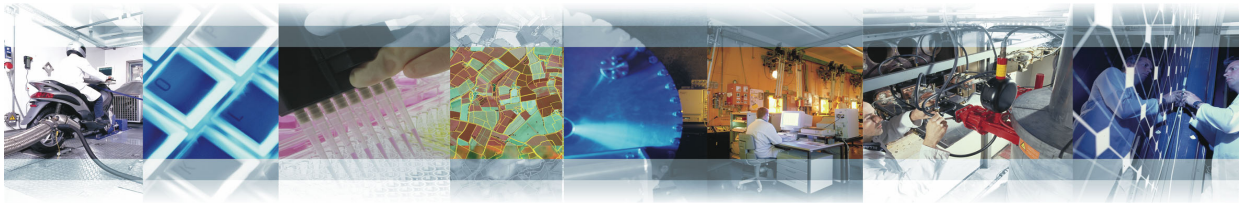


Report on the first inter-laboratory comparison test organised by the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons

15+1 EU priority PAHs in acetonitrile

Jose Angel Gomez Ruiz, Laszlo Hollosi, Lubomir Karasek, Rupert Simon, and Thomas Wenzl

EUR 22696 EN

2007

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

CRL
Polycyclic Aromatic Hydrocarbons

The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies.

European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Dr. Thomas Wenzl
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

E-mail: thomas.wenzl@ec.europa.eu

Tel.: +32 (0)14 571 320
Fax: +32 (0)14 571 873

http://www.irmm.jrc.be
http://www.jrc.ec.europa.eu

EUR 22696 EN
ISSN 1018-5593

Printed in Belgium

CRL

Polycyclic Aromatic Hydrocarbons

Report on the first inter-laboratory comparison test – 15 EU priority PAHs in acetonitrile

Jose Angel Gomez Ruiz, Laszlo Hollosi, Lubomir Karasek, Rupert Simon, and Thomas Wenzl

EC-JRC-IRMM

February 2007

Table of Contents

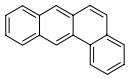
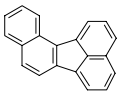
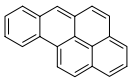
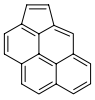
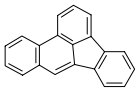
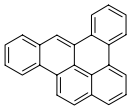
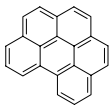
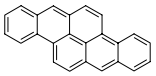
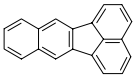
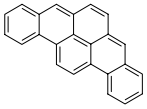
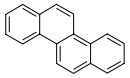
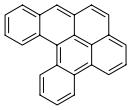
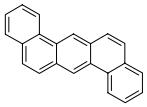
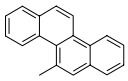
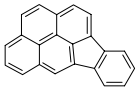
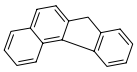
1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Joint Research Centre hosts the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons in Food (CRL-PAH). One of its core tasks is to organise inter-laboratory comparisons (ILCs) for the National Reference Laboratories (NRLs). This report presents the results of the 1st ILC of the CRL-PAH on the determination of the 15+1 EU priority PAHs in acetonitrile, which was conducted along the lines of the International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories.
The test material used in this exercise was a solution of the 15+1 EU priority PAHs in acetonitrile. The solution was prepared gravimetrically.
The assigned concentrations were calculated from the gravimetric data.
The uncertainty of the assigned value was determined for each analyte taking into account the uncertainty of the certified mass fraction of the neat substance as well as the uncertainty stemming from all manipulations of the material. Uncertainties are reported as expanded uncertainty with a coverage factor of 2.
The results of the laboratories were not rated.

2 Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings. PAHs may be formed during the incomplete combustion of organic compounds and can be found ubiquitously distributed in the environment. In food, PAH may be formed during processing and domestic food preparation, such as smoking, drying, roasting, baking, frying or grilling.
In 2002 the European Commission's Scientific Committee on Food identified 15 individual PAHs as of major concern for human health. These 15 EU priority PAHs should be monitored in food to enable long-term exposure assessments and to verify the validity of the use of the concentrations of benzo[*a*]pyrene (BaP) as a marker for a "total-PAH content" (EU 2002). The toxicological importance of these compounds was confirmed in October 2005 by the International Agency for Research on Cancer (IARC), which classified BaP as carcinogen to human beings (IARC group 1), cyclopenta[*cd*]pyrene, dibenz[*a*,*h*]anthracene, and dibenzo[*a*,*l*]pyrene as probably carcinogenic to human beings (group 2a), and 9 other EU priority PAHs as possibly carcinogenic to human beings (IARC 2006).
As a consequence, the European Commission (EC) issued Regulation (EC) No 208/2005 amending Regulation (EC) No 466/2001 setting maximum levels of benzo[*a*]pyrene in food, Commission Directive 2005/10/EC laying down sampling methods and the methods of analysis for the official control of benzo[*a*]pyrene levels in foodstuffs, and Commission Recommendation 2005/108/EC on the further investigation into the levels of polycyclic aromatic hydrocarbons in certain foods.
The European Food Safety Authority (EFSA) is evaluating the suitability of benzo[*a*]pyrene as a marker for the total PAH content of food. For that reason, EFSA asked the EU Member States to submit monitoring data on levels of the 15 EU priority PAHs and in addition benzo[*c*]fluorene to its database on PAH levels in food (EFSA 2006). The monitoring of latter PAH was recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in 2005 (JECFA 2005). In order to distinguish this set of PAHs from a set of PAHs that is prioritised by the US Environmental Protection Agency (US EPA), the terminology 15+1 EU priority PAHs was chosen. They are listed in Table 1.

Table 1: Names and structures of 15+1 EU priority PAHs

1	Benz[*a*] anthracene (BaA)		9	Benzo[*j*] fluoranthene (BjF)	
2	Benzo[*a*] pyrene (BaP)		10	Cyclopenta [*cd*]pyrene (CPP)	
3	Benzo[*b*] fluoranthene (BbF)		11	Dibenzo [*a,e*]pyrene (DeP)	
4	Benzo[*ghi*] perylene (BgP)		12	Dibenzo [*a,h*]pyrene (DhP)	
5	Benzo[*k*] fluoranthene (BkF)		13	Dibenzo [*a,i*]pyrene (DiP)	
6	Chrysene (CHR)		14	Dibenzo [*a,l*]pyrene (DlP)	
7	Dibenz[*a,h*] anthracene (DhA)		15	5-Methyl chrysene (5MC)	
8	Indeno[1,2,3-*cd*]pyrene (IcP)		+ 1	Benzo[*c*]fluorene	

3 Scope

As stated in Article 32 of Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with food and feed law, animal health and animal welfare rules (EU 2004), one of the core duties of the CRL-PAH is to organise inter-laboratory comparison tests (ILCs).

The ILC was designed and the reported data were processed along the lines of the International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories (Thompson *et al.* 2006).

4 Time frame

The ILC was announced to the NRLs at the CRL-PAH kick-off meeting in Geel on 26 and 27 September 2006. Invitation letters were sent to the laboratories in October 2006 (cf Annex) and the planned ILC was published on the IRMM web page (IRMM 2006). Test samples were dispatched beginning of November and the deadline for reporting of results was 1st December 2006. However, the deadline for submitting analysis results was extended on request of some participants twice to finally mid January 2007.

5 Test material

5.1 Preparation

The test material for the ILC was prepared from neat Certified Reference Materials (CRMs, Institute for Reference Materials and Measurements, Geel Belgium) except cyclopenta[*cd*]pyrene, which was manufactured on request (Biochemisches Institut für Umweltkarzinogene, Großhansdorf, Germany). Stock standard solutions of each analyte were produced by differential weighing of neat substance on a microbalance and dissolution in toluene. The mixed standard solution as well as the subsequent dilution were prepared gravimetrically. Acetonitrile was used as solvent. The concentrations of the standards and the test material were calculated applying the density equation. The uncertainty of the analyte concentration was determined for each analyte separately taking into account the uncertainty of the certified purity of the neat substance as well as the uncertainty stemming from all manipulations of the material. Uncertainties are reported as expanded uncertainty with a coverage factor of 2. The analyte concentration of the test material as well as the respective expanded uncertainties are given in Table 2.

About 180 ampoules containing each 5 mL of test samples were filled under inert atmosphere, sealed and stored refrigerated until dispatch.

Table 2: Analyte content of the test material

Analyte	**Concentration [µg/L]**	**Expanded uncertainty (*k*=2) [µg/L]**
benz[*a*]anthracene	63.75	0.17
benzo[*b*]fluoranthene	52.43	0.25
benzo[*j*]fluoranthene	91.0	0.4
benzo[*k*]fluoranthene	39.15	0.21
benzo[*c*]fluorene	36.11	0.25
benzo[*ghi*]perylene	53.46	0.28
benzo[*a*]pyrene	97.9	0.5
chrysene	53.6	0.5
cyclopenta[*cd*]pyrene	43.78	0.21
dibenz[*a,h*]anthracene	52.8	0.4
dibenzo[*a,e*]pyrene	70.0	0.4
dibenzo[*a,h*]pyrene	68.72	0.19
dibenzo[*a,i*]pyrene	85.8	0.6
dibenzo[*a,l*]pyrene	56.81	0.25
indeno[1,2,3-*cd*]pyrene	37.62	0.26
5-methylchrysene	74.2	0.5

5.2 Verification of the analyte concentration

The concentration of the test material was verified by GC/MS as well as HPLC-FLD, applying self prepared standard solutions as well as standard solutions from external suppliers (LGC Promochem and NIST). The measurement results deviated maximum 3% from the known concentrations of the test material.

5.3 Homogeneity

As the material consisted of a solution of the analytes in solvent, homogeneity can be assumed. However a number of 15 randomly selected ampoules were analysed in duplicate. Results were evaluated by ANOVA. Statistically significant differences of the analyte concentration of different ampoules were not found.

5.4 Stability

The test material concentration was monitored at begin of the study as well as after receipt of the results of the participants. Statistically significant differences of the results of analysis gained on the two mentioned dates were not found. Test samples were stored refrigerated for the period of the study.

5.5 Distribution

The samples were dispatched from IRMM on 3rd November 2006. Each participant received with the shipment a sample receipt form (Annex 1), an accompanying letter with instructions for sample handling, measurement, and reporting (Annex 2), the Material Safety Data Sheet for acetonitrile, and two ampoules containing the test material.

6 Outline of the study

Details of this ILC were presented to the participating NRLs at the kick-off meeting. Concrete instructions were published on the internet and given in a letter that accompanied the samples. The analytes and matrix were clearly defined as the 15+1 EU priority PAHs in acetonitrile and a concentration range, in which the values of the analyte contents were to be expected, was given.

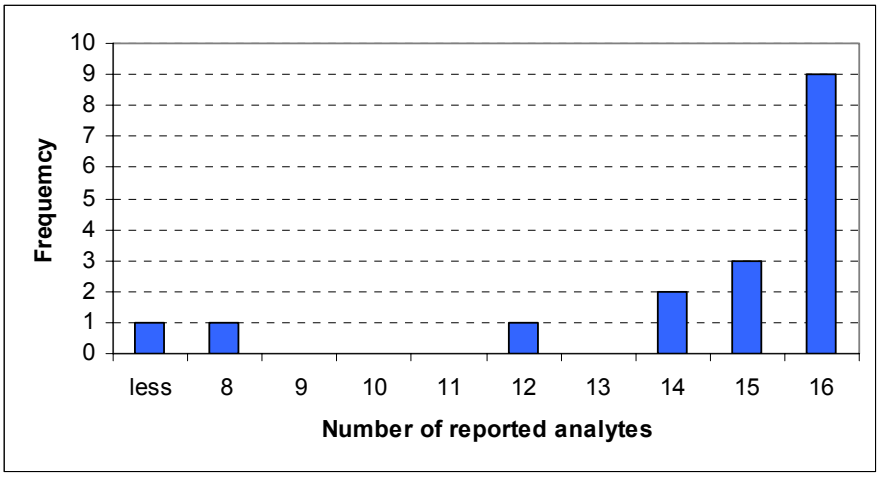
The participants were asked to use an analysis method of their choice, and to determine the analyte content of each ampoule on different days in triplicate, by applying two independent instrument calibrations. The analysis results had to be reported to an online-database at IRMM. The filling-in of a brief questionnaire (see Annex 3) was requested too.

7 Evaluation of the results

7.1 General observations

Analysis results were received from 17 out of 22 NRLs that were supplied with test samples. The missing laboratories were repeatedly reminded to submit their data, but they either stated not to be able to analyse the test material or did simply not respond to the reminders. Therefore the CRL closed the web interface for data submission mid of January.
The majority of laboratories reported results for all 15+1 PAHs. Three laboratories reported the sum of two analytes, which was a consequence of co-elution of benzo[*b*]fluoranthene and benzo[*j*]fluoranthene. Three NRLs submitted results for half or less of the number of analytes. Details on the composition of the received data sets can be taken from Figure 1.

Figure 1: Frequency distribution of reported data in terms of total number of analysed PAHs



7.2 Evaluation criteria

In the kick-off meeting it was agreed to omit the attribution of scores. The reason for that is that scores could be misleading if presented to third parties because they could be mixed up with scores that were gained for the whole analysis of real food, which includes sample preparation. The present study focused only on one, albeit important part of the analysis, the calibration. Therefore the submitted analysis data were evaluated for their percentage deviation from the known concentration of the individual analyte.

7.3 Laboratory results

The gravimetrically established concentration values were applied for the evaluation of the reported results.
On the following pages the results from the inter-laboratory comparison test on the 15+1 EU priority PAHs in acetonitrile are presented. In the first part the results for each analyte are evaluated individually.
The figures show for each analyte the percentage deviation of each measurement result submitted by the respective participant. In addition the mean value, calculated from the reported replicates (without exclusion of any potential outlier) is depicted. Due to different scaling of the figures and hence for better orientation, a deviation of ±10% from the assigned value is indicated by blue lines. The red line marks the known concentration and the black dotted line the expanded uncertainty of the known concentration.
The Kernel density plots show the distribution of the data and indicate for many analytes that data are not normally distributed and that outliers are in the data set (manifested by multimodality).
The cumulative frequency plot gives information on the magnitude and frequency of deviations from the assigned value, which is an indicator for the overall performance of the ensemble of NRLs. Typically 60 % to 80 % of the results were within the range of ±10 % from the assigned value. More difficulties caused the analysis of cyclopenta[*cd*]pyrene and of some dibenzopyrenes.
The analysis results and, if reported, corresponding measurement uncertainties are listed for the replicate measurements in Table 3 to 19. The presented data were harmonized in terms of applied concentration units and coverage factor of the reported uncertainties. A coverage factor of 2 was applied.

The percentage deviation of the average result for each analyte from the target concentration is depicted in Figure 51 for the individual participant. The aim of this evaluation was to highlight any systematics in the deviations from the assigned values for the whole set of PAHs.

Benz[*a*]anthracene

Figure 2: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): 63,75±0,17 µg/L; the blue lines indicate a 10% deviation from the known value.

