



## **Summary of Quarterly Operations April – June 2009**

**EPA Project No. 68-D-03-052**

### **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 2009. The results presented for filter pack data collection and field calibrations are generated from data extracted from the CASTNET Data Management Center (DMC) database using the CASTNET Data Management System Application (CDMSA). 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 second quarter 2009, data sets were examined for evidence characterizing laboratory handling-related effect on the precision of filter pack concentrations. Given the internal QA/QC checks and monitoring in place and the successful analyses performed by the laboratory for Environment Canada proficiency tests and U.S. Geological Survey (USGS) intercomparison studies, it is unlikely that laboratory handling significantly affects the precision of filter pack concentrations.

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 the quarter 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 this quarter.

## Sample Receipt Statistics

For the current CASTNET project, which began on July 30, 2003, EPA requires that 95 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 6 presents the relevant sample receipt statistics for second quarter 2009.

## Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for second quarter 2009. All results were within the criteria listed in Table 4 with the exception of several individual RP results. However, these are considered reasonable since higher relative percent differences generally correlate with lower sample concentrations. An examination of long-term RF results shows that the average calcium recovery over the first two quarters of 2008 was 102 percent, while the average calcium recovery over the same span for 2009 was 106 percent. The higher recovery percentages resulted from an error in the certified value for calcium in a particular manufacturing lot of the reference standard as reported by the reference standard manufacturer. The manufacturer provided confirmation of this error in July of 2009. The error introduced a false positive bias of approximately six percent for this manufacturing lot. Quarterly averages are all within criteria.

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 2009.

**Blank Results**

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for second quarter 2009. All results were within criteria (two times the reporting limit) listed in Table 4.

**Suspect/Invalid Filter Pack Samples**

Table 7 presents the filter pack samples that were flagged as suspect or invalid during second quarter 2009. As of report publication, no second quarter 2009 filter pack samples had been flagged as suspect or invalid.

**Field Problem Count**

Table 8 presents counts of field problems affecting continuous data collection during second quarter 2009. 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 20 sites during second quarter 2009. All sites and parameters were within the criteria listed in Table 3 with the exception of the parameters at the nine sites that listed in Table 9.

## Tables and Figures

**Table 1.** Data Validated to Level 3 during Second Quarter 2009

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-1/SE-5	August 2008 – January 2009	6	Quarter 4 2008	1
MW-7/W-9	September 2008 – February 2009	6	Quarter 4 2008	1
E-2/MW-8	October 2008 – March 2009	6	Quarter 4 2008 – Quarter 1 2009	2

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

**Table 2.** Field Calibration Schedule

Calibration Group Number	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

**Note:** °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	10	90 - 110	0.020 *	0.5
Sodium (Na <sup>+</sup> )	F	ICP-AES	5	95 - 105	0.005	0.125
Potassium (K <sup>+</sup> )	F	ICP-AES	5	95 - 105	0.006	0.15
Magnesium (Mg <sup>2+</sup> )	F	ICP-AES	5	95 - 105	0.003	0.075
Calcium (Ca <sup>2+</sup> )	F	ICP-AES	5	95 - 105	0.006	0.15
Chloride (Cl <sup>-</sup> )	F	IC	5	95 - 105	0.020	0.5
Nitrate (NO <sub>3</sub> <sup>-</sup> )	F	IC	5	95 - 105	0.008 *	0.2
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	F	IC	5	95 - 105	0.040	1.0

**Note:** <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 ICP-AES precision RPD criterion changed from 10 percent to 5 percent at the onset of the new contract beginning on July 30, 2003. The precision criterion is applied as described below:

QC conditions: (v1 = initial response; v2 = replicate response; RL = nominal reporting limit)

Condition 1: if (v1 or v2 < RL and the absolute value of (v1 - v2) < RL) = OK

Condition 2: if (v1-v2) < RL and v1 < 5 x RL) = OK

Condition 3: if (v1 > 5\*RL and RPD < 5%) = OK

Status: one of the conditions is OK = Precision QC Passes

<sup>2</sup> This column lists laboratory accuracy goals based on reference standards and continuing calibration verification spikes. The goal for the ICP-AES accuracy criterion changed from 90 – 110 percent to 95 – 105 percent for continuing calibration verification spikes at the onset of the new contract beginning on July 30, 2003. The criterion remains 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 Quality Assurance Project Plan (QAPP), Revision 4.1 (MACTEC, 2008).

