CCQM-K184

Low-Polarity Analytes in Abiotic Matrix: Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment

Key Comparison
Track A

Final Report
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SUMMARY

The CCQM-K184 comparison, undertaken with a parallel pilot study CCQM-P235 was coordinated by NIM on behalf of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) Organic Analysis Working Group (OAWG). This comparison was classified as a Track A comparison.

Polycyclic aromatic hydrocarbons (PAHs) are a class of carcinogenic organic compounds which can be introduced to the aquatic environments by various processes: incomplete combustion of fossil fuels and organic material and following dispersal via long-range transport (pyrolytic origin), spillage of crude oil and its refined products (petrogenic/fossil origin), and post-depositional transformation of biogenic precursors (diagenetic origin). Due to their hydrophobic nature, PAHs tend to accumulate in sediments and are considered critical indicators of environmental pollution. They pose significant ecological and human health risks as many are classified as carcinogens, mutagens, and teratogens. Accurate measurement of PAHs is essential to support global environmental monitoring efforts and regulatory frameworks such as Sediment Quality Guidelines. Evidence of successful participation in formal, relevant international comparisons is needed to document measurement capability claims (CMCs) made by national metrology institutes (NMIs) and designated institutes (DIs). To enable NMIs and DIs to update or establish, the CCQM Organic Analysis Working Group sponsored CCQM-K184 "Low-Polarity Analytes in Abiotic Matrix: Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment".

Seventeen National Metrology Institutes (NMIs) and Designated Institutes (DIs) participated in CCQM-K184 Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment. Participants were requested to evaluate the mass fractions of fluoranthene, Benzo[*a*]pyrene, Benzo[*ghi*]perylene, and optionally phenanthrene in a river sediment sample collected from a tributary of the Taizi River in China.

Successful participation in CCQM-K184 demonstrates the following measurement capabilities in determining mass fraction of organic compounds, with molecular mass of 170 g/mol to 500 g/mol, having low polarity pKow < -2, in mass fraction range from 100 µg/kg to 1,000,000 µg/kg in an abiotic dried matrix such as sediment: (i) value assignment of primary reference standards; (ii) value assignment of calibration solutions; (iii) extraction of analyte of interest from the matrix; (iv) clean-up and separation of analyte of interest from other interfering matrix or extract components; (v) separation and quantification using techniques such as GC-IDMS, GC-IDMS/MS, and HPLC-FLD.

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ACRONYMS

ASE	accelerated solvent extraction
BAM	Bundesanstalt fuer Materialforschung und –pruefung, NMI: Germany
B*a*P	benzo[*a*]pyrene
B*ghi*P	benzo[*ghi*]perylene
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CENAM	Centro Nacional de Metrologia, NMI: Mexico
CIL	Cambridge Isotope Laboratories, Inc.
CMC	Calibration and Measurement Capability
CRM	certified reference material
CV	coefficient of variation, expressed in %: $\mathrm{CV} = 100 \cdot \mathrm{s}/\bar{x}$
DI	designated institute
DoE	degrees of equivalence
Flu	fluoranthene
GC-GC	two-dimensional gas chromatography
GC-HRMS	gas chromatography with high-resolution mass spectrometry detection
GC-IT-MS	gas chromatography with ion trap mass spectrometry detection
GC-MS	gas chromatography with mass spectrometry detection
GC-MS/MS	gas chromatography with tandem mass spectrometry detection
GC-TOFMS	gas chromatography with time-of-flight mass spectrometry detection
GLHK	Government Laboratory of the Hong Kong SAR, DI: Hong Kong Special Administrative Region (HKSAR), China
GPC	gel permeation chromatography
HPLC-DAD	high pressure liquid chromatography with diode array detection
IAEA	International Atomic Energy Agency Marine Environment Laboratories (IAEA),
ID	isotope dilution
IH	Instituto Hidrográfico, NMI: Portugal
INM	Instituto Nacional de Metrología de Colombia, NMI: Colombia
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnologia, NMI: Brazil
INTI	Instituto Nacional de Tecnología Industrial, NMI: Argentina
KC	Key Comparison
KCRV	Key Comparison Reference Value
KRISS	Korea Research Institute of Standards and Science, NMI: Republic of Korea
LC	liquid chromatography
LGC	Laboratory of the Government Chemist, NMI: United Kingdom
LNE	Laboratoire National de Métrologie et d'Essais, NMI: France
MRM	multiple reaction monitoring
METAS	Federal Institute of Metrology, NMI: Switzerland
NIM	National Institute of Metrology, NMI: China
NIMT	National Institute of Metrology, Thailand, NMI: Thailand
NIST	National Institute of Standards and Technology, NMI: USA
NMI	National metrology institute
NMIA	National Measurement Institute Australia, NMI: Australia
NMR	nuclear magnetic resonance spectroscopy
OAWG	Organic Analysis Working Group
pK_{ow}	logarithm of the octanol-water partition coefficient
Phe	Phenanthrene

QuEChERS	“Quick, Easy, Cheap, Effective, Rugged, Safe” liquid/solid extraction
SIM	selected ion monitoring
SPE	solid phase extraction
SRM	Standard Reference Material, a NIST CRM
UME	National Metrology Institute of Turkey, NMI: Turkey
VNIIM	D.I. Mendeleyev Institute for Metrology, NMI: Russia

SYMBOLS

d_i	absolute degree of equivalence: x_i - KCRV
$\%d_\mathrm{i}$	relative degree of equivalence: $100 \cdot d_\mathrm{i}$/KCRV
k	coverage factor: $\mathrm{U(x)} = k \cdot u(\mathrm{x})$
n	number of quantity values in a series of quantity values
s	standard deviation of a series of quantity values: $s = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)}$
$u(x_i)$	standard uncertainty of quantity value x_i
$U(x)$	expanded uncertainty
x	a quantity value
x_i	the i^{th} member of a series of quantity values
$\bar{x}$	mean of a series of quantity values: $\bar{x} = \sum_{i=1}^{n} x_i/n$

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of carcinogenic organic compounds composed of two or more fused aromatic rings. They are present in fossil fuels and further generated from the incomplete combustion of organic matter at high-temperatures from multiple sources, including industrial emissions, motor vehicle emissions, tobacco smoke, and other human activities [1]. They have a wide existence in the entire ecosystem especially the aquatic environment [2]. PAHs may accumulate at high levels in sediments because of their hydrophobic nature [3]. Research showed that many PAHs are widely classified as carcinogens, mutagens, and teratogens [4]. Analysis of PAHs in sediments is particularly important because they are considered pollution indicators, since they present a view of the spatial distribution of pollutants. Furthermore, many Sediment Quality Guidelines for individual and total PAH were compiled [5]. The concentration of PAHs in sediment is geographically variable and influenced by human activities, PAH levels in sediment have been found to vary from 10 to 1,000,000 µg/kg [6-10].

At the CCQM OAWG meeting held in April 2023, it was agreed to have a comparison on the determination of polycyclic aromatic hydrocarbons in sediment as a Track A study. This comparison meets the OAWG strategy document for 2021-2030 for services in support of the environmental sector, in the category of "analyte in abiotic matrix". Participation in CCQM-K184 will demonstrate the following measurement capabilities for the determination of low-polarity contaminants, with molecular mass of 170 g/mol to 500 g/mol, having Low polarity $pK_{ow} < -2$, in mass fraction range from 100 [µg/kg] to 1000000 [µg/kg] in abiotic dried matrix.

As a Track A comparison, it was expected that all NMIs or DIs who had or expected to have services related to the capabilities related to the “How far does the light shine” statement for this key comparison would participate.

TIMELINE

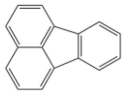
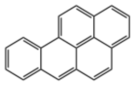
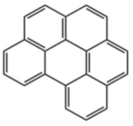
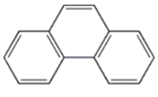
Table 1. Timeline for CCQM-K184

Date	Action
Dec. 2022	Proposed to CCQM
Jul. 2023	Draft protocol presented to OAWG as potential Track A Key Comparison
Aug. 2023	OAWG authorized [CCQM-K184] as a Track A Key Comparison; protocol approved
Aug. 2023	Call for participation to OAWG members
Oct. 2023	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
Jun 2024	Results due to coordinating laboratory
March 2025	Draft A report
Oct. 2025	Draft B report

MEASURANDS

The minimum reporting requirements for participants in CCQM-K184 are the mass fractions (on a dry mass basis) of fluoranthene (Flu), benzo[*a*]pyrene (B*a*P), and benzo[*ghi*]perylene (B*ghi*P). Phenanthrene (Phe), a volatile three-ring PAH, has been selected as an optional analyte for the CCQM-K184 measurands. This selection supports claims covering the volatility and lower molecular mass range of PAHs commonly quantified in environmental samples. Table 1 below provides detailed information on these compounds.

Table 2. Selected PAHs as study measurands for CCQM-K184

Compound	**CAS**	**Structural Formula**	**Chemical Formula (MW g/mol)**	**pK_{ow}**
Fluoranthene	206-44-0		$C_{16}H_{10}$ (202.25)	-5.16 [11]
Benzo[*a*]pyrene	50-32-8		$C_{20}H_{12}$ (252.31)	-6.13 [12]
Benzo[*ghi*]perylene	191-24-2		$C_{22}H_{12}$ (276.33)	-6.63 [13]
Phenanthrene	85-01-8		$C_{14}H_{10}$ (178.23)	-4.46 [14]

STUDY MATERIALS

The study material is river sediment collected at 41°70'55.79" N, 123°19'40.76" E from the tributary of Taizi River in Liaoning Province, China. Sediment in this river was naturally contaminated by industrial emissions from several heavy industrial plants over decades. The material underwent a series of processing steps: air-drying, sieving (178 µm), γ-irradiation and homogenization. The final powdered sediment was dispensed in portions of about 10 g into 30 mL amber glass jars with screw caps, and then vacuum sealed within plastic-lined aluminum bags.

Each participant received 3 samples of 10 g each. The recommended minimum sample amount for analysis is at least 1.0 g. The samples are to be stored at 20°C or below; under the absence of light. Before opening, the samples should be allowed to equilibrate to room temperature. Measurement results were to be reported on a dry-mass basis. Dry mass correction should be carried out simultaneously as the test sample portion is to be analyzed in the same package of the sample aliquot in which PAH measurements are performed.

Dry Mass Determination

A minimum of three subsamples (recommended sample size of 1 g each) of the sediment should be dried in an oven at (105 ± 2) °C until constant mass is reached. The correction used for dry-mass conversion shall be reported.

Methods

The study will require extraction, clean-up, analytical separation, and selective detection of the analytes in sediment. Participants are anticipated to perform measurements with appropriately validated methods with demonstrated metrological traceability.

Homogeneity Assessment of Study Material

The homogeneity of the sediment material was assessed by analyzing duplicate 1.0 g subsamples from each of 12 jars of sediment. The material was extracted by accelerated solvent extraction (ASE) with hexane/acetone (1:1 volume fraction) at 160 ºC for 6 cycles. The extracts were concentrated to 1 mL. Then 0.5 mL supernatant was eluted through a silica gel SPE cartridge with dichloromethane /hexane (3:7 volume fraction) and the eluent was concentrated to 0.5 mL. The samples were analyzed by GC-MS; GBW08736 Aromatic Hydrocarbons in acetonitrile was used as a calibrant. Based on the measurements from the homogeneity assessment, the target mass fraction ranges were as follows: 400 µg/kg - 4000 µg/kg.

The results of the homogeneity assessment reported as the coefficient of variation (CV) for the 4 target PAHs are listed in Table 3. One-way ANOVA with F-test in accordance with the requirements as stipulated in ISO Guide 35 was used to test whether there were significant between-packet differences in the concentration of the measurand (Table 3). The estimated between-packet standard deviations proved to be smaller than within-group standard deviations. The value of the relevant F-test ratios, F, is small, and P-value is larger than the usual critical 0.05 confidence level, which indicates that the inhomogeneity was not statistically significant.

Table 3. Results of the homogeneity assessment for four PAHs in sediment sample

ANOVA Estimate	**Fluoranthene**	**Benzo[*a*]pyrene**	**Benzo[*ghi*]perylene**	**Phenanthrene**
Within-packet, CV_{wth}:	1.50%	1.52%	1.93%	1.68%
Between-packet, CV_{btw}:	2.31%	2.22%	2.46%	1.88%
Total analytical variability, CV:	1.93%	1.89%	2.20%	1.78%
p-value（Probability of falsely rejecting the hypothesis that all samples have the same concentration）:	0.076	0.107	0.211	0.355

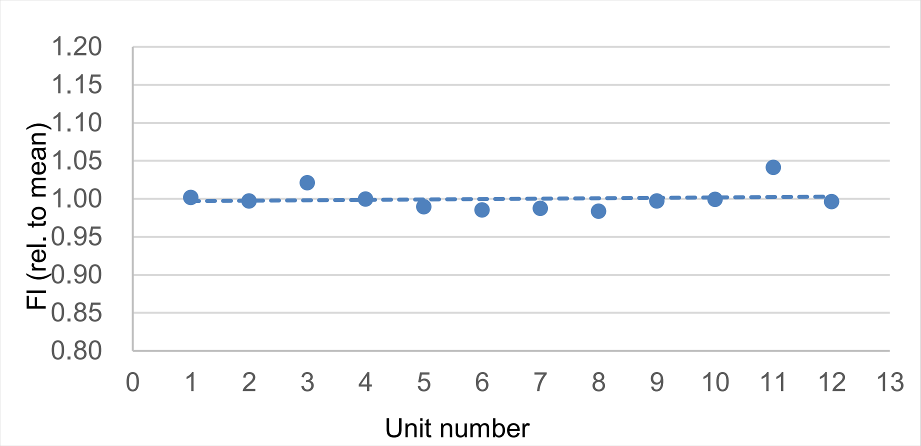


Figure 1: Homogeneity of Fluoranthene in sediment

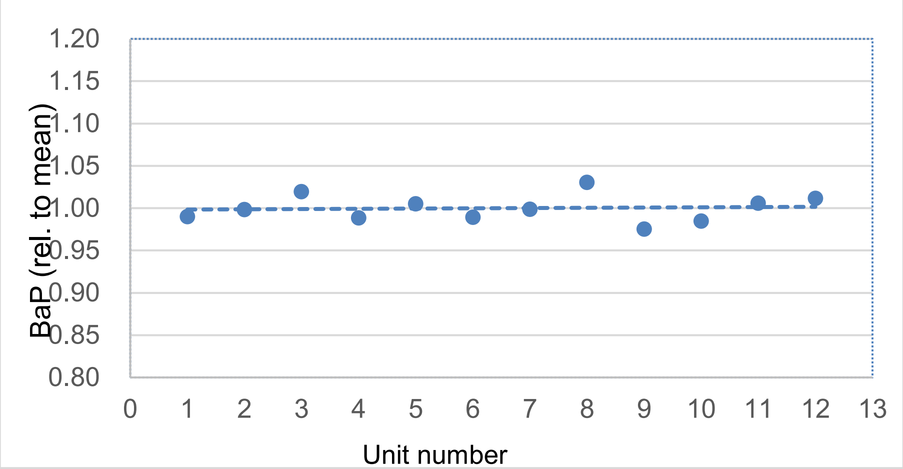


Figure 2: Homogeneity of Benzo[*a*]pyrene in sediment

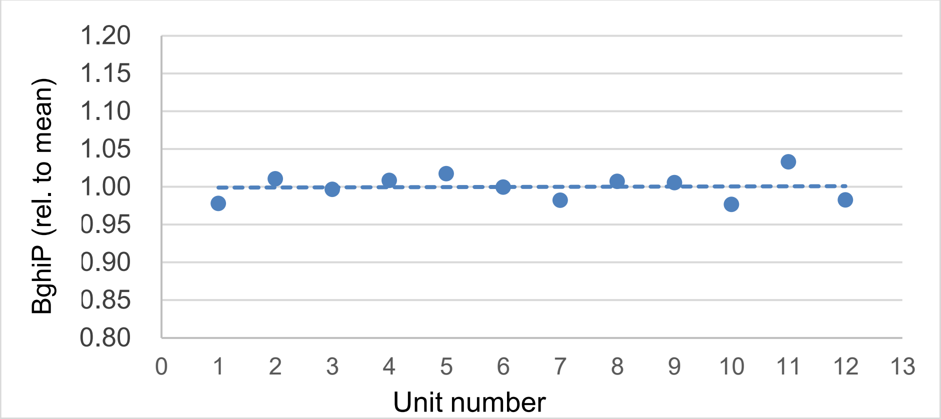


Figure 3: Homogeneity of Benzo[*ghi*]perylene in sediment

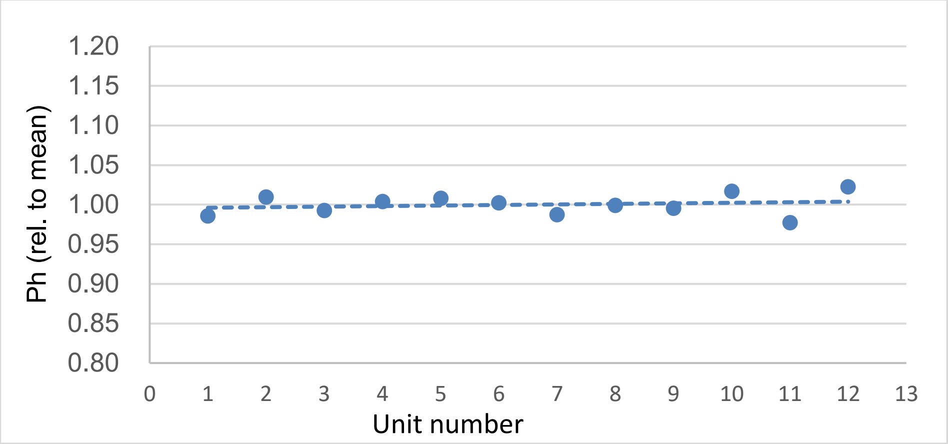


Figure 4: Homogeneity of phenanthrene in sediment

Stability Assessment of the Study Materials

Long-term stability assessment was conducted at two storage conditions: -18 °C, and 20 °C. Two samples were selected randomly at the storage condition of -18 °C for testing at 0, 6, 12, 24, and 36 months and analyzed in duplicate by GC-IDMS. Similarly, stability studies were performed for 4 time points (0, 1, 3 and 5 months) at a temperature of +20 °C. The trend graphs of stability are shown in Figures 5 and 6. The trend-analysis technique proposed by ISO Guide 35 was applied to assess the stability. The effect of time on the stability was evaluated using a linear approximation model by fitting linear regression lines to the data set ($Y=\beta_0-\beta_1X$). The statistical results indicated that no significant trend at 95% confidence level was detected as the absolute values of β_1 (ie., the slope of the regression line) were smaller than the critical values of β_1, which were the uncertainty associated with the slope of the regression line for the stability times the respective Student's t-factor. Hence, the instability of the material was insignificant at the study temperature over the study period.

Short-term stability was not performed for this sediment material. Based on previous transportation conditions for CCQM comparison samples of PAHs in matrix, the sample is inferred to be stable during transportation.

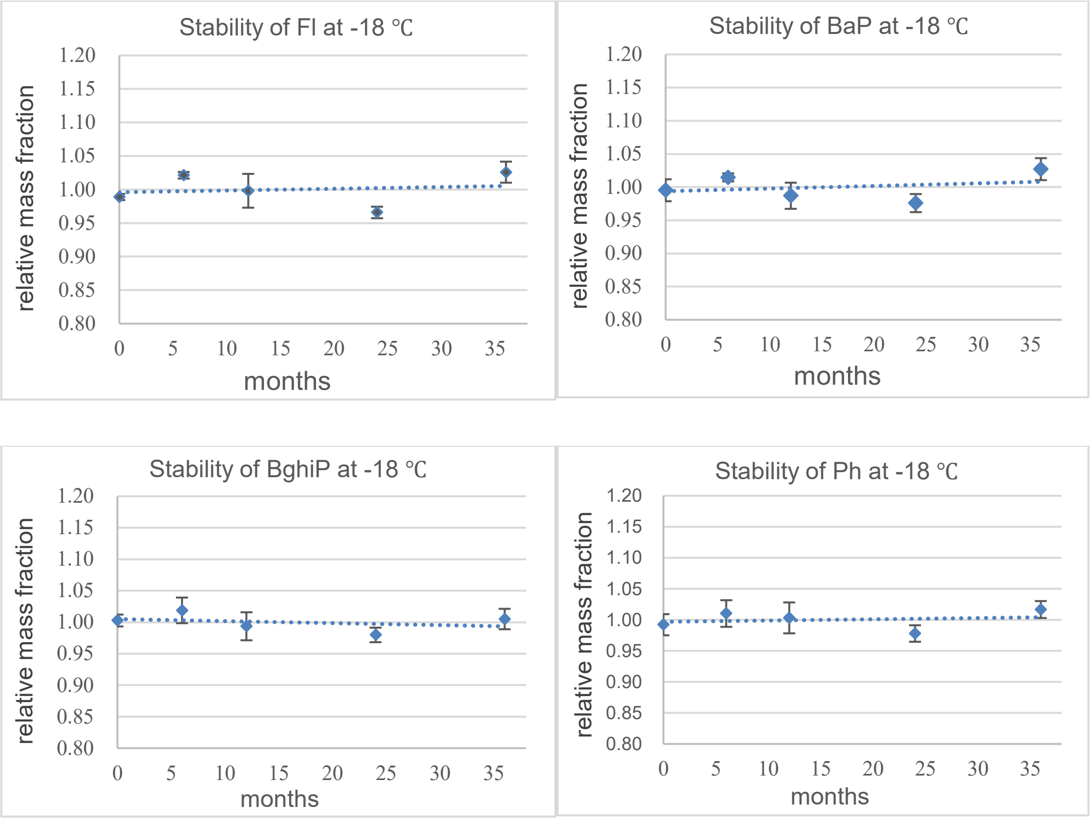
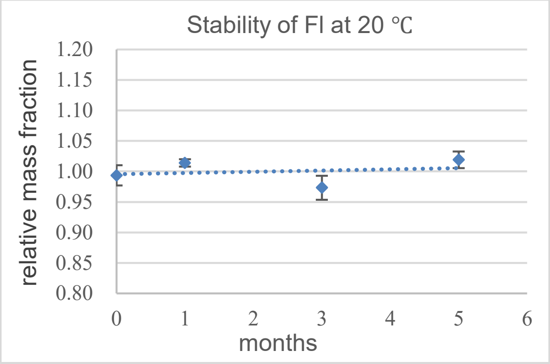
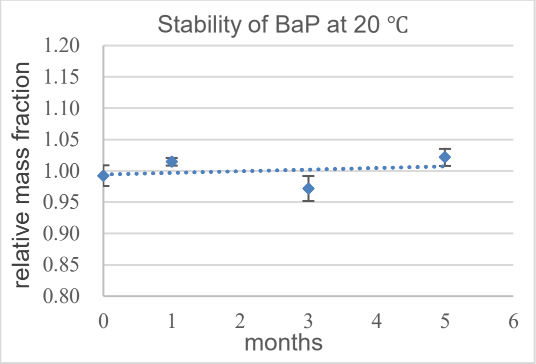


Figure 5: Long-term stability of 4 PAHs at -18 °C





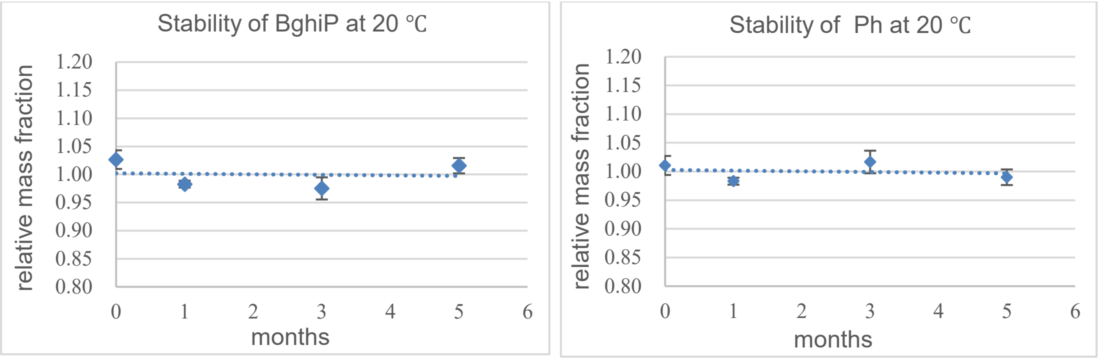


Figure 6: Long-term stability of 4 PAHs at 20°C

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was distributed in Aug-2023 with the intent to distribute samples on 31st Oct-2023. Due to customs issues, the last set of materials was delivered on 3rd Dec-2023. Because of these delays and some issues encountered by some participating laboratories during the comparison experiment, the deadline for submission of results was postponed from 31 March to 31st June 2024. This extension enabled the results to be discussed at the Fall 2024 OAWG meeting on 23rd October 2024. See Table 1 for the study timeline. Appendix A reproduces the Call for Participation; Appendix B reproduces the study Protocol.

Table 4 lists the institutions that registered for CCQM-K184.

Table 4. Institutions Registered for CCQM-K184

NMI or DI	Country	Contact
KRISS	South Korea	Song-Yee Baek, Kihwan Choi
LNE	France	Béatrice LALERE and Carine FALLOT
NIST	America	Catherine Rimmer, Alix Rodowa
CENAM	Mexican	Mariana Arce Osuna
VNIIM	Russia	Anatoliy I. Krylov, Alena Yu. Mikheeva
IH	Portugal	Carla Palma
INM	Colombia	Mr Julian Herney Pulido Vargas
INMETRO	Brazil	Eliane Cristina Pires do Rego
NIM	China	Tang Hua, HanYaxin
NIMT	Thailand	Ms. Nittaya Sudsiri
GLHK	Hong Kong, China	Yee-lok WONG, Hei-man Vincent TANG
BAM	Germany	Roland Becker
NMIA	Australia	Mark Lewin
INTI	Argentina	Julián Gigena
TUBITAK_UME	Turkey	Mine Bilsel, Taner Gokcen
METAS	Switzerland	Simon Lobsiger
LGC	United Kingdom	Chris Hopley

The reporting requirements for the CCQM-K184 Comparison on PAHs in sediment stipulate that participants must analyze two subsamples from the provided river sediment material and report the overall mean mass fraction of the target PAHs (fluoranthene, benzo[*a*]pyrene, and benzo[*ghi*]perylene) in units of ng/g (µg/kg) on a dry mass basis. The results should include the standard uncertainty (u) and the expanded uncertainty (U) at the 95% confidence level, calculated with a coverage factor (k = 2). Calibration must be performed using certified reference materials (CRMs) with traceability ensured through their certification. The uncertainty budget should detail contributions from sampling, extraction, clean-up, instrumental calibration, and calculation errors. Participants are required to provide a comprehensive description of their analytical procedure, including extraction methods, clean-up steps, analytical conditions, and quantification approaches, as well as details on the purity and assessment of calibration and internal standards used.

RESULTS

Participants were requested to report a single estimate of the mass fraction (µg/kg) for the 3 or 4 target PAHs based on measurements for 3 subsamples from each of two sample unites of the sediment (i.e., three independent replicates) on a dry-mass basis. The moisture content of the sample was to be determined using the described protocol, then reported, and applied to the reported mass fractions.

In addition to the quantitative results, participants were to describe their extraction, clean-up, column, and analytical conditions, quantification approach, calibration standards, the internal standards, any quality control materials, the number of replicates, quantification approach for mass fractions, estimation of measurement uncertainty and the Core Competencies they felt were demonstrated in this study. Appendices C, D, and E reproduce the several report forms.

CCQM-K184 results were received from 17 of the 17 institutions that received samples. After the comparison results discussion meeting, IH withdrew all their comparison results due to issues with the traceability of the calibration materials. INM and INTI withdrew all their comparison results due to technical problems. NIMT withdrew the reported data on benzo[ghi]perylene, LGC withdrew the reported results on benzo[a]pyrene and benzo[ghi]perylene, and CENAM withdrew the results for phenanthrene and fluoranthene due to technical problems.

Brief descriptions of the analytical methods used by the participants, including sample preparation, analytical technique, calibrants, and quantification approach are summarized in Appendix F. The participants' approaches to estimating uncertainty are provided in Appendix G. The participants' results, as reported, are provided in Appendix H.

Calibration Materials Used by Participants

Participants established the metrological traceability of their results using certified reference materials (CRMs) with stated traceability and/or commercially available high-purity materials for which they determined the purity. Table 5 lists the calibration standards used by the participants in CCQM-K184.

Table 5. Calibrants used by the participants

Participant	Calibrants' Source	Determined purity or certified value where not assessed in house	Purity assessment	Evidence of competence
KRISS	sigma-aldrich Supelco Accustandard, neat	Flu: 98.80 ± 0.13 % BaP: 98.76 ± 0.50 % BghiP: 97.59 ± 0.35 %	Purity was assayed by KRISS with mass-balance method. The purities of the primary materials were determined following protocols maintained in KRISS. GC-FID was used for the analysis of structurally related impurities, Karl-Fischer Coulometry for water content, thermogravimetric analysis for non-volatile impurities, and headspace-GC/MS for residual solvents.	Purity assay was provided through participation of CCQM - K55a, K55b, 55c, and 55d. Preparation and verification of the calibration was verified through participation of CCQM-K131.
LNE	NIST (SRM 2260a) Solution SRM	Phe:(11.57 ± 0.12) µg/g Flu: (8.324±0.087) µg/g BaP: (4.71 ± 0.17) µg/g BghiP:(5.669 ± 0.069) µg/g	N/A	N/A
NIST	NIST (SRM 2260a) Solution SRM	Phe:(11.57 ± 0.12) µg/g Flu: (8.324±0.087) µg/g BaP: (4.71 ± 0.17) µg/g BghiP:(5.669 ± 0.069) µg/g	N/A	N/A
CENAM	Aldrich Chem Aldrich Chem Supelco Ultra scientific neat	Phe: (992.5 ± 4.4) mg/g Flu: (986.5 ± 3.8) mg/g BaP (975.8 ± 4.3) mg/g BghiP (989.5 ± 6.4) mg/g	Purity was assessed by mass balance approach: GC-FID with two different columns and water content by Karl Fischer titration	Purity value assignment was supported through participation in CCQM-K55a, K55b, K55c and K55d. Preparation and verification of the calibration solution

				was supported through participation in CCQM-K131.
VNIIM	NIST (SRM 1647f) Solution SRM	Phe:(4.57± 0.05) mg/kg Flu: (9.71± 0.16) mg/kg BaP:(6.22±0.11) mg/kg BghiP:(4.64±0.12) mg/kg	N/A	N/A
IH	Dr Ehrenstorfer, Solution Mixture	Phe: (2000±110) µg/mL Flu: (2008±100) µg/mL BaP: (1999±130) µg/mL BghiP: (2000±130) µg/mL	-	-
INM	NIST (SRM 1647f) Solution SRM	Phe:(4.57±0.05) mg/kg Flu: (9.71±0.16) mg/kg BaP:(6.22±0.11) mg/kg BghiP:(4.64 ± 0.12) mg/kg	N/A	N/A
INMETRO	Sigma-Aldrich Sigma-Aldrich Dr. Ehrenstorfer Sigma-Aldrich，neat	Phe: (996.0 ± 2.8) mg/g Flu: (993.8 ± 1.7) mg/g BaP: (971.6 ± 3.8) mg/g BghiP: (980.1 ± 2.0) mg/g	qNMR Purity value assignment was performed by qNMR using the following Inmetro's internal standards: CRM 8792 - Maleic acid, for Phenanthrene and Fluoranthene; CRM 8783 - Dimethyl sulfone, for Benzo[*a*]pyrene; and CRM 8784 - Dimethyl terephthalate, for Benzo[*ghi*]perylene	Broad CMC for “Mass fraction purity of organic compounds of low polarity (pKOW < -2) with molar mass below 500 g/mol” and “Mass fraction purity of organic compounds of high polarity (pKOW > -2) with molar mass below 500 g/mol”. Individual CMC for Dimethyl terephthalate CRM (IS for qNMR). Evidence of competence through regular participation on purity key comparisons (CCQM-K55a, K55b, 55c, 55d, 148a and 148b). Additional evidence: participation on

				CCQM-K131 (Low-Polarity Analytes in a Multicomponent Organic Solution – PAHs in acetonitrile). Broad CMC for organic solutions “PAHs in toluene of molar mass > 150 g/mol and less than 280 g/mol”.
NIM	Supelco Chem Service Cerilliant AccuStandard neat	Phe: (98.9 ± 0.44) % Flu: (98.3± 0.80) % BaP: (99.4 ± 0.27) % BghiP:(98.3 ± 0.23) %	Mass- balance methods: HPLC-DAD and GC-FID were employed to identify related structural impurities. Moisture content was determined via Karl Fischer titration. Residual solvents were analyzed using headspace-GC/MS, while inorganic content was assessed by ICP-MS.	The purity value of 4 PAHs was assessed in NIM by using the mass balance method. The ability for purity assignment has been supported by NIM's participation in K148a, K55b, 55c, and 55d. CCQM-K131 provides further evidence with demonstrated ability for preparation and verification of calibration solution.
NIMT	NIM (GBW(E)080477) NIST (SRM 1647f) NIST (SRM 1647f), Solution SRM	Flu: 7.50μg/mL ± 2.9% Phe:(4.57±0.05) mg/kg BghiP:(4.64±0.12) mg/kg	N/A	N/A
GLHK	NIM (GBW 08736), Solution CRM	Flu: 5.00 μg/g, U=2% BaP: 4.88 μg/g, U=2% BghiP:4.89μg/g, U=2%	N/A	N/A
BAM	NIST (SRM 1647f / SRM 2260a), Solution SRM	Phe:(4.57 ± 0.05) mg/kg Flu: (9.71 ± 0.16) mg/kg BaP:(6.22 ± 0.11) mg/kg BghiP: (4.64 ± 0.12) mg/kg	N/A	N/A

	1647f as calibrant used			
NMIA	NIST (SRM 2260a) Solution SRM	Phe:(11.57 ± 0.12) µg/g Flu:(8.324 ± 0.087) µg/g BaP: (4.71 ± 0.17) µg/g BghiP:(5.669 ±0.069) µg/g	N/A	N/A
INTI	NIST (SRM 1647f / SRM 2260a), Solution SRM 1647f for the quantification, 2260a for the study of bias	Phe:(4.57± 0.05) mg/kg Flu: (9.71±0.16) mg/kg BaP: (6.22± 0.11) mg/kg BghiP: (4.64 ± 0.12) mg/kg	N/A	N/A
TUBITAK_UME	NIST (SRM 1647f), Solution SRM	Phe:(4.57 ± 0.05) mg/kg Flu: (9.71 ± 0.16) mg/kg BaP:(6.22±0.11) mg/kg BghiP:(4.64±0.12) mg/kg	N/A	N/A
METAS	NIST (SRM 1647f), Solution SRM	Phe:(4.57±0.05) mg/kg Flu: (9.71±0.16) mg/kg BaP:(6.22±0.11) mg/kg BghiP:(4.64±0.12) mg/kg	N/A	N/A
LGC	NIST (SRM 1647f), Solution SRM	Phe:(4.57 ± 0.05) mg/kg Flu: (9.71 ± 0.16) mg/kg BaP:(6.22± 0.11) mg/kg BghiP:(4.64 ± 0.12) mg/kg	N/A	N/A

Solution SRMs or CRMs of PAHs are available from NIST and NIM China.

Most of the participating laboratories (12 out of 17) used solution CRMs that were assessed by the OAWG to meet the CIPM traceability requirements. Four laboratories used pure PAHs as the source of traceability, all of which assessed the purity of the PAHs using in-house methods (e.g., qNMR, mass-balance method). IH used a mixed PAHs solution from Dr. Ehrenstorfer without further assessment, so their results are not compliant with CIPM traceability requirements and were therefore not included in the KCRV calculation. The results from CENAM were excluded from the KCRV calculation due to traceability issues arising from their use of the partial mass-balance method.

Methods Used by Participants

The methods for extraction, clean-up, instrumental techniques, internal standards as well as the calibration type used by the participants in CCQM-K184 are listed in Table 6. The full details on the analytical methods, as reported by each participant, are given in Appendix F.

Table 6. Summary of analytical methods used by the participants in CCQM-K184

Participant	Sample intake / bottle number(s)	Extraction	Clean-up	Instrumental technique	Internal standard(s)	Calibration
KRISS	1 g / (46, 118)	ASE	SPE	GC/MS	Fluoranthene-D10 Benzo[*a*]pyrene-13C4 Benzo[*ghi*]perylene-13C12	IDMS Single point
KRISS supplementary method		ASE	-	GC-MS		
LNE	1 g / (77, 173)	Microwave	Filtration	GC-MS	Phenanthrene 13C6 Fluoranthene 13C6 Benzo[*a*]pyrene 13C4 Benzo[*ghi*]perylene 13C12	IDMS 6 point calibration curve
NIST	1 g / (147, 149)	ASE	Filtration	GC/MS	phenanthrene-D10 Fluoranthene-D10 Benzo[*a*]pyrene-D12 Benzo[*ghi*]perylene-D12	IDMS Multipoint calibration
CENAM	1 g / (110, 147, 27)	Automated Soxhlet extraction	SPE	GC-MS/MS, GC-MS HPLC-FLD HPLC-DAD	Phenanthrene-D10 Fluoranthene-D10 Benzo[*a*]pyrene-D12 benzo[*ghi*]perylene-D12 Peryelene-D12	IDMS HPLC: Internal standard 4-5 points, calibration curve
VNIIM	0.5 g / (125, 212)	Soxhlet extraction	SPE	GC-MS/MS	US EPA PAH Cocktail (13C, 99%)	IDMS Single point
IH	2 g / (47, 202)	ASE	Copper for removing sulfur and Column purification	GC-MS	Phenanthrene-D10 Chrysene-D12 Peryelene-D12	Internal standard calibration
INM	2 g / (62, 131)	Ultrasonic extraction	d-SPE	GC-MS/MS	Fluoranthene-D10 Benzo[*a*]pyrene-D12 Benzo[*ghi*]perylene-D12	Internal standard Bracketing, Matrix matched calibration
INMETRO	1 g / (40, 174)	Ultrasonic extraction	SPE	GC-MS/MS	Phenanthrene-D10 Fluoranthene-D10 Benzo[*a*]pyrene-D12	IDMS Bracketing

					Benzo[*ghi*]perylene-D12	
NIM	1 g / (12, 187)	ASE	SPE	GC-MS	Phenanthrene 13C12 Fluoranthene 13C6 Benzo[*a*]pyrene 13C4 Benzo[*ghi*]perylene 13C12	IDMS Single point
NIMT	1 g / (98, 154)	ASE	-	GC-MS/MS	Phenanthrene-D10 Fluoranthene-D10 Benzo[*ghi*]perylene-D12	Exact-matching IDMS for Fluoranthene and multi-point with isotopically internal standard for Phenanthrene and Benzo[*ghi*)]perylene.
GLHK	1 g / (86, 153)	Sonication-assisted saponification with KOH/MeOH, followed by hexane extraction	Activated copper for removal of sulphur-containing compounds, Column chromatography	GC-MS GC-HRMS	Fluoranthene-D10 Benzo[*a*]pyrene-D12 Benzo[*ghi*]perylene-13C12	IDMS 4 point calibration curve and IDMS with bracketing.
BAM	1 g / (104, 169)	ASE	Filtration	GC-MS	Deuterated PAH-Mix 9	IDMS 4-10 point calibration curves
NMIA	1 g / (25, 94)	ASE	Filtration	GC-MS/MS	Phenanthrene 13C6 Fluoranthene 13C6 Benzo[*a*]pyrene 13C4 Benzo[*ghi*]perylene 13C12	IDMS 8 point calibration curve
INTI	2 g / (5, 34)	ASE	Column Chromatography	GC-MS	SRM 2269, SRM 2270	Calibration curve.
TUBITAK_UME	1 g / (56, 160)	Soxhlet (Buchi b 811)	SPE	GC-MS (Thermo TSQ Quantum XLS)	phenanthrene-D10 Fluoranthene-D10 Benzo[*a*]pyrene-D12 Benzo[*ghi*]perylene-D12	Calibration curve.

METAS	1 g / (58, 126)	ASE	SPE	GC-MS/MS (Thermo Scientific TSQ 8000 Evo / Trace 1310)	phenanthrene-D10 Fluoranthene-D10 Benzo[*a*]pyrene-D12 Benzo[*ghi*]perylene-D12	IDMS 9-point calibration
LGC	1 g / (50, 122)	Soxhlet extraction	-	Shimadzu GC system Nexis GC-2030 coupled to Shimadzu GCMS-TQ8050NX QQQ	Fluoranthene-D10 Benzo[*a*]pyrene-D12 Benzo[*ghi*]perylene-D12	Double Exact Matching Isotope Dilution Mass Spectrometry (DEM-IDMS)

Participant Results for 4 PAHs

The results for CCQM-K184 for the determination of moisture and 4 PAHs are detailed in Tables 7-10 and presented graphically in Figures 7-10.

