

Clean Air Status and Trends Network

First Quarter 2024 Quality Assurance Report

Summary of Quarterly Operations (January through March) EPA Contract No. 68HERH21D0006 EPA Project No. 68HERH23F0263

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 2024. The various QA/QC criteria and policies are documented in the CASTNET Quality Assurance Project Plan [QAPP; WSP USA Environment & Infastructure Inc. (WSP), 2024]. 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

On January 24, 2024, WSP submitted results of analyses for proficiency test (PT) 123 for Rain and Soft Waters from the Water Science and Technology Directorate (WS&TD), a branch of Environmental Science and Technology Laboratories with Environment and Climate Change Canada. On March 25, 2024, WSP received final results and a laboratory performance assessment score for PT 123 from the WS&TD. WSP's final results were assessed as "Very Good." WSP was the only laboratory that participated in PT 123 to receive this rating. WSP's five-year historical performance is rated as "Good."

The site operator for the MKG113, PA site suffered a broken foot in December 2023 and was unable to perform his site operator duties through first quarter 2024. As a result of the data loss at the MKG113 site due to the site operator's injury, corrective action 0126 (CA_0126) was initiated. Tickets have customarily been opened in the field problem ticketing system by field or data personnel pursuant to problems with equipment or continuous data collection. Under this corrective action, a problem ticket will be opened for any issue adversely affecting the collection of data, including issues that interrupt or compromise filter pack sampling (e.g., if a site operator is unable to service their site). Filter pack sampling resumed March 24, 2024, and the regular site operator returned to duty on April 23. Ozone measurements continued without interruption throughout the quarter.

Documentation was requested by the American Association for Laboratory Accreditation (A2LA) in support of continuation of International Organization for Standardization (ISO)/International Electrotechnical Commission (IEC) 17025:2017 accreditation of WSP's analytical and field laboratories. The CASTNET QA Manager worked with the CASTNET Laboratory Operations Manager and CASTNET Field Operations Manager to compile the necessary annual review documentation. The annual review documentation provided by WSP was accepted by the A2LA, and the A2LA reaffirmed WSP's ISO/IEC 17025:2017 accreditation until May 31, 2025.

The QA Manager received comments and recommendations for changes to the draft CASTNET QAPP Revision 10.1 from EPA's Office of Atmospheric Protection. The QA Manager began incorporating the recommendations and changes to the QAPP Revision 10.1. The updated, final version of the QAPP will be resubmitted to EPA in early second guarter 2024.

WSP attended EPA's Office of Air Quality Planning and Standards National Performance Audit Program training during the week of March 4, 2024. The training included a review of regulation changes and the new addition of Nafion dryers. Greg Noah (EPA) credited the work done by the WSP field technicians and CASTNET for the acceptance of Nafion in a regulatory ozone system.

The QA Manager continued working with the EPA Region 3 QA Coordinator regarding the mini technical systems audit (TSA) of the PAR107, VA ozone system on August 21, 2023. During March 2024, the Region 3 QA Coordinator requested additional information for the TSA report. In particular, he asked for the residence time, how often residence time is tested, and the schedule of maintenance procedures such as tubing exchanges.

Table 1 lists the quarters of data that were validated to Level 3 during first quarter 2024 by the 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 2024.

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 2024.

Data Quality indicator (DQI) Results

Figures 1 through 3 present the results of RF, CCV, and RP QC sample analyses for first quarter 2024. All results were within the criteria listed in Table 3.

Table 8 presents summary statistics of critical criteria measurements at ozone sites collected during first quarter 2024. 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. If a cell is shaded, the result either exceeds documented criteria or is 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 2024. 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. If a cell is shaded, the result either exceeds documented criteria or is otherwise notable. 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 2024. All recovery values were between 91 percent and 103 percent.

Blank Results

Figures 5 through 7 present the results of MB, LB, and FB QC sample analyses for first quarter 2024. All first quarter results were within criteria (two times the reporting limit) listed in Table 3 (with the exception of one cellulose SO₂ FB result reported at 4.2 parts per billion).

