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 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.

During third quarter 2010, the Environmental Protection Agency (EPA); MACTEC Engineering and Consulting, Inc. (MACTEC); the National Park Service (NPS); and Air Resource Specialists, Inc. (ARS) worked to develop a proposal for a joint ozone data screening protocol that can be applied to ozone data collected from all sites. The screening protocol includes rules for annual review screening and validation. Some of the rules include identifying percentiles out of bounds, discontinuities in concentration data, correlation with site visits, and correlation with synoptic weather patterns. Ozone data identified by the screening will require additional review. Data may also be compared to data from nearby sites.

Possible sources for the suspected intermittent potassium contamination of filters used for filter packs and filter blanks continued to be investigated during third quarter 2010. Audits of all stages of handling procedures (e.g., filter pack packing and unpacking, extraction and analysis, and impregnation of the potassium carbonate filters) indicated that standard operating procedures (SOPs) are followed, and contamination is not likely to be introduced by current handling methods. Additionally, the reagents used were checked and verified to be stored properly and in leak-proof containers. It is believed that the upgrade of the heating, ventilation, and air conditioning (HVAC) system and resultant construction for installation of new ducts, vents, and

thermostats at MACTEC's laboratory is the most likely source of contamination. Currently, the room where filters are handled is being isolated during handling procedures. Only filter packs and filter blanks showed evidence of contamination. Method blanks and all other QC samples remained within normal limits.

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 third 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 third 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 third quarter 2010.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for third quarter 2010. All results were within the criteria listed in Table 4 with the exception of RP results for a single metal cations sample. Investigation revealed that the sample vessel was empty when the duplicate analysis was performed. These results have been omitted from Figure 3 to permit proper scaling for the other RP sample results. RF sample results for metal cations show a shift upward in August 2010 that coincides with the use of newly prepared calibration standards. Please note that the format for Figure 3 has been changed starting with this report to match the presentation format of all other QC sample result figures (Figures 1, 2, and 5 through 8).

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 third 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 third quarter 2010. All results were within criteria (two times the reporting limit) listed in Table 4 with the exception of two potassium FB results. These two values were at four and five times the reporting limit, respectively. Please refer to the introduction to this report for discussion of potassium contamination and actions taken. Additionally, there were two cellulose filter FB results that were essentially at two times the reporting limit at 4.1 total micrograms.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during third 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 third quarter, 18 filter pack samples were invalidated. Some samples have not been validated to Level 3 and, therefore, may be recovered during the validation process.

Field Problem Count

Table 8 presents counts of field problems affecting continuous data collection for more than one day during third 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 24 sites during third 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 Third Quarter 2010

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10†	November 2009 – April 2010	6	Quarter 1 2010	1
SE-4/MW-6‡	January 2010 – June 2010	6	Quarter 1 2010 – Quarter 2 2010	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 (19 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 (5 Sites)	April/October	SAL133, IN HOX148, MI	ANA115, MI UVL124, MI	LYK123, OH	
Western Sites (10 Total)					
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**
Filter pack flow	Mass flow controller	± 10%	± 5%
Ozone	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†
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 third
RTD = resistance-temperature device
UV = ultraviolet

* Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments
† For target value of 0.50 inch

Table 4. Data Quality Indicators for CASTNET Laboratory Measurements

Analyte	Medium	Method	Precision[1] (MARPD)	Accuracy[2] (%)	Nominal Reporting Limits	
					mg/L	µg/Filter
Ammonium (NH_4^+)	F	AC	20	90 - 110	0.020 *	0.5
Sodium (Na^+)	F	ICP-AES	20	95 - 105	0.005	0.125
Potassium (K^+)	F	ICP-AES	20	95 - 105	0.006	0.15
Magnesium (Mg^{2+})	F	ICP-AES	20	95 - 105	0.003	0.075
Calcium (Ca^{2+})	F	ICP-AES	20	95 - 105	0.006	0.15
Chloride (Cl^-)	F	IC	20	95 - 105	0.020	0.5
Nitrate (NO_3^-)	F	IC	20	95 - 105	0.008 *	0.2
Sulfate (SO_4^{2-})	F	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. The goal for the RPD criterion changed to 20 percent at the onset of the CASTNET IV contract beginning on August 11, 2009.

[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.

