EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022

EURL-PT-POP_2203-FM

FEED

Report

PBDEs and HBCDDs

(Report Version 1.0)

28 July 2023

EURL for halogenated POPs in Feed and Food
c/o State Institute for Chemical and
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Summary

Test sample	**FEED:** Fish Meal [2203-FM]
Analytes of interest **Mandatory** for NRLs:	**PBDEs** (BDE-28, -47, -49, -99, -100, -153, -154, -183, -209) **HBCDDs** (α-HBCDD, β-HBCDD, γ-HBCDD or total HBCDD)
Methods	Any kind of method
Participants	NRLs, OFLs, other official laboratories, commercial laboratories performing the analysis of samples taken by feed business operators
Statistical evaluation	ISO 13528:2022 [1], IUPAC Protocol [2]
Report of final results	28 July 2023 (Version 1.0)
Publication	EURL POPs reserves all rights to publish and present the anonymised results of the interlaboratory study in scientific journals and/or during conferences.

1. Structure of the PT, test material and analytes

This proficiency test (PT) on the determination of **PCDD/Fs, PCBs, PBDEs, HBCDDs** and **PFASs** in **fish meal** was organized by European Union Reference Laboratory (EURL) for halogenated persistent organic pollutants (POPs) in Feed and Food to be performed between September and November 2022. The objective was to assess analytical performance of laboratories and interlaboratory comparability of results from analyses of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in one sample of **fish meal**.

National Reference Laboratories (NRLs) for halogenated POPs in Feed and Food from EU member states were requested to participate as part of their work programme for 2022. NRLs were invited to encourage the participation of Official Laboratories (OFLs) from their member states as part of their duties following Article 101 of regulation (EU) 2017/625 of the European Parliament and of the Council of 15 March 2017. Furthermore, participation of OFLs allowed the extension of the data basis for calculation of assigned values and evaluation of results. **Other official laboratories** and **commercial laboratories** performing the analysis of samples taken by feed business operators were invited to participate in this proficiency test.

The evaluated results were discussed by representatives of European Commission, NRLs and the EURL at the EURL/NRL workshop on 29 and 30 November 2022.

1.1. Samples and coding

The test sample was prepared from commercially available feed, naturally contaminated with PCDD/Fs, PCBs and PFASs and fortified with analytes of interest using technical mixtures of PBDEs and HBCDDs. Each participant received about **90 g** of the test sample in a HDPE bottle.

Fish Meal	**Sample no. 2203-FM-xxx**

1.2. Analytes of interest

NRLs for halogenated POPs in feed and food were requested to determine the following parameters:

Polybrominated diphenyl ethers (PBDEs)

- Individual congeners: BDE-28, -47, -49, -99, -100, -153, -154, -183, -209
- Sum of 8 PBDEs (without BDE-209)
- Sum of 9 PBDEs (with BDE-209)

Hexabromocyclododecanes (HBCDDs)

- α-HBCDD, β-HBCDD, γ-HBCDD stereoisomers
- Sum of α-, β-, γ-HBCDD (using HPLC methods)
- Total HBCDD (using GC methods)

1.3. Methods

All kinds of detection and quantification methods could be applied.

1.4. Coding of laboratories and confidentiality

The identity of participating laboratories will be kept confidential and will not be revealed to other participants.
For NRLs of EU member states, the suggested "protocol for management of underperformance in comparative testing or lack of collaboration of National Reference Laboratories (NRLs)" will be followed. The confidentiality of NRLs will be kept according to this protocol. For OFLs of EU member states cooperating with NRL, the respective NRLs will inform the EURL for halogenated POPs about the participating OFLs and will receive the respective laboratory codes, invoices for participation fee and certificates of participation of the OFLs.

1.5. Results of PBDEs and HBCDDs

Laboratories should:

- use their own reference standards for identification and quantification,
- report results for each analyte,
- report the limit of quantification (LOQ), at least for each non-quantified analyte,
- give method information and
- give information about the accreditation of the laboratory according to ISO/IEC 17025 *(for metrological traceability of consensus values of participants used as assigned values).*

Results had to be reported in **µg/kg, relative to a feed with a moisture content of 12 %,** for PBDEs and HBCDDs.

2. Participating laboratories

This proficiency test was open for participation of:

- National Reference Laboratories (NRLs) of EU member states
- National Reference Laboratories of other European countries
- Official laboratories
- Commercial laboratories

113 laboratories registered for this proficiency test. For PBDE and HBCDD, 27 and 19 sets of results were reported, respectively.

Table 1: Participating laboratories

Participating laboratories	Region	No. of participants
National Reference Laboratories	European Union Other Countries	19 2
Official Laboratories	European Union Other European Countries Africa Americas Asia Oceania	6 - - - - 1
Commercial Laboratories	European Union Other European Countries Africa Americas Asia Oceania	1 - - - - -
	Total	**29**

2.1. Number of reported results

Table 2: Reported results for PBDEs and moisture content for fish meal (2203-FM)

Reported results (2203-FM)	All laboratories
BDE-28	27
BDE-47	27
BDE-49	24
BDE-99	27

Reported results (2203-FM)	All laboratories
BDE-100	27
BDE-153	27
BDE-154	27
BDE-183	26
BDE-209	22
Sum of 8 PBDEs (without BDE-209) (ub)	26
Sum of 8 PBDEs (without BDE-209) (lb)	26
Sum of 9 PBDEs (with BDE-209) (ub)	23
Sum of 9 PBDEs (with BDE-209) (lb)	23
Moisture content	26

Table 3: Reported results for HBCDDs for fish meal (2203-FM)

Reported results (2203-FM)	All laboratories
α-HBCDD	18
β-HBCDD	18
γ-HBCDD	18
Sum of α-, β-, γ-HBCDD (ub)	17
Sum of α-, β-, γ-HBCDD (lb)	17
Total HBCDD (using GC methods)	2

2.2. Accreditation

Table 4: Reported accreditation according to ISO/IEC 17025 by participants for PBDEs and HBCDDs

Fish Meal	PBDEs	HBCDDs
Accreditation	20	7
No accreditation	7	11

2.3. Detection methods

The following detection methods were applied:

- GC-HRMS-, GC-MS/MS, GC-NCI-MS-methods for PBDEs
- GC-HRMS-, LC-MS/MS-, LC-HRMS-methods for HBCDDs

Table 5: Overview of chromatographic separation and detection methods for the determination of PBDEs and HBCDDs for fish meal (2203-FM)

Detection methods	PBDEs	HBCDDs
GC-HRMS	17	2
GC-MS/MS	9	-
GC-NCI-MS	1	-
LC-MS/MS	-	15
LC-HRMS	-	3

3. Test for sufficient homogeneity

The test for sufficient homogeneity was performed according to ISO 13528:2022 [1] and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [2]. Therefore, 10 portions of the test samples 2203-FM were analyzed in duplicate for PBDEs. The test for sufficient homogeneity was performed for individual congeners and sum parameters. The test materials showed sufficient homogeneity and stability for PBDEs for this proficiency test. Homogeneity can be concluded also for HBCDDs, due to similar physico-chemical properties. The stability check of the analytes of interest applying room temperature storage was performed according to ISO 13528:2022 [1]. The test material showed sufficient stability for this proficiency test.

4. Determination of the assigned value

Statistical evaluation of the PT results was performed by the EURL for halogenated POPs in feed and food according to DIN ISO 13528:2022 [1] and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [2].
The determination of the assigned value was performed according [1] by estimating of the assigned value as the consensus of participants' results (using only results of physico-chemical methods). The Huber robust mean is taken as assigned value after excluding extreme outliers (outside the range of ± 50 % of the median of all reported results) and examination of the distribution of the remaining results using histogram and Kernel density estimation, if necessary.

Assigned values were calculated for individual PBDE congeners, sum of 8 (without BDE-209) and sum of 9 (with BDE-209) PBDEs, for individual HBCDD diastereomers, sum of α-, β- and γ-HBCDD and total HBCDD (including limits of quantification (LOQs)), if possible. Additionally the median of all values was calculated.
For individual congeners (including LOQs) assigned values were only calculated according to the above mentioned procedure, if more than 2/3 of all results are above the LOQ and less than 1/3 of all results (including LOQs) are outside the range of ± 50 % of the median of all reported results. Levels for individual congeners are only taken for evaluation and calculation if these levels are equal to or above the LOQ; otherwise the LOQ will be taken instead.
Due to high variation of participants' results in the range of the respective LOQ or too few results, no assigned values could be calculated for:

- (+/–)-γ-HBCDD
- Total HBCDD (using GC-methods)

Since there are no traceable reference values available, the assigned values in this PT were calculated based on the Huber robust mean of the participants' results. Therefore, the assigned values are only traceable to the results of the participants. Additionally the results of all participants reporting results and the results of participants having accreditation according to ISO/IEC 17025 were compared for PBDE sum parameters. 20 of 27 participating laboratories were accredited according to ISO/IEC 17025 for PBDEs. No significant differences (0 to 2 %) between the assigned values calculated for both data sets for PBDEs were observed. For HBCDDs only 7 out of 19 participating laboratories were accredited according to ISO/IEC 17025. Therefore, no assigned values for HBCDDs could be calculated for this group of participants (Table 6).

Table 6: Comparison of assigned values for all participants and participants with reported accreditation according to ISO/IEC 17025 for PBDE and HBCDD sum parameters

Sum parameters	Assigned value All participants	Assigned value ISO/IEC 17025 accreditation	Deviation
	µg/kg product (12 % moisture content)		%
Sum of PBDE without BDE-209 (ub)	1.08	1.08	-
Sum of PBDE without BDE-209 (lb)	1.08	1.08	-
Sum of PBDE including BDE-209 (ub)	1.55	1.55	-
Sum of PBDE including BDE-209 (lb)	1.55	1.52	2
α-HBCDD	0.205	-*	-
β-HBCDD	0.0192	-*	-
Sum of α-, β-, γ-HBCDD (ub)	0.240	-*	-
Sum of α-, β-, γ-HBCDD (lb)	0.227	-*	-

*only very few results from accredited laboratories to calculated an assigned value

4.1. PBDEs – individual congeners and sum parameter

The assigned values for the test sample 2203-FM were calculated as consensus of participants' results for individual PBDEs and sum parameters, taking into account the calculation criteria described above (Table 7 ; tabular summary see annex 1; Figure 1).

Table 7: Assigned values for PBDEs (rounded to three significant figures)

Fish Meal (2203-FM)	Assigned value µg/kg product (12 % moisture content)
BDE-28	0.0435
BDE-47	0.350
BDE-49	0.156
BDE-99	0.0941
BDE-100	0.0804
BDE-153	0.0442
BDE-154	0.126
BDE-183	0.188
BDE-209	0.445
Sum of 8 PBDEs (without BDE-209) (ub)	1.08
Sum of 8 PBDEs (without BDE-209) (lb)	1.08
Sum of 9 PBDEs (with BDE-209) (ub)	1.55
Sum of 9 PBDEs (with BDE-209) (lb)	1.55

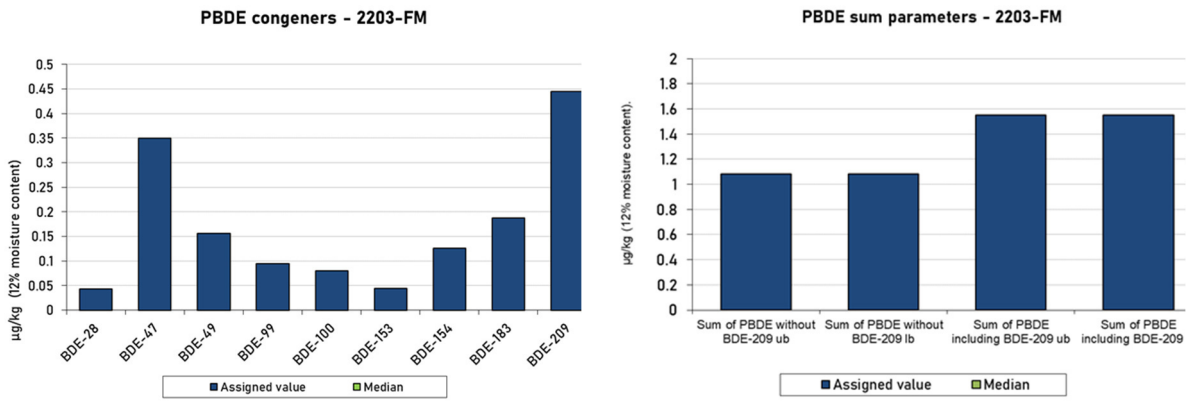


Figure 1: Assigned values (blue) for PBDE individual congeners and sum parameters for fish meal (2203-FM) [µg/kg product (12% moisture content)]

4.2. HBCDDs – individual stereoisomers and sum parameter

The assigned values for the test sample 2203-FM were calculated as consensus of participants' results for individual HBCDDs and sum parameters, taking into account the calculation criteria described above (Table 8 ; tabular summary see annex 1; Figure 2).

Table 8: Assigned values for HBCDDs (rounded to three significant figures)

Fish Meal (2203-FM)	Assigned value µg/kg product (12 % moisture content)
(+/–)-α-HBCDD	0.205
(+/–)-β-HBCDD	0.0192
Sum of α-, β-, γ-HBCDD (ub)	0.240
Sum of α-, β-, γ-HBCDD (lb)	0.227

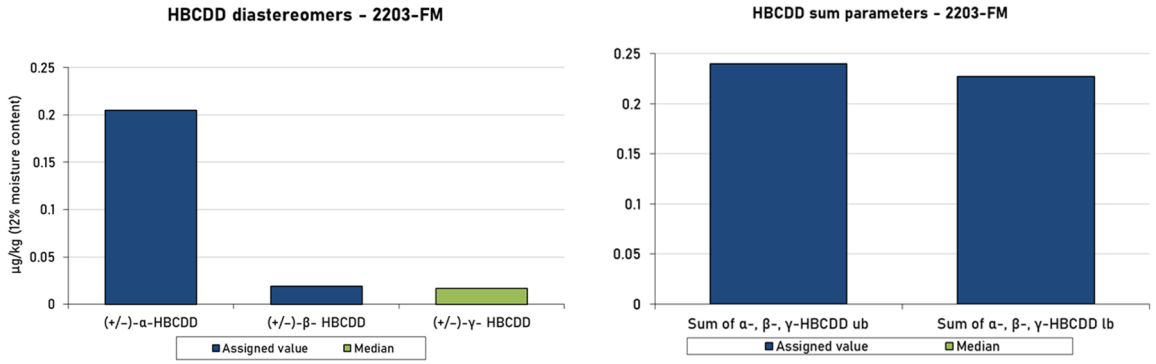


Figure 2: Assigned values (blue) and median values (green) for HBCDD individual congeners and sum parameters for fish meal (2203-FM) [µg/kg product (12% moisture content)]

4.3. Moisture content

For the moisture content an assigned value of 10.7 % for the test sample 2203-FM was calculated as a consensus of the participants' results, taking into account the calculation criteria described above.

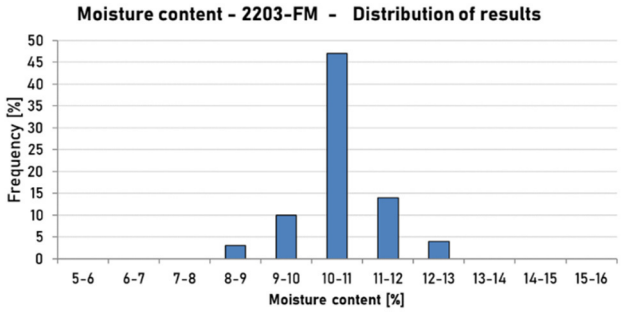


Figure 3: Distribution of participant's results of the moisture content in % for fish meal (2203-FM)

4.4. Comparison of assigned values with recommended LOQs

The limits of quantification are currently based on the values specified in Commission Recommendation of 3 March 2014, on the monitoring of trace levels of brominated flame retardants in food (2014/118/EU). For PBDEs the recommended LOQ value is 0.01 µg/kg w.w. for individual congeners. However, it was discussed in the meetings of the core working group "Brominated Contaminants and PCNs" of the EURL/NRL network that for feed an LOQ value of 0.01 µg/kg product, compared to a feed with a moisture content of 12%, is preferable for all congeners and given that some feeds show concentrations below this an even lower targeted LOQ of 0.001 µg/kg product (12% moisture content), except for BDE-209 was recommended (Table 9). Valid data on the background contamination of feedstuffs with BFRs is particularly important for a reliable risk assessment. For HBCDDs the recommended LOQ value is at 0.01 µg/kg product, compared to a feed with a moisture content of 12% for α-, β- and γ-stereoisomers (Table 9). For total HBCDD measured by GC-MS, the corresponding LOQ value is 0.003 µg/kg product (12% moisture content), as cumulative response of all possible HBCDD diastereomers (Table 9).

Table 9: Analytical recommendations from "Guidance document on analytical parameters for the determination of organobromine contaminants in food and feed" (CWG "BCons and PCNs")

Undesirable Substances in Feed	Limit of quantification per congener/stereoisomer µg/kg product (12 % moisture content)
PBDEs	0.01 and 0.001 (all congeners except BDE-209)
HBCDDs	0.01 (sum of HBCDDs) and 0.003 (total HBCDD)

PBDEs:

The calculated assigned values were all four to forty times higher than the recommended LOQs for the test sample fish meal (2203-FM).

