

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 2011. The results presented for filter pack data collection and field calibrations are generated from data extracted from the CASTNET Data Management Center (DMC) database using the CASTNET Data Management System Application (CDMSA). The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP). The QAPP is comprehensive and includes standards and policies for all components of project operation from site selection through final data reporting. It is reviewed annually and updated as warranted.

MACTEC is continuing to investigate the cause of occasional low-level potassium contamination on the Teflon filters. New procedures were implemented for coding wet filters returning from the field. Now, exposed filters are coded as being wet if even slightly wet since potassium from impregnated cellulose filters can migrate when the filters are wet. The desiccation procedure for preparation of impregnated cellulose filters was investigated and found to be producing sufficiently dry batches of impregnated filters with sufficiently uniform results regardless of the filter's location within the desiccator.

The CASTNET QAPP Revision 7.0 was approved by EPA during February 2011.

During March 2011, MACTEC received final results and rankings for proficiency test (PT) study 0097 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 QA services. MACTEC tied for first place out of the 33 competing laboratories. Results for MACTEC showed no flags and no indication of bias. All parameters tested were appraised as "ideal." MACTEC's laboratory was rated, "Good," the highest rating available. MACTEC's

5-year historical average for Environment Canada PT studies is rated "Good," which shows MACTEC's consistent performance for laboratory analyses.

Collocated filter pack precision data and completeness data for continuous field 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 first quarter 2011 by the data operations group. Table 2 lists the sites in each calibration group along with the calibration schedule.

As of January 2011, meteorological parameters were measured at only four of the EPA-sponsored CASTNET sites: PAL190, TX; CHE185, OK; BVL130, IL; and BEL116, MD. Data for meteorological parameters collected prior to January 2011 were validated to Level 3 during the quarter; therefore, completeness data are presented as in previous reports. Beginning with the third quarter 2011 report, continuous measurements validated to Level 3 will exclusively consist of ozone and flow rate with the exception of the four sites listed previously. To ensure clarity, the presentation of summary data will change from that report forward.

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 Air Quality System (AQS) criteria for QA/QC procedures and are operated in accordance with Part 58 of Title 40 of the Code of Federal Regulations (40CFR).

# **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 2011.

# **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 2011.

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

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for first quarter 2011. All results were within the criteria listed in Table 4 with the exception of one Teflon filter RP result. The QC criterion for in-run precision is 20 percent. However, since the measured concentration of this sample was between 2 and 3 times the analyte reporting limit, this result is considered reasonable since higher relative percent differences generally correlate with lower sample concentrations.

Figure 4 presents completeness statistics for continuous measurements validated to Level 3 during the quarter. All parameters met the 90 percent criterion.

Table 8 presents summary statistics of critical criteria measurements at AQS-protocol ozone sites validated during the quarter. All data associated with failure to meet the criteria listed in Table 5 were invalidated. The QC results at BFT142, NC were affected by problems with the zero air system that lasted for several days. Five days of the KNZ184, KS results were affected by a program error that resulted in erroneous lamp drive settings for the on-site transfer standard. Ice in the calibration line at ROM206, CO affected QC results from late December 2010 through early January 2011. Finally, QC results at SUM156, FL were affected by failure of the site analyzer's pressure transducer, which was repaired within 12 days.

# **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 5 presents LCS analysis results for first quarter 2011.

#### **Blank Results**

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for first quarter 2011. All results were within criteria (two times the reporting limit) listed in Table 4 with the exception of two Teflon filter FB results. All values were less than three times the reporting limit. No systemic problems were indicated upon review.

# Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during first quarter 2011 are listed in Table 9. This table includes associated site identification and a brief description of the reason the sample was flagged. During first quarter, twenty-one filter pack samples were invalidated due to data polling problems or insufficient flow volume. The data logger and data importer software

were updated at several sites during the quarter resulting in the polling program failing to import data until sites were properly recognized in the system. Data were stored on-site in the data logger. Several of the noted samples should be recovered during Level 3 data validation.

### **Field Problem Count**

Table 10 presents counts of field problems affecting continuous data collection for more than one day during first quarter 2011. 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 25 sites during first quarter 2011. All sites and parameters were within the criteria listed in Table 3.

