



Preliminary results for CCQM-K184/P235 :

PAHs in sediment

Track A environmental key comparison:

Low-polar Analytes in Abiotic Matrix: PAHs in Sediment

NIM CHINA

October 24, 2024



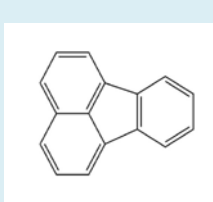
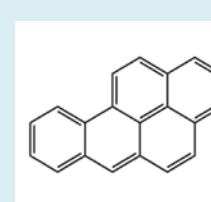
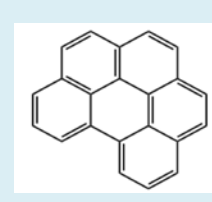
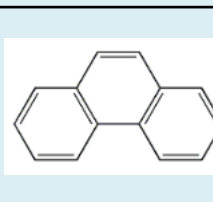
Outline

- ✓ **The Progress of CCQM-K184/P235.**
- ✓ **Summary and analysis of reported results for CCQM-K184/P235.**
- ✓ **Discussion meeting on October 16, 2024.**



The Progress of CCQM-K184/P235

- **CCQM-K184/P235 PAHs in sediment.**
 - ▶ **Matrix: River sediment**
 - ▶ **Measurands: 4 PAHs**
 - **Fluoranthene, Benzo[a]pyrene, Benzo[ghi]perylene.**
 - **Optional analyte: Phenanthrene** (volatility and lower molecular PAHs).
 - ▶ **Mass fraction rang of 3 PAHs: 400- 4000 µg/kg**

Fluoranthene		Benzo[a]pyrene		Benzo[ghi]perylene		Phenanthrene	
CAS	206-44-0	CAS	50-32-8	CAS	206-44-0	CAS	85-01-8
Molecular formula	$C_{16}H_{10}$	Molecular formula	$C_{20}H_{12}$	Molecular formula	$C_{22}H_{12}$	Molecular formula	$C_{14}H_{10}$
M_W	202.25	M_W	252.31	M_W	276.33	M_W	178.23
pK_{ow}	-5.16	pK_{ow}	-6.13	pK_{ow}	-6.63	pK_{ow}	-4.46
Structure		Structure		Structure		Structure	



How far does the light shine

- ✓ The analyte (PAHs) : **Low-polarity ($pK_{ow} < -2$).**
- ✓ Matrix type: **Abiotic dried Matrix.**
- ✓ Molecular mass: **170g/mol to 500g/mol.**
- ✓ Mass fraction range: **100 $\mu\text{g}/\text{kg}$ to 1000000 $\mu\text{g}/\text{kg}$.**



Sample Description

- ▶▶ Sample: PAHs in river sediment.
- ▶▶ Mass-fraction : (400 ~ 4000 $\mu\text{g}/\text{kg}$) samples.
- ▶▶ Each participant received: **Three** packages of sediment (10 g/pack) ;
- ▶▶ Each participant is requested to determine the mass fractions (in $\mu\text{g}/\text{kg}$) of PAHs: **Phenanthrene (Optional), Fluoranthene, Benzo[a]pyrene, Benzo[ghi]perylene** with their preferred methods.
- ▶▶ The minimum sample intake: 1 g.



Result in Report

- The results for 4 PAHs are reported in $\mu\text{g}/\text{kg}$ on a **dry mass basis**;
- The **standard and expanded uncertainties** with detailed description of the **full uncertainty budget**.
- The reported result will be the **mean value** of 2 sample units.
- A description of the **analytical procedure** (extraction, clean-up, GC-MS column and conditions, quantification approach).
- **Details of purity statement** and/or laboratory assessment for calibration and internal standards.



Timeline of CCQM-K184/P235

2023

Registration

6th Oct. 2023

19 labs registered to participate CCQM-K184/ P235, 17 labs registered for CCQM-K184, 2 labs registered for CCQM-P235.

Sample distribution

31th Oct. 2023

Samples were sent to participants.

3rd Dec. 2023

All registered labs received samples of CCQM-K184/ P235.

2024

Submission of results

30th Jun. 2024

18 labs submitted their results for CCQM-K184 / P235 (17 results for CCQM-K184, 1 result for CCQM-P235), except for NBL-Phil.

Confirmation of results

14th Sept. 2024

Preliminary results summary of CCQM-K184/P235 were sent to participants for confirmation.

8th Oct. 2024

All participating laboratories affirmed the summary of preliminary results of CCQM-K184/P235, and a few proposed alterations.

Discussion of results

16th Oct. 2024

Online discussion of the preliminary results of CCQM-K184/P235.

24th Oct. 2024

OAWG meeting



Reported Results-Moisture

Code	Moisture		
	Bottle 1	Bottle 2	Average
Lab 1	1.90%	1.95%	1.93%
Lab 2	1.76%	1.78%	1.77%
Lab 3	1.96%	1.92%	1.94%
Lab 4	1.90%		1.90%
Lab 5	1.8%	1.9%	1.85%
Lab 6	1.93%	1.97%	1.95%
Lab 7	2.02%	2.08%	2.05%
Lab 8	1.90%	1.94%	1.92%
Lab 9	2.20%	2.21%	2.21%
Lab 10	2.65%	3.09%	2.87%
Lab 11	2.12%	2.11%	2.12%
Lab 12	2.12%	2.29%	2.21%
Lab 13	3.1%	2.8%	2.95%
Lab 14	1.77%	1.78%	1.77%
Lab 15	1.9%	1.9%	1.90%
Lab 16	1.55%	1.36%	1.45%
Lab 17	2.03%	2.23%	2.13%
mean	2.05%		
Median	1.94%		
Lab 18	1.26%	1.19%	1.23%

- The 18 Labs were randomly numbered and represented by Lab+code.
- The 17 labs from Lab1 to Lab17 participated in CCQM-K184.
- Lab 18 participated in CCQM-P235, is not in the results statistics.
- Lab1 provides the results of another extraction method, but is not put into the results statistics.
- The average value of moisture measurement by 17 labs was 1.45%~ 2.95%.



