DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENT

PROFICIENCY TESTING PROGRAM

APLAC T068

FINAL REPORT

11 May 2009

CONTENTS

Summary of Results

1. The proficiency testing program (APLAC T068) aimed at evaluating the testing capability of participants on the quantitative analysis of five polycyclic aromatic hydrocarbons, *viz.* phenanthrene (PHE), fluoranthene (FLT), benzo(a)anthrancene (BAA), benzo(a)pyrene (BAP) and benzo(ghi)perylene (BGP), in sediment.

2. A total of 58 laboratories from 23 economies enrolled in the program and 54 of them returned results to the organizer.

3. The reference values of polycyclic aromatic hydrocarbons were assigned by the organizers using isotope dilution gas chromatography-mass spectrometry (ID-GCMS) technique. The standard deviations for proficiency assessment were calculated using the Horwitz Equation[8.1]. z-Score was used as the numerical indicator to assess individual participant's competence in the program.

4. z-Scores for the five polycyclic aromatic hydrocarbons are summarized as follows:

Performance	Number of Participants / Percentage				
	PHE	**FLT**	**BAA**	**BAP**	**BGP**
$\|z\| \le 2$	34	35	38	35	31
	64.2%	66.0%	70.4%	64.9%	62.0%
$2 < \|z\| < 3$	11	12	10	15	11
	20.8%	20.6%	18.5%	27.8%	22.0%
$\|z\| \ge 3$	8	6	6	4	8
	15.1%	11.3%	11.1%	7.4%	16.0%
Total:	53	53	54	54	50
	100%	100%	100%	100%	100%

1. Introduction

1.1. Polycyclic aromatic hydrocarbons (PAHs) are components of crude petroleum and coal. Many PAHs are persistent in soil and sediment, and are known to exhibit carcinogenic and mutagenic properties.

1.2. A proficiency testing program (APLAC T068) on the quantitative analysis of five polycyclic aromatic hydrocarbons, *viz.* phenanthrene (PHE), fluoranthene (FLT), benzo(a)anthrancene (BAA), benzo(a)pyrene (BAP) and benzo(ghi)perylene (BGP) in sediment, was organised by the Hong Kong Government Laboratory (HKGL), 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 September 2008 and completed in April 2009 (Table I).

1.3. A total of 58 laboratories from 23 economies enrolled in the program and 54 of them returned their results on or before the deadline (Table II). Each participant was confidentially assigned with a unique laboratory code (1 to 54) and the code was used throughout the program.

2. Objectives

2.1. The main objective of this program is to assess the performance of participants in the analysis of five PAHs in sediment through inter-laboratory comparison.

2.2. Test results from participants are evaluated according to the statistical techniques outlined in ISO13528:2005[8.2] "Statistical methods for use in proficiency testing by inter-laboratory comparisons" and in the international harmonized protocol for the proficiency testing of analytical chemistry laboratories[8. 3]. z-Score was used as a numerical indicator to assess individual participant's proficiency.

3. Test Material

3.1. About 20 kg contaminated sediment samples were collected from a coastal site near an industrial plant in Hong Kong. The samples were immersed in about 10L of acetone for removing trapped moisture and to kill microbes. The slurry mixture was continuously stirred for thirty minutes and then placed inside a fume hood in a clean room (Class 1000) for air-drying at room temperature. The dried samples were filtered through 1.7 mm sieves

in order to get rid of brick and stone fragments, shell debris, and other foreign substances. The collected sediment particulates were grounded to fine powder with high speed blenders, and then sieved through 250 μm sieves. All batches of fine powder were combined and placed in a 3-dimensional mixer and mixed for more than 7 days. The mixing condition of the powder was monitored by sampling some portions for homogeneity trials. The homogenized fine powder was then packed into cleaned and nitrogen-flush amber glass bottles, in 15 g portions. More than 400 bottles of sediment samples was finally prepared and stored at room temperature before shipment.

3.2. Homogeneity (performed in August 2008) and stability tests (September 2008 and March 2009) of the samples were determined in accordance with the procedures stipulated in APPENDICES I and II. Results indicate the samples are suitable to be used as the proficiency testing materials for the program.

3.3. Samples together with "Instructions to Accreditation Bodies", "Receipt Form", "Instructions to Participating Laboratories", and "Result Proformas" were sent to participating accreditation bodies (AB) in November 2008. A specimen copy of these instructions was given in APPENDICES IV to VIII.

3.4. All AB were requested to read the "Instructions to Accreditation Bodies" and to redirect the sample(s) and the attached documents to their nominated laboratories as soon as possible.

3.5. Each participant was provided with one bottle of 15 g of test sample.

4. Test Required

4.1. Participants were required to determine, preferably in triplicate, the concentration of PHE, FLT, BAA, BAP and BGP in the test sample by their appropriate validated methods.

4.2. Participants were requested to report results in mg/kg to three significant figures or three decimal places, whichever was appropriate.

4.3. Participants were also requested to report the expanded measurement uncertainty and technical information of the method used.

4.4. All the analytical results and information were reported in the Result Proformas provided.

5. Statistical Evaluation

5.1. Participants' test results

5.1.1. Test results received from participants are presented in TABLES III to VII. Their methodologies and techniques employed as well as their accreditation status are tabulated in TABLES VIII to IX.

5.2. Performance evaluation

5.2.1. Performance of each participant was evaluated by means of a performance index, z-score, which is calculated as:

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

where x_i = reported mean of individual participant
m = assigned reference values
S = standard deviation (in mg/kg) estimated from Horwitz Equation

5.2.2. z-Score is interpreted as follows:

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

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

5.3. An interim report containing participants' data and the respective z-score results was issued to participants and their ABs on 13 February 2009. Participants were requested to check the correctness of their submitted data and to inform the organizers of any mistakes found on or before 28 February 2009 prior to the issuance of Final Report.

6. Results and Discussions

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

	PHE	FLT	BAA	BAP	BGP
No. of data submitted	54	54	54	54	52
No. of valid numeric data	53	53	54	54	50

6.2. Assignment of reference values for performance assessment

6.2.1. Assigned reference values of the five PAHs were determined by 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 potential primary methods and is a preferred analytical methods for the provision of accurate and precise results. IDMS technique involves the use of isotopic analogues as internal standards for the above target PAHs. These analogues are referred to as "spike" and are added to both the sample and the calibration standards during analysis. The calibration procedure of the present ID-GCMS was based on the single point calibration technique, which involved spiking a similar amount of the isotope-labelled solution to both the samples and the calibration standards, and the amount of PAHs in the calibration standard was close to that in the sample. This resulted 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 samples by Soxhlet extraction using an acetone/hexane mixture, followed by a clean-up step using solid phase extraction (SPE). The ID-GCMS procedure in this program had been employed for the analysis of PAHs in sediment in the CCQM inter-laboratory key comparison programs (CCQM-P69 in 2005 and CCQM-K50 in 2007). The results were found to show high degree of equivalence with those of other participated national measurement institutes in both programs, and demonstrated that the ID-GCMS procedure used for the determination of reference value assignment is of high reliability. The use of reference values instead of the consensus means of participants is because of the particular challenges presented to the participants in the analysis of trace organics in sediment and soil samples. There is a possibility that the consensus mean of participants is biased and hence it is not used in this program.

6.2.2. Results of assigned reference values:

	PHE	FLT	BAA	BAP	BGP
Assigned ref. value (mg/kg)	14.41	10.92	8.98	4.84	6.21
MU (mg/kg) at k = 2	0.14	0.10	0.14	0.17	0.08

6.3. Horwitz's standard deviation used for performance assessment:

	PHE	FLT	BAA	BAP	BGP
Horwitz's SD (%)	10.65	11.10	11.43	12.54	12.08
Horwitz's SD (mg/kg)	1.53	1.21	1.03	0.61	0.75

6.4. An overview of participants' results:

6.4.1. The robust mean values are 12.02 mg/kg for PHE, 9.14 mg/kg for FLT, 7.83 mg/kg for BAA, 3.94 mg/kg for BAP and 4.96 mg/kg for BGP, and are comparably lower than the assigned reference values by 13 to 20%.

6.4.2. Between-laboratory variations (relative sd) of the five PAHs range from 14% to 18%, which are slightly higher than the Horwitz SD (%) (clause 6.3).

	PHE	FLT	BAA	BAP	BGP
Participants' Mean (mg/kg)	12.02	9.14	7.83	3.94	4.96
Deviation from assigned ref. values (%)	-16.6	-16.3	-12.8	-18.6	-20.1
Between-laboratory variation (relative sd %)	17.1	14.0	16.9	16.6	17.7

6.4.3. z-Scores of individual participant are presented in TABLE X and displayed graphically in CHART I to V. The z-score distribution skews to the right hand side, which indicates negative deviation of participants' results from the reference values in general (Clause 6.4.2.). z-Score performance of participants is summarized as follows:

Performance	Number of Participants / Percentage				
	PHE	FLT	BAA	BAP	BGP
$\|z\| \leq 2$	34	35	38	35	31
	64.2%	66.0%	70.4%	64.9%	62.0%
$2 < \|z\| < 3$	11	12	10	15	11
	20.8%	20.6%	18.5%	27.8%	22.0%
$\|z\| \geq 3$	8	6	6	4	8
	15.1%	11.3%	11.1%	7.4%	16.0%
Total:	53	53	54	54	50
	100%	100%	100%	100%	100%

In brief, 18 participants (Lab. 1, 4, 5, 13, 21, 22, 23, 26, 29, 30, 39, 41, 43, 47, 49, 50, 51, 54) were identified as having reported one or more unsatisfactory results; and 32 out of the 264 results (12.1 %) submitted were identified as unsatisfactory results.

6.5. Majority of the participants used GC-MS (43 laboratories) for the analysis. Nine of them used HPLC with UV or fluorescence detection, and two used GC-FID. Almost all the GC-MS users employed deuteriated PAHs as their quantification techniques. In general, the recovery of PAHs is good, mostly in the 80 to 100% range. About 70% or 38 participants' methods are accredited (Table VIII and IX).

