

# Summary of Quarterly Operations (January through March) EPA Contract No. EP-W-15-003

#### 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 2015. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; AMEC, 2014). 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.

## **Quarterly Summary**

During January 2015, comments received from EPA on the CASTNET QAPP Revision 8.2 were incorporated into the QAPP, and Revision 8.2 was finalized. After EPA approved the final version of the QAPP Revision 8.2, it was distributed to the designated recipients.

AMEC received Contract Modification 0066 to the CASTNET IV contract (EP-W-09-028) on January 14, 2015, which modified the Key Personnel clause to replace W. Charles Greer, Jr. with Ann Bernhardt as AMEC's CASTNET QA Supervisor.

On January 26, 2015, AMEC submitted sample analyses for proficiency test (PT) study 0105 for Rain and Soft Waters to the National Laboratory of Environmental Testing (NLET), a branch of the National Water Research Institute (NWRI) with Environment Canada that provides QA services. AMEC received the results from PT study 0105 in March. A low bias was indicated for the pH analyses. One sample was flagged "action high" for potassium and chloride. AMEC was rated good for the study overall. An investigation and corrective action will be initiated for the low bias and "action high" flags.

AMEC's next surveillance assessment required to maintain International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025:2005 accreditation by the American Association for Laboratory Accreditation (A2LA) is scheduled to

take place during second quarter 2015. During first quarter, AMEC reviewed procedures and laboratory documentation to verify that everything had been updated and documented as required to maintain 17025:2005 accreditation. After the April 2015 assessment, the next assessment will be performed around May 2017. Assessments occur once every two years.

Table 1 lists the quarters of data that were validated to Level 3 during first quarter 2015 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 laboratory filter pack measurements. These criteria apply to the QC samples listed in the following section of this report. Table 4 presents the critical criteria for ozone monitoring. Table 5 presents the critical criteria for trace-level gas monitoring.

## **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 2015.

## **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 2015.

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

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for first quarter 2015. All results were within the criteria listed in Table 3. Two RF samples reported in support of cellulose filter analyses appear to be outside of established criteria as plotted on the graph. These samples were within criteria per the established rule for rounding results at 94.7 and 105.3 percent recovery.

Table 8 presents summary statistics of critical criteria measurements at ozone sites collected during first quarter 2015. The statistics presented contain data validated at Level 2 and Level 3. All data associated with QC checks that fail to meet the criteria listed in Table 4 were or will be invalidated unless the cause of failure has no affect on ambient data collection, and passing results still meet frequency criteria. Results in the shaded cell either exceeded documented

criteria or are otherwise notable. Table 9 presents observations associated with the shaded cell results in Table 8.

Table 10 presents summary statistics of critical criteria measurements at trace-level gas monitoring sites collected during first quarter 2015. The statistics presented contain data validated at Level 2 and Level 3. All data associated with QC checks that fail to meet the criteria listed in Table 5 were or will be invalidated unless the cause of failure has no affect on ambient data collection, and passing results still meet frequency criteria. During first quarter 2015, no results exceeded documented criteria or were otherwise notable.

## **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. Figure 4 presents LCS analysis results for first quarter 2015. All recovery values were between 85 percent and 110 percent.

#### **Blank Results**

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for first quarter 2015. All first quarter results were within criteria (two times the reporting limit) listed in Table 3.

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

Filter pack samples that were flagged as suspect or invalid during first quarter 2015 are listed in Table 11. This table also includes associated site identification and a brief description of the reason the sample was flagged. During first quarter, 10 filter pack samples were invalidated.

#### **Field Problem Count**

Table 12 presents counts of field problems affecting continuous data collection for more than one day for first quarter 2015. 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.

#### References

- AMEC Environment & Infrastructure, Inc. (AMEC). 2014. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 8.2.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-09-028. Gainesville, FL. http://java.epa.gov/castnet/documents.do.
- American Society for Testing and Materials (ASTM). 2008. ASTM E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications. ASTM International, West Conshohocken, PA, DOI:10.1520/E0029-08. www.astm.org.
- U.S. Environmental Protection Agency (EPA). 2014. Appendix A to Part 58 Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS), Special Purpose Monitors (SPMs), and Prevention of Significant Deterioration (PSD) Air Monitoring. *Title 40 Code of Federal Regulations Part 58*.

