



APTIM FEDERAL SERVICES, LLC
QATS Program
2700 Chandler Avenue, Building C
Las Vegas, Nevada 89120

Technical Memorandum - Final

To: Justine Barton, Environmental Review and Sediment Management Unit, EPA Region 10
Elisabeth Novak, QATS Task Order 1029 EPA Task Order Contracting Officer's Representative

From: Keith Strout, APTIM Federal Services, LLC – EPA QATS Program

Through: Brett Moody, QATS Program EPA Contracting Officer's Representative

Date: July 30, 2023

Subject: Puget Sound Sediment Reference Material SR0431 – Advisory Control Limits Update

1.0 Introduction

In cooperation with the United States Environmental Protection Agency (EPA) Region 10, and the EPA Analytical Services Branch (ASB) Office of Superfund Remediation and Technology Innovation (OSRTI), a Puget Sound Sediment Reference Material (SRM) was developed and produced at the Quality Assurance Technical Support (QATS) Laboratory in Las Vegas, Nevada in November, 2013. The SRM is designated as Puget Sound SRM SR0431. The QATS Laboratory is operated by APTIM Federal Services, LLC under EPA Contract Number EP-W-16-016.

The Puget Sound SRM was prepared from marine sediment material sampled from Puget Sound in Washington State, and it was developed as a quality assurance (QA) material to assist in the verification and validation of measurement accuracy, and to evaluate and monitor laboratory performance when analyzing sediment samples with low level contamination field-collected from Puget Sound. The Puget Sound SRM was developed for use with high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS) extraction and analysis methods for chlorinated dibenzo-p-dioxin / chlorinated dibenzofuran (CDD/CDF) and chlorinated biphenyl congener (CBC) analytes, as well as for Aroclors using gas chromatography / electron capture detection (GC/ECD) methods. Certified values and advisory control limits for many of the organic analytes in the SRM were initially established using the statistics derived from round-robin, QATS Laboratory, and EPA Contract Laboratory Program (CLP) analyses. All of the analytes in Puget Sound SRM SR0431, for which certified values and advisory control limits were established, were present in the field-collected sediment before processing and were not spiked in the laboratory.

2.0 Background

The QATS Program document titled "Development and Production of the Puget Sound Sediment Reference Material SR0431" (QATS Document ID#: 2029-11132013-1), submitted to EPA Region 10 on November 13, 2013, describes in detail the development and production of the Puget Sound SRM at the EPA QATS Laboratory, including receipt and processing of the starting material, characterization, preliminary and round-robin analysis of the sediment with sample sizes (n) of 12 for the Aroclors and 9

Expect the Extraordinary.



The Quality Assurance Technical Support (QATS) contract is operated by APTIM Federal Services, LLC. The QATS Program's Quality Management System is certified to the ISO 9001:2015 International Standard.



to 10 for the CDD/CDFs, development of certified analyte values and advisory control limits, and packaging and storage of the finished Puget Sound SRM. Control Limits define a range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged to determine if the SRM results may potentially impact the project sample results. The Puget Sound SRM control limits are advisory control limits.

Since the time of its development in November, 2013, the Puget Sound SRM has been stored, maintained, and shipped from the QATS Facility in Las Vegas, Nevada. The inventory and management responsibilities of the SRM were transferred from the QATS Laboratory to the USEPA Region 10 Laboratory in Port Orchard, Washington in March, 2023.

3.0 2023 Puget Sound SRM Advisory Control Limits Update

In May, 2023, the QATS Program was tasked to recalculate, statistically evaluate, and update the Aroclor 1260 and CDD/CDF advisory control limits for the SRM using the initial data combined with additional data (referred to in this report as “composite”) which has become available since the onset of SRM distribution for Puget Sound projects. For the advisory control limits update project, a total of 92 Aroclor sample results and 76 CDD/CDF sample results were available for statistical processing, including those from the initial 2013 study and various subsequent Region 10 and Puget Sound projects.

During the initial SRM development project, the Aroclor raw data submitted by the laboratories were reviewed for identification and quantitation validity using the criteria in the CLP Statement of Work (SOW) and EPA Method 8082, as well as the USEPA CLP National Functional Guidelines (NFG) for Superfund Organic Methods Data Review (June 2008). Aroclor 1260 was the only target Aroclor positively identified and reported. The 2013 initial average Aroclor result and associated statistics and calculated advisory control limits are presented in Table 1 below.

The 2023 updated average Aroclor result and associated statistics and calculated advisory control limits are presented in Table 2 below. The Grubbs’ Test for outliers was performed on the available data (alpha value = 0.05 significance level) and there were no statistical outliers detected in the data set. The QATS Program maintains a historic database of results and statistics derived from the CLP proficiency testing (PT) round-robin events. Based on these historical statistics, the relative standard deviation (RSD) value of 17.0 percent derived from the 2023 statistical evaluation was within the expected range for Aroclors in soil. The historical statistical database for Aroclors in soil samples may not necessarily apply to Aroclors in sediment samples; however, it does provide a useful statistical comparison for this project.

