# Clean Air Status and Trends Network Quality Assurance Report

EPA Contract No.: 68-D-03-052 (Base Program)

**MACTEC Project No.:** 6064079000

**Reporting Period:** Second Quarter 2008 (April - June)

### **Summary of Quarterly Operations**

#### 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 second quarter 2008. 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 updated annually.

During second quarter 2008, the CASTNET QAPP, Revision 4.1 was approved by the Environmental Protection Agency (EPA). Also during second quarter 2008, MACTEC continued installing Campbell Scientific, Inc. (Campbell) Model CR3000 data loggers at the Environmental Protection Agency (EPA)-sponsored CASTNET sites. Documentation regarding installation, operation, and maintenance of the CR3000 data loggers is required to maintain consistent data collection across all sites. Checklists, standard operating procedures (SOP), and other documentation were prepared and evaluated during second quarter. MACTEC expects to complete the final revisions during third quarter 2008. This documentation will be incorporated into Appendix 1 (Field SOP) of the CASTNET QAPP at the upcoming annual revision.

In addition, during second quarter 2008, MACTEC and EPA continued work to evaluate requirements to make ozone measurements compliant with 40 CFR Part 58 at five CASTNET sites for the 2008 ozone season. SOP in support of this effort are being prepared to document installation procedures, operational requirements, and monitoring criteria. This documentation effort is expected to be completed during 2008. Prior to a requiring a site to be compliant with Part 58 monitoring criteria, a CR3000 data logger and a Thermo Fisher Scientific, Inc. (Thermo) Model 49i ozone analyzer must be installed. As sites are upgraded across the network, they will be required to meet Part 58 monitoring criteria.

The SOP for operation, calibration, maintenance, and data management activities of the tracelevel gas continuous monitoring equipment for sulfur dioxide (SO<sub>2</sub>), total reactive oxides of nitrogen (NO/NO<sub>y</sub>), and carbon monoxide (CO), located at the CASTNET site in Beltsville, MD (BEL116), were finalized and approved by EPA during second quarter 2008.

Data and QA personnel recoded the QC field in the LABDATA\_QC database table during second quarter 2008. The table contains laboratory QC data that were generated by the Chemical Laboratory Analysis and Scheduling System (CLASS™), the laboratory information management system (LIMS) used prior to Element DataSystem™, the LIMS currently in use. The QC data fields used by each LIMS were not consistent to one another making it necessary to standardize the QC data fields across all years to enhance the functionality of the LABDATA and LABDATA\_QC database tables and the usability of the data contained therein. The recoded LABDATA and LABDATA\_QC database tables will be resubmitted to EPA in their entirety during third quarter 2008.

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 the quarter 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 this quarter.

#### **Sample Receipt Statistics**

For the current CASTNET project, which began on July 30, 2003, EPA requires that 95 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 6 presents the relevant sample receipt statistics for second quarter 2008.

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

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for second quarter 2008. All results were within the criteria listed in Table 4 with the exception of several individual RP results. However, these are considered reasonable since higher relative percent differences generally correlate with lower sample concentrations. Quarterly averages are all within criteria.

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

#### **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 second quarter 2008.

#### **Blank Results**

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for second quarter 2008. All results were within criteria (two times the reporting limit) listed in Table 4 with the exception of one Teflon<sup>®</sup> filter FB result for nitrate that was just over twice the reporting limit and one Teflon<sup>®</sup> filter LB result for potassium that was far outside of the established criterion. The LB result was investigated and the contamination was confirmed but apparently anomalous. The cause was indeterminate. All LB samples are prepared in sets of two and the other LB in this set showed no such contamination. Similarly, all other QC blanks in the analysis batch showed no contamination. All other blank values for all filter types were less than three times the reporting limit. No systemic problems were indicated upon review.

#### Suspect/Invalid Filter Pack Samples

Eight filter pack samples were invalidated due to communication problems, which resulted in insufficient collection of flow data. These data may be recovered during the Level 3 validation process. The samples and associated site identification are presented in Table 7.

