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Report on the 4th inter-laboratory comparison test organised by the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons

15 + 1 EU priority PAHs in fish and acetonitrile

Donata Lerda, Laszlo Hollosi, Patricia Lopez, Szilard Szilagyi, and Thomas Wenzl

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CRL Polycyclic Aromatic Hydrocarbons

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Summary

This report presents the results of the 4th inter-laboratory comparison (ILC) organised by the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons (CRL PAH) on the determination of the 15+1 EU priority PAHs in fish and acetonitrile. It was conducted in accordance with the IUPAC International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories.
In agreement with the National Reference Laboratories, the three test materials used in this exercise were smoked salmon meat spiked with 15 + 1 EU priority PAHs, a raw salmon meat spiked with an extract of contaminated smoke flavourings and a solution in acetonitrile respectively. The materials were prepared gravimetrically and the analyte contents verified by isotope dilution gas chromatography mass spectrometry.
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 the latter 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 by z-scores, which were calculated from the results reported for the fish samples. The reported values of the laboratories for PAHs in acetonitrile were not rated.

A summary of the performance of the participants for the two fish test material is given in the following table.

Participants	**Reporting laboratories**	**Total number of calculated z-scores**		**z-scores ≤ |2|**		**z-scores ≤ |2|**	
number	**number**	**number**		**number**		**%**	
		Fish C	Fish D	Fish C	Fish D	Fish C	Fish D
27	25	379	88	356	78	94	89

For the test material Fish C (smoked salmon spiked with the 15+1 EU priority PAHs) 379 out of 400 possible individual results were received, of which 94 % were rated as satisfactorily with regard to performance. The respective figures for the Fish D test material (fresh salmon spiked with an extract of contaminated smoke flavouring) are 88 results of 100 possible, and 89 % satisfactory performance.

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) [i, ii].

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic substances. The chemical structure of PAHs consists of two or more fused aromatic rings. PAHs may be formed during the incomplete combustion of organic compounds and can be found 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" [iii]. 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), dibenzo[*a,h*]anthracene, and dibenzo[*a,l*]pyrene as probably carcinogenic to human beings (group 2a), and nine other EU priority PAHs as possibly carcinogenic to human beings [iv].

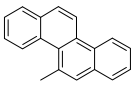
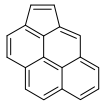
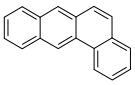
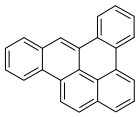
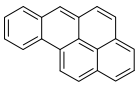
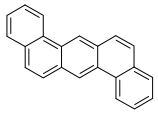
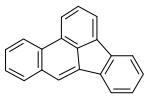
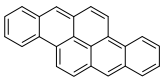
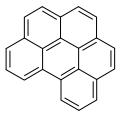
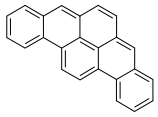
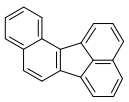
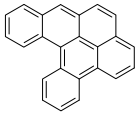
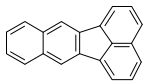
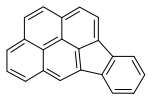
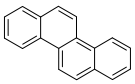
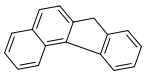
As a consequence, the European Commission (EC) issued Commission Regulation (EC) No 1881/2006 setting maximum levels of benzo[a]pyrene in food, Commission Regulation (EC) No 333/2007 laying down sampling methods and the performance criteria and fitness-for-purpose approach for the methods of analysis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

In order to distinguish this set of PAHs from a set of PAHs that has 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 [ix]. The results indicated that the use of BaP as marker was questionable [x].

A scientific opinion on polycyclic aromatic hydrocarbons in food was published recently by EFSAs Panel on Contaminants in the Food Chain [xi]. 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 official food control should focus in future on the set of four PAHs (benzo[*a*]pyrene, chrysene, benzo[*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	Benzo[*a*]anthracene (BaA)		10	Dibenzo[*a,e*]pyrene (DeP)	
3	Benzo[*a*]pyrene (BaP)		11	Dibenzo[*a,h*]anthracene (DhA)	
4	Benzo[*b*]fluoranthene (BbF)		12	Dibenzo[*a,h*]pyrene (DhP)	
5	Benzo[*ghī*]perylene (BgP)		13	Dibenzo[*a,ī*]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 specified in 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 [ii], one of the core duties of CRLs is organising inter-laboratory comparison tests (ILCs).

This inter-laboratory comparison study aimed to evaluate the comparability of analysis results reported by National Reference Laboratories for the 15+1 EU priority PAHs in smoked fish, 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 [xii].

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 (TAIEX) programme of the European Commission were admitted as participants.

Table 2: List of participants to the ILC round

Institute	*Country*
Österreichische Agentur für Gesundheit und Ernährungssicherheit, Kompetenzzentrum Cluster Chemie	Austria
Scientific Institute of Public Health	Belgium
SGL - State General Laboratory, Environmental and other Food Contaminantion Laboratory	Cyprus
Nàrodní referenční laboratoř pro polycyklické aromatické uhlovodíky - Státní veterinární ústav Praha	Czech Republic
Danish Institute for Food and Veterinary Research, Department of Food Chemistry	Denmark
Danish Plant Directorate, Laboratory for Feed and Fertilizers	Denmark
Tartu Laboratory of Health Protection Inspectorate	Estonia
Finnish Food Safety Authority Evira	Finland
LABERCA, LABoratoire d'Etude des Résidus et des Contaminants dans les Aliments	France
BVL (Bundesamt für Verbraucherschutz und Lebensmittelsicherheit)	Germany
General Chemical State Laboratory (GCSL) Food Division - Laboratory	Greece
Central Agricultural Office, Food & Feed Safety Directorate, Food Residues Toxicological Dept.	Hungary
Central Agricultural Office, Food and Feed Safety Directorate, Feed Investigation NRL	Hungary
Public Analyst Laboratory	Ireland
"Centro nazionale per la qualità e per i rischi alimentari (CNQRA)	Italy
Istituto Superiore di Sanità (ISS)"	Latvia
National Diagnostic Centre, Laboratory of Food and Environmental Investigations (LFEI)	Lithuania
Laboratory of the Food and Consumer Product Safety Authority	The Netherlands
RIKILT- Institute of Food Safety	The Netherlands
Laboratory of Department of Food and Consumer Articles Research -National Institute of Hygiene	Poland
INETI	Portugal
State Veterinary and Food Institute Dolný Kubín (SVPUDK)	Slovak Republic
Institute of Public Health Maribor, Institute of Environmental Protection	Slovenia
Centro Nacional de Alimentación.	Spain
Agencia Española de Seguridad Alimentaria y Nutrición (AESAN)	Sweden
Livsmedelsverket (SLV)	United Kingdom
Faculty of Technology, University of Novi Sad*	Serbia

* covered by TAIEX

Two NRLs did not report results. Justification for non-participation was requested from them by the CRL PAH and will be, as requested, reported to DG SANCO.

Time frame

The ILC was agreed with the NRLs at the CRL-PAH workshop in Geel on 24 and 25 March 2009. The planned ILC was published on the IRMM web page and invitation letters were sent to the laboratories on 07 May 2009. Test samples were dispatched 02 June 2009 and the deadline for reporting of results was 11 September 2009.
The documents sent to the participants are depicted in Annex 5.

Test materials

Preparation and verification

The test materials of this PT round were:

1. smoked salmon meat spiked with 15+1 EU priority PAHs, in the following denoted as Fish C. This matrix is mimicking the food category " muscle meat of smoked fish and smoked fishery products, excluding bivalve molluscs " in Commission Regulation (EC) No1881/2006, with a maximum level for BaP of 5,0 µg/kg
2. raw salmon meat spiked with an extract of contaminated smoke flavourings in the following denoted as Fish D. This test material is representing also the food category "muscle meat of smoked fish and smoked fishery products, excluding bivalve molluscs", with a maximum level for BaP of 5,0 µg/kg.
3. A solution of the 15+1 EU Priority PAHs in acetonitrile (in the following denoted as: ACN) with undisclosed concentration, which served for checking instrument calibration.

A common calibrant (in the following denoted as: CAL) containing the 15+1 EU priority PAHs in a toluene/cyclohexane mixture was supplied to the participants for instrument calibration.

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). Single 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 spiked edible oil was used to prepare the test material Fish C, which consisted of smoked salmon. Test material Fish D consisted of raw salmon meat. It was spiked with the extract into olive oil of a highly contaminated liquid smoke flavouring sample to a benzo[*a*]pyrene content of about 1 µg/kg. The liquid smoke flavouring sample was a waste product of industry and not intended to be used for food production.
The olive oil extract was applied for the test material preparation analogous to the preparation of test material Fish C. In contrast to Fish C this test material was preserved after canning into aluminium jars. Both materials were prepared at the Max Rubner Institut (Kulmbach, Germany).

The analyte content of the test material Fish C was calculated from gravimetrical preparation data and verified by isotope dilution GC-MS applying bracketing calibration against, where applicable, the certified reference material (CRM) SRM 2260a (National Institute of Standards and Technology, Gaithersburg, MD, USA). The differences between the gravimetric preparation data and the analysis

results were smaller than the associated measurement uncertainties. Hence the gravimetric preparation data were applied as assigned values.
For test material Fish D gravimetric preparation data were not available. The assigned values were derived from the homogeneity test experiments and verified by isotope dilution GC-MS applying bracketing calibration.

About 500 cans of each of the two fish materials were produced and were stored at a temperature below 10 ºC respectively 0°C (Fish C) until dispatch. The amount of material in each can was about 50 g.

The calibrant and the PAH solution in acetonitrile were prepared from the same single PAH stock solutions. The concentrations of the standard preparations were verified where applicable against SRM 2260a. Isotope dilution gas chromatography mass spectrometry and bracketing calibration was used for that purpose. Statistical significant differences of the analyte concentration were not found for any of the 15+1 EU priority PAHs which are contained in the CRM. The uncertainties of the standard preparations were determined from the individual uncertainty contributions of the purity of the applied CRMs and all handling steps applying the law of error propagation.

About 200 ampoules of a volume of 5 mL containing each 4 mL of acetonitrile test material were filled under inert atmosphere and flame sealed. The ampoules were stored at a temperature below 10 ºC until dispatch.

Table 3: Analyte contents of the test materials for this PT round

	Fish C	Fish D	PAHs in acetonitrile		PAHs in calibrant	
Analyte	**content [µg/kg]**	**content µg/kg]**	**Conc. [µg/l]**	**RU* [%]**	**Conc. [mg/l]**	**RU* [%]**
5MC	4,8	<LOD	64,7	0,4	9,9	1
BaA	4,8	1,9	46,1	0,4	10,0	1
BaP	5,6	0,94	50,2	0,3	10,1	1
BbF	5,6	0,70	89,8	0,3	9,9	1
BcL	4,7	*4,1***	72,7	0,4	7,8	1
BgP	5,5	0,39	42,8	0,3	8,9	1
BjF	4,8	0,49	54,4	0,2	10,0	1
BkF	4,9	0,36	65,8	0,5	9,1	1
CHR	5,2	2,4	118,1	0,3	10,0	1
CPP	5,2	0,33	106,1	0,4	9,6	1
DeP	5,2	<LOQ	102,9	0,3	9,1	1
DhA	5,4	<LOQ	75,0	0,5	9,5	1
DhP	4,6	<LOD	159,9	0,3	10,1	1
DiP	5,1	<LOD	15,5	0,9	5,4	1
DlP	5,2	<LOD	72,0	0,4	10,1	1
IcP	4,1	0,33	41,2	0,4	10,0	1

*RU: relative expanded measurement uncertainty (k=2)
** only indicative

Each participant received at least one ampoule of the PAHs solution in cyclohexane/toluene, one ampoule of the PAHs solution in acetonitrile with unknown concentration (ACN) and two cans of each of the two fish materials (Fish C and Fish D).

Homogeneity and stability

Homogeneity of the fish test samples was tested according to ISO standard 13528. Both fish test materials were rated sufficiently homogeneous. Details of the homogeneity tests are given for selected analytes in Annex 1.

Stability of the test materials was assessed under both recommended and suboptimal storage conditions applying an isochronous experimental design. Samples stored at recommended conditions were kept for the whole period between sample dispatch and deadline for reporting of results at below 10°C, while suboptimal conditions included at the begin of the stability study a two weeks period of storage at room temperature, which aimed to mimic breakage of the cooling chain during transport, respectively improper storage of samples. Both sample types were analysed after the end of the reporting period under repeatability condition by isotope dilution GC-MS. Significant differences of the analyte contents of the two sample types were not found. The results agreed also with results gained before dispatch of the sample. Thus stability of the samples over the whole study period can be assumed.

Design of the PT

The design of the PT foresaw replicate analyses of the test samples (three for ACN and Fish D, five for Fish C) and reporting of both the individual results of the replicate analyses and a "final result". The final result had to be reported together with the accompanying expanded measurement uncertainty (with a coverage factor of 2). This final result was used for performance assessment.
Participants were asked to report besides analysis results also details of the applied analysis method.

Evaluation of the results

General

The most important evaluation parameter was the performance of the laboratories in the determination of the target PAHs in the fish materials, which was expressed by z-scores. Besides this other aspects were studied based on the reported data too.

The influence of the source of reference material on the comparability of analysis results was eliminated by the application of a common calibrant (CAL) for instrument calibration. The correctness of instrument calibration was checked by including a standard solution in acetonitrile with undisclosed content in the sample set. This solution was traceable to the standard preparation from which the calibrant was prepared. Furthermore the influence of instrument calibration on the results for the fish samples was evaluated.

The agreement of performance indicators for the two fish test samples was evaluated as well.

Finally the compliance of method performance characteristics for the determination of BaP was evaluated for compliance with legislation.

An overview of the number of analytes reported by participants for this PT round and a comparison with previous rounds is given in Figure 1 and Figure 2. The percentage of participants reporting results for a certain number of analytes is plotted on the abscissa.

Figure 1: number of PAHs reported by the participants

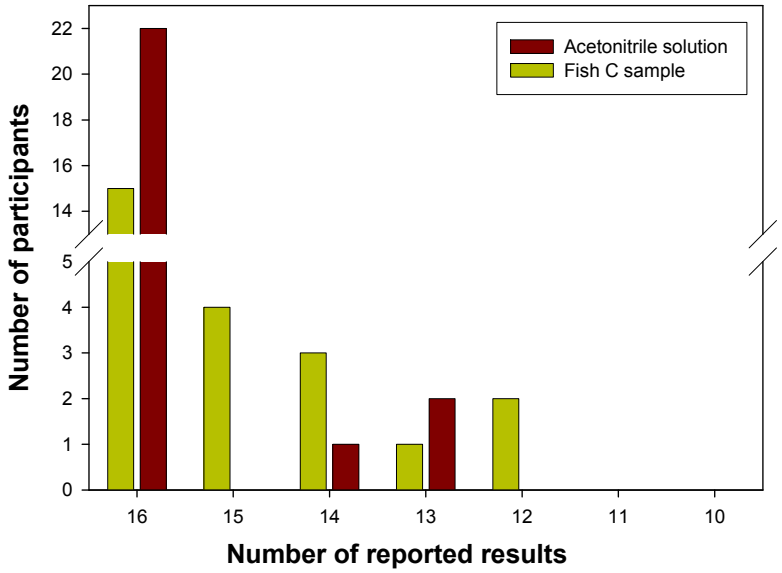
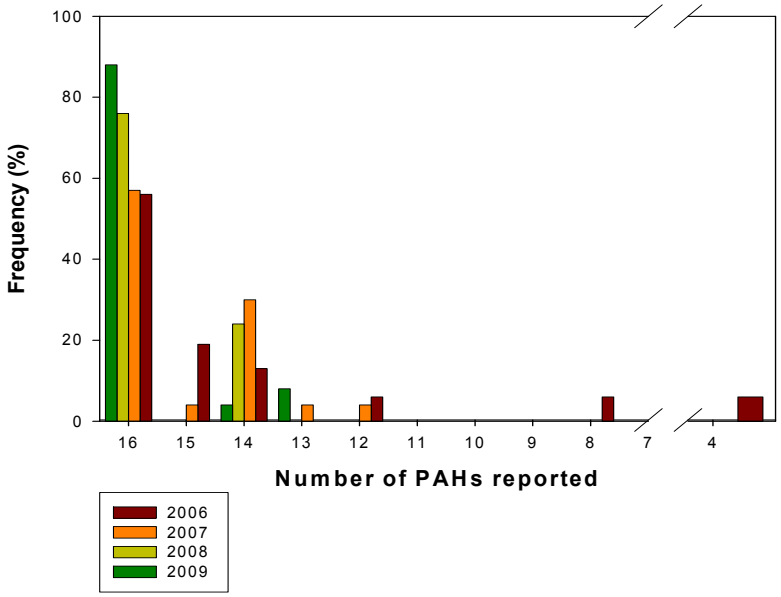


Figure 2: survey of reported results for the acetonitrile solution in the last 4 PT rounds



Evaluation criteria

In the 2008 workshop it was already agreed to omit the attribution of scores for the results 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. Hence the results for the acetonitrile standard solution were evaluated for their percentage deviation from the known concentration of the individual analyte only.
For the fish materials z-scores were calculated for the "final values" according to the formula

Equation 1 $$z = (x - X) / \sigma_P$$

where z refers to the z-score, x to the reported "final value", X to the assigned value, and σ_P to the standard deviation for proficiency testing.

For benzo[*a*]pyrene, the standard deviation for proficiency testing σ_P was set equal to the maximum tolerated standard measurement uncertainty U_f as defined by Commission Regulation (EC) No 333/2007 [xiii]:

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

where U_f relates to the maximum tolerated 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 for benzo[*a*]pyrene of 5.6 µg/kg and the maximum tolerated value of LOD of 0.3 µg/kg results in a value for U_f of 2,3 µg/kg for the test material Fish C. The value of *Uf* calculated for Fish D was 0,48 µg/kg.
For all other analytes the relative standard deviation for proficiency testing was set to 22 % of the assigned value, as suggested by Thompson, and agreed upon in the preparatory workshop [xiv].

The performance of the laboratories was classified according to ISO Guide 43-1 [xv] and the Harmonised Protocol [xvi]

$|z| \leq 2$ = satisfactory
$2 < |z| \leq 3$ = questionable
$|z| > 3$ = unsatisfactory

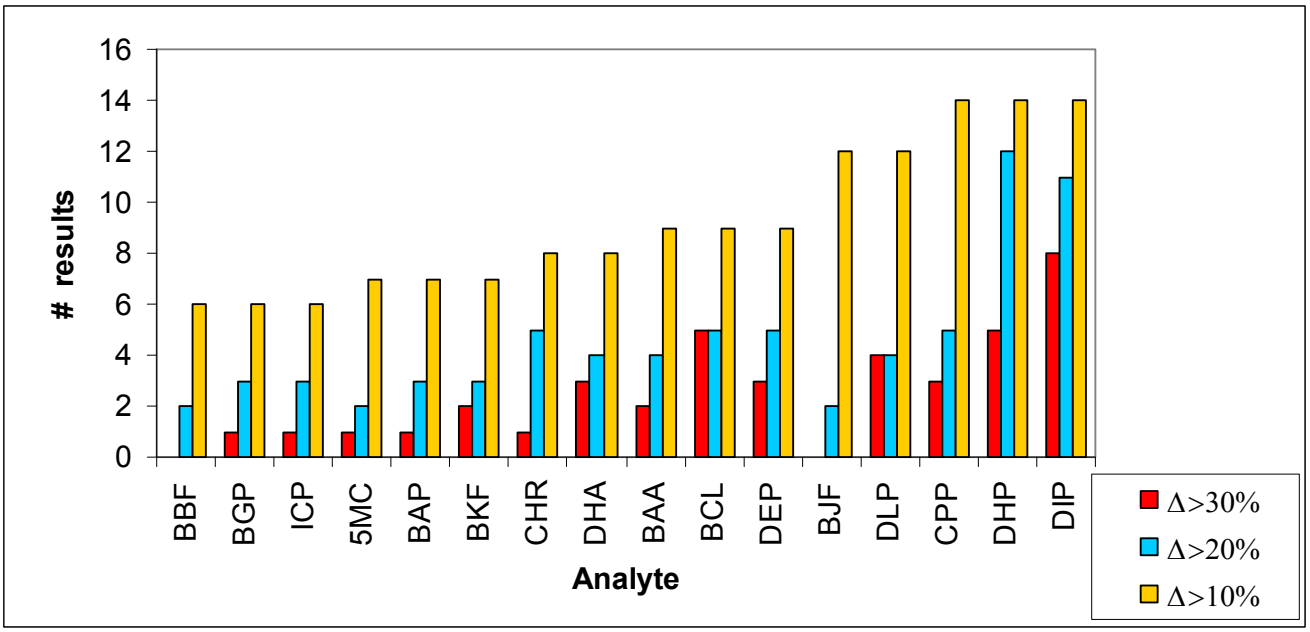
Evaluation of results for the standard solution in acetonitrile

The concentration of the standard solution in acetonitrile was not disclosed to the participants. It served for checking the correctness of instrument calibration, since this part of the analytical process has major influence on the trueness of the results. The data reported by the participants were evaluated with regard to the performance of both the individual participant and to the whole network of NRLs. Also performance over time was investigated.

For some analytes the median of the results of all laboratories results was lower than the assigned value calculated from gravimetric data. However the deviation was for most analytes marginal and was in general within the uncertainty of the estimates.
In addition a systematic error in the preparation of the acetonitrile solution, e.g. dilution error, can be excluded since the gravimetric preparation concentration of the acetonitrile solution was verified for eight analytes against SRM 2260a (NIST).

Some analytes caused difficulties to the whole group of participants. This concerns especially six analytes, the four dibenzopyrenes, benzo[*j*]fluoranthene and cyclopenta[*cd*]pyrene, for which the average of the reported results for at least halve of the participants deviated more than 10 % from the assigned value. This can be reasoned by the physicochemical properties of these substances that hamper either gas chromatographic analysis (dibenzopyrenes) or analysis by high performance liquid chromatography with fluorescence detection (cyclopenta[*cd*]pyrene). Benzo[*j*]fluoranthene provides problems with both chromatographic techniques, because it is difficult to separate from the other two benzofluoranthenes by GC and shows weak fluorescence impeding HPLC-FLD analyses. Figure 3 shows for each analyte the number of average results deviating within certain ranges from the assigned value. The minimum number of laboratories reporting results outside the range of ±10% of the assigned value was six, which is equal to almost one quarter of the whole population.

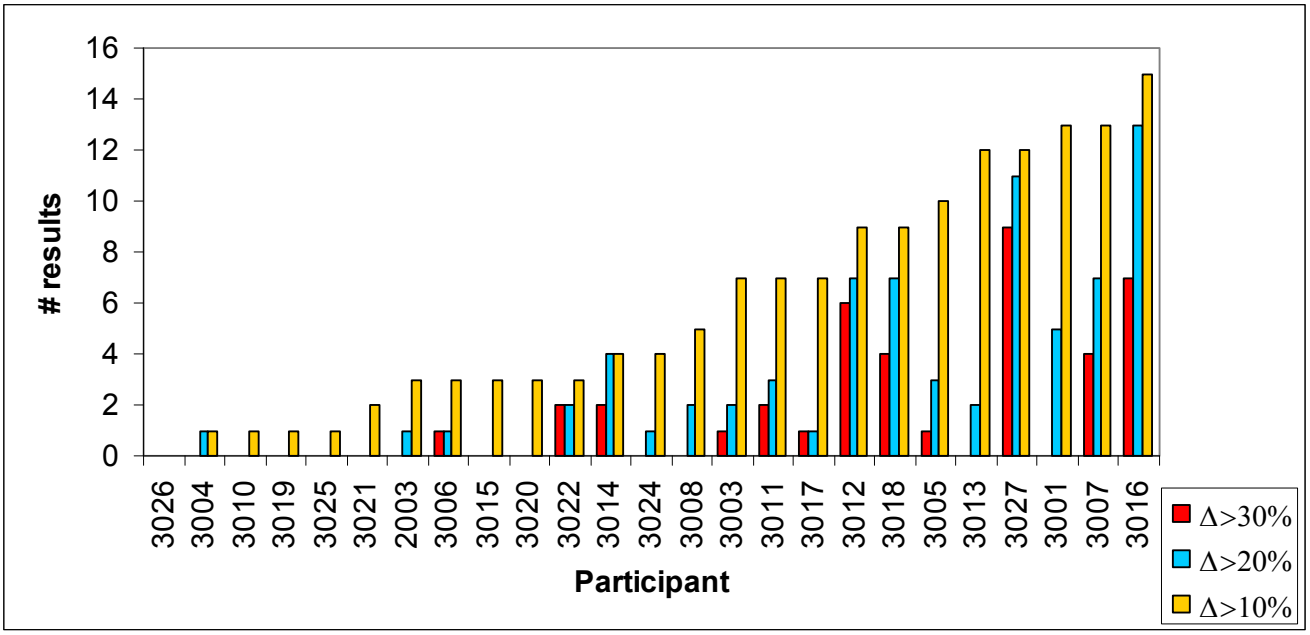
Figure 3: Cumulative frequency of averages of reported results deviating from the assigned value for the particular analyte by more than 30%, more than 20%, or more than 10% of the assigned values respectively



This evaluation suggests that methods for analysis of PAHs need improvement. However when looking to the performance of the individual participant, it becomes clear that the experienced deviations from the assigned values are rather systematic than random. Hence it may be concluded that biased standard preparation or mistakes during handling of the unknown standard solution in

acetonitrile (e.g. biased dilution) caused the deviations and not problems with the analysis methods. For example participant 3016 reported for all but one analyte results with negative relative bias exceeding the level of 10 %. The results of some other participants show similar trends. This is displayed in Figure 4, which presents the number of mean values of the results reported by a particular participant deviating from the assigned value by more than certain thresholds.

Figure 4: Cumulative sum of averages of reported results of a particular participant deviating from the assigned value by at least 30%, 20 %, or more than 10% of the assigned value.



Details on the performance of the participants for the individual analyte are given in Table 4 and Table 5. Cells containing a hyphen indicate deviations from the assigned value of maximum ± 10 %. The pattern in Tables 4 and Table 5 demonstrates clearly that the majority of large deviations from the assigned values was linked to the results of six to seven participants, and to the results for the most difficult analytes (the four dibenzopyrenes, CPP and BjF).

Table 4: Percent deviations of the average of reported results for the PAH solution in acetonitrile exceeding certain thresholds for the 4 target PAHs. Hyphens indicate results that deviated less than ±10 % from the assigned value. Results were not reported in case of empty cells.

Participant	BaA	BaP	BbF	CHR
	%	%	%	%
3026	–	–	–	–
3004	–	–	–	–
3010	–	–	–	–
3019	–	–	–	–
3025	–	–	–	–
3021	–	–	–	–
2003	–	–	–	–
3006	–	–	–	–
3015	–	–	–	–
3020	–	–	–	–
3022	–	–	–	–
3014	–	–	–	Δ>20%
3024	–	–	–	–
3008	–	–	Δ>10%	–
3003	Δ>10%	–	Δ>20%	–
3011	–	–	–	–
3017	Δ>30%	–	–	Δ>10%
3012	–	Δ>10%	–	–
3018	Δ>20%	–	–	Δ>20%
3005	Δ>10%	Δ>10%	–	Δ>10%
3013	Δ>10%	Δ>10%	Δ>10%	Δ>10%
3027	Δ>30%	Δ>30%		Δ>30%
3001	Δ>10%	Δ>10%	Δ>10%	Δ>20%
3007	Δ>10%	Δ>20%	Δ>10%	–
3016	Δ>20%	Δ>20%	Δ>20%	Δ>20%

Table 5: Percent deviations of the average of reported results for the PAH solution in acetonitrile exceeding certain thresholds for the other 12 PAHs. Hyphens indicate results that deviated less than ±10 % from the assigned value. Results were not reported in case of empty cells.

Participant	5MC	BcL	BgP	BjF	BkF	CPP	DeP	DhA	DhP	DiP	DlP	IcP
	%	%	%	%	%	%	%	%	%	%	%	%
3026	–	–	–	–	–	–	–	–	–	–	–	–
3004	–	–	–	–	–	–	–	–	–	Δ>20%	–	–
3010	–	–	–	–	–	Δ>10%	–	–	–	–	–	–
3019	–	–	–	–	–	Δ>10%	–	–	–	–	–	–
3025	–	–	–	Δ>10%	–	–	–	–	–	–	–	–
3021	–	–	–	–	–	Δ>10%	–	Δ>10%	–	–	–	–
2003	–	Δ>10%	–	–	–	–	–	–	Δ>20%	Δ>10%	–	–
3006	–	–		Δ>10%	–	–	–			Δ>30%	–	Δ>10%
3015	–	–	–	Δ>10%	–	Δ>10%	Δ>10%	–	–	–	–	–
3020	–	–	–	–	–	–	Δ>10%	–	Δ>10%	–	–	Δ>10%
3022	–	Δ>30%	–	–	–	–	–	–	–	Δ>30%	Δ>10%	–
3014	–	Δ>30%	–		–		–	–	Δ>20%	Δ>30%	–	
3024	–	–	–	Δ>10%	–	Δ>10%	–	–	Δ>20%	Δ>10%	–	–
3008	–	–	–	Δ>10%	Δ>20%	–	–	–	Δ>20%	–	Δ>10%	–
3003	Δ>10%	–	–	Δ>10%	–	–	–	Δ>10%	–	Δ>30%	Δ>10%	–
3011	Δ>10%	Δ>30%	–	–	–	Δ>10%	Δ>20%	–	Δ>30%	Δ>10%	Δ>10%	–
3017	–	–	–	Δ>10%	Δ>10%	Δ>10%	–	–	Δ>10%	–	Δ>10%	–
3012	–	Δ>30%	Δ>10%	Δ>20%	–	Δ>30%	Δ>30%	–	Δ>30%	Δ>30%	Δ>30%	–
3018	–	Δ>30%	Δ>20%	–	–	–	Δ>10%	Δ>30%	Δ>30%	Δ>30%	Δ>10%	–
3005	Δ>10%	–	Δ>10%	–	Δ>10%	Δ>30%	–	Δ>10%	Δ>20%	–	–	Δ>20%
3013	Δ>10%	–	–	Δ>10%	–	Δ>10%	Δ>10%	–	Δ>20%	Δ>20%	Δ>10%	Δ>10%
3027	Δ>30%	Δ>10%	Δ>30%		Δ>30%	Δ>20%	–	Δ>30%	–	Δ>20%	Δ>30%	Δ>30%
3001	Δ>10%	Δ>10%	–	Δ>20%	Δ>10%	Δ>20%	Δ>20%	Δ>10%	Δ>20%	–	Δ>10%	–
3007	–	Δ>10%	Δ>20%	Δ>10%	Δ>10%	Δ>10%	Δ>30%	Δ>10%	Δ>30%	Δ>30%	Δ>30%	–
3016	Δ>20%	–	Δ>10%	Δ>10%	Δ>30%	Δ>30%	Δ>30%	Δ>30%	Δ>30%	Δ>30%	Δ>30%	Δ>20%

Details of the evaluation of the results analyte by analyte are given in the Annex 2.
There the first figure shows for the individual analyte the results reported by the participants for the three replicate measurements. In addition, the assigned (reference) value is depicted as red solid line and the mean of the results of the participants, equal to the median, as blue solid line. The black dotted lines represent a deviation of ± 10 %, 20 %, and 30 % respectively from the assigned value.
The blue box indicates the standard deviation of the three measurements with the blue horizontal line indicating the mean of the three results.

The Kernel density plots show the distribution of the data: the mean and the assigned value are depicted as a green and a blue line respectively.

The figures are complemented by tables, containing all results reported by the participants.

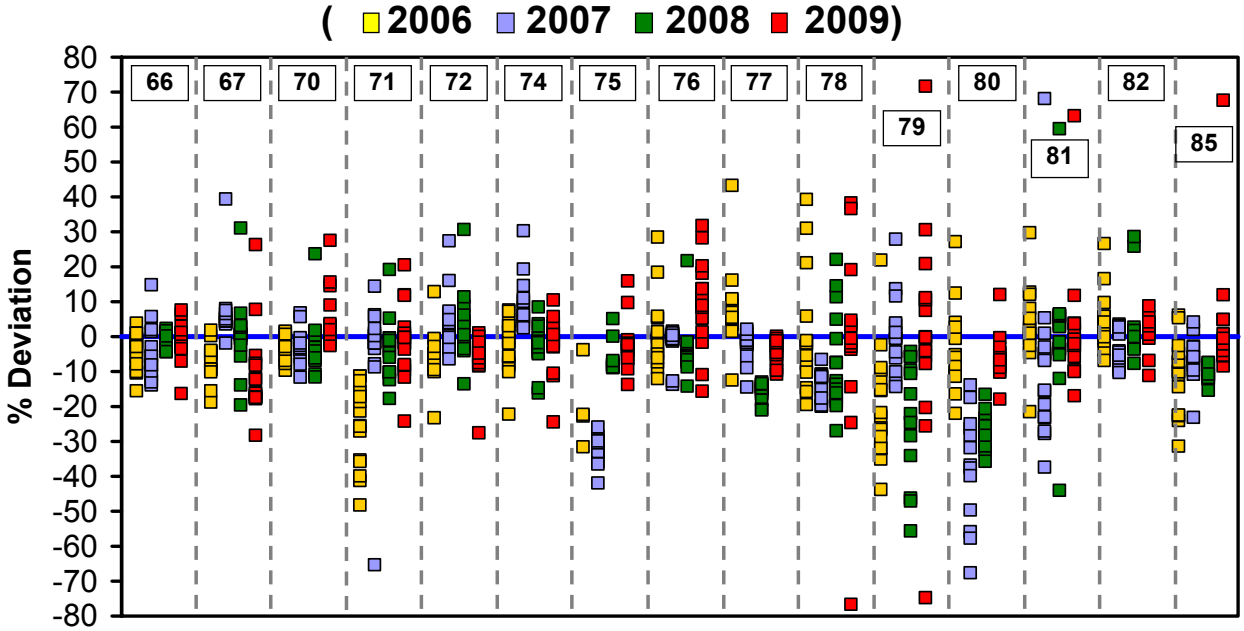
The Kernel density plots indicated that the reported data were normally distributed for most analytes. However for some analytes deviations from normal distribution and multimodality were found.
Multimodality was evident especially for BcL, DhP and DeP. This seemed to be caused by the analysis technique.

For DhP the median of the results obtained with GC is 121,2 µg/l against 155,9 µg/l obtained with HPLC methods. The mean of all results (130,6 µg/l) is much lower than the assigned value of 159,9

µg/l due to the influence of strongly biased results reported by a few laboratories, 3011, 3007, 3012, 3016, and 3018, which applied GC based methods. Finally, in the case of DiP the robust mean (median) of the results obtained with GC is 15,3 µg/l against 15,9 µg/l obtained with HPLC methods. Four laboratories reported highly biased results: two using GC-MS methods (3012 and 3018), and two using HPLC-FLD methods (3006 and 3022). The mean of all results (19,8 µg/l) is higher than the assigned value (15,5 µg/l, obtained applying GC-MS) due to the impact of results reported by those four laboratories.

The analysis of an unknown solution of PAHs in acetonitrile was already requested from the NRLs in the previous three PT rounds. Since the composition of the participants stayed to a great extend unchanged in the different PT rounds, the question about performance over time came into mind. Figure 5 presents the percent deviation of the results for the undisclosed PAH standard solutions in acetonitrile for 15 laboratories participating to all four PT rounds organised so far.
The blue line in Figure 5 indicates no deviation at all. However the scaling of the Figure was chosen to best visualise the dispersion of results. Consequently some outliers were cut off. However this data does not influence the outcome of the study.
Most laboratories improved their performance over the years. This can be partially attributed to the application of a common calibrant (since 2007), containing the whole set of analytes, which for many participants significantly reduced the number of production steps in standard preparation. Consequently the number of possible sources of bias and the total uncertainties of the concentrations of the analytes in the calibration standards is reduced.
However the constantly high variability of the analysis results of the participants 78 and 79 is independent of the kind of applied calibrant. This variability seems to be caused by the applied analysis method. Hence those two laboratories are advised to investigate into the source of the inconsistent and for some analytes high mismatch between the reported results and the assigned values.

Figure 5: Comparison of % deviations of the results reported in the 4 ILCs organised by CRL PAH so far for the 16 target analytes in ACN solutions from the assigned values



Evaluation of results for the fish test samples

The participants were requested to report for all analytes the results of replicate measurements and a "final result", which is the result they wish to be applied in the proficiency assessment. z-Scores were attributed only to these final results. The individual results of replicate analyses were not rated but in case of test sample Fish C used to determine precision parameters.

Evaluation of test sample Fish C

The 25 participants in the study reported in total 379 results, which equals to about 95 % of the maximum 400 possible. About 82 % of the reported results were rated satisfactorily.
Figure 6 gives an overview of the performance indicators assigned to the respective results. The larger the triangles, the larger were the differences to the assigned values. Red triangles indicate z-scores outside the satisfactory range. About 55 % of the 31 non-satisfactory results were reported by three laboratories only, e.g. the performance of participant 3024 was not satisfactory for halve of the target analytes.

The numerical values of the calculated z-scores are compiled in Table 6. z-Scores with an absolute value of above 2 are given in bold font (for BaP in red bold font).

Figure 6: Overview of performance of participants in the analysis of target analytes. The larger the triangle the greater was the deviation from the assigned value. Red triangles indicate non-satisfactory performance.

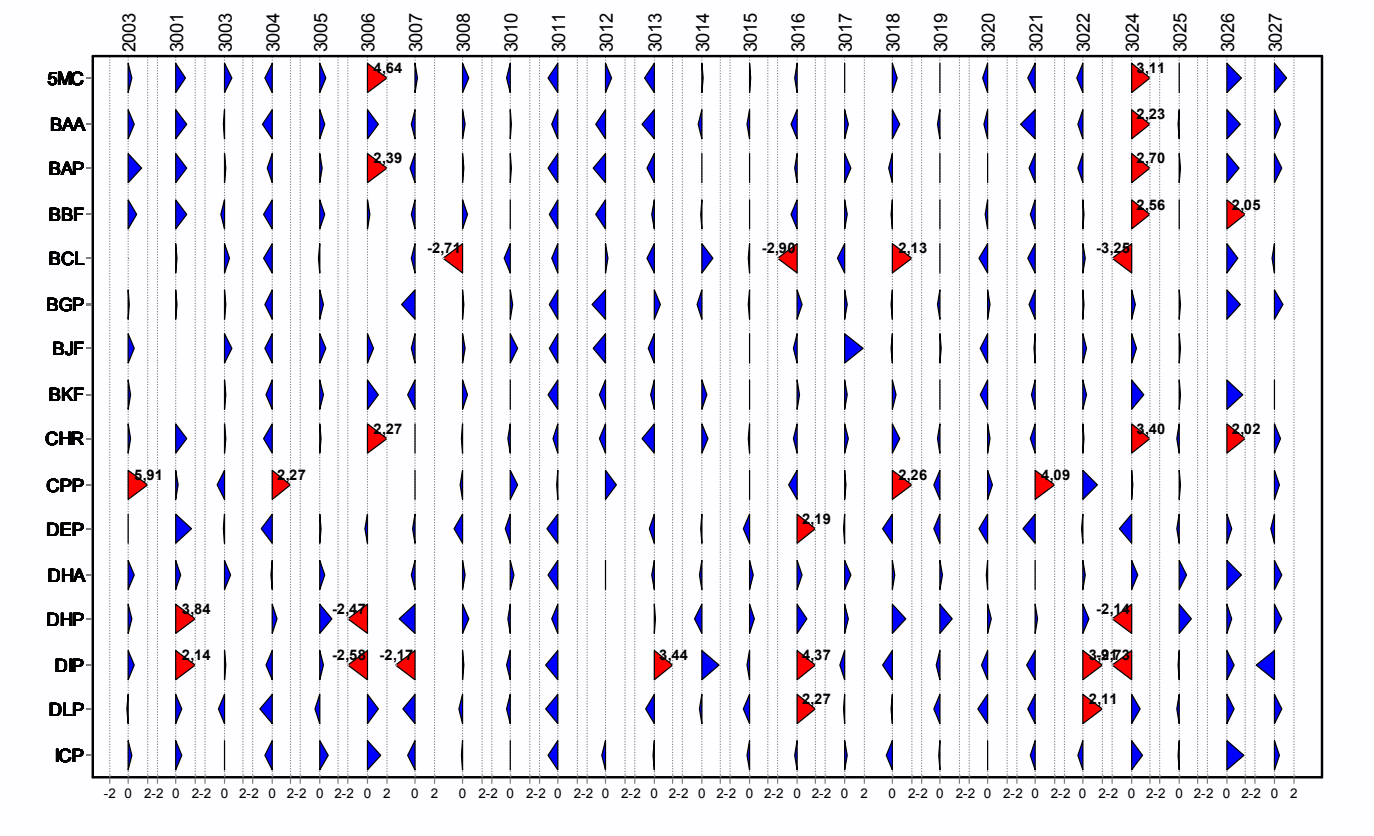


Table 6: Compilation of z-scores calculated from the "final values" for test material Fish C: z-scores outside the satisfactory range (|z| ≥ 2) are indicated by bold /red-bold (for BaP) font; N.R. denotes analytes for which "final results" were not reported.

Lab code	5MC	BaA	BaP	BbF	BcL	BgP	BjF	BkF	CHR	CPP	DeP	DhA	DhP	DiP	DlP	IcP
2003	0,34	0,56	1,30	0,84	**N.R.**	0,13	0,60	0,21	0,20	**5,91**	0,01	0,61	0,32	0,62	-0,13	0,39
3001	0,92	1,10	1,06	1,10	0,02	0,03	**N.R.**	**N.R.**	1,04	0,16	1,67	0,40	**3,84**	**2,14**	0,53	0,62
3003	0,81	-0,09	0,24	-0,33	0,55	0,22	0,85	0,16	0,13	-0,66	-0,12	0,76	**N.R.**	0,21	-0,59	0,12
3004	-0,69	-0,99	-0,52	-0,82	-0,82	-0,76	-0,75	-0,57	-0,87	**2,27**	-1,07	-0,10	0,51	-0,62	-1,19	-0,72
3005	0,62	0,59	0,27	0,60	-0,15	0,37	0,69	0,45	0,11	N.R.	0,13	0,60	1,27	0,36	-0,44	0,87
3006	**4,64**	1,14	**2,39**	0,33	**N.R.**	**N.R.**	0,66	1,11	**2,27**	**N.R.**	-0,18	**N.R.**	**-2,47**	**-2,59**	1,14	1,44
3007	0,27	-0,32	-0,55	-0,42	-0,33	-1,34	-0,42	-0,74	-0,05	-0,02	-0,21	-0,35	-1,66	**-2,18**	-1,26	-0,71
3008	0,66	0,19	0,18	0,49	**-2,71**	0,08	0,28	0,46	-0,09	-0,26	-0,87	0,25	0,69	0,18	-0,35	-0,11
3010	-0,38	0,09	0,17	-0,04	-0,68	0,22	0,69	-0,02	-0,30	0,74	-0,54	0,31	-0,32	-0,39	-0,46	0,01
3011	-1,10	-0,69	-1,02	-0,93	-0,68	-0,93	-0,87	-1,03	-0,61	-0,11	-1,18	-1,03	-0,71	-1,35	-1,33	-1,11
3012	0,57	-1,04	-1,33	-1,06	0,19	-1,41	-1,33	-0,65	-0,70	1,14	**N.R.**	0,00	**N.R.**	**N.R.**	**N.R.**	-0,44
3013	-0,94	-1,26	-0,70	-0,24	-0,75	0,70	-0,60	-0,29	-1,27	**N.R.**	-0,46	-0,14	0,21	**3,44**	-0,87	-0,11
3014	0,19	-0,38	0,00	-0,08	1,26	-0,41	**N.R.**	0,56	0,70	0,00	-0,09	-0,17	-0,69	1,87	-0,26	**N.R.**
3015	0,12	-0,17	-0,02	0,09	-0,16	-0,07	0,10	0,07	-0,14	-0,01	-0,59	0,42	0,55	-0,21	-0,61	-0,20
3016	-0,28	-0,57	-0,27	-0,57	**-2,90**	0,58	-0,38	0,28	-0,35	-0,87	**2,19**	0,59	1,09	**4,37**	**2,27**	-0,22
3017	0,00	0,38	0,62	0,33	-0,77	0,25	1,99	0,28	0,44	0,18	-0,18	0,59	0,40	-0,54	-0,18	0,22
3018	0,48	0,80	-0,36	-0,15	**2,13**	-0,17	-0,12	0,39	0,80	**2,26**	-1,07	0,26	1,38	-1,05	-0,12	-0,60
3019	-0,03	-0,29	-0,08	0,04	-0,05	-0,27	0,16	-0,07	-0,26	-0,62	-0,64	0,25	1,28	-0,42	-0,61	-0,11
3020	-0,57	-0,38	-0,09	-0,24	-0,87	0,17	-0,76	-0,84	0,18	0,44	-0,96	-0,17	0,40	-0,62	-1,05	0,00
3021	-0,77	-1,61	-0,69	-0,61	-0,85	-0,64	-0,13	-0,37	-0,52	**4,09**	-1,36	-0,09	0,15	-0,95	-0,82	-0,58
3022	-0,66	-0,60	-0,60	0,13	0,14	0,00	0,38	0,33	0,04	1,48	-0,23	0,24	0,60	**3,91**	**2,11**	-0,55
3024	**3,11**	**2,24**	**2,70**	**2,57**	**-3,25**	0,41	0,63	1,31	**3,40**	0,12	-1,22	0,67	**-2,14**	**-2,73**	1,00	1,16
3025	0,00	-0,10	0,18	0,08	**N.R.**	0,17	0,19	0,19	-0,18	0,18	-0,18	0,76	1,29	-0,09	-0,26	-0,11
3026	1,60	1,49	1,26	**2,05**	1,12	1,48	**N.R.**	1,75	**2,02**	N.R.	0,56	1,60	0,55	0,78	0,80	1,82
3027	1,25	0,63	0,82	**N.R.**	-0,19	0,95	**N.R.**	0,04	0,60	0,55	-0,43	0,83	0,78	-1,94	0,78	0,55

Precision parameters were determined from the results of five replicate analyses of test sample Fish C to see whether the applied target standard deviations for proficiency testing were realistic. The repeatability relative standard deviations (RSD_r) and reproducibility relative standard deviations (RSD_R) were calculated from the mean sums of squares from one way analysis of variance (ANOVA). They are listed in Table 7. All data was applied in the calculations, despite the precision of analysis data of some laboratories was much worse than the average precision. The reason was that these "worse" data were not outliers, but simply generated with a less precise analysis method. Hence they were considered for the estimation of the average performance characteristics of analytical methods applied in this study. In addition it guaranteed that the precision estimates were not too optimistic.
The two parameters RSD_r and RSD_R were for most of the analytes quite low. The calculated values were also significantly lower than the applied standard deviations for proficiency testing. The only

exception is CPP. The data for this PAH are strongly influenced by a few laboratories, which reported results of replicate analyses with high variability.

Table 7: Repeatability relative standard deviation and reproducibility relative standard deviation of the determination of the target PAHs in test sample Fish C.

	RSD_r	RSD_R		RSD_r	RSD_R
Analyte	%	%	Analyte	%	%
5MC	14,6	18,8	CHR	8,6	13,1
BaA	10,2	13,4	CPP	22,7	30,2
BaP	7,7	11,2	DeP	6,9	10,7
BbF	7,1	10,7	DhA	8,3	12,6
BcL	8,0	15,5	DhP	9,8	16,2
BgP	7,3	9,5	DiP	8,6	20,3
BjF	7,3	9,9	DlP	7,9	12,5
BkF	7,0	9,5	IcP	7,5	10,2

Looking at both the performance of a particular laboratory for this test sample and at the precision of reported results it may be said that a lack of accuracy of results cannot be attributed to a lack of precision of the replicate determinations. Participant 3024, whose performance was rated for eight out of 16 analytes not satisfactorily, reported results of replicate determinations with relative standard deviations of mostly below 5,5 %. Hence the problem seems to be related to bias. This could be caused by erroneous instrument calibration, respectively wrong recovery estimates. However, it would be very much appreciated if root cause analysis would be performed by the respective participant and if the identified reason for the deviations would be reported to the NRLs at the next workshop.

