



Summary of Quarterly Operations (October – December) with 2013 Annual Summary

EPA Contract No. EP-W-09-028

Introduction

This quarterly report summarizes results from the Clean Air Status and Trends Network (CASTNET) quality assurance/quality control (QA/QC) program for data collected during fourth quarter 2013. It also provides an annual summary that includes data from the three previous quarters. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; AMEC, 2012; 2013). The QAPP is comprehensive and includes standards and policies for all components of project operation from site selection through final data reporting. It is reviewed annually and updated as warranted.

Significant Events for 2013

AMEC's analytical laboratory received International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025:2005 accreditation by the American Association for Laboratory Accreditation (A2LA) on April 19, 2013 for its defined chemical testing scope, including, but not limited to, CASTNET laboratory test procedures.

AMEC submitted a Notice of Key Personnel Change to EPA during March 2013, which was approved by EPA. W. Charles Greer replaced William Imbur as the CASTNET QA Supervisor.

Beginning with the February 2013 data submittal, trace-level gas data from the BVL130, IL site were included in the raw data submittal to EPA's Air Quality System (AQS). Beginning with the March 2013 data submittal, trace-level gas data from the BEL116, MD and HWF187, NY sites were included with the BVL130 data and submitted to AQS. Beginning with the August 2013 data submittal, trace-level gas data from the PND165, WY site also were included and submitted to AQS. Additionally, trace-level gas instrument suites were installed and began operating at PNF126, NC and ROM206, CO during fourth quarter 2013. Submission of data to AQS will begin for these two sites in 2014.

During 2013, AMEC participated in two proficiency test (PT) studies (101 and 102) for Rain and Soft Waters from the National Laboratory of Environmental Testing (NLET), a branch of the National Water Research Institute (NWRI) with Environment Canada that provides QA services. Overall, AMEC's laboratory was rated, "very good", the highest rating available, for PT study 101 and PT study 102. The laboratory's analyses for both studies showed no flags and no indication of bias. An "Ideal" rating was assigned to each parameter tested and submitted. AMEC's 5-year median rating remained "Very Good" for Environment Canada PT studies, which shows AMEC's consistent performance for laboratory analyses. AMEC regularly participates in laboratory intercomparison tests offered by Environment Canada and the U.S. Geological Survey.

During 2013, AMEC worked with Teledyne Advanced Pollution Instrumentation (TAPI) to resolve multiple issues with the trace-level gas instruments. TAPI's product group reviewed AMEC's questions and comments and provided feedback. A TAPI technical specialist met with AMEC personnel in the Gainesville, FL office and again later at the BVL130, IL site so he could see the analyzers in situ and work with AMEC technicians on troubleshooting activities. Most issues were resolved. Significant and/or ongoing issues include the following:

- ▶ Comparison of fourth quarter 2012 trace-level gas concentrations and filter pack concentrations at the BEL116, MD and BVL130, IL sites indicated that weekly average sulfur dioxide (SO₂) concentrations from the TAPI analyzer were about 25 percent lower than the corresponding filter pack concentrations and concentrations from the Monitors for Aerosols and Gases in Ambient Air (MARGA), located at the BEL116, MD site. TAPI recommended using a single gas cylinder for routine QC and calibration checks. Per TAPI, the blended gas cylinders currently used may lower concentrations reported by the TAPI instrument by introducing an uncorrected positive interference from nitric oxide (NO) during instrument calibration. During December 2013, AMEC began testing with a single gas cylinder to evaluate whether use of blended gas is the cause of the disparity in concentration measurements.
- ▶ AMEC continued working with TAPI to address problems with the adaptive signal filtering of the TAPI trace-level gas analyzers. A fast response is needed for QC measurements, but available options are not sufficient to engage this mode reliably under current operational protocols.
- ▶ While the zero/precision/span QC checks remained within criteria, the TAPI trace-level gas monitoring system at the BEL116, MD site was only intermittently reporting an expected (i.e. "target") value. AMEC developed a data logger program to correct the problem. The program was deployed to the trace-level monitoring sites during third quarter 2013 after testing confirmed its effectiveness.

The QA Manager performed six laboratory audits during 2013 in accordance with AMEC's analytical laboratory's ISO/IEC 17025:2005 accreditation. The QA Supervisor conducted the annual management review in accordance with the laboratory's accreditation during April 2013.

During the site visit in late September, the mass flow controller (MFC) at UND002, VT was found to be out of calibration criterion. The MFC was replaced during the visit. Additional investigations in Gainesville determined that the MFC had been accidentally set to the wrong gas type during troubleshooting performed by the site operator. AMEC is establishing preventive actions to preclude this from happening in the future. As part of this preventive action, during 2014, AMEC will make changes to site infrastructure and the data logger program to allow remote monitoring of internal MFC system data and remote control of MFC settings.

The CASTNET QAPP Revision 8.1 was approved by EPA during October 2013.

During third and fourth quarter, AMEC worked with EPA and RTI International, Inc. (RTI), the auditing organization, to coordinate a technical systems audit (TSA) of the National Park Service's (NPS's) contractor's ozone facilities in Fort Collins, CO and at the ROM406, CO field site. A TSA of the monitoring organization's facility is required by EPA every three years. Air Resource Specialists, Inc. (ARS) is the monitoring organization in charge of NPS-sponsored CASTNET AQS-protocol sites. The auditor with RTI interviewed ARS staff and observed activities related to various procedures. The audit report covered his visits to the CASTNET field site at ROM406 and the Fort Collins facility. The final report (in press) will be posted on the EPA CASTNET website. The TSA for the AMEC facility (the monitoring organization in charge of EPA-sponsored sites) was performed in 2012.

The ozone analyzers at several sites reported negative concentration values intermittently for zero phase QC checks. During 2014, AMEC will begin making changes to the ozone sample lines at CASTNET sites to lessen the potential influence of ambient conditions, including dew point, on the zero/precision/ span QC checks and routine measurements.

Providing a safe working environment is one of AMEC's goals. Sites are routinely checked for safe working conditions at each calibration (i.e., twice per year). Beginning in November 2012 and continuing through 2013, AMEC performed internal safety audits of selected sites. These safety audits provide a more in-depth review of site safety and include a safety-related evaluation of infrastructure condition and maintenance, use of equipment, site operator activities at the site, and verification that procedures are understood and followed by site personnel. There were no findings during 2013.

Quarterly/Annual Summary

Table 1 lists the quarters of data that were validated to Level 3 during 2013 by site calibration group. Table 2 lists the sites in each calibration group along with the calibration schedule. Table 3 presents the measurement criteria for continuous field measurements. These criteria apply to the instrument challenges performed during site calibrations. Table 4 presents the measurement criteria for laboratory filter pack measurements. These criteria apply to the QC samples listed in the following section of this report. Table 5 presents the critical criteria for ozone monitoring at sites that are configured to meet EPA's AQS criteria for QA/QC procedures and are operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (CFR; EPA, 2012). Table 6 presents the critical criteria for AQS-protocol trace-level gas monitoring.

Quality Control Analysis Count

The QC sample statistics presented in this report are for reference standards (RF) and continuing calibration verification spikes (CCV) used to assess accuracy and for replicate sample analyses (RP) used to assess "in-run" precision. In addition, laboratory method blanks (MB) containing reagents without a filter; laboratory blanks (LB) containing reagents and a new, unexposed filter; and field blanks (FB) containing reagents and an unexposed filter that was loaded into a filter pack assembly and shipped to and from the monitoring site while remaining in sealed packaging are also included. Tables 7 through 10 present the number of analyses in each category that were performed during each quarter of 2013.

Sample Receipt Statistics

Ninety-five percent of field samples from EPA-sponsored sites must be received by the CASTNET laboratory in Gainesville, FL no later than 14 days after removal from the sampling tower. Table 11 presents the relevant sample receipt statistics for each of the four quarters of 2013 together with an annual summary for each category.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for fourth quarter 2013. All results were within the criteria listed in Table 4. Table 12 presents the percent recoveries and standard deviations for RF, CCV, and RP QC sample analyses for 2013. Quarterly averages are all within criteria.

Table 13 presents quarterly collocated filter pack precision results for data validated to Level 3 during the year. Results for MCK131/231, KY and ROM406/206, CO were within the criterion for all of the 11 parameters reported.

Figure 4 presents completeness statistics for continuous measurements validated to Level 3 during the year. All parameters met the 90 percent criterion.

Table 14 presents summary statistics of critical criteria measurements at AQS-protocol ozone sites collected during fourth quarter 2013. All data associated with QC checks that fail to meet the criteria listed in Table 5 were or will be invalidated. Results in shaded cells either exceed documented criteria or are otherwise notable. Table 15 presents observations associated with the shaded cell results in Table 14.