#### **Field Problem Count**

Table 8 presents counts of field problems affecting continuous data collection during second quarter 2008. 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 29 sites during second quarter 2008. All sites and parameters were within the criteria listed in Table 3 with the exception of the parameters at the 13 sites that listed in Table 9.

## **Tables and Figures**

Table 1. Data Validated to Level 3 during Second Quarter 2008

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
2	August 2007 – January 2008	6	Quarter 4 2007	1
3 <sup>†</sup>	September 2007 – February 2008	6	Quarter 4 2007	1
4	October 2007 – March 2008	6	Quarter 4 2007 – Quarter 1 2008	2

Note:

Table 2. Field Calibration Schedule

Calibration					
Group Number	Months Calibrated	Sites Calibrated			
1	January/July	SND152, AL GAS153, GA CDZ171, KY	BFT142, NC CND125, NC COW137, NC	PNF126, NC ESP127, TN SPD111, TN	PED108, VA VPI120, VA
2	February/August	CAD150, AR IRL141, FL SUM156, FL	BEL116, MD BWR139, MD CVL151, MS	WSP144, NJ CTH110, NY CHE185, OK	ARE128, PA PSU106, PA ALC188, TX
3	March/September	ALH157, IL BVL130, IL STK138, IL	VIN140, IN KNZ184, KS CKT136, KY	MCK131, KY MCK231, KY SAN189, NE	DCP114, OH OXF122, OH PRK134, WI
4	April/October	ABT147, CT SAL133, IN ASH135, ME	HOW132,ME ANA115, MI HOX148, MI	UVL124, MI WST109, NH CAT175, NY	HWF187, NY LYK123, OH EGB181, ON
5	May/November	CON186, CA ROM206, CO GTH161, CO	QAK172, OH KEF112, PA LRL117, PA	MKG113, PA PAL190, TX CDR119, WV	PAR107, WV CNT169, WY PND165, WY

<sup>\*</sup> The sites contained in each calibration group are listed in Table 2.

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

 Table 3. Data Quality Indicators for CASTNET Continuous Measurements

Measurement		Criteria <sup>*</sup>		
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)	± 5%, rel. hum. > 85% ± 20%, rel. hum. ≤ 85%	
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	
$O_3$	UV Absorbance	± 10% (of reading)	± 10%	
Filter Pack Flow	Mass Flow Controller	± 10%	± 5%	
Surface Wetness	Conductivity Bridge	Undefined	Undefined	

Note:

°C degrees Celsius m/s meters per second rel. hum. = relative humidity

RTD resistance-temperature device

UV ultraviolet

 $<sup>^{\</sup>ast}$  Precision criteria apply to collocated instruments, and accuracy criteria apply to calibration of instruments  $^{\dagger}$  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	Medium	Method	(MARPD)	(%)	mg/L	μg/Filter
Ammonium (NH <sub>4</sub> <sup>+</sup> )	F	AC	10	90 - 110	0.020 *	0.5
Sodium (Na <sup>+</sup> )	F	ICP-AES	5	95 - 105	0.005	0.125
Potassium (K <sup>+</sup> )	F	ICP-AES	5	95 - 105	0.006	0.15
Magnesium (Mg <sup>2+</sup> )	F	ICP-AES	5	95 - 105	0.003	0.075
Calcium (Ca <sup>2+</sup> )	F	ICP-AES	5	95 - 105	0.006	0.15
Chloride (Cl <sup>-</sup> )	F	IC	5	95 - 105	0.020	0.5
Nitrate (NO <sub>3</sub> )	F	IC	5	95 - 105	0.008 *	0.2
Sulfate (SO <sub>4</sub> <sup>2</sup> )	F	IC	5	95 - 105	0.040	1.0

Note:

QC conditions: (v1 = initial response; v2 = replicate response; RL = nominal reporting limit)