The results of the evaluation of the data reported for the individual analytes are given in Annex 3.
For each analyte the first figure shows the individual analysis results of the five replicate determinations. In addition, the assigned value is shown as red solid line. The arithmetic means of the results of the participants are indicated by blue solid lines. The black dotted lines represent deviations from the assigned value of $\pm 1\sigma_p$, $\pm 2\sigma_p$, and $\pm 3\sigma_p$ respectively.
The blue boxes represent the expanded uncertainties as reported by participants for the "final results".
The arithmetic mean of all replicate analysis results was for most of the analytes slightly higher, but considering the uncertainty of the estimates, in good agreement with the assigned value. The sole exceptions were BcL, for which multimodality was evident, and CPP, which was influenced by outliers.

The second figure shows Kernel density plots, which indicate the distribution of the data. The robust mean and the assigned value are depicted as a green and a blue line respectively.
The Kernel density plots indicated for some analytes deviations from normal distribution, the presence of outliers in the data set, and that multimodality occurred. However, significant deviations from Gaussian distribution were not detected for most of the PAHs.

The individual results of the replicate measurements and the "final result" with its accompanying expanded measurement uncertainty (k=2) are listed in the tables in Annex 3 as well.

Evaluation of test sample Fish D

Fish D was prepared by spiking of raw salmon with an extract of a liquid smoke flavouring sample that was highly contaminated with PAHs. The amount of extract used for spiking was adjusted to give a BaP level in the test material of about 1 µg/kg.

The natural variability of the PAH contents in the liquid smoke flavouring sample caused compared to test material Fish C a broader distribution of the analyte content levels. Content values were assigned only to nine out of the 16 target analytes. The residual seven analytes were either at content levels below the limit of detection of the isotope dilution GC-MS method applied at the CRL PAH (six analytes), or a value could not be assigned (BcL).

Performance indicators were only calculated for analytes that were at a content level equal or higher than the maximum level of LOQ specified in legislation for BaP, which is 0,9 µg/kg. One exception is provided by BcL, for which the mismatch between the mean of the results reported by the participants and the content level determined in the homogeneity and stability study differed significantly. The Kernel density plot showed also multimodality. Therefore the given content level is only indicative and performance was not rated for this analyte.

Slight differences between the mean value derived from the reported results and the assigned value were also found for other PAHs, but the difference between the two values was smaller than the combined uncertainty of the two values, which means that they were not statistically significantly different. For example, the assigned value of BaA was 1,88 µg/kg with an expanded uncertainty of 0,09 µg/kg, whereas the arithmetic mean of the results of participants was 1,79 µg/kg, and the expanded uncertainty of the arithmetic mean was 0,20 µg/kg.

z-Scores were calculated from the "final result" that participants were requested to report. However, performance indicators were attributed to the results of the participants for BaA, BaP, and CHR only. The contents of the other PAHs were either below the maximum permissible value for the LOQ of BaP (0,9 µg/kg), which was used also for the other target PAHs as a threshold for performance assessment, or, as for BcL, a content value was not assigned to the test material.

The performance indicators are listed in Table 8. z-Scores exceeding an absolute value of two are reported in bold font.

Table 8: Compilation of z-scores calculated from the reported "final values": z-scores outside the satisfactory range(|z| ≥ 2) are given in bold/red bold (for BaP); N.R. denotes analytes for which "final results" were not received

Lab code	BaA	BaP	CHR	Lab code	BaA	BaP	CHR
2003	-0,96	0,13	-0,76	3015	-0,67	-0,48	-1,27
3001	-0,93	0,74	-1,04	3016	-1,44	-1,48	-1,33
3003	-1,32	-0,17	-0,13	3017	-0,24	0,00	-0,38
3004	**-3,90**	**-3,04**	-1,63	3018	1,03	-0,48	0,10
3005	**N.R.**	**4,39**	-1,12	3019	**-3,09**	-0,52	**-3,09**
3006	**N.R.**	**N.R.**	**N.R.**	3020	-0,72	0,00	0,38
3007	**N.R.**	**N.R.**	1,65	3021	-1,65	**2,61**	**2,25**
3008	-0,24	-0,43	-1,14	3022	-1,22	-0,22	-1,48
3010	0,81	-0,70	-0,63	3024	1,05	**3,61**	**N.R.**
3011	-1,03	-0,57	-0,15	3025	-0,48	-0,43	-1,14
3012	-1,20	-0,43	-1,33	3026	**3,06**	**3,39**	**3,56**
3013	-0,36	-0,87	-1,67	3027	**5,65**	**5,17**	**6,04**
3014	0,72	0,00	-2,27				

In addition to BaA, BaP, and CHR six other analytes were determined during the homogeneity study in test sample Fish D. However a special situation was faced in the evaluation of the results for these compounds, because many laboratories reported "below LOD" or "below LOQ" instead of numerical values. As there is not any guidance on minimum method performance criteria for the determination of PAHs besides BaP, it cannot be expected that all laboratories developed their methods to a level that allows the determination of such low contents. To avoid applying double standards, the results were not rated, but only compiled and checked if the laboratories were able to detect the analytes. The compilation of results is given in Table 9. Results respectively reported content ranges deviating by from the assigned value by more than 50 % of the assigned value are highlighted.

Notably the majority of laboratories was able to quantify the analytes even at such low content levels. The agreement among the numerical results was good, which is promising with respect of coming changes in legislation.

The results of the evaluation of the data reported for the individual analytes are given in Annex 4.
For each analyte the first figure shows the individual analysis results of the three replicate determinations. In addition, the assigned value is shown as red solid line. The robust means (medians) of the results of the participants are indicated by blue solid lines.
The blue boxes represent the expanded uncertainties as reported by participants for the "final results".

The second figure shows Kernel density plots, which indicate the distribution of the data. The robust mean and the assigned value are depicted as a green and a blue line respectively.
The Kernel density plots indicated for some analytes deviations from normal distribution, the presence of outliers in the data set, and that multimodality occurred.

The individual results of the replicate measurements and the "final result" with its accompanying expanded measurement uncertainty (k=2) are listed in the tables in Annex 4 as well.

Table 9: Compilation of results reported for analytes in test sample Fish D with content levels below 0,9 µg/kg.

	BbF	BgP	BjF	BkF	CPP	ICP
Assigned value	**0,7 µg/kg**	**0,4 µg/kg**	**0,5 µg/kg**	**0,4 µg/kg**	**0,3 µg/kg**	**0,3 µg/kg**
Participant	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
2003	0,6	0,87	0,1<[BjF]<0,3	0,42	1<[CPP]<3,5	0,31
3001	1,06	2,09			1,12	1,09
3003	0,49	0,36	0,54	0,24	0,11	0,3
3004	0,15<[BbF]<0,45	<0,15	<1	0,02<[BkF]<0,06	<1	<0,8
3005	<0,2	<0,4	<0,75	<0,2	<7,5	<0,2
3006	0,22<[BbF]<0,66		<1,02	0,64		0,11<[IcP]<0,33
3007	<2	<2	<2	<2	<2	<2
3008	0,6	0,4	0,5	0,3	0,3	0,3
3010	0,72	0,48	<0,2	0,26	0,1<[CPP]<0,2	0,24
3011	0,64	0,34	0,42	0,26	0,21	0,27
3012	0,6	1,4	0,4	0,4	0,4	1,3
3013	0,49	0,43	<0,34	0,24	3,13<[CPP]<6,27	0,21<[IcP]<0,42
3014	0,6	0,54<[BgP]<1,08		0,3		
3015	0,55	0,31	0,39	0,23	0,17	0,26
3016	0,46	0,29	0,5	0,35	1,8	0,15
3017	<0,2	0,4	2,1	<0,2	1	<0,2
3018	<1,11	0,38	<1,28	<0,83	0,38	<0,43
3019	0,48	<0,38	0,46	<0,39	<0,95	<0,35
3020	0,7	0,9	0,5	0,4	1,3	0,4
3021	0,97	0,64	0,2<[BjF]<0,8	0,41		<0,2
3022	0,61	0,41	0,49	0,28		0,29
3024	0,4<[BbF]<1,2	0,63	<0,3	0,8	0,37<[CPP]<1,1	<0,3
3025	0,6	0,4	0,4	0,2<[BkF]<0,59	<0,21	0,3
3026	0,97	8,1	<10	0,71	<50	1,53
3027		1,3		0,8	0,64	0,72

Evaluation of the influence of calibration on results

The influence of calibration on the results for the fish test samples was evaluated by comparing the relative deviations of the reported results for the unknown standard solution in acetonitrile from the preparation values to the relative deviations from the assigned values of the results for the fish samples. This was done by means of Youden plots.

As examples the evaluations for BaP are given in Figure 7 and 8. The different separation techniques (GC and HPLC) are marked by different colours. The red line indicates identical relative deviations for both samples.
As can be seen data points accumulate in quadrant one and three. Therefore it may be concluded that there is significant influence of the calibration on the results for the fish test samples. However it has also to be said that the deviations from the assigned values were in general low. Most of the results shown in Figures 7 and 8 were within the range of ± 20%. Clear evidence of superior performance of one chromatographic technique compared to the other was not retrieved from the data.

Figure 7: Youden plot for BaP in ACN and Fish C with GC and HPLC techniques

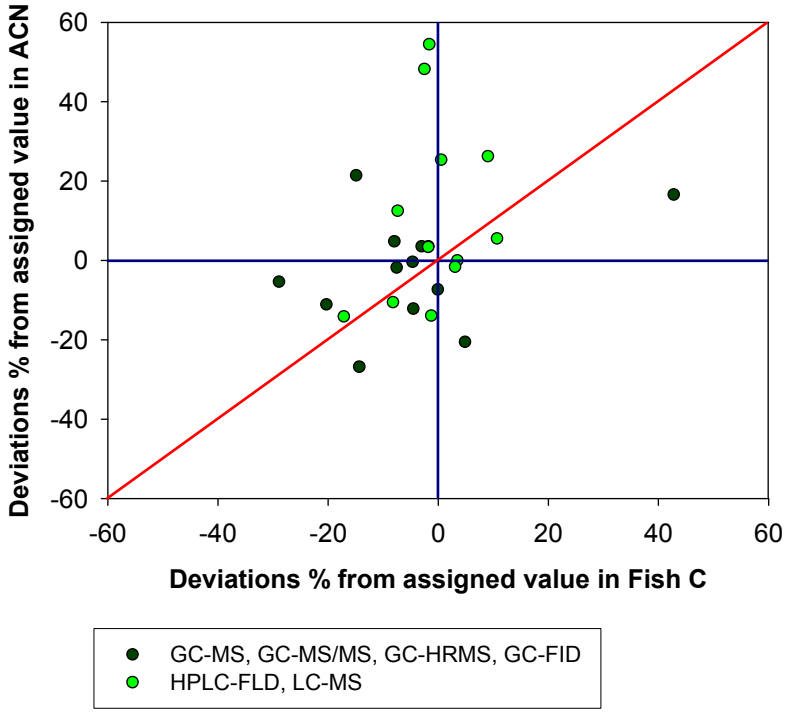
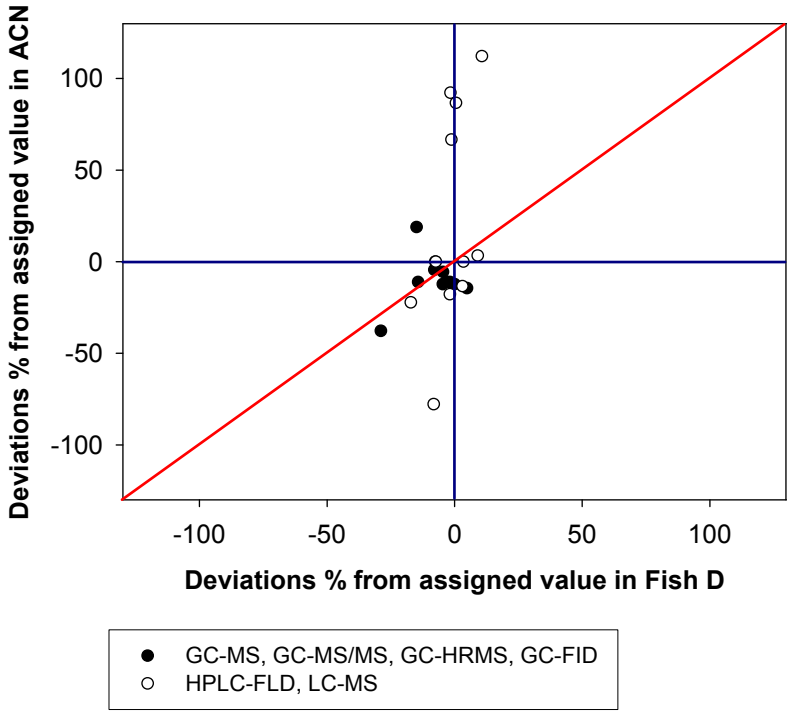


Figure 8: Youden plot for BaP in ACN and Fish D with GC and HPLC techniques

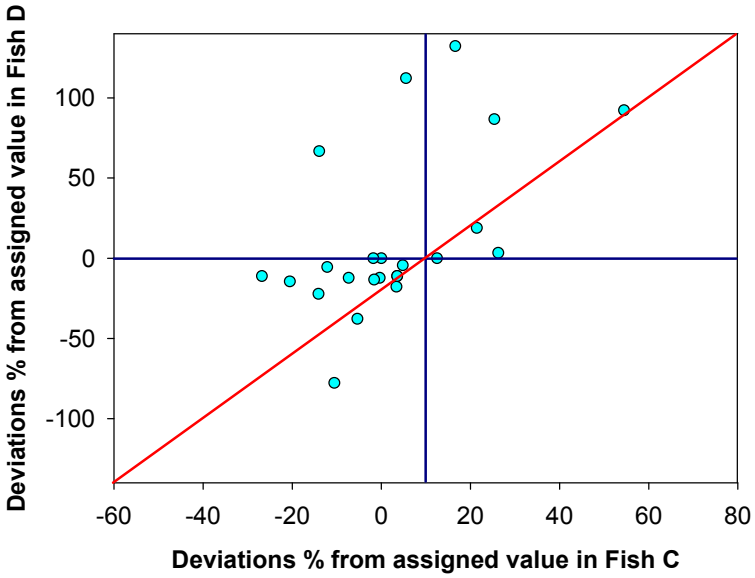


Method performances for the two fish samples

The consistency of performance of the laboratories in the analysis of PAHs in fish was evaluated by comparing the relative deviations of the reported results for BaP from the assigned values for Fish C and Fish D. This was done by means of a Youden plot. The red line indicates identical relative deviations for both samples.

As can be seen in Figure 9, data points accumulate in quadrant one and three. Therefore it may be concluded that the performance of the participants is consistent, and systematic effects might be responsible for large deviations. However, it should be highlighted that deviations are much higher for sample D, as could be expected due to the lower content of BaP in Fish D (0,94 µg/kg) than in Fish C (5,6 µg/kg).

Figure 9: Youden plot for BaP in Fish C and Fish D



Evaluation of compliance with legislation

The data for BaP were evaluated for compliance with the provisions given in Commission Regulation (EC) No 333/2007. Table 7 contains an overview on the results of the evaluation. Empty cells indicate compliant data.

Table 10: Compliance of data reported fro BaP with the criteria given by Commission Regulation (EC) No 333/2007.

	LOD	LOQ	Precision Fish C	Recovery	U Fish C	U Fish D
Participant			$HO_r < 2$		Uf=1,1 µg/kg	Uf=0,2 µg/kg
2003						
3001						
3003						
3004						
3005						
3006	***0,55***	***1,65***				***N.R***
3007	*N.R.*	***2***			***N.R.***	***N.R***
3008						
3010					***N.R.***	***N.R***
3011						
3012			*			
3013						
3014						
3015						
3016						
3017						***0,25***
3018	***0,37***	***1,2***				
3019						
3020						
3021					***1,29***	***0,27***
3022					***N.R.***	***N.R***
3024						
3025						
3026						***0,21***
3027						

N.R. not reported (non compliant)
HOr $Horrat_r$ ratio for repeatability calculated from $RSD_r/(RSD_H*0.66)$
* not evaluated - less than 3 values reported

Follow-up actions for underperforming laboratories

The CRL will set up follow-up measures in due time for all participating laboratories that received z-scores > |3| as required by Regulation (EC) 882/2004, and to the Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with Community reference laboratories (CRLs) activities.

Conclusions

Twenty-five of 27 participants reported their analysis results on time. The performance of most participants was good. In total about 90 % of the attributed z-scores were below an absolute value of two. About half of the z-scores exceeding this level were attributed to the results of three laboratories only. Six analytes, benzo[*c*]fluorene, cyclopenta[*cd*]pyrene and the four dibenzopyrenes, caused most difficulties to the participants. However these substances are not among the four that will be applied for future control of the levels of PAHs in food within the EU.
The majority of NRLs applied in this inter-laboratory comparison test analysis methods which were with regard to performance characteristics compliant with EU legislation.
The influence of instrument calibration on the results for the food samples were evaluated. Deviations of results for the fish samples from the assigned values seemed to be rather systematic than random. This conclusion is supported by the high precision of the results of replicate analyses. The findings underpin the importance of accurate instrument calibration.

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Annex 1: Homogeneity data

Homogeneity data for PAH4 in test material Fish C

sample id	rep 1	rep 2	count	sum	square	average	variance
1	4,41	4,40	2	8,8	77,6	4,406	0,000
2	4,57	4,91	2	9,5	89,8	4,739	0,056
3	4,58	4,71	2	9,3	86,2	4,642	0,008
4	4,59	4,65	2	9,2	85,4	4,621	0,002
5	4,92	4,53	2	9,5	89,4	4,728	0,077
6	4,42	4,33	2	8,8	76,6	4,377	0,004
7	4,61	4,47	2	9,1	82,5	4,543	0,010
8	4,44	4,45	2	8,9	79,0	4,445	0,000
9	4,52	4,32	2	8,8	78,2	4,422	0,020
10	4,44	4,39	2	8,8	78,0	4,416	0,001

mean	sd	cv
4,53	0,17	3,68

BaA

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,349	9	0,039	2,162	0,123	3,020
Within Groups	0,179	10	0,018			
Total	0,528	19				

Sufficient Homgeneity

target σ	F<Fcrit?	s_s/σ
1,632		0,063
		critical $s_s/\sigma = 0.3$
	ACCEPT	

sample id	rep 1	rep 2	count	sum	square	average	variance
1	5,86	5,59	2	11,5	131,1	5,725	0,038
2	5,66	5,74	2	11,4	130,1	5,703	0,003
3	5,79	5,71	2	11,5	132,2	5,749	0,003
4	5,83	5,76	2	11,6	134,3	5,795	0,002
5	6,04	5,76	2	11,8	139,3	5,901	0,039
6	5,55	5,37	2	10,9	119,2	5,459	0,016
7	5,77	5,76	2	11,5	132,8	5,763	0,000
8	5,53	5,46	2	11,0	120,8	5,495	0,002
9	5,47	5,29	2	10,8	115,7	5,378	0,017
10	5,60	5,57	2	11,2	124,7	5,583	0,000

mean	sd	cv
5,66	0,18	3,22

BaP

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,507	9	0,056	4,649	0,012	3,020
Within Groups	0,121	10	0,012			
Total	0,628	19				

Sufficient Homgeneity

target σ	F<Fcrit?	s_s/σ
1,974		0,075
		critical $s_s/\sigma = 0.3$
	no->ss	ACCEPT

sample id	rep 1	rep 2	count	sum	square	average	variance
1	5,46	5,70	2	11,2	124,6	5,581	0,027
2	5,32	5,74	2	11,1	122,3	5,529	0,089
3	5,60	5,65	2	11,3	126,8	5,630	0,001
4	5,63	5,23	2	10,9	118,0	5,430	0,078
5	5,94	5,28	2	11,2	126,0	5,612	0,217
6	5,60	5,39	2	11,0	120,7	5,493	0,021
7	5,39	5,23	2	10,6	112,8	5,311	0,013
8	5,39	5,56	2	10,9	119,9	5,474	0,014
9	5,50	4,97	2	10,5	109,6	5,236	0,138
10	5,42	4,79	2	10,2	104,2	5,104	0,198

mean	sd	cv
5,44	0,26	4,87

BbF

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,536	9	0,060	0,748	0,664	3,020
Within Groups	0,797	10	0,080			
Total	1,333	19				

Sufficient Homgeneity

target σ	F<Fcrit?	s_s/σ
1,909		
		critical $s_s/\sigma = 0.3$
	ACCEPT	

sample id	rep 1	rep 2	count	sum	square	average	variance
1	4,85	4,81	2	9,7	93,2	4,828	0,001
2	4,97	5,25	2	10,2	104,5	5,110	0,039
3	4,75	4,86	2	9,6	92,4	4,806	0,005
4	4,93	4,91	2	9,8	96,7	4,916	0,000
5	5,17	5,00	2	10,2	103,6	5,089	0,014
6	4,75	4,64	2	9,4	88,2	4,696	0,006
7	4,85	4,77	2	9,6	92,6	4,812	0,004
8	4,80	4,74	2	9,5	91,1	4,773	0,002
9	4,76	4,83	2	9,6	91,9	4,794	0,003
10	4,81	4,74	2	9,5	91,2	4,774	0,003

mean	sd	cv
4,86	0,15	3,05

CHR

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,342	9	0,038	4,938	0,010	3,020
Within Groups	0,077	10	0,008			
Total	0,418	19				

Sufficient Homgeneity

target σ	F<Fcrit?	s_s/σ
1,735		0,071
		critical $s_s/\sigma = 0.3$
	no->ss	ACCEPT

Homogeneity data for BaA, BaP, and CHR in test material Fish D

sample id	rep 1	rep 2	count	sum	square	average	variance
1	1,92	1,93	2	3,8	14,8	1,923	0,000
2	1,95	1,84	2	3,8	14,3	1,894	0,006
3	1,91	1,94	2	3,8	14,8	1,923	0,000
4	1,91	1,86	2	3,8	14,3	1,889	0,001
5	1,88	1,95	2	3,8	14,7	1,915	0,002
6	1,89	1,89	2	3,8	14,3	1,889	0,000
7	1,87	1,86	2	3,7	13,9	1,865	0,000
8	1,85	1,81	2	3,7	13,4	1,829	0,001
9	1,83	1,89	2	3,7	13,9	1,862	0,002
10	1,84	1,86	2	3,7	13,7	1,853	0,000

mean	sd	cv
1,88	0,04	2,16

BaA

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,018	9	0,002	1,479	0,275	3,020
Within Groups	0,013	10	0,001			
Total	0,031	19				

Sufficient Homgeneity

target σ	F<Fcrit?	s_s/σ
0,774		0,023
		critical $s_s/\sigma = 0.3$

ACCEPT

sample id	rep 1	rep 2	count	sum	square	average	variance
1	1,08	0,99	2	2,1	4,3	1,036	0,004
2	1,01	0,88	2	1,9	3,6	0,946	0,008
3	1,03	0,94	2	2,0	3,9	0,989	0,004
4	0,97	0,93	2	1,9	3,6	0,953	0,001
5	0,94	0,94	2	1,9	3,5	0,937	0,000
6	0,91	0,92	2	1,8	3,4	0,916	0,000
7	0,92	0,90	2	1,8	3,3	0,911	0,000
8	0,91	0,88	2	1,8	3,2	0,897	0,000
9	0,89	0,93	2	1,8	3,3	0,911	0,001
10	0,88	0,88	2	1,8	3,1	0,879	0,000

mean	sd	cv
0,94	0,05	5,83

BaP

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,039	9	0,004	2,431	0,091	3,020
Within Groups	0,018	10	0,002			
Total	0,057	19				

Sufficient Homgeneity

target σ	F<Fcrit?	s_s/σ
0,428		0,083
		critical $s_s/\sigma = 0.3$

ACCEPT

sample id	rep 1	rep 2	count	sum	square	average	variance
1	2,39	2,46	2	4,9	23,6	2,426	0,002
2	2,45	2,40	2	4,8	23,5	2,423	0,001
3	2,44	2,46	2	4,9	24,0	2,449	0,000
4	2,31	2,40	2	4,7	22,2	2,357	0,005
5	2,41	2,42	2	4,8	23,3	2,415	0,000
6	2,37	2,37	2	4,7	22,4	2,367	0,000
7	2,36	2,31	2	4,7	21,8	2,336	0,002
8	2,32	2,37	2	4,7	22,0	2,344	0,001
9	2,35	2,34	2	4,7	22,0	2,345	0,000
10							

mean	sd	cv
2,38	0,05	2,05

CHR

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0,030	8	0,004	3,119	0,055	3,230
Within Groups	0,011	9	0,001			
Total	0,041	17				

Sufficient Homgeneity

target σ	F<Fcrit?	s_s/σ
0,947		0,038
		critical $s_s/\sigma = 0.3$

ACCEPT

Annex 2: Data for the solution of the 15+1 EU priority PAHs in acetonitrile (ACN)

5-methylchrysene (5MC)

Figure 10 : Individual results of replicate measurements (▲) of 5MC in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 64,7 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

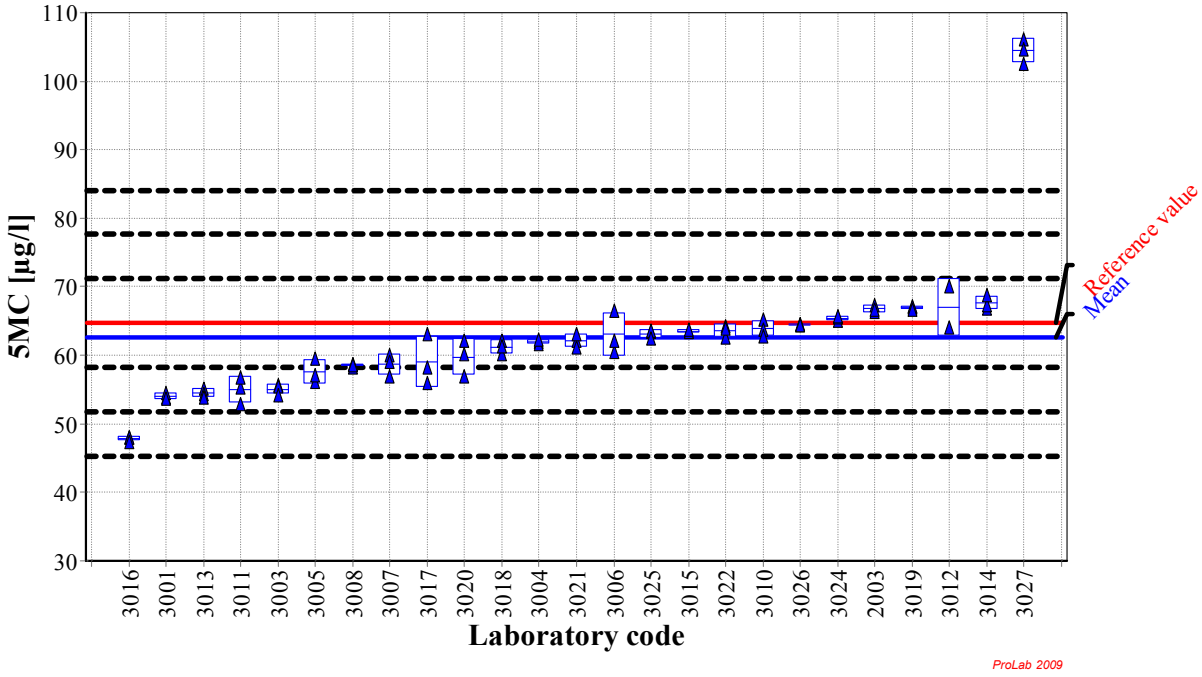

Figure 11: Kernel Density Plot

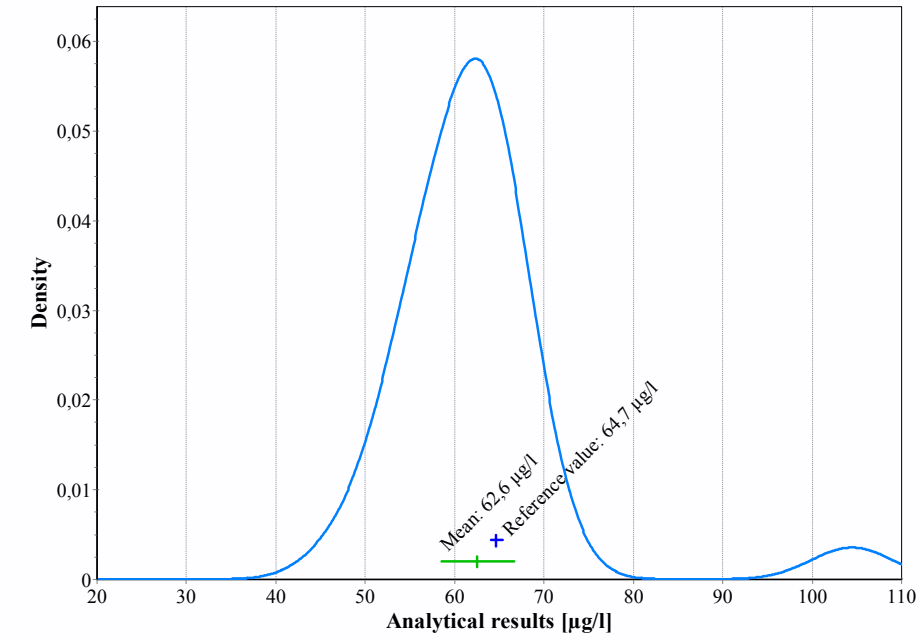

Table 11: Individual results of replicate measurements of 5MC in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	66,32	67,37	66,68
3001	53,82	54,5	53,7
3003	55,6	55,4	54,2
3004	61,94	61,69	62,33
3005	56,2	57,1	59,6
3006	66,5	60,5	62,1
3007	60	57	59
3008	58,3	58,7	58,6
3010	65,17	63,81	62,78
3011	52,9	55,3	56,7
3012	70	64	
3013	55,13	54,32	53,86
3014	66,8	67,3	68,8
3015	63,4	63,4	63,7
3016	48,06	47,99	47,39
3017	58,2	55,9	63,1
3018	62,2	60,2	61,3
3019	67	67,2	66,6
3020	62,2	60,2	56,9
3021	62,15	61,23	63,14
3022	64,26	62,55	63,94
3024	65,05	65,61	65,64
3025	63,4	63,6	62,4
3026	64,6	64,4	64,4
3027	106,1	104,7	102,5

Benzo[*a*]anthracene (BaA)

Figure 12: Individual results of replicate measurements (▲) of BaA in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 46,1 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

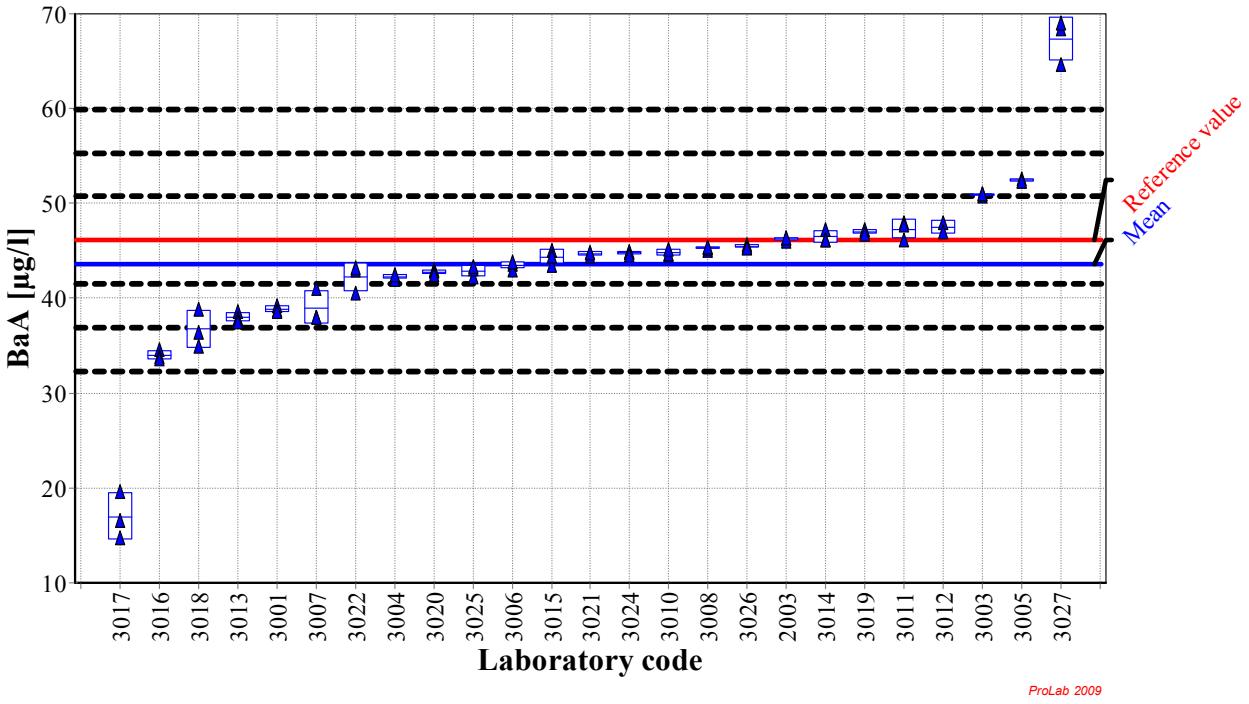

Figure 13: Kernel Density Plot

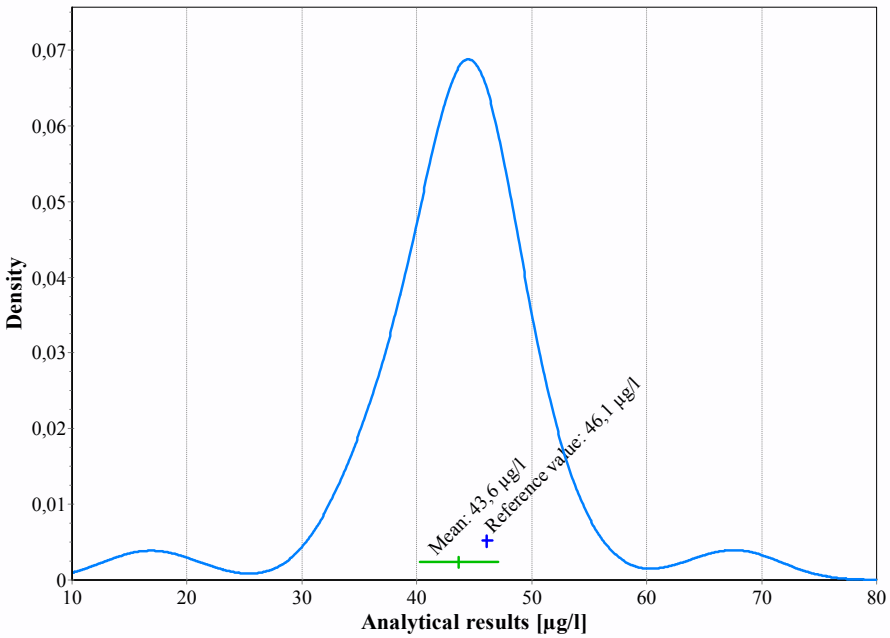

Table 12: Individual results of replicate measurements of BaA in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	46,22	46,01	46,42
3001	38,69	39,24	38,65
3003	50,8	51	51
3004	42,28	41,97	42,46
3005	52,3	52,6	52,4
3006	43,6	43	43,8
3007	41	38	38
3008	45,1	45,3	45,4
3010	44,56	44,73	45,18
3011	46,1	48	47,7
3012	48	47	
3013	38,55	37,85	37,55
3014	47,2	46,1	46,1
3015	43,5	45,1	44,4
3016	34,58	33,82	33,56
3017	16,6	14,7	19,6
3018	34,9	36,4	38,9
3019	47	47,2	46,8
3020	43	42,8	42,5
3021	44,44	44,82	44,85
3022	42,96	43,24	40,5
3024	44,81	44,89	44,56
3025	42,2	43,1	43,3
3026	45,7	45,4	45,3
3027	68,4	69	64,7

Benzo[*a*]pyrene (BaP)

Figure 14: Individual results of replicate measurements (▲)of BaP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 50,2 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

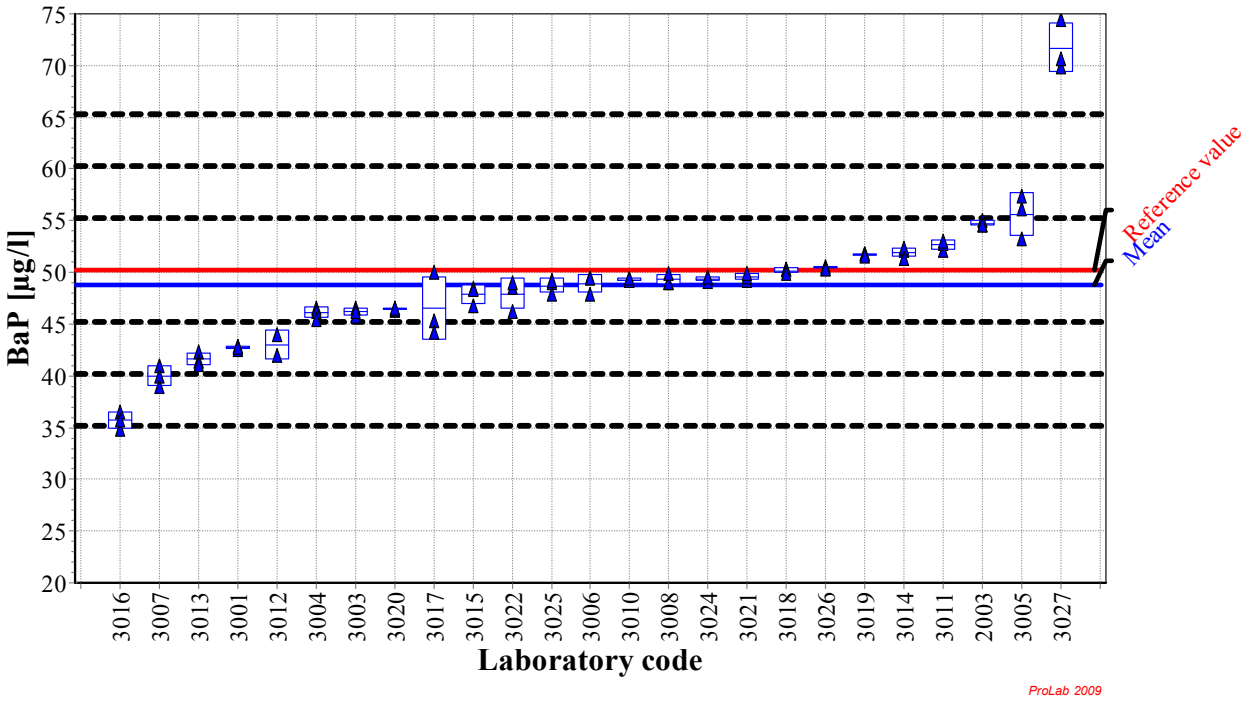

Figure 15: Kernel Density Plot

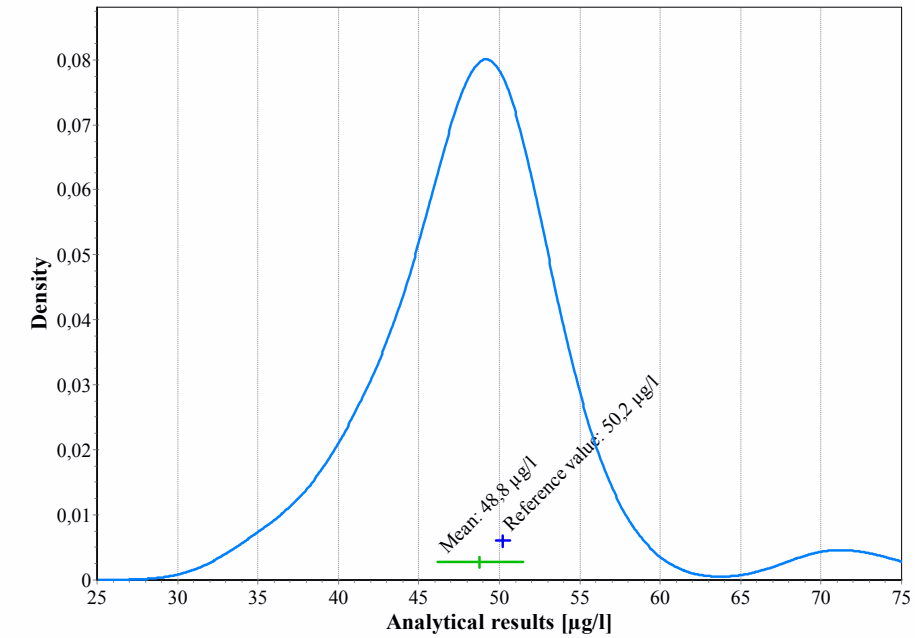

Table 13: Individual results of replicate measurements of BaP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	54,6	55,05	54,55
3001	42,84	42,52	42,79
3003	45,8	46,6	46,2
3004	46,57	46,17	45,49
3005	53,2	56,1	57,4
3006	49,4	49,5	47,9
3007	41	40	39
3008	49	49	49,9
3010	49,18	49,25	49,42
3011	52,1	52,8	53
3012	42	44	
3013	42,29	41,45	41,03
3014	52,1	52,3	51,4
3015	46,8	48,5	48,3
3016	36,49	34,84	35,73
3017	45,3	44,2	50
3018	50,4	50,2	49,9
3019	51,8	51,8	51,6
3020	46,3	46,4	46,5
3021	49,21	49,58	49,9
3022	48,56	49,02	46,2
3024	49,46	49,14	49,53
3025	49	49,2	47,9
3026	50,4	50,6	50,4
3027	69,9	70,7	74,4

Benzo[*b*]fluoranthene (BbF)

Figure 16: Individual results of replicate measurements (▲)of BbF in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 89,8 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

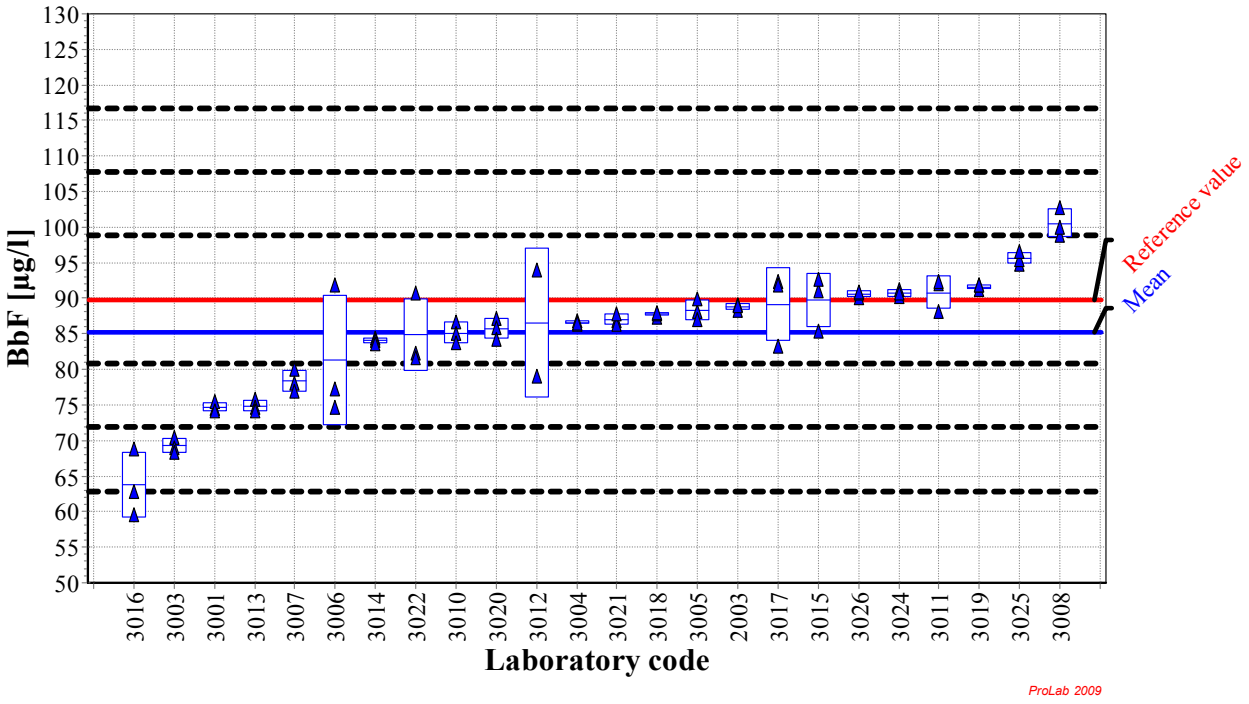

Figure 17: Kernel Density Plot

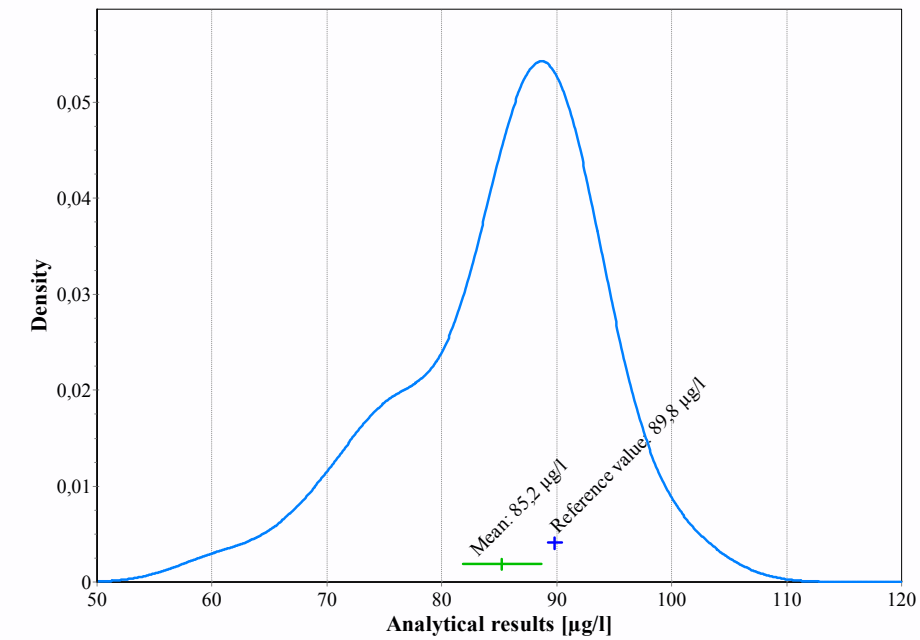

Table 14: Individual results of replicate measurements of BbF in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	88,23	89,1	89,01
3001	74,43	75,4	74,25
3003	70,4	69	68,4
3004	86,33	86,87	86,48
3005	88,2	87	89,9
3006	91,8	74,7	77,3
3007	80	78	77
3008	98,8	100	102,8
3010	86,69	84,99	83,68
3011	88,1	92	92,3
3012	94	79	
3013	75,77	74,6	74,21
3014	84,4	84,1	83,6
3015	85,4	91	92,7
3016	68,78	62,8	59,58
3017	92,3	83,2	91,9
3018	87,4	87,8	88
3019	91,2	91,8	91,8
3020	87,2	85,8	84,3
3021	86,86	86,36	87,88
3022	82,23	90,76	81,58
3024	90,17	91,23	90,66
3025	94,8	95,5	96,5
3026	90	90,8	90,9
3027			

Benzo[*c*]fluorene (BcL)

