Summary of Quarterly Operations (October through December) with 2021 Annual Summary

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 fourth quarter 2021. It also provides an annual summary that includes data from the three previous quarters. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan (QAPP; Wood, 2020; 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.

Significant Events for 2021

During first quarter, approximately 35 sites received a weekly filter pack shipment with the incorrect quick connect. Most sites were able to use the next week's filter pack instead. About six sites did not have an extra filter pack and ran two-week samples. Replacement filter packs were shipped to the sites that needed them. Laboratory identification numbers were adjusted as filter packs were received to indicate the actual sampling period. Corrective Action No. 0104 was initiated. Actions included retraining personnel, further separation of storage for differing filter pack configurations, and posting a visual reference guide.

During first quarter, the CASTNET QA Manager documented the results of co-located testing that compared MTL nylon filters from lots 709 and 710. The filters compared well. Wood began using nylon filters from lot 710 in CASTNET filter packs during first quarter beginning sampling week 7.

The QA Manager completed review of the metrics for the annual site operator performance assessment during first quarter. These metrics are evaluated annually to determine where additional training is needed.

NADP hosted a Data Quality Objective (DQO) Summit during January 2021. Marcus Stewart, Wood's CASTNET QA Manager, served as a moderator. Previously, Mr. Stewart worked closely with EPA during the development of CASTNET DQO and data quality indicators.

The surveillance assessment required to continue International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025:2017 accreditation by the American Association for Laboratory Accreditation (A2LA) took place April 12–14, 2021, as a virtual assessment. During first quarter, documentation was reviewed and updated as needed. The assessor requested advance, electronic copies of general documentation along with many laboratory and field-related records. Wood supplied the requested documentation and answered questions from the assessor to

help make the audit go smoothly. Additionally, Wood worked with the assessor so he could securely access the Wood network for the remote audit. The virtual assessment went well. There were four findings that required corrective action. Wood addressed the corrective actions. Certified, adjustable pipettes with appropriate certification documentation were ordered. Documentation and other issues were addressed, and the appropriate updates/additions were prepared and provided to A2LA. Wood's ISO/IEC 17025:2017 re-accreditation was approved by A2LA and will continue through May 2023.

During second quarter 2021, the CASTNET QA Manager prepared the annual management review summary presentation as required to maintain ISO/IEC 17025:2017 accreditation by the A2LA. During third quarter, the presentation was distributed to the CASTNET management team, and the annual management review meeting was held to discuss the presentation. The meeting attendees included the CASTNET management team, Wood's Florida Regional Manager, and Wood's East US QA Lead.

In second quarter, Wood learned that the potassium carbonate (K_2CO_3) used to impregnate the cellulose filters was backordered by J.T. Baker, Wood's usual supplier, until January 2022. Wood's supply on-hand was sufficient only through August 2021. Wood began acceptance testing K_2CO_3 from other vendors. During July, Wood conducted a field study to confirm the performance of the K_2CO_3 that passed acceptance testing from four vendors. The study included filters exposed to active and passive flow, laboratory blanks, and field blanks. Wood was looking for K_2CO_3 that not only passed acceptance and field testing but was also the most comparable with J.T. Baker's performance. After all test results were reviewed, Wood selected Fisher as the one vendor to use. Wood verified that Fisher had a sufficient quantity to ensure availability. Wood began using Fisher K_2CO_3 for the solution used to impregnate the cellulose filters for September 2021 sampling activities. The CASTNET QA Manager prepared a summary of the K_2CO_3 testing and results and submitted it to EPA as an attachment to the CASTNET Third Quarter 2021 Quality Assurance Report.

The CASTNET QAPP Revision 9.4 was approved by EPA in early July 2021. As a result of the mid-year approval of Revision 9.4, both QAPP Revision 9.3 and QAPP Revision 9.4 are applicable to CASTNET activities for 2021. Revision 9.3 covers first and second quarter 2021, and Revision 9.4 covers third and fourth quarter 2021.

Wood continued the process of transitioning from hardcopy to electronic documentation. For the CASTNET QAPP Revision 9.4, Wood received approval from EPA to modify statements on double entry to indicate that only items that directly affect atmospheric concentration data (e.g., dates) from the Site Status Report Forms (SSRF) require double entry. During July, the new SSRF dashboard began being tested in iCASTNET. Only two fields on the hard copy SSRF now require double entry in the new dashboard.

During third quarter, The CASTNET QA Manager began working with field personnel to develop a detailed procedure for checking the pressure of gas cylinders while minimizing the risk of contamination. Wood has found empty or nearly empty cylinders in inventory with the manufacturer's seal still intact. A procedure to check pressure without causing contamination will help Wood maintain an adequate number of cylinders ready to go to the sites. Gas cylinders have a long lead-time to delivery.

Wood began evaluating how changes to the new Ozone Technical Assistance Document (TAD; EPA, 2020) will affect ozone criteria and reporting for CASTNET sites. Wood had multiple meetings with EPA, NPS, and ARS to discuss the changes proposed as they pertain to CASTNET. Wood provided comments and observations to EPA's Clean Air Markets Division (CAMD) regarding the new TAD worksheet/spreadsheets.

The draft of the CASTNET QAPP Revision 9.5 was submitted to EPA on November 1, 2021.

The BFT142, NC site failed a NPAP ozone system audit by EPA Region 4 in September 2021. Wood believes the audit was not performed under routine operational conditions because the audit was performed without purge flow to the Nafion dryer. Wood's CASTNET QA Manager issued a corrective action, which included training site operators at sites with Nafion dryers on proper operation of the Nafion dryer during an audit by using a quick connect to allow the dryer to run without a filter pack installed. Additionally, guidelines were provided for site operators and auditors to use for reference. The BFT142 site passed two subsequent PE audits by two different auditors during fourth quarter 2021 indicating the site is operating within criteria when audited under normal operating conditions with purge flow to the Nafion dryer.

Providing a safe working environment is one of Wood's goals. Sites are routinely checked for safe working conditions at each calibration (i.e., twice per year). During 2021, Wood performed internal safety audits of selected sites. These safety audits provide a more in-depth review of site safety and include a safety-related evaluation of infrastructure condition and maintenance, use of equipment, site operator activities at the site, and verification that procedures are understood and followed by site personnel. There were no findings during 2021.

Quarterly/Annual Summary

Table 1 lists the quarters of data that were validated to Level 3 during 2021 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. Table 5 presents the critical criteria for ozone monitoring. Table 6 presents the critical criteria for trace-level gas monitoring.

Laboratory Intercomparison Results Summary

Wood's CASTNET laboratory regularly participates in the Environment and Climate Change Canada (ECCC) Proficiency Testing (PT) Program for Inorganic Environmental Substances. The results reported by the participating laboratories are evaluated for systematic bias and precision. Systematic bias is assessed using the Youden (1969) non-parametric analysis, while precision is calculated using algorithm A from the ISO standard 13528 (ISO, 2005). Laboratory results are considered systematically biased when individual parameters are ranked by the Youden analysis to be consistently and significantly higher or lower than the assigned value without regard to flagged results. The CASTNET laboratory's proficiency testing plan requires action for individual test results that are greater than three standard deviations from the assigned value, bias 5 percent or higher for a single parameter,

three or more biased results of any magnitude in a single study, or a consecutive study result indicating bias of any magnitude for a given parameter.

During second quarter 2021, Wood received results for sample analyses for PT study 117 for Rain and Soft Waters submitted to the Environmental Science and Technology Laboratories Division, a branch of the Water Science and Technology Directorate with ECCC that provides QA services. Sodium was flagged high but within limits. No corrective actions were required. Analyses of all parameters were rated as "good" for PT study 117 (ECCC, 2021). Wood's 5-year average was also rated as "good" (ECCC, 2021).