**Table 5.** QC Analysis Count for Second Quarter 2009

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon <sup>®</sup>	SO <sub>4</sub> <sup>2-</sup>	34	168	75	17	26	73
	NO <sub>3</sub> <sup>-</sup>	34	168	75	17	26	73
	NH <sub>4</sub> <sup>+</sup>	32	168	79	16	26	83
	Cl <sup>-</sup>	34	168	75	17	26	73
	Ca <sup>2+</sup>	32	171	79	16	26	83
	Mg <sup>2+</sup>	32	171	79	16	26	83
	Na <sup>+</sup>	32	171	79	16	26	83
	K <sup>+</sup>	32	171	79	16	26	83
Nylon	SO <sub>4</sub> <sup>2-</sup>	35	171	79	17	28	86
	NO <sub>3</sub> <sup>-</sup>	35	171	79	17	28	86
Cellulose	SO <sub>4</sub> <sup>2-</sup>	45	174	82	23	26	105

**Table 6.** Filter Pack Receipt Summary

Count of samples received more than 14 days after removal from tower:	7
Count of all samples received:	760
Fraction of samples received within 14 days:	0.991
Average interval in days:	4.27
First receipt date:	04/01/2009
Last receipt date:	06/29/2009

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

Site ID	Sample ID	Reason
No filter packs were flagged during second quarter 2009		

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

Days to Resolution	Problem Count
30	89
60	11
90	1
Unresolved by date of publication	6

**Note:** Counts were extracted using the problem tracking system (PTS) feature of the CDMSA. Problems requiring corrective action are flagged by field personnel with a ticket number.