Table 1 Data Validated to Level 3 during First Quarter 2015

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10 <sup>†</sup>	May 2014 – October 2014	6	Quarter 3 2014	1
SE-4/MW-6 <sup>‡</sup>	July 2014 – December 2014	6	Quarter 3 2014 – Quarter 4 2014	2

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

† Contains ROM206 of the ROM406/ROM206 collocated pair

Table 2 Field Calibration Schedule for 2015

Calibration Group	Months Calibrated			tes orated			
Group	Camprateu	Eastern Sites (2		rateu			
E 1	F-1/A/	`		ADE 120 DA	DED 100 V/A		
E-1	February/August	BEL116, MD	WSP144, NJ	ARE 128, PA	PED108, VA		
(8 Sites)		BWR139, MD	CTH110, NY	PSU106, PA	VPI120, VA		
E-2	April/October	ABT147, CT	WST109, NH	WFM105, NY	UND002, VT		
(10 Sites)		ASH135, ME	CAT175, NY	NIC001, NY			
		HOW191, ME	HWF187, NY	EGB181, ON			
E-3	May/November	KEF112, PA	LRL117, PA	CDR119, WV			
(5 Sites)		MKG113, PA	PAR107, WV				
		Southeastern Si	ites (10 Total)				
SE-4	January/July	SND152, AL	BFT142, NC	COW137, NC			
(6 Sites)		GAS153, GA	CND125, NC	SPD111, TN			
SE-5	February/August	CAD150, AR	IRL141, FL				
(4 Sites)		CVL151, MS	SUM156, FL				
		Midwestern Sit	es (19 Total)				
MW-6	January/July	CDZ171, KY	MCK131, KY	PNF126, NC			
(6 Sites)		CKT136, KY	MCK231, KY	ESP127, TN			
MW-7	March/September	ALH157, IL	VIN140, IN	OXF122, OH			
(9 Sites)	•	BVL130, IL	RED004, MN	QAK172, OH			
		STK138, IL	DCP114, OH	PRK134, WI			
MW-8	April/October	SAL133, IN	ANA115, MI				
(4 Sites)	•	HOX148, MI	UVL124, MI				
	Western Sites (10 Total)						
W-9	March/September	KNZ184, KS	CHE185, OK	ALC188, TX			
(5 Sites)	•	KIC003, KS	SAN189, NE				
W-10	May/November	GTH161, CO	CNT169, WY	PAL190, TX			
(5 Sites)		ROM206, CO	PND165, WY	•			

<sup>‡</sup> Contains MCK131/231 collocated pair

**Table 3** Data Quality Indicators for CASTNET Laboratory Measurements

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

AC = automated colorimetry IC = ion chromatography

ICP-OES = inductively coupled plasma-optical emission spectrometry

MARPD = mean absolute relative percent difference

mg/L = milligrams per liter  $\mu g/Filter$  = micrograms per filter \* = as nitrogen

Values are rounded according to American Society for Testing and Materials (ASTM) E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications (ASTM, 2008).

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP, (AMEC, 2014).

**Table 4** Ozone Critical Criteria\*

Type of Check	Analyzer Response
Zero	Less than ± 3 parts per billion (ppb)
Span	Less than or equal to $\pm$ 7 percent between supplied and observed concentrations
Single Point QC	Less than or equal to $\pm$ 7 percent between supplied and observed concentrations

Notes: \*Applies to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (EPA, 2014). The minimum frequency for these checks is once every two weeks.

Values are rounded according to ASTM E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications (ASTM, 2008).

replicate samples.

<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-OES reference standards.

**Table 5** Trace-level Gas Monitoring Critical Criteria\*

	Analyzer Response					
Parameter	Zero Check	Span Check / Single Point QC Check				
SO <sub>2</sub>	Less than ± 3 ppb					
NO <sub>y</sub>	Less than ± 3 ppb	Less than or equal to $\pm$ 10 percent between supplied and observed concentrations				
СО	Less than ± 40 ppb					

Notes: \*Applies to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (EPA, 2014). The minimum frequency for these checks is once every two weeks.

Values are rounded according to ASTM E29-08, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications E29 (ASTM, 2008).

