1.0 INTRODUCTION

This report summarizes the validation of analytical results generated from field sampling in 2005, in support of the Vieques Island Biota Sampling Project. Sampling and analyses were performed according to the *Laboratory Quality Assurance Project Plan* (QAPP), (Ridolfi Inc. and NOAA ORR, June 2005). The criteria applied for this validation are consistent with U.S. EPA SW-846 analytical methods, laboratory established criteria, and the *U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review* (*Functional Guidelines*), (U.S. EPA, 1999) and *U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (*Functional Guidelines*), (U.S. EPA, 2004). Data qualifiers applied to sample results are in accordance with the *Functional Guidelines*; qualifiers applied are summarized below:

- U: The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
- J: The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
- UJ: The analyte was not detected above the sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
- i: The method reporting limit (MRL) is elevated due to matrix interference. This is a laboratory-applied qualifier and is left for the convenience of the user.

2.0 **LIPIDS** - CAS SOP Lipids in Tissue, Bligh & Dyer Modified Method

Percent lipids determinations were performed by Columbia Analytical Services (CAS) Laboratory of Kelso, Washington, in accordance with the requirements of the QAPP.

One hundred twelve samples were analyzed for percent lipids. The laboratory provided U.S. EPA CLP style deliverables for all sample delivery groups.

Sample Documentation, Custody and Holding Conditions / Times: All samples were handled and delivered to the laboratory according to chain-of-custody procedure. Laboratory data deliverables were complete. The tissue samples were received at temperatures ranging from -0.7 to 11.7° C, and stored frozen at -20° C until extraction. Maximum sample holding times for frozen tissues have not been established for lipids determination.

Duplicate/Triplicate Analyses: Samples S7-FD-01-03, RB-FD-01-03, KA-LC-01-04, S4-FD-01-03 were analyzed in duplicate and triplicate per the laboratory SOP. The relative percent differences for the duplicate (%RPD) analyses ranged from 7 to 22%, and percent relative standard deviation (%RSD) of the triplicate analyses ranged from 4% to 12%. There are no control limits established for triplicate determination.

Lipid Quantitation and Reported Detection/Quantitation Limits: The laboratory bench sheets were reviewed for transcription errors; no errors noted.

Field Replicates: There were no field replicates submitted for the project.

Overall Assessment: All deliverables required by the project are present and data packages are complete. Sample conditions and holding times are considered acceptable. The duplicate and triplicate analyses were within specification. Lipids determination (quantitation) and method

reporting limits are deemed sufficient. Overall analytical performance is considered acceptable, and data quality is sufficient for project use.

3.0 PESTICIDES - U.S. EPA SW-846, Method 8081A.

Pesticides analyses were performed by Columbia Analytical Services (CAS) of Kelso, Washington, in accordance with the requirements of the QAPP. The samples were analyzed using EPA SW-846 method 8081A.

One hundred twelve samples were analyzed for pesticides. The laboratory provided U.S. EPA CLP style deliverables for all sample delivery groups.

Sample Documentation, Custody and Holding Conditions / Times: All samples were handled and delivered to the laboratory according to chain-of-custody procedure. Laboratory data deliverables were complete. The tissue samples were received at temperatures ranging from -0.7 to 11.7° C, and stored frozen at -20° C until extraction. Maximum sample holding times for frozen tissues have not been established for pesticides analysis. Regional guidance generally recommends a maximum holding time of one year for frozen samples. Since the samples were stored at -20°C, the sample integrity is considered to have been maintained until extraction; additionally, all samples were extracted within one year. Extracts were evaluated using a holding time of 40 days from extraction until analysis.

Instrument Performance: The breakdown of 4,4'-DDT and endrin were evaluated at the beginning of every 12-hour shift and after the analysis of ten samples using a standard that contained 4,4'-DDT and endrin. The percent breakdown of the two compounds was less than 20%, and is acceptable.

Initial Calibration: Initial five point calibrations were performed for the majority of pesticides at 2, 5, 20, 50, 100 and 200 ppb, while toxaphene was calibrated at 100, 250, 500, 1000, 2000 and 5000 ppb and chlordane was calibrated at 25, 50, 100, 500, 1000, 2000 ppb. Response factors were defined for each compound at each calibration concentration. The relative standard deviations for initial calibration are <20% per method 8081A, demonstrating acceptable linearity. The laboratory also analyzed a second source calibration which consisted of 40 ppb of each pesticide (with the exception of toxaphene and chlordane which were analyzed at a concentration of 1000 ppb). The laboratory notes the percent difference criteria of ±15% was met for all of the second source calibration analyses with the exception the drift of 16% for one second source calibration (run date 8/24/05) for the primary column for chlordane. No action was taken.

Continuing Calibration: Per method 8081, calibration verification was performed every 12 hours. Calibration standards were injected after the analysis of ten samples and at the end of each analytical sequence. The laboratory notes in the case narratives that the primary evaluation criteria were exceeded for several analytes in the packages. In accordance with CAS standard operating procedures, the alternative evaluation specified in the EPA method was performed using the average percent recovery of all analytes in the verification standard, which met the alternative evaluation criteria.

