Summary of Quarterly Operations (July through September)

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 third quarter 2018. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; Wood, 2017). 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

The annual management review report in support of International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025:2005 accreditation was completed and distributed to the Wood QA and management teams for review and comment. The meeting to discuss the report was held July 30, 2018. The management team was complimentary of the program. A recommendation for improvement was to purchase an additional ion chromatography instrument for the CASTNET analytical laboratory. It was also recommended that the management review meeting be held earlier in the year in 2019, as has been done in previous years. Additionally, the management team requested a written report on the VPNFilter malware attack outlining the risks and corrective actions taken.

The State of North Carolina Department of Environmental Quality (NCDEQ) audited the four CASTNET ozone sites in the state during July 2018. Three of the four sites failed the performance evaluation audit at the 15 parts per billion challenge point. The failures were unexpected since the sites passed daily zero, span, and precision QC checks. The NCDEQ used a Thermo PS transfer standard for the audit. Wood plans to meet with the auditor and other NCDEQ personnel at a CASTNET site during fourth quarter to work out why the sites failed the audits.

Investigation into possible potassium and calcium contamination of filter packs continued. It was determined that the foil used to line the bins for the washing and drying of filter pack parts was the source of the contamination. In late July 2018, use of foil was discontinued. Laboratory and field blanks continued to be tested through third quarter. A set of filter packs was prepared each week during July and August for testing as process blanks to verify the effectiveness of the corrective actions taken. As of September, none of the filter blanks analyzed exceeded the acceptance criterion for either potassium or calcium.

Wood continued to work with MTL Corp to develop an acceptable standard operating procedure (SOP) for consistently providing pre-washed nylon filters that pass CASTNET acceptance tests. Comments were provided to MTL on their draft SOP by the CASTNET QA Manager and CASTNET

Laboratory Operations Manager. Until the SOP is finalized by MTL and approved by Wood, Wood will continue washing the MTL nylon filters in-house.

Breakthrough testing of the MTL Corp nylon filters continued during third quarter. Wood's test results did not show evidence of breakthrough while the Canadian Air and Precipitation Monitoring Network (CAPMoN) continues to detect breakthrough. Wood worked with personnel from CAPMoN to investigate why test results between the two networks differ. A small aliquot from select CASTNET filter extracts was sent to CAPMoN's laboratory for evaluation. CAPMoN uses different ion chromatography equipment, and the associated analytical method used by CAPMoN provides a lower detection limit than that used for CASTNET. CAPMoN did not find evidence of breakthrough in the CASTNET filter extracts. CAPMoN is now investigating whether the filter pack housings used by the two networks are a factor.

Wood received the report on the laboratory intercomparison proficiency test (PT) to verify that the Wisconsin State Laboratory of Hygiene meets the National Atmospheric Deposition Program's standards as its Central Analytical Laboratory. The Wood analytical laboratory compared well with the other laboratories.

During August 2018, Wood received preliminary results for sample analyses submitted for PT study 112 for Rain and Soft Waters to the National Laboratory of Environmental Testing, a branch of the National Water Research Institute with Environment Canada that provides quality assurance services. Preliminary results indicated a flag for sulfate due to a data entry error. A corrective action was initiated, and the CASTNET QA Manager developed a spreadsheet to facilitate double entry and detect data entry errors.

Table 1 lists the quarters of data that were validated to Level 3 during third quarter 2018 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 third quarter 2018.

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 third quarter 2018.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for third quarter 2018. All results were within the criteria listed in Table 3.

Table 8 presents summary statistics of critical criteria measurements at ozone sites collected during third quarter 2018. 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 third quarter 2018. 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. During third quarter, no values exceeded documented criteria or were otherwise notable.

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. Figure 4 presents LCS analysis results for third quarter 2018. All recovery values were between 94 percent and 108 percent.

Blank Results

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for third quarter 2018. All third quarter results were within criteria (two times the reporting limit) listed in Table 3 with the exception of two Teflon FB calcium results at 2.3 and 2.4 times the reporting limit and one Teflon FB potassium result at 2.3 times the reporting limit.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during third quarter 2018 are listed in Table 11. This table also includes associated site identification and a brief description of the reason the sample was flagged. During third quarter, 10 filter pack samples were invalidated.

Field Problem Count

Table 12 presents counts of field problems affecting continuous data collection for more than one day for third quarter 2018. 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

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.

International Organization for Standardization (ISO). 2005. *Statistical Methods for the Use in Proficiency Testing by Interlaboratory Comparisons, Annex C, Robust Analysis, Section C.1: Algorithm A*. Standard 13528. ISO 13528:2005(E).

U.S. Environmental Protection Agency (EPA). 2017. Title 40 *Code of Federal Regulations* Part 58, "Appendix A to Part 58 – Quality Assurance Requirements for Monitors used in Evaluations of National Ambient Air Quality Standards."