 $SO_2 = sulfur dioxide$ 

NO<sub>y</sub> = total reactive oxides of nitrogen

CO = carbon monoxide ppb = parts per billion

Table 6 QC Analysis Count for First Quarter 2015

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	$SO_4^{2-}$	53	201	86	18	26	130
	$NO_3$	53	201	86	18	26	130
	$\mathrm{NH}_{4}^{^{+}}$	36	185	89	18	26	130
	Cl	53	201	86	18	26	130
	$Ca^{2+}$	36	186	88	18	26	130
	$\mathrm{Mg}^{^{2+}}$	36	186	88	18	26	130
	Na <sup>+</sup>	36	186	88	18	26	130
	$\mathbf{K}^{\scriptscriptstyle{+}}$	36	186	88	18	26	130
Nylon	SO <sub>4</sub> <sup>2-</sup>	36	183	83	18	26	130
	NO <sub>3</sub>	48	195	89	24	26	136
Cellulose	SO <sub>4</sub> <sup>2-</sup>	37	185	82	18	26	130

Table 7 Filter Pack Receipt Summary for First Quarter 2015

Count of samples received more than 14 days	
after removal from tower:	22
Count of all samples received:	875
Fraction of samples received within 14 days:	0.975
Average interval in days:	5.19
First receipt date:	01/02/2015
Last receipt date:	03/31/2015

Table 8 Ozone QC Summary for First Quarter 2015 (1 of 2)

Site ID	% Span Pass <sup>1</sup>	<b>Span</b>  % <b>D</b>   <sup>2</sup>	% Single Point QC Pass <sup>1</sup>	Single Point QC  %D  <sup>2</sup>	Single Point QC CL <sup>3</sup>	% Zero Pass <sup>1</sup>	Zero Average (ppb) <sup>2</sup>
ABT147, CT	100.00	1.71	100.00	1.54	0.10	100.00	0.29
ALC188, TX	100.00	0.60	98.94	0.90	0.28	100.00	0.38
ALH157, IL	100.00	1.65	100.00	0.80	0.07	100.00	0.14
ANA115, MI	100.00	0.91	100.00	0.92	0.12	100.00	0.11
ARE128, PA	97.80	3.52	97.80	1.45	0.23	97.80	1.49
ASH135, ME	100.00	1.31	100.00	1.20	0.10	100.00	0.22
BEL116, MD	96.74	3.56	92.39	4.14	0.27	100.00	1.47
BFT142, NC	97.89	2.59	97.89	2.06	0.71	95.79	1.28
BVL130, IL	100.00	0.58	100.00	1.53	0.14	100.00	1.19
BWR139, MD	100.00	1.57	100.00	2.11	0.23	100.00	0.11
CAD150, AR	100.00	1.62	100.00	1.88	0.28	98.68	0.64
CDR119, WV	97.75	1.53	100.00	1.53	0.12	100.00	0.24
CDZ171, KY	100.00	0.48	100.00	0.56	0.10	100.00	0.14
CKT136, KY	100.00	1.00	100.00	1.95	0.14	100.00	0.16
CND125, NC	100.00	0.50	100.00	0.54	0.10	100.00	0.19
CNT169, WY	100.00	0.92	100.00	1.57	0.25	100.00	0.69
COW137, NC	100.00	2.01	100.00	2.65	0.10	100.00	0.13
CTH110, NY	100.00	1.25	100.00	1.13	0.18	100.00	0.35
CVL151, MS	100.00	0.74	100.00	0.73	0.17	100.00	0.32
DCP114, OH	96.70	3.69	97.78	2.85	2.46	100.00	0.21
ESP127, TN	100.00	0.81	98.86	0.68	0.15	100.00	0.18
GAS153, GA	100.00	0.43	98.92	0.99	0.14	100.00	0.19
GTH161, CO	100.00	1.06	100.00	1.32	0.13	100.00	0.18
HOX148, MI	93.75	6.63	93.75	7.21	4.00	100.00	0.65

Table 8 Ozone QC Summary for First Quarter 2015 (2 of 2)

