Summary of Quarterly Operations (April – June)

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 second 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.

RTI International (RTI) audited MACTEC's analytical laboratory during the week of April 25, 2011. The audit was very thorough and covered all laboratory activities described in the CASTNET QAPP and standard operating procedures. Findings indicated that the MACTEC laboratory personnel are qualified, properly trained, and adhere to documented project procedures. There were no major findings. Minor findings included the need to reconcile nomenclature between project documents.

Final results were received in April 2011 for MACTEC's analytical laboratory's 2010 analyses of U.S. Geological Survey (USGS) interlaboratory comparison test samples. Results indicated good performance. MACTEC submitted analyses of interlaboratory comparison test samples to USGS each quarter of 2010. MACTEC is currently participating in the 2011 USGS interlaboratory comparison program.

Data for the trace-level gas analyzers at the BEL116, MD site are currently reported as measured with no reporting limit filters. During May, calibration data were evaluated, and reporting limits for the trace-level gas analyzers at the BEL116, MD site were developed. The proposed reporting limits were sent to EPA for review and approval.

MACTEC continued investigating the cause of the intermittent potassium contamination. The contamination correlates with high temperatures in the filter pack shipping tube and primarily occurs during the warmest months and in warmer regions. Moisture may also be a factor. MACTEC is evaluating other carbonates for impregnation of the cellulose filters. Rubidium and cesium salts are options. Other salts without target analytes are not sufficiently water soluble.

During June 2011, MACTEC's CASTNET QA Manager verified that corrective action either has been taken or is in process with regard to the findings from the November 2010 annual internal technical systems audits of the CASTNET analytical laboratory and the CASTNET field instrumentation laboratory. For example, a standard operating procedure for supply inventory and invoicing has been drafted for inclusion with the next QAPP revision. These audits are designed to verify conformance of laboratory activities with those established by the CASTNET QAPP and associated standard operating procedures. The follow-up of the audit indicated general compliance by MACTEC personnel.

In early June 2011, MACTEC traveled to the ROM406/206, CO site to work with the National Park Service (NPS) contractor, Air Resource Specialists, Inc. (ARS), to identify any differences that may be the potential cause(s) of observed ozone measurement bias. Transfer standard readings were compared. Calibration procedures and associated equipment configuration were also compared. While differences in instruments and procedures were noted, no one procedure stood out as the cause of the bias nor was the cumulative error observed sufficient to account for it. Data from the comparisons, as well as configuration and procedural differences, will be further evaluated to try to isolate the cause(s) of the continued bias.

Collocated filter pack precision data and completeness data for meteorological measurements are presented for data validated to Level 3 during the quarter. Table 1 lists the quarters of data that were validated to Level 3 during second 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 Air Quality System (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 second 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 second quarter 2011.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for second quarter 2011. All results were within the criteria listed in Table 4.

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

Table 8 presents summary statistics of critical criteria measurements at AQS-protocol ozone sites collected during the quarter. All data that fail to meet the criteria listed in Table 5 will be invalidated. The QC results at BEL116, MD; CTH110, NY; and SND152, AL were affected by problems with their zero air systems. The analyzer at BVL130, IL experienced drift in its calibration during April, resulting in a site visit to correct the problem. The site analyzer was replaced at CAD150, AR in May due to a malfunction affecting the optical bench. Finally, QC results at WSP144, NJ were affected by failure of the site analyzer's pressure transducer.

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. These limits may change as data are collected and analyzed. Figure 5 presents LCS analysis results for second quarter 2011. All recovery values were between 95 percent and 105 percent.

Blank Results

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for second quarter 2011. All results were within criteria (two times the reporting limit) listed in Table 4 with

the exception of one cellulose LB sample and one Teflon FB sample (potassium). The cellulose LB value was an error resulting from a mislabeled peak. The actual sample result was below the reporting limit. The potassium FB value was approximately five times the reporting limit.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during second quarter 2011 are listed in Table 9. This table includes associated site identification and a brief description of the reason the sample was flagged. During second quarter, 22 filter pack samples were invalidated.

Field Problem Count

Table 10 presents counts of field problems affecting continuous data collection for more than one day during second 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 19 sites during second quarter 2011. All sites and parameters were within the criteria listed in Table 3 with the exception of those parameters at the 5 sites that are listed in Table 11.

Tables and Figures

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

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-1/SE-5	August 2010 – January 2011	6	Quarter 4 2010	1
MW-7/W-9	September 2010 – February 2011	6	Quarter 4 2010	1
E-2/MW-8	October 2010 – March 2011	6	Quarter 4 2010 – Quarter 1 2011	2

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

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	± 10% (of reading)	± 10%
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.

