



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 2011. 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.

One of the more stable parameters measured at CASTNET sites is filter pack flow. It is uncommon for flow to fail a calibration audit. Recently, AMEC E&I, Inc. (AMEC) noted an unusual series of flow calibration failures (please refer to the Second Quarter 2011 Quality Assurance Report, Table 11). The majority of the failures were biased the same direction (low) and were eventually found to correlate with two flow transfer standards being used for field calibrations. Subsequent AMEC testing indicated that these standards were suspect. They have been returned to the manufacturer for further evaluation and servicing. Results of this evaluation will be incorporated in corrective actions regarding the associated data. Additionally, other standards were tested under various operating conditions (fully charged, plugged in/charging, warmed up, cold started, etc.) to determine the best operating configuration for consistent results. A memorandum containing best practice operating guidelines was developed for use by field personnel to minimize errors. The new procedures will be implemented during fourth quarter 2011 calibrations.

AMEC and the National Park Service (NPS)'s contractor, Air Resource Specialists, Inc. (ARS), continued to evaluate possible causes of the bias in ozone concentrations seen at the ROM406/206, CO collocated site. Data from the comparisons, as well as configuration and

procedural differences, were further evaluated to try to isolate the cause(s) of the continued bias. The results were inconclusive.

During a general review of data for all sites, it was noted that wind speed data for PRK134, WI should have been invalidated, but were not. Further review of all data for all sites and discussion of the findings will be scheduled prior to invalidation of the PRK134 wind speed data.

AMEC continued to work with Thermo Scientific (Thermo) to determine possible causes of the ozone pressure transducer failures. Thermo is working with AMEC to trace the serial numbers of the failed transducers to production runs in order to determine the scope of the problem. AMEC continued to work with EPA to establish a protocol for component replacement at affected sites.

During September, AMEC began officially submitting ozone data from EPA-sponsored sites to the EPA Air Quality System (AQS). Beginning in fourth quarter, AMEC will submit data to AQS on a monthly basis for all EPA-sponsored sites that measure ozone.

During September 2011, AMEC received final results and rankings for proficiency test (PT) study 0098 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. AMEC tied for first place out of the 31 competing laboratories. Results for AMEC showed no flags and no indication of 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 2011 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.

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 2011.

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 2011.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for third quarter 2011. All results were within the criteria listed in Table 4. The CCV value for “WSO2” that appears low in Figure 2 is displayed at 94.8 percent, which becomes 95 percent after rounding rules are applied.

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 current action limits for LCS recovery are 80 percent and 120 percent. Figure 4 presents LCS analysis results for third quarter 2011. 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 2011. All results were within criteria (two times the reporting limit) listed in Table 4 with the exception of one Teflon filter LB result for calcium.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during third quarter 2011 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, 15 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 2011. 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 26 sites during third quarter 2011. 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.

Tables and Figures

Table 1. Data Validated to Level 3 during Third Quarter 2011

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10 [†]	November 2010 – April 2011	6	Quarter 1 2011	1
SE-4/MW-6 [‡]	January 2011 – June 2011	6	Quarter 1 2011 – Quarter 2 2011	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 (20 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 (7 Sites)	April/October	ABT147, CT WST109, NH	HOW132, ME ASH135, 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 four of the EPA-sponsored CASTNET sites: PAL190, TX; CHE185, OK; BVL130, IL; and BEL116, MD.

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 7.0 (MACTEC Engineering and Consulting, Inc., now known as AMEC, 2011)

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: * Applies to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations

Table 6. QC Analysis Count for Third Quarter 2011

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	165	73	17	26	81
	NO ₃ ⁻	34	165	82	17	26	81
	NH ₄ ⁺	34	168	89	17	26	81
	Cl ⁻	34	165	70	17	26	81
	Ca ²⁺	35	165	78	17	26	81
	Mg ²⁺	35	165	78	17	26	81
	Na ⁺	35	165	78	17	26	81
	K ⁺	35	165	78	17	26	81
Nylon	SO ₄ ²⁻	33	165	70	16	26	81
	NO ₃ ⁻	33	165	78	16	26	81
Cellulose	SO ₄ ²⁻	49	183	90	23	26	81

Table 7. Filter Pack Receipt Summary for Third Quarter 2011

Count of samples received more than 14 days after removal from tower:	7
Count of all samples received:	692
Fraction of samples received within 14 days:	0.990
Average interval in days:	4.029
First receipt date:	07/01/2011
Last receipt date:	09/28/2011

Table 8. AQS-Protocol Ozone QC Summary (1 of 2)

