State of Connecticut

Department of Energy and Environmental Protection

# Recommended Reasonable Confidence Protocols

# Quality Assurance and Quality Control Requirements

# Chlorinated Herbicides by SW-846 Method 8151

Version 3.0

May 2024

Written by the Connecticut DEEP QA/QC Workgroup

| Revision | Comments | Date |
|---|---|---|
| 1.0 | First version for publication | 7/05/2005 |
| 2.0 | Final version based upon public comments | July 2006 |
| 3.0 | Updates to reflect CAM method updates to improve consistency between different states. | May 2024 |

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## Acronym List

| ACRONYM | DEFINITION |
|---|---|
| BFB | Bromofluorobenzene |
| CASN | Chemical Abstracts Service Number |
| CCV | Continuing calibration verification |
| %D | Percent difference or percent drift |
| 2.4-D | 2,4-Dichlorophenoxy acetic acid |
| 2,4-DB | 2,4-Dichlorophenoxy butyric acid |
| DBOFB | 4,4'-Dibromooctafluorobiphenyl |
| DCAA | 2,4-Dichlorophenylacetic acid |
| DF | Dilution factor |
| ECD | Electron capture detector |
| DEEP | CT Department of Energy and Environmental Protection |
| DF | Dilution factor |
| ECD | Electron capture detector |
| EP | Environmental Professional |
| g | grams |
| GC | Gas chromatograph |
| GC/MS | Gas chromatography/mass spectrometry |
| ICV | Initial calibration verification |
| LCS/LCSD | Laboratory control sample |
| LCSD | Laboratory control duplicate |
| LLOQ | Lower Limit of Quantitation |
| MCPA | 2-Methyl-4-chlorophenoxy acetic acid |
| MCPP | 2-(2-methyl-4-chlorophenoxy) propionic acid |
| MD | Matrix duplicate |
| mL | Milliliters |
| MS | Matrix spike |
| MSD | Matrix spike duplicate |
| NA | Not applicable |
| OHM | Oil and Hazardous Materials |
| QA | Quality assurance |
| QC | Quality control |
| $r/r^2$ | Correlation coefficient |
| %R | Percent recovery |
| %RSD | Percent relative standard deviation |
| RCP | Reasonable Confidence Protocol |
| RF | Response factor |
| RL | Reporting limit |
| RPD | Relative percent difference |
| RSR/RSRs | Remediation Standard Regulations |
| 2,4,5-T | 2,4,5-Trichlorophenoxy acetic acid |
| µg/kg | micrograms per kilogram |
| µg/L | micrograms per liter |
| µL | microliters |

# *1.0 Quality Assurance and Quality Control Requirements for SW-846 Method 8151*

## *1.1 Method Overview*

SW-846 Method 8151 is a gas chromatography ("GC") procedure used for the analysis of chlorinated herbicides in a variety of matrices including waters, soils, sediments, wastes, etc. This procedure requires an experienced GC analyst familiar with the Quality Assurance and Quality Control ("QA/QC") requirements of the method. The sample introduction procedure requires the use of a solvent extraction followed by a derivitization procedure.

Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151 utilizes a hydrolysis step to convert herbicide esters into the acid form prior to derivatization. This hydrolysis step is required to produce data of Reasonable Confidence. Herbicide esters generally have a half-life of less than one week in soil.

Open-tubular, capillary columns are employed with electron capture detectors ("ECD"). The target analytes may be determined with either a single- or dual-column chromatographic system. Second column confirmation is required for all herbicide analyses.

All method references are to the latest promulgated version of the method found in *Test Methods for Evaluating Solid Waste, SW-846*.

## *1.2 Summary of SW-846 Method 8151*

### 1.2.1 Sample Extraction and Cleanup

Samples for analysis by SW-846 Method 8151 require extraction by one of the following methods presented in Table 1.0. Laboratories must use the solvents listed for extraction and follow the extraction procedures in SW-846 Method 8151.

