Summary of Quarterly Operations (January through March)

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 first quarter 2022. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; Wood, 2021). 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 QA Manager reviewed the metrics for the annual site operator performance assessment. The metrics are evaluated to determine where additional training is needed. For 2021, problems with site operations were not related to training issues. Problems mainly stemmed from issues related to shipping, weather, and COVID-19. Additionally, Wood's QA Manager completed the annual review of site operator quality management system training and identified those site operators that had not completed training questionnaires. The site operators were contacted and requested to complete the required training documentation.

American Association for Laboratory Accreditation (A2LA) requested updated documentation be submitted by March 3, 2022, as part of the annual renewal in support of International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025:2017 accreditation. The CASTNET Laboratory Operations Manager and QA Manager compiled the requested documentation and submitted it to A2LA. Wood's ISO/IEC 17025:2017 accreditation was reaffirmed by A2LA through May 31, 2023.

Preparation began on the annual management review report in support of ISO/IEC 17025:2017 accreditation. The report will be distributed to the CASTNET management team during second quarter 2022.

Work continued on the CASTNET QAPP Revision 9.5. Wood's CASTNET QA Manager reviewed the checklist of requests for future changes made by the EPA CAMD QA Manager during work on Revision 9.4. The CASTNET QA Manager also worked with EPA CAMD staff to ensure all previously requested changes were addressed.

Wood completed compiling information and data on Nafion dryers in response to the failed NPAP audit at the BFT142, NC site and submitted the information to EPA. Region 4 reviewed the data and agreed the NPAP audit of the BFT142 site was faulty, and the audit should be removed from AQS.

EPA requested Wood's CASTNET QA Manager provide an audit of polyfluorinated alkyl substances (PFAS) data quality for samples collected during 2020 as part of the National Atmospheric Deposition Program (NADP) PFAS Wet Deposition Pilot Study. The QA Manager used the EPA Office of Research and Development PFAS QAPP and NADP Central Analytical Laboratory standard operating procedures in addition to PFAS laboratory data reports, chains-of-custody, etc. during the audit. There were no findings.

Wood received final results for analyses of samples for proficiency test (PT) study 118 for Rain and Soft Waters. Wood's laboratory analyses were rated, "very good." Out of the 19 laboratories that participated in PT study 118, only two laboratories (Wood plus one other) were rated, "very good." PT study 118 was overseen by the Water Science and Technology (WS&T) Directorate, a branch of Environmental Science and Technology Laboratories with ECCC. The WS&T Directorate provides quality assurance and proficiency testing services.

The USGS resumed sending interlaboratory comparison samples for analysis to Wood on a monthly basis. During 2021, USGS was sending samples every other month.

Table 1 lists the quarters of data that were validated to Level 3 during first quarter 2022 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 first quarter 2022.

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 2022. Return delivery service was often delayed due to policy and procedure decisions made by the U.S. Postal Service, which resulted in an 87 percent average for first quarter. Near the end of first quarter, Wood's analytical laboratory began the process of upgrading return shipping labels from standard shipping to priority mail to speed up shipping. All sites will be using upgraded return shipping labels by early second quarter.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for first quarter 2022. All results were within the criteria listed in Table 3. Figure 3 depicts two Teflon calcium RP results at 25

and 26 percent, respectively. The original sample concentrations were between two and three times the reporting limit. As noted in Table 3, the 20 percent criterion only applies to values greater than or equal to five times the reporting limit; otherwise, the criterion is \pm the reporting limit. The quarterly averages met this criterion.

Table 8 presents summary statistics of critical criteria measurements at ozone sites collected during first quarter 2022. 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 first quarter 2022. 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. During first 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 first quarter 2022. All recovery values were between 90 percent and 106 percent.

Blank Results

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for first quarter 2022. All first quarter results were within criteria (two times the reporting limit) listed in Table 3 with the exception of one Teflon FB potassium result and one Teflon FB ammonium result both at three times the reporting limit. All other associated QC were within criteria, and the data from the associated sites (BUF603, WY and LRL117, PA) were reasonable.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during first quarter 2022 are listed in Table 11. This table also includes associated site identification and a brief description of the reason the sample was flagged. During first quarter, six 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 first quarter 2022. 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

- 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."
- Wood Environment & Infrastructure Solutions, Inc. (Wood) 2021. *Clean Air Status and Trends Network (CASTNET) Quality Assurance Project Plan* (QAPP) Revision 9.4. Prepared for U.S. Environmental Protection Agency (EPA), Office of Air and Radiation, Clean Air Markets Division, Washington, DC. Contract No. EP-W-16-015. Gainesville, FL. https://java.epa.gov/castnet/documents.do.

