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Ampelisca abdita CHRONIC EXPOSURE SEDIMENT ASSAY

STUDY # 7814-14	SAMPLE ID: E4 SED SMP	DILUENT: Hampton Estuary	START DATE:

DAY	REP A				REP B				REP C				INITIALS
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	
0	21	6.8	4.25**	27	21	6.9	3.71**	27	21	6.9	3.90**	27	JL
1	22	6.4	7.37	29	22	6.8	7.16	29	22	6.7	6.74	29	JL
2	22	6.8	6.84**	28	22	7.0	5.51**	27	22	7.1	5.04**	27	—
3	22	7.5	7.25	27	22	7.5	7.23	26	22	7.5	7.20	27	—
4	22	6.6	7.17	27	22	6.5	7.14	26	22	6.8	7.11	27	JL
5	22	6.8	6.75	30	22	6.9	5.89	30	22	7.0	6.55*	30	KHS
6	22	6.9	7.47	27	22	7.1	6.26	27	22	7.1	7.10	28	—
7	22	6.9	7.26	27	22	7.0	6.48	26	22	7.0	6.48	28	—
8	21	7.6	6.36	27	21	7.5	6.06	27	21	7.5	6.44	28	CW
9	21	5.8	7.22	27	21	5.7	1.99	26	21	5.9	7.97	27	JL
10	21	6.1	7.28	27	21	6.1	7.17	27	21	5.9	7.16	27	CA
# ALIVE	8				10				13				

DAY	REP D				REP E				AMMONIA*				
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	A	B	C	D	E
0	21	6.9	4.41**	27	21	6.9	4.38**	27	X	X	X	X	X
1	22	6.6	6.75	29	22	6.7	6.75	29					
2	22	7.0	5.51*	29	22	7.1	5.38**	28					
3	22	7.5	7.16	28	22	7.4	7.17	28					
4	22	6.6	7.12	28	22	6.7	7.14	27					
5	22	7.0	6.99	30	22	6.9	6.85	30	KHS				
6	22	7.1	7.26	28	22	7.0	7.27	28					
7	22	6.9	6.89	27	22	6.9	6.90	27					
8	21	7.5	6.95	28	21	7.5	6.60	29					
9	21	5.9	7.02	26	21	5.8	7.05	29					
10	21	5.8	7.25	27	21	5.7	7.28	28	CA				
# ALIVE	9				5								

* - Ammonia values on Day 0 were measured on the porewater. Ammonia on Days 5 and 10 were measured on the overlying water.

** - See misc Doc.

Ampelisca abdita CHRONIC EXPOSURE SEDIMENT ASSAY

STUDY # 7814-15	SAMPLE ID: F1-SEDSMP	DILUENT: Hampton Estuary	START DATE:

DAY	REP A				REP B				REP C				INITIALS
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	
0	21	6.9	799	29	21	6.9	8.00	29	21	6.9	7.95	29	JE
1	22	7.1	7.74	31	22	6.9	7.91	31	22	6.8	7.98	31	JLh
2	22	6.8	7.78	30	22	7.0	8.03	30	22	7.0	8.05	30	—
3	22	7.3	8.14	28	22	7.4	8.16	29	22	7.5	8.17	29	—
4	22	6.7	8.14	28	22	6.7	8.29	28	22	6.7	8.32	28	JLh
5	22	6.8	8.43	30	22	6.8	8.58	30	22	6.7	8.51	30	JLH
6	22	6.9	8.43	29	22	7.0	8.58	29	22	7.0	8.58	29	—
7	22	6.8	8.46	29	22	6.9	8.49	29	22	6.9	8.48	29	—
8	21	7.5	8.40	29	21	7.5	8.33	30	21	7.5	8.36	30	EW
9	21	5.9	8.45	29	21	6.1	8.44	30	21	6.3	8.44	29	JLh
10	21	6.1	8.33	29	21	6.1	8.33	29	21	6.1	8.35	29	CR
# ALIVE	9				10				13				

DAY	REP D				REP E				AMMONIA*				
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	A	B	C	D	E
0	21	6.9	8.00	29	21	6.8	7.90	29	JE	/	/	/	/
1	22	7.0	8.04	31	22	6.9	8.04	31					
2	22	7.0	8.06	29	22	7.1	8.07	29					
3	22	7.4	8.17	29	22	7.4	8.16	29					
4	22	6.8	8.27	28	22	6.6	8.26	28					
5	22	6.8	8.44	30	22	6.8	8.42	30	JLH				
6	22	7.0	8.47	30	22	6.9	8.46	29					
7	22	6.9	8.47	30	22	6.9	8.46	29					
8	21	7.5	8.38	31	21	7.5	8.48	30					
9	21	5.9	8.45	30	21	6.0	8.52	30					
10	21	6.3	8.38	29	21	6.8	8.45	30	CR				
# ALIVE	14				9								

* - **Ammonia values on Day 0 were measured on the porewater. Ammonia on Days 5 and 10 were measured on the overlying water.**

Ampelisca abdita CHRONIC EXPOSURE SEDIMENT ASSAY

STUDY # 7814 -16	SAMPLE ID: F-2 SED SMP	DILUENT: Hampton Estuary	START DATE:

DAY	REP A				REP B				REP C				INITIALS
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	
0	21	6.6	8.01	29	21	6.6	7.99	29	21	6.7	7.98	29	[illegible]
1	22	6.4	8.03	31	22	6.6	8.04	31	22	6.6	8.06	31	[illegible]
2	22	6.7	8.10	29	22	6.9	8.10	30	22	7.0	8.11	30	—
3	22	7.4	8.13	27	22	7.5	8.11	28	22	7.4	8.10	29	—
4	22	6.5	8.10	27	22	6.9	8.08	27	22	6.6	8.07	28	[illegible]
5	22	6.8	8.14	30	22	6.8	8.12	30	22	6.8	8.09	30	[illegible]
6	22	7.1	8.16	29	22	7.1	8.11	29	22	7.1	8.10	29	—
7	22	6.9	8.09	28	22	6.9	8.00	28	22	6.7	7.86	28	—
8	21	7.5	7.65	28	21	7.5	7.96	30	21	7.4	7.86	29	[illegible]
9	21	6.2	8.27	28	21	6.3	8.18	30	21	6.1	8.02	28	[illegible]
10	21	5.9	8.18	28	21	6.1	8.08	29	21	6.3	7.97	29	[illegible]
# ALIVE	17				12				15				[illegible]

DAY	REP D				REP E				AMMONIA*				
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	A	B	C	D	E
0	21	6.7	7.98	29	21	6.8	7.96	29	[illegible]	/	/	/	/
1	22	6.4	8.07	31	22	6.9	8.04	31					
2	22	7.0	8.10	30	22	6.9	8.08	30					
3	22	7.4	8.08	29	22	7.5	8.08	29					
4	22	6.9	8.06	28	22	6.7	8.06	27					
5	22	6.8	8.12	30	22	6.8	8.10	30	[illegible]				
6	22	7.2	8.08	29	22	7.0	8.06	30					
7	22	6.8	7.92	29	22	6.8	7.92	28					
8	21	7.4	7.97	31	21	7.5	7.92	30					
9	21	6.3	8.06	31	21	6.3	8.05	29					
10	21	6.7	8.04	29	21	6.4	8.04	28	[illegible]				
# ALIVE	16				16								

* - **Ammonia values on Day 0 were measured on the porewater. Ammonia on Days 5 and 10 were measured on the overlying water.**

Ampelisca abdita CHRONIC EXPOSURE SEDIMENT ASSAY

STUDY # 7814 – 17	SAMPLE ID: F-3-SED-SMP	DILUENT: Hampton Estuary	START DATE:

DAY	REP A				REP B				REP C				INITIALS
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	
0	20	6.6	8.04	28	21	6.5	8.00	28	21	6.5	8.08	28	X
1	22	6.5	8.06	30	22	6.6	8.07	30	22	6.2	8.10	30	LL
2	22	6.6	8.11	29	22	6.8	8.16	30	22	7.0	8.18	30	—
3	22	7.3	8.08	28	22	7.4	8.12	28	22	7.5	8.14	28	—
4	22	6.6	8.11	29	22	6.8	8.16	30	22	6.6	8.12	29	LL
5	22	6.8	8.18	30	22	6.7	8.18	30	22	6.8	8.18	30	XFS
6	22	7.1	8.18	29	22	7.1	8.18	29	22	7.1	8.17	29	—
7	22	6.8	8.15	27	22	7.0	8.14	23	22	7.0	8.13	28	—
8	21	7.4	7.99	29	21	7.4	8.19	29	21	7.4	8.18	29	
9	21	6.1	8.34	28	21	6.3	8.42	28	21	6.2	8.41	29	LL
10	21	5.9	8.33	28	21	6.1	8.29	28	21	6.3	8.31	29	CF
# ALIVE	14				12				16				HA

DAY	REP D				REP E				AMMONIA*				
	TEMP	D.O.	pH	SAL.	TEMP	D.O.	pH	SAL.	A	B	C	D	E
0	21	6.5	8.03	28	21	6.5	8.08	28	X	✓	✓	✓	✓
1	22	6.2	8.08	31	22	6.3	8.10	30					
2	22	7.0	8.17	30	22	7.0	8.15	29					
3	22	7.4	8.15	28	22	7.4	8.15	28					
4	22	6.6	8.12	28	22	6.8	8.13	28					
5	22	6.9	8.17	30	22	6.8	8.17	30	XFS				
6	22	7.1	8.16	28	22	7.1	8.16	28					
7	22	6.9	8.12	28	22	6.9	8.09	28					
8	21	7.5	8.09	29	21	7.5	8.07	29					
9	21	6.3	8.26	29	21	6.1	8.21	29					
10	21	6.3	8.31	29	21	6.3	8.16	28	CF				
# ALIVE	13				10								

* - **Ammonia values on Day 0 were measured on the porewater. Ammonia on Days 5 and 10 were measured on the overlying water.**

DOCUMENTATION FORM

STUDY No.: 7814 STUDY DIRECTOR: K. Simon

PROJECT TITLE: Raymark 1999 - HA 10 DCR

GENERATED BY: D. Harris DATE: 4/22/99

The following information is
- ☑ Miscellaneous Documentation
- ☐ A Deviation from the Protocol
- ☐ A Deviation from SOP _____

A pore water sample was taken from each test sediment. Samples were evaluated for Ammonia

APPROVED BY: _____ DATE: _____

DOCUMENTATION FORM

STUDY No.: 7814 STUDY DIRECTOR: K. Simon

PROJECT TITLE: SAIC - Raytheon 1995

GENERATED BY: W. Harris DATE: 4/23/95

The following information is

- ☑ Miscellaneous Documentation
- ☐ A Deviation from the Protocol
- ☐ A Deviation from SOP _____

pH of the overlying water initially ranged from 3.71 SU to 4.41 SU.