Upon consultation with the Puget Sound SRM Interagency Workgroup, the 2013 initial advisory control limits for Aroclor 1260 in Puget Sound SRM SR0431 of 41 ug/Kg to 180 ug/Kg were set using the calculated 95% confidence interval (CI) around the average concentration of 108 ug/Kg. The updated calculated 95% CI around the updated average result is substantially narrower than the initial interval, resulting in narrower advisory control limits of 75 ug/Kg to 151 ug/Kg for Aroclor 1260. Typically, the 99% CI is used as the control limit interval for performance evaluation samples (PES). The 99% CI advisory control limits were not used in 2013 because the Interagency Workgroup decided that because they were established using a limited number of data points, the resulting limits were too wide. The updated calculated 99% CI around the updated average of 113 ug/Kg, resulting in advisory control limits of 62 ug/Kg to 164 ug/Kg for Aroclor 1260, is statistically more appropriate for the 2023 updated data set. Using the 99% CI limits, a total of one of the 2023 composite analytical results was outside



the advisory control limits, whereas using the 95% CI limits, a total of five of the 2023 composite analytical results were outside the advisory control limits. Therefore, we recommend using the advisory control limits based on the 99% CI presented in Table 2 in evaluating Puget Sound SRM Aroclor 1260 results for Puget Sound projects. It should be noted that the majority of the Aroclor results used for the advisory control limits update project (68 of 92) were derived from SRM analyses from one laboratory.

In addition to reporting detected results for Aroclor 1260, some of the laboratories reported detected results for Aroclor 1254. As mentioned above, using the criteria in the analytical method, as well as the NFG cited above, the reported results for Aroclor 1254 could not be authenticated upon review. Aroclor 1260 is the only Aroclor in the Puget Sound SRM with a certified average value and advisory control limits. Reported detected results for any other Aroclors in the Puget Sound SRM should be classified as “not evaluated”, unless they are misidentifications of Aroclor 1260, or if they can be classified as false positive results based on blank sample or other QA sample results. In either case, the non-Aroclor 1260 results should be qualified appropriately.

The following is a list of definitions for the acronyms used in the tables in this report

Acronym	Definition	Acronym	Definition
% Diff.	Percent difference	Min	Minimum value in sample set
Avg.	Average	Max	Maximum value in sample set
CAS No.	Chemical Abstracts Service number	n	Number of values
Conc.	Concentration	QL	Quantitation limit
CI	Confidence interval	RSD	Relative standard deviation
LCS	Laboratory control sample	SD	Standard deviation

Table 1: Puget Sound SRM 2013 Initial Composite Laboratory Results and Advisory Control Limits - Aroclors

	Aroclor Target Analyte	CAS No.	QL ug/Kg	Avg. Conc. ug/Kg	SD ug/Kg	RSD	Min ug/Kg	Max ug/Kg	n	Advisory Control Limits** (ug/Kg)	
										Low	High
1	Aroclor 1016	12674-11-2	33	33 U*	-----	-----	-----	-----	----	-----	-----
2	Aroclor 1221	11104-28-2	33	33 U	-----	-----	-----	-----	----	-----	-----
3	Aroclor 1232	11141-16-5	33	33 U	-----	-----	-----	-----	----	-----	-----
4	Aroclor 1242	53469-21-9	33	33 U	-----	-----	-----	-----	----	-----	-----
5	Aroclor 1248	12672-29-6	33	33 U	-----	-----	-----	-----	----	-----	-----
6	Aroclor 1254	11097-69-1	33	33 U	-----	-----	-----	-----	----	-----	-----
7	Aroclor 1260	11096-82-5	33	108	29	27.1	59	150	12	41	180
8	Aroclor 1262	37324-23-5	33	33 U	-----	-----	-----	-----	----	-----	-----
9	Aroclor 1268	11100-14-4	33	33 U	-----	-----	-----	-----	----	-----	-----

*U = Not detected above the required quantitation limit (RQL)

** The 2013 Advisory Control Limits were set using the calculated 95% CI around the average concentration.



Table 2: Puget Sound SRM 2023 Updated Composite Laboratory Results and Advisory Control Limits - Aroclors

	Aroclor Target Analyte	CAS No.	QL ug/Kg	Avg. Conc. ug/Kg	SD ug/Kg	RSD	Min ug/Kg	Max ug/Kg	n	Advisory Control Limits** (ug/Kg)	
										Low	High
1	Aroclor 1016	12674-11-2	33	33 U*	-----	-----	-----	-----	-----	-----	-----
2	Aroclor 1221	11104-28-2	33	33 U	-----	-----	-----	-----	-----	-----	-----
3	Aroclor 1232	11141-16-5	33	33 U	-----	-----	-----	-----	-----	-----	-----
4	Aroclor 1242	53469-21-9	33	33 U	-----	-----	-----	-----	-----	-----	-----
5	Aroclor 1248	12672-29-6	33	33 U	-----	-----	-----	-----	-----	-----	-----
6	Aroclor 1254	11097-69-1	33	33 U	-----	-----	-----	-----	-----	-----	-----
7	Aroclor 1260	11096-82-5	33	113	19.2	17.0	59	162	92	62	164
8	Aroclor 1262	37324-23-5	33	33 U	-----	-----	-----	-----	-----	-----	-----
9	Aroclor 1268	11100-14-4	33	33 U	-----	-----	-----	-----	-----	-----	-----

*U = Not detected above the RQL

** The 2023 Advisory Control Limits were set using the calculated 99% CI around the average concentration. The data used to calculate these limits includes the 2013 data.

