Suomen ympäristökeskuksen moniste

347

Irma Mäkinen and Jari Nuutinen

SYKE Proficiency Test 3/2005

PCB compounds from polluted soils

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Finnish Environment Institute

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CONTENT

APPENDICES

1 INTRODUCTION

The Finnish Environment Institute carried out the proficiency test for the determination of ten PCB congeners (PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p,-DDE and p,p-DDT) and total PCB from polluted soils in 2005.

The proficiency test was carried out in accordance with the international guidelines, ISO/IEC Guide 43 1 [1] and ILAC Requirements [2], IUPAC Recommendations [3] and ISO/DIS 13528 [4].

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

The responsibilities in organizing the proficiency test were as follows:
Irma Mäkinen, SYKE, coordinator
Jari Nuutinen, SYKE, analytical expert
Anne Markkanen, analytical assistant.

2.2 Participants

A total of 12 laboratories from Finland, Denmark, Sweden and Norway participated in the proficiency test (Appendix 1). The samples were distributed to 14 laboratories, but two laboratories did not reported the results. One laboratory reported only the results of the p,p-DDE and p,p-DDT.

2.3 Samples

2.3.1 Testing of purity of sample bottles

Purity of the sample bottles was checked before sample preparation. Ten randomly selected bottles were rinsed with iso-octane. Iso-octane was evaporated to a small volume (about 0.5 ml) and analyzed by GC-ECD. PCBs were not detected.

2.3.2 Sample preparation and delivery

Firstly, a standard solution containing a known concentration of different PCBs was prepared (see Table 1). The solution S1 was prepared in iso-octane. Before delivery, the sample ampoules were weighed to check the possible solvent evaporation. Evaporation has not obtained. The preparation of the sample has been presented in Appendix 2.

Secondly, the sample M1, the certified reference material (CRM LGC6113) was delivered. A supply of soil was obtained in industrial site. Eight bottles of CRM LGC6113 were purchased for preparation of the sample M1. The contents were combined, mixed and divided into a bottles containing about 30 g of soil. The soil sample M2 was sealant contaminated with PCBs. To achieve homogeneity, the soil sample M2 was dried at room temperature and sieved through a 0.5 mm sieve.

The sieved bulk materials were manually mixed until the sample was sufficiently homogenous. The sample M2 was divided into 64 portions containing about 100 g of soil. This was done using a rotary sample divider equipped with a vibratory sample feeder.

The proficiency test took place between 3 May and 8 August, 2005.

The results were asked to return until 9 August 2005. Two laboratories did not reported results.

Table 1. Samples and PCB congeners

Samples and PCB congeners	Sample type
S1: PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p-DDT, p,p-DDE	1 synthetic solution
M1: PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p-DDT, p,p-DDE and total PCB	1 certified reference material
M2: PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p-DDT, p,p-DDE and total PCB	1 contaminated soil

2.4 Sample testing

2.4.1 Homogeneity study

The soil sample M1 was a certified reference material. The uncertainties of eight PCBs have been reported in Appendix 3. The sample M2 was tested for homogeneity in the proficiency test 5/2001. The results were recalcualted using the new procedure for homogeneity testing [3] and the target deviations in this proficiency test. The sample M2 was considered homogenous.

2.4.2 Stability study

Stability of the sample S1 was tested, even PCB-compounds can be regarded stable (Appendix 4). There was not detected any changes in the sample.

2.5 Comments sent by the participants

The laboratory 3 commented on their own results. In calculation of the results for the samples M1 and M2 they had used an "old" calibration factor. The recalculated results are presented in Appendix 5.

2.6 Analytical methods and their uncertainties

2.6.1 Analytical methods

Various analysis methods were used for the PCB determination. Majority of them were in-house methods based on instrument applications or standard methods (Nordtest 1143-93 [5], ISO 10382 [6], EN-ISO 6468 [7]). Analytical methods are presented in Appendix 6. Two laboratories (lab 6 and lab10) did not reported their analytical methods.

For the extraction, six laboratories used shaking in 1 - 18 hours. The others used sonic water bath or stirring. The most common solvent combination used was acetone/hexane. Two laboratories used dichloromethne for extraction.

Only four laboratories reported the procedures for the clean-up. One laboratory used TBA-solution (Tetra-n-butylammonium hydrogen sulfate) and sulfuric acid for the clean-up. Other laboratories used sulfuric acid treatment followed by column chromatography either with aluminium oxide or silica.

For the detection, the laboratories used mass selective detector (MSD) or electron capture detector (ECD). Three of these ECD laboratories used two columns with different polarities attached to one injector. The length of columns varied from 30 m to 60 m. The laboratories 4, 5, 8, 9 and 11 used the column, which was shorter than 50 m. Splittless-injection was most commonly used.

Many various methods were used for the calculation of total PCB (Appendix 7). The most common ways were to calculate the sum of selected congeners (five or fifteen) or multiply the sum with an appropriate factor.

2.6.2 Uncertainties of the analytical methods

Most of the participants had estimated the uncertainties of their analytical methods (Appendix 8 and 9). The estimations were based mainly on the data of internal quality control procedures and the data obtained in method validation. The reported uncertainties varied mainly 20 - 40 %. One participant (lab 4) had reported the much lower uncertainties (4 – 9 %) than the others (Appendix 9). The uncertainties corresponded fairly well to the performance of the laboratories (Appendix 9). However, one should keep in mind that in this interlaboratory comparison the samples were dried, sieved and homogenized. Therefore, the reported uncertainty could be overestimated compared to real life laboratory samples.

Most of the laboratories reported same uncertainties for the standard solutions as for the soil samples. However, it is obvious, that uncertainties in analysis of standard solutions are smaller than uncertainties in analysis of soil samples.

2.7 Data treatment

2.7.1 Test of outliers and normality of data

Normality of the data was tested according to Kolmogorov-Smirnov normality test. The Hampel's test was used for rejecting of outliers before calculation of the mean value. Also before calculation of the robust mean from 1 to 4 outliers were rejected.

2.7.2 Assigned value and its uncertainty

The calculated value in the dilution of the solution was used as the assigned value for the PCBs in solvent sample S1 (Appendix 10).

The assigned values for the PCBs in the sample M1 (CRM LGC6113) were as reported in the certificate except PCB-28 and PCB-52. In these cases the robust mean (after rejection of outliers) was used as the assigned value. The robust mean values obtained in this proficiency were slightly lower than the certified values (Appendix 10). However, in each case the uncertainty of the certified value covered also the robust mean value.

The assigned value for the soil sample M2 was the robust mean of the results. The calculated values were compared with the mean value of the group of the laboratories, which obtained the results in the certified range (or close to the range) in analysis of the sample M1. There were only small differences between the robust mean of the data or the mean value of this group of the laboratories.

Because of few participants or accepted results the assigned values had not been reported in analysis of p,p-DDE and p,p-DDT from the samples M1 and M2, in analysis of PCB-156 from the sample M1 and in analysis of PCB-170 from the samples M1 and M2.

The uncertainty of the assigned value was estimated for the sample M2. For the estimation of uncertainty, the robust standard deviation of the results used for calculation of the assigned values was used [4]. The uncertainties are presented in Appendix 10.

2.7.3 Target value for total deviation

The total target deviation (s_{target}, %) used for calculation of the z scores was estimated from the robust standard deviations of the results, the uncertainty of the CRM (the sample M1) and the measurements uncertainties reported by the participants (Table 1). The s_{target} was 20 % (95 % confidence level) in analyses of the solvent sample S1. In analysis of the soil samples it was 26 - 40 %. After reporting of the preliminary data the target deviations had been raised in analysis of the sample M2. However, in analyses of PCB's of the soil sample the ratio u/s_{target} was at least 4. It was higher than the new criteria ($u/s_{target} < 0,3$) presented in the new version of our protocol prepared after this proficiency test was started.

2.7.4 Evaluation of performance

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

$$z = (x_i - X)/s$$

where
x_i = the reported value of the participant
X = the assigned value
s = the target total deviation ($s_{target\,(\%)}$).

z scores can be interpreted as follows:

$\|z\| < 2$	"satisfactory" results
$2 \leq \|z\| \leq 3$	"questionable" results
$\|z\| > 3$	"unsatisfactory" results.

The z scores are presented in Appendix 12 (the results of each participant) and the summary of z scores is presented in Appendix 13.

The organizing laboratory (SYKE) had the code 2 in this proficiency test.

3. RESULTS AND DISCUSSION

3.1 Results

The robust standard deviation of the results was in general 20 - 40 % in analysis of the soil samples M1 and M2. Of course, it was lower (3 - 20 %) in analysis the synthetic sample S1. The results varied most in analysis of p,p-DDT, PCB-170, PCB-28, PCB-52 and total PCB. One reason can be the use of several methods or method modifications. The variation of the results has varied even more (45 - 60 %) in the Polish proficiency test for analysis of PCBs in sediment [8]. However, in the Polish profiency test the concentrations of PCB were some lower than in this proficiency test.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
p,p-DDE	M1	µg/kg		5.50	5.47	5.35	1.12	20,5	4		
	M2	µg/kg		27.07	35.80	36.00	0.94	2,6	6		
	S1	µg/ml	0,133	0.13	0.13	0.13	0.029	22,3	4		
p,p-DDT	M1	µg/kg		5.35	4.95	4.76	1.57	31,7	6		
	M2	µg/kg		14.43	14.43	11.20	18.48	128	4		
	S1	µg/ml	0,128	0.12	0.12	0.11	0.033	28,4	4	20	50
PCB-101	M1	µg/kg	23	19.70	20.48	21.00	4.42	21,6	10	26	80
	M2	µg/kg	242	227.85	234.06	237.95	50.30	21,5	11	35	91
	S1	µg/ml	0,081	0.082	0.086	0.084	0.009	10	11	20	73
PCB-105	M1	µg/kg	13,3	13.78	13.30	13.60	1.56	11,7	5		
	M2	µg/kg	90,8	90.82	90.82	93.70	20.81	22,9	6	40	100
	S1	µg/ml	0,051	0.050	0.051	0.050	0.005	9,9	6	20	83
PCB-118	M1	µg/kg	28	27.63	26.70	27.20	4.70	17,6	9	32	89
	M2	µg/kg	224	209.59	215.05	212.50	45.02	20,9	10	30	90
	S1	µg/ml	0,098	0.093	0.096	0.096	0.011	11,2	10	20	80
PCB-138	M1	µg/kg	43	38.52	40.07	40.75	9.31	23,2	10	30	80
	M2	µg/kg	235	220.88	226.39	227.00	56.49	25	11	35	91
	S1	µg/ml	0,132	0.13	0.14	0.14	0.017	11,9	11	20	64
PCB-153	M1	µg/kg	42	34.04	34.65	34.90	8.55	24,7	10	29	80
	M2	µg/kg	179	180.49	178.76	178.00	37.06	20,7	11	35	73
	S1	µg/ml	0,128	0.14	0.14	0.14	0.011	7,7	11	20	82
PCB-156	M1	µg/kg		8.58	8.58	8.40	2.40	27,9	4		
	M2	µg/kg	27,8	27.80	30.20	29.80	7.81	25,9	5		
	S1	µg/ml	0,029	0.030	0.031	0.029	0.006	19	5	20	60
PCB-170	M1	µg/kg		13.50	14.07	15.50	6.55	46,6	3		
	M2	µg/kg		33.70	33.70	31.10	21.70	64,4	3		
	S1	µg/ml	0,028	0.058	0.028	0.028	0.002	6,6	3		
PCB-180	M1	µg/kg	29	26.96	27.64	27.70	7.42	26,9	10	28	70
	M2	µg/kg	68,4	68.19	68.38	72.00	16.84	24,6	11	35	82
	S1	µg/ml	0,08	0.080	0.080	0.079	0.011	13,3	11	20	82
PCB-28	M1	µg/kg	11	10.21	11.53	11.10	3.03	26,3	9	25	67
	M2	µg/kg	13,6	12.88	11.19	11.46	9.24	82,6	10		
	S1	µg/ml	0,048	0.058	0.057	0.057	0.010	18,1	10	20	50
PCB-52	M1	µg/kg	8,7	8.26	8.24	8.35	3.04	36,9	10	30	60
	M2	µg/kg	150	143.23	150.02	140.00	49.02	32,7	11	40	73
	S1	µg/ml	0,052	0.055	0.056	0.056	0.005	9,3	11	20	91
Total-PCB	M1	µg/kg	452	464.00	489.56	436.00	186.78	38,2	9		
	M2	µg/kg	3301	3921.00	3711.65	3410.50	1818.60	49	10		

Table 1. Summary of the proficiency test

3.2 Effect of different analytical methods on the results

3.2.1 Effect of different analytical methods

The laboratories used mainly one of the PCB congener as an internal standard (30, 53, 77, 185, 208 or 209). The results were not satisfactory, when the internal standard was something else (e.g. Naphthalene-D8 or decafuorobiphenyl) than a PCB congener (lab 3 and 4). The laboratories used from three to five calibration points for the calibaration. Mass-labelled PCB congeners ($^{13}C_{12}$) are recomended to use for the internal standards in MS measurements.

3.2.2 Chromatography

According to some chromatograms, coelution can occurr and the result for PCB 28 can been overestimated. Using a short column (≤ 30 m), PCB 28 can coelute with PCB 31. Some laboratories report routinely the sum of PCB 28 and 31, and they did not report PCB 28 in this intercomparison. No major interferences are usually observed for PCBs 52, 153, 170 and 180.

When using a short (DB 5 type) column the following interferences may occure according to literature [9]:
- PCBs 84 and 90 may interfere PCB 101.
- PCB 105 can coelute with PCB 132
- PCB 118 can coelute with PCB 149.
- PCB 138 can coelute with PCBs 160 and 163.

PCB 138 has usually one of the largest peaks. PCB 156 also has its coeluters PCBs 171 and 202.

Coelution can be excluded with MSD, if the coeluted PCB congeners have different masses for the selection of the ions for quantitation. If PCB 28 and 31 are eluated at the same time, it can be impossible to separate them from each other even in use of MSD.

It is also highly recommended to use columns over 50 m long due to the coelution problems [10]. When using short columns, the resolution is quite poor for many PCBs and severe coelution may occur. This problem seemed to be prevalent, if an ECD with only one column was employed. The resolution could improve by changing the oven program to have a slower temperature gradient in the middle of the program, or higher starting temperature for the GC oven.

3.2.3 Total PCB

There were several different ways to calculate the total PCB (see Appendix 7). The laboratories used more or less similar approach in calculations. Five laboratories calculated the total PCB by summing selected PCB congeners (five to fifteen). Four laboratories calcutated the sum of selected PCB congeners and multiplied the sum with an appropriate factor. Only one laboratory used a fixed formula.

According to some experts, the only way is to determine all the PCBs and report the sum of these as a total PCB. On the other hand, the use of multipliers have been regarded as an adequate procedure. Calculation of PCB content is presented in EN 12766-2 standard; the sum of six PCB congeners (28, 52, 101, 153, 138, 180) is multiplied with multiplication factor of five [11].

In many environmental samples, especially in sediments or in biological samples, the resemblance to the technical PCB mixtures is not that obvious due to the metabolism and other alterations. Also organochlorine pesticides may interfere. In these cases the mixture of different technical mixtures should be used for multiplier determination. However, information about individual PCB congeners is often more important than the total PCB for toxicity or risk evaluation.

3.4 Estimation of performance

In this proficiency test 77 % of the participating laboratories were able to report satisfactory results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval (Appendix 13).

In analysis of PCB's 101, 138, 156 and 28 from the solvent sample S1, only 50 – 73 % of the results were satisfactory when the target standard deviation was 20 % (Appendix 13). This means, that there have been serious problems in calibration procedure of these congeners. In analysis of other congeners from the sample S1 80 – 91 % of the results were satisfactory.

In analysis of PCBs 101,105, 118 and 138 from the soil samples M1 and M2 the results were most satisfactory (≥ 80 %). The PCB congeners 28 and 52 turned to be most critical analytes. The performance in analysis of PCB 105 (the sample M1), PCBs 156 and 170 (the samples M1 and M2), total PCB and p,p-DDE and p,p-DDT had not been evaluated because of few reported results. Different calculation procedures used in estimation of total PCB have effected on the variation of the results, which was 34 – 37 %.

However, in analysis of the certified material M1, 56 – 80 % of the results were inside the confidence intervals reported in the certificate. In particular, on the basis of the results, the PCB congeners 28, 52, 138 and 180 seemed to be most critical. The calculated robust mean was much lower than the reported certified value in ananlysis of PCBs 28 and 52. Thus the former value was used as the assigned value instead of the certified value. The performance in analysis of PCB 105 was not evaluated due to few participants.

The SYKE proficiency test for analyses of PCB compounds from polluted soils was carried out for the second time. The results of this PT were fairly similar than in the first PT in analysis of most PCB congeners. However, quality of the results can be improved by applying efficient validation procedures and quality assurance systems and the participants should check particularly calibrants and some technical procedures. Harmonization of analytical methods for analysis of PCBs could be reasonable.

4 SUMMARY

The Finnish Environment Institute carried out the interlaboratory comparison test for the determination of ten PCB congeners (PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p,-DDE and p,p-DDT) and total PCB from polluted soils in summer 2005. The samples were distributed to 14 laboratories, but two laboratories did not reported the results. One laboratory reported only the results of the p,p-DDE and p,p-DDT.

One standard solution containing a known concentration of different PCBs were prepared. The certified reference material (CRM LGC6113) and one soil sample contaminated with PCBs were delivered to the participating laboratories.

Various analysis methods were used for the PCB determination. Most of them were in-house methods based on instrument applications or standard methods. Particularly, for the determination of total PCB several different procedures, were used.

As the assigned value for the PCBs, the calculated concentration was used in solvent samples, the certified values the robust mean values were used for the soil samples.

In this proficiency test, 77 % of the participating laboratories were able to report satisfactory results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval. In analysis of PCBs 101,105, 118 and 138 from the soil samples the results were most satisfactory. The PCB congeners 28 and 52 turned to be most critical analytes. Performance has not been evaluated for each sample in analysis of PCBs 105, 156 and 170, total PCB and p,p-DDE and p,p-DDT.

The SYKE proficiency test for analysis of PCB compounds from polluted soils was carried out for the second time. The results were fairly satisfactory in analysis of most PCB congeners, when compared with some international comparisons.

5 YHTEENVETO

Suomen ympäristökeksuksen laboratorio järjesti kesällä 2005 pätevyyskokeen PCB-yhdisteiden (PCB 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p,-DDE ja p,p-DDT) ja kokonais-PCB:n analysoimiseksi saastuneista maista. Pätevyyskokeeseen ilmoittautui 14 laboratoriota, joista kaksi laboratoriota ei toimittanut tuloksia. Lisäksi yksi laboratorio analysoi vain yhdisteet p,p-DDE ja p,p-DDT.

Pätevyyskokeessa toimitettiin standardiseos, saastuneesta maasta valmistettu varmennettu vertailumateriaali ja saastunut maanäyte.

Laboratoriot käyttivät useita analyysimenetelmiä tai eri menetelmien variaatioita. Varsinkin kokonais-PCB:n laskemiseen käytettiin useita eri menettelyjä.

Tässä pätevyyskokeessa 77 % tuloksista oli tyydyttäviä, kun pätevyyden arvioinnissa käytettiin kokonaishajonnan tavoitearvoa 20 – 40 % vertailuarvosta 95 % merkitsevyystasolla. PCB-yhdisteiden 101, 105, 118 ja 138 tuloksista oli eniten tyydyttäviä (≥ 80). PCB-yhdisteet 28 ja 52 osoittautuvat vaikeimmin analysoitavaksi. PCB-yhdisteiden 105, 156 ja 170, kokonais-PCB sekä p,p-DDE ja p,p-DDT tuloksille ei arviointia tehty ainakaan kaikille näytteille raportoitujen tulosten vähäisen lukumäärän vuoksi.