**Table 1.0: Extraction Methods**

| SW-846 Method | Matrix | Method |
|---|---|---|
| 3510 | Aqueous | Separatory Funnel Liquid-Liquid Extraction. |
| 3545 | Soil/Sediment | Sonication, Pressurized Fluid |
| 8151 | Soil/Sediment | Shaker extraction |
| 3580 | Waste | Waste Dilution |
| 8151 | Extract Concentration | SW-846 Method 8151 |
| 8151 | Derivatization | SW-846 Method 8151 |

### 1.2.2 GC Analysis

The herbicides are extracted from the sample using the appropriate method. Water samples are extracted with diethyl ether and then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by gas chromatography with an electron capture detector ("GC/ECD"). The results are reported as acid equivalents.

Soil and waste samples are extracted with the appropriate extraction method according to SW-846 Method 8151 indicated in Table 1.0. The extracts are then esterified with either diazomethane or pentafluorobenzyl bromide. The derivatives are determined by GC/ECD. The results are reported as acid equivalents. Herbicide esters are required to be determined using this method, and hydrolysis conditions for the esters in water and soil extracts must be employed.

Preliminary identification of target analytes is accomplished by comparing the retention time of the chromatographic peaks of the sample to known herbicides analyzed under the exact same conditions. Confirmation is accomplished either by analysis of the same extract on a dissimilar column, again comparing the retention times of the chromatographic peaks of the sample to known pesticides analyzed under the exact same conditions, or by using at least one other independent qualitative technique such as gas chromatography/mass spectrometry ("GC/MS"). Quantitation is accomplished by constructing a calibration curve of herbicide concentration vs. peak area. Confirmation is not required in the case where herbicides are not detected above their specific reporting limit.

## *1.3 Method Interferences*

Refer to SW-846 Methods 3500, 3600, and 8000 for a detailed discussion of interferences and corrective actions which may be taken to eliminate contamination. Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

Sources of interference in this method can be grouped into four broad categories:

- Contaminated solvents, reagents, or sample processing hardware,
- Contaminated GC carrier gas, parts, column surfaces, or detector surfaces,
- Non-target compounds simultaneously extracted from the sample matrix which cause a detector response, and
- Co-elution of target analytes.

### 1.3.1 Chemical Contaminants

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Analysis of blanks provides information about the presence of contaminants. When potential interfering peaks or high levels of target compounds are detected in blanks, the laboratory should try and find the source of the contamination and eliminate it. **Subtracting blank concentrations from sample results is not permitted.** Any method blank exceedances should be fully documented in the laboratory report narrative.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from sample to sample depending upon the nature and diversity of the matrix being sampled.

Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive, and more prone to interferences from the presence of organic acids or phenols than by methylation.

The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

### 1.3.2 Cross-contamination/Carryover

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of chlorinated herbicides. After the analysis of a sample containing high concentrations of chlorinated herbicides, one or more blanks should be analyzed to check for potential cross-contamination/carryover. Concentrations of chlorinated herbicides which exceed the upper limit of calibration should prompt the analyst to check for potential cross-contamination/carryover. In addition, samples containing large amounts of water-soluble materials, suspended solids, or high boiling point compounds may also present potential for cross-contamination/carryover. Laboratories should be aware that carryover from high boiling point compounds may not appear until a later sample analysis. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections.

### 1.3.3 Special Precautions

Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

Esterification duration is critical to the herbicide recoveries. Methylated extracts are subject to trans- esterification and other unwanted side reactions. Sample extracts must be analyzed immediately after the methylation procedure has been performed in order to minimize the trans-esterification and other potential reactions that may occur. This is critical in the evaluation of whether the holding time criteria were achieved.

## *1.4 Quality Control Requirements for SW-846 Method 8151*

### 1.4.1 Reporting Limits/Lower Limits of Quantitation for SW-846 Method 8151

The reporting limit (“RL”), or lower limit of quantitation (“LLOQ”), for a compound is dependent on the concentration of the lowest standard in the initial calibration, sample weight/volume, extraction procedure, and moisture content. Table 2.0 presents approximate RL/LLOQs for various matrices utilizing a GC/ECD. Solid matrices in this table assume 100% solids.

