Asia Pacific Laboratory Accreditation Cooperation

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENT

PROFICIENCY TESTING PROGRAM APLAC T078

FINAL REPORT

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PTP 001

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CONTENTS

Summary of Results

1. The proficiency testing program (APLAC T078) aimed at evaluating the testing capability of participants on the quantitative analysis of five polycyclic aromatic hydrocarbons, *viz.* phenanthrene (PHE), fluoranthene (FLT), benzo(a)anthracene (BAA), benzo(a)pyrene (BAP) and benzo(ghi)perylene (BGP), in sediment.

2. A total of 69 laboratories from 25 economies enrolled in the program and 67 of them returned results to the organizers.

3. The reference values and standard deviations for performance assessment were respectively assigned by the organizers using an isotope dilution gas chromatography-mass spectrometry (ID-GCMS) technique and calculated using the Horwitz Equation[8.1]. The z-score was used as the numerical indicator to show participants' performance with respect to the assigned values in the program.

4. The z-scores of the five polycyclic aromatic hydrocarbons are summarized as follows:

z-Score	Number of Participants (Percentage)				
	PHE	**FLT**	**BAA**	**BAP**	**BGP**
$\|z\| \leq 2$	52 (78.8%)	54 (81.8%)	55 (84.6%)	42 (63.6%)	44 (66.7%)
$2 < \|z\| < 3$	6 (9.1%)	6 (9.1%)	5 (7.7%)	11 (16.7%)	11 (16.6%)
$\|z\| \geq 3$	8 (12.1%)	6 (9.1%)	5 (7.7%)	13 (19.7%)	11 (16.6%)
Total:	66 (100%)	66 (100%)	65 (100%)	66 (100%)	66 (100%)

1. Introduction

1.1. Polycyclic aromatic hydrocarbons (PAH) are components of crude petroleum and coal. Due to the continuous consumption of fossil fuels from anthropogenic activities, many PAH are present as common contaminants in the environments such as soil and sediment. PAH are known to exhibit carcinogenic and mutagenic properties and therefore monitoring of these compounds is deemed important.

1.2. A proficiency testing program (APLAC T078) on the quantitative analysis of five PAH, *viz.* phenanthrene (PHE), fluoranthene (FLT), benzo(a)anthracene (BAA), benzo(a)pyrene (BAP) and benzo(ghi)perylene (BGP) in sediment was organised by the Government Laboratory of Hong Kong (GLHK), in collaboration with Hong Kong Accreditation Service (HKAS), and under the auspices of the Asia-Pacific Laboratory Accreditation Co-operation (APLAC). The program was approved by APLAC PT Committee in July 2010 and was expected to be completed in February 2011 (TABLE I). It is the 2nd round APLAC PT for PAHs in sediment where the 1st round was conducted in 2009.

1.3. A total of 69 laboratories from 25 economies enrolled in the program and 67 of them returned their results on or before the deadline (TABLE II). Participants were confidentially assigned with a unique laboratory code (01 to 69) and the code was used throughout the program.

2. Objectives

2.1. The main objective of this program is to evaluate the capability of participants on the quantitative analysis of five PAH in sediment with respect to the assigned reference values provided by the organizers.

2.2. Test results from participants are processed in accordance with the statistical techniques outlined in ISO13528:2005 - Statistical Methods for Use in Proficiency Testing by Inter-laboratory Comparisons[8.2] and in the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories[8.3].

3. Test Material

3.1. About 6 kg sediment samples were collected from a coastal site in Hong Kong. The samples were found to contain insignificant amount of PHE, FLT, BAA, BAP and BGP. The samples were stirred with about 30 L of acetone for an hour to remove odour, trapped moisture and microbes. The solvent was

decanted and the residues were air dried overnight. The washed samples were placed in a metal barrel and added with 20 L acetone that containing appropriate quantity (16 to 51 mg) of the five PAH (APPENDIX I). The PAH spiked samples were mixed for three hours before transferred to a clean room (Class 1000) for air dried at room temperature overnight. The dried samples were filtered through 1.7 mm sieves in order to get rid stone fragments, shell debris and other foreign substances. The collected sediment particulates were grounded to fine powder with high speed blenders and were sifted with 500 μm sieves. All batches of fine powder were combined and placed in a rotating drum for a 7-day mixing. The well mixed powder was then packed into cleaned and nitrogen-flush amber glass bottles, each in 20 g portion. More than 150 bottles of sediment test material were finally prepared and stored in the clean room at around 20°C before shipment.

3.2. The tests for sample homogeneity (performed in May 2010) and stability (September 2010 and November 2010) were carried out in accordance with the procedures stipulated in APPENDIX II and III. Results indicated the testing materials are suitable to be used in the proficiency testing program.

3.3. Participants were provided with one bottle containing about 20 g of sediment powder. The test materials labelled as PAH in sediment were dispatched to participants by courier mail in mid September 2010. Relevant documents included “Program Instruction”, “Receipt Form”, and “Result Proforma” were also provided via emails at the time of dispatch. A specimen copy of these instructions was illustrated in APPENDIX IV to VIII.

3.4. Upon receipt of the test material, participants were requested to check the physical conditions of the bottle and promptly acknowledge the organizers by returning the “Receipt Form” to T78@govtlab.gov.hk. Replacement would be arranged if any defect was detected. The organizers received no abnormality report in this program.

4. Test Required

4.1. Participants were required to determine the concentration of PHE, FLT, BAA, BAP and BGP in the test material using their appropriate validated methods.

4.2. Results should be reported in mg/kg with three significant figures or three decimal places, whichever was appropriate.

4.3. Expanded measurement uncertainty and technical information of the

method used were required.

4.4. All the analytical results and information should be reported in the Result Proforma provided.

5. Statistical Evaluation

5.1. Performance evaluation

5.1.1. Performance of participants was assessed using z-score, which is calculated as:

$$z = \frac{x_i - m}{S}$$

where x_i : reported mean from individual participant
m : assigned reference values
S : standard deviation (in mg/kg) calculated from the Horwitz Equation = $0.02\ m^{0.8495}$

5.1.2. z-Score is interpreted as follows:

(a)	$\|z\| \leq 2$	Satisfactory
(b)	$2 < \|z\| < 3$	Questionable
(c)	$\|z\| \geq 3$	Unsatisfactory

5.1.3. Participants having z-scores ≥ 3 or ≤ -3 should thoroughly investigate their results and report the findings to their AB. Participants having z-score(s) in the range $2 < |z| < 3$ are encouraged to review their results.

5.2. An interim report containing participants' data and the respective z-score results was issued to participants and their ABs on 26 November 2010. Participants were requested to check the correctness of their submitted data and to inform the organizers of any mistakes found on or before 30 December 2010 prior to the issuance of the Final Report.

6. Results and Discussions

6.1. Test results and the technical information of methods used by participants are presented in TABLE III to VII.

6.2. Number of participants' data submitted is summarized as follows:

	PHE	FLT	BAA	BAP	BGP
No. of numeric data	66	66	65	66	66

6.3. Assigned reference values for performance assessment

6.3.1. Assigned reference values of the five PAHs were determined using an isotope dilution gas chromatography mass spectrometry (ID-GCMS) technique. Isotope dilution mass spectrometry is considered by the Comité Consultatif pour la Quantité de Matière (CCQM)[8.4] as one of the preferable analytical methods for the provision of accurate and precise measurement. The ID-GCMS involves the use of gravimetrical spikes of isotopic analogues as internal standards for the above target PAHs. These analogues were added to both the sample and the calibration standard during the analysis. The calibration procedure of the present ID-GCMS was based on the single point calibration technique, which involved spiking a known amount of the isotope-labelled PAH (C^{13}) to both the samples and the calibration standards, and the known amount of PAH (C^{12}) to the calibration standard. The relative amount of C12 and C13 PAH in should close to that in the sample. This might result in producing a calibration blend with isotope amount ratio (R_{BC}) similar to that of the sample blend (R_B). The analytical method involved the extraction of the sediment test materials by Soxhlet extraction using an acetone/hexane mixture, followed by a clean-up step using solid phase extraction (SPE). The ID-GCMS in this program had been previously employed for the analysis of PAHs in organic solution and sediment in the CCQM pilot study (CCQM-P69) in 2005 and key comparison programs (CCQM-K50) in 2007. Our results were of good degree of equivalence with those of the participating national measurement institutes. Hence, the ID-GCMS technique used for the assignment of reference value assignment is demonstrated to have high measurement reliability.

6.3.2. Two ID-GCMS measurements were respectively performed in July and November 2010. The average values of the two measurements are the assigned reference values for the five PAH. Experimental

details and results of the determinations are attached in APPENDIX IX and X.

6.3.3. Assignment of reference values:

	PHE	FLT	BAA	BAP	BGP
Reference value (mg/kg)	5.68	4.35	3.43	2.01	2.89
Expanded relative MU (%) at $k = 2$	4.9	4.2	4.3	8.4	4.0

6.4. Horwitz's standard deviation used for assessment:

	PHE	FLT	BAA	BAP	BGP
Horwitz's SD (%)	12.2	12.7	13.2	14.3	13.5
Horwitz's SD (mg/kg)	0.70	0.55	0.45	0.29	0.39

6.5. An overview of participants' results:

6.5.1. Robust mean values are 4.96 mg/kg for PHE, 3.70 mg/kg for FLT, 2.98 mg/kg for BAA, 1.62 mg/kg for BAP and 2.32 mg/kg for BGP. These values are comparably lower than the assigned reference values by 12 to 20%. Between-laboratory variations (RSD) range from 14% to 26%. Comparing with the Horwitz SD (%) in cl. 6.4, the values are slightly higher in FLT and BAA, but significantly higher in PHE, BAP and BGP.

	PHE	FLT	BAA	BAP	BGP
Robust Mean (mg/kg)	4.96	3.70	2.98	1.62	2.32
Deviation from Reference values (%)	-12.7	-14.9	-13.1	-19.4	-19.7
Between-laboratory variation (RSD %)	20.0	14.7	14.7	26.2	25.7

6.5.2. Participants' *z*-scores for the five PAH are presented in TABLE VIII. As illustrated in FIGURE I (a) to V (a). The patterns of *z*-score distributions are found to be skewed to the left hand side, indicating the presence of negative deviations from the reference values (Clause

6.3.3.). The reported mean PAH concentrations, in ascending order, for all participants are shown in FIGURE I (b) to V (b).

6.5.3. Performance of participants, in terms of z-score, is summarized as follow:

z-Score	Number of Participants (Percentage)				
	PHE	**FLT**	**BAA**	**BAP**	**BGP**
$\|z\| \leq 2$	52 (78.8%)	54 (81.8%)	55 (84.6%)	42 (63.6%)	44 (66.7%)
$2 < \|z\| < 3$	6 (9.1%)	6 (9.1%)	5 (7.7%)	11 (16.7%)	11 (16.6%)
$\|z\| \geq 3$	8 (12.1%)	6 (9.1%)	5 (7.7%)	13 (19.7%)	11 (16.6%)
Total:	66 (100%)	66 (100%)	65 (100%)	66 (100%)	66 (100%)

In brief, 16 participants (code 02, 07, 09, 12, 19, 33, 34, 35, 36, 43, 47, 55, 59, 60, 61, 66, 69) were identified as having reported one or more unsatisfactory results; and 43 out of the 329 results (13.1%) submitted were identified as unsatisfactory results.

6.6. Instrumental methods:

6.6.1. GC-MS offers the advantage of reliable confirmation of mass ions being determined and the use of labelled internal standards in quantification. Hence, it becomes a popular method for PAH measurement than others. As shown in TABLE IX, majority of the participants used GC-MS (49 laboratories) that equipped with DB5 or similar types of capillary columns for the analysis. Twelve of them used HPLC with UV or fluorescence detection with common reversed phase columns (such as C_{18}), three used high resolution GC-MS, two used GC-FID and one used GC-MS/MS. Forty of the GC-MS users employed deuteriated PAH (same or similar analogues) and three employed C^{13}-PAH as the internal standards to improve the precision of the quantification.

6.6.2. No significant performance difference between the GC-MS and the LC techniques is observed. Twelve out of the fifty-three GC-MS (GC-MS, -MS/MS & -HRMS) gave at least one unsatisfactory z-scores compared with two participants out of the twelve who used LC (TABLE IX).

6.7. Extraction methods:

6.7.1. Participants commonly used acetone, dichloromethane, hexane pet ether, toluene or a combination of these organic solvents as their extraction media. Thirty-nine participants used sonication or agitation/shaking for the PAH extraction, and the others used Soxhlet extraction (eleven), accelerated solvent extraction (eleven), microwave-assisted extraction (four). Extraction recovery was generally good, mostly higher than 70%, only a very few laboratories reported low recovery for individual PAH (eg. code 49 reported a recovery of 20%). Forty-three participants had not taken the recovery correction in their calculation, while the others (twenty-two) had done so (TABLE X).

6.7.2. Sonication and agitation are relatively low cost methods (less solvents and energy consumption) and they are the preferred methods by commercial laboratories. However, it was reported that more rigorous extraction conditions should be used for PAH in environmental samples[8.5]. Another comparative study on PAH in clay soil showed the problem of underestimation in sonication extraction[8.6]. In addition, the organizers had carried out the stability tests by both sonication and Soxhlet extraction in the previous PT program on PAH in sediment. It was noted that the amount of extractable PAH in Soxhlet extraction was having 13 to 31% higher than that of the sonication. Further analysis of participants' data from sonication/agitation and other rigorous extraction (Soxhlet, microwave and accelerated solvent extraction) showed that the average reported concentration of PHE, FLT, BAA and BGP from the latter are higher than those of using sonication by 4.0% to 15%, although no statistical difference for the two average values (due to large deviation of data). The value of BAP is higher by sonication probably because of an extremely high value reported by one participant (code 09).

6.7.3. The overall underestimated trends for all the five PAH in this program and the previous program (from -13 to -20% in the APLAC T068) are an important issue that needs to be paid attention to. Participants should review their methods (eg. extraction time of sonication/agitation) so as to ensure the methods are adequate for the analysis of PAH in sediment. If participants used spiked samples for their recovery studies, they are recommended to use relevant certified reference materials to check the actual bias of their methods.

6.8. Accreditation Status versus Performance

6.8.1. Fifty-four participants claimed their methods are accredited for all or part of the five PAH. Only twelve do not have the accreditation status.

6.8.2. No significant difference in performance between the accredited laboratories and the non-accredited counterparts in this program. Fifty-five out of two hundred and thirty-four data (or 24%) from the accredited laboratories were identified as unsatisfactory, while there are eleven out of fifty-nine (or 19%) from the non-accredited laboratories.

7. Remarks

7.1. Contributions from all ABs and participants to this program are gratefully noted. Special thanks are also extended to APLAC PT Committee, HKAS Executive and the Government Chemist of GLHK for their support to the program.

7.2. For further comments or disagreement with the report, please promptly contact the organizers by mail or email:

Dr. Yiu-chung WONG
GLHK, 7/F. Homantin Government Offices,
88 Chung Hau Street, KLN, Hong Kong.
email: ycwong@govtlab.gov.hk

7.3. The organizer (GLHK) is not accredited for providing those technical commentaries listed in Section 6.

7.4. Use of this report by participants shall only be allowed with the written permission of the program's organizers.

8. References

8.1. W. Horwitz. Evaluation of analytical methods used for regulations of food and drugs, *Anal. Chem.*, **1982**, 54: 67A-76A.

8.2. ISO 13528:2005. Statistical methods for use in proficiency testing by interlaboratory comparisons, **2005**, Geneva, Switzerland.

8.3. M. Thompson, S.L. Ellison, R. Wood. The International harmonized protocol for the proficiency testing of analytical chemistry laboratories (IUPAC technical report), *Pure Appl. Chem.*, **2006**, 78: 146-196.

8.4. R. Kaarl, T.J. Quinn. The Comite Consultatif pour la Quantite de Matiere:a brief review of its origin and present activities, *Metrologia*, **1997**, 37: 1-5.

8.5. D.L. Stephens, T. McFadden, O.D. Heath, R.F. Mauldin. The effect of sonication in the recovery of polycyclic aromatic hydrocarbons from coal stack ashes surfaces. *Chemosphere*, **1994**, 28:1741-1747.