Wood generally participates in two ECCC PT studies each year. However, because of difficulties caused by the COVID-19 pandemic, ECCC did not run the PT 116 study. The study number 116 was retired in order to preserve the naming convention.

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. Tables 7 through 10 present the number of analyses in each category that were performed during each quarter of 2021.

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 11 presents the relevant sample receipt statistics for each of the four quarters of 2021 together with an annual summary for each category. Due to issues arising from the pandemic and U.S. Postal Service policy decisions, mail delivery service was often delayed resulting in an eighty-seven percent average for 2021.

Data Quality Indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for fourth quarter 2021. All results were within the criteria listed in Table 4. Table 12 presents the percent recoveries and standard deviations for RF, CCV, and RP QC sample analyses for 2021. Quarterly averages are all within criteria.

Table 13 presents quarterly co-located filter pack precision results for data validated to Level 3 during the year. Results for MCK131/231, KY were within the criterion for all of the 11 parameters reported. The MARPD values for K^+ and Cl^- exceeded the 20 percent criterion for ROM406/206 during first quarter 2021. The sample concentrations at these sites were low, averaging about four times the reporting limit for K^+ and less than two times the reporting limit for Cl^-. As noted in Table 4, the

20 percent criterion only applies to values greater than or equal to five times the reporting limit; otherwise, the criterion is ± the reporting limit. The quarterly averages met this criterion.

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

Table 14 presents summary statistics of critical criteria measurements at ozone sites collected during fourth quarter 2021. 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. Table 15 presents observations associated with the shaded cell results in Table 14.

Table 16 presents summary statistics of critical criteria measurements at trace-level gas monitoring sites collected during fourth quarter 2021. 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 6 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 17 presents observations associated with the shaded cell results in Table 16.

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. Figure 5 presents LCS analysis results for fourth quarter 2021. All recovery values were between 92 percent and 112 percent.

Blank Results

Figures 6 through 8 present the results of MB, LB, and FB QC sample analyses for fourth quarter 2021. All fourth quarter results were within criteria (two times the reporting limit) listed in Table 4 with the exception of two cellulose filter FB results. All other associated QC were within criteria, and the data from associated sites (CDR119, WV and CDZ171, KY) were reasonable. Table 18 summarizes the record of filter blanks for 2021. All 2021 results were within criteria listed in Table 4 with the exception of the fourth quarter FB results discussed above and several second and third quarter cellulose filter acceptance test results. All failing cellulose filter acceptance test results were associated with Wood acceptance testing the candidate vendor K_2CO_3 to determine the best replacement for J.T. Baker K_2CO_3 as discussed in the Significant Events section. All other blank QC checks in their respective batches were within criteria.

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during each of the four quarters of 2021 are listed in Table 19. This table also includes associated site identification and a brief description of the reason the sample was flagged. During fourth quarter, nine filter pack samples were invalidated.

Field Problem Count

Table 20 presents counts of field problems affecting continuous data collection for more than one day for each quarter during 2021. 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

A summary of field calibration failures by parameter for each quarter of 2021 is listed in Table 21. Calibrations were performed at 17 sites during fourth quarter 2021. During 2021, all sites and parameters were within the criteria listed in Table 3 with the exception of the parameters at the six sites that are listed in Table 21.

Table 22 presents field accuracy results for 2021 based on instrument challenges performed using independent reference standards during site calibration visits. Each parameter was within its criterion with at least 90 percent frequency except wind speed greater than 5 meters per second at 87.5 percent frequency and solar radiation at 87.5 percent frequency. Per CASTNET project protocols, data are flagged but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within two times the criterion). All calibration failures reported in 2021 for the indicated parameters were within two times the criterion with the exception of wind speed at IRL141, FL and flow rate at ALC188, TX; CAT175, NY; OXF122, OH; and PAL190, TX. Data associated with these failures were invalidated.

References

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Table 1 Data Validated to Level 3 through Fourth Quarter 2021

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
SE-4/MW-6†	July 2020 – June 2021	12	Quarter 3 2020 – Quarter 2 2021	4
E-1/SE-5	August 2020 – July 2021	12	Quarter 4 2020 – Quarter 2 2021	3
MW-7/W-9	September 2020 – August 2021	12	Quarter 4 2020 – Quarter 2 2021	3
E-2/MW-8	October 2020 – September 2021	12	Quarter 4 2020 – Quarter 3 2021	4
E-3/W-10‡	May 2020 – April 2021	12	Quarter 3 2020 – Quarter 1 2021	3

Notes: * The sites contained in each calibration group are listed in Table 2.
† Contains MCK131/231 co-located pair
‡ Contains ROM206 of the ROM406/ROM206 co-located pair

Table 2 Field Calibration Schedule for 2021

Calibration Group	Months Calibrated	Sites Calibrated				
Eastern Sites (22 Total)						
E-1 (8 Sites)	February/August	BEL116, MD	WSP144, NJ	ARE128, PA	PED108, VA	
		BWR139, MD	CTH110, NY	PSU106, PA	VPI120, VA	
E-2 (9 Sites)	April/October	ABT147, CT	WST109, NH	HWF187, NY[1]	WFM105, NY	UND002, VT
		ASH135, ME	CAT175, NY	NIC001, NY	EGB181, ON	
E-3 (5 Sites)	May/November	KEF112, PA	LRL117, PA	CDR119, WV		
		MKG113, PA	PAR107, WV			
Southeastern Sites (11 Total)						
SE-4 (7 Sites)	January/July	SND152, AL	BFT142, NC	COW137, NC	SPD111, TN	
		GAS153, GA	CND125, NC	DUK008, NC[1]		
SE-5 (4 Sites)	February/August	CAD150, AR	SUM156, FL			
		IRL141, FL	CVL151, MS			
Midwestern Sites (19 Total)						
MW-6 (6 Sites)	January/July	CDZ171, KY	MCK131, KY	PNF126, NC[1]		
		CKT136, KY	MCK231, KY	ESP127, TN		
MW-7 (9 Sites)	March/September	ALH157, IL	STK138, IL	RED004, MN	OXF122, OH	PRK134, WI
		BVL130, IL[2]	VIN140, IN	DCP114, OH	QAK172, OH	
MW-8 (4 Sites)	April/October	SAL133, IN	ANA115, MI			
		HOX148, MI	UVL124, MI			
Western Sites (12 Total)						
W-9 (5 Sites)	March/September	KNZ184, KS	CHE185, OK	ALC188, TX		
		KIC003, KS	SAN189, NE			
W-10 (7 Sites)	May/November	GTH161, CO	NPT006, ID	UMA009, WA	PND165, WY[3]	
		ROM206, CO[3]	PAL190, TX	CNT169, WY		

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

Measurement		Criteria[1]	
Parameter[2]	Method	Precision	Accuracy
Filter pack flow	Mass flow controller	± 10%	± 5%
Ozone[3]	UV absorbance	All points within ± 2% of full scale of best fit straight line Linearity error < 5%	
Wind speed	Anemometer	± 0.5 m/s	The greater of ± 0.5 m/s for winds < 5 m/s or ± 5% for winds ≥ 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[4]
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

[1]Precision criteria apply to co-located instruments, and accuracy criteria apply to calibration of instruments. Co-located precision criteria do not apply to CASTNET sites that are configured and operated in accordance with Part 58 of Title 40 of the *Code of Federal Regulations* (EPA, 2020)

[2]Meteorological parameters are only measured at five of the EPA-sponsored CASTNET sites: IRL141, FL: BVL130, IL; BEL116, MD; CHE185, OK; and PND165, WY.