6.6. Extraction methods:

6.6.1. Participants used ultrasonic (14 laboratories) or agitation/shaking (13) or both (2) as their choice of extraction, and 8 laboratories did not state which one (agitation or ultrasonic) they actually used. The others used Soxhlet extraction (9), accelerated solvent extraction (6), microwave-assisted extraction (1) and saponification extraction (1). Most of them used acetone and/or dichloromethane or a combination of acetone or dichloromethane with other organic solvents such as hexane, methanol and toluene. (TABLE VIII). Since PAHs are bound tightly to soil and sediment, the recovery of PAHs depends on the extraction techniques. Literature information showed that rigorous conditions are required to be used for PAHs in soil and sediment samples. For examples, Soxhlet extraction and accelerated solvent extraction reported to be more efficient than sonication[8.6, 8.7] in the recovery of PAHs. Sonication extraction, which is one of the US EPA official methods (3550), was used by a number of participants in this program. However, the US EPA method does not specify solvents nor the length of time required for the extraction and the potential problem of underestimation was reported when using the 3550 method for the analysis of PAHs in soil and sediment [8.7]. An analysis of participants' data from sonication and Soxhlet extraction showed that the average values of the five

PAHs from Soxhlet extraction were higher than those of the sonication by 3.0% to 12.8% (mean at 9.3%), although no statistical difference for the two average values could be found (due to large deviation of data).

6.6.2. The PAHs in the PT samples were extracted with sonication (30 minutes duration) in the homogeneity and stability tests due to simplicity and convenience. During the course of the study, we also compared the extraction efficiency between sonication and Soxhlet extraction. An additional experiment was performed by using Soxhlet extraction (24 hours duration) in the stability test (in September 2008) and we found that the results differed significantly (APPENDIX III). The concentrations of PAHs obtained from the Soxhlet extraction were having 13 to 31% higher than those of the sonication under the same experimental conditions. The results further indicated the choice of extraction for the analysis of PAH in soil and sediment is of critical importance.

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 the Government Laboratory for their support of the program.

7.2. For further comments, participants are welcome to contact the organizers in following address:

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The Proficiency Test Advisory Board,
Hong Kong Government Laboratory,
7/F. Homantin Government Offices,
88 Chung Hau Street, KLN, Hong Kong.

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8. References

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TABLE I: Timeline of the Program

EVENT	SCHEDULE
Preparation of sample	Apr – Jul 2008
Homogeneity testing	Aug 2008
Submission of proposal to APLAC PT Committee for approval	Sept 2008
Invitation of participants	Oct – Nov 2008
Dispatch of samples	Nov/Dec 2008
Stability testing	Sept 2008 – Mar 2009
Deadline for result submission	31 Jan 2009
Statistical analysis of pooled data	Feb 2009
Interim report	Feb – Mar 2009
Preparation of draft report	Mar 2009
Submission of draft report to APLAC PT Committee for approval	Mar 2009
Distribution of final report	Apr 2009

TABLE II: List of Participating Accreditation Bodies

No.	ECONOMIES	PARTICIPANTS ENROLLED	RETURNED RESULTS
1	Argentina	1	1
2	Australia	4	4
3	Belgium	1	1
4	Brazil	2	2
5	Canada	6	6
6	Chile	3	3
7	China	4	4
8	Costa Rica	2	2
9	Czech	2	2
10	Ecuador	2	2
11	Finland	2	2
12	Germany	3	3
13	Hong Kong	4	4
14	Israel	2	2
15	New Zealand	2	2
16	Norway	2	2
17	Portugal	2	2
18	Russia	4	4
19	Slovenia	2	2
20	Sweden	2	2
21	Taiwan	2	1
22	Uruguay	2	0
23	Vietnam	2	1
	Total:	**58**	**54**

TABLE III: Participants' Results for Phenanthrene (PHE)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	7.78	7.77	8.19	7.92	2.92	2
2	11.7	11.6	11.5	11.6	6.148	2
3	11.9	12.0	12.1	12.0	0.43	2
4	6.651	6.632	6.598	6.627	0.399	2.03
5	10.2	10.0	9.78	9.99	2.06	2
6	11.514	11.277	11.295	11.362	4.60	2
7	13.7	13.5	13.0	13.4	0.3	2
8	15.4	10.9	11.9	12.7	1.36	2
9	11.9	12.3	12.4	12.2	0.31	3.2
10	11.65	11.31	11.01	11.32	4.53	2
11	15.4	14.5	14.5	14.8	5.0	2
12	13.195	13.263	12.958	13.138	1.971	2
13	8.69	9.46	8.20	8.79	2.00	2
14	13.6	13.4	13.1	13.4	0.55	2
15	13.8	13.5	13.7	13.7	3.92	2
16	13.303	13.218	13.207	13.243	0.106	2
17	12.5	13.2	12.7	12.8	2.82	2
18	13.588	14.079	13.661	13.776	0.530	2
19	11.3	11.8	11.9	11.7	3.66	2
20	10.1	11.3	10.6	10.7	2.1	2
21	9.6	10.2	9.8	9.9	---	---
22	11.443	10.807	12.094	11.448	1.187	2
23	10.0	9.2	8.9	9.4	0.4	2
24	14.5	15.0	14.4	14.6	5.84	2
25	11.0	11.2	11.3	11.2	2.55	2
26	1.578	1.608	1.559	1.582	0.04	2
27	10.3	11.2	10.7	10.7	1.6	2
28	13.31	13.10	13.09	13.17	1.751	2
29	11.1	11.1	10.6	10.9	2.18	2
30	12.40	12.54	11.30	12.08	2.04	3
31	12.2	12.2	14.5	13.0	3.06	2
32	11.8	12.1	12.3	12.1	1.82	2
33	13.6	15.7	14.1	14.5	4.35	2
34	11.9	11.8	12.4	12.1	3.3	2
35	13.8	13.1	13.1	13.3	2.66	2
36	15	15.6	---	15.3	2	2
37	11.0	11.1	11.0	11.0	1.76	2
38	13.1	13.4	13.3	13.3	3.99	2
39	8.337	8.564	8.739	8.547	1.755	2
40	13.4	13.2	13.0	13.2	2.32	2
41	17.6	18.1	19.0	18.2	0.565	2
42	14.5	---	---	14.5	5.8	2
43	11.630	11.666	11.757	11.684	0.003	2
44	10.5	10.5	10.6	10.5	2.63	2
45	13.3	13.0	13.5	13.3	4.7	2
46	11.8	12.1	12.0	12.0	1.2	2
47	7.54	7.58	---	7.56	1.77	2
48	13.089	12.864	12.240	12.731	0.080	2
49	7.685	7.874	7.907	7.822	0.202	2
50	11.9	11.7	12.0	11.9	2.08	2
51	< 0.92	< 0.92	< 0.92	< 0.92	---	---
52	12.7	12.7	12.6	12.7	0.77	---
53	17.6	18.0	17.9	17.8	1	2
54	10.4	11.2	11.2	10.9	3.3	2

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

TABLE IV: Participants' Results for Fluoranthene (FLT)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	6.60	6.60	6.93	6.71	2.48	2
2	8.44	8.43	8.34	8.40	4.452	2
3	9.55	9.55	9.62	9.57	0.19	2
4	5.200	5.136	5.149	5.162	0.662	2.03
5	7.47	7.39	7.28	7.38	1.60	2
6	8.799	8.454	8.550	8.601	3.48	2
7	9.51	9.42	8.99	9.31	0.10	2
8	12.7	9.14	9.92	10.6	0.976	2
9	10.1	10.2	10.9	10.4	0.33	3.2
10	9.15	8.68	8.57	8.80	3.52	2
11	9.73	9.67	9.50	9.63	3.0	2
12	10.534	10.460	10.397	10.464	2.197	2
13	8.27	8.88	8.03	8.39	1.60	2
14	9.94	9.79	10.1	9.94	0.43	2
15	9.59	9.43	9.38	9.47	2.92	2
16	9.493	9.453	9.350	9.432	0.148	2
17	9.83	11.4	10.3	10.5	2.31	2
18	9.334	9.682	9.339	9.452	0.399	2
19	10.1	10.4	10.9	10.5	3.15	2
20	8.87	10.3	10.1	9.76	1.76	2
21	9	9.1	9.4	9.2	---	---
22	16.427	15.343	15.102	15.024	2.295	2
23	9.1	7.8	7.6	8.2	0.7	2
24	11.2	11.1	11.0	11.1	4.44	2
25	7.94	8.22	8.21	8.12	2.03	2
26	8.680	8.680	8.686	8.682	0.22	2
27	7.86	8.43	8.13	8.14	1.1	2
28	10.41	10.14	10.15	10.23	1.380	2
29	8.30	8.30	7.90	8.20	1.80	2
30	7.24	7.26	6.52	7.01	1.26	3
31	8.37	8.23	9.50	8.70	0.16	2
32	8.27	8.21	8.38	8.29	1.24	2
33	9.64	10.9	9.85	10.1	3.03	2
34	9.5	9.3	9.8	9.5	4.4	2
35	10.2	9.80	9.80	9.93	1.99	2
36	12.5	12.8	---	12.6	1.2	2
37	9.03	8.91	8.77	8.90	1.69	2
38	10.3	10.8	10.7	10.6	2.12	2
39	7.265	7.505	7.799	7.523	2.501	2
40	10.6	10.3	9.99	10.3	1.29	2
41	0.235	0.233	0.241	0.236	0.004	2
42	9.74	---	---	9.74	4.26	2
43	9.368	9.285	9.229	9.294	0.003	2
44	8.37	8.04	8.04	8.15	1.30	2
45	9.99	9.89	9.84	9.91	3.07	2
46	9.18	9.35	9.33	9.29	0.9	2
47	5.94	5.76	---	5.85	1.32	2
48	8.058	7.840	7.523	7.807	0.054	2
49	7.194	7.515	7.688	7.465	0.423	2
50	9.36	9.29	9.43	9.36	1.89	2
51	< 0.83	< 0.83	< 0.83	< 0.83	---	---
52	10.0	9.98	9.76	9.91	1.16	-
53	9.81	9.98	10.1	9.96	1	2
54	8.55	9.22	9.16	8.98	2.69	2

