Suomen ympäristökeskuksen moniste

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Irma Mäkinen, Pirjo Sainio, Kirsti Erkomaa and Sami Huhtala

SYKE Proficiency test 3a/2004

PAHs from polluted soil

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SUOMEN YMPÄRISTÖKESKUS

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CONTENT

1 INTRODUCTION

The Finnish Environment Institute carried out the proficiency test for the determination of PAH's from polluted soil. The test was carried out in accordance with the international guidelines, ISO/IEC Guide 43 1 (1) and ILAC Requirements (2) and ISO/DIS 13528 (3).

The proficiency test was carried out in the framework of the EU/CoEPT Project "Compara-bility of the Operation and Evaluation Protocols of European Proficiency Testing Schemes" (4).

2 ORGANIZING THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Finnish Environment Institute (SYKE), Laboratory
Hakuninmaantie 6, 00430 Helsinki
tel. +358 9 403 000, telecopy +358 9 4030 0890

The responsibilities in organizing the proficiency testwere as follows:
Irma Mäkinen, SYKE, coordinator
Sami Huhtala, SYKE, technical coordinator
Pirjo Sainio and Kirsti Erkomaa, analytical experts

2.2 Participants

In total 21 laboratories (one Danish laboratory, two Norwegian, five Swedish and thirteen Finnish laboratories) participated in the proficiency test (Annex 1). One laboratory reported two sets of the results obtained using two different measurement methods.

2.3 Sample and its delivery

One soil sample was delivered to the European organizers of proficiency tests participating in the EU/ CoEPT Project, which SYKE delivered forward to the participants of this PT test. The sample was the certified reference material (CRM LGC6144), which was contaminated soil taken from gas works (Annex 2).

The sample was delivered 10 March 2004 and it was asked to analyze before 5 August 2004. The sample was asked to keep cool (4 °C).

The results were asked to return before 9 August 2004. All participating laboratories reported results.

The preliminary lists of the results were delivered during the week 38.

2.4 Comments sent by the participants

The participants sent comments on their analytical methods and their results. Some participants were not able to measure benzo(b)fluoranthene and benzo(k)fluoranthene separately. The participants using the HPLC method were not able to report acenaphtalene, because it does not fluoresce. Two participants had reported their results in the wrong places and the organizer had corrected the results in the datafile.

2.5 Analytical methods

For analysis of PAH's in soil using GC-MS has been prepared the draft standard ISO/DIS 18287 (5). The draft standard is based on extraction acetone and petroleum ether. However, a few participants has used the draft standard (Annex 4). The method published by Nordtest (Report TR 329) was rather commonly used (6). The method based on the extraction with sodium pyrophosphate solution together with toluene at rt for 16 h. The extract is analysed by GC-MS. Many participants used their own "in house" methods.

The soil sample was extracted using several different solvents or solvent mixtures. Eleven different solvents or solvent mixtures had been used. The mixture of acetone and hexane was most commonly used or another solvent besides acetone. The participants used the sample intake between some hundreds milligrams and 20 grams. The intake of 10 – 20 g was mainly used. Extraction was carried out mainly by shaking or by soxhlet. Only one participant (lab 2) used sonication for extraction of the soil sample.

For measurement of PAH's the GC-MS- method was commonly used. One participant (lab 17) measured PAHs using the GC-FID-method and three participants (lab 7, 15 and 21) measured PAH's using the HPLC technique.

Several standards or standard mixtures were used as internal standards. Also deuterated standards were used rather commonly.

2.6 Data treatment

2.6.1 Testing of outliers and normality of data

The participants were requested to report three results. Measurement uncertainties were asked to report for each result, too.

Before the statistical treatment, the data was tested according to Kolmogorov-Smirnov normality test and it was normally distributed in each case. Outliers were rejected according to the Cochran test (replicates) or Hampel test (mean values). The results were calculated using the Robust algorithm A (3).

2.6.2 Assigned value and its uncertainty

The robust-mean was used as the assigned value except fluoranthene, for which the median was used. The certified value reported by the provider of the CRM was not used as the assigned value, because there were large differences between the assigned values calculated from the results of this PT test and the certified values, e.g. in analysis of acenaphtylene, anthracene, benzo(a)pyrene, fluorine and total PAH. In addition, the reported uncertainties for the certified values were rather large.

The uncertainty of the assigned values was calculated using the standard deviation based on Robust algorithm. The uncertainty of the assigned value was between 11 % and 21 %, (95 % confidence interval) and in many cases it was smaller than the uncertainty reported in the certificate (Annex 2).

2.6.3 Target value for total standard deviation

The target total standard deviation (s_{target}, %) used for calculation of the z scores was estimated on basis of PAH contents in the sample and the uncertainties of the assigned values. The s_{target} was 30 % or 40 % (95 % confidence interval). The target standard deviations of 15 % or 20 % was used in calculating of z scores.

2.6.4 Evaluation of performance

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

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

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:

$\lvert z \rvert \leq 2$	"satisfied" results
$2 < \lvert z \rvert < 3$	"questionable" results
$\lvert z \rvert \geq 3$	"unsatisfied" results.

The calculated z scores are presented in the results of each participant (Annex 8) and the summary of z scores is presented in Annex 9. Explanations to terms are presented in Annex 7.

The organizing laboratory (SYKE) had the code 7 in this proficiency test (HPLC method).

3. RESULTS AND PERFORMANCE

3.1 Results

All of the results reported by the laboratories are presented in Annex 4. Statistically treated results for each laboratory are presented in Annex 8. The graphical presentations of the results and the uncertainty estimations are presented in Annex 6.

Table 1. Results of triplicate determinations (ANOVA statistics)

Analyte	Sample	Unit	Ass. val	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Ac-cepted z-val %
A-naphthy	P	mg/kg	8,45	8,464	8,97	0,7918	3,521	3,609	9,4	42	43	40	18	61
Acenaph	P	mg/kg	2,05	2,327	2,035	0,223	1,41	1,427	9,6	61	61	40	19	89
Anthrac	P	mg/kg	7,95	7,913	7,232	0,5688	2,903	2,959	7,2	37	37	40	21	67
Benzo-A-P	P	mg/kg	15,5	15,54	15,06	1,151	3,718	3,892	7,4	24	25	40	22	91
Benzo-ant	P	mg/kg	28,5	28,36	26,97	1,749	6,616	6,843	6,2	23	24	40	20	85
Benzo-B-F	P	mg/kg	24,4	26,3	23,24	1,977	9,19	9,401	7,5	35	36	40	21	76
Benzo-K-F	P	mg/kg	16,6	17,35	15,95	1,365	6,635	6,774	7,9	38	39	40	18	78
Benzo-per	P	mg/kg	17,3	17,61	18,1	1,459	5,23	5,43	8,3	30	31	40	22	91
Chrysene	P	mg/kg	33,7	33,41	31,2	2,295	8,049	8,37	6,9	24	25	30	21	76
Dibenz-ah	P	mg/kg	3,27	3,074	3,328	0,2738	0,7982	0,8439	8,9	26	27	40	21	76
Fluoran	P	mg/kg	89,7	93,27	89,2	5,169	18,28	19	5,5	20	20	30	22	82
Fluorene	P	mg/kg	8,57	8,277	8,423	0,6344	1,51	1,638	7,7	18	20	30	20	70
Indeno	P	mg/kg	16,7	17,01	16,7	1,717	5,036	5,32	10	30	31	40	22	86
Napht	P	mg/kg	5,86	5,918	5,2	0,6209	2,287	2,37	10	39	40	40	19	84
Phenan	P	mg/kg	120	117,3	115	8,9	19,9	21,8	7,6	17	19	30	21	81
Pyrene	P	mg/kg	91,1	91,53	89,02	5,323	18,32	19,08	5,8	20	21	30	21	86
tot-PAH	P	mg/kg	483	474,2	468	21,57	83,79	86,52	4,5	18	18	40	18	94

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

The results were asked to report as triplicates. The repeatability (the within-laboratory standard deviation, s_w) of PAH's was between 4.5 % and 10 % and the reproducibility (s_t) was between 17 % and 61 % (Table 1). The ratio s_t/s_w, a measure for the robustness of the methods used, was mainly higher than 3. Only in case of dibenz(ah)anthracene, fluorine and indeno it was smaller than 3. The ratio s_t/s_w should be between 2 and 3 for robust methods (7).

Table 3. Summary of the proficiency test

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Ac-cepted z-val%
Acenaph	P	mg/kg	2,05	2,33	2,02	2,04	0,39	19,5	20	40	89
A-naphthy	P	mg/kg	8,45	8,46	8,45	8,97	3,1	36,6	19	40	61
Anthrac	P	mg/kg	7,95	7,91	7,95	7,55	3,02	38	21	40	71
Benzo-ant	P	mg/kg	28,5	28,36	28,53	27,7	6,94	24,3	20	40	85
Benzo-A-P	P	mg/kg	15,5	15,54	15,46	15,06	3,54	22,9	22	40	91
Benzo-B-F	P	mg/kg	24,4	26,3	24,38	23,24	6,29	25,8	21	40	76
Benzo-K-F	P	mg/kg	16,6	17,35	16,64	15,95	5,69	34,2	18	40	78
Benzo-per	P	mg/kg	17,3	17,61	17,32	18,1	5,05	29,1	22	40	91
Chrysene	P	mg/kg	33,7	33,41	33,72	32,85	7,91	23,5	21	30	76
Dibenz-ah	P	mg/kg	3,27	3,07	3,29	3,39	0,89	26,9	21	40	76
Fluoran	P	mg/kg	89,7	93,27	93,27	89,7	19,14	20,5	22	30	82
Fluorene	P	mg/kg	8,57	8,28	8,57	8,6	1,71	20	20	30	70
Indeno	P	mg/kg	16,7	17,01	16,74	16,7	4,08	24,4	22	40	86
Napht	P	mg/kg	5,86	5,92	5,86	5,2	2,13	36,4	20	40	84
Phenan	P	mg/kg	120	117,35	120,23	119	26,86	22,3	21	30	81
Pyrene	P	mg/kg	91,1	91,53	91,07	90,35	19,92	21,9	21	30	86
tot-PAH	P	mg/kg	483	474,24	482,54	472,5	95,52	19,8	18	40	94

where,

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

Differences between the results obtained using different extraction solvents were not possible to evaluate due to a great variety of solvents in this PT test. However, according to the report of the European project HORIZONTAL a polar solvent should be used in determination of PAHs because of its limited solubility in unpolar (8). According to the HORIZONTAL report he choice of extraction solvent is more crucial than the procedure and the extraction devices itself for the extraction of PAH's from the matrices. PAH's are not very good soluble in the ordinary solvents such as petroleum ether and other hydrocarbons. The choice of solvents has to be made in accordance with the expected contamination level and with the measurement techniques.

The sample intake and particularly the ratio "the sample intake/the volume of solvent" is supported to have an influence on the results in this PT test. In the delivered soil sample the content of PAH's was rather high. It is obvious that the laboratories 13 and 17 reported too low contents of PAH's because of too large sample intake, in extraction.

Table 3. The mean values of the results (mg/kg) obtained using GC (n= 19) or HPLC (n=3) in analysis of some PAH's

	Acenaph	**Antrac**	**Benzo-ant**	**Chrysene**	**Fluoran**	**Indeno**	**Napht**	**Phenan**	**Pyrene**
GC	2.02	7.93	28.5	33.7	89.7	16.7	6.1	118	87.7
HPLC	1.83	8.61	26.9	33.3	93.3	16.7	4.5	114	97.3

In this PT test the results obtained using GC and HPLC techniques were fairly simialr as the table 3 shows. Acenaphthylene cannot be detected using HPLC/FL. Interaction of emission signals with the matrix compounds, such as quenching effect is possible which leads to error in PAH-determination (8). It should be also notified, that the proper choice of a capillary GC-column is the prerequisite for the gas chromatographic separation of PAH's.

The used calibration range varied greatly from one laboratory to the other. In most cases the number of calibration points was at least four. Internal standards (e.g. deutered C 13-isotopic PAH's are necessary for quantification in GC/MS technique(8).

The total PAH had is calculated as the sum of each 16 PAHs. The results of the total PAH agreed rather well (Appendix 7). One participant reported too high value.

There was variation in the reported uncertainties of the analytical methods used by the laboratories (Appendix 7 and 9). Estimation based on validation and intern quality control data was the most common procedure for calculation of the measurement uncertainty. According to this proficiency test a few participants had overestimated their measurement uncertainty (> 50 %) comparing with their performance, but some of them had reported rather low uncertainties
(< 10 %) in 95 % confidence level. Measurement uncertainties had been estimated for analysis of less polluted samples than for the sample in this proficiency test

3.2 Estimation of performance

In this PT test, 81 % of the participating laboratories reported satisfied results, based on the target total standard deviation between 30 % and 40 % used in calculating of z scores in 95 % confidence level (Appendix 6 and 10). The variation of the results in analysis of different PAH's was between 20 % and 38 %. SYKE has not carried out the proficiency test before for analysis of PAH's from soil. By taking into

that some laboratories might have participated the first time in the test for PAH's, the laboratories performed rather well.

The participants used many different methods for analysis of PAH's and this might have had some influence on the variation of the results. At least too large sample intake showed to have some effect on results of some participants. Use of a proper and sufficiently effective, polar solvent is crucial in analysis of PAH's, Use of uniform and proper methods e.g. in extraction step could improve a quality of results in analysis of PAH's from soils.

3.3 Results obtained in the EU/CoEPT Project

The proficiency test was carried out within the framework of the EU/CoEPT Project "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes". In the 1st step of the project the statistical protocols of the PT providers have been assessed and their validity has been checked. In the 2nd step, in this proficiency test, a common soil sample (CRM) was distributed among the European providers, who delivered it among their our clients. The providers were asked to establish reference and consensus values, to rate performance of the participating laboratories and to estimate uncertainty of assigned values.

In total eight providers from five countries reported the results in the 2nd step of the project. The preliminary results of the 2nd step showed as follows:

- Generally there was a good agreement between providers in estimation of assigned values by taking into account difficulty of PAH analysis. For some invidual PAH's (e.g. acepnaphthylene) there were significant differences between PT providers.
- There was a good agreement between the results of different participants. Differences came mainly from differences of analytical methods used by the participants.
- Main differences came from different statistical protocols used by the providers e.g. in estimation of performance of participants. However, most PT providers did reasonable agreement on the value of the target standard deviation.
- Uncertainty of assigned values is seldom reported in European proficiency tests at this moment. There were some differences in the uncertainties reported by the providers.

4 SUMMARY

The Finnish Environment Institute carried out the proficiency test for the determination of PAH's from polluted soil. The proficiency test was carried out in the framework of the EU/CoEPT Project "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes". In total, 21 laboratories (one Danish laboratory, two Norwegian, five Swedish and thirteen Finnish laboratories) participated in the proficiency test

One sample was delivered to the participating laboratories, which was a certified reference material prepared from highly contaminated soil.

The method published by Nordtest (Report TR 329) or different "in house" methods were rather commonly used in theanalysis of PAH's. A few participants used the draft standard ISO/DIS 18287. Variation of the results in the analysis of different PAH's was between 20 % and 38 %. Use of different methods or method variations might have let to thevariation of the results. There was variation e.g. in the sample intake, in the extraction solvents and in internal standards. Use of a proper and sufficiently effective, polar solvent is

crucial in the analysis of PAHs from polluted soil.

In this proficiency test, the robust mean value was used as the assigned value. When the target total standard deviation of 30 % or 40 % was used in calculation of z scores (95 % confidence level) 81 % of the participating laboratories reported satisfied results.

The SYKE proficiency test for analysis of PAH's in polluted soil was carried out for the first time. By taking into account that some laboratories might have participated the first time in the test for PAHs, the laboratories performed rather well. Use of uniform and proper methods e.g. in the extraction step could improve the quality of results in the analysis of PAH's from soils.

The proficiency test was carried out within the framework of the EU/CoEPT Project "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes". Generally there was a good agreement between providers in estimation of assigned values and here was also a good agreement between the results of different participants. Main differences came from different statistical protocols used by the providers e.g. in estimation of performance of participants.

5 YHTEENVETO

Suomen ympäristökeskus järjesti toukokuussa 2004 pätevyyskokeen 16 PAH-yhdisteiden määrittämiseksi maasta. Pätevyyskoe oli osa EU-hanketta "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes" (CoEPT). Pätevyyskokeeseen osallistui kaikkiaan 21 laboratoriota Suomesta, Norjasta, Ruotsista ja Tanskasta.

Pätevyyskokeen näytteenä oli yksi sertifioitu vertailumateriaali, joka oli valmistettu saastuneesta maasta.

Analysoinnissa käytettiin useita menetelmiä, yleisimmin Nordtestin raportin TR 329 mukaista menetelmää tai erilaisia laboratorioiden omia menetelmiä. Vain harva osallistuja käytti vielä toistaiseksi kansainvälisen standardiehdotuksen ISO/DIS 18287 mukaista menettelyä. Mm. määritykseen käytetty näytemäärä, uuttoliuottimet ja kalibrointiliuokset vaihtelivat eri laboratorioissa. Riittävän polaarisen liuottimen käyttö on ensisijaisen tärkeää PAH-yhdisteiden uutossa maanäytteistä. Tulosten hajonta oli 20 % – 38 % eri PAH-yhdisteille ja hajontaan vaikutti mm. eri menetelmävariaatioiden runsaus.

Vertailuarvona käytettiin robusti-keskiarvoa. Tässä pätevyyskokeessa 81 % tuloksista oli tyydyttäviä, kun kokonaiskeskihajonnan tavoitearvona käytettiin 30 % tai 40 % (95 % merkitsevyystaso).

Pätevyyskoe PAH-yhdisteiden määrittämiseksi pilaantuneesta maasta järjestettiin ensimmäisen kerran Suomessa. Joiden laboratorioiden osallistuminen ensimmäistä kertaa PAH-yhdisteiden pätevyyskokeeseen on voinut vaikuttaa suoriutumiseen.

Pätevyyskoe oli osa EU/CoEPT-hanketta, jonka alustavat tulokset raportoitiin helmikuussa 2005. Niiden perusteella eurooppalaisten järjestäjien asettamat vertailuarvot olivat pääasiassa yhteneväisiä ottaen huomioon PAH-yhdisteiden analytiikan vaikeudet. Myös eri laborato-rioiden tulokset olivat keskenään vertailukelpoisia. Eroja esiintyi pätevyyden arvioinnissa sekä vertailuarvon mittausepävarmuuden arvioinnissa.

