Summary of Quarterly Operations (January – March)

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 first quarter 2012. 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.

EPA issued Contract Modification 0032 to the CASTNET IV contract (EP-W-09-028) on April 6, 2012 to accept AMEC E&I, Inc.'s name change to AMEC Environment & Infrastructure, Inc. (AMEC).

AMEC has continued working with the manufacturer of the flow transfer standards used for the network to resolve the measurement errors AMEC discovered in 2011. The manufacturer has identified a defect in the model used for network calibrations between 2000 and 2011, which affects all units of this model. The defect affects ambient pressure readings used to calculate "standard" flow rates (i.e., rates scaled to standard temperature and pressure). At pressures below one atmosphere, these units read erroneously high pressure values. The magnitude of the error increases as the ambient pressure decreases. The faulty units are no longer manufactured. AMEC began using the replacement model in the field along with the older units during 2011. The differences between these models sparked the subsequent investigations. The replacement model has been verified to accurately measure ambient pressures in the range expected for CASTNET sites, including the high elevation sites in the network. The issue was discussed by project participants during a summit meeting in March 2012. EPA made the decision to make the documented transition to the newer, replacement standards at the beginning of 2013. In the

meantime, AMEC and the manufacturer will continue investigating with the goal of quantifying the error and providing users with a measure of uncertainty for affected data. The corrective actions to be implemented by AMEC include:

- Requiring documentation from the manufacturer that verifies pressure readings in the range expected at network sites. This information will be added to all flow standard certification documents produced by the manufacturer for AMEC standards.
- Collecting audit data from both flow standard models during all calibrations through the end of 2012.

During first quarter 2012, the CASTNET QA Manager completed an audit of the preparation, use, and return of the calibration and repair kits. The first phase of the audit focused on the procedures and preparation of the calibration and repair kits used by site calibrators and technicians. A few minor items were missing from the calibration kit. The checklists used when packing the kits will be revised to provide additional details for the packers. Implementation of a peer review process will be evaluated. The second phase consisted of an audit of the process and procedures for handling the kits after they are returned to AMEC. The repair and calibration kits returned by one of AMEC's field subcontractors did not have complete documentation. Making modifications to select forms in order to provide reminders was recommended. Kits returned by other AMEC field subcontractors also will be audited. A follow up audit to verify that findings and recommendations resulting from the audit have been addressed will take place during second quarter 2012.

AMEC continued planning for an on-site technical systems audit (TSA) of AMEC's CASTNET field instrumentation laboratory. A TSA of the ozone monitoring support provided by the facility is required by EPA since AMEC is the monitoring organization in charge of EPA-sponsored CASTNET Air Quality System (AQS)-protocol sites. AMEC contacted RTI International about performing the audit. The audit will occur no sooner than late June, and could take place as late as September 2012.

During March 2012, AMEC received results from sample analyses for proficiency test (PT) study 0099 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 quality assurance (QA) services. AMEC's laboratory received a warning flag for being biased high on two ammonia sample results. The laboratory identified the source of the error and will implement corrective action during second quarter 2012. Overall, the laboratory was rated "Good" for PT 0099 analyses, and AMEC's 5-year median rating remained "Very Good." AMEC regularly participates in laboratory intercomparison tests offered by Environment Canada and the U.S. Geological Survey.

Table 1 lists the quarters of data that were validated to Level 3 during first quarter 2012 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 first quarter 2012.

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 first quarter 2012.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for first quarter 2012. All results were within the criteria listed in Table 4.

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 unless there is documented evidence that the problem can be verifiably traced to a system or subsystem that does not affect reported data. 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 first quarter 2012. 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 first quarter 2012. All results were within criteria (two times the reporting limit) listed in Table 4.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during first quarter 2012 are listed in Table 10. This table includes associated site identification and a brief description of the reason the sample was flagged. During first quarter, seven 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 first quarter 2012. 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 24 sites during first quarter 2012. 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.

Table 1. Data Validated to Level 3 during First Quarter 2012

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-2/MW-8	April 2011 – September 2011	6	Quarter 2, 2011 – Quarter 3, 2011	2
E-3/W-10†	May 2011 – October 2011	6	Quarter 3, 2011	1
SE-4/MW-6‡	July 2011 – December 2011	6	Quarter 3, 2011 – Quarter 4, 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 third
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 First Quarter 2012

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	176	77	17	26	118
	NO_3^-	34	176	84	17	26	118
	NH_4^+	36	178	97	18	26	118
	Cl^-	34	176	84	17	26	117
	Ca^{2+}	34	175	84	17	26	117
	Mg^{2+}	34	175	84	17	26	117
	Na^+	34	175	84	17	26	117
	K^+	34	175	84	17	26	117
Nylon	SO_4^{2-}	28	153	67	14	24	81
	NO_3^-	28	153	75	14	24	81
Cellulose	SO_4^{2-}	44	166	81	21	24	81

