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CONTENT

1 INTRODUCTION

The Finnish Environment Institute (SYKE) carried out the proficiency test for the analysis of PCB, PBDE and PCDDs/PCDF compounds in sediment in August 2007. The test was carried out in accordance with the international guidelines, ISO/IEC Guide 43 1 [1], ILAC Requirements [2], ISO 13528 [3] and IUPAC Recommendations [4]. SYKE is the Proficiency Testing Provider No. PT01 accredited by the Finnish Accreditation Service. The proficiency testing service in SYKE conforms to the requirements of the Guide ISO/IEC 43-1:1997. However, the organising of tests for PDBE and PCDD/PCDF compounds is not included in the accredited scope.

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Finnish Environment Institute (SYKE), Laboratory
Hakuninmaantie 6, 00430 Helsinki
tel. +358 20 490 123, fax +358 20 490 2890

Subcontractor: Axys Analytical Services, Canada, PBDEs and PCDDs/PCDFs.

The responsibilities in organizing the proficiency test were as follows:
Kaija Korhonen, coordinator
Sami Huhtala, analytical expert (PBDEs and PCDDs/PCDFs)
Jari Nuutinen, analytical expert (PCBs)
Anne Markkanen, technical assistent
Helena Pyykönen, technical assistant
Markku Ilmakunnas, layout of the report

2.2 Participants

In total, 10 laboratories (Appendix 11) from Finland, Belgium, Denmark and Sweden participated in this proficiency test. The samples were distributed to eleven laboratories. Ten laboratories reported their results. Five laboratories used accredited methods for PCB analysis and three laboratories for PBDE analysis as well as for PCDD/PCDF analysis. The organizing laboratory (SYKE) has the code 1 in the result tables.

2.3 Samples and their delivery

The preparation of the samples is presented in Appendix 2.

Artificial samples (S1, S2 and S3) were commercial reference solutions diluted to final concentration.

Sediment sample (M1) was a clayey river estuary sediment collected from the river estuary of River Vantaa in Helsinki. The sediment was air dried and sieved to < 2 mm.

The samples were delivered August 7th 2007. They were requested to be analyzed and to reported

before November 30th 2007. Later on the reporting time was extended to the end of December 2007.

The samples and the requested measurands were as follows:

Sample, code	Measurand	Amount (approximately)
Artificial sample, S1	PCBs, concentration in isooctane, ng/ml	1 ml
Artificial sample, S2	PBDEs, concentration in nonane, ng/ml	1 ml
Artificial sample, S3	PCDDs/PCDFs, concentration in nonane, ng/ml	1 ml
Sediment, M1	PCBs, PBDEs and PCDDs/PCDFs, concentration, µg/kg	60 g

2.4 Homogeneity of the samples

Homogeneity of the sample M1 was tested by analyzing PCB-101, PCB-153 and PCB-180 as duplicate determinations from eight sub samples (Appendix 3). According to the homogeneity test results the sample M1 was considered homogenous.

The sample M1 was tested also by analysing PBDE congeners BDE-47, BDE-99 and BDE-209. Because of the low levels and thus high analytical deviations these results could not be treated statistically.

2.5 Stability studies

Because all compounds (PCB, PBDE and PCDD/PCDF) included in this test are known to be persistent in soil and sediment any stability study for the analytes in the sample M1 was not considered relevant. The stability of the artificial samples S1, S2 and S3 during the transport were checked. The sample vials were weighed at SYKE before the delivering and reweighed at the participating laboratory after the receiving. The differences of these two measurements were less than 0.5 % which means that significant solvent evaporation was not observed.

2.6 Comments sent by the participants

Appendix 4 contains the comments sent by the participants.

2.7 Analytical methods

The analytical methods used by the participants are presented in Appendix 5.1 (PCBs), Appendix 5.2 (PBDEs) and Appendix 5.3 (PCDDs/PCDFs). Laboratory 4 did not give any information about the analytical methods though it was asked.

PCBs

Five laboratories used GC-ECD technique. Three of them had the protocol based on the standard method ISO 10382 [5]. One laboratory analyzed only total PCB as Arochlor 1242 and the method based

on the standard ISO 15318 [6]. All used at least one PCB congener as an internal standard. ^{13}C-labelled congeners as internal standards were used in three laboratories using mass spectrometric method.

Total PCB
Laboratories were asked to report also the total PCB in the sediment sample. There were three different principles to calculate total PCB. One laboratory reported total PCB as Arochor 1242 [6] and one laboratory as toxicity equivalency (WHO TEQ) [7]. The third way was to summarize the analysed congeners.

PBDEs
The analysis of PBDE compounds is still relative new methodology even thought there is ISO and US EPA standards already available (ISO 22032 [8], US EPA 1614 [9]). Nevertheless, the determination of PBDEs is sensitive to errors: e.g. the distraction of chromatography and ionization caused by sulphur, thermal degradation of higher brominated congeners as well as contamination of the samples by dust containing PBDEs. The sulphur content of the sediment sample (M1) was determined to be 2300 mg/kg. Special care should be taken to avoid these potential sources of error.

All four participated laboratories used mass spectrometric method (one single and one triple quadrupole instrument and two high resolution instruments). Also ^{13}C-labelled standards were used at the determination of PBDEs in all laboratories.

PCDDs/PCDFs
There was only three laboratories analysing PCDD/PCDF compounds. Participants did not report literature references for their methods. However, there is international standards (US EPA 1613/1613B [10] and US EPA 8230 [11], ISO 18073:2004 [12]) available for the determination of PCDD/PCDF compounds.

The sediment sample was extracted with toluene or combination of toluene and ethanol and the extract was cleaned with column clean up (silica, alumina, active carbon). All participants used mass spectrometric methods (two high resolution instruments and one low resolution instrument). Also ^{13}C-labelled standards were used in all the laboratories.

2.8 Data treatment

2.8.1 Testing of outliers and normality of data

Before the statistical treatment, the data was tested according to the Kolmogorov-Smirnov normality test and the outliers were rejected according to the Hampel test. One result of PCB-52, PCB-138 as well as PCB-180 deviated over 50 % from the mean of the reported results were rejected before the robust statistic calculation.

2.8.2 Assigned values and their uncertainties

The assigned values and their uncertainties are presented in Appendix 6. The calculated concentrations were used as the assigned values for measurands in the artificial samples S1, S2 and S3. The uncertainty given is the expanded combined uncertainty and based on the combination of uncertainties associated with each individual operation involved in the preparation of the sample. The main individual source of uncertainty was the uncertainty of the concentration in the stock solution.

The robust mean of the reported results was used as the assigned value for the measurands in the sediment sample M1. However, the indicative assigned value was used instead of the assigned value when the uncertainty of the assigned value was over 25 % or when it could not be calculated.

The uncertainty of the assigned value was calculated using the robust standard deviation of the reported results as follows:

$$U\% = \frac{100 \times \left(\frac{2 \times 1.25 \times s_{rob}}{\sqrt{n}} \right)}{AV}$$

where:

AV = assigned value
U% = expanded uncertainty of the assigned value
s_{rob} = robust standard deviation
n = number of the results

In the final data treatment all assigned values for the measurands in the artificial samples were changed a little because the calculation of the theoretical concentration was based on the gravimetric results instead of the volumetric results. Consequently most z scores changed a little. Also the assigned value for PCB-138 as well as for PCB-52 in sediment changed in the final data treatment.

2.8.3 Target value for total deviation

The target value for the total deviation used for calculation of the z scores was estimated on basis of the type of the sample, the concentration of the analyte, the results of homogeneity testing and the uncertainties of the assigned values. The total target deviation was 20 % for all measurands in the artificial samples. The total target deviation for the concentrations of PCB compounds in the sediment sample were between 30–50 %. In the final data treatment the total target deviation for PCB-52 and PCB-138 were set 50 % because of the large uncertainty of the assigned value. Any target deviation for PBDEs and PCDDs/PCDFs in sediment could not be set because of the low number of the participants/results (PBDEs 4 lab., PCDDs/PCDFs 3 lab.).

2.8.4 Evaluation of performance

The performance evaluation was carried out by using the z scores. The z scores were calculated using the following equation:

$$z = \frac{(x_i - X)}{s}$$

where:

x_i = the reported value by the participant
X = the assigned value
s = the target value for total deviation/2

z scores were interpreted as follows:

$\lvert z \rvert \leq 2$	satisfactory result
$2 < \lvert z \rvert < 3$	questionable result
$\lvert z \rvert \geq 3$	unsatisfactory result.

3 RESULTS AND PERFORMANCE

3.1 Results

The results and the performance of each laboratory are presented in Appendix 7.1 (PCBs and PBDEs) and Appendix 7.2 (PCDDs/PCDFs). Explanations to terms used in the result tables are presented in Appendix 8.

Most participants reported their measurement uncertainties and they were mainly estimated using the data of validation and internal quality control (Appendix 9). The uncertainties varied between 10–60 % for PCBs, 15–50 % for PBDEs and 10–50 % for PCDDs/PCDFs. Laboratory 5 reported that the methods were accredited but did not give any uncertainties with the results.

The results and their uncertainties reported by the participants are presented graphically in Appendix 10 and the summaries of the proficiency test are presented in the tables 1 (PCBs and PBDEs) and 2 (PCDDs/PCDFs).

Table 1. Summary of the proficiency test 5/2007, PCBs and PBDEs

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
BDE100	M1	µg/kg	0,045	0.045	0.045	0.048	0.016	36,3	3		
	S2	ng/ml	257	247.25	245.30	244.00	12.41	5,1	4	20	100
BDE153	M1	µg/kg	0,096	0.096	0.096	0.095	0.031	32,2	3		
	S2	ng/ml	257	240.67	246.25	245.50	15.06	6,1	4	20	75
BDE17	M1	µg/kg		0.025		0.025			1		
	S2	ng/ml	257	247.50		247.50			1	20	100
BDE183	M1	µg/kg		0.040		0.040			3		
	S2	ng/ml	257	248.50	240.18	239.00	7.58	3,2	4	20	100
BDE209	M1	µg/kg	5,49	5.00	5.49	5.63	0.65	11,8	3		
	S2	ng/ml	514	508.25	518.69	514.50	21.52	4,1	3	20	67
BDE28	M1	µg/kg		0.020		0.020			2		
	S2	ng/ml				0.000			1	20	
BDE47	M1	µg/kg	0,12	0.10	0.12	0.12	0.018	15,9	4		
	S2	ng/ml	257	242.25	240.64	240.50	8.75	3,6	4	20	100
BDE66	M1	µg/kg	0,032	0.032	0.032	0.033	0.028	88,3	2		
	S2	ng/ml	257	234.50	235.39	234.50	2.81	1,2	3	20	100
BDE99	M1	µg/kg	0,21	0.21	0.21	0.22	0.092	42,7	4		
	S2	ng/ml		3.20		3.20			2		
PCB101	M1	µg/kg	1,19	1.21	1.19	1.20	0.088	7,4	8	30	100
	S1	ng/ml	21,16	21.42	21.42	21.44	2.49	11,6	8	20	100
PCB105	M1	µg/kg	0,12	0.12	0.12	0.13	0.092	75,3	3		
	S1	ng/ml	14,54	14.53	13.68	14.06	1.76	12,9	3	20	67
PCB118	M1	µg/kg	0,54	0.54	0.53	0.54	0.085	16	8	30	100
	S1	ng/ml	14,54	13.87	13.89	14.25	1.94	14	9	20	78
PCB126	M1	µg/kg	0,15	0.15	0.15	0.009	0.23	150,8	2		
	S1	ng/ml	14,54	14.97	14.97	14.75	0.84	5,6	2	20	100
PCB128	M1	µg/kg		0.88		0.88			1		
	S1	ng/ml	14,54	14.23	14.23	14.09	0.43	3	2	20	100
PCB138	M1	µg/kg	2,56	2.35	2.43	2.46	0.83	34,1	9	50	89
	S1	ng/ml	14,54	12.83	12.83	13.05	2.40	18,7	9	20	78
PCB153	M1	µg/kg	3,17	3.18	3.17	3.11	0.31	9,8	8	30	100
	S1	ng/ml	69,76	68.81	68.42	70.44	9.99	14,6	8	20	75
PCB156	M1	µg/kg	0,25	0.26	0.25	0.23	0.10	40,7	4		
	S1	ng/ml	14,54	14.25	14.60	14.82	0.80	5,5	4	20	100
PCB169	M1	µg/kg	0,81	0.81	0.81	0.80	1.30	160,1	2		
	S1	ng/ml	14,54	15.18	15.18	14.95	0.52	3,4	2	20	100
PCB170	M1	µg/kg	1,08	1.08	1.08	1.08	0.004	0,4	2		
	S1	ng/ml	14,54	13.61	13.61	13.41	1.43	10,5	2	20	100
PCB180	M1	µg/kg	2,37	2.37	2.32	2.35	0.29	12,7	9	30	89
	S1	ng/ml	42,73	39.09	39.09	39.60	8.72	22,3	9	20	67
PCB28	M1	µg/kg	0,16	0.18	0.16	0.15	0.088	54,2	6		
	S1	ng/ml	14,54	13.15	13.33	14.00	2.24	16,8	7	20	71
PCB31	M1	µg/kg	0,1	0.10	0.10	0.11	0.007	6,6	2		
	S1	ng/ml	14,54	10.41	10.41	10.52	2.46	23,6	2	20	50
PCB52	M1	µg/kg	0,28	0.34	0.35	0.37	0.29	81,1	8	50	60
	S1	ng/ml	37,39	36.38	36.06	37.10	3.87	10,7	9	20	78
PCB77	M1	µg/kg		0.073		0.073			1		
	S1	ng/ml	14,54	14.43	14.43	14.40	0.63	4,4	3	20	100

Table 2. Summary of the proficiency test 5/2007, PCDDs/PCDFs in the sample S3

Analyte	Unit	Ass value	Mean	SD %	Num of labs	2*TargSD, %	Accepted z-val%
2,3,7,8-TCDD	ng/mL	20.94	20,08	8,5	3	20	100
2,3,7,8-TCDF	ng/mL	20.94	19,38	8,6	3	20	100
1,2,3,7,8-PeCDD	ng/mL	52,34	49,95	6,4	3	20	100
1,2,3,7,8-PeCDF	ng/mL	52,34	48,42	3,4	3	20	100
2,3,4,7,8-PeCDF	ng/mL	52,34	49,42	10	3	20	100
1,2,3,4,7,8-HxCDD	ng/mL	52,34	48,33	13	3	20	67
1,2,3,6,7,8-HxCDD	ng/mL	52,34	48,48	10	3	20	100
1,2,3,7,8,9-HxCDD	ng/mL	52,34	51,80	19	3	20	67
1,2,3,4,7,8-HxCDF	ng/mL	52,34	49,93	9,6	3	20	100
1,2,3,6,7,8-HxCDF	ng/mL	52,34	50,67	3,4	3	20	100
2,3,4,6,7,8-HxCDF	ng/mL	52,34	50,60	9,9	3	20	100
1,2,3,7,8,9-HxCDF	ng/mL	52,34	53,18	21	3	20	67
1,2,3,4,6,7,8-HpCDD	ng/mL	52,34	53,42	3,1	3	20	100
1,2,3,4,6,7,8-HpCDF	ng/mL	52,34	50,72	1,8	3	20	100
1,2,3,4,7,8,9-HpCDF	ng/mL	52,34	51,80	16	3	20	100
OCDD	ng/mL	104,68	100,3	6,2	3	20	100
OCDF	ng/mL	104,68	104,4	12	3	20	100

where

Ass. val.	the assigned value
Mean	the mean value
Mean rob	robust mean
Md	the median value
SD %	the standard deviation as percent
SD rob	the robust standard deviation
SD rob %	the robust standard deviation as percents
Num of Labs	the number of participants
2*Targ. SD%	the target total deviation at 95% confidence level
Accepted z-val%	the satisfied z values: the results (%), where $\lvert z \rvert \leq 2$.

3.2 Evaluation of performance

The evaluation of the participants was based on z scores which were calculated using the estimated target values for the total deviation. The calculated z scores are presented with the results of each participant (Appendices 7.1 and 7.2) and the summary of z scores is presented in Appendix 10.

The total target deviation was 20 % for all measurands in the artificial samples and 30–50 % for PCBs in sediment. In this proficiency test from the artificial sample 84 % of the PCB results, 92 % of PBDE results and 94 % of PCDD/PCDF results were satisfactory.

From the PCB results in the sediment sample 87 % were satisfactory. The evaluation of PBDE and PCDD/PCDF results in sediment could not be carried out owing to the small number of the participants.

The calculated robust mean values for some of the PBDE and PCDD/PCDF compounds as well as the results of subcontractor are only indicative results. However, all the z scores of the results in both the sample S2 and S3 reported by the subcontractor lay within $|z| \leq 2$ (Appendix 11).

In the proficiency test 3/2005 [13] 75 % of the laboratories reported the satisfactory PCB results from the artificial sample and 75 % and 85 % from the soil samples M1 (CRM soil) and M2 (sealant contaminated soil), respectively.

In QUASIMEMEs Laboratory performance study for brominated flame retardants [14] sediment sample was submitted which contained similar PBDE levels with SYKE 5/2007 sediment sample M1. From results in QUASIMEME study 69 % were considered satisfactory. For BDE-28 and BDE-209 only indicative values were given.

The Ministry of Environment in Finland has published the guideline for dredging and placement of sediment [15]. The guideline provides that at PCB compounds 28, 52, 101, 118, 138, 153 and 180 are analysed. Three laboratories analysed all of these congeners satisfactory and two laboratories analysed six congeners satisfactory but did not analyse PCB-28 or reported sum of PCB-28 and -31. Using short (≤30m) colum, PCB-28 can coelute with PCB-31, and the results may be overestimated. Some high z scores for the PCB-138 in the M1 sample may be a consequence of coelution with PCBs 160 and 163. The coelution of the PCB congeners can be excluded e.g. with longer columns.

4 SUMMARY

The Finnish Environment Institute carried out the proficiency test for the analysis of PCBs, PBDEs and PCDDs/PCDFs in sediment in autumn 2007. In total, the samples were delivered to 11 laboratories from which ten laboratories reported PCB results, four laboratories PBDE results and three laboratories PCDD/PCDF results. One laboratory did not reported any results.

One artificial sample and one sediment sample were delivered to the laboratories for the analysis of each measurand.

The calculated concentrations were used as the assigned values for measurands in the artificial sample and the robust means of the reported results for the measurands in the sediment. The assessment of performance was based on the z score which was calculated using the target value for total deviation at 95% confidence level. The target value for the total deviation was set 20 % for the measurands in the artificial samples and varied from 30 % to 50 % for PCBs in sediment. Any target deviation for PBDEs and PCDDs/PCDFs in sediment could not be set because of the low number of the participants. In total, 86 % of the participating laboratories reported the satisfactory results.

5 YHTEENVETO

Suomen ympäristökeskus järjesti elokuussa 2007 pätevyyskokeen PCB-, PBDE- ja PCDD/PCDF -yhdisteiden määrittämiseksi sedimentistä. Sedimenttinäytteen lisäksi toimitettiin synteettinen näyte, jonka avulla laboratoriot saivat tarkistaa mittaussysteeminsä kalibroinnin. Näytteet toimitettiin 11 laboratoriolle, joista kymmenen laboratoriota palautti PCB -tulokset, neljä laboratoriota PBDE -tulokset ja kolme laboratoriota PCDD/PCDF -tulokset.

Synteettiset näytteet valmistettiin sertifioiduista vertailuaineista laimentamalla. Niissä mittaussuureen ver-

tailuarvona käytettiin laskennallista pitoisuutta. Sedimenttinäytteessä mittaussuureelle vertailuarvoksi asetettiin osallistujien tulosten robusti keskiarvo, mikäli tulosten robustin keskihajonnan avulla laskettu laajennettu mittausepävarmuus oli alle 20 %. Jos vertailuarvon mittausepävarmuus oli yli 25 %, vertailuarvon sijasta ilmoitettiin ainoastaan viitteellinen vertailuarvo. Kaikille mittaussuureille ei voitu laskea edes viitteellistä vertailuarvoa vähäsen tulosmäärän vuoksi.

Tulosten arviointi tehtiin z-arvon avulla, joka laskettiin etukäteen asetetun kokonaishajonnan tavoitearvon avulla. Tavoitehajontaa asetettaessa otettiin huomioon mittaussuureen pitoisuus, vertailuarvon mittausepävarmuus sekä näytteen homogeenisuustestin tulokset. Tulosten arviointia ei tehty, jos mittaussuureen vertailuarvon mittausepävarmuus oli yli 25 % tai jos epävarmuutta ei voitu laskea.

Synteettisen näytteen PCB -tuloksista 84 % oli hyväksyttäviä, PBDE -tuloksista 92 % ja PCDD/PCDF -tuloksista 94 %, kun tuloksissa sallittiin 20 % poikkeama vertailuarvosta. Sedimenttinäytteen PCB -tuloksista 86 % oli hyväksyttäviä, kun tuloksissa sallittiin PCB-kongeneerista riippuen 30–50 % poikkeama vertailuarvosta. Sedimenttinäytteen PBDE- ja PCDD/PCDF -tulosten arviointia ei voitu tehdä vähäisen osallistujamäärän vuoksi. Yhteensä tässä pätevyyskokeessa arvioiduista tuloksista oli hyväksyttäviä 86 %.

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APPENDIX 1. PARTICIPANTS IN THE PROFICIENCY TEST SYKE 5/2007

Alcontrol Ab, Lidköping, Sweden

Ekokem Oy Ab, Riihimäki, Finland

Eurofins Miljö A/S, Vallensbak Strand, Denmark

Jyväskylän yliopisto, Ympäristöntutkimuskeskus, Jyväskylä, Finland

Kansanterveyslaitos, Kuopio, Finland

Novalab Oy, Karkkila, Finland

Oy Keskuslaboratorio – Centrallaboratorium Ab, Espoo, Finland

Ramboll Analytics Oy, Hollola, Finland

SGS Belgium NV, Belgium

SGS Inspection Services Oy, Hamina, Finland

Suomen ympäristökeskus (SYKE), laboratorio, Helsinki, Finland

APPENDIX 2. PREPARATION OF THE SAMPLES

Sample S1 PCBs

Individual stock solutions

1. PCB 52: 69,4 µg/mL in isooctane
2. PCB 101: 20,0 µg/mL in isooctane
3. PCB 153: 167,7 µg/mL in isooctane
4. PCB 180: 83,7 µg/mL in isooctane

Stock solution PCB Mix 4: 0,5 mL of the individual stock solutions PCB 52 (1), PCB 101 (2), PCB 153 (3) and PCB 180 (4) were mixed.

