ERM-CC013a: Polycyclic aromatic hydrocarbons in soil

Certification Report

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List of Abbreviations

BIPM	International Bureau of Weights and Measures
CCQM	Consultative Committee for Amount of Substance – Metrology in Chemistry
CIPM	International Committee for Weights and Measures
CIPM MRA	Mutual Recognition Arrangement of CIPM members
DAD	Diode array detector
EPA	U. S. Environmental Protection Agency
ERM®	European Reference Materials
F	Fluorescence detector
FBE	Fluidised bed extraction
GC	Gas chromatography
HPLC	High performance liquid chromatography
IRMM	Institute for Reference Materials and Measurements
LOD	Limit of detection
MS	Mass spectrometry
PFE	Pressurised fluid extraction
PTFE	Polytetrafluoroethylene
UV	Ultraviolet detector

1 Introduction

1.1 PAH congeners of interest and available analytical procedures

Polycyclic aromatic hydrocarbons (PAHs) are among the most important organic pollutants in environmental matrices and are widely monitored by field laboratories. The quantification of PAHs in soil using liquid chromatography (HPLC-UV/DAD/F) has been standardised nearly ten years ago [1] and the application of GC-MS for this purpose has been recently standardised as well [2].

ERM-CC013a replaces the certified reference materials ERM-CC013 and ERM-CC014 which displayed similar PAH contents in the mg/kg level in a similar soil matrix and have been sold out meanwhile. The measurements aimed at the extractable contents of 16 priority pollutant PAHs according to the EPA list.

1.2 Strategy of the certification project

A real world material, representative for a moderately polluted industrial soil from a former gasworks site with regard to PAH contents and congener pattern was sampled from the Berlin area and preliminarily checked for its appropriateness regarding contents of congeners. Fortification of environmental matrices with respective analytes is generally avoided wherever possible. GC-MS and HPLC are the two analytical procedures available and are equally often used in practice. Therefore, both chromatographic procedures along with usually applied extraction procedures were employed for the characterisation of the PAH contents. This certification exercise was done at BAM employing a number of independent operator/equipment combinations in-house rather than an external intercomparison since the calibration and measurement capability (CMC) of BAM with regard to PAHs has internationally been recognised by way of key comparisons [3] of the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) of the International Bureau of Weights and Measures (BIPM). Every operator analysed two different units of the candidate material and two control solutions containing the congeners of question. Traceability was established using calibration standard solutions certified for the contents of these congeners and in case of GC-MS additionally deuterated PAHs were applied as internal standards (see clause 5.3.3).

2 Candidate material

The loamy sandy soil was sampled from a former gasworks site in Berlin-Mariendorf, Berlin, Germany. The specific location was chosen because it displayed a PAH pattern typical for an aged contamination originating from industrial immission over decades. Particles larger than 6 mm were removed from the bulk on the site and the material was air-dried to constant weight before further processing. After drying to constant weight, the bulk material (104 kg) was passed through a pin mill to gently smash the brittle agglomerates contained in the material. After classification by means of an automatic sieving station a total amount of 29.05 kg of the fraction ≤ 63 µm was collected. Thereafter, this material was homogenised by means of a 120 L stainless steel barrel in a drum hoop mixer (J. Engelsmann AG, Ludwigshafen; Germany). The barrel was equipped with a mixing insert inside for improving the mixing intensity and moved for several days (approx. 110 h total). Further homogenisation and bottling was achieved using a VIS type mixer (AMK, Aachen, Germany) equipped with a helically shaped mixing blade inclined 45°. The trough is equipped with an automatic partitioning device that allows bottling of the individual units under precise gravimetric control.

A total of 493 units was bottled in 100 mL amber screw-capped glass bottles containing (81.5 ± 0.3) g each and units were numbered in the order of leaving the bottling process. The screw caps equipped with PTFE foil inserts were tightly closed and sealed with shrinking foil. All units were stored at -20 °C directly after bottling. Table 1 comprises the chemical and physical characterisation of the matrix of the candidate material. The relatively high water content of the soil is at equilibrium with the ambient atmosphere under typical laboratory conditions and corresponds to the relatively high content of organic carbon.

Table 1: Matrix characterisation of ERM-CC013a

Measurand	**Value**	**Method**
Particle size range	≤ 63 µm	Sieving
Water content	(6.32 ± 0.03) %	*Karl Fischer* titration
Drying loss	(5.82 ± 0.08) %	Gravimetry after drying to constant weight at 105 °C (ISO 11465:1993)
Total organic carbon	(18.1 ± 0.3) mg g^{-1}	ISO 10694:1995
Total inorganic carbon	(6.44 ± 0.05) mg g^{-1}	ISO 10694:1995
CHN-Analysis (in %)	C: 2.132 ± 0.008; H: 1.124 ± 0.005; N: 0.088 ± 0.003	Combustion
pH	7.79 ± 0.03	ISO 10390:2005

3 Homogeneity study

The procedure employed for this study was pressurized fluid extraction (PFE) with methanol followed by HPLC-DAD/F. Details can be found in ANNEX B.1. The minimum sample intake for one determination was chosen in a way that no significant heterogeneity within the bottle is to be expected. Measurements with sample intakes of 2 g, 4 g, and 7 g (six replicate determinations each) revealed no significantly different standard deviations. Therefore, a mass of 3 g was used for each replicate determination during the homogeneity study and is recommended as minimum sample intake in the certificate.

A total of 15 units was selected equidistantly from the whole set of 493 units in the order of bottling. The selected units were analysed four times each using a sample intake of 3 g. The extraction procedure and instrumental parameters are given in ANNEX B1. All 15 units were extracted once under repeatability conditions on four consecutive days. All extracts were analysed under repeatability conditions in those all 60 extracts were quantified against one calibration after randomisation. (For the individual measurement results see ANNEX C). Table 2 reveals the results of the 1-way analysis of variance (ANOVA).

Table 2: Results of the 1-way ANOVA on the candidate material

PAH congener	MS_{within} [a] (mg^2 kg^{-2})	$MS_{between}$ [b] (mg^2 kg^{-2})	F_{obs} [c]	F_{crit} [d]	u_{bb} [e] (mg kg^{-1})
Naphthalene	0.00372	0.005890	1.5839	1.9236	0.02330
Acenaphthene	0.0014	0.0019	1.3941	1.9182	0.01165
Fluorene	0.0015	0.0009	0.6380	1.9182	0.008745
Phenanthrene	0.2004	0.1079	0.5384	1.9182	0.10276
Anthracene	0.0021	0.0012	0.5538	1.9182	0.01047
Fluoranthene	0.1024	0.1281	1.2515	1.9182	0.08023
Pyrene	0.2136	0.0848	0.3969	1.9182	0.10610
Benz[*a*]anthracene	0.0163	0.0195	1.1919	1.9182	0.03992
Chrysene	0.0181	0.0132	0.7318	1.9182	0.03088
Benzo[*b*]fluoranthene	0.0378	0.0354	0.9363	1.9182	0.04464
Benzo[*k*]fluoranthene	0.00504	0.00500	0.9924	1.9182	0.01629
Benzo[*a*]pyrene	0.0302	0.0207	0.6838	1.9182	0.03992
Dibenz[*ah*]anthracene	0.0019	0.0006	0.3287	1.9182	0.01014
Benzo[*ghi*]perylene	0.0117	0.0085	0.7323	1.9182	0.02480
Indeno[1,2,3-*cd*]pyrene	0.0579	0.0527	0.9102	1.9182	0.05524

[a] *Mean of squared deviations within bottles (from 1-way ANOVA)*
[b] *Mean of squared deviations between bottles (from 1-way ANOVA)*
[c] *Observed F-value: $MS_{between}/MS_{within}$*
[d] *Critical F-value for the respective degrees of freedom*
[e] *Estimate of inhomogeneity contribution to total uncertainty according to [6].*

No evidence suggesting a rejection of the hypothesis that the material is homogeneous was observed. The estimates of inhomogeneity contribution to total uncertainty u_{bb} were estimated according to ISO Guide 35 as the maximum of the values obtained with Eq. (1) and (2).

$$u_{bb} = \sqrt{\frac{MS_{among} - MS_{within}}{n}} \quad (1) \qquad u_{bb} = \frac{S_{method}}{n}\sqrt[4]{\frac{2}{N(n-1)}} \quad (2)$$

Where:

S_{method} = Method variability $(=\sqrt{MS_{within}})$
n = Number of replicate determinations
N = Number of bottles analysed

4 Stability study

4.1 Initial stability study

From earlier experience with PAHs in various matrices a temperature-driven deterioration of the PAH content was to be expected also for this material. Selected units of the candidate material were submitted to a so-called isochronous [4] accelerated ageing at temperatures between 4 and 60 °C over periods of 1-6 months as shown in Table 3. After the respective periods of time individual units were stored at -20 °C. All units were analysed for PAH using the PFE/HPLC procedure under repeatability conditions together with reference samples which had been kept at -20 °C since bottling. For the individual data see ANNEX C.

Table 3: Accelerated ageing of exposed units

Ageing time [Months]	***+4 °C***	***+20 °C***	***+40 °C***	***+60 °C***	***Remark***
1	263	270	279	283	*initial study*
3	264	271	280	284	*initial study*
6	265	272	281		*initial study*
12	266	273	282		*post certification monitoring*
24	267	274			*post certification monitoring*
36	268	275			*post certification monitoring*

Data evaluation and expiry date estimation strictly follow the procedures as comprehensively described in [5]: From semi-logarithmic plots of measured single values over time, effective deterioration rates were determined and tested against an Arrhenius model describing the dependence on temperature of the deterioration rates. Most of the PAHs matched the model, some of them excellently. Activation energies as determined from the model were in the region between 20 and 105 kJ mol^{-1} depending on the PAHs considered. Figure 4.1 shows the dependence of the logarithm of the effective deterioration rate k_eff on the inverse temperature by way of example for benzo[*a*]pyrene and benzo[*a*]anthracene. The activation energy ΔE is 77.2 kJ mol^{-1} and 81.2 kJ mol^{-1}, respectively.