[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
ICP-AES = inductively coupled plasma-atomic emission spectrometry
IC = ion chromatography
MARPD = mean absolute relative percent difference
* = as nitrogen

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP, Revision 7.0 (MACTEC, 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 Second 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-}	32	167	82	16	26	80
	NO_3^-	32	167	82	16	26	80
	NH_4^+	32	168	81	16	26	80
	Cl^-	32	167	75	16	26	80
	Ca^{2+}	32	172	75	16	26	80
	Mg^{2+}	32	172	75	16	26	80
	Na^+	32	172	75	16	26	80
	K^+	32	172	75	16	26	80
Nylon	SO_4^{2-}	34	162	77	15	26	80
	NO_3^-	34	162	77	15	26	80
Cellulose	SO_4^{2-}	37	152	78	19	26	80

Table 7. Filter Pack Receipt Summary for Second Quarter 2011

Count of samples received more than 14 days after removal from tower:	6
Count of all samples received:	727
Fraction of samples received within 14 days:	0.992
Average interval in days:	4.27
First receipt date:	04/01/2011
Last receipt date:	06/30/2011

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)
ALC188, TX	100.00	2.15	100.00	2.63	0.47	97.83	-0.86
ALH157, IL	100.00	5.68	95.88	5.77	0.36	100.00	-0.67
ARE128, PA	100.00	1.74	88.12	4.31	0.62	100.00	0.13
BEL116, MD	88.04	12.88	88.04	11.86	3.15	85.87	2.73
BFT142, NC	100.00	2.65	100.00	2.06	0.32	100.00	0.46
BVL130, IL	59.17	4.47	59.66	4.53	0.83	100.00	-0.59
BWR139, MD	100.00	1.09	100.00	0.99	0.51	100.00	-0.10
CAD150, AR	81.72	9.62	81.72	9.62	3.01	93.55	2.34
CDR119, WV	97.83	1.09	97.83	1.12	0.43	100.00	-2.04
CDZ171, KY	100.00	0.91	97.87	1.13	1.60	98.94	-3.05
CKT136, KY	98.96	8.24	100.00	2.22	0.42	100.00	0.09
CND125, NC	96.95	5.84	87.02	6.69	1.55	96.21	2.32
COW137, NC	100.00	0.71	100.00	0.74	0.37	100.00	-0.12
CTH110, NY	68.60	12.93	77.91	13.36	2.93	88.37	5.86
CVL151, MS	95.42	10.92	94.77	6.98	5.85	100.00	-0.06
DCP114, OH	100.00	1.54	100.00	0.83	0.28	100.00	1.03
ESP127, TN	100.00	2.92	100.00	2.95	0.40	100.00	-0.75
GAS153, GA	99.11	8.72	96.43	8.04	7.97	100.00	-2.73
IRL141, FL	100.00	2.52	100.00	2.56	0.24	100.00	0.17
KNZ184, KS	100.00	0.73	100.00	0.33	0.42	100.00*	0.45*
LRL117, PA	100.00	1.85	98.94	2.40	5.36	100.00	-0.18
MCK131, KY	100.00	2.70	100.00	3.03	0.37	98.91	-0.74
MCK231, KY	96.74	4.96	96.74	4.90	1.52	95.65	-0.48
OXF122, OH	100.00	3.10	100.00	3.52	0.35	100.00	-0.33
PED108, VA	92.31	6.72	92.31	5.12	1.75	91.21	0.36
PNF126, NC	100.00	2.85	100.00	3.28	0.35	100.00	0.29
PRK134, WI	98.91	3.03	98.91	2.55	0.25	100.00	0.55
PSU106, PA	100.00	2.00	100.00	1.51	5.48	100.00	-0.45
QAK172, OH	100.00	2.80	98.91	2.58	0.32	98.91	-1.10
ROM206, CO	100.00	1.73	100.00	2.57	0.39	100.00	-0.98
SAN189, NE	100.00	0.85	100.00	0.72	0.28	100.00	-0.17
SND152, AL	87.60	13.29	87.60	10.45	3.03	86.89	3.39
SPD111, TN	84.88	2.75	93.02	2.11	0.43	97.70	-0.30
STK138, IL	98.94	2.58	100.00	2.46	0.28	100.00*	0.09*

Table 8. AQS-Protocol Ozone QC Summary (2 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)
SUM156, FL	95.45	1.89	98.86	1.72	0.48	100.00	-0.02
VIN140, IN	100.00	1.26	100.00	1.59	0.31	100.00	0.23
VPI120, VA	96.74	3.50	97.83	2.78	0.30	100.00	2.06
WSP144, NJ	92.93	23.33	92.93	25.62	17.83	98.99	-0.44

Notes: [1] Percentage of span comparisons that pass the 7% criterion

[2] Absolute value of the average percent differences between the on-site transfer standard and the site monitor

[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.

