8 TIER 2: CHEMICAL TESTING

Following an assessment of existing information for a project in Tier 1, chemical testing of the dredged material is usually required. Chemical analysis includes both the measurement of "conventional" parameters and the measurement of concentrations of chemicals which have been identified by DMMP as chemicals of concern (COCs) for the project.

8.1 SEDIMENT CONVENTIONAL PARAMETERS

Sediment conventionals provide information about the physical nature of the dredged material and aid in interpreting chemical and biological test results. Table 6-1 lists the conventional parameters required for analysis and recommended analytical methods.

Table 8-1. Sediment Conventionals and Recommended Analytical Methods

SEDIMENT CONVENTIONAL	ANALYSIS METHOD
Total solids	PSEP (1986)
Total volatile solids (TVS)	PSEP (1986)
Grain size	PSEP (1986)/ASTM D-422 (modified)
Total organic carbon (TOC)	EPA 5310B/EPA 9060 (modified)
Total sulfides	PSEP (1986)/Plumb (1981)
Ammonia	Plumb (1981)

Grain size may be determined using either PSEP (1986) or ASTM Method D-422 (modified), which subdivide the silt-clay fraction by pipette and hydrometer respectively. One of the following sieve series must be used: 1) Modified EPA - sieve numbers 4, 10, 18, 35, 60, 120, 230 or 2) Modified ASTM - sieve numbers 4, 10, 20, 40, 60, 140, 230. The fine-grained fraction must be classified by phi size (+5, +6, +7, +8, >8). The delineation of sand vs. gravel fractions is achieved through use of the #10 sieve (2 mm). Similarly, the delineation of fines (silt and clay) vs. sand is achieved through use of the #230 sieve (62.5 microns). It is therefore critical that these two sieve sizes be used in analyzing grain size. The following general classifications are used in the DMMP:

- **Gravel**: >2,000 microns (2 mm)
- **Sand**: 62.5 to 2,000 microns
- **Silt**: 3.9 to 62.5 microns
- **Clay**: 0 to 3.9 microns

Appendix D of *Recommended Guidelines for Measuring Organic Compounds in Puget Sound Water, Sediment and Tissue Samples* (PSEP, 1997b) must be consulted for required modifications of methods EPA 5310B and EPA 9060 for the analysis of TOC.

8.2 STANDARD LIST OF CHEMICALS OF CONCERN

Chemicals of concern generally have the following characteristics:

- A demonstrated or suspected effect on ecological receptors or human health.
- One or more present or historical sources, resulting in high concentration when compared to natural conditions, and of sufficient magnitude to be of concern.
- A potential for persisting in a toxic form for long periods in the environment.
- A potential for entering the food web (bioavailability).

Chemicals of concern that have been shown to be widespread in the environment are included on the standard list of DMMP COCs. Chemical testing, when required, will involve analysis of these COCs. **Table 8-2** lists these chemicals and presents the currently-used marine and freshwater guideline values for each chemical.

Table 8-2. DMMP COCs and regulatory guidelines

	CHEMICAL	CAS[1] NUMBER	USE FOR MARINE PROJECTS. TBT, DIOXINS/FURANS AND GUAIACOLS ARE REQUIRED ONLY ON A PROJECT-SPECIFIC BASIS.			USE FOR FRESHWATER DREDGED MATERIAL WITHIN DMMP JURISDICTION.	
			DMMP MARINE GUIDELINES			**SMS FRESHWATER**	
			SL	**BT**	**ML**	**SL1**	**SL2**
STANDARD CHEMICALS OF CONCERN	METALS (mg/kg dry weight)						
	Antimony	7440-36-0	150	---	200	---	---
	Arsenic	7440-38-2	57	507.1	700	14	120
	Cadmium	7440-43-9	5.1	11.3	14	2.1	5.4
	Chromium	7440-47-3	260	260	---	72	88
	Copper	7440-50-8	390	1,027	1,300	400	1,200
	Lead	7439-92-1	450	975	1,200	360	> 1,300
	Mercury	7439-97-6	0.41	1.5	2.3	0.66	0.8
	Nickel	7440-02-0	---	---	---	38[2]	110
	Selenium	7782-49-2	---	3	---	11	>20
	Silver	7440-22-4	6.1	6.1	8.4	0.57	1.7
	Zinc	7440-66-6	410	2,783	3,800	3,200	>4,200
	ORGANOMETALLIC COMPOUNDS						
	Tributyltin ion (interstitial water; ug/L)	36643-28-4	---	0.15	---	---	---
	Tributyltin ion (bulk; ug/kg)[3]	36643-28-4	---	73	---	47	320
	Monobutyltin ion (bulk; ug/kg)	78763-54-9	---	---		540	>4,800
	Dibutyltin ion (bulk; ug/kg)	10-53-502	---	---		910	130,000
	Tetrabutyltin ion (bulk; ug/kg)	1461-25-2	---	---		97	>97
	PAHs (µg/kg dry weight)						
	Naphthalene	91-20-3	2,100	---	2,400	---	---
	Acenaphthylene	208-96-8	560	---	1,300	---	---
	Acenaphthene	83-32-9	500	---	2,000	---	---
	Fluorene	86-73-7	540	---	3,600	---	---
	Phenanthrene	85-01-8	1,500	---	21,000	---	---
	Anthracene	120-12-7	960	---	13,000	---	---
	2-Methylnaphthalene[4]	91-57-6	670	---	1,900	---	---
	Total LPAH	**---**	**5,200**	**---**	**29,000**	---	---
	Fluoranthene	206-44-0	1,700	4,600	30,000	---	---
	Pyrene	129-00-0	2,600	11,980	16,000	---	---
	Benz(a)anthracene	56-55-3	1,300	---	5,100	---	---
	Chrysene	218-01-9	1,400	---	21,000	---	---
	Benzofluoranthenes (b, j ,k)	205-99-2 205-82-3 207-08-9	3,200	---	9,900	---	---
	Benzo(a)pyrene	50-32-8	1,600	---	3,600	---	---
	Indeno(1,2,3-c,d)pyrene	193-39-5	600	---	4,400	---	---

	CHEMICAL	CAS[1] NUMBER	USE FOR MARINE PROJECTS. TBT, DIOXINS/FURANS AND GUAIACOLS ARE REQUIRED ONLY ON A PROJECT-SPECIFIC BASIS.			USE FOR FRESHWATER DREDGED MATERIAL WITHIN DMMP JURISDICTION.	
			DMMP MARINE GUIDELINES			**SMS FRESHWATER**	
			SL	**BT**	**ML**	**SL1**	**SL2**
	Dibenz(a,h)anthracene	53-70-3	230	---	1,900	---	---
	Benzo(g,h,i)perylene	191-24-2	670	---	3,200	---	---
	Total HPAH	**---**	**12,000**	**---**	**69,000**	---	---
	Total PAHs[5]	**---**				**17,000**	**30,000**
	CHLORINATED HYDROCARBONS (µg/kg dry weight)						
	1,4-Dichlorobenzene	106-46-7	110	---	120	---	---
	1,2-Dichlorobenzene	95-50-1	35	---	110	---	---
	1,2,4-Trichlorobenzene	120-82-1	31	---	64	---	---
	Hexachlorobenzene (HCB)	118-74-1	22	168	230	---	---
	beta-Hexachlorocyclohexane					7.2	11
	PHTHALATES (µg/kg dry weight)						
	Dimethyl phthalate	131-11-3	71	---	1,400	---	---
	Diethyl phthalate	84-66-2	200	---	1,200	---	---
	Di-n-butyl phthalate	84-74-2	1,400	---	5,100	380	1,000
	Butyl benzyl phthalate	85-68-7	63	---	970	---	---
	Bis(2-ethylhexyl) phthalate	117-81-7	1,300	---	8,300	500	22,000
	Di-n-octyl phthalate	117-84-0	6,200	---	6,200	39	>1,100
STANDARD CHEMICALS OF CONCERN	PHENOLS (µg/kg dry weight)						
	Phenol	108-95-2	420	---	1,200	120	210
	2-Methylphenol	95-48-7	63	---	77	---	---
	4-Methylphenol	106-44-5	670	---	3,600	260	2,000
	2,4-Dimethylphenol	105-67-9	29	---	210	---	---
	Pentachlorophenol	87-86-5	400	504	690	1,200	>1,200
	MISCELLANEOUS EXTRACTABLES (µg/kg dry weight)						
	Benzyl alcohol	100-51-6	57	---	870	---	---
	Benzoic acid	65-85-0	650	---	760	2,900	3,800
	Dibenzofuran	132-64-9	540	---	1,700	200	680
	Hexachlorobutadiene	87-68-3	11	---	270	---	---
	N-Nitrosodiphenylamine	86-30-6	28	---	130	---	---
	Carbazole	86-74-8				900	1,100
	PESTICIDES & PCBs (µg/kg dry weight)						
	4,4'-DDD 4,4'-DDE 4,4'-DDT sum of 4,4'-DDD, 4,4'-DDE and 4,4'-DDT	72-54-8 72-55-9 50-29-3 ---	16 9 12 ---	--- --- --- 50	--- --- --- 69	---	---

