

CCQM-K50 „Polycyclic Aromatic Hydrocarbons (PAHs) in Soil/Particulate Matter“

Draft B Report (final version May 2009)

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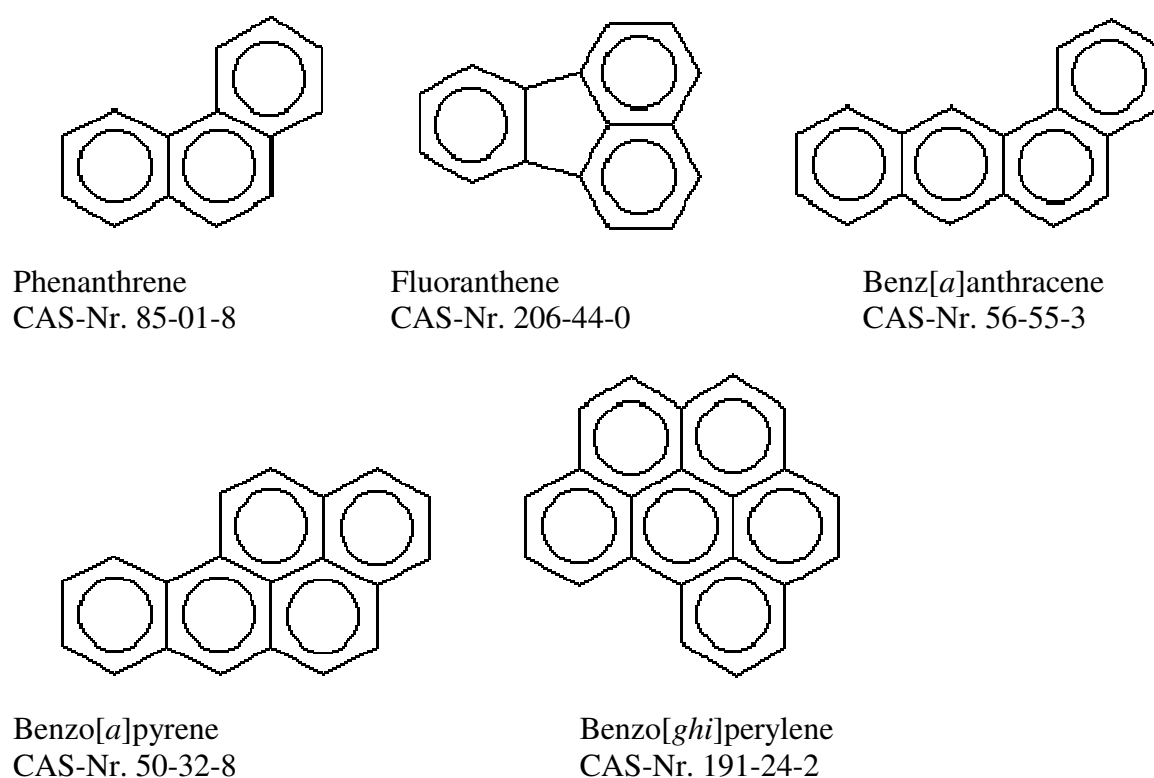
1. Introduction

For the Mutual Recognition Arrangement (MRA) developed by the CIPM, there are numerous Calibration and Measurement Capability Claims (CMCs) on PAH analysis in various matrices published in the BIPM key comparison database, Appendix C. By July 2007 such CMCs were released in Category 10 Biological fluids and materials, Subcategory 10.4 Tissues, Category 11 Food, Subcategory 11.2 Contaminants and Category 13 Sediments, soils, ores and particulates, Subcategories 13.1 Sediments, 13.2 Soils and 13.4 Particulates. Additional CMCs are being proposed and reviewed. Evidence of successful participation in formal, relevant international comparisons is needed to support these claims.

At the CCQM Organic Working Group meeting held at IRMM in September 2005, results of a pilot study CCQM-P69 “PAHs in Soil/Sediment” were discussed and it was decided to proceed with a key comparison and a subsequent pilot study CCQM-K50/P69.1. CENAM and BAM agreed to serve as the coordinating laboratories. The measurand of the study was specified as amount of specific PAHs in solid matrices as extracted under exhaustive extraction conditions.

PAHs constitute a large class of organic substances containing two or more fused aromatic rings made up of carbon and hydrogen atoms. PAHs result from combustion or pyrolysis sources and are ubiquitous in environmental samples. PAHs are known as carcinogenic or mutagenic and give rise to serious health concern. As for CCQM-P31a, CCQM-K38 “PAHs in Organic Solution” and the preceding pilot study CCQM-P69 “PAHs in Soil/Sediment” five target PAHs, phenanthrene (Ph), fluoranthene (Fl), benz[*a*]anthracene (B[*a*]A), benzo[*a*]pyrene (B[*a*]P), and benzo[*ghi*]perylene (B[*ghi*]P), were selected as representative of the measurement of individual compounds. They span the volatility and concentration range of the PAHs commonly quantified in environmental samples and are of toxicological relevance. B[*a*]P is often used as a marker for total PAH exposure. The target compounds also include some potentially problematic GC separations (phenanthrene/anthracene, B[*a*]A/ triphenylene/chrysene).

Figure 1: Structure of target analytes for CCQM-K50



2. Sample materials

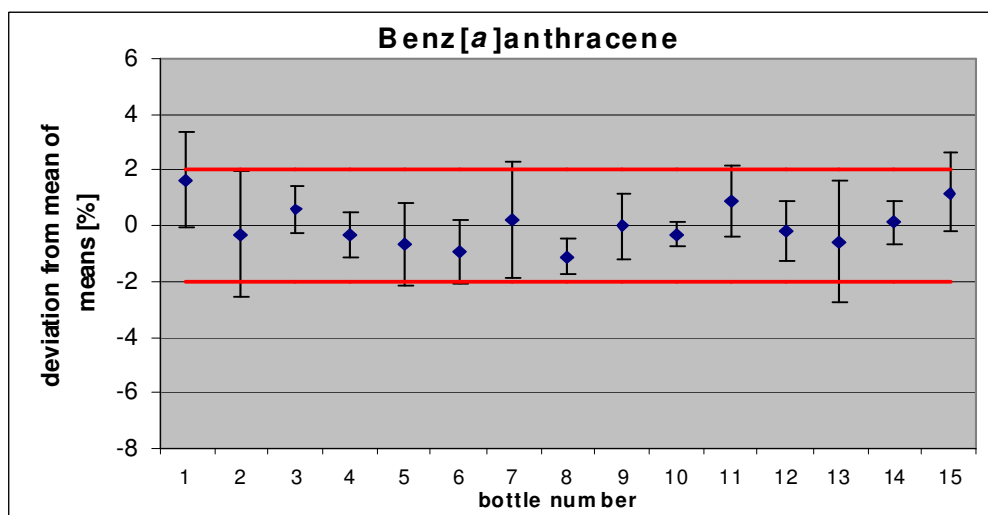
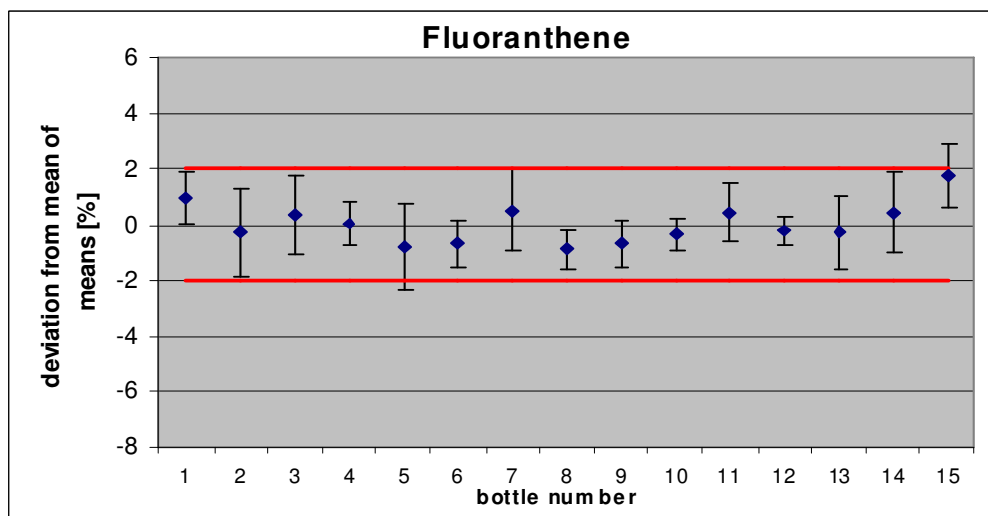
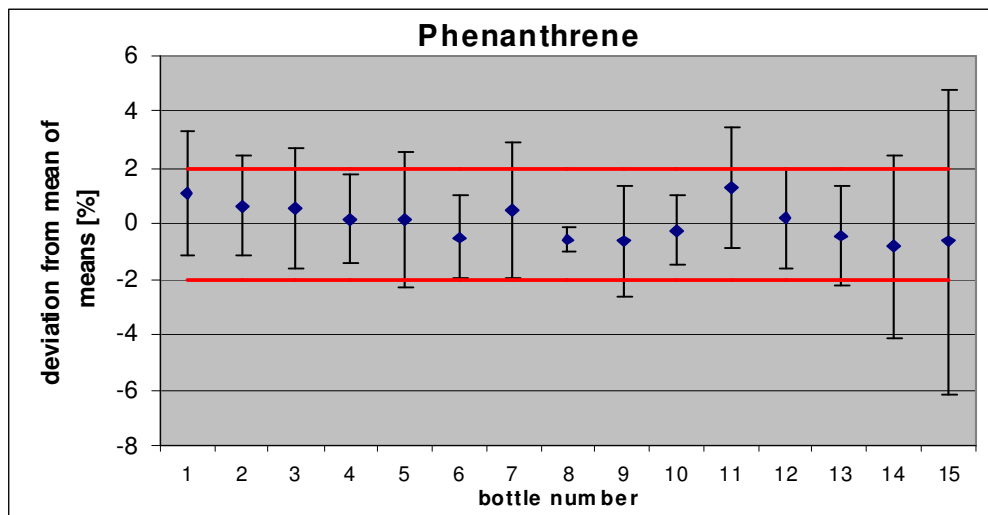
Since some of the CMC entries for PAHs in the BIPM database have very low uncertainties, a degree of inhomogeneity of less than 2% was regarded as necessary for a candidate sample material for K50 to verify these entries. At the OAWG meeting at KRISS in November 2006 BAM and NIST presented homogeneity and sample size data of two candidate materials, a soil (BAM) and a particulate matter (NIST) which meet this requirement. It was decided to use both materials to extend the concentration range and scope of the study. NIST also offered SRM 1649a Urban Dust for use as a control material.