Table 1 Data Validated to Level 3 during First Quarter 2022

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10 [†]	May 2021 – October 2021	6	Quarter 3 2021	1
SE-4/MW-6 [‡]	July 2021 – December 2021	6	Quarter 3 2021 – Quarter 4 2021	2

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

Table 2 Field Calibration Schedule for 2022

Calibration Group	Months Calibrated			Sites Calibrated		
Group	Calibrated	Γ-	atawa Citaa (22)			
			stern Sites (22			
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	WST109, NH	HWF187, NY ¹	WFM105, NY	UND002, VT
(9 Sites)		ASH135, ME	CAT175, NY	NIC001, NY	EGB181, ON	
E-3	May/November	KEF112, PA	LRL117, PA	CDR119, WV		
(5 Sites)		MKG113, PA	PAR107, WV			
		South	neastern Sites (11 Total)		
SE-4	January/July	SND152, AL	BFT142, NC	COW137, NC	SPD111, TN	
(7 Sites)		GAS153, GA	CND125, NC	DUK008, NC ¹		
SE-5	February/August	CAD150, AR	SUM156, FL			
(4 Sites)		IRL141, FL	CVL151, MS			
		Mid	western Sites (1	9 Total)		
MW-6	January/July	CDZ171, KY	MCK131, KY	PNF126, NC ¹		
(6 Sites)		CKT136, KY	MCK231, KY	ESP127, TN		
MW-7	March/September	ALH157, IL	STK138, IL	RED004, MN	OXF122, OH	PRK134, WI
(9 Sites)		BVL130, IL ²	VIN140, IN	DCP114, OH	QAK172, OH	
MW-8	April/October	SAL133, IN	ANA115, MI			
(4 Sites)		HOX148, MI	UVL124, MI			
	Western Sites (12 Total)					
W-9	March/September	KNZ184, KS	CHE185, OK	ALC188, TX		
(5 Sites)		KIC003, KS	SAN189, NE			
W-10	May/November	GTH161, CO	NPT006, ID	UMA009, WA	PND165, WY ³	
(7 Sites)		ROM206, CO ³	PAL190, TX	CNT169, WY		

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

[†] Contains ROM206 of the ROM406/ROM206 co-located pair

[‡] Contains MCK131/231 co-located pair

 $^{^{\}rm 2}$ Trace-level gas calibrations are performed quarterly in March, June, September, and December.

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

Table 3 Data Quality Indicators for CASTNET Laboratory Measurements

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

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, (Wood, 2021).

Table 4 Ozone Critical Criteria*

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

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).

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.

² 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.

 $^{^{3}}$ The reporting limit for sulfate on cellulose filters is 0.080 mg/L (2.0 μ g/filter).

Table 5 Trace-level Gas Monitoring Critical Criteria*

	Analyzer Response				
Parameter	Zero Check	Span Check / Single Point QC Check			
SO ₂	Less than ± 1.51 ppb				
NO _y	Less than ± 1.51 ppb	Less than ± 10.1 percent between supplied and observed concentrations			
СО	Less than \pm 30.1 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_y = total reactive oxides of nitrogen

CO = carbon monoxide ppb = parts per billion

Table 6 QC Analysis Count for First Quarter 2022

		RF	CCV	RP	МВ	LB	FB
Filter		Sample	Sample	Sample	Sample	Sample	Sample
Туре	Parameter	Count	Count	Count	Count	Count	Count
Teflon	SO ₄ ²⁻	74	211	87	19	24	106
	NO ₃	74	211	87	19	24	106
	NH_4^+	38	175	87	19	24	106
	Cl ⁻	74	211	87	19	24	106
	Ca ²⁺	38	190	86	19	24	106
	Mg ²⁺	38	190	86	19	24	106
	Na⁺	38	190	86	19	24	106
	$K^{^{+}}$	38	190	86	19	24	106
Nylon	SO ₄ ²⁻	45	184	79	14	24	130
	NO ₃	45	184	79	14	24	130
Cellulose	SO ₄ ²⁻	51	184	85	17	26	136

