

**Summary of Quarterly Operations (July–September)** 

EPA Contract No. EP-W-09-028 AMEC Project No.: 6064130418

### 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 2013. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; AMEC, 2012). 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**

Comparison of trace-level gas concentrations with filter pack concentrations at the BEL116, MD and BVL130, IL sites have indicated that weekly average trace-level gas sulfur dioxide (SO<sub>2</sub>) concentrations from the Teledyne API (API) analyzer were lower than the corresponding filter pack concentrations. Comparison of trace-level gas concentrations with filter pack concentrations and concentrations from the Monitors for Aerosols and Gases in Ambient Air (MARGA), located at the BEL116, MD site, indicated that filter pack and MARGA concentrations were comparable. API has recommended using a single gas cylinder for routine QC and calibration checks. Per API, the blended gas cylinders currently used are the suspected cause of the lower concentrations measured by the API instrument by introducing an uncorrected positive interference from nitric oxide (NO) during instrument calibration. AMEC is purchasing a single gas cylinder for testing.

During third quarter 2013, AMEC continued working with API on the adaptive signal filtering of the API trace-level gas analyzers. A fast measurement response is needed for collecting QC data, but available options are not sufficient to engage this mode under current operational protocols. AMEC also continued working with API on other various problems encountered during operation of the API gas analyzers. An API technical specialist met with AMEC personnel in the Gainesville, FL office and again later at the BVL130, IL site so he could see the analyzers in situ and work with AMEC technicians on troubleshooting activities.

While the zero/precision/span quality control checks have remained within criteria, the API trace-level gas monitoring system at the BEL116, MD site has been only intermittently reporting an expected (i.e. "target") value. During second quarter, AMEC developed a new program to correct the problem. AMEC tested the new program before deploying it to the sites during third quarter.

During September 2013, AMEC received results from sample analyses for proficiency test (PT) study 102 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 tied with two other competing laboratories for first place. Results for AMEC showed no flags and no indication of bias. An "Ideal" rating was assigned to each parameter tested and submitted. AMEC's laboratory performance rating was "Very Good," the highest rating available. AMEC's 5-year historical average for Environment Canada PT studies is rated "Very Good," which shows AMEC's consistent performance for laboratory analyses.

AMEC conducted a safety audit of the IRL141, FL site during September 2013. The site operator was observed performing his routine duties. Documentation at the site was evaluated as was the site itself. There were no negative findings. One recommendation is to post a sign on the fence stating, "Only authorized personnel allowed," since the site is located near a public campground.

Table 1 lists the quarters of data that were validated to Level 3 during third quarter 2013 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 (EPA, 2010). Table 6 presents the critical criteria for AQS-protocol 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 7 presents the number of analyses in each category that were performed during third quarter 2013.

## **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 8 presents the relevant sample receipt statistics for third quarter 2013.

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

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for third quarter 2013. All results were within the criteria listed in Table 4.

Table 9 presents summary statistics of critical criteria measurements at AQS-protocol ozone sites collected during the quarter. All data associated with QC checks that failed to meet the criteria listed in Table 5 were or will be invalidated. Results in shaded cells either exceeded documented criteria or are otherwise notable. Table 10 presents observations associated with the shaded cell results in Table 9.

Table 11 presents summary statistics of critical criteria measurements collected during the quarter for the AQS-protocol trace-level gas monitoring sites. All data associated with QC checks that failed to meet the criteria listed in Table 6 were invalidated. Results in shaded cells either exceeded documented criteria or are otherwise notable. Table 12 presents observations associated with the shaded cell results in Table 11.

### **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 third quarter 2013. All recovery values were between 90 percent and 110 percent.

#### **Blank Results**

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for third quarter 2013. 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 third quarter 2013 are listed in Table 13. 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 for one or more of the measured parameters.

### **Field Problem Count**

Table 14 presents counts of field problems affecting continuous data collection for more than one day during third quarter 2013. 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). 2012. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 8.0.* 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). 2010. 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. 40 *CFR* Part 58.