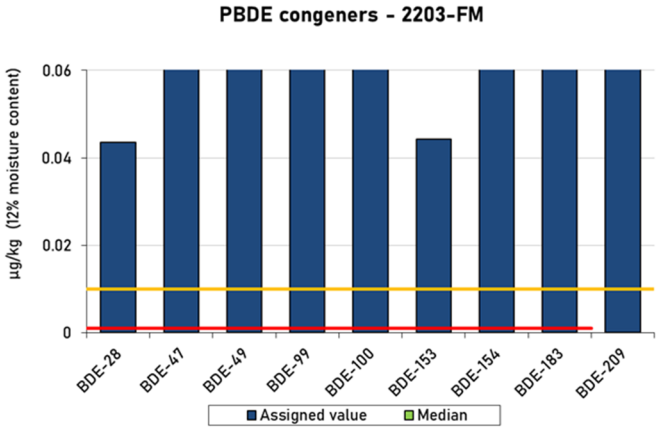


Figure 4: Comparison of assigned values for PBDE congeners with recommended LOQs (yellow line at 0.01 µg/kg product and red line at 0.001 µg/kg product) in fish meal (2203-FM)

HBCDDs:

For γ-HBCDD no assigned values could be calculated, because less than 2/3 of all reported results were above the LOQs (see calculation criteria section 4). Therefore, the median value was taken for comparison with the recommended LOQ. The median value for γ-HBCDD (0.0168 µg/kg) was in the range of the recommended LOQ of 0.01 µg/kg product, showing that the majority of the laboratories in this PT could not reliably report results for γ-HBCDDs in fish meal in this low concentration range. However, for β-HBCDD an assigned value of 0.0200 µg/kg could be calculated, also in the range of the recommended LOQ.

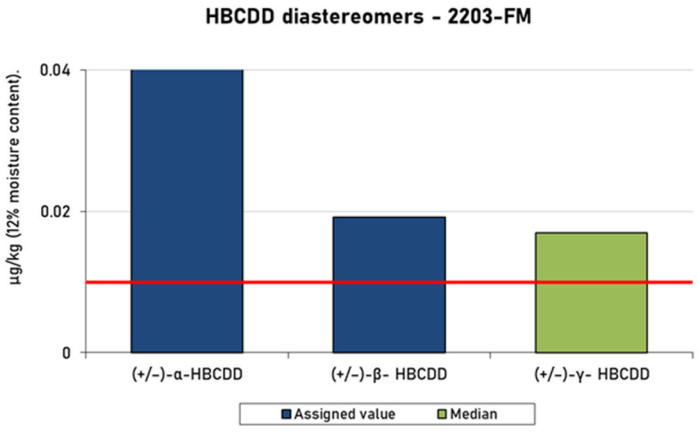


Figure 4: Comparison of assigned values for HBCDD stereoisomers with recommended LOQs (red line at 0.01 µg/kg product) in fish meal (2203-FM)

5. Evaluation of results

5.1. Z-scores calculation

Criteria for successful participation of laboratories were based on the evaluation of the results of individual congeners and sum parameters. For evaluation of results of physico-chemical methods the z-scores were calculated according to the following formula:

$$z = \frac{(x - x_a)}{\sigma_p}$$

x: *participant's result*

x_a: *assigned value*

σ_p: *fitness-for-purpose-based standard deviation for proficiency assessment*

For individual PBDE congeners, individual HBCDD diastereomers and PBDE and HBCDD sum parameters, the standard deviation for proficiency assessment σ_p is defined as 20 %.

Z-scores for individual congeners / substances and diastereomers are only calculated and reported if levels for these congeners are equal to or above the LOQ. Otherwise, no z-scores will be given.

Interpretation of z-scores:

$\lvert z\text{-score} \rvert \leq 2$	*satisfactory performance*
$2 < \lvert z\text{-score} \rvert < 3$	*questionable performance (warning signal)*
$\lvert z\text{-score} \rvert \geq 3$	*unsatisfactory performance (action signal)*

5.2. PBDEs - Participants' z-scores

Table 10: Distribution of participants' z-scores for PBDEs for fish meal (2203-FM)

Percentage of participants' results	$\lvert z\text{-score} \rvert \leq 2$	$2 < \lvert z\text{-score} \rvert < 3$	$\lvert z\text{-score} \rvert \geq 3$
BDE-28	100%	-	-
BDE-47	96%	4%	-
BDE-49	88%	4%	8%
BDE-99	96%	4%	-
BDE-100	100%	-	-
BDE-153	96%	-	4%
BDE-154	100%	-	-

Percentage of participants' results	|z-score| ≤ 2	2 < |z-score| < 3	|z-score| ≥ 3
BDE-183	96%	-	4%
BDE-209	90%	5%	5%
Sum of 8 PBDEs without BDE-209 (ub)	100%	-	-
Sum of 8 PBDE including BDE-209 (lb)	100%	-	-
Sum of 9 PBDE including BDE-209 (ub)	100%	-	-
Sum of 9 PBDE including BDE-209 (lb)	100%	-	-

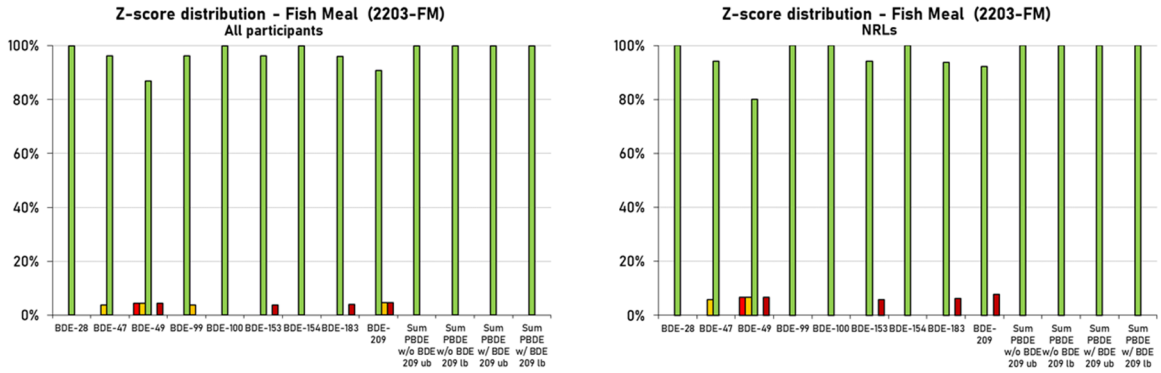


Figure 7: Distribution of participants' z-scores and NRLs only for PBDE congeners / sum parameters for fish meal (2203-FM) [Green bars: -2 ≤ z-score ≤ 2, orange bars: -3 < z-score < -2, 2 < z-score < 3, red bars: z-score ≤ -3, z-score ≥ 3]

5.3. HBCDDs - Participants' z-scores

HBCDD stereoisomers undergo thermal isomerization at temperatures above 160 °C. With GC elution temperature of these compounds of normally above 160 °C a separation of HBCDD stereoisomers using GC analysis is not possible. Only one unresolved peak is obtained. Additional thermal decomposition of HBCDDs is reported for temperatures above 240 °C. Therefore, in case of applying GC-MS methods for HBCDD analysis determination of total HBCDD (as sum of all originally present HBCDD diastereomers) is possible only.

Due to the low numbers of results for total HBCDD the sum of α-, β-, γ-HBCDD (using LC separation) was taken for comparison.

Table 11: Distribution of participants' z-scores for HBCDD for fish meal (2203-FM)

Percentage of participants' results	|z-score| ≤ 2	2 < |z-score| < 3	|z-score| ≥ 3
(+/–)-α-HBCDD	94%	-	6%
(+/–)-β-HBCDD	86%	14%	-
Sum of α-, β-, γ-HBCDD (ub)	76%	6%	18%
Sum of α-, β-, γ-HBCDD (lb)	88%	-	12%
Total HBCDD*	100%	-	-

*Comparison of participants' results for total HBCDD with assigned value for sum of α-, β-, γ-HBCDD

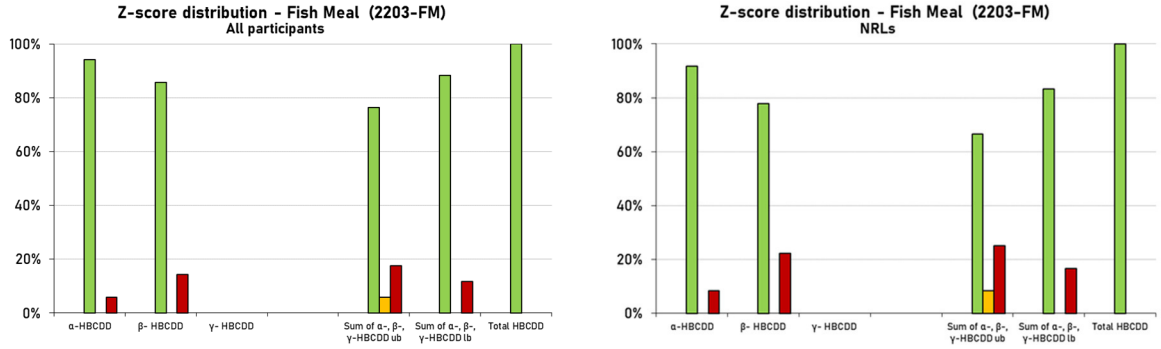


Figure 8: Distribution of participants' z-scores and NRLs only for HBCDD stereoisomers / sum parameters for fish meal (2203-FM) [Green bars: -2 ≤ z-score ≤ 2, orange bars: -3 < z-score <-2, 2 < z-score < 3, red bars: z-score ≤ -3, z-score ≥ 3]

6. Participants' feedback

A questionnaire for feedback from participants of this EURL proficiency test was available as online survey between 28 November 2022 and 23 January 2023. The survey was anonymous, but participants could also give their laboratory name. The identity of the laboratories is kept confidential. The survey included several questions related to different topics (participants' information, organization of the proficiency test, PT test samples and evaluation of results and summary of data) and a possibility to include comments and further suggestions.

In total, 9 laboratories (8 % of all PT participants) replied to this survey.

Table 12: Participating laboratories in the feedback survey

Type of laboratory	Answers
National Reference Laboratory (NRL)	2
Official Laboratory (OFL)	5
Commercial laboratory	2
Other (e.g. research and development)	0
No Answer	0

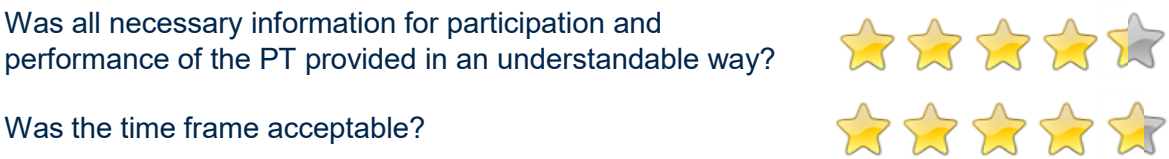
General aspect

How satisfied are you with the organization of this proficiency test in general? Please rate the parts below according to your experience, with 0 stars meaning "no opinion" and 5 stars meaning "full satisfaction".

Did the proficiency test meet expectations?

Specific aspects of this proficiency test

We would like to know a bit more about specific aspects of this proficiency test. Please rate the aspects below according to your experience, with 0 stars meaning "no opinion" and 5 stars meaning "full satisfaction".



Was the handling of EUSurvey as webtool for reporting and source of instructions manageable?

Was the evaluation of participant's results and the information in the preliminary report clear and comprehensible?

Was the selected sample adequate for the goal to assess analytical performance of laboratories in relevant matrices?

Choice of matrix

Level of contamination

The following comments or suggestions for improvements were submitted:
"To the EUSurvey webtool: the person-related application is impractical; it would be better to create an access option for several people in a laboratory."; "timing to perform test was very good (enough time); timing to send the preliminary results was very good (short)"

7. Quality control

The Deutsche Akkreditierungsstelle GmbH attests that the provider of proficiency testing Chemisches und Veterinäruntersuchungsamt Freiburg, EU Reference Laboratory (EURL) for halogenated persistent organic pollutants (POPs) in feed and food is competent under the terms of DIN EN ISO/IEC 17043:2010 to carry out proficiency testing in the testing field of determination of halogenated persistent organic pollutants (POPs) in food and feed (Accreditation number: D-EP-18625-01-00).

8. Results of participants

An overview of the PBDE and HBCDD results for the PT test sample fish meal (2203-FM) are given in the following annexes. Laboratories are coded according to the laboratory codes sent after registration.

9. References

[1] ISO 13528:2022, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization

[2] M. Thompson, S.L.R. Ellison, R. Wood: The International Harmonized Protocol For The Proficiency Testing Of Analytical Chemistry Laboratories, Pure Appl. Chem., Vol. 78, No. 1, pp. 145-196, 2006.

10. Annex

Fish meal – 2203-FM	
Annex-1	Assigned values – PBDEs, HBCDDs
Annex-2	Participants' results – Tables – PBDEs, HBCDDs
Annex-3	Participants' z-scores – Tables – PBDEs, HBCDDs
Annex-4	Participants' z-scores – Charts – PBDEs, HBCDDs
Annex-5	Homogeneity and stability test – PBDE
Annex-6	Participants' methods – PBDE, HBCDD
Annex-7	Participants' methods – Measurement uncertainty and Limits of detection - PBDE, HBCDD

EURL for halogenated POPs in Feed and Food
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EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs,HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

28 July 2023

Annex 1: Assigned values of PBDEs and HBCDDs

Test sample - Fish Meal (2203-FM)

Assigned values of sum parameters and individual congeners

Estimation of the assigned value as the consensus of participants' results
Assigned value = Huber robust mean after exlusion of extreme outliers

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)
PBDE - Assigned values

Analyte		Result µg/kg (12% moisture content)	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
BDE-28	2,2′,4-tribromodiphenyl ether		0.0435	0.0040	0.00097	26	0.0442
BDE-47	2,2′,4,4′-tetrabromodiphenyl ether		0.350	0.043	0.011	26	0.355
BDE-49	2,2′,4,5′-tetrabromodiphenyl ether		0.156	0.025	0.0067	21	0.158
BDE-99	2,2′,4,4′,5-pentabromodiphenyl ether		0.0941	0.0096	0.0024	26	0.0943
BDE-100	2,2′,4,4′,6-pentabromodiphenyl ether		0.0804	0.0082	0.002	26	0.0792
BDE-153	2,2′,4,4′,5,5′-hexabromodiphenyl ether		0.0442	0.0032	0.00081	25	0.0451
BDE-154	2,2′,4,4′,5,6′-hexabromodiphenyl ether		0.126	0.0150	0.0037	26	0.125
BDE-183	2,2′,3,4,4′,5′,6-heptabromodiphenyl ether		0.188	0.016	0.0042	24	0.186
BDE-209	2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether		0.445	0.077	0.021	21	0.453
Sum of 8 PBDE	without BDE-209 (ub)		1.08	0.11	0.028	25	1.07
Sum of 8 PBDE	without BDE-209 (lb)		1.08	0.11	0.028	25	1.07
Sum of 9 PBDE	including BDE-209 (ub)		1.55	0.16	0.042	22	1.56
Sum of 9 PBDE	including BDE-209 (lb)		1.55	0.16	0.042	22	1.56

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
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Fish Meal (2203-FM)
HBCDD - Assigned values

Analyte		Result µg/kg (12% moisture content)	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
(+/–)-α-HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane)		0.205	0.026	0.0081	16	0.203
(+/–)-β- HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane)		0.0192	0.002	0.00081	13	0.0200
(+/–)-γ- HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane)						0.0168
Sum of α-, β-, γ-HBCDD	(ub)		0.240	0.034	0.012	13	0.248
Sum of α-, β-, γ-HBCDD	(lb)		0.227	0.024	0.0077	15	0.227
Total HBCDD	(using GC-methods)						0.213

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)
Moisture content (BFR) - Assigned value

Analyte	Result %	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
Moisture content		10.7	0.601	0.14	27	10.7

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs,HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

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Annex 2: Participants' results of PBDEs and HBCDDs

Test sample - Fish Meal (2203-FM)

* Modified/additional results reported after distribution of preliminary results to all participating laboratories

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)
PBDE - Results

LC	Sample	Result µg/kg (12% moisture content)	2,2',4-tribromodiphenyl ether **BDE-28**	2,2',4,4'-tetrabromodiphenyl ether **BDE-47**	2,2',4,5'-tetrabromodiphenyl ether **BDE-49**	2,2',4,4',5-pentabromodiphenyl ether **BDE-99**	2,2',4,4',6-pentabromodiphenyl ether **BDE-100**	2,2',4,4',5,5'-hexabromodiphenyl ether **BDE-153**	2,2',4,4',5,6'-hexabromodiphenyl ether **BDE-154**	2,2',3,4,4',5',6-heptabromodiphenyl ether **BDE-183**	2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether **BDE-209**	**Sum of 8 PBDE** without BDE-209 (ub)	**Sum of 8 PBDE** without BDE-209 (lb)	**Sum of 9 PBDE** including BDE-209 (ub)	**Sum of 9 PBDE** without BDE-209 (lb)
3	2203-FM		0.045	0.4	0.16	0.1	0.082	0.043	0.15	0.23	0.47	1.21	1.21	1.68	1.68
4	2203-FM		0.0421	0.289	0.174	0.0638	0.0773	0.0458	0.127	0.218	0.375	1.04	1.04	1.41	1.41
5	2203-FM		0.045	0.332	0.152	0.08	0.072	0.041	0.114	0.181	0.443	1.02	1.02	1.46	1.46
7	2203-FM		0.0398	0.332		0.0821	0.0727	0.0444	0.136						
12	2203-FM		0.0384	0.293	0.081	0.0864	0.0685	0.04	0.105	0.17		0.881	0.881		
16	2203-FM														
17	2203-FM		0.038	0.313	0.141	0.083	0.074	0.045	0.111	0.175	0.433	0.98	0.98	1.41	1.41
21	2203-FM		0.0463	0.362	0.0172	0.0989	0.088	0.0824	0.117	0.357	0.817	1.17	1.17	1.99	1.99
23	2203-FM		0.049	0.382	0.167	0.113	0.087	0.046	0.126	0.177	0.47	1.15	1.15	1.62	1.62
25	2203-FM		0.0443	0.206	0.349	0.0934	0.0772	0.0473	0.15	0.177	0.511	1.14	1.14	1.66	1.66
26	2203-FM		0.052	0.331	0.156	0.095	0.072	0.049	0.124	0.191	0.375	1.07	1.07	1.44	1.44
28	2203-FM		0.0368	0.312	0.136	0.0856	0.0766	0.0464	0.107	0.181	0.454	0.981	0.981	1.44	1.44
29	2203-FM		0.0388	0.346	0.139	0.0919	0.0889	0.0431	0.111	0.197	0.616	1.06	1.06	1.67	1.67
32	2203-FM		0.0431	0.412	0.18	0.134	0.0972	0.0451	0.14	0.183	0.48	1.23	1.23	1.71	1.71
39	2203-FM		0.0419	0.336	0.144	0.0913	0.076	0.0375	0.133	0.188	0.353	1.05	1.05	1.4	1.4
46	2203-FM		0.045	0.286	0.107	0.097	0.082	0.037	0.079	0.186	0.451	0.92	0.92	1.37	1.37
49	2203-FM		0.0438	0.391	0.206	0.1	0.0795	0.0463	0.119	0.18		1.17	1.17		
56	2203-FM		0.049	0.43	0.18	0.11	0.089	0.045	0.12	0.23		1.25	1.25	2.05	1.25
59	2203-FM		0.0471	0.398	0.186	0.102	0.0888	0.0479	0.125	0.195	0.527	1.19	1.19	1.72	1.72
61	2203-FM		0.0481	0.378		0.099	0.0839	0.0442	0.134	0.196		0.983	0.983		
62	2203-FM														
63	2203-FM		0.0466	0.405	0.172	0.0968	0.088	0.0497	0.123	0.211	0.528	1.19	1.19	1.72	1.72
64	2203-FM		0.0466	0.357	0.112	0.0929	0.0771	0.0451	0.138	0.191	0.363	1.06	1.06	1.42	1.42
83	2203-FM		0.044	0.385	0.165	0.103	0.09	0.046	0.13	0.221	0.468	1.18	1.18	1.65	1.65
86	2203-FM		0.0447	0.367		0.0912	0.0702	0.0423	0.121	0.179	0.659	0.916	0.916	1.57	1.57
92	2203-FM		0.041	0.36	0.17	0.11	0.099	0.042	0.14	0.18	0.41	1.14	1.14	1.55	1.55
97	2203-FM		0.044	0.363	0.158	0.095	0.082	0.041	0.119	0.167	0.372	1.07	1.07	1.44	1.44
106	2203-FM		0.0444	0.352	0.178	0.0936	0.0788	0.0452	0.161	0.204	0.418	1.16	1.16	1.58	1.58
109	2203-FM		0.0358	0.332	0.143	0.0839	0.0742	0.041	0.118	0.134	0.272	0.962	0.962	1.23	1.23

