DATA QUALITY ASSESSMENT REPORT

MONTROSE SETTLEMENTS RESTORATION PROGRAM

BALD EAGLE EGG STUDY

Prepared for:

U.S. Department of Interior
Fish and Wildlife Service

U.S. Department of Commerce
National Oceanic and Atmospheric Administration

State of California
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1.0 INTRODUCTION

This report documents the results of a quality assurance review of data from eagle egg samples collected in support of the Montrose Settlements Restoration Program (MSRP). The eggs were analyzed for PCB congeners, PCB homologue groups, total PCBs, DDT isomers, total DDTs, percent lipids, and percent moisture.

A total 30 eggs were submitted for analysis, 21 eggs from the 2003 Bald Eagle Study and nine eggs from the 2004 Bald Eagle Study. These samples were analyzed in two analytical batches, laboratory numbers 0403104 and 0404028. The egg tissue was prepped, extracted, and analyzed by the Woods Hole Group Environmental Laboratories (Raynham, Massachusetts) using laboratory Standard Operating Procedures (SOPs) that were submitted and reviewed by EcoChem, Inc. prior to sample receipt.

Each sample extract was injected onto the instrument three different times, once for the PCB congeners, once for the DDT isomers, and once for the dilution of the 4,4´-DDE result.

2.0 DATA VALIDATION PROCEDURES

Data validation was based on the quality assurance/quality control (QA/QC) criteria documented in the *Addendum to the USEPA/MSRP Quality Assurance Plan for the Palos Verdes Shelf "Fish in Ocean" Sampling & Analysis Project*, April 14, 2004, and USEPA *National Functional Guidelines for Organic Data Review*, 1999, and the following laboratory SOPs:

- SOP # HR NRDA Project Tissue Prep: Tissue Preparation and Homogenization, Revision #1.0, 9/25/02
- SOP # OP-016: Microscale Solvent Extraction (MSE), Revision #1.0, 1/29/04
- SOP # O-010: Determination of PCB Homologues and Individual Congeners by GC/MS - SIM, Revision # 2.2, 10/24/02
- SOP # HR NRDA % Lipids: Percent Lipids Determination, Revision # 0.0, 9/9/02
- SOP # W-001: Percent Solids Determination, Revision # 2.1, 9/25/02
- Additional cleanup, sample handling, storage, custody SOPs as necessary.

Sample results and related QC data were received in both an electronic and hard copy format. Electronic data were verified against the hard copy data package. One package received full validation; the other package received summary validation.

The following QC elements were reviewed for data packages undergoing summary validation:

- Analytical holding times
- Chain of custody and sample handling
- GC/MS tune verification (from summary forms)
- Method blank contamination (from summary forms)
- Initial and continuing calibration (from summary forms)
- Analytical accuracy: surrogates, matrix spike samples, laboratory control samples, and standard reference material results (from summary forms)
- Analytical precision: laboratory duplicate samples (from summary forms)
- Internal standard areas (from summary forms)
- Reported detection limits (from sample result summaries)

Full validation included review of all the items listed above for summary validation, plus the following QC elements:

- Compound identification (from raw data)
- Compound quantitation, transcription and calculation checks performed at a frequency of 10% from raw data. If an error was noted, 100% of the calculations and transcriptions for that data set were verified.

This report summarizes the results of data validation relative to the analytical data quality objectives (ADQO) for precision, accuracy, and completeness. The report also provides a quantitative and qualitative assessment of the data and identifies potential sources of error, uncertainty, and bias that may affect the overall usability.

Laboratory QC samples were used to assess the effectiveness of homogenization procedures and to evaluate laboratory-derived contamination, laboratory performance, and sample matrix effects. Quality control samples included: method blanks, laboratory control samples (LCS), matrix spike (MS) samples, laboratory duplicate samples, and standard reference material (SRM) analyses. Surrogates were added to each sample analyzed for PCB congeners to further assess the effects of sample matrix on accuracy.

Data were qualified when associated QC sample results were outside the QC limits. The following definitions provide brief explanations of the qualifiers assigned to results in the data validation process:

J **Estimated**: The associated numerical value is an estimated quantity. The analyte was detected, but the reported value may not be accurate or precise. The "J" qualification

indicates the data fell outside the QC limits, but the exceedance was not sufficient to cause rejection of the data.