The percent differences of the calibration verification solution exceeded the control limits (CAS uses ±15% for the evaluation) for several compounds. Several detected results were qualified in accordance with the *Functional Guidelines*. Non-detected results were qualified if the calibration

percent difference was biased low. Continuing calibrations exceeding control limits and subsequent qualification are summarized below:

Compounds	Samples Affected	Qualification
4,4'-DDE	PF-LC-01-04, PF-LC-01-06	J
4,4'-DDD	BT-LC-01-01,PF-FD-01-03/03bcomposite JR-FD-01-01, BB-LC-01-03, BB-LC-01-05 RB-LC-01-04, RB-LC-01-03, BT-LC-01-02 RB-LC-01-01	J
4,4'-DDE, 4,4'-DDD	BB-LC-01-06, RB-LC-01-05	J
4,4'-DDE, g-chlordane	PF-LC-01-02, PF-LC-01-03, PF-LC-01-05 PF-LC-01-07	J
Toxaphene, chlordane	RB-LC-01-07	J
Chlordane	LA-LC-01-04, VR-LC-01-06, LA-FD-01-04, S4-FD-01-01, S4-FD-01-02, S4-FD-01-03, BT-FD-01-01, BT-FD-01-02, BT-FD-01-03, LI-FD-01-01, LI-LC-01-01, LI-LC-01-03, LI-LC-01-04, LI-LC-01-05	J
Trans-nonachlor	BT-FD-01-01, VR-LC-01-06, LA-FD-01-04, S4-FD-01-01, S4-FD-01-02, S4-FD-01-03	J
Endrin ketone	RB-FD-01-01, RB-FD-01-03	J
Toxaphene, chlordane	S4-LC-01-01, S4-LC-01-02, S4-LC-01-05, S4-LC-01-06, S4-LC-01-04, S4-LC-01-08, SB-LC-01-01, SB-LC-01-02, SB-LC-01-03, SB-LC-01-05, SB-LC-01-06, KA-LC-01-01, KA-LC-01-03, KA-LC-01-04, KA-LC-01-05, KA-LC-01-06, LA-LC-01-02, LA-LC-01-03, LA-LC-01-04	J/UJ
Endrin ketone	S4-LC-01-06, S4-LC-01-08, SB-LC-01-01, SB-LC-01-02, SB-LC-01-03, SB-LC-01-05, SB-LC-01-06, KA-LC-01-01, KA-LC-01-03, KA-LC-01-04, KA-LC-01-05, KA-LC-01-06, LA-LC-01-02, LA-LC-01-03, LA-LC-01-04	J/UJ
Mirex	S4-LC-01-06, KA-LC-01-01, KA-LC-01-02, KA-LC-01-04, KA-LC-01-05, KA-LC-01-06, LA-LC-01-02, LA-LC-01-03, LA-LC-01-04	J/UJ
d-bhc, endrin ketone, toxaphene, chlordane, mirex	VR-LC-01-06, LA-FD-01-03, S4-FD-01-01, S4-FD-01-02, S4-FD-01-03	J/UJ
endrin ketone, toxaphene, mirex	LA-FD-01-02, BB-FD-01-01, BB-FD-01-02, BB-FD-01-03, LI-FD-01-02, LI-FD-01-03, SB-FD-01-01, SB-FD-01-02, SB-FD-01-03, S7-FD-01-01, S7-FD-01-02, S7-FD-01-03, PG-FD-01-01, PG-FD-01-02, PG-FD-01-03, RB-FD-01-01, RB-FD-01-02, RB-FD-01-03, KA-FD-01-01, KA-FD-01-02, KA-FD-01-03	J/UJ

Blanks: Method blanks were analyzed for each analytical group. Method blanks show no detections of target analytes above the method detection limits.

Surrogate Compound Performance: Surrogate compounds tetrachloro-m-xylene and decachlorobiphenyl were added to each sample prior to analysis to assess analytical performance on each sample. Acceptance limits were 10-158%R for tetrachloro-m-xylene and 10-178%R for decachlorobiphenyl. All surrogate recoveries are within limits with the exception of samples analyzed at dilutions, from which data were not qualified.

Matrix Spike/Matrix Spike Duplicate Analyses: Matrix spike and matrix spike duplicate analyses were performed on samples JR-LC-01-05, BB-LC-01-03, BB-LC-01-02, PF-LC-01-06, RB-LC-01-04, BT-LC-01-05, RB-LC-01-01, BB-LC-01-01 and batch (for two data sets). All target compounds were spiked at a concentration of 19.9 or 20 μg/kg (wet weight) with the exception of toxaphene and chlordane, which were spiked at 200 μg/kg (wet weight). The acceptance limits are as follows:

Compound	Acceptance Limits (%R)
a-bhc	51-122
b-bhc	13-162
g-bhc	40-133
d-bhc	36-140
Heptachlor	41-128
Aldrin	30-140
Isodrin	70-130
Heptachlor epoxide	43-129
g-chlordane	32-132
Endosulfan I	17-141
a-chlordane	41-129
Dieldrin	25-148
4,4′-DDE	10-166
Endrin	46-135
Endosulfan II	29-139
4,4′-DDD	16-161
Endrin aldehyde	10-109
Endosulfan sulfate	31-137
4,4′-DDT	24-151
Endrin ketone	41-139
Methoxychlor	31-148
Toxaphene	70-130
Chlordane	70-130
Chloropyrifos	70-130
Oxychlordane	21-154
cis-Nonachlor	70-130
trans-Nonachlor	54-110
Mirex	38-128
2,4′-DDE	20-176
2,4′-DDD	10-231
2,4′-DDT	10-196