In order to raise pH, overlying water was decanted + replenished with fresh salt water + allowed to settle.

New pH values were:

A	6.53
B	6.51
C	6.45
D	6.53
E	6.54

APPROVED BY: _____ DATE: _____

DOCUMENTATION FORM

STUDY No.: 7814 STUDY DIRECTOR: K Simon

PROJECT TITLE: SAIC

GENERATED BY: P Lymani DATE: 4/25/94

The following information is
- ☑ Miscellaneous Documentation
- ☐ A Deviation from the Protocol
- ☐ A Deviation from SOP _____

pH of the overlying water initially ranged from 5.04 su to 6.24 su

In order to raise pH overlying water was decanted + replenished with fresh salt water + allowed to settle

New pH values were:

A 6.36
B 6.35
C 6.33
D 6.34
E 6.40

APPROVED BY: _____ DATE: _____

ESI SAMPLE RECEIPT RECORD

EnviroSystems, Inc.
P.O. Box 778, One Lafayette Road
Hampton, N.H. 03842
(603) 926-3345

ESI STUDY NUMBER: 7814

SAMPLE RECEIPT DATE: 4/20/99 TIME: 1000 am

SAMPLE RECEIVED BY: BB

DELIVERED VIA: ☒ FED X ☐ CARRIER ☐ CLIENT ☐ COURIER

SAMPLE CONDITION:

CHAIN OF CUSTODY:	☒ YES	☐ NO
CHAIN OF CUSTODY SIGNED:	☒ YES	☐ NO
CHAIN OF CUSTODY COMPLETE:		
SAMPLE DATE:	☑ YES	☐ NO
SAMPLE TIME RECORDED:	☑ YES	☐ NO
SAMPLE TYPE IDENTIFIED:	☒ YES	☐ NO
CUSTODY SEAL IN PLACE:	☑ YES	☐ NO
SHIPPING CONTAINER INTACT:	☑ YES	☐ NO
SAMPLE TEMPERATURE (AT ARRIVAL):	____	°C

COMMENTS: 17 x 1gal Sediment
See Attached Misc. Doc

COOLER NUMBER: Green Igloo (no #)
127, 115
~~444~~ 215
206
232

Science Applications International Corporation

Chain of Custody Record

Environmental Testing Center / 165 Dean Knauss Dr. / Narragansett, RI 02882 / Tel. (401) 782-1900 / Fax (401) 782-2330

Project: RAYMARK 1999	Client Name and Contact: USACE

Sample No.	Containers No.	Containers Type	Collection Date	Collection Time	Sample Description			Requested Parameters
C-1-SED-SMP	1	1 gal	4/16	2:20	SEDIMENT (GRAB)	—	—	TOXICITY
C-2-SED-SMP	1			1:37		—	—	
C-3-SED-SMP	1			12:50		—	—	
D-1-SED-SMP	1			12:16		—	—	
D-2-SED-SMP	1			12:35		—	—	
D-3-SED-SMP	1			2:00		—	—	
D-4-SED-SMP	1			0:20		—	—	
D-5-SED-SMP	1			2:45		—	—	
D-6-SED-SMP	1			1:20		—	—	
D-6-SED-FD	1			3:07		—	—	
E-1-SED-SMP	1			10:65		—	—	
E-2-SED-SMP	1			9:50		—	—	
E-3-SED-SMP	1			11:15		—	—	
E-4-SED-SMP	1			11:21		—	—	
EEF-1-SED-SMP	1	"	"	2:35	"	—	—	"
Total:	15							

Packed/Released By: SAIC Signature: Printed Name: Cornelia Hullek Date Time 4/19/99 1430 pm	*Received By:* ESL Signature: Printed Name: Brian Beezley Date Time 4/20/99 1000am	Remarks: SAMPLES WERE REFRIGERATED UNTIL RELEASED. CM 4/16/99 - 4/19/99
Released By: Signature: Printed Name: Date Time	*Received By:* Signature: Printed Name: Date Time	
Final Destination: ENVIROSYSTEMS, INC	Contact Name and Phone Number PETRA KARIBE 60392.63345	
Shipping Method: FED EX	Page 1 of 1	

Cornelia Fax 401 849 1585

Science Applications International Corporation

Chain of Custody Record

Environmental Testing Center / 165 Dean Knauss Dr. / Narragansett, RI 02882 / Tel. (401) 782-1900 / Fax (401) 782-2330

Project: RAYMARK 1999	Client Name and Contact: USACE

Sample No.	Containers No.	Containers Type	Collection Date	Collection Time	Sample Description			Requested Parameters
F-2-SED-SHP	1	1gal	4/16	12:00	SEDIMENT (GRAB)	—	—	TOXICITY
F-3-SED-SHP	1	1gal	4/16	3:25	SEDIMENT (GRAB)	—	—	TOXICITY
Total :	2							

Packed/Released By: SAIC Signature: Printed Name: Cornelia Hueller Date Time: 4/19/99 4:50pm	*Received By:* Signature: Printed Name: Brian Buzby Date Time: 4/20/99 1000am	Remarks: SAMPLES WERE REFRIGERATED UNTIL RELEASED on 4/16/99 4/19/99
Released By: Signature: Printed Name: Date Time	*Received By:* Signature: Printed Name: Date Time	
Final Destination: ENVIROSYSTEMS, INC.	Contact Name and Phone Number: PATRA KARBE 6039263345	
Shipping Method: FED EX	Page 2 of 2	

CORNELIA FAX 401 849 1585

DOCUMENTATION FORM

STUDY No.: 7814 STUDY DIRECTOR: K. Simon

PROJECT TITLE: SAIC - Raymark 1995

GENERATED BY: D. Helms DATE: 4/20/95

The following information is
- ☑ Miscellaneous Documentation
- ☐ A Deviation from the Protocol
- ☐ A Deviation from SOP _____

EST #	SAIC #	Amount
7814-1	C-1-SED-SMP	1x1g
7814-2	C-2-SED-SMP	1x1c
7814-3	C-3-SED-SMP	1x1g
7814-4	D-1-SED-SMP	1x1g
7814-5	D-2-SED-SMP	1x1g
7814-6	D-3-SED-SMP	1x1g
7814-7	D-4-SED-SMP	1x1g
7814-8	D-5-SED-SMP	1x1g
7814-9	D-6-SED-SMP	1x1g
7814-10	D-6-SED-FD	1x1g
7814-11	E-1-SED-SMP	1x1g
7814-12	E-2-SED-SMP	1x1g
7814-13	E-3-SED-SMP	1x1g
7814-14	E-4-SED-SMP	1x1g
7814-15	F-1-SED-SMP	1x1g
7814-16	F-2-SED-SMP	1x1g
7814-17	F-3-SED-SMP	1x1g

APPROVED BY: _____ DATE: _____

APPENDIX C
QA/QC AND DATA VALIDATION

APPENDIX C-1
SEDIMENT CHEMISTRY

Science Applications International Corporation
An Employee-Owned Company

MEMORANDUM

Date: May 28, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Sediment Set 1 - Pesticide data for 10 samples

As requested, I have reviewed the results of the 1999 Raymark sediment sample data for the organochlorine pesticide analyses in Set 1. The analyses were performed by The Woods Hole Group (WHG), on 10 samples collected by SAIC on April 15, 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
HB-1-SED-SMP	42279-1
HB-2-SED-SMP	42279-2
HB-3-SED-SMP	42279-3
HB-4-SED-SMP	42279-4
HB-5-SED-SMP	42279-5
HB-6-SED-SMP	42279-6
HB-6-SED-FD	42279-7
HB-7-SED-SMP	42279-8
HB-8-SED-SMP	42279-9
HB-9-SED-SMP	42279-10

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples other than sediments and analyzed by CLP methods, which are not the methods designated for this project.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks

- Matrix spike and matrix spike duplicate results
- Laboratory control sample results
- Surrogate recoveries
- Endrin and DDT breakdown

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

As noted by the laboratory, the use of the amino-propyl cleanup column does not provide consistent recoveries of the target analyte endrin aldehyde. According to the narrative, the situation was discussed with SAIC and it was agreed that for this project, all endrin aldehyde results would be flagged "J" as estimated. Endrin aldehyde was not detected in any of the samples, thus all results for this analyte are reported as "UJ," for not detected and estimated. Unfortunately, the laboratory did not provide any data from reference materials, spiked samples, or laboratory control samples that included this analyte. Therefore, it is not possible to determine from the data in the package if the laboratory could have detected endrin aldehyde at all. Therefore, the reviewer suggests that the endrin aldehyde be deleted from the list of target analytes, or simply be reported as "NA" for not analyzed.