2.1. K50a soil

The soil sample material, **K50a**, was prepared and characterized at BAM. It was a sandy soil collected near a former gasworks site in Berlin, Germany. It was naturally contaminated by industrial emission over decades. It has not been enriched or spiked. The material was air-dried and sieved. The particle size fraction <63 μm was homogenized and bottled. Each bottle

contained about 20 g of soil in 50 mL brown glass jar with a Teflon-lined screw cap. The concentration of each of the five target PAHs in the soil was between 1 µg/g to 20 µg/g. The material was tested for homogeneity according to ISO Guide 35 (ANOVA, single factor analysis of variance, 95% level). 15 bottles of the material were used, 4 determinations per bottle were carried out using 3 g sample. Extraction was done with methanol by Accelerated Solvent method (ASE), measurement by HPLC-FLD/DAD.

Figure 2: Homogeneity study for K50a soil. Symbols are the mean of 4 determinations per bottle, uncertainty bars are the relative standard deviation of the 4 determinations. Red lines display the $\pm 2\%$ level.



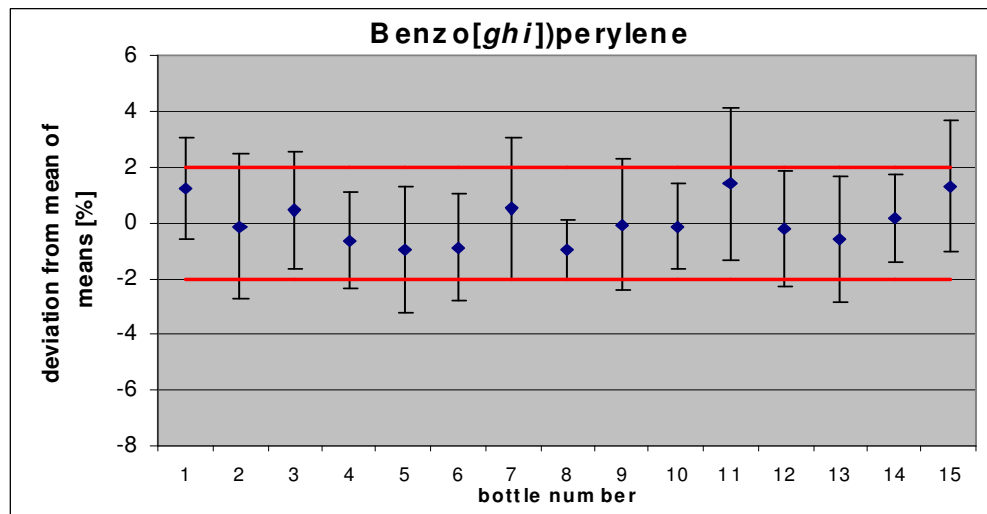
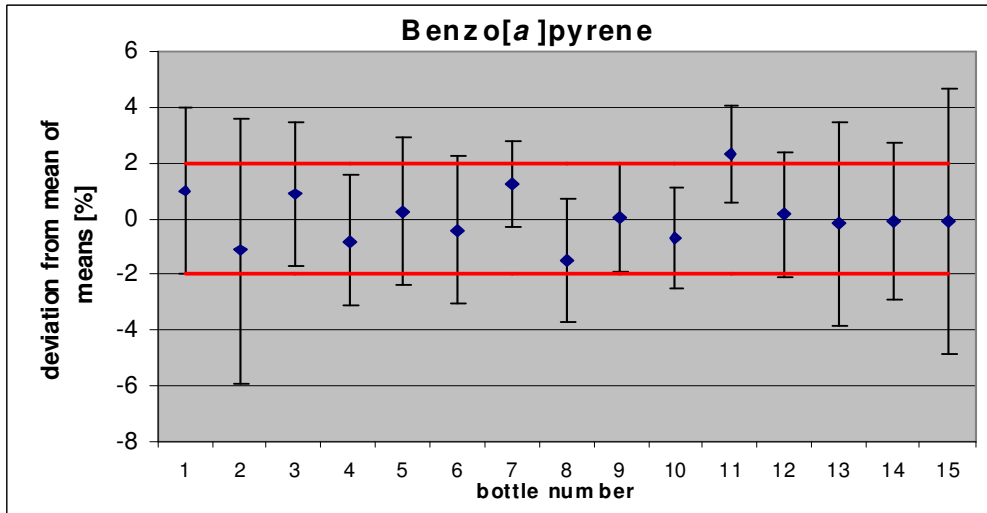


Table 1: Results of the homogeneity study (ANOVA) of K50a soil sample

	within bottle standard deviation sqrt(MS_{within})	between bottle standard deviation sqrt($MS_{between}$)	uncertainty between bottles
Ph	2,40%	1,21%	0,56%
Fl	1,13%	1,44%	0,44%
B[a]A	1,39%	1,50%	0,32%
B[a]P	2,88%	1,61%	0,66%
B[ghi]P	2,07%	1,49%	0,48%

*the larger value of s_{bb} and u_{bb} was used

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (1)$$

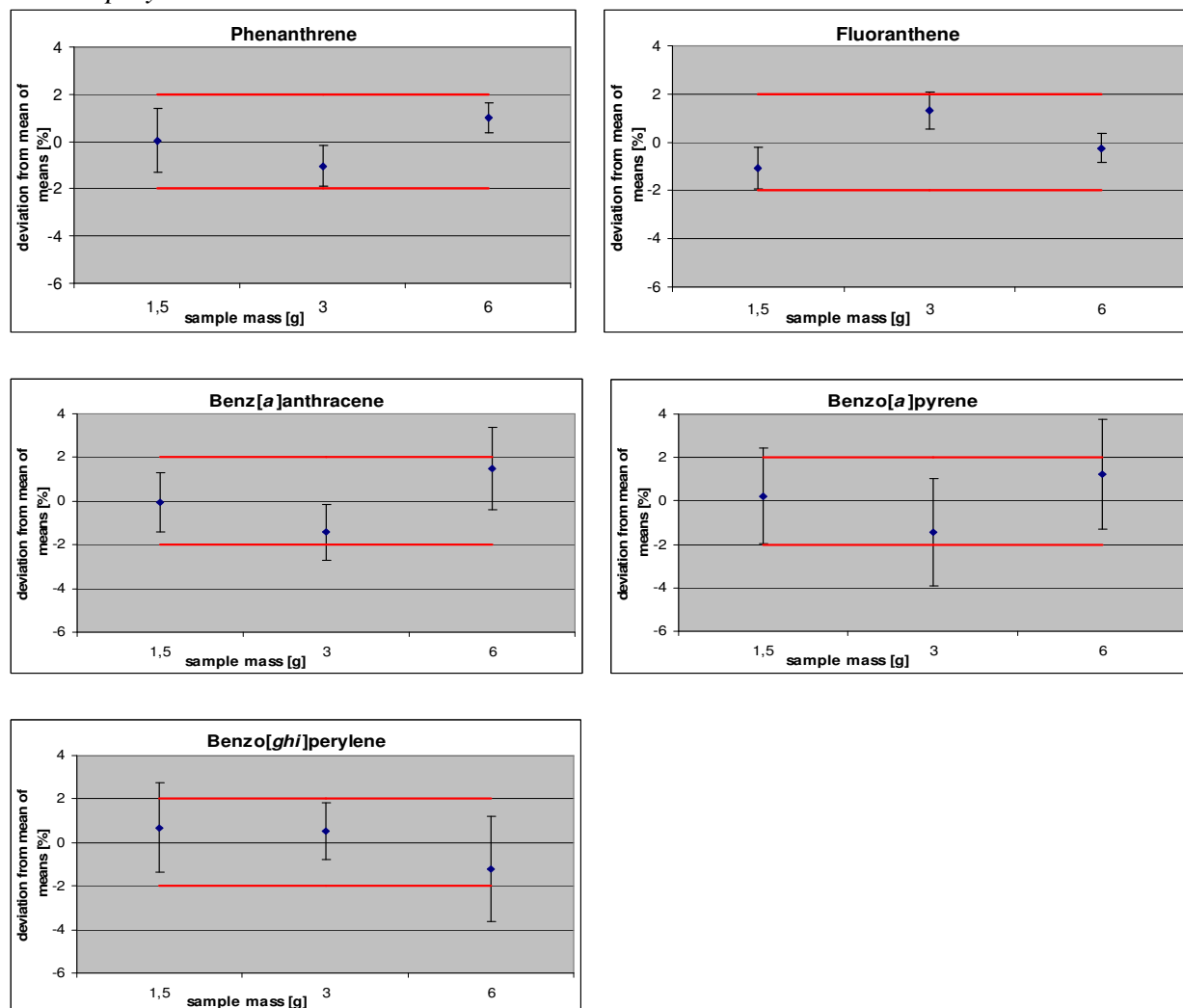
$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt{\frac{2}{v_{MS_{within}}}} \quad (2)$$

MS_{within} and $MS_{between}$ are the within and between group variances, n the number of measurements per bottle and $v_{MS_{within}}$ the degrees of freedom within group.

Results show that the material is homogeneous, the between bottle inhomogeneity is less than 2% for all analytes.

The sample size study was carried out with three different sample masses (1.5 g, 3 g, 6 g). Five replicate measurements per sample mass were performed (extraction with toluene by ASE or FlexIka, measurement by GC-MS). No statistically significant dependence of analytical results on sample mass intake was observed within the mass range 1.5 g to 6 g.

Figure 3: Sample size study for K50a soil. Symbols are the mean of 5 determinations per mass, uncertainty bars are the relative standard deviation of the mean of replicate determinations. Red lines display the $\pm 2\%$ level.



2.2. K50b particulate matter

The particulate sample material, **K50b**, was prepared and characterized at NIST. It is an air particulate which was collected in an urban area over a period in excess of 12 months using a baghouse. The material was removed from the baghouse filter bags and combined in a single lot. The lot was passed through a 63 μm sieve and mixed in a V-blender. The mean particle size of the material is 20 μm . This material has not been enriched or spiked. Each jar contains approximately 2 g of particulate. The concentration of each of the five target PAHs in the particulate is between 1 $\mu\text{g/g}$ to 7 $\mu\text{g/g}$.

