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

Site: PHSS-Swan Island Basin	SDG #: 20634
Laboratory: Cape Fear Analytical (CFA)	Project #: DT2002.03.03.04.01
HydroGeoLogic, Inc. Validator: Ken Rapuano	Validation Date: 09.05.23
HGL Peer Reviewer: Joseph Vilain (2b) Jennifer Chandler (L4)	Peer Review Date: 10/10/23 (2b) 08/17/2023

Client Sample ID	Laboratory Sample ID	Matrix
SIB-075-MLW-0-1-10132022	20634001	Riverbank Soil
SIB-075-OHW-0-1-10132022	20634002	Riverbank Soil
SIB-075-OHW-0-1-10132022MS	20634003	Riverbank Soil MS
SIB-075-OHW-0-1-10132022SD	20634004	Riverbank Soil MSD
SIB-075-TOB-0-1-10132022	20634005	Riverbank Soil
SIB-074-MLW-0-1-10132022	20634006	Riverbank Soil
SIB-074-OHW-0-1-10132022	20634007	Riverbank Soil
SIB-074-TOB-0-1-10132022	20634008	Riverbank Soil
SIB-073-MLW-0-1-10132022	20634009	Riverbank Soil
SIB-073-OHW-0-1-10132022	20634010	Riverbank Soil
SIB-073-TOB-0-1-10132022	20634011	Riverbank Soil
FD07-10132022	20634012	Riverbank Soil
SIB-072-MLW-0-1-10132022	20634013	Riverbank Soil
SIB-072-OHW-0-1-10132022	20634014	Riverbank Soil
SIB-072-TOB-0-1-10132022	20634015	Riverbank Soil
SIB-071-MLW-0-1-10132022	20634016	Riverbank Soil
SIB-071-OHW-0-1-10132022	20634017	Riverbank Soil
SIB-071-TOB-0-1-10132022	20634018	Riverbank Soil
SIB-070-MLW-0-1-10132022	20634019	Riverbank Soil
SIB-070-OHW-0-1-10132022	20634020	Riverbank Soil
SIB-069-MLW-0-1-10142022	20634021	Riverbank Soil
SIB-069-OHW-0-1-10142022	20634022	Riverbank Soil
SIB-069-TOB-0-1-10142022	20634023	Riverbank Soil
SIB-068-TOB-0-1-10142022	20634024	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 13 and 14, 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.

Qualification: None required.

Sample Delivery and Condition – The samples arrived at the laboratory in acceptable condition and temperature. All samples were collected on October 13 and 14, 2022. The samples were shipped on October 18, 2022, and arrived at the laboratory on October 19, 2022. Per the field team leader, the samples were stored refrigerated before shipping. All samples arrived at the laboratory at temperatures of 2.3 to 3.7 °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 EB02-10102022 (results reported in SDG 20186) is associated with all riverbank soil samples reported in this SDG. 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 soil samples. OCDD was detected in the rinse blank, but the detected concentration was similar to the concentration in the associated aqueous method blank. The OCDD detected in the rinse blank is attributable to laboratory contamination in aqueous sample preparation and no qualification of solid matrix samples is required.

Qualification: None required.

Field Duplicates – Sample FD07-10132022 is a field duplicate of sample SIB-073-MLW-0-1-10132022. All results in the duplicate pair met precision criteria.

Qualification: None required.

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 with one exception. The peak for m/z 354 at the close of run e04apr23a was off center and a substantial portion of the peak was outside the mass window. The laboratory was contacted, and the lead analyst indicated that there is

an interference (column bleed peak) in the 354 window that is sometimes observed at the end of a sequence. The TCDF and 13C-TCDF peaks are bracketed by the 292 and 318 peaks, so there is no impact on the associated sample data.

Qualification: None required.

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, and a six-point ICal was performed on instrument HRP791_3 (DB-5 column) on January 2, 2023. These ICals are associated with all PCDD/PCDF results reported in this SDG. The ICal 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 52214 was contaminated with 1.21 pg/g OCDD and 0.374 pg/g 1,2,3,4,6,7,8-HpCDF, leading to qualification levels of 6.05 pg/g and 1.87 pg/g, respectively. All associated results for these two compounds were detections greater than the qualification threshold and no qualification is required. The method blank associated with batch 52237 was free from contamination.