UJ **Estimated/Not detected**: An analysis was performed for the compound or analyte, but it was not detected and the sample quantitation or detection limit may be inaccurate or imprecise. The associated numerical result is the detection limit.

NJ **Tentatively Identified/Estimated**: The analyte was tentatively identified and the associated numerical value is an estimated quantity.

3.0 DATA QUALITY ASSESSMENT

The data package submitted by the laboratory was reviewed to determine whether the analytical data quality objectives (ADQO) specified in the *Analytical Quality Assurance Plan* were met. Each quality control element is discussed briefly below. More details are available in the individual data validation report presented in **Attachment A**.

3.1 Holding Times and Sample Preservation

The primary analytes of concern for this study are persistent compounds, which have been found to remain stable in tissue after several years of storage. Due to this, no maximum holding time criterion was established. All sample extracts were analyzed within 30 days from sample extraction. Samples were kept frozen by the laboratory at the required temperature of -20^{o}C ±2^{o}.

Sample 03-0041 was inadvertently left at room temperature for an undetermined length of time prior to submission to the laboratory. The sample was placed in the freezer upon discovery of this discrepancy. As the impact on the reported results cannot be determined, positive values and/or reporting limits were estimated.

3.2 Instrument Calibration

3.2.1 Initial Calibration (ICAL)

The ADQO specification for the initial calibration is that a minimum of a five point calibration would be performed for all analytes, and that the percent relative standard deviation (%RSD) values for all analytes are less than 20%.

The %RSD value for 4,4´-DDT was greater than the 20% control limit. One data point (a positive value for 4,4´-DDT in Sample 04-0006) was estimated based on the %RSD value outlier. All other submitted ICAL data met the specified ADQO.

3.2.2 Continuing Calibration (CCAL)

The ADQO specified for the continuing (or daily) calibrations is that a CCAL must be analyzed at the beginning and end of each analytical sequence (or every 12 hours, whichever is more frequent), and that all percent difference (%D) values must be less than 20% for the PCB congeners, and less than 25% for the DDT isomers. However, up to 10% of the analyte %D values can be greater than 20% provided that all %D values are less than 30%.

Eight of the 21 CCAL did not meet the specified ADQO, in that one or more analyte %D values were greater than 30% in the CCAL. All of the %D outliers indicate a potential high bias. The associated positive results were estimated (J), the detection limits for non-detected results were judged not affected. A total of 42 data points were estimated based on CCAL %D outliers.

3.3 GC/MS Tune

GC/MS instrument tuning verifications were performed at the proper frequency, prior to each analytical sequence. All GC/MS tunes met the acceptance criteria specified in the laboratory standard operating procedures.

3.4 Blank Analyses

Low levels of 4,4´-DDE were detected in both method blanks. As the values for this analyte in the samples were significantly greater (>100 times) the amount reported in the blank; no action was taken.

3.5 Accuracy

Accuracy is evaluated by comparison of an analytical concentration to a known (true) value. Accuracy was monitored through the use of surrogate compounds in each sample, and SRM, MS, and LCS (blank spike) analyses. Each QC element is discussed below. Overall, accuracy was acceptable.

3.5.1 Surrogate Compounds

Two surrogate compounds, ^{13}C-PCB19 and ^{13}C-PCB202, were added to each sample prior to extraction. The ADQO specified for surrogate compounds is that all percent recovery (%R) values would be within the 50% - 125% acceptance window. The recovery value from the late eluting surrogate (^{13}C-PCB202) is used for the quantitation of the reported target analyte concentrations.

As noted in the introduction, each sample extract was analyzed three times. However, due to the dilution factor necessary for the high levels of 4,4´-DDE present in the samples, no surrogates were recovered from the dilution analyses. See **Section 3.7 Reporting Limits** for further discussion of the dilution analyses. The surrogate recoveries from the PCB congener analyses and DDT isomer analyses were acceptable with the following exceptions.

The ^{13}C-PCB202 %R value was greater than 125% in the DDT isomer analysis of Sample 04-0009 (at 138%). The positive results for 4,4´-DDD, 4,4´-DDE, 2,4´-DDE, and Total DDTs were estimated (J). Both surrogate %R values were less than 50% in the PCB congener analysis of Sample 03-0024. All PCB congener, homologue group, and total PCBs positive results and detection limits were estimated (J/UJ) in this sample. A total of 58 data points were estimated (J/UJ) based on surrogate %R outliers.

