Final Data Validation Report

USACE Fort Wingate Depot Activity
New Mexico

Project No: **Eco-18-1237**

SDG #23D322 Analytical Data Package

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

This data validation report presents the evaluation and validation of the analytical data for samples collected in April 2023 as part of water monitoring, Fort Wingate Depot Activity, New Mexico (NM). EMAX Laboratories in Torrance, California performed the chemical analysis of these samples. The United States Army Corps of Engineers and the State of California have certified EMAX Laboratories to perform the analysis described within this project, (QAPP, Eco & Associate, Inc. Project number Eco-18-1237, April 2019).

A total of nine (9) water samples were collected on 04-27-23. EMAX Laboratories received the samples on 04-28-23. The data was delivered in one package as stage 2b and stage 3 deliverable. Ten percent of the data was subjected to validation equivalent to stage 3 deliverable. Raw data for all samples were submitted for the requested analytical methods. Two samples from this sample delivery group, MW38042023(Lab ID#D322-03) and TMW32042023(Lab ID#D322-04) were designated as stage 3 deliverable. Raw data for these samples were compared to the reported summary tables for each method and went through comprehensive data validation review. No sample was designated to be spiked as MS/MSD on the chain of custody. Therefore, the results and recoveries of LCS/LCSD was used for both accuracy and precision for each method. Raw data for method blank and LCS/LCSD for each method were cross checked with the corresponding summary table results.

Stage 2b data validation examined quality assurance/quality control (QA/QC) elements such as holding time, (both extraction and analysis), extraction logs, instrument injection logs, method blank results, QC summary results and recoveries, LODs/LOQs, summaries of initial and continuing calibrations and completeness of results for the following requested EPA methods of analysis:
EPA Method 3050B/8260C: Volatile Organics by GC-MS (9 samples)
EPA Method 3520C/8270D: Semi-Volatile Organics by GC/MS (6 samples)
EPA Method SW846 3535A/8330B: Nitroaromatics and Nitramines (8 samples)
EPA Method SW8332: Nitroglycerine and PETN (8 samples)
EPA Method 8081B: Organochlorine Pesticides (6 samples)

EPA Method 8082A: Polychlorinated Biphenyls; PCBs (2 sample)

EPA Method 8151A: Chlorinated herbicides (2 sample)

EPA Method 8015D: Total Petroleum Hydrocarbons (GROs) (5 samples)

EPA Method 8015D: Total Petroleum Hydrocarbons; extractable (DROs) (4 samples)

EPA Method 6850: Perchlorate (7 samples)

EPA Method SW6020A: Dissolved and total Metals by ICP-MS (8 samples)

EPA Method 7470A: Mercury & Dissolved Mercury (8 samples)
EPA Method SW9056A: Nitrate-N, Nitrite, Orthophosphate, Bromide, Chloride, Fluoride and Sulfate (7 samples)

The analytical results, QC results, initial calibration summary table and initial calibration verification (ICV) data were comprehensively compared with the corresponding raw data and chromatograms presented for stage 3 data validation.

All the requested samples were analyzed for each of the components listed in the corresponding EPA Methods (QAPP; final version, Eco & Associate, Inc. April 2019). The evaluation indicated that all the analytical work was performed as requested on the chain of custody. The extraction and analytical holding times were met for each method and all the related samples. The deviations, if any, are discussed in Section 4.0 for each method.

The SDG # 23D322 analytical data evaluated in this data validation report has met the data quality and usability requirement as defined in the data quality objectives. While very few analytical QC exceedances were observed, it was not significant for any data qualifiers. Overall data is of acceptable quality and considered usable for its intended purpose.

1.0 INTRODUCTION

This report presents the evaluation and validation of analytical data for water samples collected as a part of water monitoring at Fort Wingate, New Mexico (NM).

1.1 Objectives and Scope of Data

The main objective of this report is to assess the acceptability of the data generated by the designated laboratory. The data validation was performed according to the analytical requirements of the method in the *Quality Assurance Project Plan, final Draft, USACE Fort Wingate New Mexico,* (Project No: Eco-18-1237, April 2019)*, USEPA Analytical Operations/Data Quality Center (AOC) National Functional Guidelines for Organic Data Review* (USEPA, January 2017), *National Functional Guidelines for Inorganic Data Review* (USEPA, September 2016), US DoD General Data Validation Guideline, February 2018, *EM 200-1-10 Guidance for Evaluating Performance-based Chemical Data, US Army Corps of Engineers (USACE). June 2005 and DoD Quality* System Manual DoD *QSM 5.3, 2019.* The Approved site-specific Quality Assurance Project Plan (ECO QAPP) has the highest hierarchy.

1.2 Organization of the Report

Section 2.0 describes the components of the data review. Section 3.0 provides the qualitative quality assurance objectives. Section 4.0 summarizes the findings and conclusions of the data validation.

2.0 DATA REVIEW AND VALIDATION

Data validation is a systematic method for reviewing and qualifying the presented analytical data for their intended use. The objective of this data validation report is to identify any unacceptable or faulty measurements, as reported by the laboratory.

EMAX Laboratories in Torrance, California performed the chemical analysis of the samples. Army Corps of Engineers and the State of California has certified this laboratory for performing the analysis described within this report.

A total of nine (9) water samples were collected on 04-27-23. EMAX Laboratories received the samples on 04-28-23.

2.1 Data Reporting

The data was delivered in one package as stage 2b and stage 3 deliverables. 10% of the data was subjected to validation to the equivalent of stage 3.

EMAX Laboratories provided the following information in one data package:

- Sample identification number;
- Date of sample collection;
- Sample matrix type;
- Analysis method;
- Target lists and results of analysis;
- Limit of Detection (LOD);
- Limit of Quantitation (LOQ);
- Laboratory qualifiers and qualifier definitions;
- Copies of sample logs and chain-of-custody logs;
- Sample preparation logs (with the sample extraction dates);
- Sample Analysis logs (Instrument injection logs with sample analysis dates);
- Results and percent recoveries of Matrix Spike Samples (MS/MSD), if submitted
- Results and percent recoveries of Lab Control Samples (LCS/LCSD)

- Summary of initial calibration, initial calibration verification (ICV) and continuing calibration verification (CCV) standards;
- Case narrative for each method;
- Raw data for all the initial calibrations, initial calibration verifications, continuing calibrations, Tune check standards (where applicable), internal standard responses and chromatograms for the sample/samples at Stage 3 deliverable and related QC samples.

Data validation was performed by initial review of the analytical reports and QA/QC results and recoveries using summary tables. Next, selected analytical reports including QA/QC information was cross checked with raw data. The analysis and extraction sequence logs for each method were examined. Overall review assessed the effects of QA/QC results on the data usability. The review included such parameters as holding times, LODs/LOQs, initial and continuing calibration method requirements, surrogate recoveries, MS/MSD and lab control samples (LCS/LCSD) results and percent recoveries for accuracy and precision.

Stage 3 review compared the reported analytical results with those obtained from the raw data. Raw data for each analytical method requested on the chain of custody were submitted for all samples. Two field samples MW38042023 (Lab ID #D322-03) and TMW32042023 (Lab ID #D322-04) from this sample delivery group were designated for stage 3 data review. Raw data for these samples was evaluated comprehensively. No sample was designated to be spiked as MS/MSD on the chain of custody. Raw data for method blank and LCS/LCSD was reviewed for each method in detail. Calculations and corresponding equations, as well as analyte identification were randomly checked and verified.

2.2 Data Evaluation

The following parameters were evaluated in the preliminary data review:

- Analysis performed and sample identifications were verified to be in accordance with the information provided on the chain-of-custody (COC);

- Technical holding times were confirmed for all samples with regard to the requested method of analysis (collection to extraction and extraction to analysis);
- Limit of quantitation (LOQ) for each analyte reported were compared with the project measurement objectives;
- Initial calibration and initial calibration verification standards were evaluated;
- Continuing calibration standards were evaluated
- Trip blank results (Method 8260C and TPH by purge & trap only) were evaluated;
- MS/MSD results and recoveries were evaluated; only for total metals
- LCS/LCSD results and recoveries were evaluated; and
- Method blank results as well as surrogate recoveries, internal standards and instrument performance check compounds (for GC-MS) and DDT/Endrin breakdown (Method 8081B) were evaluated.