Reported Results-4PAHs

Code	Phenanthrene (optional), µg/kg				Fluoranthene, µg/kg				Benzo[a]pyrene, µg/kg				Benzo[ghi]perylene, µg/kg			
	<i>x</i>	<i>u(x)</i>	<i>k</i>	<i>U(x)</i>	<i>x</i>	<i>u(x)</i>	<i>k</i>	<i>U(x)</i>	<i>x</i>	<i>u(x)</i>	<i>k</i>	<i>U(x)</i>	<i>x</i>	<i>u(x)</i>	<i>k</i>	<i>U(x)</i>
Lab 1	NA	NA	NA	NA	2602	51	2.36	120	728	32	2.78	89	637	25	2.36	59
Lab 2	2255	69	2	138	2297	82	2	164	839	34	2	68	708	27	2	53
Lab 3	2573	50	2.145	106	2130	58	2.138	123	656	41	2.13	87	700	24	2.139	51
Lab 4	885.1	105	2	210	1243	95	2	190	907.3	43.8	2	87.6	619	46.8	2	93.6
Lab 5	2920	111	2	230	2490	105	2	210	776	32	2	64	728	35	2	70
Lab 6	1781	221	2	442	2012	250	2	500	504	64	2	128	444	68	2	136
Lab 7	726.84	54.07	2	108.15	1020.64	32.93	2	65.86	418.57	19.66	2	39.33	357.47	16.2	2	32.4
Lab 8	2437	58	2	115	2238	63	2	126	853	27	2	54	630	23	2	45
Lab 9	2724	111.3	2	223	2419	89.5	2	179	749	22.6	2	45.2	680	23.7	2	47.5
Lab 10	2235	162	2	324	2277	105	2.03	213	NA	NA	NA	NA	474.25	31	2	62
Lab 11	NA	NA	NA	NA	2100	130	2	260	742	88	2	180	742	37	2	74
Lab 12	3010	96.65	2	193	2538	89.95	2	180	882.9	40.51	2	81	673	30.54	2	61.1
Lab 13	2550	91	2.09	190	2300	66	2.12	140	748	28	2.31	64	643	39	2.11	82
Lab 14	1580	108	2	216	1400	110	2	221	427	55	2	111	417	44	2	87
Lab 15	2528	114	2	228	2183	103	2	206	699	33	2	66	665	54	2	108
Lab 16	2562	74	2	149	2172	66	2	133	710	31	2	63	668	26	2	53
Lab 17	NA	NA	NA	NA	2299	68	2	136	531	17	2	34	474	14	2	28
mean	2197.6				2101.2				698.2				603.5			
Median	2483				2238				735				643			
Lab 18	2360	103	2	205	1907	100	2	201	608	77.2	2	154	418	36.3	2	72.7
Lab 1*	NA	NA	NA	2283	43	2.31	100	547	16	2.78	45	495	17	2.78	48	NA

Summary of Key Technologies

- ▶ **Extraction method.**
- ▶ **Clean-up Methods .**
- ▶ **Analytical Techniques & Type of Calibration;**
- ▶ **Source of Traceability**
- ▶ **Moisture determination**



Extraction method-Key Factors

➤ Extraction techniques: 4 extraction techniques.

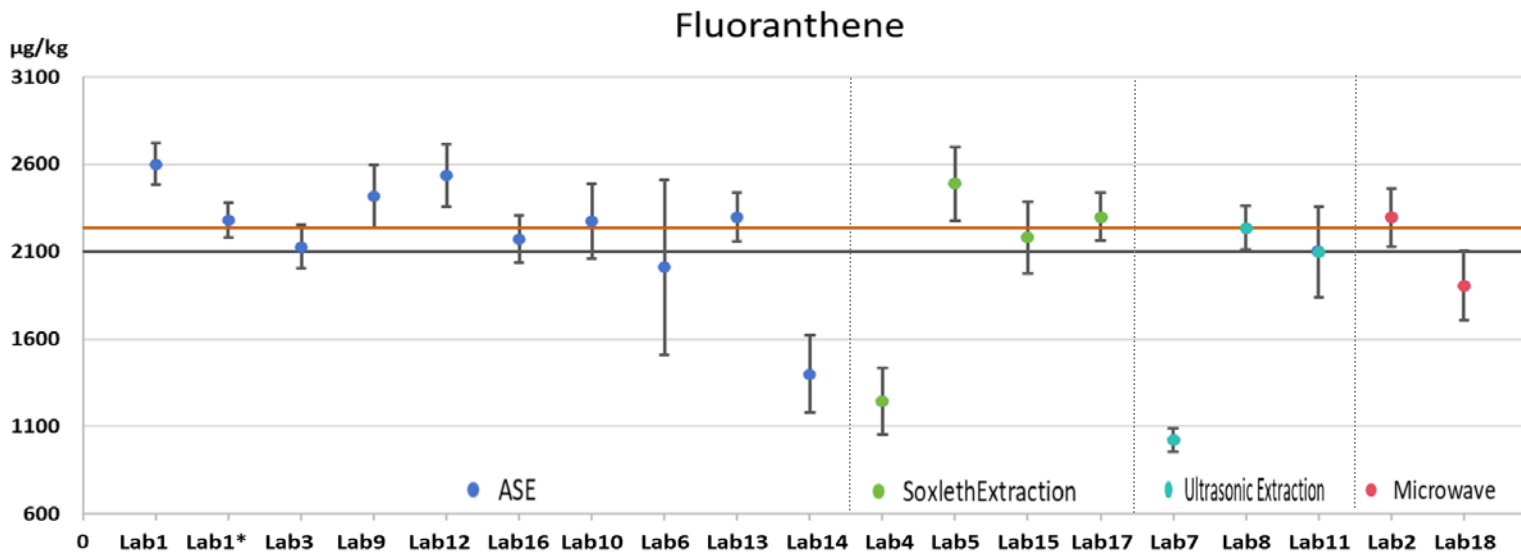
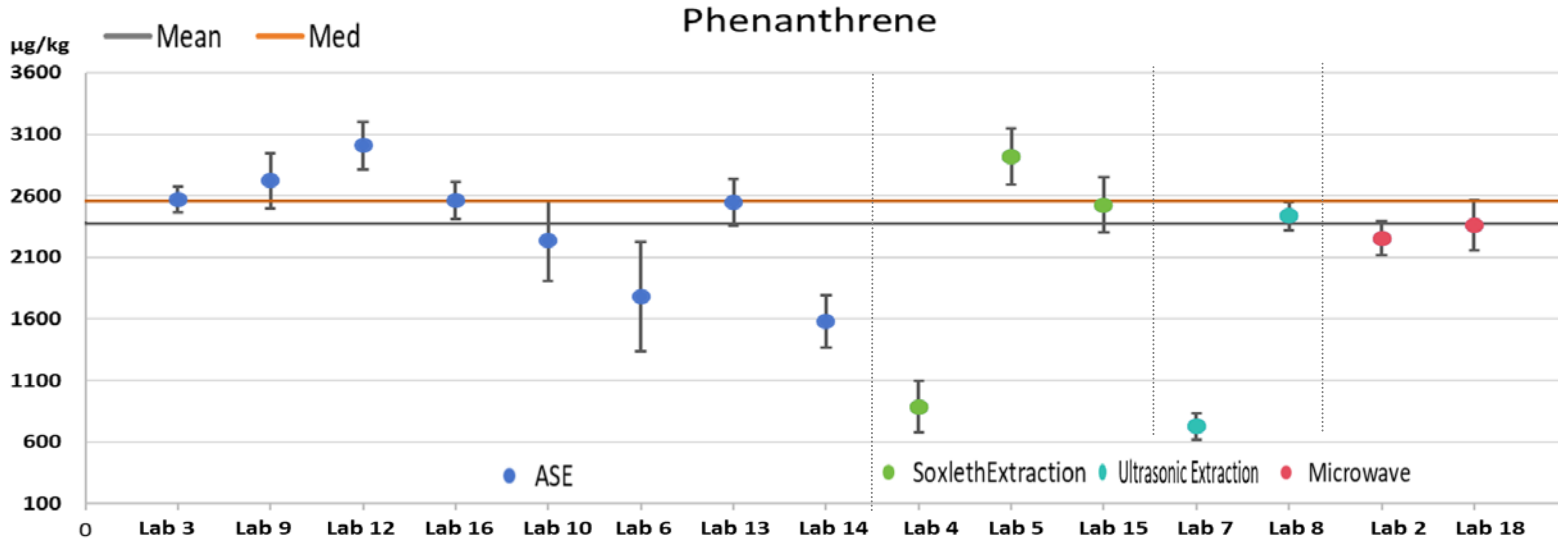
- ◆ ASE - 9 labs;
- ◆ Soxhlet extraction- 4 labs;
- ◆ Ultrasonic extraction- 3 labs;
- ◆ Microwave extraction - 2 lab.