Table 7. Filter Pack Receipt Summary for First Quarter 2012

Count of samples received more than 14 days after removal from tower:	10
Count of all samples received:	783
Fraction of samples received within 14 days:	0.987
Average interval in days:	4.58
First receipt date:	01/03/2012
Last receipt date:	03/30/2012

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	100.00	1.20	100.00	1.33	0.09	98.84	0.97
ALC188, TX	94.19	282.22	86.05	207.74	206.82	79.78	5.27
ALH157, IL	100.00	0.93	100.00	0.79	0.06	100.00	0.34
ANA115, MI	100.00	0.88	100.00	1.04	0.08	100.00	0.32
ARE128, PA	88.04	13.61	88.04	14.22	6.42	98.92	1.02
ASH135, ME	100.00	4.29	100.00	4.28	0.08	100.00	0.26
BEL116, MD	100.00	1.09	100.00	1.66	0.09	100.00	0.25
BFT142, NC	100.00	1.40	100.00	1.43	0.20	100.00	1.02
BVL130, IL	100.00	3.38	100.00	3.77	0.11	100.00	0.53
BWR139, MD	100.00	0.58	100.00	0.63	0.12	100.00	0.40
CAD150, AR	98.91	2.33	97.83	2.52	1.77	100.00	0.38
CDR119, WV	100.00	0.75	100.00	0.74	0.06	100.00	1.14
CDZ171, KY	96.81	3.16	96.81	3.06	2.57	98.94	0.93
CKT136, KY	100.00	1.28	98.96	1.11	0.19	100.00	1.04
CND125, NC	91.49	8.01	91.49	7.66	3.94	91.49	3.01
CNT169, WY	100.00	0.86	100.00	2.28	0.24	98.68	0.78
COW137, NC	96.74	2.23	96.74	2.21	0.38	100.00	0.36
CTH110, NY	100.00	1.70	100.00	1.24	0.10	100.00	0.38
CVL151, MS	95.70	4.16	95.65	4.65	2.70	94.62	2.48
DCP114, OH	97.87	14.54	97.87	14.80	15.56	100.00	0.41
ESP127, TN	100.00	0.38	100.00	0.47	0.08	100.00	0.78
GAS153, GA	98.81	0.67	100.00	0.99	0.10	100.00	0.60
GTH161, CO	96.74	3.82	96.70	2.55	1.34	96.74	1.83
HOW132, ME	100.00	1.53	100.00	1.53	0.05	100.00	1.53
HOX148, MI	100.00	0.31	100.00	0.35	0.05	100.00	0.23
HWF187, NY	90.22	2.99	93.48	2.67	0.26	100.00	0.71
IRL141, FL	100.00	0.59	100.00	0.34	0.04	100.00	1.16
KEF112, PA	100.00	0.34	100.00	0.47	0.08	100.00	2.06
KNZ184, KS	100.00	0.34	100.00	0.58	0.07	100.00	0.85
LRL117, PA	100.00	1.90	96.39	2.10	0.41	97.87	1.08
MCK131, KY	100.00	2.91	100.00	3.15	0.08	100.00	0.31
MCK231, KY	100.00	2.27	100.00	2.24	0.17	98.89	1.08

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	91.95	7.26	90.80	7.41	3.68	90.91	2.80
OXF122, OH	100.00	2.90	100.00	3.27	0.28	100.00	0.30
PAL190, TX	100.00	1.32	100.00	1.26	0.07	100.00	0.33
PAR107, WV	84.04	78020.63	84.04	27529.41	15217.62	100.00	0.34
PED108, VA	100.00	0.99	100.00	0.92	0.08	100.00	0.29
PND165, WY	100.00	1.68	100.00	0.90	0.10	100.00	0.52
PNF126, NC	100.00	0.33	100.00	0.44	0.08	100.00	0.20
PRK134, WI	85.11	11.81	86.17	7.41	2.75	89.36	4.86
PSU106, PA	100.00	1.39	100.00	1.37	0.09	100.00	0.29
QAK172, OH	92.47	1.91	92.47	2.32	0.29	100.00	0.62
ROM206, CO	97.83	3.88	98.91	3.17	0.89	96.81	1.79
SAL133, IN	100.00	0.65	100.00	0.81	0.07	100.00	1.93
SAN189, NE	100.00	0.99	100.00	0.77	0.07	100.00	0.22
SND152, AL	100.00	1.41	100.00	1.26	0.07	100.00	0.20
SPD111, TN	100.00	0.80	100.00	0.58	0.08	100.00	0.29
STK138, IL	98.92	3.79	98.92	3.64	0.98	98.92	1.06
SUM156, FL	100.00	0.74	100.00	0.73	0.11	100.00	0.19
UVL124, MI	100.00	2.73	100.00	3.12	0.18	100.00	0.40
VIN140, IN	96.88	15.99	96.88	15.92	15.92	100.00	0.56
VPI120, VA	100.00	0.96	100.00	0.91	0.11	100.00	0.73
WSP144, NJ	100.00	0.35	100.00	0.86	0.06	100.00	0.44
WST109, NH	97.80	7.05	97.80	7.01	1.83	98.90	1.30