[3]Ozone is not measured at eight EPA-sponsored CASTNET sites: KIC003, KS; KNZ184, KS; RED004, MN; EGB181, ON; CAT175, NY; NIC001, NY; WFM105, NY; and UND002, VT.

[4]For target value of 0.50 inch

Table 4 Data Quality Indicators for CASTNET Laboratory Measurements

Analyte	Method	Precision[1] (MARPD)	Accuracy[2] (%)	Nominal Reporting Limits	
				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

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 µg/filter).

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, 2020; 2021).

Table 5 Ozone Critical Criteria*

Type of 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 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).

Table 6 Trace-level Gas Monitoring Critical Criteria*

Parameter	Analyzer Response	
	Zero Check	Span Check / Single Point QC Check
SO_2	Less than ± 1.51 ppb	Less than ± 10.1 percent between supplied and observed concentrations
NO_y	Less than ± 1.51 ppb	
CO	Less than ± 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 7 QC Analysis Count for First Quarter 2021

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-}	75	211	87	19	26	97
	NO_3^-	75	211	87	19	26	97
	NH_4^+	38	179	88	19	26	101
	Cl^-	75	211	87	19	26	97
	Ca^{2+}	38	194	88	19	26	101
	Mg^{2+}	38	194	88	19	26	101
	Na^+	38	194	88	19	26	101
	K^+	38	194	88	19	26	101
Nylon	SO_4^{2-}	58	203	82	18	26	100
	NO_3^-	58	203	82	18	26	100
Cellulose	SO_4^{2-}	51	184	84	19	26	100

Table 8 QC Analysis Count for Second Quarter 2021

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-}	75	211	83	18	24	97
	NO_3^-	75	211	83	18	24	97
	NH_4^+	36	171	82	18	22	93
	Cl^-	75	211	83	18	24	97
	Ca^{2+}	36	188	82	18	22	93
	Mg^{2+}	36	188	82	18	22	93
	Na^+	36	188	82	18	22	93
	K^+	36	188	82	18	22	93
Nylon	SO_4^{2-}	54	203	88	18	24	94
	NO_3^-	54	203	88	18	24	94
Cellulose	SO_4^{2-}	51	192	88	20	24	94

Table 9 QC Analysis Count for Third Quarter 2021

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-}	63	182	74	15	24	47
	NO_3^-	63	182	74	15	24	47
	NH_4^+	30	141	71	15	22	47
	Cl^-	63	182	74	15	24	47
	Ca^{2+}	30	161	71	15	22	47
	Mg^{2+}	30	161	71	15	22	47
	Na^+	30	161	71	15	22	47
	K^+	30	161	71	15	22	47
Nylon	SO_4^{2-}	45	178	75	15	24	47
	NO_3^-	45	178	75	15	24	47
Cellulose	SO_4^{2-}	53	171	74	16	22	47

Table 10 QC Analysis Count for Fourth Quarter 2021

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-}	69	197	81	17	24	54
	NO_3^-	69	197	81	17	24	54
	NH_4^+	36	159	79	17	22	54
	Cl^-	69	197	81	17	24	54
	Ca^{2+}	39	193	90	19	24	89
	Mg^{2+}	39	193	90	19	24	89
	Na^+	39	193	90	19	24	89
	K^+	39	193	90	19	24	89
Nylon	SO_4^{2-}	41	174	77	14	24	64
	NO_3^-	41	174	77	14	24	64
Cellulose	SO_4^{2-}	53	180	79	15	24	92

Table 11 Filter Pack Receipt Summary for 2021

Description	First Quarter	Second Quarter	Third Quarter	Fourth Quarter	Annual Summary
Count of samples received more than 14 days after removal from tower:	231	73	38	27	369
Count of all samples received:	611	743	685	710	2749
Fraction of samples received within 14 days:	0.622	0.902	0.945	0.962	0.866
Average interval in days:	14.309	8.382	7.409	8.066	9.542*
First receipt date:	01/07/2021	04/01/2021	07/01/2021	10/04/2021	01/07/2021
Last receipt date:	03/18/2021	06/24/2021	09/14/2021	12/21/2021	12/21/2021

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

Table 12 Filter Pack QC Summary for 2021

Filter Type	Parameter	Reference Sample[1] Recovery (%R)			Continuing Calibration Verification Samples (%R)			In-Run Replicate[2] (RPD)		
		Mean	Std. Dev.	Count[3]	Mean	Std. Dev.	Count[3]	Mean	Std. Dev.	Count[3]
Teflon	SO_4^{2-}	102.02	1.31	290	101.05	1.38	825	0.85	0.83	336
	NO_3^-	101.16	1.48	290	99.40	1.20	825	1.32	1.40	336
	NH_4^+	99.93	1.83	146	99.97	1.13	678	0.58	0.71	335
	Cl^-	100.69	1.46	290	100.91	1.77	825	1.85	1.66	336
	Ca^{2+}	101.13	2.24	145	100.64	1.00	747	1.89	2.74	336
	Mg^{2+}	99.76	1.47	145	99.90	0.82	747	1.92	2.05	336
	Na^+	96.96	1.17	145	99.89	0.92	747	1.27	1.61	336
	K^+	97.77	1.52	145	99.92	0.79	747	2.21	2.48	336
Nylon	SO_4^{2-}	101.67	1.35	201	100.36	1.50	770	4.18	3.88	327
	NO_3^-	101.08	1.43	201	99.52	2.04	770	2.05	2.17	327
Cellulose	SO_4^{2-}	101.09	1.01	212	100.42	0.84	732	1.65	1.87	331

Notes: % R = percent recovery
RPD = relative percent difference

[1]Results of reference sample analyses provide accuracy estimates
[2]Results of replicate analyses provide precision estimates
[3]Number of QC Samples

Table 13 Precision Results for Third Quarter 2016 through Second Quarter 2021

Quarter	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	HNO_3	SO_2	Total NO_3^-
MCK131/231, KY											
2020 Q3	2.46	6.01	3.73	5.74	3.79	4.65	2.81	0.21	2.77	4.49	2.74
2020 Q4	7.07	8.76	7.46	7.98	5.85	6.40	9.73	5.41	9.86	6.00	8.12
2021 Q1	2.08	5.21	3.85	7.14	5.60	3.29	3.41	8.92	7.97	4.19	2.70
2021 Q2	2.39	7.96	2.81	8.19	9.12	2.79	14.01	0.39	3.14	1.92	3.48
Average	3.50	6.99	4.46	7.26	6.09	4.28	7.49	3.73	5.94	4.15	4.26
ROM406/206, CO											
2020 Q3	3.21	7.92	7.30	7.38	9.22	4.67	5.94	13.41	5.53	6.79	4.59
2020 Q4	7.27	9.52	12.24	10.03	13.08	11.63	10.36	18.97	4.97	12.27	4.86
2021 Q1*	5.03	11.03	7.19	11.97	16.53	10.84	22.90	21.47	14.24	9.93	8.86
2021 Q2	3.61	9.35	6.92	7.86	9.55	14.28	9.48	13.86	9.84	17.58	5.18
Average	4.78	9.46	8.41	9.31	12.10	10.36	12.17	16.93	8.65	11.64	5.87

Notes: 2 of 88 site-quarter-parameters were outside criterion

*As noted in Table 4, the 20 percent criterion only applies to values greater than or equal to five times the reporting limit; otherwise, the criterion is ± the reporting limit. The quarterly averages met this criterion.