Figure 18: Individual results of replicate measurements (▲)of BcL in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 72,7 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

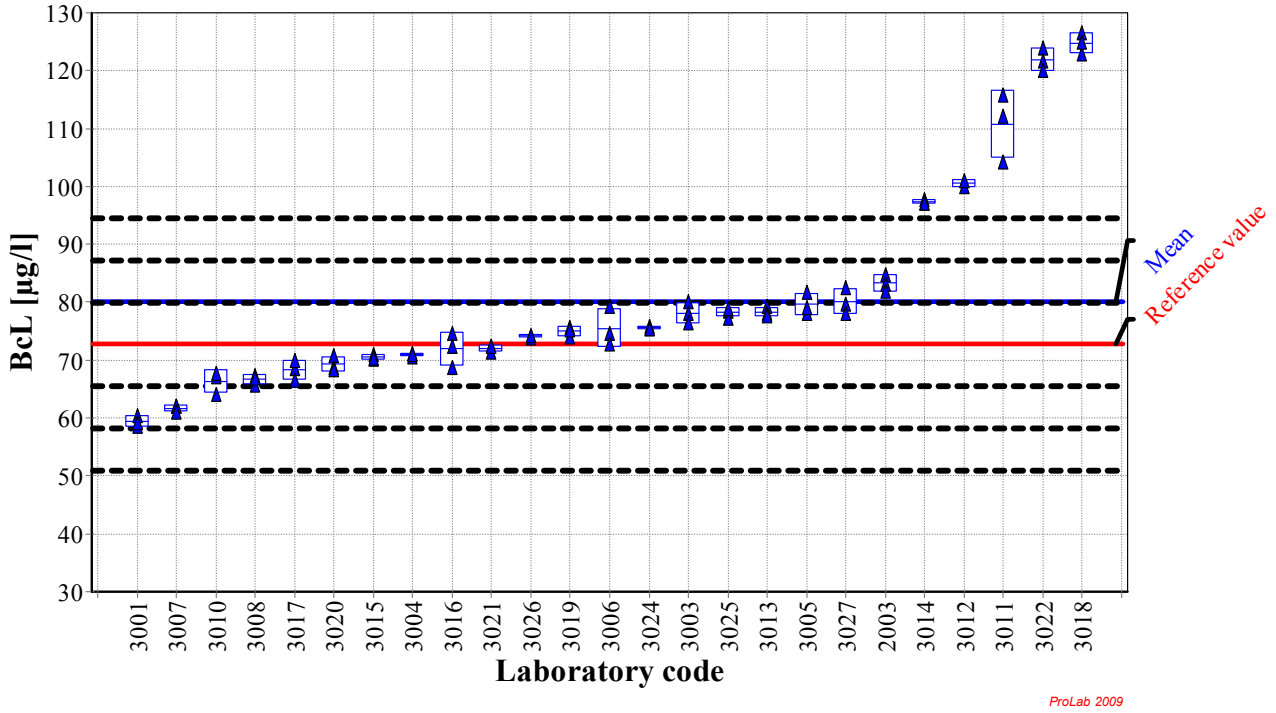

Figure 19: Kernel Density Plot

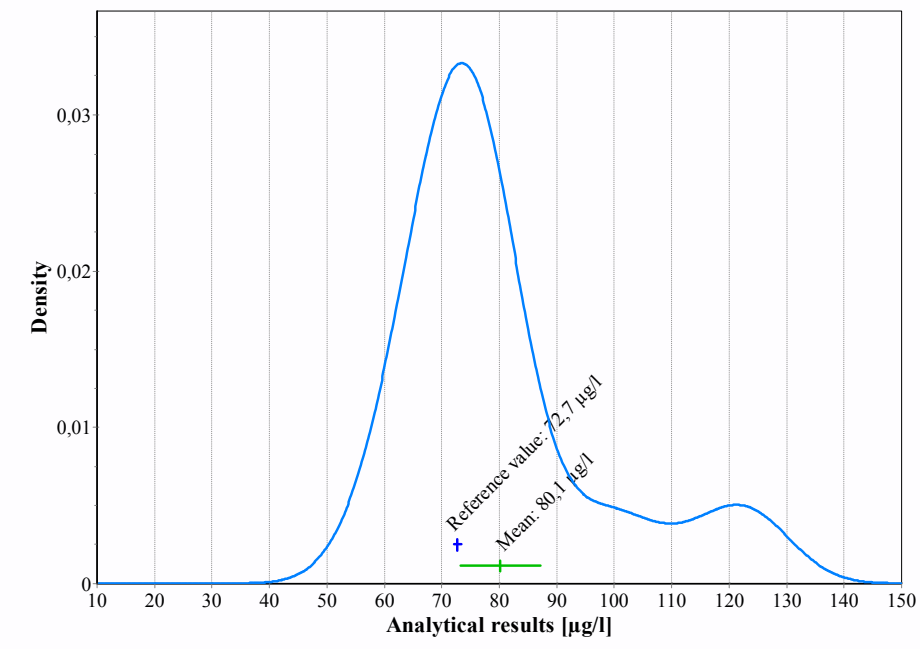

Table 15: Individual results of replicate measurements of BcL in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	88,23	89,1	89,01
3001	74,43	75,4	74,25
3003	70,4	69	68,4
3004	86,33	86,87	86,48
3005	88,2	87	89,9
3006	91,8	74,7	77,3
3007	80	78	77
3008	98,8	100	102,8
3010	86,69	84,99	83,68
3011	88,1	92	92,3
3012	94	79	
3013	75,77	74,6	74,21
3014	84,4	84,1	83,6
3015	85,4	91	92,7
3016	68,78	62,8	59,58
3017	92,3	83,2	91,9
3018	87,4	87,8	88
3019	91,2	91,8	91,8
3020	87,2	85,8	84,3
3021	86,86	86,36	87,88
3022	82,23	90,76	81,58
3024	90,17	91,23	90,66
3025	94,8	95,5	96,5
3026	90	90,8	90,9
3027			

Benzo[*ghi*]perylene (BgP)

Figure 20: Individual results of replicate measurements (▲)of BgP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 42,8 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

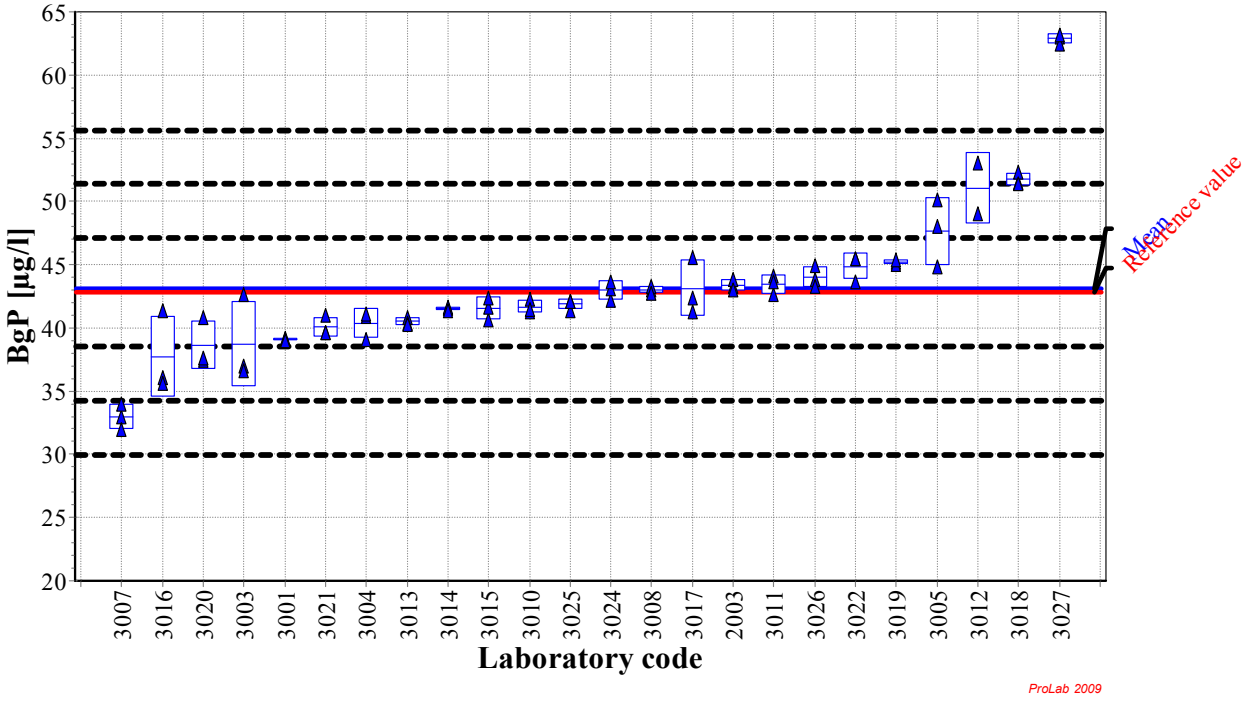

Figure 21: Kernel Density Plot

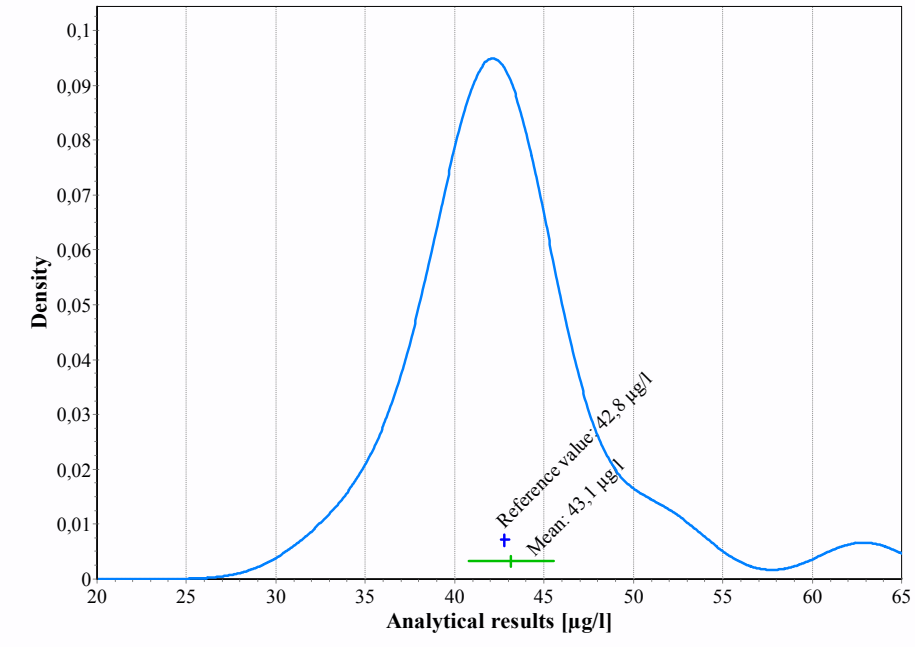

Table 16: Individual results of replicate measurements of BgP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	43,26	43,83	43,01
3001	39,08	39,14	39,01
3003	42,6	37	36,6
3004	40,89	41,13	39,04
3005	48	44,8	50,1
3006			
3007	33	34	32
3008	43	43,3	42,7
3010	41,26	42,26	41,49
3011	44,1	42,6	43,6
3012	53	49	
3013	40,85	40,38	40,26
3014	41,5	41,6	41,4
3015	40,6	41,6	42,4
3016	41,36	36,09	35,65
3017	45,6	41,3	42,4
3018	51,5	52,3	51,4
3019	45,2	45	45,4
3020	40,8	37,4	37,6
3021	40,97	39,63	39,61
3022	45,46	45,5	43,64
3024	42,16	43,08	43,63
3025	42,1	41,4	42,1
3026	43,8	43,3	44,9
3027	63	62,4	63,2

Benzo[*j*]fluoranthene (BjF)

Figure 22: Individual results of replicate measurements (▲)of BjF in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 54,4 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

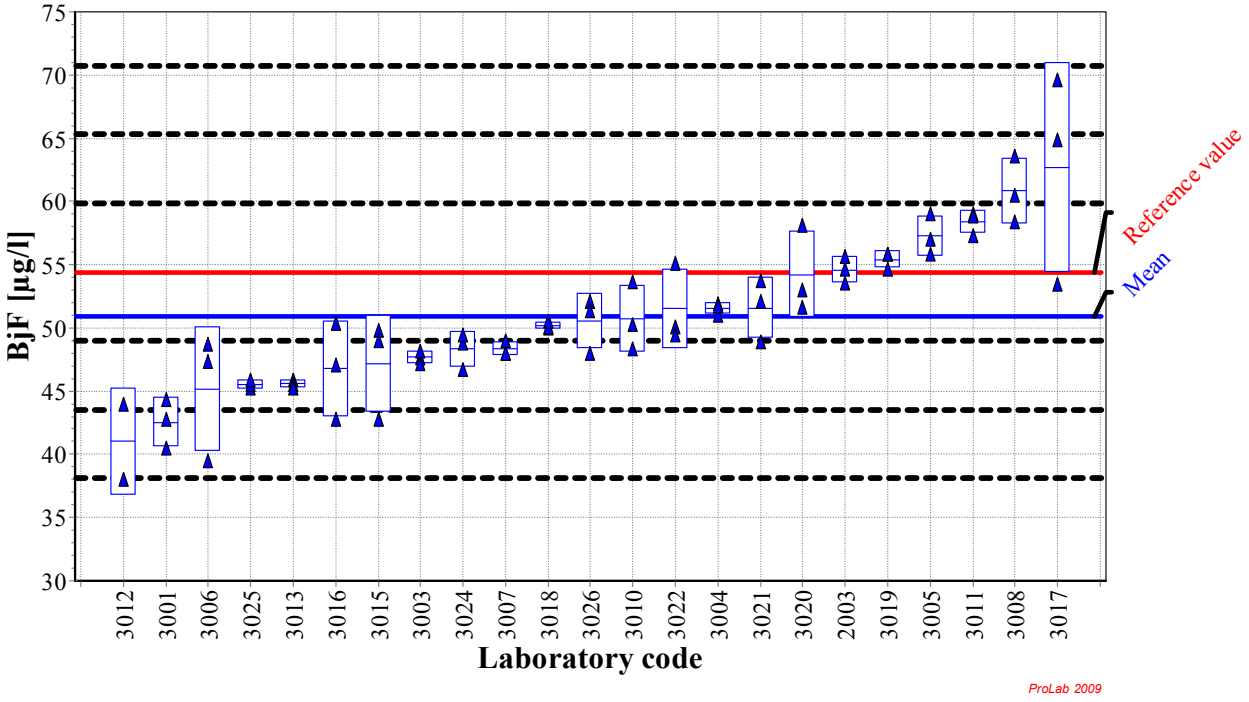

Figure 23: Kernel Density Plot

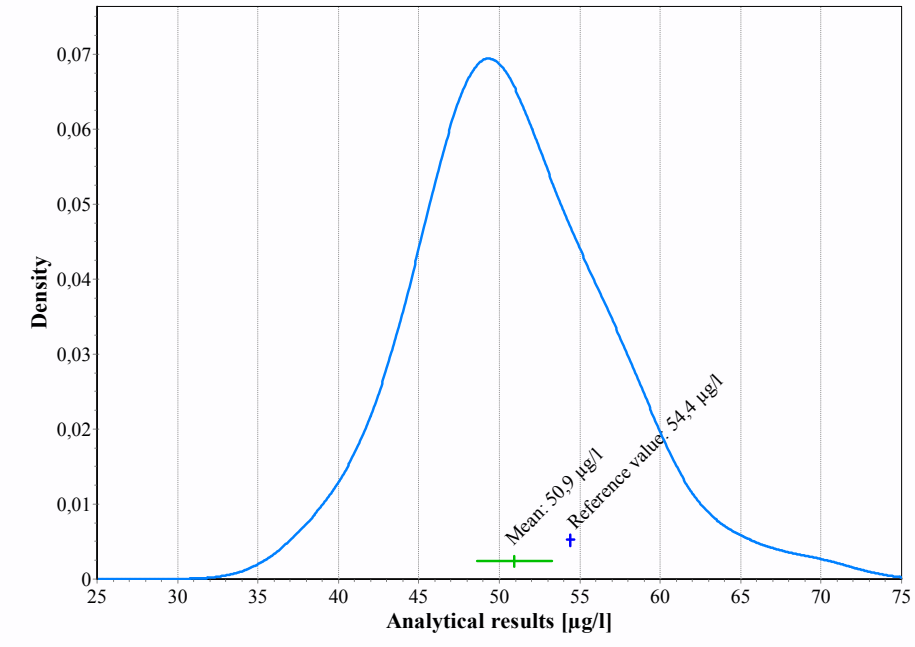

Table 17: Individual results of replicate measurements of BjF in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	53,53	54,61	55,62
3001	40,47	42,81	44,37
3003	47,6	48,2	47,2
3004	51	51,92	51,74
3005	55,8	59	57
3006	39,5	47,3	48,7
3007	49	48	48
3008	58,4	63,6	60,5
3010	53,63	48,36	50,22
3011	57,3	59	58,8
3012	38	44	
3013	45,9	45,56	45,25
3014			
3015	49,8	49	42,8
3016	50,39	47,11	42,76
3017	69,6	53,5	64,9
3018	50	50,1	50,5
3019	54,6	55,8	55,8
3020	58,1	51,6	53
3021	52,13	48,9	53,73
3022	50,04	55,1	49,4
3024	46,7	48,84	49,4
3025	45,2	45,5	45,9
3026	52,1	48	51,4
3027			

Benzo[*k*]fluoranthene (BkF)

Figure 24: Individual results of replicate measurements (▲)of BkF in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 54,4 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

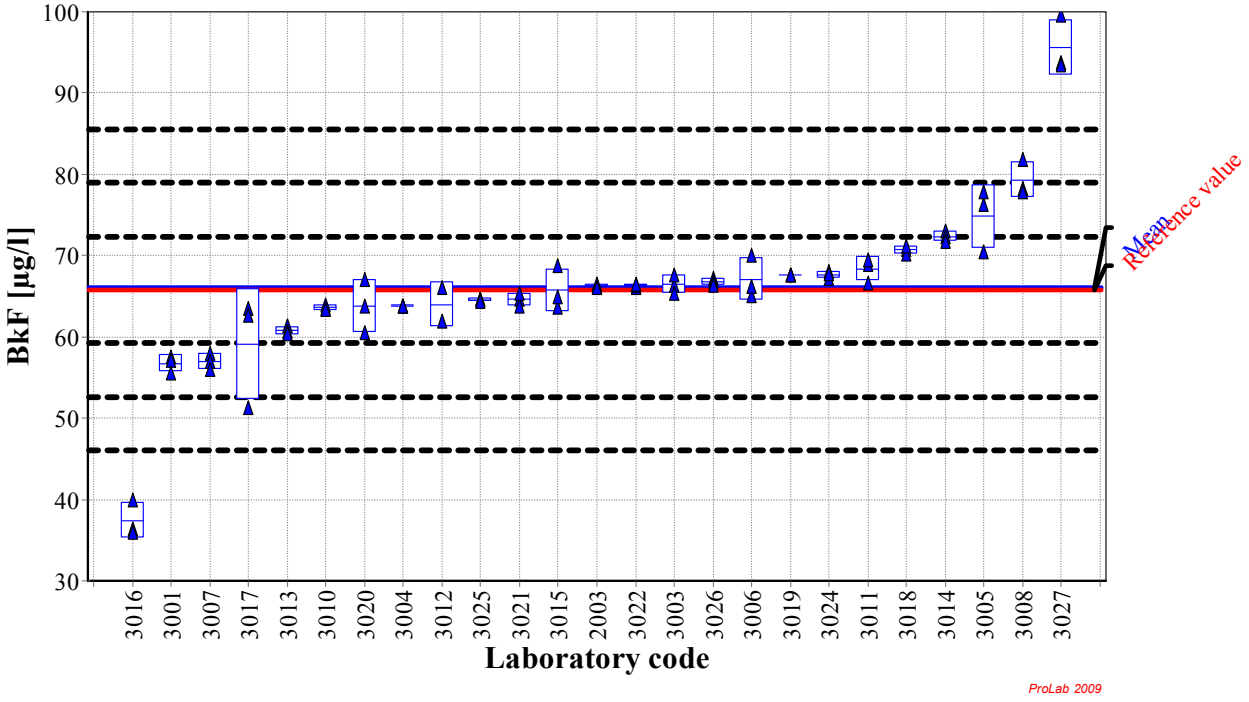

Figure 25: Kernel Density Plot

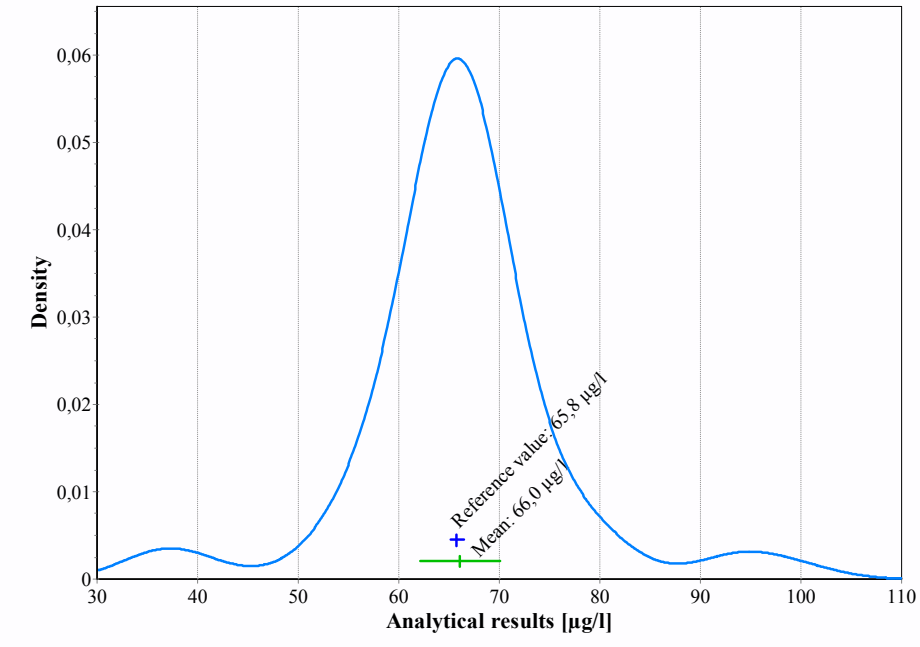

Table 18: Individual results of replicate measurements of BkF in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	66,27	66,5	66,07
3001	57,49	57,18	55,53
3003	66,4	67,6	65,4
3004	63,79	63,85	63,86
3005	70,4	76,3	77,8
3006	65	66,2	70,1
3007	58	57	56
3008	78,3	77,9	81,8
3010	63,56	63,91	63,3
3011	66,7	68,9	69,5
3012	66	62	
3013	61,32	60,62	60,33
3014	73	72,3	71,7
3015	63,6	64,9	68,7
3016	39,91	36,38	35,93
3017	63,5	51,3	62,7
3018	70,8	70,2	71,2
3019	67,6	67,6	67,6
3020	67,1	60,5	63,8
3021	64,58	63,85	65,36
3022	66,12	66,37	66,42
3024	67,21	68,03	67,73
3025	64,7	64,6	64,4
3026	67,2	66,8	66,4
3027	93,8	93,5	99,6

Chrysene (CHR)

Figure 26: Individual results of replicate measurements (▲)of CHR in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 118,1 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

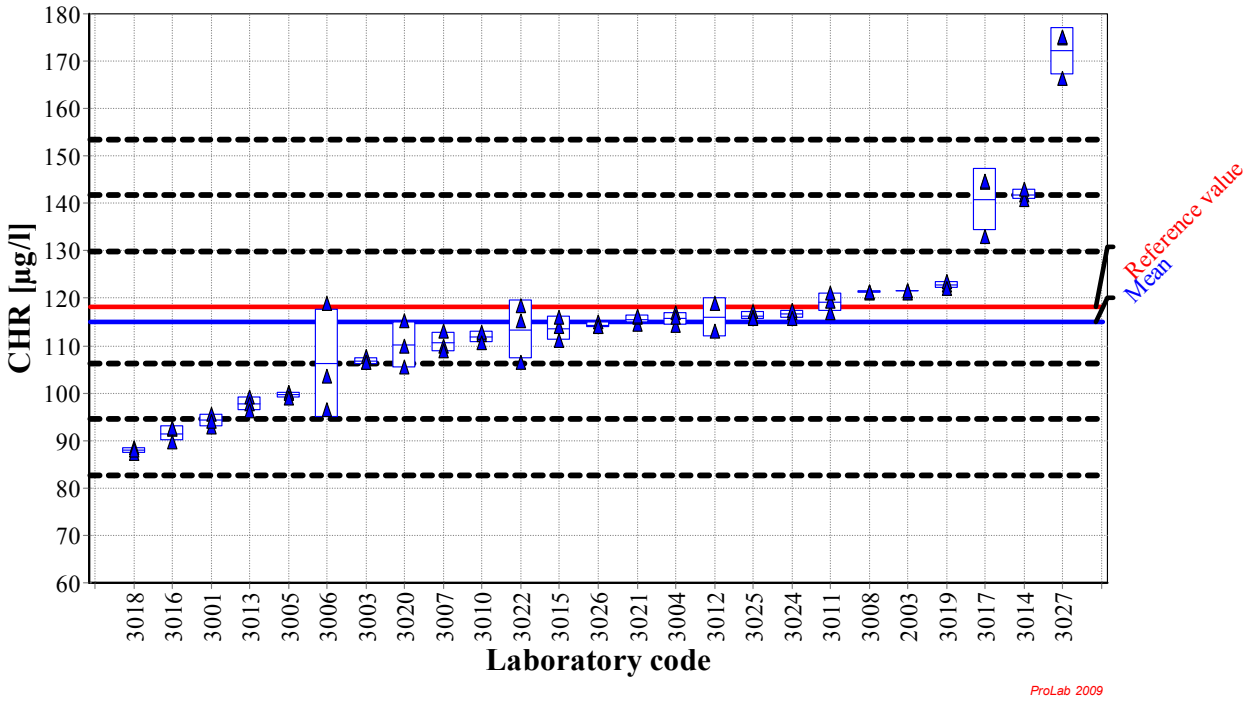

Figure 27: Kernel Density Plot

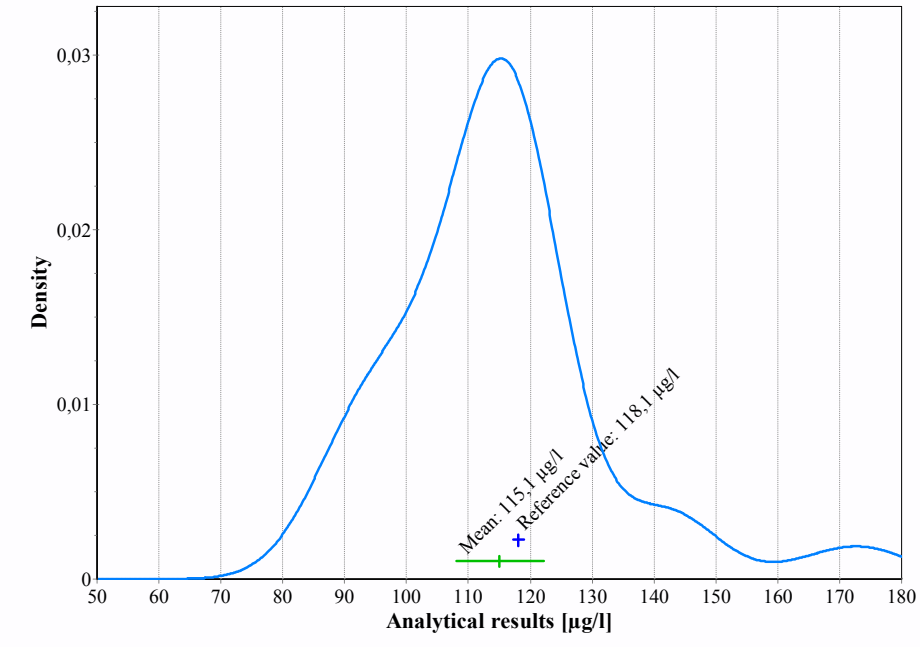

Table 19: Individual results of replicate measurements of CHR in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	121,6	121,2	121,6
3001	92,98	95,64	94,18
3003	107,6	106,4	106,4
3004	116,85	114,24	115,92
3005	100,2	99,8	99
3006	118,8	103,5	96,5
3007	113	110	109
3008	121,1	121,4	121,4
3010	112,44	112,77	110,53
3011	117	119,5	121
3012	113	119	
3013	99,19	97,61	96,32
3014	141,9	140,7	143
3015	111	114	116
3016	92,28	92,63	89,62
3017	144,5	144,7	133,1
3018	88,5	87,3	88
3019	122,8	123,6	122
3020	109,8	115,2	105,6
3021	114,62	115,97	116,23
3022	115,35	118,3	106,43
3024	116,84	117,42	115,74
3025	117,3	116	115,7
3026	114	115	114
3027	174,9	175,2	166,3

Cyclopenta[*cd*]pyrene (CPP)

Figure 28: Individual results of replicate measurements (▲)of CPP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 106,1 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

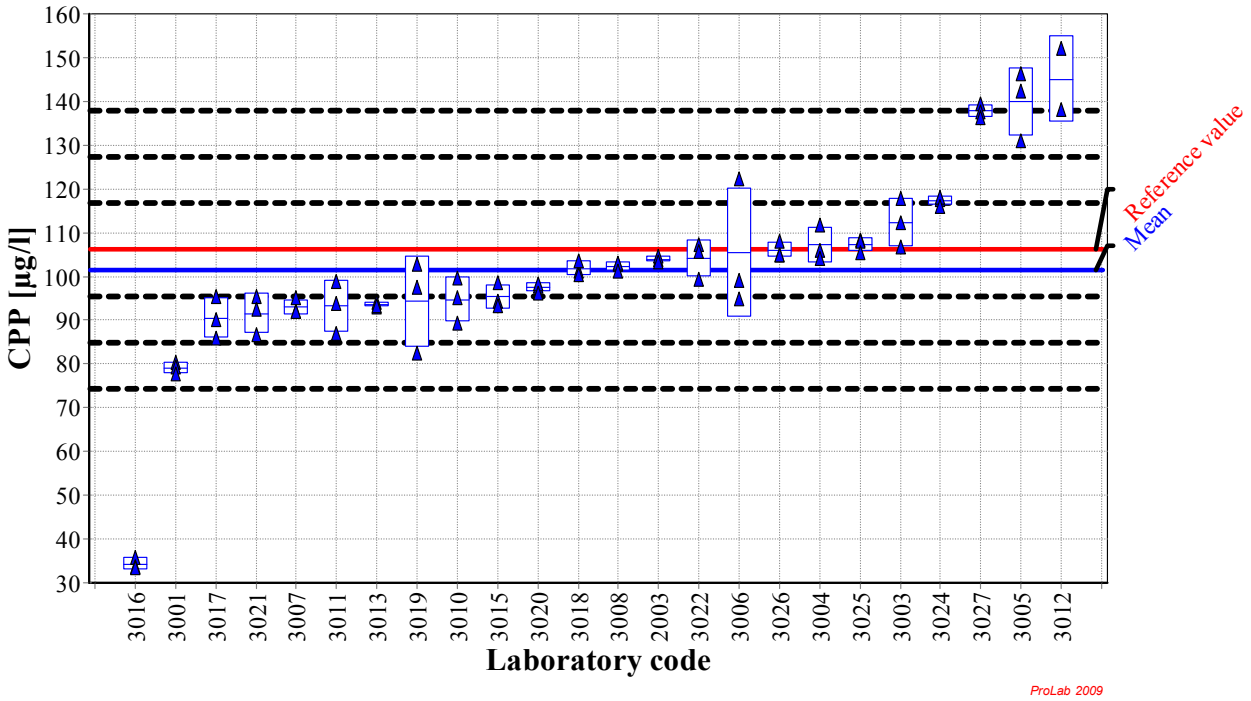

Figure 29: Kernel Density Plot

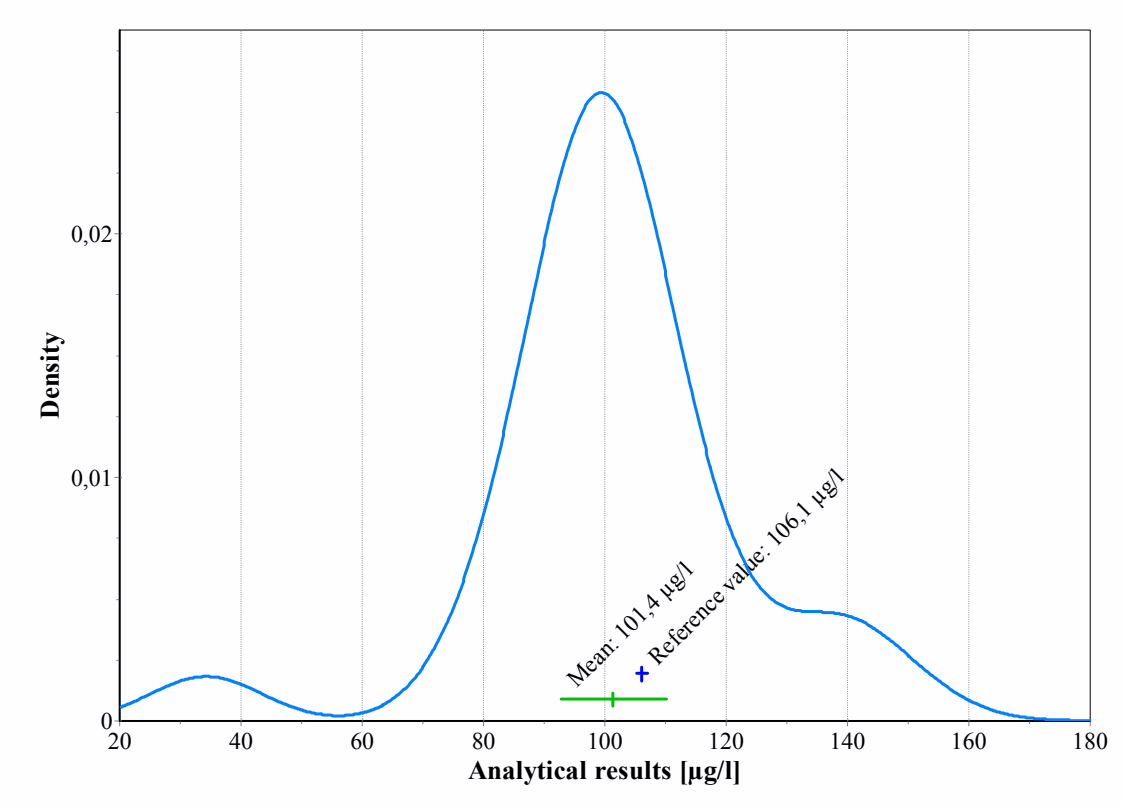

Table 20: Individual results of replicate measurements of CPP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	103,9	104,6	103,2
3001	80,34	79,3	77,77
3003	112,4	117,8	106,8
3004	111,86	105,85	103,98
3005	146,2	142,3	131,1
3006	99,1	94,8	122,2
3007	95	92	92
3008	102,7	103,1	101,1
3010	95,23	99,51	89,35
3011	87	98,7	93,8
3012	138	152	
3013	94,15	93,12	93,16
3014			
3015	94,4	93,2	98,5
3016	35,91	33,63	33,34
3017	86	90,2	95,3
3018	101,3	100,3	103,7
3019	82,6	102,8	97,4
3020	97,9	98,2	96,2
3021	86,58	95,49	92,5
3022	107,33	105,66	99,42
3024	117,48	118,14	116,06
3025	108,4	108,1	105,5
3026	108	105	105
3027	139,4	137,5	136,3

Dibenzo[*a*,*e*]pyrene (DeP)

Figure 30: Individual results of replicate measurements (▲)of DeP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 102,9 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

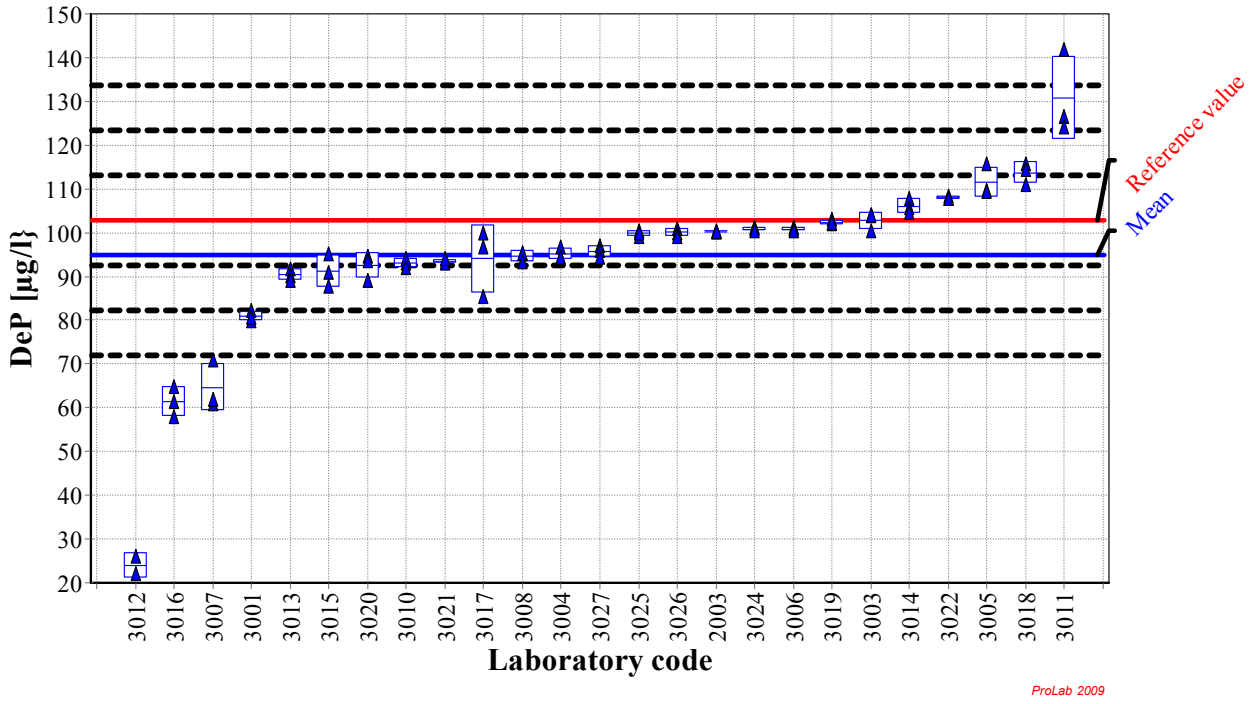

Figure 31: Kernel Density Plot

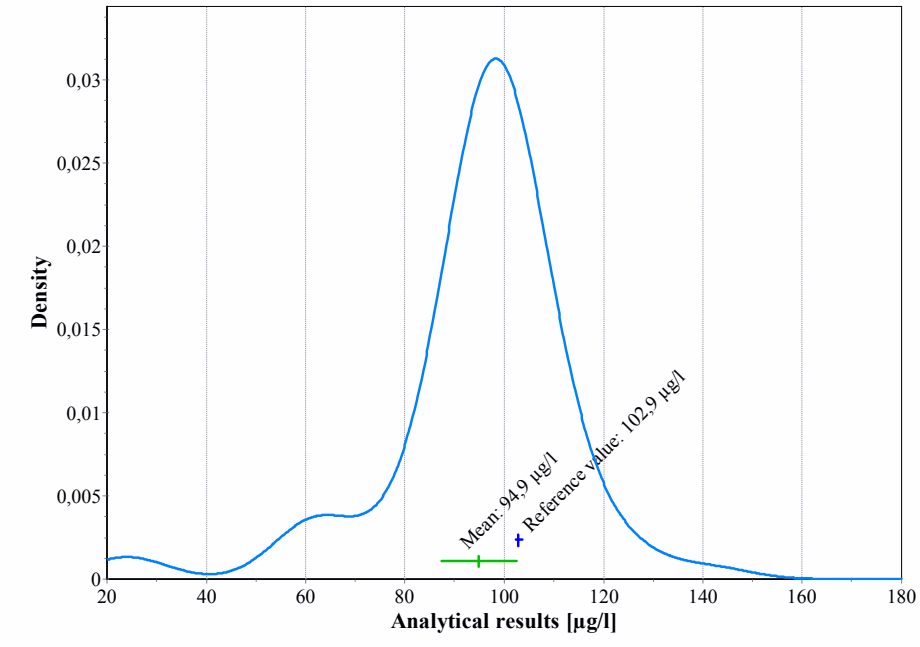

Table 21: Individual results of replicate measurements of DeP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	100,4	100,2	100,2
3001	79,84	82,13	80,78
3003	100,4	103,8	104
3004	96,75	94,44	94,47
3005	109,6	109,3	115,6
3006	101,1	100,9	100,4
3007	71	61	62
3008	95,2	95,5	93,2
3010	93,07	94	91,92
3011	141,7	126,5	124,2
3012	26	22	
3013	91,77	90,04	89,2
3014	107,9	105,6	104,7
3015	91	95,1	87,7
3016	64,89	57,9	61,38
3017	96,7	85,3	100
3018	115,8	111	114,4
3019	103	102	102,2
3020	94,5	93,7	89,1
3021	93,23	93,04	93,99
3022	107,7	108,45	107,73
3024	100,87	101,09	100,32
3025	100,5	99,2	99,8
3026	101	100	99,2
3027	96,9	95,9	94,4

Dibenzo[*a*,*h*]anthracene (DhA)

Figure 32: Individual results of replicate measurements (▲)of DhA in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 75,0 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

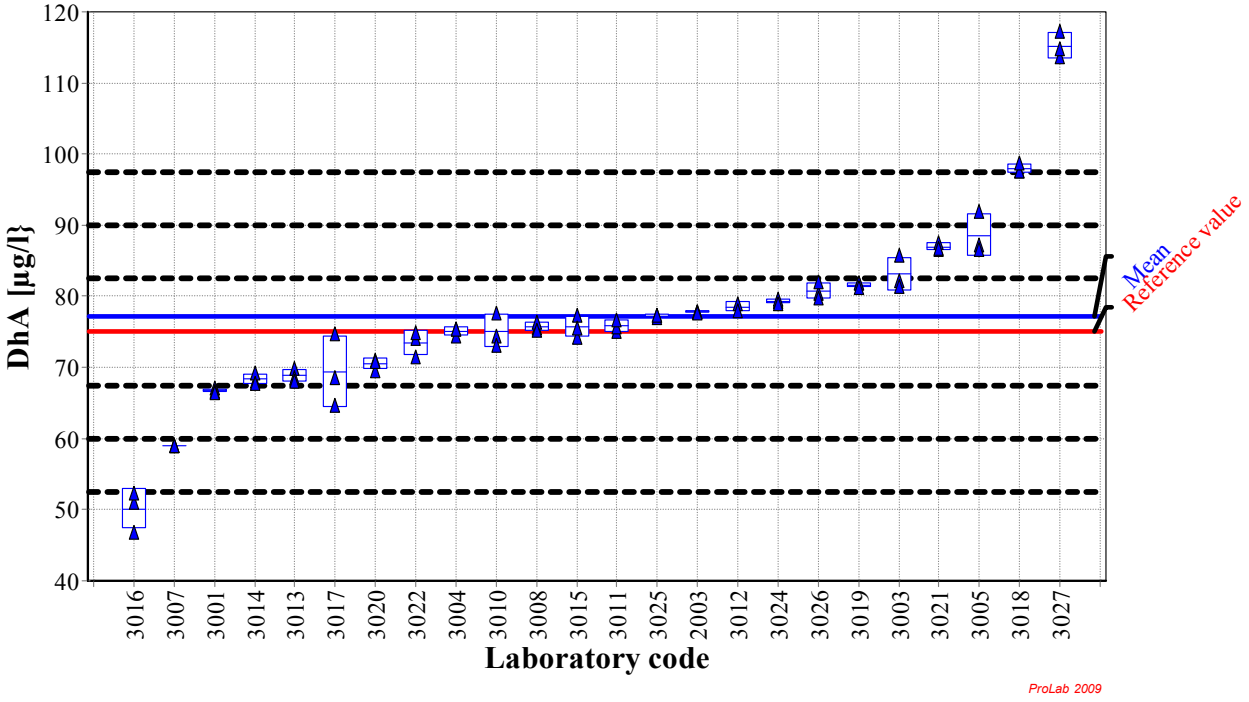

Figure 33: Kernel Density Plot

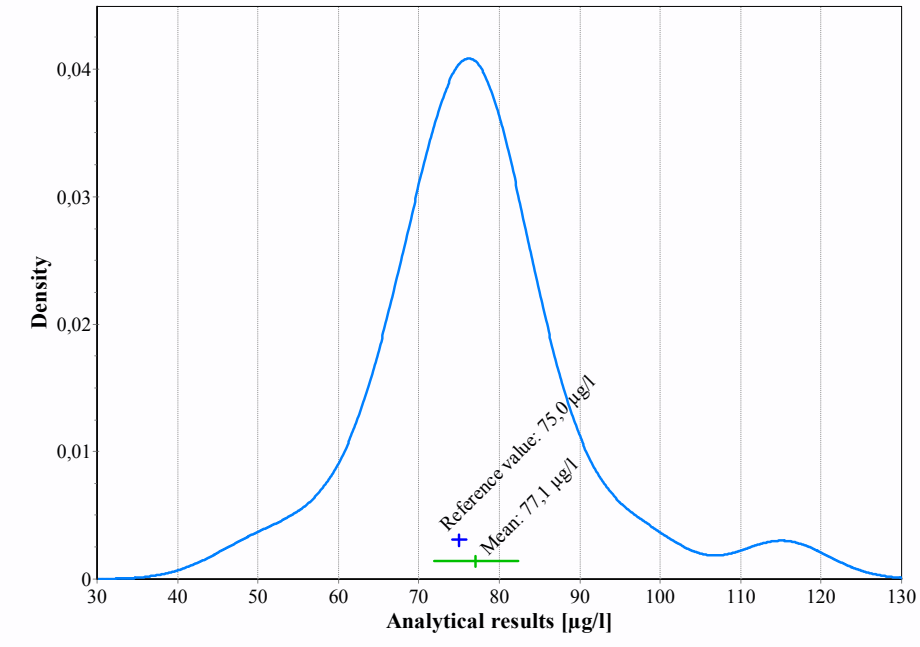

Table 22: Individual results of replicate measurements of DhA in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	77,88	77,85	77,68
3001	67,02	66,62	66,49
3003	85,8	82,2	81,4
3004	75,36	74,36	75,45
3005	87,2	86,6	92
3006			
3007	59	59	59
3008	75,5	76,4	75,2
3010	77,7	74,41	73,15
3011	75	75,7	76,7
3012	79	78	
3013	69,83	68,55	68,1
3014	68,1	69,2	67,7
3015	74,3	77,3	75,5
3016	50,96	46,89	52,38
3017	68,6	64,7	74,7
3018	97,6	97,6	98,7
3019	81,8	81,8	81,2
3020	69,5	71	70,9
3021	87,59	86,56	86,68
3022	74,13	74,83	71,47
3024	79,31	79,64	78,98
3025	77,4	77	77,3
3026	80,4	79,8	82
3027	113,6	114,8	117,2

Dibenzo[*a*,*h*]pyrene (DhP)

Figure 34: Individual results of replicate measurements (▲)of DhP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 159,9 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

