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

15 + 1 EU priority PAHs in sausage meat and acetonitrile

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CRL Polycyclic Aromatic Hydrocarbons

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Summary

This report presents the results of the 3rd inter-laboratory comparison (ILC) of the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons (PAHs) on the determination of the 15+1 EU priority PAHs in sausage meat and acetonitrile, which was conducted along the lines of the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories.

In agreement with the National Reference Laboratories, the test materials used in this exercise were a canned sausage meat preparation spiked with the 15+1 EU priority PAHs and a solution of the analytes in acetonitrile, respectively. The materials were prepared gravimetrically.

The assigned concentration values of PAHs in sausage meat and in acetonitrile were calculated from the gravimetric preparation data.

Only officially nominated National Reference Laboratories of the EU Member States and from countries covered by the Technical Assistance and Information Exchange programme of the European Commission were admitted as participants. However, from latter countries only one laboratory reported results. The participants were free to choose the method for the analysis of the materials.

The performance of the participating laboratories was expressed as z-scores, which were calculated from the participants reported "final result" for the analytes' contents in the sausage meat material, based on gravimetrical preparation. The reported values of the laboratories for PAHs in acetonitrile were not rated.

For the sausage meat material 88 % of the reported values were attributed with z-scores $\leq |2|$), indicating that most of the participating laboratories were performing satisfactorily with respect to internationally accepted standards. However, in some cases bias and/or a high variability were discovered, and some analytes consistently caused specific problems. It is therefore recommended to investigate this further.

Introduction

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) [1, 2].

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings (see Table 1). PAHs may be formed during the incomplete combustion of organic compounds and can be found in the environment. In food, PAHs 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 being 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" [3]. 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 (CPP), dibenz [*a,h*]anthracene, and dibenz [*a,l*]pyrene as probably carcinogenic to human beings (group 2a), and nine other EU priority PAHs as possibly carcinogenic to human beings [4].

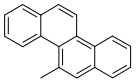
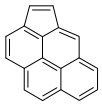
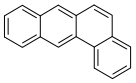
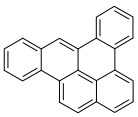
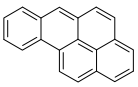
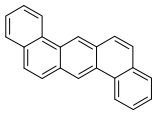
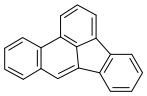
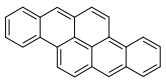
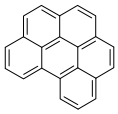
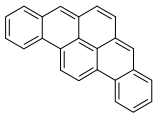
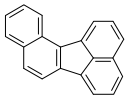
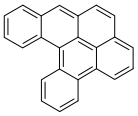
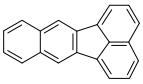
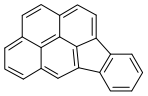
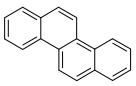
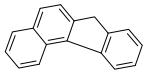
As a consequence, the European Commission (EC) issued Commission Regulation (EC) No 1881/2006 setting maximum levels of benzo[a]pyrene in food, Commission Regulation (EC) No 333/2007 laying down sampling methods and the performance criteria and fitness-for-purpose approach for the methods of analysis in use 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 PAHs in certain foods [5-7]. Additionally, the monitoring of BcL had been recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in 2006 [8].

In order to distinguish this set of PAHs from a set of PAHs that have been addressed by a method of the US Environmental Protection Agency, known as the 16 EPA PAHs, the terminology 15+1 EU priority PAHs was chosen. They are listed in Table 1.

To evaluate the suitability of BaP as a marker for the total PAH content of food the European Food Safety Authority (EFSA) had asked the EU Member States to submit monitoring data on levels of the 15+1 EU priority PAHs to its database on PAH levels in food [9]. The results indicated that the use of BaP as marker was questionable [10].

A scientific opinion on polycyclic aromatic hydrocarbons in food was published recently by EFSAs Panel on Contaminants in the Food Chain [11]. The Contaminants Panel confirmed the limited suitability of BaP as marker for the total PAH content and recommended to focus for official food control purposes instead on BaP only onto groups of four respectively eight PAHs. The Standing Committee On The Food Chain And Animal Health held in Brussels on 12 December 2008, Section "Toxicological Safety Of The Food Chain" agreed that the occurrence data, in view of a future review of current legislation, should focus on the PAH 4 individually (benzo[*a*]pyrene, chrysene, benz[*a*]anthracene and benzo[*b*]fluoranthene, which make up a sub-set of the EU 15+1 PAHs). In addition, the Committee encouraged, if possible to analyse all relevant toxic PAHs in food, and thus underpins the importance of this ILC.

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

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

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 [2], one of the core duties of the CRL-PAH is organising inter-laboratory comparison tests (ILCs).

This study aimed to evaluate the comparability of analysis results for the 15+1 EU priority PAHs in sausage meat reported by National Reference Laboratories, and to assess the influence of standard preparation and instrument calibration on the performance of the individual participant.

The ILC was designed and evaluated along the lines of the International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories, further denoted as Harmonized Protocol [12].

Participating Laboratories

Only officially nominated National Reference Laboratories of the EU Member States and laboratories from countries covered by the Technical Assistance and Information Exchange programme of the European Commission were admitted as participants.

Time frame

The ILC was agreed with the NRLs at the CRL-PAH workshop in Geel on 25 and 26 February 2008. The planned ILC was published on the IRMM web page and invitation letters were sent to the laboratories on 20 May 2008 (see Annex 1 and IRMM web page [13]). Test samples were dispatched 3 July 2008 and the deadline for reporting of results was 12 September 2008. However, the deadline for submitting analysis results was extended on request of participants to finally 31 October 2008.

Test material

Preparation

The test materials for the ILC were prepared from neat certified reference materials (BCR®, Institute for Reference Materials and Measurements, Geel, Belgium) except cyclopenta[*cd*]pyrene (Biochemisches Institut für Umweltkarzinogene, Großhansdorf, Germany), benzo[*c*]fluorene (Dr. Ehrenstorfer, Germany), and dibenzo[*a,i*]pyrene (Campro Scientific, Germany). Standard stock solutions of each analyte were produced by substitution weighing of neat substance on a microbalance and dissolution in toluene. The standard stock solutions as well as the subsequent dilutions were prepared gravimetrically. Toluene was used as solvent of the stock solutions. These stock solutions were added to gravimetrically determined amounts of acetonitrile (ca 0.5 l) and edible oil (ca 4.5 l), respectively. The materials were homogenised by vigorously stirring for several hours. The edible oil was used to prepare the sausage meat material, which was canned before use in the ILC (Max Rubner Institut, Kulmbach, Germany). The acetonitrile was used as such. The concentrations of the independently prepared standards and the test materials were calculated from the results of mass determinations and applying the density equation when required.

The uncertainties of the analyte concentrations of the acetonitrile solution were determined using the law of error propagation 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 were reported as expanded uncertainty with a coverage factor of 2.

The values of the analyte concentrations in the test materials are given in Table 2.

The PAH concentration of the acetonitrile test material was at a level that allows adding of internal standards respectively that considers frequently found analyte enrichment factors. The relative uncertainties did not differ much from analyte to analyte.

About 100 ampoules containing each 5 mL of acetonitrile test material were filled under inert atmosphere and flame sealed. 100 cans containing each 50 g of sausage meat testing material were selected from the production batch. Both materials were stored at 4º C until dispatch.

Table 2: Analyte content of the test materials (in alphabetical order of the analyte)

	Sausage Meat	Acetonitrile	
Analyte	**content [µg/kg]**	**content [µg/l]**	**expanded uncertainty (k=2) [µg/l]**
5-methylchrysene	6.2	67.1	0.4
benzo[*a*]anthracene	5.9	63.3	0.3
benzo[*a*]pyrene	5.3	57.2	0.2
benzo[*b*]fluoranthene	4.1	53.7	0.4
benzo[*c*]fluorene	3.9	29.5	0.2
benzo[*ghi*]perylene	4.7	52.5	0.2
benzo[*j*]fluoranthene	9.2	66.1	0.3
benzo[*k*]fluoranthene	5.2	46.5	0.2
chrysene	6.4	47.7	0.4
cyclopenta[*cd*]pyrene	6.0	51.1	0.3
dibenzo[*a,e*]pyrene	7.1	47.5	0.2
dibenz[*a,h*]anthracene	7.7	49.1	0.2
dibenzo[*a,h*]pyrene	9.9	58.0	0.2
dibenzo[*a,i*]pyrene	5.6	48.3	0.2
dibenzo[*a,l*]pyrene	7.7	48.0	0.2
indeno[*1,2,3,-cd*]pyrene	5.2	65.6	0.3

Verification of the analyte concentration

The concentrations of the analytes in the acetonitrile test material was verified by high performance liquid chromatography - fluorescence detection (HPLC-FLD) and gas chromatography – mass spectrometry (GC-MS), applying independent standard solutions prepared from the CRMs used for the preparation of the test materials as well as where applicable a certified reference material containing in total 36 aromatic hydrocarbons from the National Institute for Standards and Technology (SRM® 2260a, Gaithersburg, MD, USA). Isotope dilution with bracketing calibration was applied for the GC-MS analyses.

The analyte contents of the sausage meat sample were verified applying a self developed analysis method, which is based on pressurised liquid extraction, gel permeation chromatography, and solid phase extraction prior to GC-MS analysis. Isotope dilution method and standards prepared from CRMs were applied for the analyses.

Homogeneity

For the test solution in acetonitrile sufficient homogeneity was assumed as it consisted of a well mixed solution of the analytes in a solvent of low viscosity. For the sausage meat material 10 randomly selected tins were analysed in duplicate. Results were evaluated by one-way analysis of variances and sufficient homogeneity was judged based on provisions given in chapter 3.11.1 of the Harmonized Protocol [12]. All analyses complied with the provisions given by the Harmonized Protocol and the sausage meat test material was found sufficiently homogeneous.

Stability

The test material concentration was monitored at the beginning of the study as well as after receipt of the results from the participants (chapter 3.11.5 of the Harmonized Protocol [12]). Statistically significant differences of the results of analysis obtained before and after termination of the study were not found, thus indicating the stability of the test material. Test samples were stored refrigerated for the period of the study.

Distribution

The samples were dispatched from IRMM on 1 July 2008. Each participant received (together with the shipment) a sample receipt form (Annex 2), an accompanying letter with instructions for sample handling, measurement, and reporting (Annex 3), the respective Material Safety Data Sheet for acetonitrile and cyclohexane (solvent of commercial standard solution), and two aluminium tins with the sausage meat test material, one ampoule with the acetonitrile solution and a commercial standard solution (Dr. Ehrenstorfer GmbH) containing the 16 analytes in cyclohexane with known concentrations to be used for instrument calibration.

Outline of the study

Details of this ILC were presented to the participating NRLs at the CRL workshop. Explicit instructions were published on the internet and given in a letter that accompanied the samples. The analytes and test matrices were clearly defined as the 15+1 EU priority PAHs in sausage meat and acetonitrile. Furthermore, concentration ranges, within which the values of the analyte contents were to be expected, were given.

The participants were asked to use a method of analysis of their choice and to determine in triplicate the analyte contents of each sample. For the sausage meat a nested design was chosen: the two tins, each containing sausage meat material, were to be analysed on two different days (in triplicate) applying two independent instrument calibrations. The results of the individual analyses had to be reported to a database at IRMM via an internet interface. Additionally the laboratories were asked to report a “final value” for the content of each analyte in the sausage meat sample. These "final values" were used for the determination of the z-scores. The filling-in of a brief questionnaire (see Annex 4) was requested too.

Evaluation of the results

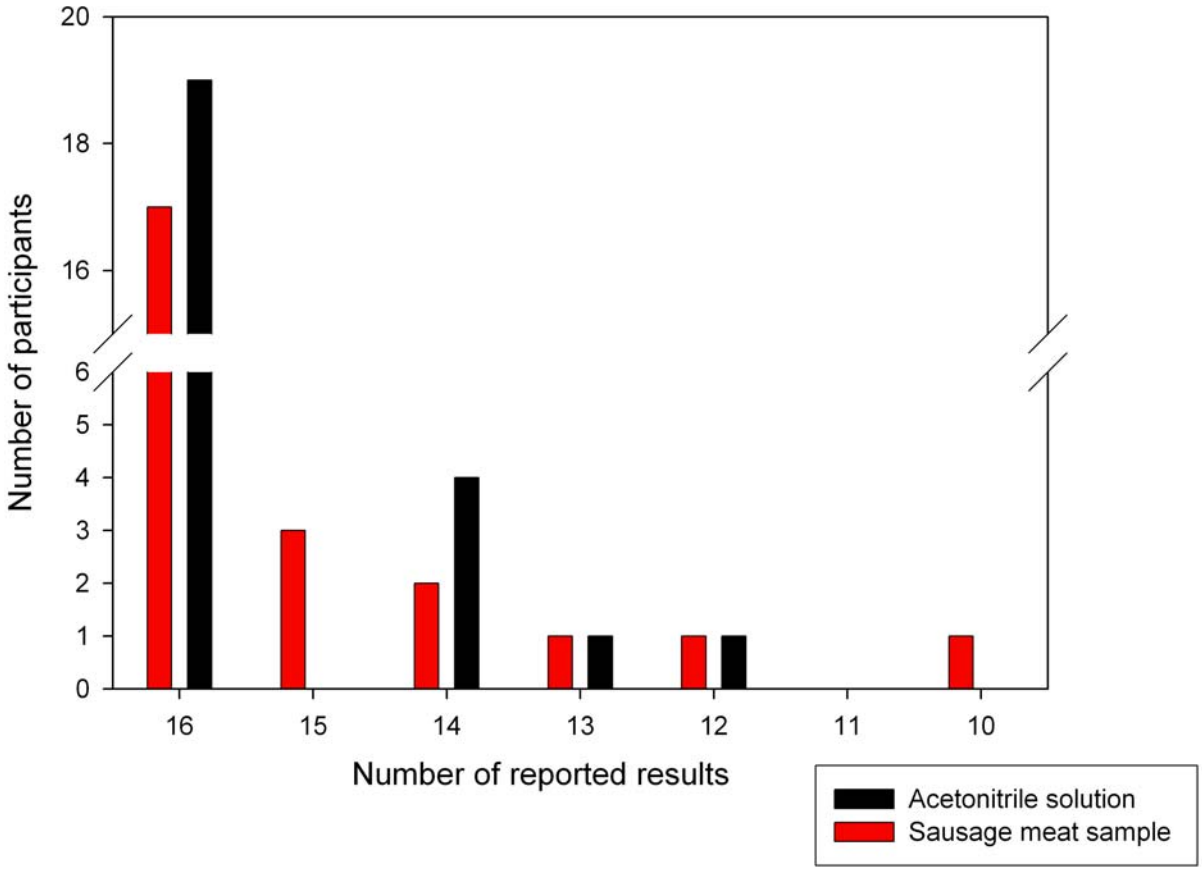
General observations

Analytical results were received from all 25 participants that were supplied with test samples. This is a positive development in respect to the PT in 2007 when only 23 of 25 laboratories reported results. The CRL, upon request from the participants, extended the original deadline of 12 September 2008 to 31 October 2008.

The majority of laboratories analysed all 15+1 PAHs (19), whereas six laboratories were unable to analyse either two (4), three (1), or four (1) of the 15 + 1 analytes. The slight increase of these numbers with respect to the PT conducted in 2007 when 20, 2, and 1 laboratory analysed 16, 15, and 14 of the analytes respectively might be the consequence of reporting provisions, since the reporting of combined values for the analytes BbF, BjF, and BkF were, in contrast to 2007, not anymore accepted.

An overview on the frequency of results reported for the individual analytes is given in Figure 1.

Figure 1: Counts of reported data in terms of total number of analysed PAHs in sausage meat and acetonitrile



Evaluation criteria

In the 2008 workshop it was agreed to omit the attribution of scores for the values reported for the acetonitrile solution. The reason is that such scores could be misleading if presented to third parties because they could be mistaken as scores related to the analysis of food samples, which would include sample preparation. The results for the acetonitrile standard solution were evaluated for their percentage deviation from the known concentration of the individual analyte.

For the sausage meat material z-scores were calculated according to the formula

$$\text{Equation 1} \qquad z = (x - X) / \sigma_P$$

where z refers to the z-score, x to the reported "final value", X to the assigned value (=gravimetric preparation data), and σ_P to the target standard deviation.

For benzo[*a*]pyrene, the target standard deviation σ_P was set equal to the maximum standard measurement uncertainty U_f as defined by Commission Regulation (EC) No 333/2007 (Annex Part C Paragraph C.3.3.2) [7]:

$$\text{Equation 2} \qquad U_f = \sqrt{(\text{LOD}/2)^2 + (\alpha \text{C})^2}$$

where U_f relates to the maximum standard measurement uncertainty, LOD to the required limit of detection, α to a numeric factor depending on the concentration C as given in Commission Regulation (EC) No 333/2007, Annex Part C, Table 8.

The application of Equation 2 with the assigned value of 5.3 µg/kg for benzo[*a*]pyrene as C and the maximum tolerable value of 0.3 µg/kg as LOD results in a value for U_f of 1.1 µg/kg (20.2%) for the sausage meat material.

For all other analytes the value of 22 % given by the modified Horwitz equation, as suggested by Thompson and agreed upon in the preparatory workshop, was taken as target standard deviation [14].

Formal compliance with legal requirements

Table 7 of Commission Regulation (EC) No 333/2007 lays down minimum performance criteria for methods used for the official control of the levels of benzo[*a*]pyrene in foodstuff [7]. The parameters addressed are listed in Table 3 together with reported values of the participants, preserving the number of significant figures reported. The purpose of this compilation was to evaluate if the applied methods fulfil the provisions laid down in Commission Regulation (EC) No 333/2007. Non-compliant rated were data that did not fulfil the criteria specified in the Commission Regulation. Over two thirds of the participants (18) succeeded in fulfilling the formal requirements and it should be noted that five laboratories reporting non-compliant method performance data performed well in the determination of benzo[*a*]pyrene in the sausage meat test material.

Table 3: Minimum method performance criteria for benzo[*a*]pyrene given by Commission Regulation (EC) No 333/2007 and values as reported by the participants[*)].

	LOD [µg/kg]	LOQ [µg/kg]	Recovery [%]	Uncertainty [µg/kg]
required minimum performance	**0.3**	**0.9**	**50 – 120**	**1.1****
laboratory (down)				
1991	0.08	0.15	100	0.2
1992	0.025	0.05	79	1.1
1993	0.1	0.2	100	0.5
1995	0.2	0.3	101	0.6
1996	0.2	0.7	100	0.9
1997	0.02	0.1	80.3	0.5
1998	0.3	0.6	96	0.4
1999	0.26	0.52	72.99	0.5
2000	0.05	0.2	95	0.8
2001	0.004	0.52	95.5	0.6
2002	0.03	0.3	103	0.5
2003	0.02	0.08	60	0.9
2004	NR	NR	97.3	NR
2010	***0.4***	0.8	71	NR
2011	0.1	0.25	104	0.7
2012	0.2	0.6	101	***1.9***
2030	0.01	0.03	73	0.8
2031	***1***	***2***	87	NR
2050	0.008	0.024	90	1.1
2051	***0.4***	0.8	104	1.1
2052	0.1	0.5	90	0.8
2053	0.06	0.2	90	1.1
2056	0.01	0.02	80	NR
2070	***0.5***	***1.5***	91	0.3
2090	0.003	0.008	84.6	0.9

*) *NR* = not reported,.

**) Maximum permitted uncertainty for the assigned value given by Equation 2

Non compliant values are displayed in bold-italic font

Laboratory results for PAHs in acetonitrile

The gravimetrically established concentration values were applied for the evaluation of the reported results (= assigned values).

The results from the inter-laboratory comparison test on the 15+1 EU priority PAHs in acetonitrile are presented in Figure 2 to Figure 33.

For each analyte the first figures show the results from individual measurements as reported by the participants. In addition, the assigned value is depicted as purple solid line and the robust mean of the results of the participants as red solid line. The blue dotted lines represent a deviation of ± 10 %, 20 %, and 30 % from the assigned value.

The Kernel density plots showed the distribution of the data and indicated for several analytes that data were not normally distributed, that outliers were in the data set, and multimodality occurred.

The analytical results were listed for the replicate measurements in Table 4 to Table 19. The data were presented with significant figures as reported.

The percentage deviation of the average result for each analyte from the target concentration had been calculated for each individual participant for the acetonitrile material. The aim of this evaluation was to highlight systematic deviations from the assigned values for the whole set of PAHs. Figure 81 showed that most of the reported values deviated less than ± 20 % from the assigned value. However, for one laboratory (Lab-code 1993) all reported values lay outside of this range and the results of two participants covered large ranges of deviations: -80 % to +100 % (Lab-Code 2053), and -20 % to 230 % (Lab-Code 2030).

For most analytes the mean of the laboratories results (= consensus value, calculated as robust mean according ISO 13528) was slightly lower than the assigned value calculated from gravimetric data (see Figure 2 to Figure 32). The reason for these deviations has not been identified yet. A systematic error in the preparation of the acetonitrile solution, e.g. dilution error, has to be excluded since the gravimetrical preparation concentration of the acetonitrile solution was verified for eight analytes against the SRM 2260a. A systematic error would also not explain the fact that the consensus values for benzo[*j*]fluoranthene and cyclopenta[*cd*]pyrene agreed very well with the assigned values and that for benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene the maxima of the major modes were much closer to the assigned values than the robust means. Additionally Figure 81 showed that the negative bias was not a general phenomenon, but rather cumulated at certain laboratories. After all it seemed that the genesis of the phenomenon was related to some of the laboratories rather than to the material used.

The consensus value for DeP was for the solvent material in agreement with the assigned value (Figure 22). However the distribution of the values shown by the kernel density plot indicated two main modes (Figure 23). The relative deviations of the reported values sorted by the chromatographic method used at the laboratories showed a positive bias for the results related to HPLC (Figure 43), while the results related to GC were widely scattered, but on the average in agreement with the assigned value (Figure 42). Thus, related to the analysis of DeP, the methods employing HPLC needed improvement.

For dibenzo[*a,h*]pyrene (DhP) and dibenzo[*a,i*]pyrene (DiP) the deviations were larger (14.8 % and 16.4 %) indicating that these two analytes caused extra difficulties during the analysis. The agreement of the robust mean value of the participants with the assigned value was in the 2008 ILC worse than in the 2007 ILC. Plotting the differences of the reported values from the assigned value sorted by the analytical method used (Figure 42 and Figure 43) it became clear that the results reported by the laboratories using gas chromatography (GC) had a negative bias while the ones reported by laboratories using HPLC did not. Therefore it was concluded that the methods based on GC need to be scrutinised for the reason of this bias. The same was true for DiP (Figure 46 and Figure 47).

As a follow-up from last years ILC the differences from the reported values to the assigned values were also plotted separately for the analytical method used for BaP, BjF, BkF, and CCP (

Figure 34 to Figure 41). For BaP no major differences in performance were detected for the two chromatographic methods, while for BjF and BkF the data generated using HPLC seemed a bit more consistent than the GC-MS data. It is also remarkable that in 2008 practically all laboratories using GC reported values for BjF, which is roughly double the rate of 2007. However, neither for BaP nor for the two benzofluoranthenes significant bias was found. For CPP the GC-data showed a negative bias of about 10 %, while the data from laboratories using HPLC were far-scattered around the assigned value.

5-Methylchrysene

Figure 2: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 67.1 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

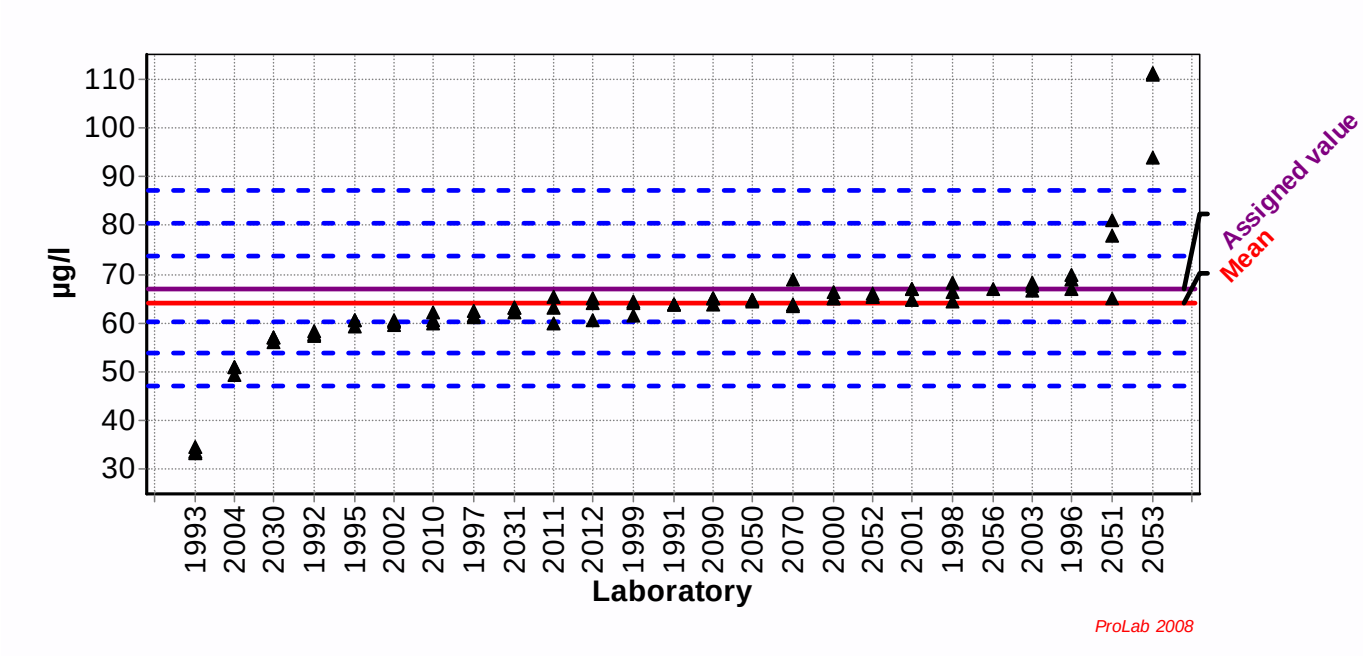


Figure 3: **Kernel Density Plot**

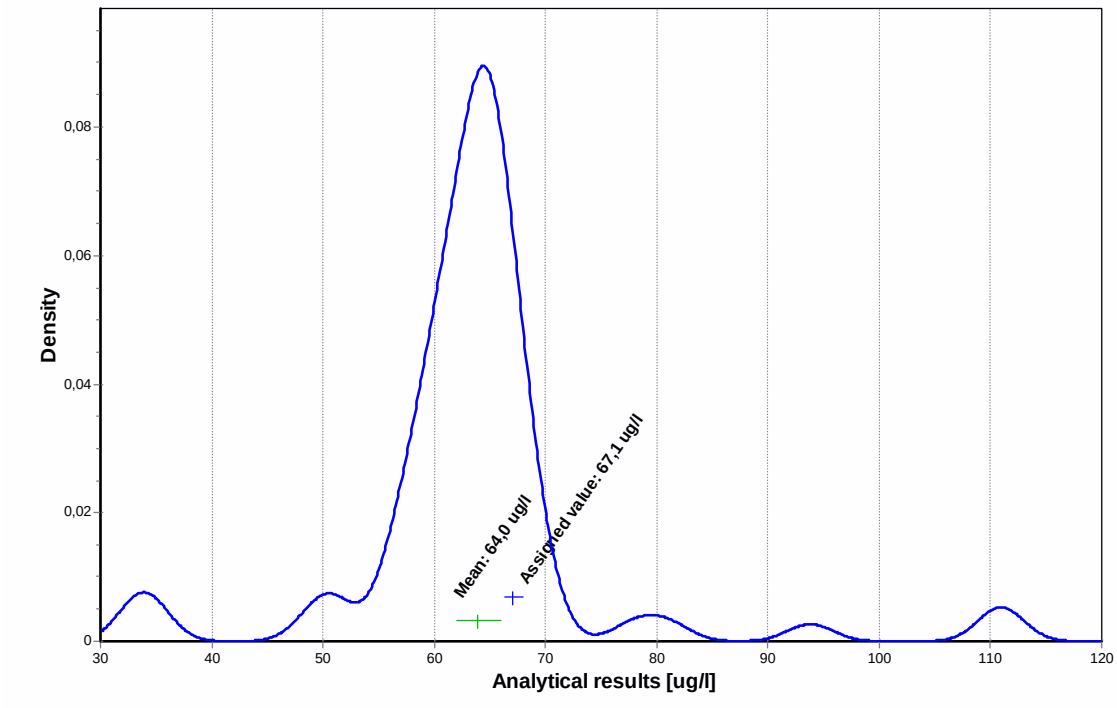


Table 4: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	63.9	63.6	63.6
1992	57.26	57.78	58.16
1993	34.73	33.65	33.34
1995	59.4	60.7	60.4
1996	68.8	69.9	67.1
1997	62.6	61.2	61.6
1998	66.4	68.2	64.5
1999	61.38	64.16	64.46
2000	64.95	65.17	66.22
2001	64.8	66.9	66.9
2002	60.7	60.3	59.7
2003	68.1	67.7	66.7
2004	49.2	51.1	50.8
2010	60.46	62.29	60.06
2011	59.8	65.4	63.2
2012	60.65	65.1	63.99
2030	56.18	57.02	56.95
2031	63	62	63
2050	64.55	64.56	64.85
2051	81	65	78
2052	65.46	65.47	65.92
2053	111	110.9	93.8
2056	67		
2070	68.8	63.67	63.35
2090	65.093	65.07	63.704

Benzo[*a*]anthracene

Figure 4: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 63.2 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

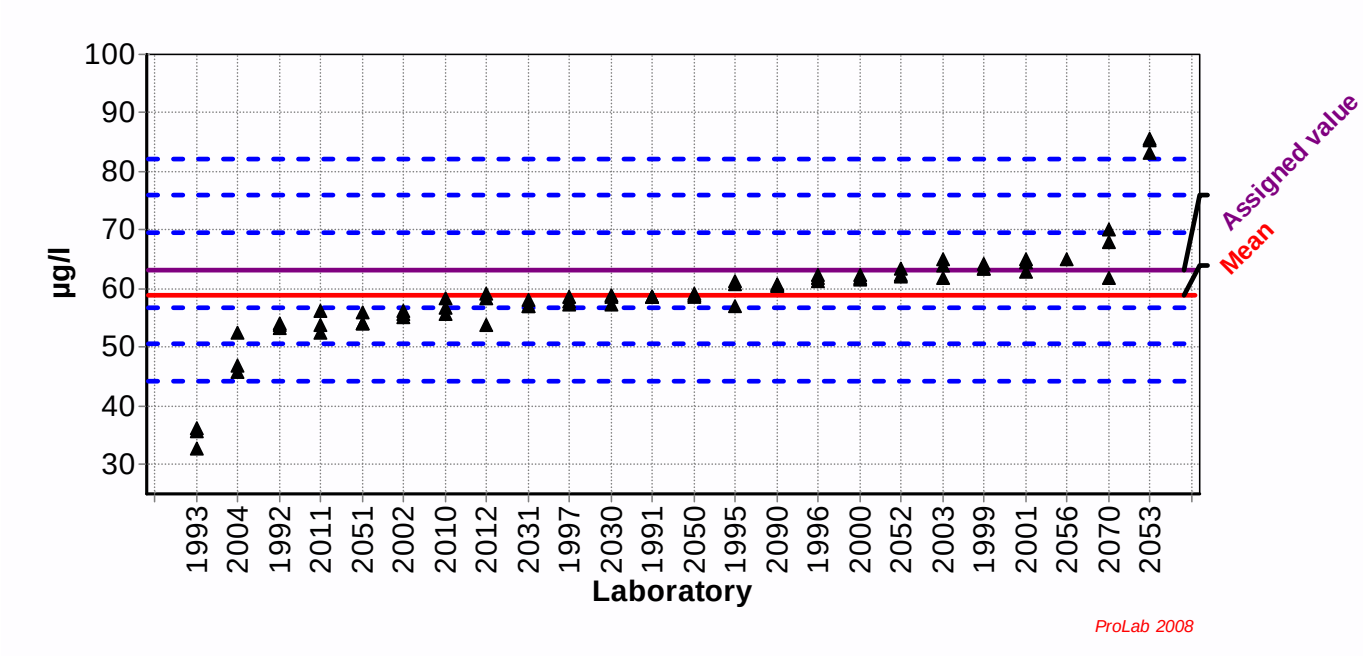


Figure 5: **Kernel Density Plot**

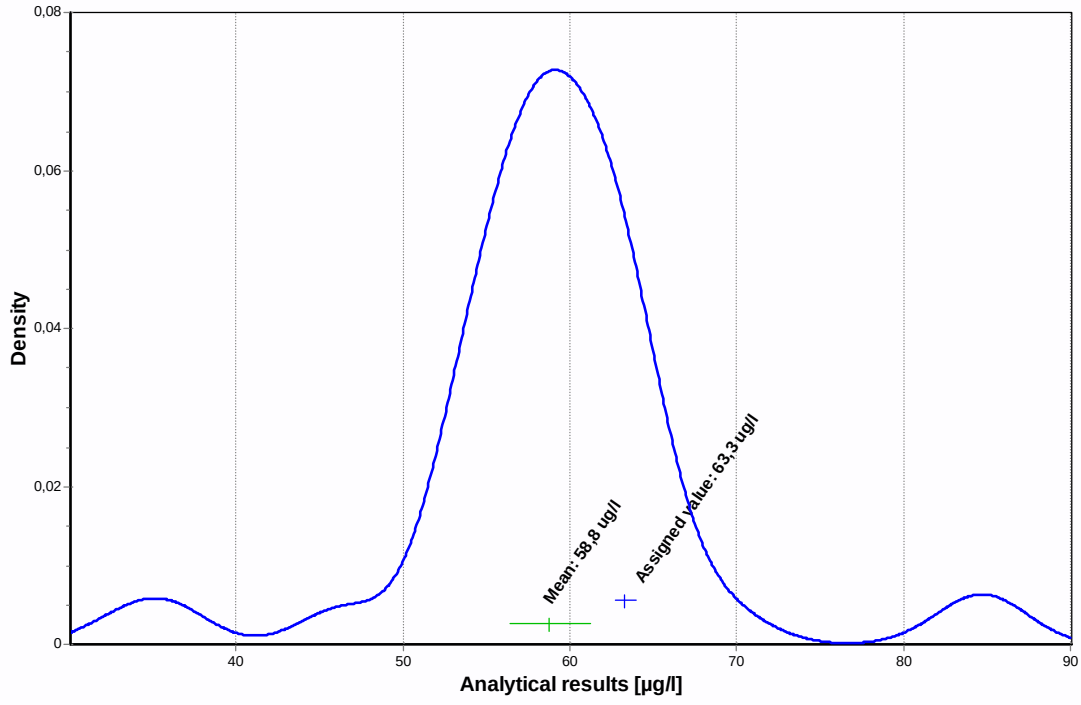


Table 5: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	58.6	58.5	58.7
1992	53.26	53.8	54
1993	32.87	35.73	36.16
1995	60.7	61.2	56.9
1996	62.4	61.4	61.8
1997	58.6	57.7	57.3
1998			
1999	63.32	63.5	64.12
2000	61.6	61.95	62.44
2001	62.8	65	64.6
2002	56.1	55.7	55.1
2003	64	65	61.9
2004	45.9	52.6	46.8
2010	56.71	58.42	55.71
2011	52.6	53.8	56.1
2012	53.93	58.38	59.24
2030	58.85	57.2	58.59
2031	58	57	57
2050	59.08	58.73	58.97
2051	54	56	54
2052	62.43	62.22	63.53
2053	85.2	85.5	83.2
2056	65		
2070	70.15	68	61.74
2090	60.522	60.561	60.683
1991	58.6	58.5	58.7

Benzo[*a*]pyrene

Figure 6: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 57.2 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

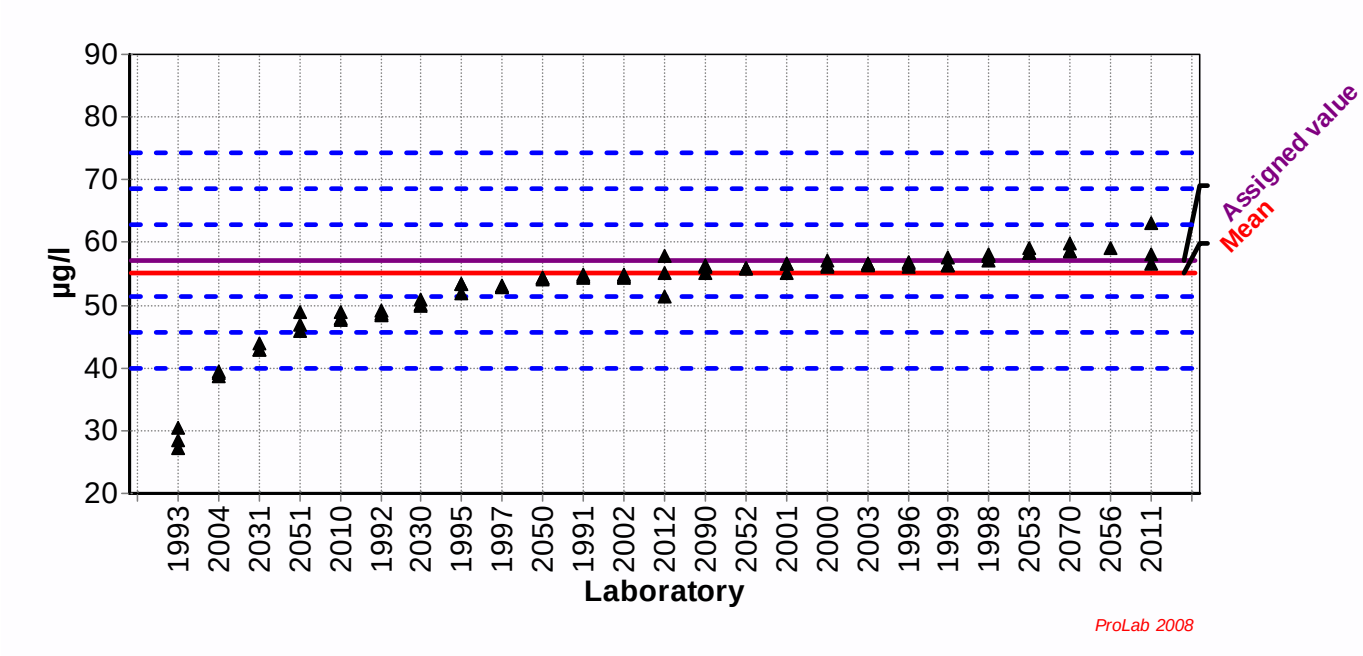


Figure 7: **Kernel Density Plot**

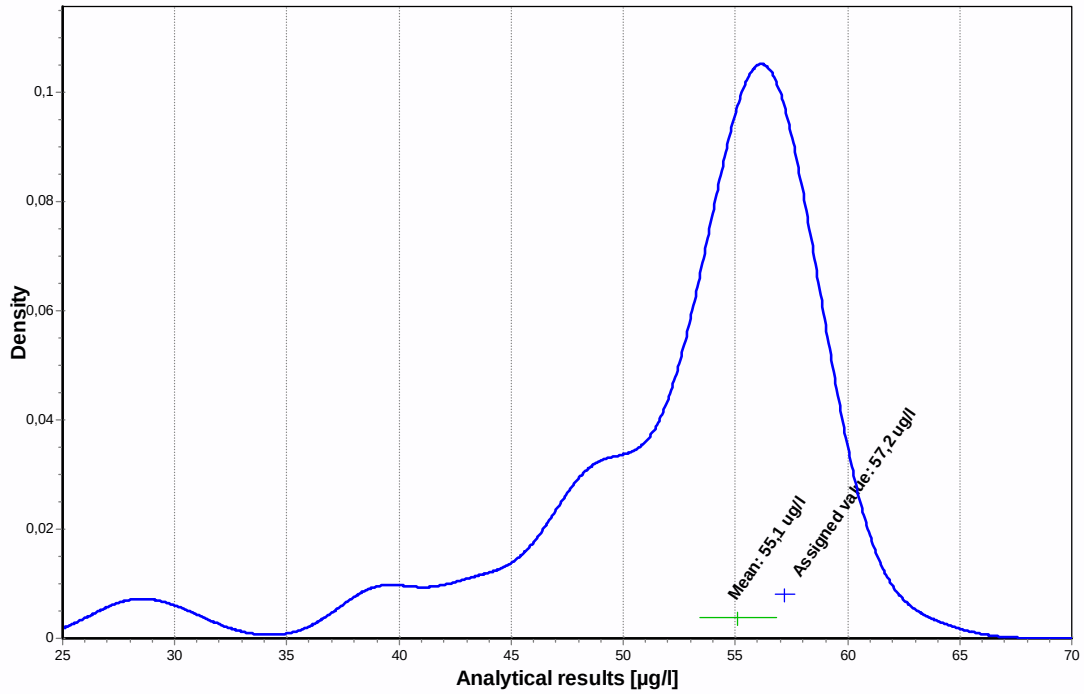


Table 6: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	54.7	54.8	54.3
1992	48.4	48.63	49.17
1993	28.43	27.31	30.37
1995	53.3	51.8	53.4
1996	56	56.9	56.7
1997	53.2	52.9	53
1998	58.2	57.8	57.1
1999	56.34	56.44	57.7
2000	56.13	56.28	57.01
2001	55.2	56.7	56.6
2002	54.5	54.6	54.9
2003	56.7	56.5	56.4
2004	39.4	39.3	38.6
2010	47.66	48.87	47.99
2011	63	58.2	56.6
2012	51.4	55.08	57.83
2030	50.25	51.01	49.89
2031	44	43	43
2050	54.49	54.08	54.31
2051	46	49	47
2052	55.88	55.93	55.87
2053	59.2	58.3	58.3
2056	59.2		
2070	58.55	58.6	59.97
2090	56.228	56.325	55.022

Benzo[*b*]fluoranthene

Figure 8: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 53.7 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