Calibrations

Initial calibrations and continuing calibrations were performed as required. The results for several of the continuing calibration standards included one or more analytes that demonstrated a difference of more than 15% between the amount found and the true concentration of the standard. However, in every such instance, the results for the same standard analyzed on the second GC column were within the acceptance limits. Therefore, the laboratory reported the results for those analytes from the GC column that met the specifications. Most of the instances involved the amount found being greater than the true value, and many of the analytes were not found in any of the samples. The %D values in question were typically 16 to 21%, versus the 15% limit.

Given these calibration data, there is no reason to qualify any of the sample results.

Surrogate Recoveries

The laboratory employed two surrogate compounds for these analyses, 4,4'-dibromooctafluorobiphernyl (DBOB) and the PCB congener BZ202. The recoveries of BZ202 were well above the upper limit of the laboratory's acceptance limits of 30-150% in the initial analyses of five of the field samples. The recoveries for HB-2-SED-SMP, HB-3-SED-SMP, HB-4-SED-SMP, HB-6-SED-SMP, and HB-6-SED-FD were all above 150%. However, given that there were relatively few target analytes detected in these samples and the recoveries of the other surrogate were within the acceptance limits, there is no reason to qualify the sample results due to high surrogate recoveries.

There were several instances noted by the laboratory of low recoveries of the DBOB surrogate. However, all of these occurred in the analyses of diluted sample extracts, and in each case, the initial, undiluted, analyses had acceptable DBOB recoveries. Since the recoveries in the initial analyses were acceptable, there is no reason to qualify the results from the diluted analyses due to surrogate concerns.

Comparisons Between Results from Two GC Columns

SW-846 Method 8000B recommends that the quantitative results from both GC columns be compared during dual-column analyses such as used here for the pesticides. As noted by the laboratory, there were a two instances in which the quantitative results from the two GC columns used for the analyses differed by more than 40%. In those instances, the laboratory reviewed the chromatograms and if no evidence of a problem was found, they took the conservative approach and reported the higher of the two results. The results for o,p'-DDE in Sample HB-6-SED-FD and the results for p,p'-DDD in sample HB-7-SED-SMP were flagged "P" by the laboratory to indicate that the higher value was reported. The results for o,p'-DDE were 1.8 and 3.8 µg/kg on the two columns in HB-6-SED-SMP. The results for p,p'-DDD in sample HB-7-SED-SMP were 1.3 and 2.3. SAIC has reviewed the chromatograms for these samples and agrees that the higher values be reported and there is no need for qualification.

In sample HB-6-SED-SMP, the laboratory took the opposite approach, and after examining the chromatograms, they reported the lower value for p,p'-DDD in this sample. The result of 3.6 µg/kg was reported because the result of 5.7 was derived from a peak with an apparent positive interference. Similarly, in sample HB-6-SED-FD, the laboratory reported the results for p,p'-DDD as the lower of the two values 4.0 and 7.9 µg/kg. The lower results for both samples were flagged "I" by the laboratory. SAIC has reviewed the chromatograms for these samples agrees that the lower values be reported and there is no need for qualification.

Field Duplicate Precision

Sample HB-6-SED-FD is a field duplicate. As part of this validation effort, the results for the field duplicate were compared to the original field sample, HB-6-SED-SMP. The RPDs between the results for each detected pesticide were calculated by the reviewer, and are shown below.

Analyte	HB-6-SED-SMP	HB-6-SED-FD	RPD
gamma-Chlordane	4.6 µg/kg	4.6 µg/kg	0%
o,p'-DDE	ND	3.8 µg/kg	NA
p,p'-DDT	ND	3.7 µg/kg	NA
p,p'-DDD	3.6 µg/kg	7.9 µg/kg	75%

Two of the analytes were not detected (ND) in the initial sample (-SMP), o'p'-DDE and p,p'-DDT. Therefore, no RPD calculation was possible and the RPD values are listed above as "NA" for not applicable. The gamma-Chlordane results indicated excellent precision, with RPD=0%. Conversely, the p,p'-DDD results exhibited poorer precision between these two samples, with an RPD=75%. However, these samples were taken from different cores collected

in approximately the same location and do not represent samples split from the same core. Thus, the precision for DDD may not be a major concern. Field duplicate precision is *not* within the control of the laboratory, but is discussed here in terms of the overall validation of the sampling and analysis effort.

Overall Assessment

Overall, the results for these 10 samples meet the objectives of the sampling and analysis effort. The only qualification is that endrin aldehyde should not be considered to be a target analyte and the non-detect results for it should be considered to be "not analyzed" instead.

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MEMORANDUM

Date: June 1, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Sediment Set 2 - Pesticide data for 17 samples

As requested, I have reviewed the results of the 1999 Raymark sediment sample data for the organochlorine pesticide analyses in Set 2. The analyses were performed by The Woods Hole Group (WHG), on 17 samples collected by SAIC on April 16, 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
C-1-SED-SMP	42280-1
C-2-SED-SMP	42280-2
C-3-SED-SMP	42280-3
D-1-SED-SMP	42280-4
D-2-SED-SMP	42280-5
D-3-SED-SMP	42280-6
D-4-SED-SMP	42280-7
D-5-SED-SMP	42280-8
D-6-SED-SMP	42280-9
D-6-SED-FD	42280-10
E-1-SED-SMP	42280-11
E-2-SED-SMP	42280-12
E-3-SED-SMP	42280-13
E-4-SED-SMP	42280-14
F-1-SED-SMP	42280-15
F-2-SED-SMP	42280-16
F-3-SED-SMP	42280-17

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples

other than sediments and analyzed by CLP methods, which are not the methods designated for this project.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike and matrix spike duplicate results
- Laboratory control sample results
- Surrogate recoveries
- Endrin and DDT breakdown

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

As noted by the laboratory, the use of the amino-propyl cleanup column does not provide consistent recoveries of the target analyte endrin aldehyde. According to the narrative, the situation was discussed with SAIC and it was agreed that for this project, all endrin aldehyde results would be flagged "J" as estimated. Endrin aldehyde was not detected in any of the samples, thus all results for this analyte are reported as "UJ," for not detected and estimated. Unfortunately, the laboratory did not provide any data from reference materials, spiked samples, or laboratory control samples that included this analyte. Therefore, it is not possible to determine from the data in the package if the laboratory could have detected endrin aldehyde at all. Therefore, the reviewer suggests that the endrin aldehyde be deleted from the list of target analytes, or simply be reported as "NA" for not analyzed.

Calibrations

Initial calibrations and continuing calibrations were performed as required. The results for several of the continuing calibration standards included one or more analytes that demonstrated a difference of more than 25% between the amount found and the true concentration of the standard. However, in most such instances, the results for the same standard analyzed on the second GC column were within the acceptance limits. Therefore, the laboratory reported the results for those analytes from the GC column that met the specifications. Most of the instances involved the amount found being greater than the true value, and many of the analytes were not found in any of the samples.

The only exceptions were for the continuing calibration standards analyzed on 5/8/99 at 7:31 AM and 5/8/99 at 9:12PM. For the 7:31 AM standard, the results for Methoxychlor were above the acceptance limit on both columns A and B. Similarly, for the 9:12PM analysis, the results for gamma-BHC were above the limits on both columns. However, neither of these

compounds was reported as found in any of the samples. Since the continuing calibration standard results were higher than expected, there is no risk that the analytes may have been present in the samples but not detected because of the drift in the results for the continuing calibration standard.

Given these calibration data, there is no reason to qualify any of the sample results.

Surrogate Recoveries

The laboratory employed two surrogate compounds for these analyses, 4,4'-dibromooctafluorobiphernyl (DBOB) and the PCB congener BZ202. The recoveries of BZ202 were well above the upper limit of the laboratory's acceptance limits of 30-150% in the analyses of two of the field samples. The BZ202 recoveries for D-5-SED-SMP and E-1-SED-SMP were above 250%. However, the only analyte detected was p,p'-DDD in sample D-5-SED-SMP. The recoveries of the other surrogate were within the acceptance limits in both samples. Therefore, there is no reason to qualify the sample results due to high surrogate recoveries.

Comparisons Between Results from Two GC Columns

SW-846 Method 8000B recommends that the quantitative results from both GC columns be compared during dual-column analyses such as used here for the pesticides. As noted by the laboratory, there were a two instances in which the quantitative results from the two GC columns used for the analyses differed by more than 40%. In those instances, the laboratory reviewed the chromatograms and if no evidence of a problem was found, they took the conservative approach and reported the higher of the two results. Results were flagged "P" in the following samples:

SAIC Sample ID	Analyte	Result Reported with "P" Flag
D-4-SED-SMP	p,p'-DDD	3.7 P
D-5-SED-SMP	p,p'-DDD	20 P
E-2-SED-SMP	p,p'-DDD	58 P
E-4-SED-SMP	p,p'-DDD	24 P
F-1-SED-SMP	p,p'-DDD	36 P
F-2-SED-SMP	p,p'-DDT	24 P

SAIC has reviewed the chromatograms for these samples and agrees that the higher values be reported and there is no need for qualification, *with one exception*. The results for p,p'-DDD in sample E-2-SED-SMP are also associated with one of the calibration verification standards with an analyte above the acceptance limits. In this instance, the p,p'-DDD continuing calibration results had a percent difference from the initial calibration of 44% on Column A. The laboratory reported the results for this compound as "58 P," using the data from Column A. SAIC disagrees, and believes that the results should be reported from Column B, as 23 µg/kg.

