



Summary of Quarterly Operations (July – September)

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 third quarter 2012. The results presented for filter pack data collection and field calibrations are generated from data extracted from the CASTNET Data Management Center database using the CASTNET Data Management System Application. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP). 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.

During third quarter, the designation for the ozone monitor at ROM206, CO was changed in EPA's Air Quality System (AQS) to a non-regulatory monitor.

During third quarter, AMEC Environment & Infrastructure, Inc. (AMEC) and the National Park Service contractor, Air Resource Specialists, Inc. (ARS), met at the ROM406/206 sites to audit the ozone monitoring systems at each site and evaluate differences in systems and procedures. The ARS and AMEC transfer standards were compared to one another and to the site analyzers. Further comparisons were made using the different transfers at different settings with calibration lines of different inner diameter and different venting locations. Testing of Thermo PS model standards indicated that greater pressure in the calibration line results in a greater imbalance in the detector cells, affecting their performance. This pressure difference can be the result of smaller inner diameter calibration tubing (e.g., 3 millimeter), longer calibration tubing, or increased gas flow rate. The inner diameter and length of the sample tubing does not affect the performance of a transfer standard if it is not a PS model. If it is necessary to use a PS model, a minimum of 4.7 millimeter inner diameter calibration line tubing and an open vent at the back of the instrument are recommended to limit pressure imbalance in the detector cells to less than 10 millimeters of mercury.

A technical systems audit (TSA) of AMEC's ozone facilities in Gainesville, FL and at two field sites in North Carolina (CND125 and BFT142) took place during late August and early September 2012. A TSA of the facility is required by EPA since AMEC is the monitoring organization in charge of CASTNET AQS-protocol sites. The auditor with RTI International, Inc. (RTI), the auditing organization, interviewed AMEC staff and site operators and observed activities related to various procedures. The preliminary audit report covered his visits to the two CASTNET field sites as well as the Gainesville facility audit. The preliminary report was good with only minor findings. The auditor suggested that AMEC improve documentation of site operator training and independently confirm the status of documents stored onsite. The draft audit report will be available in October 2012 with the final report submitted to AMEC by November 30, 2012.

AMEC's analytical laboratory is pursuing International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025 accreditation by the American Association for Laboratory Accreditation (A2LA). AMEC is providing corporate funding to support this effort. During September 2012, AMEC submitted materials to the accreditation body. The accreditation process is expected to take until early April 2013 to complete.

During September 2012, AMEC received final results and rankings for proficiency test (PT) study 0100 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 quality assurance services. Results for AMEC showed no flags and no indication of bias. An "Ideal" rating was assigned to all parameters assessed for bias. AMEC's laboratory was rated, "Very Good," the highest rating available. AMEC's 5-year historical average for Environment Canada PT studies is rated "Very Good," which shows AMEC's consistent performance for laboratory analyses.

Table 1 lists the quarters of data that were validated to Level 3 during third quarter 2012 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. All EPA-sponsored CASTNET sites that monitor ozone are configured to meet EPA's AQS criteria for QA/QC procedures and are operated in accordance with Title 40 of the Code of Federal Regulations Part 58.

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 2012.

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 2012.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for third quarter 2012. All results were within the criteria listed in Table 4.

Table 8 presents summary statistics of critical criteria measurements at AQS-protocol ozone sites collected during the quarter. All data associated with QC checks that fail to meet the criteria listed in Table 5 will be invalidated. 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.

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 action limits for LCS recovery are 80 percent and 120 percent. Figure 4 presents LCS analysis results for third quarter 2012. All recovery values were between 95 percent and 110 percent.

Blank Results

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for third quarter 2012. All results were within criteria (two times the reporting limit) listed in Table 4.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during third quarter 2012 are listed in Table 10. This table includes associated site identification and a brief description of the reason the sample was flagged. During third quarter, nine filter pack samples were invalidated.

Field Problem Count

Table 11 presents counts of field problems affecting continuous data collection for more than one day during third quarter 2012. 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

Calibrations were performed at 24 sites during third quarter 2012. All sites and parameters were within the criteria listed in Table 3 with the exception of one parameter at the site listed in Table 12.

Table 1. Data Validated to Level 3 during Third Quarter 2012

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10 [†]	November 2011 – April 2012	6	Quarter 1 2012	1
SE-4/MW-6 [‡]	January 2012 – June 2012	6	Quarter 1 2012 – Quarter 2 2012	2

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

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

[‡] Contains MCK131/231 collocated pair

Table 2. Field Calibration Schedule

Calibration Group	Months Calibrated	Sites Calibrated			
Eastern Sites (21 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 (8 Sites)	April/October	ABT147, CT WST109, NH	ASH135, ME HOW132, ME	HOW191, ME CAT175, NY	HWF187, NY EGB181, ON
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 As of January 2011, meteorological parameters were only measured at five of the EPA-sponsored CASTNET sites: PAL190, TX; CHE185, OK; BVL130, IL; BEL116, MD; BFT142, NC.