	CHEMICAL	CAS[1] NUMBER	USE FOR MARINE PROJECTS. TBT, DIOXINS/FURANS AND GUAIACOLS ARE REQUIRED ONLY ON A PROJECT-SPECIFIC BASIS.			USE FOR FRESHWATER DREDGED MATERIAL WITHIN DMMP JURISDICTION.	
			DMMP MARINE GUIDELINES			SMS FRESHWATER	
			SL	BT	ML	SL1	SL2
	2,4'-DDD and 4.4'-DDD 2,4'-DDE and 4,4'-DDE 2,4'-DDT and 4,4'-DDT	--- --- ---	---	---	---	310 21 100	860 33 8,100
	Aldrin	309-00-2	9.5	---	---	---	---
	Total Chlordane (sum of cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, oxychlordane)	5103-71-9 5103-74-2 5103-73-1 39765-80-5 27304-13-8	2.8	37	---	---	---
	Dieldrin	60-57-1	1.9	---	1,700	4.9	9.3
	Heptachlor	76-44-8	1.5	---	270	---	---
	Endrin ketone	53494-70-5				8.5	>8.5
	Total PCBs (Aroclors)	---	130	38 [6]	3,100	110	2,500
	BULK PETROLEUM HYDROCARBONS (mg/kg)						
	TPH – Diesel	---				340	510
	TPH – Residual	---				3,600	4,400
NON-STANDARD COCs [7]	DIOXINS/FURANS						
	Total TEQ (pptr dry wt)	See DMMO Dioxin page	4 - 10[8]	10[8]	---	---	---
	GUAIACOLS						
	Guaiacol (2-methoxyphenol) and chlorinated guaiacols (3,4,5-trichloroguaiacol; 4,5,6-trichloroguaiacol; tetrachloroguaiacol)	---	No guidelines determined				

[1] Chemical Abstract Service Registry Number
[2] This Nickel SL1 value is based on the 90th percentile of soil background data from WA state (Ecology, 1994), and was adopted by the DMMP agencies at the 2014 SMARM (DMMP/RSET, 2014b)
[3] Bulk sediment measurement of TBT is used for z-sample evaluations or when porewater extraction cannot be accomplished.
[4] 2-Methylnaphthalene is not included in the summation for total LPAH.
[5] Total PAHs include sum of all PAHs listed, plus 1-methylnaphthalene
[6] This value is normalized to total organic carbon, and is expressed in mg/kg carbon.
[7] Analyses required only when there is sufficient reason-to-believe for presence in given project or location.
[8] Puget Sound only; see the text for other areas in Washington State.
Analytes printed in blue apply ONLY to freshwater.

8.2.1 Chemical Evaluation Guidelines

Apparent Effects Threshold values (AETs) were the main basis for establishing DMMP evaluation guidelines for marine sediment. For freshwater sediment, the floating percentile method (FPM) was used. For details regarding AETs, see PSDDA, 1988. For details regarding FPM, see SAIC and Avocet, 2003. The Department of Ecology adopted new freshwater sediment standards in February 2013. These new standards were adopted at SMARM 2014 and are now reflected in the freshwater standards shown in **Table 8-2**.

Screening and Maximum Levels

The "screening level" (SL) is defined as the chemical concentration at or below which there is no reason to believe that dredged material disposal would result in unacceptable adverse effects. For most COCs, the SL is set equal to the lowest Apparent Effects Threshold (LAET). DMMUs with chemical concentrations present at levels above the SL require biological testing before a decision can be made on the suitability for unconfined, open water disposal.

The "maximum level" (ML) is equal to the highest Apparent Effects Threshold (HAET) – a chemical concentration at which all biological indicators with AETs show significant effects. The ML values are no longer used by the DMMP agencies as pass/fail indicators, but rather serve to provide valuable information to project proponents. While some DMMUs with ML exceedances have passed biological testing, the majority have failed. By comparing sediment chemical data to the MLs, a dredging proponent can better judge how to proceed with the project, i.e., whether to invest more time and money into further testing for unconfined, open-water disposal, or to rechanneled that effort into other disposal options and testing for those options (e.g., leachate tests for upland disposal).

With regard to the SLs and MLs, the following scenarios are possible:

1. All chemicals are **at or below their SLs**; no biological testing is needed; the DMMU is considered suitable for unconfined, open water disposal at any DMMP site.
2. One or more chemicals are present at levels **between SL and ML**; standard biological testing is needed (see Chapter 9).
3. One or more chemicals are present at levels above the ML. Standard biological testing may still be pursued but there is a high probability that the dredged material will fail Tier 3 testing.

Bioaccumulation Trigger

Bioaccumulation trigger (BT) values are used as guidelines to determine when bioaccumulation testing is required. If any chemical of concern exceeds the bioaccumulation trigger guideline value, additional information gained via bioaccumulation testing will be required in order to determine whether dredged material is suitable for unconfined, open-water disposal. Discussion on bioaccumulation testing is presented in Chapter 10.

8.2.2 Analytical Methods

There are no required analytical methods for standard chemicals of concern in the Dredged Material Management Program. Any established and well-documented method that is capable of meeting the QC requirements outlined in this chapter may be used. The Puget Sound Estuary Program protocols should be consulted for sample cleanup procedures and method modifications.

The methods to be used for a project must be clearly articulated in the SAP and approved by the DMMP agencies prior to testing. **Table 8-3** lists the most commonly used sediment methods for the standard COCs.

Table 8-3. Analytical Methods for Standard COCs

CHEMICAL Standard Chemicals of Concern	PREP METHOD	ANALYSIS METHOD
METALS:		
Antimony, Arsenic, Cadmium, Chromium, Copper, Lead, Silver, Zinc	EPA 3050B	EPA 6010/6020
Selenium	EPA 3050B	EPA 6020/7440
Mercury	CLP-M-245.5	EPA 7471
PAHs	EPA 3541/3550	EPA 8270D
CHLORINATED HYDROCARBONS:		
1,2-Dichlorobenzene, 1,4-Dichlorobenzene, 1,2,4-Trichlorobenzene	EPA 3550	EPA 8260B/8270D
Hexachlorobenzene (HCB)	EPA 3540/3550	EPA 8270D/8081
PHTHALATES	EPA 3550	EPA 8270D
PHENOLS	EPA 3550	EPA 8270D
MISCELLANEOUS EXTRACTABLES:		
Benzyl alcohol, Benzoic acid, Dibenzofuran, N-Nitrosodiphenylamine	EPA 3550	EPA 8270D
Hexachlorobutadiene	EPA 3540/3550	EPA 8270D/8081
PESTICIDES & PCBs:		
Pesticides	EPA 3540/3541/3550	EPA 8081
PCB Aroclors	EPA 3540/3550	EPA 8082
TOTAL PETROLEUM HYDROCARBONS	NWTPH-Dx[1]	NWTPH-Dx[1]

[1] Total Petroleum Hydrocarbons by GC/FID – Analytical Methods for Petroleum Hydrocarbons, Ecology 1997. Other methods may be used with DMMP approval.