Field Duplicate Precision

Sample D-6-SED-FD is a field duplicate. As part of this validation effort, the results for the field duplicate were compared to the original field sample, D-6-SED-SMP. The only analyte detected in either analysis was p,p'-DDD, reported at 1.8 µg/kg in sample D-6-SED-SMP. This analyte was not detected in the field duplicate. Therefore, the RPD calculation is not appropriate. These two samples were collected from different cores collected in approximately the same location and do not represent samples split from the same core. Field duplicate precision is *not* within the control of the laboratory, but is discussed here in terms of the overall validation of the sampling and analysis effort.

Overall Assessment

Overall, the results for these 17 samples meet the objectives of the sampling and analysis effort. Only two qualifications were made by the reviewer:

- Endrin aldehyde should not be considered to be a target analyte and the non-detect results for it should be considered to be "not analyzed" instead.

- The p,p'-DDD result in sample E-2-SED-SMP should be revised to 23 µg/kg, instead of the "58 P" value reported by the laboratory.

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MEMORANDUM

Date: May 28, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Sediment Set 1 - PCB congener data for 10 samples

As requested, I have reviewed the results of the 1999 Raymark sediment sample data for the PCB congener analyses in Set 1. The analyses were performed by The Woods Hole Group (WHG), on 10 samples collected by SAIC on April 15, 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
HB-1-SED-SMP	42279-1
HB-2-SED-SMP	42279-2
HB-3-SED-SMP	42279-3
HB-4-SED-SMP	42279-4
HB-5-SED-SMP	42279-5
HB-6-SED-SMP	42279-6
HB-6-SED-FD	42279-7
HB-7-SED-SMP	42279-8
HB-8-SED-SMP	42279-9
HB-9-SED-SMP	42279-10

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples other than sediments and analyzed by CLP methods, which are not the methods designated for this project.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks

- Matrix spike and matrix spike duplicate results
- Laboratory control sample results
- Surrogate recoveries

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

Calibrations

Initial calibrations and continuing calibrations were performed as required. The results for several of the continuing calibration standards included one or more analytes that demonstrated a difference of more than 15% between the amount found and the true concentration of the standard. However, in every instance but one, the results for the same standard analyzed on the second GC column were within the acceptance limits. Therefore, the laboratory reported the results for those analytes from the GC column that met the specifications.

The exception was for the calibration verification analyzed on May 10, 1999, at 2:18 PM. In this instance, the %D values for the surrogate 4,4'-dibromooctafluorobiphernyl (DBOB) were both outside the 15% acceptance limit (-26% for Channel A and -22% for Channel B). Three field samples were analyzed after that verification standard: HB-3-SED-SMP, and the diluted analyses of both HB-2-SED-SMP and HB-6-SED-FD. Given that the latter two samples were diluted analyses and the surrogate recoveries in both the initial and diluted analyses met the QC limits, there is no need to qualify the sample results. For HB-3-SED-SMP, the surrogate recovery for DBOB was well within the acceptance limits, so no qualification is necessary either.

Surrogate Recoveries

The laboratory employed two surrogate compounds for these analyses, 4,4'-dibromooctafluorobiphernyl (DBOB) and the PCB congener BZ202. The recoveries of BZ202 were well above the upper limit of the laboratory's acceptance limits of 30-150% in the initial analyses of five of the field samples. The recoveries for HB-2-SED-SMP, HB-3-SED-SMP, HB-4-SED-SMP, HB-6-SED-SMP, and HB-6-SED-FD were all above 150%. The laboratory attributed the high recoveries to a matrix interference and analyzed a dilution of each extract. The BZ202 recovery remained high in each diluted extract analysis, indicating that the interference was likely due to a matrix effect.

Given the high recoveries and the fact that they were reproducible upon dilution, SAIC does not believe that qualification of any samples results is warranted.

Comparisons Between Results from Two GC Columns

SW-846 Method 8000B recommends that the quantitative results from both GC columns be compared during dual-column analyses such as used here for the PCBs. As noted by the

laboratory, there were a number of instances in which the quantitative results from the two GC columns used for the analyses differed by more than 40%. In those instances, the laboratory reviewed the chromatograms and if no evidence of a problem was found, they took the conservative approach and reported the higher of the two results, flagging those values with a "P" to indicate that the higher value was reported.

If, after examining the chromatograms, they found evidence of a positive interference on one of the columns, or if there was evidence that the baseline had been incorrectly established by the software, the laboratory reported the lower of the two results, flagging those values with a "I" to indicate that the lower value was reported, due to an interference.

SAIC has reviewed the chromatograms for these samples and agrees that the laboratory's reported results were appropriate and there is no need for qualification of the results.

Field Duplicate Precision

Sample HB-6-SED-FD is a field duplicate. As part of this validation effort, the results for the field duplicate were compared to the original field sample, HB-6-SED-SMP. The RPDs between the results for each detected pesticide were calculated by the reviewer, and are shown below.

Analyte	HB-6-SED-SMP	HB-6-SED-FD	RPD
PCB52	3.3	ND	NA
PCB66	ND	3.9	NA
PCB101	8.3	9.8	17%
PCB105	ND	2.3	NA
PCB118	ND	2.6	NA
PCB126	9.9	10	1%
PCB138	5.2	6.9	3%
PCB153	7.0	7.9	14%
PCB170	5.0	5.4	8%
PCB180	30	36	18%
PCB187	26	27	4%
PCB195	11	13	17%
PCB200	4.8	6.8	34%
PCB206	65	100	42%
PCB209	10	13	26%

Four of the analytes were not detected (ND) in either the original sample or the duplicate sample. Therefore, no RPD calculation was possible and the RPD values are listed above as "NA" for not applicable. The results for the sample in which these congeners were detected are all only slightly above the laboratory's reporting limits, and therefore, the detect/nondetect situation is not unexpected.

The results for the eight analytes that were detected in both analyses indicate excellent precision, with all RPD values less than 20%. The last three PCB congeners exhibited lesser precision, but still had RPD values less than 45%. PCB206 had the highest RPD value, 42%, and involved the results from a diluted analysis of the field duplicate sample. The dilution of the sample extract may have introduced some portion of the difference between these two results.

These samples were taken from different cores collected in approximately the same location and do not represent samples split from the same core. The precision exhibited by these results is well within the expected range for field duplicate samples, and there is no reason to qualify any sample results. Field duplicate precision is *not* within the control of the laboratory, but is discussed here in terms of the overall validation of the sampling and analysis effort.

Overall Assessment

Overall, the results for these 10 samples meet the objectives of the sampling and analysis effort. The results may be used without qualification.

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MEMORANDUM

Date: June 2, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Sediment Set 2 - PCB congener data for 17 samples

As requested, I have reviewed the results of the 1999 Raymark sediment sample data for the PCB congener analyses in Set 2. The analyses were performed by The Woods Hole Group (WHG), on 17 samples collected by SAIC on April 16, 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
C-1-SED-SMP	42280-1
C-2-SED-SMP	42280-2
C-3-SED-SMP	42280-3
D-1-SED-SMP	42280-4
D-2-SED-SMP	42280-5
D-3-SED-SMP	42280-6
D-4-SED-SMP	42280-7
D-5-SED-SMP	42280-8
D-6-SED-SMP	42280-9
D-6-SED-FD	42280-10
E-1-SED-SMP	42280-11
E-2-SED-SMP	42280-12
E-3-SED-SMP	42280-13
E-4-SED-SMP	42280-14
F-1-SED-SMP	42280-15
F-2-SED-SMP	42280-16
F-3-SED-SMP	42280-17

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples

other than sediments and analyzed by CLP methods, which are not the methods designated for this project.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike and matrix spike duplicate results
- Laboratory control sample results
- Surrogate recoveries

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

Calibrations

Initial calibrations and continuing calibrations were performed as required. The results for two of the continuing calibration standards included one or more analytes that demonstrated a difference of more than 25% between the amount found and the true concentration of the standard. However, in both instances, the results for the same standard analyzed on the second GC column were within the acceptance limits. Therefore, the laboratory reported the results for those analytes from the GC column that met the specifications.

Surrogate Recoveries

The laboratory employed two surrogate compounds for these analyses, 4,4'-dibromooctafluorobiphernyl (DBOB) and the PCB congener BZ202. Samples D-5-SED-SMP and E-1-SED-SMP required large dilutions of the extracts in order to bring all of the target congeners within the calibration range of the instrument. As a result of these large dilutions, the surrogates were diluted out in the final analyses. Given the extent of the required dilutions, this is not surprising and is not cause to qualify the results for these samples. The laboratory reported the undiluted results for D-5-SED-SMP, which, while the PCB congener results themselves are not usable, do indicate acceptable surrogate recoveries.