8.6. T.F. Guerin. The extraction of aged polycyclic aromatic hydrocarbon (PAH) residues from a clay soil using sonication and a Soxhlet procedure: a comparative study. *J. Environ. Monit.*, **1999**, 1:63-67.

TABLE I: Program Timeline

EVENT	SCHEDULE
Preparation of sample	Mar – Apr 2010
Homogeneity testing	May 2010
Submission of proposal to APLAC PT Committee for approval	Jun 2010
Stability testing	Jul – Oct 2010
Invitation of participants	Jul - Aug 2010
Dispatch of samples	Sept 2010
Submission of results	Oct 2010
Statistical analysis of results	Nov 2010
Interim report	Nov 2010
Submission of draft report to APLAC PT Committee	Jan 2011
Approval of draft report by APLAC PT Committee	Feb 2011
Distribution of final report	Feb 2011

TABLE II: Geographical Distribution of Participants

No.	ECONOMIES	PARTICIPANTS ENROLLED	RETURNED RESULTS
1	Australia	4	4
2	Belgium	4	4
3	Canada	8	8
4	China	4	4
5	Czech Republic	3	3
6	Estonia	1	1
7	France	3	3
8	Germany	1	1
9	Hong Kong	3	3
10	Hungary	4	3
11	Israel	1	1
12	Italy	4	4
13	Japan	1	1
14	Kuwait	1	1
15	Latvia	2	2
16	New Zealand	3	3
17	Portugal	3	3
18	Slovakia	4	4
19	Slovenia	1	1
20	Sri Lanka	1	1
21	Sweden	4	4
22	Switzerland	1	1
23	Taiwan	3	3
24	Thailand	1	1
25	United Kingdom	4	3
	Total:	**69**	**67**

TABLE III: Participants' Results for PHE

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	4.76	4.87	4.80	4.81	0.207	2
2	2.67	2.52	--	2.59	0.41	2
3	3.947	4.062	3.708	3.906	1.172	2
4	7.38	7.35	7.40	7.38	0.97	2
5	4.86	4.86	4.80	4.84	0.015	2
6	4.74	4.82	4.69	4.75	0.42	2
7	4.41	4.71	4.89	4.67	--	--
8	5.54	5.41	5.45	5.47	0.133	2
9	3.620	3.448	3.080	3.383	0.038	2
10	6.69	6.29	5.76	6.25	0.016	2
11	5.06	4.98	5.01	5.02	0.60	2
12	5.323	5.219	--	5.271	0.66	2
13	3.67	4.44	4.05	4.05	1.01	2
14	5.231	5.100	5.200	5.177	1.3	2
15	4.34	4.60	4.78	4.57	0.85	2
16	4.15	4.25	4.12	4.17	1.04	2
17	4.91	5.32	4.91	5.05	0.47	2
18	5.9	--	--	5.9	0.8	--
19	3.028	2.987	--	3.008	--	--
20	5.073	--	--	5.073	0.507	--
21	5.43	5.44	5.58	5.48	1.42	--
22	4.87	5.13	5.00	5.00	0.01	--
23	5.62	5.74	5.51	5.62	0.94	2.45
24	4.27	5.32	5.54	5.04	1.4	2
25	5.92	--	--	5.92	1.95	2
26	5.120	5.151	5.204	5.158	1.032	2
27	5.82	6.70	5.82	6.12	0.9	2
28	4.65	4.61	4.61	4.62	0.26	2
29	4.023	3.948	4.002	3.991	0.798	2
30	--	--	--	4.73	--	--
31	4.26	4.31	4.39	4.32	0.11	3.2
32	4.668	5.005	--	4.837	--	--
33	1.98	1.98	1.95	1.97	0.03	3.18
34	5.16	5.19	--	5.18	0.39	--
35	5.58	5.77	5.90	5.75	0.32	2
36	2.79	3.15	3.28	3.07	0.614	2
37	4.50	4.97	4.03	4.50	0.99	2

TABLE III: Participants' Results for PHE (Cont'd)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
38	5.74	5.75	5.59	5.79	0.04	0.95
39	4.98	5.25	ND	5.12	0.50	2
40	***	***	***	***	***	***
41	4.321	4.497	4.102	4.307	0.710	2
42	4.42	4.88	4.80	4.70	0.74	2
43	3.27	3.15	3.25	3.22	--	--
44	5.5	5.4	5.4	5.4	1.5	2
45	6.34	6.12	6.53	6.33	1.71	2
46	4.97	4.90	4.86	4.91	1.228	2
47	2.64	2.69	2.77	2.70	0.645	2
48	4.71	4.51	4.28	4.5	1.72	0.95
49	3.75	3.81	4.48	4.01	0.69	2
50	5.330	5.269	5.323	5.307	1.327	--
51	4.85	4.83	4.64	4.77	0.42	2
52	4.380	5.570	4.602	4.851	1.698	2
53	6.83	6.15	6.49	6.49	0.857	2
54	4.8	--	--	4.8	1.5	--
55	4.20	4.30	4.42	4.31	--	--
56	5.32	4.93	5.20	5.15	--	--
57	6.64	6.66	5.7	6.33	1.88	2
58	4.59	4.28	4.51	4.46	0.32	2
59	6.78	6.25	6.44	6.49	0.467	3
60	5.13	5.21	5.46	5.26	0.67	2
61	6.31	6.22	5.91	6.15	0.476	2
62	6.098	6.583	6.101	6.228	1.03	0.95
63	6.239	6.292	6.284	6.271	1.129	2
64	6.192	6.559	6.693	6.481	0.55	2
65	4.53	4.26	4.76	4.51	1.28	2
66	3.22	3.23	2.93	3.13	0.114	1.96
67	***	***	***	***	***	***
68	5.07	4.89	5.21	5.04	1.26	2
69	--	--	--	--	--	--

"--" denotes data/information was not provided by participants

"***" denotes no return of results to the organizers

TABLE IV: Participants' Results for FLT

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	4.33	4.44	4.33	4.37	0.194	2
2	2.66	2.51	--	2.58	0.40	2
3	3.267	3.373	3.245	3.295	0.988	2
4	4.56	4.32	4.57	4.48	0.67	2
5	3.70	3.73	3.70	3.71	0.014	2
6	3.84	3.94	4.01	3.93	0.32	2
7	3.27	3.39	3.39	3.35	0.17	0.98
8	3.68	3.68	3.69	3.68	0.012	2
9	3.013	2.998	2.992	3.001	0.034	2
10	4.57	4.35	4.00	4.31	0.008	2
11	3.85	3.77	3.81	3.81	0.29	2
12	3.991	3.827	--	3.909	0.49	2
13	3.54	4.00	3.13	3.56	0.89	2
14	3.769	3.800	3.900	3.823	1.8	2
15	3.56	3.44	3.67	3.56	0.66	2
16	3.48	3.49	3.45	3.47	0.87	2
17	3.48	3.42	4.01	3.64	0.65	2
18	4.9	--	--	4.9	--	--
19	1.795	1.741	--	1.768	--	--
20	3.838	--	--	3.838	0.384	--
21	3.87	3.83	3.76	3.82	0.726	--
22	--	--	--	--	--	--
23	4.23	4.18	4.18	4.20	0.67	2.45
24	4.55	5.18	5.22	4.98	0.5	2
25	4.33	--	--	4.33	1.43	2
26	3.898	3.842	3.975	3.905	0.781	2
27	3.79	3.85	3.77	3.80	0.4	2
28	4.16	4.14	4.17	4.16	0.23	2
29	3.169	3.194	3.077	3.147	0.629	2
30	--	--	--	3.53	--	--
31	3.34	3.14	3.00	3.16	0.10	3.2
32	3.437	3.684	--	3.561	--	--
33	4.10	4.21	4.17	4.16	0.10	3.18
34	3.00	3.48	--	3.24	0.93	--
35	1.40	1.2	0.70	1.10	0.72	2
36	1.98	2.33	2.35	2.22	0.444	2
37	3.57	3.61	3.42	3.53	0.78	2

TABLE IV: Participants' Results for FLT (Cont'd)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
38	4.26	4.27	4.33	4.29	0.55	0.95
39	3.63	3.61	ND	3.62	0.36	2
40	***	***	***	***	***	***
41	3.381	3.615	3.450	3.482	0.574	2
42	3.45	3.31	3.80	3.52	0.58	2
43	2.82	2.71	2.75	2.76	--	--
44	4.0	3.8	3.8	3.9	1.8	2
45	4.54	4.39	4.64	4.52	1.27	2
46	3.90	3.64	3.58	3.71	0.928	2
47	1.90	2.00	2.01	1.97	0.327	2
48	3.67	3.51	3.3	3.49	1.39	0.95
49	3.76	3.75	3.75	3.75	0.66	2
50	4.013	4.007	4.094	4.038	1.010	-
51	3.67	3.56	3.61	3.61	0.36	2
52	3.427	4.027	3.594	3.683	1.289	2
53	4.67	4.66	4.70	4.68	0.637	2
54	3.7	--	--	3.7	1.1	--
55	4.43	4.58	4.14	4.38	--	--
56	4.13	3.95	3.94	4.01	1.20	0.30
57	4.67	5.04	3.99	4.57	1.02	2
58	3.23	3.03	3.35	3.20	0.33	2
59	3.44	3.31	3.38	3.38	0.116	3
60	3.80	3.88	4.07	3.91	0.58	2
61	3.52	3.64	3.29	3.48	0.259	2
62	4.012	4.210	4.029	4.080	1.05	0.95
63	4.445	3.945	3.821	4.070	0.855	2
64	3.650	3.527	3.663	3.614	1.15	2
65	3.48	3.30	3.67	3.48	0.85	2
66	2.82	2.82	2.61	2.75	0.100	1.96
67	***	***	***	***	***	***
68	3.81	4.02	3.94	3.92	0.99	2
69	--	--	--	2.67	1.4	2

"--" denotes data/information was not provided by participants

"***" denotes no return of results to the organizers

TABLE V: Participants' Results for BAA

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	3.15	3.18	3.17	3.17	0.221	2
2	2.27	2.17	--	2.22	0.36	2
3	2.564	2.430	2.589	2.528	0.758	2
4	3.50	3.26	3.42	3.39	0.45	2
5	2.60	2.63	2.61	2.61	0.015	2
6	3.56	3.53	3.66	3.58	0.40	2
7	2.47	2.52	2.61	2.53	0.20	0.96
8	2.80	2.88	2.94	2.87	0.141	2
9	2.793	2.990	3.039	2.941	0.034	2
10	3.18	3.06	2.83	3.02	0.010	2
11	2.98	2.95	3.00	2.98	0.36	2
12	4.620	4.278	--	4.449	0.56	2
13	4.65	3.55	3.40	3.87	0.97	2
14	3.154	3.200	3.400	3.251	4.0	2
15	3.14	2.82	2.93	2.96	0.55	2
16	2.98	3.12	3.07	3.06	0.77	2
17	2.94	2.90	3.02	2.95	0.12	2
18	2.7	--	--	2.7	0.9	--
19	1.241	1.230	NT	1.236	--	--
20	2.809	--	--	2.809	0.281	--
21	2.74	3.44	2.83	3.00	0.540	--
22	--	--	--	--	--	--
23	3.39	3.27	3.33	3.33	0.49	2.45
24	3.72	4.06	4.07	3.95	0.3	2
25	3.34	--	--	3.34	0.935	2
26	4.265	3.584	3.802	3.884	0.777	2
27	3.40	3.47	3.10	3.32	0.3	2
28	3.06	3.10	3.09	3.08	0.17	2
29	2.668	2.699	2.462	2.670	0.534	2
30	--	--	--	2.87	--	--
31	2.72	2.77	2.81	2.77	0.027	3.2
32	2.433	2.759	--	2.596	--	--
33	1.25	1.20	1.27	1.24	0.07	3.18
34	1.98	2.07	--	2.03	0.65	--
35	3.14	3.05	3.18	3.12	0.13	2
36	1.43	1.64	1.67	1.58	0.316	2
37	3.24	3.23	2.56	3.01	0.66	2

TABLE V: Participants' Results for BAA (Cont'd)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
38	3.29	3.33	3.33	3.32	1.14	0.95
39	2.50	2.58	ND	2.54	0.26	2
40	***	***	***	***	***	***
41	2.669	3.359	3.277	3.102	0.512	2
42	2.20	2.54	2.82	2.52	0.65	2
43	2.37	2.30	2.31	2.33	--	--
44	2.9	2.9	2.9	2.9	1.6	2
45	3.71	3.58	3.80	3.70	0.703	2
46	3.05	2.97	2.90	2.97	0.683	2
47	1.33	1.42	1.46	1.40	0.472	2
48	3.23	3.25	3.25	3.24	1.04	0.95
49	3.01	3.36	2.80	3.06	0.55	2
50	3.232	3.120	3.165	3.172	0.793	--
51	2.78	2.72	2.62	2.71	0.27	2
52	2.843	3.217	2.830	2.963	1.037	2
53	3.05	3.11	3.22	3.13	0.385	2
54	--	--	--	2.8	0.84	--
55	4.01	4.00	3.80	3.94	--	--
56	3.02	2.80	2.96	2.93	--	--
57	2.96	3.18	2.99	3.04	1.66	2
58	3.64	3.27	3.44	3.45	0.37	2
59	2.61	2.68	2.88	2.72	0.242	3
60	2.27	2.36	2.43	2.35	0.50	2
61	3.09	3.24	3.41	3.25	0.358	2
62	2.901	3.755	3.529	3.395	1.08	0.95
63	3.233	3.081	3.132	3.132	0.846	2
64	3.974	3.822	3.828	3.875	0.25	2
65	2.80	2.61	3.00	2.80	0.88	2
66	3.05	3.02	2.95	3.01	0.110	1.96
67	***	***	***	***	***	***
68	2.81	3.00	2.96	2.92	0.73	2
69	--	--	--	--	--	--

"--" denotes data/information was not provided by participants

"***" denotes no return of results to the organizers

TABLE VI: Participants' Results for BAP

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	1.58	1.60	1.61	1.60	0.280	2
2	1.11	1.05	--	1.08	0.18	2
3	1.453	0.911	1.228	1.197	0.479	2
4	1.99	1.90	2.03	1.97	0.28	2
5	1.66	1.68	1.67	1.67	0.017	2
6	1.39	1.37	1.34	1.37	0.34	2
7	1.06	0.87	1.11	1.01	0.13	0.99
8	1.64	1.62	1.65	1.64	0.031	2
9	53.679	47.666	46.052	49.132	0.347	2
10	1.58	1.43	1.31	1.44	0.010	2
11	1.40	1.42	1.43	1.42	0.67	2
12	0.842	0.818	--	0.830	0.10	2
13	2.56	1.84	1.72	2.04	0.51	2
14	2.077	2.100	2.300	2.159	5.7	2
15	1.80	1.76	1.88	1.81	0.34	2
16	1.40	1.44	1.45	1.43	0.36	2
17	1.92	1.91	1.96	1.93	0.05	2
18	1.7	--	--	1.7	0.5	--
19	0.683	0.644	NT	0.664	--	--
20	1.551	--	--	1.551	0.155	--
21	1.62	1.53	1.57	1.57	0.911	--
22	--	--	--	--	--	--
23	2.07	1.97	2	2.01	0.30	2.45
24	2.05	2.08	2.21	2.11	0.7	2
25	2.08	--	--	2.08	0.686	2
26	1.825	1.818	1.933	1.859	0.372	2
27	1.91	1.94	1.90	1.92	0.2	2
28	1.50	1.48	1.53	1.50	0.08	2
29	1.909	1.938	1.924	1.924	0.384	2
30	--	--	--	1.69	--	--
31	1.39	1.34	1.37	1.37	0.038	3.2
32	1.718	1.641	--	1.680	--	--
33	8.22	8.94	8.59	8.58	0.66	3.18
34	1.63	1.67	--	1.65	0.38	--
35	1.76	1.51	1.71	1.66	0.26	2
36	0.73	0.85	0.85	0.81	0.162	2
37	1.86	1.83	1.53	1.74	0.38	2