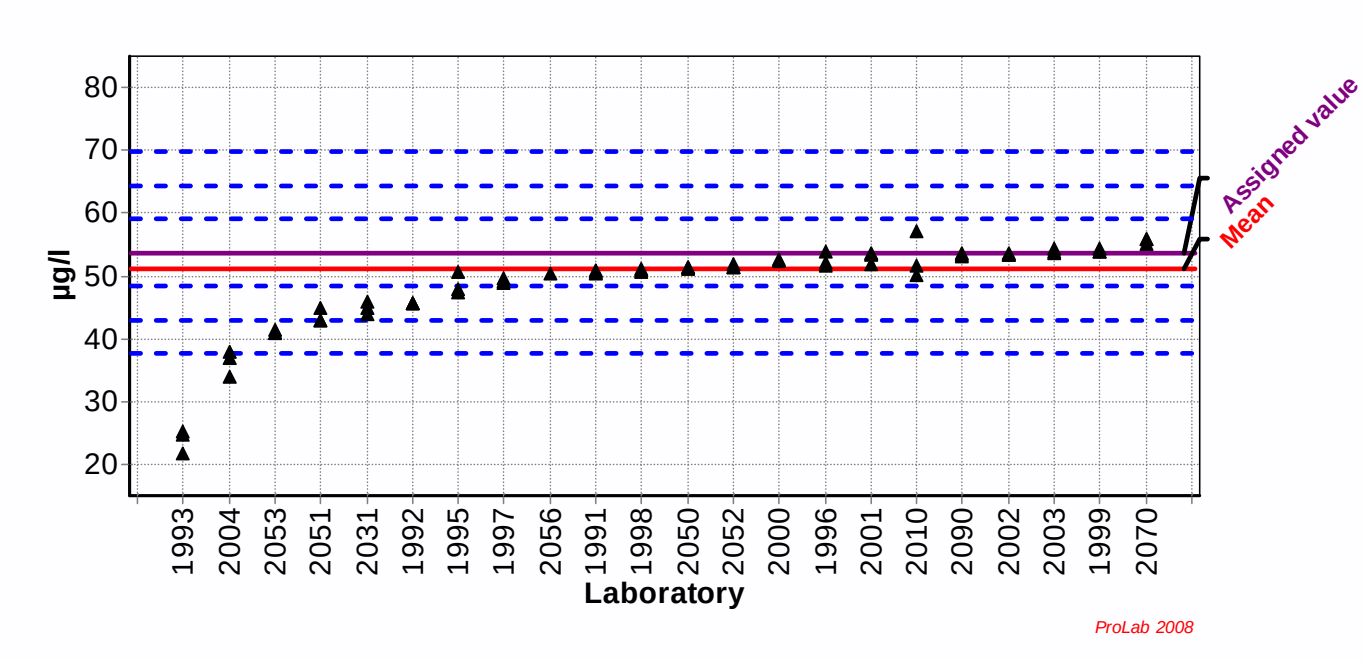


Figure 9: **Kernel Density Plot**

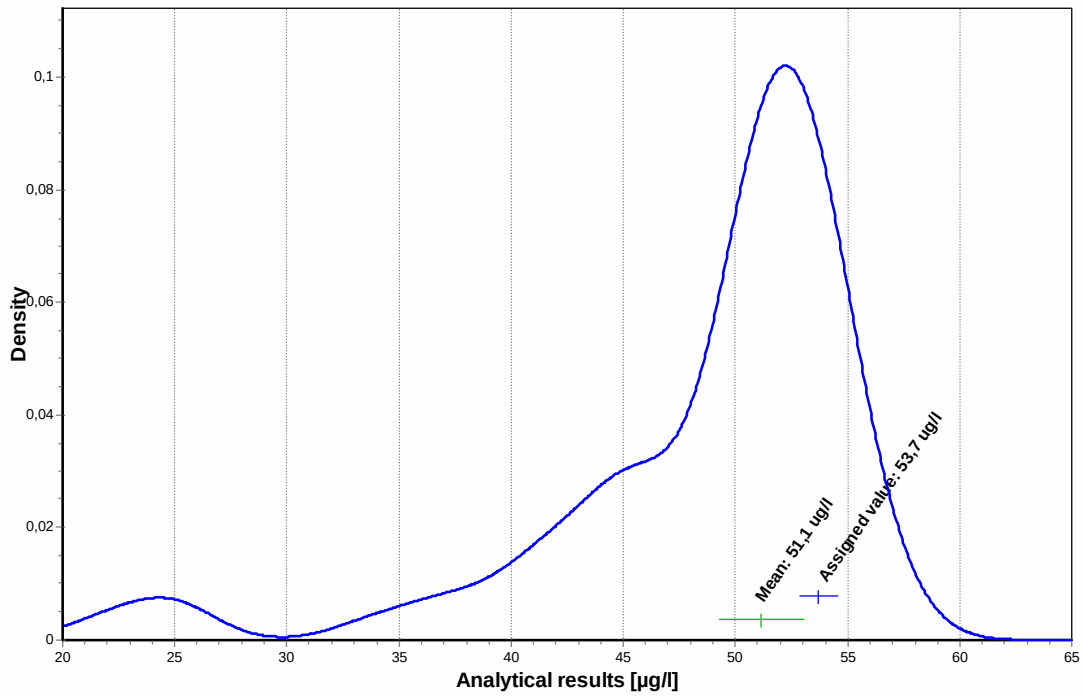


Table 7: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	50.6	50.3	50.9
1992	45.56	45.65	45.7
1993	21.79	24.66	25.1
1995	50.5	47.9	47.4
1996	52	51.7	53.9
1997	49.6	48.9	49.1
1998	50.7	50.9	51.2
1999	53.96	53.94	54.28
2000	52.43	52.73	52.33
2001	51.9	53.6	53.4
2002	53.4	53.7	53.3
2003	53.6	54.4	53.9
2004	36.8	37.9	34
2010	50.18	51.73	57.08
2011			
2012*	147	156	156.6
2030			
2031	46	45	44
2050	51.49	51.24	51.4
2051	45	43	43
2052	51.4	51.81	51.25
2053	40.8	41.3	40.8
2056	50.4		
2070	55.95	55.89	55
2090	53.184	53.713	53.453

** The values reported represent the sum of the contents of the three benzofluoranthenes. They were not included into the evaluation of the individual analytes*

Benzo[*c*]fluorene

Figure 10: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 29.5 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

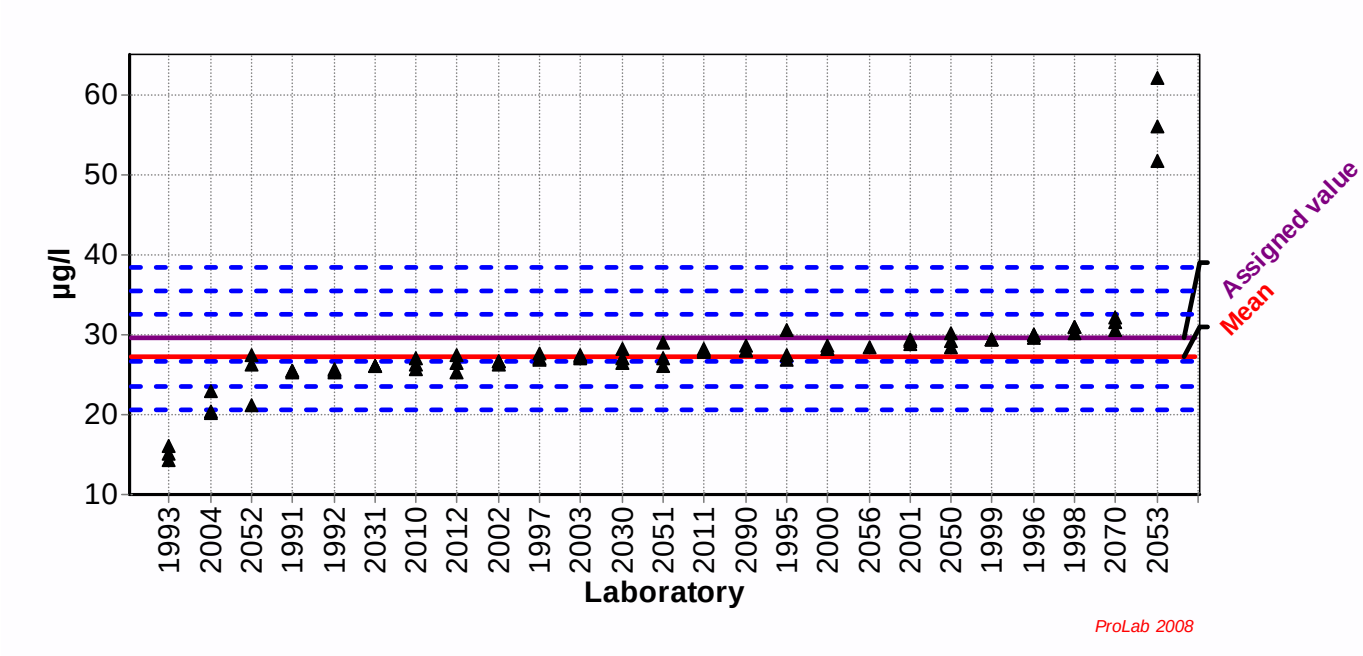


Figure 11: **Kernel Density Plot**

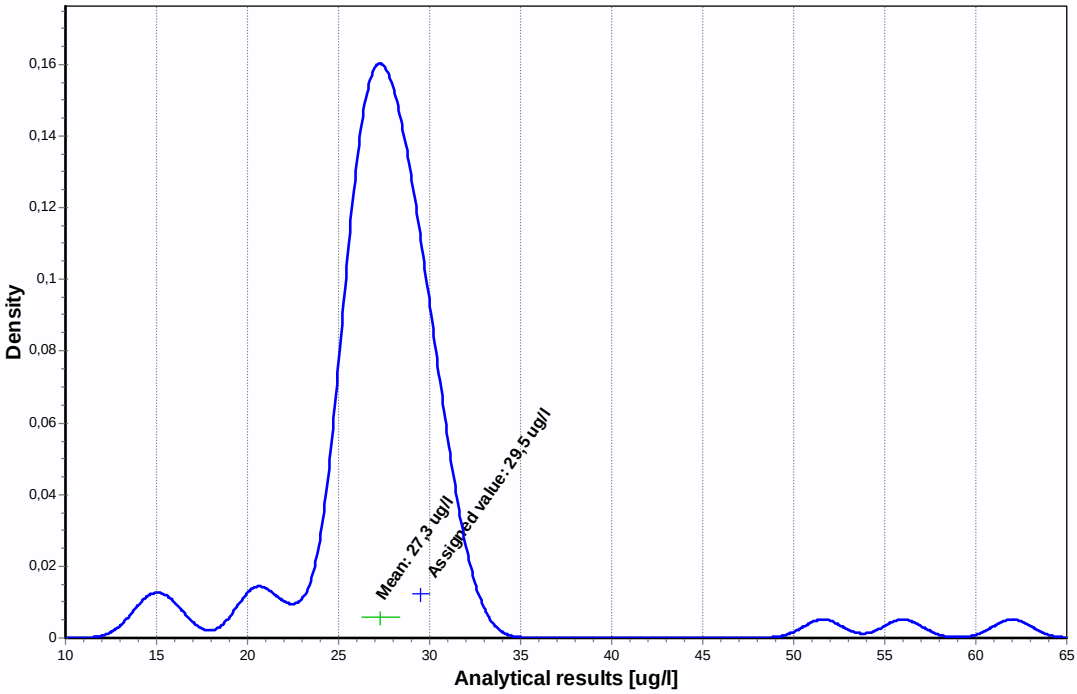


Table 8: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	25.4	25.4	25.2
1992	25.26	25.42	25.6
1993	15	15.97	14.3
1995	27.4	30.5	26.8
1996	30	30	29.6
1997	27.6	26.8	27
1998	30.9	30.9	30.1
1999	29.34	29.32	29.44
2000	28.2	28.25	28.5
2001	28.7	29.3	29.2
2002	26.6	26.6	26.3
2003	27.3	27	27.4
2004	20.2	23	20.3
2010	26.16	26.97	25.71
2011	28.1	27.9	28.3
2012	25.25	26.47	27.49
2030	28.3	27.1	26.52
2031	26	26	26
2050	30.23	29.22	28.32
2051	29	27	26
2052	27.45	21.25	26.33
2053	56	62	51.6
2056	28.4		
2070	32.15	31.48	30.49
2090	27.987	28.601	27.941

Benzo[*ghi*]perylene

Figure 12: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 52.5 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

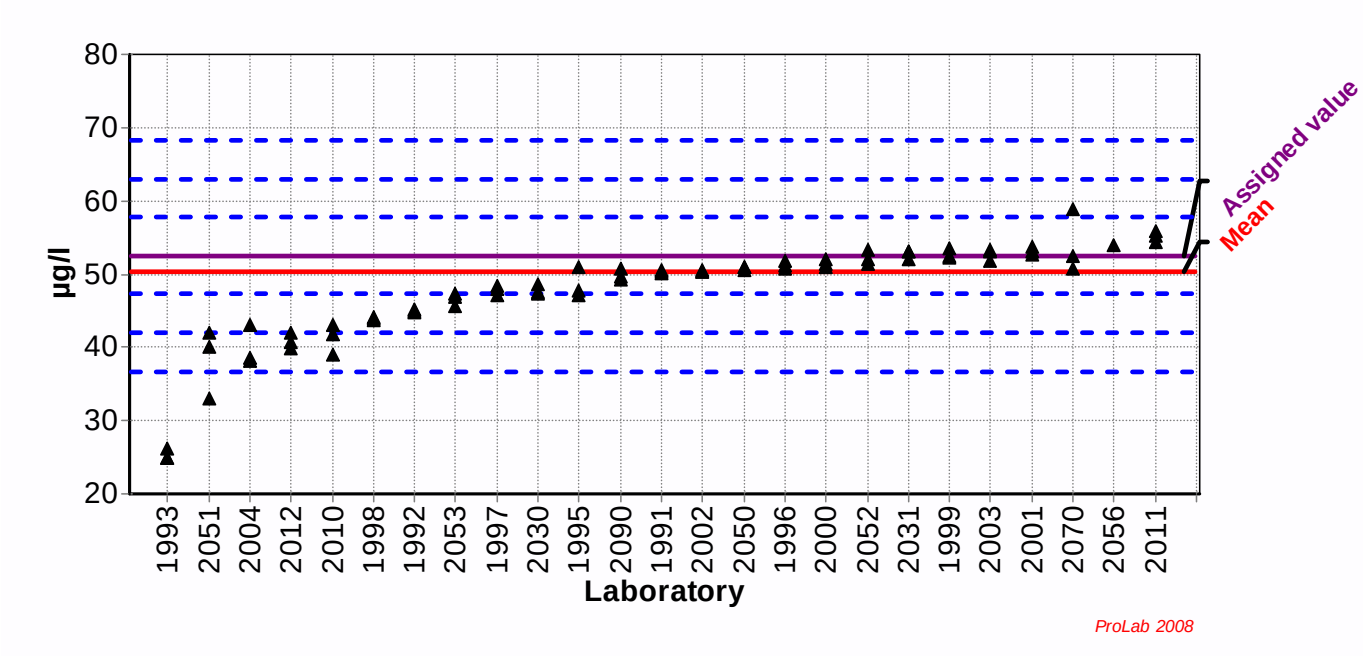


Figure 13: **Kernel Density Plot**

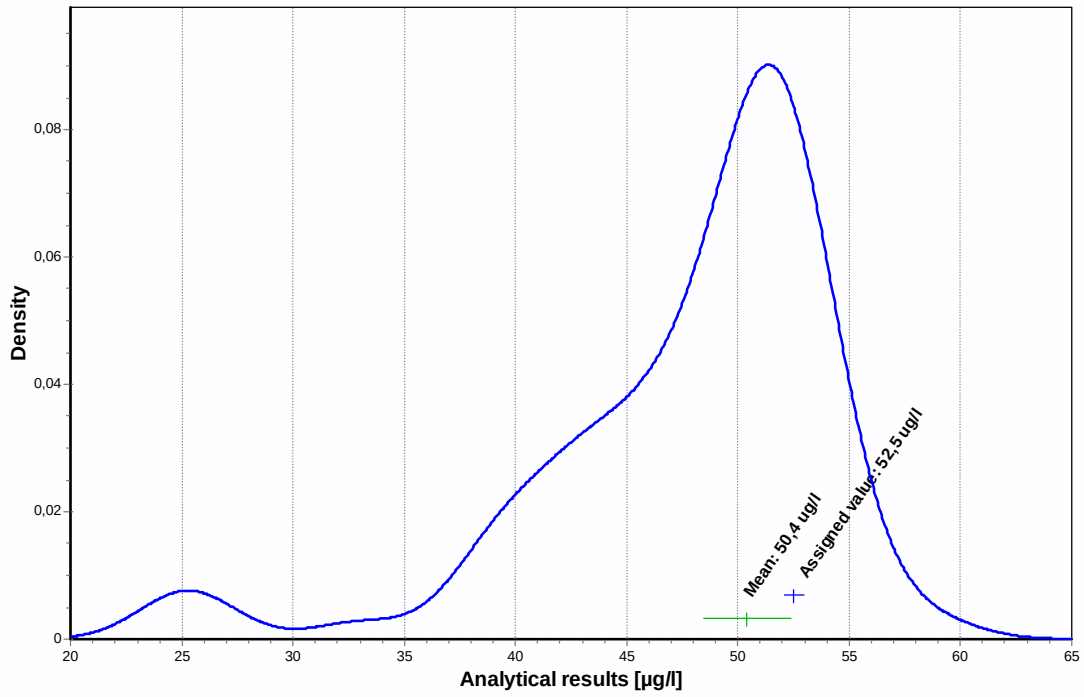


Table 9: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	50.1	50.5	50.4
1992	44.72	44.95	45.23
1993	24.91	24.85	26.14
1995	50.9	47.7	47.2
1996	51.9	50.7	51.1
1997	47.1	47.9	48.4
1998	44.1	43.7	44
1999	52.4	52.34	53.46
2000	50.86	51.41	51.95
2001	53	53.7	52.7
2002	50.5	50.4	50.4
2003	53.2	53.3	51.8
2004	38.5	43	38.2
2010	38.95	43.06	41.83
2011	55.2	54.3	55.9
2012	39.87	42.02	40.74
2030	48.66	47.49	47.27
2031	52	53	53
2050	50.99	51.01	50.58
2051	33	42	40
2052	53.25	52.07	51.47
2053	47.4	46.8	45.6
2056	54		
2070	58.8	52.35	50.67
2090	49.244	49.648	50.81

Benzo[*j*]fluoranthene

Figure 14: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 66.1 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

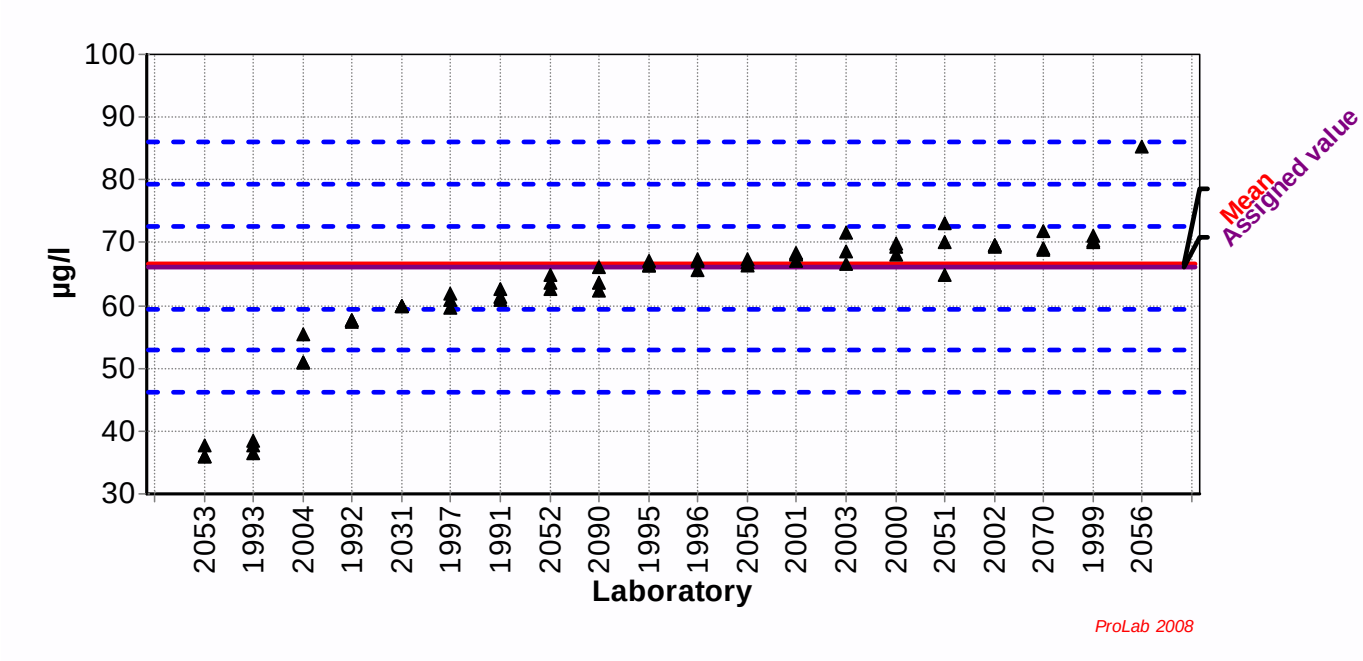


Figure 15: **Kernel Density Plot**

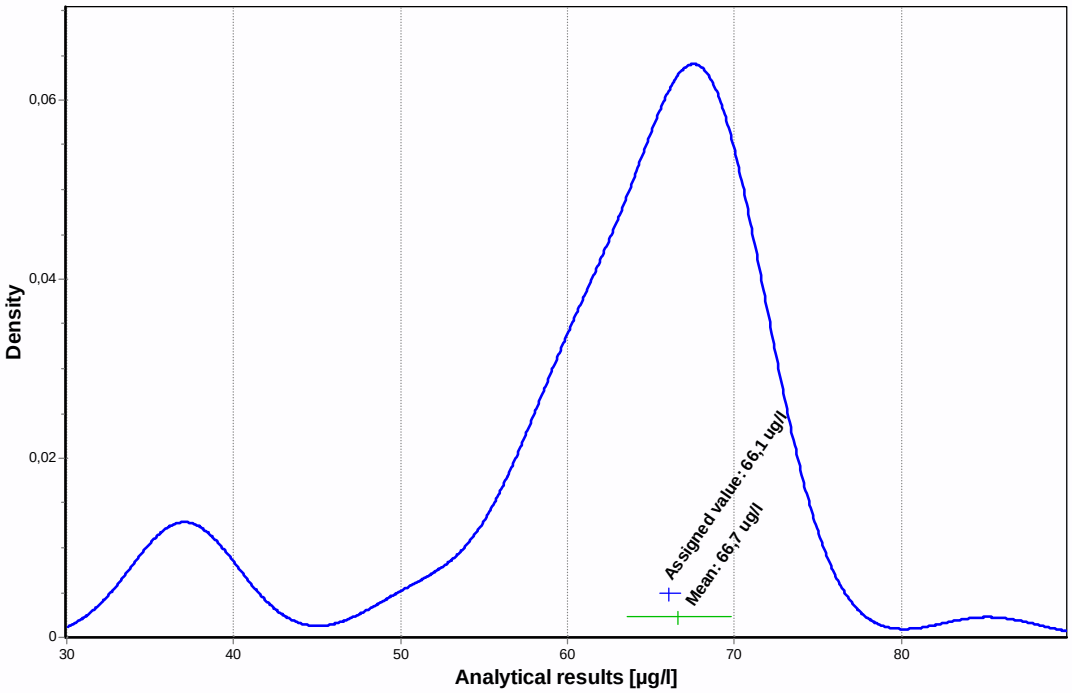


Table 10: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	60.8	61.5	62.6
1992	57.3	57.55	57.62
1993	36.56	37.64	38.5
1995	66.3	66.4	67.2
1996	65.6	67.1	67.3
1997	62	60.9	59.6
1999	70.1	70.24	71.1
2000	68.12	69.43	69.8
2001	67.1	68	68.4
2002	69.6	69.6	69.4
2003	66.6	68.7	71.7
2004	50.9	55.4	51
2010			
2011			
2012*	147	156	156.6
2030			
2031	60	60	60
2050	67.46	66.93	66.47
2051	73	70	65
2052	62.67	64.99	63.52
2053	35.9	37.7	36
2056	85.2		
2070	68.8	71.97	69
2090	66.108	62.476	63.628

** The values reported represent the sum of the contents of the three benzofluoranthenes. They were not included into the evaluation of the individual analytes*

Benzo[*k*]fluoranthene

Figure 16: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 46.5 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

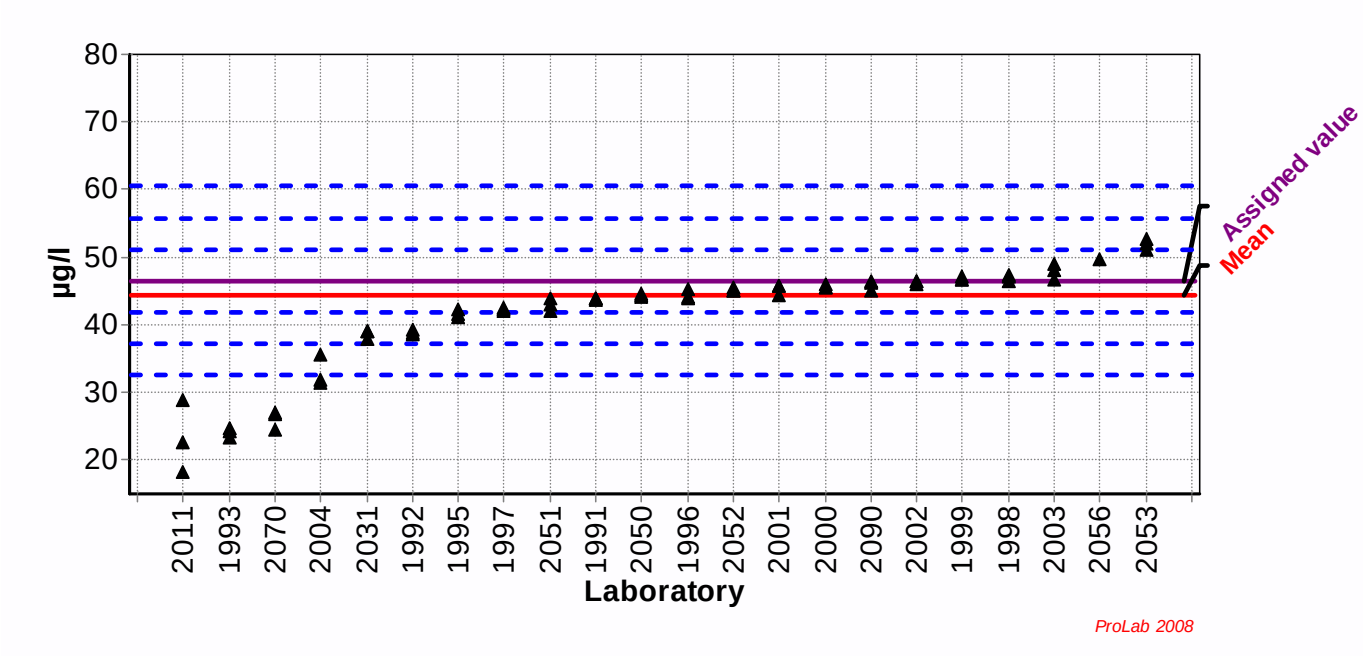


Figure 17: **Kernel Density Plot**

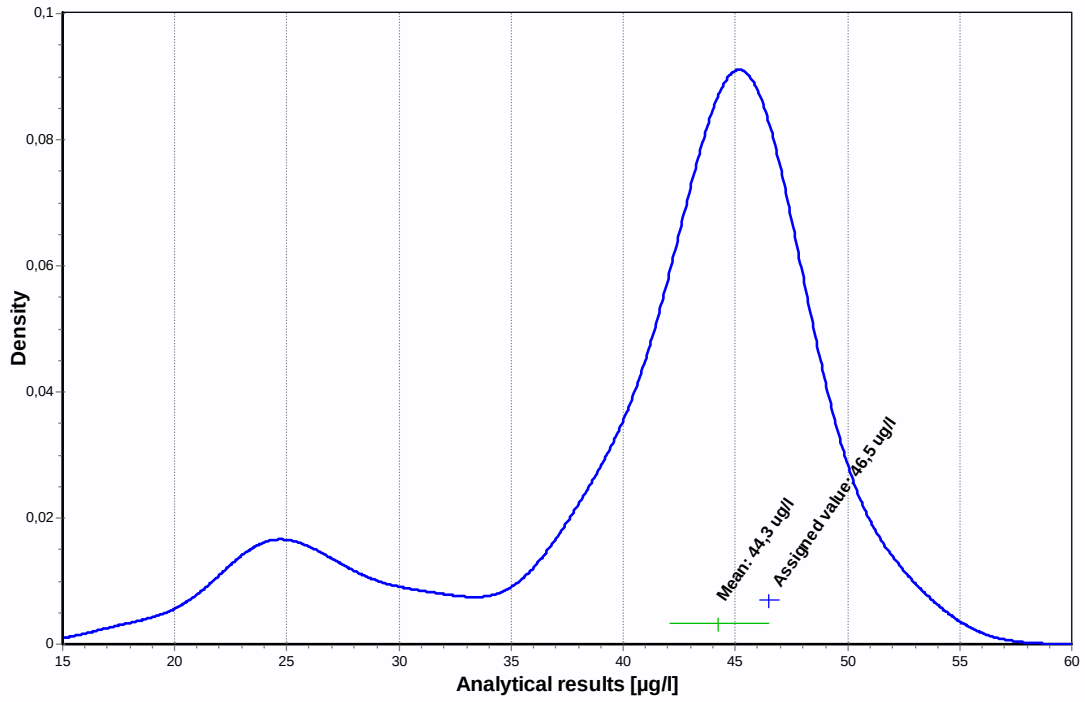


Table 11: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	44	44	43.7
1992	38.48	38.86	39.21
1993	24.65	23.28	24.14
1995	41.7	42.4	41.1
1996	44.2	45.4	43.9
1997	42.6	42.1	42.4
1998	47.4	47.1	46.5
1999	46.76	46.76	47.06
2000	45.44	45.57	45.96
2001	44.4	45.8	45.7
2002	46.1	46.4	46.4
2003	49.1	48	46.8
2004	32	35.5	31.5
2010			
2011	28.8	22.7	18.3
2012*	147	156	156.6
2030*	149.19	146.47	149.66
2031	39	39	38
2050	44.52	44.2	44.35
2051	44	43	42
2052	45.09	45.5	44.98
2053	51.9	52.7	51.1
2056	49.7		
2070	26.7	26.95	24.43
2090	46.423	46.141	44.978

** The values reported represent the sum of the contents of the three benzofluoranthenes. They were not included into the evaluation of the individual analytes*

Chrysene

Figure 18: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 47.7 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

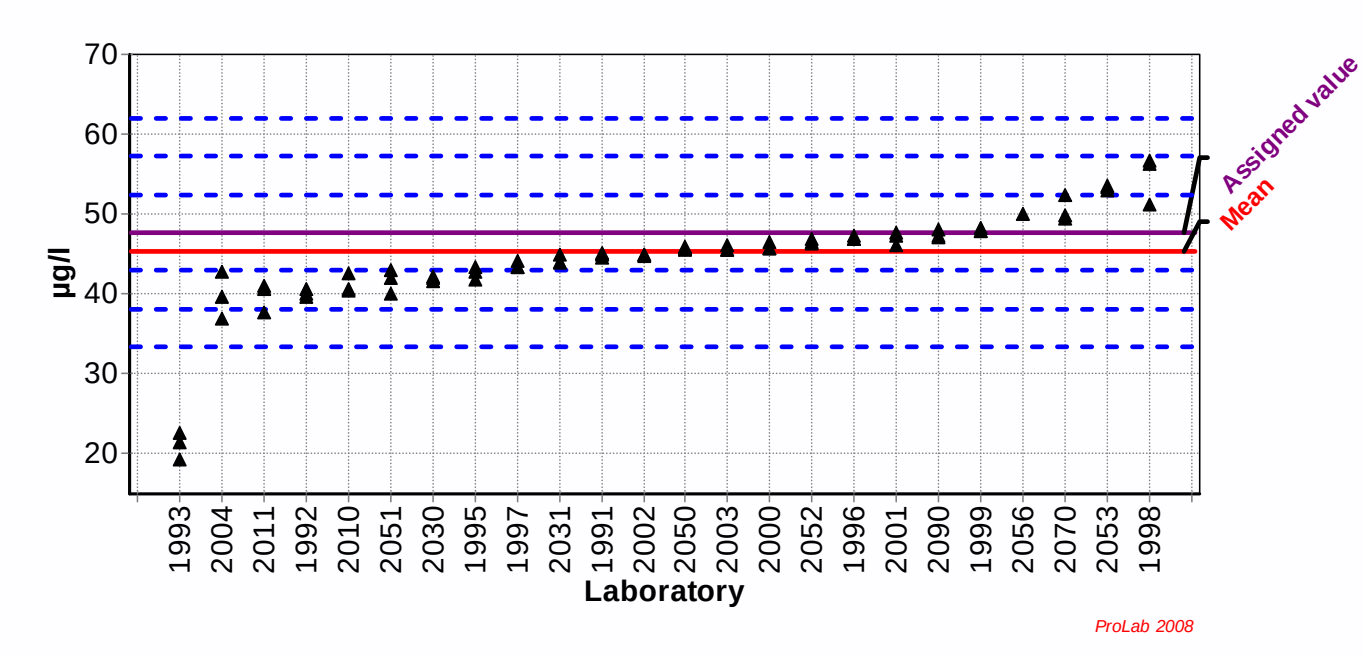


Figure 19: **Kernel Density Plot**

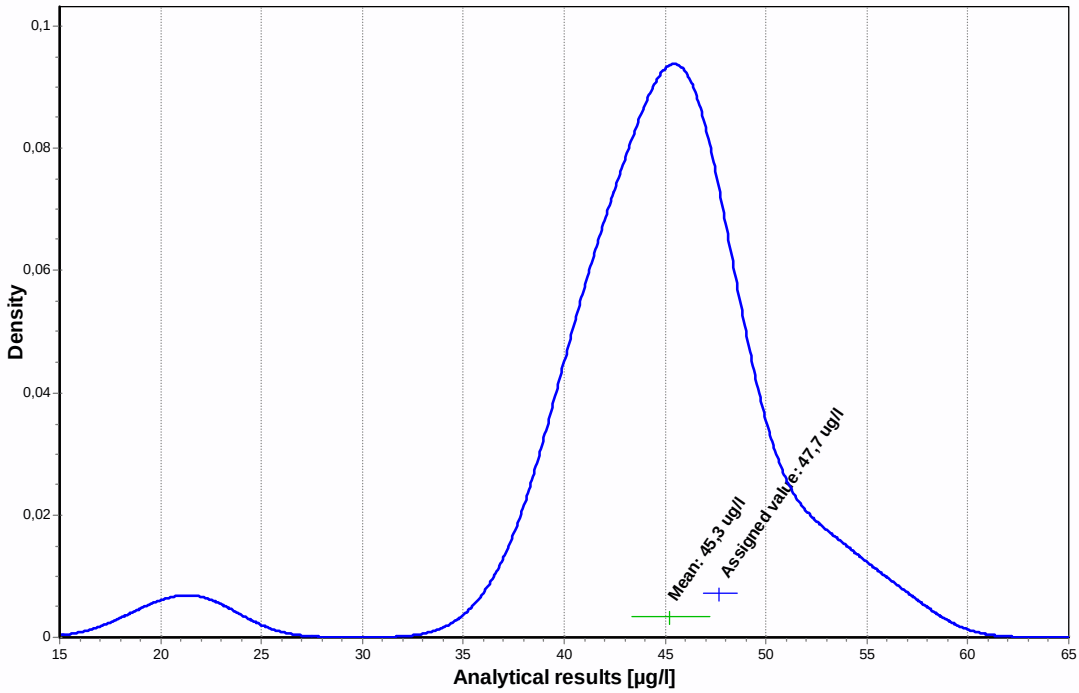


Table 12: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	45.1	44.9	44.5
1992	39.72	40.05	40.62
1993	21.51	19.26	22.56
1995	41.9	43.3	42.8
1996	46.9	46.9	47.3
1997	44.1	43.4	43.3
1998	56.7	56.3	51.2
1999	47.82	47.8	48.3
2000	45.71	45.76	46.6
2001	46.2	47.7	47.3
2002	44.9	44.9	44.8
2003	46.1	45.5	45.6
2004	37	42.7	39.7
2010	40.61	42.63	40.47
2011	37.8	41.1	40.7
2012	42.69	46.28	45.86
2030	42.21	42.09	41.58
2031	45	44	44
2050	45.67	45.62	45.87
2051	40	43	42
2052	46.36	46.46	46.98
2053	53.3	53.6	53
2056	50		
2070	49.8	52.47	49.5
2090	47.078	47.317	48.15

Cyclopenta[*cd*]pyrene

Figure 20: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 51.1 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

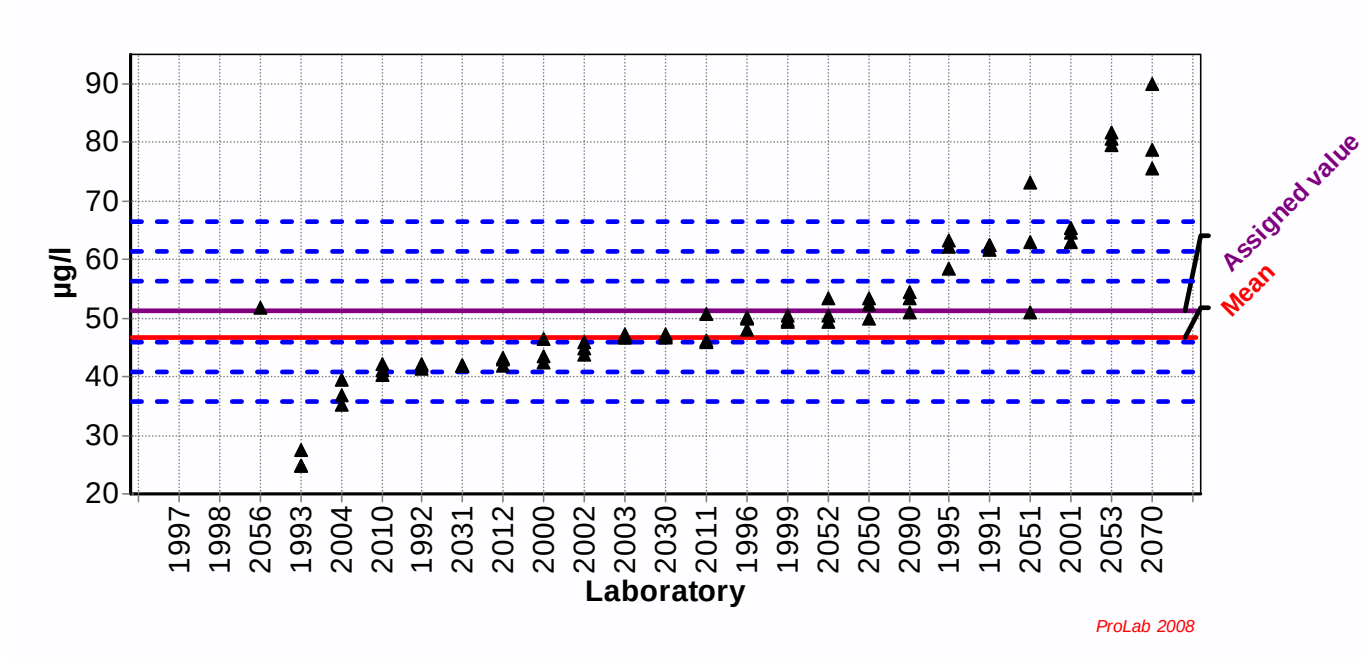


Figure 21: **Kernel Density Plot**

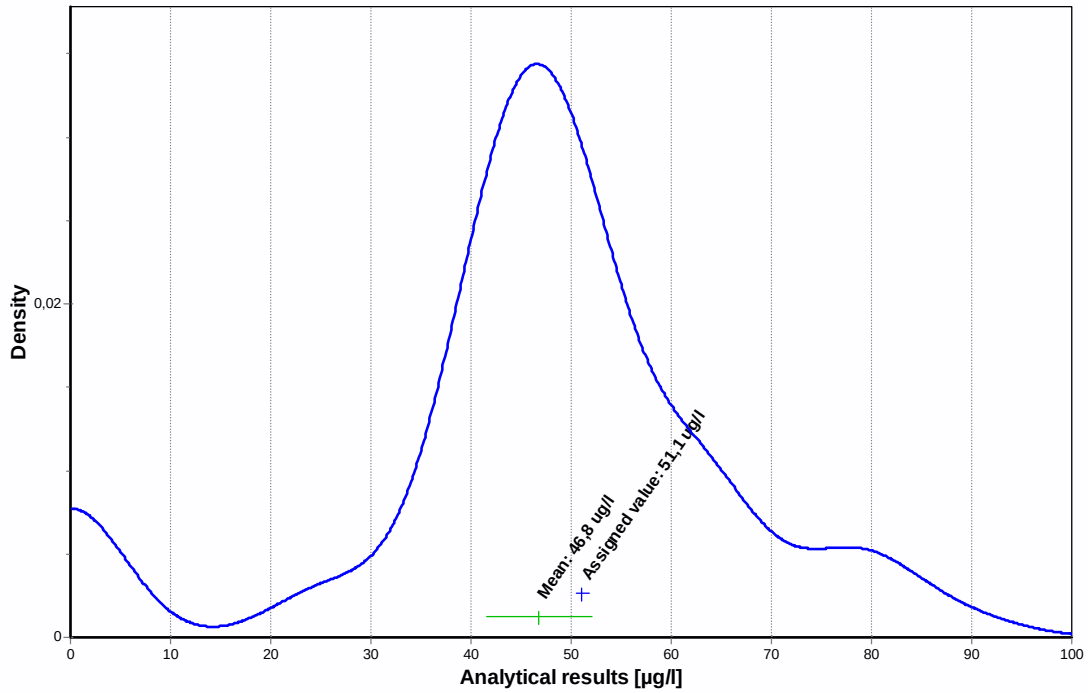


Table 13: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	61.6	62.5	62.4
1992	41.34	41.88	42.05
1993	24.76	27.59	24.69
1995	58.5	63.2	62.3
1996	47.9	50.2	49.9
1997			
1998			
1999	50.46	49.54	49.44
2000	43.52	46.51	42.42
2001	65.3	64.6	62.9
2002	45.8	44.7	43.8
2003	46.7	46.8	47.2
2004	36.8	39.5	35.1
2010	40.36	42.28	40.97
2011	45.9	46.2	50.8
2012	41.76	42.98	43.33
2030	47.11	46.58	47.09
2031	42	42	42
2050	53.36	49.82	52.31
2051	73	51	63
2052	50.42	49.42	53.25
2053	80.5	81.7	79.5
2056	51.8		
2070	78.8	90	75.5
2090	53.3	54.5	51

Dibenzo[*a,e*]pyrene

Figure 22: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 47.4 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

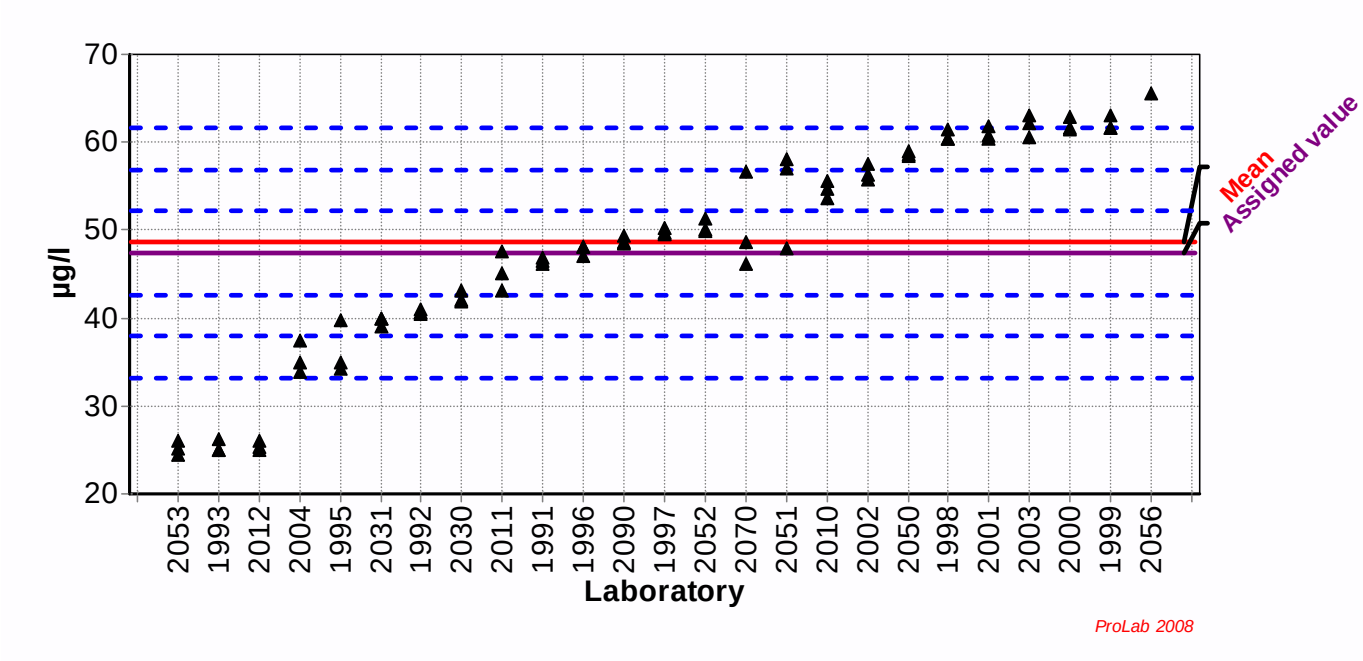


Figure 23: **Kernel Density Plot**

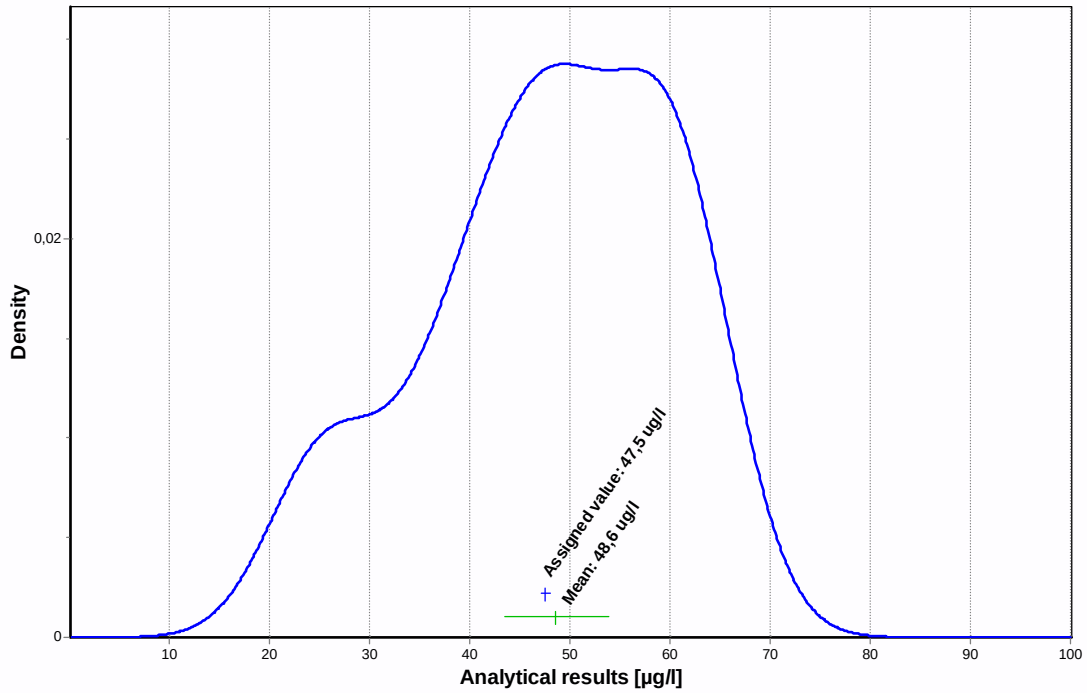


Table 14: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	46.1	46.9	46.5
1992	40.38	40.63	40.95
1993	25.03	26.26	24.96
1995	39.8	34.3	35
1996	47	48.1	48.2
1997	49.8	49.6	50.2
1998	61.4	60.4	60.4
1999	61.72	61.72	63.08
2000	61.47	61.6	62.82
2001	60.4	61.8	60.8
2002	57.6	56.3	55.7
2003	63	62.1	60.6
2004	34.9	37.4	33.8
2010	53.67	54.74	55.56
2011	45.01	47.6	43.1
2012	25.3	25.05	26.13
2030	43.12	42.05	41.83
2031	40	40	39
2050	58.65	58.51	58.88
2051	48	58	57
2052	50.06	51.27	49.92
2053	24.4	25.2	26
2056	65.5		
2070	56.7	48.62	46.22
2090	48.611	49.442	48.493