Table 3 below presents a side-by-side comparison of the 2013 and 2023 composite statistical results for Aroclor 1260, indicating that the 2023 updated average is 4.6 percent greater than the 2013 average, and the 2023 RSD value indicates a higher degree of analytical accuracy and precision compared to the 2013 data set. Table 4 below presents a side-by-side comparison of the 2013 and 2023 calculated advisory control limits for Aroclor 1260. As stated above, the calculated advisory control limits of 75 ug/Kg to 151 ug/Kg based on the 95% CI using the 2023 data set is substantially narrower than the current advisory control limits of 41 ug/Kg to 180 ug/Kg, which is, in part, why we recommend using the calculated advisory control limits based on the 99% CI. The narrower 99% CI Advisory Control Limits of 62 ug/Kg (low) to 164 ug/Kg (high) based on the 2023 data set are also an indication of a higher degree of accuracy and precision in the 2023 data set.

Table 3: Puget Sound SRM 2013 and 2023 Composite Statistical Results Comparison - Aroclors

Aroclor Target Analyte	CAS No.	QL ug/Kg	2013 Avg. Conc. ug/Kg	2023 Avg. Conc. ug/Kg	Avg. Conc. % Diff.	2013	2023	2013	2023
						RSD	RSD	n	n
Aroclor 1260	11096-82-5	33	108	113	4.6	27.1	17.0	12	92

Table 4: Puget Sound SRM 2013 and 2023 Advisory Control Limits Comparison - Aroclors

Aroclor Target Analyte	QL ug/Kg	2013 Avg. Conc. ug/Kg	2023 Avg. Conc. ug/Kg	2013 95% CI Advisory Control Limits (ug/Kg)		2023 99% CI Advisory Control Limits (ug/Kg)	
				Low	High	Low	High
Aroclor 1260	33	108	113	41	180	62	164

The initial average CDD/CDF results and associated statistics and calculated advisory control limits are presented in Table 5 below. The 2023 updated average CDD/CDF results and associated statistics and calculated advisory control limits, using the 99% CIs, are presented in Table 6 below. The Grubbs' Test for outliers was performed on the available data (alpha value = 0.05 significance level) and a total of 32 of the 1,292 2,3,7,8-chlorinated target CDD/CDF congeners (2.5% of the data set) were identified as statistical outliers in the data set and were removed from further statistical processing. The QATS Program maintains a historic database of results and statistics derived from the CLP CDD/ PT round-robin events. Based on these historical statistics, the RSD values for the remaining individual CDD/CDF congener data (minus outliers) from the 2023 statistical evaluation were within the expected range for CDD/CDF analytes in soil. The historical statistical database for CDD/CDF analytes in soil samples may not necessarily apply to CDD/CDF analytes in sediment samples; however, it does provide a useful statistical comparison for this project.

Upon consultation with the Puget Sound SRM Interagency Workgroup, the 2013 initial advisory control limits for 2,3,7,8-chlorinated CDD/CDF congeners in Puget Sound SRM SR0431 were set at $\pm 50\%$ around the average concentrations. Using the 2023 updated data and statistics, advisory control limits were calculated using the 95% CIs, 99% CIs, $\pm 30\%$ around the average concentrations, $\pm 50\%$ around the average concentrations, and \pm the EPA Method 1613 laboratory control sample (LCS) limits around the average concentrations. Table 7 presents the number of CDD/CDF results exceeding the various calculated advisory control limits listed above. The lowest number of CDD/CDF results exceeding any of the calculated advisory control limits listed above is 21 for the $\pm 99\%$ CIs advisory control limits (1.7% of the data set). The 2013 CDD/CDF advisory control limits are based on $\pm 50\%$ around the average results, and 35 of the data points exceed the 2023 updated $\pm 50\%$ advisory control limits. Using the calculated advisory control limits based on the 99% CIs around the average results has a higher degree of statistical defensibility than using arbitrary advisory control limits based on $\pm 50\%$ around the average results. Therefore, we recommend using the advisory control limits based on the 99% CI presented in Table 6 in evaluating Puget Sound SRM 2,3,7,8-chlorinated CDD/CDF congener results for Puget Sound projects. It should be noted that the majority of the CDD/CDF results used for the advisory control limits update project (50 of 76) were derived from SRM analyses from one laboratory.

Table 5: Puget Sound SRM 2013 Initial Composite Laboratory Results and Advisory Control Limit – CDD/CDF Analytes