Site ID	% Span Pass <sup>1</sup>	<b>Span</b>  % <b>D</b>   <sup>2</sup>	% Single Point QC Pass <sup>1</sup>	Single Point QC  %D  <sup>2</sup>	Single Point QC CL <sup>3</sup>	% Zero Pass <sup>1</sup>	Zero Average (ppb) <sup>2</sup>
HWF187, NY	98.92	3.85	77.42	5.83	0.30	100.00	1.29
IRL141, FL	100.00	0.82	100.00	1.20	0.12	100.00	0.17
KEF112, PA	98.85	6.41	100.00	0.87	0.10	100.00	0.25
LRL117, PA	100.00	0.78	100.00	0.47	0.11	100.00	0.21
MCK131, KY	100.00	0.48	100.00	0.50	0.08	100.00	0.21
MCK231, KY	100.00	0.66	100.00	0.75	0.10	100.00	0.22
MKG113, PA	100.00	0.33	100.00	0.35	0.05	100.00	0.18
OXF122, OH	94.05	5.96	95.24	4.88	3.35	100.00	0.74
PAL190, TX	100.00	0.54	100.00	0.93	0.12	100.00	0.17
PAR107, WV	98.92	0.54	98.92	1.04	0.81	100.00	0.49
PED108, VA	100.00	1.88	100.00	1.88	0.28	100.00	0.10
PND165, WY	100.00	1.64	100.00	2.65	0.13	100.00	1.17
PNF126, NC	100.00	1.01	100.00	2.39	0.24	100.00	1.44
PRK134, WI	100.00	0.58	100.00	0.47	0.09	100.00	0.45
PSU106, PA	94.44	6.71	95.56	4.05	1.34	95.56	2.08
QAK172, OH	100.00	1.14	100.00	0.46	0.08	100.00	0.17
ROM206, CO	100.00	0.51	97.87	1.92	0.27	100.00	1.06
SAL133, IN	100.00	0.89	100.00	1.04	0.15	100.00	0.13
SAN189, NE	100.00	0.41	100.00	0.41	0.04	100.00	0.18
SND152, AL	100.00	1.15	98.91	1.50	0.13	100.00	0.19
SPD111, TN	100.00	1.03	100.00	1.42	0.12	100.00	0.22
STK138, IL	100.00	0.93	100.00	0.38	0.06	100.00	0.60
SUM156, FL	97.96	0.85	95.92	1.99	1.18	97.96	1.01
UVL124, MI	100.00	0.55	100.00	0.78	0.08	100.00	0.18
VIN140, IN	100.00	0.43	100.00	0.68	0.14	100.00	0.24
VPI120, VA	98.73	1.60	98.73	1.52	0.72	98.73	0.82
WSP144, NJ	100.00	1.11	100.00	0.95	0.21	93.48	2.44
WST109, NH	100.00	0.47	100.00	0.40	0.07	100.00	0.10

Notes: <sup>1</sup> Percentage of comparisons that pass the criteria listed in Table 4. Values falling below 90 percent are addressed in Table 9.

 $\%\,D\ =\ percent\ difference$ 

CL = confidence limit

ppb = parts per billion

<sup>&</sup>lt;sup>2</sup> Absolute value of the average percent differences between the on-site transfer standard and the site monitor. Values exceeding the criteria listed in Table 4 are addressed in Table 9.

<sup>&</sup>lt;sup>3</sup> 90 percent confidence limit of the coefficient of variation. This should be less than or equal to the 7 percent single point QC check critical criterion. Values exceeding this criterion are addressed in Table 9.

Table 9 Ozone QC Observations for First Quarter 2015

Site ID	QC Criterion	Comments
HWF187, NY	% Single Point QC Pass	The site analyzer malfunctioned. Associated data were invalidated.

Table 10 Trace-level Gas QC Summary for First Quarter 2015

Parameter	% Span Pass <sup>1</sup>	<b>Span</b>  % <b>D</b>   <sup>2</sup>	% Single Point QC Pass <sup>1</sup>	Single Point QC  %D  <sup>2</sup>	Single Point QC CL <sup>3</sup>	% Zero Pass <sup>1</sup>	Zero Average (ppb) <sup>2</sup>
			BEL116	, MD			
$SO_2$	97.78	4.53	100.00	3.74	0.45	100.00	1.16
$NO_y$	100.00	1.46	100.00	3.57	0.46	97.37	1.03
			BVL13	0, IL			
$SO_2$	100.00	2.91	100.00	1.42	0.28	100.00	0.62
$NO_y$	100.00	2.01	100.00	1.97	0.27	100.00	0.26
CO	100.00	1.02	90.32	5.84	1.27	90.91	14.43
			HWF18	7, NY			
$NO_y$	100.00	2.69	100.00	1.78	0.28	100.00	0.76
			PND165	, WY			
$NO_y$	100.00	1.25	100.00	4.78	0.52	100.00	0.23
	PNF126, NC						
$NO_y$	97.73	5.21	97.73	5.76	4.84	95.45	2.28
	ROM206, CO						
$NO_y$	100.00	0.72	100.00	0.64	0.13	100.00	0.35

Notes: <sup>1</sup> Percentage of comparisons that pass the criteria listed in Table 5. No values fell below 90 percent.