**Table 2.0: Typical Reporting Limits/Lower Limits of Quantitation**

| Matrix | Typical Reporting Limit |
|---|---|
| Water | 0.5 to 2.0 µg/L (MCPA/MCPP 100 µg/L) |
| Soil | 5 to 80 µg/kg (MCPA/MCPP 3300 µg/kg) |
| [1]Note these values are intended to serve as guidance to EPs when planning analytical needs to achieve the data quality objectives to meet project-specific goals. These tables are not intended to dictate what RL/LLOQs laboratories must report. | |

Moisture content of soils and sediments will raise the RL/LLOQ, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL/LLOQs to be raised. It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analytes to meet the project Data Quality Objectives (“DQOs”). To meet the RLs/LLOQs

applicable to project DQOs, it may be necessary to modify the analytical method by using increased sample volume or mass. In such cases the modifications must be noted in the laboratory report narrative.

### 1.4.2 General Quality Control Requirements

This protocol is restricted to use by, or under the supervision of, analysts experienced in the use of GC instrumentation as a quantitative tool and skilled in the interpretation of chromatograms for chlorinated herbicides.

Refer to SW-846 Method 8000 for general quality control ("QC") requirements for all chromatographic methods, including SW-846 Method 8151. These requirements ensure that each laboratory maintain a formal quality assurance ("QA") program and records to document the quality of all chromatographic data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the GC system operation may be found in SW-846 Method 8000 and include evaluation of retention time windows, initial and verification of instrument calibrations and chromatographic performance of sample analyses. Instrument quality control and method performance requirements for the GC system may be found in SW-846 Method 8151.

The minimum requirements for a formal QA program include Initial Demonstration of Laboratory Capability ("IDOC"), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples ("LCS") and/ or matrix spikes ("MS") to assess accuracy and LCS duplicates ("LCSD") and matrix spike duplicates ("MSD") to assess precision. The use of site-specific MS/MSD's is highly recommended for each site and each matrix type sampled. Evaluation of sample matrix effects on compound recovery is key to making informed decisions. Percent recovery data from site-specific samples allow the environmental professional ("EP") to make informed decisions regarding contamination levels at the site. Batch MS/MSD results do not give any indication of site-specific matrix interferences or analytical problems related to the specific site matrices. Field, rinsate, or other blanks should not be used for MS/MSD's.

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative method being used. An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform this method. These data must meet or fall within the performance standards as presented in Section 1.4 and Table 1A of this RCP. See SW-846 Method 8000 for the procedure. The IDOC must include the following elements in Table 3.0:

**Table 3.0: IDOC Requirements**

| QC Element | Performance Criteria |
|---|---|
| Initial Calibration | Table 1A |
| Continuing Calibration | Table 1A |
| Method Blanks | Table 1A |
| Average Recovery | Table 1A |
| % Relative Standard Deviation | Table 1A |
| Surrogate Recovery | Table 1A |
| Internal Standards (Optional) | Table 1A |

Because of the extensive analyte list and number of QC elements associated with the IDOC it should be expected that one or more analytes may not meet the performance standards for one or more QC elements. The laboratory should make every effort to find and correct the problem and repeat the analysis. All non-conforming analytes along with the laboratory acceptance criteria should be noted in the IDOC data. This information should be kept on-file at the laboratory.

Laboratories are required to generate laboratory specific performance criteria for LCS compound recovery limits, matrix spike/matrix spike duplicate compound recovery and relative percent difference ("RPD") limits, and surrogate recovery limits. These limits must be equal to or fall within the limits specified in Table 1A.

### 1.4.3 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151

Specific QA/QC requirements and performance standards for SW-846 Method 8151 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide the EP with “Reasonable Confidence” regarding the usability of analytical data to support environmental decisions. The concept of "Reasonable Confidence" is explained on the CT Department of Energy and Environmental Protection (“DEEP”) website.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will generally accept “Reasonable Confidence” data. In order to achieve “Reasonable Confidence” parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate all protocol non-compliances and implement, as necessary, required corrective actions and analytical response actions for all non-conforming analytical performance standards; and

3. Retain reported and unreported analytical data and information for a period of 5 years or as required under applicable accreditation criteria.