³ Ozone is not measured at two EPA-sponsored CASTNET sites: EGB181, ON and CAT175, NY.

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
 * = as nitrogen

Values are rounded according to American Society for Testing and Materials (ASTM) (Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications E 29).

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP, Revision 8.0 (AMEC, 2012)

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
One Point QC	Less than or equal to ± 7 percent between supplied and observed concentrations

Note: * All EPA-sponsored CASTNET sites that monitor ozone (except HOW191, ME) 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.

Table 6. QC Analysis Count for Third Quarter 2012

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⁻	37	175	71	18	26	82
	NO ₃ ⁻	37	175	83	18	26	82
	NH ₄ ⁺	36	174	93	18	26	82
	Cl ⁻	37	175	70	18	26	81
	Ca ²⁺	36	177	82	18	26	82
	Mg ²⁺	36	177	82	18	26	82
	Na ⁺	36	177	82	18	26	82
	K ⁺	36	177	82	18	26	82
Nylon	SO ₄ ²⁻	34	163	68	17	26	82
	NO ₃ ⁻	34	163	80	17	26	82
Cellulose	SO ₄ ²⁻	32	158	77	16	26	81

Table 7. Filter Pack Receipt Summary for Third Quarter 2012

Count of samples received more than 14 days after removal from tower:	3
Count of all samples received:	1059
Fraction of samples received within 14 days:	0.997
Average interval in days:	3.34
First receipt date:	07/02/2012
Last receipt date:	09/28/2012

Table 8. AQS-Protocol Ozone QC Summary (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	0.28	100.00	0.38	0.07	100.00	1.03
ALC188, TX	70.83	24.65	69.79	23.05	5.45	87.50	5.52
ALH157, IL	98.91	2.11	98.91	1.53	0.97	98.92	2.61
ANA115, MI	100.00	0.89	100.00	1.07	0.12	100.00	0.40
ARE128, PA	100.00	0.51	96.74	0.79	0.34	96.74	2.01
ASH135, ME	100.00	4.62	100.00	4.57	0.08	100.00	0.79
BEL116, MD	89.87	8.46	91.14	9.00	4.26	96.25	1.20
BFT142, NC	94.90	3.90	91.84	3.64	1.87	94.90	2.60
BVL130, IL	97.96	2.89	89.80	4.74	0.35	66.34	7.05
BWR139, MD	90.53	11.09	81.05	21.79	17.46	84.38	12.85
CAD150, AR	96.91	1.59	91.75	2.88	1.02	95.92	1.74
CDR119, WV	100.00	0.82	100.00	0.61	0.07	100.00	3.43
CDZ171, KY	100.00	0.65	100.00	0.58	0.12	100.00	0.63
CKT136, KY	100.00	1.72	100.00	2.02	0.09	100.00	0.90
CND125, NC	98.92	1.67	98.92	1.61	1.39	98.92	1.39
CNT169, WY	100.00	0.87	100.00	1.75	0.23	100.00	0.33
COW137, NC	95.83	1.25	98.96	1.01	0.28	100.00	0.77
CTH110, NY	100.00	1.64	100.00	1.12	0.10	100.00	0.61
CVL151, MS	96.84	2.43	90.53	3.19	0.54	98.95	2.51
DCP114, OH	98.92	1.90	98.94	2.18	0.45	100.00	0.95
ESP127, TN	97.96	2.31	95.92	1.77	1.38	87.76	4.97
GAS153, GA	98.96	2.14	96.88	2.16	1.72	92.71	2.96
GTH161, CO	100.00	1.94	100.00	1.80	0.17	100.00	0.18
HOW132, ME	91.49	8.05	91.40	8.53	4.33	92.55	2.57
HOX148, MI	88.42	3.86	89.47	3.67	1.07	98.95	0.78
HWF187, NY	92.63	3.83	94.79	3.81	0.28	100.00	0.67
IRL141, FL	100.00	1.68	100.00	2.56	0.20	97.89	2.74
KEF112, PA	100.00	0.72	100.00	0.82	0.09	100.00	0.60
KNZ184, KS	98.96	1.49	98.96	1.24	1.01	94.79	4.43
LRL117, PA	86.81	2.93	87.64	2.97	0.41	100.00	0.65
MCK131, KY	100.00	2.85	100.00	3.07	0.21	100.00	0.37
MCK231, KY	98.96	2.89	98.96	2.18	0.59	95.83	2.15