Table 7. Reported Results for Moisture and Phenanthrene

NMI	% Moisture	Phenanthrene (optional), μg/kg					
		x	*u*(*x*)	*u*(*x*) %	*k*	*U*(*x*)	*U*(*x*) %
KRISS	1.93%	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
LNE	1.77%	2255	69	3.1%	2	138	6.1%
NIST	1.94%	2573	50	1.9%	2.145	106	4.1%
CENAM	1.90%	885.1	105	11.9%	2	210	23.7%
VNIIM	1.85%	2920	111	3.8%	2	230	7.9%
IH	1.95%	1781	221	12.4%	2	442	24.8%
INM	2.05%	726.84	54.07	7.4%	2	108.15	14.9%
INMETRO	1.92%	2437	58	2.4%	2	115	4.7%
NIM	2.21%	2724	111.3	4.1%	2	223	8.2%
NIMT	2.87%	2235	162	7.2%	2	324	14.5%
GLHK	2.12%	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
BAM	2.21%	3010	96.65	3.2%	2	193	6.4%
NMIA	2.95%	2550	91	3.6%	2.09	190	7.5%
INTI	1.77%	1580	108	6.8%	2	216	13.7%
TUBITAK_ UME	1.90%	2528	114	4.5%	2	228	9.0%
METAS	1.45%	2562	74	2.9%	2	149	5.8%
LGC	2.13%	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
KRISS*	NA	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
n	17	14					
$\bar{x}$	2.05%	2197.6					
s	0.37%	705.4					
CV	18.0	32.1					

n = number of results included in summary statistics; $\bar{x}$ = mean; *s* = standard deviation;
CV = $100 \cdot s/\bar{x}$

KRISS*: KRISS's supplementary result with extraction condition (2).

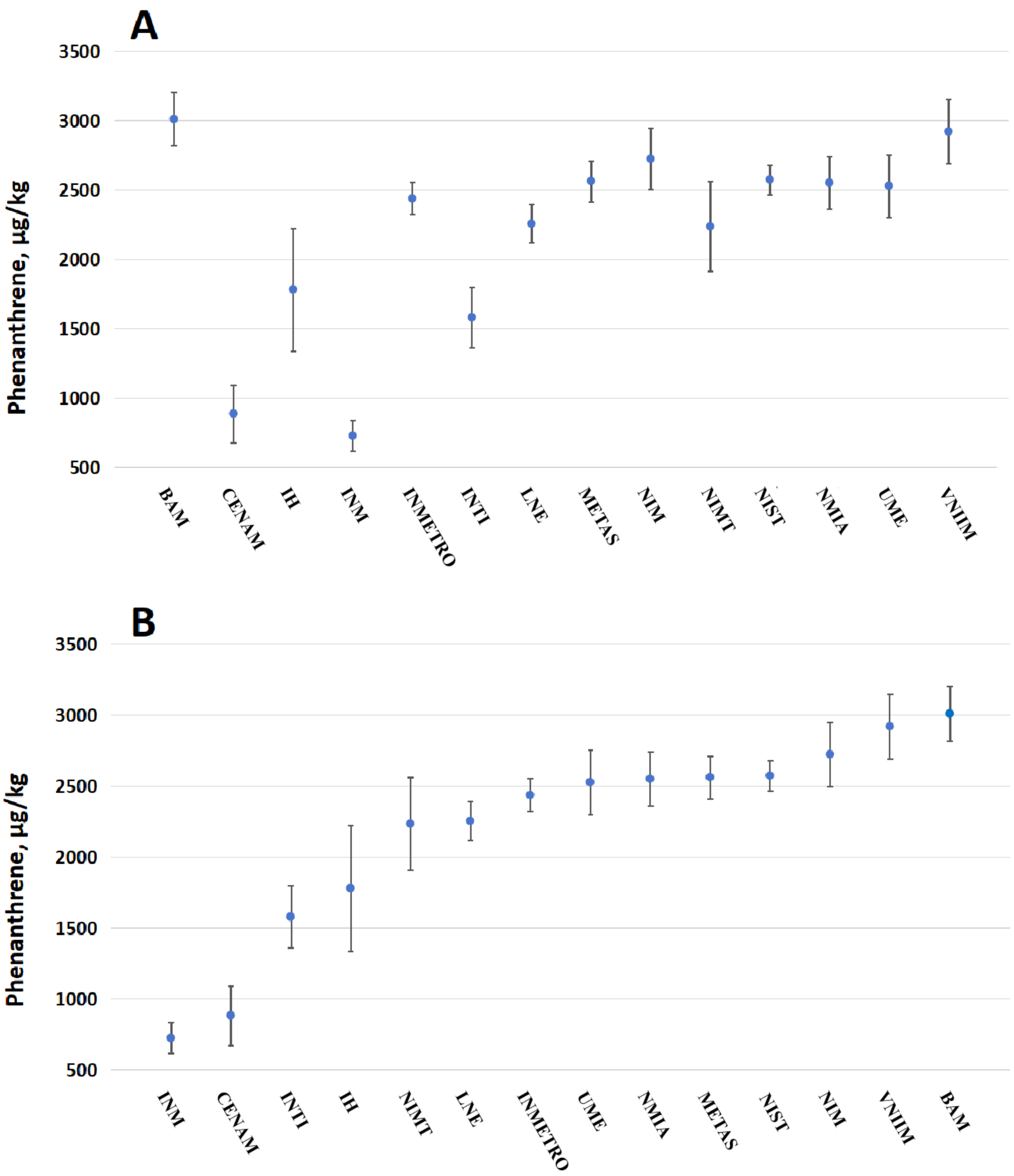


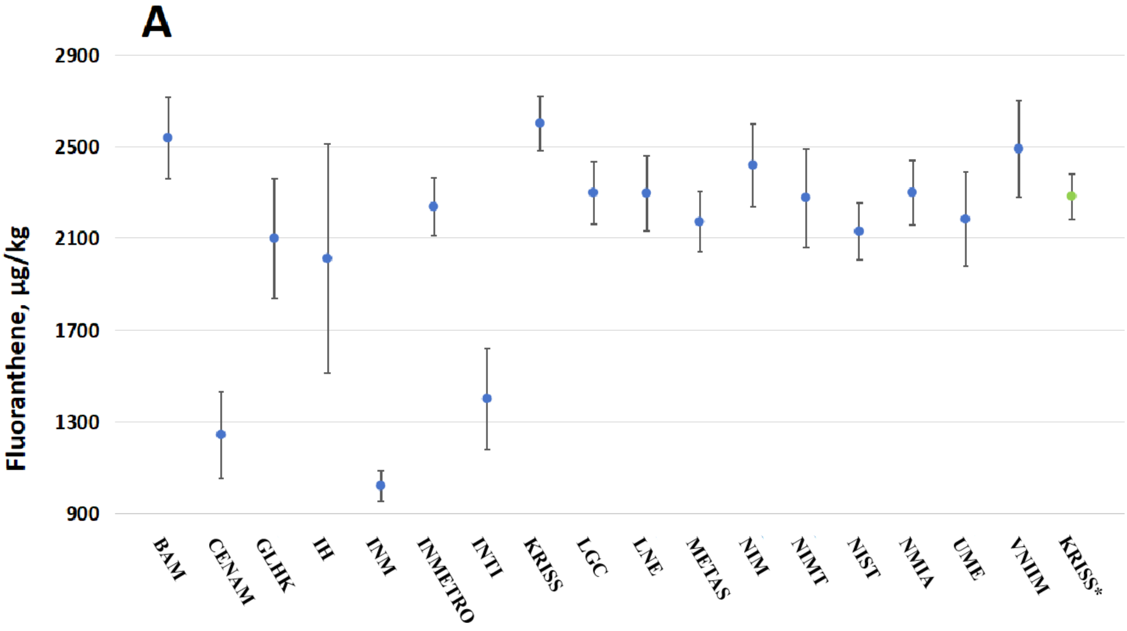
Figure 7: Illustrated Reported Results for Phenanthrene, µg/kg

Panels A and B display the reported results for phenanthrene; panel A displays the results sorted alphabetically by NMI acronym, panel B displays results sorted by increasing reported value. Dots represent the reported mean values, *x*; bars their reported expanded uncertainties, *U*(*x*). The thin horizontal gridlines are provided for visual guidance.

Table 8. Reported Results for Fluoranthene

NMI	Fluoranthene, µg/kg					
	x	$u(x)$	$u(x)$ %	k	$U(x)$	$U(x)$ %
KRISS	2602	51	2.0%	2.36	120	4.6%
LNE	2297	82	3.6%	2	164	7.1%
NIST	2130	58	2.7%	2.138	123	5.8%
CENAM	1243	95	7.6%	2	190	15.3%
VNIIM	2490	105	4.2%	2	210	8.4%
IH	2012	250	12.4%	2	500	24.9%
INM	1020.64	32.93	3.2%	2	65.86	6.5%
INMETRO	2238	63	2.8%	2	126	5.6%
NIM	2419	89.5	3.7%	2	179	7.4%
NIMT	2277	105	4.6%	2.03	213	9.4%
GLHK	2100	130	6.2%	2	260	12.4%
BAM	2538	89.95	3.5%	2	180	7.1%
NMIA	2300	66	2.9%	2.12	140	6.1%
INTI	1400	110	7.9%	2	221	15.8%
TUBITAK_UME	2183	103	4.7%	2	206	9.4%
METAS	2172	66	3.0%	2	133	6.1%
LGC	2299	68	3.0%	2	136	5.9%
KRISS*	2283	43	1.9%	2.31	100	4.4%
n	18					
$\bar{x}$	2111.3					
s	441.1					
CV	20.9					

n = number of results included in summary statistics; $\bar{x}$ = mean; s = standard deviation;
CV = $100 \cdot s/\bar{x}$
KRISS*: KRISS's supplementary result with extraction condition (2).



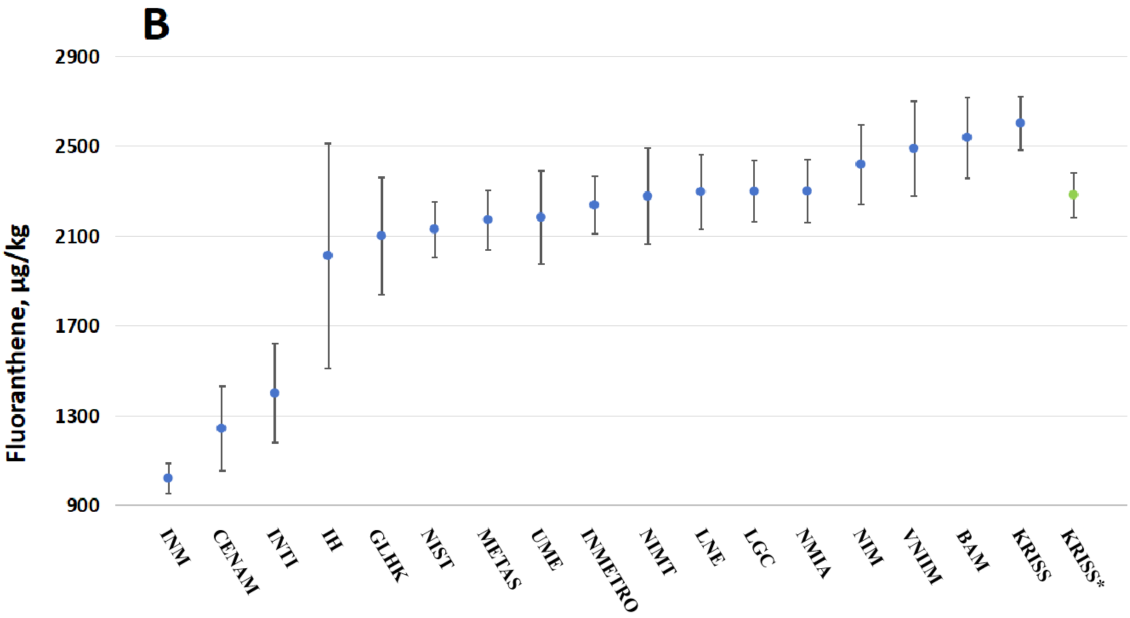


Figure 8: Illustrated Reported Results for Fluoranthene, µg/kg

Panels A and B display the reported results for fluoranthene; panel A displays the results sorted alphabetically by NMI acronym, panel B displays results sorted by increasing reported value. Dots represent the reported mean values, *x*; bars their reported expanded uncertainties, *U*(*x*). The thin horizontal gridlines are provided for visual guidance.

Table 9. Reported Results for Benzo[*a*]pyrene

NMI	Benzo[*a*]pyrene, µg/kg					
	x	*u*(*x*)	*u*(*x*) %	*k*	*U*(*x*)	*U*(*x*) %
KRISS	728	32	4.4%	2.78	89	12.2%
LNE	839	34	4.1%	2	68	8.1%
NIST	656	41	6.3%	2.13	87	13.3%
CENAM	907.3	43.8	4.8%	2	87.6	9.7%
VNIIM	776	32	4.1%	2	64	8.2%
IH	504	64	12.7%	2	128	25.4%
INM	418.57	19.66	4.7%	2	39.33	9.4%
INMETRO	853	27	3.2%	2	54	6.3%
NIM	749	22.6	3.0%	2	45.2	6.0%
NIMT	**NA**	**NA**	**NA**	**NA**	**NA**	**NA**
GLHK	742	88	11.9%	2	180	24.3%
BAM	882.9	40.51	4.6%	2	81	9.2%
NMIA	748	28	3.7%	2.31	64	8.6%
INTI	427	55	12.9%	2	111	26.0%
TUBITAK_UME	699	33	4.7%	2	66	9.4%
METAS	710	31	4.4%	2	63	8.9%
LGC	531	17	3.2%	2	34	6.4%
KRISS*	547	16	2.9%	2.78	45	8.2%
n	17					
$\bar{x}$	689.3					
s	153.4					
CV	22.3					

n = number of results included in summary statistics; $\bar{x}$ = mean; *s* = standard deviation;

CV = $100 \cdot s/\bar{x}$

KRISS*: KRISS's supplementary result with extraction condition (2).

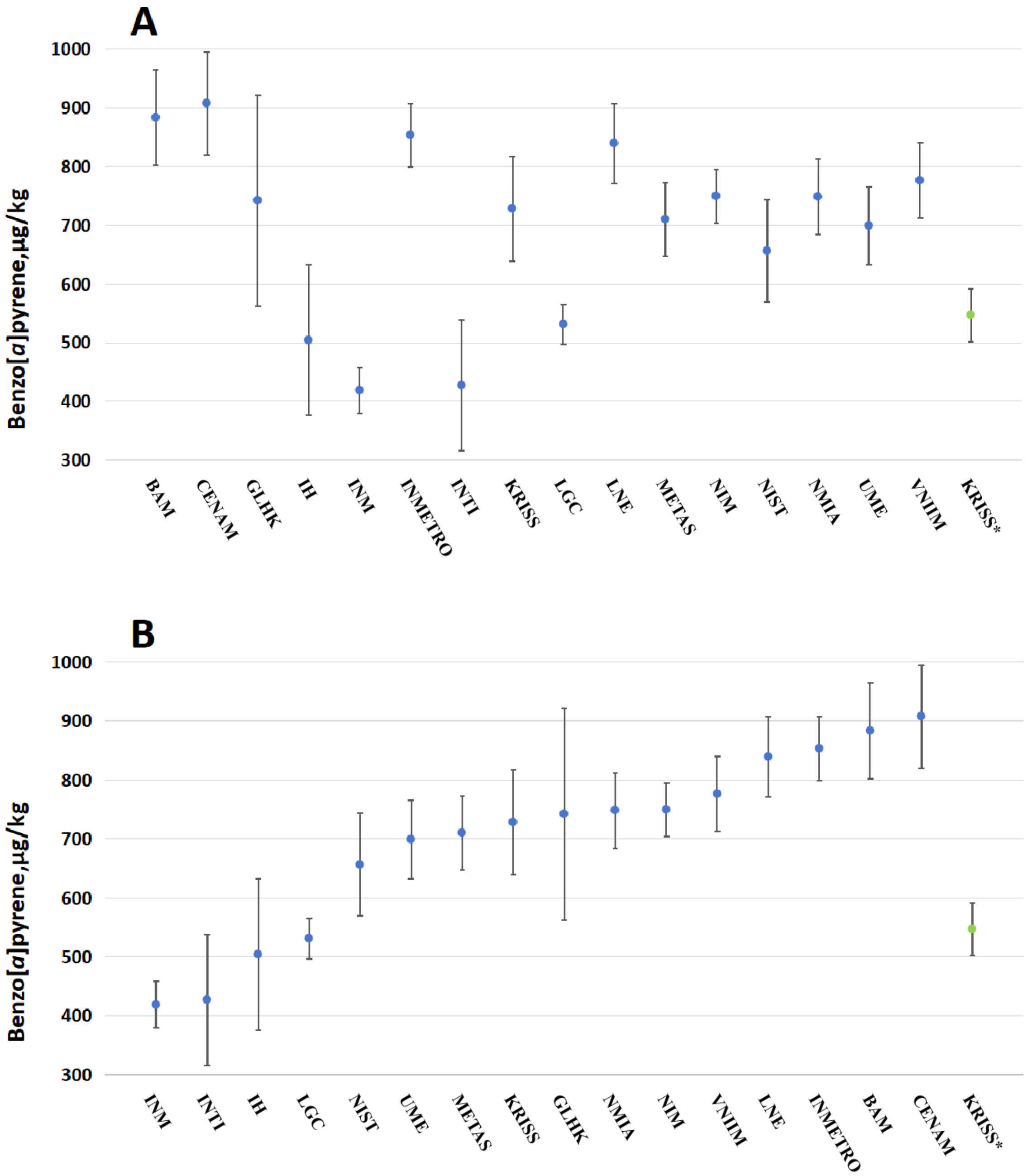


Figure 9: Illustrated Reported Results for Benzo[*a*]pyrene, µg/kg

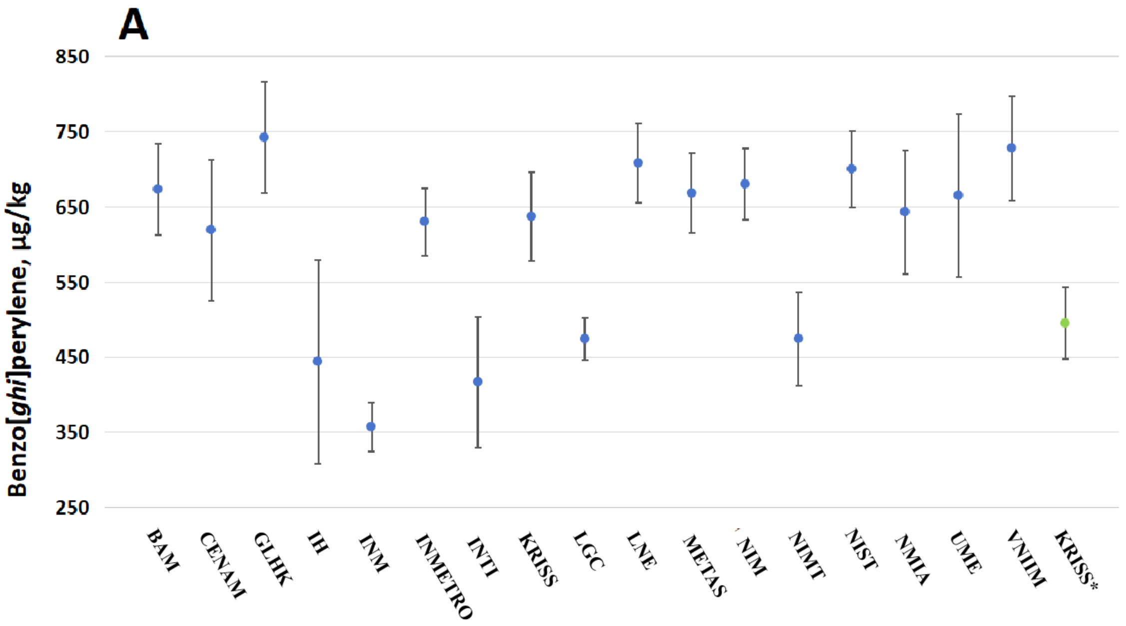
Panels A and B display the reported results for benzo[*a*]pyrene; panel A displays the results sorted alphabetically by NMI acronym, panel B displays results sorted by increasing reported value. Dots represent the reported mean values, *x*; bars their reported expanded uncertainties, *U*(*x*). The thin horizontal gridlines are provided for visual guidance.

Table 10. Reported Results for Benzo[*ghi*]perylene

NMI	Benzo[*ghi*]perylene, µg/kg					
	x	*u*(*x*)	*u*(*x*) %	*k*	*U*(*x*)	*U*(*x*) %
KRISS	637	25	3.9%	2.36	59	9.3%
LNE	708	27	3.8%	2	53	7.5%
NIST	700	24	3.4%	2.139	51	7.3%
CENAM	619	46.8	7.6%	2	93.6	15.1%
VNIIM	728	35	4.8%	2	70	9.6%
IH	444	68	15.3%	2	136	30.6%
INM	357.47	16.2	4.5%	2	32.4	9.1%
INMETRO	630	23	3.7%	2	45	7.1%
NIM	680	23.7	3.5%	2	47.5	7.0%
NIMT	474.25	31	6.5%	2	62	13.1%
GLHK	742	37	5.0%	2	74	10.0%
BAM	673	30.54	4.5%	2	61.1	9.1%
NMIA	643	39	6.1%	2.11	82	12.8%
INTI	417	44	10.6%	2	87	20.9%
TUBITAK_UME	665	54	8.1%	2	108	16.2%
METAS	668	26	3.9%	2	53	7.9%
LGC	474	14	3.0%	2	28	5.9%
KRISS*	495	17	3.4%	2.78	48	9.7%
n	18					
$\bar{x}$	597.5					
s	119.4					
CV	20.0					

n = number of results included in summary statistics; $\bar{x}$ = mean; *s* = standard deviation; CV = $100{\cdot}s/\bar{x}$

KRISS*: KIRSS's supplementary result with extraction condition (2).



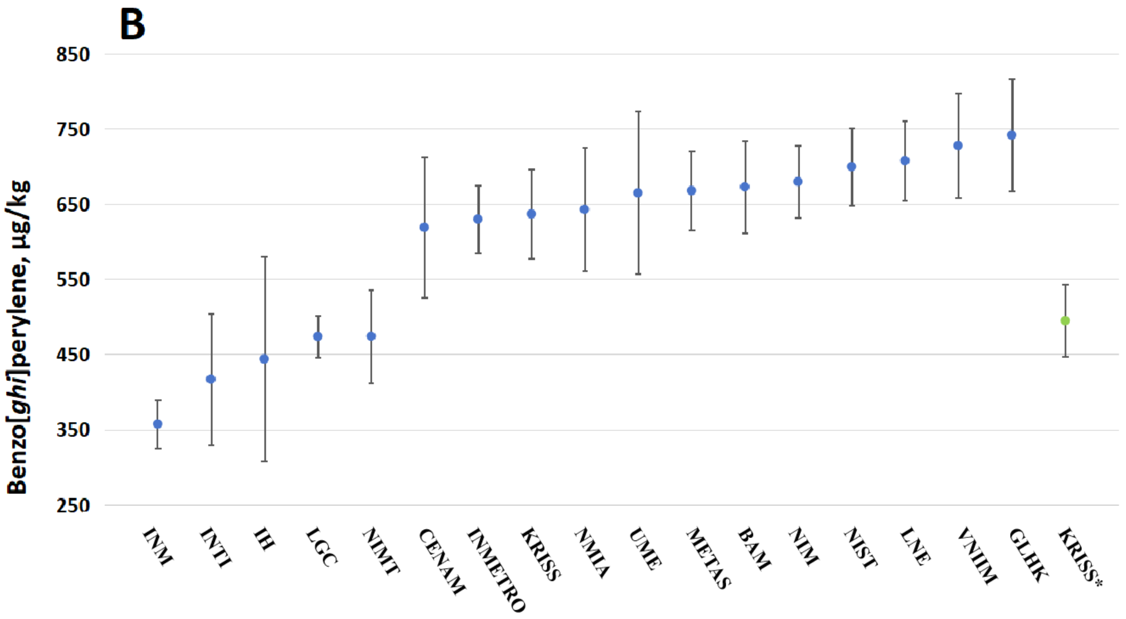


Figure 10: Illustrated Reported Results for Benzo[*ghi*]perylene, µg/kg
Panels A and B display the reported results for benzo[*ghi*]perylene; panel A displays the results sorted alphabetically by NMI acronym, panel B displays results sorted by increasing reported value. Dots represent the reported mean values, *x*; bars their reported expanded uncertainties, *U*(*x*). The thin horizontal gridlines are provided for visual guidance.

KEY COMPARISON REFERENCE VALUE (KCRV)

All datasets from CCQM-K184 were included in the Key Comparison Reference Value (KCRV) calculation for all measurands, with the following exceptions: CENAM and IH (excluded due to traceability issues), INM and INTI (excluded due to technical issues), NIMT (which did not submit data for benzo[a]pyrene and withdrew data for benzo[*ghi*]perylene due to technical issues), LGC (which withdrew results for both benzo[*a*]pyrene and benzo[*ghi*]perylene due to technical issues), and KRISS's supplementary result. The NIST Consensus Builder (NICOB) was employed to calculate the KCRV, associated uncertainty (u(KCRV)), and Degrees of Equivalence (DoE) values for comparison[15]. The specific parameters used in the NICOB calculations can be found in Appendix I.

Table 11. KCRVs and associated standard uncertainty of PAHs in sediment

	Phenanthrene (optional), µg/kg	Fluoranthene, µg/kg	Benzo[*a*]pyrene, µg/kg	Benzo[*ghi*]perylene, µg/kg
n	10	13	11	11
$\bar{x}$	2579.4	2311.2	762.1	679.5
s	251.7	158.1	69.9	36.7
$\bar{u}$	98.8	85.8	40.8	32.6
CV	9.8	6.8	9.2	5.4
Median	2556	2297	748	673

Selected Procedure	Hierarchical Bayes (Gaussian)	Hierarchical Bayes (Gaussian)	Hierarchical Bayesian (Gaussian)	Hierarchical Bayes (Gaussian)
KCRV	2581	2314	763.4	677
Standard uncertainty	82.53	48.84	22.5	11.81
95% coverage interval	(2417, 2742)	(2216, 2410)	(719.5, 808.9)	(654.1, 700.7)
Dark uncertainty (tau)	236.9	149	62.66	20.87

n = number of results included in summary statistics;

$\bar{x}$ = mean;

s = standard deviation;

$\bar{u} = \sqrt{\sum_i^n u^2(x_i)/n}$, the "average" reported uncertainty

CV = $100 \cdot \frac{s}{\bar{x}}$;

The KCRV calculation was performed using the NIST Consensus Builder (NICOB) in accordance with the KCRV QuickGuide (OAWG-100-KCRV-QuickGuide-V2)[16]. Both the DerSimonian-Laird (DSL) and Hierarchical Bayes Random-Effects Model (HB REM) statistical models were considered as potential candidates for the KCRV computation.

Although no significant differences were observed between the KCRV estimates derived from the DSL and HB REM models, our analysis revealed that the standard deviation (s) of the measured values $\{x_i\}$ was approximately three times greater than the typical within-laboratory standard uncertainty. This observed "excess" variance suggests that participating laboratories may have overlooked or underestimated certain significant uncertainty sources, referred to as dark uncertainty (τ).

While the DSL method generally requires fewer assumptions than the HB REM approach, both methods make comparable assumptions regarding uncertainty analysis. Importantly, the Bayesian methodology addresses a critical limitation of the conventional DSL uncertainty evaluation - its failure to account for uncertainty in estimating τ.

Consequently, the Hierarchical Bayes approach was selected as more appropriate for this analysis, as it effectively accommodates both the substantial dark uncertainty (excess variance) present in these limited datasets and the reported uncertainties from participants.

Shapiro-Wilk test was used to test the normality of datasets. 4 PAHs all met the normality assumption. Therefore, Hierarchical Bayesian (Gaussian) statistical models were used for 4 PAHs.

The participants' results with their standard uncertainties and the KCRV and its associated standard uncertainty are plotted in Figures 11-14 for 4 PAHs in sediment.

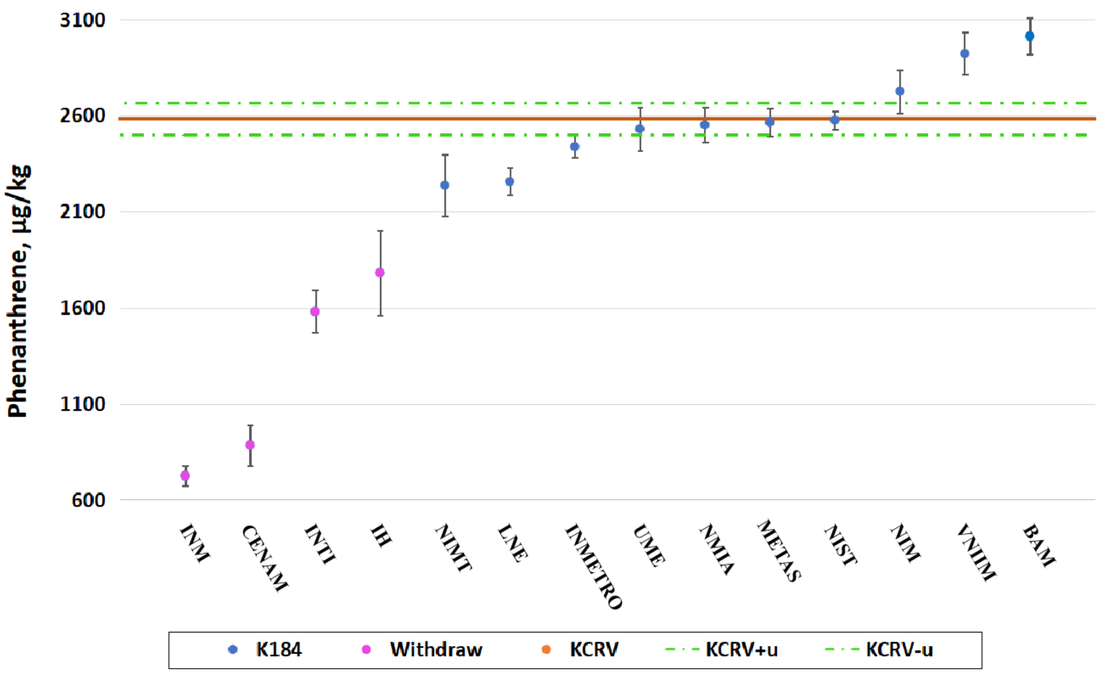


Figure 11: KCRV and participants' results for Phenanthrene in Sediment

Dots represent the reported mean values, *x*; bars their standard uncertainties, *u*(x). The brown horizontal line denotes the KCRV. The bracketing green lines denote the standard uncertainty of the KCRV.

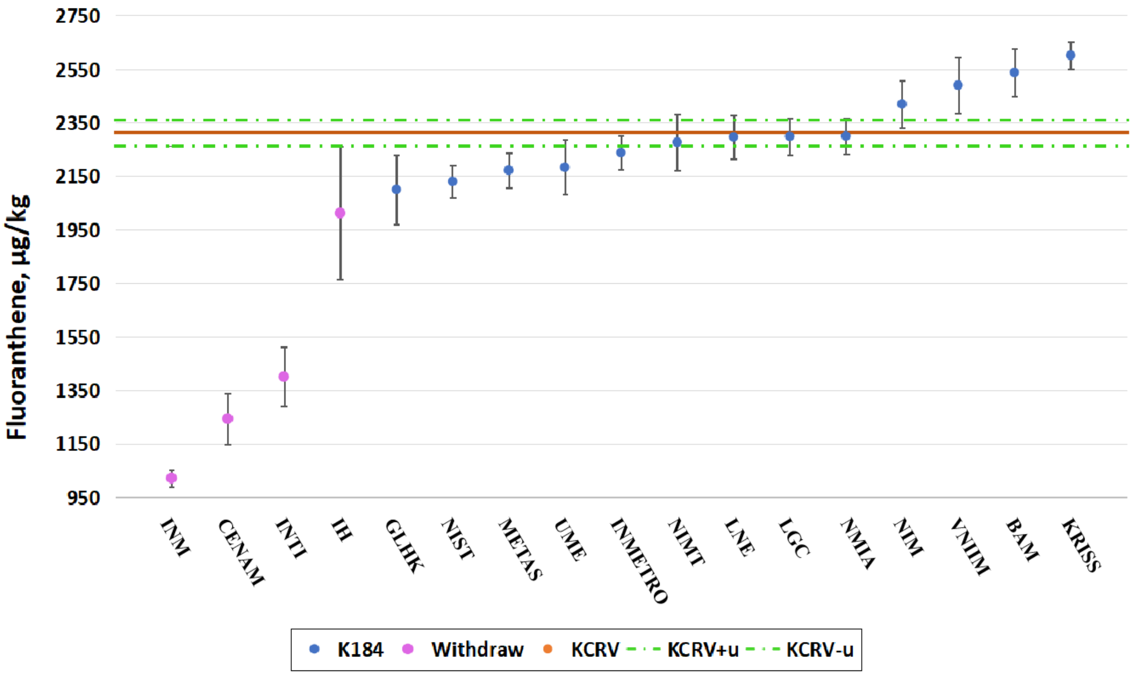


Figure 12: KCRV and participants' results for Fluoranthene in Sediment

Dots represent the reported mean values, x; bars their standard uncertainties, *u*(x). The brown horizontal line denotes the KCRV. The bracketing green lines denote the standard uncertainty of the KCRV.

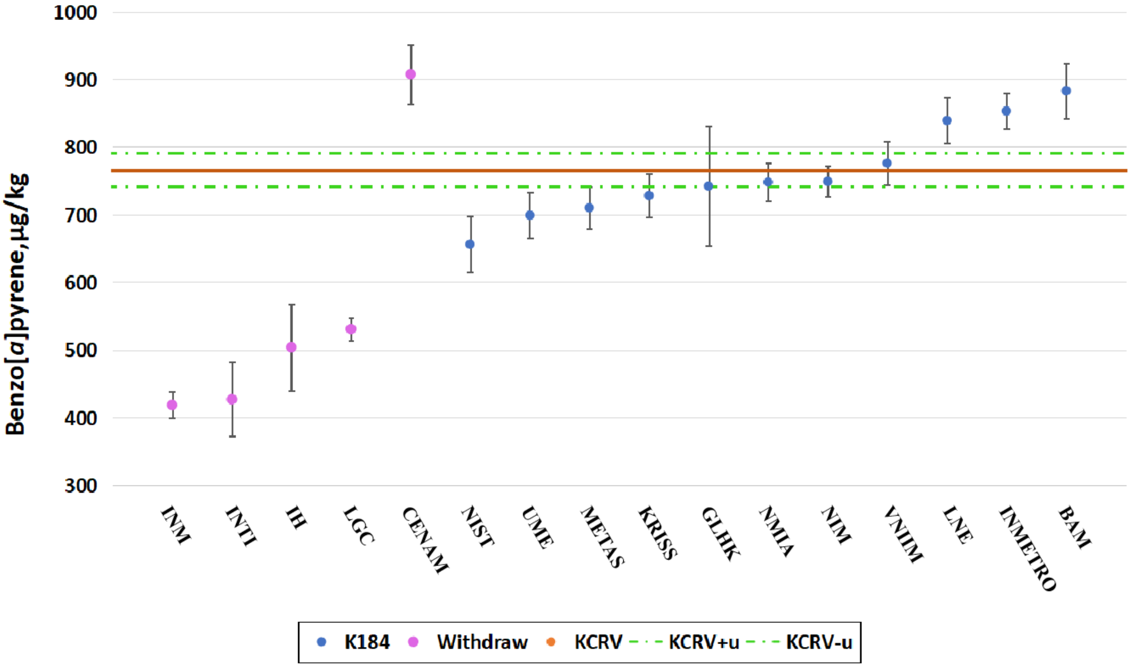


Figure 13: KCRV and participants' results for Benzo[a]pyrene in Sediment

Dots represent the reported mean values, x; bars their standard uncertainties, *u*(x). The brown horizontal line denotes the KCRV. The bracketing green lines denote the standard uncertainty of the KCRV.

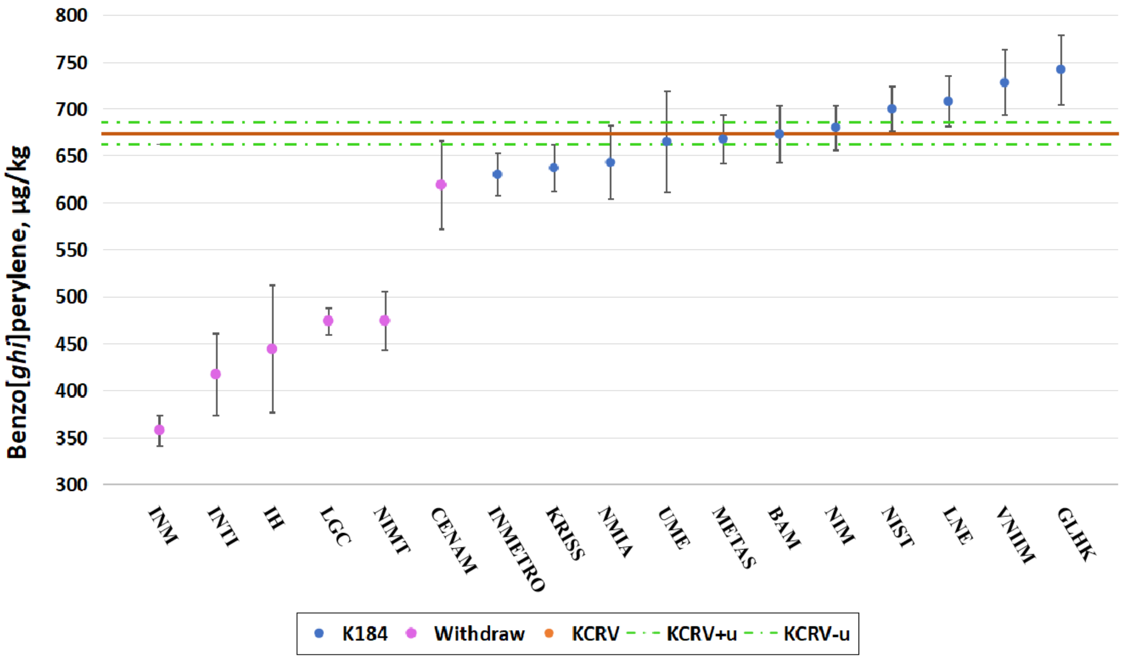


Figure 14: KCRV and participants' results for Benzo[ghi]perylene in Sediment

Dots represent the reported mean values, x; bars their standard uncertainties, *u*(x). The brown horizontal line denotes the KCRV. The bracketing green lines denote the standard uncertainty of the KCRV.

DEGREES OF EQUIVALENCE (DoE)

The Degree of Equivalence (DoE), d_i, for a given result, x_i, is:

$$d_i = x_i - \text{KCRV}.$$

Where x_i is the result reported by participants. The DoEs and uncertainties for 4 PAHs were determined using the NICOB Hierarchical Bayes (Gaussian) procedure.

To enable comparison with the DoE estimates from other studies, it is convenient to express the d_i and $U(d_i)$ as percentages relative to the KCRV:

$$\%d_i = 100 \cdot d_i/\text{KCRV}$$

$$U(\%d_i) = 100 \cdot U(d_i)/\text{KCRV}.$$

Figures 15-22 display the absolute $d_i \pm U(d_i)$ and the relative $\%d_i \pm U(\%d_i)$ for all participants in CCQM-K184.

Table 12. DoEs and their uncertainties for Phenanthrene in Sediment

NMIs	d_i	$U(d_i)$	$\%d_i$	$U(\%d_i)$
LNE	-325.5	549.0	-12.63	21.27
NIST	-7.518	550.3	-0.31	21.32
VNIIM	339.5	575.7	13.13	22.31
INMETRO	-143.5	541.1	-5.58	20.96
NIM	143.5	570.4	5.52	22.10
NIMT	-345.5	605.5	-13.41	23.46
BAM	429.5	559.1	16.62	21.66
NMIA	-30.52	558.3	-1.20	21.63
TUBITAK_UME	-52.52	562.2	-2.05	21.78
METAS	-18.52	548.8	-0.74	21.26
CENAM*	-1695	562.4	-65.71	21.79
IH*	-799.5	683.3	-31.00	26.47
INM*	-1854	538.4	-71.84	20.86
INTI*	-1001	558.2	-38.78	21.63

KCRV: 2581 µg/kg, u=82.53, 95% coverage interval (2417, 2742)

* The corresponding measurement results were excluded from the calculation of the KCRV and the evaluation of the associated uncertainty, but the DoEs and corresponding uncertainties of these laboratory results were calculated.