Stock solution PCB Mix 20: Dr. Ehrenstorfer certificated PCB Mix 20 in isooctane

Preparation step 1: 0,782 g of PCB Mix 20, 0,714 g of PCB Mix 4 and 15,697 g of isooctane were mixed
Preparation step 2: 0,891 g of the solution from the step 1 and 27,013 g isooctane were mixed

Compound	Concentration in stock solution PCB Mix 4 µg/mL	Concentration in stock solution PCB Mix 20 µg/mL	Final concentration in the sample S1, ng/mL
PCB 28		10,0	14,54
PCB 31		10,0	14,54
PCB 52	17,23	10,0	37,39
PCB 77		10,0	14,54
PCB 101	5,00	10,0	21,16
PCB 105		10,0	14,54
PCB 118		10,0	14,54
PCB 126		10,0	14,54
PCB 128		10,0	14,54
PCB 138		10,0	14,54
PCB 153	41,64	10,0	69,76
PCB 156		10,0	14,54
PCB 169		10,0	14,54
PCB 170		10,0	14,54
PCB 180	21,26	10,0	42,73

Sample S2 PBDEs

Stock solution: Wellington certificated BDE-MXD Brominated diphenyl ethers in nonane.
Preparation: 1,1506 g of the stock solution and 21,239 g of nonane were mixed

Compound	Concentration in stock solution, µg/mL	Final concentration in the sample S2 ng/mL
BDE 17, BDE 47, BDE 66, BDE 100, BDE 153, BDE 183	5	257
BDE 209	10	514

Sample S3 PCDDs/PCDFs

Stock solution: Wellington certificated EPA-8290STN PCDD/PCDF in nonane.
Preparation: 0,4027 g of the stock solution and 18,83 g of nonane were mixed

Compound	**Concentration in stock solution, µg/mL**	**Final concentration in the sample S3, ng/mL**
2378-TCDD, 2378-TCDF	1,0	20,94
12378-PeCDD, 123478-HxCDD, 123678-HxCDD, 123789-HxCDD, 1234678.HpCDD, 12378-PeCDF, 23478-PeCDF, 123478-HxCDF, 123678-HxCDF, 123789-HxCDF, 234678-HxCDF, 1234678-HpCDF, 123789-HpCDF,	2,5	52,34
OCDD, OCDF	5,0	104,68

Sample M1

The polluted sediment taken from the bottom of a river close to Helsinki. The sediment was dried at room temperature and sieved through a 0.250 µm sieve. The dried and sieved sample was mixed by a mechanized sample mixer and distributed in sub samples of 60 g using a rotary sample divider equipped with vibratory sample feeder.

APPENDIX 3. TESTING OF HOMOGENEITY

Sediment sample S1	Conc. µg/kg	s_t%	s_t	s_a	s_a/s_t	Was s_a/s_t<0.5?	s_{bb}	s_{bb}^2	c	Was s_{bb}^2<c?
PCB 101	1,049	15	0,157	0,062	0,394	yes	0,029	0,001	0,009	yes
PCB 153	2,801	15	0,420	0,130	0,309	yes	0,057	0,003	0,053	yes
PCB 180	2,215	15	0,332	0,081	0,243	yes	0,065	0,004	0,028	yes

Conc. = Concentration

s_t = target deviation, total target deviation/2

s_t% = target deviation as percent, total target deviation/2

s_a = analytical deviation, mean standard deviation of results in a sub sample

s_{bb} = between-sample deviation, standard deviation of results between sub samples

$c = F1 \bullet s_{all}^2 + F2 \bullet s_a^2$
where:

$s_{all}^2 = (0,3s_t)^2$
F1 = 2,01 when the number of sub samples is 8
F2 = 1,25 when the number of sub samples is 8

Conclution: In each case $s_a/s_{ta}<0.5$ and $s_{bb}^2 < c$. The samples were homogenous.

APPENDIX 4. COMMENTS SENT BY THE PARTICIPANTS

Lab	Comment	Action/SYKE
2	Lab usually determinates PCB congeners 28, 52, 101, 118, 153, 138 and 180	
9	The reported HpCDD1234678 results 0,0263 and 0,0351 µg/kg but in the preliminary lists the results were 0,0263 and 0,437 µg/l.	The mistake was corrected before the final result treatment.
7	Laboratory reweighed the sample S1 18 September and the loss of the weight was ca. 1 %.	This means ca. 1 % change in the concentration.

APPENDIX 5.1 ANALYTICAL METHODS FOR PCBs

Analytical Methods for PCBs, GC-ECD conditions							
Lab	**Extraction - method - solvent - volume - time - temperature**	**Clean-up**	**Injection - mode - volume - temperature**	**Mobile phase Flow rate**	**Oven temperature program**	**MS conditions - instrument - ionization mode - resolution - monitored ions**	**Calibration - internal standard - range - calibration points - curve fitting - weighting mode**
1	Ultrasonication Acetone, hexane 3 x 100 mL 60 min Cool ca. 4 °C	H_2SO_4 TBA sulphide	Split/splitless 1 µL 270 °C	Helium 1 mL/min	90 °C 20min, 3 min, 30 °C/min ->215 °C, 42 min, 5 °C/min -> 270 °C, 10 min	PCB 53 and TeCN 0,23 - 26 ng/mL 4 points Quatratic	ISO 10382
2	Shaking Acetone, hexane 2 x 50 mL 2 x 60 min 23 °C	H_2SO_4 Silica TBA sulphide	Splitless 1 µL 280 °C	Helium 1,3 mL/min	50 °C 1 min, 40 °C/min ->168 °C, 4 °C/min -> 310 °C	PCB 209 10 – 300 ng/mL 3 points Linear Equal	ISO 10382
3	Ultrasonic Acetone, hexane 10 + 5 mL 30 min 20 - 30 °C	H_2SO_4 Silica TBA sulphide	Split/splitless 1 µL 300 °C	Helium 1 mL/min	50 °C 2 min, 20 °C/min ->160 °C, 5 °C/min -> 310 °C, 2 min	PCB 204 0 – 100 ng/mL 2 points Linear	ISO 10382
6	Soxhlet KHO, EtOH (2 %) 50 mL 60 min Boiling	SPE, C18, with Hexane	On-column 1 µL 50 °C	Helium 4,3 mL/min	50 °C 20min, 30 °C/min ->160 °C, 4 °C/min -> 250 °C, 10 °C/min -> 300 °C, 5 min	PCB 30 - 1 point Linear, origin included Equal	ISO 15318
8	Shaking Acetone, hexane 30 mL 16 hrs 15 - 25 °C		PTV Splitless, 2 µL	Nitrogen 0,9 mL/min	60 °C 0,4 min, 40 °C/min ->90 °C, 2 min, 40 °C/min -> 150 °C, 5 °C/min -> 280 °C Post temp 320 °C 2 min	PCB 53 (2, 2',5,6'TeCB) 1-50 ng/mL 5 points	SNVs report 3829

Analytical Methods for PCBs, GC-MS conditions

Lab	Extraction - method - solvent - volume - time - temperature	Clean-up	Injection - mode - volume - temperature	Mobile phase Flow rate	Oven temperature program	MS conditions - instrument - ionization mode - resolution - monitored ions	Calibration - internal standard - range - calibration points - curve fitting - weighting mode	Reference
5	Soxhlet Toluene 250 mL 24 hrs	Mixed silica layer column Alumina column	Split/splitless 1 µL 280 °C	Helium 1 mL/min	Confedential	Waters Autospec Ultima Electron ionization 10 000 amu	^{13}C-labelled congeners 0,1 – 800 ng/mL 7 points	EPA 1668 and
7	Shaking Acetone, hexane 30 mL 16 hrs 15 - 25 °C	Al_2O_3	Splitless 2 µL 250 °C	Helium 1 mL/min	150 °C 0,5 min, 12 °C/min ->190 °C, 2 min, 10 °C/min -> 290 °C, 3 min	HP 5973 GC/MSD Electron ionization High	No 5 – 1000 ng/mL 6 points	Nordtest TC 329
9	ASE Toluene 10 ml Shaking 16 hrs Ambient	Florisil H_2SO_4	Spitless 1 µL 270 °C	Helium 0,7 mL/min	80 °C 1 min, 15 °C/min ->220 °C, 2 °C/min -> 270 °C, 30 °C/min -> 320 °C, 5 °C	Agilent 5973N Electron ionization	^{13}C-labelled congeners 0 – 1000 ng/mL 6 points Linear	
10	Soxhlet Ethanol, toluene 300 mL 20 hrs		Spitless 2 µL 270 °C	Helium 1 mL/min	60 °C 3 min, 20 °C/min ->200 °C, 4 °C/min -> 270 °C, 14 °C	VG 70-250 SE Electron ionization 10 000 amu	PCB 30 ^{13}C-labelled congeners - 1 point	

APPENDIX 5.2 ANALYTICAL METHODS FOR PBDEs

Analytical Methods for PBDEs, GC-MS conditions								
Lab	**Extraction - method - solvent - volume - time - temperature**	**Clean-up**	**Injection - mode - volume - temperature**	**Mobile phase Flow rate**	**Oven temperature program**	**MS conditions - instrument - ionization mode - resolution - monitored ions**	**Calibration - internal standard - range - calibration points - curve fitting - weighting mode**	**Reference**
1	ASE Dichloromethane 3 x 10 min 100 °C	Multilayer column: Acidic silica Basic silica $AgNO_3$ silica	PTV Splitless 1 µl Temp. program: Int. 100 °C 200 °C/min ->300 °C	Helium 1,2 mL/min	120 °C 2 min, 15 °C/min ->250 °C, 12.5 °C/min -> 320 °C, 4.5 min	Varian triple quadrupole 1200L Electron ionization Unit resolution MS/MS technique	^{13}C-labelled congeners 0,2 – 2000 ng/mL 10 points Linear 1/nx	Partially ISO 22032
5	Soxhlet Toluene 250 mL 24 hrs	Silica Alumina	Split/splitless 1 µL 280 °C	Helium 1 mL/min	Confidential	Waters Autospec Ultima Electron ionization 10 000 amu	^{13}C-labelled congeners 0,1 – 500 ng/mL 6 points	Based on EPA 1613
9	ASE Acetone, hexane 2 x 10 min 150 °C		Splitless 1 µL 270 °C	Helium 0,7 mL/min	120 °C 3 min, 15 °C/min ->280 °C, 3 min 10 °C/min -> 320 °C, 10 min	HP5973 Electron ionization	^{13}C-labelled congeners 0 – 400 4 points Linear	
10	Soxhlet Ethanol, toluene 300 mL 20 hrs		Splitless 2 µL 300 °C except BDE209: 130 °C	Helium 1 mL/min	100 °C 3 min, 25 °C/min ->240 °C, 4 °C/min -> 300 °C, 25 min BDE209: 100 °C, 1 min, 40 °C/min ->300 °C, 7 min	Autospec Ultima GC-MS Electron ionization 10 000 amu	^{13}C-labelled congeners - 1 point	

APPENDIX 5.3 ANALYTICAL METHODS FOR PCDDs/PCDFs

Analytical Methods for PCDD/PCDFs, GC-ECD conditions								
Lab	**Extraction** **- solvent** **- volume** **- method** **- time** **- temperature**	**Clean-up**	**Injection** **- mode** **- volume** **- temperature**	**Mobile phase** **Flow rate**	**Oven temperature program**	**MS conditions** **- instrument** **- ionization mode** **- resolution** **- monitored ions**	**Calibration** **- internal standard** **- range** **- calibration points** **- curve fitting** **- weighting mode**	**Reference**
5	Toluene 250 mL Soxhlet 24 hrs	Silica Alumina	Split/splitless 1 µL 280 °C	Helium 1 mL/min	Confidential	Waters Autospec Ultima Electron ionization 10 000 amu	^{13}C-labelled congeners 5 – 200 ng/mL 5 points	
9	Toluene ASE 2 x 10 min 190 °C	Acidified silica H_2SO_4 Al_2O_3 Carbon column	Splitless, pulsed 2 µL 300 °C	Helium 0,7 mL/min	180 °C 2 min, 3 °C/min ->280 °C 20 min, 30 °C/min -> 320 °C, 5 min	Agilent 5973N Electron ionization	^{13}C-labelled congeners 5 – 400 ng/mL 3 points Isotope dilution	
10	Ethanol, toluene 300 mL Soxhlet 21 hrs		Splitless 2 µL 270 °C	Helium 1 mL/min	140 °C 4 min, 20 °C/min ->180 °C, 2 °C/min -> 270 °C, 36 min	VG 70-250 SE Electron ionization 10 000 amu ^{13}C-labelled congeners	^{13}C-labelled congeners - 1 point	

APPENDIX 6. ASSIGNED VALUES AND THEIR UNCERTAINTIES

The samples S1, S2 S3 and M1:

Analyte	Sample	Unit	Assigned value */Indicative assigned value*	Estimation of assigned value	Uncertainty ($U = 2\ u_c$) %
PCB 28	S1	ng/mL	14,54	Calculated	1,0
	M1	*µg/kg*	*0,16*	*Robust mean*	*55*
PCB 31	S1	ng/mL	14,54	Calculated	1,0
	M1	*µg/kg*	*0,1*	*Robust mean*	-
PCB 52	S1	ng/mL	37,39	Calculated	3,1
	M1	µg/kg	0,28	Robust mean	20
PCB 77	S1	ng/mL	14,54	Calculated	1,0
	M1	-	-	-	
PCB 101	S1	ng/mL	21,16	Calculated	3,1
	M1	µg/kg	1,19	Robust mean	6,4
PCB 105	S1	ng/mL	14,54	Calculated	1,0
	M1	*µg/kg*	*0,12*	-	-
PCB 118	S1	ng/mL	14,54	Calculated	1,0
	M1	µg/kg	0,54	Robust mean	14
PCB 126	S1	ng/mL	14,54	Calculated	1,0
	M1	*µg/kg*	*0,15*	-	-
PCB 128	S1	ng/mL	14,54	Calculated	1,0
	M1	-	-	-	-
PCB 138	S1	ng/mL	14,54	Calculated	1,0
	M1	µg/kg	2,56	Robust mean	23
PCB 153	S1	ng/mL	69,76	Calculated	3,1
	M1	µg/kg	3,17	Robust mean	8,5
PCB 156	S1	ng/mL	14,54	Calculated	1,0
	M1	*µg/kg*	*0,25*	*Robust mean*	-
PCB 169	S1	ng/mL	14,54	Calculated	1,0
	M1	*µg/kg*	*0,81*	-	-
PCB 170	S1	ng/mL	14,54	Calculated	1,0
	M1	*µg/kg*	*1,08*	-	-
PCB 180	S1	ng/mL	42,73	Calculated	3,1
	M1	µg/kg	2,37	Robust mean	9,0
BDE 17	S2	ng/mL	257	Calculated	5,0
	M1	*µg/kg*	*0,045*	-	-
BDE 47	S2	ng/mL	257	Calculated	5,0
	M1	*µg/kg*	*0,12*	*Robust mean*	*18*
BDE 66	S2	ng/mL	257	Calculated	5,0
	M1	*µg/kg*	*0,032*	-	
BDE 99	S2	ng/mL	257	Calculated	5,0
	M1	*µg/kg*	*0,21*	-	
BDE 100	S2	ng/mL	257	Calculated	5,0
	M1	*µg/kg*	*0,045*	*Robust mean*	*50*
BDE 153	S2	ng/mL	257	Calculated	5,0
	M1	*µg/kg*	*0,096*	*Robust mean*	*46*
BDE 183	S2	ng/mL	257	Calculated	5,0
	M1	µg/kg	-	-	-
BDE 209	S2	ng/mL	514	Calculated	5,0
	M1	*µg/kg*	*5,49*	*Robust mean*	*17*

Analyte	Sample	Unit	Assigned value	Estimation of assigned value	Uncertainty ($U = 2\ u_c$) %
2378-TCDD	S3	ng/mL	20,94	Calculated	5,0
	M1	ng/kg			
2378-TCDF	S3	ng/mL	20,94	Calculated	5,0
	M1	ng/kg			
12378-PeCDD	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
123478-HxCDD	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
123678-HxCDD	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
123789-HxCDD	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
1234678.HpCDD	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
12378-PeCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
23478-PeCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
123478-HxCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
123678-HxCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
123789-HxCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
234678-HxCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
1234678-HpCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
123789-HpCDF	S3	ng/mL	52,34	Calculated	5,0
	M1	ng/kg			
OCDD	S3	ng/mL	104,68	Calculated	5,0
	M1	ng/kg			
OCDF	S3	ng/mL	104,68	Calculated	5,0
	M1	ng/kg			

If the assigned value was calculated its uncertainty was estimated on the basis of the sample preparation.

Otherwise $U\% = 100*(2*1,25*s_{rob}/\sqrt{n})/AV$

where:

s_{rob} = robust standard deviation

n = number of the results

AV = Assigned value (*Indicative assigned value printed in Italics)*

LIITE 7.1.

Appendix 7.1. Results of each participant, PCBs and PBDEs

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	Robust mean	SD%	SD% rob	Num of labs
Laboratory 1														
BDE100	µg/kg	M1			yes	0,045		0,035	0,0475	0,04525	0,045	27,6	31,3	3
	ng/ml	S2		-0,450	yes	257	20	245,5	244	247,3	245,949	5,6	5,27	4
BDE153	µg/kg	M1			yes	0,096		0,115	0,095	0,09575	0,096	23,7	26,9	3
	ng/ml	S2		-0,430	yes	257	20	246	245,5	240,7	249,105	4,8	8,38	4
BDE17	µg/kg	M1			yes			0,025	0,025	0,025	0,025	28,2	32,0	1
	ng/ml	S2		-0,370	yes	257	20	247,5	247,5	247,5	247,5	6	6,80	1
BDE183	µg/kg	M1			yes			0,04	0,04	0,04	0,04	0	0	3
	ng/ml	S2		-0,580	yes	257	20	242	239	248,5	241,921	8,6	4,74	4
BDE209	µg/kg	M1			yes	5,49		3,405	5,63	5,003	5,489	25,5	10,7	3
	ng/ml	S2		6,200	H	514	20	830,5	514,5	508,3	519,602	2,3	4,30	3
BDE28	µg/kg	M1			yes			0,02	0,02	0,02	0,02	0	0	2
BDE47	µg/kg	M1			yes	0,12		0,035	0,116	0,1004	0,115	41,1	14,0	4
	ng/ml	S2		0,000	yes	257	20	257	240,5	242,3	241,462	4,1	4,05	4
BDE66	µg/kg	M1			yes	0,032		0,05	0,0325	0,03225	0,032	63,5	72,0	2
	ng/ml	S2		-0,820	yes	257	20	236	234,5	234,5	234,5	1,8	1,99	3
BDE99	µg/kg	M1			yes	0,21		0,105	0,2165	0,2133	0,216	37,0	38,6	4
PCB101	µg/kg	M1		-0,310	yes	1,19	30	1,134	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		0,095	yes	21,16	20	21,36	21,44	21,42	21,475	10,5	8,81	8
PCB105	µg/kg	M1			yes	0,12		0,18	0,126	0,1225	0,122	55,3	62,7	3
	ng/ml	S1		-0,330	yes	14,54	20	14,06	14,06	14,53	13,676	3,8	11,5	3
PCB118	µg/kg	M1		0,056	yes	0,54	30	0,5445	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		0,930	yes	14,54	20	15,89	14,25	13,87	13,926	16,3	13,6	9
PCB128	ng/ml	S1		-0,400	yes	14,54	20	13,96	14,09	14,23	14,118	3,8	2,63	2
PCB138	µg/kg	M1		-0,160	yes	2,56	50	2,457	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		-0,320	yes	14,54	20	14,07	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		0,036	yes	3,17	30	3,187	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		0,140	yes	69,76	20	70,75	70,44	68,81	68,996	14,6	12,6	8
PCB156	µg/kg	M1			yes	0,25		0,172	0,225	0,2332	0,219	35,4	25,3	4
	ng/ml	S1		-0,093	yes	14,54	20	14,41	14,82	14,25	14,621	9,2	5,00	4
PCB170	µg/kg	M1			yes	1,08		1,081	1,081	1,078	1,078	14,8	16,7	2
	ng/ml	S1		-1,300	yes	14,54	20	12,71	13,41	13,61	13,597	8,2	9,12	2
PCB180	µg/kg	M1		0,470	yes	2,37	30	2,535	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		-0,049	yes	42,73	20	42,52	39,6	39,09	39,034	19,5	21,8	9
PCB28	µg/kg	M1			yes	0,16		0,1965	0,1535	0,1837	0,167	60,1	53,1	6
	ng/ml	S1		-0,250	yes	14,54	20	14,17	14	13,15	13,207	17,2	18,7	7
PCB31	µg/kg	M1			yes	0,1		0,109	0,109	0,1047	0,108	20,5	15,8	2
	ng/ml	S1		-1,800	yes	14,54	20	11,95	10,52	10,41	10,412	17,1	19,4	2
PCB52	µg/kg	M1		-0,840	yes	0,28	50	0,221	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		-0,005	yes	37,39	20	37,37	37,1	36,38	36,18	10,4	9,67	9
PCB77	ng/ml	S1		-0,480	yes	14,54	20	13,84	14,4	14,43	14,43	4,2	4,70	3
Laboratory 2														
PCB101	µg/kg	M1		0,056	yes	1,19	30	1,2	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		-1,000	yes	21,16	20	19,05	21,44	21,42	21,475	10,5	8,81	8
PCB118	µg/kg	M1				0,54	30	<1,0	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		-1,500	yes	14,54	20	12,4	14,25	13,87	13,926	16,3	13,6	9
PCB138	µg/kg	M1		0,530	yes	2,56	50	2,9	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		-1,700	yes	14,54	20	12	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		-0,150	yes	3,17	30	3,1	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		-0,690	yes	69,76	20	64,95	70,44	68,81	68,996	14,6	12,6	8
PCB180	µg/kg	M1		-0,200	yes	2,37	30	2,3	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		-1,300	yes	42,73	20	37,15	39,6	39,09	39,034	19,5	21,8	9
PCB28	µg/kg	M1				0,16		<1,0	0,1535	0,1837	0,167	60,1	53,1	6
	ng/ml	S1		-1,600	yes	14,54	20	12,25	14	13,15	13,207	17,2	18,7	7
PCB52	µg/kg	M1				0,28	50	<1,0	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		-0,850	yes	37,39	20	34,2	37,1	36,38	36,18	10,4	9,67	9