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 Third 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_4^{2-}	41	196	91	20	26	83
	NO_3^-	41	196	91	20	26	83
	NH_4^+	40	206	103	19	26	83
	Cl^-	41	196	90	20	26	83
	Ca^{2+}	39	203	99	19	26	83
	Mg^{2+}	39	203	99	19	26	83
	Na^+	39	203	99	19	26	83
	K^+	39	203	99	19	26	83
Nylon	SO_4^{2-}	41	200	95	19	28	81
	NO_3^-	41	200	95	19	28	81
Cellulose	SO_4^{2-}	41	178	90	22	26	83

Table 6. Filter Pack Receipt Summary for Third Quarter 2010

Count of samples received more than 14 days after removal from tower:	10
Count of all samples received:	758
Fraction of samples received within 14 days:	0.987
Average interval in days:	5.431
First receipt date:	07/01/2010
Last receipt date:	09/30/2010

Table 7. Filter Packs Flagged as Suspect or Invalid

Site ID	Sample No.	Reason
ARE128, PA	1030001-06 1031001-06	Insufficient flow Insufficient flow
BEL116, MD	1030001-09	Insufficient flow
BWR139, MD	1033001-12	Insufficient flow
CTH110, NY	1037001-25	Insufficient flow
GRB411, NV	1032001-34 1033001-34	Insufficient flow Insufficient flow
JOT403, CA	1035001-42	Insufficient flow
LYK123, OH	1029001-47	Insufficient flow
PAL190, TX	1033001-55	Insufficient flow
PET427, AZ	1032001-58	Insufficient flow
PNF126, NC	1030001-61	Insufficient flow
PSU106, PA	1032001-63	Insufficient flow
ROM206, CO	1028001-65	Insufficient flow
SAL133, IN	1029001-67	Insufficient flow
VPI120, VA	1031001-79 1032001-79	Insufficient flow Insufficient flow
WNC429, SD	1031001-80	Insufficient flow

Table 8. Field Problems Affecting Data Collection

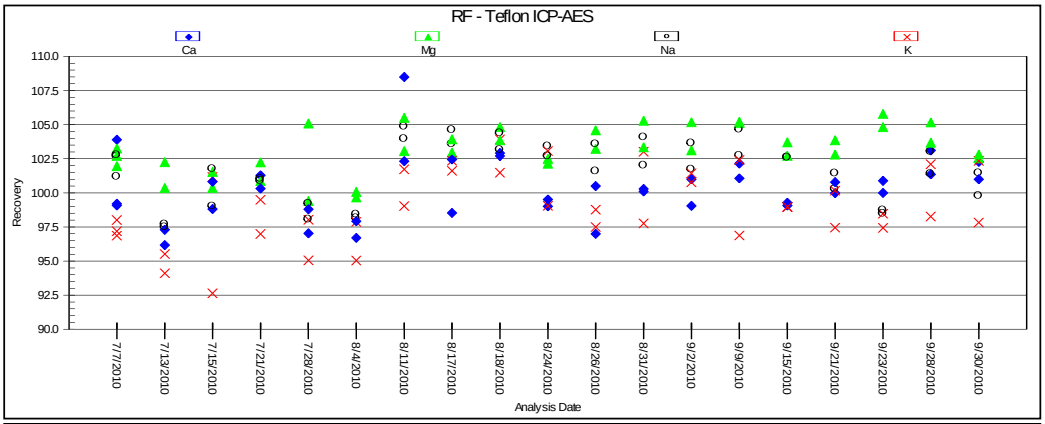
Days to Resolution	Problem Count
30	146
60	8
90	1
Unresolved by End of Quarter	3

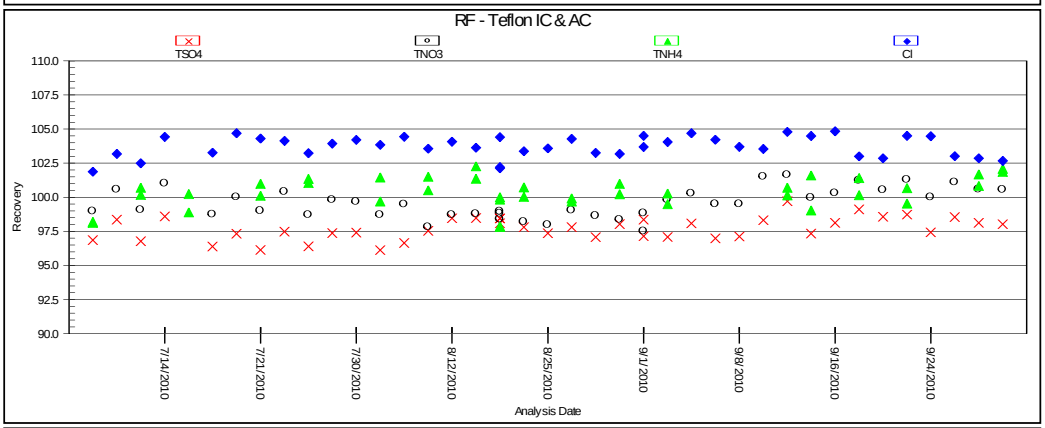
Table 9. Field Calibration Failures by Parameter