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Fish Meal (2203-FM)
HBCDD - Results

LC	Sample	Result µg/kg (12% moisture content)	(+/–)-α-HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane	(+/–)-β- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane	(+/–)-γ- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane		Sum of α-, β-, γ-HBCDD (ub)	Sum of α-, β-, γ-HBCDD (lb)	Total HBCDD (using GC-methods)
3	2203-FM		0.23	< 0.03	< 0.03		0.29	0.23	
4	2203-FM		0.192	0.0203	0.0123		0.225	0.225	
5	2203-FM		0.187	0.02	0.02		0.227	0.227	
7	2203-FM		0.215	0.02	0.013		0.248	0.248	
12	2203-FM								
16	2203-FM		0.232	0.02	< 0.039		0.291	0.252	
17	2203-FM		0.198	0.0183	0.0114		0.227	0.227	
21	2203-FM								
23	2203-FM								
25	2203-FM		0.19	< 0.1	< 0.1		0.39	0.19	
26	2203-FM		< 0.9	< 0.9	< 0.9				
28	2203-FM		0.186	0.0169	0.0122		0.215	0.215	
29	2203-FM		0.188	0.0193	0.0123		0.22	0.22	
32	2203-FM								
39	2203-FM		0.244	0.0174	0.0165		0.278	0.278	
46	2203-FM		0.172	0.023	0.014		0.209	0.209	0.196
49	2203-FM								
59	2203-FM								
61	2203-FM		0.264	0.072	0.043		0.379	0.379	
62	2203-FM		1.05	0.11	0.05		1.21	1.21	
63	2203-FM		0.204	< 0.1	< 0.1		0.404	0.204	
64	2203-FM								0.23
83	2203-FM		0.201	0.019	0.014		0.234	0.234	
86	2203-FM								
92	2203-FM		0.179	0.013	0.01		0.202	0.202	
97	2203-FM								
106	2203-FM		0.224	0.017	0.017		0.258	0.258	
109	2203-FM								

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Fish Meal (2203-FM)
Moisture content - Results

LC	Sample	Result %	Moisture content PBDE	Moisture content HBCDD	Moisture content Mean
3	2203-FM		10.7	10.7	10.7
4	2203-FM		12.6	12.6	12.6
5	2203-FM		10.7	10.7	10.7
7	2203-FM		10.3	10.3	10.3
12	2203-FM		11.6		11.6
16	2203-FM			9.8	9.8
17	2203-FM		9.6	9.6	9.6
21	2203-FM		12.3		12.3
23	2203-FM				
25	2203-FM		10.6	10.6	10.6
26	2203-FM		10.8	10.8	10.8
28	2203-FM		9.6	9.6	9.6
29	2203-FM		10.8	10.8	10.8
32	2203-FM		10.5		10.5
39	2203-FM		10.3	10.3	10.3
46	2203-FM		10.1	10.1	10.1
49	2203-FM		10.9		10.9
56	2203-FM		10.7		10.7
59	2203-FM		10.9		10.9
61	2203-FM		10.7	10.7	10.7
62	2203-FM			11.4	11.4
63	2203-FM		10.5	10.5	10.5
64	2203-FM		11.1	11.1	11.1
83	2203-FM		10.9	10.9	10.9
86	2203-FM		10.5		10.5
92	2203-FM		10.8	10.8	10.8
97	2203-FM		9.6		9.6
106	2203-FM		11.2	11.2	11.2
109	2203-FM		10.7		10.66

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Annex 3: Participants' z-scores of PBDEs and HBCDDs - Tables

Test sample - Fish Meal (2203-FM)

Z-scores of sum parameters and individual results

Calculation of z-score on basis of assigned value

$$z = (x - x_a) / \sigma_p$$

x_a: assigned value

x: participant's result

σ_p: fitness-for-purpose-based standard deviation for proficiency assessment

20%: Evaluated individual PBDE congeners and HBCDD diastereomers and sum

* Modified/additional results reported after distribution of preliminary results to all participating laboratories

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
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Fish Meal (2203-FM)
PBDE - Z-scores

LC	Sample	Z-score [σ_p = 20 %]	2,2',4-tribromodiphenyl ether **BDE-28**	2,2',4,4'-tetrabromodiphenyl ether **BDE-47**	2,2',4,5'-tetrabromodiphenyl ether **BDE-49**	2,2',4,4',5-pentabromodiphenyl ether **BDE-99**	2,2',4,4',6-pentabromodiphenyl ether **BDE-100**	2,2',4,4',5,5'-hexabromodiphenyl ether **BDE-153**	2,2',4,4',5,6'-hexabromodiphenyl ether **BDE-154**	2,2',3,4,4',5',6-heptabromodiphenyl ether **BDE-183**	2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether **BDE-209**	**Sum of 8 PBDE** without BDE-209 (ub)	**Sum of 8 PBDE** without BDE-209 (lb)	**Sum of 9 PBDE** including BDE-209 (ub)	**Sum of 9 PBDE** without BDE-209 (lb)
3	2203-FM		0.2	0.7	0.1	0.3	0.1	-0.1	1.0	1.1	0.3	0.6	0.6	0.4	0.4
4	2203-FM		-0.2	-0.9	0.6	-1.6	-0.2	0.2	0.0	0.8	-0.8	-0.2	-0.2	-0.5	-0.5
5	2203-FM		0.2	-0.3	-0.1	-0.7	-0.5	-0.4	-0.5	-0.2	0.0	-0.3	-0.3	-0.3	-0.3
7	2203-FM		-0.4	-0.3		-0.6	-0.5	0.0	0.4						
12	2203-FM		-0.6	-0.8	-2.4	-0.4	-0.7	-0.5	-0.8	-0.5		-0.9	-0.9		
16	2203-FM														
17	2203-FM		-0.6	-0.5	-0.5	-0.6	-0.4	0.1	-0.6	-0.3	-0.1	-0.5	-0.5	-0.5	-0.5
21	2203-FM		0.3	0.2	-4.4	0.3	0.5	4.3	-0.4	4.5	4.2	0.4	0.4	1.4	1.4
23	2203-FM		0.6	0.5	0.4	1.0	0.4	0.2	0.0	-0.3	0.3	0.3	0.3	0.2	0.2
25	2203-FM		0.1	-2.1	6.2	0.0	-0.2	0.4	1.0	-0.3	0.7	0.3	0.3	0.4	0.4
26	2203-FM		1.0	-0.3	0.0	0.0	-0.5	0.5	-0.1	0.1	-0.8	0.0	0.0	-0.4	-0.4
28	2203-FM		-0.8	-0.5	-0.6	-0.5	-0.2	0.2	-0.8	-0.2	0.1	-0.5	-0.5	-0.4	-0.4
29	2203-FM		-0.5	-0.1	-0.5	-0.1	0.5	-0.1	-0.6	0.2	1.9	-0.1	-0.1	0.4	0.4
32	2203-FM		0.0	0.9	0.8	2.1	1.0	0.1	0.6	-0.1	0.4	0.7	0.7	0.5	0.5
39	2203-FM		-0.2	-0.2	-0.4	-0.1	-0.3	-0.8	0.3	0.0	-1.0	-0.1	-0.1	-0.5	-0.5
46	2203-FM		0.2	-0.9	-1.6	0.2	0.1	-0.8	-1.9	-0.1	0.1	-0.7	-0.7	-0.6	-0.6
49	2203-FM		0.0	0.6	1.6	0.3	-0.1	0.2	-0.3	-0.2		0.4	0.4		
56	2203-FM		0.6	1.1	0.8	0.8	0.5	0.1	-0.2	1.1		0.8	0.8	1.6	-1.0
59	2203-FM		0.4	0.7	1.0	0.4	0.5	0.4	0.0	0.2	0.9	0.5	0.5	0.5	0.5
61	2203-FM		0.5	0.4		0.3	0.2	0.0	0.3	0.2		-0.4	-0.4		
62	2203-FM														
63	2203-FM		0.4	0.8	0.5	0.1	0.5	0.6	-0.1	0.6	0.9	0.5	0.5	0.5	0.5
64	2203-FM		0.4	0.1	-1.4	-0.1	-0.2	0.1	0.5	0.1	-0.9	-0.1	-0.1	-0.4	-0.4
83	2203-FM		0.1	0.5	0.3	0.5	0.6	0.2	0.2	0.9	0.3	0.5	0.5	0.3	0.3
86	2203-FM		0.1	0.2		-0.2	-0.6	-0.2	-0.2	-0.2	2.4	-0.8	-0.8	0.1	0.1
92	2203-FM		-0.3	0.1	0.4	0.8	1.2	-0.2	0.6	-0.2	-0.4	0.3	0.3	0.0	0.0
97	2203-FM		0.1	0.2	0.1	0.0	0.1	-0.4	-0.3	-0.6	-0.8	0.0	0.0	-0.4	-0.4
106	2203-FM		0.1	0.0	0.7	0.0	-0.1	0.1	1.4	0.4	-0.3	0.4	0.4	0.1	0.1
109	2203-FM		-0.9	-0.3	-0.4	-0.5	-0.4	-0.4	-0.3	-1.4	-1.9	-0.5	-0.5	-1.0	-1.0

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Fish Meal (2203-FM)
HBCDD - Z-scores

LC	Sample	Z-score [σ_p = 20 %]	(+/–)-α-HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane	(+/–)-β- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane	(+/–)-γ- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane		Sum of α-, β-, γ-HBCDD (ub)	Sum of α-, β-, γ-HBCDD (lb)	Total HBCDD* (using GC-methods)
3	2203-FM		0.6				1.0	0.1	
4	2203-FM		-0.3	0.3			-0.3	0.0	
5	2203-FM		-0.4	0.2			-0.3	0.0	
7	2203-FM		0.2	0.2			0.2	0.5	
12	2203-FM								
16	2203-FM		0.7	0.2			1.1	0.6	
17	2203-FM		-0.2	-0.2			-0.3	0.0	
21	2203-FM								
23	2203-FM								
25	2203-FM		-0.4				3.1	-0.8	
26	2203-FM								
28	2203-FM		-0.5	-0.6			-0.5	-0.3	
29	2203-FM		-0.4	0.0			-0.4	-0.2	
32	2203-FM								
39	2203-FM		1.0	-0.5			0.8	1.1	
46	2203-FM		-0.8	1.0			-0.6	-0.4	-0.7
49	2203-FM								
59	2203-FM								
61	2203-FM		1.4	13.8			2.9	3.3	
62	2203-FM		20.6	23.6			20.2	21.7	
63	2203-FM		0.0				3.4	-0.5	
64	2203-FM								0.1
83	2203-FM		-0.1	-0.1			-0.1	0.2	
86	2203-FM								
92	2203-FM		-0.6	-1.6			-0.8	-0.6	
97	2203-FM								
106	2203-FM		0.5	-0.6			0.4	0.7	
109	2203-FM								

* Z-scores for information only; calculation based on assigned value for sum of α-, β-, γ-HBCDD (lb)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)
Moisture content - Results

LC	Sample	Z-score [σ_p = 10 %]	Moisture content	Moisture content	Moisture content
			PBDE	HBCDD	Mean
3	2203-FM		0.0	0.0	0.0
4	2203-FM		1.8	1.8	1.8
5	2203-FM		0.0	0.0	0.0
7	2203-FM		-0.4	-0.4	-0.4
12	2203-FM		0.8		0.8
16	2203-FM			-0.8	-0.8
17	2203-FM		-1.0	-1.0	-1.0
21	2203-FM		1.5		1.5
23	2203-FM				
25	2203-FM		-0.1	-0.1	-0.1
26	2203-FM		0.1	0.1	0.1
28	2203-FM		-1.0	-1.0	-1.0
29	2203-FM		0.1	0.1	0.1
32	2203-FM		-0.2		-0.2
39	2203-FM		-0.4	-0.4	-0.4
46	2203-FM		-0.5	-0.5	-0.5
49	2203-FM		0.2		0.2
59	2203-FM		0.0		0.0
61	2203-FM		0.2		0.2
62	2203-FM		0.0	0.0	0.0
63	2203-FM			0.7	0.7
64	2203-FM		-0.2	-0.2	-0.2
83	2203-FM		0.4	0.4	0.4
86	2203-FM		0.2	0.2	0.2
92	2203-FM		-0.2		-0.2
97	2203-FM		0.1	0.1	0.1
106	2203-FM		-1.0		-1.0
109	2203-FM		0.5	0.5	0.5

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs,HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

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Annex 4: Participants' z-scores of PBDEs and HBCDDs - Charts

Test sample - Fish Meal (2203-FM)

Z-scores of sum parameters and individual results

Calculation of z-score on basis of assigned value

$$z = (x - x_a) / \sigma_p$$

x_a: assigned value

x: participant's result

σ_p: fitness-for-purpose-based standard deviation for proficiency assessment

20%: Evaluated individual PBDE congeners and HBCDD diastereomers and sum

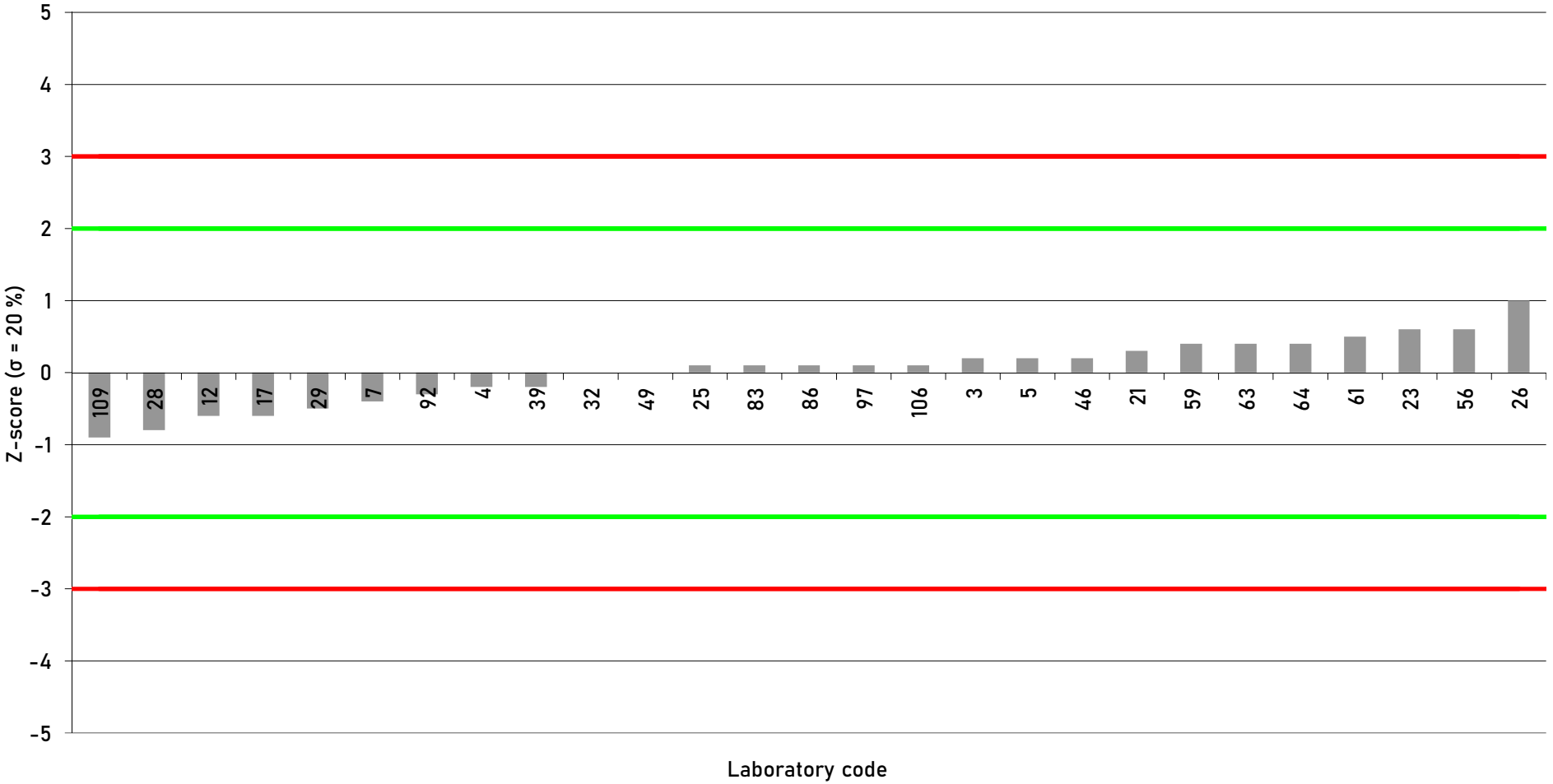
± 2 z-scores:

± 3 z-scores:

Fish Meal (2203-FM)

BDE-28

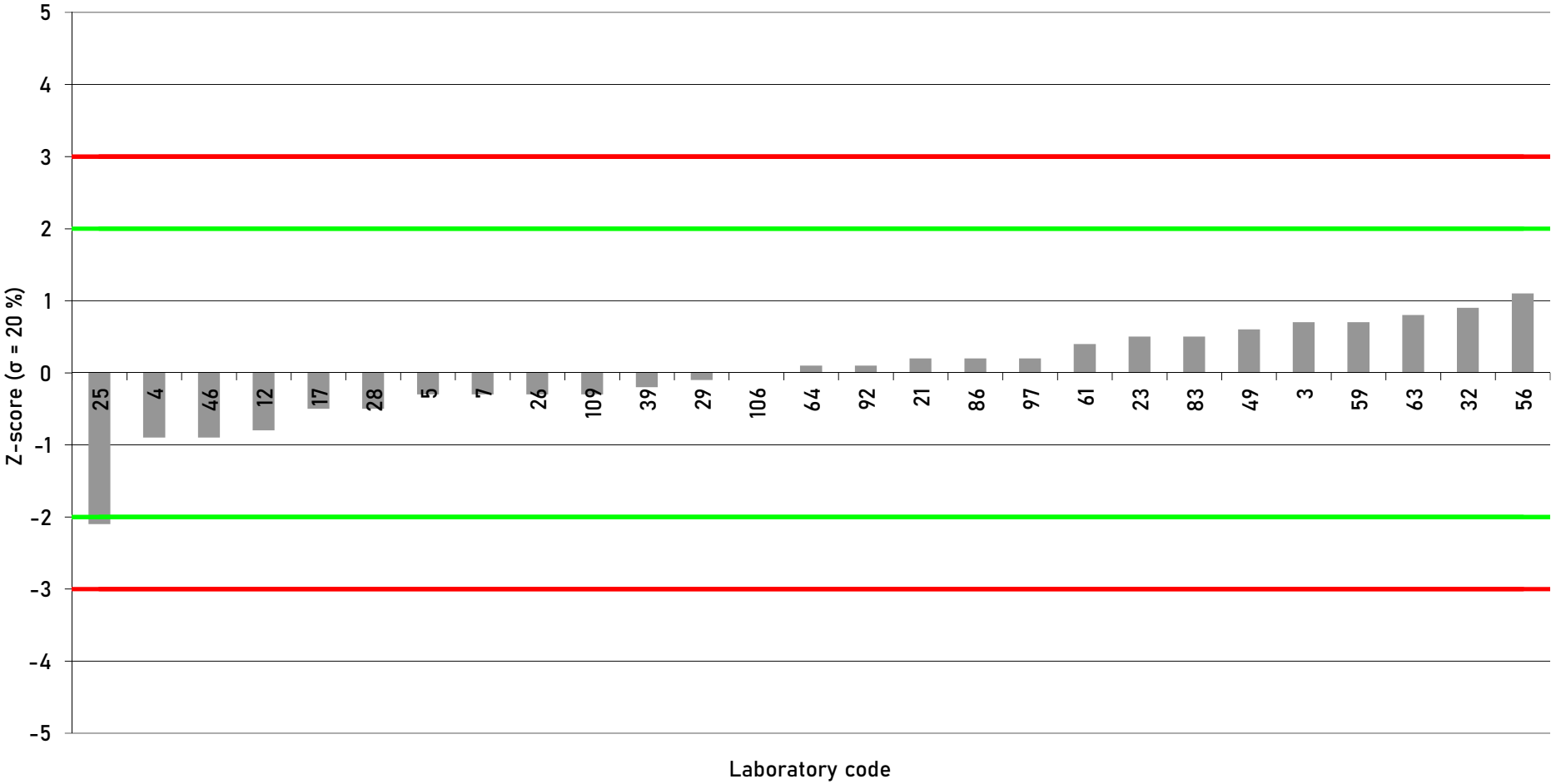
Assigned value: 0.0435 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

BDE-47

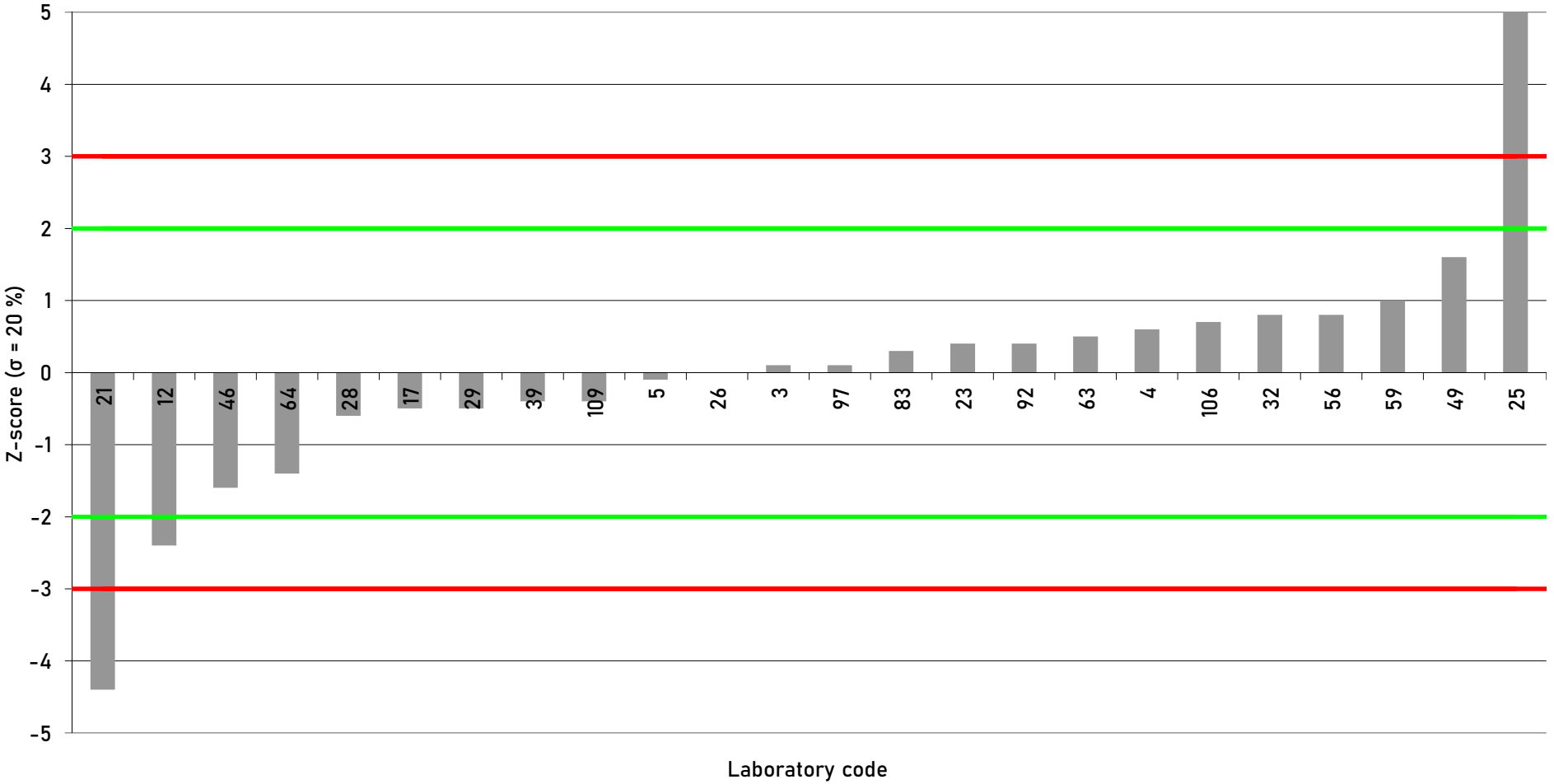
Assigned value: 0.35 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

BDE-49

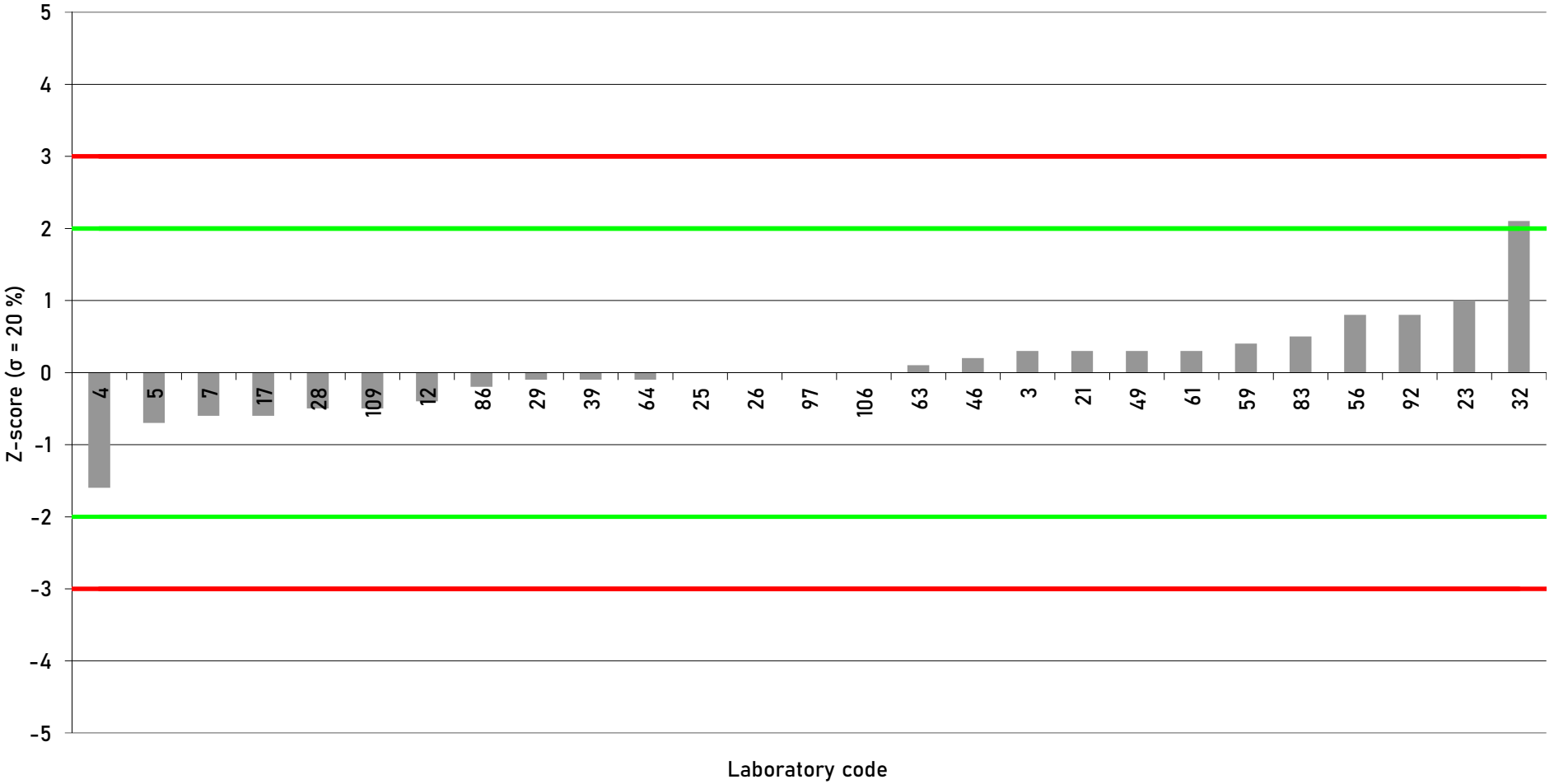
Assigned value: 0.156 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

BDE-99

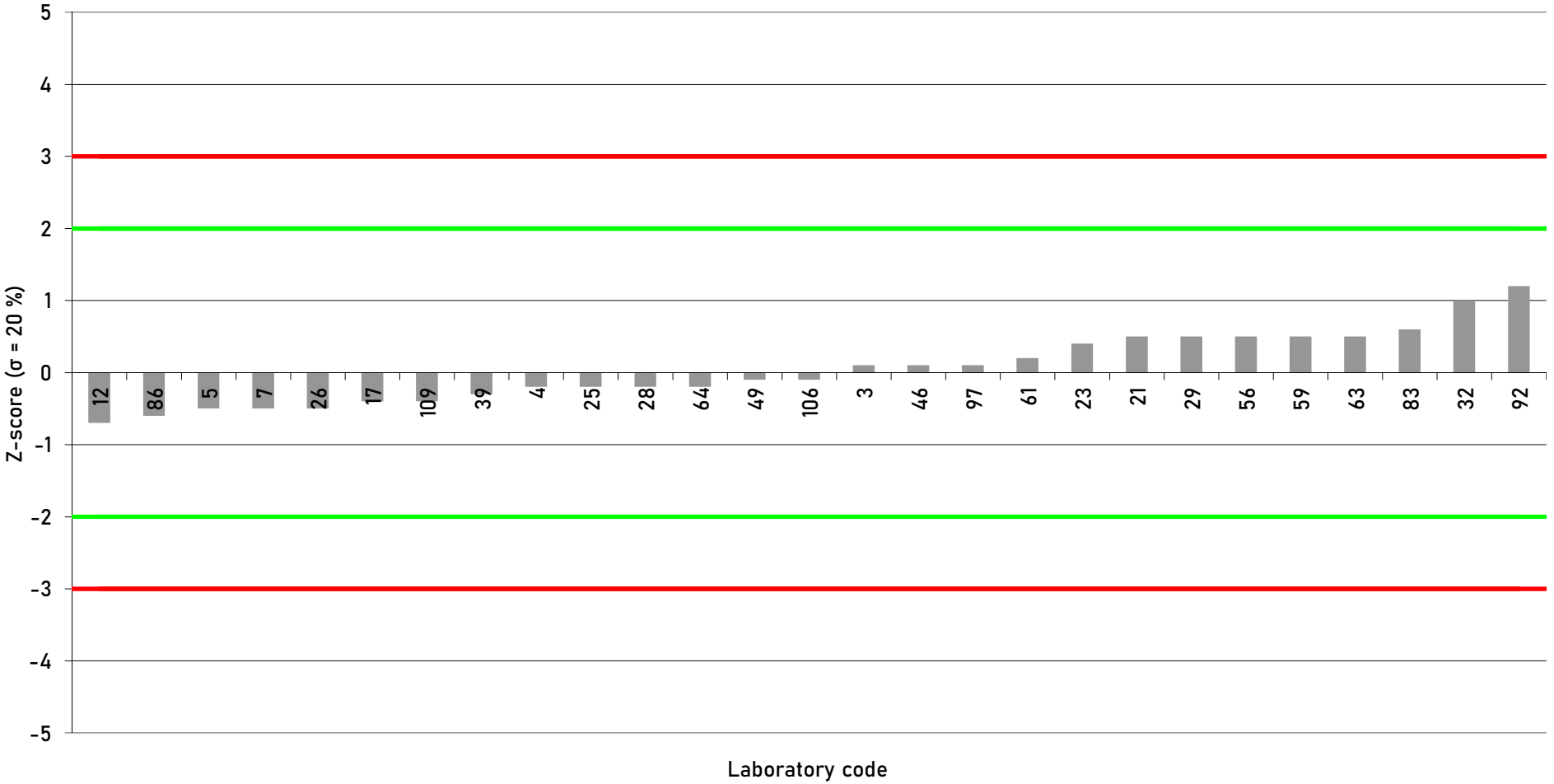
Assigned value: 0.0941 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

BDE-100

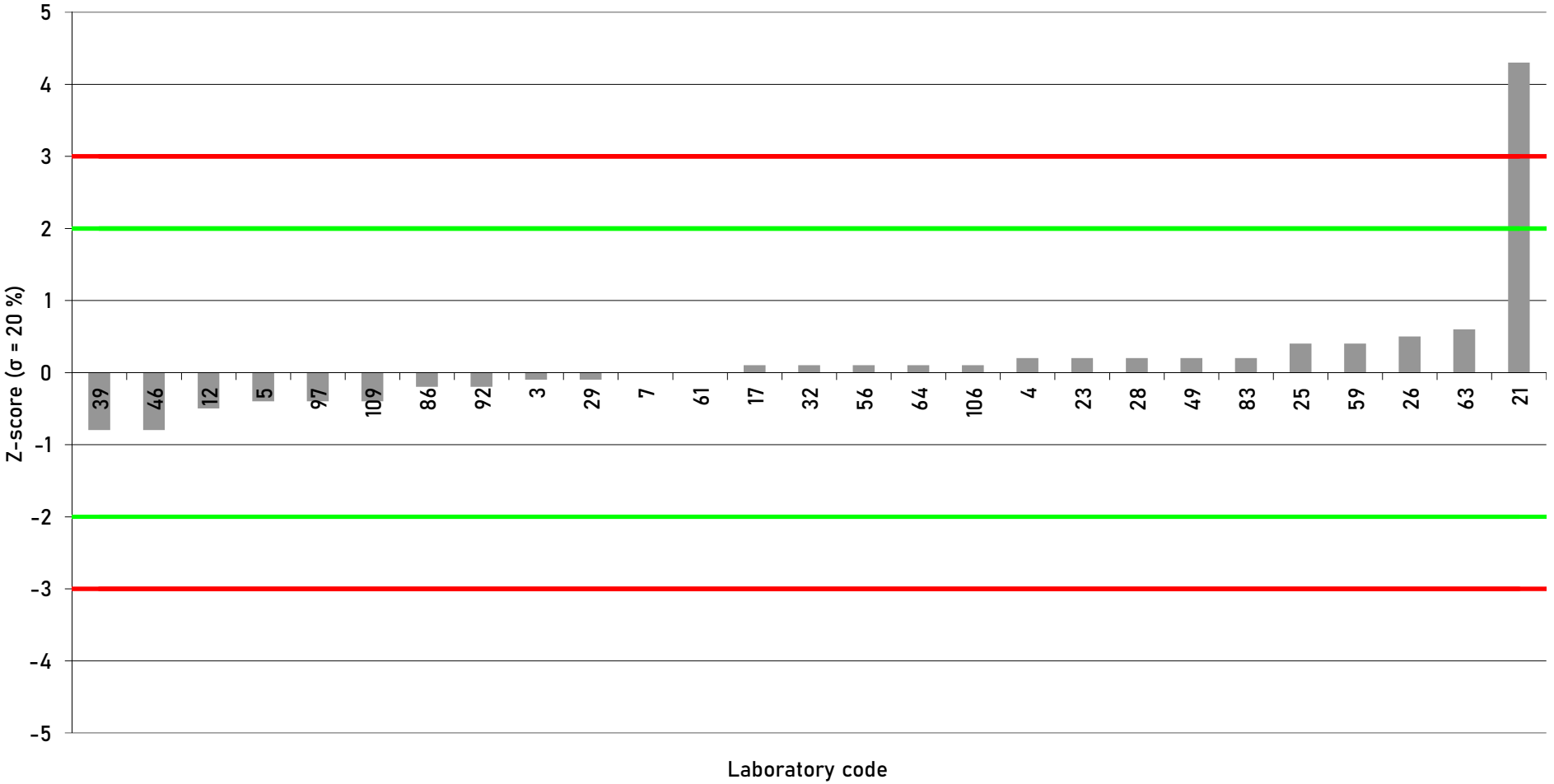
Assigned value: 0.0804 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