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	Robust mean	SD%	SD% rob	Num of labs
Laboratory 3														
PCB101	µg/kg	M1		0,620	yes	1,19	30	1,3	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		0,400	yes	21,16	20	22	21,44	21,42	21,475	10,5	8,81	8
PCB118	µg/kg	M1				0,54	30	<1	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		-0,028	yes	14,54	20	14,5	14,25	13,87	13,926	16,3	13,6	9
PCB138	µg/kg	M1		-0,950	yes	2,56	50	1,95	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		-1,400	yes	14,54	20	12,5	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		-0,780	yes	3,17	30	2,8	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		-1,300	yes	69,76	20	61	70,44	68,81	68,996	14,6	12,6	8
PCB180	µg/kg	M1		-1,000	yes	2,37	30	2	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		-2,200	yes	42,73	20	33,5	39,6	39,09	39,034	19,5	21,8	9
PCB28	µg/kg	M1				0,16		<1	0,1535	0,1837	0,167	60,1	53,1	6
	ng/ml	S1		0,320	yes	14,54	20	15	14	13,15	13,207	17,2	18,7	7
PCB52	µg/kg	M1				0,28	50	<1	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		-0,100	yes	37,39	20	37	37,1	36,38	36,18	10,4	9,67	9
Laboratory 4														
PCB105	µg/kg	M1				0,12		<0,2	0,126	0,1225	0,122	55,3	62,7	3
	ng/ml	S1		-3,800	H	14,54	20	9,044	14,06	14,53	13,676	3,8	11,5	3
PCB118	µg/kg	M1		-1,000	yes	0,54	30	0,459	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		-3,900	yes	14,54	20	8,92	14,25	13,87	13,926	16,3	13,6	9
PCB138	µg/kg	M1		-3,200	yes	2,56	50	0,484	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		-3,500	yes	14,54	20	9,48	13,05	12,83	12,842	16,6	16,7	9
PCB156	µg/kg	M1				0,25		<0,1	0,225	0,2332	0,219	35,4	25,3	4
	ng/ml	S1		-1,500	yes	14,54	20	12,29	14,82	14,25	14,621	9,2	5,00	4
PCB180	µg/kg	M1		-5,700	H	2,37	30	0,328	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		-3,300	yes	42,73	20	28,84	39,6	39,09	39,034	19,5	21,8	9
PCB28	µg/kg	M1			yes	0,16		0,09815	0,1535	0,1837	0,167	60,1	53,1	6
	ng/ml	S1		-2,900	yes	14,54	20	10,29	14	13,15	13,207	17,2	18,7	7
PCB31	µg/kg	M1			yes	0,1		0,1004	0,109	0,1047	0,108	20,5	15,8	2
	ng/ml	S1		-3,900	yes	14,54	20	8,88	10,52	10,41	10,412	17,1	19,4	2
PCB52	µg/kg	M1				0,28	50	<0,2	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		-3,400	H	37,39	20	24,71	37,1	36,38	36,18	10,4	9,67	9
Laboratory 5														
BDE100	µg/kg	M1				0,045		<0,0999	0,0475	0,04525	0,045	27,6	31,3	3
	ng/ml	S2		0,390	yes	257	20	267	244	247,3	245,949	5,6	5,27	4
BDE153	µg/kg	M1				0,096		<0,0999	0,095	0,09575	0,096	23,7	26,9	3
	ng/ml	S2		-0,450	yes	257	20	245,5	245,5	240,7	249,105	4,8	8,38	4
BDE183	µg/kg	M1						<0,0999	0,04	0,04	0,04	0	0	3
	ng/ml	S2		-0,910	yes	257	20	233,5	239	248,5	241,921	8,6	4,74	4
BDE209	µg/kg	M1			yes	5,49		5,63	5,63	5,003	5,489	25,5	10,7	3
	ng/ml	S2		-0,220	yes	514	20	502,5	514,5	508,3	519,602	2,3	4,30	3
BDE28	µg/kg	M1						<0,0999	0,02	0,02	0,02	0	0	2
	ng/ml	S2					20	<20	9,401E-		0,02		0	1
BDE47	µg/kg	M1			yes	0,12		0,1145	0,116	0,1004	0,115	41,1	14,0	4
	ng/ml	S2		-0,720	yes	257	20	238,5	240,5	242,3	241,462	4,1	4,05	4
BDE99	µg/kg	M1			yes	0,21		0,213	0,2165	0,2133	0,216	37,0	38,6	4
	ng/ml	S2						<20	3,2	3,2	3,2	0	0	2
PCB101	µg/kg	M1		-0,640	yes	1,19	30	1,075	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		-0,380	yes	21,16	20	20,35	21,44	21,42	21,475	10,5	8,81	8
PCB118	µg/kg	M1		0,890	yes	0,54	30	0,612	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		-0,200	yes	14,54	20	14,25	14,25	13,87	13,926	16,3	13,6	9
PCB126	µg/kg	M1			yes	0,15		0,0092	0,0092	0,1061	0,009	158,	0	2
	ng/ml	S1		-0,062	yes	14,54	20	14,45	14,75	14,97	14,829	4,9	3,60	2
PCB138	µg/kg	M1		-1,500	yes	2,56	50	1,625	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		-1,600	yes	14,54	20	12,15	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		0,500	yes	3,17	30	3,41	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		-0,600	yes	69,76	20	65,55	70,44	68,81	68,996	14,6	12,6	8
PCB156	µg/kg	M1			yes	0,25		0,226	0,225	0,2332	0,219	35,4	25,3	4
	ng/ml	S1		0,520	yes	14,54	20	15,3	14,82	14,25	14,621	9,2	5,00	4
PCB169	µg/kg	M1			yes	0,81		0,0013	0,7957	0,8132	0,813	115,	130,	2
	ng/ml	S1		0,210	yes	14,54	20	14,85	14,95	15,18	14,968	3,7	1,20	2
PCB180	µg/kg	M1		0,028	yes	2,37	30	2,38	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		-0,920	yes	42,73	20	38,8	39,6	39,09	39,034	19,5	21,8	9
PCB52	µg/kg	M1		1,300	yes	0,28	50	0,3735	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		-0,770	yes	37,39	20	34,5	37,1	36,38	36,18	10,4	9,67	9
PCB77	µg/kg	M1			yes			0,073	0,073	0,073	0,073	0	0	1
	ng/ml	S1		0,280	yes	14,54	20	14,95	14,4	14,43	14,43	4,2	4,70	3

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	Robust mean	SD%	SD% rob	Num of labs
Laboratory 7														
PCB101	µg/kg	M1		-0,140	yes	1,19	30	1,165	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		1,800	yes	21,16	20	25	21,44	21,42	21,475	10,5	8,81	8
PCB105	µg/kg	M1			yes	0,12		0,065	0,126	0,1225	0,122	55,3	62,7	3
	ng/ml	S1		0,320	yes	14,54	20	15	14,06	14,53	13,676	3,8	11,5	3
PCB118	µg/kg	M1		-0,310	yes	0,54	30	0,515	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		0,660	yes	14,54	20	15,5	14,25	13,87	13,926	16,3	13,6	9
PCB126	µg/kg	M1			yes	0,15		0,30	0,0092	0,1061	0,009	158,	0	2
	ng/ml	S1		0,660	yes	14,54	20	15,5	14,75	14,97	14,829	4,9	3,60	2
PCB128	µg/kg	M1			yes			0,875	0,875	0,875	0,875	5,7	6,41	1
	ng/ml	S1		-0,028	yes	14,54	20	14,5	14,09	14,23	14,118	3,8	2,63	2
PCB138	µg/kg	M1		1,800	yes	2,56	50	3,69	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		1,000	yes	14,54	20	16	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		1,100	yes	3,17	30	3,68	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		2,400	yes	69,76	20	86,5	70,44	68,81	68,996	14,6	12,6	8
PCB156	µg/kg	M1			yes	0,25		0,37	0,225	0,2332	0,219	35,4	25,3	4
	ng/ml	S1		0,320	yes	14,54	20	15	14,82	14,25	14,621	9,2	5,00	4
PCB169	µg/kg	M1			yes	0,81		1,625	0,7957	0,8132	0,813	115,	130,	2
	ng/ml	S1		0,660	yes	14,54	20	15,5	14,95	15,18	14,968	3,7	1,20	2
PCB170	µg/kg	M1			yes	1,08		1,075	1,081	1,078	1,078	14,8	16,7	2
	ng/ml	S1		-0,028	yes	14,54	20	14,5	13,41	13,61	13,597	8,2	9,12	2
PCB180	µg/kg	M1		1,000	yes	2,37	30	2,725	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		1,600	yes	42,73	20	49,5	39,6	39,09	39,034	19,5	21,8	9
PCB28	µg/kg	M1			yes	0,16		0,34	0,1535	0,1837	0,167	60,1	53,1	6
	ng/ml	S1		-0,028	yes	14,54	20	14,5	14	13,15	13,207	17,2	18,7	7
PCB52	µg/kg	M1		39,000	H	0,28	50	3	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		1,100	yes	37,39	20	41,5	37,1	36,38	36,18	10,4	9,67	9
PCB77	ng/ml	S1		-0,028	yes	14,54	20	14,5	14,4	14,43	14,43	4,2	4,70	3
Laboratory 8														
PCB101	µg/kg	M1		1,200	yes	1,19	30	1,4	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		-1,300	yes	21,16	20	18,35	21,44	21,42	21,475	10,5	8,81	8
PCB118	µg/kg	M1		-1,100	yes	0,54	30	0,45	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		-4,200	H	14,54	20	8,365	14,25	13,87	13,926	16,3	13,6	9
PCB138	µg/kg	M1		1,000	yes	2,56	50	3,2	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		-2,700	yes	14,54	20	10,55	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		0,270	yes	3,17	30	3,3	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		-2,400	yes	69,76	20	52,89	70,44	68,81	68,996	14,6	12,6	8
PCB180	µg/kg	M1		-0,620	yes	2,37	30	2,15	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		-3,000	yes	42,73	20	29,77	39,6	39,09	39,034	19,5	21,8	9
PCB28	µg/kg	M1			yes	0,16		0,1	0,1535	0,1837	0,167	60,1	53,1	6
	ng/ml	S1		-3,000	yes	14,54	20	10,18	14	13,15	13,207	17,2	18,7	7
PCB52	µg/kg	M1		-4,000	M	0,28	50	0	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		-2,100	yes	37,39	20	29,39	37,1	36,38	36,18	10,4	9,67	9
Laboratory 9														
BDE100	ng/ml	S2		-0,950	yes	257	20	232,5	244	247,3	245,949	5,6	5,27	4
BDE153	ng/ml	S2		-1,000	yes	257	20	230,5	245,5	240,7	249,105	4,8	8,38	4
BDE183	ng/ml	S2		-0,800	yes	257	20	236,5	239	248,5	241,921	8,6	4,74	4
BDE47	µg/kg	M1			yes	0,12		0,118	0,116	0,1004	0,115	41,1	14,0	4
	ng/ml	S2		-0,970	yes	257	20	232	240,5	242,3	241,462	4,1	4,05	4
BDE66	ng/ml	S2		-1,100	yes	257	20	230	234,5	234,5	234,5	1,8	1,99	3
BDE99	µg/kg	M1			yes	0,21		0,2255	0,2165	0,2133	0,216	37,0	38,6	4
PCB101	µg/kg	M1		-0,220	yes	1,19	30	1,15	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		0,280	yes	21,16	20	21,75	21,44	21,42	21,475	10,5	8,81	8
PCB118	ng/ml	S1		-0,340	yes	14,54	20	14,05	14,25	13,87	13,926	16,3	13,6	9
PCB138	µg/kg	M1		-0,410	yes	2,56	50	2,3	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		0,520	yes	14,54	20	15,3	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		-0,670	yes	3,17	30	2,85	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		0,690	yes	69,76	20	74,55	70,44	68,81	68,996	14,6	12,6	8
PCB180	µg/kg	M1		-0,056	yes	2,37	30	2,35	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		-0,230	yes	42,73	20	41,75	39,6	39,09	39,034	19,5	21,8	9
PCB28	ng/ml	S1		0,760	yes	14,54	20	15,65	14	13,15	13,207	17,2	18,7	7
PCB52	ng/ml	S1		0,300	yes	37,39	20	38,5	37,1	36,38	36,18	10,4	9,67	9

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	Robust mean	SD%	SD% rob	Num of labs
Laboratory 10														
BDE100	µg/kg	M1			yes	0,045		0,0555	0,0475	0,04525	0,045	27,6	31,3	3
	ng/ml	S2		-0,510	yes	257	20	244	244	247,3	245,949	5,6	5,27	4
BDE153	µg/kg	M1			yes	0,096		0,0765	0,095	0,09575	0,096	23,7	26,9	3
	ng/ml	S2		3,200	H	257	20	339	245,5	240,7	249,105	4,8	8,38	4
BDE183	µg/kg	M1						<0,05	0,04	0,04	0,04	0	0	3
	ng/ml	S2		0,970	yes	257	20	282	239	248,5	241,921	8,6	4,74	4
BDE209	µg/kg	M1			yes	5,49		5,975	5,63	5,003	5,489	25,5	10,7	3
	ng/ml	S2		0,000	yes	514	20	514	514,5	508,3	519,602	2,3	4,30	3
BDE47	µg/kg	M1			yes	0,12		0,134	0,116	0,1004	0,115	41,1	14,0	4
	ng/ml	S2		-0,600	yes	257	20	241,5	240,5	242,3	241,462	4,1	4,05	4
BDE66	µg/kg	M1			yes	0,032		0,0145	0,0325	0,03225	0,032	63,5	72,0	2
	ng/ml	S2		-0,760	yes	257	20	237,5	234,5	234,5	234,5	1,8	1,99	3
BDE99	µg/kg	M1			yes	0,21		0,3095	0,2165	0,2133	0,216	37,0	38,6	4
	ng/ml	S2			yes			3,2	3,2	3,2	3,2	0	0	2
PCB101	µg/kg	M1		0,250	yes	1,19	30	1,235	1,2	1,207	1,192	9,5	6,72	8
	ng/ml	S1		1,100	yes	21,16	20	23,5	21,44	21,42	21,475	10,5	8,81	8
PCB118	µg/kg	M1		1,100	yes	0,54	30	0,6295	0,5445	0,535	0,535	14,9	16,9	8
	ng/ml	S1		0,630	yes	14,54	20	15,45	14,25	13,87	13,926	16,3	13,6	9
PCB138	µg/kg	M1		-0,055	yes	2,56	50	2,525	2,457	2,348	2,425	39,0	34,4	9
	ng/ml	S1		-0,780	yes	14,54	20	13,4	13,05	12,83	12,842	16,6	16,7	9
PCB153	µg/kg	M1		-0,160	yes	3,17	30	3,095	3,111	3,178	3,172	10,3	9,25	8
	ng/ml	S1		0,650	yes	69,76	20	74,3	70,44	68,81	68,996	14,6	12,6	8
PCB180	µg/kg	M1		0,460	yes	2,37	30	2,535	2,355	2,372	2,325	10,6	13,2	9
	ng/ml	S1		1,700	yes	42,73	20	50	39,6	39,09	39,034	19,5	21,8	9
PCB52	µg/kg	M1		1,900	yes	0,28	50	0,4165	0,372	0,337	0,351	28,4	76,1	8
	ng/ml	S1		0,320	yes	37,39	20	38,6	37,1	36,38	36,18	10,4	9,67	9

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

APPENDIX 7.2. RESULTS OF EACH LABORATORY, PCDDs/PCDFs

Sample S3	Unit	Assigned value	2*TargSD %	Lab5		Lab9		Lab10		Accepted z-val%
				Result	z value	Result	z value	Result	z value	
TriCDD/CDFs										
TetraCDD/CDFs										
2,3,7,8-TCDD	ng/mL	20,94	20	18,75	-0,10	19,50	-0,07	22,00	0,05	100
2,3,7,8-TCDF		20,94	20	18,30	-1,26	18,55	-0,11	21,30	0,02	100
PentaCDD/CDFs										
1,2,3,7,8-PeCDD	ng/mL	52,34	20	49,70	-0,50	46,90	-1,04	53,25	0,17	100
1,2,3,7,8-PeCDF	ng/mL	52,34	20	46,55	-1,11	49,15	-0,61	49,55	-0,53	100
2,3,4,7,8-PeCDF	ng/mL	52,34	20	44,75	-1,45	48,50	-0,73	55,00	0,51	100
HexaCDD/CDFs										
1,2,3,4,7,8-HXCDD	ng/mL	52,34	20	49,10	-0,62	41,65	-2,04	54,25	0,36	67
1,2,3,6,7,8-HxCDD	ng/mL	52,34	20	47,70	-0,89	44,00	-1,59	53,75	0,27	100
1,2,3,7,8,9-HxCDD	ng/mL	52,34	20	58,85	1,24	40,80	-2,20	55,75	0,65	67
1,2,3,4,7,8-HxCDF	ng/mL	52,34	20	46,70	-1,08	47,60	-0,91	55,50	0,60	100
1,2,3,6,7,8-HxCDF	ng/mL	52,34	20	50,95	-0,27	48,80	-0,68	52,25	-0,02	100
2,3,4,6,7,8-HxCDF	ng/mL	52,34	20	49,75	-0,49	46,05	-1,20	56,00	0,70	100
1,2,3,7,8,9-HxCDF	ng/mL	52,34	20	47,55	-0,92	45,75	-1,26	66,25	2,66	67
HeptaCDD/CDFs										
1,2,3,4,6,7,8-HpCDD	ng/mL	52,34	20	54,70	0,45	51,55	-0,15	54,00	0,32	100
1,2,3,4,6,7,8-HpCDF	ng/mL	52,34	20	51,50	-0,16	50,90	-0,28	49,75	-0,49	100
1,2,3,4,7,8,9-HpCDF	ng/mL	52,34	20	49,75	-0,49	44,90	-1,42	60,75	1,61	100
OctaCDD/CDFs										
OCDD	ng/mL	104,68	20	96,30	-0,80	97,05	-0,73	107,50	0,27	100
OCDF	ng/mL	104,68	20	100,95	-0,36	94,40	-0,98	118,00	1,27	100
Accepted z-val%					100		88		94	

Sample M1	Unit	Lab5	Lab9	Lab10	Mean	Axys
TetraCDD/CDFs						
2,3,7,8-TCDD	ng/kg	0,088				0,19
2,3,7,8-TCDF	ng/kg	1,890		3,045	2,47	3,36
PentaCDD/CDFs						
1,2,3,7,8-PeCDD	ng/kg	0,511		1,085	0,80	0,56
1,2,3,7,8-PeCDF	ng/kg	1,055		0,730	0,89	0,93
2,3,4,7,8-PeCDF	ng/kg	1,650		1,780	1,72	1,81
HexaCDD/CDFs						
1,2,3,4,7,8-HxCDD	ng/kg	0,607		0,550	0,58	0,52
1,2,3,6,7,8-HxCDD	ng/kg	2,090		3,125	2,61	2,36
1,2,3,7,8,9-HxCDD	ng/kg	0,673		1,595	1,13	2,14
1,2,3,4,7,8-HxCDF	ng/kg	1,770		1,555	1,66	1,45
1,2,3,6,7,8-HxCDF	ng/kg	1,400		1,470	1,44	1,49
2,3,4,6,7,8-HxCDF	ng/kg	1,540		1,630	1,59	1,85
1,2,3,7,8,9-HxCDF	ng/kg	0,163				
HeptaCDD/CDFs						
1,2,3,4,6,7,8-HpCDD	ng/kg	25,50	30,70	24,40	26,9	27,0
1,2,3,4,6,7,8-HpCDF	ng/kg	45,45	45,50	47,40	46,1	46,9
1,2,3,4,7,8,9-HpCDF	ng/kg	0,841		1,205	1,02	0,92
OctaCCD/CDFs						
OCDD	ng/kg	141,0	173,50	137,5	151	155
OCDF	ng/kg	65,90	50,90	60,7	59,2	54,5

Mean = the mean of the results reported by participants
Axys = the result of Axys analytical service

APPENDIX 8. EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant

Analyte
Unit
Sample The code of the sample
z-Graphics z score - the graphical presentation
z-value z-score, calculated as follows:
$z = (x_i - X)/s$, where
x_i = the result of the individual laboratory
X = the reference value (the assigned value)
s = the target value for the deviation (s_{target}).
Outl test OK yes - the result passed the outlier test
H = Hampel test (a test for the mean value)
In addition, in robust statistics results deviating at least 50 % from the original robust mean have been rejected.
Assigned value the reference value
2* Targ SD % the target value for total deviation at 95 % confidence level
Lab's result the result reported by the participant (the mean value of the replicates)
Md. Median
Mean Mean
SD Standard deviation
SD % Standard deviation, %
Passed The results passed the outlier test
Missing i.e. < DL
Num of labs the total number of the participants

Summary on the z scores

A - accepted ($-2 \le z \le 2$)
p - questionable ($2 < z \le 3$), positive error, the result > X
n - questionable ($-3 \le z < -2$), negative error, the result < X
P - non- accepted ($z > 3$), positive error, the result >>> X
N - non- accepted ($z < -3$), negative error, the result <<< X (X = the reference value)

Robust analysis

The items of data is sorted into increasing order, $x_1, x_2, \ldots, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
$X^* =$ median of x_i $(i = 1 \ldots p)$
$s^* = 1.483$ median of $| x_i - x^* |$ $(i = 1 \ldots p)$

For each x_i is calculated:
$x_i^* = x^* - \varphi$ if $x_i < x^* - \varphi$
$x_i^* = x^* + \varphi$ if $x_i > x^* + \varphi$
$x_i^* = x_i$ otherwise

The new values of x^* and s^* are calculated from:
$X^* = \sum x_i^* / p$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

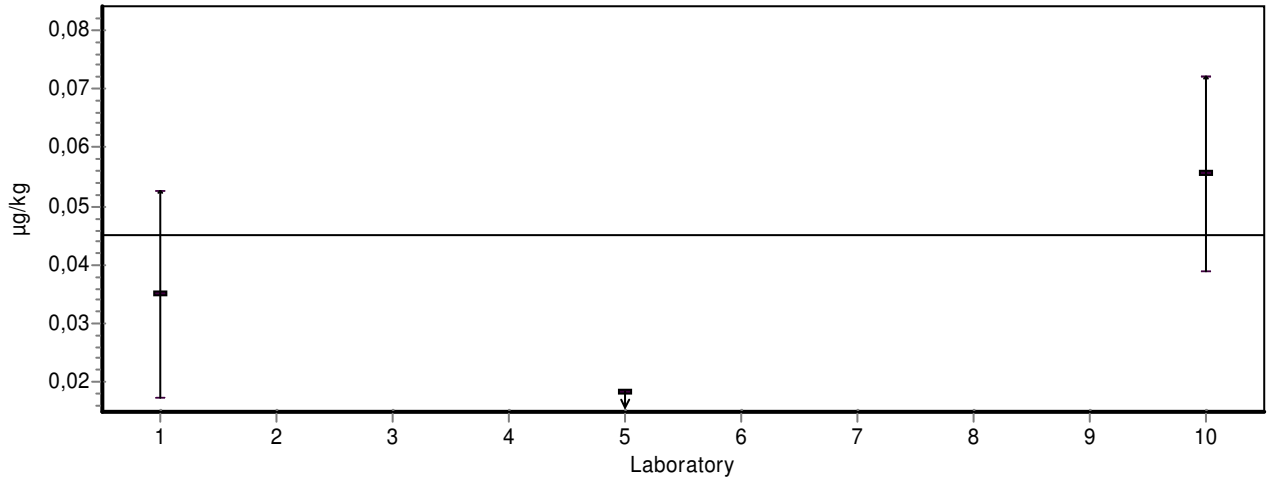
The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences.

