

## Clean Air Status and Trends Network

Second Quarter 2023 Quality Assurance Report

# Summary of Quarterly Operations (April through June) EPA Contract No. 68HERH21D0006

#### 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 2023. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; WSP, 2022). 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**

The biennial onsite assessment of WSP's analytical and field laboratories by the American Association for Laboratory Accreditation (A2LA) to continue WSP's International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025:2017 accreditation took place on April 3–5, 2023. The assessor looked at WSP's quality management system as well as the technical capabilities of WSP's CASTNET personnel. The assessor was very complimentary and impressed with the staff's openness with explanations. There were two deficiencies: one relating to the supplier list not being inclusive (e.g., needed to include EPA Regions for level 2 certifications and A2LA for accreditation) and the other relating to the need to document quality and schedule evaluations for suppliers in addition to the documented technical evaluations. WSP addressed the deficiencies noted in the A2LA assessment and submitted the documentation of root cause, corrective action, and resolution to A2LA, as required, within the 30-day post-assessment period on May 3, 2023. After review of WSP's documentation, on May 22, 2023, A2LA approved WSP's field and analytical laboratory for ISO/IEC 17025:2017 reaccreditation through May 2025.

WSP's CASTNET QA Manager was asked to perform an audit of data quality for the second cloud water PFAS data set covering the period June 2020 to August 2021. There were no findings. The audit was performed, and the report was submitted to EPA on June 6, 2023.

Preparation of the annual management review and report in support of ISO/IEC 17025:2017 accreditation was completed. Work on the presentation related to the report began.

Greg Wetherbee *et al.* (2023) of the U. S. Geological Survey (USGS) published a project report summarizing the results of the 2019 through 2020 USGS Interlaboratory Comparison Program. WSP has been, and continues to be, a regular participant in this program. Out of 11 laboratories, only the WSP analytical laboratory and one other showed "no practically significant bias" for all analytes reported. (<a href="https://pubs.er.usgs.gov/publication/sir20235045">https://pubs.er.usgs.gov/publication/sir20235045</a>).

Table 1 lists the quarters of data that were validated to Level 3 during second quarter 2023 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 second quarter 2023.

#### **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 second quarter 2023.

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

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for second quarter 2023. All results were within the criteria listed in Table 3.

Table 8 presents summary statistics of critical criteria measurements at ozone sites collected during second quarter 2023. 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 effect on ambient data collection, and passing results still meet frequency criteria. Results in shaded cells either exceed 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 second quarter 2023. 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 effect on ambient data collection, and passing results still meet frequency criteria. Results in shaded cells either exceed documented criteria or are otherwise notable. During second quarter, no values 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. 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 second quarter 2023. All recovery values were within the criterion.

#### **Blank Results**

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for second quarter 2023. All second quarter results were within criteria (two times the reporting limit) listed in Table 3 with the exception of one potassium FB and one calcium FB between 2 and 4 times the reporting limit.

#### Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during second quarter 2023 are listed in Table 11. This table also includes associated site identification and a brief description of the reason the sample was flagged. During second quarter, four 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 second quarter 2023. The problem counts are sorted by a 30-, 60-, or 90-day time period to resolution. A category for unresolved problems is also included.

#### References

- 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). 2020. Title 40 Code of Federal Regulations Part 58, "Appendix A to Part 58 – Quality Assurance Requirements for Monitors used in Evaluations of National Ambient Air Quality Standards."
- Wetherbee, G. A., Martin, R. and Liethen, A. 2023. External Quality-Assurance Project Report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2019–20. U.S. Geological Survey Scientific Investigations Report 2023-5045, https://pubs.er.usgs.gov/publication/sir20235045.
- WSP USA Environment & Infrastructure Inc. (WSP) formerly known as Wood USA Environment & Infrastructure Inc. 2022. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan (QAPP) Revision 9.5.* Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. 68HERH21D0006. Gainesville, FL. https://java.epa.gov/castnet/documents.do.