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ANNEX 1. PARTICIPANTS IN THE PROFICIENCY TEST SYKE 3a/2004

Alcontrol Ab, Linköping, Sweden

Alcontrol Ab, Skara, Sweden

Analycen Oy, Tampere, Finland

Analycen Nordic Ab, Lidköping, Sweden

Ekokem Oy Ab, Riihimäki, Finland

Eurofins Danmark A/S, Vallensbak Str., Denmark

Eurofins A/S, Norway

Fortum Oil Oy, Porvoo, Finland

Golder Associates Oy, Helsinki, Finland

Helsingin kaupungin ympäristökeskus, Helsinki, Finland

Insinööritoimisto Paavo Ristola Oy, Hollola, Finland

IVL, Institut för Vatten och Luft, Göteborg, Sweden

Oy Juve AC Ltd., Rovaniemi, Finland

Jyväskylän yliopisto, Ympäristöntutkimuskeskus, Jyväskylä, Finland

Lahden Tutkimuslaboratorio, Finland

PSV-Maa ja Vesi Oy, Oulu, Finland

SGS Inspection Services Oy, Hamina, Finland

SINTEF Materials and Chemistry, Department of Marine Environmental Technology, Trondheim, Norway

VA-Verket Vattenlaboratoriet, Malmö, Sweden

VTT/Prosessit, Espoo, Finland

SYKE, Laboratory, Helsinki Finland

ANNEX 2. CERTIFIED VALUES AND THE CALCULATED ASSIGNED VALUES OF THE SOIL SAMPLE AND UNCERTAINTIES

	CV[1]		U_{CV} [1]	U_{CV} % [1]	ASSIGNED VALUE[2]	$U_{ASS.VAL}$	$U_{ASS.VAL}$ % [3]	$2s_{target}$ % [4]
Acenaph	5	(6,9-3,1)	1,9	38	2,05	0,22	11	40
A-naphthy	7,8	(10,6-5,0)	2,8	36	8,45	1,75	21	40
Anthrac	16,7	(18,5-14,9)	1,8	11	7,95	1,62	20	40
Benzo-ant	28	(32-24)	4	14	28,5	3,82	13	40
Benzo-A-P	22	(25-19)	3	14	15,5	1,86	12	40
Benzo-B-F	26	(32-20)	6	23	24,4	3,38	14	40
Benzo-K-F	17,5	(22,3-12,7)	4,8	27	16,6	3,3	20	40
Benzo-per	22	(26,2-17,8)	4,2	19	17,3	2,65	15	40
Chrysene	34	(39-29)	5	15	33,7	4,25	13	30
Dibenz-ah	3,8	(5,0-2,6)	1,2	32	3,27	0,476	15	40
Fluoran	84	(92-76)	8	9,5	93,3	10	11	30
Fluorene	21	(24-18)	3	14	8,57	0,941	11	30
Indeno	19,6	(25,1-14,1)	5,5	28	16,7	2,14	13	40
Napht	6,6	(8,3-4,9)	1,7	28	5,86	1,17	20	40
Phenan	106	(116-96)	10	9,4	120	14,4	12	30
Pyrene	88	(98-78)	10	11	91,1	10,7	12	30
tot-PAH	510	(565-455)	55	11	483	55,4	11	40

1) Certified values (CRM LGC6144) and uncertainties

2) Assigned value = X_{rob} (except Fluoran, in which it was median value)

3) $U_{ASS.VAL} = 100 \times 2 \times 1{,}23 \times s_{Rob}/X_{Rob}$ or median

4) $2\,s_{target}$ % = the total target standard deviation used in evaluation of performance at 95 % confidence interval, (in calculating of z score the percent 15 % or 20 % of the assigned value is used as a standard deviation)

ANNEX 3. COMMENTS SENT BY THE PARTICIPANTS

Comments on the reported results:

Lab 1: Sulphur removed with TBA according to ISO 10382. Removal of sulphur was carried out prior to Al_2O_3 clean-up.

Lab 4: The results given to benzo(b)fluoranthene indicates the sum of benzo(b)fluoranthene and benzo(k)fluoranthene

Lab 7: I excepted that benzoperfluoranthene was benzo(ghl) fluoranthene

Lab 9: The laboratory had put some results in the wrong place – the organizer has corrected the results in the data file.

Lab 10: The laboratory had put some results in the wrong place – the organizer has corrected the results in the data file.

Lab 11: The laboratory does not measure benzo(b)fluoranthene and benzo(k)fluoranthene separately, the result of benzo(b)fluoranthene

Lab 14 The laboratory does not measure benzo(b)fluoranthene and benzo(k)fluoranthene separately, the result was reported as benzo(b)fluoranthene

Lab 15: Acenaphtalene does not fluoresce – not measured

Lab 18: Because of the high content of PAHs in the sample, in extraction has been used too large intake of the sample

Lab 21: Acenaphtalene does not fluoresce – not measured

ANNEX 4. ANALYTICAL METHODS

Lab	Intake, g	Extr.solvent, vol (ml)/time (min)	Extr.method	Separation	Acetone/remove
1	10	25 ml H_2O, 20g NaCl, 50ml acetone, 25 ml hexane	ultrasonic, 2h + shaking 16h	separatory funnel	shaking 2 times with 100 ml H_2O
2	7	acetone 30 ml, 30 min	ultrasonic	centrifuge	
3					
4	20	dichloromethane			
5	2	dichloromethane 20ml	shaking	centrifuge	
6	5	10 ml ethylacetate/cyklohexane during 60 min	shaking	centrifuge	
7	0-5	hexane-acetone-toluene(10+5+1), DCM-acetone(1+1)	ultrasonic, soxhlet, ASE	centrifuge	water extraction
8	~0. 1	20 ml aceton, 10 ml n-hexan	shaking	centrifuge	shaking with dimetylformamide
9	1.0-3.0	ca.200 ml toluene	soxhlet	filtering (Na_2SO_4)	
10	5	8 ml cyclohexane, 15 ml acetone	shaking table		water
11	~19	20 ml acetone, 20 ml pentane			
12	4	n-hexane 30 ml, acetone 50 ml	solid/liquid	centrifuge	evaroration
13	20	200 ml toluene	soxhlet		
14	0.1-0.5	90 ml toluene	soxhlet		rotavapour
15	8	cycloheksane	Dionex ASE 200		
16	2	10ml acetonitrile, 20ml 0,05 m Na-pyrophosphate-dekahydrate, 10ml toluene	shaking	centrifuge	
17	5-20	20 ml toluene	shaking	centrifuge	
18	16-21	120 ml dichlorometane	soxhlet		
19	5	50 ml acetone-hexane	shaking	centrifuge	
20		alkaline methanol with dichloromethane			
21	0.2	acetone/hexane 2590 ml, 24 h (75/25)	Soxhlet		pentane/water 2% H_2SO_4
22	2	acetone/hexane 2590 ml, 24 h (75/25)	Soxhlet		pentane/water 2% H_2SO_4

Lab	GC-columns and dimens.(m/mm/μm)	Carrier gas and ml/min	Injection technig and T °C	Oven-T °C/min
1	HP-5 MS, 30 m, 0,25 mm, 0,25 μm	helium, 1,6 ml/min	splitless, 275° C, 1,5 min	60°/2 min, 25°/min to 160°, 3°/min to 280°, 25°/min to300° 1 min
2	HP-5 MS, 30 m, 0,25 mm, 0,25 μm	helium, 1 ml/min	splittless, 300° C	60°/2 min, 20°/min to 180°, 8°/min to 280° 10 min
3				
4	HP-5 MS, 30 m, 0,25 mm, 0,25 μm	helium, 1 ml/min	splittless, 280° C	40°/1 min, 15°/min to 280°
5	DP-5MS, 30 m, 250 μm, 0,5μm	1 ml/min	pulse spittless 208° C	60°/1 min, 12°/min to 310° 10 min
6	DB 5MS, i:20 m ID:0,18 mm, film:0,18μm	helium, 0,8 ml/min	PVT/injector, 310° C	60°/1 min, 7°/min to 310° 7 min
7	HPLC			
8	varian VF-5 ms 30m 0,25mm ID, 0,25μm film	helium, 1,2 ml/min	automatic autosampler	70°/2 min, 7°/min to 290° 11 min
9	DB-17, 30m, 0,25mm, 0,15μm	helium, 2 ml/min	split 275° C	60°/0,8 min, 35°/min to 160°, 3°/min to 300° 16 min
10	HP-5 MS, 30 m, 0,25 mm, 0,25 μm	helium, 1,3 ml/min	PTV	60°/2 min, 10°/min to 180°, 15°/min to 300°, 30°/min to 340o 3 min
11				
12	HP-1, 50m, 0,32 mm, 0,52μm	nitrogen 2 ml/min	split	90°/2 min, 5°/min to 300° 8 min
13	DB-5 30m, 0,25 mm, 0,2μm	helium, 1 ml/mil	split	90°/2 min, 10°/min to 325° 10 min
14	HP-5 MS, 30 m, 0,25 mm, 0,25 μm	helium, 1 ml/mil	split	50°/6 min, 10°/min to 300° 20 min
15	HPLC			
16	ZB-5, 60m, 0,25mm, 0,25μm	helium, 0,7 ml/min	split	80°/2 min, 25°/min to 285°, 1°/min to 310°
17	NB 1701, 25m, 0,32mm, 0,1 μm (GC-FID)	helium, 5,7 ml/min	split	100°, 6°/min to 280° 1 min
18	DB-5 30m, 0,32mm, 0,25μm	helium, 1,3 ml/min	split	100°/2 min, 10°/min to 300° 40 min
19	HP-5 MS, 30 m, 0,25 mm, 0,25 μm	1,3 ml/min	split	60°/1 min, 15°/min to 170°, 3°/min to 300°, 10°/min to325°
20				
21	Chromspher PAH, 5 μm C18 packed HPLC	Acetonitrile/water 50:50, 1 ml/min		28°
22	VF-5ms, 30 m x 0,25mmx0,25 μm	helium, i ml/min	splitless 290°C	50°/1 min, 26°/min to 120°, 5°/min to 300°, 300° 20 min

Lab	Cal.range	No of standards	Internal standard	Calc. of tot-PAH	References
1	0.1-2.5 mg/l	7	acenaphtene-d10, chrysene-d12, naphtalene-d8, phenantrene-d12, perylene-d12	Sum of 16 PAHs	ISO/DIS 18287, modified
2	1-25 µg/ml	4	d10-fenantreeni	the 16 reported PAHs+ benzopyrene	Nordtest TR 329 and ISO/DIS 18287
3					Nordtest
4	0.1 - >10 mg/l	4	Naph-d8, phen-d10, fluoranthan-d10, penzopyren-d12, dibenzanthacen-d14		
5	0.01-1.0 mg/l in extract	3	Naph-d8, phen-d10, fluranthan-d10, penzopyren-d12, dibenzanthacen-d14	sum US EPA 16	"In house" method
6	0.03-5 mg/kg	3	Naftalene-d8, pyrene d-10, perylene-d12		
7	10-300 ng/ml	5			DIONEX Application Note 313 and Analytica Chim. Acta 383(1999)263
8	0.125-1 µg/ml	4	pyrene d-10	sum of 16 PAH	SNV Report nr 3829
9	0.6-3,4 µg/ml	4	b,b-binaftyyli ja indeno (1,2,3,cd) fluorantene	sum of invidual compounds	"In house" method
10	0.25-11.3 ng/ml	4	pyrene d-10 and d12-perylene	addition of each separate PAH	ISO/DIS 16703, modified
11	0.008-3.2 mg/kg		phenantrene-d10, fluorantene-d10, penzepyrene-d12	sum of individual compounds	SNV Report nr 4199
12	0.4-8 mg/l	4	3,6 dimethylphenanthrene, 2,2 binaphtyl	sum of individual compounds	"In house" method
13	0.5-100 mg/kg	7	1,1 binaphthyl	sum of 24 PAH-compounds	
14	0.200 µg/l	3	D10-pyrene		
15		15			
16	50-2000µg/l		pyrene-d10, 2,2-binaftyl, indeno(1,2,3,c,d)fluorantene	sum of 16 PAH	Nordtest TR 329
17		3	1,3,5-trifenylbenzene		Nordtest TR 329
18		16	d10-antrasene	sum of invidual compounds	"In house" method
19	10-10000ng/ml	4	asenaphtalene-d10, phenantrene-d10, crysene-d12, perylene-d12	sum of invidual compounds	Nordtest TR 329
20			d-PAH internal standards		
21	0.01-25 ng/g	5	b,b-binaphthyl	sum of analyzed PAHs	
22		1	naph-d8, phen-d10, fluoranth-d10, benzopyren-d12, benzoper-d12, acepnaph-d18, pyr-d10	sum of analyzed PAHs	