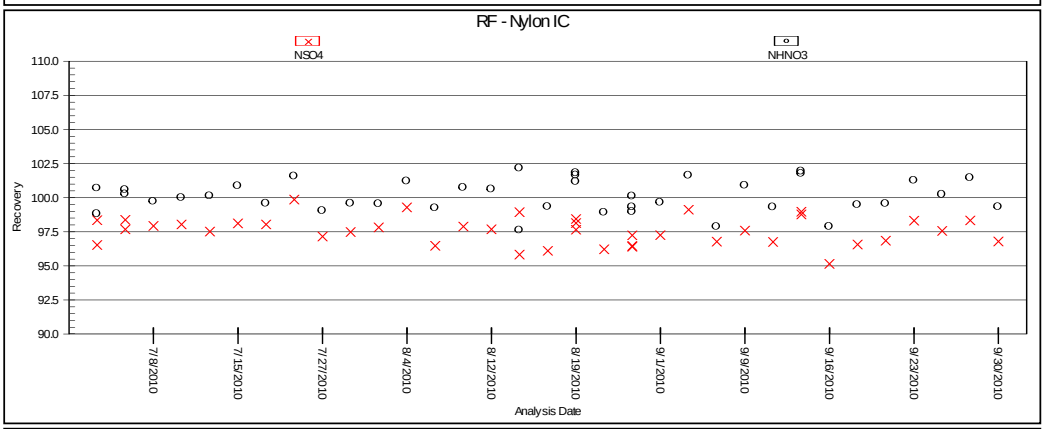
Site ID	Parameter(s)
PED108, VA	Precipitation
PNF126, NC	Solar Radiation
VPI120, VA	Relative Humidity

Note: Per CASTNET project protocols, data 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 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 Third Quarter 2010 (percent recovery)