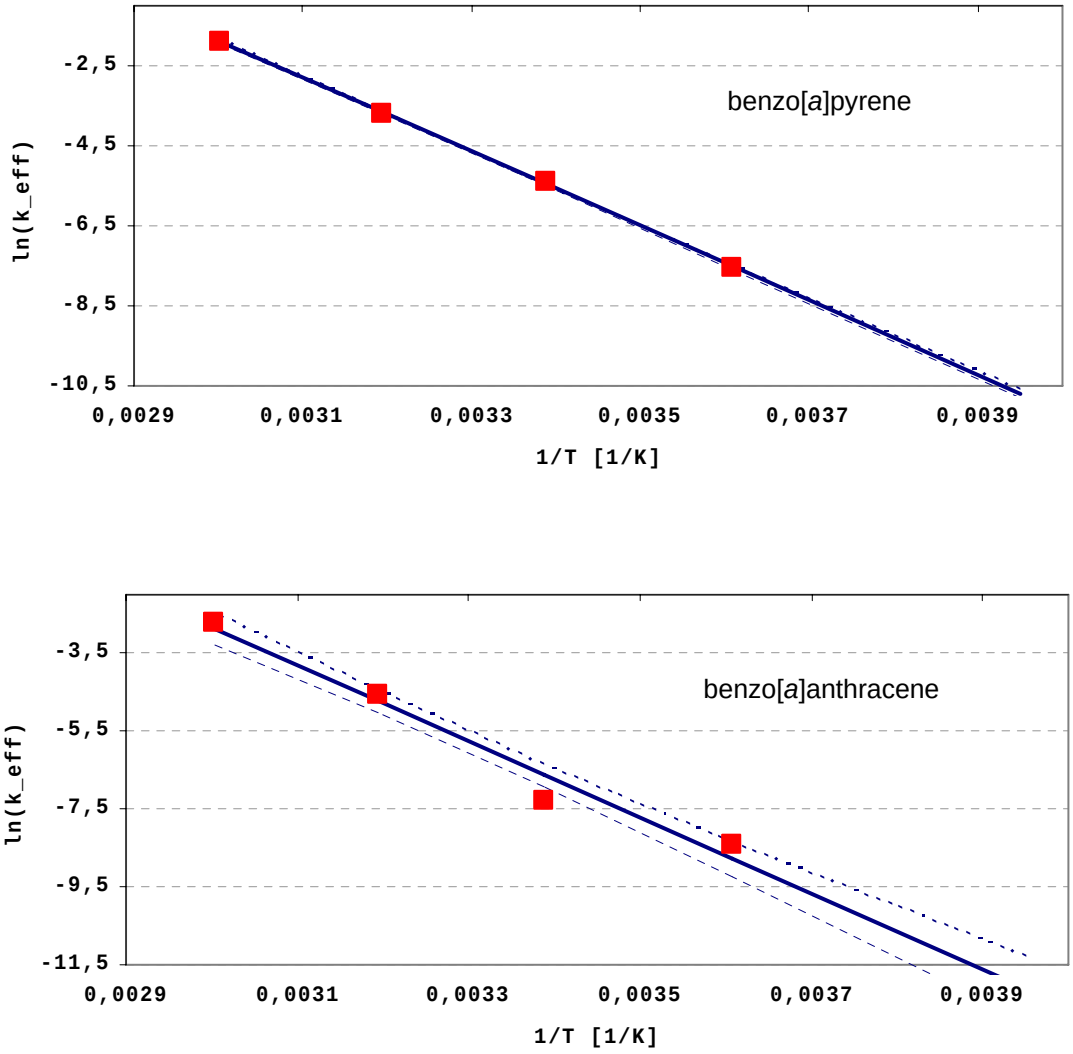

Fig. 4.1: Effective deterioration rate versus inverse temperature for benzo[*a*]pyrene and benzo[*a*]anthracene.

Using the value at the upper confidence bound of the regressed line as a worst-case estimate for the rate of deterioration to be expected, the expiry term estimates as summarised in table 4 were calculated. The period given in table 4 started with the storage of the whole batch directly after production on 24 August 2005.

Although shelf life at a storage temperature of -20 °C is quite considerable for many of the PAHs considered, any exposure to room or even higher temperatures may drastically reduce the time of validity of certified PAH contents of ERM-CC013a. Therefore, a unique expiry date of **one year after dispatch from BAM** is established. Transportation/delivery time should be kept at the possible minimum and any exposure to heat or strong light should be avoided.

For acenaphthene, a deterioration at higher temperatures was visible already from the raw data, while the match with the model was relatively poor for dibenz[*ah*]anthracene. The bad expiry term for the latter is thus caused by a broad confidence interval rather than a real, observable deterioration. However, both analytes are excluded from certification due to the results of the stability study and other considerations.

Table 4: Estimated period in months after which the certified values fall out of their certified uncertainties U

PAH congener	- 20 °C	+ 4 °C	+ 20 °C	+ 40 °C	+ 60 °C
Naphthalene	448.8	98.3	33.2	9.8	2.4
Acenaphthene	10971.9	204.6	14.1	1.1	0.1
Fluorene	1433.8	54.5	6.5	0.9	0.1
Phenanthrene	28748.9	1016.5	104.0	10.3	0.8
Anthracene	11518.2	306.7	29.5	3.6	0.4
Fluoranthene	1551.1	192.1	45.9	10.5	2.1
Pyrene	11099.8	409.0	48.7	7.3	1.1
Benz[*a*]anthracene	6725.5	347.4	48.2	7.1	0.9
Chrysene	355.2	114.8	49.0	17.3	4.8
Benzo[*b*]fluoranthene	1570.6	220.1	56.6	13.7	2.8
Benzo[*k*]fluoranthene	278.5	96.5	39.5	11.1	2.0
Benzo[*a*]pyrene	5414.2	238.7	31.7	5.2	0.9
Dibenz[*ah*]anthracene	177.6	119.5	85.0	51.5	26.2
Benzo[*ghi*]perylene	392.1	95.2	35.9	13.0	4.2
Indeno[1,2,3-*cd*]pyrene	9018.6	876.7	184.2	40.3	7.9

4.2 Post-certification stability monitoring

The first rough estimation of stability will be updated by further measurements of units stored at +4°C and +20°C over the period of availability of the material. The post-certification measurements will be conducted according to the information given in table 3. Several units investigated during the initial stability study were stored again at +4 °C or +20 °C, respectively. That way, information on the long term stability of units of ERM-CC013a having been opened at least once for withdrawal of material is expected in the course of the post certification monitoring. Earlier experience with ERM-CC013 and ERM-CC014 does not indicate any enhanced deterioration of once opened bottles if they are closed and stored thereafter according to the instructions given in the certificate (see also clause 6.2).

5 Certification study

5.1 Selection of participants and methods

Since the calibration and measurement capability of BAM for PAHs in natural matrices was demonstrated in several key comparisons conducted by the CCQM (see above) and is recognised under the CIPM MRA, it was decided to conduct the certification study based on in-house capabilities.

Six different operator/equipment combinations from BAM (in the following called “laboratories”) were invited to participate in the certification exercise. The methods employed covered both methods GC and HPLC as well as modern and classical extraction procedures. The equivalence of Soxhlet, pressurised fluid extraction (PFE), fluid bed extraction (FBE), and sonication was investigated prior to the certification exercise with one operator/equipment combination under repeatability conditions.

5.2 Design of the study

Two units of the candidate material were to be analysed by each laboratory in triple each. A rough information on the level of content of the PAH congeners to be expected was provided in order to allow a reasonable adjustment of individual calibrations. Certified calibration standards SRM 1647d, SRM 2260, and LGC PAH mix were used as calibrants (see also clause 5.3.3). Each laboratory was to prepare its independent calibration from the purchased CRMs. In addition, participants received two control solutions of PAHs in toluene with concentrations unknown to them. These solutions were prepared gravimetrically from the calibration standard SRM 1647d such that roughly correspond to the lower and upper region of the calibration range (see ANNEX B). Laboratories using GC-MS applied the respective deuterated PAH congeners as internal standards (CIL, Andover, MA, USA), while HPLC measurements were done with external calibration.
Extraction methods and solvents to be used by each laboratory are listed in Table 5. In order to allow an assessment of the interlaboratory variability each laboratory was asked to analyse two extracts prepared and also measured by the respectively indicated other laboratory. Results for the contents of

PAH congeners were to be reported on basis of total mass intake, no dry mass determinations were asked for.

Table 5: Extraction and determination methods

Laboratory	Extraction	Determination method	Exchange of extracts
1	PFE/toluene	GC-MS (trace QSQ)	With Laboratory 4
2	Soxhlet/toluene	GC-MS (ion trap)	With Laboratory 3
3	FBE/toluene	GC-MS	With Laboratory 2
4	Sonication/acetone/cyclohexane	GC-MS (EI, 70 eV)	With Laboratory 1
5	PFE/methanol	HPLC-DAD/F	With Laboratory 5
6	Sonication/acetonitrile	HPLC-DAD/F	With Laboratory 6

5.3 Evaluation of results and certified values

The results of the certification study are listed comprehensively in Table 6 and were evaluated in accordance with ISO Guide 35 [6] and the specific requirements of the ERM agreement [7]. For all measurement data see ANNEX B.3. The computer software SoftCRM [8] was partially used for statistical tests and data treatment.

5.3.1 Technical evaluation

A thorough investigation of all measurement results led to the identification of several data from some operator/equipment combinations which are biased due to an obvious technical reason such as interference by other substances and other chromatographic reasons. In case of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene the well-known problem of their separation from benzo[*j*]fluoranthene was tackled using the information supplied by each operator/equipment combination on which of both congeners is affected by benzo[*j*]fluoranthene. This influence was eliminated as described below.

Let $y_{ih}(b)$ and $y_{ih}(k)$ be the response (peak area) for replicate *h* measured by laboratory *i* as benzo[*b*]fluoranthene and benzo[*k*]fluoranthene, respectively. This response consists of the signal due to the "true" content *m(b)* and *m(k)* of these analytes in the sample and, in case of unsufficient separation, a certain fraction originating from benzo[*j*]fluoranthene with (unknown) content *m(j)*. With $r_i(b)$, $r_i(k)$, and $r_i(j)$ being the response factors of laboratory *i* for the corresponding analyte, one can write

$$\begin{aligned} y_{ih}(b) &= r_i(b)\cdot m(b) + r_i(j)\cdot m(j) + \varepsilon_{ih}(b) \\ y_{ih}(k) &= r_i(k)\cdot m(k) + r_i(j)\cdot m(j) + \varepsilon_{ih}(k) \end{aligned} \qquad (3)$$

where the second term has to be taken into account only where applicable (lacking separation power), and the $\varepsilon_{ih}(b)$ and $\varepsilon_{ih}(k)$ denominate the residual scatter. The $r_i(b)$ and $r_i(k)$ were determined in corresponding calibration experiments by all laboratories and used for deriving the estimates $m'_{ih}(b)$ and $m'_{ih}(k)$ (which are affected by *m(j)* where applicable) from the measured signals according to

$$\begin{aligned} m'_{ih}(b) &= m(b) + \frac{r_i(j)}{r_i(b)}\cdot m(j) + \varepsilon_{ih}(b) = m(b) + \alpha_i(j,b)\cdot m(j) + \varepsilon_{ih}(b) \\ m'_{ih}(k) &= m(k) + \frac{r_i(j)}{r_i(k)}\cdot m(j) + \varepsilon_{ih}(k) = m(k) + \alpha_i(j,k)\cdot m(j) + \varepsilon_{ih}(k) \end{aligned} \qquad (4)$$

where the $\alpha_i(j,b)$ and $\alpha_i(j,k)$ are the ratios of the response factors for benzo[*j*]fluoranthene and benzo[*b*]fluoranthene (resp. benzo[*k*]fluoranthene). The ε_{ih} are scaled by the corresponding response factor, but since they also describe the residual scatter and follow a similar distribution, the same symbols were used for simplicity.