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
ALC188, TX	Span |%D|, % Single Point QC Pass, Single Point QC |%D|, Single Point QC CL, % Zero Pass	There was a flow leak in a zero air canister connection that lasted for approximately three days. Ambient data were not affected.
ARE128, PA	% Span Pass, Span |%D|, % Single Point QC Pass, Single Point QC |%D|	The analyzer's sample pump failed affecting reported values for three weeks until the analyzer was replaced.
CND125, NC	Span |%D |, Single Point QC |%D|	Investigation is inconclusive to date. If no source of error is found, the associated data will be invalidated.
DCP114, OH	Span |%D |, Single Point QC |%D|, Single Point QC CL	The pressure transducer in the site analyzer was malfunctioning.
MKG113, PA	Span |%D |, Single Point QC |%D|	The pressure transducer in the site analyzer was malfunctioning.
PAR107, WV	%Span Pass, Span |%D|, % Single Point QC Pass, Single Point QC |%D|, Single Point QC CL	The site transfer standard internal solenoid malfunctioned. The transfer standard was replaced in about one week. Ambient data were not affected.
PRK134, WI	%Span Pass, Span |%D|, % Single Point QC Pass, Single Point QC |%D|, % Zero Pass	The zero air tubing was disconnected for about one week. Ambient data were not affected.
VIN140, IN	Span |%D|, Single Point QC |%D|, Single Point QC CL	The pressure transducer in the site analyzer was malfunctioning.
WST109, NH	Span |%D|, Single Point QC |%D|	There was a flow leak in one of the zero air canisters that lasted for approximately two days. Ambient data were not affected.

Notes: %D = percent difference
CL = confidence limit

Table 10. Filter Packs Flagged as Suspect or Invalid

Site ID	Sample No.	Reason
BFT142, NC	1202001-10	Polling problems
	1203001-10	Polling problems
	1206001-10	Polling problems
	1207001-10	Polling problems
CKT136, KY	1208001-20	Insufficient flow volume
CNT169, WY	1203001-22	Polling problems
GAS153, GA	1201001-31	Polling problems

Table 11. Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	162
60	9
90	0
Unresolved by End of Quarter	4

Table 12. Field Calibration Failures by Parameter

Site ID	Parameter(s)
COW137, NC	Flow Rate

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 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 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 First Quarter 2012 (percent recovery)