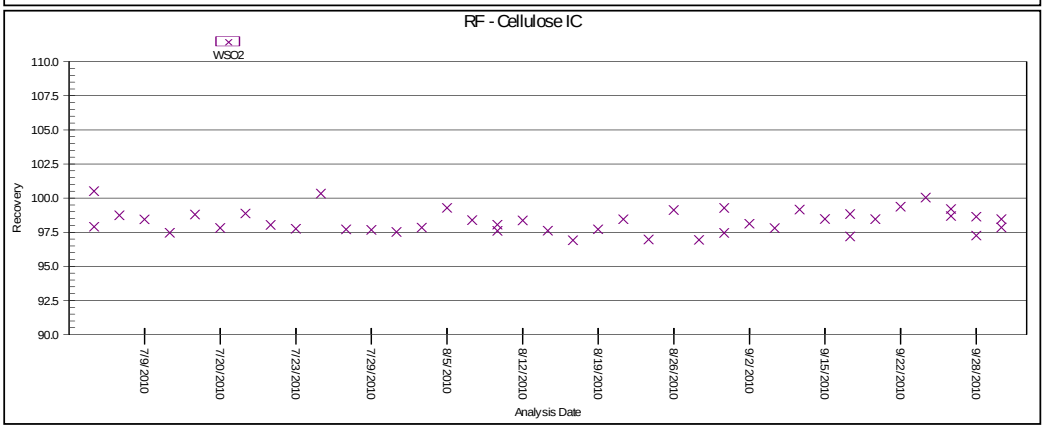
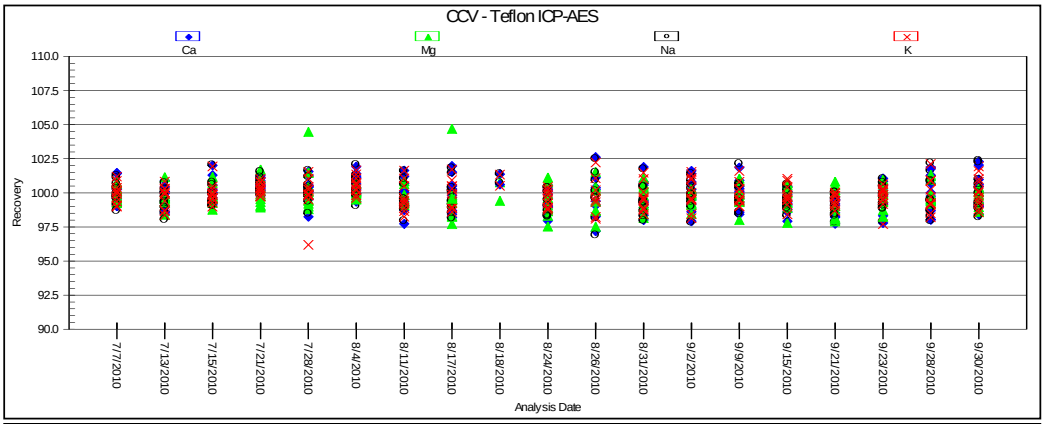
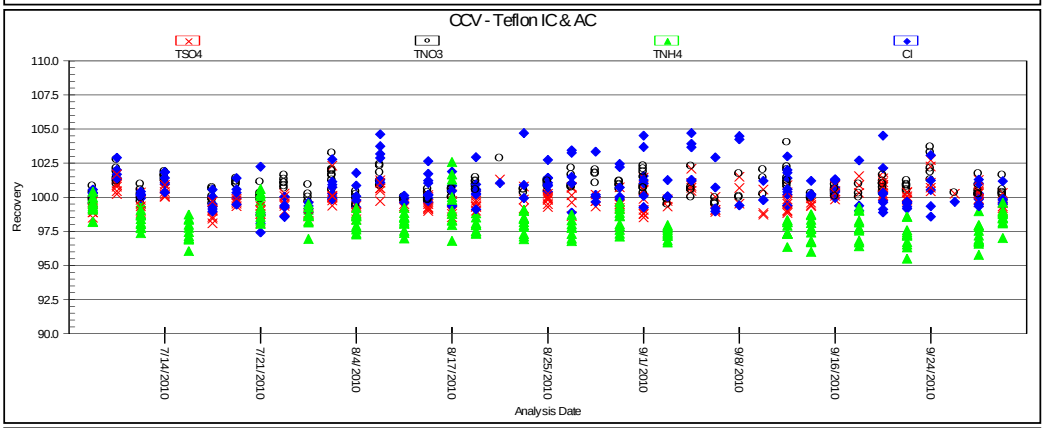
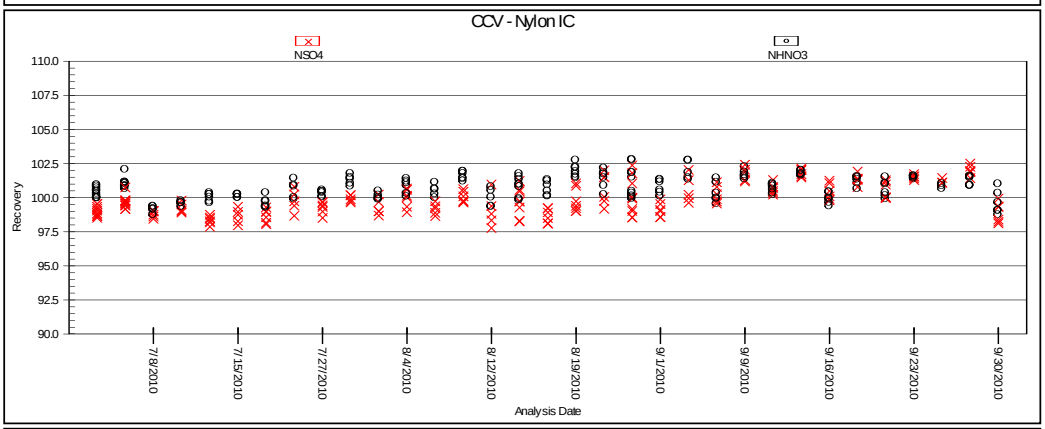


Figure 2. Continuing Calibration Spike Results for Third Quarter 2010 (percent recovery)







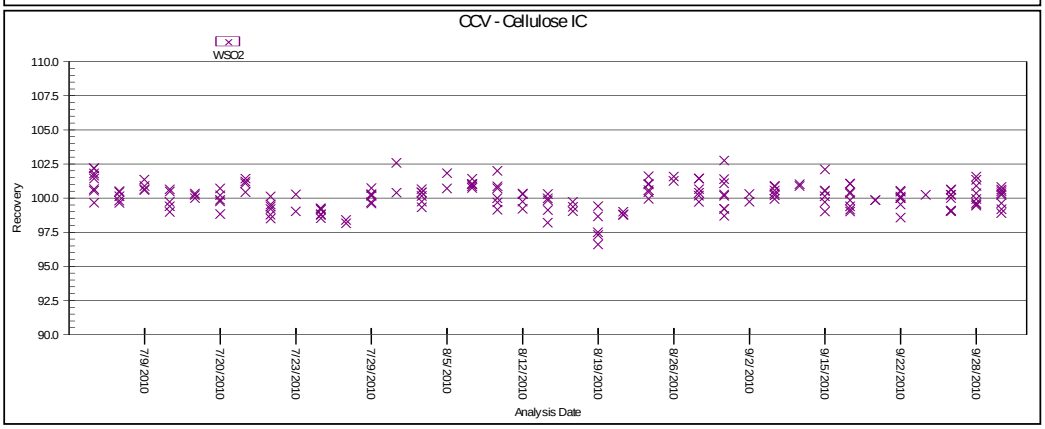


Figure 3. Replicate Sample Analysis Results for Third Quarter 2010 (relative percent difference)

