

APPENDIX B: MS/MSD RESULTS AND CORRECTIVE ACTION MEMO

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**Table B-1. MS/MSD results for butyltin analysis
(accuracy limits 20-130%, precision 50%)**

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
LDW-T1-M-ES-WB-comp-3			
Monobutyltin	69	71	3
Dibutyltin	74	74	1
Tributyltin	64	69	5
Tetrabutyltin	75	90	18
LDW-T1-M-ES-WB-comp-5			
Monobutyltin	75	76	0
Dibutyltin	77	79	0
Tributyltin	72	75	2
Tetrabutyltin	95	96	1
LDW-T1-M-DC-EM-comp-2			
Monobutyltin	59	55	7
Dibutyltin	70	71	1
Tributyltin	53	53	1
Tetrabutyltin	34	46	32
LDW-T2-M-ES-WB-comp-1			
Monobutyltin	4 ^a	4 ^a	0
Dibutyltin	12 ^a	10 ^a	10
Tributyltin	12 ^a	10 ^a	11
Tetrabutyltin	41	43	4
LDW-T3-F-PS-WB-comp-1			
Monobutyltin	76	75	3
Dibutyltin	79	76	6
Tributyltin	75	75	2
Tetrabutyltin	84	62	32
LDW-T3-M-ES-WB-comp-4			
Monobutyltin	61	61	0
Dibutyltin	67	66	3
Tributyltin	61	62	1
Tetrabutyltin	80	81	1
LDW-T4-A-PS-WB-comp-1			
Monobutyltin	68	70	1
Dibutyltin	72	74	0
Tributyltin	62	67	3
Tetrabutyltin	49	65	27

^a Sample result does not meet accuracy criteria. Associated laboratory control sample recovery is within limits.

**Table B-2. MS/MSD results for organochlorine pesticide analysis
(accuracy limits 30-150%, precision 50%)**

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
LDW-T1-M-DC-EM-comp-1			
alpha-BHC	87	90	3
Hexachlorobenzene	81	82	2
beta-BHC	84	87	4
gamma-BHC (Lindane)	78	75	3
delta-BHC	76	92	19
Heptachlor	89	97	9
Aldrin	90	89	0
Heptachlor Epoxide	97	90	7
gamma-Chlordane	94	98	4
Endosulfan I	87	89	3
alpha-Chlordane	93	97	4
Dieldrin	78	81	4
4,4'-DDE	93	112	18
Endrin	99	104	5
Endosulfan II	90	95	6
4,4'-DDD	92	103	11
Endrin Aldehyde	27 ^a	32	16
Endosulfan Sulfate	89	98	9
4,4'-DDT	91	95	4
Endrin Ketone	104	108	4
Methoxychlor	85	91	6
2,4'-DDE	112	107	4
2,4'-DDD	102	92	10
2,4'-DDT	107	93	12
LDW-T1-M-ES-WB-comp-2			
alpha-BHC	69	74	7
Hexachlorobenzene	67	72	7
beta-BHC	77	82	6
gamma-BHC (Lindane)	67	70	4
delta-BHC	61	62	1
Heptachlor	64	71	10
Aldrin	85	65	27
Heptachlor Epoxide	54	44	11
gamma-Chlordane	59	55	4
Endosulfan I	61	63	2
alpha-Chlordane	63	66	4
Dieldrin	69	68	2
4,4'-DDE	75	75	1
Endrin	65	70	7
Endosulfan II	103	106	3
4,4'-DDD	78	78	1
Endrin Aldehyde	71	74	3
Endosulfan Sulfate	72	77	6