Comparisons Between Results from Two GC Columns

SW-846 Method 8000B recommends that the quantitative results from both GC columns be compared during dual-column analyses such as used here for the PCBs. As noted by the laboratory, there were a number of instances in which the quantitative results from the two GC columns used for the analyses differed by more than 40%. In those instances, the laboratory reviewed the chromatograms and if no evidence of a problem was found, they took the

conservative approach and reported the higher of the two results, flagging those values with a "P" to indicate that the higher value was reported.

If, after examining the chromatograms, they found evidence of a positive interference on one of the columns, or if there was evidence that the baseline had been incorrectly established by the software, the laboratory reported the lower of the two results, flagging those values with a "I" to indicate that the lower value was reported, due to an interference.

SAIC has reviewed the chromatograms for these samples and agrees that the laboratory's reported results were appropriate and there is no need for qualification of the results.

Field Duplicate Precision

Sample D-6-SED-FD is a field duplicate. As part of this validation effort, the results for the field duplicate were compared to the original field sample, HB-6-SED-SMP. The RPDs between the results for each detected pesticide were calculated by the reviewer, and are shown below.

Analyte	D-6-SED-SMP	D-6-SED-FD	RPD
PCB28	1.3	--	NA
PCB52	2.3	--	NA
PCB66	--	1.9	NA
PCB105	1.7	--	NA
PCB138	1.4	--	NA
PCB153	2.2	--	NA
PCB180	3.9	7.7	66
PCB187	3.2	3.5	9
PCB188	1.2	1.5	22
PCB195	1.1	2.0	58
PCB206	4.0	5.1	24

Six of the analytes were not detected (ND) in either the original sample or the duplicate sample. Therefore, no RPD calculation was possible and the RPD values are listed above as "NA" for not applicable. The results for many of the samples in which these congeners were detected are only slightly above the laboratory's reporting limits, and therefore, the detect/nondetect situation is not unexpected.

These samples were taken from different cores collected in approximately the same location and do not represent samples split from the same core. The precision exhibited by these results is generally within the expected range for field duplicate samples, and there is no reason to qualify any sample results. Field duplicate precision is *not* within the control of the laboratory, but is discussed here in terms of the overall validation of the sampling and analysis effort.

Overall Assessment

Overall, the results for these 17 samples meet the objectives of the sampling and analysis effort. The results may be used without qualification.

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MEMORANDUM

Date: June 17, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Sediment dioxin data for 17 samples

As requested, I have reviewed the results of the 1999 Raymark sediment data for PCDDs/PCDFs. The analyses were performed by Midwest Research Institute (MRI) on 17 sediment samples collected by SAIC in April 1999. The laboratory used the SAIC sample numbers, as shown below:

SAIC Sample ID	
C-1-SED-SMP	D-6-SED-FD
C-2-SED-SMP	E-1-SED-SMP
C-3-SED-SMP	E-2-SED-SMP
D-1-SED-SMP	E-3-SED-SMP
D-2-SED-SMP	E-4-SED-SMP
D-3-SED-SMP	F-1-SED-SMP
D-4-SED-SMP	F-2-SED-SMP
D-5-SED-SMP	F-3-SED-SMP
D-6-SED-SMP	

While an attempt was made to perform a Tier II validation, using the EPA Region 1 data validation guidance, the level of validation that was possible for these results was very limited. Although the method employed, Method 1613B, contains an extensive quality control protocol, the data there were provided are limited to tabular summaries of the results for the samples, the recoveries of the isotopically-labeled compounds added to the sample prior to extraction, and the laboratory control sample (LCS) results. No raw data were provided, nor were any data on mass calibration, the window defining mixture analyses, initial calibration, calibration verification, or the ion abundance ratios.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Blanks
- Labeled compound recoveries
- Laboratory control sample results
- Compound identification

The results were evaluated in the context of the requirements of Method 1613B. Where no comments are made, no problems were identified.

Blanks

The laboratory provided summary data for two method blanks. The first blank was associated with 16 of the samples. The second blank was associated with one sample, D-5-SED-SMP, that required re-extraction by the laboratory due to a malfunction of the gel permeation chromatography (GPC) cleanup apparatus.

Only four of the 17 target analytes were found in the methods blanks. 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, OCDF, and OCDD were detected in both blanks at low levels. The reviewers have used the "5 times" rule to qualify any sample results that are not at least 5 times the associated blank result. Only three sample results required qualification.

The 1,2,3,4,6,7,8-HpCDD and the 1,2,3,4,6,7,8-HpCDF results in D-1-SED-SMP were qualified as estimated and flagged "J," due to the blank results. The 1,2,3,4,6,7,8-HpCDF result in D-2-SED-SMP is similarly qualified. None of the OCDD or OCDF results were qualified.

The reporting practices used by MRI lead to some confusion with regard the to analytes found in the blanks. See the discussion of compound identification later in this review.

Labeled Compound Recoveries

^{13}C-labeled analogs of the target analytes are added to each sample prior to extraction and the recoveries of those compounds are used to perform isotope dilution quantitation of the target analytes. The method contains acceptance criteria for the labeled compounds in the form of limits for the percent recovery. MRI has used the consensus limits of 25-150% from the original publication of Method 1613. Since that time, EPA has slightly revised and widened those limits as a result of a interlaboratory study of the method.

MRI flagged two recoveries as being outside of their in-house limit. The recovery of ^{13}C-2,3,7,8,-TCDF was flagged in samples E-3-SED-SMP and E-4-SED-SMP. Sample F-2-SED-SMP also had a recovery outside of MRI's in-house limits, but it was not flagged in the data summary. Based on the latest EPA acceptance criteria, this labeled standard should be recovered in the range 24-169%. The recovery in E-4-SED-SMP was reported as 23.8%, which when rounded to the appropriate number of significant figures becomes 24%, and falls within the method-specified acceptance limit. Therefore, there is no issue for that sample. The recoveries in the E-3-SED-SMP and F-2-SED-SMP were reported as 12.7% and 20.7%, respectively, and both

values are outside the method-specified limits. Therefore, the results for 2,3,7,8-TCDF in these two samples are qualified as estimates, and flagged "J" by the reviewers.

Compound Identification

Method 1613 includes specific requirements for identifying a compound as one of the 17 2,3,7,8-substituted PCDDs/PCDFs that are the target analytes in the method. Among those requirements is the ratio of the two characteristic ions that are monitored for each analyte. If that ratio falls outside of a consensus window for the analyte, then the peaks cannot be definitively identified as the analyte, and the results may include a contribution from some non-target analyte. The laboratory will then typically report the results as a worst case estimate called an estimated maximum possible concentration (EMPC).

The laboratory employed an unusual reporting scheme for these samples, in that they often reported results as "U (###) EMPC," where "###" represents the sample-specific detection limit calculated on the basis of the observed noise. The EMPC qualifier normally indicates that the results did not meet the ion abundance ratio criteria for identifying a target analyte. The reviewers have questioned the laboratory about this practice, and as a result of those discussions, any results reported by MRI in this fashion are considered to be not detected (e.g., "U") at the detection limit reported in parentheses. MRI's unusual use of the EMPC qualifier essentially indicates that the detection limit is a worst case limit for this sample. SAIC does not believe that there is a meaningful difference between the worst case detection limit and a noise-based detection limit that would be reported otherwise.

In addition, to the method specifications for the ion abundance ratio, the GC column used for the analysis cannot absolutely separate 2,3,7,8-TCDF from other TCDF isomers. Therefore, the method specifies that whenever 2,3,7,8-TCDF is found in a sample, the sample extract should be reanalyzed on a different GC column that can separate the TCDF isomers, but that is not suitable for the analysis of all of the other target analytes. MRI reported 2,3,7,8-TCDF in 14 of the 17 sediment samples. Based on a conversation with the laboratory, they will provide the second column confirmation data as soon as possible. SAIC will review those results as soon as they are received.

Given the need to validate these sample results quickly, SAIC will only revise this review in the event that the second column confirmation results demonstrate that 2,3,7,8-TCDF was not present in one of those 14 samples.

Finally, the results for OCDD in sample E-1-SED-SMP was reported by the laboratory as 7900 pg/g, with a flag that indicated that the peak was saturated. Given this saturation of the detector, it may be possible that the reported concentration is lower than the true concentration. Therefore, SAIC has flagged that OCDD results as estimated.

Overall Assessment

The majority of the results for the PCDDs/PCDFs in these 17 samples met the data quality objectives and may be used without qualification.

The results for 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were flagged as estimates in sample D-1-SED-SMP and the 1,2,3,4,6,7,8-HpCDD result in D-2-SED-SMP was also flagged as an estimate.

All results reported by MRI with both the "U" and "EMPC" qualifiers are to be considered not detected and reported simply as "u" values.

The 2,3,7,8-TCDF results in samples E-3-SED-SMP and F-2-SED-SMP were flagged as estimates due to low recoveries of the associated labeled standard.

SAIC expects to receive the results for 2,3,7,8-TCDF confirmation of 14 of the 17 samples in the near future. *SAIC will only revise this review in the event that the second column confirmation results demonstrate that 2,3,7,8-TCDF was not present in one of those 14 samples.*

APPENDIX C-2
SEDIMENT POREWATER CHEMISTRY

Science Applications International Corporation
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MEMORANDUM

Date: June 11, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Porewater metals data for 17 samples

As requested, I have reviewed the results of the 1999 Raymark porewater metals data. The analyses were performed by the University of Rhode Island (URI) Paleomagnetics Laboratory on 17 sediment samples collected by SAIC in April 1999. The laboratory used the SAIC sample numbers, as shown below:

SAIC Sample Number	
C-1-PW	D-6-FD
C-2-PW	E-1-PW
C-3-PW	E-2-PW
D-1-PW	E-3-PW
D-2-PW	E-4-PW
D-3-PW	F-1-PW
D-4-PW	F-2-PW
D-5-PW	F-3-PW
D-6-PW	

While an attempt was made to perform a Tier II validation, using the EPA Region 1 data validation guidance, the level of validation that was possible for these results was very limited. The data reported by URI are limited to tabular summaries only.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike results
- Duplicate samples
- Blank spikes

The results were evaluated in the context of the data quality objectives (DQOs) provided by the laboratory. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

The data package is limited to tabular summaries. No raw data were provided. Since this is a Tier II validation effort, the raw data were not absolutely needed, but the lack of raw data would limit any further evaluation in the future.