Table 8. AQS-Protocol Ozone QC Summary (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
MKG113, PA	98.92	1.28	98.92	1.77	0.94	98.92	1.17
OXF122, OH	100.00	1.22	100.00	1.20	0.10	100.00	1.36
PAL190, TX	100.00	1.11	100.00	0.81	0.07	100.00	0.87
PAR107, WV	100.00	0.47	100.00	0.48	0.13	98.39	1.37
PED108, VA	100.00	1.02	100.00	0.82	0.12	100.00	0.93
PND165, WY	100.00	0.87	100.00	0.94	0.14	100.00	1.00
PNF126, NC	100.00	0.44	100.00	0.43	0.05	100.00	0.41
PRK134, WI	98.80	1.13	97.62	1.08	0.24	100.00	1.25
PSU106, PA	100.00	1.04	100.00	1.10	0.06	100.00	0.21
QAK172, OH	97.53	2.00	93.83	3.11	0.71	88.89	3.19
ROM206, CO	90.43	10.36	91.49	10.63	4.65	98.94	0.78
SAL133, IN	100.00	0.88	98.91	1.00	0.22	100.00	0.81
SAN189, NE	97.87	2.53	97.87	2.79	2.45	97.87	1.87
SND152, AL	97.85	3.12	97.85	2.59	1.63	97.87	1.00
SPD111, TN	100.00	0.76	100.00	0.64	0.10	100.00	0.28
STK138, IL	97.53	4.80	98.77	3.58	1.55	98.77	0.59
SUM156, FL	100.00	1.33	100.00	1.97	0.20	100.00	0.71
UVL124, MI	100.00	1.37	100.00	1.29	0.07	100.00	0.27
VIN140, IN	100.00	0.86	100.00	0.90	0.15	100.00	0.40
VPI120, VA	97.50	2.53	96.25	2.54	0.94	97.50	7.70
WSP144, NJ	100.00	0.96	100.00	1.16	0.11	100.00	0.80
WST109, NH	100.00	2.28	100.00	2.72	0.14	100.00	0.92

Notes: ¹ Percentage of comparisons that pass the criteria listed in Table 5. 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 5 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 one 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. AQS-Protocol Ozone QC Observations

Site ID	QC Criterion	Comments
ALC188, TX	% Span Pass; Span %D ; % Single Point QC Pass; Single Point QC %D ; % Zero Pass	A leak in the sampling train required invalidation of associated ambient data.
BEL116, MD	Span %D ; Single Point QC %D	There were problems with the zero air system in July and September. Ambient data collection was not affected.
BVL130, IL	% Zero Pass	The associated ambient data were invalidated.
BWR139, MD	Span %D ; % Single Point QC Pass; Single Point QC %D ; % Single Point QC CL; % Zero Pass; Zero Average	The site analyzer was malfunctioning. The associated ambient data were invalidated.
ESP127, TN	% Zero Pass	The associated ambient data were invalidated.
HOW132, ME	Span %D ; Single Point QC %D	The zero air compressor was deactivated in error for approximately one week. Ambient data were not affected.
HOX148, MI	% Span Pass	There was a leak affecting calibration gas delivery. Ambient data were not affected.
LRL117, PA	% Span Pass; % Single Point QC Pass	The sample pump failed resulting in the invalidation of two weeks of ambient data during September.
QAK172, OH	% Zero Pass	The associated ambient data were invalidated.
ROM206, CO	Span %D ; Single Point QC %D	A faulty Ethernet connection resulted in erroneous data collection for approximately one week. The associated ambient data were invalidated.

Notes: %D = percent difference
CL = confidence limit

Table 10. Filter Packs Flagged as Suspect or Invalid

Site ID	Sample No.	Reason
BBE401, TX	1229001-08	Insufficient valid flow
BFT142, NC	1228001-10	Insufficient valid flow
BVL130, IL	1230001-11	Insufficient valid flow
GLR468, MT	1227001-32	Insufficient valid flow
PRK134, WI	1231001-62	Insufficient valid flow
	1232001-62	Insufficient valid flow
UVL124, MI	1232001-76	Insufficient valid flow
VPI120, VA	1227001-79	Insufficient valid flow
WNC429, SD	1230001-80	Insufficient valid flow

Table 11. Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	139
60	9
90	8
Unresolved by End of Quarter	7

Table 12. Field Calibration Failures by Parameter

Site ID	Parameter(s)
BFT142, NC	Solar Radiation

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 criteria, these data are adjusted per approved protocol described in the CASTNET QAPP, Revision 8.0 (AMEC, 2012). Please refer to Table 8 for documentation of the QC failures affecting the validity of AQS-protocol ozone data.

