



## 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 2010. 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.

The CASTNET QAPP Revision 6.0 was approved by EPA during May 2010.

During second quarter, MACTEC upgraded the laboratory instruments used for CASTNET. MACTEC ordered four new autosamplers, two new ion chromatographs, and a new inductively coupled argon plasma atomic emission spectrometer. The standard operating procedures (SOPs) for the new instruments were modified as needed and will be included in the CASTNET QAPP Revision 7.0. Data comparisons were run to ensure proper operation and compatibility with CASTNET analyses.

During March 2010, final results were received by MACTEC for analyses completed for proficiency test (PT) study (0095) 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. MACTEC performed well on the analyses for all parameters except conductivity. Conductivity is not required for CASTNET analyses; however, it is required for the cloud water samples obtained through the Mountain Acid Deposition Program (MADPro). MACTEC tested the conductivity meter and discovered that it

was no longer functioning reliably. The meter and probe were replaced prior to the start of the 2010 cloud water sampling season for MADPro.

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 2010 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.

### **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 5 presents the number of analyses in each category that were performed during second quarter 2010.

### **Sample Receipt Statistics**

EPA requires that 95 percent of field samples from EPA-sponsored sites be received by the CASTNET laboratory in Gainesville, FL no later than 14 days after removal from the sampling tower. Table 6 presents the relevant sample receipt statistics for second quarter 2010.

### **Data Quality Indicator (DQI) Results**

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for second quarter 2010. All results were within the criteria listed in Table 4 with the exception of one RP sample. Investigation revealed that the duplicate calculation referenced the wrong sample. This has been corrected in the batch and will be submitted as an update to the database.

Average recoveries for sulfate RF samples have declined from levels reported in September 2009, while average recoveries for chloride RF samples have risen from levels reported in January 2009. While the average recovery range has shifted, there is no persistent change in a single direction through consecutive analyses. Changes such as these can be expected as the result of changes between manufacturing lots or even within the manufacturer’s tolerance level

in the same lot, as different shipments are received and different containers utilized. Manufacturing tolerance for the aforementioned analytes is approximately 3 percent.

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

### **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 2010. All recovery values were between 90 percent and 110 percent.

### **Blank Results**

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for second quarter 2010. All results were within the criteria (two times the reporting limit) listed in Table 4 with the exception of several field blanks. One Teflon filter potassium FB response was at about six times the reporting limit, and one cellulose filter sulfur dioxide FB response was at about five times the reporting limit. Six nylon sulfate FB responses were between two and seven times the reporting limit with five sharing the same sample preparation and analysis batches. All of these FB responses are under investigation. The cause of the nylon sulfate excursions is currently undetermined but appears to be isolated affecting only field blanks.

### **Suspect/Invalid Filter Pack Samples**

Filter pack samples that were flagged as suspect or invalid during second quarter 2010 are listed in Table 7. This table includes associated site identification and a brief description of the reason the sample was flagged. During second quarter, 10 filter pack samples were invalidated.

### **Field Problem Count**

Table 8 presents counts of field problems affecting continuous data collection for more than one day during second quarter 2010. 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. The time period does not correlate with the quantity of data affected. For example, if a 5-hour block of missing data takes 60 days to replace, it will show up in the 60-day category. By the same token, a site missing 200 hours of data due to the damage caused by a lightning strike will show up in the 30-day category if the site is repaired within 30 days, even though the data cannot be replaced.

### **Field Calibration Results**

Calibrations were performed at 21 sites during second quarter 2010. All sites and parameters were within the criteria listed in Table 3 with the exception of those parameters at the three sites that are listed in Table 9.

## **Tables and Figures**

**Table 1.** Data Validated to Level 3 during Second Quarter 2010

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-1/SE-5	August 2009 – January 2010	6	Quarter 4 2009	1
MW-7/W-9	September 2009 – February 2010	6	Quarter 4 2009	1
E-2/MW-8	October 2009 – March 2010	6	Quarter 4 2009 – Quarter 1 2010	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			
<b>Eastern Sites (20 Total)</b>					
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	
<b>Southeastern Sites (10 Total)</b>					
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		
<b>Midwestern Sites (19 Total)</b>					
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 (5 Sites)	April/October	SAL133, IN HOX148, MI	ANA115, MI UVL124, MI	LYK123, OH	
<b>Western Sites (10 Total)</b>					
W-9 (4 Sites)	March/September	KNZ184, KS CHE185, OK	SAN189, NE ALC188, TX		
W-10 (6 Sites)	May/November	CON186, CA PAL190, TX	GTH161, CO ROM206, CO	CNT169, WY PND165, WY	