Table 1 Data Validated to Level 3 during Third Quarter 2012

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10 <sup>†</sup>	November 2012 – April 2013	6	Quarter 1 2013	1
SE-4/MW-6 <sup>‡</sup>	January 2013 – June 2013	6	Quarter 1 2013 – Quarter 2 2013	2

Note: \* 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

Calibration Group	Months Calibrated		Sites Calibrated				
22004		Eastern Site					
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 S	Sites (10 Total)				
SE-4	January/July	SND152, AL	BFT142, NC	COW137, NC			
(6 Sites)		GAS153, GA	CND125, NC	PNF126, NC			
SE-5	February/August	CAD150, AR	IRL141, FL				
(4 Sites)		CVL151, MS	SUM156, FL				
		Midwestern S	ites (18 Total)				
MW-6	January/July	CDZ171, KY	MCK131, KY	ESP127, TN			
(6 Sites)		CKT136, KY	MCK231, KY	SPD111, TN			
MW-7	March/September	ALH157, IL	STK138, IL	DCP114, OH	QAK172, OH		
(8 Sites)		BVL130, IL	VIN140, IN	OXF122, OH	PRK134, WI		
MW-8	April/October	SAL133, IN	ANA115, MI				
(4 Sites)		HOX148, MI	UVL124, MI				
		Western Sit	tes (9 Total)				
W-9	March/September	KNZ184, KS	SAN189, NE				
(4 Sites)	_	CHE185, OK	ALC188, TX				
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 Continuous Measurements

Measu	rement	Criteria <sup>1</sup>			
Parameter <sup>2</sup>	Method	Precision	Accuracy		
Filter pack flow	Mass flow controller	± 10%	± 5%		
Ozone <sup>3</sup>	UV absorbance	All points within ± 2% of full scale of best f straight line			
		Linearity of	error < 5%		
Wind speed	Anemometer	± 0.5 m/s	The greater of $\pm$ 0.5 m/s for winds < 5 m/s or $\pm$ 5% for winds $\geq$ 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 <sup>4</sup>		
Solar radiation	Pyranometer	± 10% (of reading taken at local noon)	± 10%		
Surface wetness	Conductivity bridge	Undefined	Undefined		

Notes:  $^{\circ}C$  = 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. Collocated precision criteria do not apply to AQS-protocol ozone measurements.

<sup>&</sup>lt;sup>2</sup> As of the end of third quarter 2013, meteorological parameters were only measured at five of the EPA-sponsored CASTNET sites: PAL190, TX; CHE185, OK; BVL130, IL; BEL116, MD, and IRL141, FL.

<sup>&</sup>lt;sup>3</sup> Ozone is not measured at six EPA-sponsored CASTNET sites: EGB181, ON; CAT175, NY; NIC001, NY; WFM105, NY; UND002, VT; and KNZ184, KS.

<sup>&</sup>lt;sup>4</sup> For target value of 0.50 inch

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

		Dun atat au 1	A2	Nominal Reporting Limits	
Analyte	Method	Precision <sup>1</sup> (MARPD)	Accuracy <sup>2</sup> (%)	mg/L	μg/Filter
Ammonium (NH <sub>4</sub> <sup>+</sup> )	AC	20	90 - 110	0.020*	0.5
Sodium (Na <sup>+</sup> )	ICP-AES	20	95 - 105	0.005	0.125
Potassium (K <sup>+</sup> )	ICP-AES	20	95 - 105	0.006	0.15
Magnesium (Mg <sup>2+</sup> )	ICP-AES	20	95 - 105	0.003	0.075
Calcium (Ca <sup>2+</sup> )	ICP-AES	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-AES = inductively coupled plasma-atomic emission spectrometry

MARPD = mean absolute relative percent difference

 $\begin{array}{lll} mg/Liter & = milligrams \ per \ liter \\ \mu g/Filter & = micrograms \ per \ filter \\ * & = as \ nitrogen \end{array}$ 

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, Revision 8.0 (AMEC, 2012)

 Table 5
 AQS-Protocol Ozone Critical Criteria\*

Type of Check	Analyzer Response
Zero	Less than ± 10 parts per billion
Span	Less than or equal to $\pm$ 7 percent between supplied and observed concentrations
Single 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 (EPA, 2010). 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).