Table 1 Data Validated to Level 3 through Second Quarter 2023

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-1/SE-5	August 2022– January 2023	6	Quarter 4 2022	1
MW-7/W-9	September 2022– February 2023	6	Quarter 4 2022	1
E-2/MW-8	October 2022– March 2023	6	Quarter 4 2022– Quarter 1, 2023	2

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

Table 2 Field Calibration Schedule for 2023

Calibration					
Group	Months Calibrated		Sites	Calibrated	
		Eastern	Sites (22 Total)		
E-1	February/August	BEL116, MD	WSP144, NJ	ARE128, PA	PED108, VA
(8 Sites)		BWR139, MD	CTH110, NY	PSU106, PA	VPI120, VA
E-2	April/October	ABT147, CT	CAT175, NY	NIC001, NY	
(9 Sites)		ASH135, ME	HWF187, NY <sup>1</sup>	EGB181, ON	
		WST109, NH	WFM105, NY	UND002, VT	
E-3	May/November	KEF112, PA	LRL117, PA	CDR119, WV	
(5 Sites)		MKG113, PA	PAR107, WV		
	Southeastern Sites (11 Total)				
SE-4	January/July	SND152, AL	BFT142, NC	COW137, NC	SPD111, TN
(7 Sites)		GAS153, GA	CND125, NC	DUK008, NC1	
SE-5	February/August	CAD150, AR	SUM156, FL		
(4 Sites)		IRL141, FL	CVL151, MS		
		Midwester	rn Sites (18 Total)		
MW-6	January/July	CDZ171, KY	MCK131, KY	PNF126, NC <sup>1</sup>	
(6 Sites)		CKT136, KY	MCK231, KY	ESP127, TN	
MW-7	March/September	BVL130, IL <sup>2</sup>	VIN140, IN	DCP114, OH	QAK172, OH
(8 Sites)		STK138, IL	RED004, MN	OXF122, OH	PRK134, WI
MW-8	April/October	SAL133, IN	ANA115, MI		
(4 Sites)		HOX148, MI	UVL124, MI		
		Western	Sites (13 Total)		
W-9	March/September	KNZ184, KS	CHE185, OK	ALC188, TX	
(5 Sites)		KIC003, KS	SAN189, NE		
W-10	May/November	LPO010, CA	ROM206, CO <sup>3</sup>	PAL190, TX	CNT169, WY
(8 Sites)		GTH161, CO	NPT006, ID	UMA009, WA	PND165, WY <sup>3</sup>

Notes: <sup>1</sup> Trace-level gas calibrations are performed quarterly in January, April, July, and October.

<sup>2</sup> Trace-level gas calibrations are performed quarterly in March, June, September, and December.

<sup>3</sup> Trace-level gas calibrations are performed quarterly in February, May, August, and November.

Table 3 Data Quality Indicators for CASTNET Laboratory Measurements

		Precision <sup>1</sup>	Accuracy <sup>2</sup>	Nominal Reporting Limits <sup>3</sup>		
Analyte	Method	(MARPD)	(%)	mg/L	μg/Filter	
Ammonium (NH <sup>+</sup> <sub>4</sub> )	AC	20	90-110	0.020 <sup>*</sup>	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: ¹ This column lists precision goals for both network precision calculated from co-located filter samples and laboratory precision based on replicate samples for samples > five times the reporting limit. The criterion is ± the reporting limit if the sample is ≤ five times the reporting limit.

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 µg/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, (WSP, 2022).

Table 4 Ozone Critical Criteria\*

Type Check	Analyzer Response
Zero	Less than ± 3.1 parts per billion (ppb)
Span	Less than ± 7.1 percent between supplied and observed concentrations
Single Point QC	Less than ± 7.1 percent between supplied and observed conentrations

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, 2020). 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-OES reference standards. The criterion for all laboratory control samples is 80-120 percent.

<sup>3</sup> The reporting limit for sulfate on cellulose filters is 0.080 mg/L (2.0 µg/filter).