Dibenz[*a*,*h*]anthracene

Figure 24: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 49.0 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

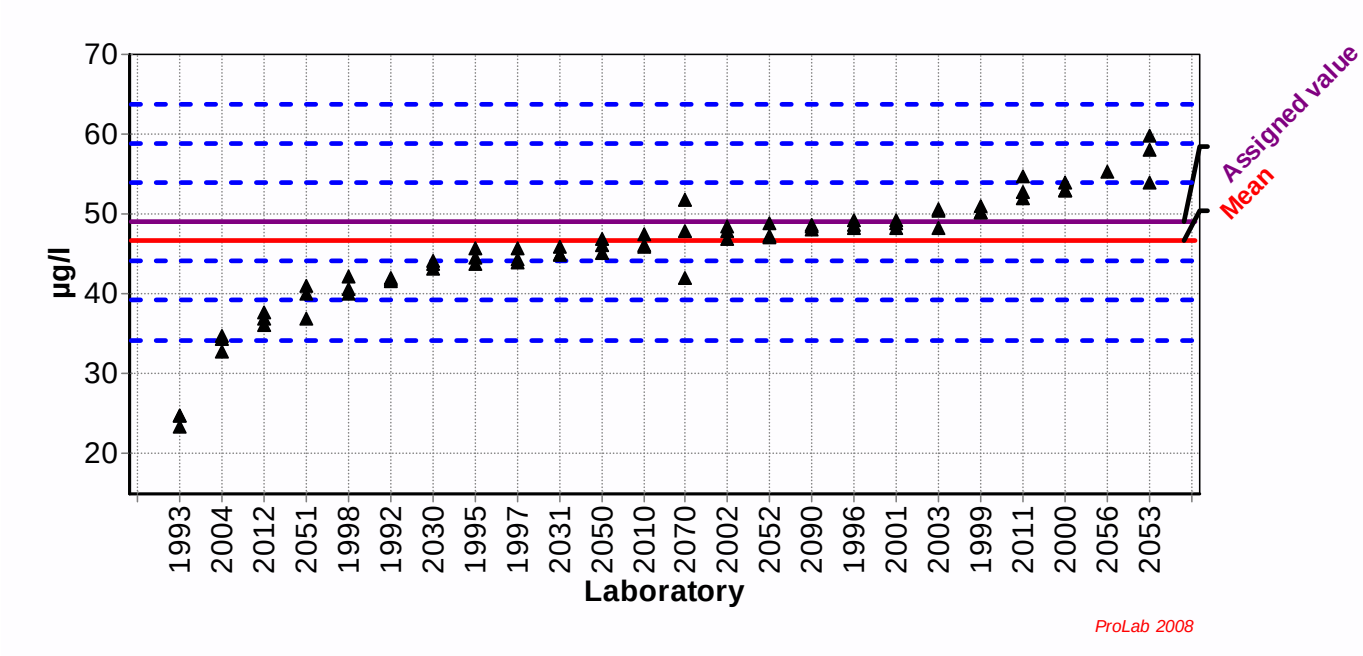


Figure 25: **Kernel Density Plot**

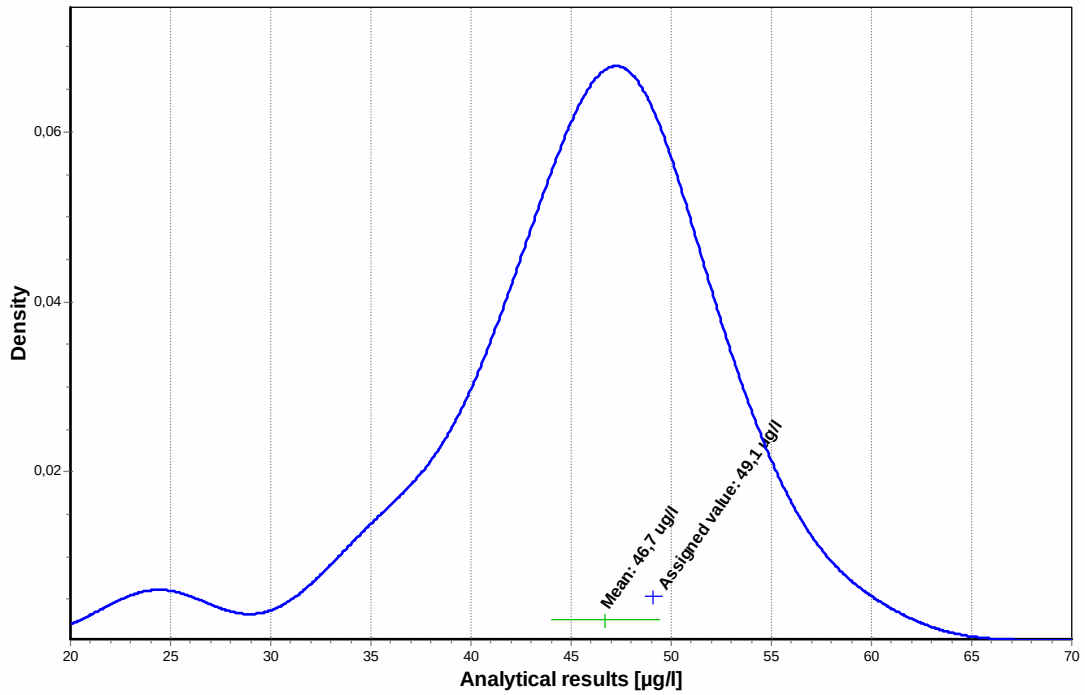


Table 15: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991			
1992	41.58	41.72	42.08
1993	23.36	24.87	24.84
1995	44.5	43.7	45.8
1996	49.2	48.3	48.7
1997	44	44.4	45.8
1998	42.3	40.1	40.6
1999	50.24	50.26	50.96
2000	52.9	53.04	53.93
2001	48.9	49.3	48.2
2002	48.5	47.8	47
2003	50.4	50.6	48.3
2004	34.8	34.3	32.9
2010	46.05	45.93	47.53
2011	54.7	52	52.7
2012	36.22	37.61	36.98
2030	43.69	43.16	44.11
2031	45	45	46
2050	45.14	46.87	46.06
2051	37	41	40
2052	47.3	48.82	47.18
2053	53.9	59.8	58.1
2056	55.4		
2070	47.9	41.99	51.77
2090	48.056	48.426	48.642

Dibenzo[*a,h*]pyrene

Figure 26: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 57.9 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

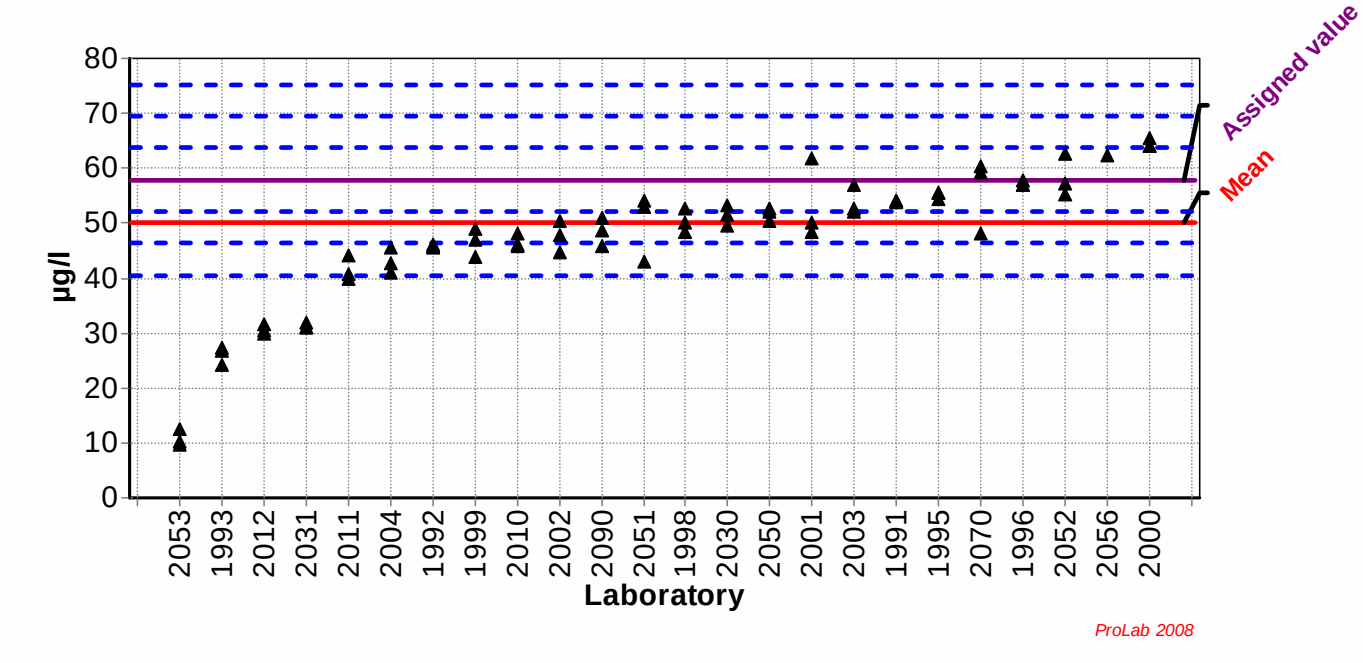


Figure 27: **Kernel Density Plot**

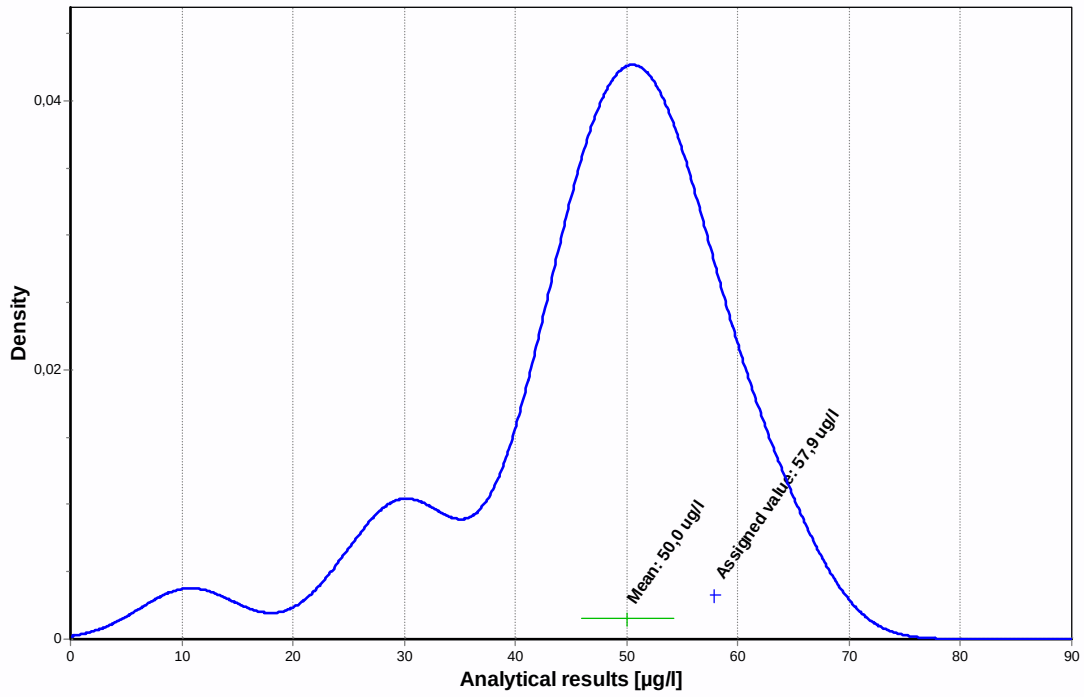


Table 16: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	54.2	54.1	53.9
1992	45.5	45.95	46.17
1993	26.76	27.33	24.3
1995	54.4	55.5	55.4
1996	57.7	57	57
1997			
1998	52.8	50	48.4
1999	46.98	48.88	43.88
2000	64.19	64	65.38
2001	61.9	48.4	50.1
2002	50.5	47.7	44.8
2003	52	56.8	52.6
2004	42.8	45.5	41
2010	45.98	45.89	48.07
2011	39.9	40.8	44.1
2012	29.86	30.35	31.73
2030	53.37	51.58	49.54
2031	31	31	32
2050	50.25	52.75	52.12
2051	43	53	54
2052	57.35	55.3	62.59
2053	10.2	12.5	9.7
2056	62.3		
2070	48.1	59.35	60.27
2090	48.696	45.947	51.013

Dibenzo[*a,i*]pyrene

Figure 28: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 50.2 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

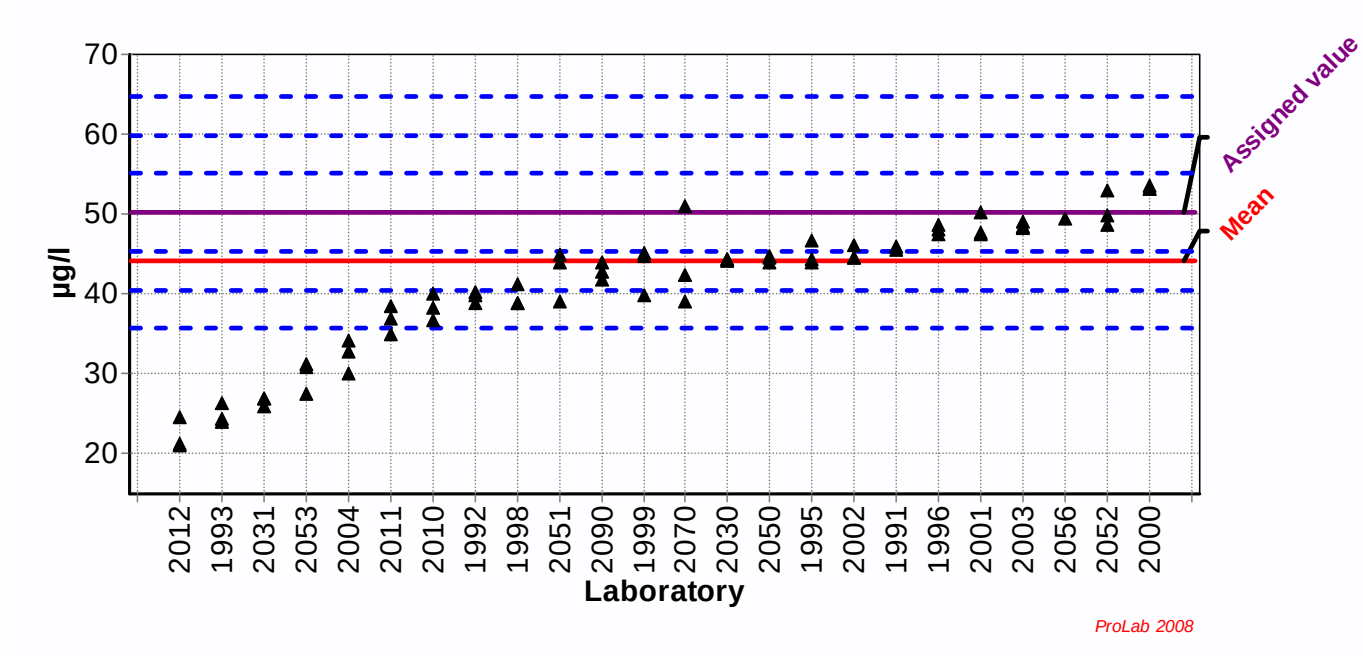


Figure 29: **Kernel Density Plot**

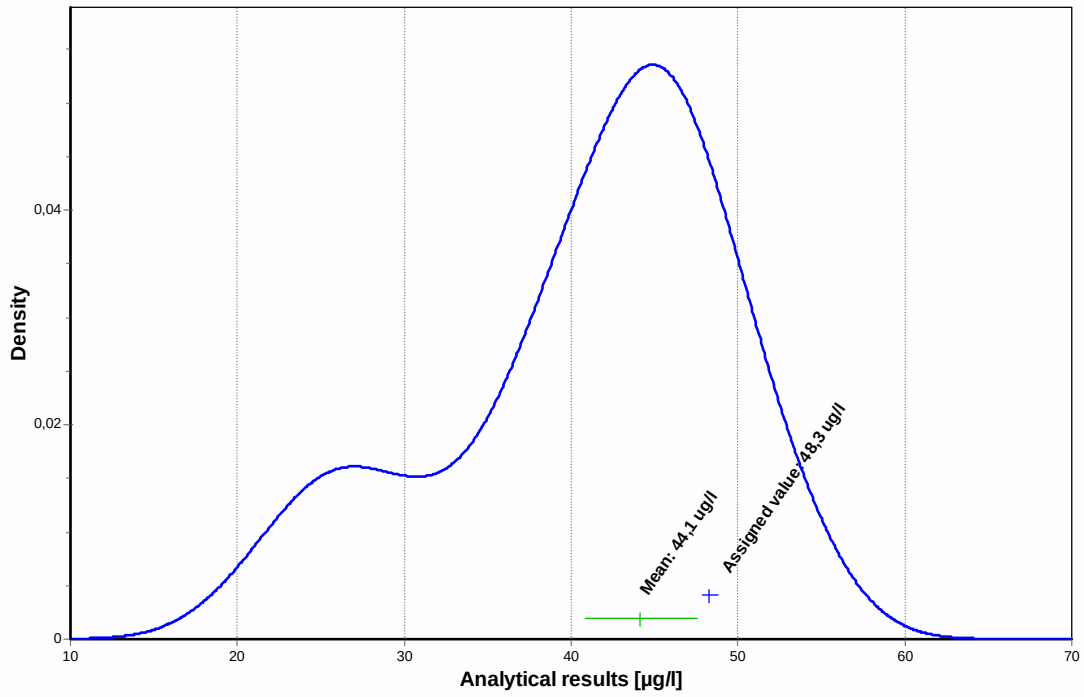


Table 17: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991	46	46	45.6
1992	38.84	39.87	40.29
1993	23.98	24.38	26.34
1995	43.9	44.3	46.7
1996	48.7	48	47.5
1997			
1998	41.3	38.8	38.9
1999	44.82	45.08	39.9
2000	53.22	53.14	53.63
2001	50.3	47.6	47.4
2002	44.6	44.6	46.2
2003	48.3	48.5	49
2004	32.8	34.1	30
2010	36.69	38.27	40.09
2011	36.9	35	38.5
2012	21.04	21.28	24.56
2030	44.21	44.37	44.42
2031	26	27	27
2050	44.03	44.49	44.71
2051	39	45	44
2052	49.91	48.69	53.06
2053	27.6	31.3	30.9
2056	49.4		
2070	42.45	39.12	51.07
2090	42.738	41.745	44.055

Dibenzo[*a,l*]pyrene

Figure 30: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 48.0 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

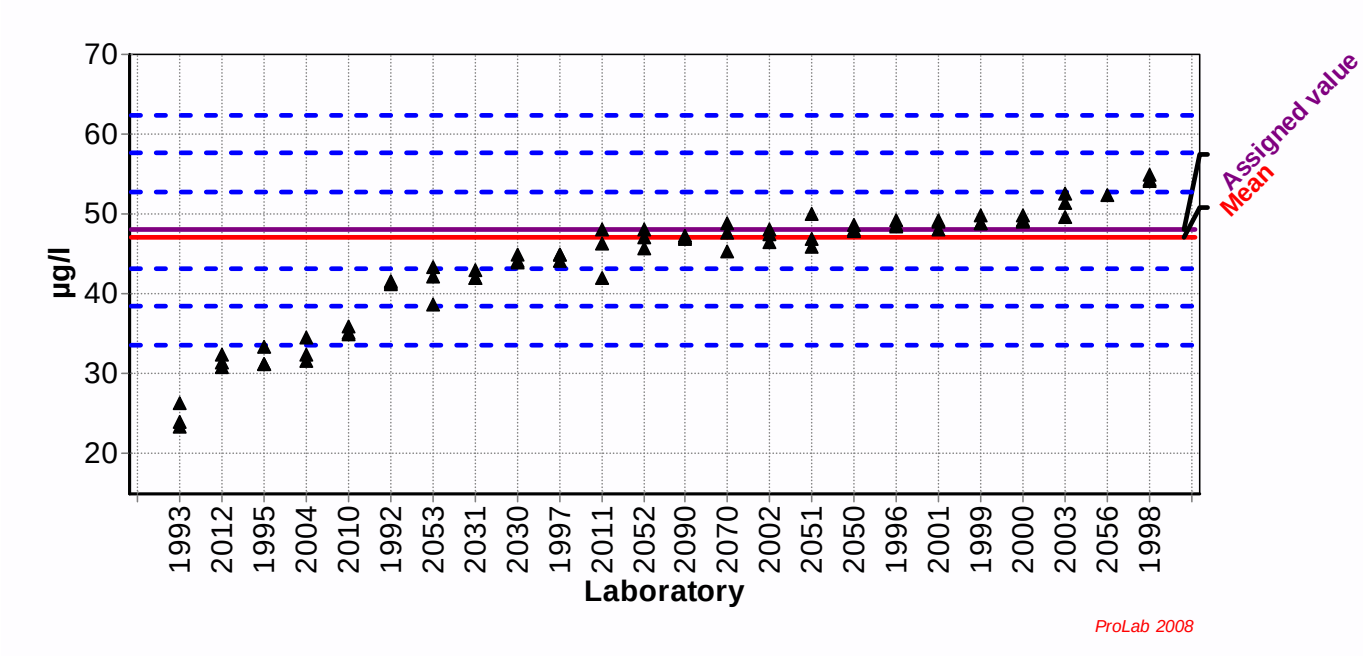


Figure 31: **Kernel Density Plot**

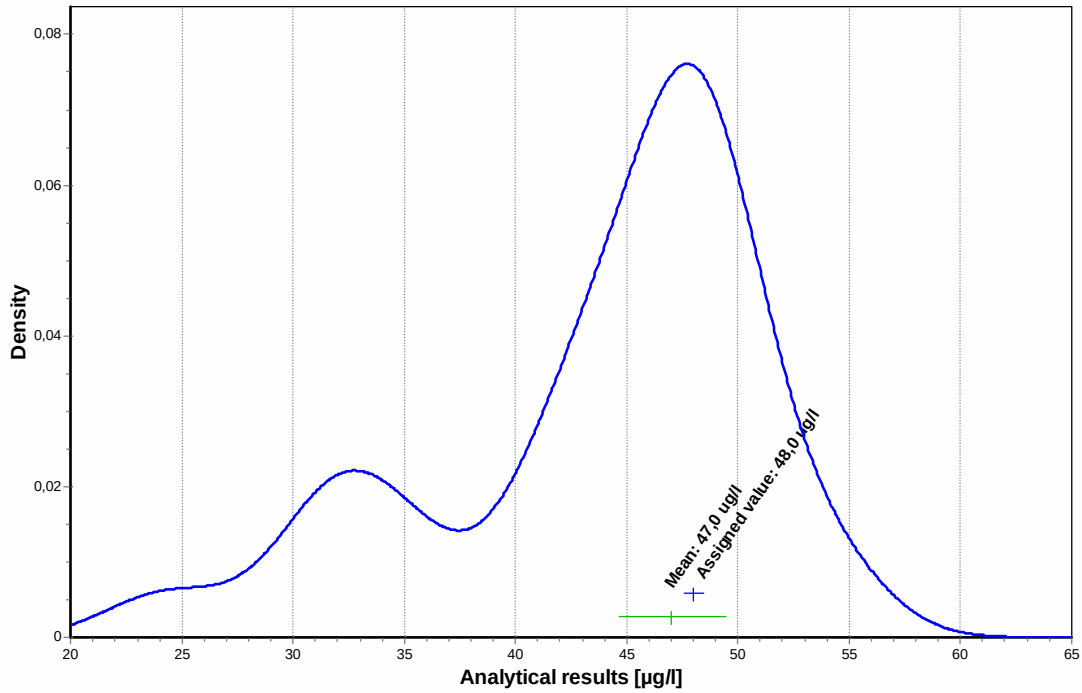


Table 18: Individual results of replicate measurements in µg/l (blank cells indicate missing data)

laboratory	Result 1	Result 2	Result 3
1991			
1992	41.22	41.46	41.61
1993	24.1	23.4	26.31
1995	33.4	31.2	31.2
1996	48.6	48.5	49.2
1997	44.2	44.9	44.9
1998	54.9	54.2	54.4
1999	48.88	48.92	49.92
2000	49.03	49.17	49.83
2001	48	49.3	49.1
2002	48	47.5	46.6
2003	52.5	51.4	49.7
2004	31.7	34.6	32.5
2010	35.01	35.14	35.97
2011	48	42	46.4
2012	31.47	30.86	32.51
2030	44.95	44.03	44.24
2031	42	43	42
2050	47.89	48.01	48.61
2051	50	46	47
2052	48	45.75	47.19
2053	38.7	42.3	43.4
2056	52.4		
2070	48.85	45.25	47.67
2090	47.072	47.334	46.98

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

Figure 32: **Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 65.6 µg/l (purple), and a ± 10 %, 20 %, and 30 % deviation thereof (blue dotted).**

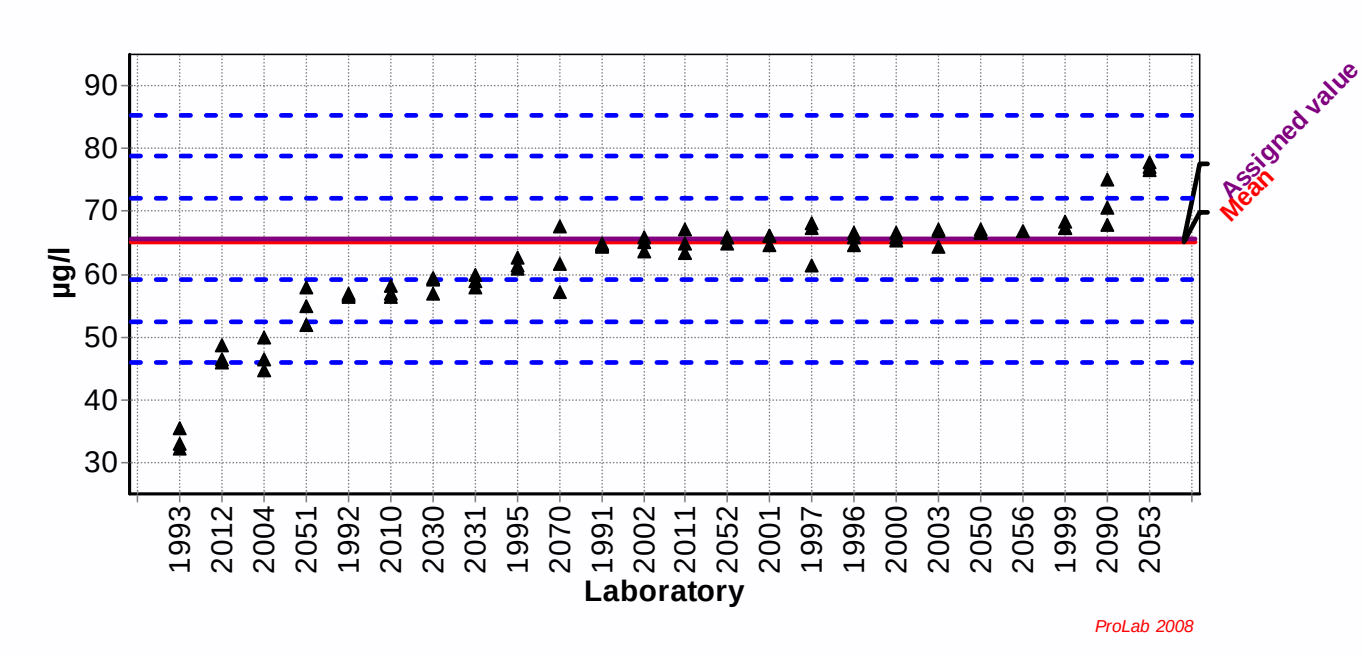


Figure 33: **Kernel Density Plot**

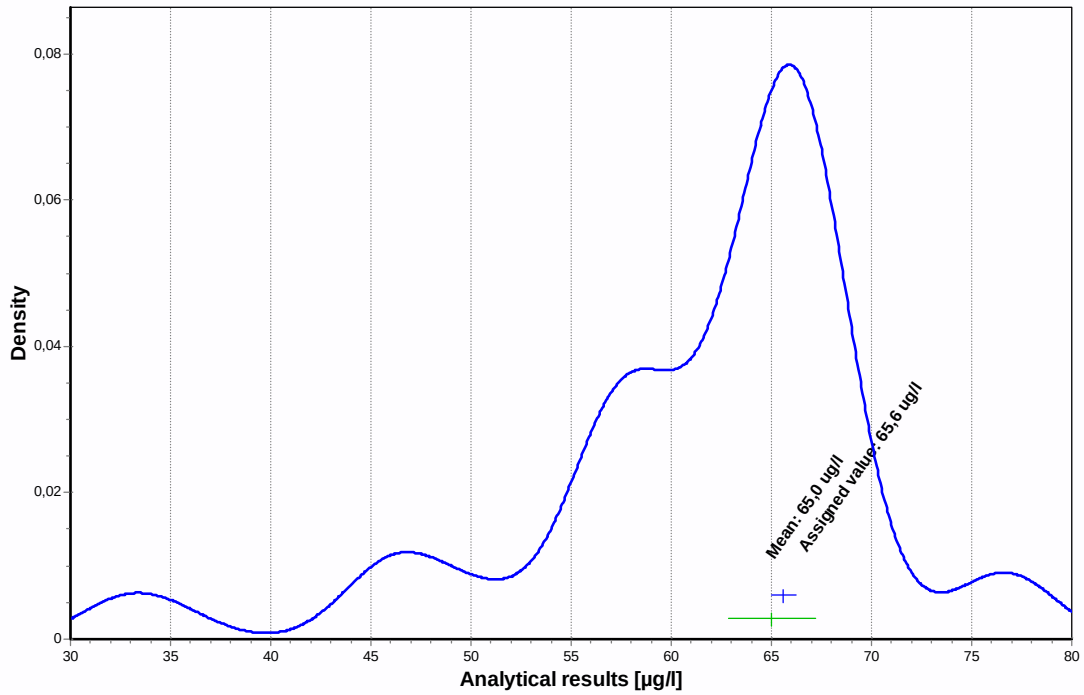


Table 19: Indeno[1,2,3-*cd*]pyrene: Individual results of replicate measurements in µg/l; blank cells indicate missing data

laboratory	Result 1	Result 2	Result 3
1991	64.9	64.5	64.3
1992	56.5	56.74	56.97
1993	33.08	32.15	35.42
1995	61.4	62.5	60.9
1996	65.9	64.6	66.5
1997	61.4	67.4	68.1
1998			
1999	67.26	67.4	68.3
2000	65.4	65.77	66.52
2001	64.6	66.1	66
2002	65.8	63.7	65.1
2003	66.8	67	64.3
2004	46.5	49.9	44.7
2010	56.39	57.01	58.16
2011	67.2	64.9	63.3
2012	45.85	48.61	46.44
2030	56.98	59.46	59.16
2031	59	58	60
2050	66.52	66.68	67.05
2051	52	58	55
2052	65.91	65.73	64.88
2053	77.9	77	76.6
2056	66.8		
2070	67.55	61.74	57.1
2090	74.95	67.882	70.532

Evaluation of potential influences on results for individual analytes in acetonitrile

In the following graphs the percent deviation of the results of selected analytes for the acetonitrile solution is depicted based on the applied analysis technique. This evaluation aims to identify bias of the results depending of the chromatographic technique applied. The agreement of results obtained by GC-MS and HPLC-FLD is good for BaP, BjF, and BkF. The deviations of the results of some participants are for these analytes rather systematic than random. For CPP, DhP and DiP the results gained by GC-MS are underestimated compared to HPLC-FLD, for which they are nearly evenly distributed around zero. Especially the latter two analytes are due to their low volatility challenging in GC-MS analysis. The results reported by laboratories applying HPLC-FLD were positively biased for DeP, whereas results obtained by GC-MS were for this analyte despite scattered evenly distributed around zero.

The respective graphs are shown from Figure 34 to Figure 47.

Figure 34: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*a*]pyrene in acetonitrile analysed by GC

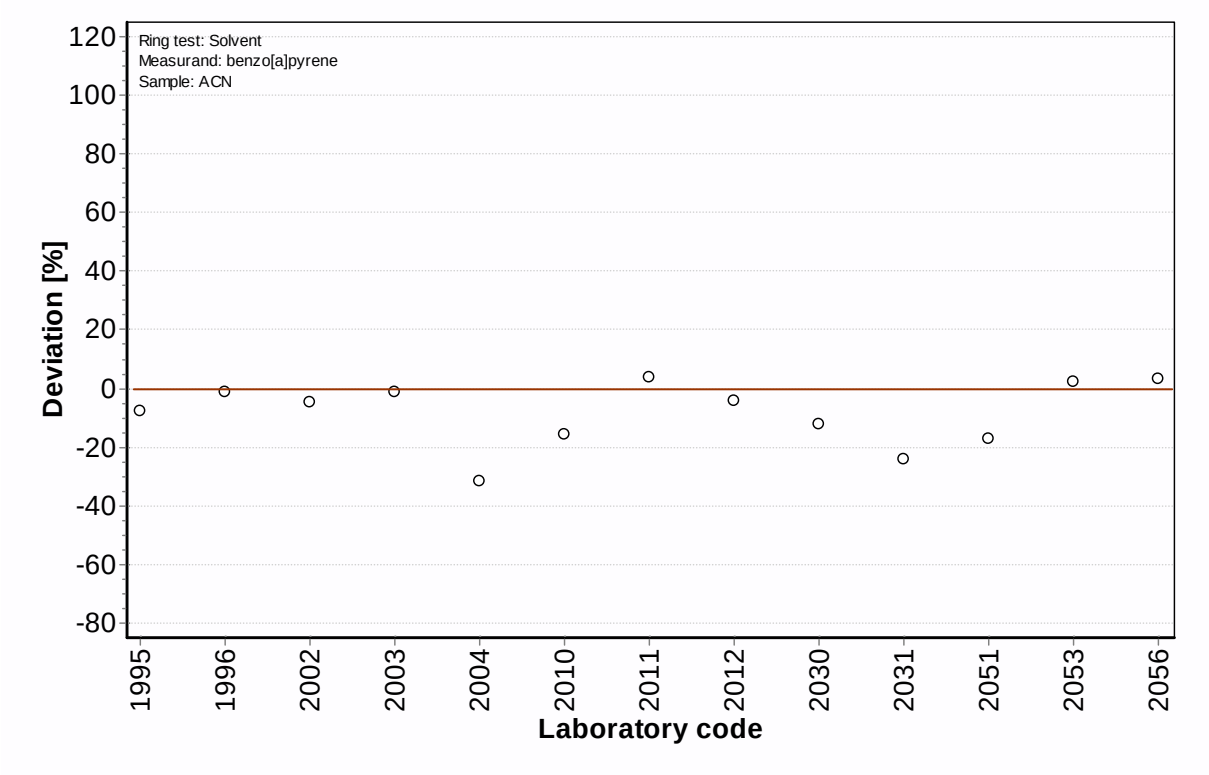


Figure 35: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*a*]pyrene in acetonitrile analysed by HPLC

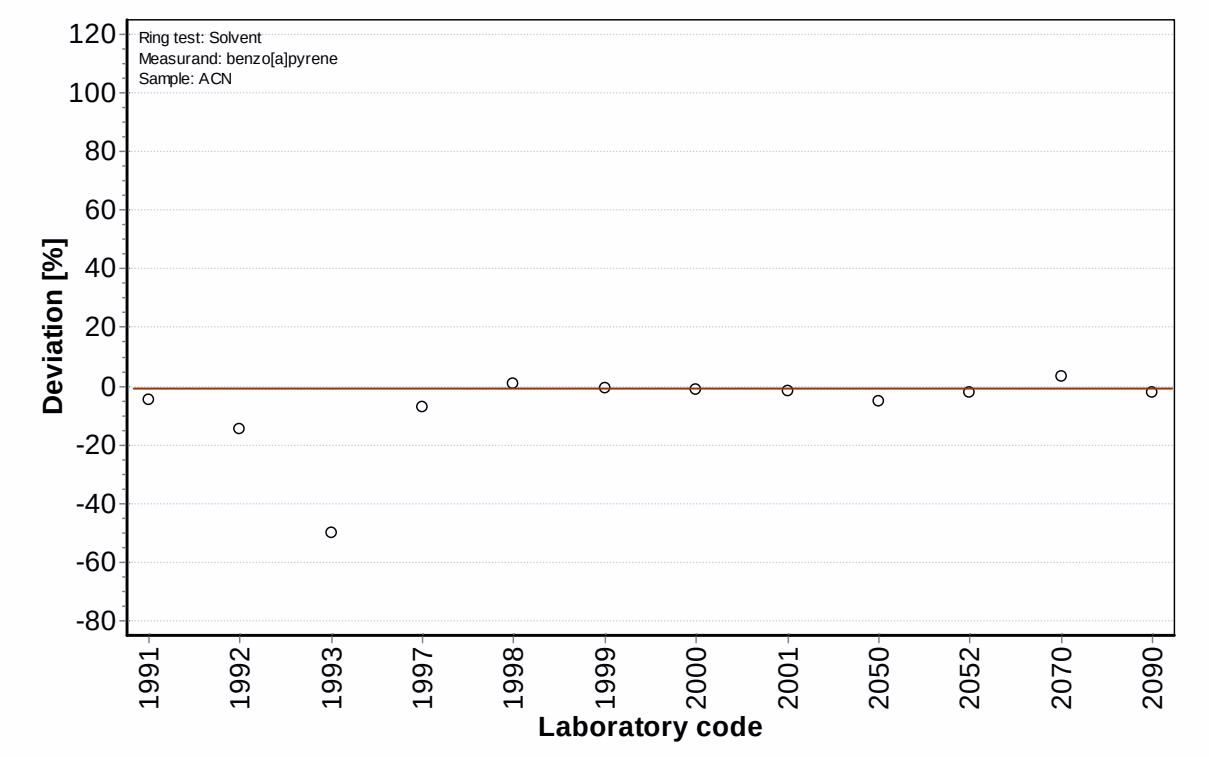


Figure 36: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*j*]fluoranthene in acetonitrile analysed by GC

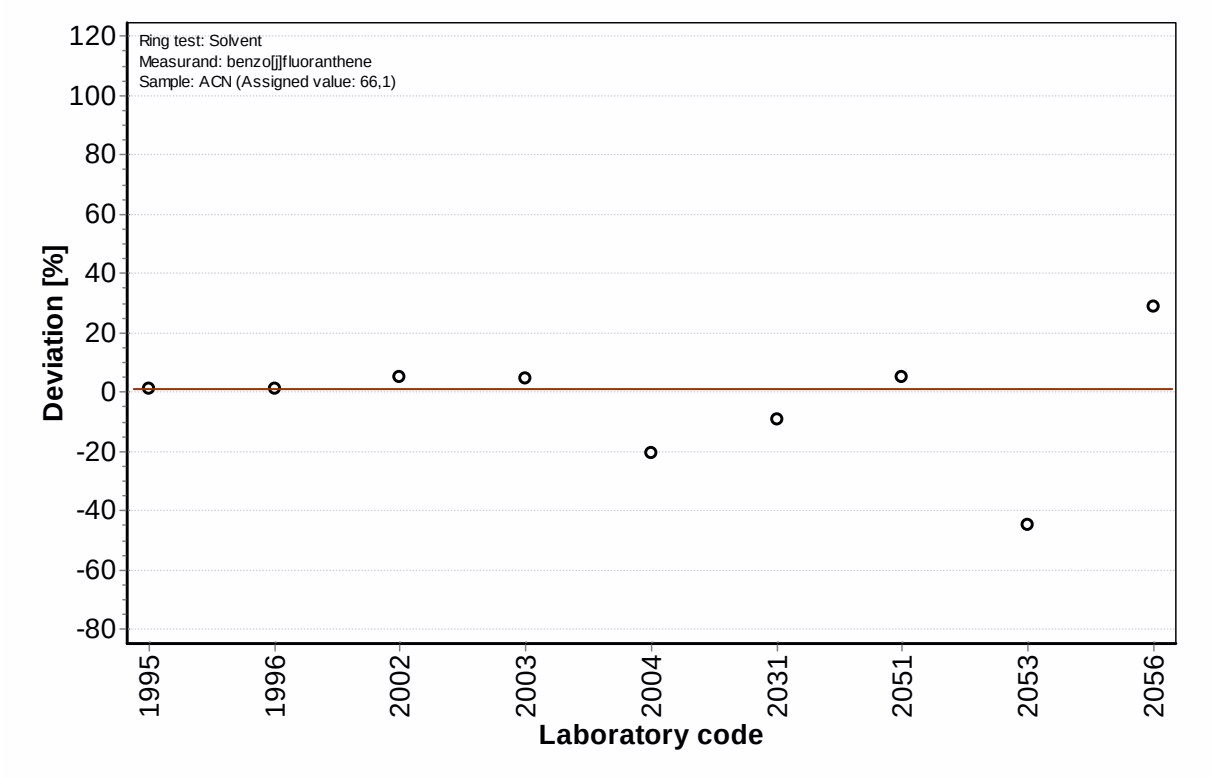


Figure 37: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*j*]fluoranthene in acetonitrile analysed by HPLC