**Table 3.** Data Quality Indicators for CASTNET Continuous Measurements

Measurement		Criteria*	
Parameter	Method	Precision	Accuracy
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
Relative humidity	Thin film capacitor	± 10% (of full scale)	± 10%
Solar radiation	Pyranometer	± 10% (of reading taken at local noon)	± 10%
Precipitation	Tipping bucket rain gauge	± 10% (of reading)	± 0.05 inch <sup>†</sup>
Ambient temperature	Platinum RTD	± 1.0°C	± 0.5°C
Delta temperature	Platinum RTD	± 0.5°C	± 0.5°C
Ozone	UV absorbance	± 10% (of reading)	± 10%
Filter pack flow	Mass flow controller	± 10%	± 5%
Surface wetness	Conductivity bridge	Undefined	Undefined

Notes: °C = degrees Celsius  
m/s = meters per second  
RTD = resistance-temperature device  
UV = ultraviolet

\* Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments

<sup>†</sup> For target value of 0.50 inch

**Table 4.** Data Quality Indicators for CASTNET Laboratory Measurements

Analyte	Medium	Method	Precision <sup>1</sup> (MARPD)	Accuracy <sup>2</sup> (%)	Nominal Reporting Limits	
					mg/L	µg/Filter
Ammonium (NH <sub>4</sub> <sup>+</sup> )	F	AC	20	90 - 110	0.020 *	0.5
Sodium (Na <sup>+</sup> )	F	ICP-AES	20	95 - 105	0.005	0.125
Potassium (K <sup>+</sup> )	F	ICP-AES	20	95 - 105	0.006	0.15
Magnesium (Mg <sup>2+</sup> )	F	ICP-AES	20	95 - 105	0.003	0.075
Calcium (Ca <sup>2+</sup> )	F	ICP-AES	20	95 - 105	0.006	0.15
Chloride (Cl <sup>-</sup> )	F	IC	20	95 - 105	0.020	0.5
Nitrate (NO <sub>3</sub> <sup>-</sup> )	F	IC	20	95 - 105	0.008 *	0.2
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	F	IC	20	95 - 105	0.040	1.0

**Notes:** <sup>1</sup> This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples. The goal for the RPD criterion changed to 20 percent at the onset of the CASTNET IV contract beginning on August 11, 2009.

<sup>2</sup> 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.

F = filter pack samples  
 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 6.0 (MACTEC, 2010).

**Table 5.** QC Analysis Count for Second Quarter 2010

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	SO <sub>4</sub> <sup>2-</sup>	37	186	89	18	28	86
	NO <sub>3</sub> <sup>-</sup>	37	186	89	18	28	86
	NH <sub>4</sub> <sup>+</sup>	34	182	94	17	28	86
	Cl <sup>-</sup>	37	186	89	18	28	86
	Ca <sup>2+</sup>	34	189	92	17	28	86
	Mg <sup>2+</sup>	34	189	92	17	28	86
	Na <sup>+</sup>	34	189	92	17	28	86
Nylon	SO <sub>4</sub> <sup>2-</sup>	45	180	88	20	24	101
	NO <sub>3</sub> <sup>-</sup>	45	180	88	20	24	101
Cellulose	SO <sub>4</sub> <sup>2-</sup>	50	184	90	23	26	84

**Table 6.** Filter Pack Receipt Summary for Second Quarter 2010

Count of samples received more than 14 days after removal from tower:	1
Count of all samples received:	761
Fraction of samples received within 14 days:	0.999
Average interval in days:	4.947
First receipt date:	04/01/2010
Last receipt date:	06/30/2010

**Table 7.** Filter Packs Flagged as Suspect or Invalid

Site ID	Sample No.	Reason
CKT136, KY	1015001-20	Insufficient flow
CON186, CA	1019001-23	Insufficient flow
SUM156, FL	1023001-74	Insufficient flow
THR422, ND	1019001-75	Insufficient flow
VOY413, MN	1021001-78	Insufficient flow
WNC429, SD	1015001-80	Insufficient flow
	1016001-80	
	1017001-80	
	1021001-80	
	1022001-80	