The material was tested for homogeneity and minimum sample size using the following approach: The observed (overall) variance (S_{obs}^2) of repetitive analysis includes both analytical measurement (S_m^2) and subsampling (S_s^2) variances.

$$S_{obs}^2 = S_m^2 + S_s^2 \quad (3)$$

The analytical measurement (S_m^2) variance can be estimated by processing calibration solutions prepared so that concentrations mimic those in the samples of interest through the entire analytical procedure from extraction to analysis.

Figure 4: Observed variance S_{obs} , measurement variance S_m and variance due to subsampling S_s as a function of sample mass.

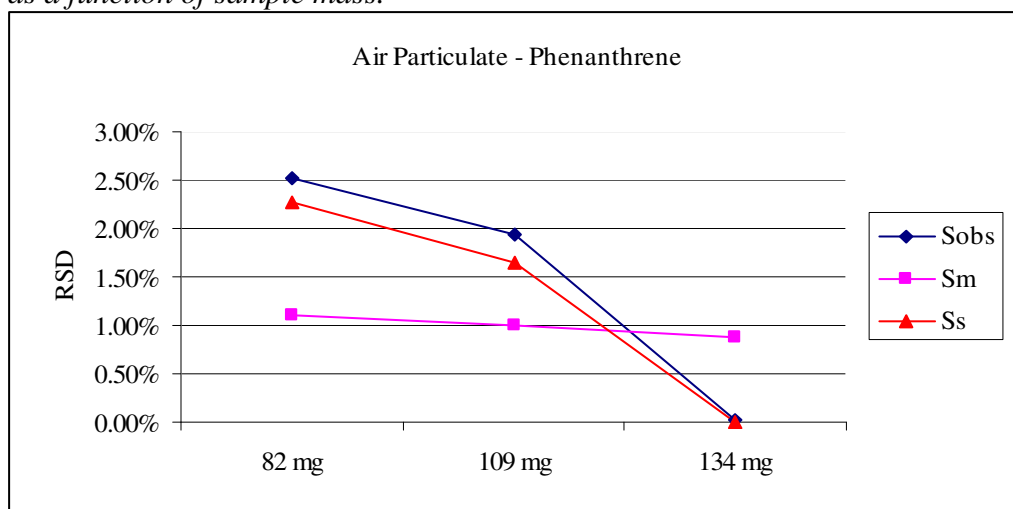
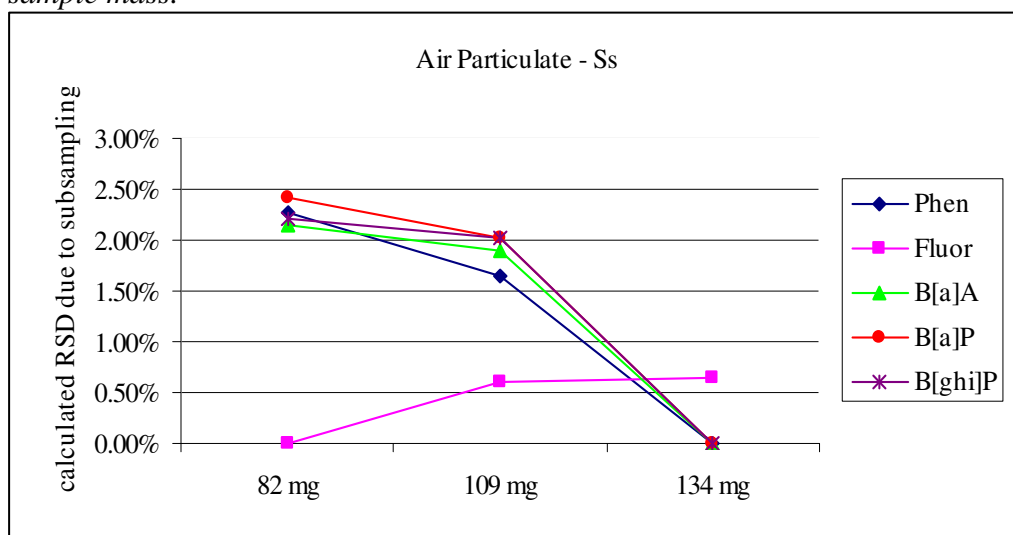


Figure 5: Variance due to subsampling S_s , calculated according to eqn. (1), as a function of sample mass.



As a result of that study a minimum subsample size of 135 mg is recommended for K50b sample. This sample size will ensure that the component of uncertainty due to subsampling is less than 1%.

3. Conduct of the study

According to the project protocol agreed to at the November 2006 OAWG meeting samples were distributed in February 2007. The laboratories receiving samples for CCQM-K50 were:

BAM	[Germany]
CENAM	[Mexico]
Government Lab (GL)	[Hong Kong]
INMETRO	[Brazil]
IRMM	[EU]
KRISS	[Korea]
LGC	[Great Britain]
LNE	[France]
NIST	[USA]
NMIJ	[Japan]

All participants returned results. KRISS and GL measured the K50a soil sample only.

In parallel with CCQM-K50 another pilot study CCQM-P69.1 was initiated. Two labs received samples for this intercomparison.

Each participant received two bottles of K50a, two bottles of K50b and one bottle of SRM 1649a. The exercise instructions requested the analysis of three aliquots from each of the four bottles (total of six determinations per sample). Analysis of the SRM1649a (control sample) was optional, but participants were strongly encouraged to report results for this material too. The amount of the control sample supplied to the participants was about 500 mg, which was sufficient for up to three replicate measurements.

The material within the bottles was to be mixed thoroughly by stirring or shaking before subsampling. For extraction of the K50a material a sample mass between 1.5 g and 6 g was recommended. For extraction of the K50b material, the minimum sample intake was to be 135 mg. Participants were asked to use their routine analytical procedures for the determination of PAHs in solid matrices.

Results were to be reported as mass fractions of the target analytes on a dry-mass basis, therefore, the residual moisture in the samples was to be determined and reported. A complete uncertainty budget was also requested.

4. Methods

All participants applied GC-MS with either deuterated or ¹³C isotopes as internal standards. Extractions were done by Soxhlet or Accelerated Solvent Extraction (ASE), also known as Pressurized Fluid Extraction (PFE). For calibration, certified organic solutions of PAHs (NIST CRMs) were used by BAM, GL and NIST. All other participants used neat crystalline substances from different commercial sources, among them BCR certified reference materials which were available for fluoranthene, B[a]A and B[ghi]P. For the non BCR commercial standards, all participants except INMETRO, IRMM and LNE performed a purity assessment.

Details of the analytical methods and the sources of calibration standards are summarized in the following tables.

Table 4: Sources of calibration standards

	Phenanthrene	Fluoranthene	B[a]A	B[a]P	B[ghi]P	purity assessment
BAM	NIST SRM 1647d "16 priority pollutant polycyclic hydrocarbons in acetonitrile"					
GL	NIST SRM 2260a "36 aromatic hydrocarbons in toluene"					
CENAM	Chem Service	Aldrich	Supelco	Ultra Scientific	Ultra Scientific	yes
INMETRO	Sigma-Aldrich	Sigma-Aldrich	Sigma-Aldrich	AccuStandard	Sigma-Aldrich	no
IRMM	Dr Ehrenstorfer	Dr Ehrenstorfer	BCR271	Dr Ehrenstorfer	BCR52	no
KRISS	Aldrich	BCR	BCR	Chem Service	BCR	yes
LGC	Aldrich	Aldrich	BCR271	QMx labs (Dr Ehrenstorfer)	BCR52	yes
LNE	Dr Ehrenstorfer	Dr Ehrenstorfer	Dr Ehrenstorfer	Dr Ehrenstorfer	Dr Ehrenstorfer	no
NIST	NIST SRM 2260a "36 aromatic hydrocarbons in toluene"					
NMIJ	Supelco	TCI	TCI	TCI	AccuStandard	yes

Table 2: Participant's methods for the analysis of K50a soil

laboratory	sample mass [g]	extraction			clean-up	column type	length [m], inner diameter [mm], film thickness [µm]	calibration		dry mass determination
		solvent	method	conditions				internal standard	mode	
BAM	3	toluene	ASE	140 bar, 100°C, 10 min static, 2 cycles	Na ₂ SO ₄ drying	Varian factorFOUR VF-5ms, equivalent to 5% phenyl 95% dimethylpolysiloxane	30, 0.25, 0.25	deuterated	5 point curve	Karl-Fischer titration
CENAM	1.5	toluene	Soxhlet	18 h, 4 cycles/min	Filtration	5%-Phenyl-methylpolysiloxane (ZB-5) and 50%-Phenyl-methylpolysiloxane (HP-50+)	60, 0.25, 0.25	deuterated	4 point curve, standard addition	oven drying
GL	1.5	hexane/acetone, 50:50 v/v	Soxhlet	24 h	Silica	DB-5ms	60, 0.25, 0.25	¹³ C labelled	single point	oven drying
INMETRO	1.5	dichloro-methane	Soxhlet	18-20 h, (~ 200 cycles)	Silica, 500mg/3ml	5% phenyl 95% methylpolysiloxane Low Bleed	30, 0.25, 0.25	deuterated Ph, Fl, B[a]A, B[a]P	6 to 8 point curve	oven drying
IRMM	1.5	dichloro-methane	ASE	100°C, 2000 psi, 2 cycles, 5 min, 60% flush, 90 s purge	SPE, AccuBondII, 1000mg/6ml	J&W DB5-MS; J&W DB17-MS	30, 0.25, 0.25; 30, 0.32, 0.15	deuterated	2 to 4 point curve	Karl-Fischer titration
KRISS	2 to 3	acetone/hexane, 50:50 v/v	Soxhlet	14 h, 110 ml	None	RTX-5MS	30, 0.25, 0.25	deuterated	single point	oven drying
LGC	2	toluene	ASE	preheat 2min, heat 6min, static 5min, flush 40%vol., purge 100s, 1500psi, 125°C, 5 cycles	None	intermediate polarity deactivated ret.gap + VF-5ms + DB-17ms (coupled in series)	1.7+30+30; 0.25, 0.25	¹³ C labelled	exact matching	oven drying
LNE	2	dichloro-methane	ASE	100 bar, 120°C, static 6 min, flush 70v%, purge 100s, 3 cycles of 2 extractions	Alumina	5% phenyl Polysilphenylene-siloxane	60, 0.25, 0.25	deuterated	8 point curve	oven drying
NIST	1.5 to 2.8	dichloro-methane	Soxhlet	20 h	aminopropyl solid phase extraction cartridge eluted with 40 mL of 20% methylene chloride in hexane (volume fraction)	DB-17	60, 0.25, 0.25	deuterated	bracketing	vacuum freeze drying
NMIJ	3	toluene	PFE	190°C, 20 MPa, 10 min, 2 cycles	Silica, 500mg, twice	DB-17MS	30, 0.25, 0.25	deuterated	single point	oven drying