Table 5 Trace-level Gas Monitoring Critical Criteria\*

	<u> </u>					
	Analyzer Response					
Parameter	Zero Check	Span Check / Single Point QC Check				
SO <sub>2</sub>	Less than ± 1.51 ppb	Less than ± 10.1 percent between supplied and				
NO <sub>y</sub>	Less than ± 1.51 ppb	observed concentrations				
CO	Less than ± 50 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, 2020). 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).

 $SO_2$  = sulfur dioxide

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

CO = carbon monoxide ppb = parts per billion

## Table 6 QC Analysis Count for Second Quarter 2023

Filter Type	Parameter	RF Sample Count	CCV Sample Count	RP Sample Count	MB Sample Count	LB Sample Count	FB Sample Count
Teflon	SO <sub>4</sub> <sup>2-</sup>	56	161	68	14	22	43
	NO <sub>3</sub>	56	161	68	14	22	43
	NH <sup>+</sup> <sub>4</sub>	29	148	68	14	22	43
	Cl	56	161	68	14	22	43
	Ca <sup>2+</sup>	28	146	68	14	22	43
	Mg <sup>2+</sup>	28	146	68	14	22	43
	Na <sup>⁺</sup>	28	146	68	14	22	43
	K⁺	28	146	68	14	22	43
Nylon	SO <sub>4</sub> <sup>2-</sup>	31	144	71	10	24	43
	NO <sub>3</sub>	31	144	71	10	24	43
Cellulose	SO <sub>4</sub> <sup>2-</sup>	48	172	76	15	28	84

Table 7 Filter Pack Receipt Summary for Second Quarter 2023

Count of samples received more than 14 days after removal from tower:	11
Count of all samples received	642
Fraction of samples received within 14 days:	0.983
Average interval in days:	4.117
First receipt date:	04/01/2023
Last receipt date:	06/30/2023

Note: Sample shipments for the Egbert, Ontario site (EGB181) are in groups of four. Samples associated with EGB181 are excluded from this statistic.

Table 8 Ozone QC Summary for Second Quarter 2023 (1 of 2)

		/ for Occorra G	% Single			Zero
	% Span		Point QC	Single Point	% Zero	Average
Site ID	Pass <sup>1</sup>	Span [%D] <sup>2</sup>	Pass <sup>1</sup>	QC [%D] <sup>2</sup>	Pass <sup>1</sup>	(ppb) <sup>2</sup>
ABT147, CT	100.00	2.95	97.87	3.28	100.00	0.26
ALC188, TX	98.91	2.00	100.00	1.29	100.00	0.26
ANA115, MI	100.00	1.41	100.00	2.63	100.00	0.16
ARE128, PA	97.94	2.59	94.85	2.73	100.00	1.04
ASH135, ME <sup>3</sup>	N/A	N/A	N/A	N/A	N/A	N/A
BEL116, MD	100.00	0.82	100.00	0.65	100.00	0.45
BFT142, NC	100.00	4.94	100.00	4.98	100.00	0.28
BVL130, IL	98.80	0.68	100.00	0.80	100.00	0.25
BWR139, MD	100.00	1.54	100.00	1.27	97.87	0.58
CAD150, AR	95.74	6.51	95.74	6.69	97.87	0.54
CDR119, WV <sup>3</sup>	N/A	N/A	N/A	N/A	N/A	N/A
CDZ171, KY <sup>3</sup>	N/A	N/A	N/A	N/A	N/A	N/A
CKT136, KY	100.00	0.75	100.00	0.77	100.00	0.14
CND125, NC	98.97	3.67	100.00	2.71	100.00	0.39
CNT169, WY	100.00	0.44	100.00	0.87	100.00	0.31
COW137, NC	100.00	0.46	100.00	1.11	100.00	0.27
CTH110, NY	100.00	0.87	100.00	0.97	100.00	0.17
CVL151, MS	91.40	9.52	91.40	9.87	100.00	0.30
DCP114, OH <sup>3</sup>	N/A	N/A	N/A	N/A	N/A	N/A
DUK008, NC	100.00	2.79	100.00	2.31	100.00	0.94
ESP127, TN	95.51	4.34	95.51	3.47	100.00	0.89
GAS153, GA	100.00	0.87	100.00	1.56	100.00	0.47
GTH161, CO	100.00	1.50	98.89	1.65	97.78	0.78
HOX148, MI	100.00	4.38	100.00	4.57	100.00	0.26
HWF187, NY <sup>3</sup>	N/A	N/A	N/A	N/A	N/A	N/A
IRL141, FL	98.96	2.83	100.00	1.80	100.00	0.79
KEF112, PA	100.00	2.21	100.00	0.88	100.00	0.61
LPO010, CA	100.00	1.34	98.91	1.88	100.00	0.66
LRL117, PA	96.43	2.75	97.59	1.72	97.59	1.41
MCK131, KY	100.00	0.36	100.00	0.47	100.00	0.20
MCK231, KY	100.00	2.28	100.00	1.74	100.00	0.22