**Table 8.** Field Problems Affecting Data Collection

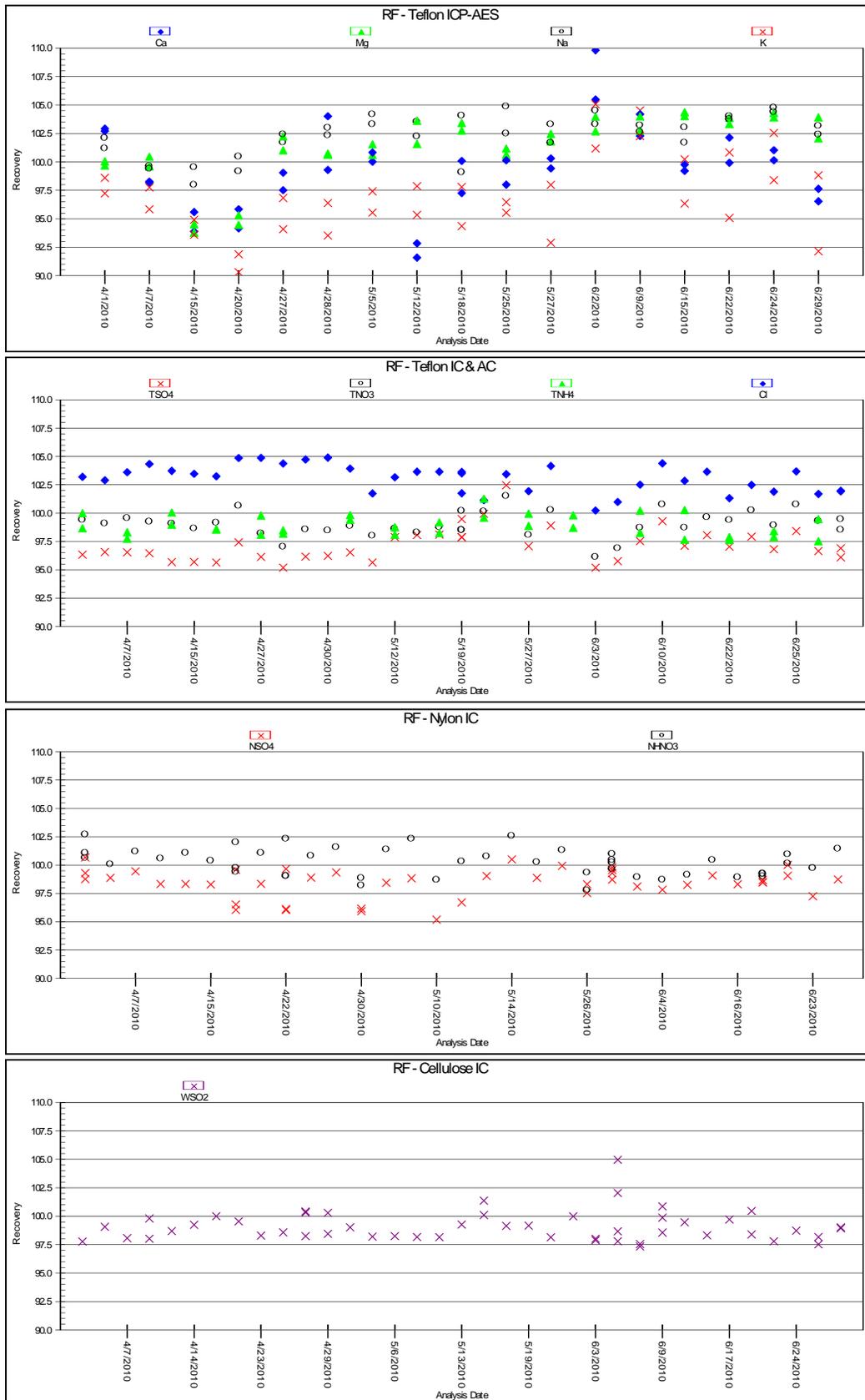
Days to Resolution	Problem Count
30	132
60	14
90	1
Unresolved by End of Quarter	12