**Table 1A: Specific QA/QC Requirements and Performance Standards for RCP Method 8151**

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| Initial Demonstration of Capability ("IDOC") | Laboratory Analytical Accuracy & Precision | (1) Must be performed prior to using method on samples.<br>(2) Must be performed for each matrix.<br>(3) Must contain all target analytes.<br>4 Must follow procedure in SW-846 8000. | No | Refer to SW-846 8000 and Section 1.4.2 of this protocol. | N/A |
| Retention Time Windows | Laboratory Analytical Accuracy | (1) Prior to or during the initial calibration when a new column is installed.<br>(2) Calculate according to the Method SW-846 8000. | No | N/A | N/A |
| Initial Calibration ("ICAL") | Laboratory Analytical Accuracy | (1) Must be analyzed with dual columns at least once prior to analyzing samples, when initial calibration verification or continuing calibration does not meet the performance standards, and when major instrument maintenance is performed.<br>(2) Minimum of 5 standards (or 6 if non-linear regression used).<br>(3) Low standard must be ≤RL/LLOQ.<br>(4) % RSD ≤20, r≥0.99 (linear regression), or $r^2$≥0.99 (non-linear regression) for each target herbicide.<br>(5) If RSD% >20, linear or non-linear regression must be used.<br>(6) Must contain all target herbicides.<br>(7) Calibration must be performed under the same conditions as the samples.<br>(8) If linear or non-linear regression used, verify the RL/LLOQ by recalculating concentrations in lowest calibration standard using the final calibration curve; recoveries must be 70-130%.<br>(9) Curves must be verified with initial calibration verification (ICV) prior to sample analysis.<br>(10) All standards must be derivatized using the same procedure used for samples, whether prepared in lab or purchased from a vendor.<br>(11) If curves are used, curve must NOT be forced through origin. Must use additional standards as specified in Method 8000. | No | (1) Recalibrate as required by method.<br>(2) If recalculated concentrations from the lowest calibration standard are outside of 70-130% recovery range, either:<br>(a) The RL/LLOQ limit must be reported as an estimated value; or<br>(b) The RL/LLOQ must be raised to the concentration of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration curve. | Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds (%RSD >20, r <0.99, or $r^2$ <0.99) in laboratory report narrative. If non-linear regression (i.e., quadratic equation) is used for calibration, this must be noted in laboratory report narrative along with the compounds affected. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| Initial Calibration Verification ("ICV") | Laboratory Analytical Accuracy | (1) Immediately after each initial calibration.<br>(2) Concentration level near midpoint of curve.<br>(3) Prepared using standard source different than used for initial calibration.<br>(4) Must contain all target herbicides.<br>(5) Percent recoveries must be between 80-120% for each target analyte. | No | Locate source of problem; recalibrate if >10% of all analytes are outside of criteria. | If recovery is outside of 80-120% for any analyte, report non-conforming compounds in laboratory report narrative. |
| Continuing Calibration Verification ("CCV") | Laboratory Analytical Accuracy | (1) Prior to samples, every 12 hours or every 10 samples, whichever is more frequent, and at the end of the analytical sequence.<br><br>NOTE: if internal standard calibration used, the continuing calibration at the end of the analytical sequence is not required.<br><br>(2) Concentration level near midpoint of curve.<br>(3) Must contain all target herbicides.<br>(4) %D must be ≤15% for each target analyte.<br>(5) Verify that all analytes fall within retention time windows.<br>(6) Area count of internal standard in continuing calibration must be within ±50% of the average area count in the associated initial calibration.<br>(7) All standards must be derivatized using the same procedure used for samples, whether prepared in lab or purchased from a vendor. | No | (1) Perform instrument maintenance, reanalyze CCV and/or recalibrate as required by method.<br>(2) Reanalyze associated samples if beginning or ending CCV exhibited low response.<br>(3) Reanalyze associated samples if beginning or ending CCV exhibited high response and associated herbicides were detected in the "associated samples".<br><br>NOTE: Associated samples refers to all samples analyzed since the last acceptable CCV.. | Report non-conforming compounds (%D > 15%) and associated samples in laboratory report narrative. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| Method Blank ("MB") | Laboratory Method Sensitivity (contamination evaluation) | (1) Extracted with every batch or every ≤20 field samples, whichever is more frequent.<br>(2) Matrix-specific (e.g., water, soil).<br>(3) Target analytes must be <RL/LLOQ. | Yes | (1) If concentration of contaminant in sample is <10x concentration in blank**,** locate source of contamination; correct problem; re-extract and re-analyze method blank and associated samples.