Wood Environment & Infrastructure Solutions, Inc. (Wood) formerly known as Amec Foster Wheeler Environment & Infrastructure, Inc. 2017. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan* (QAPP) Revision 9.1. 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. https://java.epa.gov/castnet/documents.do.

Table 1 Data Validated to Level 3 during Third Quarter 2018

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10†	November 2016 – April 2018	6	Quarter 1 2018	1
SE-4/MW-6‡	January 2018 – June 2018	6	Quarter 1 2018 – Quarter 2 2018	2

Notes: * The sites contained in each calibration group are listed in Table 2.
† Contains ROM206 of the ROM406/ROM206 co-located pair
‡ Contains MCK131/231 co-located pair

Table 2 Field Calibration Schedule for 2018

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[2]	NIC001, 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 (6 Sites)	January/July	SND152, AL GAS153, GA	BFT142, NC CND125, NC	COW137, NC SPD111, TN	
SE-5 (5 Sites)	February/August	CAD150, AR IRL141, FL	SUM156, FL CVL151, MS	DUK008, NC[1]	
Midwestern Sites (19 Total)					
MW-6 (6 Sites)	January/July	CDZ171, KY CKT136, KY	MCK131, KY MCK231, KY	PNF126, NC[2] ESP127, TN	
MW-7 (9 Sites)	March/September	ALH157, IL BVL130, IL[3] 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[1]	NPT006, ID CNT169, WY	PND165, WY[1] PAL190, TX	

Notes: [1] Trace-level gas calibrations are performed quarterly in February, May, August, and November.
[2] Trace-level gas calibrations are performed quarterly in January, April, July, and October.
[3] Trace-level gas calibrations are performed quarterly in March, June, September, and December.

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 co-located 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, (Wood, 2017).

Table 4 Ozone Critical Criteria*

Type of Check	Analyzer Response
Zero	Less than ± 3.1 parts per billion (ppb)
Span	Less than ± 7.1 percent between supplied and observed concentrations
Single Point QC	Less than ± 7.1 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, 2017). 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 ± 1.51 ppb	Less than ± 10.1 percent between supplied and observed concentrations
NO_y	Less than ± 1.51 ppb	
CO	Less than ± 30.1 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, 2017). 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).

SO_2 = sulfur dioxide
NO_y = total reactive oxides of nitrogen
CO = carbon monoxide
ppb = parts per billion

Table 6 QC Analysis Count for Third Quarter 2018

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-}	52	198	85	17	24	95
	NO_3^-	52	198	85	17	24	95
	NH_4^+	34	179	85	17	24	95
	Cl^-	52	198	85	17	24	95
	Ca^{2+}	34	182	87	17	24	95
	Mg^{2+}	34	182	87	17	24	95
	Na^+	34	182	87	17	24	95
	K^+	34	182	87	17	24	95
Nylon	SO_4^{2-}	50	201	75	17	24	95
	NO_3^-	50	201	75	17	24	95
Cellulose	SO_4^{2-}	51	175	79	17	24	94

Table 7 Filter Pack Receipt Summary for Third Quarter 2018

Count of samples received more than 14 days after removal from tower:	18
Count of all samples received:	814
Fraction of samples received within 14 days:	0.978
Average interval in days:	4.966
First receipt date:	07-02-2018
Last receipt date:	09-28-2018

Table 8 Ozone QC Summary for Third Quarter 2018 (1 of 2)

Site ID	% Span Pass[1]	Span |%D|[2]	% Single Point QC Pass[1]	Single Point QC |%D|[2]	% Zero Pass[1]	Zero Average (ppb)[2]
ABT147, CT	100.00	2.32	100.00	2.34	96.81	0.58
ALC188, TX	100.00	0.71	100.00	1.39	100.00	0.58
ALH157, IL	98.91	2.44	100.00	2.00	100.00	0.35
ANA115, MI	98.96	1.14	100.00	1.88	100.00	0.14
ARE128, PA	100.00	1.88	100.00	1.69	100.00	0.38
ASH135, ME	100.00	1.32	100.00	1.31	98.91	0.29
BEL116, MD	100.00	0.68	100.00	0.71	100.00	0.37
BFT142, NC	100.00	1.25	100.00	1.79	100.00	0.52
BVL130, IL	100.00	1.04	98.94	0.89	96.81	0.52
BWR139, MD	100.00	2.16	100.00	1.84	100.00	0.48
CAD150, AR	100.00	0.83	100.00	1.75	100.00	0.54
CDR119, WV	100.00	1.92	100.00	1.16	100.00	0.12
CDZ171, KY	100.00	0.83	100.00	1.17	100.00	0.15
CKT136, KY	100.00	0.45	100.00	0.55	100.00	0.15
CND125, NC	97.96	4.86	93.88	3.16	98.98	0.57
CNT169, WY	100.00	0.47	100.00	0.65	100.00	0.21
COW137, NC	100.00	0.58	100.00	0.81	100.00	0.25
CTH110, NY	100.00	1.45	100.00	1.11	100.00	0.48
CVL151, MS	96.91	3.77	94.85	1.86	100.00	0.18
DCP114, OH	100.00	0.86	100.00	1.29	100.00	0.36
ESP127, TN	100.00	1.43	100.00	1.89	100.00	0.57
GAS153, GA	100.00	1.51	90.48	2.88	94.05	1.55
GTH161, CO	100.00	2.00	100.00	1.89	100.00	0.22
HOX148, MI	100.00	1.46	100.00	0.63	100.00	0.67
HWF187, NY	100.00	2.45	95.83	2.90	100.00	0.31