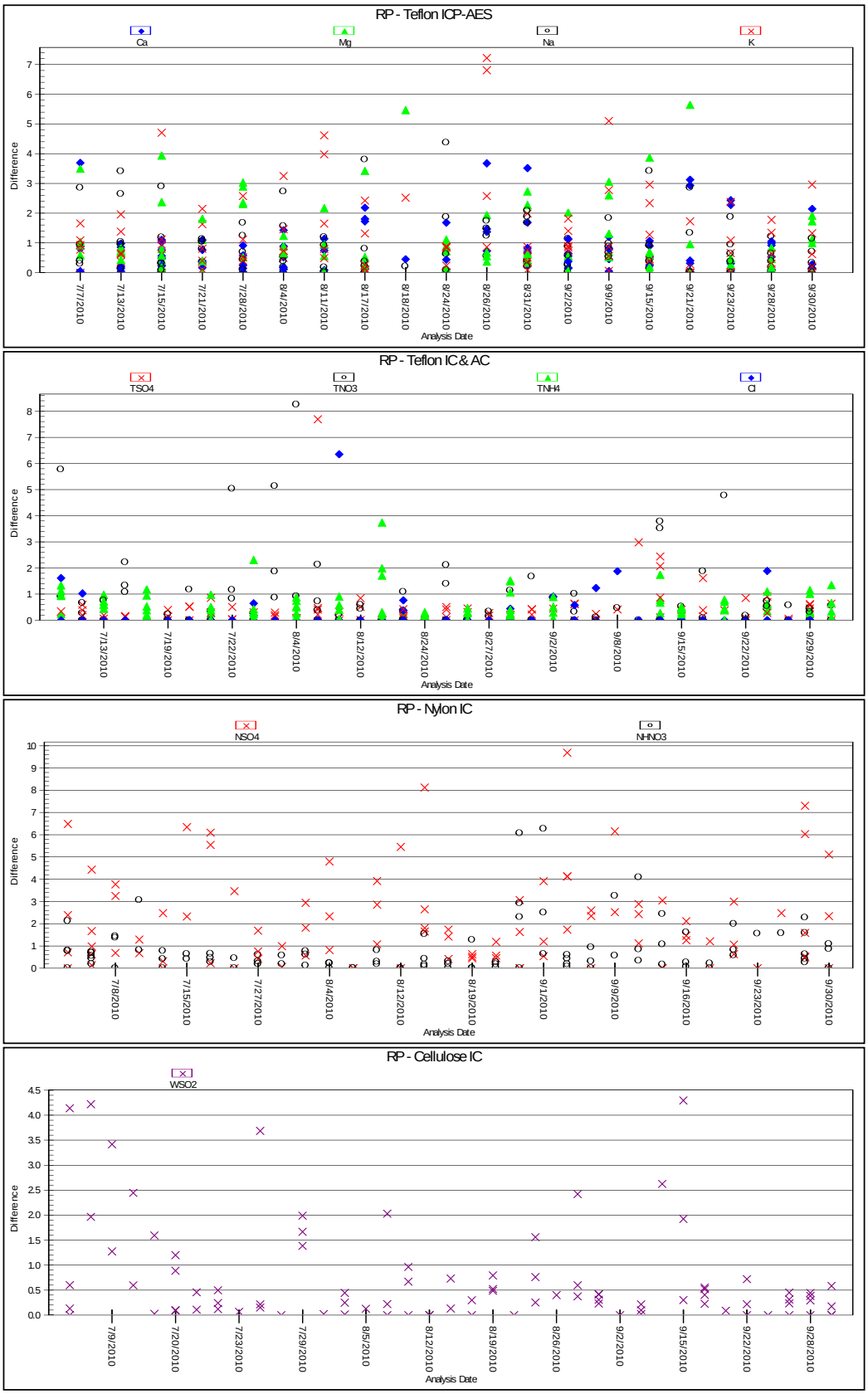
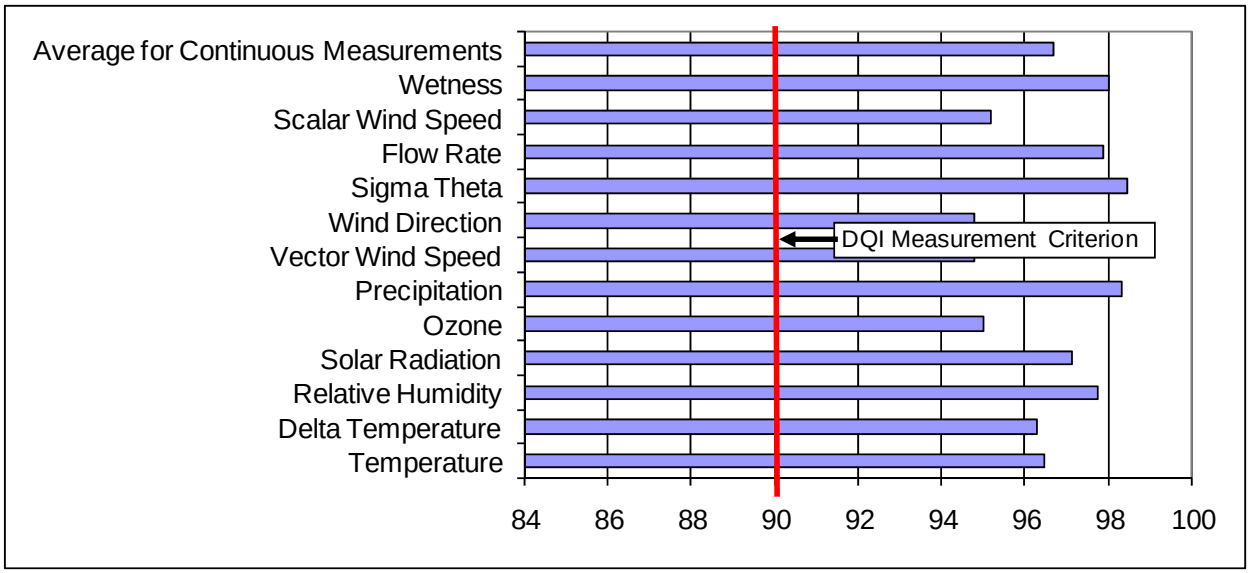