SYKEn pätevyyskoe PCB-yhdisteiden määrittämiseksi saastuneista maista järjestettiin toisen kerran. Tulokset olivat jokseenkin tyydyttäviä useimpien PCB-yhdisteiden osalta myös verrattaessa niitä kansainvälisiin pätevyyskokeisiin.

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APPENDIX 1. PARTICIPANTS IN THE PROFICIENCY TEST 3/2005

Alcontrol Laboratories, Linköping, Sweden

Analycen Nordic AB, Lindköping, Sweden

Ekokem Oy Ab, Riihimäki, Finland

Eurofins Norge A/S, Oslo, Norway

Helsingin kaupungin ympäristökeskus, ympäristölaboratorio, Helsinki, Finland

Insinööritoimisto Paavo Ristola Oy, Hollola, Finland

IVL, Swedish Environmental Institute, Göteborg, Sweden

Jyväskylän yliopisto, Ympäristöntutkimus, Jyväskylä, Finland

Lahden tiede- ja yrityspuisto Oy, Lahden tutkimuslaboratorio, Lahti, Finland

Milana A/S, Helsingør, Denmark

SGS Inspection Services Oy, Hamina, Finland

Suomen ympäristökeskus, laboratorio, Helsinki, Finland

APPENDIX 2. PREPARATION OF THE SAMPLES

The synthetic sample S1

The synthetic sample S1 was a dilution of combined PCB and Pesticide solutions. PCB solution contained 23 PCB-congeners (8, 18, 28, 31, 52, 66, 77, 101, 105, 110, 118, 126, 128, 129, 138, 149, 153, 156, 169, 170, 180, 187 and 194) and Pesticide solution contained 14 pesticides, both in iso-octane. The concentration of the compounds in the solutions are presented in the following table. The PCB and Pesticide stock solutions were made of single PCB congeners (AccuStandard) and pesticides (Dr. Ehrenstorfer), respectively. The solutions were then diluted by weighing 3 ml of the both solutions and 24 ml iso-octane. For calculations, densities of 0,6919 g/ml was used for iso-octane.

PCBs	Pesticides	Iso-octane	Iso-octane + PCBs + Pesticides
~ 3 ml	~3 ml	~24 ml	~30 ml
2,0597 g	2,1094 g	16,6203 g	20,7894 g

	Dilution factor
PCBs	2,0597 g / 20,7894 g = 0,099075
Pesticides	2,1094 g / 20,7894 g = 0,101465

PCBs		**S1**
	ng/ml	**ng/ml**
PCB28	487,46	**48,29**
PCB52	518,99	**51,42**
PCB101	815,62	**80,81**
PCB118	985,76	**97,66**
PCB153	1287,84	**127,59**
PCB105	516,29	**51,15**
PCB138	1330,64	**131,83**
PCB156	292,75	**29,00**
PCB180	809,82	**80,23**
PCB170	284,03	**28,14**

Pesticides		**S1**
	ng/ml	**ng/ml**
PDDE	1312,95	**133,218**
PDDT	1260,89	**127,937**

The prepared dilution was carefully mixed and sampled into a 1,5 ml portions. Small amber glass bottles with a teflon-lined seal and a screw cap was used. Bottles were labelled and numbered according to filling order.

The weight of each tube was recorded at SYKE and at the participating laboratory. The differences of these two weights were as follows:

Tube	SYKE (g)	Participating laboratory (g)	Difference - %
2	7,5526	7,5711	0,24
5	7,5560	7,561	0,07
6	7,5279	7,5332	0,07
11	7,5473	7,5516	0,06
13	7,6220	7,6239	0,02
14	7,6467	7,6488	0,03
15	7,5880	7,5924	0,06
16	7,4895	7,4939	0,06
17	7,5980	7,6032	0,07
18	7,5072	7,5112	0,05
19	7,4970	7,5078	0,14

The soil sample M1

The sample was the certified soil sample (CRM LGC6113). The values for PCB-28, PCB-52, p,p-DDE and p,p-DDT were not certified.

Sample	PCB µg/kg							
M1	101	105	118	138	153	180	28	52
µg/kg	23	13,3	28	43	42	29	14 (X_{rob} = 11)	11 (X_{rob} = 8,7)

The soil sample M2

The sample M2 was the contaminated soil containing sealant and it was distibuted also in the proficiency test SYKE 5/2001.

The obtained robust means were as follows:

Sample	PCB µg/kg								
M2	101	105	118	138	153	156	180	28	52
µg/kg	242	90,8	224	235	179	27,8	68,4	13,6	150

APPENDIX 3. RESULTS OF THE HOMOGENEITY STUDY

The synthetic sample S1

Three tubes of the sample S1 was tested. There were not differences between the results.

The soil sample M1

The sample was a certified reference material (CRM LGC6113).

The soil sample M2

Homogeneity was tested as duplicate determinations from eight bottles of the sample M2. The analytical variation s_a and the between bottle variation s_{bb} was calculated using one-way variance analysis. For this proficiency test the results were recalculated by taking into account the new procedure (3) for the treatment of homogeneity testing data and the target values of total deviation.

PCB	PCB µg/kg	s_{target}	$0{,}3s_t$	s_a	s_a	$s_a/s_{target}<0{,}5$	s_{bb}	s_{bb}	$s_{bb}^2<c$
		%			%			%	
101	259,4	**17,5**	13,62	**4,96**	1,9	yes	**3,5**	1,4	yes
105	94,18	**20**	5,65	**1,4**	1,4	yes	**0,99**	1,1	yes
118	261,7	**15**	11,78	**3,61**	1,4	yes	**2,77**	1,1	yes
138	222	**17,5**	11,66	**3,2**	1,4	yes	**2,26**	1	yes
153	194	**17,5**	10,19	**2,6**	1,3	yes	**2,46**	1,3	yes
180	72,25	**17,5**	3,79	**1,39**	1,9	yes	**1,34**	1,9	yes
52	164,3	**20**	9,86	**2,81**	1,7	yes	**2,58**	1,6	yes

The analytical variation s_a was accepted, because $s_a/s_{target}<0{,}5$.

The between-bottle variation s_{bb} was smaller than the criteria $c = F1 \cdot s_{all}^2 + F2 \cdot s_a^2$, where $s_{all}^2 = (0{,}3s_{target})^2$,
F1 = 2,01 and F2 = 1,25, when the number of bottles was eight.

APPENDIX 4. RESULTS OF THE STABILITY STUDY

Stability of the synthetic sample S1 was tested. The results (µg/ml) were as follows:

PCB	After preparation	After 21 Days	After 68 Days	after 112 Days
101	80,35	81,04	83,41	81,26
105	50,34	52,17	53,74	51,16
118	97,32	99,17	103	97,99
138	130,9	132,7	136,6	131,3
153	126,8	130,0	134,3	128,8
156	28,69	29,35	30,15	28,53
170	28,04	28,94	29,24	28,16
180	80,35	81,30	83,03	79,47
28	48,07	48,74	48,81	47,15
52	50,68	51,73	51,55	50,03
p,p-DDE	130,6	132,6	137,0	132,2
p,p-DDT	126,9	127,4	139,0	127,0

On the basis of the standard deviation of the regression line tested with t-statistics the significant trend was not obtained.

APPENDIX 5. COMMENTS SENT BY THE PARTICIPANTS

<table>
<tr><th>Lab</th><th>Comment</th><th>Action/SYKE</th></tr>
<tr><td>3</td><td>The laboratory calculated the results for the samples M1 and M2 using the "old" calibration factor. The new results (µg/kg) were as follows:
<table>
<tr><th>PCB</th><th>M1</th><th>M2</th></tr>
<tr><td>28</td><td>15</td><td>17</td></tr>
<tr><td>52</td><td>8</td><td>110</td></tr>
<tr><td>101</td><td>20</td><td>182</td></tr>
<tr><td>118</td><td>27</td><td>218</td></tr>
<tr><td>153</td><td>36</td><td>185</td></tr>
<tr><td>105</td><td>24</td><td>129</td></tr>
<tr><td>138</td><td>30</td><td>165</td></tr>
<tr><td>170</td><td>13</td><td>34</td></tr>
<tr><td>180</td><td>23</td><td>60</td></tr>
<tr><td>total PCB</td><td>660</td><td>3590</td></tr>
</table></td><td>No action</td></tr>
</table>

APPENDIX 6. ANALYTICAL METHODS

Lab[1)]	Extr.solvent	Extr.method/time	Clean-up	Injection, vol.	1: Column m/mm/µm 2: Column		Oven-T °C/min	Detector	Gas mL/min	Standard, µg/ml
1	acetone/n-hexane	stirring 90 min	TBA/H_2SO_4	splitless, 2 µl	CP-Sil 5 CB CP-Sil 8 CB	50/0,25/0,25 50/0,25/0,25	125°,7.5°/1 to 190°, 2°/1 to 275°/10	ECD	H_2, 1,6	PCB 53; 0,01 - 0,05
2	acetone/hexane	ultrasonic. 60 min		splitless, 1 µl	HP 1701 HP-5	60/0,25/0,25 60/0,25/0,25	90°/3, 30°/1 to 215°/42, 5°/1 to 270°/10	ECD	Helium	PCB 53; 0,23-10-42
3	acetone/hexane	ultrasonic. 60 min		splitless, 1 µl				ECD	Helium	Decafluorobiphenyl 0,004 - 0,4
4	dichloromethane	shaker 1080 min		split/splitless	HP 5 MS	30/0,25/0,25	40°, 20°/1 to 200°, 8°/1 to 290°, 20°/1 to 325°	MS	Helium	Naphtalen D8
5	dichloromethane	shaking 120 min		split/splitless 1 µl	DB-5MS	30/0,25/0,5	60°, 12°/1 to 310°/10	MS: HP 5973	Helium, 1	PCB 77; 0,01 - 1,0
7	acetone/hexane	ultrasonic. and shaking 60 minx2	H_2SO_4 + alumina column	splitless 1 µl	Zebron ZB 5 ms	60/0,25/0,25	80°/1, 15°/1 to 220°, 2°/1 to 270°, 30°/1 to 320°/5	MS	Helium, 0,7	2,4,6-trichlorobiphenyl; 0,005 - 1,1
8	acetone/hexane	ultrasonic. 30 min		pulsed splitless 1 µl	HP-5	30/0,25/0,25	80°/1.5, 7.5°/1 to 310°/5	MSD	Helium, 1	PCB 185; 0,02 - 0,4
9	acetone/hexane	shaking 60 min ultrasonic. 20 min		autom. sampler 1 µl	NB-54 NB-1701	30/0,32/0,25 30/0,32	150°, 5°/1 to 250°/20	ECD	Helium, 1	PCB 30; 0,1 - 0,4
11	acetone/hexane	ultrasonication 5 min shaking 60 min	H_2SO_4 + Na_2SO_4 + silica	splitless 1 µl	DB-35MS (HP 123-3832)	30/0,32/0,25	50°/2, 20°/1 to 150°, 6°/1 to 260°/15	ECD	Helium, 2	PCB 209; 0,01 - 0,3
12	acetone/hexane		H_2SO_4 + Na_2SO_4- concentration + alumina column	on column 0,8 µl	CP-SIL 8CB	50/0,25/0,25	60-280°	ECD	Helium, 1,5	Nonachlorobiphenyl (PCB 208); 0,0002 - 0,1

[1)] lab 6 and 10 did not reported their analytical methods.

The reported references of the analytical methods: ISO 10387, Nordtest TR 329, ISO 10382, EN ISO 6468 and in-house methods.

APPENDIX 7. METHODS USED FOR DETERMINATION OF TOTAL PCB

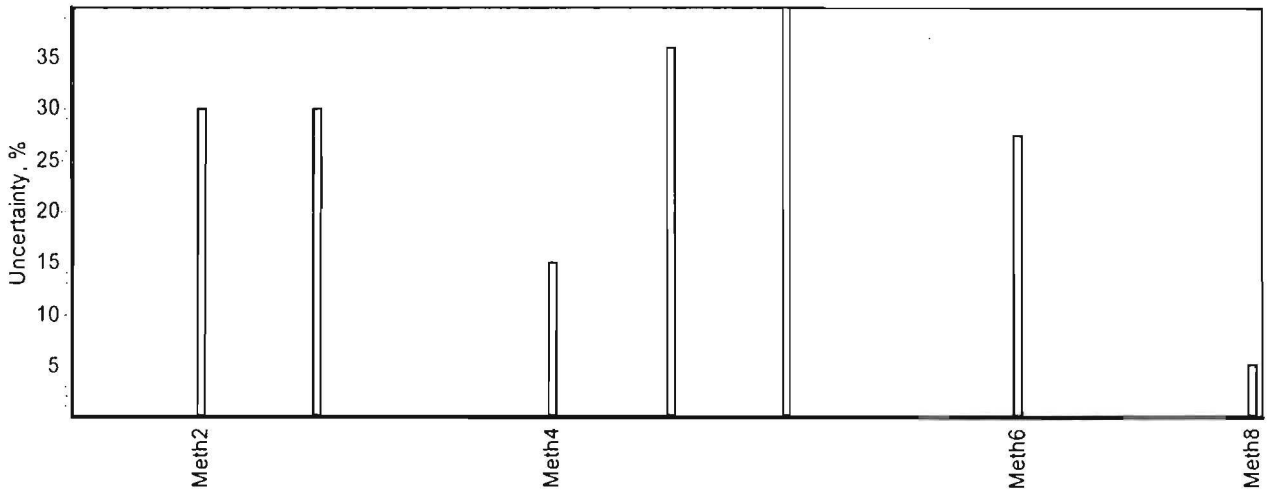
Lab	Calculation method for total PCB
1	Sum of seven congeners (28, 52, 101, 118, 138, 153 and 180) multiplied with factor 3. The pattern in the sample was Aroclor 1260 that gave the factor.
3	Sum of six congeners (28, 52, 101, 138, 153 and 180) multiplied with factor 5.
4	Sum of 15 congeners (28, 31, 52, 77, 101, 105, 118, 126, 128, 138, 153, 156, 169, 170 and 180).
5	Sum of seven congeners (28, 52, 101, 118, 138, 153 and 180).
6	The pattern of the sample chromatogram was compared with technical solutions. The amount of total PCB in the sample was estimated with the selected congeners and summing them.
7	Sum of nine congeners (28, 52, 101, 105, 118, 138, 153, 156 and 180) multiplied with factor 3,303
8	The pattern of the sample chromatogram was compared with Aroclor solutions. Sum of seven congeners (28, 52, 105, 118, 138, 153 and 180) were calculated in the selected Aroclor solution, divided with the concentration of the Aroclor solution and multiplied by one hundred (= Aroclor-%). In the sample the same congeners were added together, multiplied by one hundred and divided with Aroclor-%.
9	Sum of 10 peaks. The results of the sample were calculated comparing with Chlophen A60.
10	Sum of 5 to 7 peaks. The pattern of the sample chromatogram was compared with Aroclor and Chlophen solutions.
11	The pattern of the sample chromatogram was compared with Aroclor solutions. M1: Sum of six congeners (31/28, 52, 101, 138, 153 and 180).The factor was 4,5. M2: Sum of six congeners (31/28, 52, 101, 138, 153 and 180).The factor was 3,8

APPENDIX 8. MEASUREMENT UNCERTAINTIES REPORTED BY THE PARTICIPANTS

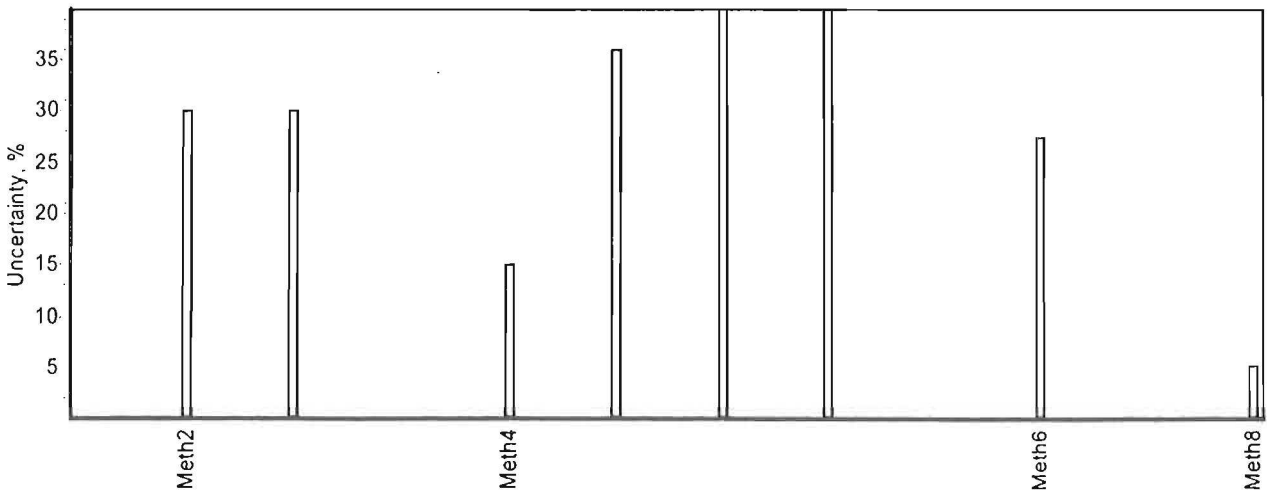
Measurement uncertainties were estimated by using the procedures as follows:

1. the variation of the results in X chart (for artificial samples)
2. the variation of the results in X chart and the variation of the replicates (r- or R- chart for real samples)
3. the variation of the data obtained in analysis of CRM
4. the data obtained in method validation (and IQC)
5. the EURACHEM-Guide "Quantifying Uncertainty in Analytical Measurements"
6. the NORDTEST report TR 537
8. other procedure

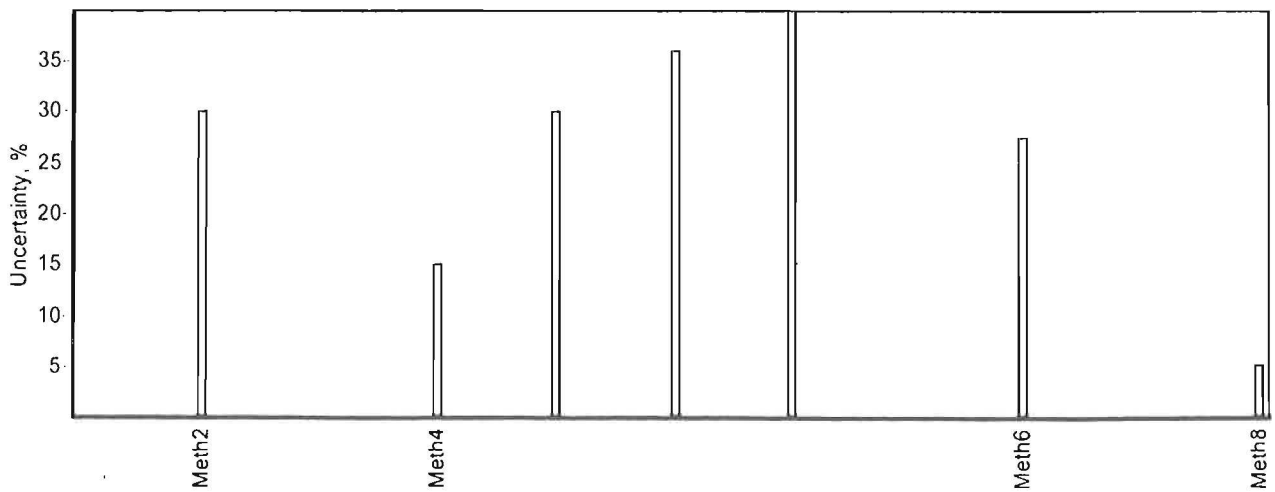
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* M1