Table 8 Ozone QC Summary for Third Quarter 2018 (2 of 2)

Site ID	% Span Pass[1]	Span |%D|[2]	% Single Point QC Pass[1]	Single Point QC |%D|[2]	% Zero Pass[1]	Zero Average (ppb)[2]
IRL141, FL	95.79	1.43	94.74	1.60	100.00	0.46
KEF112, PA	92.47	2.60	92.47	2.62	95.70	0.78
LRL117, PA	100.00	0.80	100.00	0.64	100.00	0.16
MCK131, KY	92.52	2.46	91.59	2.86	92.52	1.58
MCK231, KY	98.91	3.43	98.92	3.87	97.83	1.44
MKG113, PA	100.00	1.11	100.00	0.87	100.00	0.49
NPT006, ID	100.00	1.24	100.00	0.59	100.00	0.37
OXF122, OH	98.75	1.86	97.50	2.16	97.50	0.98
PAL190, TX	100.00	0.81	100.00	0.97	100.00	0.92
PAR107, WV	100.00	0.97	100.00	1.15	100.00	0.23
PED108, VA	100.00	0.92	100.00	0.86	100.00	0.17
PND165, WY	98.91	2.06	100.00	1.89	100.00	0.63
PNF126, NC	83.00	3.01	86.00	3.49	100.00	0.54
PRK134, WI	100.00	2.54	100.00	2.35	98.94	0.61
PSU106, PA	100.00	2.42	100.00	2.80	100.00	0.27
QAK172, OH	98.92	3.03	97.85	3.70	100.00	1.02
ROM206, CO	100.00	1.98	100.00	2.24	100.00	0.22
SAL133, IN	100.00	4.25	100.00	4.30	100.00	0.25
SAN189, NE	100.00	1.90	100.00	1.86	100.00	0.66
SND152, AL	100.00	1.84	96.08	2.65	98.04	0.78
SPD111, TN	100.00	1.03	100.00	1.33	97.83	0.68
STK138, IL	98.90	2.89	100.00	2.40	100.00	0.37
SUM156, FL	100.00	0.76	100.00	0.51	100.00	0.95
UVL124, MI	100.00	1.54	98.94	1.27	97.87	0.44
VIN140, IN	100.00	0.85	100.00	1.98	100.00	1.12
VPI120, VA	100.00	2.03	97.78	1.88	98.89	0.76
WSP144, NJ	100.00	2.64	98.88	2.29	97.75	0.91
WST109, NH	98.94	2.06	96.81	2.25	100.00	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.

%D = percent difference

ppb = parts per billion

Table 9 Ozone QC Observations for Third Quarter 2018

Site ID	QC Criterion	Comments
PNF126, NC	% Span Pass % Single Point QC Pass	The sample pump failed on 8-10-2018 and was replaced on 8-16-2018.

Table 10 Trace-level Gas QC Summary for Third Quarter 2018

Parameter	% Span Pass[1]	Span |%D|[2]	% Single Point QC Pass[1]	Single Point QC |%D|[2]	% Zero Pass[1]	Zero Average (ppb)[2]
BVL130, IL						
SO_2	100.00	0.96	100.00	3.03	100.00	0.42
NO_y	100.00	0.73	100.00	3.03	95.24	0.89
CO	100.00	1.08	92.68	5.83	90.48	14.55
DUK008, NC						
NO_y	100.00	6.69	100.00	5.51	90.91	0.87
HWF187, NY						
NO_y	100.00	0.60	100.00	1.37	100.00	0.34
PND165, WY						
NO_y	100.00	1.75	98.00	3.96	100.00	0.37
PNF126, NC						
NO_y	100.00	0.93	100.00	1.42	100.00	0.84
ROM206, CO						
NO_y	100.00	1.67	100.00	3.52	100.00	0.57

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.