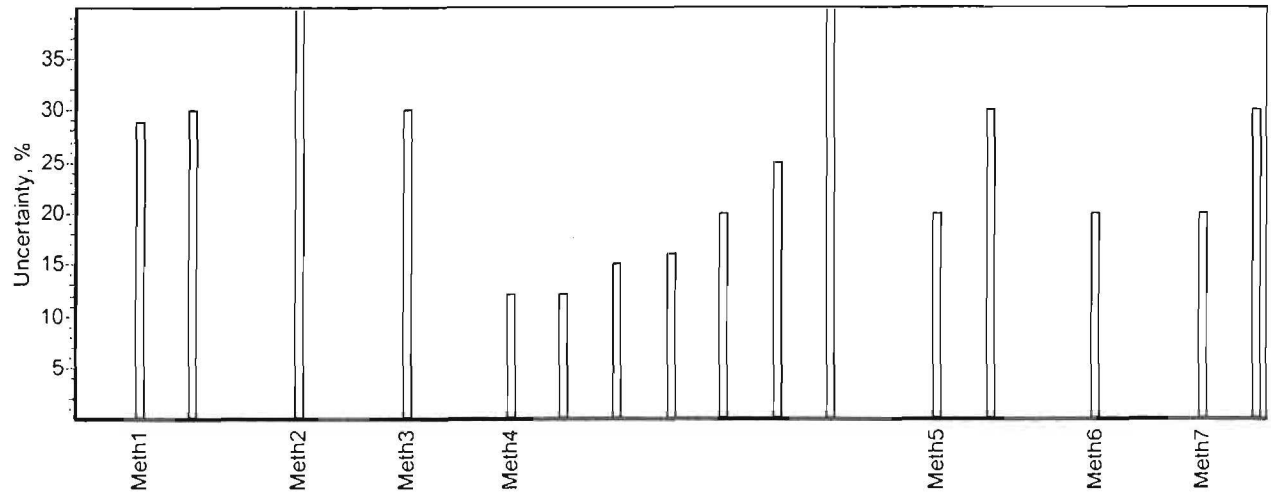
ANNEX 5. RESULTS REPORTED BY THE LABORATORIES

Analyte	Sample	Unit	1				2				3				4			
A-naphthy	P	mg/kg	4,27	3,62	4,78	1	12.3	12.1	12.1	1	9,318	9	9,266	1	12,376	12,234		1
Acenaph	P	mg/kg	1,79	1,69	1,73	1	2.0	2.0	2.0	1	1,768	1,835	1,834	1	2,992	2,958		1
Anthrac	P	mg/kg	5,65	5,46	5,68	1	11.8	11.8	11.8	1	6,278	6,326	6,345	1	10,691	10,412		1
Benzo-A-P	P	mg/kg	13,7	13,6	14,6	1	14.7	14.5	14.3	1	15,058	14,727	14,46	1	16,566	16,761		1
Benzo-ant	P	mg/kg	23,1	22,6	23,2	1	35.5	34.8	34.6	1	28,246	28,09	27,462	1	26,331	26,470		1
Benzo-B-F	P	mg/kg	16,6	16,1	17,0	1	20.8	19.1	19.2	1	24,102	22,164	22,059	1	47,044	46,345		1
Benzo-K-F	P	mg/kg	15,9	15,1	15,6	1	24.4	23.9	23.7	1	21,81	22,302	21,382	1				
Benzo-per	P	mg/kg	14,1	12,7	13,8	1	18.9	18.5	18.2	1	13,226	12,461	10,956	1	19,888	19,147		1
Chrysene	P	mg/kg	27,9	26,4	27,0	1	27.6	27.1	26.8	1	35,21	34,491	33,825	1	34,252	35,103		1
Dibenz-ah	P	mg/kg	3,68	3,64	3,87	1	3.5	3.4	3.3	1	1,596	1,726	1,532	1	3,469	3,643		1
Fluoran	P	mg/kg	69,1	71,5	70,0	1	91.5	89.7	88.2	1	87,358	84,25	80,308	1	89,077	89,290		1
Fluorene	P	mg/kg	7,38	7,49	7,33	1	9.6	9.0	8.7	1	7,442	7,712	7,666	1	11,918	11,715		1
Indeno	P	mg/kg	14,9	13,9	15,3	1	18.6	16.7	16.6	1	13,506	12,496	11,709	1	18,875	18,022		1
Napht	P	mg/kg	4,74	4,49	4,83	1	4.2	4.2	4.2	1	3,388	3,322	3,23	1	8,602	8,406		1
Phenan	P	mg/kg	92,0	98,8	94,4	1	120	118	115	1	111,77	110,77	109,27	1	135,87	133,97		1
Pyrene	P	mg/kg	71,1	72,0	70,9	1	92.5	91.5	90.2	1	86,272	82,834	80,616	1	88,490	89,017		1
tot-PAH	P	mg/kg	386	389	390	1	526	514	506	1	466,35	454,50	441,92	1				
Analyte	Sample	Unit	5				6				7				9			
A-naphthy	P	mg/kg	10,383	10,519	10,953	1	7,6	7,5	7,4	1					3,34	3,12	3,39	1
Acenaph	P	mg/kg	2,227	2,307	2,274	1	2,2	2,1	2,2	1					1,45	1,31	1,27	1
Anthrac	P	mg/kg	9,492	8,151	9,535	1	7,9	7,6	7,9	1	3,21	4,23	4,42	3	11,6	10,1	10,0	1
Benzo-A-P	P	mg/kg	12,718	12,694	12,943	1	13,1	12,9	13,7	1	15,2	18,6	19,8	3	12,0	11,9	11,9	1
Benzo-ant	P	mg/kg	22,618	22,170	22,542	1	22,4	24,5	23,7	1	28,6	32,6	35,4	3	21,8	21,7	21,2	1
Benzo-B-F	P	mg/kg	23,575	23,489	24,286	1	26,8	26,6	26,9	1	19,4	21,3	22,5	3	12,9	12,8	12,9	1
Benzo-K-F	P	mg/kg	11,094	11,530	11,429	1	9,6	10,6	10,4	1	13,4	15,3	16,8	3	8,99	8,76	8,95	1
Benzo-per	P	mg/kg	14,721	14,537	14,894	1	15,1	14,1	13,1	1	13,5	16,3	16,8	3	15,0	13,8	13,9	1
Chrysene	P	mg/kg	28,901	27,368	28,394	1	27,8	30,0	29,9	1	29,2	33,1	36,3	3	18,8	17,9	17,9	1
Dibenz-ah	P	mg/kg	3,355	3,377	3,403	1	3,1	3,0	3,3	1	3,40	4,45	3,91	3	1,94	1,82	1,81	1
Fluoran	P	mg/kg	67,521	64,265	67,280	1	82,9	84,1	89,2	1	69,7	78,3	84,9	3	131	126	123	1
Fluorene	P	mg/kg	8,487	8,414	8,601	1	9,5	9,5	10,0	1					5,42	5,16	5,01	1
Indeno	P	mg/kg	12,653	12,498	12,860	1	16,3	17,0	16,4	1	14,5	16,4	18,4	3	14,4	13,7	14,1	1
Napht	P	mg/kg	7,292	7,231	7,479	1	4,8	5,1	4,6	1					3,65	4,14	3,42	1
Phenan	P	mg/kg	85,908	83,383	87,082	1	118	121	132	1	93,5	98,6	114	3	162	159	156	1
Pyrene	P	mg/kg	65,390	64,531	66,914	1	86,7	90,5	97,1	1	76,5	87,7	92,6	3	135	129	123	1
tot-PAH	P	mg/kg	386,33	376,35	390,87	1	454	466	489	1					559	540	528	1
Analyte	Sample	Unit	10				11				12				13			
A-naphthy	P	mg/kg	9,10	8,74	8,94	1	9,10	9,14	8,73	1					10,5	9,69	9,56	1
Acenaph	P	mg/kg	1,85	1,81	1,79	1	1,64	1,61	1,60	1					2,24	2,01	1,99	1
Anthrac	P	mg/kg	8,27	8,04	7,96	1	13,6	14,7	12,6	1					12,6	12,7	13,0	1
Benzo-A-P	P	mg/kg	15,4	15,3	16,7	1	11,8	11,7	11,3	1	16,0	16,6	19,9	2	18,9	18,0	17,8	1
Benzo-ant	P	mg/kg	32,0	31,2	32,1	1	23,7	23,8	22,3	1					39,6	37,5	38,4	1
Benzo-B-F	P	mg/kg	32,3	32,7	35,5	1				1	35,7	38,5	37,2	2	19,9	18,5	18,3	1
Benzo-K-F	P	mg/kg	14,4	15,6	15,3	1					14,4	15,2	16,2	2	29,6	30,2	28,9	1
Benzo-per	P	mg/kg	18,2	18,1	19,6	1	11,7	11,5	11,1	1	19,3	20,1	20,2	2	25,5	23,8	20,9	1
Chrysene	P	mg/kg	42,2	41,0	41,8	1	28,9	29,0	27,6	1					41,2	40,1	40,5	1
Dibenz-ah	P	mg/kg	3,87	3,82	4,65	1	2,61	2,36	2,12	1					6,92	6,20	6,47	1
Fluoran	P	mg/kg	103	102	103	1	79,5	78,8	75,4	1	151	170	160	2	179	168	154	1
Fluorene	P	mg/kg	9,56	9,39	9,29	1	8,22	8,35	8,26	1					14,1	12,8	12,6	1
Indeno	P	mg/kg	17,4	17,2	18,6	1	10,4	10,2	10,4	1	17,3	18,0	12,9	2	21,6	20,2	18,5	1
Napht	P	mg/kg	5,62	5,68	5,58	1	3,65	3,56	3,45	1					7,93	7,12	7,16	1
Phenan	P	mg/kg	138	134	135	1	109	108	104	1					216	198	202	1
Pyrene	P	mg/kg	105	104	104	1	78,1	77,3	73,2	1					169	159	159	1
tot-PAH	P	mg/kg	556	549	560	1	424	422	403	1	304	332	320	2	888	831	806	1
Analyte	Sample	Unit	14				15				16				17			
A-naphthy	P	mg/kg	6.30	6,43	5,8	1	ND	ND	ND	3	6,97	6,51	6,80	1	8,5	7,6	12	2
Acenaph	P	mg/kg	2,53	2.21	2,07	1	<3	<3	<3	3	2,76	2,69	2,76	1	8,0	7,4	8,0	2
Anthrac	P	mg/kg	5.68	5,48	5,90	1	4,19	4,00	4,19	3	6,94	6,14	7,05	1	9,0	14	9,3	2
Benzo-A-P	P	mg/kg	10,7	10,0	11,9	1	16,7	16,2	16,7	3	14,0	15,2	13,9	1	27	24	22	2
Benzo-ant	P	mg/kg	17,0	17,9	15,5	1	25,3	24,8	25,6	3	27,7	29,1	32,9	1	45	43	37	2
Benzo-B-F	P	mg/kg	27,0	26,6	23,6	1	21,5	21,0	21,9	3	21,2	20,0	23,5	1	35	35	29	2
Benzo-K-F	P	mg/kg					12,1	11,8	12,3	3	11,2	11,00	10,8	1	37	34	29	2
Benzo-per	P	mg/kg	12,5	10,3	11,7	1	23,1	19,8	23,6	3	15,5	19,2	16,4	1	31	34	27	2
Chrysene	P	mg/kg	23,5	24,8	21,2	1	30,9	30,3	31,2	3	28,7	30,1	35,6	1	68	62	56	2
Dibenz-ah	P	mg/kg	2,83	3,07	2,97	1	2,51	2,46	2,59	3	2,16	2,45	2,21	1	13	11	10	2
Fluoran	P	mg/kg	87,5	90,5	87,8	1	93,3	91,4	94,3	3	83,1	86,5	93,6	1	146	141	122	2
Fluorene	P	mg/kg	8,12	8,71	8,50	1	7,88	7,62	7,78	3	9,92	9,58	9,90	1	17	16	14	2
Indeno	P	mg/kg	11,8	10,5	12,5	1	21,0	14,3	21,9	3	15,9	19,3	16,7	1	26	31	24	2
Napht	P	mg/kg	13,2	12,4	11,7	1	ND	ND	ND	3	7,60	7,31	7,74	1	3,6	3,0	5,1	2
Phenan	P	mg/kg	112	115	109	1	128	125	129	3	125	122	130	1	208	191	172	2

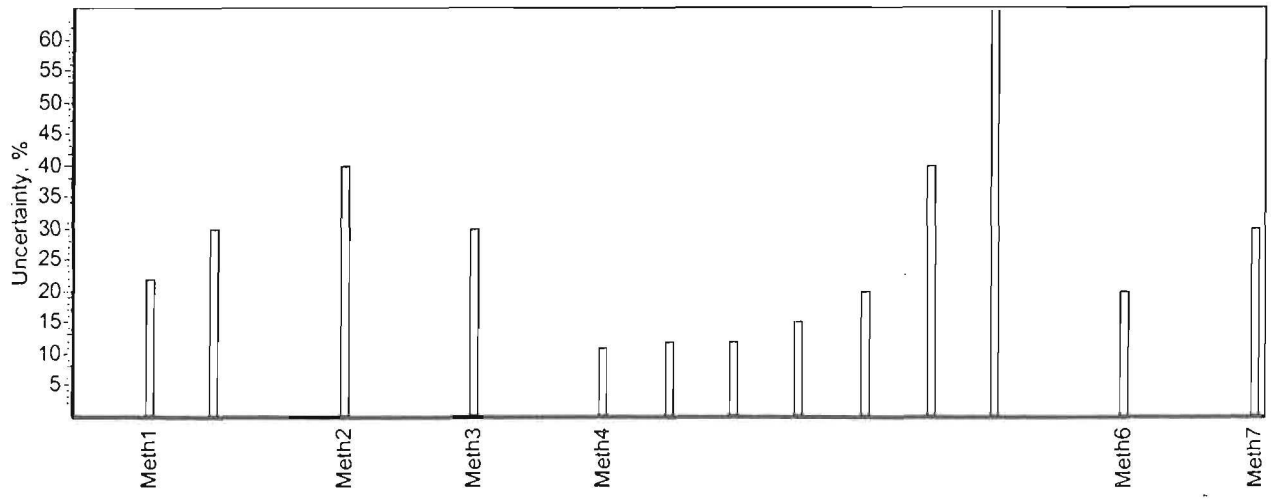
Analyte	Sample	Unit	14				15				16				17			
Pyrene	P	mg/kg	76,2	77,5	72,5	1	104	101	104	3	83,7	87,3	95,5	1	143	134	118	2
tot-PAH	P	mg/kg					492	471	497	3	462	474	506	1				
Analyte	Sample	Unit	18				19				20				21			
A-naphthy	P	mg/kg	8,97	7,53	9,82	1	9,92	9,81	9,26	1	4,02			1				
Acenaph	P	mg/kg	1,90	1,35	1,62	1	2,06	2,16	1,95	1	1,41			1	1,3	2,1	2,1	3
Anthrac	P	mg/kg	10,9	9,42	11,1	1	7,23	6,94	6,21	1	7,09			1	4,2	4,9	4,6	3
Benzo-A-P	P	mg/kg	7,52	6,63	10,4	1	13,4	13,8	12,98	1	15,5			1	20	21	19	3
Benzo-ant	P	mg/kg					24,9	22,2	20,9	1	26,3			1	33	37	33	3
Benzo-B-F	P	mg/kg	21,5	19,4	29,5	1	19,8	18,2	17,7	1	21,5			1	23	26	23	3
Benzo-K-F	P	mg/kg					22,6	20,5	20,0	1	18,1			1	16	17	15	3
Benzo-per	P	mg/kg	8,24	7,17	10,6	1	18,3	18,2	16,2	1	14,3			1	24	25	22	3
Chrysene	P	mg/kg	37,1	37,1	48,1	1	33,3	30,8	29,0	1	32,6			1	37	41	37	3
Dibenz-ah	P	mg/kg	1,74	1,49	2,21	1	3,6	3,6	3,18	1	3,37			1	3,8	4,0	3,5	3
Fluoran	P	mg/kg	88,6	90,5	89,3	1	89,2	84,9	80,22	1	66,8			1	100	120	110	3
Fluorene	P	mg/kg	7,73	5,61	6,43	1	9,73	9,58	8,70	1	5,69			1	4,9	6,2	6,5	3
Indeno	P	mg/kg	6,30	5,45	8,12	1	17,0	17,8	15,72	1	16,1			1	22	23	20	3
Napht	P	mg/kg	4,50	3,62	4,10	1	7,47	7,89	7,23	1	7,91			1	3,2	5,2	5,2	3
Phenan	P	mg/kg	110,2	86,2	92,6	1	99,3	97,3	94,8	1	80,2			1	100	130	110	3
Pyrene	P	mg/kg	68,5	65,3	73,1	1	88,5	82,5	77,9	1	65,0			1	100	110	100	3
tot-PAH	P	mg/kg	384	347	397	1	466,3	446,2	422,0	1	468			1	490	570	510	3
Analyte	Sample	Unit	22															
A-naphthy	P	mg/kg	1,5	2,4	2,4	1												
Acenaph	P	mg/kg	1,4	2,3	2,5	1												
Anthrac	P	mg/kg	4,2	6,2	6,1	1												
Benzo-A-P	P	mg/kg	20	19	20	1												
Benzo-ant	P	mg/kg	53	57	61	1												
Benzo-B-F	P	mg/kg	41	42	42	1												
Benzo-K-F	P	mg/kg	17	16	16	1												
Benzo-per	P	mg/kg	21	20	20	1												
Chrysene	P	mg/kg	54	50	55	1												
Dibenz-ah	P	mg/kg	4,2	4,2	4,3	1												
Fluoran	P	mg/kg	110	110	100	1												
Fluorene	P	mg/kg	6,6	9,5	10	1												
Indeno	P	mg/kg	28	28	28	1												
Napht	P	mg/kg	4,9	7,7	7,7	1												
Phenan	P	mg/kg	120	160	170	1												
Pyrene	P	mg/kg	93	100	110	1												
tot-PAH	P	mg/kg	580	630	660	1												

ANNEX 6. ESTIMATION OF METHOD UNCERTAINTIES

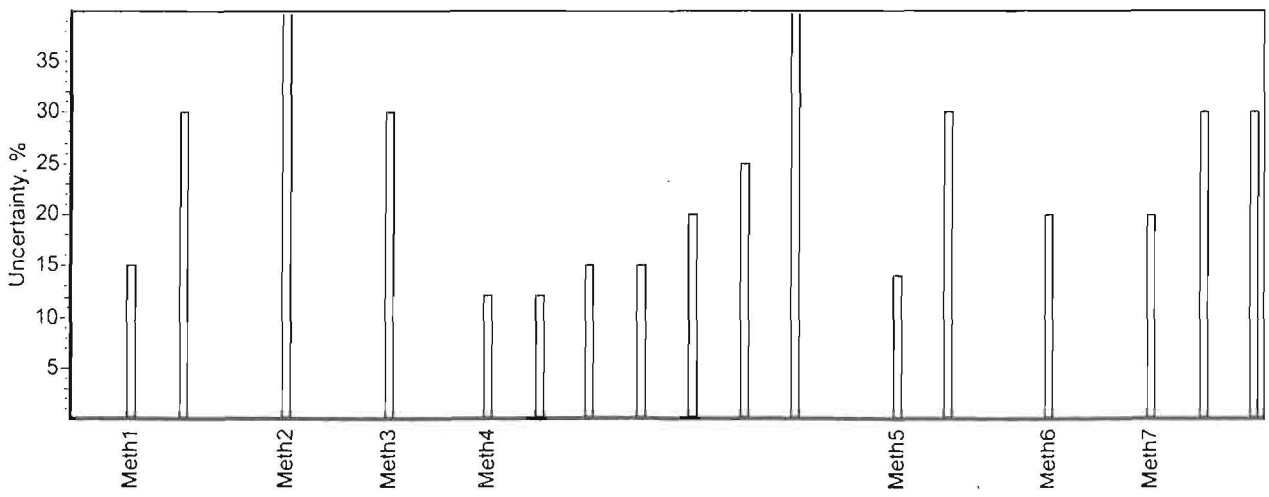
Analyytti *(Analyte)* **Acenaph** Näyte *(Sample)* P



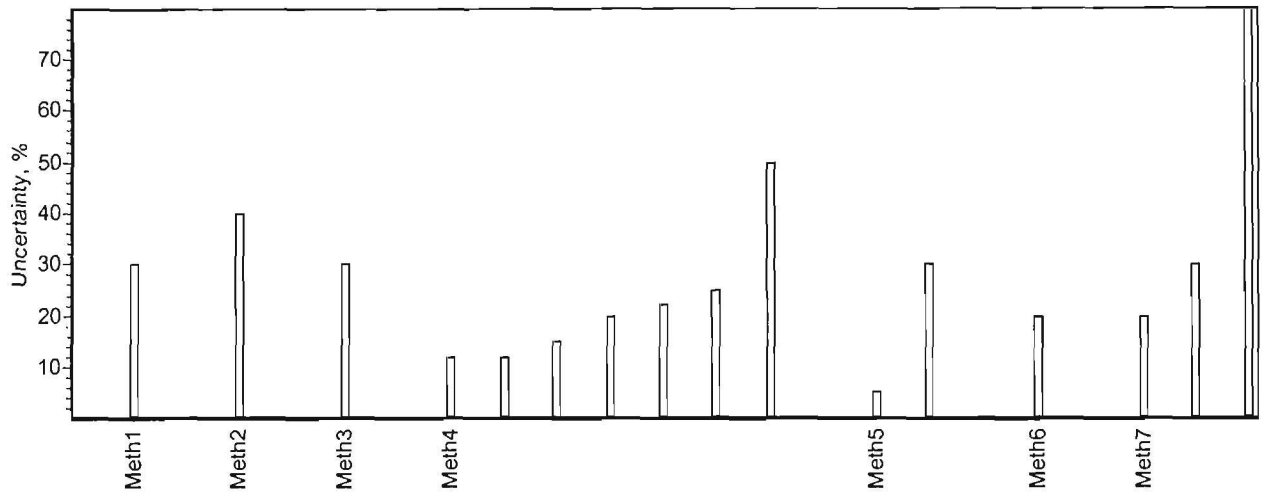
Analyytti *(Analyte)* **A-naphthy** Näyte *(Sample)* P



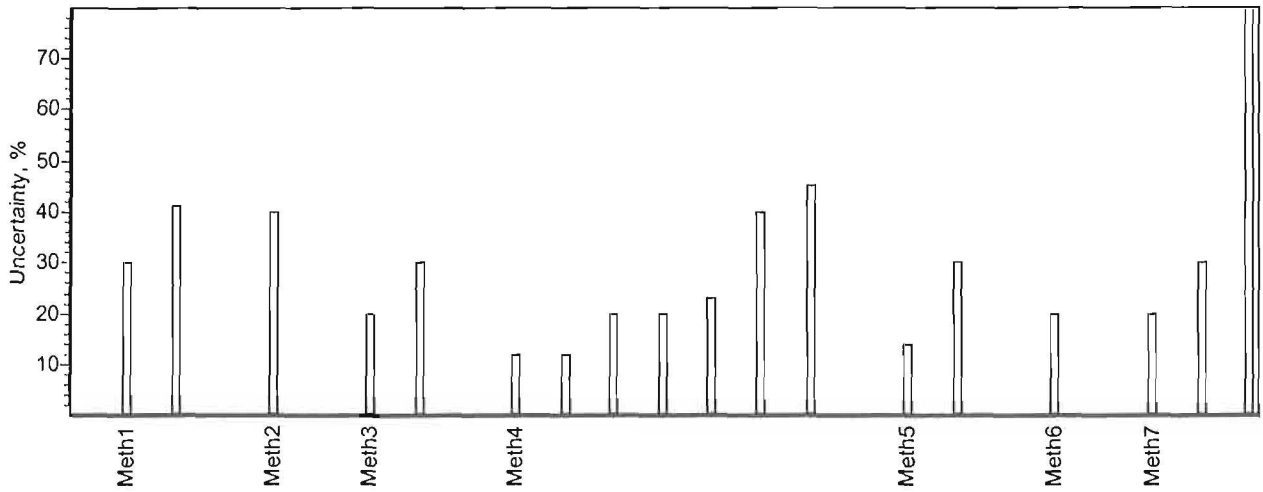
Analyytti *(Analyte)* **Anthrac** Näyte *(Sample)* P