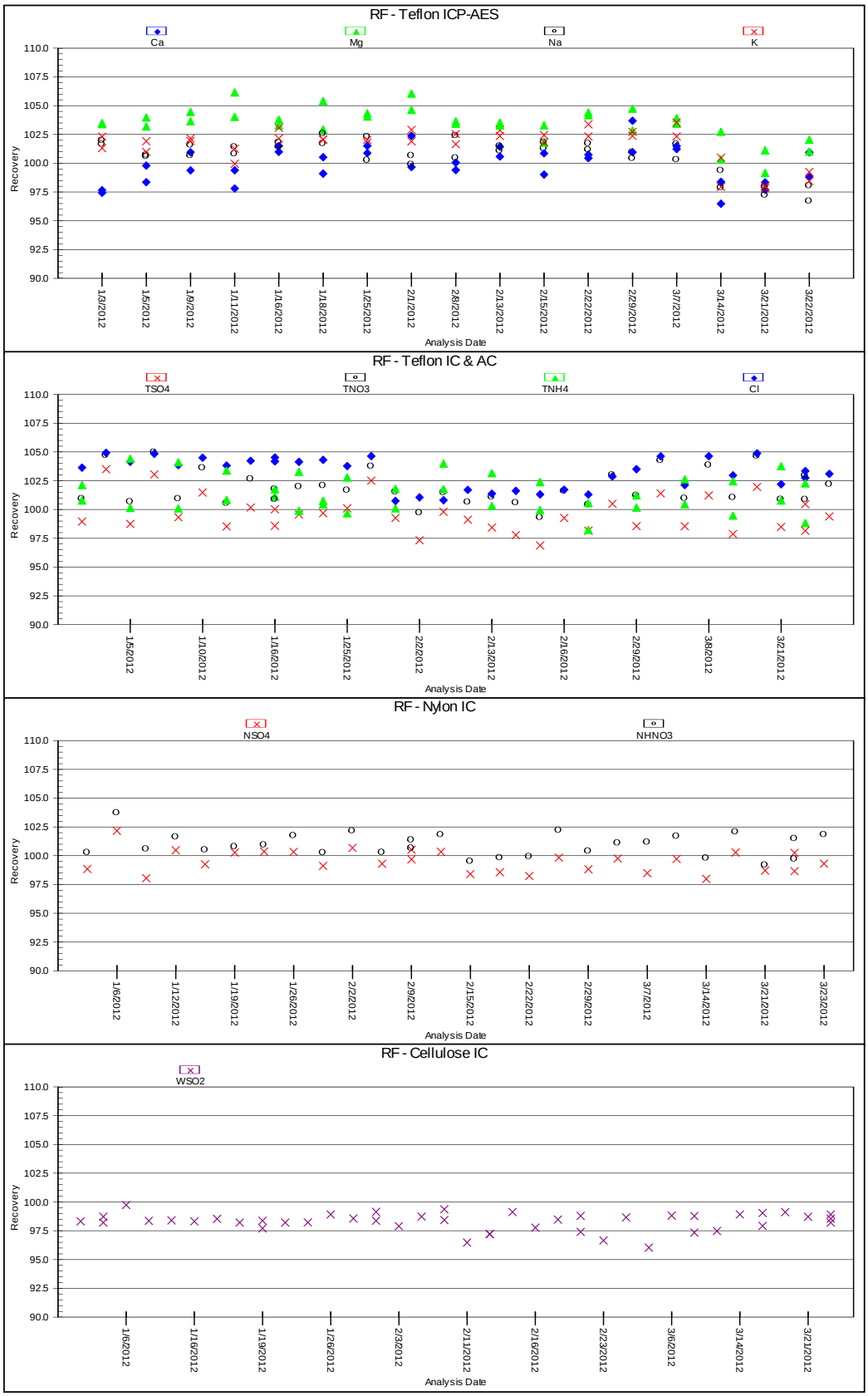


Figure 2. Continuing Calibration Spike Results for First Quarter 2012 (percent recovery)