Qualification: None required.

Labeled Standards – All labeled standard %Rs met the method control limits. All IARs were in control for labeled standards, with the following exceptions. In all cases, the labeled standards in the associated calibration standard analyses were in control and the affected sample results should be qualified J (detections) or UJ (non-detections).

- 13C-12378-PeCDF in sample SIB-074-OHW-0-1-10132022; the corresponding detection of 1,2,3,7,8-PeCDF should be qualified J-IAR
- 13C-12378-PeCDF in sample SIB-072-TOB-0-1-10132022; the corresponding detection of 1,2,3,7,8-PeCDF should be qualified J-IAR

***Qualification*: The detected 1,2,3,7,8-PeCDF results for samples SIB-074-OHW-0-1-10132022 and SIB-072-TOB-0-1-10132022 are qualified J-IAR.**

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

Qualification: None required.

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MS/MSD – An MS/MSD was performed using sample SIB-075-OHW-0-1-10132022. All MS/MSD %Rs and RPDs were in control with the exception of a very low %R for OCDD in the MS, high %Rs for 1,2,3,4,6,7,8-HpCDD and OCDD in the MSD, and high MS/MSD RPDs for 1,2,3,4,6,7,8-HpCDD and OCDD. The OCDD %R discrepancies are not considered applicable because the sample concentration is >4x the spike concentration. The OCDD result reported for sample SIB-075-OHW-0-1-10132022 should be qualified J-MSP; the 1,2,3,4,6,7,8-HpCDD result for sample SIB-075-OHW-0-1-10132022 should be qualified J-MSH,MSP.

> ***Qualification*: The OCDD result reported for sample SIB-075-OHW-0-1-10132022 should be qualified J-MSP; the 1,2,3,4,6,7,8-HpCDD result for sample SIB-075-OHW-0-1-10132022 should be qualified J-MSH,MSP.**

Raw Data Review – Samples SIB-073-TOB-0-1-10132022 and SIB-069-TOB-0-1-10142022 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 affected results 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.**

Calculation and Transcription Verification – Samples SIB-073-TOB-0-1-10132022 and SIB-069-MLW-0-1-10142022 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.2.

> *Qualification*: None required.

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

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

SDG: 20634
Laboratory: Cape Fear Analytical
Validator: Ken Rapuano, HGL
Validation Date: 8.20.23

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-075-MLW-0-1-10132022 (20634001)	No qualification required					
SIB-075-OHW-0-1-10132022 (20634002)	1,2,3,4,6,7,8-HpCDD	199	--	**J**	**J**	**MSH,MSP**
	OCDD	1540	--	**J**	**J**	**MSP**
	2,3,7,8-TCDF (DB-5MS column)	1.16	K	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	1.26	--	--	--	--
SIB-075-TOB-0-1-10132022 (20634005)	2,3,7,8-TCDF (DB-5MS column)	2.2	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	1.14	U			
SIB-074-MLW-0-1-10132022 (20634006)	No qualification required					
SIB-074-OHW-0-1-10132022 (20634007)	2,3,7,8-TCDF (DB-5MS column)	19.8	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	7.96	--	--	--	--
	1,2,3,7,8-PeCDF	40.1	--	**J**	**J**	**IAR**
SIB-074-TOB-0-1-10132022 (20634008)	2,3,7,8-TCDF (DB-5MS column)	1.9	K	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	1.8	--	--	--	--
SIB-073-MLW-0-1-10132022 (20634009)	No qualification required					
SIB-073-OHW-0-1-10132022 (20634010)	2,3,7,8-TCDF (DB-5MS column)	6.81	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	5.21	--	--	--	--
SIB-073-TOB-0-1-10132022 (20634011)	2,3,7,8-TCDF (DB-5MS column)	2.95	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	2.6	--	--	--	--
FD07-10132022 (20634012)	No qualification required					
SIB-072-MLW-0-1-10132022 (20634013)	No qualification required					
SIB-072-OHW-0-1-10132022 (20634014)	2,3,7,8-TCDF (DB-5MS column)	1.55	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	1.92	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]**
SIB-072-TOB-0-1-10132022 (20634015)	OCDD	6840	E	**J**	**J**	**ACR[5]**
	2,3,7,8-TCDF (DB-5MS column)	33.2	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	14.2	--	--	--	--
	1,2,3,7,8-PeCDF	89.6	--	**J**	**J**	**IAR**
SIB-071-MLW-0-1-10132022 (20634016)	No qualification required					
SIB-071-OHW-0-1-10132022 (20634017)	2,3,7,8-TCDF (DB-5MS column)	1.62	--	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	1.34	--	--	--	--
SIB-071-TOB-0-1-10132022 (20634018)	No qualification required					
SIB-070-MLW-0-1-10132022 (20634019)	2,3,7,8-TCDF (DB-5MS column)	1.45	K	**DNR**	**DNR**	**EXC[4]**
	2,3,7,8-TCDF (DB-225 column)	1.66	--	--	--	--
SIB-070-OHW-0-1-10132022 (20634020)	No qualification required					
SIB-069-MLW-0-1-10142022 (20634021)	No qualification required					
SIB-069-OHW-0-1-10142022 (20634022)	No qualification required					
SIB-069-TOB-0-1-10142022 (20634023)	No qualification required					
SIB-068-TOB-0-1-10142022 (20634024)	No qualification required					
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”)
IAR = ion abundance ratio not met in associated labeled standard
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”

