Suomen ympäristökeskuksen moniste

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Interlaboratory comparison 5/2001

PCB compounds from polluted soils

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PCB compounds from polluted soils

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FINNISH ENVIRONMENT INSTITUTE

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Content

1 INTRODUCTION

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) and total PCB from polluted soils in October 2001.

The interlaboratory comparison was carried out in accordance with the international guidelines, ISO/IEC Guide 43-1 (1) and ILAC Requirements (2) and some other publications (3, 4, 5 and 6).

2 ORGANIZING THE INTERLABORATORY COMPARISON

2.1 Responsibilities

The responsibilities in organizing the interlaboratory comparison were as follows:
Irma Mäkinen, SYKE, coordinator
Sami Huhtala, SYKE, technical coordinator
Anna-Mari Suortti, SYKE, analytical expert
Seppo Pönni, Pirkanmaa Regional Environment Centre, preparation of the soil samples.
Leena Sihvonen, analytical assistant.

2.2 Participants

A total of 14 laboratories from Finland, one German laboratory and one Estonian laboratory participated (Annex 1). Two laboratories participated only in the determination of the total PCB.

2.3 Samples

2.3.1 Testing of purity of the sample bottles

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

2.3.2 Sample preparation and delivery

Firstly, two standard solutions containing a known concentration of different PCBs were prepared (see Table 1). The solution L1 was prepared in iso-octane and the solution L2 in iso-octane, which contained eight volume percent of cyclohexane. The sample preparation is presented in Annex 2. Before delivery, the sample ampoules were weighed to check the possible solvent evaporation.

Secondly, a certified reference material (BCR CRM 536, freshwater harbour sediment), and two soil samples contaminated with PCBs were delivered to the participating laboratories. Four bottles of CRM 536 was purchased. The contents were combined, throughly mixed and divided

into a small glass bottles containing about 8 g of sediment (sample M0). Soil sample M1 was contaminated with small particles of PCB containing sealant and soil sample M2 with PCB containing engine oil. Both soils were excavated from contaminated sites.

To achieve homogeneity, the soil samples M1 and M2 were dried at room temperature and sieved through a 2.0 mm and 0.5 mm sieve, respectively. The sieved bulk materials were manually mixed until the samples were sufficiently homogenous. Finally, the samples M1 and M2 were divided into 64 portions containing about 100 g of soil. This was done using a rotary sample divider equipped with a vibratory sample feeder. Moisture content of both samples was less than 2 %. The amount of organic matter, measured as ignition loss, was 7 % and 4 % for M1 and M2, respectively.

The interlaboratory comparison took place between October 9 and 24, 2001.

The results were asked to return during the week 49 (2001). All participating laboratories reported results.

Table 1. Samples and PCB congeners

Samples and PCB congeners	Sample type
L1: PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180	1 synthetic solution
L2: total PCB	1 synthetic solution
M0: PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180	1 certified reference material
M1 and M2: PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170, 180 and total PCB	2 contaminated soils

2.4 Sample testing

2.4.1 Homogeneity study

The soil samples M1 and M2 were tested for homogeneity. For this purpose, eight samples of all the prepared samples were randomly selected. The samples were analysed as duplicates, and the results were estimated using one-way analysis of variance (3). The within-bottle standard deviation including analytical variation (s_{wb} %) was lower than 6 % in the sample M1 and lower than 3 % in the sample M2 (Annex 3). Higher s_{wb} was even expected, since the sample M1 was more coarse-grained than the sample M2.

The between-bottle standard deviation (s_{bb} %) was lower than 4 % in the sample M1 and lower than 3 % in the sample M2. In general, s_{bb} was at least five times lower than the reproducibility standard deviations of this interlaboratory comparison, s_b (Table 3).

However, s_{wb} and s_{bb} were low enough compared to the target total standard deviation (30 % or 40 % in 95 % confidence interval) in analysis of the samples M1 and M2. Thus the samples were considered homogenous to be used in this interlaboratory comparison. The between-bottle standard deviation (s_{bb}) was included in the uncertainty estimation of the assigned values.

2.4.2 Stability study

Stability testing of the samples was based on the analyses carried out at four times: once before the delivery and three times during the interlaboratory comparison. Stability of the samples L1, L2, M1 and M2 was tested.

Stability data was tested using regression analysis (4). The standard deviation of the regression line was tested for significance with t-statistics with n-2 degrees of freedom, by comparing the ratio of a degradation rate and a standard deviation of the regression line. In two cases the significant negative trend was present (Annex 4). The standard deviation of the regression line was included in the uncertainty estimation of the assigned values also when its value was not significant.

The results in the stability study of the sample L1 varied due to the high dilution needed for EC detector. The concentration of the sample was set to be adapted also for MSD measurements.

2.5 Comments sent by the participants

The participants commented mainly on some analytical problems (Annex 5).

The sample M2 contained mineral oil about 15000 mg/kg. This interfered severely the PCB analysis when mass selective detector was used. Because of oil interferences, the sample extract needed more spesific clean-up than normally used. Therefore the laboratories 1, 5 and 7 could not report results for M2.

The laboratory 16 commented mainly on their own results. In their opinion, the sample M2 was not throughly homogenous on the basis of variation of their replicate determinations. As a matter of fact, the results of homogeneity testing showed, that the within-bottle variation (s_{wb}) was highest (5.5 %) in determination of PCB-180 from the sample M1.

2.6 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 (ISO/DIS 10382, ISO 6468). Analytical methods are presented in Annex 6.

For the extraction, six laboratories used Soxhlet with extraction time of 2 - 8 hours. One laboratory used accelerated solvent extraction (ASE) and one supercritical fluid extraction (SFE). The others used traditional liquid extraction with shaking or sonic water bath, or combination of these. The most common solvent combination used was acetone:hexane (1:1 v/v), but also other combinations were used (see Annex 6).

Half of the laboratories used only sulfuric acid treatment for the extract clean-up. Four laboratories used sulfuric acid treatment followed by column chromatography either with aluminium oxide or silica. Three laboratories used only column chromatography either with Florisil, aluminium oxide or aluminium oxide combined with acidic silica. One laboratory didn't use clean-up at all.

For the detection, seven laboratories used mass selective detector (MSD) either in the SCAN or SIM mode. Nine laboratories used electron capture detector (ECD). Six of these ECD

laboratories used two columns with different polarities attached to one injector. From all the laboratories, only four used columns over 50 m long. Splittless-injection was most commonly used.

Various methods were also used for the determination of total PCB (Table 2).

Table 2. Methods used for determinaton of total PCB

Meth	Lab	Determination method for total PCB
1	1, 2, 3, 4, 8, 11, 12, 13, 14 and 16	For the sum of 4 - 15 PCB congeners appearing in technical PCB mixtures, a percentual part of the total content or a response factor is determined in each laboratory. In most of the laboratories, technical PCB mixture is chosen to resemble the PCB distribution in the sample. Using this defined percent or response factor, the total PCB in the sample is calculated.
2	5	The concentrations of congeners appearing in 10 peaks were calculated on the basis of the weight-% distribution of the individual congeners in the Aroclor 1260 mixture (7). The relation between the response areas and the concentratios was determined. The total PCB content for each sample was the sum of the peak concentrations.
	6	Sum of 33 PCB congeners
	7	Using 20 PCBs, retention time windows and mean response factors are determined for each chlorination isomer groups. Isomers are calculated using these response factors and sum of all isomers is reported as total PCB.
	9	Sum of seven congeners (28, 52, 101, 118, 138, 153 and 180)
	10	The total peak area between internal standard (not spesified) and PCB 189 was determined in samples and compared with peak area of known amount of Aroclor 1254.
	15	2,7 x sum of seven congeners (28, 52, 101, 118, 138, 153 and 180)

2.7 Data treatment

2.7.1 Testing of outliers and normality of data

Except for the sample M0, the participants were requested to report duplicate results. Measurement uncertainties were asked for all the results. Before the statistical treatment, the data was tested according to Cochran's (5), Hampel's (6) or Grubbs's outlier test (6), and Kolmogorov-Smirnov normality test. Outliers were rejected from the further data handling.

2.7.2 Assigned value and its uncertainty

The solvent samples L1 and L2 were prepared by diluting the commercial solution. Calculated values were used as the assigned values for the PCB congeners. The assigned values for the PCBs in the sample M0 (CRM 536) are as reported in the certificate.

The mean values of the results analyzed by a selected group of participants were used as the assigned values of the PCB congeners for soil samples M1 and M2. These "expert" laboratories reported accepted results (in or close to the 95 % confidence interval) for the CRM 536 and they had in total a good performance in this interlaboratory comparison.

For some PCB congeners (28, 105 and 170 in the sample M1 and 170 in the sample M2) the median values were used as the assigned values. Because of few participants or accepted values, the assigned values should be regarded only as indicative values.

The median value was used as the assigned value for the total PCB in the samples M1 and M2. The assigned values are presented in Annex 7.

The uncertainty of the assigned value was estimated. For the estimation of uncertainty, the standard deviation of the results used for calculation of the assigned values as well as the uncertainties obtained in the homogeneity and stability tests were used. The uncertainties are presented in Annex 8.

2.7.3 Target value for total standard deviation

The target total standard deviation (s_{target}, %) used for calculation of the z scores was estimated from the results of homogeneity and stability tests, the reproducibility standard deviations and the measurements uncertainties reported by the participants. The s_{target} was 20 % (95 % confidence interval) in analyses of the solvent sample L1. In the analyses of the soil samples it was 30 %, in general. However, in analyses of PCB 28 and PCB 52 in the sample M2 and in analyses of total PCB in both samples, the s_{target} was 40 %.

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 standard 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 Annex 12 (the results of the individual laboratories) and the summary of z scores is presented in Annex 18. Explanations to these Anneces are precented in Annex 11.

The organizing laboratory (SYKE) had the code 12 in this interlaboratory comparison.

3. RESULTS AND DISCUSSION

All of the results reported by the laboratories are presented in Annex 10. Statistically treated results of the individual laboratories are presented in Annex 12. The graphical presentations of the results and the uncertainty estimations are presented in Annex 13.

3.1 Repeatability and reproducibility

The repeatability (the within-laboratory standard deviation, s_w) was 2 - 4 % in analysis of the solvent samples L1 and L2, and 5 - 12 % in analysis of the soil samples M0, M1 and M2 (Table 3). In analysis of PCBs 105, 156 and 170 in the sample M1, the repeatability was about twice as much as in analysis of the sample M2 mainly due to analytical problems (see 3.4.2).

Table 3. Results of duplicate determinations (ANOVA statistics)

Analyte	Sample	Unit	Ass. val.	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Accepted. z-val %
PCB-101	L1	µg/l	699	682	679	20,7	55,6	59,3	3	8,1	8,7	20	14	93
	M1	µg/kg	355	356	362	16,4	69,5	71,4	4,6	19	20	30	14	86
	M2	µg/kg	258	278	265	17,1	54,9	57,5	6,1	20	21	30	12	83
PCB-105	L1	µg/l	699	723	722	19	71,7	74,1	2,6	9,9	10	20	11	82
	M1	µg/kg	18	20,5	18	2,49	7,8	8,19	12	38	40		8	
	M2	µg/kg	110	122	117	10,4	28,7	30,6	8,6	24	25	30	9	67
PCB-118	L1	µg/l	699	672	709	14,7	112	113	2,2	17	17	20	13	85
	M1	µg/kg	118	114	115	7,99	24,8	26,1	7	22	23	30	13	69
	M2	µg/kg	264	262	252	18,4	55,6	58,6	7	21	22	30	11	91
PCB-138	L1	µg/l	699	694	694	19,6	48,8	52,6	2,8	7	7,6	20	14	86
	M1	µg/kg	719	732	739	41,1	228	231	5,6	31	32	30	14	79
	M2	µg/kg	241	233	237	14,2	24,7	28,5	6,1	11	12	30	12	83
PCB-153	L1	µg/l	699	687	698	20,5	66,1	69,2	3	9,6	10	20	14	86
	M1	µg/kg	714	692	716	43,2	130	137	6,2	19	20	30	14	86
	M2	µg/kg	216	203	200	16,4	30,4	34,5	8,1	15	17	30	12	92
PCB-156	L1	µg/l	699	699	704	16,4	72,3	74,1	2,3	10	11	20	9	89
	M1	µg/kg	73,3	79,5	74,2	6,48	20,5	21,5	8,2	26	27	30	9	56
	M2	µg/kg	28	29,2	30,3	1,27	3,54	3,76	4,3	12	13	30	7	100
PCB-170	L1	µg/l	699	735	745	16,7	87,1	88,7	2,3	12	12	20	6	83
	M1	µg/kg	316	302	316	37,3	76,7	85,3	12	25	28		6	
	M2	µg/kg	43,1	43,6	43,1	2,6	5,73	6,29	6	13	14		5	
PCB-180	L1	µg/l	699	686	677	20,4	117	119	3	17	17	20	14	79
	M1	µg/kg	448	445	449	38,4	82,8	91,3	8,6	19	21	30	14	71
	M2	µg/kg	82,3	78,8	77,5	2,22	14,9	15,1	2,8	19	19	30	12	83
PCB-28	L1	µg/l	699	716	708	13	57,6	59,1	1,8	8	8,2	20	11	64
	M1	µg/kg	6,05	6,05	6,05	0,354			5,8				1	
	M2	µg/kg	18,5	18,6	18,9	2,17	4,21	4,74	12	23	26	30	8	75
PCB-52	L1	µg/l	699	659	677	17,7	90,2	91,9	2,7	14	14	20	14	86
	M1	µg/kg	30,1	29,3	29,8	1,71	8,14	8,31	5,8	28	28	30	13	77
	M2	µg/kg	157	181	160	10,1	58,1	59	5,6	32	33	30	12	75
Total-PCB	L2	mg/l	7,97	8,59	8,54	0,297	2,84	2,86	3,5	33	33	40	16	75
	M1	mg/kg	7,12	7,07	7,12	0,6	1,26	1,4	8,5	18	20	40	16	81
	M2	mg/kg	3,45	3,33	3,45	0,182	1,21	1,22	5,4	36	37	40	13	69

Ass. val. - assigned value, Md - median, sw - repeatability standard error, sb - standard error between laboratories, st - reproducibility standard error

On the other hand, the reproducibility (s_R) was 8 - 36 %. The majority of the obtained reproducibilities in analysis of soil samples was between 15 % and 25 %, and it was more than 30 % only in analyses of PCB 105 and PCB 138 from the sample M1 and PCB 52 from the sample M2.

The relative standard deviation (SD %) of the total PCB varied 20 - 36 % (Table 4). Most of the results for the total PCB were based on calculations, not on the actual determinations. Differences in calculating procedures can be seen also in the reproducibility of the results.

The results of the standard solution (the sample L1) showed a good agreement between the calculated, the mean value and the median value of the data (Table 4). However, in analysis of PCBs 105 and 170 the mean and the median values of the data were higher than the calculated concentration. In analysis of PCBs 52 and 180, the mean and median values were lower than the calculated concentration. The relative standard deviation varied 9 - 17 % mainly because of the differences in calibration solutions used by the participants or different sentivities of measurement techniques.

Compared to the other intercomparisons, the PCB concentrations in the sample M0 were fairly close to the concentrations of the samples in the QUASIMEME interlaboratory comparisons carried out in 1999 - 2001 (10). The results of the QUASIMEME comparisons varied 25 - 50 %, and the variation of the Finnish data in analysis of the sample M0 was rather similar.

As well, the variation of the Finnish data was compared with the results presented in the draft ISO/DIS 10382 (8). In analysis of PCBs from sand matrix (the sample SS155) the results varied 23 - 103 %. The PCB concentrations in this sample (260 - 700 µg/kg) were fairly close to the PCB concentration in the samples M1 and M2.

Table 4. Summary of the interlaboratory comparison

Analyte	Sample	Unit	Ass. val.	Mean	Md.	SD	SD%	2*Targ SD%	Num of labs	Ac-cepted. z-val %
PCB-101	L1	µg/l	699	682	679	58,2	8,54	20	14	93
	M0	µg/kg	44	39,9	40,5	6,59	16,5	30	14	79
	M1	µg/kg	355	356	362	70,1	19,7	30	14	86
	M2	µg/kg	258	278	265	56,4	20,3	30	13	83
PCB-105	L1	µg/l	699	723	722	72,3	10	20	11	82
	M0	µg/kg	3,5	11,8	9,1	9,4	79,9	30	11	29
	M1	µg/kg	18	20,5	18	7,76	37,9		11	
	M2	µg/kg	110	122	117	29,8	24,5	30	10	67
PCB-118	L1	µg/l	699	672	709	111	16,5	20	13	85
	M0	µg/kg	28	27	25,6	5,88	21,8	30	13	77
	M1	µg/kg	118	114	115	25,5	22,4	30	13	69
	M2	µg/kg	264	262	252	57,3	21,9	30	12	91
PCB-138	L1	µg/l	699	694	694	51,6	7,43	20	14	86
	M0	µg/kg	27	33,1	30,5	12,2	36,9	30	14	57
	M1	µg/kg	719	732	739	227	31	30	14	79
	M2	µg/kg	241	233	237	27,9	12	30	13	83
PCB-153	L1	µg/l	699	687	698	68	9,89	20	14	86
	M0	µg/kg	50	48	45,4	9,55	19,9	30	14	86
	M1	µg/kg	714	692	716	134	19,4	30	14	86
	M2	µg/kg	216	203	200	33,9	16,7	30	13	92
PCB-156	L1	µg/l	699	699	704	71,7	10,3	20	9	89
	M0	µg/kg	3	3,47	3,28	0,628	18,1	30	9	67
	M1	µg/kg	73,3	79,5	74,2	20,8	26,2	30	9	56
	M2	µg/kg	28	29,2	30,3	3,63	12,4	30	8	100
PCB-170	L1	µg/l	699	735	745	84,8	11,5	20	7	83
	M0	µg/kg	13,4	15,6	15,3	4,09	26,3	30	7	67
	M1	µg/kg	316	302	316	82,1	27,2		7	
	M2	µg/kg	43,1	43,6	43,1	6	13,7		7	
PCB-180	L1	µg/l	699	686	677	117	17	20	14	79
	M0	µg/kg	22	20,8	20,1	4,26	20,5	30	14	71
	M1	µg/kg	448	445	449	89,6	20,1	30	14	71
	M2	µg/kg	82,3	78,8	77,5	14,7	18,7	30	13	83
PCB-28	L1	µg/l	699	716	708	56,9	7,94	20	11	64
	M0	µg/kg	44	52	43	24,6	47,4	30	11	55
	M1	µg/kg	6,05	6,05	6,05	0,354	5,84		11	
	M2	µg/kg	18,5	18,6	18,9	4,61	24,8	30	10	75
PCB-52	L1	µg/l	699	659	677	90,3	13,7	20	14	86
	M0	µg/kg	38	35,9	32	11,6	32,2	30	14	64
	M1	µg/kg	30,1	29,3	29,8	8,15	27,8	30	14	77
	M2	µg/kg	157	181	160	57,6	31,8	30	13	75
Total-PCB	L2	mg/l	7,97	8,59	8,54	2,81	32,7	40	16	75
	M1	mg/kg	7,12	7,07	7,12	1,38	19,5	40	16	81
	M2	mg/kg	3,45	3,33	3,45	1,19	35,8	40	14	69

Ass. val.	the assigned value *(vertailuarvo)*
Mean	the mean value *(keskiarvo)*
Md:	the median value *(mediaani)*
SD:	the standard deviation *(keskihajonta)*
SD %:	the standard deviation as percents *(keskihajonta prosentteina)*
2*Targ. SD%	Acceptance level : the highest accepted deviation = the target total standard deviation, 95 % confidence level) *(hyväksymisraja: suurin sallittu poikkeama = kokonais-keskihajonnan tavoitearvo, 95 % todennäköisyys)*
Num of Labs	number of participants *(ko. määrityksen tehneiden laboratorioiden lukumäärä)*
Accepted z-val%	Accepted z values: the results (%), where $\|z\| < 2$ *(hyväksytyt z arvot = niiden tulosten osuus (%). joissa $\|z\| < 2$)*

3.2 Quality assurance procedures carried out by the participants

In this interlaboratory comparison, four participants had accredited their analytical methods (see Annex 9 and 18). Six laboratories had participated in international interlaboratory comparisons for analyses of PCBs from soil or sediment, and three of them were regarded as the "expert" laboratories in calculations of the assigned values. Four laboratories reported that they occasionally use reference materials (BCR CRM 481 or 365, RM LGC6113) in PCB analyses.

3.3 Uncertainties reported by the participants

Most of the participants had estimated the uncertainty of their analytical methods (Annex 13). The estimations were based mainly on the data of internal quality control procedures. The reported uncertainties varied mainly 20 - 30 %. Three participants (11, 12 and 14) had reported some higher uncertainties than the others, 36 - 60 %. In some cases, the uncertainties did not correspond well to the performance of the laboratories. Estimation of the measurement uncertainty seems to be partly at the stage of development. However, one should keep in mind that in this interlaboratory comparison the samples were dried, sieved and homogenized. Therefore, the reported uncertainties 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 uncertainty in analysis of standard solutions is smaller than uncertainty in analysis of soil samples.

3.4 Effect of different analytical methods on the results

3.4.1 Effect of different analytical methods

For dry sediment samples, Soxhlet extraction may be more efficient than liquid extraction with shaking or sonic extraction (11). At least, in SYKE it was observed that when the sample M0 was prewetted with water (0,5 ml/2 g), extraction recoveries using sonication were higher. For samples M1 and M2, prewetting was not tested.

The sample amount and the volume of the extraction solvent differed a lot. For the soil samples M1 and M2, laboratories extracted 1 - 25 g of soil with 3 - 210 ml of solvent (see Annex 6 for details). The homogeneity of these samples was tested with 10 g of soil. Especially in sample M1, the small sample intakes may not be representative and homogenous enough.

Three laboratories were not able to report results for the sample M2 due to the oil interference (see 2.5). Interference was observed also in some ECD chromatograms. Some laboratories had impurities in M0 extract, maybe due to deficient sulphur removal.

Many laboratories used commercial standard mixtures for instrument calibration. However, it is highly recommended to prepare standard solutions from certified, crystalline PCBs (11).

The calculated z scores of the laboratories were subjected to principal component analysis (PCA). The first PC represents the major part of the overall variance of the z scores. Due to the small number of participants and some missing values, the PCA figures can be regarded only as indicative (Annex 14). Although many of the results obtained using acetone:hexane as the extracting solvent were close to the origin of the coordinate system, almost all extreme values were obtained using the same solvent mixture. As well, the plotted data for the PCB 180 on the

basis of the results using different extraction solvents shows that variation of the results obtained using acetone:hexane was higher than variation of the results obtained by other solvents (petroleum ether:acetone:hexane:diethyl ether) (Annex 15).

3.4.2 Chromatography

Laboratories were asked to send chromatograms of samples, blank and calibration solution. Following observations were made. Some examples of peaks are presented in Annex 16.

PCB 28: Using a short column (≤ 30 m), 28 can coelute with PCB 31. According to some chromatograms, coelution has occurred and the result for 28 has been overestimated. Fairly few laboratories had 31 in their standard solution to control the resolution between these congeners. Some laboratories report routinely the sum of 28 and 31, and they didn't report 28 in this intercomparison. Some laboratories had interferences (unpurified sulphur, mineral oil) in the chromatogram.

PCB 52: No major interferences. Some laboratories had interferences (unpurified sulphur, mineral oil) in the chromatogram. According to organizer's experience, one phtalate may interfere in DB 5 type column.

PCB 101: According to literature (7,12), PCBs 84 and 90 may interfere especially when using a short DB 5 type column.

PCB 105: Most likely many laboratories had difficulties in identification of 105. According to literature (12), 105 can coelute with PCB 132, especially when using a short column. In the samples M0 and M1, the concentration of 105 was much smaller than that of 132. Therefore when using ECD, 105 can't be separated properly from 132. Obviously, 132 was quantified as 105 in many laboratories.

PCB 118: It is well known, that 118 can coelute with PCB 149 in DB 5 type columns and especially on short columns. According to some chromatograms, coelution has occurred and the result for 118 has been overestimated. Fairly few laboratories had 149 in their standard solution to control the resolution between these congeners.

PCB 138: It is well known, that 138 can coelute with PCBs 160 and 163. According to the certificate, sample M0 contains 17 µg/kg PCB 163. This interference may be one reason for high SD% (see Table 3). 138 is usually one of the largest peaks. Therefore there may be some problems in linearity of the ECD.

PCB 153: No major interferences. 153 is usually one of the largest peaks. Therefore there may be some problems in linearity of the ECD.

PCB 156: 156 is a very small peak in the samples M0 and M2. 156 also has its coeluters (PCBs 171 and 202) on DB 5 type columns, which may interfere especially on short columns.

PCB 170: No major interferences. Some coelution with PCB 190 may occur in DB 5 type columns.

PCB 180: No major interferences. As a late eluting compound and due to high temperatures, there may be some baseline problems when integrating the peak.

It is also highly recommended to use columns over 50 m long due to the coelution problems (13). 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. In general, the total elution time for all the PCBs was 10 - 15 minutes in 30 - 45 total run time. In one laboratory the PCBs eluted in less than seven minutes in a 45 total run time. This laboratory could improve the resolution by changing the oven program to have a slower temperature gradient in the middle of the program. On the other hand the laboratory 15 was able to achieve a good resolution even with 30 m columns. They had a total run time of 60 minutes and PCBs eluted in approx. 30 minutes. They used very slow temperature gradient in the middle of the oven program.

3.4.3 Total PCB

Seven different procedures were used for calculations of the total PCB (see Table 2). Ten laboratories used more or less similar approach in calculations, where laboratory determines the multiplier by itself. Only laboratory 15 used a fixed formula, which was derived in Finland in the 1980's to be commonly used for the calculation of total PCB. Laboratories 6 and 7 determined all or allmost all of the individual PCBs and summed them up. This can be done only with MSD. In general, the results in method group 2 were lower than in method group 1 (Table 2 and Annex 17).

At present, there are a lot of discussions about the proper way to estimate the total PCB. According to some experts, the only way is to determine all the individual PCBs and report the sum of these as a total PCB. Laboratories 6 and 7 were representing this way of calculation. On the other hand, the use of multipliers have been regarded as an adequate procedure. There is not yet a ISO standard method for calculating the total PCB in soil samples. However, the preparation of this standard will be started in near future by the ISO Soil quality TC 190/SC3/Working Group 7.

In these samples the calculation of total PCB was quite straightforward. The samples M1 and M2 resembled quite distinctly the technical mixtures Aroclor 1260 (or Clophen A60) and 1254 (or Clophen A50), respectively. In many environmental samples, especially in sediments or in biological samples, the resemblance 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 result of the total PCB for toxicity or risk evaluation.

3.5 Estimation of performance

In this interlaboratory comparison, 80 % of the participating laboratories were able to report acceptable results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval (Annex 18). The results were most satisfactory (87 %) in analysis of PCBs 101, 153 and total PCB. The PCB congeners 28, 52, 105 and 170 turned to be most critical analytes. The target standard deviation was highest for total PCB.

In analysis of the solvent sample L1, more than 80 % of the results were satisfactory when the target standard deviation was 20 %. This means, that there have not been serious problems in calibration procedures. In analysis of total PCB from the solvent sample L2, 75 % of the results

were satisfactory. Different calculation procedures used in estimation of total PCB have effected the variation of the results.

However, in analysis of the certified material M0, fairly few results were inside the confidence intervals reported in the certificate. In particular, on the basis of the results, the PCB congeners 28, 105 and 138 seemed to be most critical. In some cases, PCB 105 was incorrectly identified. As well, the confidence intervals of this CRM were widest for the PCBs 105 and 138.

In analysis of the soil sample M2 more results were satisfactory than in analysis of the sample M1. The sample M2 seemed to be easier to analyze, although it included mineral oil as interfering compound. Sample M1 may not have been as representative as M2 because it was more coarse grained than M2.

The Finnish interlaboratory comparison for analyses of PCB compounds from polluted soils was carried out for the first time. The results were promising in analysis of most PCB congeners, also when compared with some international comparisons. However, quality of the results can be improved by applying efficient validation procedures and quality assurance systems.

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) and total PCB from polluted soils in October 2001. A total of 14 laboratories from Finland, one German laboratory and one Estonian laboratory participated. Two laboratories participated only in the determination of the total PCB.

Two standard solutions containing a known concentration of different PCBs were prepared. A certified reference material (BCR CRM 536), and two soil samples contaminated with PCBs were also delivered to the participating laboratories.

Various analysis methods were used for the PCB determination. Majority of them were in-house methods based on instrument applications or standard methods (ISO/DIS 10382, ISO 6468). The method combinations were subjected to principal component analysis (PCA). For the determination of total PCB, there were seven different procedures.

As the assigned value for the PCBs, the calculated concentration was used in solvent samples, the certified values were used for the CRM 536 and a mean value of the results analyzed by a selected group of participants was used for the soil samples. The median value was used as the assigned value for the total PCB in the soil samples.

In this interlaboratory comparison, 80 % of the participating laboratories were able to report acceptable results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval. The results were most satisfactory (87 %) in analysis of PCBs 101, 153 and total PCB. The PCB congeners 28, 52, 105 and 170 turned to be most critical analytes.

The Finnish interlaboratory comparison for analyses of PCB compounds from polluted soils was carried out for the first time. The results were promising in analysis of most PCB congeners, also when compared with some international comparisons.

