



Clean Air Status and Trends Network

Second Quarter 2016 Quality Assurance Report

Summary of Quarterly Operations (April through June)

EPA Contract No. EP-W-16-015

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 second quarter 2016. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; Amec Foster Wheeler, 2014). 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.

Quarterly Summary

Investigation into the cause of the anomalous sulfur dioxide (SO₂) filter pack concentration measurements for third and fourth quarter 2015 continued. The laboratory had changed to a different supplier of the cellulose filter impregnation solution in April 2015, which continued through October 2015 and affected filter pack samples from mid-May through December 2015. During April 2016, SO₂ data from EPA-sponsored sites in calibration groups E-1 and SE-5 for January 2016 were reviewed and validated at Level 3, the final data validation level. January SO₂ values were reasonable and comparable with historical trends.

Amec Foster Wheeler completed the statistical analyses to evaluate the Teflon and nylon filter sulfate (SO₄²⁻) concentrations. The results were documented and archived. Improvements to the filter pack data review process were implemented through better outlier screening. Concentration data were reviewed from 2000 through 2015. No other year has the same distribution as 2015. Additionally, Amec Foster Wheeler is re-evaluating the reporting limit and acceptance test criteria for cellulose filters in order to establish an acceptance testing procedure with an established 95 percent confidence for a given set of cellulose filters.

A flagging system was approved by EPA for the third and fourth quarter 2015 SO₂ data where lower values will be invalidated, midrange values will be flagged as suspect, and upper values will be valid with a comment code. During third quarter 2016, data flags will be applied to these 2015 data and uploaded to EPA with the final, validated 2015 dataset.

The CASTNET QAPP Revision 8.3 was approved by EPA, the National Park Service, and Bureau of Land Management-Wyoming State Office. Before the QAPP Revision 8.3 was finalized for distribution, the zero QC check guidelines were changed from 3 parts per billion (ppb) to 1.5 ppb for ozone, SO₂ and nitrogen oxides (NO)/reactive oxides of nitrogen (NO_y) and from 40 ppb to 30 ppb for carbon monoxide. Amec Foster Wheeler will submit the finalized

QAPP Revision 8.3, including signatures, to EPA for upload to the CASTNET website in early third quarter 2016.

Table 1 lists the quarters of data that were validated to Level 3 during second quarter 2016 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 laboratory filter pack measurements. These criteria apply to the QC samples listed in the following section of this report. Table 4 presents the critical criteria for ozone monitoring. Table 5 presents the critical criteria for 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. Table 6 presents the number of analyses in each category that were performed during second quarter 2016.

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 7 presents the relevant sample receipt statistics for second quarter 2016.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for second quarter 2016. All results were within the criteria listed in Table 3. There were three nylon filter CCV results between 94.5 and 95 percent and one cellulose filter RP result less than 20.5 percent. All are within established criteria per the established rounding rules (ASTM, 2008).

Table 8 presents summary statistics of critical criteria measurements at ozone sites collected during second quarter 2016. The statistics presented contain data validated at Level 2 and Level 3. All data associated with QC checks that fail to meet the criteria listed in Table 4 were or will be invalidated unless the cause of failure has no effect on ambient data collection, and passing results still meet frequency criteria. Results in shaded cells either exceed documented criteria or are otherwise notable. Table 9 presents observations associated with the shaded cell results in Table 8.

Table 10 presents summary statistics of critical criteria measurements at trace-level gas monitoring sites collected during second quarter 2016. The statistics presented contain data validated at Level 2 and Level 3. All data associated with QC checks that fail to meet the criteria

listed in Table 5 were or will be invalidated unless the cause of failure has no effect on ambient data collection, and passing results still meet frequency criteria. Results in shaded cells either exceed documented criteria or are otherwise notable. Table 11 presents observations associated with the shaded cell results in Table 10.

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. 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. Figure 4 presents LCS analysis results for second quarter 2016. All recovery values were between 87 percent and 107 percent.

Blank Results

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for second quarter 2016. All second quarter results were within criteria (two times the reporting limit) listed in Table 3.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during second quarter 2016 are listed in Table 12. This table also includes associated site identification and a brief description of the reason the sample was flagged. During second quarter, 13 filter pack samples were invalidated.

Field Problem Count

Table 13 presents counts of field problems affecting continuous data collection for more than one day for second quarter 2016. 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.

References

Amec Foster Wheeler Environment & Infrastructure, Inc. (Amec Foster Wheeler). 2014. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 8.2*. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-16-015. 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). 2015. 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 during Second Quarter 2016

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-1/SE-5	August 2015 – January 2016	6	Quarter 4 2015	1
MW-7/W-9	September 2015 – February 2016	6	Quarter 4 2015	1
E-2/MW-8	October 2015 – March 2016	6	Quarter 4 2015 – Quarter 1 2016	2