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
4,4'-DDT	67	75	4
Endrin Ketone	75	77	3
Methoxychlor	67	69	3
2,4'-DDE	108	91	18
2,4'-DDD	89	82	8
2,4'-DDT	65	68	1
LDW-T2-M-ES-WB-comp-3			
alpha-BHC	49	62	24
Hexachlorobenzene	67	69	4
beta-BHC	75	82	10
gamma-BHC (Lindane)	77	82	7
delta-BHC	57	65	12
Heptachlor	60	65	8
Aldrin	47	54	11
Heptachlor Epoxide	52	62	13
gamma-Chlordane	49	67	12
Endosulfan I	67	75	12
alpha-Chlordane	68	75	9
Dieldrin	62	70	12
4,4'-DDE	122	79	30
Endrin	75	87	15
Endosulfan II	111	126	13
4,4'-DDD	68	75	7
Endrin Aldehyde	72	83	14
Endosulfan Sulfate	77	72	6
4,4'-DDT	-173 ^a	-149 ^a	9
Endrin Ketone	72	77	6
Methoxychlor	64	68	6
2,4'-DDE	78	85	9
2,4'-DDD	84	86	3
2,4'-DDT	71	70	0
LDW-T3-B-PS-WB-comp-1			
alpha-BHC	78	77	1
Hexachlorobenzene	75	79	5
beta-BHC	59	63	5
gamma-BHC (Lindane)	76	77	0
delta-BHC	73	82	12
Heptachlor	68	75	11
Aldrin	87	93	7
Heptachlor Epoxide	78	86	10
gamma-Chlordane	67	81	13
Endosulfan I	81	85	4
alpha-Chlordane	89	101	13
Dieldrin	78	85	8
4,4'-DDE	142	142	0
Endrin	90	95	6

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
Endosulfan II	90	98	9
4,4'-DDD	90	95	5
Endrin Aldehyde	50	53	6
Endosulfan Sulfate	77	83	7
4,4'-DDT	72	94	11
Endrin Ketone	80	87	9
Methoxychlor	73	79	8
2,4'-DDE	111	107	3
2,4'-DDD	104	93	11
2,4'-DDT	95	80	6
LDW-T3-E-PS-WB-comp-1			
alpha-BHC	70	80	12
Hexachlorobenzene	70	76	8
beta-BHC	91	99	8
gamma-BHC (Lindane)	70	78	10
delta-BHC	80	87	8
Heptachlor	83	92	10
Aldrin	80	89	11
Heptachlor Epoxide	60	68	10
gamma-Chlordane	102	111	9
Endosulfan I	79	87	9
alpha-Chlordane	85	91	8
Dieldrin	81	87	8
4,4'-DDE	107	117	8
Endrin	89	98	10
Endosulfan II	80	93	13
4,4'-DDD	86	94	9
Endrin Aldehyde	85	92	8
Endosulfan Sulfate	81	88	8
4,4'-DDT	183 ^b	204 ^b	11
Endrin Ketone	84	93	10
Methoxychlor	75	82	9
2,4'-DDE	124	119	4
2,4'-DDD	102	91	8
2,4'-DDT	79	89	4
LDW-T4-M-ES-WB-comp-2			
alpha-BHC	64	65	1
Hexachlorobenzene	70	69	1
beta-BHC	91	117	24
gamma-BHC (Lindane)	94	88	6
delta-BHC	69	86	22
Heptachlor	71	78	9
Aldrin	68	78	13
Heptachlor Epoxide	57	78	26
gamma-Chlordane	109	133	20
Endosulfan I	65	78	18