%D = percent difference
ppb = parts per billion

Table 11 Filter Packs Flagged as Suspect or Invalid during Third Quarter 2018

Site ID	Sample No.	Reason
CHA467, AZ	1829003-04	Polling issue
CNT169, WY	1827001-15	Polling issue
HOX148, MI	1835001-26	Polling issue
JOT403, CA	1831003-12	Polling issue
KIC003, KS	1830004-03	Power failure
UND002, VT	1827001-51	Intermittent power failures
	1828001-51	
	1831001-51	
	1833001-51	
YEL408, WY	1833003-24	Polling issue

Table 12 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	653
60	17
90	2
Unresolved by End of Quarter	15

Figure 1 Reference Standard Results for Third Quarter 2018 (percent recovery)

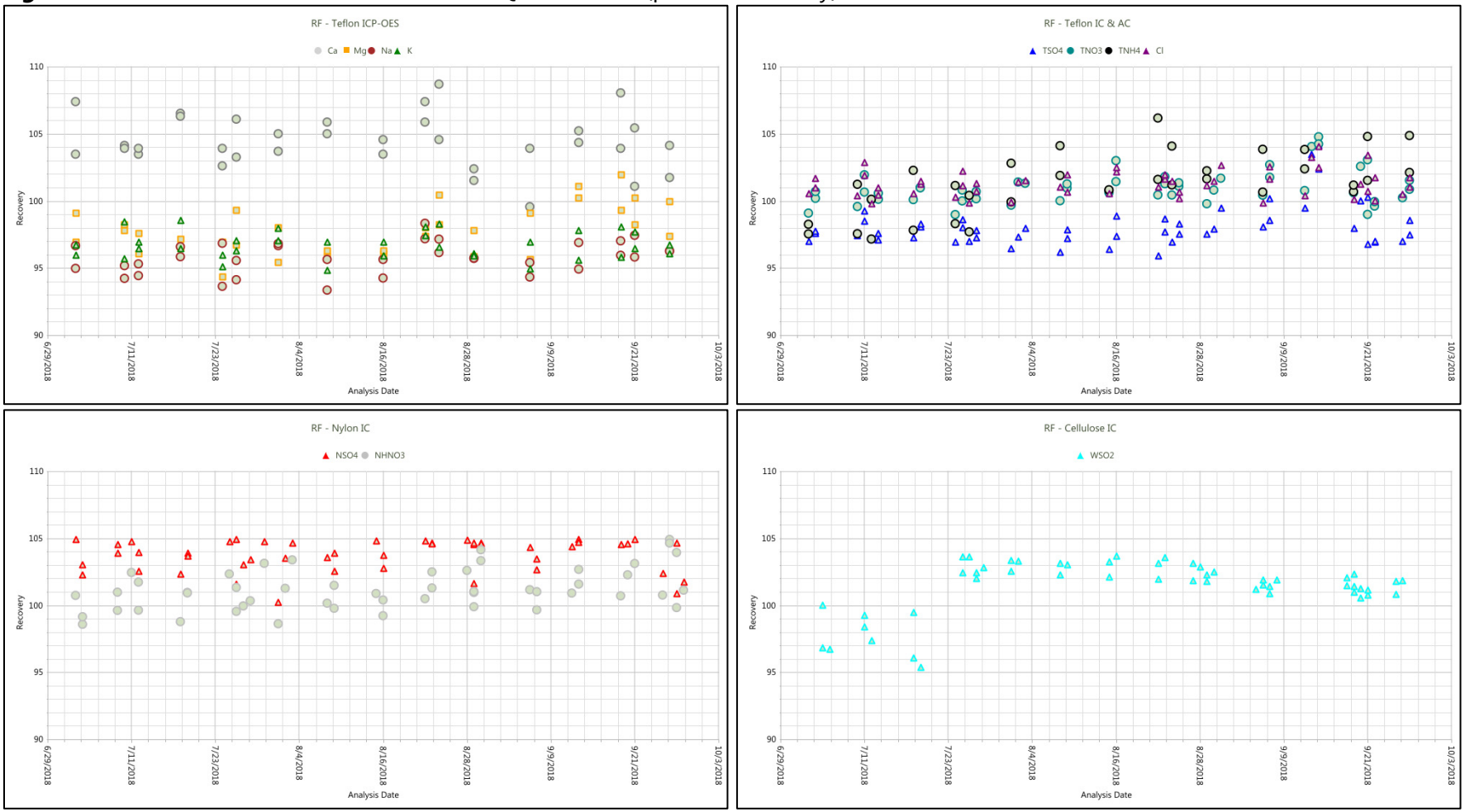

Figure 2 Continuing Calibration Spike Results for Third Quarter 2018 (percent recovery)