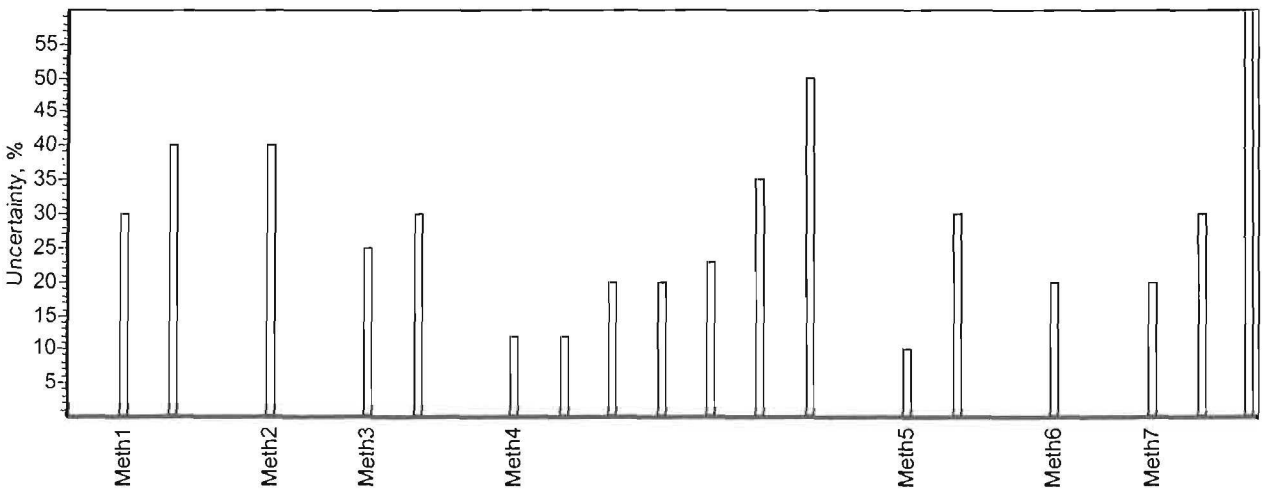
Analyytti *(Analyte)* **Benzo-ant** Näyte *(Sample)* P



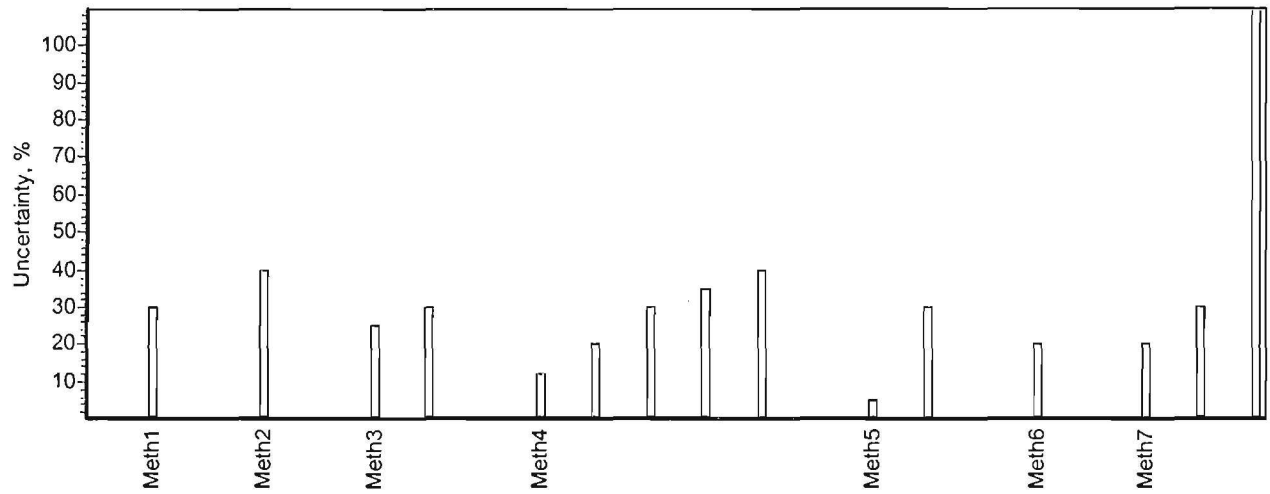
Analyytti *(Analyte)* **Benzo-A-P** Näyte *(Sample)* P



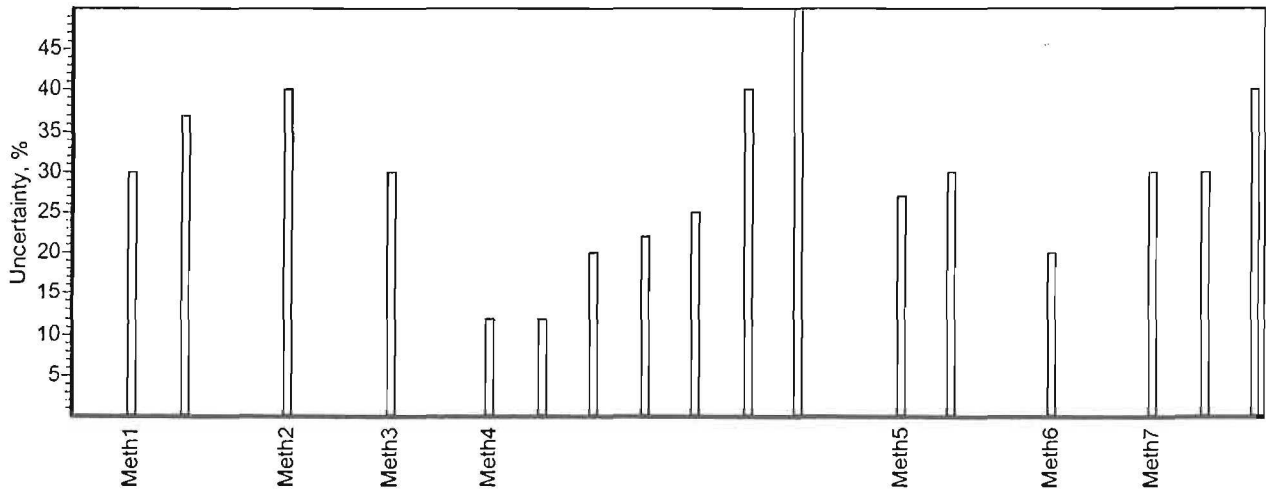
Analyytti *(Analyte)* **Benzo-B-F** Näyte *(Sample)* P



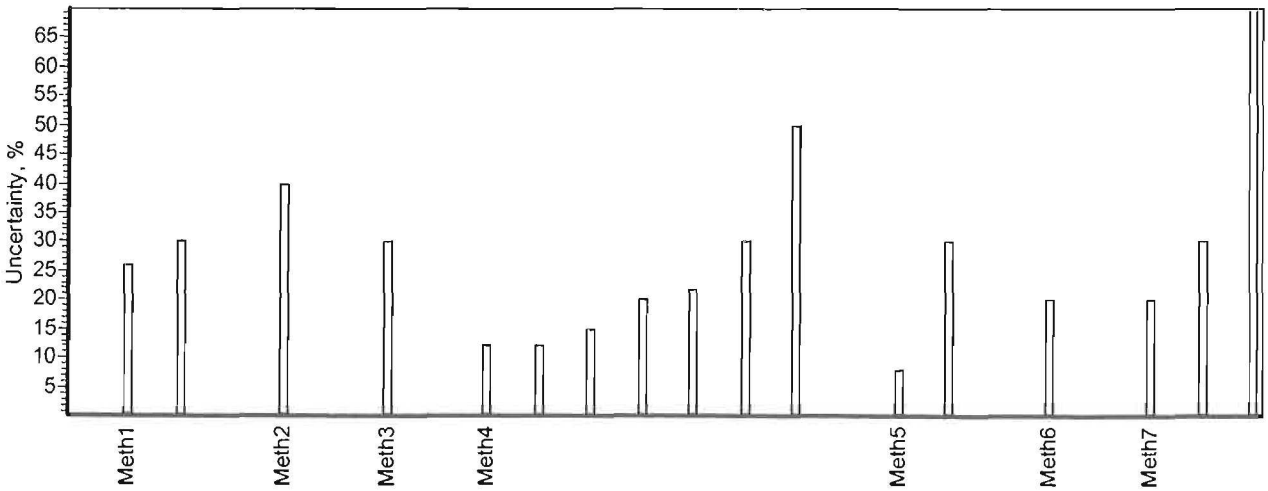
Analyytti *(Analyte)* **Benzo-K-F** Näyte *(Sample)* P



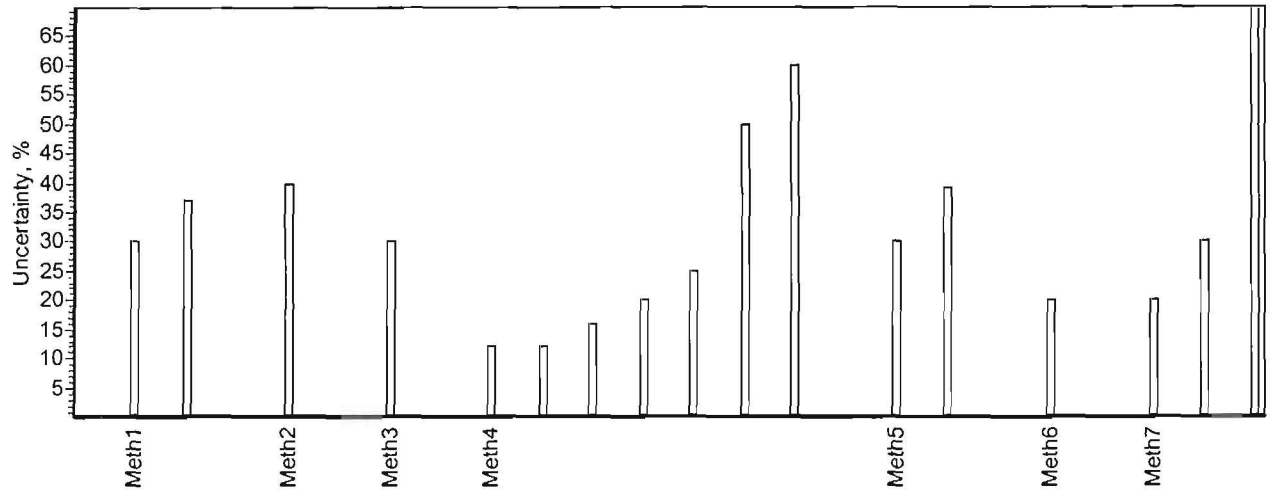
Analyytti *(Analyte)* **Benzo-per** Näyte *(Sample)* P



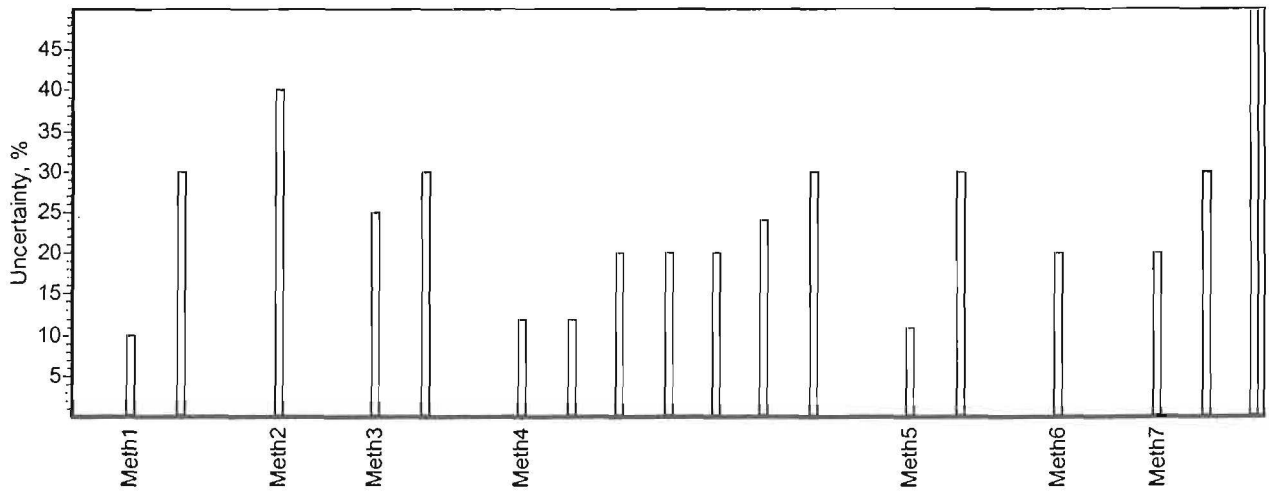
Analyytti *(Analyte)* **Chrysene** Näyte *(Sample)* P



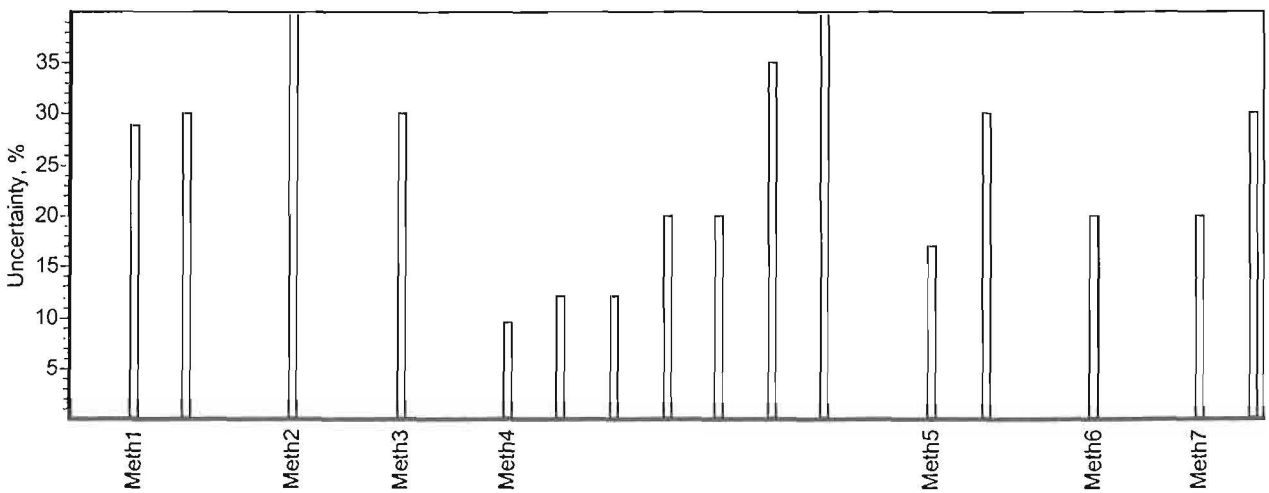
Analyytti *(Analyte)* **Dibenz-ah** Näyte *(Sample)* P



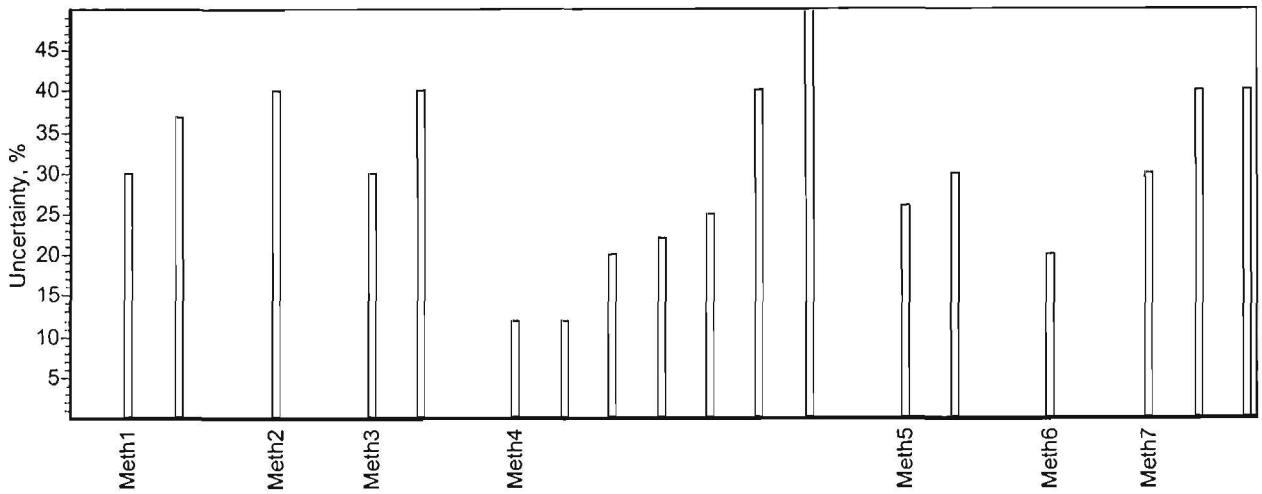
Analyytti *(Analyte)* **Fluoran** Näyte *(Sample)* P



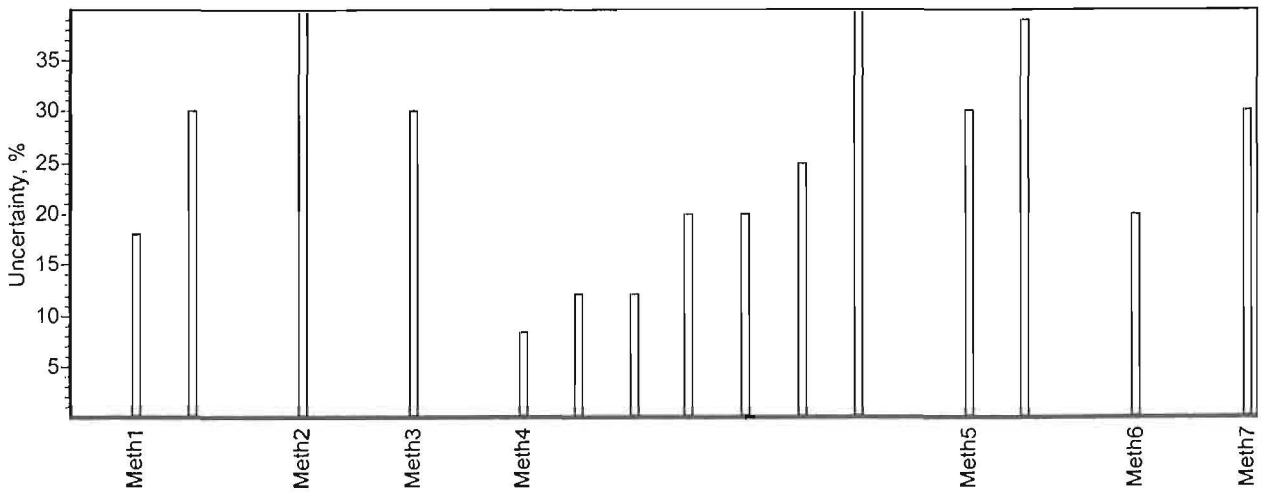
Analyytti *(Analyte)* **Fluorene** Näyte *(Sample)* P