Table 8 Ozone QC Summary for Second Quarter 2023 (2 of 2)

Site ID	% Span Pass¹	Span [%D] <sup>2</sup>	% Single Point QC Pass <sup>1</sup>	Single Point QC [%D] <sup>2</sup>	% Zero Pass¹	Zero Average (ppb) <sup>2</sup>
MKG113, PA	92.47	2.77	90.32	2.82	100.00	0.26
NPT006, ID	100.00	1.98	100.00	1.63	100.00	0.11
OXF122, OH	100.00	0.86	100.00	0.71	100.00	0.22
PAL190, TX	100.00	1.53	100.00	1.48	100.00	0.27
PAR107, WV	100.00	1.12	100.00	0.94	100.00	0.17
PED108, VA	100.00	2.51	100.00	2.33	100.00	0.21
PND165, WY	100.00	2.50	100.00	1.47	100.00	1.33
PNF126, NC <sup>3</sup>	N/A	N/A	N/A	N/A	N/A	N/A
PRK134, WI	98.80	1.37	100.00	1.24	100.00	0.19
PSU106, PA	100.00	1.66	100.00	0.93	100.00	0.19
QAK172, OH	100.00	1.10	100.00	1.97	100.00	0.60
ROM206, CO	100.00	1.31	100.00	2.06	98.92	0.27
SAL133, IN	100.00	0.42	100.00	0.48	100.00	0.32
SAN189, TX	95.70	6.11	95.70	6.98	97.85	1.26
SND152, AL	100.00	0.53	100.00	1.04	100.00	0.53
SPD111, TN	100.00	1.02	100.00	1.61	100.00	0.25
STK138, IL	100.00	2.41	100.00	1.93	100.00	0.47
SUM156, FL	100.00	2.61	100.00	1.25	100.00	0.20
UMA009, WA	100.00	0.61	100.00	0.84	100.00	0.31
UVL124, MI	100.00	2.24	100.00	1.25	100.00	0.55
VIN140, IN	100.00	0.73	100.00	0.80	100.00	0.13
VPI120, VA	98.90	1.10	100.00	1.32	100.00	0.36
WSP144, NJ	95.24	6.39	92.77	8.18	98.80	0.26
WST109, NH <sup>3</sup>	N/A	N/A	N/A	N/A	N/A	N/A

**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 ppb = parts per billion

Table 9 Ozone QC Observations for Second Quarter 2023

Site ID	QC Criterion	Comments
CVL151, MS	Span  %D  Single Point QC  %D	The analyzer sample pump failed 5/8/2023 and was replaced 5/12/2023.
WSP144, NJ	Single Point QC  %D	The analyzer sample malfunctioned 5/31/2023 and was replaced 6/3/2023.

Note: %D = percent difference

<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> Site mothballed due to EPA budget constraints.

