

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 2010. The results presented for filter pack data collection and field calibrations are generated from data extracted from the CASTNET Data Management Center database using the CASTNET Data Management System Application. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP). The QAPP is comprehensive and includes standards and policies for all components of project operation from site selection through final data reporting. It is reviewed annually and updated as warranted.

During January 2010, EPA met with MACTEC in Gainesville, FL for a CASTNET technical meeting. During the meeting, updating of the CASTNET QAPP and related standard operating procedures (SOPs) was discussed. During March 2010, MACTEC prepared and submitted samples of the new SOP format, applying it to field, laboratory, and data SOPs. EPA approved the proposed changes, which include flow charts, photographs, and illustrations along with rewritten text to better explain the steps required.

Restrictions on the availability of auditor findings and comments were lifted by EPA. During the CASTNET III contract, only audit findings of unsafe conditions were immediately released to the contractor operating the site (i.e., MACTEC or Air Resource Specialists, Inc.). Review of audit report findings was restricted to the QA Manager until after the site's subsequent calibration. As of March 2010, spot reports and audit findings for EPA-sponsored sites will be disseminated to MACTEC as soon as they are available.

Collocated filter pack precision data and completeness data for meteorological measurements are presented for data validated to Level 3 during the quarter. Table 1 lists the quarters of data that

were validated to Level 3 during first quarter 2010 by site calibration group. Table 2 lists the sites in each calibration group along with the calibration schedule.

Table 3 presents the measurement criteria for continuous field measurements. These criteria apply to the instrument challenges performed during site calibrations. Table 4 presents the measurement criteria for laboratory filter pack measurements. These criteria apply to the QC samples listed in the following section of this report.

Quality Control Analysis Count

The QC sample statistics presented in this report are for reference standards (RF) and continuing calibration verification spikes (CCV) used to assess accuracy and for replicate sample analyses (RP) used to assess "in-run" precision. In addition, laboratory method blanks (MB) containing reagents without a filter; laboratory blanks (LB) containing reagents and a new, unexposed filter; and field blanks (FB) containing reagents and an unexposed filter that was loaded into a filter pack assembly and shipped to and from the monitoring site while remaining in sealed packaging are also included. Table 5 presents the number of analyses in each category that were performed during first quarter 2010.

Sample Receipt Statistics

EPA requires that 95 percent of field samples from EPA-sponsored sites be received by the CASTNET laboratory in Gainesville, FL no later than 14 days after removal from the sampling tower. Table 6 presents the relevant sample receipt statistics for first quarter 2010.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for first quarter 2010. All results were within the criteria listed in Table 4. Average recoveries for chloride reference samples rose by one percent in March 2010. MACTEC will monitor recoveries for trending and take corrective action if necessary.

Figure 4 presents completeness statistics for continuous measurements validated to Level 3 during the quarter. All parameters met the 90 percent criterion. Completeness values for wind direction parameters are in the low 90 percent range due to calibration failures at three sites and invalidation of suspect data at a fourth.

Laboratory Control Sample Analysis

The laboratory control sample (LCS) is a reagent blank spiked with the target analytes from the established analytical methods and carried through the same extraction process that field samples must undergo. The LCS is not required by the CASTNET QA/QC program. LCS analyses are performed by the laboratory to monitor for potential sample handling artifacts and provide a means to identify possible analyte loss from extraction to extraction. The current action limits for

LCS recovery are 80 percent and 120 percent. These limits may change as data are collected and analyzed. Figure 5 presents LCS analysis results for first quarter 2010. All recovery values were between 90 percent and 110 percent.

Blank Results

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for first quarter 2010. All results were within criteria (2 times the reporting limit) listed in Table 4 with the exception of one LB and several FB results. One Teflon filter LB showed a response for potassium at approximately 4 times the reporting limit (RL). All QC analyses associated with this batch, including an additional LB, were well within criteria. There were three Teflon filter FB samples showing potassium values at approximately 3 to 5 times RL and five nylon FB samples with sulfate values between 2 and 6 times RL. Other QC blanks in the data batches associated with these samples were within their established criteria, as were the RF, RP and CCV samples. Filter media acceptance tests were also within criteria. Additionally, the laboratory routinely analyses the solutions used to extract filter media. No responses were detected during these tests. While no systemic problems were indicated upon review, these results are unusual. FB samples were re-analyzed and reported results confirmed. Further testing will be performed until appropriate corrective action is determined.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during first quarter 2010 are listed in Table 7. This table includes associated site identification and a brief description of the reason the sample was flagged. During first quarter, 14 filter pack samples were invalidated.