**Table 9.** Field Calibration Failures by Parameter

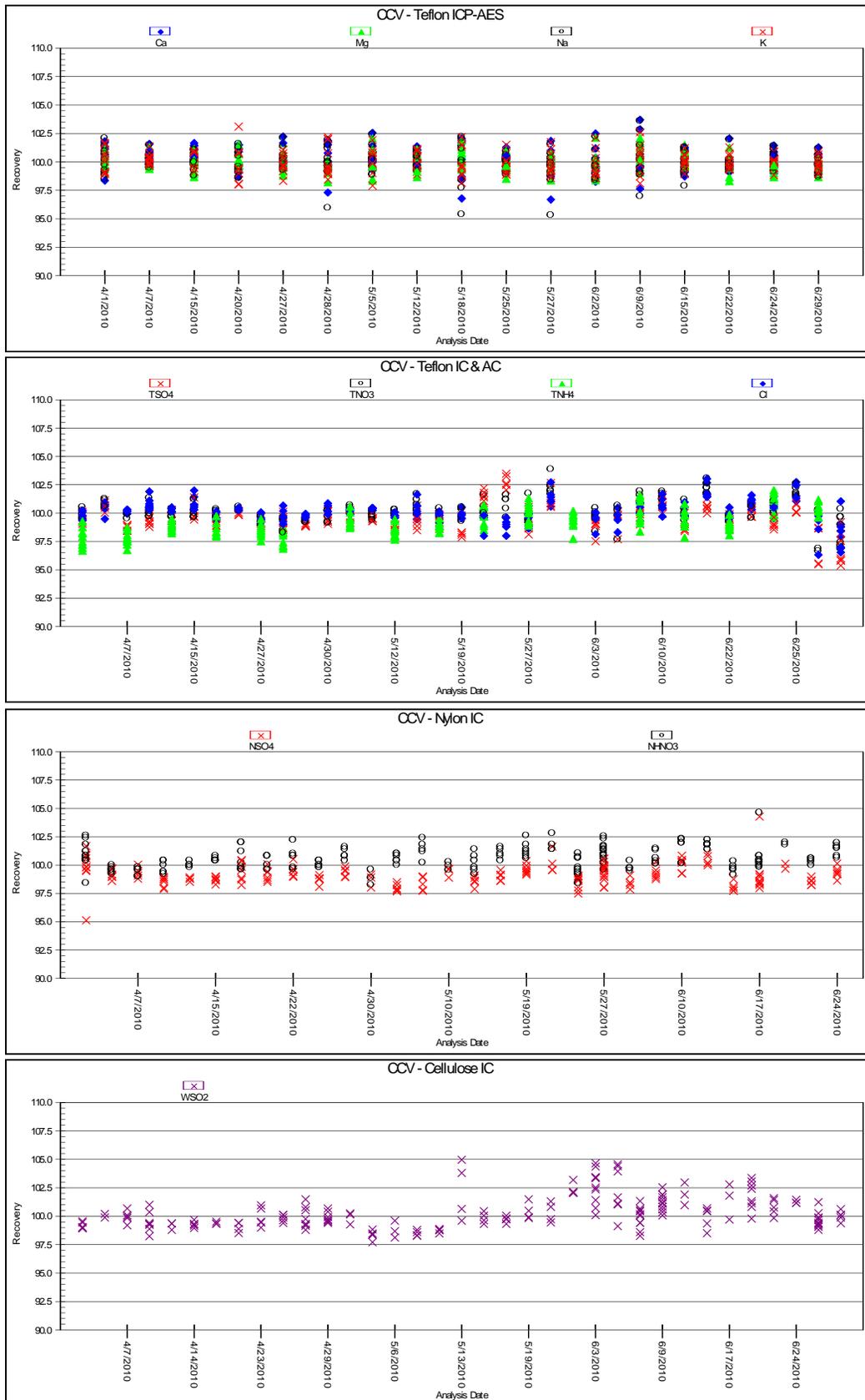
Site ID	Parameter(s)
CON186, CA	Solar Radiation
GTH161, CO	Ozone
HOX148, MI	Precipitation

**Note:** Per CASTNET project protocols, data 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 ozone or flow calibrations fall within 2x the criteria, these data are adjusted per approved protocol described in the CASTNET QAPP, Revision 6.0 (MACTEC, 2010).