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
alpha-Chlordane	69	82	17
Dieldrin	78	83	7
4,4'-DDE	67	93	19
Endrin	82	95	15
Endosulfan II	92	81	12
4,4'-DDD	73	83	11
Endrin Aldehyde	35	42	21
Endosulfan Sulfate	77	82	7
4,4'-DDT	146	166 ^b	13
Endrin Ketone	69	81	17
Methoxychlor	66	71	8
2,4'-DDE	57	41	14
2,4'-DDD	87	83	4
2,4'-DDT	62	61	1
LDW-T4-M-SF-FL-comp-1			
alpha-BHC	90	99	10
Hexachlorobenzene	83	89	7
beta-BHC	90	102	12
gamma-BHC (Lindane)	90	101	11
delta-BHC	102	113	10
Heptachlor	88	119	30
Aldrin	88	97	10
Heptachlor Epoxide	102	92	10
gamma-Chlordane	107	118	10
Endosulfan I	91	100	10
alpha-Chlordane	97	108	11
Dieldrin	90	99	10
4,4'-DDE	106	108	2
Endrin	96	108	11
Endosulfan II	94	102	8
4,4'-DDD	96	92	3
Endrin Aldehyde	76	82	7
Endosulfan Sulfate	95	103	9
4,4'-DDT	85	91	4
Endrin Ketone	85	90	6
Methoxychlor	84	91	8
2,4'-DDE	117	119	1
2,4'-DDD	107	104	3
2,4'-DDT	88	84	3

^a Sample result does not meet accuracy criteria. Associated laboratory control sampler recovery is within limits.

^b Analyte not detected in original sample. Results unaffected by high bias.

**Table B-3. MS/MSD results for PCB analysis (Aroclors)
(accuracy limits 38-150%, precision 50%)**

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
LDW-T1-M-DC-EM-comp-1			
Aroclor-1016	91	91	1
Aroclor-1260	82	89	8
LDW-T1-M-DC-EM-comp-2			
Aroclor-1016	96	96	1
Aroclor-1260	91	93	4
LDW-T2-M-ES-WB-comp-1			
Aroclor-1016	193 ^a	190 ^a	3
Aroclor-1260	99	102	0
LDW-T2-M-ES-WB-comp-2			
Aroclor-1016	224 ^a	188 ^a	19
Aroclor-1260	183 ^b	116	17
LDW-T2-A-PS-WB-comp-1			
Aroclor-1016	106	108	2
Aroclor-1260	91	94	2
LDW-T4-E-PS-WB-comp-1			
Aroclor-1016	92	92	1
Aroclor-1260	75	72	1
LDW-T4-M-ES-WB-comp-2			
Aroclor-1016	106	103	2
Aroclor-1260	70	66	2

^a Analyte not detected in original sample. Results unaffected by high bias.

^b Sample result does not meet accuracy criteria. Associated laboratory control sampler recovery is within limits.

**Table B-4. MS/MSD results for SVOC analysis
(accuracy limits 20-130%, precision 50%)**

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
LDW-T1-D-PS-WB-comp-1			
Phenol	80	83	4
2-Chlorophenol	90	94	5
1,4-Dichlorobenzene	78	76	1
N-Nitrosodi-n-propylamine	81	86	7
1,2,4-Trichlorobenzene	86	90	5
4-Chloro-3-methylphenol	112	127	14
4-Nitrophenol	90	102	13
2,4-Dinitrotoluene	105	114	9
Pentachlorophenol	49	74	40
Acenaphthene	86	93	8
Pyrene	75	81	8
LDW-T1-M-DC-EM-comp-1			
Phenol	92	83	9
2-Chlorophenol	94	88	6
1,4-Dichlorobenzene	55	67	20
N-Nitrosodi-n-propylamine	84	78	7
1,2,4-Trichlorobenzene	73	79	8
4-Chloro-3-methylphenol	116	115	1
4-Nitrophenol	118	105	12
2,4-Dinitrotoluene	115	108	6
Pentachlorophenol	46	35	28
Acenaphthene	84	85	1
Pyrene	84	81	4
LDW-T1-M-DC-EM-comp-2			
Phenol	70	79	11
2-Chlorophenol	82	91	11
1,4-Dichlorobenzene	67	72	6
N-Nitrosodi-n-propylamine	72	84	15
1,2,4-Trichlorobenzene	76	84	9
4-Chloro-3-methylphenol	106	112	5
4-Nitrophenol	90	94	4
2,4-Dinitrotoluene	100	107	7
Pentachlorophenol	34	28	21
Acenaphthene	81	86	6
Pyrene	76	83	9
LDW-T1-M-ES-WB-comp-3			
Phenol	83	96	13
2-Chlorophenol	91	92	1
1,4-Dichlorobenzene	82	78	4
N-Nitrosodi-n-propylamine	83	82	2
1,2,4-Trichlorobenzene	85	84	2
4-Chloro-3-methylphenol	120	117	2
4-Nitrophenol	119	116	3