Field Problem Count

Table 8 presents counts of field problems affecting continuous data collection for more than one day during first quarter 2010. The problem counts are sorted by a 30-, 60-, or 90- day time period to resolution. A category for unresolved problems is also included. Time to resolution indicates the period taken to implement corrective action. The time period does not correlate with the quantity of data affected. For example, if a 5-hour block of missing data takes 60 days to replace, it will show up in the 60-day category. By the same token, a site missing 200 hours of data due to the damage caused by a lightning strike will show up in the 30-day category if the site is repaired within 30 days, even though the data cannot be replaced.

Field Calibration Results

Calibrations were performed at 23 sites during first quarter 2010. All sites and parameters were within the criteria listed in Table 3 with the exception of those parameters at the seven sites that are listed in Table 9.

Tables and Figures

Table 1. Data Validated to Level 3 during First Quarter 2010

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-2/MW-8	April 2009 – September 2009	6	Quarter 2 2009 – Quarter 3 2009	2
E-3/W-10 [†]	May 2009 – October 2009	6	Quarter 3 2009	1
SE-4/MW-6 [‡]	July 2009 – December 2009	6	Quarter 3 2009 – Quarter 4 2009	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 (19 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	LYK123, OH	
(5 Sites)		HOX148, MI	UVL124, MI		
Western Sites (10 Total)					
W-9	March/September	KNZ184, KS	SAN189, NE		
(4 Sites)		CHE185, OK	ALC188, TX		
W-10	May/November	CON186, CA	GTH161, CO	CNT169, WY	
(6 Sites)		PAL190, TX	ROM206, CO	PND165, WY	

[†] Contains ROM206 of the ROM406/ROM206 collocated pair

[‡] Contains MCK131/231 collocated pair

 Table 3. Data Quality Indicators for CASTNET Continuous Measurements

Measurement		Criteria [*]		
Parameter	Method	Precision	Accuracy	
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	
Relative humidity	Thin film capacitor	± 10% (of full scale)	± 10%	
Solar radiation	Pyranometer	± 10% (of reading taken at local noon)	± 10%	
Precipitation	Tipping bucket rain gauge	± 10% (of reading)	$\pm 0.05 \text{ inch}^{\dagger}$	
Ambient temperature	Platinum RTD	± 1.0°C	± 0.5°C	
Delta temperature	Platinum RTD	± 0.5°C	± 0.5°C	
Ozone	UV absorbance	± 10% (of reading)	± 10%	
Filter pack flow	Mass flow controller	± 10%	± 5%	
Surface wetness	Conductivity bridge	Undefined	Undefined	

°C = degrees Celsius m/s = meters per second Notes: °C

RTD = resistance-temperature device

UV = ultraviolet

 $^{^{\}ast}$ Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments † For target value of 0.50 inch

Table 4. Data Quality Indicators for CASTNET Laboratory Measurements

					Nomina	al
			Precision ¹	Accuracy ²	Reporting I	Limits
Analyte	Medium	Method	(MARPD)	(%)	mg/L	μg/Filter
Ammonium (NH ₄ ⁺)	F	AC	20	90 - 110	0.020 *	0.5
Sodium (Na ⁺)	F	ICP-AES	20	95 - 105	0.005	0.125
Potassium (K ⁺)	F	ICP-AES	20	95 - 105	0.006	0.15
Magnesium (Mg ²⁺)	F	ICP-AES	20	95 - 105	0.003	0.075
Calcium (Ca ²⁺)	F	ICP-AES	20	95 - 105	0.006	0.15
Chloride (Cl ⁻)	F	IC	20	95 - 105	0.020	0.5
Nitrate (NO ₃)	F	IC	20	95 - 105	0.008 *	0.2
Sulfate (SO ₄ ²)	F	IC	20	95 - 105	0.040	1.0

Notes: ¹ This column lists precision goals for both network precision calculated from collocated filter samples and laboratory precision based on replicate samples. The goal for the RPD criterion changed to 20 percent at the onset of the CASTNET IV contract beginning on August 11, 2009.

F = filter pack samples AC = automated colorimetry

ICP-AES = inductively coupled plasma-atomic emission spectrometry

C = ion chromatography

 $MARPD \ = \ mean \ absolute \ relative \ percent \ difference$

' = as nitrogen

For more information on analytical methods and associated precision and accuracy criteria, see the CASTNET QAPP, Revision 4.1 (MACTEC, 2008).