No.	CDD/CDF Target Analyte	CAS No.	QL ng/Kg	Avg. Conc. ng/Kg	SD ng/Kg	RSD	Min ng/Kg	Max ng/Kg	n	Advisory Control Limits* (ng/Kg)	
										Low	High
1	2,3,7,8-TCDD	1746-01-6	1.0	1.05	0.25	24.1	0.695	1.50	10	0.525	1.57
2	1,2,3,7,8-PeCDD	40321-76-4	5.0	1.08	0.39	35.6	0.630	1.72	10	0.542	1.63
3	1,2,3,4,7,8-HxCDD	39227-28-6	5.0	1.59	0.46	28.6	0.930	2.43	10	0.797	2.39
4	1,2,3,6,7,8-HxCDD	67653-85-7	5.0	3.88	0.73	18.7	2.35	4.72	10	1.94	5.82
5	1,2,3,7,8,9-HxCDD	19408-74-3	5.0	3.04	0.74	24.3	1.47	3.80	10	1.52	4.55
6	1,2,3,4,6,7,8-HpCDD	35822-46-9	5.0	90.6	12.78	14.1	64.0	106	10	45.3	136
7	OCDD	3268-87-9	10.0	811	106.51	13.1	620	937	10	406	1220
8	2,3,7,8-TCDF	51207-31-9	1.0	1.11	0.50	44.8	0.688	2.10	10	0.557	1.67
9	1,2,3,7,8-PeCDF	57117-41-6	5.0	1.23	0.57	46.5	0.794	2.65	10	0.613	1.84
10	2,3,4,7,8-PeCDF	57117-31-4	5.0	1.07	0.41	38.5	0.673	2.01	10	0.533	1.60
11	1,2,3,4,7,8-HxCDF	70648-26-9	5.0	3.02	0.58	19.3	2.17	3.81	10	1.51	4.53
12	1,2,3,6,7,8-HxCDF	57117-44-9	5.0	1.09	0.33	29.9	0.680	1.61	10	0.545	1.64



Table 5: Puget Sound SRM 2013 Initial Composite Laboratory Results and Advisory Control Limit – CDD/CDF Analytes

No.	CDD/CDF Target Analyte	CAS No.	QL ng/Kg	Avg. Conc. ng/Kg	SD ng/Kg	RSD	Min ng/Kg	Max ng/Kg	n	Advisory Control Limits* (ng/Kg)	
										Low	High
13	1,2,3,7,8,9-HxCDF	72918-21-9	5.0	0.511	0.35	68.3	0.071	1.16	9	0.255	0.77
14	2,3,4,6,7,8-HxCDF	60851-34-5	5.0	1.83	0.59	32.3	1.04	2.78	10	0.917	2.75
15	1,2,3,4,6,7,8-HpCDF	67562-39-4	5.0	18.7	2.94	15.7	13.8	22.1	10	9.36	28.1
16	1,2,3,4,7,8,9-HpCDF	55673-89-7	5.0	1.63	0.44	27.3	1.14	2.42	10	0.815	2.44
17	OCDF	39001-02-0	10.0	58.4	8.99	15.4	45.0	71.0	10	29.2	87.6

* The 2013 Advisory Control Limits for 2,3,7,8-chlorinated CDD/CDF congeners in Puget Sound SRM SR0431 were set at $\pm 50\%$ around the average concentrations.

Table 6: Puget Sound SRM 2023 Updated Composite Laboratory Results and Advisory Control Limits CDD/CDF Analytes

No.	CDD/CDF Target Analyte	CAS No.	QL ng/Kg	Avg. Conc. ng/Kg	SD ng/Kg	RSD	Min ng/Kg	Max ng/Kg	n	Advisory Control Limits* (ng/Kg)	
										Low	High
1	2,3,7,8-TCDD	1746-01-6	1.0	1.04	0.14	13.4	0.695	1.50	74	0.671	1.42
2	1,2,3,7,8-PeCDD	40321-76-4	5.0	1.17	0.23	19.5	0.630	1.91	75	0.562	1.79
3	1,2,3,4,7,8-HxCDD	39227-28-6	5.0	1.51	0.25	16.5	0.915	2.31	75	0.844	2.17
4	1,2,3,6,7,8-HxCDD	67653-85-7	5.0	3.95	0.55	14.0	2.35	5.13	76	2.48	5.42
5	1,2,3,7,8,9-HxCDD	19408-74-3	5.0	2.92	0.40	13.8	1.96	3.80	74	1.85	3.99
6	1,2,3,4,6,7,8-HpCDD	35822-46-9	5.0	103	9.83	9.6	79.7	126	74	76.3	129
7	OCDD	3268-87-9	10.0	888	113	12.8	620	1170	75	584	1190
8	2,3,7,8-TCDF	51207-31-9	1.0	0.917	0.16	16.9	0.384	1.39	70	0.505	1.33
9	1,2,3,7,8-PeCDF	57117-41-6	5.0	1.10	0.22	20.1	0.430	1.74	73	0.510	1.69
10	2,3,4,7,8-PeCDF	57117-31-4	5.0	0.915	0.19	20.2	0.589	1.50	74	0.421	1.41
11	1,2,3,4,7,8-HxCDF	70648-26-9	5.0	2.95	0.40	13.6	1.67	3.9	73	1.88	4.01
12	1,2,3,6,7,8-HxCDF	57117-44-9	5.0	1.04	0.22	20.9	0.331	1.60	76	0.457	1.61
13	1,2,3,7,8,9-HxCDF	72918-21-9	5.0	0.604	0.24	39.5	0.071	1.34	73	NL	1.24
14	2,3,4,6,7,8-HxCDF	60851-34-5	5.0	1.83	0.44	24.1	0.498	2.79	76	0.655	3.01
15	1,2,3,4,6,7,8-HpCDF	67562-39-4	5.0	19.8	2.09	10.5	13.8	25.9	74	14.2	25.3
16	1,2,3,4,7,8,9-HpCDF	55673-89-7	5.0	1.65	0.26	15.8	1.14	2.42	74	0.957	2.35
17	OCDF	39001-02-0	10.0	60.9	11.6	19.0	29.2	102	74	30.1	91.7

* The 2023 Advisory Control Limits for 2,3,7,8-chlorinated CDD/CDF analytes are based on updated results and associated statistics using the 99% CI around the average concentrations. The data used to calculate these limits includes the 2013 and 2023 data.