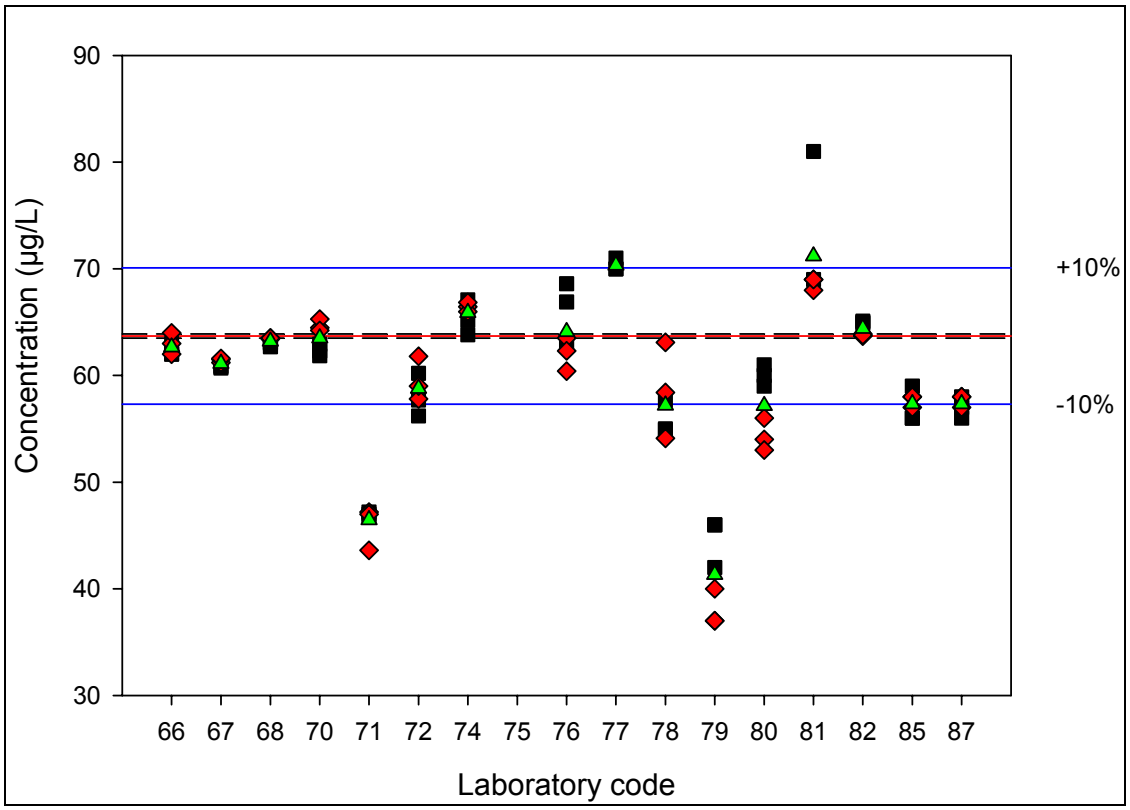


Figure 3: Kernel density plot of the reported results

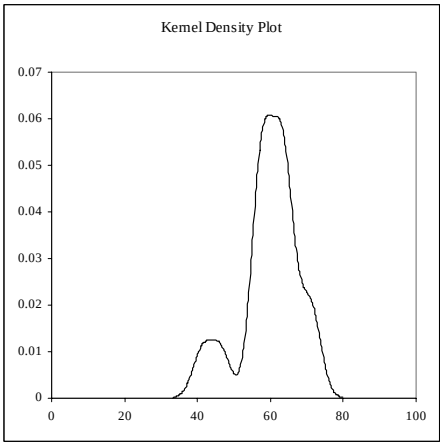


Figure 4: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

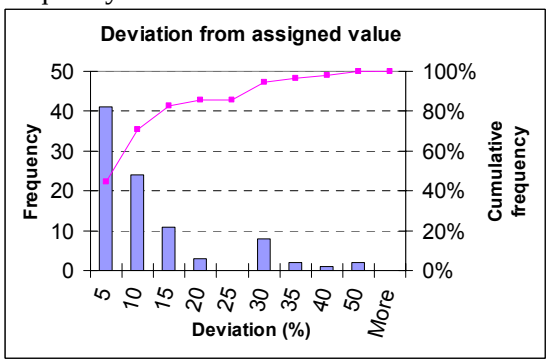


Table 3: **Benz[*a*]anthracene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); blank cells indicate missing data

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	63.00	6.00		63.00	6.00
66	62.00	6.00		62.00	6.00
66	62.00	6.00		64.00	6.00
67	60.90			61.20	
67	60.80			61.50	
67	60.70			61.60	
68	63.10	3.20		63.40	3.20
68	63.00	3.10		63.50	3.20
68	62.70	3.10		63.50	3.20
70	62.93			64.47	
70	61.85			65.28	
70	62.30			64.21	
71	47.20	11.80		47.20	11.80
71	46.80	11.70		47.00	11.80
71	47.00	11.80		43.60	10.90
72	57.70	3.30		57.80	3.30
72	56.20	3.20		59.00	3.40
72	60.20	3.60		61.80	3.60
74	67.10	3.30		66.44	0.86
74	63.82	3.30		65.98	0.86
74	65.17	3.30		66.84	0.86
75					
75					
75					
76	68.60	5.90		63.50	3.00
76	62.90	5.90		60.40	3.00
76	66.90	5.90		62.30	3.00
77	71.00	7.00			
77	70.00	7.00			
77	70.00	7.00			
78	55.00	8.30		58.40	8.80
78	57.70	8.70		54.10	8.10
78	54.90	8.20		63.10	9.50
79	46.00	14.00		40.00	12.00
79	42.00	13.00		37.00	11.00
79	46.00	14.00		37.00	11.00
80	61.00			54.00	
80	60.00			56.00	
80	59.00			53.00	
81	69.00	5.00		69.00	2.00
81	81.00	5.00		68.00	2.00
81				69.00	2.00
82	65.10	2.70		63.70	0.80
82	64.90	2.60		63.90	0.80
82	65.00	2.70		63.80	0.80
85	56.00			58.00	
85	56.00			58.00	
85	59.00			57.00	
87	58.00	0.50		57.00	0.50
87	57.00	0.50		58.00	0.50
87	56.00	0.50		58.00	0.50

Benzo[*b*]fluoranthene

Figure 5: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **52,43±0,25 µg/L**; the blue lines indicate a 10% deviation from the known value.

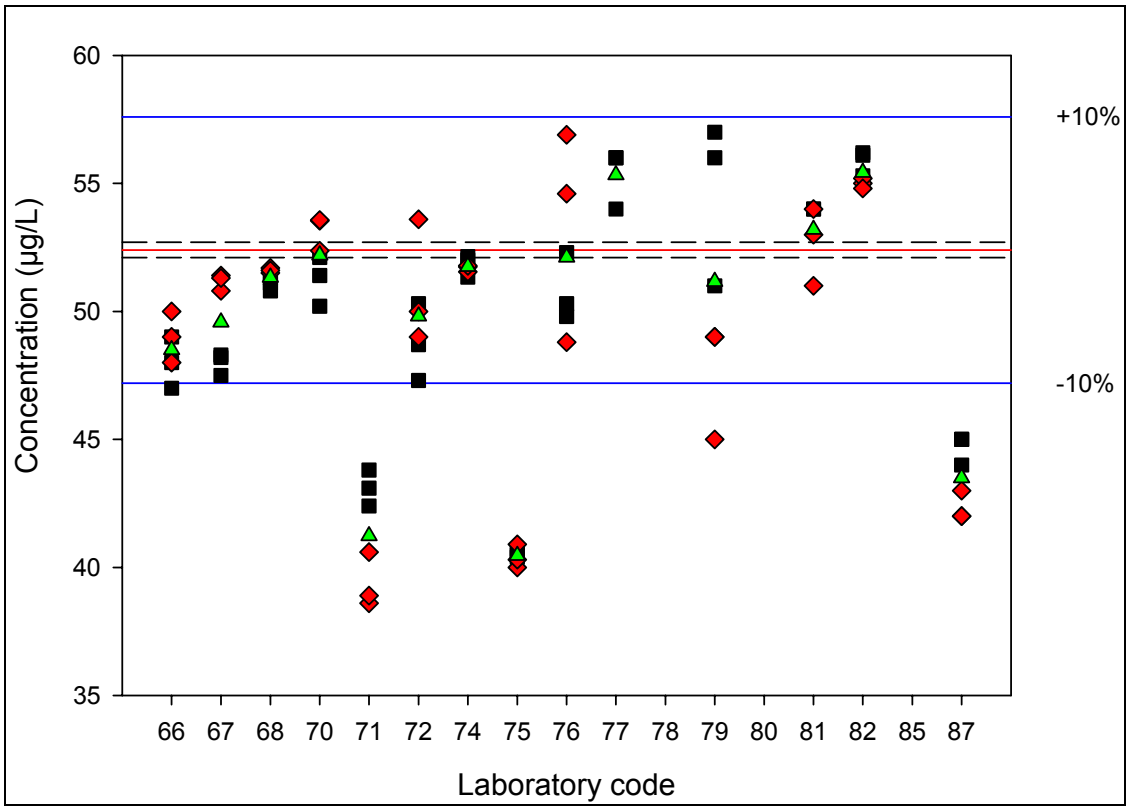


Figure 6: Kernel density plot of the reported results

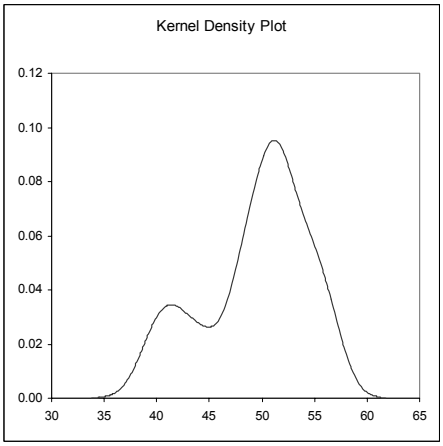


Figure 7: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

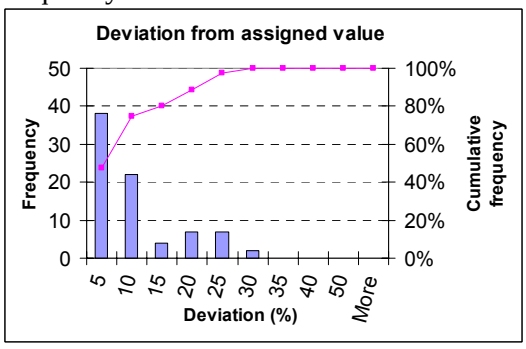


Table 4: **Benzo[*b*]fluoranthene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); blank cells indicate missing data

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	47.00	5.00		48.00	5.00
66	49.00	5.00		49.00	5.00
66	48.00	5.00		50.00	5.00
67	48.30			51.40	
67	48.20			50.80	
67	47.50			51.30	
68	51.30	2.60		51.50	2.60
68	51.10	2.60		51.70	2.60
68	50.80	2.50		51.60	2.60
70	51.40			52.37	
70	50.20			53.54	
70	52.11			53.57	
71	43.10	7.80		40.60	7.30
71	43.80	7.90		38.60	6.90
71	42.40	7.60		38.90	7.00
72	48.70	2.90		49.00	2.90
72	47.30	2.80		50.00	3.00
72	50.30	3.00		53.60	3.20
74	52.01	0.86		51.74	0.26
74	51.34	0.86		51.54	0.26
74	52.14	0.86		51.78	0.26
75	40.50	2.00		40.00	5.30
75	40.40	3.20		40.30	4.30
75	40.70	4.60		40.90	3.90
76	49.80	2.60		54.60	8.30
76	50.30	2.60		48.80	8.30
76	52.30	2.60		56.90	8.30
77	56.00	3.00			
77	54.00	3.00			
77	56.00	3.00			
78	127.20	25.40		145.90	21.90
78	134.60	20.20		138.30	30.70
78	129.30	19.40		131.10	19.70
79	56.00	17.00		49.00	15.00
79	57.00	17.00		49.00	15.00
79	51.00	15.00		45.00	13.00
80	172.00			181.00	
80	173.00			185.00	
80	172.00			173.00	
81	54.00	2.00		51.00	2.00
81	54.00	2.00		53.00	2.00
81				54.00	2.00
82	56.20	2.90		55.00	0.60
82	56.10	2.90		55.20	0.60
82	55.30	2.80		54.80	0.60
85	142.00			138.00	
85	139.00			136.00	
85	141.00			137.00	
87	45.00	0.50		42.00	0.50
87	45.00	0.50		43.00	0.50
87	44.00	0.50		42.00	0.50

Benzo[*j*]fluoranthene

Figure 8: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **91,0±0,4 µg/L**; the blue lines indicate a 10% deviation from the known value.

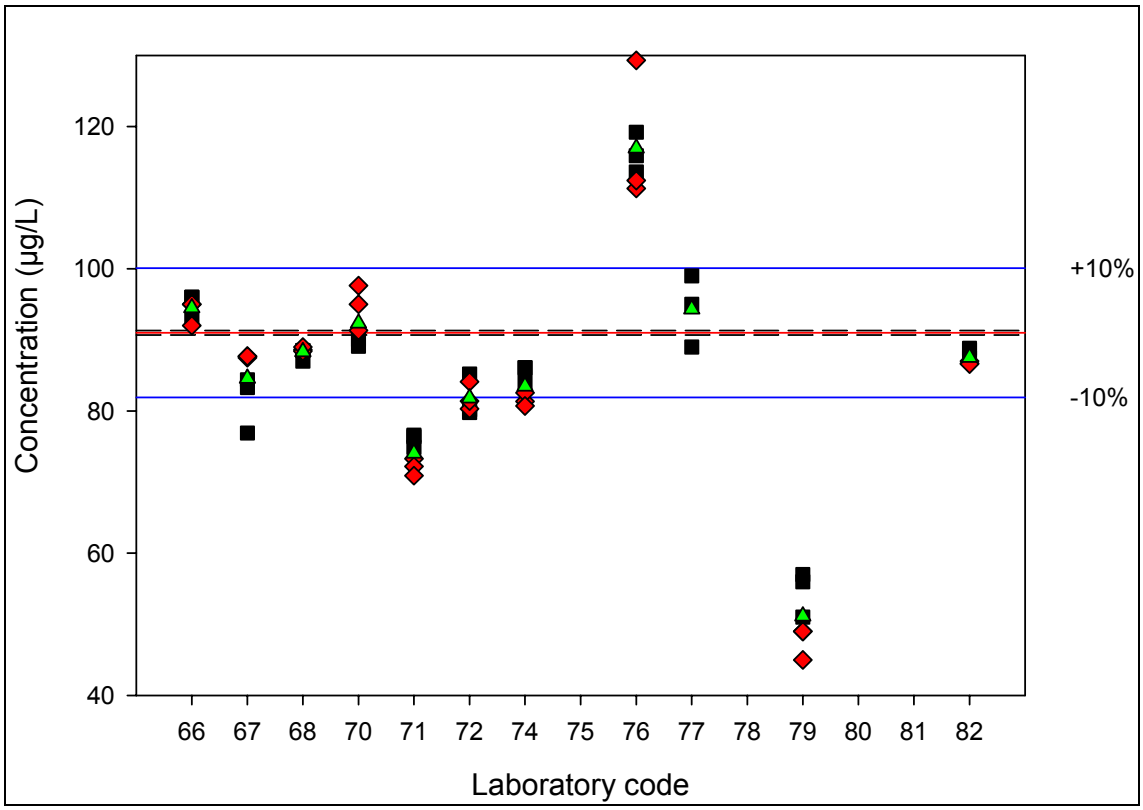


Figure 9: Kernel density plot of the reported results

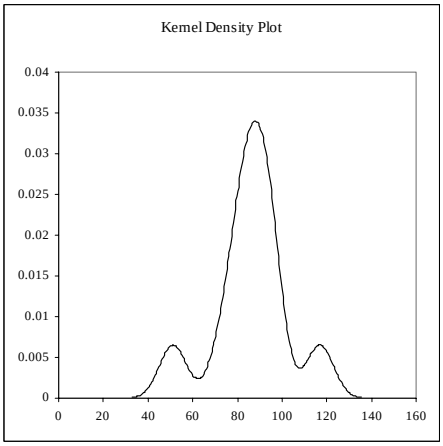


Figure 10: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

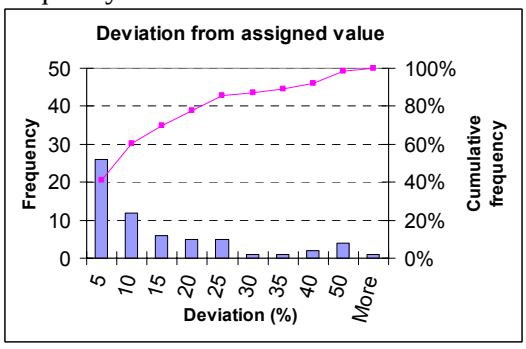


Table 5: **Benzo[*j*]fluoranthene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	93.00	9.00		95.00	9.00
66	96.00	10.00		95.00	9.00
66	96.00	10.00		92.00	9.00
67	76.90			87.50	
67	84.40			87.70	
67	83.30			87.70	
68	88.50	7.10		88.60	7.10
68	88.50	7.10		88.40	7.10
68	87.00	7.00		89.00	7.10
70	90.97			91.33	
70	89.09			95.02	
70	90.04			97.62	
71	76.60	13.80		73.30	13.20
71	76.40	13.80		72.20	13.00
71	74.90	13.50		70.90	12.80
72	85.20	5.80		84.10	5.70
72	79.80	5.40		80.30	5.50
72	80.20	5.50		81.40	5.50
74	86.08	2.33		81.35	1.88
74	84.07	2.33		82.55	1.88
74	86.09	2.33		80.70	1.88
75					
75					
75					
76	115.90	6.10		111.30	20.20
76	113.60	6.10		112.40	20.20
76	119.20	6.10		129.30	20.20
77	95.00	10.00			
77	99.00	11.00			
77	89.00	10.00			
78					
78					
78					
79	56.00	17.00		49.00	15.00
79	57.00	17.00		49.00	15.00
79	51.00	15.00		45.00	13.00
80					
80					
80					
81					
81					
81					
82	88.80	4.50		86.70	0.60
82	88.60	4.50		87.00	0.60
82	87.50	4.50		86.60	0.60
85					
85					
85					
87					
87					
87					

Sum of Benzo[*b*]fluoranthene and benzo[*j*]fluoranthene

Figure 11: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **143,4±0,5 µg/L**; the blue lines indicate a 10% deviation from the known value.

