

ATTACHMENT H.5
TECHNICAL MEMORANDUM – INTERLABORATORY COMPARISON OF
PV SHELF SSRM (MARINE SEDIMENT SR0326)

Technical Memorandum

To: Palos Verdes Technical Information Exchange Group

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Date: 14 November 2012

Subject: Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

1.0 Introduction

The United States Environmental Protection Agency (EPA) Region 9 coordinated an interlaboratory comparison study related to DDT analyses of a site-specific reference material (SSRM) of sediment collected at the Palos Verdes (PV) Shelf, Operable Unit (OU) 5 of the Montrose Chemical Corporation Superfund Site, Torrance, California. The SSRM material is designated as Marine Sediment SR0326. This effort was not intended to validate a test method or to provide certified DDT concentrations for the SSRM, but rather to provide a valid statistical approach to attain confidence in past, present, and future results from laboratories working on PV Shelf sediment projects, including the results generated during the sediment sampling event conducted by EPA at PV Shelf in fall 2009 (report pending).

2.0 Origin of Marine Sediment SR0326

Marine Sediment SR0236 was derived from a box core of seabed sediment collected at PV Shelf by Dr. Robert Eganhouse of the United States Geological Survey (USGS), Reston, Virginia, during spring 2010. The core was collected near Station 6C, established by the Sanitation Districts of Los Angeles County (LACSD) for its sampling program related to the National Pollutant Discharge Elimination System (NPDES) permit for the Joint Water Pollution Control Plant (JWPCP), Carson, California. Station 6C is situated in the Pacific Ocean approximately 2.3 miles west-southwest (WSW) of White Point on the PV Peninsula; the measured depth of the water column at the time of core collection was 59 meters (193.5 feet).

A subcore of the seabed box core was retrieved and frozen on board the project research vessel and shipped to EPA's Quality Assurance Technical Support (QATS) laboratory in Las Vegas, Nevada. At QATS, the material was designated as Marine Sediment SR0326; the subcore was thawed, air-dried for 3 days, sieved, ball-milled, and homogenized. After this processing, it yielded approximately 2 kilograms (kg) of dry sediment. The sediment was divided into 30-gram (g) aliquots and transferred into amber screw-cap glass bottles with Teflon-lined caps. The bottles were placed into storage in a deep freezer (-20°C). More details of the naming, processing, and storage of the SSRM are provided in the attached report from the Shaw Group (Shaw), Las Vegas, Nevada, contracted to EPA under the QATS program (Attachment 1).

EPA directed Shaw to perform initial characterization of SR0326 by testing for pesticides per Contract Laboratory Program (CLP) SOM01.2 protocol (EPA, 2007). The standard SOM01.2 analyte list was expanded to include DDT analytes 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDMU,

and 4,4'-DDNU. Attachment 1 includes the DDT results of the initial characterization tests conducted at the QATS laboratory.

In late spring 2012, EPA requested Shaw to ship SR0326 aliquots to the outside laboratories participating in this interlaboratory study. Samples were shipped to the labs under ambient-temperature conditions.

3.0 Approach to DDT Analysis

This interlaboratory comparison evaluated the DDT results for Marine Sediment SR0326 reported by the QATS laboratory and by the five outside participating laboratories listed below.

- Calscience Environmental Laboratories, Garden Grove, California, the commercial laboratory that performed tests for EPA's PV Shelf sediment sampling event conducted in fall 2009
- Institute for Integrated Research in Materials, Environments, and Society (IIRMES), Long Beach, California
- Water Quality Laboratory at LACSD's JWPCP
- Southern California Coastal Water Research Project (SCCWRP), Costa Mesa, California
- USGS Environmental Organic Geochemistry Laboratory, Reston, Virginia

The laboratories were instructed to select their preferred analytical methods for pesticide compounds, and to report results for the following forms of DDT, referred to herein as "DDT analytes":

2,4'-DDD	4,4'-DDD	2,4'-DDE	4,4'-DDE
2,4'-DDT	4,4'-DDT	4,4'-DDMU	4,4'-DDNU

The DDT analytes 4,4'-DDMU and 4,4'-DDNU are of interest because they have been identified as being part of the DDT degradation pathway at PV Shelf (Eganhouse and Pontolillo, 2008). Results of the PV Shelf sediment sampling event conducted by EPA in fall 2009 indicate that 4,4'-DDMU was detected generally at high concentrations relative to the other DDT analytes, second only to 4,4'-DDE (report pending).

Results for the DDT analytes were reported in terms of dry weight. Results for moisture content (MC) and total organic carbon (TOC) were optional. LACSD and QATS reported MCs of 0.8 percent and 1.2 percent, respectively. All other laboratories assumed an MC value of zero due to the drying steps taken during preparation of the SSRM.

Each laboratory performed multiple analyses of the PV Shelf SSRM employing the techniques and methods routinely used in their laboratory to measure DDTs in marine sediments. The analytical instruments used were gas chromatograph (GC) combined with either electron capture detector (ECD) or mass spectrometer (MS). Table 1 summarizes the procedures used by each laboratory, including methods for extraction, extract cleanup, and instrumental analysis.

4.0 Analytical Results

DDT results from each laboratory are presented in Tables 2 through 7, respectively. Reports submitted by the five outside laboratories are presented in Attachments 2 through 6. As indicated, most laboratories analyzed and detected all eight requested DDT analytes with the following exceptions:

- 2,4'-DDT was reported as non-detected for all analytical runs by three laboratories (IIRMES, QATS, and SCCWRP). For the 13 runs by USGS, 2,4'-DDT was detected in one run, not detected in six runs, and not reported for six runs.
- 4,4'-DDNU was not reported by IIRMES and LACSD.
 - IIRMES stated that a calibration standard for 4,4'-DDNU was not available.
 - LACSD stated that their method for 4,4'-DDNU analysis had not been fully developed.
- 4,4'-DDNU results from QATS were reported as qualified (of poor quality), due to high variability from their dual GC/ECD columns and possible interference in the analysis.

The statistical analysis herein was not carried through for 2,4'-DDT and 4,4'-DDNU because of the reasons below.

- For 2,4'-DDT, fewer than six laboratories reported analytical results (ASTM International [ASTM], 2011).
- For 4,4'-DDNU, most results were below detection limits or not reported (Schantz *et al.*, 2008, p. 11).

5.0 Statistical Approaches

5.1 Basis of Evaluation

Statistical approaches used herein generally followed guidelines from the National Institute of Standards and Technology (NIST) and ASTM. NIST web pages were accessed for general guidance (NIST [1], [2], [3]). Specific guidelines include Taylor and Kuyatt, 1994, and ASTM, 2011. Definitions of terminology used in this memorandum are provided below.

- C = the value of a characteristic obtained by carrying out a specified test method (ASTM, 2011). In this study C refers to a reported or calculated concentration.
- C_i = an individual analyte concentration for each sample, replicate, or duplicate reported by a laboratory.
- C_L = the mean analyte concentration value reported by a laboratory for all runs, for each DDT analyte (based on averaging the C_i s); also referred to as the "laboratory analyte mean".
- C_{uw} = the unweighted mean concentration for each analyte (based on all analytical runs).
- C_w = the weighted mean concentration for each analyte (based on averaging the C_L s).

- Individual Standard Uncertainty of an individual measurement (u_i) = standard deviation (s) (Taylor and Kuyatt, 1994).
- Coverage Factor (k) = a factor used in the calculation of “expanded uncertainty” (below) relating to the number of standard deviations within the desired “confidence interval”, the interval selected to define the probability that the measurement falls within the interval.
- Expanded Uncertainty (U) = the acceptance interval based on the probability defined by the coverage factor k (based on Taylor and Kuyatt, 1994).