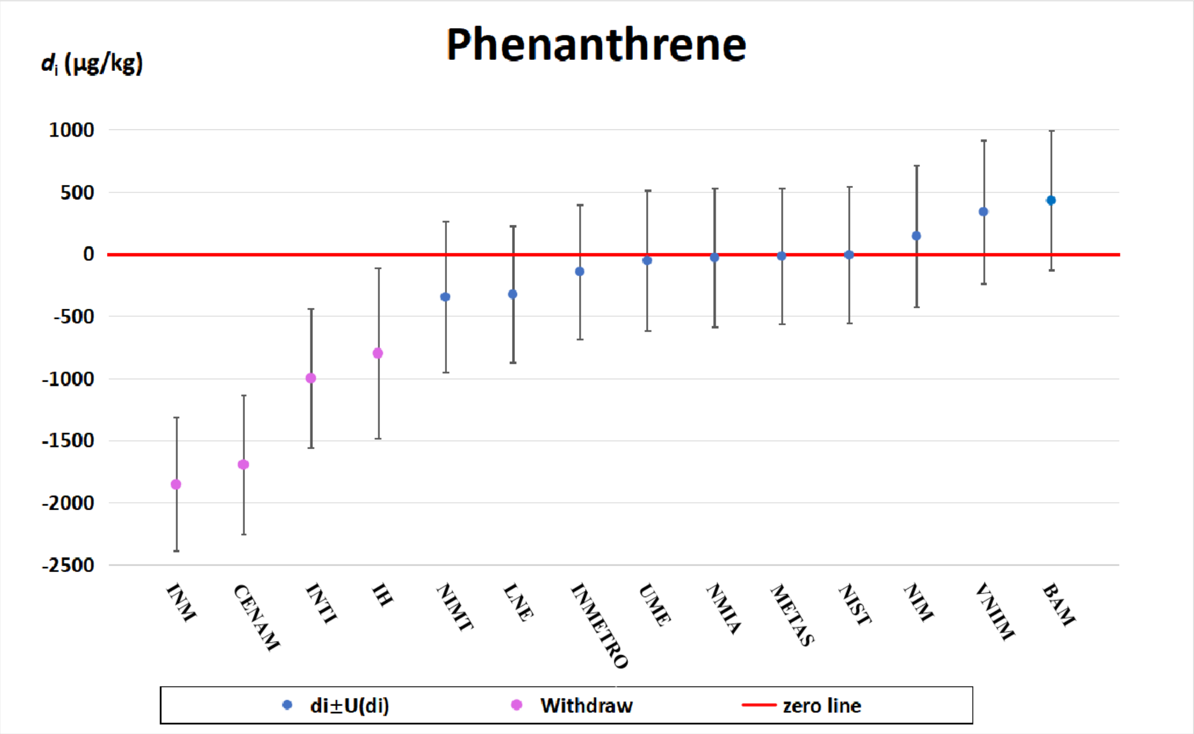


Figure 15: Absolute DoEs of Phenanthrene with the KCRV

All results are sorted by increasing *x*. Dots represent the d_i; bars their expanded uncertainties, $U(d_i)$.The thick red horizontal line denotes perfect agreement with the KCRV.

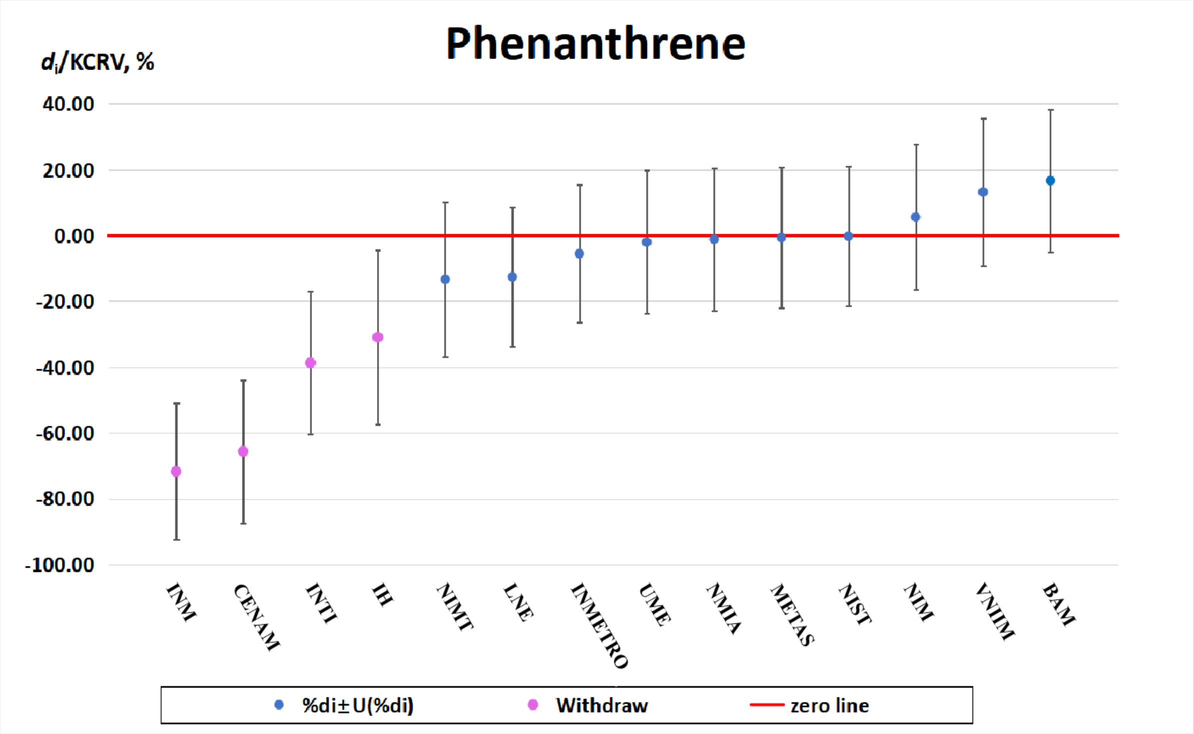


Figure 16: Relative DoEs of Phenanthrene with the KCRV

Dots represent the $\%d_i$; bars their expanded uncertainties, $U(\%d_i)$. The thick red horizontal line denotes perfect agreement with the KCRV.

Table 13. DoEs and their uncertainties for Fluoranthene in Sediment

NMIs	d_i	$U(d_i)$	$\%d_i$	$U(\%d_i)$
KRISS	287.7	346.8	12.43	14.99
LNE	-17.33	367.3	-0.75	15.87
NIST	-184.3	346.9	-7.96	14.99
VNIIM	175.7	390.5	7.59	16.88
INMETRO	-76.33	344.9	-3.30	14.90
NIM	104.7	368.5	4.52	15.92
NIMT	-37.33	384.7	-1.61	16.62
GLHK	-214.3	408	-9.26	17.63
BAM	223.7	367.1	9.67	15.86
NMIA	-14.33	348.7	-0.62	15.07
TUBITAK_UME	-131.3	382	-5.67	16.51
METAS	-142.3	347.1	-6.15	15.00
LGC	-15.33	349.1	-0.66	15.09
CENAM*	-1071	365.3	-46.28	15.79
IH*	-302.3	591.5	-13.06	25.56
INM*	-1294	325.9	-55.92	14.08
INTI*	-914.3	387.2	-39.51	16.73

KCRV: 2314 µg/kg, u=48.84, 95% coverage interval (2216, 2410)

* The corresponding measurement results were excluded from the calculation of the KCRV and the evaluation of the associated uncertainty, but the DoEs and corresponding uncertainties of these laboratory results were calculated.

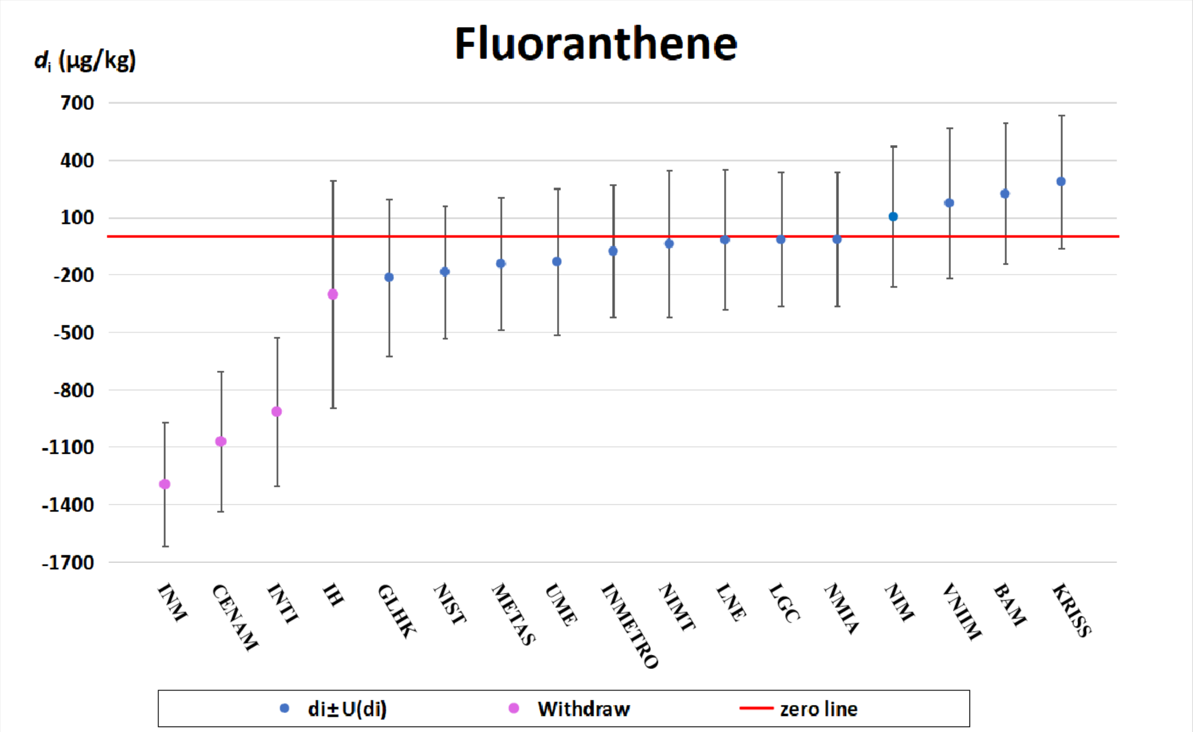


Figure 17: Absolute DoEs of Fluoranthene with the KCRV

Dots represent the d_i; bars their expanded uncertainties, $U(d_i)$. The thick red horizontal line denotes perfect agreement with the KCRV.

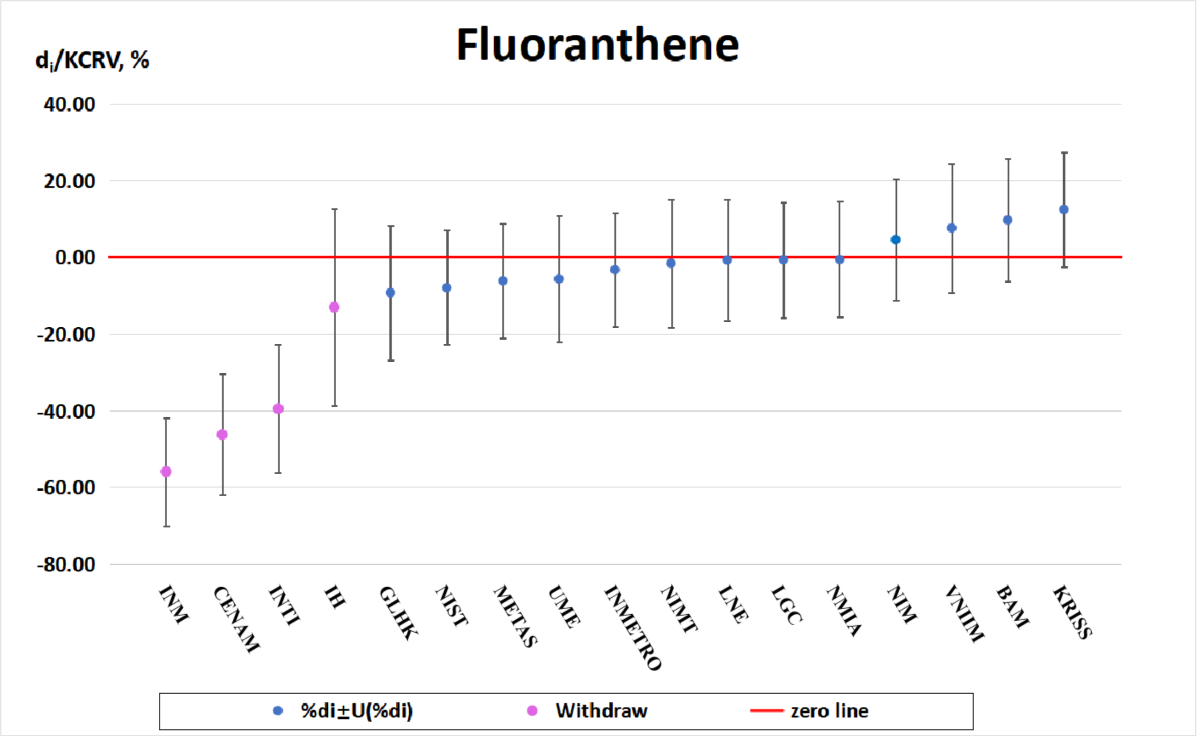


Figure 18: Relative DoEs of Fluoranthene with the KCRV

Dots represent the %d_i; bars their expanded uncertainties, $U(\%d_i)$. The thick red horizontal line denotes perfect agreement with the KCRV.

Table 14. DoEs and their uncertainties for Benzo[*a*]pyrene in Sediment

NMIs	d_i	$U(d_i)$	$\%d_i$	$U(\%d_i)$
KRISS	-35.43	153.2	-4.64	20.07
LNE	75.57	154.6	9.90	20.25
NIST	-107.4	161.5	-14.07	21.16
VNIIM	12.57	154.3	1.65	20.21
INMETRO	89.57	146.4	11.73	19.18
NIM	-14.43	151	-1.89	19.78
GLHK	-21.43	223.3	-2.81	29.25
BAM	119.5	161.9	15.65	21.21
NMIA	-15.43	151.9	-2.02	19.90
TUBITAK_UME	-64.43	153.6	-8.44	20.12
METAS	-53.43	149.3	-7.00	19.56
CENAM*	143.9	160.1	18.85	20.97
IH*	-259.4	185.8	-33.98	24.34
INM*	-344.9	146.8	-45.18	19.23
INTI*	-336.4	176	-44.07	23.05
LGC*	-232.4	141.8	-30.44	18.57

KCRV: 763.4 µg/kg, *u*=22.5, 95% coverage interval (719.5, 808.9)

* The corresponding measurement results were excluded from the calculation of the KCRV and the evaluation of the associated uncertainty, but the DoEs and corresponding uncertainties of these laboratory results were calculated.

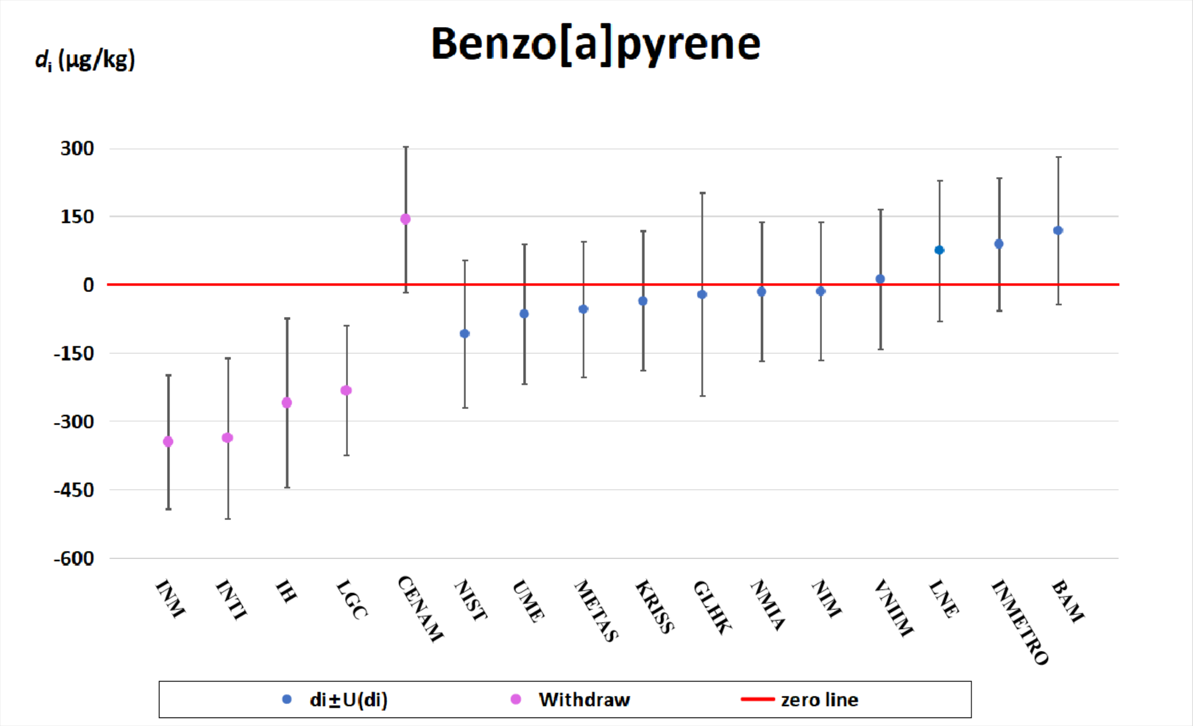


Figure 19: Absolute DoEs of Benzo[*a*]pyrene with the KCRV

Dots represent the d_i; bars their expanded uncertainties, $U(d_i)$. The thick red horizontal line denotes perfect agreement with the KCRV.

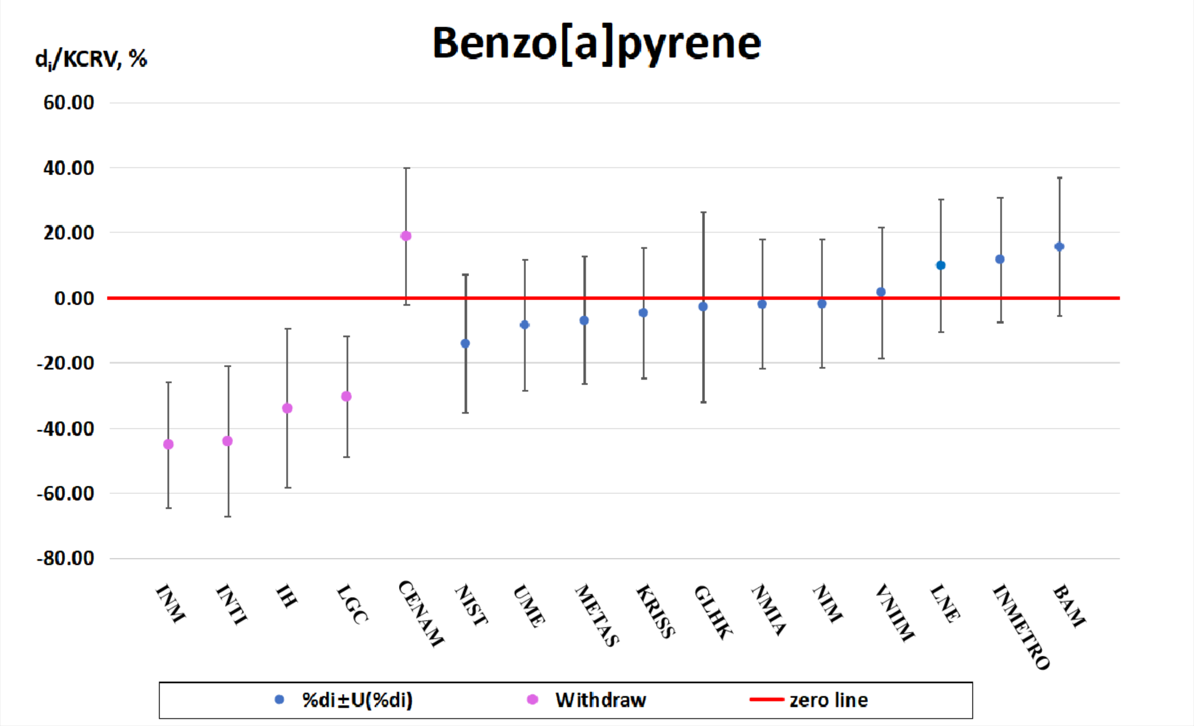


Figure 20: Relative DoEs of Benzo[*a*]pyrene with the KCRV

Dots represent the $\%d_i$; bars their expanded uncertainties, $U(\%d_i)$. The thick red horizontal line denotes perfect agreement with the KCRV.

Table 15. DoEs and their uncertainties for Benzo[*ghi*]perylene in Sediment

NMIs	d_i	$U(d_i)$	$\%d_i$	$U(\%d_i)$
KRISS	-40	72.68	-5.91	10.74
LNE	31	75.86	4.58	11.21
NIST	23	72.92	3.40	10.77
VNIIM	51	87.57	7.53	12.94
INMETRO	-47	70.84	-6.94	10.46
NIM	3	72.14	0.44	10.66
GLHK	65	91.46	9.60	13.51
BAM	-4	81.54	-0.59	12.04
NMIA	-34	94.03	-5.02	13.89
TUBITAK_UME	-12	119.5	-1.77	17.65
METAS	-9	74.45	-1.33	11.00
CENAM*	-58	106.7	-8.57	15.76
IH*	-233	143.1	-34.42	21.14
INM*	-319.5	64.92	-47.19	9.59
NIMT*	-202.7	82.27	-29.94	12.15
INTI*	-260	101.4	-38.40	14.98
LGC*	-203	62.75	-29.99	9.27

KCRV: 677 µg/kg, u=11.81, 95% coverage interval (654.1, 700.7)

* The corresponding measurement results were excluded from the calculation of the KCRV and the evaluation of the associated uncertainty, but the DoEs and corresponding uncertainties of these laboratory results were calculated.

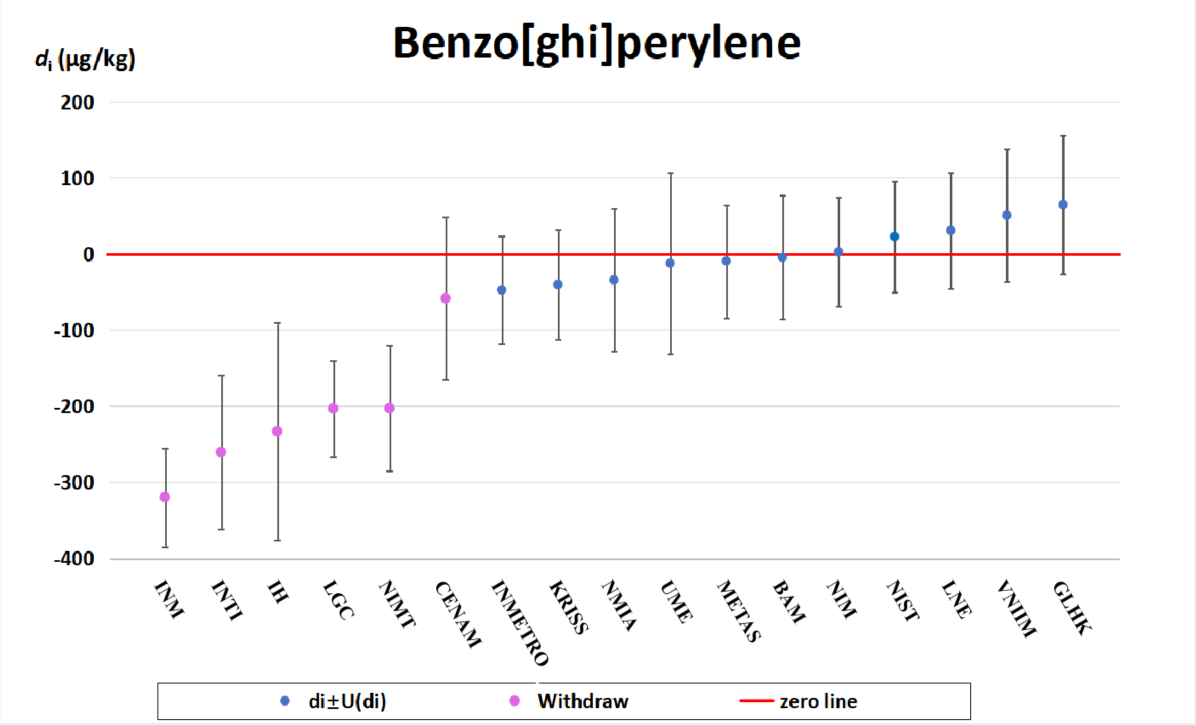


Figure 21: Absolute DoEs of Benzo[ghi]pyrene with the KCRV

Dots represent the d_i; bars their expanded uncertainties, $U(d_i)$. The thick red horizontal line denotes perfect agreement with the KCRV.

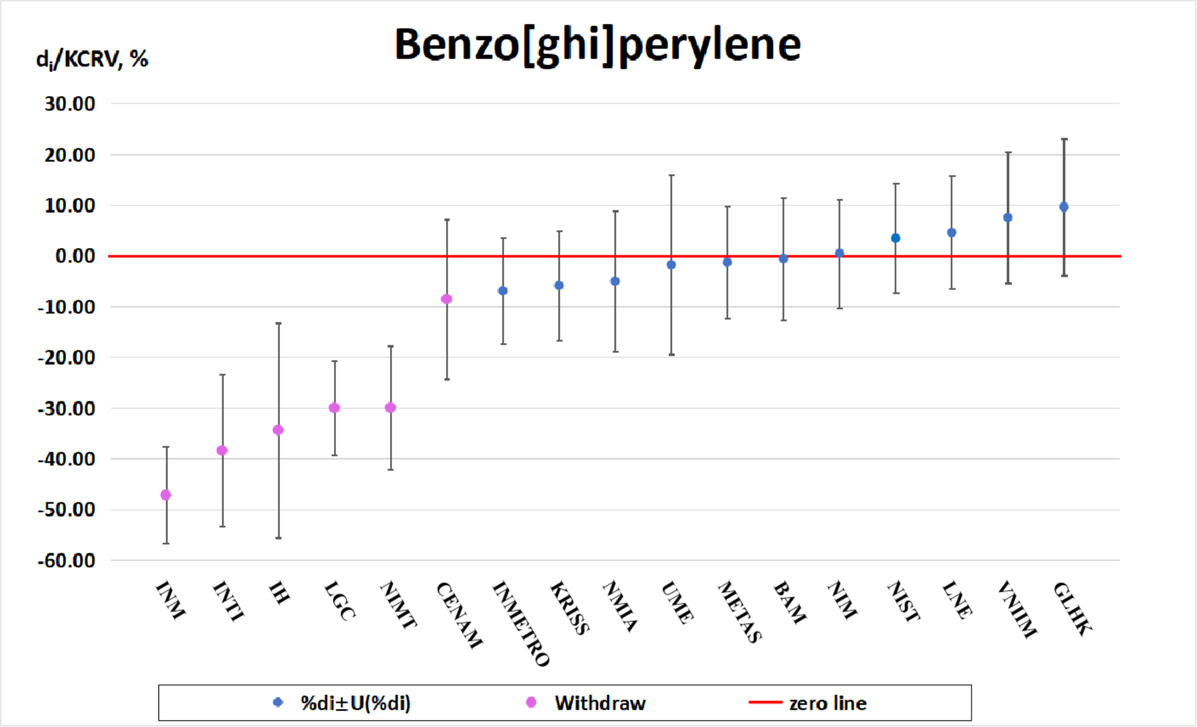


Figure 22: Relative DoEs of Benzo[ghi]pyrene with the KCRV

Dots represent the %d_i; bars their expanded uncertainties, U(%d_i). The thick red horizontal line denotes perfect agreement with the KCRV.

USE OF CCQM-K184 (PAHs in Sediment) IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far the Light Shines

Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes ($pK_{ow} < -2$) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix.
This includes demonstrating capabilities in:
(1) value assignment of primary reference standards;
(2) value assignment of calibration solutions;
(3) extraction of analyte of interest from the matrix;
(4) clean-up and separation of analyte of interest from other interfering matrix or extract components;
(5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC-FLD, etc.

Core Competency Statements

Appendix E-a to E-r list the Core Competencies claimed by the participants in CCQM-K184. The information in these Tables is as provided by the participants; however, the presentation of many entries has been condensed and standardized. Details of the analytical methods used by each participant in this study are provided in Appendix F.

CONCLUSIONS

Most of the participants in CCQM-K184 successfully determined the mass fraction of PAHs in the study samples. They were able to demonstrate their capabilities in determining low-polarity analytes in sediment through the key comparison.

ACKNOWLEDGEMENTS

The study coordinators thank the participating laboratories for providing the requested information used in this study.

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APPENDIX A: Call for Participation

From: Maria Fernandes-Whaley<MFWhaley@nmisa.org>

Sent: Thursday, 31 August 2023 14:28
To:

Subject: Call for participation CCQM-K184/P235 PAHs in sediment

Dear OAWG Colleagues

This is the formal call for participation in our next Track A comparison for PAHs in sediment which will start next month.

The key comparison CCQM-K184 is being run in parallel with the pilot study CCQM-P235. This is a Track A comparison, in our Environmental Sector Focus area, thus institutes that need to demonstrate their capabilities in the measurement of low-polarity analytes in an abiotic matrix should participate in CCQM-K184.

NMIs/DIs that wish to participate are requested to please register by 30 September 2023 using the attached form and then submit by email to Tang Hua (tanghua@nim.ac.cn).

At our April meeting, the coordinating laboratory (NIM), was invited to consider including an optional PAH to cover volatility and the minimum molar mass of 170 g/mol which could be incorporated in the "HFTLS". Although naphthalene was suggested, as a volatile PAH, it would be very challenging to accommodate this volatility within the current comparison study material. NIM has therefore included phenanthrene (molar mass 178 g/mol), which has a lower volatility and experiences less interferences than naphthalene, as the optional measurand.

The HFTLS statement covers the majority of Institute mass fraction ranges that require underpinning in this space. Institutes with much lower mass fraction ranges may need to refer to our OAWG guideline document for the evidence needed to extend the claim.

Participants are kindly reminded that they need to use CRMs that meet the CIPM traceability requirements as sources of traceability in the study.

Many thanks again to NIM for coordinating this study.

Best regards

Maria

APPENDIX B: Protocol
CCQM-K184/CCQM-P235

Low-polarity analytes in abiotic matrix:
PAHs in Sediment
Key Comparison /Pilot Study
Track A
Draft Study Protocol

August 2023

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of carcinogenic organic compounds composed of two or more fused aromatic rings. They are mainly generated from the incomplete combustion of organic matter at high-temperatures from multiple sources including industrial emissions, motor vehicle emissions, tobacco smoke, and other human activities [1]. They have a wide existence in the entire ecosystem especially the aquatic environment [2]. PAHs may accumulate at high levels in sediments because of their hydrophobic nature [3]. Research showed that many PAHs are widely classified as carcinogens, mutagens, and teratogens [4]. Analysis of PAHs in sediments is particularly important because they are considered pollution indicators, since they present a view of the spatial distribution of pollutants. Furthermore, many Sediment Quality Guidelines for individual and total PAH were compiled [5]. The concentration of PAHs in sediment showed obvious regional variance. In southern Brazil, the concentration of PAHs in sediment samples ranged from 15.5 to 133.6 μg/kg [6], meanwhile it ranges from 11.7 to 129.21 μg/kg in eastern China [7], 37.3 to 1973 ng/g in Norway [8], 213 to 1291 μg/kg in southern USA [9], and 10000-100000 μg/kg in polluted areas of Canada [10].

At the CCQM OAWG meeting held in April 2023, it was agreed to have a comparison on the determination of polycyclic aromatic hydrocarbons in sediment as a Track A study. This comparison meets the OAWG strategy document for 2021-2030 for services in support of the environmental sector, in the category of "analyte in abiotic matrix". Participation in CCQM-K184 will demonstrate the following measurement capabilities for the determination of low-polarity contaminants, with molecular mass of 170 g/mol to 500 g/mol, having Low polarity $pK_{ow} < -2$, in mass fraction range from 100 [μg/kg] to 1000000 [μg/kg] in abiotic dried matrix.

As a Track A comparison, it is expected that all NMIs or DIs who have or expect to have services related to the capabilities related to the “How far does the light shines” statement for this key comparison will participate.

TIMELINE

The proposed timeline for the comparison is given in Table 1:

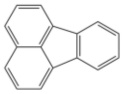
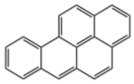
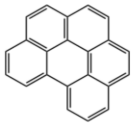
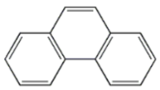
Table 1: Proposed timeline for CCQM-K184/CCQM-P235

Date	Action
Nov. 2019	Sample Preparation
Dec. 2019	Homogeneity Testing
From Dec. 2019	Stability Testing
Aug. 2023	Call for participation to OAWG members
30 Sept. 2023	Deadline for registration
31 Oct. 2023	Dispatch of samples
31 Mar. 2024	Deadline for submission of results
Apr. 2024	Preliminary Discussion of Results

MEASURANDS

Minimum reporting requirements for participants to CCQM-K184 are the mass fractions (on a dry mass basis) of fluoranthene (Fl), benzo[a]pyrene (B[a]P), and benzo[ghi]perylene (B[ghi]P). Based on the discussion at OAWG meeting, Phenanthrene (Ph), a volatile three-rang PAH was added as an optional analyte to the list of CCQM-K184 measurands to support claims that could cover the volatility and lower molecular mass range of PAHs commonly quantified in environmental samples. Table 2 below displays information of these compounds.

Table 2: Physico-chemical parameters for the four PAHs

Compound	**CAS**	**Structural Formula**	**Chemical Formula (MW g/mol)**	**pK_{ow}**
Fluoranthene	206-44-0		$C_{16}H_{10}$ (202.25)	-5.16 [11]
Benzo[a]pyrene	50-32-8		$C_{20}H_{12}$ (252.31)	-6.13 [12]
Benzo[ghi]perylene	191-24-2		$C_{22}H_{12}$ (276.33)	-6.63 [13]
Phenanthrene	85-01-8		C14H10 (178.23)	-4.46 [14]

STUDY MATERIAL

The test material is river sediment collected at 40°55'16.8" N, 29°12'43.6" E from the tributary of Taizi River in Liaoning Province, China. Sediment in this river was naturally contaminated by industrial emissions from several heavy industrial plants over decades. The material underwent a series of processing steps: air-drying, sieving (178 μm), γ-irradiation and homogenization. The final powdered sediment was dispensed in portions of about 10 g into 30 mL amber glass jars with screw caps, and then vacuum sealed within plastic-lined aluminum bags.

Methods

The study will require extraction, clean-up, analytical separation, and selective detection of the analytes in sediment. Participants are anticipated to perform measurements with appropriately validated methods with demonstrated metrological traceability.

Recommended Minimum Sample Amount

Participants will receive 3 samples of 10 g each. The recommended minimum sample amount for analysis is at least 1.0 g. The samples are to be stored at 20°C or below; under the absence of light. Before opening, the samples should be allowed to equilibrate to room temperature.

Dry Mass Determination

Participants are required to carry out a dry mass correction. Dry mass correction should be carried out simultaneously as the test sample portion to be analyzed in the same package of the sample aliquot in which PAH measurements are performed. The moisture content should be measured using the following drying method. A minimum of three subsamples (recommended sample size of 1 g each) of the sediment should be dried in an oven at (105 ± 2) °C until constant mass is reached. The correction used for dry-mass conversion shall be reported.

Homogeneity Assessment of Study Material

The homogeneity of the sediment material was assessed by analyzing duplicate 1.0 g subsamples from each of 12 jars of sediment. The material was extracted by accelerated-solvent-extraction (ASE) with hexane/acetone (1:1 volume fraction) at 160 ºC for 6 cycles. The extracts were concentrated to 1 mL. Then 0.5 mL supernatant was eluted through a silica gel SPE cartridge with dichloromethane /hexane (3:7 volume fraction) and the eluent was concentrated to 0.5 mL. The samples were analyzed by GC-MS; GBW08736 Aromatic Hydrocarbons in acetonitrile was used as a calibrant. Based on the measurements from the homogeneity assessment, the target mass fraction ranges were as follows: 400 μg/kg - 4000 μg/kg.

The results of the homogeneity assessment reported as the coefficient of variation (CV) for the 4 target PAHs are listed in Table 3. One-way ANOVA with F-test in accordance with the requirements as stipulated in ISO Guide 35 was used to test whether there were significant between-packet differences in the concentration of the measurand (Table 3). The estimated between-packet standard deviations proved to be smaller than within group standard deviations. The value of the relevant F-test ratios, F, is small, and P-value is larger than the usual critical 0.05 confidence level, which indicates that the inhomogeneity was not statistically significant.

Table 3: Results of the homogeneity assessment for four PAHs in sediment sample

ANOVA Estimate	**Fluoranthene**	**Benzo[a]pyrene**	**Benzo[ghi]perylene**	**Phenanthrene**
Within-packet, CV_{wth}:	1.50%	1.52%	1.93%	1.68%
Between-packet, CV_{btw}:	2.31%	2.22%	2.46%	1.88%
Total analytical variability, CV:	1.93%	1.89%	2.20%	1.78%
p-value（Probability of falsely rejecting the hypothesis that all samples have the same concentration）:	0.076	0.107	0.211	0.355

Stability Assessment of the Study Material

Long-term stability assessment at two storage conditions, -18 °C, and 20 °C. Two samples were selected randomly at the storage condition of -18 °C for testing at the 0, 6, 12, 24, and 36 months and analyzed in duplicate by GC-IDMS. Similarly, stability studies were performed for 4 time points (0, 1, 3 and 5 months) at a temperature of +20 °C. The trend graphs of stability are shown in Figures 5 and 6. The trend-analysis technique proposed by ISO Guide 35 was applied to assess the stability. The effect of time on the stability was evaluated using a linear approximation model by fitting linear regression lines to the data set ($Y=\beta_0-\beta_1X$). The statistical results indicated that no significant trend at 95% confidence level was detected as the absolute values of β_1 (ie., slope of the regression line) were smaller than the critical values of β_1, which were the uncertainty associated with the slope of the regression line for the stability times the respective Student's t-factor. Hence, the instability of the material was insignificant at the study temperature over the study period.

Short-term stability was not performed for this sediment material. Based on previous transportation conditions for CCQM comparison samples of PAHs in matrix, The sample is inferred to be stable during transportation.

INSTRUCTIONS AND SAMPLE DISTRIBUTION

Each participant will receive 3 jars, each containing 10 g of sediment. One sample jar is intended for method development and the other two are to be used for determining the final results. The material within the jars is suggested to be mixed thoroughly by stirring or shaking before subsampling. The minimum sample intake of 1.0 g is recommended. Participants may use their preferred laboratory procedures. For long term storage, the sample temperature should be kept below 20 °C.

At the time of sample dispatch, a sample receipt form will be provided electronically to all participants that must be completed and returned by email to the study coordinator (tanghua@nim.ac.cn, tanghua16@163.com) on receipt of the shipment. The result reporting form and core competency template will be provided to each participant via email.

RESULTS

Reporting of Results

Each participant must provide results using the result reporting form provided with the samples including the core competency table. The results should be emailed to the study coordinator (tanghua@nim.ac.cn) before the submission deadline. The results should be reported in the unit of µg/kg for 3 or 4 PAHs on a dry-mass basis (dry-mass correction should be reported). The reported mass fraction will be the mean value from measurements of two sample units, reporting should include the three subsamples values of each sample unit. Information on the measurement procedure should also be reported: extraction, clean-up, column and analytical conditions, quantification approach, the calibration standards, the internal standard, any quality control materials, the number of replicates, the calculation of the results and the estimation of measurement uncertainty should be included.

Evaluation of Results

All the results of the pilot and key comparison will be evaluated against the key comparison reference value (KCRV). The KCRV will be determined from the results of all NMIs/DIs participating in the key comparison that would use appropriately validated methods with demonstrated metrological traceability. The draft A report will provide candidate estimates of the KCRV and its uncertainty for review and discussion by the OAWG.

Available Calibration Materials

Participants are reminded to meet the Metrological Traceability requirements of the Comparison Calibrator Materials used, as defined by the CIPM MRA, and described in section 7.7 of the OAWG Practices and Guidelines (version 8). The value assigned to the primary calibrant used in a key comparison can only be established from the NMI/DI's own primary realization or from that of another recognized NMI/DI, in both cases with evidence of relevant track A purity assignment competencies. Details of the sources of CRMs and isotopically labeled PAHs are summarized in table 4 and table 5. Table 6 lists matrix CRMs that are available to assist with method validation.