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
2,4-Dinitrotoluene	102	107	5
Pentachlorophenol	98	78	23
LDW-T1-M-ES-WB-comp-4			
Phenol	100	84	17
2-Chlorophenol	103	90	14
1,4-Dichlorobenzene	86	77	10
N-Nitrosodi-n-propylamine	93	79	16
1,2,4-Trichlorobenzene	93	85	9
4-Chloro-3-methylphenol	124	115	7
4-Nitrophenol	128	115	11
2,4-Dinitrotoluene	118	105	11
Pentachlorophenol	87	73	18
Acenaphthene	95	86	9
Pyrene	81	74	8
LDW-T4-D-PS-WB-comp-1			
Phenol	74	94	25
2-Chlorophenol	81	105	26
1,4-Dichlorobenzene	66	85	26
N-Nitrosodi-n-propylamine	73	95	27
1,2,4-Trichlorobenzene	79	101	25
4-Chloro-3-methylphenol	112	142 ^a	25
4-Nitrophenol	83	109	27
2,4-Dinitrotoluene	97	124	25
Pentachlorophenol	68	93	32
Acenaphthene	81	103	24
Pyrene	73	91	22
LDW-T4-M-ES-WB-comp-2			
Phenol	85	84	1
2-Chlorophenol	99	99	0
1,4-Dichlorobenzene	82	83	1
N-Nitrosodi-n-propylamine	90	92	3
1,2,4-Trichlorobenzene	92	91	1
4-Chloro-3-methylphenol	129	132 ^a	2
4-Nitrophenol	134 ^a	112	18
2,4-Dinitrotoluene	110	109	1
Pentachlorophenol	81	87	7

^a Analyte not detected in original sample. Results unaffected by high bias.

**Table B-5. MS/MSD results for PAH analysis
(accuracy limits 20-130%, precision 50%)**

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
LDW-T1-M-ES-WB-comp-3			
Naphthalene	81	59	32
2-Methylnaphthalene	90	68	29
Acenaphthylene	100	88	13
Acenaphthene	92	77	17
Dibenzofuran	95	87	8
Fluorene	99	91	9
Phenanthrene	92	85	8
Anthracene	102	94	9
Fluoranthene	102	95	7
Pyrene	92	85	8
Benz(a)anthracene	104	97	8
Chrysene	96	89	7
Benzo(b)fluoranthene	99	94	6
Benzo(k)fluoranthene	93	81	14
Benzo(a)pyrene	106	99	7
Indeno(1,2,3-cd)pyrene	111	108	3
Dibenz(a,h)anthracene	106	104	2
Benzo(g,h,i)perylene	94	88	7
LDW-T1-M-ES-WB-comp-5			
Naphthalene	74	73	1
2-Methylnaphthalene	82	83	1
Acenaphthylene	93	94	1
Acenaphthene	84	86	1
Dibenzofuran	92	93	1
Fluorene	96	99	3
Phenanthrene	90	92	2
Anthracene	101	102	1
Fluoranthene	99	102	3
Pyrene	90	91	1
Benz(a)anthracene	107	110	3
Chrysene	99	101	2
Benzo(b)fluoranthene	101	107	6
Benzo(k)fluoranthene	94	98	4
Benzo(a)pyrene	107	110	3
Indeno(1,2,3-cd)pyrene	110	114	3
Dibenz(a,h)anthracene	106	110	4
Benzo(g,h,i)perylene	93	95	3
LDW-T4-M-ES-WB-comp-2			
Naphthalene	61	79	25
2-Methylnaphthalene	71	88	22
Acenaphthylene	86	97	13
Acenaphthene	77	90	15
Dibenzofuran	88	94	7

