High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry
PCDD/PCDFs (EPA Method 1613B)
EPA Stage 4 Review

Site: PHSS-Swan Island Basin	SDG #: 20665
Laboratory: Cape Fear Analytical (CFA)	Project #: DT2002.03.03.04.01
HydroGeoLogic, Inc. Validator: Ken Rapuano	Validation Date: 09.07.23
HGL Peer Reviewer: Jospeh Vilain (2b) Jennifer Chandler (L4)	Peer Review Date: 10/10/23 (2b) 08/17/2023 (L4)

Client Sample ID	Laboratory Sample ID	Matrix
SIB-046-TOB-0-1-10242022	20665001	Riverbank Soil
SIB-046-OHW-0-1-10242022	20665002	Riverbank Soil
SIB-045-TOB-0-1-10242022	20665003	Riverbank Soil
SIB-045-OHW-0-1-10242022	20665004	Riverbank Soil
SIB-044-TOB-0-1-10242022	20665005	Riverbank Soil
SIB-044-TOB-0-1-10242022MS	20665006	Riverbank Soil MS
SIB-044-TOB-0-1-10242022SD	20665007	Riverbank Soil MSD
SIB-044-OHW-0-1-10242022	20665008	Riverbank Soil
SIB-043-TOB-0-1-10242022	20665009	Riverbank Soil
SIB-043-OHW-0-1-10242022	20665010	Riverbank Soil
FD13-10242022	20665011	Riverbank Soil
SIB-042-OHW-0-1-10242022	20665012	Riverbank Soil
SIB-042-MLW-0-1-10242022	20665013	Riverbank Soil
SIB-041-OHW-0-1-10242022	20665014	Riverbank Soil
SIB-041-MLW-0-1-10242022	20665015	Riverbank Soil
SIB-040-OHW-0-1-10242022	20665016	Riverbank Soil
SIB-040-MLW-0-1-10242022	20665017	Riverbank Soil

CFA performed analyses for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by EPA Method 1613B on riverbank soil samples collected October 24, 2022. Analyses were performed in accordance with the project Quality Assurance Project Plan (HGL, 2022).

The data were validated in accordance with the following documents:

- Uniform Federal Policy-Quality Assurance Project Plan (UFP-QAPP), Revision 3; Remedial Design Services, Swan Island Basin Project Area, CERCLA Docket No. 10-2021-001, Portland Harbor Superfund Site Portland, Multnomah County, Oregon (HGL, 2022)
- USEPA National Functional Guidelines for High Resolution Superfund Methods Data Review (NFG) (EPA, 2020)
- HGL SOP HGL SOP 412.501 – Data Validation, U.S. EPA Stage 2A and Stage 2B (HGL, 2021)

In some cases, the calibration criteria presented in the QAPP did not correspond to the criteria presented in the laboratory analytical SOPs. In these cases, the laboratory criteria were used to evaluate calibration performance.

The qualifiers defined in Table 1 of EPA, 2020 have been applied to any results requiring qualification as described in this data validation report; the historical site data set uses only the J qualifier for estimated results (i.e., does not include the directional J+ and J− qualifiers) and this convention was retained in this DV report. The qualifiers have also been applied as the final qualifier to the electronic data deliverable (EDD) file provided by the laboratory. Any non-standard qualifiers and informational flags reported by the

laboratory in the laboratory qualifier field of this EDD are not included in the final qualifier field. A qualification summary table is provided at the end of this report as Attachment A.

In the text of the data validation report, assigned qualifiers are presented in the format "[qualifier]-[reason code(s)]" for ease of description. When presented in tabular format, the qualifier and the reason codes are presented in the columns named as presented in the EDD. The HGL data validation SOP does not include a reason code for ion abundance ratio discrepancies in labeled standards or for analyte results reported as estimated potential maximum concentrations (EMPCs); the reason codes IAR and EMPC are used, respectively, where applicable.

Narrative and Completeness Review – The case narrative and data package were checked for completeness. No completeness issues were noted. The narrative noted chlorinated diphenyl ether interferences affected the quantitation of PCDD/PCDF peaks for several samples. The affected results were reported with a laboratory qualifier of P and the narrative indicates that these results are potentially biased high. The results reported with a P qualifier by the laboratory are laboratory-calculated totals for homologs and no target 2,3,7,8-substituted congeners were affected. No additional qualification is required.