Table 4: List of pure and solution PAHs CRMs available as calibrants

Supplier	CRM	Certified value		Expanded uncertainty
HSA	Benzo[a]pyrene	Benzo[a]pyrene	995 mg/g	3.5 mg/g
NIM	Benzo[a]pyrene in Acetonitrile (GBW08734)	Benzo[a]pyrene	8.00 µg/g	0.16 µg/g (*k*=2)
NMIJ	Benzo[a]pyrene in 2,2,4-trimethylpentane (CRM 4213-a)	Benzo[a]pyrene	99.2 mg/kg	3.9 mg/kg (*k*=2)
NIM	Phenanthrene in Methanol (GBW(E)080477)	Phenanthrene	7.5 µg/mL	2.9% (*k*=2)
NIM		Phenanthrene	5.02 µg/g	2% (*k*=2)

	16 Polycyclic Aromatic Hydrocarbons in Acetonitrile (GBW08736)	Fluoranthene	5.00 µg/g	2% (*k*=2)
		Benzo[a]pyrene	4.88 µg/g	2% (*k*=2)
		Benzo[ghi]perylene	4.89 µg/g	2% (*k*=2)
NIST	Priority Pollutant Polycyclic Aromatic Hydrocarbons in Acetonitrile (SRM1647f)	Phenanthrene	4.57 mg/kg	0.05 mg/kg (*k*=2)
		Fluoranthene	9.71 mg/kg	0.16 mg/kg (*k*=2)
		Benzo[a]pyrene	6.22 mg/kg	0.11 mg/kg (*k*=2)
		Benzo[ghi]perylene	4.64 mg/kg	0.12 mg/kg (*k*=2)
NIST	Aromatic Hydrocarbons in Toluene (SRM2260a)	Phenanthrene	11.57 µg/g	0.12 µg/g (*k*=3)
		Fluoranthene	8.324 µg/g	0.087 µg/g (*k*=3)
		Benzo[a]pyrene	4.71 µg/g	0.17 µg/g (*k*=3)
		Benzo[ghi]perylene	5.669 µg/g	0.069 µg/g (*k*=3)

Table 5: List of isotopically labeled PAHs internal standards

Producer	Isotopically-labeled PAHs	Product Form	Concentration	Item No.
Cambridge Isotope Laboratories	Fluoranthene -$^{13}C_6$	Single Solution	100 µg/mL in Nonane	CLM-3597
	Benzo[a]pyrene-$^{13}C_4$	Single Solution	100 µg/mL in Nonane	CLM-2722
	Benzo[ghi]perylene-$^{13}C_{12}$	Single Solution	100 µg/mL in Nonane	CLM-1364
	Phenanthrene-$^{13}C_6$	Single Solution	100 µg/mL in Nonane	CLM-2451
	Fluoranthene-D_{10}	Single Solution	200 µg/ml in Isooctane	DLM-2140
	Benzo[a]pyrene-D_{12}	Single Solution	200 µg/mL in Isooctane	DLM-258
	Benzo[ghi]perylene- D_{12}	Single Solution	200 µg/mL in Toluene-D_8	DLM-2135
	Phenanthrene-D_{10}	Single Solution	200 µg/mL in Isooctane	DLM-371
	Fluoranthene-D_{10}	Neat	/	C20795100

Dr. Ehrenstorfer	Benzo[a]pyrene-D_{12}	Neat	/	C20635100
	Phenanthrene-D_{10}	Neat	/	C20920100
TRC	Benzo[ghi]perylene-D_{12}	Neat	/	B207702
	Benzo[a]pyrene-D_{12}	Neat	/	B287527
	Fluoranthene-D_{10}	Neat	/	F461992
	Phenanthrene-D_{10}	Neat	/	P294801
NIST	Fluoranthene-D_{10}	Mixed Solution	(41.6 ± 1.1) µg/mL in hexane/toluene (96:4 volume fraction)	SRM2269
	Phenanthrene-D_{10}	Mixed Solution	(24.76 ± 0.64) µg/mL in hexane/toluene (96:4 volume fraction)	SRM2269
	Benzo[a]pyrene D_{12}	Mixed Solution	(24.80 ± 0.73) µg/mL in hexane/toluene (96:4 volume fraction)	SRM2270
	Benzo[ghi]perylene- D_{12}	Mixed Solution	(23.49 ± 0.62) µg/mL in hexane/toluene (96:4 volume fraction)	SRM2270

Table 6: List of matrix PAHs CRMs available

Supplier	**CRM**	**Certified value**		**Expanded uncertainty**
BAM	Polycyclic Aromatic Hydrocarbons in Soil (BAM-U013c)	Phenanthrene	7.0 mg/kg	0.5 mg/kg (k=2)
		Fluoranthene	14.2 mg/kg	0.7 mg/kg (k=2)
		Benzo[a]pyrene	8.1 mg/kg	0.8 mg/kg (k=2)
		Benzo[ghi]perylene	5.5 mg/kg	0.4 mg/kg (k=2)
NIST	Great Lakes Sediment (SRM1936)	Benzo[ghi]perylene	1690 ng/g	$U_{95\%}$= 90 ng/g
NIST	Organics in Marine Sediment (SRM1941b)	Phenanthrene	406 µg/kg	44 µg/kg (k=2)
		Fluoranthene	651 µg/kg	50 µg/kg (k=2)
		Benzo[a]pyrene	358 µg/kg	17 µg/kg (k=2)
		Benzo[ghi]perylene	307 µg/kg	45 µg/kg (k=2)
NIST	New York/New Jersey Waterway Sediment (SRM1944)	Phenanthrene	5.27 mg/kg	$U_{95\%}$=0.22 mg/kg
		Fluoranthene	8.92 mg/kg	$U_{95\%}$=0.32 mg/kg
		Benzo[a]pyrene	4.30 mg/kg	$U_{95\%}$=0.13 mg/kg
		Benzo[ghi]perylene	2.84 mg/kg	$U_{95\%}$=0.10 mg/kg
NIST	Organic Contaminants in House Dust (SRM2585)	Phenanthrene	1920 µg/kg	20 µg/kg (k=4)
		Fluoranthene	4380 µg/kg	100 µg/kg (k=2)
		Benzo[a]pyrene	1140 µg/kg	10 µg/kg (k=4)
		Benzo[ghi]perylene	2280 µg/kg	40 µg/kg (k=2)

NIST	New Jersey Soil Organics and Trace Elements (SRM706)	Phenanthrene	0.471 mg/kg	0.046 mg/kg (*k*=2)
		Fluoranthene	0.516 mg/kg	0.066 mg/kg (*k*=2)
		Benzo[a]pyrene	0.255 mg/kg	0.032 mg/kg (*k*=2)
		Benzo[ghi]perylene	0.363 mg/kg	0.060 mg/kg (*k*=2)

USE OF CCQM-K184 (PAHs in Sediment) IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far Does the Light Shine

Successful participation in CCQM-K184 demonstrate participants' capabilities in determining low-polarity analytes (pK_{ow} < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in abiotic dried matrix.

This may include demonstration of measurement capabilities such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC-FLD or LC-MS, etc.

Update, 18-Mar-2024

From: Tanghua < tanghua@nim.ac.cn >
Sent: Monday, March 18, 2024 10:48 AM
Subject: Deadline of CCQM-K184/P235 extended to June 30, 2024

Dear Colleagues,

Due to the reported problems from participants， the deadline for reporting CCQM-K184/P235 results is extended to June 30, 2024. I would appreciate getting your result forms before this deadline.

Best regards

Tang Hua

Organic Chemistry Group
Division of Chemical Metrology and Analytical Science
National Institute of Metrology, China

APPENDIX C: Registration Form

REGISTRATION FORM

CCQM-K184 or CCQM-P235

Low-Polarity Analytes in Abiotic Matrix: PAHs in Sediment

REQUEST FOR REGISTRATION TO PARTICIPATE IN:

☐CCQM-K184
☐ CCQM-P235
(Click to check your selection. Participation in the CCQM-K184 comparison is only allowed for NMIs or Designated Institutes recognized under the CIPM MRA)

INSTITUTE / LABORATORY:

____

____

FULL ADDRESS FOR SHIPMENT OF SAMPLES

____

____

____

CONTACT PERSON

(Prof / Dr / Mr / Ms) ____

E-MAIL, TELEPHONE and FAX

____

____

____

SIGNATURE ____

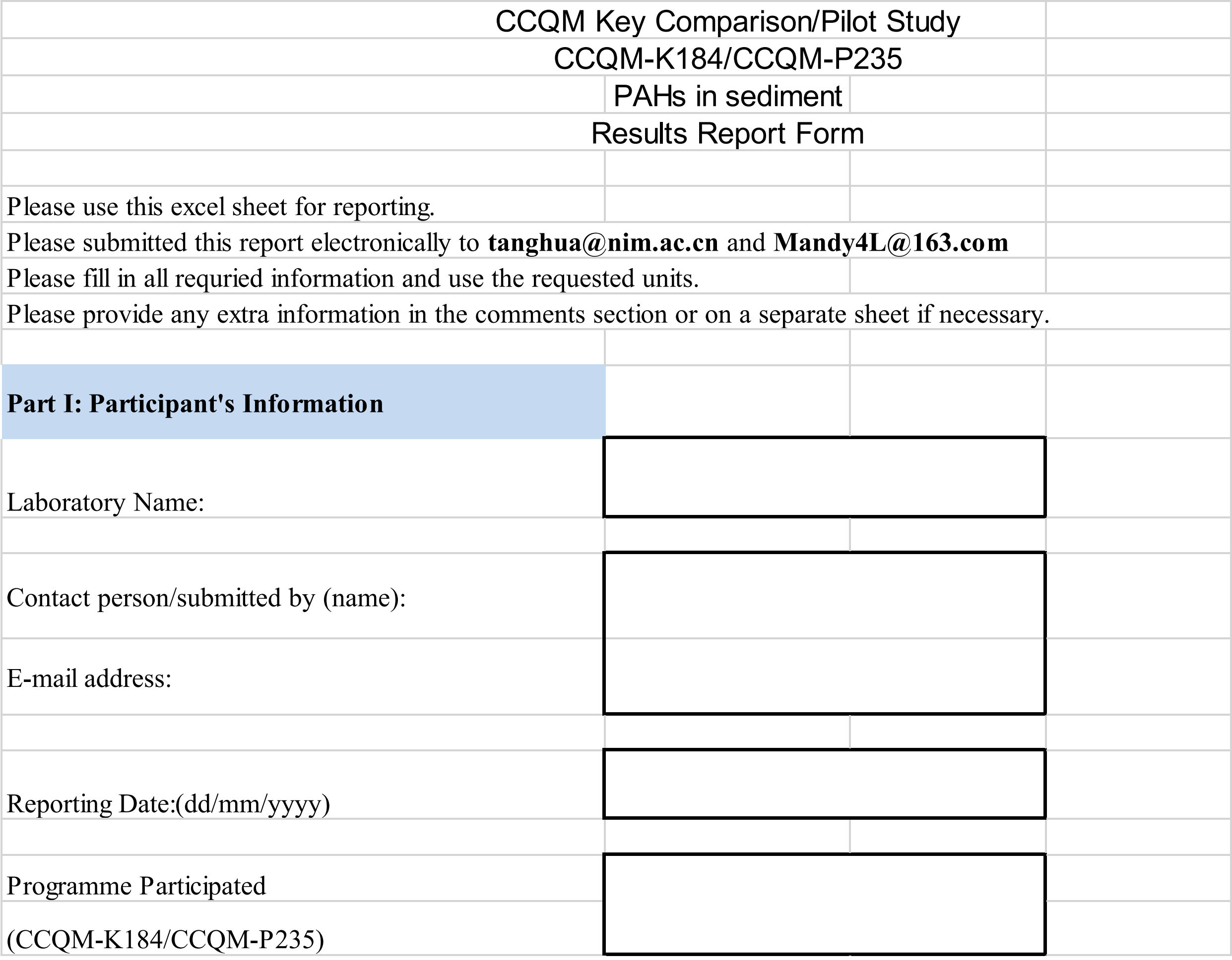
DATE ____

Complete and return to tanghua@nim.ac.cn & Mandy4L@163.com **before September 30, 2023.** If you do not receive an acknowledgement from us within 4 working days, please send us an email.

APPENDIX D: Reporting Form

The original form was distributed as an Excel workbook. The following are pictures of the relevant portions of the workbook's three worksheets.

"Participant Details" worksheet



CCQM Key Comparison/Pilot Study
CCQM-K184/CCQM-P235
PAHs in sediment
Results Report Form

Please use this excel sheet for reporting.
Please submitted this report electronically to **tanghua@nim.ac.cn** and **Mandy4L@163.com**
Please fill in all requried information and use the requested units.
Please provide any extra information in the comments section or on a separate sheet if necessary.

Part I: Participant's Information

Laboratory Name:	
Contact person/submitted by (name):	
E-mail address:	
Reporting Date:(dd/mm/yyyy)	
Programme Participated (CCQM-K184/CCQM-P235)	

Part II: Results:

Sample No. used for reporting		
Moisture content (w/w %)		

Analyte/ Mass Fraction	**Sample No.**		**Mass Fraction (µg/kg)**	**Overall Mean value (µg/kg)**	**Combined Standard Uncertainty (µg/kg)**	**Coverage Factor (k)**	**Expanded Uncertainty (µg/kg)**
Phenanthrene (optional)		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					
		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					
Fluoranthene		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					
		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					
Benzo[a]pyrene		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					
		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					
Benzo[ghi]perylene		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					
		SubSample 1					
		SubSample 2					
		SubSample 3					
		Mean					

Note: Please refer to the OAWG guidance document on significant figures when reporting values.

Part III: Information about the analytical procedure	
Sample amount used for analysis (g)	
Moisture content method (Please briefly describe the moisture determination procedure)	
Extraction method/conditions (Please briefly describe the extraction procedures, e.g., Soxhlet, ASE, Ultrasonic, solvent, etc., solvents, volumne, time, temperature etc.)	
Post extraction clean-up method and the transformation procedure, if any (e.g., SPE, etc)	
Analytical instrument (s) used (e.g., GC-MS, HPLC-FLD, LC-MS/MS, etc) (Please specify the model)	
Chromatographic Column (i.e., specify type and manufacturer)	
The chromatographic condition(s) (e.g., GC temperature program, LC mobile phase and gradient, etc)	
MS Settings	
Method of quantification (e.g., external calibration, internal standard calibration, IDMS, etc)	
Type of calibration (e.g., single-point, bracketing, three-point calibration curve, etc.)	
Native calibration standards: source, confirmation of identity, value assignment, uncertainty and traceability	
Reference material used for calibration is in compliance with the requirements for Traceabilty in CIPM MRA (Document No.: CIPM 2009-24; latest update: Revised 13 Oct. 2009):	

Indicate ion/MRM monitored in Mass Spectrometer

Internal standards used (if applicable)

(Please specify the compounds, sourse, and at which stage of the analysis were the internal standards added)

Part IV: Uncertainty budget

The measurement equations used to calculate the mass fraction of each analyte. Please provide details of all the factors listed in the equations and indicate how these values were determined.

Estimation of uncertainty for each factor. Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

Part V: Comments / additional information

Other information, observation or evidences, if any, that can further support your results.

APPENDIX E: Core Competency Claimed by Participant

Table E-a: Core Competencies Demonstrated in CCQM-K184 by KRISS

CCQM-K184	***KRISS***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓, ×, or N/A**	**Specific Information as Provided by *KRISS***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Neat commercial calibrants for fluoranthene, benzo(a)pyrene, benzo(ghi)perylene from sigma-aldrich, SUPELCO, Accustandard, respectively. Purity of each compounds were assayed by KRISS with mass-balance method.
Identity verification of analyte(s) in calibration material. #	√	ID-GC/MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	√	The purities of the primary materials were determined following protocols maintained in KRISS. GC-FID used for the analysis of structurally related impurities, Karl-Fischer Coulometry for water content, thermogravimetric analysis for non-volatile impurities, headspace-GC/MS for residual solvents. As a result, the purities of fluoranthene, benzo(a)pyrene, benzo(ghi)perylene were 98.80 ± 0.13 % (k=2.04) .98.76 ± 0.50 % (k = 2.05), 97.59 ± 0.35 % (k=2.45), respectively.
For calibrants which are a calibration solution: Value-assignment method(s).#	√	Calibration solutions were gravimetrically prepared in KRISS and verified by cross-checking of multiple calibration solutions.
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	GC retention time, mass spec ion ratios, comparison of GC/MS measurement results by low and high resolution SIM.
Extraction of analyte(s) of interest from matrix	√	ASE, 1500 psi, toluene:methanol (1:1, v:v), 200 °C, 20 min, 2 cycles

Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	silica SPE, hexane:DCM (4:1, v:v) elution
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC/MS, Resolution = 1000 (verified by high resolution MS R=10000)
Calibration approach for value-assignment of analyte(s) in matrix	√	Gravimetrically prepared calibration solution was used as a calibrant. For ID-GC/MS analysis, calibration blend was prepared by gravimetrically mixing the calibration solution and the internal standard solutions (Fluor-d10, $^{13}C_4$-BaP, $^{13}C_{12}$-BghiP). IDMS with exact matching single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Calibration solutions were gravimetrically prepared in KRISS and verified by cross-checking of multiple calibration solutions. NIST SRM 2260a (PAHs in toluene) was also used for secondary confirmation, which were good agreement with the KRISS calibration solutions. As the confirmation for instrumental analysis, we also applied high resolution MS condition (R=10,000) to the same samples, which were good agreement with the primary method (GC/MS: R =1000). NIST SRM 1941b was used for the verification of analytical method. When extracting naturally contaminated environmental samples, it has been reported that extraction efficiency may vary depending on the solvent used, extraction temperature, and extraction method in many previous studies. Even if IDMS was applied. Because the sample amount of K184 was very limited, some tests were conducted on ASE extraction solvents and temperatures using SRM 1941b, and it was observed that the results were quite different depending on the solvent and the extraction temperature of ASE. Considering these verification results, the K184 sediment samples from the same bottle were extracted in two different conditions. (1) toluene:methanol (1:1, *v*:*v*), 200 °C, 20 min, 2 cycles and (2) hexane:acetone (1:1, *v*:*v*), 5 min, 160 °C, 5 cycles. The results from two different extraction condition were not agreed within the uncertainty. Condition (2) is a similar method that NIM China used to evaluate the homogeneity of K184 samples. We finally submit the results with (1) condition as we think that harsher conditions better extract PAHs adsorbed and absorbed on the sediment samples. However, due to differences in the results depending on the extraction solvent or the extraction temperature of ASE, it needs to be discussed.

		As supplementary results, the results with (2) condition (hexane:acetone (1:1), 160 °C, 5 cycles) are also attached (in the supplementary sheet).
Other	N/A	

Table E-b: Core Competencies Demonstrated in CCQM-K184 by LNE

CCQM-K184	***LNE***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *LNE***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Calibration solution: NIST 2260a
Identity verification of analyte(s) in calibration material. #	√	Mass spectra, Retention time, individual calibrants
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	/
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	/
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time, mass ratio
Extraction of analyte(s) of interest from matrix	√	Microwave
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	/
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	/
Analytical system	√	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	√	a) IDMS b) 6-points calibration curve
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	/
Other	N/A	/

Table E-c: Core Competencies Demonstrated in CCQM-K184 by NIST

CCQM-K184	***NIST***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *NIST***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	**√**	NIST SRM 2260a Aromatic Hydrocarbons in Toluene was used for calibration solutions. SRMs 2269 Perdeuterated PAH-I solution in hexane/toluene and 2270 Perdeuterated PAH-II solution in hexane/toluene were used for isotope dilution.
Identity verification of analyte(s) in calibration material. #	**√**	Information from the SRM 2260a certificate of analysis, chromatographic retention, mass spectrometry.
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	**√**	The PAH components used to produced SRM 2260a were purity assigned by qNMR. Mass fractions were determined via gravimetry and measurements with independent calibration solutions.
For calibrants which are a calibration solution: Value-assignment method(s).#	**√**	SRM 2260a was gravimetrically diluted with hexanes, the diluted solutions were gravimetrically spiked with SRMs 2269 and 2270 to add the internal standard. An internal standard approach to calibration was used with a linear regression forced through zero.
Sample Analysis Competencies		
Identification of analyte(s) in sample	**√**	Retention times, specific mass/charge (m/z) spectrometric ratios for targeted PAHs, presence of quant/qual ions.
Extraction of analyte(s) of interest from matrix	**√**	Pressurized liquid extraction with hexane/acetone (50/50 by volume) at 160 ^{o}C, two sequential extractions combined.

Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Filtration with 0.45 µM PTFE syringe filter to remove any particles.
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	Not used
Analytical system	√	Gas chromatography/mass spectrometry (GC/MS), single quadrupole.
Calibration approach for value-assignment of analyte(s) in matrix	√	a) Indicate quantification mode used (i.e. IDMS, internal standard, external standard, other): *IDMS* b) Indicate calibration mode used (i.e, single-point calibration, bracketing, x-point calibration curve, other): *Multipoint calibration spanning above and below the concentrations of the relevant PAHs in the CCQM material and in the NIST SRM 1941b used as control[.*]*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Indicate any confirmative method(s) used, if any: *SRM 1941b Organics in Marine Sediment used as a control*
Other	N/A	Indicate any other competencies demonstrated: *None*

Table E-d: Core Competencies Demonstrated in CCQM-K184 by CENAM

Remark: results were not included in the calculation of the KCRV as the purity assignment of the calibrator did not meet CIPM metrological traceability requirements.

<table>
<tr><th>CCQM-K184</th><th colspan="2"><i>CENAM</i></th><th>PAHs in Sediment</th></tr>
<tr><td colspan="4">Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities.

such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.</td></tr>
<tr><td colspan="2">Competency</td><td>✓,⍰, or N/A</td><td>Specific Information as Provided by <i>CENAM</i></td></tr>
<tr><td colspan="4">Competencies for Value-Assignment of Calibrant</td></tr>
<tr><td colspan="2">Calibrant: Did you use a “highly-pure substance” or calibration solution?</td><td>√</td><td>Highly pure substance: Benzo[a]pyrene, Supelco; Benzo[ghi]perylene, Ultra scientific; Phenanthrene, Aldrich Chem; Fluoranthene, Aldrich Chem.</td></tr>
<tr><td colspan="2">Identity verification of analyte(s) in calibration material. #</td><td>√</td><td>Retention time and SIM GC-MS: Phenanthrene, ion 178; Phenanthrene d12 ion 188, Fluoranthene, ion 202, Fluoranthene d10, ion 212, Benzo[a]pyrene, ion 252, Benzo[a]pyrene d12, ion 264, Benzo[g,h,i]perylene, ion 276, Benzo[g,h,i] perylene d12, ion 288.

MRM: Phenanthrene, 178->177; Phenanthrene d12, 188>184, Fluoranthene, 202 -> 201, Fluoranthene d10, 212>208, Benzo[a]pyrene, 252.1 -> 250.1, Benzo[a]pyrene d12, 264.1 -> 260.1, Benzo[g,h,i]perylene, 276 -> 274, Benzo[g,h,i]perylene d12, 288 -> 284. time retention LC- DAD-FLD at 254 nm wavelength,</td></tr>
<tr><td colspan="2">For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#</td><td>√</td><td>The purity value was calculated using the mass balance method.
GC-FID with three columns with different stationary phase were used and for determination of water content was used Karl Fischer method.</td></tr>
<tr><td colspan="2">For calibrants which are a calibration solution: Value-assignment method(s).#</td><td>N/A</td><td></td></tr>
<tr><td colspan="4">Sample Analysis Competencies</td></tr>
<tr><td colspan="2">Identification of analyte(s) in sample</td><td>√</td><td>Retention time and SIM or MRM ion pairs Phenanthrene, ion 178; Phenanthrene d12 ion 188, Fluoranthene, ion 202, Fluoranthene d10, ion 212, Benzo[a]pyrene, ion 252, Benzo[a]pyrene d 12, ion 264, Benzo[g,h,i]perylene, ion 276, Benzo[g,h,i]perylene d12, ion 288. MRM:</td></tr>
</table>

		Phenanthrene, 178->177; Phenanthrene d12, 188->184, Fluoranthene, 202 -> 201, Fluoranthene d10, 212->208, Benzo[a]pyrene, 252.1 -> 250.1, Benzo[a]pyrene d 12, 264.1 -> 260.1, Benzo[g,h,i]perylene, 276 -> 274, Benzo[g,h,i]perylene d12, 288 -> 284. time retention LC- DAD-FLD at 254 nm wavelength
Extraction of analyte(s) of interest from matrix	√	Automated Soxhlet Extraction by using Hexane:acetone 1:1, 60 cycles
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Silica SPE Cartridge 1g , eluting with 3 mL of hexane-acetone mixture, sample and finally 1 mL of hexane, Evaporation to dryness and reconstitution with 200 µL of acetonitrile, Filtration with PVDF acrodisc of 0.2 µm
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS/MS and LC-DAD-FLD
Calibration approach for value-assignment of analyte(s) in matrix	√	Internal standard; 5-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Certified reference material SRM-1941b as control
Other	N/A	

The expanded uncertainty for the degree of equivalence of phenanthrene and fluoranthene does not cross zero, indicating that their values are not consistent with the KCRV.

Table E-e: Core Competencies Demonstrated in CCQM-K184 by VNIIM

CCQM-K184	***VNIIM***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *VNIIM***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Calibration solution NIST SRM 1647f
Identity verification of analyte(s) in calibration material. #	√	GC-MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	√	Certificate of Analysis Standard Reference Material 1647f (Certificate Issue Date: 13 May 2021)
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time, ions ratio in the mass spectrum
Extraction of analyte(s) of interest from matrix	√	Soxhlet extraction, 24 h
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS/MS Agilent 7000D GC/MS Triple Quad
Calibration approach for value-assignment of analyte(s) in matrix	√	IDMS single-point calibration
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	Supelco CRM104 PAH - Sediment 1
Other	N/A	Indicate any other competencies demonstrated.

Table E-f: Core Competencies Demonstrated in CCQM-K184 by IH

Remark: results were withdrawn for Phenanthrene, Fluoranthene, Benzo[a]pyrene, Benzo[ghi]perylene – competencies cannot be claimed.

CCQM-K184	***IH***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *IH***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	It was used several calibration solutions (0.100 µg/mL to 2.23 µg/mL) prepared by dilution from the certified reference materials: - ampoule "EPA Method 610/8100 PAH Mixture" (Dr Ehrenstorfer, Refª DRE-GA09000161BD, Batch 2-H473805NA) with phenanthrene, fluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene at 2000 µg/mL; - ampoule "EPA Method 8270 Internal Standard Mixture 2000" (Dr Ehrenstorfer, Refª DRE-YS09000038DI, Batch 2 H470128DI) with phenanthrene-d10, chrysene-d12 and perylene-d12 at 2000 µg/mL (internal standards).
Identity verification of analyte(s) in calibration material. #	√	Chromatographic identification was accepted if the two requirements below are met: - the peak retention time deviation in the sample is less than 0.100 min compared to the retention time defined as a reference; - the deviation of the abundance ratio between the confirmation fragment and the quantification fragment is lower than the defined tolerance (http://data.europa.eu/eli/dec/2002/657/oj) in comparison with the abundance ratio stipulated as a reference.
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	√	The value-assigning, purity and assessment methods of the calibrants used were obtained from the certificates of the calibrants (certified reference

		materials). The certified value is based on gravimetric and volumetric preparation of the certified reference materials confirmed by GC-MS analysis.
For calibrants which are a calibration solution: Value-assignment method(s).#	√	The concentrations of the analytes in the calibration solutions were obtained by calculation, considering the dilution volumes and the certified value of the analyte concentration present in the certificate of analysis of the certified reference material.
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Chromatographic identification was accepted if the two requirements below are met: - the peak retention time deviation in the sample is less than 0.100 min compared to the retention time defined as a reference by a calibration solution; - the deviation of the abundance ratio between the confirmation fragment and the quantification fragment is lower than the defined tolerance (http://data.europa.eu/eli/dec/2002/657/oj) in comparison with the abundance ratio stipulated as a reference by a calibration solution.
Extraction of analyte(s) of interest from matrix	√	Extraction was performed by Accelerated Solvent Extraction (ASE)
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Purification of extracts was carried out by adsorption chromatography in a glass column containing silica gel and basic aluminum oxide, both deactivated at 5%.
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	The instrumental analysis was performed by GC-MS with a mass spectrometry scanning mode in selected ion monitoring mode (SIM)
Calibration approach for value-assignment of analyte(s) in matrix	√	a) Quantification mode used: internal standard b) Calibration mode used: 8-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other		The method used is an internal method applied to determine the 16 PAHs considered priority substances by the US EPA. The determination of the 16 PAHs, as well as the triphenylene and benzo(j)fluoranthene, is currently accredited under NP EN ISO/IEC 17025:2018.The dry mass determination was carried out using an internal method accredited under NP EN ISO/IEC 17025:2018 (subsample size of 1 g each, dried in an oven at (105 ± 2) ºC until constant mass reached).

The values for phenanthrene, fluoranthene, benzo[a]pyrene and benzo[ghi]pyrene are not consistent with the KCRV, as evidenced by their degrees of equivalence having expanded uncertainties that do not cross zero.

Table E-g: Core Competencies Demonstrated in CCQM-K184 by INM

Remark: results were withdrawn for Phenanthrene, Fluoranthene, Benzo[a]pyrene, Benzo[ghi]perylene – competencies cannot be claimed.

CCQM-K184	***INM***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *INM***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Calibrant solution: Priority Pollutant Polycyclic Aromatic Hydrocarbons in Acetonitrile (SRM1647f) by NIST: Phenanthrene 4.57 mg/kg U= 0.05 mg/kg (k=2) Fluoranthene 9.71 mg/kg U= 0.16 mg/kg (k=2) Benzo[a]pyrene 6.22 mg/kg U= 0.11 mg/kg (k=2) Benzo[ghi]perylene 4.64 mg/kg U= 0.12 mg/kg (k=2)
Identity verification of analyte(s) in calibration material. #	√	Retention time, mass spectrometry ion ratios by GC-MS/MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	√	According to the certificate, concentrations were obtained by multiplying the certified values in milligrams per kilogram by the density of acetonitrile at 23 °C (0.7789 g/mL), and an allowance for the change in this density over the rang 20 °C to 25 °C is included in the uncertainty.
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time, mass spectrometry ion ratios

	Transition	Qualifier
Phenanthrene	178.0 -> 152.0	178.0 -> 177.0
		176.0 -> 149.8
		152.0 -> 125.8
Fluoranthene D10	212.1 -> 208.1	106.0 -> 92.0
		208.1 -> 180.0
		208.1 -> 156.1
Fluoranthene	202.0 -> 200.0	101.0 -> 88.0
		200.0 -> 174.0
		200.0 -> 150.0
Benzo-a-pyrene D12	132.0 -> 118.0	264.1 -> 260.1
		118.0 -> 104.0
Benzo-a-pyrene	252.0 -> 250.0	126.0 -> 113.0
		113.0 -> 111.2
		250.0 -> 224.0
Benzo-ghi-perylene_D12	142.0 -> 140.0	144.0 -> 130.0
		144.0 -> 142.0
		288.0 -> 284.1
Benzo-ghi-perylene	138.0 -> 137.0	276.0 -> 274.0
		138.0 -> 124.9
		125.0 -> 123.2

Extraction of analyte(s) of interest from matrix	√	A 2.00 g sub-sample of the KC item was weighed in a 50 mL flask, and 6.8 g of a n-hexane:acetone (1:1, v/v) mixture was added. After that, an aliquot of 0.14 g of internal standard solution was added. This mixture was vigorously shaken by hand for 30 seconds. Subsequently, 1.0 g of magnesium sulfate was added, shaking immediately by hand for one minute, and then ultrasonicated for 15 minutes. Finally, the tubes were centrifuged at 7500 xg for 5 minutes at 15 °C.
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	6 mL of the crude extract was subjected to cleaning by dispersive solid-phase extraction (d-SPE) using a mixture consisting of 900 mg of anhydrous magnesium sulfate, 150 mg of PSA, and 150 mg of C18, followed by shaking for 30 s. Finally, the mixture was centrifuged at 7500 xg for 5 minutes at 15 °C. 4.00 g of the clean extract were filtered through a PTFE filter and dried under a nitrogen stream at 35 °C and reconstituted with 1.00 g of ethyl acetate
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	Indicate chemical transformation method(s), if any, (i.e., hydrolysis, derivatization, other)
Analytical system	√	Gas chromatograph Agilent 8890 Mass spectrometer Agilent 7000E Hydrogen generator Peak 450 Hydrogen as a carrier gas
Calibration approach for value-assignment of analyte(s) in matrix	√	Internal standard Bracketing
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Reference material LGC6188 River sediment- PAHs by LGC was used as a quality control, for method and extraction procedures development and bias evaluation
Other	N/A	

The values for phenanthrene, fluoranthene, benzo[a]pyrene and benzo[ghi]pyrene are not consistent with the KCRV, as evidenced by their degrees of equivalence having expanded uncertainties that do not cross zero.

Table E-h: Core Competencies Demonstrated in CCQM-K184 by INMETRO

CCQM-K184	***INMETRO***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,□, or N/A**	**Specific Information as Provided by *INMETRO***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Highly-pure substance. PAH purity determined by ^{1}H-qNMR.
Identity verification of analyte(s) in calibration material. #	√	Identity of each analyte in the calibration material was performed by NMR spectrum.
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	√	Purity value assignment of each PAH was performed by qNMR using the following Inmetro' internal standards: CRM 8792 - Maleic acid, for Phenanthrene and Fluoranthene; CRM 8783 - Dimethyl sulfone, for Benzo[a]Pyrene; and CRM 8784 - Dimethyl terephthalate, for Benzo[ghi]Perylene. Purity values assigned and expanded uncertainties (k=2, 95%): Phenantrene (996.0 ± 2.8) mg/g, Fluoranthene (993.8 ± 1.7) mg/g, Benzo[a]Pyrene (971.6 ± 3.8) mg/g and Benzo[ghi]Perylene (980.1 ± 2.0) mg/g.
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention times and ions monitored (m/z) in GC-MS/MS
Extraction of analyte(s) of interest from matrix	√	Analytes were extracted from matrix by ultrasonic extraction.
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Solid phase extraction with silica column, addition of Zn/Cu mixture and sodium sulfate (Na2SO4), elution with hexane/dichloromethane (70:30, v:v).

Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS/MS (Triple Quadrupole)
Calibration approach for value-assignment of analyte(s) in matrix	√	a) Quantification mode used: IDMS. b) Calibration mode used: bracketing calibration.
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Two calibration solutions were prepared independently and used for cross-confirmation of the results. Certified Reference Materials (SRM 1941b, SRM 1944, and BCR 524) were used as Control samples.
Other	N/A	

Table E-i: Core Competencies Demonstrated in CCQM-K184 by NIM

CCQM-K184	***NIM***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *NIM***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Highly-pure substances were used. Phenanthrene was obtained from Supelco, fluoranthene was obtained from Chem Service, benzo[a]pyrene was obtained from Cerilliant and benzo[ghi]perylene AccuStandard.
Identity verification of analyte(s) in calibration material. #	√	Mass fractions were determined via gravimetry and measurements with independent calibration solutions.
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	√	HPLC-DAD and GC-FID were employed to identify related structural impurities. Moisture content was determined via Karl Fischer titration. Residual solvents were analyzed using headspace-GC/MS, while inorganic content was assessed by ICP-MS.. The purity value was calculated using the mass balance method.
For calibrants which are a calibration solution: Value-assignment method(s).#	√	Gravimetric control of dilutions
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention times, mass spec ion ratios, comparison with authentic compounds from other sources
Extraction of analyte(s) of interest from matrix	√	ASE with toluene
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	SPE with silica column
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	√	a) GC-IDMS with 13C isotopes of PAHs as internal standard b) Single-point calibration was used for both PAHs
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

Table E-j: Core Competencies Demonstrated in CCQM-K184 by NIMT

Remark: results were withdrawn for Benzo[ghi]perylene and Benzo[a]pyrene was not submitted – competencies cannot be claimed for these parameters.

CCQM-K184	***NIMT***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *NIMT***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	A calibration solution (GBW(E)080477 was used for fluoranthene analysis. A mixture of PAH standards (SRM 1647f) was used for phenanthrene and benzo(ghi) perylene analyses.
Identity verification of analyte(s) in calibration material. #	√	MRM in GC-MS/MS
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	√	Gravimetric
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	MRM in GC-MS/MS
Extraction of analyte(s) of interest from matrix	√	50:50 Acetone: Dichloromethane, ASE
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS/MS
Calibration approach for value-assignment of analyte(s) in matrix	√	7-point calibration curve for Phenanthrene and Benzo(ghi)perylene. Exact-matching IDMS for Fluoranthene.
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Analysis of SRM 1941b: Organics in marine sediment was use as quality control.
Other	N/A	

The value for benzo[ghi]pyrene is not consistent with the KCRV, as evidenced by its degree of equivalence having an expanded uncertainty that does not cross zero. The value for benzo[a]pyrene was not submitted.

Table E-k: Core Competencies Demonstrated in CCQM-K184 by GLHK

CCQM-K184	***GLHK***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *GLHK***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Calibration solution from NIM (GBW08736)
Identity verification of analyte(s) in calibration material. #	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time, mass spec ion ratios, HRMS accurate mass measurement
Extraction of analyte(s) of interest from matrix	√	Sonication followed by saponification with potassium hydroxide in methanol, and liquid/liquid extraction by hexane.
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Activated copper granule for removal of sulphur-containing compounds, Activated silica gel chromatography
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS, GC-HRMS
Calibration approach for value-assignment of analyte(s) in matrix	√	IDMS with 4-point calibration curve and IDMS with bracketing
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

Table E-l: Core Competencies Demonstrated in CCQM-K184 by BAM

CCQM-K184	***BAM***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *BAM***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	Certified reference materials: NIST 1647f and NIST 2260a
Identity verification of analyte(s) in calibration material. #	√	Retention times, mass spec ion ratios, comparison with authentic compounds from other sources
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	√	Gravimetric control of dilutions
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Methods used to identify analytes in the sample: Retention time, mass spec ion ratios
Extraction of analyte(s) of interest from matrix	√	Extraction technique(s) used: ASE with toluene
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Filtration of fine particles
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	√	a) IDMS with labelled PAHs as internal standards b) 4-10-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Confirmative method(s): HPLC-DAD-F, two other GC-MS systems, two different CRMs for calibration; independent sets of calibration curves; intercalibration
Other	N/A	

Table E-m: Core Competencies Demonstrated in CCQM-K184 by NMIA

CCQM-K184	***NMIA***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *NMIA***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	NIST 2260a
Identity verification of analyte(s) in calibration material. #	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time on two separate columns and response on six or more MRMs
Extraction of analyte(s) of interest from matrix	√	ASE
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC- MSMS
Calibration approach for value-assignment of analyte(s) in matrix	√	IDMS using 8 point calibration
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	Two solvent systems used for ASE extraction and two chromatographic columns
Other	N/A	

Table E-n: Core Competencies Demonstrated in CCQM-K184 by INTI

Remark: results were withdrawn for Phenanthrene, Fluoranthene, Benzo[a]pyrene, Benzo[ghi]perylene – competencies cannot be claimed.

CCQM-K184	***INTI***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *INTI***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	NIST, SRM 1647f
Identity verification of analyte(s) in calibration material. #	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time and Mass spec ion ratios
Extraction of analyte(s) of interest from matrix	√	ASE. Extration solvent: dichloromethane/acetone 1:1. Temperature: 100°C. Pressure: 1500 psi. Cycles: 2.
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Silica gel column. Eluent solvent: Pentane/dichloromethane 3:2.
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	√	a) External standard. b) Calibration curve. Phenanthrene: 8-point. Fluoranthene: 8-point. Benzo[a]pyrene: 4-point. Benzo[ghi]perylene: 5-point.
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	√	1) NIST, SRM 2260a used as reference material for calibration 2)NIST, SRM 2269 and SRM 2270 were used as surrogates. Both were spiked before extraction for recovery control.

The values for phenanthrene, fluoranthene, benzo[a]pyrene and benzo[ghi]pyrene are not consistent with the KCRV, as evidenced by their degrees of equivalence having expanded uncertainties that do not cross zero.

Table E-o: Core Competencies Demonstrated in CCQM-K184 by TUBITAK_UME

CCQM-K184	***TUBITAK_UME***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *TUBITAK_UME***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	NIST, SRM 1647f
Identity verification of analyte(s) in calibration material. #	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time, mass ion
Extraction of analyte(s) of interest from matrix	√	Soxhlet
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	Sep-Pak silica SPE 1 g 6 cc
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS
Calibration approach for value-assignment of analyte(s) in matrix	√	a) IDMS b) 6-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	NIST SRM 1941b
Other		

Table E-p: Core Competencies Demonstrated in CCQM-K184 by METAS

CCQM-K184	***METAS***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *METAS***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	NIST, SRM 1647f
Identity verification of analyte(s) in calibration material. #	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	Retention time, mass spec ion ratios
Extraction of analyte(s) of interest from matrix	√	ASE
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	√	SPE
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS/MS
Calibration approach for value-assignment of analyte(s) in matrix	√	a) linear regression IDMS b) 9-point calibration curve
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	BAM-U013c was used as matrix CRM to verify method performance
Other	N/A	

Table E-q: Core Competencies Demonstrated in CCQM-K184 by LGC

Remark: results were withdrawn for Benzo[a]pyrene and Benzo[ghi]perylene – competencies cannot be claimed.

CCQM-K184	***LGC***	**PAHs in Sediment**
Scope of Measurement: Successful participation in CCQM-K184 demonstrates participants' capabilities in determining low-polarity analytes (pKow < -2) with molecular mass range from 170 to 500 g/mol at mass fraction levels of 100 [µg/kg] to 1000 000 [µg/kg] in an abiotic dried matrix. This may include demonstration of measurement capabilities. such as: (1) value assignment of primary reference standards; (2) value assignment of calibration solutions; (3) extraction of analyte of interest from the matrix; (4) clean-up and separation of analyte of interest from other interfering matrix or extract components; (5) separation and quantification using techniques such as GC-MS, GC-MS/MS, GC-HRMS, HPLC- FLD or LC-MS, etc.		
Competency	**✓,⍰, or N/A**	**Specific Information as Provided by *LGC***
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	NIST Calibration solution SRM 1647f Priority Pollutant Polycyclic Aromatic Hydrocarbons in Acetonitrile.
Identity verification of analyte(s) in calibration material. #	N/A	
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	2 MRM transitions, retention time, peak shape
Extraction of analyte(s) of interest from matrix	√	Soxhlet extraction – 1g of sediment extracted with 250 mL DCM:MeOH 2:1 v/v
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	GC-MS/MS
Calibration approach for value-assignment of analyte(s) in matrix	√	a) Quantification mode - double exact matching IDMS b) Calibration mode - bracketed single point
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	QC (CRM 104 LRAD7551) verified in house
Other	N/A	

The values for benzo[a]pyrene and benzo[ghi]pyrene are not consistent with the KCRV, as evidenced by their degrees of equivalence having expanded uncertainties that do not cross zero.