<sup>&</sup>lt;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.

**Table 6** AQS-Protocol Trace-level Gas Monitoring Critical Criteria\*

	Analyzer Response					
Parameter	Zero Check	Span Check	Single Point QC Check			
$SO_2$	Less than ± 3 parts per billion (ppb)	Less than or equal to ± 10 percent between supplied and observed concentrations	Less than or equal to $\pm$ 10 percent between supplied and observed concentrations			
NO <sub>y</sub>	Less than ± 3 ppb	Less than or equal to ± 10 percent between supplied and observed concentrations	Less than or equal to ± 10 percent between supplied and observed concentrations			
СО	Less than ± 40 ppb	Less than or equal to ± 10 percent between supplied and observed concentrations	Less than or equal to ± 10 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 (EPA, 2010). 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

Table 7 QC Analysis Count for Third Quarter 2013

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	$\mathrm{SO}_{\scriptscriptstyle{4}}^{\scriptscriptstyle{2-}}$	28	153	70	14	26	87
	$NO_3$	28	153	70	14	26	87
	$NH_4^+$	28	153	76	14	26	87
	Cl¯	28	153	70	14	26	87
	Ca <sup>2+</sup>	29	160	72	14	26	87
	$\mathrm{Mg}^{^{2+}}$	29	160	72	14	26	87
	Na <sup>+</sup>	29	160	72	14	26	87
	$\mathbf{K}^{\scriptscriptstyle{+}}$	29	160	72	14	26	87
Nylon	$\mathrm{SO}_{\scriptscriptstyle{4}}^{\scriptscriptstyle{2-}}$	33	169	76	16	26	87
	$NO_3$	33	169	76	16	26	87
Cellulose	SO <sub>4</sub> <sup>2-</sup>	40	195	85	20	26	87

Table 8 Filter Pack Receipt Summary for Third Quarter 2013

Count of samples received more than 14 days after removal from tower:	12
Count of all samples received:	857
Fraction of samples received within 14 days:	0.986
Average interval in days:	3.927
First receipt date:	07/01/2013
Last receipt date:	09/30/2013

Table 9 AQS-Protocol Ozone QC Summary (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	100.0	0.4	100.0	0.7	0.1	100.0	2.4
ALC188, TX	93.3	4.2	67.3	8.8	2.8	75.0	9.0
ALH157, IL	100.0	1.3	100.0	1.2	0.1	100.0	1.4
ANA115, MI	100.0	0.9	100.0	1.1	0.2	96.6	1.6
ARE128, PA	100.0	1.1	100.0	1.1	0.1	97.8	3.5
ASH135, ME	98.9	1.1	91.2	2.1	0.4	94.5	3.7
BEL116, MD	100.0	1.0	97.8	1.0	0.3	94.4	4.1
BFT142, NC	99.0	1.2	92.9	2.1	0.5	97.0	2.8
BVL130, IL	100.0	1.0	97.9	2.2	0.2	96.8	3.5
BWR139, MD	100.0	1.4	98.8	1.7	0.3	95.4	2.1
CAD150, AR	99.0	2.8	90.2	5.0	1.5	80.6	4.9
CDR119, WV	98.9	2.2	98.9	2.4	0.3	100.0	1.0
CDZ171, KY	98.9	1.8	92.5	2.9	1.3	93.7	3.2
CKT136, KY	100.0	1.2	100.0	1.4	0.1	100.0	0.9
CND125, NC	100.0	0.4	100.0	1.0	0.1	92.9	2.6
CNT169, WY	100.0	1.6	98.9	1.8	0.3	100.0	0.8
COW137, NC	100.0	0.7	100.0	0.8	0.2	100.0	1.6
CTH110, NY	100.0	1.9	100.0	1.2	0.1	100.0	0.9
CVL151, MS	100.0	0.8	100.0	0.7	0.1	100.0	1.2
DCP114, OH	100.0	0.7	100.0	0.7	0.1	98.8	1.6
ESP127, TN	100.0	0.7	99.0	0.6	0.4	95.7	2.1
GAS153, GA	96.7	3.8	95.6	3.1	1.6	92.2	5.4
GTH161, CO	100.0	2.5	100.0	2.5	0.1	100.0	0.2
HOX148, MI	100.0	0.6	100.0	0.5	0.1	97.9	1.7