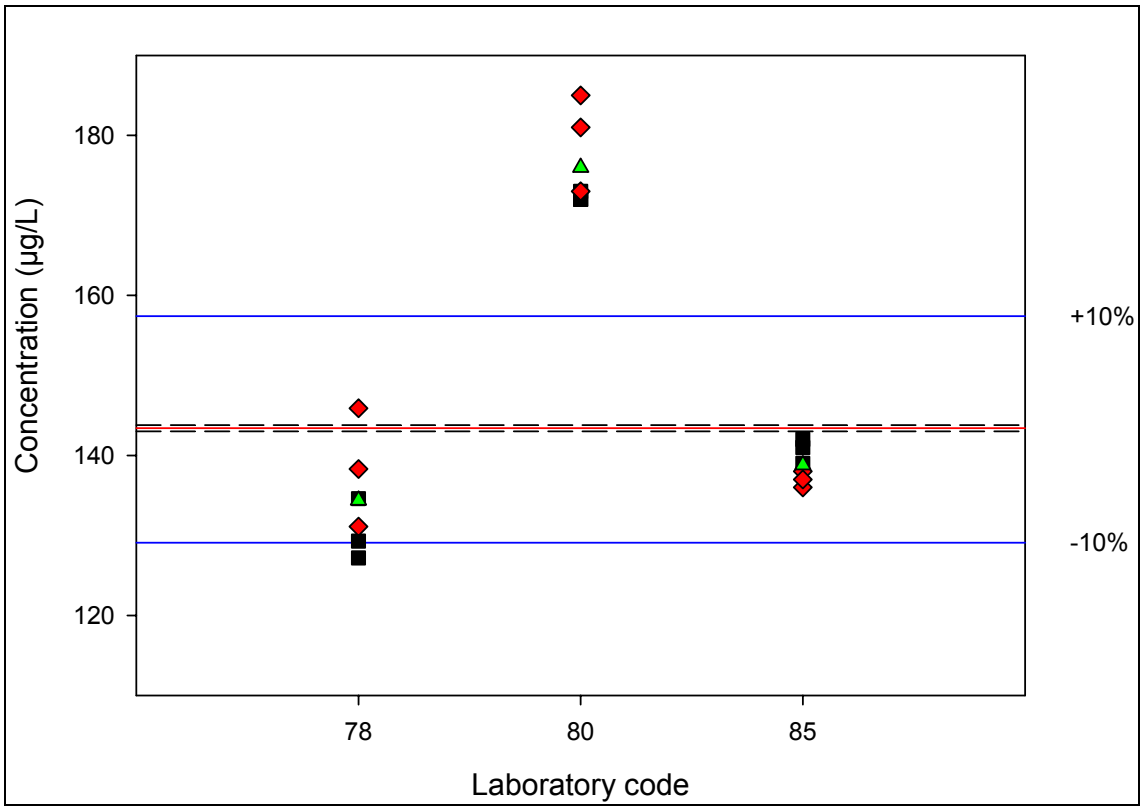


Table 6: **Sum of benzo[*b*]fluoranthene and benzo[*j*]fluoranthene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
78	127.2	25.4		145.9	21.9
78	134.6	20.2		138.3	30.7
78	129.3	19.4		131.1	19.7
80	172			181	
80	173			185	
80	172			173	
85	142			138	
85	139			136	
85	141			137	

Benzo[*k*]fluoranthene

Figure 12: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **39,15±0,21 µg/L**; the blue lines indicate a 10% deviation from the known value.

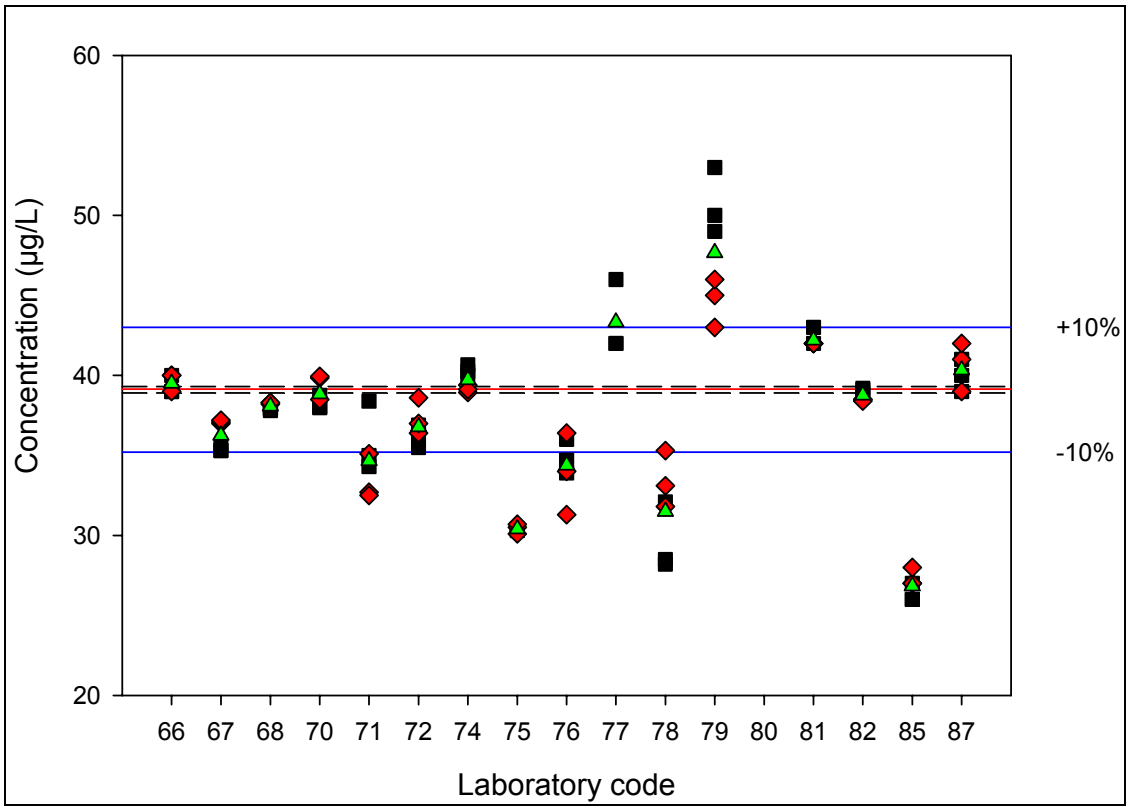


Figure 13: Kernel density plot of the reported results

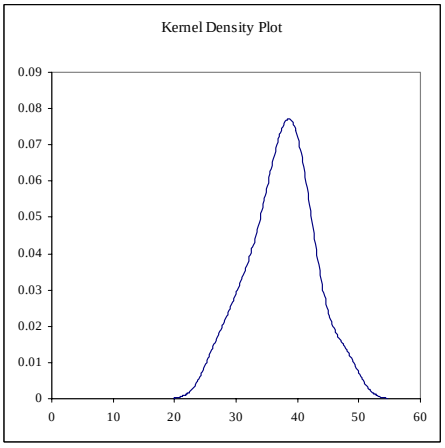


Figure 14: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

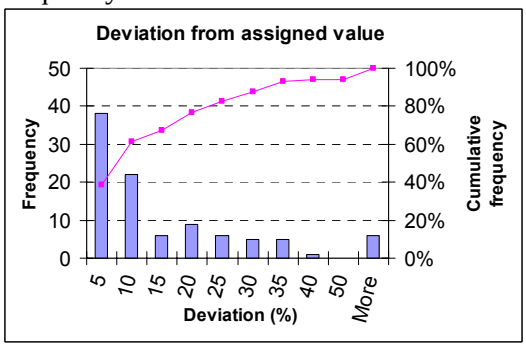


Table 7: **Benzo[*k*]fluoranthene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	39.00	4.00		39.00	4.00
66	40.00	4.00		40.00	4.00
66	39.00	4.00		40.00	4.00
67	35.60			37.00	
67	35.30			37.10	
67	35.30			37.20	
68	38.00	1.90		38.20	1.90
68	37.90	1.90		38.30	1.90
68	37.80	1.90		38.30	1.90
70	38.76			38.50	
70	37.98			39.84	
70	38.05			39.94	
71	38.40	6.90		35.10	6.30
71	34.30	6.20		32.70	5.90
71	35.00	6.30		32.50	5.80
72	36.30	1.60		36.40	1.60
72	35.50	1.50		37.00	1.60
72	36.90	1.60		38.60	1.70
74	40.25	0.66		39.39	0.46
74	40.01	0.66		38.93	0.46
74	40.67	0.66		39.13	0.46
75	30.30	3.40		30.50	3.80
75	30.40	1.50		30.10	1.80
75	30.40	1.70		30.70	3.10
76	34.70	2.10		34.00	5.20
76	33.90	2.10		31.30	5.20
76	36.00	2.10		36.40	5.20
77	42.00	5.00			
77	42.00	5.00			
77	46.00	5.00			
78	28.50	4.30		31.80	4.80
78	32.10	4.80		33.10	5.00
78	28.20	5.00		35.30	5.30
79	49.00	15.00		45.00	14.00
79	53.00	16.00		43.00	13.00
79	50.00	15.00		46.00	14.00
80					
80					
80					
81	42.00	2.00		42.00	2.00
81	43.00	2.00		42.00	2.00
81				42.00	2.00
82	39.20	1.60		38.50	0.40
82	39.10	1.60		38.50	0.40
82	38.90	1.60		38.40	0.40
85	27.00			27.00	
85	26.00			27.00	
85	26.00			28.00	
87	39.00	0.50		39.00	0.50
87	40.00	0.50		41.00	0.50
87	41.00	0.50		42.00	0.50

Benzo[*c*]fluorene

Figure 15: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **36,11±0,25 µg/L**; the blue lines indicate a 10% deviation from the known value.

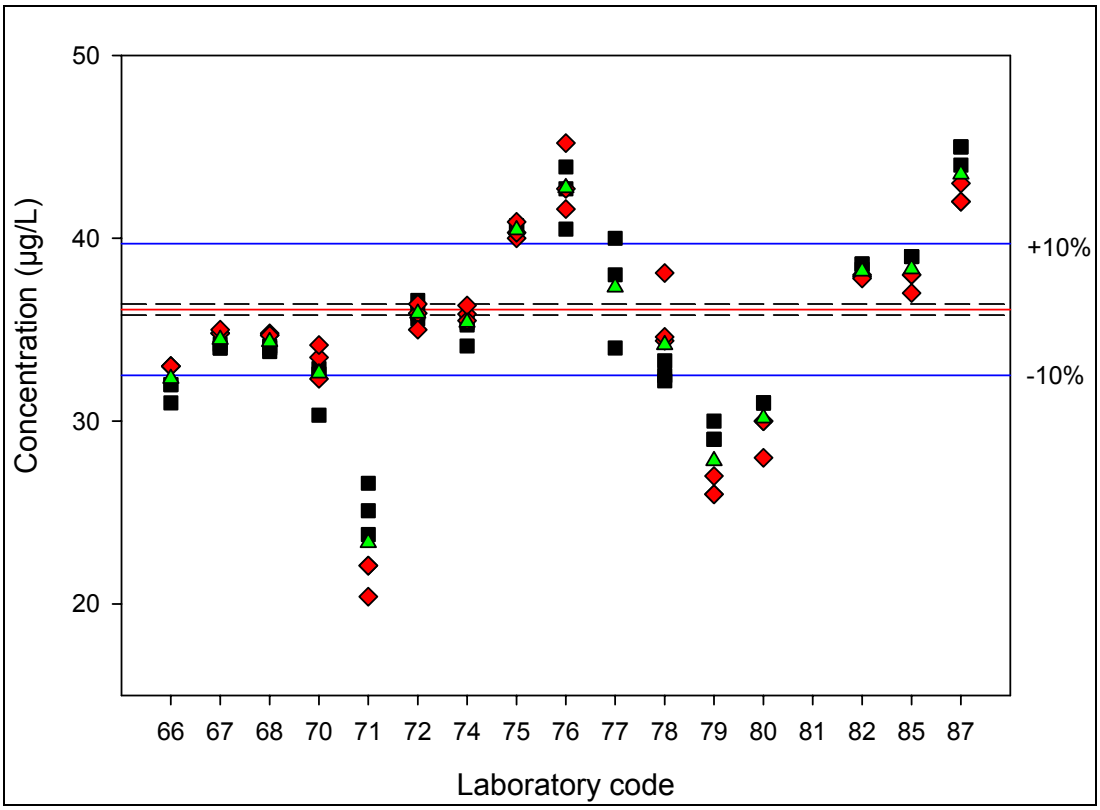


Figure 16: Kernel density plot of the reported results

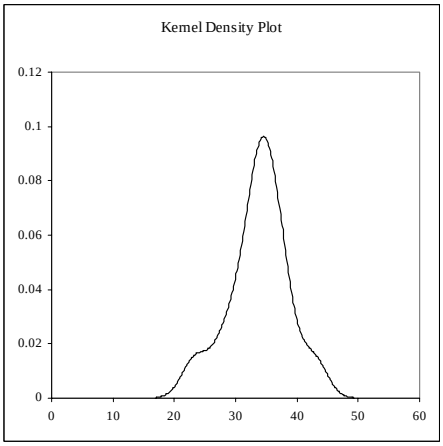


Figure 17: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

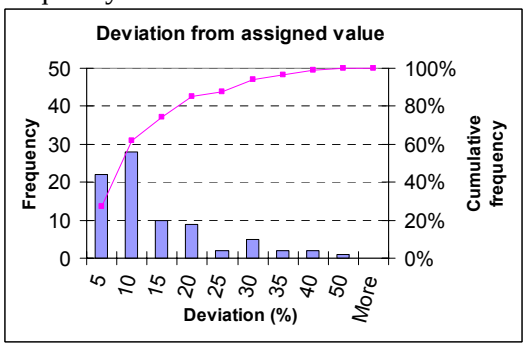


Table 8: **Benzo[*c*]fluorene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	32.00	3.00		33.00	3.00
66	32.00	3.00		33.00	3.00
66	31.00	3.00		33.00	3.00
67	34.20			34.80	
67	34.00			34.80	
67	34.00			35.00	
68	34.10	1.70		34.70	1.70
68	34.00	1.70		34.80	1.70
68	33.80	1.70		34.70	1.70
70	32.58			32.31	
70	30.33			33.49	
70	32.88			34.16	
71	26.60			22.10	
71	25.10			22.10	
71	23.80			20.40	
72	35.90	1.80		35.90	1.80
72	35.60	1.80		35.00	1.80
72	36.60	1.80		36.40	1.80
74	35.26	1.40		35.86	0.83
74	34.12	1.40		35.49	0.83
74	35.39	1.40		36.32	0.83
75					
75					
75					
76	42.70	3.40		41.60	1.20
76	40.50	3.40		42.70	1.20
76	43.90	3.40		45.20	1.20
77	38.00	6.00			
77	40.00	6.00			
77	34.00	5.00			
78	32.20	4.80		38.10	5.70
78	33.30	5.00		34.40	5.20
78	32.50	4.90		34.60	5.20
79	30.00	9.00		27.00	8.00
79	29.00	9.00		26.00	8.00
79	29.00	9.00		26.00	8.00
80	31.00			30.00	
80	31.00			30.00	
80	31.00			28.00	
81					
81					
81					
82	38.60	1.40		38.00	0.40
82	38.60	1.40		37.90	0.40
82	38.30	1.40		37.80	0.40
85	39.00			37.00	
85	39.00			38.00	
85	39.00			38.00	
87					
87					
87					

Benzo[*ghi*]perylene

Figure 18: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **53,46±0,28 µg/L**; the blue lines indicate a 10% deviation from the known value.