Table 7 Filter Pack Receipt Summary for First Quarter 2022

Count of samples received more than 14 days after removal from tower:	92
Count of all samples received:	697
Fraction of samples received within 14 days:	0.868
Average interval in days:	9.175
First receipt date:	01/03/2022
Last receipt date:	03/23/2022

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 First Quarter 2022 (1 of 2)

Site ID	% Span Pass ¹	Span %D ²	% Single Point QC Pass ¹	Single Point QC %D ²	% Zero Pass ¹	Zero Average (ppb) ²
ABT147, CT	100.00	0.49	100.00	0.52	100.00	0.18
ALC188, TX	98.82	2.96	100.00	2.13	100.00	0.44
ALH157, IL	100.00	0.76	100.00	0.92	100.00	0.13
ANA115, MI	100.00	2.15	100.00	1.96	100.00	1.05
ARE128, PA	100.00	1.00	100.00	1.14	100.00	0.32
ASH135, ME	100.00	1.57	100.00	1.92	100.00	0.26
BEL116, MD	100.00	1.34	100.00	0.92	100.00	0.44
BFT142, NC	95.56	5.28	95.56	4.65	95.56	0.84
BVL130, IL	100.00	2.48	100.00	2.48	100.00	0.41
BWR139, MD	100.00	1.52	100.00	1.90	100.00	0.35
CAD150, AR	95.45	5.47	95.56	5.86	100.00	0.32
CDR119, WV	100.00	0.78	100.00	0.88	100.00	0.23
CDZ171, KY	100.00	0.96	100.00	0.95	100.00	0.26
CKT136, KY	100.00	0.36	100.00	0.42	100.00	0.09
CND125, NC	100.00	1.65	100.00	1.20	100.00	0.68
CNT169, WY	86.60	13.85	86.60	13.98	100.00	0.26
COW137, NC	100.00	0.43	100.00	0.69	100.00	0.28
CTH110, NY	100.00	1.98	100.00	2.09	100.00	0.17
CVL151, MS	95.74	4.90	95.74	4.69	100.00	0.45
DCP114, OH	100.00	2.06	100.00	1.25	100.00	0.66
DUK008, NC	100.00	2.48	100.00	2.97	100.00	1.25
ESP127, TN	100.00	0.93	100.00	0.95	100.00	0.25
GAS153, GA	84.03	16.36	83.90	12.76	83.90	3.08
GTH161, CO	100.00	0.63	100.00	0.70	100.00	0.18

Table 8 Ozone QC Summary for First Quarter 2022 (2 of 2)

	-		% Single	Single		Zero
	% Span		Point QC	Point QC	% Zero	Average
Site ID	Pass ¹	Span %D ²	Pass ¹	%D ²	Pass ¹	(ppb) ²
HOX148, MI	93.62	3.84	93.62	2.42	93.62	1.22
HWF187, NY	100.00	1.80	97.87	2.16	100.00	0.63
IRL141, FL	100.00	1.25	100.00	1.49	100.00	0.82
KEF112, PA	100.00	0.58	100.00	0.50	100.00	0.14
LRL117, PA	93.68	4.62	93.68	5.05	100.00	0.28
MCK131, KY	100.00	0.82	100.00	0.77	100.00	0.18
MCK231, KY	100.00	0.71	100.00	0.74	100.00	0.19
MKG113, PA	100.00	1.12	100.00	1.62	100.00	0.25
NPT006, ID	97.65	5.25	97.65	3.48	100.00	0.17
OXF122, OH	100.00	1.30	100.00	1.57	100.00	0.44
PAL190, TX	100.00	2.58	100.00	1.98	100.00	0.27
PAR107, WV	100.00	0.41	100.00	0.54	100.00	0.19
PED108, VA	100.00	1.09	100.00	1.12	100.00	0.18
PND165, WY	100.00	1.19	100.00	1.17	100.00	0.23
PNF126, NC	100.00	0.39	100.00	0.61	100.00	0.40
PRK134, WI	100.00	2.04	100.00	1.94	100.00	0.20
PSU106, PA	100.00	0.58	100.00	0.76	100.00	0.24
QAK172, OH	100.00	1.81	100.00	1.87	100.00	0.32
ROM206, CO	100.00	0.58	100.00	0.73	100.00	0.22
SAL133, IN	100.00	0.66	100.00	0.50	100.00	0.16
SAN189, NE	100.00	1.43	100.00	1.39	100.00	0.27
SND152, AL	100.00	2.68	100.00	3.07	100.00	0.29
SPD111, TN	100.00	2.35	100.00	2.64	100.00	0.33
STK138, IL	72.28	19.86	74.23	9.99	74.23	6.72
SUM156, FL	100.00	2.63	100.00	2.20	100.00	0.18
UMA009, WA	100.00	1.74	100.00	1.48	100.00	0.20
UVL124, MI	100.00	0.91	100.00	0.85	100.00	0.22
VIN140, IN	100.00	0.84	100.00	1.41	100.00	0.23
VPI120, VA	100.00	1.14	100.00	1.21	100.00	0.24
WSP144, NJ	100.00	0.88	100.00	0.87	100.00	0.17
WST109, NH	100.00	0.37	100.00	0.47	100.00	0.30