➤ Parameters of Extraction:

- ◆ Type and amount of solvent;
- ◆ Temperature;
- ◆ Extraction cycles;
- ◆ Duration time

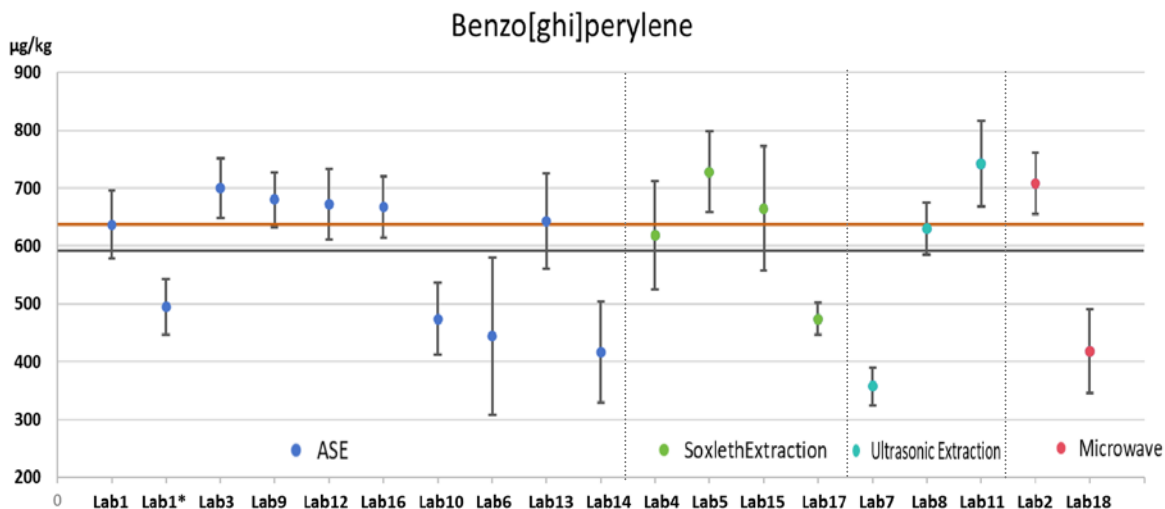
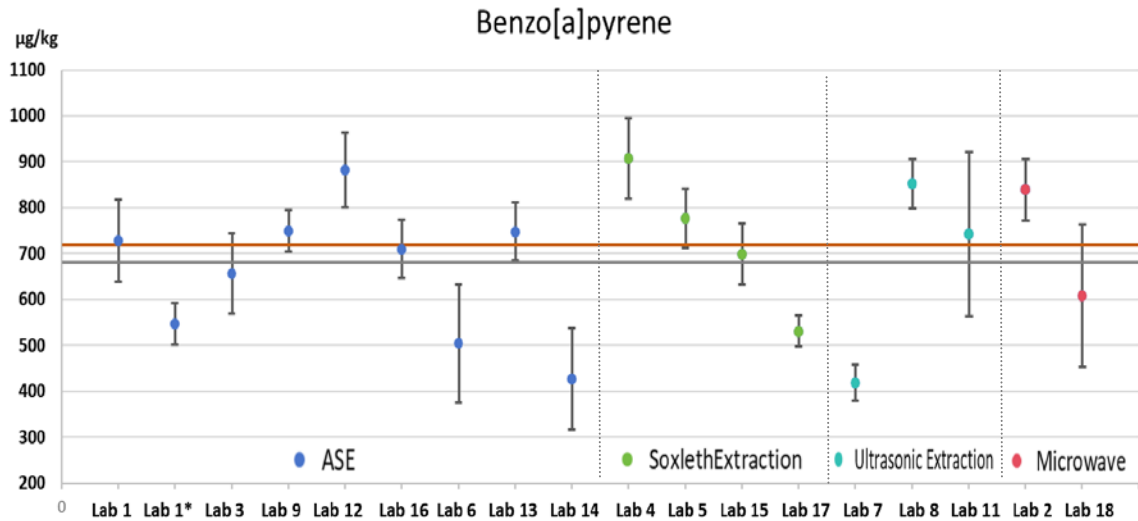


Results of different extraction technique





Results of different extraction methods



► None of the extraction methods demonstrated significant extraction superiority.

► The key parameters in each extraction method may be the decisive factors affecting the extraction efficiency.



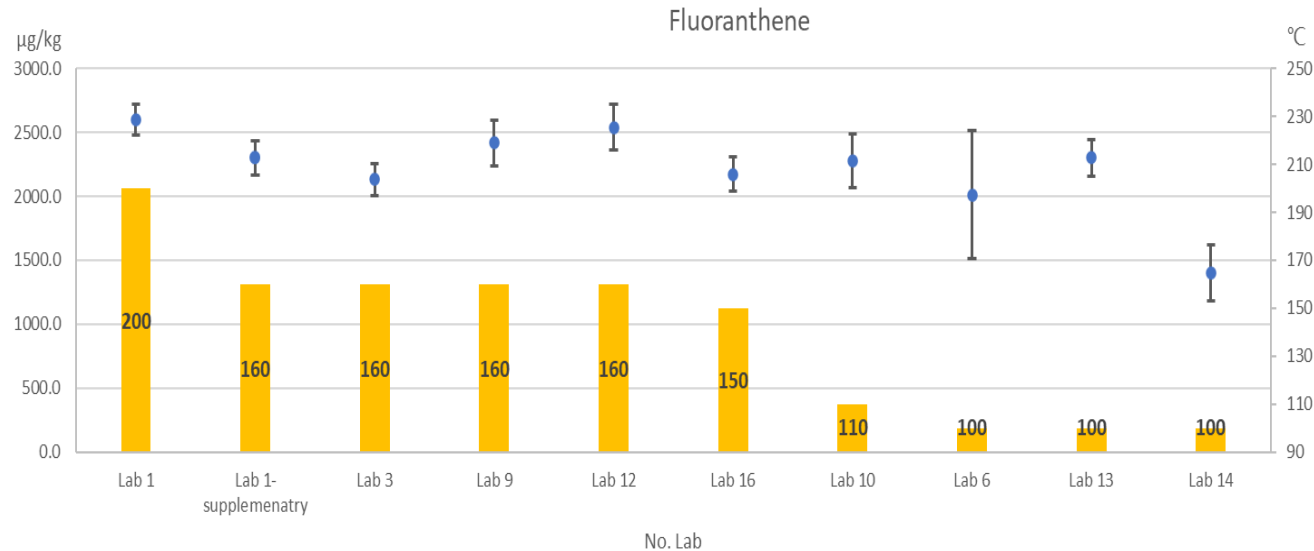
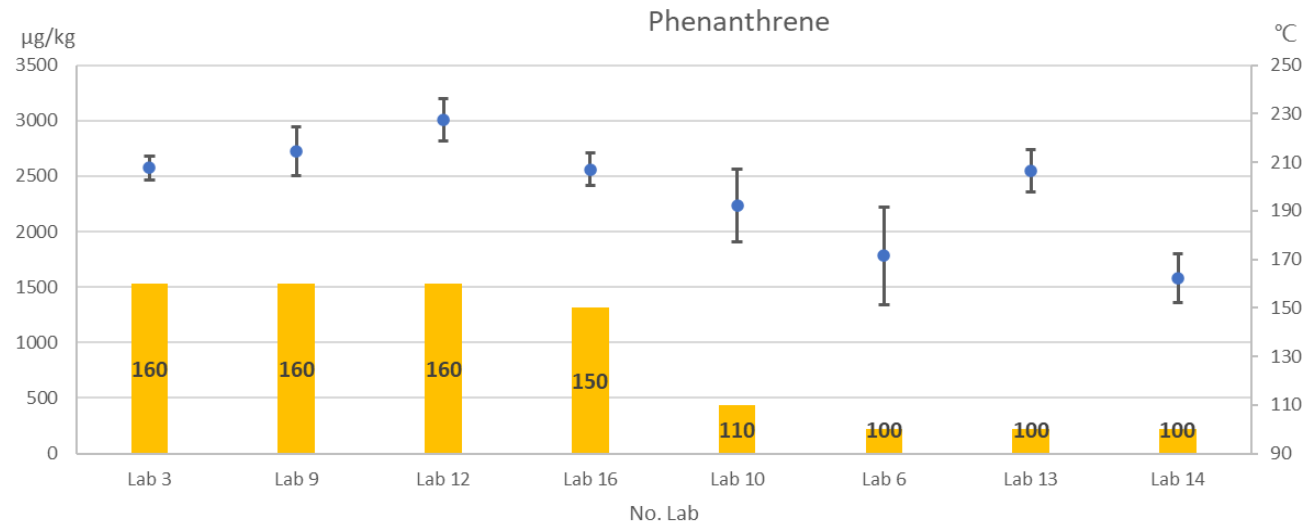
Extraction-ASE extraction