Table 10 Trace-level Gas QC Summary for Second Quarter 2023

Parameter	% Span Pass¹	Span [%D] <sup>2</sup>	% Single Point QC Pass <sup>1</sup>	Single Point QC [%D] <sup>2</sup>	% Zero Pass¹	Zero Average (ppb) <sup>2</sup>
			BVL130, IL			
SO <sub>2</sub>	100.00	0.88	100.00	5.49	100.00	0.82
NO <sub>y</sub>	100.00	2.46	100.00	5.24	100.00	0.76
CO	100.00	0.88	100.00	3.54	100.00	17.67
			DUK008, NC			
NO <sub>y</sub>	100.00	1.73	100.00	1.63	100.00	0.41
			HWF187, NY			
NO <sub>y</sub>	N/A	N/A	N/A	N/A	N/A	N/A
	-	-	PND126, NC			
NO <sub>y</sub>	100.00	2.45	100.00	2.34	100.00	0.57
	PNF126, NC					
NOy	N/A	N/A	N/A	N/A	N/A	N/A
	ROM206, CO					
NOy	100.00	3.23	100.00	2.90	100.00	0.44

%D = percent difference ppb = parts per billion

Table 11 Filter Packs Flagged as Suspect or Invalid During Second Quarter 2023

Site ID	Sample No.	Reason
ALC188, TX	2316004-01	Sample was invalidated for suspect data.
EGB181, ON	2314001-21	The site had a polling issue, and flow data were missing for five out of seven days.
SUM156, FL	2315001-49 2316001-49	The site had a polling issue, and flow data were missing for several days, which affected two samples.

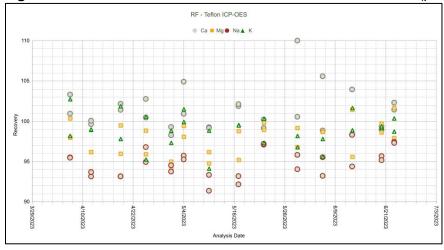
Table 12 Field Problems Affecting Data Collection

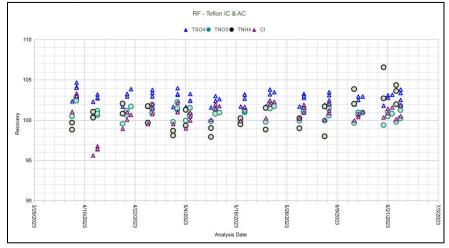
Days to Resolution	Problem Count
30	216
60	2
90	0
Unresolved by end of quarter	3

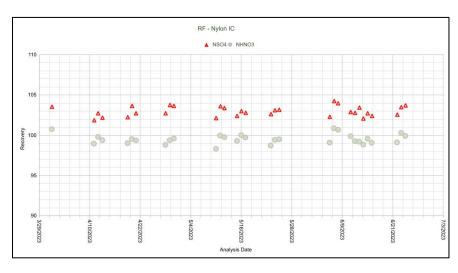
Notes: <sup>1</sup>Percentage of comparisons that pass the criteria listed in Table 5.

<sup>2</sup>Absolute value of the average percent differences between the supplied and observed concentrations.

Figure 1 Reference Standard Results for Second Quarter 2023 (percent recovery)