Depending on the assumptions on the ε_{ih}, different optimisation problems can be formulated from the set of equations (4). Homoscedasticity was assumed here, i.e. all follow the same $N(0, \sigma)$ distribution, resulting in the following minimisation problem

$$\arg\min_{m(b),m(k),a_i(j,b),a_i(j,k)} \sum_{i,h} [m'_{ih}(b) - \alpha_i(j,b) \cdot m(j) - m(b)]^2 + [m'_{ih}(k) - \alpha_i(j,k) \cdot m(j) - m(k)]^2 \quad (5)$$

Note that the term containing *m(j)* is taken into account only where applicable. Problem (5) has unique solutions for *m(b)*, *m(k)*, and the products α_i*(j,b)* · *m(j)* (resp. α_i*(j,k)* · *m(j)*), while multiple solutions for the value of *m(j)* and the corresponding response ratios are possible. This corresponds to the fact that without knowledge of the individual response factor for benzo[*j*]fluoranthene, its quantification is impossible.

Problem (5) was solved based on a data set consisting of all replicate measurements the 6 participating laboratories had carried out on their own extracts and on the extracts prepared by another participating laboratory according to the cyclic permutation scheme. Two laboratories were identified for problems with the *(b,j)*, and one with the *(k,j)* separation. For the (b,j) separation, a common response factor ratio (not common response factors) was assumed for both laboratories. Minimum variance of equation (5) was attained for the following parameters

$m(b) = 7.11483$
$m(k) = 3.44456$
$m(j) = 1.64532$
$\alpha(j,b) = 0.67186$
$\alpha(j,k) = 1.502209$

(where the ratios are those most symmetric to unity), which were used to correct the initial data set (i.e. for the conversion from *m'(b)* to *m(b)*, and *m'(k)* to *m(k)*). Thereafter this corrected data set was fed into the statistical evaluation as described in chapter 5.3.2.

5.3.2 Statistical evaluation

Since the participants in the intercomparison used different extraction techniques and solvents, followed their own procedures, and applied both GC and HPLC for separation, a certain scatter of results was to be expected from experience. Thus there was no good reason for assuming that the single values measured by the different laboratories would belong to a common mother distribution. This was confirmed by the statistical analysis within which the following statistical parameters were calculated:

- *the mean of laboratory means*
- *the standard deviation of the distribution of laboratory means, and the standard deviation of the mean of laboratory means*
- *the confidence interval of the mean of laboratory means at the 0.05 significance level*

and the following statistical tests were carried out (at significance levels of 0.05 and 0.01):

- *Cochran test for the identification of outliers with respect to laboratory variance*
- *Grubbs test for the identification of outliers with respect to the mean*
- *Dixon and Nalimov test for the verification of possible outlier indications*
- *Kolmogorov-Smirnov Test (Lilliefors version) for the normality test*
- *Test for skewness and kurtosis*

The results of the above calculations and tests for a data evaluation based upon the laboratory means are given in table 7 ct. The main features are as follows:

- *Scheffé- und Snedecor-F-Test: Data sets differ significantly.*
- *Bartlett-Test: Variances are inhomogeneous (at the significance level of 0.01).*
- *Cochran-Test: No outliers detected (significance level 0.05 and 0.01).*
- *Dixon-, Grubbs- und Nalimov-Test: Laboratory means do not contain outliers (significance level 0.01).*
- *Kolmogorov-Smirnov and skewness/kurtosis test: Based on the available data, the hypothesis of normality cannot be rejected.*

Table 6: Data sets received from the participating laboratories (mean±standard deviation)

	No. 1	**No. 2**	**No. 3**	**No. 4**	**No. 5**	**No. 6**
	Mean ± SD (mg kg^{-1})	Mean ± SD (mg kg^{-1})	Mean ± SD (mg kg^{-1})	Mean ± SD (mg kg^{-1})	Mean ± SD (mg kg^{-1})	Mean ± SD (mg kg^{-1})
Naphthalene	2.262±0.182	1.952±0.312	2.908±0.079	2.747±0.041	2.054±0.076	2.746±0.085
Acenaphthene	0.654±0.063	0.758±0.023	0.816±0.013	0.772±0.012	2.472±0.051	0.737±0.005
Fluorene	1.001±0.080	1.244±0.072	1.167±0.067	1.106±0.027	1.126±0.043	1.165±0.003
Phenanthrene	11.132±0.578	12.402±0.293	12.678±0.265	11.284±0.304	12.644±0.139	11.933±0.034
Anthracene	1.355±0.027	1.438±0.085	1.813±0.036	1.030±0.018	1.275±0.043	1.520±0.016
Fluoranthene	11.478±0.387	12.629±0.317	13.709±0.254	12.986±0.272	13.688±0.531	12.815±0.020
Pyrene	9.434±0.252	9.993±0.404	9.589±0.115	9.728±0.173	9.242±0.401	9.344±0.066
Benz[*a*]anthracene	5.141±0.159	7.719±1.232	5.568±0.173	5.813±0.187	6.242±0.546	5.309±0.083
Chrysene	4.063±0.133	5.735±0.399	5.364±0.255	6.606±0.334	5.031±0.080	4.716±0.047
Benzo[*b*]fluoranthene*	7.203±0.331	7.026±0.207	5.697±0.443	6.169±0.461	7.576±0.537	9.017±0.063
Benzo[*k*]fluoranthene*	3.380±0.197	4.291±0.883	3.210±0.131	3.445±0.900	3.104±0.163	3.238±0.030
Benzo[*a*]pyrene	4.768±0.512	4.269±0.289	3.729±0.270	5.298±0.145	5.741±0.206	5.292±0.025
Dibenz[*ah*]anthracene		1.185±0.088	1.394±0.101	0.915±0.050	1.707±0.073	0.530±0.025
Benzo[ghi]perylene	4.307±0.134	5.808±0.987	4.228±0.134	5.13±0.103	4.794±0.204	4.196±0.047
Indeno[1,2,3-*cd*]pyrene	5.639±0.376	4.229±0.285	4.262±0.167	4.924±0.214	5.188±0.259	5.188±0.259

*corrected, see chapter 5.3.1.

According to these results, the means of laboratory means were taken as the best estimates w_{char} for the values to be certified, and the standard deviations of the mean of laboratory means were taken as the uncertainty contributions u_{char} from characterisation by this intercomparison exercise.

Table 7: Values and statistical parameters for the intercomparison (all values in mg kg^{-1})

PAH congener	value [a]	s [b]	u [c]	CI [d]	TI [e]	data sets	pooling
Naphthalene	2.449	0.404	0.165	0.424	1.784	6	no
Acenaphthene	0.751	0.052	0.023	0.065	0.266	5	no
Fluorene	1.14	0.072	0.029	0.075	0.317	6	no
Phenanthrene	12.014	0.675	0.276	0.709	2.981	6	no
Anthracene	1.406	0.261	0.107	0.274	1.152	6	no
Fluoranthene	12.904	0.781	0.319	0.82	3.449	6	no
Pyrene	9.562	0.273	0.111	0.286	1.203	6	no
Benz[*a*]anthracene	5.622	0.424	0.190	0.527	2.154	5	no
Chrysene	5.258	0.866	0.354	0.909	3.822	6	no
Benzo[*b*]fluoranthene*	7.115	1.162	0.474	1.220	5.129	6	no
Benzo[*k*]fluoranthene*	3.445	0.433	0.176	0.454	1.908	6	no
Benzo[*a*]pyrene	4.856	0.747	0.305	0.783	3.295	6	no
Dibenz[*ah*]anthracene	1.146	0.45	0.201	0.559	2.286	5	no
Benzo[*ghi*]perylene	4.562	0.419	0.187	0.52	2.129	5	no
Indeno[1,2,3-*cd*]pyrene	5.231	1.062	0.434	1.114	4.687	6	no

[a] *mean of laboratory means*
[b] *standard deviation of the population of laboratory means*
[c] *standard deviation of the mean of means*
[d] *confidence interval*
[e] *tolerance interval*
** corrected, see chapter 5.3.1.*

Table 7 continued

PAH	Scheffé[f]	Bartlett[g]	outlier tests[h]				normality
			Cochran	Grubbs-1	Grubbs-2	Nalimov	
Naphthalene	No	inhom	2, 1	-(-)	-(-)	-(-)	yes
Acenaphthene	No	inhom	1	-(-)	-(-)	-(-)	yes
Fluorene	No	inhom	-	-(-)	-(-)	-(-)	yes
Phenanthrene	No	inhom	1	-(-)	-(-)	-(-)	yes
Anthracene	No	inhom	2	-(-)	-(-)	-(-)	yes
Fluoranthene	No	inhom	-	-(-)	-(-)	-(1)	yes
Pyrene	no	inhom	-	-(-)	-(-)	-(-)	yes
Benz[*a*]anthracene	no	inhom	5	-(-)	-(-)	-(-)	yes
Chrysene	no	inhom	-	-(-)	-(-)	-(-)	yes
Benzo[*b*]fluoranthene*	no	inhom	-	-(-)	-(-)	-(-)	yes
Benzo[k]fluoranthene*	no	inhom	n/a	-(2)		2(2)	yes [*]
Benzo[*a*]pyrene	no	inhom	-	-(-)	-(-)	-(-)	yes
Dibenz[*ah*]anthracene	No	hom	-	-(-)	-(-)	-(-)	yes
Benzo[*ghi*]perylene	No	hom	-	-(-)	-(-)	-(-)	yes
Indeno[1,2,3-*cd*]pyrene	No	hom	-	-(-)	-(-)	-(-)	yes

[f] *Scheffé test for two-by-two data set compatibility*
[g] *Bartlett test for homogeneity of laboratory variances (significance level 0.01)*
[h] *outlier tests: outlying laboratory values are indicated, significance level 0.01 (0.05 in brackets)*
[*] *normal only at a signifcance level of 0.01*
** corrected, see chapter 5.3.1.*

5.3.3 Traceability

All certified values refer to the extractable amount of PAHs and are conventional to this extent. However, different extraction methods and solvents have been used such that systematic biases will (at least partially) cancel out. The completeness of extraction was investigated by extraction. It was demonstrated that any further extraction provided extracts with PAH contents below the limit of detection (LOD). The LOD was included in the uncertainty budget as a worst-case estimate for the possibly unextractable remainder of the analytes in the sample.