Code	Sample size	Extraction solvent	Temp/°C	Extraction cycles	Extraction time
Lab 1	1 g	Toluene: MeOH (1:1, v:v)	200	2	20 min
Lab 1 supplemenatry	1 g	Acetone/Hexane (1:1, v:v)	160	5	25 min, 5 min
Lab 3	1 g		160	6 cycles, 2 rounds	5 min static,
Lab 6	2 g		100	2	5 min/cycle
Lab 16	1 g	15mL Acetone/n-Hexane (1:1, v:v) for each cycle	150	6	15mL, 3 min/cycle.
Lab 9	1 g	Toluene	160	8	Static time/cycle: 10 min
Lab 12	1 g		160	6	30min
Lab 10	1 g	Acetone/DCM (1:1, v/v)	110	6	15 min for 6 cycles
Lab 14	2 g		100	2	20 time
Lab 13	1 g	2 mL of DCM was added mixed with the sample. Phenanthrene & fluoranthene with DCM: ACN; benzo(a)pyrene & benzo(ghi)perylene with both solvent mixtures (1:1 hexane:acetone & 9:1 DCM: ACN.	100	2	5 min/cycle



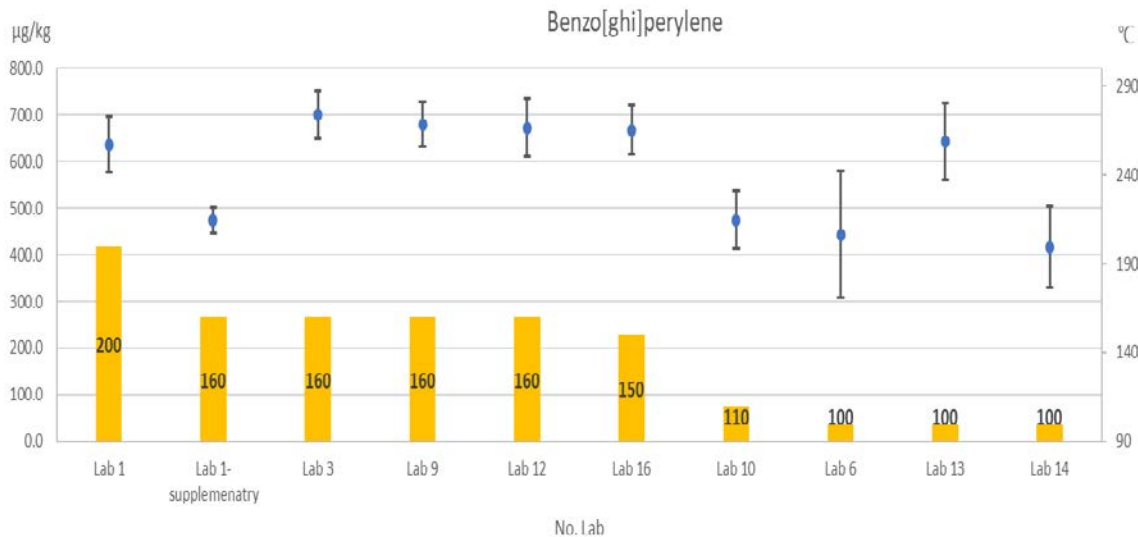
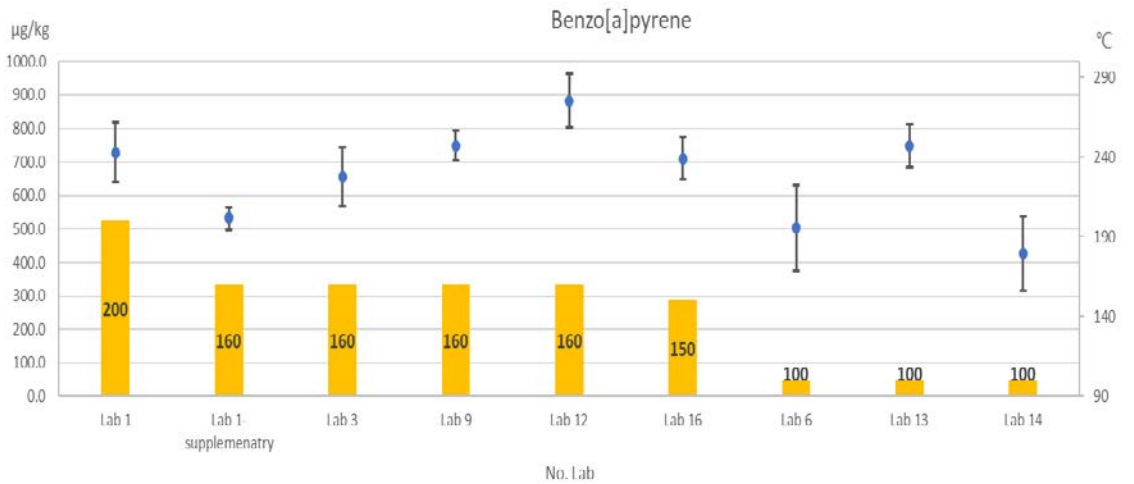
Effect of Temperature of ASE

➤ Results from 9 labs using ASE extraction are listed in order of extraction temperature from highest to lowest.





Extraction-ASE extraction



➤ The overall performance shows that extraction at higher temperatures ($\geq 150^{\circ}\text{C}$) shows higher results.