Notes: ¹Percentage of comparisons that pass the criteria listed in Table 4. Values falling below 90 percent are addressed in Table 9.

²Absolute 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.

[%]D = percent difference

ppb = parts per billion

Table 9 Ozone QC Observations for First Quarter 2022

Site ID	QC Criterion	Comments
CNT169, WY	% Span Pass Span %D % Single Point QC Pass Single Point QC %D	The analyzer sample pump failed on 1/18/2022 and was replaced on 1/25/2022.
GAS153, GA	% Span Pass Span %D % Single Point QC Pass Single Point QC %D % Zero Pass	A system leak affected data from 1/30/2022 through 2/8/2022 when it was repaired.
STK138, IL	% Span Pass Span %D % Single Point QC Pass Single Point QC %D % Zero Pass Zero Average	A system leak affected data from 1/15/2022 through 1/27/2022 when it was repaired.

Note: %D = percent difference

Table 10 Trace-level Gas QC Summary for First Quarter 2022

Parameter	% Span Pass ¹	Span %D ²	% Single Point QC Pass ¹	Single Point QC %D ²	% Zero Pass ¹	Zero Average (ppb) ²
		-	BVL130, IL	-		
SO ₂	100.00	0.99	100.00	4.13	94.12	0.80
NO _y	100.00	1.62	100.00	1.78	100.00	0.28
СО	96.55	1.76	100.00	4.28	100.00	11.85
		-	DUK008, NC			
NO _y	100.00	2.44	100.00	1.59	100.00	0.17
		ŀ	- - - - - - - - - - - - - - - - - - -			
NO _y	100.00	1.66	100.00	2.92	96.08	0.36
		F	ND165, WY			
NO _y	100.00	2.06	100.00	2.69	94.44	0.62
	PNF126, NC					
NO _y	100.00	1.88	100.00	1.96	100.00	0.28
	ROM206, CO					
NO _y	100.00	1.63	100.00	3.16	100.00	0.15

Notes: ¹Percentage of comparisons that pass the criteria listed in Table 5.

%D = percent difference ppb = parts per billion

Table 11 Filter Packs Flagged as Suspect or Invalid during First Quarter 2022

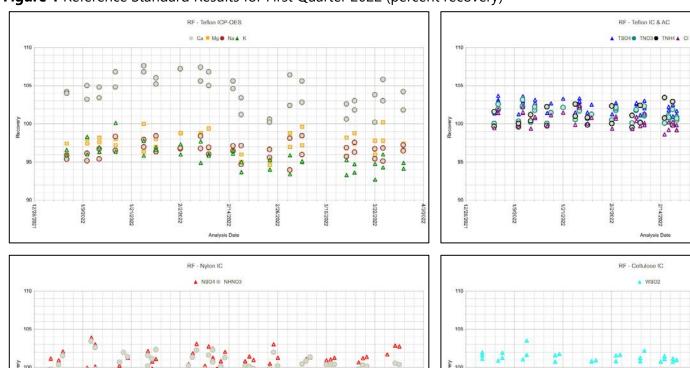
Site ID	Sample No.	Reason
CDR119, WV	2201001-12 2203001-12	A polling issue caused missing data. Data may be recovered during the validation process. Additionally, the data logger malfunctioned and was replaced on 1/25/2022.
NPT006, ID	2201004-04	Power failure
RED004, MN	2203004-05	Power failure
SHN418, VA	2201003-20	Power failure
STK138, IL	2204001-49	There was hole in the Teflon filter.