<br>(2) No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample. | (1) If sample re-extraction is not possible, report non-conformance in laboratory report narrative.<br>(2) If contamination of method blanks is suspected or present, the lab, using a "B" suffix or some other convention, should qualify the sample results. Blank contamination should also be documented in the laboratory report narrative.<br>(3) If re-extraction is performed within holding time and yields acceptable method blank results, the lab may report results of the re-extraction only.<br>(4) If re-extraction is performed outside of holding time, the lab must report results of both the initial extraction and re-extraction. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| Laboratory Control Sample ("LCS") | Laboratory Analytical Accuracy | (1) Every ≤20 field samples or each batch, whichever is more frequent.<br>(2) Standard source different from initial calibration source.<br>(3) Concentration level should be near or at the mid-point of the initial calibration.<br>(4) Must contain all target analytes.<br>(5) Matrix specific (e.g., soil, water).<br>(6) Percent recoveries must be between 40-140% for all target analytes.<br>(7) Must be prepared in a water-miscible solvent (e.g., acetone, methanol). | Yes | (1) Locate source of problem; re-extract and re-analyze LCS and associated samples if >10% of all analytes are outside of criteria.<br>(2) If ≤10% of compounds are outside of the acceptance criteria, re-extraction is not required as long as recoveries are >10%.<br>(3) If >10% of compounds are above the acceptance criteria (>140%) re-extraction is not required if affected compounds were not detected in associated samples.<br>(4) If MS/MSD in the same batch compare to determine if problem isolated to LCS.<br>(5) Re-extract LCS and samples if compounds outside acceptance criteria and no MS/MSD with acceptable criteria. | (1) If sample re-extraction is not possible, report non-conformance in laboratory report narrative.<br>(2) If recovery is outside of 40-140% for any analyte, report non-conforming compounds in laboratory report narrative.<br>(3) If re-extraction is performed within holding time and yields acceptable LCS results, the lab may report the re-extraction only.<br>(4) If re-extraction is performed outside holding time, the lab must report results of both the initial and re-extraction.<br>(5) Individual labs must identify and document problem analytes that routinely fall outside the limits. Any non-conformances must be noted in laboratory report narrative. Data to support lab problem compounds kept on file at. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| LCS Duplicate ("LCSD") | Laboratory Analytical Accuracy & Precision | (1) Extracted every batch or every ≤20 field samples, whichever is more frequent.<br>(2) Concentration level near midpoint of curve.<br>(3) Must contain all target herbicides.<br>(4) Matrix-specific (e.g., soil, water).<br>(5) Percent recoveries must be between 40-140% for all target analytes.<br>(6) RPDs must be ≤20% for waters and ≤30% for solids.<br>(7) Must be prepared in water-miscible solvent (e.g., acetone, methanol). | Yes | (1) Locate source of problem; re-extract and re-analyze LCS and associated samples if >10% of all analytes are outside of recovery acceptance criteria.<br>(2) If ≤10% of compounds are outside of the recovery acceptance criteria, re-extraction is not required as long as recoveries are >10%.<br>(3) If >10% of compounds are above the recovery acceptance criteria (>140%), re-extraction is not required if affected compounds were not detected in associated samples. | (1) If sample re-extraction is not possible, report non-conformance in laboratory report narrative.<br>(2) If recovery is outside of 40-140% for any analyte or if RPD is outside of criteria, report non-conforming compounds in laboratory report narrative.<br>(3) If re-extraction is performed within holding time and yields acceptable LCS results, the lab may report results of the re-extraction only.<br>(4) If re-extraction is performed outside of holding time, the lab must report results of both the initial extraction and re-extraction. |
| Matrix Spike / Matrix Spike Duplicate ("MS/MSD") (Site Specific) | Method Accuracy & Precision in Sample Matrix | (1) Every ≤20 field samples per matrix (at discretion of lab or at request of data user).<br>(2) Matrix specific (e.g., aqueous, soil).<br>(3) Spike concentration near midpoint of curve.<br>(4) Must contain all target analytes.<br>(5) Percent recoveries between 30-150%.<br>(6) RPDs ≤20% for waters and ≤30% for solids.<br>(7) Must be prepared in water-miscible solvent (e.g., acetone, methanol).<br>(8) Field blanks, trip blanks, etc. cannot be used for MS/MSDs. | Yes<br><br>ONLY when requested by data user | Check LCS; If recoveries are acceptable in LCS, narrate non-conformance. | Note non-conformances in laboratory report narrative. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| Surrogates | Method Accuracy in Sample Matrix | (1) Minimum 1 surrogate across retention times of GC run and does not interfere with target analytes. Recommended compound DCAA.