APPENDIX F: Summary of Participants' Analytical Information

The following Tables summarize the detailed information about the analytical procedures each participant provided in their "Analytical Information" worksheets. The presentation of the information in many entries has been consolidated and standardized.

The participant's measurement uncertainty statements are provided verbatim in Appendix G.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in these Tables to specify adequately experimental conditions or reported results. Such identification does not imply recommendation or endorsement by the National Institute of Metrology or other participant in this Key Comparison, nor does it imply that the equipment, instruments, or materials identified are necessarily the best available for the purpose.

Table F-1: Summary of Sample Size, Extraction, and Clean up for CCQM-K184

Participant	Extraction method	Sample size	Extraction solvent	Temp/°C	Other conditions for Extraction method	Clean-up method	Details for Clean-up method and the transformation procedure
KRISS	ASE	1 g	Toluene: Methanol (1:1, v:v)	200	1500 psi, 20 min, 2 cycles	SPE	Silica SPE, hexane:DCM (4:1, v:v) elution
KRISS supplementary method	ASE	1 g	Acetone/Hexane (1:1, v:v)	160	1500 psi, 25 min, 5 min, 5 cycles		
LNE	Microwave	1 g	20 mL Acetone/Hexane (1:1, v:v)	increase temperature during 3 mins from ambiant temperature to 110°C, 110°C during 15min and then final temperature: 45°C	850W and 600rpm	-	The extract is centrifuged and the supernatant is evaporated to dryness using a speedvack at 45°C. The final solvent is toluene
NIST	ASE	1 g	Acetone/Hexane (50/50 v/v)	160	5 min heat, 5 min static, 100% flush, purge for 90 s, 6 cycles, two rounds of extraction were combined	Filtration	Filtered concentrated extract through 0.45 µm Teflon syringe filter into 2 mL amber vial, diluted to 1 mL with hexanes (if necessary).
CENAM	Automated Soxhlet extraction	1 g	Acetone/Hexane (1:1, v:v)	-	60 cycles Duration of extraction: 4 hours	SPE	Silica Cartridge 1g, eluting with 3 mL of hexane-acetone mixture, sample and finally 1 mL of hexane, Evaporation to dryness and reconstitution with 200 µL of acetonitrile.

Table F-1: Summary of Sample Size, Extraction, and Clean up for CCQM-K184 (Continued)

Participant	Extraction method	Sample size	Extraction solvent	Temp/ °C	Other conditions for Extraction method	Clean-up method	Details for Clean-up method and the transformation procedure
VNIIM	Soxhlet extraction	0.5 g	Toluene /Acetone (50/50)	-	24 hours	-	-
IH	ASE	2 g	Hexane/ Acetone (50:50, v/v (%))	100	2000 psi, with 2 cycles of 5 min each, pre-heating time of 1 min, heating time of 5 min	Copper for removing sulfur and Column purification	2 g of copper strips were added to remove sulfur, leaving the extracts in contact with copper overnight. The purification of ASE extracts, previously concentrated to approximately 1 mL using a Turbovap equipment, was carried out by adsorption chromatography in a glass column containing 5 g of silica gel and 5 g of basic aluminum oxide, both deactivated at 5%. The elution was performed using 50 mL of hexane: dichloromethane (90:10, v/v (%)). The purified extracts were concentrated to approximately 1 mL using Turbovap and a stream of N2 (g), the necessary amount of a solution containing the internal standards was added, and the extracts were rigorously adjusted to a final volume of 1 mL.
INM	Ultrasonic extraction	2 g	6.8g n-hexane: acetone (1:1, v/v)	-	This mixture was vigorously shaken by hand for 30 seconds. Subsequently, 1.0 g of magnesium sulfate was added, shaking immediately by hand for one minute, and then ultrasonicated for 15 minutes.	d-SPE	6 mL of the crude extract was subjected to cleaning by dispersive solid-phase extraction (d-SPE) using a mixture consisting of 900 mg of anhydrous magnesium sulfate, 150 mg of PSA, and 150 mg of C18, followed by shaking for 30 s. Finally, the mixture was centrifuged at 7500*g* for 5 minutes. 4.00 g of the clean extract were filtered through a PTFE filter and dried under a nitrogen stream at 35 °C and reconstituted with 1.00 g of ethyl acetate.

Table F-1: Summary of Sample Size, Extraction, and Clean up for CCQM-K184(Continued)

Participant	Extraction method	Sample size	Extraction solvent	Temp/ °C	Other conditions for Extraction method	Clean-up method	Details for Clean-up method and the transformation procedure
INMETRO	Ultrasonic extraction	1 g	25 mL Dichloromethane/Hexane (50:50, v:v) for each circle	70	4 cycles of 20 minutes at a temperature of 70 °C	SPE	Solid phase extraction with silica column (SiO2, 1000 mg, 6 mL), addition 30:9 m:m Zn/Cu mixture and sodium sulfate (Na2SO4), 6 mL of a mixture of hexane/dichloromethane (70:30, v:v) was used as a carrier.
NIM	ASE	1 g	toluene	160	Static extraction time: 10 min； extraction cycles: 8; purge time: 100s; flush volume: 80%	SPE	The tube used in SPE is LC-Si (1g/6mL）. PAHs were eluted with 8 mL cyclohexane-DCM (7:3, v/v), which was followed by nitrogen blowing concentration.
NIMT	ASE	1 g	Acetone/Dichloromethane (1:1, v/v)	110	15 min for 6 cycles	-	-
GLHK	Sonication followed by saponification with potassium hydroxide in methanol, and liquid/ liquid extraction by hexane	1 g	Potassium hydroxide in methanol, hexane	-	-	Activated copper for removal of sulphur-containing compounds, Column chromatography	Activated copper granule for removal of sulphur-containing compounds, Column chromatography (silica gel)

Table F-1: Summary of Sample Size, Extraction, and Clean up for CCQM-K184 (Continued)

Participant	Extraction method	Sample size	Extraction solvent	Temp/°C	Other conditions for Extraction method	Clean-up method	Details for Clean-up method and the transformation procedure
BAM	ASE	1 g	Toluene	160	6 cycles for 30min	Filtration	Filtration of fine particles
NMIA	ASE	1 g	Either 1:1 hexane:acetone or 9:1 dichloromethane: acetonitrile Note: Phenanthrene and fluoranthene reported from samples extracted with dichloromethane: acetonitrile, and benzo(a)pyrene and benzo(ghi)perylene reported from separate extractions using both solvent mixtures.	100	5 min/cycle, 2 cycles, 1500 psi, flush volume 150%	Filtration	1 g aliquots of sample were weighed into glass vessels. 450 uL of internal standard solution was added gravimetrically. 2 mL of dichloromethane was added to the vessel and briefly vortexed to mix. The solvent was evaporated on a hot block at 50 C. Once dry, the sample was transferred to a 34 mL ASE cell partially filled with hydromatrix. The remaining cell volume was filled with hydromatrix before being subjected to accelerated solvent extraction. Extracts were reduced with solvent exchange to acetonitrile to 2 mL, and 1 mL of dichloromethane added before being filtered through a 0.2 um nylon filter.
INTI	ASE	2 g	Acetone / Dichloromethane (1:1, v/v)	100	1500 psi, 2 cycle, 20 time	Column Chromatography	Column (Silica Gel). Eluent solvent: Pentane/Dichloromethane 3:2

Table F-1: Summary of Sample Size, Extraction, and Clean up for CCQM-K184 (Continued)

Participant	Extraction method	Sample size	Extraction solvent	Temp/°C	Other conditions for Extraction method	Clean-up method	Details for Clean-up method and the transformation procedure
TUBITAK_UME	Soxhlet (Buchi b 811)	1 g	130 mL Acetone/Hexane (1:1, v:v)	-	18 hours	SPE	Extracts evaporated under nitrogen stream at 35 °C to 1 mL. Silica SPE (Sep-Pak) 1 g 6 cc used for cleanup. PAHs eluted with 10 mL hexane:DCM (8:2) (v/v). Eluent evaporated to 1 mL then 0.5 mL toluene added as solvent keeper and evaporated to 0.5 mL under gentle nitrogen stream at 35 °C.
METAS	ASE	1 g	15mL Acetone/n-Hexane (1:1, v:v) for each cycle	150	6 cycles, for each cycle: 15 mL solvent, n-hexane: acetone (1:1), 150 °C, 3 min. hold time	SPE	SPE (Restek Resprep Silica, RT-28978)
LGC	Soxhlet extraction	1 g	250 mL DCM/MeOH (2:1, v/v)	-	72 hours	-	-

Table F-2: Summary of Analytical Techniques for CCQM-K184

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
KRISS	GC/MS (Agilent 7890 GC/Jeol 800D-UF MS)	Rxi-PAH (40 m x 0.18 mm x 0.07 µm)	90 °C (3min) - 8 °C/min - 320 °C (8 min)	SIM mode, low resolution R=1000 (verified by high resolution MS R=10000)	Fluoranthene (m/z 202.0783), Fluoranthene-d10 (m/z 212.1410), Benzo(a)pyrene (m/z 252.0939), Benzo(a)pyrene-$^{13}C_4$ (m/z 256.1073), Benzo(g,h,i)perylene (m/z 276.0939), Benzo(g,h,i)perylene-$^{13}C_{12}$ (m/z 288.1342)
LNE	GC-MS	DB-EUPAH (60 m × 0.25 mm×0.25 µm)	Injector temp : 280°C Injection Mode : Splitless Injection volume : 1µl Gas : He/ Flow: 1,2ml/min Oven program temperature : 80°C hold time 3 min, ramp 45°C/min to 200°C, ramp 10°C/min to 250°C, ramp 30°C/min to 320°C hold time 26min, Thermal Aux : 300°C	MS source temperature: 230°C MS Quad temperature: 150°C	Phenanthrene : 178/184, Fluoranthene : 202/208, Benzo(a)pyrene : 252/256, Benzo(ghi)perylene : 276/288
NIST	GC-MS (Agilent 8890/5977b)	Rxi-PAH (60 m x 0.25 mm x 0.25 µm)	2 ml/min constant flow helium, 40 ºC, 50 ºC/min to 100 ºC, 3 ºC/min to 320 ºC for 10 min.	MS source temperature : 230°C MS Quad temperature : 150°C Interface temperature: 300°C	Phenanthrene : 178/188, Fluoranthene : 202/212, Benzo(a)pyrene : 252/264, Benzo(ghi)perylene : 276/288

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
CENAM	GC-MS/MS(Agilent 7000C), GC-MS (Agilent 6890N), HPLC-FLD (Waters 2475) HPLC-DAD (Waters 2996)	GC: HP-5 (30 m x 0.32 mm x 0.25 µm) LC: WP Octadecyl C18 (4.6×250 mm,5 µm)	GC: Column flow: 1.3 mL/min initial temp 100°C for 1 min, 10 °C/min to 260°C for 5 min, 40°C/min to 300°C for 10 min LC: Flow 0.5 mL 100% methanol isocratic mode DAD: Phenanthrene and Fluoranthene: 254 nm; Perylene D12: 432 nm, Benzo[a]pyrene and Benzo[g,h,i]perylene: 298 nm FLD: Excitation wavelength 260 nm, emission wavelength 410nm, Perylene d12 was used as IS for HPLC	-	GC-MS: Phenanthrene, ion 178; Phenanthrene d12 ion 188, Fluoranthene, ion 202, Fluoranthene d10, ion 212, Benzo[a]pyrene, ion 252, Benzo[a]pyrene d 12, ion 264, Benzo[g,h,i]perylene, ion 276, Benzo[g,h,i]perylene d12, ion 288. MRM: Phenanthrene, 178->177; Phenanthrene d12, 188->184, Fluoranthene, 202 -> 201, Fluoranthene d10, 212->208, Benzo[a]pyrene, 252.1 -> 250.1, Benzo[a]pyrene d 12, 264.1 -> 260.1, Benzo[g,h,i]perylene, 276 -> 274, Benzo[g,h,i]perylene d12, 288 -> 284.
VNIIM	GC-MS/MS (Agilent 7000D), GC/MS Triple Quad	Rtx-Dioxin2 (60 m x 0.25mm x 0.25 µm)	Inlet 280˚C; Oven: 70˚C (1 min)-5˚C/min to 250-10˚C/min to 280˚C (1 min)-5˚C/min to 320 (30 min)	MS source temperature : 230°C MS Quad 1 temperature : 150°C MS Quad 2 temperature : 150°C	MRM Phenanthrene : 178→176 Fluoranthene : 202→200 Benzo(a)pyrene : 252→250 Benzo(ghi)perylene : 276→274
IH	GC-MS(Agilent 6890N/5975B)	one meter of deactivated fused silica capillary pre-column with 0.53 mm internal diameter DB-5 (60 m x 0.25 mm x 0.25 µm)	Injection port temperature: 3 °C above oven temperature Oven temperature program: 60 °C (1 min), 9 °C/min up to 100 °C, 5 °C/min up to 310 °C and isothermal at 310 ºC during 30 min	MS source temperature : 230°C MS Quad temperature : 150°C Electron impact energy: 70 eV	Fluoranthrene: Qion: 202, Cion: 200 Benzo(a)pyrene: Qion: 252, Cion: 250 Benzo(g,h,i)perylene: Qion:276. Cion: 274 Phenanthrene-d10: Qion:188, Cion:184 Chrysene-d12: Qion:240, Cion :236 Perylene-d12: Qion :264, Cion :260

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
INM	Gas chromatograph Agilent 8890 Mass spectrometer Agilent 7000E Hydrogen generator Peak 450 Hydrogen as a Carrier gas	Two Agilent HP-5MS UI with a backflush system	Oven: 100˚C (1 min)-25˚C/min to 200°C-4˚C/min to 215°C-25˚C/min to 280°C-10˚C/min to 305°C (4 min)	Source temperature: 300 °C Scan type: dMRM Total MRMs: 32 Number of MRM groups: 10 Minimum Concurrent MRMs: 3 Maximum concurrent MRMs: 9 Minimum Dwell time (ms): 2.02 Maximum Dwell time (ms): 48.48 Minimum cycle time (ms): 11.75 Cycles per second: 10 Calculate dwell using response level	Phenanthrene: Transition: 178→152, Qualifier: 178/177, 176/149.8, 152/125.8; Fluoranthrene: Transition: 202→200, Qualifier: 101/88, 200/174, 200/150; Fluoranthrene D10: Transition: 212.1→208.1, Qualifier: 106/92, 208.1/180, 208.1/156.1; Benzo(a)pyrene: Transition: 252→250, Qualifier: 126/113, 113/111.2, 250/224; Benzo(a)pyrene D12: Transition: 132→118, Qualifier: 264.1/260.1, 118/104; Benzo(g,h,i)perylene: Transition: 138→137, Qualifier: 276/274, 138/124.9, 125/123.2; Benzo(g,h,i)perylene D12: Transition: 142→140, Qualifier: 144/130, 144/142, 288/284.1;
INMETRO	GC-MS/MS (Agilent 8890 GC coupled to an Agilent 7000D GC/TQ system)	DB-5MS UI (30 m x 0.25 mm x 0.25 µm)	Injection Volume: 1.0 µL. Injecton temp.: 350°C. Injection mode: pulsed splitless, 16 psi until 0.7 min, purge flow to split vent of 10 mL/min at 0.7 min. Oven: 60 °C (2 min), 23°C/min until 150°C, 2.5°C/min until 200 °C, 7°C/min until 280°C (13 min), 20°C/min until 300 °C (1 min.), 20°C/min until 325°C (3 min).	MSD transferline temperature: 325 °C. Scan type: Selected ion monitoring (SIM). Source temp.: 320 °C, Quad temp.: 150 °C.	Phenantrene: 178, Phenantrene-d10: 188, Fluoranthene: 202, Fluoranthene-d10: 212, Benzo[a]pyrene: 252, Benzo[a]pyrene-d12: 264, Benzo[ghi]perylene: 276, Benzo[ghi]perylene-d12: 288.

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
NIM	GC-MS (Agilent 7890B- 5977B), GC-MS (Agilent 6890N-5975)	Agilent DB-XLB (30 m x 0.25 mm x 0.25 µm); Agilent DB EU-PAH (60 m x 0.25 mm x 0.25 µm)	Injector temp : 300°C, Injection Mode : Splitless, Injection volume : 1µL, Gas : He, Thermal Aux : 280°C For DB-XLB: Flow: 1.0 mL/min, Oven program temperature : 70°C hold time 1 min, ramp 25°C/min to 180°C hold time 2 min, ramp 5°C/min to 260°C, ramp 2.5°C/min to 300°C, ramp 5°C/min to 310°C, ramp 10°C/min to 320°C hold time 3 min. For EU-PAH: Flow: 1.2 mL/min, Oven program temperature : 80°C hold time 1 min, ramp 15°C/min to 220°C, ramp 5°C/min to 290°C, ramp 2°C/min to 320°C hold time 15 min.	For DB-XLB: EI source, ion source temp:250°C, Aux temp:280°C, Quantitative analysis was conducted by SIM mode. For EU-PAH: EI source, ion source temp:260°C, Aux temp:280°C, Quantitative analysis was conducted by SIM mode.	Phenanthrene 178, $^{13}C_6$-Phenanthrene 184, Fluoranthene 202, $^{13}C_6$-Fluoranthene 208, Benzo[a]pyrene 252, $^{13}C_4$-Benzo[a]pyrene 256, Benzo[ghi]perylene 276, $^{13}C_{12}$-Benzo[ghi]perylene 288.
NIMT	GC-MS/MS (Agilent 7000D)	HP-5MS UI (30 m x 0.32 mm x 0.25 µm)	Injection Mode: Splitless, Flow: 1.0 mL/min, Inlet temp.: 300°C. Oven: 60˚C (1 min)-25˚C/min to 200°C (3 min)-8˚C/min to 300°C (7 min), Post run 300 °C for 2 min. Transfer line: 300°C	-	Phenanthrene: quantitative:177.9/176.1, confirmation:177.9/152.1; Phenanthrene D10: quantitative:188.2/160.3, confirmation:188.2/184.5 Fluorathene: quantitative:201.9/200.1, confirmation:201.9/152.1 Fluorathene D10: quantitative:212.2/208.1, confirmation:212.2/210 Benzo(ghi)perylene:quantitative:276.0/274.1, confirmation:138/137.1 Benzo(ghi)perylene D12: quantitative:288/284.1, confirmation:288/286.2

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
GLHK	**GC-MS** 1. GC: 7890A, Agilent; MS: 5975C MSD, Agilent 2. GC: 7890B, Agilent; MS: 7010 GC-MS Triple Quad, Agilent **GC-HRMS** 1. GC: Trace 1310, Thermo Scientific; HRMS: DFS, Thermo Scientific 2. GC: 7890A, Agilent; HRMS: Autospec Premier, Waters	DB-17 MS (60 m, 0.25 mm, 0.25 µm) DB-5MS (60 m, 0.25 mm, 0.25 µm)	GC temperature programme for DB-17 MS: 85 °C (hold 1 min) Ramp1 rate 30 °C/min to 210 °C (hold 8 min) Ramp2 rate 5 °C/min to 250 °C (hold 8 min) Ramp3 rate 5 °C/min to 300 °C (hold 9.5 min) Ramp4 rate 30 °C/min to 315 °C (hold 16 min) Transfer line temperature: 315 °C Flow rate: 1.5mL/min for 48.5 min, then 2.0 mL/min for 27min GC temperature programme for DB-5MS: 85 ºC (hold 1 min) Ramp1 rate 30 ºC/min to 210 ºC (hold 8 min) Ramp2 rate 5 ºC/min to 250 ºC (hold 8 min) Ramp3 rate 5 ºC/min to 300 ºC (hold 26 min) Transfer line temperature: 300 °C Flow rate: 1.5mL/min (constant flow)	GC-MS Ionization mode: Electron Impact (EI) Source temperature: 300°C quadrupole temperature: 150°C GC-HRMS Ionization mode: Electron Impact (EI) Electron energy: ~35 eV Source temperature: 300°C Resolution: 10,000 (at 10% valley)	GC-MS Fluoranthene: 202, 200, 201 Fluoranthene-D10: 212, 213, 208 Benzo[a]pyrene: 252, 250, 253 Benzo[a]pyrene-D12: 264, 265, 260 Benzo[ghi]perylene: 276, 277, 274 Benzo[ghi]perylene-13C12: 288, 286, 287 GC-HRMS: Fluoranthene: 202.0783, 203.0816, 200.0626 Fluoranthene-D10: 212.1410, 213.1444, 208.1128 Benzo[a]pyrene: 252.0939, 253.0973, 250.0783 Benzo[a]pyrene-D12: 264.1692, 265.1726, 260.1410 Benzo[ghi]perylene: 276.0939, 277.0973, 274.0783 Benzo[ghi]perylene-13C12: 288.1342, 289.1375, 286.1185

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
BAM	GC-MS	PAH select (30m x 0.25mm x 0.18µm); ZB-PAH-CT (40m x 0.18mm x 0.14µm)	GC temperature programme for PAH select: 70°C (0.7min) with 85°C/min; 180°C (0min) with 3°C/min to 230°C (7min) with 28°C/min to 280°C (10min) with 14°C/min to 350°C (3min); He-flow 2ml/min; 5µL LVI GC temperature programm for ZB-PAH-CT: 45°C (0,8min) with 45°C/min to 200°C (0min) with 3°C/min to 265°C (5min) with 1°C/min to 270°C (0min) with 10°C/min to 320°C (5min); He-Flow 2ml/min; 5µL LVI	For both method: Source-Temp 276°C;	Phenanthrene: 178 / 176 / 179 Phenanthrene-D10: 188 Fluoranthene: 202 / 201 / 203 Fluoranthene-D10: 212 Benzo[*a*]pyrene: 252 / 250 / 253 Benzo[*a*]pyrene D12: 264 Benzo[*ghi*]perylene: 276 / 274 Benzo[*ghi*]perylene-D12: 288

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
NMIA	GC-MS/MS(Agilent 8890-7010C)	DB-17MS (30 m x 0.25 mm x 0.25 µm), VF-5MS (30 m x 0.25 mm x 0.25 µm)	Column flow: 1.2 mL/min helium, Injection volume: 0.8 µL, Inlet mode: Splitless, Inlet temperature: 300°C, Oven:100°C(1min), 50°C/min to 150°C, 5°C/min to 330°C (6 min)	Transfer line temperature: 300°C	13C6 Phenanthrene: 184>129, 184>132, 184>133, 184>134, 184>154, 184>155, 184>181, 184>182, 184>183 Phenanthrene: 178>125, 178>126, 178>127, 178>128, 178>150, 178>151, 178>175, 178>176, 178>177 13C6 Fluoranthene: 208>153, 208>156, 208>180, 208>204, 208>205, 208>206, 208>207 Fluoranthene: 202>150, 202>151, 202>175, 202>198, 202>199, 202>200, 202>201 13C4 Benzo(a)pyrene: 256>226, 256>228, 256>252, 256>253, 256>254, 256>255 Benzo(a)pyrene: 252>224, 252>226, 252>248, 252>249, 252>250, 252>251 13C12 Benzo(ghi)perylene: 288>259, 288>260, 288>284, 288>285, 288>286, 288>287 Benzo(ghi)perylene: 276>248, 276>249, 276>272, 276>273, 276>274, 276>275

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	Ion/MRM monitored
INTI	GC-MS (Agilent 7890A)	DB-5 MS UI, Agilent J&W	Initial Temperature: 120°C. Gradient: 5°C/ min. Final Temperature: 300°C.	Interface Temperature: 350°C. Source Temperature: 230°C. Quadrupole Temperature: 150°C.	Phenanthrene: 178,1. Fluoranthene: 202,1. Benzo[a]pyrene: 252,1. Benzo[ghi]perylene: 276,1.
TUBITAK_UME	GC-MS (Thermo TSQ Quantum XLS)	VF-17ms from Varian	Oven Program: 100℃ (1 min), 10 ℃/min to 200, 2 ℃/min to 320 (33 min). Splitless 1 uL injection	MS Mode: SIM Source temp: 270 ℃ MS Transfer Line: 300 ℃ Inlet Temp: 250 ℃	Phenanthrene: 178 IS: 188 Fluoranthene: 202 IS: 212 Benzo(a)pyrene: 252 IS: 264 Benz(ghi)perylene: 276 IS: 288
METAS	GC-MS/MS (Thermo Scientific TSQ 8000 Evo / Trace 1310)	Pre-column: Restek Rxi Guard Column, 5 m x 0.25 mm (10029) Column: Agilent J&W Select PAH, 30 m x 0.25 mm; 0.15 µm (CP7462)	70 °C (0.7 min.) → (85 °C/min.) 180 °C (0 min.) →(3 °C/min.) 230 °C (7 min.) → (28 °C/min.) 280 °C (10 min.) → (14 °C/min.) 330 °C (3 min.)	GC-MS interface: 300 °C Ion source: 300 °C Ionization: 70 eV (EI) Polarity: positive Scan type: SRM	PAH: m/z precursor → m/z fragment (collision energy (eV)) Phenanthrene: 178.1→152.1 (20) [quant.]; 178.1→176.0 (30) [conf.] Phenanthrene-d10: 188.2→184.1 (20) [quant.]; 188.2→160.1 (30) [conf.] Fluoranthene: 202.1→200.1 (30) [quant.]; 202.1→176.1 (30) [conf.] Fluoranthene-d10: 212.2→208.1 (20) [quant.]; 212.2→184.2 (30) [conf.] Benzo[a]pyrene: 252.1→250.1 (30) [quant.]; 252.1→225.9 (30) [conf.] Benzo[a]pyrene-d12: 264.2→260.2 (30) [quant.]; 264.2→236.1 (30) [conf.] Benzo[ghi]perylene: 276.1→274.0 (30) [quant.]; 276.1→275.2 (30) [conf.] Benzo[ghi]perylene-d12:

					288.2→284.1 (30) [quant.]; 288.2→260.1 (30) [conf.]

Table F-2: Summary of Analytical Techniques for CCQM-K184 (Continued)

Participant	Analytical Technique	Chromatographic Column	Chromatographic Conditions	Mass Spectrometry Conditions	ion/MRM monitored
LGC	Shimadzu GC system Nexis GC-2030 coupled to Shimadzu GCMS-TQ8050NX QQQ	DB-EUPAH (60 m × 0.25 mm×0.25 µm)	Injection volume: 1uL Injector: Split/Splitless Mode: Pulsed splitless Temp: 320C. Oven program: Intial temp 50°C (2 min), 80°C/min to 275°C (7 min), 50°C/min to320°C (10 min), 50°C/min to 325°C (13 min).	Transfer line Temp: 310°C, Source temperature: 230°C, EI ionisation, MRM	Fluoranthene: 202/202, CE: 20eV Qualifier: 202>156 CE 55 Fluoranthene D10: 212/212, CE: 20eV Qualifier: 212>156 CE55 Benzo[a]pyrene: 252/252, CE: 20eV Qualifier: 252>224 CE55 Benzo[a]pyrene D12: 264/264, CE: 20eV Qualifier: 264>232 CE55 Benzo[ghi]perylene: 276/276, CE: 20eV Qualifier: 276>274 CE42 Benzo[ghi]perylene D12: 288/288, CE: 20eV

Table F-3: Summary of Calibrants and Standards for CCQM-K184

Participant	**Type of Calibration**	**Analyte**	**Source of Traceability**	**Material**	**Purities/Concentration and Uncertainties (95% CI)**	**Purity techniques**	**Evidence of Competence**
KRISS	IDMS Single point	Fluoranthene	KRISS	sigma-aldrich	98.80 ± 0.13 % (k=2.04)	mass- balance	Purity assay was provided through participation of CCQM-K55a, K55b, 55c, and 55d. Preparation and verification of the calibration was verified through participation of CCQ0M-K131.
		Benzo[a]pyrene	KRISS	Supelco	98.76 ± 0.50 % (k=2.05)	mass- balance	
		Benzo[ghi]perylene	KRISS	Accustandard	97.59 ± 0.35 % (k=2.45)	mass- balance	
LNE	IDMS 6 point calibration curve	4 PAHs	SRM 2260a	NIST		N/A	
NIST	IDMS Multipoint calibration spanning above and below the concentrations of the relevant PAHs in the CCQM material and in the NIST SRM 1941b used as control.	4 PAHs	SRM 2260a	NIST		N/A	
CENAM	GC: IDMS; HPLC: Internal standard 4-5 points, calibration curve	Phenanthrene	CENAM	Aldrich Chem	-	Mass balance: GC-FID with two different columns and water content by Karl Fischer titration	Purity value assignment was supported through participation in CCQM-K55a, K55b, K55c and K55d. Preparation and verification of the calibration solution was supported through participation in CCQM-K131.
		Fluoranthene	CENAM	Aldrich Chem	-		
		Benzo[a]pyrene	CENAM	Supelco	-		
		Benzo[ghi]perylene	CENAM	Ultra scientific	-		

Table F-3: Summary of Calibrants and Standards for CCQM-K184 (Continued)

Participant	Type of Calibration	Analyte	Source of Traceability	Material	Purities/Concentration and Uncertainties (95% CI)	Purity techniques	Evidence of Competence
VNIIM	IDMS Single point	4 PAHs	SRM 1647f	NIST		N/A	
IH	Internal standard calibration 8-point calibration curve with linear regression between 0,100 µg/mL to 2,23 µg/mL	Phenanthrene	EPA Method 610/8100 PAH Mixture	Dr Ehrenstorfer, Refª DRE-GA09000161BD, Batch 2-H473805NA	(2000 ± 110) µg/mL	-	-
		Fluoranthene			(2008 ± 100) µg/mL	-	
		Benzo[a]pyrene			(1999 ± 130) µg/mL	-	
		Benzo[ghi]perylene			(2000 ± 130) µg/mL	-	
INM	Internal standard Bracketing, Matrix matched calibration	Phenanthrene	SRM 1647f	NIST	4.57 mg/kg, U= 0.05 mg/kg (k=2)	N/A	
		Fluoranthene			9.71 mg/kg, U= 0.16 mg/kg (k=2)		
		Benzo[a]pyrene			6.22 mg/kg, U= 0.11 mg/kg (k=2)		
		Benzo[ghi]perylene			4.64 mg/kg, U= 0.12 mg/kg (k=2)		
INMETRO	IDMS Bracketing	Phenanthrene	INMETRO	Sigma-Aldrich	(996.0 ± 2.8) mg/g	q-NMR	Purity value assignment was performed by qNMR using the following Inmetro' internal standards: CRM 8792 - Maleic acid, for Phenanthrene and Fluoranthene; CRM 8783 - Dimethyl sulfone, for Benzo[a]Pyrene; and CRM 8784 - Dimethyl terephthalate, for Benzo[ghi]Perylene.
		Fluoranthene	INMETRO	Sigma-Aldrich	(993.8 ± 1.7) mg/g		
		Benzo[a]pyrene	INMETRO	Dr. Ehrenstorfer GmbH	(971.6 ± 3.8) mg/g		
		Benzo[ghi]perylene	INMETRO	Sigma-Aldrich	(980.1 ± 2.0) mg/g		

Table F-3: Summary of Calibrants and Standards for CCQM-K184 (Continued)

Participant	Type of Calibration	Analyte	Source of Traceability	Material	Purities/ Concentration and Uncertainties (95% CI)	Purity techniques	Evidence of Competence
NIM	IDMS Single point	Phenanthrene	NIM	Supelco	98.9%, u_{rel}=0.44%	Mass- balance: HPLC-DAD, GC-FID and moisture content by Karl Fischer titration, Residual solvents were analyzed using headspace-GC/MS, while inorganic content was assessed by ICP-MS.	The purity value of 4 PAHs was assessed in NIM by using the mass balance method. The ability for purity assignment has been supported by NIM's participation in K148a, K55b, 55c, and 55d. CCQM-K131 provides further evidence with demonstrated ability for preparation and verification of calibration solution.
		Fluoranthene		Chem Service	98.3%, u_{rel}=0.80%		
		Benzo[a]pyrene		Cerilliant	99.4%, u_{rel}=0.27%		
		Benzo[ghi]perylene		AccuStandard	98.3%, u_{rel}=0.23%		
NIMT	Exact-matching IDMS for Fluoranthrene and multi-point with isotopically internal standard for Phenanthrene and Benzo(ghi) perylene Single-point, bracketing calibration and 5-7 point calibration curve.	Fluoranthene	GBW(E)080477	NIM	7.50 ug/mL ± 2.9 % (at 95 %CI)	N/A	
		Phenanthrene	SRM 1647f	NIST	4.57 mg/kg ± 0.05 mg/kg (at 95 %CI)		
		Benzo(ghi)perylene	SRM 1647f	NIST	4.64 mg/kg ± 0.12 mg/kg (at 95 %CI)		
GLHK	IDMS 4 point calibration curve and IDMS with bracketing	Fluoranthene	GBW 08736	NIM	5.00 µg/g, U=2% (*k*=2)	N/A	
		Benzo[a]pyrene			4.88 µg/g, U=2% (*k*=2)		
		Benzo[ghi]perylene			4.89 µg/g, U=2% (*k*=2)		

Table F-3: Summary of Calibrants and Standards for CCQM-K184 (Continued)

Participant	Type of Calibration	Analyte	Source of Traceability	Material	Purities/Concentration and Uncertainties (95% CI)	Purity techniques	Evidence of Competence
BAM	IDMS 4-10 point calibration curves	4 PAHs	SRM 1647f / SRM 2260a	NIST		N/A	
NMIA	IDMS 8 point calibration curve	4 PAHs	SRM 2260a	NIST		N/A	
INTI	8 point Calibration curve	Phenanthrene and Fluoranthene	SRM 1647f / SRM 2260a	NIST		N/A	
	4 point calibration curve	Benzo[a]pyrene					
	5 point calibration curve	Benzo[ghi]perylene					
TUBITAK_UME	IDMS 6 point calibration curve	4 PAHs	SRM 1647f	NIST		N/A	
METAS	IDMS 9-point calibration	4 PAHs	SRM 1647f	NIST		N/A	
LGC	Double Exact Matching Isotope Dilution Mass Spectrometry (DEM-IDMS) Bracketed single point exact matching	4 PAHs	SRM 1647f	NIST		N/A	

Table F-4 Summary of Internal Standards for CCQM-K184

Participant	**Analyte**	**Source(s)**
KRISS	Fluoranthene-D10	Cerilliant-CIL
	Benzo(a)pyrene-$^{13}C_4$	Cerilliant-CIL
	Benzo(ghi)perylene-$^{13}C_{12}$	Cerilliant-CIL
LNE	Phenanthrene $^{13}C_6$	CLM- 2451-1,2
	Fluoranthene $^{13}C_6$	CLM-3597-1,2
	Benzo(a)pyrene $^{13}C_4$	CLM-2722-1,2
	Benzo(ghi)perylene $^{13}C_{12}$	CLM-1364-1,2
NIST	phenanthrene-D10	Sourced from SRMs 2269 Perdeuterated PAH-I solution in hexane/toluene and 2270 Perdeuterated PAH-II solution in hexane/toluene
	Fluoranthene-D10	
	Benzo(a)pyrene-D12	
	Benzo[ghi]perylene-D12	
CENAM	Phenanthrene-D10	Aldrich, Lot: 12114TI
	Fluoranthene-D10	Aldrich, Lot: 07605BQ
	Benzo(a)pyrene-D12	CIL, Co, Lot: PR-13182
	benzo[ghi]perylene-D12	CDN/ Isotopes, Lot: F204P9
	Peryelene-D12	
VNIIM	US EPA PAH Coktail (13C, 99%)	CIL # ES-4087
IH	Phenanthrene-D10	EPA Method 8270 Internal Standard Mixture 2000, (Dr Ehrenstorfer, Refª DRE-YS09000038DI, Batch 2 H470128DI)\
	Chrysene-D12	
	Peryelene-D12	

Table F-4 Summary of Internal Standards for CCQM-K184 (Continued)

Participant	Analyte	Source(s)
INM	Fluoranthene-D10	By LGC
	Benzo(a)pyrene-D12	By LGC
	Benzo[ghi]perylene-D12	By LGC
INMETRO	Phenanthrene-D10	Cerilliant-CIL
	Fluoranthene-D10	Cerilliant-CIL
	Benzo(a)pyrene-D12	Cerilliant-CIL
	Benzo[ghi]perylene-D12	Cerilliant-CIL
NIM	Phenanthrene $^{13}C_{12}$	Cambridge Isotope Laboratories CLM- 2451-1.2
	Fluoranthene $^{13}C_{6}$	Cambridge Isotope Laboratories CLM-3597-1.2
	Benzo(a)pyrene $^{13}C_{4}$	Cambridge Isotope Laboratories CLM-2722-1.2
	Benzo(ghi)perylene $^{13}C_{12}$	Cambridge Isotope Laboratories CLM-1364-1.2.
NIMT	Phenanthrene-D10	DR Ehrenstorfer
	Fluoranthene-D10	
	Benzo[ghi]perylene-D12	
GLHK	Fluoranthene-D10	Dr. Ehrenstorfer
	Benzo(a)pyrene-D12	Cambridge Isotope Laboratories
	Benzo(ghi)perylene-13C12	Cambridge Isotope Laboratories
BAM	Deuterated PAH-Mix 9	(LGC/Dr. Ehrenstorfer)

Table F-4 Summary of Internal Standards for CCQM-K184 (Continued)

Participant	Analyte	Source(s)
NMIA	Phenanthrene $^{13}C_6$	Cambridge Isotopes
	Fluoranthene $^{13}C_6$	Cambridge Isotopes
	Benzo(a)pyrene $^{13}C_4$	Cambridge Isotopes
	Benzo(ghi)perylene $^{13}C_{12}$	Cambridge Isotopes
INTI	SRM 2269, SRM 2270	NIST
TUBITAK_UME	phenanthrene-D10	LinkChem (Batch #: LK-795248-2309001)
	Fluoranthene-D10	Cambridge Isotope Laboratories (Lot #: PR-20668/08189FT1)
	Benzo(a)pyrene-D12	Cambridge Isotope Laboratories (Lot #: PR-22264)
	Benzo[ghi]perylene-D12	Cambridge Isotope Laboratories (Lot #: PR-21753)
METAS	phenanthrene-D10	16 EPA Priority PAHs mix (Chiron AS, Trondheim, Norway, S-4513-K-T)
	Fluoranthene-D10	
	Benzo(a)pyrene-D12	
	Benzo[ghi]perylene-D12	
LGC	Fluoranthene-D10	Cambridge Isotopes, Reference: DLM-2140-0, Batch:PR-32557A
	Benzo(a)pyrene-D12	Cambridge Isotopes, Reference: DLM-258-0, Batch:PR-31995
	Benzo[ghi]perylene-D12	Cambridge Isotopes, Reference: DLM-2135-0, Batch:PR-28694

Table F-5: Additional Comments for CCQM-K184

Participant	Additional Comments
KRISS	Calibration solutions were gravimetrically prepared in KRISS and verified by cross-checking of multiple calibration solutions. NIST SRM 2260a (PAHs in toluene) was also used for secondary confirmation, which were good agreement with the KRISS calibration solutions. As the confirmation for instrumental analysis, we also applied high resolution MS condition (R=10,000) to the same samples, which were good agreement with the primary method (GC/MS: R =1000). NIST SRM 1941b was used for the verification of analytical method. When extracting naturally contaminated environmental samples, it has been reported that extraction efficiency may vary depending on the solvent used, extraction temperature, and extraction method in many previous studies. Even if IDMS was applied. Because the sample amount of K184 was very limited, some tests were conducted on ASE extraction solvents and temperatures using SRM 1941b, and it was observed that the results were quite different depending on the solvent and the extraction temperature of ASE. Considering these verification results, the K184 sediment samples from the same bottle were extracted in two different conditions. (1) toluene:methanol (1:1=v:v), 200 °C, 20 min, 2 cycles and (2) hexane:acetone (1:1=v:v), 5 min, 160 °C, 5 cycles. The results from two different extraction condition were not agreed within the uncertainty. Condition (2) is a similar method that NIM China used to evaluate the homogeneity of K184 samples. We finally submit the results with (1) condition as we think that harsher conditions better extract PAHs adsorbed and absorbed on the sediment samples. However, due to differences in results depending on the extraction solvent or the extraction temperature of ASE, it needs to be discussed. As supplementary results, the results with (2) condition (hexane:acetone (1:1), 160 °C, 5 cycles) are also attached (in the supplementary sheet).
LNE	NA
NIST	Used the same pressurized fluid extraction conditions and instrument as those used by organizers but found two sequential extractions were needed to insure complete extraction of the targeted PAHs. These two extract fractions were combined prior to subsequent processing.
CENAM	Although isotopic dilution was chosen to determine the measurands, the results had a lot of dispersion, and for some of the measurands, significant bias, so it was decided to apply other methods to obtain more conclusive results.
VNIIM	1) The preparing of calibration solutions and adding the IS into the sample were performed by the volumetric method. Uncertainty was calculated based on the syringes specifications. 2) 2 calibration solutions were prepared. 3) Mettler Toledo XP105 accuracy specifications based on Certificate of Calibration. 4) The mass of sample was reduced to 0,5 g because the lack of IS solution (not enough for equal amount of native and isotop labeled PAH).