BDE-153

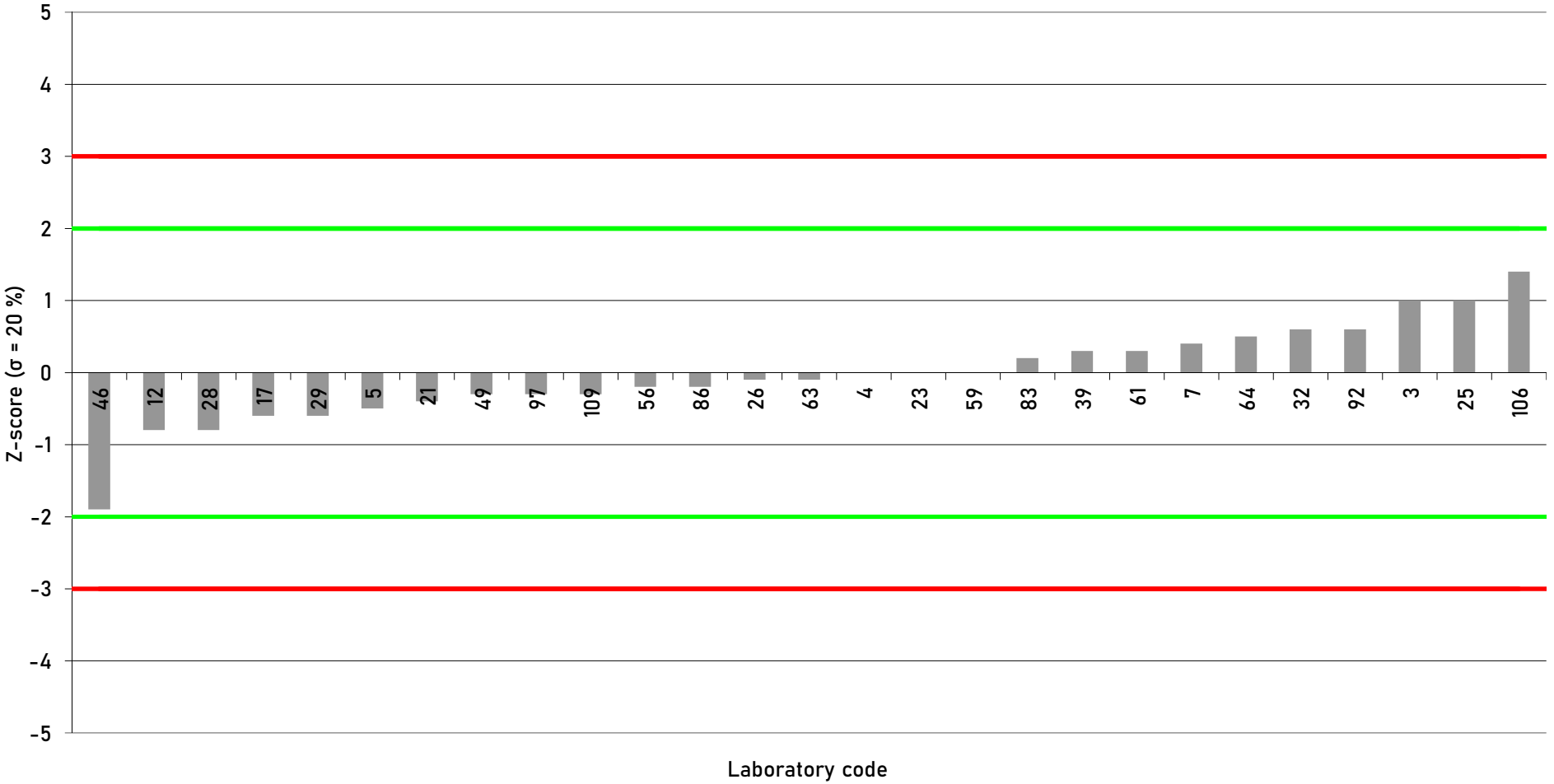
Assigned value: 0.0442 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

BDE-154

Assigned value: 0.126 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

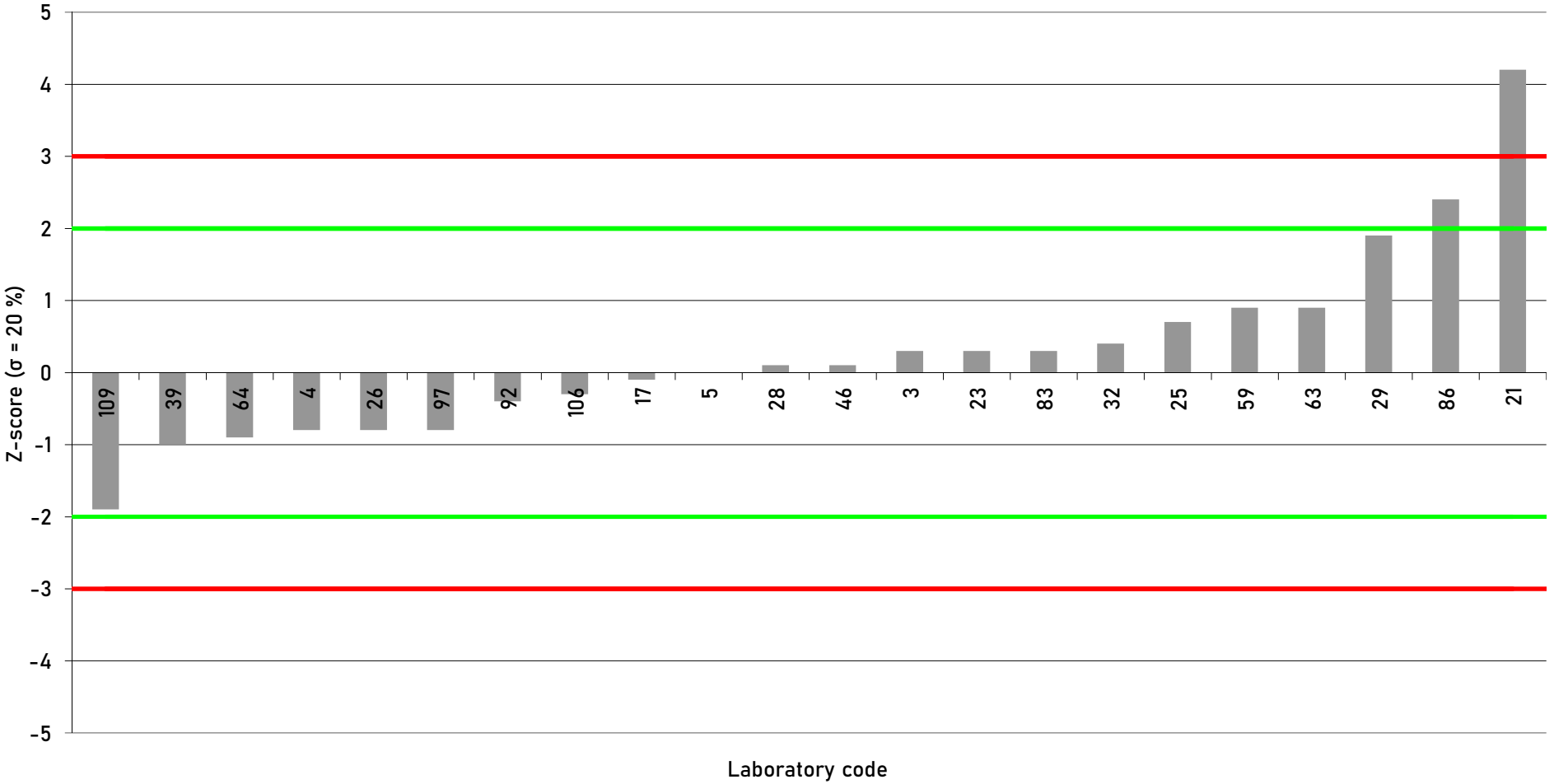
BDE-183

Assigned value: 0.188 µg/kg product (12 % moisture content)

Fish Meal (2203-FM)

BDE-209

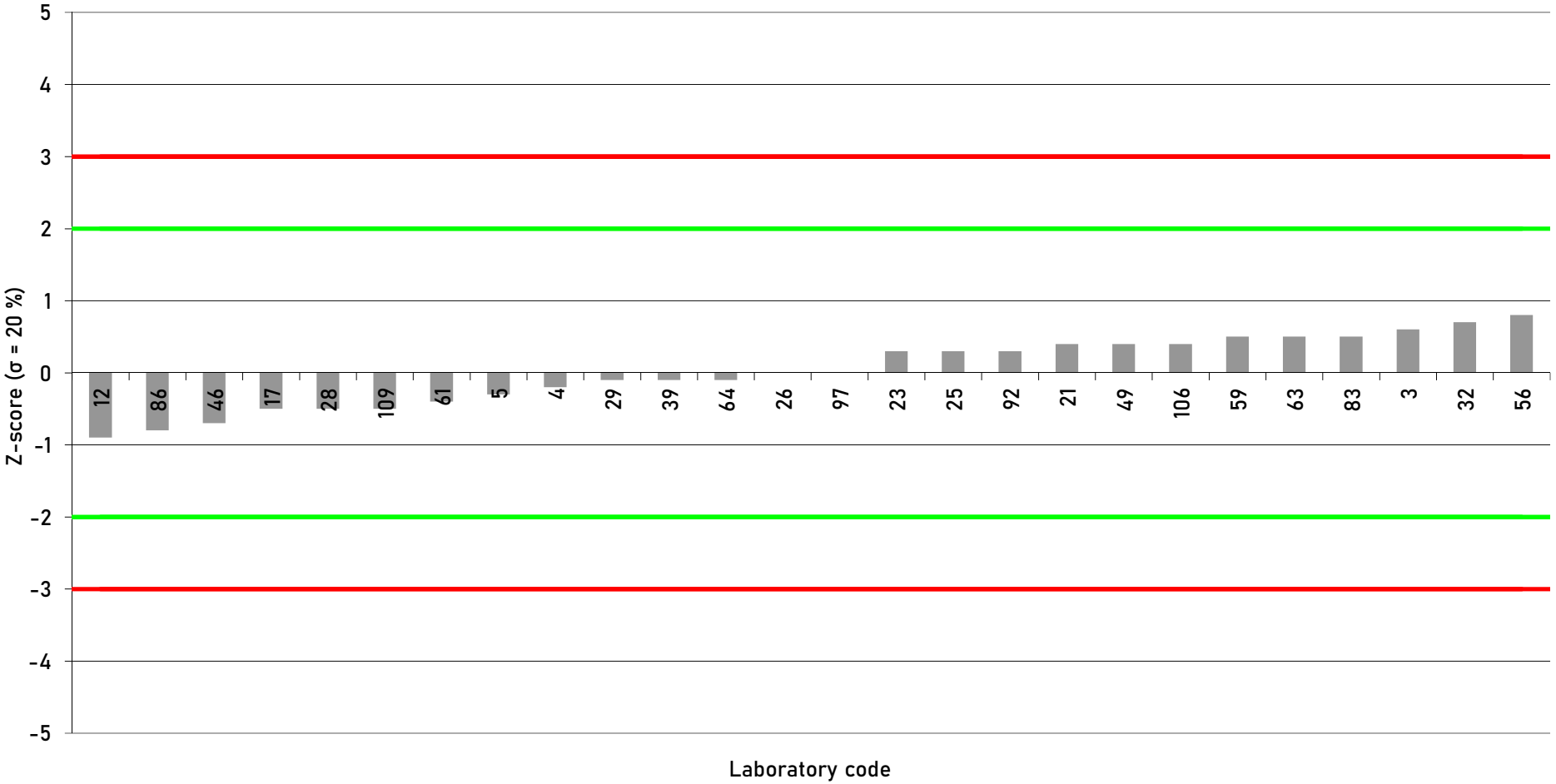
Assigned value: 0.445 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

Sum of PBDE without BDE-209 ub

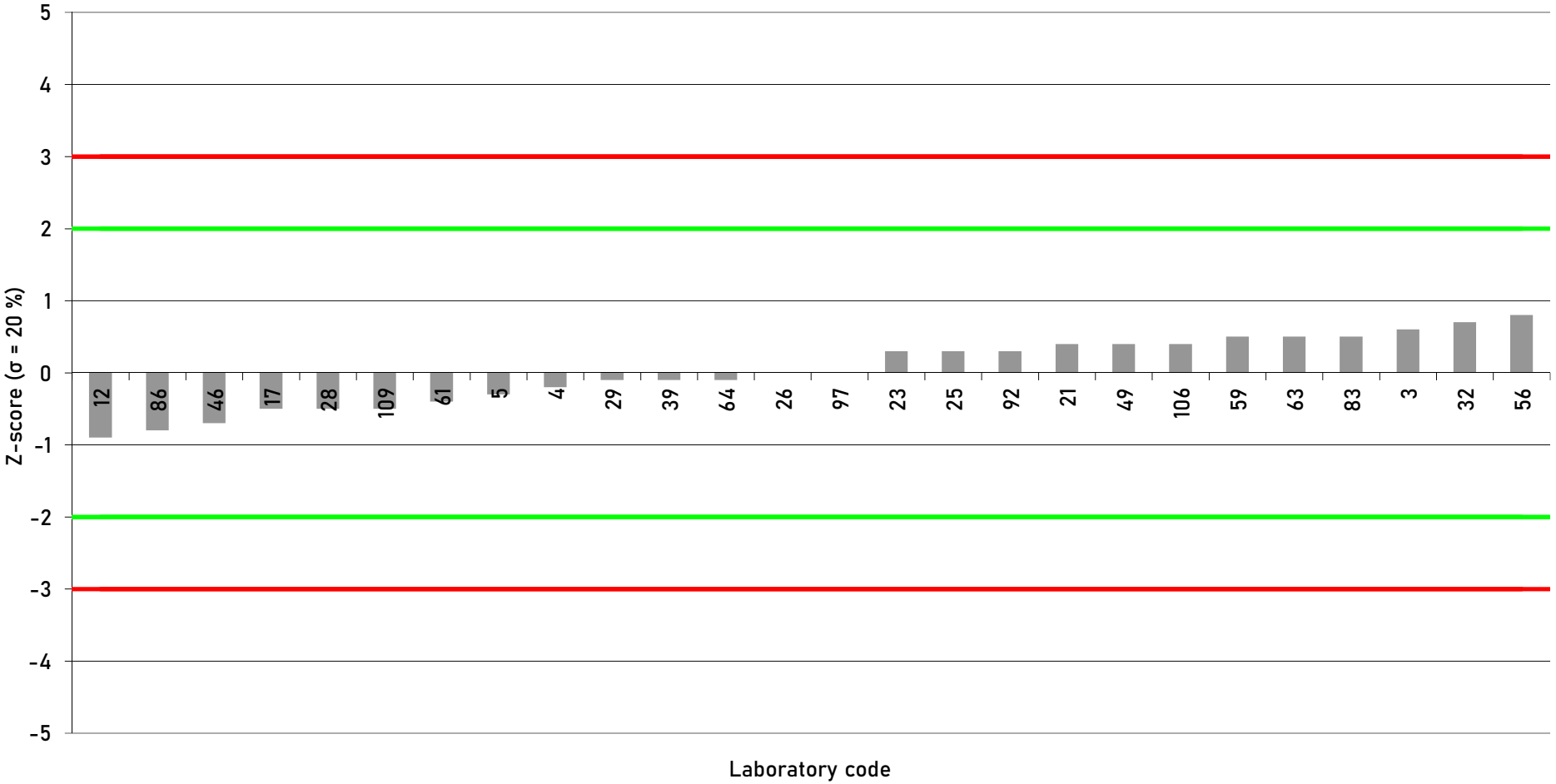
Assigned value: 1.08 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