* Spike (> 7,000 ppb) removed

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

Table 9. Filter Packs Flagged as Suspect or Invalid

Site ID	Sample No.	Reason
ABT147, CT	1114001-01	Polling problems
ALC188, TX	1115001-03	Insufficient flow volume
BBE401, TX	1115001-08	Suspect potassium value
BEL116, MD	1116001-09	Polling problems
	1119001-09	Polling problems
	1121001-09	Polling problems
	1123001-09	Polling problems
BFT142, NC	1118001-10	Insufficient flow volume
CNT169, WY	1119001-22	Polling problems
GRC474, AZ	1123001-34	Insufficient flow volume
GRS420, TN	1117001-35	Insufficient flow volume
HOW132, ME	1122001-37	Insufficient flow volume
HWF187, NY	1120001-39	Insufficient flow volume
JOT403, CA	1116001-41	Insufficient flow volume
	1117001-41	Insufficient flow volume
	1119001-41	Insufficient flow volume
LRL117, PA	1114001-45	Insufficient flow volume
OXF122, OH	1119001-52	Insufficient flow volume
PND165, WY	1117001-58	Polling problems
SHN418, VA	1120001-68	Insufficient flow volume
SND152, AL	1117001-69	Polling problems
YEL408, WY	1121001-81	Insufficient flow volume

Table 10. Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	161
60	3
90	0
Unresolved by End of Quarter	33

Table 11. Field Calibration Failures by Parameter

Site ID	Parameter(s)
BVL130, IL	Ozone
CNT169, WY	Flow Rate
GTH161, CO	Flow Rate
MKG113, PA	Flow Rate
PND165, WY	Flow Rate

Note: Per CASTNET project protocols, data for all parameters except flow and ozone are flagged as "suspect" (S) but still considered valid if the calibration criterion is not exceeded by more that 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, 2011). The protocol used for flow is applied to ozone except at sites configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations.

Figure 1. Reference Standard Results for Second Quarter 2011 (percent recovery)