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

Table 2 Field Calibration Schedule for 2016

Calibration Group	Months Calibrated	Sites Calibrated			
Eastern Sites (24 Total)					
E-1 (8 Sites)	February/August	BEL116, MD BWR139, MD	WSP144, NJ CTH110, NY	ARE128, PA PSU106, PA	PED108, VA VPI120, VA
E-2 (11 Sites)	April/October	ABT147, CT ASH135, ME HOW191, ME	WST109, NH CAT175, NY HWF187, NY	NIC001, NY WFM007, NY WFM105, NY	EGB181, ON UND002, VT
E-3 (5 Sites)	May/November	KEF112, PA MKG113, PA	LRL117, PA PAR107, WV	CDR119, WV	
Southeastern Sites (11 Total)					
SE-4 (7 Sites)	January/July	SND152, AL GAS153, GA	BFT142, NC CND125, NC	COW005, NC COW137, NC	SPD111, TN
SE-5 (4 Sites)	February/August	CAD150, AR CVL151, MS	IRL141, FL SUM156, FL		
Midwestern Sites (19 Total)					
MW-6 (6 Sites)	January/July	CDZ171, KY CKT136, KY	MCK131, KY MCK231, KY	PNF126, NC ESP127, TN	
MW-7 (9 Sites)	March/September	ALH157, IL BVL130, IL STK138, IL	VIN140, IN RED004, MN DCP114, OH	OXF122, OH QAK172, OH PRK134, WI	
MW-8 (4 Sites)	April/October	SAL133, IN HOX148, MI	ANA115, MI UVL124, MI		
Western Sites (11 Total)					
W-9 (5 Sites)	March/September	KNZ184, KS KIC003, KS	CHE185, OK SAN189, NE	ALC188, TX	
W-10 (6 Sites)	May/November	GTH161, CO ROM206, CO	NPT006, ID CNT169, WY	PND165, WY PAL190, TX	

Table 3 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-OES	20	95 - 105	0.005	0.125
Potassium (K ⁺)	ICP-OES	20	95 - 105	0.006	0.15
Magnesium (Mg ²⁺)	ICP-OES	20	95 - 105	0.003	0.075
Calcium (Ca ²⁺)	ICP-OES	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-OES reference standards.

AC = automated colorimetry

IC = ion chromatography

ICP-OES = inductively coupled plasma-optical 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 Foster Wheeler, 2014).

Table 4 Ozone Critical Criteria*

Type of Check	Analyzer Response
Zero	Less than ± 1.5 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

Notes:* Applies to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (EPA, 2015). 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 5 Trace-level Gas Monitoring Critical Criteria *

Parameter	Analyzer Response	
	Zero Check	Span Check / Single Point QC Check
SO ₂	Less than ± 1.5 ppb	Less than or equal to ± 10 percent between supplied and observed concentrations
NO _y	Less than ± 1.5 ppb	
CO	Less than ± 30 ppb	

Notes: *Applies to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (EPA, 2015). 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

ppb = parts per billion

Table 6 QC Analysis Count for Second Quarter 2016

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⁻	63	176	75	15	24	90
	NO ₃ ⁻	63	176	75	15	24	90
	NH ₄ ⁺	31	162	75	15	24	90
	Cl ⁻	63	176	75	15	24	90
	Ca ²⁺	31	166	75	15	24	90
	Mg ²⁺	31	166	75	15	24	90
	Na ⁺	31	166	75	15	24	90
	K ⁺	31	166	75	15	24	90
Nylon	SO ₄ ²⁻	44	183	75	17	24	90
	NO ₃ ⁻	44	183	75	17	24	90
Cellulose	SO ₄ ²⁻	42	191	76	18	24	90

Table 7 Filter Pack Receipt Summary for Second Quarter 2016

Count of samples received more than 14 days after removal from tower:	8
Count of all samples received:	863
Fraction of samples received within 14 days:	0.991
Average interval in days:	4.388
First receipt date:	04/01/2016
Last receipt date:	06/30/2016

Table 8 Ozone QC Summary for Second Quarter 2016 (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	100.00	0.60	100.00	0.63	0.10	100.00	0.18
ALC188, TX	100.00	1.82	98.81	1.63	0.26	100.00	0.26
ALH157, IL	100.00	0.82	100.00	0.65	0.10	100.00	0.12
ANA115, MI	100.00	0.95	100.00	0.82	0.08	98.78	0.35
ARE128, PA	100.00	1.27	100.00	1.35	0.13	98.88	0.39
ASH135, ME	100.00	0.89	100.00	0.67	0.10	100.00	0.17
BEL116, MD	100.00	0.92	98.91	0.73	0.28	100.00	0.16
BFT142, NC	96.88	1.71	97.92	1.77	0.25	100.00	0.23
BVL130, IL	97.87	3.07	97.87	3.05	1.35	97.87	0.95
BWR139, MD	98.91	2.13	89.13	4.57	1.72	83.53	2.68
CAD150, AR	97.85	1.17	97.85	1.01	0.28	98.92	0.38
CDR119, WV	100.00	1.39	100.00	1.51	0.12	100.00	0.32
CDZ171, KY	100.00	0.77	98.94	0.76	0.26	100.00	0.17
CKT136, KY	100.00	0.53	100.00	0.78	0.09	100.00	0.14
CND125, NC	100.00	1.78	100.00	1.19	0.21	96.97	0.36
CNT169, WY	100.00	2.32	100.00	1.34	0.11	100.00	0.72
COW137, NC	100.00	1.23	100.00	1.74	0.11	100.00	0.26
CTH110, NY	100.00	0.75	100.00	1.07	0.13	100.00	0.32
CVL151, MS	98.94	0.70	100.00	0.44	0.06	100.00	0.26
DCP114, OH	100.00	0.98	100.00	1.08	0.15	98.90	0.12
ESP127, TN	100.00	1.51	100.00	1.05	0.13	100.00	0.14
GAS153, GA	98.90	0.47	100.00	0.41	0.05	100.00	0.41
GTH161, CO	98.92	2.57	97.85	2.30	0.28	100.00	0.16