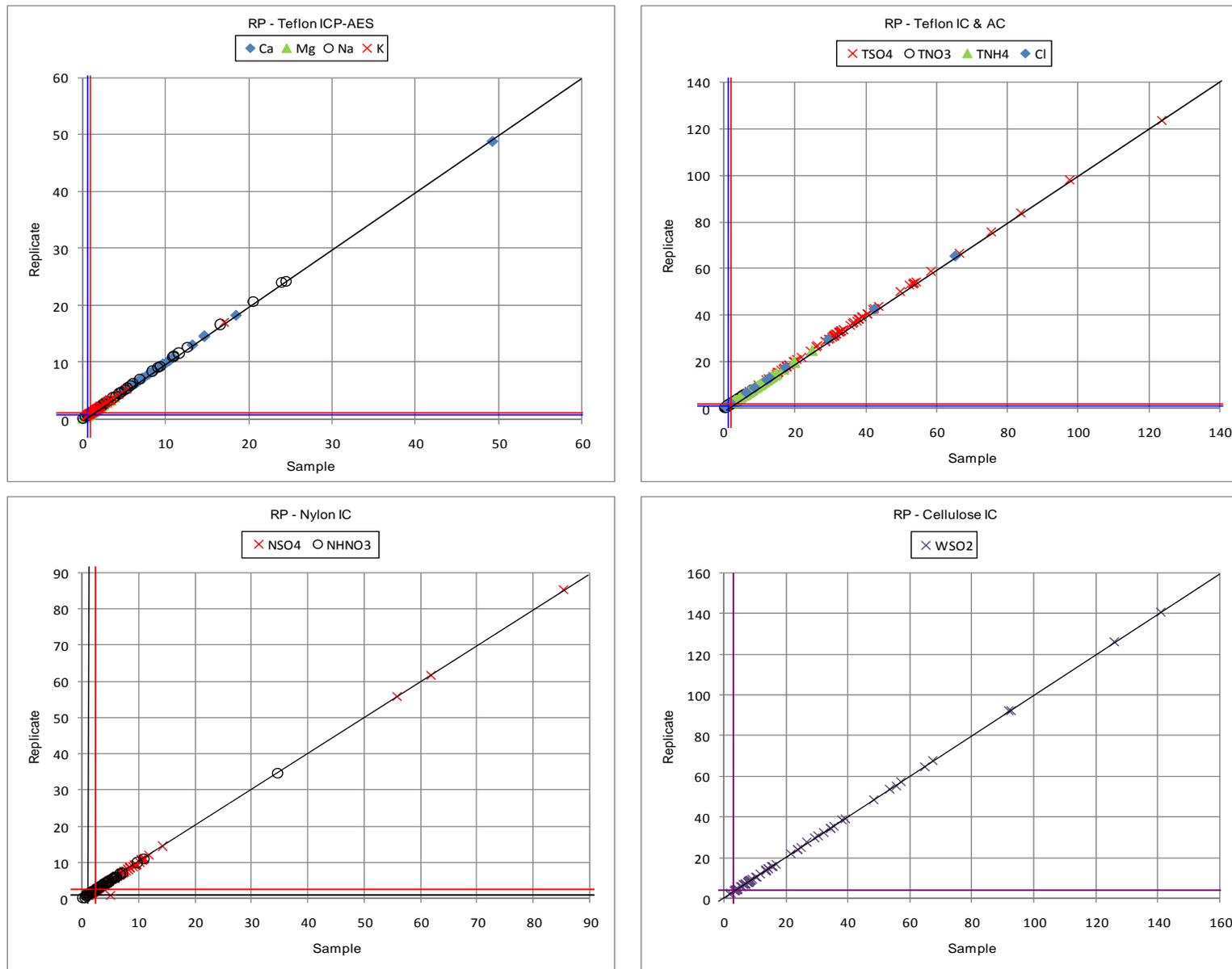
**Figure 1.** Reference Standard Results for Second Quarter 2010 (percent recovery)



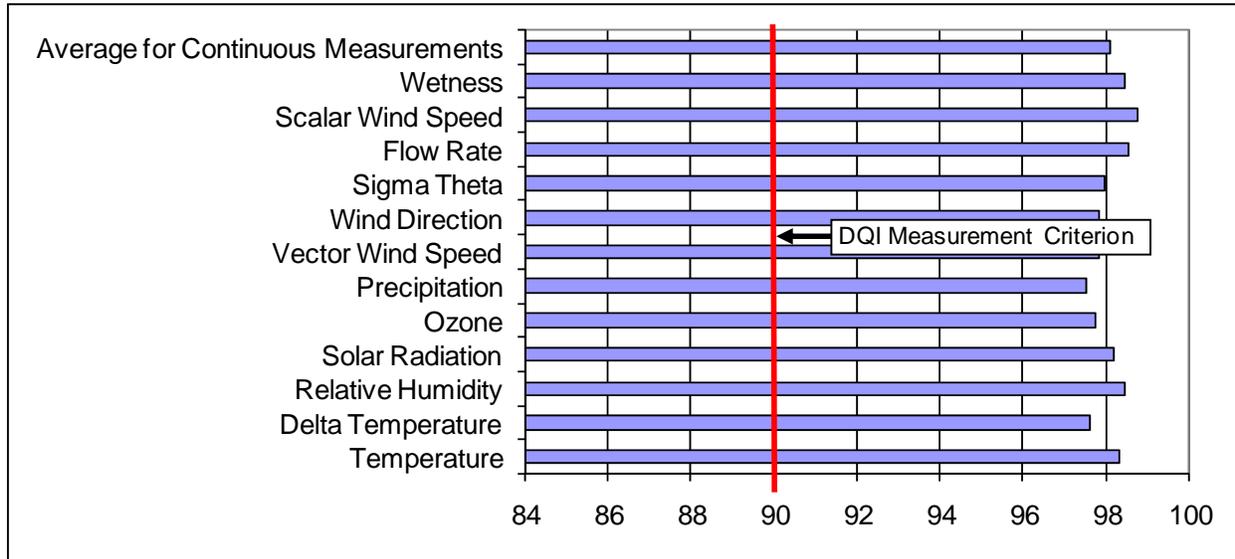
**Figure 2.** Continuing Calibration Spike Results for Second Quarter 2010 (percent recovery)