The matrix spike recoveries were outside control limits for several compounds, for which the parent sample was qualified as estimated as follows:

Sample	Compound	Qualification
JR-LC-01-05, PF-LC-01-06 LA-FD-01-01,	endrin aldehyde	J/UJ
BB-LC-01-03, RB-LC-01-04 SB-LC-01-03, S4-FD-01-03 S7-FD-01-02	Toxaphene, chlordane	J/UJ
BB-LC-01-01, SB-LC-01-04 LA-FD-01-03, SB-FD-01-02 PG-FD-01-03	chlorpyrifos	J/UJ
S4-LC-01-01	isodrin	J/UJ
PG-FD-01-02	a-bhc, heptachlor, isodrin, endrin aldehyde, methoxychlor	J/UJ
RB-FD-01-01	Chlorpyrifos, cis-nonaclor	J/UJ

The laboratory notes in the case narrative that the control limits are considered default limits temporarily in use until sufficient data points are generated to calculate statistical control limits and based on the method and historic data the recoveries observed were in the range expected for the procedure. Therefore, only the parent spiked samples were qualified. For the 'batch QC' analyses, in which the recoveries were not met, data was not qualified since the parent sample was from another SDG.

Laboratory Control Samples: Twenty spiked blanks (LCS) were analyzed. The acceptance limits are as follows:

Compound	Acceptance Limits (%R)
a-bhc	58-124
b-bhc	55-118
g-bhc	61-122
d-bhc	58-135
Heptachlor	52-115
Aldrin	55-118
Isodrin	49-116
Heptachlor epoxide	53-120
g-chlordane	53-120
Endosulfan I	43-114
a-chlordane	53-116
Dieldrin	56-122
4,4'-DDE	52-128
Endrin	57-128
Endosulfan II	52-111
4,4'-DDD	49-132
Endrin aldehyde	12-104
Endosulfan sulfate	57-118
4,4'-DDT	53-136
Endrin ketone	57-118
Methoxychlor	56-129
Toxaphene	55-128
Chlordane	70-130
Chloropyrifos	45-133
Oxychlordane	21-154
cis-Nonachlor	56-112
trans-Nonachlor	54-108
Mirex	52-112
2,4'-DDE	42-146
2,4'-DDD	46-148
2,4'-DDT	41-156

For SDGs K0501162 and K0501711, the LCS recovery for chlordane was low in all of the LCS samples, resulting in estimated qualification of chlordane for all samples.

For SDGs K0501249, the LCS recovery for chlordane was low in all of the LCS samples with the exception of sample associated with extraction lot KWG0514038. All other samples were qualified as estimated for chlordane.

Target Compound Identification and Reporting Limits: The compounds reported are within established retention time windows. The laboratory reported several compounds with an "i" qualifier, indicating the method detection limit is elevated because matrix interference prevented adequate resolution of the target compound at the reporting limit.

In SDG K0501162, sample RB-LC-01-04 was reported by the laboratory at a concentration above the calibration range for 4,4'-DDE. The result was qualified as estimated in the original sample, and the diluted result was sent to the validator on 9/23/05.

All g-chlordane results have a marker by the compound on the result form, noting "for the analyte (CAS number 5103-74-2), USEPA has corrected the name to beta-chlordane or trans-chlordane".

Certain results were flagged by the laboratory as "P", which indicates the relative percent difference between the two analytical columns (primary and confirmation) is greater than 40%. As a result, the following results are qualified as estimated:

Sample	Compound	Qualification
BB-LC-01-03, LA-LC-01-02, S4-FD-01-03, BT-FD-01-02, L1-LC-01-04, L1-LC-01-03, SB-LC-01-03, SB-LC-01-06, KA-LC-01-05, S7-LC-01-05, LA-FD-01-02, SB-FD-01-03, S7-FD-01-03	2,4-DDT	J
HR-FD-01-03	Endrin aldehyde	J
KA-LC-01-03	Endosulfan sulfate	J
LA-LC-01-04	Chlordane	J
BT-FD-01-01	Trans-nonachlor	J
BB-FD-01-02	4,4'-DDD, endrin aldehyde	J
L1-FD-01-02	Mirex	J
L1-FD-01-03	4,4'-DDT	J
SB-FD-01-01	2,4'-DDE	J
KA-FD-01-01	Dieldrin, 2,4'-DDT	J
KA-FD-01-02	Dieldrin	J
RB-FD-01-01, RB-FD-01-03	Endrin ketone	J

The laboratory noted when the column difference exceeds 40%, the higher value is reported if no anomalies are identified. However, the lower value was reported for 2,4-DDT for S7-LC-01-05, L1-LC-01-03, LA-FD-01-02, LA-FD-01-02 and mirex for L1-FD-01-02 since anomalies were identified.