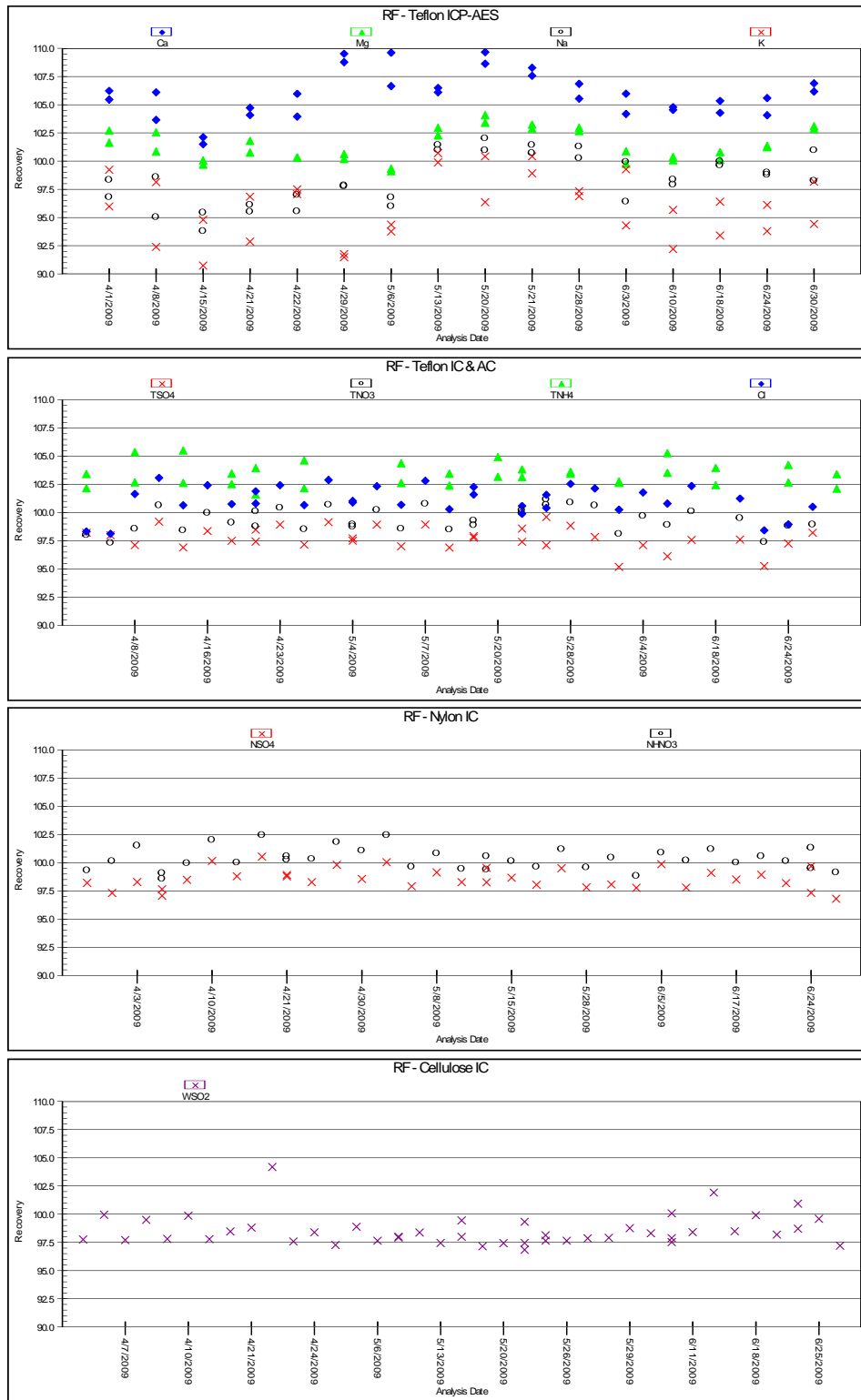


**Table 9.** Field Calibration Failures by Parameter

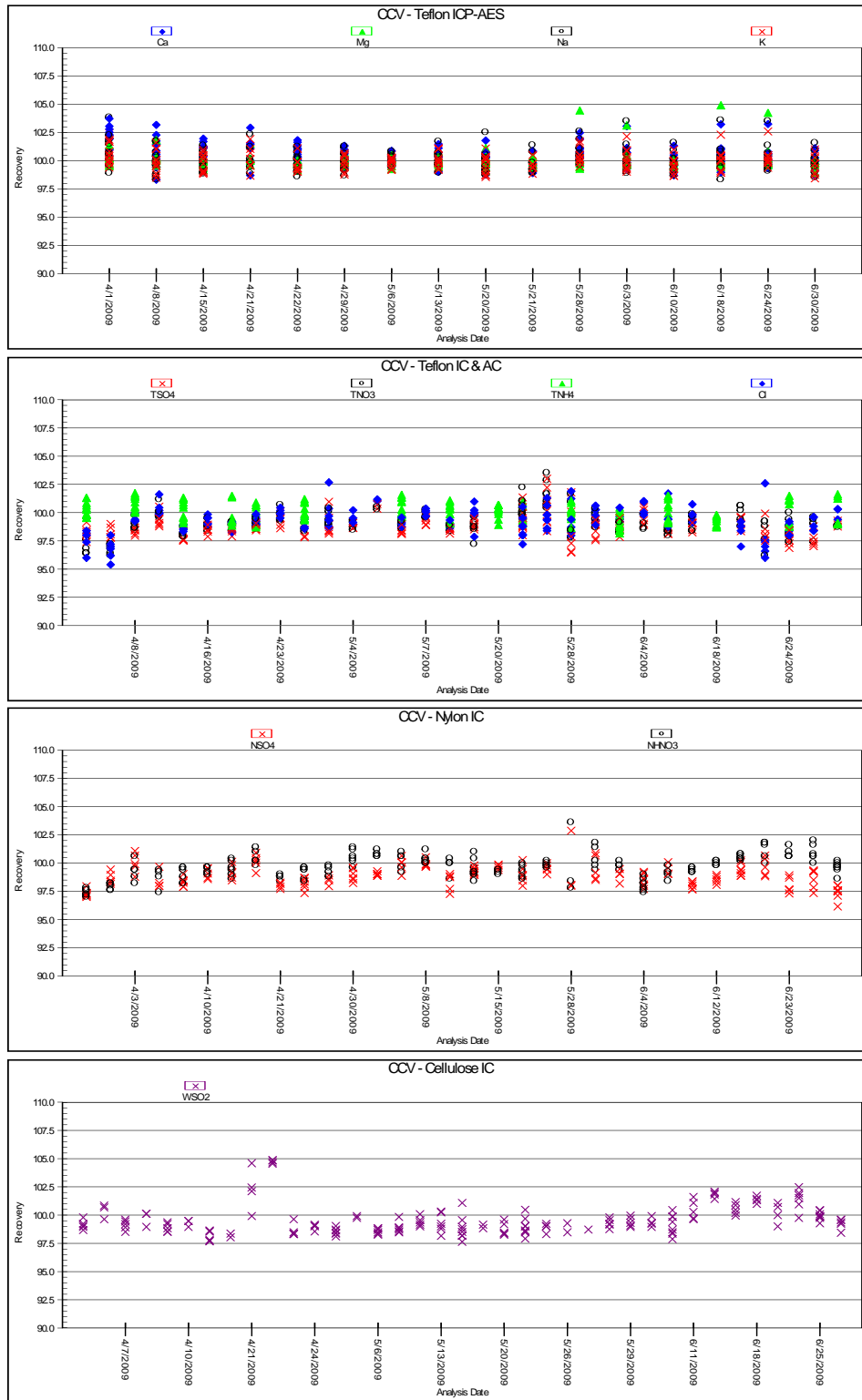
Site ID	Parameter(s)
ABT147, CT	Relative Humidity
CNT169, WY	Surface Wetness
CON186, CA	Relative Humidity
EGB181, ON	Solar Radiation
HOX148, MI	Flow Rate
LRL117, PA	Wind Speed
LYK123, OH	Relative Humidity
SAL133, IN	Wind Speed
UVL124, MI	Relative Humidity Wind Direction