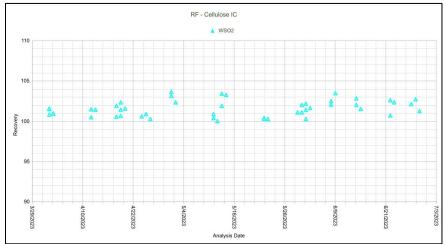
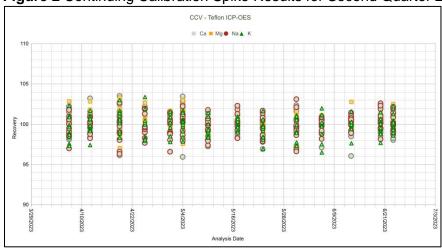
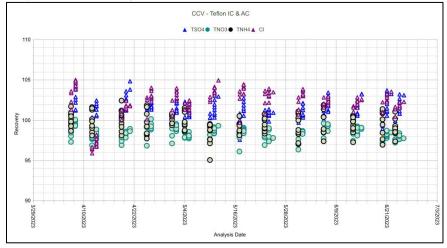
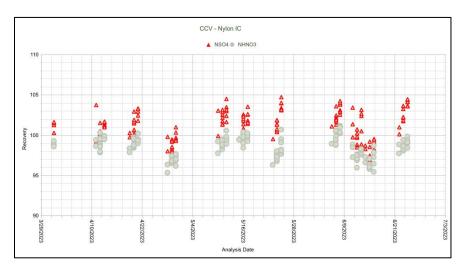


Figure 2 Continuing Calibration Spike Results for Second Quarter 2023 (percent recovery)







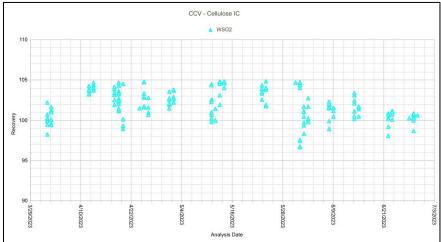
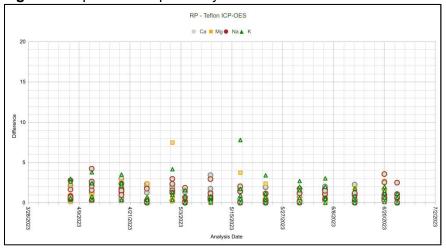
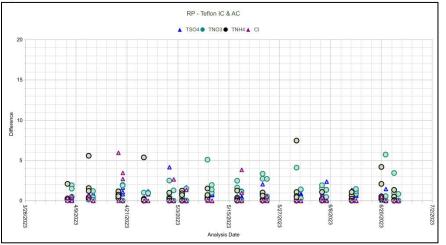
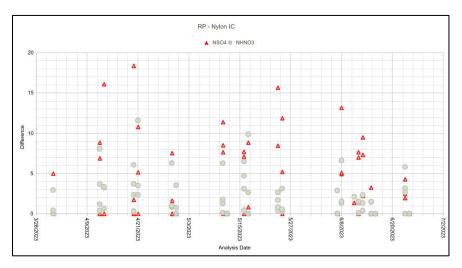


Figure 3 Replicate Sample Analysis Results for Second Quarter 2023 (percent difference)







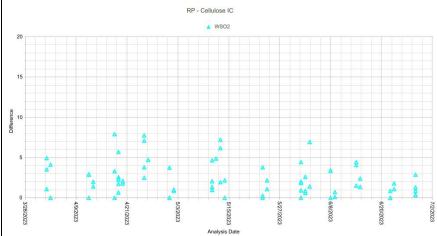
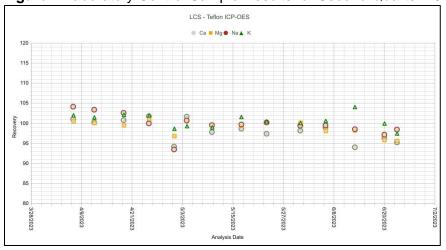
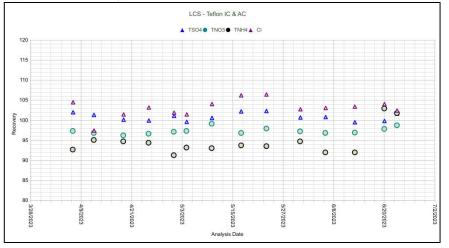
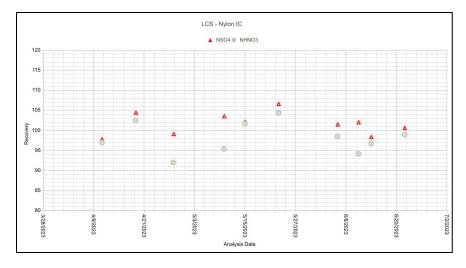