**Figure 3.** Replicate Sample Analysis Results for Second Quarter 2010 (total micrograms)

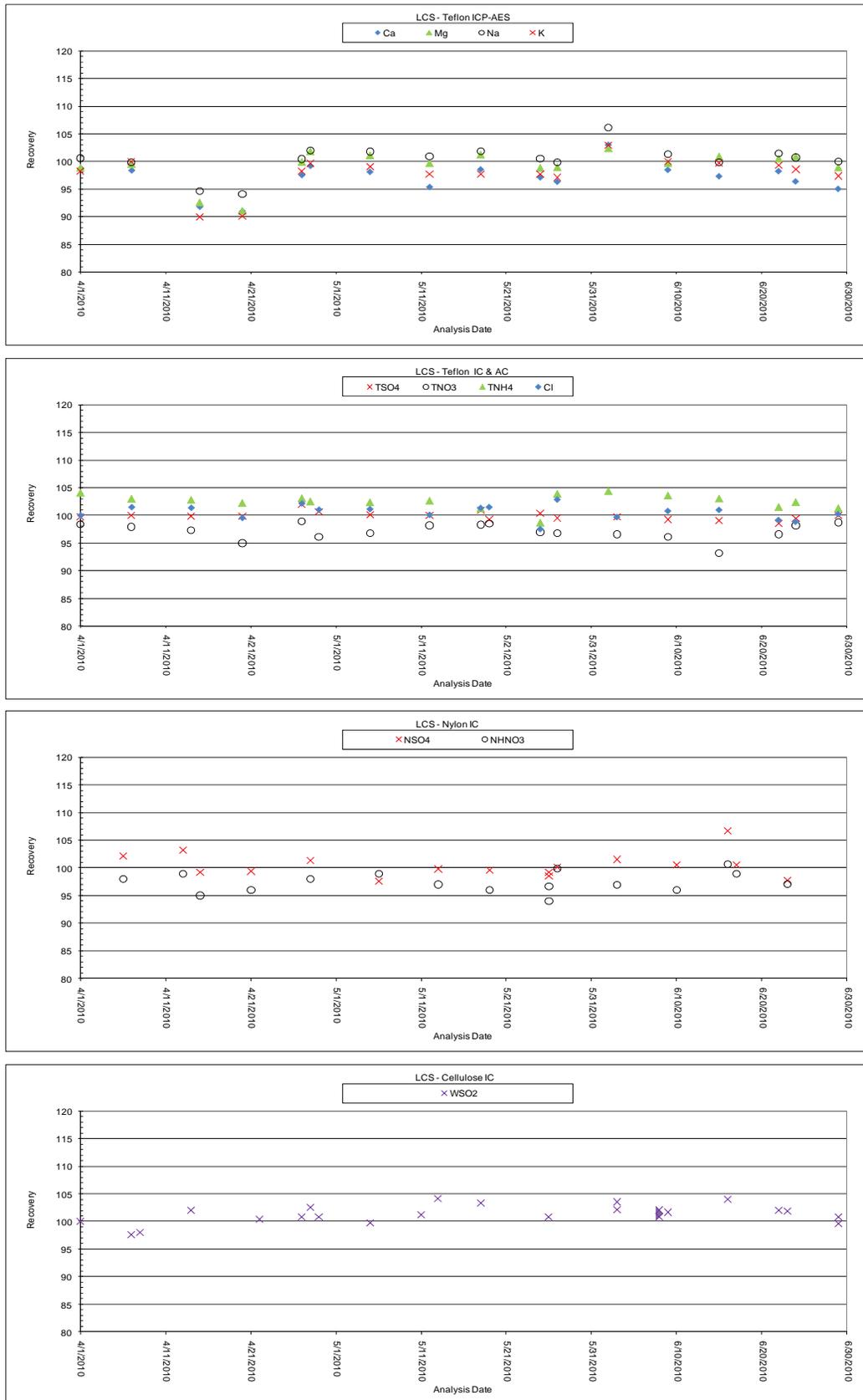


**Figure 4.** Percent Completeness of Measurements for Fourth Quarter 2009 through First Quarter 2010\*

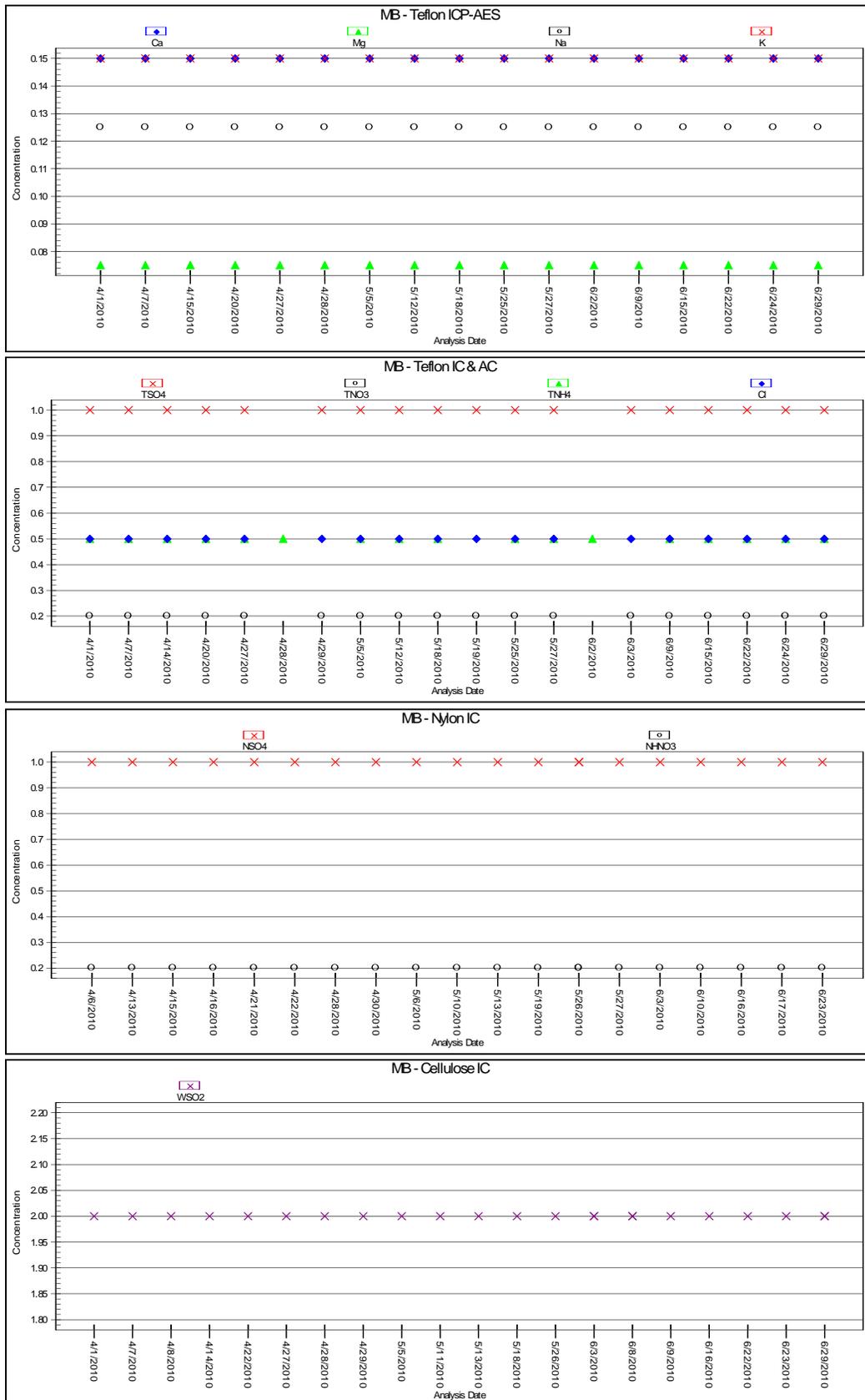