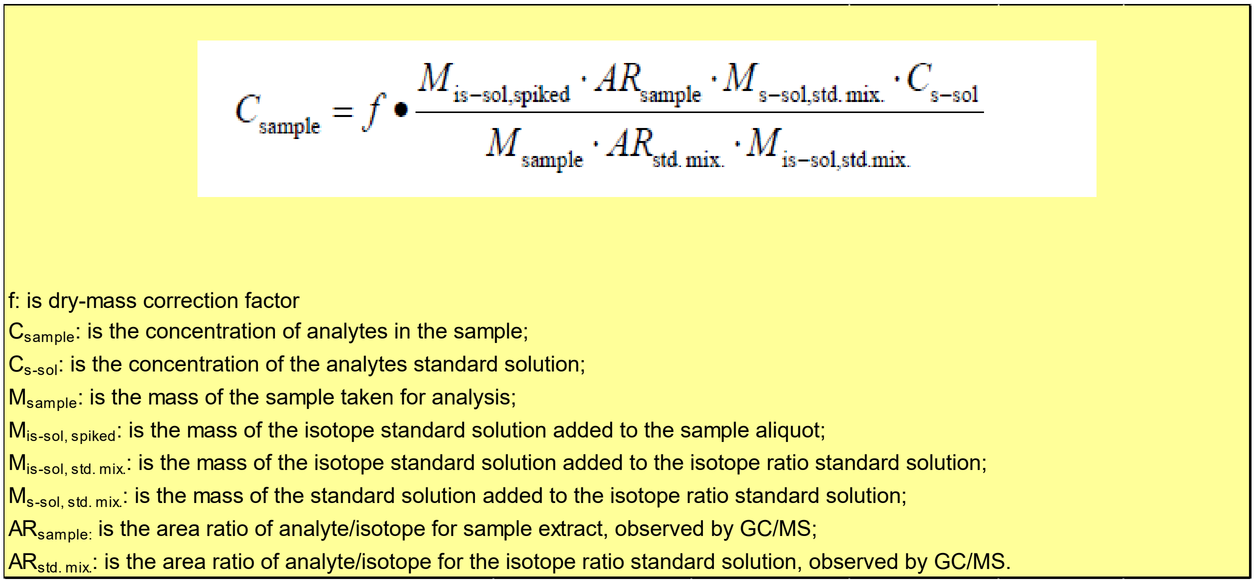
Table F-5: Additional Comments for CCQM-K184 (Continued)

Participant	Additional Comments
IH	Blank test, recovery in inert matrix test and reference material were analysed in parallel with the samples. All satisfied the method quality control criteria for each of the PAHs. Control solutions, prepared from a different source than the calibration solutions, were also analysed, making it possible to ensure that the determination of the PAH content is carried out correctly by GC-MS.
INM	Reference material LGC6188 River sediment- PAHs was used as a quality control, for method and extraction procedures development and bias evaluation
INMETRO	Two independent working solutions containing the four analytes were used to prepare independent calibration blends. These solutions were prepared from the same analyte pure standards however from different preparations of stock solutions. The samples were quantified using the two calibration blends in order to support the results. Equivalent results were obtained using both calibration blends. Certified Reference Materials (SRM 1941b, SRM 1944, and BCR 524) were used as Control samples.
NIM	Analytical method with Agilent DB EU-PAH (60 m x 0.25 mm x 0.25 µm) column was used for confirmation and support of the results . The internal standard used in the method with DB EU-PAH column is phenanthrene-D10, fluoranthene-D10, benzo(a)pyrene-D12 and benzo[ghi]perylene-D12. The results with two columns and two kinds of isotope internal standard (Deuterium internal standards and 13C internal standards) are agreed within the uncertainty. In each batch test, a blank test sample and a blank matrix addition sample (for whole-process recovery monitoring) were determined in parallel with the samples.
NIMT	
GLHK	
BAM	
NMIA	
INTI	
TUBITAK_UME	NIST 1941b was used as control sample for each sample preparation and measurement sequence.
METAS	The certified reference material BAM-U013c was used as control sample for each sample preparation/measurement sequence.
LGC	During the measurement process equal amounts material from pots 50 and 122 were combined into a single pot, this was then mixed prior to the taking of aliquots for measurement and dry mass correction.

APPENDIX G: Summary of Participants' Uncertainty Estimation Approaches

The following are pictures of the uncertainty-related information provided by the participants in the "Analytical Information" worksheet of the "Reporting Form" Excel workbook. The information is grouped by participant and presented in the order of the randomly assigned laboratory codes.

Uncertainty Information from KRISS



$$C_{\text{sample}} = f \bullet \frac{M_{\text{is-sol,spiked}} \cdot AR_{\text{sample}} \cdot M_{\text{s-sol,std. mix.}} \cdot C_{\text{s-sol}}}{M_{\text{sample}} \cdot AR_{\text{std. mix.}} \cdot M_{\text{is-sol,std.mix.}}}$$

f: is dry-mass correction factor

C_{sample}: is the concentration of analytes in the sample;

$C_{\text{s-sol}}$: is the concentration of the analytes standard solution;

M_{sample}: is the mass of the sample taken for analysis;

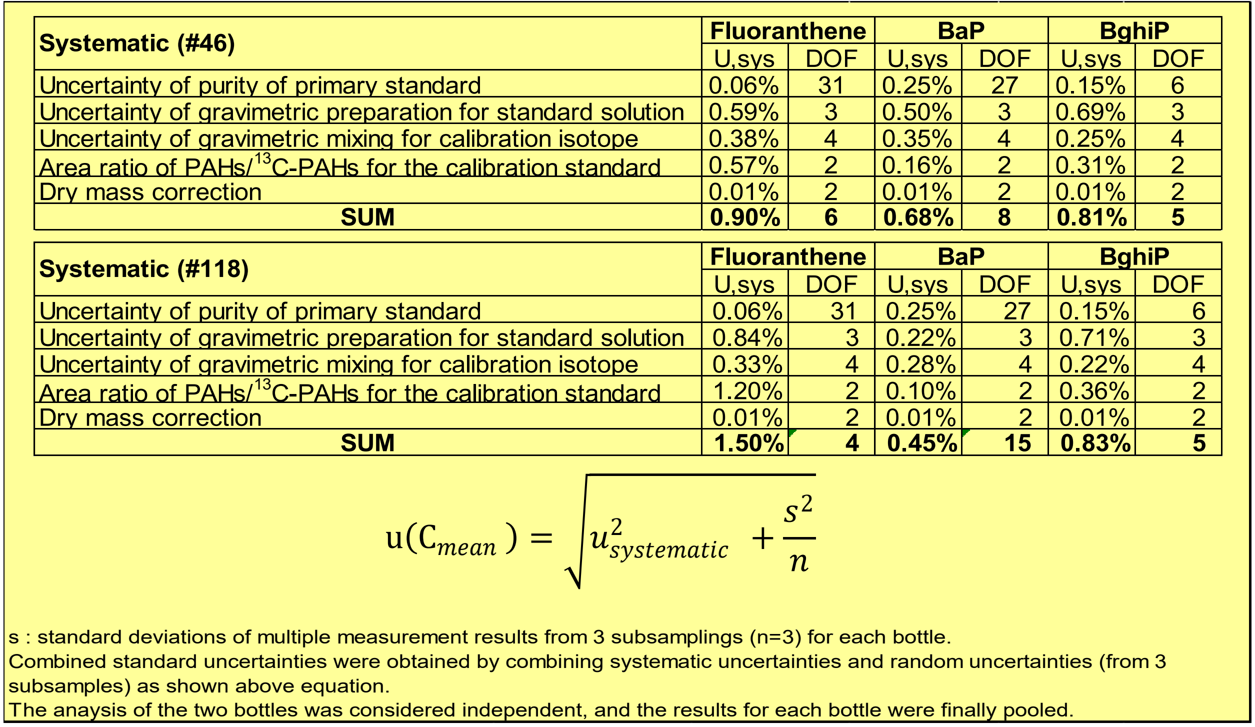
$M_{\text{is-sol, spiked}}$: is the mass of the isotope standard solution added to the sample aliquot;

$M_{\text{is-sol, std. mix.}}$: is the mass of the isotope standard solution added to the isotope ratio standard solution;

$M_{\text{s-sol, std. mix.}}$: is the mass of the standard solution added to the isotope ratio standard solution;

$AR_{\text{sample:}}$ is the area ratio of analyte/isotope for sample extract, observed by GC/MS;

$AR_{\text{std. mix.}}$: is the area ratio of analyte/isotope for the isotope ratio standard solution, observed by GC/MS.



Systematic (#46)	**Fluoranthene**		**BaP**		**BghiP**	
	U,sys	DOF	U,sys	DOF	U,sys	DOF
Uncertainty of purity of primary standard	0.06%	31	0.25%	27	0.15%	6
Uncertainty of gravimetric preparation for standard solution	0.59%	3	0.50%	3	0.69%	3
Uncertainty of gravimetric mixing for calibration isotope	0.38%	4	0.35%	4	0.25%	4
Area ratio of PAHs/^{13}C-PAHs for the calibration standard	0.57%	2	0.16%	2	0.31%	2
Dry mass correction	0.01%	2	0.01%	2	0.01%	2
SUM	**0.90%**	**6**	**0.68%**	**8**	**0.81%**	**5**

Systematic (#118)	**Fluoranthene**		**BaP**		**BghiP**	
	U,sys	DOF	U,sys	DOF	U,sys	DOF
Uncertainty of purity of primary standard	0.06%	31	0.25%	27	0.15%	6
Uncertainty of gravimetric preparation for standard solution	0.84%	3	0.22%	3	0.71%	3
Uncertainty of gravimetric mixing for calibration isotope	0.33%	4	0.28%	4	0.22%	4
Area ratio of PAHs/^{13}C-PAHs for the calibration standard	1.20%	2	0.10%	2	0.36%	2
Dry mass correction	0.01%	2	0.01%	2	0.01%	2
SUM	**1.50%**	**4**	**0.45%**	**15**	**0.83%**	**5**

$$\mathrm{u}(\mathrm{C}_{mean}) = \sqrt{u_{systematic}^2 + \frac{s^2}{n}}$$

s : standard deviations of multiple measurement results from 3 subsamplings (n=3) for each bottle.
Combined standard uncertainties were obtained by combining systematic uncertainties and random uncertainties (from 3 subsamples) as shown above equation.
The anaysis of the two bottles was considered independent, and the results for each bottle were finally pooled.

Uncertainty Information from LNE

$$C_{PAH/sediment} \frac{C_{PAH*/sediment} \times m_{PAH*/sediment}}{m_{sediment}} \times (a \times R_{sediment} + b) \times 1000 \times f_{humidity} \times f_{standard} + f_{F}$$

$C_{PAH/sediment}$: mass fraction of PAH in sediment in µg/kg
$C_{PAH*/sediment}$: mass fraction of PAH* in sediment in µg/g
$m_{PAH*/sediment}$: mass of labelled solution in sediment in g
$m_{sediment}$: mass of sediment in g
$R_{sediment}$: unlabeled/labeled ion peak area ratio in sediment
a : gradient of the slope for linear regression plot
b : intercept onn y axis for linear regression plot
$f_{humidity}$: humidity correction
$f_{standard}$: correction factor due to the standard solutions uncertainty
$f_{intermediate\ precision}$: correction factor due to measurment intermediate precision

	TYPE (A or	RELATIVE UNCERTAINTY
Phenanthrene		
Preparation of sediment (weighings)	B	18%
Calibration model	B	32%
Preparation of calibration blends (weighings + CRM uncertainty)	B	8%
Intermediate Precision	B	42%
Fluoranthene		
Preparation of sediment (weighings)	B	14%
Calibration model	B	0%
Preparation of calibration blends (weighings + CRM uncertainty)	B	5%
Intermediate Precision	B	81%
Benzo(a)pyrene		
Preparation of sediment (weighings)	B	11%
Calibration model	B	3%
Preparation of calibration blends (weighings + CRM uncertainty)	B	22%
Intermediate Precision	B	64%
Benzo(ghi)perylene		
Preparation of sediment (weighings)	B	12%
Calibration model	B	4%
Preparation of calibration blends (weighings + CRM uncertainty)	B	6%
Intermediate Precision	B	78%

Uncertainty Information from NIST

	Sensitivity Coefficients for Each PAH				Standard Uncertainty Values for Each PAH					
Variable Name	Phenant	Fluoran	Benzo[a	Benzo[g	Phenant	Fluoran	Benzo[a	Benzo[g	Degrees of Freedom for Each Std Unc	Uncertainty Estimate Type
w.CS	0.222	0.256	0.139	0.123	0.004	0.029	0.057	0.023	60	B
beta0	−0.842	−1.357	−0.747	−0.877	0.050	0.037	0.055	0.028	14	A
beta1	−0.668	−1.240	−0.372	−0.386	0.094	0.070	0.104	0.053	14	A
beta2	0.000	−0.237	0.000	0.000	0.085	0.063	0.094	0.047	14	A
yn1	0.147	0.237	0.131	0.153	0.092	0.068	0.101	0.051	14	A
m.Smp1	−0.470	−0.342	−0.121	−0.127	0.000	0.000	0.000	0.000	999	B
m.IS1	1.883	1.370	0.483	0.509	0.000	0.000	0.000	0.000	999	B
x1i1	−0.045	−0.056	−0.018	−0.015	0.000	0.000	0.000	0.000	999	B
yn2	0.188	0.303	0.167	0.195	0.092	0.068	0.101	0.051	14	A
m.Smp2	−0.518	−0.444	−0.140	−0.144	0.000	0.000	0.000	0.000	999	B
m.IS2	1.628	1.395	0.440	0.453	0.000	0.000	0.000	0.000	999	B
x1i2	−0.058	−0.071	−0.023	−0.019	0.000	0.000	0.000	0.000	999	B
yn3	0.168	0.271	0.149	0.175	0.092	0.068	0.101	0.051	14	A
m.Smp3	−0.474	−0.407	−0.125	−0.130	0.000	0.000	0.000	0.000	999	B
m.IS3	1.660	1.423	0.436	0.454	0.000	0.000	0.000	0.000	999	B
x1i3	−0.052	−0.064	−0.021	−0.017	0.000	0.000	0.000	0.000	999	B
yn4	0.167	0.270	0.149	0.174	0.092	0.068	0.101	0.051	14	A
m.Smp4	−0.526	−0.435	−0.121	−0.145	0.000	0.000	0.000	0.000	999	B
m.IS4	1.853	1.532	0.424	0.509	0.000	0.000	0.000	0.000	999	B
x1i4	−0.051	−0.064	−0.021	−0.017	0.000	0.000	0.000	0.000	999	B
yn5	0.171	0.276	0.152	0.179	0.092	0.068	0.101	0.051	14	A
m.Smp5	−0.508	−0.442	−0.131	−0.134	0.000	0.000	0.000	0.000	999	B
m.IS5	1.747	1.520	0.452	0.459	0.000	0.000	0.000	0.000	999	B
x1i5	−0.053	−0.065	−0.021	−0.018	0.000	0.000	0.000	0.000	999	B
mmc	−2.624	−2.172	−0.669	−0.714	0.000	0.000	0.000	0.000	4	A
Combined Standard Uncertainty, mg/kg					0.050	0.058	0.041	0.024		
Effective Degrees of Freedom					14.010	14.475	15.107	14.399		
Coverage Factor					2.145	2.138	2.130	2.139		
Expanded Uncertainty at the 95% Confidence Level, mg.kg					0.106	0.123	0.087	0.051		

Correlation Matrix for Variable Values

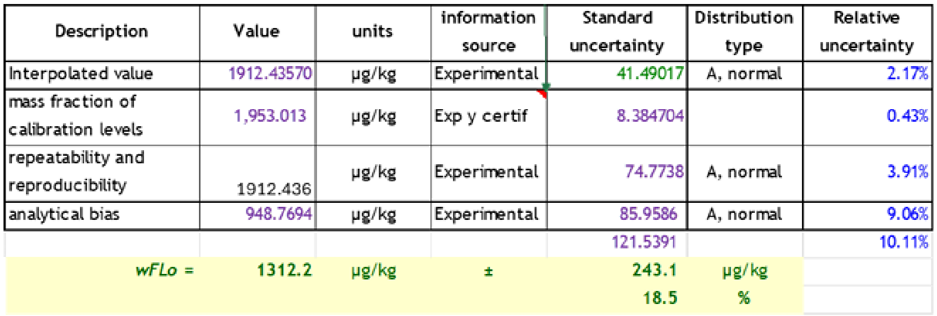
	w.CS	beta0	beta1	beta2	yn1	m.Smp1	m.IS1	x1i1	yn2	m.Smp2	m.IS2	x1i2	yn3	m.Smp3	m.IS3	x1i3	yn4	m.Smp4	m.IS4	x1i4	yn5	m.Smp5	m.IS5	x1i5	mmc
w.CS	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
beta0	0.00	1.00	-0.85	0.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
beta1	0.00	-0.85	1.00	-0.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
beta2	0.00	0.53	-0.82	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
yn1	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.Smp1	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.IS1	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
x1i1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
yn2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.Smp2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.IS2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
x1i2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
yn3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.Smp3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.IS3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
x1i3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
yn4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.Smp4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
m.IS4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
x1i4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
yn5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
m.Smp5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00
m.IS5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00
x1i5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
mmc	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00

Note: Mass values are listed in the measurement function and the uncertainty budget to aid automation of computations. These values were all treated as known (i.e., standard uncertainty = 0) by assumption. Based on experience, we feel this assumption is reasonable given the standard uncertainties of the instrumental readings, the calibration standards, the fit of the calibration model, and the drying.

Note: Standard uncertainties for beta0, beta1, beta2, yn1, yn2, yn3, yn4, and yn5 are all based on the single residual standard deviation from the fit of the calibration model. Thus those standard uncertainty estimates are completely dependent on one another, which must be taken into account when computing effective degrees of freedom using the Welch-Satterthwaite formula (which we have done).

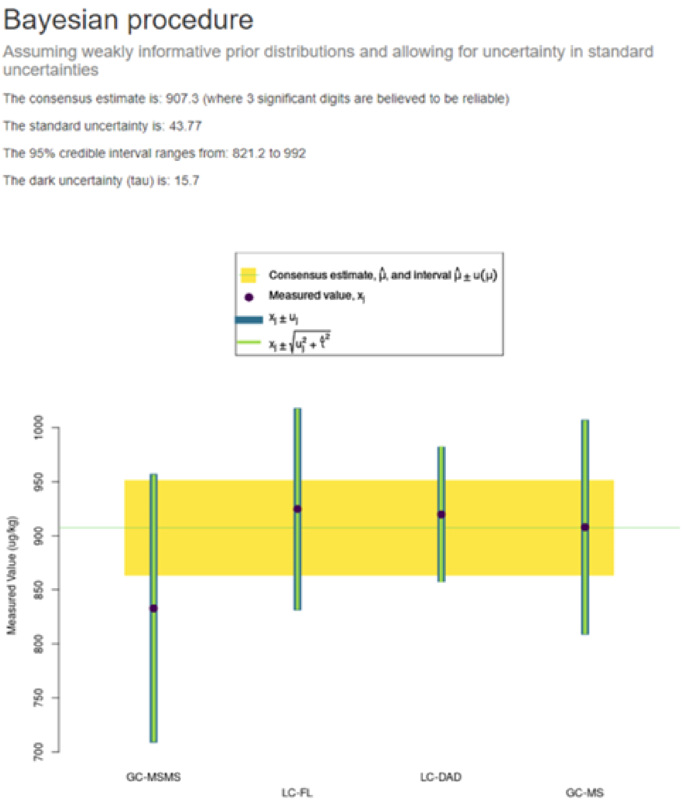
Uncertainty Information from CENAM

Several uncertainty sources were combined: Calibration curve residual variation, dilution factor variation (including weight repeatability and balance calibration); variation IS mass fraction (weighting process variation, variation of purity measurements), repeatability of sample measurements, and variance of dry mass correction. For de combination of all sources (relative uncertainties) Law of Propagation of Uncertainty was used. The expanded uncertainty was obtained by multiplying the combined standards uncertainty by the cover factor with a 95 % level of confidence.



Description	Value	units	information source	Standard uncertainty	Distribution type	Relative uncertainty
Interpolated value	1912.43570	µg/kg	Experimental	41.49017	A, normal	2.17%
mass fraction of calibration levels	1,953.013	µg/kg	Exp y certif	8.384704		0.43%
repeatability and reproducibility	1912.436	µg/kg	Experimental	74.7738	A, normal	3.91%
analytical bias	948.7694	µg/kg	Experimental	85.9586	A, normal	9.06%
				121.5391		10.11%
wFLo =	1312.2	µg/kg	±	243.1	µg/kg	
				18.5	%	

GC-MSMS GC-MS, LC-FL, LC-DAD results of the measurements with these methods were combined with the NIST Consensus Builder, chossing Bayesian method



Bayesian procedure

Assuming weakly informative prior distributions and allowing for uncertainty in standard uncertainties

The consensus estimate is: 907.3 (where 3 significant digits are believed to be reliable)

The standard uncertainty is: 43.77

The 95% credible interval ranges from: 821.2 to 992

The dark uncertainty (tau) is: 15.7

Uncertainty Information from VNIIM

The measurement equations used to calculate the mass fraction of each analyte. Please provide details of all the factors listed in the equations and indicate how these values were determined.

$w_{an} = \frac{A_{an} \times m_{IS}}{A_{IS} \times RRF \times m_{sample}} \times f_1$	w_{an}	– the mass fraction of the analyte in the sample, mkg/kg;
	A_{an}	– the area of the analyte (sample);
	A_{IS}	– the area of the IS (sample);
	m_{IS}	– the mass of the IS added to sample, mkg;
	m_{sample}	– the mass of the sample, kg;
	f_1	– the correction factor to moisture content;
	RRF	– the relative response factor of analyte;
$RRF = \frac{A_{an} \times m_{IS}}{A_{IS} \times m_{an}}$	A_{an}	– the area of the analyte (calibration solution);
	A_{IS}	– the area of the IS (calibration solution);
	m_{an}	– the mass of the analyte (calibration solution), mkg
	m_{IS}	– the mass of IS (calibration solution), mkg.

Estimation of uncertainty for each factor. Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

$$u_{w_{an}} = \sqrt{(u_{cal})^2 + (u_{meas})^2 + (u_{bl})^2}$$

u_{cal}	- the relative standard uncertainty of the calibration;
u_{meas}	- the relative standard uncertainty of measuring PAH in the sample;
u_{bl}	- the relative standard uncertainty of method blank

$$u_{cal} = \sqrt{(u_{RRF})^2 + (u_{IS})^2 + (u_{PAH})^2 + (u_{SRM})^2}$$

u_{RRF}	- the relative standard uncertainty of RRF averaging;
u_{IS}	- the relative standard uncertainty of calibration solution preparing (addition of IS);
u_{PAH}	- the relative standard uncertainty of calibration solution preparing (addition of calibrant - SRM);
u_{SRM}	- the relative standard uncertainty of PAH certified value.

$$u_{meas} = \sqrt{(u_{RSD})^2 + (u_{IS})^2 + (u_m)^2 + (u_{H2O})^2}$$

u_{RSD}	- the relative standard uncertainty of measurement results (RSD);
u_{IS}	- the relative standard uncertainty of sample preparing (addition of IS);
u_m	- the relative standard uncertainty of sample preparing (sample weighing);
u_{H2O}	- the relative standard uncertainty of the moisture content measuring.

Source of uncertainty	Type	u, % (Phenanthrene)	u, % (Fluoranthene)	u, % (Benzo[a]pyrene)	u, % (Benzo[ghi]perylene)
u_{RRF}	A	2.04	1.88	1.46	2.26
u_{IS}	B	1.44	1.44	1.44	1.44
u_{PAH}	B	1.44	1.44	1.44	1.44
u_{SRM}	B	0.70	0.93	1.03	1.39
u_{cal}		2.97	2.92	2.71	3.35
u_{RSD}	A	1.50	2.28	2.38	2.67
u_{IS}	B	1.44	1.44	1.44	1.44
u_{m}	B	0.0083	0.0083	0.0083	0.0083
u_{H2O}	B	1.11	1.11	1.11	1.11
u_{meas}		2.36	2.92	3.00	3.23
u_{bl}	B	0.016	0.006	0	0
Relative Standard Uncertainty		3.79	4.13	4.04	4.65
Relative expanded uncertainty (k=2)		**7.6**	**8.4**	**8.2**	**9.4**

Uncertainty Information from IH

$$\frac{A_{PAH}^{Std}}{A_{PAH}^{Std}} = m \cdot \frac{C_{PAH}^{Std}}{C_{IS}^{Std}} + b$$

C_{PAH}^{Std} - Concentration of the PAH in the calibration solution (μg/mL);
C_{IS}^{Std} - Concentration of the internal standard in the calibration solution (μg/mL);
A_{PAH}^{Std} - Area of the chromatographic peak (quantification ion chromatogram) of PAH in the calibration solution (dimensionless);
A_{PAH}^{Std} - Area of the chromatographic peak (quantification ion chromatogram) of PAH in the calibration solution (dimensionless);
m - slope of the linear regression;
b - intercept of the linear regression.

$$C_{PAH}^{E} = \frac{\left(\frac{A_{PAH}^{E}}{A_{IS}^{E}} - b\right)}{m} \cdot C_{IS}^{E}$$

C_{PAH}^{E} - Concentration of the PAH in the subsample extract analysed (μg/mL);
C_{IS}^{E} - Concentration of the internal standard in the subsample extract analysed (μg/mL);
A_{PAH}^{E} - Area of the chromatographic peak (quantification ion chromatogram) of PAH in the subsample extract analysed (dimensionless);
A_{PAH}^{E} - Area of the chromatographic peak (quantification ion chromatogram) of PAH in the subsample extract analysed (dimensionless).

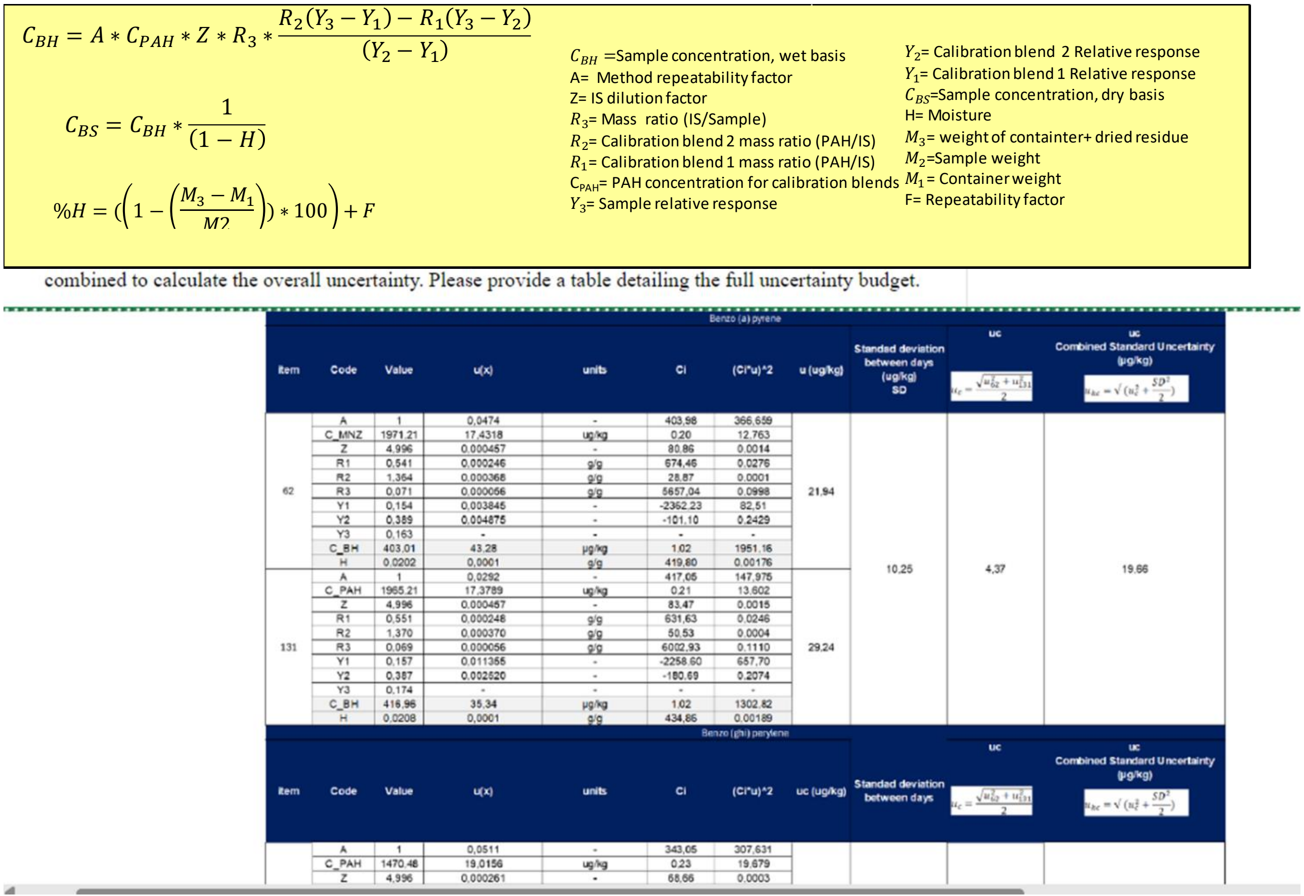
$$C_{PAH}^{S} = \frac{C_{PAH}^{E} \cdot V_{E}}{m_{S}} \cdot \frac{100}{MC}$$

C_{PAH}^{S} - Concentration of the PAH in the subsample (μg/kg dry basis);
C_{PAH}^{E} - Concentration of the PAH in the subsample extract (μg/mL), appyling the data from the internal standard calibration and the areas of the chromatographic peaks of PAH and internal standard quantified in the chromatogram of the subsample extract;

The combined uncertainty takes into account the uncertainty associated with both the precision and trueness components.
The uncertainty associated with the precision component takes into account the repeatability and intermediate precision components.
The uncertainty associated with the repeatability component was estimated using duplicate analysis conducted on different sediment samples under repeatability conditions (expressed by the ratio of the mean amplitude of the duplicate analysis to the factor of 1.128).
The uncertainty associated with the intermediate precision component was determined using data from a fortification analysis performed on different days while analysing distinct sets of samples (indicated by the dispersion of recoveries obtained in these analysis).
The uncertainty associated with the trueness component was evaluated using data from interlaboratory tests conducted by the laboratory, taking into account the observed recovery and the uncertainty associated with the reference value.
More information about the estimation of uncertainty provide in the sheet "Uncertainty".

			Equation	
Repetibility	Phenanthrene	6.22%	$u'_{rep} = \frac{\bar{A}'}{1{,}128}$	$\bar{A}'$ - relative amplitude of the concentrations observed in the two replicates u'_{rep} - relative uncertainty of the precision component (repetibility)
	Fluoranthene	7.00%		
	Benzo(a)pyrene	5.42%		
	Benzo(g,h,i)perylene	5.69%		
Intermediate precision	Phenanthrene	7.95%	$u_{IP} = \sqrt{\frac{\sum_{i=1}^{n}(R_i - \bar{R})}{n-1}}$ $u'_{IP} = \frac{u_{IP}}{\bar{R}}$	R_i - recovery obtained in each analysis $\bar{R}$ - mean recovery of *n* analysis u_{IP} - absolute uncertainty of the precision component (intermediate precision) u'_{IP} - relative uncertainty of the precision component (intermediate precision)
	Fluoranthene	7.62%		
	Benzo(a)pyrene	8.66%		
	Benzo(g,h,i)perylene	11.6%		
Trueness	Phenanthrene	7.76%	$u'_{ver} = \sqrt{\left(\frac{{s_R}^2}{n \cdot {\bar{R}_{EIL}}^2}\right) + \left(\frac{RSD_{EIL}}{\sqrt{m}}\right)^2_{max}}$	s_R - standard deviation of the recoveries obtained of *n* analysis of samples from proficiency tests $\bar{R}_{EIL}$ - mean recovery of *n* analysis of samples from proficiency tests $(RSD_{EIL}/\sqrt{m})_{max}$ - maximum value of the ratio between the relative standard deviation of the reference value of the proefficiency test sample and the square root of the number of participants who contributed to establish the reference value u'_{ver} - relative uncertainty of the trueness component
	Fluoranthene	6.65%		
	Benzo(a)pyrene	7.58%		
	Benzo(g,h,i)perylene	8.70%		
Combined	Phenanthrene	12.4%	$u'_{PAH} = \sqrt{{u'_{rep}}^2 + {u'_{IP}}^2 + (\bar{R}_{EIL} \cdot u'_{ver})^2}$	u'_{PAH} - relative combined uncertainty $\bar{R}_{EIL} \cdot u'_{ver}$ - used because the $\bar{R}_{EIL}$ are not significant different from 100% (recovery correction not applied) The uncertainty values of the three components were not limited in terms of significant digits to calculate the combined uncertainty.
	Fluoranthene	12.4%		
	Benzo(a)pyrene	12.7%		
	Benzo(g,h,i)perylene	15.3%		
Expanded (coverage factor = 2)	Phenanthrene	24.8%	$U'_{PAH} = 2 \cdot u'_{PAH}$	U'_{PAH} - Expanded relative uncertainty
	Fluoranthene	24.8%		
	Benzo(a)pyrene	25.4%		
	Benzo(g,h,i)perylene	30.6%		

Uncertainty Information from INM



$$C_{BH} = A * C_{PAH} * Z * R_3 * \frac{R_2(Y_3 - Y_1) - R_1(Y_3 - Y_2)}{(Y_2 - Y_1)}$$

$$C_{BS} = C_{BH} * \frac{1}{(1 - H)}$$

$$\%H = (\left(1 - \left(\frac{M_3 - M_1}{M2}\right)) * 100\right) + F$$

C_{BH} =Sample concentration, wet basis
A= Method repeatability factor
Z= IS dilution factor
R_3= Mass ratio (IS/Sample)
R_2= Calibration blend 2 mass ratio (PAH/IS)
R_1= Calibration blend 1 mass ratio (PAH/IS)
C_{PAH}= PAH concentration for calibration blends
Y_3= Sample relative response
Y_2= Calibration blend 2 Relative response
Y_1= Calibration blend 1 Relative response
C_{BS}=Sample concentration, dry basis
H= Moisture
M_3= weight of containter+ dried residue
M_2=Sample weight
M_1= Container weight
F= Repeatability factor

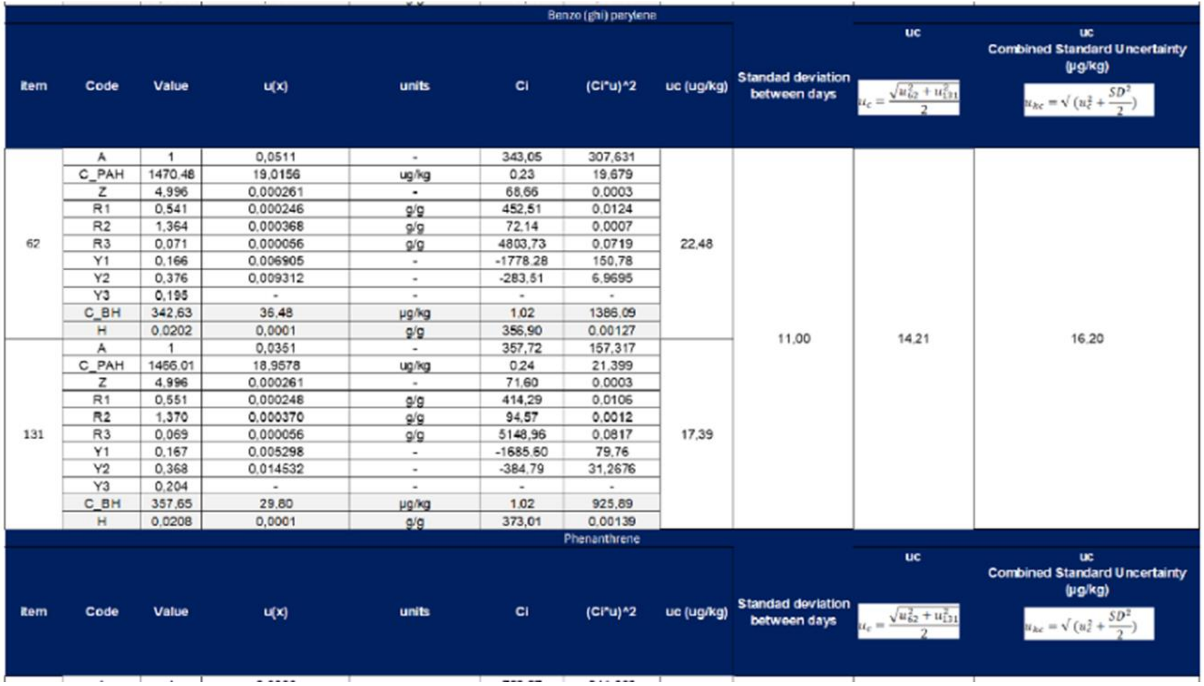
combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

Benzo (a) pyrene

Item	Code	Value	u(x)	units	Ci	(Ci*u)^2	u (ug/kg)	Standad deviation between days (ug/kg) SD	uc $u_c = \frac{\sqrt{u_{62}^2 + u_{131}^2}}{2}$	uc Combined Standard Uncertainty (µg/kg) $u_{kc} = \sqrt{(u_c^2 + \frac{SD^2}{2})}$
62	A	1	0,0474	-	403,98	366,659	21,94	10,25	4,37	19,66
	C_MNZ	1971,21	17,4318	ug/kg	0,20	12,763				
	Z	4,996	0,000457	-	80,86	0,0014				
	R1	0,541	0,000246	g/g	674,46	0,0276				
	R2	1,364	0,000368	g/g	28,87	0,0001				
	R3	0,071	0,000056	g/g	5657,04	0,0998				
	Y1	0,154	0,003845	-	-2362,23	82,51				
	Y2	0,389	0,004875	-	-101,10	0,2429				
	Y3	0,163	-	-	-	-				
	C_BH	403,01	43,28	µg/kg	1,02	1951,16				
	H	0,0202	0,0001	g/g	419,80	0,00176				
131	A	1	0,0292	-	417,05	147,975	29,24			
	C_PAH	1965,21	17,3789	ug/kg	0,21	13,602				
	Z	4,996	0,000457	-	83,47	0,0015				
	R1	0,551	0,000248	g/g	631,63	0,0246				
	R2	1,370	0,000370	g/g	50,53	0,0004				
	R3	0,069	0,000056	g/g	6002,93	0,1110				
	Y1	0,157	0,011355	-	-2258,60	657,70				
	Y2	0,387	0,002620	-	-180,69	0,2074				
	Y3	0,174	-	-	-	-				
	C_BH	416,96	35,34	µg/kg	1,02	1302,82				
	H	0,0208	0,0001	g/g	434,86	0,00189				

Benzo (ghi) perylene

Item	Code	Value	u(x)	units	Ci	(Ci*u)^2	uc (ug/kg)	Standad deviation between days	uc $u_c = \frac{\sqrt{u_{62}^2 + u_{131}^2}}{2}$	uc Combined Standard Uncertainty (µg/kg) $u_{kc} = \sqrt{(u_c^2 + \frac{SD^2}{2})}$
	A	1	0,0511	-	343,05	307,631				
	C_PAH	1470,48	19,0156	ug/kg	0,23	19,679				
	Z	4,996	0,000261	-	68,66	0,0003				

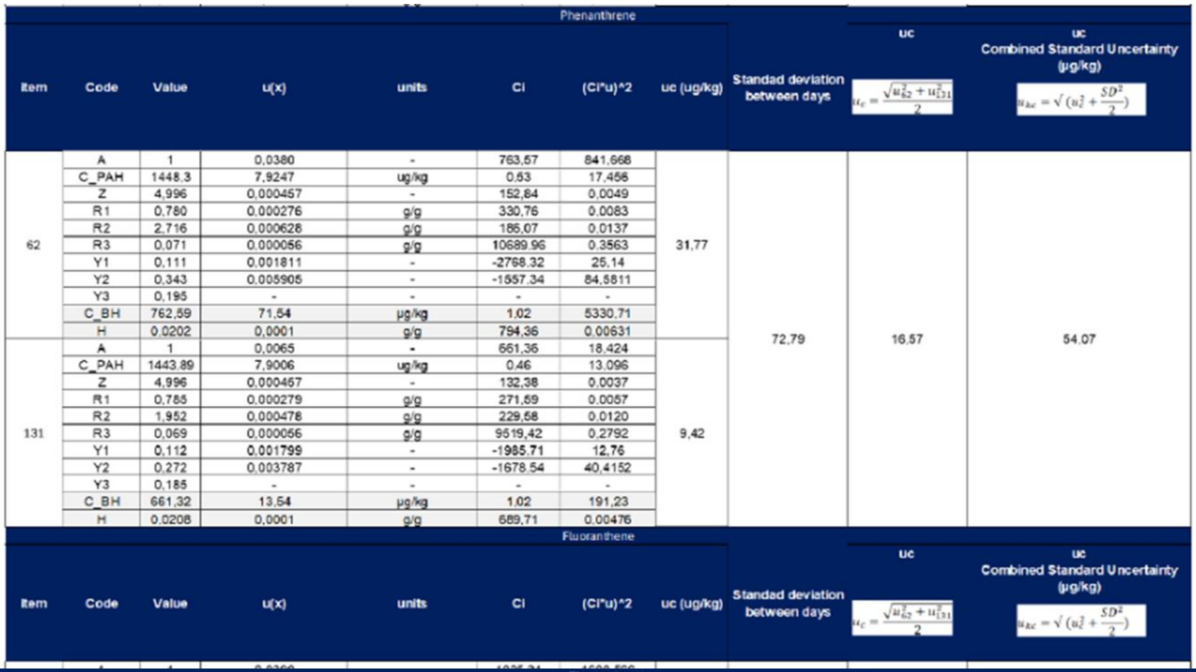


Benzo (ghi) perylene

Item	Code	Value	u(x)	units	Ci	(Ci*u)^2	uc (ug/kg)	Standad deviation between days	uc $u_c = \frac{\sqrt{u_{62}^2 + u_{131}^2}}{2}$	uc Combined Standard Uncertainty (µg/kg) $u_{kc} = \sqrt{(u_c^2 + \frac{SD^2}{2})}$
62	A	1	0,0511	-	343,05	307,631	22,48	11,00	14,21	16,20
	C_PAH	1470,48	19,0156	ug/kg	0,23	19,679				
	Z	4,996	0,000261	-	68,66	0,0003				
	R1	0,541	0,000246	g/g	452,51	0,0124				
	R2	1,364	0,000368	g/g	72,14	0,0007				
	R3	0,071	0,000056	g/g	4803,73	0,0719				
	Y1	0,166	0,006905	-	-1778,28	150,78				
	Y2	0,376	0,009312	-	-283,51	6,9695				
	Y3	0,195	-	-	-	-				
	C_BH	342,63	36,48	µg/kg	1,02	1386,09				
	H	0,0202	0,0001	g/g	356,90	0,00127				
131	A	1	0,0351	-	357,72	157,317	17,39			
	C_PAH	1466,01	18,9578	ug/kg	0,24	21,399				
	Z	4,996	0,000261	-	71,60	0,0003				
	R1	0,551	0,000248	g/g	414,29	0,0106				
	R2	1,370	0,000370	g/g	94,57	0,0012				
	R3	0,069	0,000056	g/g	5148,96	0,0817				
	Y1	0,167	0,005298	-	-1685,60	79,76				
	Y2	0,368	0,014532	-	-384,79	31,2676				
	Y3	0,204	-	-	-	-				
	C_BH	357,65	29,80	µg/kg	1,02	925,89				
	H	0,0208	0,0001	g/g	373,01	0,00139				