Table 7: Puget Sound SRM – Number of CDD/CDF Results Exceeding Various 2023 Updated Advisory Control Limits

No.	CDD/CDF Target Analyte	CAS No.	QL ng/Kg	Avg. Conc. ng/Kg	# Outside 95% CI	# Outside 99% CI	# Outside $\pm 30\%$ of Avg.	# Outside $\pm 50\%$ of Avg.	# Outside $\pm LCS$ Limits
1	2,3,7,8-TCDD	1746-01-6	1.0	1.04	4	1	2	0	1
2	1,2,3,7,8-PeCDD	40321-76-4	5.0	1.17	4	1	11	1	9
3	1,2,3,4,7,8-HxCDD	39227-28-6	5.0	1.51	6	1	6	1	4



Table 7: Puget Sound SRM – Number of CDD/CDF Results Exceeding Various 2023 Updated Advisory Control Limits

No.	CDD/CDF Target Analyte	CAS No.	QL ng/Kg	Avg. Conc. ng/Kg	# Outside 95% CI	# Outside 99% CI	# Outside ±30% of Avg.	# Outside ±50% of Avg.	# Outside ±LCS Limits
4	1,2,3,6,7,8-HxCDD	67653-85-7	5.0	3.95	4	2	2	0	4
5	1,2,3,7,8,9-HxCDD	19408-74-3	5.0	2.92	4	0	3	0	0
6	1,2,3,4,6,7,8-HpCDD	35822-46-9	5.0	103	6	0	0	0	0
7	OCDD	3268-87-9	10.0	888	4	0	2	0	4
8	2,3,7,8-TCDF	51207-31-9	1.0	0.917	4	2	6	2	3
9	1,2,3,7,8-PeCDF	57117-41-6	5.0	1.10	5	2	8	3	12
10	2,3,4,7,8-PeCDF	57117-31-4	5.0	0.915	3	1	9	3	2
11	1,2,3,4,7,8-HxCDF	70648-26-9	5.0	2.95	4	1	2	0	1
12	1,2,3,6,7,8-HxCDF	57117-44-9	5.0	1.04	7	2	8	5	16
13	1,2,3,7,8,9-HxCDF	72918-21-9	5.0	0.604	9	1	21	14	24
14	2,3,4,6,7,8-HxCDF	60851-34-5	5.0	1.83	4	2	13	4	7
15	1,2,3,4,6,7,8-HpCDF	67562-39-4	5.0	19.8	6	2	2	0	4
16	1,2,3,4,7,8,9-HpCDF	55673-89-7	5.0	1.65	4	1	5	0	9
17	OCDF	39001-02-0	10.0	60.9	3	2	5	2	1
Total					81	21	105	35	101

Table 8 below presents a side-by-side comparison of the 2013 and 2023 composite statistical results for the CDD/CDF analytes, indicating the percent differences between the 2023 updated averages compared to the 2013 averages, which range from -17.4% to +18.2%. The 2023 RSD values are lower than the 2013 RSD values with the exception of OCDF. This generally indicates a higher degree of analytical accuracy and precision for the 2023 data set compared to the 2013 data set. Table 9 below presents a side-by-side comparison of the 2013 and 2023 calculated advisory control limits for the CDD/CDF analytes. The proposed 2023 advisory control limits are generally slightly narrower than the 2013 advisory control limits, with the 2023 limits based on the 99% CIs and the 2013 limits based on ±50% around the average results.

Table 8: Puget Sound SRM 2013 and 2023 Composite Statistical Results Comparison – CDD/CDF Analytes

CDD/CDF Target Analyte	CAS No.	QL ng/Kg	2013 Avg. Conc. ng/Kg	2023 Avg. Conc. ng/Kg	Avg. Conc. % Diff.	2013 RSD	2023 RSD	2013 n	2023 n
2,3,7,8-TCDD	1746-01-6	1.0	1.05	1.04	-0.6	24.1	13.4	10	74
1,2,3,7,8-PeCDD	40321-76-4	5.0	1.08	1.17	8.7	35.6	19.5	10	75
1,2,3,4,7,8-HxCDD	39227-28-6	5.0	1.59	1.51	-5.0	28.6	16.5	10	75
1,2,3,6,7,8-HxCDD	67653-85-7	5.0	3.88	3.95	1.8	18.7	14.0	10	76
1,2,3,7,8,9-HxCDD	19408-74-3	5.0	3.04	2.92	-4.0	24.3	13.8	10	74
1,2,3,4,6,7,8-HpCDD	35822-46-9	5.0	90.6	103	13.7	14.1	9.6	10	74
OCDD	3268-87-9	10.0	811	888	9.5	13.1	12.8	10	75
2,3,7,8-TCDF	51207-31-9	1.0	1.11	0.917	-17.4	44.8	16.9	10	70
1,2,3,7,8-PeCDF	57117-41-6	5.0	1.23	1.10	-10.7	46.5	20.1	10	73
2,3,4,7,8-PeCDF	57117-31-4	5.0	1.07	0.915	-14.5	38.5	20.2	10	74