No action was taken for results reported by the laboratory with a JP qualifier, since the J indicates the results on both columns are below the method reporting limit and the confirmation criteria are not considered applicable.

System Performance: System and analytical performance was evaluated by the breakdown of 4,4'-DDT in addition to a review of chromatograms and quantitation reports. No problems identified during review of the raw data. No abrupt baseline shifts were identified during chromatogram review.

Field Replicates: Field replicates were not collected for this dataset.

Overall Assessment: All deliverables required by the project are present and data packages are complete. Recommended sample holding times and conditions were met. Calibration requirements were met and acceptable with the exception of qualified data. The matrix spike

and LCS results are acceptable as qualified. Method blanks show no detection of target analytes. Compound identification and quantitation are acceptable as qualified. Overall analytical performance is considered acceptable, and data quality is sufficient for project use.

4.0 Polychlorinated Biphenyls - U.S. EPA SW-846, Method 8082.

Polychlorinated biphenyls (PCBs) analyses were performed by CAS of Kelso, Washington, in accordance with the requirements of the QAPP. The samples were analyzed for PCBs using EPA SW-846 method 8082.

One hundred twelve samples were analyzed for PCBs. The laboratory provided U.S. EPA CLP style deliverables for all sample delivery groups.

Sample Documentation, Custody and Holding Conditions / Times: All samples were handled and delivered to the laboratory according to chain-of-custody procedure. Laboratory data deliverables were complete. The tissue samples were received at temperatures ranging from -0.7 to 11.7° C, and stored frozen at -20° C until extraction. Maximum sample holding times for frozen tissues have not been established for PCB analysis. Regional guidance generally recommends a maximum holding time of one year for frozen samples. Since the samples were stored at -20°C, the sample integrity is considered to have been maintained until extraction; additionally, all samples were extracted within one year. Extracts were evaluated using a holding time of 40 days from extraction until analysis.

Initial Calibration: Initial five point calibrations were performed for Aroclors 1016 and 1260 at 2.5, 5, 50, 1000, 2000 and 5000 ppb. Single standards of each of the other Aroclors were also analyzed at the mid-point of the linear range of the detector. Calibration factors for each Aroclor were established. The percent relative standard deviations for the calibration factors in the initial calibrations were <20%, demonstrating acceptable linearity. A second source calibration consisting of all Aroclors at 1000 ppb was also performed.

Continuing Calibration: Calibration verification was performed every 12 hours or every 10 samples. Mid-level standards were injected at the required frequency and at the end of each analytical sequence. The laboratory noted that the alternative calibration criteria (average percent difference) were used and the results were acceptable with the exception of the following:

AR1260 for the continuing calibration analyzed on 8/19/05, which resulted in estimated qualification of AR1260 for JR-LC-01-01, JR-LC-01-03, JR-LC-01-04, JR-LC-01-05, JR-LC-01-06, JR-FD-01-01, JR-FD-01-02, JR-FD-01-03 and PG-LC-01-01.

AR1260 for the continuing calibration analyzed on 9/12/05, which resulted in estimated qualification of AR1260 for SD-F4-01-02, SD-F4-01-03, BT-FD-01-01, BT-FD-01-02, BT-FD-01-03, LI-FD-01-01, LI-LC-01-01, LI-LC-01-03, LI-LC-01-04, LI-LC-01-05, LI-LC-01-06.

Blanks: Method blanks were analyzed for each analytical group. Method blanks show no detections of target analytes above reporting limits.

Surrogate Compound Performance: Surrogate compound decachlorobiphenyl was added to each sample prior to analysis to assess analytical performance on each sample. Acceptance limits are 37-124%R. All surrogate recoveries are acceptable.

Matrix Spike/Matrix Spike Duplicate Analyses: Matrix spike and matrix spike duplicate analyses were performed on PF-FD-01-03/03bcomposite, PF-LC-01-05, S4-FD-01-03, S7-FD-01-03, RB-FD-01-03 and 'batch QC'. Analyte spike concentrations for Aroclors 1016 and 1260 are 200 μg/kg. The acceptance windows for the analysis are as follows:

Compound	Acceptance Limits (%R)
Aroclor 1016	65-125
Aroclor 1260	48-142

The matrix spike recoveries were acceptable.

Laboratory Control Samples: LCS samples were analyzed with acceptable results. The acceptance windows for the analysis are as follows:

Compound	Acceptance Limits (%R)
Aroclor 1016	62-124
Aroclor 1260	62-129

Target Compound Identification and Reporting Limits: There were no problems noted during review of the chromatograms.

Field Replicates: Field replicates were not collected for this dataset.

System Performance: The chromatograms were reviewed for baseline shifts, Aroclor patterns and general instrument response. No problems were identified during review of the raw data.

Overall Assessment: All deliverables required by the project are present and data packages are complete. Recommended sample holding times and conditions were met. Initial and continuing calibration requirements were acceptable with exceptions noted above. Method blanks show no presence of target analytes. Compound identification and quantitation is acceptable. Raw data show no indications of system performance degradation. The laboratory did note that degradation was noted in the samples. No data qualification resulted, however, the case narrative also mentions the analyst used professional judgment for identification of the detected aroclors. The MS/MSD and LCS recoveries were acceptable. Overall analytical performance is considered acceptable, and data quality is sufficient for project use.