Selected ion monitoring (SIM) may be used in the event that reporting limits cannot be brought below SL.

8.2.3 Summing PAHs, Benzofluoranthenes, DDT, Chlordane and PCBs

For comparison to SL, BT and ML values, a group summation is performed for the following families of chemicals using all detected concentrations. Undetected results are not included in the sum. Estimated values between the method detection limit and the laboratory reporting limit (i.e., J-flagged values) are included in the summation at face value. If all constituents of a group are undetected, the group sum is reported as undetected, and the single highest laboratory reporting limit of all the constituents is reported as the group sum.

- LPAH is the sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene.
- HPAH is the sum of benzofluoranthenes, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene.
- Total PAHs are the sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, 1-methylnaphthalene, 2-methylnaphthalene, anthracene, benzofluoranthenes, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene and benzo(g,h,i)perylene.
- Benzofluoranthenes are the sum of the i, j and k isomers.
- For marine guidelines, total DDT is the sum of 4,4'-DDD, 4,4'-DDE and 4,4'-DDT.
- For freshwater guidelines, DDT, DDD and DDE values are the sum of both the 2,4'- and 4,4'-isomers
- Total chlordane is the sum of cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor and oxychlordane.
- Total PCBs include the sum of the following Aroclors: 1016, 1221, 1232, 1242, 1248, 1254, and 1260. If present, Aroclor-1262 and 1268 should be reported but not included in the total PCB summation.

The group sums, as well as the concentrations of individual constituents, must be included in the sediment characterization report.

8.3 DIOXINS

Polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) are commonly referred to together as "dioxins", or simply "dioxin." Dioxins are a group of 210 chlorinated organic compounds with similar chemical structures, or congeners. The toxicity of the various congeners varies considerably. The 17 congeners that have chlorine atoms located in the 2,3,7,8 positions (e.g., 2,3,7,8-TCDD or 1,2,3,7,8-PeCDF) are the dioxins of known concern for health effects in fish, wildlife, and humans. Of these, 2,3,7,8-TCDD is considered the most toxic and is used as a benchmark for estimating the toxicity of the other 16 congeners; as such, it is assigned a toxic equivalency factor (TEF) of 1.0. **Table 8-4** provides the human/mammalian TEFs for all 17 congeners of regulatory concern. The Toxicity Equivalence (TEQ) is calculated by multiplying the TEF of each congener by the concentration of the congener, and summing the results. The resulting TEQ is used in evaluating the suitability of dredged material for open-water disposal.

Dioxins are produced by natural events and are also unintentional byproducts of certain industrial processes. Natural events include forest fires or volcanic activity. Industrial processes include incomplete combustion of materials in the presence of chloride, such as burning of fuels, municipal and domestic waste incineration, as well as chlorine bleaching of pulp and paper, and creosote and chlorinated pesticide manufacturing. Structural fires may also be a source of dioxins.

Like the standard DMMP chemicals of concern, dioxins are widespread in the environment. However, due to the cost of analysis, dioxins are only required to be analyzed when there is a

reason to believe they might be present at a project site, or when dredged material is proposed for dispersive disposal.

Table 8-4. Toxicity Equivalency Factors (TEFs) for PCDDs and PCDFs[1]

	CONGENERS / ISOMERS	TOXIC EQUIVALENCY FACTOR (TEF)
Dioxins	2,3,7,8-TCDD	1
	1,2,3,7,8-PeCDD	1
	1,2,3,4,7,8-HxCDD	0.1
	1,2,3,6,7,8-HxCCD	0.1
	1,2,3,7,8,9-HxCDD	0.1
	1,2,3,4,6,7,8-HpCDD	0.01
	OCDD	0.0003
Furans	2,3,7,8-TCDF	0.1
	1,2,3,7,8-PeCDF	0.03
	2,3,4,7,8-PeCDF	0.3
	1,2,3,4,7,8-HxCDF	0.1
	1,2,3,6,7,8-HxCDF	0.1
	2,3,4,6,7,8-HxCDF	0.1
	1,2,3.7,8,9-HxCDF	0.1
	1,2,3,4,6,7,8-HpCDF	0.01
	1,2,3,4,7,8,9-HpCDF	0.01
	OCDF	0.0003

[1] World Health Organization Human and Mammalian TEFs, from van den Berg et al (2006)

8.3.1 Dioxin Reason-to-Believe Guidelines

Testing for dioxins and furans is required on a case-by-case basis in areas where there is reason to suspect presence of these chemicals. Significant factors which can trigger a "reason-to-believe" that dioxin may be present and thus result in the requirement for dioxin testing include the following:

- Location within an urban bay and having no historical data showing that dioxin is below interim guidelines.
- Proximity to current or historical point sources, such as outfalls.
- Proximity to chlor-oxide bleach process pulp mills, chlor-alkali or chlorinated solvent manufacturing plants, former wood treatment sites, phenoxy herbicide manufacture and/or use and handling areas.
- Proximity to areas with high polychlorinated biphenyl (PCB) concentrations.
- Proximity to former hog fuel burners/boilers and areas with previous structural, vessel or other fires or incineration sources.
- Proximity to areas previously sampled that showed elevated levels of dioxin.

Dioxin testing will be required for all projects meeting one or more of the reason-to-believe factors described above. Deeper underlying sediments, which are confirmed as "native," may be exempt

from testing. Native material within the dredge prism, and lying directly under sediment that is being tested for dioxins, should be archived for possible dioxin analysis.

8.3.2 Guidelines for Dioxin Evaluation in Puget Sound

In December of 2010, the DMMP agencies implemented guidelines for dredging projects in Puget Sound (DMMP, 2010a). The guidelines included a Disposal Site Management Objective of 4 pptr TEQ, which was derived from data on background concentrations of dioxins in the Sound. Due to differences in the nature of dispersive and nondispersive disposal sites, separate guidelines were developed to achieve the Site Management Objective at the two types of sites.

1. ***Dispersive Sites:*** Dredged material placed at dispersive sites does not stay on site, but is rapidly dispersed with the tides. Post-disposal monitoring is not possible. Therefore, only DMMUs meeting the Disposal Site Management Objective of 4 pptr TEQ may be placed at dispersive sites.

   In addition, because post-disposal monitoring is not possible at dispersive sites, projects for which dioxin testing would not normally be required under the reason-to-believe guidelines, may be required to undergo dioxin analysis of a reduced number of sediment samples. The decision to conduct this testing will be based on the size of the project, the grain-size characteristics of the dredged material, and the availability of dioxin data in the vicinity of the dredging project.

   The Puget Sound dispersive-site guidance applies to the Port Angeles, Port Townsend and Rosario Strait disposal sites.

2. ***Nondispersive Sites:*** Dredged material placed at nondispersive sites stays on site, and sequential disposal events result in a combination of mixing with, and burial of, previously-placed dredged material. This mixing and burial allowed the DMMP agencies to adopt more flexible guidelines for nondispersive disposal, while still achieving the Disposal Site Management Objective of 4 pptr TEQ in surface sediment. Further, periodic post-disposal monitoring provides the feedback necessary to ensure that the Disposal Site Management Objective is being met.

   For nondispersive sites, DMMUs with dioxin concentrations below 10 pptr TEQ will be allowed for disposal as long as the volume-weighted average concentration of dioxins in material from the entire dredging project does not exceed the Disposal Site Management Objective of 4 pptr TEQ. Where possible, disposal of DMMUs is sequenced such that those with higher dioxin concentrations are disposed before those with lower concentrations.