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

<sup>&</sup>lt;sup>2</sup> Absolute value of the average percent differences between the supplied and observed concentrations. No values exceeded the criteria

<sup>&</sup>lt;sup>3</sup> 90 percent confidence limit of the coefficient of variation. This should be less than or equal to the 10 percent single point QC check critical criterion. No values exceeded this criterion.

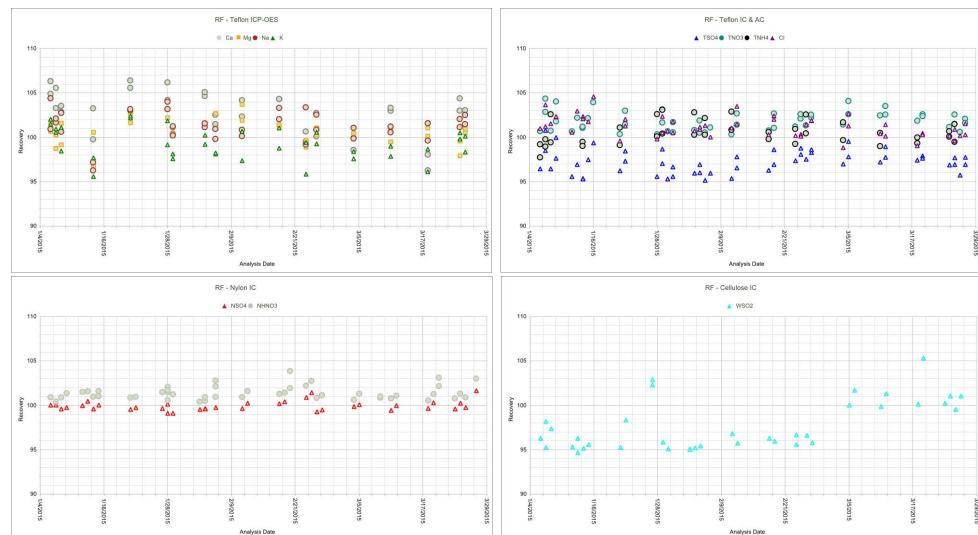
Table 11 Filter Packs Flagged as Suspect or Invalid during First Quarter 2015

Site ID	Sample No.	Reason
ALC188, TX	1502001-03	Potassium deemed suspect and flagged as invalid.
CAN407, UT	1505001-14	Insufficient flow volume
CDR119, WV	1503001-16	Concentration data deemed suspect and flagged as invalid.
CDZ171, KY	1507001-17	Insufficient flow volume
GRS420, TN	1502001-36	Concentration data deemed suspect and flagged as invalid.
KIC003, KS	1503001-44	Insufficient flow volume
LAV410, CA	1506001-46	Flow system malfunctioned
LRL117, PA	1502001-47	Concentration data deemed suspect and flagged as invalid for all
	1503001-47	three samples.
	1505001-47	

Table 12 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	230
60	8
90	3
Unresolved by End of Quarter	10

Figure 1 Reference Standard Results for First Quarter 2015 (percent recovery)



12

Figure 2 Continuing Calibration Spike Results for First Quarter 2015 (percent recovery)