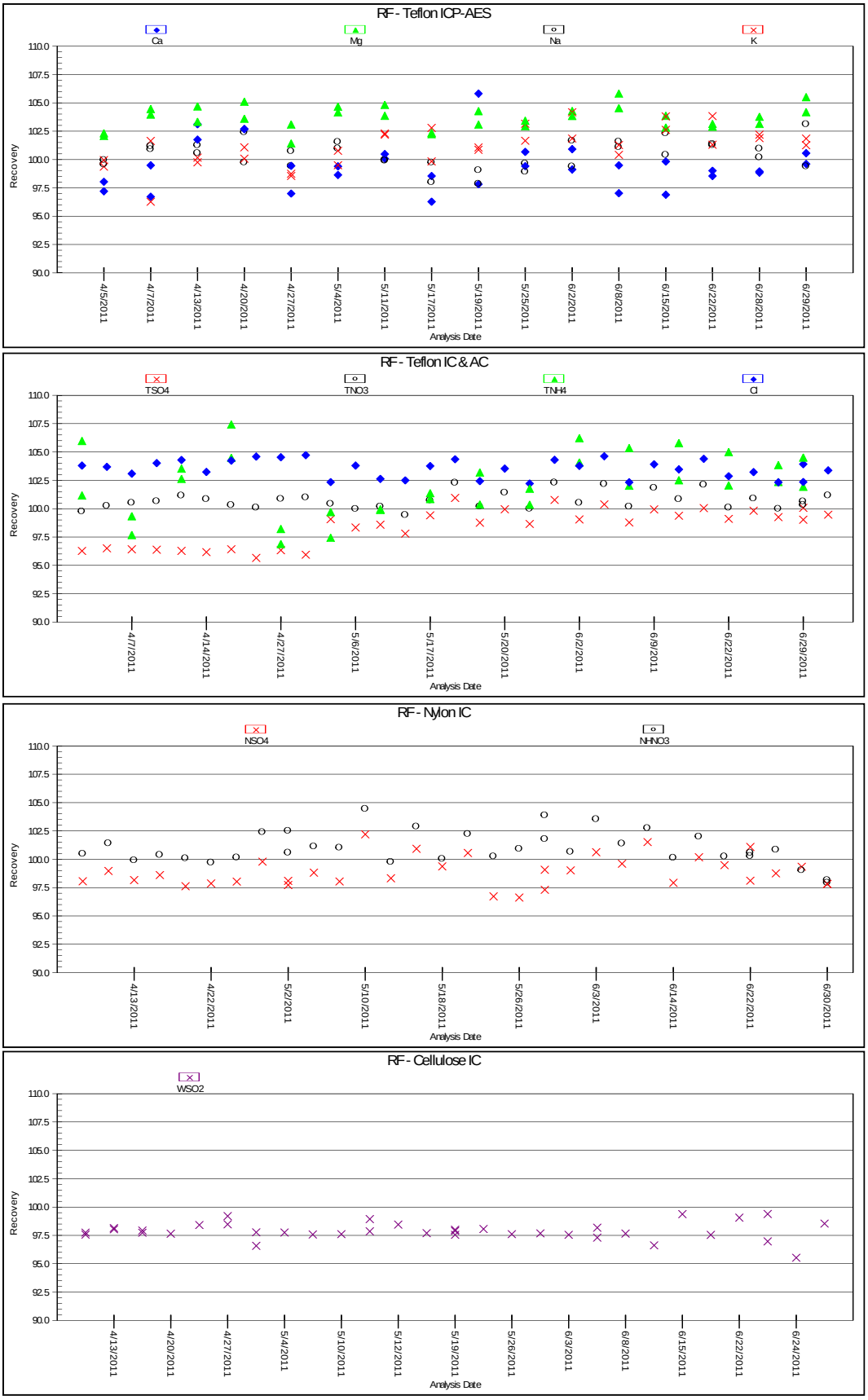


Figure 2. Continuing Calibration Spike Results for Second Quarter 2011 (percent recovery)