5.0 METALS ANALYSES - U.S. EPA SW-846 Methods.

Metals analyses were performed by Columbia Analytical Services (CAS) Laboratory of Kelso, Washington, in accordance with the requirements of the QAPP. All samples were analyzed according to the U.S. EPA referenced methods, and calibrations and performance criteria are consistent with the U.S. EPA CLP Statement of Work. Aluminum, barium, calcium, chromium, copper, iron, magnesium, manganese, potassium, sodium, vanadium and zinc were analyzed by the Inductively Coupled Plasma–Atomic Emission Spectrometry method (ICP–AES, Method 6010B). Arsenic, beryllium, cadmium, cobalt, lead, nickel, silver, thallium and uranium were analyzed by the Inductively Coupled Plasma–Mass Spectrometry method (ICP-MS, Method 200.8). Selenium was analyzed by the Graphite Furnace Atomic Absorption method (GFAA, Method 7740). Mercury was analyzed by the Cold Vapor Atomic Absorption method (CVAA, Method 7471A).

One hundred twenty-six samples were analyzed for metals. The laboratory provided U.S. EPA CLP style deliverables for all sample delivery groups.

Sample Documentation, Custody and Holding Conditions / Times: All samples were handled and delivered to the laboratory according to chain-of-custody procedure. Laboratory data deliverables are complete. No preservatives were added to the tissue samples. The tissue samples were received from -0.7 to 11.7° C, and stored frozen at -20° C until preparation and analysis. Maximum sample holding times for frozen tissues have not been established for metals analyses. Regional guidance generally recommends a maximum holding time of one year for frozen samples. All analyses were performed within one year of sampling.

Initial Calibration: The laboratory performed initial instrumental calibrations daily using at least the minimum required number of data points to establish the analytical curve for each method: a blank and one standard for ICP analyses, a blank and three standards for GFAA analyses and a blank and five standards for mercury analyses. Correlation coefficients for all GFAA and mercury initial calibrations are ≥ 0.995, as required.

Initial Calibration Verification: The laboratory performed initial calibration verification checks (ICVs) immediately after initial instrumental calibrations during all ICP, GFAA and mercury analytical sequences, as required. All ICV recoveries are within acceptance limits (90–110% for ICP/GFAA; 80–120% for mercury). A spot check of ICV recoveries shows no calculation errors.

Continuing Calibration Verification: The laboratory analyzed continuing calibration verification standards (CCVs) at the required frequency for all ICP, GFAA and mercury analytical sequences (at the beginning and end of each run; at a frequency of ≥ 10% or every two hours, whichever is more frequent). All CCV recoveries are within acceptance limits (90–110% for ICP/GFAA; 80–120% for mercury). A spot check of CCV recoveries shows no calculation errors.

Blanks: Initial calibration blanks (ICBs) were analyzed immediately after ICVs, and continuing calibration blanks (CCBs) were analyzed immediately after CCVs during all ICP, GFAA and mercury analytical sequences, as required. The CLP *Functional Guidelines* require that positive sample results less than 5 times the amount in any blank be qualified as "U" (quantitation limit). All positive sample results associated with blank positive results are greater than 5 times the amount in an associated calibration blank.

Preparation blanks were analyzed for all target analytes at the required frequency (one per matrix per preparation batch). The CLP *Functional Guidelines* require that positive sample results less than 5 times the amount in the preparation blank be qualified as "U" (quantitation limit). All positive sample results associated with blank positive results are greater than 5 times the amount in an associated preparation blank with the exception of silver, which was used to assign a U qualifier to samples HR-01, HR-03, HR-04, HR-05, HR-06, KA-FD-01-02 and KA-FD-01-03.

Interference Check Samples: ICP interference check solutions (ICS) were analyzed for the target analytes at the beginning of each ICP analytical run, as required by the method. Recoveries for all required target analytes in all check samples are within acceptance limits (80–120%). A spot check of ICS recoveries shows no calculation errors.

Laboratory Control Samples: Laboratory control samples (LCS) were analyzed at the required frequency (at least one sample per preparation batch). The LCSs are NRCC (National Research

Council of Canada) Dorm-2 and NRCC Dolt-3 reference material. Control limits for target analytes for this LCS are NRCC's certified advisory limits. All analytes are within the advisory ranges for these reference materials with the exception of Dolt-3 aluminum (36.2%, limit = 18.2 – 31.9%) for LCS2 and Copper (38.9%, limit = 24.2 – 38.6%) for LCS 8. Since the laboratory analyzed both a Dorm-2 and Dolt-3 sample with each sample batch, and all of the Dorm-2 recoveries were acceptable, no data qualification was made. A spot check of LCS recoveries shows no calculation errors.

Duplicate Sample Analyses: Laboratory duplicate samples were analyzed for the target analytes at the required frequency (at least one sample per preparation batch). Acceptance limits applied in this evaluation of duplicate sample analyses are in accordance with the requirements of the U.S. EPA *Functional Guidelines* (results ≥ 5X the reporting limit, ≤ 20% Relative Percent Difference (RPD); results < 5X the reporting limit ± 1X the reporting limit). Results of all duplicate analyses meet these criteria with the exception of the duplicate analysis for SDGs K0501711 and K0501162 for chromium, which resulted in J/UJ qualification of chromium for associated samples. A comparison of raw data and reporting forms shows no transcription errors. A recalculation of RPDs shows no calculation errors.