   Case-by-case decisions to allow disposal of material not meeting these guidelines may be made by the DMMP agencies based on the overall goal of meeting the Disposal Site Management Objective. Case-by-case considerations will include the following: (a) material placement sequencing; (b) consideration of the possible cumulative effects of other bioaccumulative compounds within the project sediments; and (c) the frequency of disposal site use.

   When the sediment dioxin concentration in a dredging unit exceeds the 10 pptr TEQ screening level and the dredging unit is found unacceptable for nondispersive disposal under case-by-case decision-making, the dredging proponent will have the option of

pursuing bioaccumulation testing to determine whether or not individual DMMUs could qualify for open-water disposal.

Small businesses[1] with total dredged volume less than 4,000 cubic yards may not be required to meet the volume-weighted average concentrations of 4 pptr if dioxin in all suitable DMMUs is less than 10 pptr TEQ and DMMP review determines that the Disposal Site Management Objective of 4 pptr will likely be met on an annual average basis, based on knowledge of other anticipated use of the identified disposal site.

The Puget Sound nondispersive-site guidance applies to the Bellingham Bay, Port Gardner, Elliott Bay, Commencement Bay and Anderson-Ketron disposal sites.

8.3.3 Guidelines for Dioxin Evaluation in Grays Harbor

Dioxin evaluation guidelines in Grays Harbor are based on a risk assessment conducted for a navigation improvement project in the early 1990's (USACE, 1991). For the dispersive sites in Grays Harbor, each disposed DMMU must have a 2,3,7,8-TCDD concentration less than or equal to 5 ng/kg and a TEQ of less than or equal to 15 ng/kg. DMMUs with concentrations above these levels would be required to undergo bioaccumulation testing in order to qualify for open-water disposal.

8.3.4 Guidelines for Dioxin Evaluation in Other Areas of Washington State

Dioxin evaluation guidelines have not been developed in other areas of Washington State. Dioxin results for areas outside of Puget Sound and Grays Harbor will be evaluated on a case-by-case basis. For non-Port projects on the Washington side of the Columbia River, dioxin concentrations in dredged material have been compared to background values for sediment samples taken downstream of Puget Island, which ranged from 0.65 to 2.89 pptr TEQ as of 2009.

8.3.5 Dioxin Analysis and Reporting

Specifying data analysis procedures for PCDD/F is considerably more difficult than for other chemicals in the DMMP list. The DMMP clarified preferred analysis methods at the 2010 SMARM, in *Polychlorinated Dioxins and Furans (PCDD/F): Revisions to the Supplemental Quality Assurance Project Plan* (DMMP, 2010b) and *Revised Supplemental Information on Polychlorinated Dioxins and Furans (PCDD/F) for use in Preparing a Quality Assurance Project Plan (QAPP)* (DMMP, 2010c). **Please refer to the full documents for complete guidance.** In summary, for dioxin analysis, the DMMP requires:

1. **Sediment sampling and holding.** These procedures are generally similar to semivolatile chemicals in the DMMP. Frozen samples may be held for one year prior to extraction.
2. **Analytical method.** The identification of PCDD/F congeners at low concentrations is difficult, and there is significant possibility of interfering compounds (such as chloro-diphenyl ethers) causing the reporting of artificially elevated values. The DMMP agencies recommend EPA Method 1613B: Tetra- Through Octa-Chlorinated Dioxins and Furans by

[1] "Small business" means any business entity, including a sole proprietorship, corporation, partnership, or other legal entity, that is owned and operated independently from all other businesses, and t hat has fifty or fewer employees. (RCW Chapter 19.85)

Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry as the most suitable method for sediment.

3. **Data evaluation/validation methods.** Because of the complexity of the method, the extremely low reporting limits, and the high potential for interfering compounds such as chloro-diphenyl ethers, it is recommended that the dioxin data be subjected to Stage 4 data validation by an experienced independent validator.

   Full validation is highly recommended by the DMMP. However, if the applicant chooses not to validate the data, the primary method of data evaluation will consist of analysis of the Puget Sound Sediment Reference Material (PS-SRM). The DMMP will review the primary results against the Method 1613B acceptance limits or those in the QAPP. Based upon the DMMP review of precision, accuracy, representativeness, and completeness measures as well as the PS-SRM, full validation of the dioxin raw data may, nevertheless, be required. Should the DMMP request validation, the project must provide it, using a person with demonstrated experience accomplishing validation for PCDD/F. The raw data associated with the analysis of dioxins must be made available to the DMMP agencies upon their request.

4. **Data Reporting**. The laboratory shall report each of the 2,3,7,8-chlorine substituted PCDD/F congeners on a dry-weight basis. Estimated detection limits (EDLs) and reporting limits shall be reported for each of these congeners. The 17 congeners of interest shall be tabulated as TEQ, both with nondetected values (U) = ½ EDL and with U = 0. (The difference between these values gives data reviewers an idea of how much the EDL substitution affects the TEQ summation.) For the purpose of TEQ summation, detections at concentrations >EDL but <RL, and which were reported as estimated maximum potential concentrations (EMPCs) shall be reported as non-detects (U) elevated at the EMPC value. EMPC values >RLs with mass- ion ratios adjusted to meet the criteria are flagged as estimated and reported as detected compounds. Details regarding EDLs are as follows:

   <u>Estimated Detection Limit</u>

   The estimated detection limit is a sample- and analyte-specific detection limit that is based on the signal-to-noise ratio present in the sample for each analyte at the time of analysis. This is the best value to use to get the lowest defensible TEQ values.

   The estimated detection limit is defined as follows:

$$\mathrm{EDL} = \frac{2.5 \times \mathrm{H}_x \times \mathrm{Q}_{is}}{\mathrm{H}_{is} \times \mathrm{W} \times \overline{\mathrm{RF}}_n}$$

   where:

   EDL = estimated detection limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

   H_x = sum of the height of the noise level for each quantitation ion for the unlabeled PCDDs/PCDFs.

   H_{is} = sum of the height of the noise level for each quantitation ion for the labeled internal standard.

W = weight, in g, of the sample.

$\overline{RF}_n$ = calculated mean relative response factor for the analyte (with n = 1 to 17 for the seventeen 2,3,7,8-substituted PCDDs/PCDFs).

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction.

5. **Deliverables Necessary for Stage IV data validation:**

- **Case narrative** per batch of samples, including: a summary of samples received and samples analyzed; list of analytical methods used and modifications; samples requiring dilutions and re-analysis and reasons; description of any problems encountered during sample shipment, extraction and/or analysis; corrective actions taken and any data limitations; list of manually integrated peaks with the original and manually reintegrated peak areas;, and definitions of all laboratory qualifiers applied.
- **PCDD/PCDF Data**
- **Summary of analytical results** arranged in chronological order. Example calculations. Tabulated analytical results (identification and quantitation) of the specified target analytes, mass-ion ratios and recoveries of the associated labeled compounds. Include lab name, lab sample ID, lab file ID, sample prep method, date received, date extracted, date analyzed, sample matrix, amount of sample extracted, dilution factor (if any), injection volume, final extract volume, and sample specific EDLs and RLs. For solids, reporting units and concentrations need to be identified on a dry weight basis (include percent moisture).
- **Toxicity Equivalence Summary** - Tabulated adjusted concentrations for the target analytes based on toxicity equivalent factors. PCDD/PCDF toxicity of the 17 congeners of interest shall be calculated and tabulated as TEQs, using the product of the TEFs with (1) non-detected values (U) = ½ EDLs and (2) with non-detected values (U) = 0. **Table 8-4** presents the specified mammalian TEFs for each of the 17 congeners. **Tabulated total homologue co**ncentrations shall be completed for each sample, blank, and Quality Control (QC) sample analyzed. EMPC values shall be flagged "*", and the Estimated Detection Limit (EDL) shall be qualified "U" on the form.
- Complete data system report, including but not limited to quantitation reports and area summaries, selected ion current profile (SICP) for each sample including dilution and re-analysis. SICPs must be presented so the two major quantitation ions, the relevant labeled compounds and chlorinated diphenyl ether (CDPE) interferences are on one page. The internal standards can be presented on another page. The SICPs must show the full retention time window scanned for each ion. Enlarge any SICP peak for any 2,3,7,8-substituted congener present below the signal-to noise (S/N) ratio of 10 or below the RLs.
    - The following information shall be included in all laboratory “raw data sheets”: sample number, date and time of analysis, retention time or scan number of the identified target compound, ions used for quantitation with measured areas, area table, on-column concentration including units, S/N ratios, lab file ID, Analyst ID.
    - In all instances where the data system report has been edited, or where manual integration or quantitation has been performed, the HRGC/HRMS operator shall identify the changes made to the report, by initialing and dating all handwritten

changes, and shall include the integration scan range. In addition, a hardcopy printout of the chromatogram displaying the manual integration shall be included in the raw data.