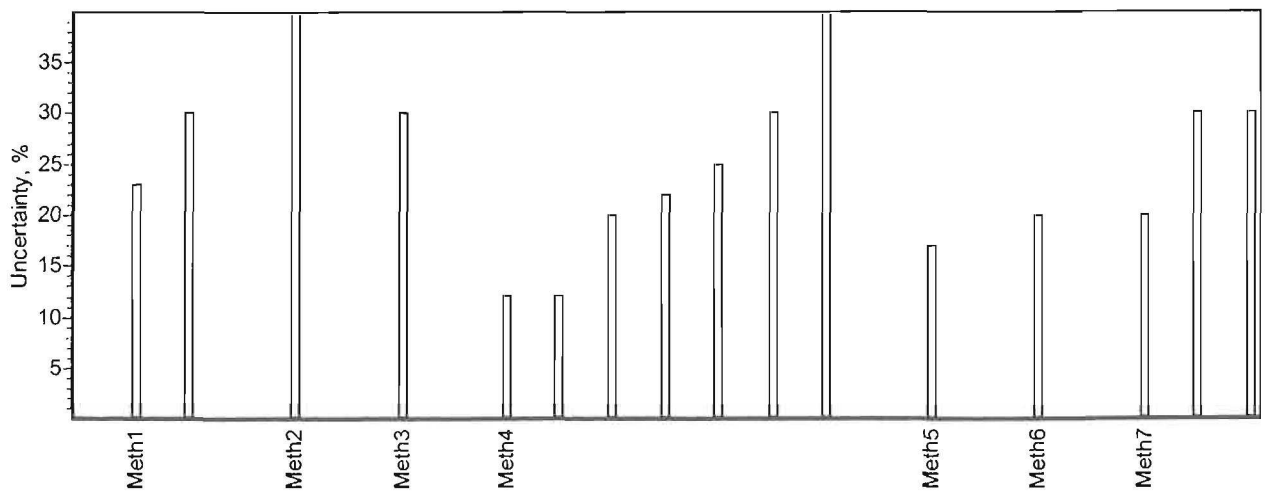
Analyytti *(Analyte)* **Indeno** Näyte *(Sample)* P

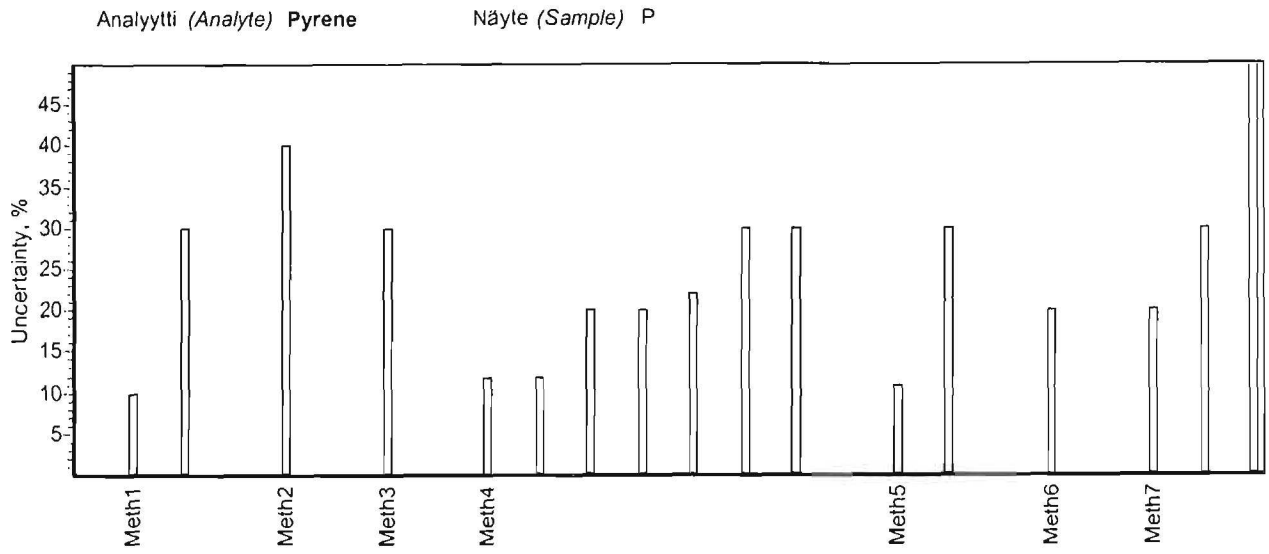


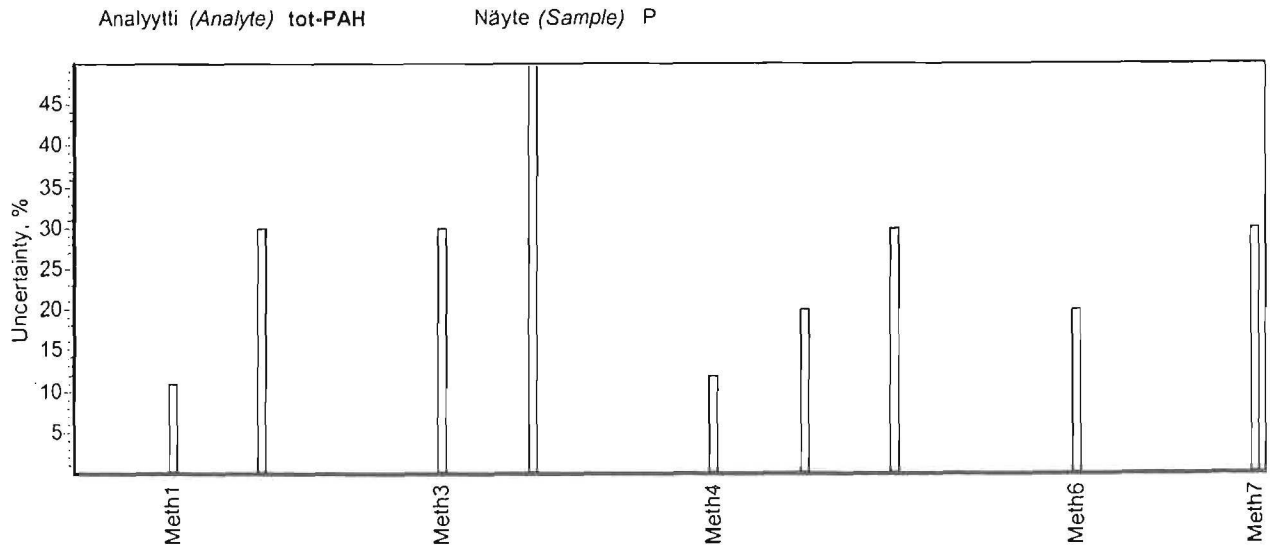
Analyytti *(Analyte)* **Napht** Näyte *(Sample)* P



Analyytti *(Analyte)* **Phenan** Näyte *(Sample)* P



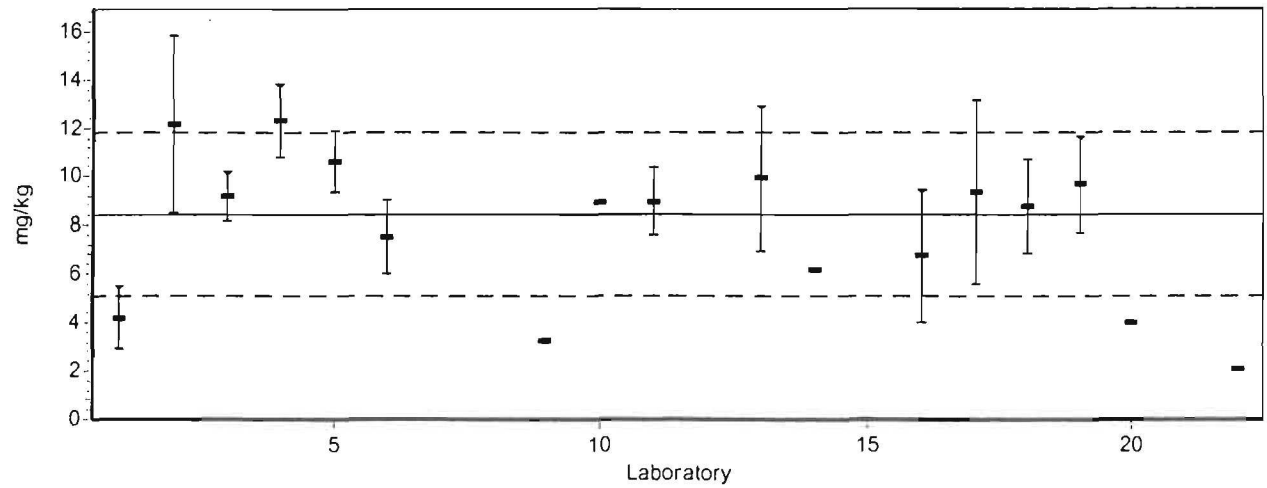




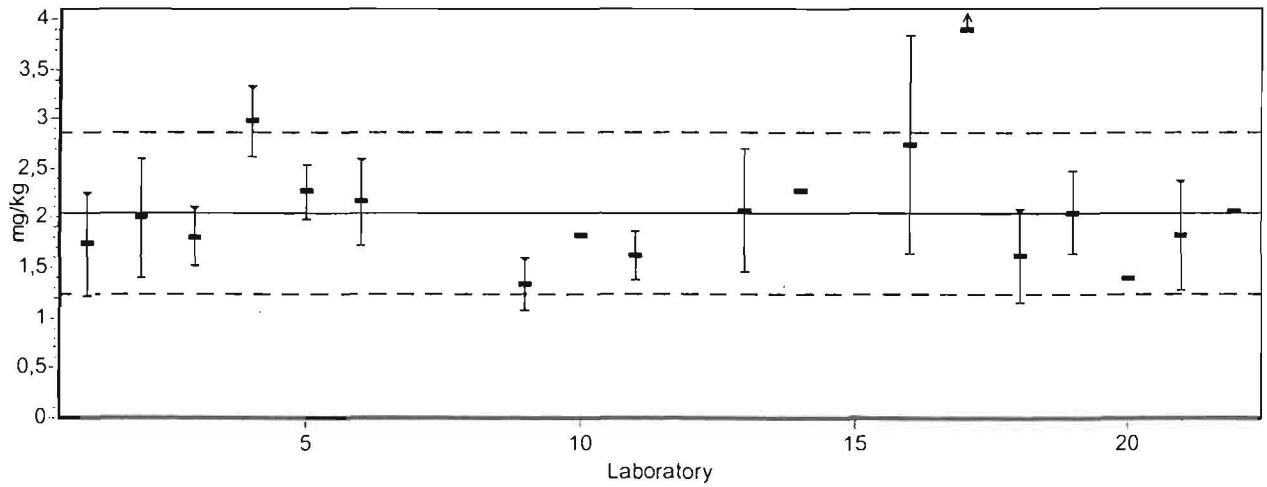
Meth 1: using the variation of the results in X chart (for artificial samples)
Meth 2: using the variation of the results in X chart and the variation of the replicates (r %- or R-chart)
Meth 3: using the variation of the data obtained in analysis of CRM
Meth 4: using the data obtained in method validation (and IQC)
Meth 5: using the EURACHEM- Guide "Quantifying Uncertainty in Analytical measurements"
Meth 6: adapting the EURACHEM- Guide "Quantifying Uncertainty in Analytical measurements"
Meth 7: Other procedure

ANNEX 7. RESULTS AND THEIR UNCERTANTIES

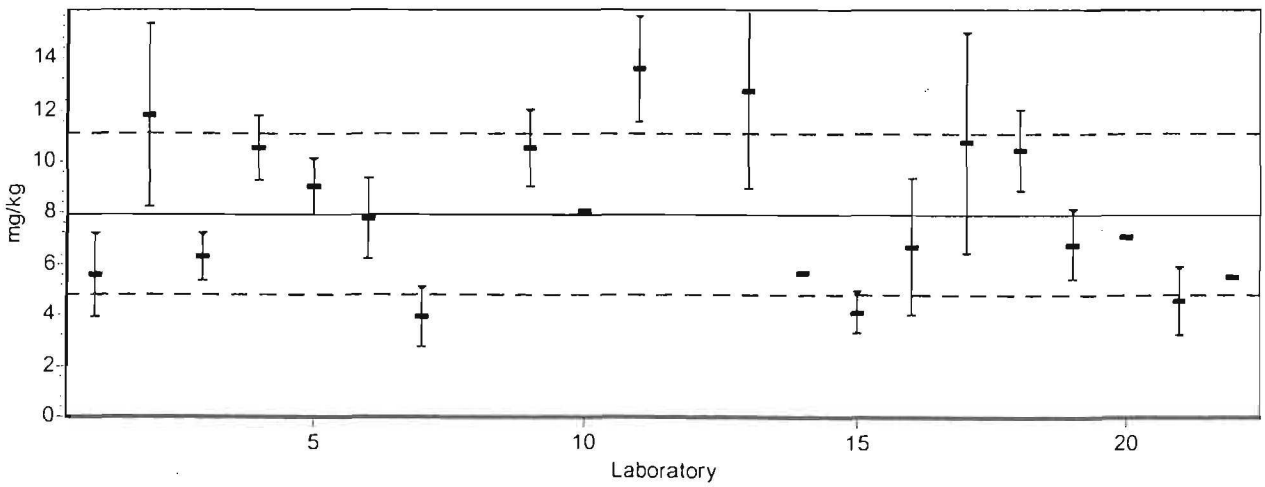
Analyytti *(Analyte)* **A-naphthy** Näyte *(Sample)* P



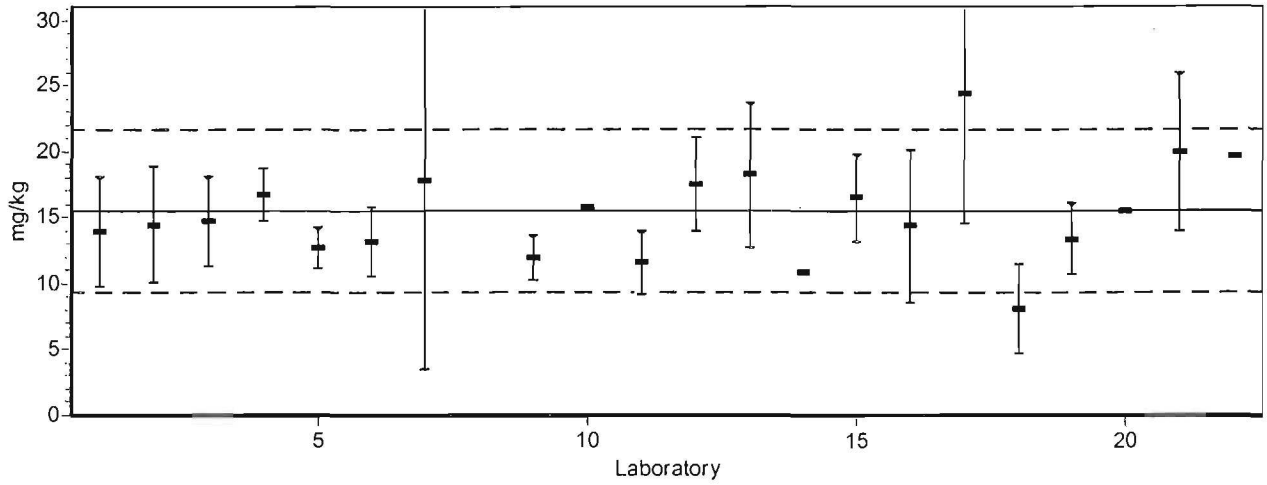
Analyytti *(Analyte)* **Acenaph** Näyte *(Sample)* P



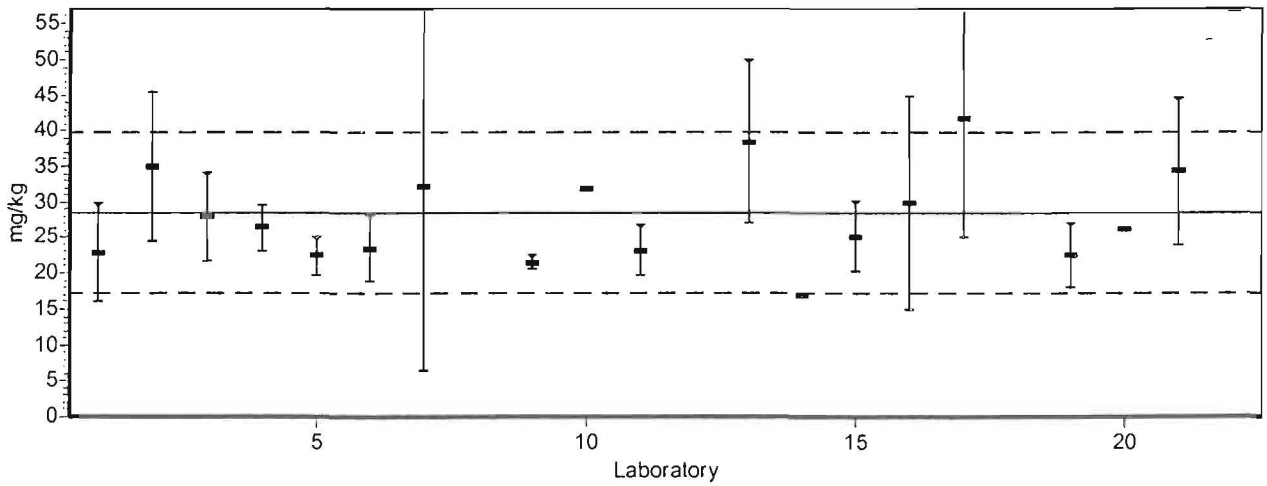
Analyytti *(Analyte)* **Anthrac** Näyte *(Sample)* P