Site ID	% Span Pass ¹	Span %D ²	% One Point QC Pass	One Point QC %D	One Point QC CL ³	% Zero Pass	Zero Average (ppb)
ABT147, CT	89.74	2.34	89.87	2.27	0.59	100.00	0.31
ALC188, TX	100.00	1.31	97.25	1.75	0.24	97.25	2.52
ALH157, IL	100.00	2.75	100.00	2.72	0.29	98.08	1.61
ANA115, MI	100.00	0.85	99.05	1.12	0.30	99.05	1.18
ARE128, PA	100.00	2.33	100.00	1.22	0.08	100.00	1.55
ASH135, ME	100.00	3.18	100.00	3.04	0.18	98.08	1.69
BEL116, MD	92.31	4.00	91.35	3.69	1.69	95.10	2.36
BFT142, NC	97.50	4.58	79.17	5.61	0.99	92.50	3.34
BVL130, IL	98.98	2.60	97.96	2.63	0.33	93.88	1.85
BWR139, MD	100.00	1.19	100.00	1.46	0.17	100.00	1.01
CAD150, AR	95.19	6.87	95.19	5.68	2.96	98.08	1.27
CDR119, WV	100.00	0.36	100.00	0.37	0.07	96.15	4.90
CDZ171, KY	99.06	1.88	99.05	1.96	1.34	100.00	1.17
CKT136, KY	100.00	1.75	99.07	1.62	0.20	100.00	0.42
CND125, NC	100.00	2.60	100.00	2.99	0.15	100.00	0.40
CNT169, WY	100.00	0.98	99.01	1.37	0.20	100.00	0.32
COW137, NC	100.00	0.40	100.00	0.77	0.07	93.27	3.08
CTH110, NY	100.00	1.53	100.00	1.23	0.16	100.00	0.29
CVL151, MS	97.98	3.22	97.98	4.07	2.10	97.98	1.86
DCP114, OH	100.00	1.40	98.77	1.72	0.49	100.00	1.26
ESP127, TN	100.00	0.84	96.30	64.38	103.58	100.00	0.61
GAS153, GA	100.00	2.53	100.00	0.92	0.13	98.08	3.64
GTH161, CO	94.23	4.67	96.15	3.06	1.47	96.15	2.44
HOW132, ME	99.28	1.12	100.00	1.05	0.08	100.00	1.32
HOX148, MI	100.00	2.02	100.00	1.07	0.11	97.83	1.21
HWF187, NY	91.51	8.19	91.51	7.62	3.77	97.20	2.16
IRL141, FL	99.04	2.15	99.04	1.79	0.74	99.04	0.84
KEF112, PA	100.00	1.09	100.00	1.10	0.14	98.06	1.47
KNZ184, KS	98.21	6.62	98.88	8.87	13.25	98.88	0.73
LRL117, PA	100.00	1.75	100.00	1.57	0.11	97.92	2.27
MCK131, KY	91.54	3.12	89.11	3.60	0.61	100.00	0.70
MCK231, KY	83.02	12.28	83.02	14.09	3.68	83.02	7.32

Table 8. AQS-Protocol Ozone QC Summary (2 of 2)

Site ID	% Span Pass ¹	Span %D ²	% One Point QC Pass ¹	One Point QC %D ²	One Point QC CL ³	% Zero Pass ¹	Zero Average (ppb) ²
MKG113, PA	100.00	2.72	99.03	2.10	0.26	100.00	0.94
OXF122, OH	99.25	2.93	98.97	3.21	0.19	98.99	1.86
PAL190, TX	76.52	4.37	94.78	5.54	4.77	98.26	2.16
PAR107, WV	97.32	1.50	92.86	2.17	0.42	92.04	4.00
PED108, VA	100.00	1.01	100.00	1.10	0.23	100.00	0.91
PND165, WY	97.89	1.32	98.97	2.16	1.68	100.00	0.62
PNF126, NC	95.37	2.91	96.30	2.16	0.30	100.00	0.22
PRK134, WI	87.74	4.04	86.79	4.17	0.74	100.00	0.91
PSU106, PA	100.00	1.79	98.99	1.49	0.28	100.00	0.29
QAK172, OH	100.00	2.45	97.17	2.83	0.40	97.17	2.73
ROM206, CO	98.10	5.56	98.10	6.23	5.14	100.00	0.86
SAL133, IN	94.17	2.16	95.15	2.17	1.00	99.03	1.36
SAN189, NE	100.00	0.78	100.00	0.47	0.05	100.00	1.32
SND152, AL	100.00	3.55	100.00	3.67	0.17	97.94	1.06
SPD111, TN	92.66	8.05	90.83	7.78	3.71	99.08	1.06
STK138, IL	97.09	2.44	99.16	2.84	0.08	100.00	0.47
SUM156, FL	100.00	1.09	100.00	1.15	0.11	98.82	0.71
UVL124, MI	97.12	2.91	98.08	2.07	0.40	100.00	0.43
VIN140, IN	100.00	1.73	100.00	1.83	0.22	100.00	0.83
VPI120, VA	100.00	1.46	97.12	1.33	0.25	95.19	1.76
WSP144, NJ	100.00	1.18	100.00	0.77	0.12	99.01	0.80
WST109, NH	100.00	4.17	100.00	4.43	0.09	100.00	0.86