TABLE VI: Participants' Results for BAP (Cont'd)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
38	1.99	2.01	2.05	2.02	0.55	0.95
39	1.25	1.30	ND	1.27	0.13	2
40	***	***	***	***	***	***
41	1.531	1.795	1.740	1.689	0.279	2
42	1.64	1.59	1.81	1.68	0.30	2
43	1.38	1.35	1.35	1.36	--	--
44	1.8	1.8	1.8	1.8	0.9	2
45	1.97	1.91	2.01	1.96	0.725	2
46	1.65	1.57	1.55	1.59	0.366	2
47	0.732	0.728	0.727	0.729	0.118	2
48	1.84	1.85	1.84	1.84	0.65	0.95
49	1.72	1.62	1.56	1.63	0.32	2
50	1.604	1.595	1.660	1.620	0.648	--
51	1.25	1.33	1.26	1.28	0.54	2
52	1.500	1.712	1.578	1.597	0.559	2
53	1.92	2.01	2.01	1.98	0.741	2
54	1.5	--	--	1.5	0.47	--
55	3.25	4.16	4.01	3.81	--	--
56	2.43	1.64	1.74	1.94	0.58	0.30
57	1.36	1.53	1.11	1.33	0.24	2
58	1.35	1.20	1.28	1.28	0.14	2
59	1.27	1.34	1.28	1.29	0.063	3
60	0.937	0.933	0.922	0.954	0.45	2
61	0.999	0.998	1.09	1.03	0.156	2
62	2.101	2.350	2.495	2.317	0.41	0.95
63	2.078	1.927	1.923	1.976	0.356	2
64	2.771	2.915	2.808	2.831	0.40	2
65	1.51	1.42	1.48	1.47	0.39	2
66	1.07	1.14	1.07	1.09	0.040	1.96
67	***	***	***	***	***	***
68	1.54	1.68	1.69	1.64	0.41	2
69	--	--	--	0.250	0.1	2

"--" denotes data/information was not provided by participants

"***" denotes no return of results to the organizers

TABLE VII: Participants' Results for BGP

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	2.39	2.40	2.38	2.39	0.301	2
2	1.62	1.52	--	1.57	0.24	2
3	2.212	2.303	2.287	2.267	0.907	2
4	2.09	2.03	2.27	2.13	0.34	2
5	2.33	2.39	2.41	2.38	0.016	2
6	2.31	2.21	2.18	2.23	0.46	2
7	1.29	1.35	1.42	1.35	0.160	0.98
8	2.31	2.36	2.39	2.35	0.081	2
9	3.015	2.867	3.063	2.982	0.0635	2
10	2.44	2.13	2.00	2.19	0.009	2
11	1.99	2.10	2.09	2.06	0.72	2
12	0.783	0.774	--	0.779	0.10	2
13	2.33	1.48	1.81	1.87	0.47	2
14	2.385	2.500	2.800	2.562	8.4	2
15	2.71	2.42	2.27	2.47	0.46	2
16	2.31	2.33	2.49	2.38	0.60	2
17	2.92	3.02	2.52	2.82	0.53	2
18	2.8	--	--	2.8	--	--
19	0.772	0.779	--	0.776	--	--
20	2.069	--	--	2.069	0.207	--
21	2.45	2.50	2.61	2.52	0.454	--
22	--	--	--	--	--	--
23	2.98	2.88	2.86	2.91	0.42	2.45
24	2.45	2.63	2.62	2.57	0.4	2
25	2.75	--	--	2.75	0.853	2
26	2.334	2.379	2.357	2.357	0.471	2
27	2.73	2.72	2.70	2.72	0.3	2
28	2.64	2.58	2.70	2.64	0.15	2
29	2.259	2.246	2.293	2.266	0.453	2
30	--	--	--	2.34	--	--
31	2.17	1.99	1.99	2.05	0.089	3.2
32	3.804	4.058	--	3.931	--	--
33	0.93	1.22	1.12	1.09	0.27	3.18
34	2.25	2.07	--	2.16	0.19	--
35	2.75	2.52	2.77	2.68	0.27	2
36	1.03	1.21	1.22	1.15	0.230	2
37	2.36	2.77	2.62	2.58	0.57	2

TABLE VII: Participants' Results for BGP (Cont'd)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
38	3.10	3.07	3.23	3.13	1.95	0.95
39	2.31	2.25	ND	2.28	0.23	2
40	***	***	***	***	***	***
41	3.478	3.275	3.217	3.323	0.548	2
42	2.23	2.28	2.37	2.29	0.49	2
43	1.32	1.32	1.33	1.32	--	--
44	2.4	2.4	2.3	2.4	1.0	2
45	2.92	2.77	3.01	2.90	0.928	2
46	2.62	2.60	2.55	2.59	1.03	2
47	1.19	1.30	1.27	1.26	0.306	2
48	2.25	2.05	2.07	2.12	1.07	0.95
49	2.16	2.16	2.06	2.13	0.41	2
50	2.468	2.428	2.479	2.458	0.863	--
51	1.81	1.98	1.87	1.89	0.19	2
52	1.717	1.971	1.776	1.821	0.747	2
53	3.51	3.17	3.36	3.35	0.750	2
54	1.9	--	--	1.90	0.57	--
55	3.40	3.46	3.40	3.42	--	--
56	2.86	2.15	2.64	2.55	1.15	0.45
57	2.64	2.37	2.05	2.35	0.82	2
58	2.73	2.47	2.56	2.59	0.26	2
59	1.71	1.65	1.67	1.68	0.048	3
60	1.97	1.87	2.03	1.96	0.48	2
61	1.42	1.58	1.46	1.49	0.207	2
62	3.299	3.054	3.201	3.185	1.02	0.95
63	3.021	2.988	3.116	3.042	0.730	2
64	3.867	3.654	3.626	3.716	0.55	2
65	1.96	1.84	2.15	1.98	0.66	2
66	1.17	1.19	1.09	1.15	0.042	1.96
67	***	***	***	***	***	***
68	2.26	2.49	2.49	2.14	0.55	2
69	--	--	--	2.64	1.3	2

"--" denotes data/information was not provided by participants

"***" denotes no return of results to the organizers

TABLE VIII: *z*-Scores of Participants

Lab Code	z-Scores				
	PHE	FLT	BAA	BAP	BGP
1	-1.3	0.03	-0.58	-1.4	-1.3
2	-4.4	-3.2	-2.7	-3.2	-3.4
3	-2.6	-1.9	-2.0	-2.8	-1.6
4	2.4	0.24	-0.08	-0.13	-1.9
5	-1.2	-1.2	-1.8	-1.2	-1.3
6	-1.3	-0.76	0.34	-2.2	-1.7
7	-0.31	-2.0	-2.0	-3.5	-3.9
8	-0.31	-1.2	-1.2	-1.3	-1.4
9	-3.3	-2.4	-1.1	164	0.23
10	0.81	-0.08	-0.90	-2.0	-1.8
11	-0.95	-0.97	-1.0	-2.1	-2.1
12	-0.59	-0.80	2.2	-4.1	-5.4
13	-2.3	-1.4	1.0	0.10	-2.6
14	-0.72	-0.95	-0.39	0.52	-0.84
15	-1.6	-1.4	-1.0	-0.68	-1.1
16	-2.2	-1.6	-0.82	-2.0	-1.3
17	-0.91	-1.3	-1.1	-0.28	-0.18
18	0.32	0.99	-1.6	-1.1	-0.23
19	-3.8	-4.7	-4.8	-4.7	-5.4
20	-0.87	-0.92	-1.4	-1.6	-2.1
21	-0.28	-1.0	-0.94	-1.5	-0.94
22	-1.0	NA	NA	NA	NA
23	-0.08	-0.28	-0.22	0.01	0.04
24	-0.92	1.1	1.1	0.36	-0.83
25	0.35	-0.04	-0.20	0.24	-0.36
26	-0.75	-0.80	1.0	-0.53	-1.4
27	0.63	-1.0	-0.24	-0.32	-0.44
28	-1.5	-0.35	-0.77	-1.8	-0.64
29	-2.4	-2.2	-1.7	-0.30	-1.6
30	-1.4	-1.5	-1.2	-1.1	-1.4
31	-2.0	-2.1	-1.5	-2.2	-2.1
32	-1.2	-1.4	-1.8	-1.1	2.7
33	-5.3	-0.34	-4.8	23	-4.6
34	-0.73	-2.0	-3.1	-1.3	-1.9
35	0.10	-5.9	-0.68	-1.2	-0.54
36	-3.7	-3.8	-4.1	-4.2	-4.4
37	-1.7	-1.5	-0.93	-0.94	-0.78

TABLE VIII: *z*-Scores of Participants (Cont'd)

Lab Code	z-Scores				
	PHE	**FLT**	**BAA**	**BAP**	**BGP**
38	0.16	-0.11	-0.25	0.02	0.62
39	-0.81	-1.3	-2.0	-2.6	-1.6
40	***	***	***	***	***
41	-2.0	-1.6	-0.72	-1.1	1.1
42	-1.4	-1.5	-2.0	-1.1	-1.5
43	-3.5	-2.9	-2.4	-2.3	-4.0
44	-0.35	-0.87	-1.2	-0.73	-1.3
45	0.93	0.31	0.59	-0.16	0.03
46	-1.1	-1.2	-1.0	-1.5	-0.77
47	-4.3	-4.3	-4.5	-4.5	-4.2
48	-1.7	-1.5	-0.41	-0.58	-2.0
49	-2.4	-1.1	-0.82	-1.3	-1.9
50	-0.54	-0.56	-0.57	-1.4	-1.1
51	-1.3	-1.3	-1.6	-2.5	-2.6
52	-1.2	-1.2	-1.0	-1.4	-2.7
53	1.2	0.59	-0.67	-0.10	1.2
54	-1.3	-1.2	-1.4	-1.8	-2.5
55	-2.0	0.06	1.1	6.2	1.4
56	-0.76	-0.62	-1.1	-0.26	-0.87
57	0.94	0.39	-0.85	-2.4	-1.4
58	-1.8	-2.1	0.04	-2.6	-0.77
59	1.2	-1.8	-1.6	-2.5	-3.1
60	-0.60	-0.79	-2.4	-3.7	-2.4
61	0.67	-1.6	-0.40	-3.4	-3.6
62	0.84	-0.49	-0.08	1.1	0.75
63	0.85	-0.50	-0.66	-0.12	0.39
64	1.2	-1.3	0.98	2.9	2.1
65	-1.7	-1.6	-1.4	-1.9	-2.3
66	-3.7	-2.9	-0.93	-3.2	-4.4
67	***	***	***	***	***
68	-0.92	-0.77	-1.1	-1.3	-1.2
69	NA	-3.0	NA	-6.1	-0.64

"NA" denotes not applicable
z-Scores ≥ 3 or ≤ -3 are underlined
"***" denotes no submission of results to the organizers

TABLE IX: Instrumentation and Extraction Techniques

Lab Code	Analytical Instrument	Analytical Column	Internal Standard	Extraction Solvent(s)	Extraction Technique
1	GC-MSD	Phenomenex ZB-5MS (30 m x 0.25 mm x 0.25 mm)	PHE-d10, chrysene-d12, perylene-d12	Acetone: DCM (1:1)	Tumbler Extraction
2	GC-FID	CP SIL 5CB 8752 WCOT	b-b' Binaftile	Toluene	Ultrasonic
3	LC-FLD	Varian - Pursuit PAH (25 cm x 4.6mm,5 µm)	--	DCM	ASE
4	GC-MSD	Valco Bond VB 5 (60 mx0.25 mmx0.25 mm)	None	Hexane: Acetone (6:4)	Ultrasonic
5	GC-MSD	RTX-5MS (30 m x 0.25 mm x 0.25 mm)	PHE-C13, perylene-d12	DCM (Distilled in glass)	ASE
6	GC-MSD	DB 5-MS (30 m x 0.25 mm x 0.25 mm)	PHE-d10	Acetone: Hexane (1:1)	Microwave
7	GC-MSD	Rxi-XLB (30mx0.25mmx0.25mm)	Deuterated PAH	DCM	Ultrasonic
8	GC-MSD	B 5 (30mx0.25mmx0.25mm)	Deuterated PAH	Acetone	Ultrasonic
9	HPLC-PDA	ODS-P (25 cm x 4.6 mm,5 µm)	--	Toluene: Ethanol (16:4)	Ultrasonic
10	GC-MSD	DB 5 (30mx0.25mmx0.25mm)	Naphthalene-d8, anthracene-d10, 1,3,5-triphenylbenzene	Toluene	Ultrasonic
11	GC-MSD	HP 5MS (30 m x 0.25 mm x 0.25 mm)	Pyrene-d10, perylene-d12	Cyclohexane	Soxhlet
12	GC-MSD	Varian VF-5MS (30 m x 0.25 mm x 0.25 mm)	deuterated PHE, acenaphthene, chrysene, perylene and dichlorobenzene	DCM : Acetone (1:1)	ASE
13	GC-MSD	DB 5MS (30 m x 0.25 mm x 0.25 mm)	Yes, only in calibration, not surrogates	DCM	Soxhlet
14	GC-MSD	DB-5 (30m x 0.25 mm x 0.25 mm)	--	DCM	Agitation/Ultrasonic
15	GC-MSD	DB-5MS (60mx0.32mmx0.25mm)	C13-labeled product mix	Toluene	Ultrasonic, 60°C 1hour
16	GC-MSD	HP-5MS (60mx0.25mmx0.25mm)	Deuterated PAH's	Acetone: Hexane (1:1)	Soxhlet
17	GC-MSD	RTX-5 Sil MS (30 m x 0.25 mm x 0.25 mm) + 5m IntegraGuard	PHE-d10, chrysene-d12, perylene-d12	Acetone, DCM	Ultrasonic
18	GC-MSD	Factor four DB5 (30 m x 0.25 mm x 0.25 mm)	1,4-Dichlorobenzene-d4, naphthalene-d8, acenapthene-d10, PHE-d10, chrysene-d12	DCM: Acetone (1:1)	Agitation/Ultrasonic

TABLE IX: Instrumentation and Extraction Techniques (Cont'd)

Lab Code	Analytical Instrument	Analytical Column	Internal Standard	Extraction Solvent(s)	Extraction Technique
19	GC-MSD	ZB-5MS (30 m x 0.25 mm x 0.25 mm)	--	Acetone: Hexane (50:50)	Agitation/Ultrasonic
20	LC-FLD	C_{18} (25 cm x 4.6 mm,5 µm)		ACN	Agitation/Ultrasonic
21	GC/HRMS	DB 5 (30 m x 0.25 mm x 0.25 mm)	PHE-d10, FLT-d10, chrysene-d12, BAP-d12, dibenz(a,h)anthracene-d14	Acetone: Hexane (1:1)	Soxhlet
22	HPLC-UV	C18 (15 cm x 2.1 mm, 5 µm)	--	--	Solvent Extraction; SPE (C_{18}, Florisil)
23	HRGC/HRMS	DB-EUPAH (20m; 0.15mm; 0.14mm film)	16 PAH C13	Acetone: DCM (1:1)	ASE
24	GC-MSD	Restek RTX-5MS (30 m x 0.25 mm x 0.25 mm)	1,4-Dichlorobenzene-d4, naphthalene-d8, acenphthene-d10, PHE-d10, chrysene-d12, perylene-d12	Hexane: DCM (1:1 v/v)	Soxhlet
25	GC-MSD	VF-17ms (30 m x 0.25 mm x 0.25 mm)	PHE-d10, FLT- d10, BAA- d12, BAP- d12, BGP- d12	n-Hexane: Acetone (50:50 v/v)	ASE
26	LC-FLD	SUPELCOSIL™ LC-PAH (25 cm x 46 mm,5 µm)	PHE-d10, Benzo(b)fluoranthene-d12	Hexane: Acetone: Toluene (2:1:1)	Agitation/Ultrasonic
27	GC-MSD	RTX-5(30 m x 0.25 mm x 0.25 mm)	PHE-d10, FLT-d10, BAA- d12, BAP- d12, BAP- d12	DCM	Soxhlet
28	GC-MSD	DB 5 (60 m x 0.32 mm x 0.25 mm)	--	Hexane: Acetone (1:1)	ASE (DIONEX ASE 300)
29	LC-FLD	Waters PAH; C_{18}(25 cm x 4.6 mm, 5 µm)	No	Acetone: Hexane (1:1)	Soxhlet (18hrs)
30	GC-MSD	DB 5ms (60 m x 0.25 mm x 0.25 mm)	Napthalene-d8, acenaphthalene-d10, PHE-d10, chrysene-d12, perylene-d12	n-Hexane, Acetone	Microwave extraction
31	GC-MSD	2B-5 (30 m x 0.25 mm x 0.25 mm)	Deuterated PAH mix	Acetone, Hexane	Ultrasonic
32	GC-MSD	HP5-MS	--	Acetone: n-Hexane (50:50)	Agitation
33	GC-MSD	Zebron ZB-5 (60 m x 0.25 mm x 0.30 mm)	2-fluoro-biphenyl; p-terphenil-d14	n-Hexane	Ultrasonic
34	GC-MSD	XTI-5M (5 m x 250 µm x 25 µm)	Acenaphthene-d10, PHE-d10, naphthalene-d10, chrysene-d10, perylene-d10	DCM, solvent exchange into hexane	Solvent extraction (rolling)
35	GC-MSD	ZB-5MS (30 m x 0.25 mm x 0.25 mm)	Phenanthrene-d10, Chrysene-d10, Perylene-d12	Toluene	--
36	GC-MSD	DB5-MS (20 m x 0.18 mm x 0.18 mm)	Naphthalene-d8, pyrene-d10, perylene-d12	Cyclohexane: Ethyl Acetate 50%	Agitation