Overall, surrogate accuracy was judged acceptable. Only five surrogate %R values (out of 160 total surrogate %R values for all samples and QC analyses) were outside the 50% - 125% control limits.

3.5.2 Standard Reference Material Analyses

An SRM was extracted and analyzed with each analytical batch. The SRM used for the Eagle Egg Study was 1974b, Organics in Mussel Tissue. This SRM has certified values for 27 PCB congeners.

The ADQO for the SRM is that the reported value must be within ±25% of the 95% confidence interval of the true value for congeners with concentrations in the SRM greater than five times the method detection limit (MDL).

Overall, SRM accuracy results were acceptable. Two SRM results (4,4´-DDE and PCB180) were greater than the +25% upper control limit. The 4,4´-DDE concentration in the SRM is two orders of magnitude lower than the levels found in the samples. The level of 4,4´-DDE in the SRM was considered to be not representative of the samples, and no data were qualified. For the PCB180 outlier, as the result may indicate a possible high bias, positive results associated were estimated (J). A total of 21 data points were estimated based on SRM outliers.

Table 1 summarizes the SRM results for this study.

3.5.3 Laboratory Control Samples

The laboratory performed LCS analyses at the required frequency of one for each analytical batch. The ADQO for the LCS analyses is that all %R values must be within the acceptance limits of 75% to 125%.

Seven LCS %R values were outside the 75% to 125% control limits. The LCS %R values were greater than the upper control limit, indicating a potential high bias. Associated positive results were estimated (J); reporting limits were judged as unaffected and no action was taken. Fifty data points were estimated based on the LCS %R outliers.

All other LCS %R values met the ADQO.

3.5.4 Matrix Spike Samples

The laboratory performed the MS analysis at the required frequency of each analytical batch. Six DDT isomers and 43 PCB congeners were spiked into each MS, for a total of 98 results. The ADQO

for MS analyses is that all %R values should be within the 50% to 125% control limits. The ADQO does not apply if the concentration in the parent sample is greater than five times the concentration in the spiking solution.

In the two MS analyses, a potential high bias was indicated by the recoveries for 24 compounds, as the %R values were greater than 125% (ranging from 127% to 360%). Half of the outliers were associated with positive results, which were estimated (J) to indicate a potential high bias. No action was taken if the compound was not detected.

Qualifiers were issued only to the target analyte in the parent sample associated with the MS %R outlier. A total of twelve data points were estimated (J).

3.5.5 Internal Standards

Internal standards were added to each field and QC sample prior to injection onto the analytical instrument. The ADQO for internal standards is that the area of the internal standards in each analysis must be within ±50% of the area of the internal standard in the associated CCAL. All sample internal standard areas met the ADQO.

3.6 Precision

Precision is evaluated through replicate analyses of a sample. For the eagle egg study, a laboratory duplicate and SRM were analyzed with each analytical batch. No field duplicates were submitted. Overall, precision was acceptable.

3.6.1 Standard Reference Material Analyses

Section 3.5.2 describes the frequency and criteria for the SRM analyses performed with each analytical batch. The results for the eagle egg SRM analyses are summarized in **Table 1**.

The relative percent difference (RPD) values for the eagle egg SRM results ranged from 0.0% to 19.2% for each of the congeners with values greater than five times the MDL, with the exception of the congeners with outliers discussed in **Section 3.5.2**. Most RPD values are less than 10%, indicating good overall precision between analytical batches.

3.6.2 Laboratory Duplicate Samples

For PCB congeners and DDT isomers, if the positive results are greater than or equal to five times the MDL, the ADQO specified relative percent difference (RPD) control limit for laboratory duplicates is 30%. For percent lipids and percent moisture analyses, the RPD control limit is 15%. Two laboratory duplicates were analyzed.

For the PCB congeners, one RPD value (for PCB114) was greater than 30%. Target analytes associated with RPD outliers were estimated (J) in the parent sample. One value was estimated due to laboratory precision outliers.

Table 2 summarizes the results of the laboratory duplicate analyses.