# **Tables and Figures**

Table 1. Data Validated to Level 3 during First Quarter 2011

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-2/MW-8	April 2010 – September 2010	6	Quarter 2 2010 – Quarter 3 2010	2
E-3/W-10 <sup>‡</sup>	May 2010 – October 2010	6	Quarter 3 2010	1
SE-4/MW-6 <sup>†</sup>	July 2010 – December 2010	6	Quarter 3 2010 – Quarter 4 2010	2

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

Table 2. Field Calibration Schedule

Calibration	Months		Sit	tes		
Group	Calibrated	Calibrated				
		Eastern Site	es (20 Total)			
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	HOW132, ME	CAT175, NY	EGB181 ON	
(7 Sites)	_	WST109, NH	ASH135, ME	HWF187, NY		
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 Sites (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

<sup>‡</sup> Contains ROM206 of the ROM406/ROM206 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	± 10% (of reading)	± 10%	
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: °C = degrees Celsius m/s = meters per second

RTD = resistance-temperature device

UV = ultraviolet

<sup>&</sup>lt;sup>1</sup> Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments.

<sup>&</sup>lt;sup>2</sup> 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.

 $<sup>^{\</sup>rm 3}$  Ozone is not measured at two EPA-sponsored CASTNET sites: EGB181, ON and CAT175, NY.

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

**Table 4.** 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-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: 1 This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on

= automated colorimetry

ICP-AES = inductively coupled plasma-atomic emission spectrometry

= ion chromatography

MARPD = mean absolute relative percent difference

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP Revision 7.0 (MACTEC, 2011).

Table 5. AQS-Protocol Ozone Critical Criteria\*

Type of Check	Analyzer Response			
Zero	Less than $\pm$ 10 parts per billion (ppb)			
Span	Less than or equal to $\pm$ 7 percent between supplied and observed concentrations			
One Point QC	Less than or equal to $\pm$ 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

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-AES reference standards.

Table 6. QC Analysis Count for First Quarter 2011

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	$SO_4^{2-}$	32	169	80	16	28	83
	$NO_3$	32	169	80	16	30	83
	$\mathrm{NH}_{\scriptscriptstyle{4}}^{\scriptscriptstyle{+}}$	34	181	86	17	30	120
	Cl	32	169	78	16	28	83
	$\operatorname{Ca}^{^{2+}}$	34	180	83	17	30	120
	$\mathrm{Mg}^{^{2+}}$	34	180	83	17	30	120
	$\mathbf{Na}^{\scriptscriptstyle +}$	34	180	83	17	30	120
	$\mathbf{K}^{\scriptscriptstyle +}$	34	180	83	17	30	120
Nylon	$\mathrm{SO}_{\scriptscriptstyle{4}}^{\scriptscriptstyle{2-}}$	32	165	81	16	26	81
	$NO_3$	32	165	81	16	26	81
Cellulose	SO <sub>4</sub> <sup>2-</sup>	44	176	88	22	28	95

Table 7. Filter Pack Receipt Summary for First Quarter 2011

Count of samples received more than 14 days after removal from tower:	3
Count of all samples received:	597
Fraction of samples received within 14 days:	0.995
Average interval in days:	4.54
First receipt date:	01/03/2011
Last receipt date:	03/28/2011