Figure 1. Reference Standard Results for Third Quarter 2012 (percent recovery)

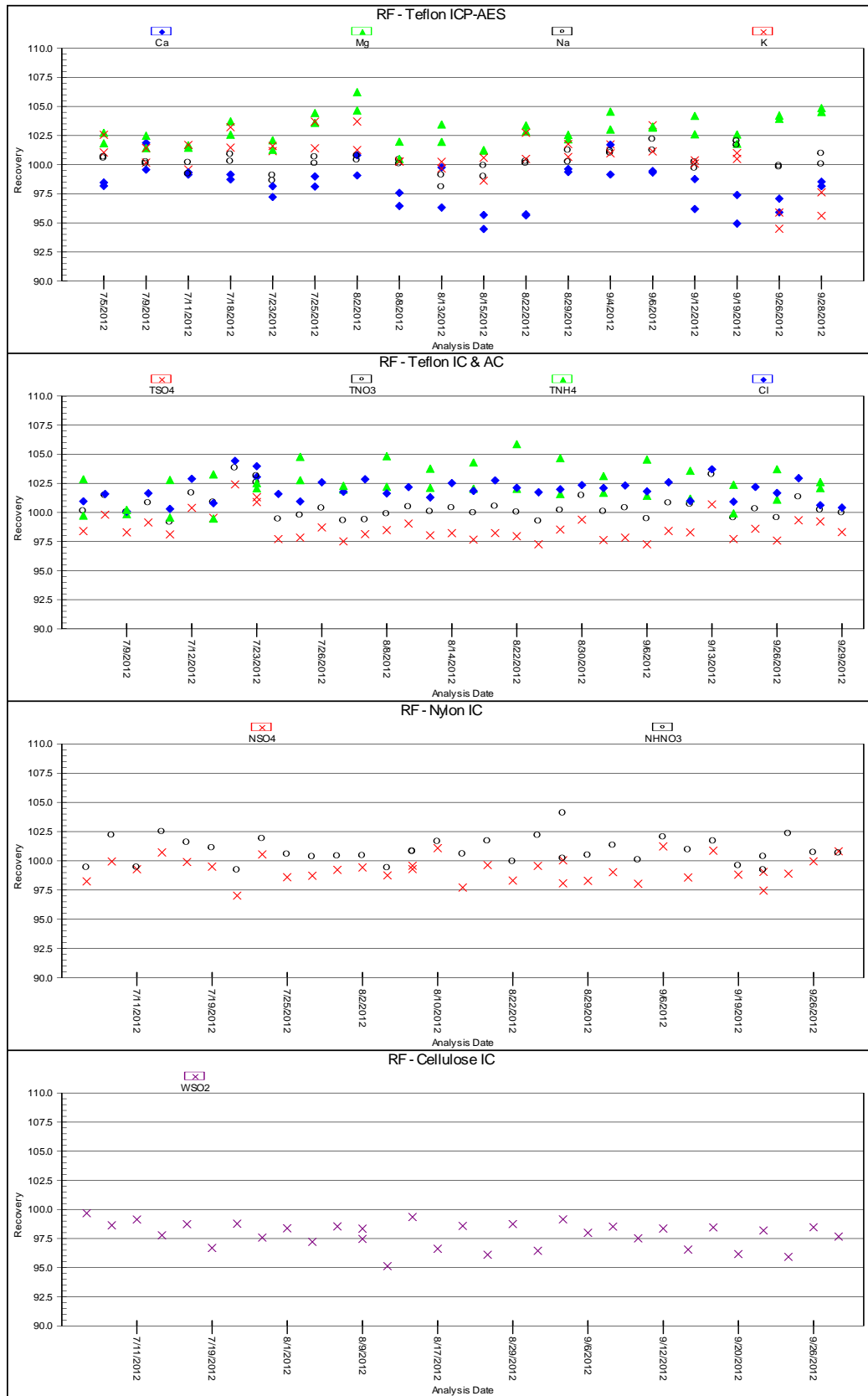


Figure 2. Continuing Calibration Spike Results for Third Quarter 2012 (percent recovery)