3.7 Reporting Limits and Sample Results

MDLs were determined using low level spikes on chicken eggs following procedures outlined in the *US Code of Federal Regulations* (40 CFR Part 136, Appendix B). The detection limits for target congeners were generally in the range of 0.04 µg/Kg to 0.30 µg/Kg. There were 11 target congeners with MDL values greater than the 0.1 µg/Kg target MDL. Of these, only one congener MDL value was greater than 0.3 µg/Kg: The MDL value for PCB169 was elevated at 2.21 µg/Kg due to interferences which could not be resolved using the selected method.

The laboratory did not have method detection limit (MDL) values established for all target analytes for this project. When an MDL value was not established for a PCB congener, the MDL value for a similar PCB was used. For the DDT compounds, the reporting limit was based on the lowest concentration standard used in the ICAL. Concentrations less than the concentration of the lowest calibration standard were not reported for the DDT compounds.

All samples required dilution for 4,4´-DDE. The level of dilution was such that the surrogates were not recovered in the dilution analysis, so the laboratory reported the 4,4´-DDE results with no surrogate recovery correction. To ensure that all data were comparable, the 4,4´-DDE results from the dilution analyses were recovery corrected by the data reviewer using the C_{13}-PCB202 %R values from the initial analysis. The revised results were added to the sample results summary forms and also to the database.

For many of the samples, the values reported for one or more homologue groups were less than the sums of the individual PCB congeners from the homologue group. PCB congener response factors are generated for each target congener during the calibration process. The relative area of a peak is divided by the appropriate response factor to calculate the concentration of the congener. For the homologue groups (monochlorobiphenyl, dichlorobiphenyl, etc.), a representative response factor is derived from the average response factors of the first and last eluting congener of that homologue groups. For example, the octachlorobiphenyl homologue group RRF is the average of the PCB202 and PCB205 response factors. Unless all 209 congeners are calibrated, any reported total for a chlorination level will have some inherent variability. The differences noted for the Total Homologue values were less than 1%, and are within the variability of the method. No action was taken.

The separation and spectral fit for any positive result for the coplanar congeners (PCB77, PCB81, PCB126, and PCB169) were evaluated. PCB77 was detected in one sample; no other coplanar congeners were detected. PCB110 was found to interfere with PCB77. The spectral match met general identification criteria, so the laboratory correctly reported the PCB77 result as a positive

result. However, due to the interference, the result may be a false positive or may be biased high. The potential interferences cannot be resolved without further extract cleanup (e.g., carbon column cleanup). Thus, the positive result PCB77 in Sample 01-0018 was qualified as tentatively identified at an estimated concentration (NJ-21).

Chromatography and mass spectral identification were reviewed for a minimum of 10% of the reported congeners. No other instances of potential interference were noted. All reported positive results met the identification criteria, and chromatographic peak shapes were acceptable.

3.8 Completeness

For the eagle egg analyses, no data were rejected out of the 1890 data points (thirty samples, each with 43 congener results, ten homologue groups, total PCBs, six DDT isomers, total DDTs, percent lipids and total solids). The completeness level attained for the analysis of the field samples is 100%.

Note that there are 54 PCB congeners reported instead of the requested 45 PCB congeners. However, due to co-elution of some congeners, there are only 43 unique congener results for each sample. The following PCB congeners co-elute: PCB5 and PCB8, PCB28 and PCB31, PCB43 and PCB49, PCB84, PCB89, and PCB101, PCB132 and PCB168, PCB138 and PCB163, PCB167 and PCB128, PCB170 and PCB190, PCB182 and PCB187, and PCB196 and PCB203.

3.9 Summary of Data Usability

Out of 1890 results reported by the laboratory, a total of 221 (12%) data points were qualified as estimated (J). Of the 221 data points that were estimated, 162 (8.6% of the total results) were due to laboratory accuracy or precision outliers. Sixty-three data points were qualified due to the sample being left at room temperature (four of these data points were also qualified for other reasons). The overall quality of the data is acceptable and the results, as qualified, are considered usable.