Figure 4. Percent Completeness of Measurements for Fourth Quarter 2009 through Third Quarter 2010*



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

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

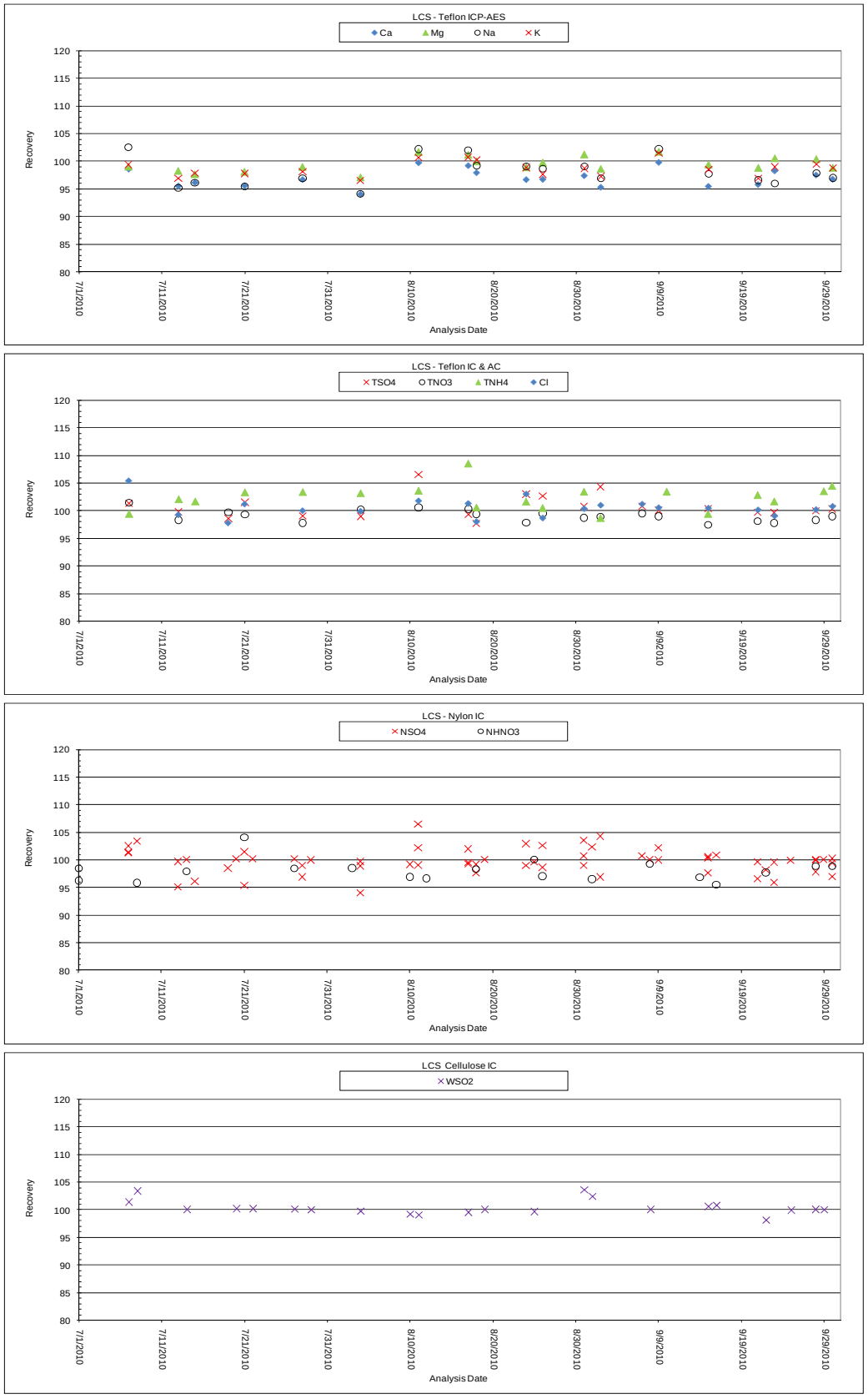