In order to ensure traceability of the extractable content as defined above, calibration standards SRM 1647d, LGC 16 EPA PAH, and SRM 2260 were employed. Outside of this study it had been established before that these standard solutions were equivalent to standards prepared using pure crystalline PAH congeners with certified purity and available as BCR CRM from the IRMM in Geel, Belgium. While this study was conducted several of those BCR CRMs were no longer available.

5.3.4 Certified values and combined uncertainties

As mentioned in clause 5.3.2, the means of laboratory means were taken as the best estimates w_{char} for the values to be certified. The standard deviations of the mean of laboratory means were taken as the uncertainty contributions u_{char} from characterisation.
Besides this uncertainty of characterisation u_{char}, the contribution from a possibly undetected inhomogeneity u_{bb}, the uncertainty estimate for possibly incomplete extraction (see clause 5.3.3) u_{ext}, and the uncertainty of the calibration standard u_{pur} contribute to the combined uncertainty according to

$$u_{com,\,r}^{\,2} = u_{char,\,r}^{\,2} + u_{bb,\,r}^{\,2} + u_{ext,r}^{\,2} + u_{pur,\,r}^{\,2}$$

where the index r refers to the corresponding relative uncertainties. The uncertainties of the calibration standards were taken from the certificate of SRM-1647d, u_{char} are given in clause 5.3.2), u_{ext} was estimated as described in clause 5.3.3, and u_{bb} are evaluated in clause 3.

The final values are given in table 8 where the expansion factor for the expanded uncertainties is $k = 2$. The value and the expanded uncertainty are rounded according to the recommendations of [9] and are given with respect to raw sample mass. The water content of ERM-CC013a was seen to remain stable if the material is handled according to the instructions in the certificate (see also clause 6).

Table 8 : Certified mass fractions of PAH congeners in ERM-CC013a (before rounding)

PAH	w_{char} (mg kg^{-1})	u_{char} (mg kg^{-1})	u_{bb} (mg kg^{-1})	u_{ext} (mg kg^{-1})	u_{pur} (mg kg^{-1})	u_{com} (mg kg^{-1})
Naphthalene	2.449	0.165	0.023	0.166	0.016	0.236
Fluorene	1.14	0.029	0.009	0.045	0.006	0.055
Phenanthrene	12.014	0.276	0.103	0.052	0.096	0.314
Anthracene	1.406	0.107	0.010	0.012	0.014	0.109
Fluoranthene	12.904	0.319	0.080	0.031	0.072	0.338
Pyrene	9.562	0.111	0.106	0.024	0.048	0.163
Benz[*a*]anthracene	5.622	0.190	0.040	0.125	0.021	0.232
Chrysene	5.258	0.354	0.031	0.093	0.022	0.368
Benzo[*b*]fluoranthene	7.115	0.474	0.045	0.074	0.035	0.483
Benzo[*k*]fluoranthene	3.445	0.176	0.016	0.019	0.022	0.179
Benzo[*a*]pyrene	4.856	0.305	0.040	0.058	0.035	0.315
Benzo[*ghi*]perylene	4.562	0.187	0.025	0.073	0.072	0.215
Indeno[1,2,3-*cd*]pyrene	5.231	0.434	0.055	0.129	0.048	0.458

6 Information on the proper use of ERM-CC013a

6.1 Shelf life

From the initial stability study a preliminary shelf life of two years at storage temperatures not higher than +4 °C is estimated. Since the dispatch to the end user may occur at any time during this period the certified properties will be valid for 12 months beginning with the dispatch of the material from BAM. The validity of this information will be maintained by post-certification stability monitoring.

6.2 Transport, storage and use

The stability of the content of PAH allows the dispatch of the material at ambient temperature. On receiving, it is to be stored at -20 °C. Before withdrawing a sub-sample the bottle has to have reached ambient temperature. Thereafter, the bottle must be closed tightly and stored at –20 °C. The water content remains stable when the material is treated as described.

6.3 Safety instructions

The sediment was not sterilised, however, it is supposed to not exhibit any biological activity due to having been dried to constant weight. No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of environmental matrices moderately contaminated with polycyclic aromatic hydrocarbons.

It is strongly recommended to handle and dispose the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal.

6.4 Legal notice

Neither the Federal Institute for Materials Research and Testing (BAM) nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document may not infringe privately owned rights, or assume any liability with respect to the use of, or damages resulting from the use of any information, material, apparatus, method or process disclosed in this document.

7 References

[1] ISO 13877:1998 – Soil quality -- Determination of polynuclear aromatic hydrocarbons -- Method using high-performance liquid chromatography

[2] ISO 18287:2006 – Soil quality -- Determination of polycyclic aromatic hydrocarbons (PAH) -- Gas chromatographic method with mass spectrometric detection (GC-MS)

[3] *http://www.bipm.fr/en/committees/cc/ccqm/*

[4] A. Lamberty, H. Schimmel, J. Pauwels. The study of the stability of reference materials by isochronous measurements. *Fres. J. Anal. Chem.* (1998) 360: 359–361

[5] W. Bremser, R. Becker, H. Kipphardt, P. Lehnik-Habrink, U. Panne and A. Töpfer. Stability testing in an integrated scheme. Accred Qual Assur (2006) 11: 489–495.

[6] ISO Guide 35:2006. Reference materials – General and statistical principles for certification. ISO, Geneva, Switzerland

[7] For detailed information on the ERM agreement see: www.erm-crm.org/ermcrm

[8] SoftCRM V.1.22 (developed and funded under Contract SMT4 - CT98 – 6533 of the STANDARDS, MEASUREMENTS & TESTING PROGRAMME)

[9] Guide To The Expression Of Uncertainty In Measurement. ISO, Geneva (1993). (ISBN 92-67-10188-9, Reprinted 1995)

ANNEX A: Measurement methods

Six independent operator/equipment combinations took part in the certification study. The following procedural details were employed:

Method	Extraction	Chromatography	Detection
1	Pressurised fluid extraction (PFE, here: ASE® 200, Dionex), toluene (2 cycles)	GC; column: DB-5MS 60 m x 0.25 ID x 0.25 µm film	MS Trace DSQ
2	Soxhlet, 8 h, toluene	GC; column: DB 5 MS, 30 m, 0.25 mm ID, 0.25 µm film	MS 4000 Varian Ion Trap
3	Fluidised bed extraction (FBE, here: FexIKA®), 15 cycles (2.5 h), toluene	Varian GC CP-3800; column: VF-5ms, 30 m, 0.25 mm ID, 0.25 µm film	Varian MS 1200L
4	Sonication, 2 x 1 h, 40 °C, cyclohexane/acetone (1:1)	Agilent GC 6890N; column: ZB-5, 30 m, 0.25 mm ID, 0.25 µm film	Agilent MS5973N, EI, 70 eV
5	Pressurised fluid extraction (PFE, here: ASE® 200, Dionex), methanol, 100 °C (2 cycles)	HP 1100 Liquid chromatograph; column: UltraSep ES PAH 250x3 mm, acetonitrile/water, gradient	DAD/F
6	Sonication, 2 x 1 h, 40 °C, acetonitrile	Gynkotek HPLC, methanol/water, gradient	DAD/F

Sample intake for a single determination: 3 g
GC: Deuterated PAHs were used as internal standards

ANNEX B: Measurement results

Method no. 5 was used for the homogeneity and stability study.

The measurements for the homogeneity and stability study were both performed under repeatability conditions with a randomised order of extracts.

In order to control any possible drift of the chromatographic system (e. g. the detector) a calibration solution was injected after every seventh run in the homogeneity and stability studies (data not given). No significant variability compared with the variability of analytical results obtained from replicate extractions of the candidate material was observed.

B.1 Homogeneity study

Naphthalene				
Bottle	Replicate determination (mg kg^{-1})			
22	2.79	2.79	2.71	2.78
55	2.78	2.75	2.31	2.73
88	2.76	2.74	2.59	2.76
121	2.73	2.75	2.56	2.71
154	2.75	2.69	2.58	2.68
187	2.67	2.66	2.56	2.62
220	2.66	2.73	2.64	2.68
253	2.65	2.67	2.66	2.66
286	2.73	2.62	2.63	2.65
319	2.78	2.61	2.68	2.68
352	2.84	2.74	2.66	2.68
385	2.77	2.60	2.71	2.66
418	2.75	2.67	2.65	2.61
451	2.80	2.70	2.73	2.69
484	2.77	2.65	2.60	2.67

Acenaphthene				
Bottle	Replicate determination (mg kg^{-1})			
22	0.79	0.77	0.79	0.89
55	0.79	0.77	0.68	0.77
88	0.77	0.84	0.79	0.79
121	0.83	0.79	0.76	0.83
154	0.79	0.79	0.75	0.76
187	0.80	0.83	0.80	0.80
220	0.82	0.78	0.79	0.81
253	0.80	0.80	0.80	0.78
286	0.88	0.88	0.82	0.79
319	0.80	0.77	0.83	0.82
352	0.81	0.76	0.77	0.81
385	0.78	0.77	0.76	0.83
418	0.90	0.80	0.84	0.76
451	0.76	0.89	0.81	0.81
484	0.80	0.85	0.75	0.80

Fluorene

Bottle	Replicate determination (mg kg^{-1})			
22	1.21	1.20	1.16	1.19
55	1.21	1.22	0.95	1.19
88	1.18	1.21	1.20	1.23
121	1.18	1.20	1.19	1.21
154	1.21	1.20	1.18	1.19
187	1.20	1.18	1.19	1.15
220	1.17	1.20	1.17	1.19
253	1.18	1.19	1.21	1.15
286	1.17	1.21	1.19	1.18
319	1.20	1.20	1.20	1.21
352	1.23	1.20	1.18	1.19
385	1.21	1.18	1.21	1.18
418	1.22	1.20	1.20	1.13
451	1.19	1.21	1.20	1.19
484	1.23	1.21	1.19	1.18