➤ Lab13 was extracted at 100°C , the results remained stably in the same level range as the results of other higher temp extraction.

➤ Lab13 is mixed sample with DCM before ASE extraction, and extracted with 34mL extraction cell.



Extraction method other than ASE

Code	Extraction method	Sample size	Extraction solvent	Temp/°C	Other key parameters	
					Cycles	Time
Lab 4	Automated Soxleth extraction	1 g	Acetone/Hexane (1:1, v:v)	-	60 cycles	4 hours
Lab 5	Soxhlet extraction	0.5 g	Toluene /Acetone (50/50)	-	-	24 hours
Lab 15	Soxhlet (Buchi b 811)	1 g	Acetone/Hexane (1:1, v:v) (130 mL)	-	-	18 hours
Lab 17	Soxhlet extraction	1 g	250 mL DCM/MeOH (2:1, v/v)	-	-	72 hours
Lab 7	Ultrasonic extraction	2 g	6.8g , n-Hexane: Acetone (1:1, v/v)	-		15 minutes.
Lab 8	Ultrasonic extraction	1 g	25 mL DCM/Hexane (50:50, v:v) each circle	70	4 cycles	20 minutes
Lab 11	Sonication-saponification -liquid/ liquid extraction	1 g	Potassium hydroxide in MeOH, hexane	-	-	-
Lab 2	Microwave	1 g	20 mL Acetone/Hexane (1:1, v:v)	In 3 mins, increase temperature to 110°C (for 15min) , final temperature 45°C	850W and 600rpm	
Lab 18	Microwave	1.2 g	40 mL n-Hexane/ DCM(1:1)	the temperature is programmed to 115 °C in 10 min. and then isothermal at 115 °C for 30 min.	The oven is set at 1200 Watts	



Clean-up Methods

Code	Clean-up method	Sorbent of SPE/ Column purification
Lab 1	SPE	Silica
Lab 4		Silica 1g
Lab 8		Silica 1g , 30:9 m:m Zn/Cu mixture and sodium sulfate (Na ₂ SO ₄)
Lab 9		Silica 1g
Lab 15		Silica 1g
Lab 16		Silica
Lab 18		Si/CN-S 1g/0.5g
Lab 6		Copper for removing sulfur & Column purification
Lab 11	Activated copper granule, silica gel	
Lab 14	Column Chromatography	Silica Gel
Lab 7	d-SPE	900 mg of anhydrous magnesium sulfate, 150 mg of PSA, and 150 mg of C18,
Lab 3, Lab 12, Lab 13	Filtration	-
Lab 2, Lab 5, Lab 10, Lab 17		-

- 11 labs used adsorbents to purify the extracted sample solution.
- 3 Labs used filtration, and 4 Labs have no Clean-up steps.
- Most laboratories use silica gel as the adsorbent in purification, and copper is also used in some laboratories to purify possible sulfur.



Analytical Techniques & Type of Calibration

Code	Analytical Technique	Type of Calibration
Lab 1	GC-IDMS	Single point
Lab 2	GC-IDMS	6 point calibration curve
Lab 3	GC-IDMS	Multipoint calibration
Lab 4	GC-IDMS/MS, GC-IDMS, IS method of HPLC-FLD, IS method of HPLC-DAD	Internal standard, 4-5 points, calibration curve
Lab 5	GC-IDMS/MS	Single point
Lab 6	GC-IDMS	8-point calibration curve
Lab 7	GC-IDMS/MS	Bracketing, Matrix matched calibration
Lab 8	GC-IDMS	Bracketing
Lab 9	GC-IDMS	Single point
Lab 10	GC-IDMS/MS	Single-point, bracketing calibration and 5-7 point calibration curve
Lab 11	GC-IDMS, GC-HR-IDMS	4 point calibration curve and IDMS with bracketing
Lab 12	GC-IDMS	4-10 point calibration curves
Lab 13	GC-IDMS/MS	8 point calibration curve
Lab 14	GC-IDMS/MS	Calibration curve
Lab 15	GC-IDMS	6 point calibration curve
Lab 16	GC-IDMS/MS	9-point calibration
Lab 17	GC-IDMS/MS	Bracketed single point exact matching
Lab 18	GC-IDMS	Single point

- 9 labs adopted GC-IDMS method, Lab 11 also uses an additional GC-HR-IDMS approach.
- 7 labs adopted GC-IDMS/MS method.
- Lab 4 used 4 methods .
- Lab 6 only uses the isotope diluent for Phenanthrene, and the other internal standard is Chrysene-D12, Perylene-D12.



Calibrants and Traceability-Solution CRM

Code	Analyte	Source of Traceability	Producer
Lab 2	4 PAHs	SRM 2260a	NIST
Lab 3	4 PAHs	SRM 2260a	NIST
Lab 5	4 PAHs	SRM 1647f	NIST
Lab 7	4 PAHs	SRM 1647f	NIST
Lab 10	Fluoranthene	GBW(E)080477	NIM
	Phenanthrene, Benzo(ghi)perylene	SRM 1647f	NIST
Lab 11	3 PAHs	GBW 08736	NIM
Lab 12	4 PAHs	SRM 1647f / SRM 2260a	NIST
Lab 13	4 PAHs	SRM 2260a	NIST
Lab 14	4 PAHs	SRM 1647f / SRM 2260a	NIST
Lab 15	4 PAHs	SRM 1647f	NIST
Lab 16	4 PAHs	SRM 1647f	NIST
Lab 17	4 PAHs	SRM 1647f	NIST
Lab 18	4 PAHs	SRM 2260a	NIST

➤ 13 laboratories adopted certified solution reference materials from NIST or NIM.

➤ In addition to GBW(E)080477, the other 3 CRMs used are all multi-PAH CRMs, including not only the 4 PAHs in this comparison.



Calibrants and Traceability - Certified purity PAHs

Code	Analyte	Source of Traceability	Producer	Purities/Concentration and Uncertainties (95% CI)	Purity techniques
Lab 1	Fluoranthene	Lab 1	sigma-aldrich	98.80 ± 0.13 % (k=2.04)	mass- balance
	Benzo[a]pyrene		Supelco	98.76 ± 0.50 % (k=2.05)	
	Benzo[ghi]perylene		Accustandard	97.59 ± 0.35 % (k=2.45)	
Lab 4	Phenanthrene	Lab 4	Aldrich Chem	(992.5 ± 4.4) mg/g	GC-FID with two different columns and water content by Karl Fischer titration
	Fluoranthene		Aldrich Chem	(986.5 ± 3.8) mg/g	
	Benzo[a]pyrene		Supelco	(975.8 ± 4.3) mg/g	
	Benzo[ghi]perylene		Ultra scientific	(989.5 ± 6.4) mg/g	
Lab 8	Phenanthrene	Lab 8	Sigma-Aldrich	(996.0 ± 2.8) mg/g	q-NMR
	Fluoranthene		Sigma-Aldrich	(993.8 ± 1.7) mg/g	
	Benzo[a]pyrene		Dr. Ehrenstorfer GmbH	(971.6 ± 3.8) mg/g	
	Benzo[ghi]perylene		Sigma-Aldrich	(980.1 ± 2.0) mg/g	
Lab 9	Phenanthrene	Lab 9	Supelco	98.9%, urel=0.44%	Mass- balance: HPLC-DAD, GC-FID and moisture content by Karl Fischer titration
	Phenanthrene		Supelco	98.9%, urel=0.45%	
	Benzo[a]pyrene		Cerilliant	99.4%, urel=0.27%	
	Benzo[ghi]perylene		AccuStandard	98.3%, urel=0.23%	

➤ 4 labs used calibration solution made from certified pure products of PAHs.