Calibration

The graphite furnace atomic absorption spectrophotometer (GFAA) was calibrated for all eight metals and those calibrations met the linearity criteria described in the laboratory's data quality objectives. However, two of the continuing calibration blanks (CCBs) exceeded the target values for arsenic. One CCB in each of the two analysis batches reported by URI exceeded the acceptance limit of 5.0 µg/L, with both values at 5.6 µg/L. The laboratory's DQOs do not specify an allowance for any CCB results to exceed this value, nor would one be expected. There is no indication that the laboratory took any corrective action when the CCB results failed to meet the acceptance limits.

Arsenic was reported in six of the 17 samples, at levels ranging from 10.3 to 42.9 µg/L. The other 11 samples were all reported to be below the detection limit of 10.0 µg/L. The arsenic results for the method, or procedural, blank were reported as <10.0 µg/L, meeting the laboratory's DQOs. However, given the level of arsenic in the two CCBs and the low levels reported in four of the six positive samples, it is not possible to determine how much, if any, of those results were due to the background levels of arsenic in the laboratory. The validators have used the "five times rule" to evaluate these results, whereby any sample result less than five times the CCB result is considered to be an estimate of the sample concentration that may reflect a significant contribution from the CCB. The results for samples C-2-PW, E-1-PW, E-3-PW, and F-3-PW are all below 28 µg/L (5.6 x 5). Therefore, the arsenic results for these four samples are all flagged "J" as estimated. The arsenic results for sample C-1-PW and E-2-PW are not affected, since they are more than five times the CCB results. The non-detect results for the remaining samples are not affected.

Matrix Spike Results

The laboratory reported the results for a matrix spike of sample C-1-PW. The laboratory's DQOs specify a recovery range of 50-150%, with no more than 30% of the analytes falling outside that range. For these samples, five of eight metals had matrix spike recoveries within the acceptance range, and three metals fell outside the limits. Thus, 37.5% of the metal recoveries fell outside of the acceptance limits. Arsenic, lead, and silver had recoveries of 35%, 30%, and 24% respectively, well below the laboratory's acceptance limits. There is no indication that the laboratory took any corrective action when more than 30% of the results failed to meet the acceptance limits.

The laboratory also analyzed a blank spike, or laboratory control sample, containing all eight metals. The recoveries of all of the metals where in the range of 71-103%, including

arsenic, lead and silver. These blank spike data indicate that the recovery problems may be associated with the porewater matrix itself. Thus, the issue is not necessarily one of laboratory performance, but rather the ability of the selected sample preparation procedures to determine the analytes in the porewater matrix.

Silver was not detected in any of the 17 porewater samples. Given the reported matrix spike recovery (24%), and without the raw data from the analyses, it is not possible to say that the silver results are not false negatives. Therefore, all the silver results are flagged "UJ" to indicate the uncertainty associated with the reported detection limits.

Arsenic and lead were each reported as present in six of the 17 samples, although both metals were not necessarily reported in the same sample. All but one of the lead results were only slightly above the reported detection limit (results ranged from 2.9 to 3.7 µg/L, versus a detection limit of 2.9). Four of the six arsenic results were similarly close to the reported detection limit of 10 µg/L.

The arsenic data for those four samples are already qualified as estimated due to the CCB issue described above. Given the reported matrix spike recovery, the non-detect results for arsenic in samples C-3-PW, D-1-PW, D-2-PW, D-3-PW, D-4-PW, D-5-PW, D-6-PW, D-6-FD, E-4-PW, F-1-PW, and F-2-PW are flagged as "UJ" to indicate the uncertainty associated with the reported detection limits.

The lead results for C-3-PW, D-1-PW, D-2-PW, D-3-PW, AND E-4-PW are flagged "J" as estimated due to the low matrix spike recovery. The non-detect results for C-1-PW, C-2-PW, D-4-PW, D-5-PW, D-6-PW, D-6-FD, E-1-PW, E-3-PW, F-1-PW, F-2-PW, and F-3-PW are flagged as "UJ" to indicate the uncertainty associated with the reported detection limits.

Duplicate Sample Results

The laboratory analyzed one sample, D-4-PW, in duplicate. Unfortunately, this sample contained only two metals above the reported detection limits. Therefore, the precision of the analysis could only be assessed on the basis of those two results. The relative percent difference (RPD) was reported as 11% for chromium and 79% for zinc. The zinc results are well outside of the laboratory's 30% acceptance limit, but their DQOs allow for up to 35% of the analytes to fail this criterion (Note: The laboratory's DQO statement refers to the "recoveries," not the RPD, and is an obvious typographical error).

Zinc was reported as present in 14 of the 17 samples. Given the relatively high RPD for the duplicate analyses, all of the detected results have been flagged "J" as estimates. Only the non-detect results for C-1-PW, E-1-PW, and E-2-PW are unaffected.

Overall Assessment

The results for the analyses of cadmium, chromium, copper, and nickel may all be used without qualification. However, all of the results for silver are non-detects and are qualified as estimates. The reported detection limits should be used with appropriate caution if silver is an analyte of concern at this site.

All of the non-detect results for arsenic and lead are similarly qualified due to low matrix spike recoveries and the reported detection limits should be used with appropriate caution if these analytes are of concern at this site.

A number of the results for samples in which either lead or arsenic were reported as detected are also qualified as estimates either due to the potential contributions from the blank (for arsenic) or due to low matrix spike recoveries (for arsenic and lead).

The reported results for zinc are qualified as estimates, due to the relatively poor precision between the duplicate analyses. This qualification may adversely affect comparisons of zinc results between different samples.

APPENDIX C-3
TISSUE CHEMISTRY

Science Applications International Corporation
An Employee-Owned Company

MEMORANDUM

Date: June 25, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Tissue Data Validation
Metals data for 9 samples

As requested, I have reviewed the results of the 1999 Raymark tissue sample data for the metals analyses. The analyses were performed by The Woods Hole Group (WHG), on 9 ribbed mussel samples collected by SAIC in April 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
C-1-TISS-SMP	42274-1
C-2-TISS-SMP	42274-2
C-3-TISS-SMP	42274-3
D-1-TISS-SMP	42274-4
D-2-TISS-SMP	42274-5
D-3-TISS-SMP	42274-6
D-4-TISS-SMP	42274-7
D-6-TISS-SMP	42274-8
HB-9-TISS-SMP	42274-9

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples other than tissues and analyzed by CLP methods, which are not the methods designated for this project.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike and duplicate sample results

- Laboratory control sample results
- ICP serial dilution results
- ICP interference check results
- Graphite furnace post-digestion spike results

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

Duplicate Sample Results

The laboratory performed a duplicate analysis of sample C-1-TISS-SMP. The precision results for all the metals were within the acceptance limits except for arsenic, cadmium, and nickel. The RPD for arsenic was 23.8%, 32% for cadmium, and 20.6% for nickel.

The precision for nickel is so close to the limit that no qualification of the data is needed. The precision for arsenic in only slightly outside the limit, while the cadmium results demonstrate more variability. Both metals were reported in all of the tissue samples. Therefore, all of the results for arsenic and cadmium are considered to be estimates and are flagged "J."

Laboratory Control Sample

The laboratory analyzed a standard reference material, SRM 2976, as a laboratory control sample. As noted by the laboratory, the results for chromium and cadmium were outside of the acceptance limits for this SRM. The recovery of cadmium was 37.5% and 134% for chromium. The laboratory attributes these recovery problems to a sample matrix interference.

SAIC has reviewed the results. Because the matrix spike results are well within the acceptance limits, there is no need to qualify the sample results for cadmium or chromium on the basis of the SRM results.

Overall Assessment

Overall, the majority of the results for these 9 tissue samples meet the objectives of the sampling and analysis effort and they may be used without qualifications. All results for arsenic and cadmium are flagged "J," as estimated, due to the difficulties noted with the duplicate analysis.

Science Applications International Corporation
An Employee-Owned Company

MEMORANDUM

Date: June 25, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Tissue Data Validation
PAH data for 9 samples

As requested, I have reviewed the results of the 1999 Raymark tissue sample data for the PAH analyses. The analyses were performed by The Woods Hole Group (WHG), on 9 ribbed mussel samples collected by SAIC in April 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
C-1-TISS-SMP	42274-1
C-2-TISS-SMP	42274-2
C-3-TISS-SMP	42274-3
D-1-TISS-SMP	42274-4
D-2-TISS-SMP	42274-5
D-3-TISS-SMP	42274-6
D-4-TISS-SMP	42274-7
D-6-TISS-SMP	42274-8
HB-9-TISS-SMP	42274-9

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples other than tissues and analyzed by CLP methods, which are not the methods designated for this project. Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike and matrix spike duplicate results
- Laboratory control sample results
- Surrogate recoveries

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

Laboratory Control Sample Results

According to the narrative, the laboratory analyzed a standard reference material, SRM 1974a, in conjunction with these samples, as a laboratory control sample (LCS). The results for this SRM were reported with a recovery correction that was based on the recoveries of the four surrogates added to all the samples. According to the narrative, this recovery correction was made by the laboratory because the certified values for the SRM are based on the use of isotope dilution quantitation, which includes an inherent recovery correction for each analyte.