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% confidence limit of the coefficient of variation. This should be less than or equal to the 7% 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
BFT142, NC	% One Point QC Pass	The zero air canisters were installed in incorrect order during August. Ambient data were not affected.
ESP127, TN	One Point QC %D One Point QC CL	Statistics affected by single failure. All checks are within criteria with this outlier removed.
HWF187, NY	Span %D One Point QC %D	The zero air compressor did not operate for one week. Ambient data were not affected.
KNZ184, KS	One Point QC %D One Point QC CL	The pressure transducer failed in the site analyzer.
MCK131, KY	% One Point QC Pass	The pressure transducer in the site transfer standard failed in mid-September. Ambient data were not affected.
MCK231, KY	% Span Pass; Span %D % One Point QC Pass One Point QC %D % Zero Pass	There was a flow leak in one of the zero air canisters that lasted for approximately three weeks. Ambient data were not affected.
PAL190, TX	% Span Pass	There was a leak in the calibration gas line. Ambient data were not affected.
PRK134, WI	% Span Pass % One Point QC Pass	The pressure transducer failed in the site analyzer.
SPD111, TN	Span %D One Point QC %D	The sample line was disconnected from the inlet probe during the first week in August.

Notes: %D = percent difference
CL = confidence limit

Table 10. Filter Packs Flagged as Suspect or Invalid

Site ID	Sample No.	Reason
ABT147, CT	1130001-01	Polling problem
BEL116, MD	1130001-09	Insufficient flow volume*
CHA467, NM	1127001-18	Power failure
CKT136, KY	1128001-20	Flow channel down
	1129001-20	Flow channel down
CNT169, WY	1128001-22	Flow channel down
EVE419, FL	1129001-30	Missing flow data
	1130001-30	Missing flow data
	1131001-30	Missing flow data
GLR468, MT	1127001-32	Missing flow data
GRB411, NV	1129001-33	Suspect data
MCK131, KY	1130001-47	Insufficient flow volume
MCK231, KY	1130001-48	Insufficient flow volume
	1131001-48	Insufficient flow volume
OXF122, OH	1128001-52	Insufficient flow volume

Notes: *Due to installation of new monitoring shelter

Table 11. Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	160
60	14
90	0
Unresolved by End of Quarter	23

Table 12. Field Calibration Failures by Parameter

Site ID	Parameter(s)
SUM156, FL	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 criteria, these data are adjusted per approved protocol described in the CASTNET QAPP, Revision 7.0 (MACTEC Engineering and Consulting, Inc., now known as AMEC, 2011). 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 2011 (percent recovery)