Sum of PBDE without BDE-209 lb

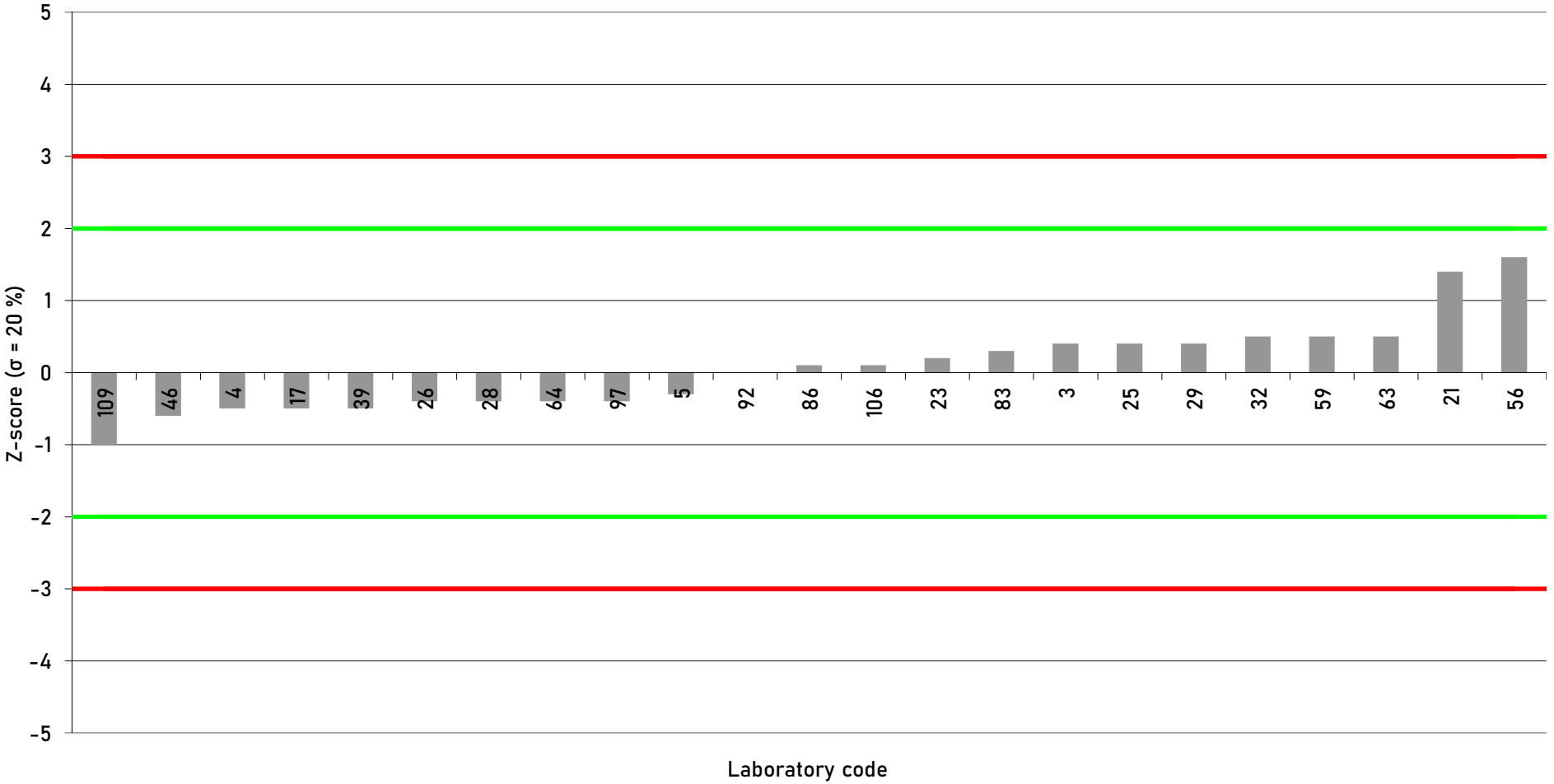
Assigned value: 1.08 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

Sum of PBDE including BDE-209 ub

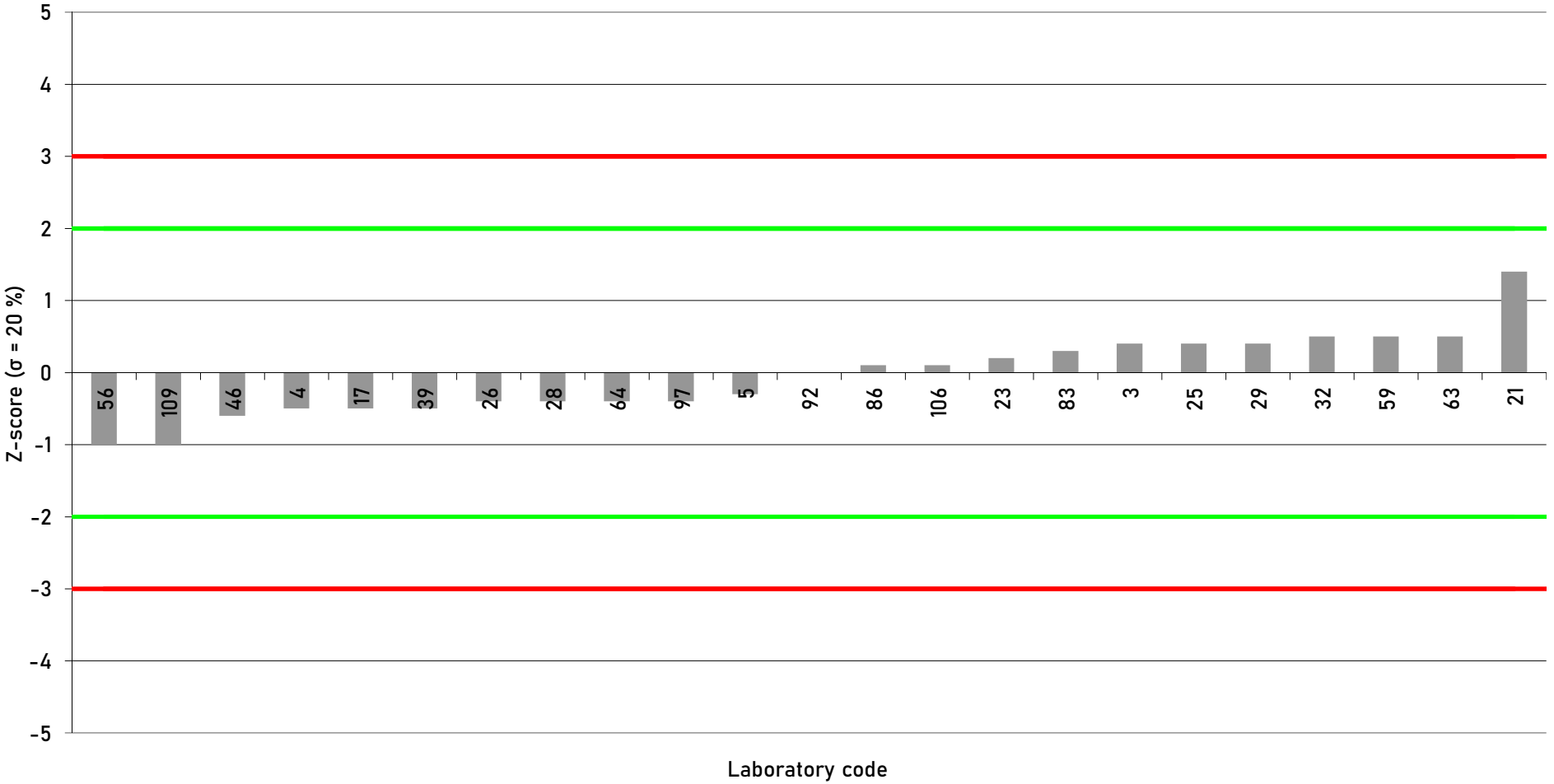
Assigned value: 1.55 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

Sum of PBDE including BDE-209 lb

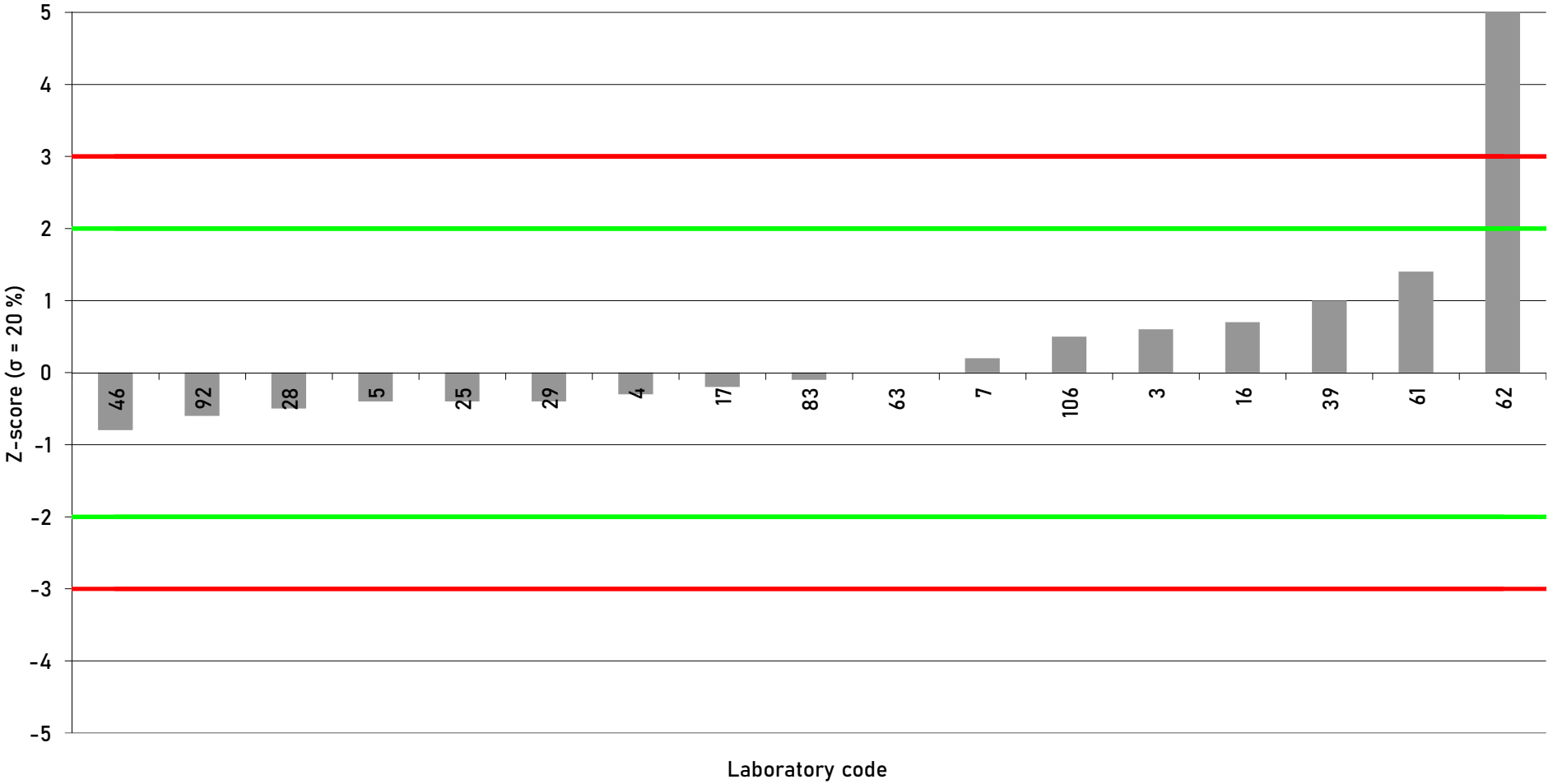
Assigned value: 1.55 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

(+/–)-α-HBCDD

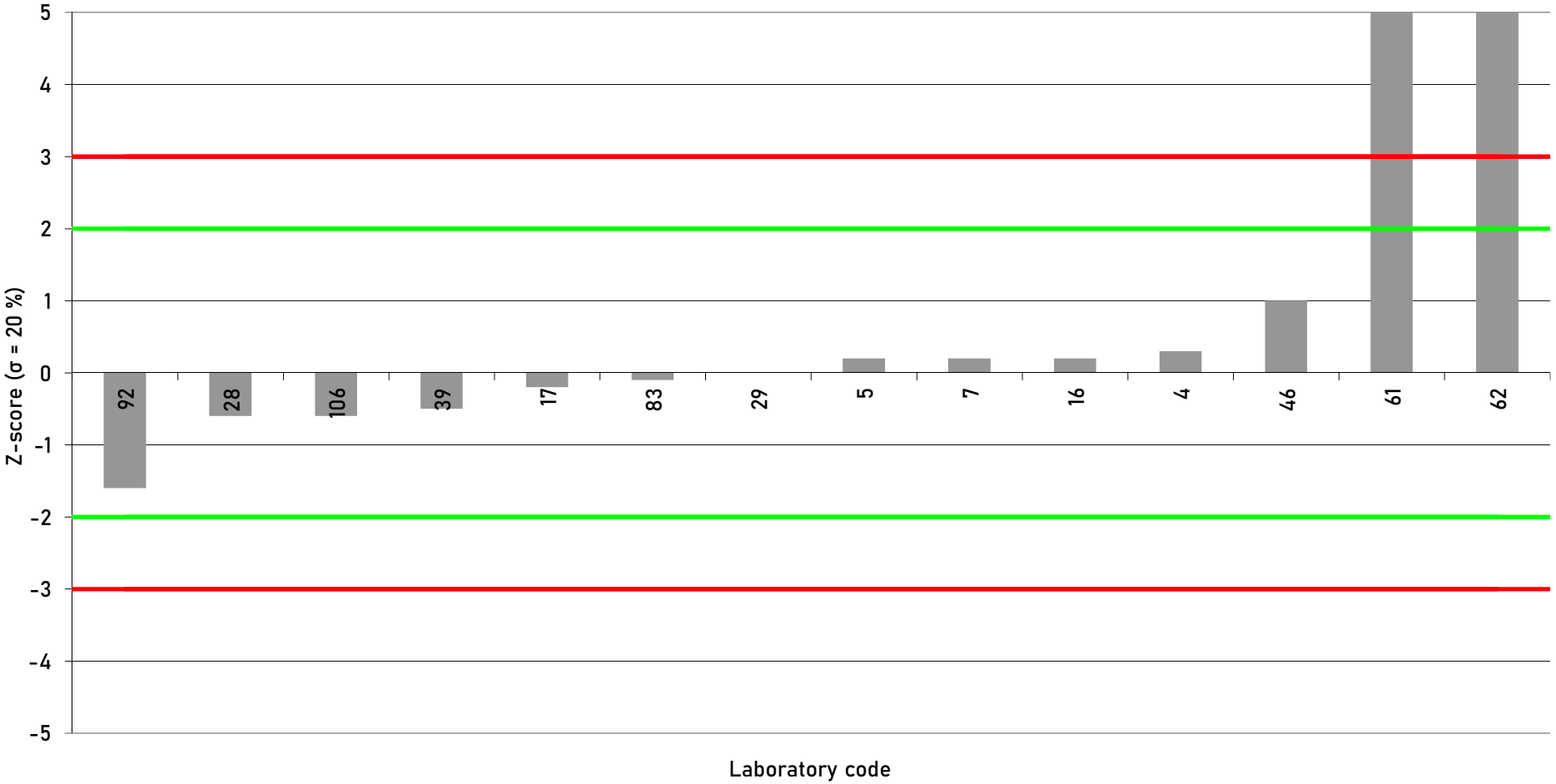
Assigned value: 0.205 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

(+/–)-β- HBCDD

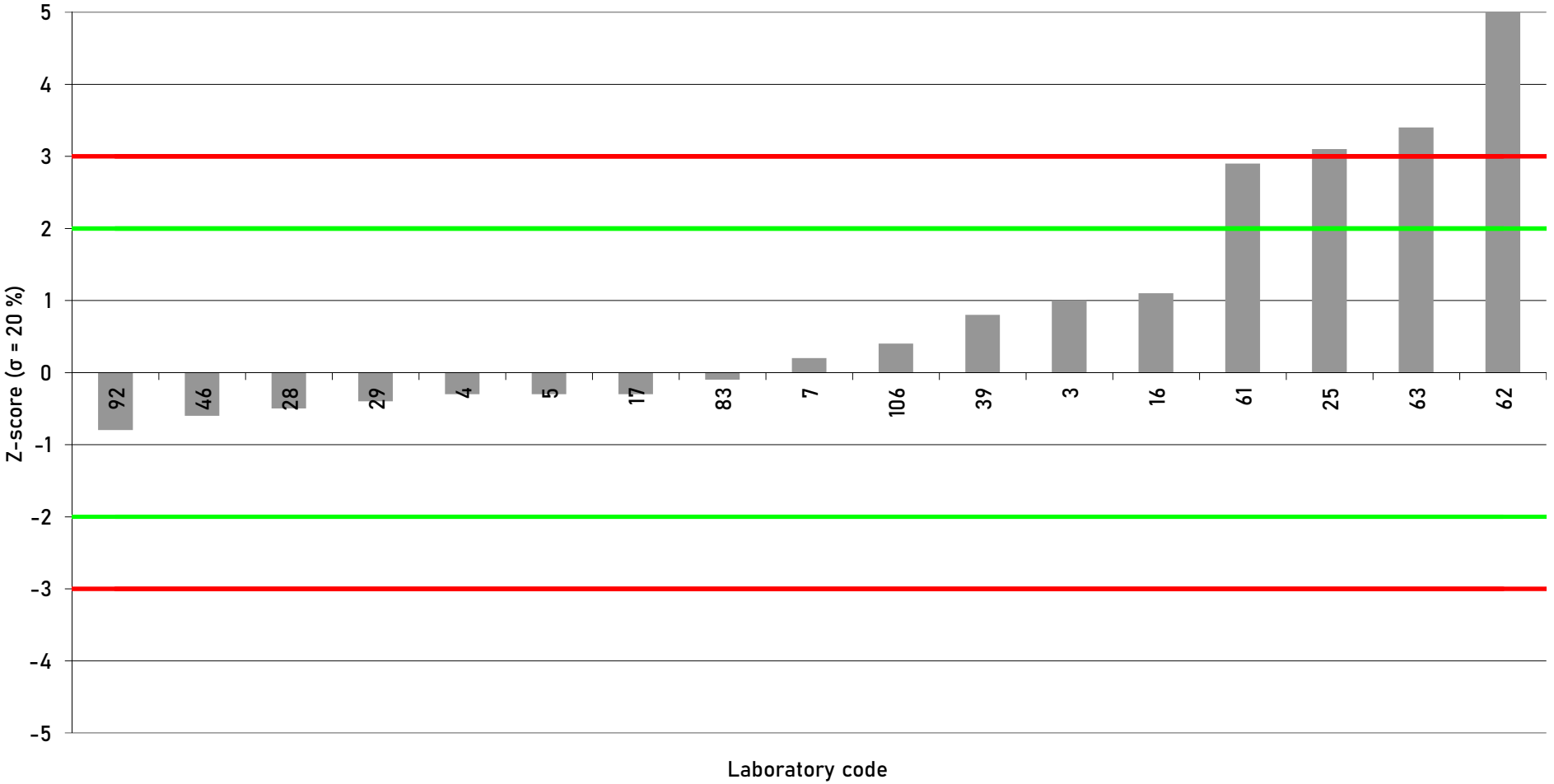
Assigned value: 0.0192 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