Table 8 Ozone QC Summary for Second Quarter 2016 (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
HOX148, MI	97.89	2.36	97.89	2.56	2.13	97.89	0.97
HWF187, NY	98.92	0.85	100.00	0.83	0.09	100.00	0.15
IRL141, FL	97.94	1.50	94.85	2.35	1.28	95.88	1.78
KEF112, PA	100.00	0.79	100.00	1.14	0.16	98.84	0.28
LRL117, PA	100.00	0.33	100.00	0.68	0.07	100.00	0.18
MCK131, KY	95.65	2.99	97.83	1.71	0.96	97.83	1.08
MCK231, KY	100.00	1.04	100.00	1.16	0.18	100.00	0.27
MKG113, PA	100.00	0.61	100.00	0.63	0.07	97.75	0.25
OXF122, OH	95.10	1.99	93.14	3.25	1.05	91.00	1.49
PAL190, TX	95.06	1.70	98.75	1.59	0.24	93.75	0.66
PAR107, WV	100.00	1.00	98.94	1.03	0.23	98.94	0.21
PED108, VA	100.00	2.32	96.81	2.67	0.22	98.94	0.25
PND165, WY	100.00	1.24	100.00	2.61	0.14	100.00	0.58
PNF126, NC	100.00	2.03	100.00	2.20	0.16	98.78	0.22
PRK134, WI	100.00	2.13	98.94	1.81	0.28	98.94	0.36
PSU106, PA	100.00	0.77	100.00	0.56	0.08	100.00	0.39
QAK172, OH	96.81	2.23	93.41	3.88	2.42	92.31	1.57
ROM206, CO	100.00	0.66	100.00	0.67	0.10	100.00	0.18
SAL133, IN	98.84	1.65	100.00	0.75	0.11	100.00	0.18
SAN189, NE	100.00	0.54	100.00	0.88	0.09	100.00	0.16
SND152, AL	94.05	1.75	98.80	1.36	0.20	100.00	0.25
SPD111, TN	100.00	0.84	98.94	0.64	0.13	100.00	0.24
STK138, IL	98.94	2.52	98.94	1.02	0.27	92.55	0.71
SUM156, FL	97.85	1.67	100.00	1.04	0.19	100.00	0.24
UVL124, MI	100.00	0.96	100.00	0.86	0.10	100.00	0.15
VIN140, IN	100.00	3.53	100.00	3.65	0.31	100.00	0.27
VPI120, VA	90.82	7.61	91.84	3.50	2.08	91.84	2.94
WSP144, NJ	100.00	0.65	100.00	0.76	0.13	97.83	0.50
WST109, NH	100.00	0.47	100.00	0.54	0.09	97.85	0.18

Notes: ¹ Percentage of comparisons that pass the criteria listed in Table 4. Values falling below 90 percent are addressed in Table 9.

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 4 are addressed in Table 9.

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 9.

%D = percent difference

CL = confidence limit

ppb = parts per billion

Table 9 Ozone QC Observations for Second Quarter 2016

Site ID	QC Criterion	Comments
BWR139, MD	% Single Point QC Pass % Zero Pass Zero Average	The site analyzer malfunctioned at the end of March and was replaced early April. Associated data were invalidated.
IRL141, FL	Zero Average	There were intermittent system moisture issues in early to mid-June. Associated data were invalidated.
QAK172, OH	Zero Average	There were system moisture issues in early June. Associated data were invalidated.
VPI120, VA	Span %D Zero Average	The site analyzer was left in service mode in early June. The sampling line broke at the tower hinge point (5.5 meters) at the end of June. Associated data were invalidated.

Notes: %D = percent difference

Table 10 Trace-level Gas QC Summary for Second Quarter 2016

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	100.00	2.16	100.00	1.04	0.22	100.00	0.96
NO _y	63.64	27.52	66.67	25.05	8.86	93.94	0.27
BVL130, IL							
SO ₂	100.00	2.14	100.00	0.81	0.16	100.00	0.26
NO _y	100.00	1.34	100.00	1.46	0.30	100.00	1.04
CO	100.00	0.59	93.02	3.79	1.12	93.33	11.27
HWF187, NY							
NO _y	100.00	1.22	100.00	1.13	0.24	100.00	0.24
PND165, WY							
NO _y	100.00	0.84	100.00	5.06	0.79	100.00	0.12
PNF126, NC							
NO _y	100.00	1.68	100.00	2.23	0.34	97.14	0.91
ROM206, CO							
NO _y	100.00	1.32	100.00	1.47	0.27	97.06	0.88

Notes: ¹ Percentage of comparisons that pass the criteria listed in Table 5. Values falling below 90 percent are addressed in Table 11.