PCDD/PCDF ICal Calculations
CFA SDG 20634
Instrument HRP791_3 (DB-5MS Column)
Analyzed 11/22/22
Summary Data pp. 903-913
Raw Data pp. 915-1011

File ID	Analyte Conc	Analyte Resp	IS Conc	IS Resp	RRF	Reported RRF
c02jan23a-3	1.25	1.60E+04	100	1.23E+06	1.041	1.046
c02jan23a-4	2.5	3.58E+04	100	1.36E+06	1.053	1.053
c02jan23a-5	10	2.07E+05	100	1.86E+06	1.113	1.110
c02jan23a-6	50	1.04E+06	100	1.88E+06	1.106	1.112
c02jan23a-7	200	4.57E+06	100	2.04E+06	1.120	1.119
c02jan23a-8	1000	2.83E+07	100	2.52E+06	1.123	1.120
		Calc	Rep			
	Mean RRF	1.093	1.094			
	%RSD	3.31371	3.14458			

File ID	Analyte Conc	Analyte Resp	IS Conc	IS Resp	RRF	Reported RRF
c02jan23a-3	1.25	2.64E+04	100	1.87E+06	1.129	1.129
c02jan23a-4	2.5	5.69E+04	100	2.07E+06	1.100	1.098
c02jan23a-5	10	3.20E+05	100	2.76E+06	1.159	1.160
c02jan23a-6	50	1.62E+06	100	2.71E+06	1.196	1.195
c02jan23a-7	200	7.25E+06	100	3.01E+06	1.204	1.202
c02jan23a-8	1000	4.44E+07	100	3.73E+06	1.190	1.191
		Calc	Rep			
	Mean RRF	1.163	1.162			
	%RSD	3.58375	3.59891			

Instrument HRP757_3 (DB-225 Column)
Analyzed 11/22/22
Summary Data p. 869
Raw Data pp. 872-885

File ID	Analyte Conc	Analyte Resp	IS Conc	IS Resp	RRF	Reported RRF
e22nov22a-4	0.25	2.15E+03	100	8.34E+05	1.031	1.031
e22nov22a-5	0.5	2.52E+03	100	4.95E+05	1.018	1.019
e22nov22a-6	2	8.86E+03	100	4.76E+05	0.931	0.930
e22nov22a-7	10	4.68E+04	100	4.86E+05	0.963	0.962
e22nov22a-8	40	1.72E+05	100	4.52E+05	0.951	0.953
e22nov22a-9	200	1.01E+06	100	5.17E+05	0.977	0.981
		Calc	Rep			
	Mean RRF	0.979	0.979			
	%RSD	3.98941	3.97932			

1,2,3,7,8-PeCDD
IS = C13-1,2,3,7,8-PeCDD

1,2,3,6,7,8-HxCDF
IS = C13-1,2,3,6,7,8-HxCDF

2,3,7,8-TCDF
IS = C13-2,3,7,8-TCDF