5.2 Assumptions

- Given that all samples analyzed were taken from aliquots derived from a homogenized source (Marine Sediment SR0326), it was assumed that the analytical results form a normal (Gaussian) distribution, with variances in the individual analyzed samples distributed evenly around the mean.
- Individual sample results were “in control”, i.e., the results passed internal quality control (QC) requirements for each laboratory. This assumption allowed each laboratory/method to be evaluated with respect to the others for systematic analytical variations.

5.3 Initial Statistical Steps

Three initial steps were taken to assess the analytical data, as described below.

- Laboratory results for all analytical runs were combined and averaged to produce an unweighted study mean (C_{uw}) for each of the DDT analytes where sufficient data were available. Table 8 lists the unweighted study means by analyte.
- Each data set submitted by each laboratory was examined separately to produce a laboratory analyte mean (C_L) for the six DDT analytes where adequate data were available. Tables 2 through 7 list the C_L s for each laboratory for each DDT analyte.
- The C_L s were averaged to produce a weighted study mean (C_w) for each of the DDT analytes. Table 8 lists the weighted study means by analyte.

5.4 Standard Uncertainties

Standard uncertainties (standard deviations) were calculated for the unweighted data, where each analytical result was individually examined regardless of source laboratory, and the weighted data, where laboratory analytes means were used.

For the unweighted standard uncertainty, the sample standard deviation function (STDEV.S) of Microsoft Excel™ 2010 was applied as follows:

$$u_{cuw} = s_{uw} = \sqrt{\frac{\sum_{i=1}^n (C_i - C_{ave})^2}{(n-1)}}$$

where:

u_{cuw} = the unweighted standard uncertainty

s_{uw} = the unweighted standard deviation

C_i = an individual analytical result

C_{ave} = the unweighted study mean = C_{uw} , and
 n = the sample size = the total number of analytical runs for each analyte

For the weighted sample standard uncertainty, the STDEV.S function was applied as follows:

$$u_{cw} = s_w = \sqrt{\frac{\sum_{i=1}^n (C_L - C_{ave})^2}{(n-1)}}$$

where:

u_{cw} = the laboratory-weighted standard uncertainty
 s_w = the laboratory-weighted standard deviation
 C_L = the laboratory analyte mean for each laboratory
 C_{ave} = the weighted study mean = C_w , and
 n = the sample size = number of laboratories

Table 8 provides results for both the weighted and unweighted standard uncertainties.

5.5 Coverage Factor

NIST by convention, by current international practice, and by policy, generally uses a coverage factor $k = 2$ (Taylor and Kuyatt, 1994 §6.5; Wise and Watters, 2012). This value was used herein. Values of k can be correlated to confidence intervals using published tables of probability distribution (Taylor and Kuyatt, 1994, Table B.1).

5.6 Expanded Uncertainty about the Mean

Calculating an expanded uncertainty (U) allows for the definition of an interval within which a measurement is confidently believed to fall. Similar to approaches typically used by NIST, statistical methods were applied to the data set of DDT analyte results to calculate expanded uncertainties about both the unweighted and weighted study means (Taylor and Kuyatt, 1994; Schantz *et al.*, 2008; Wise and Watters, 2012) for each DDT analyte.

The expanded uncertainty, U , can be calculated using the following formula (Taylor and Kuyatt, 1994):

$$U = ku_c$$

where:

k = coverage factor

u_c = standard uncertainty of the mean = standard deviation of the mean

As this formula indicates, U is obtained by multiplying the standard uncertainty (equal to the standard deviation), u_c , by the coverage factor, k . Table 9 presents the values of expanded uncertainties for both unweighted and weighted approaches. By using coverage factor $k = 2$ and Taylor and Kuyatt, 1994, a DDT analyte result that is trusted will fall within this interval with a level of confidence approximated at 95 percent, as follows:

$$[C_{ave} - U] \leq C \leq [C_{ave} + U]$$

6.0 Discussion of Laboratory Performance

The intervals of analyte-specific expanded uncertainties can be used to evaluate whether a result is statistically acceptable relative to the study mean. For this interlaboratory comparison, the approach for each DDT analyte was to select (and apply) the higher of the two values of standard deviation (and therefore, expanded uncertainty), whether the value was derived from the unweighted or weighted calculations (see Tables 8 and 9).

When applying the selected expanded uncertainties to individual analytical results for the entire data set for the six DDT analytes where adequate data were available, five results of 142 total results fell outside the range of interest, i.e., 97 percent of the results fell within the acceptable range. All results reported from three laboratories, Calscience, IIRMES, and SCCWRP, fell within the acceptable range. For the 18 analytical results reported by LACSD, one value fell outside the range of interest (Table 4), correlating to a 94-percent-acceptable performance. For the 36 analytical results reported by QATS, one value fell outside the range of interest (Table 5), correlating to a 97-percent-acceptable performance. For the 78 results reported by USGS, three values fell outside the range of interest (Table 7), correlating to a 96-percent-acceptable performance.

When applying the selected expanded uncertainties to the correlating laboratory analyte means, all mean results for all laboratories fell within the expanded uncertainty range, i.e., all laboratory mean results are considered acceptable.

Calscience was the analytical laboratory used for EPA's fall 2009 sediment sampling event covering the PV Shelf study area. For that sampling event, Calscience used identical methods of sediment extraction and analysis as for this interlab study of Marine Sediment SR0326, including a secondary cleanup step (see Attachment 2). All Calscience analytical results for Marine Sediment SR0326 were acceptable, based on the confidence intervals described herein. This performance helps to provide an additional level of confidence in the accuracy of the fall 2009 chemistry data set. EPA's full report on the fall 2009 sediment sampling event is due to be released in early 2013.

7.0 Summary

For the six DDT analytes where sufficient data were available, the performance of each laboratory evaluated in this study was acceptable, in that (1) the overwhelming majority (97 percent) of individual analytical results fell within the selected acceptance interval, and (2) all laboratory-specific analyte mean values fell within the selected acceptance interval.

The value and statistical quality of this comparison study could be enhanced in the future if the evaluated laboratories can conduct additional testing of Marine Sediment SR0326, or if additional laboratories can participate.

8.0 Acknowledgements

The following individuals contributed to this effort: Dr. Robert Eganhouse of USGS, Reston, Virginia, collected the original SSRM cores at the shelf, spearheaded the effort to develop the SSRM, and graciously reviewed this memorandum; Mr. Keith Strout at the QATS laboratory

provided processing, handling, distribution, and the initial characterization of the SSRM; Dr. Michele Schantz of NIST, Gaithersburg, Maryland, offered valuable technical assistance for the statistical approaches and provided comments for this memorandum; and the following individuals assisted by volunteering lab services and arranging for the tests of the SSRM: Mr. Bob Stearns and Ms. Danielle Gonsman at CalScience; Mr. Richard Gossett at IIRMES; Mr. Chi-Li Tang and Ms. Janice Chen at LACSD; and Mr. Keith Maruya at SCCWRP.