Phenanthrene

Item	Code	Value	u(x)	units	Ci	(Ci*u)^2	uc (ug/kg)	Standad deviation between days	uc $u_c = \frac{\sqrt{u_{62}^2 + u_{131}^2}}{2}$	uc Combined Standard Uncertainty (µg/kg) $u_{kc} = \sqrt{(u_c^2 + \frac{SD^2}{2})}$

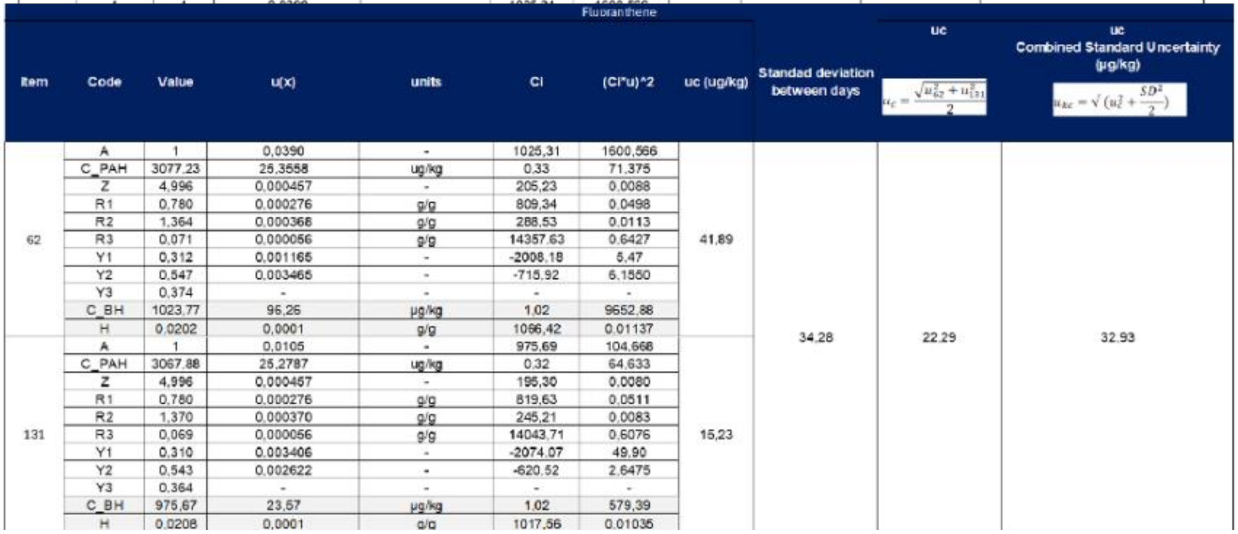


Phenanthrene

Item	Code	Value	u(x)	units	Ci	(Ci*u)^2	uc (ug/kg)	Standad deviation between days	uc $u_c=\frac{\sqrt{u_{62}^2+u_{131}^2}}{2}$	uc Combined Standard Uncertainty (µg/kg) $u_{kc}=\sqrt{(u_c^2+\frac{SD^2}{2})}$
62	A	1	0,0380	-	763,57	841,668	31,77	72,79	16,57	54,07
	C_PAH	1448,3	7,9247	ug/kg	0,53	17,456				
	Z	4,996	0,000457	-	152,84	0,0049				
	R1	0,780	0,000276	g/g	330,76	0,0083				
	R2	2,716	0,000628	g/g	186,07	0,0137				
	R3	0,071	0,000056	g/g	10689,96	0,3563				
	Y1	0,111	0,001811	-	-2768,32	25,14				
	Y2	0,343	0,005905	-	-1557,34	84,5811				
	Y3	0,195	-	-	-	-				
	C_BH	762,59	71,54	µg/kg	1,02	5330,71				
	H	0,0202	0,0001	g/g	794,36	0,00631				
131	A	1	0,0065	-	661,36	18,424	9,42			
	C_PAH	1443,89	7,9006	ug/kg	0,46	13,096				
	Z	4,996	0,000467	-	132,38	0,0037				
	R1	0,785	0,000279	g/g	271,59	0,0057				
	R2	1,952	0,000478	g/g	229,58	0,0120				
	R3	0,069	0,000056	g/g	9519,42	0,2792				
	Y1	0,112	0,001799	-	-1985,71	12,76				
	Y2	0,272	0,003787	-	-1678,54	40,4152				
	Y3	0,185	-	-	-	-				
	C_BH	661,32	13,54	µg/kg	1,02	191,23				
	H	0,0208	0,0001	g/g	689,71	0,00476				

Fluoranthene

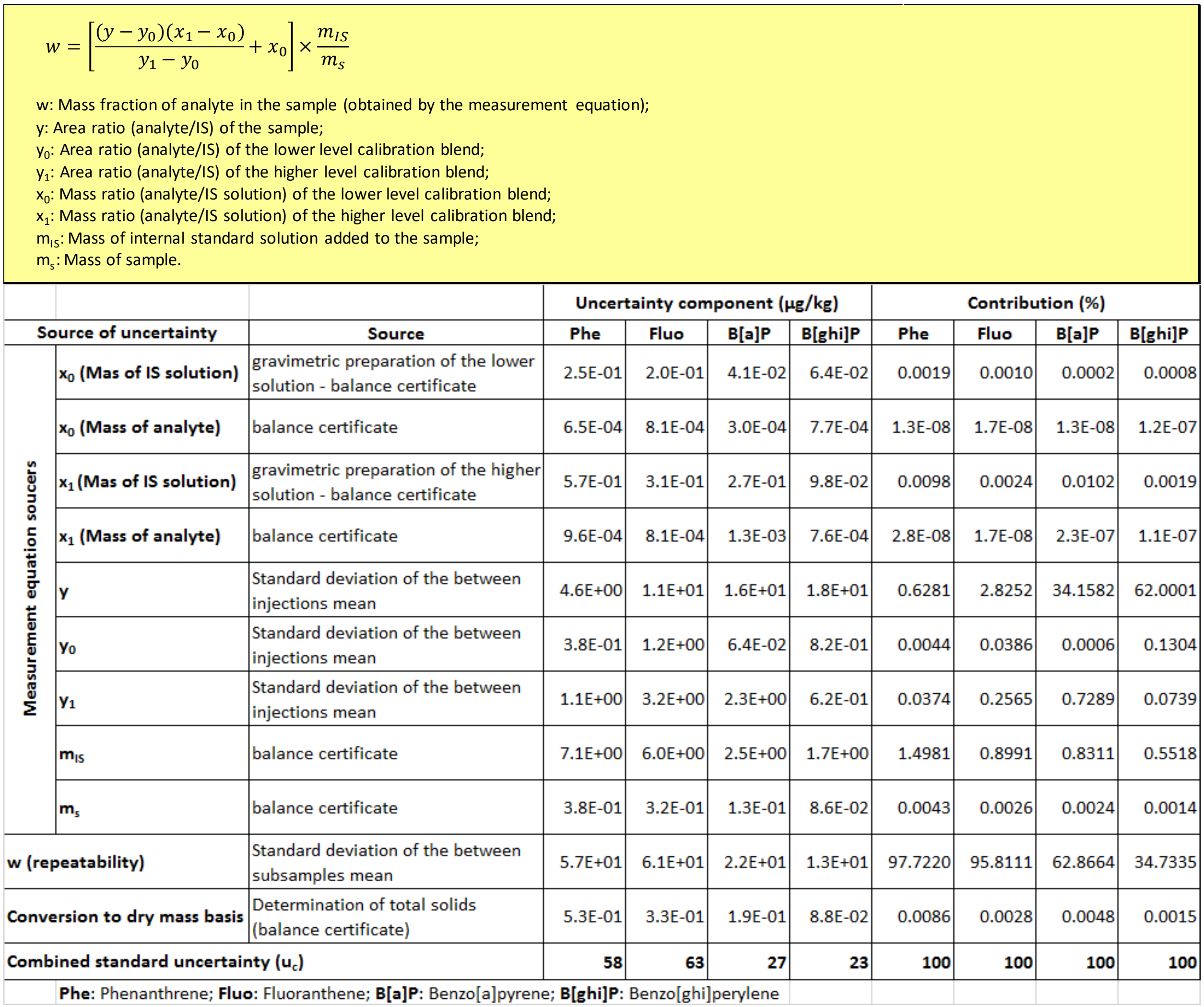
Item	Code	Value	u(x)	units	Ci	(Ci*u)^2	uc (ug/kg)	Standad deviation between days	uc $u_c=\frac{\sqrt{u_{62}^2+u_{131}^2}}{2}$	uc Combined Standard Uncertainty (µg/kg) $u_{kc}=\sqrt{(u_c^2+\frac{SD^2}{2})}$



Fluoranthene

Item	Code	Value	u(x)	units	Ci	(Ci*u)^2	uc (ug/kg)	Standad deviation between days	uc $u_c=\frac{\sqrt{u_{62}^2+u_{131}^2}}{2}$	uc Combined Standard Uncertainty (µg/kg) $u_{kc}=\sqrt{(u_c^2+\frac{SD^2}{2})}$
62	A	1	0,0390	-	1025,31	1600,566	41,89	34,28	22,29	32,93
	C_PAH	3077,23	25,3558	ug/kg	0,33	71,375				
	Z	4,996	0,000457	-	205,23	0,0088				
	R1	0,780	0,000276	g/g	809,34	0,0498				
	R2	1,364	0,000368	g/g	288,53	0,0113				
	R3	0,071	0,000056	g/g	14357,63	0,6427				
	Y1	0,312	0,001165	-	-2008,18	5,47				
	Y2	0,547	0,003465	-	-715,92	6,1550				
	Y3	0,374	-	-	-	-				
	C_BH	1023,77	96,26	µg/kg	1,02	9652,88				
	H	0,0202	0,0001	g/g	1066,42	0,01137				
131	A	1	0,0105	-	975,69	104,668	15,23			
	C_PAH	3067,88	25,2787	ug/kg	0,32	64,633				
	Z	4,996	0,000457	-	195,30	0,0080				
	R1	0,780	0,000276	g/g	819,63	0,0511				
	R2	1,370	0,000370	g/g	245,21	0,0083				
	R3	0,069	0,000056	g/g	14043,71	0,6076				
	Y1	0,310	0,003406	-	-2074,07	49,90				
	Y2	0,543	0,002622	-	-620,52	2,6475				
	Y3	0,364	-	-	-	-				
	C_BH	975,67	23,57	µg/kg	1,02	579,39				
	H	0,0208	0,0001	g/g	1017,56	0,01035				

Uncertainty Information from INMETRO



$$w = \left[\frac{(y - y_0)(x_1 - x_0)}{y_1 - y_0} + x_0\right] \times \frac{m_{IS}}{m_s}$$

w: Mass fraction of analyte in the sample (obtained by the measurement equation);
y: Area ratio (analyte/IS) of the sample;
y_0: Area ratio (analyte/IS) of the lower level calibration blend;
y_1: Area ratio (analyte/IS) of the higher level calibration blend;
x_0: Mass ratio (analyte/IS solution) of the lower level calibration blend;
x_1: Mass ratio (analyte/IS solution) of the higher level calibration blend;
m_{IS}: Mass of internal standard solution added to the sample;
m_s: Mass of sample.

			Uncertainty component (µg/kg)				**Contribution (%)**			
Source of uncertainty		**Source**	**Phe**	**Fluo**	**B[a]P**	**B[ghi]P**	**Phe**	**Fluo**	**B[a]P**	**B[ghi]P**
Measurement equation soucers	**x_0 (Mas of IS solution)**	gravimetric preparation of the lower solution - balance certificate	2.5E-01	2.0E-01	4.1E-02	6.4E-02	0.0019	0.0010	0.0002	0.0008
	x_0 (Mass of analyte)	balance certificate	6.5E-04	8.1E-04	3.0E-04	7.7E-04	1.3E-08	1.7E-08	1.3E-08	1.2E-07
	x_1 (Mas of IS solution)	gravimetric preparation of the higher solution - balance certificate	5.7E-01	3.1E-01	2.7E-01	9.8E-02	0.0098	0.0024	0.0102	0.0019
	x_1 (Mass of analyte)	balance certificate	9.6E-04	8.1E-04	1.3E-03	7.6E-04	2.8E-08	1.7E-08	2.3E-07	1.1E-07
	y	Standard deviation of the between injections mean	4.6E+00	1.1E+01	1.6E+01	1.8E+01	0.6281	2.8252	34.1582	62.0001
	y_0	Standard deviation of the between injections mean	3.8E-01	1.2E+00	6.4E-02	8.2E-01	0.0044	0.0386	0.0006	0.1304
	y_1	Standard deviation of the between injections mean	1.1E+00	3.2E+00	2.3E+00	6.2E-01	0.0374	0.2565	0.7289	0.0739
	m_{IS}	balance certificate	7.1E+00	6.0E+00	2.5E+00	1.7E+00	1.4981	0.8991	0.8311	0.5518
	m_s	balance certificate	3.8E-01	3.2E-01	1.3E-01	8.6E-02	0.0043	0.0026	0.0024	0.0014
w (repeatability)		Standard deviation of the between subsamples mean	5.7E+01	6.1E+01	2.2E+01	1.3E+01	97.7220	95.8111	62.8664	34.7335
Conversion to dry mass basis		Determination of total solids (balance certificate)	5.3E-01	3.3E-01	1.9E-01	8.8E-02	0.0086	0.0028	0.0048	0.0015
Combined standard uncertainty (u_c)			**58**	**63**	**27**	**23**	**100**	**100**	**100**	**100**

Phe: Phenanthrene; **Fluo**: Fluoranthene; **B[a]P**: Benzo[a]pyrene; **B[ghi]P**: Benzo[ghi]perylene

Uncertainty Information from NIM

Measurement equation was showed as following

$$C_{sample} = \frac{R_{SM} \times C_{calib} \times f_{purity} \times M_{spike(sample)}}{R_{CM} \times M_{sample} \times f_{dry} \times C_{spike(calib)}}$$

R_{SM} : Area ratio of target compound and labeled compound in sample solution.
R_{CM} : Area ratio of target compound and labeled compound in calibration.
C_{calib}: Mass faction of standard solution,by weighing.
$M_{spike(sample)}$: Mass of labeled compound to added into sample, by weighing .
$C_{spike(calib)}$: Mass fractionof labeled compound to add into calibration soultion, by weighing.
M_{sample}: Sample mass, by weighing.
f_{purity} : Calibrate Purity
f_{dry} : Ratio of the sample mass before drying and after drying

Parameter of **Phenanthrene**	Standard Uncertainty (ng/g)	Degrees of freedom	Type
Method precision	41.89	5	A
Efficiency of extraction procedure	100.59	large	B
Purity of pure standard	11.99		A+B
Mass fraction of internal standard	8.17	large	A+B
Mass fraction of sample	4.09	large	A+B
Mass fraction calibration standard	4.90	large	A+B
Matrix effects in calibration blend	10.90	large	B
Influnce of peak seperation	8.17		B
Pollution introduced from the environment	8.17		B
Combined standard uncertainty	111.30		
Coverage factor	2		
Combined expanded uncertainty	223		

Parameter of **Fluoranthene**	Standard Uncertainty (ng/g)	Degrees of freedom	Type
Method precision	39.59	5	A
Efficiency of extraction procedure	76.83	large	B
Purity of pure standard	19.35		A+B
Mass fraction of internal standard	7.26	large	A+B
Mass fraction of sample	3.63	large	A+B
Mass fraction calibration standard	4.35	large	A+B
Matrix effects in calibration blend	7.26	large	B
Influnce of peak seperation	2.42		B
Pollution introduced from the environment	2.42		B
Combined standard uncertainty	89.5		
Coverage factor	2		
Combined expanded uncertainty	179		

Parameter of **Benzo[a]pyrene**	Standard Uncertainty (ng/g)	Degrees of freedom	Type
Method precision	10.00	5	A
Efficiency of extraction procedure:	19.61	large	B
purity of pure standard	2.02		A+B
Mass fraction of internal standard	2.25	large	A+B
Mass fraction of sample	1.12	large	A+B
Mass fraction calibration standard	1.35	large	A+B
Matrix effects in calibration blend	2.25	large	B
Influnce of peak seperation	3.00		B
Combined standard uncertainty	22.6		
Coverage factor	2		
Combined expanded uncertainty	45.2		

Parameter of Benzo[ghi]perylene	Standard Uncertainty (ng/g)	Degrees of freedom	Type
Method precision	6.93	5	A
Efficiency of extraction procedure:	22.28	large	B
purity of pure standard	1.56		A+B
Mass fraction of internal standard	2.04	large	A+B
Mass fraction of sample	1.02	large	A+B
Mass fraction calibration standard	1.22	large	A+B
Matrix effects in calibration blend	2.04	large	B
Influnce of peak seperation	0.68		B
Combined standard uncertainty	23.7		
Coverage factor	2		
Combined expanded uncertainty	47.5		

Method precision:	Reproducibility of sample determination
Efficiency of extraction procedure:	Comparison of results from different extraction techniques and different extraction time.
Purity of pure standard:	Type A uncertainty (combined uncertainty of 3 method for purity determination),type B uncertainty
Mass fraction of internal standard:	Type A uncertainty (reproducibility of weighing, n=6) and type B uncertainty (linearity of weighing,
Mass fraction of sample:	Type A uncertainty (reproducibility of weighing, n=6) and type B uncertainty (linearity of weighing,
Mass fraction calibration standard:	Type A uncertainty (reproducibility of weighing, n=6) and type B uncertainty (linearity of weighing,
Matrix effects in calibration blend:	Comparison of results from calibration blends prepared from solvent and sediment matrix
Influnce of peak seperation	Influnce of interfernce peak to analyte peak area
Pollution introduced from the environment	Target compounds that are inevitably introduced from the environment during extraction and clean-up process.

Uncertainty Information from NIMT

$$W_x = F_P . W_z . \frac{m_y . m_{zc}}{F_{recovery} . F_{dry\,mass} . m_x . m_{yc}} . \frac{R'_b}{R'_{bc}}$$

Where:
wx = mass fraction of Fluoranthene in sediment
wzc = mass fraction of Fluoranthrene in the calibration solution used to prepare the calibration blend
my = mass of spike solution (internal standard) added to sample blend
myc = mass of spike solution (internal standard) added to calibration blend
mzc= mass of standard solution added to calibration blend
mx = mass of sample added to sample blend
FP = method precision factor, given a value of 1
F drymass = dry mass correction factor obtained from moisture content analysis and R'bc = observed isotope amount ratios in the sample blend and the calibration blend, respectively.
F recovery = recovery factor obtained from SRM 1941 b anaysis.

An external calibration curve for Phenanthrene and Benzo(ghi)perylene measurement equation:

$$w_x = F_{std} \cdot F_{Precision} \cdot \frac{[W_0]}{m_x . F_{dry\,mass} . F_{recovery}}$$

wx = Mass fraction of measurand in sample (ng/g)
wo = amount of measurand obtained from the calibration curve (ng)
mx= Mass of sample (g)
F dry mass= dry mass correction factor
F std= given a value of 1 but accounting for the uncertainty including bias and random effects of calibration standard (type B and type A)
F Recovery =The uncertainty from revovery will take to account if the recovery factor is significantly different to 1

Combined uncertainty for Fluoranthene:

$$\frac{u(w_x)}{w_x} = \sqrt{\left(\frac{u(w_{zc})}{w_{zc}}\right)^2 + \left(\frac{u(m_y)}{m_y}\right)^2 + \left(\frac{u(m_{yc})}{m_{yc}}\right)^2 + \left(\frac{u(m_{zc})}{m_{zc}}\right)^2 + \left(\frac{u(m_x)}{m_x}\right)^2 + \left(\frac{u(F_{drymass})}{F_{drymass}}\right)^2 + \left(\frac{u(R'_b)}{R'_b}\right)^2 + \left(\frac{u(R'_{bc})}{R'_{bc}}\right)^2 + \left(\frac{u(F_{recovery}}{F_{recovery}}\right)^2 + \left(\frac{u(F_P)}{F_P}\right)^2}$$

Where:

u(wz,c) is the standard uncertainty of the mass fraction of analyte in the calibration solution used to prepare the calibration blend. The value was evaluated from the purity of MNZ standard, masses weighed for preparation of stock solutions and uncertainty using different standards (standard comparison).

u(my), u(my,c), u(mx) and u(mz,c) are standard uncertainties of the masses. These values were evaluated from the bias and precision effect of the balance.
u (FP) is the standard uncertainty of the precision factor. This value was evaluated from standard deviation of the multiple IDMS results.
u(Fdrymass) is the standard uncertainty of the dry mass correction factor which was evaluated from the moisture content analysis.
u(R'b) andvu(R'b,c) are standard uncertainties of the measured isotope amount ratios of the analyte and the internal standard in the sample and calibration blend. These value were evaluated from the precison on these ratios.
u(recovery) is the standard uncertainty of the recovery factor.

Combined uncertainty for Phenanthrene and Benzo(ghi)perylene:

$$\frac{u(w_x)}{w_x} = \sqrt{\left(\frac{u(w_0)}{w_0}\right)^2 + \left(\frac{u(F_{std})}{F_{std}}\right)^2 + \left(\frac{u(m_x)}{m_x}\right)^2 + \left(\frac{u(F_{drymass})}{F_{drymass}}\right)^2 + \left(\frac{u(F_{recovery})}{F_{recovery}}\right)^2 + \left(\frac{u(F_P)}{F_P}\right)^2}$$

$u(m_x)$ = standard uncertainties due to weighing estimated from bias of balance
$u(w_0)$= standard uncertainty of the amount of measurand obtained from the calibration curve (ng) estimated from the regression
u(Fstd) = standard uncertainty of mid concentration calibration standard estimated from bias and random effects (type B and type A)
$u(F_{drymass})$ = standard uncertainty of dry mass correction factor
$u(F_P)$ = standard uncertainty of method precision
u(Recovery) = standard uncertainty of recovery

Combination of Uncertainties of Fluoranthene

Factor	Values	Uncertainties	
	x	u(x)	u(x)/(x)
Measurement equation factors			
Method Precision	1.000	0.029098	2.910%
mzc	0.637	0.000019	0.0030%
my	0.210	0.000019	0.0091%
myc	0.215	0.000019	0.0089%
mx	1.016	0.000019	0.0019%
wz	3423.435	107.157712	3.1301%
R'b	1.3941	0.008212	0.5890%
R'bc	1.3074	0.005421	0.4146%
Additional Factors		Enter u(x) = 0 and veff = 1 for unused factors.	
Moisture content	0.9735	0.0005	0.0005
Recovery	1.0206	0.0154	1.5095%

Uncertainty Analysis Results of Fluoranthene

wx=	**2276.58**	ng/g
u(x) =	104.488	ng/g
u(x)/x =	4.59%	
Veff(total) =	35.973	
k=	2.03	(@ 95% level)
U(x) =	**212.121**	
%U(x) =	**9.32%**	

Combination of Uncertainties of Phenanthrene

Factor	Values	Uncertainties	
Measurement equation factors			
method precision	1.000	0.030484	3.048%
w0	2662.265	18.234786	0.6849%
mx	1.016	0.000031	0.0030%
calibrant Type A	3352.116	18.337680	0.5470%
Calibrant type B	4.570	0.025000	0.5470%
Additional Factors		Enter u(x) = 0 and veff = 1 for unused factors.	
Moisture content	0.9735	0.0005	0.0005
Recovery	1.1768	0.0764	6.4949%

Uncertainty Analysis Results of Phenanthrene

wx=	**2234.72**	ng/g
u(x) =	161.994	ng/g
u(x)/x =	7.22%	
Veff(total) =	4360924.081	
k=	2.00	(@ 95% level)
U(x) =	**316.261**	
%U(x) =	**14.15%**	

Combination of Uncertainties of Benzo(ghi)perylene

Factor	Values	Uncertainties	
Measurement equation factors			
method precision	1.000	0.038607	3.861%
w0	496.685	15.352538	3.091%
mx	1.016	0.000031	0.003%
calibrant Type A	3403.462	8.802061	0.259%
Calibrant type B	4.640	0.060000	1.293%
Additional Factors		Enter u(x) = 0 and veff = 1 for unused factors.	
Moisture content	0.9735	0.0529%	0.054%
Recovery	1.0302	3.882%	3.77%

Uncertainty Analysis Results of Benzo(ghi)perylene

wx=	**474.25**	ng/g
u(x) =	30.143	ng/g
u(x)/x =	6.36%	
Veff(total) =	3467.669	
k=	2.00	(@ 95% level)
U(x) =	**59.100**	
%U(x) =	**12.46%**	

Uncertainty Information from GLHK

1. Calculate the signal response ratio (*Rsp*) of fluoranthene (FLUT), benzo[*a*]pyrene (BAPY) and benzo[*ghi*]perylene (BGPE) for each standard as follows:

$$Rsp = \frac{A}{A_{IS}}$$

where

A = Q1 peak area of the target analyte
A_{IS} = Q1 peak area of the corresponding labelled standard

2. Calculate the amount ratio (Amt_{Ratio}) of fluoranthene (FLUT), benzo[*a*]pyrene (BAPY) and benzo[*ghi*]perylene (BGPE) for each standard as follows:

$$Amt_{Ratio} = \frac{Amt}{Amt_{IS}}$$

where

Amt = amount of the target analyte used in ng
Amt_{IS} = amount of the corresponding labelled standard used in ng

3. Establish a calibration bracket by plotting the response ratios (*Rsp*) versus the amount ratios (Amt_{Ratio}). Obtain the following linear equation from the graph:

$$(Rsp) = (m)(Amt_{Ratio}) + b$$

where

Rsp = signal response ratio of the target analyte (y-axis)
m = slope of the linear equation
Amt_{Ratio} = amount ratio of the corresponding labelled standard (x-axis)
b = y-intercept

4. Calculate the amount of fluoranthene (FLUT), benzo[*a*]pyrene (BAPY) and benzo[*ghi*]perylene (BGPE) in sample (*Spl_Amt*) in ng using the following equation:

$$Spl\_Amt = \frac{\left({A_{spl}}/{A_{IS}}\right) - b}{m} \times Amt_{IS}$$

where

A = Q1 peak area of the target analyte in sample solution
A_{IS} = Q1 peak area of the corresponding labelled standard in sample solution
b = y-intercept of the linear equation as obtained in Clause 3
m = slope of the linear equation as obtained in in Clause 3
Amt_{IS} = amount of labelled standard in sample in ng

5. Calculate the concentration of fluoranthene (FLUT), benzo[*a*]pyrene (BAPY) and benzo[*ghi*]perylene (BGPE) in sample in ng/g as follows:

$$C_{Sample} = \frac{Spl\_Amt}{W_{Sample}}$$

where

Spl_Amt = amount of the target analyte found in sample in ng
W_{sample} = sample used in g

6. The moisture content (%*M*) in the sample is calculated as follows:

$$\%M = \frac{W2 - W3}{W2 - W1} \times 100\%$$

where

$W3$ = weight of glass vial with sample after drying, in g
$W2$ = weight of glass vial with sample before drying, in g
$W1$ = weight of glass vial, in g

7. The moisture-corrected analyte content (C_{sample_MC}), in ng/g or µg/kg is calculated as follows:

$$C_{Sample,MC} = C_{Sample} \div \left(1 - \frac{\%M}{100\%}\right)$$

where

C_{sample} = concentration of target analyte in sample as obtained in Clause 5, in ng/g or µg/kg
$\%M$ = moisture content in sample as obtained in Clause 6

Uncertainties were estimated based on contribution from four factors: 1) method precision, 2) method bias, 3) purity of reference standards, 4) uncertainty from moisture content determination.

Fluoranthene

Description	Relative standard Uncertainty u(x)
Precision u_{pre}	0.05872
Bias (Cal std) u_{bias}	0.00465
CRM $u_{Calibrant}$	0.01000
Moisture content $u_{moisture}$	0.00035
Relative combined standard uncertainty (u)	0.05975

Relative Expanded Uncertainty (U) = Relative combined standard uncertainty (u) × Coverage factor
=0.05975 x 2
=0.11950
~12%

Benzo[a]pyrene

Description	Relative standard Uncertainty u(x)
Precision u_{pre}	0.11702
Bias (Cal std) u_{bias}	0.00292
CRM $u_{Calibrant}$	0.01000
Moisture content $u_{moisture}$	0.00035
Relative combined standard uncertainty (u)	0.11748

Relative Expanded Uncertainty (U) = Relative combined standard uncertainty (u) × Coverage factor
=0.11748 x 2
=0.23496
~24%

Benzo[ghi]perylene

Description	Relative standard Uncertainty u(x)
Precision u_{pre}	0.04760
Bias (Cal std) u_{bias}	0.00176
CRM $u_{Calibrant}$	0.01000
Moisture content $u_{moisture}$	0.00035
Relative combined standard uncertainty (u)	0.04867

Relative Expanded Uncertainty (U) = Relative combined standard uncertainty (u) × Coverage factor
=0.04867 x 2
=0.09734
~10%

where

Relative combined standard uncertainty (u) = $\sqrt{\ }(u_{\text{pre}}^2 + u_{\text{bias}}^2 + u_{\text{calibrant}}^2 + u_{\text{moisture}}^2)$

*Coverage factor k = 2, at approximate 95% confidence level

Uncertainty Information from BAM

$$x_{sample} = \frac{r - i_c}{sl} \cdot \frac{m_{is}}{m_{sample}} \cdot F_{pur} \cdot F_{dry\ mass}$$

x_{sample}: mass fraction of the respective PAH congener in the sediment sample
r: area ratio native/internal standard
i_c: intercept of calibration curve
sl: slope of calibration curve
m_{IS}: mass of internal standard added to
m_{sample}: mass of sediment sample
F_{pur}: purity of respetive PAH congener in the calibation standard according to certificate
$F_{dry\ mass}$: Dry $mass_{sample}$/total $mass_{sample}$

$$U = k \cdot u_c = k \cdot x_{sample} \cdot \sqrt{(u_{x,r})^2 + (u_{cal,r})^2 + (u_{pur,r})^2 + (u_{dry\ mass,r})^2}$$

Symbol	Description	Unit	Value			
			Phenanthrene	Fluoranthene	Benzo[*a*]pyrene	Benzo[*ghi*]perylene
x_{sample}	mean value of PAH congener content in the sample	µg/kg	3010	2538	882.9	673.0
$SD_{mean,PAH}$	standard deviation of the mean PAH congener content in the sample	µg/kg	28.75	42.34	29.50	21.09
$u_{x,r}$	rel. standard uncertainty of measurement: $SD_{mean;PAH}/x_{sample}$	–	0.009552	0.01668	0.03342	0.03134
$u_{cal,r}$	rel. uncertainty of calibration acc. to EURACHEM CITAC Guide	–	0.03	0.03	0.03	0.03
F_{pur}	purity of PAH congener in the standard acc. to certificate	g/g	1	1	1	1
$u_{pur,r}$	rel. uncertainty of PAH congener content in the standard (purity): u_{pur}/F_{pur}	–	0.005470	0.008239	0.008842	0.012931
$SD_{mean,dry\ mass}$	standard deviation of the mean dry mass content of the sample	%	0.307	0.307	0.307	0.307
$u_{dry\ mass,r}$	rel. uncertainty of dry mass $SD_{dry\ mass}/F_{dry\ mass}$	%/%	0.0031396	0.0031396	0.0031396	0.0031396
$F_{dry\ mass}$	Dry $mass_{sample}$/total $mass_{sample}$	%	0.9774	0.9774	0.9774	0.9774
$u_{c,r}$	rel. combined standard uncertainty	-	0.0321	0.0354	0.0459	0.0454
u_c	combined standard uncertainty	µg/kg	96.65	89.95	40.51	30.54
k	coverage factor	-	2	2	2	2
U	expanded uncertainty (95% confidence)	µg/kg	193	180	81.0	61.1

Uncertainty Information from NMIA

Measurement Equation:

$$w_x = P.\frac{m_{istd}}{m_{sample}}.F_{MF}.F_{Cal}.F_{ExtB}.F_{ExtS}.F_{Chro}.F_{MS}.F_{Reg}$$

Where $P = \frac{r_R - b}{a}$

w_x	sample mass fraction
m_{istd}	internal standard mass (bias only) determined from balance calibration data
m_{sample}	sample mass (bias only) determined from balance calibration data
F_{MF}	Moisture factor correction, determined from moisture determination precision and balance calibration data.
F_{Cal}	Calibrator uncertainty, determined from the certificate uncertainty values
F_{ExtB}	Potential bias from incomplete extraction, determined by analysis of re-extracted ASE cells
F_{ExtS}	Potential bias from extraction solvent choice, determined by comparing results from two ASE colvent conditions.
F_{Chro}	Potential chromatographic biases, determined by comparing results from two chromatographic columns
F_{MS}	Potential mass spectrometric biases, determined by comparing results from multiple MRMs
F_{Reg}	Potential bias from regression model, determined by comparing results from ordinary least squares and Pade[1,1] regression models
P	Precision, which includes components of response ratio variance, regression constants, and sample mass variance. Note that individual components of precision could not be individually assessed.

Factors are combined according to JCGM 100:2008

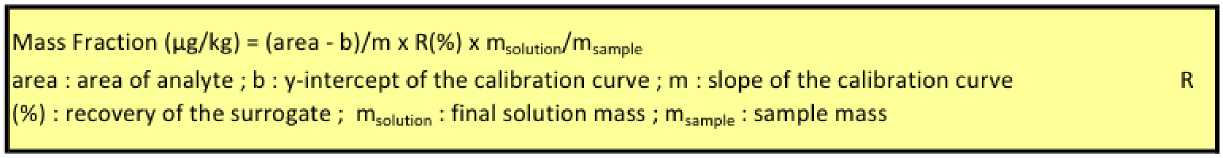
Phenanthrene				
Factor	Value	u(x)	u(x)/x	Veff
P	0.627	0.00529	0.00844	5
mistd	0.343	0.00006	0.00018	400
msample	1.004	0.00018	0.00018	400
F MF	1.030	0.00304	0.00295	5.07
F Cal	11.57	0.04000	0.00346	20
F ExtB	1	0.02887	0.02887	10
F ExtS	1	0.00000	0.00000	1
F Chro	1	0.00790	0.00790	11
F MS	1	0.01660	0.01660	8
F Reg	1	0.00394	0.00394	23

Fluoranthene				
Factor	Value	u(x)	u(x)/x	Veff
P	0.787	0.00292	0.00371	5
mistd	0.343	0.00006	0.00018	400
msample	1.004	0.00018	0.00018	400
F MF	1.030	0.00304	0.00295	5.07
F Cal	8.324	0.02900	0.00348	20
F ExtB	1	0.01732	0.01732	10
F ExtS	1	0.00000	0.00000	1
F Chro	1	0.00715	0.00715	11
F MS	1	0.02099	0.02099	6
F Reg	1	0.00112	0.00112	23

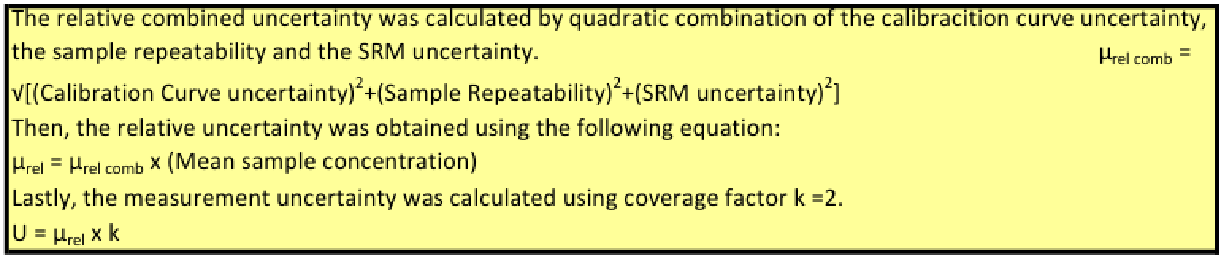
Benzo(a)pyrene				
Factor	Value	u(x)	u(x)/x	Veff
P	0.451	0.00356	0.00789	11
mistd	0.343	0.00006	0.00018	400
msample	1.004	0.00018	0.00018	400
F MF	1.030	0.00304	0.00295	5.07
F Cal	4.71	0.05667	0.01203	20
F ExtB	1	0.01155	0.01155	10
F ExtS	1	0.02088	0.02088	1
F Chro	1	0.01236	0.01236	11
F MS	1	0.02035	0.02035	5
F Reg	1	0.00237	0.00237	23

Benzo(ghi)perylene				
Factor	Value	u(x)	u(x)/x	Veff
P	0.322	0.00243	0.00753	11
mistd	0.343	0.00006	0.00018	400
msample	1.004	0.00018	0.00018	400
F MF	1.030	0.00304	0.00295	5.07
F Cal	5.669	0.02300	0.00406	20
F ExtB	1	0.00577	0.00577	10
F ExtS	1	0.01792	0.01792	1
F Chro	1	0.04865	0.04865	11
F MS	1	0.02992	0.02992	5
F Reg	1	0.00107	0.00107	23

Uncertainty Information from INTI



Mass Fraction (μg/kg) = (area - b)/m x R(%) x $m_{solution}/m_{sample}$
area : area of analyte ; b : y-intercept of the calibration curve ; m : slope of the calibration curve R
(%) : recovery of the surrogate ; $m_{solution}$: final solution mass ; m_{sample} : sample mass



The relative combined uncertainty was calculated by quadratic combination of the calibracition curve uncertainty, the sample repeatability and the SRM uncertainty. $\mu_{rel\ comb}$ =
√[(Calibration Curve uncertainty)^2+(Sample Repeatability)^2+(SRM uncertainty)^2]
Then, the relative uncertainty was obtained using the following equation:
$\mu_{rel} = \mu_{rel\ comb}$ x (Mean sample concentration)
Lastly, the measurement uncertainty was calculated using coverage factor k =2.
U = μ_{rel} x k

Uncertainty Information from TUBITAK_UME

$$\frac{u_c(Analyte)}{c_{Analyte}} = \sqrt{\left(\frac{u(m_{SI})}{m_{SI}}\right)^2 + \left(\frac{u(c_{LSS})}{c_{LSS}}\right)^2 + \left(\frac{u(c_{NSS})}{c_{NSS}}\right)^2 + \left(\frac{u(V_{SLL})}{V_{SLL}}\right)^2 + \left(\frac{u(R_m)}{R_m}\right)^2 + \left(\frac{u(r)}{r}\right)^2 + \frac{u(Drymass)}{WaterContent} + \left(\frac{u(Cal)}{C_0}\right)^2}$$

Uncertainty Budget of Phe

Parameters	Value (X)	u(x)	u(x)/X
Mass of sample intake	1	0.00008	7.92E-05
Labelled stock solution	26466	229	8.67E-03
Native stock solution	4570	25	5.47E-03
Spiking of labelled stock solution	0.043	0.00008	1.84E-03
Recovery	1.51	0.06	3.74E-02
Repeatability	2528	53	2.10E-02
Dry Mass Corretion	1.85	0.017	9.21E-03
Calibration Graph	2528	0.03	1.35E-05
Relative Standard Measurement Uncertainty			0.045
Result (ng/g)	2528		
Combined Standard Measurement Uncertainty		114	
Expanded Uncertainty (k=2)		228	
Relative Mesurement Uncertainty (%)		9	