Table 16 presents summary statistics of critical criteria measurements at AQS-protocol trace-level gas monitoring sites collected during fourth quarter 2013. All data associated with QC checks that fail to meet the criteria listed in Table 6 were or will be invalidated. Results in shaded cells either exceed documented criteria or are otherwise notable. Table 17 presents observations associated with the shaded cell results in Table 16.

Laboratory Control Sample Analysis

The laboratory control sample (LCS) is a reagent blank spiked with the target analytes from the established analytical methods and carried through the same extraction process that field samples must undergo. The LCS is not required by the CASTNET QA/QC program. LCS analyses are performed by the laboratory to monitor for potential sample handling artifacts and provide a means to identify possible analyte loss from extraction to extraction. The current action limits for LCS recovery are 80 percent and 120 percent. Figure 5 presents LCS analysis results for fourth quarter 2013. All recovery values were between 84 percent and 112 percent.

Blank Results

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for fourth quarter 2013. All fourth quarter results were within criteria (two times the reporting limit) listed in Table 4. Table 18 summarizes the record of filter blanks for 2013. All 2013 results were within criteria listed in Table 4 with the exception of a single calcium FB value and a single sulfur dioxide FB value that occurred during different weeks of second quarter. Both results appeared to be random contamination. All other blank QC checks in their respective batches were within criteria, and all other FB results for 2013 were within criteria.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during each of the four quarters of 2013 are listed in Table 19. This table also includes associated site identification and a brief description of the reason the sample was flagged. During fourth quarter, 14 filter pack samples were invalidated.

Field Problem Count

Table 20 presents counts of field problems affecting continuous data collection for more than one day for each quarter during 2013. The problem counts are sorted by a 30-, 60-, or 90- day time period to resolution. A category for unresolved problems is also included. Time to resolution indicates the period taken to implement corrective action.

Field Calibration Results

A summary of field calibration failures by parameter for each quarter of 2013 is listed in Table 21. Calibrations were performed at 20 sites during fourth quarter 2013. During 2013, all sites and parameters were within the criteria listed in Table 3 with the exception of the parameters at the five sites that are listed in Table 21.

Table 22 presents field accuracy results for 2013 based on instrument challenges performed using independent reference standards during site calibration visits. Each parameter was within its criterion with at least 90 percent frequency except relative humidity at 88.9 percent and solar radiation at 77.8 percent frequency. Per CASTNET project protocols, data are flagged but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). All calibration failures reported in 2013 for the indicated parameters were within 2x the criterion with the exception of temperature at QAK172, OH in March 2013. Data associated with the failure at QAK172 were invalidated.

References

AMEC Environment & Infrastructure, Inc. (AMEC). 2013. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 8.1*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. <http://java.epa.gov/castnet/documents.do>.

AMEC Environment & Infrastructure, Inc. (AMEC). 2012. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 8.0*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. <http://java.epa.gov/castnet/documents.do>.

American Society for Testing and Materials (ASTM). 2008. *ASTM E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications*. ASTM International, West Conshohocken, PA, DOI:10.1520/E0029-08. www.astm.org.

U.S. Environmental Protection Agency (EPA). 2012. Appendix A to Part 58 – Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS), Special Purpose Monitors (SPMs), and Prevention of Significant Deterioration (PSD) Air Monitoring. 40 *CFR* Part 58.

Table 1 Data Validated to Level 3 through Fourth Quarter 2013

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
SE-4 MW-6 [†]	July 2012 – June 2013	12	Quarter 3 2012 – Quarter 2 2013	4
E-1 SE-5	August 2012 – July 2013	12	Quarter 4 2012 – Quarter 2 2013	3
MW-7 W-9	September 2012 – August 2013	12	Quarter 4 2012 – Quarter 2 2013	3
E-2 MW-8	October 2012 – September 2013	12	Quarter 4 2012 – Quarter 3 2013	4
E-3 W-10 [‡]	May 2012 – April 2013	12	Quarter 3 2012 – Quarter 1 2013	3

Notes: * The sites contained in each calibration group are listed in Table 2.

[†] Contains MCK131/231 collocated pair

[‡] Contains ROM206 of the ROM406/ROM206 collocated pair

Table 2 Field Calibration Schedule for 2013

Calibration Group	Months Calibrated	Sites Calibrated			
Eastern Sites (23 Total)					
E-1 (8 Sites)	February/August	BEL116, MD BWR139, MD	WSP144, NJ CTH110, NY	ARE 128, PA PSU106, PA	PED108, VA VPI120, VA
E-2 (10 Sites)	April/October	ABT147, CT ASH135, ME HOW191, ME	WST109, NH CAT175, NY HWF187, NY	WFM105, NY NIC001, NY EGB181 ON	UND002, VT
E-3 (5 Sites)	May/November	KEF112, PA MKG113, PA	LRL117, PA PAR107, WV	CDR119, WV	
Southeastern Sites (10 Total)					
SE-4 (6 Sites)	January/July	SND152, AL GAS153, GA	BFT142, NC CND125, NC	COW137, NC PNF126, NC	
SE-5 (4 Sites)	February/August	CAD150, AR CVL151, MS	IRL141, FL SUM156, FL		
Midwestern Sites (18 Total)					
MW-6 (6 Sites)	January/July	CDZ171, KY CKT136, KY	MCK131, KY MCK231, KY	ESP127, TN SPD111, TN	
MW-7 (8 Sites)	March/September	ALH157, IL BVL130, IL	STK138, IL VIN140, IN	DCP114, OH OXF122, OH	QAK172, OH PRK134, WI
MW-8 (4 Sites)	April/October	SAL133, IN HOX148, MI	ANA115, MI UVL124, MI		
Western Sites (9 Total)					
W-9 (4 Sites)	March/September	KNZ184, KS CHE185, OK	SAN189, NE ALC188, TX		
W-10 (5 Sites)	May/November	GTH161, CO ROM206, CO	CNT169, WY PND165, WY	PAL190, TX	

Table 3 Data Quality Indicators for CASTNET Continuous Measurements

Measurement		Criteria ¹	
Parameter ²	Method	Precision	Accuracy
Filter pack flow	Mass flow controller	± 10%	± 5%
Ozone ³	UV absorbance	All points within ± 2% of full scale of best fit straight line Linearity error < 5%	
Wind speed	Anemometer	± 0.5 m/s	The greater of ± 0.5 m/s for winds < 5 m/s or ± 5% for winds ≥ 5 m/s
Wind direction	Wind vane	± 5°	± 5°
Sigma theta	Wind vane	Undefined	Undefined
Ambient temperature	Platinum RTD	± 1.0°C	± 0.5°C
Delta temperature	Platinum RTD	± 0.5°C	± 0.5°C
Relative humidity	Thin film capacitor	± 10% (of full scale)	± 10%
Precipitation	Tipping bucket rain gauge	± 10% (of reading)	± 0.05 inch ⁴
Solar radiation	Pyranometer	± 10% (of reading taken at local noon)	± 10%
Surface wetness	Conductivity bridge	Undefined	Undefined

Notes: °C = degrees Celsius
m/s = meters per second
RTD = resistance-temperature device
UV = ultraviolet

¹ Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments. Collocated precision criteria do not apply to AQS-protocol ozone measurements.

² During 2013, meteorological parameters were only measured at five of the EPA-sponsored CASTNET sites: PAL190, TX; CHE185, OK; BVL130, IL; BEL116, MD, and IRL141, FL.

³ Ozone is not measured at six EPA-sponsored CASTNET sites: EGB181, ON; CAT175, NY; NIC001, NY; WFM105, NY; UND002, VT; and KNZ184, KS.

⁴ For target value of 0.50 inch

Table 4 Data Quality Indicators for CASTNET Laboratory Measurements

Analyte	Method	Precision ¹ (MARPD)	Accuracy ² (%)	Nominal Reporting Limits	
				mg/L	µg/Filter
Ammonium (NH ₄ ⁺)	AC	20	90 - 110	0.020*	0.5
Sodium (Na ⁺)	ICP-AES	20	95 - 105	0.005	0.125
Potassium (K ⁺)	ICP-AES	20	95 - 105	0.006	0.15
Magnesium (Mg ²⁺)	ICP-AES	20	95 - 105	0.003	0.075
Calcium (Ca ²⁺)	ICP-AES	20	95 - 105	0.006	0.15
Chloride (Cl ⁻)	IC	20	95 - 105	0.020	0.5
Nitrate (NO ₃ ⁻)	IC	20	95 - 105	0.008*	0.2
Sulfate (SO ₄ ²⁻)	IC	20	95 - 105	0.040	1.0

Notes: ¹ This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples.

² This column lists laboratory accuracy goals based on reference standards and continuing calibration verification spikes. The criterion is 90–110 percent for ICP-AES reference standards.

AC = automated colorimetry
 IC = ion chromatography
 ICP-AES = inductively coupled plasma-atomic emission spectrometry
 MARPD = mean absolute relative percent difference
 mg/L = milligrams per liter
 µg/Filter = micrograms per filter
 * = as nitrogen

Values are rounded according to American Society for Testing and Materials (ASTM) E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications (ASTM, 2008).