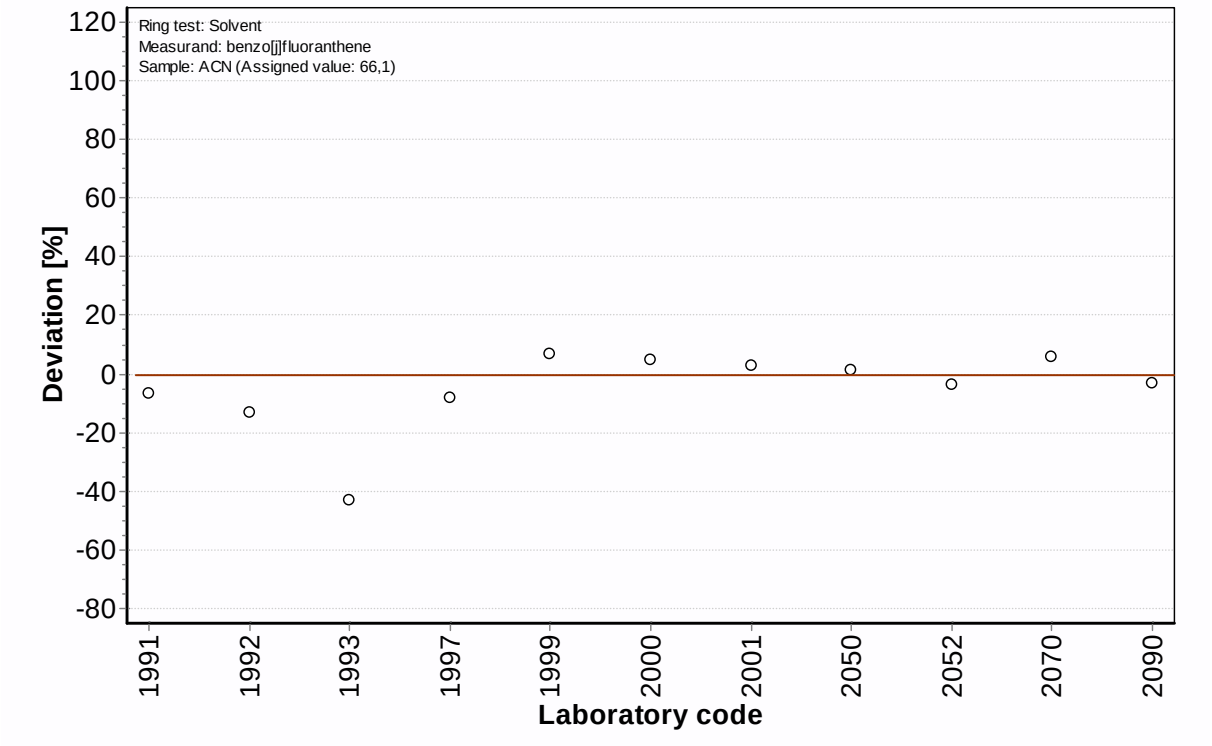


Figure 38: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*k*]fluoranthene in acetonitrile analysed by GC

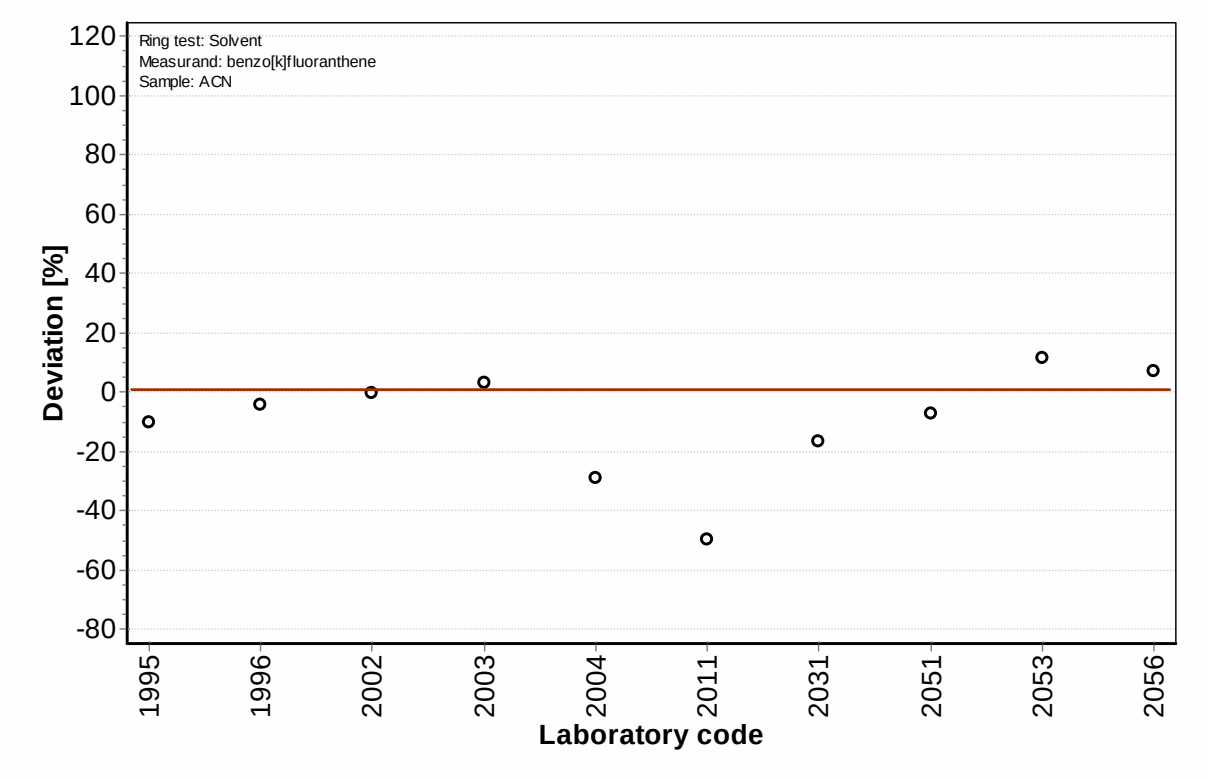


Figure 39: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*k*]fluoranthene in acetonitrile analysed by HPLC

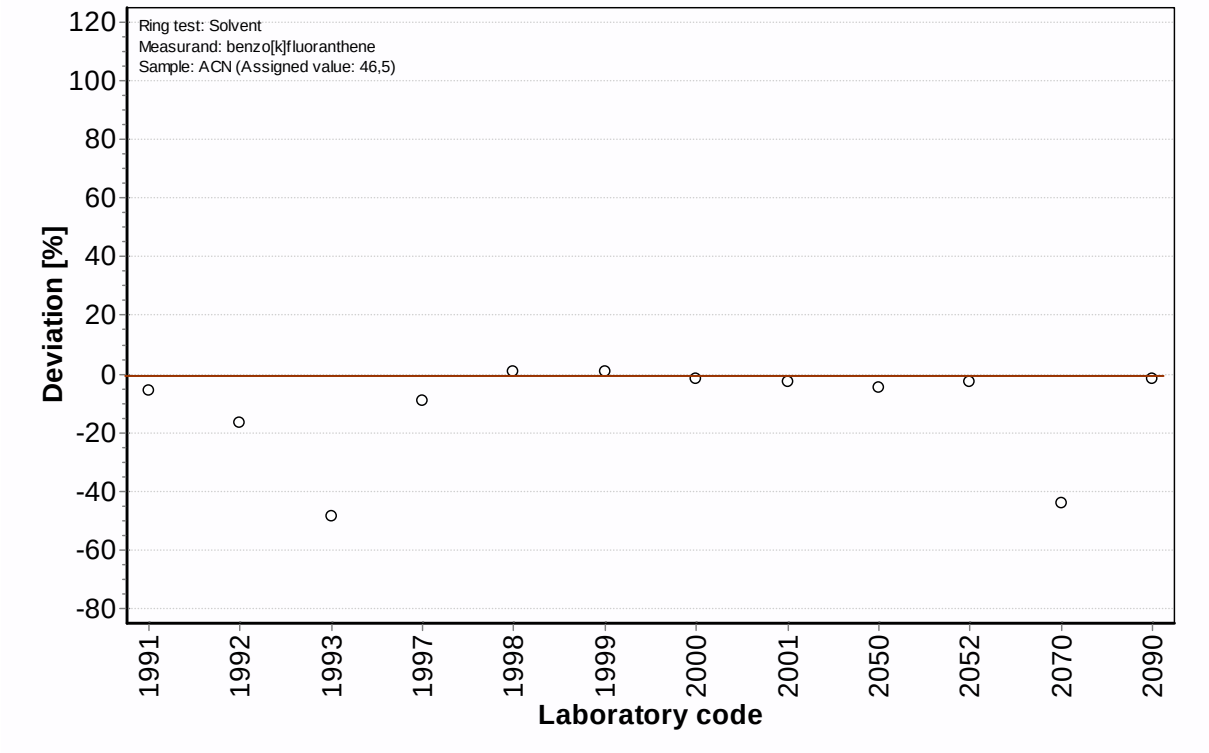


Figure 40: Relative deviations of the individual laboratories mean values from the assigned value of cyclopenta[*cd*]pyrene in acetonitrile analysed by GC

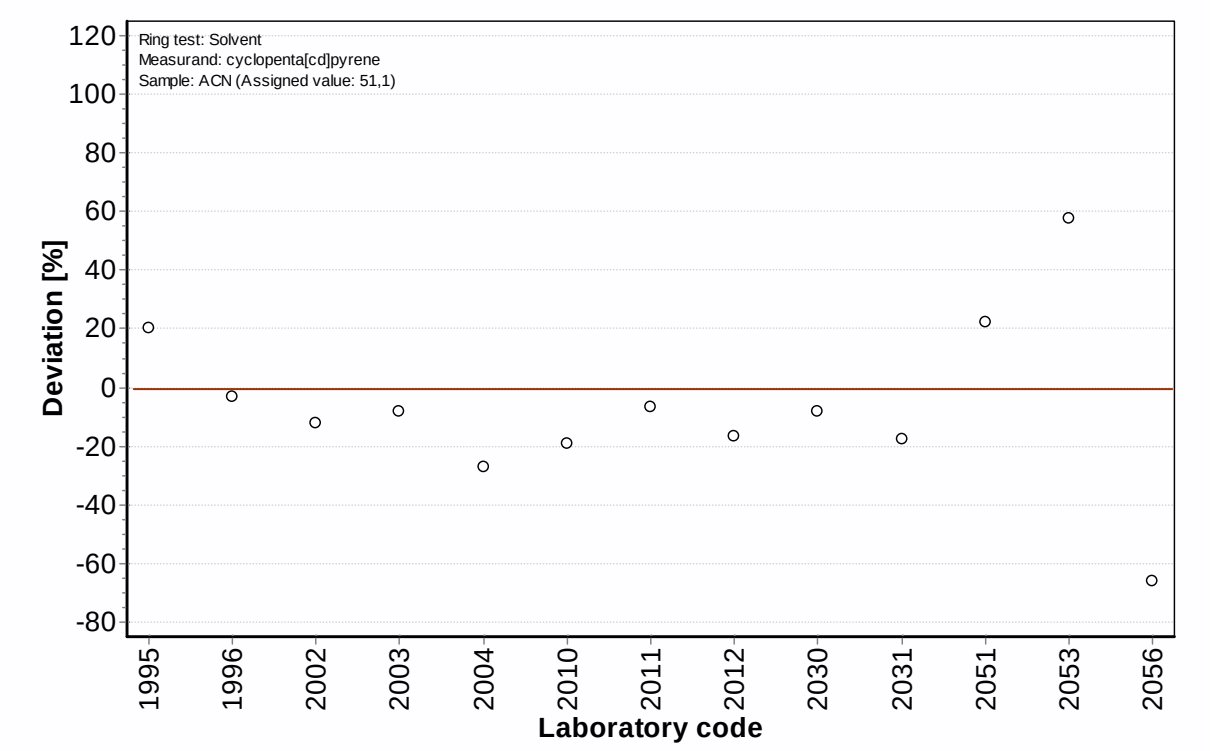


Figure 41: Relative deviations of the individual laboratories mean values from the assigned value of cyclopenta[*cd*]pyrene in acetonitrile analysed by HPLC

Figure 42: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,e*]pyrene in acetonitrile analysed by GC

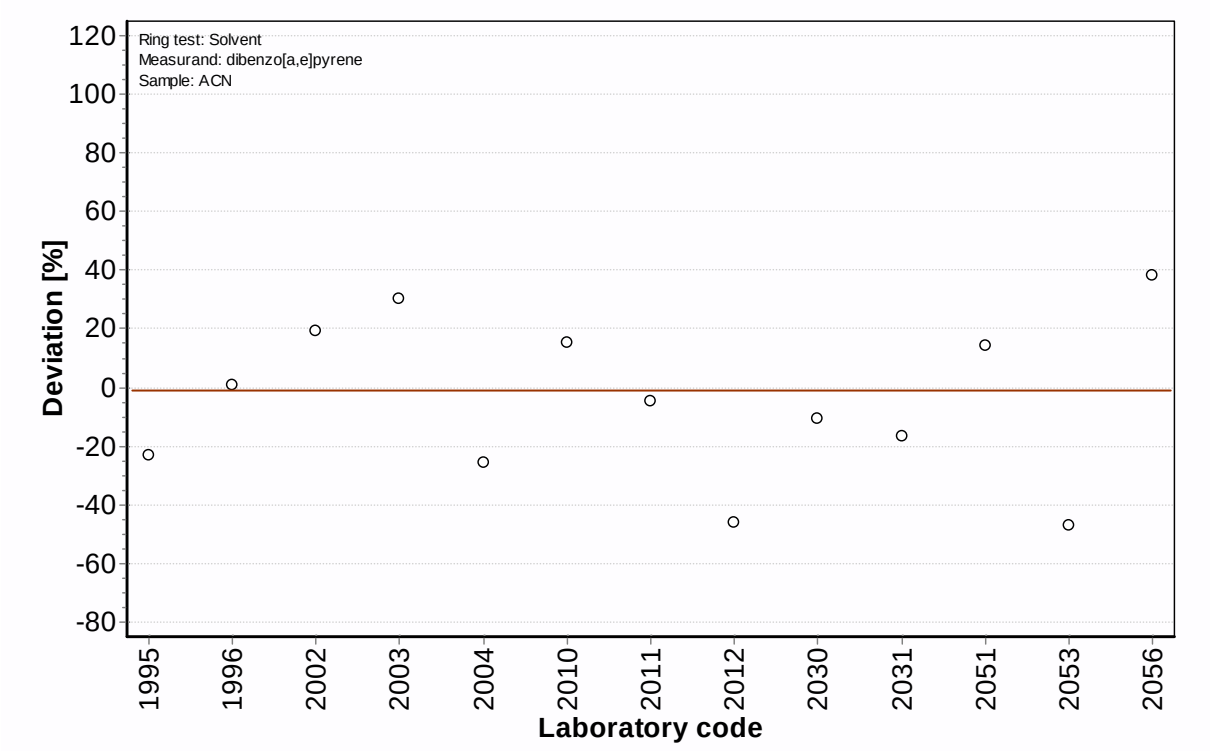


Figure 43: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,e*]pyrene in acetonitrile analysed by HPLC

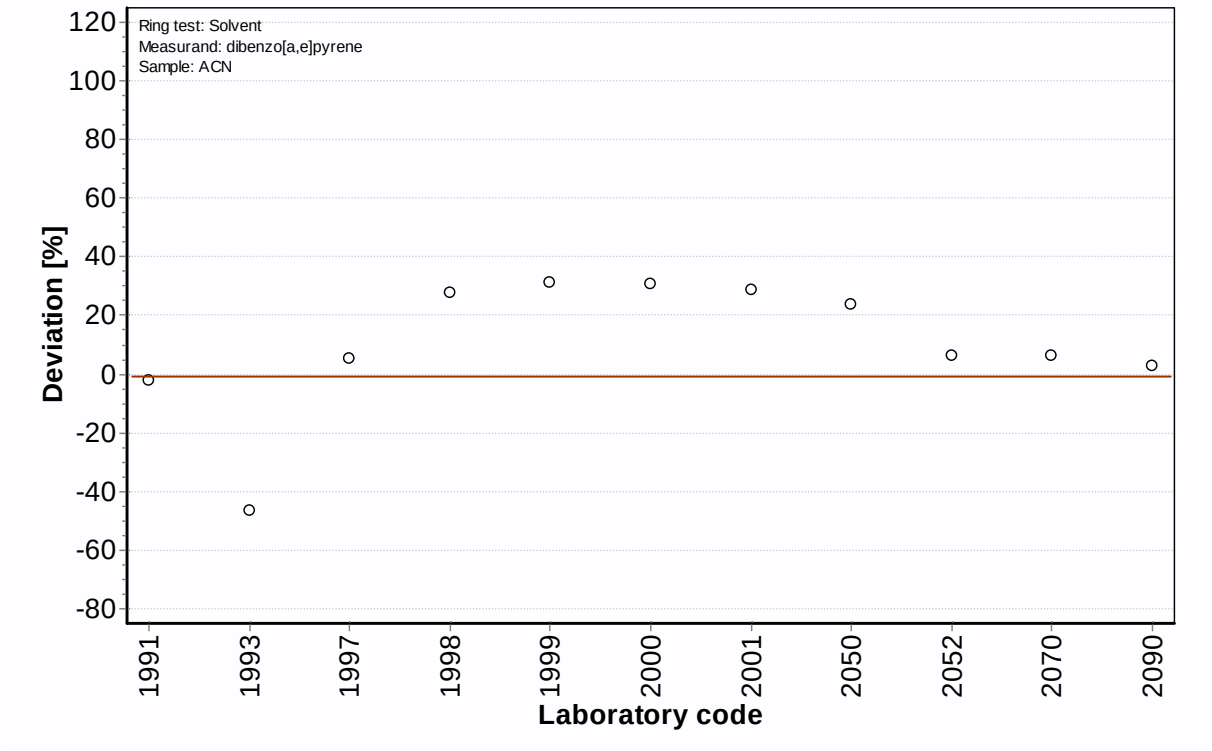


Figure 44: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,h*]pyrene in acetonitrile analysed by GC

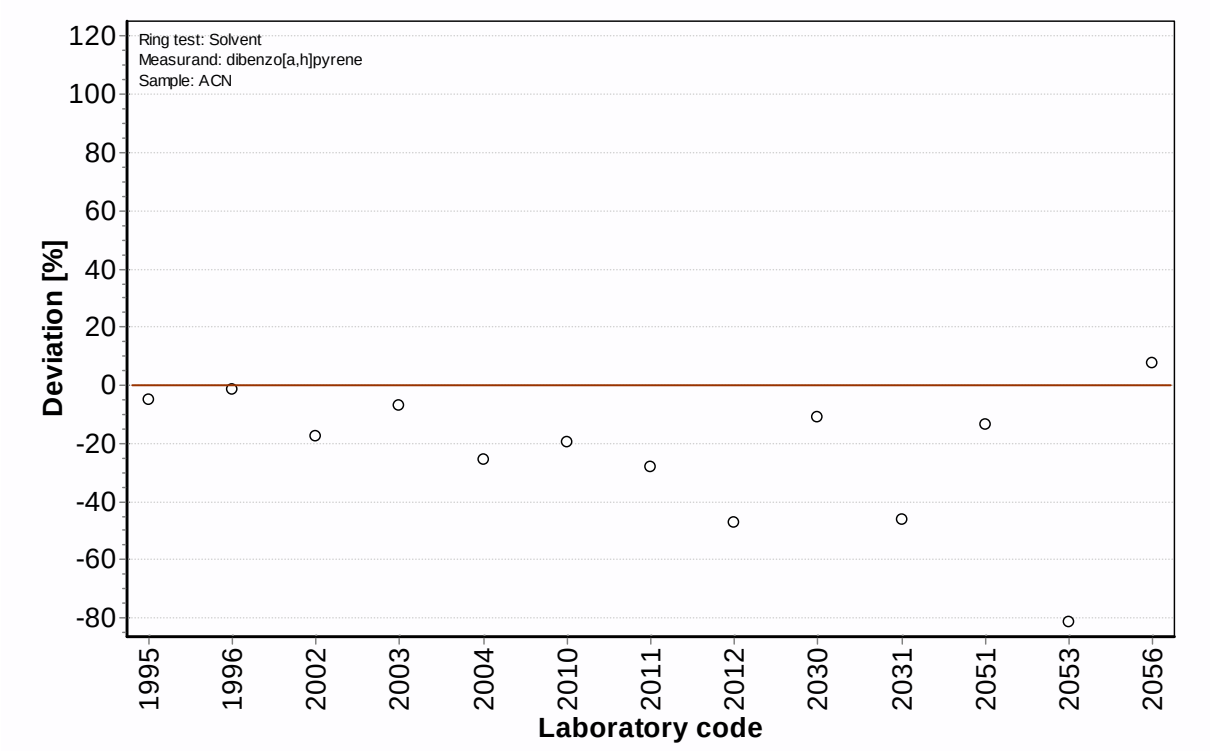


Figure 45: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,h*]pyrene in acetonitrile analysed by HPLC

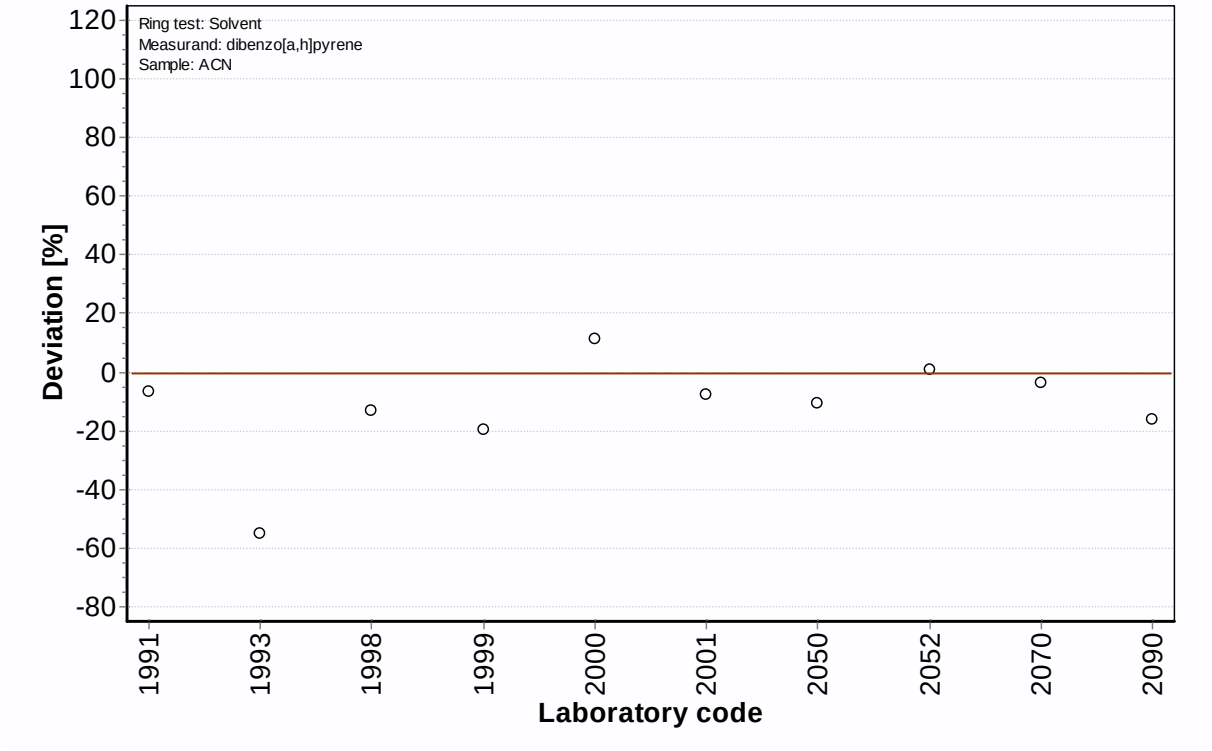


Figure 46: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,i*]pyrene in acetonitrile analysed by GC

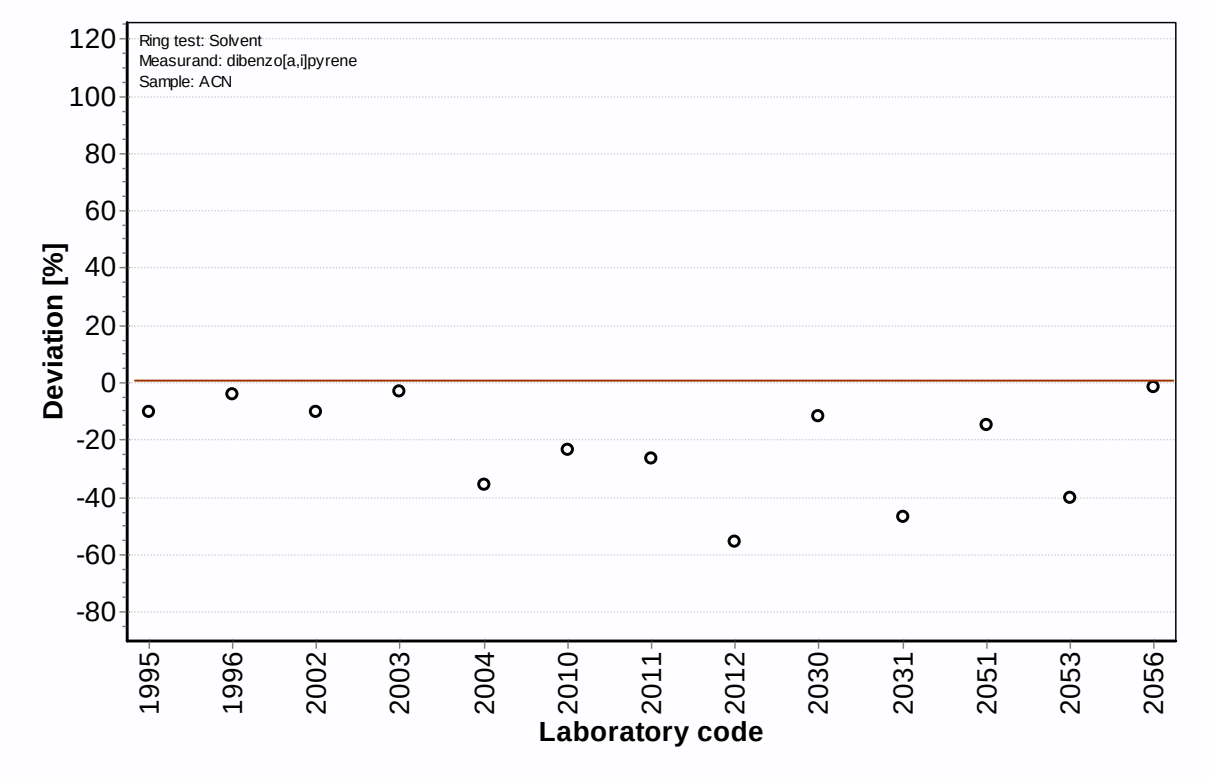
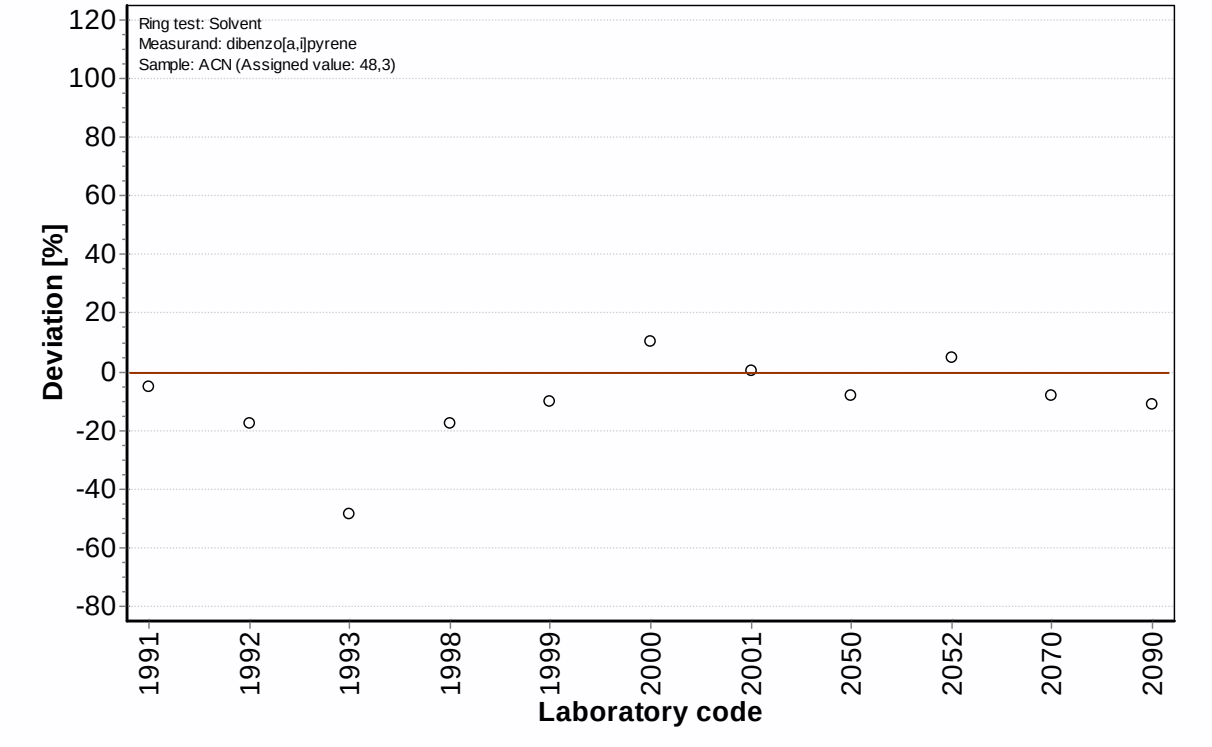


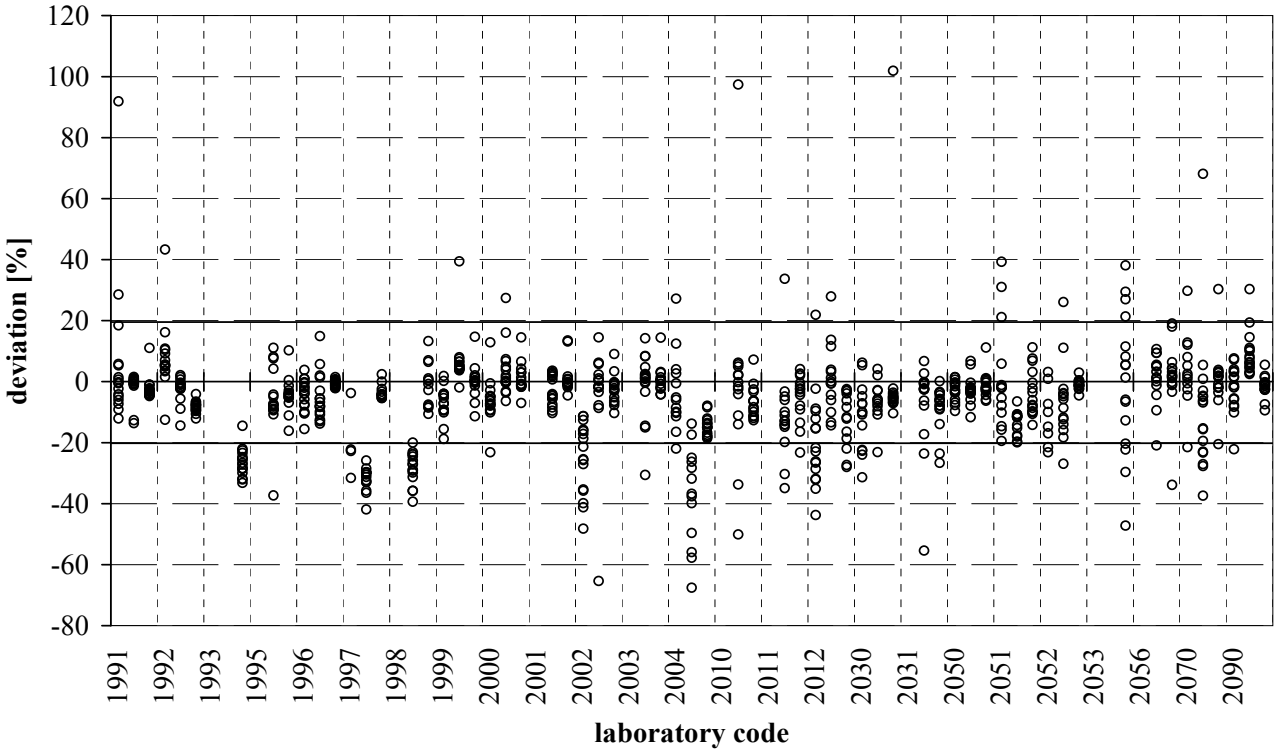
Figure 47: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,i*]pyrene in acetonitrile analysed by HPLC



Development over time of the reported values for acetonitrile

The first inter-laboratory comparison (ILC) of the CRL on PAHs in 2006 focussed on the calibration process [15]. The test material applied in that study consisted of a solvent solution of the analytes in question. In the two following ILCs of 2007 [16] and 2008 similar solvent solutions were distributed to the NRLs and results of the analysis thereof had been reported. Figure 48 showed the relative deviation of the reported values for all analytes sorted by laboratory and year. The laboratory codes indicated in Figure 48 referred to the codes given in 2008. It should be noted that more than 50 % of the participants improved their performance in terms of either precision or bias since last year. Especially obvious is the improvement of performance since the first participation of the respective laboratory in the ILCs. Most participants that reported in their first round either biased results (e.g. 1998 or 2004) or results with high variability (e.g. 2030, 2051, or 2070) reported in this ILC more accurate results. Laboratories participating this time for the first time in an ILC organised by the CRL (1993, 2053) had similar problems as many other NRLs in their first participation. This indicates clearly the benefits of regular participation in ILCs.

Figure 48: Relative deviations of the individual laboratory mean values from the assigned values for the concentrations of the analytes in acetonitrile in the PTs from 2006, 2007, and 2008. The data of the individual laboratories are separated by vertical, dotted lines. Data for the year 2006 are in each column at the very left, data for the year 2008 at the very right.



Laboratory results for sausage meat

The gravimetrically established concentration values (= assigned values) were applied for the evaluation of the reported results.

z-Scores were calculated from the final value, that participants were requested to report for the sausage meat sample. However, two laboratories did not report any final values, but only the results of the replicate analyses. Hence the mean value of the individual results was used for the performance assessment. From 400 expected results (25 laboratories report for 16 analytes in one material) 373 (93 %) were reported. 329 (88 %) of the reported 373 data were rated satisfactory. Counting the not reported values as not-satisfactory, the percentage of satisfactory data decreases slightly to 83 %. However, participant 2010 identified after submission of results problems with the instrument used for the analysis. This laboratory informed the CRL that corrective action had been taken. Since correction of results was at that stage not anymore possible, they were kept as they were reported and a remark was added to the data. The z-scores for all participants and all analytes are compiled in Table 20. Results between -1.0 and 1.0 were achieved for 253 (63 %) reported values. The latter results deviated from the assigned values less than the single target standard deviation of the PT.

The results from the inter-laboratory comparison test on the 15+1 EU priority PAHs in sausage meat are presented in Figure 49 to Figure 79.

For each analyte the first figures show the results of each laboratory from (six) individual measurements, with different symbols for the two analytical sequences, the average thereof, and the associated expanded measurement uncertainty (coverage factor = 2), as reported by the participants. In addition the robust mean off all results (red) and the assigned value (purple) are depicted as solid lines. The blue broken lines indicate a deviation from the assigned value of ± 1, 2, and 3 times the target standard deviation (22 % according to the modified Horwitz equation for all analytes except of 20.2 % for benzo[*a*]pyrene calculated according to equation 2 [7]).

In many cases the robust mean of the reported values (consensus value) was lower than the assigned value. This offset varied between almost naught for CPP, BkF, BjF, BcL, DeP, DlP and DhA to more than 22 % for DiP and DhP. For the remaining analytes the offset lay between 5 % and 10 % of the assigned value. It seemed from Figure 82 that this offset was at least partly cumulated on certain laboratories, except for DhP and DiP, which obviously proved to be analytically difficult.

In some cases the individual data indicated the day-to-day variability clearly. In other cases the agreement of results gained on different days was good. From the graphs of the individual results, the reported measurement uncertainty could be matched against the dispersion of the analytical data. It showed that some laboratories clearly underestimated measurement uncertainty, because the dispersion of the analytical results was larger than the measurement uncertainty.

Kernel density plots showed the distribution of the data and indicated that for many analytes the values of the data were not normally distributed, the data set contained outliers, and/or the data distribution was multimodal

The numerical values of the individual analytical results and, if reported, their corresponding measurement uncertainties with a 95 % confidence interval are listed for the replicate measurements in Table 21 to Table 36 using the same number of significant figures as reported by the respective participant.

Table 20: Compilation of z-scores calculated from the reported "final values", respectively where they were not available from the mean values of the replicate analyses : z-Scores outside the satisfactory range are indicated by bold figures; empty cells denote analytes for which results were not received; the asterisk with the results of participant 2010 indicate a malfunctioning analysis instrument.

Laboratory code	5-methylchrysene	benz[*a*]anthracene	benzo[*a*]pyrene	benzo[*b*]fluoranthene	benzo[*c*]fluorene	benzo[*ghi*]perylene	benzo[*j*]fluoranthene	benzo[*k*]fluoranthene	chrysene	cyclopenta[*cd*]pyrene	dibenzo[*a,e*]pyrene	dibenz[*a,h*]anthracene	dibenzo[*a,h*]pyrene	dibenzo[*a,i*]pyrene	dibenzo[*a,l*]pyrene	indeno[1,2,3-*cd*]pyrene
1991	-1.1	-1.5	-1.3	-1.0	-1.9	-0.9	-1.3	-1.2	-1.8		-1.0		-1.6	-1.5		-0.9
1992	-0.1	-0.5	0.1	0.7	1.3	0.3	-1.8	-0.4	-0.7	-0.9	-0.3	-0.8	**-2.1**	0.6	-0.2	0.8
1993	-0.2	-0.6	-0.3	-1.6	-0.4	-0.4	0.5	-0.4	-0.5	-0.1	-0.2	-0.5	-1.4	-1.1	0.0	0.1
1995	-0.5	-0.4	-0.2	-0.1	0.1	-0.2	-0.1	-0.2	-0.3	-0.3	0.9	-0.2	-1.0	-0.9	**2.1**	0.1
1996	-0.5	-0.2	-0.2	-0.4		-0.1	0.1	-0.2	-0.4	-0.4	-0.1	-0.1	0.1	-0.6	0.1	-0.1
1997	-1.5	-1.1	-1.7	-1.6	**-2.1**	-1.3	-1.9	-1.6	-1.6		-1.2	-1.8			-1.5	-1.6
1998	-0.1		-0.1	-0.3	0.4	-0.6		0.0	0.3		1.1	-0.8	-1.6	-1.4	0.4	
1999	0.3	0.5	0.4	0.4	0.3	0.7	0.3	0.3	0.1	2.0	1.7	0.4	0.0	0.1	0.5	1.1
2000	-0.6	-0.6	-0.6	-0.6	0.1	-0.6	0.4	-0.6	-0.7	0.0	0.4	-0.2	0.1	-0.6	-0.7	-0.5
2001	-0.2	-0.5	-0.6	0.0	-0.4	-0.5	0.3	-0.5	-0.5	1.5	0.9	-0.6	-0.8	-1.1	-0.2	-0.4
2002	0.2	-0.4	-0.1	-0.1		-0.1	0.3	-0.1	-0.5	0.3	1.1	0.3	0.1	-0.6	0.9	0.2
2003	0.3	-0.3	-0.2	-0.3	1.6	-0.2	0.1	-0.3	-0.4	**-2.1**	1.0	0.0	**-2.9**	-0.7	-0.1	0.0
2004	**-3.4**	**-3.0**	**-2.2**	-1.7	**-3.0**	-1.4	-1.9	-1.8	**-2.4**	**-2.2**	**-2.1**	-1.8	-2.0	**-2.2**	-1.8	-1.0
2010*	**-3.4**	**-3.0**	**-2.2**	0.1		**-2.5**			**-2.9**	**-2.4**	**-2.4**				**-2.6**	**-3.4**
2011	-0.4	-0.4	0.3		**-3.6**	0.3		0.3	-0.1	-0.4	**2.4**	0.1	**5.4**	**3.4**	**7.6**	-0.5
2012	0.3	0.2	**-3.8**	NE	-0.1	-1.2	NE	NE	-0.4	0.7	**-2.2**	-1.1	**-2.3**	**-2.7**	-0.9	-1.1
2030	-0.7	-0.7	-0.9		-1.4	-0.3		NE	-1.2	0.0	-0.5	-1.0	-0.7	-1.2	0.4	-0.4
2031	-0.4	-0.9	-1.4	-1.1	-0.5	-1.8	-1.1	-1.1	-1.0	-1.2	-1.9	-1.2	**-2.7**	**-2.6**	-2.0	-1.4
2050	-0.2	-0.3	-0.4	-0.1		-0.5	0.6	-0.4	-0.7	**3.2**	0.7	0.0	-1.2	-1.1	0.1	0.1
2051	0.0	-0.4	-0.5	-0.9	-0.4	-1.3	0.3	0.0	-0.8	0.2	0.6	-0.5	-1.9	-1.2	0.3	-0.5
2052	-0.2	-0.6	-1.0	-0.2	**3.0**	-0.6	0.0	-0.4	-0.4	-0.7	-0.9	-0.9	**-3.2**	**-2.2**	-1.1	-0.5
2053	0.0	0.3	0.3	1.3	-0.1	0.1	-1.2	**5.0**	-0.1	0.2	0.3	1.2	**-2.3**	**3.7**	-0.5	0.4
2056	-0.3	-0.4	-0.3	-1.0	0.6	-0.5	0.3	-0.5	-0.5	-0.1	1.2	-0.2	0.0	-0.8	0.6	-0.2
2070	0.0	0.4	0.0	0.4	0.9	-0.7	0.4	**-2.6**	-0.4	-0.5	-0.3	0.0	-1.5	-1.6	0.3	0.0
2090	1.0	0.5	1.0	0.6	**5.4**	0.5	0.5	0.8	0.6	**2.1**	0.3	0.9	0.1	**2.3**	1.1	1.3

NE: not evaluated, since the reported results represented the sum of the contents of BbF, BjF, and BkF

** participant 2010 identified and reported a problem with the applied analysis instrument*

5-Methylchrysene

Figure 49: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 6.2 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