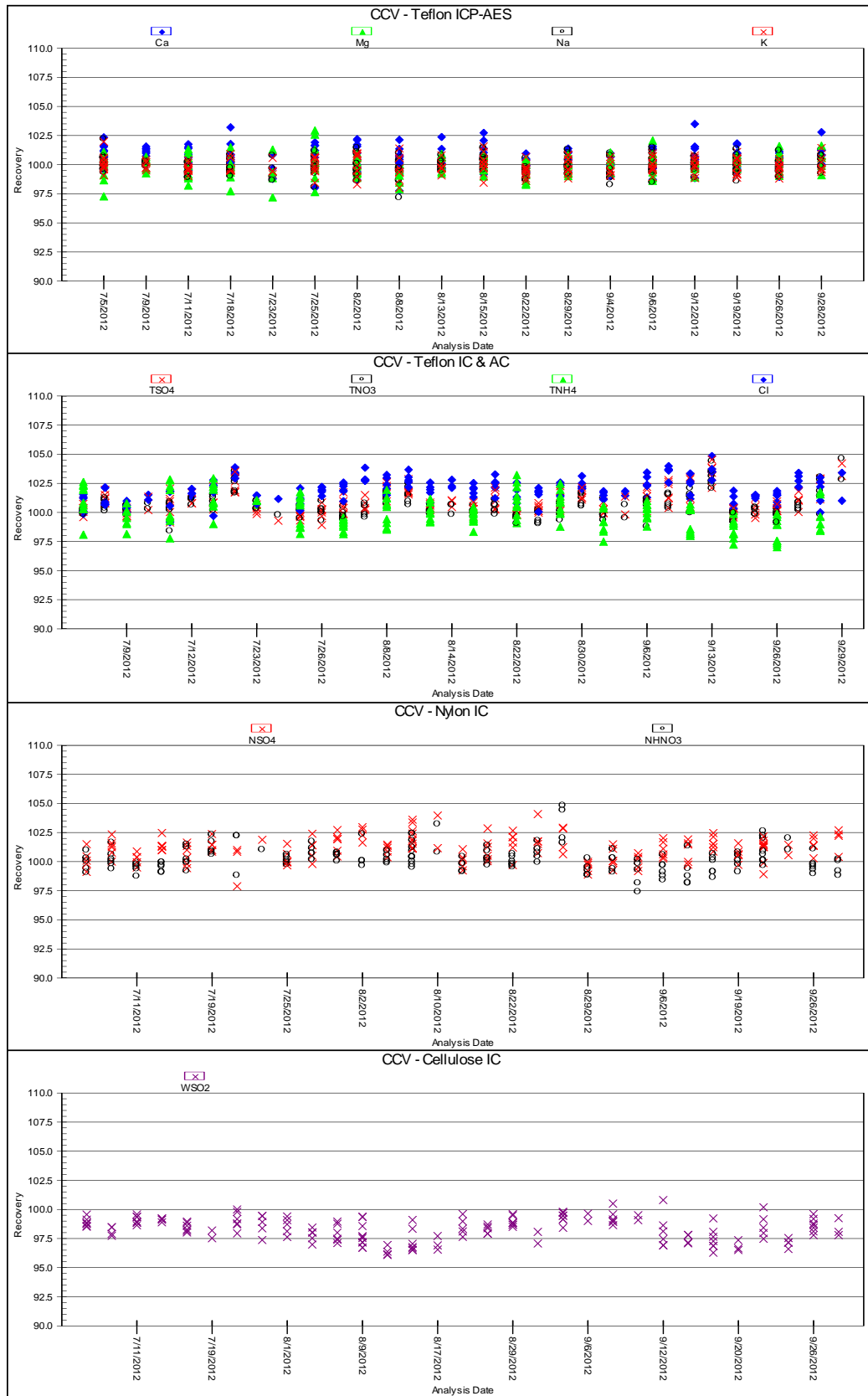


Figure 3. Replicate Sample Analysis Results for Third Quarter 2012 (percent difference)