Table 14 Ozone QC Summary for Fourth Quarter 2021 (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	0.34	100.00	0.35	100.00	0.13
ALC188, TX	100.00	1.32	100.00	1.12	100.00	0.35
ALH157, IL	100.00	0.78	100.00	1.08	100.00	0.16
ANA115, MI	100.00	1.43	100.00	2.32	100.00	1.06
ARE128, PA	100.00	1.03	100.00	1.00	100.00	0.18
ASH135, ME	82.35	8.12	82.35	8.02	100.00	0.25
BEL116, MD	100.00	1.31	100.00	1.22	100.00	0.57
BFT142, NC	100.00	0.75	100.00	0.99	100.00	0.37
BVL130, IL	100.00	5.66	97.89	5.79	100.00	0.17
BWR139, MD	100.00	0.96	100.00	1.23	98.95	0.37
CAD150, AR	100.00	2.26	98.53	2.60	100.00	0.37
CDR119, WV	100.00	1.21	100.00	1.18	100.00	0.24
CDZ171, KY	98.92	1.59	100.00	0.67	100.00	0.29
CKT136, KY	100.00	0.50	100.00	0.54	100.00	0.12
CND125, NC	100.00	1.66	98.90	1.68	98.90	0.92
CNT169, WY	100.00	0.69	100.00	0.48	100.00	0.25
COW137, NC	100.00	0.52	100.00	0.98	98.97	0.52
CTH110, NY	100.00	2.75	100.00	2.85	100.00	0.14
CVL151, MS	100.00	1.15	100.00	0.66	100.00	0.30
DCP114, OH	100.00	1.31	100.00	1.29	100.00	0.91
ESP127, TN	100.00	0.87	100.00	0.96	100.00	0.25
GAS153, GA	92.47	9.82	92.47	9.23	97.89	1.25
GTH161, CO	100.00	0.82	100.00	1.16	100.00	0.20
HOX148, MI	100.00	1.43	100.00	1.61	100.00	0.16
HWF187, NY	98.94	2.82	98.94	1.94	100.00	0.46
IRL141, FL	100.00	1.98	100.00	2.62	100.00	0.83
KEF112, PA	100.00	0.94	100.00	0.82	100.00	0.15
LRL117, PA	100.00	1.19	100.00	1.13	100.00	0.32
MCK131, KY	100.00	1.53	98.94	1.73	100.00	0.19
MCK231, KY	100.00	0.38	100.00	0.53	100.00	0.17
MKG113, PA	100.00	1.32	100.00	2.07	100.00	0.25
NPT006, ID	98.90	2.42	100.00	1.56	100.00	0.19

Table 14 Ozone QC Summary for Fourth Quarter 2021 (2 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]
OXF122, OH	100.00	0.88	100.00	1.27	100.00	0.52
PAL190, TX	98.92	3.71	100.00	3.08	100.00	0.24
PAR107, WV	100.00	1.30	100.00	1.31	100.00	0.24
PED108, VA	100.00	0.83	100.00	1.15	100.00	0.32
PND165, WY	95.51	6.09	95.51	6.29	100.00	0.17
PNF126, NC	95.65	3.96	95.65	2.83	95.65	2.27
PRK134, WI	100.00	0.64	100.00	0.70	100.00	0.17
PSU106, PA	100.00	0.53	100.00	0.78	100.00	0.17
QAK172, OH	96.97	3.43	93.88	5.52	93.88	2.19
ROM206, CO	98.95	0.81	98.95	1.06	100.00	0.17
SAL133, IN	100.00	0.57	100.00	0.55	100.00	0.22
SAN189, NE	100.00	1.57	100.00	1.22	100.00	0.23
SND152, AL	100.00	0.49	100.00	0.83	100.00	0.38
SPD111, TN	100.00	0.66	97.85	5.49	100.00	0.15
STK138, IL	97.85	2.03	97.85	4.34	97.85	1.89
SUM156, FL	100.00	2.63	100.00	2.19	100.00	0.17
UMA009, WA	100.00	1.61	100.00	1.51	100.00	0.27
UVL124, MI	97.92	3.33	100.00	1.17	100.00	0.21
VIN140, IN	100.00	0.90	100.00	1.22	100.00	0.35
VPI120, VA	100.00	0.74	100.00	0.76	100.00	0.17
WSP144, NJ	100.00	0.99	100.00	0.87	100.00	0.22
WST109, NY	98.94	0.65	100.00	0.43	100.00	0.23

Notes: [1]Percentage of comparisons that pass the criteria listed in Table 5. Values falling below 90 percent are addressed in Table 15.

[2]Absolute value of the average percent differences between the on-site transfer standard and the site monitor. Values exceeding the criteria listed in Table 5 are addressed in Table 15.

%D = percent difference

ppb = parts per billion

Table 15 Ozone QC Observations for Fourth Quarter 2021

Site ID	QC Criterion	Comments
ASH135, ME	% Span Pass Span |%D| % Single Point QC Pass Single Point QC |%D|	The ozone sample pump failed on 11/3/2021 and was replaced 11/12/2021.
GAS153, GA	Span |%D| Single Point QC |%D|	The sample pump failed from 10/24/2021 to 10/27/2021.

Note: %D = percent difference

Table 16 Trace-level Gas QC Summary for Fourth Quarter 2021

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	1.33	100.00	1.67	100.00	0.37
NO_y	100.00	0.98	100.00	1.47	100.00	0.55
CO	92.31	2.76	57.69	22.82	52.83	52.02
DUK008, NC						
NO_y	100.00	2.49	100.00	2.26	100.00	0.34
HWF187, NY						
NO_y	100.00	2.69	100.00	2.85	98.00	0.62
PND165, WY						
NO_y	100.00	2.99	100.00	4.43	100.00	0.30
PNF126, NC						
NO_y	100.00	1.17	100.00	2.70	100.00	0.21
ROM206, CO						
NO_y	100.00	2.38	100.00	4.93	100.00	0.11

Notes: [1]Percentage of comparisons that pass the criteria listed in Table 6. Values falling below 90 percent are addressed in Table 17.

[2]Absolute value of the average percent differences between the supplied and observed concentrations. Values exceeding the criteria listed in Table 6 are addressed in Table 17.

%D = percent difference
ppb = parts per billion

Table 17 Trace-level Gas QC Observations for Fourth Quarter 2021

Site ID	Parameter	QC Criterion	Comments
BVL130, IL	CO	% Single Point QC Pass Single Point QC |%D| % Zero Pass Zero Average	The CO analyzer malfunctioned and was replaced in December 2021.

Notes: %D = percent difference

Table 18 Summary of Filter Blanks for 2021 (1 of 2)

Parameter Name	Detection Limit Total μg	Total Number	Number > Detection Limit	Average Total μg	Average Absolute Deviation	Maximum Total μg
FIELD BLANKS						
Teflon-NH_4^+-N	0.500	336	0	0.500	0.000	0.500
Teflon- NO_3^--N	0.200	336	0	0.200	0.000	0.200
Teflon- SO_4^{2-}	1.000	336	0	1.000	0.000	1.000
Cl^-	0.500	336	0	0.500	0.000	0.500
Ca^{2+}	0.150	336	3	0.150	0.001	0.225
Mg^{2+}	0.075	336	0	0.075	0.000	0.075
Na^+	0.125	336	0	0.125	0.000	0.125
K^+	0.150	336	9	0.151	0.002	0.215
Nylon- NO_3^--N	0.200	336	0	0.200	0.000	0.200
Nylon - SO_4^{2-}	1.000	336	0	1.000	0.000	1.000
Cellulose - SO_4^{2-}	2.000	336	47	2.110	0.191	8.910
LABORATORY BLANKS						
Teflon-NH_4^+-N	0.500	104	0	0.500	0.000	0.500
Teflon- NO_3^--N	0.200	104	0	0.200	0.000	0.200
Teflon- SO_4^{2-}	1.000	104	0	1.000	0.000	1.000
Cl^-	0.500	104	0	0.500	0.000	0.500
Ca^{2+}	0.150	104	1	0.150	0.000	0.155
Mg^{2+}	0.075	104	0	0.075	0.000	0.075
Na^+	0.125	104	0	0.125	0.000	0.125
K^+	0.150	104	2	0.151	0.001	0.180
Nylon- NO_3^--N	0.200	104	1	0.201	0.003	0.340
Nylon -SO_4^{2-}	1.000	104	3	1.009	0.018	1.475
Cellulose -SO_4^{2-}	2.000	104	0	2.000	0.000	2.000