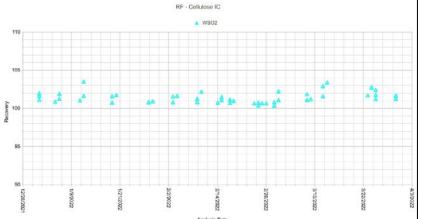
Table 12 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	242
60	6
90	0
Unresolved by end of quarter	3

²Absolute value of the average percent differences between the supplied and observed concentrations.

Figure 1 Reference Standard Results for First Quarter 2022 (percent recovery)

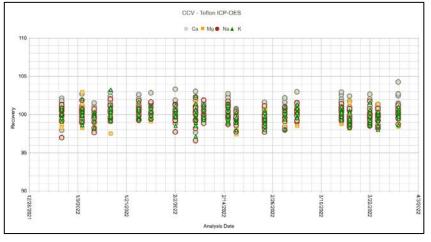


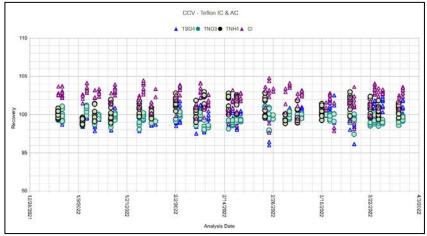


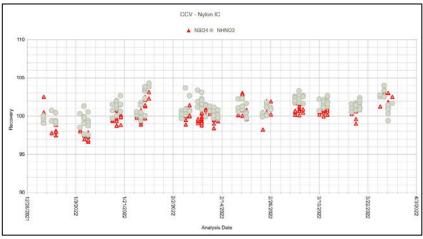
Analysis Date

RF - Teflon IC & AC

Figure 2 Continuing Calibration Spike Results for First Quarter 2022 (percent recovery)







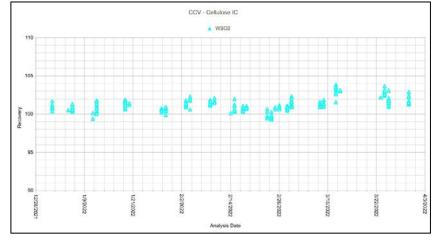
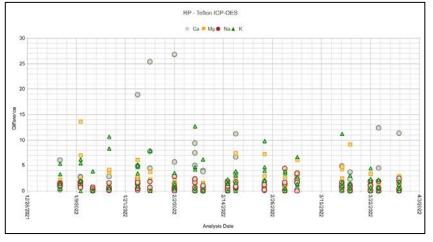
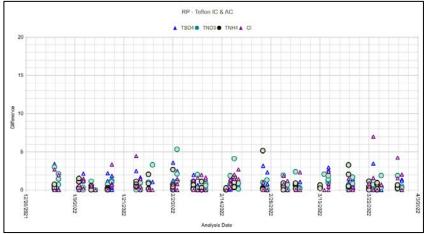
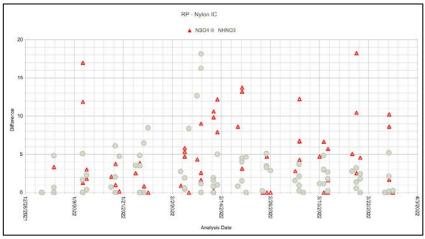


Figure 3 Replicate Sample Analysis Results for First Quarter 2022 (percent difference)







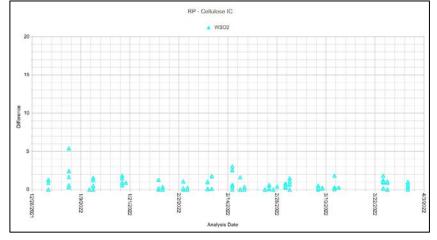
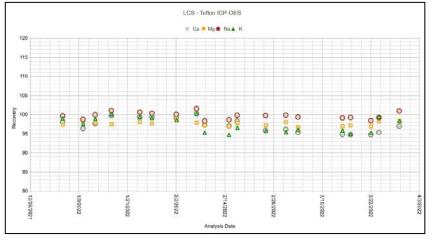
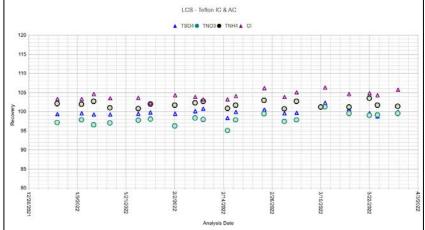
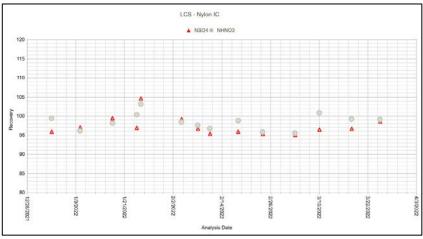