Phenanthrene

Bottle	Replicate determination (mg kg^{-1})			
22	12.82	12.54	12.16	12.64
55	12.73	12.43	9.87	12.29
88	12.70	12.51	12.08	12.59
121	12.61	12.54	12.18	12.36
154	12.65	12.69	12.05	12.30
187	12.58	12.40	12.19	12.21
220	12.63	12.78	12.09	12.35
253	12.38	12.28	12.30	12.38
286	12.62	12.38	12.03	12.27
319	12.54	12.32	12.18	12.45
352	12.87	12.48	12.34	12.35
385	12.72	12.36	12.19	12.45
418	12.60	12.45	12.25	12.10
451	12.52	12.60	11.72	12.36
484	12.90	12.81	12.13	11.45

Anthracene

Bottle	Replicate determination (mg kg^{-1})			
22	1.61	1.63	1.58	1.65
55	1.61	1.63	1.39	1.59
88	1.57	1.63	1.59	1.65
121	1.60	1.62	1.58	1.61
154	1.53	1.62	1.51	1.60
187	1.59	1.57	1.61	1.59
220	1.58	1.62	1.60	1.59
253	1.59	1.60	1.60	1.50
286	1.59	1.62	1.60	1.50
319	1.55	1.61	1.62	1.62
352	1.55	1.63	1.61	1.60
385	1.60	1.51	1.61	1.61
418	1.60	1.61	1.61	1.55
451	1.59	1.59	1.53	1.61
484	1.59	1.61	1.60	1.52

Fluoranthene				
Bottle	Replicate determination (mg kg^{-1})			
22	13.61	13.48	13.32	13.52
55	13.47	13.41	11.13	13.08
88	13.23	13.37	13.33	13.67
121	13.25	13.50	13.32	13.38
154	13.21	13.53	13.03	13.23
187	13.39	13.28	13.12	13.27
220	13.23	13.70	13.37	13.39
253	13.20	13.21	13.37	13.17
286	13.17	13.38	13.35	13.18
319	13.27	13.30	13.24	13.42
352	13.46	13.52	13.25	13.16
385	13.31	13.39	13.38	13.24
418	13.37	13.41	13.44	13.06
451	13.63	13.50	13.34	13.18
484	13.74	13.71	13.47	13.45

Pyrene				
Bottle	Replicate determination (mg kg^{-1})			
22	10.31	9.87	9.08	10.04
55	10.10	9.60	7.57	9.64
88	10.00	9.81	9.25	9.97
121	9.83	9.65	9.47	9.75
154	9.88	9.89	9.34	9.68
187	9.89	9.77	9.51	9.66
220	9.85	10.02	9.11	9.75
253	9.74	9.45	9.62	9.78
286	10.05	9.77	9.14	9.73
319	9.88	9.64	9.26	9.88
352	10.05	9.75	9.70	9.77
385	10.04	9.61	9.37	9.83
418	9.84	9.79	9.22	9.58
451	9.82	9.96	8.30	9.79
484	10.05	9.99	9.11	9.40

Benzo[*a*]anthracene				
Bottle	Replicate determination (mg kg^{-1})			
22	6.07	5.90	5.83	5.94
55	5.92	5.86	5.05	5.67
88	5.89	5.90	5.80	5.90
121	5.80	5.88	5.82	5.78
154	5.83	5.91	5.73	5.73
187	5.83	5.84	5.77	5.70
220	5.83	6.03	5.80	5.75
253	5.74	5.77	5.82	5.76
286	5.85	5.83	5.92	5.76
319	5.82	5.81	5.85	5.80
352	5.97	5.87	5.82	5.77
385	5.92	5.79	5.82	5.78
418	5.92	5.86	5.81	5.63
451	5.87	5.89	5.84	5.78
484	6.00	5.96	5.82	5.86

Chrysene

Bottle	Replicate determination (mg kg^{-1})			
22	5.14	4.99	4.87	5.12
55	5.03	5.02	4.24	4.89
88	5.01	5.08	4.83	4.99
121	4.95	5.12	4.93	4.93
154	4.98	5.11	4.84	4.86
187	4.98	4.99	4.91	4.86
220	5.01	5.10	4.95	4.96
253	4.91	4.91	4.98	4.94
286	5.13	5.06	4.95	4.86
319	5.04	4.90	4.97	4.92
352	5.14	5.03	4.90	4.90
385	5.10	4.98	4.93	4.93
418	5.07	5.03	4.96	4.79
451	5.05	5.01	5.00	4.89
484	5.15	5.12	4.96	4.97

Benzo[*b*]anthracene

Bottle	Replicate determination (mg kg^{-1})			
22	9.45	9.45	9.28	9.52
55	9.53	9.39	8.22	9.22
88	9.46	9.53	9.29	9.37
121	9.34	9.41	9.30	9.23
154	9.36	9.35	9.16	9.08
187	9.38	9.28	9.35	9.27
220	9.31	9.42	9.40	9.19
253	9.10	9.35	9.40	9.29
286	9.25	9.35	9.39	9.22
319	9.19	9.28	9.36	9.44
352	9.33	9.53	9.36	9.37
385	9.16	9.32	8.77	9.32
418	9.25	9.32	9.37	8.99
451	9.22	9.31	9.45	9.34
484	9.38	9.43	9.30	9.43

Benzo[*k*]anthracene

Bottle	Replicate determination (mg kg^{-1})			
22	3.17	3.13	3.06	3.15
55	3.20	3.13	2.67	3.02
88	3.12	3.19	3.11	3.18
121	3.08	3.15	3.09	3.05
154	3.10	3.13	3.07	3.03
187	3.11	3.10	3.08	3.09
220	3.15	3.19	3.11	3.12
253	3.05	3.09	3.09	3.10
286	3.10	3.09	3.14	3.10
319	3.05	3.07	3.14	3.11
352	3.19	3.12	3.12	3.05
385	3.12	3.12	3.09	3.10
418	3.12	3.14	3.14	3.04
451	3.14	3.13	3.14	3.06
484	3.17	3.21	3.13	3.11

Benzo[*a*]pyrene

Bottle	Replicate determination (mg kg^{-1})			
22	5.55	5.46	5.22	5.26
55	5.51	5.25	4.59	5.01
88	5.47	5.45	5.16	5.39
121	5.35	5.40	5.24	5.12
154	5.39	5.49	5.29	5.16
187	5.42	5.34	5.33	5.10
220	5.33	5.51	5.36	5.35
253	5.18	5.30	5.37	5.12
286	5.40	5.38	5.32	5.17
319	5.31	5.34	5.35	5.14
352	5.52	5.47	5.34	5.17
385	5.47	5.36	5.30	5.18
418	5.41	5.48	5.32	5.03
451	5.40	5.47	5.24	5.14
484	5.52	5.45	5.34	4.95

Dibenz[*ah*]anthracene

Bottle	Replicate determination (mg kg^{-1})			
22	0.60	0.53	0.52	0.53
55	0.69	0.53	0.47	0.49
88	0.58	0.51	0.52	0.49
121	0.51	0.54	0.49	0.50
154	0.64	0.54	0.53	0.50
187	0.57	0.53	0.47	0.50
220	0.57	0.55	0.51	0.54
253	0.55	0.51	0.56	0.50
286	0.58	0.52	0.58	0.47
319	0.57	0.51	0.49	0.50
352	0.50	0.52	0.57	0.53
385	0.59	0.54	0.52	0.49
418	0.54	0.58	0.51	0.50
451	0.51	0.50	0.52	0.51
484	0.55	0.54	0.55	0.50

Benzo[*ghi*]perylene

Bottle	Replicate determination (mg kg^{-1})			
22	4.30	4.30	4.14	4.28
55	4.30	4.23	3.70	4.08
88	4.28	4.28	4.09	4.25
121	4.21	4.27	4.12	4.12
154	4.20	4.28	4.11	4.07
187	4.23	4.24	4.12	4.08
220	4.28	4.35	4.17	4.12
253	4.22	4.14	4.18	4.12
286	4.35	4.17	4.17	4.13
319	4.29	4.14	4.20	4.17
352	4.39	4.24	4.16	4.17
385	4.33	4.14	4.18	4.15
418	4.28	4.23	4.16	4.06
451	4.25	4.29	4.17	4.15
484	4.37	4.32	4.16	4.20

Indeno[123*cd*]pyrene				
Bottle	Replicate determination (mg kg^{-1})			
22	7.57	7.53	7.31	7.49
55	7.90	7.22	6.78	7.07
88	7.04	7.15	6.96	7.36
121	7.30	7.23	7.14	7.29
154	7.43	7.44	7.18	6.98
187	7.38	7.21	7.57	7.27
220	7.68	7.42	7.07	7.71
253	7.66	7.03	6.79	7.26
286	7.26	7.48	7.24	7.01
319	7.32	7.26	7.31	6.75
352	7.59	7.38	7.40	7.31
385	7.61	7.62	7.51	7.06
418	7.58	7.20	7.15	7.14
451	7.26	7.37	7.37	7.23
484	7.66	7.16	7.49	7.28

B.2 Stability study

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Naphthalene	255	ref	-20	2.43	2.36	2.18	2.33
Naphthalene	256	ref	-20	2.31	2.32	2.28	2.38
Naphthalene	256	ref	-20	2.62	2.88	3.03	2.97
Naphthalene	257	ref	-20	3.02	2.89	2.87	2.88
Naphthalene	263	1	4	2.30	2.32	2.46	2.25
Naphthalene	264	3	4	2.38	2.28	2.37	2.25
Naphthalene	265	6	4	2.87	2.29	2.32	2.30
Naphthalene	265	6	4	3.08	2.99	2.88	2.96
Naphthalene	266	12	4	2.96	3.00	2.92	2.92
Naphthalene	270	1	22	2.76	2.30	2.33	2.18
Naphthalene	271	3	22	2.25	2.43	2.38	2.26
Naphthalene	272	6	22	2.38	2.28	2.34	2.30
Naphthalene	272	6	22	2.94	2.95	2.84	2.95
Naphthalene	273	12	22	2.89	2.89	2.91	3.06
Naphthalene	279	1	40	2.66		2.35	2.33
Naphthalene	280	3	40	2.30	2.16	2.06	2.26
Naphthalene	281	6	40	2.17	2.14	2.21	2.16
Naphthalene	281	6	40	2.64	2.70	2.62	2.67
Naphthalene	282	12	40	2.51	2.62	2.54	2.52
Naphthalene	283	1	60	1.89	2.09	2.01	2.12
Naphthalene	284	3	60	1.87	1.74	1.83	1.81