Table 8. AQS-Protocol Ozone QC Summary

Site ID	% Span Pass <sup>1</sup>	<b>Span</b>  % <b>D</b>   <sup>2</sup>	% One Point QC Pass	One Point QC  %D	One Point QC CL <sup>3</sup>	% Zero Pass	Zero Average (ppb)
ARE128, PA	100.00	0.75	100.00	1.44	0.22	99.25	1.57
BFT142, NC	82.76	13.93	80.14	13.67	9.85	97.26	1.71
BWR139, MD	100.00	0.41	96.08	1.23	1.56	100.00	0.63
CAD150, AR	100.00	1.08	98.67	0.95	0.46	100.00	1.59
CND125, NC	91.03	3.15	91.08	3.19	0.57	99.36	1.29
COW137, NC	100.00	1.44	98.68	2.52	1.19	100.00	0.49
CTH110, NY	98.00	3.19	98.01	2.57	1.07	97.39	1.44
CVL151, MS	98.68	1.02	98.04	1.29	1.19	99.34	0.87
GAS153, GA	98.67	2.60	96.69	2.40	1.86	98.01	1.05
IRL141, FL	90.11	3.47	92.31	3.27	0.99	99.45	0.66
KNZ184, KS	96.10	55.62	94.81	4.92	2.32	100.00	0.84
PED108, VA	100.00	0.73	98.01	1.19	1.20	100.00	1.35
PNF126, NC	100.00	0.58	98.71	1.35	1.06	100.00	0.67
QAK172, OH	98.69	0.94	98.04	0.99	0.81	100.00	0.98
ROM206, CO	83.22	13.63	80.54	9.68	1.97	82.17	8.06
SAN189, NE	99.35	3.35	98.08	2.27	1.28	99.36	0.54
SND152, AL	98.70	1.95	99.35	2.65	1.86	100.00	0.73
SUM156, FL	92.31	50.50	90.45	50.22	19.58	99.36	0.86
WSP144, NJ	100.00	2.63	98.69	3.38	1.48	100.00	0.43

**Notes:** <sup>1</sup> Percentage of span comparisons that pass the 7% criterion.

%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

<sup>&</sup>lt;sup>3</sup> 90% confidence limit of the coefficient of variation. This should be less than or equal to the 7% one point QC check critical criterion.

Table 9. Filter Packs Flagged as Suspect or Invalid

Site ID	Sample	Reason
ALC188, TX	1106001-03	Polling problems
ARE128, PA	1104001-06	Polling problems
	1105001-06	Polling problems
BEL116, MD	1104001-09	Power outage
	1108001-09	Polling problems
CAD150, AR	1107001-13	Polling problems
CNT169, WY	1106001-22	Polling problems
CVL151, MS	1107001-25	Polling problems
EGB181, ON	1109001-28	Polling problems
ESP127, TN	1104001-29	Polling problems
GLR468, MT	1106001-32	Insufficient flow
JOT403, CA	1108001-41	Insufficient flow
OXF122, OH	1105001-52	Polling problems
	1106001-52	Polling problems
QAK172, OH	1105001-62	Polling problems
SHN418, VA	1104001-68	Insufficient flow
STK138, IL	1105001-71	Data logger power problems
VPI120, VA	1109001-77	Polling problems
WNC429, SD	1105001-78	Insufficient flow
	1108001-78	Insufficient flow
	1110001-78	Insufficient flow

Table 10. Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	97
60	7
90	0
Unresolved by End of Quarter	10

Table 11. Field Calibration Failures by Parameter

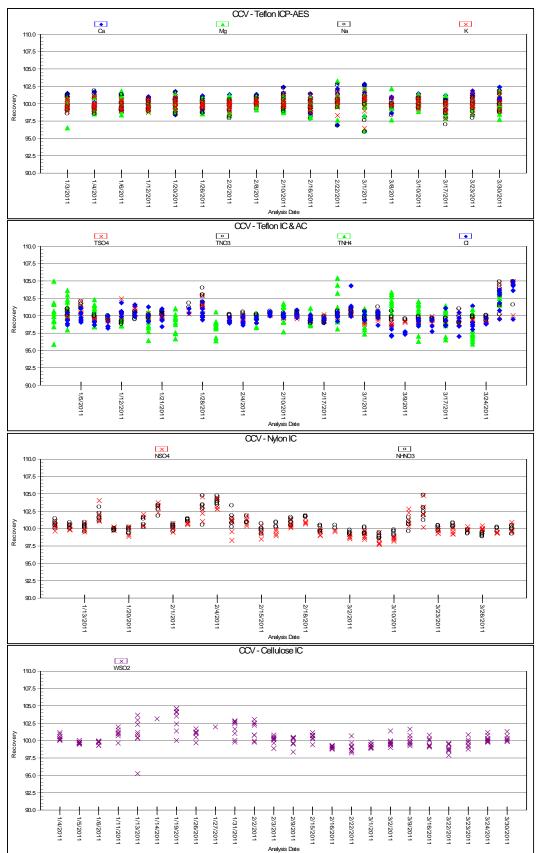
Site ID	Site ID Parameter(s)		
There wer	re no calibration failures during first quarter 2011.		

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 7.0 (MACTEC, 2011).