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP, (AMEC, 2012; 2013)

Table 5 AQS-Protocol Ozone Critical Criteria*

Type of Check	Analyzer Response
Zero	Less than ± 10 parts per billion (ppb)
Span	Less than or equal to ± 7 percent between supplied and observed concentrations
Single Point QC	Less than or equal to ± 7 percent between supplied and observed concentrations

Note: * Applies to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (EPA, 2012). The minimum frequency for these checks is once every two weeks.

Values are rounded according to ASTM E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications (ASTM, 2008).

Table 6 AQS-Protocol Trace-level Gas Monitoring Critical Criteria *

Parameter	Analyzer Response		
	Zero Check	Span Check	Single Point QC Check
SO ₂	Less than ± 3 parts per billion (ppb)	Less than or equal to ± 10 percent between supplied and observed concentrations	Less than or equal to ± 10 percent between supplied and observed concentrations
NO _y	Less than ± 3 ppb	Less than or equal to ± 10 percent between supplied and observed concentrations	Less than or equal to ± 10 percent between supplied and observed concentrations
CO	Less than ± 40 ppb	Less than or equal to ± 10 percent between supplied and observed concentrations	Less than or equal to ± 10 percent between supplied and observed concentrations

Note: *Applies to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (EPA, 2012). The minimum frequency for these checks is once every two weeks.

Values are rounded according to ASTM E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications E29 (ASTM, 2008).

SO₂ = sulfur dioxide

NO_y = total reactive oxides of nitrogen

CO = carbon monoxide

Table 7 QC Analysis Count for First Quarter 2013

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	SO ₄ ²⁻	34	177	81	17	28	87
	NO ₃ ⁻	34	177	81	17	28	87
	NH ₄ ⁺	34	176	84	17	28	87
	Cl ⁻	34	177	81	17	28	87
	Ca ²⁺	36	179	82	17	28	87
	Mg ²⁺	36	179	82	17	28	87
	Na ⁺	36	179	82	17	28	87
Nylon	K ⁺	36	179	82	17	28	87
	SO ₄ ²⁻	38	183	85	19	28	88
Cellulose	NO ₃ ⁻	38	183	85	19	28	88
	SO ₄ ²⁻	42	192	86	21	28	88

Table 8 QC Analysis Count for Second Quarter 2013

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	SO ₄ ²⁻	34	161	72	16	24	45
	NO ₃ ⁻	34	161	72	16	24	45
	NH ₄ ⁺	32	159	74	16	24	45
	Cl ⁻	32	161	72	16	24	45
	Ca ²⁺	32	166	72	16	24	45
	Mg ²⁺	32	166	72	16	24	45
	Na ⁺	32	166	72	16	24	45
	K ⁺	32	166	72	16	24	45
Nylon	SO ₄ ²⁻	31	150	68	15	24	45
	NO ₃ ⁻	31	150	68	15	24	45
Cellulose	SO ₄ ²⁻	38	182	82	19	24	45

Table 9 QC Analysis Count for Third Quarter 2013

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	SO ₄ ²⁻	28	153	70	14	26	87
	NO ₃ ⁻	28	153	70	14	26	87
	NH ₄ ⁺	28	153	76	14	26	87
	Cl ⁻	28	153	70	14	26	87
	Ca ²⁺	29	160	72	14	26	87
	Mg ²⁺	29	160	72	14	26	87
	Na ⁺	29	160	72	14	26	87
	K ⁺	29	160	72	14	26	87
Nylon	SO ₄ ²⁻	33	169	76	16	26	87
	NO ₃ ⁻	33	169	76	16	26	87
Cellulose	SO ₄ ²⁻	40	195	85	20	26	87

Table 10 QC Analysis Count for Fourth Quarter 2013

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	SO ₄ ²⁻	42	168	75	15	24	85
	NO ₃ ⁻	42	168	75	15	24	85
	NH ₄ ⁺	28	148	74	14	24	85
	Cl ⁻	42	168	75	15	24	85
	Ca ²⁺	28	150	71	14	24	85
	Mg ²⁺	28	150	71	14	24	85
	Na ⁺	28	150	71	14	24	85
	K ⁺	28	150	71	14	24	85
Nylon	SO ₄ ²⁻	30	155	72	15	24	85
	NO ₃ ⁻	30	155	72	15	24	85
Cellulose	SO ₄ ²⁻	36	162	79	18	24	85

Table 11 Filter Pack Receipt Summary for 2013

Description	First Quarter	Second Quarter	Third Quarter	Fourth Quarter	Annual Summary
Count of samples received more than 14 days after removal from tower:	36	12	12	13	73
Count of all samples received:	1,185	847	857	806	3695
Fraction of samples received within 14 days:	0.970	0.986	0.986	0.984	0.980
Average interval in days:	4.612	3.965	3.927	4.763	4.317*
First receipt date:	01/02/2013	04/01/2013	07/01/2013	10/2/2013	01/02/2013
Last receipt date:	03/29/2013	06/28/2013	09/30/2013	12/31/2013	12/31/2013

Note: *annual average

Table 12 Filter Pack QC Summary for 2013

Filter Type	Parameter	Reference Sample ¹ Recovery (%R)			Continuing Calibration Verification Samples (%R)			In-Run Replicate ² (RPD)		
		Mean	Std. Dev.	Count ³	Mean	Std. Dev.	Count ³	Mean	Std. Dev.	Count ³
Teflon	SO ₄ ²⁻	98.3	1.9	143	100.5	1.5	685	0.8	1.4	310
	NO ₃ ⁻	101.1	1.6	143	99.8	1.4	685	1.5	2.0	310
	NH ₄ ⁺	100.2	3.2	128	100.2	2.3	668	1.0	1.5	324
	Ca ²⁺	102.0	2.0	143	101.4	1.5	685	1.9	2.3	310
	Mg ²⁺	101.7	1.9	131	100.6	1.1	688	1.0	1.0	312
	Na ⁺	102.4	1.4	131	99.9	0.9	688	1.2	1.5	312
	K ⁺	100.3	1.5	131	100.0	1.0	688	1.1	1.1	312
	Cl ⁻	99.2	2.3	131	100.0	0.9	688	1.6	1.7	312
Nylon	SO ₄ ²⁻	99.1	1.7	134	101.0	1.4	668	1.5	1.8	306
	NO ₃ ⁻	101.4	1.5	134	100.2	1.3	668	1.1	1.0	306
Cellulose	SO ₄ ²⁻	99.2	1.6	158	100.6	1.7	742	1.3	1.4	337

Notes: % R = percent recovery
RPD = relative percent difference

¹ Results of reference sample analyses provide accuracy estimates

² Results of replicate analyses provide precision estimates

³ Number of QC Samples

Table 13 Precision Results for Third Quarter 2012 through Second Quarter 2013

Site Pairs	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HNO ₃	SO ₂	Total NO ₃
MCK131/231, KY											
2012 Q3	3.05	7.77	2.59	6.11	5.98	4.15	4.84	1.98	5.08	6.81	4.67
2012 Q4	4.25	5.60	3.84	9.22	9.03	5.57	5.43	4.71	3.36	4.51	4.29
2013 Q1	2.51	6.22	3.82	10.50	10.03	5.07	6.20	4.67	4.88	4.21	4.19
2013 Q2	3.52	7.88	3.17	7.37	6.79	3.64	5.59	0.45	3.46	4.19	4.63
Average	3.33	6.87	3.36	8.30	7.96	4.61	5.52	2.95	4.20	4.93	4.45
ROM406/206, CO											
2012 Q3	4.51	10.28	5.34	4.79	5.3	5.35	8.13	6.34	7.74	6.77	7.22
2012 Q4	3.56	13.87	7.53	5.56	7.54	7.45	14.52	3.66	9.36	12.17	7.66
2013 Q1	6.76	11.12	6.21	8.81	8.57	11.8	8.51	6.51	9.64	8.56	7.84
2013 Q2	4.96	10.55	7.60	7.38	6.96	8.83	8.26	9.88	13.50	10.98	8.08
Average	4.95	11.46	6.67	6.64	7.09	8.36	9.86	6.60	10.06	9.62	7.70

Note: 0 of 88 site-quarter-parameters were outside criterion
MARPD = mean absolute relative percent difference

Table 14 AQS-Protocol Ozone QC Summary for Fourth Quarter 2013 (1 of 2)