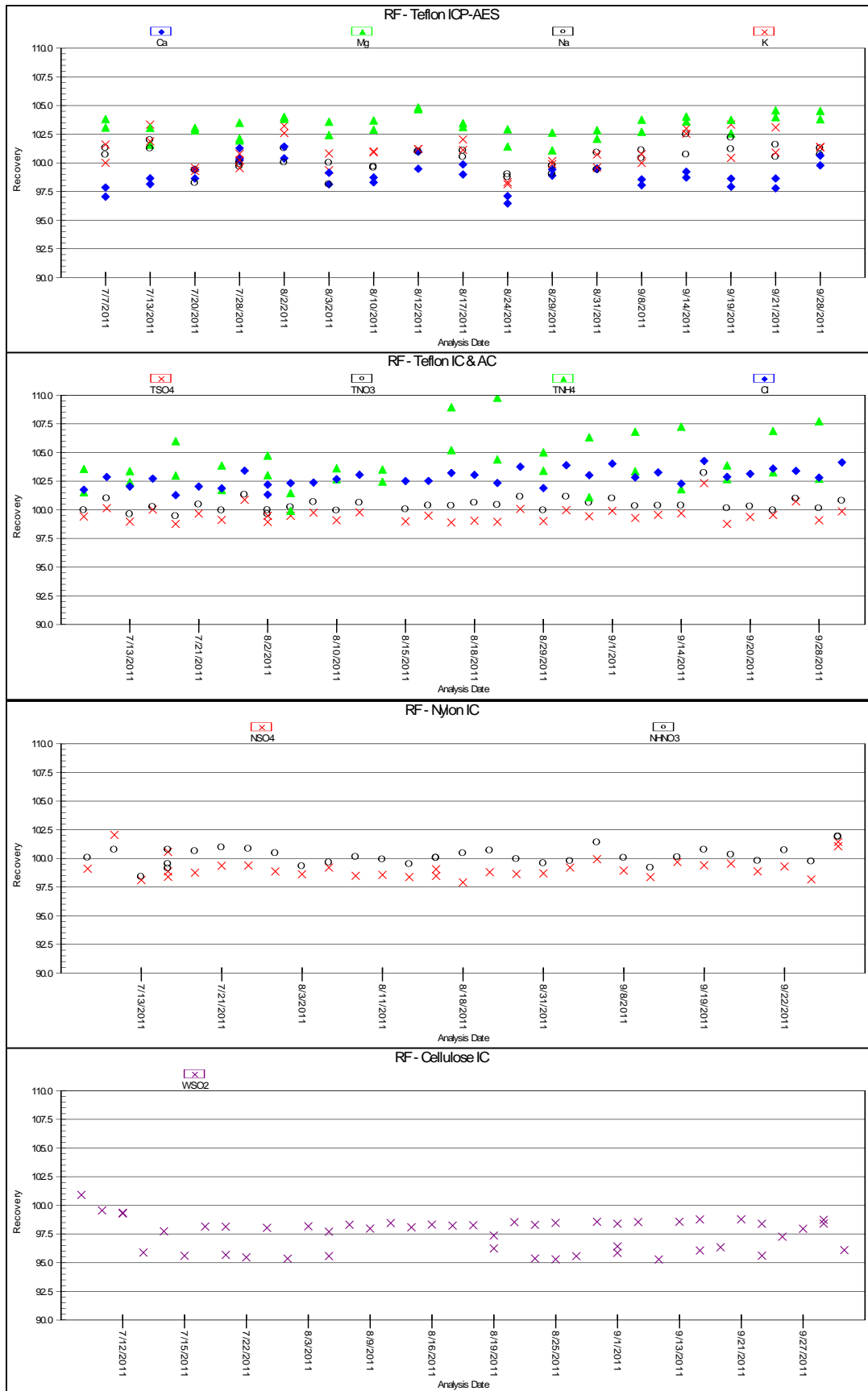


Figure 2. Continuing Calibration Spike Results for Third Quarter 2011 (percent recovery)