ATTACHMENT A

Data Validation Reports
by Sample Delivery Group (SDG)

DATA VALIDATION REPORT - FULL REVIEW
Montrose Eagle Eggs
DDTs and Polychlorinated Biphenyl Congeners, Percent Lipids and Total Solids
SDG: 0403104
Woods Hole Group

This report documents the review of analytical data from the analysis of eagle egg samples and the associated laboratory quality control samples. Samples were analyzed by Woods Hole Group Environmental Laboratories, Raynham, Massachusetts. The following table is a list of samples reviewed.

Field ID	Laboratory ID	Common Name
01-0017	0403104-01	Eagle egg
01-0030	0403104-02	Eagle egg
01-0018	0403104-03	Eagle egg
01-0025	0403104-04	Eagle egg
01-0031	0403104-05	Eagle egg
01-0010	0403104-06	Eagle egg
02-0017	0403104-07	Eagle egg
02-0018	0403104-08	Eagle egg
02-0023	0403104-09	Eagle egg
01-0009	0403104-10	Eagle egg
03-0023	0403104-11	Eagle egg
03-0021	0403104-12	Eagle egg
03-0022	0403104-13	Eagle egg
03-0024	0403104-14	Eagle egg
03-0036	0403104-15	Eagle egg
03-0041	0403104-16	Eagle egg
03-0037	0403104-18	Eagle egg
03-0042	0403104-19	Eagle egg
02-0025	0403104-20	Eagle egg
02-0028	0403104-21	Eagle egg
02-0056	0403104-22	Eagle Egg

I. DATA PACKAGE COMPLETENESS

All required deliverables were submitted by the laboratory. The laboratory followed adequate corrective action processes, and all anomalies were discussed in the case narrative.

II. TECHNICAL DATA VALIDATION

The quality control (QC) requirements that were reviewed are listed below.

2	Technical Holding Times and Sample Receipt	2	Standard Reference Material (SRM)
	GC/MS Instrument Performance Check		Laboratory Duplicate
1	Initial Calibration (ICAL)		Internal Standards
2	Continuing Calibration (CCAL)	2	Compound Identification
1	Blanks		Calculation Verification
2	Surrogate Compounds	1	Reporting Limits
2	Matrix Spike (MS)		DDT Degradation
2	Laboratory Control Samples (LCS)		

[1] ***Quality control results are discussed below, but no data were qualified.***
[2] ***Quality control outliers that impact the reported data were noted. Data qualifiers were issued as discussed below.***

Technical Holding Times and Sample Receipt

A note on the chain of custody (COC) form stated that Sample 03-0041 was inadvertently left at room temperature for an undetermined length of time prior to submission to the laboratory. The sample was placed in the freezer upon discovery of this discrepancy. As the impact on the reported results cannot be determined, positive values and/or reporting limits were estimated (J/UJ-1).

Sample 02-0018 consisted of a yolk sac only, so a limited volume was present for analysis. No qualifiers were assigned on this basis, however the data user should be aware of the impact this may have on the data.

Initial Calibration (ICAL)

The analyte 4,4´-DDT was calibrated using a quadratic curve, with an acceptable r^2 value of 1.00. The percent relative standard deviation (%RSD) values for all other analytes were less than the control limit of 20%, and were acceptable.

Continuing Calibration (CCAL)

The percent difference (%D) value for 4,4´-DDT was greater than the ±25% control limit in all eight pesticide CCAL standards. The %D value for 2,4´-DDT was greater than the ±25% control limit in seven of the pesticide CCAL standards. The %D value for PCB158 was greater than the control limit of ±20% in two of the PCB CCAL standards.

All samples were associated with these outliers. The positive results for 4,4´-DDT, 2,4´-DDT and PCB158 were estimated (J-5B) in all samples. As the %D outliers indicate a potential high bias, reporting limits were judged to be unaffected and no action was taken for non-detected compounds.

Blanks

The target compound 4,4´-DDE was present in the method blank at a concentration less than the reporting limit. Additionally, a positive value for percent lipids was reported in the method blank. All sample values were significantly greater than the levels in the blanks, and no action was taken.

Surrogate Compounds

The percent recovery (%R) values for both surrogate compounds (^{13}C-PCB19 and ^{13}C-PCB202) were less than the 50% lower control limit in the PCB congener analysis of Sample 03-0024. All positive values and reporting limits for PCB congeners and homologue groups were estimated (J/UJ-13) in this sample.