Qualification: None required.

Sample Delivery and Condition – The samples arrived at the laboratory in acceptable condition and temperature. All samples were collected on October 24, 2022. The samples were shipped on October 25, 2022, and arrived at the laboratory on October 26, 2022. Per the field team leader, the samples were stored refrigerated before shipping. All samples arrived at the laboratory at temperatures of 4.7 °C.

Qualification: None required.

Holding Times – All samples were extracted within the 1-year holding time from collection; all analyses were performed within the 1-year holding time for extracts.

Qualification: None required.

Field Blanks – Equipment blank EB04-10262022 (results reported in SDG 20699) is associated with all samples collected on 10.24.22. Due to the differences in mass extracted, the concentrations reported as pg/L in EBs correspond to the 0.1 x concentration in pg/g in oil samples. OCDD was detected in rinse blank EB04-10262022 at 3.95 pg/L, leading to a qualification level of 1.975 pg/g. All OCDD results in associated samples were greater than the qualification level and no qualification is required.

Qualification: None required.

Field Duplicates – Sample FD13-10242022 is a field duplicate of sample SIB-045-TOB-0-1-10242022. The results for 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF, and OCDF did not meet the precision criteria. The 1,2,3,4,6,7,8-HpCDD, OCDD, and OCDF results for samples SIB-045-TOB-0-1-10242022 and FD13-10242022 should be qualified J-FDPR and the 1,2,3,4,6,7,8-HpCDF results should be qualified J-FDPA.

***Qualification*: The 1,2,3,4,6,7,8-HpCDD, OCDD, and OCDF results for samples SIB-045-TOB-0-1-10242022 and FD13-10242022 are qualified J-FDPR and the 1,2,3,4,6,7,8-HpCDF results for samples SIB-045-TOB-0-1-10242022 and FD13-10242022 are qualified J-FDPA.**

Mass Tuning – Mass tuning was performed before the ICal sequence, before each daily analytical sequence, and at the end of each daily analytical sequence. Data was not provided to calculate the resolving power; however, all peaks appeared to be fully resolved and Gaussian in form.

Qualification: None required.

SDG 20665 - HRGC_HRMS_Stage_4

Column Check – Column check data for each analytical sequence showed acceptable separation for TCDD and TCDF.

Qualification: None required.

Initial Calibration – A six-point ICal was performed on instrument HRP757_3 (DB-225 column) on November 22, 2022, a six-point ICal was performed on instrument HRP763_1 (DB-5MS column) on November 2, 2022, and a six-point ICal was performed on instrument HRP791_3 (DB-5MS column) on January 2, 2023. These ICals are associated with all PCDD/PCDF results reported in this SDG. The ICals included all target analytes required by the method. All target analytes and labeled standards included in the ICal had %RSDs ≤20%. The ICal verification standard met all acceptance criteria for target analytes and labeled standards.

The ICal was checked by back-calculating the concentration for PCDD/PCDFs and labeled standards for each calibration level. No acceptance criteria for this back-check were provided in the analytical method or in the laboratory SOP. All back-calculated concentrations agreed with the nominal standard concentration within ±20% and in the judgment of the validator, these results are acceptable.

All ion abundance ratio (IAR) criteria were met in the ICal standards and all S/N ratios were >10.

Qualification: None required.

Continuing Calibration – Target PCDD/PCDF compounds and labeled analogs met the method %D requirement in each CCV. All IAR criteria were met in the CCV standards and all S/N ratios were >10.

Qualification: None required.

Method Blanks – The method blank associated with preparation batch 52355 was contaminated with the following PCDD/PCDF analytes:

- 0.102 pg/g 1,2,3,7,8-PeCDD, leading to a qualification level of 0.510 pg/g
- 0.240 pg/g 1,2,3,4,6,7,8-HpCDD, leading to a qualification level of 1.20 pg/g
- 0.814 pg/g OCDD, leading to a qualification level of 4.70 pg/g
- 0.134 pg/g 1,2,3,7,8-PeCDF, leading to a qualification level of 0.670 pg/g
- 0.0880 pg/g 1,2,3,4,7,8-HxCDF, leading to a qualification level of 0.440 pg/g
- 0.184 pg/g 1,2,3,4,6,7,8-HpCDF, leading to a qualification level of 0.920 pg/g

The 1,2,3,7,8-PeCDD result for sample SIB-042-OHW-0-1-10242022 is below the qualification threshold and should be qualified U-MBL.