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

TABLE V: Participants' Results for Benzo(a)anthrancene (BAA)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	5.20	5.13	5.42	5.25	1.94	2
2	8.46	8.54	8.39	8.46	4.484	2
3	7.30	7.26	7.32	7.29	0.12	2
4	4.200	4.139	4.199	4.179	0.842	2.03
5	6.48	6.63	6.30	6.47	1.35	2
6	6.944	5.885	6.535	6.455	2.61	2
7	8.04	7.86	7.64	7.85	0.14	2
8	10.7	7.29	8.12	8.70	0.834	2
9	7.15	7.22	7.61	7.33	0.07	3.2
10	7.39	7.18	6.99	7.19	2.88	2
11	9.87	9.88	9.85	9.87	1.2	2
12	8.251	8.355	8.026	8.211	1.314	2
13	7.14	7.72	7.10	7.32	1.43	2
14	8.28	8.65	8.51	8.48	0.41	2
15	8.80	8.29	8.72	8.60	2.40	2
16	7.664	7.671	7.511	7.615	0.180	2
17	7.84	8.49	8.19	8.17	2.04	2
18	7.970	8.309	8.123	8.134	0.340	2
19	7.55	8.00	8.29	7.95	2.38	2
20	6.95	8.03	7.63	7.54	1.51	2
21	7.6	8.6	8.1	8.1	---	---
22	14.314	14.086	14.407	14.269	2.240	2
23	7.1	6.7	6.2	6.7	0.7	2
24	10.1	10.3	10.3	10.3	4.10	2
25	7.37	7.35	7.38	7.37	1.84	2
26	6.707	6.697	6.686	6.697	0.17	2
27	6.49	6.79	6.49	6.59	0.84	2
28	9.57	8.86	8.82	9.08	1.415	2
29	8.40	8.40	8.00	8.30	2.49	2
30	6.60	6.54	5.77	6.30	1.38	3
31	10.9	11.5	13.4	11.9	1.8	2
32	8.68	9.87	9.02	9.19	1.38	2
33	10.4	11.5	10.3	10.7	3.21	2
34	7.9	7.7	8.0	7.8	4.3	2
35	7.81	7.42	7.47	7.57	1.89	2
36	8.98	9.22	---	9.1	1.4	2
37	7.12	7.13	6.85	7.03	1.62	2
38	8.15	8.56	8.28	8.33	1.67	2
39	5.905	6.271	5.799	5.992	1.615	2
40	8.84	8.71	8.20	8.58	2.00	2
41	20.5	19.4	22.8	20.9	1.48	2
42	8.21	---	---	8.21	3.74	2
43	7.521	7.359	7.447	7.442	0.003	2
44	6.84	6.63	6.67	6.71	1.54	2
45	8.32	8.52	8.64	8.49	2.46	2
46	7.33	7.26	7.37	7.32	0.7	2
47	4.79	4.45	---	4.62	1.02	2
48	8.036	7.853	7.467	7.785	0.051	2
49	6.494	6.235	6.735	6.640	0.423	2
50	9.10	8.74	8.91	8.92	1.69	2
51	4.78	4.16	4.16	4.37	2.185	2
52	10.5	9.97	9.64	10.0	2.67	---
53	7.55	7.75	7.62	7.64	1	2
54	7.06	7.50	7.45	7.34	2.20	2

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

TABLE VI: Participants' Results for Benzo(a)pyrene (BAP)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	3.86	3.84	4.04	3.91	1.70	2
2	3.52	3.62	3.54	3.56	1.994	2
3	3.99	4.07	4.14	4.07	0.33	2
4	2.400	2.344	2.399	2.381	1.363	2.03
5	2.15	2.22	2.13	2.17	0.33	2
6	3.532	3.196	3.298	3.342	1.35	2
7	3.86	3.79	3.14	3.59	0.04	2
8	5.40	3.81	4.04	4.42	0.419	2
9	3.83	3.77	3.87	3.82	0.11	3.2
10	4.02	3.98	3.82	3.94	1.58	2
11	4.73	5.38	5.63	5.25	0.68	2
12	4.128	4.230	4.060	4.139	0.352	2
13	3.61	3.96	3.80	3.79	0.85	2
14	4.84	4.69	4.94	4.82	0.31	2
15	3.08	3.08	3.17	3.11	0.96	2
16	3.993	3.939	3.972	3.968	0.054	2
17	4.07	4.18	4.62	4.29	0.99	2
18	4.493	4.595	4.574	4.554	0.107	2
19	4.48	4.60	4.71	4.60	1.38	2
20	3.22	3.85	3.53	3.53	0.64	2
21	6.5	6.4	7.1	6.7	---	---
22	4.193	4.783	4.719	4.565	0.840	2
23	3.2	3.1	2.9	3.1	0.3	2
24	4.44	3.94	4.00	4.13	1.65	2
25	3.57	3.27	3.17	3.34	0.868	2
26	3.677	3.669	3.677	3.674	0.09	2
27	3.56	3.79	3.64	3.66	0.46	2
28	4.42	4.40	3.85	4.22	0.720	2
29	5.70	5.70	5.50	5.60	2.41	2
30	4.28	4.19	3.65	4.04	1.02	3
31	3.22	3.07	3.62	3.30	0.66	2
32	4.28	---	5.48	4.88	0.732	2
33	3.63	4.46	4.65	4.25	1.28	2
34	3.6	4.0	4.2	3.9	1.9	2
35	3.47	3.32	3.27	3.35	0.670	2
36	4.55	5.09	---	4.8	1.7	2
37	3.39	3.43	3.40	3.41	0.99	2
38	3.44	3.56	3.33	3.44	0.69	2
39	3.383	3.428	3.700	3.504	0.690	2
40	4.10	3.97	3.88	3.98	0.778	2
41	3.43	3.73	3.49	3.55	0.135	2
42	3.78	---	---	3.78	1.07	2
43	3.143	3.139	3.255	3.179	0.003	2
44	3.67	3.48	3.73	3.63	0.62	2
45	4.35	4.68	4.54	4.52	1.45	2
46	3.97	4.04	4.02	4.01	0.4	2
47	1.64	1.48	---	1.56	0.15	2
48	4.340	4.124	3.867	4.110	0.052	2
49	3.433	3.377	3.318	3.376	0.097	2
50	5.68	5.13	5.17	5.33	1.37	2
51	4.37	4.58	2.51	3.82	0.91	2
52	5.13	5.01	4.92	5.02	1.27	---
53	3.85	4.10	3.93	3.96	0.5	2
54	3.96	4.30	4.28	4.18	1.25	2

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

TABLE VII: Participants' Results for Benzo(ghi)perylene (BGP)

Lab. Code	Concentration (mg/kg)				Expanded Measurement Uncertainty	
	Data #1	Data #2	Data #3	Mean	± mg/kg	Coverage Factor
1	3.78	3.91	4.26	3.98	1.47	2
2	4.17	4.16	4.10	4.14	2.319	2
3	4.93	4.87	4.91	4.90	0.23	2
4	2.450	2.393	2.549	2.464	3.202	2.03
5	2.97	3.06	2.86	2.96	0.60	2
6	4.496	4.048	4.133	4.242	1.72	2
7	4.57	4.48	3.69	4.25	0.05	2
8	6.49	4.78	5.17	5.48	0.575	2
9	5.10	4.81	5.05	4.99	0.22	3.2
10	5.24	5.18	4.94	5.12	2.05	2
11	5.39	5.17	4.95	5.17	0.84	2
12	5.402	5.267	4.847	5.172	0.776	2
13	5.99	6.24	6.59	6.27	2.10	2
14	5.32	5.47	5.66	5.48	0.39	2
15	4.32	4.29	4.40	4.34	1.29	2
16	4.825	4.782	4.736	4.781	0.045	2
17	5.27	5.38	5.70	5.45	1.36	2
18	5.100	5.256	5.167	5.174	0.156	2
19	4.84	5.09	5.26	5.06	1.52	2
20	4.25	4.95	4.55	4.58	1.01	2
21	Not Tested				---	---
22	5.292	5.558	5.722	5.524	1.025	2
23	4.6	4.7	4.3	4.5	0.6	2
24	5.56	5.77	5.73	5.68	2.27	2
25	4.08	4.00	4.09	4.06	1.14	2
26	5.311	5.286	5.333	5.310	0.14	2
27	4.60	4.90	4.72	4.74	0.71	2
28	5.59	5.05	5.60	5.41	0.745	2
29	11.1	11.1	10.6	10.9	3.92	2
30	5.67	5.53	4.76	5.32	1.47	3
31	4.27	4.30	4.63	4.40	1.14	2
32	4.83	5.22	5.31	5.12	0.768	2
33	4.64	5.77	5.13	5.18	1.55	2
34	5.4	5.2	5.4	5.3	2.4	2
35	4.66	4.39	4.28	4.44	1.11	2
36	5.87	6.32	---	6.1	1.3	2
37	4.88	4.92	4.88	4.89	1.61	2
38	4.21	4.26	3.97	4.15	1.24	2
39	4.530	4.702	4.590	4.607	0.980	2
40	6.56	6.31	6.24	6.37	0.859	2
41	6.57	6.89	6.31	6.59	0.233	2
42	5.97	---	---	5.97	1.67	2
43	2.347	2.315	2.280	2.314	0.003	2
44	5.37	5.38	5.57	5.44	0.82	2
45	5.50	5.62	5.66	5.59	1.57	2
46	5.28	5.41	5.36	5.35	0.6	2
47	1.78	1.65	---	1.71	0.23	2
48	Not Tested				---	---
49	< LOQ	< LOQ	< LOQ	<LOQ	---	---
50	3.70	3.87	3.94	3.84	1.35	2
51	< 0.83	< 0.83	< 0.83	< 0.83	---	---
52	6.58	6.56	6.58	6.57	1.15	---
53	5.05	5.21	5.00	5.09	0.5	2
54	1.91	2.00	2.83	2.24	0.67	2