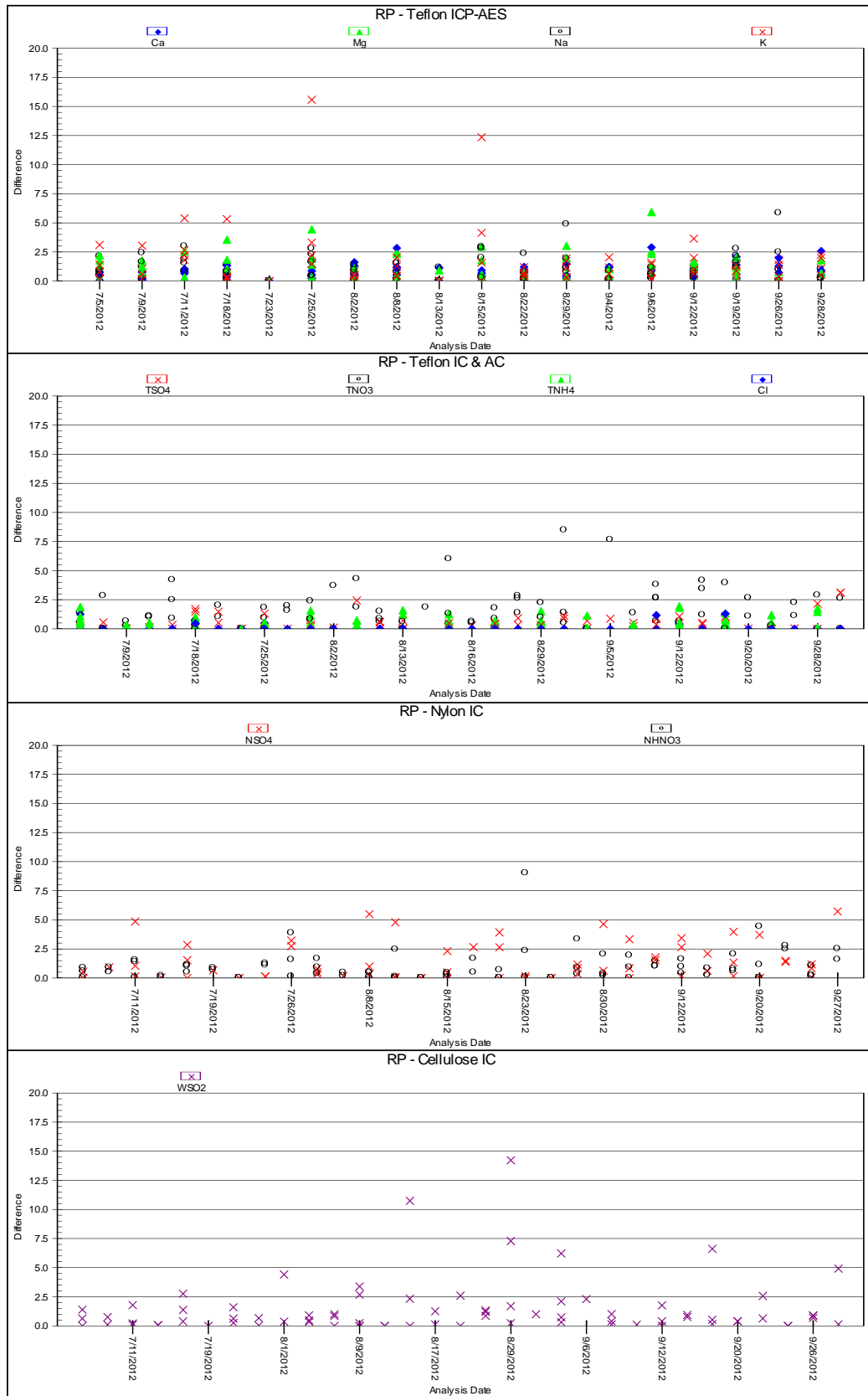


Figure 4. Laboratory Control Sample Results for Third Quarter 2012 (percent recovery)