Matrix Spike Sample Analyses: Matrix spike samples were analyzed for the target analytes at the required frequency (at least one sample per preparation batch). Samples were spiked at CLP–specified concentrations. CLP acceptance limits for matrix spike recovery are 75–125% and are applicable only to those samples in which the sample concentration does not exceed four times the spike concentration. Matrix spike recoveries are acceptable with the following exceptions:

Spike Sample	Compound	Qualification
BQ-LC-01-05S	Aluminum, iron, silver	J/UJ
S4-LC-01-01S	Iron	J/UJ
VR-LC-01-05S	Iron	J/UJ
HR-01S	Chromium, mercury	J/UJ
JR-LC-01-01S	Copper, iron, silver, zinc	J/UJ
BB-LC-01-03S	Aluminum, copper, iron, zinc	J+/J
PF-LC-01-07S	Copper, zinc	J/UJ
RB-LC-01-01S	Iron	J/UJ

All samples in the related SDGs were qualified as estimated (J) in accordance with the *Functional Guidelines*.
A comparison of raw data and reporting forms shows no transcription errors. A recalculation of recoveries shows no calculation errors.

Graphite Furnace QC: Duplicate injections were performed for all selenium analyses. Examination of raw data shows that the duplicate injections agree within ± 20% Relative Standard Deviation (%RSD). Post digestion spikes were analyzed for at least 10% of the samples at a spike level of 20 μg/L, as per Method 7740. Post digestion spike recoveries are within project–specified limits (85–115%R) with the exception of selenium for sample SB-LC-01-03 (83%), which was qualified as estimated.

ICP Serial Dilution: Although not required by Method 6010B, at least one sample was serially diluted and analyzed per ICP-AES analytical run. Results greater than 50x IDL agree within 10%D (Difference) with the exception of several analytes as follow:

Serial Dilution Sample	Compound	Qualification
KA-LC-01-05L	Calcium, magnesium, manganese, zinc	J/UJ
S4-FD-01-01L	Calcium, zinc	J/UJ
LA-FD-01-01L	Calcium, zinc	J/UJ
BB-FD-01-03L	Calcium, magnesium, zinc	J/UJ
KA-FD-01-03L	Zinc	J/UJ
PF-FD-01-01	magnesium	J/UJ

Associated results were qualified as estimated (J/UJ) in accordance with the *Functional Guidelines*.

Reported Detection/Quantitation Limits: Reported quantitation limits were acceptable. The laboratory originally reported the samples on a dry weight basis whereas analyses for all other methods were reported on a wet weight for the crab tissue. The Ridolfi Project Manager requested that the laboratory revise all metals report forms so that they are on a wet weight basis.

The 6010 metals were missing on the result form submitted by the laboratory for sample BB-FD-01-01. The laboratory was contacted and the missing analytes were added to the result form. The laboratory originally reported a 'W' flag for sample SB-LC-01-03, which was in error. The laboratory was contacted and the 'W' was omitted in the revision.

Field Replicates: Field replicates were not collected for this dataset.

Overall Assessment: All deliverables required by the project are present and data packages are complete. The laboratory originally reported the metals on a dry weight basis, but subsequently resubmitted the results as wet weight, per request by the Ridolfi Project Manager. All analyses meet recommended sample holding times. Initial and continuing calibration verification standards and blanks are acceptable. Several analytes were detected in one or more ICB/CCBs; however, associated results are greater than 5 times the blank results and are acceptable. Silver was detected in one preparation blank, resulting in qualification of several associated results that were less than 5 times the blank result as "U". Recoveries for interference check samples and laboratory control samples are acceptable. Results for analyses of laboratory control samples are within advisory limits with exceptions noted above. Laboratory duplicate sample analyses are acceptable with exceptions noted above. Several compounds in the matrix spike samples are outside acceptance limits. Associated results are qualified as estimates. One selenium result is qualified as estimated (J) because the analytical spike recovered slightly low. Results for ICP-AES serial dilution were outside limits for a few analytes, resulting in estimated qualification of associated data as noted above. Reported quantitation or lower reporting limits are acceptable. Field replicates were not submitted for this data. Overall analytical performance is considered acceptable and the data quality is sufficient for project use

6.0 Explosives - U.S. EPA SW-846, Method 8330M.

Explosive analyses were performed by CAS of Kelso, Washington, in accordance with the requirements of the QAPP.

One hundred twelve samples were analyzed for explosives. The laboratory provided U.S. EPA CLP style deliverables for all sample delivery groups. Sample results are presented with associated data qualifiers in Appendix D.

Sample Documentation, Custody and Holding Conditions / Times: All samples were handled and delivered to the laboratory according to chain-of-custody procedure. Laboratory data deliverables were complete. The tissue samples were received at temperatures ranging from -0.7 to 11.7° C, and stored frozen at -20° C until extraction. Maximum sample holding times for frozen tissues have not been established for explosives analysis. Regional guidance generally recommends a maximum holding time of one year for frozen samples. Since the samples were stored at -20°C, the sample integrity is considered to have been maintained until extraction; additionally, all samples were extracted within one year. Extracts were evaluated using a holding time of 40 days from extraction until analysis.