9.0 References

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- NIST (2): Uncertainty of Measurement Results from NIST, accessed October 2012.
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TABLES

Table 1 – Summary of Analytical Methods of Participating Laboratories
Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)
Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)
Los Angeles County, California
November 2012

<i>Laboratory name</i>	<i>Extraction method</i>	<i>Extraction solvent/mix time</i>	<i>Method of Quantification</i>	<i>Cleanup methods</i>	<i>Instrumental analysis method</i>
Calscience	EPA SW-846 3545 (using 20-g sample size)	Methylene chloride/20 min	Internal Standard (IS): acenaphthene-d10 added prior to analysis; TCMX added prior to extraction as surrogate	Sulfur cleanup followed by SPE using ENVI-Carb II/PSA'	GC/MS
IIRMES	Sohxlet (using 5-g sample size)	Methylene chloride/24 hrs	IS: 2,2'-Dibromobiphenyl, and 2,2',5,5'-Tetrabromobiphenyl added just prior to analysis; 2,4,5,6-Tetrachlorometaxylene (TCMX), PCB 30, PCB 112, and PCB 198 added prior to extraction as surrogates.	Alumina/silica	GC/MS
LACSD	In-house Open Column Extraction (PFE) for two batches; ultrasonication for one batch (using 2-g sample size)	1:1 v/v acetone/hexane; two batches used open column for 30 min extraction; one batch used SW846 3550B ultrasonic extraction	External Standard (ES): TCMX and Dichlorobiphenyl (DCB) added prior to extraction as surrogates.	EPA SW-846 3620B florisil cleanup EPA SW-846 3660B sulfur cleanup w/ granular copper EPA SW-846 3665A sulfuric acid cleanup	GC/ECD
EPA QATS Laboratory (Shaw Environmental)	CLP SOM01.1 (sonication) using 5-g sample size	Methylene chloride/acetone, 1:1, 100 ml, 3-min sonication period, performed 3 times	ES: TCMX and DCB were added prior to extraction as surrogates. (Non-CLP target analytes were also incorporated into this study: 2,4'-DDD, 2,4'-DDE, 2,4'-DDT, 4,4'-DDMU, and 4,4'-DDNU.)	GPC to remove sulfur; florisil to remove polar contaminants	GC/ECD
SCCWRP	Pressurized Fluid Extraction (using 1-g sample size)	Methylene chloride/20 min	IS: PCB 30 and PCB205 added prior to analyses; 4,4'-dibromooctofluorobiphenyl (DBOFB) and PCB 208 added prior to extraction as surrogates.	Sulfur cleanup using acid-activated copper; silica gel/alumina combination; first fraction (15 ml hexane) and second fraction (60 ml hexane/DCM at 7:3 v/v) were collected and solvent exchanged into hexane	GC/MS
USGS	EPA SW-846 3545A (PFE)	Methylene chloride/ 5-10 min per EPA SW-846 3545A	IS: TCMX, PCB 11, PCB 207 added prior to analyses; 4,4'-DDT-D8, 4,4'-DDE-D8, 4,4'-DDD-D8, PCB 30, PCB 103, PCB 121, and PCB 198 added prior to extraction as surrogates.	Silica SPE to remove undesirable polar components; SEC-HPLC to eliminate high MW constituents; activated copper to remove sulfur	GC/MS

**Table 1 – Summary of Analytical Methods of Participating Laboratories
Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)
Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)
Los Angeles County, California
May-June 2012**

Abbreviations

CLP – Contract Laboratory Program

ECD – Electron capture detector

EPA – United States Environmental Protection Agency

ES – External standard

g - Grams

GC– Gas chromatograph

GPC – Gel permeation chromatography

hr - Hours

IIRMES – Institute for Integrated Research in Materials, Environments,
and Society

IS – Internal standar

LACSD – Sanitation Districts of Los Angeles County

min – Minimum, minutes

ml – Milliliter

MS – Mass spectrometer

MW – Molecular weight

PFE – Pressurized fluid extraction

QATS – Quality Assurance and Technical Support

SCCWRP – Southern California Coastal Water Research Project

SEC-HPLC –Size-exclusion chromatography/high performance liquid chromatography

SPE – Solid-phase extraction

USGS – United States Geologic Survey

Table 2 - Calscience Results

Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)

Los Angeles County, California

November 2012

<i>Run no.</i>	<i>Sample Description</i>	<i>Test Result by Analyte (µg/kg = ppb)</i>							
		<i>2,4'-DDD</i>	<i>2,4'-DDE</i>	<i>2,4'-DDT</i>	<i>4,4'-DDD</i>	<i>4,4'-DDE</i>	<i>4,4'-DDT</i>	<i>4,4'-DDMU</i>	<i>4,4'-DDNU</i>
1	Hg and PSA/carbon cleanup - sample ID PVS0006	370	4,700	65	930	28,000	660	7,400	290
2	Hg and PSA/carbon cleanup - sample ID PVS0007	400	4,500	75	890	22,000	700	5,900	250
<i>Laboratory Analyte Mean, C_L</i>		385	4,600	-	910	25,000	680	6,650	-

Abbreviations

µg/kg - Micrograms per kilogram

Hg - Mercury

OU - Operable Unit

ppb - Parts per billion

PSA - Primary and secondary amines

Table 3 - IIRMES Results

Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)

Los Angeles County, California

November 2012

<i>Run no.</i>	<i>Test Result by Analyte (µg/kg = ppb)</i>							
	<i>2,4'-DDD</i>	<i>2,4'-DDE</i>	<i>2,4'-DDT</i>	<i>4,4'-DDD</i>	<i>4,4'-DDE</i>	<i>4,4'-DDT</i>	<i>4,4'-DDMU</i>	<i>4,4'-DDNU</i>
1	284	5,539	<1	815	32,551	650	8,617	NA
2	297	5,627	<1	857	33,643	668	8,362	NA
3	289	5,439	<1	892	32,296	668	8,157	NA
Laboratory Analyte Mean, C_L	290	5,535	-	855	32,830	662	8,379	-

Abbreviations

µg/kg - Micrograms per kilogram

IIRMES - Institute for Integrated Research in Materials, Environments, and Society

NA - Not analyzed

OU - Operable Unit

ppb - Parts per billion

Table 4 - LACSD Results

**Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)
 Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)
 Los Angeles County, California
 November 2012**

<i>Run no.</i>	<i>Test Result by Analyte (µg/kg = ppb)</i>							
	2,4'-DDD	2,4'-DDE	2,4'-DDT	4,4'-DDD	4,4'-DDE	4,4'-DDT	4,4'-DDMU	4,4'-DDNU
1	394	4,280	27.6	881	32,700	663	<i>10,100</i>	NA
2	433	4,990	24.0	722	29,500	437	9,190	NA
3	303	5,630	21.2	855	29,000	564	8,730	NA
Laboratory Analyte Mean, C_L	377	4,967	-	819	30,400	555	9,340	-

Abbreviations

µg/kg - Micrograms per kilogram

LACSD - Sanitation Districts of Los Angeles County

NA - Not analyzed

OU - Operable Unit

ppb - Parts per billion

Notes

1. Shaded results in *italic font* exceeded the expanded uncertainty (*U*) limits for *k* = 2.

Table 5 - QATS Results

Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)

Los Angeles County, California

November 2012

<i>Run no.</i>	<i>Test Result by Analyte (µg/kg = ppb)</i>							
	2,4'-DDD	2,4'-DDE	2,4'-DDT	4,4'-DDD	4,4'-DDE	4,4'-DDT	4,4'-DDMU	4,4'-DDNU
1	190	5,500	ND	710	19,000	470	7,500	24,000 (R)
2	200	4,500	ND	720	19,000	470	6,300	3,700
3	210	5,400	ND	810	18,000	490	7,400	2,500
4	180	5,100	ND	820	18,000	540	7,100	2,300
5	210	<i>6,000</i>	ND	890	20,000	560	8,200	5,100
6	170	5,000	ND	740	20,000	470	6,800	3,100
Laboratory Analyte Mean, C_L	193	5,250	-	782	19,000	500	7,217	-

Abbreviations

µg/kg - Micrograms per kilogram

ppb - Parts per billion

ND - Not detected

QATS - Quality Assurance and Technical Support Laboratory, Las Vegas, Nevada

OU - Operable Unit

R - Rejected

Notes

1. Shaded results in *italic font* exceeded the expanded uncertainty (*U*) limits for *k* = 2.

Table 6 - SCCWRP Results
Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)
Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)
Los Angeles County, California
November 2012