For Sample 03-0023MS, the %R values for the ^{13}C-PCB19 surrogate were less than the lower control limit in both the pesticide and PCB analyses. Qualifiers are not assigned to QC samples and no action was taken.

Matrix Spike (MS)

An MS was performed using Sample 03-0023. The %R values for several analytes were greater than the 125% upper control limit. If the amount of the analyte present in the parent sample was greater than four times the amount spiked, no action was taken. For the other outliers, as the %R values indicate a potential high bias, reporting limits were judged to be unaffected and only positive results were qualified. The positive values for 4,4´-DDD, 4,4´-DDT, PCB28/31, PCB66, PCB74, PCB195, and PCB206 were estimated (J-8) in the parent sample (03-0023).

Laboratory Control Sample (LCS)

The %R values of 2,4´-DDD, 4,4´-DDD, 2,4´-DDT, and 4,4´-DDT were greater than the 125% upper control limit. As the %R values indicate a potential high bias, reporting limits were judged to be unaffected and only positive results were qualified. The positive values for 4,4´-DDD, 2,4´-DDT, and 4,4´-DDT were estimated (J-10) in the samples.

Standard Reference Material (SRM)

Standard reference material 1974b, organics in mussel tissue, was analyzed with this SDG. The reported values for 2,4´-DDE, 4,4´-DDE, and PCB180 were outside of the control limits of ±25% of the 95% confidence interval. The certified value for 2,4´-DDE is less than the laboratory reporting limit, so the control limit does not apply. No action was taken.

The certified value for 4,4´-DDE is two orders of magnitude lower than the levels found in the samples. The level of 4,4´-DDE in the SRM was considered to not be representative of the samples, so no data were qualified based on the 4,4´-DDE outlier. Values for PCB180 were estimated (J-12) in the samples.

Compound Identification

The separation and spectral fit for any positive result for the coplanar congeners (PCB77, PCB81, PCB126, and PCB169) were evaluated. PCB77 was the only coplanar congener detected, and PCB110 was found to interfere with PCB77. The spectral match met general identification criteria, so the laboratory correctly reported the PCB77 result as a positive result. However, due to the interference, the result may be a false positive or may be biased high. The potential interferences cannot be resolved without further extract cleanup (e.g., carbon column cleanup). Thus, the positive result PCB77 in Sample 01-0018 was qualified as tentatively identified at an estimated concentration (NJ-21).

Chromatography and mass spectral identification were reviewed for a minimum of 10% of all other reported congeners. No other instances of potential interference were noted. All reported positive results met the identification criteria and chromatographic peak shapes were acceptable.

Reporting Limits

The laboratory did not have method detection limit (MDL) values established for all target analytes for this project. When an MDL value was not established for a PCB congener, the MDL value for a similar PCB was used. For the DDT compounds, the reporting limit was based on the lowest concentration standard used in the ICAL was used. Concentrations less than the reporting limit were not reported. The laboratory incorrectly added "J" qualifiers to DDT values equal to or up to five times greater than the reporting limit. Since these values are associated with a valid calibration, the "J" flags were removed during data validation.

All samples required dilution for 4,4´-DDE. The level of dilution was such that the surrogates were not recovered in the dilution analysis, so the laboratory reported the 4,4´-DDE results with no surrogate recovery correction. To ensure that all data were comparable, the 4,4´-DDE results from the dilution analyses were recovery corrected by the data reviewer using the C_{13}-PCB202 %R values from the initial analysis. The revised results were added to the sample results summary forms and also to the database.

Due to the dilution analyses, two sets of pesticides results were reported for each sample. As part of the data validation process, the data were reviewed to determine which set of data would provide the data user with data of the highest possible quality. To designate which data (of multiple data) should not be used, the data were flagged as do-not-report (DNR). All data flagged DNR were removed from the database provided to the data users.

For 17 of the samples, the values reported for one or more homologue groups were less than the sums of the individual PCB congeners from the homologue group. PCB congener response factors are generated for each target congener during the calibration process. The relative area of a peak is divided by the appropriate response factor to calculate the concentration of the congener. For the homologue groups (monochlorobiphenyl, dichlorobiphenyl, etc.), a representative response factor is derived from the average response factors of the first and last eluting congener of that homologue groups. For example, the octachlorobiphenyl homologue group RRF is the average of the PCB202

and PCB205 response factors. Unless all 209 congeners are calibrated, any reported total for a chlorination level will have some inherent variability. The differences noted for the Total Homologue values were less than 1%, and are within the variability of the method. No action was taken.