  - Second column confirmation is required for all samples in which 2,3,7,8-TCDF is positively identified at, or above, the RLs by analysis on a DB-5 (or equivalent) HRGC column, or if 2,3,7,8-TCDF is reported as an Estimated Maximum Possible Concentration (EMPC) at, or above, the RL.

- Quality Control and Supporting Data
- Instrument Performance Check
- Window Defining Mix Summary
- Chromatographic Resolution Checks
- Analytical Sequence Summary Checks
- Fortified blank (LCS) recovery results (1 per batch)
- SRM run and recovery results
- Method blanks and list of samples associated with the method blanks
- Initial calibration summary and raw data
- Calibration verification summary and raw data
- Miscellaneous Data
- Copy of laboratory's method SOP
- Sample receipt documentation and sample control
- Extraction, extract clean-up, and instrument run logs
- Standard Traceability documentation
- Communication logs

8.4 CHEMICALS/CONSTITUENTS OF CONCERN FOR LIMITED AREAS

In addition to the standard list of standard chemicals of concern, there are COCs that may need to be measured for certain dredging projects in certain limited areas. These chemicals include those from the following list, which are further discussed below.

- Guaiacol (2-methoxyphenol) and chlorinated guaiacols (3,4,5-trichloroguaiacol; 4,5,6-trichloroguaiacol; tetrachloroguaiacol)
- Tri-, tetra-, and pentachlorobutadienes
- Tributyltin
- Wood waste

Other COCs may need to be analyzed for specific projects depending on site-specific information.

8.4.1 Guaiacol and Chlorinated Guaiacols

Guaiacol and chlorinated guaiacols are measured in areas where kraft pulp mills are located. Only guaiacol will be measured near sulfite pulp mills (chlorinated guaiacols are not expected in processes that do not involve bleaching).

8.4.2 Tributyltin

Tributyltin (TBT) testing is indicated in areas near current or historic marinas, boatyards, shipyards, combined sewer overflows (CSOs), treatment plant outfalls and in urban areas, especially Commencement Bay, Elliott Bay, Duwamish River, Lake Washington ship canal, Salmon Bay and Lake Union.

Measurement of TBT in interstitial water may provide a more direct measure of potential bioavailability, and hence toxicity, than bulk sediment concentrations. Therefore, interstitial water analysis replaces bulk sediment analysis as the initial step in a tiered assessment of TBT toxicity for DMMP projects. Centrifugation is preferred for collecting sediment interstitial water (for detailed guidance on interstitial water collection and sample handling refer to DMMP, 1998 - Tributyltin Analysis: Clarification of Interstitial Water Extraction and Analysis Methods - Interim. Alternative interstitial water extraction methods may be used in cases where centrifugation is not an effective technique, (e.g., for very sandy sediments) and will be decided on a case-by-case basis by the DMMP agencies. In the event that interstitial water cannot be extracted or archived sediment is being analyzed, the DMMP agencies may approve the use of bulk sediment analysis on a case-by-case basis.

Acceptable methods for measuring TBT involve tropolone/methylene chloride extraction, followed by Grignard derivitization and analysis by GC/MS (e.g., Krone *et al*., 1989), GC/MS SIM (e.g., PSEP, 1997b), or GC/FPD (e.g., Unger *et al*., 1986).

If the TBT concentration in the interstitial water of a DMMU is above 0.15 ug TBT/L, bioaccumulation testing must be conducted using the DMMP bioaccumulation guidelines in effect at the time of testing. If unacceptable tissue concentrations are measured at the end of the bioaccumulation test, the sediment will be found unsuitable for open-water disposal. It should be noted that standard toxicity bioassays (amphipod mortality, larval development, and *Neanthes* growth tests) are not triggered by exceedances of the 0.15 ug TBT/L threshold, as these bioassays have been shown to be ineffective in the evaluation of TBT toxicity (PSDDA/SMS, 1996).

8.4.3 Wood Waste

Wood waste can range in size from intact logs down to fine bark and sawdust. The DMMP program requires logs and large debris to be removed prior to disposal. No debris greater than 24 inches in any dimension is allowed at the open-water disposal sites. Sediments with large pieces of wood debris may require debris removal by passing the dredged material through a 24” X 24” steel screen. The quantity of wood debris that would pass through a 24” X 24” screen must be visually assessed during field collection of sediments. If the sediment contains a significant quantity of smaller wood debris, the sediments must be analyzed in the laboratory to quantify the wood fraction.

The wood fraction can be quantified in the laboratory on either a volume or a weight-specific basis. While quantifying wood debris in sediments on a volumetric basis may be more ecologically meaningful, it is much more difficult and less accurate than quantifying it on a weight-specific basis.

Therefore, dredged material assessment of wood debris will be accomplished on a dry-weight basis, then converted to a volumetric basis by multiplying the weight-based number by two (example: 25% by weight ≅ 50% by volume). The dry-weight fraction of debris is estimated by quantifying the organic fraction. Dredged material containing an organic fraction greater than 25% dry weight will be required to undergo biological testing to assess the suitability of the material for unconfined open-water disposal. Likewise, dredged material containing an organic fraction less than 25% dry weight will be considered suitable for unconfined open-water disposal without further testing unless one or more chemicals of concern exceed chemical screening levels.

One method for determining the dry-weight fraction of wood waste is quantification by ASTM D-2974 Method C, with the sample size increased to 100-300 grams. Other methods may be proposed by the applicant in lieu of this approach, but must be included in the SAP and approved by the DMMP agencies.

For additional information see DMMP/SMS, 1997 - Management of Wood Waste under DMMP and SMS Cleanup Program.

If bioassays are triggered by wood waste, additional information must be obtained in preparation for biological testing. Sediment grain size is an important consideration when selecting the species to be used in the amphipod test and choosing appropriate reference sediments. However, the presence of wood waste in the sediment sample would bias the results of standard grain-size analysis. Therefore, in addition to the standard grain-size testing, applicants should conduct grain-size analysis on the residue left over after the wood-waste analysis. This "organic-free" grain-size distribution should be used in conjunction with the standard grain-size distribution in selecting the appropriate amphipod species and reference sediment.

8.5 QUALITY CONTROL

The quality of chemical data submitted to characterize dredged material proposed for open-water disposal at a DMMP site must be assessed before it may be used for regulatory decision-making. This section provides general quality assurance (QA) guidelines, as well as guidelines specific to the analysis of tributyltin and dioxin.

8.5.1 Laboratory Accreditation

Laboratories are required to be accredited by the Department of Ecology for sediment methods used to generate chemical and biological data for DMMP projects. Accredited labs may be found at https://fortress.wa.gov/ecy/laboratorysearch/.