Figure 4 Laboratory Control Sample Results for First Quarter 2022 (percent recovery)







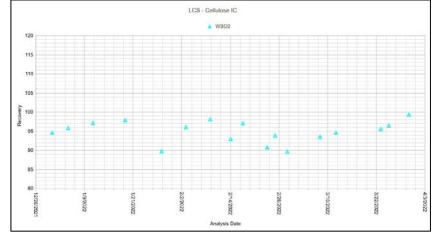
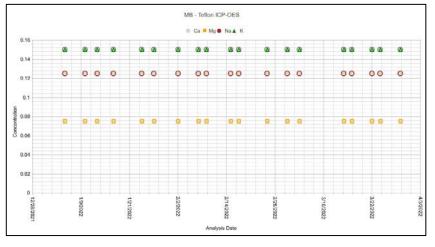
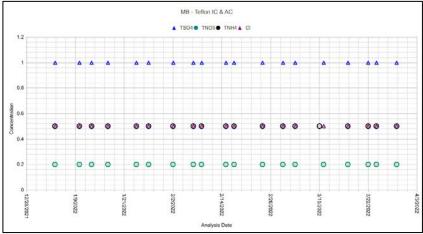
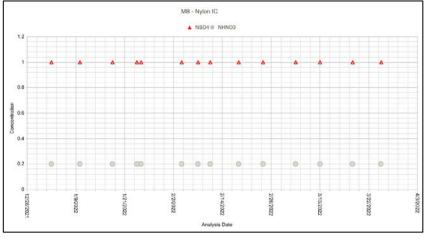


Figure 5 Method Blank Analysis Results for First Quarter 2022 (total micrograms)







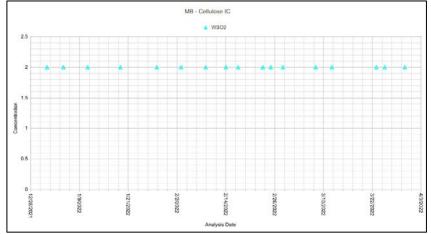
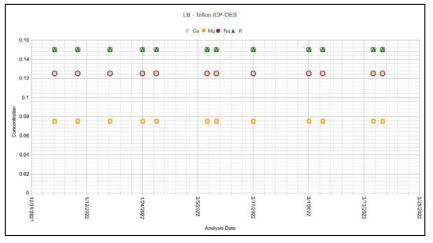
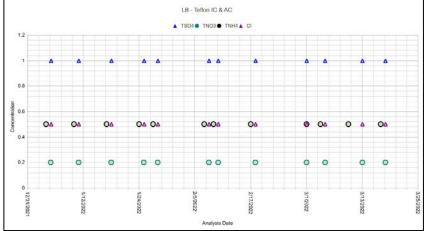
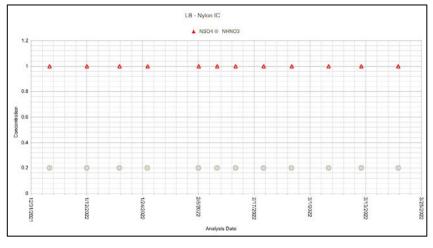


Figure 6 Laboratory Blank Analysis Results for First Quarter 2022 (total micrograms)







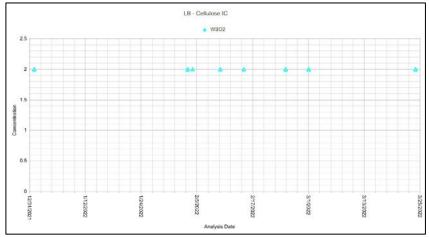


Figure 7 Field Blank Analysis Results for First Quarter 2022 (total micrograms)