Calibrants and Traceability

Code	Analyte	Source of Traceability	Producer	Purities/Concentration and Uncertainties (95% CI)	Purity techniques
Lab 6	Phenanthrene	EPA Method 610/8100 PAH Mixture	Dr Ehrenstorfer, Ref ^a DRE- GA09000161BD, Batch 2-H473805NA	(2000 ± 110) µg/mL	-
	Fluoranthene			(2008 ± 100) µg/mL	-
	Benzo[a]pyrene			(1999 ± 130) µg/mL	-
	Benzo[ghi]perylene			(2000 ± 130) µg/mL	-

➤ Lab 6 employed Dr.E's calibration solution and does not conduct purity analysis.



Moisture determination

Code	Moisture	Temperature	Number of subsamples	Sample amount (g)
Lab 1	1.93%	105°C	3	-
Lab 3	1.94%		-	1
Lab 5	1.85%		3	1
Lab 6	1.95%			
Lab 7	2.05%			
Lab 8	1.92%			
Lab 11	2.12%			
Lab 13	2.95%			
Lab 14	1.77%		-	1
Lab 15	1.90%		3	0.5
Lab 16	1.45%		-	-
Lab 18	1.23%		3	1
Lab 9	2.21%	105°C±2°C	-	-
Lab 10	2.87%		3	1
Lab 12	2.21%		-	-
Lab 17	2.13%		-	1
Lab 2	1.77%	105°C±5°C	-	1
Lab 4	1.90%	110°C	-	1

➤ In all laboratories, the moisture content was tested by oven heating method.



Discussion the Preliminary results

CCQM K184/ P235 Track A key comparison:PAHs in Sediment Seminar Agenda

10:00 -13:00 GMT on October 16, 2024

Microsoft Teams

Agenda - Wednesday 16 October 2024

10:00	Welcome – Maria Fernandes-Whaley NMISA																
10:05	<p>1. Introduction of the experiments in CCQM-K184/P235 by participants (5 min for each lab, in the following order)</p> <table border="1"> <tr><td>1.1</td><td>Lab 4</td></tr> <tr><td>1.2</td><td>Lab 11</td></tr> <tr><td>1.3</td><td>Lab 14</td></tr> <tr><td>1.4</td><td>Lab 1</td></tr> <tr><td>1.5</td><td>Lab 16</td></tr> <tr><td>1.6</td><td>Lab 3</td></tr> <tr><td>1.7</td><td>Lab 13</td></tr> <tr><td>1.8</td><td>Lab 6</td></tr> </table>	1.1	Lab 4	1.2	Lab 11	1.3	Lab 14	1.4	Lab 1	1.5	Lab 16	1.6	Lab 3	1.7	Lab 13	1.8	Lab 6
1.1	Lab 4																
1.2	Lab 11																
1.3	Lab 14																
1.4	Lab 1																
1.5	Lab 16																
1.6	Lab 3																
1.7	Lab 13																
1.8	Lab 6																
10:45	2. Preliminary results for CCQM-K184/P35 Track A key comparison: PAHs in sediment – Tang Hua -NIM																
11:10	3. Discussion – All participants																



Discussion Meeting Summary

➤ The main problem discussed:

1. The effect of extraction parameters on extraction efficiency;

◆ Lab 7 only used 6.8g n-Hexane: Acetone to extract 2g sample;

◆ Lab 14 did not perform optimization on extraction efficiency by using standard methods.

2. The validity of the certification techniques for 4 PAHs;

◆ Lab 4 only used one method (GC-FID) to determine the purities of 4 PAHs;

3. Traceability of calibrated substances;

◆ Lab 6 used Dr.E calibrant solution.

4. Whether the comparison results can be selectively withdrawn from the 3 non-selected PAHs when calculating KCRV;

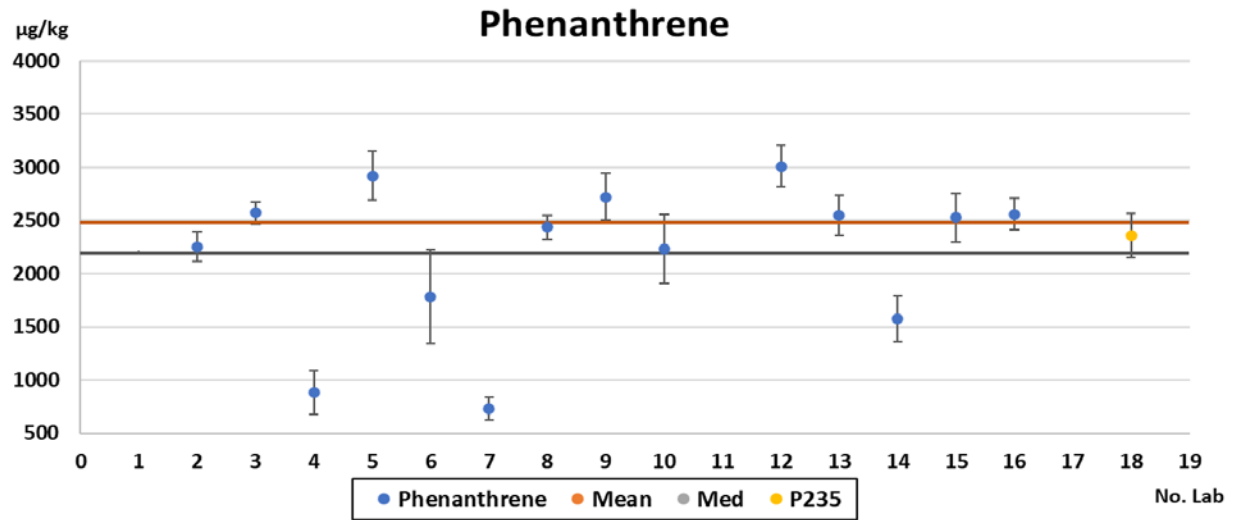
◆ Lab 11 did not submit the results of Bap.

◆ Whether other participating laboratories can selectively withdraw their results.