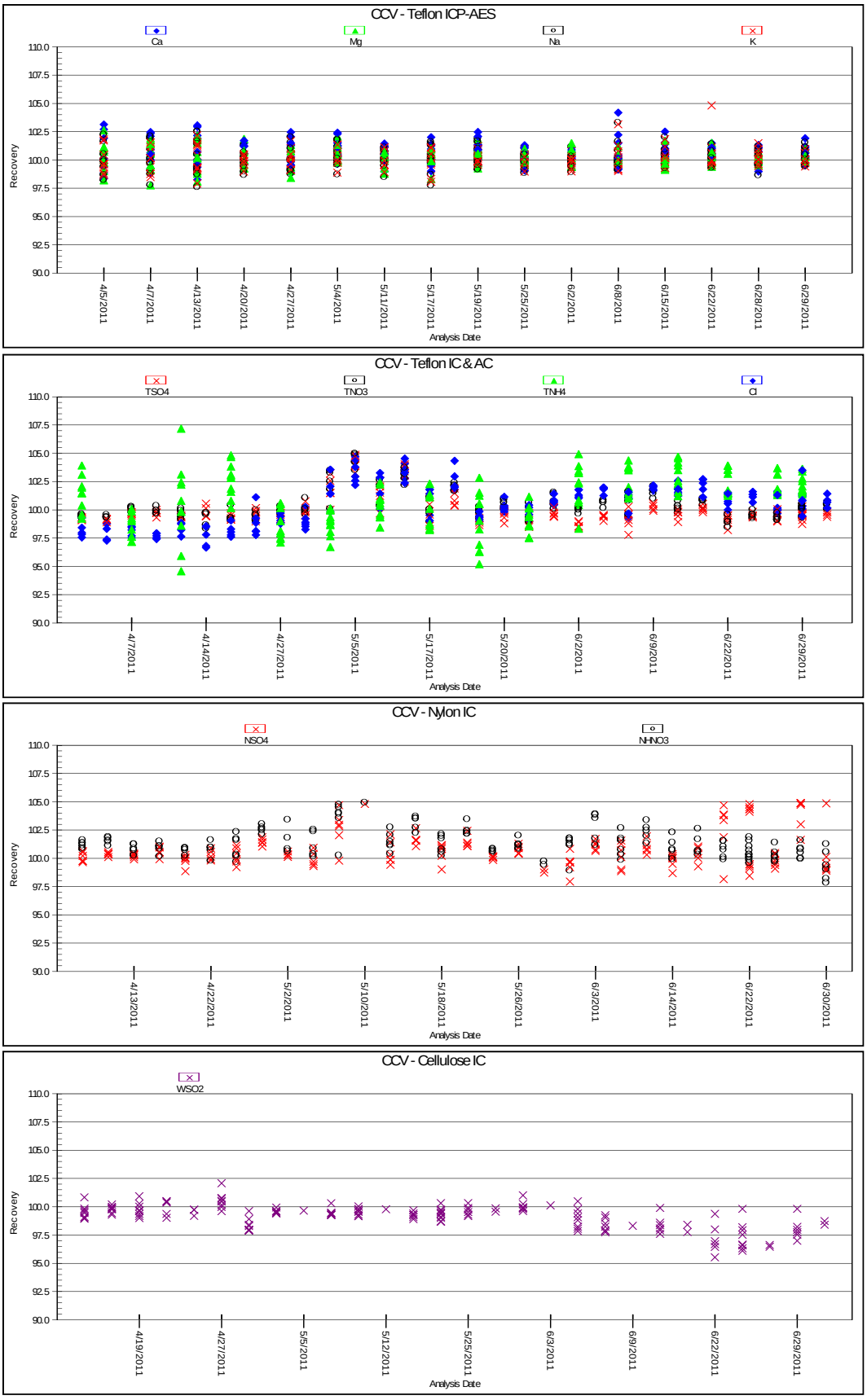


Figure 3. Replicate Sample Analysis Results for Second Quarter 2011 (total micrograms)