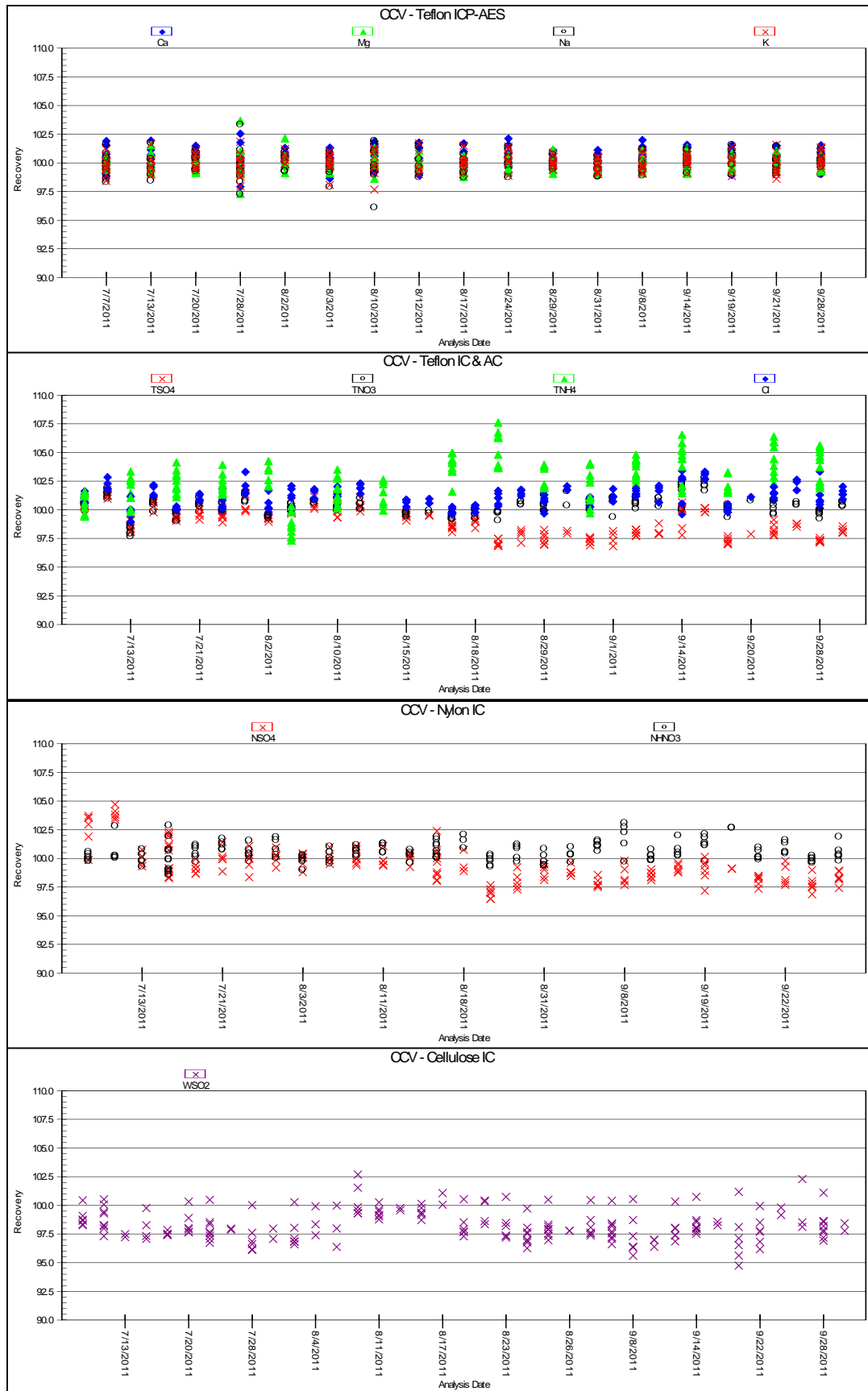


Figure 3. Replicate Sample Analysis Results for Third Quarter 2011 (total micrograms)