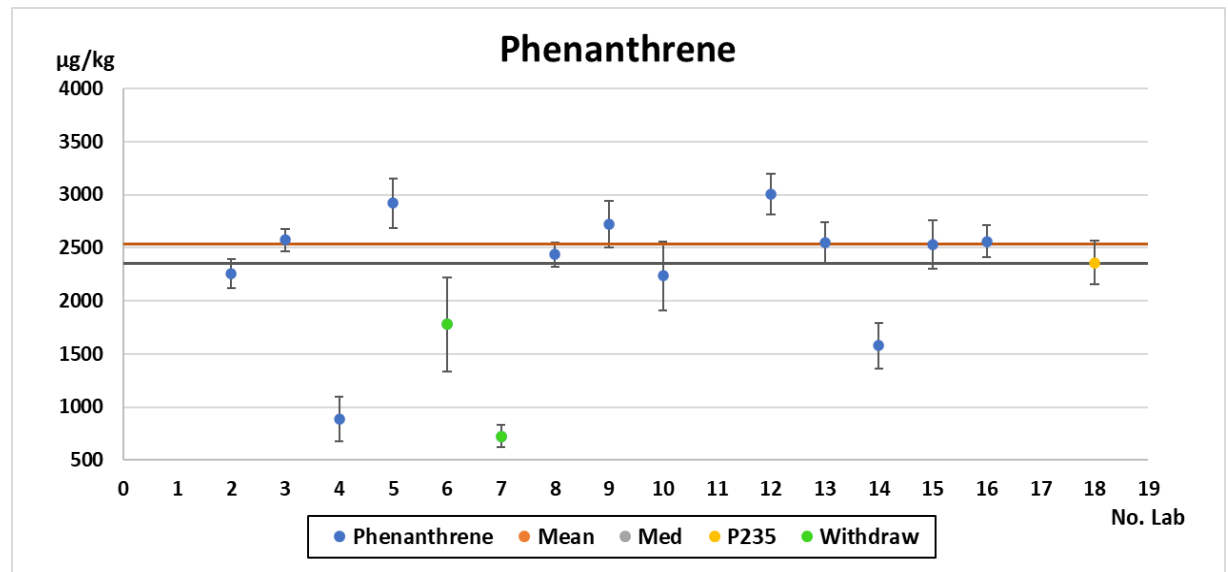


Dot-and-Bar Display of Phenanthrene

Mean and median
from 17 Labs



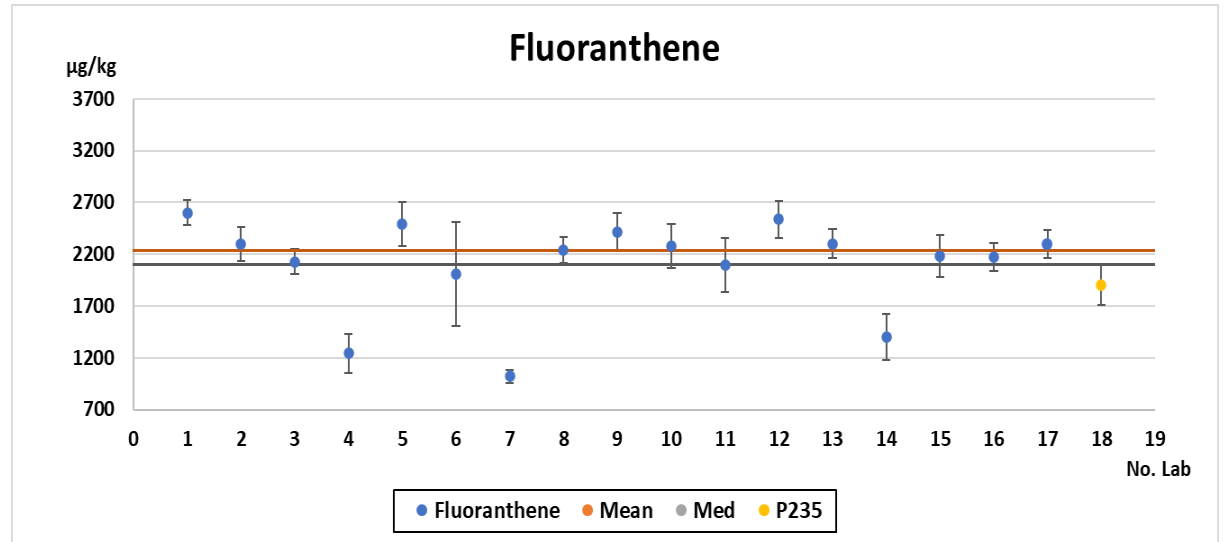
Mean and median
from 15 Labs (
Lab 6 & Lab 7
withdrew their
results).