Uncertainty Budget of FL

Parameters	Value (X)	u(x)	u(x)/X
Mass of sample intake	1	0.00008	7.92E-05
Labelled stock solution	22480	216	9.60E-03
Native stock solution	9710	80	8.24E-03
Spiking of labelled stock solution	0.043	0.00008	1.84E-03
Recovery	0.95	0.04	4.10E-02
Repeatability	2183	37	1.70E-02
Dry Mass Corretion	1.85	0.017	9.21E-03
Calibration Graph	2183	0.04	1.96E-05
Relative Standard Measurement Uncertainty			0.047
Result (ng/g)	2183		
Combined Standard Measurement Uncertainty		103	
Expanded Uncertainty (k=2)		206	
Relative Mesurement Uncertainty (%)		9	

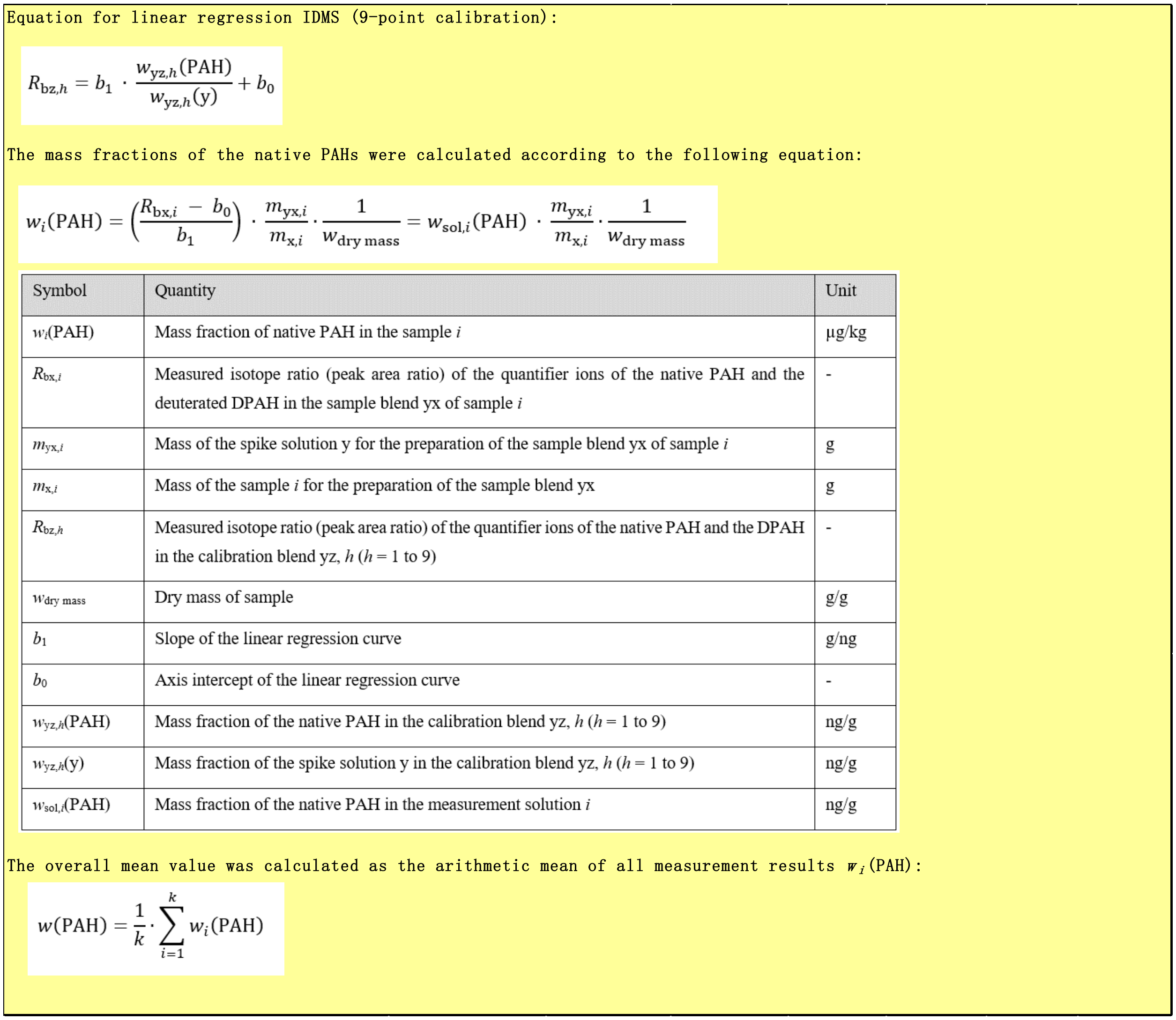
Uncertainty Budget of BaP

Parameters	Value (X)	u(x)	u(x)/X
Mass of sample intake	1	0.00008	7.92E-05
Labelled stock solution	24858	216	8.70E-03
Native stock solution	6220	55	8.84E-03
Spiking of labelled stock solution	0.043	0.00008	1.84E-03
Recovery	0.71	0.03	4.09E-02
Repeatability	699	12	1.71E-02
Dry Mass Corretion	1.85	0.017	9.21E-03
Calibration Graph	699	0.3	3.96E-04
Relative Standard Measurement Uncertainty			0.047
Result (ng/g)	699		
Combined Standard Measurement Uncertainty		33	
Expanded Uncertainty (k=2)		66	
Relative Mesurement Uncertainty (%)		9	

Uncertainty Budget of BnzGHI

Parameters	Value (X)	u(x)	u(x)/X
Mass of sample intake	1	0.00008	7.92E-05
Labelled stock solution	25543	233	9.11E-03
Native stock solution	4640	60	1.29E-02
Spiking of labelled stock solution	0.043	0.00008	1.84E-03
Recovery	1.00	0.07	7.41E-02
Repeatability	665	19	2.82E-02
Dry Mass Corretion	1.85	0.017	9.21E-03
Calibration Graph	665	0.1	1.93E-04
Relative Standard Measurement Uncertainty			0.081
Result (ng/g)	665		
Combined Standard Measurement Uncertainty		54	
Expanded Uncertainty (k=2)		108	
Relative Mesurement Uncertainty (%)		16	

Uncertainty Information from METAS



Equation for linear regression IDMS (9-point calibration):

$$R_{\mathrm{bz},h} = b_1 \cdot \frac{w_{\mathrm{yz},h}(\mathrm{PAH})}{w_{\mathrm{yz},h}(\mathrm{y})} + b_0$$

The mass fractions of the native PAHs were calculated according to the following equation:

$$w_i(\mathrm{PAH}) = \left(\frac{R_{\mathrm{bx},i} - b_0}{b_1}\right) \cdot \frac{m_{\mathrm{yx},i}}{m_{\mathrm{x},i}} \cdot \frac{1}{w_{\mathrm{dry\ mass}}} = w_{\mathrm{sol},i}(\mathrm{PAH}) \cdot \frac{m_{\mathrm{yx},i}}{m_{\mathrm{x},i}} \cdot \frac{1}{w_{\mathrm{dry\ mass}}}$$

Symbol	Quantity	Unit
w_i(PAH)	Mass fraction of native PAH in the sample *i*	µg/kg
$R_{\mathrm{bx},i}$	Measured isotope ratio (peak area ratio) of the quantifier ions of the native PAH and the deuterated DPAH in the sample blend yx of sample *i*	-
$m_{\mathrm{yx},i}$	Mass of the spike solution y for the preparation of the sample blend yx of sample *i*	g
$m_{\mathrm{x},i}$	Mass of the sample *i* for the preparation of the sample blend yx	g
$R_{\mathrm{bz},h}$	Measured isotope ratio (peak area ratio) of the quantifier ions of the native PAH and the DPAH in the calibration blend yz, *h* (*h* = 1 to 9)	-
$w_{\mathrm{dry\ mass}}$	Dry mass of sample	g/g
b_1	Slope of the linear regression curve	g/ng
b_0	Axis intercept of the linear regression curve	-
$w_{\mathrm{yz},h}$(PAH)	Mass fraction of the native PAH in the calibration blend yz, *h* (*h* = 1 to 9)	ng/g
$w_{\mathrm{yz},h}$(y)	Mass fraction of the spike solution y in the calibration blend yz, *h* (*h* = 1 to 9)	ng/g
$w_{\mathrm{sol},i}$(PAH)	Mass fraction of the native PAH in the measurement solution *i*	ng/g

The overall mean value was calculated as the arithmetic mean of all measurement results w_i(PAH):

$$w(\mathrm{PAH}) = \frac{1}{k} \cdot \sum_{i=1}^{k} w_i(\mathrm{PAH})$$

Uncertainty contribution of the measurement steps (incl. calibration):

$$u_{\mathrm{meas}}[w_i(\mathrm{PAH})] = w_i(\mathrm{PAH}) \cdot \sqrt{u_{\mathrm{rel}}^2[w_{\mathrm{sol},i}(\mathrm{PAH})] + u_{\mathrm{rel}}^2[m_{\mathrm{yx},i}] + u_{\mathrm{rel}}^2[m_{\mathrm{x},i}] + u_{\mathrm{rel}}^2[w_{\mathrm{dry\ mass}}]}$$

$$u_{\mathrm{meas}}[w(\mathrm{PAH})] = \frac{1}{k} \cdot \sum_{i=1}^{k} u_{\mathrm{meas}}[w_i(\mathrm{PAH})]$$

Uncertainty contribution of the repeatability:

$$u_{\mathrm{rep}}[w(\mathrm{PAH})] = s[w(\mathrm{PAH})] = \sqrt{\frac{\sum_{i=1}^{k}\left(w_i(\mathrm{PAH}) - w(\mathrm{PAH})\right)^2}{n-1}}$$

Uncertainty contribution of the reference standard (calibrant):

$$u_{\mathrm{ref}}[w_{\mathrm{ref}}(\mathrm{PAH})] = \frac{U_{\mathrm{ref}}[w_{\mathrm{ref}}(\mathrm{PAH})]}{k} = \frac{U_{\mathrm{ref}}[w_{\mathrm{ref}}(\mathrm{PAH})]}{2}$$

Combined standard uncertainty:

$$u_{\mathrm{c}}[w(\mathrm{PAH})] = w(\mathrm{PAH}) \cdot \sqrt{u_{\mathrm{meas,rel}}^2[w(\mathrm{PAH})] + u_{\mathrm{rep,rel}}^2[w(\mathrm{PAH})] + u_{\mathrm{ref,rel}}^2[w_{ref}(\mathrm{PAH})]}$$

Expanded uncertainty:

$$U[w(\mathrm{PAH})] = u_{\mathrm{c}}[w(\mathrm{PAH})] \cdot k$$

The following tables contain the mass fractions and estimated combined and expanded uncertainties of the four relevant PAHs phenanthrene, fluoranthene, benzo[a]pyrene and benzo[ghi]perylene in CCQM-K184 sediment. * Contribution to combined standard uncertainty. ** Percentage contribution of uj2[w(PAH)] to uc2[w(PAH)]:

PAH = Phenanthrene	Contribution j		
	Measurement (meas)	Repeatability (rep)	Calibrant (ref)
w_j(PAH) (µg/kg)	2562.2086		4570
$u_j[w_j$(PAH) (µg/kg)	22.4246	69.1953	25
$u_{j,r}[w_j$(PAH)] (-)	0.0088	0.0270	0.0055
$u_j[w$(PAH)]* (-)	22.4246	69.1953	14.0165
$\%u[w$(PAH)]** (%)	9.2	87.3	3.6
$u_c[w$(PAH)] (µg/kg)	74.076		
$U[w$(PAH)] (µg/kg)	149		

PAH = Fluoranthene	Contribution *j*		
	Measurement (meas)	Repeatability (rep)	Calibrant (ref)
w_j(PAH) (µg/kg)	2172.3818		9710
$u_j[w_j$(PAH) (µg/kg)	22.7502	59.5090	80
$u_{j:r}[w_j$(PAH)] (-)	0.0105	0.0274	0.0082
$u_j[w$(PAH)]* (-)	22.7502	59.5090	17.8981
%$u[w$(PAH)]** (%)	11.8	80.9	7.3
$u_c[w$(PAH)] (µg/kg)	66.176		
$U[w$(PAH)] (µg/kg)	133		

PAH = Benzo[a]pyrene	Contribution *j*		
	Measurement (meas)	Repeatability (rep)	Calibrant (ref)
w_j(PAH) (µg/kg)	709.9696		6220
$u_j[w_j$(PAH) (µg/kg)	14.1010	26.9658	55
$u_{j:r}[w_j$(PAH)] (-)	0.0199	0.0380	0.0088
$u_j[w$(PAH)]* (-)	14.1010	26.9658	6.2779
%$u[w$(PAH)]** (%)	20.6	75.3	4.1
$u_c[w$(PAH)] (µg/kg)	31.071		
$U[w$(PAH)] (µg/kg)	63		

PAH = Benzo[ghi]perylene	Contribution *j*		
	Measurement (meas)	Repeatability (rep)	Calibrant (ref)
w_j(PAH) (µg/kg)	667.8361		4640
$u_j[w_j$(PAH) (µg/kg)	17.6832	17.1314	60
$u_{j:r}[w_j$(PAH)] (-)	0.0265	0.0257	0.0129
$u_j[w$(PAH)]* (-)	17.6832	17.1314	8.6358
%$u[w$(PAH)]** (%)	45.9	43.1	11.0
$u_c[w$(PAH)] (µg/kg)	26.091		
$U[w$(PAH)] (µg/kg)	53		

Uncertainty Information from LGC

Equation 1:

$$W_x = W_z \cdot \frac{m_z}{m_{yc}} \cdot \frac{m_y}{m_x} \cdot \frac{R'_B}{R'_{BC}}$$

Each sample was injected five times and quantified using the standards injected immediately before and after the samples. The calculated amount of amino acid in each of the sample extracts was calculated using the simplified double IDMS equation,

Where:

Wx = the mass fraction of analyte in sample

Wz = the mass fraction of the natural analyte used to prepare the calibration blend

mz = mass of the natural analyte solution added to the calibration blend

mx = mass of the sample used

myc = mass of the labelled analyte solution added to the calibration blend

my = mass of the labelled analyte solution added to the sample blend

R’ B = measured ratio of the sample blend

R’ BC= average measured ratio of the calibration blend injected before and after the sample

Equation 2:

$$u_c = w_x \sqrt{\left(\frac{u_{W_z}}{w_z}\right)^2 + \left(\frac{u_{p_R}}{p_R}\right)^2 + \left(\frac{um_x}{m_x}\right)^2 + \left(\frac{um_y}{m_y}\right)^2 + \left(\frac{um_z}{m_z}\right)^2 + \left(\frac{um_{yc}}{m_{yc}}\right)^2}$$

DEM-IDMS allows for a calculation of the uncertainty in the mass fraction of each PAH in the samples :

Where:

UWz = the standard uncertainty associated with the mass fraction of the calibration solution

wz = the mass fraction of the calibration solution

umx = the uncertainty associated with the mass of sample used

mx = the mass of sample used

umy = the uncertainty associated with the mass of labelled analyte added to the sample

my = the mass of labelled analyte added to the sample

umz = the uncertainty associated with the mass of analyte added to the calibration blend

mz = the mass of analyte added to the calibration blend

umyc = the uncertainty associated with the mass of labelled analyte added to the calibration blend

myc = the mass of labelled analyte added to the calibration blend

uPR = the standard deviation of the ratios of R’B/R’Bc (n=5)

PR = the mean of R’B/R’Bc (n=5)

Equation 3:

$$u = \frac{\sqrt{(u_c(\overline{w}_x{}'))^2}}{\sqrt{n}}$$

The combined final measurement uncertainty was calculated by combining the mean uncertainty of all the measurements of the material over root n (n = number of analysis - 6) shown in equation 3. This was then further combined with the uncertainty for the comparison of standards.

Equation 4:

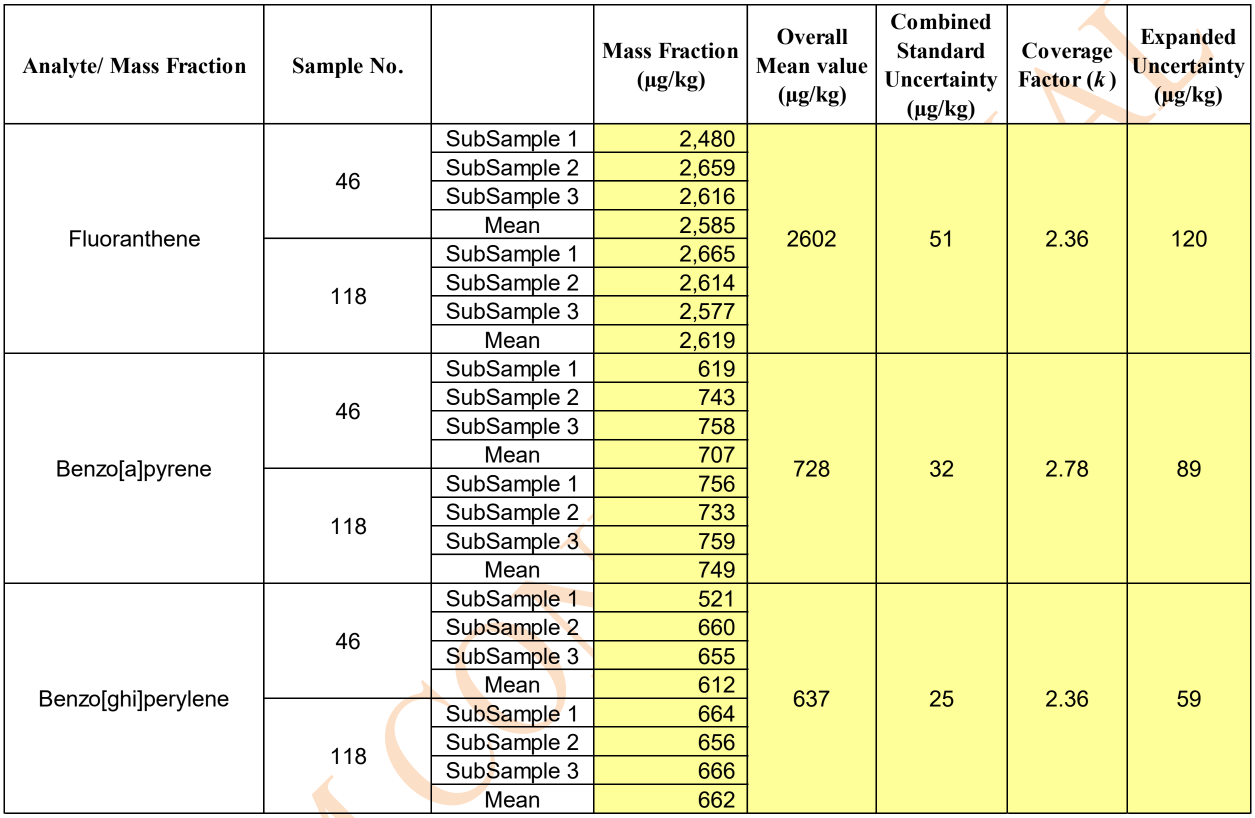
$$U = 2u$$

The uncertainty is the expanded by k=2 shown in equation 4.

APPENDIX H: Participants' Quantitative Results as Reported

The following are pictures of the quantitative results as provided by the participants in the "Results" worksheet of the "Reporting Form" Excel workbook.

Quantitative Results from KRISS



Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (*k*)	Expanded Uncertainty (µg/kg)
Fluoranthene	46	SubSample 1	2,480	2602	51	2.36	120
		SubSample 2	2,659				
		SubSample 3	2,616				
		Mean	2,585				
	118	SubSample 1	2,665				
		SubSample 2	2,614				
		SubSample 3	2,577				
		Mean	2,619				
Benzo[a]pyrene	46	SubSample 1	619	728	32	2.78	89
		SubSample 2	743				
		SubSample 3	758				
		Mean	707				
	118	SubSample 1	756				
		SubSample 2	733				
		SubSample 3	759				
		Mean	749				
Benzo[ghi]perylene	46	SubSample 1	521	637	25	2.36	59
		SubSample 2	660				
		SubSample 3	655				
		Mean	612				
	118	SubSample 1	664				
		SubSample 2	656				
		SubSample 3	666				
		Mean	662				

Moisture content method:

3 subsamples/bottle, oven drying, 105 °C, until constant mass is reached. It takes about 2~3 hours.

KRISS supplementary:

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Fluoranthene	46	SubSample 1	2,263	2283	43	2.31	100
		SubSample 2	2,377				
		SubSample 3	2,245				
		Mean	2,295				
	118	SubSample 1	2,307				
		SubSample 2	2,277				
		SubSample 3	2,228				
		Mean	2,271				
Benzo[a]pyrene	46	SubSample 1	515	547	16	2.78	45
		SubSample 2	585				
		SubSample 3	572				
		Mean	557				
	118	SubSample 1	524				
		SubSample 2	550				
		SubSample 3	538				
		Mean	537				
Benzo[ghi]perylene	46	SubSample 1	465	495	17	2.78	48
		SubSample 2	523				
		SubSample 3	538				
		Mean	509				
	118	SubSample 1	465				
		SubSample 2	497				
		SubSample 3	482				
		Mean	481				

Quantitative Results from LNE

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	Unit 77	SubSample 1	2248	2255	69	2	138
		SubSample 2	2265				
		SubSample 3	2242				
		Mean	2252				
	Unit 173	SubSample 1	2350				
		SubSample 2	2238				
		SubSample 3	2189				
		Mean	2259				
Fluoranthene	Unit 77	SubSample 1	2422	2297	82	2	164
		SubSample 2	2334				
		SubSample 3	2239				
		Mean	2331				
	Unit 173	SubSample 1	2357				
		SubSample 2	2241				
		SubSample 3	2192				
		Mean	2263				
Benzo[a]pyrene	Unit 77	SubSample 1	871	839	34	2	68
		SubSample 2	842				
		SubSample 3	844				
		Mean	852				
	Unit 173	SubSample 1	878				
		SubSample 2	809				
		SubSample 3	791				
		Mean	826				
Benzo[ghi]perylene	Unit 77	SubSample 1	757	708	27	2	53
		SubSample 2	687				
		SubSample 3	701				
		Mean	715				
	Unit 173	SubSample 1	751				
		SubSample 2	681				
		SubSample 3	669				
		Mean	700				

Moisture content method:

1g of sample is dried at 105°C ± 5°C to constant mass (NF ISO 11465)

Quantitative Results from NIST

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)		SubSample 1	2539	2573	50	2.145	106
		SubSample 2	2592				
		SubSample 3	2409				
		Mean	2513				
		SubSample 1	2676				
		SubSample 2	2649				
		SubSample 3	NA				
		Mean	2662				
Fluoranthene		SubSample 1	1847	2130	58	2.138	123
		SubSample 2	2222				
		SubSample 3	2064				
		Mean	2044				
		SubSample 1	2212				
		SubSample 2	2305				
		SubSample 3	NA				
		Mean	2259				
Benzo[a]pyrene		SubSample 1	651	656	41	2.130	87
		SubSample 2	701				
		SubSample 3	633				
		Mean	661				
		SubSample 1	613				
		SubSample 2	685				
		SubSample 3	NA				
		Mean	649				
Benzo[ghi]perylene		SubSample 1	686	700	24	2.139	51
		SubSample 2	721				
		SubSample 3	659				
		Mean	689				
		SubSample 1	735				
		SubSample 2	697				
		SubSample 3	NA				
		Mean	716				

Moisture content method:

Oven treatment of 1 g quantities of sediment at 105 ^{o}C for 4 h to constant weight as specified in protocol.

Quantitative Results from CENAM

Analytes	Mass Fraction (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Fluoranthene	1243	95	2	190
Benzo[a]pyrene	907.3	43.8	2	87.6
Benzo[g,h,i]perilene	619.0	46.8	2	93.6
Phenanthrene	885.1	105	2	210

Moisture content method:

1 g of sample, drying loss at constant weight, at 110°C oven, as indicated in protocol

Quantitative Results from VNIIM

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	125	SubSample 1	2955	2920	111	2	230
		SubSample 2	2878				
		SubSample 3	2930				
		Mean	2921				
	212	SubSample 1	2943				
		SubSample 2	2904				
		SubSample 3	2927				
		Mean	2925				
Fluoranthene	125	SubSample 1	2490	2490	105	2	210
		SubSample 2	2465				
		SubSample 3	2471				
		Mean	2475				
	212	SubSample 1	2551				
		SubSample 2	2441				
		SubSample 3	2500				
		Mean	2497				
Benzo[a]pyrene	125	SubSample 1	776	776	32	2	64
		SubSample 2	786				
		SubSample 3	776				
		Mean	779				
	212	SubSample 1	789				
		SubSample 2	754				
		SubSample 3	772				
		Mean	772				
Benzo[ghi]perylene	125	SubSample 1	722	728	35	2	70
		SubSample 2	748				
		SubSample 3	717				
		Mean	729				
	212	SubSample 1	737				
		SubSample 2	717				
		SubSample 3	728				
		Mean	727				

Moisture content method:

Three subsamples of 1 g were dried in the oven at 105˚C until constant mass

Quantitative Results from IH

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	CCQM-K184 - Unit # 47	SubSample 1	1943.288153	1781	221	2	442
		SubSample 2	1772.773106				
		SubSample 3	1756.516617				
		Mean	1824.192625				
	CCQM-K184 - Unit # 202	SubSample 1	1769.263172				
		SubSample 2	1793.485843				
		SubSample 3	1653.233593				
		Mean	1738.660869				
Fluoranthene	CCQM-K184 - Unit # 47	SubSample 1	2163.036508	2012	250	2	500
		SubSample 2	2013.760508				
		SubSample 3	1919.581693				
		Mean	2032.126236				
	CCQM-K184 - Unit # 202	SubSample 1	2041.300952				
		SubSample 2	2032.809789				
		SubSample 3	1904.366275				
		Mean	1992.825672				
Benzo[a]pyrene	CCQM-K184 - Unit # 47	SubSample 1	518.4364274	504	64.0	2	128
		SubSample 2	486.7166513				
		SubSample 3	477.7297151				
		Mean	494.2942646				
	CCQM-K184 - Unit # 202	SubSample 1	536.1213393				
		SubSample 2	511.8543031				
		SubSample 3	493.5775301				
		Mean	513.8510575				
Benzo[ghi]perylene	CCQM-K184 - Unit # 47	SubSample 1	457.7553373	444	68.0	2	136
		SubSample 2	428.290331				
		SubSample 3	410.8220761				
		Mean	432.2892481				
	CCQM-K184 - Unit # 202	SubSample 1	477.3550731				
		SubSample 2	452.388502				
		SubSample 3	439.0070771				
		Mean	456.2502174				

Moisture content method:

The sample container had been dried for half an hour at 30 °C before being weighed. A sample of about 1 g was weighed using the appropriate container (three determinations were made for each sample). Overnight, the sample was dried at 105 °C. The container was weighed followed the initial drying process. The sample was subjected to a second drying at 105 ºC for one hour and then weighed. There was no third drying process since it was determined that the mass difference between the sample mass after the first and second dryings was not significant, with the mass difference being less than the 2 mg criteria. The moisture content was reported as the percentage of dry sample mass relative to the sample mass subjected to drying (moisture content reported as the average of the three replicates).

Quantitative Results from INM

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	62	SubSample 1	806.54	726.84	54.07	2	108.15
		SubSample 2	817.75				
		SubSample 3	710.65				
		Mean	778.31				
	131	SubSample 1	679.42				
		SubSample 2	677.70				
		SubSample 3	668.99				
		Mean	675.37				
Fluoranthene	62	SubSample 1	1113.79	1020.64	32.93	2	65.86
		SubSample 2	1068.55				
		SubSample 3	952.30				
		Mean	1044.88				
	131	SubSample 1	1006.36				
		SubSample 2	1009.49				
		SubSample 3	973.33				
		Mean	996.40				
Benzo[a]pyrene	62	SubSample 1	436.27	418.57	19.66	2	39.33
		SubSample 2	423.24				
		SubSample 3	374.43				
		Mean	411.32				
	131	SubSample 1	446.53				
		SubSample 2	421.93				
		SubSample 3	408.98				
		Mean	425.81				
Benzo[ghi]perylene	62	SubSample 1	367.27	357.47	16.20	2	32.40
		SubSample 2	357.71				
		SubSample 3	324.09				
		Mean	349.69				
	131	SubSample 1	377.66				
		SubSample 2	369.41				
		SubSample 3	348.68				
		Mean	365.25				

Moisture content method:

Three sub-samples of 1.0 g were weighed in previously dried aluminum moisture tins, and dried at 105 °C. After drying, the tins were placed in a desiccator, allowed to cool at room temperature, and weighed. The procedure is repeated until constant weight is reached.

Quantitative Results from INMETRO

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	40	SubSample 1	2494	2437	58	2	115
		SubSample 2	2200				
		SubSample 3	2590				
		Mean	2428				
	174	SubSample 1	2387				
		SubSample 2	2544				
		SubSample 3	2408				
		Mean	2446				
Fluoranthene	40	SubSample 1	2265	2238	63	2	126
		SubSample 2	2017				
		SubSample 3	2479				
		Mean	2254				
	174	SubSample 1	2171				
		SubSample 2	2269				
		SubSample 3	2224				
		Mean	2221				
Benzo[a]pyrene	40	SubSample 1	872	853	27	2	54
		SubSample 2	790				
		SubSample 3	911				
		Mean	858				
	174	SubSample 1	784				
		SubSample 2	876				
		SubSample 3	883				
		Mean	848				
Benzo[ghi]perylene	40	SubSample 1	647	630	23	2	45
		SubSample 2	583				
		SubSample 3	654				
		Mean	628				
	174	SubSample 1	594				
		SubSample 2	648				
		SubSample 3	656				
		Mean	632				

Moisture content method:

Three subsamples (1 g each) from each sample (40 and 174) were weighed in glass weghing bottles and dried in an oven at 105 ℃. Every 150 min, the subsamples were removed from the oven, equilibrated to room temperature in a dessicator, and weighed again. This procedure was repeated until the subsamples reached constant masses.

Quantitative Results from NIM

Analyte/ Mass Fraction	Sample No.		Mass Fraction (μg/kg)	Overall Mean value (μg/kg)	Combined Standard Uncertainty (μg/kg)	Coverage Factor (k)	Expanded Uncertainty (μg/kg)
Phenanthrene (optional)	12#	SubSample 1	2700	2724	111.3	2	223
		SubSample 2	2724				
		SubSample 3	2749				
		Mean	2724				
	187#	SubSample 1	2739				
		SubSample 2	2719				
		SubSample 3	2710				
		Mean	2723				
Fluoranthene	12#	SubSample 1	2432	2419	89.5	2	179
		SubSample 2	2432				
		SubSample 3	2437				
		Mean	2434				
	187#	SubSample 1	2393				
		SubSample 2	2391				
		SubSample 3	2430				
		Mean	2404				
Benzo[a]pyrene	12#	SubSample 1	749	749	22.6	2	45.2
		SubSample 2	746				
		SubSample 3	741				
		Mean	745				
	187#	SubSample 1	757				
		SubSample 2	751				
		SubSample 3	749				
		Mean	752				
Benzo[ghi]perylene	12#	SubSample 1	689	680	23.7	2	47.5
		SubSample 2	688				
		SubSample 3	678				
		Mean	685				
	187#	SubSample 1	682				
		SubSample 2	676				
		SubSample 3	667				
		Mean	675				

Moisture content method:

Moisture determination by drying at 105℃ +/- 2℃, until constant mass was reached

Quantitative Results from NIMT

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	S-98	Subsample 1	2230.98	2235	162	2.0	324
		Subsample 2	2220.93				
		Subsample 3	2184.49				
		Mean					
	S-154	Subsample 1	2353.07				
		Subsample 2	2260.38				
		Subsample 3	2158.48				
		Mean					
Fluoranthene	S-98	Subsample 1	2224.09	2277	105	2.03	213
		Subsample 2	2213.91				
		Subsample 3	2250.80				
		Mean					
	S-154	Subsample 1	2253.78				
		Subsample 2	2376.69				
		Subsample 3	2340.23				
		Mean					
Benzo(a)pyrene	S-98	Subsample 1	N/A	N/A	N/A	N/A	N/A
		Subsample 2					
		Subsample 3					
		Mean					
	S-154	Subsample 1	N/A				
		Subsample 2					
		Subsample 3					
		Mean					
Benzo(ghi)perylene	S-98	Subsample 1	468.03	474.25	31	2.0	62
		Subsample 2	475.18				
		Subsample 3	497.40				
		Mean					
	S-154	Subsample 1	476.87				
		Subsample 2	442.98				
		Subsample 3	485.03				
		Mean					

Moisture content method:

The determination of dry mass content was conducted with a recommended sample size of 1 g with 3 replicates. The test sample portions were placed in the oven at (105 ± 2)°C and until a constant weight was reached.

Quantitative Results from GLHK

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Fluoranthene	86	SubSample 1	2090	2100	130	2	260
		SubSample 2	2100				
		SubSample 3	2120				
		Mean	2100				
	153	SubSample 1	2100				
		SubSample 2	2110				
		SubSample 3	2090				
		Mean	2100				
Benzo[a]pyrene	86	SubSample 1	742	742	88	2	180
		SubSample 2	738				
		SubSample 3	751				
		Mean	744				
	153	SubSample 1	742				
		SubSample 2	731				
		SubSample 3	746				
		Mean	740				
Benzo[ghi]perylene	86	SubSample 1	747	742	37	2	74
		SubSample 2	738				
		SubSample 3	755				
		Mean	747				
	153	SubSample 1	745				
		SubSample 2	726				
		SubSample 3	739				
		Mean	737				

Moisture content method:

The moisture content was measured as summarized below: Three subsamples (sample size of 1 g each) of the same sediment bottle were dried in an oven at about 105 ℃ until constant mass was reached.

Quantitative Results from BAM

Analyte/ Mass Fraction	Sample No.	Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	SubSample 1	2975	3010	96.65	2	193
	SubSample 2	3022				
	SubSample 3	2994				
	Mean	2997				
	SubSample 1	3035				
	SubSample 2	2987				
	SubSample 3	3047				
	Mean	3023				
Fluoranthene	SubSample 1	2545	2538	89.95	2	180
	SubSample 2	2494				
	SubSample 3	2571				
	Mean	2537				
	SubSample 1	2593				
	SubSample 2	2541				
	SubSample 3	2484				
	Mean	2539				
Benzo[*a*]pyrene	SubSample 1	896.8	882.9	40.51	2	81.0
	SubSample 2	832.9				
	SubSample 3	866.1				
	Mean	865.3				
	SubSample 1	887.4				
	SubSample 2	916.8				
	SubSample 3	897.4				
	Mean	900.5				
Benzo[*ghi*]perylene	SubSample 1	683.0	673.0	30.54	2	61.1
	SubSample 2	638.4				
	SubSample 3	690.2				
	Mean	670.5				
	SubSample 1	661.9				
	SubSample 2	695.2				
	SubSample 3	669.4				
	Mean	675.5				

Moisture content method:

Moisture determination by drying at 105°C +/- 2°C, until constant mass was reached (Sartorius MA30 Moisture Balance)

Quantitative Results from NMIA

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	25	SubSample 1	2590	2550	91	2.09	190
		SubSample 2	2620				
		SubSample 3	2600				
		Mean	2600				
	94	SubSample 1	2490				
		SubSample 2	2510				
		SubSample 3	2510				
		Mean	2500				
Fluoranthene	25	SubSample 1	2300	2300	66	2.12	140
		SubSample 2	2330				
		SubSample 3	2340				
		Mean	2320				
	94	SubSample 1	2280				
		SubSample 2	2290				
		SubSample 3	2280				
		Mean	2280				
Benzo[a]pyrene	25	SubSample 1	738	748	28	2.31	64
		SubSample 2	728				
		SubSample 3	784				
		Mean	750				
	94	SubSample 1	745				
		SubSample 2	749				
		SubSample 3	742				
		Mean	745				
Benzo[ghi]perylene	25	SubSample 1	632	643	39	2.11	82
		SubSample 2	623				
		SubSample 3	663				
		Mean	639				
	94	SubSample 1	647				
		SubSample 2	643				
		SubSample 3	649				
		Mean	646				

Moisture content method:

1 g aliquots were weighed into pre-dried glass vessels. The open vessels were placed in an oven at 105C for 10 days.

After removing from the oven, the vessels were placed in a dessicator to cool before reweighing.

Quantitative Results from INTI

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	5	SubSample 1	1856	1580	108	2	216
		SubSample 2	1506				
		SubSample 3	1476				
		Mean	1612				
	34	SubSample 1	1646				
		SubSample 2	1593				
		SubSample 3	1401				
		Mean	1547				
Fluoranthene	5	SubSample 1	1681	1400	110	2	221
		SubSample 2	1276				
		SubSample 3	1240				
		Mean	1399				
	34	SubSample 1	1381				
		SubSample 2	1510				
		SubSample 3	1310				
		Mean	1400				
Benzo[a]pyrene	5	SubSample 1	497	427	55	2	111
		SubSample 2	423				
		SubSample 3	371				
		Mean	430				
	34	SubSample 1	431				
		SubSample 2	438				
		SubSample 3	403				
		Mean	424				
Benzo[ghi]perylene	5	SubSample 1	519	417	44	2	87
		SubSample 2	413				
		SubSample 3	358				
		Mean	430				
	34	SubSample 1	416				
		SubSample 2	404				
		SubSample 3	395				
		Mean	405				

Moisture content method:

Three subsamples of 0,5 g each were dried in an oven at 105°C until constant mass.

Quantitative Results from TUBITAK_UME

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)		SubSample 1	2568	2528	114	2	228
		SubSample 2	2617				
		SubSample 3	2290				
		Mean	2491				
		SubSample 1	2663				
		SubSample 2	2520				
		SubSample 3	2509				
		Mean	2564				
Fluoranthene		SubSample 1	2116	2183	103	2	206
		SubSample 2	2147				
		SubSample 3	2240				
		Mean	2168				
		SubSample 1	2265				
		SubSample 2	2055				
		SubSample 3	2278				
		Mean	2199				
Benzo[a]pyrene		SubSample 1	707	699	33	2	66
		SubSample 2	698				
		SubSample 3	716				
		Mean	707				
		SubSample 1	723				
		SubSample 2	642				
		SubSample 3	709				
		Mean	691				
Benzo[ghi]perylene		SubSample 1	705	665	54	2	108
		SubSample 2	661				
		SubSample 3	663				
		Mean	676				
		SubSample 1	652				
		SubSample 2	590				
		SubSample 3	721				
		Mean	654				

Moisture content method:

In an oven at 105 °C until constant mass is reached

Quantitative Results from METAS

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Phenanthrene (optional)	58	SubSample 1	2693	2562	74	2	149
		SubSample 2	2552				
		SubSample 3	2578				
		Mean	2608				
	126	SubSample 1	2508				
		SubSample 2	2516				
		SubSample 3	2526				
		Mean	2517				
Fluoranthene	58	SubSample 1	2271	2172	66	2	133
		SubSample 2	2117				
		SubSample 3	2176				
		Mean	2188				
	126	SubSample 1	2110				
		SubSample 2	2160				
		SubSample 3	2200				
		Mean	2157				
Benzo[a]pyrene	58	SubSample 1	710	710	31	2	63
		SubSample 2	700				
		SubSample 3	672				
		Mean	694				
	126	SubSample 1	718				
		SubSample 2	705				
		SubSample 3	755				
		Mean	726				
Benzo[ghi]perylene	58	SubSample 1	691	668	26	2	53
		SubSample 2	656				
		SubSample 3	660				
		Mean	669				
	126	SubSample 1	683				
		SubSample 2	646				
		SubSample 3	671				
		Mean	667				

Moisture content method:

Three subsamples (1 g each) were dried in an oven at 105 °C until constant mass was reached (as specified in the protocol).

Quantitative Results from LGC

Analyte/ Mass Fraction	Sample No.		Mass Fraction (µg/kg)	Overall Mean value (µg/kg)	Combined Standard Uncertainty (µg/kg)	Coverage Factor (k)	Expanded Uncertainty (µg/kg)
Fluoranthene	122	SubSample 1	2268	2299	68	2	136
		SubSample 2	2331				
		SubSample 3	2318				
		Mean	2306				
	50 and 122	SubSample 1	2296				
		SubSample 2	2248				
		SubSample 3	2331				
		Mean	2292				
Benzo[a]pyrene	122	SubSample 1	517	531	17	2	34
		SubSample 2	568				
		SubSample 3	544				
		Mean	543				
	50 and 122	SubSample 1	509				
		SubSample 2	506				
		SubSample 3	543				
		Mean	519				
Benzo[ghi]perylene	122	SubSample 1	472	474	14	2	28
		SubSample 2	494				
		SubSample 3	479				
		Mean	482				
	50 and 122	SubSample 1	442				
		SubSample 2	470				
		SubSample 3	489				
		Mean	467				

Moisture content method:

~1g weighed into steel tins simultaneously to analysis sampling. Tins placed in an oven at temperature 105oC ± 2oC. Weighed daily until constant weight (3 days)

Appendix I: The Parameters Used for the NICOB Calculations

	Phenanthrene (optional), µg/kg	Fluoranthene, µg/kg	Benzo[*a*]pyrene, µg/kg	Benzo[*ghi*]perylene, µg/kg
Number of significant digits desired for results	4	4	3	3
Random number generator seed	5	5	5	5
Scale for half-Cauchy prior on between laboratory variance	212.7531	180.8772	56.3388	44.478
Scale for half-Cauchy prior on within laboratory variances	93.825	82	32	27
Total number of iterations	250000	250000	250000	250000
Length of burn in	50000	50000	50000	50000
Thinning rate	25	25	25	25