<br>(2) Recovery limits within 30-150% on both columns. | Yes (report surrogate recoveries from both columns) | If the surrogate is outside of limits on both columns:<br>(1) Re-extract the sample if surrogate recoveries are low and there is no chromatographic interference.<br>(2) Re-extract the sample if surrogate recoveries are high and herbicides were detected in the sample.<br><br>NOTE:<br>(a) If surrogate recoveries are high and target analytes are not detected in sample, re-extraction is not required.<br>(b) If chromatographic interference is present and surrogate recovery would cause rejection of data (i.e., <10%), reanalyze sample on dilution.<br>(c) If a surrogate is diluted to a concentration below that of the lowest calibration standard, re-extraction and/or reanalysis is not required.<br><br>(3)If surrogate recovery outside on one column only, and RPD of surrogate comparable (<40%), note in laboratory report narrative. | (1) Report recoveries outside of 30-150% in laboratory report narrative.<br>(2) If re-extraction yields similar surrogate non-conformances, the lab must report results of both the initial extraction and re-extraction.<br>(3) If re-extraction is performed within holding time and yields acceptable surrogate recoveries, the lab may report results of the re-extraction only.<br>(4) If re-extraction is performed outside of the holding time and yields acceptable surrogate recoveries, the lab must report results of both the initial extraction and re-extraction.<br>(5) If sample is not re-extracted due to chromatographic interference, the lab must provide the chromatogram in data report. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| Internal Standards (if employed) | Laboratory Analytical Accuracy & Method Accuracy in Sample Matrix | (1) Minimum of 1. Recommended internal standard: DBOFB.<br>(2) Area counts in sample must be between 50-200% of the area counts in the associated continuing calibration standard.<br>(3) Retention times of internal standards must be within ±30 seconds of retention times in associated continuing calibration standard. | No | If internal standard is outside of limits, re-analyze sample unless chromatographic interference present.<br><br>NOTE:<br>If chromatographic interference is present and internal standard area would cause rejection of data (i.e. <20%), reanalyze sample on dilution. | (1) Report non-conformances laboratory report narrative. Include actual recovery of internal standard and provide summary of analytes quantitated using the internal standard.<br>(2) If reanalysis yields similar internal standard non-conformances, the lab must report results of both analyses.<br>(3) If reanalysis is performed within holding time and yields acceptable internal standard recoveries, the lab may report results of the reanalysis only.<br>(4) If reanalysis is performed outside of the holding time and yields acceptable internal standard recoveries, the lab must report results of both analyses.<br>(5) If sample is not re-analyzed due to chromatographic interference, the lab must provide the chromatogram in the data report. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| Identification and Quantitation | Inter-laboratory Consistency | (1) Peak area is the expected default to be used for quantitation of herbicides under most circumstance. Regardless if peak area or peak height is used, the same method used for quantitation of samples must also be used for calibration standards.<br>(2) The laboratory must use the average CF, RF, or linear or non-linear regression curve generated from the associated initial calibration for quantitation of each target herbicide**.**<br>(3) Secondary column analysis: Laboratory must utilize a second dissimilar column to confirm positive results. The lab must report the higher of the two results unless obvious interference, in which case, report lower result. All required QC parameters (e.g., calibrations, LCSs, etc.) must be met on the secondary column as well.<br>(4) Do not report concentrations below the RL/LLOQ.<br>(5) If calibration standards are prepared using methyl esters, the calculation of concentration must include a correction for the weight of the methyl ester vs. the acid herbicide. | N/A | If RPD between the dual column results is >40%:<br>(a) determine potential interference;<br>(b) re-analyze sample on dilution; or<br>(c) additional sample cleanup techniques may be warranted; or<br>(d) re-extract sample and re-analyze. | (1) When the RPD between the dual column results is:<br>(i) <40% and there is no obvious matrix interference, the higher value shall be reported.<br>(ii) <40% and there is obvious matrix interference, the lower value shall be reported and the results shall be flagged with a “P”.<br>(iii) >40% and there is no obvious matrix interference, the higher value shall be reported and the results shall be flagged with a “P”.<br>(iv) >40% and there is obvious matrix interference, the lower value shall be reported and the results shall be flagged with a “P”.<br><br>If non-linear regression (e.g., quadratic equation) is used, must note list of affected compounds in laboratory report narrative. |