5 YHTEENVETO

Suomen ympäristökeskuksen laboratorio järjesti lokakuussa 2001 vertailukokeen kymmenen PCB-yhdisteen (28, 52, 101, 105, 118, 138, 153, 156, 170, 180) ja kokonais-PCB:n määrittämisestä pilaantuneista maista. Vertailukokeeseen osallistui yhteensä 14 suomalaista laboratoriota sekä yksi saksalainen ja yksi virolainen laboratorio.

Laboratorioille toimitettiin kaksi synteettistä liuosta, varmennettu vertailumateriaali (BCR CRM 536, sedimentti) ja kaksi PCB-yhdisteillä pilaantunutta maanäytettä.

Osallistujat käyttivät useita erilaisia analyysimenetelmiä. Menetelmistä suurin osa oli laboratorioiden sisäisiä menetelmiä, jotka pohjautuivat laitesovelluksiin tai standardimenetelmiin (ISO/DIS 10382, ISO 6468). Eri menetelmillä saatuja tuloksia tarkasteltiin pääkomponentti analyysin (PCA) avulla. Kokonais-PCB:n määrittämiseen oli käytössä seitsemän erilaista menettelyä.

Tulosten arvioimiseksi laskettiin z-arvo ja sitä varten asetettiin kokonaiskeskihajonnan tavoite-arvoksi 20 - 40 % (95 % todennäköisyys). Vertailuarvona *(the assigned value)* käytettiin synteettisille näytteille laskennallista arvoa, vertailumateriaalille sertifikaatissa ilmoitettuja arvoja ja maanäytteille valittujen laboratorioiden tulosten keskiarvoa. Kokonais-PCB:n vertailuarvona käytettiin tulosaineiston mediaania.

Vertailukokeessa 80 % laboratorioiden tuloksista oli hyväksyttäviä. Eniten tuloksia hyväksyttiin (87 %). PCB-yhdisteiden 101, 153 ja kokonais-PCB:n osalta. PCB-yhdisteistä 28, 52, 105 ja 170 osoittautuivat hankalimmiksi analysoitaviksi.

Suomen ympäristökeskuksen laboratoriossa järjestetty vertailukoe oli ensimmäinen suomalainen pilaantuneiden maiden PCB-määrityksiä koskenut vertailukoe. Vertailukokeen tulokset olivat pääsääntöisesti hyviä. Tulokset olivat hyviä myös verrattuna kansainvälisten vertailukokeiden tuloksiin.

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ANNEX 1. PARTICIPANTS IN THE INTERLABORATORY COMPARISON 5/2001

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Keski-Suomen ympäristökeskus

Lahden tutkimuslaboratorio

PSV- Maa ja Vesi Oy

SGS Inspection Services Oy

Suomen ympäristökeskus, laboratorio

Tampereen aluetyöterveyslaitos

Tampereen teknillinen korkeakoulu / Bio- ja ympäristötekniikan laitos

VTT Kemiantekniikka

ANNEX 2. PREPARATION OF THE SAMPLES

The sample L1

The standard solution L1 was a dilution of PCB Mix 20 (Dr. Ehrenstorfer, Cat.No. L200320, Lot No. 10202lO). This contained 15 PCB-congeners (28, 31, 52, 77, 101, 105, 118, 126, 128, 138, 153, 156, 169, 170 and 180) in iso-octane. Each of them had the concentration of 10.0 mg/l.

PCB Mix 20 was diluted by weighing as follows.

PCB Mix 20	Iso-octane	PCB Mix 20 + Iso-octane	The concentration of PCB in dilution
4.8316 g	**64.2580 g**	**69.0896 g (~100 ml)**	**(4.8316 g / 69.0896 g) x 10,0 mg/l = 0.6993 mg/l = 699 µg/l**

The prepared dilution was carefully mixed and sampled into a 3 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 bottle was recorded.

The sample L2

The standard solution L2 was a dilution of Aroclor 1260 (Dr. Ehrenstorfer, Cat.No. X201260, Lot No. 00809CY). This contained 100,0 mg/l of Aroclor 1260 in cyclohexane.

Aroclor 1260 was diluted by weighing as follows. For calculations, densities of 0,6919 g/ml and 0,7785 g/ml were used for iso-octane and cyclohexane, respectively.

Aroclor 1260	Iso-octane	Aroclor1260 + Iso-octane	The concentration of Aroclor 1260 in dilution
6.1888 g = 7.9496 ml	**63.4959 g = 91.7703 ml**	**7.9496 ml + 91,7703 ml = 99.7199 ml**	**(7.9496 ml / 99.7199 ml) x 100.0 mg/l = 7.9719 mg/l = 7.97 mg/l**

The prepared dilution was carefully mixed and sampled into a 3 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 bottle was recorded.

ANNEX 3. RESULTS OF THE HOMOGENEITY STUDY

Homogeneity was tested as duplicate determinations from eight bottles in samples M1 and M2. The results were calculated using one-way variance analysis.

Sample	PCB-congener	PCB µg/kg	Target SD %	s_{wb}	s_{wb} %	s_{bb}	s_{bb} %
M1	101	323.8	30	7.07	2.2	11.3	3.5
	118	114.6	30	3.36	2.3	4.11	3.6
	138	596.7	30	20.2	3.4	23.3	3.9
	153	630.3	30	22.2	3.5	21.7	3.5
	156	66.29	30	3.05	4.6	2.16 *)	3.3
	180	400.9	30	22.2	5.5	15.7 *)	3.9
	52	23.81	30	1.14	4.8	3.39 *)	1.4
M2	101	37348	30	4.96	1.9	3.51 *)	1.4
	105	94.18	30	1.4	1.4	0.99 *)	1.1
	118	261.7	30	3.61	1.4	2.77	1.1
	138	222.0	30	3.2	1.4	2.26 *)	1
	153	194	30	2.60	1.3	2.46	1.3
	156	25.46	30	0.322	1.3	0.567	2.2
	180	72.25	30	1.39	1.9	1.34 *)	1.9
	52	164.3	30	2.81	1.7	2.58	1.6
	28	13.47	30	0.329	2.4	0.232 *)	1.4

*) Because of $s_{bb}^2 < s_{wb}^2/2$, s_{bb} was estimated using the equation: $s_{bb} = \sqrt{s_{wb}^2/2}$

In general, the within bottle variation (including analytical variation), s_{wb} was less than 5 % (except PCB 180 in the sample M1) and the between bottle variation, s_{bb} was less than 4 %. However, the within-bottle variation of the sample M1 was higher than the within-bottle variation of the sample M2. The sample M1 was a soil contaminated with small particles of PCB containing sealant. It was sieved through a 2.0 mm sieve, and the sample M2 was sieved through 0.5 mm sieve. The within bottle and between bottle variations were not significant comparing with the accepted total standard deviation in this interlaboratory comparison, which was 30 % in analyses of the samples M1 and M2.

The samples were sufficiently homogenous to be used in this interlaboratory comparison.

The between bottle variations (s_{bb}) were included in the uncertainty estimation of the assigned values.

ANNEX 4. RESULTS OF THE STABILITY STUDY

Stability study was based on the analyses carried out four times during the analyzing period of the interlaboratory comparison.

Sample	PCB-compound	$s_{y/x}$ [1]	u_b [2]	$t_{calc} = \|b\|/u_b$	$t_{crit\ (0.05)}$
L1	101	19.5	0.734	0.263	2.228
	105	38.1	1.43	0.414	2.228
	118	33.7	1.27	0.02	2.228
	138	26.6	1.003	1.11	2.228
	153	21.9	0.826	0.997	2.228
	156	35.2	1.33	0.103	2.228
	180	29.9	1.13	0.522	2.228
	52	28	1.06	0.120	2.228
	28	26.1	0.98	0.165	2.228
L2	PCB-total	184	7.49	1.46	1.860
M1	101	8.04	0.118	0.217	2.306
	118	4.03	0.059	1.12	2.306
	138	13.3	0.194	2.43 [3]	2.306
	153	17.4	0.255	0.239	2.306
	156	2.11	0.031	2.43[3]	2.306
	180	12.9	0.188	0.239	2.306
	52	1.24	0.018	1.36	2.306
M2	101[4]	4.02	0.114	6.27 [3]	2.306
	105	3.76	0.106	1.68	2.306
	118	6.41	0.181	0.241	2.306
	138	2.43	0.069	0.795	2.306
	153	3.5	0.099	1.3	2.306
	156	0.781	0.022	3.24 [3]	2.306
	180	0.827	0.023	3.24 [3]	2.306
	52[4]	3.62	0.102	3.77 [3]	2.306
	28	0.349	37536	3.67[3]	2.306

[1] the standard deviation of the data

[2] the standard deviation of the slope ($y = bx + a$)

[3] $t_{calc} > t_{crit\ (0.05)}$

[4] the degradation rate was significantly negative

The standard deviation of the data ($s_{y/x}$) have been included in the uncertainty estimation of the assigned value also, when its value was not significant.

ANNEX 5. COMMENTS SENT BY THE PARTICIPANTS

Lab	Comment	Action/SYKE
1	The results of the sample M2 were not reported. Cleaning process was not effective enough for detecting of different PCB-compounds.	No action
2	The PCB 118 results in the sample M1 varied due to poor resolution. Results for 118 were obtained using different temperature program.	No action
7	In general, analyses of the samples containing high amounts of mineral oil as interference have been carried out by using ECD-detector. Unfortunately, this time the detector was broken. The results of the sample M2 were not reported.	No action
16	Comments on their own results. In the sample M0, the results were improved when results were calculated using recovery standard. In the sample M1, the replicates of the PCB-180 results varied much - the sample did not seemed to be homogenous according to other compounds either. The results for PCB 52 and total PCB in sample M2 were improved when correcting the peak integration of PCB 52.	No action

ANNEX 6. ANALYTICAL METHODS

Lab	Sample weight (approxim.)	Extraction method, solvent, volume and time	Clean up	Calibration and range	GC-injection technique, volume and temperature	GC-column(s)	Oven program	GC-detector
1	M0 2 g M1 2 g	Solvent extraction in sonic water bath: acetone:hexane (1:1) 40 ml	H_2SO_4 treatment	5 point calibration with standard solutions, range: 0,2-1200 pg/µl	T: 260 °C	DB-5 (30 m, 0.25 mm, 0.20 µm)	80°C (1.5 min), 7,5 °C/min –> 310 °C (10 min)	MSD-SIM
2	M0 4 g M1 10 g M2 10 g	ASE, petroleumether: acetone:hexane:ether (9:5.5:25:1) 25 ml, 20 min, 100 °C	H_2SO_4 treatment	2 point calibration with standard solutions	Manual injection, T: 250 °C	HP-5 and HP-50+ (30 m, 0.32 mm, 0.25 µm)	150°C,5 °C/min –> 350 °C (20 min)	ECD
3	M1 10 - 17 g M2 6 – 16 g	Soxhlet extraction, petroleumether: acetone:hexane:ether (9:5.5:25:1) 20 ml, 8 h	Al_2O_3	5 point calibration with standard solutions, range: 0,05-5 mg/l	Split, T: 250 °C	NB 54 and 1701 (25 m, 0.32 mm, 0.20 µm	80°C (1.5 min), 7,5 °C/min –> 310 °C (10 min)	ECD
4	M0 2 - 6 g M1 1 – 10 g M2 2 - 10 g	Soxhlet extraction, acetone:hexane (1:1), 6 h	H_2SO_4 treatment	3 point calibration with standard solutions, range: 5 - 100 µg/l, different congeneres, 50 – 400 µg/l, total-PCB	Splitless, T: 250 °C	NB 54 and 1701 (30 m, 0.32 mm, 0.25 µm)	150°C,5 °C/min –> 250 °C (20 min)	ECD
5	M1 2 g	Solvent extraction in sonic water bath: acetone:hexane (1:1) 2x 2ml, 2x60 min.	Florisil (100-200 mesh)	5 point calibration with standard solutions	Splitless, T: 270 °C	HP-5 (30 m, 0.25 mm, 0.25 µm)	80°C (1 min), 15 °C/min –> 150 °C, 15 °C/min –>250 °C, 15 °C/min –>315 °C	MSD-SIM
6		SFE – solid phase trap (extraction with CO_2, elution of compounds from the trap with 9 ml hexane)	Al_2O_3, M2 clean up with Al_2O_3 and acidic silica column	1 point calibration with standard solution	Splitless, T: 270 °C	DB Dioxin (60 m, 0.25 mm, 0.15 µm)	60°C (3 min), 20 °C/min –> 200 °C, 4 °C/min –> 270 °C (17 min)	HRMS-SIM

Lab	Sample weight	Extraction method, solvent, volume and time	Clean up	Calibration and range	GC-injection technique, volume and temperature	GC-column(s)	Oven program	GC-detector
7	M0 10-20 g ??? M1 10-20 g	Soxhlet extraction, acetone 20-40 ml, 2 h, 80 °C	Al_2O_3 and H_2SO_4 treatment	6 point calibration with standard solutions, d.l. 0,1 mg/kg (specific congeceres) 0,025 mg/kg total PCB	Splitless, T: 300 °C	HP-5MS (25 m, 0.25 mm, 0.25 µm)	60°C (1 min), 50 °C/min –> 230 °C, 10 °C/min –> 280 °C (10 min)	MSD-Scan
8	M0 3 g M1 8 - 10 g M2 10 g	Solvent extraction in sonic water bath, acetone:hexane (1:1) 2x50 ml, 2 h 10 min, room temp.	H_2SO_4 – mono-hydrate treatment	1 point calibration	Splitless, T: 260 °C	SPB-35 and SPB-5 (30 m, 0.25 mm, 0.25 µm)	50°C (1.5 min), 15 °C/min –> 150 °C, 4 °C/min –> 260 °C (25 min)	ECD (330 °C)
9	M0 4 g M1 25 g M2 25 g	Soxhlet extraction, acetone:hexane (1:1) 50 ml, 2 h	No clean up	7 point calibration at SIM and 10 at Scan method range: 1-100µg (SIM) 0,1-100 mg (Scan)	1 µl (Scan) 2 µl (SIM) T: 290 °C	DB-5MS (30 m, 0.25 mm, 0.50 µm)	40°C (4 min), 10 °C/min –> 300 °C (20 min)	MSD Scan (L1) SIM (L2, M0, M1, M2)
10	M0 4 g M1 3 g M2 4 g	Soxhlet extraction, acetone:hexane (1:1) 100 ml, 8 h	Silica gel, H_2SO_4 treatment	4 point calibration with standard solutions, range: 0 - 430 µg/kg		(60 m, 0.25 mm)	85°C (2 min), 80 °C/min –> 240 °C, 5 °C/min –> 325 °C (5 min)	ECD (350 °C)
11	M0 1 g M1 10 g M2 5 g	Solvent extraction, acetone: hexane (1:3) 50 ml + hexane:diethylether (1:9), 40 ml, 3x60 min., 25 °C	H_2SO_4 treatment	3 point calibration with standard solutions, range: 0,01 - 1 mg/kg	Split (1:5), 2 µl, T: 250 °C	HP-5MS (30 m, 0.25 mm, 0.25 µm)	40°C (6 min), 8 °C/min –> 300 °C (13 min)	MSD-SIM
12	M0 2 g M1 10 g M2 6 g	Solvent extraction in sonic water bath, acetone:hexane (1:1) 3x70 ml, 3x 1 h, <25 °C	H_2SO_4 treatment	6 point calibration with standard solutions, range: 0,2 - 100 µg/l	Splitless (3 min), 1 µl, T: 270 °C	HP 1701 and HP 5 (60 m, 0,25 mm, 0,25 µm)	90°C (3 min), 30 °C/min–> 215 °C (42 min), 5 °C/min–> 270 °C (10 min)	ECD (300 °C)

Lab	Sample weight	Extraction method, solvent, volume and time	Clean up	Calibration and range	GC-injection technique and temperature	GC-column(s)	Oven program	GC-detector
13	M0 3 - 5 g M1 2 - 3 g M2 2 g	Solvent extraction in sonic water bath, acetone: hexane (1:1), 3 ml	H_2SO_4 treatment	4 point calibration with standard solutions, range: 0,1-1 µg/ml	Splitless, 2 µl, T: 280 °C	HP-5 (30 m, 0.32 mm, 0.25 µm)	70°C (1 min), 15 °C/min –> 250 °C (30 min)	ECD (320 °C)
14	2 – 5 g	Solvent extraction, I acetone 50 ml, II acetone:hexane (1:3) 50 ml, 2x1 h, room temp.	H_2SO_4 treatment, Silica gel column	3 point calibration with standard solutions, range: 2-230 ng/ml (for each congenere)	Splitless, T: 250 °C	HP-35MS (30 m, 0.32 mm, 0.25 µm)	50°C (2 min), 20 °C/min –> 150 °C, 6 °C/min –> 250 °C (15 min)	ECD (320 °C)
15	M0 2 g M1 2 g M2 2 g	Soxhlet extraction, petroleumether: acetone: hexane:ether (9:5.5:25:1) 230 ml, 6 h, 180 °C	H_2SO_4 and Cu- treatment	1 point calibration with standard solution, range: 0,4-50 pg	Splitless, T: 250 °C	RTX-5 (30 m, 0.32 mm, 0.50 µm) and RTX-ClP2 (30 m, 0.32 mm, 0.25 µm)	60°C (1 min), 30 °C/min –> 170 °C (1 min) 1.5 °C/min –> 240 °C (1 min) 25 °C/min –> 290 °C (10 min)	ECD (300 °C)
16	M0 3 g M1 5 g M2 5 g	Solvent extraction by sonic water bath (5 min) and by shaking (1 h), acetone (30 ml), acetone:hexane (1:1) 30 ml, 25 °C	H_2SO_4 treatment and Al_2O_3 (M2 with silica gel)	6 point calibration with standard solutions, range: 5 - 1000 µg/l	Splitless, T: 270 °C	DB-5MS (60 m, 0.25 mm, 0.25 µm)	80°C, 15 °C/min –> 220 °C, 2 °C/min –> 270 °C, 30 °C/min –> 320 °C	MSD-SIM

ANNEX 7. THE ASSIGNED VALUES

M0, BCR CRM 536 (freshwater harbour sediment), the certified reference values

Compound	Certified value µg/kg	Uncertainty µg/kg (95 % confidence interval)	
PCB 28	44	± 5	(11 %)
PCB 52	38	± 4	(11 %)
PCB 101	44	± 4	(9.1 %)
PCB 105	3.5	± 0.6	(17 %)
PCB 118	28	± 3	(11 %)
PCB 138	27	± 4	(15 %)
PCB 153	50	± 4	(8.0 %)
PCB 156	3.0	± 0.4	(13 %)
PCB 170	13.4	± 1.4	(10 %)
PCB 180	22	± 2	(9.1 %)

L1 and L2, the solvent samples (the calculated concentrations)

Sample	Compound	Calculated value
L1	PCBs 28, 52, 101, 105, 118, 138, 153, 156, 170 and 180	699 µg/l (each)
L2	Total-PCB	7.97 mg/l

M1 and M2, the soil samples

The assigned values were calculated by using the mean value of the results reported by the "expert" laboratories, or calculated as a median value of the data as follows:

Compound	Sample	Laboratories	Assigned value: mean value of the "expert " laboratories	Assigned value: median
PCB-101 (µg/kg)	M1	6, 7, 8, 12, 14, 15, 16	355	
	M2	6, 8, 12, 14, 15	258	
PCB-105 (µg/kg)	M1			18
	M2	6, 12, 15	110	
PCB-118 (µg/kg)	M1	6, 7, 8, 12, 15, 16	118	
	M2	6, 8, 12, 15, 16	264	
PCB-138 (µg/kg)	M1	6, 7, 8, 12, 14, 15, 16	719	
	M2	6, 8, 12, 14, 15, 16	241	
PCB-153 (µg/kg)	M1	6, 7, 8, 12, 14, 15, 16	714	
	M2	6, 8, 12, 14, 15, 16	216	
PCB-156 (µg/kg)	M1	6, 7, 12, 15	73.3	
	M2	6, 12, 15	28	
PCB-170 (µg/kg)	M1			316
	M2			43.1
PCB-180 (µg/kg)	M1	6, 7, 8, 12, 14, 15	448	
	M2	6, 8, 12, 14, 15, 16	82.3	
PCB-28 (µg/kg)	M1			6.05
	M2	12, 15, 16	18.5	
PCB-52 (µg/kg)	M1	6, 7, 8, 12, 14, 15	30.1	
	M2	6, 8, 12, 14, 15	157	
Total-PCB (mg/kg)	M1			7.12
	M2			3.45

ANNEX 8. UNCERTAINTIES OF THE ASSIGNED VALUES

PCB	Sample	Conc. µg/l, µg/kg or mg/l	u_{hom} [1)]	u_{stab} [2)]	u_{char} [3)]	U	2U	2U %
101	L1	699	-	19.5	0.005	19.5	39	5.6
	M1	355	11.3	8.04	15.1	20.5	41	12
	M2	258	3.51	4.01	13.4	14.4	28.8	11
118	L1	699	-	33.7	0.005	33.7	67.4	9.6
	M1	264	4.11	4.03	4.45	7.27	14.5	5.5
	M2	264	2.77	6.41	11.7	13.6	27.2	10
138	L1	699	-	26.6	0.005	26.6	53.2	7.6
	M1	719	23.3	13.3	28.7	39.3	78.6	11
	M2	241	2.26	2.43	8	8.66	17.3	7.2
153	L1	699	-	21.9	0.005	21.9	43.2	6.3
	M1	714	21.7	17.4	32.2	42.5	85	12
	M2	216	2.46	3.5	8.08	9.1	18.2	8.4
156	L1	699	-	35.2	0.005	35.2	70.4	10
	M1	73.2	2.16	2.11	1.25	3.27	6.54	8.9
	M2	28	0.567	0.78	1.46	1.75	3.3	13
180	L1	699	-	29.9	0.005	29.9	59.8	8.6
	M1	448	15.7	12.9	14.9	25.2	50.4	11
	M2	82.3	1.34	0.827	2.47	2.93	5.86	7.1
28	L1	699	-	26.1	0.005	26.1	52.2	7.5
	M2	18.5	0.232	0.349	2.17	2.21	4.42	24
52	L1	699	-	28	0.005	28	56	8
	M1	30.1	3.39	1.24	2.36	4.31	8.62	29
	M2	157	2.58	3.62	10.7	11.6	23.2	15
105	L1	699	-	38.1	0.005	38.1	76.2	11
	M2	110	0.162	3.76	4.72	6.03	12.1	11
Total	L2	7970	-	184	0.01	184	368	4.6

[1)] u_{hom} = the between-bottle variation in testing of homogeneity
[2)] u_{stab} = the standard deviation of mesuring data in testing of stability
[3)] u_{char} = the samples M1 and M2: the standard deviation obtained in evaluation of the assigned value
the samples L1 and L2: based on the sample preparation

ANNEX 9. QUALITY ASSURANCE PROCEDURES CARRIED OUT BY THE PARTICIPANTS

Lab	Quality system	Accreditation	Participation in PT or analyses of CRM	Estimation of uncertainty
1	EN 45001 & ISO/IEC 25 or ISO 17025	No	CRM 481	On the basis of QC-data
2	EN 45001 & ISO/IEC 25 or ISO 17025	No	No	On the basis of QC-data
3	EN 45001 & ISO/IEC 25 or ISO 17025	No	No	On the basis of QC-data
4	EN 45001 & ISO/IEC 25 or ISO 17025	No	No	Own estimation
5	No	No	No	No estimation
6	EN 45001 & ISO/IEC 25 or ISO 17025	Yes	Canadian in 2000 Swedish in 2001	On the basis of QC-data
7	EN 45001 & ISO/IEC 25 or ISO 17025 and ISO 9000	No	RM LGC6113	No estimation
8	EN 45001 & ISO/IEC 25 or ISO 17025	Yes (no PCB-total)	CRM 365 British PT	Own estimation
9	No	No	No	No estimation
10	EN 45001 & ISO/IEC 25 or ISO 17025	Yes	British in 2000 and in 2001	Own estimation
11	EN 45001 & ISO/IEC 25 or ISO 17025	No	Dutch in 1999	On the basis of QC-data
12	EN 45001 & ISO/IEC 25 or ISO 17025	Yes (no PCB-total)	RM LGC6113 British in 1994-2000 Monaco in 2001	On the basis of QC-data
13	No	No	No	On the basis of response variation
14	EN 45001 & ISO/IEC 25 or ISO 17025	No	No	On the basis of QC-data
15	EN 45001 & ISO/IEC 25 or ISO 17025	No	Monaco in 2001	On the basis of QC-data
16	EN 45001 & ISO/IEC 25 or ISO 17025	No	No	On the basis of QC-data

ANNEX 10. RESULTS REPORTED BY THE PARTICIPANTS

Analyte	Sample	Unit	1			2			3			4			5			6		
PCB-101	L1	µg/l	657,40	664,00	1	451	462	1				660	630	1				744	784	1
	M0	µg/kg	39		1	28,0		1				44		1				33.2		1
	M1	µg/kg	210	214	1	383	403	1				430	430	1				376		1
	M2	µg/kg				261	258	1				230	210	1				293	295	1
PCB-105	L1	µg/l	639,65	622,75	1	415	419	1				630	650	1				685	713	1
	M0	µg/kg	eitod		1	12,8		1				9,1		1				3.24		1
	M1	µg/kg	13	13	1	<50	<50	1				150	140	1				12.8		1
	M2	µg/kg				121	117	1				110	90	1				88.3	86.2	1
PCB-118	L1	µg/l	636,00	638,60	1	445	455	1				620	640	1				730	757	1
	M0	µg/kg	25		1	22,4		1				26		1				25.2		1
	M1	µg/kg	70	74	1	244	181	1				140	130	1				114		1
	M2	µg/kg				209	210	1				190	180	1				249	247	1
PCB-138	L1	µg/l	656,15	650,05	1	430	445	1				610	640	1				656	680	1
	M0	µg/kg	45		1	28,4		1				50		1				25.4		1
	M1	µg/kg	577	591	1	918	935	1				1080	1100	1				740		1
	M2	µg/kg				260	254	1				230	220	1				248	245	1
PCB-153	L1	µg/l	655,50	657,35	1	446	404	1				630	660	1				727	757	1
	M0	µg/kg	46		1	32,0		1				45		1				45.7		1
	M1	µg/kg	434	456	1	745	777	1				750	770	1				735		1
	M2	µg/kg				189	184	1				160	150	1				220	219	1
PCB-156	L1	µg/l	663,55	655,75	1	328	343	1										699	733	1
	M0	µg/kg	eitod		1	4,5		1										3.06		1
	M1	µg/kg	40	45	1	89,1	89,6	1										68.9		1
	M2	µg/kg				26,0	22,0	1										25.0	24.9	1
PCB-170	L1	µg/l				nd	nd	1										839	868	1
	M0	µg/kg				nd		1										13.5		1
	M1	µg/kg				nd	nd	1										340		1
	M2	µg/kg				nd	nd	1										49.7	49.0	1
PCB-180	L1	µg/l	656,95	650,75	1	425	454	1				580	640	1				901	934	1
	M0	µg/kg	21		1	14,8		1				20		1				21.0		1
	M1	µg/kg	282	278	1	438	462	1				570	490	1				532		1
	M2	µg/kg				69,8	64,4	1				60	60	1				85.0	83.0	1
PCB-28	L1	µg/l	634,45	642,30	1	437	447	1				1100	1110	1				1080	1210	1
	M0	µg/kg	39		1	28,7		1				79		1				95.6		1
	M1	µg/kg	eitod	eitod	1	<40	<40	1				<10		1				< 1		1
	M2	µg/kg				<40	<40	1				23	19	1				26.2	23.6	1
PCB-52	L1	µg/l	660,20	653,65	1	466	470	1				620	620	1				682	701	1
	M0	µg/kg	32		1	21,3		1				31		1				44.9		1
	M1	µg/kg	14	15	1	<70	<70	1				35	36	1				26.9		1
	M2	µg/kg				160	159	1				190	160	1				193	191	1
Total-PCB	L2	mg/l	7,4	7,3	1	5,14	5,51	1	12.5	13.6	1	7,45	7,44	1	9,445		1	4.930	5.020	1
	M1	mg/kg	4,4	4,5	1	6,23	6,71	1	9.13	7.12	1	7,73	7,19	1	7.746	7.784	1	3.819		1
	M2	mg/kg				3,56	3,50	1	2.17	2.30	1	1,54	1,85	1				2.232	2.209	1
Analyte	Sample	Unit	7			8			9			10			11			12		
PCB-101	L1	µg/l	730	760	1	683	704	1	580	570	1	732	708	1	746.1	746.2	1	668	673	1
	M0	µg/kg	43		1	38,8		1	48,4		1	72,8		1	78.4		1	41,9		1
	M1	µg/kg	376	379	1	318	315	1	400	380	1	309	354	1	495	468	1	306	327	1
	M2	µg/kg			1	203	244	1	358	346	1	217	213	1	388	412	1	265	257	1
PCB-105	L1	µg/l	730	760	1				890	830	1	759	765	1	806.1	796.4	1	732	739	1
	M0	µg/kg			1				<0,1		1	29,5		1	<10.0		1	4,50		1
	M1	µg/kg	18	14	1				31,3	25,5	1	268,2	250,4	1	28.4	28.1	1	<4	<4	1
	M2	µg/kg			1				184	147	1	150	154	1	152	164	1	102	104	1
PCB-118	L1	µg/l	780	810	1	711	727	1	460	450	1	703	709	1	768.6	761.4	1	770	764	1
	M0	µg/kg	31		1	21,8		1	33,0		1	74,1		1	39.4		1	30,2		1
	M1	µg/kg	135	134	1	113	104	1	120	114	1	590	602	1	161	144	1	115	117	1
	M2	µg/kg			1	232	232	1	310	300	1	216	296	1	378	405	1	277	280	1
PCB-138	L1	µg/l	720	750	1	708	733	1	130	130	1	702	708	1	780.2	773.0	1	716	682	1
	M0	µg/kg	35		1	29,4		1	13,2		1	57,4		1	72.6		1	30,5		1
	M1	µg/kg	804	823	1	697	626	1	188	185	1	752	699	1	1100	1090	1	611	616	1
	M2	µg/kg			1	216	233	1	148	188	1	219	218	1	402	521	1	225	226	1
PCB-153	L1	µg/l	740	770	1	707	727	1	540	530	1	716	747	1	764.9	760.5	1	672	667	1
	M0	µg/kg	44		1	49,1		1	63,1		1	57,1		1	69.1		1	43,7		1
	M1	µg/kg	716	724	1	634	582	1	1200	920	1	628	597	1	962	890	1	660	666	1
	M2	µg/kg			1	202	201	1	291	225	1	162	162	1	431	460	1	198	199	1
PCB-156	L1	µg/l	760	780	1				590	560	1				791.2	790.4	1	757	754	1
	M0	µg/kg			1				3,58		1				<10.0		1	3,28		1
	M1	µg/kg	74	74	1				194	133	1				104	91.6	1	73,1	71,8	1
	M2	µg/kg			1				30,2	30,9	1				33.2	30.8	1	28,4	28,8	1
PCB-170	L1	µg/l	750	790	1							740	734	1	788.3	781.2	1	617	644	1