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Acenaphthene	255	ref	-20	0.26	0.30	0.24	0.29
Acenaphthene	256	ref	-20	0.27	0.21	0.26	0.28
Acenaphthene	256	ref	-20	0.40	0.30	0.32	0.33
Acenaphthene	257	ref	-20	0.31	0.28	0.28	0.30
Acenaphthene	263	1	4	0.26	0.25	0.26	0.24
Acenaphthene	264	3	4	0.30	0.22	0.25	0.22
Acenaphthene	265	6	4	0.24	0.19	0.26	0.24
Acenaphthene	265	6	4	0.30	0.33	0.28	0.31
Acenaphthene	266	12	4	0.32	0.31	0.28	0.31
Acenaphthene	270	1	22	0.23	0.21	0.22	0.22
Acenaphthene	271	3	22	0.24	0.22	0.23	0.22
Acenaphthene	272	6	22	0.20	0.27	0.19	0.19
Acenaphthene	272	6	22	0.22	0.28	0.27	0.24
Acenaphthene	273	12	22	0.22	0.20	0.17	0.17
Acenaphthene	279	1	40	0.20		0.19	0.16
Acenaphthene	280	3	40	0.07	0.02	0.02	0.08
Acenaphthene	281	6	40	0.00*	0.00*	0.00*	0.00*
Acenaphthene	281	6	40	0.00*	0.00*	0.00*	0.00*
Acenaphthene	282	12	40	0.00*	0.00*	0.00*	0.00*
Acenaphthene	283	1	60	0.00*	0.00*	0.00*	0.00*
Acenaphthene	284	3	60	0.00*	0.00*	0.00*	0.00*

* Values "0.00" represent results below the limit of determination

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Fluorene	255	ref	-20	1.11	1.18	1.08	1.10
Fluorene	256	ref	-20	1.10	1.08	1.09	1.12
Fluorene	256	ref	-20	1.11	1.09	1.12	1.12
Fluorene	257	ref	-20	1.11	1.10	1.11	1.12
Fluorene	263	1	4	1.12	1.10	1.09	1.09
Fluorene	264	3	4	1.17	1.10	1.08	1.08
Fluorene	265	6	4	1.09	1.07	1.10	1.08
Fluorene	265	6	4	1.10	1.10	1.09	1.10
Fluorene	266	12	4	1.09	1.09	1.08	1.08
Fluorene	270	1	22	1.07	1.06	1.07	1.05
Fluorene	271	3	22	1.06	1.02	1.03	1.03
Fluorene	272	6	22	0.98	1.01	0.99	0.98
Fluorene	272	6	22	0.97	0.99	0.98	0.99
Fluorene	273	12	22	0.88	0.88	0.88	0.87
Fluorene	279	1	40	0.97		0.96	0.96
Fluorene	280	3	40	0.77	0.75	0.76	0.77
Fluorene	281	6	40	0.56	0.57	0.56	0.56
Fluorene	281	6	40	0.54	0.56	0.54	0.56
Fluorene	282	12	40	0.29	0.31	0.31	0.30
Fluorene	283	1	60	0.52	0.54	0.55	0.56
Fluorene	284	3	60	0.19	0.17	0.18	0.17

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Phenanthrene	255	ref	-20	13.03	12.51	12.81	12.93
Phenanthrene	256	ref	-20	12.80	12.53	12.94	13.26
Phenanthrene	256	ref	-20	13.34	13.44	13.85	13.76
Phenanthrene	257	ref	-20	13.91	13.57	13.58	13.75
Phenanthrene	263	1	4	13.00	12.47	12.92	12.88
Phenanthrene	264	3	4	13.43	12.60	12.91	12.83
Phenanthrene	265	6	4	13.09	12.56	12.92	12.95
Phenanthrene	265	6	4	13.89	13.70	13.56	13.78
Phenanthrene	266	12	4	13.69	13.69	13.60	13.55
Phenanthrene	270	1	22	12.96	12.56	13.00	12.90
Phenanthrene	271	3	22	12.85	12.55	12.99	12.93
Phenanthrene	272	6	22	12.70	12.63	12.88	13.03
Phenanthrene	272	6	22	13.59	13.60	13.52	13.71
Phenanthrene	273	12	22	13.73	13.65	13.60	13.58
Phenanthrene	279	1	40	12.76		12.80	12.95
Phenanthrene	280	3	40	12.77	12.28	12.54	12.63
Phenanthrene	281	6	40	12.45	12.28	12.36	12.43
Phenanthrene	281	6	40	13.28	13.14	13.01	13.01
Phenanthrene	282	12	40	12.43	13.12	12.91	13.05
Phenanthrene	283	1	60	11.68	12.02	12.27	12.27
Phenanthrene	284	3	60	11.53	10.88	11.58	11.57

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Anthracene	255	ref	-20	1.75	1.74	1.71	1.74
Anthracene	256	ref	-20	1.74	1.73	1.73	1.78
Anthracene	256	ref	-20	1.56	1.60	1.67	1.64
Anthracene	257	ref	-20	1.66	1.62	1.63	1.63
Anthracene	263	1	4	1.76	1.75	1.73	1.74
Anthracene	264	3	4	1.82	1.73	1.72	1.71
Anthracene	265	6	4	1.79	1.74	1.68	1.73
Anthracene	265	6	4	1.65	1.63	1.61	1.60
Anthracene	266	12	4	1.62	1.61	1.62	1.58
Anthracene	270	1	22	1.75	1.72	1.73	1.70
Anthracene	271	3	22	1.70	1.68	1.70	1.68
Anthracene	272	6	22	1.69	1.66	1.64	1.67
Anthracene	272	6	22	1.55	1.56	1.55	1.58
Anthracene	273	12	22	1.51	1.51	1.52	1.48
Anthracene	279	1	40	1.55		1.55	1.58
Anthracene	280	3	40	1.38	1.33	1.34	1.35
Anthracene	281	6	40	1.14	1.12	1.11	1.11
Anthracene	281	6	40	1.06	1.06	1.05	1.02
Anthracene	282	12	40	0.80	0.92	0.84	0.84
Anthracene	283	1	60	0.81	0.85	0.82	0.85
Anthracene	284	3	60	0.53	0.47	0.50	0.49

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Fluoranthene	255	ref	-20	13.24	13.24	13.23	13.14
Fluoranthene	256	ref	-20	13.20	13.12	13.23	13.48
Fluoranthene	256	ref	-20	13.23	13.46	13.79	13.98
Fluoranthene	257	ref	-20	14.06	13.33	13.54	13.64
Fluoranthene	263	1	4	13.37	12.98	13.11	13.16
Fluoranthene	264	3	4	13.37	12.98	13.11	13.16
Fluoranthene	265	6	4	13.22	13.23	13.10	13.21
Fluoranthene	265	6	4	13.42	13.55	13.56	13.65
Fluoranthene	266	12	4	13.34	13.40	13.57	13.46
Fluoranthene	270	1	22	13.30	13.11	13.37	13.10
Fluoranthene	271	3	22	13.24	13.16	13.33	13.19
Fluoranthene	272	6	22	13.35	13.35	13.17	13.31
Fluoranthene	272	6	22	13.49	13.46	13.43	13.52
Fluoranthene	273	12	22	13.64	13.54	13.56	13.76
Fluoranthene	279	1	40	13.06		13.12	13.23
Fluoranthene	280	3	40	13.07	13.08	12.96	13.05
Fluoranthene	281	6	40	12.80	13.04	12.90	12.83
Fluoranthene	281	6	40	13.09	13.13	13.15	13.19
Fluoranthene	282	12	40	12.57	13.23	13.10	13.34
Fluoranthene	283	1	60	12.32	12.97	12.71	12.90
Fluoranthene	284	3	60	12.65	11.85	12.31	12.30

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Pyrene	255	ref	-20	9.50	9.70	9.46	9.55
Pyrene	256	ref	-20	9.65	9.35	9.63	9.84
Pyrene	256	ref	-20	10.65	10.11	10.26	10.26
Pyrene	257	ref	-20	10.40	10.05	10.14	10.11
Pyrene	263	1	4	9.68	9.30	9.73	9.54
Pyrene	264	3	4	9.99	9.22	9.62	9.45
Pyrene	265	6	4	9.86	9.57	9.59	9.56
Pyrene	265	6	4	10.31	10.22	10.20	10.11
Pyrene	266	12	4	10.09	10.11	10.11	10.00
Pyrene	270	1	22	9.70	9.64	9.84	9.42
Pyrene	271	3	22	9.65	9.73	9.76	9.54
Pyrene	272	6	22	9.57	9.73	9.57	9.59
Pyrene	272	6	22	9.95	10.18	10.07	10.15
Pyrene	273	12	22	10.14	10.16	10.18	10.04
Pyrene	279	1	40	9.75		9.72	9.57
Pyrene	280	3	40	10.02	9.38	9.31	9.39
Pyrene	281	6	40	9.51	9.56	9.14	9.26
Pyrene	281	6	40	9.87	9.87	10.00	9.76
Pyrene	282	12	40	9.20	9.85	9.90	9.79
Pyrene	283	1	60	8.81	9.47	9.13	9.17
Pyrene	284	3	60	8.72	8.71	8.64	8.64

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Benz[*a*]anthracene	255	ref	-20	5.95	5.72	5.65	5.76
Benz[*a*]anthracene	256	ref	-20	5.70	5.82	5.72	6.02
Benz[*a*]anthracene	256	ref	-20	5.84	5.89	6.06	6.07
Benz[*a*]anthracene	257	ref	-20	6.17	5.92	5.95	6.03
Benz[*a*]anthracene	263	1	4	5.80	5.83	5.72	5.73
Benz[*a*]anthracene	264	3	4	6.00	5.85	5.72	5.72
Benz[*a*]anthracene	265	6	4	5.87	5.80	5.69	5.78
Benz[*a*]anthracene	265	6	4	6.12	6.00	5.93	6.00
Benz[*a*]anthracene	266	12	4	5.95	5.92	5.96	5.93
Benz[*a*]anthracene	270	1	22	5.80	5.73	5.76	5.68
Benz[*a*]anthracene	271	3	22	5.72	5.75	5.69	5.69
Benz[*a*]anthracene	272	6	22	5.79	5.83	5.62	5.75
Benz[*a*]anthracene	272	6	22	5.85	5.92	5.90	5.96
Benz[*a*]anthracene	273	12	22	5.92	5.89	5.88	5.88
Benz[*a*]anthracene	279	1	40	5.64		5.64	5.72
Benz[*a*]anthracene	280	3	40	5.57	5.43	5.42	5.51
Benz[*a*]anthracene	281	6	40	5.33	5.41	5.23	5.28
Benz[*a*]anthracene	281	6	40	5.61	5.50	5.51	5.45
Benz[*a*]anthracene	282	12	40	5.01	5.30	5.26	5.33
Benz[*a*]anthracene	283	1	60	4.92	5.15	5.15	5.14
Benz[*a*]anthracene	284	3	60	4.67	4.40	4.56	4.54