Ref: Statistical methods for use in proficiency testing by interlaboratory comparisons, Annex C
ISO 13528 2005 [3].

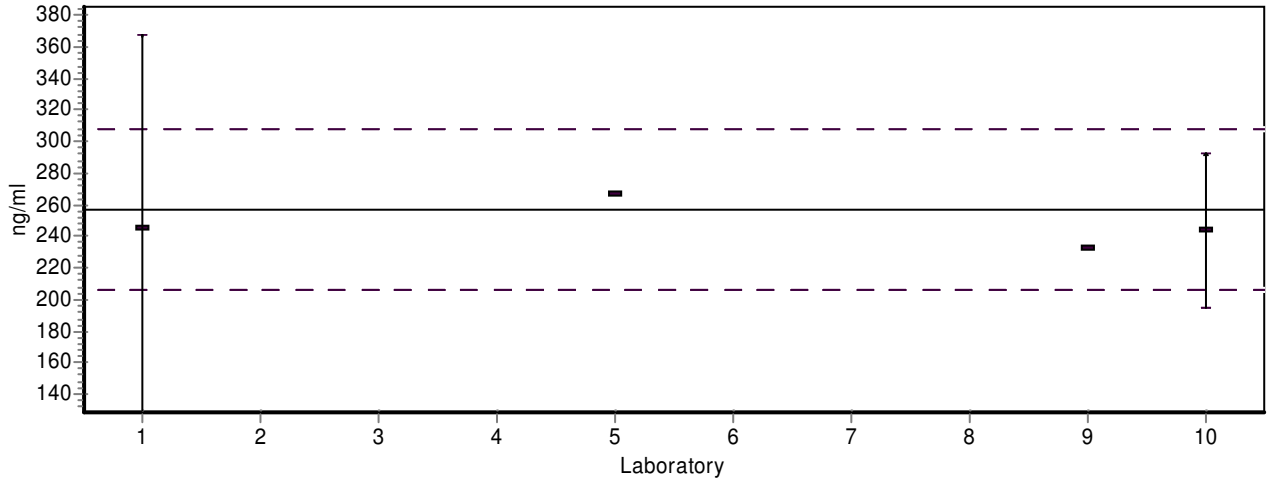
LIITE 9.

Appendix 9. Graphical presentations of the results and their uncertainties

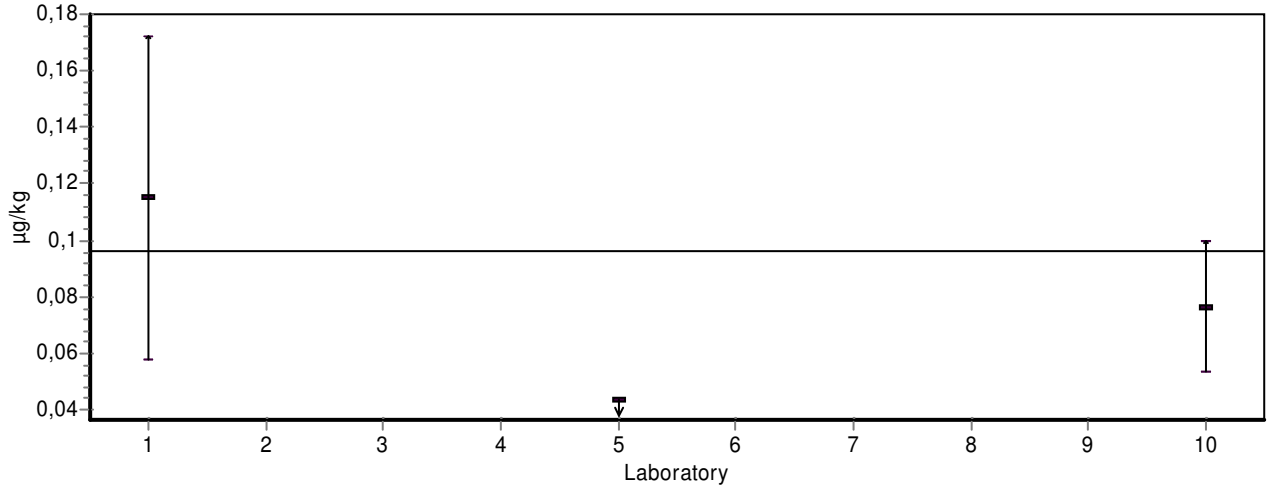
Analyytti *(Analyte)* **BDE100** Näyte *(Sample)* M1



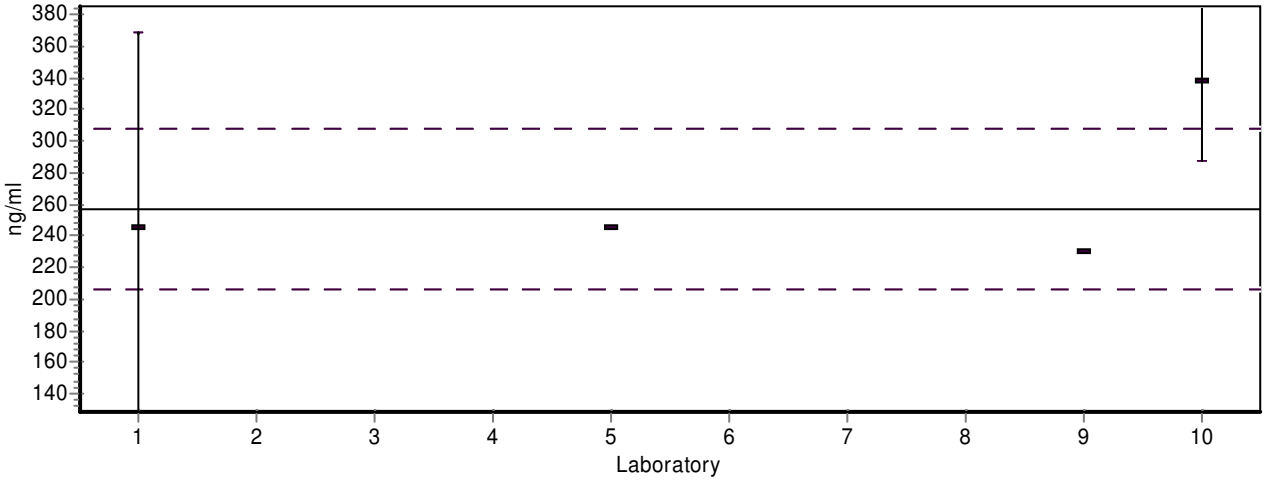
Analyytti *(Analyte)* **BDE100** Näyte *(Sample)* S2



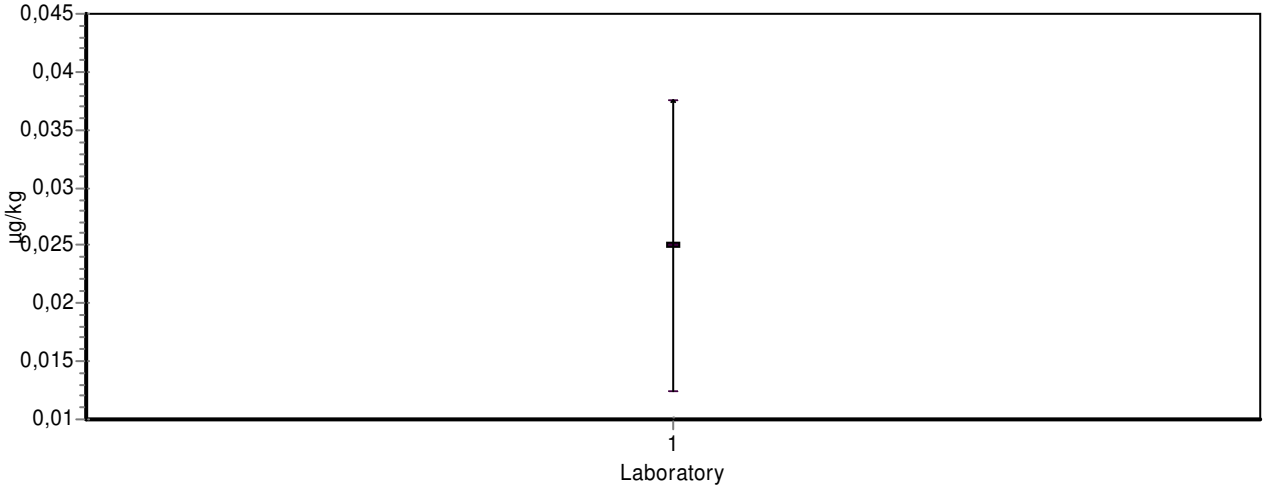
Analyytti *(Analyte)* **BDE153** Näyte *(Sample)* M1



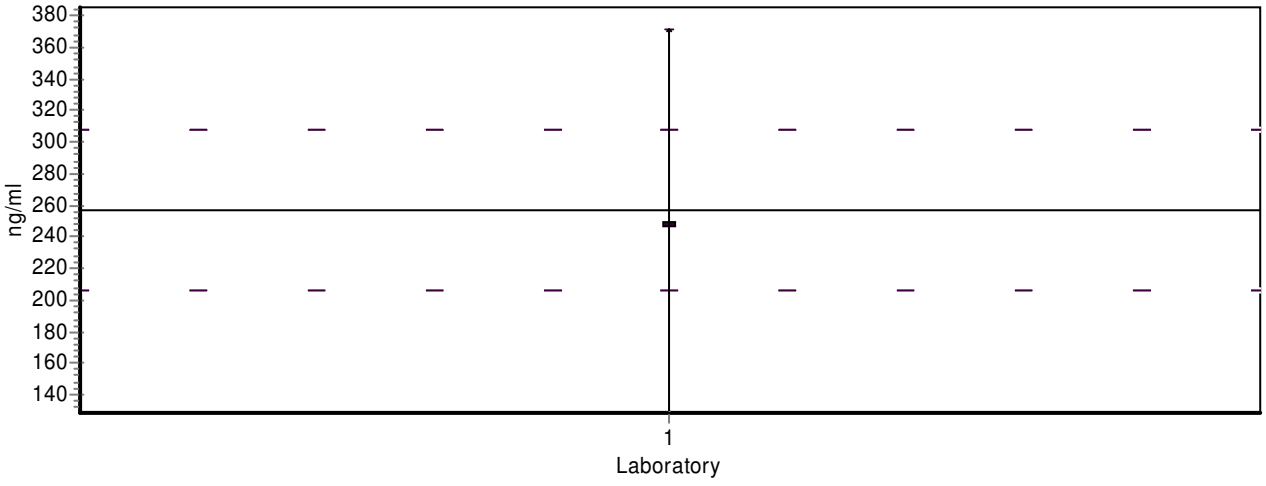
Analyytti *(Analyte)* **BDE153** Näyte *(Sample)* S2



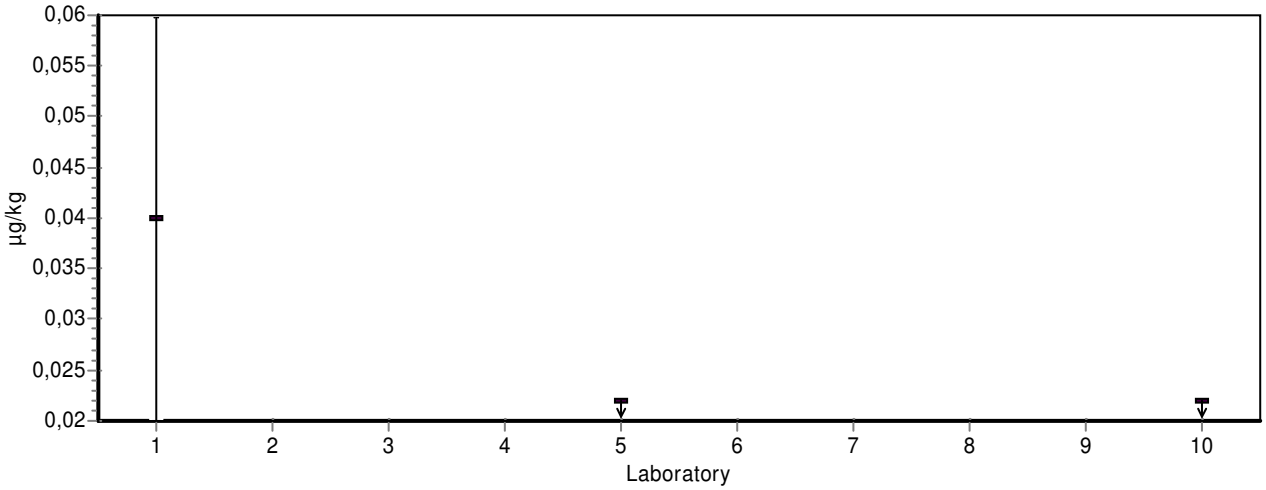
Analyytti *(Analyte)* **BDE17** Näyte *(Sample)* M1



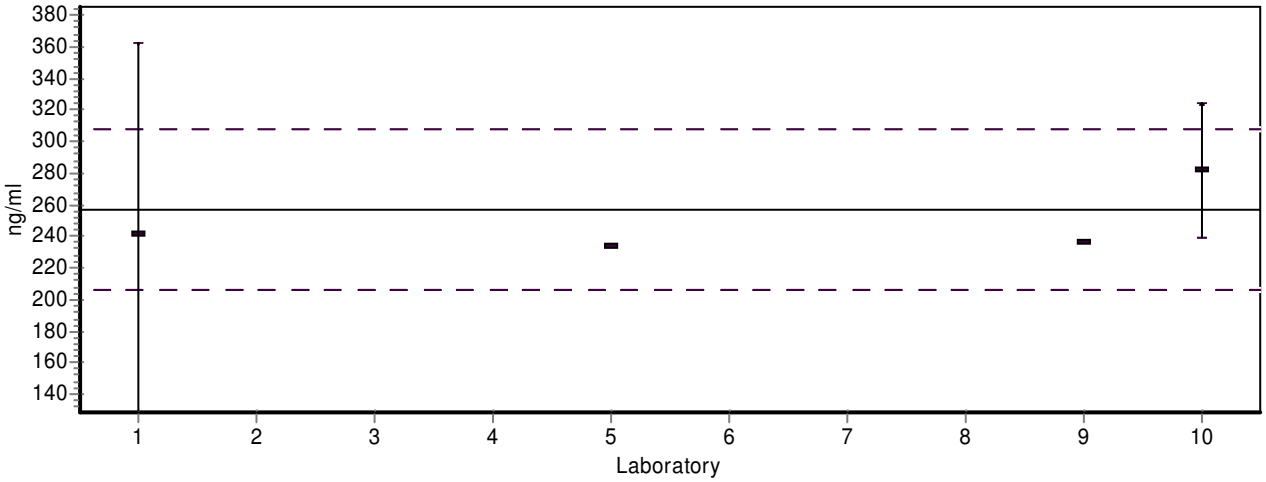
Analyytti *(Analyte)* **BDE17** Näyte *(Sample)* S2



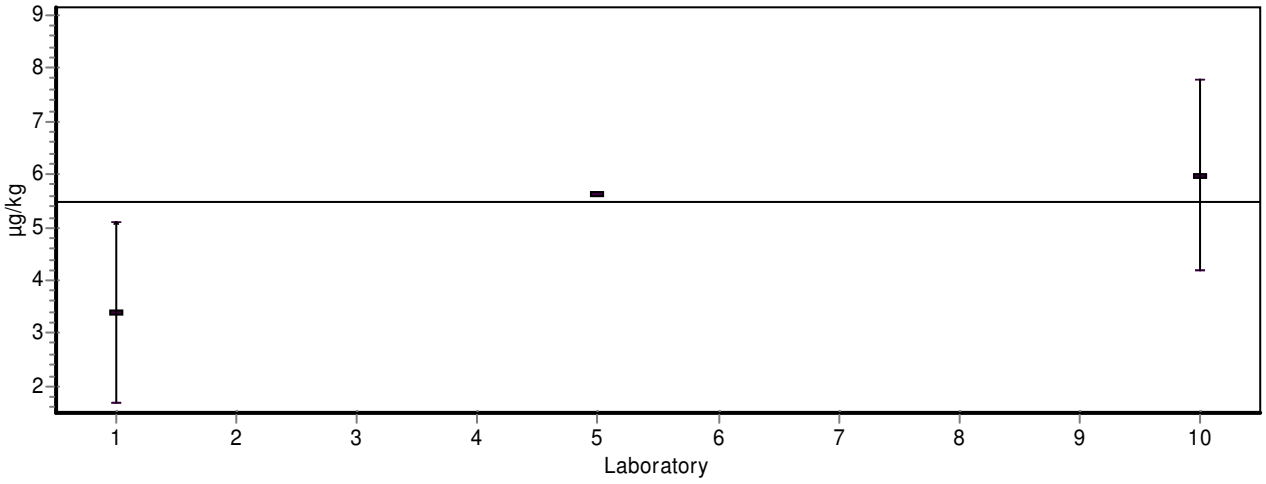
Analyytti *(Analyte)* **BDE183** Näyte *(Sample)* M1



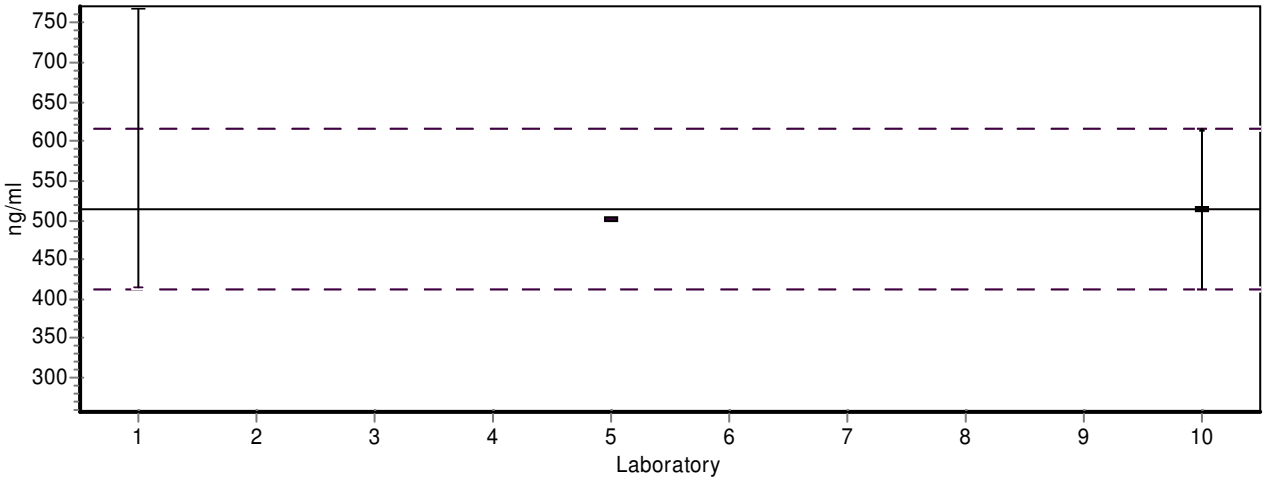
Analyytti *(Analyte)* **BDE183** Näyte *(Sample)* S2



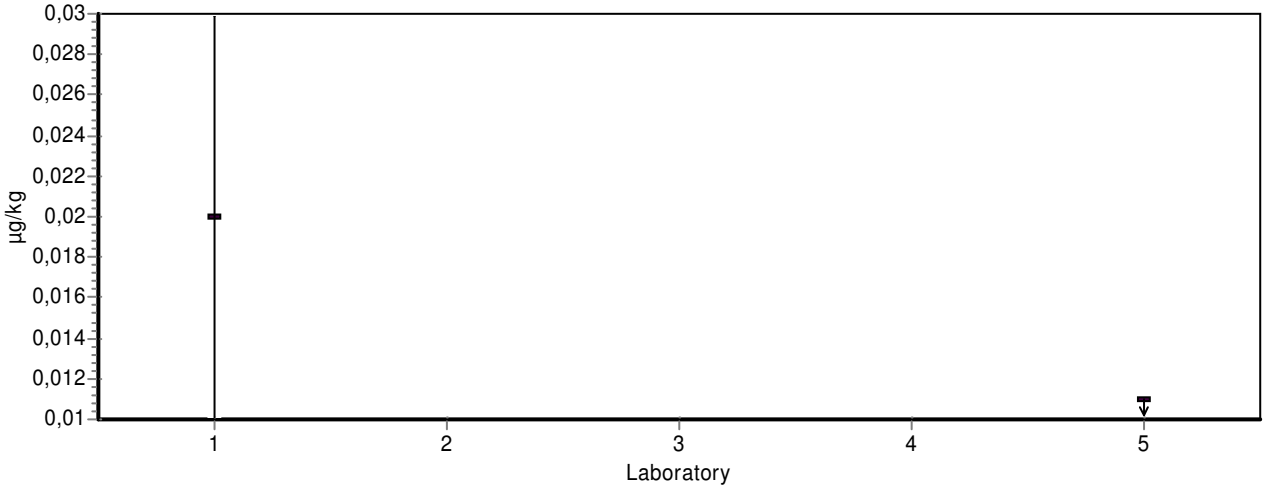
Analyytti *(Analyte)* **BDE209** Näyte *(Sample)* M1