Analyte	Sample	Unit	7			8			9			10			11			12		
PCB-170	M0	µg/kg	17		1							19,6		1	20.6		1	11,7		1
	M1	µg/kg	325	334	1							316	230	1	464	402	1	237	228	1
	M2	µg/kg			1							49,0	51,7	1	38.8	46.3	1	38,0	39,9	1
PCB-180	L1	µg/l	750	760	1	722	747	1	540	520	1	746	761	1	784.2	788.2	1	656	664	1
	M0	µg/kg	17		1	19,3		1	51,6		1	28,7		1	29.7		1	20,1		1
	M1	µg/kg	436	444	1	449	418	1	1135	736	1	468	390	1	680	552	1	413	393	1
	M2	µg/kg			1	87,6	90,8	1	174	162	1	68,4	69,8	1	111	115	1	73,3	73,9	1
PCB-28	L1	µg/l	770	770	1				1050	1030	1	777	786	1				699	700	1
	M0	µg/kg	43		1				90,8		1	44,7		1				41,2		1
	M1	µg/kg			1				<0,1	<0,1	1	6,3	5,8	1				<2	<2	1
	M2	µg/kg			1				14,6	17,0	1	18,9	22,0	1				14,4	15,2	1
PCB-52	L1	µg/l	790	780	1	709	721	1	570	560	1	728	736	1	735.5	724.8	1	672	665	1
	M0	µg/kg	30		1	32,0		1	56,5		1	45,9		1	58.1		1	33,2		1
	M1	µg/kg	26	26	1	36,2	40,9	1	30,1	27,8	1	42,5	43,5	1	36.3	35.4	1	21,7	23,9	1
	M2	µg/kg			1	126	151	1	277	295	1	163	158	1	307	295	1	159	159	1
Total-PCB	L2	mg/l	10,087	10,360	1	9,92	10,0	1	2,53	2,36	1	11,0	11,9	1	12.2	12.4	1	8,09	7,99	1
	M1	mg/kg	6,853	6,751	1	6,24	6,21	1	2,72	2,36	1	8,1	7,9	1	14.0	12.9	1	6,72	6,78	1
	M2	mg/kg			1	4,17	4,53	1	1,57	1,53	1	3,4	3,6	1	7.9	8.6	1	4,06	4,05	1
Analyte	Sample	Unit	13			14			15			16								
PCB-101	L1	µg/l	610	600	1	675	621	1	695	637	1	738	726	1						
	M0	µg/kg	48		1	35,0		1	46,9		1	33		1						
	M1	µg/kg	270	260	1	434	415	1	321	359	1	330	362	1						
	M2	µg/kg	280	280	1	217	281	1	264	259	1	324	324	1						
PCB-105	L1	µg/l	660	660	1				709	676	1									
	M0	µg/kg	18		1				5,19		1									
	M1	µg/kg	170	170	1				<0,5	<0,5	1									
	M2	µg/kg	93	92	1				118	116	1									
PCB-118	L1	µg/l	620	620	1				708	654	1	775	766	1						
	M0	µg/kg	19		1				29,9		1	21		1						
	M1	µg/kg	70	68	1				113	124	1	127	102	1						
	M2	µg/kg	220	210	1				260	254	1	304	302	1						
PCB-138	L1	µg/l	630	620	1	685	640	1	712	659	1	774	769	1						
	M0	µg/kg	39		1	21,8		1	31,9		1	23		1						
	M1	µg/kg	630	580	1	749	739	1	724	778	1	803	632	1						
	M2	µg/kg	250	240	1	208	252	1	257	252	1	257	275	1						
PCB-153	L1	µg/l	620	600	1	688	641	1	713	649	1	769	762	1						
	M0	µg/kg	41		1	43,0		1	51,2		1	42		1						
	M1	µg/kg	520	490	1	792	763	1	646	698	1	922	750	1						
	M2	µg/kg	180	180	1	195	233	1	212	209	1	251	251	1						
PCB-156	L1	µg/l	640	640	1				708	666	1									
	M0	µg/kg	10		1				2,92		1									
	M1	µg/kg	100	120	1				74,2	77,0	1									
	M2	µg/kg	34	34	1				30,7	30,3	1									
PCB-170	L1	µg/l	640	630	1															
	M0	µg/kg	11		1															
	M1	µg/kg	200	250	1															
	M2	µg/kg	37	37	1															
PCB-180	L1	µg/l	640	630	1	689	648	1	709	655	1	785	783	1						
	M0	µg/kg	17		1	18,5		1	22,4		1	21		1						
	M1	µg/kg	330	360	1	468	457	1	450	472	1	851	549	1						
	M2	µg/kg	64	63	1	75	81	1	80,1	80,8	1	90	87	1						
PCB-28	L1	µg/l	670	630	1				778	754	1	704	711	1						
	M0	µg/kg	31		1				50,1		1	29		1						
	M1	µg/kg	<1	<1	1				<0,5	<0,5	1	<5	<5	1						
	M2	µg/kg	11	11	1				19,0	18,2	1	19	25	1						
PCB-52	L1	µg/l	510	510	1	688	627	1	703	640	1	753	745	1						
	M0	µg/kg	25		1	25,5		1	40,6		1	27		1						
	M1	µg/kg	19	20	1	33	34	1	29,8	32,4	1	21	26	1						
	M2	µg/kg	130	130	1	122	137	1	166	163	1	384	391	1						
Total-PCB	L2	mg/l	10.7	10.3	1	8,54	8,25	1	7,420	7,190	1	9,79	9,67	1						
	M1	mg/kg	7.9	7.9	1	8,31	8,07	1	6,170	6,650	1	10,1	7,99	1						
	M2	mg/kg	4.3	4.6	1	3,17	3,80	1	3,400	3,310	1	5,52	5,61	1						

ANNEX 11. EXPLANATIONS FOR THE RESULT SHEETS

Results of the individual laboratories (Annex 12)

z-Graphics z score, a 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 assigned value
s = the target value for the total standrd deviation ($s_{target\,(\%)}$).

Outl test OK

yes	- a result passed the outlier test
C	- a result was rejected on the basis of Cochran test
H	- a result was rejected on the basis of Hampel test
G2	- a result was rejected on the basis of Grubbs-2 test

Cochran test: the test of the within-laboratory variances (ISO 5725-2)
Grubbs-2 test: the test of the between-laboratory varibilities (two outlying observations; to test whether the two smallest or the two highest observations may be outliers, ISO 5725-2)
Hampel test: the test of the between-laboratory varibilities (based on the absolute residuals d_i of the single data x_i from the median x_{med}; $d_i = |x_{med} - x_i|$). The data is an outlier, when $d_i > 5{,}06MAD$, where MAD is the median of the absolute residuals.

The outlier tests were carried out in 95 % confidence level.

Normality of the data was tested using the Kolmogorov-Smirnov -test.

Assigned value The calculated concentration, the mean value of the expert laboratories or the median of the data.
2* Targ SD % The target total standard deviation (95 % confidence level).
Lab's result The result reported by the participant
Md. The median value of the results
Mean The mean value of the results
SD The standard deviation
SD % The relative standard deviation
Passed The number of the laboratories that passed the outlier test
Missing The result is missing, e.g. below the detection limit
Num of labs The number of the participated laboratories

Summary of z scores (Annex 18)

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

ANNEX 12. RESULTS OF THE INDIVIDUAL LABORATORIES

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
PCB-101	µg/l	L1		-0,548	yes	699	20	661	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-0,758	yes	44	30	39	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		-2,69	yes	355	30	212	362	356	70,1	19,7	14	0	0	14
PCB-105	µg/l	L1		-0,97	yes	699	20	631	722	723	72,3	10	10	1	0	11
	µg/kg	M0				3,5	30	eitod	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			yes	18		13	18	20,5	7,76	37,9	5	3	3	11
PCB-118	µg/l	L1		-0,883	yes	699	20	637	709	672	111	16,5	13	0	0	13
	µg/kg	M0		-0,714	yes	28	30	25	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		-2,6	yes	118	30	72	115	114	25,5	22,4	11	2	0	13
PCB-138	µg/l	L1		-0,657	yes	699	20	653	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		4,44	yes	27	30	45	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		-1,25	yes	719	30	584	739	732	227	31	14	0	0	14
PCB-153	µg/l	L1		-0,609	yes	699	20	656	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-0,533	yes	50	30	46	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		-2,51	yes	714	30	445	716	692	134	19,4	13	1	0	14
PCB-156	µg/l	L1		-0,563	yes	699	20	660	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0				3	30	eitod	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		-2,8	yes	73,3	30	42,5	74,2	79,5	20,8	26,2	8	1	0	9
PCB-180	µg/l	L1		-0,646	yes	699	20	654	677	686	117	17	14	0	0	14
	µg/kg	M0		-0,303	yes	22	30	21	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		-2,5	yes	448	30	280	449	445	89,6	20,1	12	2	0	14
PCB-28	µg/l	L1		-0,867	yes	699	20	638	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		-0,758	yes	44	30	39	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05			6,05	6,05	0,354	5,8	1	0	10	11
PCB-52	µg/l	L1		-0,602	yes	699	20	657	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-1,05	yes	38	30	32	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		-3,45	yes	30,1	30	14,5	29,8	29,3	8,15	27,8	13	0	1	14
Total-PCB	mg/l	L2		-0,389	yes	7,97	40	7,35	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-1,87	yes	7,12	40	4,45	7,12	7,07	1,38	19,5	14	2	0	16
Laboratory 2																
PCB-101	µg/l	L1		-3,47	G2	699	20	457	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-2,42	yes	44	30	28,0	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		0,709	yes	355	30	393	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		0,044	yes	258	30	260	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		-4,03	H	699	20	417	722	723	72,3	10	10	1	0	11
	µg/kg	M0		17,7	yes	3,5	30	12,8	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1				18		<50	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		0,545	yes	110	30	119	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		-3,56	yes	699	20	450	709	672	111	16,5	13	0	0	13
	µg/kg	M0		-1,33	yes	28	30	22,4	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		5,34	H	118	30	213	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		-1,37	yes	264	30	210	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		-3,74	H	699	20	438	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		0,346	yes	27	30	28,4	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		1,93	yes	719	30	927	739	732	227	31	14	0	0	14
	µg/kg	M2		0,438	yes	241	30	257	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		-3,92	G2	699	20	425	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-2,4	yes	50	30	32,0	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		0,434	yes	714	30	761	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-0,906	yes	216	30	187	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		-5,2	G2	699	20	336	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0		3,33	yes	3	30	4,5	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		1,46	yes	73,3	30	89,3	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2		-0,956	yes	28	30	24	30,3	29,2	3,63	12,4	6	1	1	8
PCB-170	µg/l	L1				699	20	nd	745	735	84,8	11,5	6	0	1	7
	µg/kg	M0				13,4	30	nd	15,3	15,6	4,09	26,3	6	0	1	7
	µg/kg	M1				316		nd	316	302	82,1	27,2	6	0	1	7
	µg/kg	M2				43,1		nd	43,1	43,6	6	13,7	5	0	2	7
PCB-180	µg/l	L1		-3,71	yes	699	20	440	677	686	117	17	14	0	0	14
	µg/kg	M0		-2,18	yes	22	30	14,8	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		0,0243	yes	448	30	450	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		-1,23	yes	82,3	30	67,1	77,5	78,8	14,7	18,7	10	2	1	13

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
PCB-28	µg/l	L1		-3,68	H	699	20	442	708	716	56,9	7,9	7	4	0	11
Laboratory 2																
PCB-28	µg/kg	M0		-2,32	yes	44	30	28,7	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<40	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2				18,5	30	<40	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		-3,3	yes	699	20	468	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-2,93	yes	38	30	21,3	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1				30,1	30	<70	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		0,119	yes	157	30	160	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		-1,66	yes	7,97	40	5,33	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-0,456	yes	7,12	40	6,47	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		0,116	yes	3,45	40	3,53	3,45	3,33	1,19	35,8	12	1	1	14
Laboratory 3																
Total-PCB	mg/l	L2		3,19	yes	7,97	40	13,1	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		0,706	yes	7,12	40	8,13	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		-1,76	yes	3,45	40	2,24	3,45	3,33	1,19	35,8	12	1	1	14
Laboratory 4																
PCB-101	µg/l	L1		-0,773	yes	699	20	645	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		0	yes	44	30	44	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		1,4	yes	355	30	430	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		-0,978	yes	258	30	220	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		-0,844	yes	699	20	640	722	723	72,3	10	10	1	0	11
	µg/kg	M0		10,7	yes	3,5	30	9,1	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			H	18		145	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		-0,606	yes	110	30	100	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		-0,987	yes	699	20	630	709	672	111	16,5	13	0	0	13
	µg/kg	M0		-0,476	yes	28	30	26	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		0,96	yes	118	30	135	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		-1,99	yes	264	30	185	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		-1,06	yes	699	20	625	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		5,68	yes	27	30	50	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		3,45	yes	719	30	1090	739	732	227	31	14	0	0	14
	µg/kg	M2		-0,447	yes	241	30	225	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		-0,773	yes	699	20	645	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-0,667	yes	50	30	45	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		0,425	yes	714	30	760	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-1,88	yes	216	30	155	200	203	33,9	16,7	10	2	1	13
PCB-180	µg/l	L1		-1,27	yes	699	20	610	677	686	117	17	14	0	0	14
	µg/kg	M0		-0,606	yes	22	30	20	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		1,21	yes	448	30	530	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		-1,81	yes	82,3	30	60	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		5,81	H	699	20	1110	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		5,3	yes	44	30	79	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<10	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		0,915	yes	18,5	30	21	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		-1,13	yes	699	20	620	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-1,23	yes	38	30	31	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		1,2	yes	30,1	30	35,5	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		0,779	yes	157	30	175	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		-0,329	yes	7,97	40	7,44	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		0,239	yes	7,12	40	7,46	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		-2,54	yes	3,45	40	1,69	3,45	3,33	1,19	35,8	12	1	1	14
Laboratory 5																
Total-PCB	mg/l	L2		0,925	yes	7,97	40	9,445	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		0,453	yes	7,12	40	7,76	7,12	7,07	1,38	19,5	14	2	0	16

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 6																
PCB-101	µg/l	L1		0,93	yes	699	20	764	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-1,64	yes	44	30	33.2	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		0,39	yes	355	30	376	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		0,936	yes	258	30	294	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		0	yes	699	20	699	722	723	72,3	10	10	1	0	11
	µg/kg	M0		-0,495	yes	3,5	30	3.24	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			yes	18		12.8	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		-1,38	yes	110	30	87,3	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		0,637	yes	699	20	744	709	672	111	16,5	13	0	0	13
	µg/kg	M0		-0,667	yes	28	30	25.2	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		-0,226	yes	118	30	114	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		-0,397	yes	264	30	248	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		-0,443	yes	699	20	668	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		-0,395	yes	27	30	25.4	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		0,198	yes	719	30	740	739	732	227	31	14	0	0	14
	µg/kg	M2		0,147	yes	241	30	247	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		0,615	yes	699	20	742	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-0,573	yes	50	30	45.7	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		0,192	yes	714	30	735	716	692	134	19,4	13	1	0	14
	µg/kg	M2		0,113	yes	216	30	220	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		0,243	yes	699	20	716	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0		0,133	yes	3	30	3.06	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		-0,399	yes	73,3	30	68.9	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2		-0,73	yes	28	30	24,9	30,3	29,2	3,63	12,4	6	1	1	8
PCB-170	µg/l	L1		2,21	yes	699	20	854	745	735	84,8	11,5	6	0	1	7
	µg/kg	M0		0,0498	yes	13,4	30	13.5	15,3	15,6	4,09	26,3	6	0	1	7
	µg/kg	M1			yes	316		340	316	302	82,1	27,2	6	0	1	7
	µg/kg	M2			yes	43,1		49,4	43,1	43,6	6	13,7	5	0	2	7
PCB-180	µg/l	L1		3,13	yes	699	20	918	677	686	117	17	14	0	0	14
	µg/kg	M0		-0,303	yes	22	30	21.0	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		1,24	yes	448	30	532	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		0,138	yes	82,3	30	84	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		6,38	C	699	20	1150	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		7,82	yes	44	30	95.6	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		< 1	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		2,32	yes	18,5	30	24,9	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		-0,107	yes	699	20	692	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		1,21	yes	38	30	44.9	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		-0,703	yes	30,1	30	26.9	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		1,5	yes	157	30	192	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		-1,88	yes	7,97	40	4,97	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-2,32	yes	7,12	40	3.819	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		-1,78	yes	3,45	40	2,22	3,45	3,33	1,19	35,8	12	1	1	14

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 7																
PCB-101	µg/l	L1		0,658	yes	699	20	745	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-0,152	yes	44	30	43	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		0,418	yes	355	30	378	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2			H	258	30	<	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		0,658	yes	699	20	745	722	723	72,3	10	10	1	0	11
	µg/kg	M0				3,5	30	<	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			yes	18		16	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2				110	30	<	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		1,37	yes	699	20	795	709	672	111	16,5	13	0	0	13
	µg/kg	M0		0,714	yes	28	30	31	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		0,932	yes	118	30	135	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2				264	30	<	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		0,515	yes	699	20	735	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		1,98	yes	27	30	35	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		0,88	yes	719	30	814	739	732	227	31	14	0	0	14
	µg/kg	M2				241	30	<	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		0,801	yes	699	20	755	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-0,8	yes	50	30	44	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		0,0517	yes	714	30	720	716	692	134	19,4	13	1	0	14
	µg/kg	M2			H	216	30	<	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		1,02	yes	699	20	770	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0			H	3	30	<	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		0,065	yes	73,3	30	74	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2			H	28	30	<	30,3	29,2	3,63	12,4	6	1	1	8
PCB-170	µg/l	L1		1,02	yes	699	20	770	745	735	84,8	11,5	6	0	1	7
	µg/kg	M0		1,79	yes	13,4	30	17	15,3	15,6	4,09	26,3	6	0	1	7
	µg/kg	M1			yes	316		330	316	302	82,1	27,2	6	0	1	7
	µg/kg	M2				43,1		<	43,1	43,6	6	13,7	5	0	2	7
PCB-180	µg/l	L1		0,801	yes	699	20	755	677	686	117	17	14	0	0	14
	µg/kg	M0		-1,52	yes	22	30	17	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		-0,124	yes	448	30	440	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2			H	82,3	30	<	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		1,02	yes	699	20	770	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		-0,152	yes	44	30	43	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2				18,5	30	<	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		1,23	yes	699	20	785	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-1,4	yes	38	30	30	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		-0,903	yes	30,1	30	26	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2				157	30	<	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		1,41	yes	7,97	40	10,2	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-0,223	yes	7,12	40	6,8	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2				3,45	40	<	3,45	3,33	1,19	35,8	12	1	1	14

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 8																
PCB-101	µg/l	L1		-0.0787	yes	699	20	694	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-0,788	yes	44	30	38,8	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		-0,727	yes	355	30	317	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		-0,887	yes	258	30	224	265	278	56,4	20,3	11	1	1	13
PCB-118	µg/l	L1		0,286	yes	699	20	719	709	672	111	16,5	13	0	0	13
	µg/kg	M0		-1,48	yes	28	30	21,8	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		-0,537	yes	118	30	109	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		-0,801	yes	264	30	232	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		0,308	yes	699	20	721	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		0,593	yes	27	30	29,4	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		-0,53	yes	719	30	662	739	732	227	31	14	0	0	14
	µg/kg	M2		-0,461	yes	241	30	225	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		0,258	yes	699	20	717	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-0,12	yes	50	30	49,1	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		-0,993	yes	714	30	608	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-0,443	yes	216	30	202	200	203	33,9	16,7	10	2	1	13
PCB-180	µg/l	L1		0,508	yes	699	20	735	677	686	117	17	14	0	0	14
	µg/kg	M0		-0,818	yes	22	30	19,3	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		-0,221	yes	448	30	434	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		0,56	yes	82,3	30	89,2	77,5	78,8	14,7	18,7	10	2	1	13
PCB-52	µg/l	L1		0,229	yes	699	20	715	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-1,05	yes	38	30	32,0	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		1,88	yes	30,1	30	38,6	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		-0,774	yes	157	30	139	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		1,25	yes	7,97	40	9,96	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-0,629	yes	7,12	40	6,22	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		1,3	yes	3,45	40	4,35	3,45	3,33	1,19	35,8	12	1	1	14
Laboratory 9																
PCB-101	µg/l	L1		-1,77	yes	699	20	575	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		0,667	yes	44	30	48,4	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		0,653	yes	355	30	390	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		2,44	yes	258	30	352	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		2,3	yes	699	20	860	722	723	72,3	10	10	1	0	11
	µg/kg	M0				3,5	30	<0,1	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			yes	18		28,4	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		3,36	yes	110	30	166	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		-3,49	yes	699	20	455	709	672	111	16,5	13	0	0	13
	µg/kg	M0		1,19	yes	28	30	33,0	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		-0,0565	yes	118	30	117	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		1,04	yes	264	30	305	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		-8,14	H	699	20	130	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		-3,41	yes	27	30	13,2	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		-4,94	yes	719	30	187	739	732	227	31	14	0	0	14
	µg/kg	M2		-2,02	yes	241	30	168	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		-2,35	yes	699	20	535	698	687	68	9,9	13	1	0	14
	µg/kg	M0		1,75	yes	50	30	63,1	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		3,22	C	714	30	1060	716	692	134	19,4	13	1	0	14
	µg/kg	M2		1,3	yes	216	30	258	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		-1,77	yes	699	20	575	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0		1,29	yes	3	30	3,58	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		8,21	C	73,3	30	164	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2		0,603	yes	28	30	30,6	30,3	29,2	3,63	12,4	6	1	1	8
PCB-180	µg/l	L1		-2,42	yes	699	20	530	677	686	117	17	14	0	0	14
	µg/kg	M0		8,97	H	22	30	51,6	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		7,24	H	448	30	936	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		6,94	H	82,3	30	168	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		4,88	H	699	20	1040	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		7,09	yes	44	30	90,8	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<0,1	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		-0,963	yes	18,5	30	15,8	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		-1,92	yes	699	20	565	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		3,25	yes	38	30	56,5	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		-0,249	yes	30,1	30	28,9	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		5,5	yes	157	30	286	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		-3,47	yes	7,97	40	2,44	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-3,22	H	7,12	40	2,54	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		-2,75	yes	3,45	40	1,55	3,45	3,33	1,19	35,8	12	1	1	14

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 10																
PCB-101	µg/l	L1		0,3	yes	699	20	720	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		4,36	H	44	30	72,8	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		-0,445	yes	355	30	332	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		-1,11	yes	258	30	215	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		0,901	yes	699	20	762	722	723	72,3	10	10	1	0	11
	µg/kg	M0		49,5	yes	3,5	30	29,5	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			H	18		259	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		2,55	yes	110	30	152	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		0,1	yes	699	20	706	709	672	111	16,5	13	0	0	13
	µg/kg	M0		11	H	28	30	74,1	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		27	H	118	30	596	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		-0,195	yes	264	30	256	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		0,0858	yes	699	20	705	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		7,51	yes	27	30	57,4	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		0,0639	yes	719	30	726	739	732	227	31	14	0	0	14
	µg/kg	M2		-0,627	yes	241	30	219	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		0,465	yes	699	20	732	698	687	68	9,9	13	1	0	14
	µg/kg	M0		0,947	yes	50	30	57,1	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		-0,951	yes	714	30	613	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-1,66	yes	216	30	162	200	203	33,9	16,7	10	2	1	13
PCB-170	µg/l	L1		0,544	yes	699	20	737	745	735	84,8	11,5	6	0	1	7
	µg/kg	M0		3,08	yes	13,4	30	19,6	15,3	15,6	4,09	26,3	6	0	1	7
	µg/kg	M1			yes	316		273	316	302	82,1	27,2	6	0	1	7
	µg/kg	M2			yes	43,1		50,4	43,1	43,6	6	13,7	5	0	2	7
PCB-180	µg/l	L1		0,78	yes	699	20	754	677	686	117	17	14	0	0	14
	µg/kg	M0		2,03	yes	22	30	28,7	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		-0,288	yes	448	30	429	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		-1,07	yes	82,3	30	69,1	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		1,18	yes	699	20	782	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		0,106	yes	44	30	44,7	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1			yes	6,05		6,05	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		0,716	yes	18,5	30	20,4	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		0,472	yes	699	20	732	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		1,39	yes	38	30	45,9	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		2,87	yes	30,1	30	43	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		0,162	yes	157	30	161	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		2,18	yes	7,97	40	11,4	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		0,618	yes	7,12	40	8	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		0,0725	yes	3,45	40	3,5	3,45	3,33	1,19	35,8	12	1	1	14
Laboratory 11																
PCB-101	µg/l	L1		0,675	yes	699	20	746	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		5,21	H	44	30	78.4	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		2,37	yes	355	30	482	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		3,68	yes	258	30	400	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		1,46	yes	699	20	801	722	723	72,3	10	10	1	0	11
	µg/kg	M0				3,5	30	<10.0	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			yes	18		28,3	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		2,91	yes	110	30	158	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		0,944	yes	699	20	765	709	672	111	16,5	13	0	0	13
	µg/kg	M0		2,71	yes	28	30	39.4	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		1,95	yes	118	30	153	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		3,23	yes	264	30	392	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		1,11	yes	699	20	777	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		11,3	H	27	30	72.6	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		3,49	yes	719	30	1100	739	732	227	31	14	0	0	14
	µg/kg	M2		6,09	C	241	30	462	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		0,911	yes	699	20	763	698	687	68	9,9	13	1	0	14
	µg/kg	M0		2,55	yes	50	30	69.1	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		1,97	yes	714	30	926	716	692	134	19,4	13	1	0	14
	µg/kg	M2		7,09	H	216	30	446	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		1.31	yes	699	20	791	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0				3	30	<10.0	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		2.23	yes	73,3	30	97,8	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2		0,948	yes	28	30	32	30,3	29,2	3,63	12,4	6	1	1	8
PCB-170	µg/l	L1		1.23	yes	699	20	785	745	735	84,8	11,5	6	0	1	7
	µg/kg	M0		3,58	yes	13,4	30	20.6	15,3	15,6	4,09	26,3	6	0	1	7
	µg/kg	M1			yes	316		433	316	302	82,1	27,2	6	0	1	7

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
	µg/kg	M2			yes	43,1		42,5	43,1	43,6	6	13,7	5	0	2	7
Laboratory 11																
PCB-180	µg/l	L1		1,25	yes	699	20	786	677	686	117	17	14	0	0	14
	µg/kg	M0		2,33	yes	22	30	29.7	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		2,49	yes	448	30	616	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		2,49	yes	82,3	30	113	77,5	78,8	14,7	18,7	10	2	1	13
PCB-52	µg/l	L1		0,446	yes	699	20	730	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		3,53	yes	38	30	58.1	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		1,28	yes	30,1	30	35,9	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		6,14	yes	157	30	301	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		2,72	yes	7,97	40	12,3	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		4,45	H	7,12	40	13,4	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		6,96	G2	3,45	40	8,25	3,45	3,33	1,19	35,8	12	1	1	14
Laboratory 12																
PCB-101	µg/l	L1		-0,408	yes	699	20	671	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-0,318	yes	44	30	41,9	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		-0,727	yes	355	30	317	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		0,0828	yes	258	30	261	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		0,522	yes	699	20	736	722	723	72,3	10	10	1	0	11
	µg/kg	M0		1,9	yes	3,5	30	4,50	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1				18		<4	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		-0,424	yes	110	30	103	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		0,973	yes	699	20	767	709	672	111	16,5	13	0	0	13
	µg/kg	M0		0,524	yes	28	30	30,2	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		-0,113	yes	118	30	116	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		0,374	yes	264	30	279	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		0	yes	699	20	699	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		0,864	yes	27	30	30,5	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		-0,975	yes	719	30	614	739	732	227	31	14	0	0	14
	µg/kg	M2		-0,433	yes	241	30	226	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		-0,422	yes	699	20	670	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-0,84	yes	50	30	43,7	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		-0,48	yes	714	30	663	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-0,535	yes	216	30	199	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		0,808	yes	699	20	756	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0		0,622	yes	3	30	3,28	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		-0,076	yes	73,3	30	72,5	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2		0,139	yes	28	30	28,6	30,3	29,2	3,63	12,4	6	1	1	8
PCB-170	µg/l	L1		-0,98	yes	699	20	631	745	735	84,8	11,5	6	0	1	7
	µg/kg	M0		-0,846	yes	13,4	30	11,7	15,3	15,6	4,09	26,3	6	0	1	7
	µg/kg	M1			yes	316		233	316	302	82,1	27,2	6	0	1	7
	µg/kg	M2			yes	43,1		39	43,1	43,6	6	13,7	5	0	2	7
PCB-180	µg/l	L1		-0,558	yes	699	20	660	677	686	117	17	14	0	0	14
	µg/kg	M0		-0,576	yes	22	30	20,1	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		-0,675	yes	448	30	403	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		-0,704	yes	82,3	30	73,6	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		0,00715	yes	699	20	700	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		-0,424	yes	44	30	41,2	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<2	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		-1,32	yes	18,5	30	14,8	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		-0,436	yes	699	20	669	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-0,842	yes	38	30	33,2	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		-1,61	yes	30,1	30	22,8	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		0,0979	yes	157	30	159	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		0,0439	yes	7,97	40	8,04	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-0,26	yes	7,12	40	6,75	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		0,877	yes	3,45	40	4,06	3,45	3,33	1,19	35,8	12	1	1	14