Initial Calibration: Initial six point calibrations were performed for all explosives compounds at 0.1, 0.5, 1, 5, 10 and 50 ppm. Calibration factors for each compound were established. The percent relative standard deviations for the calibration factors in the initial calibrations were <20%, demonstrating acceptable linearity. A second source calibration consisting of all explosive compounds at 10 ppm was also performed.

Continuing Calibration: Calibration verification was performed every 10 samples, at a concentration of 10 ppm for all explosives compounds. The average percent differences of the calibration verification solutions were less than 15% for all compounds.

Blanks: Method blanks were analyzed for each analytical group. Method blanks show no detections of target analytes above reporting limits.

Surrogate Compound Performance: Surrogate compound 1-chloro-3-nitrobenzne was added to each sample prior to analysis to assess analytical performance on each sample. Acceptance limits were 70-130%R. All surrogate recoveries were acceptable with the exception of the sample VR-LC-01-05MS. No action was taken since this was a QC sample and not an actual field sample.

Matrix Spike/Matrix Spike Duplicate Analyses: Matrix spike and matrix spike duplicate analyses were performed on LI-LC-01-06, S4-LC-01-01, VR-LC-01-05, S7-FD-01-02, JR-LC-01-03 and PF-LC-01-03. Analyte spike concentrations were approximately 5 ppm (differing slightly based on actual sample weight used). The laboratory notes in the case narrative that control criteria have not been established for the matrix. Since all matrix spike samples recovered low for tetryl and the field sample results were non-detected, all data were qualified as estimated (UJ) for tetryl.

Laboratory Control Samples: LCS samples were analyzed at the frequency of one per twenty samples. The acceptance window was 70-130%. All compounds recovered within limits with the exception of tetryl, which recovered low, resulting in estimated qualification of tetryl results for all samples in SDGs K0501249 and K0501162.

Target Compound Identification and Reporting Limits: The laboratory noted that detected concentrations below the method reporting limit were not confirmed.

Field Replicates: Field replicates were not collected for this project.

System Performance: The chromatograms were reviewed for baseline shifts, general instrument response and missed peaks. The laboratory was contacted regarding the reporting and integration of HMX for sample S7-LC-01-02. The HMX was re-integrated and revised from ND 1U to 0.16 JN. Additionally, the Form 1 for sample HR-FD-01-02 was originally reported a * for RDX, which the laboratory indicated was an anomaly, therefore removed from the data point.

Overall Assessment: All deliverables required by the project are present and data packages are complete. Recommended sample holding times and conditions were met. Initial and continuing calibration requirements were acceptable. Method blanks show no presence of target analytes. Compound identification and quantitation is acceptable. Raw data show no indications of system performance degradation. The data were qualified for tetryl due to low MS/MSD and LCS recoveries. Overall analytical performance is considered acceptable, and data quality is sufficient for project use.

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MEMORANDUM

TO: Tom Bowden (Ridolfi Inc.)

FROM: Raleigh Farlow

DATE: September 20, 2005

SUBJECT: Data Assessment for Explosive Residues in Tissues; Vieques Island – 472P

Suspicious hits were reviewed for selected residues in lab (CAS) delivery group K0501249; specifically for sample K0501249-031 (field ID VR-LC-01-05). Explosive residues were analyzed and reported by U.S. EPA Method 8330, which is an HPLC screening method utilizing 254 nm absorbance for detection. Tentative hits (positive detections) on the primary HPLC column (a 0.46 x 15 cm C-18 column) are required to be confirmed on a [dissimilar] secondary column (in this case a 0.46 x 25 cm CN column coupled to a 0.46 x 10 cm C-8 column).

A summary of the primary and confirmatory analyses for sample VR-LC-01-05 are as follows:

Target analyte	Primary column result	Confirmatory column result	Comment
HMX	0.86 µg/mL	0.60 µg/mL	36% RPD; confirm. result equiv. to chromatographic background response.
RDX	0.05 µg/mL	0	nonconfirmed
1,3-DNB	0	0.16 µg/mL	nonconfirmed
Tetryl	0.23 µg/mL	0	nonconfirmed
Nitrobenzene	0.10 µg/mL	0.03 µg/mL	Less than reporting limit
2-Amino-4,6-DNT	0.06 µg/mL	0.08 µg/mL	Less than reporting limit
TNT	0	0.04 µg/mL	nonconfirmed
2,6-DNT	0.008 µg/mL	0	nonconfirmed
2,4-DNT	0.02 µg/mL	0	nonconfirmed
2-NT	0.19 µg/mL	0	nonconfirmed

The HMX result from the primary column is considered nonconfirmed due to the confirmatory column response at comparable level as the chromatographic background (bumpy baseline not allowing distinguishing between background noise and valid target analyte signal). The response on the confirmatory column is equivalent to a sample concentration of 1.2 mg/kg; just slightly greater than the method capabilities for detection. All target analyte responses via the confirmatory analyses are at levels comparable to chemical background levels – low signal to noise levels.