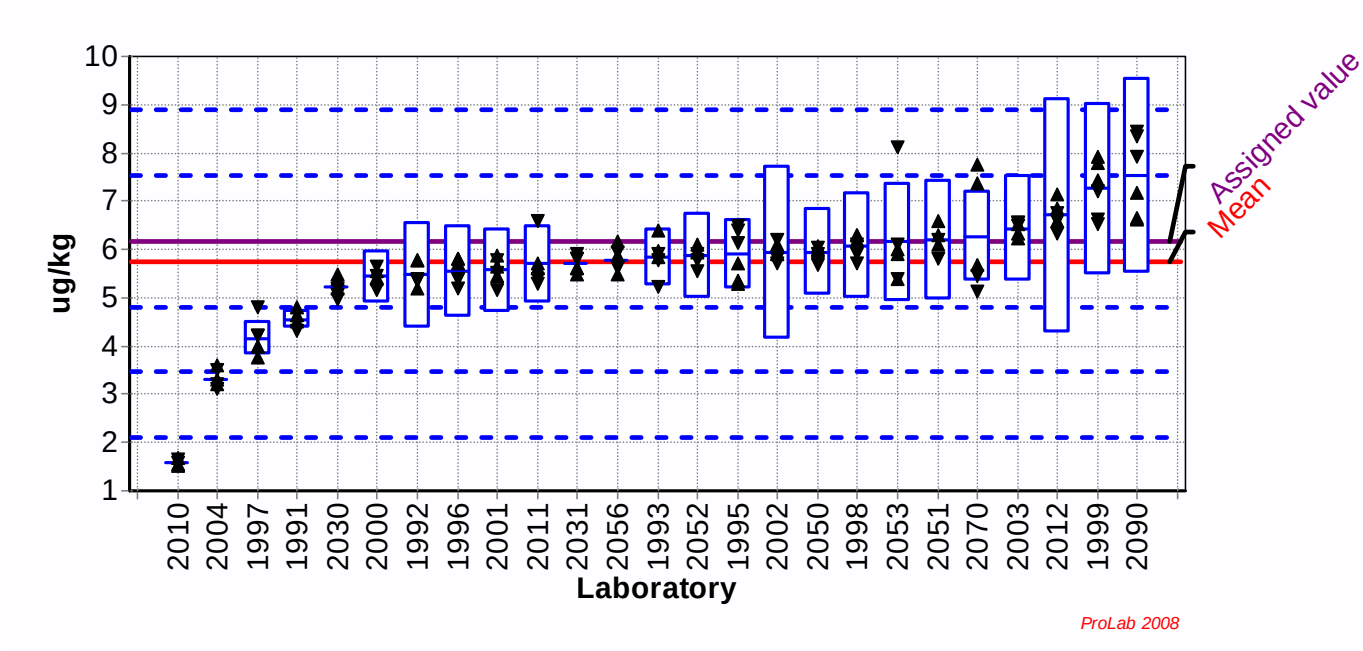


Figure 50: **Kernel density plot**

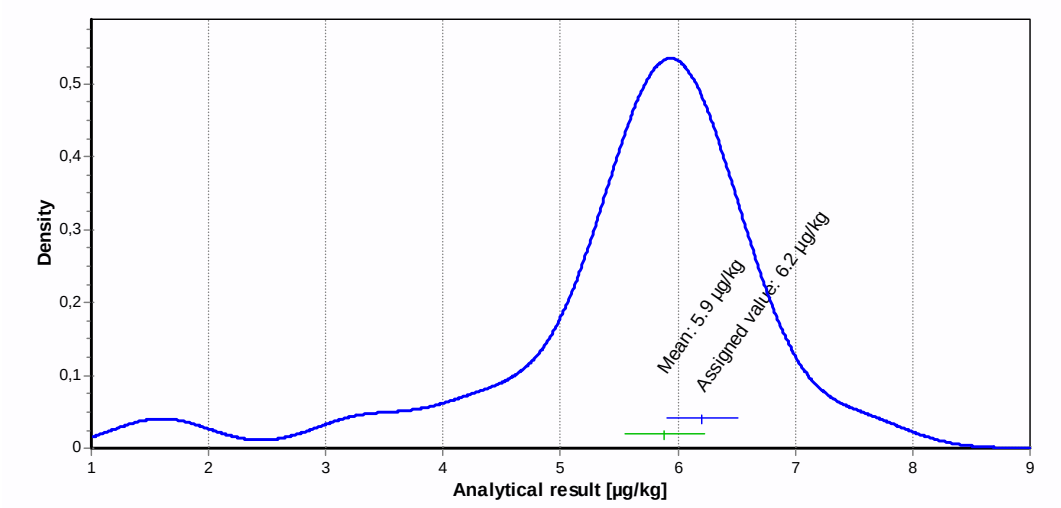


Table 21: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	4.5	4.63	4.8	4.3			4.65	0.35
1992	5.18	5.77	5.78	5.4	5.35	5.37	6.08	
1993	6.38	5.85	5.97	5.23	5.92	5.78	5.9	0.6
1995	5.3	5.72	5.35	6.13	6.5	6.4	5.46	0.7
1996	5.8	5.7	5.8	5.4	5.2	5.4	5.5	0.9
1997	3.77	3.98	3.99	4.21	4.81	4.23	4.17	0.68
1998	6.2	6.3	6.3	5.9	6.1	5.7	6.1	1.1
1999	7.8	7.93	7.43	6.63	6.53	7.22	6.58	0.99
2000	5.4	5.41	5.56	5.66	5.44	5.17	5.44	0.4
2001	5.46	5.63	5.87	5.15	5.53	5.78	5.88	0.66
2002	5.9	6.1	5.9	5.7	6.2	5.8	6	1.8
2003	6.33	6.22	6.51	6.55	6.56	6.48	6.56	1.04
2004	3.6	3.3	3.2	3.2	3.5	3.1	3.3	0.2
2010	1.51	1.56	1.69	1.59	1.64		1.6	0.19
2011	5.6	5.6	5.7	5.4	6.6	5.3		
2012	6.86	6.6	7.14	6.32	6.58	6.74	6.6	2.4
2030	5.39	5.5	5.18	5.2	5.07	4.98	5.22	
2031	5.6	5.6	5.5	5.8	5.8	5.9	5.7	
2050	5.99	6.06	5.97	5.67	6.05	5.91	5.94	0.89
2051	6.6	6.1	6.3	6.2	5.8		6.2	0.3
2052	5.94	6.11	5.96	5.89	5.76	5.55	5.87	0.88
2053	5.4	6	5.9	5.4	8.1	6.1	6.2	1.2
2056	5.48	5.87	6.17	5.63	5.62	5.94	5.84	0.36
2070	5.67	7.38	7.77	5.45	5.12			
2090	6.616	6.664	7.182	7.931	8.446	8.336	7.529	2.004

Benz[*a*]anthracene

Figure 51: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 5.9 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

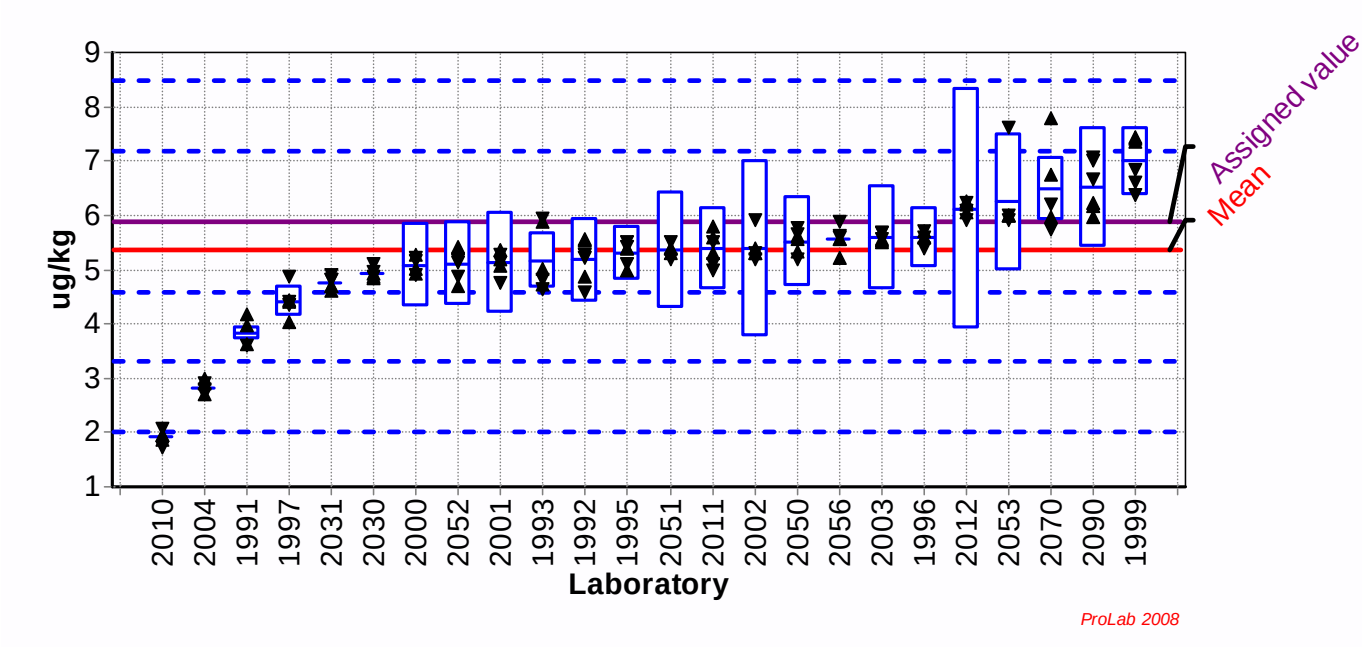


Figure 52: Kernel density plot

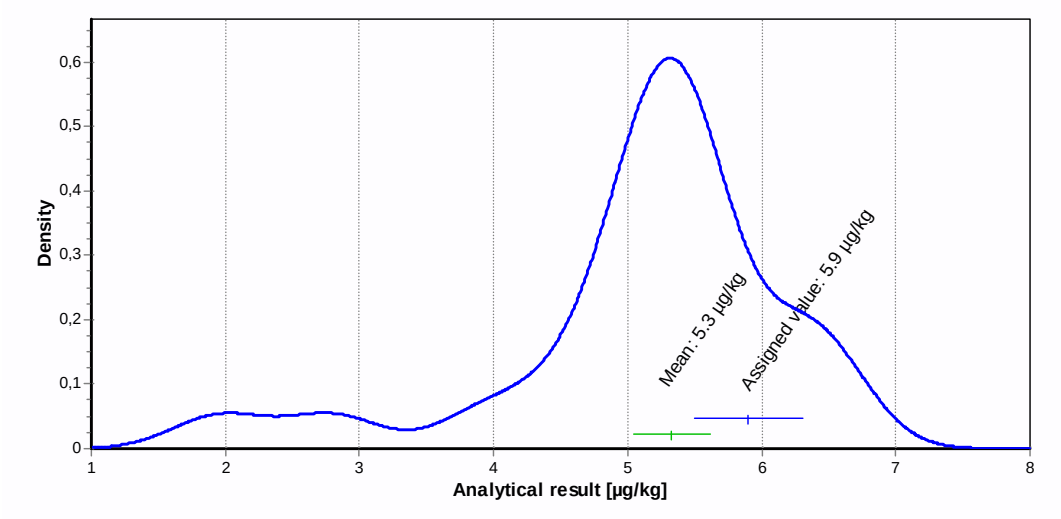


Table 22: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	3.62	3.97	4.17	3.59			3.92	0.24
1992	4.87	5.52	5.57	4.58	5.23	5.28	5.31	0
1993	4.74	5.88	5.02	5.94	4.65	4.8	5.1	0.5
1995	5	5.39	5.4	5.1	5.42	5.51	5.34	0.5
1996	5.6	5.7	5.6	5.4	5.6	5.7	5.6	0.6
1997	4.02	4.42	4.43	4.36	4.88	4.42	4.42	0.52
1998								
1999	7.41	7.45	7.35	6.6	6.36	6.82	6.48	0.72
2000	4.93	5.01	5.27	4.89	5.15	5.23	5.08	0.47
2001	5.06	5.19	5.36	4.76	5.13	5.28	5.31	0.59
2002	5.3	5.4	5.3	5.2	5.9	5.3	5.4	1.6
2003	5.51	5.55	5.54	5.67	5.57	5.68	5.57	0.9
2004	3	2.7	2.9	2.9	2.7	2.8	2.8	0.2
2010	1.95	1.87	1.94	1.72	2.08		1.96	0.23
2011	5.8	5.6	5.3	5.1	5.5	5		
2012	6.19	6.06	6.25	5.9	6.09	6.23	6.1	2.2
2030	4.87	4.94	4.84	4.88	4.97	5.11	4.94	0
2031	4.7	4.7	4.6	4.8	4.9	4.8	4.8	0
2050	5.33	5.63	5.55	5.18	5.76	5.65	5.52	0.83
2051	5.3	5.4	5.4	5.2	5.5		5.4	0.1
2052	5.43	4.69	5.38	5.12	5.18	4.87	5.11	0.77
2053	6	6	6	5.9	7.6	6	6.3	1.3
2056	5.23	5.55	5.57	5.62	5.59	5.88	5.45	0.19
2070	5.97	6.76	7.79	5.74	6.2			
2090	6.233	5.961	6.182	6.996	7.059	6.651	6.514	1.099

Benzo[*a*]pyrene

Figure 53: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 5.3 µg/kg (purple), and a ± 20.2 %, 40.4 %, and 60.6 % deviation thereof (blue dotted).**

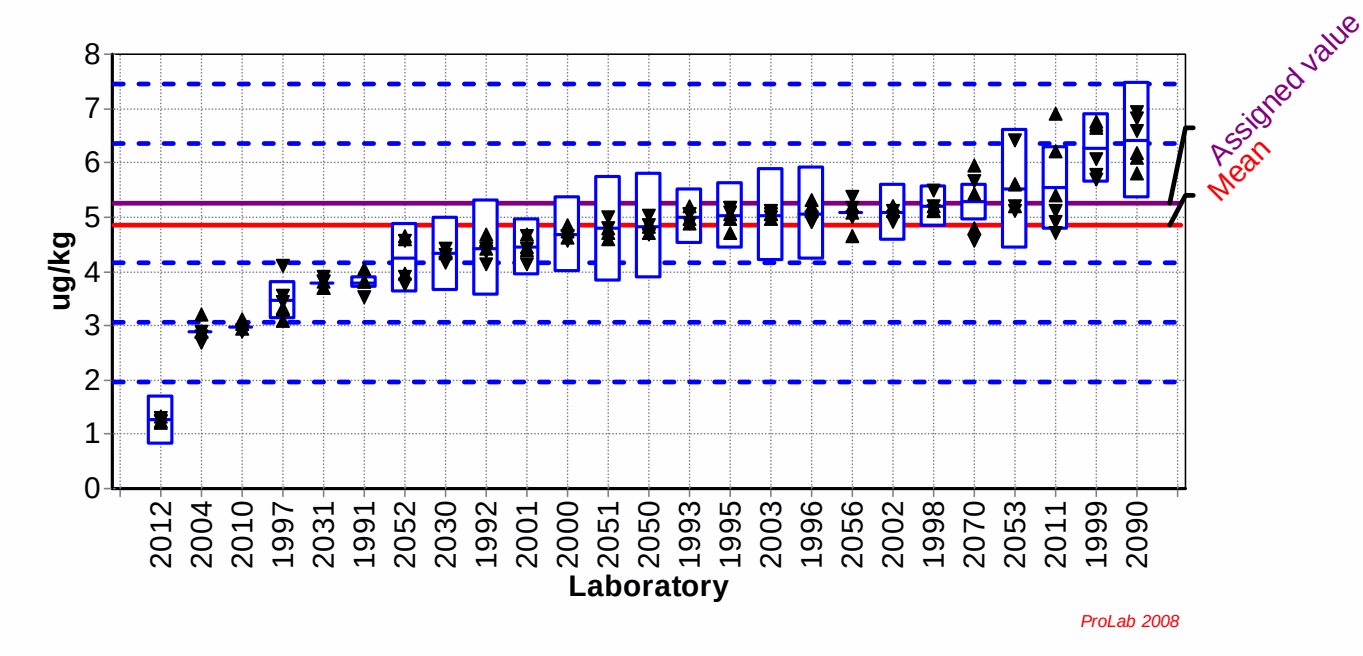


Figure 54: Kernel density plot

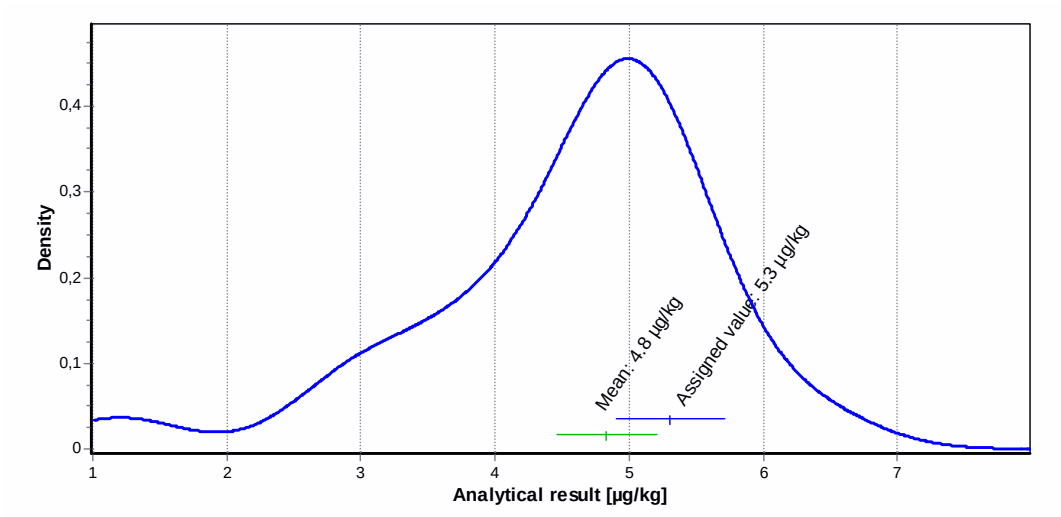


Table 23: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	3.81	3.82	4.04	3.52			3.89	0.24
1992	4.69	4.55	4.42	4.37	4.12	4.42	5.35	
1993	4.98	4.89	5.2	5.06	5.05	4.87	5	0.5
1995	4.72	5.06	4.96	5.17	5.07	5.17	5.14	0.6
1996	5.1	5.2	5.3	4.9	5	4.9	5.1	0.8
1997	3.08	3.33	3.28	3.54	4.1	3.44	3.46	0.66
1998	5.2	5.1	5.1	5.1	5.5	5.2	5.2	0.3
1999	6.71	6.77	6.64	5.78	5.68	6.06	5.73	0.92
2000	4.75	4.63	4.84	4.57	4.64	4.64	4.68	0.25
2001	4.38	4.45	4.68	4.12	4.43	4.65	4.66	0.48
2002	5.2	5.2	5.1	5	5.1	4.9	5.2	0.5
2003	5.04	4.96	5.06	5	5.04	5.11	5.04	0.9
2004	3.2	2.9	2.9	2.8	2.9	2.7	2.9	0.4
2010	2.96	3.13	3.04	2.89	2.92		2.95	0.29
2011	6.2	6.9	5.4	5.1	4.9	4.7		
2012	1.25	1.21	1.32	1.23	1.24	1.3	1.2	0.4
2030	4.32	4.36	4.37	4.31	4.15	4.41	4.32	
2031	3.7	3.7	3.8	3.8	3.9	3.8	3.8	
2050	4.7	4.88	4.83	4.68	5.03	4.85	4.83	0.97
2051	4.7	4.6	4.8	4.8	5		4.8	0.2
2052	4.58	3.96	4.65	3.91	4.55	3.76	4.25	0.64
2053	5.6	5.6	5.2	5.1	6.4	5.2	5.6	1.1
2056	4.64	5.09	5.2	5.01	5.16	5.38	4.98	0.3
2070	4.8	5.94	5.43	4.55	5.67			
2090	6.099	5.818	6.19	6.936	6.83	6.591	6.411	1.061

Benzo[*b*]fluoranthene

Figure 55: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 4.1 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

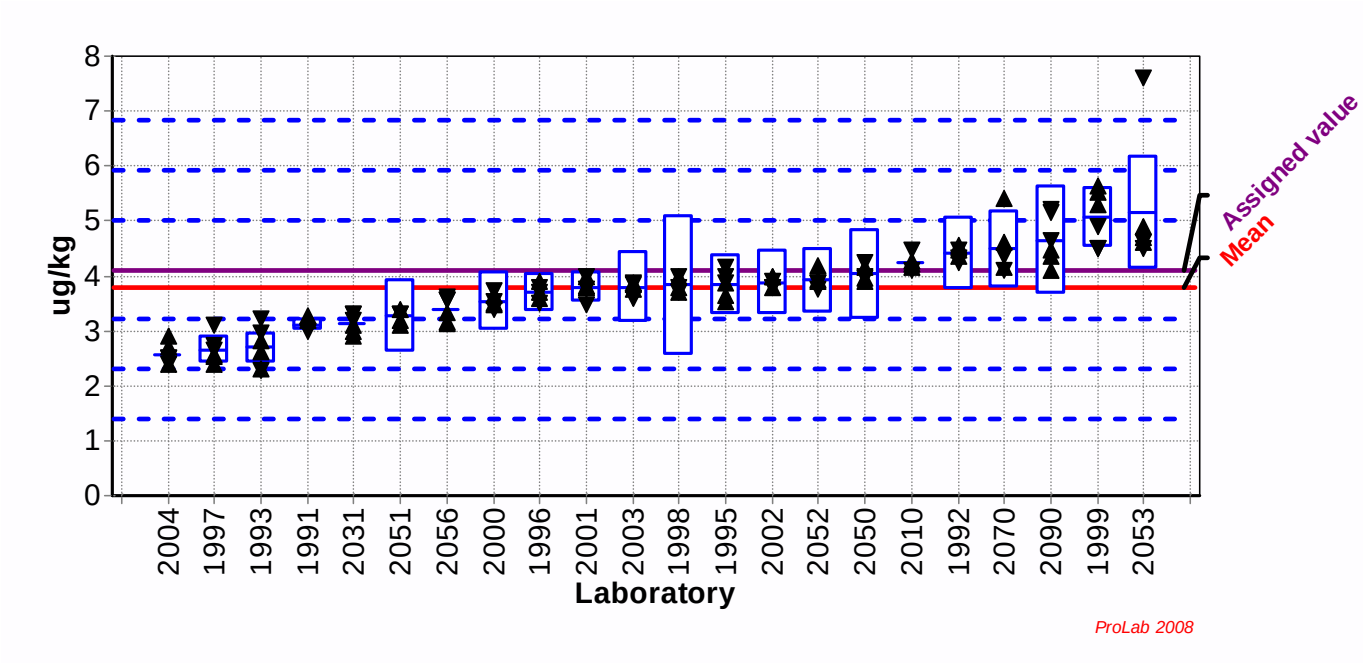


Figure 56: Kernel density plot

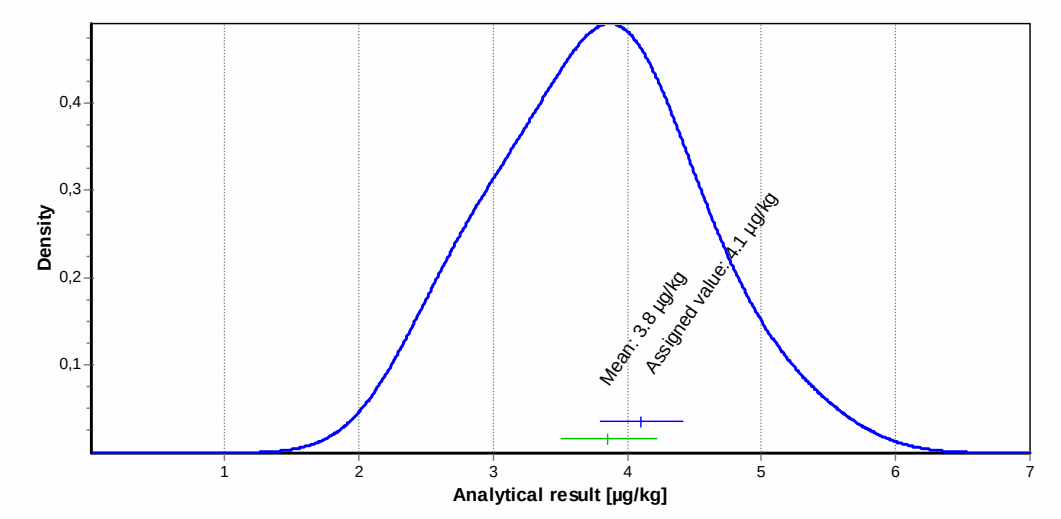


Table 24: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	3.25	3.18	3.26	2.99			3.23	0.21
1992	4.56	4.47	4.37	4.32	4.24	4.48	4.72	
1993	2.82	2.63	2.3	2.97	2.27	3.23	2.7	0.4
1995	3.52	3.86	3.64	4	3.86	4.17	4.01	0.6
1996	3.7	3.9	3.6	3.8	3.5	3.7	3.7	0.3
1997	2.39	2.56	2.52	2.72	3.11	2.64	2.66	0.47
1998	3.8	4	3.7	3.7	4	3.8	3.8	1.3
1999	5.53	5.64	5.3	4.49	4.5	4.91	4.5	0.65
2000	3.49	3.48	3.63	3.72	3.54	3.39	3.54	0.27
2001	3.78	3.81	3.98	3.46	3.75	3.99	4.06	0.43
2002	4	4	3.8	3.8	3.9	3.8	4	0.6
2003	3.87	3.77	3.85	3.59	3.86	3.83	3.86	0.71
2004	2.9	2.7	2.4	2.5	2.5	2.4	2.6	0.2
2010	4.2	4.15	4.26	4.1	4.46		4.18	0.44
2011								
2012	17.22*	17.4*	18.9*	16.38*	17.16*	17.3*	17.1*	6.2
2030								
2031	2.9	3.1	3	3.2	3.3	3.3	3.1	
2050	3.89	4.16	3.95	3.97	4.23	4	4.03	0.81
2051	3.4	3.2	3.1	3.3	3.3		3.3	0.1
2052	3.93	4.19	3.9	3.87	3.87	3.76	3.92	0.59
2053	4.7	4.9	4.6	4.5	7.6	4.6	5.3	1.1
2056	3.12	3.16	3.32	3.57	3.61	3.57	3.2	0.1
2070	4.16	4.61	5.42	4.11	4.37			
2090	4.474	4.1	4.346	5.217	5.139	4.63	4.651	0.973

** the value represents the sum of the contents of BbF, BjF and BkF and was therefore not considered in the evaluation of the individual analytes*

Benzo[*c*]fluorene

Figure 57: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 3.9 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

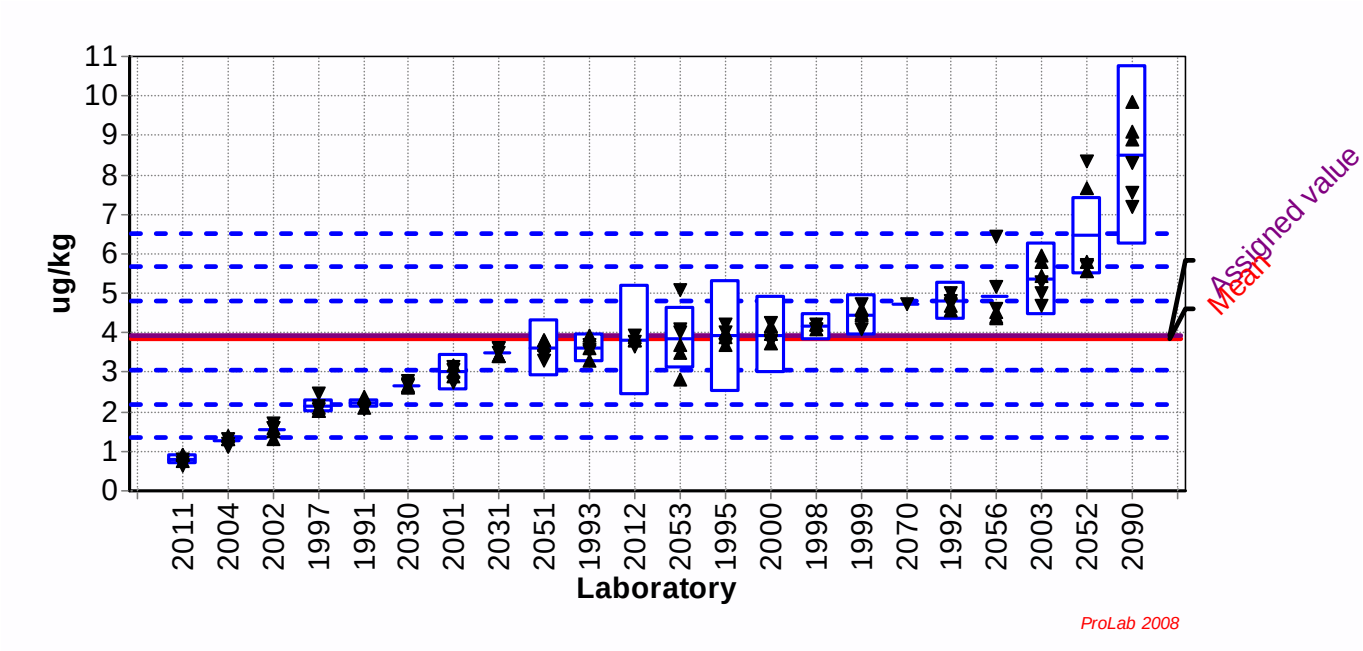


Figure 58: Kernel density plot

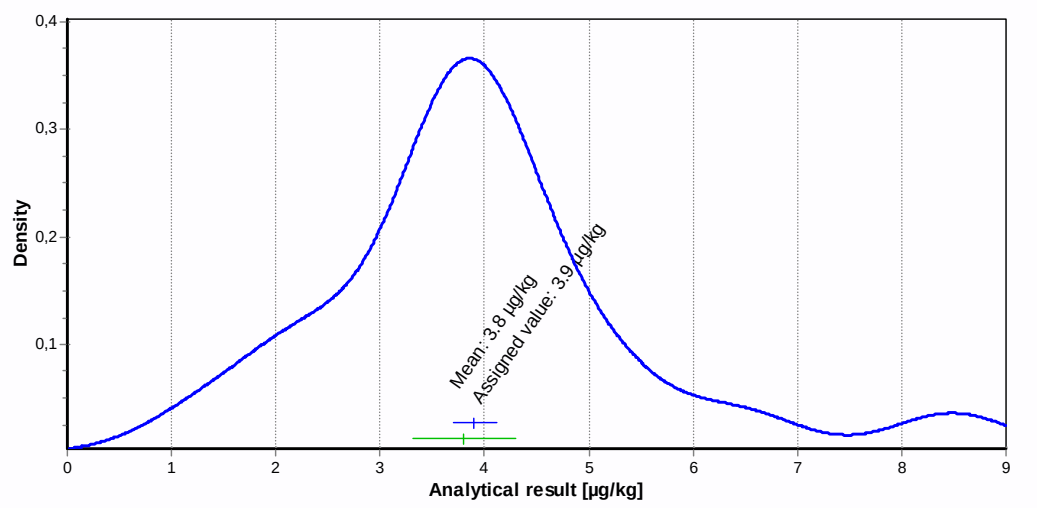


Table 25: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	2.1	2.37	2.33	2.08			2.27	0.2
1992	4.69	4.99	4.56	5.01	4.82	4.72	4.99	
1993	3.28	3.63	3.95	3.54	3.7	3.59	3.6	0.5
1995	3.68	3.88	4.02	4	4.21	3.68	3.96	1.5
1996								
1997	2.04	2.11	2.04	2.16	2.45	2.05	2.14	0.32
1998	4.2	4.2	4.1	4.1	4.2	4.1	4.2	0.3
1999	4.47	4.46	4.59	4.3	4.08	4.71	4.19	0.48
2000	4.17	3.72	3.96	3.81	4.23	3.79	3.95	0.3
2001	2.88	3	3.18	2.73	3.07	3.13	3.55	0.46
2002	1.5	1.6	1.3	1.6	1.7	1.6		
2003	5.46	5.97	5.79	5.02	5.28	4.67	5.28	1.12
2004	1.3	1.3	1.4	1.1	1.2	1.3	1.3	0.3
2010								
2011	0.92	0.77	0.92	0.71	0.81	0.62		
2012	3.9	3.81	3.82	3.66	3.77	3.92	3.8	1.4
2030	2.61	2.68	2.61	2.67	2.71	2.76	2.67	
2031	3.4	3.4	3.4	3.5	3.6	3.6	3.5	
2050							3.6	0.2
2051	3.8	3.8	3.7	3.3	3.4			
2052	5.78	5.57	7.65	8.33	5.72	5.68	6.46	0.97
2053	3.7	3.5	2.8	4.1	5.1	4	3.8	0.8
2056	4.51	4.41	4.36	4.6	5.17	6.42	4.43	0.08
2070				4.74				
2090	9.844	8.914	9.106	8.305	7.557	7.201	8.488	2.263

Benzo[*ghi*]perylene

Figure 59: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 4.7 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

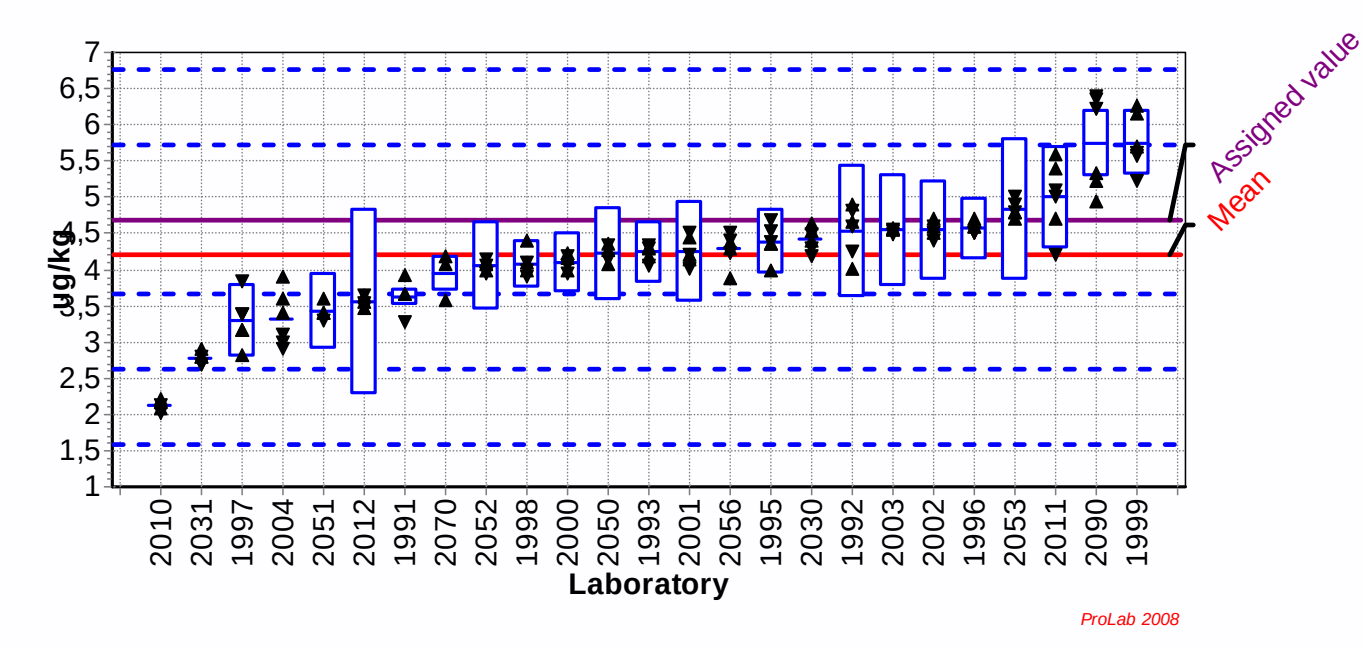


Figure 60: Kernel density plot

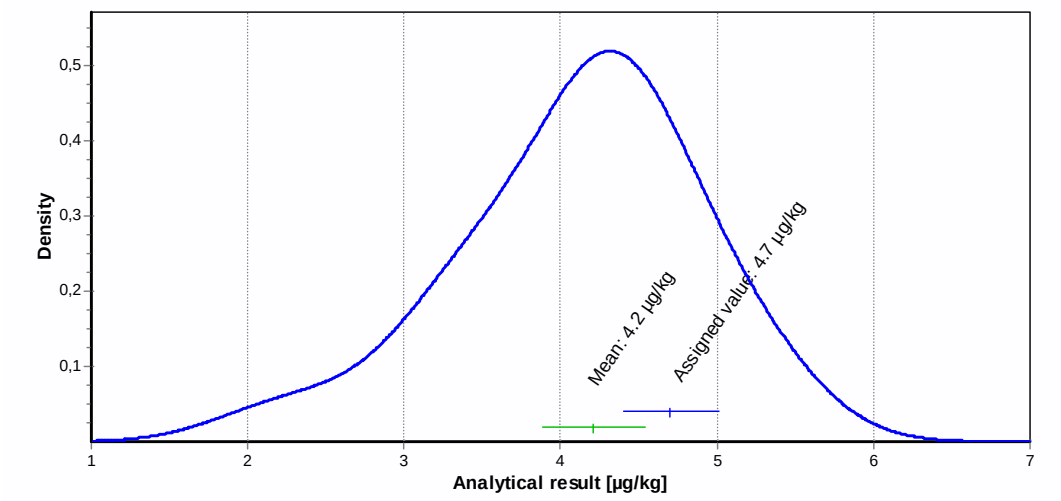


Table 26: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	3.66	3.66	3.92	3.28			3.75	0.23
1992	4.01	4.89	4.66	4.6	4.25	4.82	5.02	0
1993	4.32	4.18	4.29	4.29	4.34	4.05	4.3	0.4
1995	3.99	4.36	4.36	4.54	4.68	4.38	4.53	0.5
1996	4.7	4.6	4.6	4.5	4.5	4.5	4.6	0.4
1997	2.82	3.17	3.16	3.39	3.83	3.39	3.39	0.99
1998	4.1	4.4	4	3.9	4.1	4	4.1	0.3
1999	6.15	6.27	5.69	5.58	5.22	5.61	5.4	1.15
2000	4	4.23	4.16	4.05	4.19	3.95	4.1	0.32
2001	4.14	4.21	4.45	4.01	4.21	4.51	4.21	0.47
2002	4.7	4.6	4.5	4.5	4.6	4.4	4.6	0.7
2003	4.58	4.55	4.56	4.48	4.52	4.56	4.52	0.72
2004	3.6	3.9	3.4	3.1	2.9	3	3.3	0.3
2010	2.17	2.22	2.09	2.12	2.02		2.17	0.25
2011	5.6	5.4	4.7	5	5.1	4.2		
2012	3.56	3.48	3.64	3.46	3.64	3.53	3.5	1.3
2030	4.39	4.54	4.63	4.48	4.29	4.19	4.42	0
2031	2.8	2.8	2.9	2.7	2.8	2.7	2.8	0
2050	4.07	4.26	4.36	4.15	4.33	4.14	4.22	0.63
2051	3.4	3.6	3.4	3.3			3.4	0.1
2052	4.11	4	4.07	4.06	4.14	3.94	4.05	0.61
2053	4.8	4.7	4.8	4.8	5	4.9	4.8	1
2056	3.88	4.3	4.38	4.23	4.39	4.51	4.19	0.27
2070	4.19	3.57	4.07					
2090	5.219	4.938	5.331	6.39	6.358	6.212	5.163	0.405

Benzo[*j*]fluoranthene

Figure 61: Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 9.2 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).

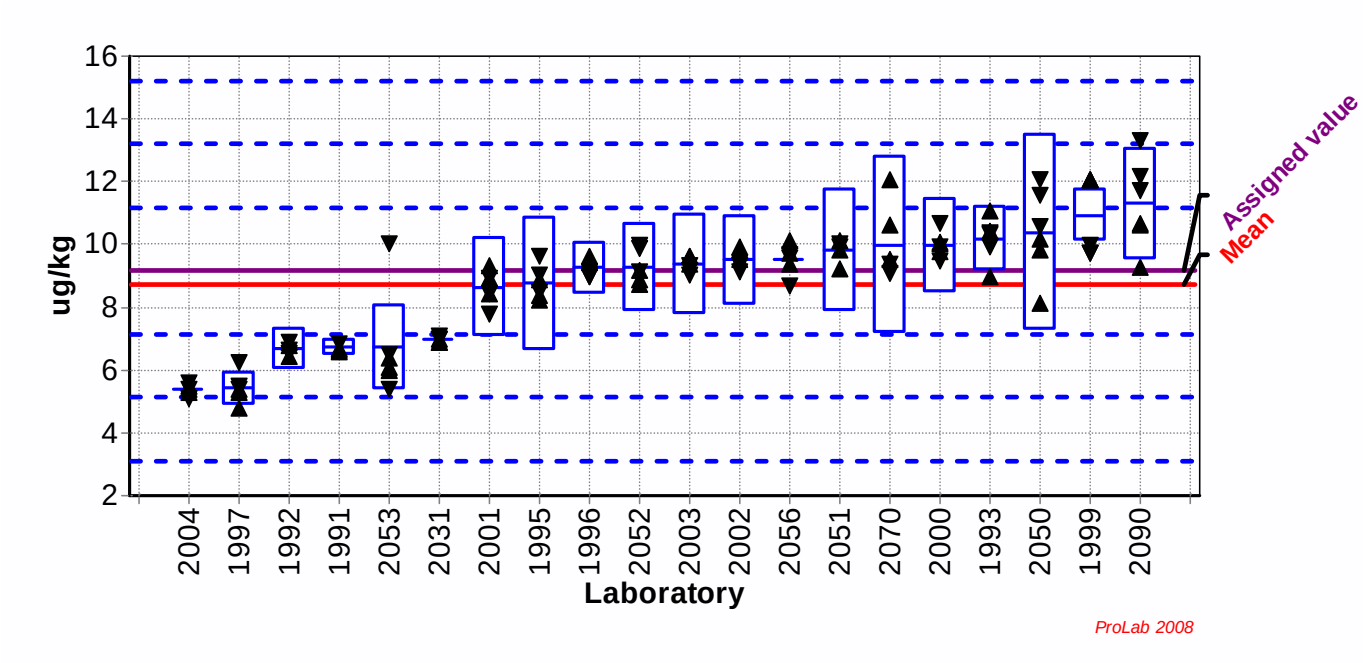


Figure 62: Kernel density plot

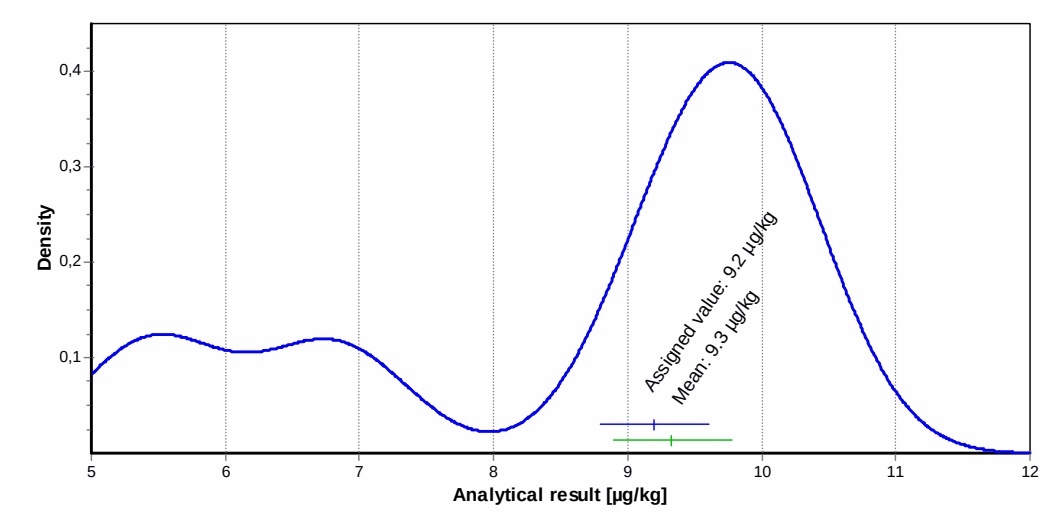


Table 27: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	6.69	6.62	6.6	6.83			6.63	0.51
1992	6.44	6.86	6.76	6.51	6.64	6.89	5.54	0
1993	8.98	10.43	11.07	9.9	10.33	10.37	10.2	1
1995	8.21	8.87	8.36	8.46	9.03	9.6	9.03	2.3
1996	9.6	9.4	9.5	9	9	9.1	9.3	0.8
1997	4.77	5.27	5.41	5.37	6.21	5.48	5.42	1.05
1998								
1999	12.06	12.05	12.07	9.71	9.72	9.96	9.72	1.46
2000	9.76	10.08	10	10.67	9.92	9.47	9.98	1
2001	8.42	8.91	9.32	7.8	8.44	8.95	9.82	1.45
2002	9.9	9.8	9.5	9.4	9.1	9.3	9.8	1.5
2003	9.63	9.39	9.64	9.03	9.33	9.18	9.33	1.58
2004	5.4	5.3	5.5	5.4	5.6	5.1	5.4	0.5
2010								
2011								
2012	17.22*	17.4*	18.9*	16.38*	17.16*	17.3*	17.1*	6.2
2030								
2031	7	6.9	6.9	7	7.1	7	7	0
2050	9.8	10.18	8.15	11.56	12.04	10.56	10.38	3.11
2051	10.1	9.2	9.8	9.9	10		9.8	0.4
2052	8.9	8.71	9.16	9.85	9.99	9.1	9.28	1.39
2053	6.1	6.4	6	5.4	10	6.5	6.8	1.4
2056	9.36	10.1	9.71	8.69	9.59	9.69	9.72	0.37
2070	9.52	10.62	12.05	9.08	9.39			
2090	10.659	9.266	10.638	12.186	13.311	11.711	10.188	1.596

** the value represents the sum of the contents of BbF, BjF and BkF and was therefore not considered in the evaluation of the individual analytes*

Benzo[*k*]fluoranthene

Figure 63: Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 5.2 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).