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 13																
PCB-101	µg/l	L1		-1,34	yes	699	20	605	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		0,606	yes	44	30	48	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		-1,69	yes	355	30	265	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		0,574	yes	258	30	280	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		-0,558	yes	699	20	660	722	723	72,3	10	10	1	0	11
	µg/kg	M0		27,6	yes	3,5	30	18	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1			H	18		170	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		-1,06	yes	110	30	92,5	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		-1,13	yes	699	20	620	709	672	111	16,5	13	0	0	13
	µg/kg	M0		-2,14	yes	28	30	19	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		-2,77	yes	118	30	69	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		-1,23	yes	264	30	215	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		-1,06	yes	699	20	625	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		2,96	yes	27	30	39	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		-1,05	yes	719	30	605	739	732	227	31	14	0	0	14
	µg/kg	M2		0,106	yes	241	30	245	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		-1,27	yes	699	20	610	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-1,2	yes	50	30	41	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		-1,95	yes	714	30	505	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-1,11	yes	216	30	180	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		-0,844	yes	699	20	640	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0		15,6	H	3	30	10	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		3,34	yes	73,3	30	110	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2		1,42	yes	28	30	34	30,3	29,2	3,63	12,4	6	1	1	8
PCB-170	µg/l	L1		-0,916	yes	699	20	635	745	735	84,8	11,5	6	0	1	7
	µg/kg	M0		-1,19	yes	13,4	30	11	15,3	15,6	4,09	26,3	6	0	1	7
	µg/kg	M1			yes	316		225	316	302	82,1	27,2	6	0	1	7
	µg/kg	M2			yes	43,1		37	43,1	43,6	6	13,7	5	0	2	7
PCB-180	µg/l	L1		-0,916	yes	699	20	635	677	686	117	17	14	0	0	14
	µg/kg	M0		-1,52	yes	22	30	17	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		-1,54	yes	448	30	345	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		-1,52	yes	82,3	30	63,5	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		-0,701	yes	699	20	650	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		-1,97	yes	44	30	31	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<1	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		-2,7	yes	18,5	30	11	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		-2,7	yes	699	20	510	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-2,28	yes	38	30	25	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		-2,34	yes	30,1	30	19,5	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		-1,14	yes	157	30	130	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		1,59	yes	7,97	40	10,5	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		0,548	yes	7,12	40	7,9	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		1,45	yes	3,45	40	4,45	3,45	3,33	1,19	35,8	12	1	1	14

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 14																
PCB-101	µg/l	L1		-0,73	yes	699	20	648	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-1,36	yes	44	30	35,0	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		1,3	yes	355	30	425	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		-0,228	yes	258	30	249	265	278	56,4	20,3	11	1	1	13
PCB-138	µg/l	L1		-0,522	yes	699	20	663	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		-1,28	yes	27	30	21,8	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		0,235	yes	719	30	744	739	732	227	31	14	0	0	14
	µg/kg	M2		-0,309	yes	241	30	230	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		-0,494	yes	699	20	665	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-0,933	yes	50	30	43,0	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		0,588	yes	714	30	778	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-0,0566	yes	216	30	214	200	203	33,9	16,7	10	2	1	13
PCB-180	µg/l	L1		-0,436	yes	699	20	669	677	686	117	17	14	0	0	14
	µg/kg	M0		-1,06	yes	22	30	18,5	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		0,21	yes	448	30	463	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		-0,348	yes	82,3	30	78	77,5	78,8	14,7	18,7	10	2	1	13
PCB-52	µg/l	L1		-0,594	yes	699	20	658	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-2,19	yes	38	30	25,5	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		0,76	yes	30,1	30	33,5	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		-1,16	yes	157	30	130	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		0,267	yes	7,97	40	8,39	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		0,751	yes	7,12	40	8,19	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		0,0507	yes	3,45	40	3,49	3,45	3,33	1,19	35,8	12	1	1	14
Laboratory 15																
PCB-101	µg/l	L1		-0,472	yes	699	20	666	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		0,439	yes	44	30	46,9	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		-0,286	yes	355	30	340	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		0,0957	yes	258	30	262	265	278	56,4	20,3	11	1	1	13
PCB-105	µg/l	L1		-0,093	yes	699	20	693	722	723	72,3	10	10	1	0	11
	µg/kg	M0		3,22	yes	3,5	30	5,19	9,1	11,8	9,4	79,9	7	0	4	11
	µg/kg	M1				18		<0,5	18	20,5	7,76	37,9	5	3	3	11
	µg/kg	M2		0,424	yes	110	30	117	117	122	29,8	24,5	9	0	1	10
PCB-118	µg/l	L1		-0,258	yes	699	20	681	709	672	111	16,5	13	0	0	13
	µg/kg	M0		0,452	yes	28	30	29,9	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		0,0282	yes	118	30	119	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		-0,169	yes	264	30	257	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		-0,193	yes	699	20	686	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		1,21	yes	27	30	31,9	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		0,3	yes	719	30	751	739	732	227	31	14	0	0	14
	µg/kg	M2		0,369	yes	241	30	255	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		-0,258	yes	699	20	681	698	687	68	9,9	13	1	0	14
	µg/kg	M0		0,16	yes	50	30	51,2	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		-0,396	yes	714	30	672	716	692	134	19,4	13	1	0	14
	µg/kg	M2		-0,165	yes	216	30	211	200	203	33,9	16,7	10	2	1	13
PCB-156	µg/l	L1		-0,172	yes	699	20	687	704	699	71,7	10,3	8	1	0	9
	µg/kg	M0		-0,178	yes	3	30	2,92	3,28	3,47	0,628	18,1	4	2	3	9
	µg/kg	M1		0,211	yes	73,3	30	75,6	74,2	79,5	20,8	26,2	8	1	0	9
	µg/kg	M2		0,591	yes	28	30	30,5	30,3	29,2	3,63	12,4	6	1	1	8
PCB-180	µg/l	L1		-0,243	yes	699	20	682	677	686	117	17	14	0	0	14
	µg/kg	M0		0,121	yes	22	30	22,4	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		0,188	yes	448	30	461	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		-0,149	yes	82,3	30	80,5	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		0,959	yes	699	20	766	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		0,924	yes	44	30	50,1	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<0,5	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		0,0481	yes	18,5	30	18,6	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		-0,393	yes	699	20	672	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		0,456	yes	38	30	40,6	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		0,228	yes	30,1	30	31,1	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		0,332	yes	157	30	165	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		-0,417	yes	7,97	40	7,31	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		-0,499	yes	7,12	40	6,41	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		-0,138	yes	3,45	40	3,36	3,45	3,33	1,19	35,8	12	1	1	14

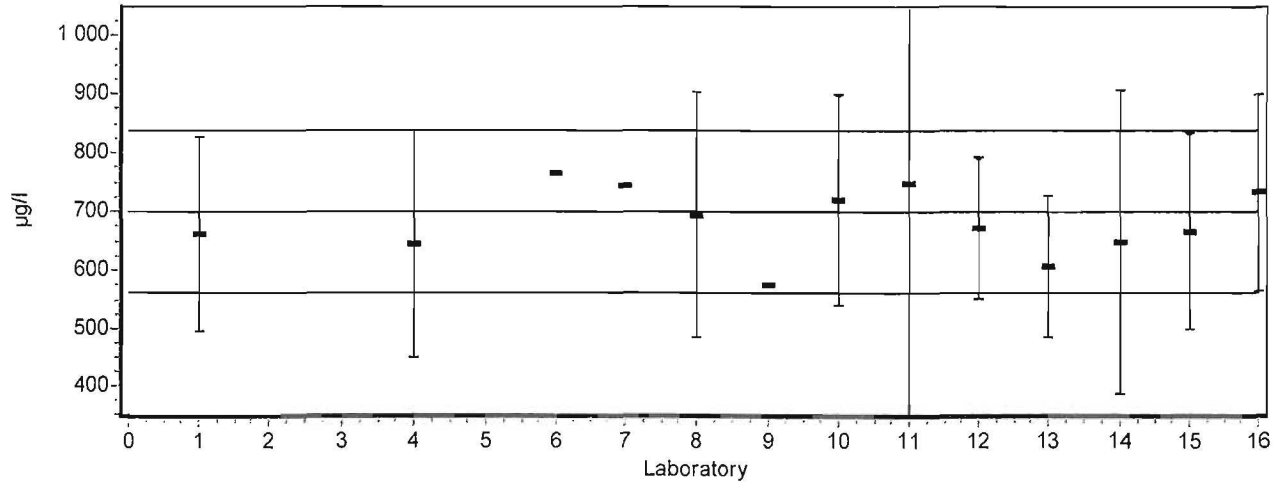
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

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	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 16																
PCB-101	µg/l	L1		0,472	yes	699	20	732	679	682	58,2	8,5	13	1	0	14
	µg/kg	M0		-1,67	yes	44	30	33	40,5	39,9	6,59	16,5	12	2	0	14
	µg/kg	M1		-0,173	yes	355	30	346	362	356	70,1	19,7	14	0	0	14
	µg/kg	M2		1,71	yes	258	30	324	265	278	56,4	20,3	11	1	1	13
PCB-118	µg/l	L1		1,02	yes	699	20	771	709	672	111	16,5	13	0	0	13
	µg/kg	M0		-1,67	yes	28	30	21	25,6	27	5,88	21,8	12	1	0	13
	µg/kg	M1		-0,198	yes	118	30	115	115	114	25,5	22,4	11	2	0	13
	µg/kg	M2		0,994	yes	264	30	303	252	262	57,3	21,9	11	0	1	12
PCB-138	µg/l	L1		1,04	yes	699	20	772	694	694	51,6	7,4	12	2	0	14
	µg/kg	M0		-0,988	yes	27	30	23	30,5	33,1	12,2	36,9	13	1	0	14
	µg/kg	M1		-0,0103	yes	719	30	718	739	732	227	31	14	0	0	14
	µg/kg	M2		0,686	yes	241	30	266	237	233	27,9	12	11	1	1	13
PCB-153	µg/l	L1		0,951	yes	699	20	766	698	687	68	9,9	13	1	0	14
	µg/kg	M0		-1,07	yes	50	30	42	45,4	48	9,55	19,9	14	0	0	14
	µg/kg	M1		1,13	yes	714	30	836	716	692	134	19,4	13	1	0	14
	µg/kg	M2		1,09	yes	216	30	251	200	203	33,9	16,7	10	2	1	13
PCB-180	µg/l	L1		1,22	yes	699	20	784	677	686	117	17	14	0	0	14
	µg/kg	M0		-0,303	yes	22	30	21	20,1	20,8	4,26	20,5	13	1	0	14
	µg/kg	M1		3,74	H	448	30	700	449	445	89,6	20,1	12	2	0	14
	µg/kg	M2		0,503	yes	82,3	30	88,5	77,5	78,8	14,7	18,7	10	2	1	13
PCB-28	µg/l	L1		0,122	yes	699	20	708	708	716	56,9	7,9	7	4	0	11
	µg/kg	M0		-2,27	yes	44	30	29	43	52	24,6	47,4	11	0	0	11
	µg/kg	M1				6,05		<5	6,05	6,05	0,354	5,8	1	0	10	11
	µg/kg	M2		1,28	yes	18,5	30	22	18,9	18,6	4,61	24,8	8	0	2	10
PCB-52	µg/l	L1		0,715	yes	699	20	749	677	659	90,3	13,7	14	0	0	14
	µg/kg	M0		-1,93	yes	38	30	27	32	35,9	11,6	32,2	14	0	0	14
	µg/kg	M1		-1,46	yes	30,1	30	23,5	29,8	29,3	8,15	27,8	13	0	1	14
	µg/kg	M2		9,82	H	157	30	388	160	181	57,6	31,8	11	1	1	13
Total-PCB	mg/l	L2		1,1	yes	7,97	40	9,73	8,54	8,59	2,81	32,7	16	0	0	16
	mg/kg	M1		1,35	yes	7,12	40	9,05	7,12	7,07	1,38	19,5	14	2	0	16
	mg/kg	M2		3,07	yes	3,45	40	5,57	3,45	3,33	1,19	35,8	12	1	1	14

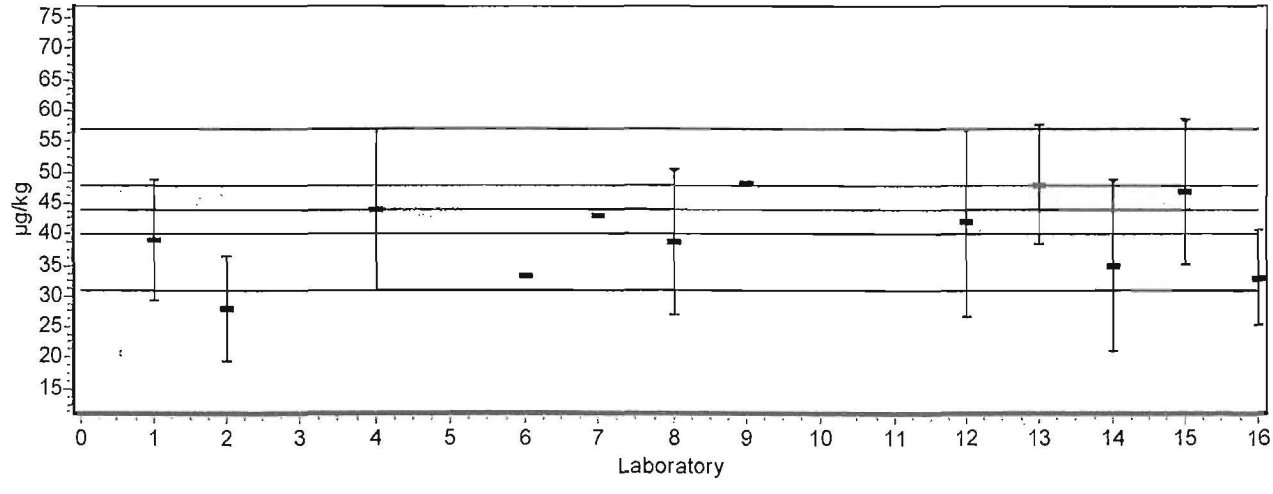
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

ANNEX 13. GRAPHICAL PRESENTATIONS OF THE RESULTS

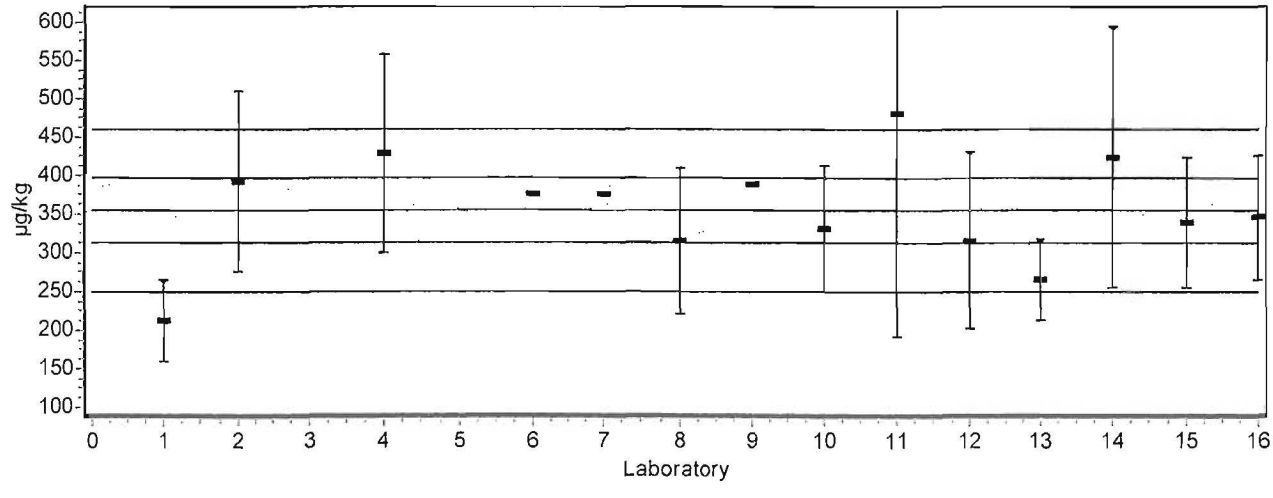
Analyytti *(Analyte)* **PCB-101** Näyte *(Sample)* L1



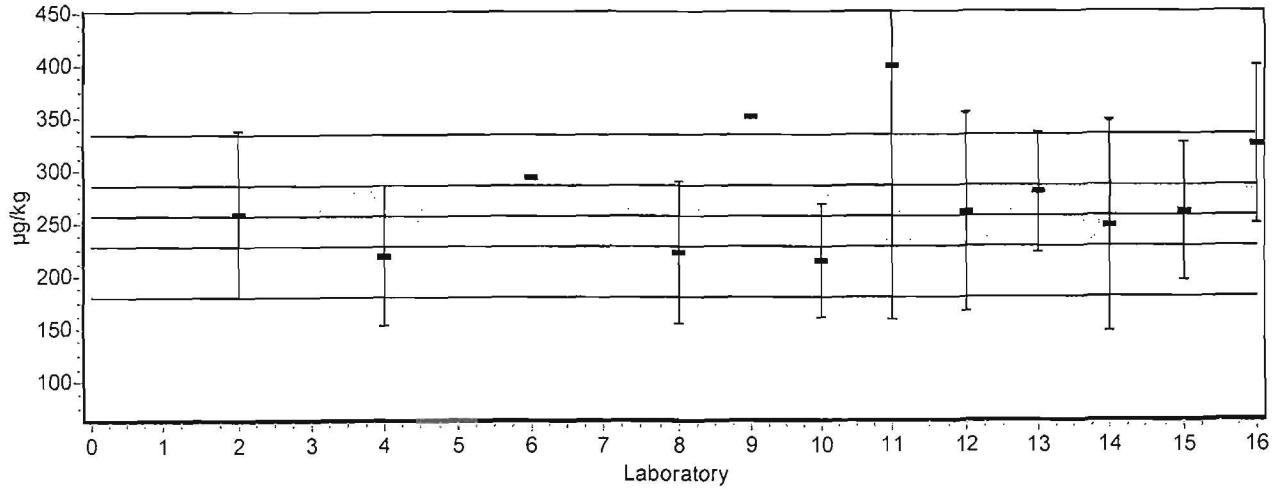
Analyytti *(Analyte)* **PCB-101** Näyte *(Sample)* M0



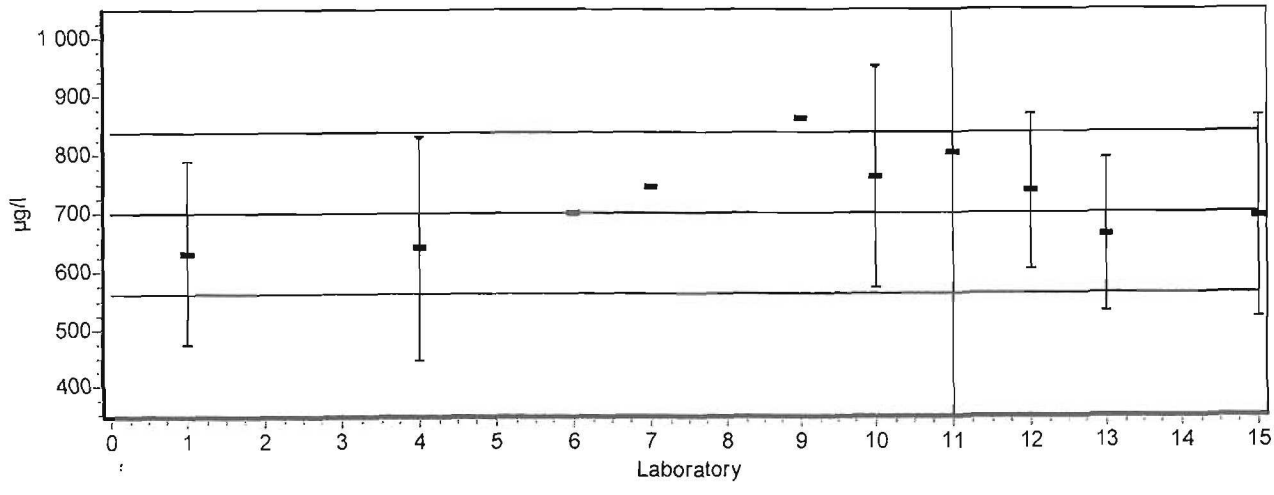
Analyytti *(Analyte)* **PCB-101** Näyte *(Sample)* M1



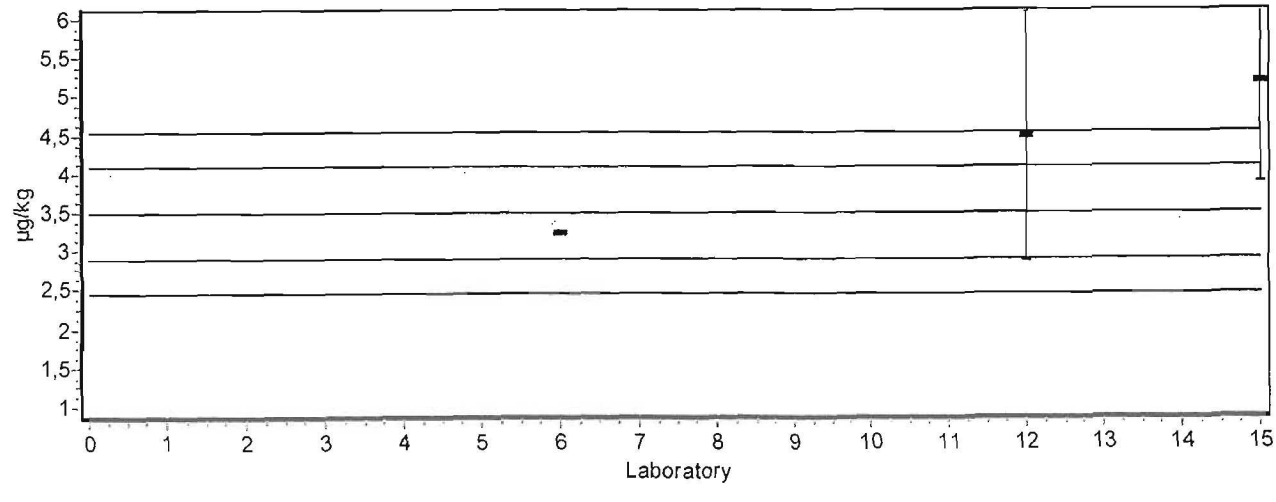
Analyytti *(Analyte)* **PCB-101** Näyte *(Sample)* M2



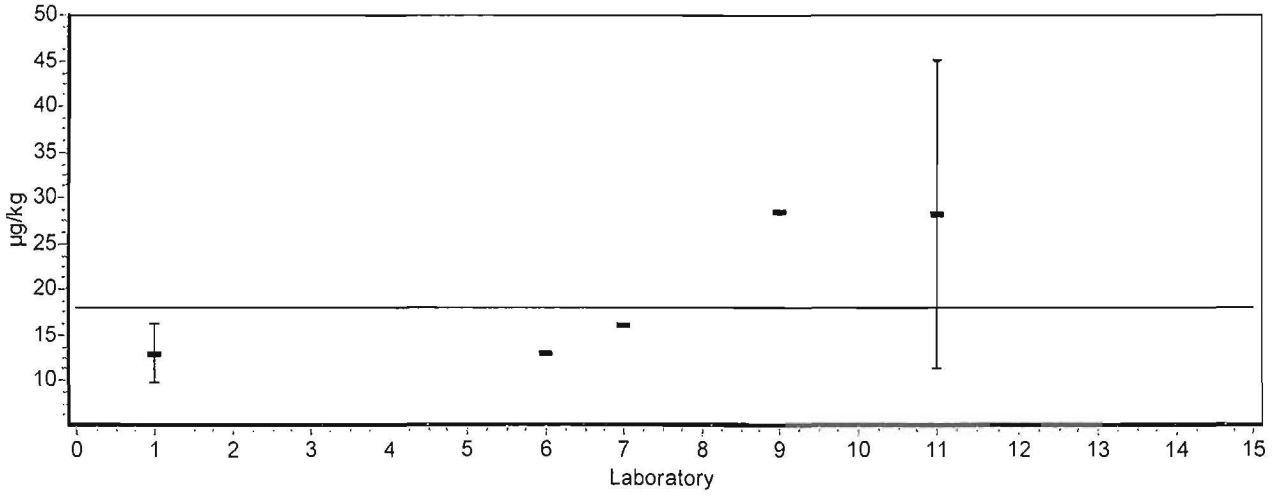
Analyytti *(Analyte)* **PCB-105** Näyte *(Sample)* L1



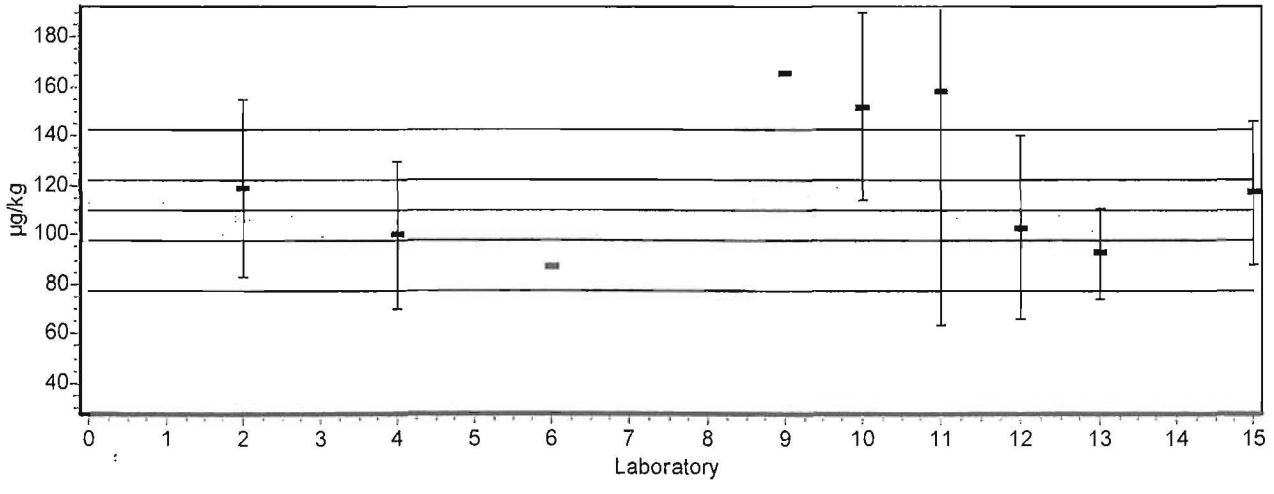
Analyytti *(Analyte)* **PCB-105** Näyte *(Sample)* M0



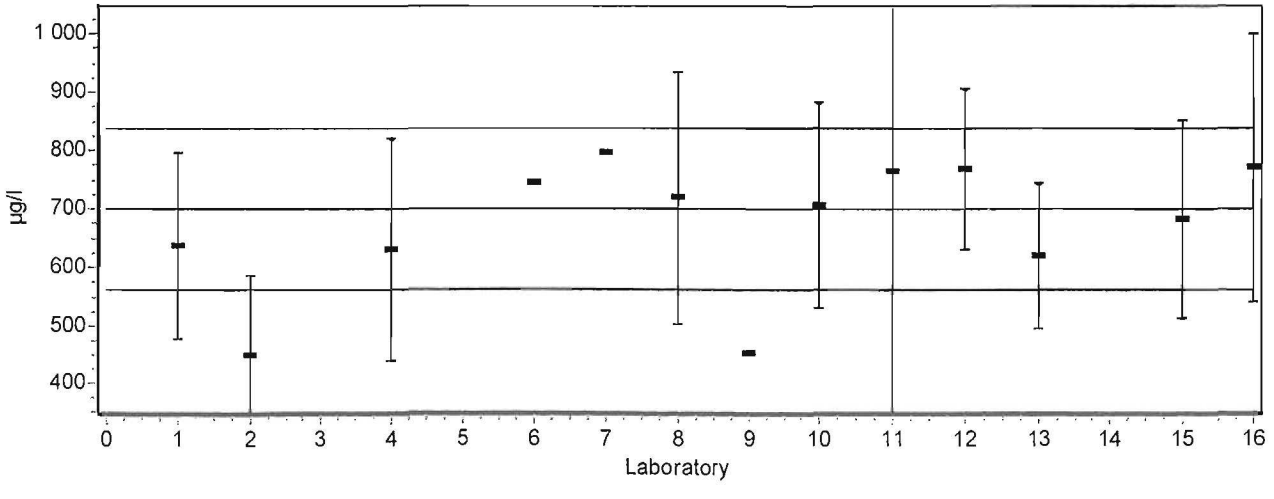
Analyytti *(Analyte)* **PCB-105** Näyte *(Sample)* M1