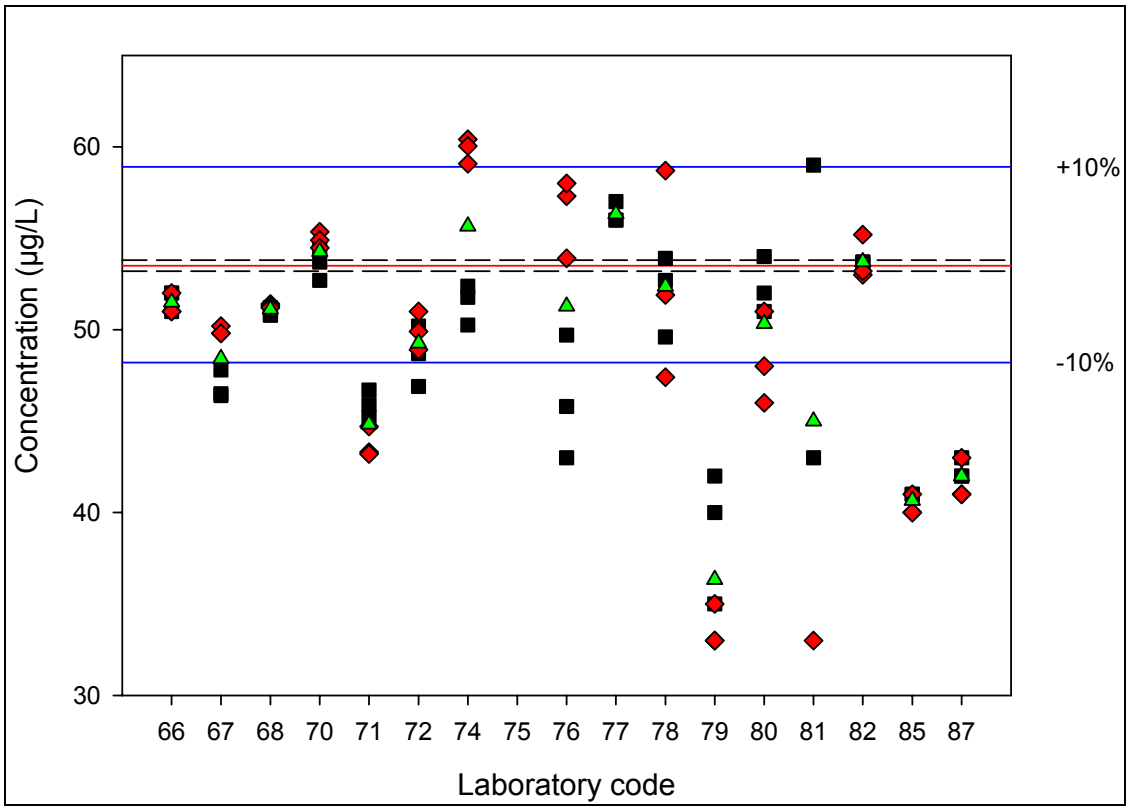


Figure 19: Kernel density plot of the reported results

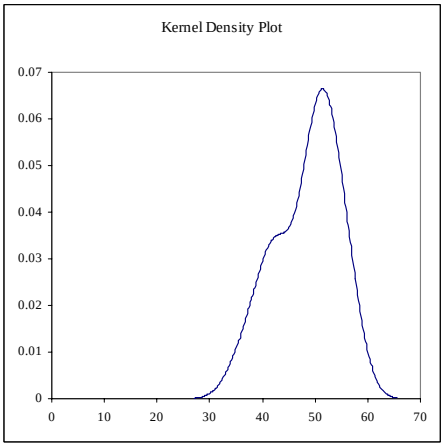


Figure 20: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

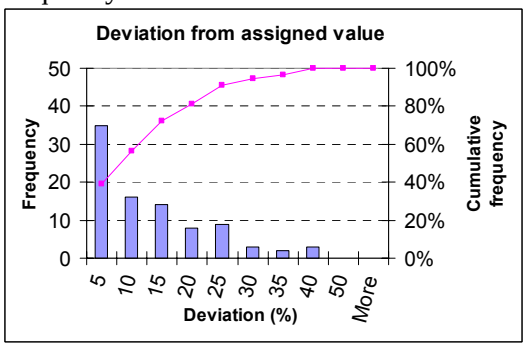


Table 9: **Benzo[*ghi*]perylene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	52.00	5.00		52.00	5.00
66	51.00	5.00		51.00	5.00
66	52.00	5.00		51.00	5.00
67	46.50			49.80	
67	46.40			50.20	
67	47.80			49.80	
68	51.20	2.60		51.40	2.60
68	50.80	2.50		51.30	2.60
68	50.80	2.50		51.20	2.60
70	53.69			55.35	
70	52.70			54.90	
70	54.51			54.47	
71	45.20	14.00		43.30	13.40
71	46.70	14.50		44.70	13.80
71	45.90	14.20		43.20	13.40
72	48.70	2.40		48.90	2.40
72	46.90	2.30		51.00	2.50
72	50.20	2.50		49.90	2.50
74	52.38	2.19		59.07	1.38
74	50.25	2.19		60.41	1.38
74	51.77	2.19		60.05	1.38
75					
75					
75					
76	43.00	6.70		53.90	4.40
76	45.80	6.70		57.30	4.40
76	49.70	6.70		58.00	4.40
77	57.00	3.00			
77	56.00	3.00			
77	56.00	3.00			
78	52.70	10.50		51.90	9.80
78	53.90	10.80		47.40	9.50
78	49.60	9.90		58.70	11.70
79	42.00	13.00		35.00	11.00
79	40.00	12.00		33.00	10.00
79	35.00	10.00		33.00	10.00
80	51.00			48.00	
80	54.00			51.00	
80	52.00			46.00	
81	59.00	5.00		33.00	
81	43.00	5.00			
81					
82	53.50	2.00		53.00	1.60
82	53.70	2.00		55.20	1.60
82	53.70	2.00		53.20	1.60
85	41.00			40.00	
85	41.00			40.00	
85	41.00			41.00	
87	42.00	0.50		43.00	0.50
87	42.00	0.50		41.00	0.50
87	43.00	0.50		41.00	0.50

Benzo[*a*]pyrene

Figure 21: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **97,9±0,5 µg/L**; the blue lines indicate a 10% deviation from the known value.

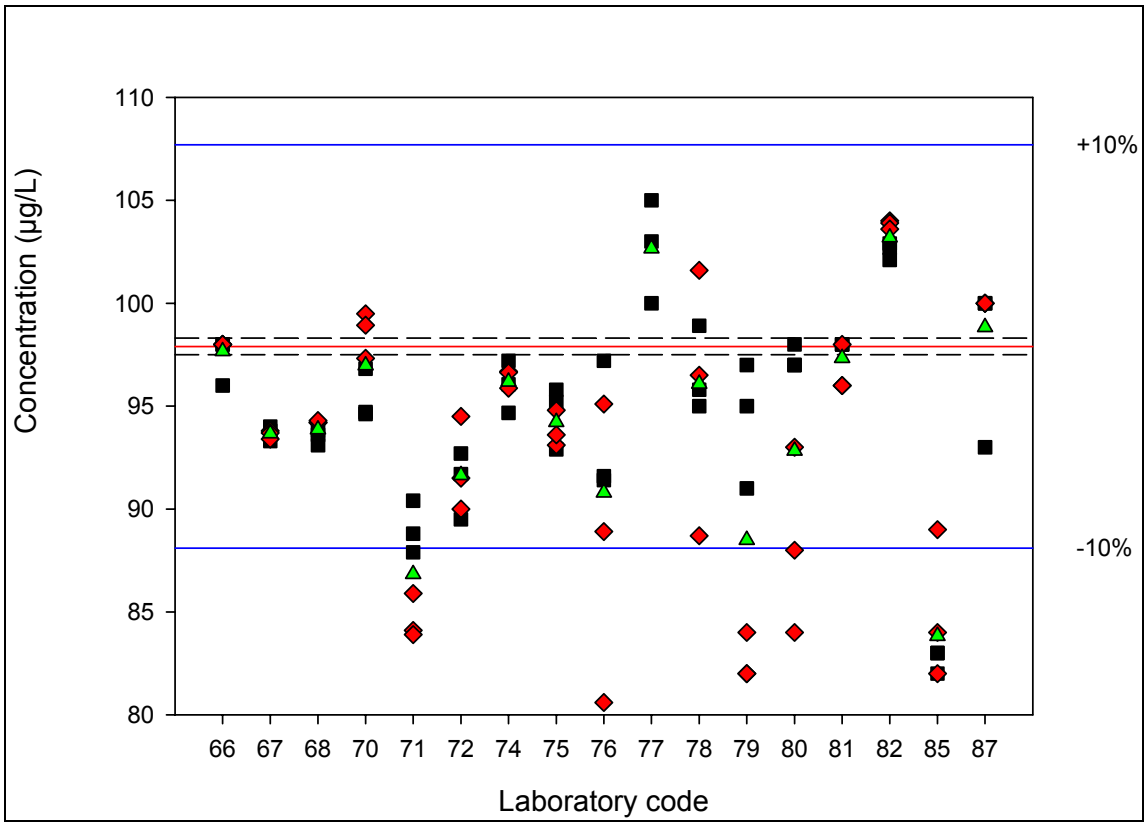


Figure 22: Kernel density plot of the reported results

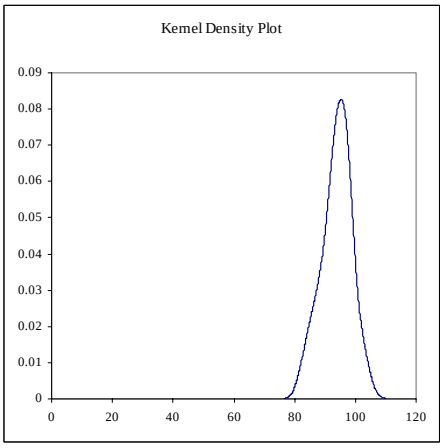


Figure 23: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

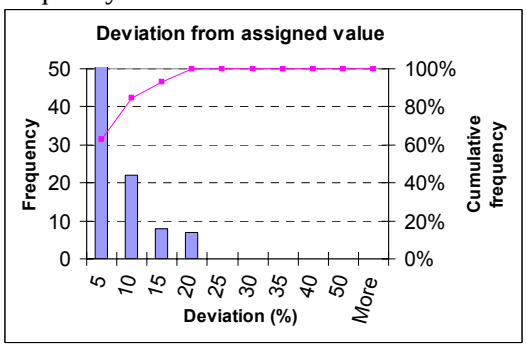


Table 10: **Benzo[*a*]pyrene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	96.00	10.00		98.00	10.00
66	98.00	10.00		98.00	10.00
66	98.00	10.00		98.00	10.00
67	94.00			93.80	
67	93.80			93.70	
67	93.30			93.40	
68	93.80	4.70		94.20	4.70
68	93.60	4.70		94.20	4.70
68	93.10	4.70		94.30	4.70
70	94.62			97.32	
70	94.71			99.49	
70	96.81			98.93	
71	88.80	8.90		85.90	8.60
71	90.40	9.00		84.10	8.40
71	87.90	8.80		83.90	8.40
72	91.70	4.80		91.50	4.80
72	89.50	4.70		90.00	4.80
72	92.70	4.90		94.50	5.00
74	97.20	2.53		96.68	0.91
74	94.67	2.53		96.63	0.91
74	96.06	2.53		95.87	0.91
75	92.90	9.60		93.10	10.60
75	95.80	11.30		93.60	11.00
75	95.20	10.50		94.80	8.50
76	91.40	6.70		95.10	14.50
76	91.60	6.70		80.60	14.50
76	97.20	6.70		88.90	14.50
77	105.00	6.00			
77	103.00	6.00			
77	100.00	6.00			
78	95.80	14.40		96.50	14.50
78	98.90	14.80		88.70	13.30
78	95.00	14.30		101.60	15.20
79	95.00	28.00		82.00	25.00
79	97.00	29.00		84.00	25.00
79	91.00	27.00		82.00	25.00
80	97.00			88.00	
80	97.00			93.00	
80	98.00			84.00	
81	98.00	2.00		96.00	2.00
81	98.00	2.00		96.00	2.00
81	98.00	2.00		98.00	2.00
82	102.10	1.00		104.00	0.80
82	102.70	1.00		103.90	0.80
82	102.90	1.00		103.60	0.80
85	83.00			84.00	
85	82.00			82.00	
85	83.00			89.00	
87	93.00	0.50		100.00	0.50
87	100.00	0.50		100.00	0.50
87	100.00	0.50		100.00	0.50

Chrysene

Figure 24: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **53,6±0,5 µg/L**; the blue lines indicate a 10% deviation from the known value.