Table 9 AQS-Protocol Ozone QC Summary (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	100.0	2.2	74.3	6.4	0.6	63.4	6.1
IRL141, FL	100.0	1.9	92.9	3.0	0.5	94.8	3.9
KEF112, PA	100.0	0.6	100.0	0.8	0.1	98.8	0.7
LRL117, PA	100.0	1.4	100.0	1.1	0.1	100.0	0.5
MCK131, KY	98.9	2.0	97.9	2.0	0.3	95.8	2.4
MCK231, KY	100.0	1.7	100.0	1.7	0.2	95.9	2.4
MKG113, PA	100.0	1.1	97.9	2.5	1.7	98.9	1.2
OXF122, OH	97.8	3.0	95.7	3.0	1.9	96.7	1.3
PAL190, TX	100.0	1.3	100.0	1.8	0.2	100.0	1.9
PAR107, WV	100.0	0.3	100.0	0.6	0.1	100.0	0.7
PED108, VA	89.9	11.3	88.9	10.9	4.7	94.9	2.0
PND165, WY	100.0	0.7	100.0	0.8	0.1	100.0	2.8
PNF126, NC	100.0	0.6	100.0	0.9	0.2	100.0	0.7
PRK134, WI	100.0	1.2	100.0	1.2	0.2	100.0	1.4
PSU106, PA	100.0	1.1	100.0	1.1	0.1	100.0	0.4
QAK172, OH	100.0	0.5	99.0	0.8	0.1	99.0	0.8
ROM206, CO	100.0	1.0	100.0	1.6	0.1	100.0	0.3
SAL133, IN	100.0	0.9	100.0	1.1	0.2	97.8	1.6
SAN189, NE	100.0	0.3	100.0	0.5	0.1	100.0	0.4
SND152, AL	100.0	1.0	100.0	1.4	0.1	100.0	1.3
SPD111, TN	99.0	1.4	96.9	1.4	0.3	92.9	2.1
STK138, IL	100.0	1.2	100.0	1.5	0.1	100.0	1.0
SUM156, FL	98.9	2.7	82.2	4.1	0.4	95.6	3.5
UVL124, MI	100.0	1.2	100.0	1.0	0.1	100.0	0.4
VIN140, IN	95.7	1.6	95.7	1.5	0.3	100.0	0.6
VPI120, VA	100.0	1.6	100.0	1.0	0.1	100.0	0.4
WSP144, NJ	100.0	1.7	96.8	1.8	0.3	100.0	0.6
WST109, NH	100.0	0.6	100.0	0.7	0.1	98.9	1.9

Notes: 1 Percentage of comparisons that pass the criteria listed in Table 5. Values falling below 90 percent are addressed in Table 10.

%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 5 are addressed in Table 10.

<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 10.