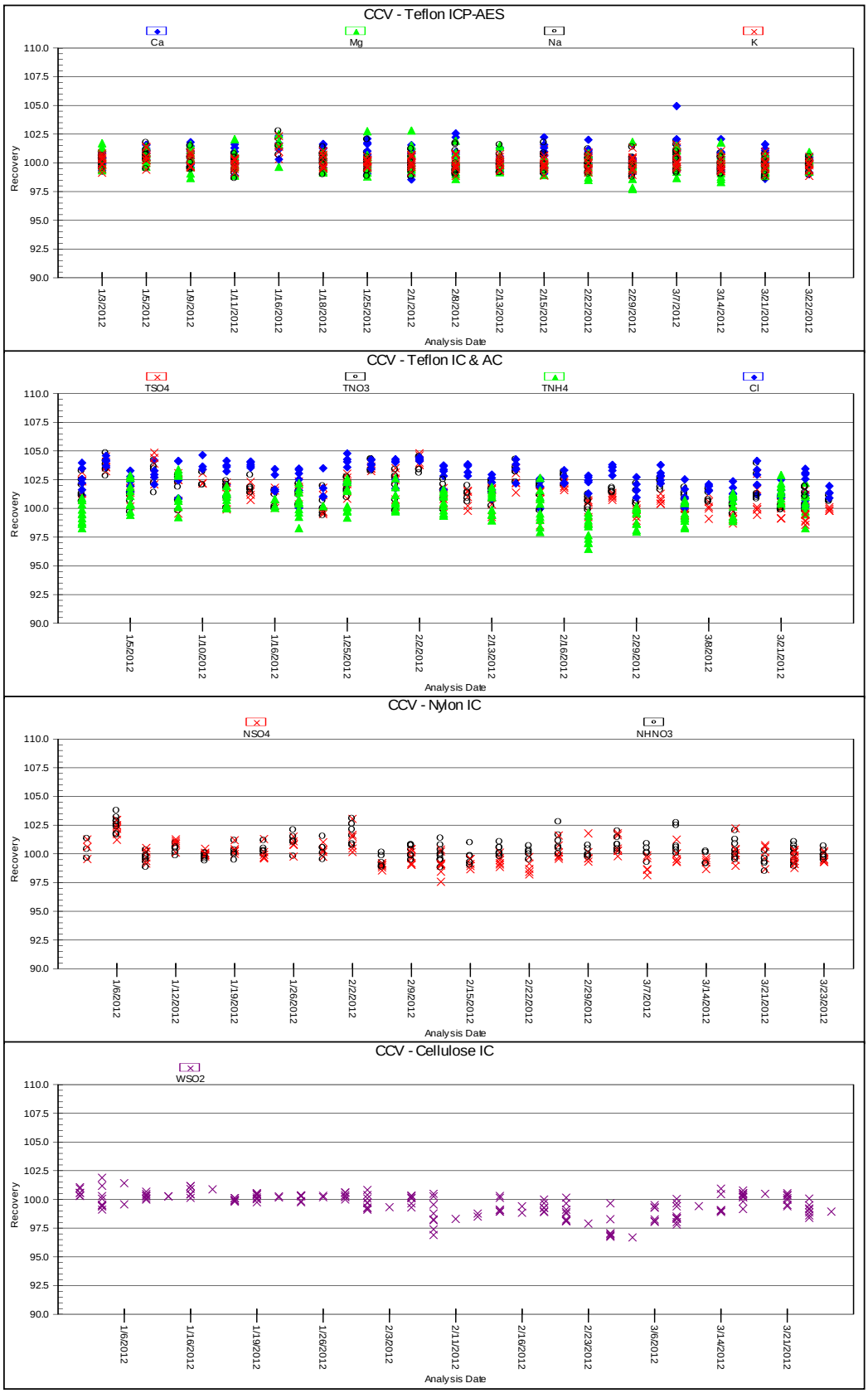


Figure 3. Replicate Sample Analysis Results for First Quarter 2012 (percent difference)