<i>Run no.</i>	<i>Sample Description</i>	<i>Test Result by Analyte (µg/kg = ppb)</i>							
		<i>2,4'-DDD</i>	<i>2,4'-DDE</i>	<i>2,4'-DDT</i>	<i>4,4'-DDD</i>	<i>4,4'-DDE</i>	<i>4,4'-DDT</i>	<i>4,4'-DDMU</i>	<i>4,4'-DDNU</i>
1	Sample 1	238	4,582	<7.29	820	24,164	602	6,996	298
2	Sample 2	226	4,512	<7.29	768	24,508	504	6,884	290
3	Sample 2 Duplicate	216	4,029	<7.29	709	22,672	449	6,268	263
4	Sample 3	218	4,309	<7.29	731	23,125	498	6,690	297
5	Sample 3 Duplicate	216	3,818	<7.29	701	20,100	422	5,814	259
<i>Laboratory Analyte Mean, C_L</i>		223	4,250	-	746	22,914	495	6,530	-

Abbreviations

µg/kg - Micrograms per kilogram

OU - Operable Unit

ppb - Parts per billion

SCCWRP - Southern California Coastal Water Research Project

Table 7 - USGS Results

Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)

Los Angeles County, California

November 2012

Run no.	Sample Description	Test Result by Analyte (µg/kg = ppb)							
		2,4'-DDD	2,4'-DDE	2,4'-DDT	4,4'-DDD	4,4'-DDE	4,4'-DDT	4,4'-DDMU	4,4'-DDNU
1	Range-finding, Sample ID RPE0172	369	4,610	28	1,138	23,233	979	7,644	232
2	Range-finding, Sample ID RPE0173	413	4,776	NR	1,239	24,147	1,624	7,912	244
3	MDL, Precision, Accuracy, Sample ID RPE0202	216	3,953	NR	727	19,709	515	6,538	220
4	MDL, Precision, Accuracy, Sample ID RPE0203	247	4,148	NR	824	21,534	556	6,996	258
5	MDL, Precision, Accuracy, Sample ID RPE0204	226	3,841	NR	722	19,493	903	6,448	223
6	MDL, Precision, Accuracy, Sample ID RPE0205	260	4,279	NR	845	22,204	652	7,150	266
7	MDL, Precision, Accuracy, Sample ID RPE0206	243	4,071	NR	781	20,735	552	6,804	234
8	Method Comparison, Sample ID RPE0238	272	4,165	<27.7	877	21,949	641	6,797	252
9	Method Comparison, Sample ID RPE0239	275	4,066	<27.1	869	18,845	699	6,617	252
10	Sample ID RPE0259	280	4,339	<27.7	963	22,951	729	7,079	240
11	Sample ID RPE0289	313	4,362	<27.1	973	21,229	807	7,147	241
12	Sample ID RPE0321	237	3,636	<27.7	756	17,717	561	6,011	193
13	Sample ID RPE0336	267	4,009	<27.1	842	19,741	618	6,497	202
Laboratory Analyte Mean, C_L		278	4,173	-	889	21,037	757	6,895	-

Table 7 - USGS Results (continued)

Interlaboratory Comparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)

Los Angeles County, California

October 2012

Abbreviations

µg/kg - Micrograms per kilogram

MDL - Method detection limit

NR - Not reported

OU - Operable Unit

ppb - Parts per billion

USGS - United States Geological Survey Laboratory, Reston, Virginia

Notes

1. Results for DDT analytes 4,4'-DDMS and 4,4'-DDNS were reported by USGS but were not included in this table.
2. Shaded results in *italic font* exceeded the expanded uncertainty (U) limits for $k = 2$.

Table 8 - Data Summary

Laboratory Intercomparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)

Los Angeles County, California

November 2012

<i>Parameter</i>	<i>Unweighted Data</i> ¹ (µg/kg = ppb)							
	2,4'-DDD	2,4'-DDE	2,4'-DDT	4,4'-DDD	4,4'-DDE	4,4'-DDT	4,4'-DDMU	4,4'-DDNU
Unweighted Study Mean, C_{uw}	262	4,476	-	813	22,477	616	7,031	-
Unweighted Standard Uncertainty, u_{cuw}	72	630	-	120	4,727	222	988	-

<i>Laboratory</i>	<i>Weighted Data</i> (µg/kg = ppb)							
	2,4'-DDD	2,4'-DDE	2,4'-DDT	4,4'-DDD	4,4'-DDE	4,4'-DDT	4,4'-DDMU	4,4'-DDNU
Calscience	385	4,600	-	910	25,000	680	6,650	-
IIRMES	290	5,535	-	855	32,830	662	8,379	-
LACSD	377	4,967	-	819	30,400	555	9,340	-
QATS	193	5,250	-	782	19,000	500	7,217	-
SCCWRP	223	4,250	-	746	22,914	495	6,530	-
USGS	278	4,173	-	889	21,037	757	6,895	-
Weighted Study Mean, C_w	291	4,796	-	833	25,197	608	7,502	-
Weighted Standard Uncertainty, u_{cw}	78	549	-	63	5,409	107	1,120	-

Table 8 - Data Summary (continued)

Laboratory Intercomparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)

Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)

Los Angeles County, California

October 2012

Abbreviations

µg/kg - Micrograms per kilogram

IIRMES - Institute for Integrated Research in Materials, Environments, and Society

LACSD - Los Angeles County Sanitation District

NA - Not analyzed

OU - Operable Unit

ppb - Parts per billion

QATS - Quality Assurance and Technical Support Laboratory, Las Vegas, Nevada

R - Rejected

SCCWRP - Southern California Coastal Water Research Project

USGS - United States Geological Survey (Laboratory in Reston, Virginia)

Notes

1. Based on all results as indicated in Tables 2-7.

2. Bold values of standard deviation (in shaded cells) were the maximum values selected for evaluating laboratory performance.

Table 9 - Values of the Study Mean with Expanded Uncertainties
Laboratory Intercomparison of the Palos Verdes Shelf Site-Specific Reference Material (Marine Sediment SR0326)
Palos Verdes Shelf (OU 5 of the Montrose Chemical Corp. Superfund Site)
Los Angeles County, California
November 2012

<i>Expanded Uncertainty Values for Unweighted Mean and Standard Uncertainties (µg/kg = ppb)</i>			
<i>Analyte</i>	<i>Study Mean, C_{uw}</i>		<i>Expanded Uncertainty, U</i>
2,4'-DDD	262	±	143
2,4'-DDE	4,476	±	1,261
2,4'-DDT	-	±	-
4,4'-DDD	813	±	241
4,4'-DDE	22,477	±	9,455
4,4'-DDT	616	±	445
4,4'-DDMU	7,031	±	1,976
4,4'-DDNU	-	±	-

<i>Expanded Uncertainty Values for Weighted Mean and Standard Uncertainties (µg/kg = ppb)</i>			
<i>Analyte</i>	<i>Study Mean, C_w</i>		<i>Expanded Uncertainty, U</i>
2,4'-DDD	291	±	156
2,4'-DDE	4,796	±	1,097
2,4'-DDT	-	±	-
4,4'-DDD	833	±	126
4,4'-DDE	25,197	±	10,818
4,4'-DDT	608	±	214
4,4'-DDMU	7,502	±	2,239
4,4'-DDNU	-	±	-

Abbreviations

OU - Operable Unit

Notes

1. Bold values of study mean and expanded uncertainty (in shaded cells) were the analyte-specific values used selected for evaluating laboratory performance.

ATTACHMENT 1
QATS DEVELOPMENT REPORT AND TEST RESULTS – MARINE SEDIMENT
SR0326

June 3, 2010

John Nebelsick
U.S. Environmental Protection Agency
Ariel Rios Bldg (5102P)
1200 Pennsylvania Ave., N.W.
Washington, DC 20460

Document ID#: 4003-06032010-1

Dear Mr. Nebelsick:

TASK ORDER 4003
DISTRIBUTION AND MAINTENANCE OF THE SUPERFUND
PERFORMANCE EVALUATION SAMPLES (PES) INVENTORY

TASK 4 – SPECIAL-REQUEST AND SITE-SPECIFIC PES
PALOS VERDE SHELF SUPERFUND SITE SRM DEVELOPMENT REPORT

At the request of Mr. Steve Remaley, USEPA Region 9, and with your approval via electronic mail on March 10, 2010, we have processed a marine sediment sample from the Palos Verde Shelf Superfund site for use as a standard reference material (SRM) for the analysis of select pesticides.