Condition 1: if (v1 or v2 < RL and the absolute value of (v1 - v2) < RL) = OK

 $\label{eq:condition 2:} \begin{array}{ll} & \text{if } (v1\text{-}v2) < RL \text{ and } v1 < 5 \text{ x RL}) = OK \\ & \text{Condition 3:} & \text{if } (v1 > 5*RL \text{ and RPD} < 5\%) = OK \\ & \text{Status: one of the conditions is } OK = \text{Precision QC Passes} \\ \end{array}$ 

F = filter pack samples AC = automated colorimetry

ICP-AES = inductively coupled plasma-atomic emission spectrometry

IC = 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 Quality Assurance Project Plan (QAPP), Revision 4.0 (MACTEC, 2007).

Table 5. QC Analysis Count for Second Quarter 2008

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon <sup>®</sup>	SO <sub>4</sub> <sup>2-</sup>	36	175	78	17	26	80
	$NO_3$	36	175	78	17	26	80
	$NH_4^+$	34	167	75	17	26	80
	Cl	36	175	75	17	26	80
	Ca <sup>2+</sup>	34	172	77	17	26	80
	$Mg^{2+}$	34	172	77	17	26	80
	Na <sup>+</sup>	34	172	77	17	26	80
	$\mathbf{K}^{\scriptscriptstyle +}$	34	172	77	17	26	80
Nylon	SO <sub>4</sub> <sup>2-</sup>	36	166	74	18	28	82
	NO <sub>3</sub>	36	166	74	18	28	82
Cellulose	SO <sub>4</sub> <sup>2-</sup>	42	166	78	21	26	82

<sup>&</sup>lt;sup>1</sup> 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 ICP-AES precision RPD criterion changed from 10 percent to 5 percent at the onset of the new contract beginning on July 30, 2003. The precision criterion is applied as described below:

 $<sup>^2</sup>$  This column lists laboratory accuracy goals based on reference standards and continuing calibration verification spikes. The goal for the ICP-AES accuracy criterion changed from 90-110 percent to 95-105 percent for continuing calibration verification spikes at the onset of the new contract beginning on July 30, 2003. The criterion remains 90-110 percent for ICP-AES reference standards.

Table 6. Filter Pack Receipt Summary

Count of samples received more than 14 days	
after removal from tower:	12
Count of all samples received:	730
Fraction of samples received within 14 days:	0.984
Average interval in days:	4.656
First receipt date:	04/02/2008
Last receipt date:	06/30/2008

Table 7. Filter Packs Flagged as Suspect or Invalid

CI. ID	G L ID
Site ID	Sample ID
ALH157, IL	0815001-04
CNT169, WY	0823001-22
CVL151, MS	0818001-26
CVL131, IVIS	0819001-26
HOW132, ME	0816001-38
110 W 132, WIE	0818001-38
LYK123, OH	0822001-47
L1K123, OI1	0823001-47

Table 8. Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	91
60	14
90	1
Unresolved by date of publication	20

**Note:** Counts were extracted using the problem tracking system (PTS) feature of the CDMSA. Problems requiring corrective action are flagged by field personnel with a ticket number.

Table 9. Field Calibration Failures by Parameter

Site ID	Parameter(s)		
ASH135, ME	Precipitation		
CDD110 WW	Relative Humidity		
CDR119, WV	Solar Radiation		
CNT169, WY	Wind Direction		
HOW132, ME	Temperature		
HOX148, MI	Relative Humidity		
HWF187, NY	Solar Radiation		
VEE112 DA	Relative Humidity		
KEF112, PA	Wind Direction		
LYK123, OH	Relative Humidity		
PAR107, WV	Solar Radiation		
	Relative Humidity		
PRK134, WI	Solar Radiation		
	Wind Direction		
ROM206, CO	Relative Humidity		
KOM200, CO	Wind Speed		
STK138, IL	Relative Humidity		
51K130, 1L	Solar Radiation		
WST109, NH	Solar Radiation		
W 5 1 107, 1111	Wind Direction		

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 4.0 (MACTEC, 2007).