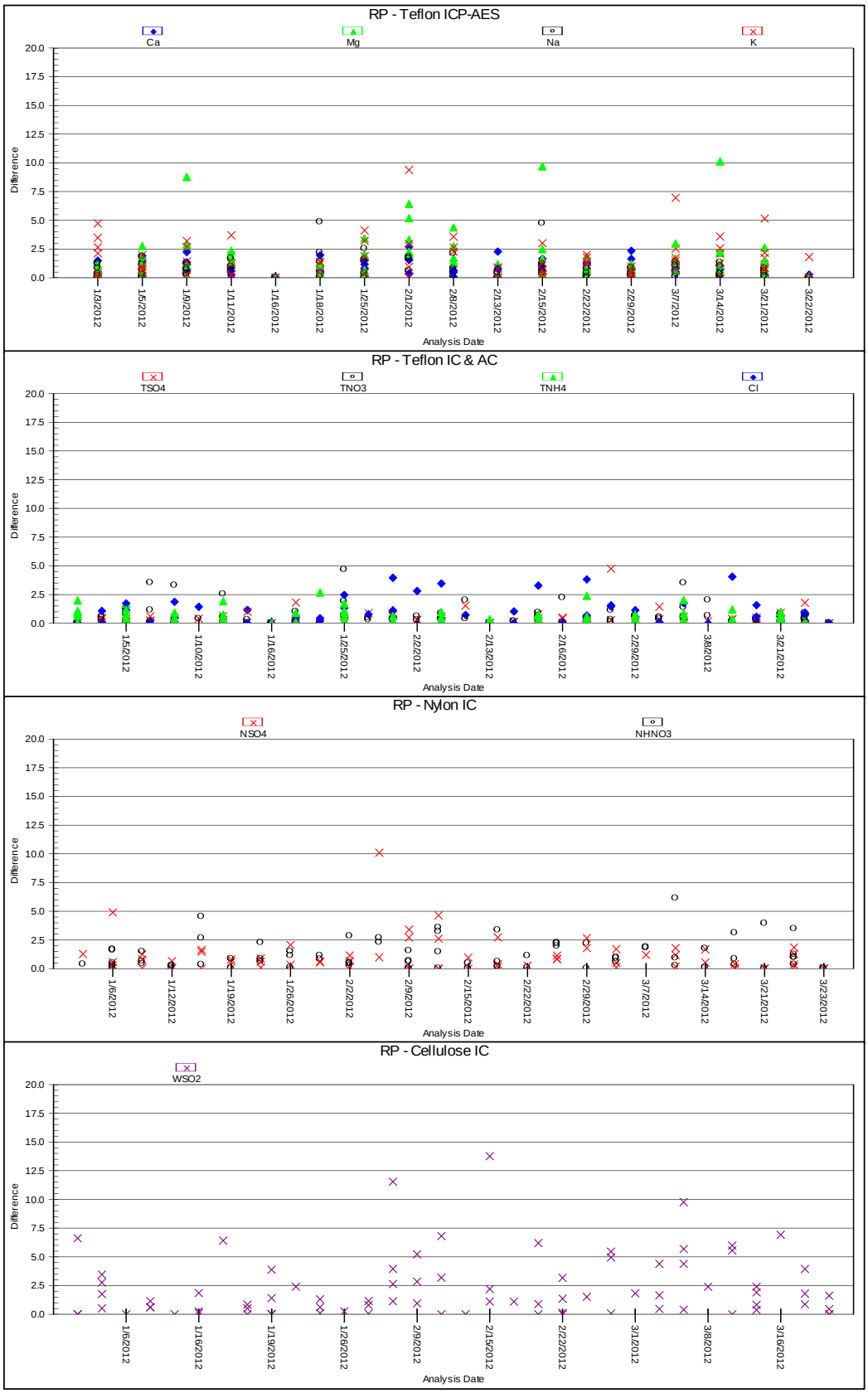
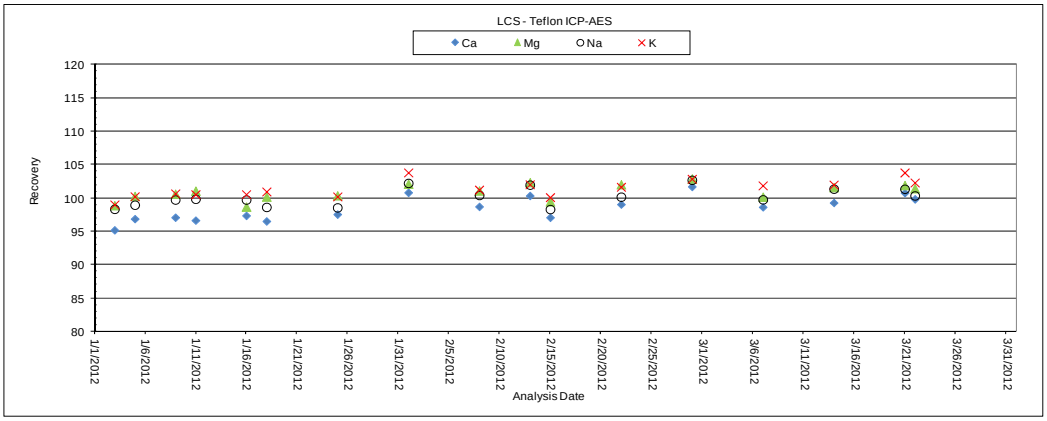
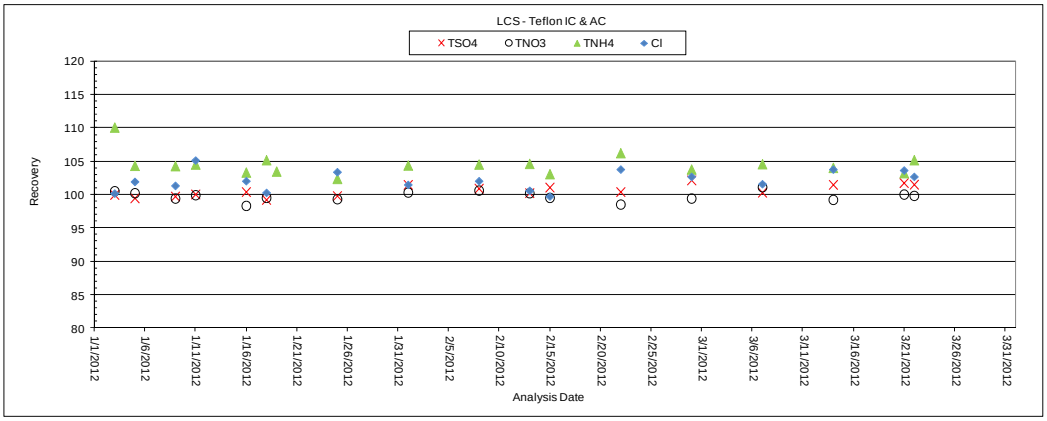
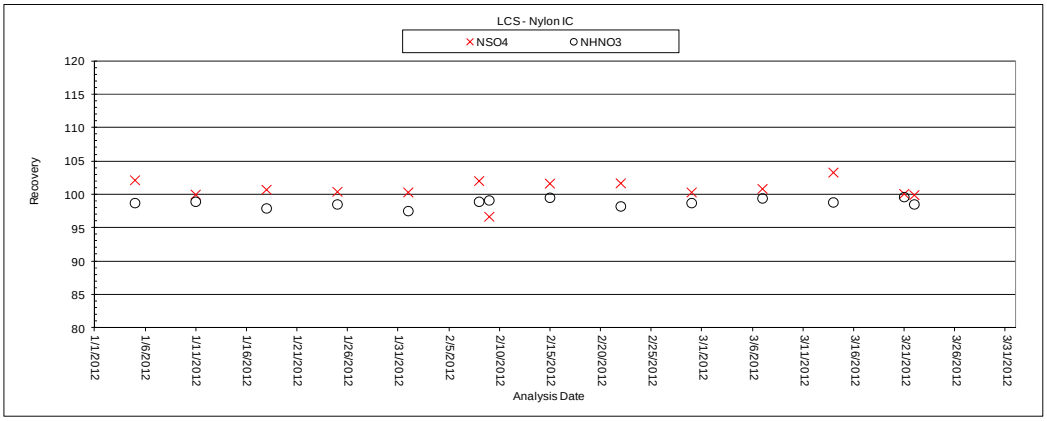


Figure 4. Laboratory Control Sample Results for First Quarter 2012 (percent recovery)