² Absolute value of the average percent differences between the supplied and observed concentrations. Values exceeding the criteria listed in Table 5 are addressed in Table 11.

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 11.

%D = percent difference

CL = confidence limit

ppb = parts per billion

Table 11 Trace-level Gas QC Observations for Second Quarter 2016

Site ID	Parameter	QC Criterion	Comments
BEL116, MD	NO _y	% Span Pass Span %D % Single Point QC Pass Single Point QC %D	The site analyzer drifted out of calibration mid-May and required servicing. The analyzer was serviced and calibrated in June. Data associated with failing QC checks in May were invalidated.

Notes: %D = percent difference

Table 12 Filter Packs Flagged as Suspect or Invalid during Second Quarter 2016

Site ID	Sample No.	Reason
ALC188, TX	1618004-01	Data logger malfunction
BFT142, NC	1615001-07	Improper installation of the filter pack
CAN407, UT	1619003-03	Insufficient valid flow volume
ESP127, TN	1619001-23	Insufficient valid flow volume
JOT403, CA	1618003-12	Insufficient valid flow volume
MAC426, KY	1615003-14	Insufficient valid flow volume
NIC001, NY	1617001-36	Insufficient valid flow volume
NPT006, ID	1618004-04	"Calibration in progress" status flags for several days. May be recoverable pending Level 3 validation.
SND152, AL	1619001-48	Data acquisition system router malfunction
SUM156, FL	1616001-51 1617001-51 1618001-51	Suspect* potassium values were invalidated. Other parameters were reported as valid.
WNC429, SD	1615003-23	Insufficient valid flow volume

*Determined to be suspect during routine review of filter pack concentrations.

Table 13 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	244
60	4
90	0
Unresolved by End of Quarter	1

Figure 1 Reference Standard Results for Second Quarter 2016 (percent recovery)

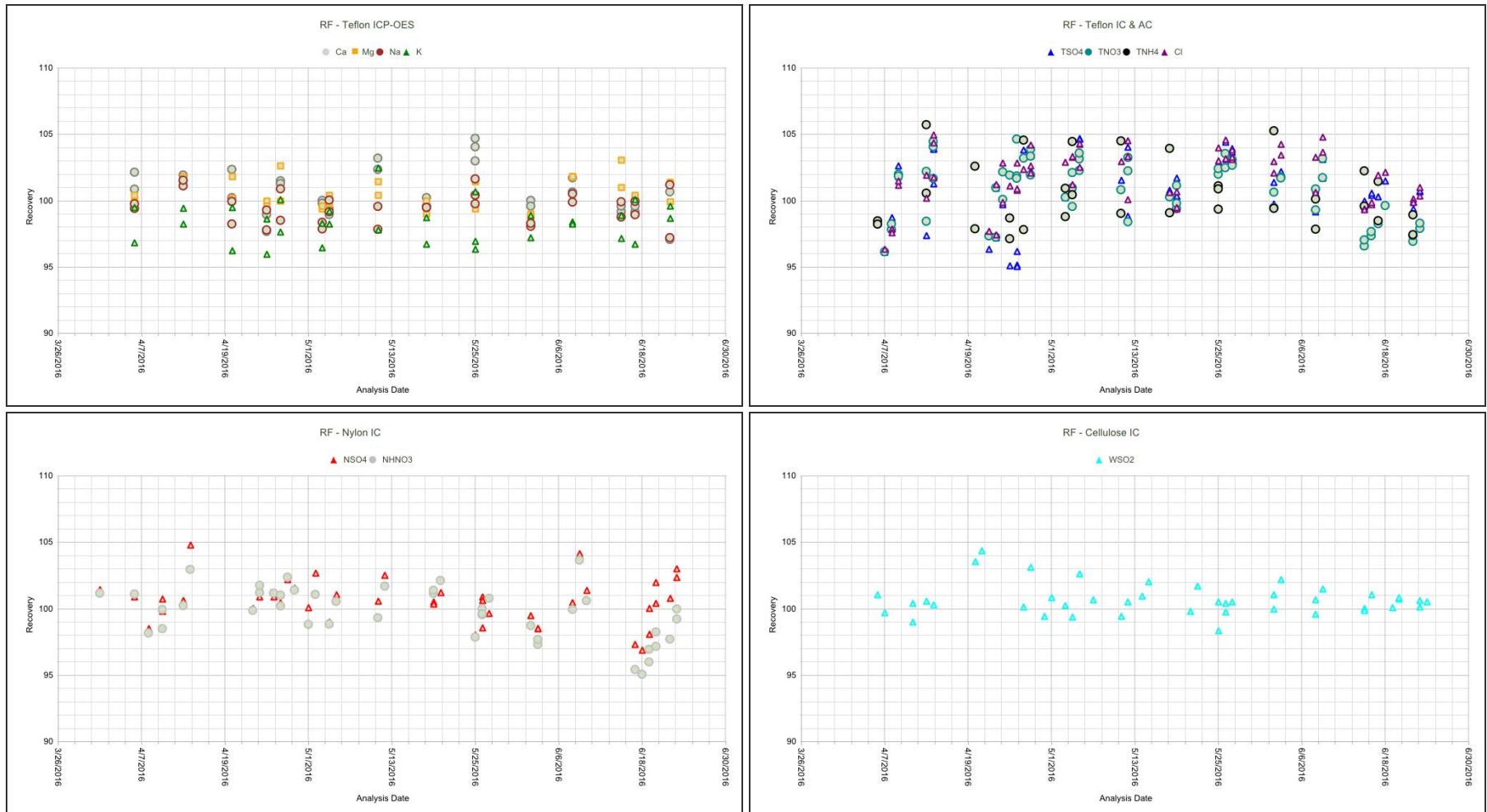


Figure 2 Continuing Calibration Spike Results for Second Quarter 2016 (percent recovery)