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

"< LOQ" denotes less than limit of quantification

TABLE VIII: Instrumentation and Extraction Techniques

Lab Code	Analytical Instrument	Analytical Column	Internal Standard	Extraction Method	Extraction Solvent(s)
1	GC-MSD	DB-5	Deuteriated IS	Shaking	Acetone, Hexane
2	GC-MSD	SLB-5MS	Deuteriated IS	Ultrasonic	Acetone,DCM
3	LC-UVD	Restek Pinnacle II PAH	benzo(j)fluoranthene	Ultrasonic	Acetone,DCM
4	GC-MSD	DB5	---	Ultrasonic	Acetone, DCM
5	GC-MSD	VB5	Deuteriated IS	Ultrasonic	DCM
6	GC-MSD	CP SIL 8	Deuteriated IS	Ultrasonic	Toluene
7	GC-MSD	RTX-35MS	Deuteriated IS	Agitation	DCM, MeOH
8	GC-MSD	DB-5MS	Deuteriated IS	Agitation	Acetone, Hexane
9	GC-MSD	DB5	Deuteriated IS	Agitation/ Ultrasonic	Acetone, Hexane
10	LC-UVD	C_{18}	---	Ultrasonic	Acetone, Hexane
11	GC-MSD	DB5	Deuteriated IS	ASE	Acetone, DCM
12	GC-MSD	VF-XMS	Deuteriated IS	ASE	Acetone, DCM
13	GC-MSD	DB5	Deuteriated IS	ASE	Acetone, Hexane
14	GC-MSD	DB-5MS	Deuteriated IS	Ultrasonic	Acetone,DCM
15	GC-MSD	DB-5.625	Deuteriated IS	Agitation/ Ultrasonic	DCM
16	GC-MSD	DB5	Deuteriated IS	Shaking	Acetone, Hexane
17	GC-MSD	VF-5MS	Deuteriated IS	Agitation and Ultrasonic	Cyclohexane, Acetone
18	GC-MSD	DB-5	Deuteriated IS	Soxhlet	Toluene
19	GC-MSD	DB-5	Deuteriated IS	Soxhlet	Acetone,DCM
20	LC-FLD	C_{18}	---	Agitation/ Ultrasonic	Diethyl ether
21	GC-MSD	ZB-5	---	Agitation/ Ultrasonic	DCM
22	LC-UVD	DUPELCO™ LC-PAH	Nitrobenzene	Agitation/ Ultrasonic	DCM
23	GC-MSD	DB-5MS	Deuteriated IS	Agitation/ Ultrasonic	Acetone, DCM
24	GC-MSD	DB-5	Deuteriated IS	Soxhlet	Acetone, n-Heptane
25	GC-MSD	ZB-5MS	Deuteriated IS	Agitation	Toluene
26	HPLC	Hypersil Green PAH	Deuteriated IS	Soxhlet	DCM
27	GC-MSD	DB-5	Deuteriated IS	Ultrasonic	Acetone, DCM
28	GC-MSD	DB-5	Deuteriated IS	Agitation	Acetone, Hexane
29	GC-MSD	DB5-17MS	Deuteriated IS	Shaking	DCM, Hexane
30	GC-MSD	DB-5	Deuteriated IS	Ultrasonic	Acetone, Hexane
31	GC-MSD	HP-5MS	Deuteriated IS	Agitation	Acetone, Pentane
32	GC-MSD	DB-5	Deuteriated IS	Soxhlet	Toluene
33	LC-FLD	Waters PAH C_{18}	---	Ultrasonic	DCM, MeOH
34	HPLC	C18-VYDAC	---	Soxhlet	Acetonitrile
35	GC-MSD	DB-5	Deuteriated IS	Agitation/ Ultrasonic	Cyclohexane, EtAc
36	GC-MSD	VF-5MS	Deuteriated IS	Ultrasonic	Acetone, DCM
37	GC-MSD	HP-5MS	Deuteriated IS	Microwave-assisted ext.	Acetone, Hexane
38	GC-MSD	DB-5MS	Deuteriated IS	Agitation/ Ultrasonic	Cyclohexane, EtAc
39	GC-MSD	DB-5	Deuteriated IS	Ultrasonic	DCM
40	GC-MSD	ZB-5MS	Deuteriated IS	Shaking	Acetone, DCM
41	GC-MSD	DB-5MS	Deuteriated IS	Low pressure ASE	Acetone, Toluene
42	GC-MSD	OB5-62S	Deuteriated IS	Agitation	Acetone, DCM
43	LC-UVD	Supelcosil-LC-PAH	---	Soxhlet	Acetonitrile
44	GC-MSD	DB-5MS	Deuteriated IS	Ultrasonic	Acetone, DCM
45	GC-MSD	VF-17MS	Deuteriated IS	ASE	Acetone, Hexane
46	GC-MSD	DB-5	Deuteriated IS	Ultrasonic	DCM
47	GC-MSD	HP-5MS	---	Soxhlet	DCM, Hexane
48	LC-UVD	C_{18}	Benzo(b)fluoranthene	Agitation/ Ultrasonic	DCM
49	GC-FID	DB-5	1-Methylpyrene, 2,2-Binaphtyl, Indeno (1,2,3-cd)fluoranthene	Soxhlet	Toluene
50	GC-MSD	DB-5	Deuteriated IS	Shaking	DCM, MeOH
51	GC-FID	Elite-SMS	---	Agitation	Hexane
52	GC-MSD	HP-5	Deuteriated IS	Saponification	MeOH/KOH, Pentane
53	GC-MSMS	VF-5MS	Deuteriated IS	ASE	Toluene
54	GC-MSD	HP-5MS	Deuteriated IS	Agitation	Acetone, Pet. ether

"---" denotes data/information was not given
"DCM" denotes dichloromethane; "EtAc" denotes ethyl acetate; "MeOH" denotes methanol

TABLE IX: Other Technical Information

Lab Code	Cleanup Method	% Recovery	Correction for Recovery	Method Accredited
1	None	102.3-128.6	No	Yes
2	Silica Gel, Na_2SO_4	62.2-94.5	No	Yes
3	Silica Gel (US EPA 3630C)	91.8-113.2	Yes	No
4	---	80	No	No
5	---	---	No	Yes
6	SPE (Silicagel)	91	No	Yes
7	---	90-106	No	Yes
8	Water displacement	71-101	No	Yes
9	---	95-102	No	No
10	SPE (XAD-2)	90-100	No	Yes
11	---	75-120	No	Yes
12	---	96.7-104.2	No	No
13	Silica gel	---	No	No
14	---	87.9-114	No	Yes
15	---	---	No	Yes
16	No	87	Yes	Yes
17	---	92-102	Yes	Yes
18	No	89	Yes	Yes
19	Silica gel, Cu powder (US EPA 3630B,C)	70.0-100.5	No	Yes
20	Na_2SO_4	60	Yes	Yes
21	Silica gel	65-76.6	Yes	No
22	Silica gel	80-120	No	No
23	Cu powder	88-111	No	Yes
24	Florisil	70	Yes	Yes
25	Florisil	79-86	No	Yes
26	Silica gel	70	No	Yes
27	---	90-110	No	Yes
28	---	90-110	No	Yes
29	Activated silica, Al_2O_3, Na_2SO_4	108	Yes	No
30	---	95	No	No
31	---	99	-	Yes
32	---	82-148	Yes	Yes
33	Florisil	70-90	Yes	Yes
34	---	84-117	No	Yes
35	---	97.8	No	Yes
36	---	110	No	Yes
37	Silica SPE	---	No	Yes
38	Sodium pyrophosphate, Na_2SO_4	96-110	No	Yes
39	---	---	No	Yes
40	---	91-111	No	Yes
41	Neutral Alumina/Silica gel/Na_2SiO_3	---	No	Yes
42	---	85-92	No	Yes
43	---	---	Yes	No
44	Silica gel SPE	78-89	No	Yes
45	Alumina and silica column	81-109	Yes	Yes
46	---	99	No	Yes
47	---	90	No	No
48	Aluminium oxide 60	85	No	No
49	Silica sel column	85.7	No	No
50	Alumina column	50-150	No	Yes
51	In-house	75.5-89.3	Yes	No
52	Silica column	---	No	Yes
53	---	70-90	No	No
54	Silica gel	100.6	Yes	No

TABLE X: *z*-Scores of Participants

Lab Code	*z*-Score				
	PHE	**FLT**	**BAA**	**BAP**	**BGP**
1	**-4.2**	**-3.5**	**-3.6**	-1.5	**-3.0**
2	-1.8	-2.1	-0.51	-2.1	-2.8
3	-1.6	-1.1	-1.6	-1.3	-1.7
4	**-5.1**	**-4.8**	**-4.7**	**-4.1**	**-5.0**
5	-2.9	-2.9	-2.4	**-4.4**	**-4.3**
6	-2.0	-1.9	-2.5	-2.5	-2.6
7	-0.66	-1.3	-1.1	-2.1	-2.6
8	-1.1	-0.26	-0.27	-0.69	-0.97
9	-1.4	-0.43	-1.6	-1.7	-1.6
10	-2.0	-1.7	-1.7	-1.5	-1.5
11	0.25	-1.1	0.87	0.68	-1.4
12	-0.83	-0.38	-0.75	-1.2	-1.4
13	**-3.7**	-2.1	-1.6	-1.7	0.08
14	-0.66	-0.81	-0.49	-0.03	-0.97
15	-0.46	-1.2	-0.37	-2.9	-2.5
16	-0.76	-1.2	-1.3	-1.4	-1.9
17	-1.0	-0.35	-0.79	-0.91	-1.0
18	-0.41	-1.2	-0.82	-0.47	-1.4
19	-1.8	-0.35	-1.0	-0.40	-1.5
20	-2.4	-1.0	-1.4	-2.2	-2.2
21	-2.9	-1.4	-0.86	**3.1**	NA
22	-1.9	**3.4**	**5.2**	-0.45	-0.91
23	**-3.3**	-2.2	-2.2	-2.9	-2.3
24	0.12	0.15	1.3	-1.2	-0.71
25	-2.1	-2.3	-1.6	-2.5	-2.9
26	**-8.4**	-1.8	-2.2	-1.9	-1.2
27	-2.4	-2.3	-2.3	-1.9	-2.0
28	-0.81	-0.57	0.10	-1.0	-1.1
29	-2.3	-2.2	-0.66	1.3	**6.3**
30	-1.5	**-3.2**	-2.6	-1.3	-1.2
31	-0.92	-1.8	2.8	-2.5	-2.4
32	-1.5	-2.2	0.20	0.07	-1.5
33	0.06	-0.68	1.7	-0.97	-1.4
34	-1.5	-1.2	-1.1	-1.5	-1.2
35	-0.72	-0.82	-1.4	-2.5	-2.4
36	0.58	1.4	0.12	-0.07	-0.15
37	-2.2	-1.7	-1.9	-2.4	-1.8
38	-0.72	-0.26	-0.63	-2.3	-2.7
39	**-3.8**	-2.8	-2.9	-2.2	-2.1
40	-0.79	-0.51	-0.39	-1.4	0.21
41	2.5	**-8.8**	**12**	-2.1	0.51
42	0.06	-0.97	-0.75	-1.7	-0.32
43	-1.8	-1.3	-1.5	-2.7	**-5.2**
44	-2.5	-2.3	-2.2	-2.0	-1.0
45	-0.72	-0.83	-0.48	-0.53	-0.83
46	-1.6	-1.3	-1.6	-1.4	-1.1
47	**-4.5**	**-4.2**	**-4.2**	**-5.4**	**-6.0**
48	-1.1	-2.6	-1.2	-1.2	NA
49	**-4.3**	-2.9	-2.3	-2.4	NA
50	-1.6	-1.3	-0.06	0.81	**-3.2**
51	NA	NA	**-4.5**	-1.7	NA
52	-1.1	-0.83	0.99	0.30	0.48
53	2.2	-0.79	-1.3	-1.4	-1.5
54	-2.3	-1.6	-1.6	-1.1	**-5.3**