Table 18 Summary of Filter Blanks for 2021 (2 of 2)

Parameter Name	Detection Limit Total μg	Total Number	Number > Detection Limit	Average Total μg	Average Absolute Deviation	Maximum Total μg
METHOD BLANKS						
Teflon-NH_4^+-N	0.500	72	0	0.500	0.000	0.500
Teflon- NO_3^--N	0.200	72	0	0.200	0.000	0.200
Teflon- SO_4^{2-}	1.000	72	0	1.000	0.000	1.000
Cl^-	0.500	72	0	0.500	0.000	0.500
Ca^{2+}	0.150	72	0	0.150	0.000	0.150
Mg^{2+}	0.075	72	0	0.075	0.000	0.075
Na^+	0.125	72	0	0.125	0.000	0.125
K^+	0.150	72	0	0.150	0.000	0.150
Nylon- NO_3^--N	0.200	66	0	0.200	0.000	0.200
Nylon -SO_4^{2-}	1.000	66	0	1.000	0.000	1.000
Cellulose -SO_4^{2-}	2.000	72	0	2.000	0.000	2.000
ACCEPTANCE TEST VALUES[1]						
Teflon-NH_4^+-N	0.500	192	0	0.500	0.000	0.500
Teflon- NO_3^--N	0.200	192	0	0.200	0.000	0.200
Teflon- SO_4^{2-}	1.000	192	0	1.000	0.000	1.000
Cl^-	0.500	192	0	0.500	0.000	0.500
Ca^{2+}	0.150	192	0	0.150	0.000	0.150
Mg^{2+}	0.075	192	0	0.075	0.000	0.075
Na^+	0.125	192	0	0.125	0.000	0.125
K^+	0.150	192	0	0.150	0.000	0.150
Nylon- NO_3^--N	0.200	240	2	0.201	0.002	0.358
Nylon -SO_4^{2-}	1.000	240	0	1.000	0.000	1.000
Cellulose -SO_4^{2-}	2.000	377	43	2.172	0.305	7.030

Note: [1]Only filter batches passing QC requirements are used for sampling and analysis.

Table 19 Filter Packs Flagged as Suspect or Invalid

Site ID	Sample	Reason
First Quarter 2021		
CAT175, NY	2107001-11	Power failures
MEV405, CO	2107003-15	Power failure
NPT006, ID	2106004-04	Power failure
PED108, VA	2107001-39	Power failure
SHE604, WY	2107005-05	Power failure
SUM156, FL	2106001-50	Suspected contamination during sampling
Second Quarter 2021		
ALC188, TX	2121004-01	Power failures affected two weeks of sampling.
BBE401, TX	2118003-02	Insufficient flow volume was caused by a flow system leak.
BUF603, WY	2121005-02	The data logger malfunctioned.
CDR119, WV	2119001-12	A power failure affected one week of sampling.
CHE185, OK	2117004-02	The sample was invalidated for suspect data.
FOR605, WY	2118005-03	A polling issue caused missing data. Data were subsequently recovered.
JOT403, CA	2118003-12	A polling issue caused missing data. Data were subsequently recovered.
LRL117, PA	2115001-31	The sample was invalidated for suspect data.
PIN414, CA	2118003-17	Insufficient flow volume was caused by a flow system leak.
PND165, WY	2120001-40	The data logger malfunctioned.
Third Quarter 2021		
CAD150, AR	2129001-10	Filter pack was invalidated for suspect data.
CDR119, WV	2128001-12 2129001-12	Particles were observed on filters downstream from the Teflon filter.
FOR605, WY	2128005-03	Power failure
JOT403, CA	2131003-12	A polling issue caused missing data. Data were subsequently recovered.
PIN414, CA	2130003-17	Flow data were flagged as invalid by ARS.
QAK172, OH	2128001-44	The site sustained storm damage.
Fourth Quarter 2021		
BVL130, IL	2142001-08	Cellulose filter results invalidated as suspect.
CND125, NC	2146001-15	MFC failed during the sampling period. New MFC installed 11/16/2021.
GRS420, TN	2144003-11	Failing flow pump
IRL141, FL	2143001-28	Cellulose filter results invalidated as suspect.
KEF112, PA	2144001-29	The Balston filter was saturated, resulting in insufficient flow volume.
KIC003, KS	2146004-03	Power failure
THR422, ND	2144003-21 2145003-21	Flow system leak
WNC429, SD	2144003-23	Flow system leak

Table 20 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
First Quarter 2021	
30	218
60	5
90	2
Unresolved by End of Quarter	3
Second Quarter 2021	
30	401
60	8
90	2
Unresolved by End of Quarter	39
Third Quarter 2021	
30	463
60	1
90	2
Unresolved by End of Quarter	4
Fourth Quarter 2021	
30	238
60	8
90	4
Unresolved by Date of Publication	25

Table 21 Field Calibration Failures by Parameter for 2021

Site ID	Parameter(s)	Quarter
ALC188, TX	Temperature (ambient)	Q1
	Flow Rate	Q3
CAT175, NY	Flow Rate	Q3
CND125, NC	Flow Rate	Q3
OXF122, OH	Flow Rate	Q3
PAL190, TX	Flow Rate	Q4
IRL141, FL	Wind speed/direction	Q1
	Solar radiation*	Q3

Note: Per CASTNET project protocols, data for all parameters except flow are flagged as "suspect" (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within two times the criterion). If flow calibrations fall within two times the criterion, these data are adjusted per approved protocol described in the CASTNET QAPP, (Wood, 2020; 2021). Please refer to Table 15 for documentation of the QC failures affecting the validity of ozone data.

*Failure was due to a faulty transfer standard and was disregarded.

Table 22 Accuracy Results for 2021 Field Measurements

Parameter	Percent Within Criterion
Flow Rate	96.2
Wind Speed < 5 m/s	100.0
Wind Speed ≥ 5 m/s*	87.5
Wind Direction North	100.0
Wind Direction South*	100.0
Temperature (0°C)	100.0
Temperature (ambient)	99.2
Delta Temperature (0°C)	100.0
Delta Temperature (ambient)	100.0
Relative Humidity	100.0
Precipitation	100.0
Solar Radiation*	87.5
Wetness (w/in 0.5 volts)	100.0

Notes: °C = degrees Celsius
m/s = meters per second
* = Per CASTNET project protocols, data are flagged as "suspect" (S) but still considered valid if the calibration criterion is not exceeded by more than its magnitude (i.e., if within two times the criterion). All calibration failures reported in 2021 for the indicated parameters were within two times the criterion with the exception of wind speed at IRL141, FL and flow rate at ALC188, TX, CAT175, NY, OXF122, OH, and PAL190, TX. Associated data were invalidated.