***Qualification*: The 1,2,3,7,8-PeCDD result for sample SIB-042-OHW-0-1-10242022 is qualified U-MBL.**

Labeled Standards – All labeled standard %Rs met the method control limits, with the exception of 13C-1,2,3,7,8,9-HxCDF which was recovered below control limits in sample SIB-045-OHW-0-1-10242022. The 1,2,3,7,8,9-HxCDF result in that sample should be qualified UJ All IARs were in control for labeled standards.

***Qualification*: The result for 13C-1,2,3,7,8,9-HxCDF in sample SIB-045-OHW-0-1-10242022 is qualified UJ.**

Laboratory Control Samples – The LCS/LCSDs associated with all PCDD/PCDF sample analyses had %Rs and RPDs in control.

Qualification: None required.

MS/MSD – An MS/MSD was performed using sample SIB-044-TOB-0-1-10242022. The MS showed high %Rs for 2,3,7,8-TCDF (DB-225 column), 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, and

1,2,3,4,6,7,8-HpCDF; the MSD showed an extremely low %R (<20%) for OCDD. All RPDs were in control. The 1,2,3,4,6,7,8-HpCDD, OCDD, and 1,2,3,4,6,7,8-HpCDF %R discrepancies are not considered applicable because the sample concentrations are >4x the spike concentrations. The 2,3,7,8-TCDF and 1,2,3,6,7,8-HxCDD results reported for sample SIB-044-TOB-0-1-10242022 should be qualified J-MSH.

***Qualification*: The 2,3,7,8-TCDF and 1,2,3,6,7,8-HxCDD results reported for sample SIB-044-TOB-0-1-10242022 are qualified J-MSH.**

Raw Data Review – Samples SIB-043-TOB-0-1-10242022 and SIB-042-OHW-0-1-10242022 were selected for in-depth review. Gas chromatograms, retention time windows, and S/N were examined. No discrepancies were noted.

Qualification: None required.

Compound Quantitation and Identification – The HGL reviewer confirmed that the laboratory uses the mean internal standard procedure described in Section 17.1.2 of Method 1613B to quantify 1,2,3,7,8,9-HxCDD.

Analyte non-detections were reported as the EDL and qualified U. Analytes detected between the EDL and PQL were reported as J-qualified results by the laboratory. These J qualifiers were retained unless superseded by a more severe qualifier.

If a detected analyte has an ion ration outside the characteristic ion ratio window, the result is reported as an estimated maximum potential concentration. All results reported as an EMPC (a "K" flag is present in the laboratory qualifier) are qualified J-EMPC unless superseded by a higher priority qualifier.

2,3,7,8-TCDF is not fully resolved on the DB-5MS column; when detected above the PQL on the DB-5MS column, the result was confirmed on a DB-225 column using the instrument ID listed in the case narrative. In cases where two results are reported for 2,3,7,8-TCDF for a sample, the result from the DB-225 column is selected for use and the result from the DB-5MS is qualified DNR-EXC.

In cases where a target analyte is detected at a concentration above the calibrated range, the laboratory's practice is to report the result with a laboratory qualifier of E without running a dilution so long as the detector is not saturated. The OCDD results for 10 affected samples are qualified J-ACR.

***Qualification:* The following results are qualified:**

- **All results reported with a laboratory qualifier of K are qualified J with reason code EMPC.**
- **All 2,3,7,8-TCDF results reported from the DB-5MS column that are paired with a 2,3,7,8-TCDF result from the DB-225 column are qualified DNR, reason code EXC; note that the reportable_result field for these results are populated with "Yes" by the laboratory and are changed to "No" for the affected results.**
- **OCDD results reported with a laboratory qualifier of E are qualified J with reason code ACR; note that the reportable_result field for these results are populated with "No" by the laboratory and are changed to "Yes" for the affected results. Some results reported for total HpCDDs or total HpCDFs are occasionally reported with E qualifiers by the laboratory; although these results are not validated, the reportable_result field has been changed from "No" to "Yes" for these results.**

Calculation and Transcription Verification – Samples SIB-043-TOB-0-1-10242022 and SIB-042-OHW-0-1-10242022 were selected for calculation and transcription verification. Recalculation was also performed on 10% of target analytes in the initial calibration. These calculation verifications used the raw data and were carried through to the results reported on summary pages and also constitute a transcription verification. Calculations are presented in Attachment B.