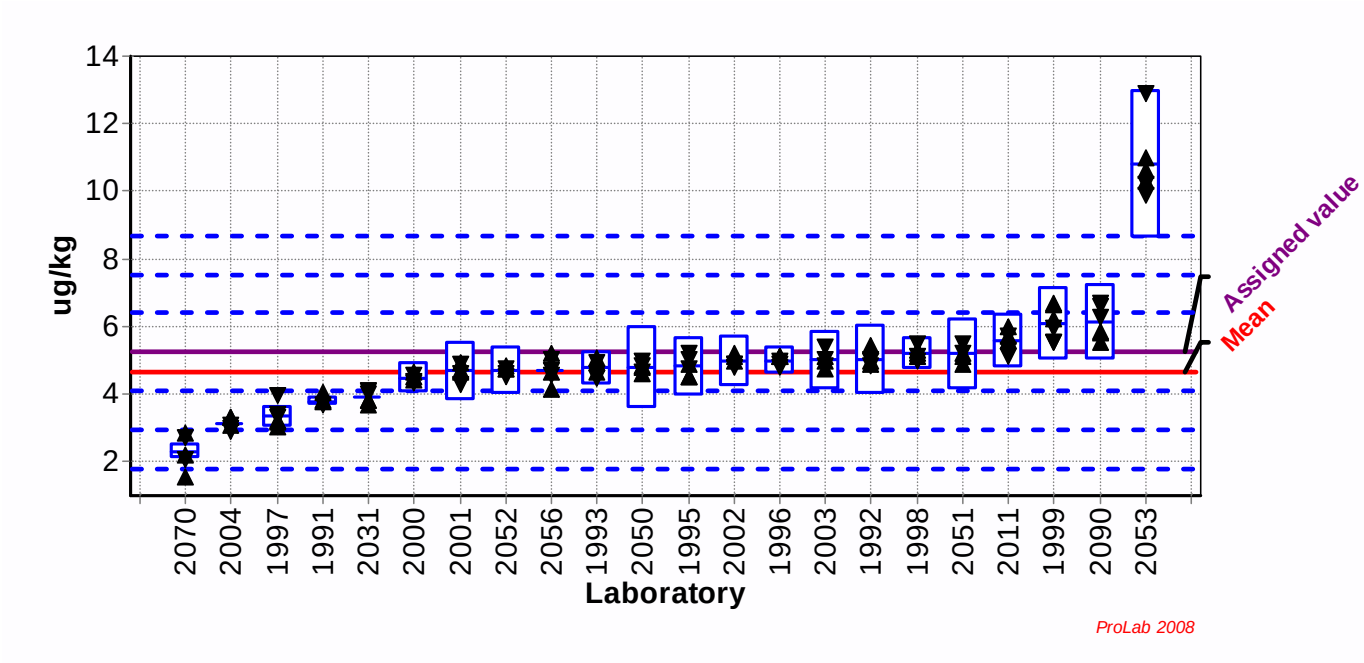


Figure 64: Kernel density plot

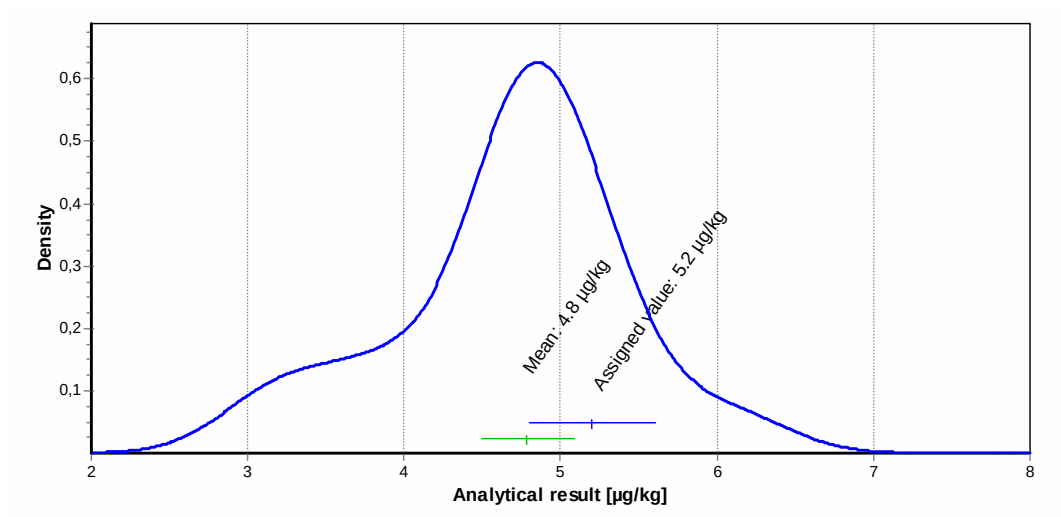


Table 28: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	3.79	3.83	4.05	3.68			3.89	0.23
1992	5.46	4.89	4.99	4.84	5	5.01	4.73	0
1993	5.08	4.66	4.93	4.63	4.47	4.91	4.8	0.5
1995	4.51	4.88	4.52	5.02	4.75	5.23	5	0.9
1996	5.1	5.1	5.1	4.9	4.8	5	5	0.4
1997	3.03	3.23	3.19	3.42	3.95	3.31	3.36	0.6
1998	5.2	5.3	5.1	5	5.5	5.1	5.2	0.5
1999	6.63	6.7	6.24	5.52	5.53	5.96	5.53	0.77
2000	4.5	4.44	4.66	4.56	4.34	4.39	4.48	0.35
2001	4.64	4.71	4.95	4.3	4.61	4.87	4.63	0.57
2002	5.2	5.1	5	4.9	4.9	4.8	5.1	0.8
2003	4.77	4.99	5.13	5.4	4.82	5.01	4.82	0.83
2004	3.3	3.3	3.1	3	3.1	2.9	3.1	0.3
2010								
2011	5.7	5.6	6	5.3	5.7	5.1		
2012	17.22*	17.4*	18.9*	16.38*	17.16*	17.3*	17.1*	6.2
2030	15.33*	16.08*	15.72*	15.72*	15.79*	15.79*	15.74*	0
2031	3.7	3.8	3.8	4	4.1	4.1	3.9	0
2050	4.61	4.82	4.79	4.64	4.98	4.85	4.78	1.2
2051	5.2	4.9	5.1	5.5	5.2		5.2	0.2
2052	4.75	4.84	4.75	4.63	4.76	4.52	4.71	0.71
2053	10.6	11	10.3	9.9	12.9	10.2	10.9	2.2
2056	4.14	4.66	5.2	5.01	4.58	4.72	4.67	0.53
2070	2.22	2.85	1.57	2.07	2.7			
2090	5.831	5.524	5.848	6.687	6.62	6.283	6.132	1.125

** the value represents the sum of the contents of BbF, BjF and BkF and was therefore not considered in the evaluation of the individual analytes*

Chrysene

Figure 65: Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 6.4 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).

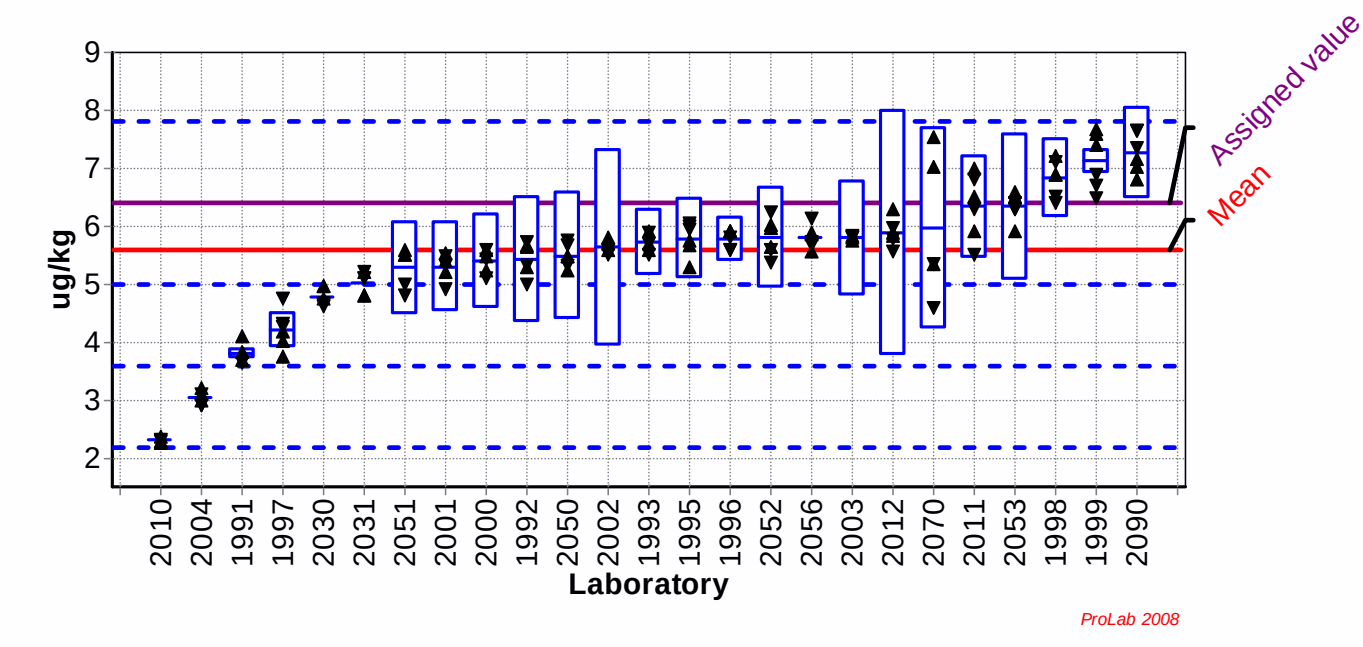


Figure 66: Kernel density plot

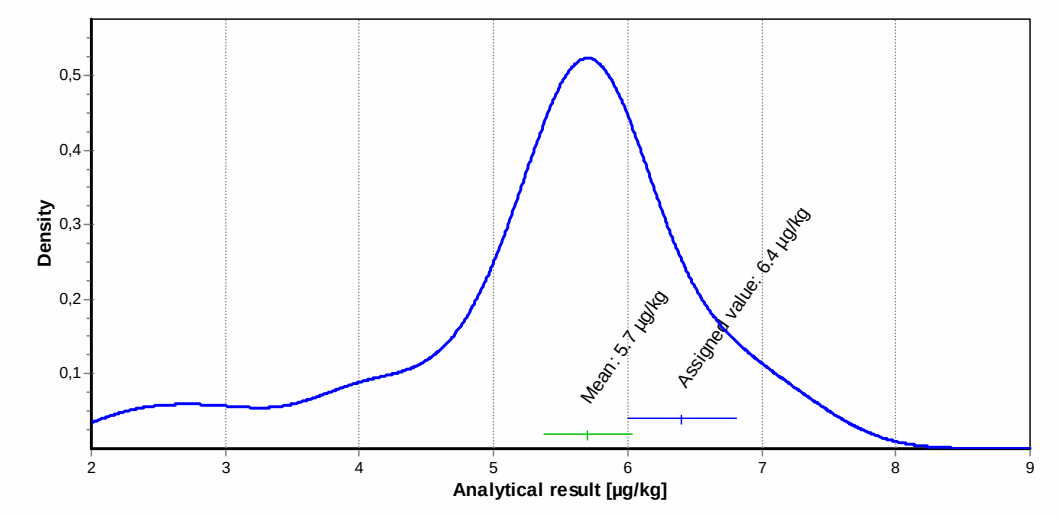


Table 29: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	3.68	3.82	4.09	3.63			3.86	0.18
1992	5.29	5.66	5.64	4.99	5.31	5.72	5.46	0
1993	5.91	5.71	5.59	5.88	5.51	5.7	5.7	0.6
1995	5.28	5.75	5.67	5.95	6.06	5.99	6	0.7
1996	5.9	5.9	5.9	5.6	5.6	5.8	5.8	0.4
1997	3.75	4.01	4.19	4.25	4.74	4.31	4.21	0.63
1998	6.9	7.2	6.9	6.4	7.1	6.5	6.8	0.7
1999	7.59	7.67	7.39	6.71	6.49	6.9	6.6	0.75
2000	5.23	5.47	5.6	5.59	5.42	5.1	5.4	0.33
2001	5.2	5.39	5.54	4.9	5.31	5.48	5.72	0.61
2002	5.8	5.7	5.6	5.6	5.6	5.5	5.7	1.7
2003	5.81	5.74	5.82	5.81	5.81	5.82	5.81	0.93
2004	3.2	3	3.1	3.1	2.9	2.9	3	0.2
2010	2.29	2.25	2.36	2.29	2.32		2.3	0.19
2011	7	6.5	5.9	6.3	6.8	5.5		
2012	5.88	5.84	6.29	5.56	5.77	5.98	5.9	2.1
2030	4.97	4.96	4.74	4.68	4.61	4.64	4.77	0
2031	4.8	5.2	4.8	5.1	5.2	5.1	5	0
2050	5.25	5.47	5.48	5.31	5.76	5.68	5.49	1.1
2051	5.6	5.5	5.5	4.8	5		5.3	0.4
2052	6.01	5.96	5.64	6.23	5.58	5.36	5.8	0.87
2053	6.6	6.5	5.9	6.3	6.4	6.3	6.3	1.3
2056	5.55	5.86	5.88	5.67	5.72	6.12	5.76	0.18
2070	5.35	7.01	7.55	5.34	4.59			
2090	6.795	7.024	7.16	7.338	7.644	7.651	7.269	0.78

Cyclopenta[*cd*]pyrene

Figure 67: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 6.0 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

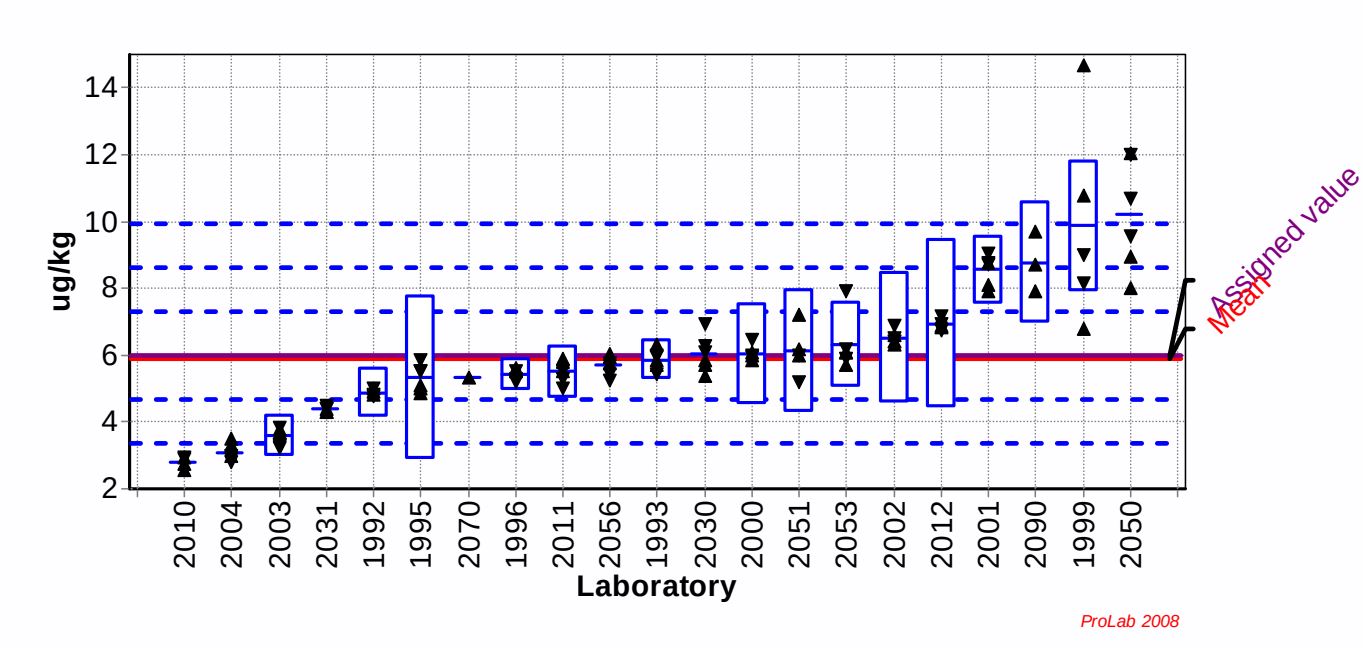


Figure 68: Kernel density plot

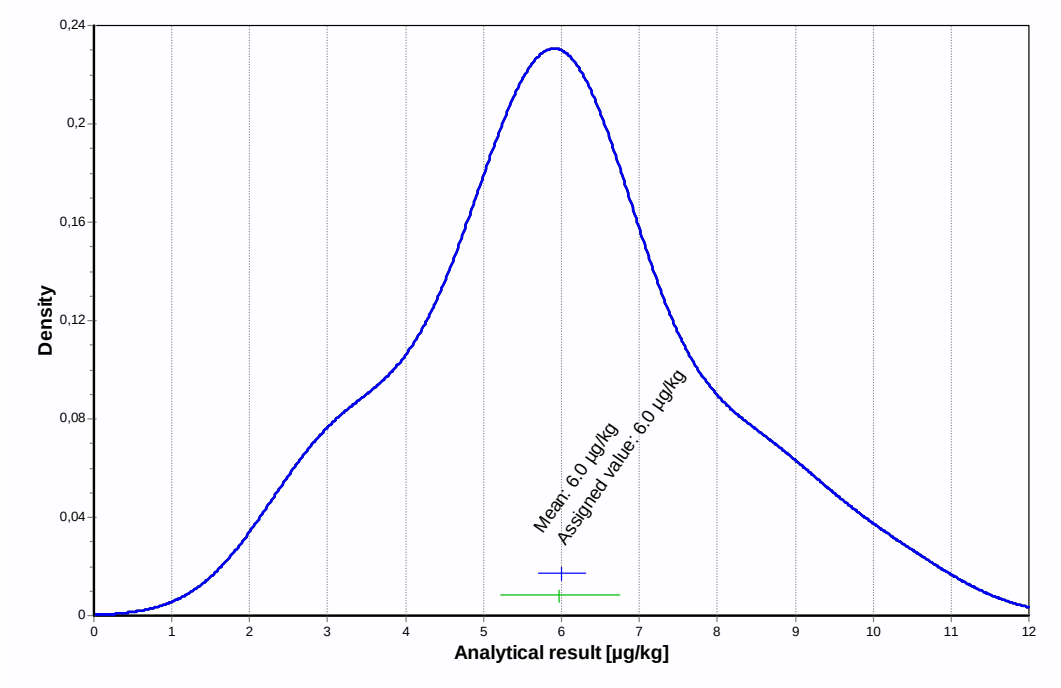


Table 30: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991								
1992	4.99	4.8	4.89	4.8	5	4.79	4.88	
1993	5.72	5.85	6.3	5.41	5.96	5.98	5.9	0.6
1995	4.99	5.12	4.88	5.53	5.53	5.85	5.64	2.7
1996	5.5	5.5	5.6	5.3	5.2	5.5	5.5	0.5
1997								
1998								
1999	10.77	14.67	6.77	8.14	9.01		8.58	3.44
2000	5.86	6.08	5.97	6.44	5.92	5.99	6.04	0.6
2001	8.12	7.91	8.78	8.73	8.76	9.03	7.93	0.97
2002	6.3	6.6	6.4	6.4	6.9	6.5	6.4	1.9
2003	3.65	3.78	3.68	3.31	3.24	3.83	3.24	0.52
2004	3.5	3	3.3	2.9	3	2.8	3.1	0.2
2010	2.73	2.57	2.96	2.87	2.94		2.88	0.2
2011	5.9	5.8	5.5	5	5.5	5.3		
2012	7.12	6.87	6.82	6.76	6.92	7.17	6.9	2.5
2030	5.4	5.85	5.69	6.1	6.92	6.28	6.04	
2031	4.4	4.3	4.3	4.4	4.5	4.4	4.4	
2050	12.05	8	8.95	10.67	11.99	9.57	10.21	
2051	7.2	6	6.2	6	5.2		6.3	0.6
2052							5.05	0.8
2053	6.1	6.1	5.7	5.9	7.9	6.2	6.3	1.3
2056	5.94	6.04	5.74	5.41	5.24	5.77	5.91	0.15
2070	5.34							
2090	9.7	7.9	8.7				8.7	1.8

Dibenzo[*a,e*]pyrene

Figure 69: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 7.1 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

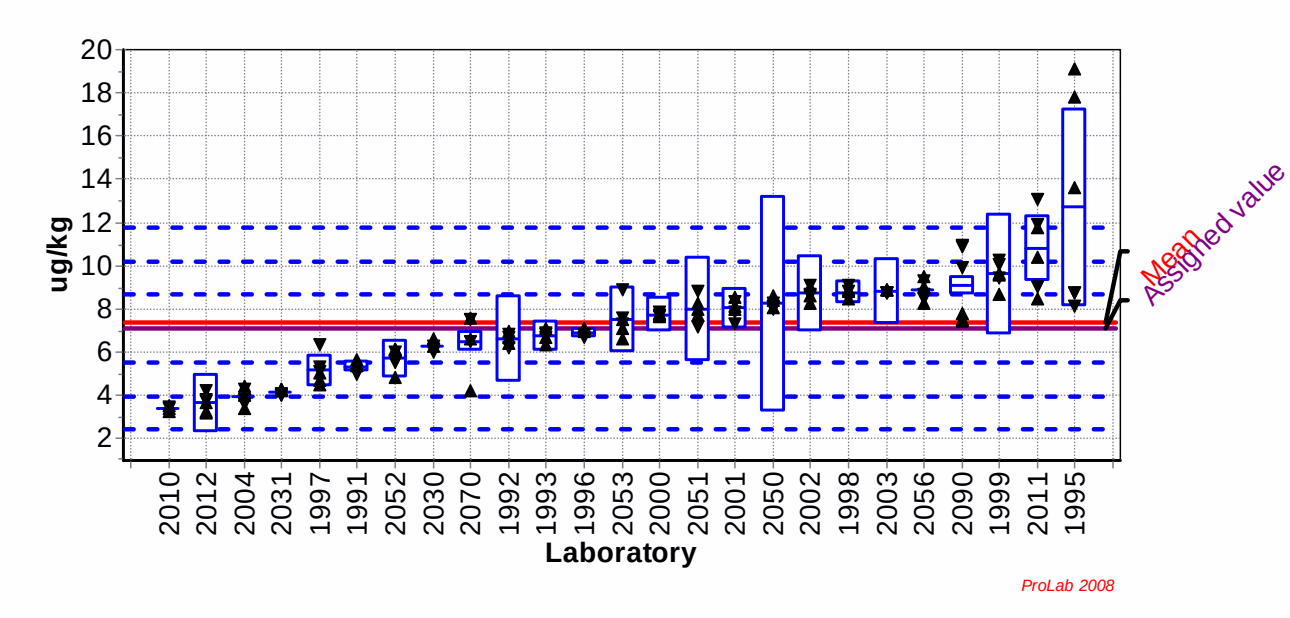


Figure 70: Kernel density plot

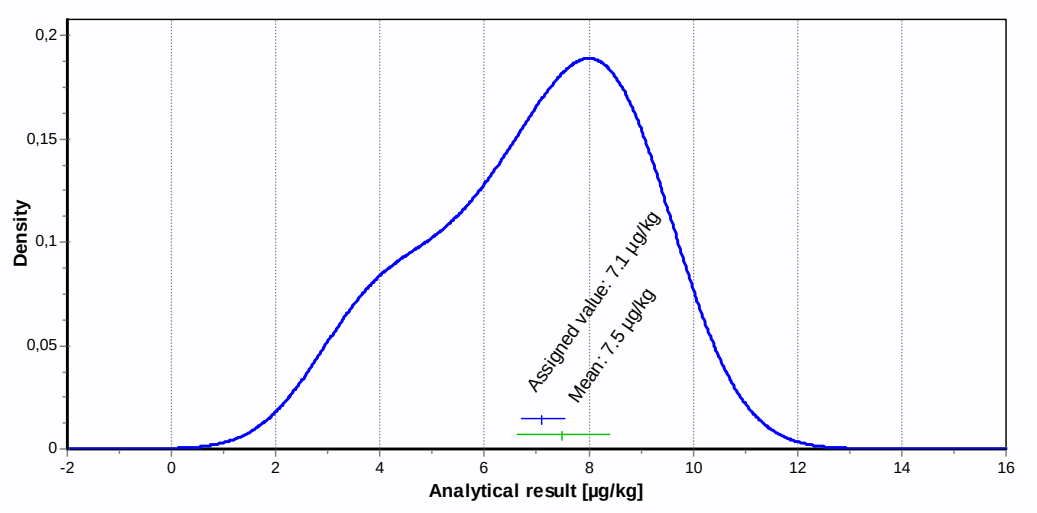


Table 31: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	5.42	5.39	5.64	4.97			5.48	0.43
1992	6.45	6.95	6.71	6.2	6.72	6.85	6.67	
1993	6.35	6.66	7.08	6.8	6.66	6.93	6.8	0.7
1995	13.6	17.8	19.1	8.77	8.78	8.13	8.56	3.2
1996	7.1	7	7.1	6.8	6.8	6.7	6.9	0.2
1997	4.71	5.06	4.5	5.29	6.34	5.14	5.17	1.4
1998	8.8	8.9	8.5	8.5	9.1	8.8	8.8	0.5
1999	9.65	9.58	8.69	10.04	9.45	10.24	9.75	2.63
2000	7.75	7.66	7.82	7.74	7.85	7.62	7.74	0.7
2001	8.02	8.13	8.56	7.32	7.88	8.34	8.57	1
2002	8.6	9	8.3	8.6	9.1	8.7	8.8	1.8
2003	8.87	8.86	8.86	8.73	8.73	8.78	8.73	1.45
2004	3.4	4	4.4	4.3	3.6	3.8	3.9	0.7
2010	3.4	3.29	3.52	3.43	3.46		3.43	0.32
2011	11.8	10.4	8.5	11.9	13.1	9		
2012	3.25	3.69	3.22	3.71	4.21	3.8	3.7	1.3
2030	6.27	6.58	6.61	6.25	6.03	6.15	6.32	
2031	4.3	4.2	4.3	4	4	4.1	4.2	
2050	8.06	8.63	8.4	7.98	8.26	8.1	8.24	4.94
2051	7.7	8.3	8	7.2	8.8		8	0.6
2052	6.14	4.81	6.14	5.61	5.98	5.54	5.7	0.86
2053	6.6	7.1	7.5	8.9	7.6	7.3	7.5	1.5
2056	8.26	9.02	9.53	8.48	8.7	9.31	8.94	0.64
2070	6.65	7.61	4.24	6.46	7.54			
2090	7.808	7.535	7.468	10.854	10.943	9.893	7.604	0.36

Dibenz[*a*,*h*]anthracene

Figure 71: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 7.7 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

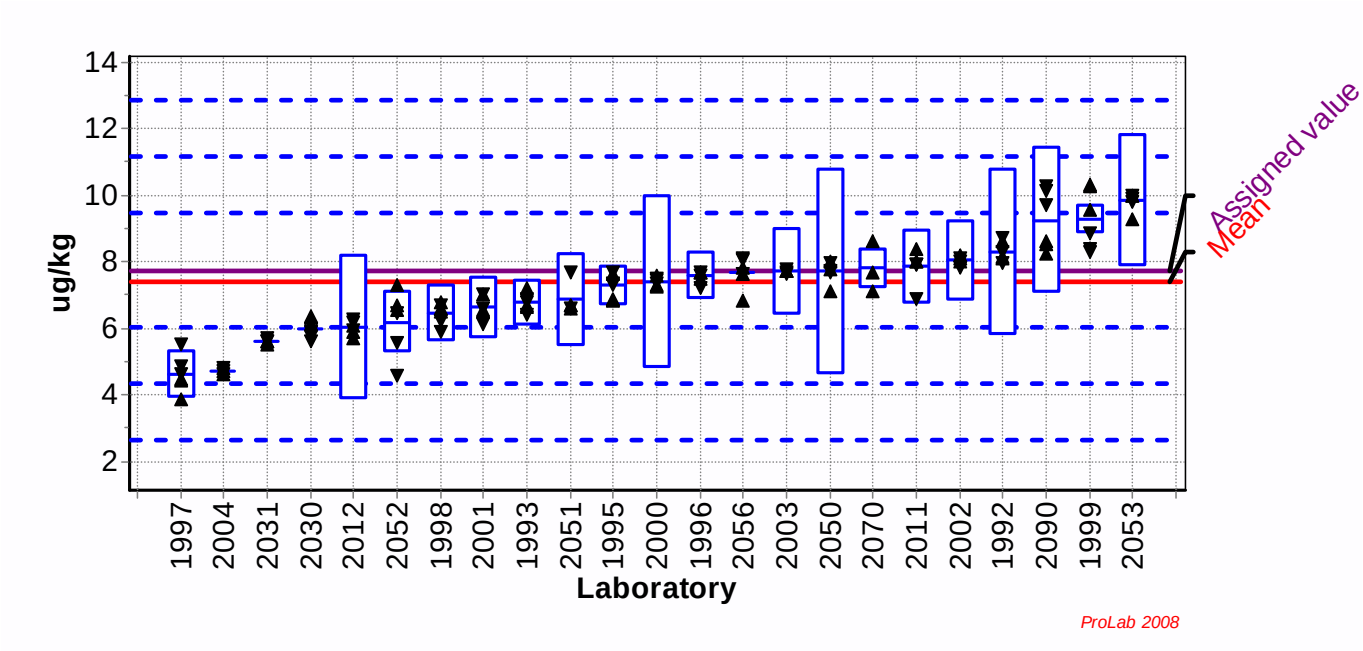


Figure 72: Kernel density plot

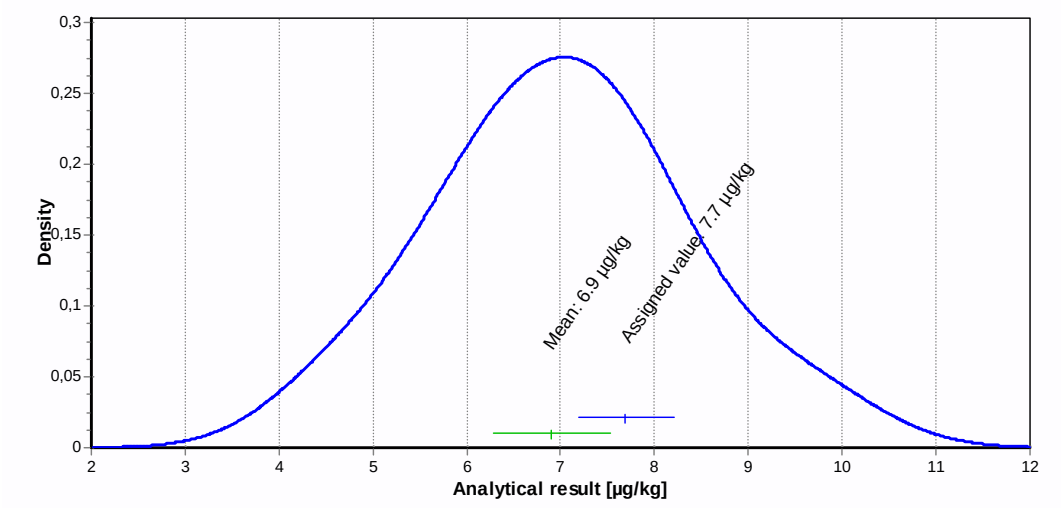


Table 32: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991								
1992	8.61	8.17	8.11	7.97	8.28	8.69	6.42	
1993	7.21	6.71	6.65	6.79	6.4	6.88	6.8	0.7
1995	6.87	7.65	6.85	7.29	7.34	7.69	7.44	0.6
1996	7.5	7.7	7.7	7.2	7.6	7.7	7.6	0.7
1997	3.86	4.42	4.48	4.62	5.52	4.85	4.63	1.35
1998	6.6	6.8	6.5	5.9	6.7	6.2	6.4	0.8
1999	10.3	10.25	9.58	8.38	8.29	8.86	8.34	1.25
2000	7.28	7.23	7.56	7.46	7.34	7.47	7.39	0.7
2001	6.5	6.55	7	6.12	6.61	7.02	6.76	0.79
2002	8.1	8.2	8	8	8.1	7.8	8.2	1.2
2003	7.72	7.71	7.74	7.63	7.69	7.75	7.69	1.22
2004	4.6	4.7	4.8	4.8	4.6	4.7	4.73	1
2010								
2011	8	8	8.4	6.9	7.9	7.9		
2012	5.7	5.88	6.1	5.95	6.26	6.16	5.9	2.1
2030	6.12	6.35	6.31	5.9	5.76	5.59	6.01	
2031	5.6	5.5	5.6	5.6	5.7	5.6	5.6	
2050	7.1	7.77	8.01	7.67	7.98	7.74	7.71	3.08
2051	6.7	6.7	6.6	6.6	7.7		6.9	0.5
2052	6.69	6.53	7.28	6.46	5.55	4.59	6.18	0.93
2053	10	10	9.3	9.9	10	9.8	9.8	2
2056	6.83	7.62	7.83	7.62	8.05	8.08	7.43	0.53
2070	7.66	8.6	7.13					
2090	8.618	8.23	8.547	10.246	10.127	9.685	9.242	2.198

Dibenzo[*a,h*]pyrene

Figure 73: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 9.9 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

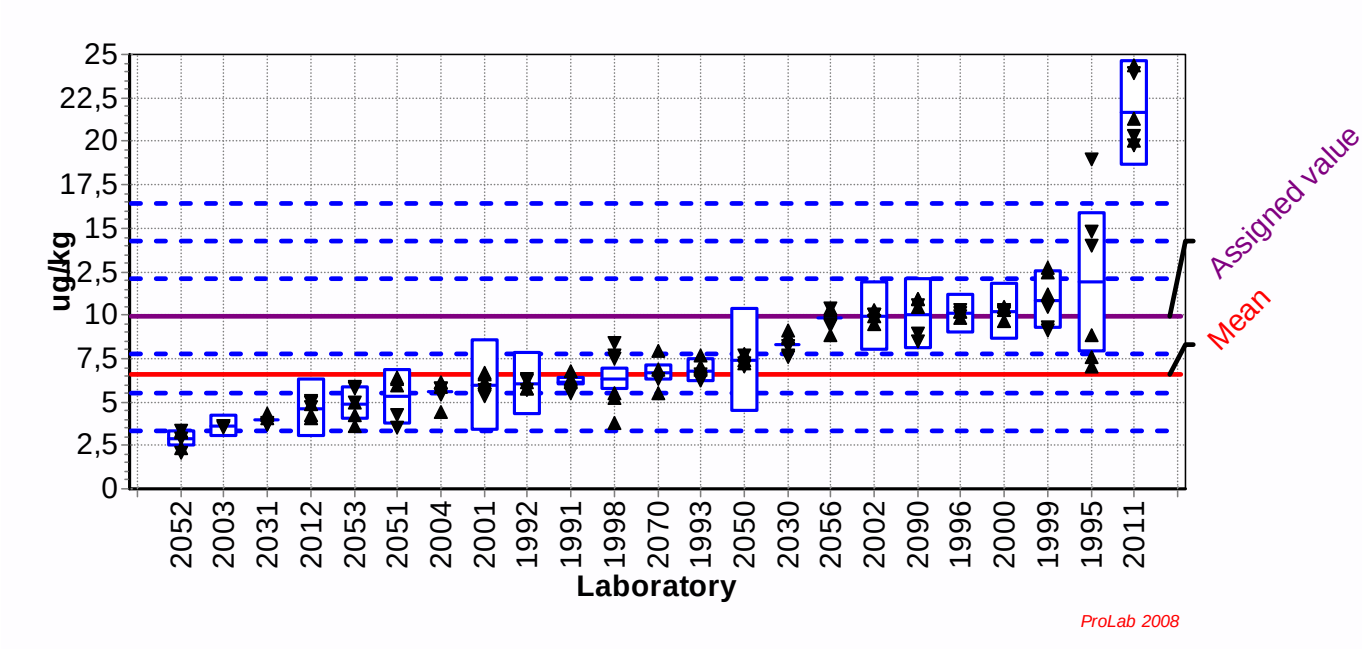


Figure 74: Kernel density plot

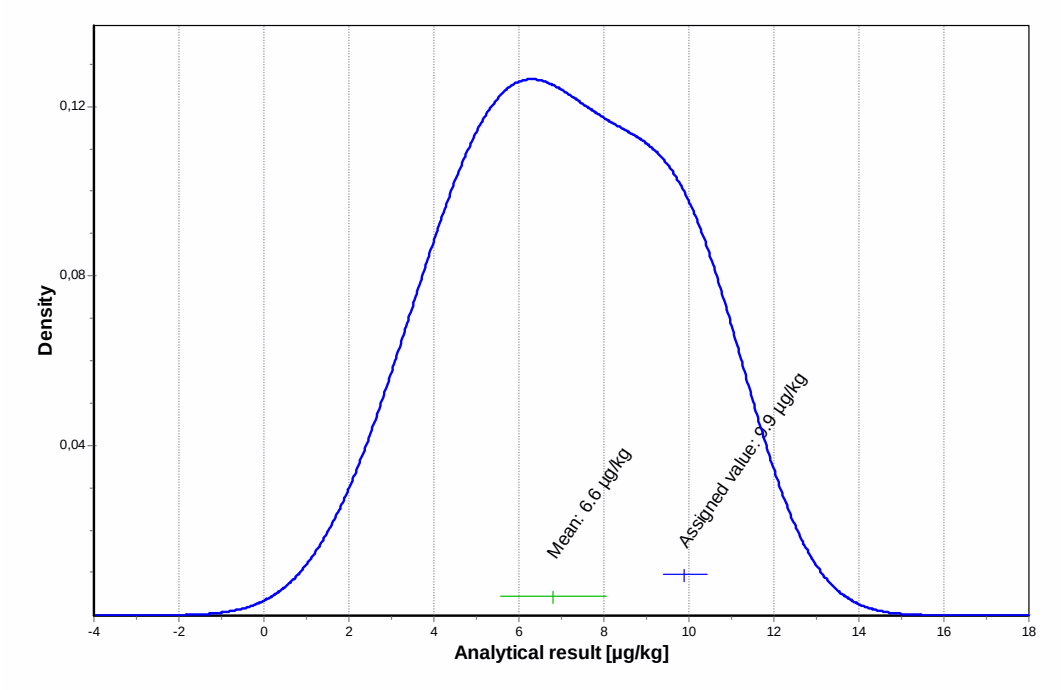


Table 33: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	6.1	6.32	6.77	5.48			6.4	0.48
1992	5.78	5.78	6.17	5.72	6.23	6.36	5.44	0
1993	7.69	6.85	7.03	6.34	6.22	6.6	6.8	0.7
1995	8.81	7.06	7.56	14.02	14.84	18.92	7.81	3
1996	10.2	9.8	10.2	10.3	10.1	9.9	10.1	1.1
1997								
1998	5.5	3.8	5.2	7.5	8.4	7.7	6.4	0.6
1999	12.42	12.69	11.17	10.46	9.31	9.08	9.89	2.45
2000	10.32	10.49	9.69	10.15	10.18	10.32	10.19	1
2001	6.64	6.61	6.1	5.42	5.71	5.32	8.07	2.13
2002	9.9	10.3	9.5	9.7	10	10	10.1	2
2003				3.52	3.63	3.64	3.63	0.61
2004	4.4	5.9	6.1	5.8	5.4	5.8	5.6	1.2
2010								
2011	24.4	21.3	20	19.8	23.9	20.3		
2012	4.2	4.85	4.1	4.94	5.07	4.69	4.9	1.8
2030	8.63	9.08	8.73	8.25	7.69	7.61	8.33	0
2031	4.2	4.1	4.3	3.7	3.8	3.7	4	0
2050	7.26	7.79	7.43	7.23	7.67	7	7.4	2.96
2051	6	6.3	6.4	3.5	4.2		5.7	1
2052	3.27	3.36	2.34	2.08	2.88	3.31	2.87	0.43
2053	3.6	4.2	5	5.9	5.8	5	4.9	1
2056	8.88	10.3	10.4	9.37	9.45	10.4	9.86	0.84
2070	6.87	7.96	5.52	6.33				
2090	10.953	10.95	10.454	8.498	10.56	8.941	10.059	2.054

Dibenzo[*a,i*]pyrene

Figure 75: Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 5.6 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).