Figure 1 Reference Standard Results for Fourth Quarter 2021 (percent recovery)

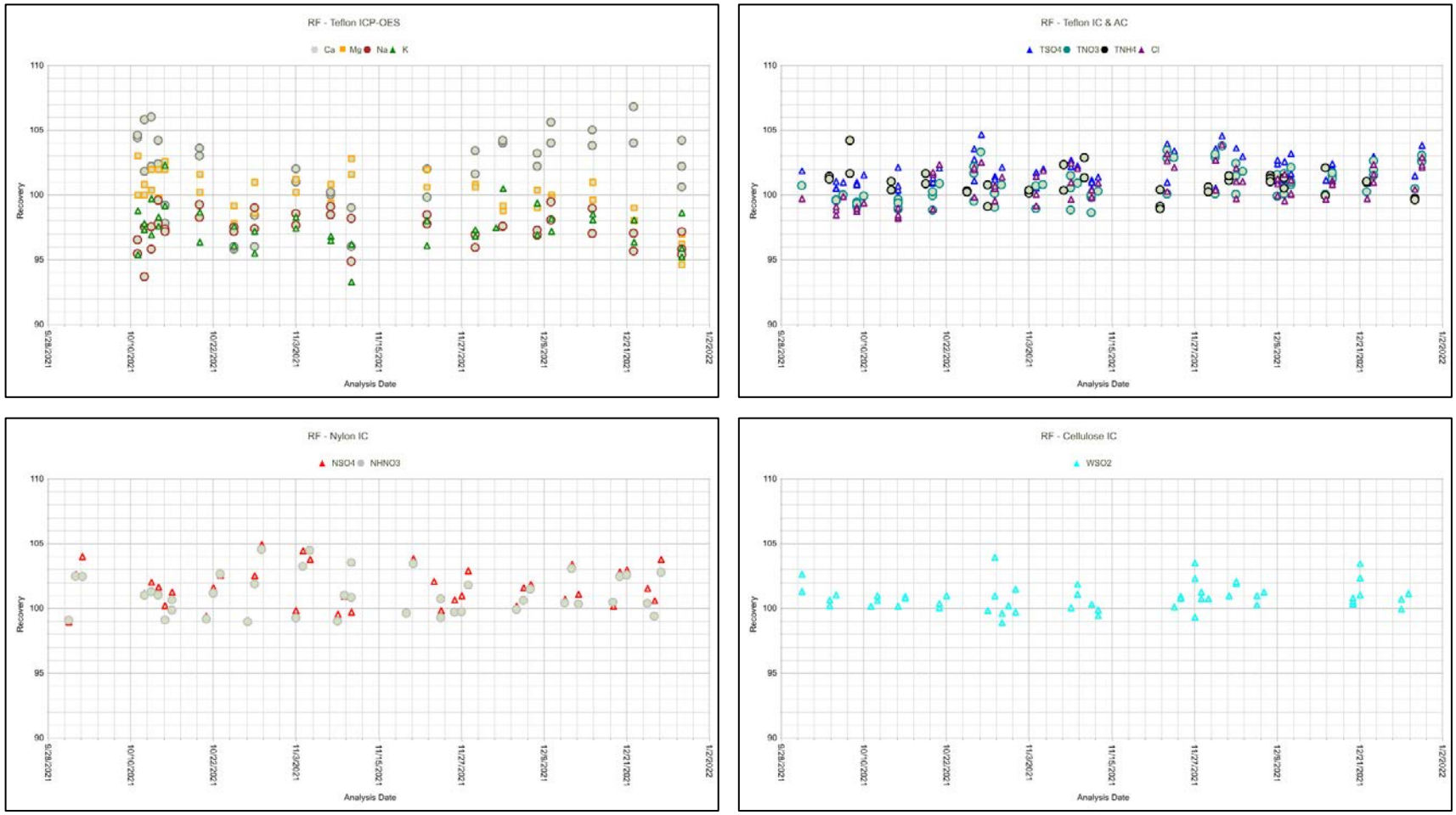


Figure 2 Continuing Calibration Spike Results for Fourth Quarter 2021 (percent recovery)

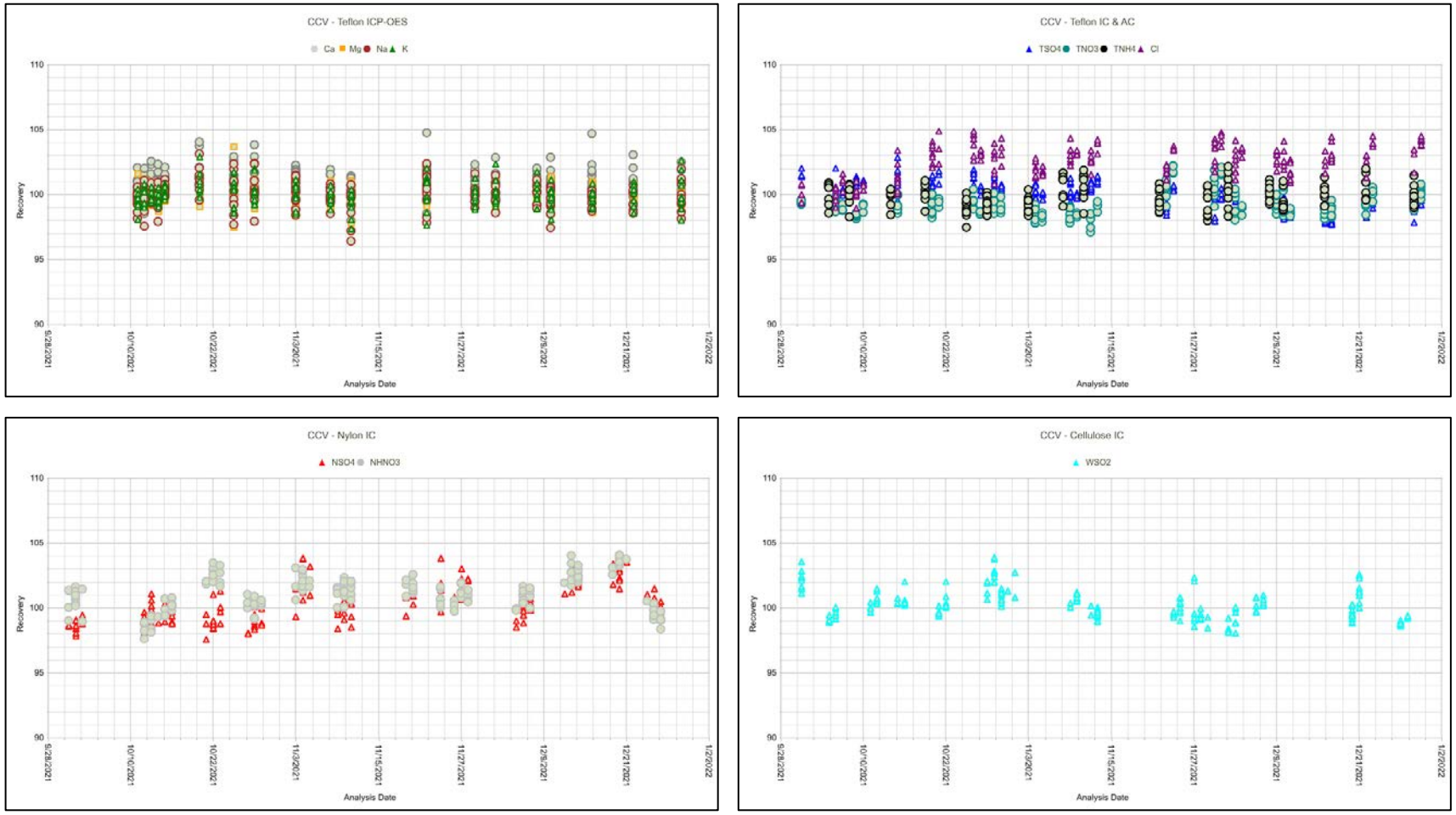


Figure 3 Replicate Sample Analysis Results for Fourth Quarter 2021 (percent difference)