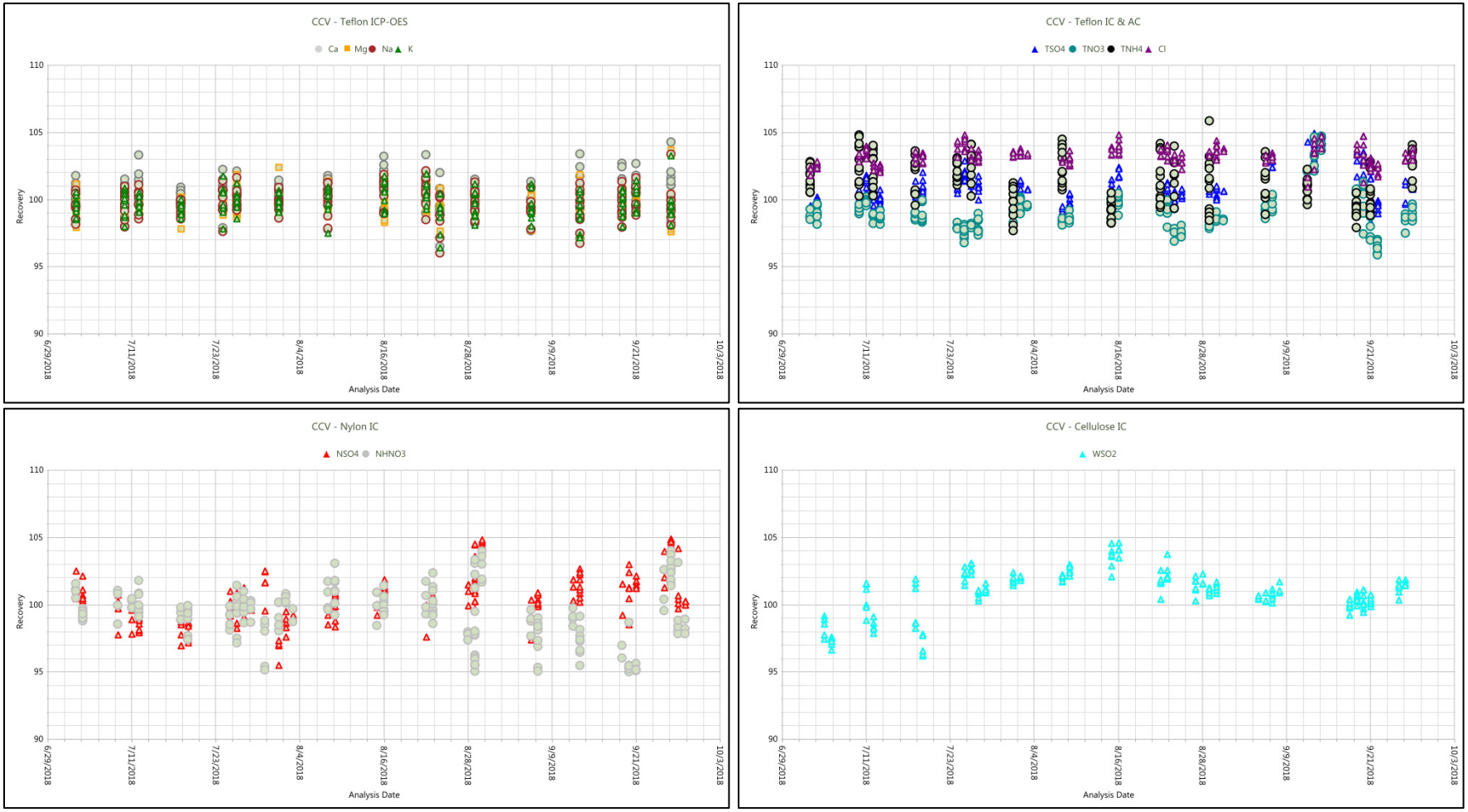

Figure 3 Replicate Sample Analysis Results for Third Quarter 2018 (percent difference)