| Required QC | Data Quality Objective | Required Performance Standard | Required Deliverable | Required Corrective Action | Required Analytical Response Action |
|---|---|---|---|---|---|
| General Reporting | N/A | (1) The laboratory must report only concentrations detected above the sample specific RL/LLOQ.<br>(2) Concentrations below the reporting limit should be reported as "ND" with the sample specific RL/LLOQ also reported.<br>(3) Dilutions: If diluted and undiluted analyses are performed, the lab should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported.<br>(4) Results for soils/sediments must be reported on dry-weight basis. | N/A | N/A | (1) The performance of dilutions must be documented in the laboratory report narrative or on the report form. Unless due to elevated concentrations of target compounds, reasons for dilutions must be explained in the laboratory report narrative.<br>(2) Complete analytical documentation for diluted and undiluted analyses must documented in laboratory report narrative and be maintained in laboratory records.<br>(3) If samples are not preserved properly or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory report narrative.<br>(4) If samples are extracted and/or analyzed outside of holding time, note the non-conformances in the laboratory report narrative. |

## *1.5 Special Analytical Considerations for Herbicides*

Because of the variable solubility, extraction efficiency and analytical sensitivity of the different compounds that are potentially analyzable by SW-846 Method 8151, the recovery ranges presented in Table 1A for laboratory control samples, matrix spikes, and surrogates should be considered general upper/lower acceptance limits. It is essential that laboratory-specific performance criteria for LCS and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table 1A to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

## *1.6 Analyte List for SW-846 Method 8151*

The DEEP analyte list for SW-846 Method 8151 is presented in Table 1B. The compounds listed are readily determined by Method 8151. Most of the compounds listed have Connecticut RSR Criteria or are listed in the Approved Criteria for Additional Polluting Substances.

**Table 1B: Analyst List For SW-846 Method 8151**

| Analyte | CAS Number |
|---|---|
| 2,5-Dichloro-6-methoxybenzoic acid (Dicamba) | 1918-00-9 |
| 2,4-Dichlorophenoxy acetic acid (2,4-D) | 94-75-7 |
| 2,4-Dichlorophenoxy butyric acid (2,4-DB) | 94-82-6 |
| 2-(2,4-Dichlorophenoxy) propionic acid (Dichloroprop) | 120-36-5 |
| 2,2-Dichloro propionic acid (Dalapon) | 75-99-0 |
| 2,4-Dinitro-6-sec-butylphenol (Dinoseb) * | 88-85-7 |
| 2-Methyl-4-chlorophenoxy acetic acid (MCPA) | 94-74-6 |
| 2-(2-Methyl-4-chlorophenoxy) propionic acid (MCPP) | 93-65-2 |
| 2,4,5- Trichlorophenoxy acetic acid (2,4,5-T) | 93-76-5 |
| 2,4,5-Trichlorophenoxy propionic acid (Silvex) | 93-72-1 |
| *Dinoseb is only a target analyte for aqueous samples. | |

### 1.6.1 Additional Reporting Requirements for SW-846 Method 8151

While it is not necessary to request and report all the analytes listed in Table 1B to obtain Reasonable Confidence status, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEEP strongly recommends that full list of analytes be reported during the initial stages of a site investigation and/or at sites with an unknown or complicated history of chemical usage or storage.