Table 3: Participant's methods for the analysis of K50b particulate and the control sample SRM 1649a

laboratory	sample mass [g]	extraction			clean-up	column		calibration		dry mass determination
		solvent	method	conditions		type	length [m], inner diameter [mm], film thickness [µm]	internal standard	mode	
BAM	0.3	toluene, dichloromethane	ASE	140 bar, 100°C, 10 min static, 3 cycles	Na ₂ SO ₄ drying	Varian factorFOUR VF-5ms, equivalent to 5% phenyl 95% dimethylpolysiloxane	30, 0.25, 0.25	deuterated	5 point curve	Karl- Fischer titration
CENAM	0.18	toluene	Soxhlet	18 h, 4 cycles/min	activated copper, filtration	5%-Phenyl-methylpolysiloxane (ZB-5)	60, 0.25, 0.25	deuterated	3 to 5 point curve, standard addition	oven drying
INMETRO	0.15	dichloromethane	Soxhlet	12-15 h, (~ 200 cycles)	Silica, 500mg/3ml	5% phenyl 95% methylpolysiloxane Low Bleed	30, 0.25, 0.25	deuterated Ph, F1, B[a]A, B[a]P	8 point curve	oven drying
IRMM	0.15	dichloromethane	ASE	100°C, 2000 psi, 2 cycles, 5 min, 60% flush, 90 s purge	SPE, AccuBondII, 1000mg/6ml	J&W DB5-MS; J&W DB17-MS	30, 0.25, 0.25; 30, 0.32, 0.15	deuterated	2 to 4 point curve	Karl- Fischer titration
LGC	0.2	toluene	ASE	preheat 2min, heat 6min, static 5min, flush 40%vol., purge 100s, 1500psi, 125°C, 5 cycles	None	intermediate polarity deactivated ret.gap + VF-5ms + DB-17ms (coupled in series)	1.7+30+30; 0.25, 0.25	¹³ C labelled	exact matching	oven drying
LNE	0.25	dichloromethane	ASE	100 bar, 120°C, static 6 min, flush 70v%, purge 100s, 3 cycles of 2 extractions	Alumina	5% phenyl Polysilphenylene-siloxane	60, 0.25, 0.25	deuterated	8 point curve	oven drying
NIST	0.13 to 0.15	dichloromethane	Soxhlet	20 h	aminopropyl solid phase extraction cartridge eluted with 40 mL of 20% methylene chloride in hexane (volume fraction)	DB-17	60, 0.25, 0.25	deuterated	bracketing	vacuum freeze drying
NMIJ	0.15	toluene	PFE	190°C, 20 MPa, 10 min, 2 cycles	Silica, 500mg, once	DB-17MS	30, 0.25, 0.25	deuterated	single point	oven drying

5. Results

Tables 5 to 7 and figures 6 to 8 summarize the results and their standard and expanded uncertainties (95% confidence interval) as reported by the participants. Mass fractions of target analytes in K50a soil and K50b particulate are the mean of six independent determinations (three per bottle). Mass fractions in the SRM 1649a control sample are the mean of one to three determinations. Together with the analytical results the key comparison reference values ($KCRV_{x_R}$) and their standard and expanded uncertainties at 95% confidence level (U_R) are displayed. Estimation of KCRV and uncertainty is described in section 6.

INMETRO submitted two sets of data. After discussion of the preliminary results at the OAWG meeting in October 2007, INMETRO assessed the purity of their commercial PAH standards and recalculated their analytical results with respect to these purity values. The tables and figures of this report display their first submission. Revised data are summarized in appendix 1.

Table 8 and figure 9 show the results of dry mass determination.

Table 5: Mass fractions of target analytes (mean of six determinations) and KCRV, $\mu\text{g/g}$, K50a soil, expanded uncertainties at the 95% confidence level

	phenanthrene			fluoranthene			B[a]A			B[a]P			B[ghi]P		
	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty
BAM	12.92	0.28	0.68	13.50	0.12	0.26	5.84	0.06	0.13	4.84	0.07	0.15	4.94	0.07	0.17
CENAM	13.22	0.25	0.50	14.31	0.25	0.50	5.80	0.11	0.23	5.03	0.11	0.21	4.97	0.09	0.19
GL	12.66	0.118	0.24	14.25	0.096	0.19	6.05	0.099	0.20	4.88	0.097	0.19	4.97	0.054	0.11
INMETRO	12.82	0.0613	0.13	14.01	0.0611	0.13	5.913	0.0286	0.061	5.314	0.0277	0.058	5.100	0.0208	0.043
IRMM	13.53	0.15	0.30	13.88	0.22	0.43	5.56	0.10	0.19	4.65	0.15	0.29	4.83	0.15	0.29
KRISS	13.264	0.112	0.250	13.770	0.139	0.283	6.033	0.049	0.101	4.807	0.045	0.091	4.875	0.048	0.097
LGC	13.91	0.17	0.35	14.54	0.16	0.32	5.87	0.05	0.10	5.35	0.05	0.10	5.06	0.04	0.08
LNE	16.49	0.21	0.42	16.38	0.20	0.40	6.30	0.10	0.20	5.56	0.09	0.18	5.62	0.09	0.18
NIST	14.05	0.15	0.35	15.63	0.16	0.37	5.99	0.12	0.27	4.96	0.09	0.24	5.09	0.07	0.13
NMIJ	14.44	0.173	0.35	14.99	0.178	0.36	6.22	0.082	0.16	5.16	0.067	0.13	5.27	0.062	0.12
KCRV	13.49	0.25	0.61	14.43	0.28	0.68	5.92	0.08	0.19	5.00	0.08	0.20	5.00	0.05	0.12

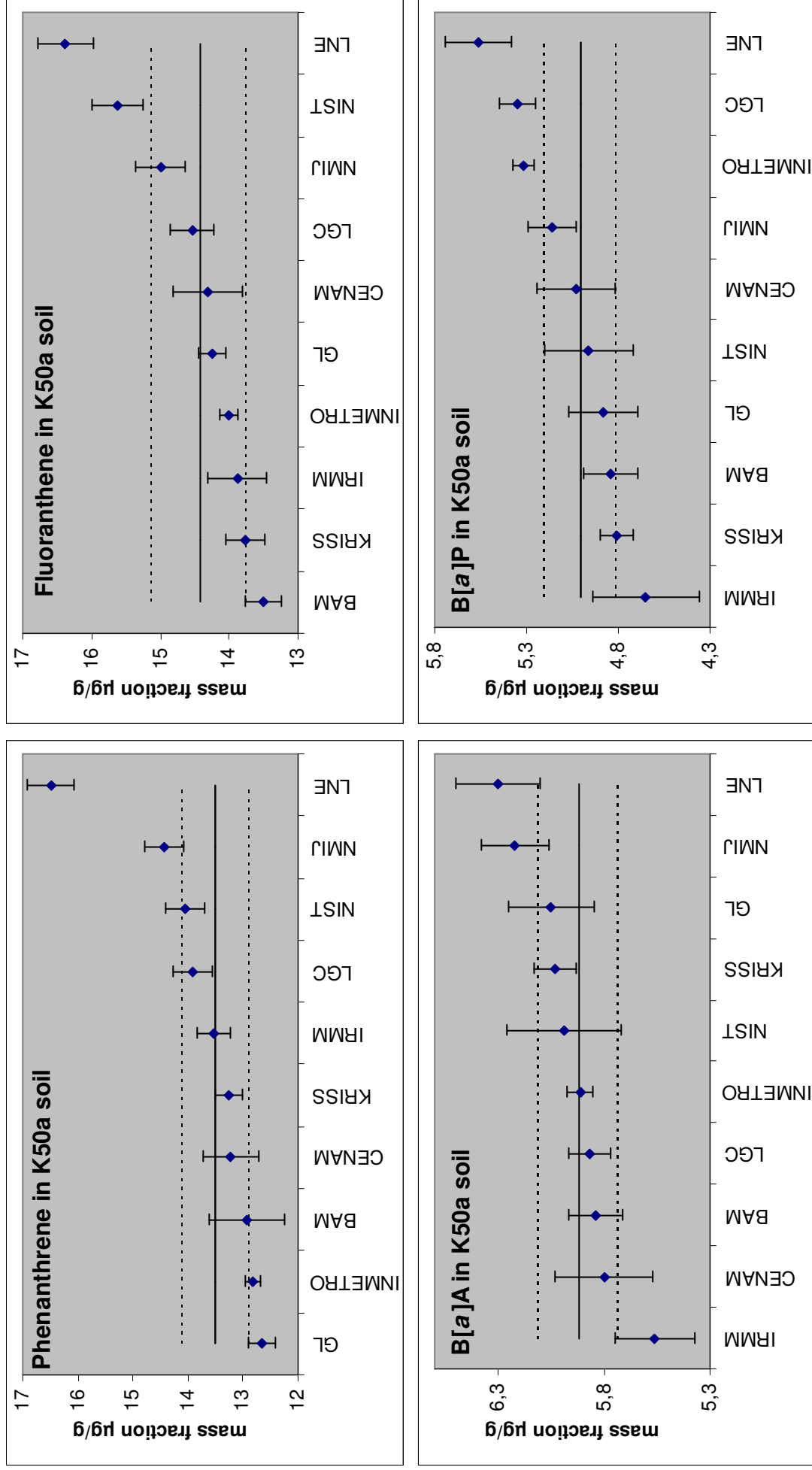
Table 6: Mass fractions of target analytes (mean of six determinations) and KCRV, $\mu\text{g/g}$, K50b particulate, expanded uncertainties at the 95% confidence level

	phenanthrene			fluoranthene			B[a]A			B[a]P			B[ghi]P		
	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty
BAM	3.93	0.07	0.15	6.27	0.08	0.17	2.17	0.02	0.04	2.32	0.05	0.12	3.88	0.07	0.14
CENAM	4.14	0.072	0.14	6.33	0.200	0.40	2.45	0.110	0.22	2.68	0.075	0.15	4.25	0.125	0.25
INMETRO	3.876	0.0408	0.092	6.01	0.0549	0.12	1.971	0.0249	0.054	2.40	0.0594	0.13	3.665	0.0360	0.078
IRMM	4.18	0.06	0.13	6.04	0.11	0.21	1.96	0.05	0.10	2.12	0.07	0.14	3.96	0.12	0.24
LGC	4.39	0.08	0.15	6.61	0.09	0.18	2.16	0.05	0.10	2.57	0.09	0.18	4.19	0.08	0.16
LNE	6.65	0.27	0.54	8.51	0.35	0.70	2.63	0.14	0.28	3.45	0.19	0.38	5.45	0.22	0.44
NIST	4.13	0.03	0.07	6.25	0.05	0.11	2.12	0.04	0.08	2.27	0.02	0.06	3.91	0.05	0.10
NMIJ	5.06	0.266	0.53	6.70	0.326	0.65	2.20	0.090	0.18	2.36	0.105	0.21	4.45	0.187	0.37
KCRV	4.33	0.20	0.55	6.43	0.10	0.28	2.18	0.07	0.18	2.44	0.08	0.22	4.11	0.10	0.26