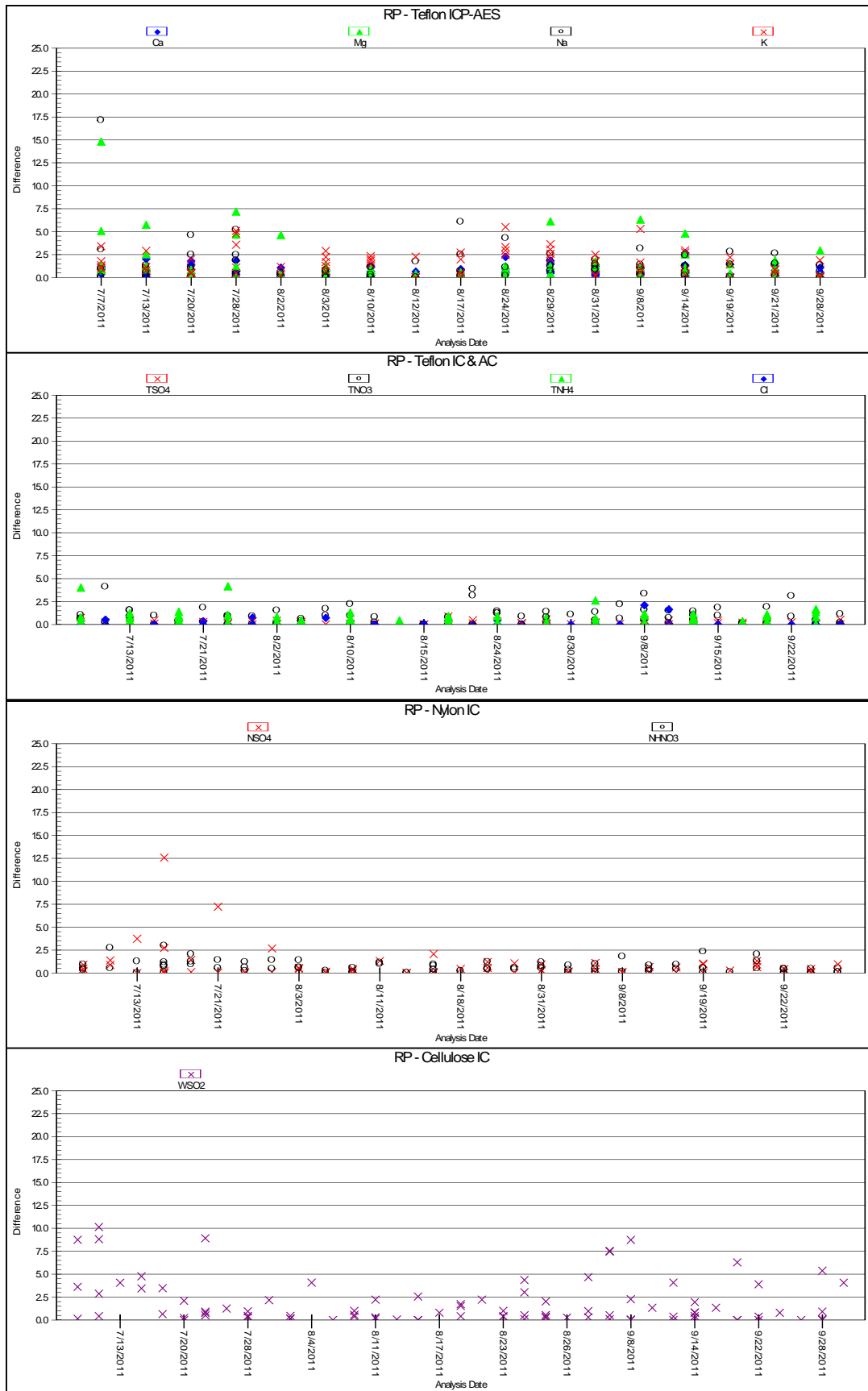


Figure 4. Laboratory Control Sample Results for Third Quarter 2011 (percent recovery)