TABLE IX: Instrumentation and Extraction Techniques (Cont'd)

Lab Code	Analytical Instrument	Analytical Column	Internal Standard	Extraction Solvent(s)	Extraction Technique
37	LC-FLD	Zorbax eclipse PAH rapid resolution HT (4.6 cm x 50 mm, 1.8 µm)	No	Acetone: n-Hexane (50:50)	Ultrasonic
38	GC-MSD	DB-35MS (30 m x 0.25 mm x 0.25 mm)	Naphthalene-d8, acenaphthene-d10, PHE-d10, chrysene-d12, perylene-d12	DCM	Agitation
39	GC-MSD	VF-5ms (30 m x 0.25 mm x 0.25 mm)	Acenaphthene-d10, chrysene-d12, perylene-d12	DCM: Acetone (1:1)	Ultrasonic
40	***	***	***	***	***
41	GC-MSD	DB 5 (30 m x 0.25 mm x 0.25 mm)	No	Pet ether, Acetone	Agitation/Ultrasonic
42	GC-MSD	DB5 MSU1x0.18x0.18	Acenaphthalene-d8, FLT-d10, perylene-d12, dibenzo(a,h)anthracene-d14	Hexane: Acetone (1:1)	Tumbler Extraction
43	LC-FLD	Acquity UPLC BEH Shield RP_{18} (15 cm x 2.1mm,1.7 µm)	PAH solution mix	Propanone: n-Hexane (1:1)	ASE
44	HPLC	ZORBAX eclipse PAH (4.6 mm x 25 cm, 5 µm)	--	ACN	Soxhlet
45	GC-MSD	DB 5MS (30 m x 0.25 mm x 1 mm)	Naphthalene-d8, acenaphthene-d10, PHE-d10, chrysene-d12, perylene-d12	--	Microwave extraction
46	GC-MSD	DB5-MS (30 m x 0.25 mm x 0.25 mm)	Naphthalene-d8, FLT-d10, chrysene-d12, perylene-d12	Pentane: Acetone (1:1)	ASE
47	GC-MSD	DB5 MS (30 m x 0.25 mm x 0.25 mm)	--	Hexane, Acetone, DCM	Trumbling minimum 4 hours
48	GC-MSD	DB 5 (30 m x 0.25 mm x 0.25 mm)	Naphthalene-d8, acenaphthene-d10, PHE-d10, Chrysene-d12, Perylene-d12	DCM	Agitation/Ultrasonic
49	LC-UVD / LC-FLD	Hypersil LC-PAH, 100 x 4.6 mm ,5 µm	PAH mix	Hexane	Soxhlet
50	GC-MSD	DB 5 (30 m x 0.25 mm x 0.25 mm)	Pyrene-d10	n-Hexane, Acetone	--
51	GC-MSD	Varian VF-5MS (30 m x 0.25 mm x 0.25 mm)	Naphthalene-d8, acenahthene-d10, PHE-d10, chrysene-d12, perylene-d12, dibenzo(an)anthracene-d14	DCM	Microwave
52	GC/MS/MS	HP 5MS (30 m x 0.25 mm x 0.25 mm)	Nitrobenzene-d5, 2-fluorobiphenyl; 2.4.6-tribromophenol; p-Terphenyl-d14	DCM	Agitation/Ultrasonic
53	GC-MSD	Thermo Gold TG-5SILMS (30 m x 0.25 mm x 0.25 mm)	Deuterated naphthalene, acenaphtene, PHE, chrysene, perylene	n-Hexane: Acetone (50:50)	ASE
54	GC-MSD	DB-5MS (30 m x 0.25 mm x 0.25 mm)	PHE-d10, Perylene	Hexane: Acetone (1:1)	Agitation

TABLE IX: Instrumentation and Extraction Techniques (Cont'd)

Lab Code	Analytical Instrument	Analytical Column	Internal Standard	Extraction Solvent(s)	Extraction Technique
55	GC-MSD / LC-DAD	DB-5 (30 m x 0.25 mm x 0.25 mm) / C_{18}(3.0 x 250 mm,5 µm)	Nitrobenzene-d5, 2-fluorophenol, phenol-d5, p-terphenyl-d14, 2-fluorobiphenyl, 2,4,6-tribromophenol	n-Hexane,& Acetone	Soxhlet
56	LC-FLD	Colonne"pinnacle PAHII" C18 (250mmx4.6mmx4mm)	No	Hexane	ASE
57	GC-MSD	DB 5MS (30mx0.25mmx0.25mm)	Naphthalene-d8, Acenaphthene-d10, PHE-d10, Pyrene-d10, Chrysene-d12, Perylene-d12, BGP-d12	DCM	Ultrasonic
58	GC-FID	RTX-5 (30mx0.32mmx0.25mm)	None	DCM	Agitation
59	GC-MSD	DB 5 (30mx0.25mmx0.25mm)	--	--	Ultrasonic
60	GC-MSD	DB-5MS (30mx0.25mmx0.25mm)	Deuterated PAHs	DCM: Acetone (1:1)	Agitation
61	GC-MSD	1. Agilent DB-5 (5mx0.15mmx0.25mm) 2. Varian Select PAH Column (15mx0.15mmx0.1mm)	Deuterated PAH standards	Hexane: DCM (2:1)	Ultrasonic
62	GC-MS HRMS	DB 5 ms (60mx0.25mmx.25mm)	Yes, only in calibration, not surrogates	Acetone, Hexane	ASE
63	GC-MSD	HP 5ms (30mx0.25mmx0.25mm)	FLT-d10; chrysene-d12, perylene-d12	Acetone: Hexane (1:1)	ASE
64	GC-MSD	DB 35ms (30mx.25mmx.25mm)	--	Acetone, n-Hexane	Agitation
65	GC-MSD	DB 5 (30mx0.25mmx0.25mm)	Naphthalene-d8, acenaphthalene-d10, PHE-d10, chrysene-d12, perylene-d12	Hexane: Acetone (50:50)	Ultrasonic
66	GC-MSD	DB-5MS (30mx0.25mmx0.25mm)	Naphthalene-d8, PHE-d10, perylene-d12	Toluene	Ultrasonic
67	***	***	***	***	***
68	LC-FLD	Lichrospher®PAH (250mmx4mmx5mm)	External standard	Acetone: n-Hexane (1:1)	Ultrasonic
69	GC-MSD	DB-5 (30mx0.25mmx0.25mm)	2,2'-binaphthyl	Hexane, Acetone	Agitation; SPE (Si60)

"---" denotes data/information was not given;
"***" denotes no return of results to the organizers;
"ACN": acetonitrile; "ASE": accelerated solvent extraction; "DCM": dichloromethane;

TABLE X: Other Technical Information

Lab Code	Cleanup Method	% Recovery	Correction for Recovery	Method Accredited
1	--	73-93%	No	Yes
2	TLC	86.50%	Yes	BAA & BGP
3	Aluminium oxide	--	No	Yes
4	NO	~ 95%	Yes	Yes
5	Silica Sep-Pak	--	Yes	Yes
6	SPE (Silica)	85-105	No	Yes
7	---	---	No	Yes (not PHE)
8	SPE (500mg SiO_2)	--	No	Yes
9	SPE (C18)	--	No	No
10	Silica gel	88.58-95.18%	No	No
11	NO	--	No	Yes
12	NO	90	No	Yes
13	Silica column	--	No	No
14	NO	ND	No	No
15	Only dilution	62-105%	Yes	Yes
16	Silica column	80	No	Yes
17	NO	60%	Yes	Yes
18	NO	--	No	Yes
19	--	98.4-98.9%	Yes	No
20	Centrifuge	100%	No	Yes
21	NO	94-106%	Yes	Yes
22	--	72	Yes	No
23	Silica gel column	75-120%	Yes	Yes
24	NO	97-130%	No	Yes
25	Open column chromatography	--	Yes	Yes
26	NO	80-115%	No	Yes

TABLE X: Other Technical Information (cont'd)

Lab Code	Cleanup Method	% Recovery	Correction for Recovery	Method Accredited
27	Silica	55-95	Yes	Yes
28	Silica gel	95.9-101.8% (Mean=99.0%)	No	Yes
29	NO	--	Yes	Yes
30	--	--	No	Yes
31	NO	--	No	Yes
32	--	--	No	No
33	Silica	62-101%	Yes	Yes
34	Florisil	--	No	Yes
35	NO	81.1%	Yes	Yes
36	NO	85-115%	No	Yes
37	NO	90	No	Yes
38	NO	107.91%	No	Yes
39	NO	99-120%	No	Yes
40	***	***	***	***
41	Aluminium oxide	95%	Yes	Yes
42	--	67-99%	No	Yes
43	GPC	81%	No	Yes
44	--	84-117%	No	Yes
45	Silica gel SPE	~80-95%	No	Yes
46	NO	--	Yes	Yes
47	NO	70-130%	No	Yes
48	--	69-77%	No	Yes
49	Silica gel	20%	Yes	Yes
50	DMF clean-up	70-80	Yes	Yes
51	--	96-110%	No	Yes
52	GPC	70% to 115%	No	--

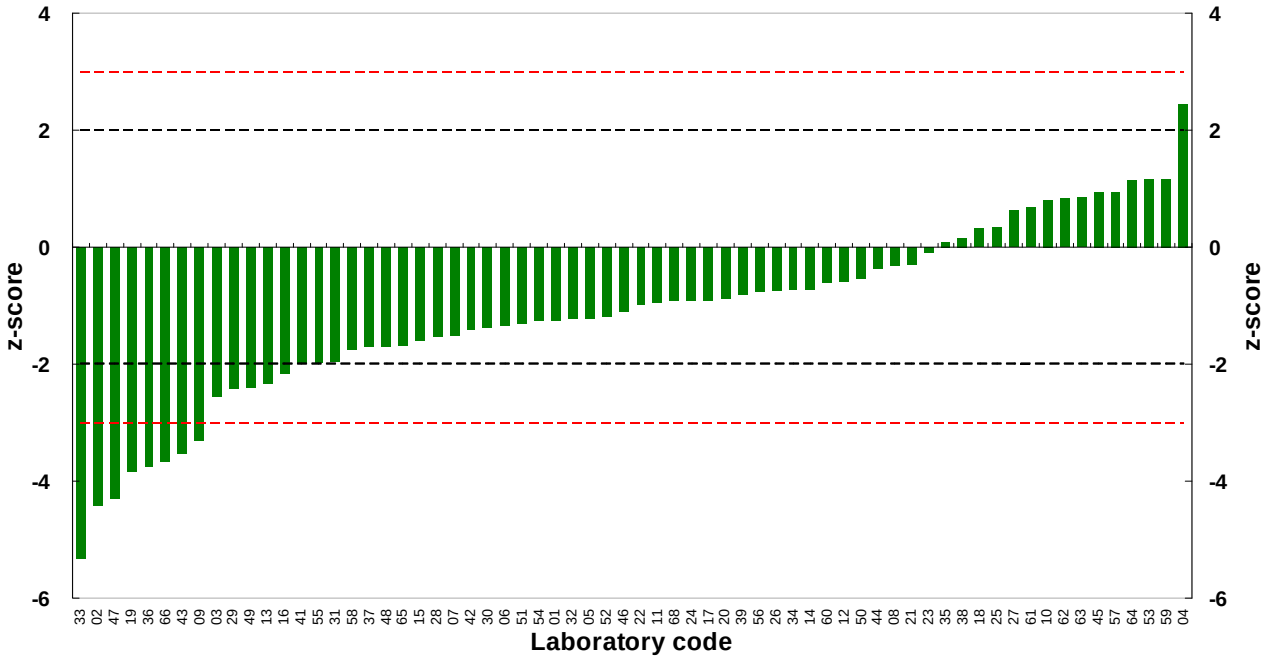
TABLE X: Other Technical Information (cont'd)

Lab Code	Cleanup Method	% Recovery	Correction for Recovery	Method Accredited
53	Silica gel	Not applicable	Yes	Yes
54	NO	57-78%	No	No
55	GPC	ND	--	Yes
56	--	No	No	No
57	Silica	--	No	Yes
58	Silica - US EPA3630	85-95%	No	No
59	--	--	Yes	Yes
60	NO	88%	No	Yes
61	NO	99.9%	No	No
62	Silica activated	90%	No	Yes
63	NO	--	No	Yes
64	Silica gel	100%	No	Yes
65	NO	--	No	No
66	NO	103%	Yes	Yes
67	***	***	***	***
68	--	100%	No	Yes
69	Si60 flash column	ND	Yes	Yes

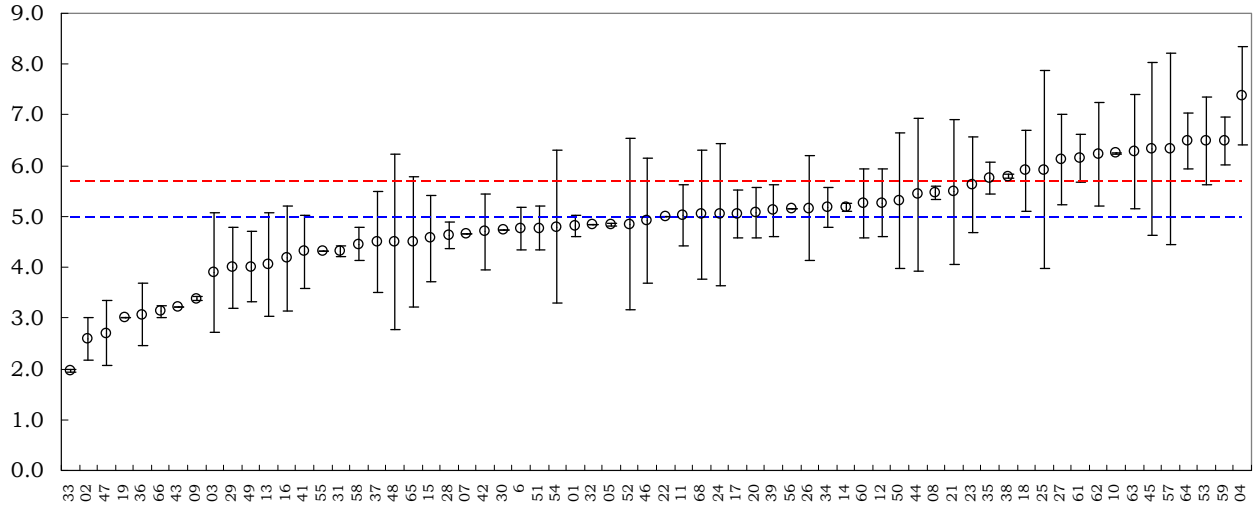
"---" denotes data/information was not given
"***" denotes no submission of results to the organizers
"ND" denotes not determined