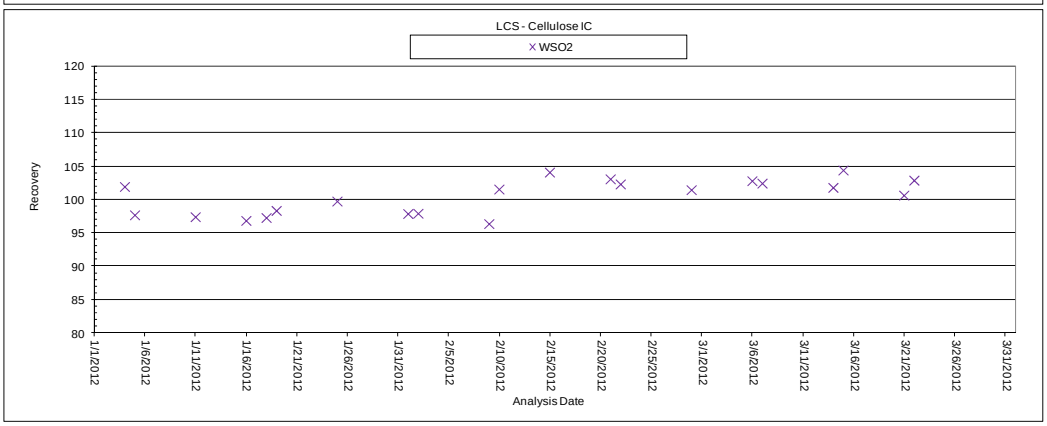


Figure 5. Method Blank Analysis Results for First Quarter 2012 (total micrograms)