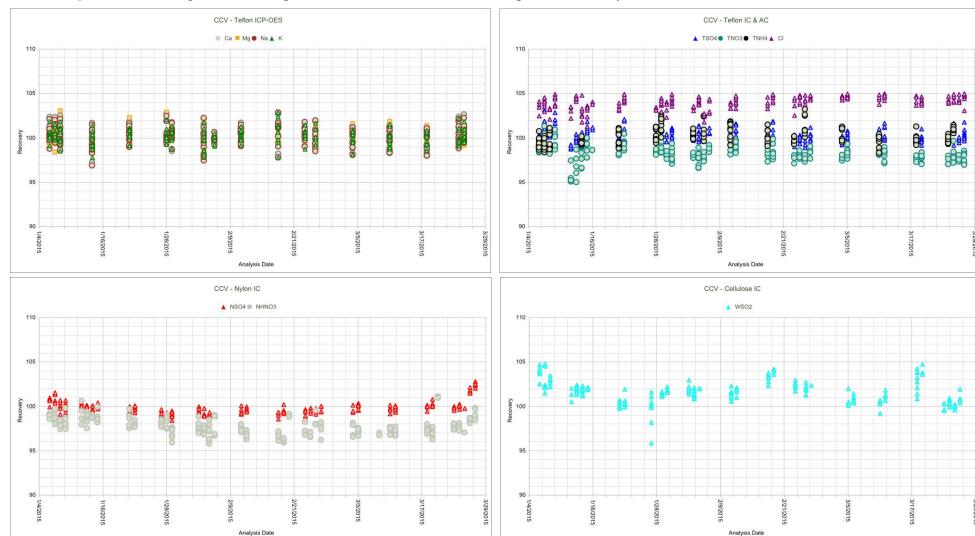


Figure 3 Replicate Sample Analysis Results for First Quarter 2015 (percent difference)

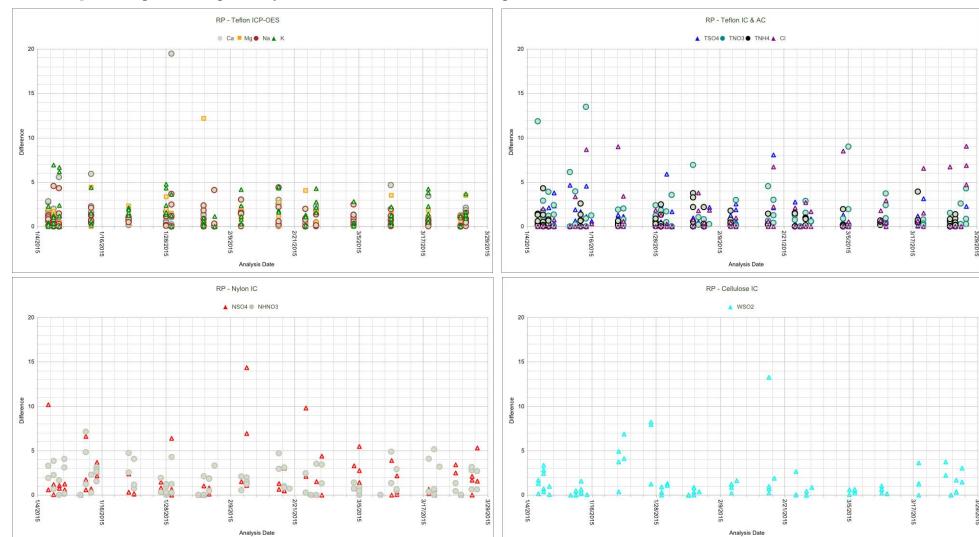


Figure 4 Laboratory Control Sample Results for First Quarter 2015 (percent recovery)