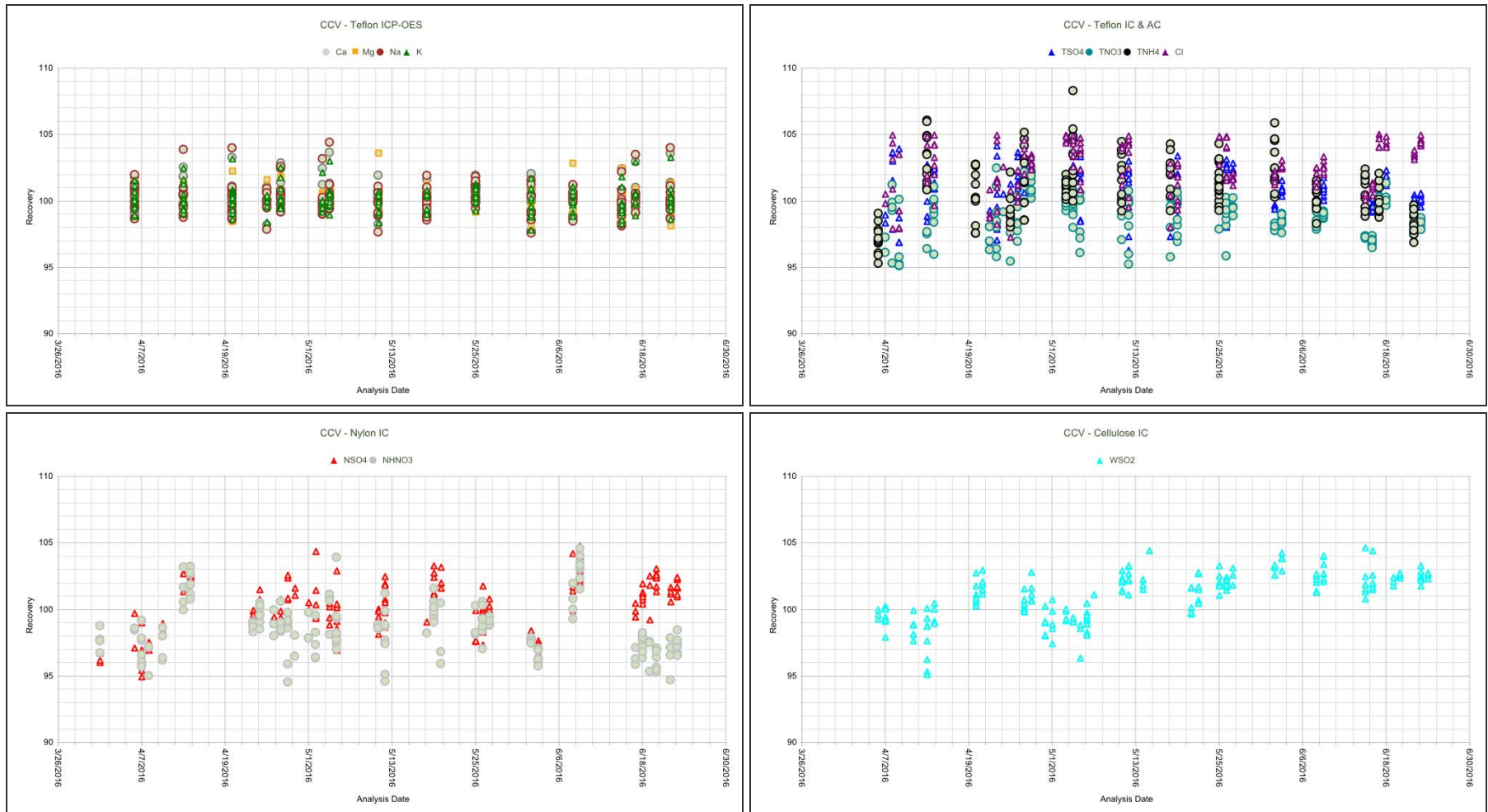


Figure 3 Replicate Sample Analysis Results for Second Quarter 2016 (percent difference)