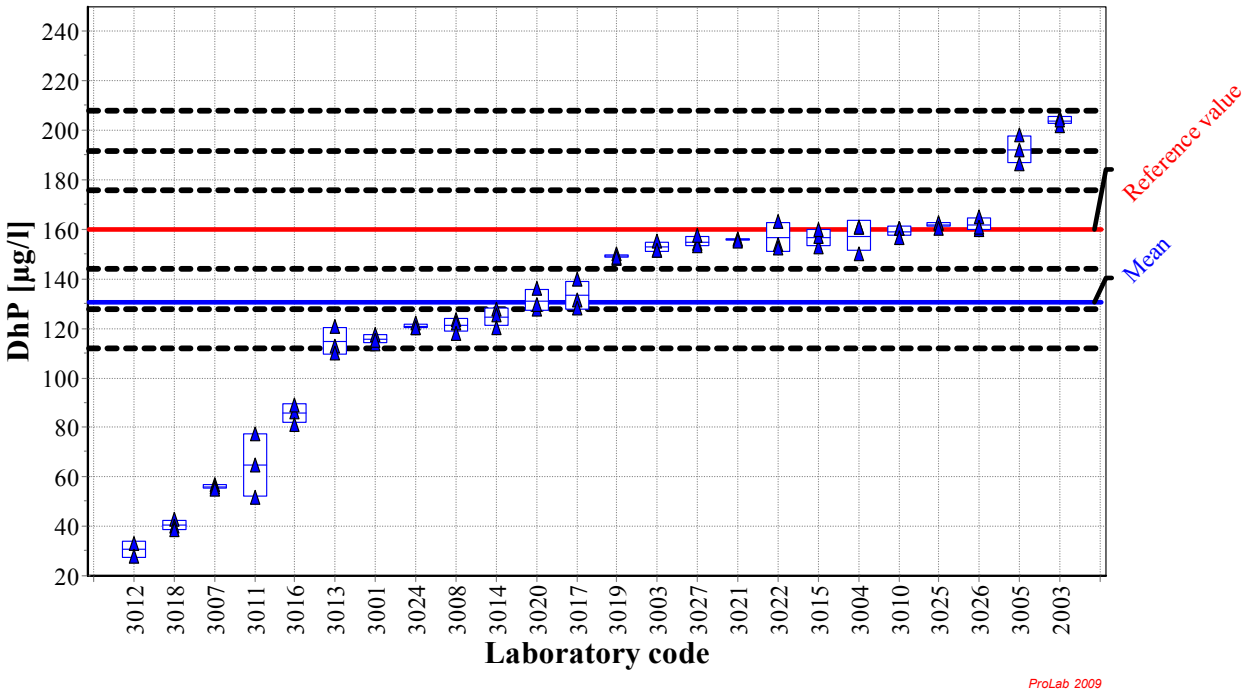

Figure 35: Kernel Density Plot

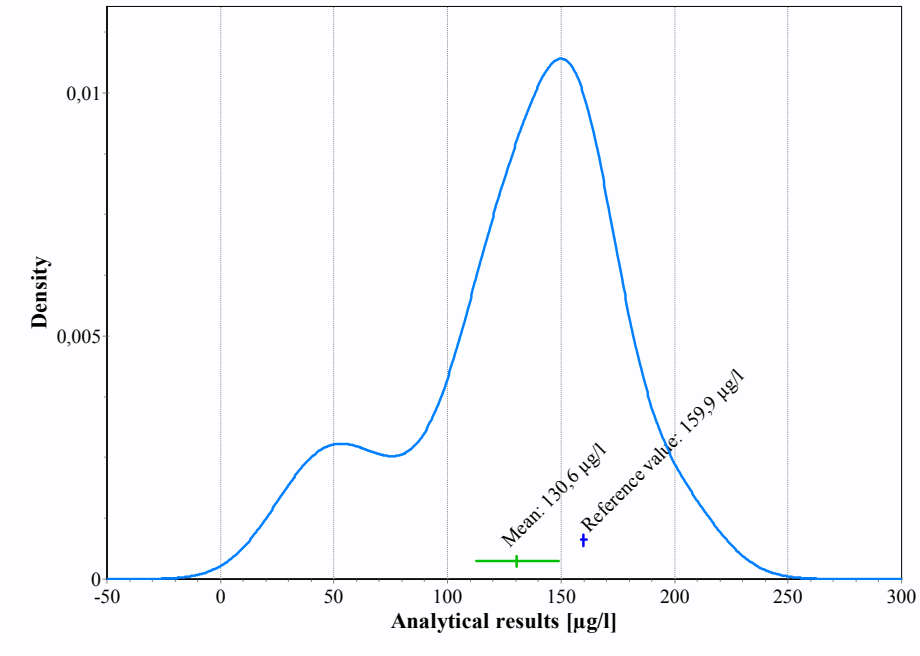

Table 23: Individual results of replicate measurements of DhP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	202,1	205,2	204,5
3001	117,63	113,89	115,07
3003	151,6	155,2	151,4
3004	160,86	149,99	161,03
3005	186,7	192	198,1
3006			
3007	57	56	55
3008	123,5	122,3	117,9
3010	160,39	160,21	156,6
3011	51,6	77,3	65
3012	33	28	
3013	120,84	113,05	110,16
3014	127,7	125,4	120,3
3015	153	157	160
3016	86,4	81,3	89,14
3017	131,5	128,4	139,8
3018	42,8	40	38,5
3019	150	148,2	148,8
3020	127,8	129,7	136,3
3021	156,4	155,71	155,48
3022	154,06	152,28	163,44
3024	120,3	121,94	120,34
3025	162,2	162,7	160,6
3026	160	165	161
3027	154,4	153,2	157,4

Dibenzo[*a*,*i*]pyrene (DiP)

Figure 36: Individual results of replicate measurements (▲)of DiP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 19,8 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

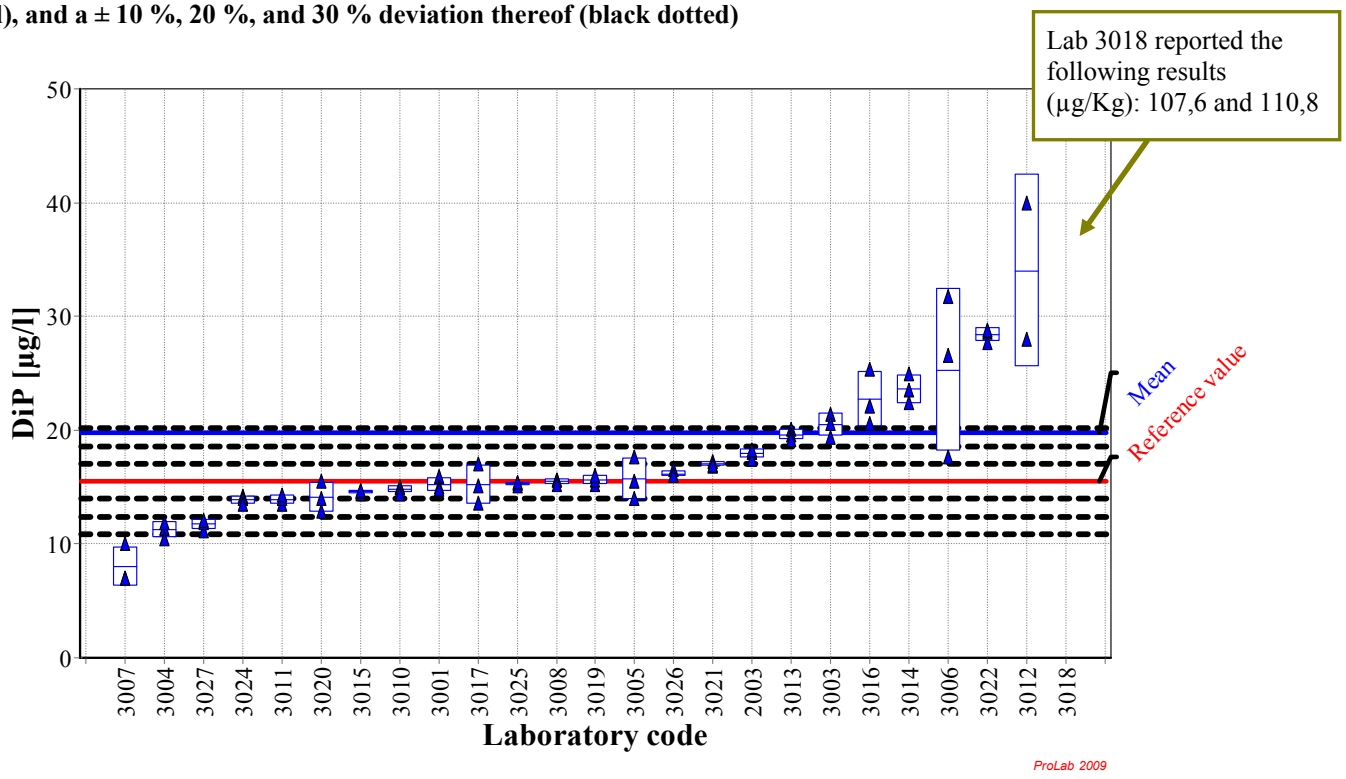

Figure 37: Kernel Density Plot

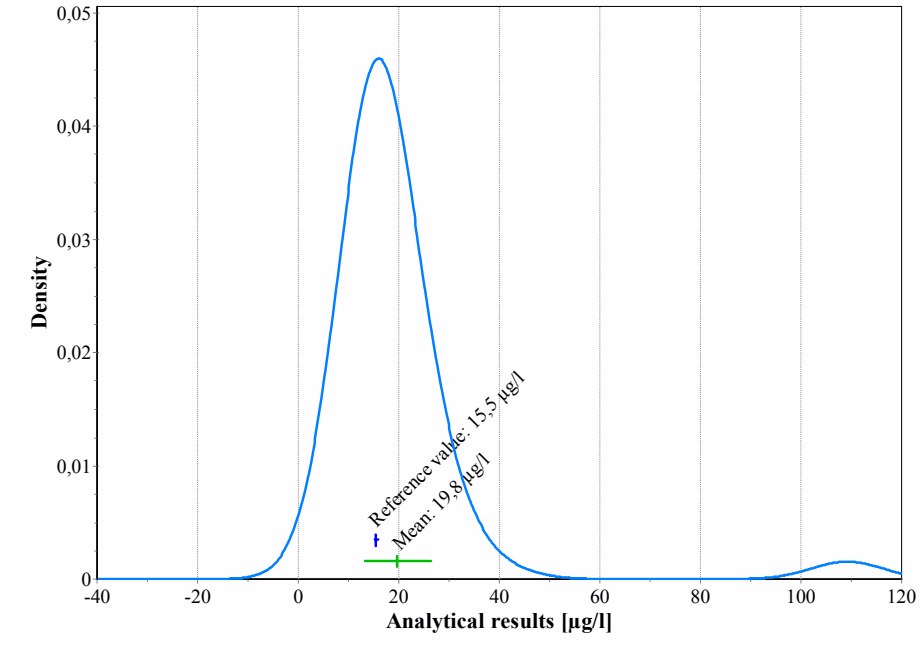

Table 24: Individual results of replicate measurements of DiP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	18,06	17,45	18,27
3001	15,92	14,96	14,82
3003	21,4	20,6	19,4
3004	11,35	11,85	10,49
3005	14	17,6	15,5
3006	17,6	26,6	31,7
3007	10	7	7
3008	15,6	15,6	15,2
3010	15,04	14,92	14,41
3011	13,5	14	14,3
3012	40	28	
3013	20,06	19,56	19,14
3014	24,9	23,5	22,4
3015	14,4	14,6	14,7
3016	25,35	22,15	20,57
3017	13,6	15,1	17
3018	107,6		110,8
3019	15,2	15,6	16
3020	15,5	12,9	14
3021	16,85	17,26	16,93
3022	28,62	27,73	28,83
3024	14,16	14	13,47
3025	15,3	15,1	15,4
3026	16	16,5	16
3027	11,2	11,9	12,1

Dibenzo[*a*,*l*]pyrene (DlP)

Figure 38: Individual results of replicate measurements (▲)of DlP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 72,0 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

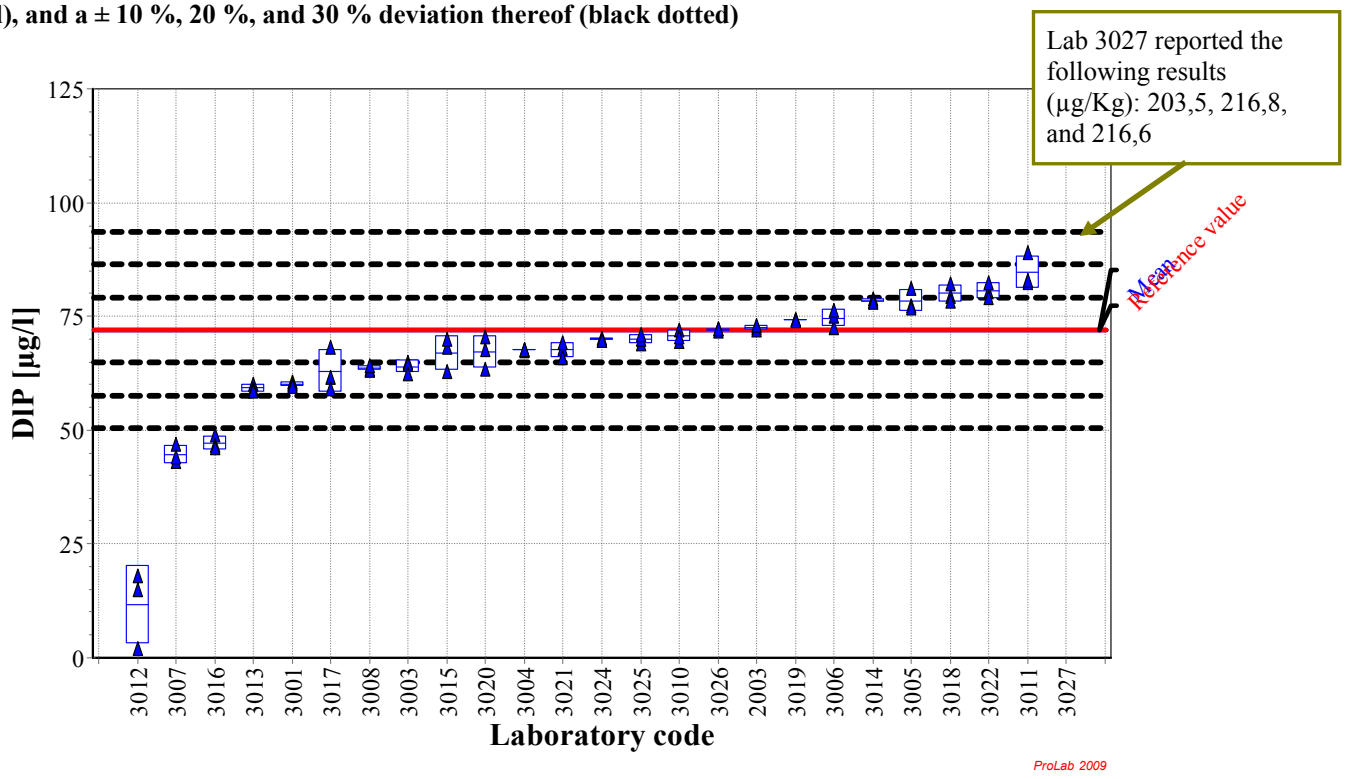

Figure 39: Kernel Density Plot

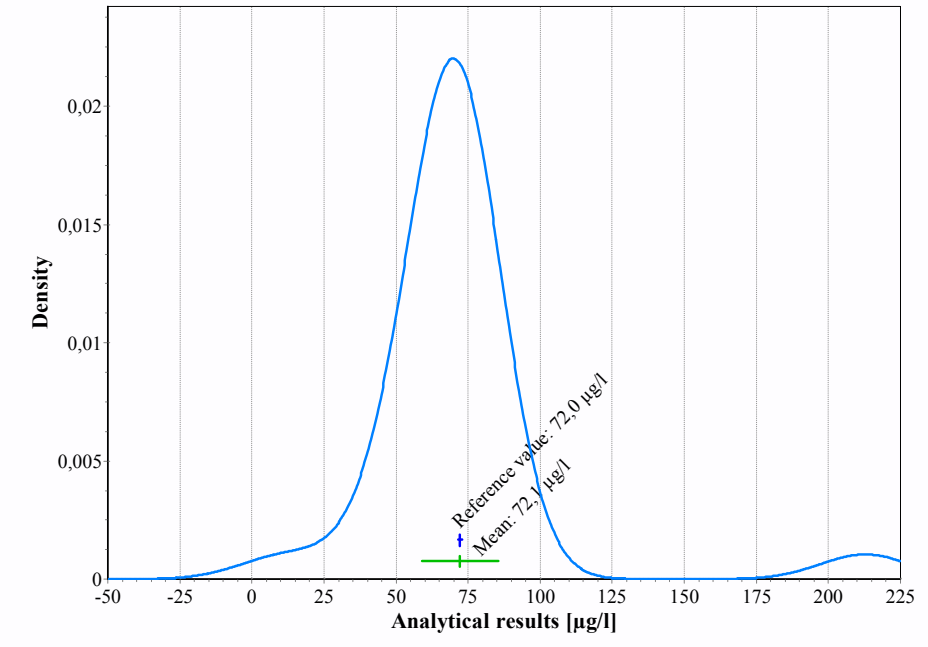

Table 25: Individual results of replicate measurements of DIP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	72,43	72,06	72,93
3001	60,59	59,98	59,53
3003	65	64,4	62,4
3004	67,36	67,59	67,81
3005	77,4	76,8	81,1
3006	72,6	75,1	76,3
3007	47	43	44
3008	63,5	63,2	64,2
3010	69,57	72,13	70,48
3011	88,9	82,4	82,9
3012	18	15	2
3013	60,12	58,98	58,52
3014	78,8	78,4	78
3015	68,2	70,1	62,8
3016	48,99	46,61	46,1
3017	61,6	59	68,2
3018	82,2	79,4	78,4
3019	74,4	74,2	74
3020	70,6	67,6	63,5
3021	67,99	65,85	69,16
3022	80,43	82,41	79,09
3024	69,82	70,35	69,83
3025	69	70	71
3026	72,3	71,8	72,2
3027	203,5	216,8	216,6

Indeno[1,2,3-*cd*]pyrene (IcP)

Figure 40: Individual results of replicate measurements (▲)of IcP in acetonitrile, sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 41,2 µg/l (red), and a ± 10 %, 20 %, and 30 % deviation thereof (black dotted)

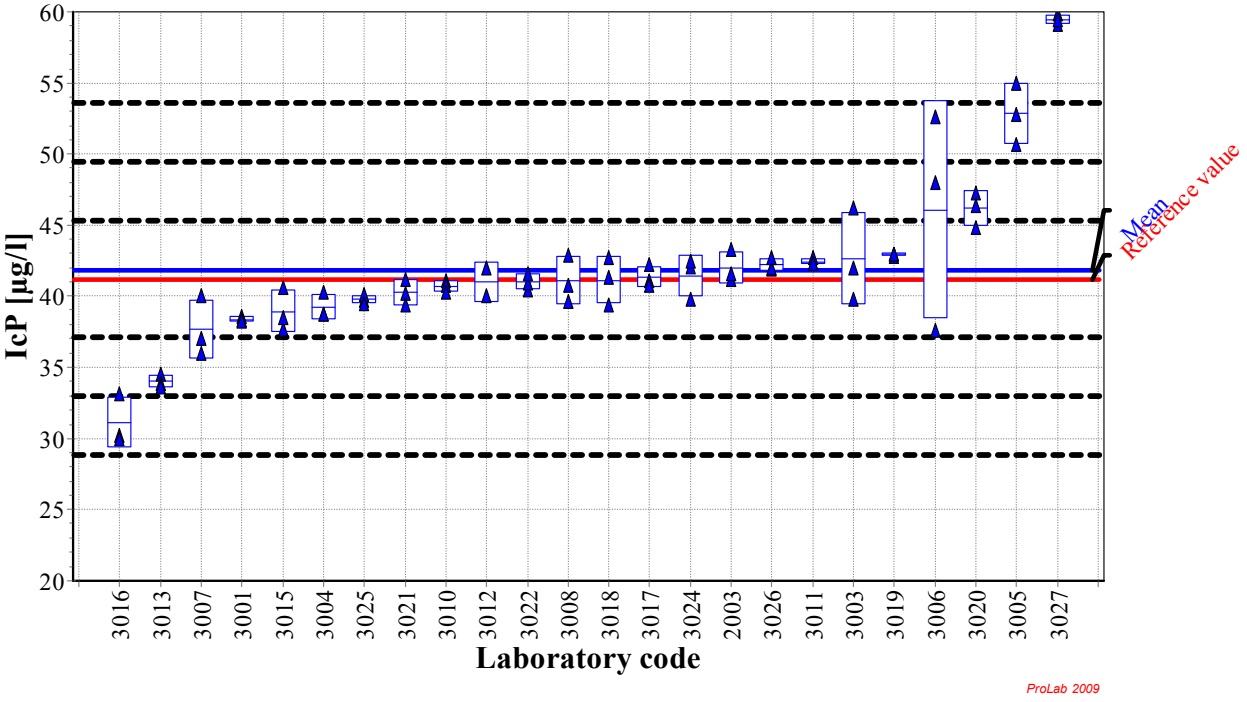

Figure 41: Kernel Density Plot

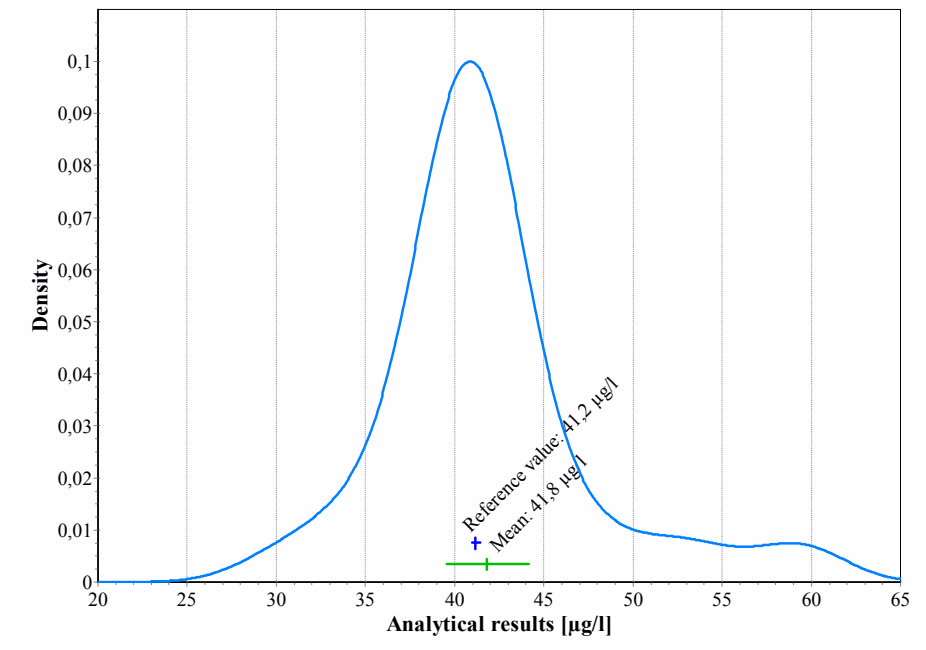

Table 26: Individual results of replicate measurements of IcP in ACN in µg/l (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3
2003	41,18	41,56	43,3
3001	38,58	38,3	38,25
3003	46,2	42	39,8
3004	38,74	38,73	40,25
3005	52,8	55	50,7
3006	37,6	52,6	48
3007	37	40	36
3008	39,6	42,9	40,8
3010	41,09	40,78	40,26
3011	42,3	42,7	42,3
3012	42	40	
3013	34,52	33,91	33,65
3014			
3015	37,7	40,6	38,5
3016	30,2	33,18	29,95
3017	41,1	42,2	40,8
3018	42,7	41,3	39,4
3019	42,8	43	43
3020	47,3	46,4	44,8
3021	40,2	39,37	41,2
3022	40,48	40,95	41,57
3024	39,76	42,08	42,47
3025	39,7	40,1	39,5
3026	41,9	42	42,7
3027	59,8	59,1	59,4

Annex 3: Data for the determination of the 15+1 Eu priority PAHs in test sample Fish C

5-Methylchrysene (5MC)

Figure 42: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 4,8 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

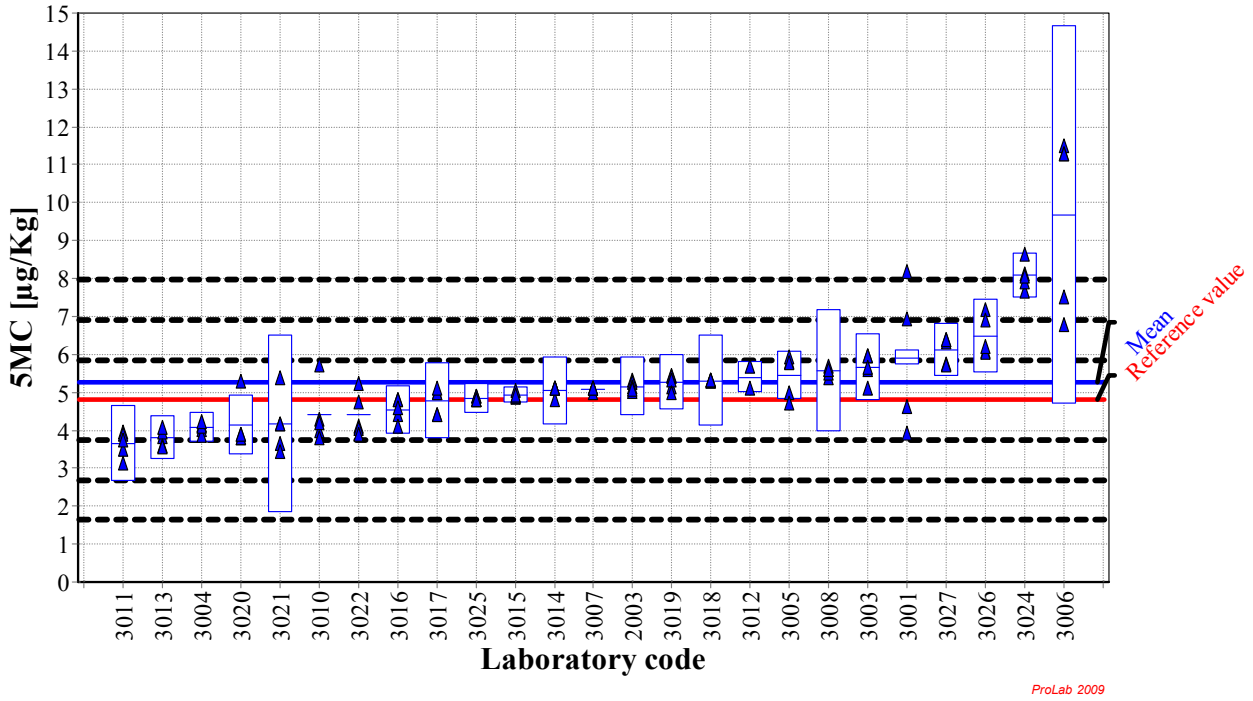

Figure 43: Kernel Density Plot

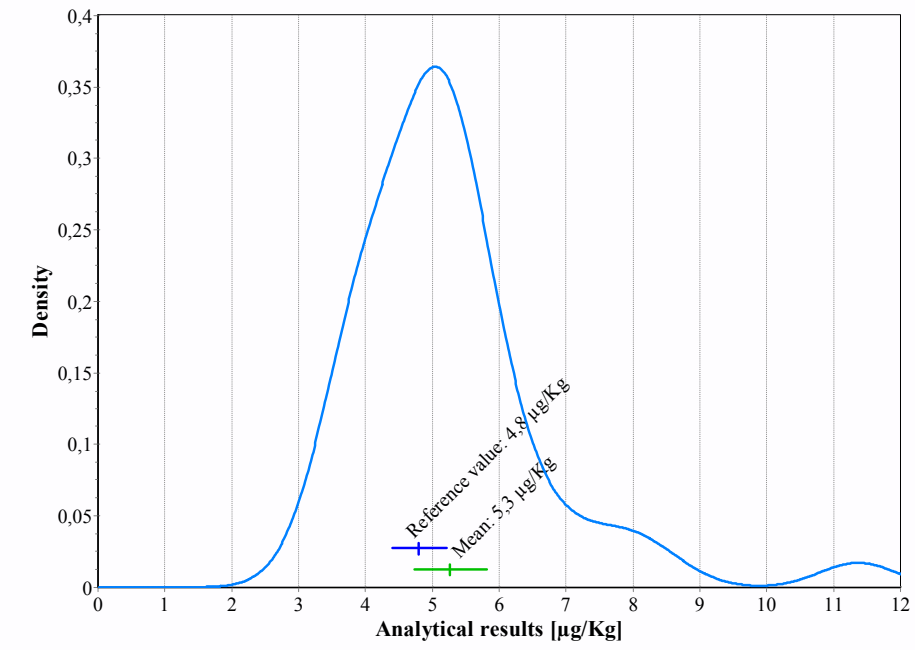

Table 27: Individual results of replicate measurements of 5MC in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,31	5,25	5,01	5,13	5,08	5,16	0,77
3001	4,61	6,94	3,93		8,18	5,77	0,2
3003	5,1	5,95	5,6	5,97	5,66	5,66	0,89
3004	4,01	4,15	3,87	4,12	4,23	4,07	0,4
3005	5,8	5,94	5	4,71	5,78	5,45	0,64
3006	6,8	7,5	11,5	11,3	11,3	9,7	5
3007	5,1	5,1	5	5,1	5,1	5,08	
3008	5,4	5,6	5,5	5,7	5,6	5,5	1,6
3010	4	3,79	4,3	4,19	5,72	4,4	
3011	3,51	3,96	3,89	3,12	3,74	3,64	1
3012	5,1	5,7				5,4	0,4
3013	3,83	3,96	3,6	4,08	3,57	3,81	0,57
3014	5,1	4,8	5,1	5,1	5,1	5	0,9
3015	4,87	4,89	4,91	5,04	4,94	4,93	0,21
3016	4,4	4,8	4,8	4,6	4,1	4,5	0,63
3017	4,4	5	4,4	5	5,1	4,8	1
3018	5,29	5,3	5,32	5,31	5,31	5,31	1,2
3019	5,13	5,45	5,43	5,33	4,98	4,77	0,66
3020	5,3	3,8	3,9	3,8	3,9	4,2	0,8
3021	4,17	4,18	5,39	3,66	3,43	3,99	2,24
3022	5,23	4,1	4,05	3,89	4,76	4,1	
3024	8,64	7,67	7,91	8,11	8,07	8,08	0,59
3025	4,8	4,8	4,9	4,9	4,8	4,8	0,4
3026	7,17	6,92	6,08	6,05	6,22	6,49	0,97
3027	6,4	5,75	6,32	6,39	5,72	6,12	0,69

Benzo[*a*]anthracene (BaA)

Figure 44: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 4,8 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

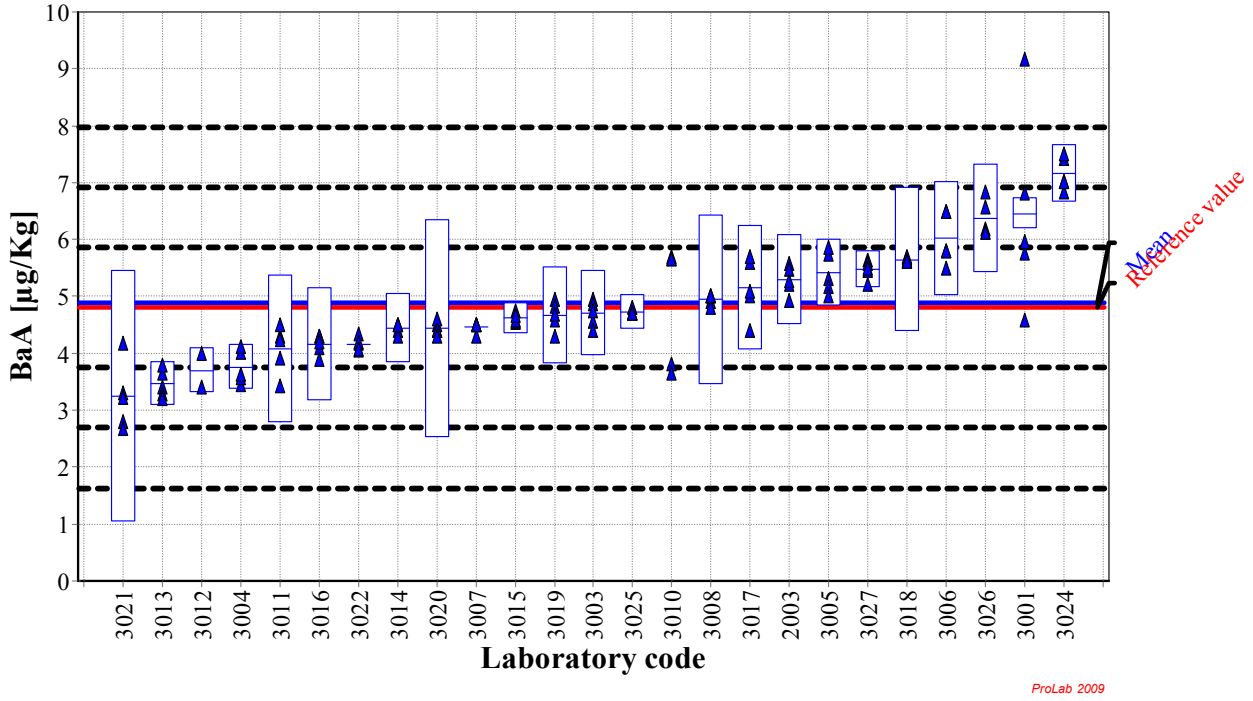

Figure 45: Kernel Density Plot

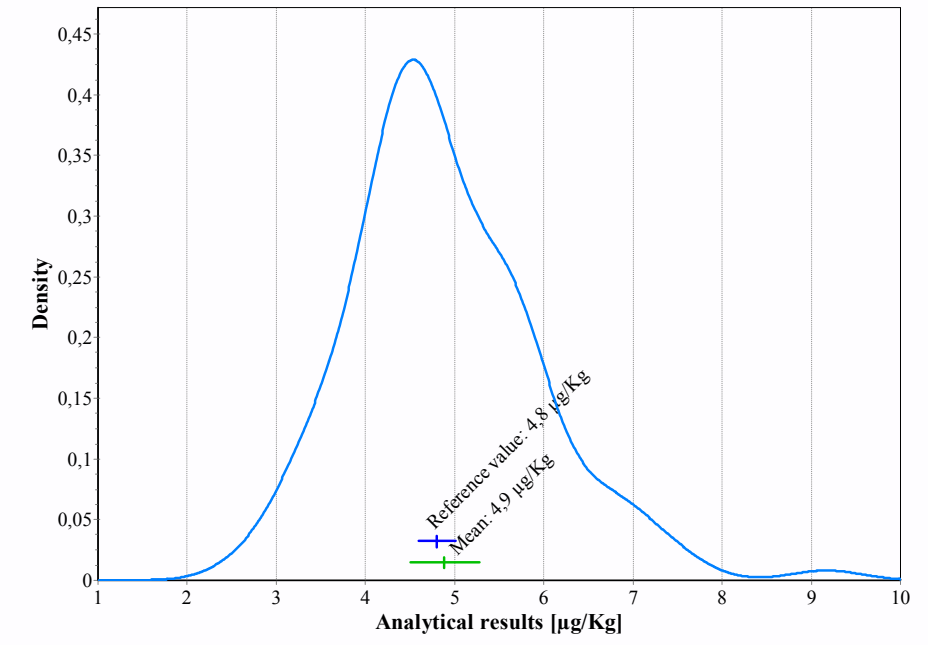

Table 28: Individual results of replicate measurements of BaA in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,58	5,48	5,21	4,92	5,28	5,39	0,81
3001	5,76	6,82	4,59	5,96	9,17	5,96	0,25
3003	4,95	4,87	4,57	4,75	4,4	4,71	0,75
3004	3,45	3,58	3,63	4,02	4,11	3,76	0,4
3005	5,32	5,75	5,18	5	5,86	5,42	0,59
3006	5,5	5,8	5,8	6,5	6,5	6	1
3007	4,5	4,3	4,5	4,5	4,5	4,46	
3008	4,9	5	4,8	5	5	5	1,5
3010	5,69	5,65	3,81	3,66	5,65	4,89	
3011	3,91	4,3	4,23	3,42	4,5	4,07	1,3
3012	3,4	4				3,7	0,4
3013	3,4	3,65	3,29	3,8	3,2	3,47	0,38
3014	4,5	4,4	4,5	4,3	4,5	4,4	0,6
3015	4,54	4,56	4,59	4,74	4,66	4,62	0,27
3016	4,3	4,1	3,9	4,3	4,2	4,2	1
3017	5	5,1	4,4	5,6	5,7	5,2	1,1
3018	5,63	5,61	5,67	5,69	5,62	5,64	1,27
3019	4,59	4,95	4,82	4,69	4,31	4,49	0,82
3020	4,5	4,6	4,4	4,4	4,3	4,4	1,9
3021	3,31	3,23	4,18	2,8	2,68	3,1	2,11
3022	4,34	4,06	4,17	4,2	4,07	4,17	
3024	7,02	6,83	7,02	7,43	7,51	7,16	0,51
3025	4,7	4,8	4,7	4,7	4,7	4,7	0,3
3026	6,83	6,58	6,18	6,13	6,12	6,37	0,96
3027	5,64	5,57	5,46	5,49	5,22	5,47	0,32

Benzo[*a*]pyrene (BaP)

Figure 46: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,6 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

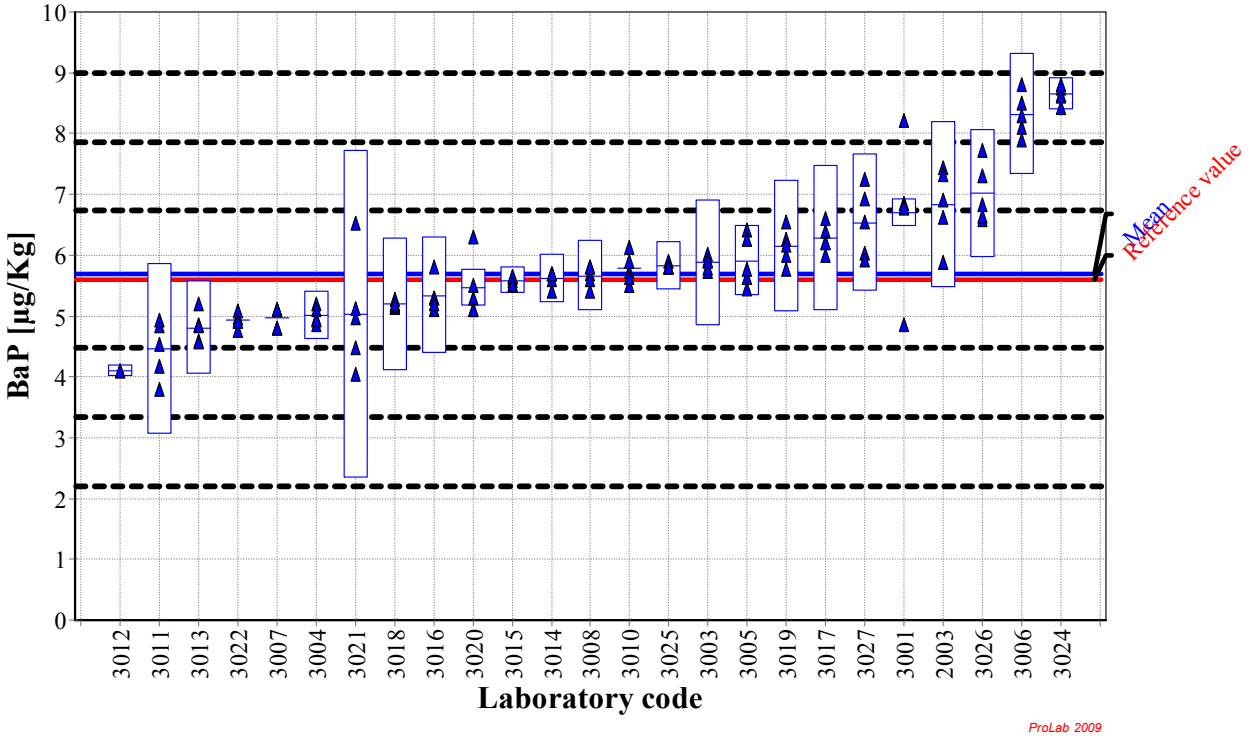

Figure 47: Kernel Density Plot

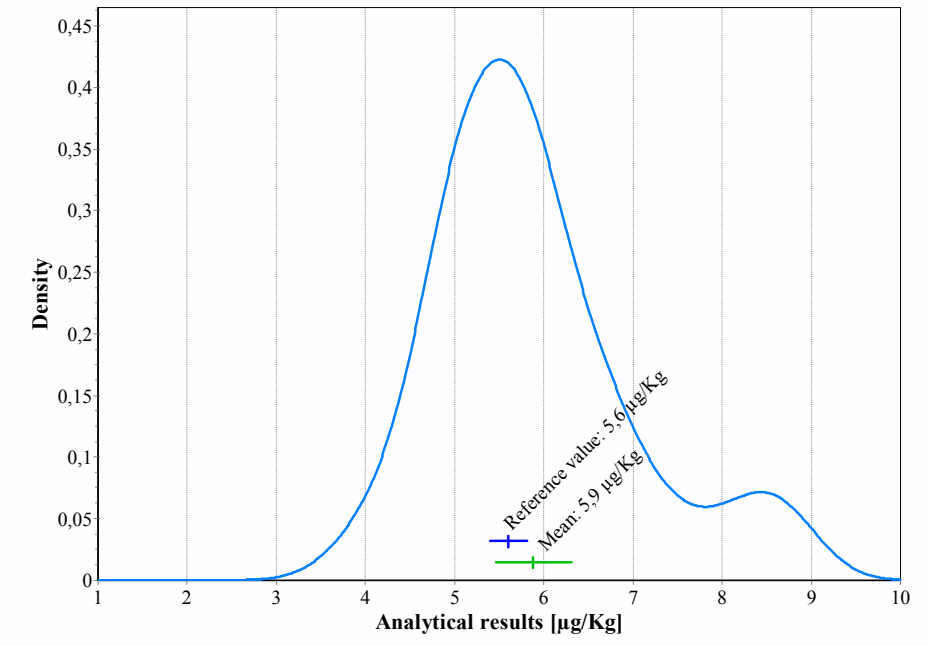

Table 29: Individual results of replicate measurements of BaP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	7,43	7,32	6,63	6,91	5,88	7,07	1,41
3001	6,78	6,85	4,85	6,8	8,22	6,8	0,24
3003	5,92	6,01	5,74	5,79	5,91	5,87	1,04
3004	4,86	4,96	5,2	5,11	4,94	5,01	0,4
3005	5,63	6,41	5,77	5,44	6,27	5,91	0,58
3006	8,1	8,8	8,5	8,3	7,9	8,3	1
3007	5,1	4,8	4,8	5,1	5,1	4,98	
3008	5,8	5,7	5,4	5,6	5,8	5,8	0,6
3010	5,51	5,74	5,91	5,64	6,13	5,79	
3011	4,17	4,83	4,53	3,8	4,94	4,45	1,4
3012	4,1	4,1				4,1	0,1
3013	4,85	4,83	4,6	5,19	4,58	4,81	0,77
3014	5,4	5,6	5,7	5,7	5,7	5,6	0,4
3015	5,5	5,58	5,64	5,66	5,53	5,58	0,22
3016	5,3	5,3	5,1	5,2	5,8	5,3	0,95
3017	6,4	6,2	6,2	6	6,6	6,3	1,2
3018	5,28	5,15	5,14	5,18	5,2	5,19	1,1
3019	5,99	6,55	6,27	6,17	5,77	5,51	0,97
3020	6,3	5,3	5,1	5,5	5,1	5,5	0,3
3021	4,97	5,13	6,52	4,48	4,05	4,82	2,58
3022	4,92	4,76	4,97	5,08	4,91	4,92	
3024	8,64	8,42	8,74	8,62	8,81	8,65	0,27
3025	5,8	5,9	5,8	5,8	5,8	5,8	0,4
3026	7,72	7,3	6,58	6,65	6,83	7,02	1,05
3027	6,92	7,24	6,54	6,03	5,92	6,53	1,13

Benzo[*b*]fluoranthene (BbF)

Figure 48: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,6 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

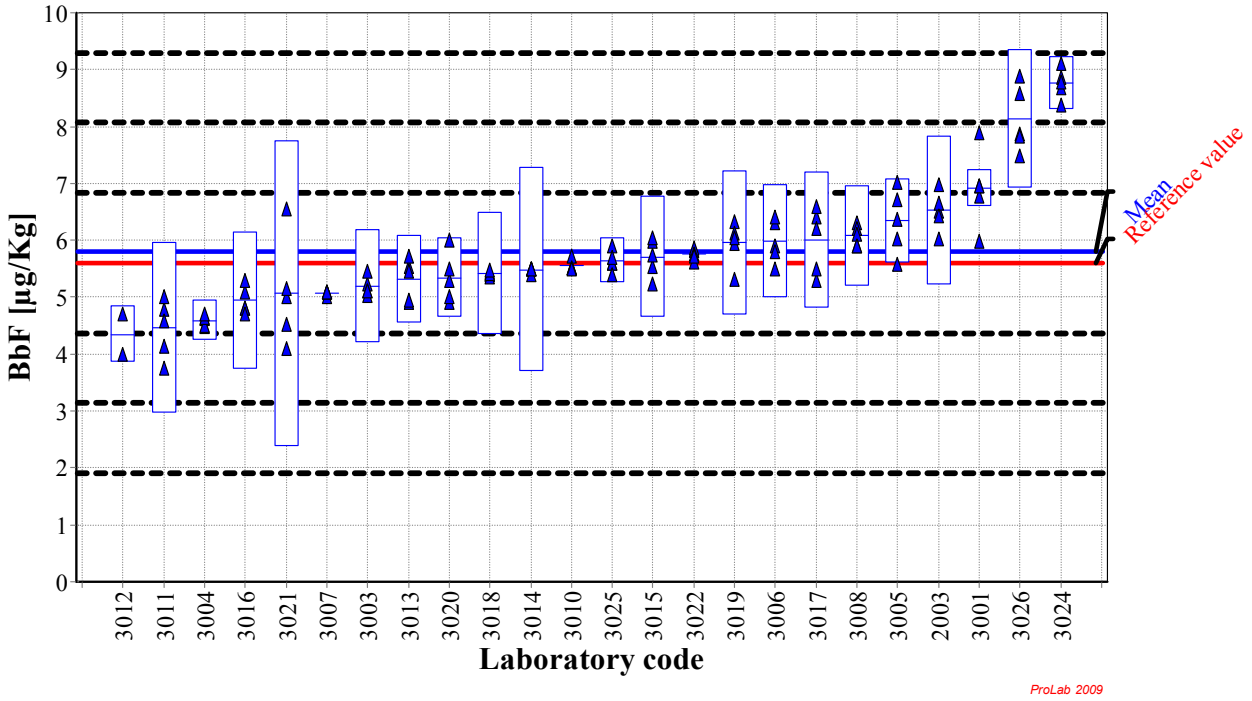

Figure 49: Kernel Density Plot

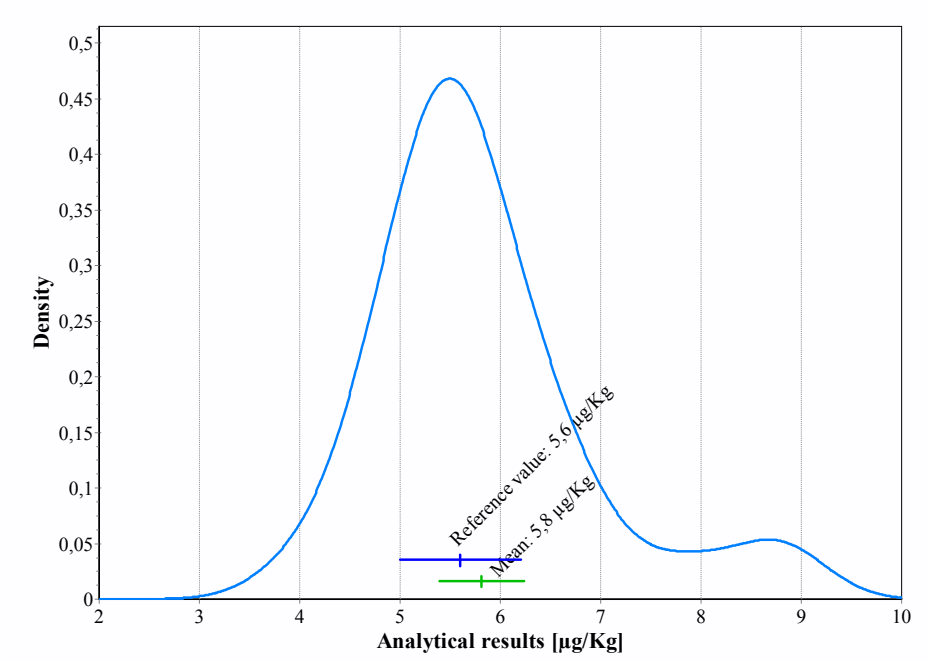

Table 30: Individual results of replicate measurements of BbF in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	6,52	6,65	6,44	6,97	6,03	6,64	1,33
3001	5,99	6,96	6,78	6,95	7,89	6,95	0,32
3003	5,23	5,12	5,04	5,11	5,46	5,19	0,99
3004	4,48	4,63	4,51	4,64	4,7	4,59	0,36
3005	6,36	7,01	6,03	5,58	6,72	6,34	0,75
3006	6,3	6,4	5,9	5,8	5,5	6	1
3007	5,1	5	5,1	5,1	5,1	5,08	
3008	6,3	6,2	5,9	6,1	5,9	6,2	0,9
3010	5,52	5,51	5,72	5,51	5,49	5,55	
3011	4,14	4,79	4,59	3,75	5,01	4,45	1,5
3012	4	4,7				4,3	0,5
3013	4,91	5,53	4,94	5,71	5,45	5,31	0,77
3014	5,5	5,5	5,5	5,4	5,5	5,5	1,8
3015	5,24	5,53	5,74	5,98	6,04	5,71	1,07
3016	4,8	5,1	4,8	4,7	5,3	4,9	1,2
3017	5,3	6,4	5,5	6,6	6,2	6	1,2
3018	5,44	5,4	5,36	5,41	5,47	5,42	1,08
3019	5,95	6,33	6,13	6,05	5,32	5,65	1,2
3020	6	4,9	5,3	5	5,5	5,3	0,7
3021	5	5,15	6,56	4,52	4,09	4,85	2,57
3022	5,82	5,87	5,76	5,61	5,73	5,76	
3024	8,87	8,37	8,68	8,78	9,1	8,76	0,46
3025	5,9	5,6	5,6	5,7	5,4	5,7	0,4
3026	8,88	8,57	7,88	7,82	7,48	8,13	1,22
3027							