i. "NA" denotes not applicable
ii. *z*-Scores ≥ 3 or ≤ -3 are bolded

CHART I: z-Scores of Participants' for PHE

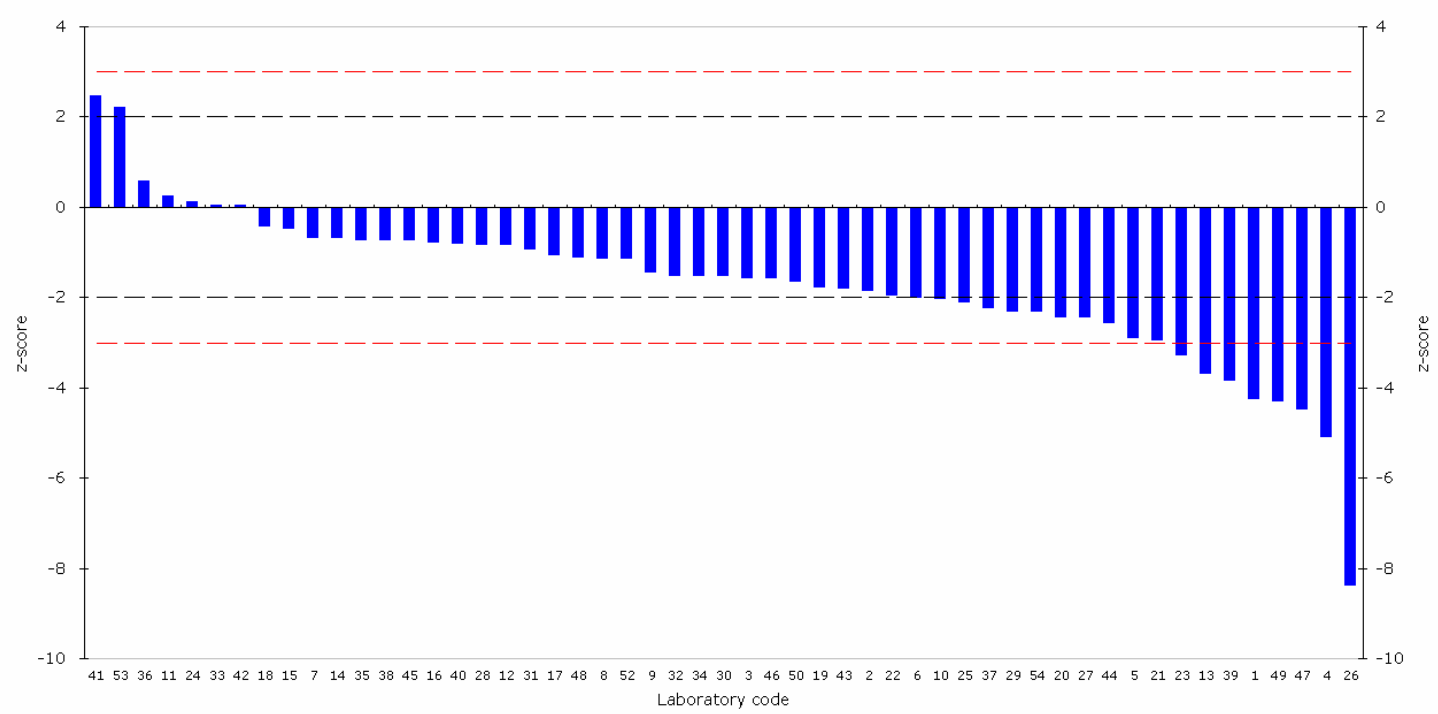


CHART II: *z*-Scores of Participants' for FLT

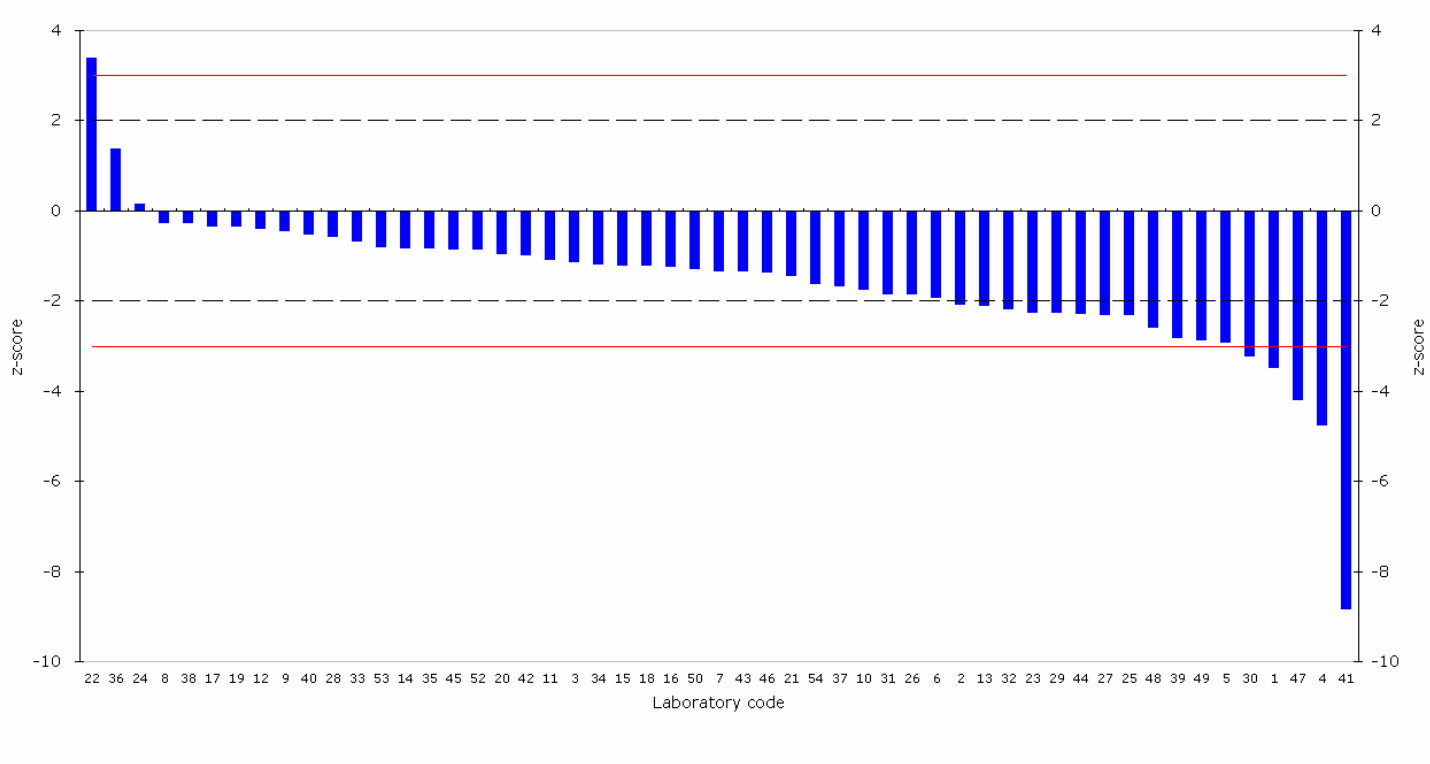


CHART III: *z*-Scores of Participants' for BAA

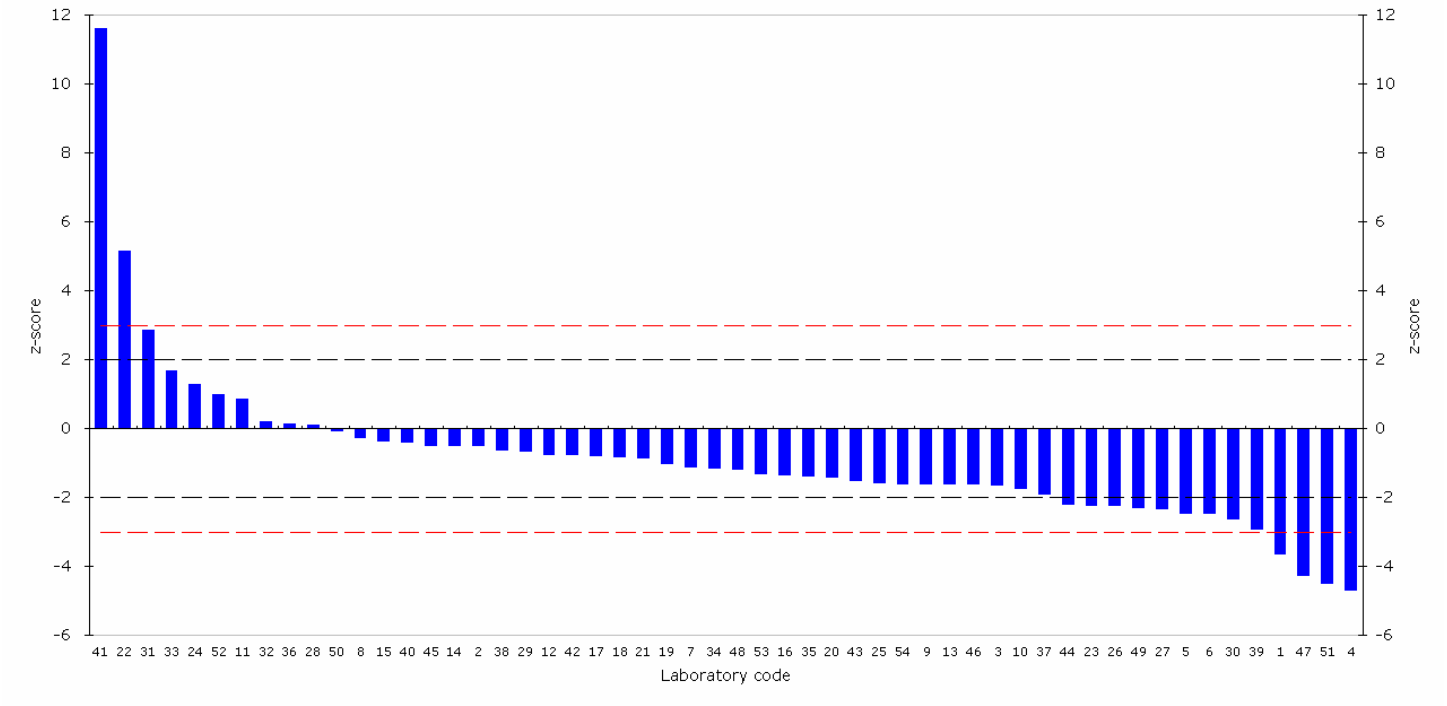


CHART IV: z-Scores of Participants' for BAP

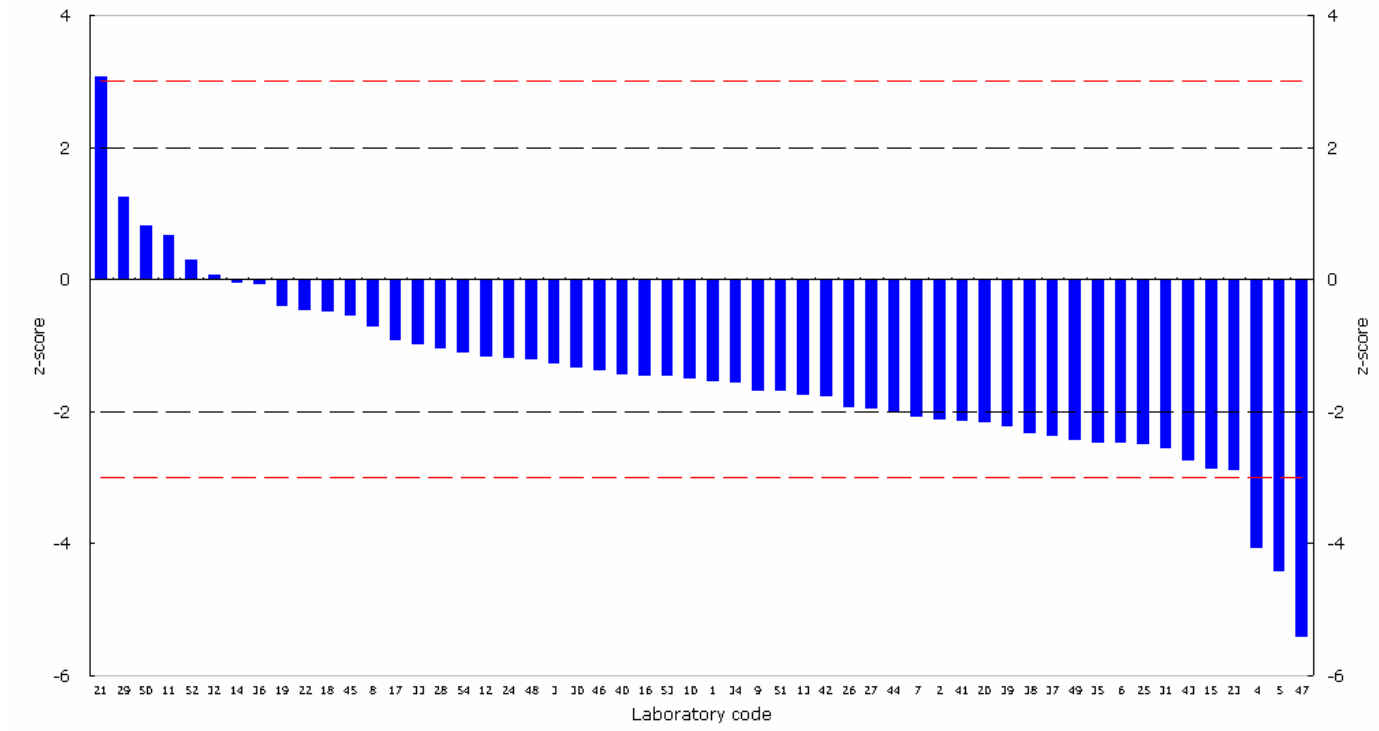
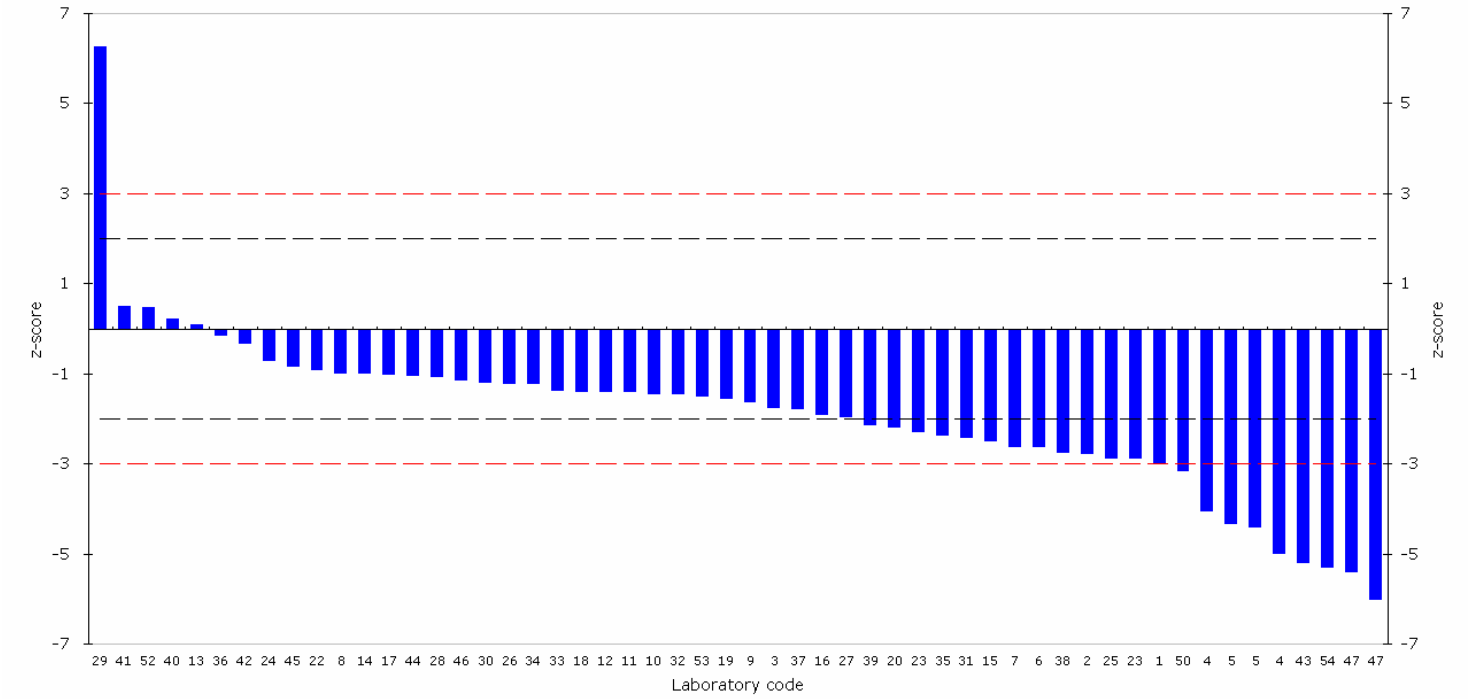


CHART V: z-Scores of Participants' for BGP



APPENDIX I: Homogeneity Test

a. A total of 12 bottles of powder were randomly selected from the bulk. Two test portions (sub-samples) of 1.0 g each taken from each bottle were carried out duplicate analysis for PHE, FLT, BAA, BAP and BGP in August 2008 using GC-MS with ultrasonic extraction.

b. 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
7	10.54	10.30	7.82	7.89	6.21	6.23	3.54	3.59	4.42	4.41
45	10.53	10.35	7.69	7.66	6.08	6.16	3.49	3.50	4.39	4.40