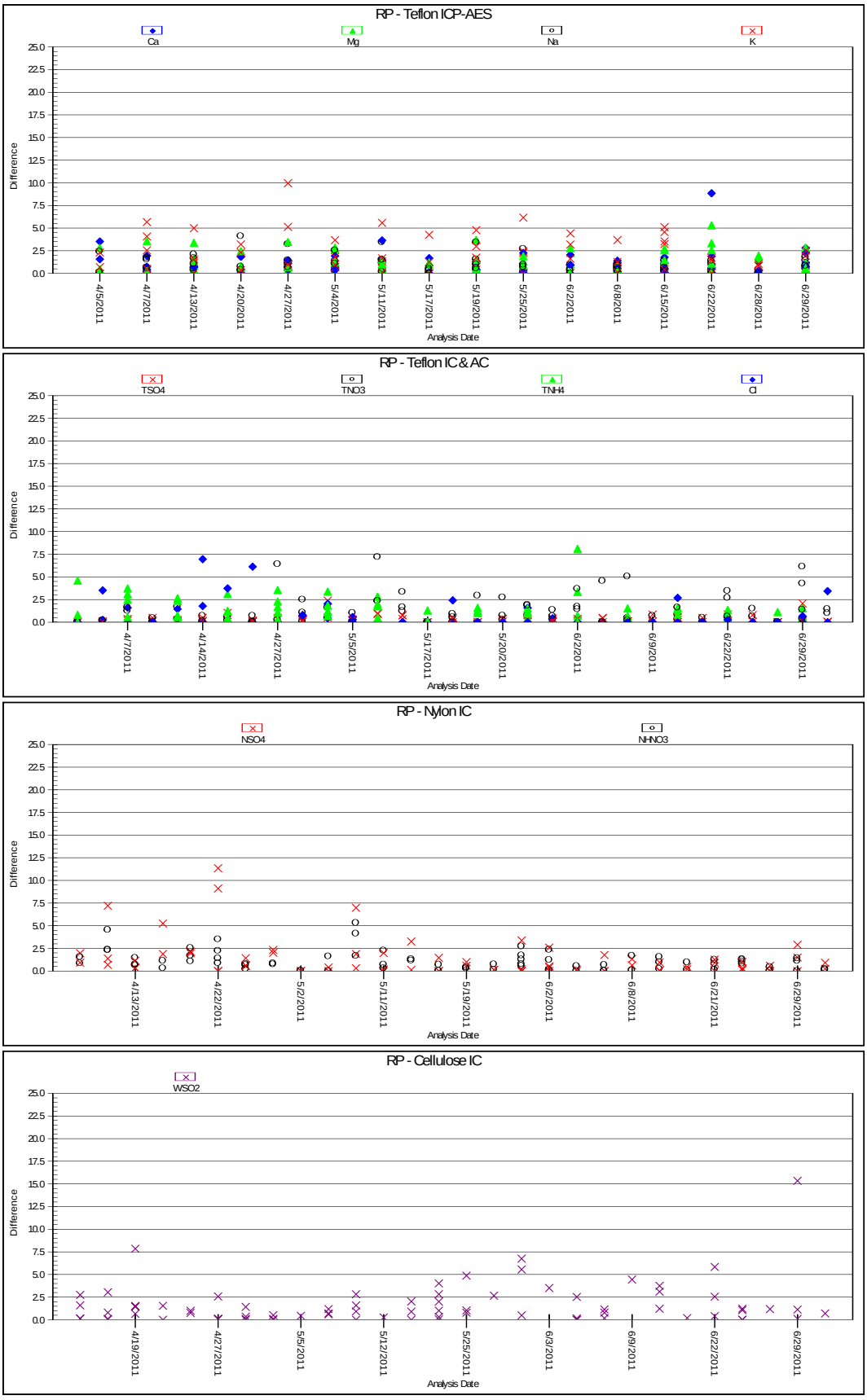
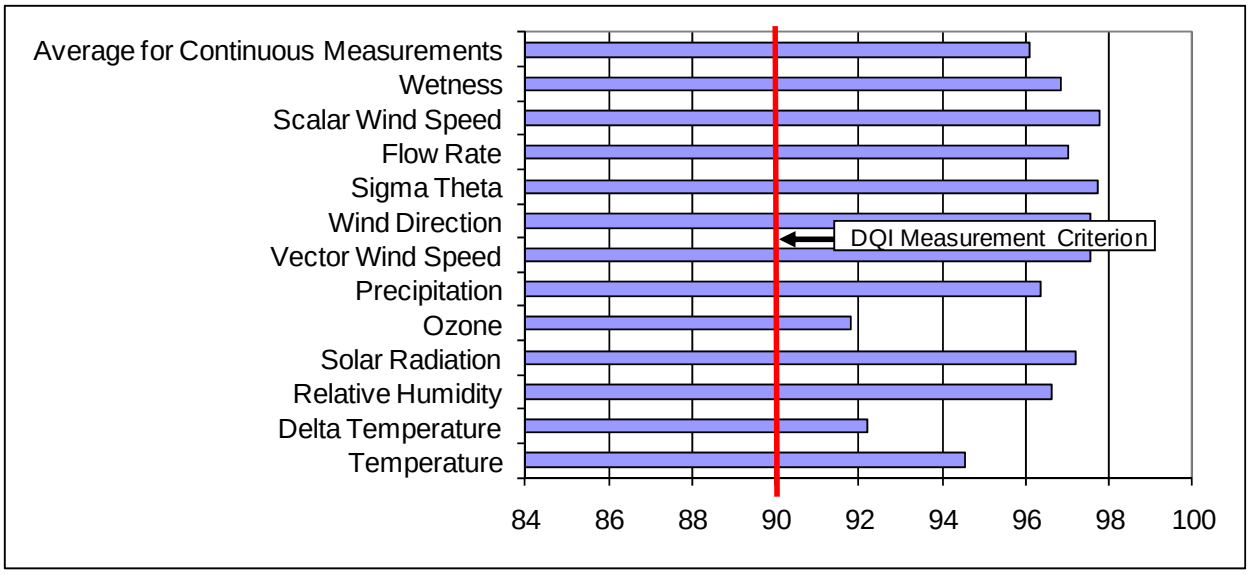