In cases where a shortened list of analytes is selected, the laboratory must still meet the method specific QC requirements and performance standards associated with the requested analytes list to obtain Reasonable Confidence.

## *1.7 Routine Reporting Deliverables for SW-846 Method 8151*

The following table (Table 4.0) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report all items in special circumstances.

**Table 4.0: Report Deliverables**

| Parameter | Deliverable | Comments |
|---|---|---|

| | | |
|---|---|---|
| Retention Time Windows | NO | |
| Initial Calibration | NO | Note non-conformances in laboratory report narrative |
| Continuing Calibration | NO | Note non-conformances in laboratory report narrative |
| Method Blanks | YES | Note non-conformances in laboratory report narrative. Flag all positive sample results above RL with “B” flag. |
| Lab Control Sample / Lab Control Sample Duplicate | YES | Note non-conformances in laboratory report narrative |
| Site Specific Matrix Spike/ Matrix Spike Duplicate | YES (If requested) | Note non-conformances in laboratory report narrative |
| Internal Standards | NO | Note non-conformances in laboratory report narrative |
| Identification and Quantitation | NO | Note non-conformances in laboratory report narrative |
| Surrogate Recoveries | YES | Note non-conformances in laboratory report narrative |
| General Reporting Issues | YES | Note non-conformances in laboratory report narrative |
| QA/QC Certification Form | YES | Signed by laboratory director or their designee. |
| Chain-of-Custody Form | YES | Signed by sample collector, courier, and laboratory. |

### 1.7.1 Reporting and Flagging of Results

The following rules apply to reporting results:

- Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Not Detected at the specified RL/LLOQ). The RL/LLOQ for each compound in each sample must be listed on the report based upon the lowest calibration standard, the exact sample mass, any dilution factors, percent moisture, etc.

- Compounds detected above the RL/LLOQ in blanks and found in samples, also above the RL/LLOQ shall be flagged with a “B” suffix (e.g., 25B).

- All soil/sediment results shall be reported on a dry weight basis.

## *1.8 Sample Containers, Preservation, and Holding Times*

Table 5.0 identifies the type of containers, preservation requirements, and holding times dependent upon analyte and matrix.

**Table 5.0: Sample Containers, Preservation, and Holding Times**

| Matrix | Container[1] | Preservation[2] | Holding Time |
|---|---|---|---|
| Aqueous with no chlorine present | 1-liter amber glass bottle with Teflon line cap | Store at 4 ± 2º C, but not frozen | 7 days to initial extraction. Initial extraction can be stored for 28 days<br><br>24 hours from esterification to analysis[4] |
| Aqueous with chlorine present | 1-liter amber glass bottle with Teflon line cap | Neutralize chlorine with sodium thiosulfate. Store at 4 ± 2º C, but not frozen. | 7 days to initial extraction. Initial extraction can be stored for 28 days<br><br>24 hours from esterification to analysis |
| Soil/Sediment samples. | 250 mL amber glass jar with Teflon lined cap. | Cool to 4 ± 2º C | 14 days to initial extraction. Initial extraction can be stored for 28 days<br><br>24 hours from esterification to analysis<br><br>Up to one year for extraction of samples frozen within 24 hours of collection.[3] |
| High Concentration Waste Samples | Collect in amber glass jar with Teflon lined cap. | Cool 4 ± 2º C. | 14 days to initial extraction. Initial extraction can be stored for 28 days<br><br>24 hours from esterification to analysis |

[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6º C are acceptable.

[3]If the freezing option is selected the sample must be frozen within 48 hours of collection. The holding time recommences when thawing begins. The total holding time is calculated from the time of collection to freezing plus the time allowed for thawing. The total elapsed time must be less than 14 days.

[4]Re-esterification may be warranted if the analyst suspects potential influence on extracts. It is at the discretion of the analyst and data user if additional QC analysis may be used to demonstrate either the potential, or absence, of bias if the extra is analyzed past 24 hours past esterification.