Suspect/Invalid Filter Pack Samples

Filter pack samples that were flagged as suspect or invalid during first quarter 2024 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, 5 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 2024. 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). 2022. ASTM E29-22, "Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications." ASTM International, West Conshohocken, PA, DOI:10.1520/E0029-22. www.astm.org.
- International Organization for Standardization (ISO). 2015. Statistical Methods for the Use in Proficiency Testing by Interlaboratory Comparisons, Annex C, Robust Analysis, Section C.1: Algorithm A. Standard 13528. ISO 13528:2015(E).
- 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://www3.epa.gov/castnet/docs/QAPP_v9-5_Main_Body.pdf.

Table 1 Data Validated to Level 3 through First Quarter 2024

Calibration Group*	Months Available	Number of Months	Complete Quarters	Number of Quarters
E-3/W-10 [†]	May 2023– October 2023	6	Quarter 3 2023	1
SE-4/MW-6 [‡]	July 2023– December 2023	6	Quarter 3 2023– Quarter 4 2023	2

Notes:

Table 2 Field Calibration Schedule for 2024

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 ¹	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, NC ¹		
SE-5	February/August	CAD150, AR	SUM156, FL			
(4 Sites)		IRL141, FL	CVL151, MS			
		Midwester	n Sites (18 Total)			
MW-6	January/July	CDZ171, KY	MCK131, KY	PNF126, NC ¹		
(6 Sites)		CKT136, KY	MCK231, KY	ESP127, TN		
MW-7	March/September	BVL130, IL ²	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 ³	PAL190, TX	CNT169, WY	
(8 Sites)		GTH161, CO	NPT006, ID	UMA009, WA	PND165, WY ³	

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

^{*} The sites contained in each calibration group are listed in Table 2.

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

[‡] Contains MCK131/231 co-located pair

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	Nominal Rep	orting Limits ³
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

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) E29-22, "Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications" (ASTM, 2022).

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, 2022). The minimum frequency for these checks is once every two weeks.

Values are rounded according to ASTM E29-22, "Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications" (ASTM, 2022).

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).

Table 5 Trace-level Gas Monitoring Critical Criteria*

	<u> </u>				
	Analyzer Response				
Parameter	Zero Check	Span Check / Single Point QC Check			
SO ₂	Less than ± 1.51 ppb	l and the second of the second back was as second in a second			
NO _y	Less than ± 1.51 ppb	Less than ± 10.1 percent between supplied and observed concentrations			
CO	Less than ± 50 ppb	SSSSIVER CONCENTIATIONS			

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, 2022). The minimum frequency for these checks is once every two weeks.

Values are rounded according to ASTM E29-22, "Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications" (ASTM, 2022).

SO₂ = sulfur dioxide

 NO_y = total reactive oxides of nitrogen

CO = carbon monoxide ppb = parts per billion

Table 6 QC Analysis Count for First Quarter 2024

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⁻	52	147	62	13	20	57
	NO ₃	52	147	62	13	20	57
	NH ⁺ ₄	26	131	58	13	20	57
	Cl	52	147	62	13	20	57
	Ca ²⁺	26	133	61	13	20	57
	Mg ²⁺	26	133	61	13	20	57
	Na [⁺]	26	133	61	13	20	57
	K ⁺	26	133	61	13	20	57
Nylon	SO ₄ ²⁻	27	125	61	9	22	57
	NO ₃	27	125	61	9	22	57
Cellulose	SO ₄ ²⁻	35	111	50	11	26	60

Table 7 Filter Pack Receipt Summary for First Quarter 2024

14
692
0.980
5.390
1/2/2024
3/30/2024

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 2024 (1 of 2)