Site ID	% Span Pass ¹	Span %D ²	% Single Point QC Pass ¹	Single Point QC %D ²	Single Point QC CL ³	% Zero Pass ¹	Zero Average (ppb) ²
ABT147, CT	100.0	0.5	100.0	0.8	0.1	100.0	1.8
ALC188, TX	97.9	0.9	95.8	1.2	0.4	100.0	0.7
ALH157, IL	96.8	6.8	96.8	10.9	9.2	100.0	1.0
ANA115, MI	100.0	0.4	100.0	0.5	0.1	100.0	0.6
ARE128, PA	100.0	1.6	100.0	1.4	0.1	98.9	3.6
ASH135, ME	100.0	0.7	100.0	0.8	0.2	100.0	1.1
BEL116, MD	93.8	82.3	92.5	91.1	88.5	97.5	1.8
BFT142, NC	100.0	0.7	100.0	0.8	0.1	100.0	1.9
BVL130, IL	97.5	3.0	96.3	4.0	1.9	97.5	2.1
BWR139, MD	100.0	2.0	100.0	1.9	0.1	100.0	1.7
CAD150, AR	98.9	4.7	96.6	4.9	0.2	100.0	0.3
CDR119, WV	100.0	0.8	100.0	0.8	0.1	100.0	0.6
CDZ171, KY	100.0	0.5	100.0	0.5	0.1	100.0	0.2
CKT136, KY	100.0	0.9	100.0	1.0	0.1	100.0	0.5
CND125, NC	100.0	0.6	100.0	0.7	0.1	100.0	1.1
CNT169, WY	86.6	13.0	86.6	7.7	2.9	86.4	6.4
COW137, NC	100.0	0.8	100.0	0.7	0.1	100.0	1.4
CTH110, NY	100.0	2.2	100.0	1.6	0.2	100.0	0.6
CVL151, MS	96.8	0.9	96.8	2.1	1.8	100.0	0.9
DCP114, OH	100.0	0.4	100.0	0.4	0.1	100.0	1.2
ESP127, TN	100.0	1.0	98.9	0.9	0.2	100.0	0.2
GAS153, GA	98.9	4.8	94.6	5.2	0.3	98.9	4.4
GTH161, CO	98.9	3.0	98.9	2.3	0.9	98.9	0.7
HOX148, MI	97.9	218.4	97.9	573.5	662.5	100.0	0.5

Table 14 AQS-Protocol Ozone QC Summary for Fourth Quarter 2013 (2 of 2)

Site ID	% Span Pass ¹	Span %D ²	% Single Point QC Pass ¹	Single Point QC %D ²	Single Point QC CL ³	% Zero Pass ¹	Zero Average (ppb) ²
HWF187, NY	100.0	1.7	92.8	4.1	0.5	98.8	2.9
IRL141, FL	100.0	0.5	100.0	0.9	0.1	92.6	4.0
KEF112, PA	100.0	1.4	100.0	1.4	0.1	100.0	0.4
LRL117, PA	100.0	1.7	100.0	1.2	0.2	100.0	0.4
MCK131, KY	100.0	2.1	98.9	2.1	0.2	100.0	1.3
MCK231, KY	100.0	3.2	100.0	3.2	0.1	100.0	1.0
MKG113, PA	100.0	0.6	100.0	0.9	0.1	100.0	0.5
OXF122, OH	100.0	1.2	100.0	1.2	0.1	100.0	0.2
PAL190, TX	99.0	1.5	99.0	1.5	1.4	99.0	0.8
PAR107, WV	97.9	2.5	97.9	2.8	2.4	100.0	1.0
PED108, VA	100.0	0.5	100.0	0.6	0.1	100.0	0.5
PND165, WY	100.0	0.7	100.0	0.8	0.1	100.0	0.7
PNF126, NC	100.0	0.9	98.8	2.2	0.3	100.0	1.3
PRK134, WI	95.7	317.2	95.7	927.4	910.1	100.0	0.6
PSU106, PA	100.0	1.1	100.0	1.0	0.1	100.0	0.5
QAK172, OH	91.7	2.3	91.7	2.3	1.1	100.0	1.0
ROM206, CO	100.0	0.7	100.0	2.3	0.2	100.0	2.2
SAL133, IN	100.0	0.5	100.0	0.5	0.1	100.0	0.5
SAN189, NE	96.5	3.7	96.5	3.3	2.7	97.7	0.8
SND152, AL	100.0	0.9	100.0	1.2	0.1	100.0	1.2
SPD111, TN	100.0	1.8	100.0	1.6	0.2	100.0	0.2
STK138, IL	100.0	1.2	100.0	1.4	0.1	100.0	0.7
SUM156, FL	100.0	3.0	97.9	4.2	0.4	95.7	3.0
UVL124, MI	100.0	1.2	100.0	1.3	0.1	100.0	0.2
VIN140, IN	100.0	4.9	100.0	4.5	0.1	100.0	0.5
VPI120, VA	100.0	1.5	100.0	1.1	0.0	100.0	0.4
WSP144, NJ	97.9	1.4	95.9	2.3	0.4	88.9	3.7
WST109, NH	100.0	0.7	100.0	0.8	0.1	100.0	0.7

Notes: ¹ Percentage of comparisons that pass the criteria listed in Table 5. Values falling below 90 percent are addressed in Table 15.

² Absolute value of the average percent differences between the on-site transfer standard and the site monitor. Values exceeding the criteria listed in Table 5 are addressed in Table 15.

³ 90 percent confidence limit of the coefficient of variation. This should be less than or equal to the 7 percent single point QC check critical criterion. Values exceeding this criterion are addressed in Table 15.

%D = percent difference
CL = confidence limit
ppb = parts per billion

Table 15 AQS-Protocol Ozone QC Observations for Fourth Quarter 2013

Site ID	QC Criterion	Comments
ALH157, IL*	Single Point QC %D Single Point QC CL	The transfer standard solenoid malfunctioned. Ambient data were not affected.
BEL116, MD*	% Span Single Point QC %D Single Point QC CL	QC failures were associated with a combination of site calibration activities and a period wherein the zero air system was not connected. Ambient data were not affected.
CNT169, WY*	Span Span %D % Single Point QC Pass Single Point QC %D % Zero Pass	There were several periods when ice clogged the calibration gas supply line. Ambient data were not affected.
HOX148, MI*	Span %D Single Point QC %D Single Point QC CL	The transfer standard solenoid malfunctioned. Ambient data were not affected.
PRK134, WI*	Span %D Single Point QC %D Single Point QC CL	The transfer standard pneumatic pump malfunctioned. Ambient data were not affected.
WSP144, NJ	% Zero Pass	Zero phase QC failures occurred intermittently (please see page 3 of this report). Associated data were invalidated.

Notes: %D = percent difference

CL = confidence limit

*The events that cause the statistical failure(s) occurred in December 2013. The events and associated data had not been validated or reported to AQS at the time of writing.

Table 16 AQS-Protocol Trace-level Gas QC Summary

Parameter	% Span Pass ¹	Span %D ²	% Single Point QC Pass ¹	Single Point QC %D ²	Single Point QC CL ³	% Zero Pass ¹	Zero Average (ppb) ²
BEL116, MD							
SO ₂	88.5	10.6	86.0	10.4	6.5	90.6	3.5
NO _y	98.1	5.9	92.3	6.4	0.7	100.0	0.8
BVL130, IL							
SO ₂	97.9	4.5	97.9	3.1	3.3	97.9	0.3
NO _y	100.0	3.8	100.0	4.3	0.6	97.8	1.3
CO	97.9	2.9	97.9	3.3	2.2	93.6	12.3
HWF187, NY							
NO _y	100.0	1.5	100.0	2.7	0.3	100.0	0.4
PND165, WY							
NO _y	100.0	2.8	100.0	2.6	0.5	100.0	0.1
PNF126, NC							
NO _y	100.0	3.1	100.0	3.1	0.6	100.0	0.3
ROM206, CO							
NO _y	100.0	0.9	100.0	1.2	0.2	100.0	0.1

Notes: ¹ Percentage of comparisons that pass the criteria listed in Table 6. Values falling below 90 percent are addressed in Table 17.

² Absolute value of the average percent differences between the supplied and observed concentrations. Values exceeding the criteria listed in Table 6 are addressed in Table 17.

³ 90 percent confidence limit of the coefficient of variation. This should be less than or equal to the 10 percent single point QC check critical criterion. Values exceeding this criterion are addressed in Table 17.