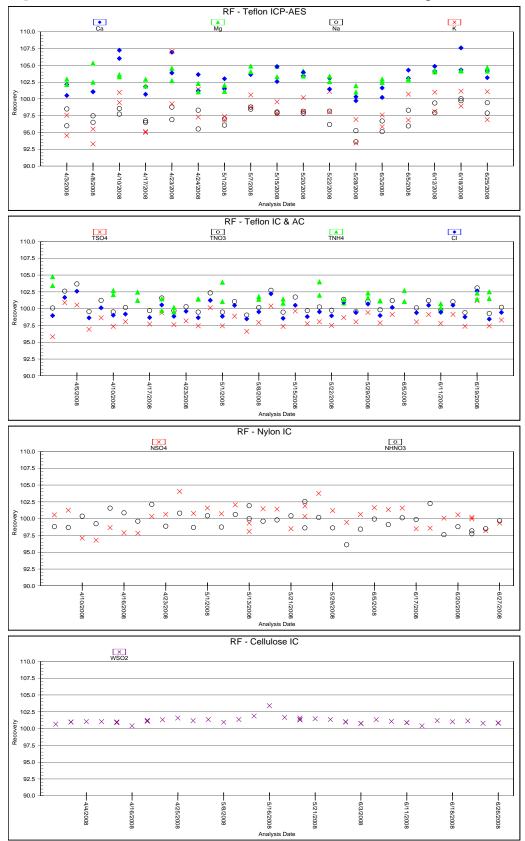


Figure 1. Reference Standard Results for Second Quarter 2008 (percent recovery)

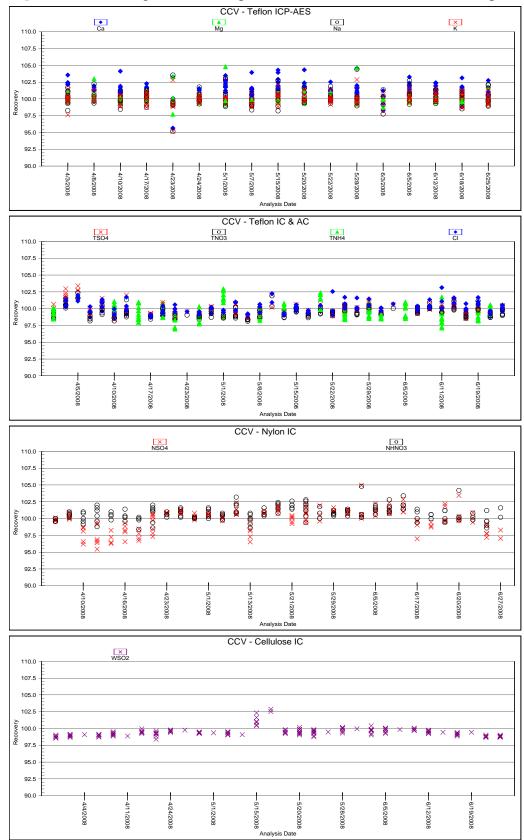


Figure 2. Continuing Calibration Spike Results for Second Quarter 2008 (percent recovery)