The following is a list of sample identifications and corresponding laboratory sample identification numbers:

Site Name: Fort Wingate, New Mexico

SDG#23D322 **Matrix: Water**

Field/Client ID	**Lab ID**	**Date collected**	**Validation stage**	**Requested Methods of Analysis**
MW39042023	23D322-01	04-27-23	S3VM	VOCs by SW5030B/8260C, Semivolatiles + APP9 Organochlorine Pesticides Nitroaromatics and Nitramines Nitroglycerine & PETN Chlorinated Herbicides Polychlorinated Biphenyls (PCBs) TPH Gasoline; TPH as DRO Mercury & Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS Perchlorate by 6850 Anions by IC
TMW25042023	23D322-02	04-27-23	S3VM	VOCs by SW5030B/8260C, Nitroaromatics and Nitramines Nitroglycerine & PETN Mercury Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS
MW38042023	23D322-03	04-27-23	S3VM	VOCs by SW5030B/8260C, Semivolatiles + APP9 Organochlorine Pesticides Nitroaromatics and Nitramines Nitroglycerine & PETN Chlorinated Herbicides Polychlorinated Biphenyls (PCBs) TPH Gasoline; TPH as DRO Mercury & Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS Perchlorate by 6850 Anions by IC
TMW32042023	23D322-04	04-27-23	S3VM	VOCs by SW5030B/8260C, Semivolatiles + APP9 Organochlorine Pesticides Nitroaromatics and Nitramines Nitroglycerine & PETN Mercury Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS Perchlorate by 6850 Anions by IC

Site Name: Fort Wingate, New Mexico

SDG#23D322 **Matrix: Water**

Field/Client ID	**Lab ID**	**Date collected**	**Validation**	**Requested Methods of Analysis**
TW38042023	23D322-05	04-27-23	S3VM	VOCs by SW5030B/8260C, Semivolatiles + APP9 Organochlorine Pesticides Nitroaromatics and Nitramines Nitroglycerine & PETN Mercury Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS Perchlorate by 6850 Anions by IC
TMW47042023	23D322-06	04-27-23	S3VM	VOCs by SW5030B/8260C, Semivolatiles + APP9 Organochlorine Pesticides Nitroaromatics and Nitramines Nitroglycerine & PETN Mercury Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS Perchlorate by 6850 Anions by IC
TMW21042023	23D322-07	04-27-23	S3VM	VOCs by SW5030B/8260C, TPH Gasoline; TPH as DRO Nitroaromatics and Nitramines Nitroglycerine & PETN Mercury & Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS Perchlorate by 6850 Anions by IC
MW22D042023	23D322-08	04-27-23	S3VM	VOCs by SW5030B/8260C, Semivolatiles + APP9 Organochlorine Pesticides Nitroaromatics and Nitramines Nitroglycerine & PETN TPH Gasoline; TPH as DRO Mercury & Dissolved Mercury Dissolved Metals by ICP-MS Total Metals by ICP-MS Perchlorate by 6850 Anions by IC
QC27042023TB09	23D322-09	04-27-23	S3VM	VOCs by SW5030B/8260C, TPH Gasoline;

TABLE 2-1

Summary of Analytical Parameters
USACE Wingate, New Mexico

Table 2-1 below shows the specified analysis for constituents in the water samples, the corresponding Environmental Protection Agency (EPA) analytical method, and the corresponding limit of quantitation (LOQ), of groups of constituents.

MATRIX	CONSTITUENT	EPA METHOD	LOQ
Water	Volatile Organic Compounds list	SW5030B/8260C	1,2 & 20 µg/L
	Semi Volatile Organic Compound List	SW3520C /8270D	10&20µg/L, (Benzidine=40µg/L)
	Nitroaromatics &Nitramines	SW3535A/8330B	0.4µg/L
	Nitroglycerine & PETN	SW3535A/8332B	0.4µg/L
	Chlorinated Herbicides	SW8151A	1µg/L, (MCPA=40µg/L)
	Organochlorine Pesticides	SW8081B	0.1µg/L Methoxychlor =1.0µg/L Toxaphene =2.0µg/L
	Polychlorinated Biphenyls (PCBs)	SW8082A	1µg/L
	Total Petroleum Hydrocarbons (GROs)	SW8015D Purge & Trap	100µg/L
	Total Petroleum Hydrocarbons (DROs)	SW8015D Extractable	0.5mg/L
	Dissolved & Total Metals By ICP-MS	SW6020A	0.5µg/L,1µg/L,20µg/L,100µg/L,200µg/L
	Dissolved Mercury/Mercury	SW7470A	0.5µg/L
	Anions by IC	SW9056A	0.1mg/L; 0.2mg/L; 0.5mg/L
	Perchlorate	SW6850	0.5µg/L

2.2.1 Sample Receipt

Documentations and recordings regarding status of each sample and cooler temperatures upon receipt in the laboratory were reviewed. Samples were received in ten ice preserved coolers.

2.2.2 Holding Times

Technical holding times are defined as the maximum time allowed between sample collection, extraction and analysis. Collection to extraction and extraction-to-analysis (40-day) was within the holding time requirement for semi-volatile organic methods. Extraction-to-analysis was within the method's holding time requirement with metals and inorganic methods. Table 2-2 presents the summary of holding time requirements with qualifications if applied.

TABLE 2-2
Summary of Analytical Methods and Holding Time Requirements
USACE Wingate, New Mexico

ANALYSIS Method	**MATRIX**	**HOLDING TIME REQUIREMENT**	**DATA QUALIFIED AS "J"**
EPA Method 5030B/8260C	Water	14days to analysis (7days if **not** acid preserved)	None. Holding times were met
Semi Volatile Organic Target List 3520C/8270D/8270SIM	Water	Collection to extraction: 7 days Extraction to analysis: 40 days	None. Holding times were met
Nitroaromatics and Nitramines	Water	Collection to extraction: 7 days Extraction to analysis: 40 days	None. Holding times were met
Nitroglycerine and PETN	Water	Collection to extraction: 7 days Extraction to analysis: 40 days	None. Holding times were met
Chlorinated Herbicides	Water	Collection to extraction: 7 days Extraction to analysis: 40 days	None. Holding times were met
Organochlorine Pesticides	Water	Collection to extraction: 7 days Extraction to analysis: 40 days	None. Holding times were met
Polychlorinated Biphenyls (PCBs)	Water	Collection to extraction: 7 days Extraction to analysis: 40 days	None. Holding times were met
Total Petroleum Hydrocarbons (GROs)	Water	14days to analysis (7days if not acid preserved)	None. Holding times were met
Total Petroleum Hydrocarbons (DROs)	Water	Collection to extraction: 7 days Extraction to analysis: 40 days	None. Holding times were met
Perchlorate	Water	Collection to Analysis: 28 days	None. Holding times were met
Dissolved and Total Metals	water	Analysis within 6 Months	None. Holding times were met
Anions by IC	Water	Analysis 48 hours from collection for Nitrate, Nitrite &Orthophosphate and 28-days for Bromide, Chloride, Fluoride and Sulfate	Holding times were met for all
Mercury & Dissolved Mercury	Water	Collection to Analysis: 28 days	None. Holding times were met

2.2.3 Laboratory and Field Blanks

The objective of laboratory and field blanks is to determine the presence and extent of contamination resulting from laboratory or field activities. Blanks reported here included method and/or extraction blanks and trip blanks (VOCs and Gasoline only). The result of analysis of method blank is discussed in Section 4.0 for each method. All samples were transported in ten ice preserved coolers and were stored in a refrigerator upon arrival to the laboratory. The cooler’s temperature was reported as low as 1.1˚C and as high as 4.2˚C upon arrival. All samples were received intact and in good condition.

3.0 QUALITY ASSURANCE OBJECTIVES

Quality assurance (QA) objectives define analytical parameters that validate the conclusions drawn from the results. Quality assurance was assessed through the following means: precision, accuracy, representativeness, completeness, and comparability (PARCC).

3.1 Qualitative QA Objectives

Qualitative aspects of QA for analytical data are characterized by completeness and representativeness.