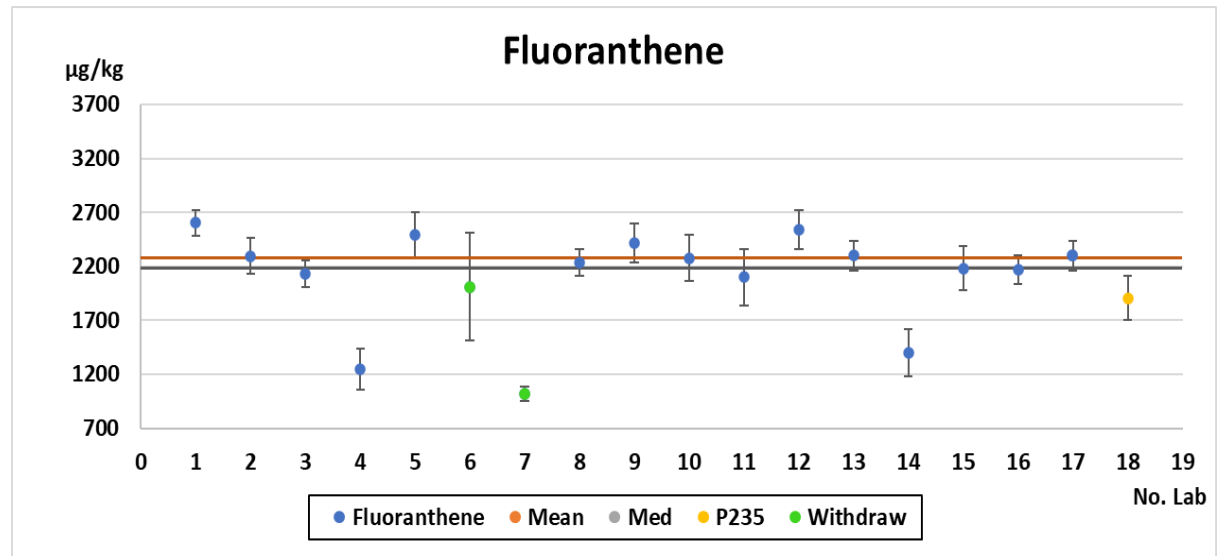


Dot-and-Bar Display of Fluoranthene

Mean and median from 17 Labs



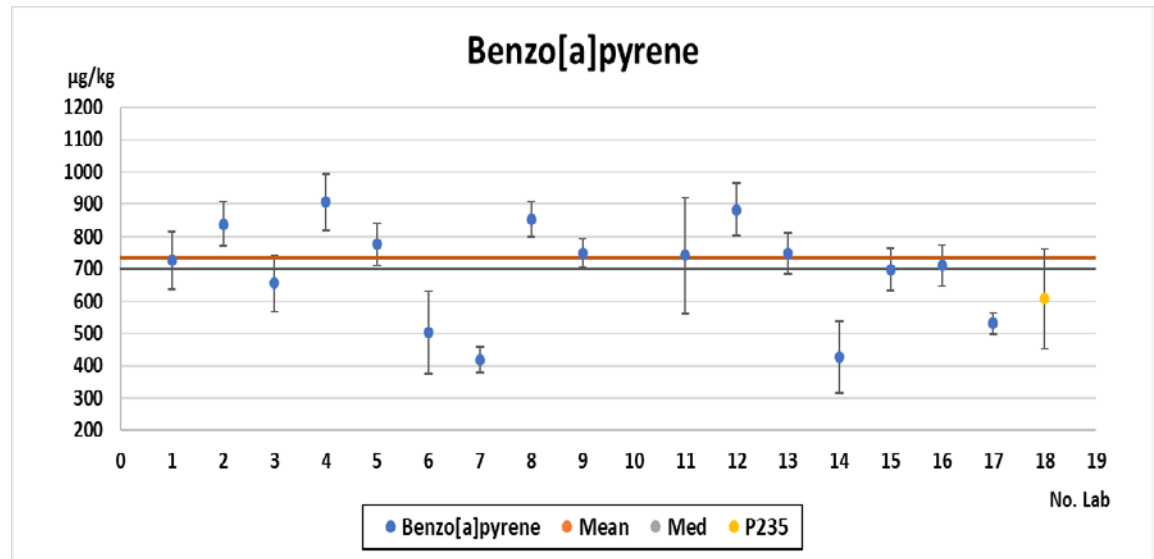
Mean and median from 15 Labs



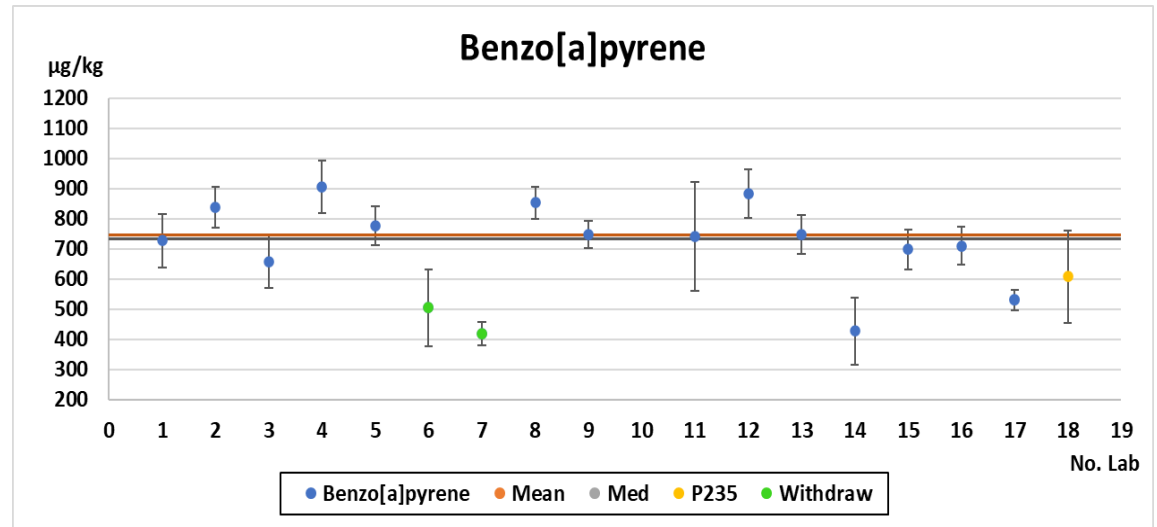


Dot-and-Bar Display of Benzo[a]pyrene

Mean and median from 16 Labs



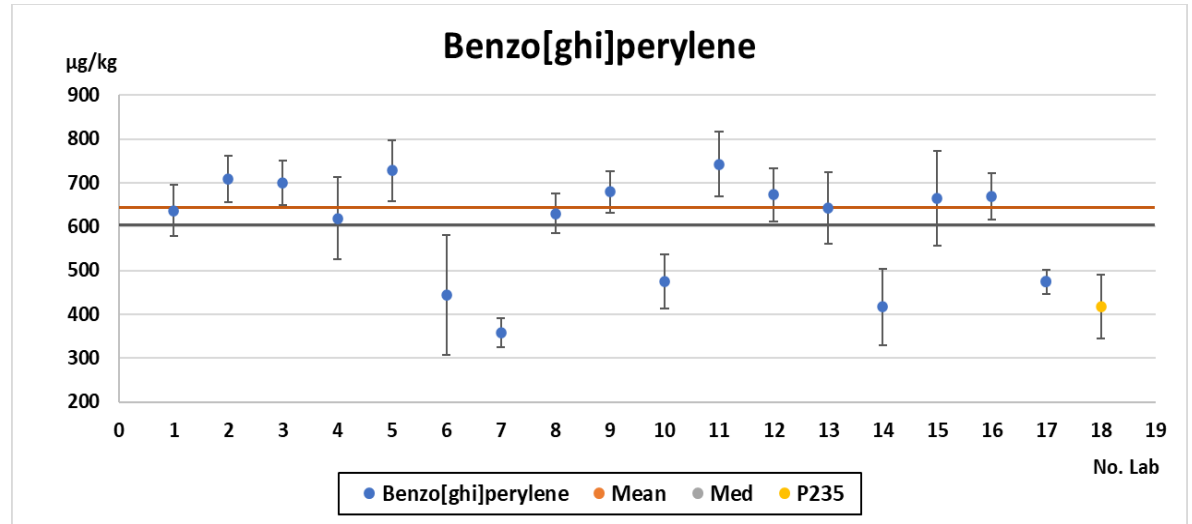
Mean and median from 15 Labs



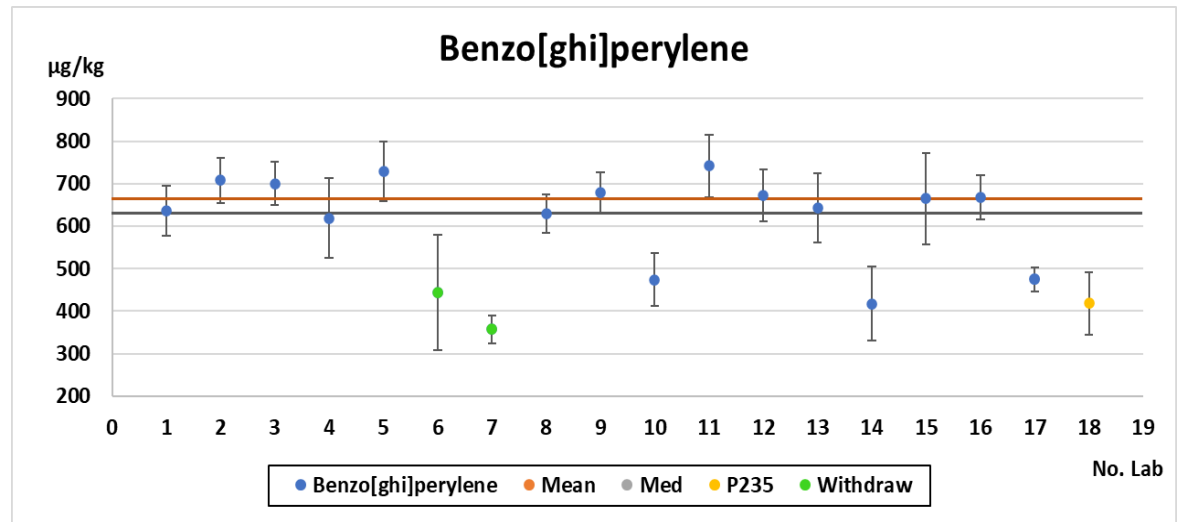


Dot-and-Bar Display of Benzo[ghi]perylene

Mean and median from 17 Labs



Mean and median from 15 Labs





Next Plan

- **We are still waiting for feedback from participating laboratories on whether to retain the comparison results in KCRV.**

- **An online meeting on KCRV calculation and evaluation is planned for November or early December.◦**



Thank You for Attention

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