Table 10 AQS-Protocol Ozone QC Observations

Site ID	QC Criterion	Comments
ALC188, TX	% Single Point QC Pass Single Point QC  %D  % Zero Pass	The causes of the failures were not determined. The site analyzer was replaced. Data associated with the failures were invalidated.
CAD150, AR	% Zero Pass	The causes of the failures were not determined. Data associated with the failures were invalidated through August. Associated September data will be invalidated during routine validation procedures. All data reported to the EPA Air Quality System (AQS) at the time of this report were invalidated prior to submission. September data were not reported to AQS at the time of this report.
HWF187, NY	% Single Point QC Pass % Zero Pass	The causes of the failures were not determined. Data associated with the failures were invalidated through August. Associated September data will be invalidated during routine validation procedures. All data reported to AQS at the time of this report were invalidated prior to submission. September data were not reported to AQS at the time of this report.
PED108, VA	Span  %D   % Single Point QC Pass Single Point QC  %D	Failures occurred for approximately one week in September due to improperly connected sample lines. Associated September data will be invalidated during routine validation procedures. September data were not reported to AQS at the time of this report.
SUM156, FL	% Single Point QC Pass	The causes of the failures were not determined. Data associated with the failures were invalidated through August. Associated September data will be invalidated during routine validation procedures. All data reported to AQS at the time of this report were invalidated prior to submission. September data were not reported to AQS at the time of this report.

Notes: %D = percent difference CL = confidence limit

Table 11 AQS-Protocol Trace-level Gas QC Summary

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			
$SO_2$	92.3	10.1	94.7	9.1	7.4	94.9	0.6
$NO_y$	84.3	5.5	82.0	17.9	7.4	82.7	3.4
			BVL13	0, IL			
$SO_2$	88.0	12.2	95.8	5.8	5.3	94.0	1.0
$NO_y$	97.4	5.1	94.7	3.4	0.8	94.7	2.2
CO	100.0	1.6	67.3	10.1	2.5	89.8	16.5
			HWF18	7, NY			
$NO_y$	100.0	2.7	100.0	1.5	0.3	100.0	0.6
	PND165, WY						
$NO_y$	97.3	5.2	91.9	5.6	1.0	100.0	0.4

Notes: 1 Percentage of comparisons that pass the criteria listed in Table 6. Values falling below 90 percent are addressed in Table 12.

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

Table 12 AQS-Protocol Trace-level Gas QC Observations

Site ID	Parameter	QC Criterion	Comments
BEL116, MD	NO <sub>y</sub>	% Span Pass	Three weeks of data were invalidated in July
		% Single Point QC Pass	due to analyzer malfunction. The analyzer was
		Single Point QC  %D	replaced in late July.
		% Zero Pass	
BVL130, IL	$SO_2$	% Span Pass	Analyzer pre-amp board required resetting.
		Span  %D	Associated data were invalidated.
	CO	% Single Point QC Pass	Baseline was elevated after a power failure.
			Associated data were invalidated. An
			uninterruptable power supply has been added to
			the system as a corrective/preventive action.

<sup>&</sup>lt;sup>2</sup> Absolute value of the average percent differences between the supplied and observed concentrations. Values exceeding the criteria listed in Table 6 are addressed in Table 12.

<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. Values exceeding this criterion are addressed in Table 12.

Table 13 Filter Packs Flagged as Suspect or Invalid

Site ID	Sample No.	Reason
ACA416, ME	1330001-02	Invalidation of suspect potassium data
ANA115, MI	1329001-05	Insufficient valid flow volume
BAS601, WY	1333001-08*	Data transfer problems
BEL116, MD	1328001-10	Insufficient valid flow volume
	1330001-10	
	1333001-10	
BUF603, WY	1333003-01*	Data transfer problems
CHA467, AZ	1328001-19*	Data transfer problems
EGB181, ON	1328001-29	Insufficient flow volume
FOR605, WY	1327003-02	Equipment problems resulted in
	1328003-02	invalidation due to suspect flow data.
	1329003-02	
	1330003-02	
	1331003-02	
GRC474, AZ	1331001-35*	Data transfer problems
MOR409, WA	1328001-53*	Data transfer problems
NEC602, WY	1333001-54*	Data transfer problems
SHE604, WY	1331003-03*	Data transfer problems

Notes:  $^*$  Data may be recovered during Level 3 validation review.