Figure 6. Method Blank Analysis Results for Third Quarter 2010 (total micrograms)

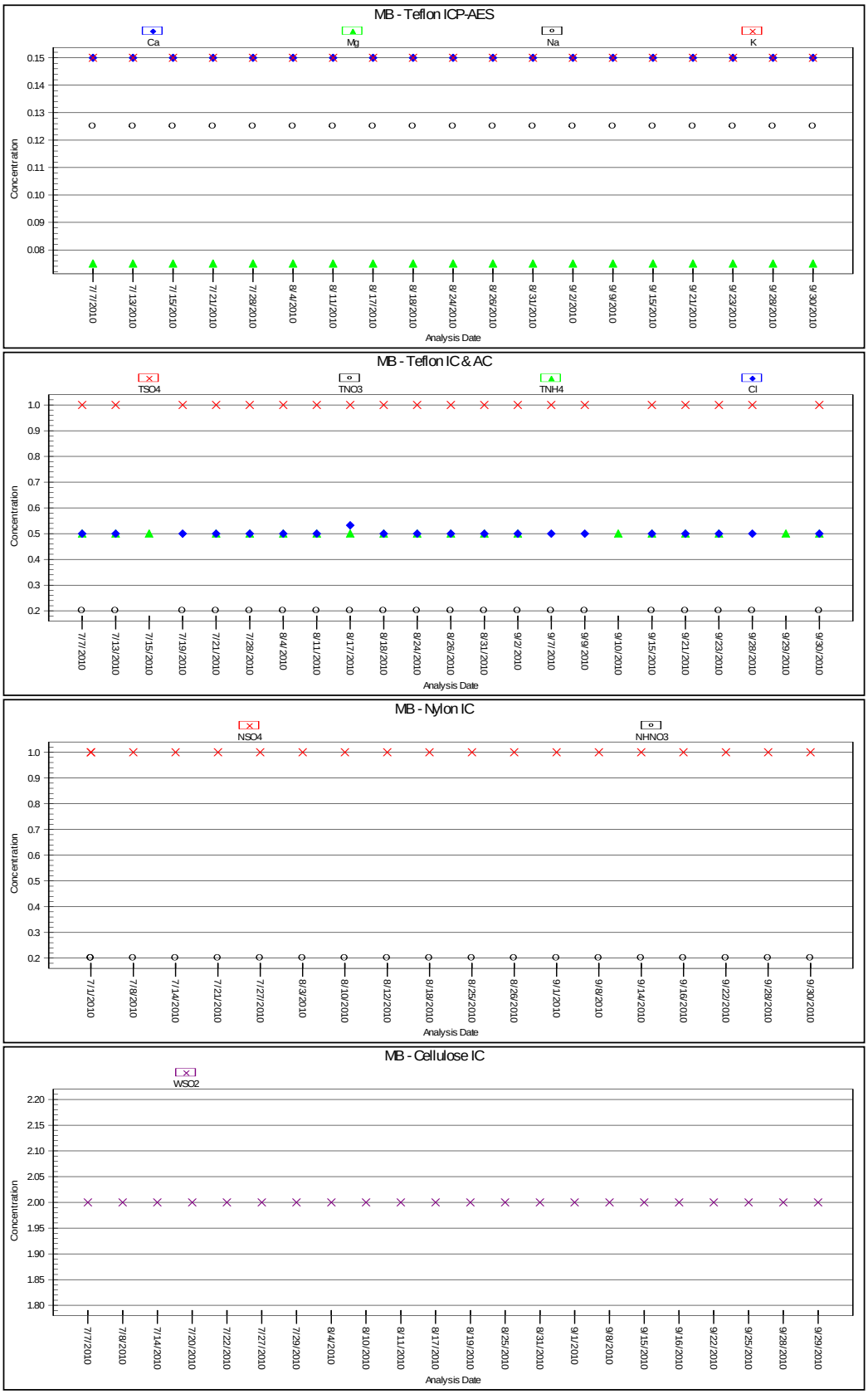


Figure 7. Laboratory Blank Analysis Results for Third Quarter 2010 (total micrograms)