SAMPLE/ANALYTE	MS % RECOVERED	MSD % RECOVERED	RELATIVE PERCENT DIFFERENCE
Fluorene	92	97	5
Phenanthrene	84	92	8
Anthracene	94	101	8
Fluoranthene	96	103	7
Pyrene	84	92	9
Benz(a)anthracene	99	102	3
Chrysene	92	94	2
Benzo(b)fluoranthene	97	91	6
Benzo(k)fluoranthene	94	98	4
Benzo(a)pyrene	103	107	3
Indeno(1,2,3-cd)pyrene	106	111	5
Dibenz(a,h)anthracene	105	113	7
Benzo(g,h,i)perylene	90	94	5

Lower Duwamish Waterway Group

Port of Seattle / City of Seattle / King County / The Boeing Company

MEMORANDUM

To: Allison Hiltner, Ginna Greppo-Grove, USEPA
From: Susan McGroddy, Windward Environmental LLC
Subject: Corrective Action for Duwamish Fish and Crab Chemical Analyses
Date: April 22, 2005

This memorandum has been prepared to document the need for corrective action for the Lower Duwamish Fish and Crab tissue analysis described in the quality assurance project plan (QAPP) (Windward 2004). This memo has been prepared in lieu of Form B-3, the Corrective Action Form, because of the complex nature of the action. All of the information required for Form B-3 is presented in this memorandum. Following the successful completion of the action described in this memorandum, the fish and crab tissue dataset will meet the quality assurance/quality control (QA/QC) requirements of EPA for use in the Phase 2 remedial investigation.

Project Name and Number

Lower Duwamish Waterway: Fish and Crab Tissue Collection and Chemical Analyses, CAS Project Number: K2409445, K2409451 and K2409809

Sample Dates Involved

July, August, September, 2004

Measurement Parameter

Polychlorinated biphenyls (PCBs), pesticides, polycyclic aromatic hydrocarbons (PAHs), semi-volatile organic compounds (SVOC), butyltins

Problem Area Requiring Corrective Action

Laboratory failure to run matrix spike/matrix spike duplicate (MS/MSD) samples for organic analytes for three sample delivery groups (SDGs). The number of samples submitted with each SDG is presented in Table 1. MS/MSD samples were required to be run at a frequency of one per SDG or 20 samples, whichever was higher. Two sets of MS/MSD samples were required for SDGs K2409445 and K2409809, and 3 sets of MS/MSD samples were required for SDG K2409451.

Table 1. Number of samples in each SDG

SDG	LAB	SVOCs	LOW LEVEL PAHs	PESTICIDES	PCBs	BUTYLINS
K2409445	Columbia	24	na	24	24	24
K2409451	Columbia	53	53	53	53	53
K2409809	Columbia	31	na	31	31	31

na-not analyzed

Measures Required to Correct Problem

The proposed solution is to run the MS/MSD samples at this time. This analysis will be in addition to the original fish and crab tissue sample analyses and will not entail a reanalysis of all of the fish and crab tissue samples from the Lower Duwamish Waterway.

In situations where sample volume is limited (i.e., most tissue analyses), it is common practice to select different samples to provide MS/MSD samples for the various analytes rather than selecting one sample to provide the MS/MSD samples for all the analytes. The proposed solution in this memorandum follows this standard approach.

The samples listed in Table 2 were selected for MS/MSD analyses to meet the required frequency for each of the SDGs. The samples have been selected based on the mass of tissue originally provided to Columbia Analytical Services (CAS) as well as the amount of tissue preserved in the archive jar stored at Axys. The selected samples had greater than 95 g of tissue in the original CAS sample and greater than 200 g in the archive sample. The goal is to ensure that sufficient tissue is available to do the MS/MSD analysis as well as to ensure that the samples selected for MS/MSD analysis will have sufficient archive material to conduct any reanalysis or additional analyses as needed. Within the groups of samples with sufficient sample mass to run an MS/MSD, samples were selected from as many different matrices as possible to provide the most representative tissue types.