Benzo[*c*]fluorene (BcL)

Figure 50: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 4,7 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

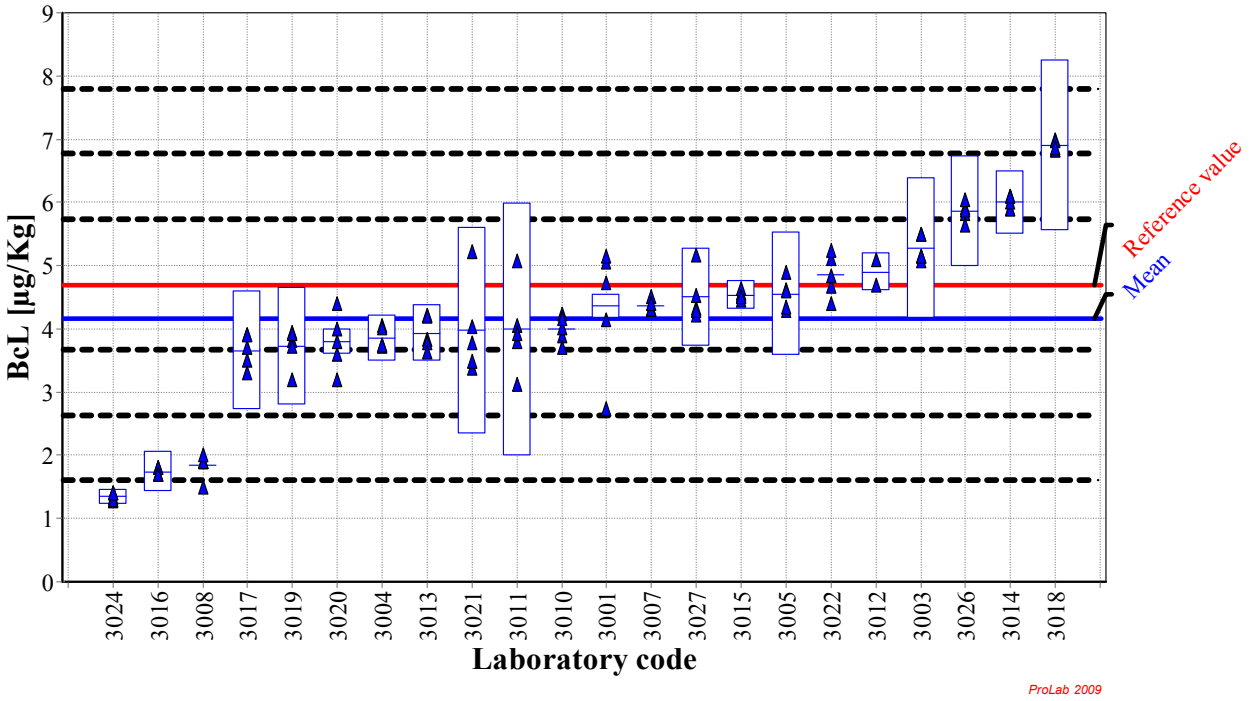

Figure 51: Kernel Density Plot

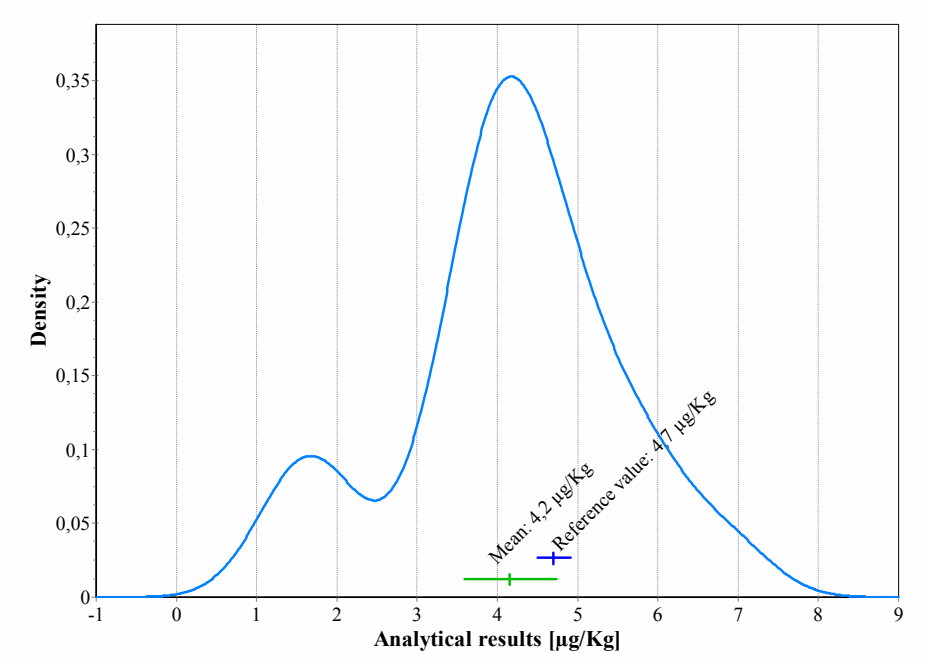

Table 31: Individual results of replicate measurements of BcL in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003							
3001	4,15	5,05	2,73	4,72	5,15	4,72	0,21
3003	5,07	5,15	5,15	5,49	5,5	5,27	1,11
3004	3,74	4,05	3,72	4,02	3,74	3,85	0,37
3005	4,29	4,62	4,6	4,34	4,89	4,55	0,98
3006							
3007	4,3	4,3	4,3	4,5	4,4	4,36	
3008	1,9	1,9	1,5	1,9	2	1,9	
3010	3,88	4,01	3,7	4,23	4,17	4	
3011	3,8	4,06	3,92	3,12	5,07	4	2
3012	4,7	5,1				4,9	0,3
3013	3,83	4,22	3,77	4,2	3,64	3,93	0,44
3014	5,9	5,9	6,1	6	6,1	6	0,5
3015	4,53	4,45	4,56	4,64	4,5	4,54	0,23
3016	1,8	1,8	1,7	1,7	1,7	1,7	0,31
3017	3,5	3,7	3,9	3,3	3,9	3,9	1
3018	6,99	6,83	6,83	6,97	6,87	6,9	1,35
3019	3,81	3,95	3,92	3,73	3,2	4,65	1,16
3020	4	4,4	3,2	3,6	3,8	3,8	0,2
3021	4,04	3,77	5,23	3,37	3,48	3,82	1,57
3022	5,12	4,67	4,4	4,84	5,24	4,84	
3024	1,28	1,34	1,29	1,41	1,4	1,34	0,12
3025							
3026	5,92	5,83	5,65	5,87	6,05	5,86	0,88
3027	5,17	4,22	4,32	4,29	4,52	4,5	0,78

Benzo[*ghi*]perylene (BgP)

Figure 52: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal olid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,5 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

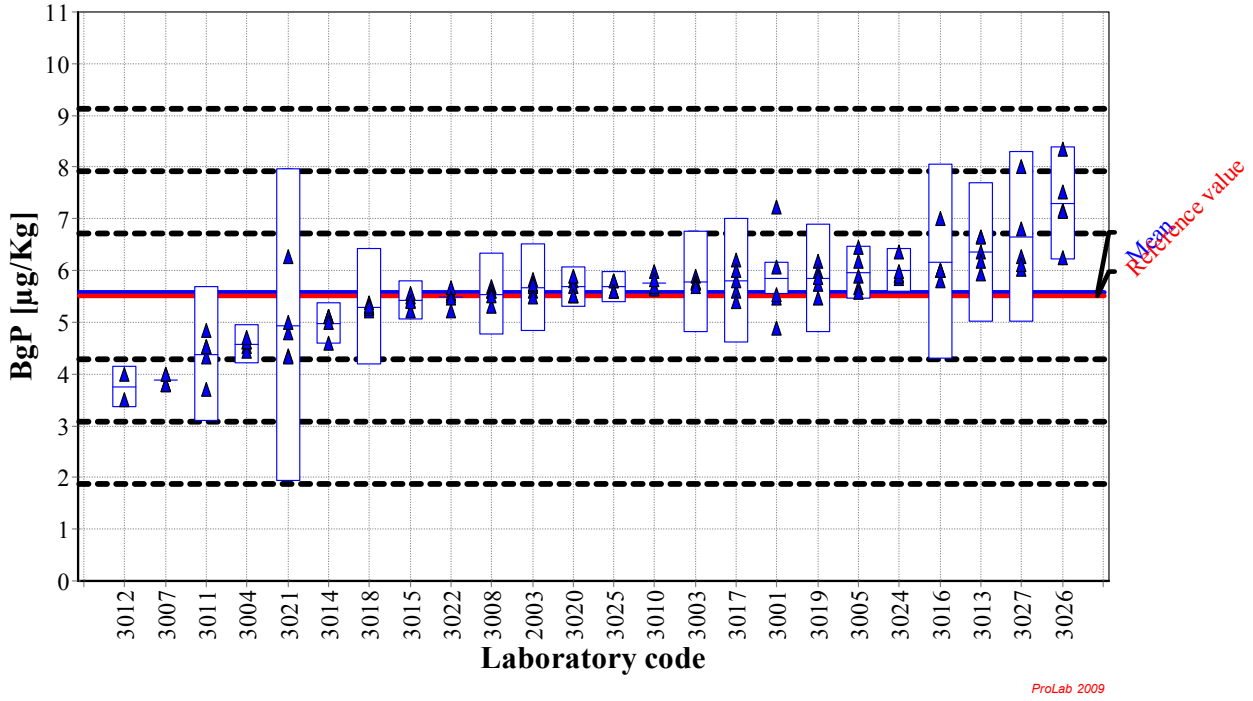

Figure 53: Kernel Density Plot

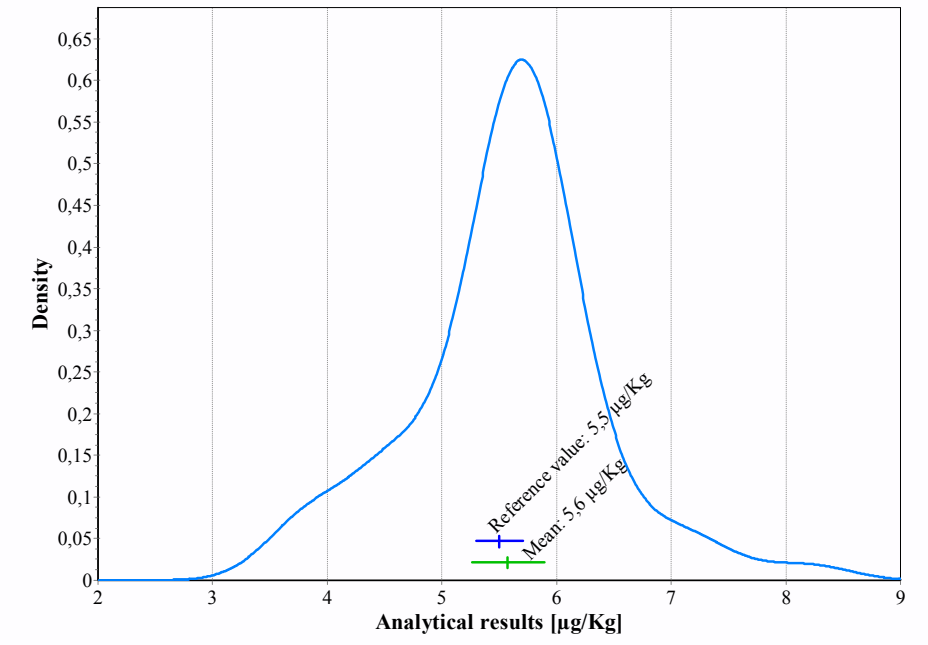

Table 32: Individual results of replicate measurements of BgP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,82	5,59	5,69	5,73	5,48	5,66	0,85
3001	4,89	6,08	5,47	5,54	7,23	5,54	0,3
3003	5,76	5,88	5,77	5,76	5,7	5,77	0,98
3004	4,53	4,61	4,44	4,62	4,71	4,58	0,38
3005	5,89	6,18	5,66	5,57	6,45	5,95	0,51
3006							
3007	4	3,8	3,8	3,8	4	3,88	
3008	5,7	5,6	5,3	5,6	5,5	5,6	0,8
3010	5,65	5,65	5,98	5,69	5,82	5,76	
3011	4,33	4,84	4,52	3,71	4,52	4,38	1,3
3012	4	3,5				3,8	0,4
3013	6,35	5,93	6,65	6,66	6,18	6,35	1,35
3014	5,1	5,1	5,1	5	4,6	5	0,4
3015	5,23	5,42	5,48	5,55	5,39	5,41	0,38
3016	6	5,8	6	6	7	6,2	1,9
3017	5,6	5,8	6,2	6	5,4	5,8	1,2
3018	5,38	5,21	5,32	5,26	5,31	5,3	1,13
3019	5,73	6,19	5,97	5,87	5,46	5,17	0,93
3020	5,8	5,7	5,5	5,9	5,5	5,7	0,4
3021	4,79	4,99	6,26	4,34	4,32	4,73	2,9
3022	5,5	5,55	5,21	5,67	5,47	5,5	
3024	6,36	5,91	5,84	5,88	5,99	6	0,42
3025	5,8	5,8	5,6	5,6	5,6	5,7	0,3
3026	8,35	7,52	7,17	6,25	7,15	7,29	1,09
3027	6,28	6,8	8,02	6,03	6,11	6,65	1,64

Benzo[j]fluoranthene (BjF)

Figure 54: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 4,8 µg/kg (red), a ±1 σ_p, ± 2 σ_p, and ± 3 σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

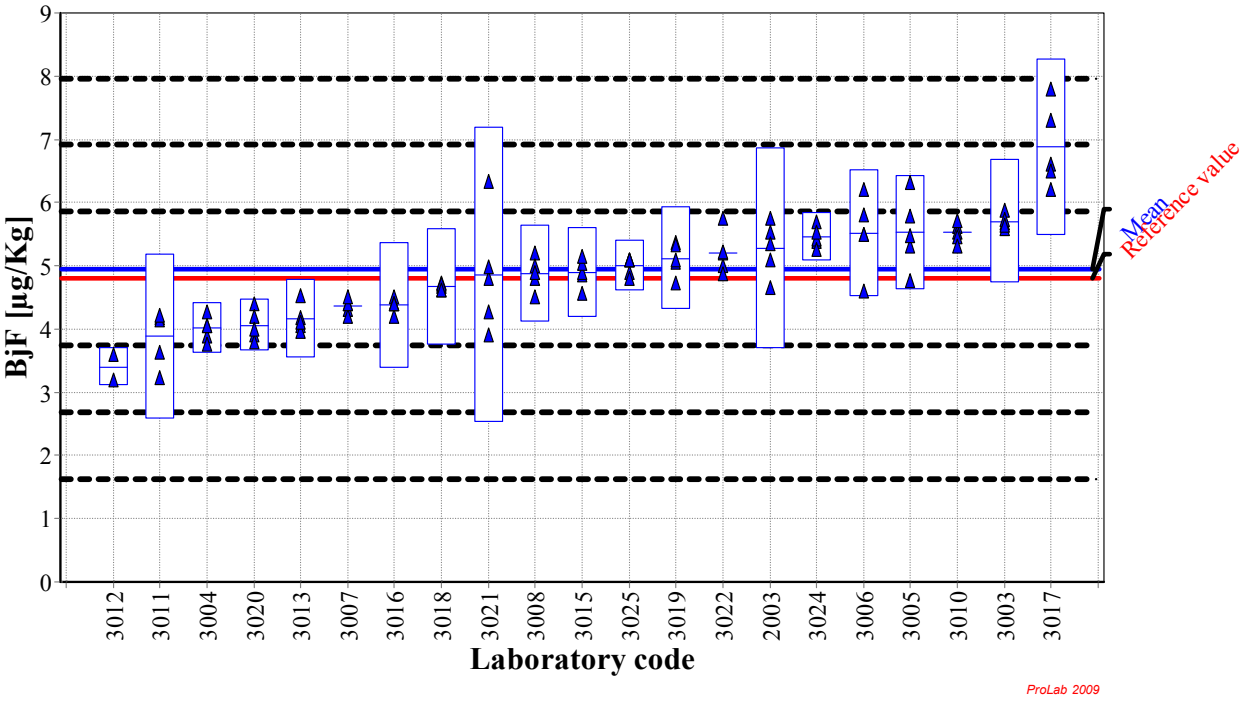

Figure 55: Kernel Density Plot

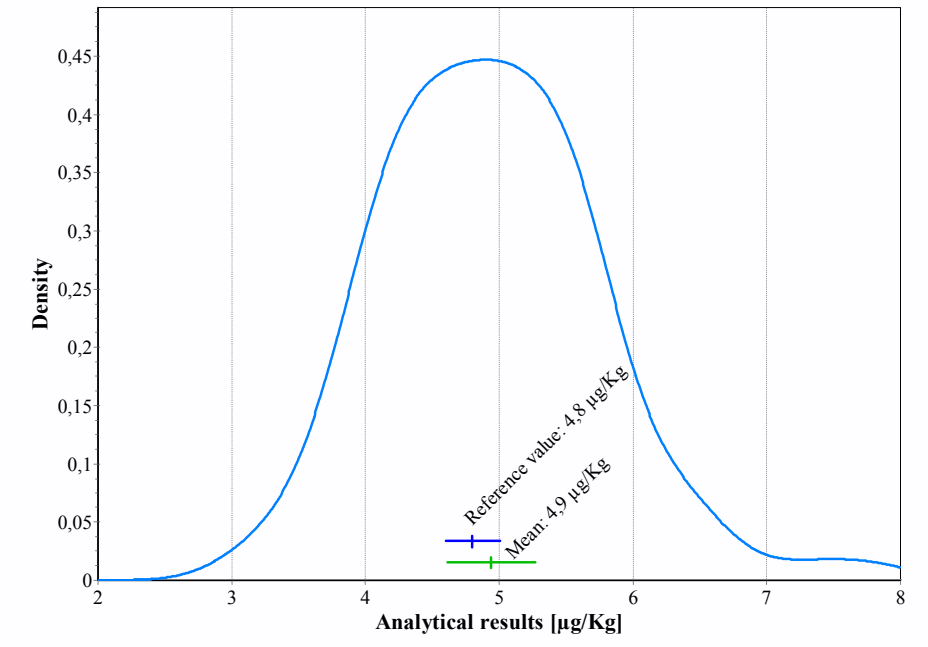

Table 33: Individual results of replicate measurements of BjF in Fish Cin µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,75	5,54	5,1	5,34	4,66	5,43	1,63
3001							
3003	5,68	5,59	5,87	5,73	5,65	5,7	0,97
3004	3,89	4,27	3,76	4,06	4,06	4,01	0,4
3005	5,31	5,78	6,31	4,76	5,48	5,53	0,9
3006	5,5	5,8	5,5	4,6	6,2	5,5	1
3007	4,4	4,3	4,2	4,4	4,5	4,36	
3008	5,2	5	4,8	4,9	4,5	5,1	0,8
3010	5,62	5,54	5,71	5,46	5,32	5,53	
3011	3,63	4,18	4,15	3,23	4,21	3,88	1,3
3012	3,6	3,2				3,4	0,3
3013	4,06	4,18	3,97	4,52	4,1	4,17	0,62
3014							
3015	4,85	4,9	5,04	4,56	5,14	4,9	0,71
3016	4,5	4,4	4,4	4,2	4,4	4,4	1
3017	6,6	7,3	7,8	6,2	6,5	6,9	1,4
3018	4,73	4,68	4,61	4,71	4,62	4,67	0,92
3019	5,05	5,37	5,33	5,09	4,73	4,97	0,79
3020	4,4	4,2	3,9	3,8	4	4	0,4
3021	4,81	4,98	6,34	4,28	3,9	4,66	2,24
3022	5	5,75	5,2	4,88	5,22	5,2	
3024	5,38	5,69	5,43	5,54	5,25	5,46	0,38
3025	4,9	5,1	5,1	5,1	4,8	5	0,4
3026							
3027							

Benzo[*k*]fluoranthene (BkF)

Figure 56: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 4,9 µg/kg (red), a ±1 σ_p, ± 2 σ_p, and ± 3 σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

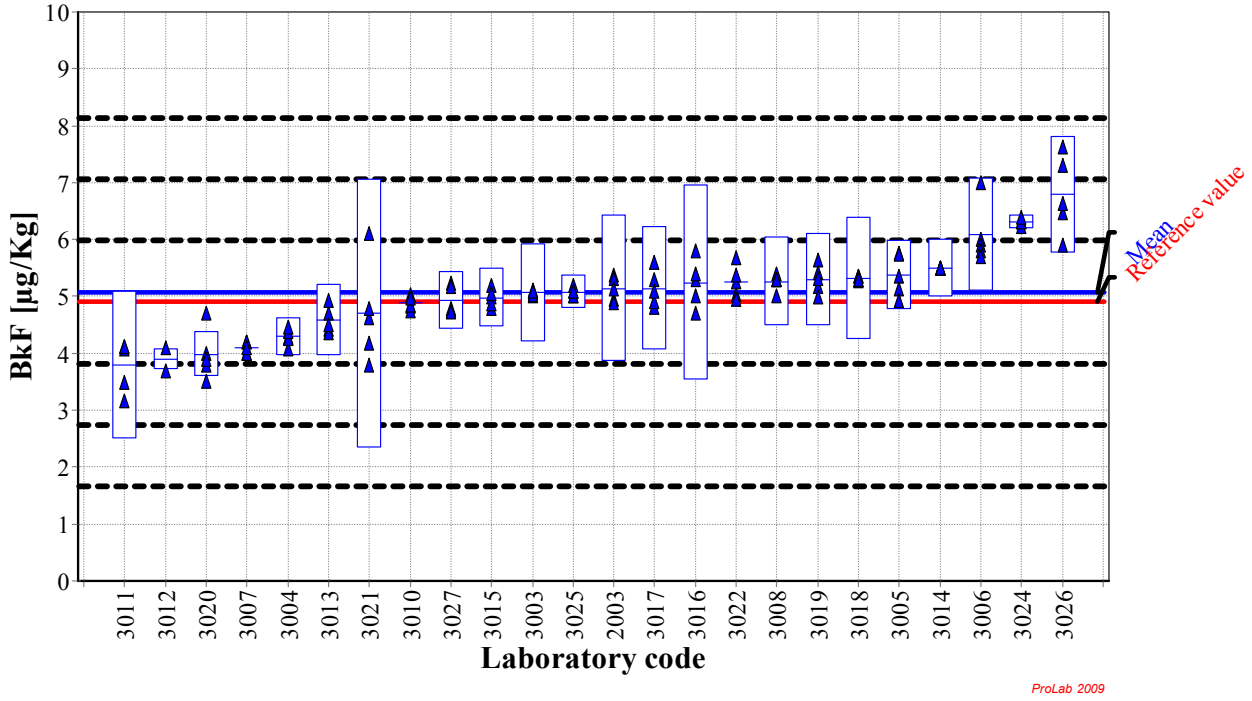

Figure 57: Kernel Density Plot

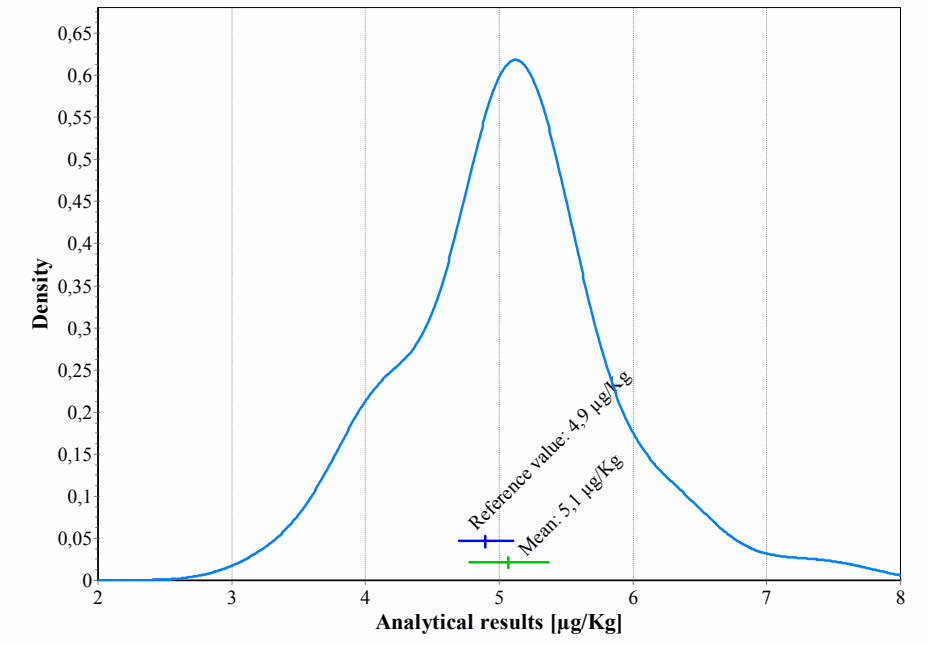

Table 34: Individual results of replicate measurements of BkF in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,38	5,31	4,95	5,14	4,88	5,13	1,29
3001							
3003	5,12	5,08	5,01	5,03	5,09	5,07	0,86
3004	4,27	4,08	4,26	4,39	4,46	4,29	0,34
3005	5,36	5,76	5,13	4,92	5,75	5,38	0,61
3006	6	5,9	5,8	5,7	7	6,1	1
3007	4,2	4	4	4,2	4,1	4,1	
3008	5,4	5,3	5	5,3	5,3	5,4	0,8
3010	4,82	4,74	5,03	4,84	4,97	4,88	
3011	3,48	4,11	4,07	3,17	4,12	3,79	1,3
3012	4,1	3,7				4,2	0,2
3013	4,42	4,71	4,36	4,93	4,5	4,59	0,64
3014	5,5	5,5	5,5	5,5	5,5	5,5	0,5
3015	4,99	4,78	4,86	5,19	5,06	4,97	0,52
3016	4,7	5	5,3	5,4	5,8	5,2	1,7
3017	4,8	5,3	4,9	5,6	5,1	5,2	1,1
3018	5,28	5,3	5,36	5,35	5,3	5,32	1,07
3019	5,17	5,63	5,41	5,31	4,98	4,83	0,74
3020	4,7	4	3,8	3,5	3,9	4	0,4
3021	4,62	4,79	6,11	4,17	3,8	4,5	2,26
3022	5,25	5,68	5,37	5,04	4,94	5,25	
3024	6,3	6,22	6,32	6,31	6,39	6,31	0,12
3025	5,1	5	5	5,2	5,1	5,1	0,3
3026	7,63	7,3	6,48	6,63	5,9	6,79	1,02
3027	5,24	5,18	4,74	4,79	4,73	4,94	0,51

Chrysene (CHR)

Figure 58: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,2 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

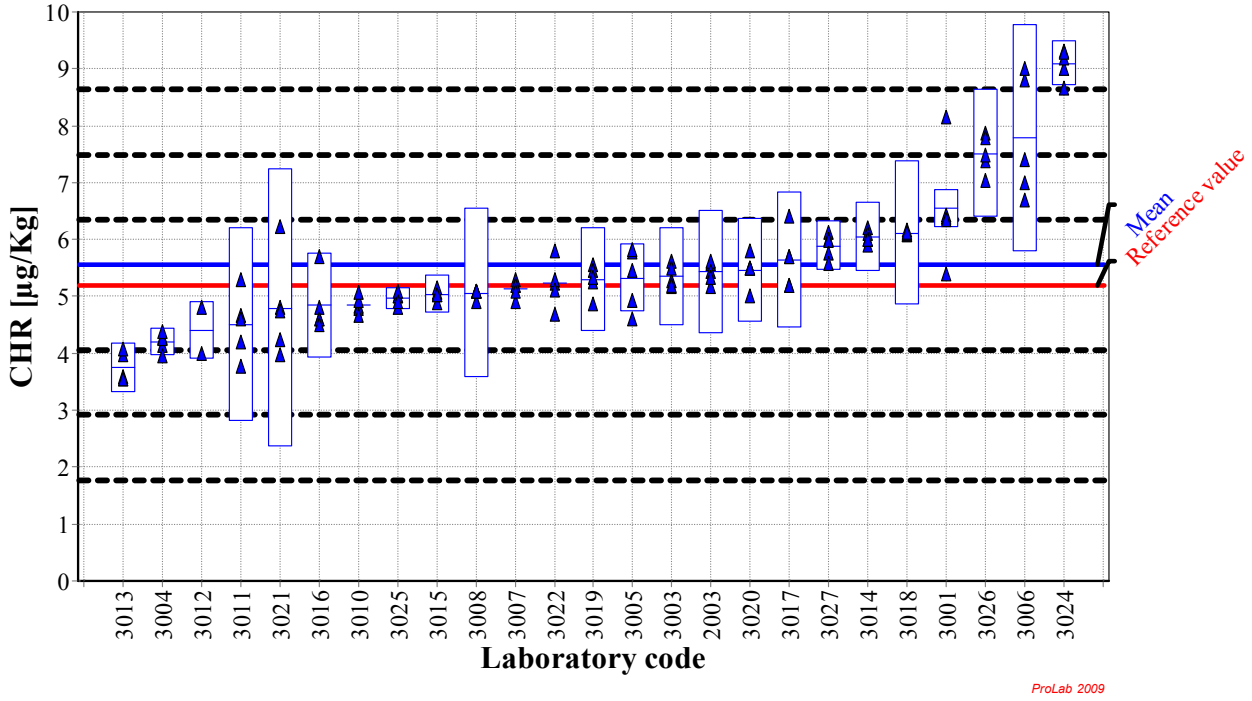

Figure 59: Kernel Density Plot

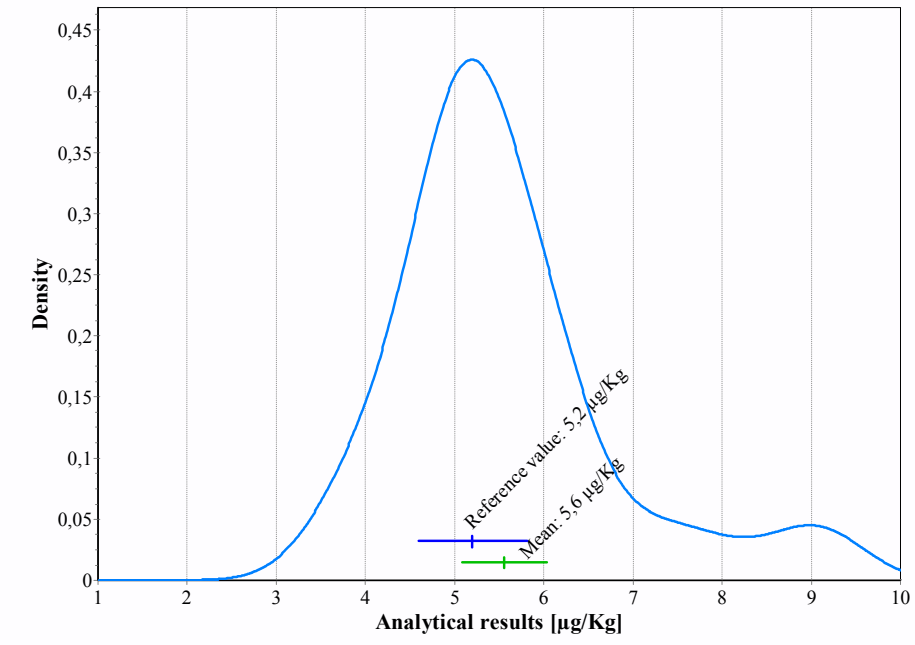

Table 35: Individual results of replicate measurements of CHR in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,57	5,62	5,18	5,44	5,33	5,43	1,09
3001	5,4	6,39	6,44	6,34	8,15	6,39	0,33
3003	5,28	5,62	5,18	5,5	5,19	5,35	0,86
3004	4,14	4,28	3,96	4,26	4,38	4,21	0,25
3005	5,45	5,78	4,93	4,61	5,82	5,32	0,6
3006	8,8	9	7,4	7	6,7	7,8	2
3007	5,3	5,2	4,9	5,2	5,1	5,14	
3008	5,1	5,1	4,9	5,1	5,1	5,1	1,5
3010	4,83	4,79	4,93	4,67	5,07	4,86	
3011	4,19	4,66	4,61	3,77	5,29	4,5	1,7
3012	4	4,8				4,4	0,5
3013	3,59	3,97	3,55	4,07	3,55	3,75	0,43
3014	6,2	5,9	6,1	6	6	6	0,6
3015	4,88	5,04	5,08	5,16	5,04	5,04	0,33
3016	4,6	4,8	4,6	4,5	5,7	4,8	0,91
3017	5,2	5,7	5,2	6,4	5,7	5,7	1,2
3018	6,09	6,08	6,11	6,17	6,12	6,11	1,27
3019	5,25	5,55	5,45	5,33	4,87	4,9	0,85
3020	5,8	5,5	5,5	5	5,5	5,4	0,9
3021	4,8	4,75	6,22	4,23	3,98	4,6	2,35
3022	4,69	5,81	5,24	5,29	5,11	5,24	
3024	9,01	8,66	9,19	9,31	9,3	9,09	0,4
3025	5	5	5,1	4,8	4,9	5	0,2
3026	7,88	7,38	7,03	7,78	7,48	7,51	1,13
3027	6,12	6	5,99	5,77	5,57	5,89	0,44

Cyclopenta[*cd*]pyrene (CPP)

Figure 60: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,2 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

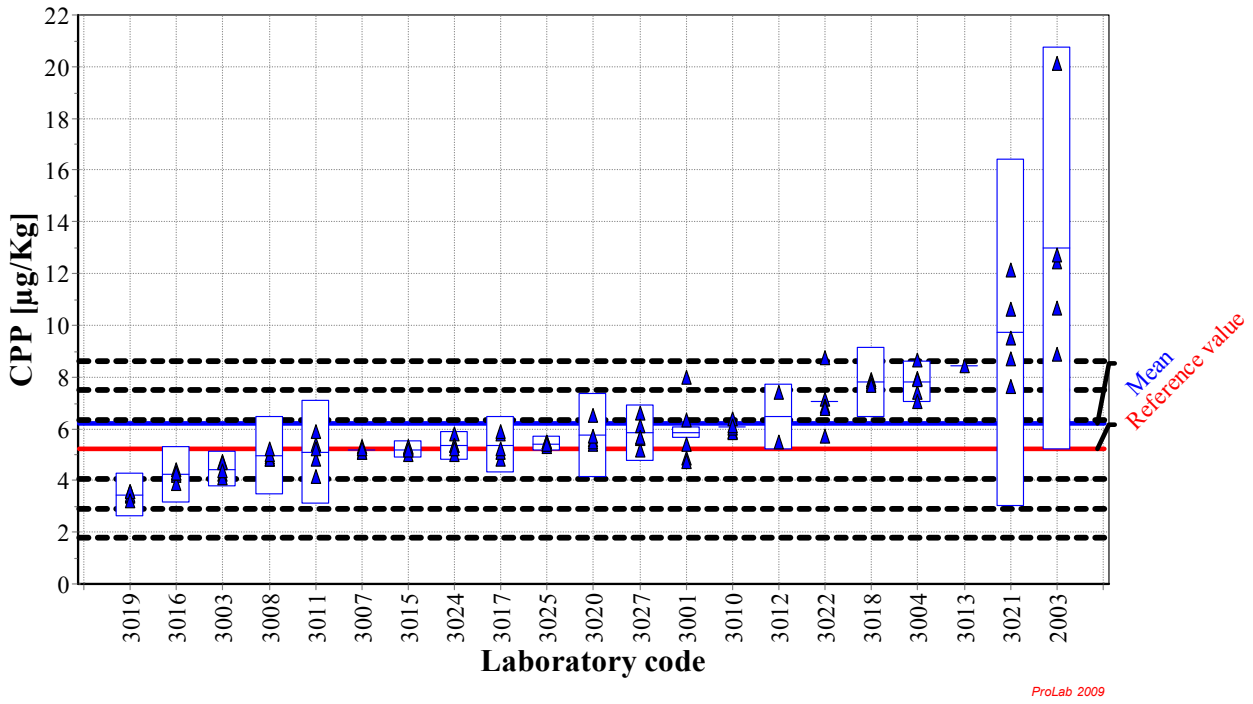

Figure 61: Kernel Density Plot

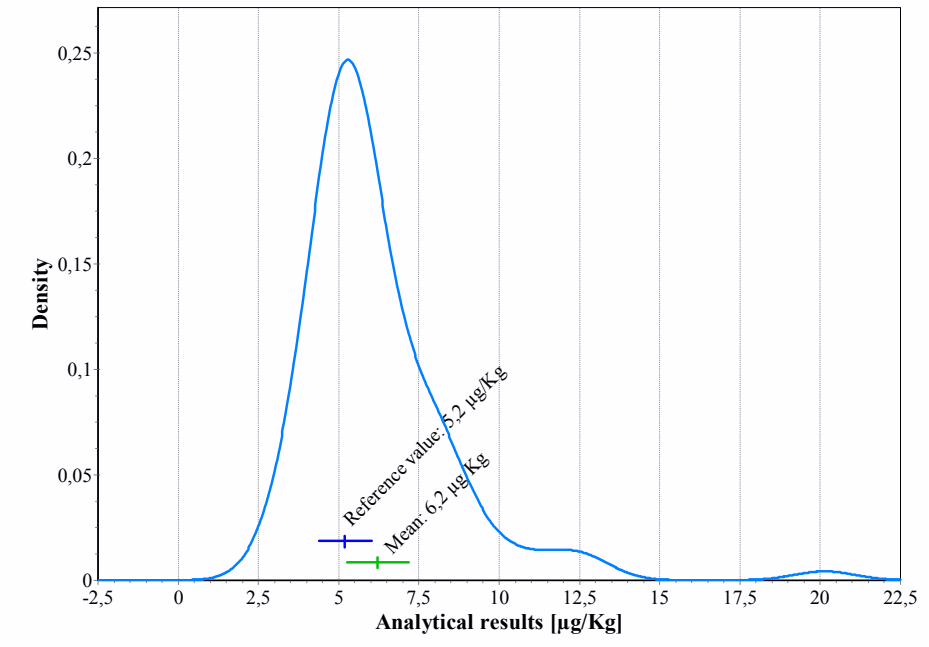

Table 36: Individual results of replicate measurements of CPP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	12,47	20,14	10,67	12,73	8,86	11,96	7,18
3001	4,86	6,32	4,73	5,38	8,01	5,38	0,2
3003	4,75	4,7	4,22	4,12	4,37	4,44	0,7
3004	8,67	7,96	7,42	7,91	7,03	7,8	0,8
3005							
3006							
3007	5,2	5,1	5,3	5,1	5,2	5,18	
3008	4,8	4,9	4,8	5	5,2	4,9	1,5
3010	6,38	5,9	5,85	6,02	6,12	6,05	
3011	4,8	5,38	5,22	4,13	5,88	5,08	2
3012	5,5	7,4				6,5	1,3
3013	8,44						
3014							
3015	5,01	5,25	5,22	5,3	5,19	5,19	0,35
3016	4,4	4,2	3,9	4,3	4,3	4,2	1,1
3017	4,8	5,8	5,1	5,9	5,2	5,4	1,1
3018	7,73	7,9	7,81	7,83	7,69	7,79	1,37
3019	3,39	3,59	3,44	3,57	3,22	4,49	1,11
3020	5,6	6,5	5,4	5,5	5,7	5,7	1,6
3021	10,63	7,61	8,69	12,15	9,52	9,88	6,83
3022	8,76	7,15	6,89	5,72	6,79	6,89	
3024	5,78	5,34	5,35	5,02	5,22	5,34	0,56
3025	5,3	5,4	5,5	5,5	5,4	5,4	0,3
3026							
3027	5,16	6,59	6,11	5,62	5,67	5,83	1,08

Dibenzo[*a*,*e*]pyrene (DeP)

Figure 62: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,2 µg/kg (red), a ±1 σ_p, ± 2 σ_p, and ± 3 σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

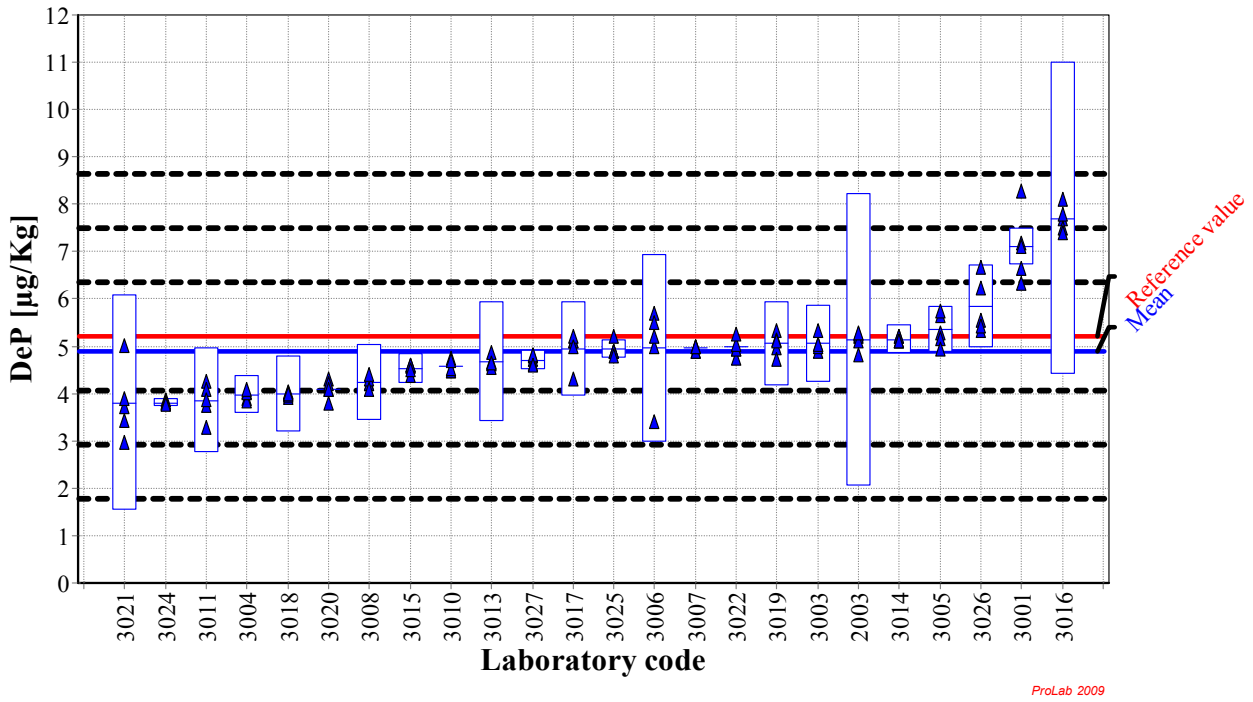

Figure 63: Kernel Density Plot

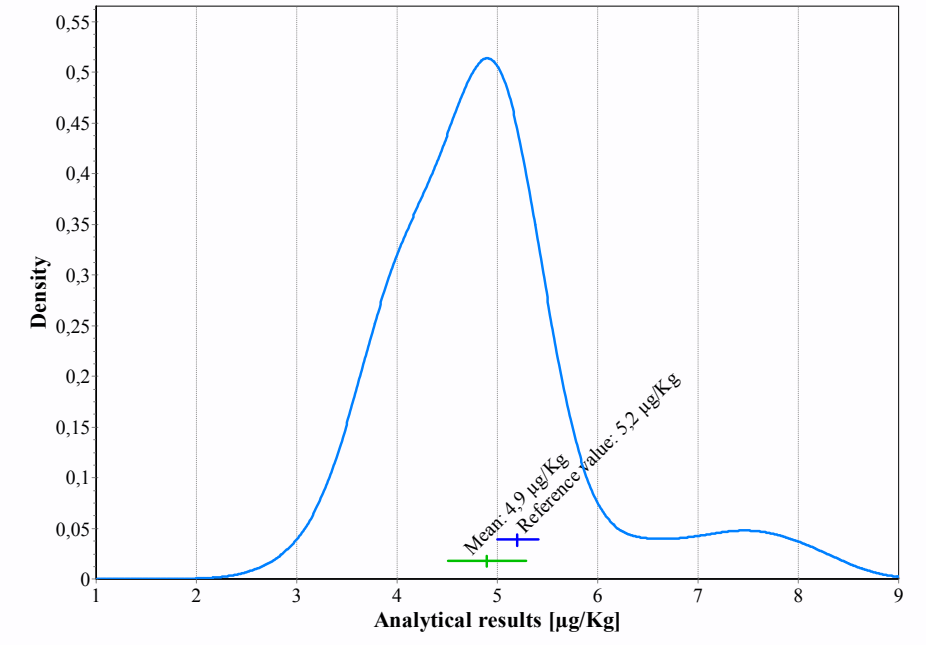

Table 37: Individual results of replicate measurements of DeP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,25	5,2	5,1	5,29	4,83	5,21	3,13
3001	6,32	7,18	7,11	6,64	8,27	7,11	0,4
3003	4,89	5,32	5	5,04	5,04	5,06	0,82
3004	3,9	4,04	3,85	4,01	4,08	3,98	0,4
3005	5,27	5,64	5,16	4,93	5,74	5,35	0,49
3006	3,4	5	5,2	5,7	5,5	5	2
3007	5	4,9	4,9	5	5	4,96	
3008	4,2	4,2	4,3	4,1	4,4	4,2	0,8
3010	4,47	4,49	4,74	4,52	4,69	4,58	
3011	3,75	4,27	4,08	3,28	3,88	3,85	1,1
3012							
3013	4,62	4,68	4,54	4,86	4,65	4,67	1,26
3014	5,1	5,2	5,2	5,1	5,1	5,1	0,3
3015	4,37	4,57	4,59	4,61	4,5	4,53	0,32
3016	7,7	7,8	8,1	7,5	7,4	7,7	3,3
3017	4,3	5,1	5,1	5,2	5	5	1
3018	4,04	3,92	4,02	3,96	3,98	3,98	0,8
3019	4,97	5,33	5,13	5,11	4,73	4,47	0,79
3020	4,1	3,8	4,3	4,2	4,1	4,1	
3021	3,73	3,89	5,01	3,43	2,96	3,64	2,18
3022	4,93	4,75	4,94	5,05	5,25	4,94	
3024	3,8	3,86	3,79	3,81	3,78	3,81	0,08
3025	4,9	4,9	4,9	5,2	4,8	5	0,2
3026	6,68	6,23	5,55	5,33	5,43	5,84	0,88
3027	4,8	4,71	4,63	4,81	4,59	4,71	0,2