%D = percent difference

CL = confidence limit

ppb = parts per billion

Table 17 AQS-Protocol Trace-level Gas QC Observations

Site ID	Parameter	QC Criterion	Comments
BEL116, MD	SO ₂	% Span Span %D % Single Point QC Pass Single Point QC %D Zero Average	Several issues: <u>Ambient data not affected</u> Adaptive signal filtering issue continued (please see page 2). The gas calibrator pressure transducer malfunctioned. <u>Ambient data affected</u> The analyzer circuit board required resetting. Associated data were invalidated

Table 18 Summary of Filter Blanks for 2013 (1 of 2)

Parameter Name	Detection Limit Total µg	Total Number	Number > Detection Limit	Average Total µg	Average Absolute Deviation	Maximum Total µg
FIELD BLANKS						
Teflon-NH ₄ ⁺ -N	0.500	350	0	0.500	0.000	0.500
Teflon- NO ₃ ⁻ -N	0.200	350	12	0.202	0.004	0.350
Teflon- SO ₄ ²⁻	1.000	350	1	1.002	0.004	1.775
Cl ⁻	0.500	350	0	0.500	0.000	0.500
Ca ²⁺	0.150	350	7	0.152	0.004	0.648
Mg ²⁺	0.075	350	0	0.075	0.000	0.075
Na ⁺	0.125	350	0	0.125	0.000	0.125
K ⁺	0.150	350	0	0.150	0.000	0.150
Nylon- NO ₃ ⁻ -N	0.200	351	0	0.200	0.000	0.200
Nylon - SO ₄ ²⁻	1.000	351	1	1.000	0.000	1.050
Cellulose - SO ₄ ²⁻	2.000	351	75	2.167	0.264	4.055
LABORATORY BLANKS						
Teflon-NH ₄ ⁺ -N	0.500	104	2	0.501	0.001	0.550
Teflon- NO ₃ ⁻ -N	0.200	104	2	0.201	0.001	0.250
Teflon- SO ₄ ²⁻	1.000	104	0	1.000	0.000	1.000
Cl ⁻	0.500	104	0	0.500	0.000	0.500
Ca ²⁺	0.150	104	1	0.150	0.000	0.168
Mg ²⁺	0.075	104	0	0.075	0.000	0.075
Na ⁺	0.125	104	0	0.125	0.000	0.125
K ⁺	0.150	104	0	0.150	0.000	0.150
Nylon- NO ₃ ⁻ -N	0.200	104	0	0.200	0.000	0.200
Nylon -SO ₄ ²⁻	1.000	104	0	1.000	0.000	1.000
Cellulose -SO ₄ ²⁻	2.000	104	3	2.008	0.016	2.480
METHOD BLANKS						
Teflon-NH ₄ ⁺ -N	0.500	64	0	0.500	0.000	0.500
Teflon- NO ₃ ⁻ -N	0.200	65	0	0.200	0.000	0.200
Teflon- SO ₄ ²⁻	1.000	65	0	1.000	0.000	1.000
Cl ⁻	0.500	65	0	0.500	0.000	0.500
Ca ²⁺	0.150	64	0	0.150	0.000	0.150
Mg ²⁺	0.075	64	0	0.075	0.000	0.075
Na ⁺	0.125	64	0	0.125	0.000	0.125
K ⁺	0.150	64	0	0.150	0.000	0.150
Nylon- NO ₃ ⁻ -N	0.200	66	0	0.200	0.000	0.200
Nylon -SO ₄ ²⁻	1.000	66	0	1.000	0.000	1.000
Cellulose -SO ₄ ²⁻	2.000	79	0	2.000	0.000	2.000

Table 18 Summary of Filter Blanks for 2013 (2 of 2)

Parameter Name	Detection Limit Total μg	Total Number	Number > Detection Limit	Average Total μg	Average Absolute Deviation	Maximum Total μg
ACCEPTANCE TEST VALUES						
Teflon-NH ₄ ⁺ -N	0.500	235	0	0.500	0.000	0.500
Teflon- NO ₃ ⁻ -N	0.200	235	0	0.200	0.000	0.200
Teflon- SO ₄ ²⁻	1.000	235	0	1.000	0.000	1.000
Cl ⁻	0.500	235	0	0.500	0.000	0.500
Ca ²⁺	0.150	235	0	0.150	0.000	0.150
Mg ²⁺	0.075	235	0	0.075	0.000	0.075
Na ⁺	0.125	235	0	0.125	0.000	0.125
K ⁺	0.150	235	0	0.150	0.000	0.150
Nylon- NO ₃ ⁻ -N	0.200	220	0	0.200	0.000	0.200
Nylon -SO ₄ ²⁻	1.000	220	0	1.000	0.000	1.000
Cellulose -SO ₄ ²⁻	2.000	288	0	2.000	0.000	2.000

Note: Cellulose filters are not analyzed for ambient NO₃⁻. The blank results are used only for QC.

Table 19 Filter Packs Flagged as Suspect or Invalid

Site ID	Sample	Reason
First Quarter 2013		
BEL116, MD	1305001-10 1306001-10 1311001-10	Low flow volume due to recurrent power failures
JOT403, CA	1309001-43	Insufficient flow volume
LRL117, PA	1305001-47	Low flow volume due to telemetry problems
SHE604, WY	1303003-03	Insufficient flow volume
SHN418, VA	1310001-72	Low flow volume due to power failure
UVL124, MI	1303001-79	Low flow volume due to power failure
VPI120, VA	1303001-82	Low flow volume due to power failure
WFM105, NY	1304001-83*	The data logger was left in calibration mode after site visit
Second Quarter 2013		
CHA467, AZ	1318001-19	Insufficient flow volume
CHE185, OK	1323001-20	Insufficient flow volume
COW137, NC	1318001-24	Insufficient flow volume
GLR468, MT	1318001-33	Insufficient flow volume
GRC474, AZ	1319001-35	Insufficient flow volume
JOT403, CA	1318001-43	Insufficient flow volume
MAC426, KY	1317001-48	Potassium data invalidated as suspect
NIC001, NY	1316001-55 1317001-55	Insufficient flow volume
SUM156, FL	1321001-76	Insufficient flow volume
UND002, VT	1317001-78 1321001-78	Insufficient flow volume
VPI120, VA	1317001-82	Insufficient flow volume

Third Quarter 2013		
ACA416, ME	1330001-02	Invalidation of suspect potassium data
ANA115, MI	1329001-05	Insufficient flow volume
BAS601, WY	1333001-08*	Data transfer problems
BEL116, MD	1328001-10 1330001-10 1333001-10	Insufficient flow volume
BUF603, WY	1333003-01*	Data transfer problems
CHA467, AZ	1328001-19	Data transfer problems
EGB181, ON	1328001-29	Insufficient flow volume
FOR605, WY	1327003-02 1328003-02 1329003-02 1330003-02 1331003-02	Insufficient flow volume
GRC474, AZ	1331001-35	Data transfer problems
MOR409, WA	1328001-53	Data transfer problems
NEC602, WY	1333001-54*	Data transfer problems
SHE604, WY	1331003-03*	Data transfer problems
Fourth Quarter 2013		
ABT147, CT	1343001-01	Insufficient flow volume
FOR605, WY	1344003-02	Insufficient flow volume
GRC474, AZ	1346001-35 1348001-35	Insufficient flow volume
JOT403, CA	1344001-43	Insufficient flow volume
LAV410, CA	1347001-46	Insufficient flow volume
LRL117, PA	1344001-47	Insufficient flow volume
ROM206, CO	1348001-67	Insufficient flow volume
SHE604, WY	1343003-03 1344003-03 1345003-03	Insufficient flow volume
UND002, VT	1340001-78	Insufficient flow volume
WFM105, NY	1348001-83	Insufficient flow volume
WSP144, NJ	1343001-85	Insufficient flow volume

Notes: * Sample later accepted as valid. Data were recovered during Level 3 validation review.

Table 20 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
First Quarter 2013	
30	145
60	9
90	0
Unresolved by End of Quarter	3
Second Quarter 2013	
30	206
60	9
90	1
Unresolved by End of Quarter	14
Third Quarter 2013	
30	176
60	24
90	10
Unresolved by End of Quarter	9
Fourth Quarter 2013	
30	194
60	6
90	2
Unresolved by Date of Publication	7

Table 21 Field Calibration Failures by Parameter for 2013

Site ID	Parameter(s)
First Quarter 2013	
BEL116, MD	Relative Humidity
BFT142, NC	Solar Radiation
QAK172, OH	Temperature
Second Quarter 2013	
PAL190, TX	Solar Radiation
Third Quarter 2013	
None	
Fourth Quarter 2013	
CNT169, WY	Temperature

Note: Per CASTNET project protocols, data for all parameters except flow are flagged as “suspect” (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). If flow calibrations fall within 2x the criterion, these data are adjusted per approved protocol described in the CASTNET QAPP, (AMEC, 2012; 2013). Please refer to Table 14 for documentation of the QC failures affecting the validity of AQS-protocol ozone data.

Table 22 Accuracy Results for 2013 Field Measurements

Parameter	Percent Within Criterion
Flow Rate	95.2
Wind Speed < 5 m/s	100.0
Wind Speed ≥ 5 m/s	100.0
Wind Direction North	100.0
Wind Direction South	100.0
Temperature (0°C)	99.2
Temperature (ambient)	98.4
Delta Temperature (0°C)	100.0
Delta Temperature (ambient)	100.0
Relative Humidity	88.9*
Precipitation	100.0
Solar Radiation	77.8*
Wetness (w/in 0.5 volts)	100.0

Notes: °C = degrees Celsius

m/s = meters per second

* = Per CASTNET project protocols, data are flagged as “suspect” (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within 2x the criterion). All calibration failures reported in 2013 for the indicated parameters were within 2x the criterion with the exception of temperature at QAK172, OH in March 2013 – associated data were invalidated.