The reviewers disagree with this approach for two reasons. First and foremost, the use of any recovery correction bears no resemblance to the approach use for the analysis of the sediment samples. Thus, the SRM results and the laboratory's success in achieving the certified values for that SRM have little meaning in the context of this project.

Secondly, the use of the surrogate data to perform the recovery correction limits the utility of the results even further. In isotope dilution methods, an isotopically-labeled analog of each target compound is added to the sample prior to extraction. In the few instances where a labeled analog is not available or cannot be used for other reasons, the recovery correction is based on the recovery of the analog of a very similar compound. In these PAH analyses, only four surrogate compounds were employed for the 24 target compounds. While all four surrogates were deuterated analogs of target PAHs, only three of those target PAHs had certified values for the SRM. Thus, the SRM results were corrected on the basis of only three surrogates. Given the wide range of structures for the 16 target PAHS in the SRM, SAIC does not believe that one can make reasonable associations between the surrogates and the target analytes for the purposes of quantitation. It is this lack of a clear association between surrogates and target analytes that has kept EPA from employing recovery corrections based on surrogate results in their analytical methods.

The net effect on the quality of the data for this project is minimal, in that only the SRM results were recovery corrected. However, SAIC believes that this approach further limits the utility of the SRM analysis as a quality control measure in relation to the sample analyses. Because the MS/MSD results reported in the data package exhibit good recoveries and excellent precision, no qualification of the sample results is required in relation to SAIC's concerns about the SRM analysis.

Overall Assessment

Overall, the results for these 9 tissue samples meet the objectives of the sampling and analysis effort and they may be used without qualifications.

Science Applications International Corporation
An Employee-Owned Company

MEMORANDUM

Date: June 18, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Tissue Data Validation
Pesticide data for 9 samples

As requested, I have reviewed the results of the 1999 Raymark tissue sample data for the organochlorine pesticide analyses. The analyses were performed by The Woods Hole Group (WHG), on 9 ribbed mussel samples collected by SAIC in April 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
C-1-TISS-SMP	42274-1
C-2-TISS-SMP	42274-2
C-3-TISS-SMP	42274-3
D-1-TISS-SMP	42274-4
D-2-TISS-SMP	42274-5
D-3-TISS-SMP	42274-6
D-4-TISS-SMP	42274-7
D-6-TISS-SMP	42274-8
HB-9-TISS-SMP	42274-9

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples other than tissues and analyzed by CLP methods, which are not the methods designated for this project.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike and matrix spike duplicate results

- Laboratory control sample results
- Surrogate recoveries
- Endrin and DDT breakdown

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

As noted by the laboratory, the use of the amino-propyl cleanup column does not provide consistent recoveries of the target analyte endrin aldehyde. According to the narrative, the situation was discussed with SAIC and it was agreed that for this project, all endrin aldehyde results would be flagged "J" as estimated. Endrin aldehyde was not detected in any of the samples, thus all results for this analyte are reported as "UJ," for not detected and estimated. Unfortunately, the laboratory did not provide any data from reference materials, spiked samples, or laboratory control samples that included this analyte. Therefore, it is not possible to determine from the data in the package if the laboratory could have detected endrin aldehyde at all. Therefore, the reviewer suggests that the endrin aldehyde be deleted from the list of target analytes, or simply be reported as "NA" for not analyzed.

Calibrations

Initial calibrations and continuing calibrations were performed as required. The results for several of the continuing calibration standards included one or more analytes that demonstrated a difference of more than 25% between the amount found and the true concentration of the standard. However, in all but one such instance, the results for the same standard analyzed on the second GC column were within the acceptance limits. Therefore, the laboratory reported the results for those analytes from the GC column that met the specifications.

The exception was for hexachlorobenzene. The continuing calibration standard analyzed on 5/15/99 at 12:01 AM, after all of the tissue samples, had a %D on Column A of -28% and -35% on Column B. This analyte was not detected in any of the 9 tissue samples. SAIC examined the chromatograms and found no evidence of peaks that would represent this analyte. However, given the continuing calibration results, there is some slim chance that the results could be false negatives. Therefore, all of the non-detect results for this analyte are flagged "UJ" to indicate that the reported quantitation limits may be estimates.

Comparisons Between Results from Two GC Columns

SW-846 Method 8000B recommends that the quantitative results from both GC columns be compared during dual-column analyses such as used here for the pesticides. As noted by the laboratory, there were a two instances in which the quantitative results from the two GC columns used for the analyses differed by more than 40%. In those instances, the laboratory reviewed the chromatograms and if no evidence of a problem was found, they took the conservative approach and reported the higher of the two results. The results for p,p'-DDE and p,p'-DDD in Sample D-

1-TISS-SMP were flagged "P" by the laboratory to indicate that the higher value was reported. SAIC has reviewed the chromatograms for these samples and agrees that the higher values be reported and there is no need for qualification.

Overall Assessment

Overall, the majority of the results for these 9 tissue samples meet the objectives of the sampling and analysis effort. The only qualifications are that endrin aldehyde should not be considered to be a target analyte and the non-detect results for it should be considered to be "not analyzed" instead, and all the reported quantitation limits for hexachlorobenzene are considered to be estimates and should be flagged "UJ."

Science Applications International Corporation
An Employee-Owned Company

MEMORANDUM

Date: June 25, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Tissue Data Validation
PCB data for 9 samples

As requested, I have reviewed the results of the 1999 Raymark tissue sample data for the PCB analyses. The analyses were performed by The Woods Hole Group (WHG), on 9 ribbed mussel samples collected by SAIC in April 1999. The SAIC and WHG sample numbers are as follows:

SAIC Sample ID	Woods Hole Group ID
C-1-TISS-SMP	42274-1
C-2-TISS-SMP	42274-2
C-3-TISS-SMP	42274-3
D-1-TISS-SMP	42274-4
D-2-TISS-SMP	42274-5
D-3-TISS-SMP	42274-6
D-4-TISS-SMP	42274-7
D-6-TISS-SMP	42274-8
HB-9-TISS-SMP	42274-9

This data validation effort approximates a Tier II validation, using the EPA Region 1 data validation guidance. It is important to note that the Region 1 guidance is intended for samples other than tissues and analyzed by CLP methods, which are not the methods designated for this project.

Our review efforts evaluated the summary level data only, and considered the following:

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike and matrix spike duplicate results

- Laboratory control sample results
- Surrogate recoveries

The results were evaluated in the context of the requirements of the project QAPP and/or laboratory SOPs, where available and applicable. Unless specific comments are made, there were no problems associated with a given evaluation criterion.

Data Completeness

Since this is a Tier II validation effort and therefore did not involve an examination of all of the raw data, there may be some raw data that are not present in the package.

Calibrations

Initial calibrations and continuing calibrations were performed as required. The results for two of the continuing calibration standards included several analytes that demonstrated a difference of more than 25% between the amount found and the true concentration of the standard. However, in most such instances, the results for the same standard analyzed on the other GC column were within the acceptance limits. Therefore, the laboratory reported the results for those analytes from the GC column that met the specifications.

The only exceptions were for the continuing calibration standards analyzed on 5/14/99 at 9:57 PM and 5/15/99 at 4:24 AM. For both of those standards, the results for PCB 18 and the surrogate compound DBOB were lower than expected, with %D values of -26% to -31% on both columns in both standards. The calibration results for the surrogate are not critical, since the surrogate recoveries for all the samples were well within the acceptance limits. The results for PCB 18 suggest that there may be some slight low bias in the affected samples.

SAIC has reviewed the specific results for the three tissue sample analyses that occurred between these two calibration standard analyses. The affected samples are D-6-TISS-SMP, HB-9-TISS-SMP, and the matrix spike duplicate aliquot prepared from sample D-4-TISS-SMP. The PCB in question was not detected in either of the unspiked samples. Therefore, given the slight potential low bias, the results for this compound in samples D-6-TISS-SMP and HB-9-TISS-SMP have been flagged "UJ" to indicate that the reported detection limit may be an estimate.

There is no apparent effect on the matrix spike duplicate results, since the recovery of PCB 18 was well within the acceptance limits and the RPD between the MS and MSD results was only 2%. Therefore, no qualification of the MSD results is required due to the calibration results.

Comparisons Between Results from Two GC Columns

SW-846 Method 8000B recommends that the quantitative results from both GC columns be compared during dual-column analyses such as used here for the PCBs. As noted by the laboratory, there were a number of instances in which the quantitative results from the two GC columns used for the analyses differed by more than 40%. In those instances, the laboratory reviewed the chromatograms and if no evidence of a problem was found, they took the conservative approach and reported the higher of the two results, flagging those values with a "P" to indicate that the higher value was reported.

If, after examining the chromatograms, they found evidence of a positive interference on one of the columns, or if there was evidence that the baseline had been incorrectly established by the software, the laboratory reported the lower of the two results, flagging those values with a "I" to indicate that the lower value was reported, due to an interference.

SAIC has reviewed the chromatograms for these samples and agrees that the laboratory's reported results were appropriate and there is no need for qualification of the results.