**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 4.1 (MACTEC, 2008).

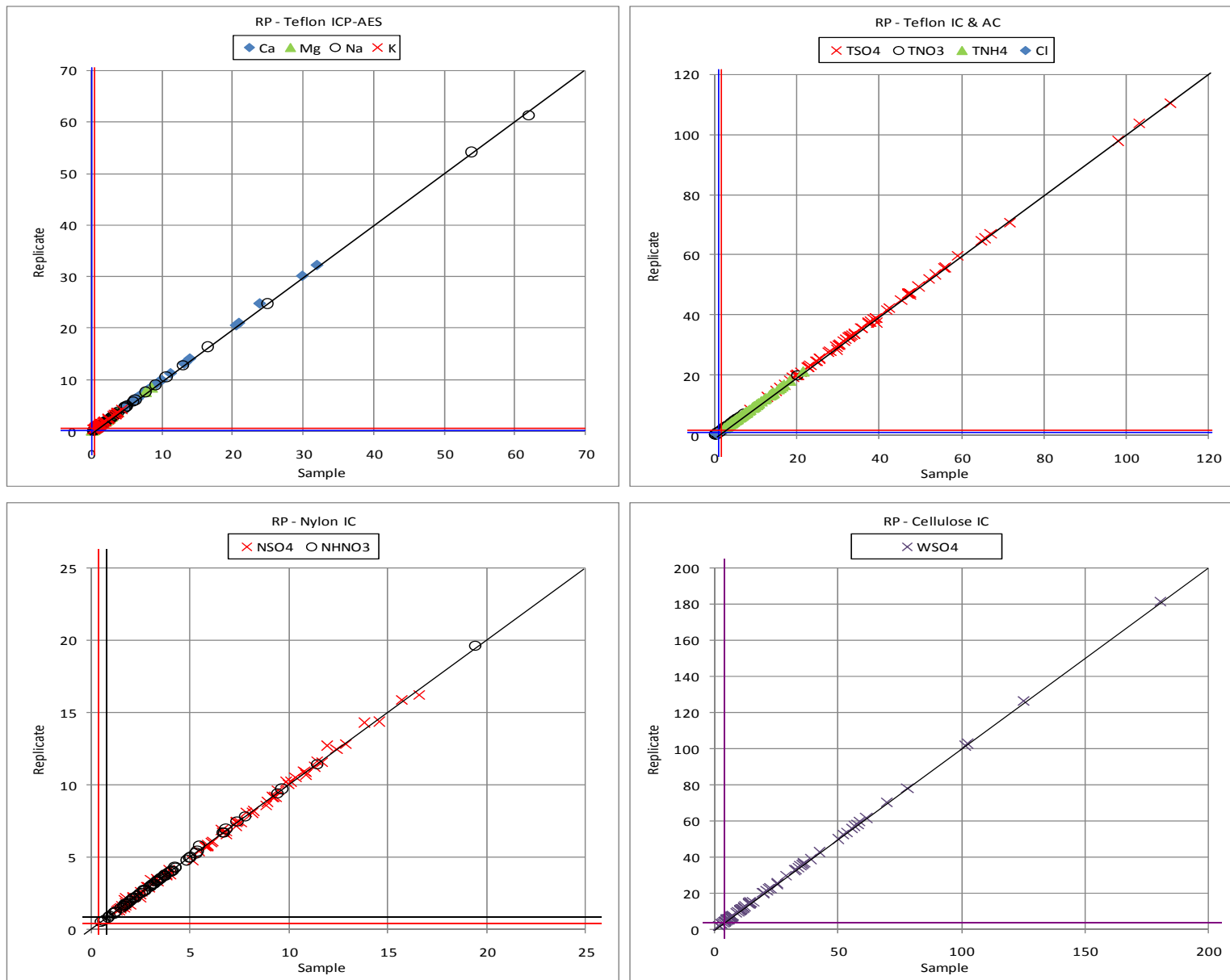
**Figure 1.** Reference Standard Results for Second Quarter 2009 (percent recovery)



