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1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate organochloride pesticide data generated by SW-846 Method 8081A for 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 8081A 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 pesticide data provided by the analytical laboratory(ies) 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 the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Method 8081A; therefore, 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/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.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 8081A.

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

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8081A (Rev 2. 12/96).

- 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 pesticide data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8081A 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 laboratories to request the correction of certain 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 subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the pesticide data based on an evaluation of the information presented in the data package deliverables. The findings of the pesticide 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 QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in the 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 (R/UR) results, tentative identifications of target compound results (N), estimated (J/UJ) results, 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 pesticide data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A. It should be noted

that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >6° but ≤10°C, no action is required. If temperature is > 10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("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 collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days after sample collection. Solid/soil samples should be extracted within 14 days after sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a 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").
GC Instrument Performance (See Note #1 for additional information.)	% Breakdown for 4,4′-DDT and endrin should be ≤15% for both GC columns.	Use professional judgement to determine if the associated sample data should be qualified if the instrument performance standard was not analyzed at the proper frequency. See Note #1 for action if the instrument performance standard criteria are not met.

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #2 for additional information.)	%RSD should be ≤20% or a calibration curve should be generated. If a curve is generated, the curve should have r (linear) or coefficient of determination (COD; quadratic) must be ≥0.99.	If target compounds have 20%<%RSD≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target compounds have 50%<%RSD≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %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) is <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").
Continuing Calibration Verification (CCV) (See Note #3 for additional information.)	%drift or %difference (%D) should be ≤15%.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. 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. 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").

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Retention Time Windows (See Note #4 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 as 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 the chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCVs, the direction of the RT drift should be applied to the sample chromatograms.
Blanks (See Note #5 and Note #10 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5x 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 both GC columns), qualify the positive results as unusable ("R") due to interference.
Internal Standards (if used)	Area counts of the internal standard peaks should be 50-200% of the internal standard area observed in the associated CCV standard. RT for any internal standard should not vary by more than ±30 seconds from RT in the associated CCV standard.	If a sample area count is outside of 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 sample 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 quantitated 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 is not necessary. Use professional judgement if peaks are observed in the sample chromatogram.

Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Surrogates (See Note #6 for additional information.)	Use laboratory acceptance limits. Use 20-150% as a default limit if the laboratory limits are unreasonable.	If samples are analyzed on two columns, samples should only be qualified if the out-of-criteria surrogate result is reported from the same column as the sample results. If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates 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 surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Matrix Spike/Matrix Spike Duplicate (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 RPDs calculated on %Rs) that are outside of criteria if the original concentration of a compound is 4× the spiking level for that compound. RPDs calculated using MS/MSD result can be used to evaluate precision. If the recovery is > 135%, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" results. If the recovery is < 50% but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <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" result. If the precision criteria (see field duplicate usability criteria) are not met for non-spiked compounds, qualify the positive result as estimated ("J") and qualify the "not-detected" result as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).

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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 in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery < 50% but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field Duplicate (See Note #7 for additional information.)	Use precision limits of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when sample results are ≥5× RL. Use limit of ± RL (±2× RL for solids) when at least one sample value is <5× RL. (Use one-half the RL as a numerical value for any "not-detected" results in the RPD calculations)..	If the criteria are not met, qualify positive results for the non-compliant compound in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with less than 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%.

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Quality Control Item	Usability Criteria	Action
Compound Quantitation (See Note #8 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"). Use professional judgement when evaluating sample reanalyses and dilutions. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J").
System Performance (See Note #9 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgement to qualify the data if it is determined that 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 Organochlorine Pesticide Data Generated by SW-846 Method 8081A

1. $$\%\ \text{breakdown for 4,4′ - DDT} = \frac{\text{Total DDT degradation peak area (DDE+ DDD)}}{\text{peak areas (DDT + DDE +DDD)}} \times 100$$

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area (Endrin aldehyde + Endrin ketone)}}{\text{peak areas (Endrin + Endrin aldehyde + Endrin ketone)}} \times 100$$