Qualification: None required.

SDG 20665 - HRGC_HRMS_Stage_4

Overall Assessment of Data - The data are usable as reported with the qualification applied by the reviewer.

SDG 20665 - HRGC_HRMS_Stage_4

Attachment A – Qualification Summary Table
PCDD/PCDFs by Method 1613B

SDG: 20665
Laboratory: Cape Fear Analytical
Validator: Ken Rapuano, HGL
Validation Date: 9.7.23

In addition to the qualifiers assigned below, all detected results <PQL retain the J qualifier assigned by the laboratory. All non-standard qualifiers assigned by the laboratory are removed and are not included as the final qualifier.

Sample ID	Analyte	Conc[1]	Lab Qual	**Val Qual**	**Final Qual[2]**	**Reason Codes[3]**
SIB-046-TOB-0-1-10242022 (20665001)	OCDD	9500	E	**J**	**J**	**ACR[5]**
	2,3,7,8-TCDF (DB-5MS column)	2.78	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	2.95	--	**--**	**--**	**--**
SIB-046-OHW-0-1-10242022 (20665002)	OCDD	4010	E	**J**	**J**	**ACR[5]**
	2,3,7,8-TCDF (DB-5MS column)	2.00	K	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	2.38	--	**--**	**--**	**--**
SIB-045-TOB-0-1-10242022 (20665003)	1,2,3,4,6,7,8-HpCDD	190	--	**J**	**J**	**FDPR**
	OCDD	2130	--	**J**	**J**	**FDPR**
	1,2,3,4,6,7,8-HpCDF	27.9	--	**J**	**J**	**FDPA**
	OCDF	124	--	**J**	**J**	**FDPR**
SIB-045-OHW-0-1-10242022 (20665004)	OCDD	9330	E	**J**	**J**	**ACR[5]**
	2,3,7,8-TCDF (DB-5MS column)	1.40	U	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	1.21	--	**--**	**--**	**--**
SIB-044-TOB-0-1-10242022 (20665005)	1,2,3,6,7,8-HxCDD	119	--	**J**	**J**	**MSH**
	OCDD	34500	E	**J**	**J**	**ACR[5]**
	2,3,7,8-TCDF (DB-5MS column)	9.48	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	8.55	K	**J**	**J**	**EMPC, MSH**
SIB-044-OHW-0-1-10242022 (20665008)	OCDD	7330	E	**J**	**J**	**ACR[5]**
	2,3,7,8-TCDF (DB-5MS column)	2.54	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	3.02	--	**--**	**--**	**--**
SIB-043-TOB-0-1-10242022 (20665009)	No qualification required					
SIB-043-OHW-0-1-10242022 (20665010)	2,3,7,8-TCDF (DB-5MS column)	6.27	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	2.9	K	**J**	**J**	**EMPC**

Attachment A – Qualification Summary Table
PCDD/PCDFs by Method 1613B

Sample ID	Analyte	Conc[1]	Lab Qual	**Val Qual**	**Final Qual[2]**	**Reason Codes[3]**
FD13-10242022 (20665011)	1,2,3,4,6,7,8-HpCDD	92.1	--	**J**	**J**	**FDPR**
	OCDD	966	--	**J**	**J**	**FDPR**
	1,2,3,4,6,7,8-HpCDF	14.4	--	**J**	**J**	**FDPA**
	OCDF	60	--	**J**	**J**	**FDPR**
SIB-042-OHW-0-1-10242022 (20665012)	1,2,3,7,8-PeCDD	0.386	BJK	**UJ**	**UJ**	**EMPC, MBL**
	2,3,7,8-TCDF (DB-5MS column)	1.56	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	2.2	K	**J**	**J**	**EMPC**
SIB-042-MLW-0-1-10242022 (20665013)	OCDD	13800	E	**J**	**J**	**ACR[5]**
	2,3,7,8-TCDF (DB-5MS column)	1.98	K	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	3.4	K	**J**	**J**	**EMPC**
SIB-041-OHW-0-1-10242022 (20665014)	OCDD	14600	E	**J**	**J**	**ACR[5]**
SIB-041-MLW-0-1-10242022 (20665015)	OCDD	35700	E	**J**	**J**	**ACR[5]**
SIB-005-MLW-0-1-10172022 (20665016)	No qualification required					
SIB-040-MLW-0-1-10242022 (20665017)	OCDD	6240	E	**J**	**J**	**ACR[5]**
All samples	Results not already addressed above	Varies	Includes K	**J**	**J**	**EMPC**