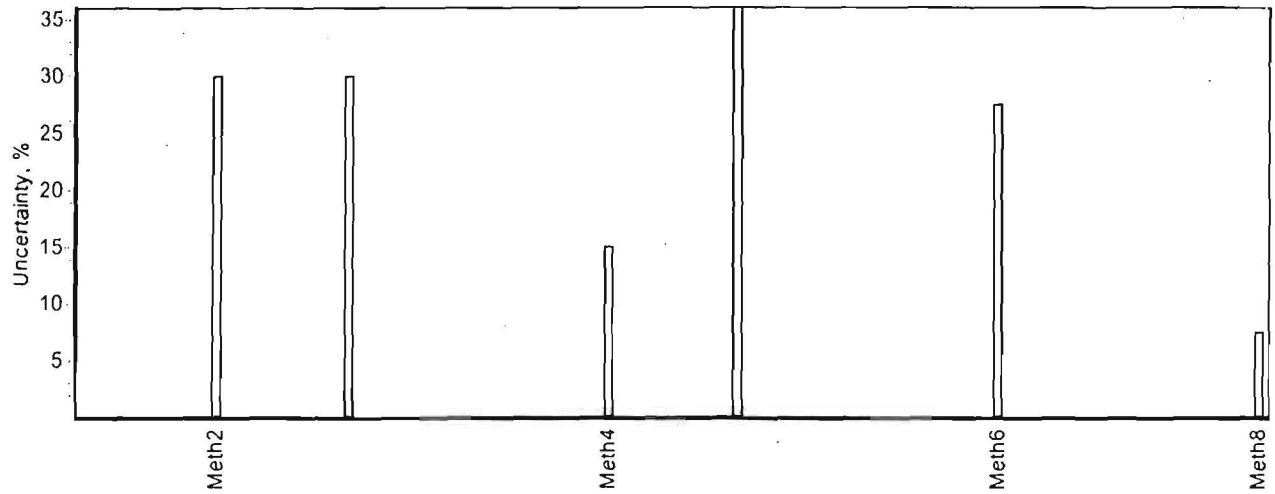
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* M2



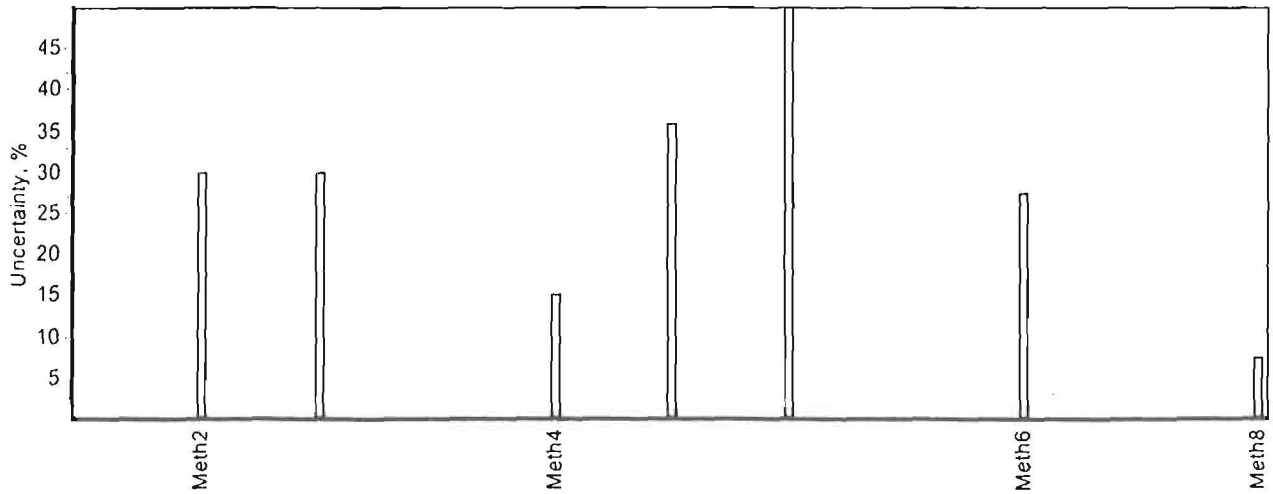
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* S1



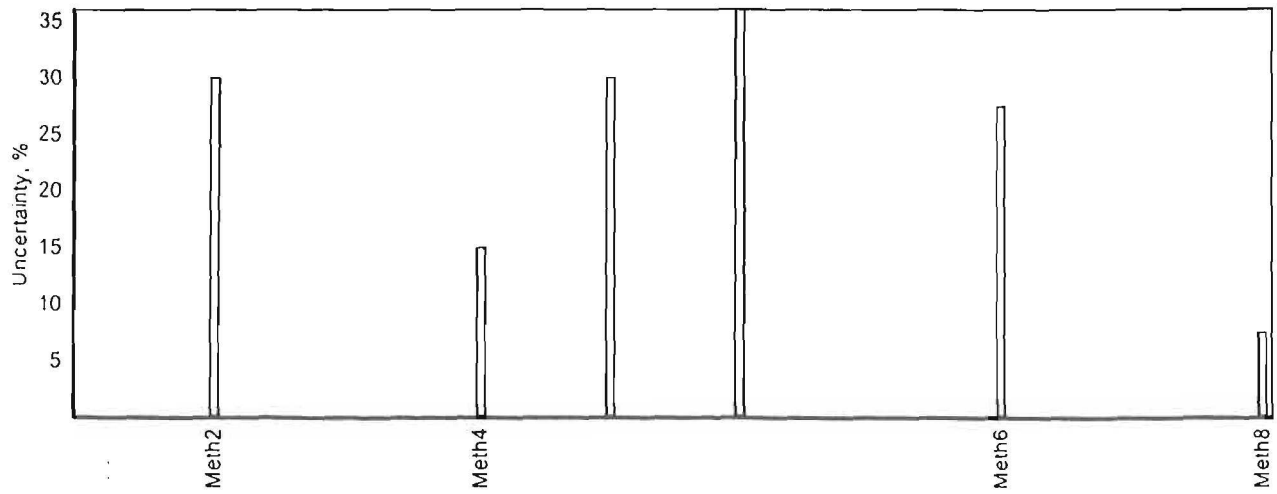
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* M1



Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* M2

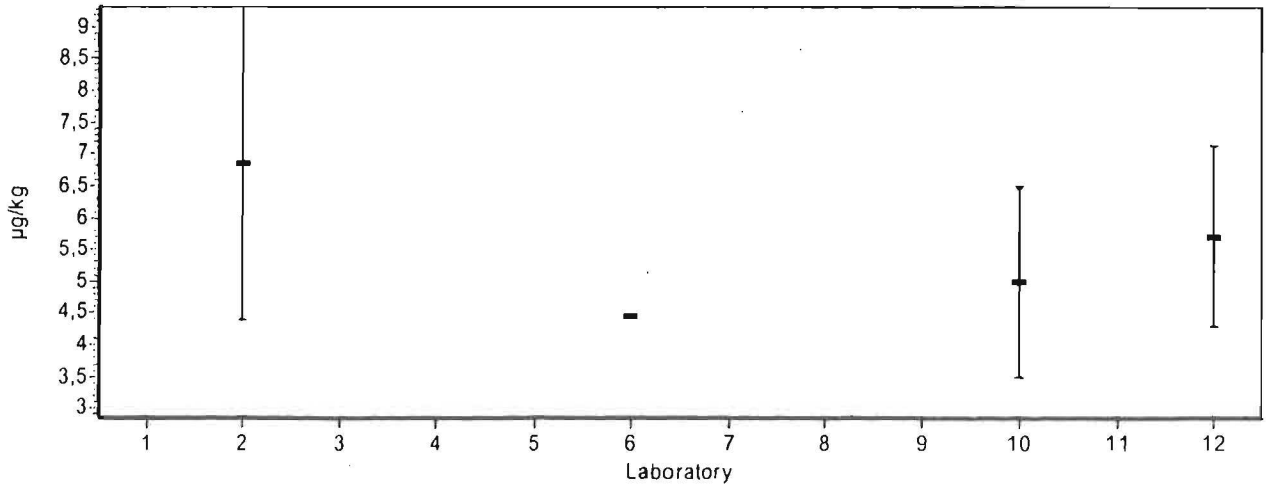


Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* S1

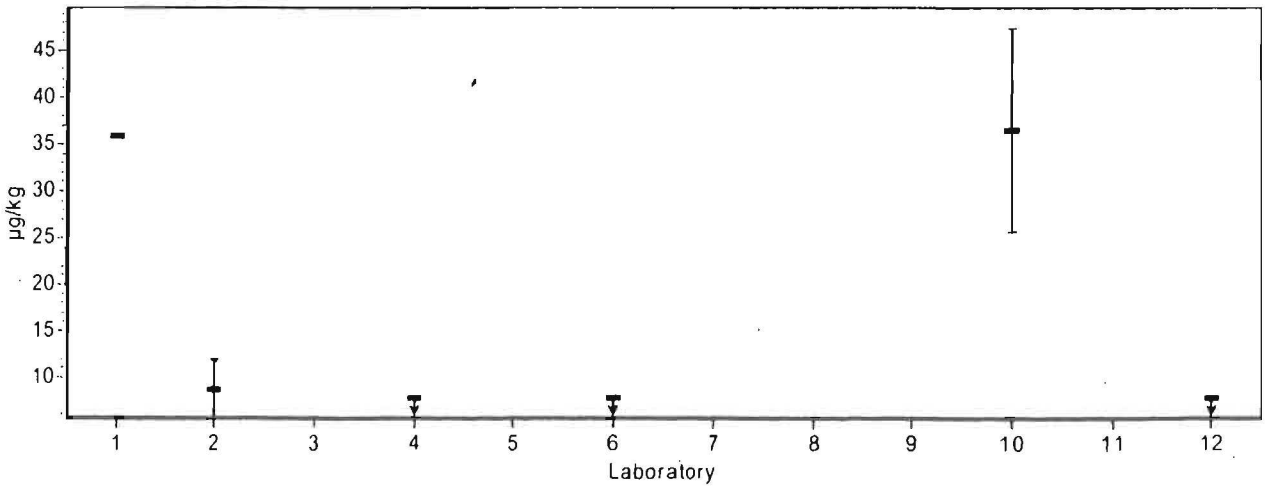


APPENDIX 9. GRAPHICAL PRESENTATION OF THE RESULTS AND THEIR MEASUREMENT UNCERTAINTIES

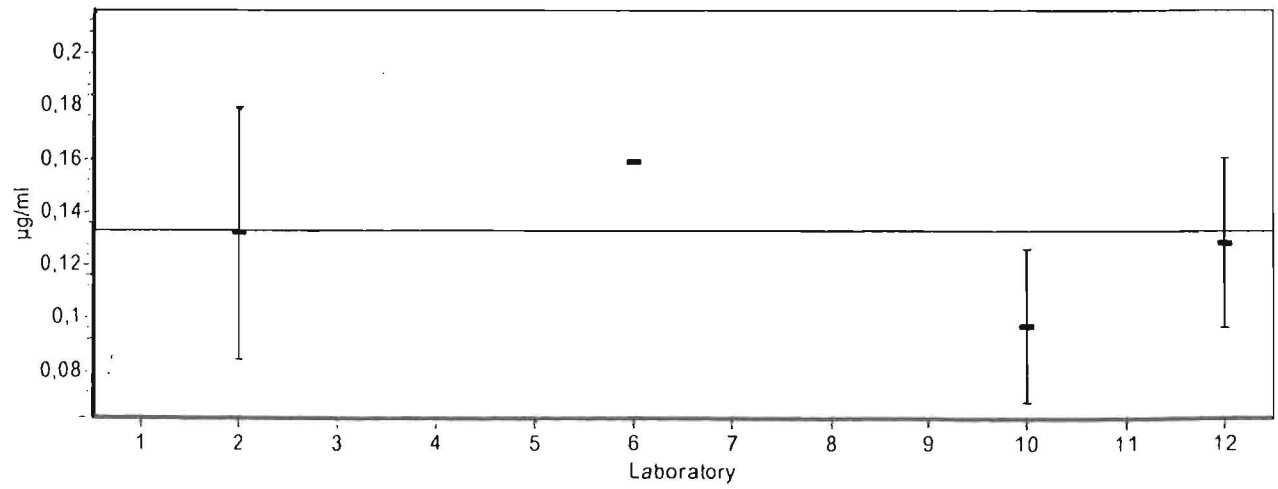
Analyytti *(Analyte)* **p,p-DDE** Näyte *(Sample)* M1



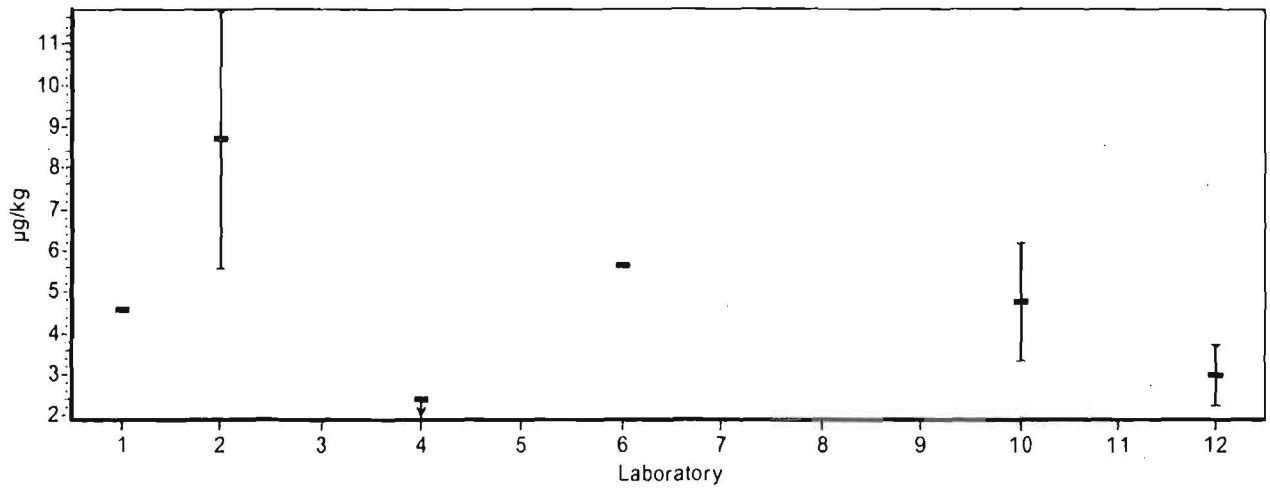
Analyytti *(Analyte)* **p,p-DDE** Näyte *(Sample)* M2



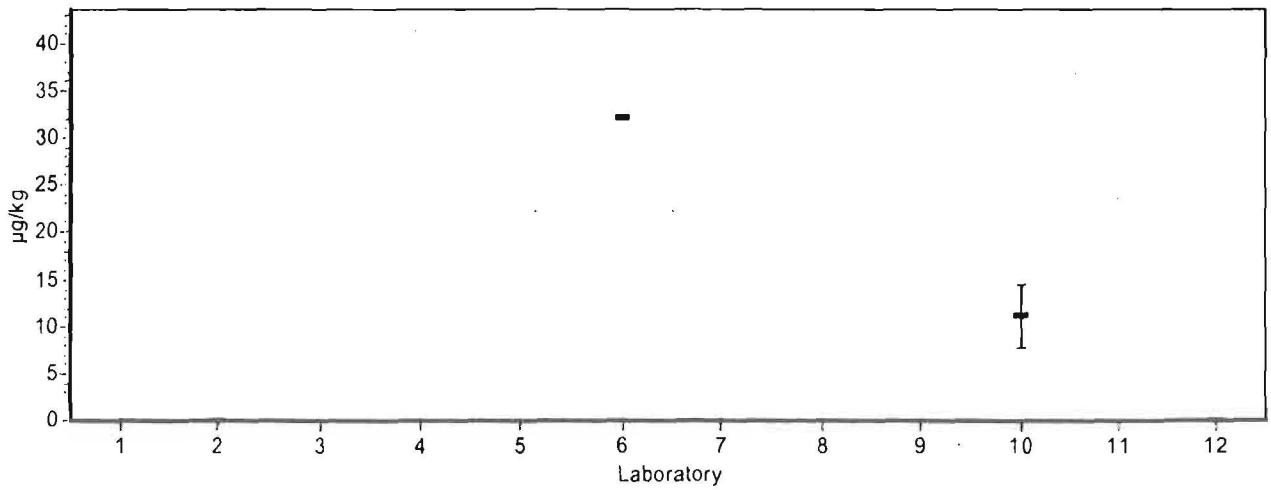
Analyytti *(Analyte)* **p,p-DDE** Näyte *(Sample)* S1



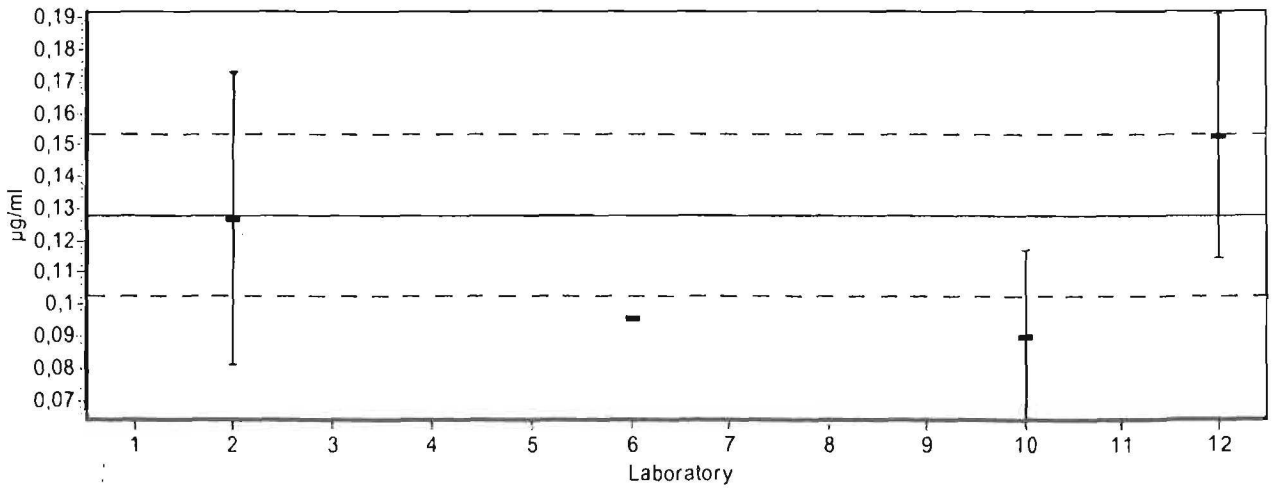
Analyytti *(Analyte)* **p,p-DDT** Näyte *(Sample)* M1



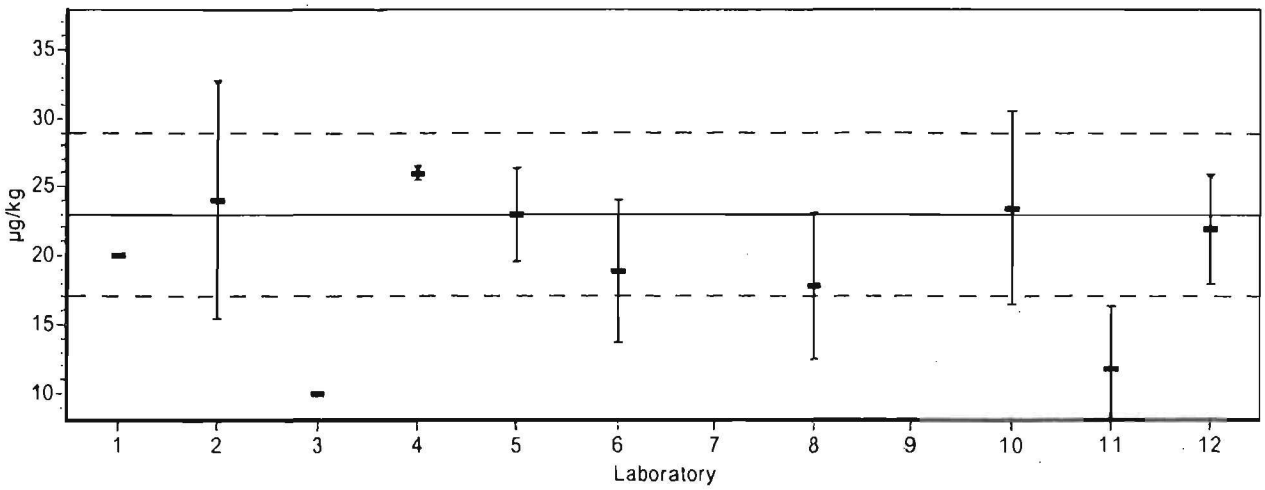
Analyytti *(Analyte)* **p,p-DDT** Näyte *(Sample)* M2