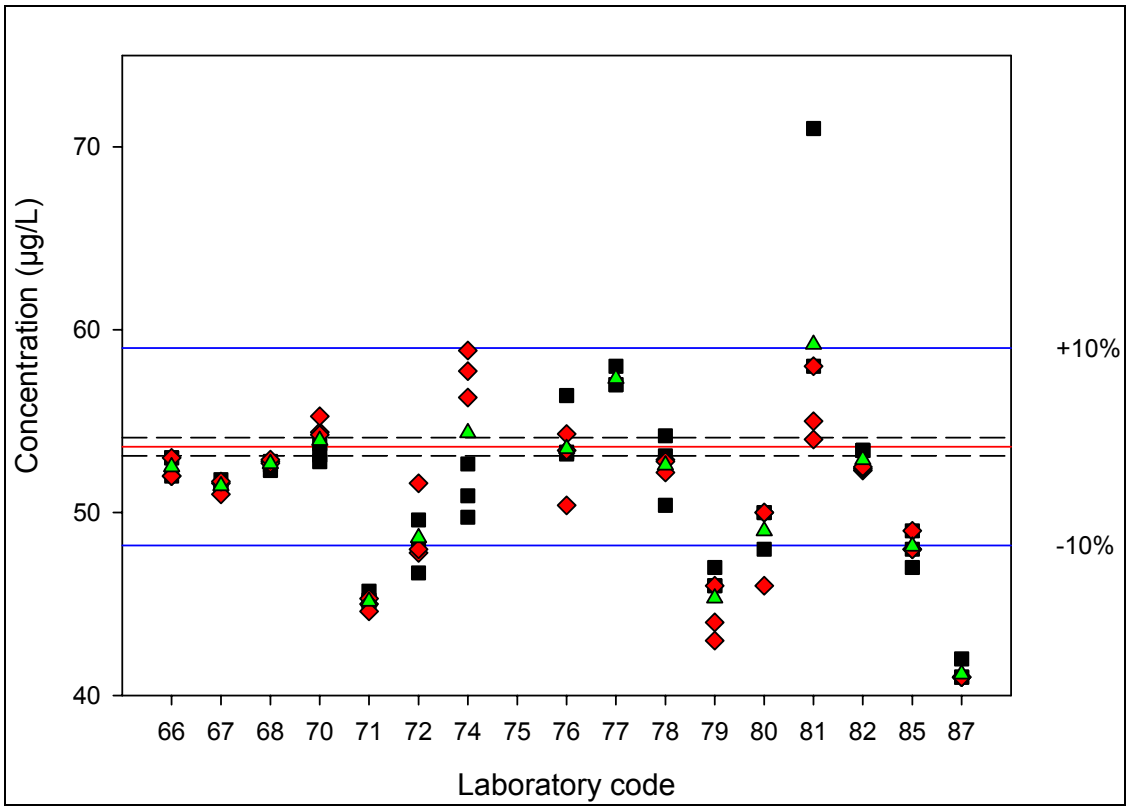


Figure 25: Kernel density plot of the reported results

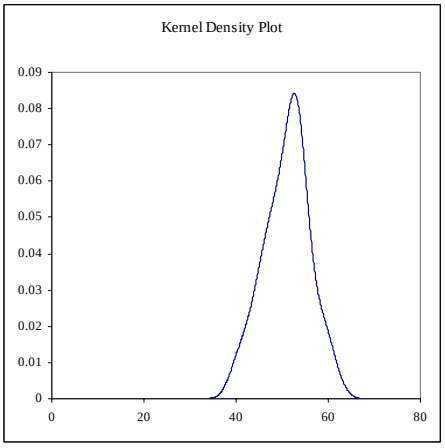


Figure 26: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

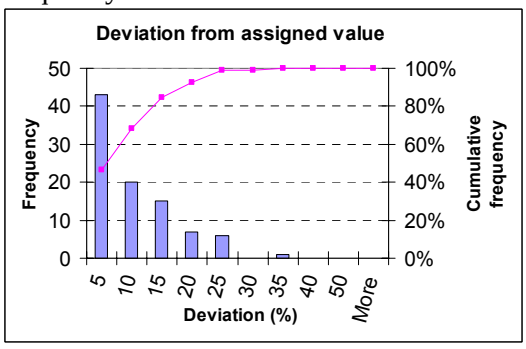


Table 11: **Chrysene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	53.00	5.00		53.00	5.00
66	53.00	5.00		52.00	5.00
66	52.00	5.00		52.00	5.00
67	51.80			51.60	
67	51.30			51.00	
67	51.40			51.70	
68	52.80	2.60		52.80	2.60
68	52.60	2.60		52.70	2.60
68	52.30	2.60		52.90	2.60
70	52.79			54.40	
70	53.15			55.27	
70	53.78			54.26	
71	45.10	11.30		45.30	11.30
71	45.20	11.30		45.00	11.20
71	45.70	11.40		44.60	11.20
72	48.10	2.60		47.80	2.60
72	46.70	2.50		48.00	2.60
72	49.60	2.70		51.60	2.80
74	50.92	2.93		57.74	2.58
74	52.66	2.93		56.29	2.58
74	49.74	2.93		58.87	2.58
75					
75					
75					
76	53.30	3.70		53.40	4.10
76	53.20	3.70		50.40	4.10
76	56.40	3.70		54.30	4.10
77	58.00	6.00			
77	57.00	6.00			
77	57.00	6.00			
78	50.40	7.60		52.90	7.90
78	54.20	8.10		52.80	7.90
78	53.10	8.00		52.20	7.80
79	46.00	14.00		46.00	14.00
79	47.00	14.00		44.00	13.00
79	46.00	14.00		43.00	13.00
80	50.00			50.00	
80	48.00			50.00	
80	50.00			46.00	
81	58.00	5.00		54.00	4.00
81	71.00	5.00		55.00	4.00
81				58.00	4.00
82	53.40	2.20		52.30	0.60
82	53.40	2.20		52.40	0.60
82	53.40	2.20		52.50	0.60
85	48.00			48.00	
85	49.00			49.00	
85	47.00			48.00	
87	42.00	0.50		41.00	0.50
87	41.00	0.50		41.00	0.50
87	41.00	0.50		41.00	0.50

Cyclopenta[*cd*]pyrene

Figure 27: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **43,78±0,21 µg/L**; the blue lines indicate a 10% deviation from the known value.

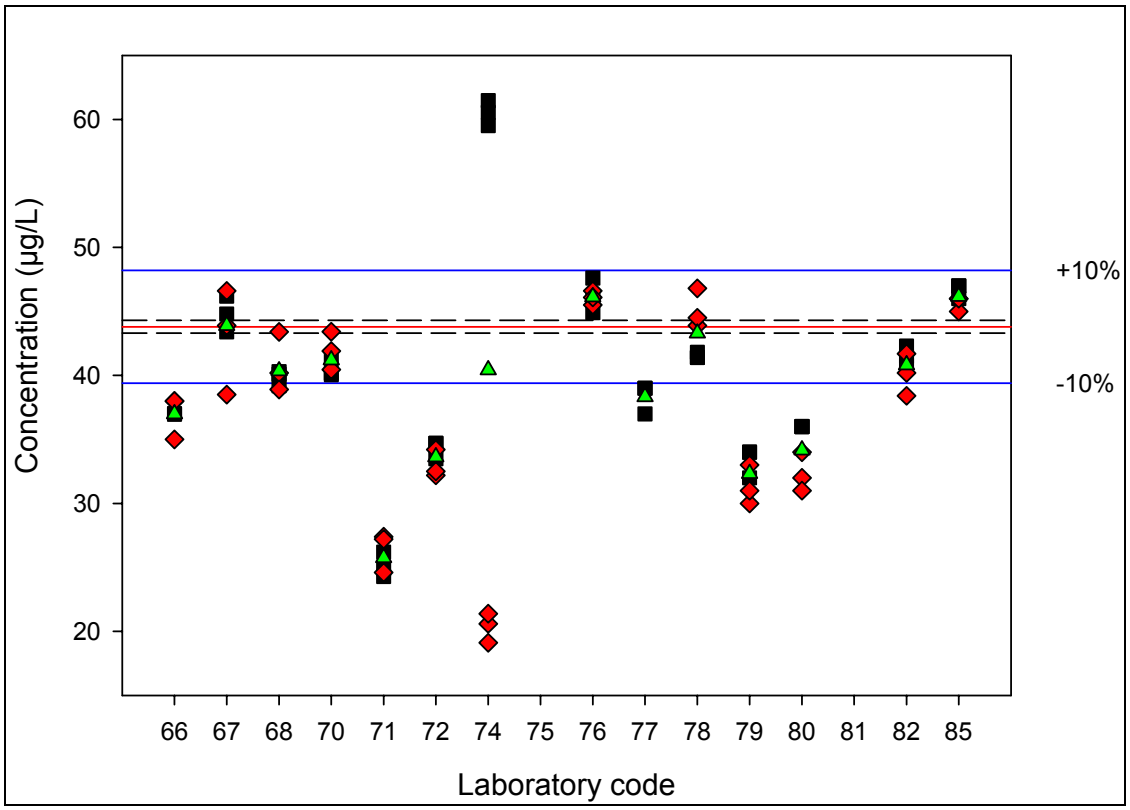


Figure 28: Kernel density plot of the reported results

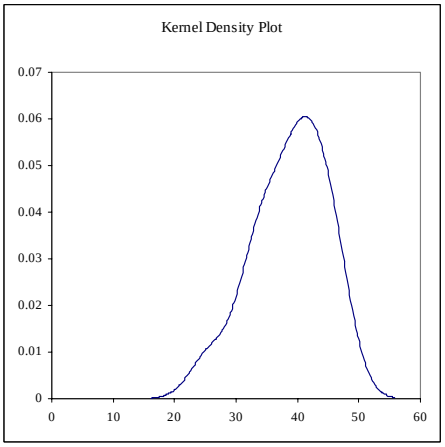


Figure 29: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

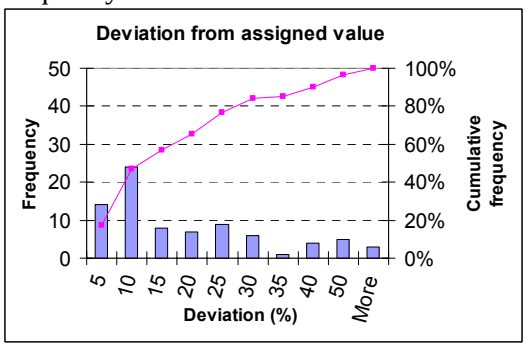


Table 12: **Cyclopenta[*cd*]pyrene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	37.00	4.00		38.00	4.00
66	37.00	4.00		38.00	4.00
66	37.00	4.00		35.00	4.00
67	44.80			43.90	
67	46.20			46.60	
67	43.40			38.50	
68	40.30	3.20		40.20	3.20
68	39.20	3.10		43.40	3.50
68	40.10	3.20		38.90	3.10
70	40.17			43.42	
70	41.32			40.45	
70	40.05			41.90	
71	26.20	6.60		27.40	6.80
71	24.90	6.20		27.20	6.80
71	24.30	6.10		24.60	6.20
72	34.70	3.50		34.20	3.40
72	34.70	3.50		32.20	3.20
72	33.50	3.40		32.50	3.30
74	61.46	1.94		19.11	2.31
74	59.52	1.94		20.59	2.31
74	60.55	1.94		21.39	2.31
75					
75					
75					
76	47.60	2.80		46.60	1.10
76	44.90	2.80		45.50	1.10
76	46.10	2.80		46.10	1.10
77	39.00	4.00			
77	37.00	4.00			
77	39.00	4.00			
78	41.40	8.30		43.90	8.80
78	41.80	8.40		46.80	9.40
78	41.40	8.30		44.50	8.70
79	34.00	10.00		33.00	10.00
79	34.00	10.00		30.00	9.00
79	32.00	10.00		31.00	9.00
80	36.00			32.00	
80	36.00			34.00	
80	36.00			31.00	
81					
81					
81					
82	42.30	3.80		38.40	3.50
82	40.80	3.60		41.70	3.80
82	41.50	3.70		40.20	3.70
85	47.00			46.00	
85	46.00			45.00	
85	47.00			46.00	
87					
87					
87					

Dibenz[*a,h*]anthracene

Figure 30: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **52,8±0,4 µg/L**; the blue lines indicate a 10% deviation from the known value.

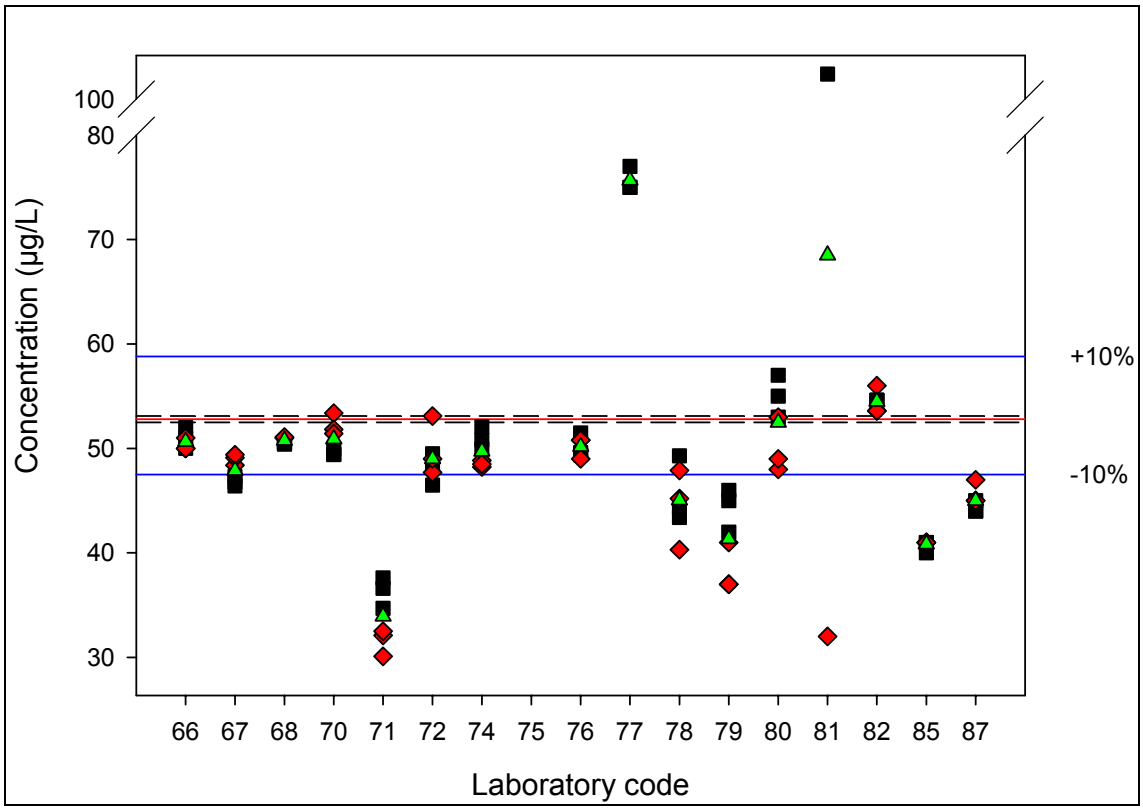


Figure 31: Kernel density plot of the reported results

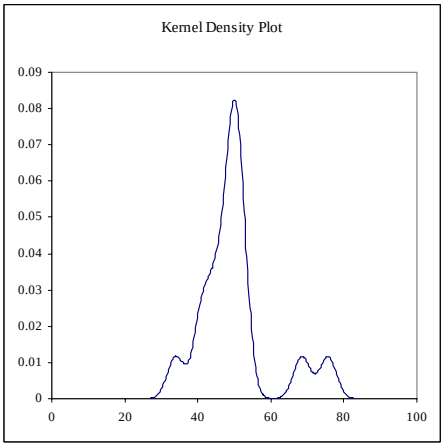


Figure 32: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

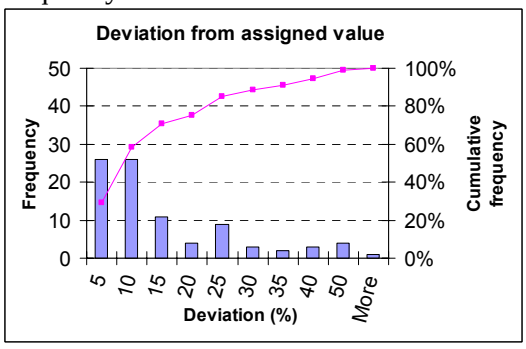


Table 13: **Dibenz[*a,h*]anthracene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	52.00	5.00		50.00	5.00
66	51.00	5.00		51.00	5.00
66	50.00	5.00		50.00	5.00
67	47.30			48.40	
67	46.40			49.10	
67	46.80			49.40	
68	50.60	2.50		51.00	2.50
68	50.50	2.50		51.00	2.50
68	50.40	2.50		51.10	2.60
70	49.43			53.37	
70	49.41			51.82	
70	49.98			51.43	
71	36.60	11.30		32.10	9.90
71	37.60	11.60		32.50	10.10
71	34.70	10.80		30.10	9.30
72	48.20	3.90		47.70	3.80
72	46.50	3.70		49.00	3.90
72	49.50	3.90		53.10	4.20
74	52.07	2.11		48.84	0.62
74	49.97	2.11		48.22	0.62
74	50.80	2.11		48.49	0.62
75					
75					
75					
76	49.40	2.30		50.80	2.10
76	51.50	2.30		49.00	2.10
76	49.60	2.30		50.80	2.10
77	77.00	8.00			
77	75.00	8.00			
77	75.00	8.00			
78	43.40	6.50		45.20	6.80
78	49.30	7.40		40.30	6.00
78	44.30	6.60		47.90	7.20
79	46.00	14.00		41.00	12.00
79	45.00	14.00		37.00	11.00
79	42.00	12.00		37.00	11.00
80	55.00			48.00	
80	57.00			53.00	
80	53.00			49.00	
81	105.00			32.00	
81					
81					
82	54.60	2.20		53.60	1.80
82	54.60	2.20		56.00	1.90
82	54.60	2.20		53.60	1.80
85	40.00			41.00	
85	41.00			41.00	
85	41.00			41.00	
87	44.00	0.50		45.00	0.50
87	44.00	0.50		45.00	0.50
87	45.00	0.50		47.00	0.50

Dibenzo[*a,e*]pyrene

Figure 33: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **70,0±0,4 µg/L**; the blue lines indicate a 10% deviation from the known value.