89	9.87	10.50	7.31	7.71	5.84	6.25	3.32	3.46	4.15	4.35
115	10.50	10.46	7.84	7.89	6.08	6.28	3.51	3.50	4.47	4.40
149	10.12	9.98	7.82	7.79	6.13	5.89	3.40	3.38	4.44	4.30
177	9.90	10.38	7.43	7.56	5.96	5.93	3.46	3.52	4.13	4.30
205	10.31	10.13	7.55	7.47	5.95	6.01	3.44	3.42	4.34	4.30
239	9.97	10.05	8.00	7.53	6.29	6.04	3.45	3.40	4.21	4.28
269	10.07	10.21	7.48	7.70	5.93	6.19	3.48	3.41	4.25	4.26
316	10.29	10.03	7.92	7.78	6.12	6.18	3.49	3.55	4.23	4.25
342	9.94	9.75	7.63	7.23	6.03	5.73	3.44	3.24	4.27	4.00
389	10.12	9.78	7.52	7.62	5.91	6.05	3.52	3.46	4.20	4.05
Mean($\bar{x}$)	10.17		7.66		6.06		3.46		4.28	
SD (S_x)	0.24		0.20		0.15		0.08		0.12	
RSD(%)	2.39		2.59		2.46		2.19		2.83	

c. According to ISO13528:2005, the samples may be considered to be adequately homogeneous if:

$$S_s \leq 0.3\sigma_R$$

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

σ_R (in percent) is estimated using Horwitz equation of $2\ c^{-0.15}$ where c was the mean concentration of analyte from homogeneity test:

PAH	$\bar{x}$ (mg/kg)	σ_R (%)	$0.3\sigma_R$ (%)	$0.3\sigma_R$ (mg/kg)
PHE	10.17	11.2	3.37	0.343
FLT	7.66	11.7	3.51	0.269
BAA	6.06	12.1	3.64	0.221
BAP	3.46	13.2	3.96	0.137
BGP	4.28	12.8	3.83	0.164

APPENDIX I: Homogeneity Test (Cont'd)

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

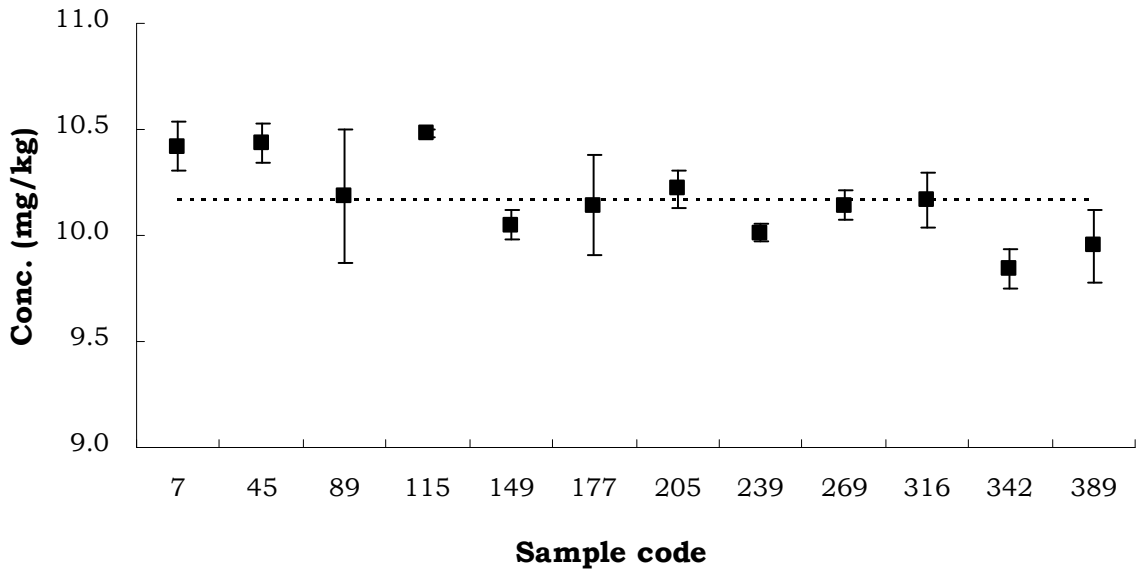
The results are summarized as follows:

PAH	n	Σw_t^2 (mg/kg)	S_w (mg/kg)	S_x (mg/kg)	S_s (mg/kg)
PHE	12	1.0075	0.0766	0.2428	0.2367
FLT	12	0.6563	0.1811	0.0393	0.1513
BAA	12	0.5244	0.1619	0.0222	0.0954
BAP	12	0.0787	0.0627	0.0758	0.0615
BGP	12	0.1961	0.0990	0.1212	0.0989

Since the between-samples standard deviations (S_s) from the homogeneity test for PHE, FLT, BAA, BAP and BGP are less than their corresponding $0.3\sigma_R$, the materials are homogeneous.

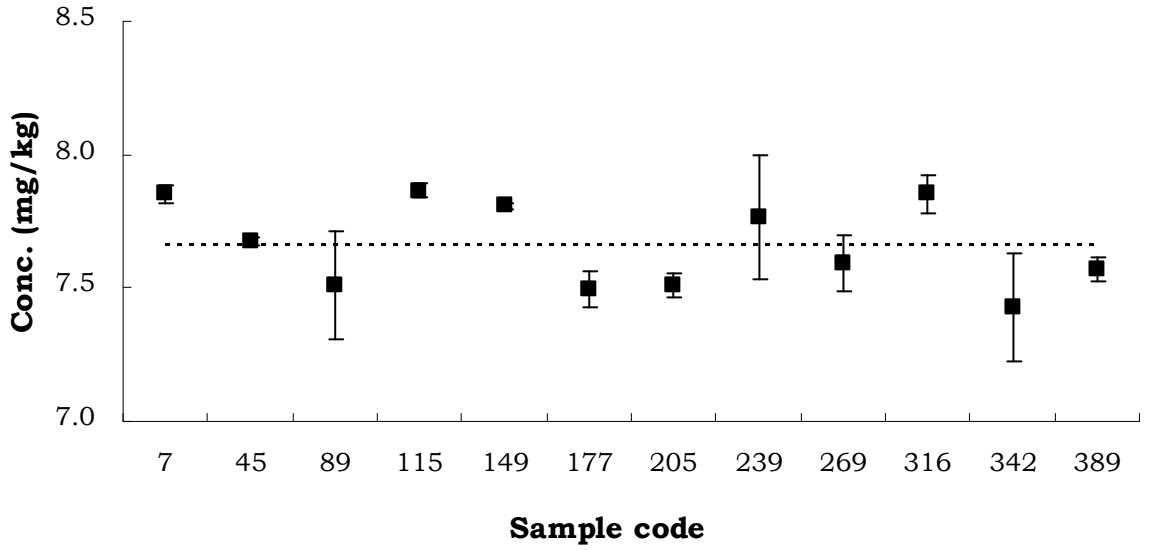
e. Graphical illustrations of random samples in the homogeneity test

(i) PHE

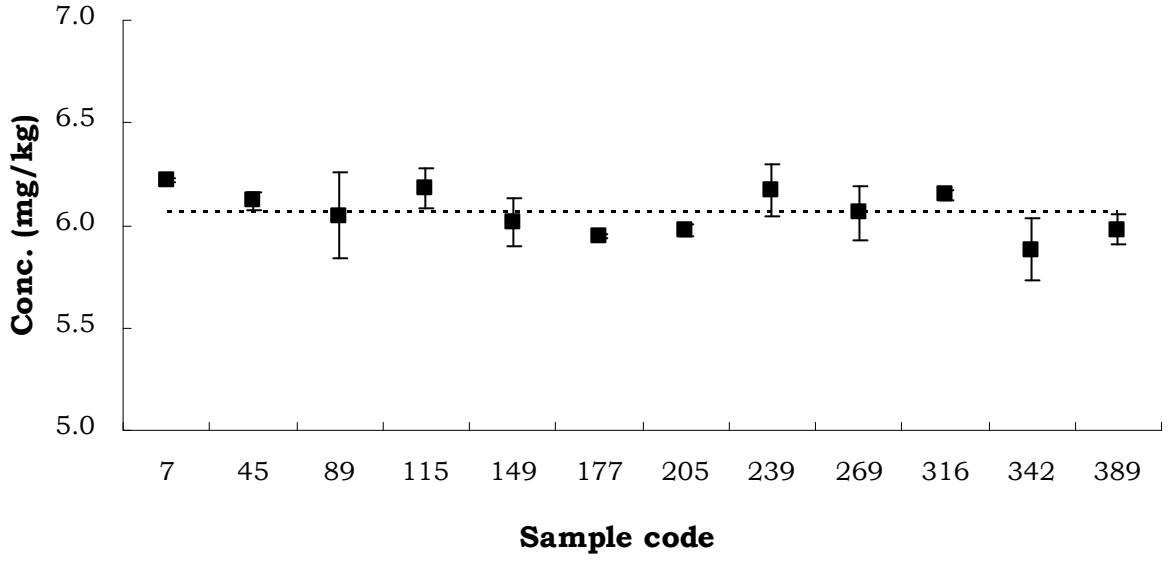


APPENDIX I: Homogeneity Test (Cont'd)