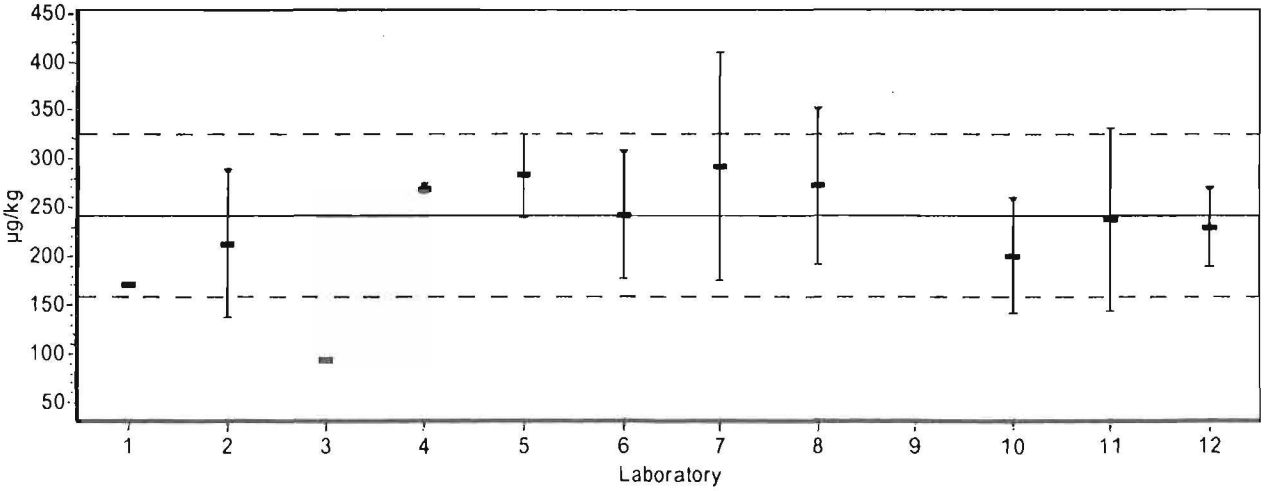
Analyytti *(Analyte)* **p,p-DDT** Näyte *(Sample)* S1



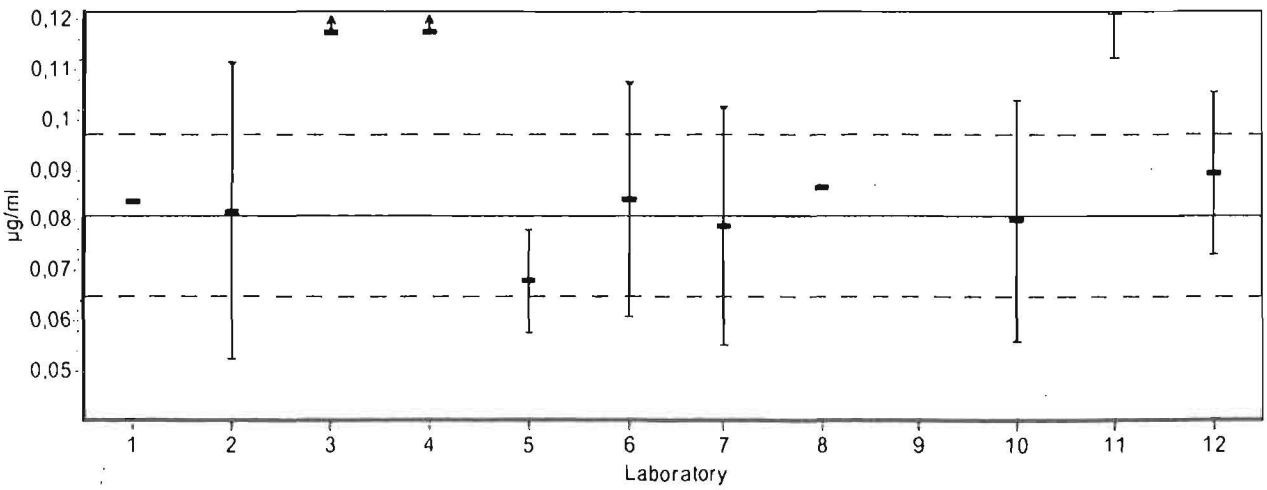
Analyytti *(Analyte)* **PCB-101** Näyte *(Sample)* M1



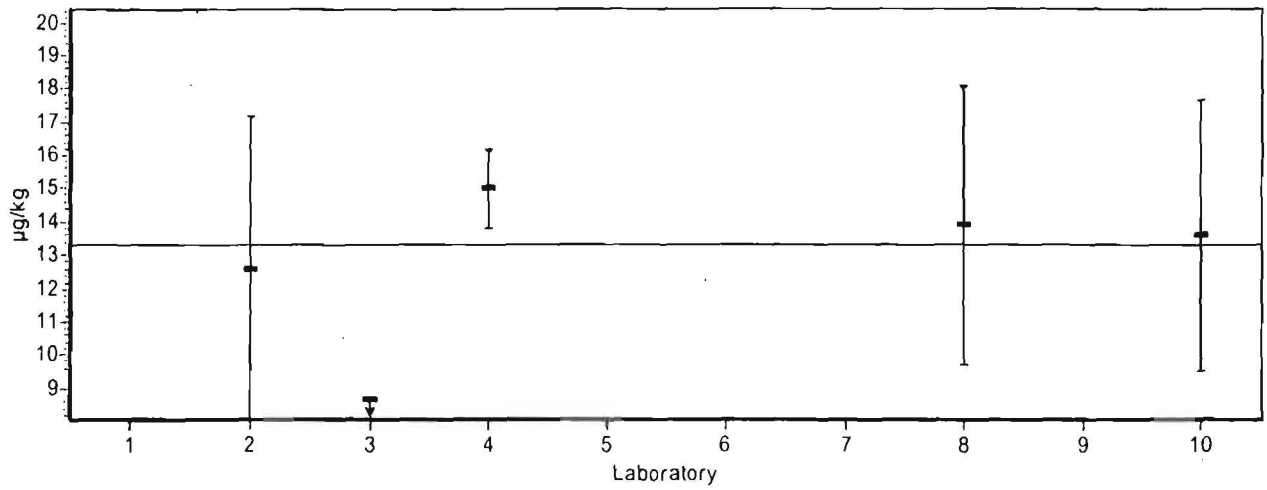
Analyytti *(Analyte)* **PCB-101** Näyte *(Sample)* M2



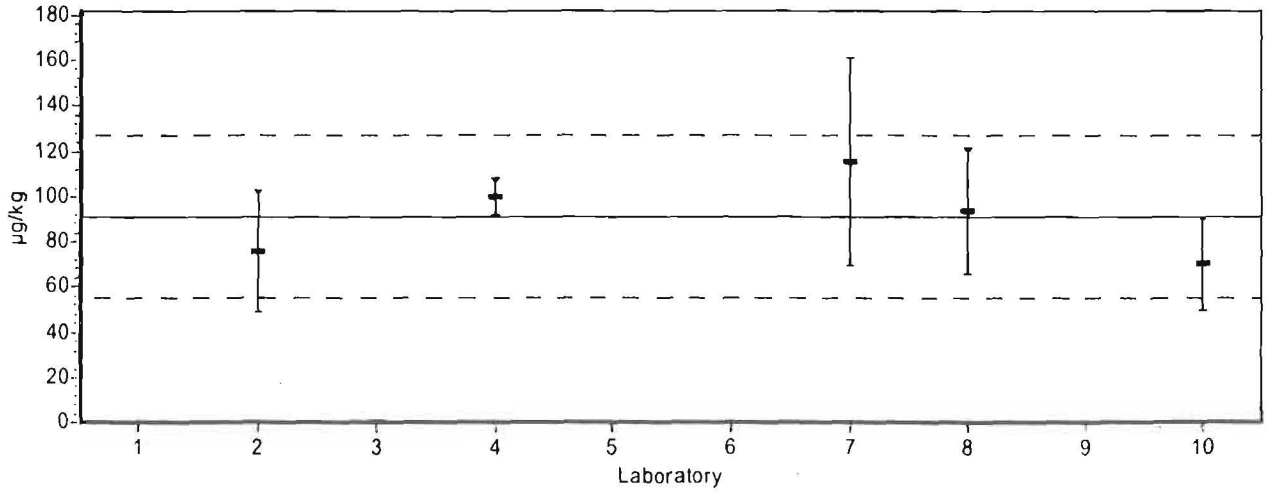
Analyytti *(Analyte)* **PCB-101** Näyte *(Sample)* S1



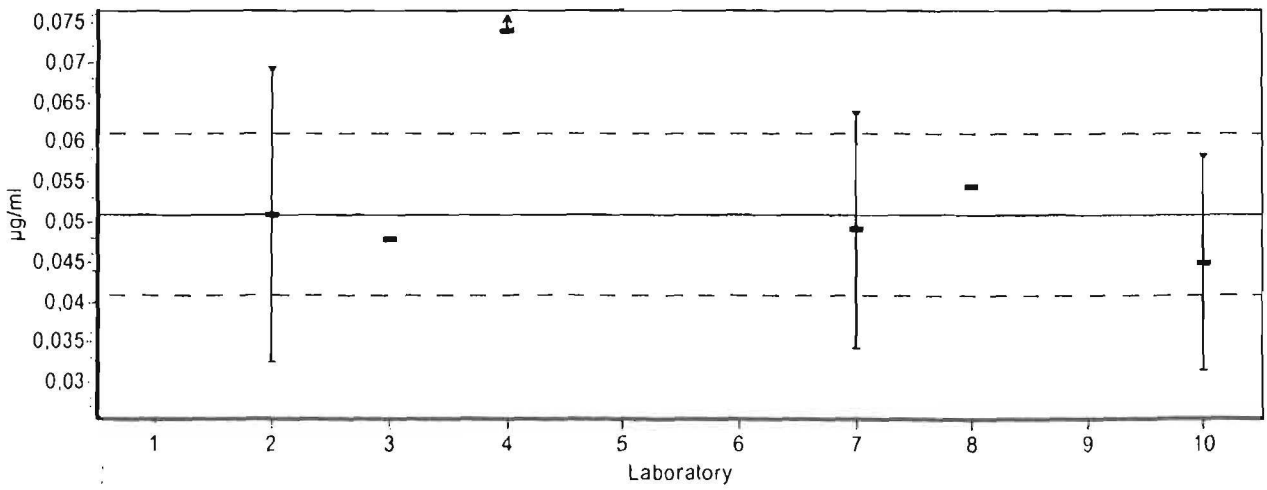
Analyytti *(Analyte)* **PCB-105** Näyte *(Sample)* M1



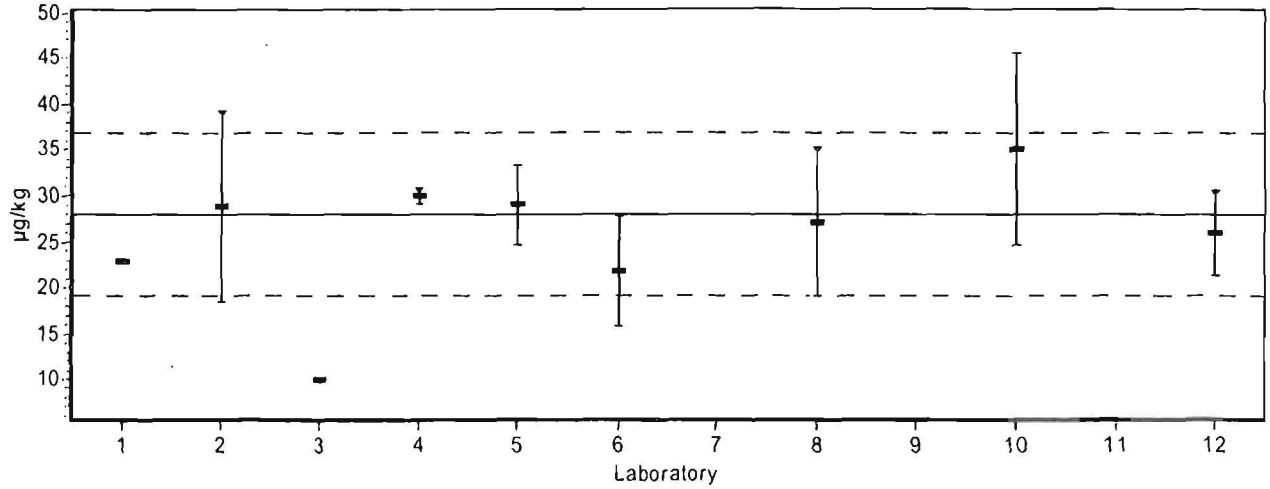
Analyytti *(Analyte)* **PCB-105** Näyte *(Sample)* M2



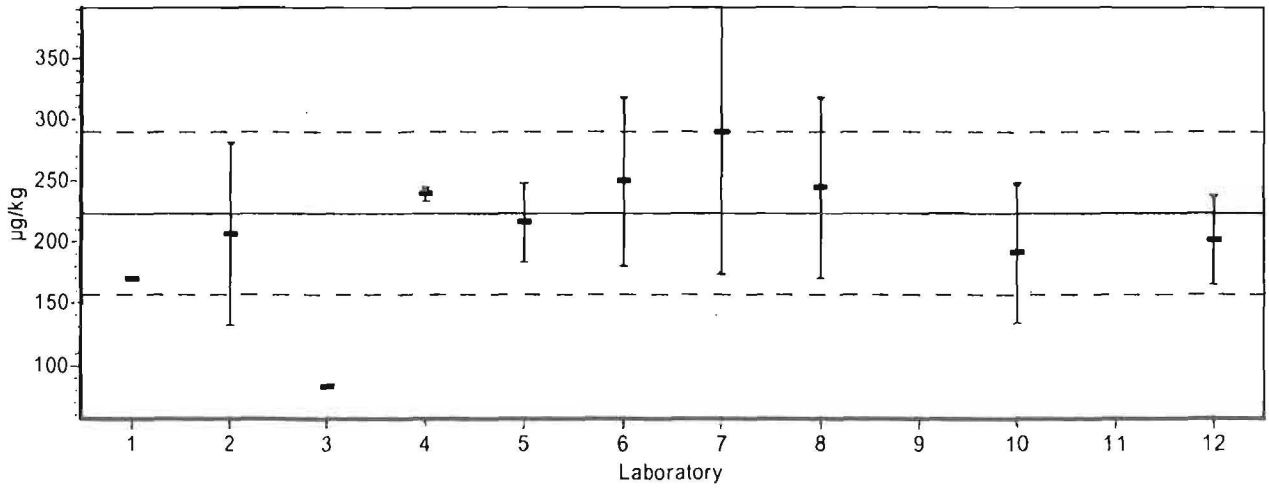
Analyytti *(Analyte)* **PCB-105** Näyte *(Sample)* S1



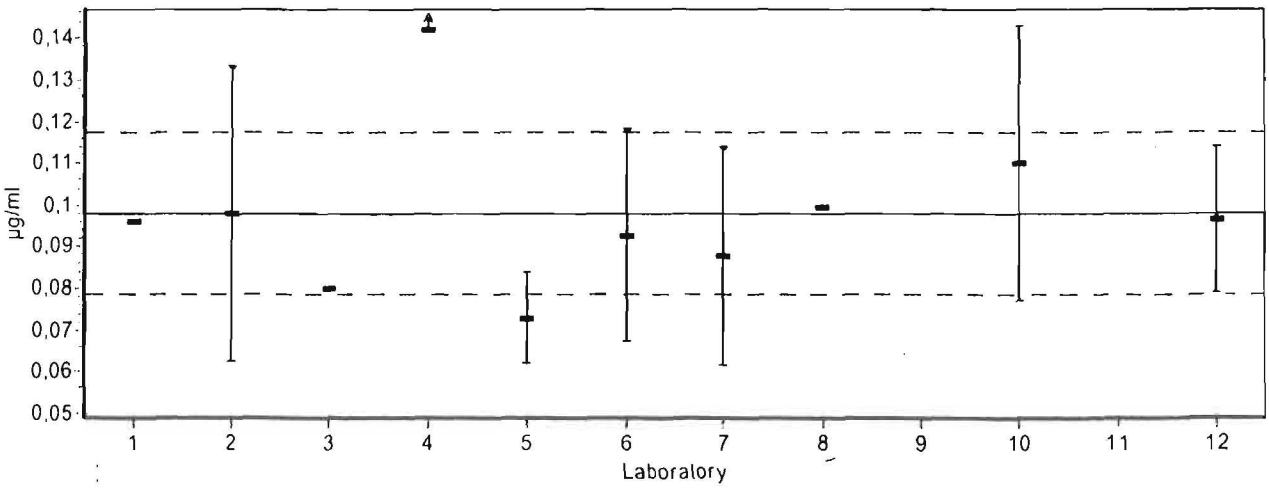
Analyytti *(Analyte)* **PCB-118** Näyte *(Sample)* M1



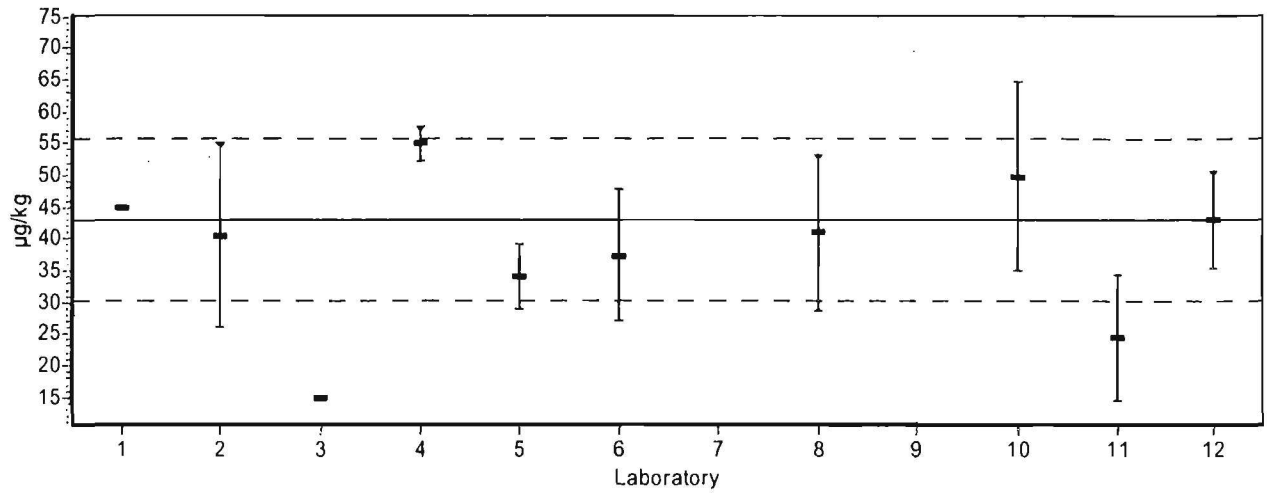
Analyytti *(Analyte)* **PCB-118** Näyte *(Sample)* M2