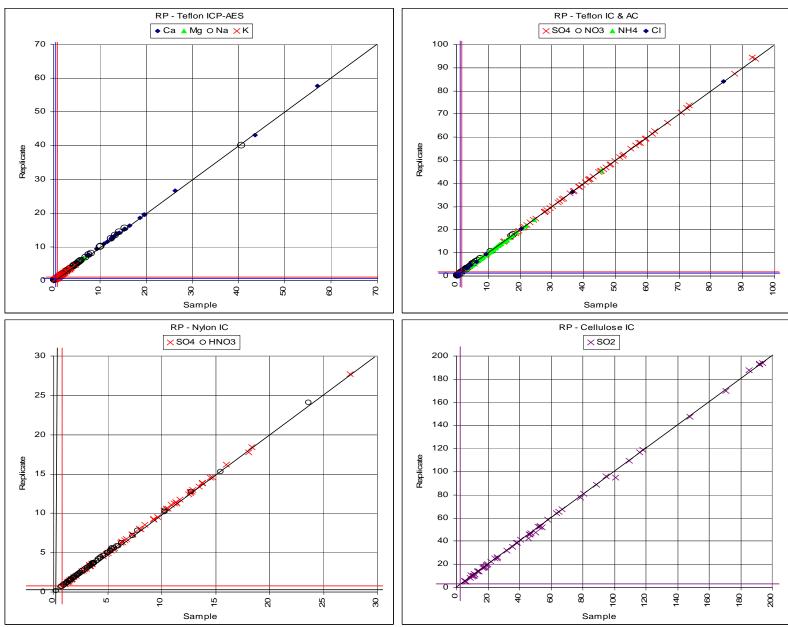
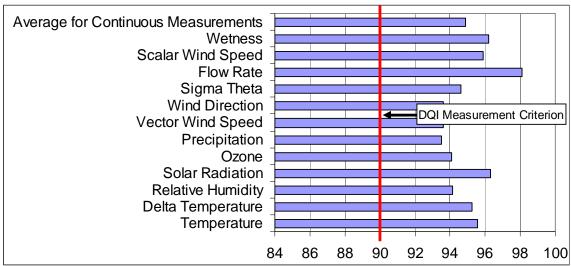
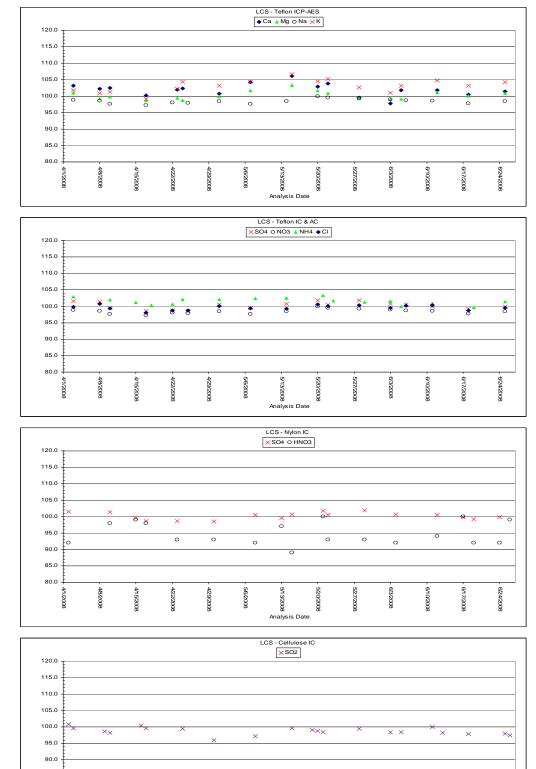


Figure 3. Replicate Sample Analysis Results for Second Quarter 2008 (total micrograms)

**Figure 4.** Percent Completeness of Measurements for Fourth Quarter 2007 through First Quarter 2008\*



Note: \*Presents Level 3 data available during the second quarter of 2008.



85.0 80.0

4,8/2008

Figure 5. Laboratory Control Sample Results for Second Quarter 2008 (percent recovery)