Dibenzo[*a*,*h*]anthracene (DhA)

Figure 64: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,4 µg/kg (red), a ±1 σ_p, ± 2 σ_p, and ± 3 σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

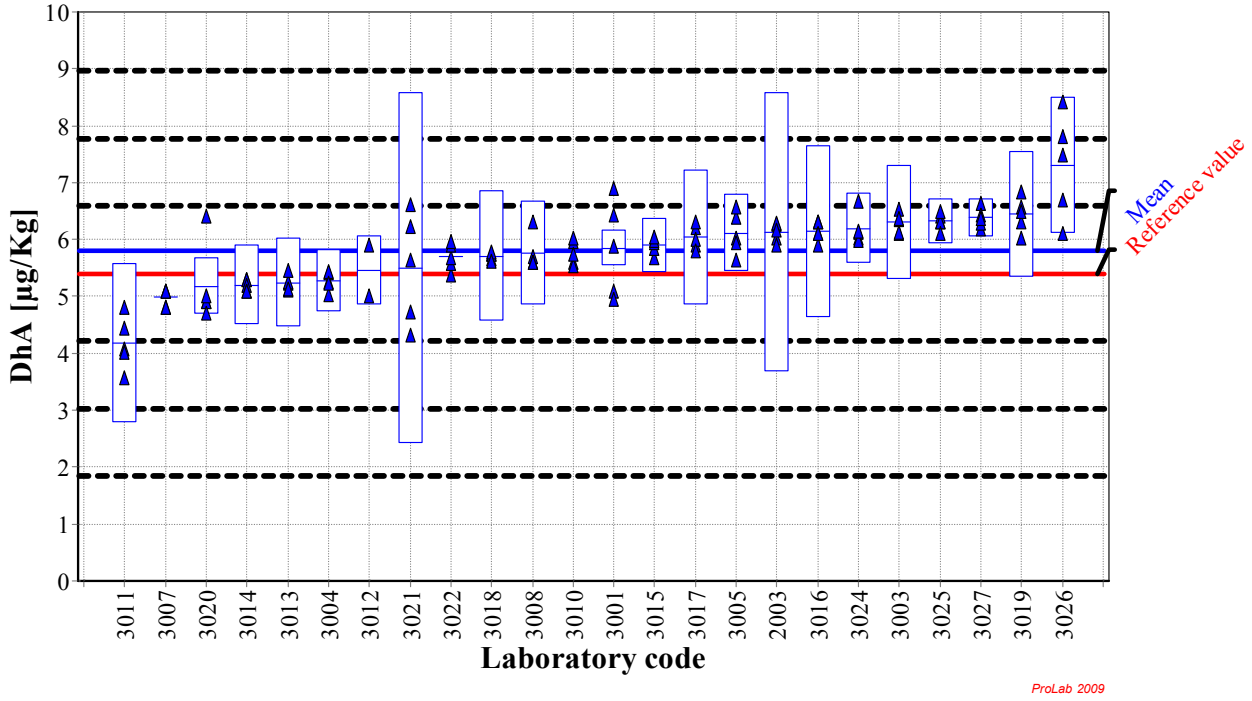

Figure 65: Kernel Density Plot

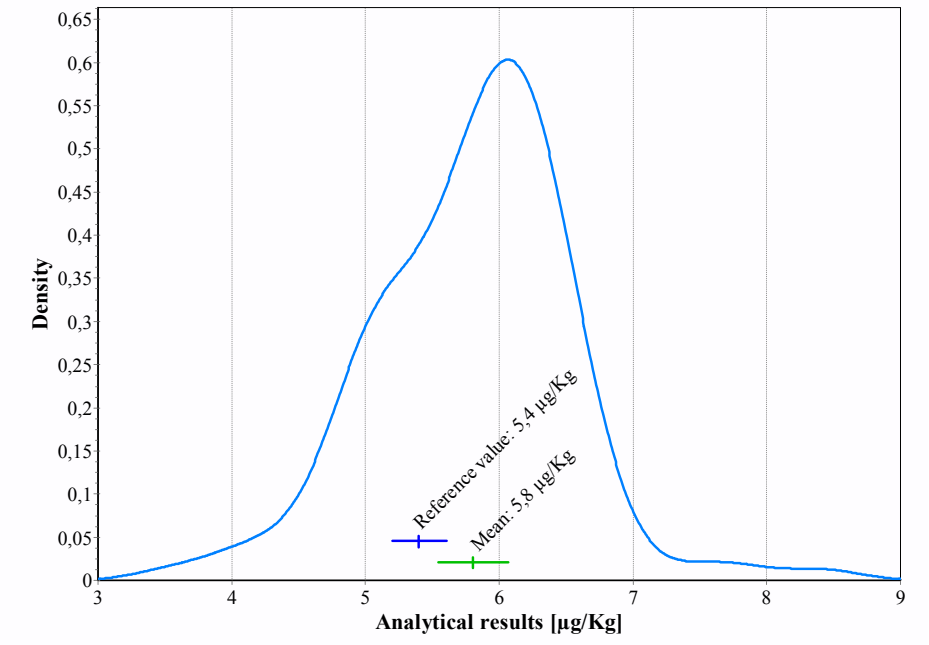

Table 38: Individual results of replicate measurements of DhA in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	6,26	6,29	6,02	6,16	5,91	6,13	2,45
3001	5,1	6,44	4,94	5,88	6,89	5,88	0,31
3003	6,11	6,54	6,13	6,35	6,37	6,3	1
3004	5,04	5,26	5,42	5,43	5,24	5,28	0,55
3005	6,02	6,39	5,95	5,63	6,57	6,11	0,68
3006							
3007	5,1	4,8	4,8	5,1	5,1	4,98	
3008	5,6	5,7	5,6	5,6	6,3	5,7	0,9
3010	5,6	5,54	5,96	5,74	6,02	5,77	
3011	4,07	4,8	4,44	3,56	4,02	4,18	1,4
3012	5	5,9				5,4	0,6
3013	5,23	5,26	5,11	5,46	5,14	5,24	0,78
3014	5,3	5,3	5,2	5,1	5,1	5,2	0,7
3015	5,67	5,84	5,95	5,98	6,05	5,9	0,48
3016	5,9	6,3	6,1	6,3	6,1	6,1	1,5
3017	6,2	5,9	6	5,8	6,3	6,1	1,2
3018	5,66	5,74	5,74	5,78	5,61	5,71	1,14
3019	6,31	6,83	6,57	6,49	6,02	5,7	0,98
3020	6,4	4,9	4,9	5	4,7	5,2	0,5
3021	5,63	6,22	6,62	4,72	4,33	5,29	2,96
3022	5,38	5,58	5,68	5,9	5,96	5,68	
3024	6,68	6,02	6,13	5,99	6,15	6,19	0,61
3025	6,3	6,4	6,3	6,1	6,5	6,3	0,4
3026	8,42	7,8	7,48	6,1	6,7	7,3	1,2
3027	6,64	6,18	6,29	6,43	6,36	6,38	0,34

Dibenzo[a,h]pyrene (DhP)

Figure 66: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 4,6 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

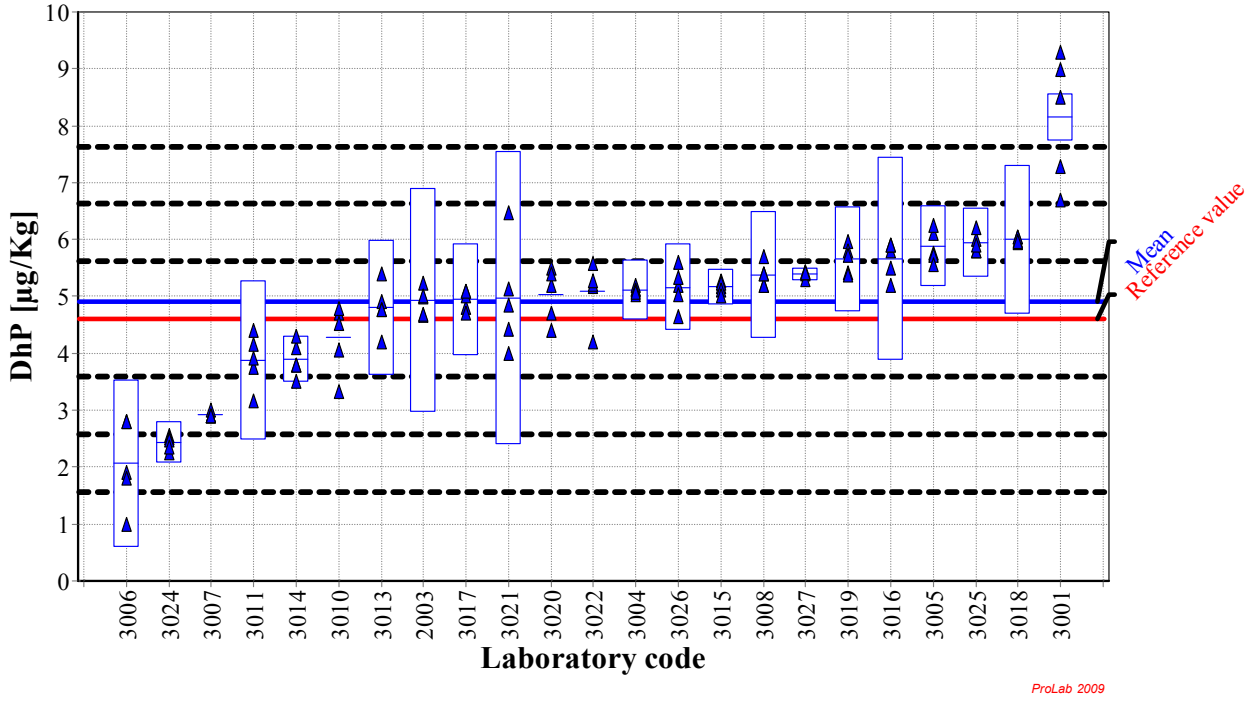

Figure 67: Kernel Density Plot

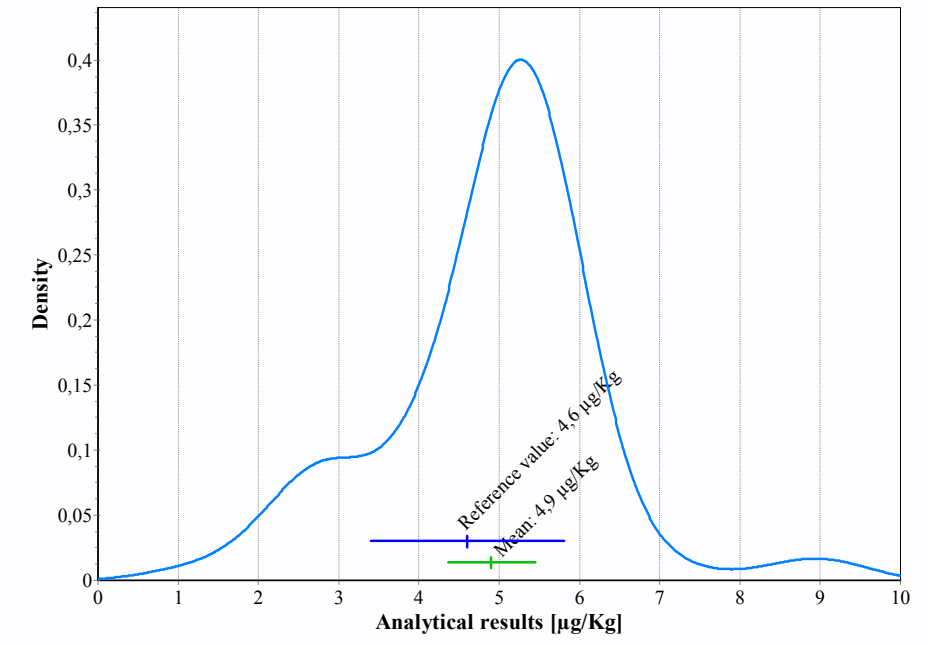

Table 39: Individual results of replicate measurements of DhP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	4,98	4,67	4,69	5,24	5,02	4,92	1,97
3001	6,7	8,98	8,49	7,28	9,28	8,49	0,43
3003							1
3004	5,14	5,2	5,12	5,04	5,08	5,12	0,52
3005	5,76	6,11	5,73	5,56	6,25	5,88	0,72
3006	1	2,8	1,9	2,8	1,8	2,1	1,5
3007	2,9	2,9	3	2,9	2,9	2,92	
3008	5,4	5,2	5,7	5,2	5,4	5,3	1,1
3010	3,32	4,05	4,71	4,78	4,52	4,28	
3011	3,75	4,41	4,16	3,17	3,91	3,88	1,4
3012							
3013	4,91	4,2	4,77	5,39	4,76	4,81	1,19
3014	3,5	4,1	4,3	3,8	3,8	3,9	0,4
3015	5,17	5,28	5,23	5,12	5,02	5,16	0,32
3016	5,5	5,8	5,9	5,9	5,2	5,7	1,8
3017	4,8	5,1	5	5,1	4,7	5	1
3018	5,94	5,99	6,04	6,05	5,96	6	1,31
3019	5,41	5,97	5,81	5,73	5,37	5,89	0,96
3020	5,5	5,2	4,7	4,4	5,4	5	
3021	4,85	5,13	6,47	4,42	3,99	4,75	2,46
3022	5,17	4,2	5,21	5,57	5,28	5,21	
3024	2,56	2,51	2,25	2,48	2,35	2,43	0,37
3025	5,8	5,8	6	6,2	5,9	5,9	0,6
3026	5,2	5,03	4,65	5,33	5,6	5,16	0,77
3027	5,44	5,39	5,3	5,41	5,41	5,39	0,11

Dibenzo[*a*,*i*]pyrene (DiP)

Figure 68: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,1µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

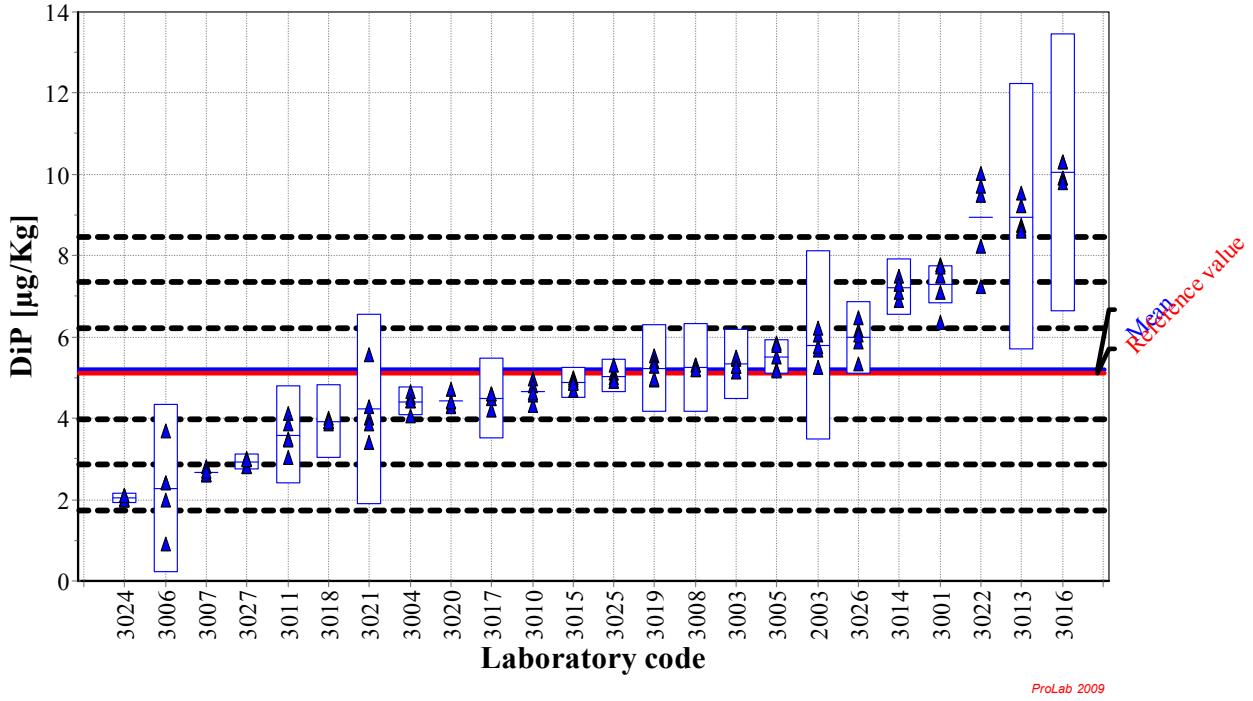

Figure 69: Kernel Density Plot

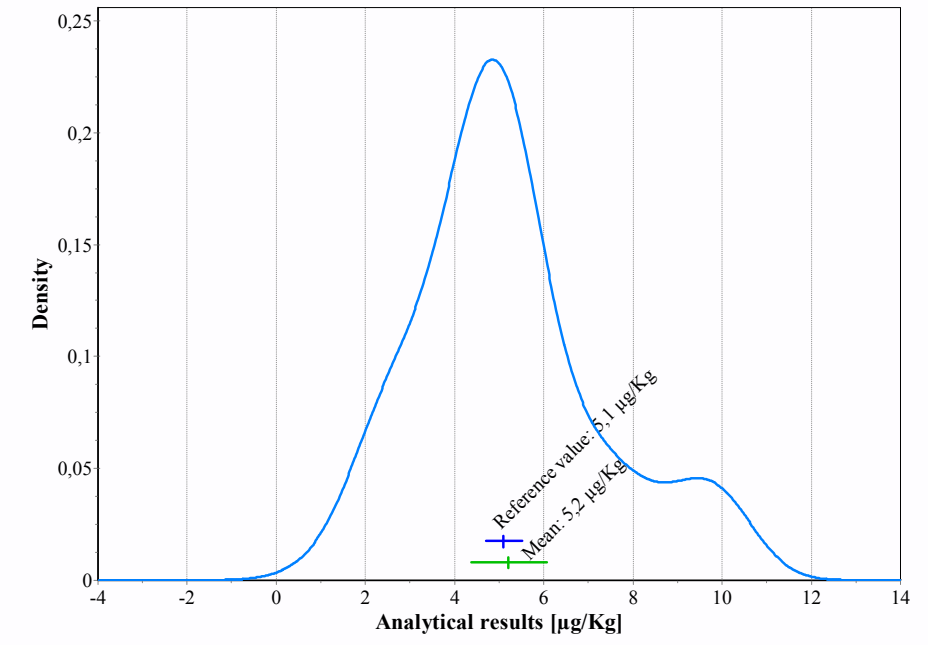

Table 40: Individual results of replicate measurements of DiP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,69	6,04	5,76	6,22	5,24	5,79	2,32
3001	6,36	7,5	7,09	7,78	7,71	7,5	0,49
3003	5,13	5,45	5,5	5,29	5,28	5,33	0,87
3004	4,05	4,42	4,51	4,67	4,42	4,41	0,36
3005	5,51	5,85	5,21	5,17	5,78	5,5	0,43
3006	3,7	2,4	0,9	2	2,4	2,2	2
3007	2,8	2,6	2,6	2,6	2,7	2,66	
3008	5,3	5,2	5,3	5,2	5,2	5,3	1,1
3010	4,31	4,58	4,97	4,81	4,62	4,66	
3011	3,5	4,11	3,86	3,03	3,46	3,59	1,2
3012							
3013	8,75	8,67	9,22	8,6	9,55	8,96	3,27
3014	6,9	7,3	7,5	7,1	7,3	7,2	0,7
3015	4,68	5	4,94	4,89	4,85	4,87	0,39
3016	9,9	10,3	10,3	9,9	9,8	10	3,4
3017	4,2	4,5	4,6	4,5	4,6	4,5	1
3018	4	3,92	3,91	3,87	3,92	3,92	0,9
3019	4,95	5,55	5,39	5,29	4,98	4,63	0,95
3020	4,7	4,3	4,4	4,3	4,4	4,4	
3021	4,01	4,28	5,57	3,85	3,4	4,04	2,25
3022	8,23	7,23	9,49	10,03	9,71	9,49	
3024	2	2,09	2,01	1,98	2,1	2,04	0,12
3025	5,1	5	4,9	5,3	4,9	5	0,4
3026	6,48	6,15	5,88	5,35	6,05	5,98	0,9
3027	2,81	2,82	2,97	3,02	2,98	2,92	0,19

Dibenzo[*a*,*l*]pyrene (DlP)

Figure 70: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 5,2µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

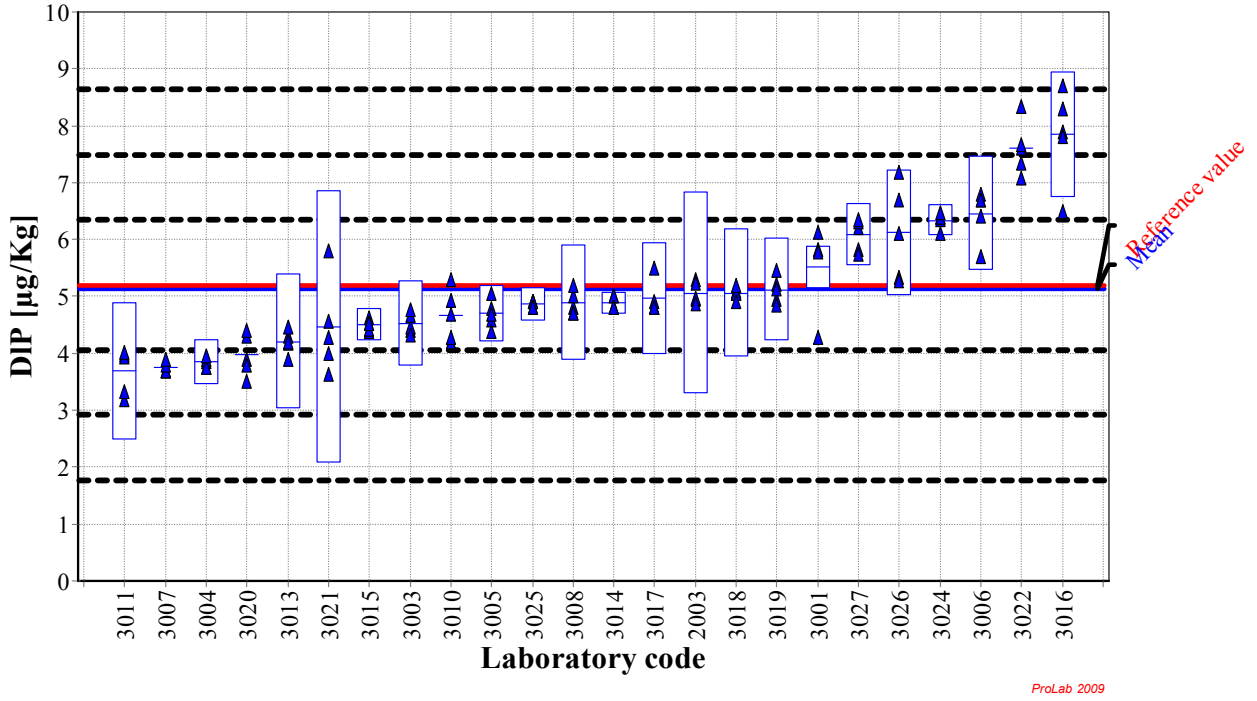

Figure 71: Kernel Density Plot

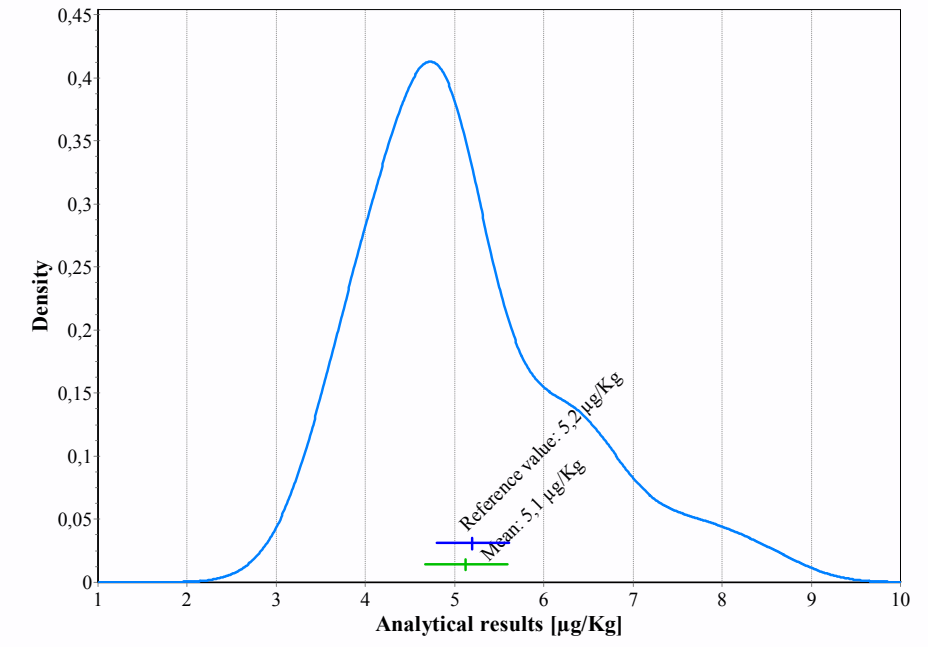

Table 41: Individual results of replicate measurements of DlP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	5,29	5,23	4,94	4,96	4,86	5,05	1,77
3001	4,28	5,83	5,79		6,13	5,81	0,4
3003	4,4	4,47	4,33	4,66	4,76	4,52	0,74
3004	3,85	3,9	3,76	3,75	3,96	3,84	0,4
3005	4,58	4,79	4,68	4,38	5,05	4,7	0,49
3006	6,4	6,7	6,8	6,7	5,7	6,5	1
3007	3,7	3,7	3,7	3,8	3,9	3,76	
3008	4,8	4,7	5	4,7	5,2	4,8	1
3010	4,19	4,28	4,93	4,68	5,29	4,67	
3011	3,98	3,93	4,01	3,18	3,32	3,68	1,2
3012							
3013	4,3	4,17	4,2	4,47	3,9	4,21	1,18
3014	4,8	5	5	4,8	4,8	4,9	0,2
3015	4,39	4,62	4,43	4,52	4,53	4,5	0,29
3016	7,9	8,3	8,7	7,8	6,5	7,8	1,1
3017	4,8	4,8	4,9	4,8	5,5	5	1
3018	5,05	5,09	5,06	4,91	5,19	5,06	1,12
3019	4,95	5,45	5,21	5,13	4,85	4,5	0,79
3020	4,3	3,5	3,9	4,4	3,8	4	
3021	4,29	4,57	5,8	4	3,63	4,26	2,29
3022	7,61	7,08	8,34	7,34	7,67	7,61	
3024	6,34	6,38	6,11	6,39	6,47	6,34	0,27
3025	4,9	4,9	4,8	4,9	4,8	4,9	0,3
3026	6,7	6,1	5,33	5,28	7,18	6,12	1,1
3027	5,83	5,75	6,21	6,31	6,34	6,09	0,55

Indeno[1,2,3-*cd*]pyrene (IcP)

Figure 72: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories mean (blue), the assigned value of 4,1µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box

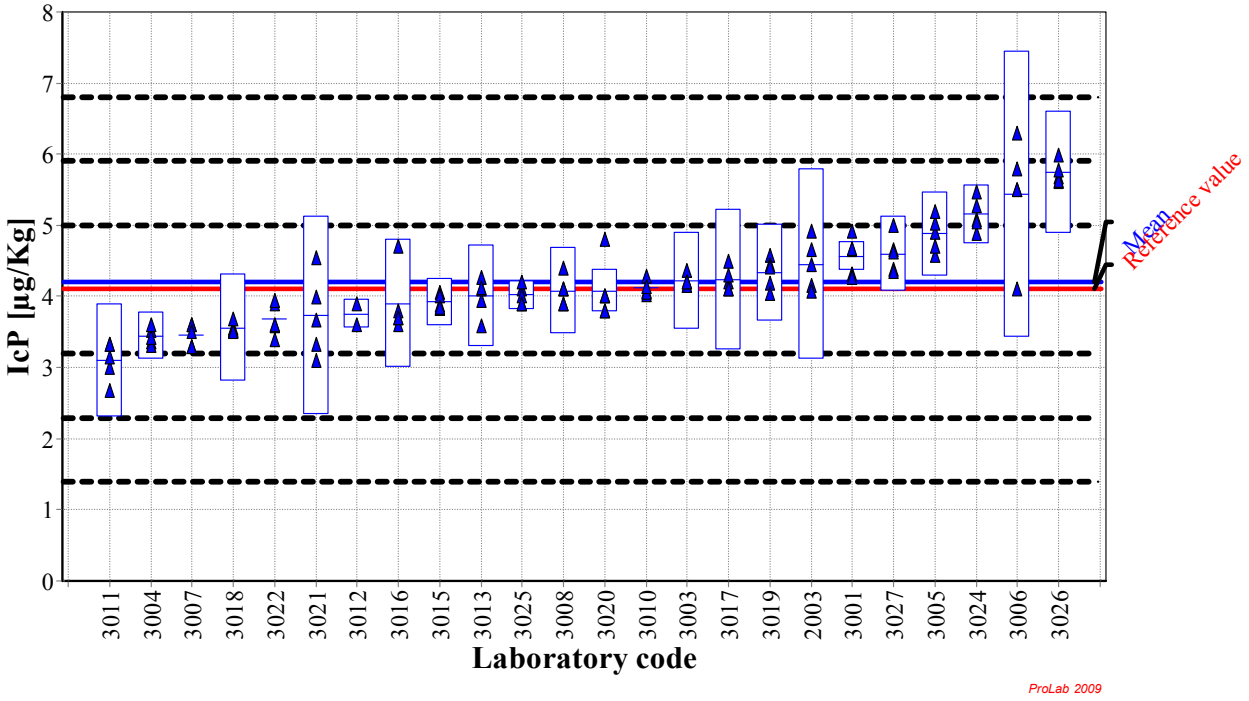

Figure 73: Kernel Density Plot

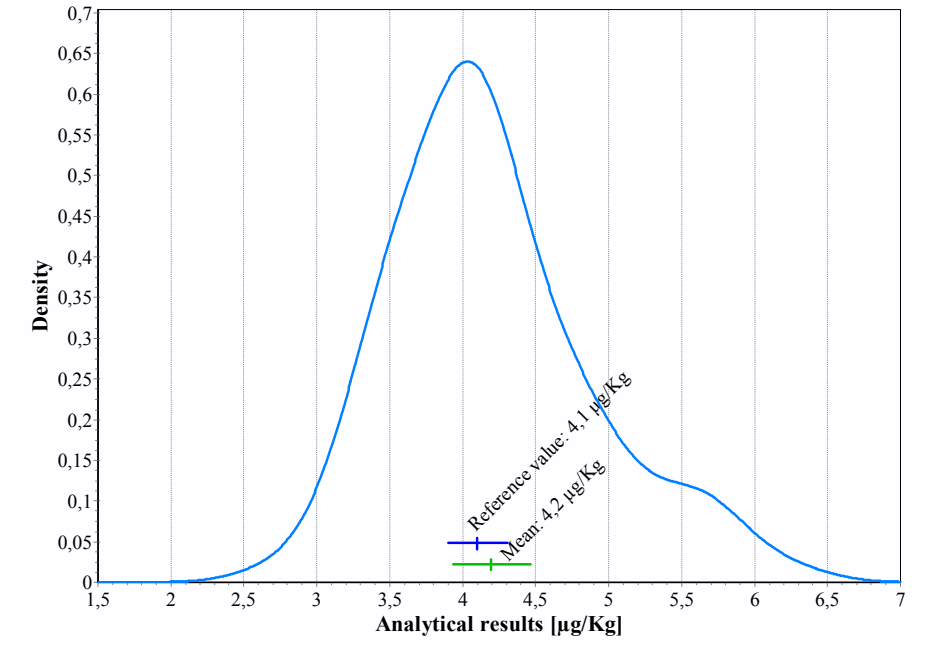

Table 42: Individual results of replicate measurements of IcP in Fish C in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Result 4	Result 5	Final results	Uncertainty (k = 2)
2003	4,92	4,65	4,45	4,16	4,08	4,45	1,34
3001	4,32	4,66	4,26	4,67	4,91	4,66	0,21
3003	4,15	4,36	4,16	4,2	4,2	4,21	0,68
3004	3,36	3,52	3,31	3,43	3,61	3,45	0,33
3005	4,57	4,9	5,03	4,7	5,2	4,88	0,59
3006	5,8	5,5	5,5	4,1	6,3	5,4	2
3007	3,6	3,3	3,3	3,6	3,5	3,46	
3008	3,9	4,1	4,1	3,9	4,4	4	0,6
3010	4,07	4,03	4,29	4,05	4,13	4,11	
3011	3,01	3,32	3,14	2,68	3,33	3,1	0,8
3012	3,6	3,9				3,7	0,2
3013	3,59	3,94	4,11	4,26	4,12	4	0,71
3014							
3015	3,88	3,83	4,05	4,01	3,84	3,92	0,33
3016	3,7	3,8	3,6	3,7	4,7	3,9	0,9
3017	4,5	4,2	4,3	4,1	4,1	4,3	1
3018	3,55	3,52	3,52	3,51	3,69	3,56	0,75
3019	4,19	4,57	4,44	4,41	4,04	4	0,63
3020	4,8	4	3,8	4	3,8	4,1	0,3
3021	3,67	3,99	4,55	3,33	3,1	3,58	1,34
3022	3,58	3,39	3,6	3,89	3,95	3,6	
3024	5,47	4,89	5,08	5,05	5,28	5,15	0,41
3025	3,9	4,1	4	3,9	4,2	4	0,2
3026	5,98	5,68	5,62	5,63	5,78	5,74	0,86
3027	4,65	5	4,62	4,38	4,35	4,6	0,53

Annex 4: Data for the determination of the 15+1 EU priority PAHs in test sample Fish D

Benzo[*a*]anthracene (BaA)

Figure 74: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories robust mean (blue), the assigned value of 1,9 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box. The green arrows indicate the LOQs reported by participants.

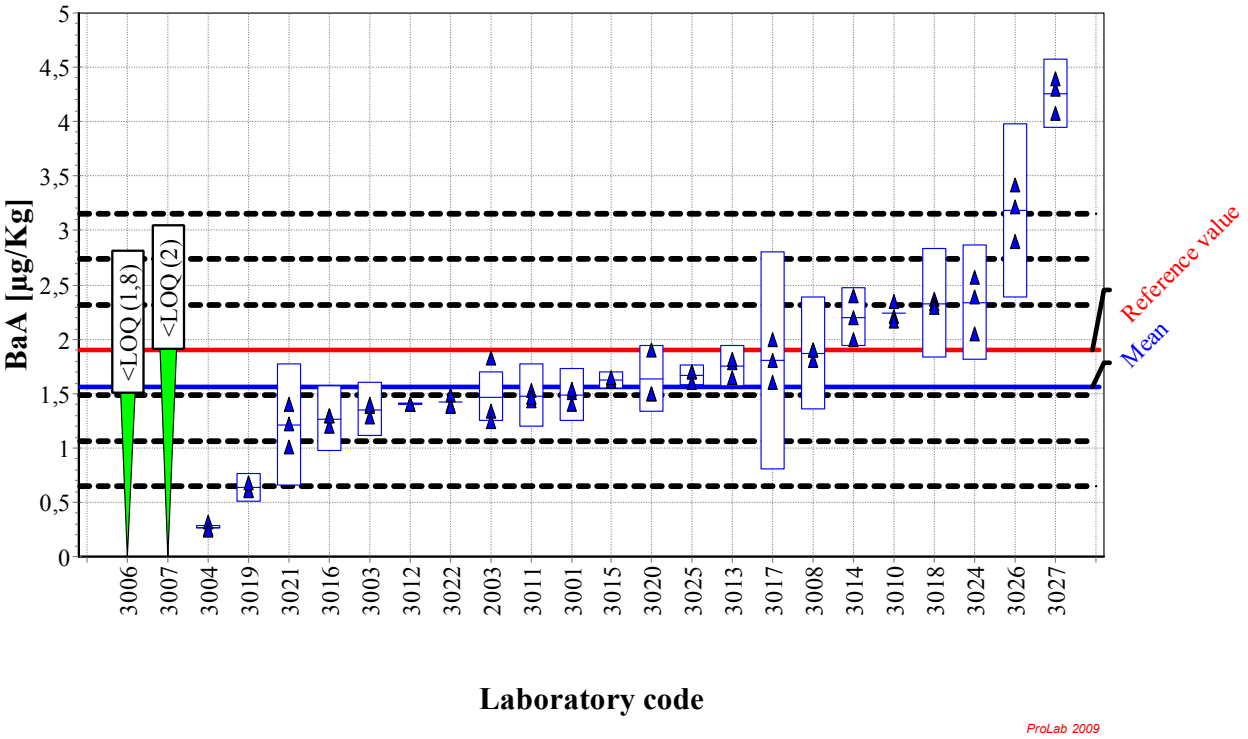

Figure 75: Kernel Density Plot

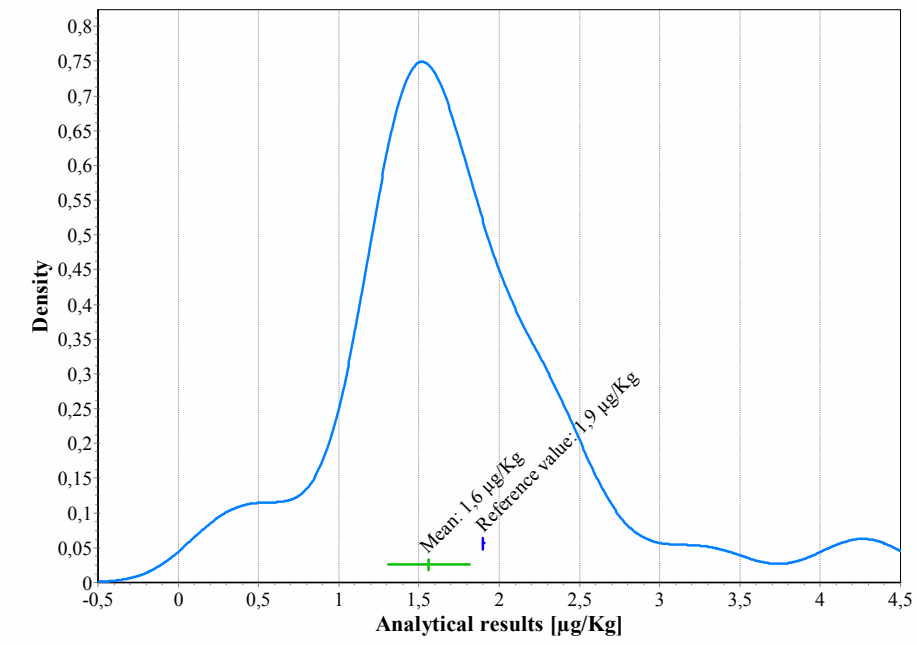

Table 43: Individual results of replicate measurements of BaA in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003	1,829	1,338	1,244	1,5	0,23
3001	1,51	1,4	1,54	1,51	0,25
3003	1,38	1,28	1,4	1,35	0,25
3004	0,25	0,32	0,24	0,27	0,02
3005					
3006					
3007					
3008	1,8	1,9	1,9	1,8	0,5
3010	2,35	2,21	2,17	2,24	
3011	1,43	1,53	1,47	1,47	0,29
3012	1,4	1,4	1,4	1,4	0,01
3013	1,78	1,82	1,65	1,75	0,19
3014	2,2	2,4	2	2,2	0,27
3015	1,61	1,61	1,65	1,62	0,08
3016	1,2	1,3	1,3	1,3	0,31
3017	1,6	2	1,8	1,8	1
3018	2,37	2,33	2,29	2,33	0,5
3019	0,62	0,6	0,68	0,61	0,13
3020	1,5	1,5	1,9	1,6	0,3
3021	1,22	1,4	1,01	1,21	0,56
3022	1,39	1,49	1,38	1,39	
3024	2,05	2,57	2,39	2,34	0,53
3025	1,7	1,7	1,6	1,7	0,1
3026	3,22	3,42	2,9	3,18	0,8
3027	4,3	4,39	4,08	4,26	0,32

Benzo[*a*]pyrene (BaP)

Figure 76: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories robust mean (blue), the assigned value of 0,9 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box. The red arrows indicate the LOQs reported by participants.

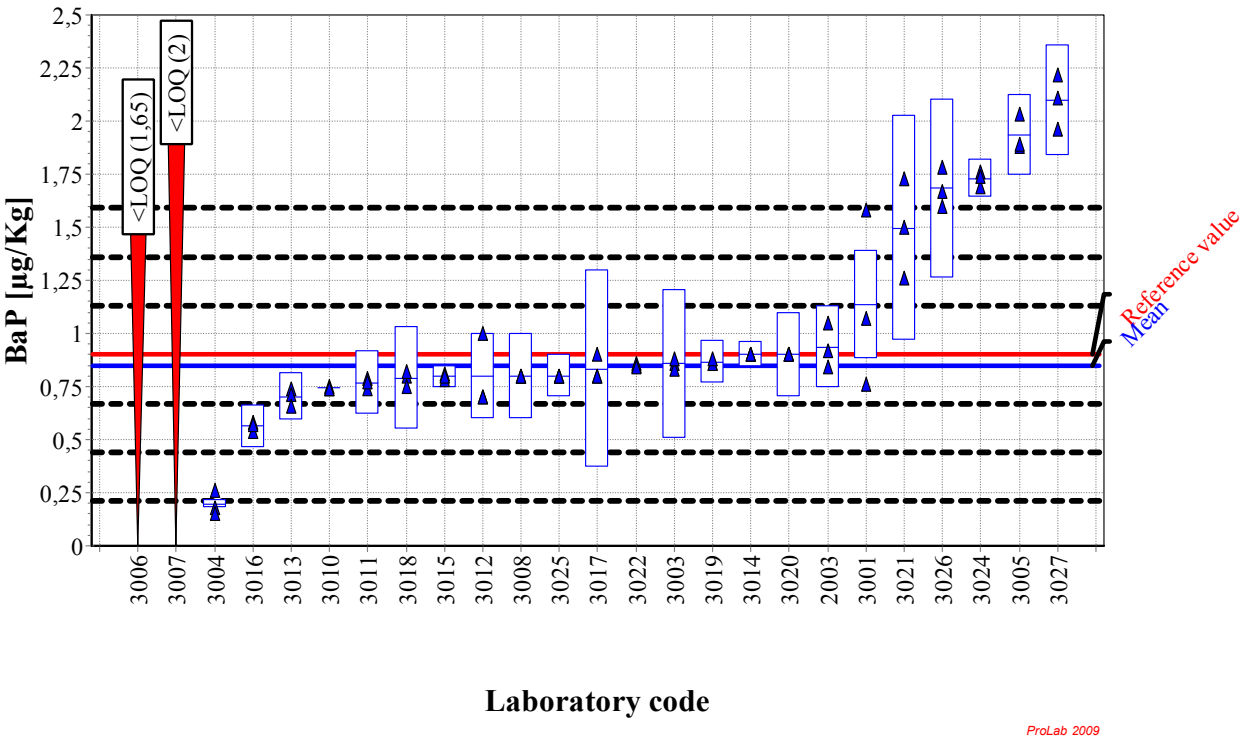

Figure 77: Kernel Density Plot

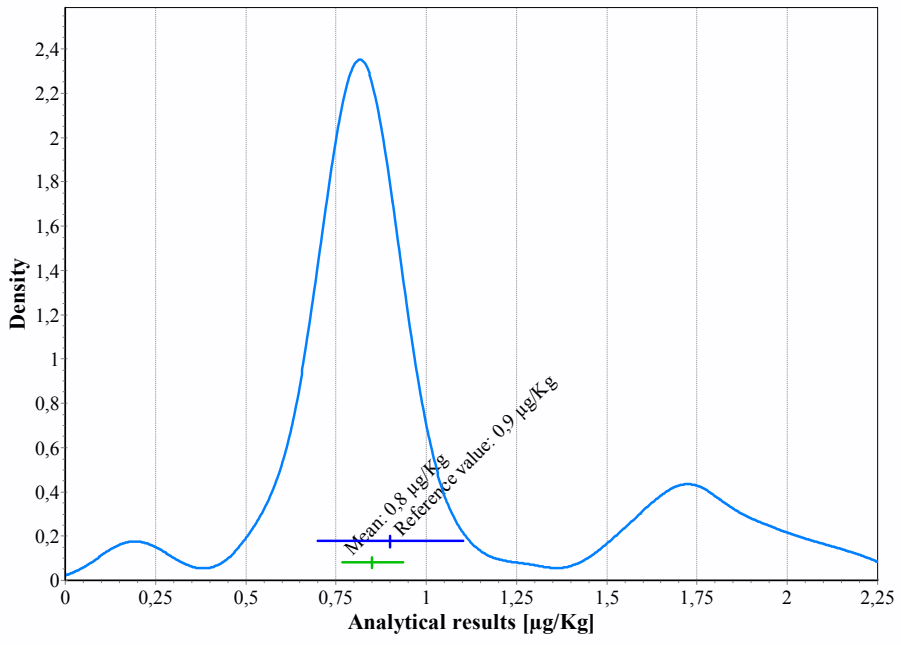

Table 44: Individual results of replicate measurements of BaP in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003	1,045	0,92	0,836	0,93	0,19
3001	1,58	0,76	1,07	1,07	0,24
3003	0,86	0,83	0,88	0,86	0,35
3004	0,26	0,18	0,15	0,2	0,02
3005	1,88	1,89	2,03	1,91	0,19
3006					
3007					
3008	0,8	0,8	0,8	0,8	0,2
3010	0,75	0,74	0,74	0,74	
3011	0,74	0,79	0,77	0,77	0,15
3012	1	0,7	0,7	0,8	0,2
3013	0,74	0,71	0,66	0,7	0,11
3014	0,9	0,9	0,9	0,9	0,06
3015	0,81	0,78	0,8	0,79	0,05
3016	0,58	0,54	0,57	0,56	0,1
3017	0,8	0,8	0,9	0,9	0,5
3018	0,8	0,82	0,75	0,79	0,24
3019	0,86	0,86	0,88	0,78	0,09
3020	0,9	0,9	0,9	0,9	0,2
3021	1,5	1,73	1,26	1,5	0,53
3022	0,85	0,86	0,84	0,85	
3024	1,76	1,69	1,74	1,73	0,09
3025	0,8	0,8	0,8	0,8	0,1
3026	1,67	1,6	1,78	1,68	0,42
3027	2,11	2,22	1,96	2,09	0,26

Benzo[*b*]fluoranthene (BbF)

Figure 78: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid lines indicate the laboratories robust mean (blue) and the assigned value of 0,7 µg/kg (red). The expanded uncertainty as reported by participants is indicated by the blue box. The green arrows indicate the LOQs reported by participants.