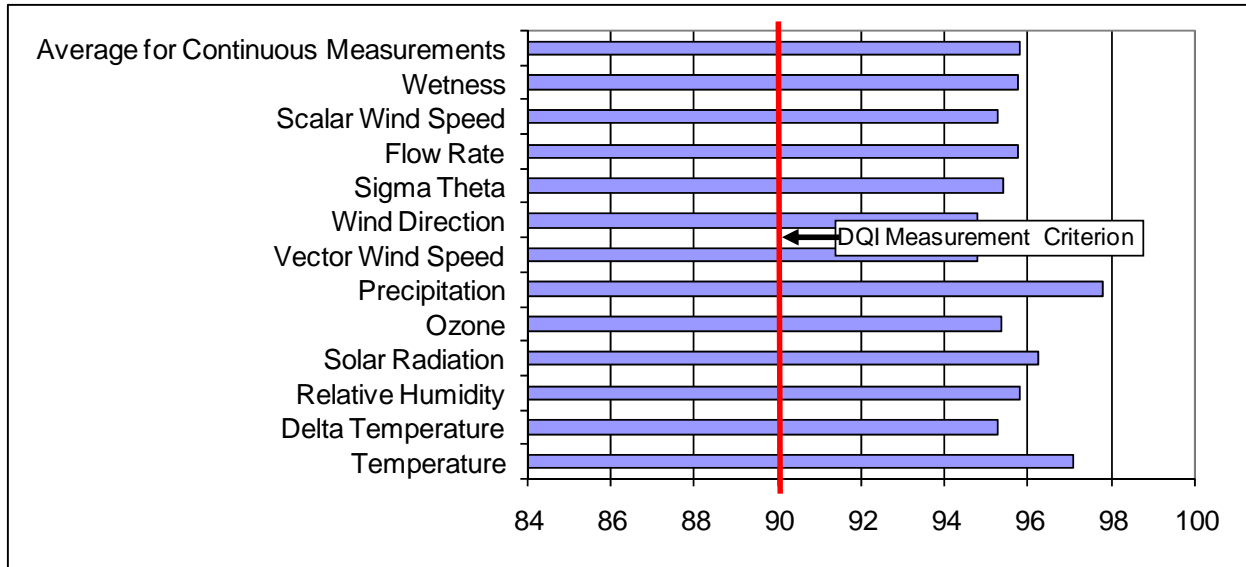
**Figure 2.** Continuing Calibration Spike Results for Second Quarter 2009 (percent recovery)