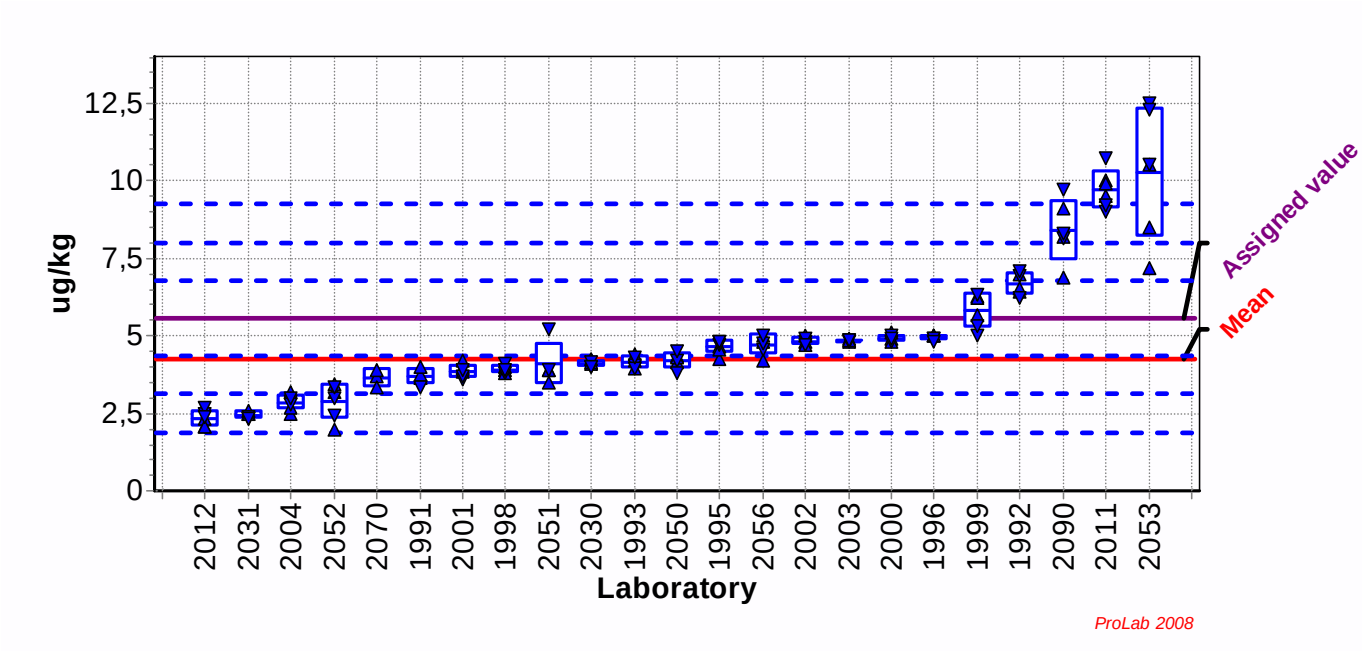


Figure 76: Kernel density plot

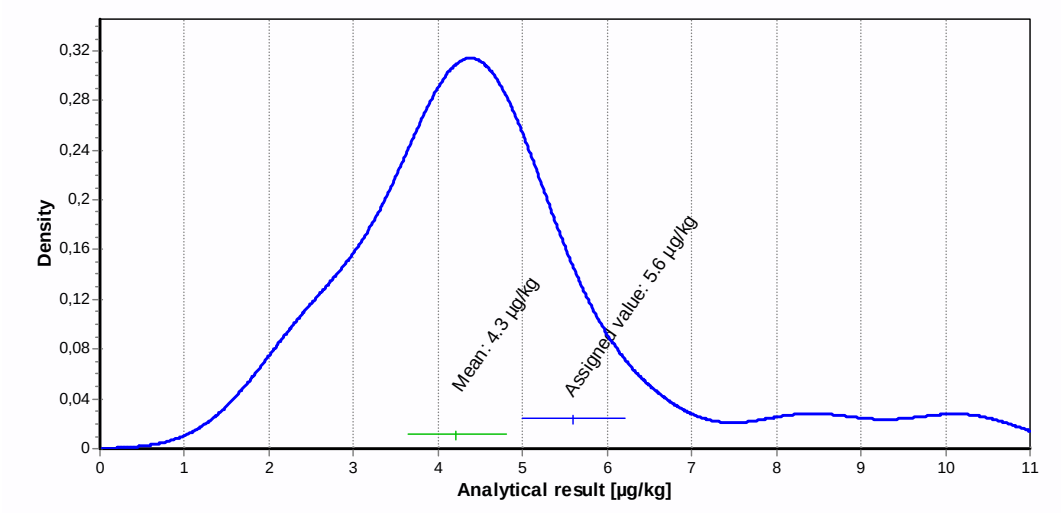


Table 34: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	3.66	3.72	3.99	3.36			3.79	0.29
1992	6.41	6.52	7	6.93	6.23	7.07	6.35	0
1993	4.38	3.95	4.22	4.05	3.96	4.32	4.2	0.4
1995	4.27	4.66	4.57	4.72	4.78	4.8	4.5	1
1996	5	5	5	4.9	4.9	4.8	4.9	0.3
1997								
1998	4	3.9	3.8	3.8	4.1	3.9	3.9	0.4
1999	6.28	6.21	5.65	6.33	5.01	5.29	5.67	2.07
2000	5.08	4.92	4.82	5	4.81	4.91	4.92	0.39
2001	3.82	3.95	4.17	3.6	3.71	3.89	4.22	0.45
2002	5	4.8	4.7	4.8	4.9	4.7	4.9	1
2003	4.88	4.78	4.83	4.83	4.8	4.83	4.8	0.78
2004	2.5	2.7	3.2	2.9	2.8	3	2.9	0.4
2010								
2011	10	9.5	9.9	9	10.7	9.2		
2012	2.07	2.3	2.05	2.47	2.68	2.39	2.3	0.8
2030	4.09	4.24	4.13	4.12	3.98	4.01	4.09	0
2031	2.5	2.5	2.6	2.3	2.4	2.3	2.4	0
2050	4.12	4.35	4.32	4.19	4.49	3.79	4.21	1.68
2051	3.5	3.9	3.9	5.2	3.9		4.1	0.7
2052	3.43	1.96	3.16	2.96	3.36	2.44	2.89	0.43
2053	7.2	8.5	10.5	12.5	12.3	10.5	10.2	2
2056	4.18	4.81	5.02	4.56	4.73	5.02	4.67	0.44
2070	3.68	3.91	3.32					
2090	8.179	6.866	9.081	8.147	8.296	9.698	8.378	0.95

Dibenzo[*a,l*]pyrene

Figure 77: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 7.7 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

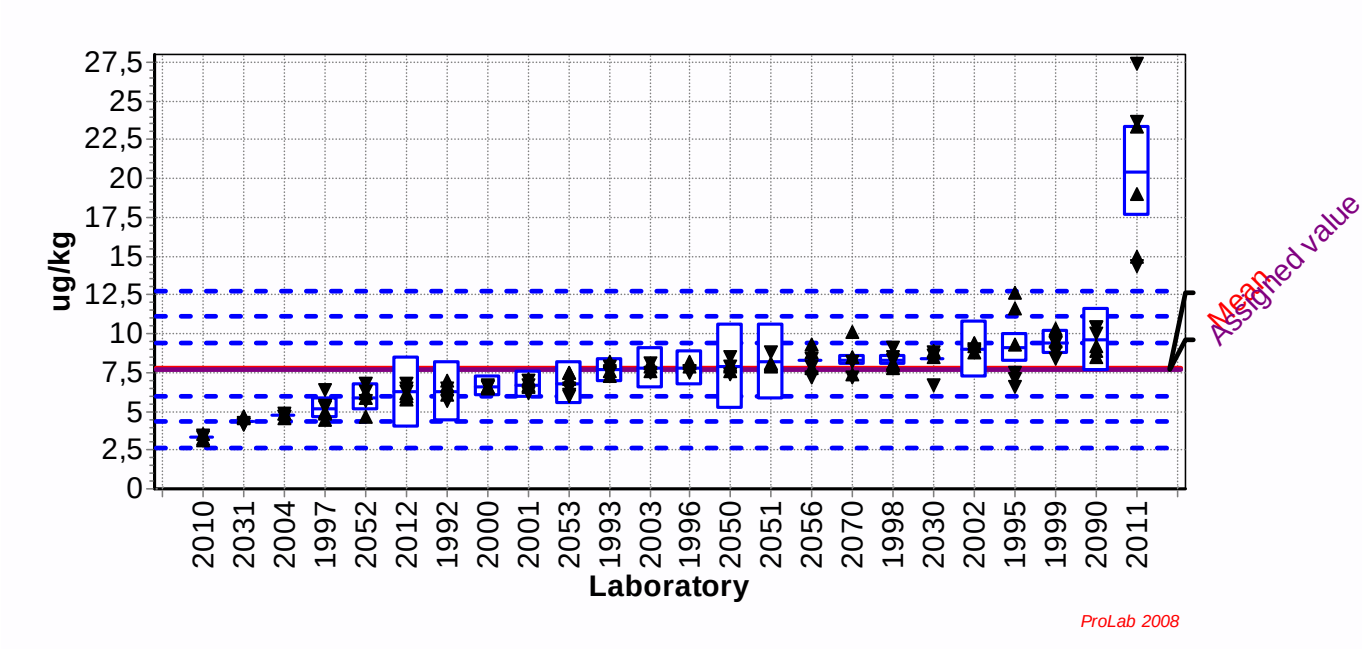


Figure 78: Kernel density plot

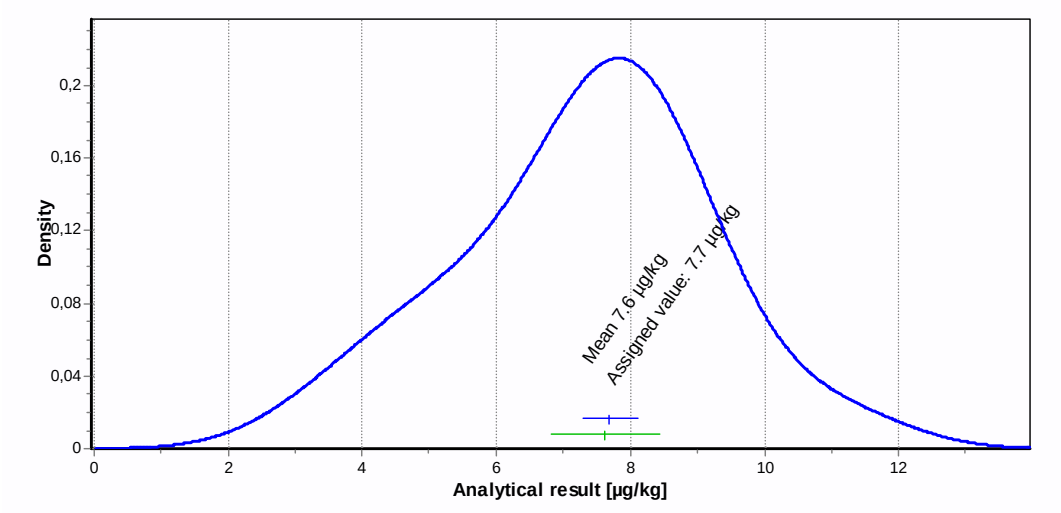


Table 35: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991								
1992	6.02	6.93	6.69	5.63	5.86	6.49	7.29	
1993	7.29	7.58	8.15	7.44	7.62	7.9	7.7	0.7
1995	9.29	11.63	12.59	7.05	7.51	6.57	11.2	1.3
1996	8.1	7.9	8.2	7.6	7.6	7.5	7.8	1.1
1997	4.44	4.89	4.92	5.39	6.37	5.22	5.21	1.27
1998	8.1	7.8	8	8.3	9.1	8.5	8.3	0.4
1999	10.33	10.18	9.47	8.83	8.4	9.37	8.62	2.41
2000	6.59	6.55	6.48	6.65	6.62	6.57	6.58	0.6
2001	6.62	6.69	7.06	6.21	6.67	7.02	7.29	0.77
2002	9.2	9.4	8.8	8.9	9	8.8	9.3	1.8
2003	7.87	7.55	8.04	7.52	8.05		7.52	1.21
2004	4.5	4.9	4.9	4.9	4.6	4.6	4.7	1
2010	3.28	3.13	3.57	3.42	3.33		3.34	0.29
2011	23.3	19	15	23.7	27.4	14.4		
2012	6	6.14	5.77	6.23	6.82	6.43	6.1	2.1
2030	8.53	8.87	8.79	8.8	6.66	8.61	8.37	
2031	4.5	4.6	4.6	4.1	4.2	4.1	4.4	
2050	7.63	8	7.93	7.39	7.91	8.5	7.89	2.76
2051	7.9	8.1	8	8.8			8.2	0.4
2052	6.2	4.64	5.89	5.71	6.76	6.27	5.91	0.89
2053	7.1	7.5	7.5	6	6.1	6.5	6.9	1.4
2056	7.82	8.82	9.27	7.21	7.89	8.42	8.64	0.74
2070	7.37	8.54	10.11	7.19	8.18			
2090	8.896	8.537	9.169	10.453	10.393	10.029	9.579	2.014

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

Figure 79: **Individual results of replicate measurements on day1 (▲) and day2 (▼), sorted by the laboratory mean values (-), and the reported expanded measurement uncertainty (k=2) (as box). The horizontal solid and dotted lines indicate the laboratory mean (red), the assigned value of 5.2 µg/kg (purple), and a ± 22 %, 44 %, and 66 % deviation thereof (blue dotted).**

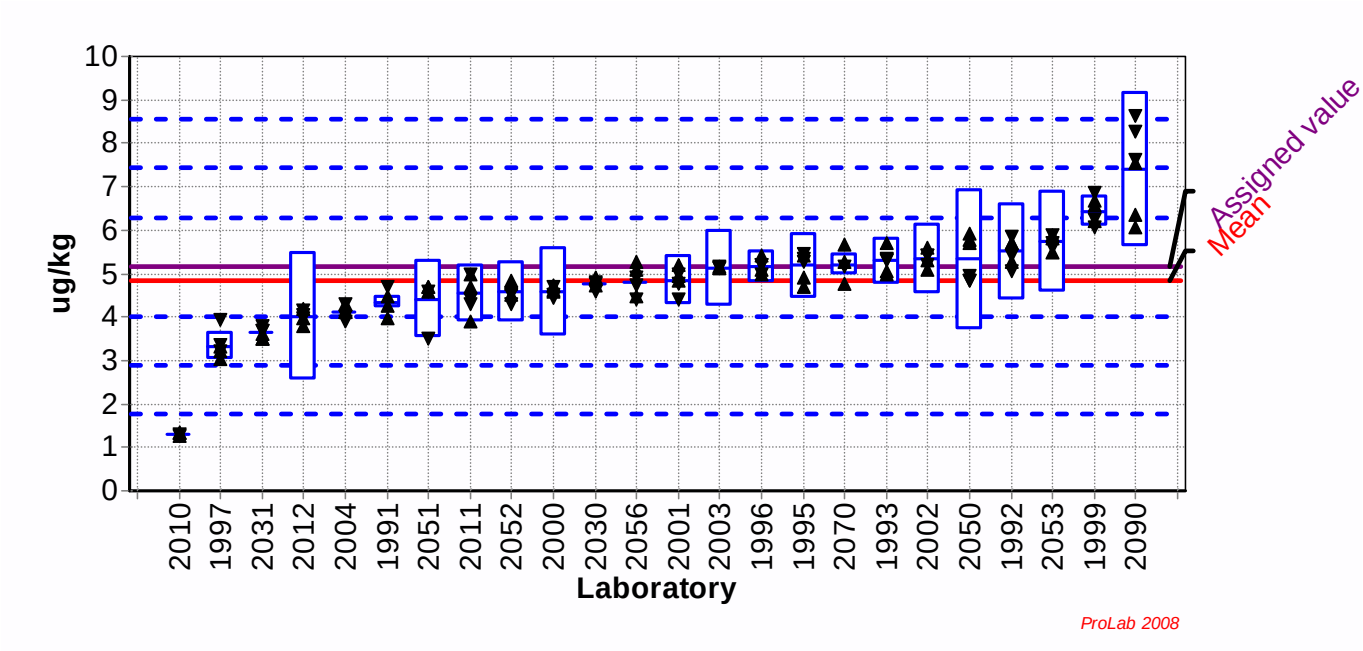


Figure 80: Kernel density plot

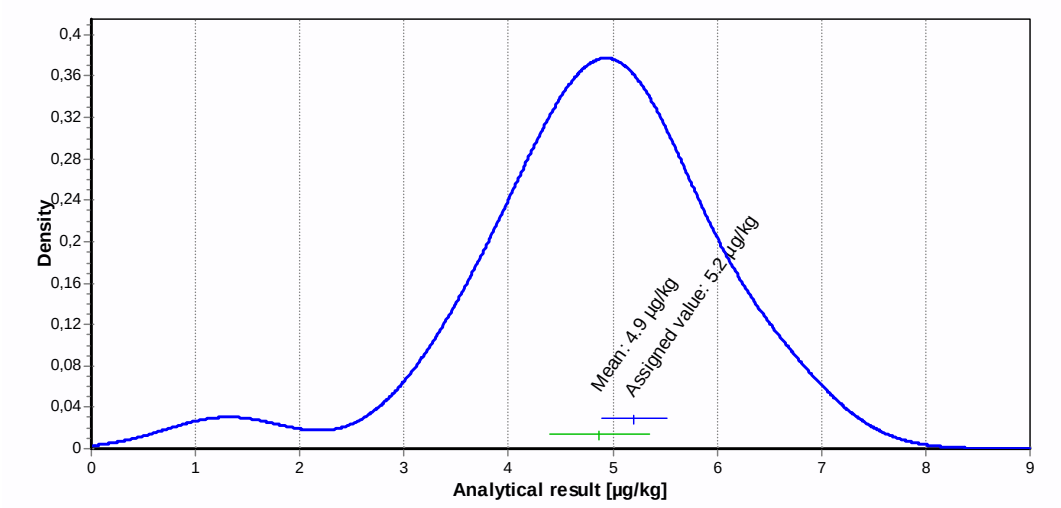


Table 36: Individual results of replicate measurements in µg/kg with expanded measurement uncertainty (k = 2); blank cells indicate missing data

laboratory	Value1	Value2	Value3	Value4	Value5	Value6	Final value	Uncertainty
1991	4.47	3.96	4.25	4.7			4.23	0.26
1992	5.28	5.72	5.71	5.06	5.43	5.86	6.08	0
1993	4.98	5.07	5.71	5.32	5.36	5.31	5.3	0.5
1995	4.9	5.41	4.71	5.26	5.45	5.36	5.36	0.8
1996	5	5.1	5.4	5	5.2	5.2	5.1	0.4
1997	3.02	3.32	3.21	3.36	3.92	3.2	3.34	0.59
1998								
1999	6.57	6.68	6.22	6.07	6.87	6.24	6.47	1.15
2000	4.59	4.63	4.74	4.69	4.45	4.5	4.6	0.46
2001	4.82	4.93	5.21	4.41	4.75	4.99	4.74	0.57
2002	5.3	5.6	5.1	5.4	5.4	5.2	5.4	0.8
2003	5.12	5.14	5.16	5.12	5.16	5.12	5.16	0.82
2004	4.1	4.1	4.3	3.9	4.3	4	4.1	0.4
2010	1.33	1.27	1.35	1.3	1.28		1.31	0.21
2011	3.9	5	4.7	4.4	5	4.3		
2012	3.78	3.98	4.2	3.97	4.15	4.05	4	1.4
2030	4.87	4.91	4.74	4.8	4.78	4.6	4.78	0
2031	3.5	3.5	3.6	3.7	3.8	3.7	3.6	0
2050	5.78	5.72	5.91	4.85	4.82	4.94	5.33	1.6
2051	4.7	4.7	4.6	3.5	4.6		4.6	0.1
2052	4.5	4.77	4.82	4.29	4.51	4.56	4.58	0.69
2053	5.9	5.8	5.5	5.7	5.6	5.9	5.7	1.1
2056	4.49	5.1	5.28	4.72	4.42	4.9	4.96	0.41
2070	5.27	5.65	4.75	5.15				
2090	7.552	6.354	6.05	8.264	8.619	7.6	6.652	1.588

Comparison of results for acetonitrile and sausage meat

The percentage deviation of the average value for each analyte from the assigned concentration had been calculated for each individual participant for the solvent solution and the sausage meat material (Figure 81 and Figure 82). The aim of this evaluation was to highlight systematic deviations from the assigned values for the whole set of PAHs.

Figure 82 showed that most of the reported values deviated not more than twice the target relative standard deviation (± 44 %) from the assigned value, which is also reflected in the z-scores (Table 20). However, for laboratory 2010 almost all reported values lay outside of the satisfactory range, which was the consequence of a malfunctioning instrument.

In many cases the comparison of the deviations of the results for the acetonitrile solution and the sausage meat material indicated that the biases and/or distribution found in the solvent material were almost completely conserved in the sausage meat (e.g. for laboratory codes 1995, 1996, 1998, 2000, 2002, 2004, 2012, 2031, 2051, 2053, and 2056). In other cases a bias and/or scatter were introduced (1991, 1997, 1999, 2001, 2003, 2010, 2050, 2052, and 2090). The results of the participants 1991 and 1997, which both applied HPLC-FLD for the analysis, might be the consequence of faulty recovery correction.

It should be emphasised at this place that bias or high uncertainty introduced by an improper calibration cannot be mended by an even very good sample preparation and determination of recovery. This becomes obvious for the results of participant 2004. The bias and dispersion of the results of this laboratory for both the acetonitrile solution and the sausage meat sample show nearly the same dispersion and similar bias.

The dispersion of the results of participant 2053 indicates chromatographic problems, since the distribution of the results of the acetonitrile solution is as broad as the one for the sausage meat sample.

Figure 81: Relative deviations of the individual laboratory mean values from the assigned values for the concentrations of the analytes in acetonitrile

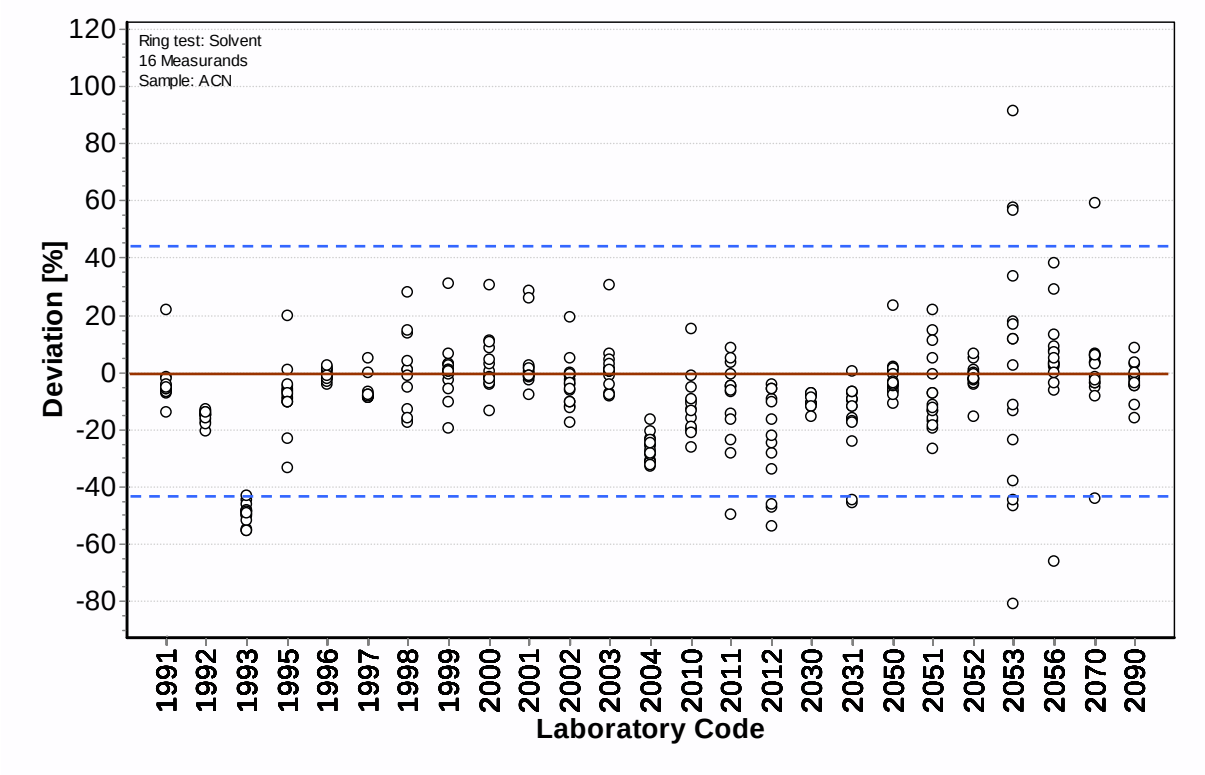
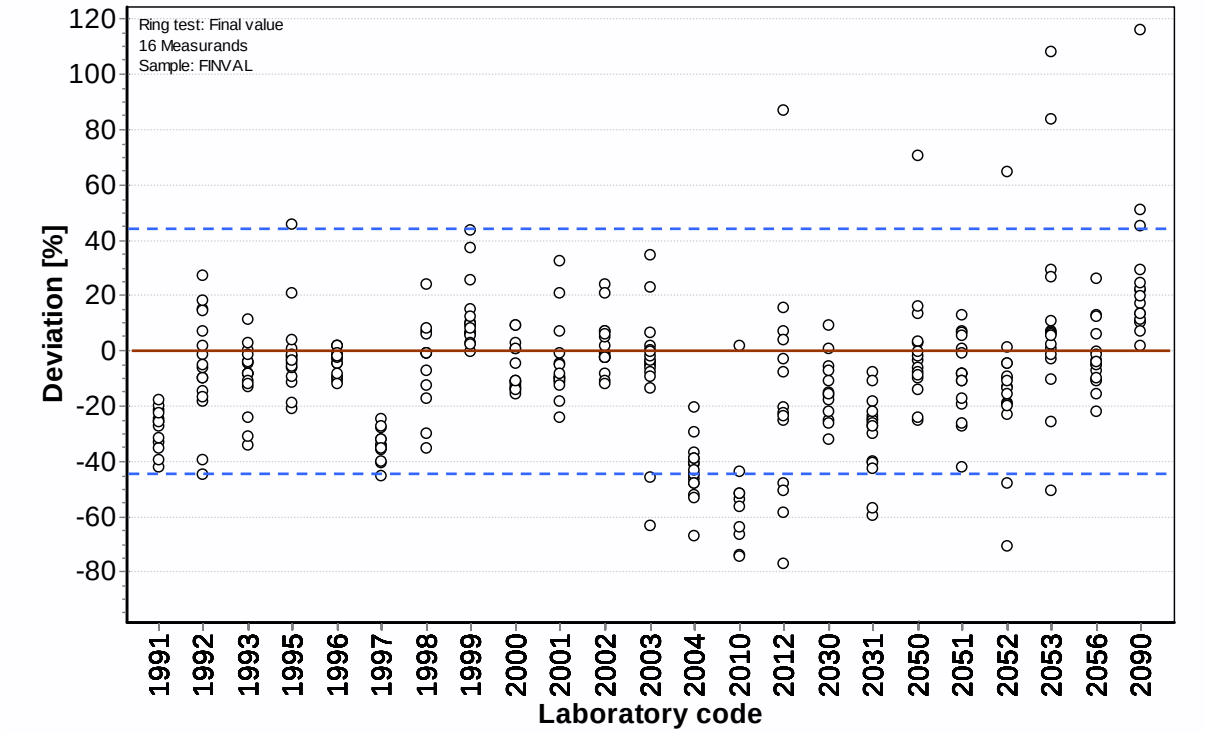


Figure 82: Relative deviations of the individual laboratory Final Values from the assigned values for the concentrations of the analytes in sausage meat



Results of the participants 2011 and 2070 are not considered in Figure 82 since they did not report Final Values.

Effect of analysis method on results for selected analytes

As a follow-up from last years PT the differences from the reported values to the assigned values were also plotted separately for the analytical method used for BaP, BjF, BkF, and CCP (Figure 83 to Figure 96). However as mentioned before, the large negative bias of the data of participant 2010 were explained by a malfunctioning instrument. No major differences in performance were detected between the two chromatographic methods for BaP, BjF, and BkF. No significant bias could be found for any of these three analytes.

For CPP the GC-data showed a better performance respective the data from laboratories using HPLC, which were more scattered and positively biased by about 20 %.

As the data for DeP in both materials indicated a bimodal distribution (Figure 23 and Figure 70) and as the consensus values for DhP and DiP deviated by more than 10 % from the respective assigned value (Figure 26, Figure 28, Figure 73, and Figure 75), the deviations from the assigned values were plotted for theses analytes as well for each analytical method separately.

In the case of DeP (Figure 91 and Figure 92), the four extreme low values had been reported by laboratories applying gas chromatography for analyte separation. However as mentioned before, the large negative bias of the data of participant 2010 were explained by a malfunctioning instrument. The other three data points could be regarded as outliers and the remaining values indicated no difference between the two methods in question.

The data for DhP indicated a bias for both chromatographic methods (Figure 93 and Figure 94). For the GC the bias was about two times as high as for the HPLC data. Six values deviated by about -50 % from the assigned value and were clearly separated from the remaining five values, which were close to zero. The large bias of some results is not surprising, since the analysis of dibenzopyrenes by GC-MS is challenging both with regard to peak tailing and to sensitivity. For the HPLC it appeared that the data were in three groups: three reported values agreed well with the assigned value, five results deviated by -20 to -40 % (still satisfactory), and one value deviated by -70 % and could be regarded as clearly outlying.

For DiP the data appeared to be closer to normal distribution for HPLC than for GC. The data for the latter method, one result was clearly lying outside with 80 % deviation, a group of three values had a deviation of about -50 %, and the remaining values grouped around -15 % deviation. Among the HPLC-data only one outlying value could be found (55 %), while the remaining data had an apparent small negative bias.

For both analytes, DhP and DiP, the relative difference of the consensus value to the assigned value found in the sausage meat material equalled in the order of magnitude the relative offset found in the solvent material (26 % vs. 18 % and 23 % vs.15 %). It could be concluded that apparently the main contribution to the bias was caused by the instrumental analysis (e.g. calibration thereof) and only a minor part originated in the sample clean-up procedure.

Figure 83: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*a*]pyrene in sausage meat analysed by GC
Participant 2010 reported a malfunctioning analysis instrument

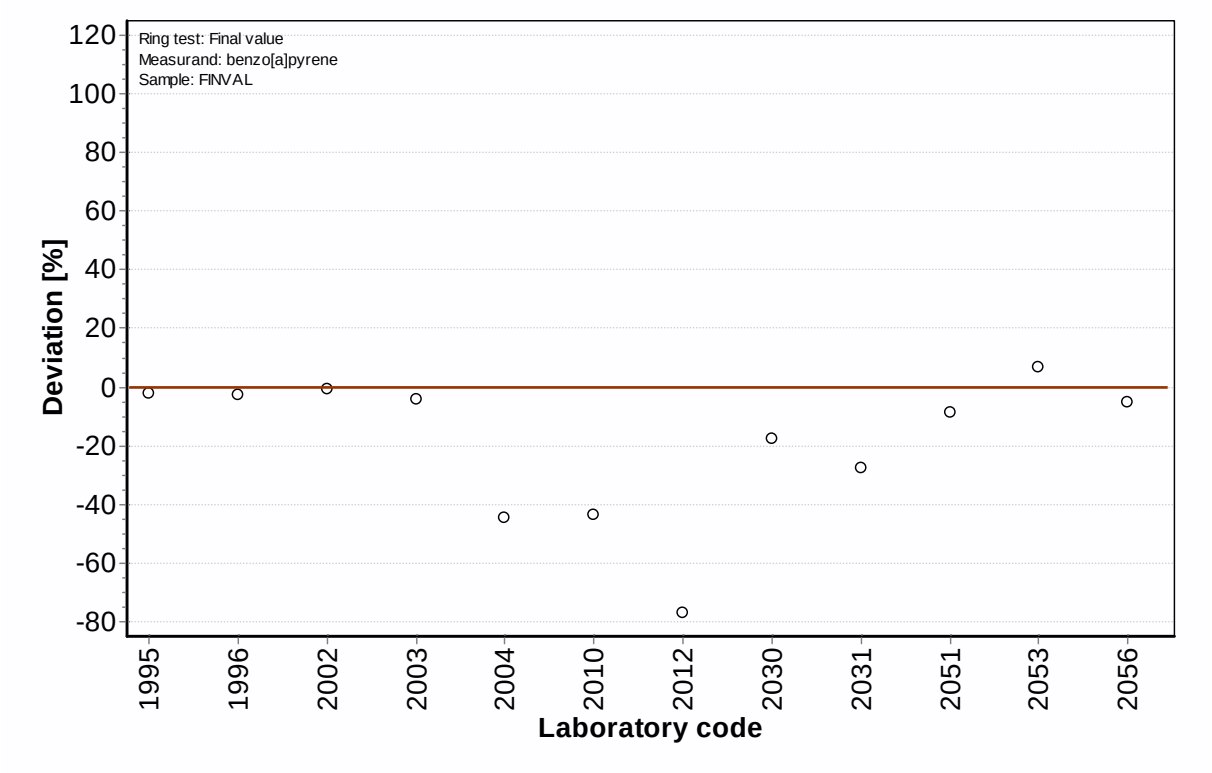


Figure 84: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*a*]pyrene in sausage meat analysed by HPLC

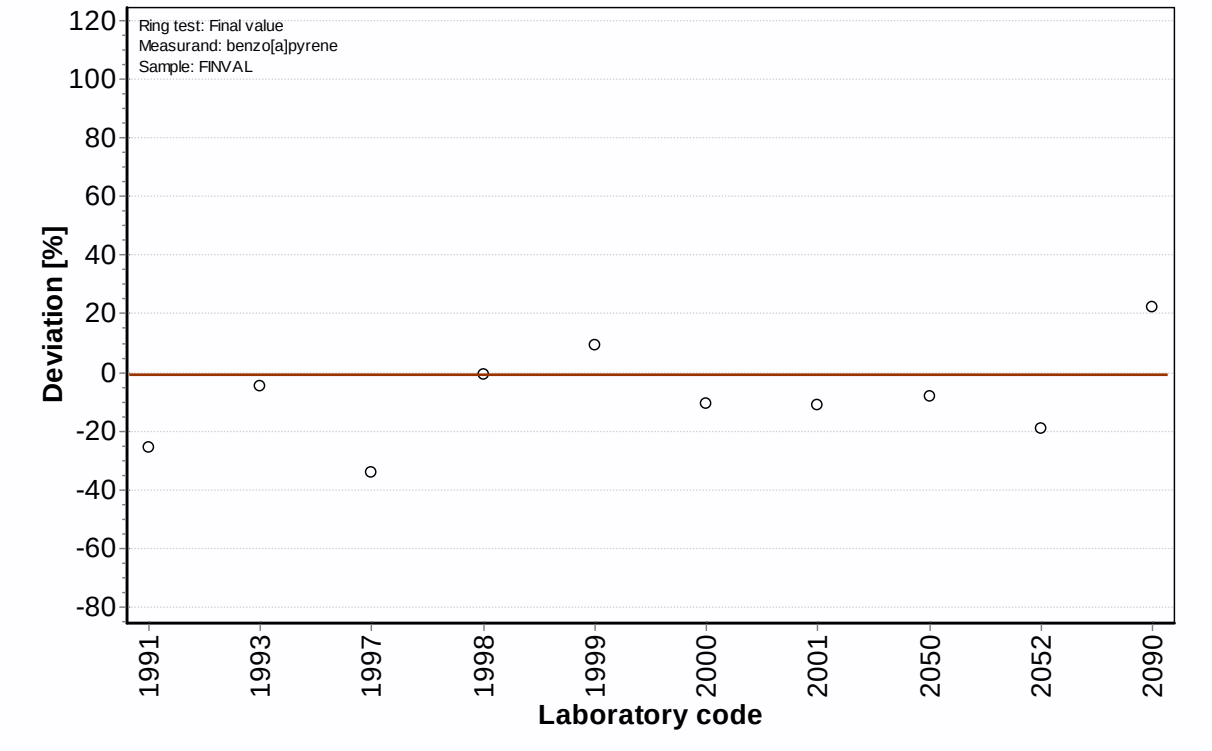


Figure 85: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*j*]fluoranthene in sausage meat analysed by GC

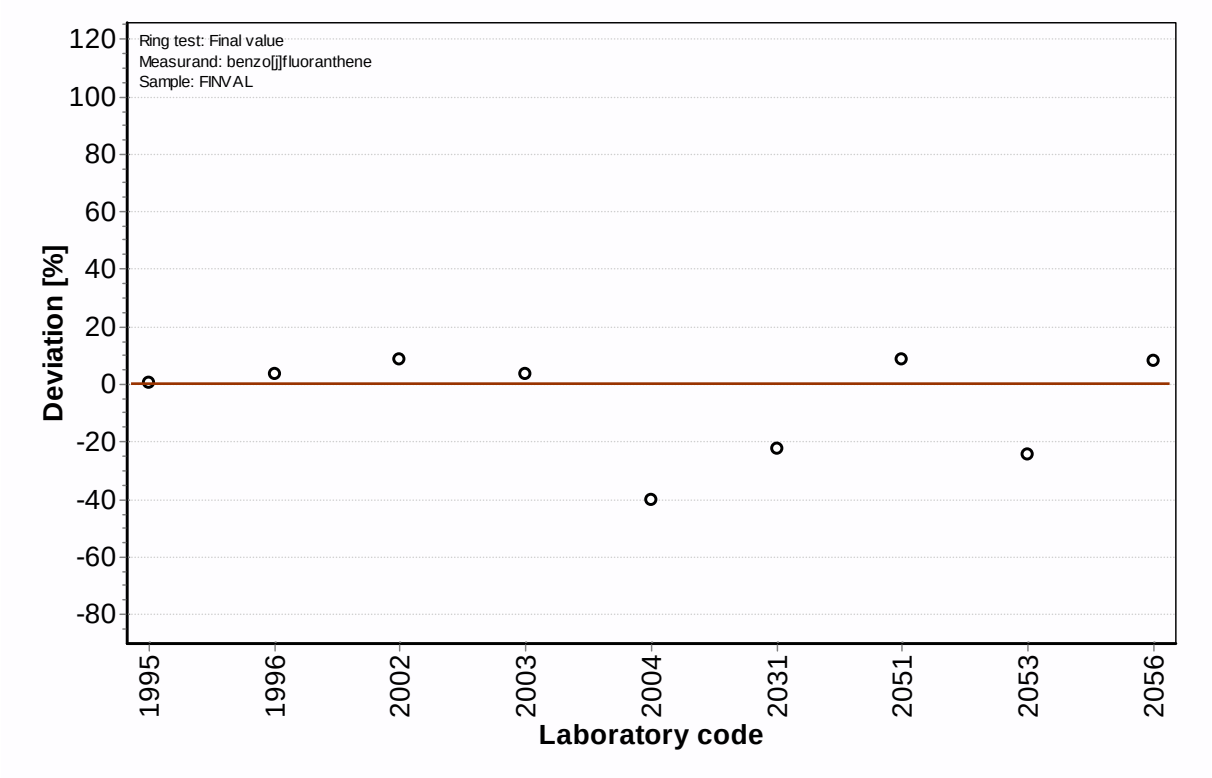


Figure 86: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*j*]fluoranthene in sausage meat analysed by HPLC

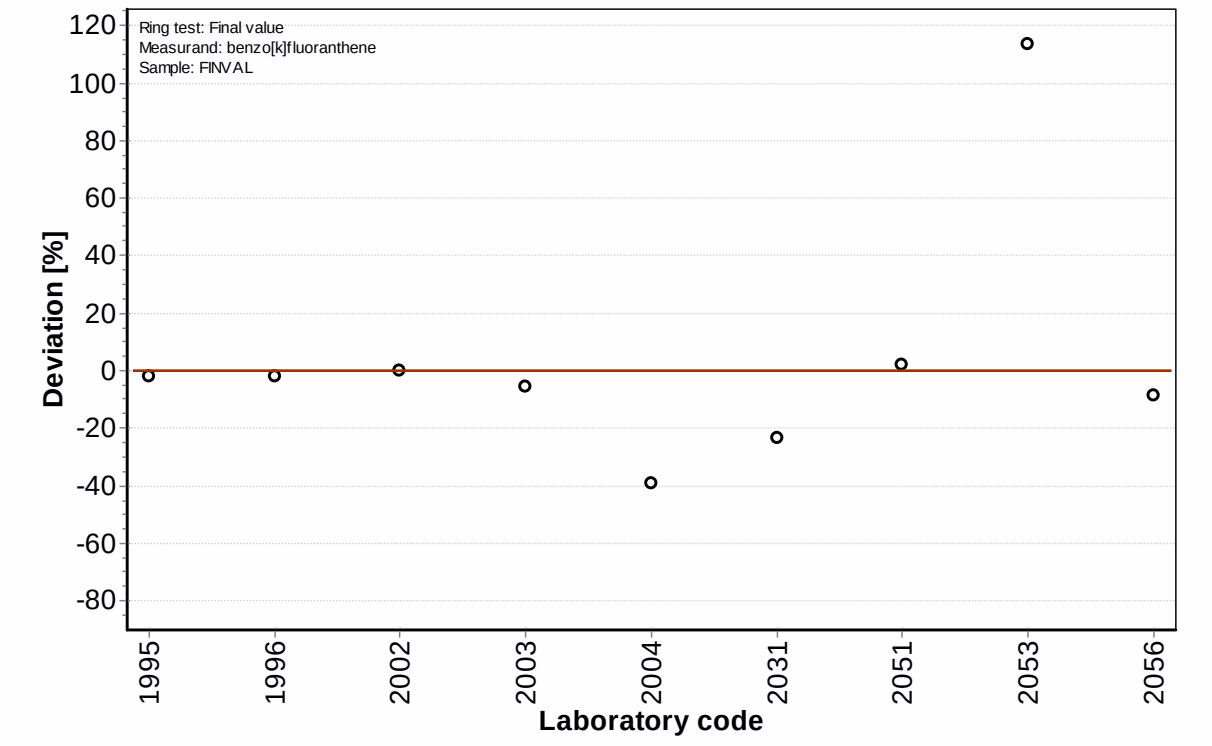


Figure 87: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*k*]fluoranthene in sausage meat analysed by GC

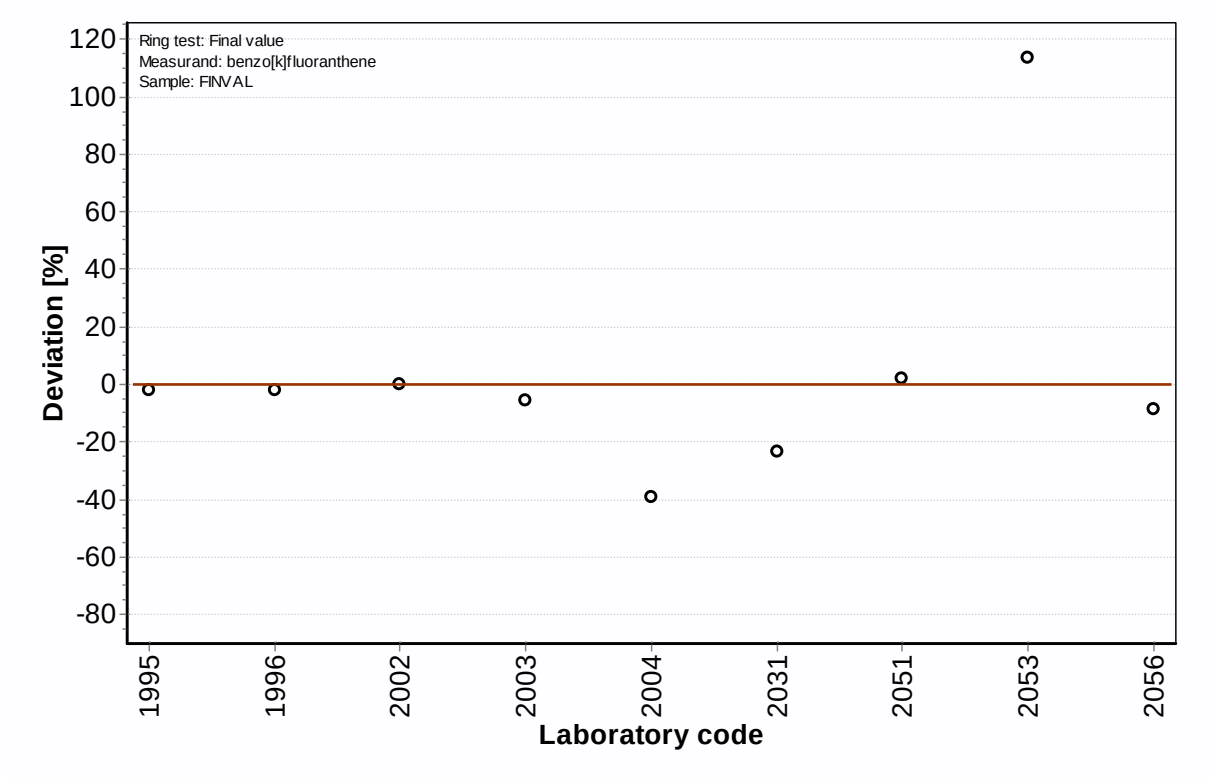


Figure 88: Relative deviations of the individual laboratories mean values from the assigned value of benzo[*k*]fluoranthene in sausage meat analysed by HPLC

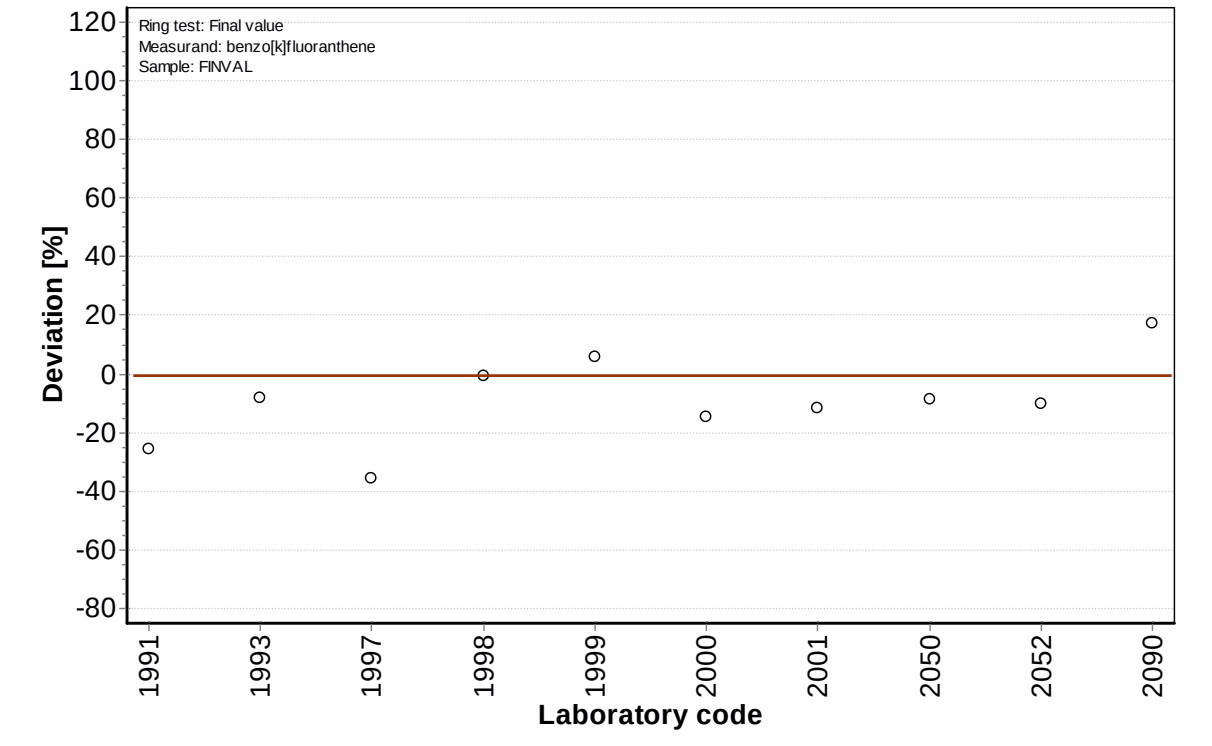


Figure 89: Relative deviations of the individual laboratories mean values from the assigned value of cyclopenta[*cd*]pyrene in sausage meat analysed by GC
Participant 2010 reported a malfunctioning analysis instrument