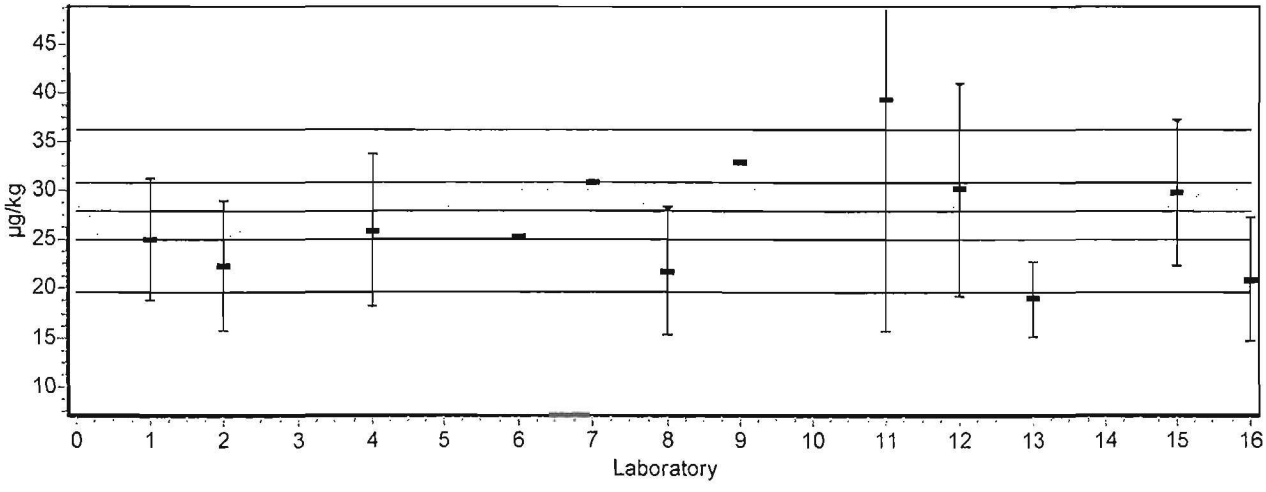
Analyytti *(Analyte)* **PCB-105** Näyte *(Sample)* M2



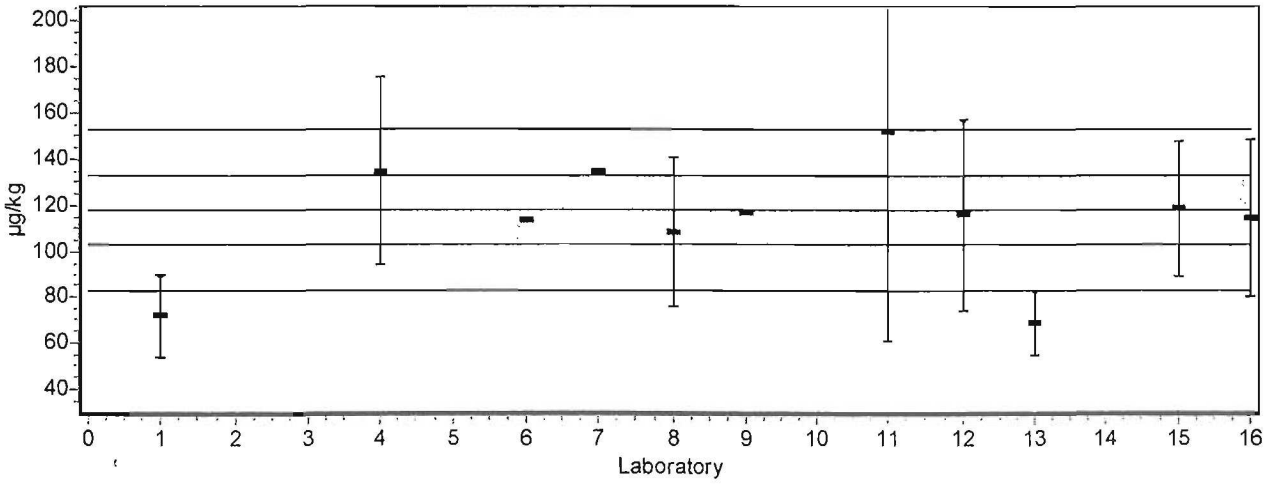
Analyytti *(Analyte)* **PCB-118** Näyte *(Sample)* L1



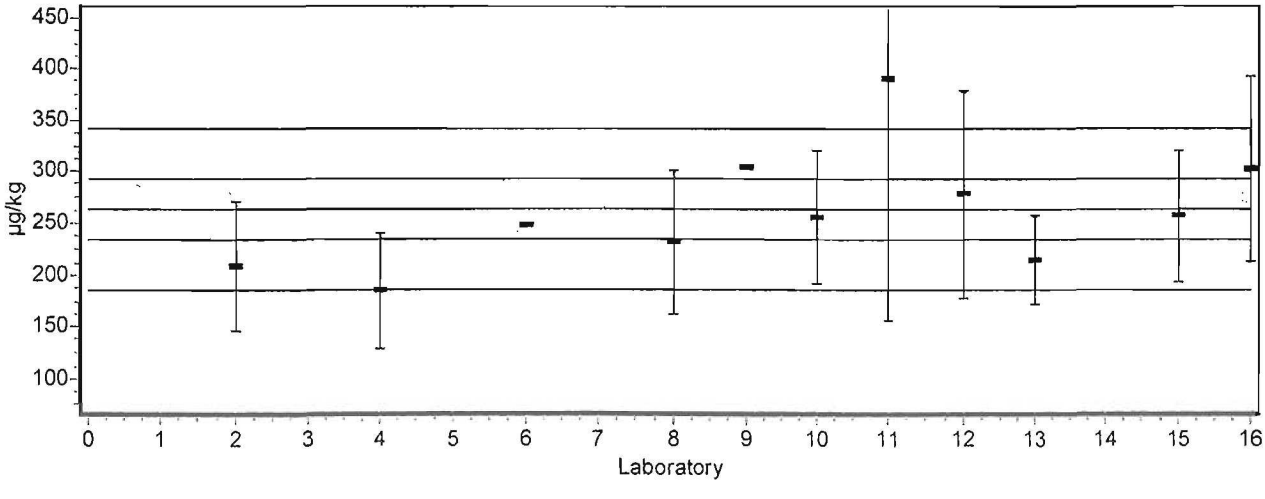
Analyytti *(Analyte)* **PCB-118** Näyte *(Sample)* M0



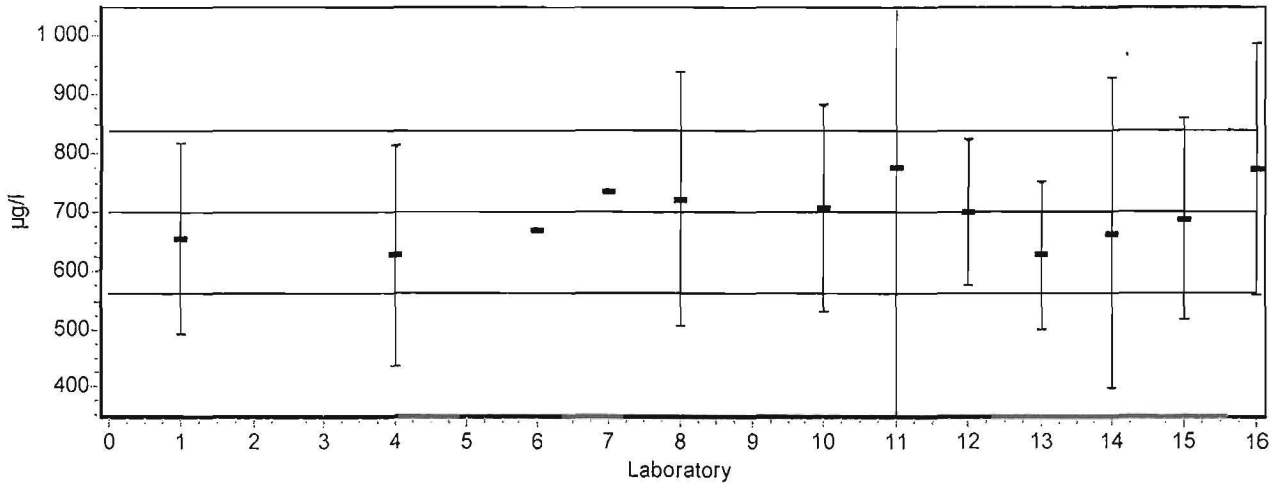
Analyytti *(Analyte)* **PCB-118** Näyte *(Sample)* M1



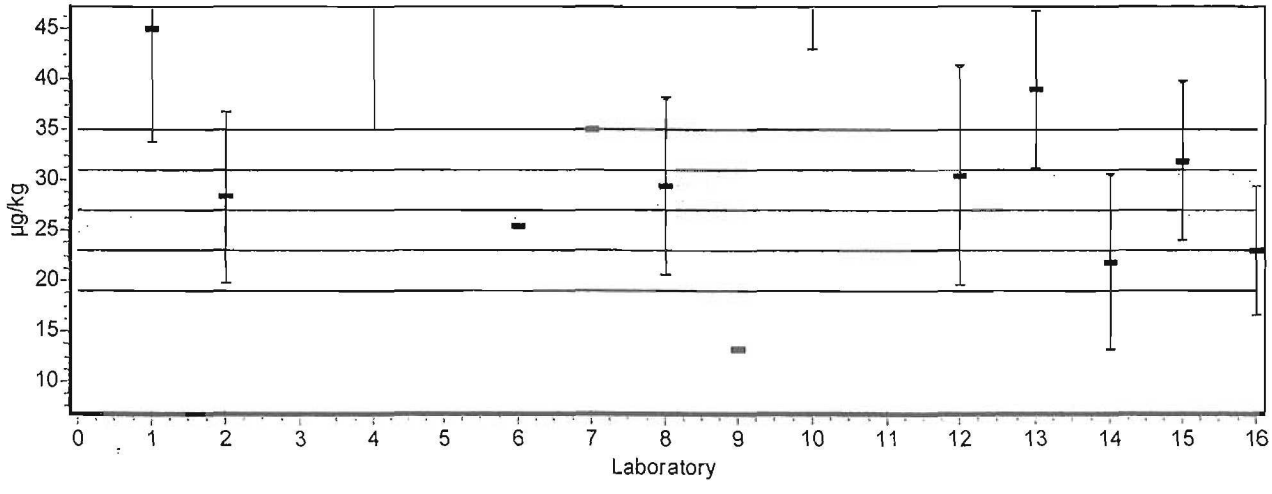
Analyytti *(Analyte)* **PCB-118** Näyte *(Sample)* M2



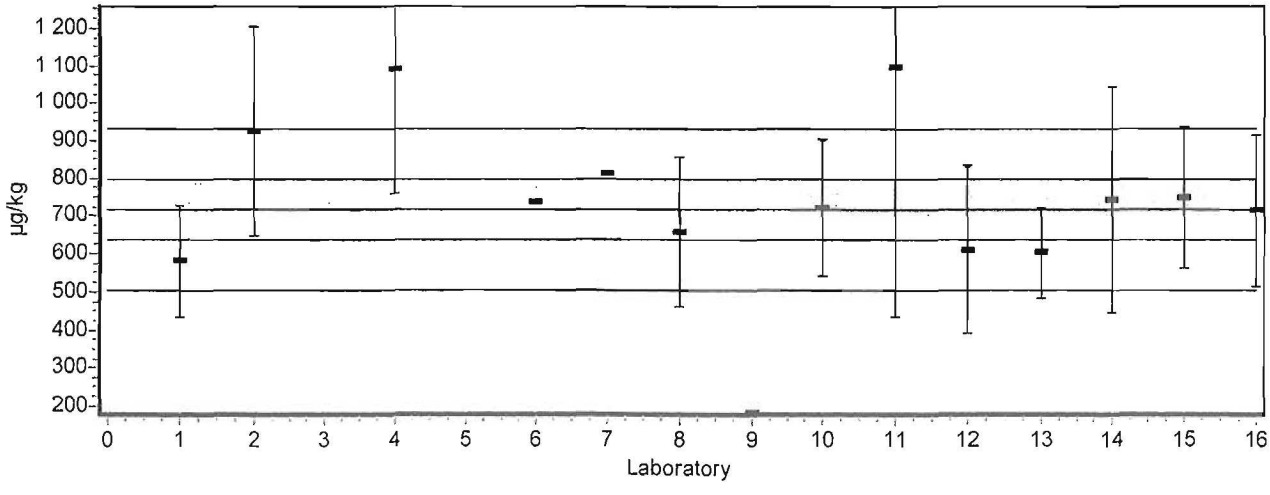
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* L1



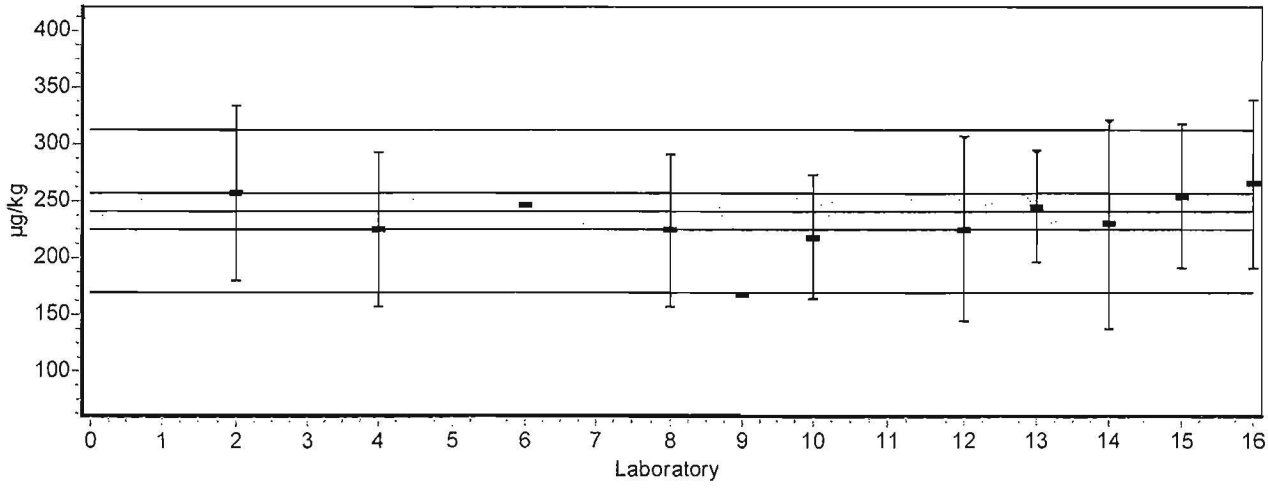
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* M0



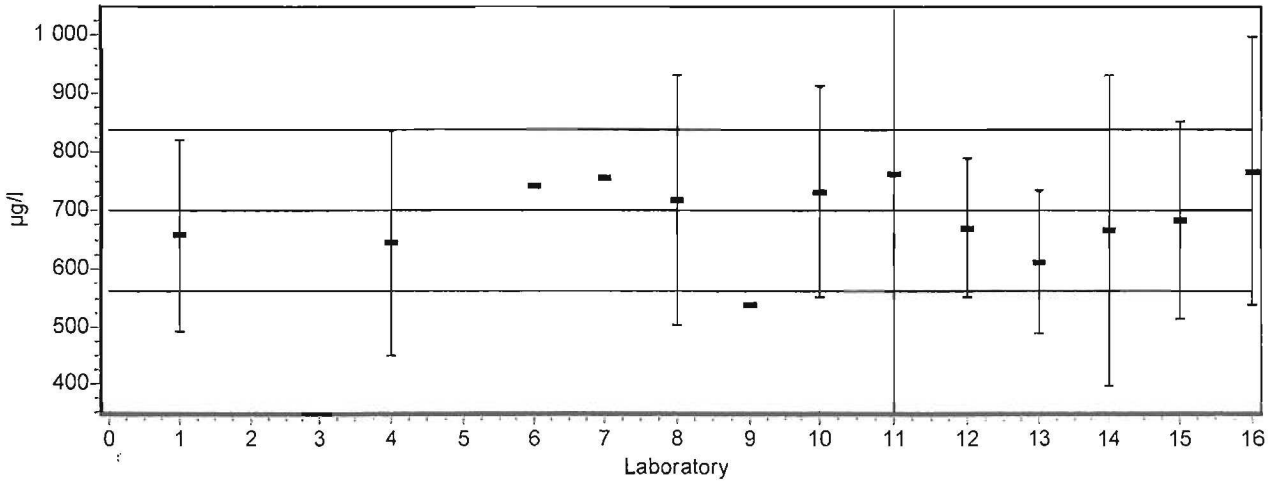
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* M1



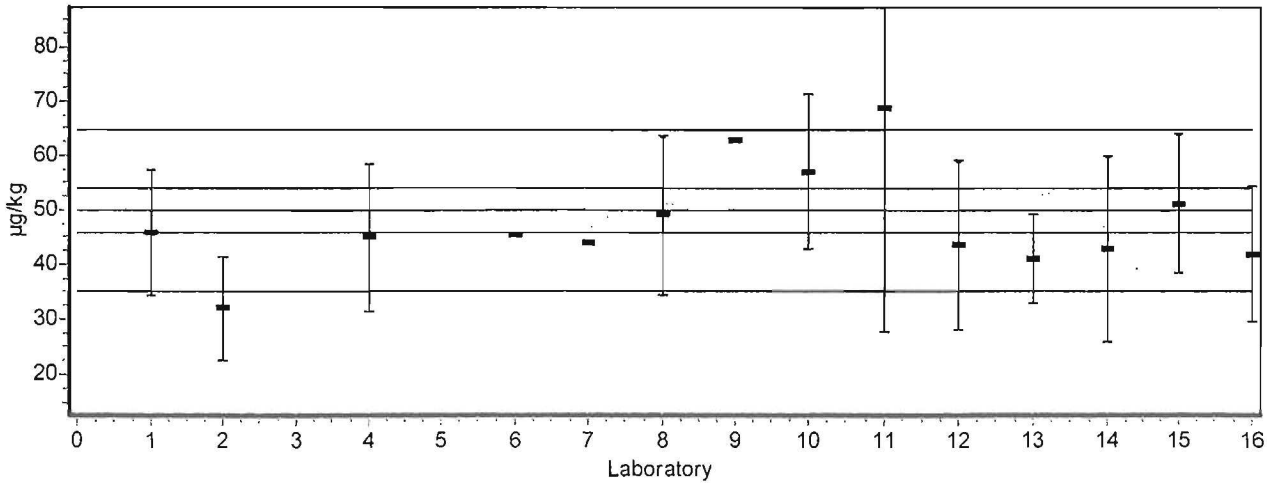
Analyytti *(Analyte)* **PCB-138** Näyte *(Sample)* M2



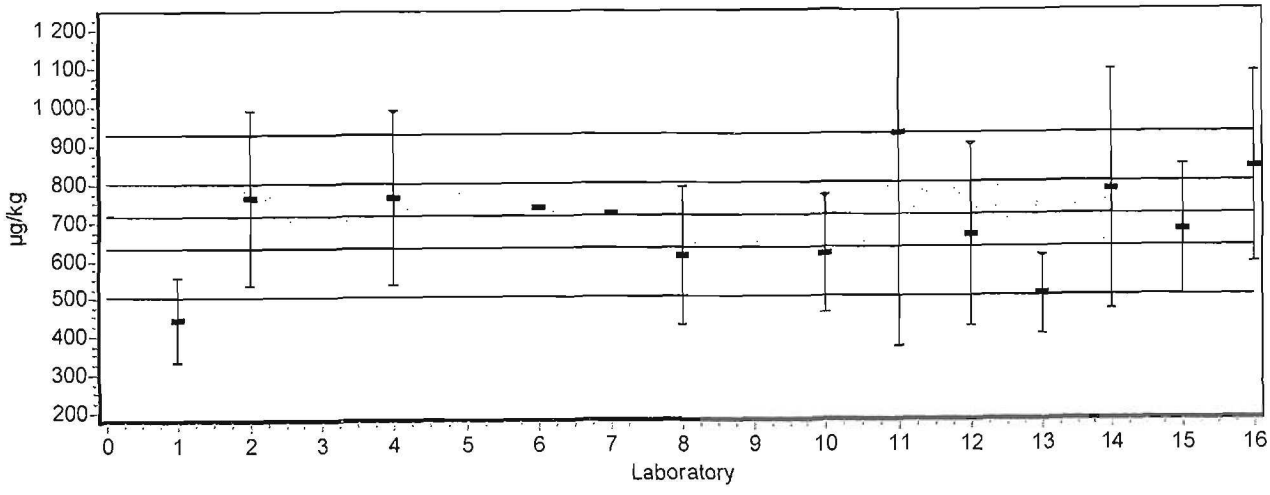
Analyytti *(Analyte)* **PCB-153** Näyte *(Sample)* L1



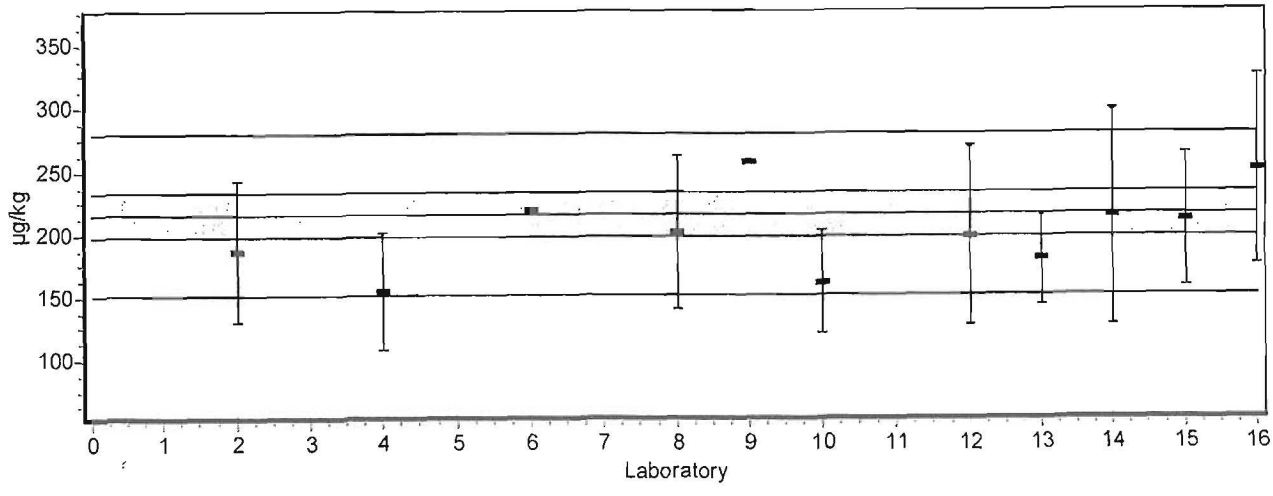
Analyytti *(Analyte)* **PCB-153** Näyte *(Sample)* M0



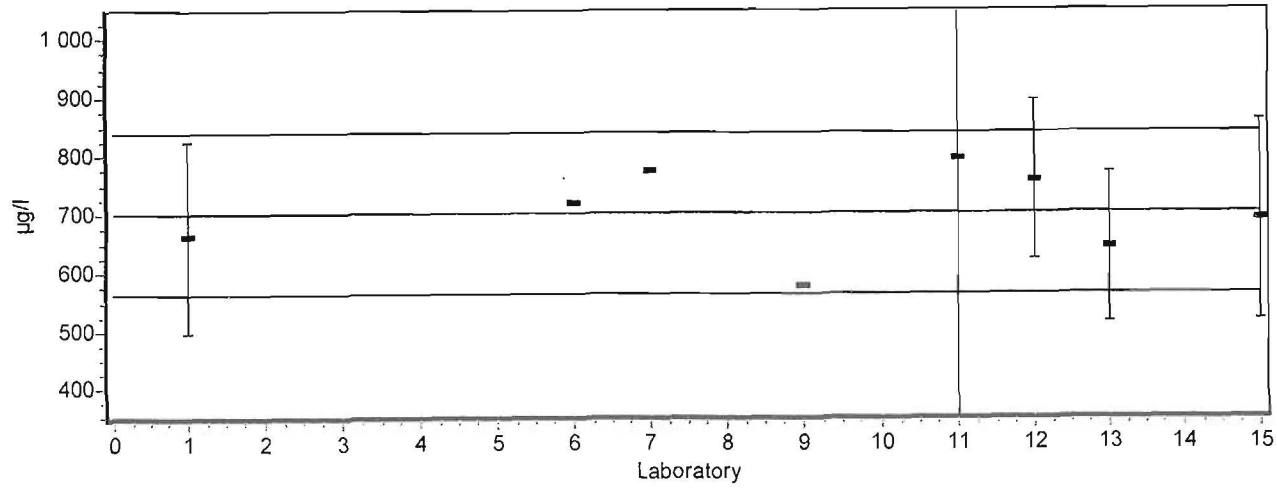
Analyytti *(Analyte)* **PCB-153** Näyte *(Sample)* M1



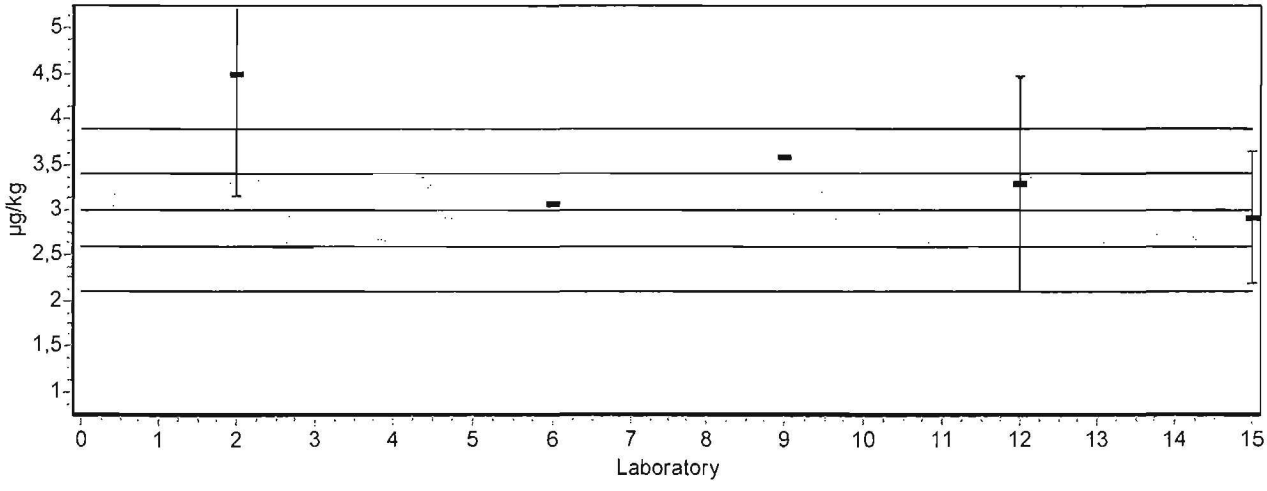
Analyytti *(Analyte)* **PCB-153** Näyte *(Sample)* M2



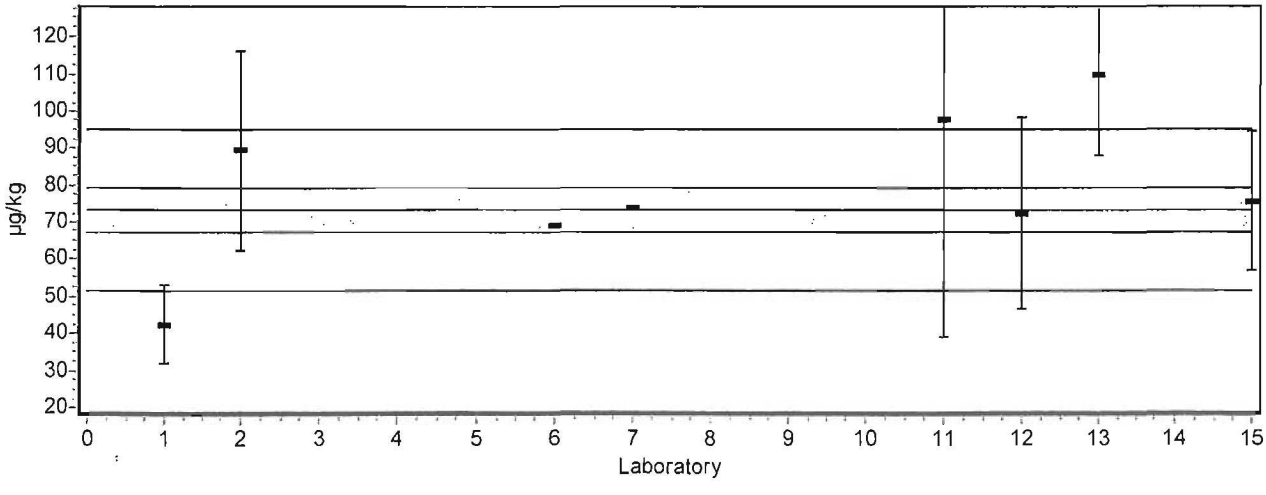
Analyytti *(Analyte)* **PCB-156** Näyte *(Sample)* L1