3.1.1 Comparability

Comparability defines the level of confidence with which one data set can be compared with another. Comparability is related to accuracy and precision. It is also a measure of the data's reliability. All units for comparability are in accordance with standard procedures so that the results could be compared with other laboratories if necessary.

3.1.2 Representativeness

Representativeness is a quantity, which presents whether the results of analysis accurately portray the actual site conditions. Representativeness is a qualitative parameter, which signifies the extent of accuracy and precision, to which the data represent a characteristic population, parameter variations at a sampling point, process condition, or environmental conditions. The sampling procedures described within the approved QAPP (Eco & Associate, Inc., April 2019) are designed to provide samples representative of the site conditions.

3.2 Quantitative QA Objectives

Quantitative QA Objectives for analytical data are defined as precision, accuracy, completeness, and method quantitation limits. These quantitative parameters are established in order to monitor the overall quality of analytical data produced by the laboratory. The laboratory performing the analytical methods specified in Table 2-1, and the case narratives, which is included in the data package from the laboratory, ensures the quality of the analytical data.

3.2.1 Precision

Precision is a measure of the closeness with which multiple analyses of a given sample agree with each other. It describes the agreement between two or more measurements that have been made in exactly the same way. Precision is measured through matrix spike/matrix spike duplicate samples, laboratory control sample/ laboratory control sample duplicate and sample/sample duplicate analysis. In the latter case, the sample with positive results can be used for this purpose. The relative percent difference (RPD) is calculated as a means of quantifying precision. The following equation is used for this purpose:

$$RPD = \frac{R_1 - R_2}{(R_1 + R_2)/2} \times 100$$

Where:

RPD = Relative percent difference

R_1 = Result of the first duplicate or measured sample concentration

R_2 = Result of the second duplicate or known sample or duplicate concentration

When analytes are present at concentrations below or near the quantitation limit, precision is measured, using MS/MSD, and/or LCS/LCSD results.
Precision results are discussed in Section 4.0 of this report.

3.2.2 Accuracy

Accuracy indicates the closeness of the measurement to its true or accepted value. Accuracy measures agreement between a result and its true value. Accuracy is measured through laboratory control sample analysis and surrogate recoveries. Method-specific QA objectives for precision and accuracy were based on the quality control limits developed by the laboratory for the analytical methods, specified in Table 2-1. These procedures may affect the accuracy of the data presented. Additionally, initial and continuing calibrations were used to verify that the analytical instrument accurately measured the compound concentrations. Calculations were independently verified for the responses and percent differences (%Ds).

3.2.3 Completeness

Completeness is defined as the percentage of total measurements, which are judged to be valid. The completeness objective is to obtain a sufficient amount of valid data to enable the goals and objectives of the project to be achieved.

Completeness is quantified by computing the fraction of reports, which remained valid after the sampling procedures were reviewed and the results conformed to QA/QC protocols. The following equation was used to calculate completeness:

$$\text{Completeness} = \frac{\text{No. of valid field samples collected and analyzed}}{\text{No. of valid field samples reported}} \text{ X } 100$$

Completeness (EPA Method 5030B/8260C: VOCs) =9/9X100=100%
Completeness (EPA Method 3520B/8270D: SVOCs) =6/6X100=100%

Completeness (EPA Method 3535A/8330B: Explosives) =8/8X100=100%

Completeness (EPA Method 8332: Nitroglycerine & PETN) =8/8X100=100%

Completeness (EPA Method 8081B: Organochlorine pesticides) =6/6X100=100%

Completeness (EPA Method 8082A: Polychlorinated Biphenyls) =2/2X100=100%

Completeness (EPA Method 8151B: Chlorinated Herbicides) =2/2X100=100%

Completeness (EPA Method 8015G: Petroleum Hydrocarbons; GRO) 5/5X100=100%

Completeness (EPA Method 8015D: Petroleum Hydrocarbons; DRO) =4/4X100=100%
Completeness (EPA Method 6850: Perchlorate) =7/7X100=100%

Completeness (EPA Method 7470A: Mercury & Dissolved Mercury) =8/8X100=100%

Completeness (EPA Method 6020A: Dissolved and Total Metals) =8/8X100=100%

Completeness (EPA Method SW9056A: Nitrate-N, Nitrite, Orthophosphate, Bromide, Chloride, Fluoride and Sulfate) =7/7X100=100%

Completeness is affected by anything that reduces the number of samples analyzed (such as a sample loss during transport or extraction), as well as acceptance or non-acceptance of analytical results.

4.0 DATA VALIDATION

This data review covers nine water samples listed on page 10 including dilutions and reanalysis if applicable. The analyses were according to the following EPA Methods:

EPA Method **5030B/8260C** for VOCs by GC/MS
EPA Method **3520C/8270D** for SVOCs by GC/MS
EPA Method **8081B** for Organochlorine pesticides by GC/ECD
EPA Method **8082A** for Polychlorinated Biphenyls
EPA Method **8151B** for Chlorinated Herbicides
EPA Method **8015D (GROs),** Total Petroleum Hydrocarbons by GC/FID
EPA Method **8015D (DROs)**, Total Petroleum Hydrocarbons by GC/FID
EPA Method **3535A/8330B** for Nitrtoaromatics and Nitramine by HPLC/UV
EPA Method **8332** for Nitroglycerine and PETN by UHPLC/UV
EPA Method **6850** for Perchlorate by HPLC/MS
EPA Method **6020A** for Dissolved and total metals by ICP/MS
Method **7470A** for Mercury & Dissolved Mercury by Cold Vapor
EPA **Method 9056A** for Anions by IC

This review follows *Quality Assurance Project Plan, final Draft, USACE Fort Wingate Depot Activity*, McKinley County, New Mexico; Project # Eco-18-1237 April 2019, EM *200-1-10 Guidance for Evaluating Performance-based Chemical Data; US Army Corps of Engineers (USACE). June 2005,* and USEPA Analytical Operations/Data Quality Center (*AOC) National Functional Guidelines for Organic Data Review* (USEPA, January 2017); DoD QSM 5.3, 2019 and *National Functional Guidelines for Inorganic Data Review* (USEPA, September 2016). The Approved site-specific Quality Assurance Project Plan has the highest hierarchy.

The following subsections correlate to the above guidelines.

The followings are definitions of the data qualifiers:

U	Indicates the analyses was analyzed for but not detected at or above Limit of Detection (LOD).
J	Indicates an estimated value with an unknown bias.

UJ	Indicates the analyte was analyzed for but not detected and reported less than LOD. However, the numerical value is approximate.
J^+	The result was estimated value and may be biased high.
J^-	The result was estimated value and may be biased low.
X	The sample results (including non-detects) were affected by serious deficiencies in the ability to analyze the sample and to meet published method and project quality criteria. The presence or absence of the analyte cannot be confirmed by the data provided. Acceptance or rejection of the data should be decided by the project team, but exclusion of the data is recommended

The following Reason codes were applied in the report:

M3	MS/MSD and/or LCS/LCSD percent recovery infraction with low bias
M4	MS/MSD or duplicate precision infraction
S1	Surrogate percent recovery infraction with high bias
S2	Surrogate percent recovery infraction with low bias
R4	Result exceeds calibration range
B6	Trip blank infraction (qualified detect)
B7	Field blank infraction (qualified detect)
B8	Equipment blank infraction (qualified detect)
D1	Field duplicate precision infraction

4.1. VOC (EPA Method 5030B/8260C)

4.1.1. Technical Holding Times

Holding time requirement was met for all nine samples. Water samples were collected on 04-27-23. Samples were analyzed on 05-04-23 within method’s requirement for holding time. (Water samples were preserved with hydrochloric acid).

The chain-of-custody was reviewed for documentation of sample information and method of analysis.

Qualification notations, if any, will be summarized in result section; section 4.1.7.

4.1.2. Tuning criteria

Performance of the instrument was checked by injection of a single component tune check standard (BFB: Bromofluorobenzene) prior to each initial calibration on 04-27-23 and at the beginning of each analysis shift on 05-04-23. It passed all the method assigned criteria.

4.1.3. Initial Calibration

Samples were analyzed with reference to one set of initial calibration using GC/MSD. Initial calibration curves were generated on 04-27-23. A multi-level calibration standard ranging from 0.3µg/L to 100µg/L was used for this purpose. Internal standard curve type was used for initial calibration and all following analysis. Minimum response factor for system performance check compounds (SPCCs) were within the method acceptable limits (Table 4.1.3.1). Response factors at each level were randomly recalculated and all agreed with the response factors submitted in the initial calibration summary table.