Figure 1 Reference Standard Results for Fourth Quarter 2013 (percent recovery)

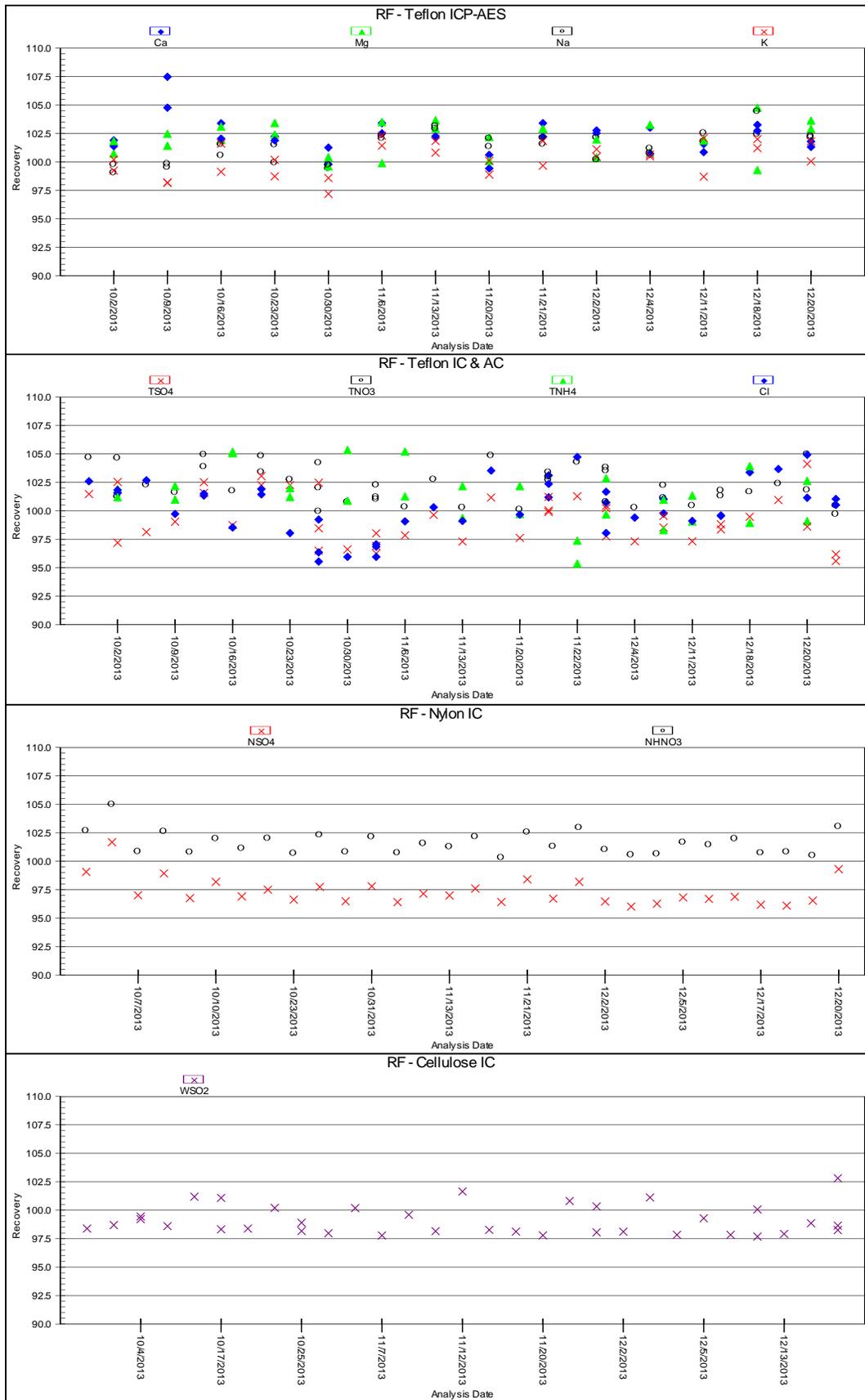


Figure 2 Continuing Calibration Spike Results for Fourth Quarter 2013 (percent recovery)

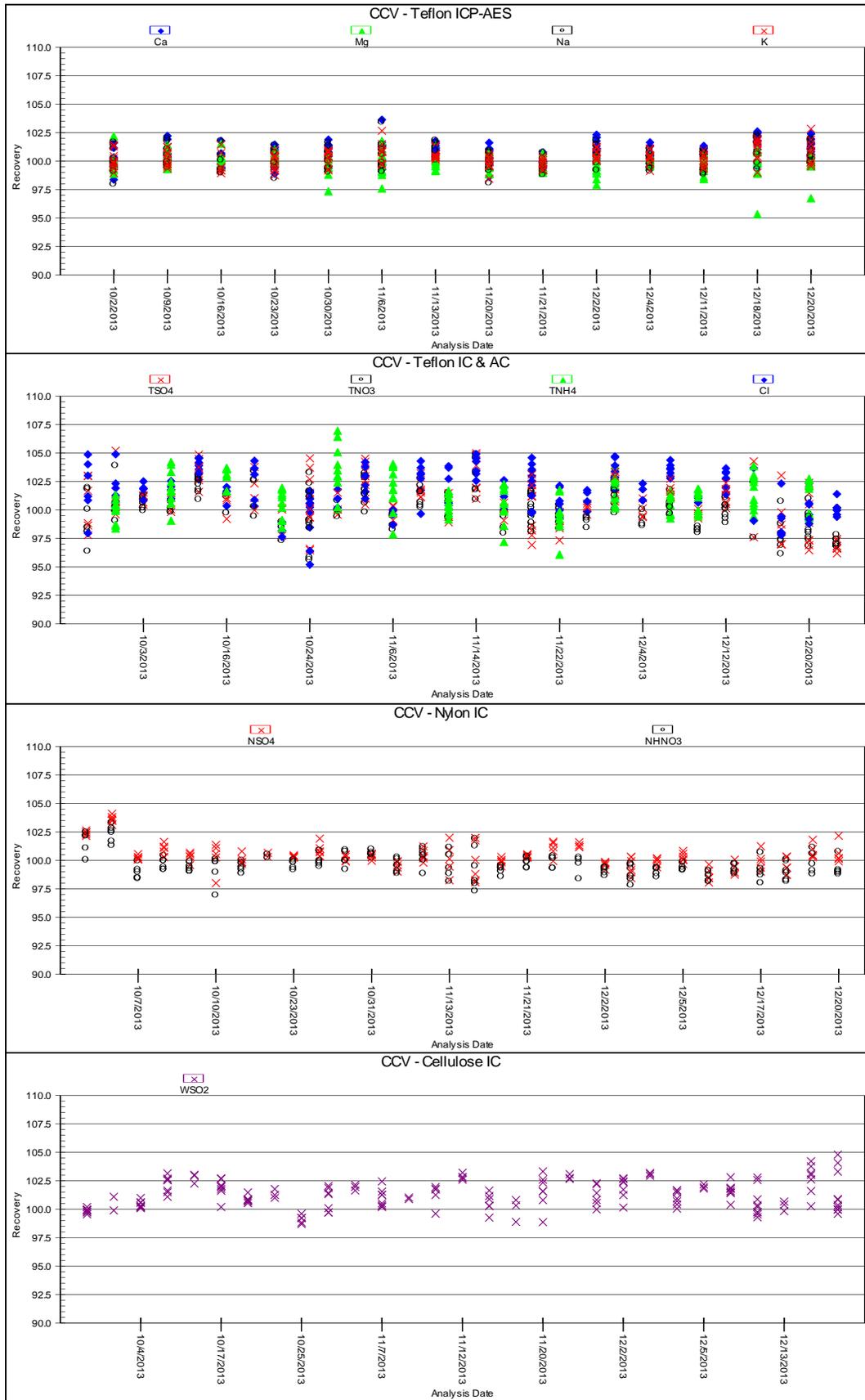


Figure 3 Replicate Sample Analysis Results for Fourth Quarter 2013 (percent difference)