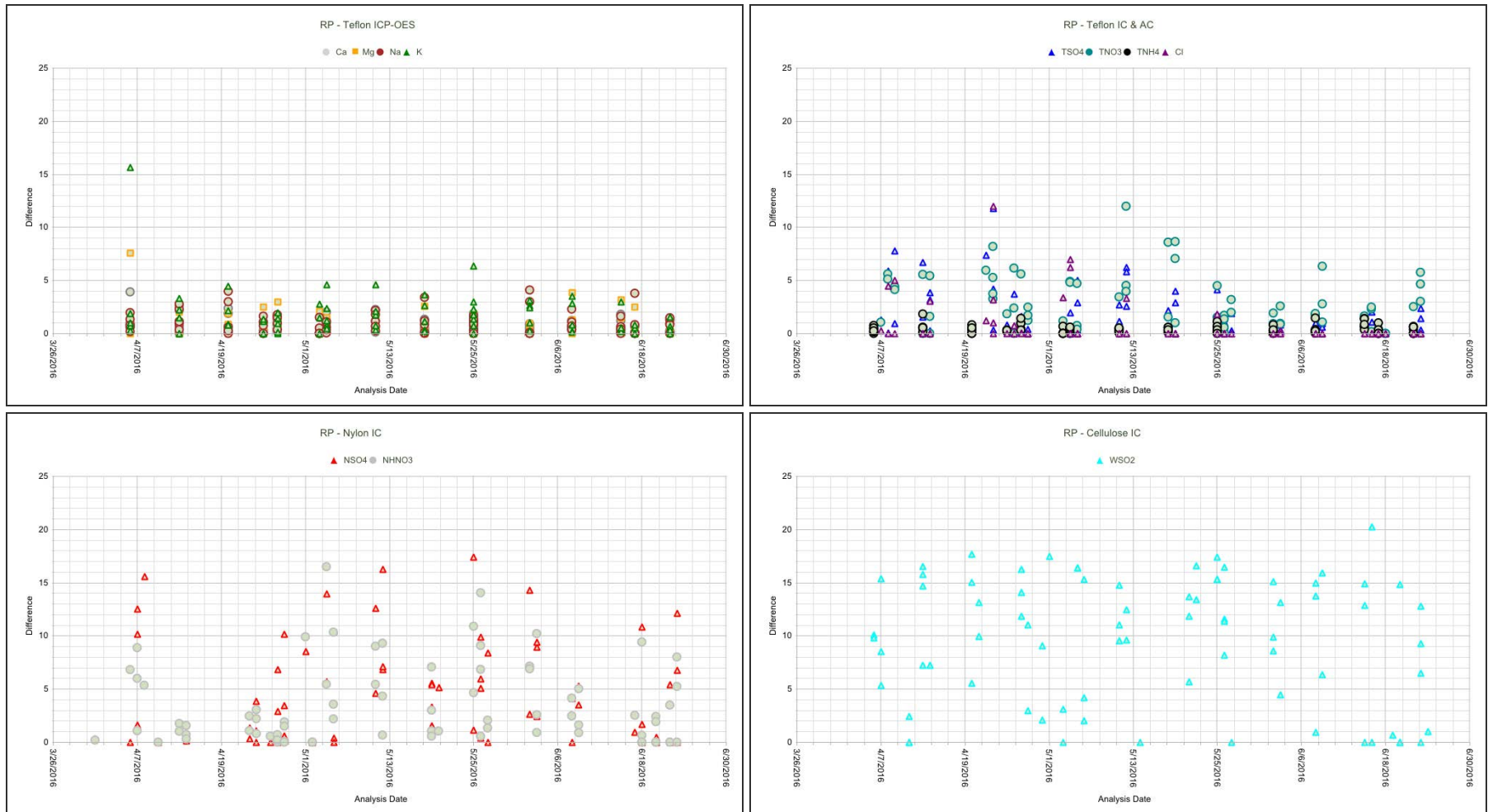


Figure 4 Laboratory Control Sample Results for Second Quarter 2016 (percent recovery)