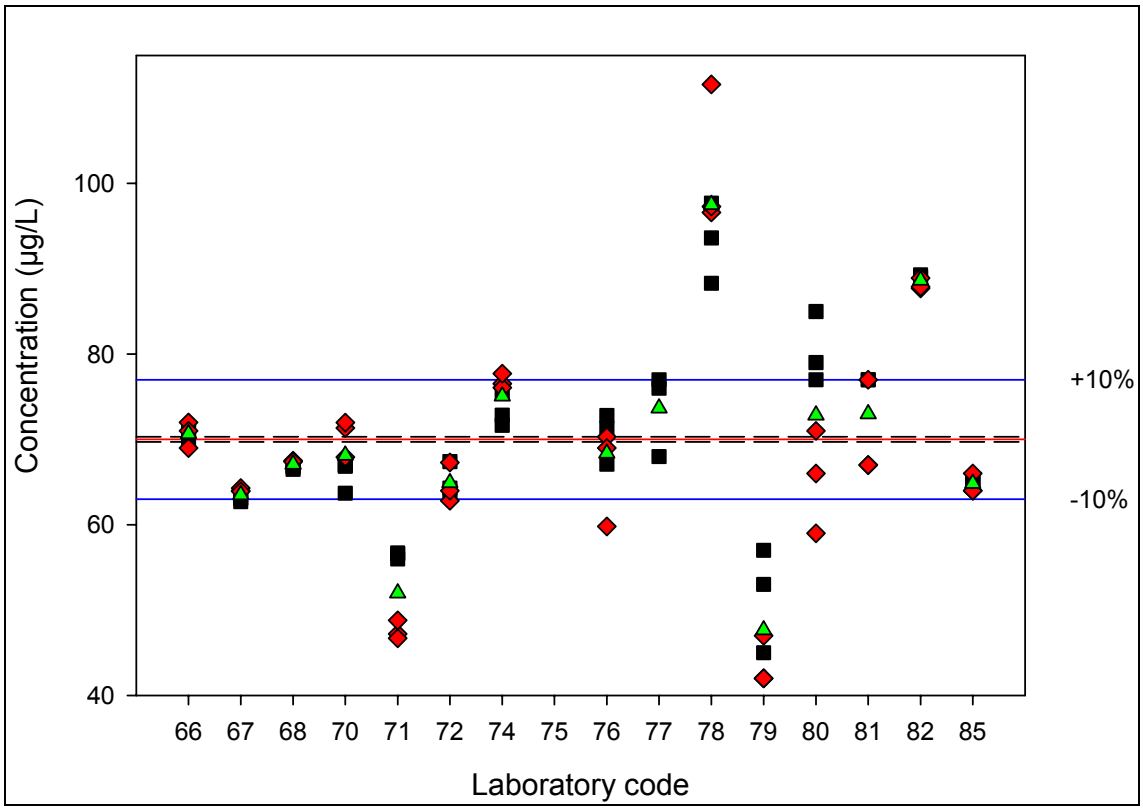


Figure 34: Kernel density plot of the reported results

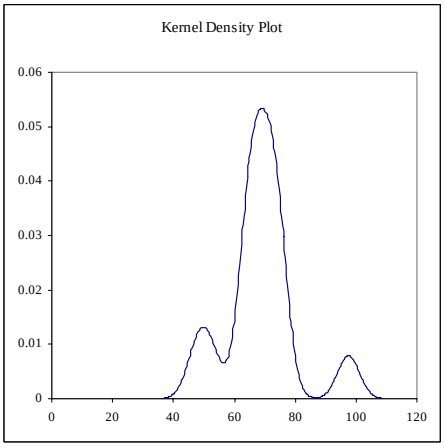


Figure 35: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

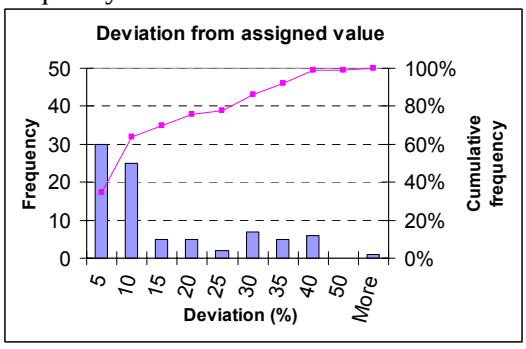


Table 14: **Dibenzo[*a,e*]pyrene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	71.00	7.00		72.00	7.00
66	71.00	7.00		71.00	7.00
66	70.00	7.00		69.00	7.00
67	63.10			64.00	
67	62.70			64.30	
67	63.10			63.90	
68	66.90	3.30		67.40	3.40
68	66.80	3.30		67.50	3.40
68	66.50	3.30		67.40	3.40
70	67.01			67.93	
70	63.70			71.35	
70	66.85			71.97	
71	56.60			47.20	
71	56.00			46.70	
71	56.70			48.80	
72	64.30	2.30		62.80	2.20
72	63.80	2.20		64.00	2.20
72	67.40	2.40		67.30	2.30
74	75.59	4.04		76.53	1.70
74	71.65	4.04		76.05	1.70
74	72.84	4.04		77.71	1.70
75					
75					
75					
76	72.80	6.00		70.30	11.50
76	67.10	6.00		59.80	11.50
76	71.30	6.00		69.00	11.50
77	77.00	8.00			
77	76.00	8.00			
77	68.00	7.00			
78	88.30	22.10		111.60	27.90
78	93.60	23.40		96.60	24.20
78	97.70	24.40		97.30	24.30
79	57.00	17.00		47.00	14.00
79	53.00	16.00		42.00	13.00
79	45.00	14.00		42.00	13.00
80	79.00			59.00	
80	85.00			71.00	
80	77.00			66.00	
81	77.00	2.00		67.00	3.00
81	77.00	2.00		67.00	3.00
81				77.00	3.00
82	89.10	4.10		87.70	1.00
82	89.30	4.10		88.90	1.00
82	89.00	4.10		87.90	1.00
85	65.00			64.00	
85	65.00			64.00	
85	65.00			66.00	
87					
87					
87					

Dibenzo[*a,h*]pyrene

Figure 36: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **68,72±0,19 µg/L**; the blue lines indicate a 10% deviation from the known value.

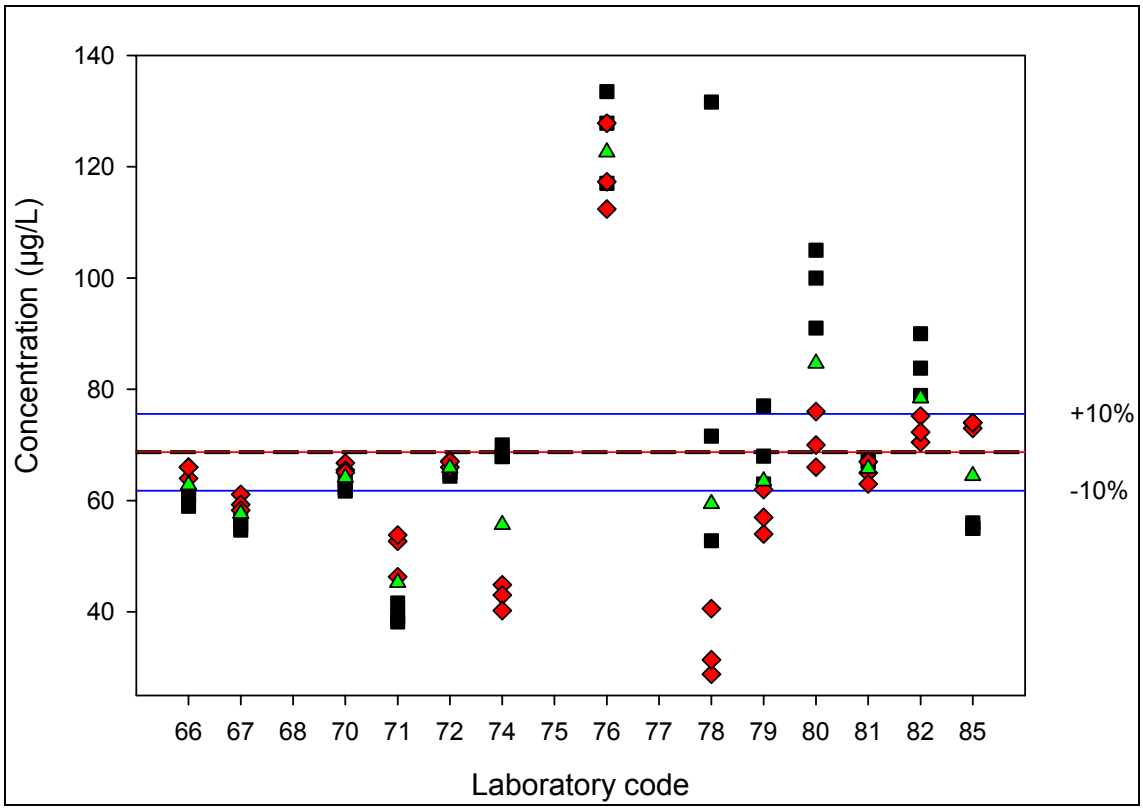


Figure 37: Kernel density plot of the reported results

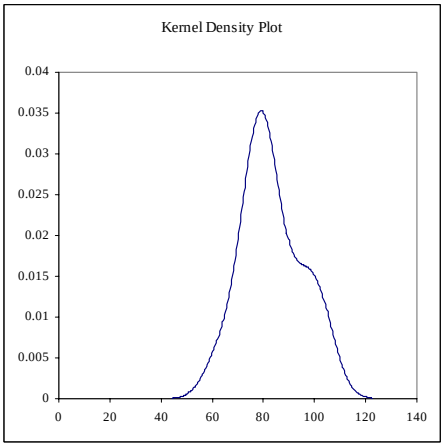


Figure 38: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

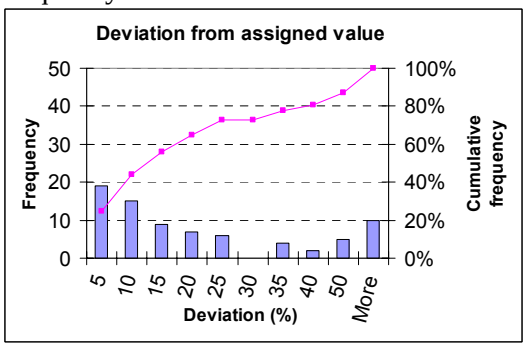


Table 15: **Dibenzo[*a,h*]pyrene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	61.00	6.00		66.00	7.00
66	59.00	6.00		64.00	6.00
66	61.00	6.00		66.00	7.00
67	54.70			61.10	
67	55.50			59.30	
67	57.20			58.30	
68					
68					
68					
70	63.71			66.76	
70	62.27			65.50	
70	61.73			65.06	
71	39.20			46.30	
71	41.60			52.70	
71	38.20			53.80	
72	65.80	5.30		67.10	4.70
72	64.40	5.20		66.00	4.60
72	65.10	5.20		67.00	4.70
74	70.01	2.39		44.88	4.66
74	67.90	2.39		43.03	4.66
74	67.98	2.39		40.25	4.66
75					
75					
75					
76	133.50	16.70		127.80	15.70
76	127.80	16.70		117.30	15.70
76	117.00	16.70		112.40	15.70
77					
77					
77					
78	52.80	13.20		28.80	7.20
78	131.60	32.90		31.40	7.90
78	71.60	17.90		40.60	10.20
79	77.00	23.00		62.00	18.00
79	63.00	19.00		54.00	16.00
79	68.00	20.00		57.00	17.00
80	100.00			66.00	
80	105.00			76.00	
80	91.00			70.00	
81	67.00	2.00		65.00	2.00
81	67.00	2.00		63.00	2.00
81				67.00	2.00
82	90.00	19.80		75.20	5.80
82	83.80	18.40		70.50	5.50
82	78.90	17.30		72.30	5.60
85	55.00			74.00	
85	55.00			73.00	
85	56.00			74.00	
87					
87					
87					

Dibenzo[*a,i*]pyrene

Figure 39: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **85,8±0,6 µg/L**; the blue lines indicate a 10% deviation from the known value.

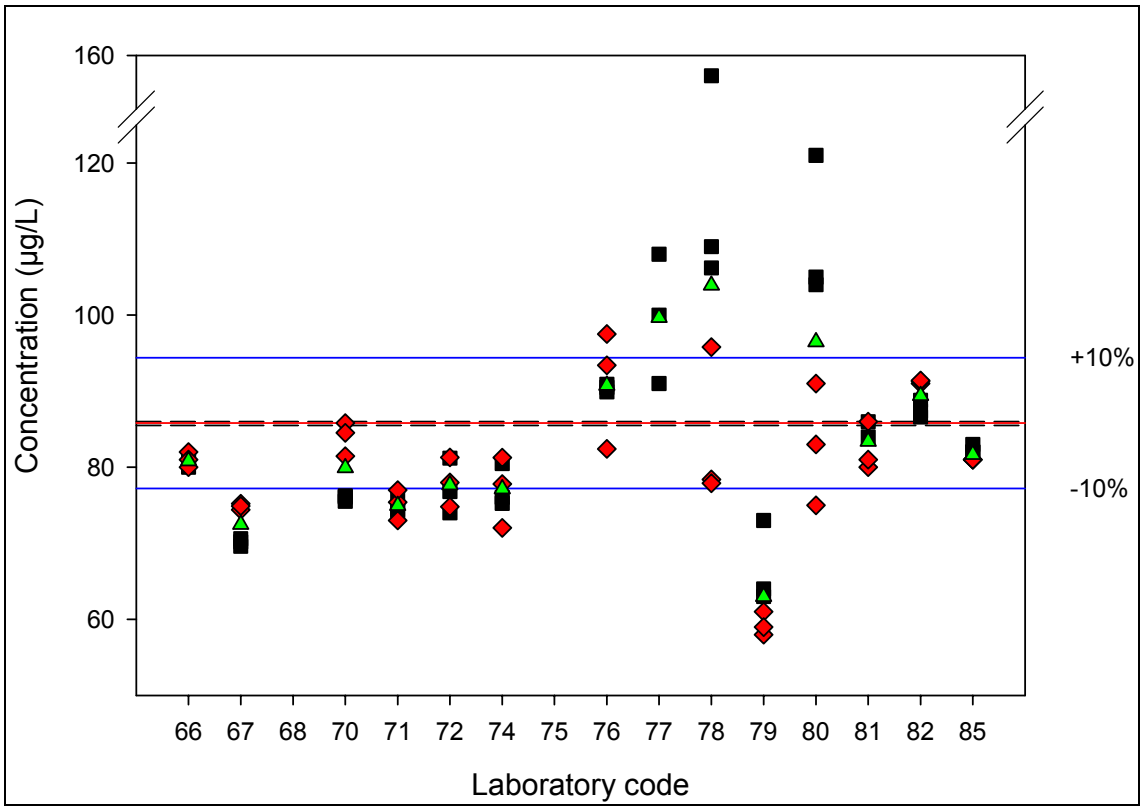


Figure 40: Kernel density plot of the reported results

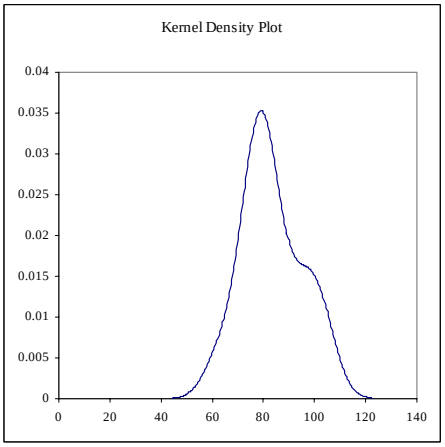


Figure 41: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

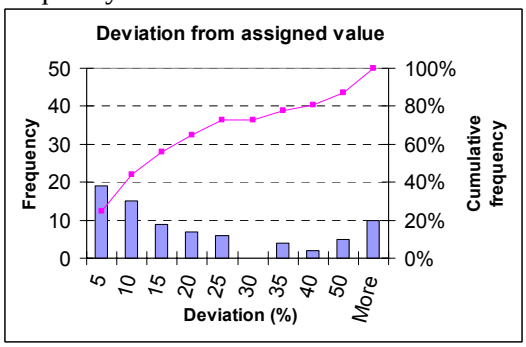


Table 16: **Dibenzo[*a,i*]pyrene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	81.00	8.00		82.00	8.00
66	81.00	8.00		81.00	8.00
66	80.00	8.00		80.00	8.00
67	70.20			75.20	
67	69.60			74.40	
67	70.60			74.90	
68					
68					
68					
70	76.26			81.45	
70	76.07			85.80	
70	75.52			84.52	
71	74.40			73.00	
71	75.90			75.40	
71	74.20			77.00	
72	81.20	6.50		81.30	6.50
72	76.80	6.10		78.00	6.20
72	74.00	5.90		74.80	6.00
74	80.49	5.64		81.27	9.35
74	75.26	5.64		77.80	9.35
74	76.04	5.64		72.02	9.35
75					
75					
75					
76	90.50	1.00		93.40	15.70
76	90.90	1.00		97.50	15.70
76	89.90	1.00		82.40	15.70
77	91.00	15.00			
77	108.00	18.00			
77	100.00	17.00			
78	109.00	27.00		78.40	19.60
78	156.20	39.10		77.90	19.50
78	106.20	26.60		95.80	24.00
79	73.00	22.00		61.00	18.00
79	63.00	19.00		58.00	17.00
79	64.00	19.00		59.00	18.00
80	104.00			75.00	
80	121.00			91.00	
80	105.00			83.00	
81	84.00	2.00		80.00	4.00
81	86.00	2.00		81.00	4.00
81				86.00	4.00
82	87.40	1.80		91.00	4.90
82	88.80	1.80		91.30	4.90
82	86.60	1.80		91.40	4.90
85	83.00			81.00	
85	82.00			81.00	
85	82.00			81.00	
87					
87					
87					

Dibenzo[*a,l*]pyrene

Figure 42: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **56,81±0,25 µg/L**; the blue lines indicate a 10% deviation from the known value.