Table 2: Selected MS/MSD samples and original and archival sample masses

SAMPLE ID	TISSUE MATRICES	CAS ORIGINAL SAMPLE MASS (g)	ARCHIVE MASS (g)
SDG K2409809			
LDW-T4-M-SF-FL-comp -1	starry flounder, fillet	105	201
LDW-T3-M-ES-WB-comp-4	English sole, whole body	109	564
LDW-T1-M-DC-EM-comp-1	Dungeness crab, edible meat	192	415
SDG K2409445			
LDW-T4-D-PS-WB-comp-1	Pacific staghorn sculpin, whole body	101	305
LDW-T4-E-PS-WB-	Pacific staghorn sculpin, whole	101	314

comp-1	body		
LDW-T3-E-PS-WB-comp-1	Pacific staghorn sculpin, whole body	102	417
LDW-T3-F-PS-WB-comp-1	Pacific staghorn sculpin, whole body	102	429
LDW-T1-D-PS-WB-comp-1	Pacific staghorn sculpin, whole body	103	372
LDW-T2-A-PS-WB-comp-1	Pacific staghorn sculpin, whole body	104	286
LDW-T3-B-PS-WB-comp-1	Pacific staghorn sculpin, whole body	104	324
LDW-T4-A-PS-WB-comp-1	Pacific staghorn sculpin, whole body	105	390
SDG K2409451			
LDW-T1-M-ES-WB-comp-4	English sole, whole body	98	545
LDW-T1-M-ES-WB-comp-5	English sole, whole body	98	563
LDW-T1-M-ES-WB-comp-2	English sole, whole body	99	512
LDW-T2-M-ES-WB-comp-3	English sole, whole body	99	553
LDW-T1-M-ES-WB-comp-3	English sole, whole body	105	545
LDW-T4-M-ES-WB-comp-2	English sole, whole body	200	636

Means of Detecting Problems and Verifying Correction

The MS/MSD analyses will include one standard reference material (SRM) and laboratory control sample/laboratory control sample duplicate (LCS/LCSD) sample per MS/MSD SDG. The results for the SRM and LCS/LCSD analyses can be compared to the SRM and LCS/LCSD results in the original dataset to identify any systematic differences between the original sample analyses and the subsequent MS/MSD analyses.

The results of the MS/MSD analyses will be compared to the project QA criteria in Table 3. The percent difference between the MS and MSD results will be compared to the project criteria for precision, and the percent recovery for each sample will be compared to the accuracy criteria for each analytical group. The results of this comparison will be presented in a memorandum that will be provided with the MS/MSD results in an addendum to the data report. If the MS/MSD, SRM and LCS results are consistent with the QC criteria, then it is unlikely that the tissue data were influenced by matrix effects. If, however, the MS/MSD results indicate potential matrix effects, then there may be uncertainty with the associated results. The tissue dataset will not be re-validated based on the MS/MSD results because functional guidelines state that no action is taken on MS/MSD data alone.

Table 3. Data quality indicators for tissue analyses

PARAMETER	UNITS	PRECISION	ACCURACY
PCBs as Aroclors	µg/kg ww	±50%	38-150%
Organochlorine pesticides	µg/kg ww	±50%	30-150%
PAHs	µg/kg ww	±50%	20-130%
SVOCs	µg/kg ww	±50%	20-130%
Tributyltin, dibutyltin, monobutyltin (as ions)	µg/kg ww	±50%	20-130%

Windward Project Manager

Name

Date

Windward QA/QC Manager

Name

Date

EPA Project Manager

Name

Date

EPA QA/QC Manager

Name

Date