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Chrysene	255	ref	-20	5.83	5.65	5.60	5.68
Chrysene	256	ref	-20	5.61	5.74	5.68	5.85
Chrysene	256	ref	-20	4.91	4.87	4.95	4.94
Chrysene	257	ref	-20	5.17	4.88	4.91	4.88
Chrysene	263	1	4	5.69	5.66	5.74	5.67
Chrysene	264	3	4	5.86	5.79	5.71	5.66
Chrysene	265	6	4	5.84	5.63	5.68	5.82
Chrysene	265	6	4	5.13	4.97	4.92	4.94
Chrysene	266	12	4	5.01	4.94	4.78	4.82
Chrysene	270	1	22	5.69	5.70	5.76	5.63
Chrysene	271	3	22	5.65	5.69	5.81	5.68
Chrysene	272	6	22	5.69	5.74	5.67	5.79
Chrysene	272	6	22	4.98	4.94	4.92	4.89
Chrysene	273	12	22	5.07	4.98	4.82	5.01
Chrysene	279	1	40	5.67		5.73	5.86
Chrysene	280	3	40	5.72	5.53	5.55	5.63
Chrysene	281	6	40	5.55	5.61	5.46	5.54
Chrysene	281	6	40	4.97	4.88	4.85	4.76
Chrysene	282	12	40	4.67	4.83	4.76	4.80
Chrysene	283	1	60	5.32	5.51	5.47	5.57
Chrysene	284	3	60	5.36	5.09	5.25	5.25

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Benzo[*b*]fluoranthene	255	ref	-20	9.59	9.40	9.23	9.49
Benzo[*b*]fluoranthene	256	ref	-20	9.36	9.43	9.41	9.77
Benzo[*b*]fluoranthene	256	ref	-20	9.04	9.31	9.48	9.38
Benzo[*b*]fluoranthene	257	ref	-20	9.66	9.18	9.15	9.39
Benzo[*b*]fluoranthene	263	1	4	9.53	9.41	9.33	9.30
Benzo[*b*]fluoranthene	264	3	4	10.12	9.42	9.30	9.38
Benzo[*b*]fluoranthene	265	6	4	9.31	9.74	9.40	9.50
Benzo[*b*]fluoranthene	265	6	4	9.48	9.31	9.24	9.10
Benzo[*b*]fluoranthene	266	12	4	9.35	9.19	9.15	9.15
Benzo[*b*]fluoranthene	270	1	22	9.52	9.32	9.49	9.27
Benzo[*b*]fluoranthene	271	3	22	9.40	9.25	9.38	9.23
Benzo[*b*]fluoranthene	272	6	22	9.43	9.41	9.26	9.40
Benzo[*b*]fluoranthene	272	6	22	9.25	9.11	9.24	9.10
Benzo[*b*]fluoranthene	273	12	22	9.36	9.37	9.14	9.12
Benzo[*b*]fluoranthene	279	1	40	9.23		8.95	9.52
Benzo[*b*]fluoranthene	280	3	40	9.05	8.70	8.96	9.07
Benzo[*b*]fluoranthene	281	6	40	8.89	8.79	8.61	8.61
Benzo[*b*]fluoranthene	281	6	40	8.81	8.64	8.73	8.38
Benzo[*b*]fluoranthene	282	12	40	8.03	8.78	8.44	8.52
Benzo[*b*]fluoranthene	283	1	60	8.07	7.97	8.05	8.16
Benzo[*b*]fluoranthene	284	3	60	7.97	7.33	7.98	7.65

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Benzo[*k*]fluoranthene	255	ref	-20	3.09	3.07	3.10	3.11
Benzo[*k*]fluoranthene	256	ref	-20	3.08	3.02	3.12	3.14
Benzo[*k*]fluoranthene	256	ref	-20	3.04	3.04	3.09	3.10
Benzo[*k*]fluoranthene	257	ref	-20	3.14	3.01	3.03	3.09
Benzo[*k*]fluoranthene	263	1	4	3.27	3.06	3.10	3.10
Benzo[*k*]fluoranthene	264	3	4	3.27	3.17	3.13	3.11
Benzo[*k*]fluoranthene	265	6	4	3.15	3.15	3.11	3.12
Benzo[*k*]fluoranthene	265	6	4	3.08	3.08	3.03	3.07
Benzo[*k*]fluoranthene	266	12	4	3.05	3.05	3.03	3.05
Benzo[*k*]fluoranthene	270	1	22	3.13	3.07	3.17	3.05
Benzo[*k*]fluoranthene	271	3	22	3.15	3.06	3.17	3.06
Benzo[*k*]fluoranthene	272	6	22	3.15	3.37	3.12	3.11
Benzo[*k*]fluoranthene	272	6	22	3.00	3.05	3.06	3.05
Benzo[*k*]fluoranthene	273	12	22	3.07	3.05	3.04	3.08
Benzo[*k*]fluoranthene	279	1	40	3.12		3.05	3.08
Benzo[*k*]fluoranthene	280	3	40	3.07	3.02	3.03	3.05
Benzo[*k*]fluoranthene	281	6	40	3.04	3.06	2.98	2.97
Benzo[*k*]fluoranthene	281	6	40	2.95	2.95	2.95	2.96
Benzo[*k*]fluoranthene	282	12	40	2.74	2.93	2.91	2.93
Benzo[*k*]fluoranthene	283	1	60	2.84	3.00	2.96	2.97
Benzo[*k*]fluoranthene	284	3	60	2.93	2.71	2.83	2.83

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Benzo[*a*]pyrene	255	ref	-20	5.51	5.43	5.34	5.41
Benzo[*a*]pyrene	256	ref	-20	5.40	5.39	5.42	5.59
Benzo[*a*]pyrene	256	ref	-20	5.51	5.60	5.95	5.70
Benzo[*a*]pyrene	257	ref	-20	5.85	5.57	5.61	5.72
Benzo[*a*]pyrene	263	1	4	5.48	5.44	5.42	5.40
Benzo[*a*]pyrene	264	3	4	5.68	5.49	5.42	5.37
Benzo[*a*]pyrene	265	6	4	5.48	5.35	5.42	5.46
Benzo[*a*]pyrene	265	6	4	5.73	5.63	5.69	5.68
Benzo[*a*]pyrene	266	12	4	5.76	5.56	5.74	5.58
Benzo[*a*]pyrene	270	1	22	5.47	5.37	5.46	5.29
Benzo[*a*]pyrene	271	3	22	5.38	5.31	5.37	5.30
Benzo[*a*]pyrene	272	6	22	5.30	5.25	5.24	5.25
Benzo[*a*]pyrene	272	6	22	5.37	5.42	5.54	5.53
Benzo[*a*]pyrene	273	12	22	5.46	5.39	5.31	5.35
Benzo[*a*]pyrene	279	1	40	5.08		5.03	5.11
Benzo[*a*]pyrene	280	3	40	4.68	4.53	4.63	4.67
Benzo[*a*]pyrene	281	6	40	4.30	4.29	4.21	4.18
Benzo[*a*]pyrene	281	6	40	4.67	4.56	4.45	4.43
Benzo[*a*]pyrene	282	12	40	3.88	4.12	4.07	4.15
Benzo[*a*]pyrene	283	1	60	3.46	3.57	3.52	3.60
Benzo[*a*]pyrene	284	3	60	2.99	2.75	2.89	2.94

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Dibenz[*ah*]anthracene	255	ref	-20	0.50	0.48	0.53	0.49
Dibenz[*ah*]anthracene	256	ref	-20	0.49	0.53	0.47	5.59
Dibenz[*ah*]anthracene	256	ref	-20	0.56	0.63	0.63	0.59
Dibenz[*ah*]anthracene	257	ref	-20	0.61	0.63	0.68	0.59
Dibenz[*ah*]anthracene	263	1	4	0.52	0.50	0.49	0.52
Dibenz[*ah*]anthracene	264	3	4	0.56	0.50	0.49	0.48
Dibenz[*ah*]anthracene	265	6	4	0.59	0.54	0.49	0.48
Dibenz[*ah*]anthracene	265	6	4	0.64	0.62	0.59	0.57
Dibenz[*ah*]anthracene	266	12	4	0.57	0.60	0.57	0.56
Dibenz[*ah*]anthracene	270	1	22	0.58	0.50	0.53	0.47
Dibenz[*ah*]anthracene	271	3	22	0.55	0.53	0.52	0.48
Dibenz[*ah*]anthracene	272	6	22	0.55	0.51	0.47	0.52
Dibenz[*ah*]anthracene	272	6	22	0.57	0.64	0.59	0.57
Dibenz[*ah*]anthracene	273	12	22	0.56	0.61	0.59	0.57
Dibenz[*ah*]anthracene	279	1	40	0.56		0.48	0.48
Dibenz[*ah*]anthracene	280	3	40	0.53	0.52	0.48	0.48
Dibenz[*ah*]anthracene	281	6	40	0.53	0.52	0.51	0.49
Dibenz[*ah*]anthracene	281	6	40	0.57	0.60	0.60	0.54
Dibenz[*ah*]anthracene	282	12	40	0.50	0.66	0.57	0.57
Dibenz[*ah*]anthracene	283	1	60	0.42	0.49	0.44	0.46
Dibenz[*ah*]anthracene	284	3	60	0.47	0.45	0.45	0.44

