurement and data processing to ensure SOPs define valid measurement methods and procedures are implemented in practice.
- Review of the measurement system:
  - Facilities
  - Station and siting sensor
  - Equipment
  - Personnel and training
  - Standard operating procedures (SOPs)
  - Record keeping (chain-of-custody)
  - Data validation and data management
  - Reporting

Performance Audit

- Conducted biannually or quarterly with independent/external personnel, equipment, and standards.
- Verify data accuracy, precision, and detection limits for sampler, analyzer, and measurements.
- Challenge the measurement system with independent standards or methods.
- Assess out-of-control sensors.
- Identify bias of sensor or network.
  - May include interlaboratory comparison and/or multi-laboratory performance testing.

Example of QC/QA Activities for Continuous Monitors

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Table 2-6. Quality Assurance Activities at the Fresno Supersite

Observable (Method)	Percent Tolerance	Instrument	Primary Standard	Calibration Standard	Calibration Frequency	Performance Test Standard	Performance Test Frequency	Performance Audit Standard	Performance Audit Frequency	Audit by[a]
I. Gases										
NO/NO_x (chemiluminescence)	±10%	TEI 42	NIST-traceable NO mixture	Certified NO mixture and dynamic dilution	Quarterly or when out of spec	Span with certified NO and zero with scrubbed air	Daily	Certified NO mixture and dynamic dilution	Yearly	ARB
O_3 (UV absorption)	±10%	API 400	ARB Primary UV Photometer	Dasibi 1003AH UV photometer	Quarterly or when out of spec	Span with internal ozone generator and zero with scrubbed air	Daily	Dasibi 1008 with temperature and pressure adjustments	Yearly	ARB
CO (infrared absorption)	±10%	Dasibi 3008	NIST-traceable CO mixture	Certified CO mixture and dynamic dilution	Quarterly or when out of spec	Span with certified CO and zero with scrubbed air	Daily	Certified CO mixture and dynamic dilution	Yearly	ARB
NMHC (flame ionization)	±10%	TEI 55C	NIST-traceable HC mixture	Certified HC gas dilution	Quarterly or when out of spec	Span with certified HC and zero with scrubbed air	Daily	Certified HC gas dilution	Yearly	ARB
NO_y, HNO_3, NO_2, PAN (chemiluminescence and Luminol)	±20%	TEI 42CY[b] UC Riverside Lumiinol	NIST-traceable NO mixture	Certified NO mixture and dynamic dilution	Quarterly or when out of spec	Span with certified NO and HNO_3 perm tube and zero with scrubbed air	Daily for NO Weekly for HNO_3	Certified NO mixture and dynamic dilution	3 times over 3 years	CRPAQS/ CE-CERT
NH_3 (chemiluminescence)	±20%	TEI 17C[b]	NIST-traceable NO mixture	Certified NO mixture and dynamic dilution	Quarterly or when out of spec	Span with certified NO and zero with scrubbed air	Daily	Certified NO mixture and dynamic dilution	3 times over 3 years	CRPAQS/ CE-CERT
II. Filter Mass and Chemistry										
TSP mass (high-volume sampler)	±5%	General Metal Works	Spirometer (>1,000 L/min)	Calibrated orifice/ roots meter	Quarterly	Calibrated orifice	Monthly	Calibrated orifice/ roots meter	Yearly	ARB
PM_{10} mass (hivol SSI sampler)	±5%	Andersen	Spirometer (>1,000 L/min)	Calibrated orifice/ roots meter	Quarterly	Calibrated orifice	Monthly	Calibrated orifice/ roots meter	Yearly	ARB
$PM_{2.5}$ and coarse mass, elements, elements, endotoxins, spores, mold, and fungi (collocated dichotomous samplers)	±5%	Andersen	NIST-certified bubblemeter (1-25 L/min)	Mass flowmeter/ bubblemeter	Quarterly	Calibrated bubblemeter	Monthly	Mass flowmeter	Yearly	ARB

Watson et al., 2000

Example of QA/QC Activities for Laboratory Analysis
(IMPROVE Carbon Measurement)