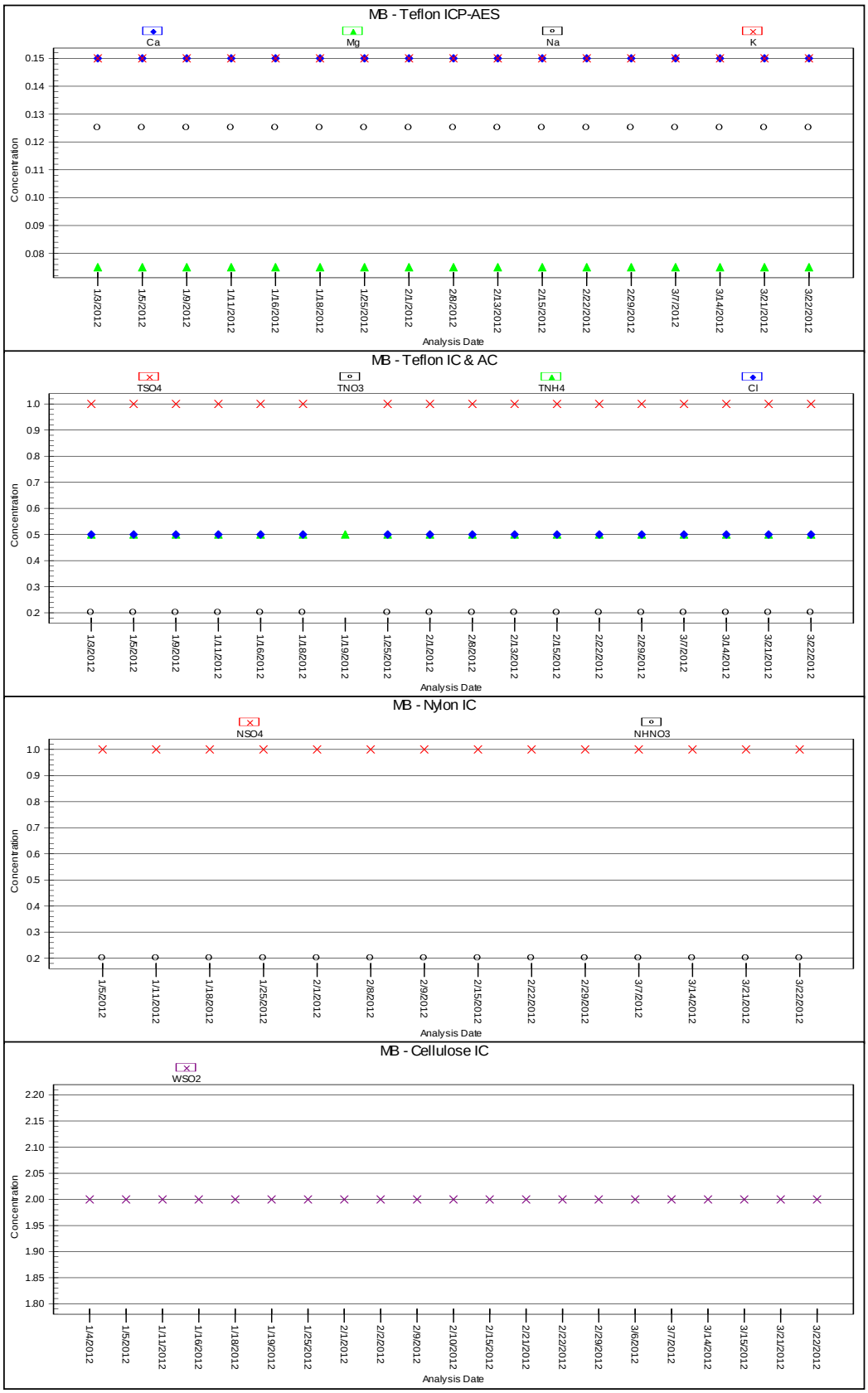


Figure 6. Laboratory Blank Analysis Results for First Quarter 2012 (total micrograms)

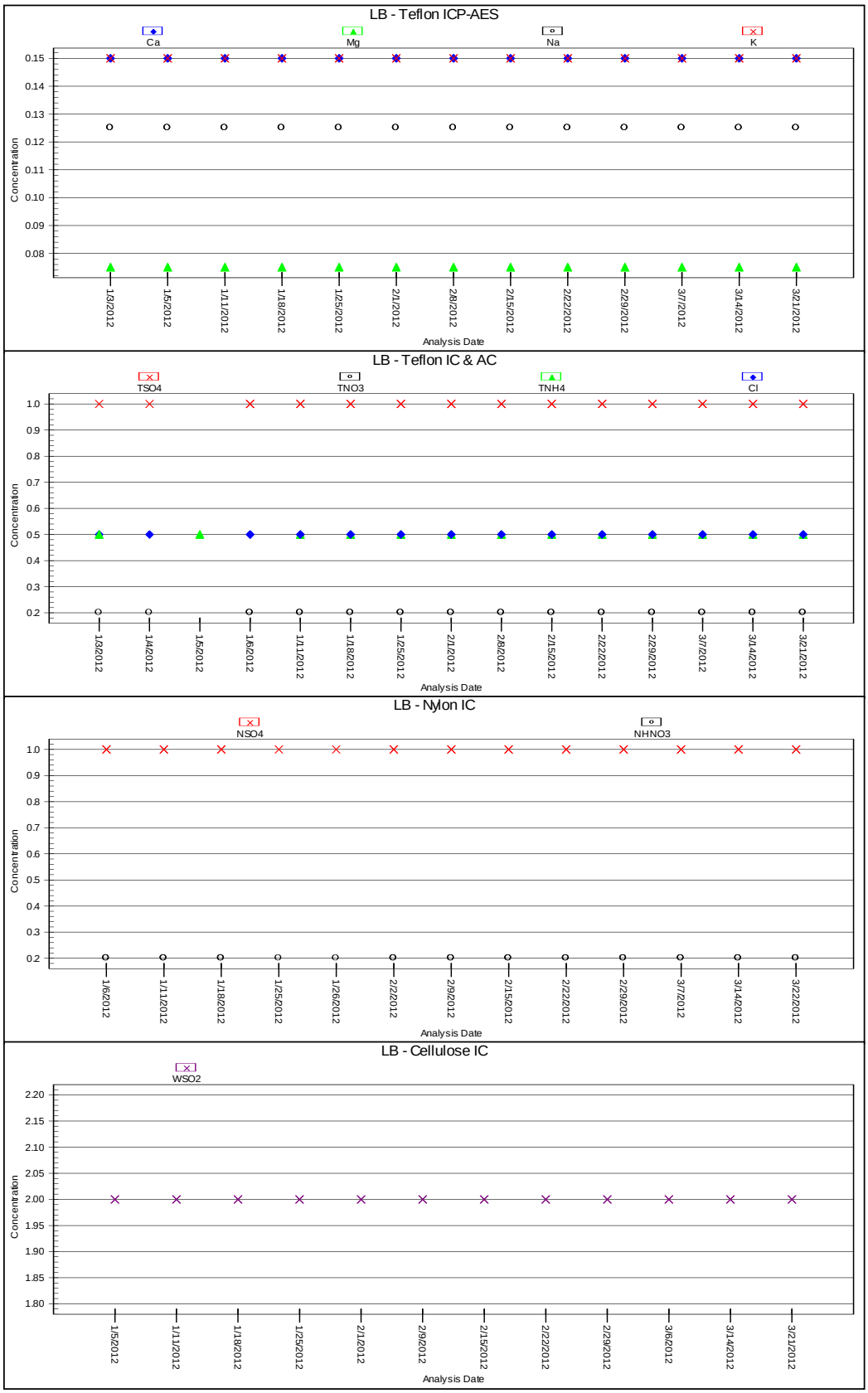


Figure 7. Field Blank Analysis Results for First Quarter 2012 (total micrograms)