8.5.2 Sample Detection Limits and Reporting Limits

Ideally, the reporting limits (*aka* limits of quantification or practical quantification limits) for all COCs will be below the SLs. If this is not possible - due to matrix interference or sample dilution - it is imperative that sample detection limits be below the SLs. **Failure to bring reported nondetects for an analyte below the SL could result in the agencies requiring the re-extraction and re-analysis of archived sediment, or biological toxicity testing, to verify the suitability of sediments for open-water disposal.**

The following guidelines must be followed when reporting results of chemical analysis:

1. Laboratories must report estimated concentrations that fall between the sample detection limit and reporting limit. Such estimated concentrations should be accompanied by a "J" qualifier.
2. Laboratories must report both the reporting limit and the sample detection limit for any COC concentration that is accompanied by a "U" flag.
3. For mixtures of chemicals, such as Total PCBs, the reported values of detected constituents - including "J" values falling between the sample detection limit and the reporting limit - will be summed. In the event that all constituents are undetected, the single highest constituent's detection limit will be used as the value for the mixture in a given sample and will be accompanied by a "U" qualifier.

The following scenarios are possible and need to be understood and handled appropriately:

1. One or more chemicals-of-concern (COC) have nondetects exceeding screening levels while all other COCs are quantitated or reported as nondetects at or below the screening levels: the requirement to conduct biological testing will be triggered solely by the nondetects. In this case the chemical testing subcontractor should do everything possible to bring sample detection limits down to or below the screening levels, including additional cleanup steps, re-extraction, etc. Selected ion monitoring may be used, if necessary. All such actions must be documented in the lab report. In the event that nondetects cannot be brought below the SLs, the Dredged Material Management Office must be contacted immediately. Failure to do so could result in the need to collect new field samples for analysis or trigger bioassays, an expensive endeavor.
2. One or more COCs are reported as nondetects above the SLs for a lab sample, but below respective bioaccumulation triggers (BT), and other COCs have quantitated concentrations above screening levels: The need to do bioassays is based on the detected exceedances of SLs and the nondetects above SL become irrelevant. No further action on the part of the chemical testing subcontractor is necessary.
3. One or more COCs are reported as nondetects above the SL and BT, and other COCs have quantitated concentrations above screening levels: the need to do bioassays is based on the detected exceedances of SLs but all other nondetects must be brought below BTs to avoid the requirement to do bioaccumulation testing. As in scenario "1" above, everything possible should be done to lower the sample detection limits.

In all cases, to avoid potential problems and leave open the option for retesting, sediments or extracts should be kept under proper storage conditions until the chemistry data are deemed acceptable by the regulatory agencies.

8.5.3 Data Quality Objectives

Data quality objectives are the quantitative and qualitative terms used to describe how good the data needs to be in order to meet the project's objectives. Typical data quality objectives include precision, accuracy, representativeness, comparability and completeness.

1. ***Precision**:* The precision is evaluated using the Relative Percent Difference (RPD) values between the duplicate sample results.

$$RPD = \frac{ABS(R1 - R2)}{\left(\frac{R1 + R2}{2}\right)} \times 100$$

R1 = Recovery for MS or duplicate 1

R2 = Recovery for MSD or duplicate 2

2. ***Accuracy**:* For parameters analyzed in the laboratory, accuracy will be evaluated using percent recovery (%R) of the target analyte in spiked samples and, where applicable, also the recoveries of the surrogates in all samples and QC samples.

$$\%Recovery = \frac{SSR - SR}{SA} \times 100$$

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

3. ***Representativeness*** is the degree to which data from the project accurately represent a particular characteristic of the environmental matrix which is being tested. Representativeness of samples is ensured by adherence to standard field sampling protocols and standard laboratory protocols. The design of the sampling scheme and number of samples should provide representativeness of each matrix being sampled.

4. ***Comparability*** is the measurement of the confidence in comparing the results of one sampling event with the results of another achieved by using the same matrix, sample location, sampling techniques and analytical methodologies.

5. ***Completeness**:* Completeness is the percentage of valid results obtained compared to the total number of samples taken for a parameter. %Completeness may be calculated using the following formula:

$$\%\,Completeness = \frac{\#\,of\ valid\ results}{\#\,of\ samples\ taken} \times 100$$

8.5.4 General Quality Assurance Guidelines

The chemistry QA/QC requirements summarized in **Table 8-5** must be met to ensure data quality and usability for dredged material characterization and suitability determinations. Due to analytical complexity, dioxin QA is covered in a separate section (8.5.4).

Table 8-5. Laboratory QA/QC Requirements for Conventionals and COCs

Analysis Type	Method Blanks[1]	Replicates[1]	Triplicates[1]	CRM/RM	MS/MSD[1]	Surrogates[2]
Semivolatiles[3,4]	X[5]	X[6]		X	X	X
Pesticides[3,4]	X[5]	X[6]		X	X	X
PCBs[3,4]	X[5]	X[6]		X[7]	X	X
Metals	X	X		X	X	
Ammonia	X		X			
Total Sulfides	X		X			
Total Organic Carbon	X		X	X		
Total Solids			X			
Total Volatile Solids			X			
Grain Size			X			
Tributyltin	X	X[6]			X	X
Dioxins/Furans	**See Table 8-8**					

Notes:

CRM = Certified Reference Material; RM = Reference Material; MS/MSD = matrix spike/matrix spike duplicate

[1] Frequency of Analysis (FOA) = 5 percent or one per batch, whichever is more frequent.

[2] Surrogate spikes required for every sample, including matrix spiked samples, blanks, and reference materials.

[3] Initial calibrations required before any samples are analyzed, after each major disruption of equipment, and when ongoing calibration fails to meet criteria.

[4] Ongoing calibration required at the beginning of each work shift, every 10–12 samples or every 12 hours (whichever is more frequent), and at the end of each shift.

[5] FOA = one per extraction batch.

[6] Matrix spike duplicates may be used.

[7] The Puget Sound Sediment Reference Material must be used for projects in Puget Sound.

Most laboratories performing DMMP chemical analysis use modified EPA Contract Lab Program (EPA CLP) methods. These methods have their own QA "control" limits for precision, matrix spike recovery and surrogate spike recovery, which have been established through inter-laboratory testing. Laboratories rely on the CLP control limits to determine when data quality may be inadequate and corrective action is necessary.

In addition to the CLP limits in common use, the Puget Sound Estuary Program (PSEP) has established both "warning" limits and "action" limits for these same QA parameters. PSEP defines warning limits as "numerical criteria that serve to alert data reviewers and users to possible problems within the analytical system. When a warning limit is exceeded, the laboratory is not obligated to halt analyses, but the reported data may be qualified during subsequent QA/QC review." Action limits are defined as "numerical criteria that, when exceeded, require specific action by the laboratory before data may be reported. Action limits are intended to serve as contractual controls on laboratory performance." The terms "action limit" and "control limit" are similar and used interchangeably.

Table 8-6 includes QA limits which are as consistent as possible with both PSEP and CLP. A system of warning and action limits, similar to PSEP, is used. In most cases, PSEP quantitative levels have been adopted as well. The warning and action limits listed in the table were adopted by the DMMP agencies for use in QA1 evaluations.

For matrix spike and surrogate spike recoveries, independent warning limits were established for volatiles, semivolatiles and pesticides. These limits meet the PSEP definition of warning limits and screen data effectively relative to the EPA CLP control limits. The chemical-specific EPA CLP control limits were adopted for use as action limits for surrogate spike recoveries and for a basis of evaluation in the application of best professional judgment for matrix spike recoveries. Where certified reference materials (CRMs) are available, the interlaboratory-derived 95% confidence interval (CI) should be used as an objective evaluation tool. This alternative is endorsed by PSEP.