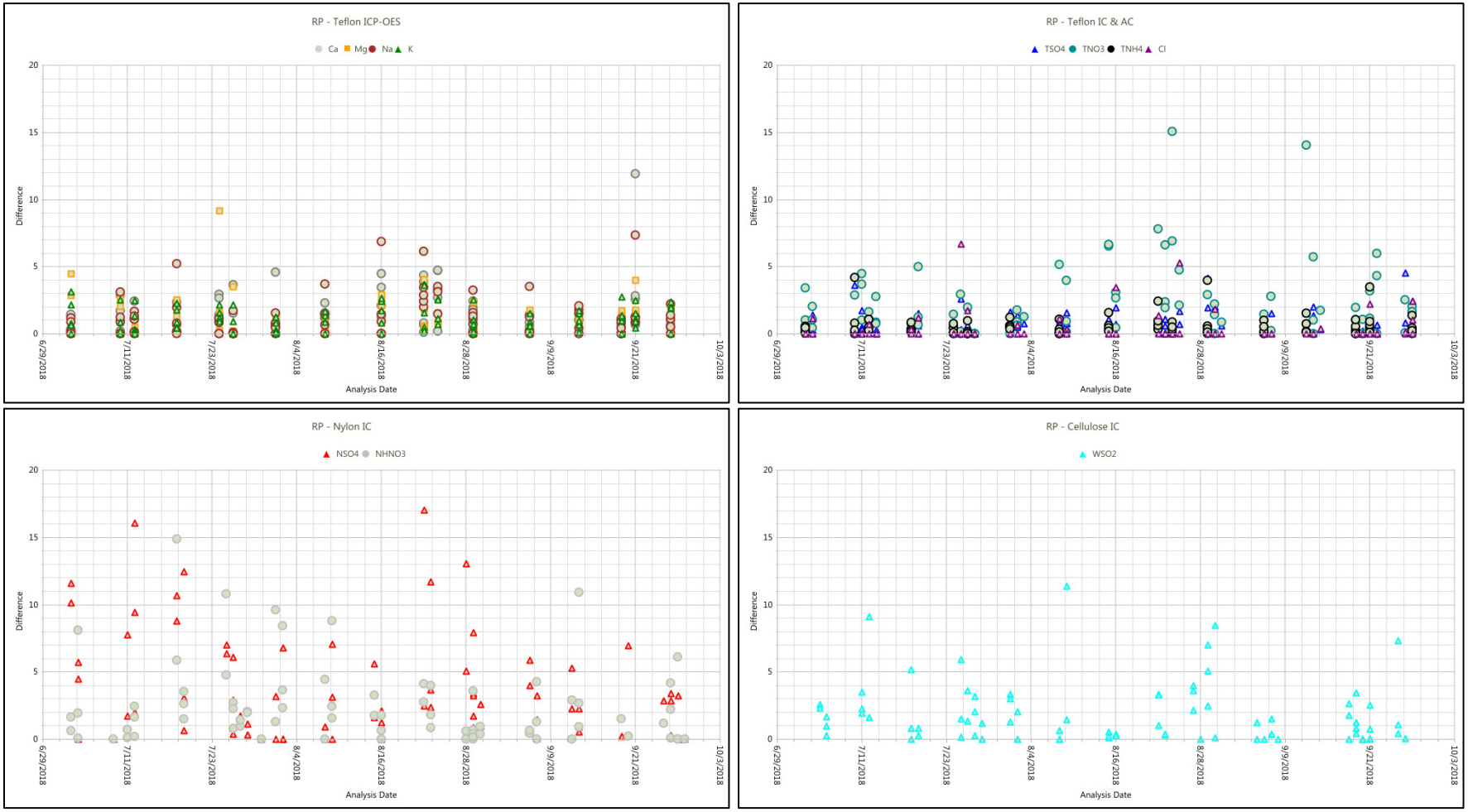

Figure 4 Laboratory Control Sample Results for Third Quarter 2018 (percent recovery)