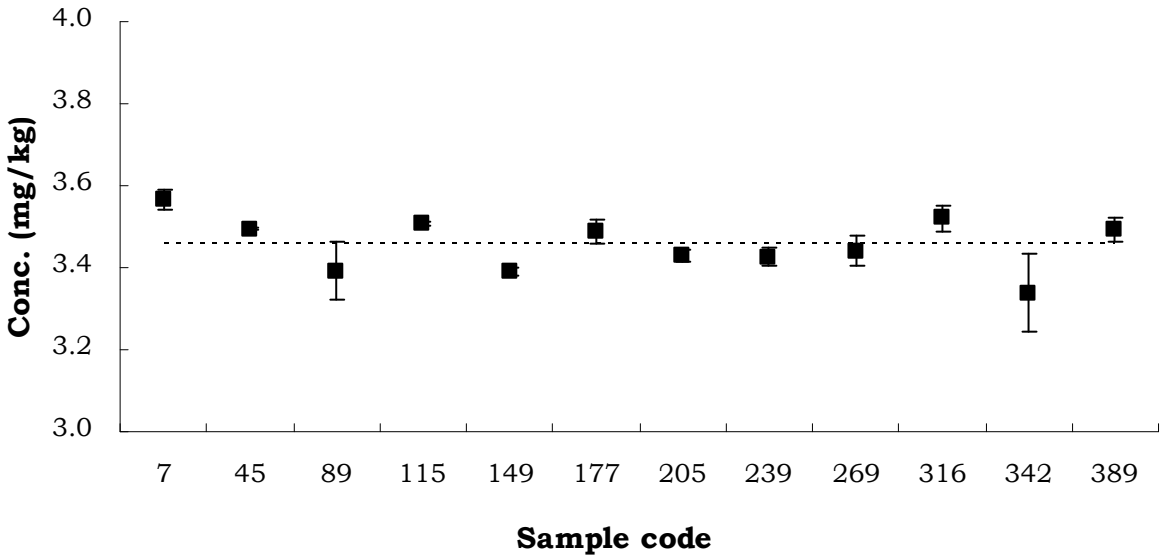
(ii) FLT



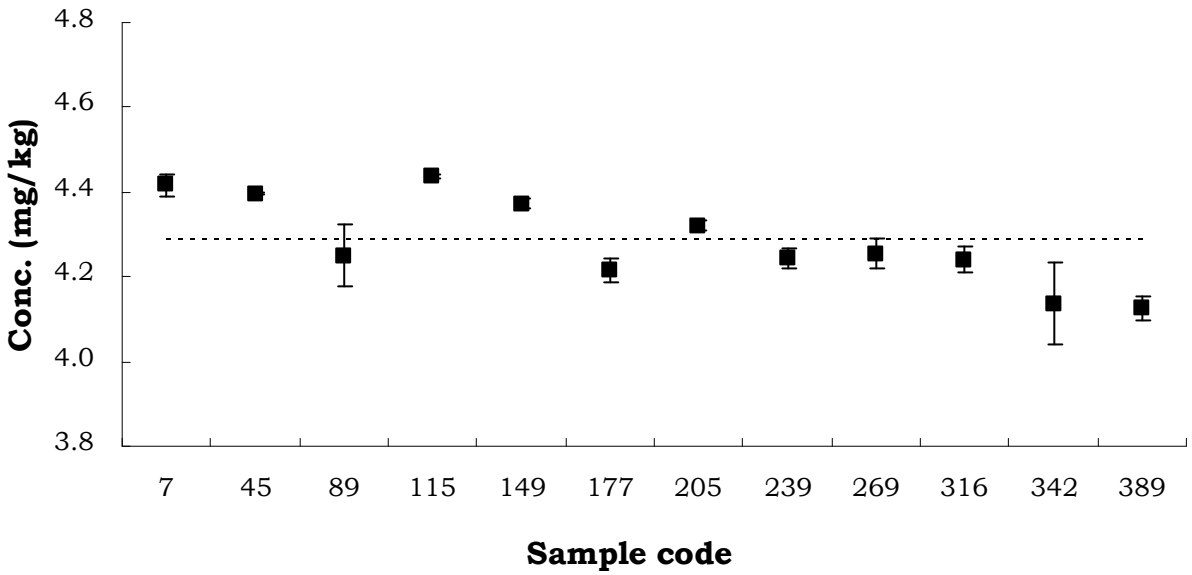
(iii) BAA



(iv) BAP


4.0
3.8
3.6
3.4
3.2
3.0
Conc. (mg/kg)
7
45
89
115
149
177
205
239
269
316
342
389
Sample code

(v) BGP


4.8
4.6
4.4
4.2
4.0
3.8
Conc. (mg/kg)
7
45
89
115
149
177
205
239
269
316
342
389
Sample code

APPENDIX II: Stability Test

a. Stability of the PHE, FLT, BAA, BAP and BGP was monitored in September 2008 and March 2009.

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 evaluated from the absolute difference between the mean value obtained in homogeneity test ($\bar{x}$) and the mean value ($\bar{yi}$) of each stability test. According to ISO13528:2005, the absolute difference should not be more than 30% of the standard deviation of the proficiency test (σ_R).

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

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 2008:	PHE	10.39	10.25	10.32	10.32	10.17	0.15	0.34	Pass
(61)	FLT	7.88	8.03	7.81	7.91	7.66	0.25	0.27	Pass
	BAA	6.45	6.34	6.03	6.27	6.06	0.21	0.22	Pass
	BAP	3.46	3.43	3.35	3.41	3.46	0.05	0.14	Pass
	BAG	4.29	4.22	4.21	4.24	4.28	0.04	0.16	Pass
Mar 2009:	PHE	10.44	10.34	10.58	10.46	10.17	0.29	0.34	Pass
(130)	FLT	7.82	8.05	7.88	7.92	7.66	0.26	0.27	Pass
	BAA	6.24	6.32	6.13	6.23	6.06	0.17	0.22	Pass
	BAP	3.56	3.62	3.58	3.58	3.46	0.12	0.14	Pass
	BAG	4.49	4.37	4.31	4.39	4.28	0.11	0.16	Pass

APPENDIX II: 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 2008:	PHE	10.31	10.22	10.01	10.18	10.17	0.01	0.34	Pass
(128)	FLT	7.33	7.42	7.43	7.40	7.66	0.26	0.27	Pass
	BAA	6.00	5.90	5.93	5.94	6.06	0.12	0.22	Pass
	BAP	3.12	3.40	3.43	3.32	3.46	0.04	0.14	Pass
	BAG	4.33	4.01	4.03	4.12	4.28	0.16	0.16	Pass
Mar 2009:	PHE	10.77	10.34	10.08	10.40	10.17	0.23	0.34	Pass
(383)	FLT	7.45	7.34	7.38	7.39	7.66	0.27	0.27	Pass
	BAA	5.94	5.76	5.96	5.89	6.06	0.17	0.22	Pass
	BAP	1.89	1.90	1.89	1.90	3.46	1.56	0.14	Fail
	BAG	4.29	4.45	4.31	4.35	4.28	0.07	0.16	Pass

f. Results showed that about 45% loss of BaP in Sample 383 at 37°C. However, the organizers considered that, with the support from the Materials Safety Data Sheet (MSDS) and literature information[8.8], the chemical should be fairly stable after the 6-month storage at that temperature. The loss was probably due to some unknown factors that might arise from during the analysis instead of chemical instability.

g Apart from item (f), the stability of the five PAHs is found to be satisfactory and the materials are suitable to be used in the PT program.

APPENDIX III: Results of PAHs by Soxhlet Extraction

(i) at 25°C (Sample code 155)

PAH	Concentration (mg/kg)			Relative % difference (from sample code 61)
	#1	#2	Average	
PHE	13.61	14.01	13.81	28.9
FLT	10.22	10.21	10.22	25.5
BAA	8.16	8.40	8.28	27.6
BAP	4.14	4.33	4.23	21.5
BGP	5.55	6.17	5.86	31.2

(ii) at 37°C (Sample code 326)

PAH	Concentration (mg/kg)			Relative % difference (from sample code 130)
	#1	#2	Average	
PHE	13.50	13.38	13.44	24.9
FLT	10.07	10.16	10.11	24.3
BAA	7.98	8.05	8.01	24.2
BAP	4.12	3.99	4.06	12.6
BGP	5.44	5.50	5.47	21.9

APPENDIX IV: Instructions to Accreditation Bodies

INSTRUCTIONS
(FOR ACCREDITATION BODIES)

1. ORGANIZATION

The PT program on "Polycyclic aromatic hydrocarbons (PAH) in sediment (APLAC T068)" is organized by the Hong Kong Government Laboratory (HKGL) in collaboration with Hong Kong Accreditation Service (HKAS) under the auspices of the Asia-Pacific Laboratory Accreditation Cooperation (APLAC). The main objective of the program is to evaluate the performance of participating laboratories on the concerned tests through inter-laboratory comparison.

2. 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 15g of dried sediment (≤ 250 μm) 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 HKGL by returning the "Receipt Form (for Accreditation Bodies)" electronically to T68@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 HKGL by returning the "Receipt Form (for Participating Laboratories)" electronically to T68@govtlab.gov.hk.

1. RESULTS

AB shall inform their respective participating laboratories complete Part I and II of the "Result Proforma" and submit electronically to the HKGL on or before **31 January 2009** to T68@govtlab.gov.hk. (Notes: 1. Unless with special reasons, results submitted after the deadline might not be accepted by the organizers. 2. To avoid poor transmission quality, results by fax are not accepted.)

2. ENQUIRIES

Please contact the HKGL for further enquiries at T68@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
The PT Advisory Board
HKGL,
Hong Kong.

Email: T68@govtlab.gov.hk

I hereby acknowledge the receipt of _____ # sample(s) for the APLAC T068 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. ORGANIZATION

The PT program on "Polycyclic aromatic hydrocarbons (PAH) in sediment (APLAC T068)" is organized by the Hong Kong Government Laboratory (HKGL) in collaboration with Hong Kong Accreditation Service (HKAS) under the auspices of the Asia-Pacific Laboratory Accreditation Cooperation (APLAC). The main objective of the program is to evaluate the performance of participating laboratories on the concerned tests through inter-laboratory comparison.

2. SAMPLE

(a) Participating laboratories will be given an amber sample bottle that containing about 15 g of dried sediment powder (≤ 250 μm) 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 HKGL to T68@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.

3. ANALYSIS

(a) Participating laboratories are required to determine the concentration (in **mg/kg**) of five PAH: Phenanthrene (PHE), fluoranthene (FLT), benzo(a)anthrancene (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 15 mg/kg. Determination should be conducted in triplicate.

(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.

4. RESULTS

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

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

APPENDIX VI: Instruction to Participating Laboratories (Cont'd)

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

(d) Submit the results electronically to the HKGL on or before **31 January 2009** to T68@govtlab.gov.hk using the soft copy of the "Result Proforma" provided. (Notes: 1. Unless with special reasons, results submitted after the deadline might not be accepted by the organizers. 2. To avoid poor transmission quality, results by fax are not accepted.)

5. ENQURIES

Please contact the HKGL at T68@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
The PT Advisory Board
Hong Kong Government
Laboratory,
Hong Kong.

Email: T68@govtlab.gov.hk

I hereby acknowledge the receipt of ONE sample for the APLAC T068 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

RESULTS PROFORMA

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

Name of Participating Laboratory: _____

_____

Contact Person / Email: _____

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)
PHE						
FLT						
BAA						
BAP						
BGP						

PHE: Phenanthrene, FLT: fluoranthene, BAA: benzo(a)anthrancene, BAP: benzo(a)pyrene (BAP) and BGP: benzo(ghi)perylene (BGP)

Note: Please fill in **<LOQ** for "less than limit of quantification"; **ND** for "not tested"

§ Report values to 3 significant figures or 3 decimal places, whichever is appropriate

‣ **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**

◆ Please submit this "Result Proforma" electronically to the HKGL at T68@govtlab.gov.hk

To be continued …

Part II: Method Information

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

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

3. (i) Mobile phase(s):
or Carrier gas
(ii) Flowrate

4. Internal standard(s)

5. Extraction solvent(s):

6. *Extraction technique: Liq-liq ext. (*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. Other additional information:

* Please circle as appropriate