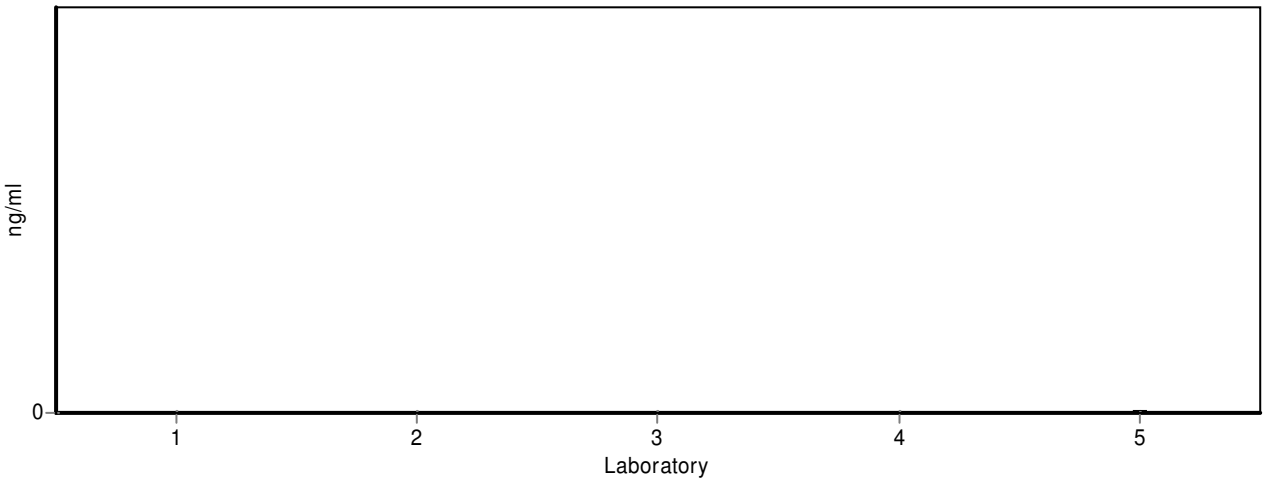
Analyytti *(Analyte)* **BDE209** Näyte *(Sample)* S2



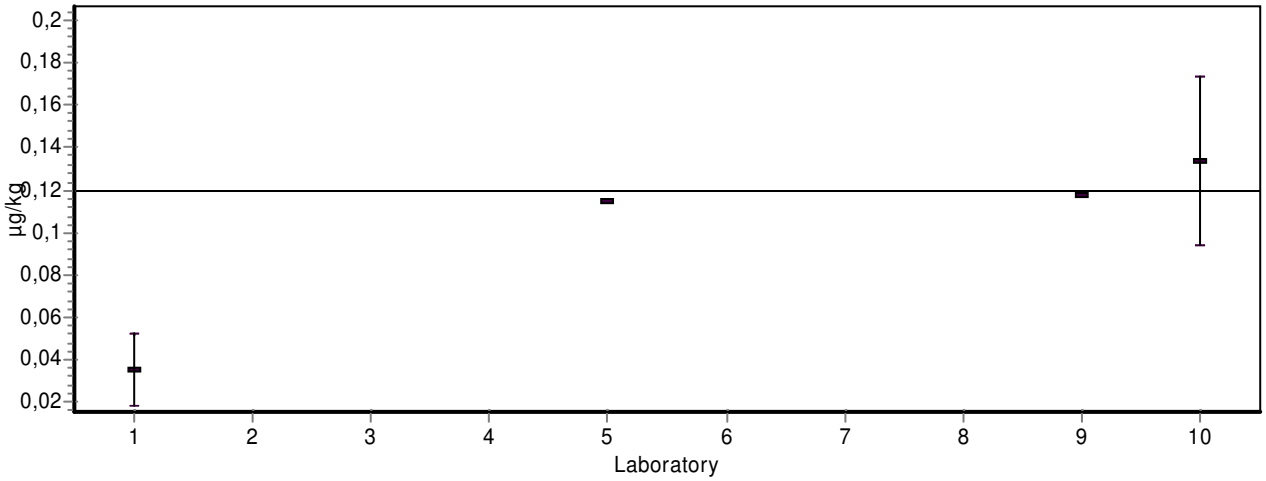
Analyytti *(Analyte)* **BDE28** Näyte *(Sample)* M1



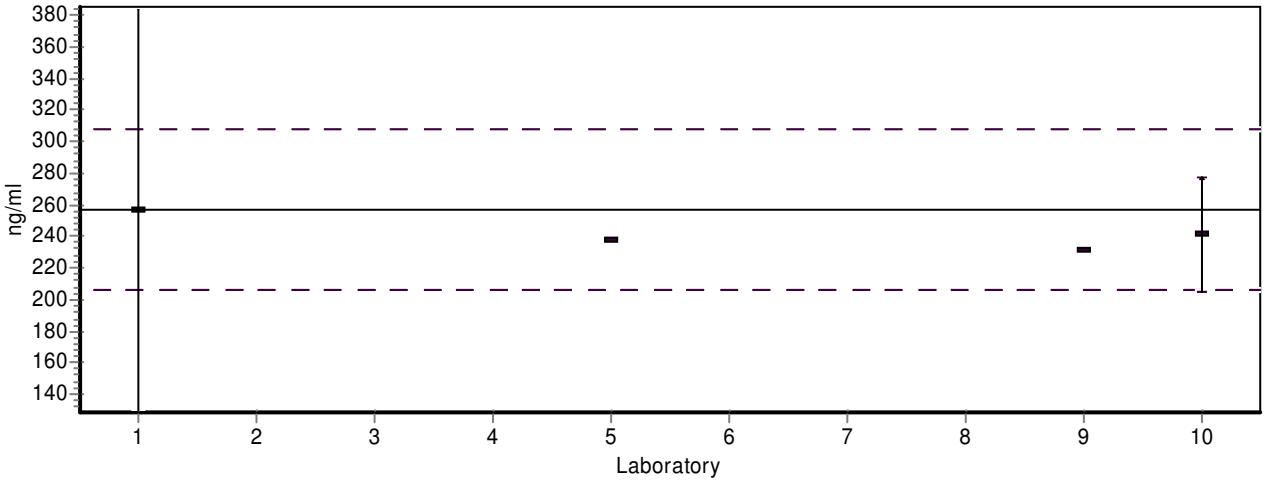
Analyytti *(Analyte)* **BDE28** Näyte *(Sample)* S2



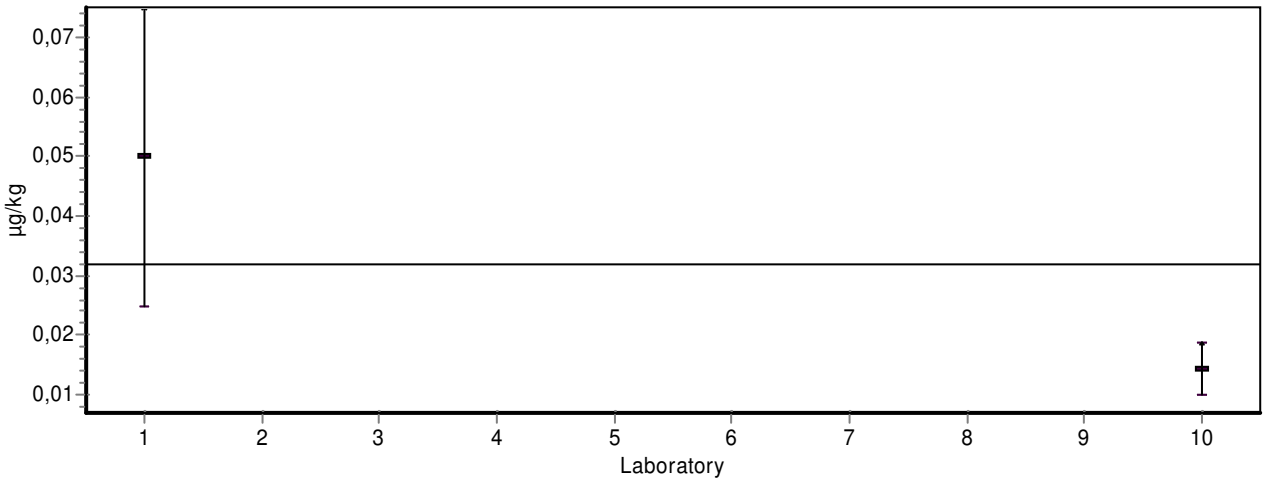
Analyytti *(Analyte)* **BDE47** Näyte *(Sample)* M1



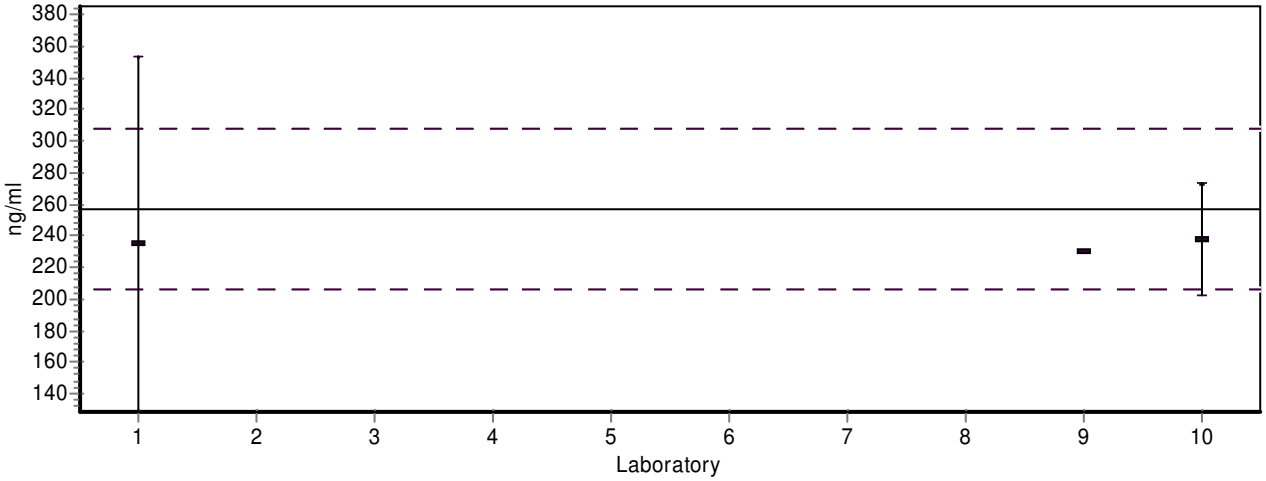
Analyytti *(Analyte)* **BDE47** Näyte *(Sample)* S2



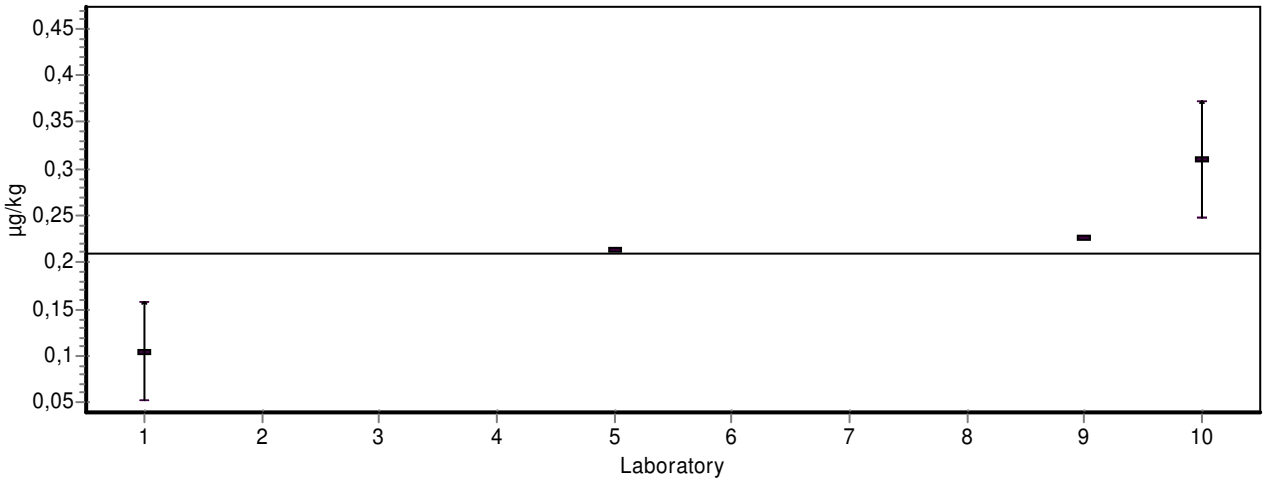
Analyytti *(Analyte)* **BDE66** Näyte *(Sample)* M1



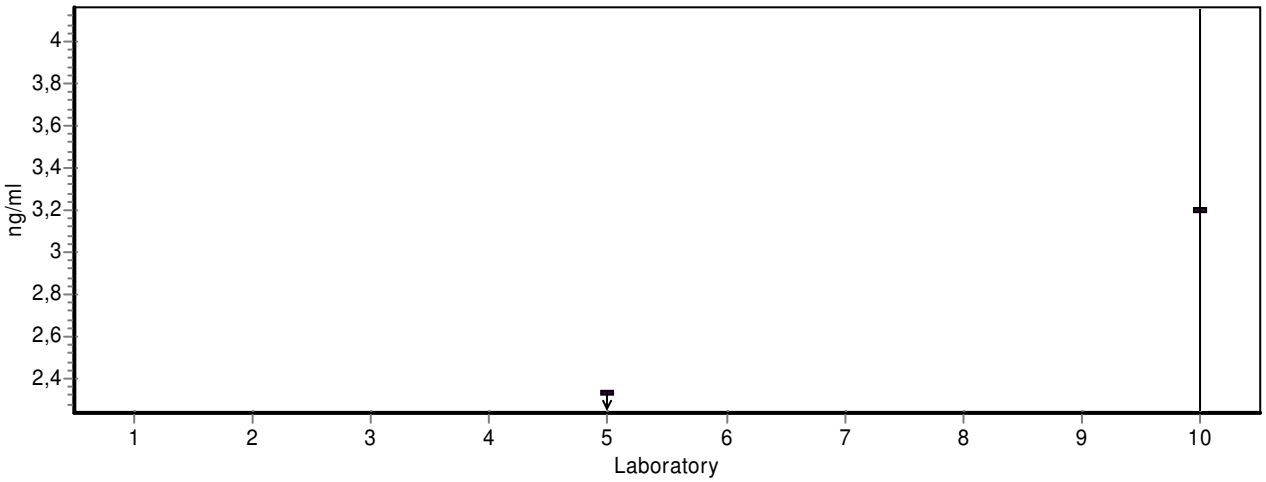
Analyytti *(Analyte)* **BDE66** Näyte *(Sample)* S2



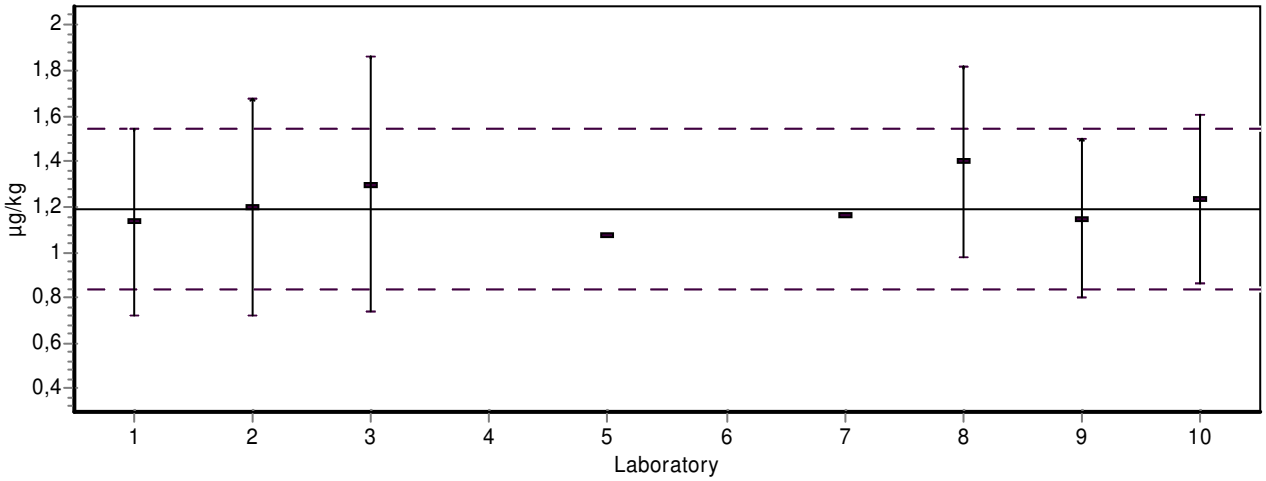
Analyytti *(Analyte)* **BDE99** Näyte *(Sample)* M1



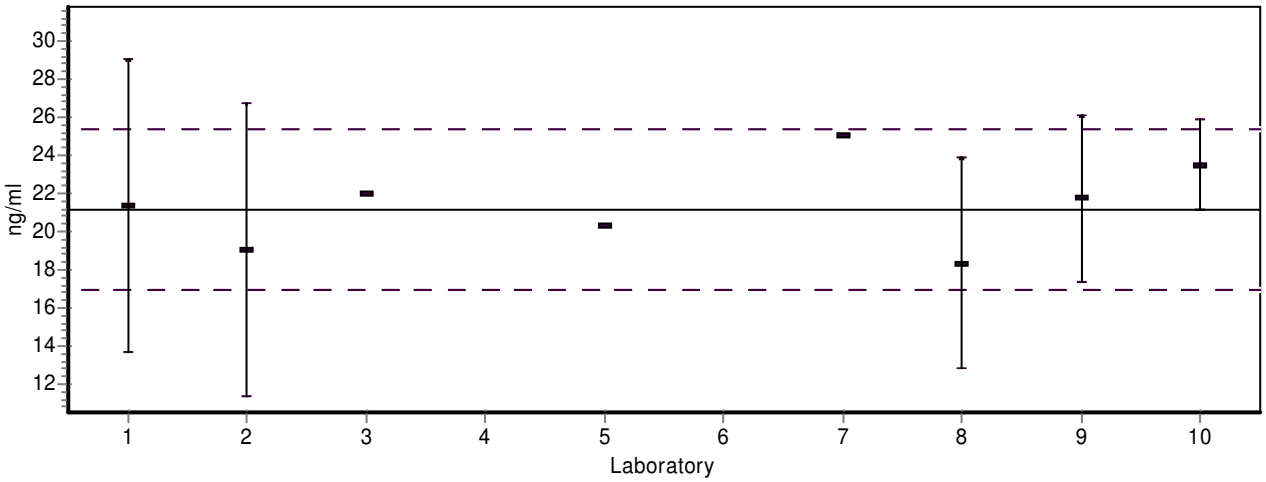
Analyytti *(Analyte)* **BDE99** Näyte *(Sample)* S2



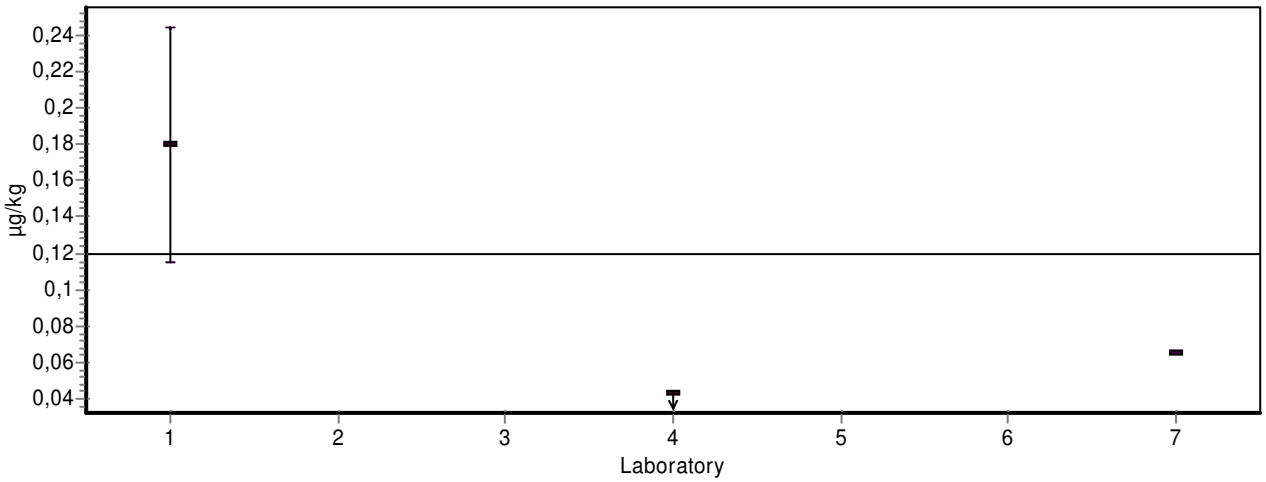
Analyytti *(Analyte)* **PCB101** Näyte *(Sample)* M1