Minimum average response factors for the system performance check compounds (SPCCs) were recognized according to the following table:

Table 4.1.3.1: System Performance Check Compounds (Initial calibration)

System Performance check compounds (SPCCs)	Minimum average response factor (requirement)	Average Response factor 04-27-23
Chloromethane	≥ 0.10	√
1,1-Dichloroethane	≥ 0.20	√
Bromoform	≥ 0.10	√
Chlorobenzene	≥ 0.50	√
1,1,2,2-Tetrachloroethane	≥ 0.30	√

√ denotes passing method acceptance limits

Average response factor curve fit was used mainly through the initial calibration. All target compounds met the maximum 15% RSD limit.

Minimum average response factors for all target compounds were within method's recommended values, except for: Acetone (0.048) and 2-Butanone (0.052). However, recoveries were within the requirement of 70-130%. Calibration check compounds (CCCs) met the acceptance criteria for %RSD among the response factors calculated for each level. Table 4.1.3.2

lists the CCCs with method requirement limits for %RSD among response factors for initial calibration.

Table 4.1.3.2 Calibration Check Compounds (CCCs) Initial Calibration

Calibration Check Compounds (CCCs)	Response Factors %RSD (Method limit)	Response Factors %RSD 04-27-23
Vinyl chloride	-≤ 20%	√
1,1-Dichloroethene	-≤ 20%	√
Chloroform	-≤ 20%	√
1,2-Dichloropropane	-≤ 20%	√
Toluene	-≤ 20%	√
Ethyl benzene	-≤ 20%	√

√ denotes passing method acceptance limits

4.1.4. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard on 04-27-23. Percent difference (%D) and/or drift between initial calibration RRFs (average response factors) and the initial calibration verification response factors (RFs) were less than or equal to 20% for all target compounds.

Continuing calibration check standard was analyzed at the beginning and end of analysis shift on 05-04-23. Prior to continuing calibration standard, **instrument performance check standard** (BFB tune check) was carried out. It passed all the method tuning criteria.

Minimum average response factors for the system performance check compounds (SPCCs) were all within the method limits according to the following table:

Table 4.1.4.1: System Performance Check Compounds (Daily calibration)

System Performance Check compounds (SPCCs)	Minimum response factor (Method limits)	Continuing cal. Response factors 05-04-23 (opening Std.)	Continuing cal. Response factors 05-04-23 (closing Std.)
Chloromethane	≥ 0.10	√	√
1,1-Dichloroethane	≥ 0.20	√	√
Chlorobenzene	≥ 0.50	√	√
Bromoform	≥ 0.10	√	√
1,1,2,2-Tetrachloroethane	≥ 0.30	√	√

√ denotes passing method acceptance limits

Calculated percent differences (%D) between initial calibration RRFs (average response factors) and the continuing calibration response factors (RFs) were less than or equal to 20% for all the Calibration Check Compounds (CCCs) and less than or equal to 20% for nearly all other target analytes. Area counts for all internal standards were within ± 50 percent of the same level in the initial calibration. The calculated % difference between RFs from continuing calibration and average response factors from initial calibration is summarized in Table 4.1.4.2 for continuing calibration reports presented with the data package.

Table 4.1.4.2 Calibration Check Compounds (CCCs): Continuing Calibration

Calibration Check Compounds (CCCs)	**%Deviation From Initial calibration (Acceptance Limit)**	**%Deviation from Initial calibration (05-04-23)** Opening Std.	**%Deviation from Initial calibration (05-04-23)** Closing Std.
Vinyl chloride	≤ 20%	√	√
1,1-Dichloroethene	≤ 20%	√	√
Chloroform	≤ 20%	√	√
1,2-Dichloropropane	≤ 20%	√	√
Toluene	≤ 20%	√	√
Ethyl benzene	≤ 20%	√	√

√ denotes passing method acceptance limits

Deviation from the initial calibration was less than 20 percent for the rest of target list, except for target analytes listed in the table below for each opening and closing daily standards. This should not affect the data quality.

Target analyte	**%Deviation From Initial calibration (Acceptance Limit)**	**%Deviation from Initial calibration (05-04-23 & 05-05-23)**	
		05-04-23 Opening Std	**05-05-23** Closing Std.
2,2-Dichloropropane	≤ 20%	√	22.6%*
Hexachlorobutadiene	≤ 20%	√	21.4%*

*Outside control limit

4.1.5. Quality Control samples reported consisted of one method blank and one set of LCS/LCSD only. No sample was designated to be analyzes as MS/MSD. The full list of target compounds was spiked and reported for LCS/LCSD. Percent recoveries and percent RPDs for QC samples reported, were within the project acceptance limits for the entire compound list. The results, percent recoveries and RPDs were recalculated randomly and all agreed with the reported QC summary table. Method blank presented with the data package, analyzed with samples did not show presence of any target compounds.

Surrogate recoveries were all within the method’s acceptable limits.

4.1.6. **Field duplicate sample** and its associated sample: No field duplicate sample was collected with this sample delivery group.

4.1.7. Raw data was submitted for all samples. Sample MW38042023 (Lab ID# 23D322-03) and MW32042023 (Lab ID# 23D322-04) were designated to be reviewed as stage 3 data deliverable. Raw data for these samples with all related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data agreed with all the results reported in data summary reports.

4.2. SVOC (EPA Method 3520C/8270D)

4.2.1. Technical Holding Times

Holding time requirement was met for six samples requested for this method. Water samples were collected on 05-27-23, extracted on 05-03-23 and were analyzed on 05-08-23 within required holding time.

The chain-of-custody was reviewed for documentation of sample information and method of analysis.

Qualification notations, if any, will be summarized in result section; section 4.2.7.

4.2.2. Tuning criteria

Performance of the instrument was checked by injection of a tune check standard (DFTPP: Decafluorotriphenylphosphine) prior to each set of initial calibration on 03-07-22, 03-31-23 and at the beginning of analysis shift on 05-08-23. It passed all the method assigned criteria. Tailing of Pentachlorophenol and Benzidine was within acceptance limit (less than 2%) and breakdown of DDT was also within methods acceptance limit of less than 20%.

4.2.3. Initial Calibration

Samples were analyzed with reference to one set of initial calibration using GC/MSD. Due to long list of analytes used for this method, three separate lists of compounds were grouped together and initial calibration was generated separately for each group.

Initial calibration curves were generated on 03-07-22, and 03-31-23. A multi-level calibration standard ranging from 4mg/L to 50mg/L was used for this purpose. Internal standard curve type was used for initial calibration and all following analysis. Minimum response factor for system performance check compounds (SPCCs) were within the method acceptable limits (Table 4.2.3.1). Response factors at each level were randomly recalculated and all agreed with the response factors submitted in the initial calibration summary table.

Minimum average response factors for the system performance check compounds (SPCCs) were recognized according to the following table.

Table 4.2.3.1: System Performance Check Compounds (Initial calibration)

System Performance check compounds (SPCCs)	Minimum average response factor (Method requirement)	Average Response factor 03-07-22
N-Nitroso-di-n-propylamine	≥ 0.5	√
Hexachlorocyclopentadiene	≥ 0.05	√
2,4-Dinitrophenol	≥ 0.01	√
4-Nitrophenol	≥ 0.01	√

√ denotes passing method acceptance limits

Average response factors for the rest of target compounds were within method’s recommended values.

Calibration check compounds (CCCs) met the acceptance criteria for %RSD (less than 20%) among the response factors calculated for each level. Table 4.2.3.2 lists the CCCs with method requirement limits and calculated %RSD among response factors for initial calibration.

