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1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate herbicide data generated by SW-846 Method 8151A for the General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8151A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program. In addition, the usability of the herbicide data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and it is not directly applicable to validation of data generated by SW-846 Method 8151A; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCEL forms:

- Organic field duplicate comparison Rev 1-01.xls
- Organic field quadruplicate comparison Rev 1-01.xls
- Organic field triplicate comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8151A and related preparation and cleanup methods.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses.

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the herbicide data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8151A and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratory(ies) to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric

Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subsection of the QAR and will be included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the herbicide data based on an evaluation of the information presented in the data package deliverables. The findings of the herbicide data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the Organic Data Evaluation Section of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), tentative identifications of target compounds (N), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Design Support Sediment Sampling and Analysis Program).

The data reviewer's criteria for evaluating the usability of the herbicide data and the resultant qualifications will be as stated on the attached Table for the Validation of

Herbicide Data Generated by SW-846 method 8151A. It should be noted that the Project Manager should be consulted when the use of "professional judgement" is indicated on the attached table.

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C, but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as "UJ". If temperature is >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory; use professional judgement if < 8 hours has elapsed from collect to receipt to determine if the qualification for elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Solid samples should be extracted within 14 days of sample collection. All matrices should be analyzed within 40 days after extraction.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results ("UJ"). If holding time is grossly exceeded (*i.e.,* >twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #1 for additional information.)	%RSD should be <20% or a calibration curve should be generated. If a curve is generated, r (linear) or coefficient of determination (COD; quadratic) should be ≥0.99.	If any target compound result is associated with a low concentration initial standard that is not visible on the chromatogram, qualify "not-detected" results for that compound as estimated ("UJ"). If the standards indicate a severe lack of sensitivity (*e.g.*, the higher calibration standards are barely visible) the reviewer may qualify the "not-detected" results for that compound as unusable ("UR"); professional judgement should be used to determine the magnitude of the bias. Compounds with 20%<%RSD≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. Compounds with 50%<%RSD≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. (See Note #1) Compounds with %RSD >90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the initial calibration standards and the samples associated were not performed similarly (*e.g.*, the initial calibration standards were analyzed under different chromatographic conditions), qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Continuing Calibration Verification (CCV) (See Note #2 for additional information.)	%drift or % difference (%D) should be ≤15%.	Qualification is for all samples on both sides of the out of criteria CCV. If target compounds have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target compounds have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. (See Note #2) If target compounds have %D>90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If any target compound is not visible in the chromatogram qualify "not-detected" results as unusable ("UR").
Internal Standards (If used)	Area counts of the internal standard peaks should be 50-200% of the area of the target analytes in the mid-point calibration analysis. RT for any internal standard changes should only be ±30 seconds from the last calibration check standard.	If an area count is outside of the criteria (50-200%), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low area counts (<25%) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds using that internal standard as unusable ("UR"). If an internal standard RT varies by more than 30 seconds and no peaks are observed in the sample chromatogram, qualification of data is not necessary. Use professional judgement if peaks are observed in the sample chromatogram.

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Retention Time Windows (See Note #3 for additional information.)	All target compound retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory or 3× the standard deviation of three non-sequential standards over a 72-hour period	If the CCV RT windows are not within the specific RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCV, apply the direction of the RT drift to the sample chromatograms.
Blanks (See Notes #4 and #9 for additional information.)	Summarize all results greater than the method detection limit (MDL) in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is detected in a blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not-detected" ("U*"). If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× the blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #5 for additional information.)	Use laboratory acceptance limits. Use 20-150% as default limits if the laboratory limits are unreasonable.	If the recoveries of one or more surrogate are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogate are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogate are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicates (MS/MSD)	For accuracy, use recovery limits of 50-135%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPD calculated on %Rs) that are outside of criteria if the original concentration of a compound is >4× spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery > 135%, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" results. If the recovery < 50% but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples estimated ("UJ"). If the recovery < 10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" results. If the precision criteria (see field duplicate usability criteria) are not met for non-spiked compounds, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if the MS/MSD recoveries or RPD are outside of the criteria (as stated above for the native sample).