Table 5. QC Analysis Count for First Quarter 2010

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	$\mathrm{SO}_{\scriptscriptstyle{4}}^{\scriptscriptstyle{2-}}$	34	172	78	17	26	115
	NO_3	34	172	78	17	26	115
	$\mathrm{NH}_{\scriptscriptstyle{4}}^{^{\scriptscriptstyle{+}}}$	32	167	80	17	26	114
	C1 ⁻	34	172	78	17	26	115
	$\operatorname{Ca}^{^{2+}}$	32	168	78	16	26	114
	$\mathrm{Mg}^{^{2+}}$	32	168	78	16	26	114
	$\mathbf{Na}^{\scriptscriptstyle +}$	32	168	78	16	26	114
	$\mathbf{K}^{\scriptscriptstyle{+}}$	32	168	78	16	26	114
Nylon	$\mathrm{SO}_{\scriptscriptstyle{4}}^{\scriptscriptstyle{2-}}$	35	167	78	18	28	91
	NO_3	35	167	78	18	28	91
Cellulose	SO_4^{2-}	44	170	85	22	28	89

August 11, 2009.

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. Filter Pack Receipt Summary for First Quarter 2010

Count of samples received more than 14 days	
1	_
after removal from tower:	5
Count of all samples received:	696
Fraction of samples received within 14 days:	0.993
· ·	
Average interval in days:	5.092
,	
First receipt date:	01/04/2010
Last receipt date:	03/26/2010

Table 7. Filter Packs Flagged as Suspect or Invalid

Site ID	Sample	Reason
CAN407, UT	1002001-14	Insufficient flow
CHE185, OK	1010001-19	Insufficient flow
CON186, CA	1004001-23	Power failure
	1005001-23	Power failure
DCP114, OH	1010001-27	Polling problems
IRL141, FL	1006001-41	Insufficient flow
KEF112, PA	1009001-43	Insufficient flow
MOR409, WA	1008001-53	Insufficient flow
OXF122, OH	1007001-54	Insufficient flow
PED108, VA	1007001-57	Insufficient flow
THR422, ND	1004001-75	Insufficient flow
	1005001-75	Insufficient flow
VOY413, MN	1004001-78	Insufficient flow
WST109, NH	1009001-82	Polling problems

Table 8. Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	96
60	7
90	1
Unresolved by End of Quarter	3

Table 9. Field Calibration Failures by Parameter

Site ID	Parameter(s)	
CDZ171, KY	Wind Direction	
CKT136, KY	Flow Rate	
CND125, NC	Solar Radiation	
	Precipitation	
ESP127, TN	Precipitation	
GAS153, GA	Solar Radiation	
MCK131, KY	Solar Radiation	
	Wind Direction	
	Wind Speed	
PSU106, PA	Wind Direction	

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 4.1 (MACTEC, 2008).

RF - Teflon ICP-AES o Na X K Ca 107.5 105.0 102.5 100.0 92.5 90.0 RF-Teflon IC & AC TSO4 a a TNH4 110.0 107.5 105.0 102.5 97.5 95.0 92.5 RF-Nylon IC 110.0 105.0 102.5 100.0 92.5 90.0 1/21/2010 RF - Cellulose IC 110.0 107.5 105.0 97.5 95.0 92.5 3/25/2010

Figure 1. Reference Standard Results for First Quarter 2010 (percent recovery)

CCV - Teflon ICP-AES Mg O Na [X] K Ca 107.5 105.0 102.5 100.0 92.5 90.0 -CCV - Teflon IC & AC TSO4 a TNH4 110.0 107.5 105.0 102.5 97.5 95.0 92.5 CCV - Nylon IC 110.0 102.5 100.0 92.5 90.0 1/21/2010 1/14/2010 CCV - Cellulose IC 107.5 105.0 97.5 95.0 92.5 -3/31/2010 2/26/2010 1/21/2010

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

Figure 3. Replicate Sample Analysis Results for First Quarter 2010 (total micrograms)