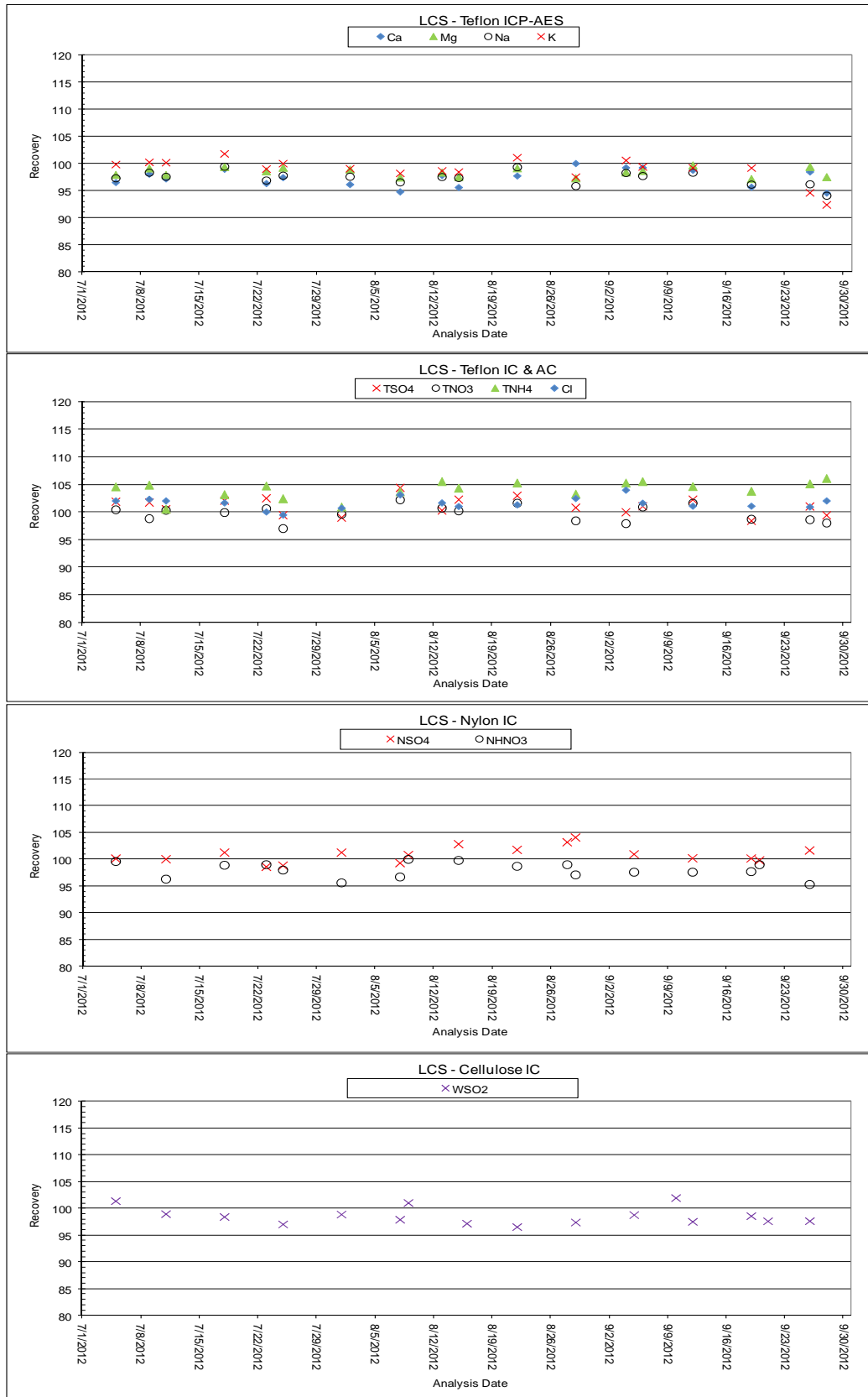


Figure 5. Method Blank Analysis Results for Third Quarter 2012 (total micrograms)