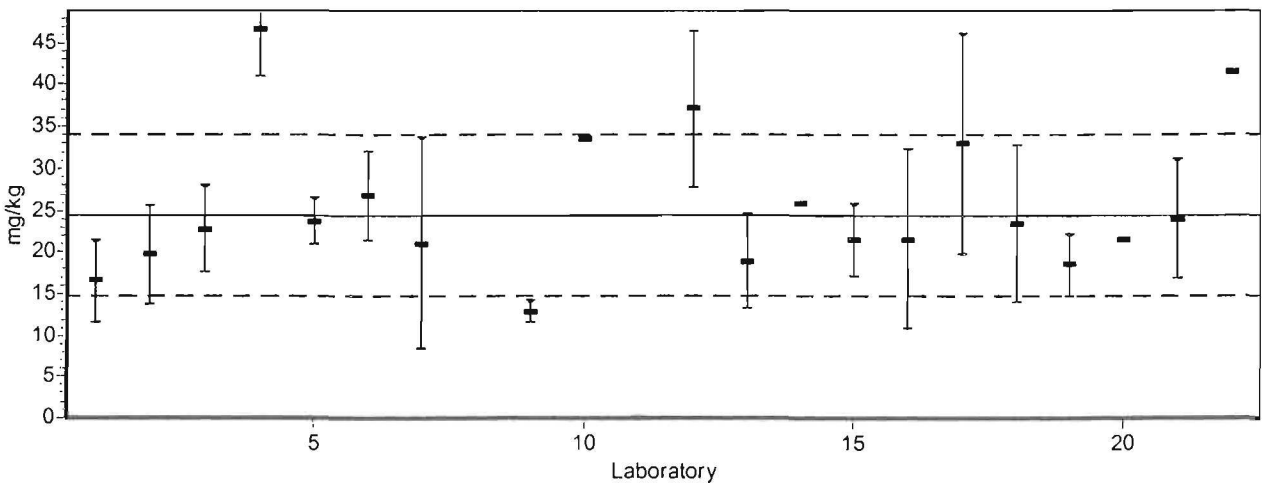
Analyytti *(Analyte)* **Benzo-A-P** Näyte *(Sample)* P



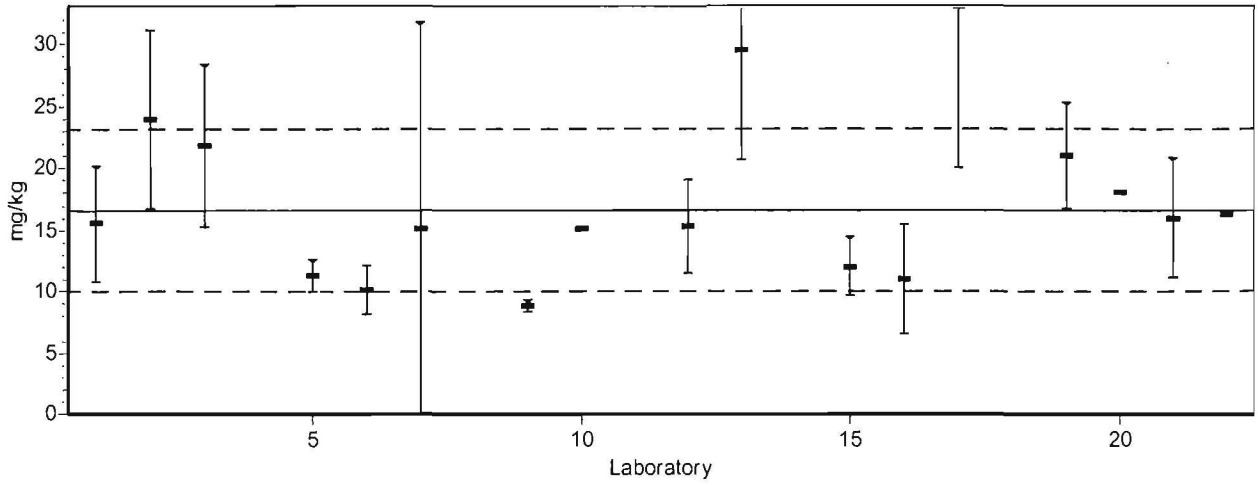
Analyytti *(Analyte)* **Benzo-ant** Näyte *(Sample)* P



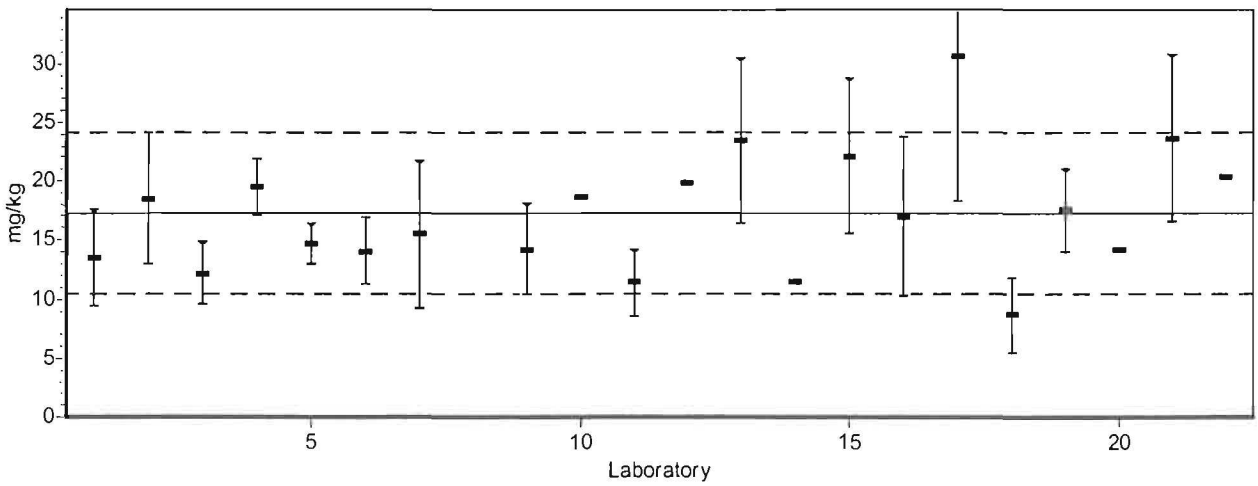
Analyytti *(Analyte)* **Benzo-B-F** Näyte *(Sample)* P



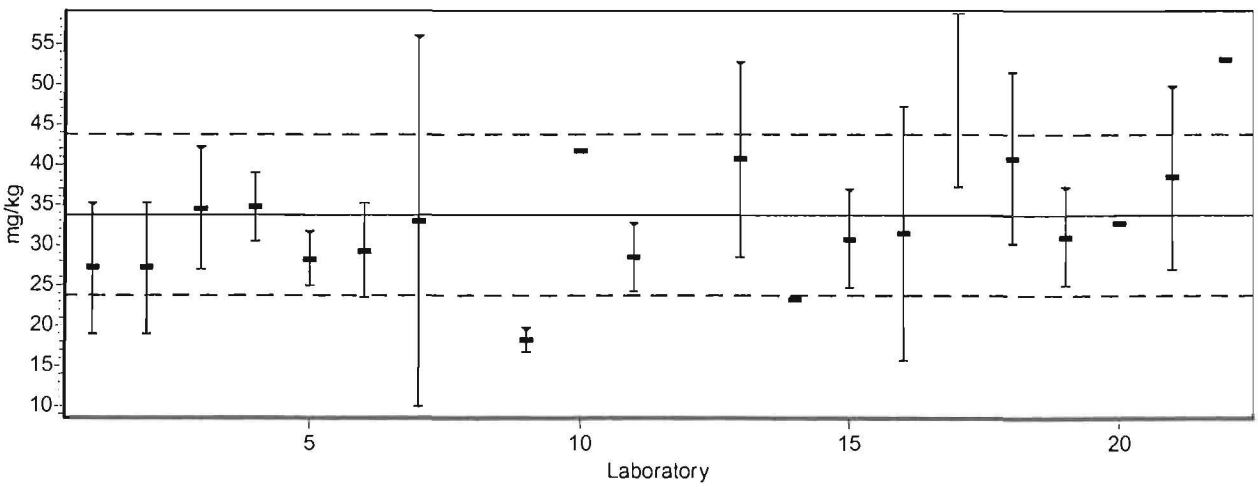
Analyytti *(Analyte)* **Benzo-K-F** Näyte *(Sample)* P



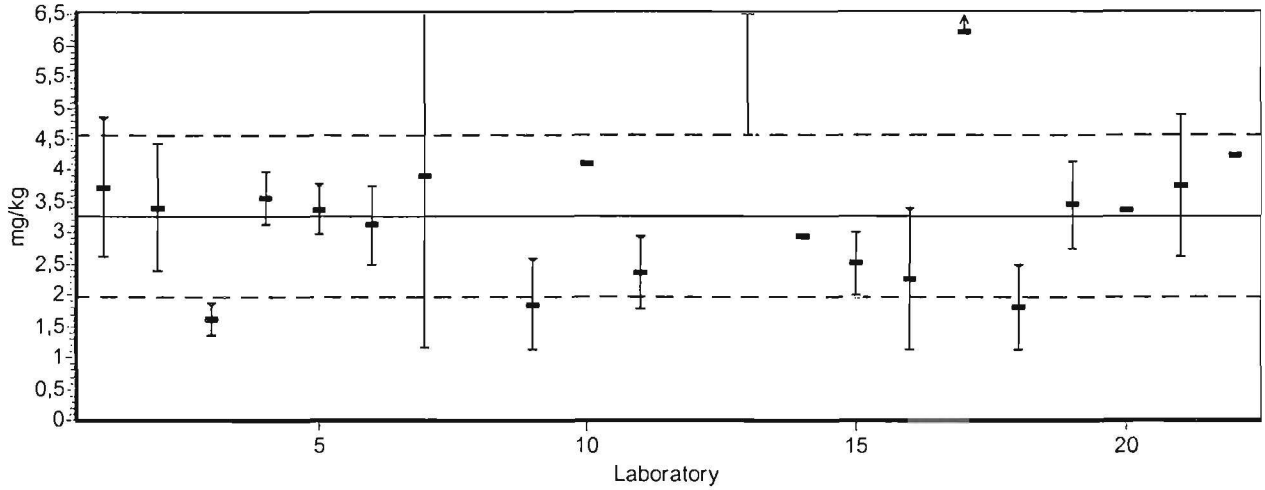
Analyytti *(Analyte)* **Benzo-per** Näyte *(Sample)* P



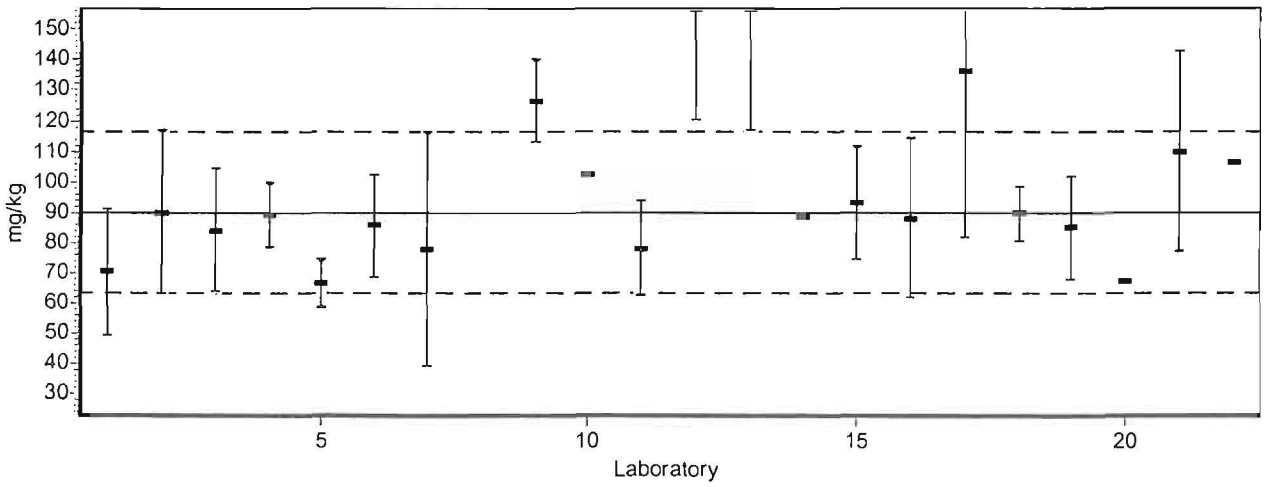
Analyytti *(Analyte)* **Chrysene** Näyte *(Sample)* P



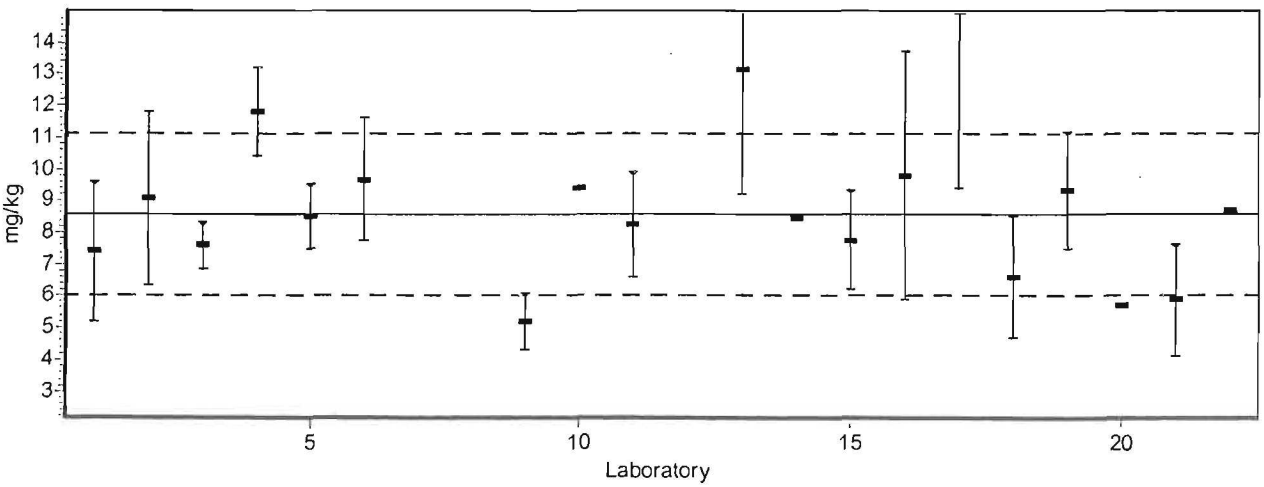
Analyytti *(Analyte)* **Dibenz-ah** Näyte *(Sample)* P



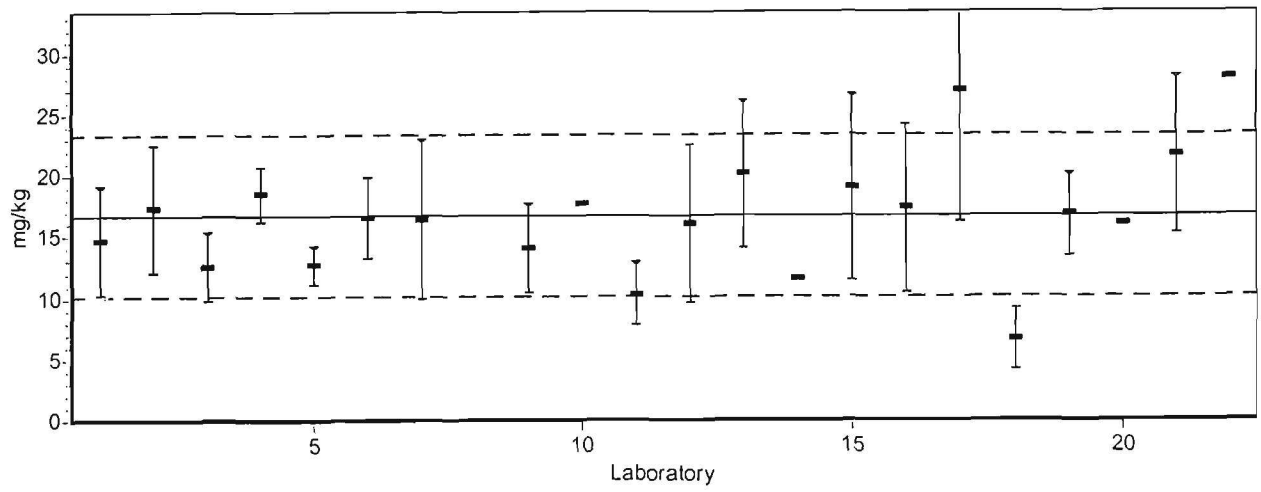
Analyytti *(Analyte)* **Fluoran** Näyte *(Sample)* P



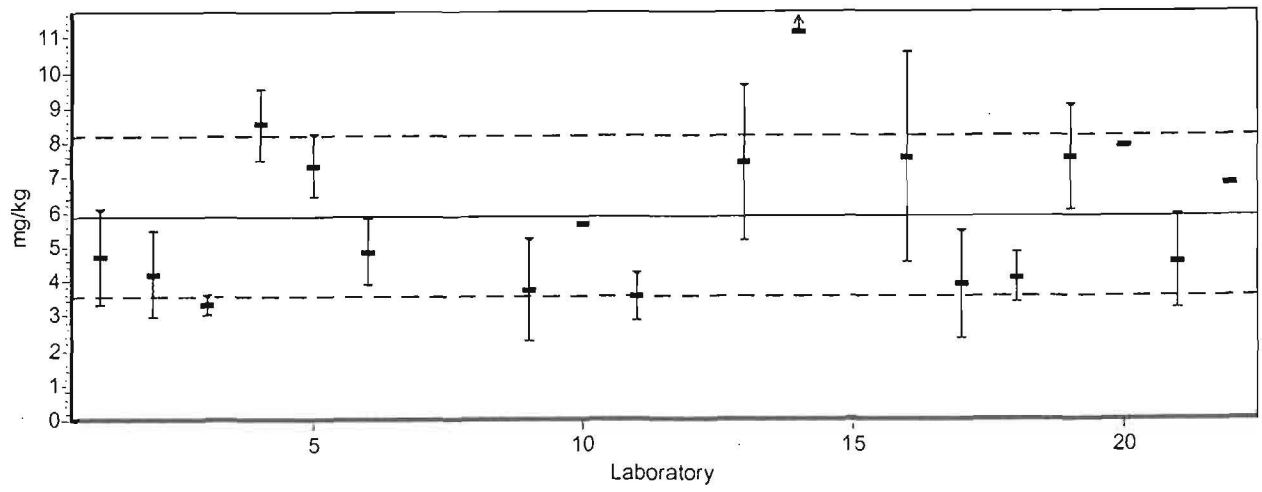
Analyytti *(Analyte)* **Fluorene** Näyte *(Sample)* P