Table 7: Mass fractions of target analytes, $\mu\text{g/g}$, SRM 1649a control sample, expanded uncertainties at the 95% confidence level

	phenanthrene			fluoranthene			B[a]A			B[a]P			B[ghi]P		
	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty	mass fraction	standard uncertainty	expanded uncertainty
BAM	4.30			6.63			2.41			2.43			4.00		
INMETRO	4.192	0.0314	0.074	6.29	0.0501	0.12	2.161	0.0173	0.037	2.58	0.0574	0.14	3.83	0.0604	0.14
IRMM	4.67	0.10	0.21	6.52	0.14	0.29	2.15	0.03	0.06	2.32	0.07	0.15	4.16	0.15	0.31
LGC	4.27	0.06	0.11	6.52	0.15	0.29	2.17	0.05	0.10	2.53	0.10	0.19	4.06	0.12	0.25
LNE	5.35	0.25	0.50	7.52	0.31	0.62	2.272	0.18	0.36	2.910	0.24	0.48	4.920	0.22	0.44
NIST	4.26			6.41			2.20			2.54			3.90		
NMIJ	5.29	0.063	0.13	6.98	0.092	0.18	2.32	0.028	0.06	2.53	0.030	0.06	4.48	0.057	0.11
certified value	4.14		0.37	6.45		0.18	2.208		0.073	2.509		0.087	4.01		0.91

Figure 6: Mass fraction of target analytes in K50a soil. Symbols: mean of six determinations as reported by the participants, uncertainty bars: expanded uncertainty 95% confidence interval as reported by the participants, black solid and dashed lines: KCRV and 95% confidence interval of the KCRV



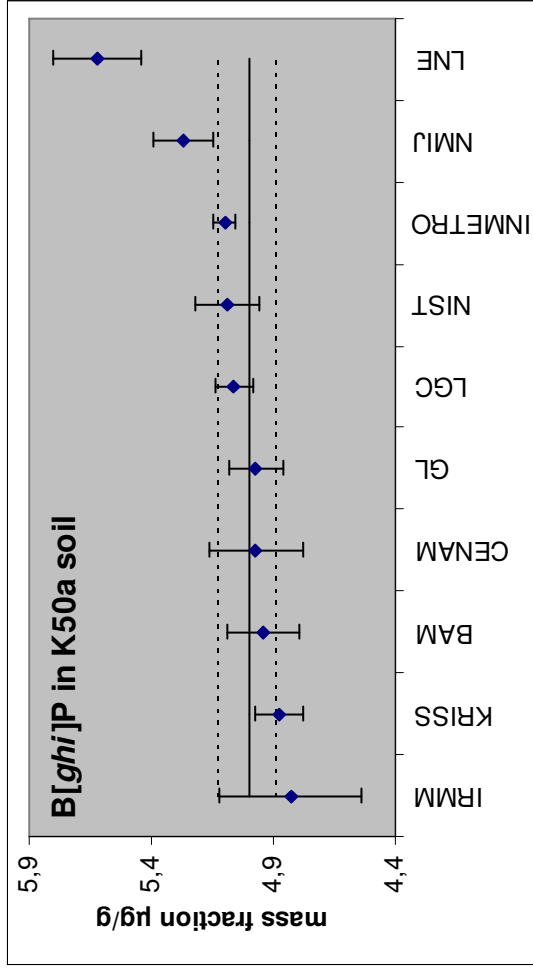
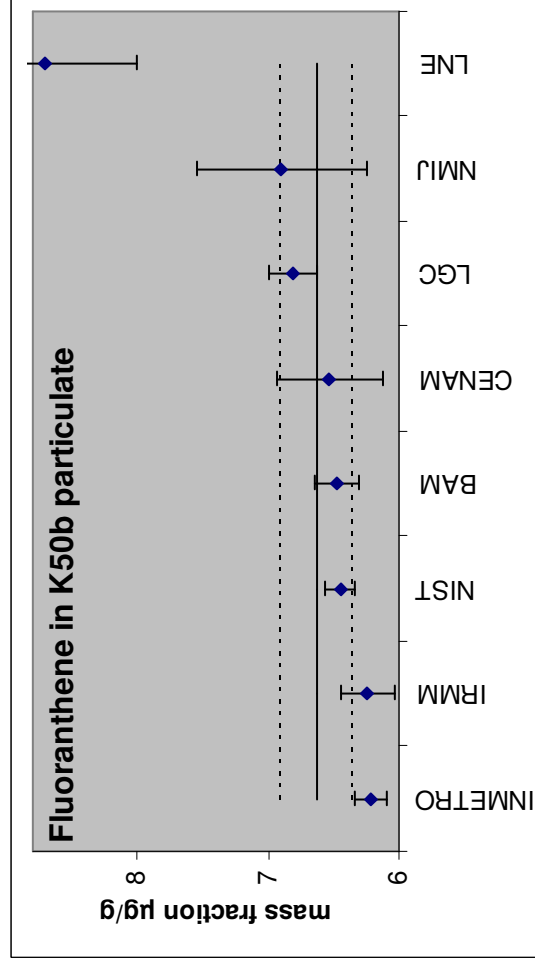
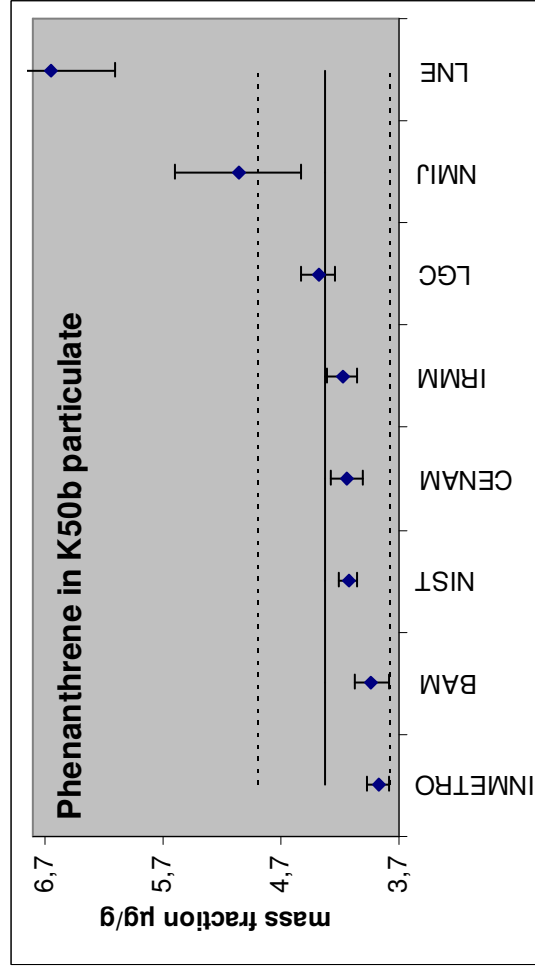


Figure 7: Mass fraction of target analytes in K50b particulate. Symbols: mean of six determinations as reported by the participants, uncertainty bars: expanded uncertainty 95% confidence interval as reported by the participants, black solid and dashed lines: KCRV and 95% confidence interval of the KCRV