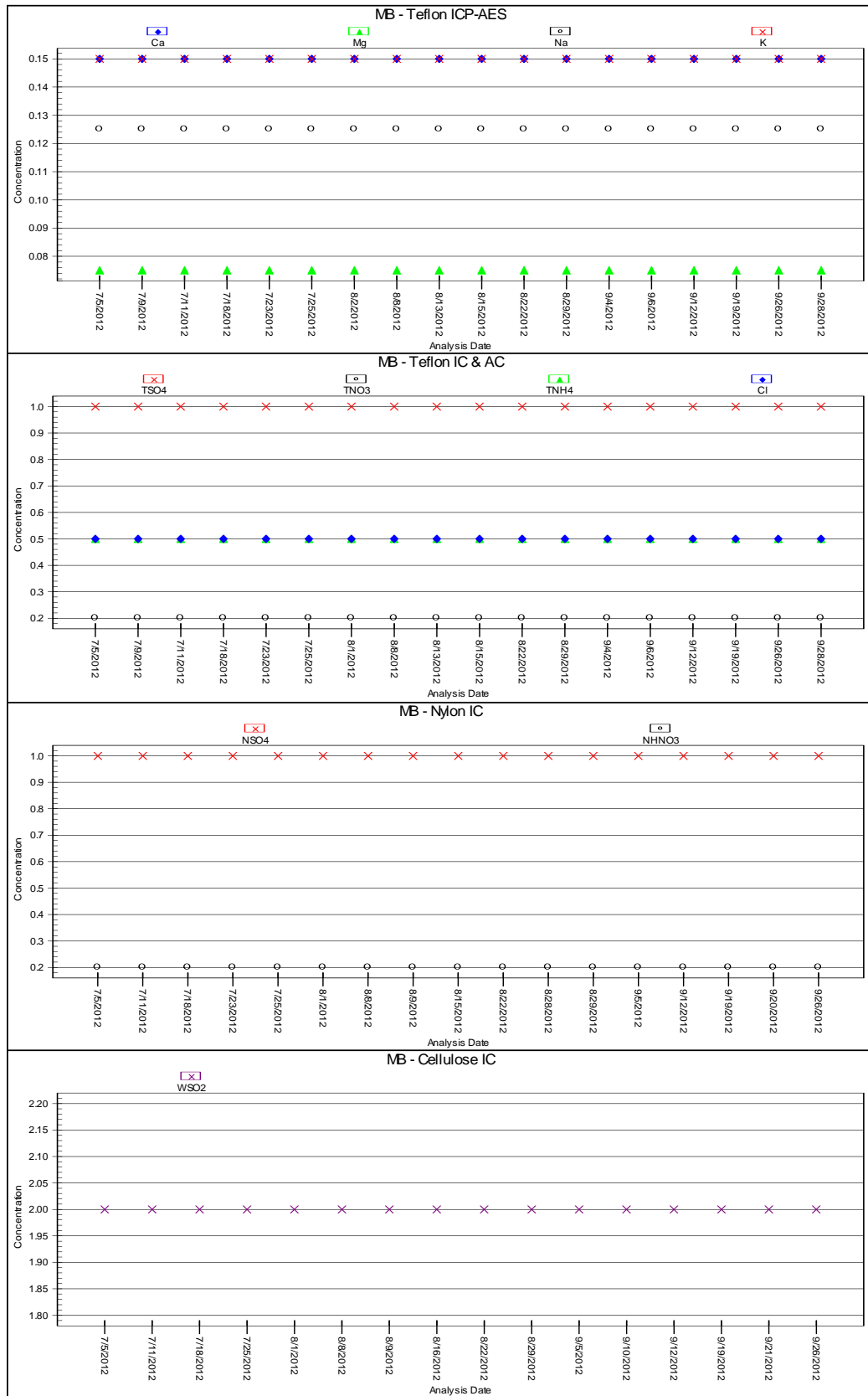


Figure 6. Laboratory Blank Analysis Results for Third Quarter 2012 (total micrograms)

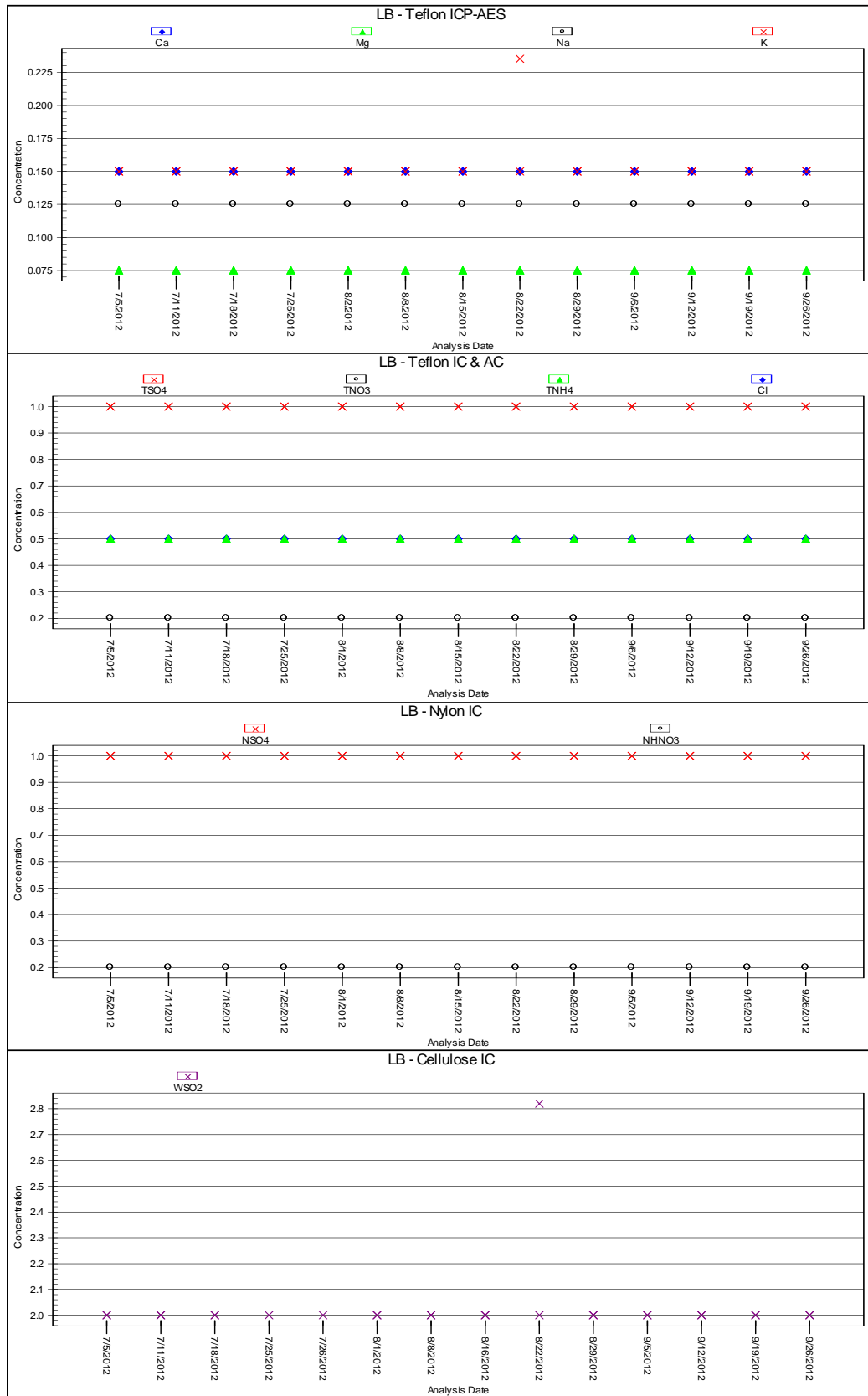


Figure 7. Field Blank Analysis Results for Third Quarter 2012 (total micrograms)