Figure 4. Percent Completeness of Measurements for Fourth Quarter 2009 through First Quarter 2011*



Note: *Presents Level 3 data available during the second quarter of 2011.

Figure 5. Laboratory Control Sample Results for Second Quarter 2011 (percent recovery)

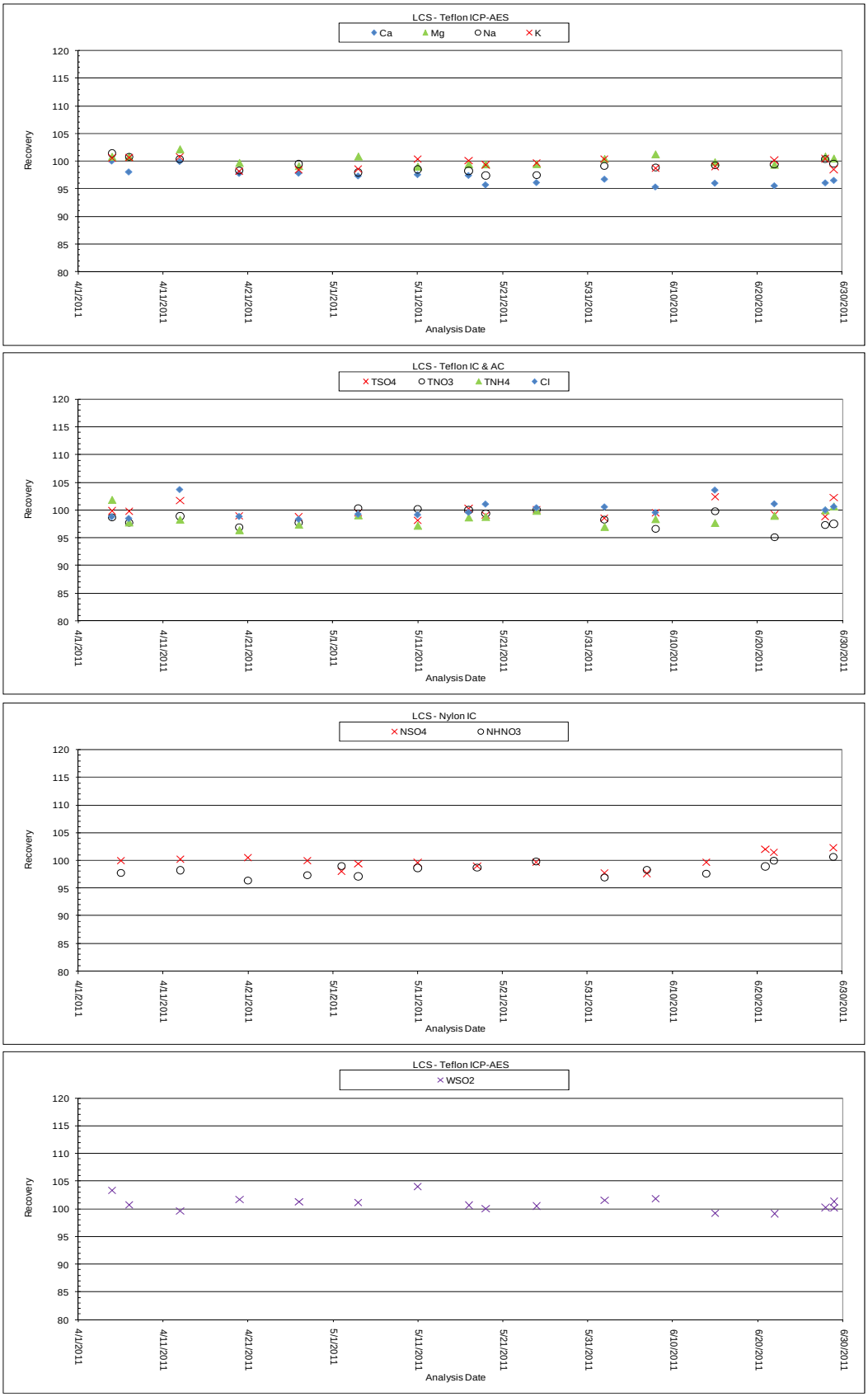


Figure 6. Method Blank Analysis Results for Second Quarter 2011 (total micrograms)