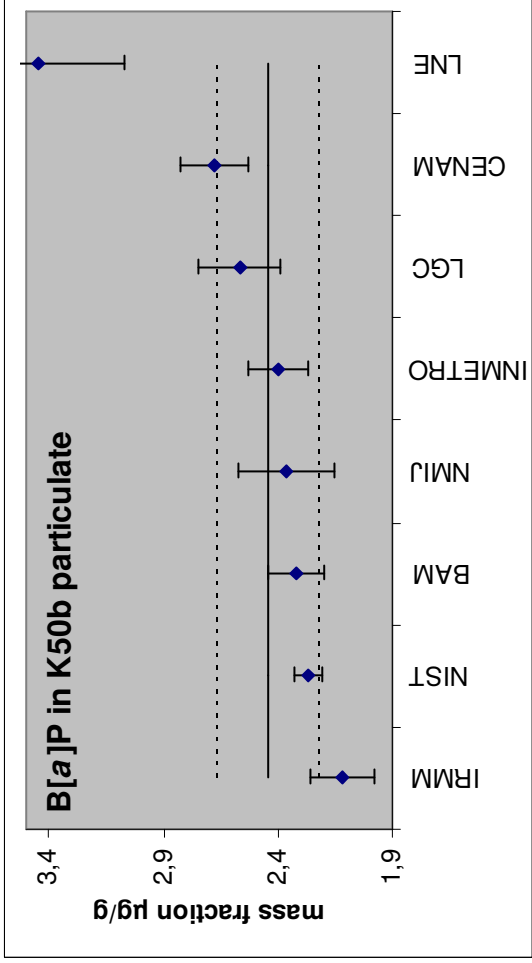
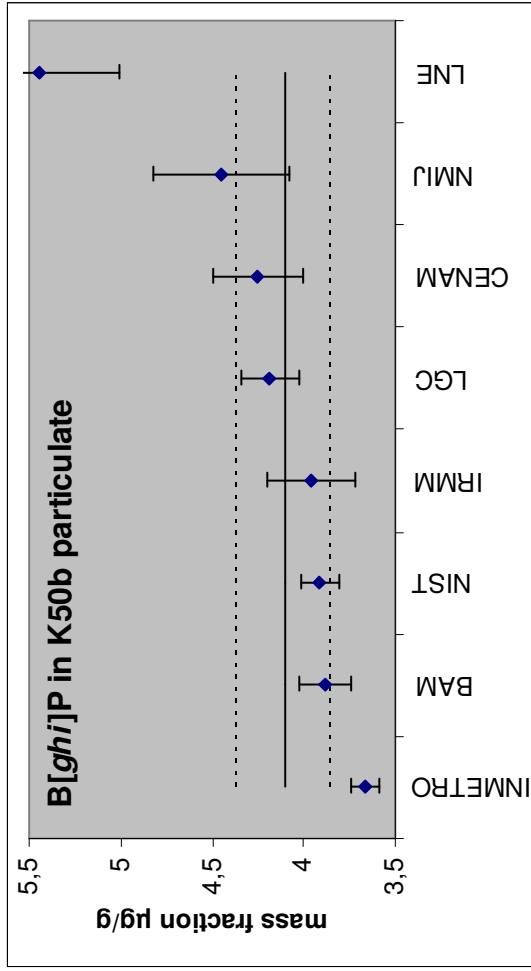
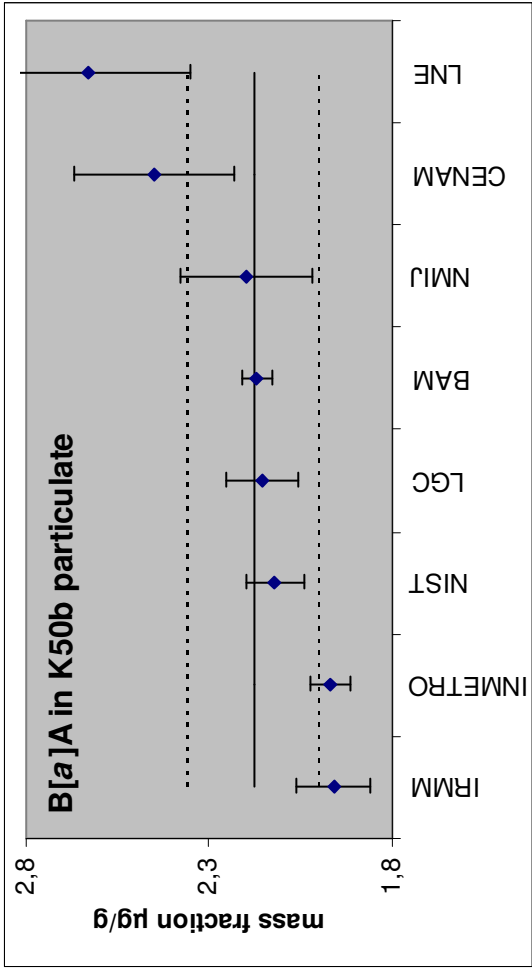
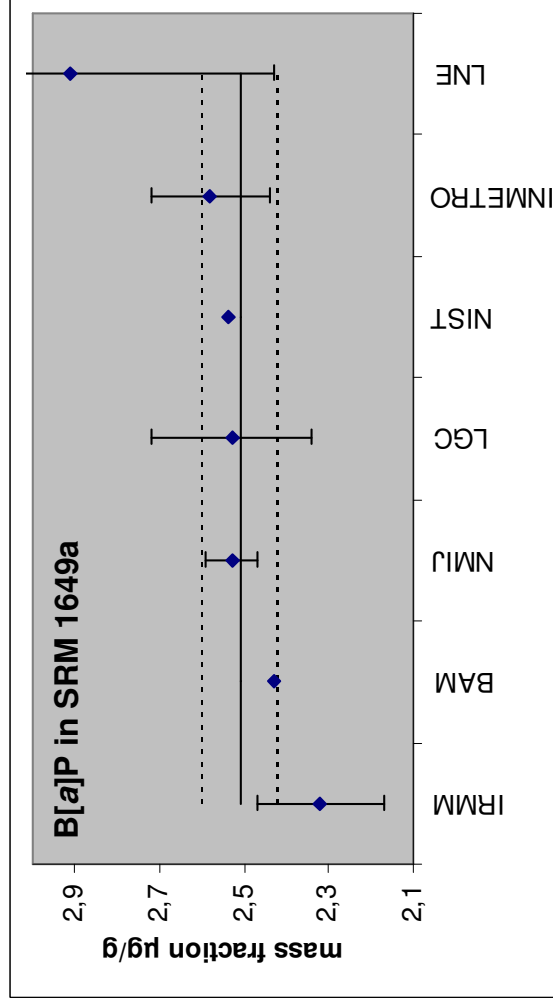
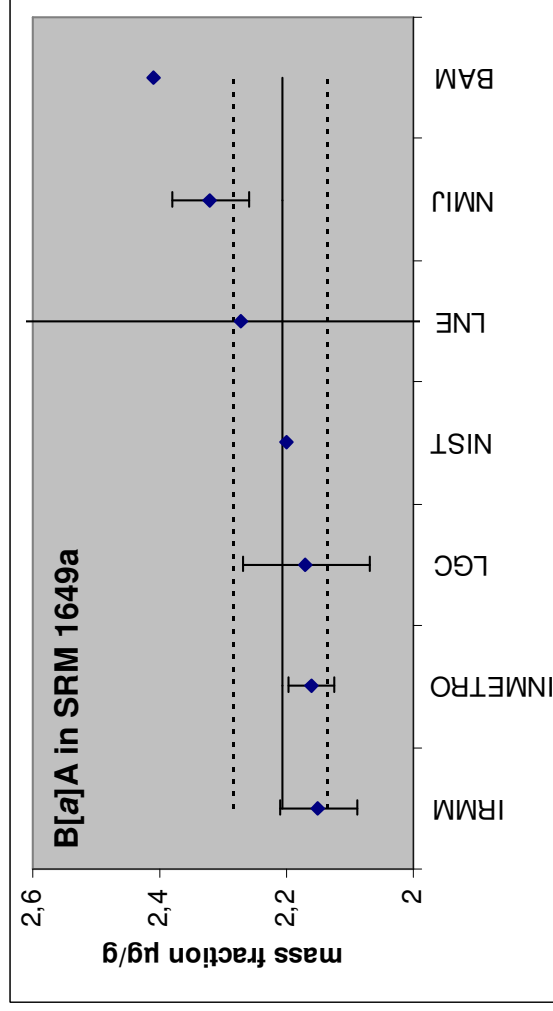
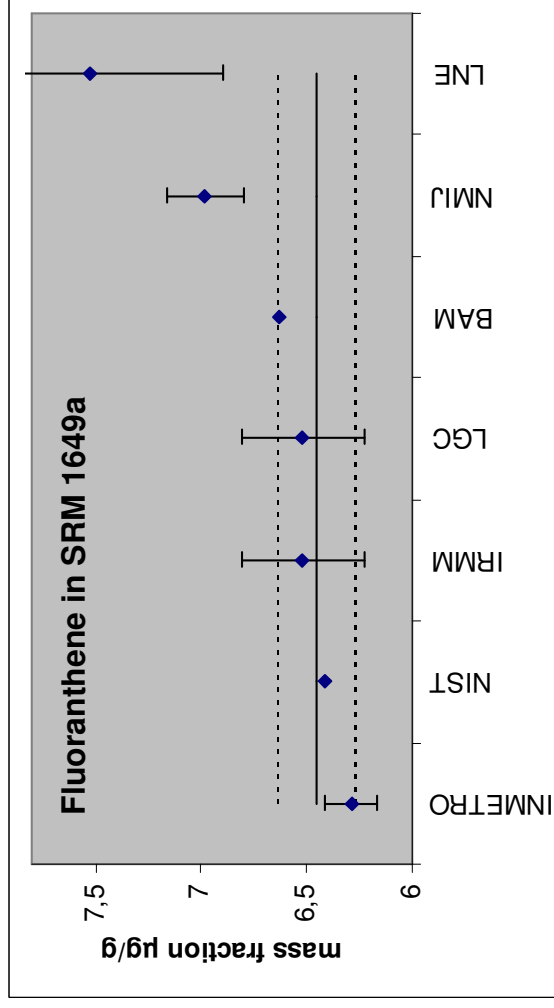
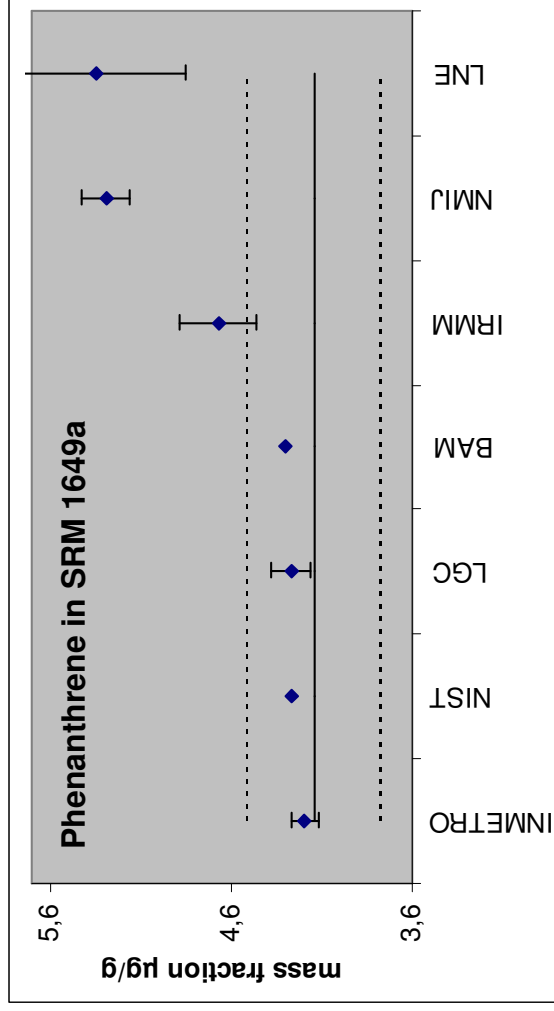


Figure 8: Mass fraction of target analytes in SRM 1649a control sample. Symbols: mean of results as reported by the participants, uncertainty bars: expanded uncertainty 95% confidence interval as reported by the participants, black solid and dashed lines: certified value and 95% confidence interval