Table 8: Puget Sound SRM 2013 and 2023 Composite Statistical Results Comparison – CDD/CDF Analytes

CDD/CDF Target Analyte	CAS No.	QL ng/Kg	2013 Avg. Conc. ng/Kg	2023 Avg. Conc. ng/Kg	Avg. Conc. % Diff.	2013	2023	2013	2023
						RSD	RSD	n	n
1,2,3,4,7,8-HxCDF	70648-26-9	5.0	3.02	2.95	-2.3	19.3	13.6	10	73
1,2,3,6,7,8-HxCDF	57117-44-9	5.0	1.09	1.04	-4.6	29.9	20.9	10	76
1,2,3,7,8,9-HxCDF	72918-21-9	5.0	0.511	0.604	18.2	68.3	39.5	9	73
2,3,4,6,7,8-HxCDF	60851-34-5	5.0	1.83	1.83	0.2	32.3	24.1	10	76
1,2,3,4,6,7,8-HpCDF	67562-39-4	5.0	18.7	19.8	5.9	15.7	10.5	10	74
1,2,3,4,7,8,9-HpCDF	55673-89-7	5.0	1.63	1.65	1.2	27.3	15.8	10	74
OCDF	39001-02-0	10.0	58.4	60.9	4.3	15.4	19.0	10	74

Table 9: Puget Sound SRM 2013 and 2023 Advisory Control Limits Comparison – CDD/CDF Analytes

CDD/CDF Target Analyte	QL ng/Kg	2013 Avg. Conc. ng/Kg	2023 Avg. Conc. ng/Kg	2013 ±50% Advisory Control Limits (ng/Kg)		2023 99% CI Advisory Control Limits (ng/Kg)	
				Low	High	Low	High
2,3,7,8-TCDD	1.0	1.05	1.04	0.525	1.57	0.671	1.42
1,2,3,7,8-PeCDD	5.0	1.08	1.17	0.542	1.63	0.562	1.79
1,2,3,4,7,8-HxCDD	5.0	1.59	1.51	0.797	2.39	0.844	2.17
1,2,3,6,7,8-HxCDD	5.0	3.88	3.95	1.94	5.82	2.48	5.42
1,2,3,7,8,9-HxCDD	5.0	3.04	2.92	1.52	4.55	1.85	3.99
1,2,3,4,6,7,8-HpCDD	5.0	90.6	103	45.3	136	76.3	129
OCDD	10.0	811	888	406	1220	584	1190
2,3,7,8-TCDF	1.0	1.11	0.917	0.557	1.67	0.505	1.33
1,2,3,7,8-PeCDF	5.0	1.23	1.10	0.613	1.84	0.510	1.69
2,3,4,7,8-PeCDF	5.0	1.07	0.915	0.533	1.60	0.421	1.41
1,2,3,4,7,8-HxCDF	5.0	3.02	2.95	1.51	4.53	1.88	4.01
1,2,3,6,7,8-HxCDF	5.0	1.09	1.04	0.545	1.64	0.457	1.61
1,2,3,7,8,9-HxCDF	5.0	0.511	0.604	0.255	0.77	NL	1.24
2,3,4,6,7,8-HxCDF	5.0	1.83	1.83	0.917	2.75	0.655	3.01
1,2,3,4,6,7,8-HpCDF	5.0	18.7	19.8	9.36	28.1	14.2	25.3
1,2,3,4,7,8,9-HpCDF	5.0	1.63	1.65	0.815	2.44	0.957	2.35
OCDF	10.0	58.4	60.9	29.2	87.6	30.1	91.7

Table 10 below presents the Toxicity Equivalency Quotient (TEQ) based on the 2013 average concentrations of the CDD/CDF congeners and the respective World Health Organization toxic equivalency factors (WHO TEF), and Table 11 below presents the TEQ based on the 2023 average concentrations of the CDD/CDF congeners and the respective WHO TEFs.

Table 10: 2013 Initial TEQ Based on Composite Laboratory Results – CDD/CDF Analytes