Requirement	Calibration Standard and Range	Calibration Frequency[b]	Acceptance Criteria	Corrective Action
System Blank Check	NA[a]	Beginning of analysis day.	≤0.2 µg C/cm^2.	Check instrument and filter lots.
Leak Check	NA	Beginning of analysis day.	Oven pressure drops less than 0.52 mm Hg/s.	Locate leaks and fix.
Laser Performance Check	NA	Beginning of analysis day.	Transmittance >700 mV; Reflectance >1500 mV	Check laser and filter holder position.
Calibration Peak Area Check	NIST 5% CH_4/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl).	Every analysis.	Counts >20,000 and 95-105% of average calibration peak area of the day.	Void analysis result and repeat analysis with second filter punch.
Auto-Calibration Check	NIST 5% CH_4/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl).	Beginning of analysis day.	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.
Manual Injection Calibration	NIST 5% CH_4/He or NIST 5% CO_2/He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl).	End of analysis day.	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.
Sucrose Calibration Check	10µL of 1800 ppm C sucrose standard; 18 µg C.	Thrice per week (began March, 2009).	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.
Multiple Point Calibrations	1800 ppm C Potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH_4/He, and NIST 5% CO_2/He gas standards; 9-36 µg C for KHP and sucrose; 2-30 µg C for CH_4 and CO_2.	Every six months or after major instrument repair.	All slopes ±5% of average.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Sample Replicates (on the same or a different analyzer)	NA	Every 10 analyses.	±10% when OC and TC ≥10 µg C/cm^2 ±20% when EC ≥ 10µg C/cm^2 or <±1 µg/cm^2 when OC and TC <10 µg C/cm^2 <±2 µg/cm^2 when EC <10µg C/cm^2	Investigate instrument and sample anomalies and rerun replicate when difference is > ±10%.
Temperature Calibrations	Tempilaq® G (Tempil, Inc., South Plainfield, NJ, USA); Three replicates each of 121, 184, 253, 510, 704, and 816 °C.	Every six months, or whenever the thermocouple is replaced.	Linear relationship between thermocouple and Tempilaq® G values with R^2>0.99.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Oxygen Level in Helium Atmosphere (using GC/MS)[c]	Certified gas-tight syringe; 0-100 ppmv.	Every six months, or whenever leak is detected.	Less than the certified amount of He cylinder.	Replace the He cylinder and/or O_2 scrubber.
Interlaboratory comparisons	NA	Once per year.	NA	Review and verify procedures.
External systems audits	NA	Once every two to three years.	NA	Take action to correct any deficiencies noted in audit report.

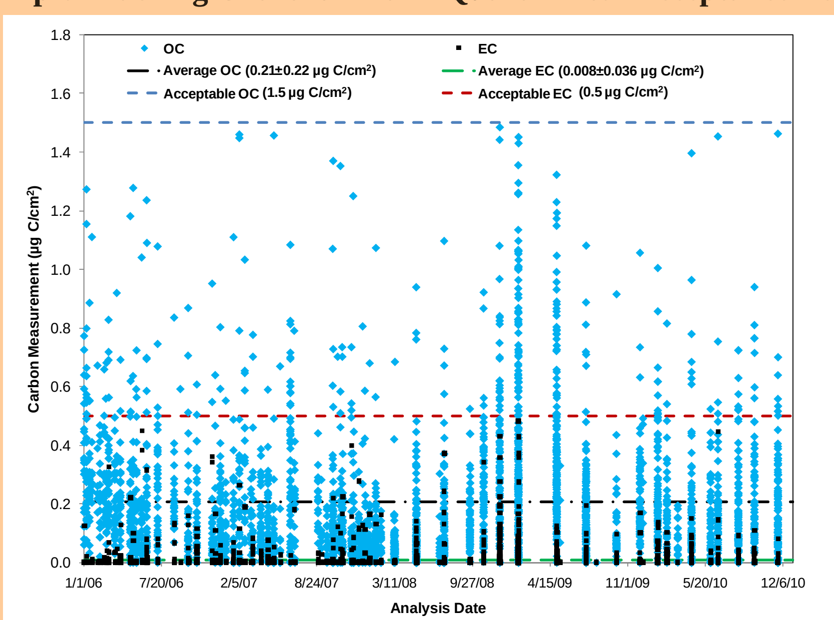
[a] NA: Not Applicable.
[b] Calibration performed by carbon analyst, except for interlaboratory comparisons and external systems audits, which are conducted by the U.S. Environmental Protection Agency (EPA) National Air and Radiation Environmental Laboratory (NAREL).
[c] Gas chromatography/mass spectrometer (Model 5975, Agilent Technology, Palo Alto, CA, USA).