FIGURE I

(a) *z*-Scores of Participants' for PHE



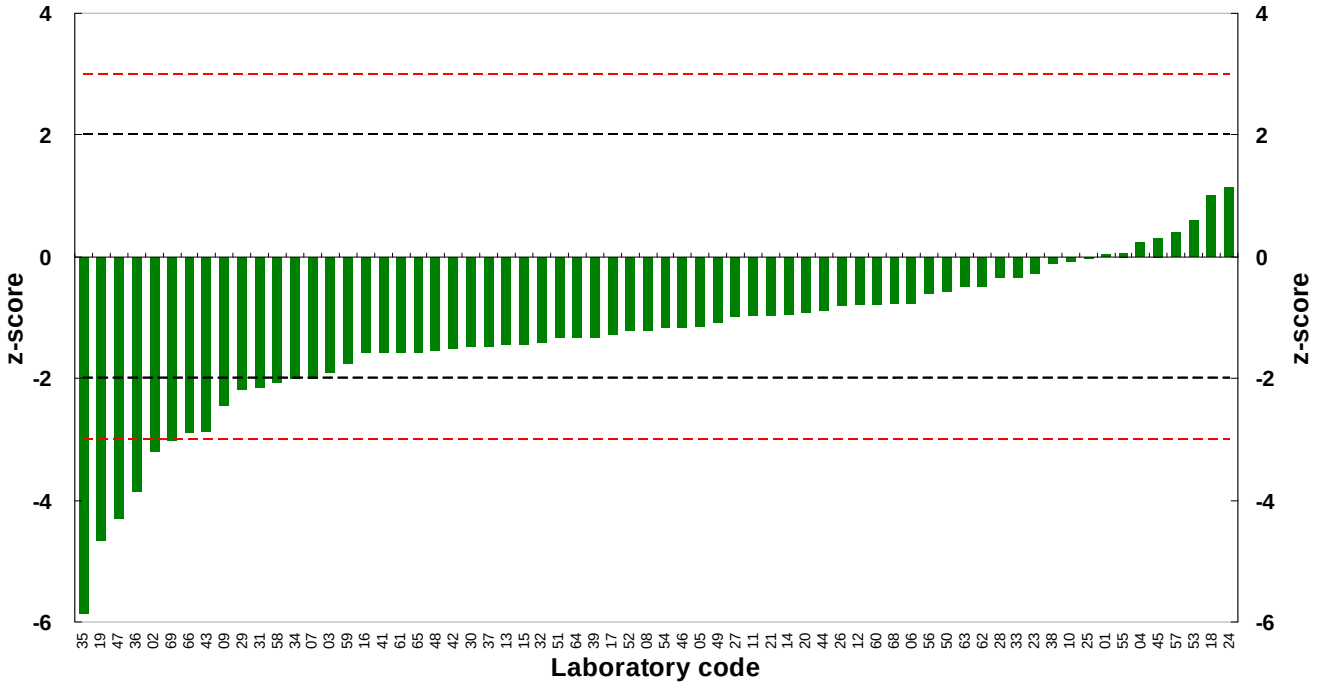
(b) Mean concentration in mg/kg of PHE (in ascending order)



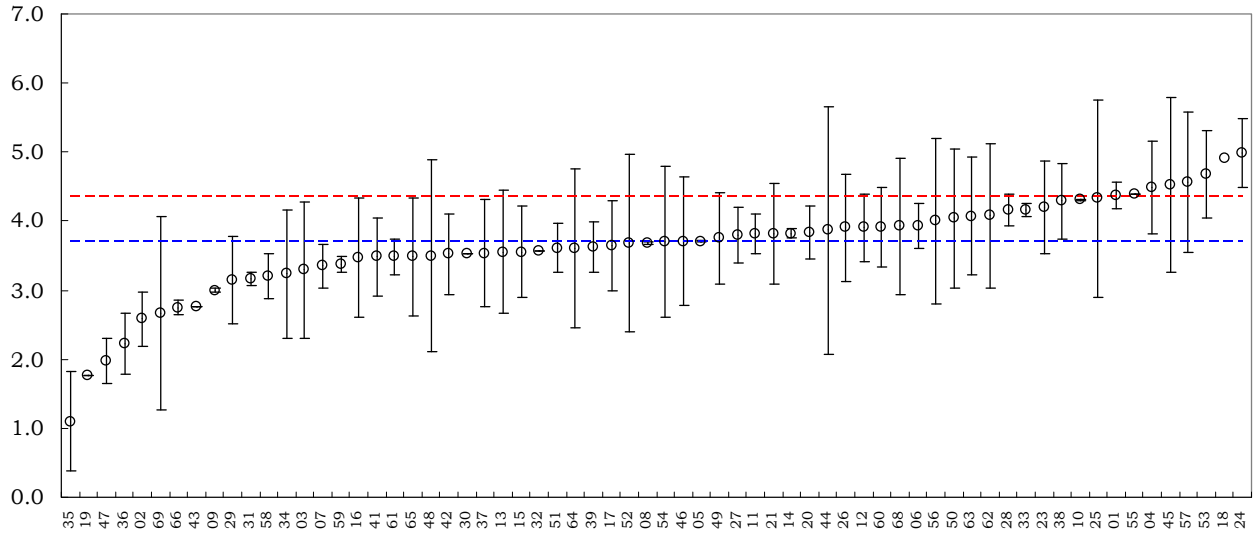
Note: Red dotted line is the assigned value; blue dotted line is the robust mean and error bars represent the expanded uncertainties

FIGURE II

(a) z-Scores of Participants' for FLT



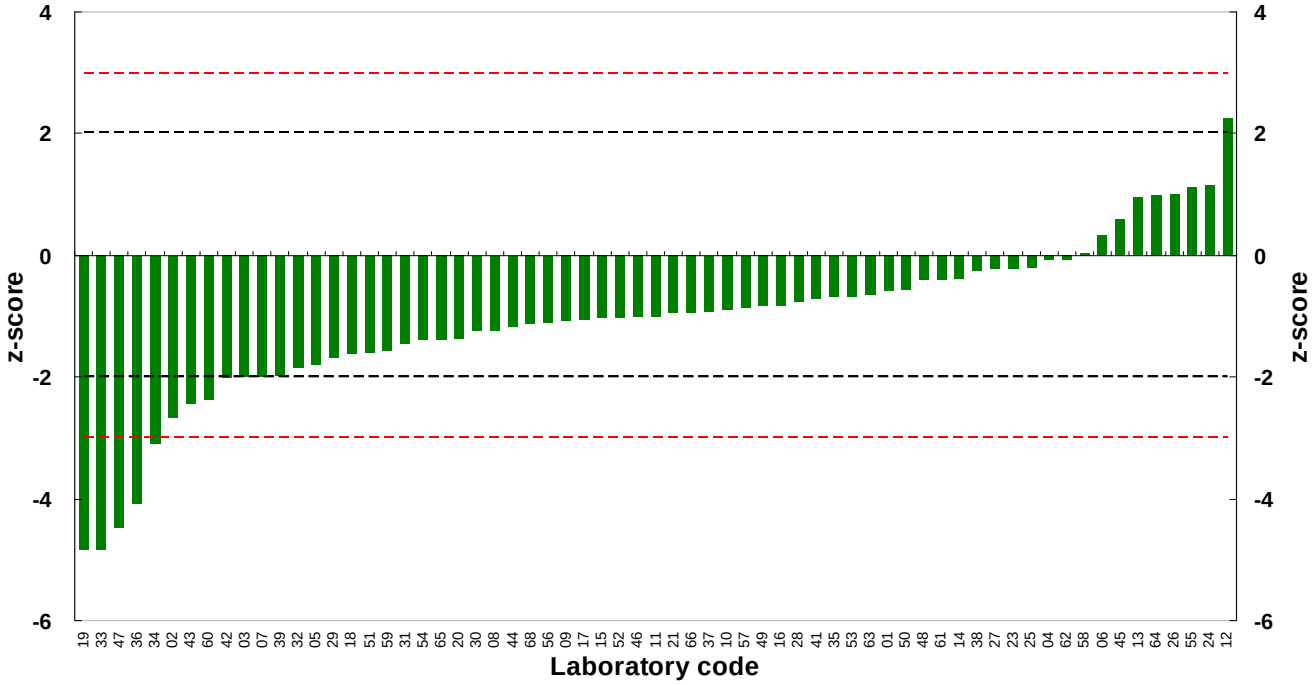
(b) Mean concentration in mg/kg of FLT (in ascending order)



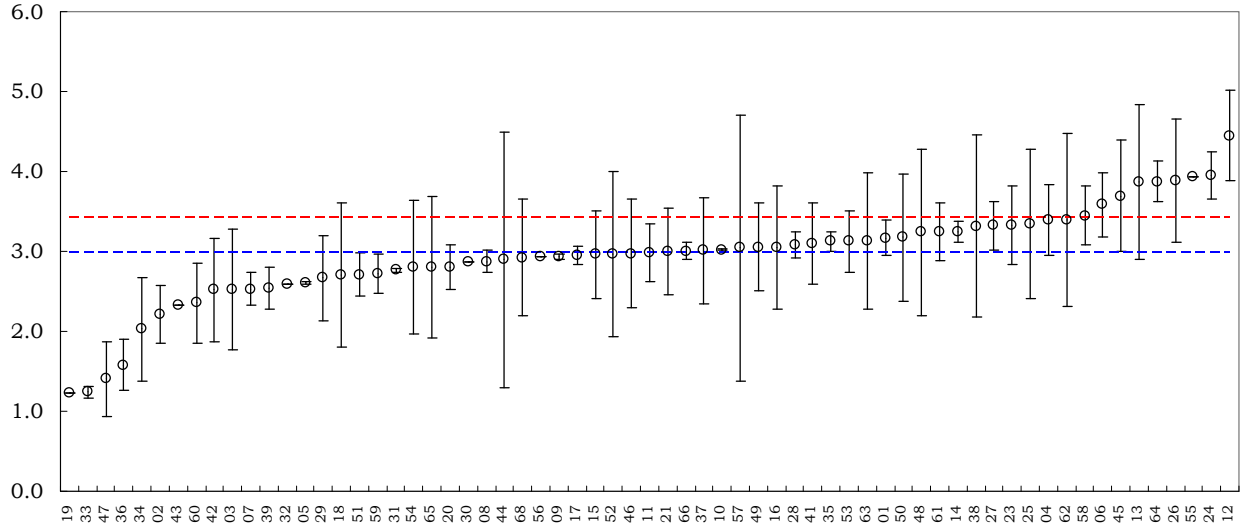
Note: Red dotted line is the assigned value; blue dotted line is the robust mean and error bars represent the expanded uncertainties

FIGURE III

(a) *z*-Scores of Participants' for BAA



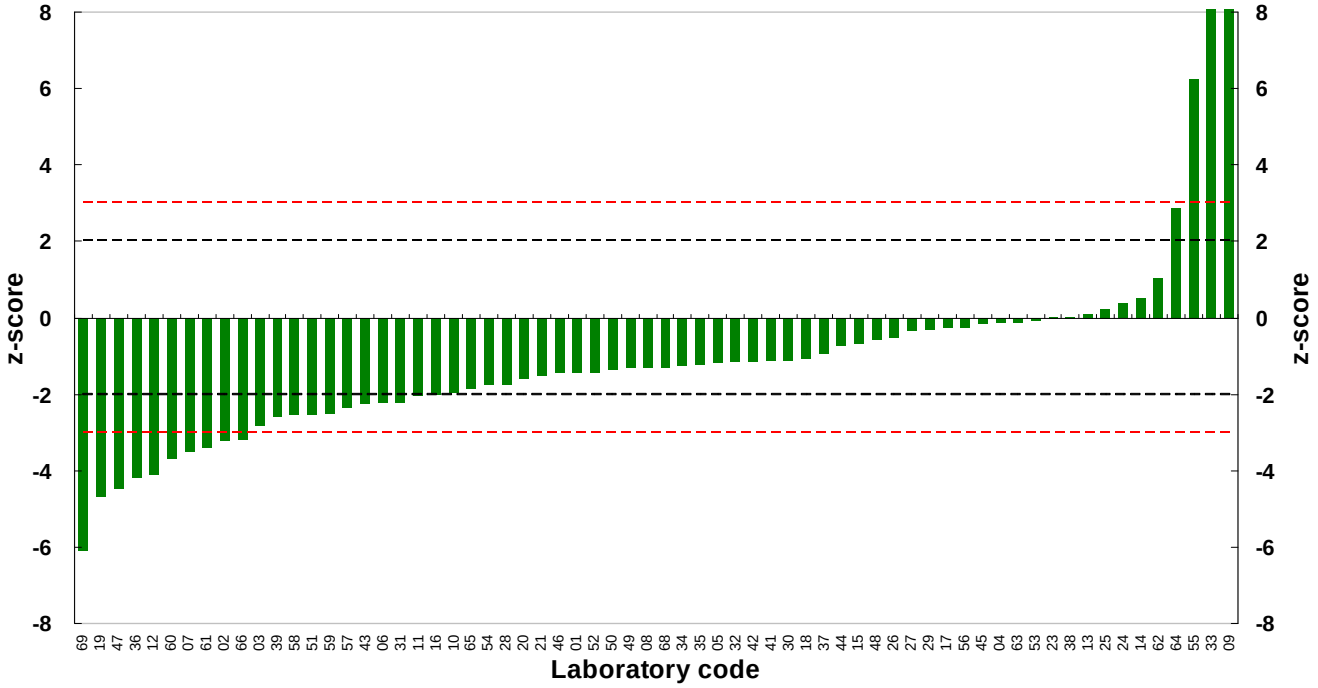
(b) Mean concentration in mg/kg of BAA (in ascending order)



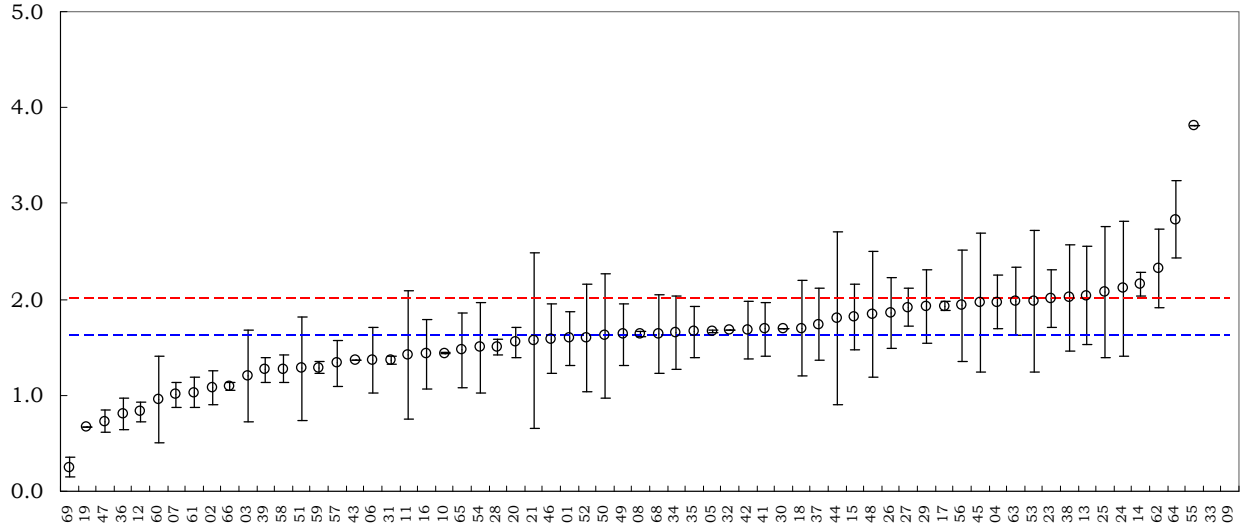
Note: Red dotted line is the assigned value; blue dotted line is the robust mean and error bars represent the expanded uncertainties