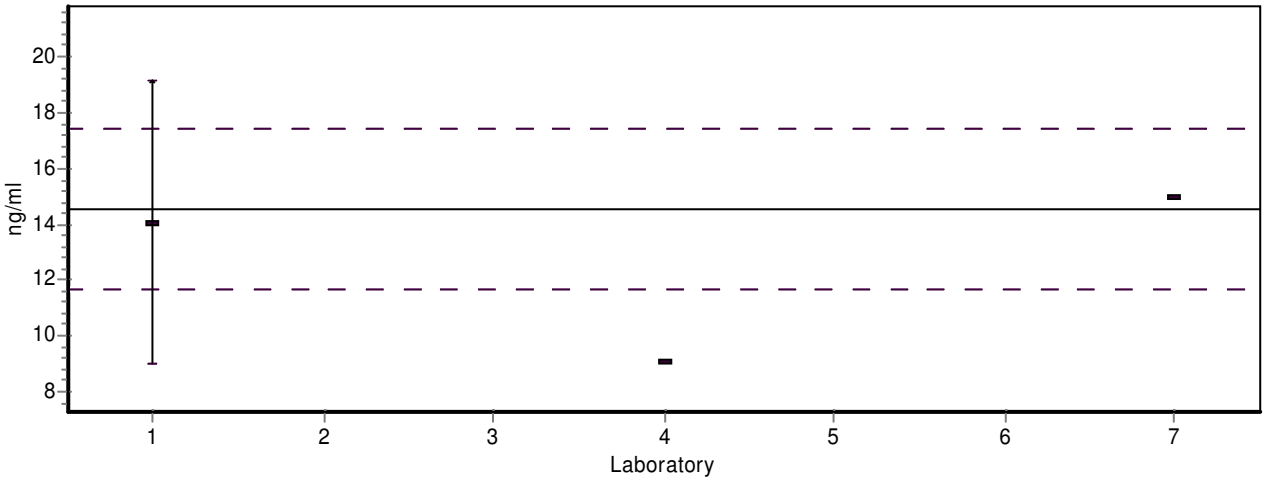
Analyytti *(Analyte)* **PCB101** Näyte *(Sample)* S1



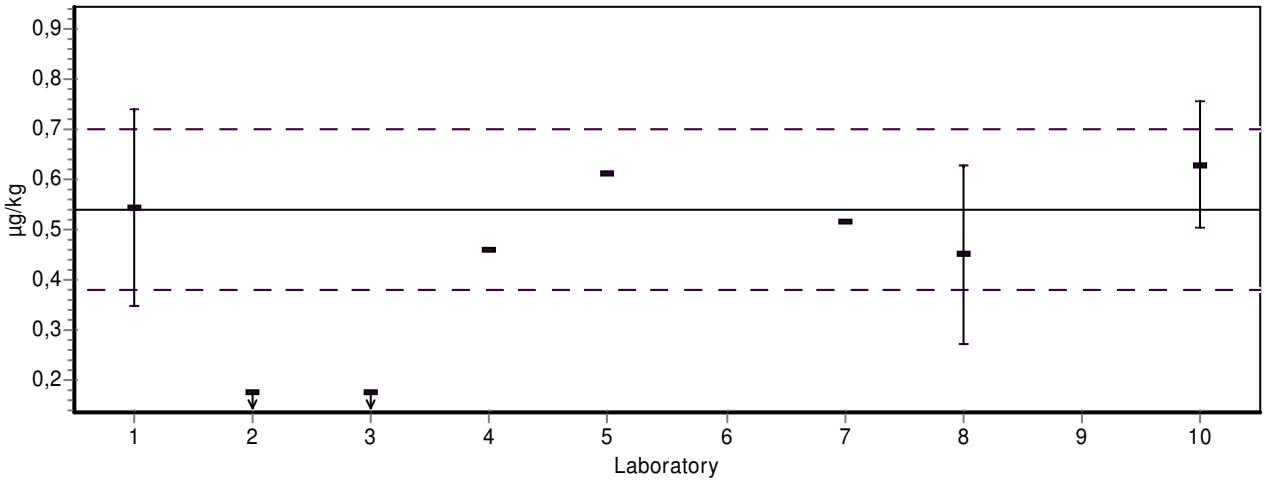
Analyytti *(Analyte)* **PCB105** Näyte *(Sample)* M1



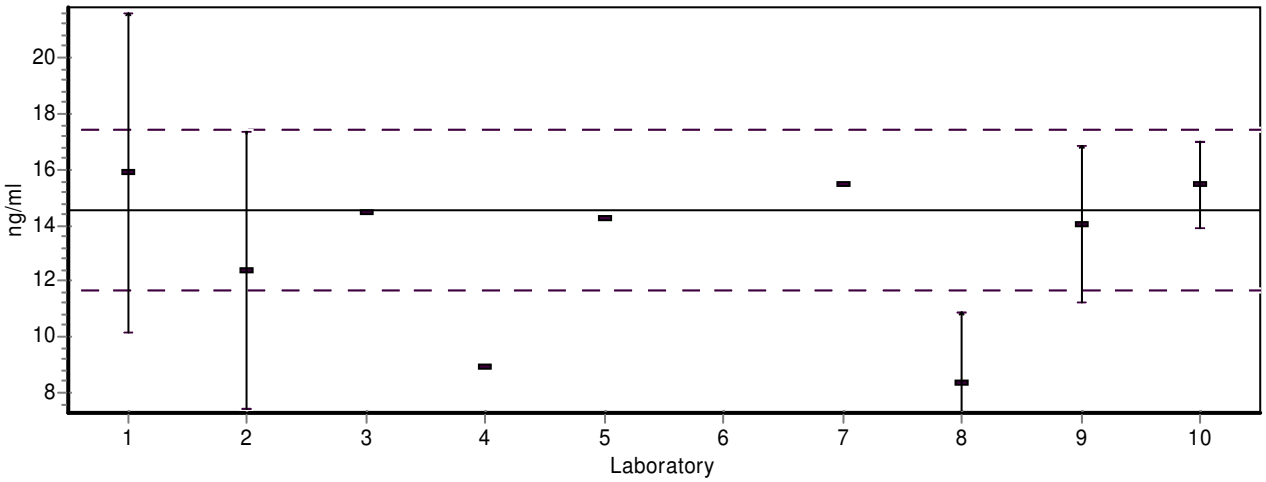
Analyytti *(Analyte)* **PCB105** Näyte *(Sample)* S1



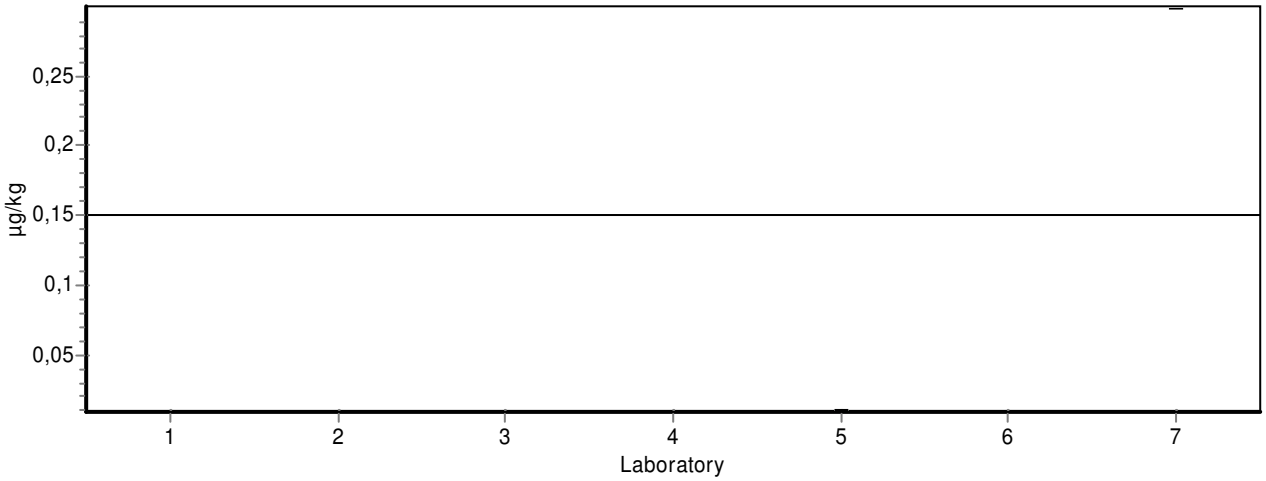
Analyytti *(Analyte)* **PCB118** Näyte *(Sample)* M1



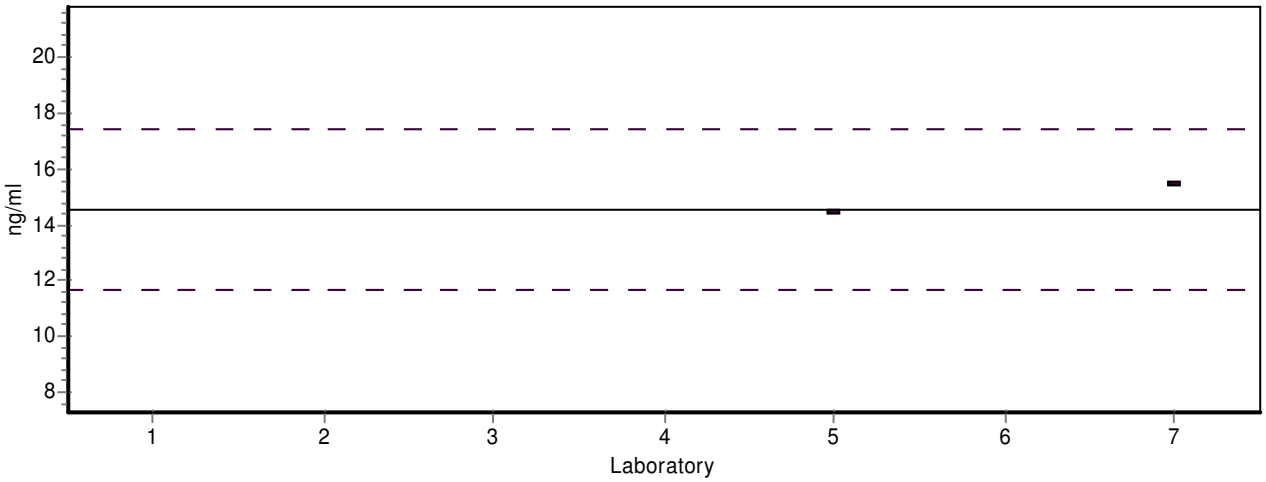
Analyytti *(Analyte)* **PCB118** Näyte *(Sample)* S1



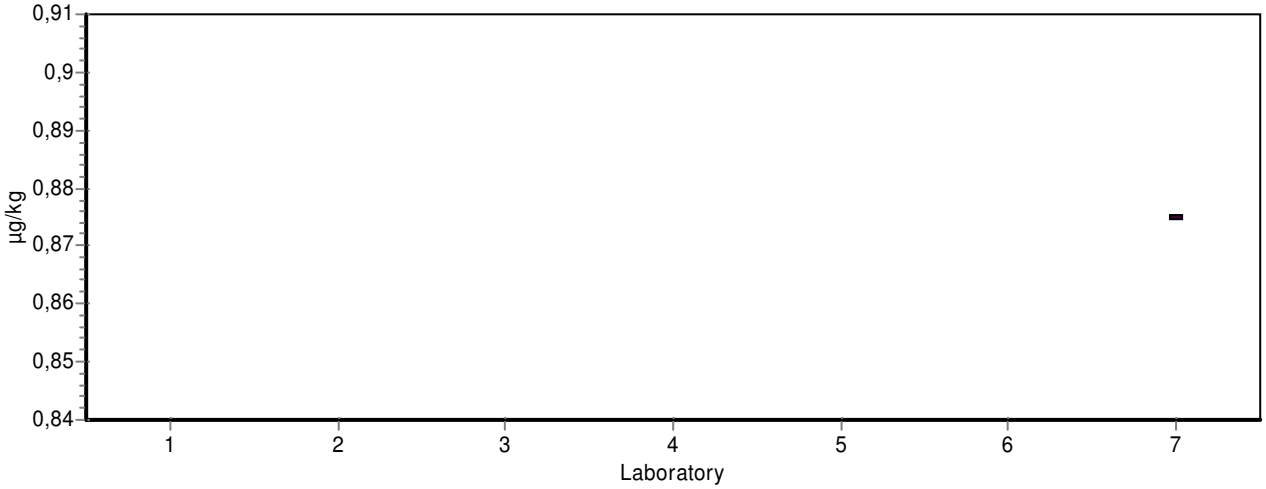
Analyytti *(Analyte)* **PCB126** Näyte *(Sample)* M1



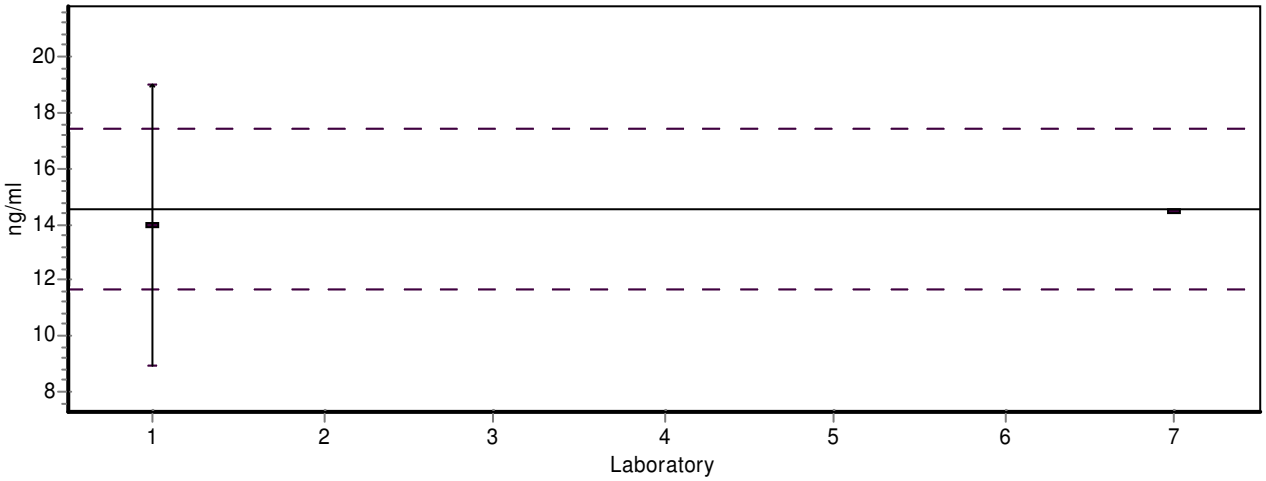
Analyytti *(Analyte)* **PCB126** Näyte *(Sample)* S1



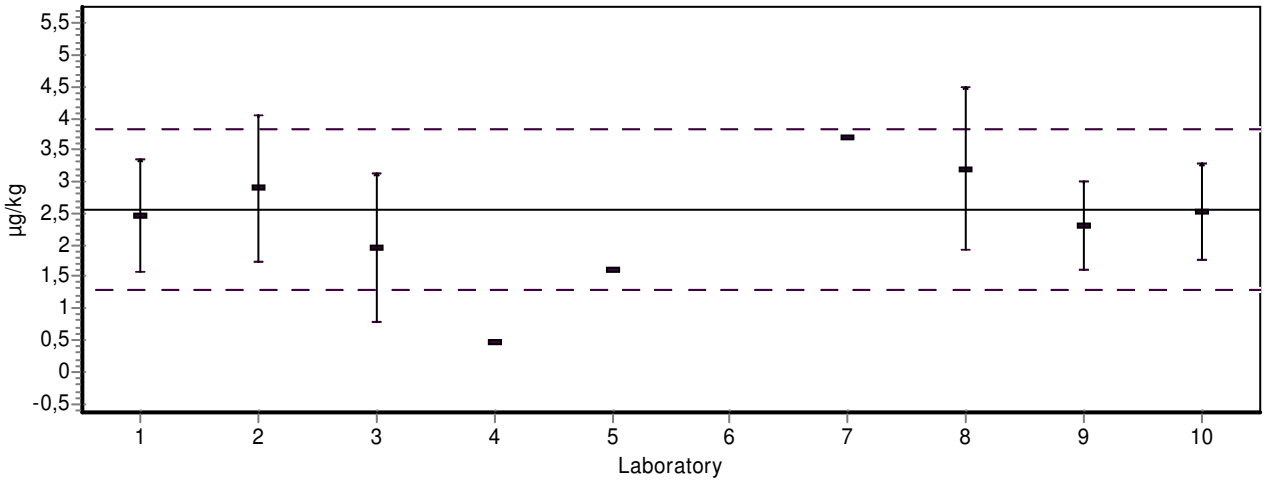
Analyytti *(Analyte)* **PCB128** Näyte *(Sample)* M1



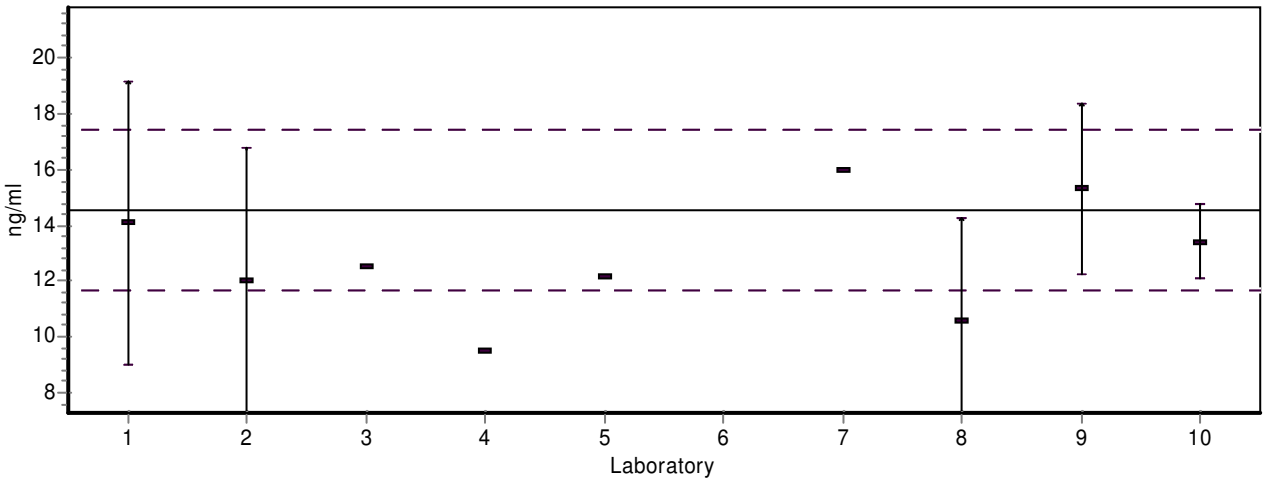
Analyytti *(Analyte)* **PCB128** Näyte *(Sample)* S1



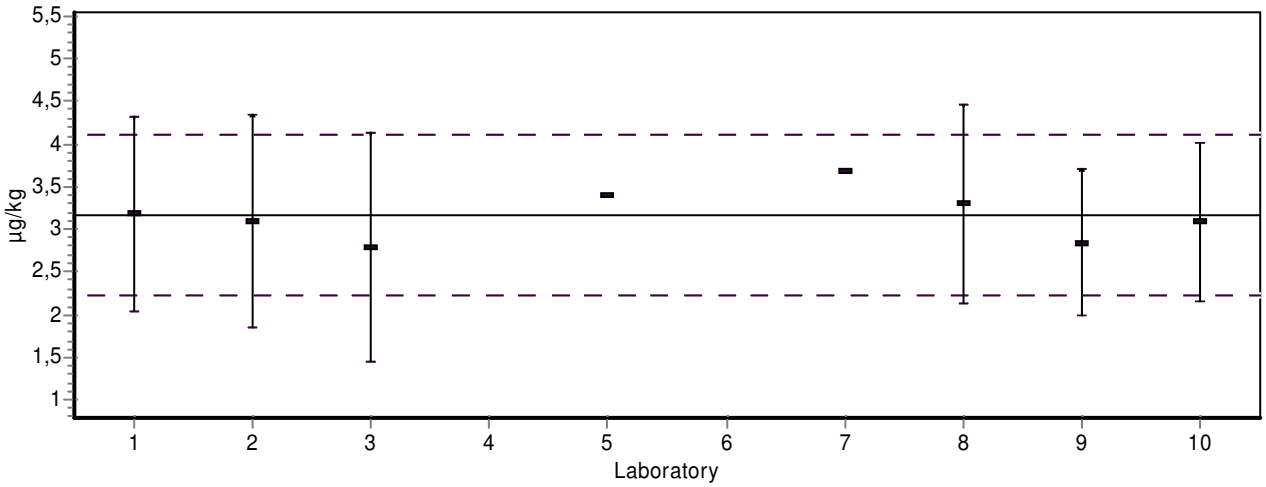
Analyytti *(Analyte)* **PCB138** Näyte *(Sample)* M1



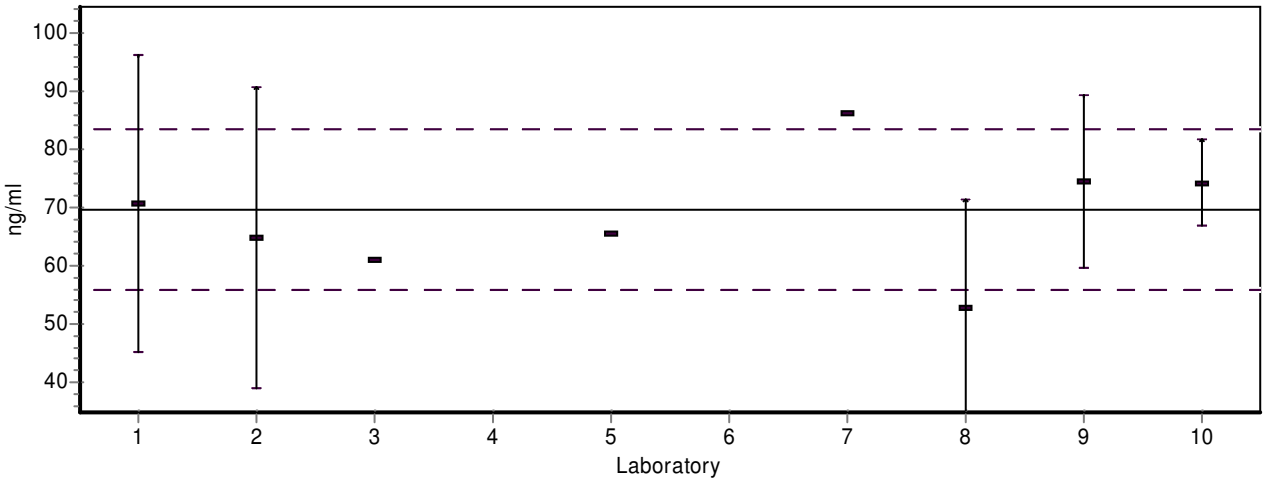
Analyytti *(Analyte)* **PCB138** Näyte *(Sample)* S1