**Figure 3.** Replicate Sample Analysis Results for Second Quarter 2009 (total micrograms)

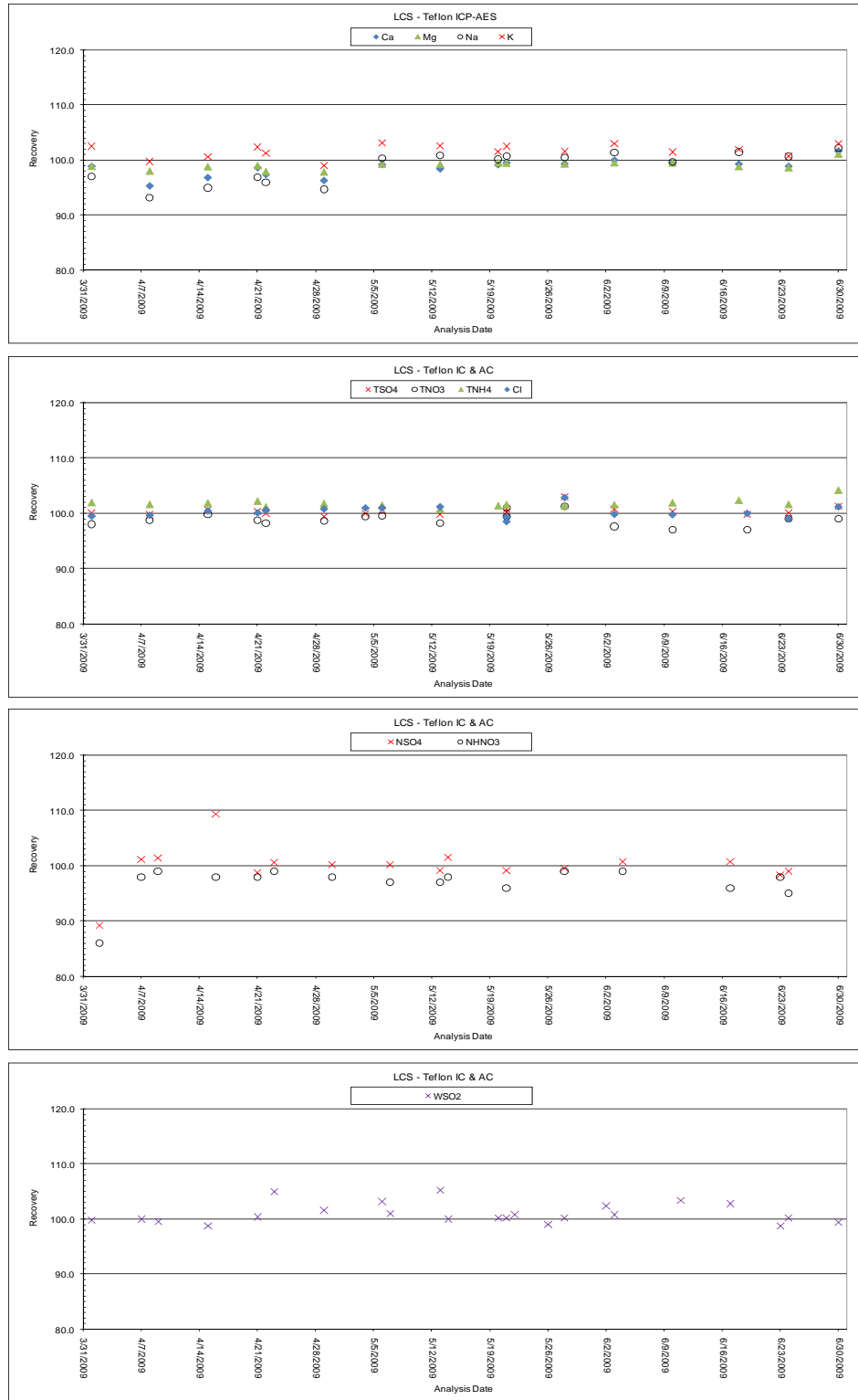


**Figure 4.** Percent Completeness of Measurements for Fourth Quarter 2008 through First Quarter 2009\*

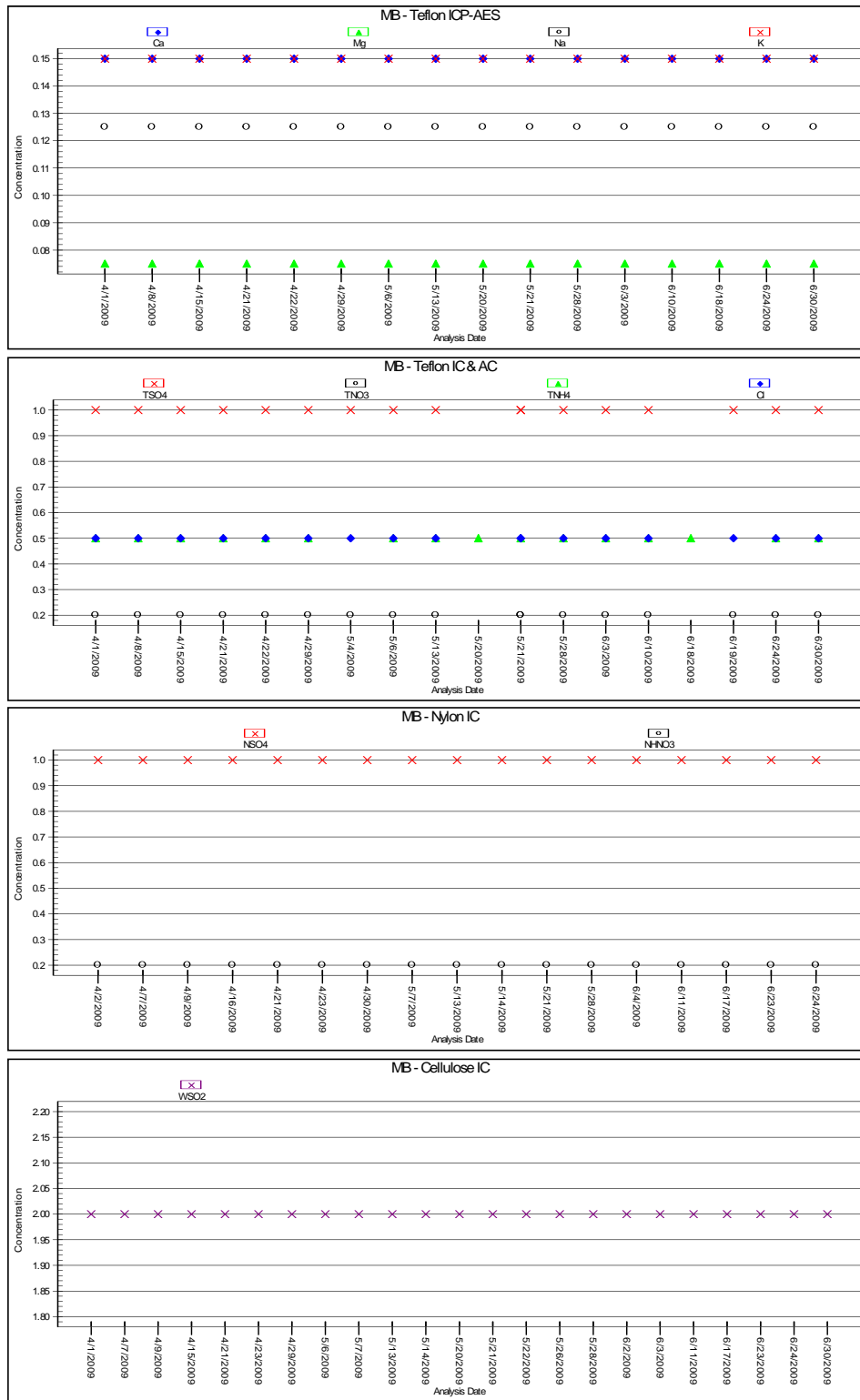


Note: \*Presents Level 3 data available during the second quarter of 2009.