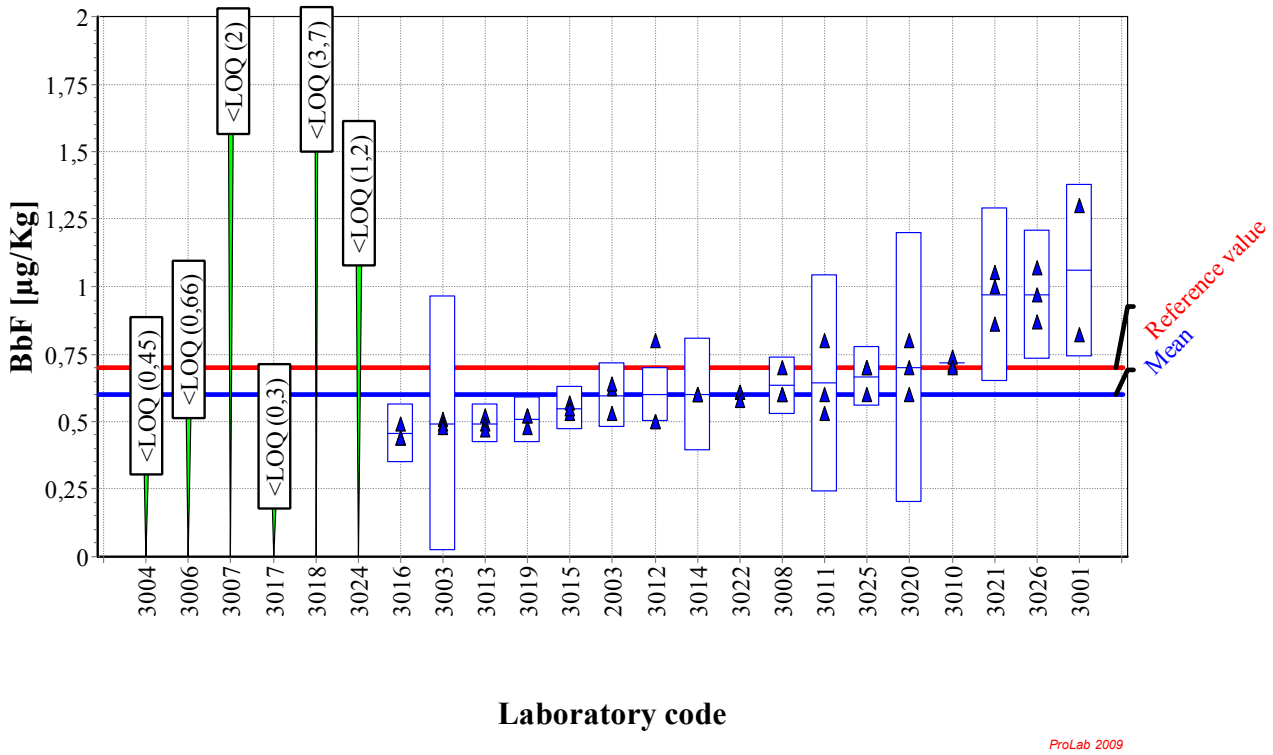

Figure 79: Kernel Density Plot

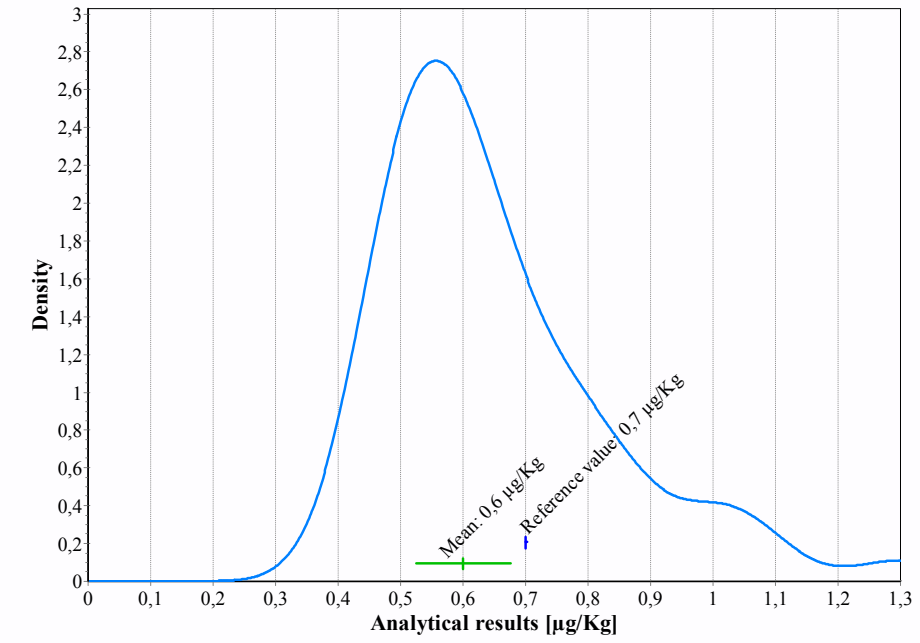

Table 45: Individual results of replicate measurements of BbF in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003	0,533	0,623	0,643	0,6	0,12
3001	0,82	1,3		1,06	0,32
3003	0,51	0,49	0,48	0,49	0,47
3004					
3005					
3006					
3007					
3008	0,6	0,7	0,6	0,6	0,1
3010	0,71	0,74	0,7	0,72	
3011	0,8	0,6	0,53	0,64	0,4
3012	0,8	0,5	0,5	0,6	0,1
3013	0,52	0,49	0,47	0,49	0,07
3014	0,6	0,6	0,6	0,6	0,21
3015	0,57	0,53	0,55	0,55	0,08
3016	0,44	0,44	0,49	0,46	0,11
3017					
3018					
3019	0,52	0,52	0,48	0,48	0,08
3020	0,6	0,8	0,7	0,7	0,5
3021	1	1,05	0,86	0,97	0,32
3022	0,61	0,61	0,58	0,61	
3024					
3025	0,7	0,6	0,7	0,6	0,1
3026	1,07	0,97	0,87	0,97	0,24
3027					

Benzo[*c*]fluorene (BcL)

Figure 80: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories robust mean (blue), the assigned value of 4,1 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box. The green arrows indicate the LOQs reported by participants.

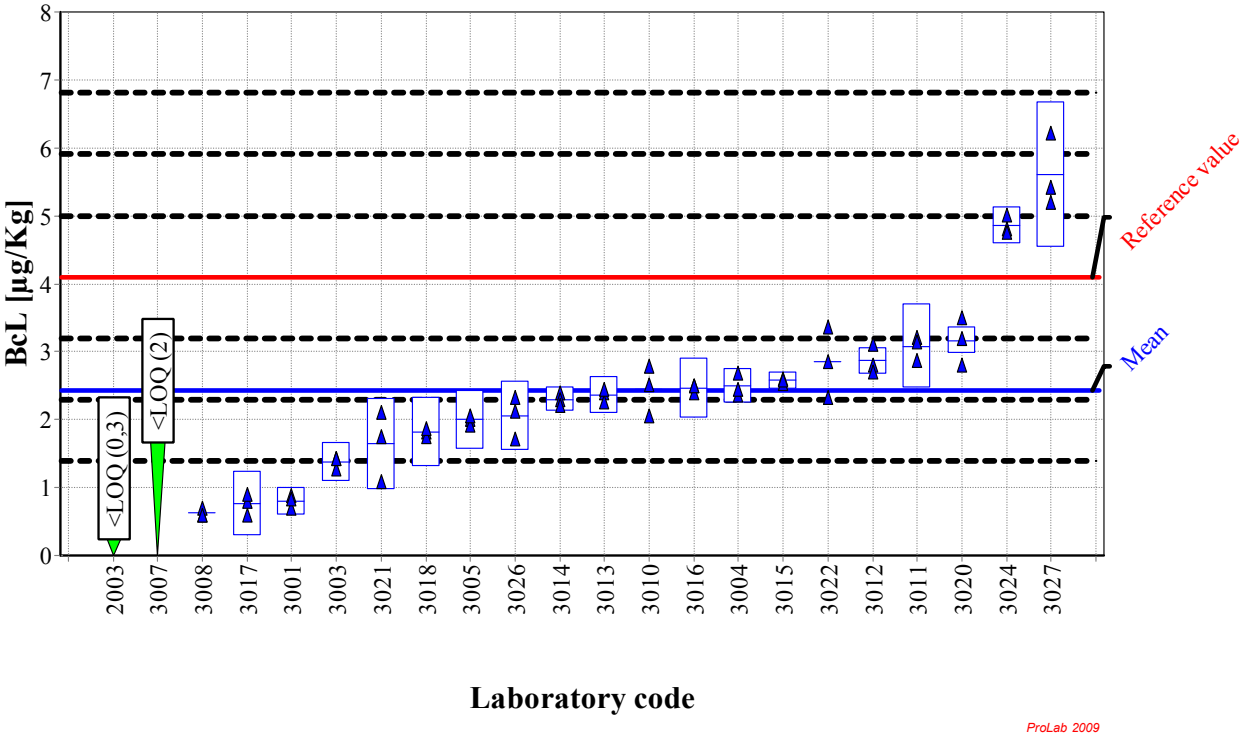

Figure 81: Kernel Density Plot

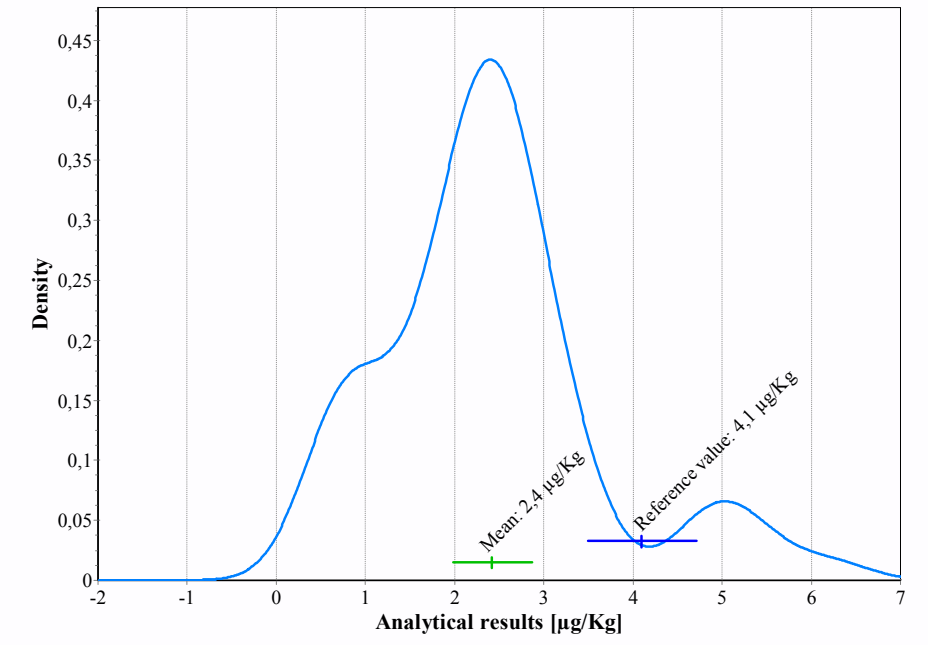

Table 46: Individual results of replicate measurements of BcL in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003					
3001	0,69	0,89	0,83	0,83	0,21
3003	1,28	1,42	1,43	1,38	0,29
3004	2,36	2,45	2,69	2,5	0,25
3005	2,01	1,92	2,06	2	0,43
3006					
3007					
3008	0,6	0,7	0,6	0,6	
3010	2,05	2,52	2,79	2,45	
3011	2,87	3,21	3,15	3,08	0,62
3012	2,8	2,7	3,1	2,9	0,2
3013	2,4	2,26	2,44	2,37	0,27
3014	2,4	2,3	2,2	2,3	0,18
3015	2,6	2,53	2,59	2,57	0,13
3016	2,5	2,4	2,5	2,5	0,45
3017	0,6	0,8	0,9	0,8	0,5
3018	1,82	1,75	1,87	1,81	0,51
3019					
3020	3,2	2,8	3,5	3,2	0,2
3021	1,08	2,1	1,75	1,64	0,67
3022	2,32	3,37	2,85	2,85	
3024	4,81	4,75	5,01	4,86	0,27
3025					
3026	2,12	1,72	2,33	2,06	0,51
3027	5,2	5,41	6,21	5,61	1,07

Benzo[*ghi*]perylene (BgP)

Figure 82: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid lines indicate the laboratories robust mean (blue) and the assigned value of 0,4 µg/kg (red). The expanded uncertainty as reported by participants is indicated by the blue box. The green arrows indicate the LOQs reported by participants.

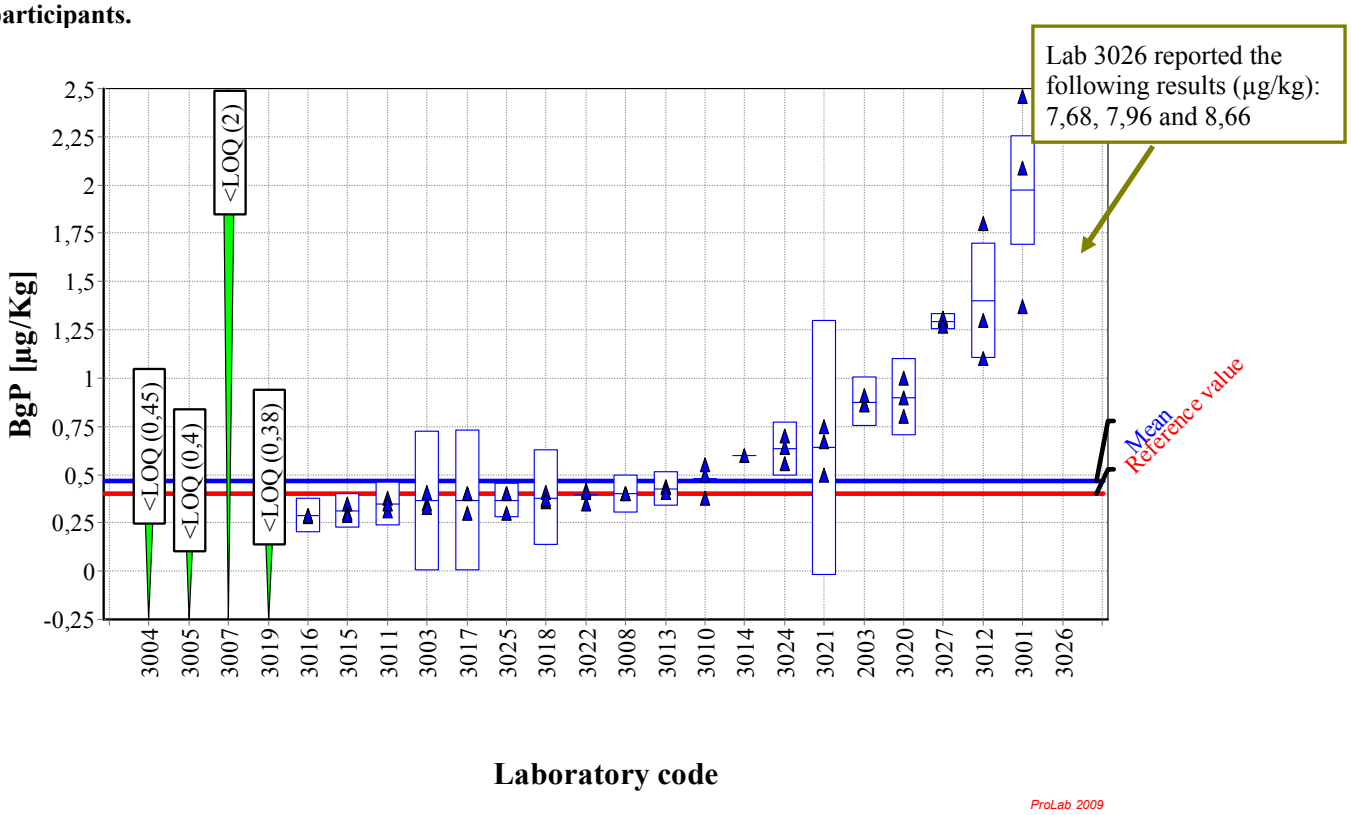

Figure 83: Kernel Density Plot

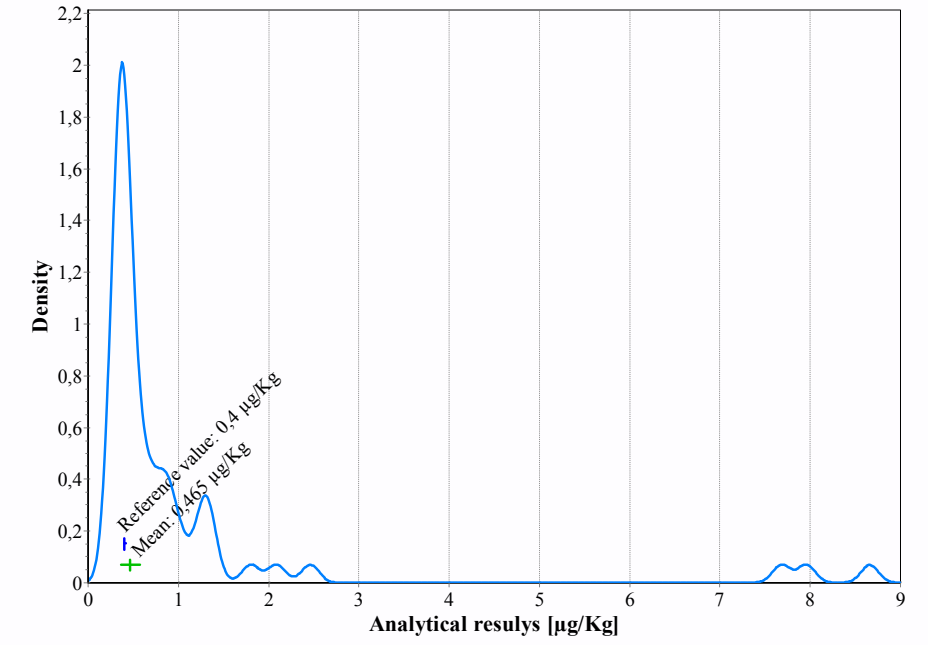

Table 47: Individual results of replicate measurements of BgP in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003	0,855	0,857	0,91	0,87	0,13
3001	2,09	2,46	1,37	2,09	0,3
3003	0,35	0,41	0,33	0,36	0,36
3004					
3005					
3006					
3007					
3008	0,4	0,4	0,4	0,4	0,1
3010	0,38	0,5	0,55	0,48	
3011	0,38	0,31	0,35	0,34	0,11
3012	1,8	1,1	1,3	1,4	0,3
3013	0,44	0,43	0,41	0,43	0,09
3014		0,6			
3015	0,35	0,3	0,29	0,31	0,09
3016	0,29	0,28	0,29	0,29	0,09
3017	0,4	0,3	0,4	0,4	0,4
3018	0,41	0,36	0,37	0,38	0,25
3019					
3020	0,8	0,9	1	0,9	0,2
3021	0,75	0,5	0,67	0,64	0,66
3022	0,35	0,42	0,41	0,41	
3024	0,56	0,64	0,7	0,63	0,14
3025	0,3	0,4	0,4	0,4	0,1
3026	7,68	7,96	8,66	8,1	1,21
3027	1,3	1,31	1,27	1,3	0,04

Benzo[*j*]fluoranthene (BjF)

Figure 84: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid lines indicate the laboratories robust mean (blue) and the assigned value of 0,5 µg/kg (red). The expanded uncertainty as reported by participants is indicated by the blue box. The green arrows indicate the LOQs reported by participants.

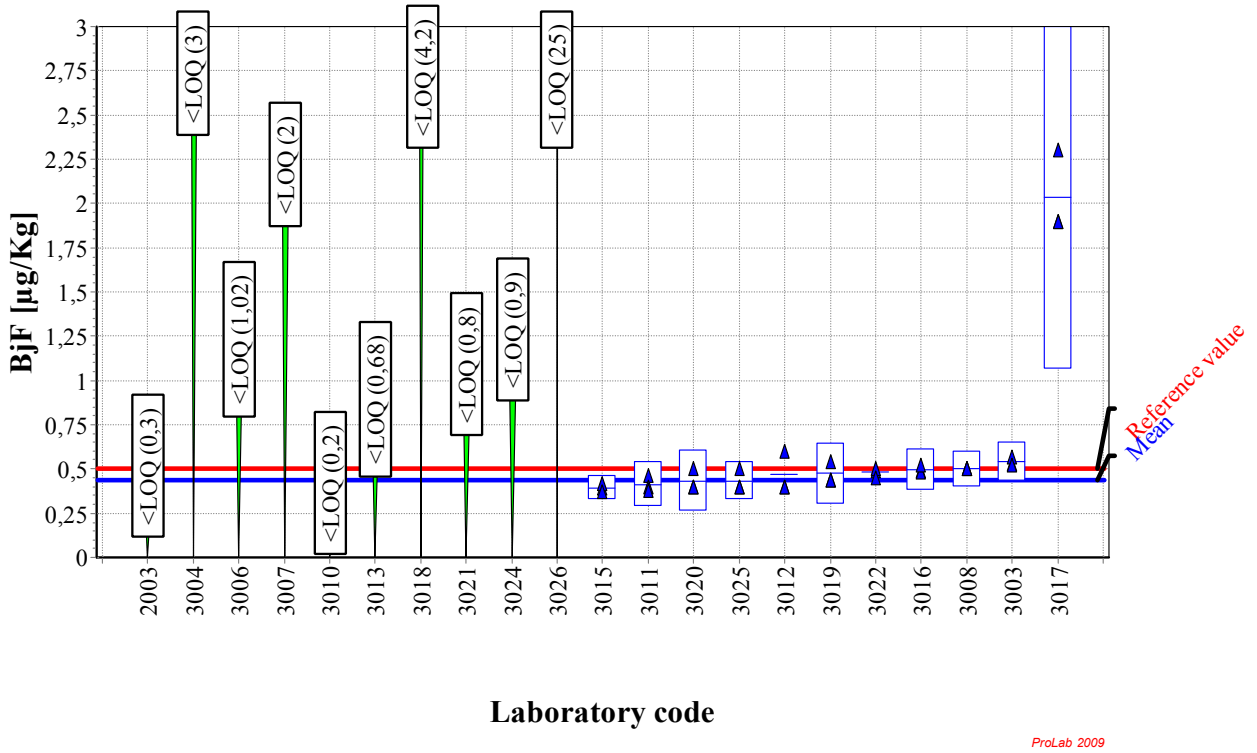

Figure 85: Kernel Density Plot

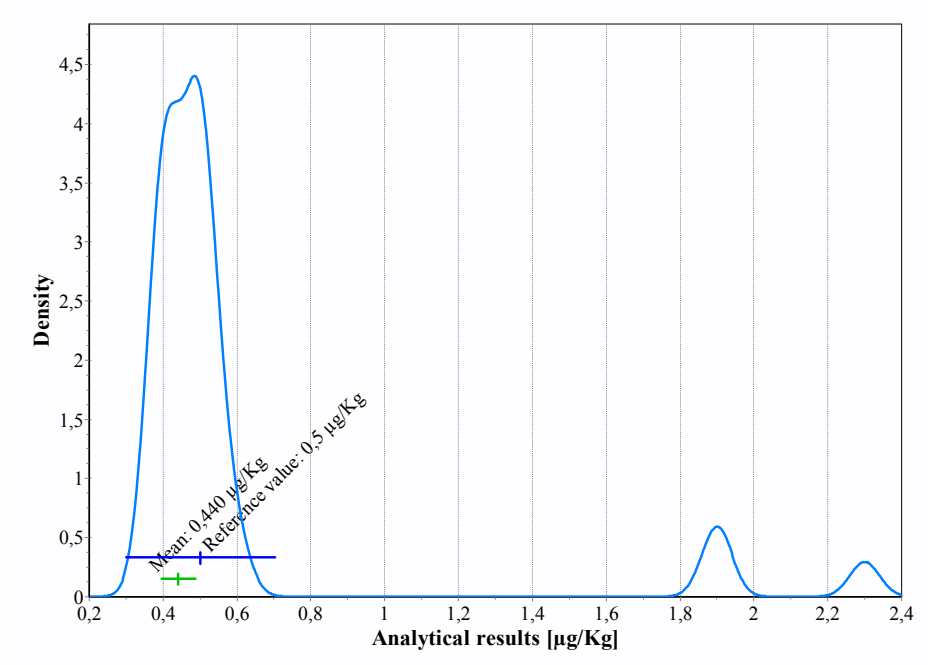

Table 48: Individual results of replicate measurements of BjF in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003					
3001					
3003	0,53	0,57	0,52	0,54	0,11
3004					
3005					
3006					
3007					
3008	0,5	0,5	0,5	0,5	0,1
3010					
3011	0,46	0,4	0,38	0,42	0,13
3012	0,6	0,4	0,4	0,4	
3013					
3014					
3015	0,39	0,42	0,37	0,39	0,07
3016	0,49	0,48	0,52	0,5	0,12
3017	1,9	2,3	1,9	2,1	1
3018					
3019	0,44	0,44	0,54	0,46	0,17
3020	0,4	0,5	0,4	0,5	0,2
3021					
3022	0,49	0,5	0,45	0,49	
3024					
3025	0,4	0,4	0,5	0,4	0,1
3026					
3027					

Chrysene (CHR)

Figure 86: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid and dotted lines indicate the laboratories robust mean (blue), the assigned value of 2,4 µg/kg (red), a ±1σ_p, ± 2σ_p, and ± 3σ_p deviation thereof (black dotted). The expanded uncertainty as reported by participants is indicated by the blue box. The green arrows indicate the LOQs reported by participants.

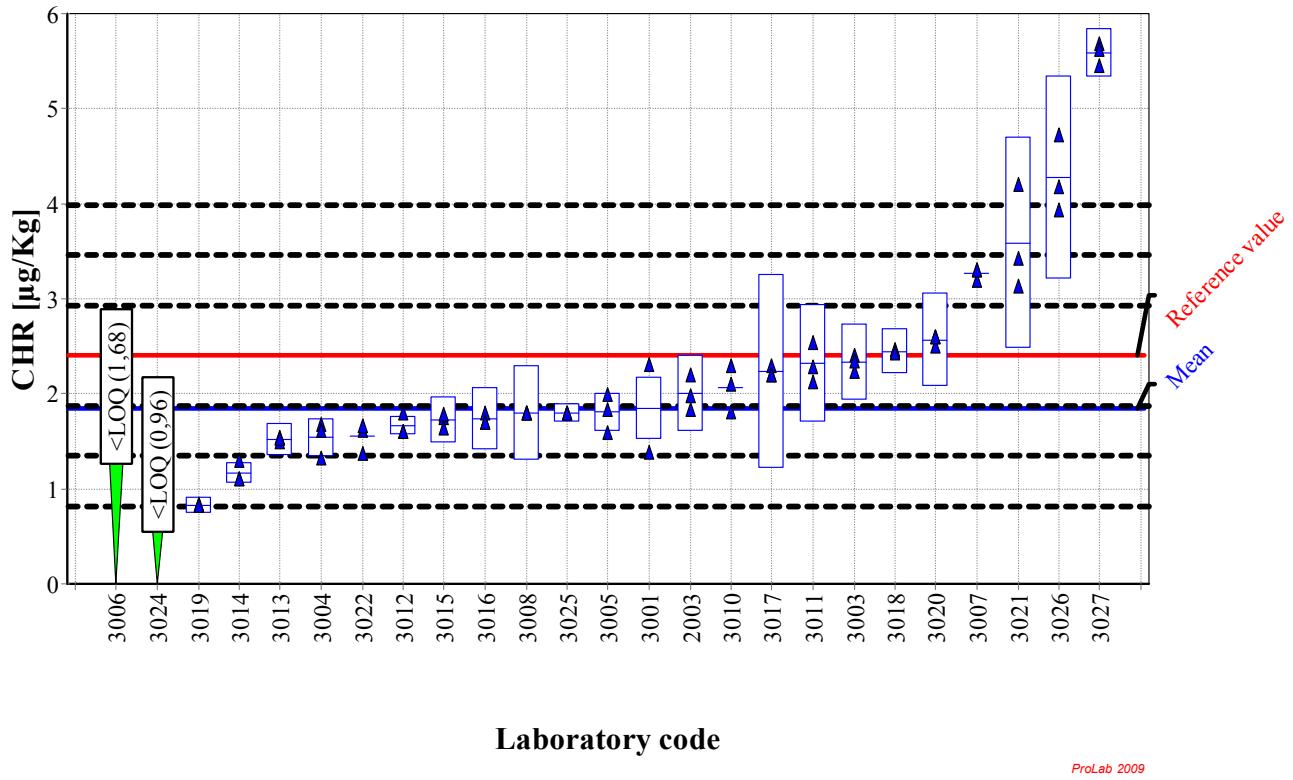

Figure 87: Kernel Density Plot

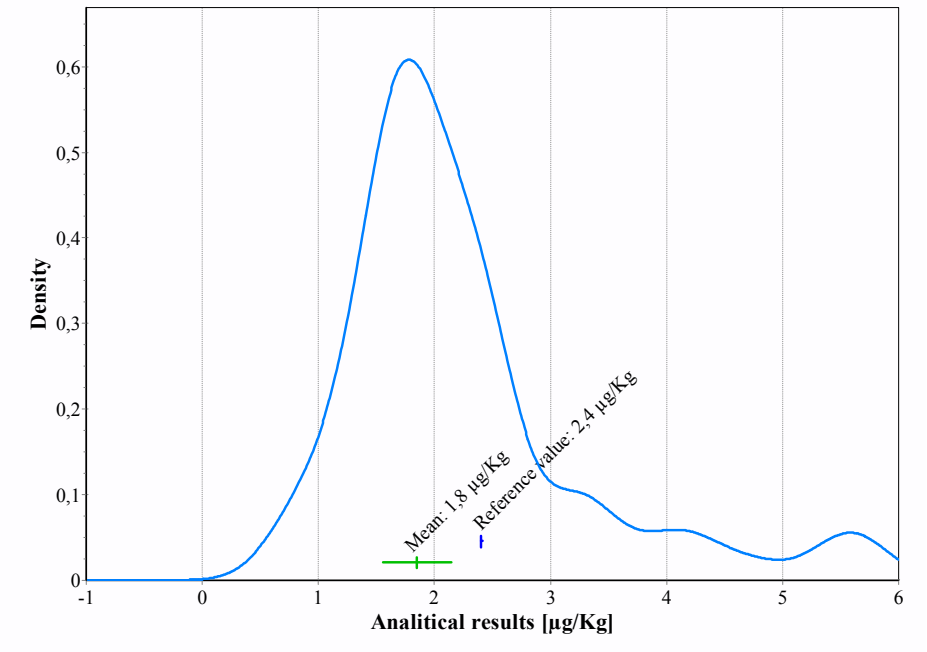

Table 49: Individual results of replicate measurements of CHR in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003	2,202	1,977	1,837	2	0,4
3001		1,39	2,31	1,85	0,33
3003	2,41	2,24	2,35	2,33	0,4
3004	1,68	1,61	1,32	1,54	0,2
3005	1,59	1,84	1,99	1,81	0,2
3006					
3007	3,3	3,2	3,3	3,27	
3008	1,8	1,8	1,8	1,8	0,5
3010	2,3	2,1	1,81	2,07	
3011	2,54	2,28	2,13	2,32	0,62
3012	1,8	1,6	1,6	1,7	0,1
3013	1,49	1,54	1,53	1,52	0,17
3014	1,1	1,1	1,3	1,2	0,11
3015	1,75	1,64	1,79	1,73	0,24
3016	1,7	1,8	1,7	1,7	0,32
3017	2,2	2,3	2,2	2,2	1
3018	2,44	2,47	2,43	2,45	0,24
3019	0,82	0,84	0,82	0,77	0,08
3020	2,5	2,6	2,6	2,6	0,5
3021	3,43	4,2	3,13	3,59	1,11
3022	1,62	1,67	1,37	1,62	
3024					
3025	1,8	1,8	1,8	1,8	0,1
3026	3,93	4,18	4,73	4,28	1,07
3027	5,69	5,62	5,45	5,59	0,25

Cyclopenta[*cd*]pyrene (CPP)

Figure 88: Individual results of replicate measurements (▲), sorted by the laboratory mean values. The horizontal solid lines indicate the laboratories robust mean (blue) and the assigned value of 0,5 µg/kg (red). The expanded uncertainty as reported by participants is indicated by the blue box. The green arrows indicate the LOQs reported by participants.

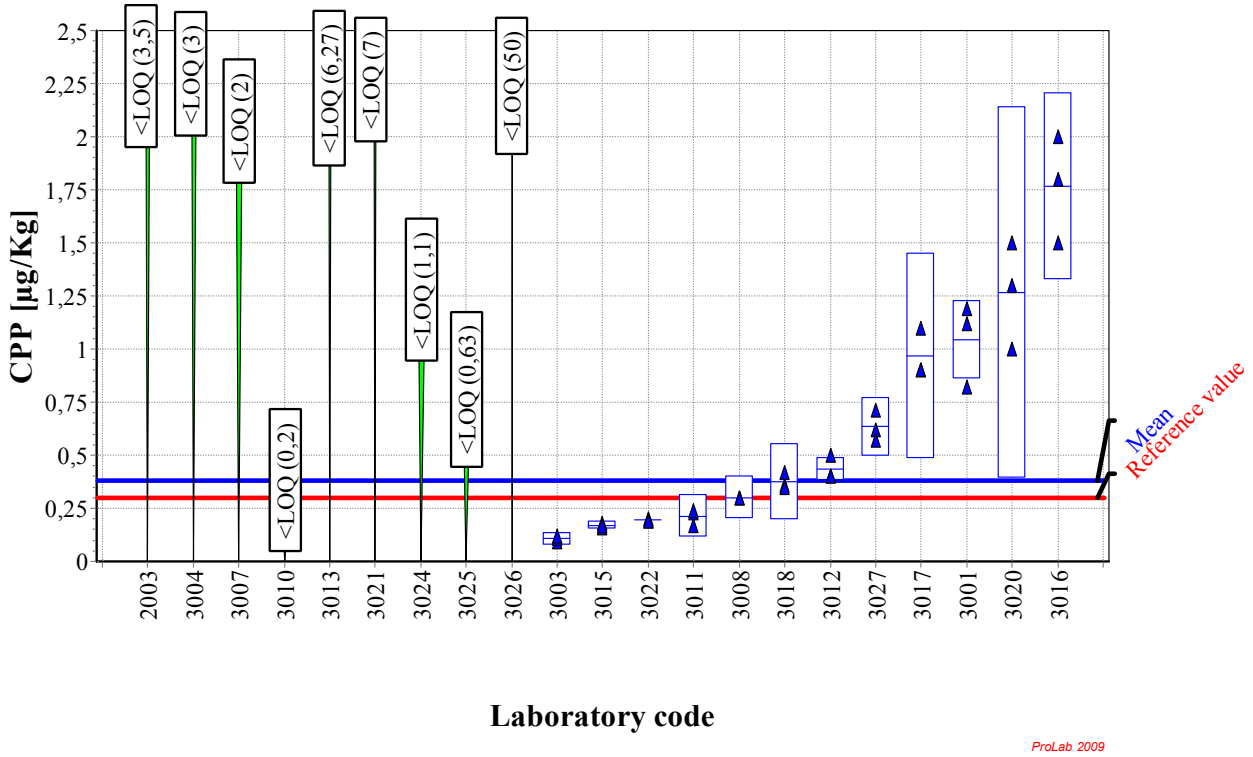

Figure 89: Kernel Density Plot

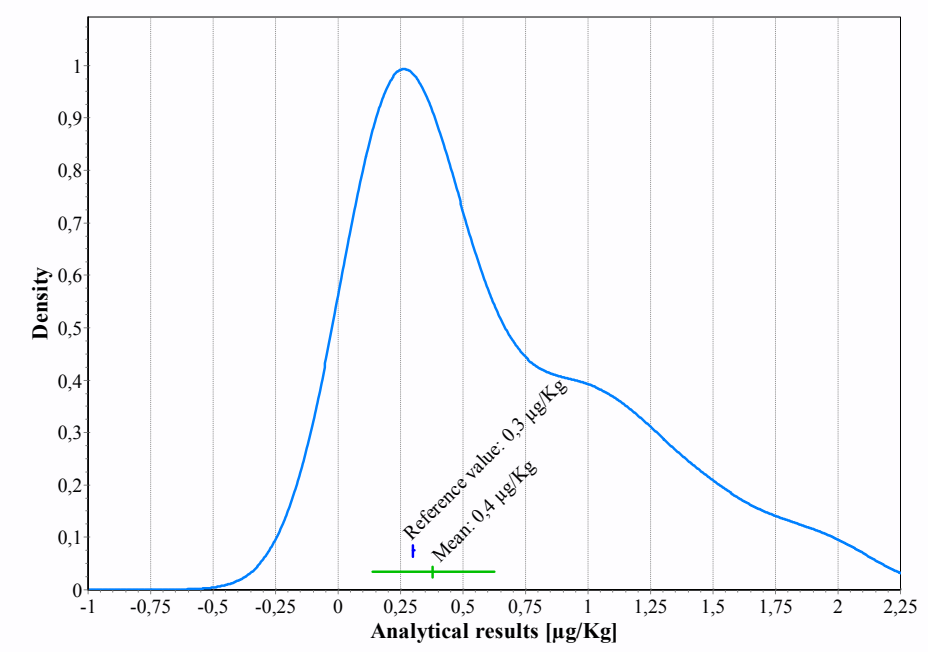

Table 50: Individual results of replicate measurements of CPP in Fish D in µg/kg (blank cells indicate missing data)

Participant	Result 1	Result 2	Result 3	Final results	Uncertainty (k = 2)
2003					
3001	0,82	1,12	1,19	1,12	0,2
3003	0,09	0,11	0,12	0,11	0,03
3004					
3005					
3006					
3007					
3008		0,3	0,3	0,3	0,1
3010					
3011	0,17	0,23	0,24	0,21	0,1
3012	0,5	0,4	0,4	0,4	0,05
3013					
3014					
3015	0,18	0,16	0,17	0,17	0,02
3016	1,8	1,5	2	1,8	0,45
3017	0,9	0,9	1,1	1	0,5
3018	0,36	0,42	0,35	0,38	0,18
3019					
3020	1,3	1	1,5	1,3	0,9
3021					
3022	0,19	0,20,19	0,19		
3024					
3025					
3026					
3027	0,71	0,62	0,57	0,64	0,14

Annex 5: Supporting documents

E-mail of announcement of the PT

From: LERDA Donata (JRC-GEEL) **On Behalf Of** JRC IRMM CRL PAH
Sent: Thursday, May 07, 2009 10:14 AM
To:
Subject: CRL PAHs 2009 PT
Importance: High

Dear Madam / Sir,

The Community Reference Laboratory for PAHs announces that the 2009 proficiency test (PT) on PAHs in smoked fish will start on the second week of June.

For correctly dispatching the sample and for the following communications, we need the name, address, and telephone + FAX numbers of the person who shall be in charge of receiving the parcel and of all next steps related to the PT organisation (communication with the CRL, reporting of results, etc.).

Please, fill in the "PT 2009 contact.xls" table, herein attached, and send it back to us with the relevant data **within the 15th of May 2009**.
Please note that, in case we do not receive any answer we shall send the parcel to the contact person included in DG SANCO official list and shall not respond, in case the data are not updated, for an NRL not being able to participate to the PT.

For third countries laboratories, we ask to express, in the answer to this e-mail, their interest in participating to the PT.

Thank you for the co-operation and 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

Announcement of material dispatch

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
Community Reference Laboratory for
Polycyclic Aromatic Hydrocarbons

CRL
Polycyclic Aromatic Hydrocarbons

Geel, 02 June 2009
CRL PAHs/DLE D(2009)

Shipment of materials for the PT-2009

«AddressBlock»

«GreetingLine»

We are planning to dispatch the materials for the next proficiency test on 9th of June via DHL. Please be prepared to receive the samples and store them in an appropriate way (cool, 4ºC, and dark).
We will inform you about the details of the shipment, the analyses to be made, deadline for reporting, and the required password as soon as the items will have left our premises.

With best regards,

Donata Lerda

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 826. Fax: (32-14) 571 783.

E-mail: donata.lerda@ec.europa.eu

DHL shipment notification

From: LERDA Donata (JRC-GEEL) On Behalf Of JRC IRMM CRL PAH
Sent: Tuesday, June 09, 2009 4:00 PM
To: ---------
Subject: FW: DHL Intraship - Shipment notification

Dear <<Title>> <<Name>>,

The material for the 'PT-2009 fish' has been dispatched. Please see below for the tracking details.

Kind 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

DHL EXPRESS
SHIPMENT ADVISORY
Subject:317/2009

The following piece has been sent by Pascal Vergucht from
IRMM via DHL Express on 09.06.2009 (AWB# 9507858636).
If you wish to track this shipment please contact your local
DHL Customer Service office or visit the DHL website at
http://www.dhl.be/

If you have a web-enabled mail reader, click the link below to view
shipment tracking details:
http://www.dhl.com/cgi-bin/tracking.pl?AWB=9507858636

or just forward this Email to tracknl@dhl.com and you will receive feedback.

SEND TO: <<Organisation>>
FAO : <<Title>> <<Name>>
<<Address>>
<<Department>>
<<Town>>
<<Zip>>
<<Country>>

SENDER : IRMM
From : ---------
Retieseweg 111
Geel - 2440 Belgium

SHIPMENT CONTENTS:
scientific samples

SHIPPER REFERENCE: ..

AWB: 9507858636
WEIGHT: 1.5
PIECES: 1
CONTENTS: scientific samples

---- DHL EXPRESS ----

Accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Community reference laboratory for polycyclic aromatic hydrocarbons

CRL
Polycyclic Aromatic Hydrocarbons

Geel, 9 June 2009
D08/TW/bk/ARES (2009) 120042

4th Inter-laboratory comparison study organised by the CRL-PAH:

CRL-PAHs-04: ***Analysis of the 15+1 EU priority PAHs in smoked fish and acetonitrile***

Dear participant,

As announced at the 4th workshop of the consortium of reference laboratories on PAHs (24-25 March 2009, Geel, Belgium), the first 2009 inter-laboratory comparison study focuses on the determination of the 15+1 EU priority PAHs in smoked fish and solvent solution.

The outline of the study was presented to the delegates of the national reference laboratories (NRLs) and of the candidate / potential candidate countries expert laboratories during the same event.

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.

The EFSA opinion Published on the EFSA Journal (2008) 724, 1-114, "Polycyclic Aromatic Hydrocarbons in Food", Adopted on 9 June 2008 brought to the consequent decision of the Standing Committee on Food Chain and Animal Health (SCFCAH) (minutes of the meeting of 12/12/2008 of the Section "Toxicological safety of food chain") to include in future legislation, beside benzo[a]pyrene, also benzo[b]fluoranthene, benzo[a]anthracene, and chrysene.

To assess the state of the art in this respect in the network of the PAHs NRLs, the CRL PAHs will check the compliancy with Regulation (EC) 333/2007 method specifications for benzo[a]pyrene and verify if for the other three PAHs those method specifications could be respected with the methods in use at present.

Each participant will be provided with a set of samples that comprises two smoked fish samples with different composition and level of concentration of PAHs (two cans for each sample), an unknown solution of the target analytes in acetonitrile, and a known, concentrated standard solution in toluene for the preparation of calibration solutions for instrument calibration.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 320. Fax: (32-14) 571 783.

E-mail: jrc-irmm-crl-pah@ec.europa.eu

Officially appointed NRLs shall participate in the study. Moreover, reference laboratories of EU Candidate / Potential candidate Countries will be supplied with samples on request.

This study is also regarded as a follow-up to the 2006, 2007, and 2008 inter-laboratory comparison studis on the determination of 15+1 PAHs in solvent solution, edible oil, and sausage meat.

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.

1. The laboratories are requested to perform **five (5) replicate analyses on the smoked fish sample (two cans were delivered to allow sufficient amount: the homogeneity of the test material was checked so that the two cans could be used indifferently).** Samples shall be analysed immediately after opening of the can(s) and the five replicates should be analysed in one day, in the same sequence with the calibration.

2. The laboratories are requested to perform **three (3) replicate analysis on the fresh fish contaminated with oil extract of smoke flavouring (two cans were delivered to allow sufficient amount: the homogeneity of the test material was checked so that the two cans could be used indifferently).** Samples shall be analysed immediately after opening of the can(s) and the three replicates should be analysed in one day, in the same sequence with the calibration

3. The **unknown solution of PAHs in acetonitrile shall be analysed in triplicate.** Samples shall be analysed immediately after opening of the ampoule and the three replicates should be analysed in one day, in the same sequence with the calibration

For all samples the participating laboratories shall apply a method of their choice, taking into account that other PAHs than the 15+1 EU priority PAHs could be present.

The laboratories shall report the results by **11th September 2009 latest** via the PDF Form they shall receive via e-mail. As participants are supposed to report on all analytes, co-eluting substances cannot be reported anymore as sum.

For each sample participants shall report all the results obtained with replicate analysis and for the two fish sample they shall also report the final value on which their performance will be assessed through the z-score. The choice of the final value (average of the replicates, robust mean of the replicates, etc.) to be reported for the PT, is with the participant.

In that PDF Form they shall be asked to report, together with the results, some method specifications concerning the 4 PAHs above mentioned and highlighted in bold character in Table 1.

In addition some general characteristics of the method applied will be asked for.

Test materials and analytes

1. Two cans, labelled as sample F (fish) / C+code, containing each about 50 g of a *spiked smoked fish sample:* The concentration of the individual analytes is in the range of about 1 to 10 µg/kg. The cans shall be considered as a single sample which shall be analysed in 5 replicates.
2. Two cans, labelled as sample F (fish) / D+code, containing each about 50 g of a *fish sample spiked with an oil extract of smoked flavouring:* The concentration of the individual analytes is in the range of about 0 to 5 µg/kg. The cans shall be considered as a single sample which shall be analysed in 3 replicates.
3. 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.
4. One ampoule with 2.5 ml of a solution of *15+1 EU priority PAHs in toluene*. Specified concentration: about 10.00 mg/l (concentrations reported on the attached certificate) for each analyte with an expanded relative uncertainty (U_{rel}) reported in the specification sheet (expansion factor k = 2). 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)

In bold are reported the 4 PAHs indicated by SCFCAH

In case of questions please do not hesitate to contact:

Donata Lerda
Institute for Reference Materials and Measurements (IRMM)
CRL Mycotoxins
Retieseweg 111
B-2440 Geel, Belgium
Tel: +32-14-571 826
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E-mail: donata.lerda@ec.europa.eu

With kind regards,

Thomas Wenzl

(Operating Manager of the Community Reference Laboratory for Polycyclic Aromatic Hydrocarbons)

Cc: Almut Bitterhof, Anne-Mette Jensen, Franz Ulberth

Standard solution (CAL) specification sheet

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Community reference laboratory for polycyclic aromatic hydrocarbons

CRL
Polycyclic Aromatic Hydrocarbons

Standard solution specification sheet **Product ID: CRL PAHs-05**

Date of production: 25/05/2009 Total volume: 2.5 mL

Expiry date: *December 2009*

Standard solution composition:

	Product name	CAS	Conc.* (µg/g)	Conc.* (µg/mL)	U** ± %
1	5-methylchrysene	3697-24-3	11,6	9,9	1
2	Benzo[a]anthracene	56-55-3	11,7	10,0	1
3	Benzo[a]pyrene	50-32-8	11,8	10,1	1
4	Benzo[b]fluoranthene	205-99-2	11,5	9,9	1
5	Benzo[c]fluorene	205-12-9	9,1	7,8	1
6	Benzo[ghi]perylene	191-24-2	10,3	8,9	1
7	Benzo[j]fluoranthene	205-82-3	11,7	10,0	1
8	Benzo[k]fluoranthene	207-08-9	10,6	9,1	1
9	Chrysene	218-01-9	11,7	10,0	1
10	Cyclopenta[cd]pyrene	27208-37-3	11,2	9,6	1
11	Dibenzo[a,e]pyrene	192-65-4	10,6	9,1	1
12	Dibenzo[a,h]anthracene	53-70-3	11,1	9,5	1
13	Dibenzo[a,h]pyrene	189-64-0	11,7	10,1	1
14	Dibenzo[a,i]pyrene	189-55-9	6,3	5,4	1
15	Dibenzo[a,l]pyrene	191-30-0	11,8	10,1	1
16	Indeno[1,2,3-cd]pyrene	193-39-5	11,7	10,0	1

** The concentrations were calculated taking into account the purity statements of the single products*

*** U is the expanded uncertainty calculated using the coverage factor 2 (corresponding to a confidence interval of 95%) multiplied by the combined standard uncertainty. The standard uncertainty is equal to the square root of the sum of the squares of the uncertainties associated with each single operation involved in the preparation of this standard solution.*

Solvent	**Ratio (g/g)**
Cyclohexane / Toluene	1 : 8,72

Analytical method for confirmation	Product ID: CRL PAHs-05

Detection: GC-MS in SIM mode (isotope dilution)

Warning	Product ID: CRL PAHs-05
	Store in the dark at 20 ºC or less The European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.
Safety of the product	The solution contains some teratogenic and carcinogenic substances. Check the attached material safety data sheets for information on hazard, exposure, and safe handling.