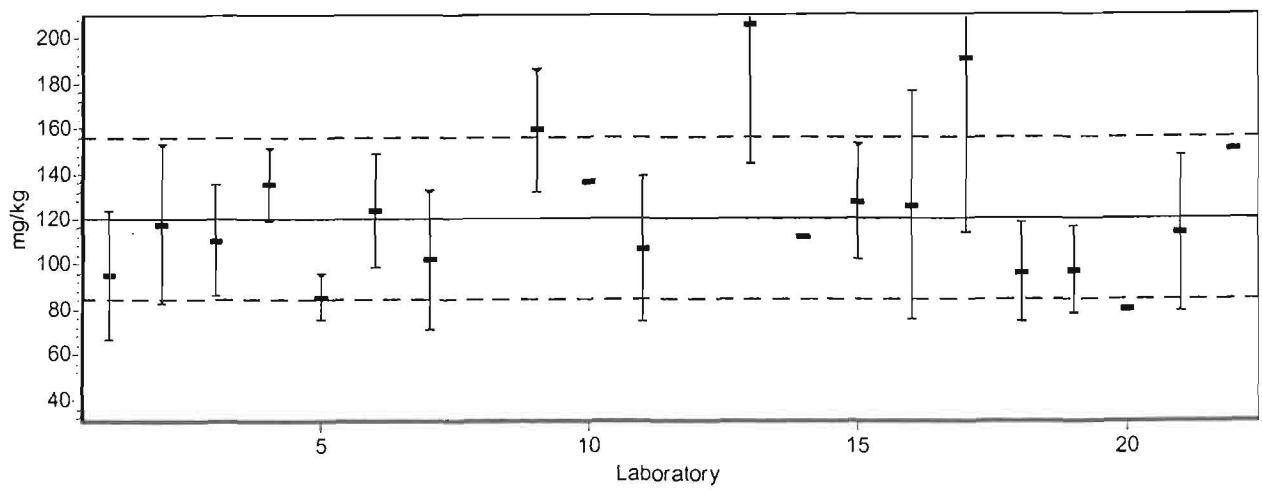
Analyytti *(Analyte)* **Indeno** Näyte *(Sample)* P



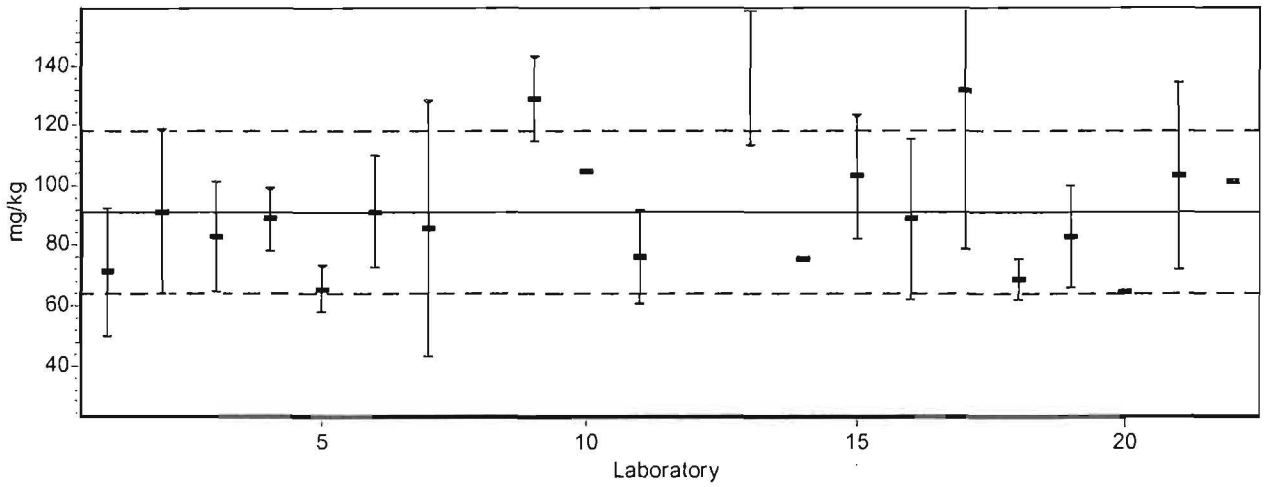
Analyytti *(Analyte)* **Napht** Näyte *(Sample)* P



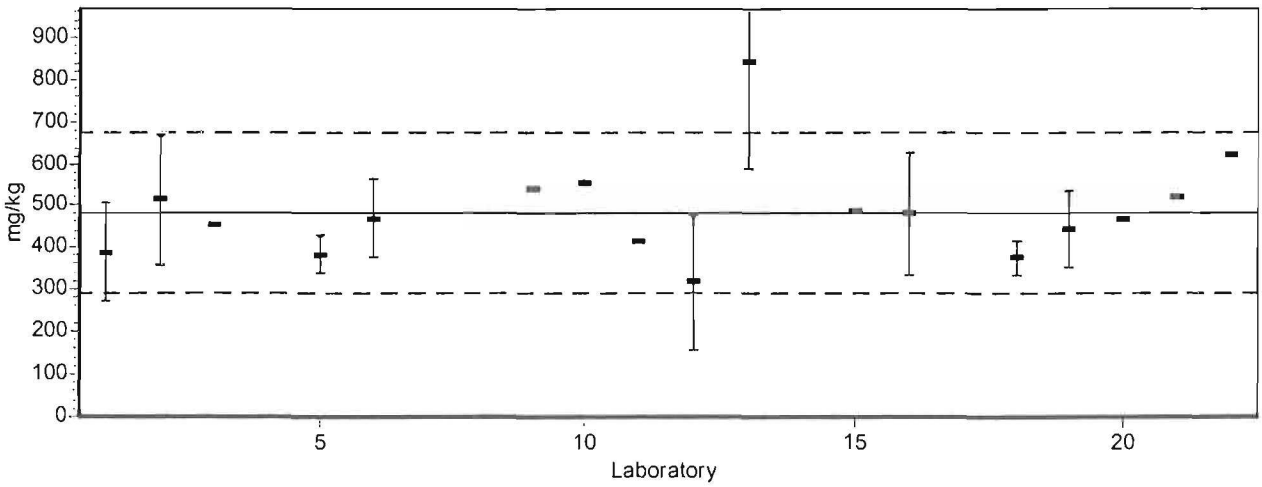
Analyytti *(Analyte)* **Phenan** Näyte *(Sample)* P



Analyytti *(Analyte)* **Pyrene** Näyte *(Sample)* P



Analyytti *(Analyte)* **tot-PAH** Näyte *(Sample)* P



ANNEX 8. EXPLANATIONS FOR THE RESULT SHEETS

Results of each participant (Annex 8):

Analyte	PAHs
Unit	mg/kg
Sample	The code of the sample
z-Graphics	z score - the graphical presentation
z-value	z-score, calculated as follows: $z = (x_i - X)/s$, where x_i = the result of the invidual laboratory X = the reference value (*the assigned value*) s = the target value for the total standard deviation (s_{target}).
Outl test OK	yes - the result passed the outlier test
Assigned value	the reference value
2* Targ SD %	the target total standard deviation (95 % confidence interval).
Lab's result	the result reported by the participant (the mean value of the replicates)
Md.	Median
Mean	Mean
SD	Standard deviation
SD%	Standard deviation, %
Passed	The results passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

Summary on the z scores (Annex 9):

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

Robust analysis (Calculation of the assigned value for the samples M1 and U1, Annex 7)

The items of data is sorted into increasing order, $x_1, x_2, \ldots, x_i, \ldots, x_p$.

Initial values for x^* and s^* are calculated as:

X^* = median of x_i $(i = 1 \ldots p)$
$S^* = 1.483$ median of $|x_i - x^*|$ $(i = 1 \ldots p)$

The values of x^* and s^* are updated by calculating
$\varphi = 1.5\, s^*$
For each x_i is calculated:

$x_i^* = x^* - \varphi$ if $x_i < x^* - \varphi$
$x_i^* = x^* + \varphi$ if $x_i > x^* + \varphi$
$x_i^* = x_i$ otherwise

The new values of x^* and s^* are calculated from:

$$X^* = \sum x_i^* / p$$

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

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

Ref: Statistical methods for use in proficiency testing by interlaboratory comparisons, Annex C (ISO/DIS 13528, Draft 2002-02-18)

ANNEX 9. RESULTS OF EACH PARTICIPANT

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																
A-naphthy	mg/kg	P		-2,501	yes	8,45	40	4,223	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-0,764	yes	2,05	40	1,737	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-1,480	yes	7,95	40	5,597	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-0,495	yes	15,5	40	13,97	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-0,971	yes	28,5	40	22,97	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-1,605	yes	24,4	40	16,57	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-0,321	yes	16,6	40	15,53	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-1,089	yes	17,3	40	13,53	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-1,306	yes	33,7	30	27,1	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,703	yes	3,27	40	3,73	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-1,449	yes	89,7	30	70,2	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-0,910	yes	8,57	30	7,4	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-0,599	yes	16,7	40	14,7	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-1,001	yes	5,86	40	4,687	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-1,385	yes	120	30	95,07	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-1,447	yes	91,1	30	71,33	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-0,980	yes	483	40	388,3	468	474,2	84,85	17,8	17	1	0	18
Laboratory 2																
A-naphthy	mg/kg	P		2,199	yes	8,45	40	12,17	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-0,122	yes	2,05	40	2	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		2,421	yes	7,95	40	11,8	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-0,323	yes	15,5	40	14,5	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		1,135	yes	28,5	40	34,97	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,963	yes	24,4	40	19,7	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		2,229	yes	16,6	40	24	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		0,357	yes	17,3	40	18,53	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-1,292	yes	33,7	30	27,17	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,199	yes	3,27	40	3,4	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		0,007	yes	89,7	30	89,8	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		0,412	yes	8,57	30	9,1	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		0,180	yes	16,7	40	17,3	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-1,416	yes	5,86	40	4,2	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-0,130	yes	120	30	117,7	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		0,022	yes	91,1	30	91,4	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		0,335	yes	483	40	515,3	468	474,2	84,85	17,8	17	1	0	18
Laboratory 3																
A-naphthy	mg/kg	P		0,441	yes	8,45	40	9,195	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-0,580	yes	2,05	40	1,812	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-1,027	yes	7,95	40	6,316	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-0,243	yes	15,5	40	14,75	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-0,100	yes	28,5	40	27,93	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,333	yes	24,4	40	22,78	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		1,576	yes	16,6	40	21,83	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-1,470	yes	17,3	40	12,21	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		0,160	yes	33,7	30	34,51	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-2,526	yes	3,27	40	1,618	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,426	yes	89,7	30	83,97	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-0,749	yes	8,57	30	7,607	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-1,236	yes	16,7	40	12,57	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-2,173	yes	5,86	40	3,313	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-0,522	yes	120	30	110,6	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-0,575	yes	91,1	30	83,24	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-0,298	yes	483	40	454,3	468	474,2	84,85	17,8	17	1	0	18

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 4																
A-naphthy	mg/kg	P		2,281	yes	8,45	40	12,31	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		2,256	yes	2,05	40	2,975	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		1,636	yes	7,95	40	10,55	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		0,375	yes	15,5	40	16,66	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-0,368	yes	28,5	40	26,4	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		4,569	yes	24,4	40	46,69	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-per	mg/kg	P		0,641	yes	17,3	40	19,52	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		0,193	yes	33,7	30	34,68	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,437	yes	3,27	40	3,556	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,038	yes	89,7	30	89,18	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		2,525	yes	8,57	30	11,82	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		0,523	yes	16,7	40	18,45	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		2,256	yes	5,86	40	8,504	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		0,829	yes	120	30	134,9	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-0,172	yes	91,1	30	88,75	89,02	91,53	18,77	20,5	20	1	0	21
Laboratory 5																
A-naphthy	mg/kg	P		1,283	yes	8,45	40	10,62	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		0,535	yes	2,05	40	2,269	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		0,698	yes	7,95	40	9,059	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-0,876	yes	15,5	40	12,78	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-1,063	yes	28,5	40	22,44	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,126	yes	24,4	40	23,78	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-1,581	yes	16,6	40	11,35	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-0,746	yes	17,3	40	14,72	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-1,084	yes	33,7	30	28,22	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,166	yes	3,27	40	3,378	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-1,735	yes	89,7	30	66,36	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-0,054	yes	8,57	30	8,501	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-1,206	yes	16,7	40	12,67	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		1,258	yes	5,86	40	7,334	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-1,919	yes	120	30	85,46	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-1,865	yes	91,1	30	65,61	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-1,019	yes	483	40	384,5	468	474,2	84,85	17,8	17	1	0	18
Laboratory 6																
A-naphthy	mg/kg	P		-0,562	yes	8,45	40	7,5	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		0,285	yes	2,05	40	2,167	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-0,094	yes	7,95	40	7,8	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-0,731	yes	15,5	40	13,23	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-0,871	yes	28,5	40	23,53	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		0,485	yes	24,4	40	26,77	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-1,928	yes	16,6	40	10,2	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-0,925	yes	17,3	40	14,1	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-0,884	yes	33,7	30	29,23	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-0,209	yes	3,27	40	3,133	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,320	yes	89,7	30	85,4	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		0,853	yes	8,57	30	9,667	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-0,040	yes	16,7	40	16,57	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-0,876	yes	5,86	40	4,833	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		0,204	yes	120	30	123,7	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		0,024	yes	91,1	30	91,43	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-0,138	yes	483	40	469,7	468	474,2	84,85	17,8	17	1	0	18
Laboratory 7																
Anthrac	mg/kg	P		-2,514	yes	7,95	40	3,953	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		0,763	yes	15,5	40	17,87	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		0,649	yes	28,5	40	32,2	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,683	yes	24,4	40	21,07	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-0,432	yes	16,6	40	15,17	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-0,511	yes	17,3	40	15,53	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-0,165	yes	33,7	30	32,87	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,994	yes	3,27	40	3,92	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,897	yes	89,7	30	77,63	89,2	93,27	18,7	20,0	20	2	0	22
Indeno	mg/kg	P		-0,080	yes	16,7	40	16,43	16,7	17,01	5,245	30,8	22	0	0	22
Phenan	mg/kg	P		-0,998	yes	120	30	102	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-0,403	yes	91,1	30	85,6	89,02	91,53	18,77	20,5	20	1	0	21

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 9																
A-naphthy	mg/kg	P		-3,057	yes	8,45	40	3,283	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-1,724	yes	2,05	40	1,343	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		1,646	yes	7,95	40	10,57	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-1,151	yes	15,5	40	11,93	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-1,216	yes	28,5	40	21,57	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-2,363	yes	24,4	40	12,87	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-2,319	yes	16,6	40	8,9	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-0,886	yes	17,3	40	14,23	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-3,066	yes	33,7	30	18,2	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-2,161	yes	3,27	40	1,857	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		2,747	yes	89,7	30	126,7	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-2,624	yes	8,57	30	5,197	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-0,788	yes	16,7	40	14,07	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-1,812	yes	5,86	40	3,737	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		2,167	yes	120	30	159	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		2,774	yes	91,1	30	129	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		0,614	yes	483	40	542,3	468	474,2	84,85	17,8	17	1	0	18
Laboratory 10																
A-naphthy	mg/kg	P		0,282	yes	8,45	40	8,927	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-0,569	yes	2,05	40	1,817	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		0,088	yes	7,95	40	8,09	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		0,097	yes	15,5	40	15,8	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		0,573	yes	28,5	40	31,77	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		1,865	yes	24,4	40	33,5	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-0,452	yes	16,6	40	15,1	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		0,385	yes	17,3	40	18,63	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		1,576	yes	33,7	30	41,67	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		1,290	yes	3,27	40	4,113	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		0,964	yes	89,7	30	102,7	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		0,656	yes	8,57	30	9,413	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		0,309	yes	16,7	40	17,73	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-0,199	yes	5,86	40	5,627	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		0,870	yes	120	30	135,7	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		0,968	yes	91,1	30	104,3	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		0,745	yes	483	40	555	468	474,2	84,85	17,8	17	1	0	18
Laboratory 11																
A-naphthy	mg/kg	P		0,320	yes	8,45	40	8,99	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-1,057	yes	2,05	40	1,617	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		3,574	yes	7,95	40	13,63	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-1,258	yes	15,5	40	11,6	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-0,918	yes	28,5	40	23,27	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P				24,4	40		23,24	26,3	9,252	35,1	20	0	1	21
Benzo-per	mg/kg	P		-1,696	yes	17,3	40	11,43	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-1,029	yes	33,7	30	28,5	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-1,386	yes	3,27	40	2,363	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,877	yes	89,7	30	77,9	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-0,228	yes	8,57	30	8,277	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-1,906	yes	16,7	40	10,33	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-1,968	yes	5,86	40	3,553	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-0,722	yes	120	30	107	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-1,090	yes	91,1	30	76,2	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-0,690	yes	483	40	416,3	468	474,2	84,85	17,8	17	1	0	18
Laboratory 12																
Benzo-A-P	mg/kg	P		0,645	yes	15,5	40	17,5	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-B-F	mg/kg	P		2,609	yes	24,4	40	37,13	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-0,402	yes	16,6	40	15,27	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		0,742	yes	17,3	40	19,87	18,1	17,61	5,35	30,3	22	0	0	22
Fluoran	mg/kg	P		5,250	H	89,7	30	160,3	89,2	93,27	18,7	20,0	20	2	0	22
Indeno	mg/kg	P		-0,190	yes	16,7	40	16,07	16,7	17,01	5,245	30,8	22	0	0	22
tot-PAH	mg/kg	P		-1,701	yes	483	40	318,7	468	474,2	84,85	17,8	17	1	0	18