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 50%-135%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	If the recovery > 135%, qualify positive results for that compound in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery < 50% but ≥ 10%, qualify positive results for that compound in all associated samples as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery <10%, qualify positive results for that compound in all associated samples as estimated and qualify "not-detected" results as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive results for that compound in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field/Laboratory Duplicate (See Note #6 for additional information.)	Use a default limit of 20% RPD (%RSD for triplicate or quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate or quadruplicate analyses) for solid samples for sample results ≥5× RL. Use a default limit of ± RL for aqueous samples and ±2× RL for solid samples when at least one sample value is <5× RL	If the criteria are not met, qualify positive results for out of criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with <50% solid content require qualification.	If a solid sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a solid sample has a percent solid content <10%.

Table for the Validation of Herbicide Data Generated by SW-846 Method 8151A

Quality Control Item	Usability Criteria	Action
Compound Quantitation (See Note #7 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution.	If a target compound result exceeds the instrument calibration range, qualify positive results as estimated ("J"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J"). Use professional judgement to determine whether sample reanalyses and dilutions should be compared to the original analysis. If the precision criteria (see field duplicate usability) between the original sample results and the reanalysis sample result is not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
System Performance (See Note #8 for additional information.)	Professional judgement should be used when assessing the degradation of the system performance during analyses.	Use professional judgement to qualify the data if it is determined that the system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Herbicide Data Generated by SW-8151A

1. If the initial calibration %RSD is >50%, the linearity of the first three initial calibration standards for the compound should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥ 0.99), do not qualify "not-detected" results. If the first thee initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the samples should be evaluated for false negatives.

2. If instrument instability (*i.e.*, several CCVs with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential CCVs, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this in the QAR support documentation.

   Positive results should only be qualified if the results were reported from the out of criteria column. If samples are analyzed on two columns and an out of criteria CCV is reported on either column, then the samples should be evaluated for tentative positive

Notes for the Validation of Herbicide Data Generated by SW-8151A

results. If a tentative positive result is observed on the compliant column, qualify "not-detected" results (laboratory should only report positive results that have been confirmed on a second column) as estimated ("UJ"). If an out of criteria CCV is reported on both columns, qualify "not-detected" results as estimated ("UJ") whether or not tentative positive results were observed.

3. Use professional judgement when evaluating sample chromatograms. If the chromatograms reveal peaks corresponding to target compounds of interest using expanded RT windows, reported positive sample results for the compound outside the RT window are replaced with the RL and qualified as "not-detected" ("U"). If chromatograms reveal peaks that interfere with potential detection of a target compound, reported positive results for the compound are qualified as unusable ("R").

4. When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples should be analyzed on at least one of those instruments. A solvent blank should be analyzed on all other instruments on which the set of samples was analyzed to demonstrate that the instrument is not contributing contaminants to the samples.

   The frequency of equipment/rinse blanks is determined during the sampling event. The results of equipment/rinse blanks should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day; however, if only one was collected for a several-day sampling event. In instances when more than one blank is

Notes for the Validation of Herbicide Data Generated by SW-8151A

associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

If a sample result qualified "U*" is less than the RL and the laboratory did not report the RL on the data tables or Form I's, then the positive result (*e.g.*, 8 µg/L) should be replaced with the RL (*e.g.*, 10 µg/L).

5. The surrogate recovery limits do not apply to samples analyzed at dilutions greater than five-fold. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, greater than a five-fold dilution will affect the ability to even detect the surrogate. If a sample was analyzed at five-fold dilution or less and the surrogate was not detected in the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicates should only be applied to the original sample and its laboratory duplicate. It is also expected that soil duplicate results will have a greater variance than aqueous duplicate results.

Notes for the Validation of Herbicide Data Generated by SW-8151A

7. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

   If the laboratory provides dual column results for samples and both columns are quantitative then the %D between the results reported for both columns needs to be evaluated. If sample results are ≥5× RL and the %D is >40% but ≤90%, qualify positive results as estimated ("J"). If sample results are >5× RL and the %Ds is >90%, qualify positive results as unusable ("R"). If sample results are <5× RL and the differences between columns is >±2×RL, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

8. Poor chromatographic performance affects both qualitative (lower dilution analyses) and quantitative results. Indications of substandard performance include:

   - high background levels or shifts in absolute retention times of internal standards
   - excessive baseline rise at elevated temperature
   - extraneous peaks
   - loss of resolution
   - peak tailing or peak splitting that may result in inaccurate quantitation

9. The RL will be defined on a project-specific basis. If the project-required RL is less than the low initial calibration standard concentration, the Project Manager should be consulted for instructions on how to apply qualification related to the RL.