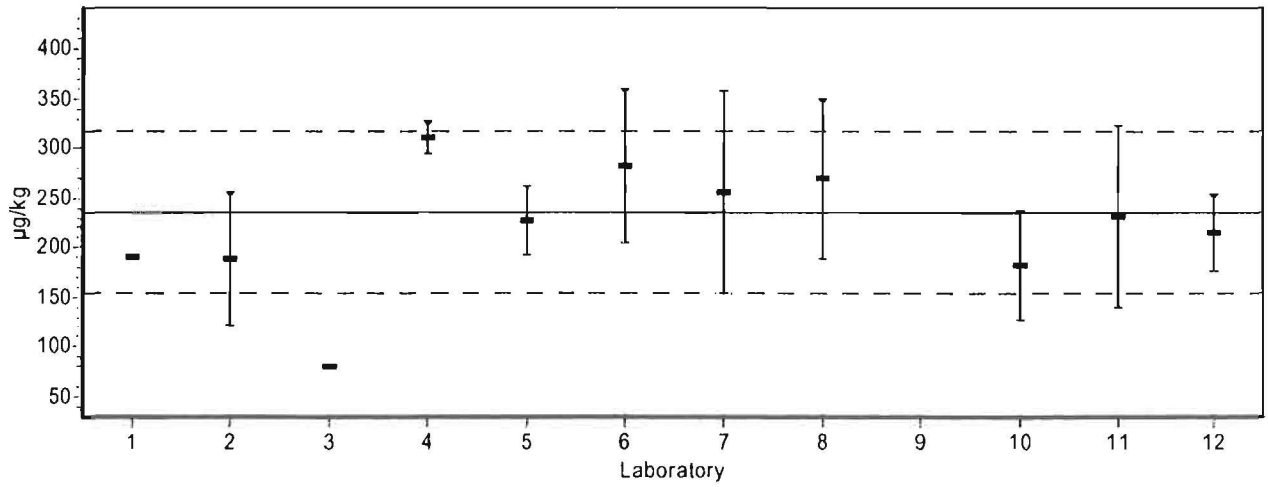
Analyytti *(Analyte)* **PCB-118** Näyte *(Sample)* S1



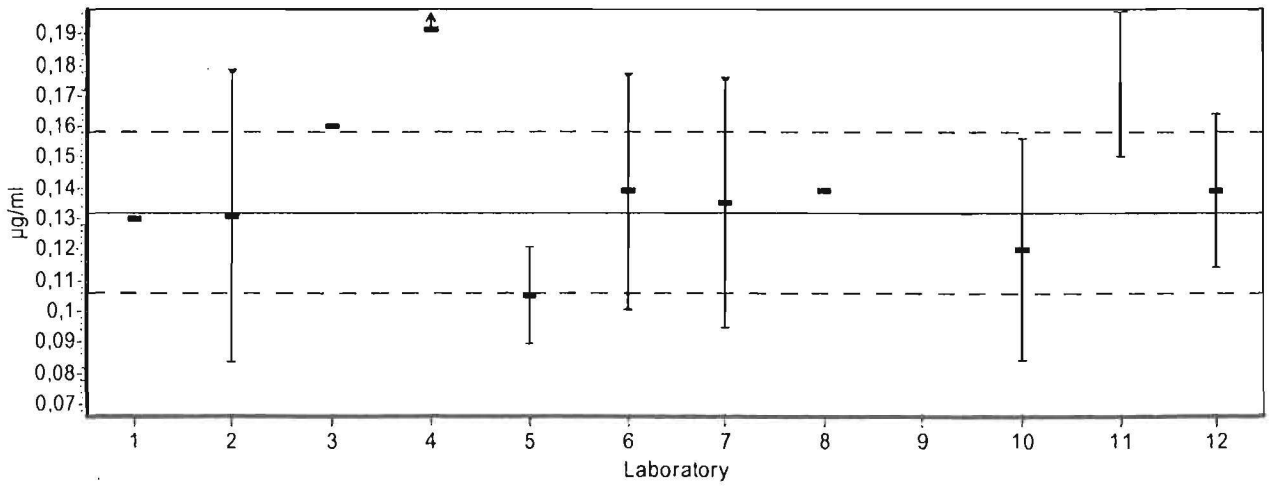
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* M1



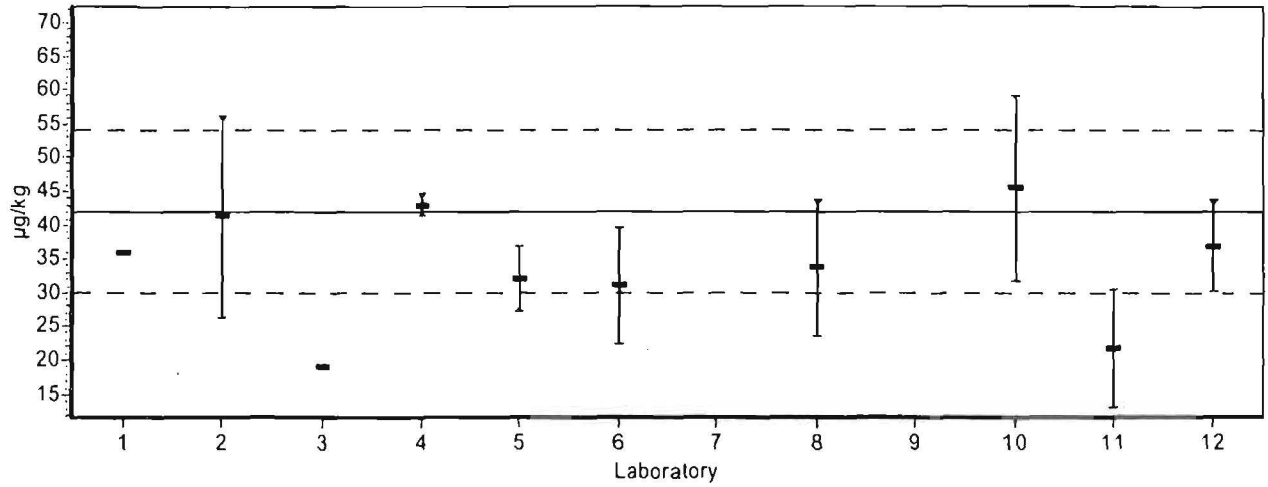
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* M2



Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* S1



Analyytti *(Analyte)* **PCB-153** Näyte *(Sample)* M1



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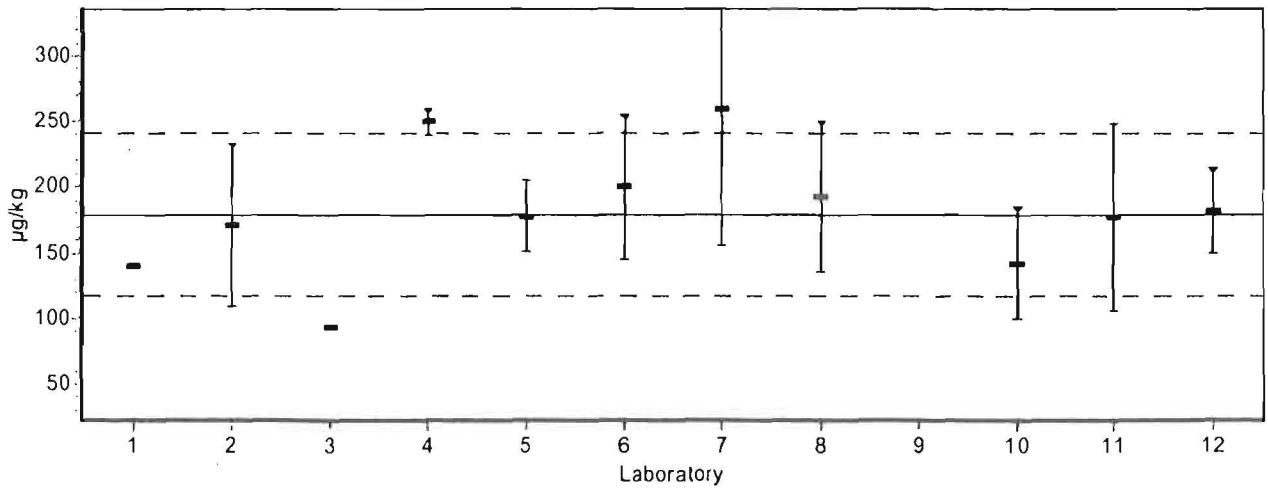
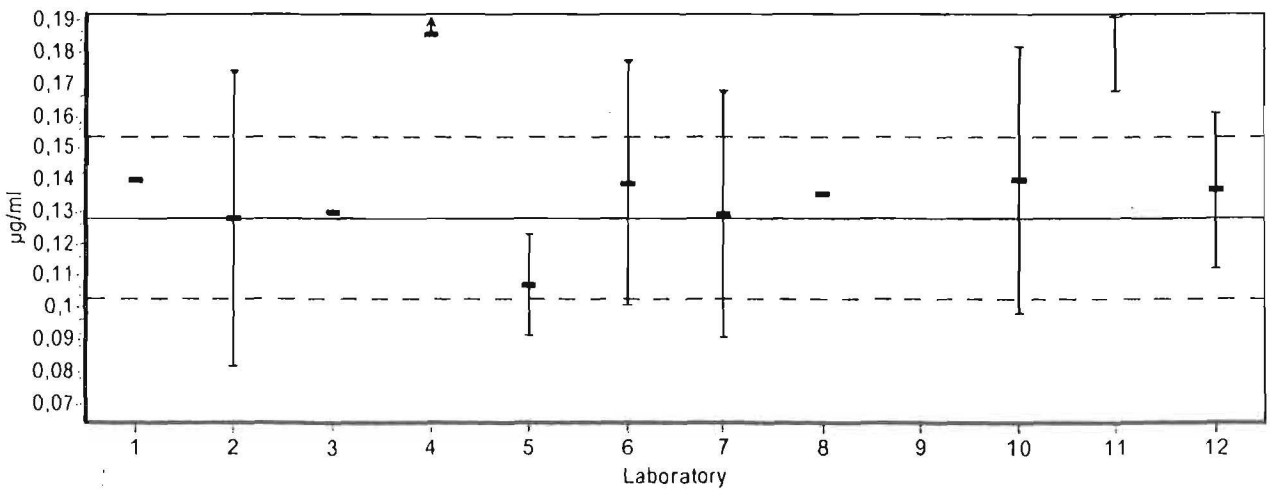
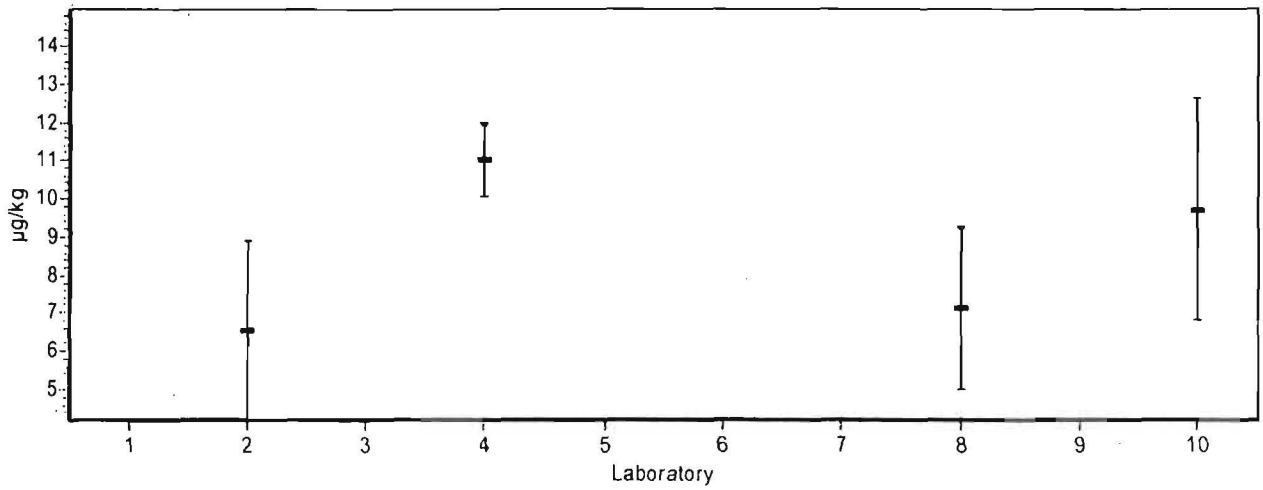


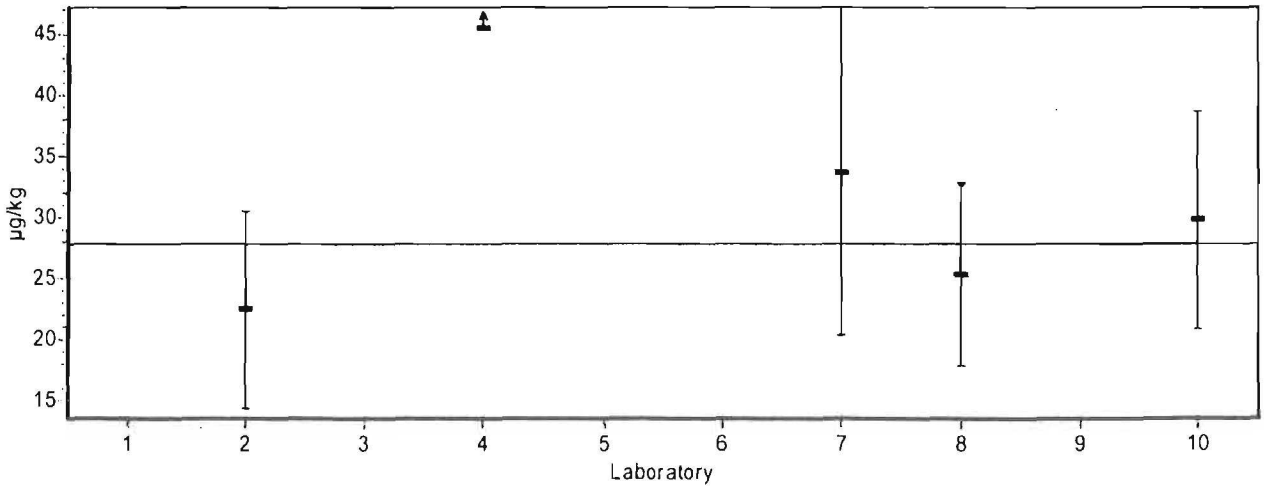
Analyytti *(Analyte)* **PCB-153** Näyte *(Sample)* S1



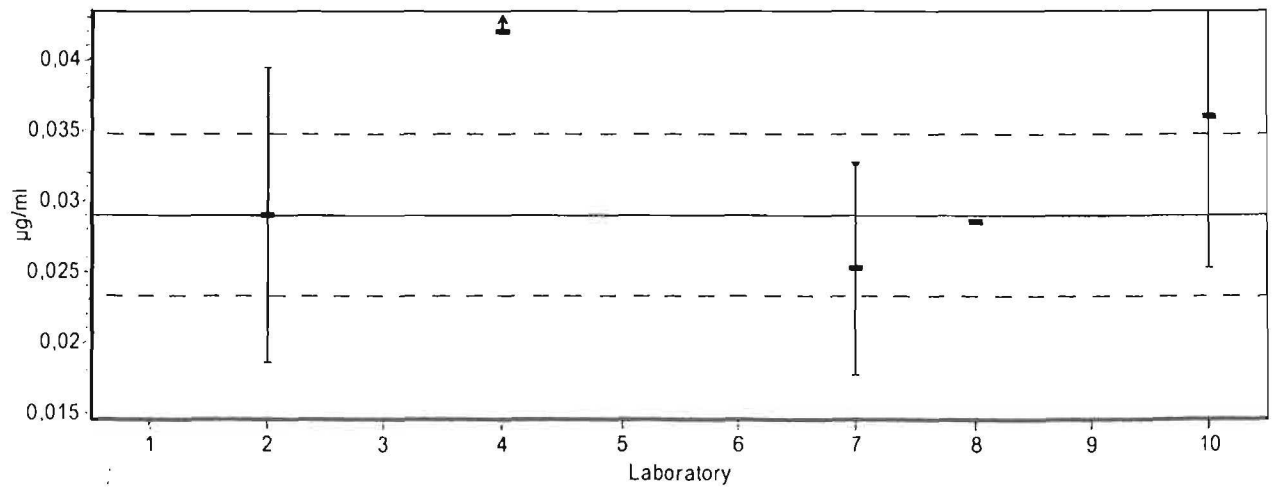
Analyytti *(Analyte)* **PCB-156** Näyte *(Sample)* M1



Analyytti *(Analyte)* **PCB-156** Näyte *(Sample)* M2



Analyytti *(Analyte)* **PCB-156** Näyte *(Sample)* S1



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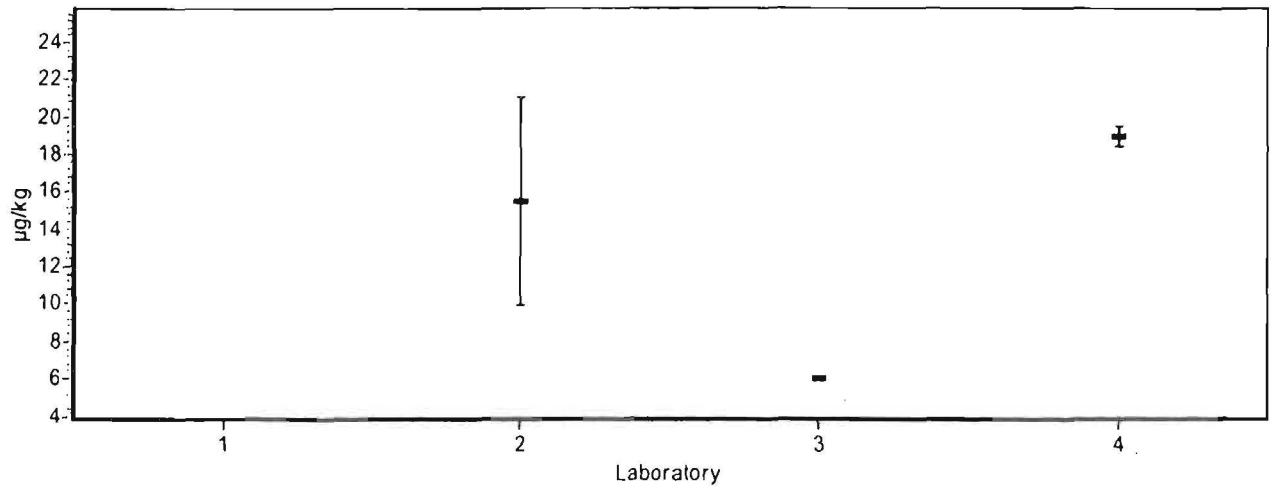