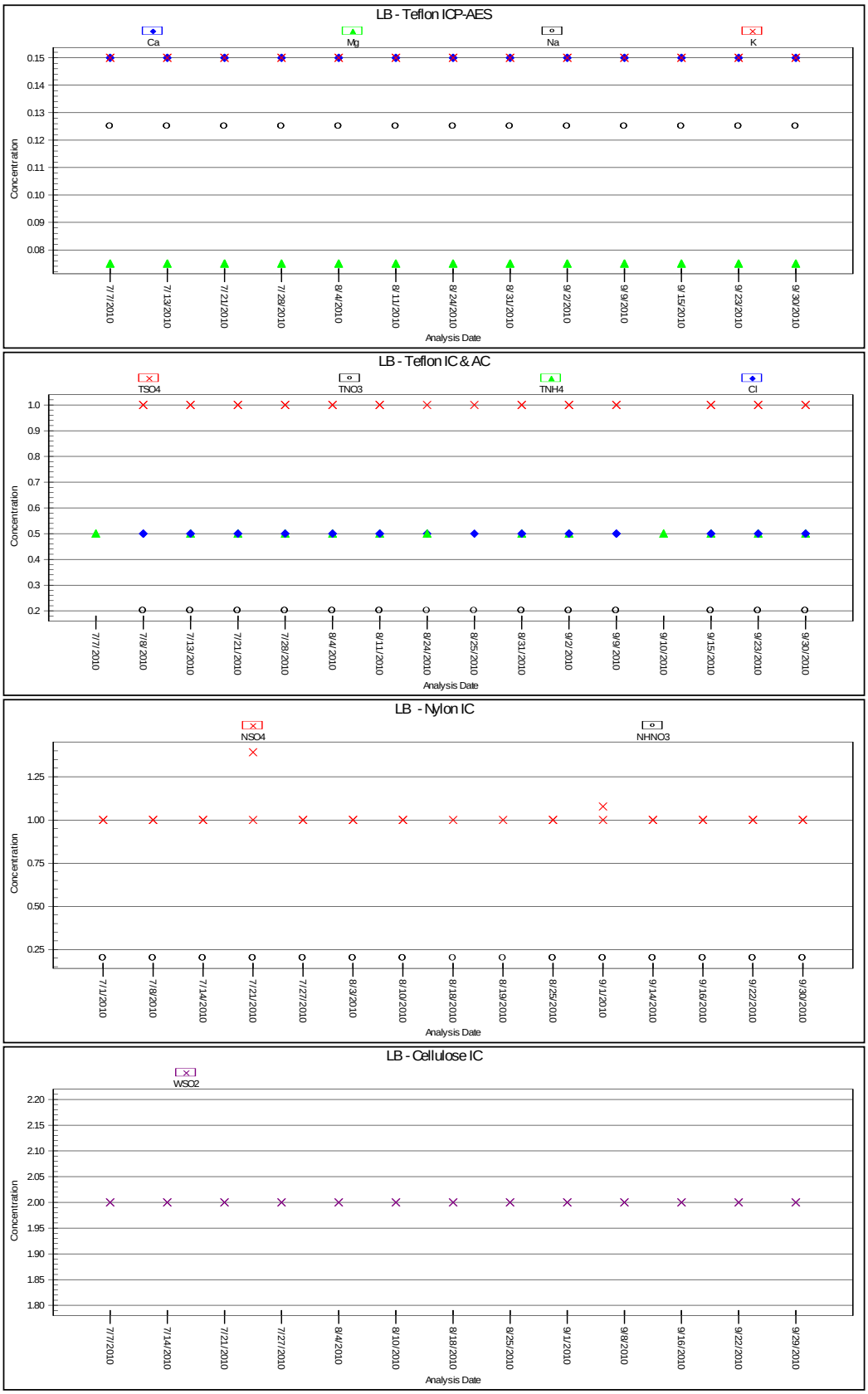


Figure 8. Field Blank Analysis Results for Third Quarter 2010 (total micrograms)