Site ID	% Span Pass¹	Span [%D]²	% Single Point QC Pass¹	Single Point QC [%D] ²	% Zero Pass¹	Zero Average (ppb) ²
ABT147, CT	100.00	1.43	100.00	1.14	100.00	0.16
ALC188, TX	100.00	1.32	100.00	1.21	100.00	0.40
ANA115, MI	100.00	1.26	100.00	1.50	100.00	0.20
ARE128, PA	100.00	1.32	100.00	1.21	100.00	0.57
ASH135, ME	N/A	N/A	N/A	N/A	N/A	N/A
BEL116, MD	100.00	0.57	100.00	0.73	100.00	0.60
BFT142, NC	100.00	1.11	100.00	0.97	100.00	0.26
BVL130, IL	85.87	15.60	85.87	15.36	100.00	0.12
BWR139, MD	100.00	0.99	100.00	1.13	100.00	0.43
CAD150, AR	100.00	1.71	100.00	1.79	100.00	0.24
CDR119, WV	N/A	N/A	N/A	N/A	N/A	N/A
CDZ171, KY	N/A	N/A	N/A	N/A	N/A	N/A
CKT136, KY	100.00	0.54	100.00	0.59	100.00	0.09
CND125, NC	100.00	1.07	100.00	1.33	100.00	0.33
CNT169, WY	100.00	0.69	100.00	0.99	100.00	0.39
COW137, NC	100.00	0.88	100.00	1.39	100.00	0.33
CTH110, NY	100.00	0.50	100.00	0.93	100.00	0.16
CVL151, MS	95.74	2.87	93.62	3.01	100.00	0.21
DCP114, OH	N/A	N/A	N/A	N/A	N/A	N/A
DUK008, NC	100.00	2.35	100.00	2.54	100.00	0.50
ESP127, TN	100.00	1.26	100.00	1.49	100.00	0.65
GAS153, GA	100.00	1.23	97.83	2.22	97.83	0.94
GTH161, CO	100.00	2.17	98.91	2.24	93.48	0.88
HOX148, MI	100.00	0.88	100.00	0.88	100.00	0.22
HWF187, NY	N/A	N/A	N/A	N/A	N/A	N/A
IRL141, FL	98.92	2.13	100.00	1.55	100.00	0.38
KEF112, PA	100.00	3.09	100.00	1.59	100.00	0.71
LPO010, CA	98.96	0.68	100.00	0.62	100.00	0.16
LRL117, PA	100.00	1.39	100.00	1.18	100.00	0.19
MCK131, KY	100.00	1.72	100.00	1.64	100.00	0.25
MCK231, KY	100.00	0.89	98.91	1.64	100.00	0.28
MKG113, PA	100.00	1.46	100.00	1.14	100.00	0.26
NPT006, ID	100.00	1.47	100.00	1.60	100.00	0.12
OXF122, OH	100.00	2.40	100.00	2.68	100.00	0.27
PAL190, TX	97.89	0.85	100.00	0.60	100.00	0.28
PAR107, WV	100.00	0.65	100.00	0.62	100.00	0.26
PED108, VA	100.00	1.26	100.00	1.17	100.00	0.23
PND165, WY	100.00	1.14	100.00	0.87	100.00	0.32
PNF126, NC	N/A	N/A	N/A	N/A	N/A	N/A
PRK134, WI	97.85	3.87	97.85	4.27	100.00	0.30
PSU106, PA	100.00	0.54	100.00	0.85	100.00	0.79
QAK172, OH	100.00	2.14	100.00	2.25	100.00	0.29

Table 8 Ozone QC Summary for First Quarter 2024 (2 of 2)