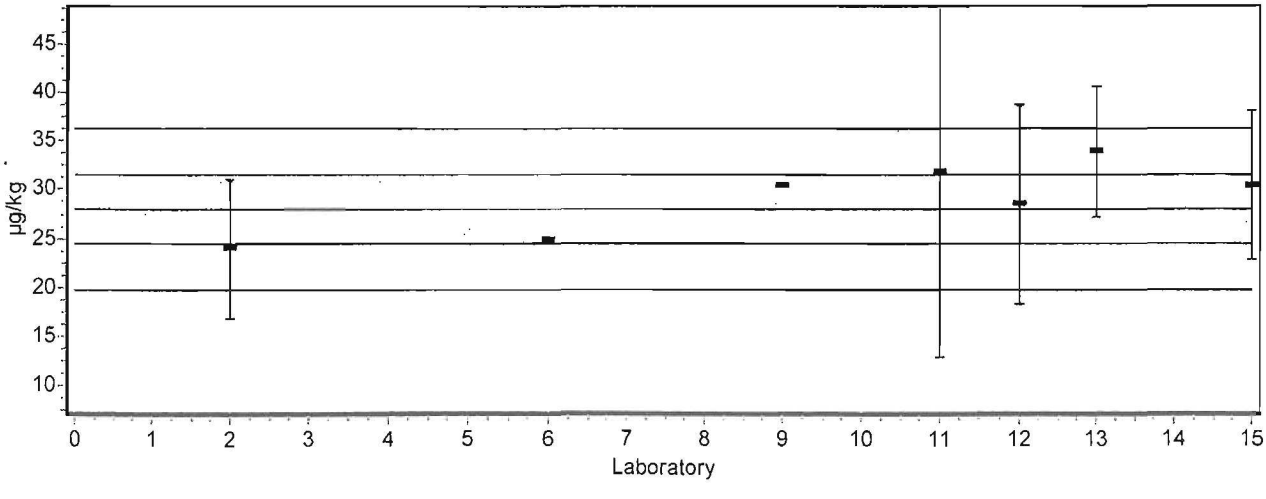
Analyytti *(Analyte)* **PCB-156** Näyte *(Sample)* M0



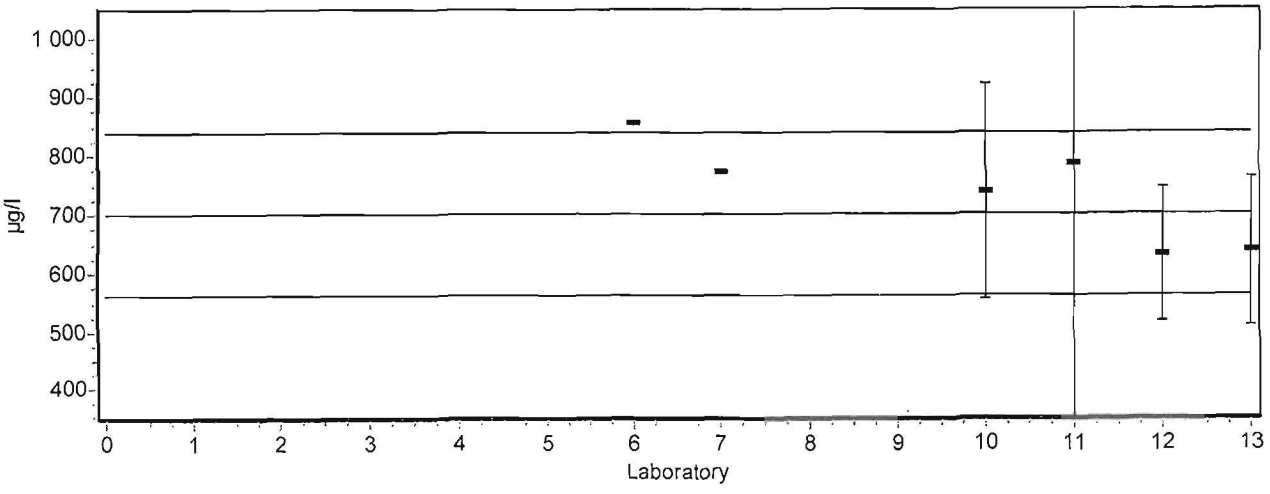
Analyytti *(Analyte)* **PCB-156** Näyte *(Sample)* M1



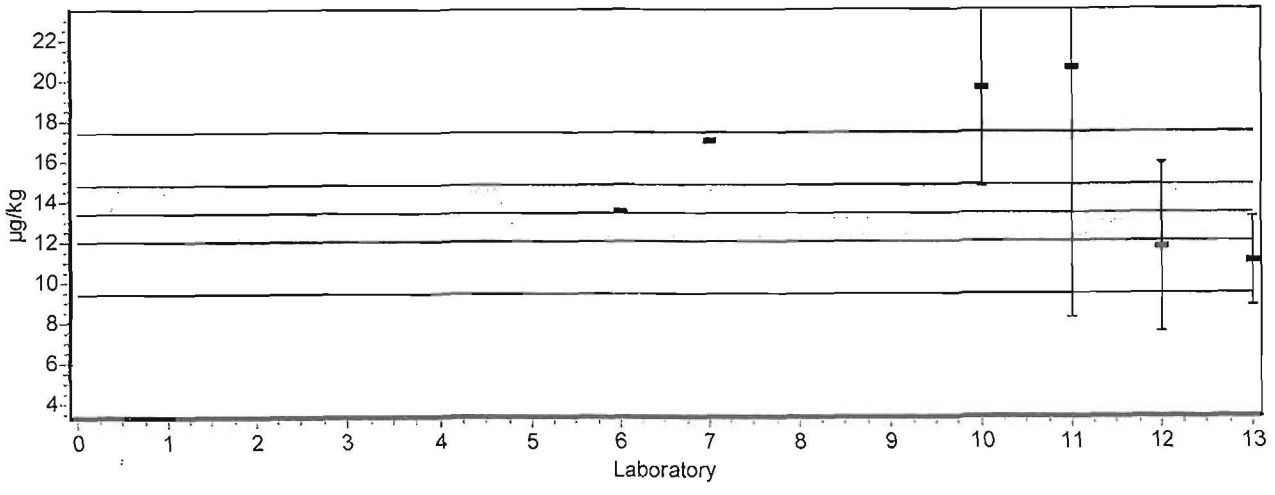
Analyytti *(Analyte)* **PCB-156** Näyte *(Sample)* M2



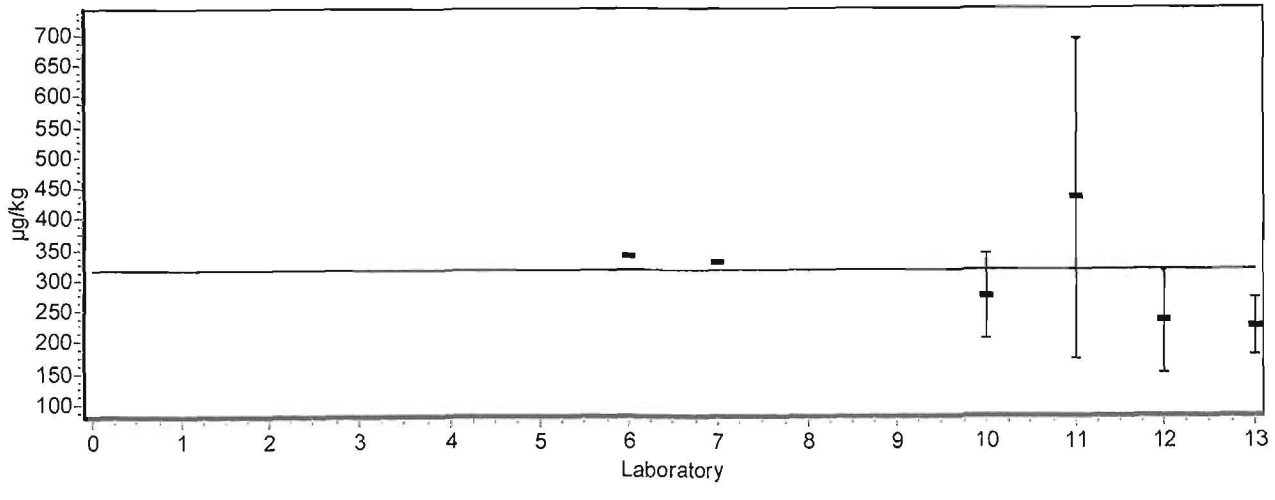
Analyytti *(Analyte)* **PCB-170** Näyte *(Sample)* L1



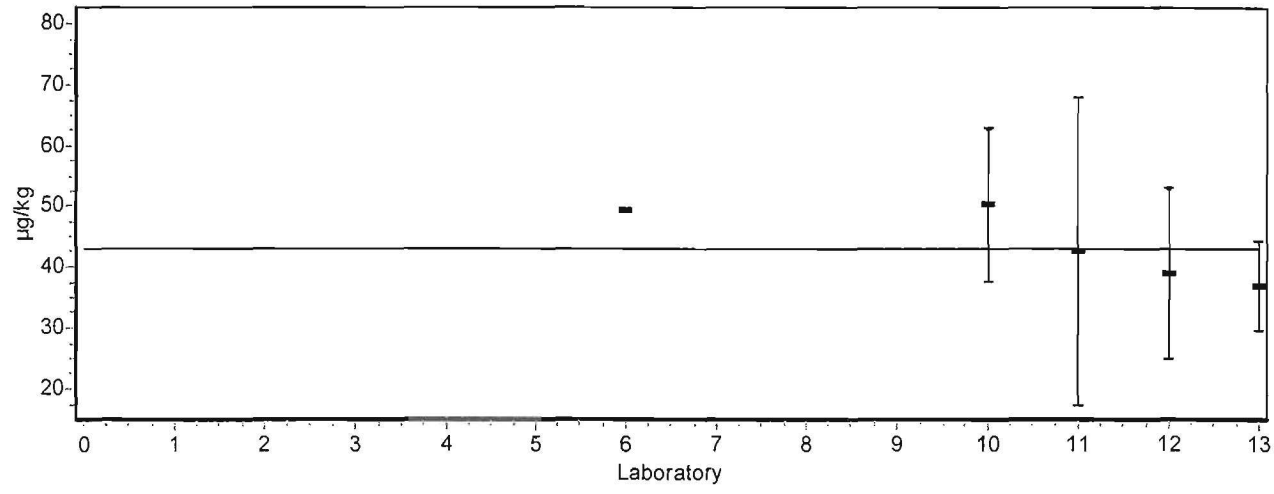
Analyytti *(Analyte)* **PCB-170** Näyte *(Sample)* M0



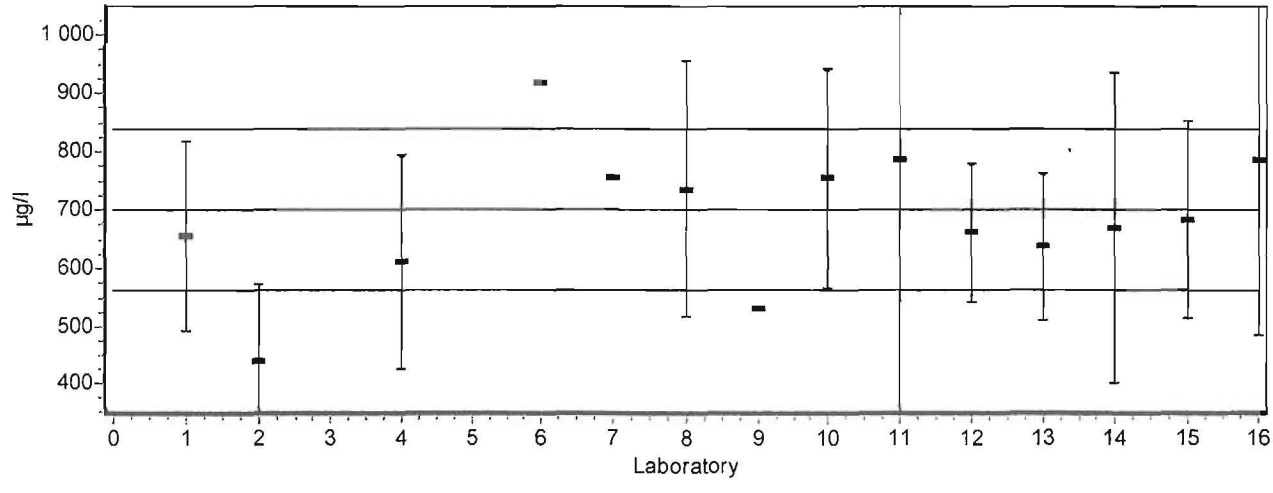
Analyytti *(Analyte)* **PCB-170** Näyte *(Sample)* M1



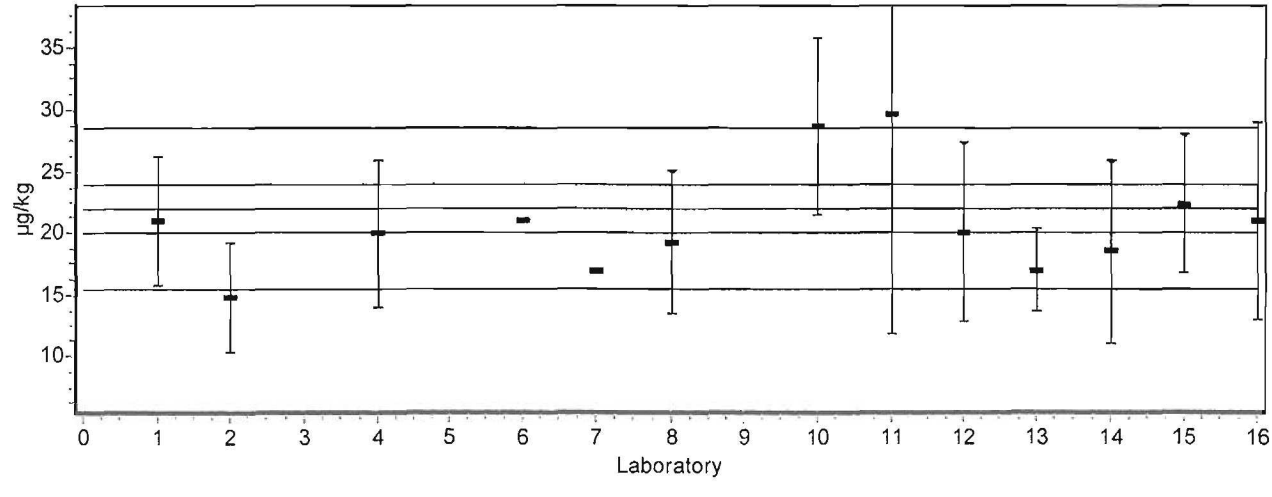
Analyytti *(Analyte)* **PCB-170** Näyte *(Sample)* M2



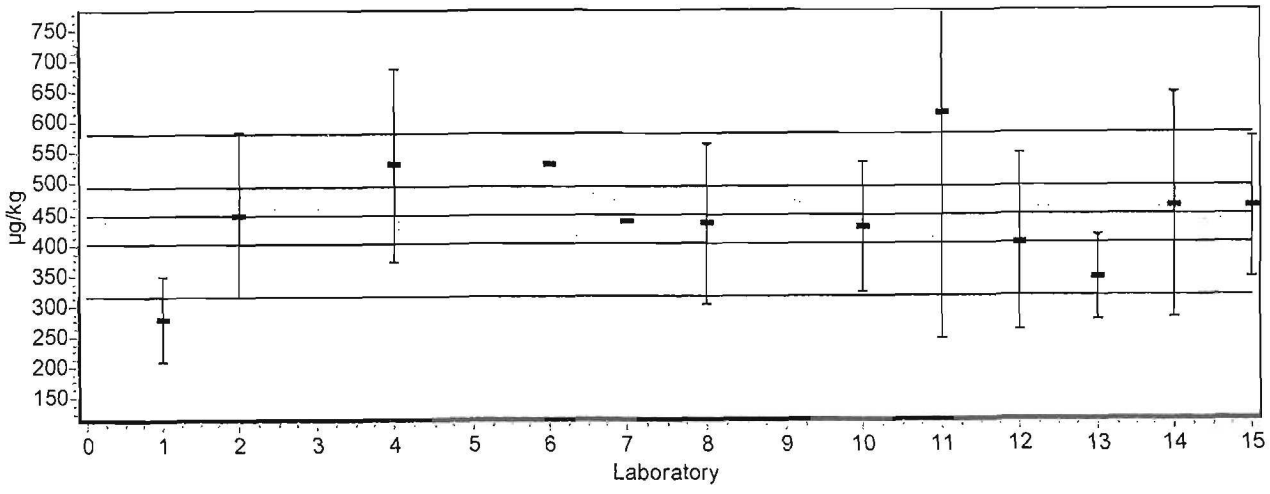
Analyytti *(Analyte)* **PCB-180** Näyte *(Sample)* L1



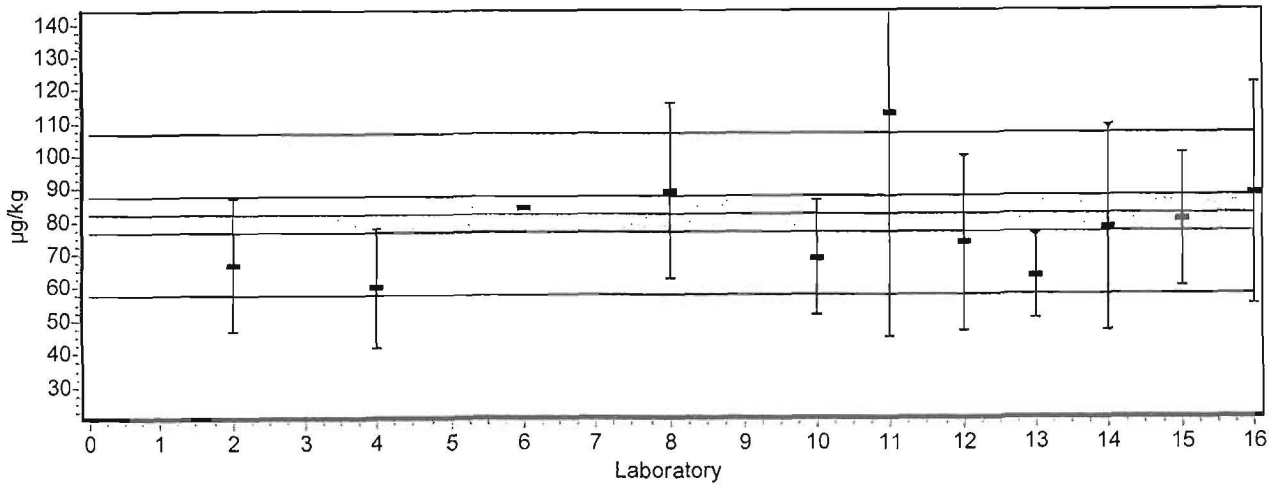
Analyytti *(Analyte)* **PCB-180** Näyte *(Sample)* M0



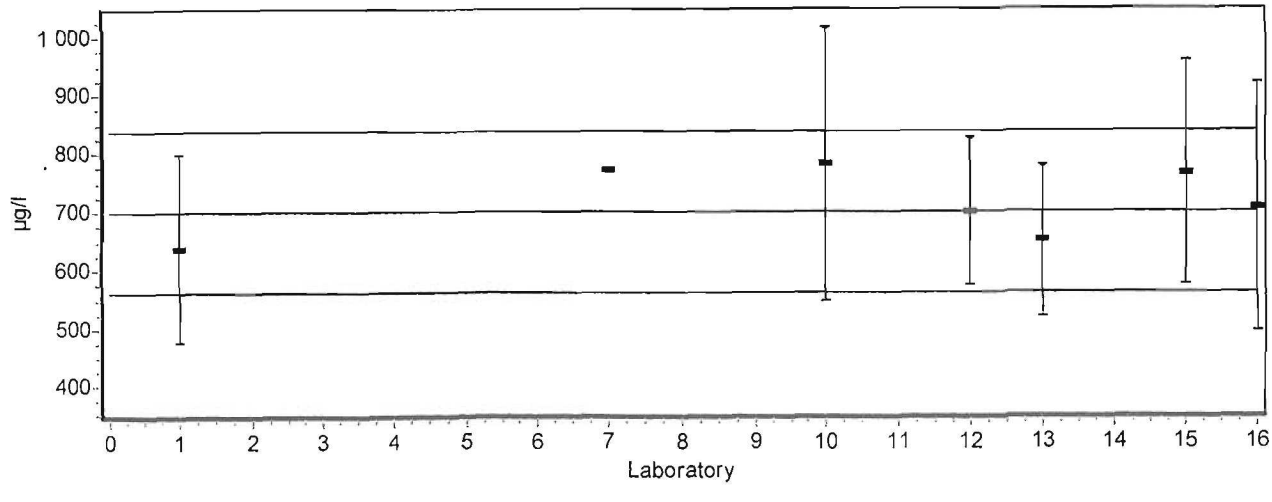
Analyytti *(Analyte)* **PCB-180** Näyte *(Sample)* M1



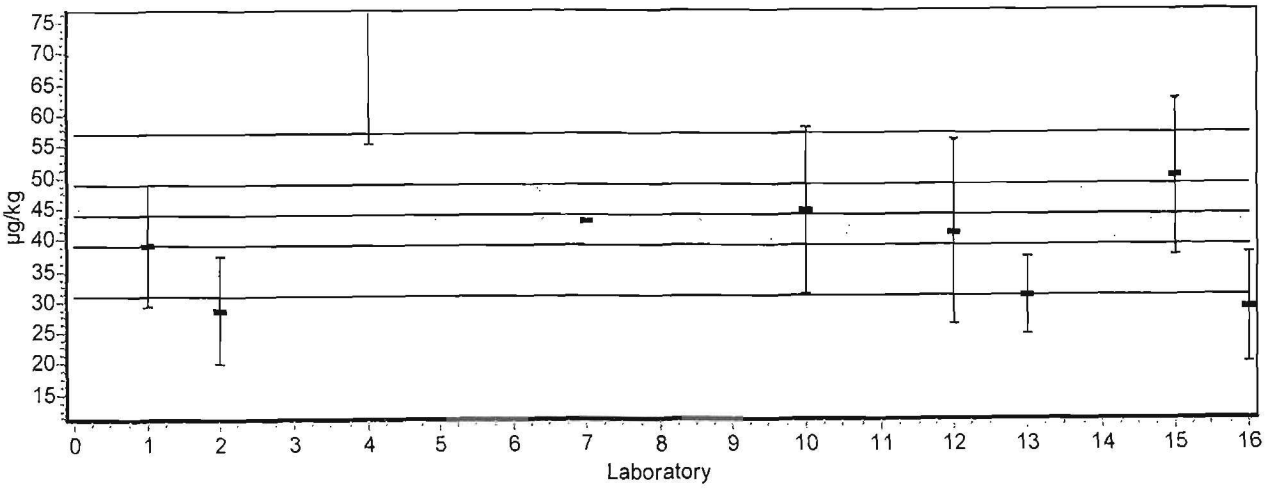
Analyytti *(Analyte)* **PCB-180** Näyte *(Sample)* M2



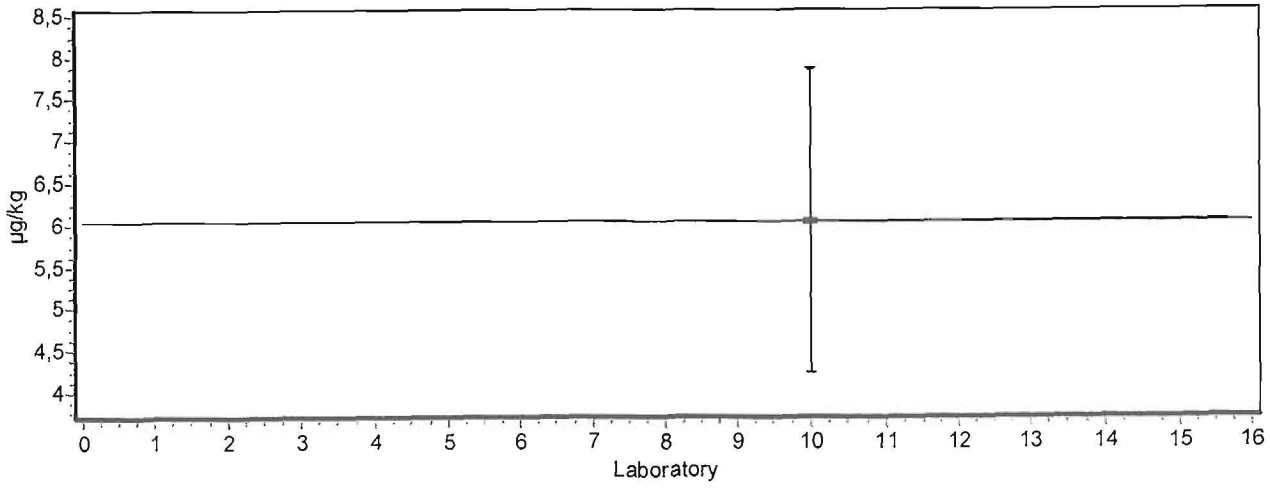
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* L1



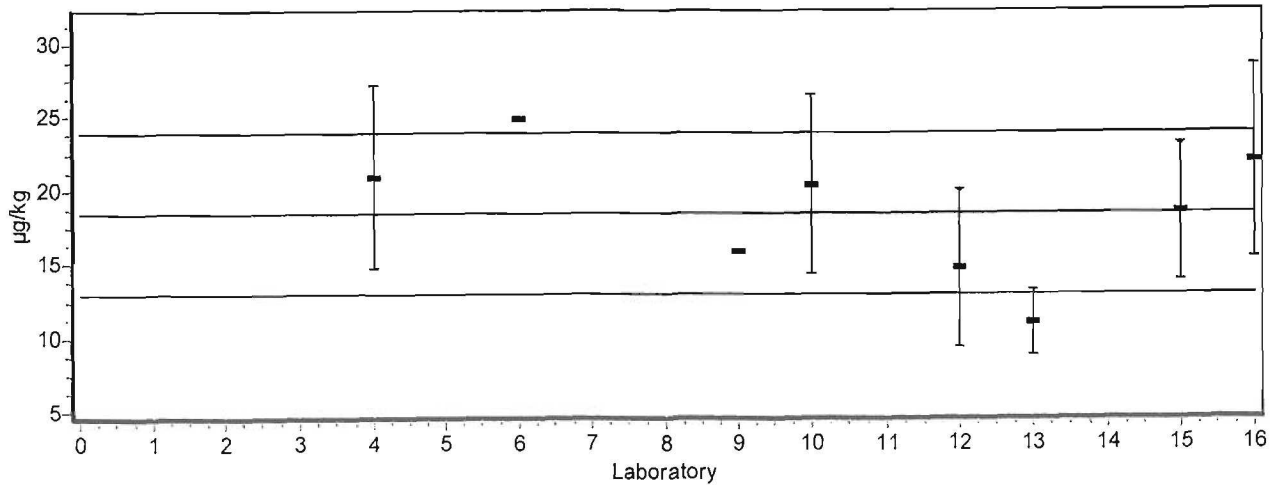
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* M0



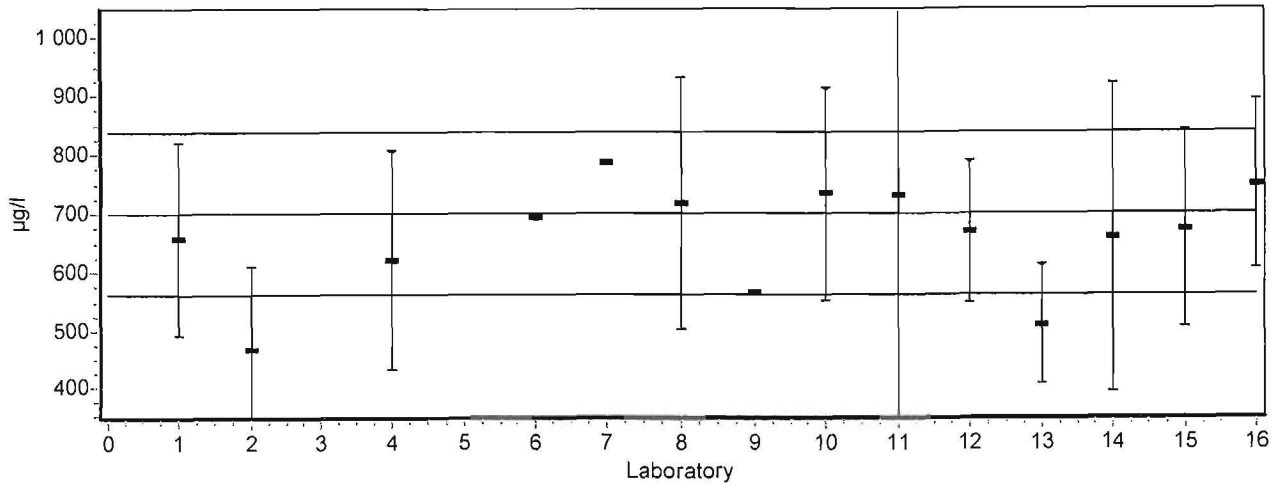
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* M1