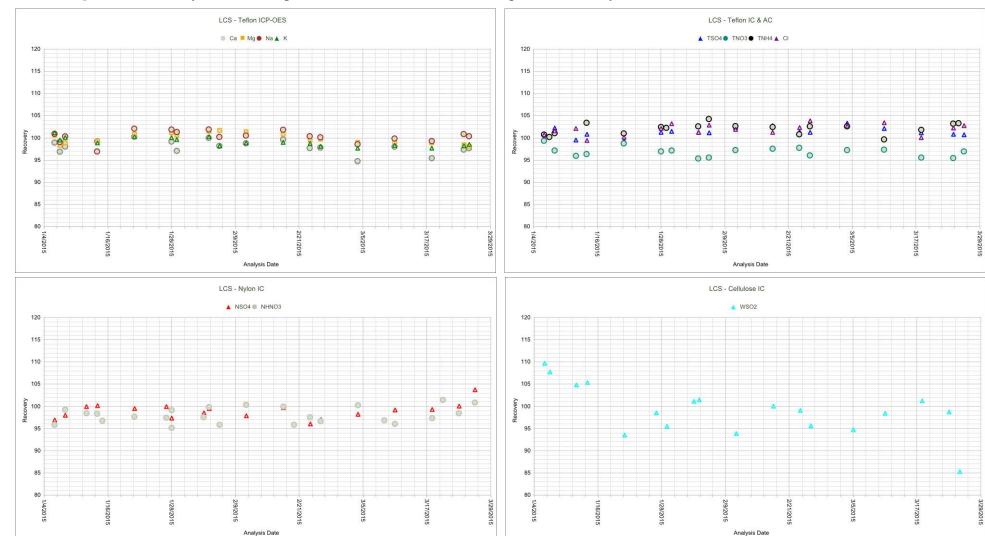
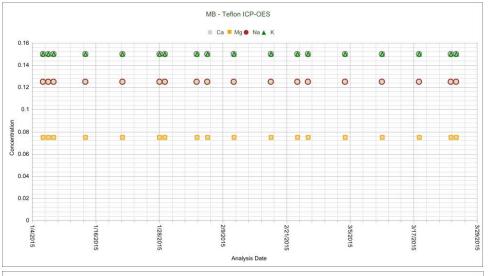
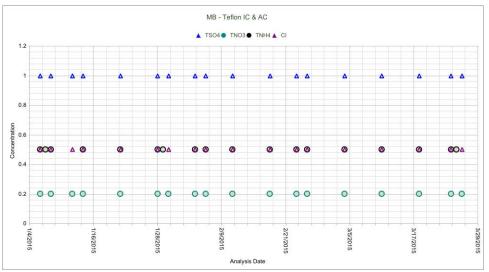
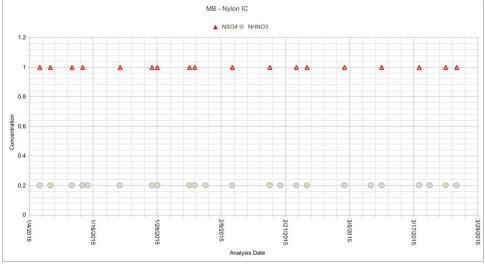


Figure 5 Method Blank Analysis Results for First Quarter 2015 (total micrograms)







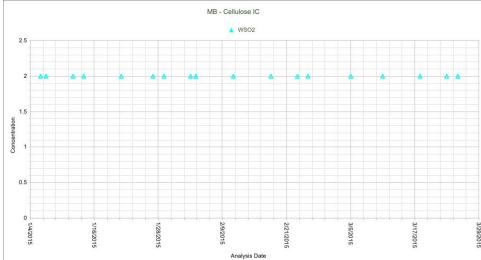
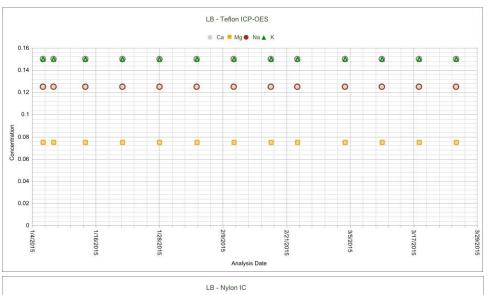
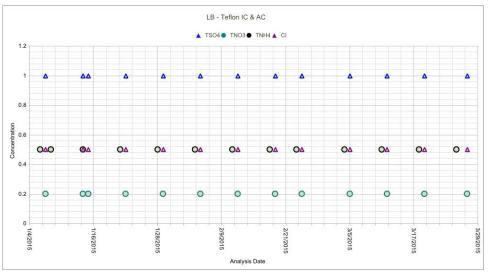
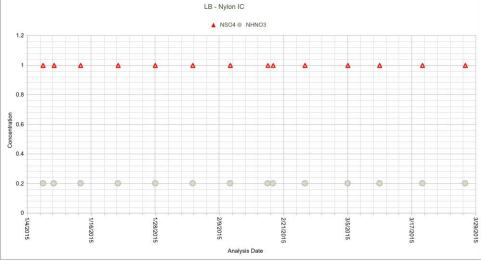


Figure 6 Laboratory Blank Analysis Results for First Quarter 2015 (total micrograms)







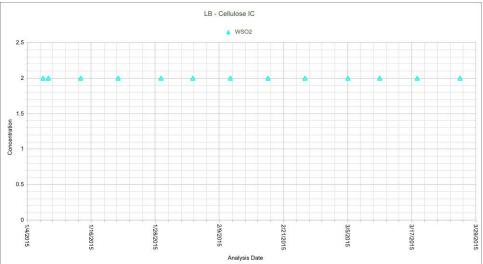


Figure 7 Field Blank Analysis Results for First Quarter 2015 (total micrograms)