 Table 14 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	176
60	24
90	10
Unresolved by End of Quarter	9

RF - Teflon ICP-AES Ca o Na × K 110.0 107.5 105.0 102.5 100.0 97.5 92.5 Analysis Date RF - Teflon IC & AC INO3 CI 110.0 107.5 105.0 102.5 0 97.5 × × 90.0 8/14/2013 8/21/2013 9/11/2013 RF - Nylon IC NHNO3 110.0 107.5 105.0 О 97.5 92.5 90.0 8/1/2013 9/11/2013 7/24/2013 Analysis Date RF - Cellulose IC 110.0 107.5 102.5 100.0 97.5 95.0 92.5 90.0 7/18/2013 8/1/2013 9/5/2013 8/14/2013 9/19/2013 9/25/2013

Figure 1 Reference Standard Results for Third Quarter 2013 (percent recovery)

110.0 107.5 95.0 92.5 90.0 CCV - Teflon IC & AC 105.0 102.5 100.0 97.5 95.0 92.5 90.0 CCV - Nylon IC 110.0 107.5 105.0 102.5 100.0 97.5 95.0 92.5 - 7/1 2/2013 - 8/1/2013 7/8/2013 Analysis Date CCV - Cellulose IC 110.0 107.5 105.0 102.5 100.0 97.5 95.0 92.5 8/14/2013 9/11/2013 9/21/2013 Analysis Date

Figure 2 Continuing Calibration Spike Results for Third Quarter 2013 (percent recovery)

□• Na 20.0 17.5 Difference 10.0 7.5 5.0 2.5 0.0 RP - Teflon IC & AC 20.0 15.0 12.5 10.0 7.5 О 5.0 2.5 7/17/2013 RP - Nylon IC NHNO3 20.0 17.5 15.0 12.5 10.0 7.5 5.0 8/1/2013 8/8/2013 8/21/2013 9/19/2013 1/12/2013 Analysis Date RP - Cellulose IC 20.0 17.5 15.0 12.5 10.0 Dillerence 7.5 7.5 × × - 8/21/2013 Analysis Date 8/13/2013 9/17/2013 9/19/2013 7/18/2013 9/25/2013

Figure 3 Replicate Sample Analysis Results for Third Quarter 2013 (percent difference)

LCS - Teflon ICP-AES ▲ Mg 120 115 110 105 100 90 80 7/1/2013 Analysis Date LCS - Teflon IC & AC ○ТNО3 120 115 110 105 100 0 0 0 95 90 85 7/1/2013 LCS - Nylon IC ×NSO4 O NHNO3 120 115 105 100 95 0 0 90 85 80 7/1/2013 7/29/2013 Analysis Date LCS - Cellulose IC 120 115 110 105  $\times_{\mathsf{X}}$ ×× × × 100 95 90 85 80 9/9/2013 8/12/2013 7/1/2013 Analysis Date

Figure 4 Laboratory Control Sample Results for Third Quarter 2013 (percent recovery)

0.14 0.13 0.12 Oucentration 0.10 0.09 0.08 -7/31/2013 -7/11/2013 7/8/2013 MB - Teflon IC & AC 1.0 0.9 0.7 0.6 0.5 0.4 0.3 MB - Nylon IC 0.6 0.5 0.4 0.3 9/9/2013 8/6/2013 7/11/2013 MB - Cellulose IC 2.20 2.15 2.10 2.05 Concentration 2.00 1.90 1.85 - 8/14/2013 - 8/12/2013 Analysis Date -8/21/2013 9/11/2013 9/17/2013 9/18/2013 7/18/2013 7/31/2013 9/20/2013

Figure 5 Method Blank Analysis Results for Third Quarter 2013 (total micrograms)

0.15 0.14 0.13 0.12 0.11 0.10 0.09 0.08 -8/7/2013 7/24/2013 8/21/2013 Analysis Date

LB - Teflon IC & AC 1.0 0.9 0.7 0.6 0.5 0.4 LB - Nylon IC 0.9 0.6 0.5 0.4 0.3 - 8/21/2013 LB - Cellulose IC 2.50 2.45 2.40 2.35 2.30 220 2.15 2.10 2.05 2.00 Analysis Date

Figure 6 Laboratory Blank Analysis Results for Third Quarter 2013 (total micrograms)

Figure 7 Field Blank Analysis Results for Third Quarter 2013 (total micrograms)