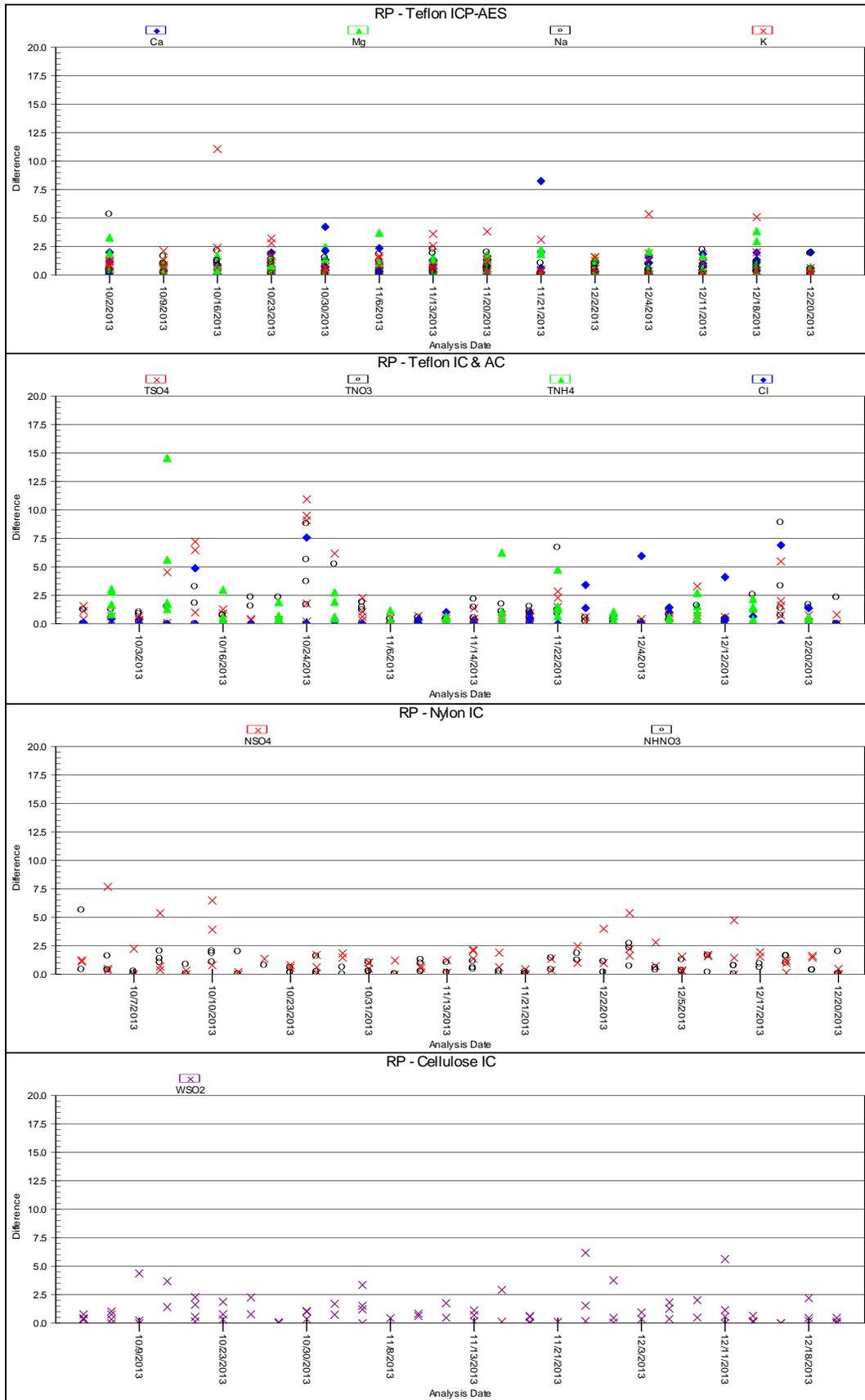
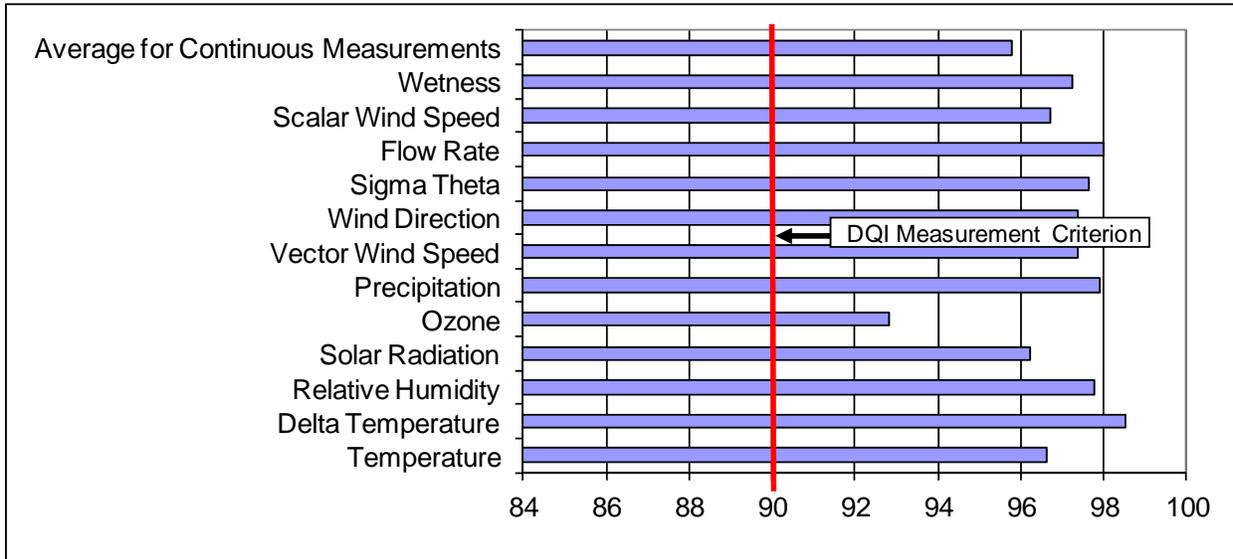


Figure 4 Percent Completeness of Measurements for Second Quarter 2012 through Third Quarter 2013*



Note: *Presents Level 3 data available during the fourth quarter of 2013

Figure 5 Laboratory Control Sample Results for Fourth Quarter 2013 (percent recovery)

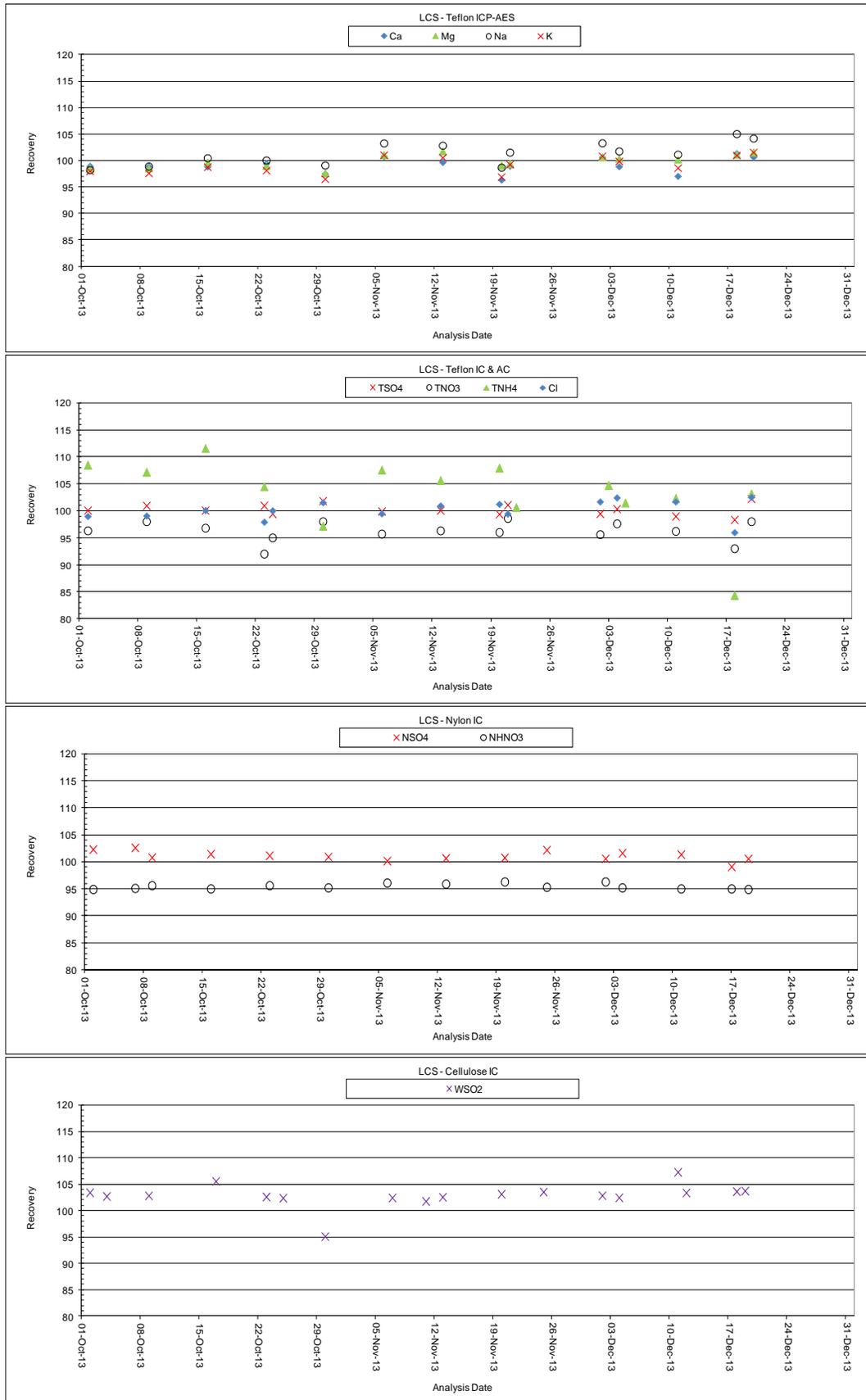


Figure 6 Method Blank Analysis Results for Fourth Quarter 2013 (total micrograms)