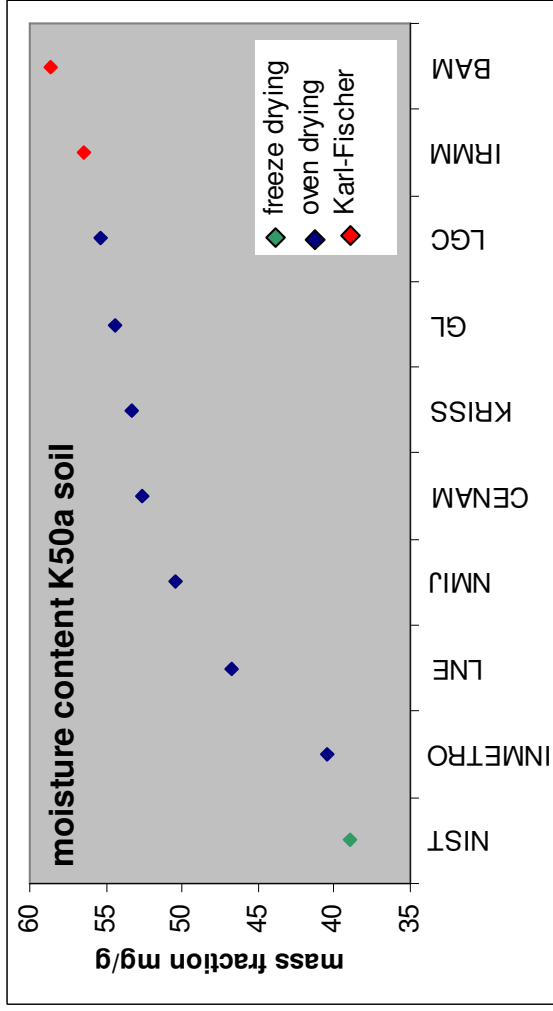
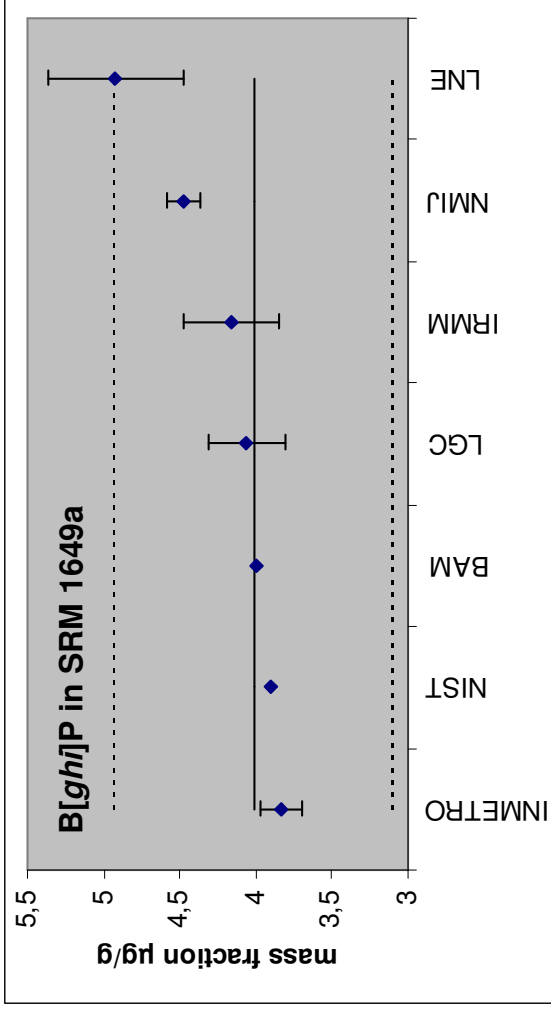


Figure 9: Moisture content as reported by the participants

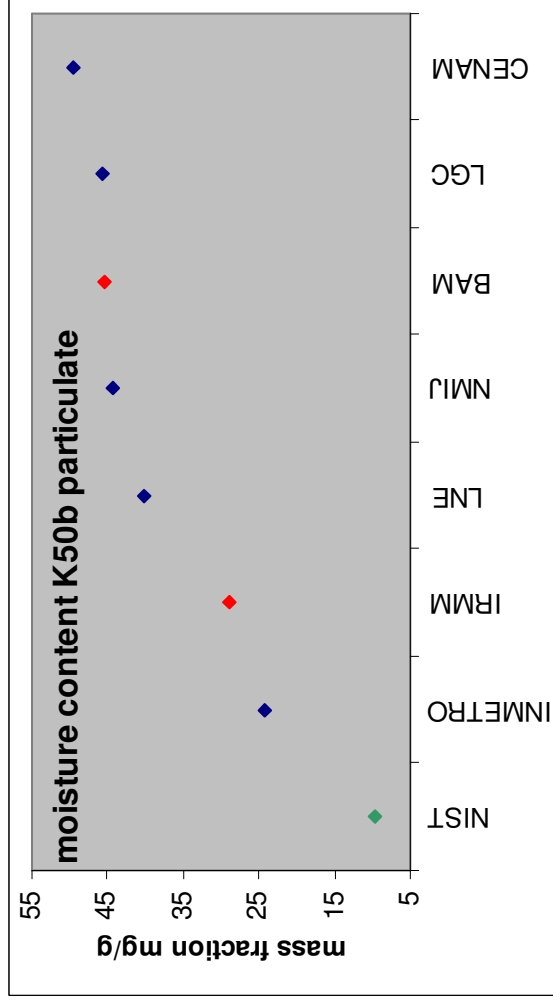


Table 8: Moisture content in mg/g as reported by the participants

laboratory	K50a soil	K50b particulate	NIST SRM 1649a
BAM	58.6	45.3	47.1
CENAM	52.6	49.55	
GL	54.46/54.36*		
INMETRO	40.52	24.29	
IRMM	56.4	28.8	
KRISS	53.32		
LGC	55.4	45.6	
LNE	46.8	40.2	
NIST	39.0	9.7	12.3
NMIJ	50.8/50.0*	44.2/44.2*	

* The moisture content was reported separately for the two sample jars.

For the control sample NIST SRM 1649a, INMETRO, LGC and NMIJ used the moisture content indicated on the certificate. IRMM used the moisture content obtained for K50b.

5.1. Basic statistics and outlier tests

The basic statistics for the data obtained on the three matrices are given in the following tables:

Table 9: Basic statistics for K50 results

Control sample

	P	F	BAA	BAP	BGHIP
N of cases	7	7	7	7	7
Minimum	4.166000	6.270000	2.146000	2.320000	3.790000
Maximum	5.350000	7.520000	2.410000	2.910000	4.920000
Median	4.300000	6.520000	2.200000	2.530000	4.060000
Mean	4.615143	6.692857	2.238286	2.547143	4.187143
95% CI Upper	5.084413	7.086893	2.330569	2.715210	4.548295
95% CI Lower	4.145873	6.298821	2.146002	2.379076	3.825990
Std. Error	0.191781	0.161034	0.037714	0.068685	0.147595
Standard Dev	0.507404	0.426056	0.099783	0.181725	0.390500
Skewness (G1)	0.886890	1.450451	0.892110	1.339467	1.268697
SE Skewness	0.793725	0.793725	0.793725	0.793725	0.793725
Kurtosis (G2)	-1.318725	1.894464	-0.351401	3.237977	1.202095
SE Kurtosis	1.587451	1.587451	1.587451	1.587451	1.587451

Soil sample

	P	F	BAA	BAP	BGHIP
N of cases	10	10	10	10	10
Minimum	12.660000	13.500000	5.560000	4.650000	4.830000
Maximum	16.490000	16.380000	6.300000	5.560000	5.620000
Median	13.397000	14.280000	5.930500	4.995000	5.012000
Mean	13.722400	14.522000	5.953400	5.051800	5.067900
95% CI Upper	14.532937	15.168244	6.106663	5.253582	5.232369
95% CI Lower	12.911863	13.875756	5.800137	4.850018	4.903431
Standard Dev	1.133053	0.903386	0.214247	0.282071	0.229912
Skewness (G1)	1.787013	1.115562	-0.071327	0.471456	1.736405
SE Skewness	0.687043	0.687043	0.687043	0.687043	0.687043
Kurtosis (G2)	3.828093	0.626432	0.257679	-0.542839	3.442113
SE Kurtosis	1.334249	1.334249	1.334249	1.334249	1.334249

Air particulate

	P	F	BAA	BAP	BGHIP
N of cases	8	8	8	8	8
Minimum	3.853000	5.990000	1.957000	2.120000	3.632000
Maximum	6.650000	8.510000	2.630000	3.450000	5.450000
Median	4.160000	6.300000	2.165000	2.370000	4.750000
Mean	4.541625	6.587500	2.205875	2.518750	4.215250
95% CI Upper	5.318639	7.268665	2.398775	2.864995	4.683130
95% CI Lower	3.764611	5.906335	2.012975	2.172505	3.747370
Standard Dev	0.929420	0.814770	0.230736	0.414158	0.559651
Skewness (G1)	2.080887	2.339044	0.927036	1.926812	1.754187
SE Skewness	0.752101	0.752101	0.752101	0.752101	0.752101
Kurtosis (G2)	4.413443	5.918293	0.357184	4.241337	3.728224
SE Kurtosis	1.480880	1.480880	1.480880	1.480880	1.480880

The basic statistics reveal a considerable deviation from normality for a number of analytes in all three matrices: Means and medians are different, and skewness and kurtosis significant, in

particular for fluoranthene in the control sample, phenanthrene and benzo[ghi]perylene (both skewed and leptokurtic) in the soil sample, and almost all analytes except benz[a]anthracene in the air particulate.

However, a formal outlier test does not indicate any value which would be subject to deletion on statistical grounds. The tables with the test statistic and the critical values for the 0.01 and 0.05 significance level are given below.