No.	CDD/CDF Target Analyte	CAS No.	Avg. Conc. ng/Kg	TEF* Mammals	TEF Adj. Conc.** Mammals ng/Kg	TEF Fish	TEF Adj. Conc. Fish ng/Kg	TEF Birds	TEF Adj. Conc. Birds ng/Kg
1	2,3,7,8-TCDD	1746-01-6	1.05	1.0	1.05	1.0	1.05	1.0	1.05
2	1,2,3,7,8-PeCDD	40321-76-4	1.08	1.0	1.08	1.0	1.08	1.0	1.08
3	1,2,3,4,7,8-HxCDD	39227-28-6	1.59	0.1	0.159	0.5	0.795	0.05	0.079
4	1,2,3,6,7,8-HxCDD	67653-85-7	3.88	0.1	0.388	0.01	0.039	0.01	0.039
5	1,2,3,7,8,9-HxCDD	19408-74-3	3.04	0.1	0.304	0.01	0.030	0.1	0.304
6	1,2,3,4,6,7,8-HpCDD	35822-46-9	90.6	0.01	0.906	0.001	0.091	0.001	0.091
7	OCDD	3268-87-9	811	0.0003	0.243	0.0001	0.081	0.0001	0.081
8	2,3,7,8-TCDF	51207-31-9	1.11	0.1	0.111	0.05	0.056	1.0	1.11
9	1,2,3,7,8-PeCDF	57117-41-6	1.23	0.03	0.037	0.05	0.062	0.1	0.123
10	2,3,4,7,8-PeCDF	57117-31-4	1.07	0.3	0.321	0.5	0.535	1.0	1.07
11	1,2,3,4,7,8-HxCDF	70648-26-9	3.02	0.1	0.302	0.1	0.302	0.1	0.302
12	1,2,3,6,7,8-HxCDF	57117-44-9	1.09	0.1	0.109	0.1	0.109	0.1	0.109
13	1,2,3,7,8,9-HxCDF	72918-21-9	0.511	0.1	0.051	0.1	0.051	0.1	0.051
14	2,3,4,6,7,8-HxCDF	60851-34-5	1.83	0.1	0.183	0.1	0.183	0.1	0.183
15	1,2,3,4,6,7,8-HpCDF	67562-39-4	18.7	0.01	0.187	0.01	0.187	0.01	0.187
16	1,2,3,4,7,8,9-HpCDF	55673-89-7	1.63	0.01	0.016	0.01	0.016	0.01	0.016
17	OCDF	39001-02-0	58.4	0.0003	0.018	0.0001	0.006	0.0001	0.006
TEQ					5.46		4.67		5.88

* TEF = Toxic Equivalency Factor from World Health Organization (WHO) (Mammal 2005, Fish and Bird 1998).

** TEF Adj. Conc. = Adjusted concentration of each congener based on the product of the detected concentration and the respective TEF.

Table 11: 2023 Updated TEQ Based on Composite Laboratory Results – CDD/CDF Analytes

No.	CDD/CDF Target Analyte	CAS No.	Avg. Conc. ng/Kg	TEF* Mammals	TEF Adj. Conc.** Mammals ng/Kg	TEF Fish	TEF Adj. Conc. Fish ng/Kg	TEF Birds	TEF Adj. Conc. Birds ng/Kg
1	2,3,7,8-TCDD	1746-01-6	1.04	1.0	1.04	1.0	1.04	1.0	1.04
2	1,2,3,7,8-PeCDD	40321-76-4	1.17	1.0	1.17	1.0	1.17	1.0	1.17
3	1,2,3,4,7,8-HxCDD	39227-28-6	1.51	0.1	0.151	0.5	0.755	0.05	0.076
4	1,2,3,6,7,8-HxCDD	67653-85-7	3.95	0.1	0.395	0.01	0.040	0.01	0.040
5	1,2,3,7,8,9-HxCDD	19408-74-3	2.92	0.1	0.292	0.01	0.029	0.1	0.292
6	1,2,3,4,6,7,8-HpCDD	35822-46-9	103	0.01	1.03	0.001	0.103	0.001	0.103
7	OCDD	3268-87-9	888	0.0003	0.266	0.0001	0.089	0.0001	0.089
8	2,3,7,8-TCDF	51207-31-9	0.917	0.1	0.092	0.05	0.046	1.0	0.917
9	1,2,3,7,8-PeCDF	57117-41-6	1.10	0.03	0.033	0.05	0.055	0.1	0.110
10	2,3,4,7,8-PeCDF	57117-31-4	0.915	0.3	0.275	0.5	0.458	1.0	0.915

Table 11: 2023 Updated TEQ Based on Composite Laboratory Results – CDD/CDF Analytes

No.	CDD/CDF Target Analyte	CAS No.	Avg. Conc. ng/Kg	TEF* Mammals	TEF Adj. Conc.** Mammals ng/Kg	TEF Fish	TEF Adj. Conc. Fish ng/Kg	TEF Birds	TEF Adj. Conc. Birds ng/Kg
11	1,2,3,4,7,8-HxCDF	70648-26-9	2.95	0.1	0.295	0.1	0.295	0.1	0.295
12	1,2,3,6,7,8-HxCDF	57117-44-9	1.04	0.1	0.104	0.1	0.104	0.1	0.104
13	1,2,3,7,8,9-HxCDF	72918-21-9	0.604	0.1	0.060	0.1	0.060	0.1	0.060
14	2,3,4,6,7,8-HxCDF	60851-34-5	1.83	0.1	0.183	0.1	0.183	0.1	0.183
15	1,2,3,4,6,7,8-HpCDF	67562-39-4	19.8	0.01	0.198	0.01	0.198	0.01	0.198
16	1,2,3,4,7,8,9-HpCDF	55673-89-7	1.65	0.01	0.017	0.01	0.017	0.01	0.017
17	OCDF	39001-02-0	60.9	0.0003	0.018	0.0001	0.006	0.0001	0.006
TEQ					5.62		4.65		5.61

* TEF = Toxic Equivalency Factor from World Health Organization (WHO) (Mammal 2005, Fish and Bird 1998).

** TEF Adj. Conc. = Adjusted concentration of each congener based on the product of the detected concentration and the respective TEF.