Sample receipt confirmation form

CRL-PAHs-04

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

Confirmation of the receipt of the samples

RECEIPT FORM

Surname of Participant	
Name of Participant	
Affiliation	
Lab ID	
Country	

Content of the parcel

a) Four 50 g aluminium tins with fish samples (of two different kinds)

b) One 5 ml brown glass ampoule with a standard solution of the 15+1 EU priority PAHs in acetonitrile (concentrations unknown)

c) One 5 ml brown glass ampoule with a standard solution of the 15+1 EU priority PAHs in toluene (concentrations known)

d) One specification sheet for the item c) content (primary standard solution)

e) One material safety data sheet for acetonitrile

f) One material safety data sheet for toluene

g) One material safety data sheet for cyclohexane

h) Safety data sheets for some of the PAHs included in the study

i) One outline of the study

j) One paper sheet with the Laboratory ID to be used in all following communications

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

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
If NO, please list damaged items according to the letters associated at each item in the list above (in case of samples, please specify the code too: e.g. a+code) Please write one item per row	
Items are missing	YES / NO
If YES, please list missing items according to the letters associated at each item in the list above Please write one item per row	
Serial numbers of the fish samples you received	
Serial number of the standard solution with unknown concentrations	

Signature .....

ATTENTION

Please, submit the filled in form by mail at the following address:

jrc-irmm-crl-pah@ec.europa.eu

or print it and send the printout by fax at the attention of Donata Lerda at the following number:

+32 – 014 - 571783

PDF form for reporting of results

Reporting of results for the
CRL PAHs PT 2009 (PAHs in fish)

This FORM has to be filled and submitted electronically by all participants to the CRL PAH. For this we need your collaboration in processing your results report in the way we propose.

Important!
Please fill all fields using Adobe Acrobat Reader. You shall **send the filled FORM by email** as well as printed and signed by FAX (in this way we have a signed proof of the results you report for this PT).
Other ways of reporting of results will not be accepted!
(Please do not print out the form, scan it, and then send by email as we need the "PDF" file generated by the above suggested procedure).
At the end of the questionnaire you will find two buttons for sending the created file submit by email and to print form. Please make use of these features and follow carefully the instructions at the end of this form.

>> Read carefully before filling-in the FORM <<

1. The fields marked with a * are mandatory: you will not be able to send the FORM if you have not filled in all the mandatory fields.
2. When the description of the field includes an indication of the format, please follow exactly the indication (e.g. Your Name (First name + SURNAME), you should write your name in normal letters and the surname in capital letters).
3. All the fields for reporting of results are numeric fields: **do not try to enter other formats**.
4. If you do not report results for a particular analyte (e.g. analyte not detectable with your method (CPP), or incomplete separation of isomers) simply leave the field empty, both for the replicates and for the final result.
5. For sample D, when you detect a certain PAH, you do not want to report numerical results for due to content below LOD or LOQ respectively, please proceed as following:
   - FOR REPLICATES: leave the field empty (*all the fields could be empty in case that none of the replicates was above your LOD or LOQ, depending on your reporting methodology, or some of them could be empty in case that one or more replicate gave a value above the LOD or LOQ of your method*)
   - FOR THE FINAL RESULT: leave the field for reporting numerical results empty and write **Y** *(for yes)* in the corresponding field in the column on the right: "Below LOD" or "Below LOQ", as applicable. Please give also numerical values for the corresponding LOD and LOQ of your method.
   - Please indicate in the fields below the table for sample D results, the statement you would use for reporting to the customer (e.g. "less than LOD")

IMPORTANT:
Please note that, for the two food samples, you should report both the results from the replicate analysis and the FINAL RESULT. The final results correspond to the result you would report to a customer and shall be obtained with a methodology chosen by you (e.g. the average of the replicates, one of the values obtained, a further analytical result).

The final result will be used for the calculation of the z-score of your laboratory.

ALL RESULTS, BOTH REPLICATES AND THE FINAL RESULT, HAVE TO BE REPORTED CORRECTED FOR RECOVERY

General information

1. Your Laboratory ID (4 digits number)*:
2. Your NRL (NRL + country abbreviation + feed / food[when applicable])*:
3. Your Affiliation (Organisation + Department)*:
4. Your Title (Mr. / Ms. / Mrs. / Dr. / Prof.):
5. Your Name (First name + SURNAME)*:
6. Your address

   Street (St. / Sq. / Bv. + Name of the street + number)*

   ZIP*:

City*:

Country*:

Phone number*:

Fax number:

Your e-mail address*:

Second contact e-mail address (if applicable):

Method description

Please report the general characteristics of the method you applied for the analysis of the fish samples received for the PT

7. Which extraction method did you use?*

PLE ○ Soxhlet ○ Saponification ○ Other ○

If other, please shortly describe

8. Which was the main purification step of your method?*

DACC ○ SPE ○ GPC ○ Solvent partitioning ○ Other ○

If other, please shortly describe

9. Which was the main instrumental-detection method you applied?*

GC-MS ○ GC-FID ○ HPLC-FLD ○ LC-MS ○ Other ○

If other, please shortly describe

Results for ACN solution (in µg/L)

Sample code (given on the ampoule e.g. '0051'):

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

**U indicates the expanded uncertainty of the measurements obtained from the standard uncertainty multiplied by the coverage factor of 2, corresponding to a confidence level of 95%*

Results for sample C (in µg/kg) **Sample codes** (written on the sample e.g. 'C 158'):

10. Did you use both sample units for the analyses? (Yes / No)* If YES, did you mix and homogenise them before aliquotation? (Yes / No)*

Analyte	Short name	Replicate 1 µg/kg	Replicate 2 µg/kg	Replicate 3 µg/kg	Replicate 4 µg/kg	Replicate 5 µg/kg	Final value µg/kg	U* (k=2) µg/kg
5-methylchrysene	5MC							
benz[*a*]anthracene	BaA							
benzo[*a*]pyrene	BaP							
benzo[*b*]fluoranthene	BbF							
benzo[*c*]fluorene	BcL							
benzo[*ghi*]perylene	BgP							
benzo[*j*]fluoranthene	BjF							
benzo[*k*]fluoranthene	BkF							
chrysene	CHR							
cyclopenta[*cd*]pyrene	CPP							
dibenzo[*a,e*]pyrene	DeP							
dibenz[*a,h*]anthracene	DhA							
dibenzo[*a,h*]pyrene	DhP							
dibenzo[*a,i*]pyrene	DiP							
dibenzo[*a,l*]pyrene	DlP							
indeno[1,2,3-*cd*]pyrene	ICP							

**U indicates the expanded uncertainty of the measurements obtained from the standard uncertainty multiplied by the coverage factor of 2, corresponding to a confidence level of 95%*

Results for sample D (in µg/kg) **Sample codes** (written on the sample e.g. 'D 288'):

11. Did you use both sample units for the analyses? (Yes / No)* If YES, did you mix and homogenise them before aliquotation? (Yes / No)*

Analyte	Short name	Replicate 1 µg/kg	Replicate 2 µg/kg	Replicate 3 µg/kg	Final value µg/kg	U* (k=2) µg/kg	Below LOD **	Below LOQ **	LOD µg/kg	LOQ µg/kg
5-methylchrysene	5MC									
benz[*a*]anthracene	BaA									
benzo[*a*]pyrene	BaP									
benzo[*b*]fluoranthene	BbF									
benzo[*c*]fluorene	BcL									
benzo[*ghi*]perylene	BgP									
benzo[*j*]fluoranthene	BjF									
benzo[*k*]fluoranthene	BkF									
chrysene	CHR									
cyclopenta[*cd*]pyrene	CPP									
dibenzo[*a,e*]pyrene	DeP									
dibenz[*a,h*]anthracene	DhA									
dibenzo[*a,h*]pyrene	DhP									
dibenzo[*a,i*]pyrene	DiP									
dibenzo[*a,l*]pyrene	DlP									
indeno[1,2,3-*cd*]pyrene	ICP									

**U indicates the expanded uncertainty of the measurements obtained from the standard uncertainty multiplied by the coverage factor of 2, corresponding to a confidence level of 95%*

*** **Please write Y if the results is below LOD or LOQ, otherwise leave it empty (see point 5 of the "Read carefully before filling-in the FORM" paragraph)***

12. Please report the statement for results below LOD, if applicable
13. Please report the statement for results below LOQ, if applicable

ATTENTION

1. Please, submit first the form by mail so we can evaluate it electronically:

   Submit by Email

2. After you have sent the form by e-mail, please print it, sign it and send the printout by fax to the following number: +32 – 14 - 571783

   Print Form

YOUR Signature: _____

Results not transmitted both by e-mail as PDF Form and by FAX will not be considered as valid

Please, remember that the deadline for reporting of results is the 11/09/2009.

There will be no possibility to extend the deadline.
The results from participants not reporting within the deadline will NOT be considered in the report and the respective participant will be asked to justify the delay.

The CRL PAHs thanks you for reporting your results.

Questionnaire on details of analysis methods

Questionnaire for the participants to CRL PAHs PT 2009 (PAHs in fish)

This FORM has to be filled and submitted electronically by all participants to the CRL PAH. For this we need your collaboration in processing this questionnaire in the way we propose.

Important!
Please fill all fields using Adobe Acrobat Reader. You shall **send the filled FORM by email** as well as printed and signed by FAX (in this way we have a signed proof of the results you report for this PT).
Other ways of reporting of results will not be accepted!
(Please do not print out the form, scan it, and then send by email as we need the "PDF" file generated by the above suggested procedure).
At the end of the questionnaire you will find two buttons for sending the created file submit by email and to print form. Please make use of these features and follow carefully the instructions at the end of this form.

>> Read carefully before filling-in the FORM <<

1. The fields marked with a * are mandatory: you will not be able to send the FORM if you have not filled in all the mandatory fields.
2. When the description of the field includes an indication of the format, please follow exactly the indication (e.g. Your Name (First name + SURNAME), you should write your name in normal letters and the surname in capital letters).
3. All the fields where you have to report the results are numeric fields: **do not try to enter other formats**.

Some of the information you have to report here are a repetition of the information you already included in the Results FORM. Please, be patient and include in this questionnaire all the information required. It will be of great help to us to treat the two set of information separately.

General information

1. Your Laboratory ID (4 digits number)*:
2. Your NRL (NRL + country abbreviation + feed / food[when applicable])*:
3. Your Affiliation (Organisation + Department)*:
4. Your Title (Mr. / Ms. / Mrs. / Dr. / Prof.):
5. Your Name (First name + SURNAME)*:
6. Your e-mail address*:
7. Second contact e-mail address (if applicable):
8. Did your laboratory perform PAHs analysis in food / feed before?

If YES, for how long?

9. Did your laboratory perform PAHs analysis in fish before?

If YES, for how long?

If YES, did the PT test samples behave similar in sample preparation and analysis to routine fish samples analysed in your laboratory?

If you answered NO to the last question, please give details on the differences

What is the extraction time?

What is the extraction temperature?

Please report other details if relevant

15. What is the first sample clean up step of your method?

DACC

Which solvents are used in the first sample clean up step?

What is the clean up time?

What is the clean up temperature?

Please report other details if relevant

16. What is the second clean up step of your method?

DACC

Which solvents are used in the second sample clean up step?

What is the clean up time?

What is the clean up temperature?

Please report other details if relevant

17. What is the third clean up step of your method?

DACC

Which solvents are used in the third sample clean up step?

What is the clean up time?

What is the clean up temperature?

Please report other details if relevant

18. What is the fourth clean up step of your method?

DACC

Which solvents are used in the first sample clean up step?

What is the clean up time?

What is the clean up temperature?

Please report other details if relevant

19. What type of analysis method did you use?

GC-FID

Details for GC method
Which injection system do you apply?

Which type of column do you apply and what are the column dimensions?

What is the oven temperature programme?

Details for HPLC method
Which type of column do you apply and what are the column dimensions?

What is the initial eluent?

What is the gradient?

Other method [please describe]

20. What type of detection system did you use?

Details for FID detection
What is the detector temperature?

Please report other details if relevant

Details for FLD detection
What are the wavelengths applied and for which groups of PAHs?

Please report other details if relevant

Details for MS detection
Do you apply electron ionisation (EI) or chemical ionisation (CI)?

If EI is applied, what is the ionisation energy?

If CI is applied, which are the ionisation gas, its pressure and flow?

If APPI (for LC-MS) is applied, please give relevant details

Do you quantify the PAHs in SCAN or SIM mode?

If in SIM, please fill in the following table

Analyte	Short name	Quantifier ion	Qualifier ion	Third ion	Fourth ion
5-methylchrysene	5MC				
benzo[*a*]anthracene	BaA				
benzo[*a*]pyrene	BaP				
benzo[*b*]fluoranthene	BbF				
benzo[*c*]fluorene	BcL				
benzo[*ghi*]perylene	BgP				
benzo[*j*]fluoranthene	BjF				
benzo[*k*]fluoranthene	BkF				
chrysene	CHR				
cyclopenta[*cd*]pyrene	CPP				
dibenzo[*a,e*]pyrene	DeP				
dibenz[*a,h*]anthracene	DhA				
dibenzo[*a,h*]pyrene	DhP				
dibenzo[*a,i*]pyrene	DiP				
dibenzo[*a,l*]pyrene	DlP				
indeno[*1,2,3,-cd*]pyrene	ICP				

21. Do you apply a confirmation method?

If YES, please describe the method

22. How did you integrate the signals (automatically or manually)?

If automatically, did you check the correctness of integration visually?

If YES, for how many peaks (in average) was it necessary to re-integrate for each chromatogram?

23. Which global settings did you use for automatic integration (e.g. valley-to-valley or horizontal baseline or tangential, etc.)?

24. Did you encounter any problems during analysis?

If YES, what were the specific problems and for which samples did you experience them?

25. Did you notice any abnormalities in the chromatogram which you however considered to have no effect on the results?

If YES, what were these observations and to which samples do they apply?

26. How long does it take the whole processing of one sample (from the preparation to the reporting of the results)?

Performance criteria for the method (Ref. Regulation (EC) 333/2007)
Please report the characteristics of the method you applied for the analysis of the fish samples received for the PT

Analyte	Short name	LOD	LOQ	Linear working range low	Linear working range high	Recovery
		µg/Kg	µg/Kg	µg/Kg	µg/Kg	%
5-methylchrysene	5MC					
benzo[*a*]anthracene	BaA					
benzo[*a*]pyrene	**BaP**					
benzo[*b*]fluoranthene	BbF					
benzo[*c*]fluorene	BcL					
benzo[*ghi*]perylene	BgP					
benzo[*j*]fluoranthene	BjF					
benzo[*k*]fluoranthene	BkF					
chrysene	CHR					
cyclopenta[*cd*]pyrene	CPP					
dibenzo[*a,e*]pyrene	DeP					
dibenz[*a,h*]anthracene	DhA					
dibenzo[*a,h*]pyrene	DhP					
dibenzo[*a,i*]pyrene	DiP					
dibenzo[*a,l*]pyrene	DlP					
indeno[*1,2,3,-cd*]pyrene	ICP					

Questions on this PT

27. Did you find the instructions distributed for this PT adequate?

If NO, which parts do you think could be improved?

28. What do you think about the reporting by electronic forms?

29. Did you have any problems in using the forms?

If YES, which were these problems?

30. Any other comments you wish to address?

ATTENTION

1. Please, submit first the form by mail so we can evaluate it electronically:

Submit by Email

2. After you have sent the form by e-mail, please print it, sign it and send the printout by fax to the following number: +32 – 14 - 571783

Print Form

YOUR Signature: _____

Questionnaires not transmitted both by e-mail as PDF Form and by FAX will not be included in the report

Please, remember that the deadline for sending back this questionnaire is the 11/09/2009.

There will be no possibility to extend the deadline.

Remember that some of the information included in this questionnaire is related to the compliancy of your method with the Regulation (EC) 333/2007 and the lack of these data will be considered as non - compliant

The CRL PAHs thanks you for answering promptly to this questionnaire.

Annex 6: Details of analysis methods applied by the participants

How do you prepare the sample? [freeze-drying, desiccant added to the sample, others]

Lab ID	Sample preparation
2003	homogenize and then store at -18°C till analyze
3001	HOMOGENIZATION, DESICCANT ADDED TO THE SAMPLE
3003	homogenised as received and whole weight aliquot extracted
3004	Hydromatrix added
3005	freeze-drying with Sodium Sulfate
3006	"We prepare/analyze the defrosted samples by milling them and adding ethanol/water/KOH. □"
3007	desiccant added to the sample
3008	Homogenise
3010	Desiccant added to the sample, spread with the sample
3011	desiccant added to sample
3012	homogenised material (fish without skin and bone) are grinded with drying material and sand. Addition of internal standard.
3014	Mix with hydromatrix (diatomaceous earth)
3015	none
3016	Homogenisation.
3017	grinding with sodium sulfate
3018	The sample is homogenized. When there is no possibility to start the analysis on the same day the homogenized sample is deep-frozen.
3019	FURTHER GRINDING OF THE RECEIVED MATERIAL
3020	Freeze-drying
3022	freeze-drying
3024	Saponification, Extraction (cyclohexane), two steps of SPE (C18 and Florisil)
3025	Homogenisation with Büchi B-400.
3026	desiccant added
3027	Homogenisation

Which extraction method do you use?
Which are the extraction solvents used?
What is the extraction time?
What is the extraction temperature?
Please report other details if relevant

LabID	Extraction method	Extraction Solvents	Extraction time	Extraction T	Extraction details
2003	Saponification	Ethanol/Water	1 hour	90 °C	
3001	SONICATION	n-HEXANE	200 min	45 °C	
3003	Saponification	Methanol, cyclohexane	30 minutes	60 celcius	
3004	PLE (Pressurized Liquid Extraction)	acetone:chloroform (1:2)	5 min	100 oC	Extraction by ASE-200 in two cycles (heating of extraction cell - 5 minutes, static extraction time - 5 minutes), purge volume 60% of capacity extraction cell (22 ml capacity)
3005	PLE (Pressurized Liquid Extraction)	Hexane	20 min	125	
3006	Saponification	Ethanol,water,cyclohexane .	1 hour	room temperature	After the extraction step we do seven extractions until the pH of the inorganic phase is below 9.The organic layer (cyclohexane) is collected and evaporated using a rotary evaporator and nitrogen.
3007	MSPD	acetonitrile	1 hour	room temperature	
3008	Saponification	3.5 M methanolic KOH	2 hours	70 °C	Saponification in a E-flask in an oven
3010	Soxhlet	Dichlomethane/Hexane (1:1)	16 hours	109 ºC	
3011	PLE (Pressurized Liquid Extraction)	toluene		80 °C	
3012	PLE (Pressurized Liquid Extraction)	acetone:hexane (50:50)	approx. 30 min.	100 degrees Celsius	2 cycles, 100% elution volume
3013	Soxhlet	hexane:dichloromethan = 3:1 (v/v)	8 hours		
3014	PLE (Pressurized Liquid Extraction)	Hexane	6 min. heating, 60 sec. purging.	120 °C	Equipment: Dionex ASE (Accelerated Solvent Extraction)

LabID	Extraction method	Extraction Solvents	Extraction time	Extraction T	Extraction details
3015	Liquid extraction according to Smedes (2-propanol/cyclohexane)	2-propanol/cyclohexane/water (10:12:13,v/ v/v)	2 minutes	ambient	The sample is first mixed with 2-propanol/cyclohexane (5:6, v/v) and thoroughly mixed with ultraturrax (2 minutes). After that water is added and mixed with ultraturrax (1 minute). After centrifugation the cyclohexane fraction is collected. The other fraction is being extracted two more times with cyclohexane and these cyclohexane fractions are added to the first cyclohexane fraction.
3016	Saponification	Potassium hydroxide, ethanol.	1,5 hours	40 C	
3017	shaking for 16 h	Hexane	16 h	room	
3018	Saponification	Methanol	2 hours	50 degrees Celsius	
3019	TREATMENT WITH DICHLOROMETHANE	DICHLOROMETHANE	3 min	AMBIENT TEMPERATURE	
3020	PLE (Pressurized Liquid Extraction)	Hexane/Acetone 1:1	20 min		
3021	Saponification	Potassium hydroxide methanolic solution	1 hour	80 oC	
3022	PLE (Pressurized Liquid Extraction)	Mixture of hexane and acetone (50/50)	25 min	100°C	"We added florisil into the extraction cell, in order to perform a pre-purification step.□"
3024	Liquid - Liquid Extraction	Cyclohexane	30min	Ambient	
3025	Saponification	75:25 methanol:water with 10 % KOH.	1 hour	60°C	Internal standard solution is added with 5 mL dioxane prior to saponification.
3026	PLE (Pressurized Liquid Extraction) extraction in ultrasonic bath (room temperature)	hexane:dichloro-methane=1:1 and ethyl-acetate:cyclohexane=1:1	3 x 30 min	room temperature	
3027	PLE (Pressurized Liquid Extraction)	Acetone, Dichloromethane	40 min	Room temperature	Liquid extreaction is used, not PLE.

What is the first sample clean up step of your method?
Which solvents are used in the first sample clean up step?
What is the clean up time?
What is the clean up temperature?
Please report other details if relevant

LabID	First clean-up method	First clean-up solvents	First clean-up time	First clean-up T	First clean-up details
2003	Solvent partitioning	Cyclohexane	5 min	90 °C	
3001	Solvent partitioning	CYCLOHEXANE, METHANOL/WATER	1 h	AMBIENT	
3003	Solvent partitioning	cyclohexane- Methanol	1-2 hours	ambient	
3004	SEC (GPC)	chloroform	40 minutes	room temperature	column BIO-BEADS S-X3 (8x500 mm), flow rate: 0,7 ml/min, fraction (20-40 minutes)
3005	DACC	Isopropanol, ACN	60 min	Room Temperature	Collection from 12 to 30 min
3006	SPE	Acetone:acetonitrile (40:60) after conditioning the SPE column with MEOH/ACN	1 hour	room temperature	Between the clean up steps the extract is centrifuged. After the clean up steps the samples are evaporated with a rotary evaporator and diluted to 1ml hexane.
3007	SPE	acetonitrile	simultaneously with extraction	room temperature	
3008	Solvent partitioning	Cyclohexane and methanol/water	2 hours	20 °C	Concentrate the cyclohexane phase to 1 ml in a rotary evaporator
3010	GPC	chloroform	30 minutes	ambient	
3011	SEC (GPC)	cyclohexane/Acetone	approx. 50 min per sample	ambient	
3012	SEC (GPC)	Cyclohexane: ethylacetate (95:5)	1.5 hr./sample	room temperature	Depending on the fat concentration of the sample, an additional clean-up cycle will be done. Injection of 5 ml in total on column, fat % larger than 15 then two injections of 2.5ml are needed (column capacity). Samples are added and collected using brown glassware.
3013	SPE	C18 2g cartridge (acetonitrile+acetone = 6:4 (v/v))		r.t.	

LabID	First clean-up method	First clean-up solvents	First clean-up time	First clean-up T	First clean-up details
3014	DACC	2-propanol	12.5 min.	25 °C	DACC Column: Varian CP 28159
3015	SEC (GPC)	cyclohexane/ethylacetate (1:1,v/v)	about 90 minutes	ambient	
3016	Solvent partitioning	Cyclohexane	2 min.	room temperature	
3017	SEC (GPC)	cyclohexane/ethylacetate	1.2 h	room	
3018	Solvent partitioning	Cyclohexane	1 hour	room temperature	
3019	SEC (GPC)	DICHLOROMETHANE	30 MINUTES	AMBIENT	
3020	SPE				
3021	Solvent partitioning	Methanol	3 min.	room	
3022	SPE	Cyclohexan, ethyl acetate, ethanol		room temperature	
3024	C18 cartridges	Acetone / Acetonitrile 40 / 60	30min	Ambient	
3025	Solvent partitioning	Cyclohexane	Not defined	Ambient	The cyclohexane is washed with an additional portion of 75:25 methanol:water and a portion of 10% aqueous ammonia.
3026	SEC (GPC)	hexane:dichloro-methane=1:1 or ethyl-acetate:cyclohexane=1:1	60 min	room temperature	
3027	SPE	Rinse: Toloulene: Hexane (1:9), and Toloulene: Hexane (1:1), Eluent: Toloulene: Hexane (1:1)	approx. 30 minutes	Room temperature	Silicagel Column clean-up is used.

What is the second clean up step of your method?
Which solvents are used in the second sample clean up step?
What is the clean up time?
What is the clean up temperature?
Please report other details if relevant

LabID	Second clean-up method	Second clean-up solvents	Second clean-up time	Second clean-up T	Second clean-up details
2003	Solvent partitioning	Cyclohexane	2 min	ambient temp.	
3001	Solvent partitioning	DMF/WATER, CYCLOHEXANE	1 h	AMBIENT	
3003	Solvent partitioning	Cyclohexane- Dimethylformamide	2 hours to overnight	Ambient	
3006	SPE florisil	Dichloromethane:Hexane (25:75) after conditioning the SPE column with Dichloromethane and Hexane	1 hour under gravity	room temperature	We pass the hexane extract from the florisil column. We then evaporate to dryness the eluate and dilute it with 1ml of ACN, filter and inject the filtrate to the HPLC.
3008	SPE, silica 5 g	cyclohexane, hexane and tert-Butyl methyl ether	30 minutes	20 °C	Concentrate to 0.5 ml in a rotary evaporator
3012	SPE	Cyclohexane	20 min.	room temperature	
3013	SPE	Silicagel 2 g cartridge (hexane+dichloromethan = 9+1 (v/v)		r.t.	
3015	SPE	hexane	10 minutes	ambient	We use basic alumina: Al2O3.14H2O
3016	Solvent partitioning	Methanol:Water (4:1)	2 min.	room temperature	
3018	SPE	Cyclohexane, methylene chloride	45 minutes	room temperature	
3021	Solvent partitioning	cyclohexane	3 min.	room	
3022	DACC				
3024	Florisil cartridges	Hexane / Dichloromethane 75 / 25	30min	Ambient	
3025	Solvent partitioning	90:10 dimethylformamide:water	Not defined, up to 24 hours.	Ambient	
3026	DACC				
3027	DACC				

What is the third clean up step of your method?
Which solvents are used in the third sample clean up step?
What is the clean up time?
What is the clean up temperature?
Please report other details if relevant

LabID	Third clean-up method	Third clean-up solvents	Third clean-up time	Third clean-up T	Third clean-up details
2003	SPE	dichloromethane/petroleum ether		ambient temp.	two spe-columns (SI 1000 mg/ CN 1000 mg)
3001	Solvent partitioning	CYCLOHEXANE, WATER	1 h	AMBIENT	
3003	Silica gel	cyclohexane	N/A	N/A	
3006	DACC				
3008	SPE, PAH HC 1g	Hexane, 2-propanole and pentane	10 minutes	20 °C	Concentrate under nitogen to 100 ul
3013	DACC				we have only two steps!
3016	Solvent partitioning	N,N-Dimethylformamide:Water (9:1)	2 min.	room temperature	
3018	SPE	Hexane, cyclohexane, pentane, isopropyl alcohol	45 minutes	room temperature	
3021	Solvent partitioning	N,N-Dimethylformamide	3 min.	room	
3022	DACC				
3025	Solvent partitioning	Back extraction into cyclohexane after addition of 1% aqueous NaCl.	Not defined	Ambient	
3026	DACC				
3027	DACC				

What is the fourth clean up step of your method?
Which solvents are used in the first sample clean up step?
What is the clean up time?
What is the clean up temperature?
Please report other details if relevant

LabID	Fourth clean-up method	Fourth clean-up solvents	Fourth clean-up time	Fourth clean-up T	Fourth clean-up details
2003	DACC				
3001	SPE	CYCLOHEXANE	2 h	AMBIENT	
3006	DACC				
3007	DACC				
3013	DACC				
3016	SPE	Cyclohexane	20 min.	room temperature	
3021	Solvent partitioning	cyclohexane	3 min.	room	
3022	DACC				
3025	Silica column	Cyclohexane	Not defined	Ambient	Silica activated at 450°C then deactivated with 5% water.
3026	DACC				
3027	DACC				

What type of analysis method did you use?

Lab ID	Analytical method
2003	HPLC-FLD
3001	GC-FID
3003	GC-MS
3004	HPLC-FLD
3005	HPLC-FLD/UV
3006	HPLC-FLD
3007	GC-MS
3008	GC-MS
3010	HPLC-FLD, GC-MS
3011	GC-High Resolution MS
3012	GC-MS
3013	HPLC-FLD
3014	HPLC-FLD
3015	GC-HRMS
3016	GC-MS
3017	LC-MS
3018	GC-MS
3019	HPLC-FLD
3020	GC-MS/MS
3021	HPLC-FLD
3022	GC-MS/MS
3025	GC-MS
3026	HPLC-FLD
3027	GC-MS

Details for GC method

Which injection system do you apply?
Which type of column do you apply and what are the column dimensions?
What is the oven temperature programme?

LabID	GC injection method	GC column	GC oven temperature
3001	SPLITLESS	Rtx-5, 30m x 0,25 mm x 0,25 µm	"70 °C, 1 min, 20 °C/min□ 160 °C, 0 min, 3 °C/min□ 180 °C, 3 min, 3 °C/min□ 200 °C, 0 min, 0,5 °C/min□ 210 °C, 0 min, 4 °C/min□ 310 °C, 10 min"
3003	PTV	DB-5 60m 0.25mmID 0.25umdf	60°C, hold 2.5 min; 7°C min to 215°C, hold 5 min; 2°C min to 260°C, hold 3 min; 3.5°C min to 340°C, hold 15 min
3007	splitless	"DB-17MS□30 m, 0.25 ID; 0.25 um"	55oC (2 min.) till 40oC/min. till 240oC (0 min.) till 10oC/min. till 300oC (50.37 min.)
3008	splittless	30 m DB 35, 0.25 mm ID, 0.25 um phase thickness	70 °C for 1 min, rate 20 °C/min to 160 °C, rate 3 °C/min to 210 °C, rate 5 °C/min to 320 °C and hold for 15 min.
3010	PTV injector operating in pulsed spiltless mode (40psi, 1.1min)	DB-17MS (30mx0.25mmx0.25µm, J&W Scientific)	100°C for 1.5min., 60°C/min. to 220°C, 2°C/min. to 270°C, hold 1.5min., 3°C/min. to 300°C, hold 5min., 120°C/min. to 320°C, hold 12.77min.
3011	split/splitless	65 % methyl/35 % phenyl ; 30 meters x 0.25 mm inner diameter; 0.25 µm film	80°C (hold 1min) - ramp 20°C/min to 230°C - ramp 2 °C/min to 310°C (hold 15 min)
3012	PTV-LVI	DB- 5MS (50mx0.25mm id x 0.25µm film thickness)	90 for 1 min, gradually raised to 270 (7/min) further raised to 280 (1/min) and finally 320 (5/min) and held at 320 for 14 min.
3015	splitless	DB5-MS, 60m x 0.25mm x 0.25µm	80°C (1 min), 15°C/min to 200 °C, 4°C/min to 310°C (10 min)
3016	Split ratio 5:1	Capillary Column Zebron-50 30m×0,25×0,25µm	80ºC, 15ºC/min to 265ºC, 5ºC/min to 290ºC, hold 5 min, 20ºC/min to 330ºC, hold 15 min
3018	splitless	HP-17MS, length: 30 m, inner diameter: 0,25 mm.	70ºC for 1 minute, 20ºC/min to 200ºC, 3ºC/min to 260ºC, hold 5 minutes, 5ºC/min to 280ºC, 3ºC/min to 290ºC, hold 5 minutes, 1,5ºC/min to 300ºC, 10ºC/min to 320ºC, hold 17 min
3020	Splitless	ZB 50, 30 m, 0,25 mm, 0,25 µm	initial temperature 80 C, 15 C/min until 265 C, 5 C/min until 290 C, 20 C/min until 320 C, 20 min.
3022	splitless injection	Zebron ZB50 - 30m * 0.25mm * 0.25 µm	110°C (2 min) - 20°C/min to 270°C - 3 °C/min to 290°C - 20°C/min to 330°C (18 min)
3025	Large volume splitless	60m x 0.25mm x 0.25µ SLB5MS	60°C (hold 3min) then to 215°C (hold 5min) @ 7°C/min then to 240°C (no hold) @ 2°C/min then to 250°C (no hold) @ 1°C/min then to 325°C (hold 10 min) @ 3.5°C/min.
3027	PTV	Varian VF 5ms, 30m×0,25mm×0,25microm	90ºC for 5 min, 20ºC/min to 200ºC, 4ºC/min to 325, hold 8,25 min

Details for HPLC method

Which type of column do you apply and what are the column dimensions?
What is the initial eluent?
What is the gradient?

LabID	HPLC column	HPLC eluent	HPLC gradient
2003	Vydac 201 TP54 250*4 mm (Vydac TP C18 PAH-1 300A 5µ)	Acetonitrile / Water	in 29min to 15/85, in 9min to 0/100, hold 41min, in 1min 50/50
3004	Waters PA C18, 4,6x250 mm, 5 um	60% acetonitrile (ACN): 40% water	Initial eluent for 2min, in 7min 100/0, in 12min 60/40
3005	Varian Pursuit 3 PAH 100x4.6 mm 3 µm	water/ACN/Methanol 15/30/55	Initial eluent for 2min, in 21min to 0/100/0, hold for 19min
3006	VYDAC C18, 250x4,6 mm	ACN:H2O(50:50)	Initial eluent for 1min, in 41min 82,5/17,5, in 30min 100/0, in 5min 75/25, hold for 10min
3010	Waters PAH C18, 5µm, 2.1x150mm	0% ethylacetate (A), 25% water (B), 75% acetonitrile (C)	Initial eluent for 2min, in 8min 100/0/0, in 3min 30/0/70
3013	Varian PAH "Pursuit" 250 mm x 4,6 mm, 5 um	acetonitrile 75%, water 25%	Initial eluent for 5min, in 40min 93/7, in 1min 100/0, hold for 29min, in 5min 75/25, hold for 5min
3014	"2 x Reversed Phase C18 in series. Type: Merck Lichrocart 250-4 Lichrospher PAH RP-18 □length: 250 mm; diameter: 4 mm; particle size: 5 µm "	85% Acetonitrile / 15% Water	Initial eluent for 26min, in 9min 90/5/5, in 10min 80/15/5, hold for 5min, in 5min 30/70/0, hold for 15min
3017	Zorbax Eclipse PAH 2.1x50 mm 1.8 µm	60/40 acetonitrile/water	Initial eluent for 1min, in 5min to 100/0, hold 5min, in 1min to 60/40
3019	PAH COLUMN (WATERS) - 250 mm x 4.6 mm - 5um	ACETONITRILE : WATER	in xmin to 100/0, in xmin to 50/50
3021	LiChroCART 250-4 LiChrosper PAH (5 µm)	Acetonitrile - water	
3024	VYDAC C18 250X4.6mm 5um pd	" 1. Acetonitrile / Water 50/50 for BcL □□ 2. Acetonitrile / Water 75/25 for the rest 15PAHs "	in 43min to 50/50, in 1 min to 65/35, in 36min to 100/0
3026	RESTEK PINNACLE II PAH 4 um x 150 mm x 4.6 mm	Water:ACN=40:60 10 min	Initial eluent for 10min, in 22min 100/0, hold for 28min, in 6min 60/40

What type of detection system did you use?

Details for FID detection
What is the detector temperature?
Please report other details if relevant

LabID	Detection method	FID temperature	FID details
2003	FLD / UV(cyclopenta[cd]pyrene)		
3001	FID	330 °C	
3003	Trace MS/ MSD		
3004	FLD+DAD		
3005	FLD/UV		
3006	FLD&PDA		
3010	FLD		
3012	Ion-trap MS		
3013	FLD, DAD		
3014	Fluorescence Detection.		
3017	APPI LC/MS/MS		
3018	MS		
3019	FLUORIMETRIC DETECTION (except for CPP)	AMBIENT TEMPERATURE	
3021	FLD, DAD		
3024	Diode Array and Fluorescence Detector		
3026	FLD		
3027	MS		

Details for FLD detection

What are the wavelengths applied and for which groups of PAHs?
Please report other details if relevant

LabID	FLD wavelengths	FLD details
2003	"A: ex290/em430: CHR, 5MC, BkF, BaP, BgP□B: ex290/em430: BcL, BaA, DhA, DeP□C: ex290/em470: BbF, DlP, ICP, DiP, DhP□D: ex290/em510: BjF□time program: 9min ex 290/em320; 12 min ex250/em385; 18 min ex265/em380; 30 min ex290/em430; 43 min ex300/em500□UV 219,5 nm: CPP"	
3004	multi chanel detection (A,B,C,D) by FLD using programing	"4 min - Ex 270, Em.A-350, Em.B-420, Em.C-470, Em.D-510□8,8 min- Ex 270, Em.A-380, Em.B-420, Em.C-470, Em.D-510□10,5 min- Ex 290, Em.A-400, Em.B-420, Em.C-470,Em.D-510□for CAP - DAD-220 nm"□
3005	"PAH . exc . em□BcL 304 353□CPP 222 -□BaA 275 389□CHR 260 381□5MC 260 376□BjF 300 512□BbF 280 438□BkF 290 412□BaP 281 407□DlP 295 424□DhA 285 396□BgP 285 416□IcP 290 499□DeP 285 398□DiP-D14 380 434□DiP 380 434□DhP 290 452□"	
3006	"270ex/420em: BaA, Chry, 5Mchry, BkF, BaP, DalP, DahA, BghiP, DaeP□270ex/470em: BbF, DahP □270ex/335em: BcF□300ex/500em: BjF, IcdP, DaiP"	"FLD 2475 Waters multi-wavelength□PDA 2996 Waters"
3010	236/384nm B(c)Fln; 270/385nm B(a)A, Chr, 5-MeChr; 238/510nm B(j)F; 295/405nm B(b)F, B(k)F, B(a)P; 269/429nm DB(al)P; 295/405nm D(ah)A, B(ghi)P; 300/500nm I(1,2,3-cd)P; 73/405nm DB(ae)P; 259/455nm DB(ai)P; 380/455nm DB(ah)P	
3013	(ex[nm]/em[nm]): 5-MeCh, CHR 266/408; BaA 286/408; BaP 380/406; BbF, Bkf 304/433; BcL 310/357; BgP 362/408; BjF 315/510; DeP, DhA 286/420; DhP 308/450; DiP 281/434; DlP 315/422; ICP 300/500	CPP (DAD): 222 nm
3014	"BcL 240/355□BaA+CHR+5MC 260/390□BbF+BkF+BaP+DlP+DhA+BgP 290/430□DeP+BbC 296/405□DiP 292/435□DhP 300/450"	BbC = control component for retention time
3019	"Excitation : 230 nm (BcL); 270 nm (BaA, CHR, 5MC); 290 nm (BkF, BaP, DlP, DhA, BgP); 294 nm (DiP); 300 nm (BjF, BbF); 302nm (IcP, DeP), 309 nm (DhP)□Emission : 357 nm (BcL); 385 nm (BaA, CHR, 5MC); 400 nm (DeP); 430 nm (BkF, BaP, DlP, DhA, BgP); 436 nm (DiP); 456 nm (DhP); 500 (BjF, BbF, IcP)"	CPP was detected at a wavelength of 254 nm
3021	BcL Ex334 Em360; BaA,CHR,5MC Ex270Em385; BjF Ex292 Em510; BbF,BkF Ex270 Em450; BaP Ex256 Em410; DlP Ex270 Em420; DhP,BghiP Ex256 Em410; IcP Ex334 Em499; DeP Ex270 Em420; DiP,DhP Ex270 Em450	for CPP DAD 275
3024	"Group A: CHR, 5MC, BkF, BaP Excitation: 290nm Emission : 400nm. □Group B: BaA, BbF, DlP, DhA, BgP Excitation: 290nm Emission : 420nm. □Group C: DeP Excitation: 270nm Emission : 420nm. □Group D: DiP, DhP Excitation: 290nm Emission : 470nm. □Group E: BjF, ICP Excitation: 290nm Emission : 510nm. □Group F: BcL Excitation: 270nm Emission : 335nm. "	For DAD Detection : CPP : 375nm
3026	270-420, 270-470, 270-370, 270-500	

Details for MS detection

Do you apply electron ionisation (EI) or chemical ionisation (CI)?
If EI is applied, what is the ionisation energy?
If CI is applied, which are the ionisation gas, its pressure and flow?
If APPI (for LC-MS) is applied, please give relevant details [no participant uses this technique]
Do you quantify the PAHs in SCAN or SIM mode?

LabID	MS: EI or CI	MS: EI energy	MS: CI details	MS: SCAN or SIM
3003	EI	70eV		SIM
3007	EI	70 eV		SIM
3008	EI	69.9		SIM
3010	EI			SIM
3011	EI	70 eV		SIM
3012	EI	70eV		SIM
3015	EI	35 eV		SIM
3016	EI	70 eV		SIM
3018	EI (positive)	69.9 eV		SIM mode
3020	EI	70 eV		MRM
3022	EI	70 eV		MRM mode, following 2 specific transitions per compounds
3025	EI	70eV		SIM
3027	EI	70 eV		SIM

Participants were asked to fill in a table with the ions used for identification / quantification in SIM. In the following table the SIM ions for the 4 PAHs BaP, BaA, BbF, CHR are listed

LabID	Quantifier BaA	Qualifier BaA	Third ion BaA	Quantifier BaP	Qualifier BaP	Third ion BaP	Quantifier BbF	Qualifier BbF	Third ion BbF	Quantifier CHR	Qualifier CHR	Third ion CHR
3003	228	226		250	252		252	250		228	226	
3007	228	114		252	126		252	126		228	113	
3008	228			252			252			228		
3010	228,05	114		252,05	126,1		252,1	125,95		228,1	114	
3011	228	229		252	253		252	253		228	229	
3012	228	226		252	250		252	250		228	226	
3015	228	229		252	253		252	253		228	229	
3016	228			252			252			228		
3018	228	229	114	252		126	252		126	228	229	114
3025	228			252			252			228		
3027	228	226		252	250		252	250		228	226	

Do you apply a confirmation method?
If YES, please describe the method

LabID	Confirmation method: Yes/No	Confirmation method details
2003	No	
3001	Yes	SECOND TEMPERATURE PROGRAMME
3003	Yes	C-13 Labelled -surrogate internal standards
3005	No	
3007	No	
3008	No	
3010	No	
3011	Yes	evaluation of retention time and mass ratio of quantifier/qualifier ion
3012	No	
3013	Yes	Injection with standard
3014	No, but we do add BbC for control purposes	BbC is added to check the DACC cleanup, recovery and the retention time.
3015	No	
3016	No	
3017	no	
3018	No	
3019	No	
3021	Partly	HPLC-DAD
3022	No	
3024	Yes	Comparison of the emission spectrums of the eluted compounds (of the unknown samples) with the emission spectrums of the relevant PAHs, in the same Retention Time
3025	No	
3026	No	
3027	No	

How did you integrate the signals (automatically or manually)?
If automatically, did you check the correctness of integration visually?
If YES, for how many peaks (in average) was it necessary to re-integrate for each chromatogram?
Which global settings did you use for automatic integration (e.g. valley-to-valley or horizontal baseline or tangential, etc.)?

LabID	Integration	Automatic Integration check	Re-integration	Settings for automatic integration
2003	manually			
3001	MANUALLY			
3003	Automatic	Yes All are checked/adjusted as necessary.	All most all are corrected/ adjusted to best fit to ensure accuracy of data.	
3004	automatically and is neede manually	Yes	4	tangential
3005	Automatically	Yes	4 for samples, 0 for standards except the fisrt calibration point	valley to valley
3006	automatically	Yes	For the most of them	Horizontal baseline
3007	manually			
3008	Automatically	Yes	6 peaks for standards and 10 peaks for sample	valley-to-valley
3010	Manually			
3011	primarily automatically, manual re-integration after visual inspection where necessary	yes	depends on concentration; almost none for sample "C": approx 1/3 for sample "D"	horizontal baseline
3012	automatically	Yes	approximately half the total number of peaks	
3013	automatically	Yes	10-12	horizontal baseline
3014	Mostly Manually			Valley-to-valley
3015	Mainly automatically, if necessary manual modifications	yes	5	horizontal baseline
3016	Automatically.	No.		Valley-to-valley.

LabID	Integration	Automatic Integration check	Re-integration	Settings for automatic integration
3017	automatically	yes	non	Valley-valley
3018	Automatically	YES	8	
3019	AUTOMATICALLY	YES	3 PEAKS in the sample contaminated at lowest level	VALLEY-TO-VALLEY
3020	automatically	yes		
3021	partly automatically	Yes	quarter	mixed
3022	automatically, and manual modification if needed	yes	2~3	"Peak to peak baseline noise : 10□Peak width at 5% height : 30"
3024	Manually			
3025	Mostly automatically	Yes	~4 mostly closely eluting peaks e.g. Benzo(b) and benzo(j)fluoranthene	The GC-MS software uses different integration algorithms e.g. ICIS and Genesis.
3026	manually			
3027	automatically	YES	3	horizontal baseline

European Commission

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Abstract
The Community Reference Laboratory for PAHs (CRL-PAHs), operated by the Institute for Reference Materials and Methods (IRMM) of the Joint Research Centre (JRC), organises yearly one or more proficiency tests (PTs) within the scope of the Regulation (EC) 882/2004.

The proficiency test here reported concerned the determination of the 15+1 EU priority polycyclic aromatic hydrocarbons (PAHs) in fish test samples. Participants to these PT were National Reference Laboratories for PAHs (NRLs-PAHs) and an expert laboratory, which was covered by the Technical Assistance and Information Exchange (TAIEX) programme for Balkan Countries. The number of invited participants was 27.
The PT was organised along the lines of the IUPAC Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories.
The test materials used were raw, frozen fish spiked with a 15 + 1 EU priority PAHs, fish spiked with an extract of a contaminated liquid smoke flavouring, and a solution of the target analytes in acetonitrile solution.
The results from participants were rated with z-scores. About 90 % of the reported results were attributed with z-scores with an absolute value of below two, which is the threshold for satisfactory performance.

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

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