QATS Laboratory personnel were provided with the sediment processing instructions from Dr. Robert Eganhouse, USGS, through Mr. Remaley in electronic mail correspondence on March 10, 2010. These instructions provided directions to air-dry, sieve, ball-mill, homogenize, and analyze the sediment sample from the Palos Verde Shelf site for pesticides. In addition to the CLP SOM01.2 SOW pesticide target analytes, we were requested to analyze for 2,4'-DDE, 2,4'-DDD, 2,4'-DDT, DDMU, and DDNU. For the past several years, we have provided special-request, site-specific pesticide PESs containing the 4,4'- and 2,4'-isomers of DDE, DDD, and DDT for this site and the Montrose Superfund site, and several of the QATS Program pesticide PESs now contain these CLP SOM01.2 SOW non-target analytes.

The Palos Verde Shelf site marine sediment core sample was received from the USGS at the QATS Laboratory on April 27, 2010 in a cooler containing ice. The sample was contained in a plastic tube with sealed end-caps secured with tape. There was no apparent leakage from the interior of the core sample. There was no chain-of-custody record with the shipment, however, field sample information was recorded on the outside of the tube including a field identification number. The sediment sample was logged into the QATS Sample Receipt Logbook and was assigned a QATS Sample Number and Sigma (PES/SRM) Number for tracking and identification purposes. The sample receipt and tracking information is listed in Table 1 below.



The Quality Assurance Technical Support Program's Quality Management System is certified to the ISO 9001:2008 International Standard

Table 1. Palos Verde Shelf Site Sediment SRM Identification and Receipt Information

Field ID No.	QATS Sample No.	QATS Sigma No.	Sample Wet Wt. (g)	Density (g/cc ³)
S-P1-10-SC (147B5-RM)	357-63-16-S	SR0326	4,030	1.48

The gross weight of the sediment core sample container and contents was recorded prior to processing. Subsequent to recording the gross weight, the sediment was transferred to two, five (5) gallon high-density polyethylene (HDPE) trays (20"L x 16"W x 5"H), broken up and spread out to increase the surface area of the sample exposed to the air, and allowed to air-dry in the fume hood in the QATS Containment Laboratory. The density of the sediment sample, listed in Table 1, was determined using the net weight of the sample and the calculated volume of the sample tube. The material was allowed to air-dry for a total of three (3) days while occasionally breaking up the material and spreading it out in the containers. The weight of the sample was recorded each morning to determine the progress of the drying process. The weight loss on drying over the three day period is presented in Table 2.

Table 2. Palos Verde Shelf Site Sediment Sample – Percent Weight Loss on Drying (3 days)

Sigma #	QATS Sample No.	Day 1	Day 2	Day 3
SR0326	357-63-16-S	17%	43.7%	48.4%

The dried sediment was screened through an ASTM E-11 No. 60 mesh (250 μ m) stainless steel sieve. All of the material, with the exception of a small amount of marine shell fragments, passed through the sieve and was collected for milling. The dried sediment material was ground in a ceramic ball mill using zirconia grinding media for a period of 10 hours. Following the milling, the sediment material was entirely screened through an ASTM E-11 No. 80 mesh (180 μ m) stainless steel sieve, placed back in the ball mill without the zirconia grinding media, and homogenized for a period of 4 hours. Therefore, the particle size of this material is classified as <180 μ m. A final percent solids determination was performed on the dried sediment material using a five (5) gram sample and drying it for a period of four (4) hours in a 105 °C oven. The percent solids value of the processed dried sediment was determined to be 98.8 percent. It was not determined if the 1.2 percent non-solid material is water, or other volatile material. Subsequent to homogenization, the entire batch of sediment material was distributed into six (6), 500 mL HDPE wide-mouth bottles for storage until sample extraction and analysis was completed. The containers of material were stored in a freezer at -20 °C until final bottling was completed.

Six (6) replicate samples of five (5) grams each were randomly selected for extraction and analysis for pesticides using the CLP SOM01.2 SOW analytical protocol. The CLP method recommends a sample size of 30 grams for extraction, however, a 5 gram sample size was selected based on concentration estimates determined from GC/MS screening analysis. The samples were extracted using the soil sonication technique, and the extracts were processed using GPC and Florisil clean-up techniques. All of the sample extracts were analyzed using 1, 5, 10, 50, and 100 fold dilutions in order to quantitate the target analytes within the demonstrated calibration range of the instrument. As previously mentioned, CLP SOM01.2 SOW non-target analytes 2,4'-DDE, 2,4'-DDD, and 2,4'-DDT, DDMU, and DDNU were added to the calibration standards for the analyses related to this project. As indicated by the GPC UV detector trace and confirmed by screening GC/MS analysis, the extracts contained high levels of sulfur, as expected for a marine sediment sample. The sulfur was removed from the extracts by GPC clean-up, thus avoiding the need for sulfur clean-up using copper powder. GC/MS screening analysis also indicated the presence of hydrocarbons in the sample, which typically do not interfere with GC/ECD analysis. The extracts were analyzed on an Agilent 6890 GC/ECD system equipped with dual ALS systems, injectors, columns, and ECD detectors. The first column is a 30 meter, 0.53 mm I.D., 0.50 micron film thickness Restek "Rtx-CLPesticides" column, and the second column is a 30 meter, 0.53 mm I.D., 0.42 micron film thickness Restek "Rtx-CLPesticides2" column. All samples were quantitated using

the front column, and the rear column was employed for analyte confirmation. Table 3 presents the analytical results and associated statistics for pesticide determination in the processed marine sediment SRM which is the subject of this report. All analytical results are reported on a dry weight basis.

Table 3. Palos Verde Site Marine Sediment – Pesticide Analytical Results (µg/Kg)

Analyte	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Average	SD	RSD
4,4'-DDE	19,000	19,000	18,000	18,000	20,000	20,000	19,000	890	4.7
4,4'-DDD	710	720	810	820	890	740	780	70	9.0
4,4'-DDT	470	470	490	540	560	470	500	40	8.0
2,4'-DDE	5,500	4,500	5,400	5,100	6,000	5,000	5,300	510	9.7
2,4'-DDD	190	200	210	180	210	170	190	16	8.4
2,4'-DDT	ND	ND	ND	ND	ND	ND	NA	NA	NA
DDMU	7,500	6,300	7,400	7,100	8,200	6,800	7,200	640	8.8
DDNU	24,000 ¹	3,700	2,500	2,300	5,100	3,100	3,300	1,100	33.7

ND = Not Detected

NA = Not Applicable

¹ = Outlier: excluded from statistical calculations.

As indicated in Table 3, 2,4'-DDT was not detected in any of the replicate samples, nor were any of the other seventeen (17) CLP SOM01.2 SOW target pesticide compounds which are not listed in Table 3. The low RSD values for all of the compounds listed in Table 3, with the exception of DDNU, indicate a high level of precision for the replicate analyses, which also indicates that the bulk sample is homogeneous. We believe that the results for DDNU are not reliable because of the high variability of the results for this analyte from the dual GC/ECD columns, as well as possible interference on the first column.

There was approximately 2,000 grams of dried Palos Verde Shelf site sediment SRM prepared from the processing effort described in this report. This material has been bottled in individual 30 gram aliquots using one (1) ounce, amber screw-cap glass bottles with Teflon-lined closures, yielding approximately 60 bottles. The individual bottles of SRM have been labeled as "Palos Verde Shelf SRM" with a unique QATS Laboratory Sample Management Program (SMP) number and barcode on each container. The individual containers are stored at the QATS Facility in a freezer at approximately -20 °C, and will be shipped as requested by authorized personnel.