Table 4.2.3.2 Calibration Check Compounds (CCCs) Initial Calibration

Calibration Check Compounds (CCCs)	Response Factors %RSD (Method limit)	Accepted Response Factors 03-07-22
Phenol	≤ 20	√
1,4-Dichlorobenzene	≤ 20	√
2-Nitrophenol	≤ 20	√
2,4-Dichlorophenol	≤ 20	√
Hexachlorobutadiene	≤ 20	√
4-Chloro-3-methylphenol	≤ 20	√
2,4,6-Trichlorophenol	≤ 20	√
Acenaphthene	≤ 20	√
N-Nitrosodiphenylamine	≤ 20	√
Pentachlorophenol	≤ 20	√
Fluoranthene	≤ 20	√
Di-n-Octylphthalate	≤ 20	√
Benzo(a)pyrene	≤ 20	√

√ denotes passing method acceptance limits

Average response factor curve fit was used mainly through the initial calibration. All target compounds met the maximum 15% RSD limit.

Least square linear regression was used for the following compounds where %RSD exceeded the maximum 15 percent limit.

Target Analytes	Least Square Linear Regression (CCF) 03-07-22
Benzoic acid	0.9969
2,4-Dinitrophenol	0.9964
4-Nitrophenol	0.9971
Di-n-Octyl phthalate	0.9972

All analytes met the acceptance criteria regarding minimum response factor and maximum %RSD.

4.2.4. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard on 03-07-22, 03-08-22 and 03-31-23. Percent difference (%D) and/or drift between initial calibration RRFs (average response factors) and the initial calibration verification response factors (RFs) were less than or equal to 20% for all target compounds. Continuing calibration check standards were analyzed at the beginning and at the end of analysis shift on 05-08-23. Prior to continuing calibration injection, instrument performance tune check standard (DFTPP) was carried out. It passed all the method tuning criteria. Tailing of Pentachlorophenol and Benzidine was within acceptance limit (less than 2%) and breakdown of DDT was also within methods acceptance limit of less than 20%.

Minimum average response factors for the system performance check compounds (SPCCs) were all within the method limits according to the following table:

Table 4.2.4.1: System Performance Check Compounds (Daily calibration)

System Performance Check compounds (SPCCs)	**Minimum response factor (Method limits)**	**Continuing cal. Response factors (05-08-23) I&II** Inst E4
N-Nitroso-di-n-propylamine	≥ 0. 5	√
Hexachlorocyclopentadiene	≥ 0.05	√
2,4-Dinitrophenol	≥ 0.01	√
4-Nitrophenol	≥ 0.01	√

√ denotes passing method acceptance limits

Calculated percent differences (%D) between initial calibration RRFs (average response factors) and the continuing calibration response factors (RFs) were less than or equal to 20% for all the Calibration Check Compounds (CCCs) and less than or equal to 20% for nearly all other target analytes. Area counts for all internal standards were within ± 50 percent of the same level in the initial calibration. Percent difference between RFs from continuing calibration and average response factors from initial calibration passed the method’s criteria as summarized in Table 4.2.4.2.

Table 4.2.4.2 Calibration Check Compounds (CCCs): Continuing Calibration

Calibration Check Compounds (CCCs)	**% Deviation From Initial calibration (Acceptance Limit)**	**Accepted Deviation from Initial calibration (05-08-23) I& II** Inst E4
Phenol	≤ 20	√
1,4-Dichlorobenzene	≤ 20	√
2-Nitrophenol	≤ 20	√
2,4-Dichlorophenol	≤ 20	√
Hexachlorobutadiene	≤ 20	√

Calibration Check Compounds (CCCs)	% Deviation From Initial calibration (Acceptance Limit)	Accepted Deviation from Initial calibration (05-08-23) I& II Inst E4
4-Chloro-3-methylphenol	≤ 20	√
2,4,6-Trichlorophenol	≤ 20	√
Acenaphthene	≤ 20	√
N-Nitrosodiphenylamine	≤ 20	√
Pentachlorophenol	≤ 20	√
Fluoranthene	≤ 20	√
Di-n-Octylphthalate	≤ 20	√
Benzo(a)pyrene	≤ 20	√

√ denotes passing method acceptance limits

Deviation from the initial calibration was less than 20 percent for the rest of target list, except for the compounds listed below in the closing continuing standard:

Target analyte	%Deviation From Initial calibration (Acceptance Limit)	%Deviation from Initial calibration (05-08-23)	
		I	II
2,4-Dinitrophenol	≤ 20%	√	22.1%*
Benzoic acid	≤ 20%	23.7%*	29.7%*
Benzo(g,h,i)Perylene	≤ 20%	√	21.4%*

*Exceeded 20% maximum allowed difference in each daily standard

This deviation should not affect quality of the presented data.

4.2.5. Quality Control samples reported consisted of one method blank and one set of LCS/LCSD. No sample was designated to be spiked as MS/MSD. The full list of target compounds was spiked and reported for LCS/LCSD. Percent recoveries and percent RPDs for all the QC samples reported were all within the project acceptance limits.

Results and recoveries of LCS/LCSD was used to evaluate accuracy and precision in this method.

Results, percent recoveries and RPDs were recalculated randomly and all agreed with the reported QC summary table. Method blank presented with the data package, analyzed with samples did not show presence of any target compounds.

Surrogate recoveries were all within the method's acceptable limits, except for three surrogates failing the lower acceptance limit in one sample as shown in the table below:

Surrogate	MW38042023 (D322-03)	**QC Limit%**
2,4,6-Tribromophenol	8%*	43-140
2-Fluorophenol	6%*	19-119
Phenol-D5	6%*	40-130

*Outside QC limit

This was attributed to matrix interference in the case narrative.

4.2.6. **Field duplicate sample** and its associated sample: No field duplicate sample was collected with this sample delivery group.

4.2.7. Raw data was submitted for all samples. Sample MW38042023 (Lab ID# 23D322-03) and sample MW32042023 (Lab ID# 23D322-04) were designated to be reviewed as stage 3 data deliverable. Raw data for these samples with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.3. ORGANOCHLORINE PESTICIDES (EPA Method 3520C/ 8081B)

4.3.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for six water samples requested for this method. Water samples were collected on 04-27-23, extracted on 05-03-23 and analyzed on 05-05-23 within required holding time.

A dual column GC equipped with two Electron Capture Detectors (ECDs) was used for analysis. The results and raw data were submitted for both channel A and B. Channel A was used for data reporting.

DDT- Endrin breakdown mix was analyzed prior to initial calibration on 01-11-23, 01-09-23 and before sample analysis on 05-05-23. Breakdown of DDT to DDE and DDD and breakdown of Endrin-to-Endrin aldehyde and Endrin ketone were within the QC limits (less than 15 percent).

4.3.2. Initial Calibration

Initial calibration was performed with eight levels of concentration for each pesticide on 01-11-23. Both channels A and B were calibrated. Calibration factor (area for each compound/concentration) was used to quantify analytes. Average response factor was used to show linearity for both channels. Percent relative standard deviation (% RSDs) among calibration factors (CFs) for both channels A and B were within method specification (less than 15%). Pesticide target list was calibrated with two separate groups of compounds for each column. Due to interference with other pesticide target compounds, a separate curve was generated for Toxaphene on 01-09-23 for both channels. %RSD among the calibration factors was less than 15 for Toxaphene.

Retention time window width were established for all target analytes at each calibration level. Retention times for further sample analyses were within the assigned retention time windows set by initial calibration.

4.3.3. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) for all pesticide target list including Toxaphene, on 01-12-23 and 01-09-23. Percent difference between initial calibration response factors (Average response factors) and the response factors calculated for each analyte were less than 20% for both channels.

Performance of instrument was monitored by analysis of DDT and Endrin breakdown mixture. Before each continuing (daily) calibration a mixture of DDT and Endrin was analyzed. Breakdown of DDT to DDE and DDD and breakdown of Endrin to Endrin-aldehyde and Endrin-ketone were all less than 15%.

A total of three continuing calibration standards were analyzed at 10-injections interval on 05-05-23, bracketing the analyses of sample and all the QC samples. Percent difference between initial calibration average response factors and the response factors calculated for each analyte from continuing calibrations, were less than 20% for target compounds for both channels A and B. In all continuing calibration standards, one mid-point concentration of 20-40µg/L was injected. Results for surrogate recoveries and QC were all calculated from channel A. Channel B was used for confirmation only.

4.3.4. Quality Control samples consisted of method blank and one set of LCS/LCSD only. No sample was designated to be spiked for MS/MSD for this method. All pesticide target list was spiked and reported for LCS/LCSD. Percent recoveries (%R) were within established QC limits. Results and recoveries of QC samples were confirmed with the reported raw data.