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																
A-naphthy	mg/kg	P		0,868	yes	8,45	40	9,917	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		0,073	yes	2,05	40	2,08	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		3,029	yes	7,95	40	12,77	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		0,882	yes	15,5	40	18,23	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		1,754	yes	28,5	40	38,5	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-1,127	yes	24,4	40	18,9	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		3,906	yes	16,6	40	29,57	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		1,763	yes	17,3	40	23,4	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		1,365	yes	33,7	30	40,6	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		4,985	H	3,27	40	6,53	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		5,745	H	89,7	30	167	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		3,576	H	8,57	30	13,17	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		1,018	yes	16,7	40	20,1	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		1,317	yes	5,86	40	7,403	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		4,741	H	120	30	205,3	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		5,213	H	91,1	30	162,3	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		3,713	H	483	40	841,7	468	474,2	84,85	17,8	17	1	0	18
Laboratory 14																
A-naphthy	mg/kg	P		-1,345	yes	8,45	40	6,177	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		0,537	yes	2,05	40	2,27	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-1,423	yes	7,95	40	5,687	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-1,495	yes	15,5	40	10,87	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-2,053	yes	28,5	40	16,8	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		0,273	yes	24,4	40	25,73	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-per	mg/kg	P		-1,676	yes	17,3	40	11,5	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-2,084	yes	33,7	30	23,17	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-0,479	yes	3,27	40	2,957	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,082	yes	89,7	30	88,6	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-0,099	yes	8,57	30	8,443	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-1,527	yes	16,7	40	11,6	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		5,609	yes	5,86	40	12,43	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-0,444	yes	120	30	112	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-1,149	yes	91,1	30	75,4	89,02	91,53	18,77	20,5	20	1	0	21
Laboratory 15																
A-naphthy	mg/kg	P				8,45	40	ND	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P				2,05	40	<3	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-2,405	yes	7,95	40	4,127	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		0,333	yes	15,5	40	16,53	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-0,573	yes	28,5	40	25,23	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,601	yes	24,4	40	21,47	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-1,365	yes	16,6	40	12,07	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		1,407	yes	17,3	40	22,17	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-0,574	yes	33,7	30	30,8	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-1,147	yes	3,27	40	2,52	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		0,245	yes	89,7	30	93	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-0,630	yes	8,57	30	7,76	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		0,709	yes	16,7	40	19,07	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P				5,86	40	ND	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		0,407	yes	120	30	127,3	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		0,871	yes	91,1	30	103	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		0,038	yes	483	40	486,7	468	474,2	84,85	17,8	17	1	0	18

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																
A-naphthy	mg/kg	P		-1,000	yes	8,45	40	6,76	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		1,675	yes	2,05	40	2,737	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-0,780	yes	7,95	40	6,71	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-0,366	yes	15,5	40	14,37	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		0,246	yes	28,5	40	29,9	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,581	yes	24,4	40	21,57	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-1,687	yes	16,6	40	11	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-0,077	yes	17,3	40	17,03	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-0,442	yes	33,7	30	31,47	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-1,524	yes	3,27	40	2,273	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,146	yes	89,7	30	87,73	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		0,957	yes	8,57	30	9,8	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		0,180	yes	16,7	40	17,3	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		1,442	yes	5,86	40	7,55	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		0,315	yes	120	30	125,7	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-0,166	yes	91,1	30	88,83	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-0,024	yes	483	40	480,7	468	474,2	84,85	17,8	17	1	0	18
Laboratory 17																
A-naphthy	mg/kg	P		0,542	yes	8,45	40	9,367	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		14,020	yes	2,05	40	7,8	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		1,771	C	7,95	40	10,77	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		2,849	yes	15,5	40	24,33	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		2,310	yes	28,5	40	41,67	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		1,762	yes	24,4	40	33	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		5,040	yes	16,6	40	33,33	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		3,863	yes	17,3	40	30,67	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		5,598	H	33,7	30	62	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		12,330	H	3,27	40	11,33	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		3,466	yes	89,7	30	136,3	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		5,521	H	8,57	30	15,67	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		3,084	yes	16,7	40	27	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-1,672	yes	5,86	40	3,9	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		3,907	H	120	30	190,3	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		2,969	yes	91,1	30	131,7	89,02	91,53	18,77	20,5	20	1	0	21
Laboratory 18																
A-naphthy	mg/kg	P		0,191	yes	8,45	40	8,773	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-1,041	yes	2,05	40	1,623	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		1,587	yes	7,95	40	10,47	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-2,360	yes	15,5	40	8,183	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-B-F	mg/kg	P		-0,191	yes	24,4	40	23,47	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-per	mg/kg	P		-2,494	yes	17,3	40	8,67	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		1,398	yes	33,7	30	40,77	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		-2,227	yes	3,27	40	1,813	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,017	yes	89,7	30	89,47	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-1,540	yes	8,57	30	6,59	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-3,017	yes	16,7	40	6,623	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-1,524	yes	5,86	40	4,073	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-1,315	yes	120	30	96,33	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-1,620	yes	91,1	30	68,97	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-1,108	yes	483	40	376	468	474,2	84,85	17,8	17	1	0	18

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 19																
A-naphthy	mg/kg	P		0,718	yes	8,45	40	9,663	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		0,016	yes	2,05	40	2,057	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-0,728	yes	7,95	40	6,793	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		-0,680	yes	15,5	40	13,39	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-1,023	yes	28,5	40	22,67	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-1,195	yes	24,4	40	18,57	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		1,335	yes	16,6	40	21,03	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		0,077	yes	17,3	40	17,57	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-0,528	yes	33,7	30	31,03	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,291	yes	3,27	40	3,46	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-0,366	yes	89,7	30	84,77	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		0,596	yes	8,57	30	9,337	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		0,042	yes	16,7	40	16,84	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		1,425	yes	5,86	40	7,53	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-1,270	yes	120	30	97,13	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-0,595	yes	91,1	30	82,97	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-0,395	yes	483	40	444,8	468	474,2	84,85	17,8	17	1	0	18
Laboratory 20																
A-naphthy	mg/kg	P		-2,621	yes	8,45	40	4,02	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		-1,561	yes	2,05	40	1,41	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-0,541	yes	7,95	40	7,09	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		0,000	yes	15,5	40	15,5	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		-0,386	yes	28,5	40	26,3	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,594	yes	24,4	40	21,5	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		0,452	yes	16,6	40	18,1	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		-0,867	yes	17,3	40	14,3	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		-0,218	yes	33,7	30	32,6	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,153	yes	3,27	40	3,37	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		-1,702	yes	89,7	30	66,8	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-2,240	yes	8,57	30	5,69	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		-0,180	yes	16,7	40	16,1	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		1,749	yes	5,86	40	7,91	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-2,211	yes	120	30	80,2	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		-1,910	yes	91,1	30	65,0	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		-0,155	yes	483	40	468	468	474,2	84,85	17,8	17	1	0	18
Laboratory 21																
Acenaph	mg/kg	P		-0,529	yes	2,05	40	1,833	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-2,128	yes	7,95	40	4,567	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		1,452	yes	15,5	40	20	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		1,023	yes	28,5	40	34,33	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		-0,082	yes	24,4	40	24	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-0,181	yes	16,6	40	16	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		1,840	yes	17,3	40	23,67	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		0,917	yes	33,7	30	38,33	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		0,759	yes	3,27	40	3,767	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		1,509	yes	89,7	30	110	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		-2,103	yes	8,57	30	5,867	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		1,487	yes	16,7	40	21,67	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		-1,132	yes	5,86	40	4,533	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		-0,370	yes	120	30	113,3	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		0,895	yes	91,1	30	103,3	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		0,418	yes	483	40	523,3	468	474,2	84,85	17,8	17	1	0	18

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 22																
A-naphthy	mg/kg	P		-3,757	yes	8,45	40	2,1	8,97	8,464	3,542	41,8	18	0	1	19
Acenaph	mg/kg	P		0,041	yes	2,05	40	2,067	2,035	2,327	1,402	60,2	19	0	1	20
Anthrac	mg/kg	P		-1,541	yes	7,95	40	5,5	7,232	7,913	2,909	36,7	20	1	0	21
Benzo-A-P	mg/kg	P		1,344	yes	15,5	40	19,67	15,06	15,54	3,836	24,6	22	0	0	22
Benzo-ant	mg/kg	P		5,000	H	28,5	40	57	26,97	28,36	6,726	23,7	19	1	0	20
Benzo-B-F	mg/kg	P		3,538	yes	24,4	40	41,67	23,24	26,3	9,252	35,1	20	0	1	21
Benzo-K-F	mg/kg	P		-0,080	yes	16,6	40	16,33	15,95	17,35	6,648	38,3	18	0	0	18
Benzo-per	mg/kg	P		0,877	yes	17,3	40	20,33	18,1	17,61	5,35	30,3	22	0	0	22
Chrysene	mg/kg	P		3,818	yes	33,7	30	53	31,2	33,41	8,235	24,6	20	1	0	21
Dibenz-ah	mg/kg	P		1,473	yes	3,27	40	4,233	3,328	3,074	0,83	27,0	19	2	0	21
Fluoran	mg/kg	P		1,261	yes	89,7	30	106,7	89,2	93,27	18,7	20,0	20	2	0	22
Fluorene	mg/kg	P		0,101	yes	8,57	30	8,7	8,423	8,277	1,611	19,4	18	2	0	20
Indeno	mg/kg	P		3,383	yes	16,7	40	28	16,7	17,01	5,245	30,8	22	0	0	22
Napht	mg/kg	P		0,774	yes	5,86	40	6,767	5,2	5,918	2,329	39,3	19	0	1	20
Phenan	mg/kg	P		1,667	yes	120	30	150	115	117,3	21,47	18,2	19	2	0	21
Pyrene	mg/kg	P		0,725	yes	91,1	30	101	89,02	91,53	18,77	20,5	20	1	0	21
tot-PAH	mg/kg	P		1,453	yes	483	40	623,3	468	474,2	84,85	17,8	17	1	0	18

ANNEX 10. SUMMARY OF z SCORES

Analyte	Sample\Lab	1	2	3	4	5	6	7	9	10	11	12	13	14	15	16	17	18	19	20	21	22	%
A-naphthy	P	n	p	A	p	A	A		N	A	A		A	A		A	A	A	A	n		N	65
Acenaph	P	A	A	A	p	A	A		A	A	A		A	A		A	P	A	A	A	A	A	89
Anthrac	P	A	p	A	A	A	A	n	A	A	P		P	A	n	A	A	A	A	A	n	A	70
Benzo-A-P	P	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	p	n	A	A	A	A	90
Benzo-ant	P	A	A	A	A	A	A	A	A	A	A		A	n	A	A	p		A	A	A	P	84
Benzo-B-F	P	A	A	A	P	A	A	A	n	A		p	A	A	A	A	A	A	A	A	A	P	80
Benzo-K-F	P	A	p	A		A	A	A	n	A		A	P		A	A	P		A	A	A	A	76
Benzo-per	P	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	P	n	A	A	A	A	90
Chrysene	P	A	A	A	A	A	A	A	N	A	A		A	n	A	A	P	A	A	A	A	P	80
Dibenz-ah	P	A	A	n	A	A	A	A	n	A	A		P	A	A	A	P	n	A	A	A	A	75
Fluoran	P	A	A	A	A	A	A	A	p	A	A	P	P	A	A	A	P	A	A	A	A	A	81
Fluorene	P	A	A	A	p	A	A		n	A	A		P	A	A	A	P	A	A	n	n	A	68
Indeno	P	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	P	N	A	A	A	P	86
Napht	P	A	A	n	p	A	A		A	A	A		A	P		A	A	A	A	A	A	A	83
Phenan	P	A	A	A	A	A	A	A	p	A	A		P	A	A	A	P	A	A	n	A	A	80
Pyrene	P	A	A	A	A	A	A	A	p	A	A		P	A	A	A	p	A	A	A	A	A	85
tot-PAH	P	A	A	A		A	A		A	A	A	A	P		A	A		A	A	A	A	A	94
%		94	82	88	67	100	100	92	47	100	93	71	53	80	93	100	25	73	100	82	88	71	
Accredited				yes	yes	yes	yes				yes	yes									yes		

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

%* - percentage of accepted results

Totally accepted, % In all: 81 In accredited: 88 In non-accredited: 78

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisuaika Helmikuu 2005
Tekijä(t)	Irma Mäkinen, Pirjo Sainio, Kirsti Erkomaa ja Sami Huhtala	
Julkaisun nimi	SYKE Proficiency test 3a/2004 (PAHs from polluted soil) SYKE Pätevyyskoe 3a/2004 (PAH yhdisteet maasta)	
Julkaisun osat/ muut saman projektin tuottamat julkaisut		
Tiivistelmä	Suomen ympäristökeskus järjesti toukokuussa 2004 pätevyyskokeen 16 PAH-yhdisteiden määrittämiseksi maasta. Pätevyyskoe oli osa EU-hanketta "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes" (CoEPT). Pätevyyskokeeseen osallistui kaikkiaan 21 laboratoriota Suomesta, Norjasta, Ruotsista ja Tanskasta. Pätevyyskokeen näytteenä oli yksi sertifioitu vertailumateriaali, joka oli valmistettu saastuneesta maasta. Analysoinnissa käytettiin useita menetelmiä. Vain harva osallistuja käytti vielä toistaiseksi kansainvälisen standardiehdotuksen ISO/DIS 18287 mukaista menettelyä. Mm. määritykseen käytetty näytemäärä, uuttoliuottimet ja kalibrointiliuokset vaihtelivat eri laboratorioissa. Tulosten hajonta oli 20 % – 38 % eri PAH-yhdisteille ja hajontaan vaikutti mm. eri menetelmävariaatioiden runsaus. Vertailuarvona käytettiin robusti-keskiarvoa. Tässä pätevyyskokeessa 81 % tuloksista oli tyydyttäviä, kun kokonaiskeskihajonnan tavoitearvona käytettiin 30 % tai 40 % (95 % merkitsevyystaso). Pätevyyskoe PAH-yhdisteiden määrittämiseksi pilaantuneesta maasta järjestettiin ensimmäisen kerran Suomessa. Joiden laboratorioiden osallistuminen ensimmäistä kertaa PAH-yhdisteiden pätevyyskokeeseen on voinut vaikuttaa suoriutumiseen. Pätevyyskoe oli osa EU/CoEPT-hanketta, jonka alustavat tulokset raportoitiin helmikuussa 2005. Niiden perusteella eurooppalaisten järjestäjien asettamat vertailuarvot olivat pääasiassa yhteneväisiä. Myös eri laboratorioiden tulokset olivat keskenään vertailukelpoisia. Eroja esiintyi pätevyyden arvioinnissa sekä vertailuarvon mittausepävarmuuden arvioinnissa.	
Asiasanat	maaperäanalytiikka, polyaromaattiset hiilivedyt (PAH), ympäristölaboratoriot, pätevyyskoe, vertailukoe	
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Painopaikka ja -aika	Helsinki 2004	
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Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date February 2005
Author(s)	Irma Mäkinen, Pirjo Sainio, Kirsti Erkomaa and Sami Huhtala	
Title of publication	SYKE Proficiency test 3a/2004 (PAHs from polluted soil)	
Parts of publication/ other project publications		
Abstract	The Finnish Environment Institute carried out the proficiency test for the determination of PAH's from polluted soil. The proficiency test was carried out in the framework of the EU/CoEPT Project "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes". In total, 21 laboratories (one Danish laboratory, two Norwegian, five Swedish and thirteen Finnish laboratories) participated in the proficiency test. One sample was delivered to the participating laboratories, which was a certified reference material prepared from highly contaminated soil. Different "in house" methods were rather commonly used in the analysis of PAH's. A few participants used the draft standard ISO/DIS 18287. There was variation e.g. in the sample intake, in the extraction solvents and in internal standards. Variation of the results in the analysis of different PAH's was between 20 % and 38 %. In this proficiency test, the robust mean value was used as the assigned value. When the target total standard deviation of 30 % or 40 % was used in calculation of z scores (95 % confidence level) 81 % of the participating laboratories reported satisfied results. The SYKE proficiency test for analysis of PAH's in polluted soil was carried out for the first time. Use of uniform and proper methods e.g. in the extraction step could improve the quality of results in the analysis of PAH's from soils. The proficiency test was carried out within the framework of the EU/CoEPT Project "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes". Generally there was a good agreement between providers in estimation of assigned values and here was also a good agreement between the results of different participants. Main differences came from different statistical protocols used by providers e.g. in performance rating.	
Keywords	soil analysis, polyaromatic hydrocarbons (PAH), proficiency test, interlaboratory comparison	
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Författare	Irma Mäkinen, Pirjo Sainio, Kirsti Erkomaa och Sami Huhtala	
Publikationens titel	SYKE Provningsjämförelse 3a/2004 (PAH jordanalyser)	
Publikationens delar/ andra publikationer inom samma projekt		
Sammandrag	Under maj 2004 genomförde Finlands Miljöcentral en provningsjämförelse, som omfattade bestämning av PAH föreningar i jord. Provningsjämförelsen ingick som en del i projektet EU-CoEPT "Comparability of the Operation and Evaluation Protocols of European Proficiency Testing Schemes". Provet var certifierade referens material, som sändes ut till 21 laboratorier. Analysmetoder varierade i olika laboratorier. Endast få laboratorier använde metoden baserade på standardförslaget ISO/DIS 18287. Provmängden, extraktionlösningar, och kalibreringlösningar varierade i olika laboratorier. Standardavvikelsen av resultaten var 20 %-38 %. Resultaten värderades med hjälp av z-värden. Beräkningen av z-värdena baserade sig på totalstandardavvikelser, som sattes till 30 % eller 40 % (95 % sannolikhetsnivå). Robust-medelvärdet användes som referensvärde (*the assigned value*). I provningsjämförelsen var 81 % av resultaten nöjaktiga. Provningsjämförelsen för analyser av PAH organiserades den första gången i Finland. På basen av preliminära resultaten i EU/CoEPT projekt, var bestämning av referensvärdet var huvudsakligen sammanfallande mellan olika europeiska anordnanden av provningsjämförelser. Även resultaten av olika laboratorier var jämförbara. Det finns ännu behov av harmonisering vid sättning av kriterier för värdering av resultaten.	
Nyckelord	jordanalyser, aromatiska kolhydrater, provningsjämförelse, miljölaboratorier	
Publikationsserie och nummer	Suomen ympäristökeskuksen moniste 312	
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