Site ID	% Span Pass¹	Span [%D]²	% Single Point QC Pass ¹	Single Point QC [%D] ²	% Zero Pass¹	Zero Average (ppb) ²
ROM206, CO	96.67	4.66	97.78	2.45	97.78	1.40
SAL133, IN	100.00	0.90	100.00	0.70	100.00	0.18
SAN189, NE	100.00	1.99	100.00	2.56	100.00	0.45
SND152, AL	100.00	1.32	100.00	1.15	100.00	0.30
SPD111, TN	100.00	2.13	100.00	1.43	100.00	0.57
STK138, IL	100.00	1.15	100.00	1.30	100.00	0.21
SUM156, FL	92.31	3.48	95.51	2.57	100.00	0.20
UMA009, WA	100.00	0.75	100.00	1.03	97.87	0.53
UVL124, MI	100.00	1.81	100.00	1.87	100.00	0.21
VIN140, IN	100.00	0.92	100.00	1.06	100.00	0.14
VPI120, VA	100.00	1.74	100.00	2.24	98.96	0.38
WSP144, NJ	100.00	0.64	100.00	0.76	100.00	0.23
WST109, NH	98.95	1.74	95.79	2.42	95.79	0.92

%D percent difference = ppb parts per billion

Table 9 Ozone QC Observations for First Quarter 2024

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Site ID	QC Criterion	Comments		
BVL130	% Span Pass Span %D % Single Point QC Pass Single Point QC %D	Site analyzer pump failed 1/26/2024 and was replaced 2/1/2024.		

Note: %D = percent difference

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

Table 10 Trace-level Gas QC Summary for First Quarter 2024

Parameter	% Span Pass ¹	Span [%D]²	% Single Point QC Pass ¹	Single Point QC [%D] ²	% Zero Pass¹	Zero Average (ppb) ²
			BVL130, IL			
SO ₂	100.00	0.97	100.00	1.55	100.00	0.36
NO _y	100.00	2.42	100.00	2.17	95.56	0.24
CO	100.00	1.41	90.00	5.15	94.00	21.16
	DUK008, NC					
NO _y	100.00	1.20	100.00	1.80	91.89	0.77
			HWF187, NY			
NO _y	N/A	N/A	N/A	N/A	N/A	N/A
	-	-	PND165, WY			
NOy	100.00	0.93	100.00	1.43	100.00	0.50
	PNF126, NC					
NO _y	N/A	N/A	N/A	N/A	N/A	N/A
	ROM206, CO					
NO _y	97.83	0.96	97.83	1.62	100.00	0.12

Notes: %D = percent difference ppb = parts per billion

Table 11 Filter Packs Flagged as Suspect or Invalid During First Quarter 2024

	<u> </u>	<u> </u>
Site ID	Sample No.	Reason
CAT175	2403001-10	Power failure.
CVL151	2402001-18	Flow rate was unknown during this sampling week.
KEF112	2402001-28	Filter pack failed leak check.
SHE604	2402005-05	Flow rate was invalidated as suspect.
SHE604	2404005-05	Invalidated for suspect data.

Table 12 Field Problems Affecting Data Collection

Days to Resolution	Problem Count
30	151
60	5
90	0
Unresolved by end of quarter	9

Figure 1 Reference Standard Results for First Quarter 2024 (percent recovery)

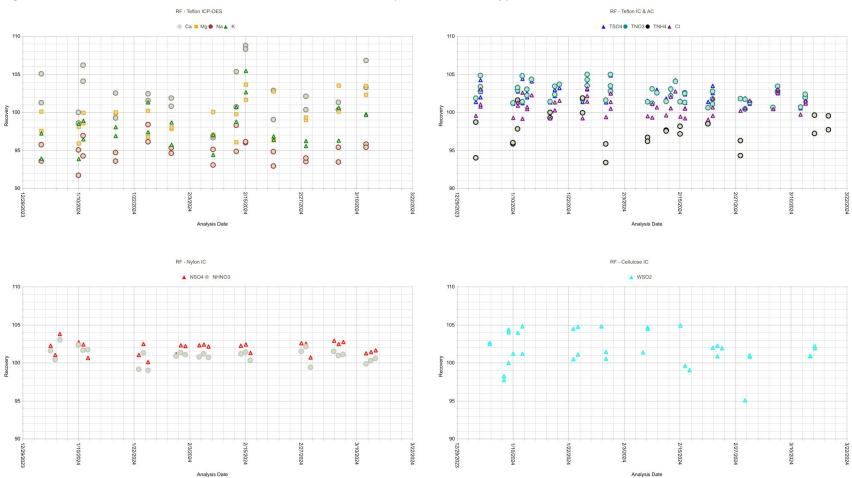


Figure 2 Continuing Calibration Spike Results for First Quarter 2024 (percent recovery)