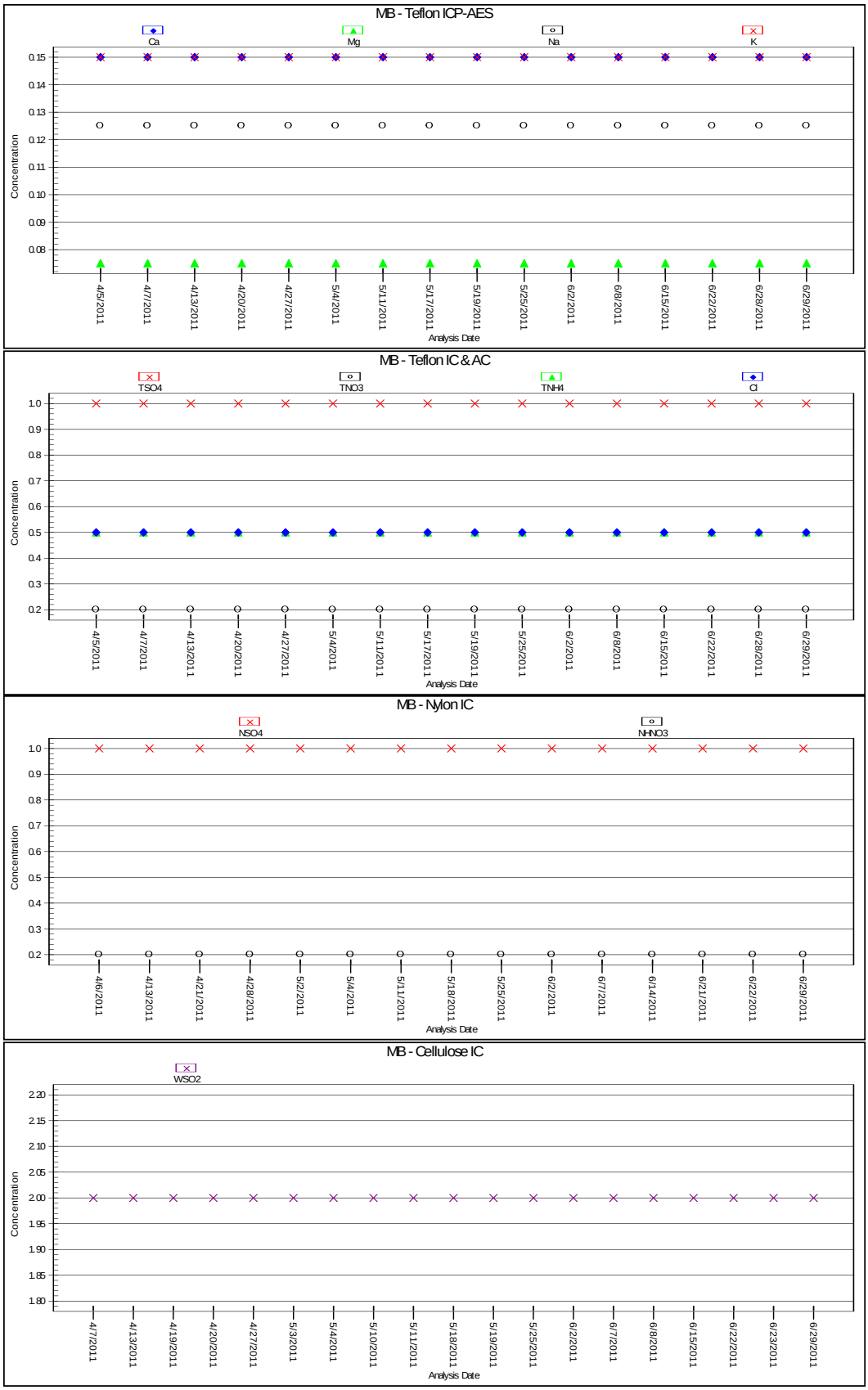


Figure 7. Laboratory Blank Analysis Results for Second Quarter 2011 (total micrograms)

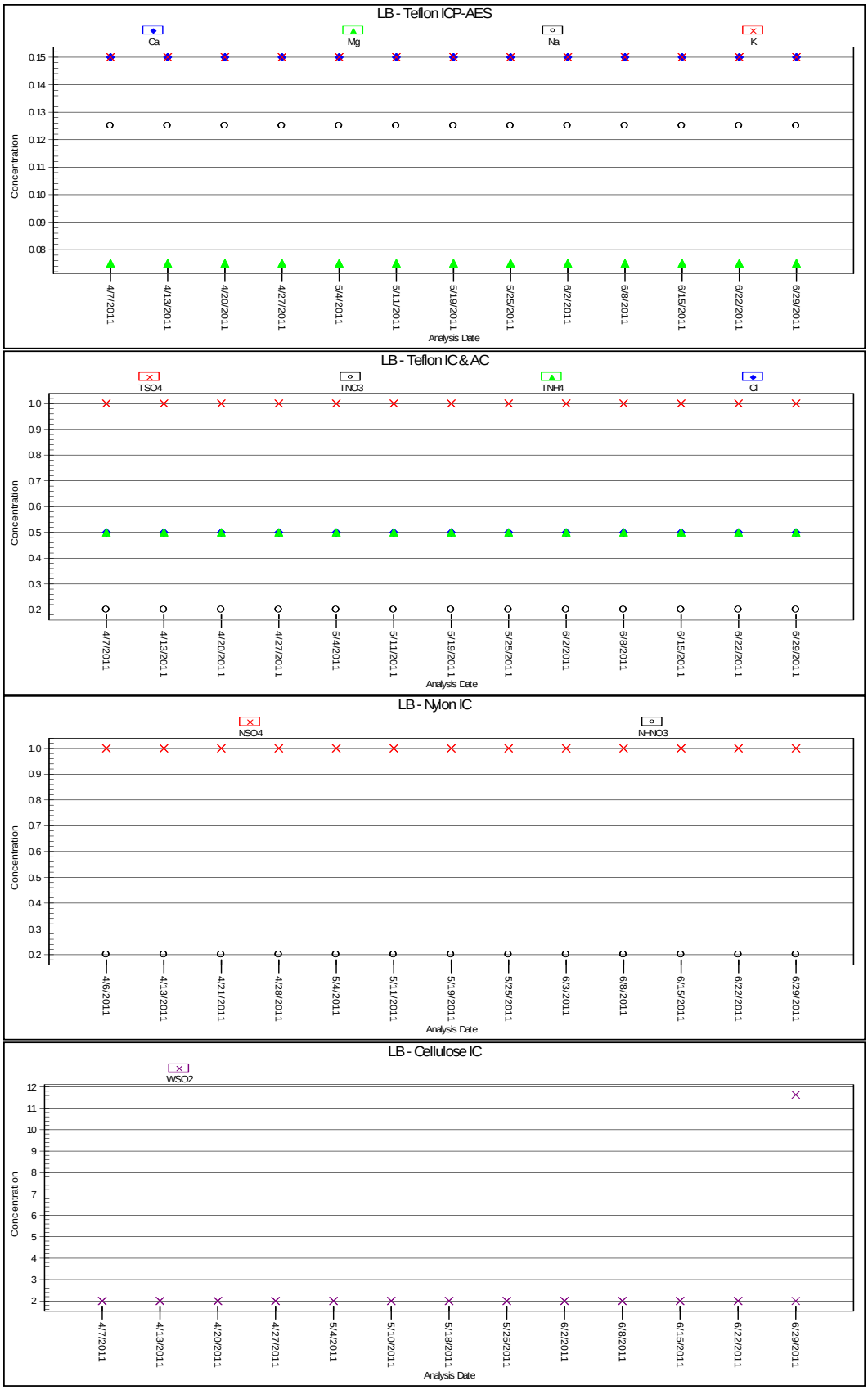


Figure 8. Field Blank Analysis Results for Second Quarter 2011 (total micrograms)