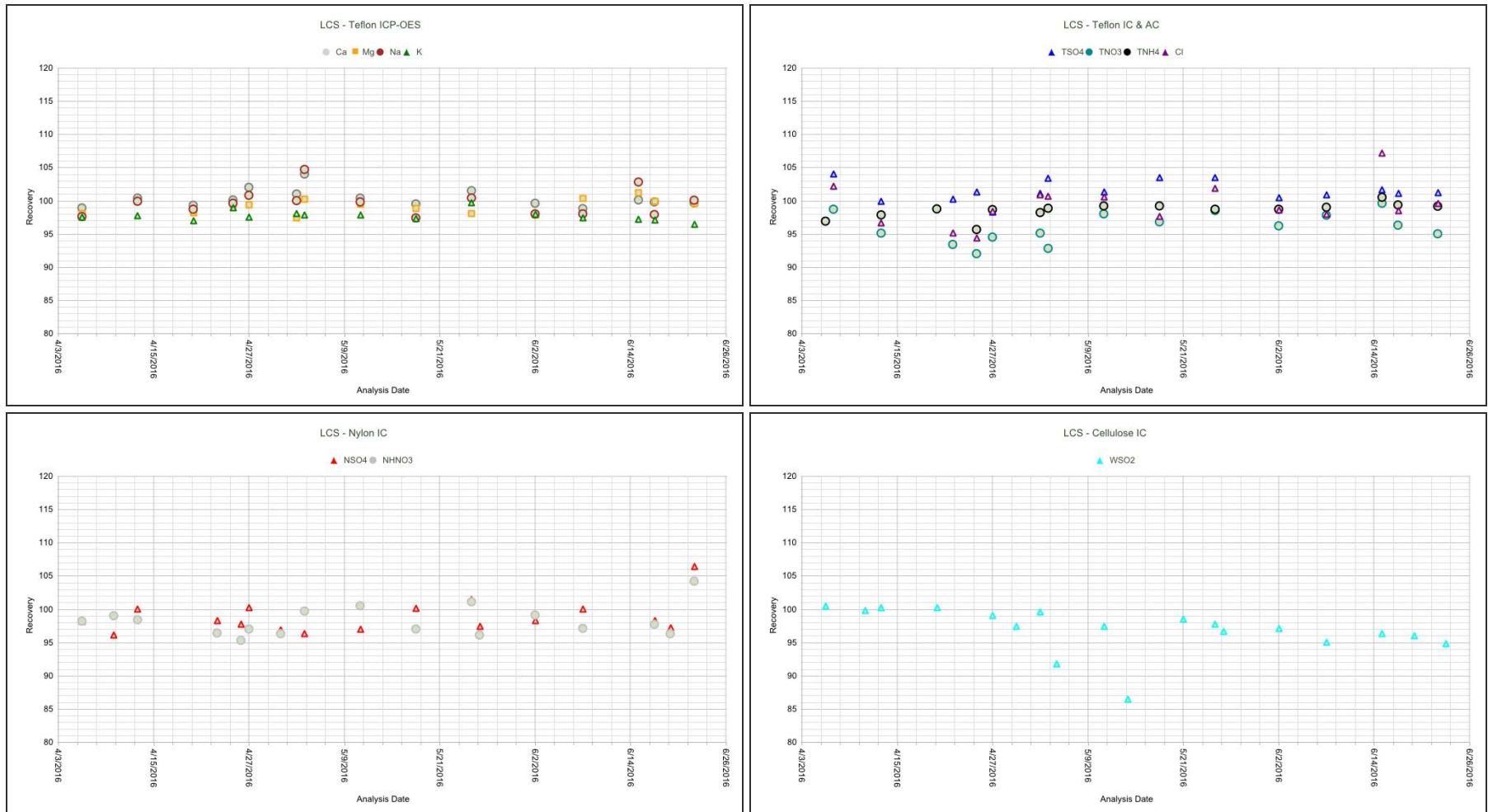


Figure 5 Method Blank Analysis Results for Second Quarter 2016 (total micrograms)