FIGURE IV

(a) *z*-Scores of Participants' for BAP



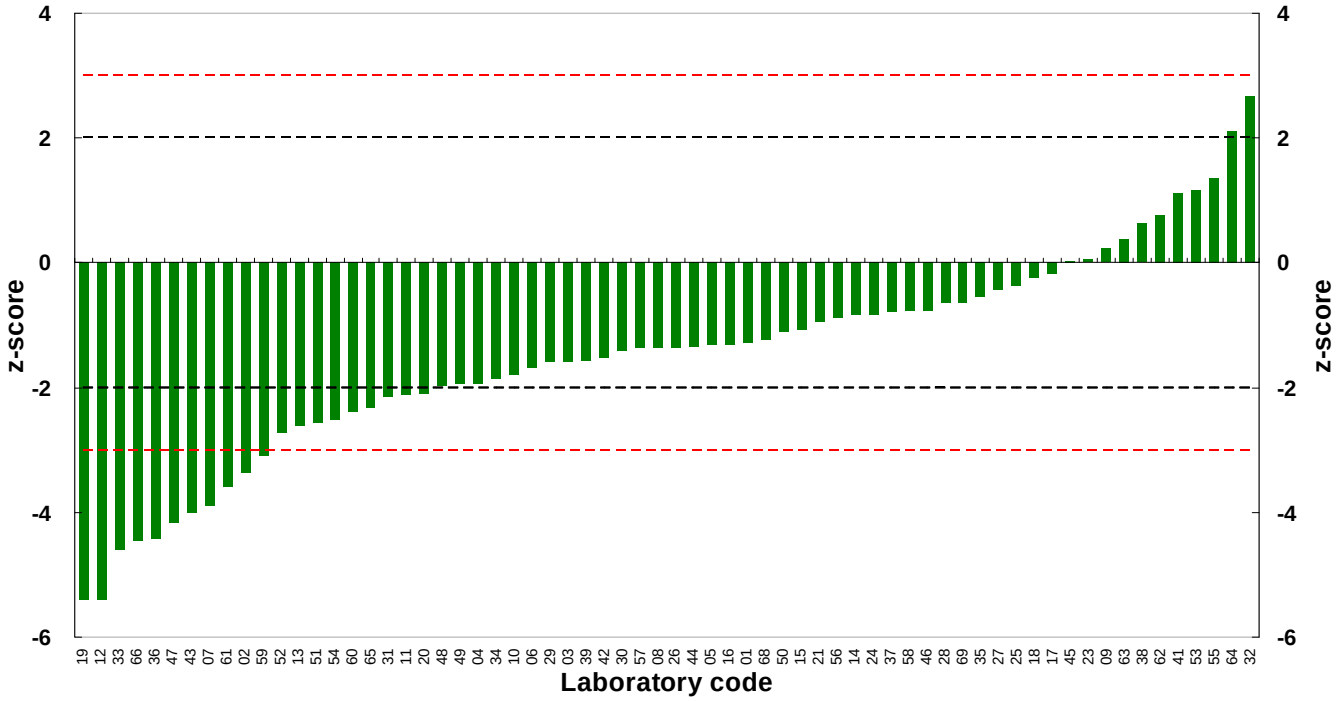
(b) Mean concentration in mg/kg of BAP (in ascending order)



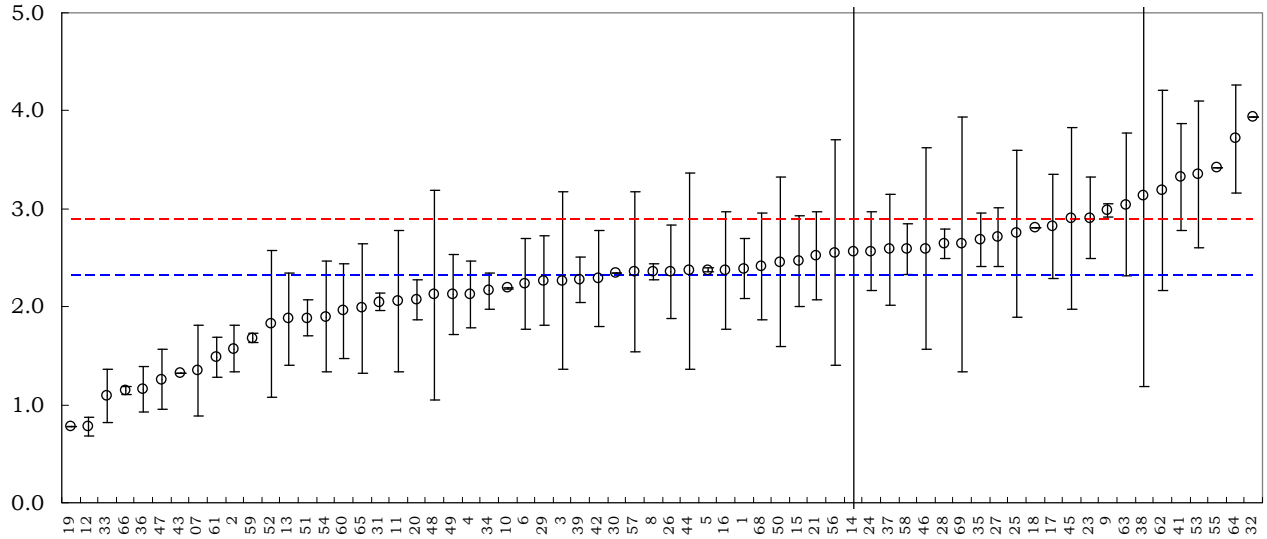
Note: Red dotted line is the assigned value; blue dotted line is the robust mean and error bars represent the expanded uncertainties

FIGURE V

(a) *z*-Scores of Participants' for BGP



(b) Mean concentration in mg/kg of BGP (in ascending order)



Note: Red dotted line is the assigned value; blue dotted line is the robust mean and error bars represent the expanded uncertainties

APPENDIX I: Preparation of PAH Spiked Sediment Testing Material

Weight of sediment = 6.004 kg

PAH std[1]	Conc. (mg/L)	Spiked volume[2] (L)	Amount spiked (mg)	Nominal conc.[3] (mg/kg)
PHE	1027.77	0.05	51.39	8.56
FLT	1042.49	0.04	41.70	6.95
BAA	406.76	0.08	32.54	5.42
BAP	207.11	0.08	16.57	2.76
BGP	407.95	0.05	20.40	3.40

[1]PAH standards were prepared by dissolving appropriate quantity of neat standards (purity >99%) in AR grade acetonitrile; [2]Aliquots taken were mixed with 20 L acetone before adding into the sediment sample; [3]Concentration in raw sediment materials

APPENDIX II: Homogeneity Test

a. A total of 12 bottles of test material were randomly selected from the bulk. Two portions (sub-samples) of about 1 g each were taken from each bottle for duplicate analysis for PHE, FLT, BAA, BAP and BGP in May 2010 using GC-MSD with 1-hour ultrasonic extraction.

b. Analysis was performed using GC-MSD with the following conditions:

Model: Agilent 6890N GC with 5973C MSD

Injection volume: 1 μL, splitless mode

Carrier gas flow rate: 1.5 mL/min

Internal standard: deuteriated PHE, FLT, BAA, BAP, BGP

Column: DB-XLB, 60 m x 250 μm x 0.25 μm

Temperature program: 40°C, hold 1 min; ramped at 30°C/min to 220°C, hold 8 min; ramped at 5°C/min to 250°C, hold 8 min; finally ramped at 5°C/min to 310°C, hold 26 min.

c. Results of the 24 sub-samples were as follows:

Sample Code	Concentration (mg/kg) of duplicate analysis									
	PHE		FLT		BAA		BAP		BGP	
	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
4	4.78	5.03	3.66	3.78	2.72	2.80	1.76	1.78	2.51	2.52
18	4.76	4.81	3.70	3.65	2.75	2.69	1.77	1.75	2.51	2.45
33	4.79	4.88	3.63	3.66	2.70	2.74	1.70	1.72	2.39	2.40
53	4.91	4.80	3.74	3.64	2.84	2.77	1.83	1.76	2.58	2.51
64	4.65	4.68	3.54	3.59	2.63	2.69	1.69	1.71	2.33	2.41
73	4.93	4.82	3.84	3.68	2.79	2.75	1.88	1.79	2.64	2.56
93	4.86	4.89	3.70	3.71	2.80	2.74	1.80	1.76	2.53	2.44
103	4.98	4.99	3.75	3.76	2.79	2.82	1.80	1.81	2.56	2.54
118	4.75	4.94	3.63	3.74	2.68	2.79	1.71	1.79	2.37	2.53
132	4.73	4.76	3.62	3.60	2.69	2.69	1.72	1.72	2.41	2.40
143	4.80	4.86	3.60	3.63	2.68	2.67	1.69	1.71	2.34	2.38
163	4.86	4.67	3.71	3.59	2.82	2.68	1.81	1.67	2.47	2.39
Mean($\bar{x}$)	4.83		3.67		2.74		1.76		2.47	
SD (S_x)	0.10		0.07		0.06		0.05		0.09	
RSD(%)	2.1		2.0		2.1		3.0		3.5	

d. According to ISO13528:2005, the test materials are of adequate homogeneity if:

$$S_s \leq 0.3\sigma_R$$

where S_s = Between-samples standard deviation
σ_R = Standard deviation for proficiency assessment

APPENDIX II: Homogeneity Test (Cont'd)

σ_R (in percent) is estimated using Horwitz equation:

PAH	$\bar{x}$ (mg/kg)	σ_R (%)	0.3σ_R (%)	0.3σ_R (mg/kg)
PHE	4.83	12.54	3.76	0.18
FLT	3.67	13.07	3.92	0.14
BAA	2.74	13.66	4.10	0.11
BAP	1.76	14.60	4.38	0.08
BGP	2.47	13.88	4.16	0.10

S_s is calculated as:

$$\sqrt{S_x^{\,2} - (S_w^{\,2}/2)}$$

Where S_x = Standard deviation of sample averages
S_w = Within-samples standard deviation

S_w is calculated as:

$$\sqrt{\sum w_t^{\,2}/(2n)}$$

where w_t = Absolute difference of the duplicate sample
n = Number tested samples

The results are summarized as follows:

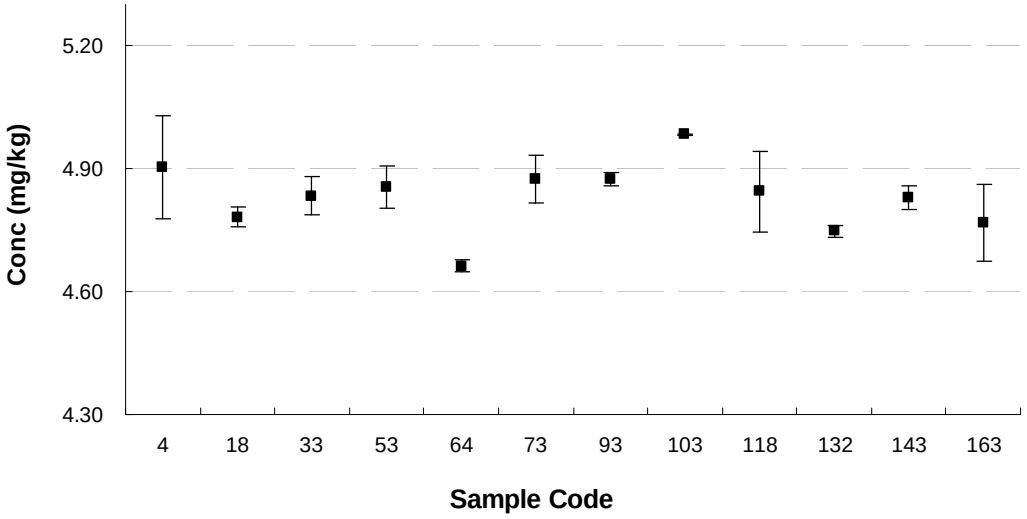
PAH	n	Σw_t^2 (mg/kg)	S_w (mg/kg)	S_x (mg/kg)	S_s (mg/kg)
PHE	12	0.1783	0.0862	0.1018	0.0816
FLT	12	0.0863	0.0600	0.0723	0.0586
BAA	12	0.0577	0.0490	0.0576	0.0460
BAP	12	0.0428	0.0422	0.0529	0.0436
BGP	12	0.0682	0.0533	0.0851	0.0763

Since the between-samples standard deviations (S_s) from the homogeneity test for PHE, FLT, BAA, BAP and BGP are less than the corresponding 0.3σ_R, the homogeneity of the test materials are satisfactory.

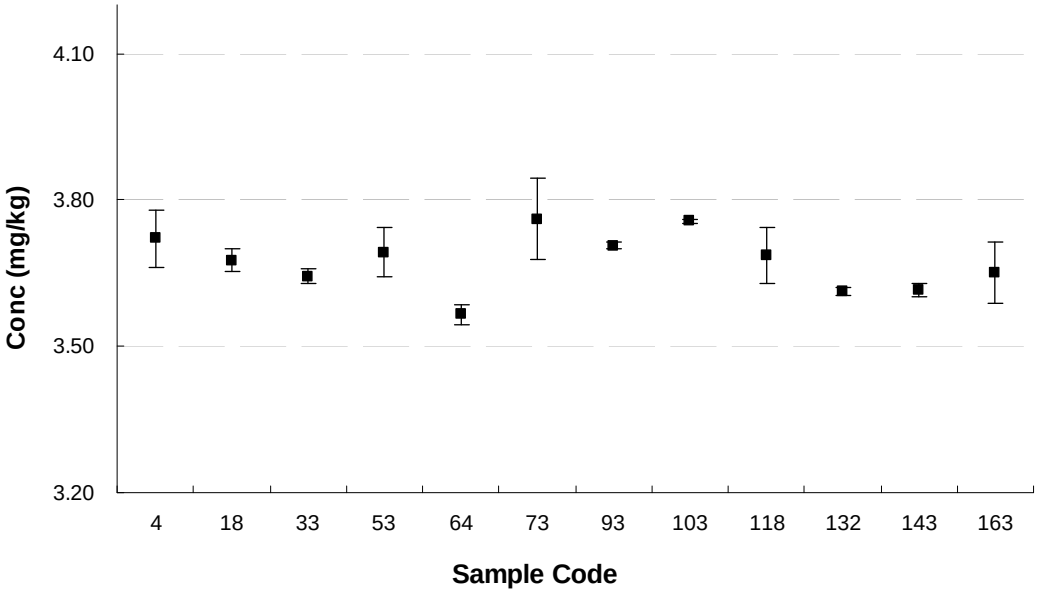
APPENDIX II: Homogeneity Test (Cont'd)