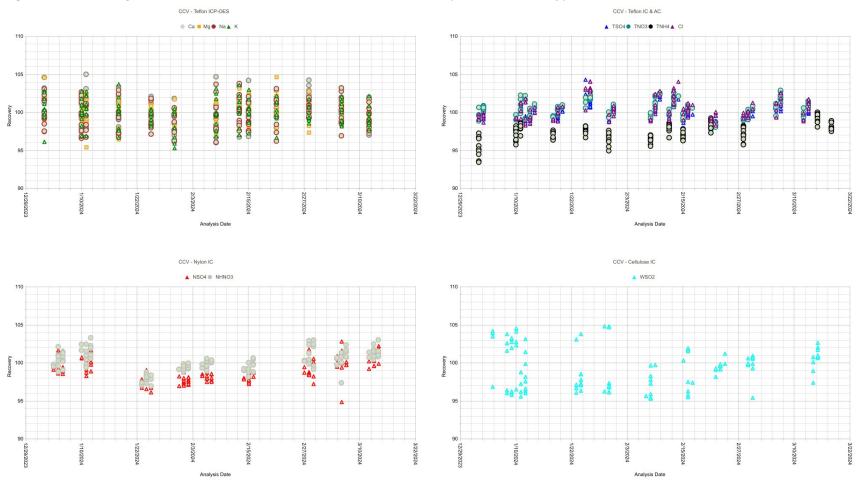


Figure 3 Replicate Sample Analysis Results for First Quarter 2024 (percent difference)

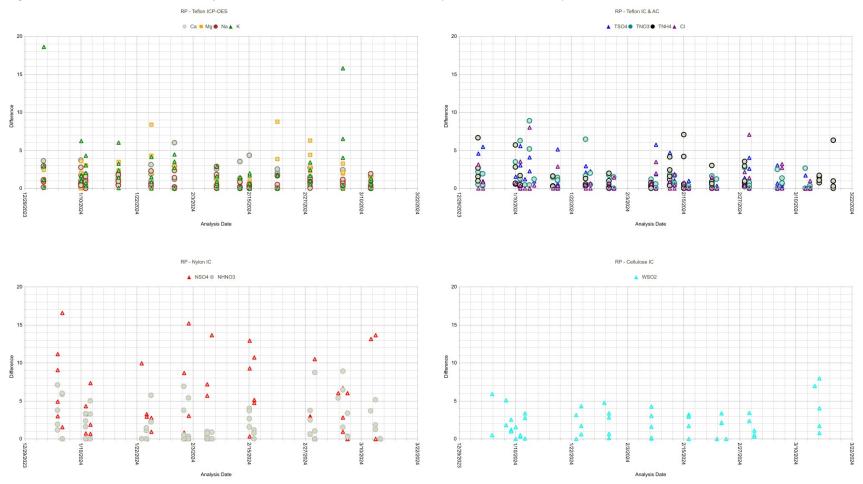


Figure 4 Laboratory Control Sample Results for First Quarter 2024 (percent recovery)