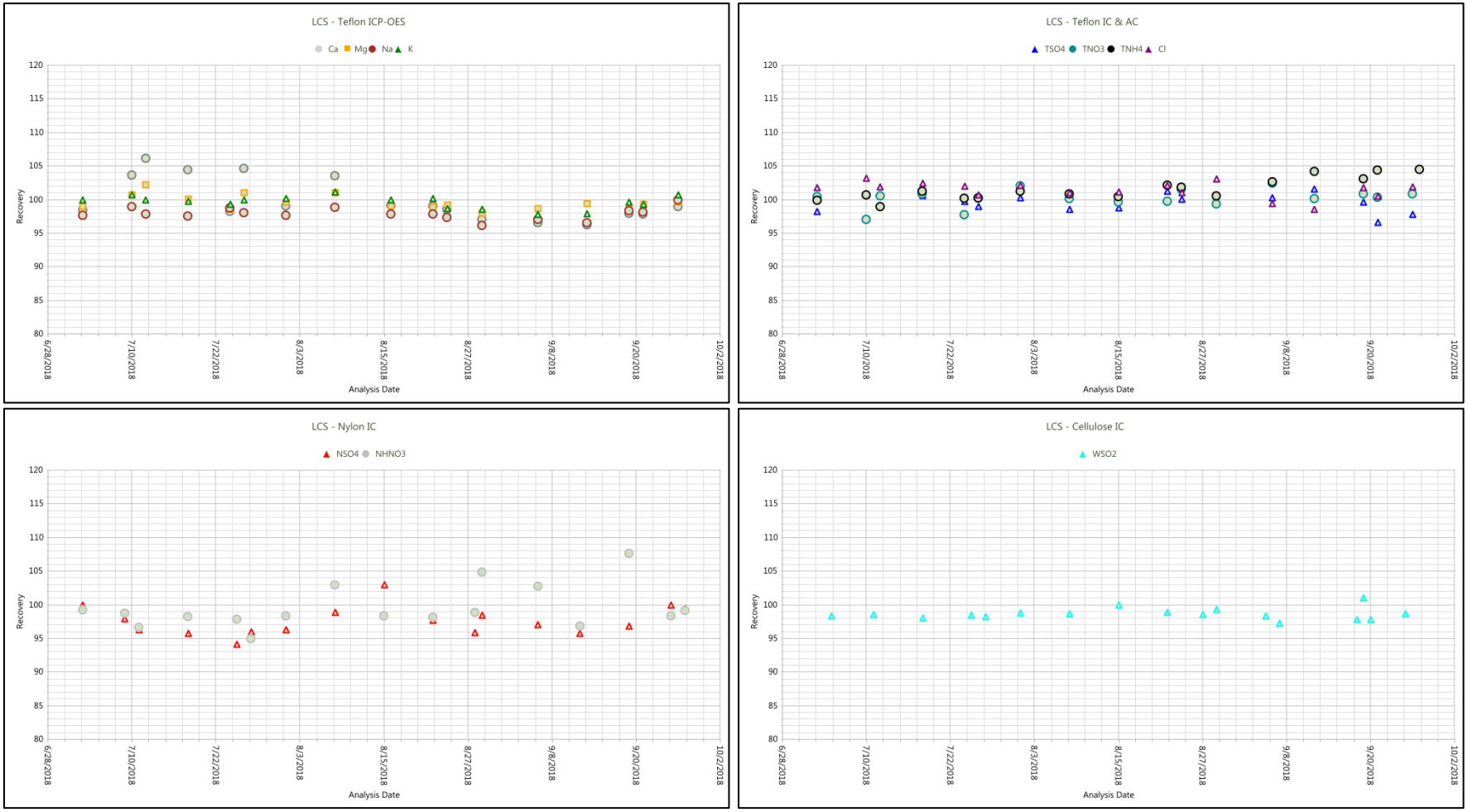

Figure 5 Method Blank Analysis Results for Third Quarter 2018 (total micrograms)