Results for method blank were reviewed for each component and no organochlorine pesticide was found in the method blank.

Surrogate recoveries were all within the method QC acceptance limits.

4.3.5. Field duplicate sample and its associated sample: No field duplicate sample was collected for this sample delivery group.

4.3.6. Raw data was submitted for all samples. Sample MW38042023 (Lab ID# 23D322-03) and TMW33042023 (Lab ID# 23D322-04) was designated to be reviewed as stage 3 data deliverable. Raw data for this sample with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.4. Polychlorinated Biphenyls (EPA Method 3520C/ 8082A)

4.4.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for water samples requested for this method. Two water samples were collected on 04-27-23, extracted on 05-03-23, and analyzed on 05-04-23.

A dual column GC equipped with two Electron Capture Detectors (ECDs) was used for analysis. The results and raw data were submitted for both channel A and B. Channel A was used for data reporting.

4.4.2. Initial Calibration

Initial calibration was performed with seven concentration levels for Aroclor 1016 and Aroclor1260 on 01-24-23. Both channels A and B were calibrated. Calibration factor (area for each compound/concentration) was used to quantify analytes. Average response factor was used to show linearity for both channels. Percent relative standard deviation (% RSDs) among calibration factors (CFs) for both channels A and B were within method specification (less than 20%).

Retention time window width were established at each calibration level. Retention times for further sample analyses were within the assigned retention time windows set by initial calibration.

4.4.3. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) for Aroclor 1016 and 1260, on 01-24-23. Percent difference between initial calibration response factors (Average response factors) and the response factors calculated for each analyte were less than 20% for both channels. After establishing linearity of the instrument through initial calibration, the rest of Aroclors, if required, were injected at single point for identification only.

Two continuing calibration standards were analyzed at 10-injections interval. It was carried out on 05-04-23, bracketing the analyses of sample and all the QC samples. Percent difference between initial calibration average response factors and the response factors calculated for each analyte from continuing calibrations, were less than 20% for each channel.

Results for surrogate recoveries and QC were all calculated from channel A. Channel B was used for confirmation only

4.4.4. Quality Control samples consisted of one method blank and one set of LCS/LCSD only. No sample was designated to be spiked as MS/MSD, therefore results and recoveries of LCS/LCSD was used for QC evaluation. Percent recoveries (%R) were within the established QC limits.

Results for method blank was reviewed for each component and no target analyte was found in the method blank.

Surrogate recoveries were all within the method QC acceptance limits.

4.4.5. Field duplicate sample: No field duplicate sample was collected with this sample delivery group.

4.4.6. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) with all related QC samples was designated to be reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.5. Chlorinated Herbicides (EPA 8151A)

4.5.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for water samples requested for this method. Two water samples were collected on 04-27-23, extracted on 04-28-23 and analyzed on 05-04-23, and 05-05-23.

A dual column GC equipped with two Electron Capture Detectors (ECDs) was used for analysis. The results and raw data were submitted for both channel A and B. Channel A was used for data reporting.

4.5.2. Initial Calibration

Initial calibration was performed with eight levels of concentration for each herbicide on 03-13-23. Both channels A and B were calibrated. Calibration factor (area for each compound/concentration) was used to quantify analytes. Average response factor was used to show linearity for both channels. Percent relative standard deviation (% RSDs) among calibration factors (CFs) for both channels A and B were within method specification (less than 20%) for all target list. Linear regression curve type with correlation coefficient of 0.9943 was used for MCPP in column B.

Retention time windows were established for all target analytes at each calibration level. Retention times for further sample analyses were within the assigned retention time windows set by initial calibration.

4.5.3. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) for all target herbicides on 03-14-23. Percent difference between initial calibration response factors (Average response factors) and the response factors calculated for each analyte were less than 20% for both channels.

Three continuing calibration standards were analyzed at 10-injections interval. It was carried out on 05-04-23 and 05-05-23, bracketing the analyses of sample and all the QC samples. Percent difference between initial calibration average response factors and the response factors calculated for each analyte from continuing calibrations, were less than 20% for all target compounds in both channels, except for two compounds as presented in the table below:

Target analyte	**%Deviation From Initial calibration (Acceptance Limit)**	**%Deviation from Initial calibration (05-04-23)**		**%Deviation from Initial calibration (05-05-23)**	
		Chanel A	Chanel B	Chanel A	Chanel B
Dinoseb	≤ 20%	35%*	√	√	√
Acifluorfen	≤ 20%	42%*	29%*	30%*	25%*

*Exceeded maximum 20% limit

Results for surrogate recoveries and QC were all reported from channel A. Channel B was used for confirmation only.

4.5.4. Quality Control samples consisted of one method blank, and one set of LCS/LCSD. No sample was designated to be spiked as MS/MSD. All herbicides target list was spiked and reported for LCS/LCSD. Percent recoveries (%R) were within established QC limits

Results for method blank was reviewed for each component and no Herbicide was found in the method blank. Surrogate recoveries were all within the method QC acceptance limits.

4.5.5. Field duplicate sample and its associated sample: No field duplicate sample was collected with this sample delivery group.

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4.5.6. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) with all related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.6. Nitroaromatics by UHPLC/UV (EPA Method3535A/ 8330B)

4.6.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for eight (8) water samples requested for this method. Water samples were collected on 04-27-23, extracted on 05-03-23 and analyzed on 05-25-22 within holding time.

A High-Performance LC (HPLC) coupled with Ultraviolet (UV) Detector was used for analysis. Positive results, if any, were confirmed with UHPLC equipped with different column (Kinetex- Biphenyl column).

4.6.2. Initial Calibration

Initial calibration was performed with seven concentration levels for each analyte on 08-25-22. Confirmation column (Biphenyl column), was calibrated on 08-23-21. Calibration factor (area for each compound/concentration) was used to quantify analytes. Average response factor was used to show linearity for both channels. Percent relative standard deviation (% RSDs) among calibration factors (CFs) was within acceptable limit (less than 15 percent.)

Retention time windows were established for each target analyte at each calibration level. Retention times for further sample analyses were within the assigned retention time windows set by initial calibration.

4.6.3. Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) for each target analyte on 08-26-22 and 08-23-21. Percent difference between initial calibration response factors (Average response factors) and the response factors calculated for each analyte were less than 15% in both columns.

Continuing calibration standards were analyzed at 10-injections interval. A total of two continuing calibration standards were analyzed on 05-25-23, bracketing the analyses of samples and all the QC samples. Four more daily standards were analyzed with confirmation column on 05-30-23. Percent difference between initial calibration average response factors and the response factors calculated for each analyte from continuing calibrations were less than 15% for all analytes for both columns.

4.6.4. Quality Control samples consisted of one method blank and one set of LCS/LCSD only. No sample was designated to be spiked as MS/MSD. The entire explosive target lists were spiked and reported for LCS/LCSD. Percent recoveries (%R) were within the QAPP established QC limits. Raw data for both un-spiked sample and spiked QC samples were matching the reported values.

Result for method blank was reviewed for each compound and no target was found in the method blank.

Surrogate recoveries were all within the method QC acceptance limits. 3,4-Dinitrotoluene was used as surrogate.

4.6.5 Field duplicate sample and its associated sample**:** No field duplicate sample was collected with this sample delivery group.

4.6.6. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) and sample MW32042023 (Lab ID#23D322-04) were designated as stage 3 data deliverable. Raw data for these samples together with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports. All positive results were confirmed with a second column (confirmation column).

4.7. Nitroglycerine and PETN by UHPLC/UV (EPA Method 8332)

4.7.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for eight water samples requested for this method. Water samples were collected on 04-27-23, extracted on 05-03-23 and analyzed on 05-16-23.

A High-Performance LC (HPLC) coupled with Ultraviolet (UV) Detector was used for analysis.

4.7.2. Initial Calibration

Initial calibration was performed with five levels of concentration for each analyte on 08-24-21. Calibration factor (area for each compound/concentration) was used to quantify analytes. Average response factor was used to show linearity. Percent relative standard deviation (% RSDs) among calibration factors (CFs) was within acceptable limit (less than 15 %.)

Retention time windows were established for each target analytes at each calibration level. Retention times for further sample analyses were within the assigned retention time windows set by initial calibration.