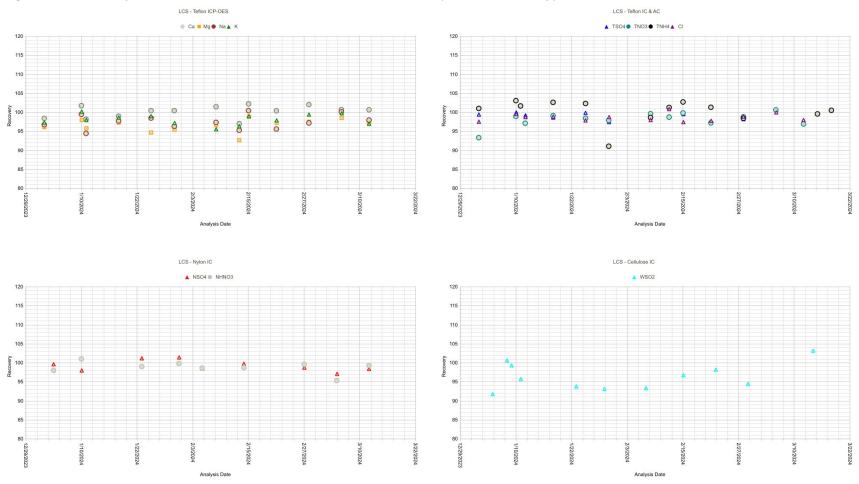


Figure 5 Method Blank Analysis Results for First Quarter 2024 (total micrograms)

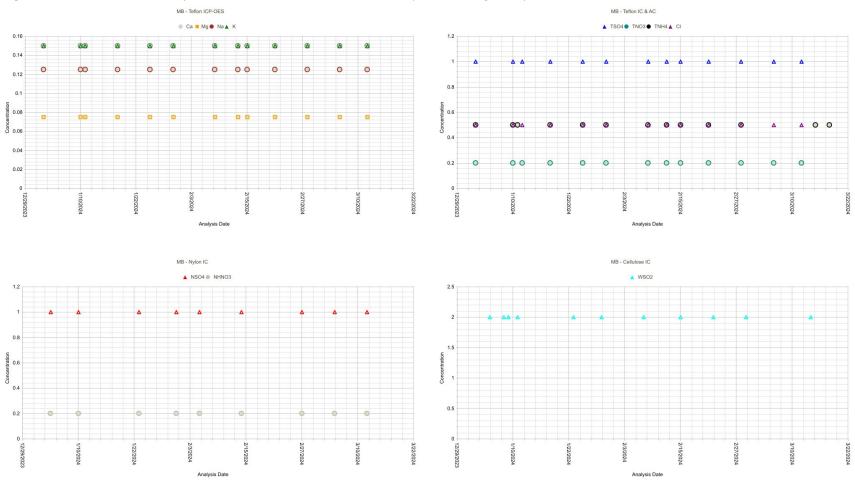


Figure 6 Laboratory Blank Analysis Results for First Quarter 2024 (total micrograms)

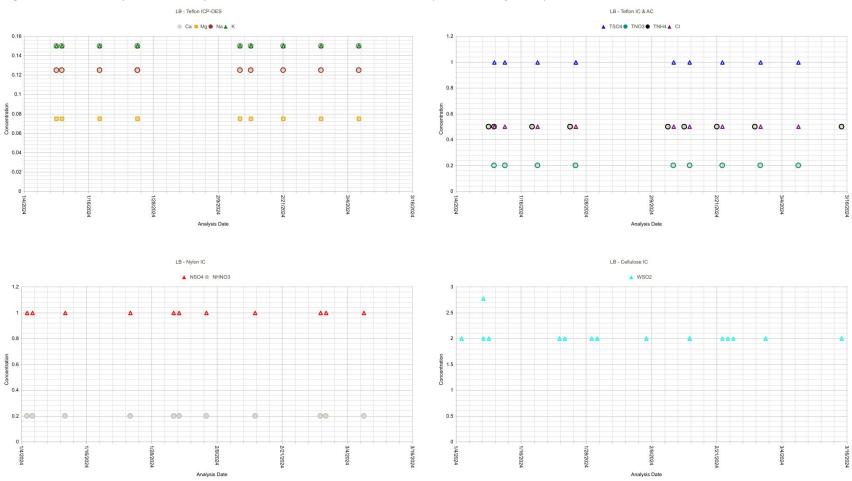


Figure 7 Field Blank Analysis Results for First Quarter 2024 (total micrograms)