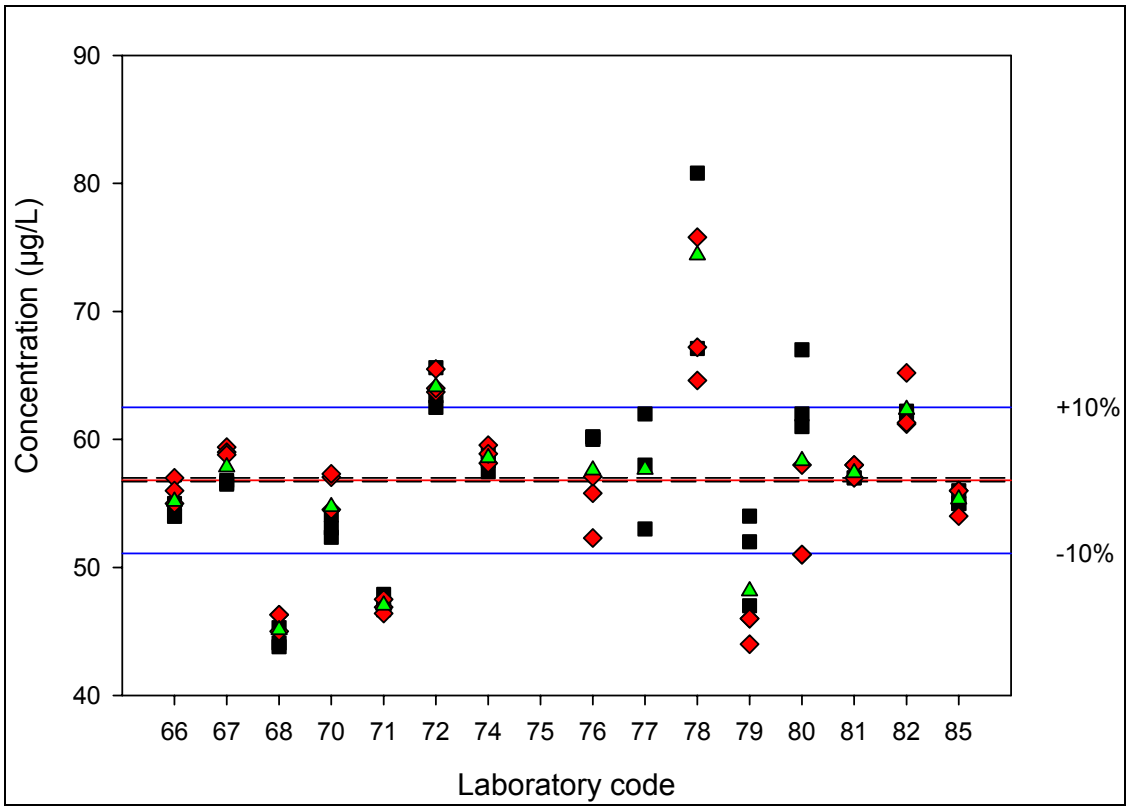


Figure 43: Kernel density plot of the reported results

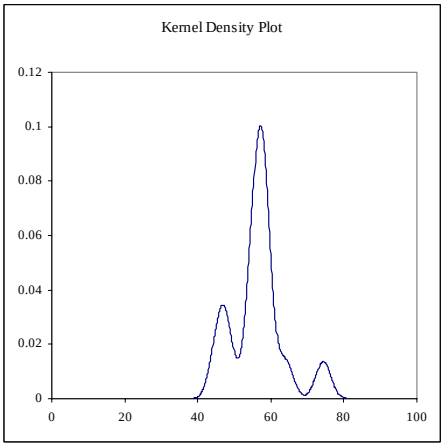


Figure 44: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

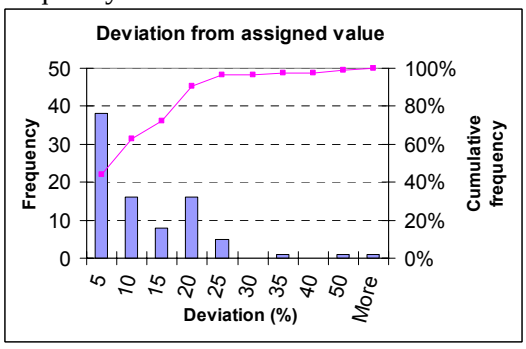


Table 17: **Dibenzo[*a,l*]pyrene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	54.00	5.00		57.00	6.00
66	55.00	5.00		56.00	6.00
66	54.00	5.00		55.00	6.00
67	56.80			59.40	
67	56.50			59.00	
67	56.60			58.80	
68	45.30	3.60		45.00	3.60
68	44.10	3.50		46.30	3.70
68	43.80	3.50		46.30	3.70
70	54.09			54.51	
70	52.35			57.06	
70	53.08			57.31	
71	46.90			47.50	
71	47.90			46.90	
71	46.70			46.40	
72	63.40	2.80		63.70	2.80
72	62.50	2.80		64.00	2.90
72	65.60	2.90		65.50	2.90
74	59.02	1.54		58.14	1.41
74	57.48	1.54		59.55	1.41
74	58.34	1.54		58.88	1.41
75					
75					
75					
76	60.20	0.30		55.80	4.90
76	60.00	0.30		52.30	4.90
76	60.20	0.30		57.10	4.90
77	62.00	6.00			
77	53.00	5.00			
77	58.00	6.00			
78	80.80	24.20		64.60	19.40
78	67.10	20.10		75.80	22.70
78	91.00	27.30		67.20	20.20
79	52.00	16.00		46.00	14.00
79	54.00	16.00		46.00	14.00
79	47.00	14.00		44.00	13.00
80	62.00			51.00	
80	67.00			58.00	
80	61.00			51.00	
81	57.00	2.00		57.00	2.00
81	57.00	2.00		58.00	2.00
81				58.00	2.00
82	62.10	2.40		61.20	2.90
82	62.20	2.50		65.20	3.10
82	62.00	2.50		61.30	3.00
85	56.00			54.00	
85	55.00			56.00	
85	55.00			56.00	
87					
87					
87					

Indeno[1,2,3-*cd*]pyrene

Figure 45: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **37,62±0,26 µg/L**; the blue lines indicate a 10% deviation from the known value.

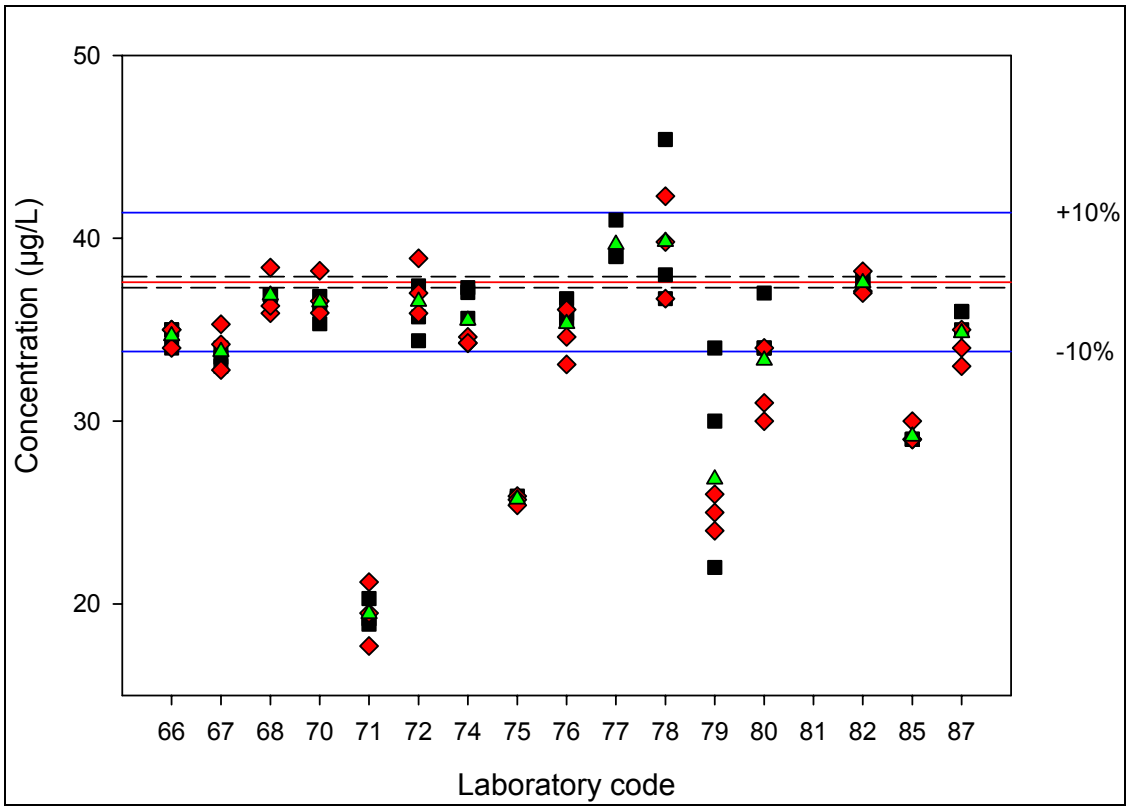


Figure 46: Kernel density plot of the reported results

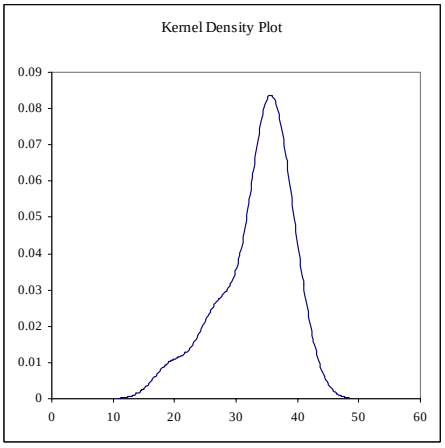


Figure 47: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

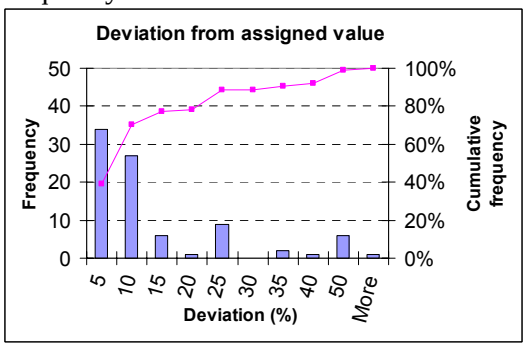


Table 18: **Indeno[1,2,3-*cd*]pyrene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	35.00	3.00		35.00	3.00
66	35.00	3.00		35.00	3.00
66	34.00	3.00		34.00	3.00
67	33.50			35.30	
67	34.00			34.20	
67	33.00			32.80	
68	36.90	3.00		35.90	2.90
68	36.90	2.90		38.40	3.10
68	36.90	2.90		36.30	2.90
70	36.82			36.56	
70	35.33			35.92	
70	36.24			38.22	
71	20.30	5.30		19.50	5.10
71	18.90	4.90		21.20	5.50
71	19.20	5.00		17.70	4.60
72	35.70	3.60		35.90	3.80
72	34.40	3.40		37.00	3.70
72	37.40	3.70		38.90	3.90
74	35.63	1.80		34.26	0.39
74	37.31	1.80		34.61	0.39
74	37.03	1.80		34.28	0.39
75	25.70	2.90		25.90	2.10
75	25.80	2.10		25.70	1.90
75	25.90	1.90		25.40	2.50
76	35.60	1.30		33.10	3.10
76	36.70	1.30		36.10	3.10
76	35.90	1.30		34.60	3.10
77	39.00	2.00			
77	39.00	2.00			
77	41.00	2.00			
78	38.00	5.70		42.30	6.30
78	45.40	6.80		39.80	6.00
78	36.70	5.50		36.70	5.50
79	34.00	10.00		26.00	8.00
79	30.00	9.00		25.00	8.00
79	22.00	6.00		24.00	7.00
80	34.00			31.00	
80	37.00			34.00	
80	34.00			30.00	
81					
81					
81					
82	37.80	1.60		37.10	0.80
82	37.80	1.60		38.20	0.80
82	37.50	1.60		37.00	0.80
85	29.00			29.00	
85	29.00			29.00	
85	29.00			30.00	
87	35.00	0.50		35.00	0.50
87	36.00	0.50		34.00	0.50
87	36.00	0.50		33.00	0.50

5-Methylchrysene

Figure 48: Plot of individual results of replicate measurements (■: results of day 1; ◆: results of day 2) and average result (▲); The red line and black dotted lines indicate the known concentration and the corresponding expanded uncertainty (k=2): **74,2±0,5 µg/L**; the blue lines indicate a 10% deviation from the known value.