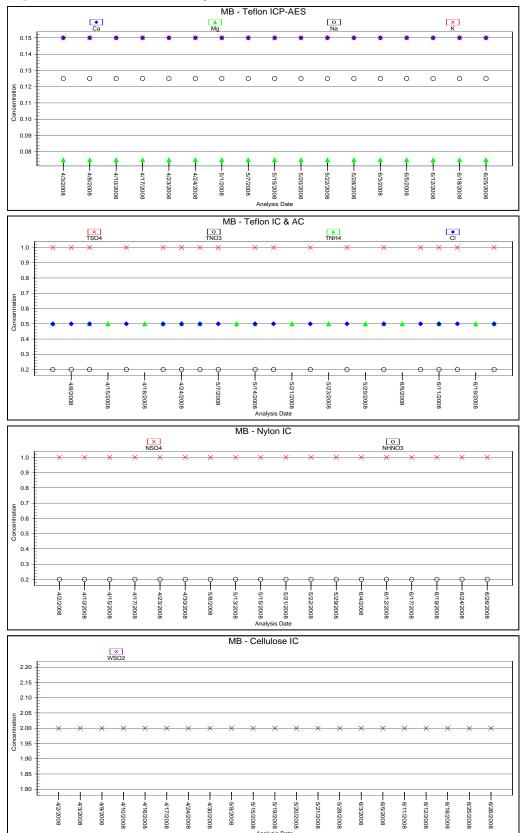


Figure 6. Method Blank Analysis Results for Second Quarter 2008 (total micrograms)

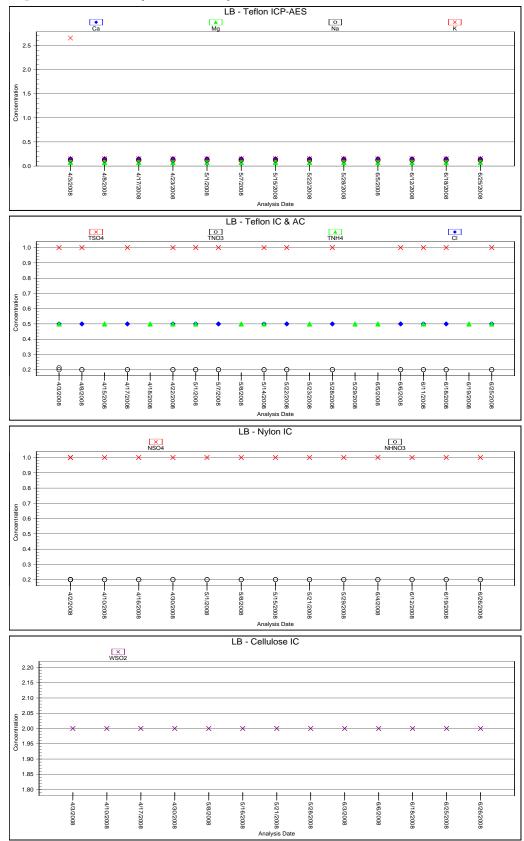


Figure 7. Laboratory Blank Analysis Results for Second Quarter 2008 (total micrograms)

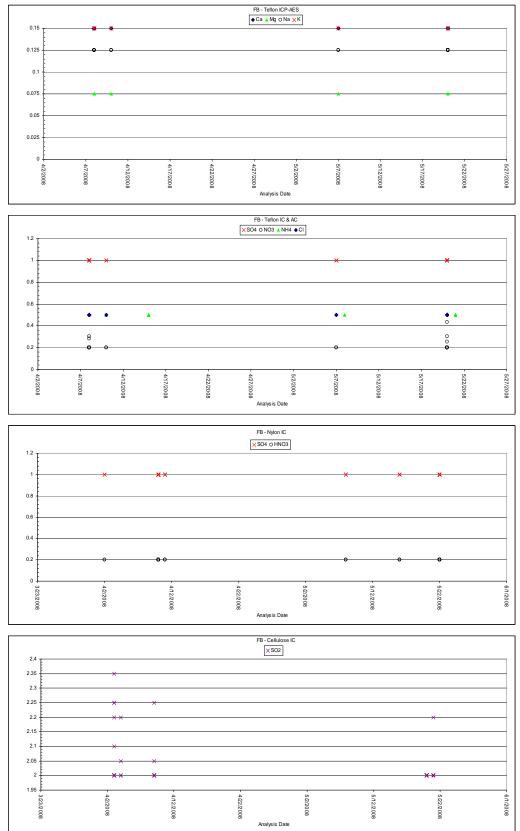


Figure 8. Field Blank Analysis Results for Second Quarter 2008 (total micrograms)