III. OVERALL ASSESSMENT

As was determined by this evaluation, the laboratory followed the specified analytical method. Accuracy was acceptable, as demonstrated by the surrogate, laboratory control sample (LCS) and matrix spike (MS) percent recovery values, with the exceptions noted above. Precision was acceptable as demonstrated by the relative percent difference values for the duplicate analyses.

Data were estimated based on surrogate, matrix spike, laboratory control sample, and standard reference material recovery outliers. Data were also estimated due to problems with sample preservation and continuing calibration outliers. Data were qualified as tentatively identified due to potential interference.

All data, as qualified, are acceptable for use.

DATA VALIDATION REPORT - SUMMARY REVIEW
Montrose Eagle Eggs
DDTs and Polychlorinated Biphenyl Congeners
Percent Lipids and Total Solids
SDG: 0404028
Woods Hole Group

This report documents the review of analytical data from the analysis of eagle egg samples and the associated laboratory quality control samples. Samples were analyzed by Woods Hole Group Environmental Laboratories, Raynham, Massachusetts. The following table lists the samples reviewed.

Field ID	Laboratory ID	Common Name
04-0005	0404028-01	Eagle egg
04-0006	0404028-02	Eagle egg
04-0009	0404028-03	Eagle egg
04-0010	0404028-04	Eagle egg
04-0013	0404028-05	Eagle egg
04-0014	0404028-06	Eagle egg
04-0015	0404028-07	Eagle egg
04-0016	0404028-08	Eagle egg
04-0017	0404028-09	Eagle egg

I. DATA PACKAGE COMPLETENESS

All required deliverables were submitted by the laboratory. The laboratory followed adequate corrective action processes, and all anomalies were discussed in the case narrative.

II. TECHNICAL DATA VALIDATION

The quality control (QC) requirements that were reviewed are listed below.

	Technical Holding Times and Sample Receipt	2	Laboratory Control Samples (LCS)
	GC/MS Instrument Performance Check		Standard Reference Material (SRM)
2	Initial Calibration (ICAL)	2	Laboratory Duplicate
2	Continuing Calibration (CCAL)	1	Internal Standards
1	Blanks		Compound Identification
2	Surrogate Compounds	1	Reporting Limits
2	Matrix Spike (MS)		DDT Degradation

[1] ***Quality control results are discussed below, but no data were qualified.***
[2] ***Quality control outliers that impact the reported data were noted. Data qualifiers were issued as discussed below.***

Initial Calibration (ICAL)

The analyte 4,4´-DDE was calibrated using a quadratic curve, with an acceptable r^2 value of 1.00. The percent relative standard deviation (%RSD) values for all other analytes were less than the control limit of 20%, with the following exception: The %RSD value for 4,4´-DDT was greater than the 20% control limit. A positive value for 4,4´-DDT was estimated (J-5A) in Sample 04-0006. Reporting limits were judged to be not affected.

Continuing Calibration (CCAL)

The percent difference (%D) value for PCB44 was greater than the control limit of ±20% in the CCAL analyzed 5/17/04 at 23:42. Positive values for PCB44 were estimated (J-5B) in the associated samples. As the outlier was indicative of a high bias, reporting limits were judged to be not affected.

The %D value for 4,4´-DDT was greater than the control limit of ±25% in the CCALs analyzed 5/4/04 at 22:32 and 5/5/04 at 4:35. There were no positive results for this analyte in the associated samples. As the outlier indicates a potential high bias, reporting limits were judged to be not affected. No qualifiers were assigned.

Blanks

A positive value for 4,4´-DDE was reported in the laboratory blank. The values for this analyte in the samples were significantly greater (>100 times) the amount reported in the blank; therefore no action was taken.

Surrogate Compounds

The percent recovery (%R) value for the ^{13}C-PCB202 surrogate compound was greater than the 125% upper control limit in the pesticide analysis of Sample 04-0009. The positive 2,4´-DDE, 4,4´-DDD, and 4,4´-DDE values in this sample were estimated (J-13). As the outlier indicates a potential high bias, reporting limits were judged not affected.