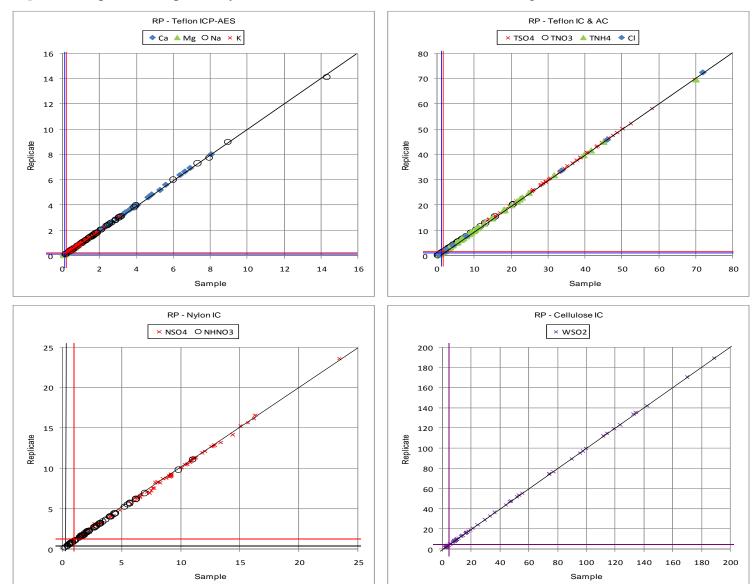
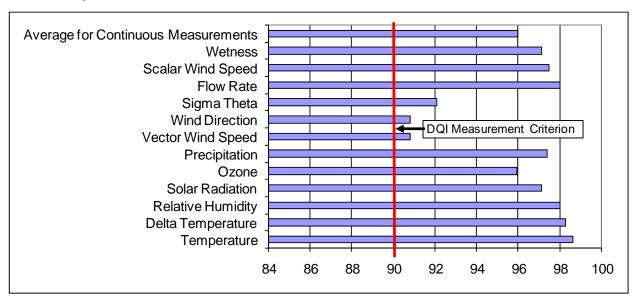
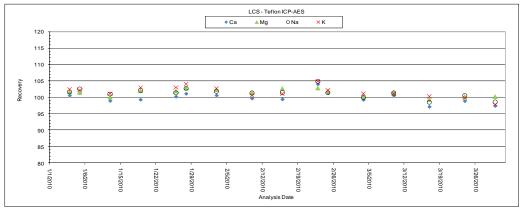


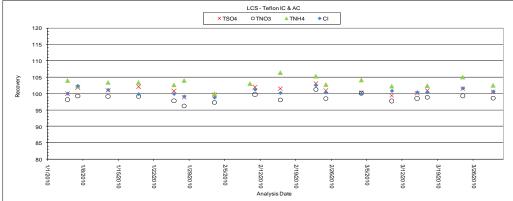
Figure 4. Percent Completeness of Measurements for Second Quarter 2009 through Fourth Quarter 2009*

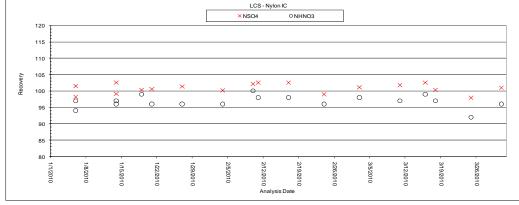


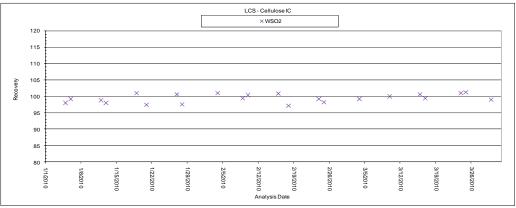
Note: *Presents Level 3 data available during the first quarter of 2010.

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



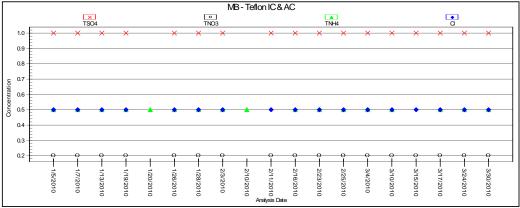


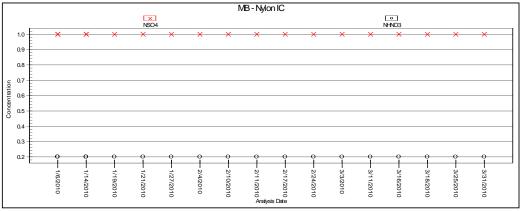


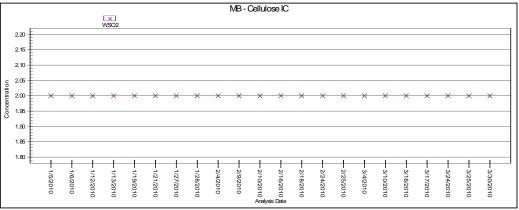


MB - Teflon ICP-AES 0.14 0.12 0.11 0.10 0.09 0.08 MB - Teflon IC & AC 1.0

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







LB - Teflon ICP-AES Ca Mg o Na K K 0.6 0.5 0.3 0.2 ***** LB-Teflon IC & AC 1.0 0.8 0.7 0.5 0.4 0.2 LB - Nylon IC 0.9 0.8 0.7 0.6 0.5 0.4 0.3 LB - Cellulose IC WSO2 2.20 2.05

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

2.00

1.85 1.80

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