It is recommended that the HMX result on the primary column of 1.7 mg/kg [tentative] be replaced by the lower reporting limit of 1.2 mg/kg (based on the confirmatory column signal to noise level) as a nondetect – **HMX @ 1.2 mg/kg U**. Background noise [chemical interference] is sufficiently high to preclude a confident assignment at these levels.

OK – what is responsible for the elevated noise level (chemical background) in the sample? A variety of substances can interfere at these analytical operating conditions; common pollutants such as PAHs and phthalate esters, for example. Note that Method 8330 is a screening method and should only be used to prescreen for tentative hits. More selective methods are available for confirmatory analyses yielding high confidence in identifications and quantitations. These methods utilize analytical techniques such as HPLC/MS, GC/ECD, and possibly a very inert GC/MS system.

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MEMORANDUM

TO: Tom Bowden (Ridolfi Inc.)
Colin Wagoner (Ridolfi Inc.)

FROM: Raleigh Farlow

DATE: September 26, 2005

SUBJECT: Data Assessment for Explosive Residues in Tissues; Vieques Island – 472P

Suspicious hits were reviewed for selected residues in 17 samples associated with lab (CAS) delivery groups K0501162, K0501249 and K0501711. Explosive residues were analyzed and reported by U.S. EPA Method 8330, which is an HPLC screening method utilizing 254 nm absorbance for detection. Tentative hits (positive detections) on the primary HPLC column (a 0.46 x 15 cm C-18 column) were reported without confirmatory analyses. The results were reported with the "JN" associated qualifier code. All reported results are **nonconfirmed** for the following samples. It is more appropriate, in these cases, to have reported the data as nondetects at the associated levels or a higher (*project-specified*) quantitation level with the "U" qualifier code.

A review was performed of the laboratory raw data, and a summary of findings is as follows:

Sample	Lab-reported result	Observations & recommendation
K0501162-007 (JR-FD-01-01)	RDX 0.08 JN	R_t shift, chemical interference. **RDX = 0.1 U**
K0501162-017 (PF-FD-01-02)	HMX 0.11 JN	R_t shift, chemical interference. **HMX = 0.1 U**
K0501162-020 (PF-FD-01-03)	HMX 0.16 JN	R_t OK, but nonconfirmed. **HMX = 0.2 U**
K0501162-032 (PF-LC-01-06)	HMX 0.64 JN	R_t OK, but nonconfirmed. **HMX = 0.6 U**
K0501162-035 (BT-LC-01-02)	HMX 0.44 JN	R_t shift, chemical interference. **HMX = 0.4 U**
K0501162-040 (HR-FD-01-01)	HMX 0.22 JN	R_t OK, but nonconfirmed. **HMX = 0.2 U**
K0501162-041 (HR-FD-01-02)	HMX 0.28 JN RDX 0.15 JN	R_t shift, chemical interference. **HMX = 0.3 U** Rt shift, chemical interference. **RDX = 0.2 U**
K0501162-045 (RB-LC-01-03)	RDX 0.098 JN	R_t shift, chemical interference. **RDX = 0.1 U**
K0501249-010 (SB-LC-01-02)	HMX 0.24 JN	R_t shift, chemical interference. **HMX = 0.2 U**
K0501249-014 (SB-LC-01-06)	HMX 0.96 JN	R_t shift, chemical interference. **HMX = 1 U**
K0501249-015 (KA-LC-01-01)	RDX 0.19 JN	R_t OK, but nonconfirmed. **RDX = 0.2 U**
K0501249-020 (KA-LC-01-06)	RDX 0.13 JN	Baseline noise; no verifiable peak. **RDX = 0.1 U**
K0501249-024 (LA-LC-01-04)	HMX 0.12 JN	R_t OK, but nonconfirmed. **HMX = 0.1 U**
K0501249-036 (S4-FD-01-03)	2-NT 0.27 JN 4-NT 0.2 JN	R_t shift (broad hump), chemical interference. **2-NT = 0.3 U** **4-NT = 0.2 U**
K0501249-044 (LI-LC-01-04)	RDX 0.12 JN 2,4-DNT 0.14 JN	R_t OK, but nonconfirmed. **RDX = 0.1 U** Broad hump, chemical interference. **2,4-DNT = 0.1 U**
K0501249-071 (PG-FD-01-01)	HMX 0.47 JN RDX 0.12 JN	R_t OK, but nonconfirmed. **HMX = 0.5 U** Rt shift, chemical interference. **RDX = 0.1 U**
K0501711-002 (HR-02 ref.)	HMX 0.19 JN	R_t shift, chemical interference. **HMX = 0.2 U**

Care must be taken to avoid over-interpreting results from a screening method. This tends to be the situation far too frequently. If positive results are observed and reported at levels of concern, then a more discriminatory and selective method is warranted for confirmation. This generally entails a greater cost per sample for analysis, however, a generally small number of samples are involved following screening. The screening method, as it is employed here, appears to be meeting the requirements of the project (based on the benchmark concentrations). Any additional work for confirmatory analyses would be warranted if the sample concentrations approached the benchmark values; which is not the case here. Appropriate analytical techniques are identified in the 9/20/05 memorandum to T. Bowden.