e. Graphical illustrations of random samples in the homogeneity test

(i) PHE

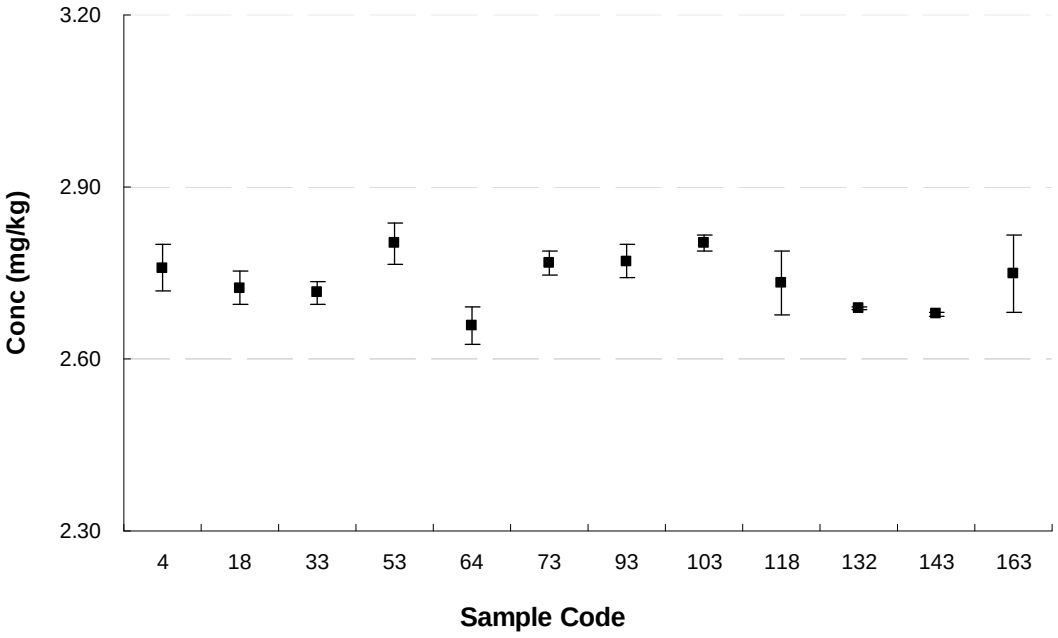


(ii) FLT

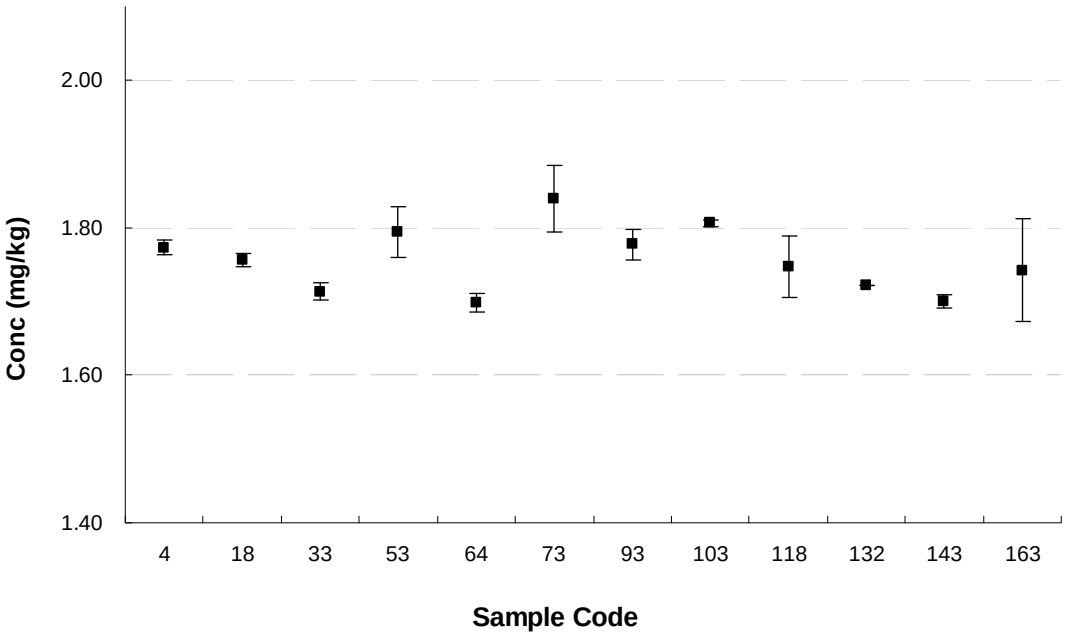


APPENDIX II: Homogeneity Test (Cont'd)

(iii) BAA

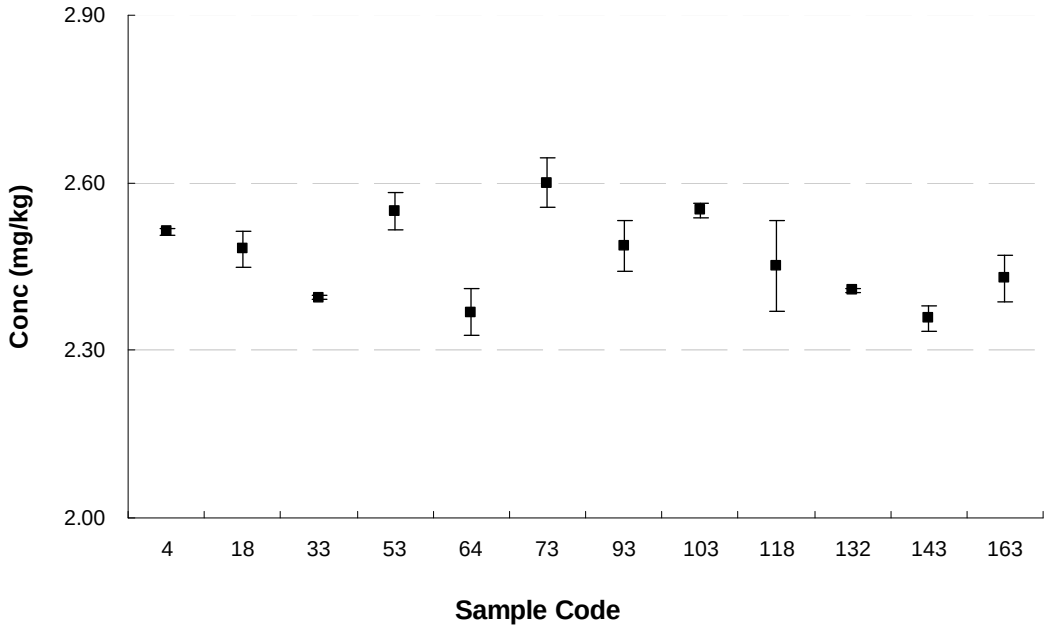


(iv) BAP

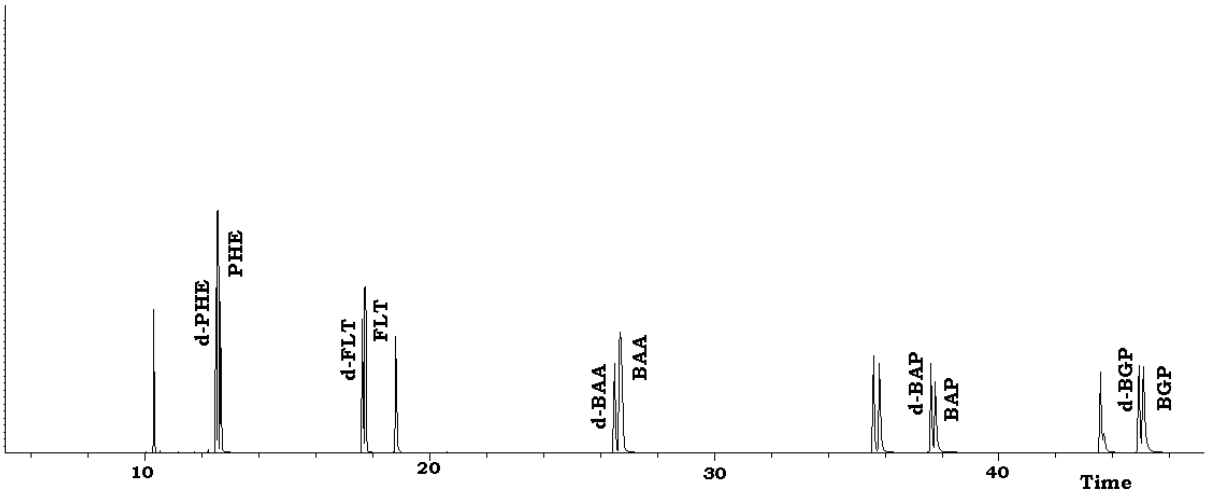


APPENDIX II: Homogeneity Test (Cont'd)

(v) BGP



f. A typical chromatogram for PAH in sediment in the homogeneity test



APPENDIX III: Stability Test

a. Stability of PHE, FLT, BAA, BAP and BGP in the test material was monitored in September 2010 and November 2010, which has fully covered the period from sample dispatch to result submission.

b. Samples selected for the stability test were stored at (i) a room temperature of 25 °C and (ii) an elevated temperature of 37 °C.

c. One sample from each temperature set was randomly selected and analyzed in duplicate or triplicate under the same operational conditions as those in homogeneity test.

d. Stability of samples was determined using the absolute difference between the mean value obtained in homogeneity test ($\bar{x}$) and the mean value ($\bar{yi}$) of each stability test. As stated in ISO13528:2005, the absolute difference should not be more than 30% of the standard deviation of the proficiency test (σ_R).

$$\text{ie.} \quad |\bar{x} - \bar{yi}| \leq 0.3\sigma_R$$

e. The stability tests at 25°C and 37°C are summarized below:

(i) at 25°C

Period (Sample Code)	PAH	Concentration (mg/kg)					$\lvert\bar{x} - \bar{yi}\rvert$	$0.3\sigma_R$	Status
		#1	#2	#3	$\bar{yi}$	$\bar{x}$			
Sep 2010:	PHE	4.98	4.95	5.04	4.99	4.83	0.16	0.18	Pass
(165)	FLT	3.72	3.71	3.77	3.73	3.67	0.06	0.14	Pass
	BAA	2.76	2.75	2.76	2.76	2.74	0.02	0.11	Pass
	BAP	1.77	1.75	1.77	1.76	1.76	0.00	0.08	Pass
	BGP	2.53	2.47	2.58	2.53	2.47	0.06	0.10	Pass
Nov 2010:	PHE	5.01	4.82	5.00	4.94	4.83	0.11	0.18	Pass
(103)	FLT	3.80	3.66	3.84	3.77	3.67	0.10	0.14	Pass
	BAA	2.76	2.74	2.91	2.80	2.74	0.06	0.11	Pass
	BAP	1.76	1.72	1.78	1.75	1.76	0.01	0.08	Pass
	BGP	2.50	2.55	2.56	2.53	2.47	0.06	0.10	Pass

APPENDIX III: Stability Test (Cont'd)

(ii) at 37°C

Period (Sample Code)	PAH	Concentration (mg/kg)					$\lvert\bar{x}-\bar{yi}\rvert$	$0.3\sigma_R$	Status
		#1	#2	#3	$\bar{yi}$	$\bar{x}$			
Sep 2010:	PHE	4.70	4.60	4.66	4.65	4.83	0.18	0.18	Pass
(49)	FLT	3.55	3.49	3.58	3.54	3.67	0.13	0.14	Pass
	BAA	2.68	2.59	2.61	2.63	2.74	0.11	0.11	Pass
	BAP	1.69	1.71	1.70	1.70	1.76	0.06	0.08	Pass
	BGP	2.47	2.33	2.42	2.41	2.47	0.06	0.10	Pass
Nov 2010:	PHE	4.61	4.72	4.70	4.68	4.83	0.15	0.18	Pass
(22)	FLT	3.51	3.56	3.59	3.55	3.67	0.12	0.14	Pass
	BAA	2.58	2.65	2.69	2.64	2.74	0.10	0.11	Pass
	BAP	1.71	1.71	1.71	1.71	1.76	0.05	0.08	Pass
	BGP	2.34	2.45	2.49	2.43	2.47	0.04	0.10	Pass

f. The stability of the five PAH inside the sample bottles is found to be satisfactory and the materials are suitable to be used in the PT program.

APPENDIX IV: Instructions to Accreditation Bodies

INSTRUCTIONS
(FOR ACCREDITATION BODIES)

1. SAMPLE

Accreditation bodies (AB) should receive the PT samples and instruction information (hard copy and soft copy) from the organizers. The samples that each contains about 30g of dried sediment are properly packaged in amber bottles. Upon receipt, AB should carefully check the samples (number of bottles, physical conditions, etc.) and shall promptly acknowledge the GLHK by returning the "Receipt Form (for Accreditation Bodies)" electronically to T78@govtlab.gov.hk. New sample(s) will be replaced for any missing and damaged bottles.

AB are recommended to promptly distribute the samples to their nominated laboratories. The samples shall be stored in a secure environment at room temperature (around 25°C) before dispatch.

AB shall remind their nominated laboratories carefully check the sample upon receipt and promptly acknowledge the GLHK by returning the "Receipt Form (for Participating Laboratories)" electronically to **T78@govtlab.gov.hk.**

2. RESULTS

AB shall inform their respective participating laboratories complete Part I and II of the "Result Proforma" and submit electronically to the organizers on or before **31 October 2010** to T78@govtlab.gov.hk. (Notes: 1. Results submitted after the deadline will not be accepted by the organizers. 2. To avoid poor transmission quality, results by fax are generally not recommended).

3. ENQUIRIES

Please contact the organizers for further enquiries at T78@govtlab.gov.hk

APPENDIX V: Receipt Form for Accreditation Bodies

RECEIPT FORM
(FOR ACCREDITATION BODIES)

From: _____
(Name of AB)

_____
(Contact Person)

Email: _____

Date: _____

To: Dr. Yiu-chung WONG
Government Laboratory
Hong Kong.

Email: T78@govtlab.gov.hk

I hereby acknowledge the receipt of _____ # sample(s) for the APLAC T078 program.

The sample(s) is/are found *(intact / damaged) and should be *(suitable / not suitable) for laboratory testing.

Remark(s) : _____

Number of samples
* Please circle as appropriate

APPENDIX VI: Instruction to Participating Laboratories

INSTRUCTIONS
(FOR PARTICIPATING LABORATORIES)

1. SAMPLE

(a) Participating laboratories will be given an amber sample bottle that containing about 30 g of dried sediment powder from the organizers or via their respective accreditation bodies (AB).

(b) Upon receipt of the sample, participating laboratories should carefully inspect the sample for any physical damages and defects.

(c) Participating laboratories shall promptly acknowledge receipt of the sample by returning the "Receipt Form (for Participating Laboratories)" electronically to the GLHK to T78@govtlab.gov.hk. New samples will be replaced for any damaged claims.

(d) Intact sample is recommended to be stored in a secure environment at room temperature (around 25°C) before use. Sample should be immediately capped after used and be kept in a dry box when not in use.

2. ANALYSIS

(a) Participating laboratories are required to determine the concentration (in **mg/kg**) of five PAH: Phenanthrene (PHE), fluoranthene (FLT), benzo(a)anthracene (BAA), benzo(a)pyrene (BAP) and benzo(ghi)perylene (BGP) in the sample. The approximate concentrations were estimated to be in the range of 1 to 10 mg/kg.

(b) Participating laboratories should use their preferable test methods (could be accredited, in-house, modified, ad hoc methods, etc.) which are normally used to test their customer samples and record the method used on the results sheet.

3. RESULTS

(a) Report all the data and the arithmetic mean in Part I of the "Results Proforma".

(b) Estimate and report the expanded uncertainty (± mg/kg) for individual analyte.

(c) Fill in the information of your performed analytical method in Part II of the "Results Proforma".

(d) Submit the results electronically to the organizers on or before **31 October 2010** to T78@govtlab.gov.hk using the soft copy of the "Result Proforma" provided. (Notes: 1. Results submitted after the deadline will not be accepted by the organizers. 2. To avoid poor transmission quality, results by fax are generally not recommended).

4. ENQURIES

Please contact the organizers at T78@govtlab.gov.hk for further enquiries concerning the program.

APPENDIX VII: Receipt Form for Participating Laboratories

RECEIPT FORM (FOR PARTICIPATING LABORATORIES)

From: _____
(Name of Participating Laboratory)

_____
(Contact Person)

Email: _____

Date: _____

To: Dr. Yiu-chung WONG
Government Laboratory
Hong Kong.

Email: T78@govtlab.gov.hk

I hereby acknowledge the receipt of ONE sample for the APLAC T078 program.

The sample(s) is/are found (damaged / satisfactory)* and should be (suitable / not suitable)* for laboratory testing.