Please contact me at (702) 895-8722, or Clyde Hedin at (702) 895-8711, if you have any questions or concerns related to the subject Palos Verde Shelf Sediment SRM, or the contents of this report.

Sincerely,



Keith Strout
Analytical Group Leader
QATS Laboratory

cc: Mr. Steve Remaley, USEPA Region 9
Dr. Robert Eganhouse, USGS
Mr. Jami Rodgers, QATS Contract Officer
Task Order 4003 files

ATTACHMENT 2
CALSCIENCE TEST RESULTS FOR MARINE SEDIMENT SR0326 AND
DESCRIPTION OF SECONDARY CLEANUP STEP

If the IS/surrogates added after extraction/cleanup extraction were used for quantitation, were results corrected for percent recovery? No
 If yes, include the associated percent recovery acceptance ranges in the table below. N/A

Calibration Curve

Number of Calibration Levels	Conc. Range	Any non-conformances with calibrations? If yes, please discuss
DDTs 5	<u>50-5000ng/mL</u>	N/A

If analyte was quantitated using a "representative compound", e.g. quantitated against an isomer, parent compound, or single alkylated compound for a group of homologs compound for a group of homologs, list the compound used in the table below.

RESULTS:

PERCENT WATER & total organic carbon, TOC (List each result if determined more than once. Enter results as a number, for example 90.0. DO NOT change format of cell to percent.)

	SR0236 (percent)	SR0326 (percent)
Percent Water	<u>NA</u>	<u>NA</u>
TOC	<u>32000 mg/kg</u>	<u>33000 mg/kg</u>

DDT ANALYSES

	SR0326	SR0326
	Batch A	Batch A
	Sample 1	Sample 2
Analyst (ID #)	<u>421</u>	<u>421</u>
Date(s) of measurements (m/d/y)	<u>5/18/2012</u>	<u>5/18/2012</u>
Sample Jar number	<u>PV0006</u>	<u>PV0007</u>

	SR0326 Sample 1 (ng/g dry mass)	SR0326 Sample 2 (ng/g dry mass)	IS/surrogate used for quantitation	Associated % recovery acceptance ranges	If "representative compound" used for quantitation list the compound used here.
2,4'-DDT	65	<u>75</u>	Acenaphthene-d10/TCMX	50-125%	N/A
4,4'-DDT	660	<u>700</u>	Acenaphthene-d10/TCMX	50-125%	N/A
2,4'-DDE	4700	<u>4500</u>	Acenaphthene-d10/TCMX	50-125%	N/A
4,4'-DDE	28000	<u>22000</u>	Acenaphthene-d10/TCMX	50-125%	N/A
2,4'-DDD	370	<u>400</u>	Acenaphthene-d10/TCMX	50-125%	N/A
4,4'-DDD	930	<u>890</u>	Acenaphthene-d10/TCMX	50-125%	N/A
4,4'-DDMU	7400	<u>5900</u>	Acenaphthene-d10/TCMX	50-125%	N/A
4,4'-DDNU	290	<u>250</u>	Acenaphthene-d10/TCMX	50-125%	N/A

(Any additional data/information should be added here.)



February 8, 2010

Ms. Kristen Craylon
Innovative Technical Solutions, Inc.
2730 Shadelands Drive, Suite 100
Walnut Creek, CA
94598-2540

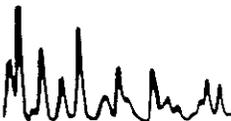
Subject: Proposal to add an additional cleanup step for pesticide samples being analyzed by EPA 8270 SIM.

Calscience Environmental Laboratories, in support of the Palos Verdes Shelf sampling, is requesting the addition of a secondary cleanup procedure for the sediment samples being analyzed for a specific list of chlorinated pesticides by EPA 8270 SIM. This cleanup step involves the use of a pre-manufactured, dual-layer, solid phase extraction cartridge which consists of an ENVI-Carb layer (carbon) on top and a PSA (primary and secondary amines) layer on the bottom.

The proposed addition to this procedure involves cleanup through a reversed-phase, anion-exchange cartridge called ENVI-Carb/PSA prior to the sulfur cleanup. According to the manufacturer (Supleco/Sigma Aldrich), the "ENVI-Carb layer has a strong affinity towards planar molecules and can isolate/remove pigments (e.g., chlorophyll and carotinoids) and sterols commonly present in foods and natural products." And, the PSA layer "has a strong affinity and high capacity for fatty acids, organic acids, and some polar pigments and sugars."

The current procedure for sediment extraction is to extract a specified volume of sample with methylene chloride using EPA method 3545 (Accelerated Solvent Extraction - ASE), solvent exchange the extract into hexane and then concentrate down to a specified final volume. The final extract is then subjected to cleanup using EPA 3660 for sulfur prior to analysis by GC/MS.

The proposed cleanup procedure would be used following the sample extraction but prior to the sulfur cleanup step and would be instituted as follows:



The cartridge is prepared for use by rinsing with 5mL of hexane, which is discarded. 1mL of sample extract is then loaded onto the cartridge and allowed to elute through, with the eluent being captured in a 40mL VOA vial. Immediately after the sample extract reaches the top of the column, 20mL of 80/20 Hexane to Methylene Chloride is then eluted through the column and is also captured in the VOA vial. The extract is then concentrated down using nitrogen to a final volume of 1mL. The 1mL aliquot is then sent for sulfur cleanup using EPA method 3660.

Calscience believes that the addition of this step will help to lessen the amount of breakdown found during analysis. This conclusion has been reached through the evaluation of continuing calibration verification samples analyzed both before and after samples that had undergone this cleanup step. Calscience also believes that the impact on data will be negligible based upon analytical trial using the ENVI-Carb/PSA solid phase extraction cartridges for cleanup of a method detection limit verification sample, method blank and laboratory quality control samples and real world sediment samples. These results are detailed in the following tables.

Table 1: MDL Verification Sample

Sample ID	Surrogate (2,4,5,6-TCMX) Amount (ppb)	Surrogate Recovered (ppb)	Surrogate Recovery %	MDL Spike Amount (ppb)	MDL Spike Recovered (ppb)	MDL % Recovery
MDL Verification	1000	638.22	63.8%	---	---	---
4,4-DDNU	---	---	---	50	42.15	84.3%
2,4-DDE	---	---	---	50	39.91	79.8%
4,4-DDMU	---	---	---	50	39.57	79.1%
4,4-DDE	---	---	---	50	43.01	86.0%
2,4-DDD	---	---	---	50	42.42	84.8%
2,4-DDT	---	---	---	50	46.59	93.2%
4,4-DDD	---	---	---	50	43.74	87.5%
4,4-DDT	---	---	---	50	69.95	139.9%