Table 8-6. DMMP Warning and Action Limits

QA Element	Warning Limits	Action Limits
Precision		
Conventionals:	None	20% coefficient of variation (CV)
Metals:	none	20% relative percent difference (RPD) or CV
Organics:	35% RPD or COV	50% CV or a factor of 2 for duplicates
Accuracy: Matrix Spikes		
Metals:	none	75-125% recovery
Organics:		none (zero percent recovery may be cause for data rejection however)[1]
Volatiles:	70-150% recovery	
Semivolatiles and Pesticides:	50-150% recovery	
Reference Materials		
Metals:	none	95% CI if specified for a particular CRM; 80-120% recovery if not.
Semivolatiles/Pesticides:	none	95% CI for CRMs. No action limit for uncertified RMs.
PCBs	PS-SRM: for Aroclor 1260 - Warning low: 41 ug/kg - Warning high: 180 ug/kg	None at this time
Surrogate Spikes		
Organics:		EPA CLP chemical-specific recovery limits
Volatiles:	85% minimum recovery	
Pesticides:	60% minimum recovery	
Semi-volatiles:	50% minimum recovery	

[1]Rigorous control limits are not recommended due to possible matrix effects and interferences.

8.5.5 Dioxin QC Performance Criteria

QC performance criteria for the analysis of dioxins must be presented in the sampling and analysis plan and approved by the DMMP agencies. Laboratories will be required to meet these performance criteria as well as take the specified corrective action if performance criteria are not met. Example criteria and corrective actions are provided in **Table 8-7** and **Table 8-8**. These tables of QC requirements are not all-inclusive of method 1613B requirements. Other method-required QC checks, criteria and corrective actions can be found in the EPA *National Functional Guidelines for Chlorinated Dioxin/Furan Data review* (EPA, 2011) and must also be followed.

It is critical for reporting limits to be sufficiently low when analyzing dredged material for dioxin. Target reporting limits for DMMP projects are presented in **Table 8-9**.

All projects will be required to analyze the Puget Sound Sediment Reference Material (PS-SRM) with each analytical batch. Acceptance criteria for the reference material must be included in the sampling and analysis plan (**Table 8-10**). If results fall outside the acceptance range, the laboratory may be required to reanalyze.

Table 8-7. Summary of Quality Control Procedures

QC Check	Minimum Frequency	Acceptance Criteria	Laboratory Corrective Action*
Ongoing Precision And Recovery	1 per analytical batch (≤ 20 samples)	Recovery within acceptance criteria in Table 8-8 of the QAPP guidance document	1. Check calculations 2. Reanalyze batch
Stable-isotope-labeled compounds	Spiked into each sample for every target analyte	Recovery within limits in Table 8-8	1. Check calculations 2. Qualify all associated results as estimated
		Ion abundance ratios must be within criteria in Table 9 of method 1613B	1. Reanalyze specific samples. 2. Reject all affected results outside the criteria 3. Alternatively, use of secondary ions that meet appropriate theoretical criteria is allowed if interferences are suspect. This alternative must be approved by the DMMP agencies.
Laboratory duplicate	5% or 1 per batch (≤ 20 samples)	Relative percent Difference ≤ 30%	1. Evaluation of the homogenization procedure and evaluation method 2. Reanalyze batch
Method blank	1 per analytical batch (≤ 20 samples)	Detection ≤ minimum level in Table 2 of Method 1613B	1. If the method blank results are greater than the reporting limit, halt analysis and find source of contamination; reanalyze batch. 2. Report project samples as non-detected for results ≤ to the reported method blank values
GC/MS Tune	At the beginnings of each 12 hour shift. Must start and end each analytical sequence.	>10,000 resolving power @ m/z304.9825 Exact mass of 380.9760 within 5 ppm of theoretical value.	1. Re-analyze affected samples 2. Reject all data not meeting method 1613B requirements
Initial Calibration	Initially and when continuing calibration fails.	Five point curve for all analytes. RSD must meet Table 4 requirements for all target compounds and labeled compounds. Signal to noise ratio	

Table 8-7. Summary of Quality Control Procedures

QC Check	Minimum Frequency	Acceptance Criteria	Laboratory Corrective Action*
		(S/N) >10. Ion abundance (IA) ratios within method specified limits.	
Window Defining/Column Performance Mix	Before every initial and continuing calibration.	Valley <25% for all peaks near 2378-TCDD/F peaks.	
Continuing Calibration	Must start and end each analytical sequence.	%D must meet Table 4 limits for target compounds & labeled compounds. S/N >10. IA ratios within method specified limits.	
Confirmation of 2,3,7,8-TCDF	For all primary-column detections of 2,3,7,8-TCDF	Confirmation presence of 2,3,7,8-TCDF in accordance with method 1613B requirements	Failure to verify presence of 2,3,7,8-TCDF by second column confirmation requires qualification of associated 2,3,7,8-TCDF results as non-detected at the associated value.
Sample data not achieving target reporting limits or method performance in presence of possibly interfering compounds	Not applicable	Not applicable	Rather than simply dilute an extract to reduce interferences, the lab should perform additional cleanup techniques identified in the method to insure minimal matrix effects and background interference. Thereafter, dilution may occur. If re-analysis is required, the laboratory shall report both initial and re-analysis results.
Puget Sound Sediment Reference Material	One per analytical batch	Result must be within acceptance ranges (**Table 8-10**)	1. Extraction and analysis should be evaluated by the lab and re-analysis performed of the entire sample batch once performance criteria can be met. 2. If analysis accompanies several batches with acceptable PS-SRM results, then the laboratory can narrate possible reason for PS-SRM outliers.

*If re-analysis is required, the laboratory shall report initial and re-analysis results

Table 8-8. QC Acceptance Criteria for PCDD/F

	Test Conc., ng/mL[1]	IPR[2]		OPR[3] (%)	I-CAL[4] %	CAL/VER[5] (%) (Coeff. of Variation)	Labeled Compound % Recovery in Sample	
		RSD (%)	Recovery				Warning Limit	Control Limit
Native Compound								
2,3,7,8-TCDD	10	28	83-129	70-130	20	78-129	-	-
2,3,7,8-TCDF	10	20	87-137	75-130	20	84-120	-	-
1,2,3,7,8-PeCDD	50	15	76-132	70-130	20	78-130	-	-
1,2,3,7,8-PeCDF	50	15	86-124	80-130	20	82-120	-	-
2,3,4,7,8-PeCDF	50	17	72-150	70-130	20	82-122	-	-
1,2,3,4,7,8-HxCDD	50	19	78-152	70-130	20	78-128	-	-
1,2,3,6,7,8-HxCDD	50	15	84-124	76-130	20	78-128	-	-
1,2,3,7,8,9-HXCDD	50	22	74-142	70-130	35	82-122	-	-
1,2,3,4,7,8-HxCDF	50	17	82-108	72-130	20	90-112	-	-
1,2,3,6,7,8-HxCDF	50	13	92-120	84-130	20	88-114	-	-
1,2,3,7,8,9-HxCDF	50	13	84-122	78-130	20	90-112	-	-
2,3,4,6,7,8-HxCDF	50	15	74-158	70-130	20	88-114	-	-
1,2,3,4,6,7,8-HpCDD	50	15	76-130	70-130	20	86-116	-	-
1,2,3,4,6,7,8-HpCDF	50	13	90-112	82-122	20	90-110	-	-
1,2,3,4,7,8,9-HpCDF	50	16	86-126	78-130	20	86-116	-	-
OCDD	100	19	86-126	78-130	20	79-126	-	-
OCDF	100	27	74-146	70-130	35	70-130	-	-
Labeled Compounds								
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	25-130	35	82-121	40-120	25-130
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	25-130	35	71-130	40-120	24-130
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	25-150	35	70-130	40-120	25-130
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	25-130	35	76-130	40-120	24-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	25-130	35	77-130	40-120	21-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	25-130	35	85-117	40-120	32-130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-130	35	85-118	40-120	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	25-130	35	76-130	40-120	26-130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	25-130	35	70-130	40-120	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	25-130	35	74-130	40-120	29-130
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	25-130	35	73-130	40-120	28-130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-130	35	72-130	40-120	23-130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	25-130	35	78-129	40-120	28-130
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	25-130	35	77-129	40-120	26-130
$^{13}C_{12}$-OCDD	200	48	20-138	25-130	35	70-130	25-120	17-130
Cleanup Standard								
$^{37}Cl_4$-2,3,7,8-TCDD	10	36	39-154	31-130	35	79-127	40-120	35-130