Chow et al., 2007, 2011

Example of Laboratory Data Validation Flags

Lab flag	Explanation
_	Indicates no flags. Used to remove null flag fields in queries
b	Blank
b1	Field/dynamic blank
b2	Laboratory blank
b3	Distilled-deionized water blank
b4	Method blank
b5	Extract/solution blank
b6	Transport blank
c	Analysis result reprocessed or recalculated
c1	XRF spectrum reprocessed using manually adjusted background
d	Sample dropped
f	Filter damaged or ripped
f1	Filter damaged outside of analysis area
f2	Filter damaged within analysis area
f3	Filter wrinkled
f4	Filter stuck to PetriSlide
f5	Teflon membrane separated from support ring
f6	Pinholes in filter
g	Filter deposit damaged
g1	Deposit scratched or scraped, causing a thin line in the deposit
g2	Deposit smudged, causing a large area of deposit to be displaced
g3	Filter deposit side down in PetriSlide
g4	Part of deposit appears to have fallen off; particles on inside of PetriSlide
g5	Ungloved finger touched filter
g6	Gloved finger touched filter

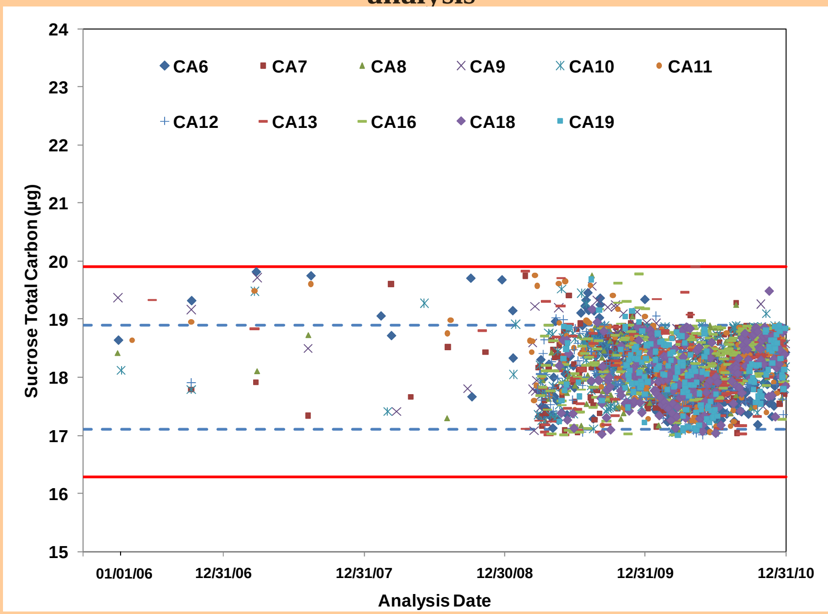
Example Tracking Chart for Blank Quartz Filter Acceptance Tests



Two filters are randomly selected from each batch of 100 quartz-fiber filters for acceptance testing

Chow et al., 2011

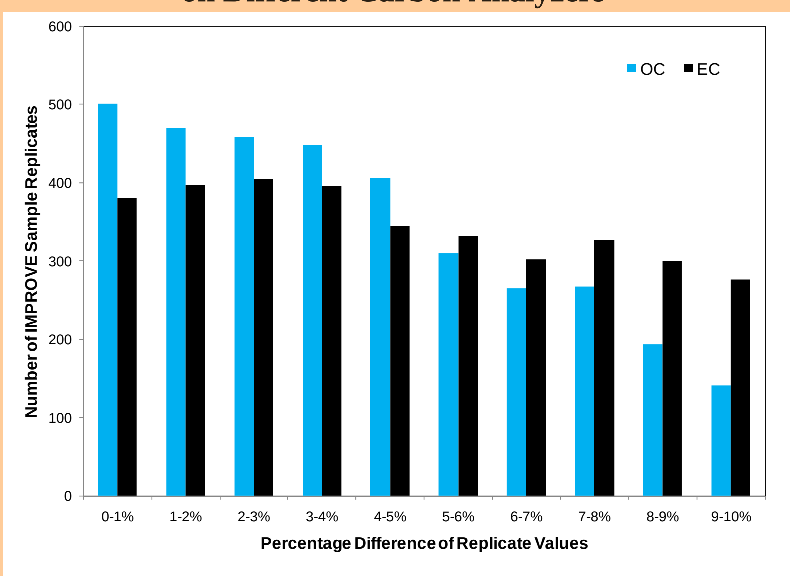
Example tracking chart for performance standards used for carbon analysis



CA: Carbon Analyzer

Chow et al., 2011

Example Distribution of Relative Differences for Replicate Analyses on Different Carbon Analyzers



Chow et al., 2011

Conclusions

- QC and QA are essential components of air quality measurement programs
- QC and QA data allow the precision, accuracy, and validity of air quality data to be quantified and expressed
- Greater resources must be directed toward QC and QA processes for emerging air quality measurement in Asia

Useful References

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