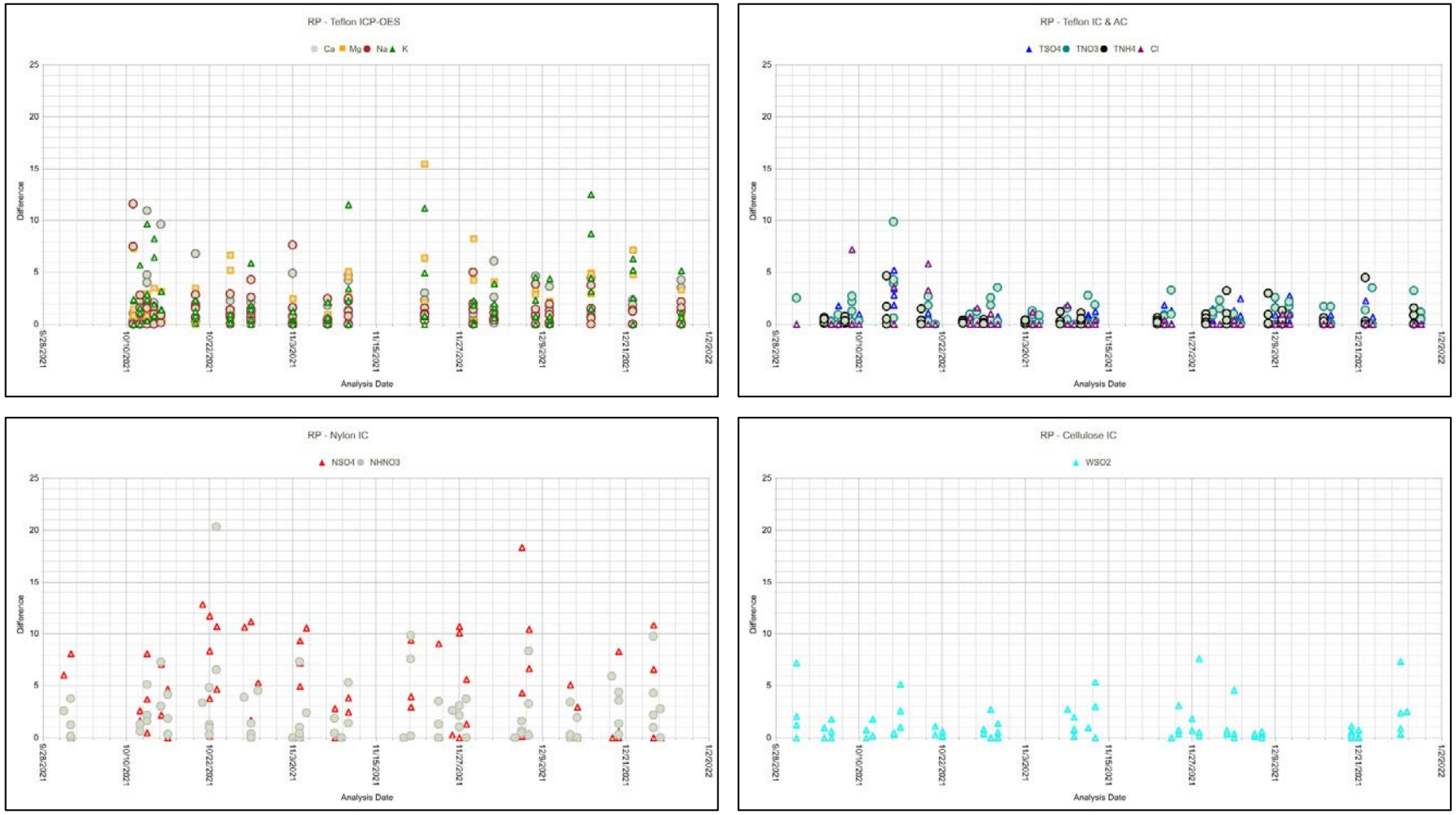
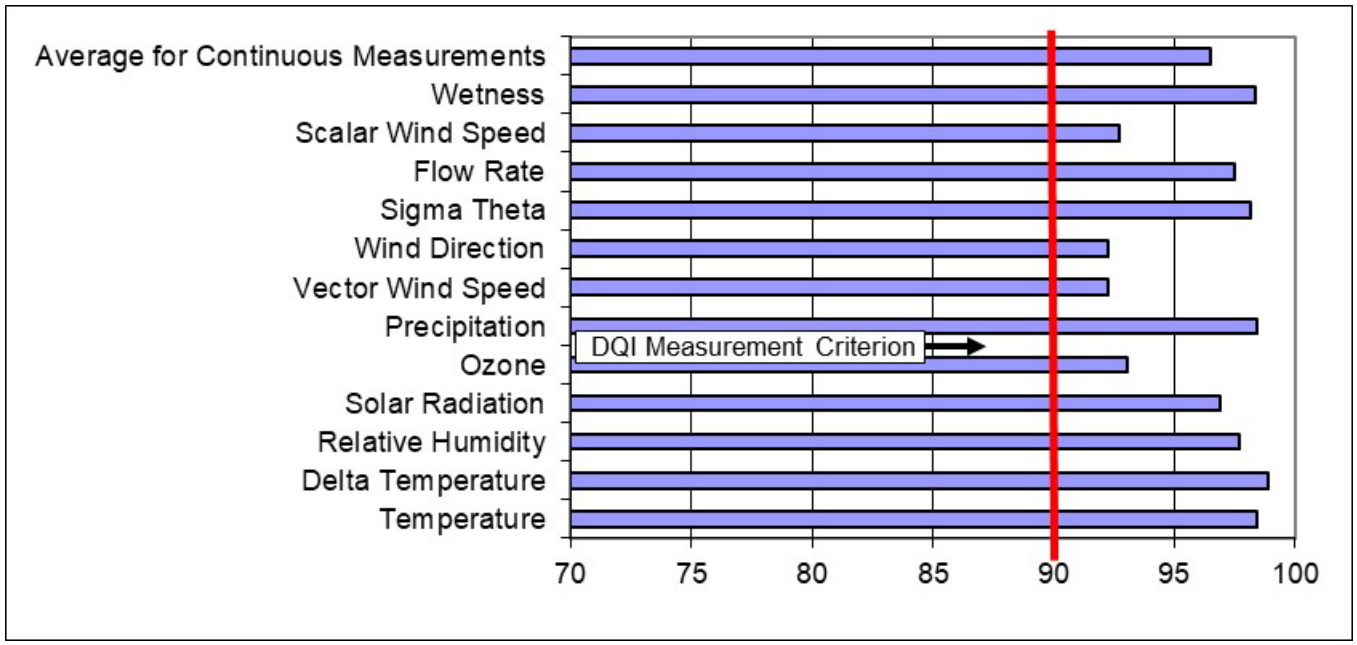


Figure 4 Percent Completeness of Measurements for Second Quarter 2020 through Third Quarter 2021*



Note: *Presents Level 3 data available during the fourth quarter of 2021

Figure 5 Laboratory Control Sample Results for Fourth Quarter 2021 (percent recovery)