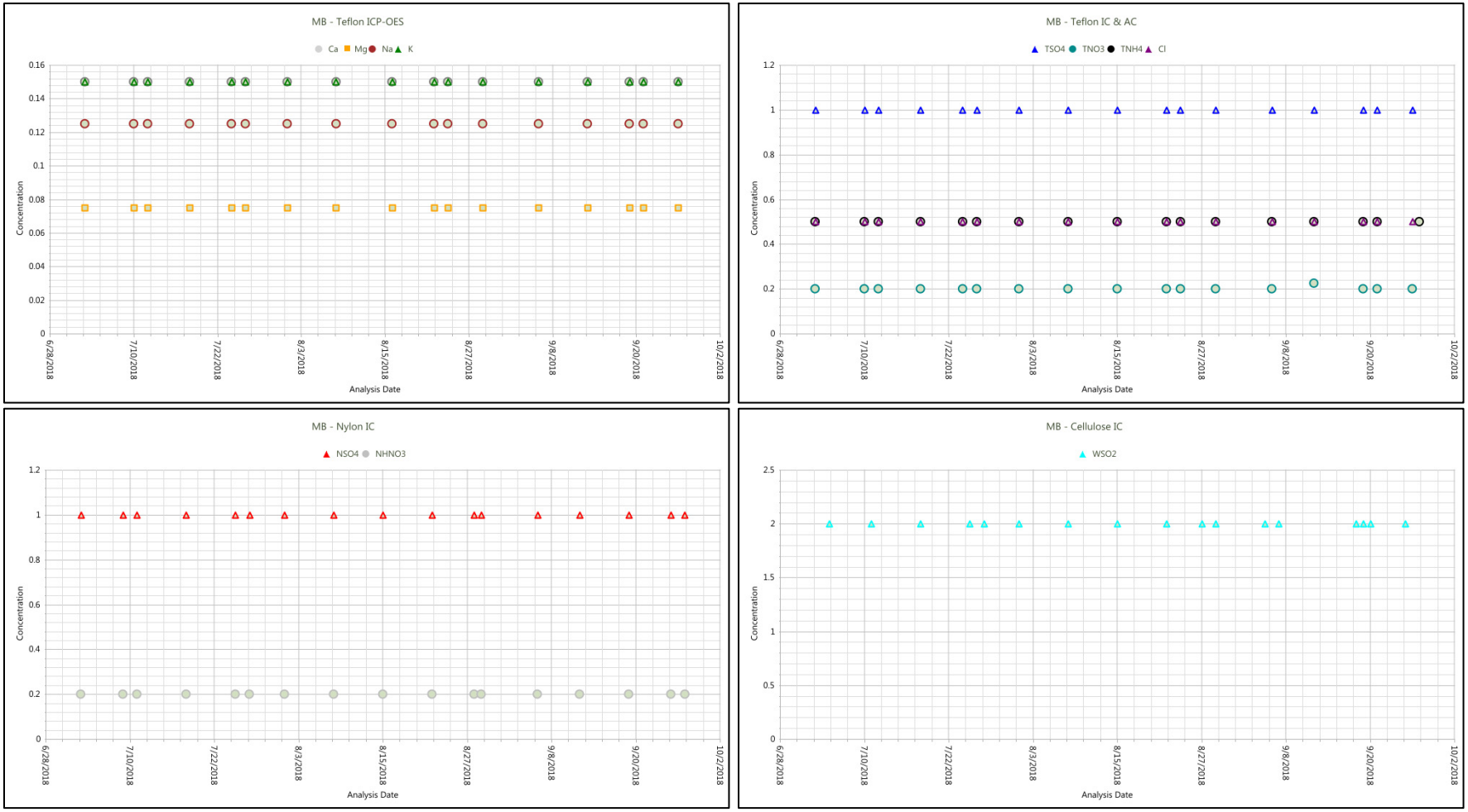

Figure 6 Laboratory Blank Analysis Results for Third Quarter 2018 (total micrograms)

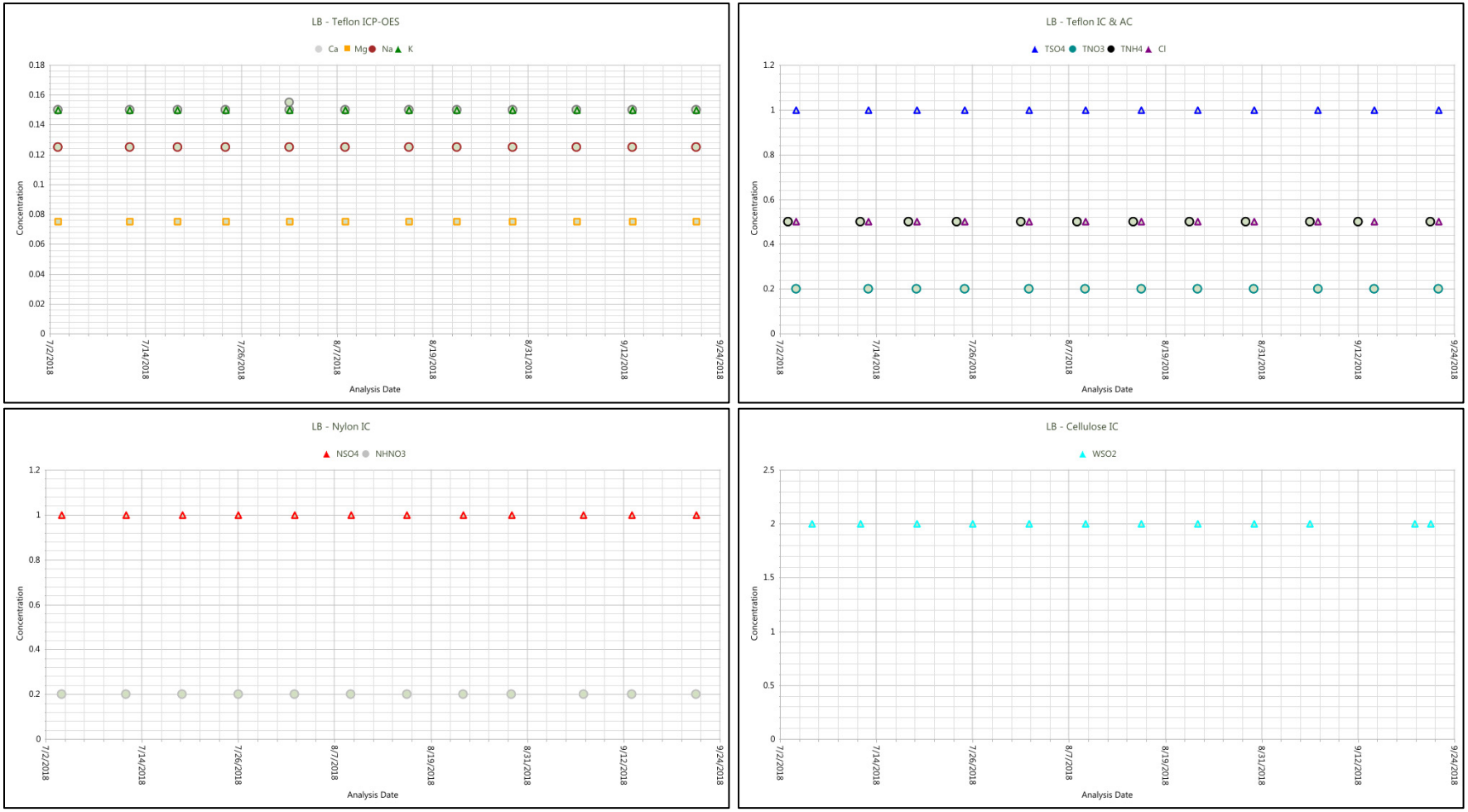

Figure 7 Field Blank Analysis Results for Third Quarter 2018 (total micrograms)