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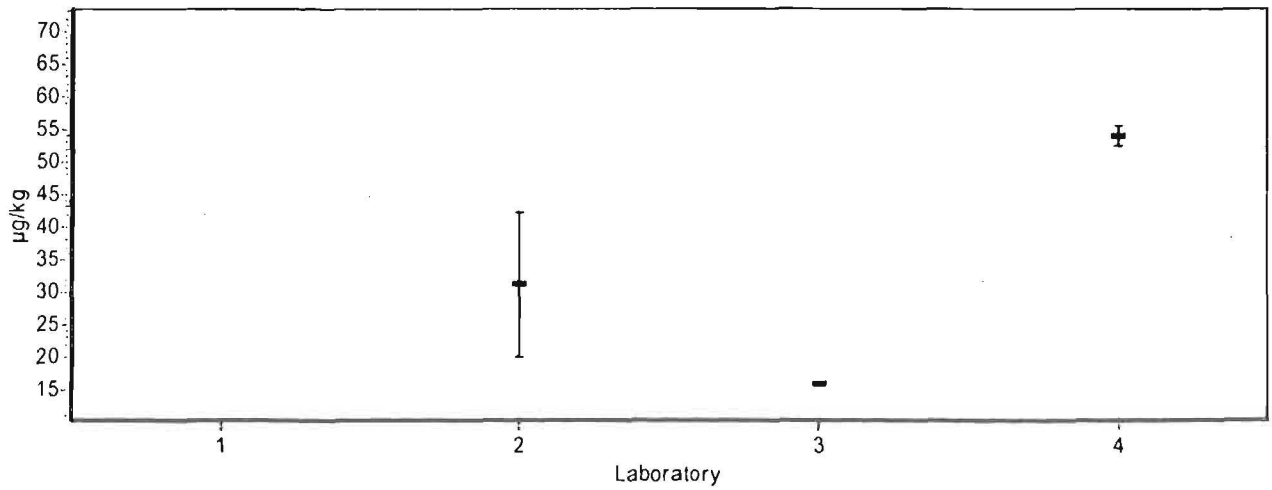
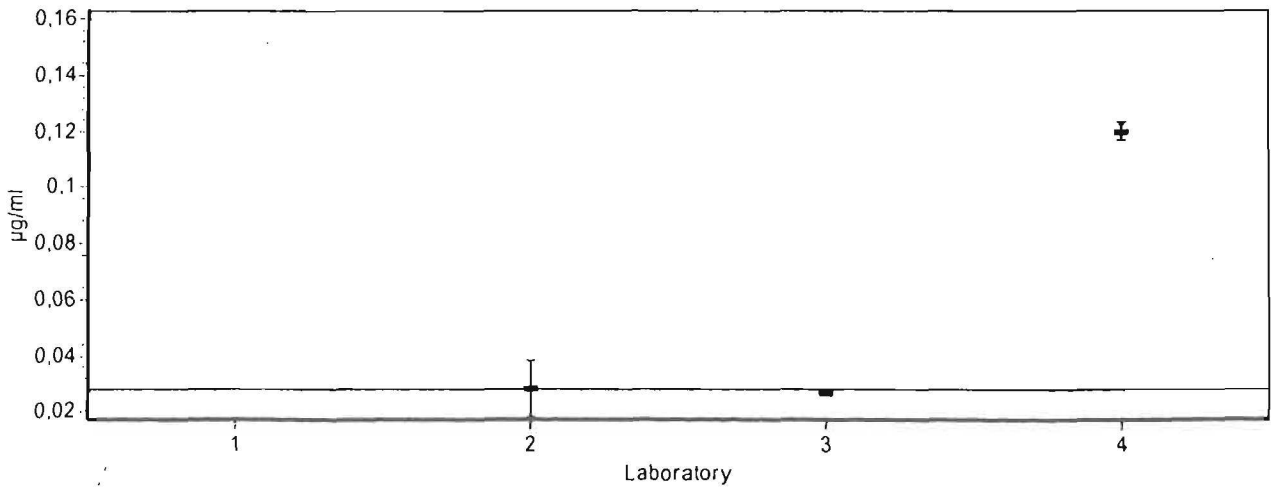
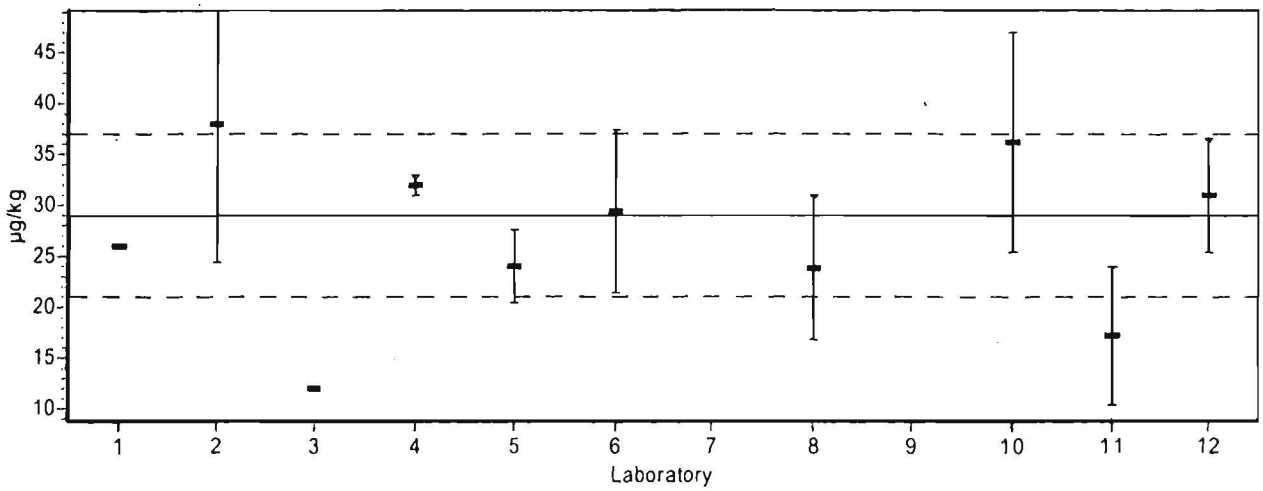


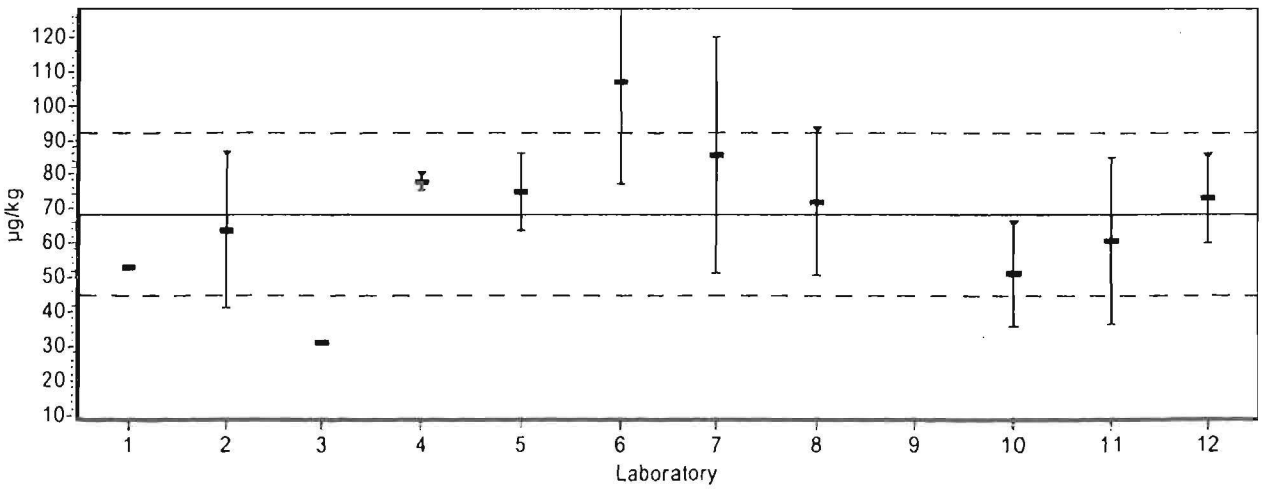
Analyytti *(Analyte)* **PCB-170** Näyte *(Sample)* S1



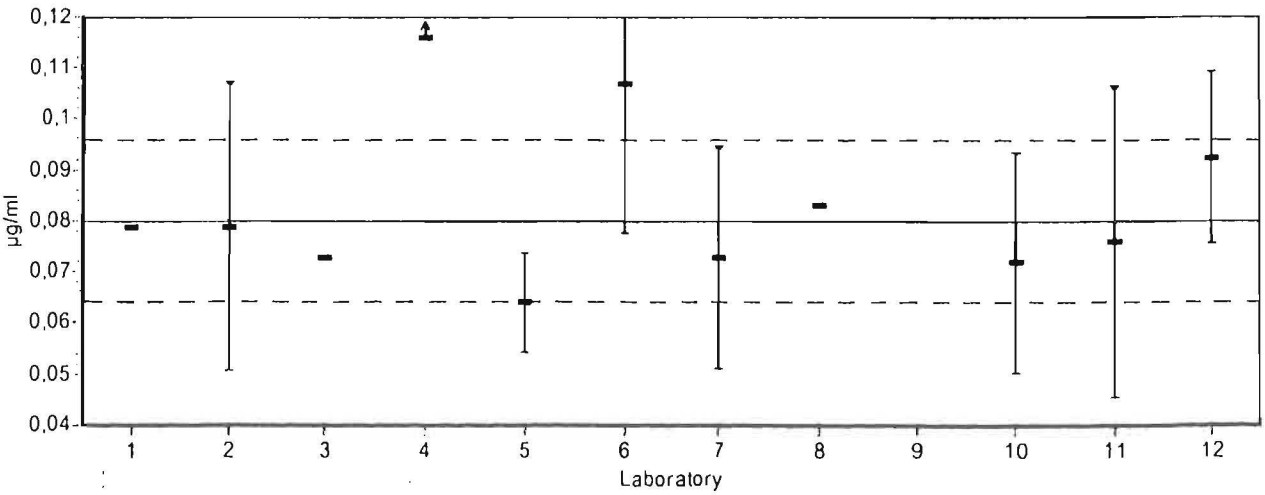
Analyytti *(Analyte)* **PCB-180** Näyte *(Sample)* M1



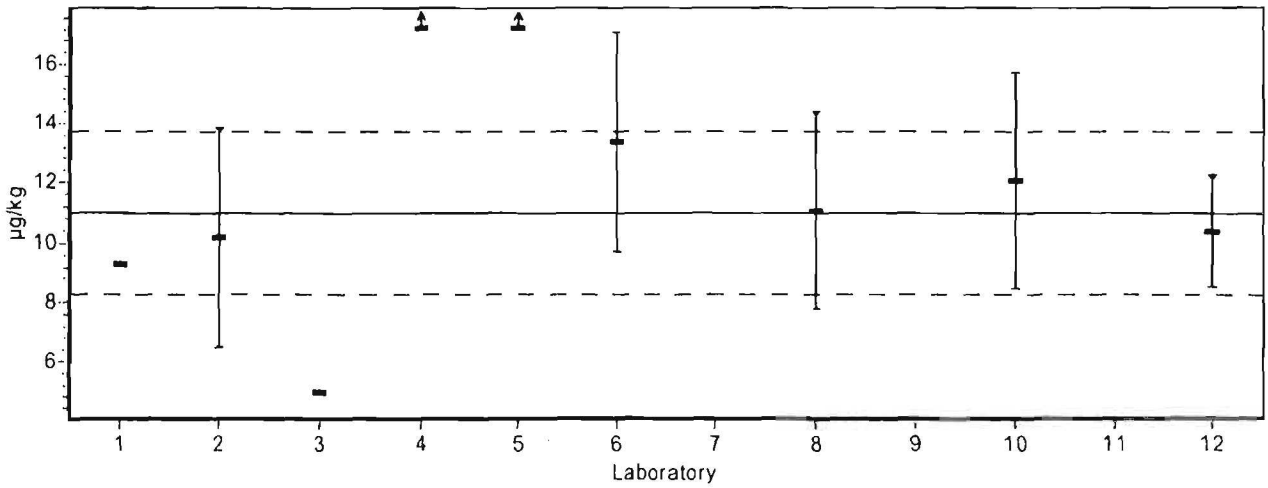
Analyytti *(Analyte)* **PCB-180** Näyte *(Sample)* M2



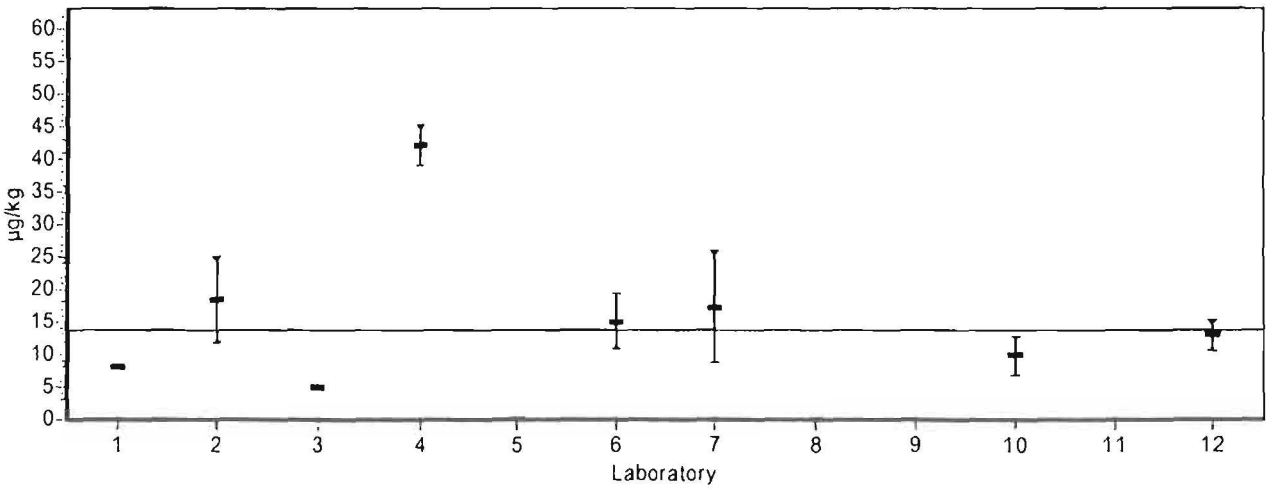
Analyytti *(Analyte)* **PCB-180** Näyte *(Sample)* S1



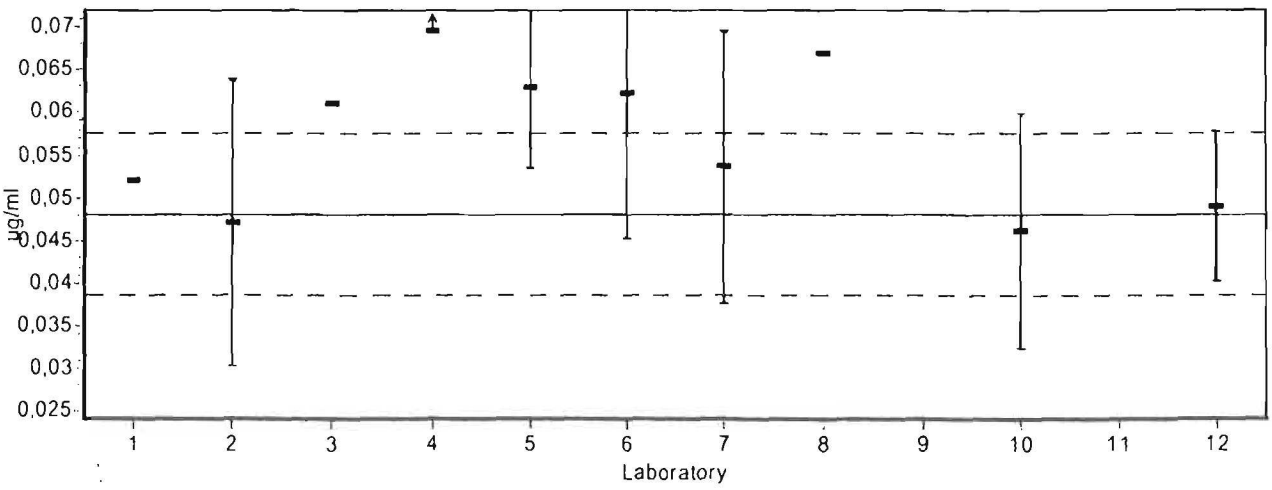
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* M1



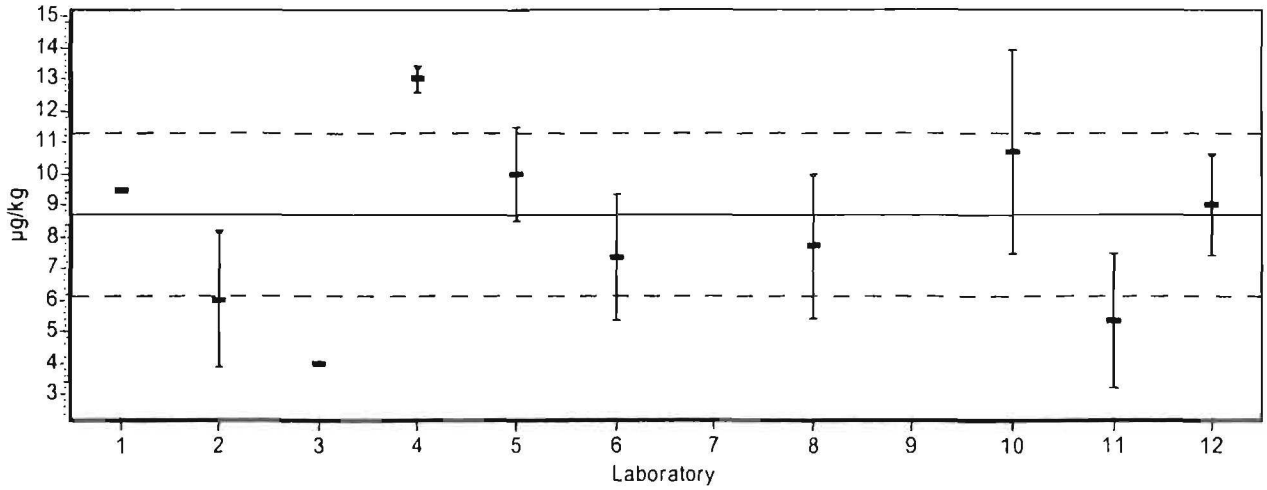
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* M2



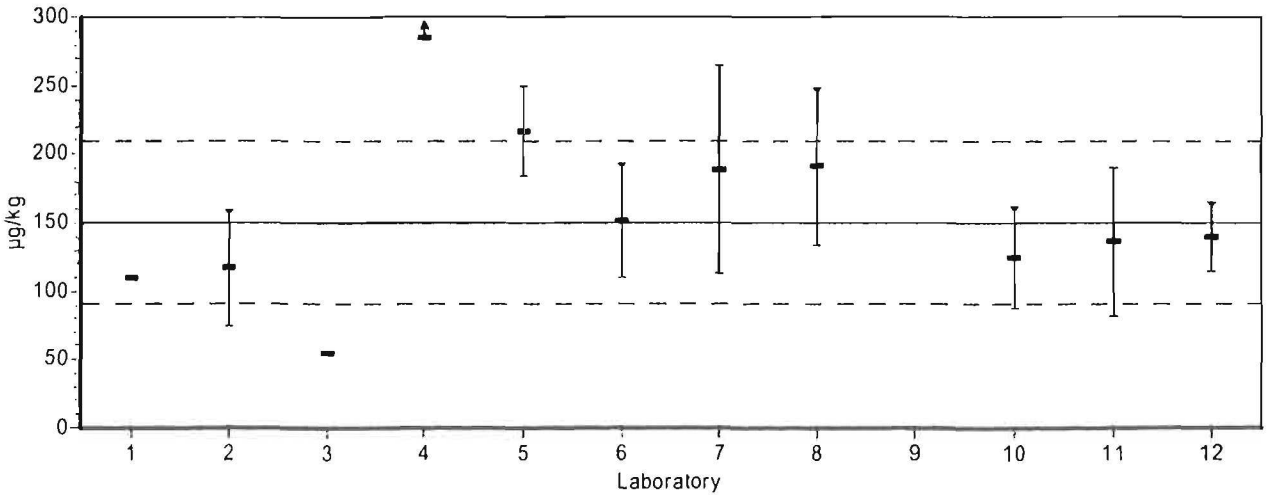
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* S1