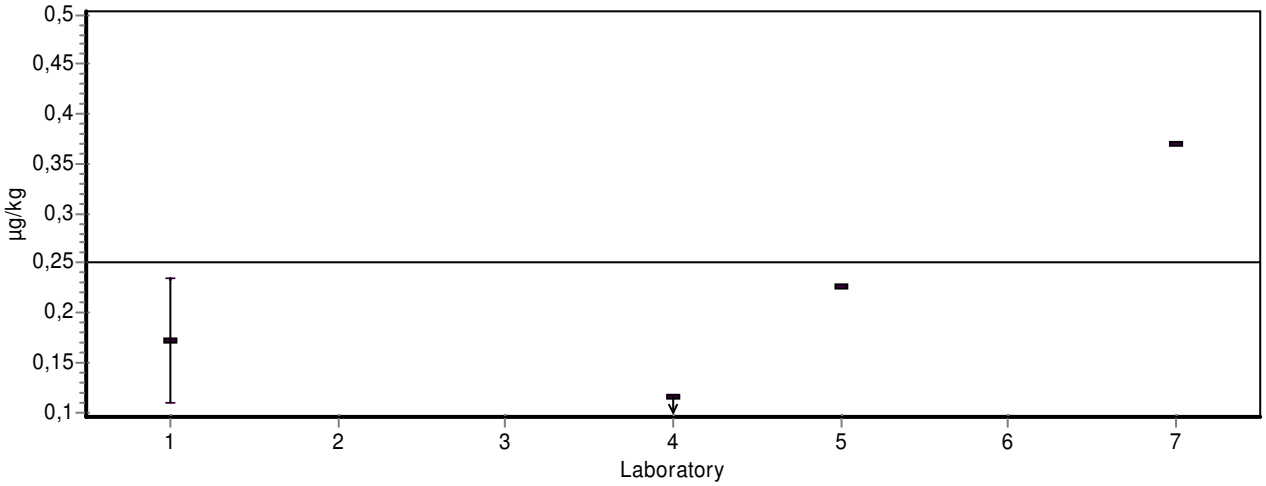
Analyytti *(Analyte)* **PCB153** Näyte *(Sample)* M1



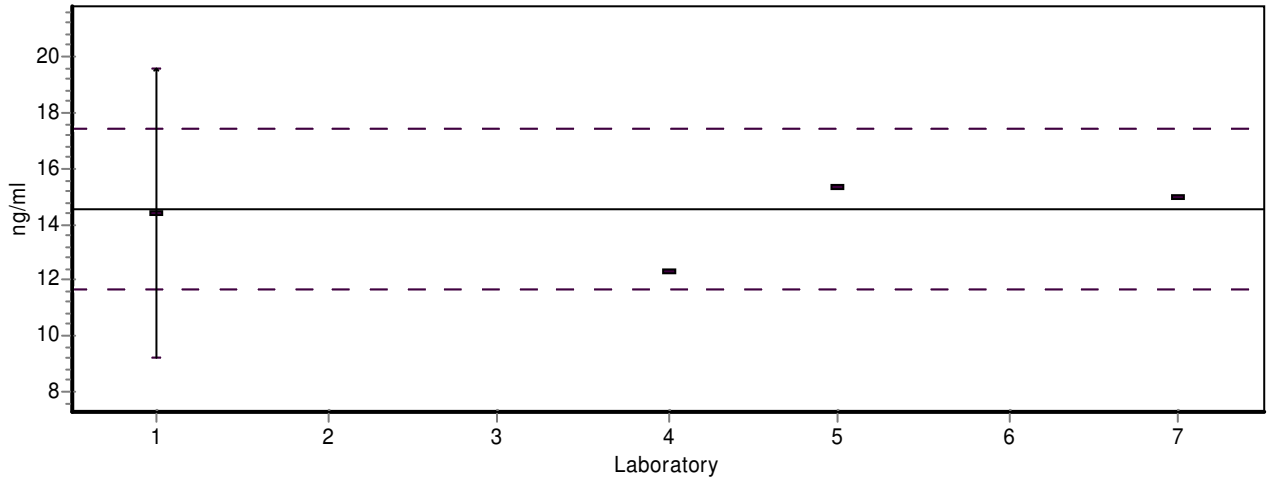
Analyytti *(Analyte)* **PCB153** Näyte *(Sample)* S1



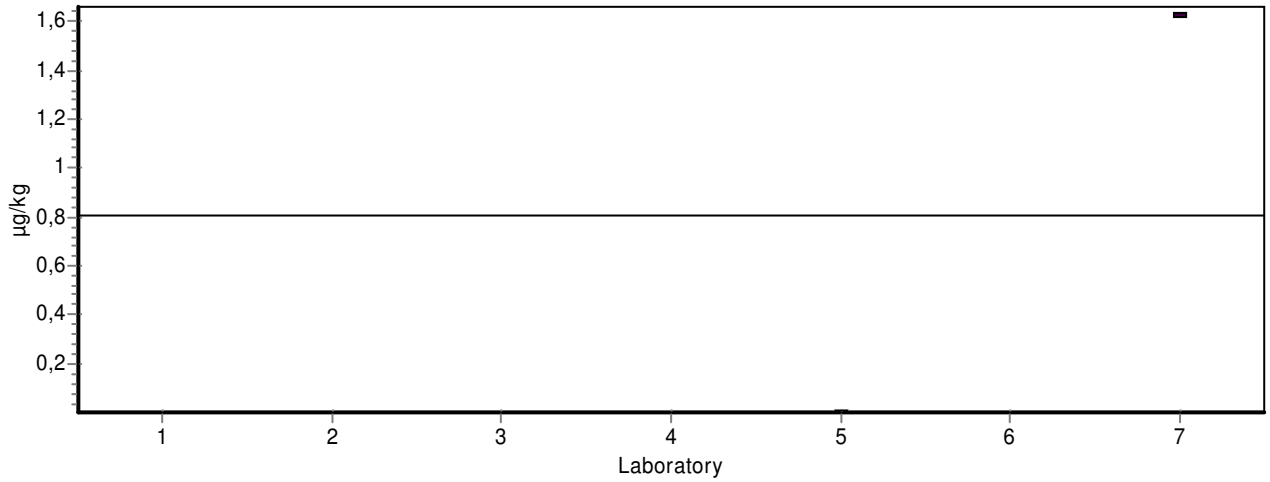
Analyytti *(Analyte)* **PCB156** Näyte *(Sample)* M1



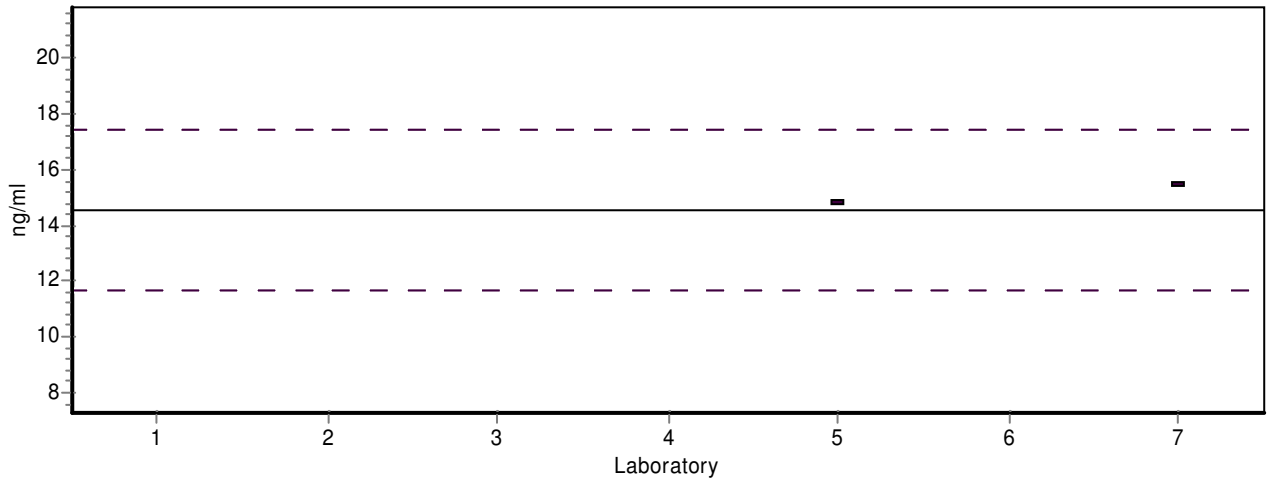
Analyytti *(Analyte)* **PCB156** Näyte *(Sample)* S1



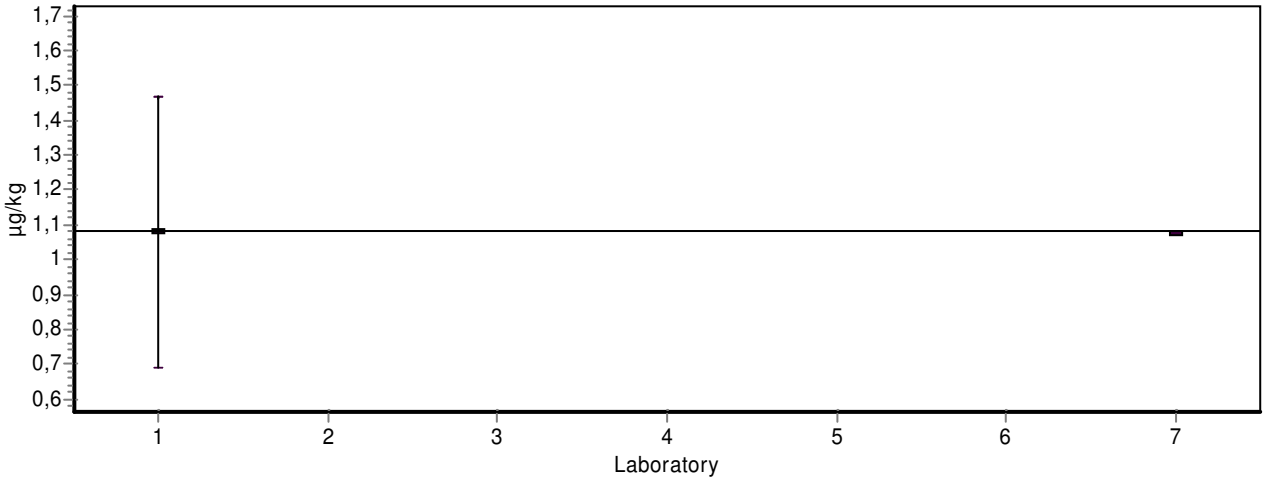
Analyytti *(Analyte)* **PCB169** Näyte *(Sample)* M1



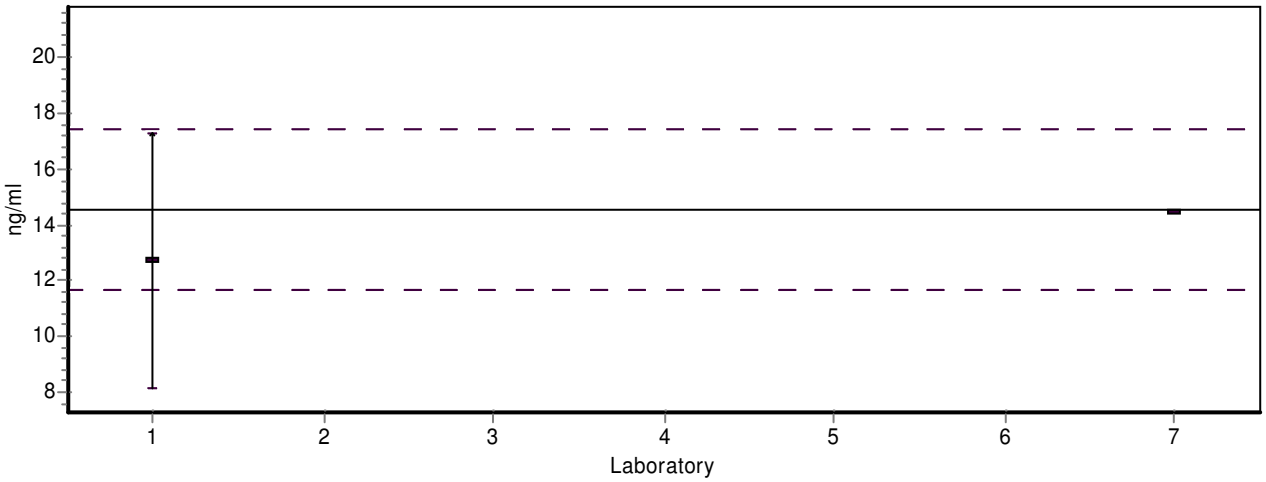
Analyytti *(Analyte)* **PCB169** Näyte *(Sample)* S1



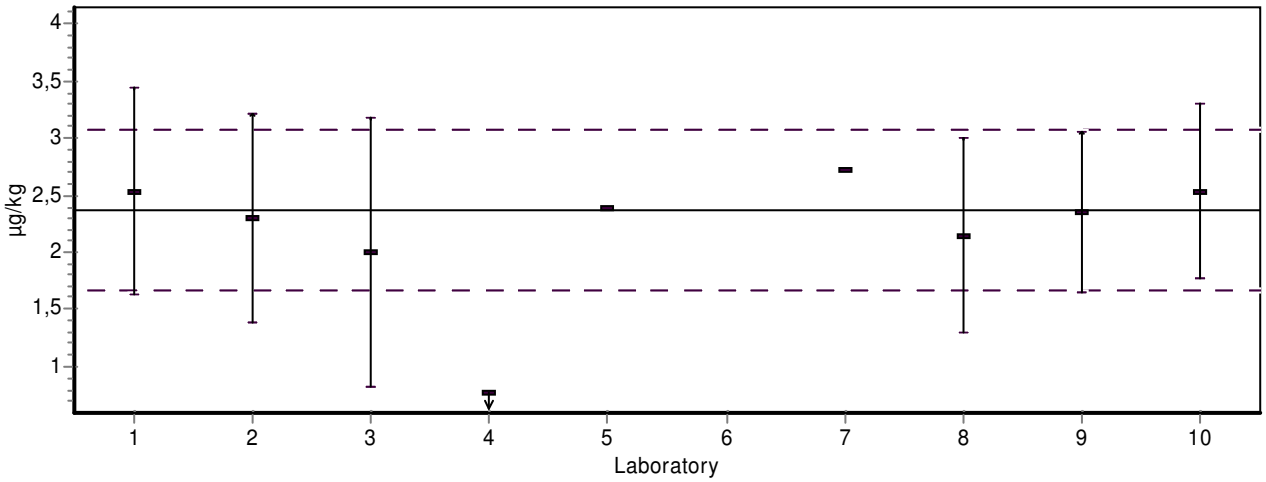
Analyytti *(Analyte)* **PCB170** Näyte *(Sample)* M1



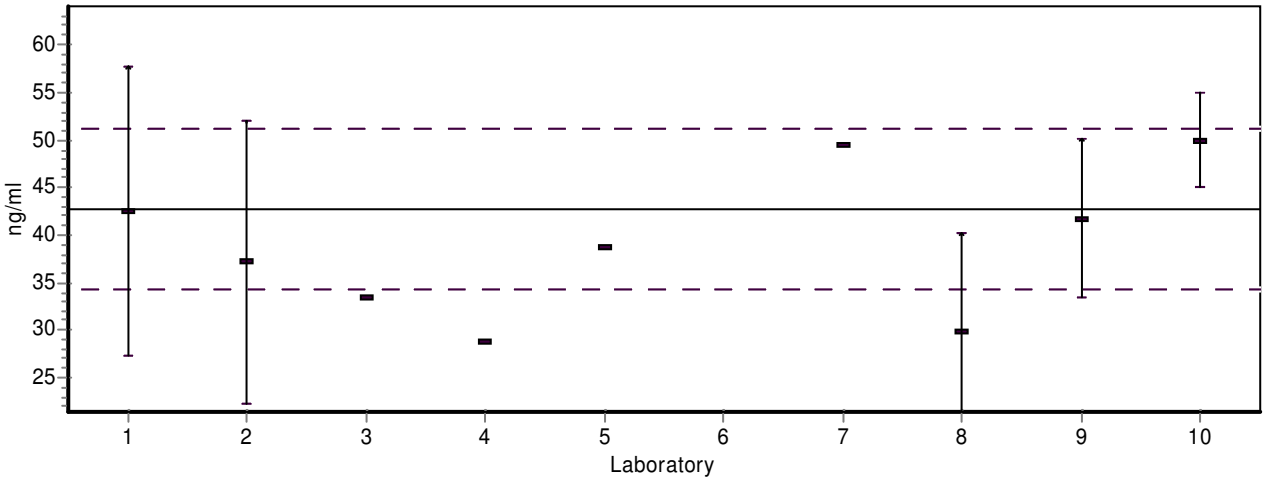
Analyytti *(Analyte)* **PCB170** Näyte *(Sample)* S1



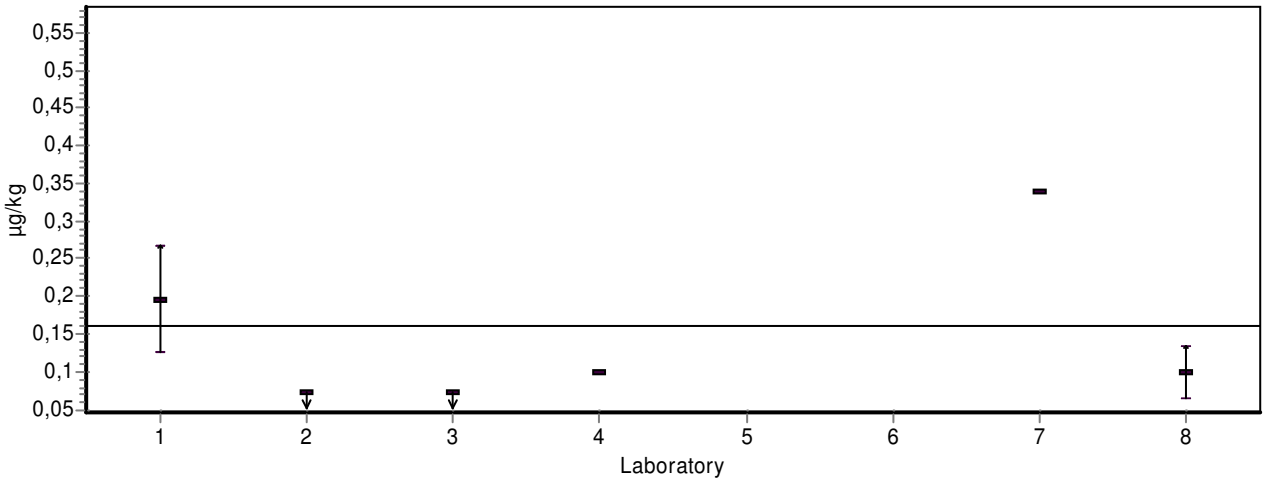
Analyytti *(Analyte)* **PCB180** Näyte *(Sample)* M1



Analyytti *(Analyte)* **PCB180** Näyte *(Sample)* S1



Analyytti *(Analyte)* **PCB28** Näyte *(Sample)* M1



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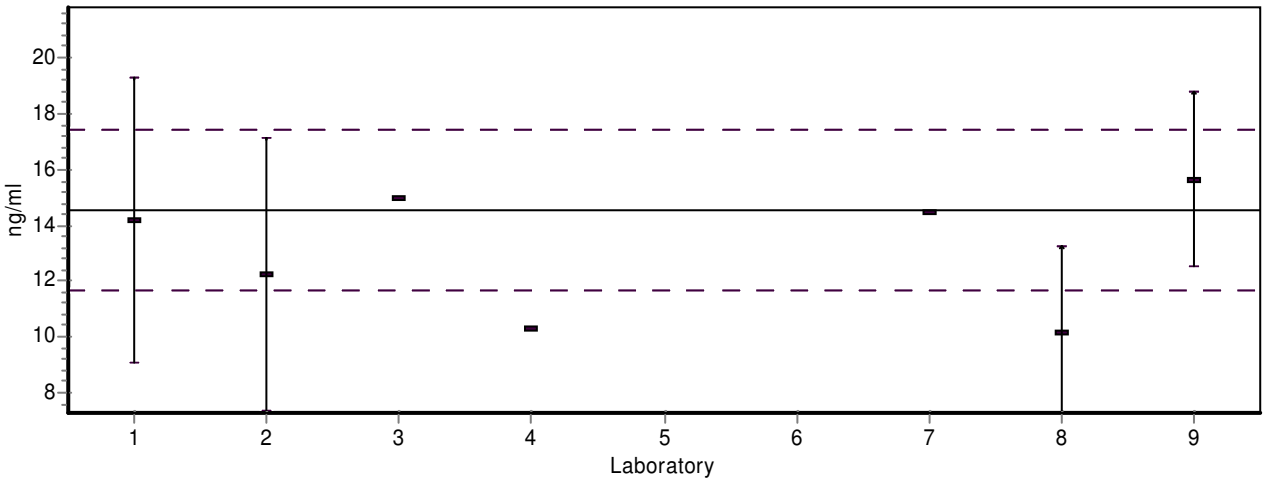