Overall Assessment

Overall, the majority of the results for these 9 tissue samples meet the objectives of the sampling and analysis effort and they may be used without qualifications.

The reported quantitation limits for PCB 18 in samples D-6-TISS-SMP and HB-9-TISS-SMP are considered to be estimates and should be flagged "UJ."

APPENDIX C-4
SEM, GRAIN SIZE, TOC, AND AVS

Science Applications International Corporation
An Employee-Owned Company

MEMORANDUM

Date: June 17, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Sediment SEM data for 17 samples

As requested, I have reviewed the results of the 1999 Raymark sediment data for simultaneously extracted metals (SEM). The analyses were performed by the University of Rhode Island (URI) Paleomagnetics Laboratory on 17 sediment samples collected by SAIC in April 1999. The laboratory used the SAIC sample numbers, as shown below:

SAIC Sample ID	
C-1-SED-SMP	D-6-SED-FD
C-2-SED-SMP	E-1-SED-SMP
C-3-SED-SMP	E-2-SED-SMP
D-1-SED-SMP	E-3-SED-SMP
D-2-SED-SMP	E-4-SED-SMP
D-3-SED-SMP	F-1-SED-SMP
D-4-SED-SMP	F-2-SED-SMP
D-5-SED-SMP	F-3-SED-SMP
D-6-SED-SMP	

While an attempt was made to perform a Tier II validation, using the EPA Region 1 data validation guidance, the level of validation that was possible for these results was very limited. The methods employed have relatively few quality control steps associated with them and the data reported by URI are limited to tabular summaries only.

Our review efforts evaluated the summary level data only, and considered the following (where applicable):

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks

- Matrix spike results
- Duplicate samples
- Blank spikes

The results were evaluated in the context of the requirements of the laboratory SOPs, where available and applicable.

Blanks

The laboratory reported the results for the procedural blank on a weight basis (e.g., µg/g) and those results have been used to evaluate the associated sample results. The procedural blank run for the SEM analysis found copper, cadmium, and nickel at levels above the levels found in many of the sediment samples. Zinc and lead were reported in the blank at levels that exceeded the results for a single sample each. The source of these metals in the blank is unclear. The calibration blanks run for each metal do not indicate that the instrument is contaminated. The levels reported in the blank do not appear to be a systematic problem. However, since many of the sample results are lower than those found in the blank, there is no means by which to determine if those low level sample results are real or the result of contamination from an unknown source.

We recognize that the SEM data are not used in the same fashion as data for total recoverable metals might be. Therefore, it is difficult to establish a firm set of rules for evaluating the SEM results relative to the observed blank results. The traditional "five times" rule would qualify any sample result that was not at least five times greater than the blank result. Using that rule, most of these SEM data would have been qualified.

Therefore, the reviewers have used the approach of qualifying all SEM results that are less than or equal to the observed blank results. Using this approach, the following results are qualified as estimates (flagged "J"). The results for the seven samples not listed in this table were *not* qualified as a result of the observed blank results.

Sample	Copper	Zinc	Lead	Nickel	Cadmium
C-1-SED-SMP	3.4 J			3.2 J	0.14 J
C-2-SED-SMP	7.7 J				0.10 J
C-3-SED-SMP				4.8 J	0.13 J
D-1-SED-SMP	4.1 J		3.3 J	2.7 J	0.18 J
D-2-SED-SMP	3.5 J			4.7 J	
D-4-SED-SMP		6.5 J			
D-5-SED-SMP	6.5 J				
D-6-SED-SMP	4.6 J				
D-6-SED-FD	11.1 J				
F-2-SED-SMP	6.9 J				

Matrix Spike Results

The DQOs provided by URI indicate that matrix spikes are not applicable to this analysis and are not included in the laboratory's SOP. However, because they were requested by SAIC for this project, URI provided data for both matrix spike and blank spike analyses. SAIC reviewed those data, and while there are no acceptance limits, the reviewers are concerned that the recovery of lead is only 55% in both the matrix spike and the blank spike. Given the identical results for the matrix spike and the blank spike, there is not an issue of a "sample matrix effect." These results raise concerns for the lead results in each sediment sample. The recoveries of the other four metals were all within a range of 90-115%.

Based on discussions with the laboratory, they believe that the relatively strong HCl concentration in the sample extracts may suppress the response for lead when using graphite furnace atomic absorption. The reviewers cannot rule out this possibility, but the issue remains that the results for lead may have a significant low bias. Therefore, all of the SEM results for lead have been qualified "J" as estimates.

Duplicate Samples

The laboratory's DQO for the precision of duplicate analyses was not met. The DQO calls for the relative percent difference between the duplicate analyses to be <30%, with an allowance for no more than 35% of the analytes to exceed that 30% limit. Of the five metals studied, three (60%) of them (copper, nickel, and zinc) exhibited RPD values in the range of 56-78%. It is important to note that these measurements were performed on duplicate aliquots of the same sample (C-1-SED-SMP) and *not* on the field duplicates collected by SAIC. The degree of blank contamination exhibited may also explain *some* of the relative imprecision observed for the duplicate analyses, since the results for copper, cadmium, and nickel in *both* the original sample and the duplicate sample were below the blank levels. However, even though the zinc results were 9 to 20 times the blank result in the sample and the duplicate, this analyte still had an RPD of 78%, indicating that the blank is not the sole contributor to the precision problems.

The sample chosen by the laboratory for the duplicate analysis was C-1-SED-SMP. The grain size data for this sample indicate that it was a coarse-grained sediment, with 78.6% sand. The laboratory believes that the coarse nature of the sediment made it very difficult to take replicate aliquots for the duplicate analyses, thus leading to the observed imprecision of the SEM results. While the grain size distribution may in fact be the cause, 8 of the 17 sediment samples were >70% sand. The reviewers also note that the other two metals, cadmium and lead, had RPD values of 7% and 1% respectively. Therefore, it cannot be the grain size alone that is determining the duplicate precision.

Whatever the cause, the results of the duplicate analyses suggest that the results for copper, nickel, and zinc may not be very precise.

Overall Assessment

Except for the four results noted in the discussion of the blank results, the SEM data for cadmium may be used without qualifications. The cadmium data for C-1-SED-SMP, C-2-SED-

SMP, D-1-SED-SMP, and D-2-SED-SMP are qualified as estimated ("J") due to potential blank contamination.

All of the results for lead are qualified as estimated ("J") due to the low recovery of this metals in both the matrix spike and blank spike analyses. The lead results in D-1-SED-SMP is also qualified as estimated on the basis of the blank results.

All of the results for copper, nickel, and zinc are qualified as estimates on the basis of the observed precision of the duplicate sample analyses. The results for many of these samples were also qualified as estimated due to potential blank contamination. See the table in the discussion of the blank results for the specific results that were qualified as estimates.

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MEMORANDUM

Date: June 11, 1999

To: Greg Tracey

From: Harry McCarty

Subject: Raymark 1999 Sediment Data Validation
Sediment Grain Size, TOC, and AVS data for 27 samples

As requested, I have reviewed the results of the 1999 Raymark sediment sample data for:

- Grain size
- Total organic carbon
- Acid volatile sulfides (AVS)

The analyses were performed by the University of Rhode Island (URI) Paleomagnetics Laboratory on 27 sediment samples collected by SAIC in April 1999. The laboratory used the SAIC sample numbers, as shown below:

SAIC Sample ID		
C-1-SED-SMP	D-6-SED-FD	HB-2-SED-SMP
C-2-SED-SMP	E-1-SED-SMP	HB-3-SED-SMP
C-3-SED-SMP	E-2-SED-SMP	HB-4-SED-SMP
D-1-SED-SMP	E-3-SED-SMP	HB-5-SED-SMP
D-2-SED-SMP	E-4-SED-SMP	HB-6-SED-SMP
D-3-SED-SMP	F-1-SED-SMP	HB-6-SED-FD
D-4-SED-SMP	F-2-SED-SMP	HB-7-SED-SMP
D-5-SED-SMP	F-3-SED-SMP	HB-8-SED-SMP
D-6-SED-SMP	HB-1-SED-SMP	HB-9-SED-SMP

While an attempt was made to perform a Tier II validation, using the EPA Region 1 data validation guidance, the level of validation that was possible for these results was very limited. The methods employed have relatively few quality control steps associated with them and the data reported by URI are limited to tabular summaries only.

Our review efforts evaluated the summary level data only, and considered the following (where applicable):

- Data completeness
- Holding times
- Calibrations (initial and continuing)
- Blanks
- Matrix spike results
- Duplicate samples
- Blank spikes

The results were evaluated in the context of the data quality objectives (DQOs) provided by the laboratory, where available and applicable. The results of this review are described below, by analysis type.

Grain Size

All of the data quality objectives provided by the laboratory were met for this analysis.

Total Organic Carbon

All of the data quality objectives provided by the laboratory were met for this analysis.

Acid volatile sulfides (AVS)

All of the data quality objectives provided by the laboratory were met for this analysis.

Overall Assessment

The data for these 27 sediment samples met the laboratory's DQOs and may be used without qualifications.

The results for the field duplicate pair D-6-SED-SMP and D-6-SED-FD in sediment set 2 support the concerns about the field duplicates that were expressed in the reviews of other analyses. The data for grain size, total organic carbon, and AVS all differ markedly between these two samples. The field duplicate pair from sediment set 1, HB-6-SED-SMP and HB-6-SED-FD, were not analyzed for AVS, but the grain size and total organic carbon data differ greatly between these two samples as well.