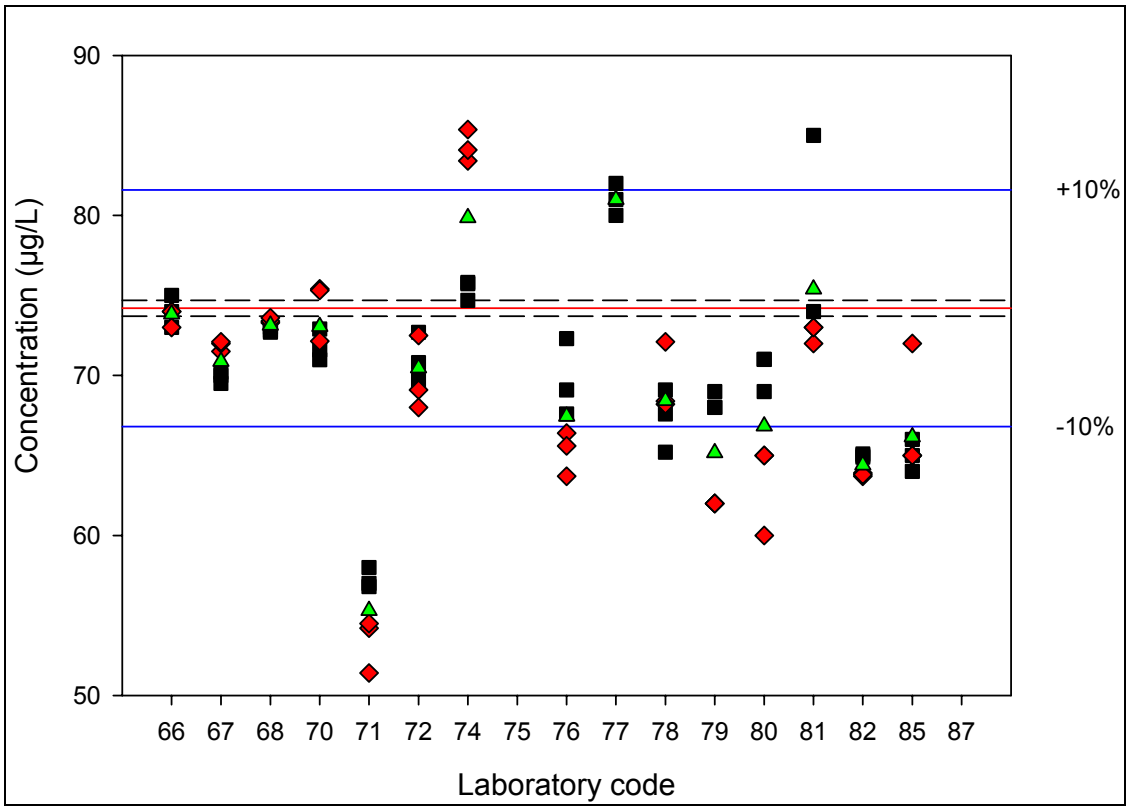


Figure 49: Kernel density plot of the reported results

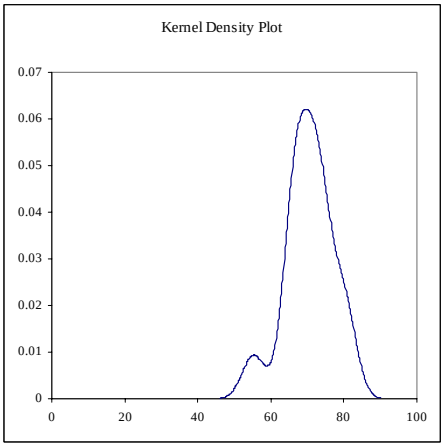


Figure 50: Frequency distribution of the deviations (in %) of individual results from the known concentration, as reported by the participants: blue bars indicate absolute frequencies; pink line: cumulative frequency

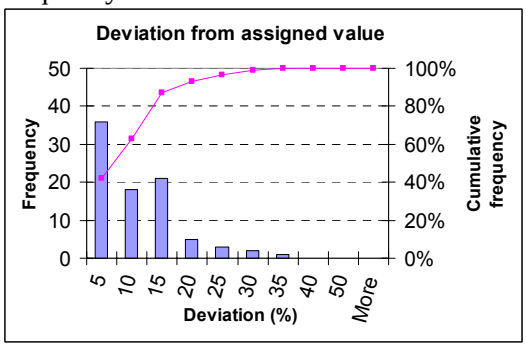


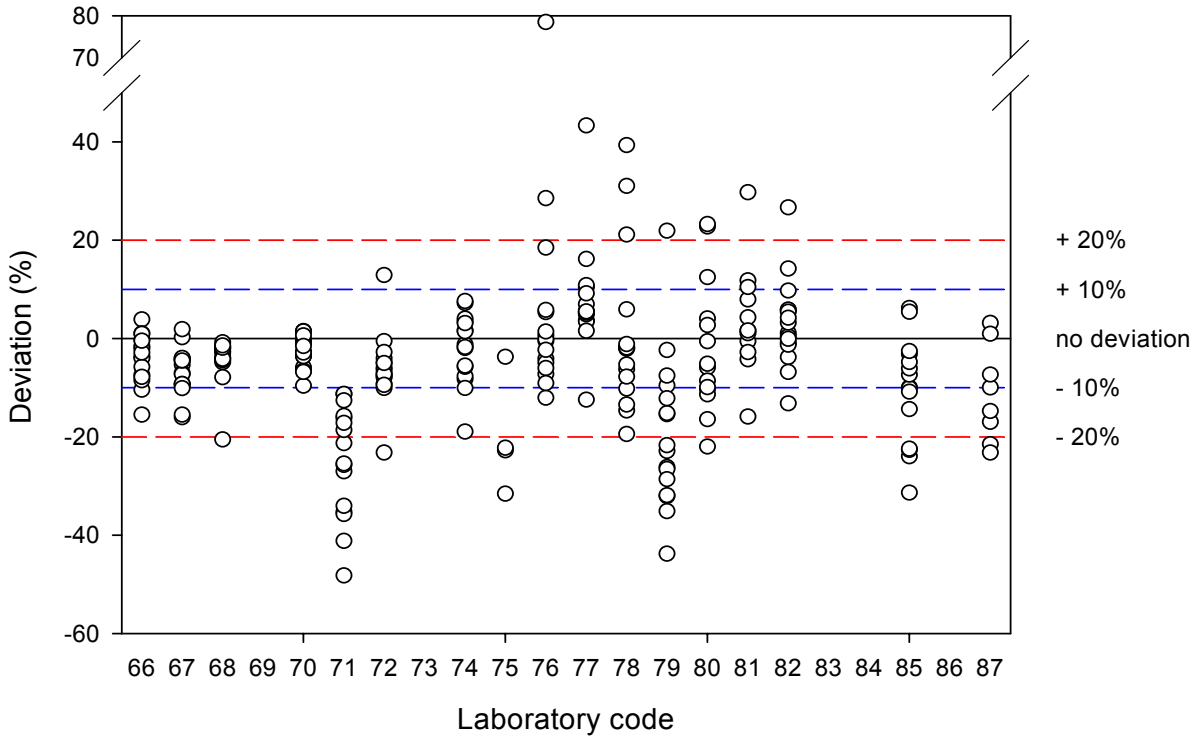
Table 19: **5-Methylchrysene**: Individual results of replicate measurements together with expanded measurement uncertainty (k=2); missing data are indicated by blank cells

	Day 1			Day 2	
Laboratory	Result	Uncertainty		Result	Uncertainty
	µg/L	µg/L		µg/L	µg/L
66	74.00	7.00		74.00	7.00
66	75.00	7.00		74.00	7.00
66	73.00	7.00		73.00	7.00
67	70.20			71.50	
67	69.50			72.00	
67	70.00			72.10	
68	73.00	3.60		73.30	3.70
68	72.80	3.60		73.40	3.70
68	72.70	3.60		73.60	3.70
70	72.90			72.14	
70	70.98			75.41	
70	71.60			75.32	
71	57.00	14.20		54.20	13.60
71	56.80	14.20		54.50	13.60
71	58.00	14.50		51.40	12.80
72	70.80	2.80		69.10	2.70
72	69.70	2.80		68.00	2.70
72	72.70	2.90		72.50	2.90
74	75.73	1.24		85.36	1.98
74	75.81	1.24		83.41	1.98
74	74.70	1.24		84.09	1.98
75					
75					
75					
76	69.10	4.80		66.40	2.80
76	72.30	4.80		63.70	2.80
76	67.60	4.80		65.60	2.80
77	82.00	12.00			
77	80.00	12.00			
77	81.00	12.00			
78	67.60	10.10		68.40	10.30
78	69.10	10.20		72.10	10.80
78	65.20	9.80		68.20	10.20
79	69.00	21.00		62.00	19.00
79	68.00	20.00		62.00	19.00
79	68.00	20.00		62.00	19.00
80	71.00			65.00	
80	69.00			65.00	
80	71.00			60.00	
81	74.00	5.00		73.00	3.00
81	85.00	5.00		72.00	3.00
81				73.00	3.00
82	65.10	2.70		63.70	0.80
82	64.90	2.60		63.90	0.80
82	65.00	2.70		63.80	0.80
85	64.00			65.00	
85	65.00			65.00	
85	66.00			72.00	
87					
87					
87					

Deviations from assigned concentrations

The deviations from the assigned concentrations were evaluated for all analytes in order to highlight any correlation. The percentage difference between the average of the results that were reported for each analyte and the assigned concentration is plotted in Figure 50 for each participant. It has to be stated that outliers were not removed for the calculation of the average result.

Figure 51: Deviation of the average result reported by the respective laboratory for each analyte from the assigned value. The deviation is expressed in percent of the assigned value. Red dotted lines indicate ±20 difference to the assigned concentration, whereas blue dotted lines indicate ±10% difference of the assigned concentration



8 Conclusions

The CRL and the NRLs agreed at the kick-off meeting of the network of reference laboratories about the importance of correct instrument calibration. Hence the first inter-laboratory comparison test on the determination of 15+1 EU priority PAHs focused on this topic. The NRLs were requested to determine the content of the 15+1 EU priority PAHs of a gravimetrically prepared solution of PAHs in acetonitrile. The majority of laboratories that were supplied with test samples reported results.

However, the results were heterogeneous in terms of completeness and variability. Good agreement of results was achieved for benzo[*a*]pyrene. More than 80 % of the reported data were within a deviation of ±10 % of the assigned value. This could be reasoned by the experience of laboratories in the determination of benzo[*a*]pyrene in food, since maximum limits for that particular substance have been set by many EU Member States already long time ago. In addition EU legislation requires its determination in a variety of foods. Another reason might be that benzo[*a*]pyrene causes, compared to other PAHs, fewer problems in instrumental analysis.

The outcome for the 6-ring PAHs was less favourable. These analytes were new to many participants. In addition their analysis is more difficult with regard to analyte separation and sensitivity. Hence, it could be expected that the results are worse than for "traditional" PAHs. About 40 % to 60 % of reported results were within a range of deviation from the assigned value of ±10 %. This is significantly less than for benzo[*a*]pyrene. Also the number of reported results was for these analytes lower than for benzo[*a*]pyrene.

The NRLs are requested to investigate and identify reasons for deviations of their results from the assigned values. The CRL attempts to perform a root cause analysis based on information on standard preparation that was supplied by the participants as well. The outcome of both analyses will be discussed at the next workshop.

9 Acknowledgements

The organisers would like to thank Mr Ulf Jacobsson for his support in the preparation of the test material.

The NRLs participating in this test –listed below- are kindly acknowledged.

ORGANISATION	COUNTRY
Österreichische Agentur für Gesundheit und Ernährungssicherheit, Kompetenzzentrum Cluster Chemie	Austria
Institute Scientifique de Santé Publique	Belgium
State General Laboratory, Environmental and other Food Contamination Laboratory	Cyprus
State Veterinary Institute Praha	Czech Republic
Danish Institute for Veterinary and Food Research, Department of Food Chemistry	Denmark
Health Protection Inspectorate, Tartu Laboratory	Estonia
Finnish Food Safety Authority Evira	Finland
LABERCA, Laboratoire d'Etude des Résidus dans les Aliments, Ecole Nationale Vétérinaire de Nantes	France
General Chemical State Laboratory, Food Division Laboratory	Greece
Central Agricultural Office, Directorate Food and Feed Safety, Central Food Investigation Laboratory	Hungary
National Food Investigation Institute	Hungary
Public Analyst Laboratory	Ireland
National Veterinary Laboratory	Lithuania
National Institute of Hygiene, Laboratory of Department of Food and Consumer Articles Research	Poland
State Veterinary and Food Institute Dolný Kubín	Slovakia
Centro Nacional de Alimentación - Agencia Española de Seguridad Alimetaria	Spain
National Food Administration, NFA	Sweden

Countries not appearing on the above list had either not nominated a National Reference Laboratory at the time when the inter-laboratory comparison test was conducted or their NRL did not submit results.

10 References

EFSA (2006). "*Invitation to submit data: 10 October 2005 – 10 October 2006*." http://www.efsa.eu.int/science/data_collection/pah/catindex_en.html

EU (2002). "*Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food*." SCF/CS/CNTM/PAH/29 Final http://europa.eu.int/comm/food/fs/sc/scf/out153_en.pdf

IARC (2006). "*Overall Evaluations of Carcinogenicity to Humans*." IARC Monographs on the Evaluation of Carcinogenic Risks to humans: (4 September 2006) http://monographs.iarc.fr/ENG/Classification/crthgr01.php

IRMM (2006). "*Inter-laboratory Comparisions at the Institute for Reference Materials and Measurements*." http://www.irmm.jrc.be/html/interlaboratory_comparisons/index.htm

JECFA (2005). *Evaluation of certain food contaminants*. WHO technical report series 930. WHO. Geneva, JECFA.

Thompson, M., S. L. R. Ellison and R. Wood (2006). "*The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories*." Pure Appl. Chem. 78(1): 145–196.

Annex 1: Sample receipt form

RECEIPT FORM

Name of Participant	
Affiliation	

Please ensure that the items listed below have been received undamaged, and then describe the relevant statement:

Date of the receipt of the test materials	
All items have been received undamaged	Yes ☐ / No ☐
Items are missing/damaged.	Yes ☐ / No ☐

Remarks (max. 700 characters):

Content of the parcel

a) Two brown glass ampoules with a solution of the 15+1 PAHs in acetonitrile

b) A safety data sheet for acetonitrile

c) A description of the exercise

d) This inter-laboratory comparison materials receipt form

Please email the completed form to

JRC-IRMM-PCRL-PAH@EC.EUROPA.EU

or fax it to +32 (14) 571-783

Annex 2: Accompanying letter with instructions

Inter-laboratory comparison on the analysis of the 15+1 EU priority PAHs in acetonitrile

Objective

The current comparison was agreed upon at the kick-off meeting of the CRL on PAHs in Geel on September 26-27 2006. The comparison intends to provide the National Reference Laboratories (NRLs) of the Member States the possibility to assess and compare the calibration of their instruments by analysing the 15+1 EU priority PAHs in a solvent solution.
Test materials and analytes
Two standard solutions containing the *15+1 EU priority PAHs* are supplied to you for analysis. The individual PAHs are each at a concentration level that allows the addition of internal standards and an overall 1:10 dilution. The solvent of both samples is *acetonitrile*. Each ampoule contains *approximately 2.5 ml of the standard solution*.
Please bear in mind that the solutions do *not contain any internal standards*.
The target analytes are (*please note the acronyms for reporting*):

Table 1: The target analytes of the comparison (15+1 EU priority PAHs)

benz[*a*]anthracene (BaA)	benzo[*a*]pyrene (BaP)
benzo[*b*]fluoranthene (BbF)	chrysene (CHR)
benzo[*j*]fluoranthene (BjF)	cyclopenta[*cd*]pyrene (CPP)
benzo[*k*]fluoranthene (BkF)	dibenz[*a,h*]anthracene (DhA)
benzo[*c*]fluorene (BcL)	dibenzo[*a,e*]pyrene (DeP)
benzo[*ghi*]perylene (BgP)	dibenzo[*a,h*]pyrene (DhP)
dibenzo[*a,i*]pyrene (DiP)	dibenzo[*a,l*]pyrene (DlP)
indeno[1,2,3-*cd*]pyrene (IcP)	5-methylchrysene (5MC)

General outline of the exercise

The laboratories are requested to perform a **triplicate analyses** on the samples applying a method of their choice. The preparation and analysis of the two samples (dilution, addition of internal standards, and injection) shall be performed **on two different days**.
The laboratories are requested to analyse the samples and report the results within three weeks after receipt of this letter and the samples. Registration and reporting of your results shall be done via the WEB interface:
http://www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=77

Geel, 27. 10. 2006

Annex 3: Questionnaire

1. **Columns used (e.g. HP5 30m 0.25mm 0.25 um):**

2. **Temp. program/gradient applied:**

   sd

3. **Calibration by the use of internal standard or external standard?**

   ◉ ISTD (internal standard) ○ ESTD (external standard)

   in case of ISTD : which compounds were used?

   sd

4. **Please give the volume of injection in ul:**

5. **Please specify your detector settings (e.g. m/z, m->m1+m2, excitation/emission wavelengths, UV absorption settings, time programming etc.)**

6. **Comments**

European Commission

EUR 22696 EN– DG Joint Research Centre, Institute for Reference Material and Measurements IRMM

Title: Report on the Inter-Laboratory Comparison Test on 15+1 EU Priority PAHs in Acetonitrile

Authors: GOMEZ RUIZ JOSE ANGEL, HOLLOSI LASZLO, KARASEK LUBOMIR, SIMON RUPERT, WENZL THOMAS

Luxembourg: Office for Official Publications of the European Communities
2007 – 55 pp. – 21 x 29.7 cm
EUR - Scientific and Technical Research series; ISSN 1018-5593

Abstract
The Institute for Reference Materials and Measurements (IRMM) of the European Commission's Joint Research Centre hosts the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons in Food (CRL-PAH). One of its core tasks is to organise inter-laboratory comparisons (ILCs) for the National Reference Laboratories (NRLs). This report presents the results of the 1st ILC of the CRL-PAH on the determination of the 15+1 EU priority PAHs in acetonitrile, which was conducted along the lines of the International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories.
The test material used in this exercise was a solution of the 15+1 EU priority PAHs in acetonitrile. The solution was prepared gravimetrically.

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

The mission of the Joint Research Centre is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of European Union policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Community. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

Publications Office
Publications.eu.int