Qualification Due to High 4,4′-DDT (or Endrin) Breakdown				
Column # / Met criteria?	If 4,4′-DDT (or Endrin):	And if 4,4′-DDD and/or 4,4′-DDE (or Endrin ketone and/or Endrin aldehyde):	Then flag 4,4′-DDT (or Endrin):	And flag **positives** for 4,4′-DDD and/or 4,4′-DDE (or Endrin ketone and/or Endrin aldehyde):
(1)/no (2)/yes	+ +	any +'s +'s or ND's	"J" column (1) OK column (2)	"JN" column (1) "N" column (2)
(1)/no (2)/yes	ND + > RL^+	any +'s +'s or ND's	ND "R"	"JN" column (1) "N" column (2)
(1)/no (2)/yes	ND + < RL^+	any +'s +'s or ND's	ND OK	"JN" column (1) "N" column (2)
(1)/no (2)/yes	+ +	all ND's +'s or ND's	*	NA
(1)/no (2)/yes	ND + or ND	all ND's +'s or ND's	ND OK	NA
(1)/no (2)/yes	+ or ND ND	+'s or ND's +'s or ND's	ND OK	OK
(1)/no (2)/no	ND + or ND	any +'s any +'s	ND "R"	"JN"
(1)/no (2)/no	+ +	any +'s any +'s	"J"	"JN"
(1)/no (2)/no	+ ND	all ND's any +'s	ND "R"**	NA
(1)/no (2)/no	+ +	all ND's all ND's	*	NA
(1)/no (2)/no	+ or ND ND	+'s or ND's all ND's	ND OK	NA

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Where:

+ A peak was observed in the RT window for this pesticide on the corresponding GC column indicating a tentative identification for this pesticide. The positive result may quantitate to be below, at, or above the RL.

ND Not Detected regardless of the RL (flat baseline was observed in the area of the chromatogram where this compound would elute if it were truly present in the sample).

RL Reporting limit (RL) – will be defined on a project basis. If the project-required RL is greater than the low initial calibration standard concentration, the Project Manager should be consulted about application of qualifications related to the RL. Positives from a non-quantitative (conformational) GC column analysis should be considered above the RL for evaluation purposes, whether or not the result was quantitated above the RL on this non-quantitative column.

NA Not Applicable. Pesticide was not detected and only positive results are impacted.

* Although high breakdown was indicated by the associated standard on at least one column used for analysis, this positive result for 4,4′-DDT (or Endrin) has <u>not</u> been qualified because the breakdown components were not detected in the sample analysis on the noncompliant column(s). It is questionable, however, whether the peak(s) used for identification on the noncompliant column(s) truly represents 4,4′-DDT (or Endrin)

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because high breakdown was indicated by the associated standard. It is highly unusual not to detect the breakdown components in the presence of 4,4′-DDT (or Endrin).

** This "not-detected" result for 4,4′-DDT (or Endrin) has been qualified as unusable ("R") because the breakdown components were observed in the sample analysis on this column on which high breakdown was indicated by the associated standard. However, it should be noted that the breakdown components were <u>not</u> detected in the sample analysis on the other column on which high breakdown was also indicated by the associated standard. It is questionable whether the peak used for identification on this other column truly represents 4,4′-DDT (or Endrin) because high breakdown was indicated by the associated standard on this other column. It is highly unusual not to detect the breakdown components in the presence of 4,4′-DDT (or Endrin).

2. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards 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 three 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 sample should be evaluated for false negatives.

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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 initial calibration is reported on either column, the sample should be evaluated for tentative positive 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 initial calibration is reported on both columns, qualify "not-detected" results as estimated ("UJ") whether or not tentative positive results were observed.

3. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "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 within the QAR support documentation.

   Positive results should only be qualified if the results were reported for the out-of-criteria column. If samples are analyzed on two columns and an out-of-criteria CCV is reported on either column, the samples should be evaluated for tentative positive results. If a tentative positive result is observed on the compliant column, qualify "not-detected"

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

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.

4. 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 of the RT window are replaced with the RL and are qualified as "not-detected" ("U"). If the chromatograms reveal peaks that interfere with potential detection of a target compound, reported positive results for that compound are qualified as unusable ("R").

5. The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected on the same day, unless only one blank was collected for a several-day sampling event. In instances when more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

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

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Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank. If a positive result for a target compound is detected on the first column and not on the second column, the positive results should be qualified as tentative in all associated samples ("N"). Use professional judgement to determine if the result should be qualified as "not-detected" ("U*").

6. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. If a sample was analyzed at a five-fold dilution or less and either surrogate was not detected in the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

7. 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. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Soil duplicate results will have greater variance than aqueous duplicate results.

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8. 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 the dual-column results for samples and both columns are quantitative, evaluate the %D between the results reported for both columns. If the sample results are ≥5× RL and the %D is >40% but ≤90%, qualify positive results as estimated ("J"). If the sample results are ≥5× RL and the %D is >90%, qualify positive results as unusable ("R"). If sample results are <5× RL and the difference between columns is >±2×RL, qualify results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

9. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   - high background levels or shifts in absolute RTs 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

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

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