**Note:** \*Presents Level 3 data available during the second quarter of 2010.

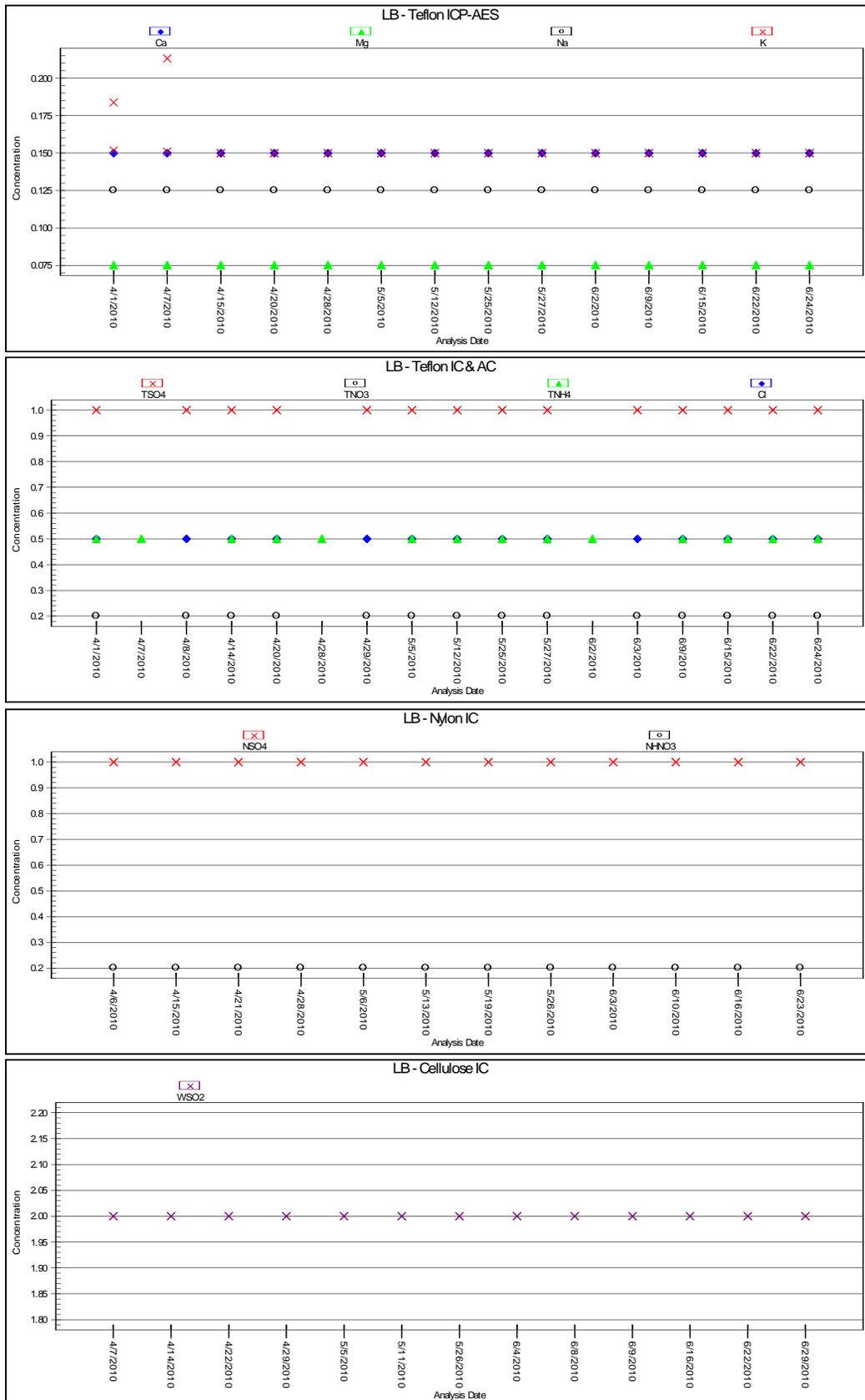
**Figure 5.** Laboratory Control Sample Results for Second Quarter 2010 (percent recovery)



**Figure 6.** Method Blank Analysis Results for Second Quarter 2010 (total micrograms)



**Figure 7.** Laboratory Blank Analysis Results for Second Quarter 2010 (total micrograms)



**Figure 8.** Field Blank Analysis Results for Second Quarter 2010 (total micrograms)