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Benzo[*ghi*]perylene	255	ref	-20	4.25	4.27	4.20	4.20
Benzo[*ghi*]perylene	256	ref	-20	4.15	4.21	4.19	4.30
Benzo[*ghi*]perylene	256	ref	-20	4.55	4.42	4.57	4.91
Benzo[*ghi*]perylene	257	ref	-20	4.68	4.86	4.86	4.54
Benzo[*ghi*]perylene	263	1	4	4.15	4.17	4.24	4.15
Benzo[*ghi*]perylene	264	3	4	4.25	4.24	4.26	4.20
Benzo[*ghi*]perylene	265	6	4	4.06	4.24	4.29	4.25
Benzo[*ghi*]perylene	265	6	4	4.72	4.96	4.82	4.94
Benzo[*ghi*]perylene	266	12	4	4.79	4.84	4.89	4.77
Benzo[*ghi*]perylene	270	1	22	4.16	4.26	4.31	4.11
Benzo[*ghi*]perylene	271	3	22	4.12	4.25	4.30	4.13
Benzo[*ghi*]perylene	272	6	22	4.19	4.28	4.22	4.26
Benzo[*ghi*]perylene	272	6	22	4.44	4.79	4.81	4.79
Benzo[*ghi*]perylene	273	12	22	4.87	4.46	4.81	4.84
Benzo[*ghi*]perylene	279	1	40	4.10		4.20	4.28
Benzo[*ghi*]perylene	280	3	40	3.98	4.12	4.10	4.18
Benzo[*ghi*]perylene	281	6	40	4.03	4.20	4.05	4.03
Benzo[*ghi*]perylene	281	6	40	4.90	4.71	4.29	4.64
Benzo[*ghi*]perylene	282	12	40	4.41	4.27	4.58	4.72
Benzo[*ghi*]perylene	283	1	60	3.75	4.12	4.02	4.08
Benzo[*ghi*]perylene	284	3	60	3.91	3.78	3.90	3.83

Stability study	Bottle	t[Months]	T[°C]	Replicates			
				-1	-2	-3	-4
Indeno[123-*cd*]pyrene	255	ref	-20	6.61	6.48	6.30	6.59
Indeno[123-*cd*]pyrene	256	ref	-20	6.57	6.59	6.63	6.83
Indeno[123-*cd*]pyrene	256	ref	-20	6.39	6.53	6.62	6.78
Indeno[123-*cd*]pyrene	257	ref	-20	6.93	6.75	6.63	6.79
Indeno[123-*cd*]pyrene	263	1	4	6.80	6.64	6.55	6.56
Indeno[123-*cd*]pyrene	264	3	4	7.10	6.71	6.70	6.52
Indeno[123-*cd*]pyrene	265	6	4	6.51	6.28	6.45	6.53
Indeno[123-*cd*]pyrene	265	6	4	6.72	6.88	6.53	6.80
Indeno[123-*cd*]pyrene	266	12	4	6.91	6.57	6.69	6.91
Indeno[123-*cd*]pyrene	270	1	22	6.65	6.58	6.63	6.41
Indeno[123-*cd*]pyrene	271	3	22	6.60	6.47	6.67	6.70
Indeno[123-*cd*]pyrene	272	6	22	6.77	6.51	6.54	6.56
Indeno[123-*cd*]pyrene	272	6	22	6.58	6.78	6.69	6.63
Indeno[123-*cd*]pyrene	273	12	22	6.80	7.01	6.66	6.97
Indeno[123-*cd*]pyrene	279	1	40	6.64		6.61	6.86
Indeno[123-*cd*]pyrene	280	3	40	6.39	6.28	6.50	6.64
Indeno[123-*cd*]pyrene	281	6	40	6.59	6.48	6.52	6.32
Indeno[123-*cd*]pyrene	281	6	40	6.56	6.51	6.68	6.38
Indeno[123-*cd*]pyrene	282	12	40	6.08	6.42	6.55	6.33
Indeno[123-*cd*]pyrene	283	1	60	5.94	6.20	6.18	6.43
Indeno[123-*cd*]pyrene	284	3	60	6.14	5.69	6.39	6.21

B.3 Certification study

Naphthalene

Laboratory	Replicate determinations (mg kg^{-1})					
1	2.073	2.068	2.216	2.447	2.488	2.431
2	2.415	2.190	2.016	1.621	1.798	1.674
3	2.925	2.958	2.991	2.763	2.908	2.903
4	2.788	2.793	2.736	2.716	2.690	2.760
5	2.054	2.202	2.017	2.042	2.001	2.005
6	2.774	2.687	2.746	2.706	2.899	2.664

Acenaphthene

Laboratory	Replicate determinations (mg kg^{-1})					
1	0.702	0.725	0.751	0.634	0.647	0.581
2	0.771	0.794	0.751	0.738	0.761	0.732
3	0.810	0.818	0.841	0.814	0.808	0.807
4	0.774	0.770	0.759	0.785	0.758	0.786
6	0.736	0.732	0.731	0.743	0.744	0.738

Fluorene

Laboratory	Replicate determinations (mg kg^{-1})					
1	1.056	0.988	1.030	1.014	1.049	1.041
2	1.270	1.375	1.202	1.197	1.239	1.182
3	1.129	1.284	1.090	1.133	1.185	1.180
4	1.139	1.123	1.095	1.125	1.074	1.080
5	1.137	1.160	1.066	1.184	1.097	1.111
6	1.168	1.162	1.163	1.167	1.167	1.162

Phenanthrene

Laboratory	Replicate determinations (mg kg^{-1})					
1	11.958	11.717	11.677	10.474	10.990	10.065
2	12.868	12.454	12.546	12.044	12.163	12.335
3	12.935	12.799	12.165	12.741	12.701	12.728
4	11.751	11.440	11.117	11.413	10.964	11.016
5	12.664	12.606	12.562	12.915	12.555	12.560
6	11.951	11.900	11.922	11.991	11.905	11.927

Anthracene

Laboratory	Replicate determinations (mg kg^{-1})					
1	1.358	1.391	1.379	1.349	1.333	1.348
2	1.540	1.542	1.405	1.376	1.424	1.339
3	1.833	1.825	1.852	1.761	1.832	1.778
4	1.048	1.032	1.024	1.054	1.005	1.018
5	1.244	1.204	1.298	1.300	1.322	1.279
6	1.528	1.529	1.530	1.531	1.506	1.495

Fluoranthene

Laboratory	Replicate determinations (mg kg^{-1})					
1	11.774	11.663	11.216	11.750	12.245	10.949
2	12.877	12.800	12.117	12.654	12.935	12.393
3	13.824	13.679	13.394	13.590	13.622	14.143
4	13.209	13.203	12.726	13.256	12.637	12.885
5	13.903	14.077	13.072	14.185	12.962	13.926
6	12.804	12.808	12.805	12.855	12.816	12.803

Pyrene

Laboratory	Replicate determinations (mg kg^{-1})					
1	9.664	9.563	9.306	9.052	9.881	9.401
2	10.241	10.398	9.267	10.108	10.129	9.814
3	9.719	9.694	9.477	9.550	9.649	9.447
4	9.948	9.843	9.467	9.788	9.603	9.720
5	8.945	8.687	9.088	9.402	9.701	9.627
6	9.305	9.247	9.310	9.400	9.412	9.388

Benzo[*a*]anthracene

Laboratory	Replicate determinations (mg kg^{-1})					
1	5.298	5.243	5.055	5.022	5.423	5.019
3	5.776	5.602	5.251	5.551	5.630	5.597
4	5.805	5.903	5.598	5.936	5.588	6.046
5	6.803	7.019	5.867	6.205	5.807	5.751
6	5.217	5.242	5.262	5.325	5.428	5.382

Chrysene

Laboratory	Replicate determinations (mg kg^{-1})					
1	4.033	4.210	4.067	3.992	4.32	3.961
2	6.410	6.022	5.388	5.607	5.532	5.450
3	5.751	5.358	5.122	5.047	5.465	5.443
4	6.518	6.559	6.314	6.649	6.356	7.238
5	4.969	4.940	5.111	5.098	5.099	4.968
6	4.770	4.659	4.662	4.759	4.732	4.711

Benzo[*b*]fluoranthene

Laboratory	Replicate determinations (mg kg^{-1})					
1	8.198	8.047	8.810	7.925	8.072	7.568
2	8.330	8.267	7.919	8.250	7.913	8.097
3	5.964	5.947	5.893	6.050	6.072	5.592
4	6.886	6.447	6.263	6.243	6.294	6.101
5	6.845	7.042	7.926	7.557	7.438	7.274
6	9.076	9.049	9.036	9.059	8.971	8.918

Benzo[*k*]fluoranthene

Laboratory	Replicate determinations (mg kg^{-1})					
1	3.220	3.619	3.267	3.274	3.117	3.287
2	3.889	6.179	3.847	4.594	4.774	3.692
3	3.384	3.335	3.136	3.287	3.268	3.182
4	4.263	6.296	5.949	6.119	5.934	7.462
5	2.988	3.085	2.959	3.098	2.982	3.015
6	3.242	3.227	3.232	3.253	3.243	3.275

Benzo[*a*]pyrene

Laboratory	Replicate determinations (mg kg^{-1})					
1	4.940	5.072	5.096	4.956	4.881	3.879
2	4.470	4.567	4.062	4.473	4.217	3.822
3	3.701	3.645	4.256	3.608	3.685	3.481
4	5.225	5.366	5.086	5.386	5.232	5.493
5	5.694	6.025	5.741	5.907	5.644	5.437
6	5.341	5.272	5.293	5.285	5.277	5.286

Dibenz[*ah*]anthracene

Laboratory	Replicate determinations (mg kg^{-1})					
2	1.168	1.193	1.080	1.285	1.285	1.099
3	1.438	1.464	1.264	1.470	1.461	1.265
4	0.894	0.888	0.883	0.922	0.892	1.013
5	1.631	1.784	1.672	1.792	1.730	1.630
6	0.566	0.517	0.534	0.550	0.506	0.505

Benzo[*ghi*]perylene

Laboratory	Replicate determinations (mg kg^{-1})					
1	4.311	4.368	4.450	4.069	4.0367	4.433
3	4.135	4.168	4.485	4.193	4.261	4.128
4	5.143	5.295	5.004	5.171	5.044	5.158
5	4.752	4.954	4.784	4.999	4.850	4.425
6	4.152	4.166	4.161	4.199	4.274	4.226

Indeno[123*cd*]pyrene

Laboratory	Replicate determinations (mg kg^{-1})					
1	6.157	5.620	5.550	6.004	5.017	5.95
2	4.470	3.969	3.785	4.360	4.473	4.314
3	4.215	4.112	4.524	4.147	4.163	4.412
4	5.058	4.927	4.725	4.840	4.720	5.273
5	5.654	5.033	5.057	5.015	5.337	5.029
6	7.306	7.011	7.042	6.983	6.993	7.054