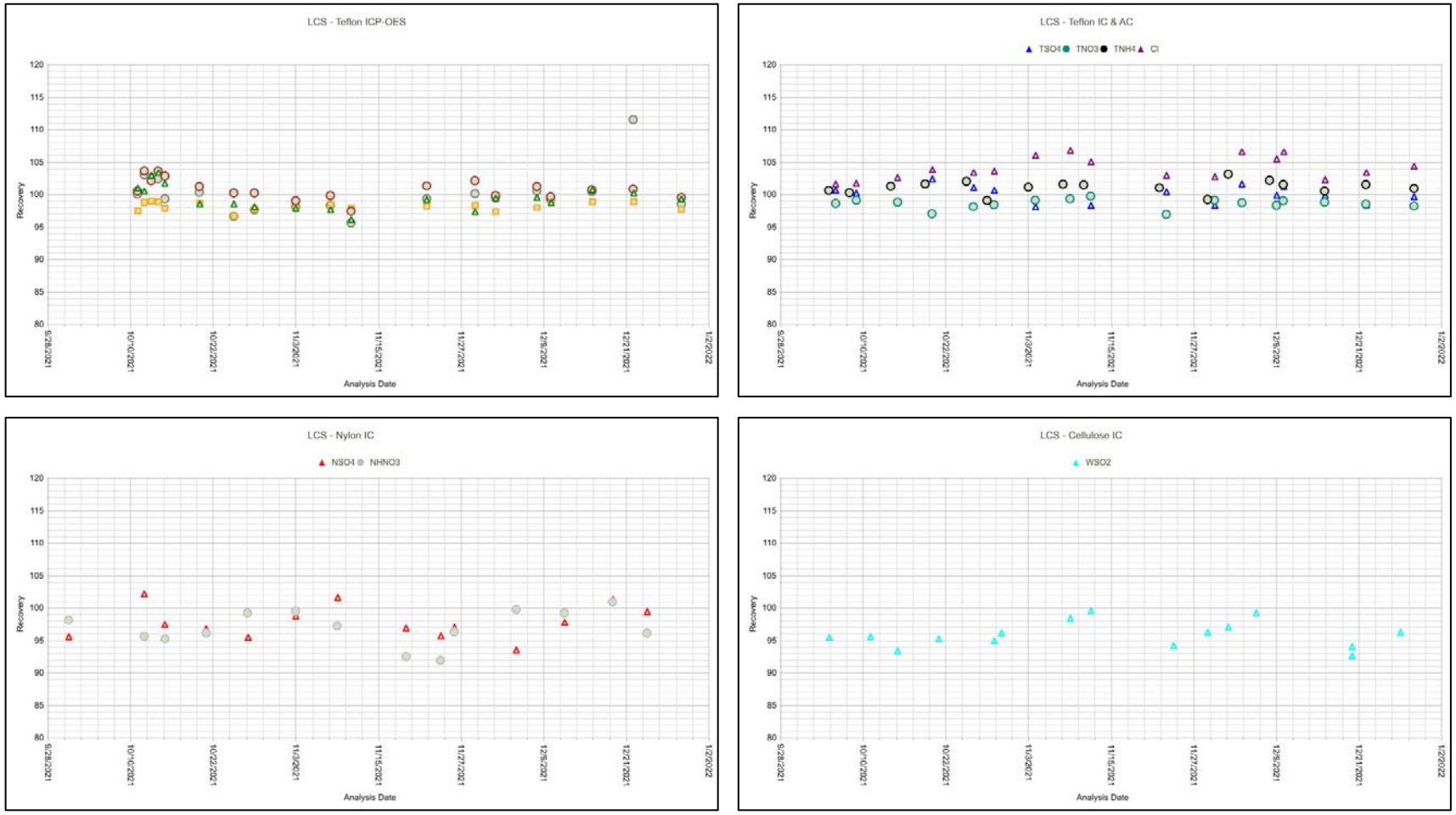


Figure 6 Method Blank Analysis Results for Fourth Quarter 2021 (total micrograms)

Figure 7 Laboratory Blank Analysis Results for Fourth Quarter 2021 (total micrograms)

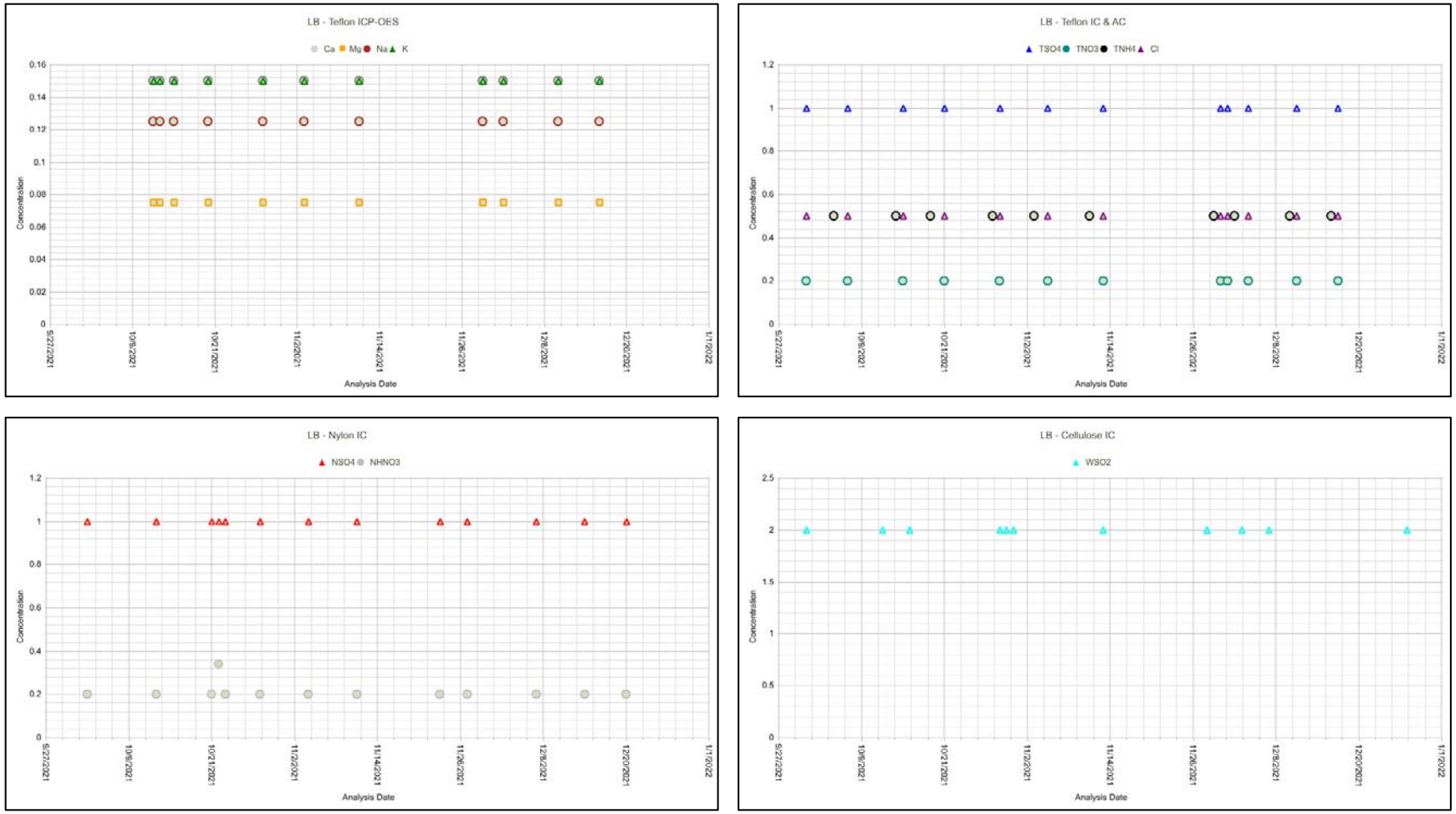


Figure 8 Field Blank Analysis Results for Fourth Quarter 2021 (total micrograms)