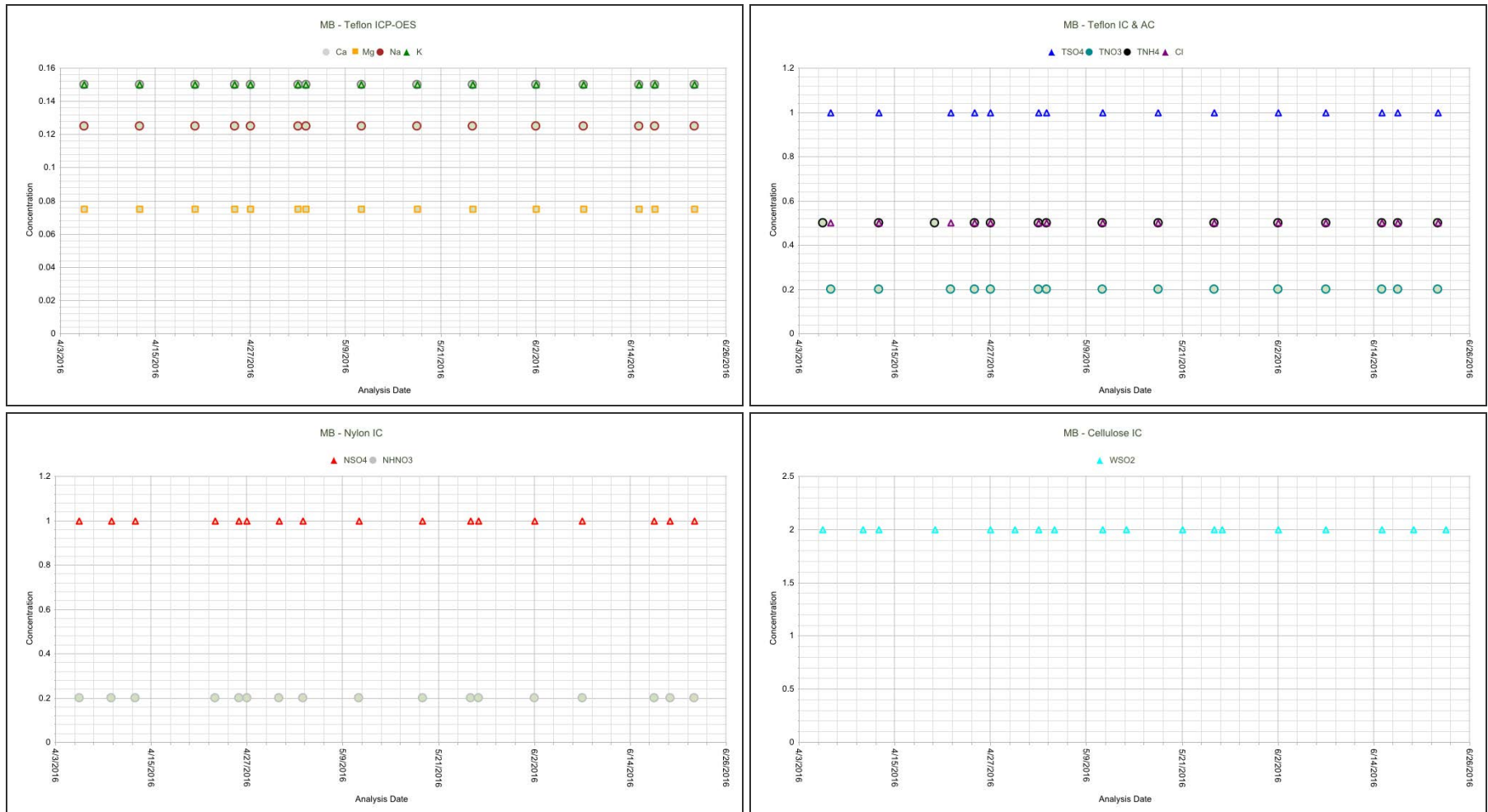


Figure 6 Laboratory Blank Analysis Results for Second Quarter 2016 (total micrograms)

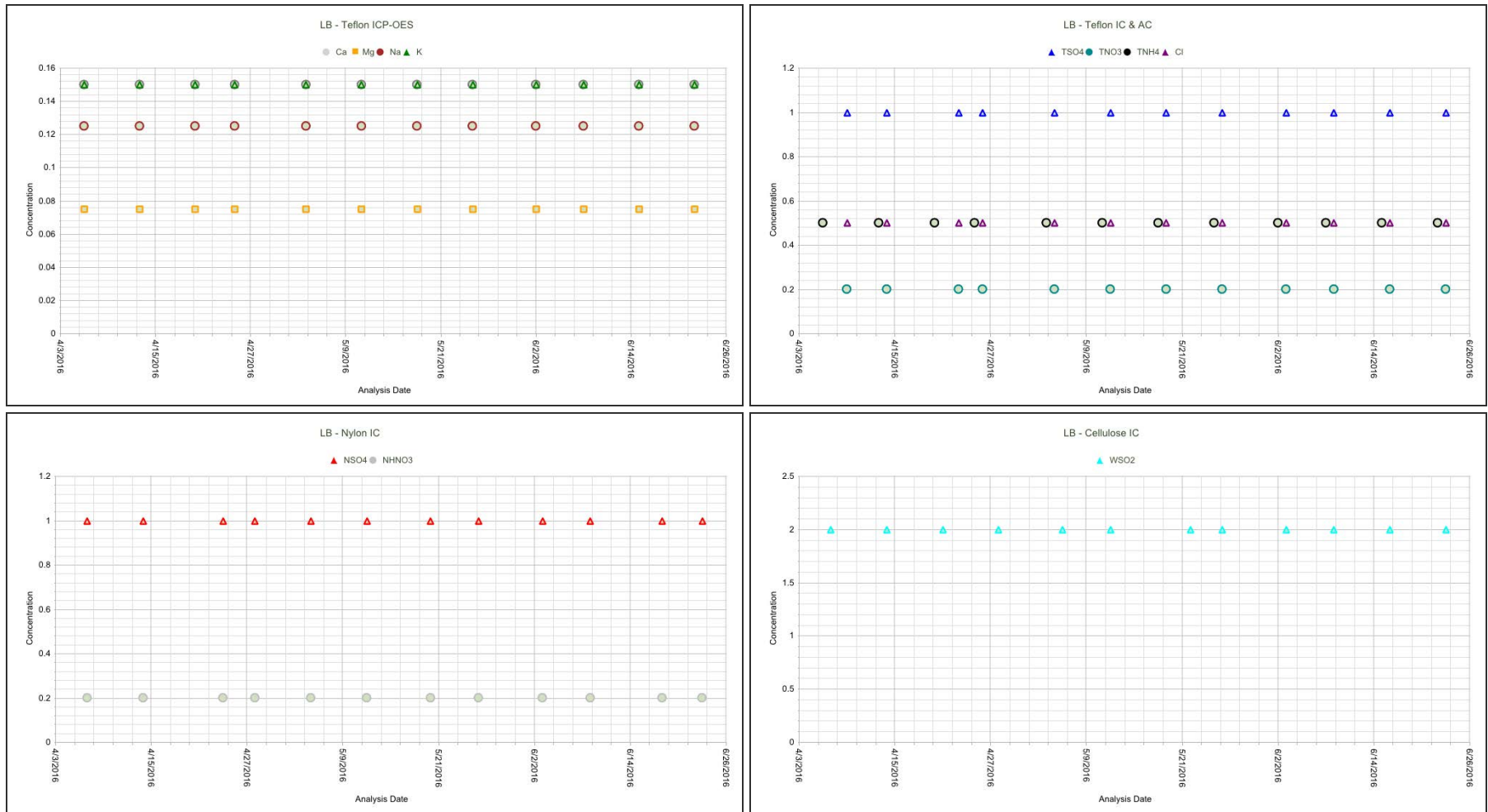


Figure 7 Field Blank Analysis Results for Second Quarter 2016 (total micrograms)