4.0 Summary, Conclusions, and Recommendations

In cooperation with the USEPA Region 10, and the EPA ASB OSRTI, a Puget Sound SRM was developed and produced at the QATS Laboratory in Las Vegas, Nevada in November, 2013. In May, 2023, the QATS Program was tasked to recalculate, statistically evaluate, and update the Aroclor 1260 and CDD/CDF advisory control limits for the SRM using the initial data combined with additional data which has become available since the onset of SRM distribution for Puget Sound projects. For the advisory control limits update project, a total of 92 Aroclor sample results and 76 CDD/CDF sample results were available from the initial study and various Puget Sound projects for statistical processing. The 2023 sample data set is significantly larger than the 2013 sample data set of 12 Aroclor sample data points and 9 to 10 CDD/CDF sample data points.

The 2023 updated average Aroclor result and associated statistics and calculated advisory control limits are presented in Table 2 of this report. The 2013 initial advisory control limits for Aroclor 1260 in the Puget Sound SRM of 41 ug/Kg to 180 ug/Kg were set using the calculated 95% CI around the average concentration. The updated calculated 95% CI around the updated average result is substantially narrower than the initial CI, resulting in narrower advisory control limits of 75 ug/Kg to 151 ug/Kg for Aroclor 1260. Typically, the 99% CI is used as the advisory control limit interval for PESs. The updated calculated 99% CI around the updated average of 113 ug/Kg, resulting in advisory control limits of 62 ug/Kg to 164 ug/Kg for Aroclor 1260, is statistically more appropriate for the 2023 updated data set. Significant summary findings for the Aroclor advisory control limits update include:

- The 2023 Aroclor 1260 average concentration is 113 ug/Kg, a 4.6% increase from the 2013 average concentration of 108 ug/Kg;
- The 2023 RSD value of 17.0% for the Aroclor 1260 results is significantly lower than the RSD value of 27.1% for the 2013 data set, indicating a higher degree of analytical precision;
- The 2023 data set (n=92) is substantially larger than the 2013 data set (n=12) resulting in a higher degree of confidence in the 2023 calculated advisory control limits;

- Based on the 99% CI limits, a total of one of the 2023 composite analytical results was outside the advisory control limits, whereas using the narrower recalculated 95% CI limits, a total of five of the 2023 composite analytical results were outside the advisory control limits; and,
- Using the advisory control limits based on the 99% CI presented in Table 2 of this report in evaluating Puget Sound SRM Aroclor 1260 results for Puget Sound projects is recommended.

The initial average CDD/CDF results and associated statistics and calculated advisory control limits are presented in Table 5 of this report. The 2023 updated average CDD/CDF results and associated statistics and calculated advisory control limits, using the 99% CIs, are presented in Table 6 of this report. The 2013 initial advisory control limits for 2,3,7,8-chlorinated CDD/CDF congeners in the Puget Sound SRM were set at ± 50 percent around the average concentrations. Using the 2023 updated data and statistics, advisory control limits were calculated using the 95% CIs, 99% CIs, $\pm 30\%$ around the average concentrations, $\pm 50\%$ around the average concentrations, and \pm the EPA Method 1613 LCS limits around the average concentrations. Table 7 of this report presents the number of CDD/CDF results exceeding the various calculated advisory control limits listed above. The lowest number of CDD/CDF results exceeding any of the calculated advisory control limits listed above is 21 for the $\pm 99\%$ CI advisory control limits. The 2013 CDD/CDF advisory control limits are based on $\pm 50\%$ around the average results, and 35 of the data points exceed the 2023 updated $\pm 50\%$ advisory control limits. Using the updated calculated advisory control limits based on the 99% CIs around the average results has a higher degree of statistical defensibility than using arbitrary advisory control limits based on $\pm 50\%$ around the average results. Significant summary findings for the CDD/CDF advisory control limits update include:

- The percent differences between the 2023 updated averages compared to the 2013 averages, range from -17.4% to +18.2%, with 12 of the 17 congeners below 10% difference;
- As indicated in Table 8 of this report, the 2023 RSD values are significantly lower than the 2013 RSD values, with the exception of OCDF, indicating a higher degree of analytical accuracy and precision for the 2023 data set compared to the 2013 data set;
- The 2023 data set (n=70 to 76) is substantially larger than the 2013 data set (n=9 or 10) resulting in a higher degree of confidence in the 2023 calculated advisory control limits;
- The proposed 2023 CDD/CDF advisory control limits are generally slightly narrower than the 2013 advisory control limits, with the 2023 limits based on the 99% CIs and the 2013 limits based on $\pm 50\%$ around the average results;
- Based on the recalculated 2023 99% CI advisory control limits, a total of 21 of the 1,260 2023 composite analytical results were outside the advisory control limits, whereas using the recalculated $\pm 50\%$ around the average results advisory control limits, a total of 35 of the 1,260 2023 composite analytical results were outside the advisory control limits; and,
- Using the advisory control limits based on the 99% CI presented in Table 6 of this report in evaluating Puget Sound SRM 2,3,7,8-chlorinated CDD/CDF results for Puget Sound projects is recommended.

In summary, using substantially more data points in the 2023 advisory control limits project than were available in 2013, the recommended 2023 updated advisory control limits for both Aroclor 1260 and the 2,3,7,8-chlorinated CDD/CDF analytes are all based on the calculated 99% CI using the updated 2023 data set. When large sample data sets are available, using advisory control limits based on calculated CI around the average results is more statistically sound and defensible than using arbitrary limits based on a \pm value around the average results. We recommend updating the advisory control limits when an additional 75 to 100 Aroclor 1260 and CDD/CDF data points become available.