Sum of α-, β-, γ-HBCDD ub

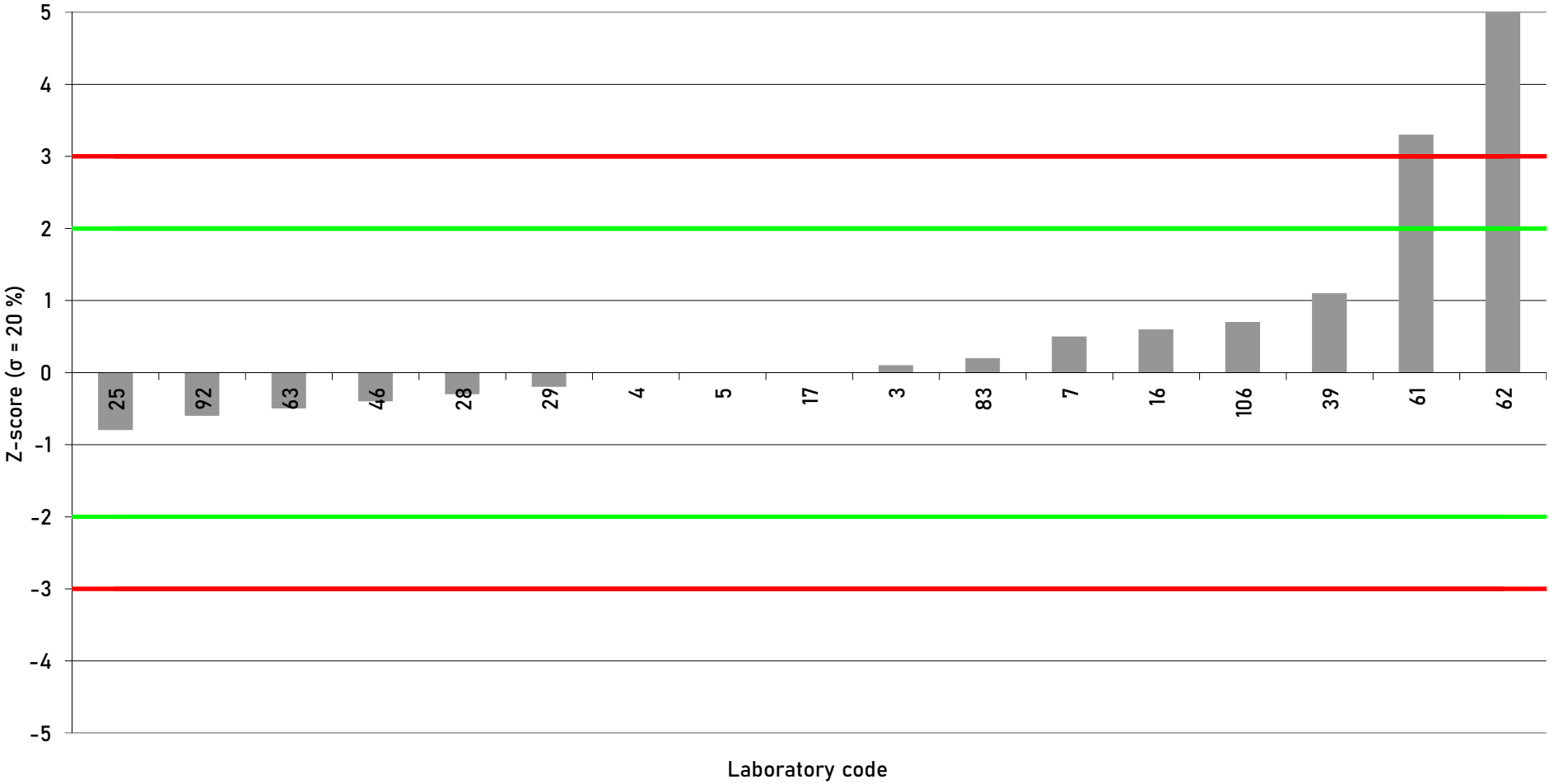
Assigned value: 0.24 µg/kg product (12 % moisture content)



Fish Meal (2203-FM)

Sum of α-, β-, γ-HBCDD lb

Assigned value: 0.227 µg/kg product (12 % moisture content)



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Annex 5: Test for sufficient homogeneity and stability for PBDEs

Test sample - Fish Meal (2203-FM)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
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Fish Meal (2203-FM)
PBDE - Homogeneity test - Data

Analyte	Result µg/kg product (12% moisture content)	**Mean** (n = 10, duplicate analysis)	**Median** (n = 10, duplicate analysis)	**Relative standard deviation** [%]
Sum of PBDE without BDE-209 ub		0.908	0.914	7%
Sum of PBDE including BDE-209 ub		1.27	1.27	7%
BDE-28		0.0347	0.0338	8%
BDE-47		0.303	0.302	7%
BDE-49		0.122	0.126	10%
BDE-99		0.0785	0.0779	9%
BDE-100		0.0677	0.0658	11%
BDE-153		0.0355	0.0352	8%
BDE-154		0.116	0.118	7%
BDE-183		0.151	0.145	11%
BDE-209		0.363	0.362	10%

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-F
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)
Selected PBDE congeners - Homogeneity test - Data

Sample	Replicate	Result µg/kg product (12% moisture content)	**BDE-209**
5	1		0.384
	2		0.370
8	1		0.377
	2		0.405
66	1		0.363
	2		0.360
79	1		0.351
	2		0.341
103	1		0.389
	2		0.454
116	1		0.351
	2		0.370
120	1		0.374
	2		0.382
146	1		0.351
	2		0.349
202	1		0.251
	2		0.352
210	1		0.330
	2		0.359
Cochran's C-test			
C			0.611
$C_{critical}$ (α = 0.05, m = 2, n = 10)			0.602
$C_{critical}$ (α = 0.01, m = 2, n = 10)			0.718
$C < C_{critical}$			yes
Outliers			no evidence for analytical outliers
Homogeneity test			
General average $\bar{x}$			0.363
Standard deviation of sample averages s_x			0.0321
Wthin-sample standard deviation s_w			0.0291
Between-sample standard deviation s_s			0.0246
Standard deviation for proficiency assessment σ_{PT}			0.0726
s_s / σ_{PT}			0.3
Test for homogeneity ($s_s \leq 0.3\ \sigma_{PT}$)			passed

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2022 [EURL-PT-POP_2203-FM]
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Fish Meal (2203-FM)
Selected congeners - Stability test - Data

Sample	Replicate	Result µg/kg product (12% moisture content)	**BDE-209**
5	1		0.373
	2		0.357
120	1		0.349
	2		0.359
210	1		0.353
	2		0.375
Stability test			
General average (stability test) $\bar{y}$			0.361
General average (homogeneity test) $\bar{x}$			0.363
Standard deviation for proficiency assessment σPT			0.0726
$\lvert \bar{y} - \bar{x} \rvert$			0.00212
Test for stability ($\lvert \bar{y} - \bar{x} \rvert \leq 0.3$ σPT)			passed

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs,HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP-2203-FM]

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Annex 6: Participants' Methods for PBDEs and HBCDDs

Test sample - Fish Meal (2203-FM)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods PBDEs - Internal standards

LC	Sample	Weighed sample [g]	Use of isotope-labelled internal standards for … PBDE congeners (yes/no)	Additional information
3	2203-FM	3	yes	
4	2203-FM	10	yes	
5	2203-FM	15.0	Yes	Moisture content analysis performed by an ISO 17025 accredited sub-contractor
7	2203-FM	10.0	28,47,99,100,154,153,183	
12	2203-FM	35.6	yes (except for BDE-49)	
16	2203-FM			
17B	2203-FM	5.0	yes	
21	2203-FM	5.0	YES	
23	2203-FM	5.37	yes	
25	2203-FM	20.0	Yes	
26	2203-FM	2.5	yes	
28	2203-FM	5.20	yes	
29	2203-FM	3	YES	
32	2203-FM	7.3	yes	
39	2203-FM	5.0	yes	
46	2203-FM	10	yes	
49	2203-FM	39.81	Yes	
56	2203-FM	25.32	YES (15)	Calculation methodology as per USEPA Method 1614
59	2203-FM	1.962	yes	
61	2203-FM	20	yes	
62	2203-FM			
63	2203-FM	20.2	yes	
64	2203-FM	20.0	yes	Extract of PBDEs together with PCBs was cleaned-up after analysis on florisil column due to high content of interferences (waxes) especially in the 5- and 6-BDE homologue group. The clean-up was not suficient enough, but it was possible to evaluate all PBDEs.
83	2203-FM	10	yes	
86	2203-FM	30	YES	
92	2203-FM	8	yes	
97	2203-FM	10	yes	Analysed from the PCBs fraction of the dioxins clean-up Method not validated for PBDEs in feed
106	2203-FM	25.0628	yes	
109	2203-FM	30	yes	

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods PBDEs - Pre-treatment and extraction

		Pre-treatment and extraction					
LC	Sample	Sample preparation/pre-treatment	Extraction technique	Extraction solvent	Extraction time [h]	Extraction temperature [ºC]	Extraction pressure [MPa]
3	2203-FM	none	Soxhlet	Toluene/Ethanol 30/70	8		
4	2203-FM	Mixed with sodium sulphate	ASE	Hexane/Acetone (70:30)	1	125	10.3
5	2203-FM	Homogenisation	SILICA GEL /SOLVENT EXTRACT- MANUAL	40:60 DCM:HEXANE	2-4HRS	AMBIENT	GRAVITY
7	2203-FM		ASE	1 cycle Toluol, 2 cycles Toluol/Ethanol (9/1)		100	10
12	2203-FM	sample mixed with sodium sulphate before extraction	Soxhlet	DCM:Hexane (50:50)	24 h		
16	2203-FM						
17B	2203-FM	homogenization, drying with polyacrylamide	cold extraction	hexane			
21	2203-FM	NO	SOXHLET	HEXANE/DCM (1/1)	24H		
23	2203-FM		ASE	Hexane	5 min x2	100	10,3
25	2203-FM	Drying in 105 degrees celsius	Soxhlet (SoxtecTM)	Hexane/DCM (1/1)	1 h 30 min	130	
26	2203-FM	/	LSE	ethyl-acetate	10m	/	/
28	2203-FM	homogenization, drying with polyacrylamide	cold extraction	hexane			
29	2203-FM	drying	PLE	Toluene/Acetone			
32	2203-FM	no	ASE	Toluen/Ethanol (90/10)	1	100	10.342
39	2203-FM	drying	soxhlet	dcm:hex 1:1	6	boiling point of solvent mixture	normal
46	2203-FM	freeze-dried	Accelerated Solvent Extraction (ASE)	dichloromethan:heksan (1:1)	2 x 5 min	125	10
49	2203-FM	No	Soxhlet	DCM	18	Boiling point	
56	2203-FM	No sample pre-treatment, used directly from container supplied.	ASE	Toluene	0.5	150	11.7
59	2203-FM		Adding silica/H2SO4 44% and then extraction with 10 ml hexane (2x). Evaporated to dryness.		over night	Room temperature	
61	2203-FM	thorough homogenization, drying with anhydrous Sodium Sulfate	Soxhlet (ultrasonic bath, agitate)	dichloromethane:acetone 3:1	21	109	0.1
62	2203-FM						
63	2203-FM	yes	ASE	ethanol-toluene (15/85)	0,2	100	100
64	2203-FM	Homogenisation, drying (only for determination of moisture content).	ASE, Soxhlet	toluene, ethanol, hexane, acethone (ASE), toluene (Soxhlet)	45min/sample (ASE), 16h (Soxhlet)	100°C (ASE)	10MPa (ASE)
83	2203-FM		Soxhlet	toluene/acetone 7/3	4		
86	2203-FM	drying	ASE	HEXANE/ACETONE 50/50	0.33	100	10.13
92	2203-FM	no	QuEChERs like-extraction	Ethyl acetate	no	no	no
97	2203-FM	-	ASE	(1) Toluene - (2) Toluene:Ethanol 90:10	0.25	100°C	10.3
106	2203-FM	Homogenisation	Soxhlet	Toluene /ethanol 50 / 50	24	120	atm
109	2203-FM		Twisselman	Toluene / Ethanol (30/70)	6		

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EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods PBDEs - Clean-up

		Clean-up						
LC	Sample	Gelchromatography	Silica/sulfuric acid column	Florisil column	Alumina column	Carbon column	Others	Final volume [µl]: PBDE
3	2203-FM	no	yes	no	yes	yes	Silica/AgNO3	100
4	2203-FM	no	yes	no	yes	no	acid hydrolysis with sulphuric acid	20
5	2203-FM	NO	YES	NO	YES	YES		50
7	2203-FM	no	yes	no	yes	yes		50
12	2203-FM	no	yes	no			basic set of "power-prep system" columns	40
16	2203-FM							
17B	2203-FM	no	yes	no	yes	no		100
21	2203-FM	NO	YES	NO	YES	NO	NO	20
23	2203-FM	no	yes	no	yes	yes	Silver nitrate, AgNO3	65 ul
25	2203-FM	Yes	Yes	Yes	No	Yes	No	50
26	2203-FM	no	yes	no	no	no	/	500
28	2203-FM	no	yes	no	yes	no		100
29	2203-FM	YES	YES	YES	NO	YES		50
32	2203-FM	no	yes	no	yes	no		200
39	2203-FM	yes	yes	no	no	yes		20
46	2203-FM	no	yes	yes	yes	no	no	50
49	2203-FM	No	Yes	No	Yes	No		50
56	2203-FM	No	Yes	No	Yes	Yes	Sample extract partitioned with concentrated sulfuric acid to remove bulk organic material residues	10µL
59	2203-FM	no	yes	no	no	no	no	250 µl
61	2203-FM	no	yes	no	yes	yes	basic silica, silver nitrate silica	50
62	2203-FM							
63	2203-FM		yes		yes	yes		500
64	2203-FM	no	yes	yes	yes	yes	PowerPrep FMS columns (basic-neutral silica, alumina, carbon)	20
83	2203-FM	no	yes	no	yes	yes		100
86	2203-FM	NO	YES	YES	NO	YES	NO	100
92	2203-FM	yes	yes	no	no	no	no	250
97	2203-FM	yes	yes	no	yes	yes	-	100
106	2203-FM	no	yes	no	yes	no		25
109	2203-FM	no	yes	no	yes	yes	acidic treatment	50

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods PBDEs - Chromatographic separation and detection method

LC	Sample	Chromatographic separation and detection method			
		GC injection	Injected volume [µl]	Chromatographic separation: Stationary phase	Detector
3	2203-FM	PTV	1	ZB - Semi Volatiles, 20m, 0.18 mm, 0.18µm	MS/MS
4	2203-FM	splitless	1	Rtx-1614 30m x 0.25mm x 0.1µm	HRMS
5	2203-FM	PTV	10µl	Rtx-1614 30m x 0.25mm x 0.1µm	HRMS
7	2203-FM	large Volume	6	Rtx-1614 (15m x 0,25 mm x 0,1 µm)	MS/MS
12	2203-FM	Splitless	1	DB-5MS (30 m, 0.25 mm id, 0,25 mm film)	HRMS (Mat-95 XP)
16	2203-FM				
17B	2203-FM	pulsed splitless	2	Diphenyl-/dimethylpolysiloxan (5%/95%)	MS/MS
21	2203-FM	SPLITLESS	1	DB-5ms 40m x 0,18 mm x 0,18 um	HRMS
23	2203-FM	Tri-hepta PBDE: Pulsed splitless / Deca PBDE: PTV splitless	2	Tri-hepta PBDE: DB-XLB / Deca PBDE: Rtx-1614, 5% diphenyl, 95% dimethyl polysiloxane	Tri-hepta PBDE: MS/MS (EI) / Deca PBDE: Single quadropol MS (NCI)
25	2203-FM	PTV	1	Rtx-1614 (20 m x 0.25 mm x 0.1 um)	Autospec Premier HRMS (SIR)
26	2203-FM	pulsed splitless	2	DB-XLB	LR-MS
28	2203-FM	pulsed splitless	2	Diphenyl-/dimethylpolysiloxan (5%/95%)	MS/MS
29	2203-FM	Splitless	2	HT8PCB	GC-HRMS
32	2203-FM	splitless	1	%5 phenyl %95 polydimethylsiloxane	APGC-MS/MS
39	2203-FM	PTV	5	5% phenyl-arylene 95% dimethylpolysiloxane	MSMS
46	2203-FM	PTV Splitless	1	60m DB-5ms; 15 m RTX 1614	HRMS
49	2203-FM	Splitless	1.5	DB-5MS	HRMS, DFS
56	2203-FM	PTV	1µL	5%-Phenyl-Arylene-95% DimethylPolysiloxane (ZB5-MS) column 30m×0.1mm×0.1µm	Thermo DFS HRMS (>10,000 Mass resolution)
59	2203-FM	PTV	10	Rtx-CIPesticides	GC-HRMS
61	2203-FM	pulsed splitless	1	DB-5MS (60m x 0,25mm x 0,10 µm)	HRMS (R>10000)
62	2203-FM				
63	2203-FM	Solvent vent	5	5% Phenyl, 95% methyl polysiloxane	MS/MS
64	2203-FM	splitless	2	DB-5ht (15m)	HRMS
83	2203-FM	splitless	2	DB 5 MS	HRMS
86	2203-FM	PTV	1	100% dimethylpolysiloxane	HRMS
92	2203-FM	PTV	10	DB5HT 15 m x 0.25 mm; 0.1 um	MS/MS
97	2203-FM	PTV	5	RTX-1614 - 15m	HRMS
106	2203-FM	splitless	1	Rtx-1614	HRMS
109	2203-FM	splitless	2.0	DB-5HT	HRMS (Autospec Ultima Waters)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)
Determination of Limit of Detection and Measurement Uncertainty (MU) - PBDEs