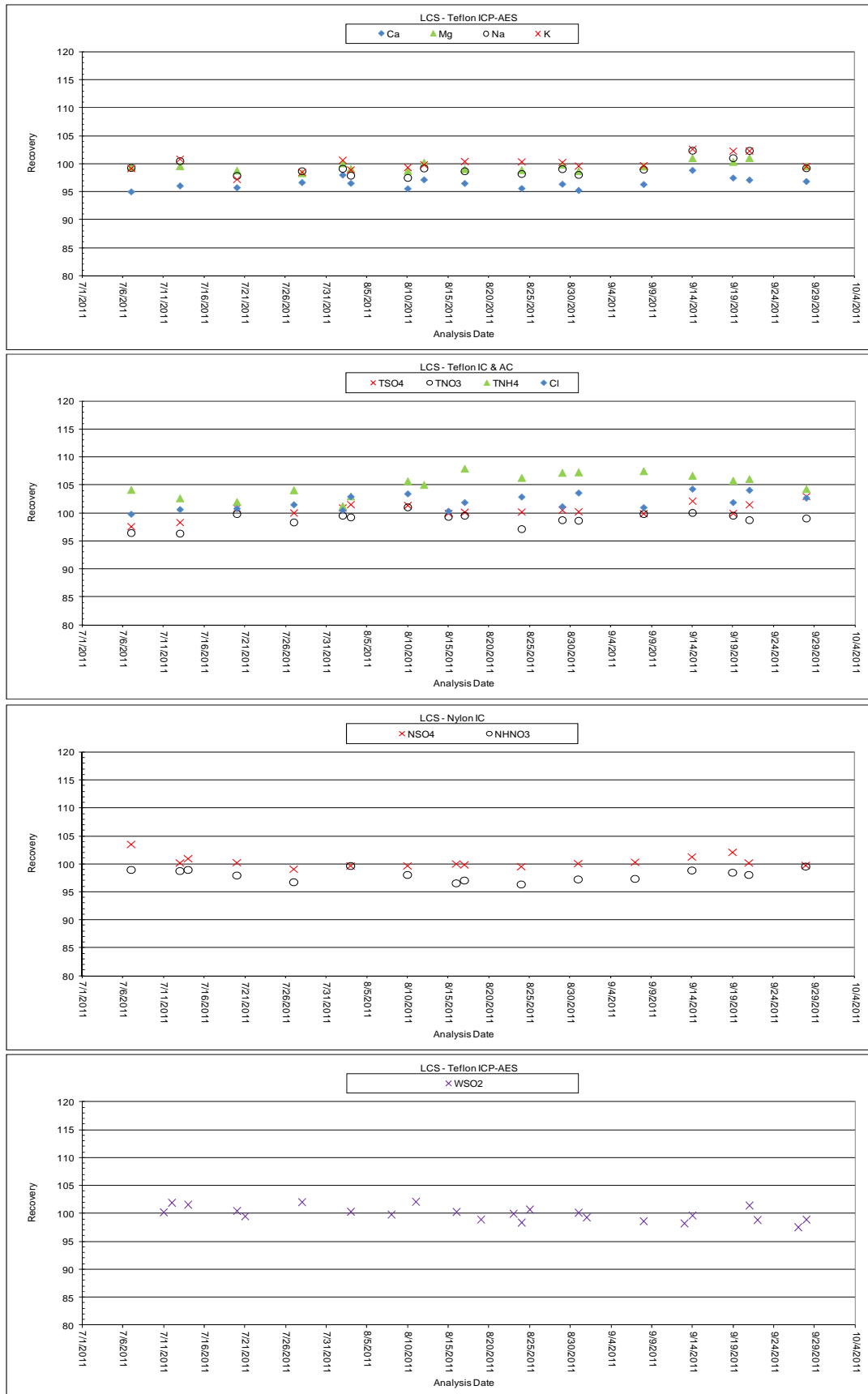


Figure 5. Method Blank Analysis Results for Third Quarter 2011 (total micrograms)

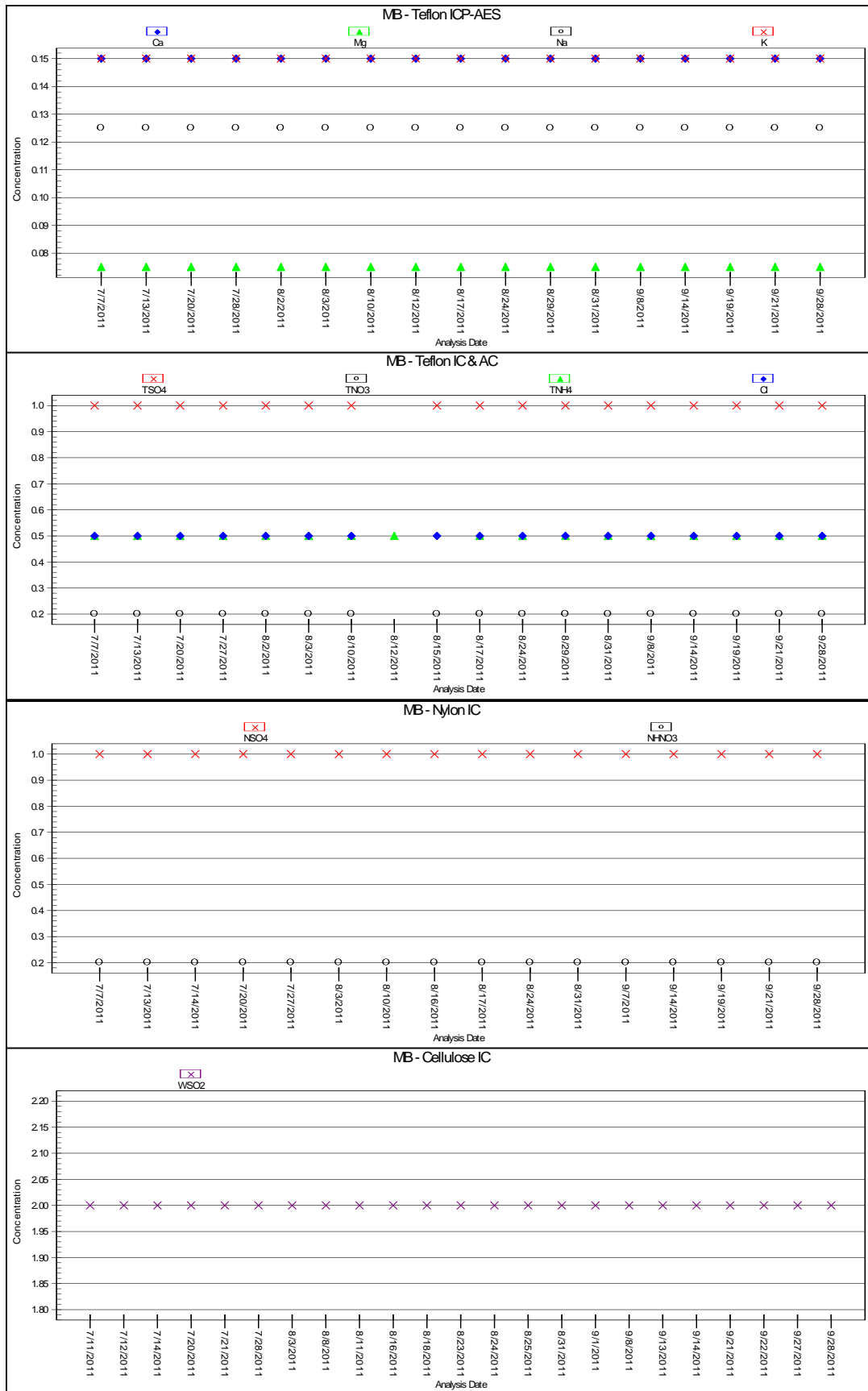


Figure 6. Laboratory Blank Analysis Results for Third Quarter 2011 (total micrograms)