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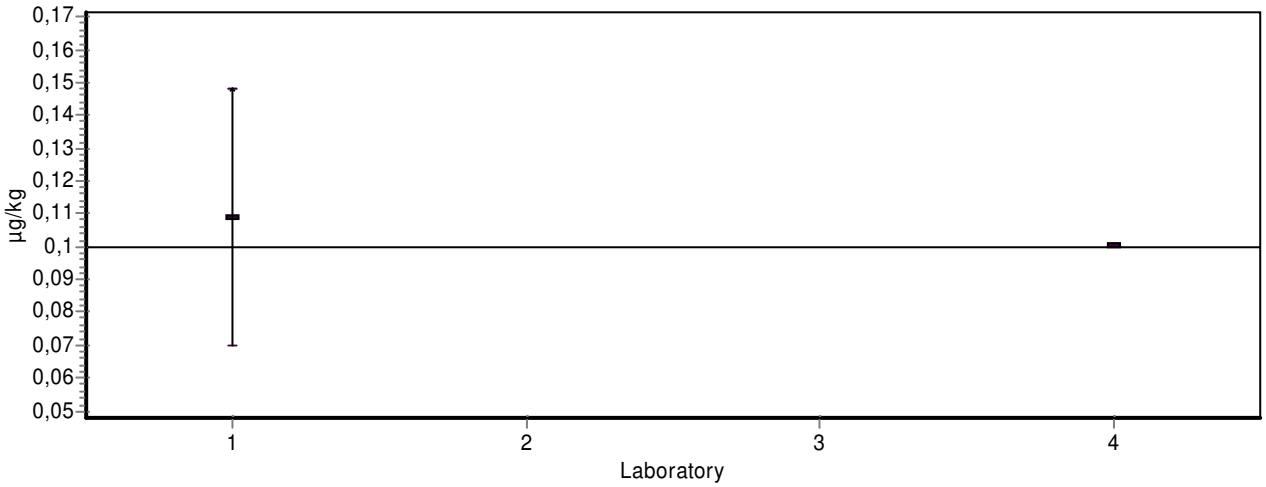

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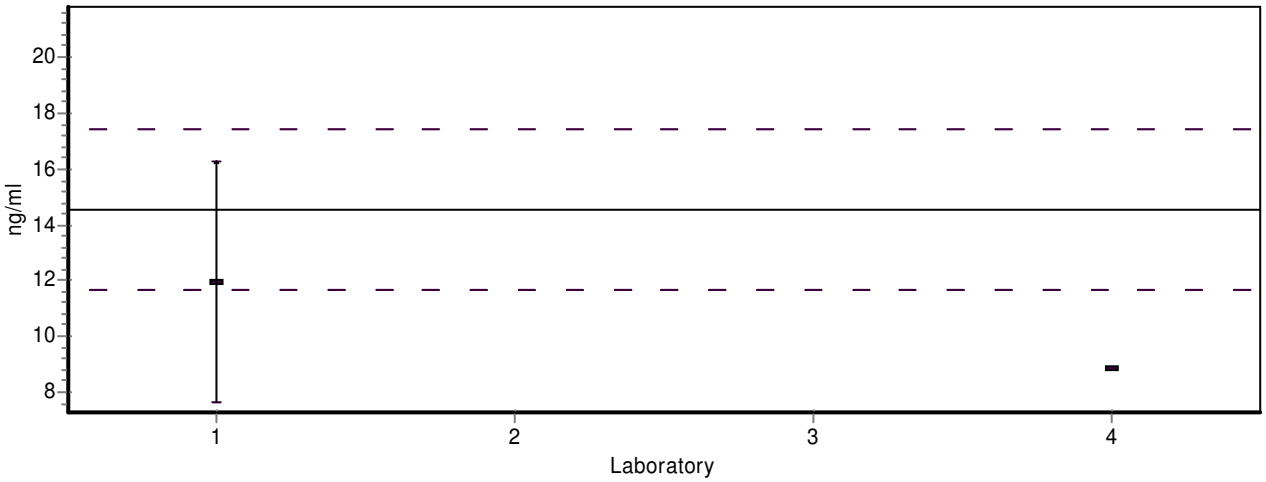
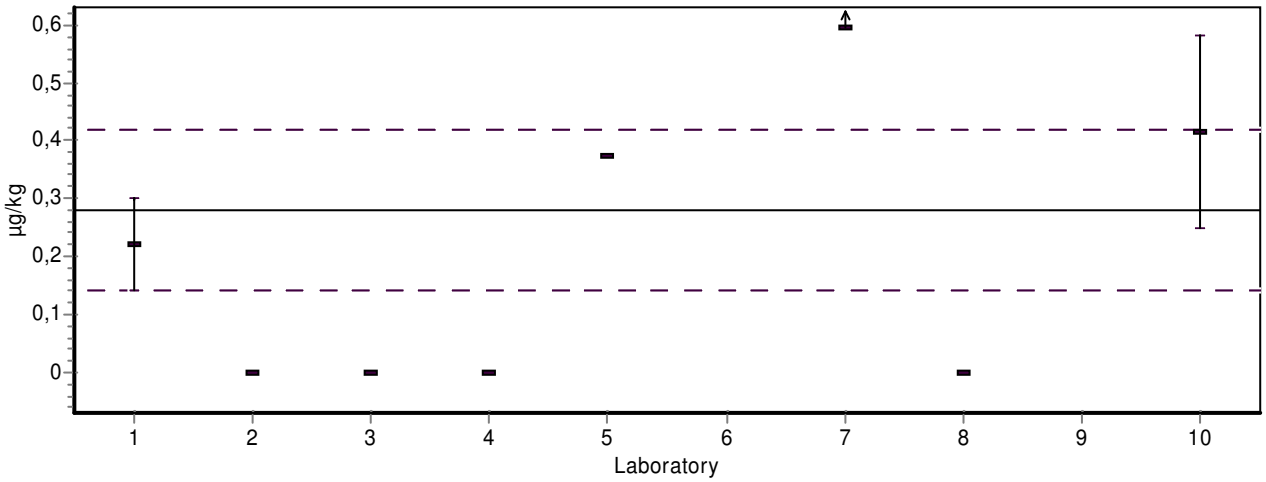
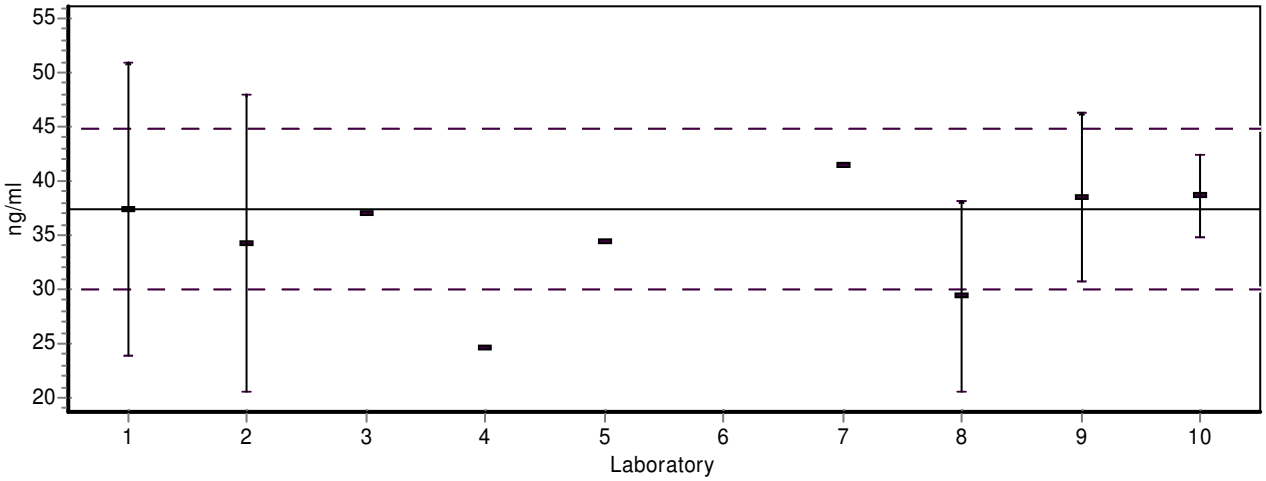


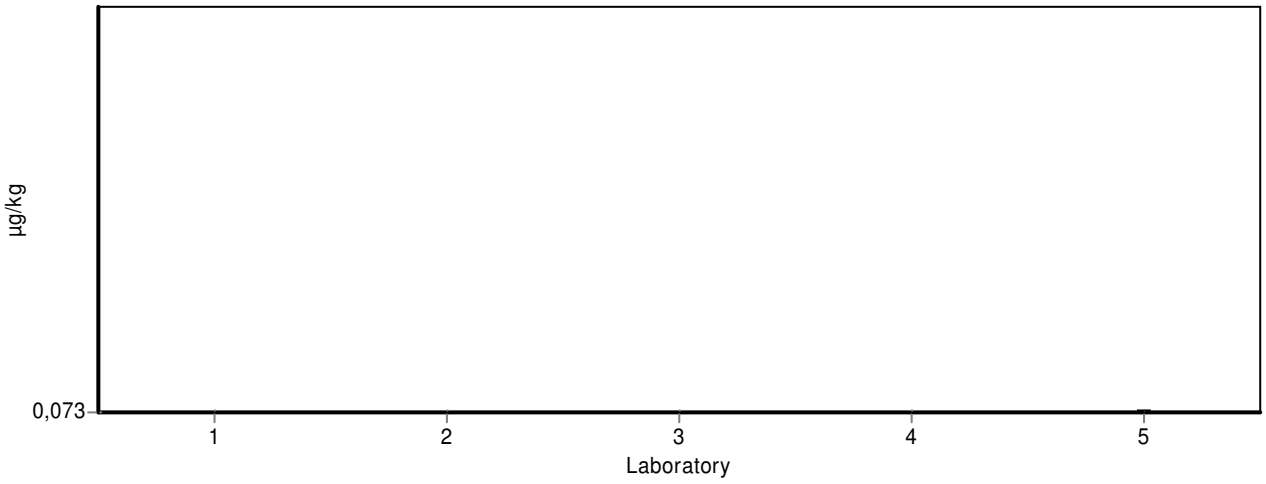
Analyytti *(Analyte)* **PCB52** Näyte *(Sample)* M1



Analyytti *(Analyte)* **PCB52** Näyte *(Sample)* S1



Analyytti *(Analyte)* **PCB77** Näyte *(Sample)* M1



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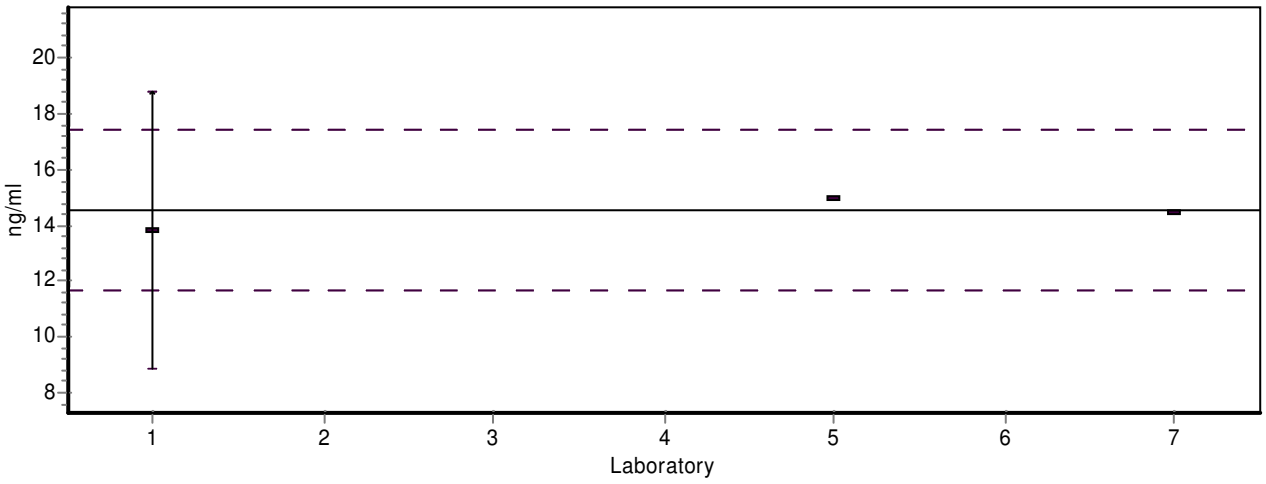

LIITE 10.

Appendix 10. Summary of the z scores

Analyte	Sample\Lab	1	2	3	4	5	7	8	9	10	%
BDE100	M1	.	.	.	.	.	.	.	.	.	
	S2	A	.	.	.	A	.	.	A	A	100
BDE153	M1	.	.	.	.	.	.	.	.	.	
	S2	A	.	.	.	A	.	.	A	**P**	75
BDE17	M1	.	.	.	.	.	.	.	.	.	
	S2	A	.	.	.	.	.	.	.	.	100
BDE183	M1	.	.	.	.	.	.	.	.	.	
	S2	A	.	.	.	A	.	.	A	A	100
BDE209	M1	.	.	.	.	.	.	.	.	.	
	S2	**P**	.	.	.	A	.	.	.	A	67
BDE28	M1	.	.	.	.	.	.	.	.	.	
	S2	.	.	.	.	.	.	.	.	.	
BDE47	M1	.	.	.	.	.	.	.	.	.	
	S2	A	.	.	.	A	.	.	A	A	100
BDE66	M1	.	.	.	.	.	.	.	.	.	
	S2	A	.	.	.	.	.	.	A	A	100
BDE99	M1	.	.	.	.	.	.	.	.	.	
	S2	.	.	.	.	.	.	.	.	.	
PCB101	M1	A	A	A	.	A	A	A	A	A	100
	S1	A	A	A	.	A	A	A	A	A	100
PCB105	M1	.	.	.	.	.	.	.	.	.	
	S1	A	.	.	**N**	.	A	.	.	.	67
PCB118	M1	A	.	.	A	A	A	A	.	A	100
	S1	A	A	A	**N**	A	A	**N**	A	A	78
PCB126	M1	.	.	.	.	.	.	.	.	.	
	S1	.	.	.	.	A	A	.	.	.	100
PCB128	M1	.	.	.	.	.	.	.	.	.	
	S1	A	.	.	.	.	A	.	.	.	100
PCB138	M1	A	A	A	**N**	A	A	A	A	A	89
	S1	A	A	A	**N**	A	A	n	A	A	78
PCB153	M1	A	A	A	.	A	A	A	A	A	100
	S1	A	A	A	.	A	p	n	A	A	75
PCB156	M1	.	.	.	.	.	.	.	.	.	
	S1	A	.	.	A	A	A	.	.	.	100
PCB169	M1	.	.	.	.	.	.	.	.	.	
	S1	.	.	.	.	A	A	.	.	.	100
PCB170	M1	.	.	.	.	.	.	.	.	.	
	S1	A	.	.	.	.	A	.	.	.	100
PCB180	M1	A	A	A	**N**	A	A	A	A	A	89
	S1	A	A	n	**N**	A	A	**N**	A	A	67
PCB28	M1	.	.	.	.	.	.	.	.	.	
	S1	A	A	A	n	.	A	**N**	A	.	71
PCB31	M1	.	.	.	.	.	.	.	.	.	
	S1	A	.	.	**N**	.	.	.	.	.	50
PCB52	M1	A	.	.	.	A	**P**	**N**	.	A	60
	S1	A	A	A	**N**	A	A	n	A	A	78
PCB77	M1	.	.	.	.	.	.	.	.	.	
	S1	A	.	.	.	A	A	.	.	.	100
%		96	100	91	18	100	90	46	100	94	
Accredited		yes		yes		yes		yes		yes	

A - accepted ($-2 \leq Z \leq 2$), p - questionable ($2 < Z \leq 3$), n - questionable ($-3 \leq Z < -2$), P - non-accepted ($Z > 3$), N - non-accepted ($Z < -3$),

%* - percentage of accepted results

Totally accepted, % In all: 86 In accredited: 89

APPENDIX 11. RESULTS OF THE AXYS ANALYTICAL SERVICES

Sample S2	Unit	Assigned value	2*TargSD %	Axys	z score		Sample M1	Unit	Axys	Note
DiBDEs							**DiBDEs**			
TriBDEs							**TriBDEs**			
17	ng/mL	257	20	299	1,63		17	µg/kg	2,99	17/25
28							28	µg/kg	0,04	28/13
TetraBDEs							**TetraBDEs**			
47	ng/mL	257	20	262	0,19		47	µg/kg	2,63	
66	ng/mL	257	20	226	-1,21		66	µg/kg	2,26	
71							71	µg/kg	<0,02	
75							75	µg/kg	0,004	K
77							77	µg/kg	0,002	K
PentaDBEs							**PentaDBEs**			
85							85	µg/kg	<0,005	
99							99	µg/kg	0,07	
100	ng/mL	257	20	259	0,08		100	µg/kg	2,59	
119							119	µg/kg	0,12	119/120
HexaBDEs							**HexaBDEs**			
138							138	µg/kg	0,02	138/166
153	ng/mL	257	20	259	0,08		153	µg/kg	2,59	
154							154	µg/kg	0,04	
HeptaBDEs							**HeptaBDEs**			
183	ng/mL	257	20	236	-0,82		183	µg/kg	2,36	
OctaBDEs							**OctaBDEs**			
203							203	µg/kg	0,09	
NonaBDEs							**NonaBDEs**			
DecaBDEs							**DecaBDEs**			
209	ng/mL	514	20	540	0,51		209	µg/kg	5,4	

K = peak detected but did not meet quantification criteria

Sample S3	Unit	Assigned value	2*TargSD %	Result	z score
TriCDD/CDFs					
TetraCDD/CDFs					
2,3,7,8-TCDD	ng/ml	20,94	20	19,10	-0,88
2,3,7,8-TCDF		20,94	20	19,60	-0,64
PentaCDD/CDFs					
1,2,3,7,8-PeCDD	ng/ml	52,34	20	48,50	-0,73
1,2,3,7,8-PeCDF	ng/ml	52,34	20	44,30	-1,54
2,3,4,7,8-PeCDF	ng/ml	52,34	20	45,20	-1,37
HexaCDD/CDFs					
1,2,3,4,7,8-HXCDD	ng/ml	52,34	20	48,20	-0,79
1,2,3,6,7,8-HxCDD	ng/ml	52,34	20	46,70	-1,08
1,2,3,7,8,9-HxCDD	ng/ml	52,34	20	46,30	-1,15
1,2,3,4,7,8-HxCDF	ng/ml	52,34	20	46,60	-1,10
1,2,3,6,7,8-HxCDF	ng/ml	52,34	20	44,70	-1,46
2,3,4,6,7,8-HxCDF	ng/ml	52,34	20	43,90	-1,61
1,2,3,7,8,9-HxCDF	ng/ml	52,34	20	46,60	-1,10
HeptaCDD/CDFs					
1,2,3,4,6,7,8-HpCDD	ng/ml	52,34	20	45,00	-1,40
1,2,3,4,6,7,8-HpCDF	ng/ml	52,34	20	44,50	-1,50
1,2,3,4,7,8,9-HpCDF	ng/ml	52,34	20	42,60	-1,86
OctaCDD/CDFs					
OCDD	ng/ml	104,68	20	99,80	-0,47
OCDF	ng/ml	104,68	20	88,90	-1,51

Documentation page

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Parts of publication/ other project publications	Publication is also available in the internet www.ymparisto.fi/julkaisut	
Abstract	The Finnish Environment Institute carried out the proficiency test for the analysis of PCBs, PBDEs and PCDDs/PCDFs in sediment in autumn 2007. In total, the samples were delivered to 11 laboratories from which ten laboratories reported PCB results, four laboratories PBDE results and three laboratories PCDD/PCDF results. One laboratory did not reported any results. The calculated concentrations were used as the assigned values for measurands in the artificial sample and the robust means of the reported results for the measurands in the sediment. The assessment of performance was based on the z score which was calculated using the target value for total deviation at 95 confidence level. The target value for the total deviation was set 20 % for the measurands in the artificial samples and varied from 30 % to 50 % for PCBs in sediment. Any target deviation for PBDEs and PCDDs/PCDFs in sediment could not be set because of the low number of the participants. In total, 86 % of the participating laboratories reported the satisfactory results.	
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Julkaisun nimi	SYKE proficiency test 5/2007 PCBs, PBDEs and PCDDs/PCDFs in sediment
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana myös internetistä www.ymparisto.fi/julkaisut
Tiivistelmä	Suomen ympäristökeskus järjesti pätevyyskokeen PCB-, PBDE, ja PCDD/PCDF-yhdisteiden määrittämisestä sedimenttinäytteestä syksyllä 2008. sedimenttinäytteen lisäksi osallistujille lähetettiin synteettinen näyte. Pätevyyskokeessa 10 laboratoriota osallistui PCB-yhdisteiden määritykseen, 4 laboratoriota PBDE-yhdisteiden määritykseen ja kolme laboratoriota PCDD/PCDF-yhdisteiden määritykseen. Määrityssuureen vertailuarvona käytettiin synteettisessä näytteessä laskennallista pitoisuutta ja sedimenttinäytteessä osallistujien tulosten robustia keskiarvoa. Tulosten arviointi tehtiin z-arvon avulla ja sen laskemisessa kokonaishajonnan tavoitearvoksi asetettiin synteettisessä näytteessä 20 % ja sedimenttinäytteessä määritettävästä yhdisteestä riippuen 30–50 %. Vähäisestä osallistujamäärästä johtuen sedimenttinäytteen PBDE- ja PCDD/PCDF-tulosten arviointia ei voitu tehdä. Tässä pätevyyskokeessa arvioituista tuloksista 86 % oli hyväksyttäviä.
Asiasanat	vesianalyysi, PCB. PBDE, PCDD, PCDF, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailukoe
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Publikationens titel	SYKE proficiency test 5/2007 PCBs, PBDEs and PCDDs/PCDFs in sediment	
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig också på internet www.ymparisto.fi/julkaisut	
Sammandrag	Under oktober 2007 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämningen av PCB, PBDE och PCDD/PCDF i sediment. Proven bestod av syntetiska och därtill ett sediment provet. Sammanlagt 10 laboratorier deltog i jämförelsen. Som referensvärde av analytens koncentration användes det teoretiska värdet eller det robust medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämförelsen var 86 % av alla resultat tillfredsställande, när i det syntetiska provet 20 % och i sediment 30–50 % av totalavvikelsen från referensvärdet accepterades.	
Nyckelord	vattenanalyser, PCB, PBDE, PCDD, PCDF, provningsjämförelse, vatten- och miljölaboratorier	
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