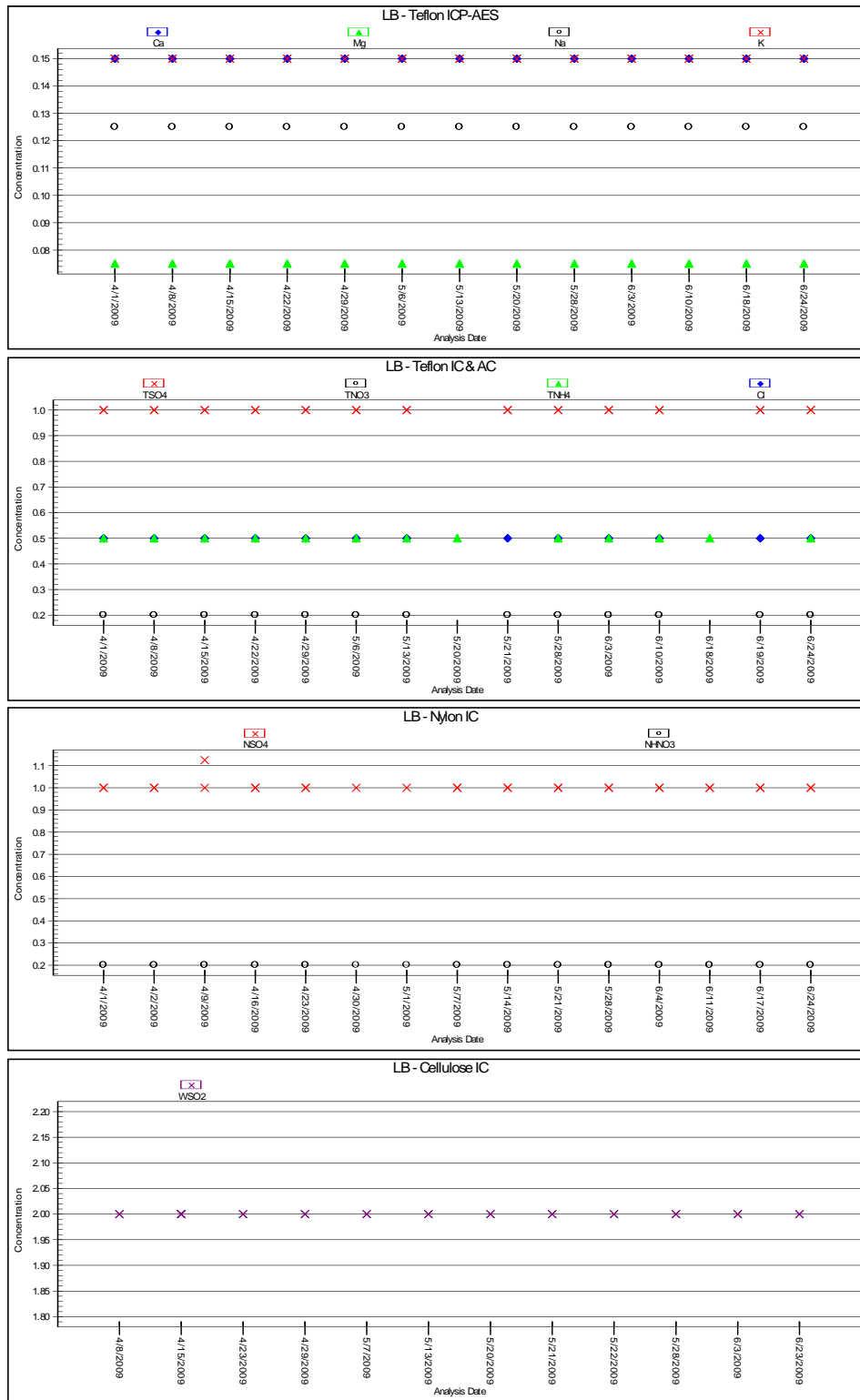
**Figure 5.** Laboratory Control Sample Results for Second Quarter 2009 (percent recovery)



**Figure 6. Method Blank Analysis Results for Second Quarter 2009 (total micrograms)**



**Figure 7.** Laboratory Blank Analysis Results for Second Quarter 2009 (total micrograms)





**Figure 8.** Field Blank Analysis Results for Second Quarter 2009 (total micrograms)