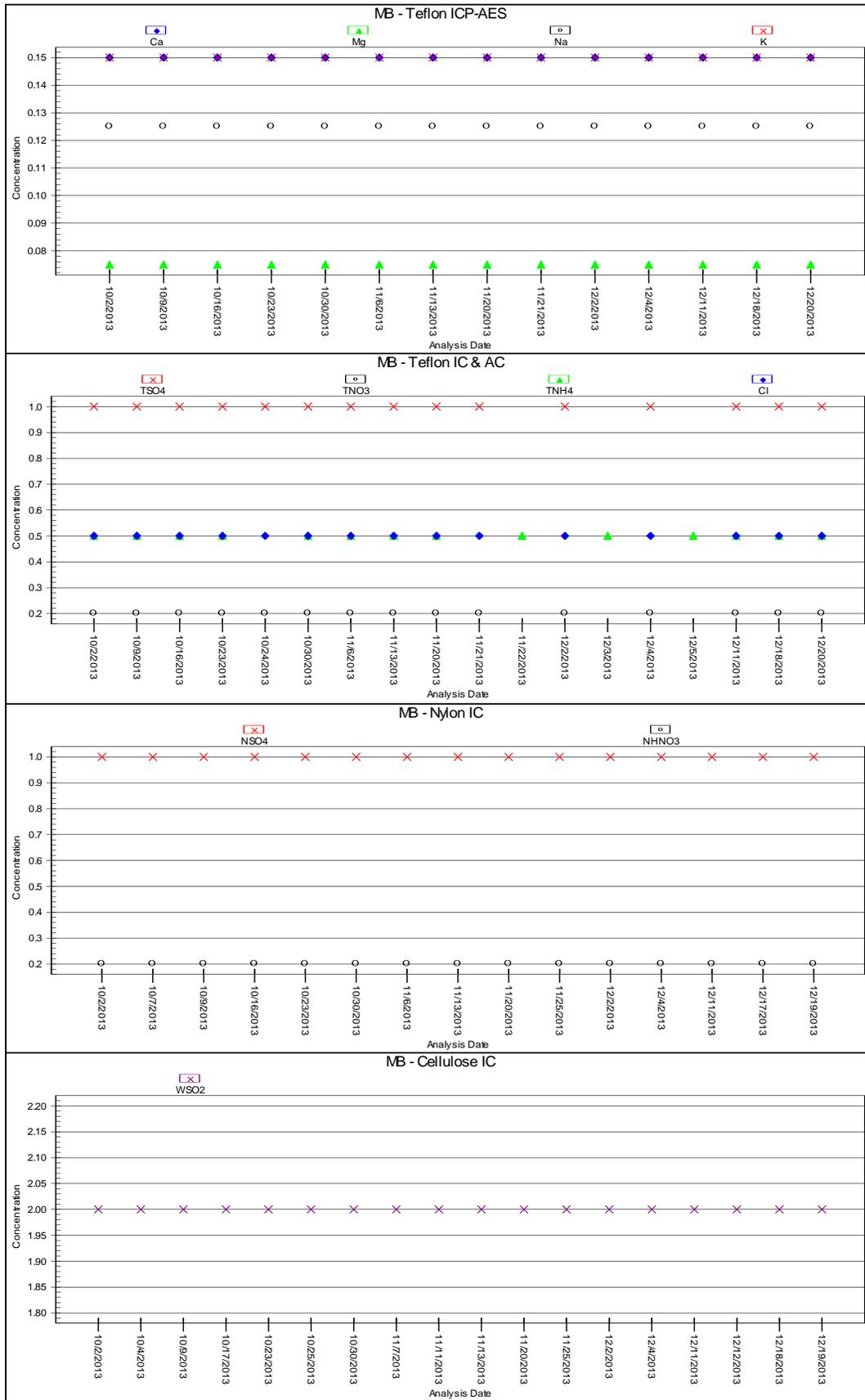


Figure 7 Laboratory Blank Analysis Results for Fourth Quarter 2013 (total micrograms)

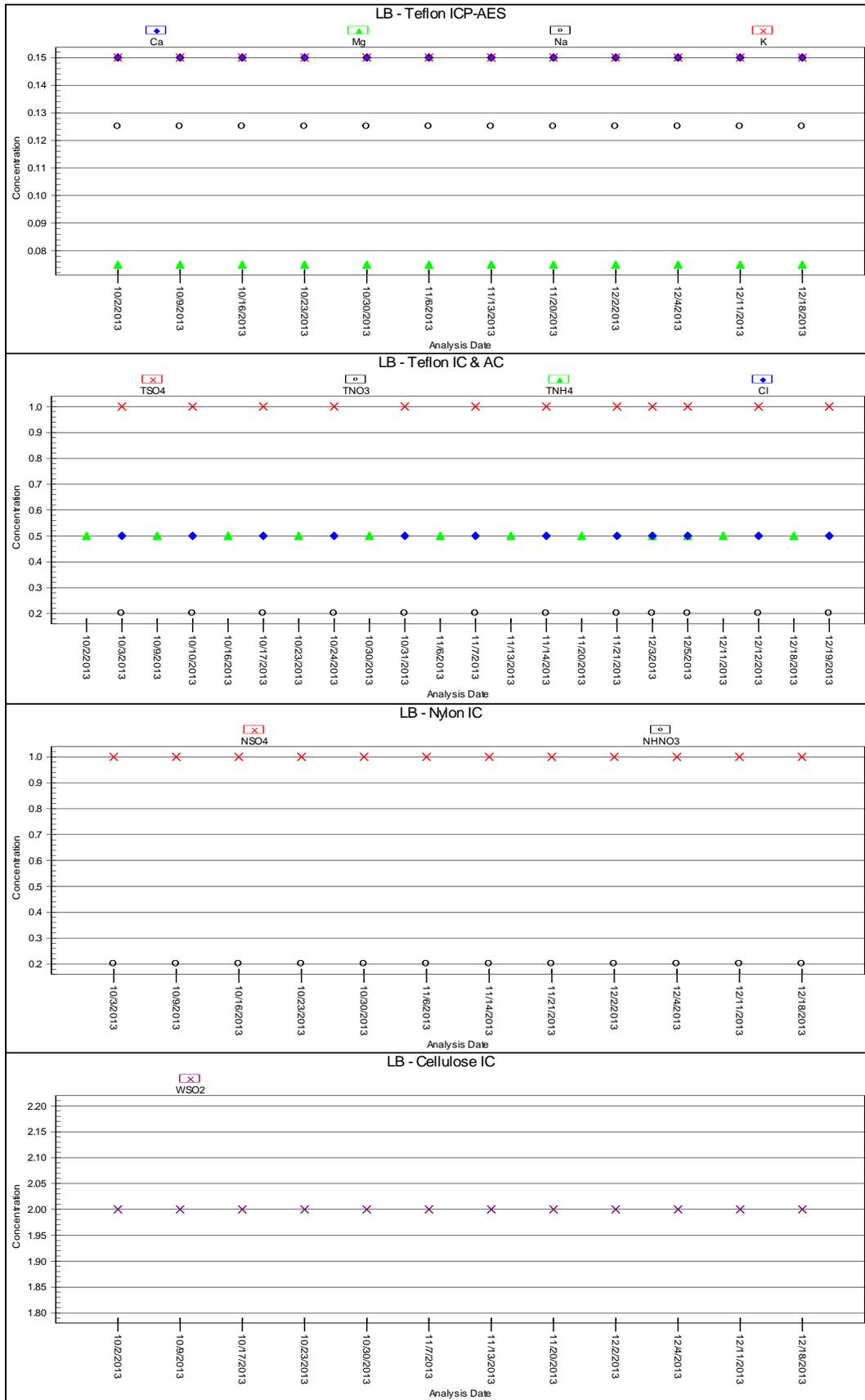


Figure 8 Field Blank Analysis Results for Fourth Quarter 2013 (total micrograms)