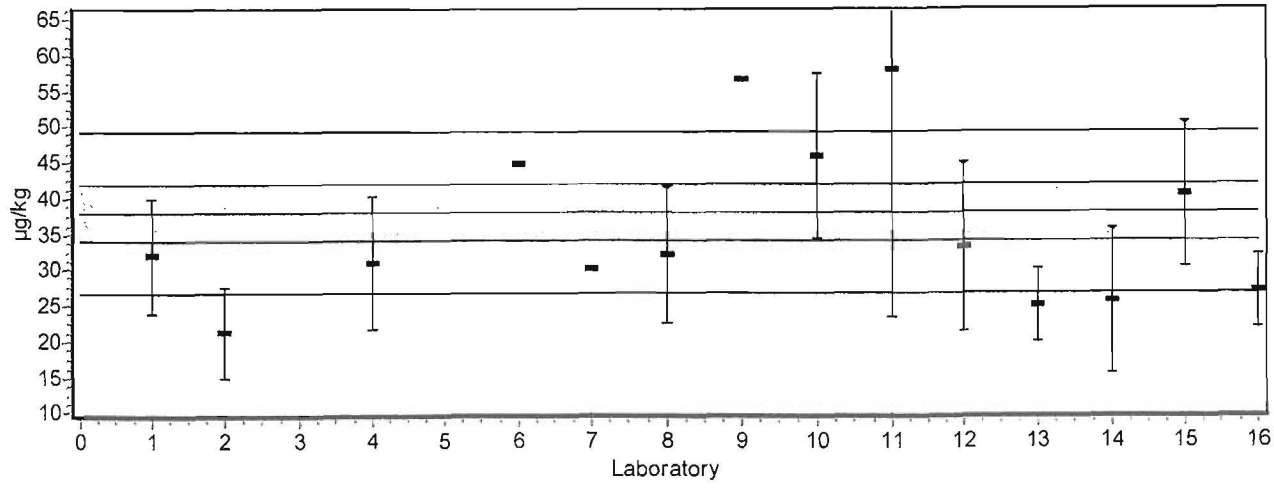
Analyytti *(Analyte)* **PCB-28** Näyte *(Sample)* M2



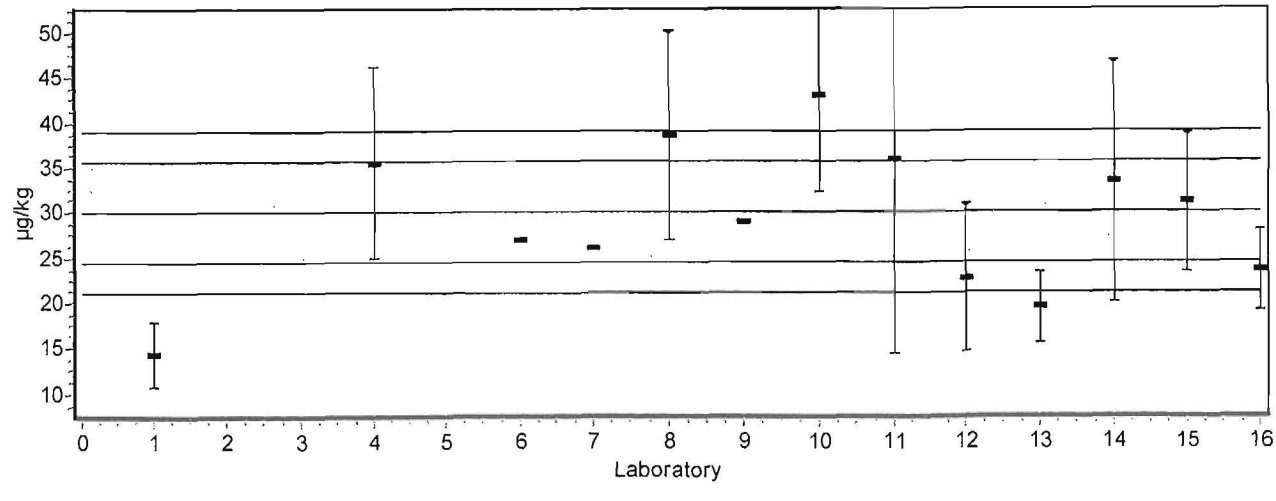
Analyytti *(Analyte)* **PCB-52** Näyte *(Sample)* L1



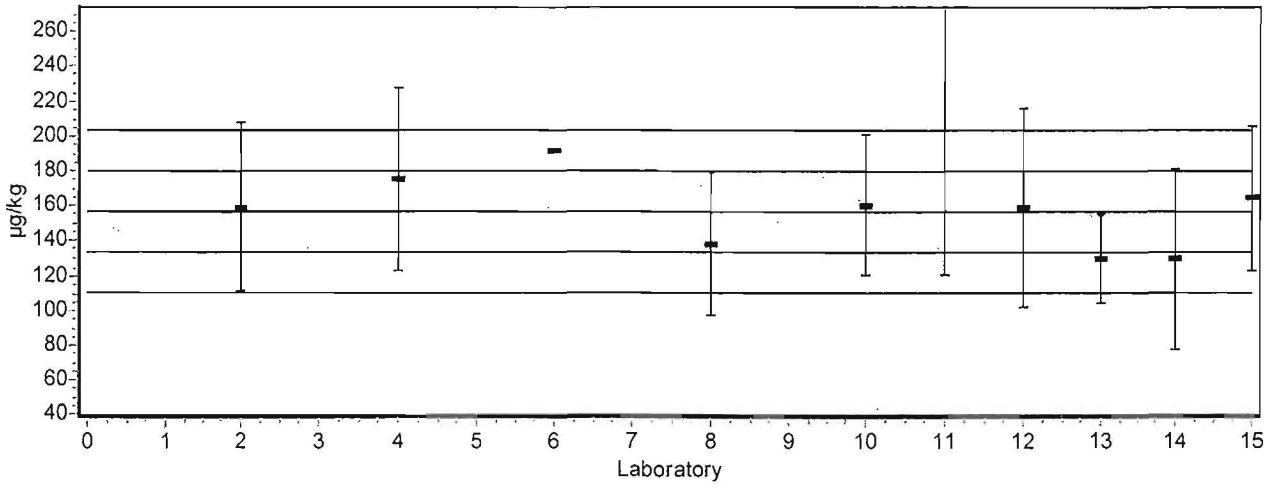
Analyytti *(Analyte)* **PCB-52** Näyte *(Sample)* M0



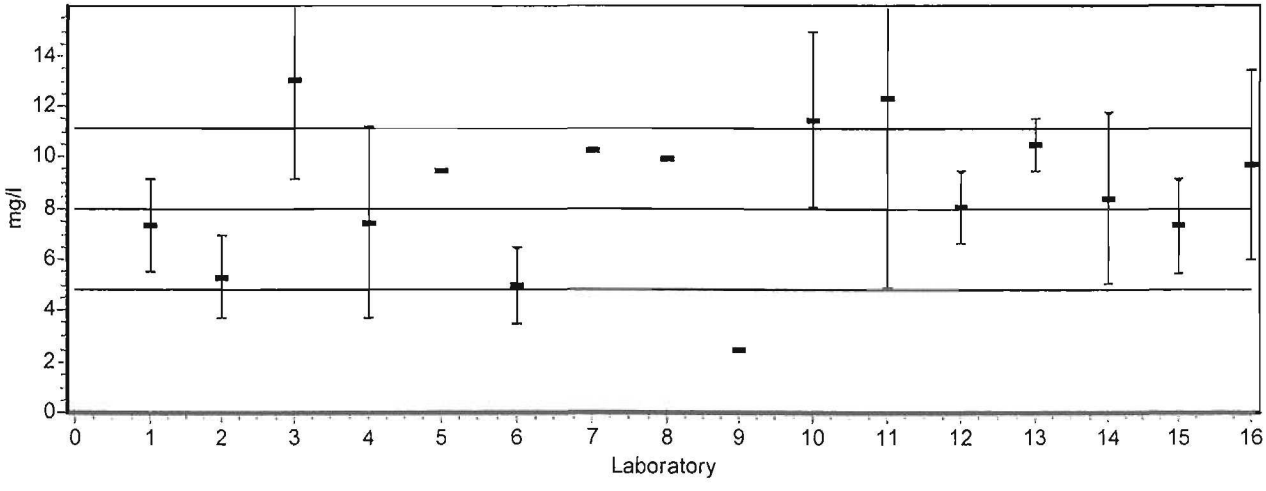
Analyytti *(Analyte)* **PCB-52** Näyte *(Sample)* M1



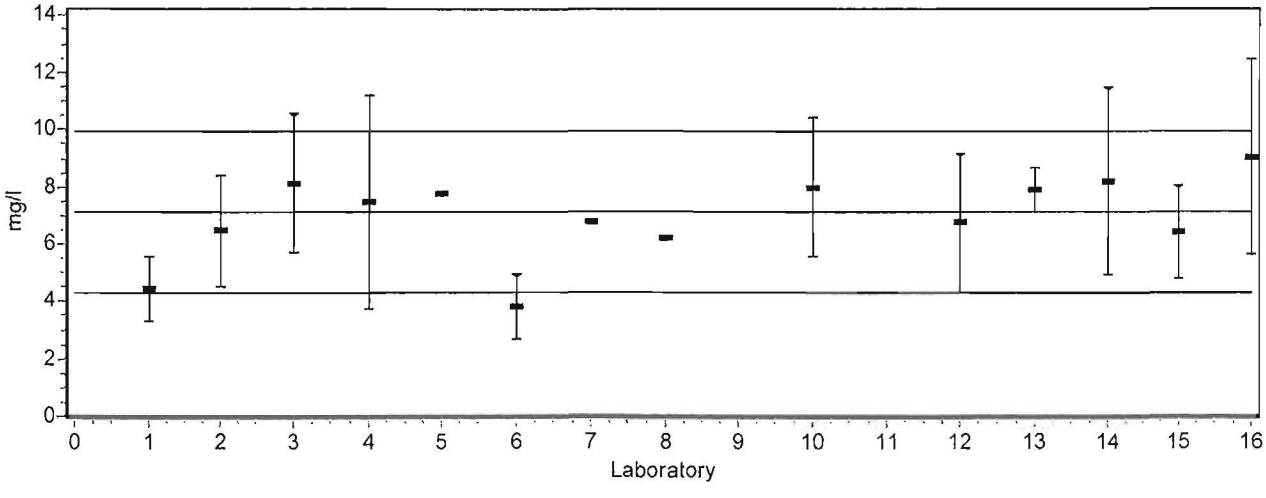
Analyytti *(Analyte)* **PCB-52** Näyte *(Sample)* M2

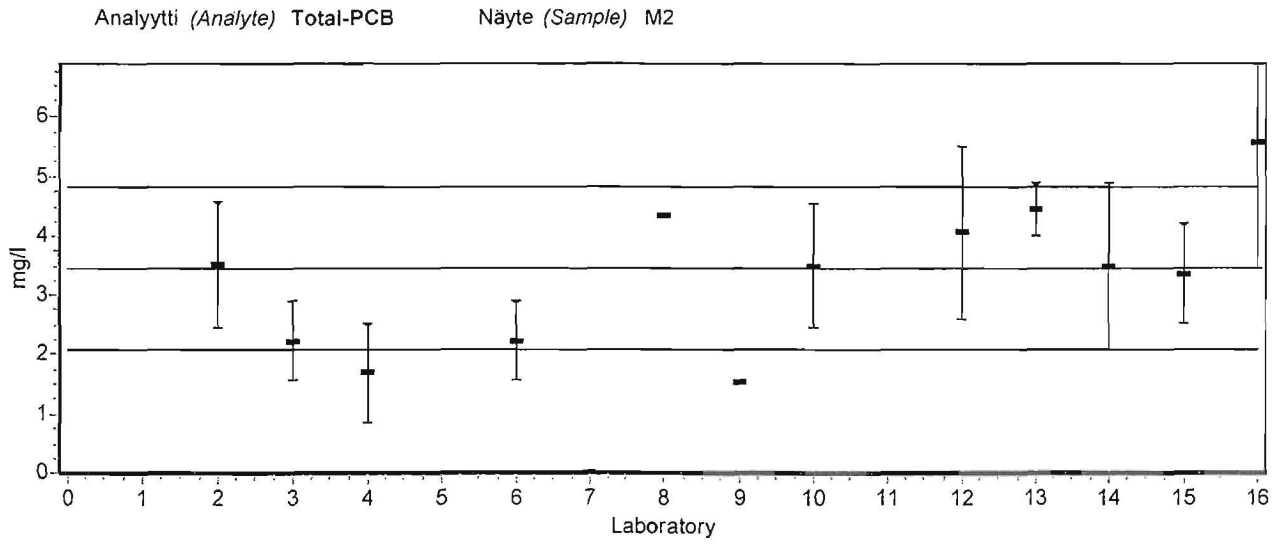


Analyytti *(Analyte)* **Total-PCB** Näyte *(Sample)* L2



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




Analyytti (Analyte) Total-PCB
Näyte (Sample) M2
mg/l
0
1
2
3
4
5
6
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Laboratory

ANNEX 14. RESULTS OF PRINCIPAL COMPONENT ANALYSIS (PCA)

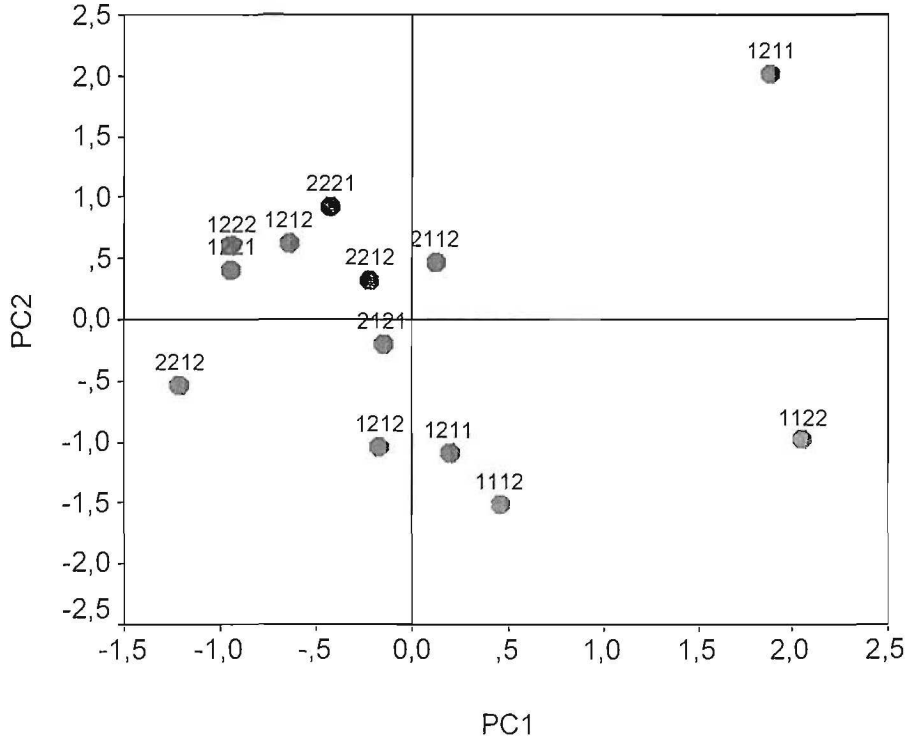
Score plots of the results shows some characteristics of the methods as follows:

Extraction solvent:	1	acetone + hexane
	2	petroleum ether + acetone + hexane + diethyl ether; acetone + hexane + diethyl ether; acetone + hexane + diethyl ether
Extraction technique:	1	Soxhlet
	2	ASE, SFE, shaking or sonic water bath
Clean-up:	1	H_2SO_4
	2	H_2SO_4 + column chromatography or column chromatography alone
Measurement:	1	GC/MS
	2	GC/ECD

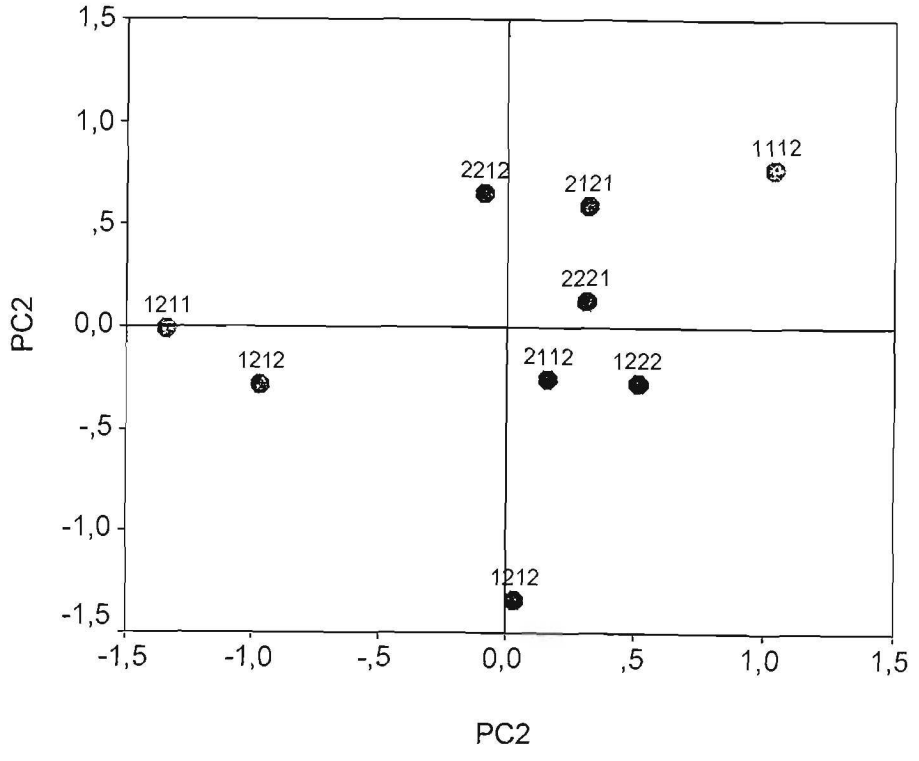
The laboratories used the combination of the methods (accepted into the score plots) as follows:

Lab	Extraction solvent	Extraction technique	Clean-up	Measurement
1	1	2	1	1
2	2	2	1	2
4	1	1	1	2
6	2	2	2	1
7	2	1	2	1
8	1	2	1	2
10	1	1	2	2
11	1	2	1	1
12	2	2	1	1
13	1	2	1	2
14	1	2	2	2
15	2	1	1	2
16	1	2	2	1

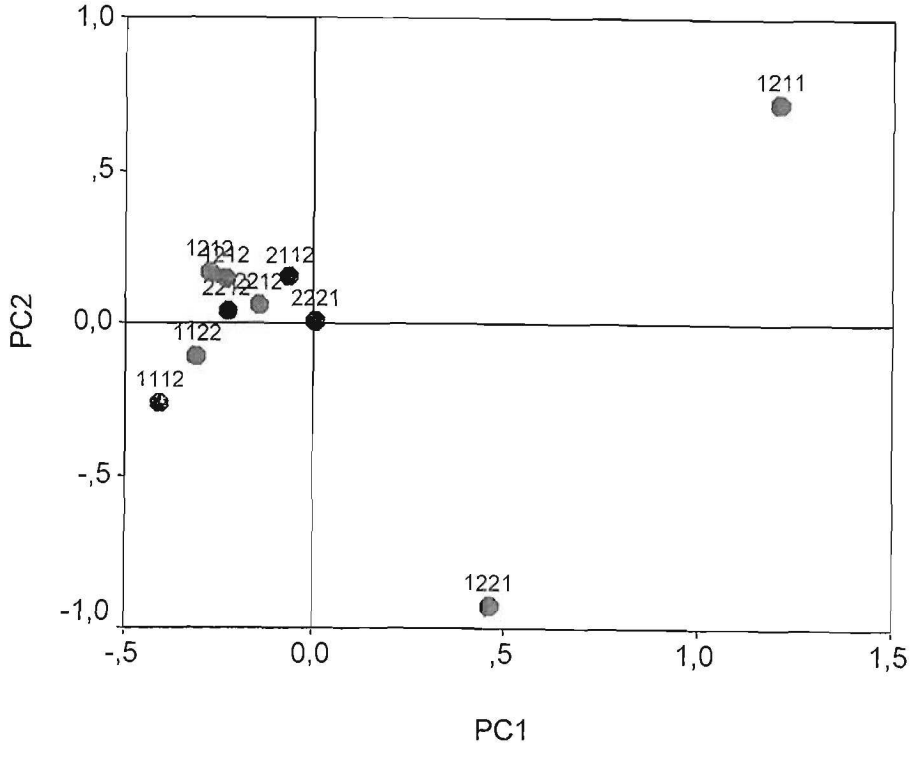
Sample M0



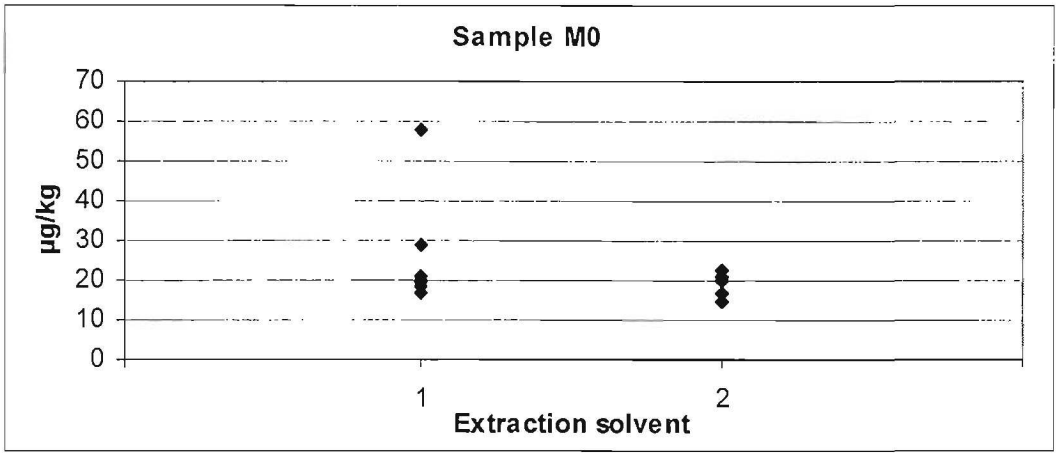
Sample M1

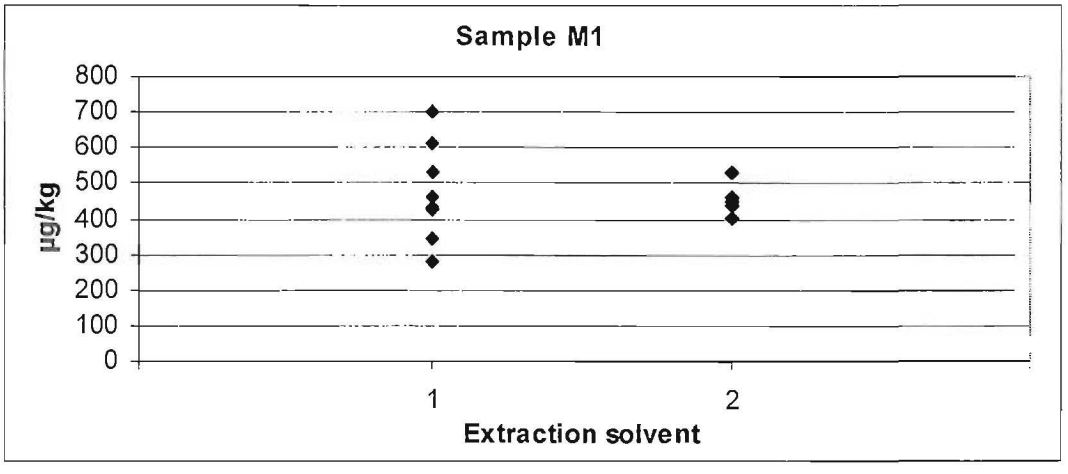


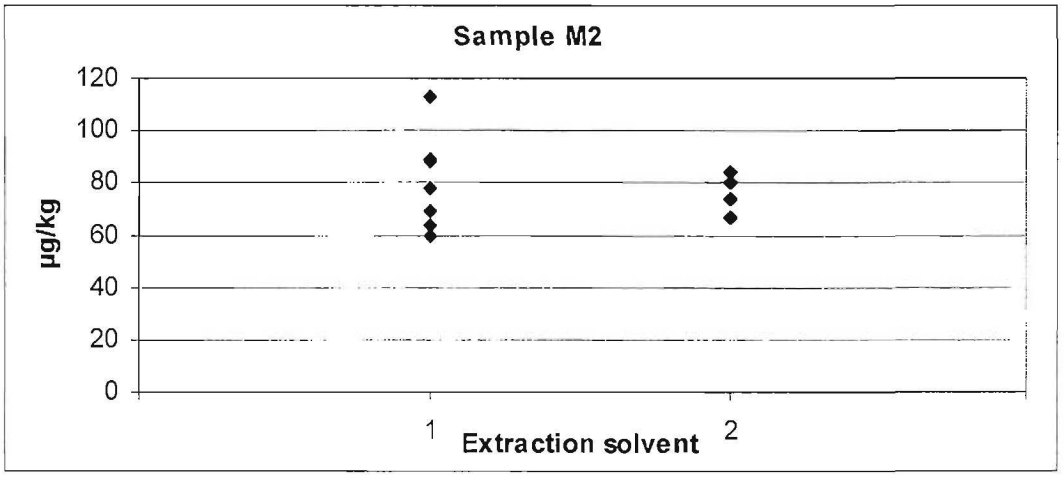
Sample M2



ANNEX 15. RESULTS OF PCB 180 USING DIFFERENT EXTRACTION SOLVENTS





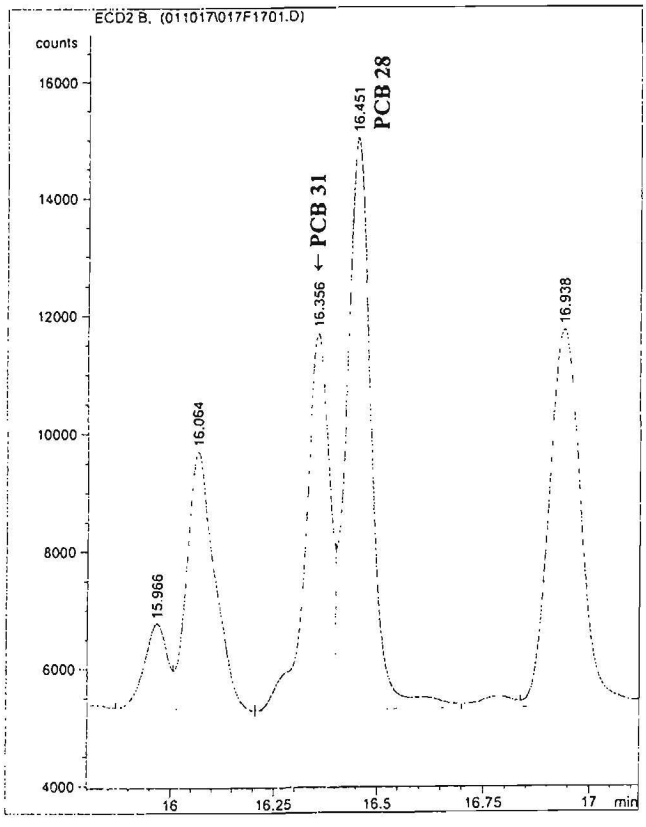


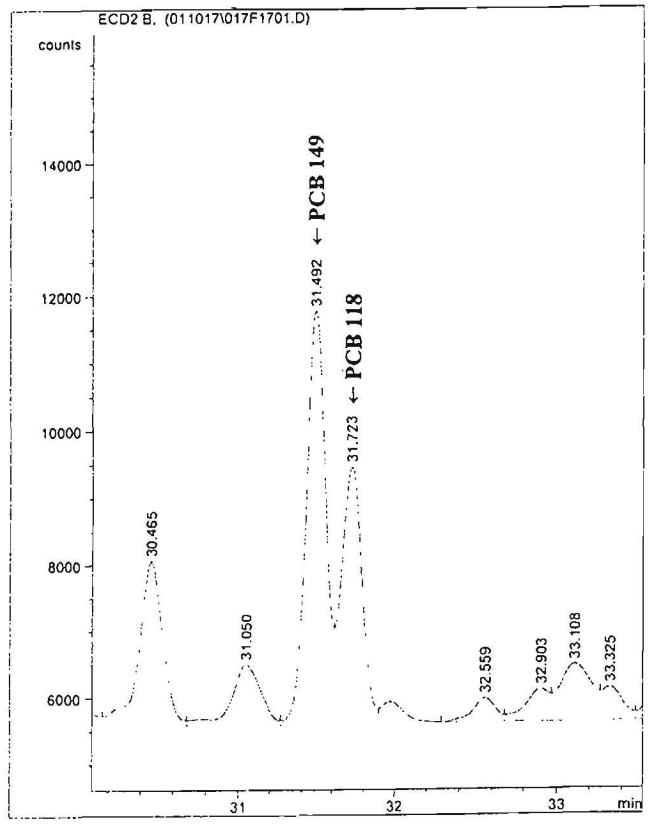
Extraction solvent:

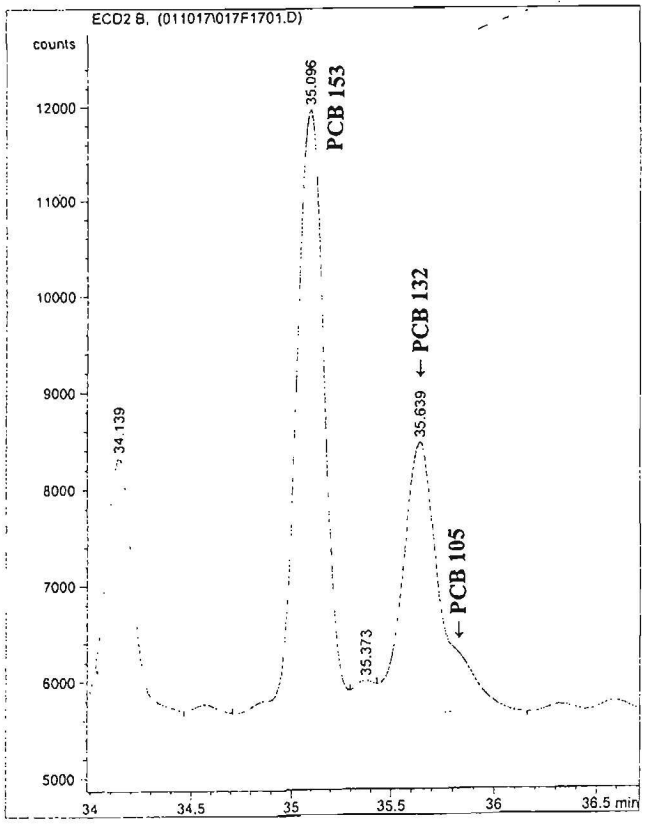
1	**acetone + hexane**
2	**petroleum ether + acetone + hexane + diethyl ether;** **acetone + hexane + diethyl ether or acetone + hexane + diethyl ether**

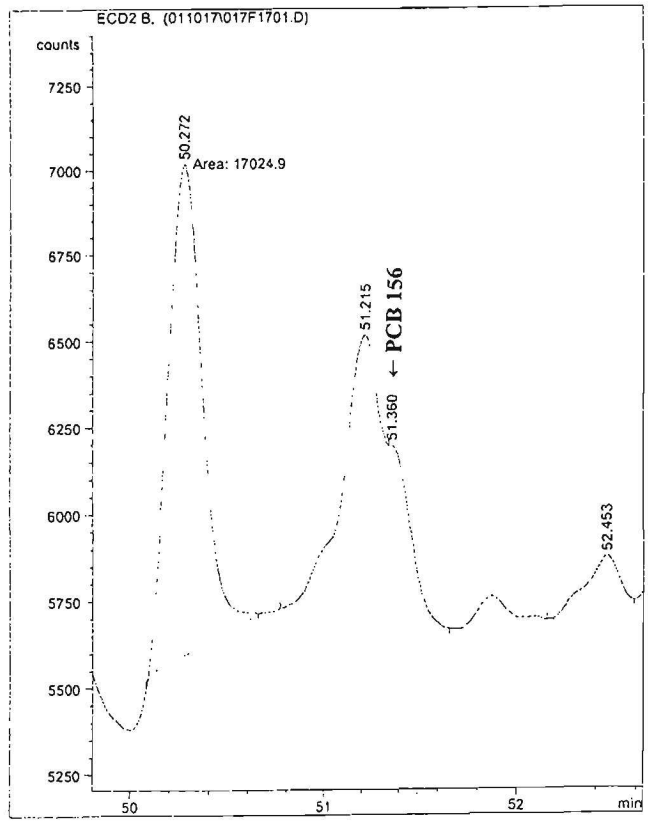
ANNEX 16. SOME EXAMPLES OF PCB PEAKS IN INTERLABORATORY SOIL SAMPLES

Sample M0 (HP 5 column, see laboratory 12 in Annex 6 for gas chromatography)

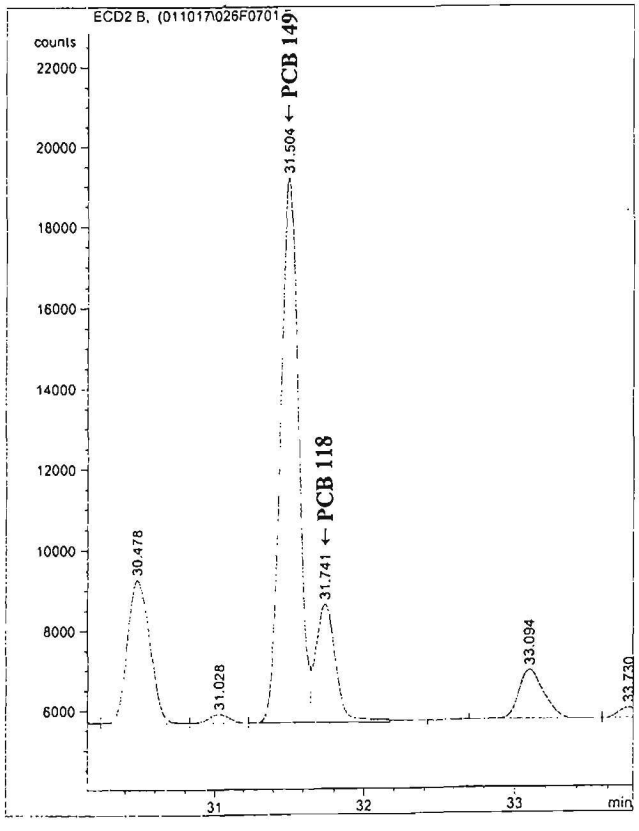


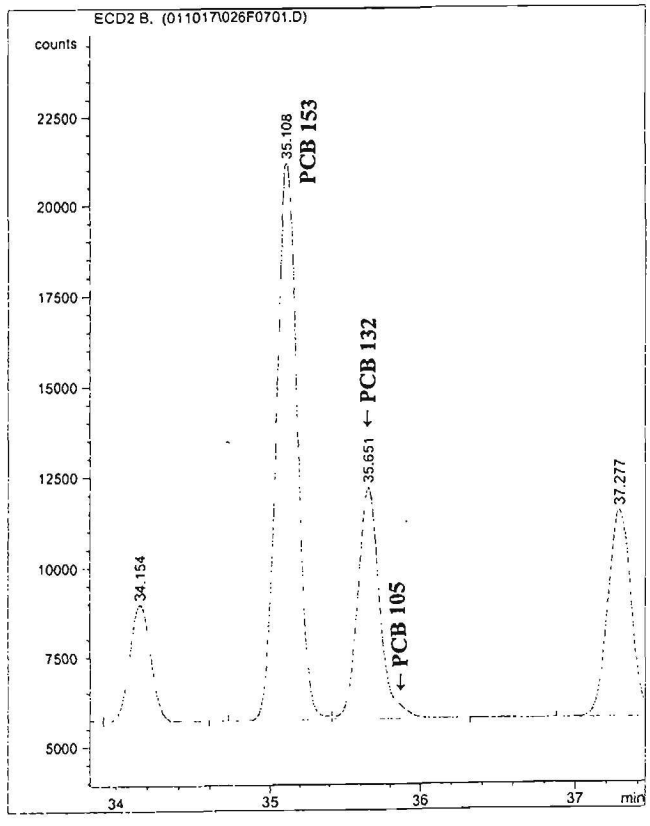


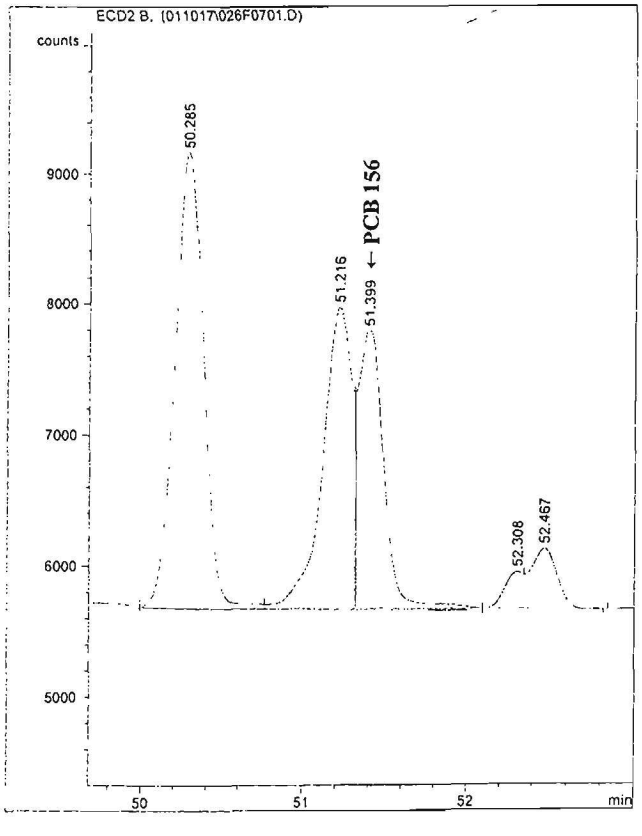




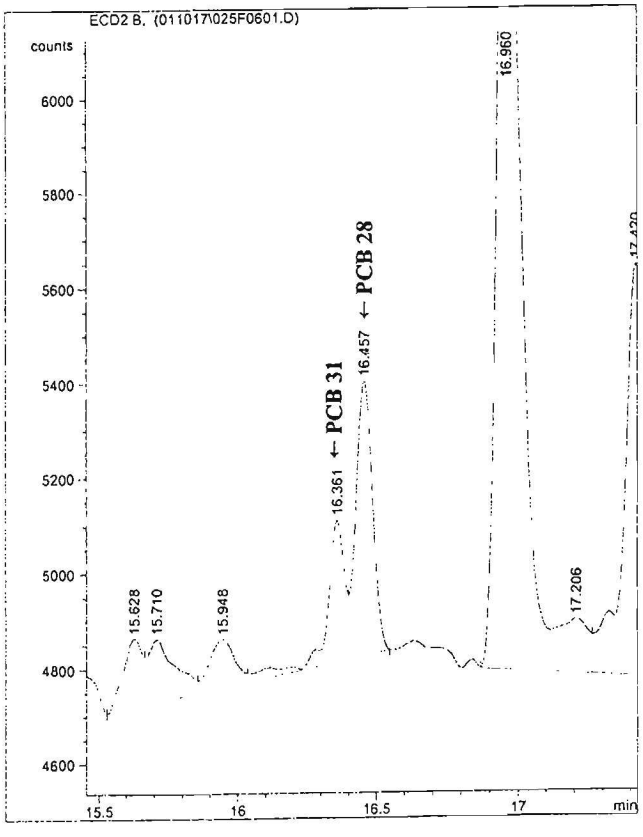
Sample M1 (HP 5 column, see laboratory 12 in Annex 6 for gas chromatography)

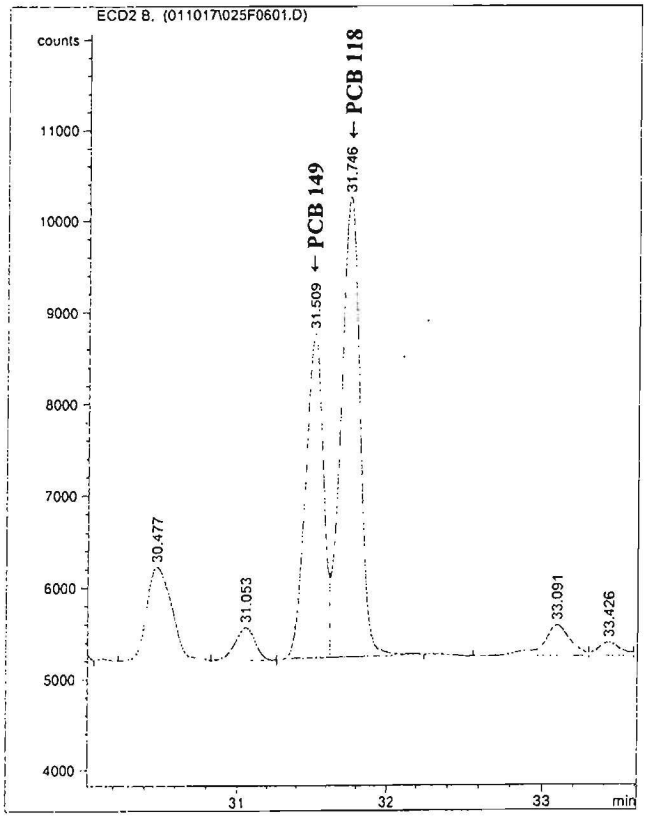


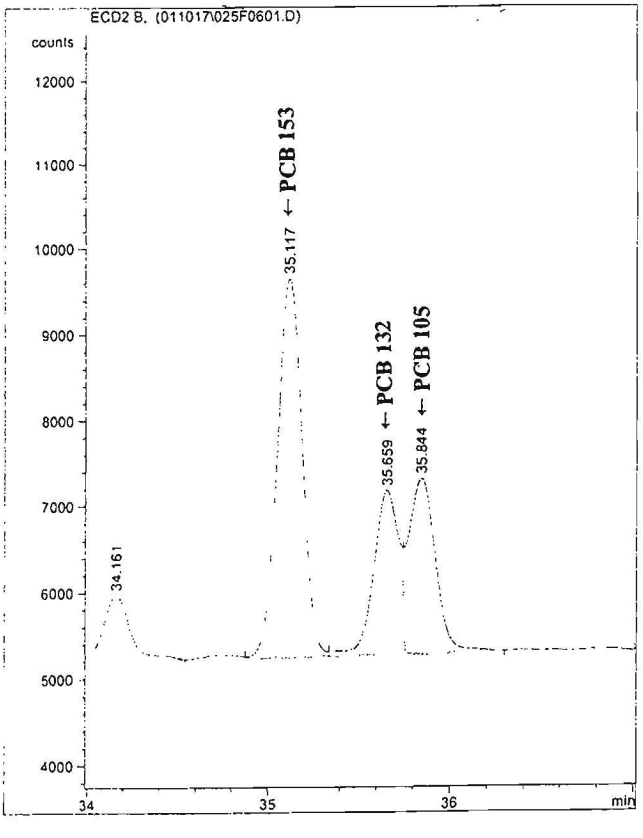


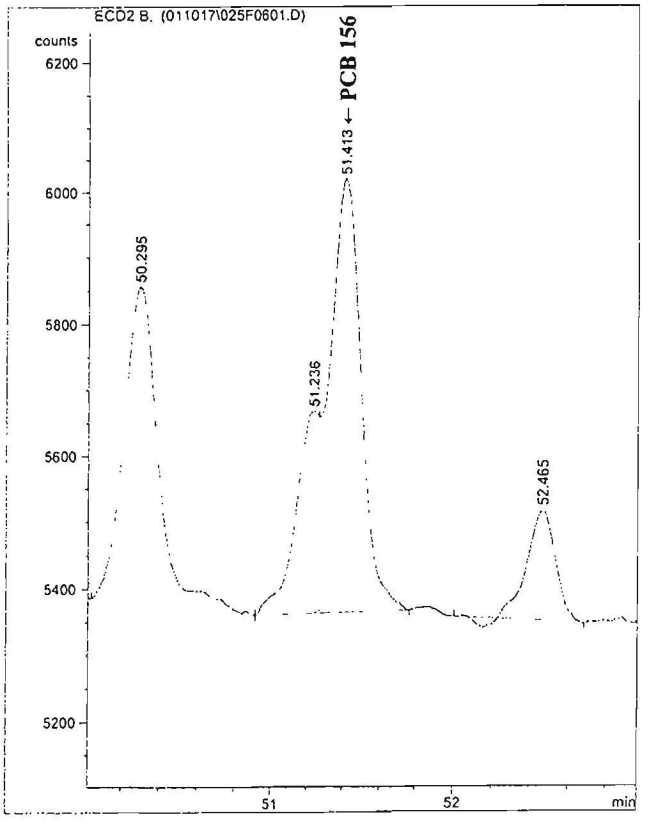


Sample M2 (HP 5 column, see laboratory 12 in Annex 6 for gas chromatography)

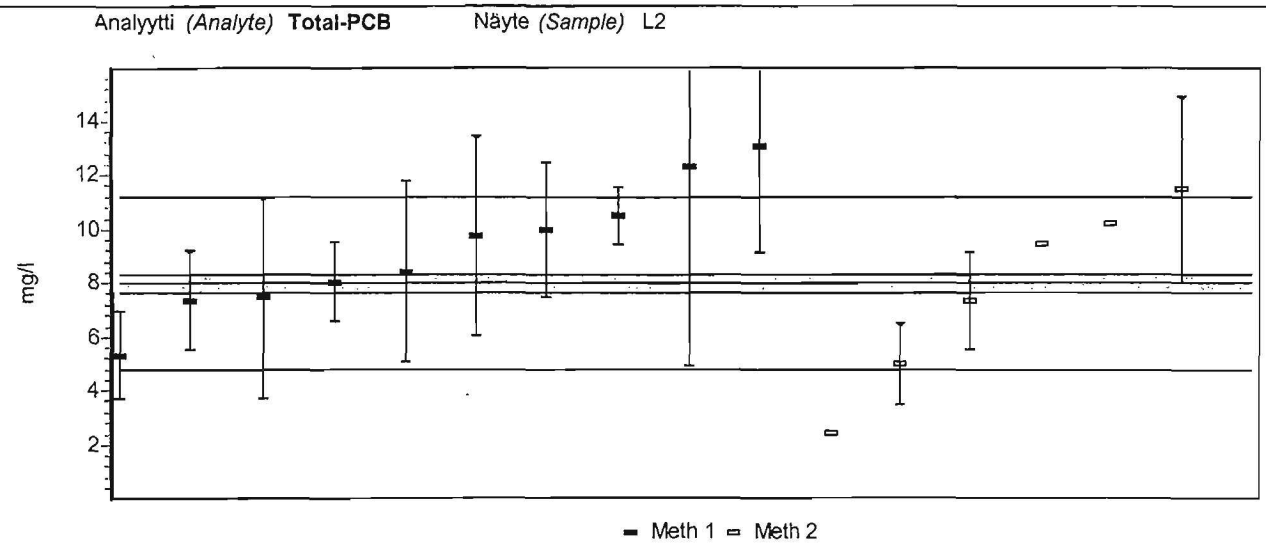


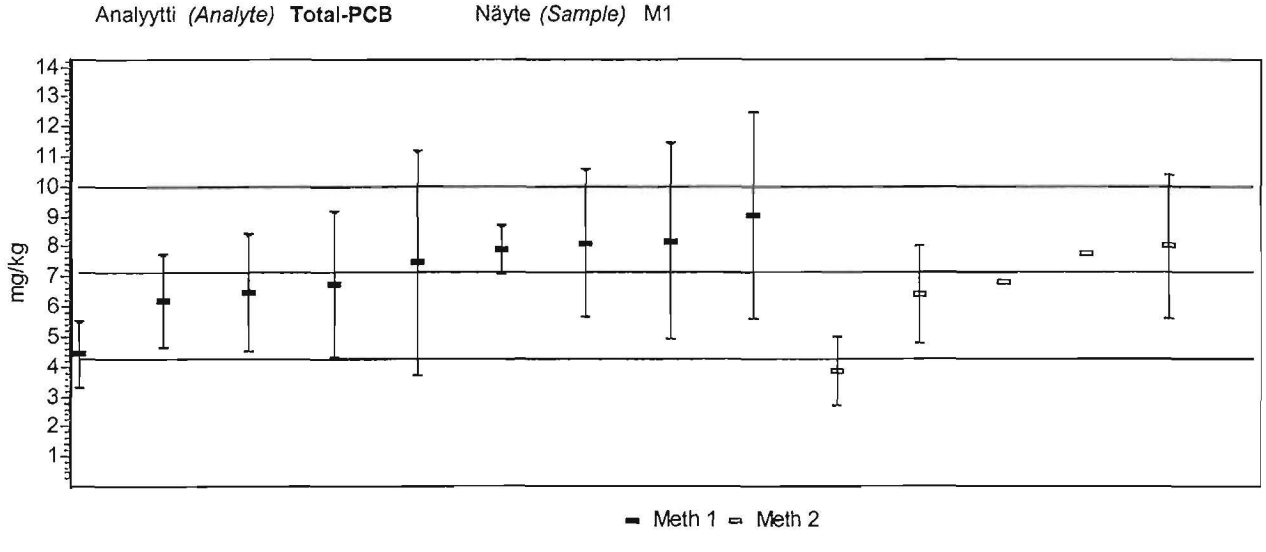


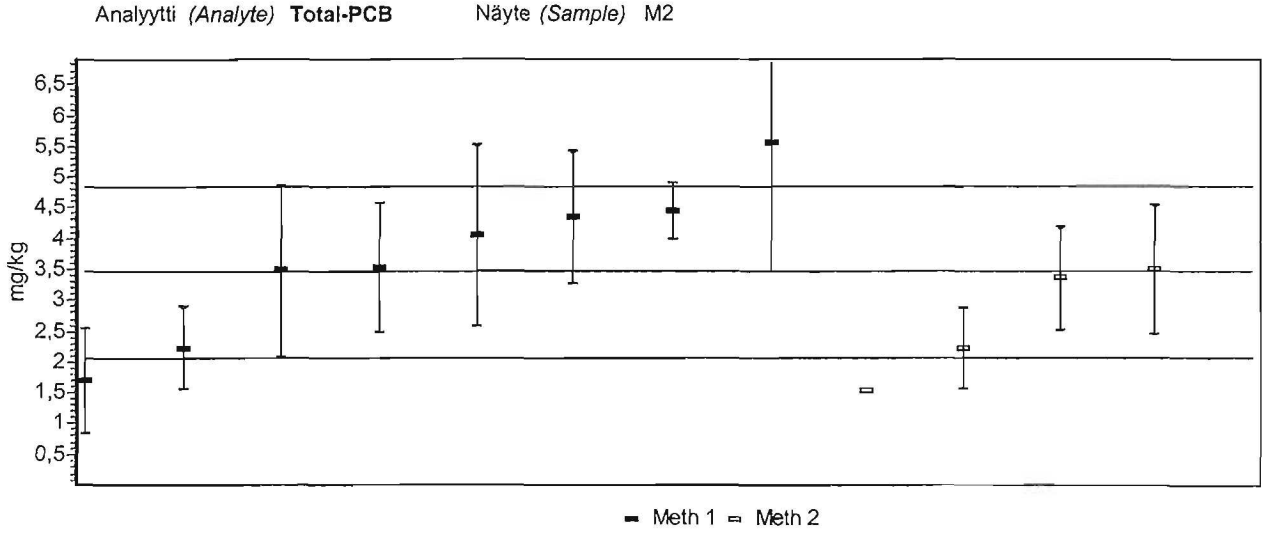




ANNEX 17. THE RESULTS FOR TOTAL PCB ACCORDING TO DIFFERENT METHODS







Meth 1 and Meth 2: see Table 2 (page 8).

ANNEX 18. SUMMARY OF THE Z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	%*
PCB-101	L1	A	N	.	A	.	A	A	A	A	A	A	A	A	A	A	A	93
	M0	A	n	.	A	.	A	A	A	A	P	P	A	A	A	A	A	79
	M1	n	A	.	A	.	A	A	A	A	A	p	A	A	A	A	A	86
	M2	.	A	.	A		A	.	A	p	A	P	A	A	A	A	A	83
PCB-105	L1	A	N	.	A	.	A	A	.	p	A	A	A	A	.	A	.	82
	M0	.	P	.	P		A	.	.	.	P	.	A	P	.	P	.	29
	M1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	0
	M2	.	A	.	A	.	A	.	.	P	p	p	A	A		A	.	67
PCB-118	L1	A	N	.	A	.	A	A	A	N	A	A	A	A	.	A	A	85
	M0	A	A	.	A	.	A	A	A	A	P	p	A	n		A	A	77
	M1	n	P	.	A	.	A	A	A	A	P	A	A	n	.	A	A	69
	M2	.	A	.	A		A	.	A	A	A	P	A	A	.	A	A	91
PCB-138	L1	A	N	.	A		A	A	A	N	A	A	A	A	A	A	A	86
	M0	P	A	.	P	.	A	A	A	N	P	P	A	p	A	A	A	57
	M1	A	A	.	P	.	A	A	A	N	A	P	A	A	A	A	A	79
	M2	.	A	.	A	.	A	.	A	n	A	P	A	A	A	A	A	83
PCB-153	L1	A	N	.	A	.	A	A	A	n	A	A	A	A	A	A	A	86
	M0	A	n	.	A	.	A	A	A	A	A	p	A	A	A	A	A	86
	M1	n	A	.	A	.	A	A	A	P	A	A	A	A	A	A	A	86
	M2	.	A	.	A	.	A	.	A	A	A	P	A	A	A	A	A	92
PCB-156	L1	A	N	.	.	.	A	A	.	A	.	A	A	A	.	A	.	89
	M0	.	P	.	.	.	A	.	.	A	.	.	A	P	.	A	.	67
	M1	n	A	.	.	.	A	A	.	P	.	p	A	P	.	A	.	56
	M2	.	A	.	.	.	A	.	.	A	.	A	A	A	.	A	.	100
PCB-170	L1	.	.	.	.	.	p	A	.	.	A	A	A	A	.	.	.	83
	M0	.	.	.	.	.	A	A		.	P	P	A	A			.	67
	M1	.	.	.	.	.	.	.	.	.	.	.		.	.	.	.	0
	M2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	0
PCB-180	L1	A	N	.	A	.	P	A	A	n	A	A	A	A	A	A	A	79
	M0	A	n	.	A	.	A	A	A	P	p	p	A	A	A	A	A	71
	M1	n	A	.	A	.	A	A	A	P	A	p	A	A	A	A	P	71
	M2	.	A	.	A	.	A	.	A	P	A	p	A	A	A	A	A	83
PCB-28	L1	A	N	.	P	.	P	A	.	P	A	.	A	A	.	A	A	64
	M0	A	n	.	P		P	A	.	P	A	.	A	A	.	A	n	55
	M1	.	.	.	.		.	.	.	.	.	.	.	.	.	.	.	0
	M2	.	.	.	A	.	p	.	.	A	A		A	n	.	A	A	75
PCB-52	L1	A	N	.	A	.	A	A	A	A	A	A	A	n	A	A	A	86
	M0	A	n	.	A	.	A	A	A	P	A	P	A	n	n	A	A	64
	M1	N	.	.	A	.	A	A	A	A	p	A	A	n	A	A	A	77
	M2	.	A	.	A	.	A	.	A	P	A	P	A	A	A	A	P	75
Total-PCB	L2	A	A	P	A	A	A	A	A	N	p	p	A	A	A	A	A	75
	M1	A	A	A	A	A	n	A	A	N	A	P	A	A	A	A	A	81
	M2	.	A	A	n	.	A	.	A	n	A	P	A	A	A	A	P	69
%*		72	51	67	82	100	85	100	100	39	71	38	100	74	96	97	87	
Accredited							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

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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) and total PCB from polluted soils in October 2001. A total of 14 laboratories from Finland and two foreign laboratories participated. Two of the laboratories participated only in the determination of the total PCB. Two standard solutions, a certified reference material (sediment) and two soil samples were delivered.

As the assigned value for the PCBs, the calculated concentration was used in solvent samples, the certified values were used for the CRM 536 and a mean value of the results analyzed by a selected group of participants was used for the soil samples. The median value was used as the assigned value for the total PCB in the soil samples.

Various analysis methods were used for the PCB determination. Majority of them were in-house methods based on instrument applications or standard methods.

In this interlaboratory comparison, 80 % of the participating laboratories were able to report acceptable results, based on the target total standard deviation 20 - 40 % used in calculating of z scores in 95 % confidence interval. The results were most satisfactory (87 %) in analysis of PCBs 101, 153 and total PCB. The PCB congeners 28, 52, 105 and 170 turned to be most critical analytes.

Keywords
soil samples, polluted soil, PCB congeners, interlaboratory comparison, performance testing, intercalibration

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Irma Mäkinen, Anna-Mari Suortti, Sami Huhtala ja Seppo Pönni

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Laboratorioiden välinen vertailukoe 5/2001

Julkaisun laji
Raportti

Toimeksiantaja

Toimielimen asettamispvm

Julkaisun osat

Tiivistelmä

Suomen ympäristökeskuksen laboratorio järjesti lokakuussa 2001 vertailukokeen kymmenen PCB-yhdisteen (28, 52, 101, 105, 118, 138, 153, 156, 170, 180) ja kokonais-PCB:n määrittämisestä pilaantuneista maista. Vertailukokeeseen osallistui yhteensä 14 suomalaista laboratoriota sekä yksi saksalainen ja yksi virolainen laboratorio. Laboratorioille toimitettiin kaksi synteettistä liuosta, yksi varmennettu vertailumateriaali (sedimentti) ja kaksi maanäytettä.

Osallistujat käyttivät useita erilaisia analyysimenetelmiä. Menetelmistä suurin osa oli laboratorioiden sisäisiä menetelmiä, jotka pohjautuivat laitesovelluksiin tai standardimenetelmiin.

Tulosten arvioimiseksi laskettiin z-arvo ja sitä varten asetettiin kokonaiskeskihajonnan tavoitearvoksi 20 - 40 % (95 % todennäköisyys). Vertailuarvona *(the assigned value)* käytettiin synteettisille näytteille laskennallista arvoa, vertailumateriaalille sertifikaatissa ilmoitettuja arvoja ja maanäytteille valittujen laboratorioiden tulosten keskiarvoa. Kokonais-PCB:n vertailuarvona käytettiin tulosaineiston mediaania.

Vertailukokeessa 80 % laboratorioiden tuloksista oli hyväksyttäviä, kun kokonaiskeskihajonnan tavoitearvona oli 20 - 40 %. Eniten tuloksia hyväksyttiin (87 %) PCB-yhdisteiden 101, 153 ja kokonais-PCB:n osalla. PCB-yhdisteistä 28, 52, 105 ja 170 osoittautuivat hankalimmiksi analysoida.

Asiasanat (avainsanat)
maanäytteiden analysointi, pilaantuneet maat, PCB-yhdisteet, vertailukoe, pätevyystesti

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