Figure 4 Laboratory Control Sample Results for Second Quarter 2023 (percent recovery)







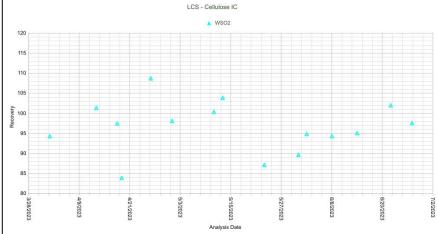
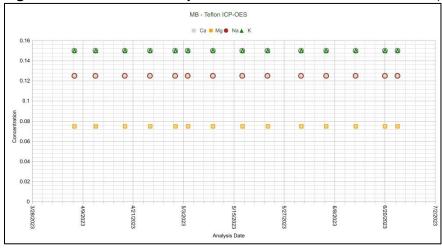
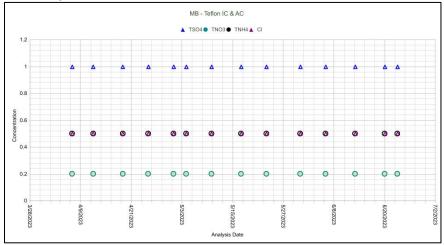
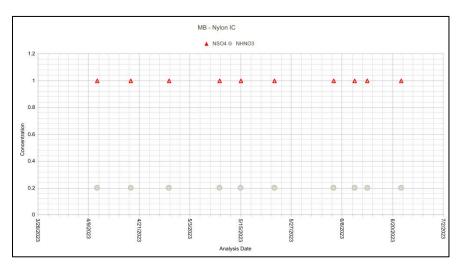


Figure 5 Method Blank Analysis Results for Second Quarter 2023 (total micrograms)







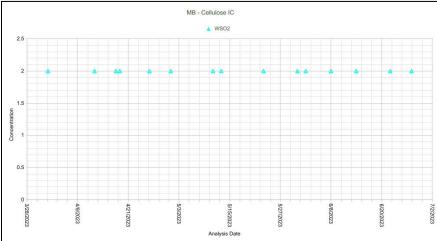
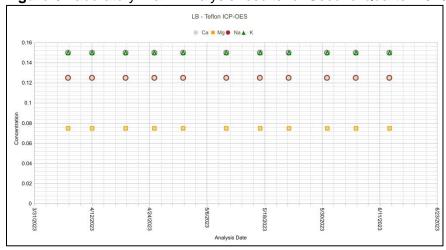
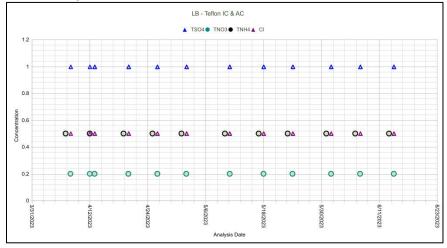
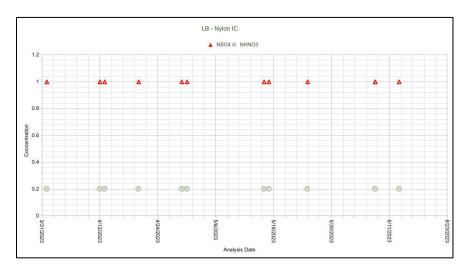


Figure 6 Laboratory Blank Analysis results for Second Quarter 2023 (total micrograms)







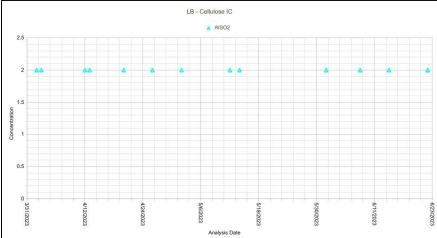


Figure 7 Field Blank Analysis Results for Second Quarter 2023 (total micrograms)