RF-Teflon ICP-AES o Na × K Ca 110.0 107.5 RF-Teflon IC & AC 110.0 107.5 105.0 102.5 100.0 1/21/2011 RF- Nylon IC 110.0 107.5 105.0 102.5 100.0 97.5 95.0 92.5 90.0 -3/2/2011 3/23/2011 RF - Cellulose IC 110.0 107.5 97.5 92.5 90.0 - 2/3/2011

Figure 1. Reference Standard Results for First Quarter 2011 (percent recovery)

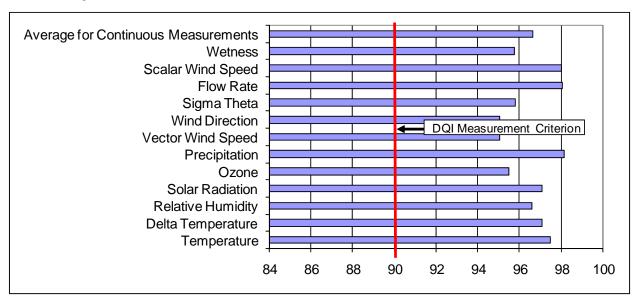
Figure 2. Continuing Calibration Spike Results for First Quarter 2011 (percent recovery)



Ca o Na × K 22.5 20.0 17.5 12.5 10.0 7.5 5.0 2.5 0.0 RP-Teflon IC&AC TNO3 a a 25.0 12.5 10.0 7.5 5.0 2.5 1/21/2011 3/9/2011 RP - Nylon IC 25.0 22.5 20.0 Difference 12.5 10.0 7.5 5.0 -3/23/2011 1/20/2011 22.5 20.0 12.5 10.0 7.5 5.0 2.5 0.0

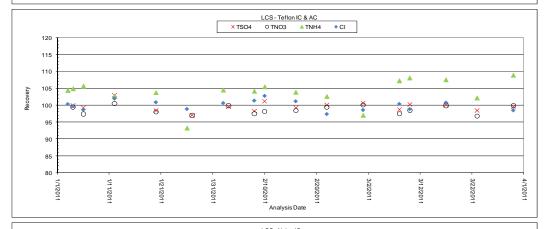
Figure 3. Replicate Sample Analysis Results for First Quarter 2011 (total micrograms)

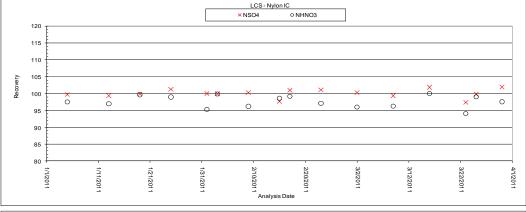
**Figure 4.** Percent Completeness of Measurements for Second Quarter 2010 through Fourth Quarter 2010\*

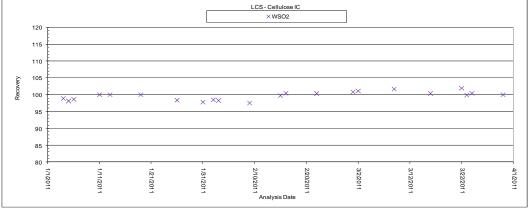


Note: \*Presents Level 3 data available during the first quarter of 2011.

Figure 5. Laboratory Control Sample Results for First Quarter 2011 (percent recovery)







Mg o Na Ca <u>들</u> 0.12 0.11 0 0 0.10 0.09 0.08 MB-Teflon IC&AC TSO4 1.0 0.9 0.7 0.6 0.5 0.4 0.3 1.0 0.6 0.5 0.4 0.2 MB - Cellulose IC 2.15 2.05 1.95 1.90 1.85

Figure 6. Method Blank Analysis Results for First Quarter 2011 (total micrograms)

0.14 0 들 0.12 0.11 0.10 0.09 0.08 LB-Teflon IC&AC 0.9 0.6 0.5 0.4 0.3 3/30/201 LB - Nylon IC 1.0 0.6 0.5 0.4 0.3 0.2 2.20 2.10 200 1.95 1.90 1.80

Figure 7. Laboratory Blank Analysis Results for First Quarter 2011 (total micrograms)

Figure 8. Field Blank Analysis Results for First Quarter 2011 (total micrograms)