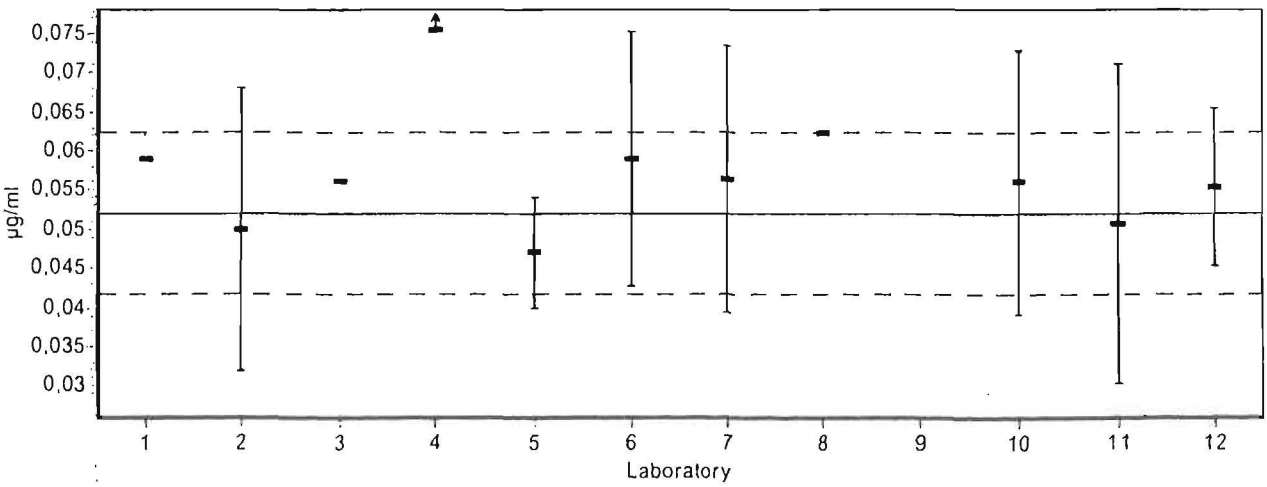
Analyytti *(Analyte)* **PCB-52** Näyte *(Sample)* M1



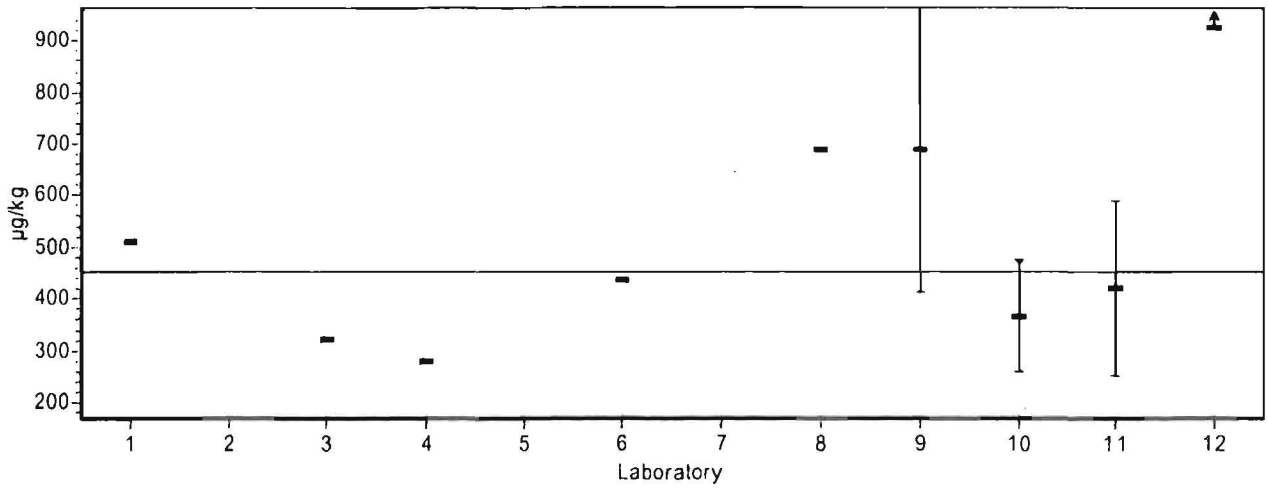
Analyytti *(Analyte)* **PCB-52** Näyte *(Sample)* M2



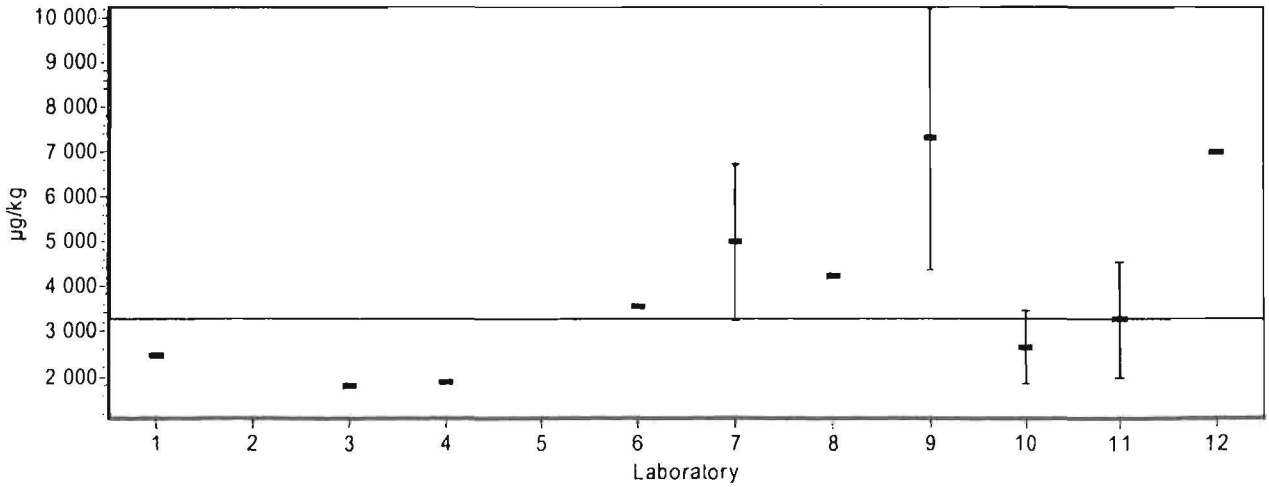
Analyytti *(Analyte)* **PCB-52** Näyte *(Sample)* S1



Analyytti *(Analyte)* **Total-PCB** Näyte *(Sample)* M1



Analyytti *(Analyte)* **Total-PCB** Näyte *(Sample)* M2



APPENDIX 10. ASSIGNED VALUES AND THEIR UNCERTAINTIES

The synthetic sample S1

The calculated concentrations were as follows:

Sample	PCB µg/ml											
S1	p,p-DDE	p,p-DDT	101	105	118	138	153	156	170	180	28	52
µg/ml	0,133	0,128	0,081	0,051	0,098	0,132	0,128	0,029	0,028	0,080	0,048	0,052

The sample M1

The soil sample was the certified reference material (CRM LGC6113). The certified values/the assigned values and their uncertainties (95 % confidence level) were as follows:

Sample	PCB µg/kg								
M1	101	105[2)]	118	138	153	180	28[1)]	52[1)]	total-PCB
µg/kg	23 ± 6	X_{rob} = 13,3 ± 1,7	28 ± 9	43 ± 13	42 ± 12	29 ± 8	X_{rob} = 11 ± 1,2 CV = 14 ± 3	X_{rob} = 8,7 ± 2,1 CV = 11 ± 3	X_{rob} = 452[2)]

[1)] The certified value had not been used as the assigned value.
[2)] The certified value had not been reported.

The assigned values had not been estimated for PCB-156, PCB-170, p,p-DDE and p,p-DDT because of a few number of the reported results.

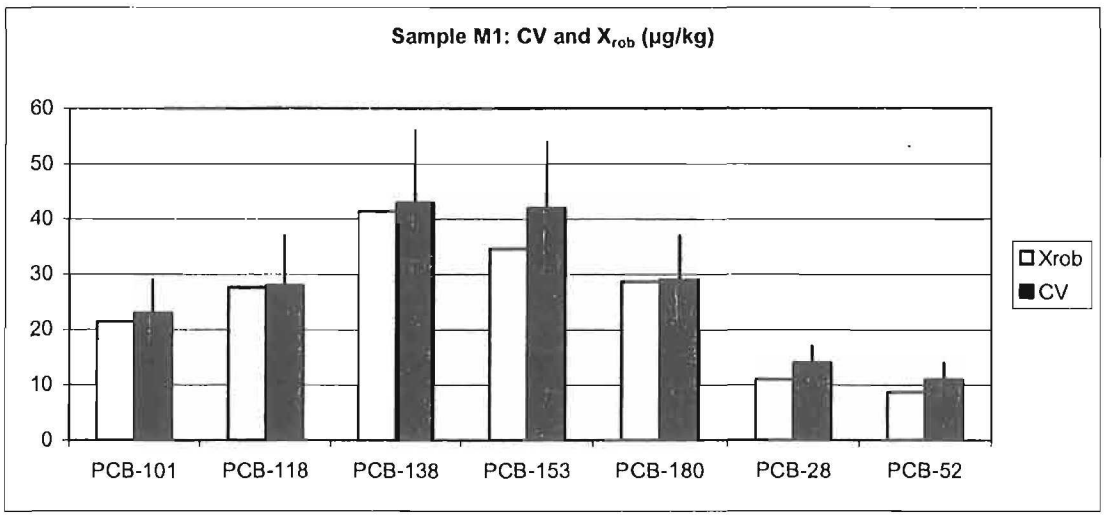


Fig. 1. The certified values (CV) and the obtained robust means (X_{rob}) in analysis of the sample M1

The sample M2

The assigned values and their uncertainties (95 % confidence level) were as follows:

Sample	**PCB µg/kg**								
M2	**101**	**105**	**118**	**138**	**153**	**156**	**180**	**28**	**52**
µg/kg	**242** ± 32 (245)	**90,8** ± 21	**224** ± 29 (222)	**235** ± 36 (227)	**179** ± 28 (178)	**27,8** ± 6,2	**68,4** ± 9,2 (74,5)	**13,6** ± 3,6 (14,1)	**150** ± 27 (133,5)

In the brackets has been reported the mean value of the results obtained by the participants, which reported the most satisfied results (inside the certified limits or close to the limits) in analysis of the sample M1.

APPENDIX 11. EXPLANATIONS FOR THE RESULT SHEETS

Results of each participants and the summary of the results:

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 invidual laboratory X = the reference value (the assigned value) s = the target value for the total deviation (s_{target}).
Outl test OK	yes - the result passed the outlier test H = Hampel test (a test of mean values) 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 total standard deviation (95 % confidence interval).
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, %
Mean rob	Robust mean
SDrob	Robust standard deviation
SDrob %	Robust 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 ($-2 \leq z \leq 2$)
p - questionable ($2 < z \leq 3$), positive error, the result > X
n - questionable ($-3 \leq z < -2$), 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/Calculation of the assigned values:

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 converges.

APPENDIX 12. RESULTS OF EACH PARTICIPANT

Analyte	Sample	Unit	z-Graphics -3 -2 -1 0 +1 +2 +3	Z-value	Assigned value	2* Targ SD%	Lab's result	R-mean	RSD	RSD %	Passed	R-adjusted	Missing	Num of labs
Laboratory 1														
p,p-DDE	M2	µg/kg					36	35,8	0,93	2,6	2	1	3	6
p,p-DDT	M1	µg/kg					4,6	4,95	1,56	31,6	4	1	1	6
PCB-101	M1	µg/kg		-1,003	23	26	20	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		-1,7	242	35	170	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		0,3704	0,081	20	0,084	0,08	0,00	10,0	7	4	0	11
PCB-118	M1	µg/kg		-1,116	28	32	23	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		-1,607	224	30	170	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		-0,2041	0,098	20	0,096	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		0,3101	43	30	45	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		-1,094	235	35	190	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		-0,1515	0,132	20	0,13	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-0,9852	42	29	36	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		-1,245	179	35	140	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0,9375	0,128	20	0,14	0,13	0,01	7,7	8	3	0	11
PCB-180	M1	µg/kg		-0,7389	29	28	26	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		-1,287	68,4	35	53	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		-0,125	0,08	20	0,079	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		-1,236	11	25	9,3	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		8,2	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		0,8333	0,048	20	0,052	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		0,613	8,7	30	9,5	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		-1,333	150	40	110	150	49,0	32,6	8	3	0	11
	S1	µg/ml		1,346	0,052	20	0,059	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		510	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		2500	3712	1819	48,9	8	2	0	10
Laboratory 2														
p,p-DDE	M1	µg/kg					6,85	5,47	1,12	20,4	3	1	0	4
	M2	µg/kg					8,72	35,8	0,93	2,6	2	1	3	6
	S1	µg/ml			0,133		0,132	0,12	0,02	22,2	4	0	0	4
p,p-DDT	M1	µg/kg					8,72	4,95	1,56	31,6	4	1	1	6
	M2	µg/kg					0	14,4	18,4	128,	3	0	1	4
	S1	µg/ml			0,128	20	0,127	0,11	0,03	28,3	3	1	0	4
PCB-101	M1	µg/kg		0,3679	23	26	24,1	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		-0,6848	242	35	213	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		0,1235	0,081	20	0,082	0,08	0,00	10,0	7	4	0	11
PCB-105	M1	µg/kg			13,3		12,6	13,3	1,55	11,7	4	1	0	5
	M2	µg/kg		-0,8535	90,8	40	75,3	90,8	20,8	22,9	5	0	1	6
	S1	µg/ml		0	0,051	20	0,051	0,05	0,00	9,9	5	1	0	6
PCB-118	M1	µg/kg		0,2009	28	32	28,9	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		-0,4762	224	30	208	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		0	0,098	20	0,098	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		-0,3876	43	30	40,5	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		-1,143	235	35	188	226,	56,4	24,9	10	1	0	11
	S1	µg/ml			0,132	20	0,131	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-0,1149	42	29	41,3	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		-0,2554	179	35	171	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0	0,128	20	0,128	0,13	0,01	7,7	8	3	0	11
PCB-156	M1	µg/kg					6,55	8,58	2,39	27,9	4	0	0	4
	M2	µg/kg			27,8		22,4	30,2	7,80	25,8	4	1	0	5
	S1	µg/ml		0	0,029	20	0,029	0,03	0,00	18,9	4	1	0	5
PCB-170	M1	µg/kg					15,5	14,0	6,55	46,5	2	1	0	3
	M2	µg/kg					31,1	33,7	21,7	64,3	3	0	0	3
	S1	µg/ml			0,028		0,028	0,02	0,00	6,6	2	1	0	3
PCB-180	M1	µg/kg		2,241	29	28	38,1	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		-0,3759	68,4	35	63,9	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		-0,125	0,08	20	0,079	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		-0,5818	11	25	10,2	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		18,3	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		-0,2083	0,048	20	0,047	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		-2,061	8,7	30	6,01	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		-1,1	150	40	117	150	49,0	32,6	8	3	0	11
	S1	µg/ml		-0,3846	0,052	20	0,050	0,05	0,00	9,3	9	2	0	11

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

Analyte	Sample	Unit	z-Graphics -3 -2 -1 0 +1 +2 +3	Z-value	Assigned value	2* Targ SD%	Lab's result	R-mean	RSD	RSD %	Passed	R-adjusted	Missing	Num of labs
Laboratory 3														
PCB-101	M1	µg/kg		-4,348	23	26	10	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		-3,518	242	35	93	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		7,284	0,081	20	0,14	0,08	0,00	10,0	7	4	0	11
PCB-105	M1	µg/kg			13,3		8	13,3	1,55	11,7	4	1	0	5
	M2	µg/kg			90,8	40	<5	90,8	20,8	22,9	5	0	1	6
	S1	µg/ml		-0,5882	0,051	20	0,048	0,05	0,00	9,9	5	1	0	6
PCB-118	M1	µg/kg		-4,018	28	32	10	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		-4,226	224	30	82	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		-1,837	0,098	20	0,080	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		-4,341	43	30	15	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		-3,745	235	35	81	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		2,121	0,132	20	0,16	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-3,777	42	29	19	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		-2,745	179	35	93	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0,1563	0,128	20	0,13	0,13	0,01	7,7	8	3	0	11
PCB-170	M1	µg/kg					6	14,0	6,55	46,5	2	1	0	3
	M2	µg/kg					16	33,7	21,7	64,3	3	0	0	3
	S1	µg/ml			0,028		0,027	0,02	0,00	6,6	2	1	0	3
PCB-180	M1	µg/kg		-4,187	29	28	12	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		-3,124	68,4	35	31	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		-0,875	0,08	20	0,073	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		-4,364	11	25	5	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		5	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		2,708	0,048	20	0,061	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		-3,602	8,7	30	4	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		-3,167	150	40	55	150	49,0	32,6	8	3	0	11
	S1	µg/ml		0,7692	0,052	20	0,056	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		320	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		1790	3712	1819	48,9	8	2	0	10
Laboratory 4														
p,p-DDE	M2	µg/kg					<10	35,8	0,93	2,6	2	1	3	6
p,p-DDT	M1	µg/kg					<10	4,95	1,56	31,6	4	1	1	6
PCB-101	M1	µg/kg		1,003	23	26	26	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		0,6612	242	35	270	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		25,8	0,081	20	0,29	0,08	0,00	10,0	7	4	0	11
PCB-105	M1	µg/kg			13,3		15	13,3	1,55	11,7	4	1	0	5
	M2	µg/kg		0,5066	90,8	40	100	90,8	20,8	22,9	5	0	1	6
	S1	µg/ml		29,22	0,051	20	0,20	0,05	0,00	9,9	5	1	0	6
PCB-118	M1	µg/kg		0,4464	28	32	30	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		0,4762	224	30	240	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		20,61	0,098	20	0,30	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		1,86	43	30	55	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		1,824	235	35	310	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		27,88	0,132	20	0,50	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		0,1642	42	29	43	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		2,267	179	35	250	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		28,28	0,128	20	0,49	0,13	0,01	7,7	8	3	0	11
PCB-156	M1	µg/kg					11	8,58	2,39	27,9	4	0	0	4
	M2	µg/kg			27,8		110	30,2	7,80	25,8	4	1	0	5
	S1	µg/ml		38,28	0,029	20	0,14	0,03	0,00	18,9	4	1	0	5
PCB-170	M1	µg/kg					19	14,0	6,55	46,5	2	1	0	3
	M2	µg/kg					54	33,7	21,7	64,3	3	0	0	3
	S1	µg/ml			0,028		0,12	0,02	0,00	6,6	2	1	0	3
PCB-180	M1	µg/kg		0,7389	29	28	32	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		0,802	68,4	35	78	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		30	0,08	20	0,32	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		15,27	11	25	32	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		42	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		6,458	0,048	20	0,079	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		3,295	8,7	30	13	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		8,667	150	40	410	150	49,0	32,6	8	3	0	11
	S1	µg/ml		22,69	0,052	20	0,17	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		280	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		1900	3712	1819	48,9	8	2	0	10