4.7.3. Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) for each analyte on 08-24-21. Percent difference between initial calibration response factors (Average response factors) and the response factors calculated for each analyte were less than 15%.

A total of three continuing calibration standards were analyzed at 10-injections interval. It was carried out on 05-16-23, bracketing the analyses of samples and all the QC samples. Percent difference between initial calibration average response factors and the response factors calculated for each analyte from continuing calibrations were less than 15% for each analyte.

4.7.4. Quality Control samples consisted of one method blank and one set of LCS/LCSD. No sample was designated to be spiked as MS/MSD. Each target compound was spiked and reported for LCS/LCSD. Percent recoveries (%R) were within the established acceptance QC limits. Raw data for both un-spiked sample and spiked QC samples were matching the reported values.

Result for method blank was reviewed for each compound and no target was found in the method blank. Surrogate recoveries were all within the method QC acceptance limits.

4.7.5. Field duplicate sample and its associated sample**:** No field duplicate sample was collected with this sample delivery group.

4.7.6. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) and sample MW32042023 (Lab ID#23D322-04) were designated as stage 3 data deliverable. Raw data for these samples with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.8. Total Petroleum hydrocarbons GRO (EPA Method 8015G)

4.8.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for five water samples requested for this method. Water samples were collected on 04-27-23. Samples were analyzed on 05-01-23 and 05-02-23 within holding time requirement.

A GC coupled with Flame Ionization Detector (FID) was used for analysis. Sample was carried through the system by purge and trap.

4.8.2. Initial Calibration

Initial calibration was performed with six levels of concentration on 05-01-23. Calibration factor (area for each compound/concentration) was used to quantify gasoline range hydrocarbons (TPH as GRO). Average response factor was used to show linearity. Percent relative standard deviation (% RSDs) among calibration factors (CFs) was within acceptable limit (less than 15%.)

Retention time window width was established by analysis of window defining hydrocarbon standard (C6-C10). Retention times for further sample analyses was used for peak identification and integration range.

4.8.3. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) on 05-01-23. Percent difference between initial calibration response factors (Average response factors) and the response factors calculated for each analyte were less than 20%

Two continuing calibration standards were analyzed at 10-injections interval. It was carried out on 05-01-23 and 05-02-23, bracketing the analyses of samples and all the QC samples. Percent difference between initial calibration average response factors and the response factors calculated for each group of GRO Hydrocarbons from continuing calibrations were less than 20%.

4.8.4. Quality Control samples consisted of one method blank and one set of LCS/LCSD. No sample was designated to be spiked as MS/MSD. Percent recoveries (%R) were within the established QC limits for LCS/LCSD. Raw data for both un-spiked sample and spiked QC samples were matching the reported values. Result for method blank was reviewed and no contamination was found in the method blank.

Surrogate recoveries were all within the method QC acceptance limits.

4.8.5. Field duplicate sample and its associated sample: No field duplicate sample was collected with this sample delivery group.

4.8.6. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) was designated as stage 3 data deliverable. Raw data for this sample with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.9. Total Petroleum hydrocarbons DRO (EPA Method 8015D)

4.9.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for four water samples requested for this method. Water samples were collected on 04-27-23, extracted on 05-03-23 and analyzed on 05-04-23 and 05-05-23, within holding time.

A GC coupled with Flame Ionization Detector (FID) was used for analysis. Heavier range of total petroleum hydrocarbons were extracted and introduced into system by direct injection.

4.9.2. Initial Calibration

Initial calibration was performed with seven levels of concentration on 02-17-23. Calibration factor (area for each compound/concentration) was used to quantify diesel range hydrocarbons (TPH as DRO). A second set of initial calibration curve was generated for lighter TPHs (Jet Fuel) and heavier TPHs (motor oil). Average response factor was used to show linearity. Percent relative standard deviation (% RSDs) among calibration factors (CFs) was within acceptable limit (less than 15 %.)

Retention time window width was established by analysis of a window defining hydrocarbon standard (C10-C40). Retention times for further sample analyses was used for peak identification and integration range.

4.9.3. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) on 02-17-23. Percent difference between initial calibration response factors (Average response factors) and the response factors calculated for each analyte were less than 20%

Three continuing calibration standards were analyzed at 10-injections interval. It was carried out on 05-04-23 and 05-05-23 bracketing the analyses of samples and all the QC samples. Percent difference between initial calibration average response factors and the response factors calculated for each DRO group from continuing calibrations were less than 20%.

4.9.4. Quality Control samples consisted of one method blank and one set of LCS/LCSD. No sample was designated for MS/MSD. Percent recoveries (%R) of LCS/LCSD were within the QAPP established QC limits. Raw data for both un-spiked sample and spiked QC samples were matching the reported values.

Result for method blank was reviewed and no contamination was found in the method blank. Surrogate recoveries were all within the method QC acceptance limits.

4.9.5. Field duplicate sample and its associated sample: No field duplicate sample was collected with this sample delivery group.

4.9.6. Raw data was submitted for all samples. Sample MW38042023(Lab ID#23D322-03) was designated to be reviewed as stage 3 data deliverable. Raw data for this sample with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.10. Perchlorate by HPLC/MS/MS (EPA Method 6850)

4.10.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for seven samples requested for this method. Water samples were collected on 04-27-23. Samples were analyzed on 05-19-23, within the required holding time.

A High-Performance LC coupled with Mass Detector (HPLC/MS) was used for analysis.

4.10.2. Initial Calibration

Initial calibration was performed with seven levels of concentration on 03-13-23. Internal standard curve type was used for quantifying Perchlorate. Isotopically-labeled Perchlorate ion ($Cl^{18}O4^{-}$) was added to serve both as internal standard and correction for Perchlorate loss from sample preparation. The correlation coefficient of 0.9962 (Perchlorate ion 83) and 0.9986 (perchlorate ion 85) was calculated to show the linearity of each curve. The concentrations used for calibration ranged from 0.1 – 7.5 µg/L.

Retention time for each isotope (ion 83 and 85) at each calibration level was within 0.2 minutes required by the method.

4.10.3. Initial Calibration Verification and Continuing Calibration

Initial calibration was verified by a second source standard (ICV) on 03-13-23. Percent recoveries were within required method limits (85-115% of the true value).

Continuing calibration standards were analyzed at 10-injections interval. A total of four daily standards were carried out on 05-19-23 bracketing analyses of samples and all the QC samples. Recoveries of continuing calibration standards were within 90-110% limit.

4.10.4. Quality Control samples consisted of one method blank and one sets of LCS/LCSD. No sample was designated to be spiked as MS/MSD. Perchlorate was spiked and reported for LCS/LCSD. Percent recoveries (%R) were within the established QC limits. Raw data for both un-spiked sample and spiked QC samples were matching the reported values.

Result for method blank was reviewed for each compound and no target was found in the method blank. No surrogate is used in this method.

4.10.5. Field duplicate sample and its associated sample: No field duplicate sample was collected with this sample delivery group.

4.10.6. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) and sample MW32042023 (Lab ID#23D322-04) were designated as stage 3 data deliverable. Raw data for these samples with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.11. TOTAL and DISSOLVED METALS BY ICP (EPA Method 6020A)

4.11.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for eight water samples requested for this method. Water samples were collected on 04-27-23. Samples were prepared (digested) for both total and dissolved metals on 05-04-23. Samples and QC samples were analyzed on 06-26-23 for total and dissolved metals by ICP MS. Some samples were re-analyzed for total metals on 06-28-23. Water samples were preserved and filtered in the lab for dissolved metals analysis. Therefore, two sets of data were generated, one for total metals and one for dissolved metals.

4.11.2. Initial Calibration and Continuing calibration standards

Initial calibration was performed at the start of each analysis day on 06-26-23 and 06-28-23. Tune performance report was generated at the start of each analysis day, before initial calibration. It was within method’s acceptance criteria. Initial instrument (ICP-MS) calibration for this method was acceptable. Five levels of concentration were used for each initial calibration. One method blank and one calibration standard was used for each daily check standard. A range of concentrations of standards was used for calibration. The concentrations used are summarized as follow:

Metals	**Concentration µg/L**
Se, Pb, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Mn, Ni, Ag, Tl, V, and Zn	50,100,500,1000
Al, Fe, Ca, Mg, Na, and K	50,000

Initial and continuing calibration verification standards for each element was within acceptable limit of 90-110 percent of the true value. Continuing calibration standards were analyzed at the frequency required by the method. Results for the ICP Interference Check Solutions (ICS-A and ICS-AB) were within the control limits of ±20% of the true value for the analytes incorporated in each solution.