Remark(s) : _____

* Please circle as appropriate

APPENDIX VIII: Results Proforma

RESULT PROFORMA

<Both Part I & II **MUST** be completed by Participating Laboratory>

Laboratory Code: _____ (will be assigned later)

Name of Participating Laboratory: _____

_____

Contact Person / Email: _____

Signature: _____

Part I: Analytical Results

Analyte	Concentration (in **mg/kg**, based on as-received weight)				Measurement Uncertainty	
	Data 1	Data 2	Data 3	Mean	Expanded Uncertainty (mg/kg)	Coverage Factor (k)
Phenanthrene						
Fluoranthene						
Benzo(a)anthracene						
Benzo(a)pyrene						
Benzo(ghi)perylene						

Note:

1. If value determined is less than the limit of quantification (LOQ), please specify (eg. if your LOQ is 5 mg/kg, pls. fill in < 5 mg/kg);
2. ND for "not tested"
3. Report values to 3 significant figures or 3 decimal places, whichever is appropriate
4. It is the responsibility of the participants to avoid collusion and falsification of result so as to ensure a reliable assessment to be made in this proficiency testing program
5. Please submit this "Result Proforma" to the organizers at T78@govtlab.gov.hk before **31 October 2010**

To be continued …

APPENDIX VIII: Results Proforma

Part II: Method Information

1. *Analytical Instrument(s): GC-FID; GC-MSD; LC-UVD; LC-Fluorescence; LC-MS/MS
Others: (please specify)

2. Chromatographic column(s): *eg. DB 5 (30m x 0.25mm x 0.25µm) or C_{18} (150mm x 2.1mm, 5µm)*

3. (i) Mobile phase(s): or (ii) GC conditions

4. Internal standard(s)

5. Extraction solvent(s):

6. *Extraction technique: Solvent extraction (*Agitation / Ultrasonic); Soxhlet; ASE; MSPD;
SPE (*C_{18}, Florisil, Alumina, others (pls. specify))
Others: (please specify)

7. Clean-up procedure:

8. Recovery (%)

9. *Correction for recovery YES; NO

10. *Method accreditation: YES; NO

11. Additional information:

* Please circle as appropriate

APPENDIX IX: Experimental Procedure for the ID-GCMS Analysis of PAH in Sediment

1. PAH Standards

(a) Calibration standard solution

A certified reference material (CRM): SRM 2260a (polycyclic aromatic hydrocarbons in toluene) obtained from the National Institute of Standards and Technology (NIST), or equivalent. The CRM contains the following PAH:

(i) PHEN: 11.57 ± 0.12 μg/g
(ii) FLUT: 8.324 ± 0.087 μg/g
(iii) BANT: 4.415 ± 0.078 μg/g
(iv) BAPY: 4.71 ± 0.170 μg/g
(v) BGPE: 5.669 ± 0.069 μg/g

(b) Control standard for verification

A CRM: SRM 1647e (polycyclic aromatic hydrocarbons in acetonitrile) obtained from the NIST, or equivalent. It is used as working standard without further dilution. The CRM contains the following PAH:

(i) PHEN: 4.52 ± 0.11 μg/g
(ii) FLUT: 9.73 ± 0.21 μg/g
(iii) BANT: 5.25 ± 0.11 μg/g
(iv) BAPY: 6.25 ± 0.15 μg/g
(v) BGPE: 4.71 ± 0.17 μg/g

(c) Isotope-labelled spiking solutions obtained from the Cambridge Isotope Laboratories (CIL) as follows:

(i) CLM-2451-1.2: $^{13}C_6$-labelled PHEN (99%, 100.0 ± 3.1 μg/mL in nonane)
(ii) CLM-3597-1.2: $^{13}C_6$-labelled FLUT (99%, 100.0 ± 3.1 μg/mL in nonane)
(iii) CLM-3602-1.2: $^{13}C_6$-labelled BANT (99%, 100.0 ± 3.1 μg/mL in nonane)
(iv) CLM-2722-1.2: $^{13}C_4$-labelled BAPY (99%, 100.0 ± 3.1 μg/mL in nonane)
(v) CLM-1364-1.2: $^{13}C_{12}$-labelled BGPE (98%, 100.0 ± 3.1 μg/mL in nonane)

Prepare a working isotope-labelled spiking solution by accurately weighing appropriate amounts of individual spiking solutions with an appropriate amount of toluene and mixing them together.

(d) Quality control check sample

A matrix CRM: SRM 1944 (polycyclic aromatic hydrocarbons in soil) obtained from the NIST, or equivalent. The certified concentration (mass fraction) of respective PAH in the material is as follows:

(i) PHEN: 5.27 ± 0.22 mg/kg
(ii) FLUT: 8.92 ± 0.32 mg/kg
(iii) BANT: 4.72 ± 0.11 mg/kg
(iv) BAPY: 4.30 ± 0.13 mg/kg
(v) BGPE: 2.84 ± 0.10 mg/kg

2. Handling of samples

(a) Store samples in a dry box at room temperature until use.

(b) Mix thoroughly the sample by shaking the sample bottle or by stirring using a stainless steel spatula.

(c) Sub-sample an adequate amount of material for each batch of analysis. After sub-sampling, the remaining sample is stored in the dry box.

3. Preparation of isotopic blends

(a) Conduct a preliminary analysis by an appropriate GC-MS method to estimate the concentrations of target PAH in the samples.

APPENDIX IX: Experimental Procedure for the ID-GCMS Analysis of PAH in Sediment (Cont'd)

(b) Preparation of sample blend or matrix CRM blend: Weigh accurately an appropriate amount of sample ($M_{x(sample)}$) or matrix CRM ($M_{x(CRM)}$) (about 1.3 g) into a glass vial. Using a gas-tight syringe, weigh a calculated weight of the isotope-labelled spiking solution (2c) ($M_{y(sample)}$ or $M_{y(CRM)}$) (about 1.3 g) into a GC vial. The molar ratio (analyte to its isotopic analogue) should be close to 1.0 as far as possible. Mix the sample with the spiking solution in the sample extraction step as in 4c to give a sample blend or matrix CRM blend.

(c) Preparation of calibration blend or control blend: Using a gas-tight syringe, weigh accurately an appropriate amount of calibration ($M_{zc(cal)}$) or control ($M_{x(cont)}$) standard solution into a glass vial. Weigh, using a gas-tight syringe, a calculated known mass of the isotope-labelled spiking solution (2c) ($M_{yc(cal)}$ or $M_{y(cont)}$) into a GC vial. The molar ratio (analyte to its isotopic analogue) should be close to 1 as far as possible. Mix the standard with the spiking solution to give a calibration blend or control blend.

(d) Preparation of blank blend: Using a gas-tight syringe, weigh accurately an appropriate amount of the isotope-labelled spiking solution (2c) ($M_{y(blk)}$) into a glass vial.

4. Extraction

(a) Place a thimble into a Soxhlet extraction apparatus. Pre-clean the whole setup by extraction with dichloromethane for at least 4 hours. After pre-extraction, cool and disassemble the apparatus. Discard the solvent and air-dry the whole setup.

(b) Add 130 mL acetone/hexane mixture (1:1, v/v) into the flat bottom flask of a pre-cleaned Soxhlet apparatus as obtained in 4a.

(c) Put the thimble together with the sample obtained in 3b into the receiver of a pre-cleaned Soxhlet extraction apparatus.

(d) Transfer the isotope-labelled spiking solution from the GC vial obtained from 3b to the sample in the thimble.

(e) Rinse the GC vial with approximately 20 mL acetone/hexane mixture (1:1) and transfer all rinsing to the sample.

(f) Assemble the apparatus and reflux the sample for at least 16 hours at approximately 4 cycles per hour.

(g) Allow the Soxhlet apparatus to cool down after extraction, disassemble the apparatus and collect all the organic solvent in the flat bottom flask.

(h) Concentrate the extract by rotary evaporation to less than 5 mL and transfer to a test tube.

(i) Proceed to 5 for performing the clean-up procedure.

(j) The matrix CRM and the blank blends obtained in 3b and 3d respectively should go through the same extraction and clean-up procedures as that of the sample blend.

5. SPE Clean-up

(a) Condition the silica SPE cartridge with 10 mL of 20% dichloromethane in hexane (v:v). Discard the eluate.

(b) Transfer the sample extract obtained in 4h quantitatively to the SPE cartridge.

(c) Elute the SPE with another 10 mL 20% dichloromethane in hexane (v:v) and collect the eluate into the same glass vial.

APPENDIX IX: Experimental Procedure for the ID-GCMS Analysis of PAH in Sediment (Cont'd)

(d) Concentrate the eluate as obtained 5c to slightly less than 1 mL under a gentle stream of nitrogen.

(e) Transfer the solution quantitatively to a pre-weighted amber GC glass vial and make up with toluene to a pre-estimated known amount, gently vortex, weigh the GC vial with sample solution and the solution is ready for IDMS analysis.

6. ID-GCMS analysis

(a) Typical gas chromatographic conditions are described below as guidelines. Other GC conditions such as DB-17MS GC column may be used whenever necessary. Record the actual experimental conditions in the worksheet for reference.

GC Column: DB-5MS, 60m, 0.25mm i.d., 0.25 m film thickness

Injector mode: Splitless

Oven temperature: 85°C (1 min); ramped at 30 °C/min to 210°C (hold8 min); ramped at 5 °C/min to 250°C (hold 8 min); ramped at 5 °C/min to 300°C (hold 26 min)

Injector: 320 °C; Detector: 300 °C; Transfer line: 280 °C

Carrier gas flow rate : 1.5 mL/min Helium

Injection volume: 1 μL

Operation mode: SIM

(b) Suggested conditions for selected ion monitoring (SIM) mode acquisition.

Group	Acquisition time (min)	Monitoring ions (*m/z*)			
1	9 – 15.6	176	178	182	184
2	15.6 – 23.4	101	202	208	--
3	23.4 – 33.4	226	228	232	234
4	33.4 – 43.1	252	253	256	--
5	43.1 – 65.2	276	277	288	--

(c) Typical ions selected for each PAH are provided as below for information:

PAHs	Retention time (min)	Monitoring ions (*m/z*)	
		Q1*	Q2#
PHEN	12.07	178	176
PHEN-$^{13}C_6$	12.07	184	182
FLUT	18.10	202	101
FLUT-$^{13}C_6$	18.09	208	--
BANT	27.27	228	226
BANT-$^{13}C_6$	27.26	234	232
BAPY	38.11	252	253
BAPY-$^{13}C_4$	38.11	256	--
BGPE	46.64	276	277
BGPE-$^{13}C_{12}$	46.63	288	--

*Q1 is the monitoring ion for quantification; #Q2 is the monitoring ion for confirmation

APPENDIX IX: Experimental Procedure for the ID-GCMS Analysis of PAH in Sediment (Cont'd)

(d) Set up an injection sequence for GC determination as follows. Each complete loop contains seven injections. Repeat the loop for at least five times for each batch of analysis.

Injections	Complete loop
1	Calibration blend
2	Control blend
3	Blank blend
4	Sample blend – Subsample 1
5	Sample blend – Subsample 2
6	Sample blend – Subsample 3 (where possible)
7	Matrix CRM blend

(e) Determine the percentage relative standard deviation (%RSD) of the MS area counts for respective PAH in each calibration, control, sub-sample and matrix CRM.

7. Measurement equations

(a) R_B is the isotope amount ratio of the sample blend which corresponds to the ratio of the area counts measures at the m/z of Q1 of the natural analogue to that of the isotope analogue for the respective PAH.

(b) R_{BC} is the isotope amount ratio of the calibration blend which corresponds to the ratio of the area counts measures at the m/z of Q1 of the natural analogue to that of the isotope analogue for the calibration standard.

(c) Calculate the sample concentration for each target PAH in μg/g, C_{PAH} as follows:

$$C_{PAH} = C_z \times (M_y/M_x) \times (M_{zc}/M_{yc}) \times (R_B/R_{BC})$$

where C_z = mass fraction of respective PAH in the calibration standard solution, in μg/g
M_y = weight of spiking solution added to the sample, in g
M_x = weight of sample taken for analysis, in g
M_{zc} = weight of standard solution taken for analysis, in g
M_{yc} = weight of spiking solution added to the standard solution, in g
R_B = isotope amount ratio of the sample blend
R_{BC} = isotope amount ratio of the calibration blend

(d) Calculate the deviation of the relative intensity for each PAH as follows:

% Deviation = (RIQ2 of sample - RIQ2 of standard)/(RIQ2 of standard) x 100%

where RIQ2 of sample = MS area count of Q2/MS area count of Q1

RIQ2 of standard = MS area count of Q2/MS area count of Q1

APPENDIX IX: Experimental Procedure for the ID-GCMS Analysis of PAH in Sediment (Cont'd)

(e) Calculate the relative retention time (RRT) for each PAH as follows:

$$RRT = \frac{RT}{RT_{IS}}$$

where RT = retention time of the natural analogue

RTIS = retention time of the isotope analogue

8. Quality control parameters

(a) Perform a blank in each analytical run. The blank blend should be processed through the entire analytical procedure with the sample blends and the calibration blends within the same batch. Acceptance limit: less than 1% of the analyses concentration determined in the sample.

(b) Analyse a control standard (1647e) to check the accuracy of the calibration standard. Acceptance limit for control standard: within the uncertainty of the control standard specified by supplier.

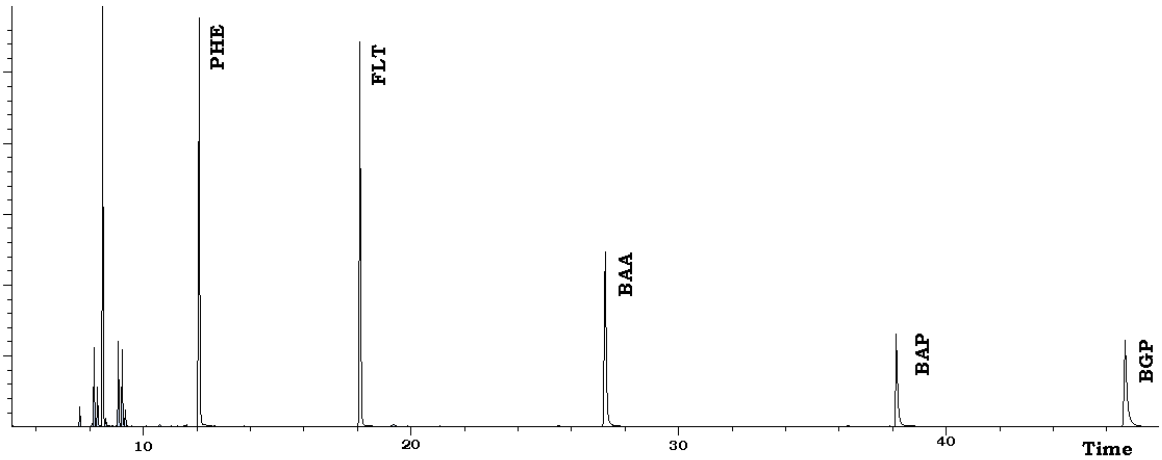
(c) Analyse a matrix reference material (SRM 1944) to check the recovery of the analytical procedure. The matrix blend should be processed through the entire analytical procedure with the sample blends and the calibration blends within the same batch. Acceptance limit for reference material: within the uncertainty of the reference material specified by supplier.

(d) The deviation of the relative intensity (Q1/Q2) for each PAH of the sample should be within ± 20% of the calibration standard.

(e) The retention time of the nature analogues should be within ± 3 seconds of those of the respective isotope analogues.

(f) Acceptance limit for the deviation of relative retention time of the respective PAHs found in the sample, control and matrix CRM from the calibration standard should be within ± 0.06 RRT unit of the standard.

9. Typical Chromatogram under the above experimental conditions



Note: C^{12} and C^{13}-PHE, FLT, BAA, BAP, BGP are overlapped in the chromatogram

APPENDIX X: Reference Values of PAH using ID-GCMS Technique

Sample	Concentration (mg/kg)				
	PHE	FLT	BAA	BAP	BGP
July 2010:					
#1	5.80	4.41	3.50	2.08	2.92
#2	5.65	4.32	3.43	2.06	2.92
#3	5.70	4.37	3.46	2.06	2.88
#4	5.70	4.39	3.48	2.07	2.90
NIST SRM1944	5.21	8.83	4.75	4.25	2.81
Deviation from certified values (%)	1.17	0.97	0.68	1.27	1.07
November 2010:					
#5	5.71	4.35	3.39	1.95	2.84
#6	5.70	4.32	3.39	1.95	2.90
#7	5.54	4.26	3.35	1.94	2.86
#8	5.63	4.34	3.41	1.97	2.87
NIST SRM1944	5.21	8.82	4.69	4.26	2.81
Deviation from certified values (%)	1.13	1.10	0.61	0.96	0.99
*Mean	5.68	4.35	3.43	2.01	2.89
RSD (%)	1.32	1.08	1.49	3.10	1.00
^Expanded rel. MU (%) at $k = 2$	4.9	4.2	4.3	8.4	4.0

* Mean values of the replicate analysis performed in July and November 2010

^Based on the relative standard deviation of replicate analysis and the average deviation of the ID-GCMS results from the certified values. Uncertainties on weighing of standards were found to have minimal contribution to the overall MU and were not taken into account in the estimation