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

Analyte	Sample	Unit	z-Graphics -3 -2 -1 0 +1 +2 +3	Z-value	Assigned value	2* Targ SD%	Lab's result	R-mean	RSD	RSD %	Passed	R-adjusted	Missing	Num of labs
Laboratory 5														
PCB-101	M1	µg/kg		0	23	26	23	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		0,9681	242	35	283	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		-1,605	0,081	20	0,068	0,08	0,00	10,0	7	4	0	11
PCB-118	M1	µg/kg		0,2232	28	32	29	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		-0,2083	224	30	217	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		-2,551	0,098	20	0,073	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		-1,395	43	30	34	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		-0,1945	235	35	227	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		-2,045	0,132	20	0,105	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-1,642	42	29	32	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg			179	35	178	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		-1,641	0,128	20	0,107	0,13	0,01	7,7	8	3	0	11
PCB-180	M1	µg/kg		-1,232	29	28	24	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		0,5514	68,4	35	75	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		-2	0,08	20	0,064	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		10,18	11	25	25	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		0	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		3,125	0,048	20	0,063	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		0,9962	8,7	30	10	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		2,233	150	40	217	150	49,0	32,6	8	3	0	11
	S1	µg/ml		-0,9615	0,052	20	0,047	0,05	0,00	9,3	9	2	0	11
Laboratory 6														
p,p-DDE	M1	µg/kg					4,45	5,47	1,12	20,4	3	1	0	4
	M2	µg/kg					<0,5	35,8	0,93	2,6	2	1	3	6
	S1	µg/ml			0,133		0,159	0,12	0,02	22,2	4	0	0	4
p,p-DDT	M1	µg/kg					5,65	4,95	1,56	31,6	4	1	1	6
	M2	µg/kg					32,1	14,4	18,4	128,	3	0	1	4
	S1	µg/ml		-2,531	0,128	20	0,095	0,11	0,03	28,3	3	1	0	4
PCB-101	M1	µg/kg		-1,371	23	26	18,9	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		0,02361	242	35	243	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		0,4074	0,081	20	0,084	0,08	0,00	10,0	7	4	0	11
PCB-118	M1	µg/kg		-1,384	28	32	21,8	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		0,7738	224	30	250	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		-0,5204	0,098	20	0,092	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		-0,8682	43	30	37,4	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		1,143	235	35	282	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		0,5303	0,132	20	0,139	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-1,806	42	29	31	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		0,6704	179	35	200	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0,8594	0,128	20	0,139	0,13	0,01	7,7	8	3	0	11
PCB-180	M1	µg/kg		0,09852	29	28	29,4	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		3,225	68,4	35	107	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		3,375	0,08	20	0,107	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		1,745	11	25	13,4	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		15,1	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		2,958	0,048	20	0,062	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		-1,034	8,7	30	7,35	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		0,06667	150	40	152	150	49,0	32,6	8	3	0	11
	S1	µg/ml		1,327	0,052	20	0,058	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		436	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		3550	3712	1819	48,9	8	2	0	10

Analyte	Sample	Unit	z-Graphics -3 -2 -1 0 +1 +2 +3	Z-value	Assigned value	2* Targ SD%	Lab's result	R-mean	RSD	RSD %	Passed	R-adjusted	Missing	Num of labs
Laboratory 7														
PCB-101	M2	µg/kg		1,204	242	35	293	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		-0,2346	0,081	20	0,079	0,08	0,00	10,0	7	4	0	11
PCB-105	M2	µg/kg		1,333	90,8	40	115	90,8	20,8	22,9	5	0	1	6
	S1	µg/ml		-0,3529	0,051	20	0,049	0,05	0,00	9,9	5	1	0	6
PCB-118	M2	µg/kg		1,964	224	30	290	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		-1,051	0,098	20	0,087	0,09	0,01	11,2	6	4	0	10
PCB-138	M2	µg/kg		0,4863	235	35	255	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		0,2273	0,132	20	0,135	0,13	0,01	11,8	7	4	0	11
PCB-153	M2	µg/kg		2,554	179	35	259	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0,07813	0,128	20	0,129	0,13	0,01	7,7	8	3	0	11
PCB-156	M2	µg/kg			27,8		33,7	30,2	7,80	25,8	4	1	0	5
	S1	µg/ml		-1,31	0,029	20	0,025	0,03	0,00	18,9	4	1	0	5
PCB-180	M2	µg/kg		1,437	68,4	35	85,6	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		-0,8875	0,08	20	0,072	0,07	0,01	13,2	8	3	0	11
PCB-28	M2	µg/kg			13,6		17,3	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		1,167	0,048	20	0,053	0,05	0,01	18,1	9	1	0	10
PCB-52	M2	µg/kg		1,3	150	40	189	150	49,0	32,6	8	3	0	11
	S1	µg/ml		0,8462	0,052	20	0,056	0,05	0,00	9,3	9	2	0	11
Total-PCB	M2	µg/kg			3301		5000	3712	1819	48,9	8	2	0	10
Laboratory 8														
PCB-101	M1	µg/kg		-1,739	23	26	17,8	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		0,7178	242	35	272,4	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		0,678	0,081	20	0,086	0,08	0,00	10,0	7	4	0	11
PCB-105	M1	µg/kg			13,3		13,9	13,3	1,55	11,7	4	1	0	5
	M2	µg/kg		0,1597	90,8	40	93,7	90,8	20,8	22,9	5	0	1	6
	S1	µg/ml		0,6727	0,051	20	0,054	0,05	0,00	9,9	5	1	0	6
PCB-118	M1	µg/kg		-0,1786	28	32	27,2	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		0,622	224	30	244,9	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		0,1455	0,098	20	0,099	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		-0,3101	43	30	41,0	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		0,8267	235	35	269,0	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		0,5476	0,132	20	0,139	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-1,346	42	29	33,8	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		0,4342	179	35	192,6	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0,6091	0,128	20	0,135	0,13	0,01	7,7	8	3	0	11
PCB-156	M1	µg/kg					7,1	8,58	2,39	27,9	4	0	0	4
	M2	µg/kg			27,8		25,3	30,2	7,80	25,8	4	1	0	5
	S1	µg/ml		-0,1303	0,029	20	0,028	0,03	0,00	18,9	4	1	0	5
PCB-180	M1	µg/kg		-1,281	29	28	23,8	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		0,3008	68,4	35	72,0	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		0,4004	0,08	20	0,083	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		0,07273	11	25	11,1	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		0	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		3,984	0,048	20	0,067	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		-0,7663	8,7	30	7,7	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		1,377	150	40	191,3	150	49,0	32,6	8	3	0	11
	S1	µg/ml		1,993	0,052	20	0,062	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		689	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		4239	3712	1819	48,9	8	2	0	10
Laboratory 9														
Total-PCB	M1	µg/kg			452		689	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		7300	3712	1819	48,9	8	2	0	10

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

Analyte	Sample	Unit	z-Graphics -3 -2 -1 0 +1 +2 +3	Z-value	Assigned value	2* Targ SD%	Lab's result	R-mean	RSD	RSD %	Passed	R-adjusted	Missing	Num of labs
Laboratory 10														
p,p-DDE	M1	µg/kg					5	5,47	1,12	20,4	3	1	0	4
	M2	µg/kg					36,5	35,8	0,93	2,6	2	1	3	6
	S1	µg/ml			0,133		0,097	0,12	0,02	22,2	4	0	0	4
p,p-DDT	M1	µg/kg					4,76	4,95	1,56	31,6	4	1	1	6
	M2	µg/kg					11,2	14,4	18,4	128,	3	0	1	4
	S1	µg/ml		-2,969	0,128	20	0,090	0,11	0,03	28,3	3	1	0	4
PCB-101	M1	µg/kg		0,1672	23	26	23,5	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		-0,9681	242	35	201	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		-0,1235	0,081	20	0,080	0,08	0,00	10,0	7	4	0	11
PCB-105	M1	µg/kg			13,3		13,6	13,3	1,55	11,7	4	1	0	5
	M2	µg/kg		-1,14	90,8	40	70,1	90,8	20,8	22,9	5	0	1	6
	S1	µg/ml		-1,176	0,051	20	0,045	0,05	0,00	9,9	5	1	0	6
PCB-118	M1	µg/kg		1,585	28	32	35,1	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		-0,9524	224	30	192	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		1,224	0,098	20	0,11	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		1,054	43	30	49,8	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		-1,289	235	35	182	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		-0,9091	0,132	20	0,12	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		0,5747	42	29	45,5	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		-1,181	179	35	142	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0,9375	0,128	20	0,14	0,13	0,01	7,7	8	3	0	11
PCB-156	M1	µg/kg					9,69	8,58	2,39	27,9	4	0	0	4
	M2	µg/kg			27,8		29,8	30,2	7,80	25,8	4	1	0	5
	S1	µg/ml		2,414	0,029	20	0,036	0,03	0,00	18,9	4	1	0	5
PCB-180	M1	µg/kg		1,773	29	28	36,2	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		-1,445	68,4	35	51,1	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		-1	0,08	20	0,072	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		0,8	11	25	12,1	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		9,91	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		-0,4167	0,048	20	0,046	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		1,533	8,7	30	10,7	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		-0,8333	150	40	125	150	49,0	32,6	8	3	0	11
	S1	µg/ml		0,7692	0,052	20	0,056	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		367	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		2660	3712	1819	48,9	8	2	0	10
Laboratory 11														
PCB-101	M1	µg/kg		-3,779	23	26	11,70	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg			242	35	237,9	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		13,09	0,081	20	0,187	0,08	0,00	10,0	7	4	0	11
PCB-138	M1	µg/kg		-2,864	43	30	24,53	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		-0,106	235	35	230,6	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		8,939	0,132	20	0,250	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-3,314	42	29	21,82	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg			179	35	177,8	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		11,88	0,128	20	0,280	0,13	0,01	7,7	8	3	0	11
PCB-180	M1	µg/kg		-2,921	29	28	17,14	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		-0,66	68,4	35	60,50	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		-0,5	0,08	20	0,076	0,07	0,01	13,2	8	3	0	11
PCB-52	M1	µg/kg		-2,59	8,7	30	5,32	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		-0,4667	150	40	136,0	150	49,0	32,6	8	3	0	11
	S1	µg/ml		-0,25	0,052	20	0,050	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		421	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		3271	3712	1819	48,9	8	2	0	10

Analyte	Sample	Unit	z-Graphics -3 -2 -1 0 +1 +2 +3	Z-value	Assigned value	2* Targ SD%	Lab's result	R-mean	RSD	RSD %	Passed	R-adjusted	Missing	Num of labs
Laboratory	**12**													
p,p-DDE	M1	µg/kg					5,7	5,47	1,12	20,4	3	1	0	4
	M2	µg/kg					<0,5	35,8	0,93	2,6	2	1	3	6
	S1	µg/ml			0,133		0,128	0,12	0,02	22,2	4	0	0	4
p,p-DDT	M1	µg/kg					3	4,95	1,56	31,6	4	1	1	6
	M2	µg/kg					<0,5	14,4	18,4	128,	3	0	1	4
	S1	µg/ml		1,947	0,128	20	0,152	0,11	0,03	28,3	3	1	0	4
PCB-101	M1	µg/kg		-0,3344	23	26	22	20,4	4,41	21,5	8	2	0	10
	M2	µg/kg		-0,2834	242	35	230	234,	50,3	21,4	10	1	0	11
	S1	µg/ml		1,054	0,081	20	0,089	0,08	0,00	10,0	7	4	0	11
PCB-118	M1	µg/kg		-0,4464	28	32	26	26,7	4,70	17,6	7	2	0	9
	M2	µg/kg		-0,6548	224	30	202	215,	45,0	20,9	8	2	0	10
	S1	µg/ml		-0,1429	0,098	20	0,096	0,09	0,01	11,2	6	4	0	10
PCB-138	M1	µg/kg		0	43	30	43	40,0	9,30	23,2	7	3	0	10
	M2	µg/kg		-0,4863	235	35	215	226,	56,4	24,9	10	1	0	11
	S1	µg/ml		0,5371	0,132	20	0,139	0,13	0,01	11,8	7	4	0	11
PCB-153	M1	µg/kg		-0,821	42	29	37	34,6	8,54	24,6	8	2	0	10
	M2	µg/kg		0,09577	179	35	182	178,	37,0	20,7	8	3	0	11
	S1	µg/ml		0,6758	0.128	20	0,136	0,13	0,01	7,7	8	3	0	11
PCB-180	M1	µg/kg		0,4926	29	28	31	27,6	7,42	26,8	7	3	0	10
	M2	µg/kg		0,3843	68,4	35	73	68,3	16,8	24,6	9	2	0	11
	S1	µg/ml		1,559	0,08	20	0,092	0,07	0,01	13,2	8	3	0	11
PCB-28	M1	µg/kg		-0,4364	11	25	10,4	11,5	3,03	26,2	6	3	0	9
	M2	µg/kg			13,6		13	11,1	9,24	82,6	9	1	0	10
	S1	µg/ml		0,1917	0,048	20	0,048	0,05	0,01	18,1	9	1	0	10
PCB-52	M1	µg/kg		0,2299	8,7	30	9	8,23	3,03	36,8	9	1	0	10
	M2	µg/kg		-0,3333	150	40	140	150	49,0	32,6	8	3	0	11
	S1	µg/ml		0,6385	0,052	20	0,055	0,05	0,00	9,3	9	2	0	11
Total-PCB	M1	µg/kg			452		1200	489,	186,	38,1	8	1	0	9
	M2	µg/kg			3301		7000	3712	1819	48,9	8	2	0	10

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

APPENDIX 13. SUMMARY OF THE z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	%
p,p-DDE	M1	.	.	.	.	.	.	.	.	.	.	.	.	
	M2	.	.	.	.	.	.	.	.	.	.	.	.	
	S1	.	.	.	.	.	.	.	.	.	.	.	.	
p,p-DDT	M1	.	.	.	.	.	.	.	.	.	.	.	.	
	M2	.	.	.	.	.	.	.	.	.	.	.	.	
	S1	.	A	.	.	.	n	.	.	.	n	.	A	50
PCB-101	M1	A	A	N	A	A	A	.	A	.	A	N	A	80
	M2	A	A	N	A	A	A	A	A	.	A	A	A	91
	S1	A	A	P	P	A	A	A	A	.	A	P	A	73
PCB-105	M1	.	.	.	.	.	.	.	.	.	.	.	.	
	M2	.	A	.	A	.	.	A	A	.	A	.	.	100
	S1	.	A	A	P	.	.	A	A	.	A	.	.	83
PCB-118	M1	A	A	N	A	A	A	.	A	.	A	.	A	89
	M2	A	A	N	A	A	A	A	A	.	A	.	A	90
	S1	A	A	A	P	n	A	A	A	.	A	.	A	80
PCB-138	M1	A	A	N	A	A	A	.	A	.	A	n	A	80
	M2	A	A	N	A	A	A	A	A	.	A	A	A	91
	S1	A	A	p	P	n	A	A	A	.	A	P	A	64
PCB-153	M1	A	A	N	A	A	A	.	A	.	A	N	A	80
	M2	A	A	n	p	A	A	p	A	.	A	A	A	73
	S1	A	A	A	P	A	A	A	A	.	A	P	A	82
PCB-156	M1	.	.	.	.	.	.	.	.	.	.	.	.	
	M2	.	.	.	.	.	.	.	.	.	.	.	.	
	S1	.	A	.	P	.	.	A	A	.	p	.	.	60
PCB-170	M1	.	.	.	.	.	.	.	.	.	.	.	.	
	M2	.	.	.	.	.	.	.	.	.	.	.	.	
	S1	.	.	.	.	.	.	.	.	.	.	.	.	
PCB-180	M1	A	p	N	A	A	A	.	A	.	A	n	A	70
	M2	A	A	N	A	A	P	A	A	.	A	A	A	82
	S1	A	A	A	P	A	P	A	A	.	A	A	A	82
PCB-28	M1	A	A	N	P	P	A	.	A	.	A	.	A	67
	M2	.	.	.	.	.	.	.	.	.	.	.	.	
	S1	A	A	p	P	P	p	A	P	.	A	.	A	50
PCB-52	M1	A	n	N	P	A	A	.	A	.	A	n	A	60
	M2	A	A	N	P	p	A	A	A	.	A	A	A	73
	S1	A	A	A	P	A	A	A	A	.	A	A	A	91
Total-PCB	M1	.	.	.	.	.	.	.	.	.	.	.	.	
	M2	.	.	.	.	.	.	.	.	.	.	.	.	
% Accredited		100	92 yes	24	43	75 yes	81 yes	94	96 yes	.	92 yes	47	100 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: 77 In accredited: 89

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Tammikuu 2006
Tekijä(t)	Irma Mäkinen ja Jari Nuutinen	
Julkaisun nimi	Laboratorioiden välinen pätevyyskoe 3/2005 PCB:t maasta	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	Suomen ympäristökeksuksen laboratorio järjesti kesällä 2005 pätevyyskokeen PCB-yhdisteiden (PCB 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p,-DDE ja p,p-DDT) ja kokonais-PCB:n analysoimiseksi saastuneista maista. Pätevyyskokeessa toimitettiin standardiseos, saastuneesta maasta valmistettu varmennettu vertailumateriaali ja saastunut maanäyte. Laboratoriot käyttivät useita analyysimenetelmiä tai eri menetelmien variaatioita. Varsinkin kokonais-PCB:n laskemiseen käytettiin useita eri menettelyjä. Tässä pätevyyskokeessa 77 % tuloksista oli tyydyttäviä, kun pätevyyden arvioinnissa käytettiin kokonaishajonnan tavoitearvoa 20 – 40 % vertailuarvosta 95 % merkitsevyystasolla. PCB-yhdisteiden 101, 105, 118 ja 138 tuloksista oli eniten tyydyttäviä. PCB-yhdisteet 28 ja 52 osoittautuvat vaikeimmin analysoitavaksi. PCB-yhdisteiden 105, 156 ja 170, kokonais-PCB sekä p,p-DDE ja p,p-DDT tuloksille ei arviointia tehty ainakaan kaikille näytteille raportoitujen tulosten vähäisen lukumäärän vuoksi.	
Asiasanat	PCB, saastuneet maat, ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailukoe	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen moniste 347	
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Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Edita Prima Ltd, Helsinki 2006	
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Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date January 2006
Author(s)	Irma Mäkinen and Jari Nuutinen	
Title of publication	SYKE Proficiency test 3/2005 PCB compounds from polluted soils	
Parts of publication/ other project publications		
Abstract	The Finnish Environment Institute carried out the interlaboratory comparison test for the determination of ten PCB congeners (PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p,-DDE and p,p-DDT) and total PCB from polluted soils in summer 2005. One standard solution containing a known concentration of different PCBs were prepared. The certified reference material (CRM LGC6113) and one soil sample contaminated with PCBs were delivered to the participating laboratories. Various analysis methods were used for the PCB determination. Most of them were in-house methods based on instrument applications or standard methods. Particularly, for the determination of total PCB several different procedures, were used. As the assigned value for the PCBs, the calculated concentration was used in the solvent samples, the certified values or the robust mean values were used for the soil samples. In this proficiency test, 77 % of the participating laboratories were able to report satisfactory results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval. In analysis of PCBs 101,105, 118 and 138 from the soil samples the results were most satisfactory. The PCB congeners 28 and 52 turned to be most critical analytes. Performance has not been evaluated for each sample in analysis of PCBs 105, 156 and 170, total PCB and p,p-DDE and p,p-DDT.	
Keywords	PCB, polluted soils, environmental laboratories, proficiency test, interlaboratory comparisons	
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Utgivare	Finlands Miljöcentral (SYKE)	Datum Januari 2006
Författare	Irma Mäkinen och Jari Nuutinen	
Publikationens titel	Provningsjämförelse 3/2005 PCB i förorenad jord	
Publikationens delar/ andra publikationer inom samma projekt		
Sammandrag	Under mars 2005 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämning av PCB föreningar (PCB 28, 52, 101, 105, 118, 138, 153, 156, 170, 180, p,p,-DDE och p,p-DDT) och total PCB i förorenad jord sommaren 2005. Ett syntetiskt prov hade preparerats. Ett sertificerat referens material (CRM LGC6113) och ett jord prov kontaminerat med PCB föreningar hade tillsats . Olika analysmetoder hade använts för PCB analys. Huvudsakligen de var "in-house" metoder, metoder baserade på instrumentaliska applikationer eller standard metoder. Särskilt, för analys av total PCB hade många olika applikationer använts. Som referensvärde (*the assigned value*) användes det teoretiska värdet (syntetiska provet) sertificerade värdet eller robust-medelvärdet (jordproven). Resultaten värderades med hjälp av z-värden. Beräkningen av z-värden baserade sig på totalstandardavvikelser, som tillsattes 20 - 40 % (95 % sannolikhetsnivå). I denna provningsjämförelse, var 77 % av resultatena tillfredsställande. I bestämmingen av PCB 101, 105, 118 och 138 i jordproven var resultatena mest tillfredsställande. Bestämningen av PCB 28 och 52 såg ut att vara mest kritisk. Kompetens i bestämningen av PCB 105, 156 och 170, total PCB och p,p-DDE och p,p-DDT hade inte evaluerats.	
Nyckelord	PCB, jord proven, provningsjämförelse, miljölaboratorier	
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