4.11.3. Quality Control samples consisted of method blank, one set of LCS/LCSD and MS/MSD for total metals. Sample MW19042023 was selected to be spiked as MS/MSD for total metals only. QC samples for dissolved metals consisted of one method blank and one set of LCS/LCSD. Recoveries of LCS/LCSD and MS/MSD were all within the acceptance limit for both total and dissolved metals. However, few metals failed the acceptable QC limits in MS/MSD for total metal analysis as shown in the table below:

ANALYTE	Total Metals			Dissolved Metals		
	MW19042023 (D322-01MS) MS%	MW19042023 (D322-01MSD) MSD%	**QC Limit %**	NA	NA	**QC Limit %**
Aluminum	120*	150*	84-117	--	--	84-117
Antimony	√	√	85-117	--	--	85-117
Arsenic	√	√	84-116	--	--	84-116
Barium	114	144*	86-114	--	--	86-114
Beryllium	√	√	83-121	--	--	83-121
Cadmium	√	√	87-115	--	--	87-115
Calcium	1000*	-167*	87-118	--	--	87-118
Chromium	√	√	85-116	--	--	85-116
Cobalt	√	√	86-115	--	--	86-115
Copper	√	√	85-118	--	--	85-118
Iron	138*	118	87-118	--	--	87-118
Lead	√	√	88-115	--	--	88-115
Magnesium	120*	110	83-118	--	--	83-118
Manganese	67*	-33*	87-115	--	--	87-115
Nickel	√	√	85-117	--	--	85-117
Potassium	√	√	85-115	--	--	85-115

ANALYTE	Total Metals			Dissolved Metals		
	MW19042023 (D322-01MS) MS%	MW19042023 (D322-01MSD) MSD%	**QC Limit %**	NA	NA	**QC Limit %**
Selenium	√	√	80-120	--	--	80-120
Silver	√	√	85-116	--	--	85-116
Sodium	1667*	667*	85-117	--	--	85-117
Thallium	√	√	82-116	--	--	82-116
Vanadium	√	√	86-115	--	--	86-115
Zinc	√	√	83-119	--	--	83-119

*Outside control limits

Therefore, positive results for the parent sample would be qualified as estimated value, “J” for these metals.

Results for method blanks were acceptable and no contamination was found in the method blanks. Calibration blanks were analyzed after each continuing calibration standard.

Sample MW19042023 was also used for serial dilution for total metals. The serial dilution analysis (at 5-fold dilution) was within 10% difference of the initial analysis. The same sample was used for spike addition (analytical spike). All results were within the QC limit of (80-120%) for total metals.

4.11.4. Field duplicate sample and its associated sample: No field duplicate sample was collected with this sample delivery group.

4.11.5. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) and sample MW32042023 (Lab ID#23D322-04) were designated as stage 3 data deliverable. Raw data for these samples with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.12. MERCURY & Dissolved Mercury by COLD VAPOR: EPA Method 7470A

4.12.1. Technical Holding Times

Holding time from sample collection to extraction and extraction to analysis was met for eight water samples requested for this method. Water samples were collected on

04-27-23. Samples were prepared (digested) on 05-24-23 for Mercury and dissolved Mercury. Samples were analyzed for Mercury and dissolved Mercury on 05-24-23. All samples were preserved and filtered in the lab for dissolved Mercury analysis.

4.12.2. Initial and continuing calibrations: The instrument calibrations for this method were acceptable. One blank and five standard levels were used for calibration curve at the beginning of analysis day on 05-24-23. The correlation coefficient of at least 0.999701 was calculated to show the linearity of calibration curve. The concentrations used for calibration ranged from 0.2 – 5.0 µg/L.

Initial calibration verification and Continuing calibration verification standards were within the acceptable range (90-110% of the spiked value).

4.12.3. Quality Control: The data for all the QC samples were within acceptable control limits. The QC samples consisted of one method blank, one set of LCS/LCSD and MS/MSD for Mercury. Sample MW22D042023 was selected to be spiked as MS/MSD for Mercury only. QC for dissolved Mercury consisted of one method blank and one set of LCS/LCSD. Percent recoveries and % differences were within the control limits for LCS/LCSD and MS/MSD for both Mercury and dissolved Mercury. Sample MW22D042023 was also used for serial dilution for Mercury. The results were all within QC acceptable limits. Method blank data was reviewed and no Mercury contamination was found in method blanks.

4.12.4. Field duplicate sample and its associated sample: No field duplicate sample was collected for this sample delivery group.

4.12.5. Raw data was submitted for all samples. Sample MW38042023 (Lab ID#23D322-03) and sample MW32042023 (Lab ID#23D322-04) were designated as stage 3 data deliverable. Raw data for these samples with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

4.13. Method SW9056A: Nitrate-N, Nitrite, Orthophosphate, Bromide, Fluoride Sulfate and Chloride

4.13.1. Technical Holding Times: Holding time from sample collection to analysis was met for analysis of seven water samples requested for this method. Water samples were collected on 04-27-23. Samples were analyzed on 04-28-23 within the required 48-hour holding time for Nitrate, Nitrite, Orthophosphate, Bromide and Fluoride. Samples were re-analyzed at higher dilutions on 04-28-23, 05-01-23 and 05-02-23 for Chloride and Sulfate within 28-day holding times.

4.13.2. Initial and continuing calibration: Anions such as Chloride, Fluoride, Bromide, Nitrite, Nitrate, Orthophosphate and Sulfate were separated from water samples by Ion chromatography. The separated anions in their acid form (very conductive) were measured by conductivity. They were identified on the basis of retention time as compared to reference standards.

Instrument was initially calibrated with nine calibration levels (0.05-20mg/L) on 11-09-22. Linear curve type with correlation coefficient of at least 0.999 for each anion was used throughout analysis. Percent RSD among calibration factors was less than 15%. Calibration curve (concentration versus area count of each anion) was presented for each anion. Area for each level was randomly checked with the values used in each calibration curve. All agreed with the raw data. A second source standard mixture (ICV) was used to verify the linearity of initial calibration on 11-09-22. Recoveries were all within 90-110% of initial true value.

Continuing Calibration standards at 10-injections interval were analyzed on 04-28-23, 04-29-23, 05-01-23 and 05-02-23. A total of nine continuing calibration standards were analyzed with analysis and re-analysis of all samples. In all continuing calibration standards submitted, the recoveries of target anions were within 90-110% of the expected values. After each continuing calibration standard, one calibration blank was injected. All the blanks were reported as non-detected regarding all the target anions. Retention time window width was established and confirmed with reference standard. It was within the assigned QC limit for each anion.

4.13.3. Quality Control Samples consisted of one method blank and one set of set LCS/LCSD only. No sample was designated to be spiked as MS/MSD. Recoveries of LCS/LCSD were all within QC acceptance limits for each anion. Percent RPDs were less than 20% for LCS/LCSD.

4.13.4. Field duplicate sample and its associated sample: No field duplicate sample was collected for this sample delivery group.

4.13.5. Raw data was submitted for all requested field samples. Sample MW38042023 (Lab ID#23D322-03) and sample MW32042023 (Lab ID#23D322-04) were designated as stage 3 data deliverable. Raw data for these samples with the related QC samples was reviewed for stage 3 data validation. The results calculated from the raw data, agreed with all the results reported in data summary reports.

5.0 CONCLUSION

SDG #23D322 analytical data evaluated in this data validation report has met the data quality and usability requirement as defined in the data quality objectives. The qualified QC data, if any, was due to matrix interference in the parent sample. Overall analytical data is of acceptable quality and considered usable for its intended purpose.

6.0 REFERENCES

1. *USEPA Analytical Operations/Data Quality Center (AOC) National Functional Guidelines for Organic Data Review* (USEPA, January 2017).

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6. Department of Defense Quality System Manual (DOD QSM), Version 5.3, 2019

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