[1] All concentrations in pg/g
[2] Where multiple qualifiers are applied to a result, the priority for assigning the final qualifier is as follows:
Detected Results: DNR > R > J > no qualifier
Non-detected results: DNR > R > UJ > U
[3] Reason Code Definitions:
ACR = Analyte reported from above the calibrated range
EMPC = Analyte identified as an EMPC; all identification criteria met except IAR
EXC = Analyte excluded (reportable_result field populated with “No”)
MBH = Analyte detected above the PQL in the associated method blank
MSP = MS/MSD precision did not meet criteria
[4] reportable_result field changed from “Yes” to “No”
[5] reportable_result field changed from “No” to “Yes”

Calculation of Field Duplicate Precision
CFA SDG 20665
Parent = Sample SIB-045-TOB-0-1-10242022 (results summary pp. 23-24)
Duplicate = Sample FD13-10242022 (results summary pp. 39-40)
Absolute comparison values are the EDL for results reported as ND.
Both samples were analyzed at the same dilution level and the higher of the two PQLs was used

Analyte	Parent Result	Parent Abs Compare Value	Parent PQL	Duplicate Result
2,3,7,8-TCDD	ND	0.250	0.5	ND
1,2,3,7,8-PeCDD	0.966	0.966	2.5	0.752
1,2,3,4,7,8-HxCDD	1.3	1.30	5	0.894
1,2,3,6,7,8-HxCDD	3.87	3.87	5	2.07
1,2,3,7,8,9-HxCDD	2.07	2.07	5	1.05
1,2,3,4,6,7,8-HpCDD	190	190	5	92.1
1,2,3,4,6,7,8,9-OCDD	2130	2130	10	966
2,3,7,8-TCDF	ND	0.390	1	ND
1,2,3,7,8-PeCDF	1.95	1.95	5	1.48
2,3,4,7,8-PeCDF	2.40	2.4	5	1.92
1,2,3,4,7,8-HxCDF	2.46	2.46	5	1.43
1,2,3,6,7,8-HxCDF	1.51	1.51	5	0.964
2,3,4,6,7,8-HxCDF	1.71	1.71	5	1.11
1,2,3,7,8,9-HxCDF	0.672	0.672	5	ND
1,2,3,4,6,7,8-HpCDF	27.9	27.9	5	14.4
1,2,3,4,7,8,9-HpCDF	1.52	1.52	5	0.784
1,2,3,4,6,7,8,9-OCDF	124	124	10	60

used for absolute difference comparisons.

Duplicate Abs Compare Value	Duplicate PQL	Units	RPD (%)	RPD Goal Met (50%)	Absolute Difference
0.260	0.5	pg/g	NC	-	0.01
0.752	2.5	pg/g	NC	-	0.214
0.894	5	pg/g	NC	-	0.406
2.07	5	pg/g	NC	-	1.8
1.05	5	pg/g	NC	-	1.02
92.1	5	pg/g	69.4	No	NA
966	10	pg/g	75.2	No	NA
0.382	1	pg/g	NC	-	0.008
1.48	5	pg/g	NC	-	0.47
1.92	5	pg/g	NC	-	0.48
1.43	5	pg/g	NC	-	1.03
0.964	5	pg/g	NC	-	0.546
1.11	5	pg/g	NC	-	0.6
0.536	5	pg/g	NC	-	0.136
14.4	5	pg/g	NC	-	13.5
0.784	5	pg/g	NC	-	0.736
60	10	pg/g	69.6	No	NA

Absolute Difference Goal (±2xPQL) Met
Yes
Yes
Yes
Yes
Yes
NA
NA
Yes
Yes
Yes
Yes
Yes
Yes
Yes
No
Yes
NA