(Table shown with permission from AXYS Analytical Services LTD (2005), Vancouver, BC, Canada. *Analysis of Polychlorinated Dioxins and Furans by Method 1613B* -- MSU-018 Rev. 5, 07-Jun-2005)

[1] QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
[2] IPR: Initial Precision and Recovery demonstration
[3] OPR: Ongoing Precision and Recovery test run with every batch of samples.
[4] Initial Calibration
[5] CAL/VER: Calibration Verification test run at least every 12 hours

Table 8-9. Target Reporting Limits for Dioxins/Furans

Dioxins and Furans	Reporting Limit (ng/kg dry wt)
2,3,7,8-TCDD	1.0
1,2,3,7,8-PeCDD	1.0
1,2,3,4,7,8-HxCDD	2.5
1,2,3,6,7,8-HxCDD	2.5
1,2,3,7,8,9-HxCDD	2.5
1,2,3,4,6,7,8-HpCDD	2.5
OCDD	5.0
2,3,7,8-TCDF	1.0
1,2,3,7,8-PeCDF	2.5
2,3,4,7,8-PeCDF	1.0
1,2,3,4,7,8-HxCDF	2.5
1,2,3,6,7,8-HxCDF	2.5
1,2,3,7,8,9-HxCDF	2.5
2,3,4,6,7,8-HxCDF	2.5
1,2,3,4,6,7,8-HpCDF	2.5
1,2,3,6,7,8,9-HpCDF	2.5
OCDF	5.0

8.5.6 Puget Sound Sediment Reference Material

The Puget Sound Sediment Reference Material (SRM) has been developed to help evaluate measurement accuracy and monitor laboratory performance when analyzing for chlorinated dioxins, furans, and biphenyl compounds in sediment samples collected from the Puget Sound area. The SRM is currently available free of charge, though recipients must pay shipping costs.

The guidance document provides instructions for obtaining, analyzing, and reporting on the SRM. The guidance and procedures are intended to ensure that SRM users:

- Report methods used for analysis
- Report QA/QC procedures used to verify and validate results, and
- Report results that can be included in periodic recalculations of acceptance limits

The Puget Sound SRM has been established for chlorinated dibenzo-p-dioxins/chlorinated dibenzofurans (CDD/CDF), and/or chlorinated biphenyl (CB) congener analysis using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) methods. This SRM is also suitable for Aroclor analysis using gas chromatography/electron capture detection (GC/ECD) methods. Use of the SRM REQUIRES submittal of data per the guidance document. The SRM may be requested through DMMP website.

Table 8-10. CDD/CDF Acceptance Limits for Puget Sound SRM

Acceptance Limits Source	Analyte	CAS No.	Avg. Conc. (ng/kg)	Action Low -50%	Action High +50%
± 50 Percent	2,3,7,8-TCDD	**1746-01-6**	1.05	**0.525**	**1.57**
	1,2,3,7,8-PeCDD	**40321-76-4**	1.08	**0.542**	**1.63**
	1,2,3,4,7,8-HxCDD	**39227-28-6**	1.59	**0.797**	**2.39**
	1,2,3,6,7,8-HxCDD	**67653-85-7**	3.88	**1.94**	**5.82**
	1,2,3,7,8,9-HxCDD	**19408-74-3**	3.04	**1.52**	**4.55**
	1,2,3,4,6,7,8-HpCDD	**35822-46-9**	90.6	**45.3**	**136**
	OCDD	**3268-87-9**	811	**406**	**1217**
	2,3,7,8-TCDF	**51207-31-9**	1.11	**0.557**	**1.67**
	1,2,3,7,8-PeCDF	**57117-41-6**	1.23	**0.613**	**1.84**
	2,3,4,7,8-PeCDF	**57117-31-4**	1.07	**0.533**	**1.60**
	1,2,3,4,7,8-HxCDF	**70648-26-9**	3.02	**1.51**	**4.53**
	1,2,3,6,7,8-HxCDF	**57117-44-9**	1.09	**0.545**	**1.64**
	2,3,4,6,7,8-HxCDF	**60851-34-5**	1.83	**0.917**	**2.75**
	1,2,3,7,8,9-HxCDF	**72918-21-9**	0.511	**0.255**	**0.77**
	1,2,3,4,6,7,8-HpCDF	**67562-39-4**	18.7	**9.36**	**28.1**
	1,2,3,4,7,8,9-HpCDF	**55673-89-7**	1.63	**0.815**	**2.44**
	OCDF	**39001-02-0**	58.4	**29.2**	**87.6**

8.5.7 TBT QC Performance Criteria: Sample Collection/Interstitial Water Analysis

The DMMP agencies recommend QC performance criteria rather than providing a step-by-step protocol for the extraction, derivitization, and analysis of TBT. The criteria presented in Table 6-10 must be met in order to verify that sample cleanup, extraction and derivitization methods are being performed correctly. Laboratories will be required to meet these performance criteria as well as take the specified corrective action if performance criteria are not met. Deviations from the specified performance criteria will be considered by the DMMP agencies on a project-specific basis. Justification for alternative performance criteria must be submitted in writing and receive agency approval prior to the initiation of testing. As discussed in earlier guidance (Michelsen, *et al.*, 1996), TBT analytical results should be reported as the TBT ion.

If the TBT concentration in the interstitial water is quantitated above 0.15 ug TBT/L, bioaccumulation testing of project sediments must be conducted using the DMMP bioaccumulation guidelines. Bioassay testing will not be required unless other chemicals of concern exceed screening levels. If unacceptable tissue concentrations are measured at the end of the bioaccumulation test, the sediment will be found unsuitable for open-water disposal. For additional information, see the SMARM issue paper Testing, Reporting, and Evaluation of Tributyltin Data in PSDDA and SMS Programs (1996).

Table 8-11. Summary of quality control procedures for TBT in interstitial water

QC CHECK	MINIMUM FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS) [1]	1 per analytical batch (≤ 20 samples)	Recovery 50 – 150%	1. Check calculations 2. Reanalyze (matrix or injection problems) 3. If still out, re-extract and reanalyze LCS and assoc. samples (if available); If not available flag data.
Matrix spike (MS) and matrix spike duplicate (MSD) [1]	1 MS/MSD pair per analytical batch (≤ 20 samples)	Recovery 50 – 150% and relative percent difference (RPD) ≤ 30%	1. Evaluate for supportable matrix effect. 2. If no interference, re-extract and reanalyze MS/MSD once (if available). 3. If still out, report both sets of data.
Surrogate spike [1] (Tripentyltin recommended)	1 per sample	Recovery 50 – 150%	1. Check calculations. 2. Evaluate for supportable matrix effect 3. If no interference is evident, re-extract and reanalyze affected sample(s) (if available) and flag any outliers.
Method blank[2]	1 per analytical batch (≤ 20 samples)	Target analyte < 3x the reporting limit (RL)	1. Flag if target > 3x RL but less than 0.075 ppb.[3] 2. Rerun batch and ID contamination source if target >0.075 ppb.

[1]All QC samples should be run using the same sample handling as is used on the environmental samples.
[2] Method blank can include centrifugation step or, alternatively a centrifugation blank can be run separately from the analytical method blank.
[3] 0.075 ppb TBT is used here as a benchmark for evaluating blank performance because it represents a concentration that is one-half the interstitial water screening level (0.15 ppb) that is being used by the DMMP agencies to determine the need for bioaccumulation testing. Note that a minimum interstitial water volume of 200-500 ml will be needed to attain reporting limits less than 0.075 ppb TBT.