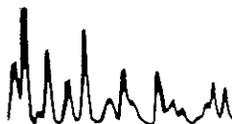


Table 2: Method Blank and Laboratory Control Sample (LCS) Results

Sample ID	Surrogate (2,4,5,6-TCMX) Amount (ppb)	Surrogate Recovered (ppb)	Surrogate Recovery %	LCS Spike Amount (ppb)	LCS Spike Recovered (ppb)	LCS % Recovery
Method Blank	1000	843.67	84.37%	---	---	---
LCS 1	1000	879.99	88.0%	---	---	---
4,4-DDNU	---	---	---	1000	1047.18	104.7%
2,4-DDE	---	---	---	1000	918.35	91.8%
4,4-DDMU	---	---	---	1000	997.36	99.7%
4,4-DDE	---	---	---	1000	958.21	95.8%
2,4-DDD	---	---	---	1000	981.05	98.1%
2,4-DDT	---	---	---	1000	1024.69	102.5%
4,4-DDD	---	---	---	1000	1006.06	100.1%
4,4-DDT	---	---	---	1000	1085.17	108.5%
LCS 2	1000	897.90	89.79%	---	---	---
4,4-DDNU	---	---	---	1000	1092.83	109.3%
2,4-DDE	---	---	---	1000	1016.12	101.6%
4,4-DDMU	---	---	---	1000	1038.79	103.9%
4,4-DDE	---	---	---	1000	1013.68	101.4%
2,4-DDD	---	---	---	1000	1015.01	101.5%
2,4-DDT	---	---	---	1000	1081.47	108.1%
4,4-DDD	---	---	---	1000	1045.53	104.6%
4,4-DDT	---	---	---	1000	1138.28	113.8%
LCS 3	1000	861.81	86.18%	---	---	---
4,4-DDNU	---	---	---	1000	1084.50	108.4%
2,4-DDE	---	---	---	1000	981.23	98.1%
4,4-DDMU	---	---	---	1000	1001.64	100.2%
4,4-DDE	---	---	---	1000	983.59	98.4%
2,4-DDD	---	---	---	1000	1001.93	100.2%
2,4-DDT	---	---	---	1000	1047.99	104.8%
4,4-DDD	---	---	---	1000	1019.71	102.0%
4,4-DDT	---	---	---	1000	1115.02	111.5%
LCS 4	1000	854.46	85.45%	---	---	---
4,4-DDNU	---	---	---	1000	1069.36	106.9%
2,4-DDE	---	---	---	1000	980.88	98.1%
4,4-DDMU	---	---	---	1000	1011.40	101.1%
4,4-DDE	---	---	---	1000	984.81	98.5%
2,4-DDD	---	---	---	1000	989.76	99.0%
2,4-DDT	---	---	---	1000	1055.31	105.5%
4,4-DDD	---	---	---	1000	1006.13	100.65
4,4-DDT	---	---	---	1000	1107.69	110.8%

Table 3: Sample and Sample Duplicate Results

Sample ID	Surrogate (2,4,5,6-TCMX) Amount (ppb)	Surrogate Recovered (ppb)	Surrogate Recovery %	Sample Amount (ppb)	Duplicate Amount (ppb)	RPD %
Sample (11-2235-13)	1000	638.22	63.8%	---	---	---
Duplicate	1000	720.83	72.1%	---	---	---
Analytes	---	---	---	---	---	---
4,4-DDNU	---	---	---	117.97	116.74	1.3%
2,4-DDE	---	---	---	168.13	153.09	9.3%
4,4-DDMU	---	---	---	366.15	358.11	2.2%
4,4-DDE	---	---	---	1069.74	972.91	9.5%
2,4-DDD	---	---	---	27.89	25.84	7.6%
2,4-DDT	---	---	---	1.17	17.63	175.1%
4,4-DDD	---	---	---	81.87	76.37	7.0%
4,4-DDT	---	---	---	41.26	49.54	18.3%

Based upon the anticipated sampling schedule, Calscience would like to begin this additional cleanup step with the next set of samples, expected to arrive on or shortly after February 9, 2010.

If you have questions or comments regarding this procedure, please do not hesitate to contact me.

Sincerely,



Linda Scharpenberg
 Technical Support Manager
 Calscience Environmental Laboratories, Inc.

cc: Bob Stearns, Calscience

ATTACHMENT 3
IIRMES TEST RESULTS – MARINE SEDIMENT SR0326

If yes, include the associated percent recovery acceptance ranges in the table below.

Calibration Curve

DDTs	Number of Calibration Levels		Any non-conformances with calibrations? If yes, please discuss
	Points	Conc. Range	
6	20ng to 800ng	n/a	

If analyte was quantitated using a "representative compound", e.g. quantitated against an isomer, parent compound, or single alkylated compound for a group of homologs compound for a group of homologs, list the compound used in the table below.

RESULTS:

PERCENT WATER & total organic carbon, TOC (List each result if determined more than once. Enter results as a number, for example 90.0.
DO NOT change format of cell to percent.)

	SR0326 (percent)	SR0326 (percent)	SR0326 (percent)
Percent Water			
TOC			

DDT ANALYSES

	SR0326 Batch A Sample 1 ADL	SR0326 Batch B Sample 2 ADL	SR0326 Batch C Sample 3 ADL
Analyst (Initials)	ADL	ADL	ADL
Date(s) of measurements (m/d/y)	6/21/2012	7/3/2012	7/9/2012
Sample Jar number	PVS0009	PVS0009	PVS0009

	SR0326 Sample 1 (ng/g dry mass)	SR0326 Sample 2 (ng/g dry mass)	SR0326 Sample 3 (ng/g dry mass)	IS/surrogate used for quantitation	Associated % recovery acceptance ranges	If "representative compound" used for quantitation list the compound used here.
2,4'-DDT	<1	<1	<1			
4,4'-DDT	650.2	667.7	667.8			
2,4'-DDE	5538.5	5626.9	5438.9			
4,4'-DDE	32551.3	33642.9	32295.5			
2,4'-DDD	283.7	296.7	289.1			
4,4'-DDD	815.0	857.4	891.9			
4,4'-DDMU	8616.9	8362.3	8157.3			
4,4'-DDNU	NA	NA	NA			

(Any additional data/information should be added here.)

ATTACHMENT 4
LACSD TEST RESULTS – MARINE SEDIMENT SR0326

Interlaboratory Analytical Comparison Study of the Palos Verdes Shelf Site-Specific Reference Material (SSRM)

Sample: SR0326

Please fill in all blanks; Use requested units of concentration; Report results as if 3 figures were significant

DO NOT INSERT ROWS OR COLUMNS WITHIN THIS TABLE. DO NOT MOVE CELLS.

- If necessary, add additional data/information at the end of the table.

- Use one of the following if no concentration is reported for an analyte:

NA = Not analyzed/determined; <"conc" = <detection limit conc.; Other = other, explain in a note at end of table

(DL = "below detection limit" may be used, but <"conc", e.g., <8, is preferable.)

Do not use parentheses or negative numbers to indicate "less than detection limit".

Reporting Date (m/d/y): 7/6/2012
 Laboratory: LACSD JWPCP
 Submitted by: Janice Chen

BRIEF DESCRIPTION OF PROCEDURES USED:

Approximate amount of sample extracted:

SR0326 2 g, wet basis;

Method used for determining percentage water: In-house method based on EPA Method 160.3 and SM 2540 G

Were "wet" or "dry" samples extracted?

SR0326 Dry

Extraction method: In-house Open Column Extraction developed by SCCWRP and EPA SW846 3550B Ultrasonic extraction

Extraction solvent: 1:1, v/v acetone/hexane

Extraction time: 30 min in open column extraction or 15 min in ultrasonic extraction

Extraction - other: The first two batches were extracted by open column and the third batch was extracted by EPA SW846 3550B ultrasonic extraction.

Sample extract cleanup method: SW846 3620B Florisil cleanup

SW846 3660B Sulfur cleanup with granular copper

SW846 3665A Sulfuric acid cleanup

Analytical method used (e.g., GC/MS):

	Analyt. Instr.	Column Phase	Col. Length, m	Col. i.d., mm	Col. film thickness, µm
DDTs	<u>GC/ECD</u>	<u>DB-5 & ZB-50</u>	<u>30</u>	<u>0.32</u>	<u>0.25</u>

Method of quantitation (IS = internal standard, ES = external standard):

DDTs ES

IF internal standard method was used, please complete the following section:

Identity of internal standards/surrogates used that were:

Added PRIOR to extraction of sample:

DDTs tetra-chloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) surrogates

Added after extraction/cleanup and JUST PRIOR to chromatographic analysis:

DDTs NA

Any others? Added at what point in analyses:

DDTs tecnazene and 2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl (PCB-208) as retention time reference prior to chromatographic analysis

IS/surrogate standards used for quantitation calculations were:

TCMX and DCB those added prior to extraction

NA those added after extraction/cleanup and just prior to chromatographic analysis

If the IS/surrogates added after extraction/cleanup extraction were used for quantitation, were results corrected for percent recovery? NA

If yes, include the associated percent recovery acceptance ranges in the table below.