Matrix Spike (MS)

An MS was performed using Sample 04-0010. The %R values for several analytes were greater than the 125% upper control limit. If the amount of the analyte present in the parent sample was greater than four times the amount spiked, no action was taken. For the other outliers, as the %R values indicate a potential high bias, reporting limits were judged to be unaffected and only positive results were qualified. The positive values for 4,4´-DDD, PCB74, PCB87, PCB151, and PCB195 were estimated (J-8) in the parent sample (04-0010).

The amount of PCB169 spiked in the MS was less than the reporting limit for this analyte. No action was taken other than to note this discrepancy.

Laboratory Control Sample (LCS)

The %R values of 4,4´-DDD, 2,4´-DDT, and 4,4´-DDT were greater than the 125% upper control limit. As the %R values indicate a potential high bias, reporting limits were judged to be unaffected and only positive results were qualified. The positive values for 4,4´-DDD and 4,4´-DDT were estimated (J-10) in the samples.

Laboratory Duplicate

A laboratory duplicate was performed using Sample 04-0010. The relative percent difference (RPD) value for PCB114 was greater than the control limit of 30%. The PCB114 result was estimated (J-9) in the parent sample.

A positive value for 2,4´-DDE was reported in the parent sample, but this analyte was not reported in the duplicate. As the value in the parent sample was less than the reporting limit in the duplicate, no action was taken.

Internal Standards

The area of the internal standard C_{13}-PCB180 in the SRM analysis was greater than the upper control limit of +50% of the area of the internal standard in the associated CCAL. Qualifiers are not assigned to QC samples and no action was taken.

Reporting Limits

The laboratory did not have method detection limit (MDL) values established for all target analytes for this project. When an MDL value was not established for a PCB congener, the MDL value for a similar PCB was used. For the DDT compounds, the reporting limit was based on the lowest concentration standard used in the ICAL was used. Concentrations less than the reporting limit were not reported. The laboratory incorrectly added "J" qualifiers to DDT values equal to or up to five times greater than the reporting limit. Since these values are associated with a valid calibration, the "J" flags were removed during data validation.

All samples required dilution for 4,4´-DDE. The level of dilution was such that the surrogates were not recovered in the dilution analysis, so the laboratory reported the 4,4´-DDE results with no surrogate recovery correction. To ensure that all data were comparable, the 4,4´-DDE results from the dilution analyses were recovery corrected by the data reviewer using the C_{13}-PCB202 %R values from the initial analysis. The revised results were added to the sample results summary forms and also to the database.

Due to the dilution analyses, two sets of pesticides results were reported for each sample. As part of the data validation process, the data were reviewed to determine which set of data would provide the data user with data of the highest possible quality. To designate which data (of multiple data) should not be used, the data were flagged as do-not-report (DNR). All data flagged DNR were removed from the database provided to the data users.

For eight of the samples, the values reported for one or more homologue groups were less than the sums of the individual PCB congeners from the homologue group. PCB congener response factors are generated for each target congener during the calibration process. The relative area of a peak is divided by the appropriate response factor to calculate the concentration of the congener. For the homologue groups (monochlorobiphenyl, dichlorobiphenyl, etc.), a representative response factor is derived from the average response factors of the first and last eluting congener of that homologue groups. For example, the octachlorobiphenyl homologue group RRF is the average of the PCB202 and PCB205 response factors. Unless all 209 congeners are calibrated, any reported total for a chlorination level will have some inherent variability. The differences noted for the Total Homologue values were less than 1%, and are within the variability of the method. No action was taken.

III. OVERALL ASSESSMENT

As was determined by this evaluation, the laboratory followed the specified analytical method. Accuracy was acceptable, as demonstrated by the surrogate, laboratory control sample (LCS) and matrix spike (MS) percent recovery values, with the exceptions noted above. Precision was acceptable as demonstrated by the relative percent difference values for the duplicate analyses.

Data were estimated due to matrix spike, laboratory control sample, and surrogate recovery outliers, initial and continuing calibration outliers, and laboratory duplicate precision outliers.

All data, as qualified, are acceptable for use.