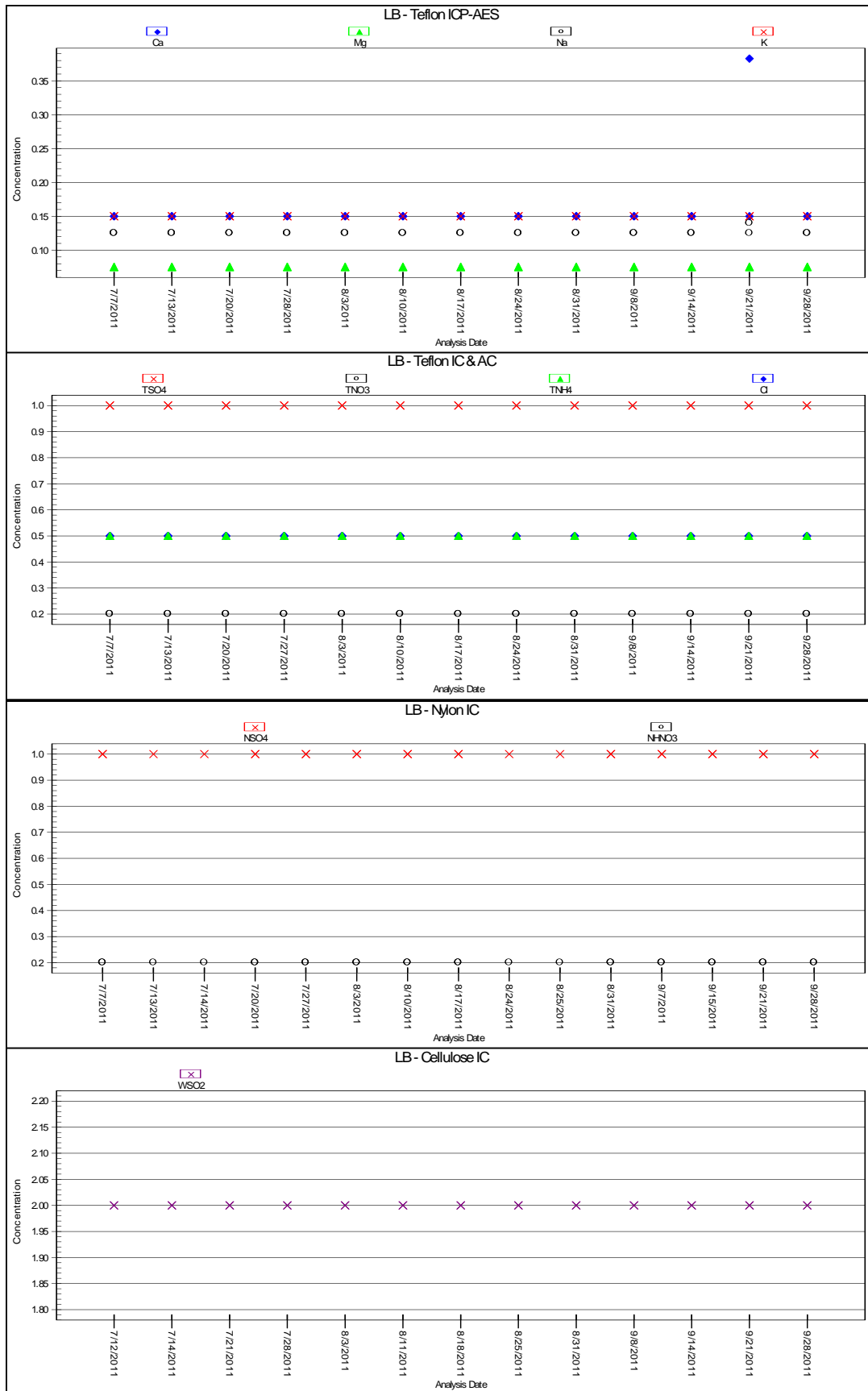


Figure 7. Field Blank Analysis Results for Third Quarter 2011 (total micrograms)