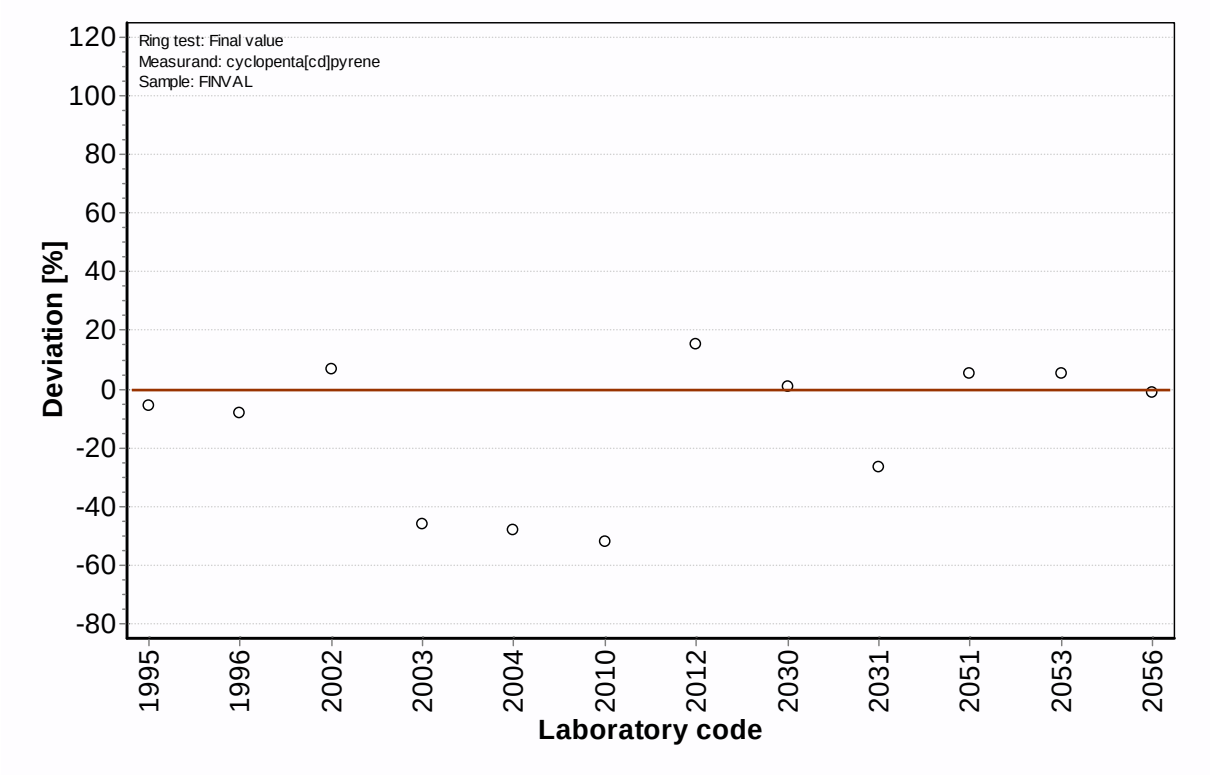


Figure 90: Relative deviations of the individual laboratories mean values from the assigned value of cyclopenta[*cd*]pyrene in sausage meat analysed by HPLC

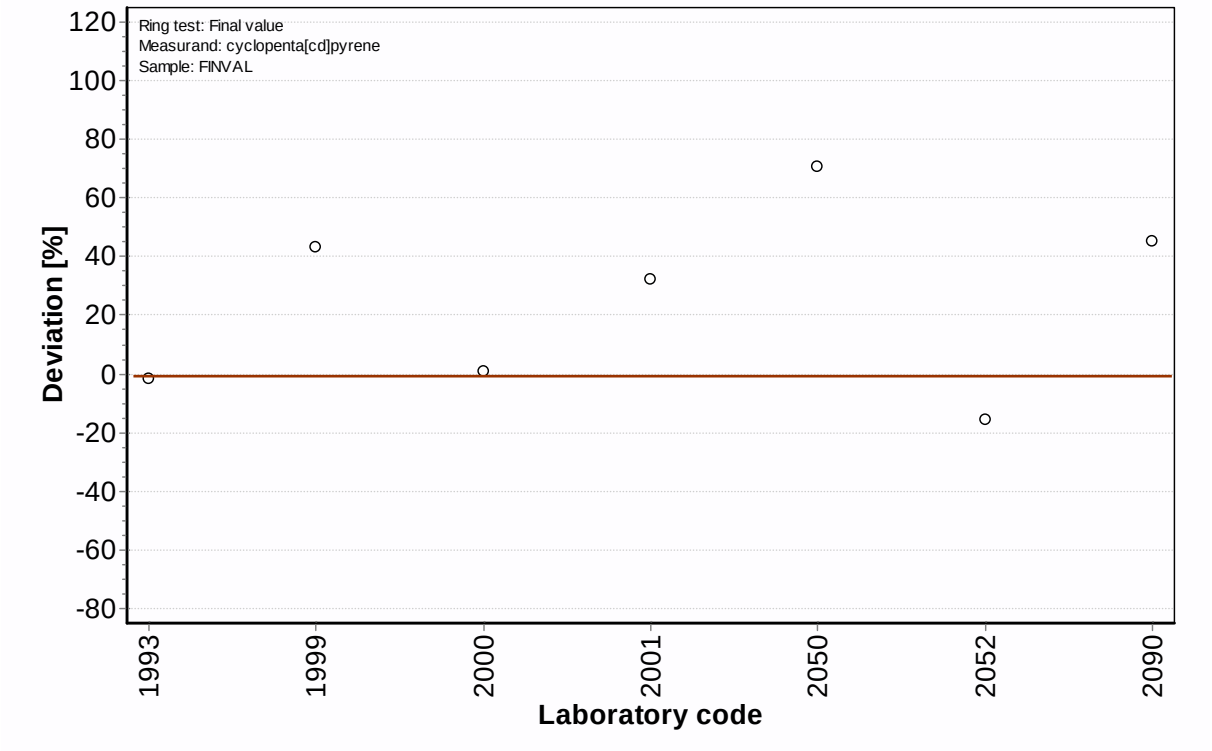


Figure 91: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,e*]pyrene in sausage meat analysed by GC

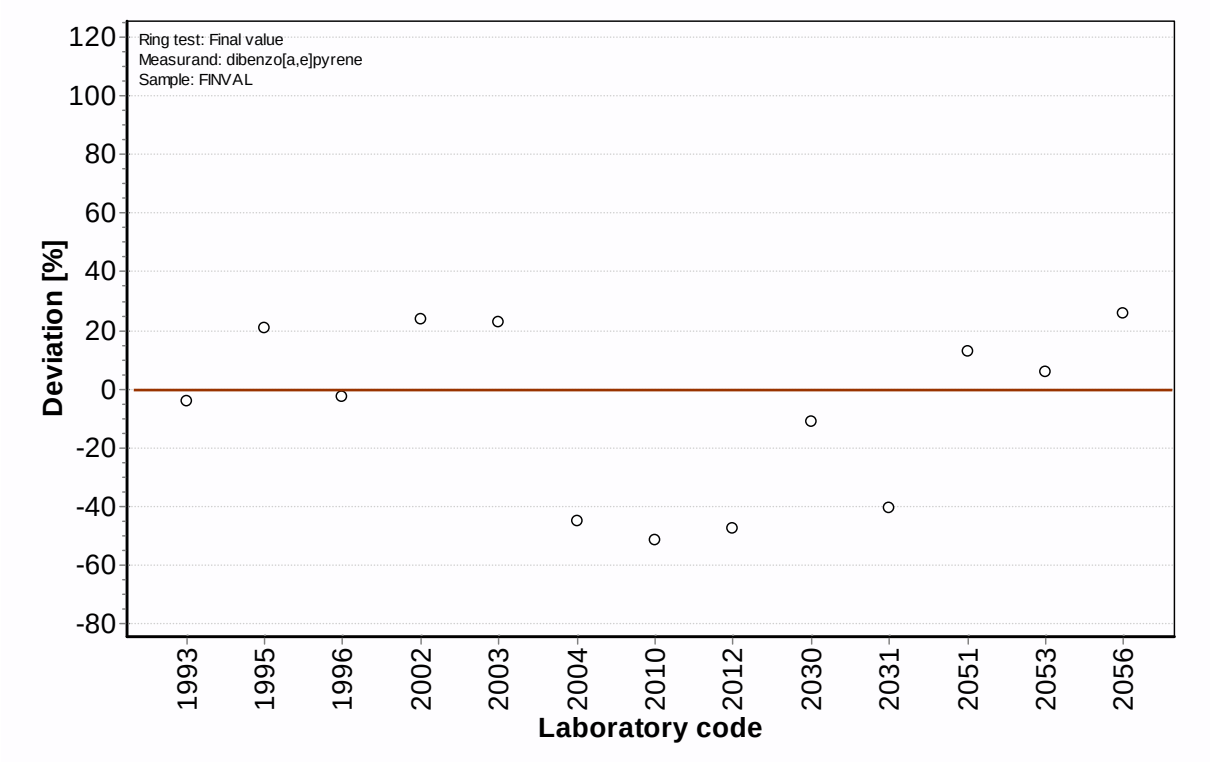


Figure 92: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,e*]pyrene in sausage meat analysed by HPLC

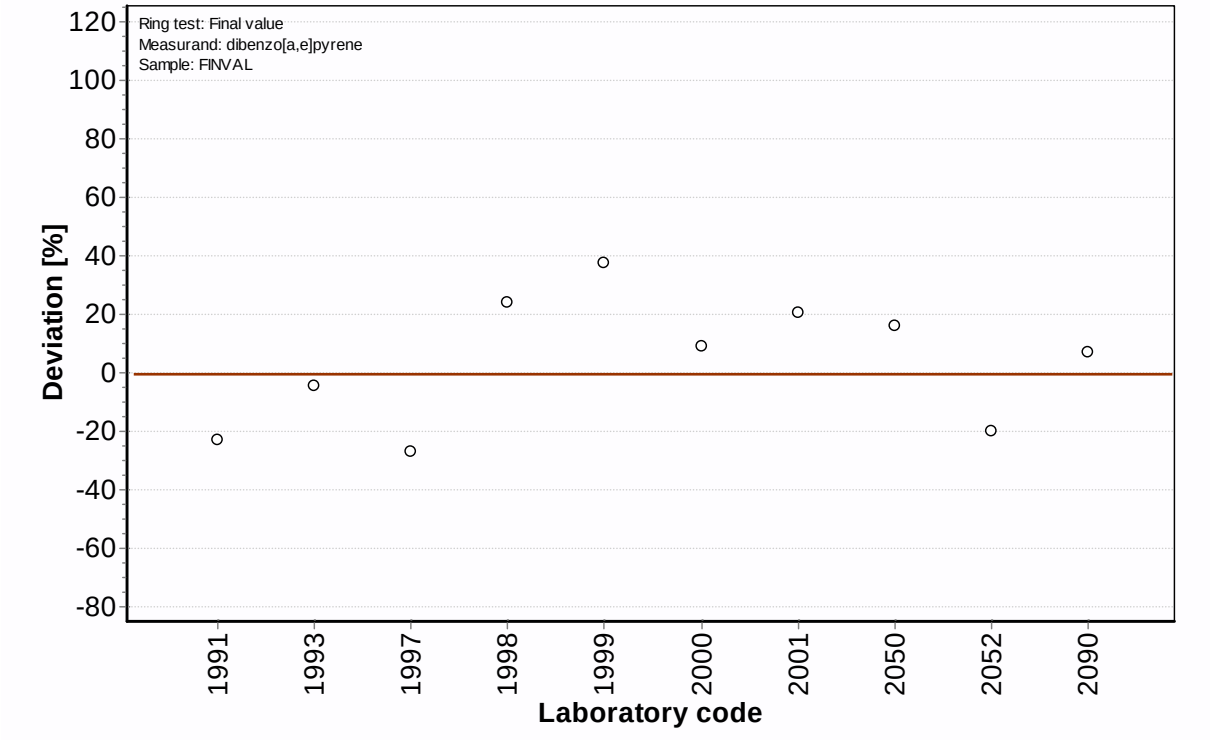


Figure 93: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,h*]pyrene in sausage meat analysed by GC

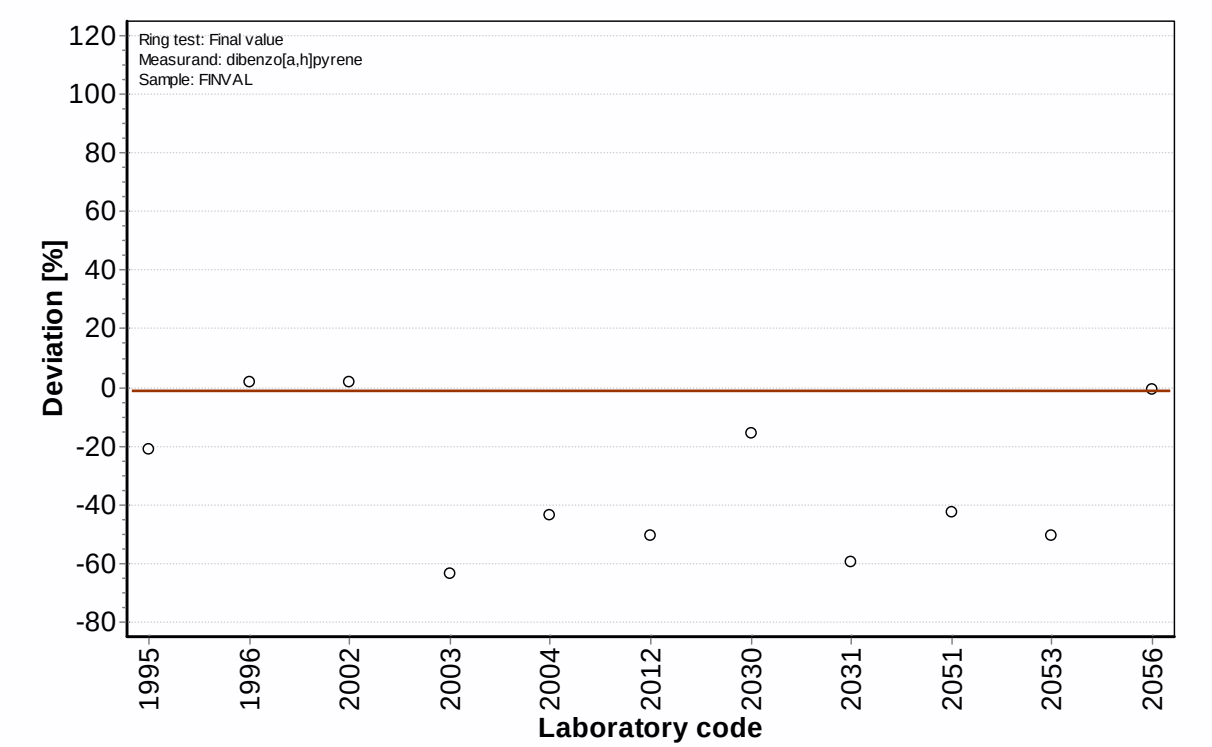


Figure 94: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,h*]pyrene in sausage meat analysed by HPLC

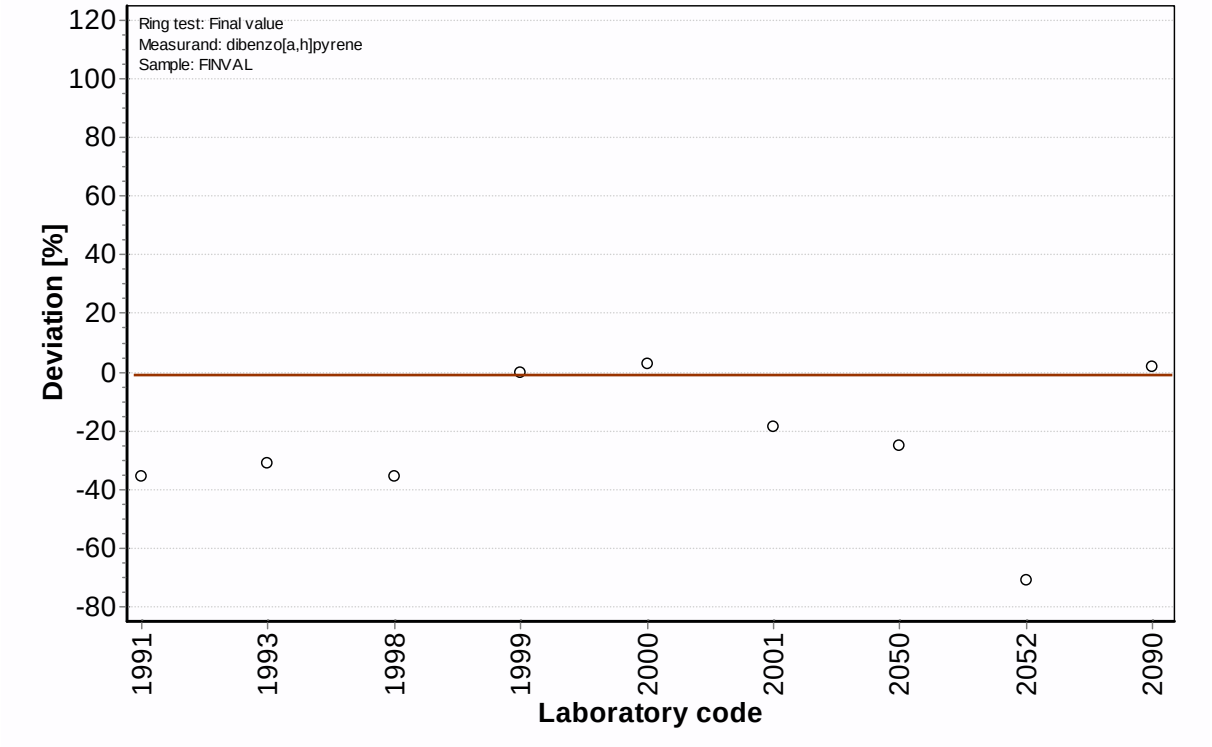


Figure 95: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,i*]pyrene in sausage meat analysed by GC

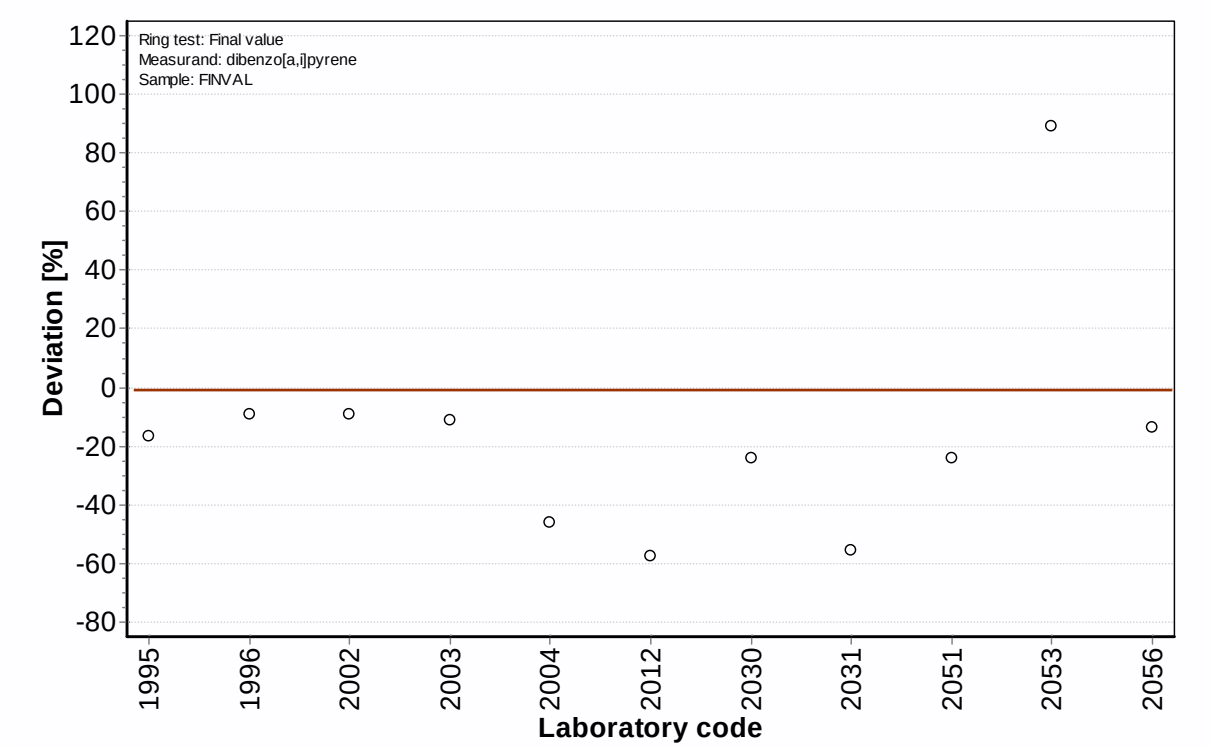
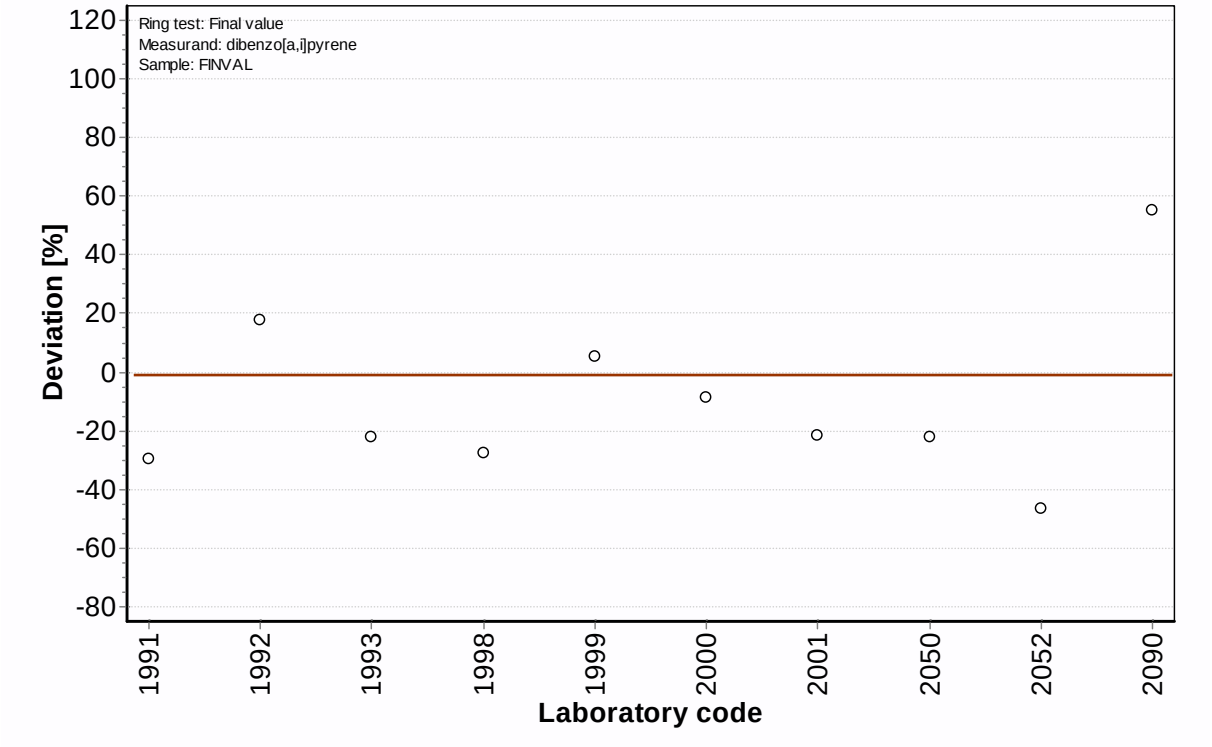


Figure 96: Relative deviations of the individual laboratories mean values from the assigned value of dibenzo[*a,i*]pyrene in sausage meat analysed by HPLC



Effect of sample preparation and measurement technique on results for all analytes

In order to identify differences between the approaches used for the chromatographic separation of the analytes and/or the preparation of the sample the relative differences of the reported to the assigned values were plotted for all analytes ordered by chromatographic method (Figure 97 and Figure 98) and/or main element of the sample preparation (Figure 99). Comparing the graphs for GC and HPLC it seemed that there is not any significant difference in the overall distribution of the data. However, in the dataset from the GC method one laboratory clearly dominated the analysis and delivered very good results (laboratory code 1996). The data of this laboratory were very precise and matched well with the assigned values.

The data for the sample preparation suggested that saponification might lead to a higher variability of the resulting values, but again the laboratory with the by far lowest distribution of values had used this approach indicating that the accuracy may depend on other variables.

Figure 97: Relative deviations of the individual laboratories values from the assigned values for the concentrations of the analytes in sausage meat (GC data)

Participant 2010 reported a malfunctioning analysis instrument

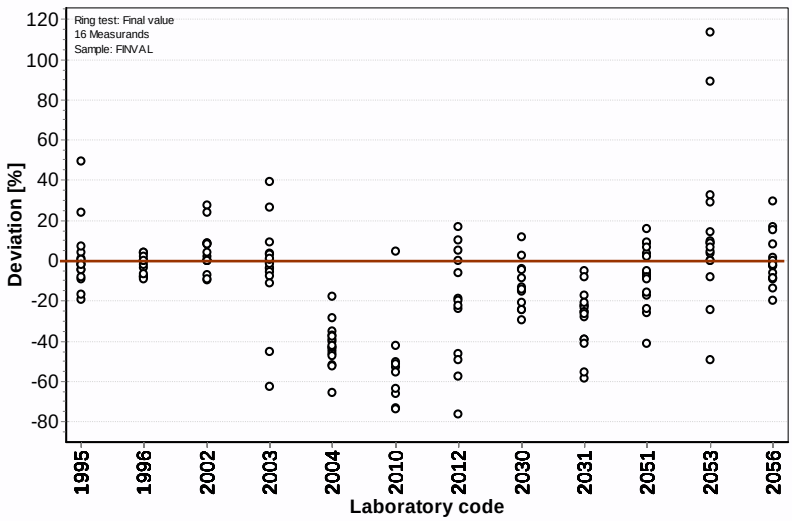


Figure 98: Relative deviations of the individual laboratories values from the assigned values for the concentrations of the analytes in sausage meat (HPLC data)

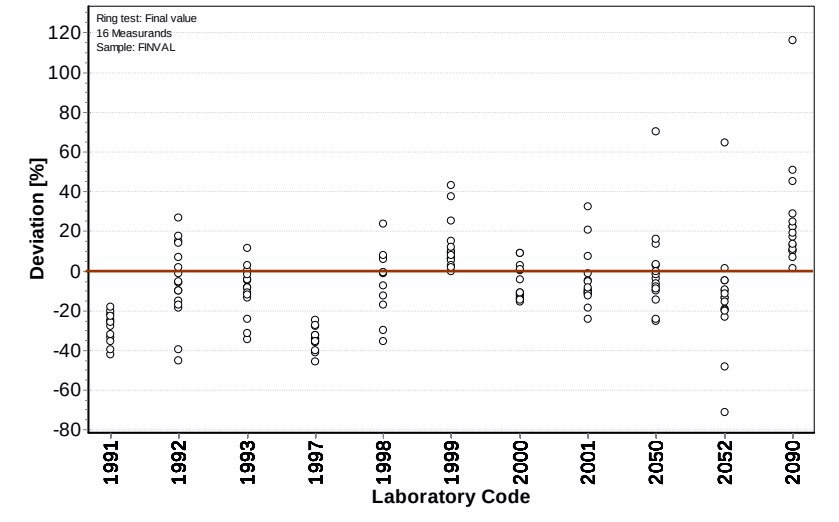
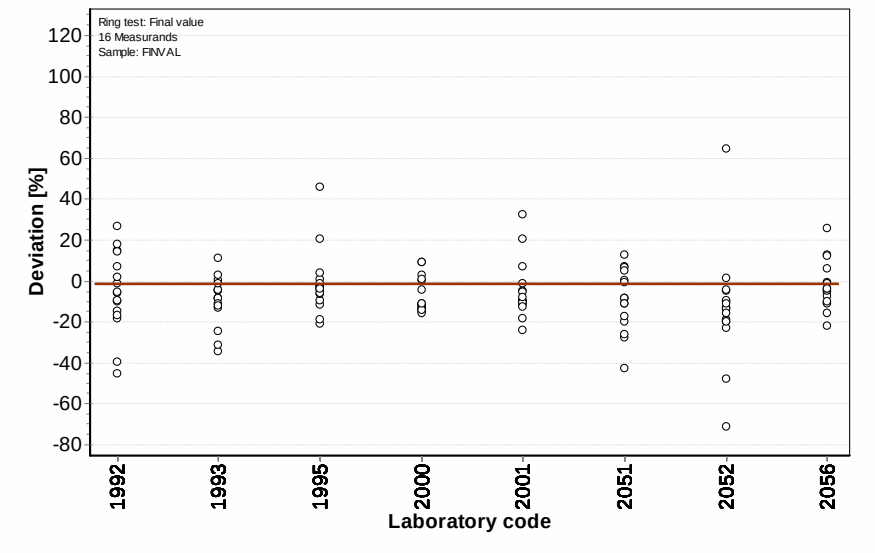
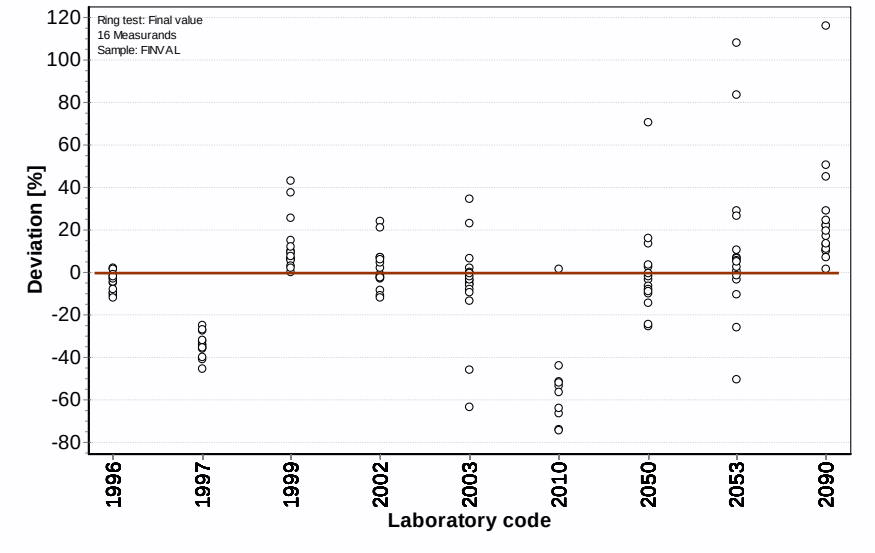


Figure 99: Relative deviations of the individual laboratories mean values from the assigned values for the concentrations of the analytes in sausage meat

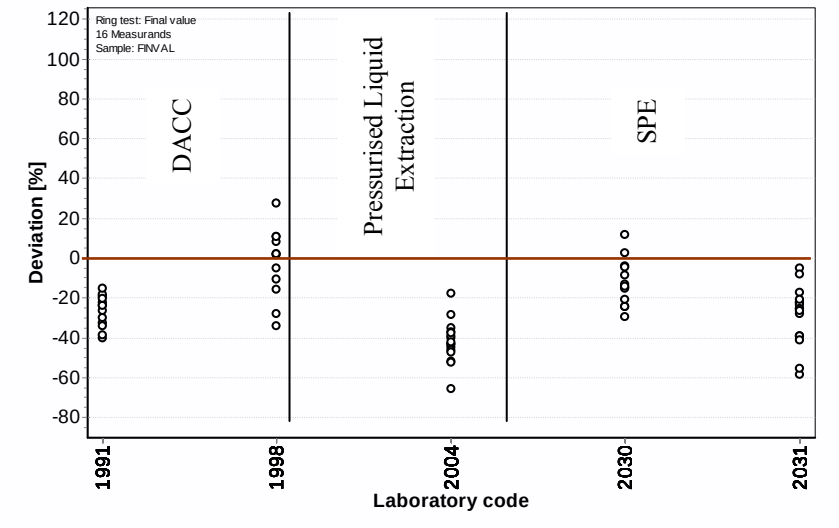
a) Gel Permeation Chromatography (GPC)



b) Saponification



c) Other methods: Donor Acceptor Complex Chromatography (DACC), Pressurised Liquid Extraction (PLE) and Solid Phase Extraction (SPE)



Conclusions

- All 25 participants reported results for the two materials sent.
- Still not all laboratories reported within the timeframe agreed upon in the preparatory workshop.
- Twenty participants, corresponding to 80%, formally fulfilled the requirements of Commission Regulation (EC) No 333/2007 on methods of sampling and analysis for the official control of the levels of benzo[*a*]pyrene in foodstuffs.
- The number of PAHs detected in acetonitrile remained at a high level, but could still be improved.
- Improvements of accuracy of determination of PAHs in acetonitrile were observed for some 14 laboratories, corresponding to more than 50%, when comparing with proficiency tests 2-3 years ago.
- The influence of instrument calibration on the results for the food sample was evaluated. The findings underpin the importance of accurate instrument calibration.
- In agreement with the results of the two previous ILCs organised by the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons, the most difficult analytes seem to be DhP, DiP, DeP, and CPP. The dibenzopyrenes were apparently giving more problems for the GC analysis, while for CPP the HPLC-based methods showed less favourable performance. A follow-up of these findings would be desirable.
- 373 of 400 possible individual results were reported for the sausage meat sample. 329 data (88 %) were within the satisfactory performance range, 253 (68 %) deviated not more than the single target standard deviation from the assigned value, resulting in absolute z-scores below or equal to one. The vast majority (26) of the 44 non-satisfactory results were reported by only four laboratories, of which 9 non-satisfactory results were attributed by one participant to a malfunctioning instrument.

Acknowledgements

The organisers would like to thank Mr Wolfgang Jira from the Max Rubner-Institute (Kulmbach, Germany), Mrs Luisa Ramos, Mr Ulf Jacobsson, and Mr Håkan Emteborg (all from IRMM, Geel, Belgium) for their support in the preparation of the test materials.

Participants

Table 37: List of participants

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
The Danish Plant Directorate	Denmark
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
Bundesamt für Verbraucherschutz und Lebensmittelsicherheit	Germany
General Chemical State Laboratory, Food Division Laboratory	Greece
Central Agricultural Office, Directorate Food and Feed Safety, Central Feed Investigation Laboratory	Hungary
Public Analyst Laboratory	Ireland
National Diagnostic Center	Latvia
National Veterinary Laboratory	Lithuania
Voedsel en Waren Autoriteit	The Netherlands
RIKILT - Instituut voor Voedselveiligheid	The Netherlands
National Institute of Hygiene	Poland
University of Novi Sad	Serbia
State Veterinary and Food Institute Dolný Kubín	Slovakia
Zavod Za Zdravstveno Varstvo Ljubljana	Slovenia
Centro Nacional de Alimentación - Agencia Española de Seguridad Alimentaría	Spain
National Food Administration, NFA	Sweden
Central Science Laboratory, CSL	United Kingdom

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Annex 1: Letter of Invitation for Registration

Dear Madame/Sir,

We would like to announce that the registration for the Inter-laboratory Comparison organised for NRLs is opened. It will regard the determination of analysis of 15+1 EU priority PAHs in sausage and solvent solution with the method in use by your laboratory.

Please find the link for registration on the IRMM home page: http://irmm.jrc.ec.europa.eu/html/homepage.htm.

It is also possible to follow the direct link to the registration page:https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=78

The registration is open until the 15th of June. In case you might need any further information or details, please do not hesitate to contact our team.

With best regards

Donata

Donata Lerda
Food Safety and Quality Unit
Institute for Reference Materials and Measurements
(EC – JRC – IRMM)
Postal address: Retieseweg 111, B-2440 Geel, Belgium

Phone: +32 14 571 826
Fax: +32 14 571 783
e-mail: donata.lerda@ec.europa.eu

Annex 2: Sample Receipt Form

SAMPLE 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 or items are damaged	Yes ☐ / No ☐
Serial number of the oil samples	and
Serial number of the standard solution with unknown concentrations	

Content of the parcel

a) Two 50 g aluminium tins with sausage meat samples

b) One 10 ml brown glass ampoule with a standard solution of the 15+1 EU priority PAHs in acetonitrile (concentrations unknown)

c) One 1 ml brown glass ampoule with a standard solution of the 15+1 EU priority PAHs in cyclohexane (concentrations known)

d) One material safety data sheet for acetonitrile

e) One material safety data sheet for cyclohexane

f) One outline of the study

g) One inter-laboratory comparison sample receipt form (= this form)

Please email the completed form to

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

or fax it to +32 (14) 571-783 at the attention of Rupert Simon

Annex 3: Outline of the Study

EUROPEAN COMMISSION

DIRECTORATE-GENERAL

JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

Community reference laboratory for Polycyclic Aromatic Hydrocarbons

Geel, 1. 7. 2008

3rd Inter-laboratory comparison study organised by the CRL-PAH:

Analysis of the 15+1 EU priority PAHs in sausage meat and acetonitrile

General

The current inter-laboratory comparison study focuses on the determination of the 15+1 EU priority PAHs in sausage meat and solvent solution.

The outline of the study was presented to the national reference laboratories (NRLs) at the 3rd workshop of the consortium of reference laboratories on PAHs (25-26 February 2008, Geel, Belgium). It was stressed that the target analytes are the 15+1 EU priority PAHs (listed in Table 1), and that the NRLs are requested to report results on as many analytes as possible, preferably on all.

Each participant will be provided with a set of samples that comprises two spiked sausage meat samples, an unknown solution of the target analytes in acetonitrile, and a known, concentrated standard solution for the preparation of calibration solutions for instrument calibration. Officially appointed NRLs shall participate in the study. Moreover, reference laboratories of EU Candidate Countries as well as EU Associated Countries will be supplied with samples on request.

This study is also regarded as a follow-up to the 2006 and 2007 inter-laboratory comparison studies on the determination of 15+1 PAHs in edible oil and solvent solution.

Outline of the study

The participants are requested to prepare their **standards for instrument calibration from the supplied concentrated standard solution**. Calibration shall be performed on each day of analysis of samples on 6 levels equally distributed over the working range.

The laboratories are requested to perform **triplicate analyses on each sausage meat sample**, and on the **unknown solution of PAHs in acetonitrile** applying a method of their choice. The two sausage meat samples (identical material) shall be analysed **on two different days (day A = sample 1 and day B = sample 2)**. Samples shall be analysed immediately after opening of the tins.

The laboratories are requested to report the results **by 12 September latest** via the WEB interface:

http://www.irmm.jrc.be/imepapp/jsp/loginResult.jsp

Test materials and analytes

1. Two tins, containing each about 50 g of a *spiked sausage meat sample:* The concentration of the individual analytes is in the range of about 1 to 10 µg/kg. The tins shall be analysed each on a different day in triplicate.
2. One ampoule containing about 4 ml of a solution of the *15+1 EU priority PAHs in acetonitrile:* The concentration of the individual analytes is in the range of 20 ng/ml to 120 ng/ml. The analyte concentration shall be determined in triplicate.
3. One ampoule with 1 ml of a solution of *15+1 EU priority PAHs in cyclohexane*. Specified concentration: 10.00 mg/l for each analyte with an expanded relative uncertainty of U_{rel} = 1.0 % (see certificate which is attached to the ampoule). The solution shall be used for the preparation of standards for instrument calibration!

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)

The results from the PT of last year showed that the collection of data on analytes which could not be separated as sum did not give additional information. Because of this, data on co-eluting substances will not be requested anymore.

Annex 4: Questionnaire

ilc questionnaire

Comparison for PAH-PT SAU-01

Please report the method performance parameter as indicated below. The dimensions for LOD, LOQ, and analytical range shall be ug/kg. The method recovery and relative uncertainty shal be reported as ratio (%). Please also indicate the key elements of the method used. Thank you for your cooperation. The CRL Team.

Submission Form

1. **Please indicate the LOD for 5MC of the method used:**
2. **Please indicate the LOQ for 5MC of the method used:**
3. **Please indicate the LOD for BaA of the method used:**
4. **Please indicate the LOQ for BaA of the method used:**
5. **Please indicate the LOD for BaP of the method used:** *
6. **Please indicate the LOQ for BaP of the method used:** *
7. **Please indicate the LOD for BbF of the method used:**
8. **Please indicate the LOQ for BbF of the method used:**
9. **Please indicate the LOD for BjF of the method used:**
10. **Please indicate the LOQ for BjF of the method used:**
11. **Please indicate the LOD for BkF of the method used:**
12. **Please indicate the LOQ for BkF of the method used:**

13. **Please indicate the LOD for BgP of the method used:**

14. **Please indicate the LOQ for BgP of the method used:**

15. **Please indicate the LOD for CHR of the method used:**

16. **Please indicate the LOQ for CHR of the method used:**

17. **Please indicate the LOD for CPP of the method used:**

18. **Please indicate the LOQ for CPP of the method used:**

19. **Please indicate the LOD for DhA of the method used:**

20. **Please indicate the LOQ for DhA of the method used:**

21. **Please indicate the LOD for DeP of the method used:**

22. **Please indicate the LOQ for DeP of the method used:**

23. **Please indicate the LOD for DhP of the method used:**

24. **Please indicate the LOQ for DhP of the method used:**

25. **Please indicate the LOD for DiP of the method used:**

26. **Please indicate the LOQ for DiP of the method used:**

27. **Please indicate the LOD for DlP of the method used:**

28. **Please indicate the LOQ for DlP of the method used:**

29. **Please indicate the LOD for IcP of the method used:**

30. **Please indicate the LOQ for IcP of the method used:**

31. **Please indicate the LOD for BcL of the method used:**

32. **Please indicate the LOQ for BcL of the method used:**

33. **Please indicate the recovery of the method used [in %]**

33.1. 5MC

33.2. BaA

33.3. BaP *

33.4. BbF

33.5. BjF

33.6. BkF

33.7. BgP

33.8. CHR

33.9. CPP

33.10. DhA

33.11. DeP

33.12. DiP

33.13. DhP

33.14. DlP

33.15. IcP

33.16. BcL

34. **Please indicate the linear working rage of your method in ug/kg**

34.1. 5MC - low

34.2. 5MC - high

34.3. BaA - low

34.4. BaA - high

34.5. BaP - low *

34.6. BaP - high *

34.7. BbF - low

34.8. BbF - high

34.9. BjF - low

34.10. BjF - high

34.11. BkF - low

34.12. BkF - high

34.13. BgP - low

34.14. BgP - high

34.15. CHR - low

34.16. CHR - high

34.17. CPP - low

34.18. CPP - high

34.19. DhA - low

34.20. DhA - high

34.21. DeP - low

34.22. DeP - high

34.23. DhP - low

34.24. DhP - high

34.25. DiP - low

34.26. DiP - high

34.27. DlP - low

34.28. DlP - high

34.29. IcP - low

34.30. IcP - high

34.31. BcL - low

34.32. BcL - high

35. **Please indicate the relative uncertainty of your method (95% confidence interval)**

35.1. for 5MC [%]

35.2. for BaA [%]

35.3. for BaP [%]

35.4. for BbF [%]

35.5. for BjF [%]

35.6. for BkF [%]

35.7. for BgP [%]

35.8. for CHR [%]

35.9. for CPP [%]

35.10. for DhA [%]

35.11. for DeP [%]

35.12. for DhP [%]

35.13. for DiP [%]

35.14. for DlP [%]

35.15. for IcP [%]

35.16. for BcL [%]

36. **The analytical method for the sample extract is:**

- ○ gc-ms
- ○ gc-ms/ms
- ○ hplc-fld
- ○ hplc-ms/ms
- ○ hplc-uv/fld
- ○ other, please specify

36.1. The method of analysis was based on:

36.2. The analytical method for the prepared sample extract is (please indicate the number):

37. **The major element of your sample preparation is:**

- ☐ 1 saponification
- ☐ 2 pressurised solvent extraction
- ☐ 3 solid phase extraction
- ☐ 4 gel permeation chromatography
- ☐ 5 Soxhlet extraction
- ☐ 6 liquid extraction
- ☐ other, please specify below

37.1. The main element of the sample preparation was:

38. **Comments**

version: 2.02

top

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EUR 23781 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: Report on the third inter-laboratory comparison test organised by the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons - 15 + 1 EU priority PAHs in sausage meat and acetonitrile

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Abstract

This report presents the results of the 3rd inter-laboratory comparison (ILC) of the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons (PAHs) on the determination of the 15+1 EU priority PAHs in sausage meat and acetonitrile, which was conducted along the lines of the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories.

In agreement with the National Reference Laboratories, the test materials used in this exercise were a canned sausage meat preparation spiked with the 15+1 EU priority PAHs and a solution of the analytes in acetonitrile, respectively. The materials were prepared gravimetrically.

The assigned concentration values of PAHs in sausage meat and in acetonitrile were calculated from the gravimetric preparation data.

Only officially nominated National Reference Laboratories of the EU Member States and from countries covered by the Technical Assistance and Information Exchange programme of the European Commission were admitted as participants. However, from latter countries only one laboratory reported results. The participants were free to choose the method for the analysis of the materials.

z-Scores were calculated for the sausage meat material from the analytes' contents based on gravimetrical preparation values and the participants reported “final result”. The reported values of the laboratories for PAHs in acetonitrile were not rated.

For the sausage meat material 89 % of the reported values lay within the 95 % confidence interval of the target standard deviation (z-scores $\leq |2|$), indicating that most of the participating laboratories were performing satisfactorily with respect to internationally accepted standards. However, in some cases bias and/or a high variability were discovered, and some analytes consistently caused specific problems. It is therefore recommended to investigate this further.

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