LC	Sample		**Methods apllied to determine** Limit of Quantification (LOQ)		Measurement Uncertainty (MU)	
3	2203-FM		blank + 3s			
4	2203-FM		The LOQs were estimated using the approach "Congener-based LOQs from S/N Calculations".	This methodology is reported in the Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food.	The MU was estimated using the "semi-empirical approach" based on the ISO Guide to the expression of Uncertainty in Measurement applied to analytical chemistry by EURACHEM/CITAC.	This approach is reported in the Guidance Document on Measurement Uncertanty for Laboratories performing PCDD/F and PCB Analysis using Isotope Dilution Mass Spectrometry
5	2203-FM					
7	2203-FM					
12	2203-FM					
16	2203-FM					
17B	2203-FM					
21	2203-FM					
23	2203-FM					
25	2203-FM					
26	2203-FM		as lowest calibration point where S/N > 10 (quantification transition) and S/N > 3 (confirmation transition)			
28	2203-FM					
29	2203-FM		S/N > 3			
32	2203-FM					
39	2203-FM					
46	2203-FM		LOQ was obtained from blank samples made in the same batch as PT samples.		Obtained during method validation additional, MUs were compared with a standard deviation of PT sample,	higher value was taken to report.
49	2203-FM					
56	2203-FM					
59	2203-FM		reporting limit = 0.005 µg/kg 12% moisture content except for BDE209 = 0.2 µg/kg 12% moisture content	according to NEN 7777	according to NEN 7777	expanded measurement uncertainty
61	2203-FM					
62	2203-FM					
63	2203-FM		Combination of low level spike and blank results.		Combination of low level spike and PT results.	
64	2203-FM		LOQ = 3 x LOD	LOD evaluated as 3 times of noise	Expanded U: Ue = k x Uc (k = 2). MU of type A is evaluated using internal RM. U of type B (includes i.a. uncertainity of weighing, volume measurements, etc.)	Uc = combined uncertainty is summed uncertainty of type A and B according the law of propagation of measurement uncertainty
83	2203-FM		S/N 3:1		Guidance document on MU; QC Samples, PT results	
86	2203-FM					
92	2203-FM		Samples spiked at LOQ level (20 pg/g; 200ppg for BDE 209); for BDE 47 LOQ (35 pg/g) was estimated from	procedural blanks run within the sample batch	Nordtest	
97	2203-FM					
106	2203-FM					
109	2203-FM					

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods HBCDDs - Internal standards

LC	Sample	**Weighed sample** [g]	**Use of isotope-labelled internal standards for …** HBCDD diastereomers (yes/no)	Additional information
3	2203-FM	2	yes	Method according to Bichon et.al. 2018
4	2203-FM	10		
5	2203-FM	4.058	yes	Moisture content analysis performed by an ISO 17025 accredited sub-contractor
7	2203-FM	10	yes	
12	2203-FM			
16	2203-FM	10.0	yes	
17B	2203-FM	5	yes	
21	2203-FM			
23	2203-FM			
25	2203-FM	2.5	Yes	
26	2203-FM	2.5	yes	
28	2203-FM	5,3g	yes	
29	2203-FM	3	YES	
32	2203-FM			
39	2203-FM	5.0	yes	
46	2203-FM	8	yes	
49	2203-FM			
56	2203-FM			
59	2203-FM			
61	2203-FM	5	yes	
62	2203-FM	10.0	Yes	
63	2203-FM	20.2	yes	
64	2203-FM	20.00	yes	
83	2203-FM	5	yes	
86	2203-FM			
92	2203-FM	8	yes	
97	2203-FM			
106	2203-FM	50.5917	yes	
109	2203-FM			

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EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods HBCDDs - Pre-treatment and extraction

LC	Sample	Pre-treatment and extraction					
		Sample preparation/pre-treatment	Extraction technique	Extraction solvent	Extraction time [h]	Extraction temperature [ºC]	Extraction pressure [MPa]
3	2203-FM		Soxhlet	Toluene	12	unknown	ambient pressure
4	2203-FM	Mixed with sodium sulphate	ASE	Hexane/Acetone (70:30)	1	125	10.3
5	2203-FM	none	acidified silica homogenisation	40/60 DCM/hexane	0.2	ambient	n/a
7	2203-FM		cold extraction	DCM/Hexan 1/1	roughly 2-3 hours	ambient	ambient
12	2203-FM						
16	2203-FM	drying		hexane:dichloromethane 50/50	0.33	ambiente	ambiente
17B	2203-FM	homogenization	QuECHERS	acetonitrile/water (1/1)			
21	2203-FM						
23	2203-FM						
25	2203-FM	Drying in 105 degrees celsius	Soxhlet (SoxtecTM)	Hexane/DCM (1/1)	1 h 30 min	130	
26	2203-FM	/	LSE	ethyl-acetate	10m	/	/
28	2203-FM	homogenization	QuEChERS	acetonitrile/water (1/1)			
29	2203-FM	drying	PLE	Toluene/Acetone			
32	2203-FM						
39	2203-FM	drying	soxhlet	hex:dcm 1:1	6	boiling point of solvent mixture	normal
46	2203-FM	no	ASE 350	dichloromethane/hexane (50/50)	0.3	120	10
49	2203-FM						
56	2203-FM						
59	2203-FM						
61	2203-FM	addition of sodium sulfate	shaking with solvent in atmospheric pressure	Dichlormethane : Acetone (2:1)	2	22	0.1
62	2203-FM	none	ASE	Hexane:Acetone 1:1	0.5	100	10.3
63	2203-FM	yes	ASE	ethanol-toluene (15/85)	0,2	100	100
64	2203-FM	Homogenisation, drying (only for determination of moisture content).	ASE, Soxhlet	toluene, ethanol, hexane, acethone (ASE), toluene (Soxhlet)	45min/sample (ASE), 16h (Soxhlet)	100°C (ASE)	10MPa (ASE)
83	2203-FM		Soxhlet	toluene/acetone 7/3	4		
86	2203-FM						
92	2203-FM		QuEChERS-like	Ethyl Acetate			
97	2203-FM						
106	2203-FM	Homogenisation	Soxhlet	Toluene /ethanol 50 / 50	24	120	atm
109	2203-FM						

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods HBCDDs - Clean-up

LC	Sample	Clean-up: Gelchromatography	Silica/sulfuric acid column	Florisil column	Alumina column	Carbon column	Others	Final volume [µl]: HBCDD
3	2203-FM	no	yes	yes	no	no	no	500
4	2203-FM	no	yes	no	no	no	acid hydrolysis with sulphuric acid	200
5	2203-FM	no	no	no	no	no	clean-up combined in extraction	150
7	2203-FM	no	yes	no	no	no	no	400
12	2203-FM							
16	2203-FM	no	yes	no	no	no		200
17B	2203-FM	no	yes	no	no	no		1000
21	2203-FM							
23	2203-FM							
25	2203-FM	No	Yes	Yes	No	No	No	50
26	2203-FM	yes	no	no	no	no	no	500
28	2203-FM	no	yes	no	no	no		1000
29	2203-FM	YES	YES	NO	NO	NO	liquid liquid extraction	50
32	2203-FM							
39	2203-FM	yes	yes	no	no	yes		200
46	2203-FM	no	yes	no	no	no	NaOH	20
49	2203-FM							
56	2203-FM							
59	2203-FM							
61	2203-FM	yes	no	no	no	no	Silica / annealed sodium sulfate	500
62	2203-FM	No	Yes	Yes	No	No	No	100
63	2203-FM		yes		yes	yes		500
64	2203-FM	no	yes	no	no	no	no	20
83	2203-FM	yes	no	no	no	no	silica column	50
86	2203-FM							
92	2203-FM	yes	no	no	no	no	Extrelut NT-3 column, acidic for H2SO4 tandem Si 1g/6 mL column	250
97	2203-FM							
106	2203-FM	no	yes	no	no	no		1000
109	2203-FM							

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Physico-chemical Methods HBCDDs - Chromatographic separation and detection method

		Chromatographic separation and detection method			
LC	Sample	Injection	Injected volume [µl]	Chromatographic separation: Stationary phase	Detector
3	2203-FM	direct injection	5, 10, 20, 40	reversed phase C18 (Eclipse XDB-C18 5µm 4,6x150mm)	MS/MS
4	2203-FM		5	BEH C18 (100 mm x 2.1 µm; 1.7 µm)	HRMS
5	2203-FM	Liquid	5	Agilent Zorbax RRHD Eclipse Plus C18 1.8 µm (150 x 2.1 mm)	LC-MS/MS
7	2203-FM		15	C18	MS/MS
12	2203-FM				
16	2203-FM	UPLC	5	Eclipse Plus C18, 2,1 x 100mm	MS/MS
17B	2203-FM	automatic sample application	10	C18	MS/MS
21	2203-FM				
23	2203-FM				
25	2203-FM	HPLC	5	C18	Orbitrap-HRMS
26	2203-FM	/	5	BEH C18 (100 × 2,1 mm; 1,7 µm)	MS/MS
28	2203-FM	automatic sample application	10	C18	MS/MS
29	2203-FM		15	Hypersil Gold	MS/MS
32	2203-FM				
39	2203-FM		70	PFP	MSMS
46	2203-FM	GC: PTV solvent split	GC: 5; LC:10	GC: DB-5MS (30m x 0.25 mm x 0.1 µm); LC:Gemini C18 (50 x 2,0 mm, 3 µm)	GC: HRMS (DFS), LC: LC-MS/MS
49	2203-FM				
56	2203-FM				
59	2203-FM				
61	2203-FM	HPLC autosampler	10	C18	MS/MS
62	2203-FM		10	C18	HRMS (Orbitrap)
63	2203-FM	syringe	5	C18	MS/MS
64	2203-FM	splitless	2	DB-5ht (15m)	HRMS
83	2203-FM	HPLC	10	RP 18	LC-MS/MS
86	2203-FM				
92	2203-FM		20 µL	KINETEX 2.6um XB-C18 100A (100 x 2.1 mm) (PHENOMENEX)	LC-MS/MS
97	2203-FM				
106	2203-FM	LC		Acquity BEH C18 150 mm	LC/MS/MS
109	2203-FM				

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal [EURL-PT-POP-2203-FM]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)
Determination of Limit of Detection and Measurement Uncertainty (MU) - HBCDDs

LC	Sample		**Methods apllied to determine** Limit of Quantification (LOQ)		Measurement Uncertainty (MU)	
3	2203-FM		calculated on base of standard with S/N 10:1 multiplied with the worst recovery rate		estimated value based on the RSD of multiple determination	
4	2203-FM		The LOQ was estimated following the "Calibration Standards" approach.	This methodology is reported in the Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food.	The MU was estimated using the Top-Down approach reported in the Guidance Document on	Measurement Uncertanty for Laboratories performing PCDD/F and PCB Analysis using Isotope Dilution Mass Spectrometry
5	2203-FM					
7	2203-FM		ten point equidistant calibration at the expected LOQ using DIN 32645			
12	2203-FM					
16	2203-FM		The LOQs corespond to the lowest validated level for validated matrices		U= k*u=((2x CVrw) + biais) for validated matrices	
17B	2203-FM					
21	2203-FM					
23	2203-FM					
25	2203-FM					
26	2203-FM		as lowest calibration point where S/N > 10 (quantification transition) and S/N > 3 (confirmation transition)			
28	2203-FM					
29	2203-FM					
32	2203-FM					
39	2203-FM					
46	2203-FM		Lowest calibration level			
49	2203-FM					
56	2203-FM					
59	2203-FM					
61	2203-FM					
62	2203-FM		Lowest validated level		to be determined	
63	2203-FM		Combination of low level spike and blank results.		Combination of low level spike and PT results.	
64	2203-FM		LOQ = 3 x LOD	LOD evaluated as 3 times of noise		
83	2203-FM		lowest calibration point		Guidance document on MU; QC Samples, PT results	
86	2203-FM					
92	2203-FM		Samples spiked at LOQ level (10 pg/g) within the batch		From validation data with a semplified bottom up approach	
97	2203-FM					
106	2203-FM					
109	2203-FM					

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs,HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP-2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

28 July 2023

Annex 7: Participants' Methods, Measurement Uncertainty and Limit of Quantification for PBDEs and HBCDDs

Test sample - Fish Meal (2203-FM)

EURL Proficiency Study on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP_2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Methods PBDEs - Measurement Uncertainty [%]

LC	Sample		BDE 28	BDE 47	BDE 49	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
3	2203-FM		30	30	30	30	30	30	30	30	40
4	2203-FM		27	34	26	28	34	35	38	40	40
5	2203-FM										
7	2203-FM										
12	2203-FM										
16	2203-FM										
17	2203-FM		25	25	25	25	25	25	25	30	30
21	2203-FM										
23	2203-FM		30	30	30	30	30	30	30	50	40
25	2203-FM										
26	2203-FM		50	50	50	50	50	50	50	50	50
28	2203-FM										
29	2203-FM										
32	2203-FM										
39	2203-FM		20	20	20	20	20	20	20	20	20
46	2203-FM		17	15	26	24	31	29	21	15	35
49	2203-FM		10	10	10	10	10	10	10	10	
59	2203-FM		25	25	25	25	25	25	25	25	50
61	2203-FM		30	30	-	30	30	30	30	30	-
62	2203-FM										
63	2203-FM		70	40	70	70	70	70	70	40	70
64	2203-FM		60	20	20	17	20	18	23	10	31
83	2203-FM		40	20	40	20	22	23	20	26	30
86	2203-FM										
92	2203-FM		59	42	42	42	59	59	42	42	59
97	2203-FM										
106	2203-FM										
109	2203-FM										

EURL Proficiency Study on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP_2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Methods PBDEs - Limit of detection (LOQ) in µg/kg product (12% moisture content)

LC	Sample		BDE 28	BDE 47	BDE 49	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
3	2203-FM		0.0031	0.04	0.029	0.016	0.004	0.003	0.014	0.019	0.140
4	2203-FM		0.0008	0.0410	0.0010	0.0130	0.0042	0.0003	0.0005	0.0007	0.0330
5	2203-FM		0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.017
7	2203-FM										
12	2203-FM		0.0001	0.0001	0.0001	0.0004	0.0005	0.0001	0.0002	0.0004	
16	2203-FM										
17	2203-FM										
21	2203-FM		0.0006	0.0010	0.0004	0.0008	0.0008	0.0024	0.0015	0.0070	0.0158
23	2203-FM		0.0050	0.0370	0.0090	0.0180	0.0180	0.0180	0.0180	0.0180	0.0370
25	2203-FM		0.0038	0.0072	0.0039	0.0050	0.0095	0.0077	0.0055	0.0055	0.0055
26	2203-FM		0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.1
28	2203-FM		0.0019	0.0019	0.0019	0.0038	0.0038	0.0058	0.0058	0.0096	0.1920
29	2203-FM										
32	2203-FM		0.0003	0.0015	0.0015	0.001	0.001	0.0008	0.0007	0.0011	0.0215
39	2203-FM										
46	2203-FM		0.001	0.001	0.002	0.004	0.003	0.001	0.001	0.003	0.031
49	2203-FM		0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	
59	2203-FM		0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.2
61	2203-FM										
62	2203-FM										
63	2203-FM		0.0016	0.0017	0.0011	0.0012	0.0012	0.0008	0.0011	0.0019	0.0212
64	2203-FM		0.0004	0.0001	0.0001	0.0006	0.0005	0.0003	0.0004	0.0008	0.0023
83	2203-FM										
86	2203-FM										
92	2203-FM										
97	2203-FM										
106	2203-FM										
109	2203-FM										

EURL Proficiency Study on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP_2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Methods HBCDDs - Measurement Uncertainty [%]

LC	Sample		(+/–)-α-HBCDD	(+/–)-β- HBCDD	(+/–)-γ- HBCDD
3	2203-FM		30	30	30
4	2203-FM		27	30	32
5	2203-FM				
7	2203-FM				
12	2203-FM				
16	2203-FM		50	50	50
17	2203-FM		30	50	30
21	2203-FM				
23	2203-FM				
25	2203-FM		20	20	20
26	2203-FM		50	50	50
28	2203-FM				
29	2203-FM				
32	2203-FM				
39	2203-FM		20	20	20
46	2203-FM				24
49	2203-FM				
59	2203-FM				
61	2203-FM				
62	2203-FM				
63	2203-FM		30	30	30
64	2203-FM				
83	2203-FM		30	30	30
86	2203-FM				
92	2203-FM		36	49	49
97	2203-FM				
106	2203-FM				
109	2203-FM				

EURL Proficiency Study on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Fish Meal 2023 [EURL-PT-POP_2203-FM]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Fish Meal (2203-FM)

Methods HBCDDs - Limit of detection (LOQ) in µg/kg product (12% moisture content)

LC	Sample		(+/–)-α-HBCDD	(+/–)-β- HBCDD	(+/–)-γ- HBCDD
3	2203-FM		0.03	0.03	0.03
4	2203-FM		0.005	0.005	0.005
5	2203-FM		0.01	0.01	0.01
7	2203-FM		0.01	0.01	0.01
12	2203-FM				
16	2203-FM		0.195	0.020	0.039
17	2203-FM				
21	2203-FM				
23	2203-FM				
25	2203-FM		0.1	0.1	0.1
26	2203-FM		0.9	0.9	0.9
28	2203-FM		0.00565	0.00565	0.00565
29	2203-FM				
32	2203-FM				
39	2203-FM				
46	2203-FM		0.005	0.005	0.005
49	2203-FM				
59	2203-FM				
61	2203-FM		0.05	0.05	0.04
62	2203-FM		0.03	0.03	0.03
63	2203-FM		0.1	0.1	0.1
64	2203-FM				
83	2203-FM				
86	2203-FM				
92	2203-FM				
97	2203-FM				
106	2203-FM				
109	2203-FM				