Calibration Curve

DDTs	Number of Calibration Levels		Any non-conformances with calibrations? If yes, please discuss
	Points	Conc. Range	
	5	0.5 - 25 ppb	NA

If analyte was quantitated using a "representative compound", e.g. quantitated against an isomer, parent compound, or single alkylated compound for a group of homologs compound for a group of homologs, list the compound used in the table below.

RESULTS:

PERCENT WATER & total organic carbon, TOC (List each result if determined more than once. Enter results as a number, for example 90.0.
DO NOT change format of cell to percent.)

	SR0326 (percent)	SR0326 (percent)	SR0326 (percent)
Percent Water	0.8	0.8	0.8
TOC	NA	NA	NA

DDT ANALYSES

	SR0326 Batch A Sample 1 KY	SR0326 Batch B Sample 2 KY	SR0326 Batch C Sample 3 KY
Analyst (Initials)			
Date(s) of measurements (m/d/y)	6/11/2012	6/19/2012	7/2/2012
Sample Jar number	PVS0005	PVS0005	PVS0005

	SR0326 Sample 1 (ng/g dry mass)	SR0326 Sample 2 (ng/g dry mass)	SR0326 Sample 3 (ng/g dry mass)		IS/surrogate used for quantitation	Associated % recovery acceptance ranges	If "representative compound" used for quantitation list the compound used here.
2,4'-DDT	27.6	24.0	21.2	24.26666667	Sample 1	TCMX	83.4
4,4'-DDT	663	437	564	554.66666667	Sample 1	DCB	90.6
2,4'-DDE	4280	4990	5630	4966.666667	Sample 2	TCMX	106
4,4'-DDE	32700	29500	29000	30400	Sample 2	DCB	98.1
2,4'-DDD	394	433	303	376.66666667	Sample 3	TCMX	83.6
4,4'-DDD	881	722	855	819.33333333	Sample 3	DCB	73.9
4,4'-DDMU	10100	9190	8730	9340			(70 -130)
4,4'-DDNU	NA	NA	NA	#DIV/0!			

(Any additional data/information should be added here.)

Two extraction methods were used in this interlaboratory study to compare the differences of the in-house open column extraction and the ultrasonic extraction. The first two batches were extracted by open column extraction developed by SCCWRP and the third batch was extracted by EPA SW846 3550B ultrasonic extraction. The results showed that the two methods are compatible with each other with percent differences less than 30% for all DDT metabolites. The SW846 3665A sulfuric acid cleanup has shown to be a useful procedure to eliminate interferences in sediment core samples without going through lengthy cleanup. The recoveries of laboratory control samples (LCS) in all three batches after sulfuric acid treatment were within the SW846 acceptance criteria of 70-130%. These indicate the stability of DDT metabolites in the presence of concentrated sulfuric acid.

ATTACHMENT 5
SCCWRP TEST RESULTS – MARINE SEDIMENT SR0326

If yes, include the associated percent recovery acceptance ranges in the table below.

Calibration Curve

DDTs	Number of Calibration Levels		Any non-conformances with calibrations? If yes, please discuss
	Points	Conc. Range	
	7	10-2000ng/mL	

If analyte was quantitated using a "representative compound", e.g. quantitated against an isomer, parent compound, or single alkylated compound for a group of homologs compound for a group of homologs, list the compound used in the table below.

RESULTS:

PERCENT WATER & total organic carbon, TOC (List each result if determined more than once. Enter results as a number, for example 90.0.
DO NOT change format of cell to percent.)

	SR0326 (percent)	SR0326 (percent)	SR0326 (percent)
Percent Water	2.0	2.0	2.1
TOC	NA	NA	NA

DDT ANALYSES

	SR0326 Batch A Sample 1	SR0326 Batch B Sample 2	SR0326 Batch C Sample 3
Analyst (Initials)	WL	WL	WL
Date(s) of measurements (m/d/y)	6/14/2012	6/14/2012	6/18/2012
Sample Jar number	PV0008	PV0008	PV0008

	SR0326 Sample 1 (ng/g dry mass)	SR0326 Sample 2 (ng/g dry mass)	SR0326 Sample 3 (ng/g dry mass)	IS/surrogate used for quantitation	Associated % recovery acceptance ranges	If "representative compound" used for quantitation list the compound used here.
2,4'-DDT	<7.29	<7.29	<7.29	PCB205/PCB208	70-130%	
4,4'-DDT	602	504	449	PCB205/PCB208	70-130%	
2,4'-DDE	4582	4512	4029	PCB205/PCB208	70-130%	
4,4'-DDE	24164	24508	22672	PCB205/PCB208	70-130%	
2,4'-DDD	238	226	216	PCB205/PCB208	70-130%	
4,4'-DDD	820	768	709	PCB205/PCB208	70-130%	
4,4'-DDMU	6996	6884	6268	PCB205/PCB208	70-130%	
4,4'-DDNU	298	290	263	PCB30/DBOFB	60-140%	

(Any additional data/information should be added here.)

	SR0326 Sample 2 duplicate (ng/g dry mass)	SR0326 Sample 3 duplicate (ng/g dry mass)
2,4'-DDT	<7.29	<7.29
4,4'-DDT	498	422
2,4'-DDE	4309	3818
4,4'-DDE	23125	20100
2,4'-DDD	218	216
4,4'-DDD	731	701
4,4'-DDMU	6690	5814
4,4'-DDNU	297	259

ATTACHMENT 6
USGS TEST RESULTS – MARINE SEDIMENT SR0326

QATS PES (SR0326) data for EPA

GC/MS run#: QATS PES bottle*	Method development studies								Sediment core analyses				Mean	Std Dev	RSD (%)	
	Range-finding		MDL, Precision, Accuracy				Method Comparison		124B1-WC (2010)		147B4-WC (2010)					
	RPE0172	RPE0173	RPE0202	RPE0203	RPE0204	RPE0205	RPE0206	RPE0238	RPE0239	RPE0259	RPE0289	RPE0321				RPE0336
	1	1	1	1	1	1	1	1	1	1	1	2				
4,4'-DDNS	190	210	154	166	144	155	157	172	165	179	184	136	163	167	20	11.9
4,4'-DDNU	232	244	220	258	223	266	234	252	252	240	241	193	202	235	21	9.0
4,4'-DDMU	7,644	7,912	6,538	6,996	6,448	7,150	6,804	6,797	6,617	7,079	7,147	6,011	6,497	6,895	511	7.4
2,4'-DDE	4,610	4,776	3,953	4,148	3,841	4,279	4,071	4,165	4,066	4,339	4,362	3,636	4,009	4,174	306	7.3
4,4'-DDMS	2,273	2,307	1,266	1,429	1,263	1,486	1,373	1,599	1,590	1,711	1,814	1,383	1,599	1,622	338	20.8
4,4'-DDE	23,233	24,147	19,709	21,534	19,493	22,204	20,735	21,949	18,845	22,951	21,229	17,717	19,741	21,037	1,879	8.9
2,4'-DDD	369	413	216	247	226	260	243	272	275	280	313	237	267	278	57	20.4
4,4'-DDD	1,138	1,239	727	824	722	845	781	877	869	963	973	756	842	889	155	17.5
2,4'-DDT	28	NR	NR	NR	NR	NR	NR	<27.7	<27.1	<27.7	<27.1	<27.7	<27.1	---	---	---
4,4'-DDT	979	1,624	515	556	903	652	552	641	699	729	807	561	618	757	296	39.1

NR = not reported by ChemStation

xx.x = less than MDL

xxx = quantitation using L4-8 MPC

xxx = quantitation using L1-8 MPC

* Bottle #1 = PVS0001, Bottle #2 = PVS0003

Major DDT compounds in PVS sediments