Table 10: Outlier test for K50 results

Grubbs test on the results for soil

	teststatistic				
	Ph	Fl	B [a]A	B [a]P	B [ghi]P
BAM	0,708175277	1,131299078	0,529296647	0,750874172	0,556299129
CENAM	0,443403862	0,234672607	0,715997404	0,077285444	0,42581458
GL	0,937643836	0,301089383	0,450882329	0,609066019	0,42581458
INMETRO	0,867038125	0,611034335	0,38460356	0,812560719	0,060457841
IRMM	0,169806734	0,710659499	1,836201947	1,424462901	1,034742477
KRIS	0,404570721	0,832423587	0,371534507	0,867865899	0,839015653
LGC	0,165570391	0,019925033	0,389271079	1,057179784	0,034360931
LNE	2,442604556	2,056706151	1,617762061	1,801672589	2,401350658
NIST	0,289130385	1,226496456	0,170831193	0,325449712	0,096123618
NMI	0,633333224	0,51805085	1,244360547	0,383591055	0,879030915
max	2,442604556	2,056706151	1,836201947	1,801672589	2,401350658
critat0.05	2,44	2,44	2,44	2,44	2,44
critat0.01	2,93	2,93	2,93	2,93	2,93

Grubbs test on the results for air particulate

	teststatistic				
	Ph	Fl	B [a]A	B [a]P	B [ghi]P
BAM	0,658071857	0,389680568	0,155480897	0,479889406	0,599034204
CENAM	0,432124439	0,316040146	1,058028544	0,389344235	0,062092285
INMETRO	0,740919244	0,733335872	1,078614865	0,335017133	1,042167634
IRMM	0,389086835	0,671968854	1,065612978	0,962796985	0,456087936
LGC	0,163139416	0,027615158	0,19882052	0,123745067	0,045117416
LNE	2,268485187	2,359561866	1,838141756	2,248538412	2,206286303
NIST	0,442883839	0,414227376	0,372179012	0,600616301	0,545429353
NMI	0,557740444	0,138075792	0,025462028	0,38330789	0,419457955
max	2,268485187	2,359561866	1,838141756	2,248538412	2,206286303
critat0.05	2,33	2,33	2,33	2,33	2,33
critat0.01	2,83	2,83	2,83	2,83	2,83

Two laboratory values are identified as stragglers (significance 0.05), namely phenanthrene in soil as submitted by LNE, and fluoranthene in air particulate, also submitted by LNE.

6. Determination of KCRV and uncertainty

At the OAWG meeting in October 2007 analytical methods of the participants were discussed. The discussion revealed no particular result to be excluded from KCRV calculation due to technical reasons. However, according to OAWG guidelines, results of institutes who did not participate in the preceding pilot study (P69) or who used neat commercial calibration standards without assessing their purity, should be excluded from the calculations. INMETRO and LNE did not participate in P69. IRMM used BCR reference materials for B[a]A and B[ghi]P but did not a purity assessment of the remaining solid calibrants. Table 11 shows which results therefore contribute to the calculation of the KCRV and its uncertainty.

Table 11: Results which contribute (+) or do not contribute (-) to the KCRV, number of contributing results n and coverage factor k (95% confidence)

	K50a soil					K50b particulate				
	Ph	Fl	B[a]A	B[a]P	B[ghi]P	Ph	Fl	B[a]A	B[a]P	B[ghi]P
BAM	+	+	+	+	+	+	+	+	+	+
CENAM	+	+	+	+	+	+	+	+	+	+
GL	+	+	+	+	+	not determined				
INMETRO	-	-	-	-	-	-	-	-	-	-
IRMM	-	-	+	-	+	-	-	+	-	+
KRISS	+	+	+	+	+	not determined				
LGC	+	+	+	+	+	+	+	+	+	+
LNE	-	-	-	-	-	-	-	-	-	-
NIST	+	+	+	+	+	+	+	+	+	+
NMIJ	+	+	+	+	+	+	+	+	+	+
n	7	7	8	7	8	5	5	6	5	6
k	2.45	2.45	2.36	2.45	2.36	2.78	2.78	2.57	2.78	2.57

OAWG agreed to use the arithmetic mean of eligible participant's results for the KCRV and the standard deviation of that mean for the standard uncertainty of KCRV. Tables 5 and 6 and figures 6 and 7 display the KCRVs and their standard and expanded uncertainty at 95% confidence level together with the analytical results.

One of the coordinating labs (BAM) developed an alternative approach for the KCRV which is entirely based on performance criteria and does not refer to any formal criterion. It was discussed by OAWG and it was decided to add this concept as an appendix (see appendix 2) to this report.

7. Degrees of equivalence

The degree of equivalence D_i of laboratory i relative to the KCRV x_R is given by a pair of terms,

$$D_i = x_i - x_R \quad (4)$$

and its expanded uncertainty U_D at a 95% level of confidence

$$U_D = \sqrt{U_i^2 + U_R^2} \quad (5)$$

x_i is the result of laboratory i . U_i and U_R are the expanded uncertainties of x_i and x_R , respectively.

Tables 12 and 13 display the degrees of equivalence of all participants for the soil and particulate matter sample. Pair-wise degrees of equivalence between two laboratories were not computed for this key comparison.

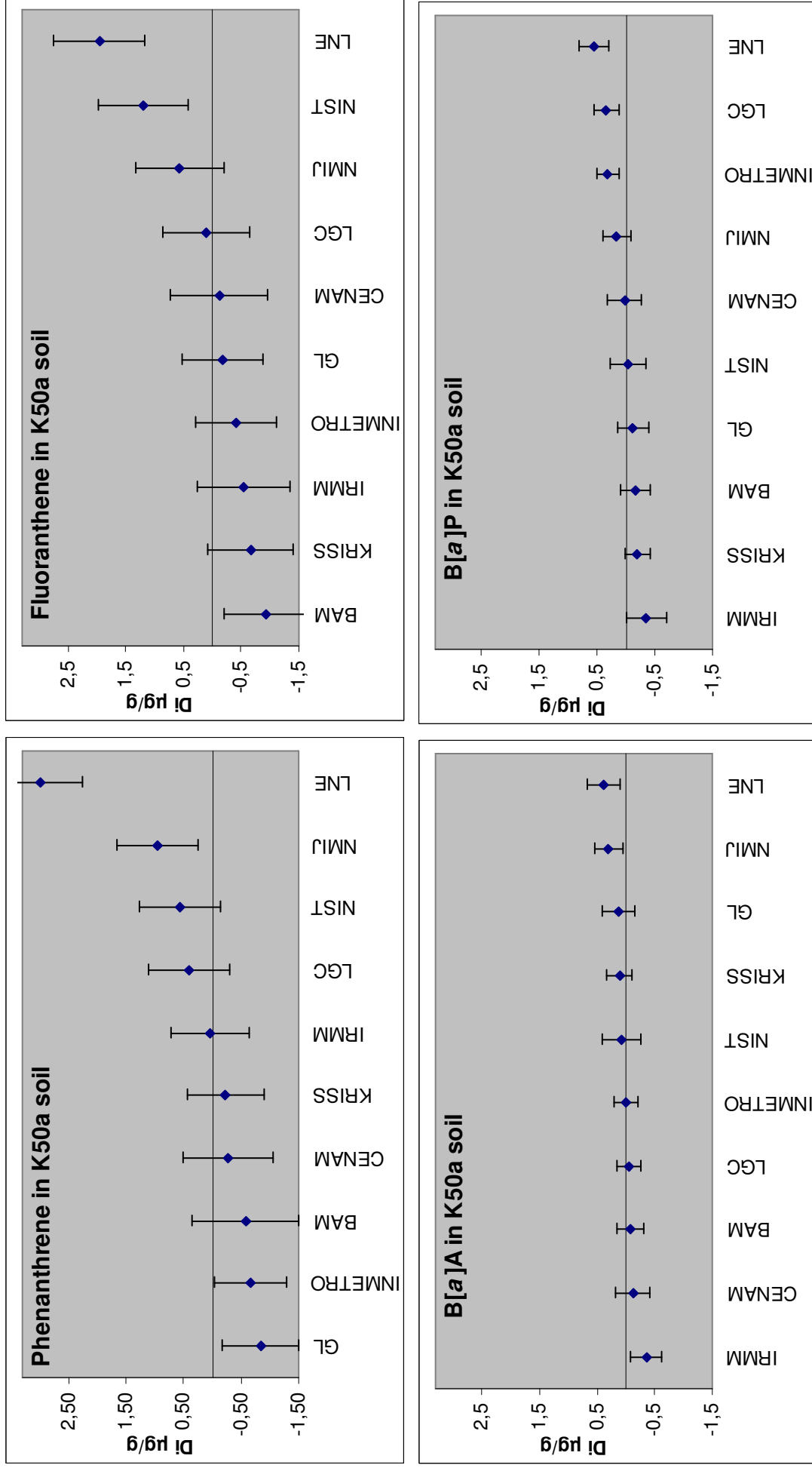
Table 12: Degrees of equivalence D_i and expanded uncertainties U_D at 95% confidence interval, in $\mu\text{g/g}$, K50a soil

	phenanthrene		fluoranthene		B[a]A		B[a]P		B[ghi]P	
	D_i	U_D	D_i	U_D	D_i	U_D	D_i	U_D	D_i	U_D
BAM	-0.57	0.91	-0.93	0.73	-0.08	0.23	-0.16	0.25	-0.06	0.19
CENAM	-0.27	0.79	-0.12	0.85	-0.12	0.30	0.03	0.29	-0.03	0.22
GL	-0.83	0.66	-0.18	0.71	0.13	0.28	-0.12	0.27	-0.03	0.16
INMETRO	-0.67	0.63	-0.42	0.70	-0.01	0.20	0.31	0.20	0.10	0.13
IRMM	0.04	0.68	-0.55	0.81	-0.36	0.27	-0.35	0.35	-0.17	0.31
KRISS	-0.23	0.66	-0.66	0.74	0.11	0.21	-0.20	0.22	-0.13	0.15
LGC	0.42	0.70	0.11	0.76	-0.05	0.21	0.35	0.22	0.06	0.14
LNE	3.00	0.74	1.95	0.79	0.38	0.28	0.56	0.27	0.62	0.22
NIST	0.56	0.70	1.20	0.78	0.07	0.33	-0.04	0.31	0.09	0.18
NMIJ	0.95	0.70	0.56	0.77	0.30	0.25	0.16	0.23	0.27	0.17

Table 13: Degrees of equivalence D_i and expanded uncertainties U_D at 95% confidence interval, in $\mu\text{g/g}$, K50b particulate

	phenanthrene		fluoranthene		B[a]A		B[a]P		B[ghi]P	
	D_i	U_D	D_i	U_D	D_i	U_D	D_i	U_D	D_i	U_D
BAM	-0.40	0.57	-0.16	0.33	-0.01	0.18	-0.12	0.25	-0.23	0.29
CENAM	-0.19	0.57	-0.10	0.49	0.27	0.28	0.24	0.27	0.14	0.36
INMETRO	-0.45	0.56	-0.42	0.30	-0.21	0.19	-0.04	0.26	-0.44	0.27
IRMM	-0.15	0.57	-0.39	0.35	-0.22	0.21	-0.32	0.26	-0.15	0.35
LGC	0.06	0.57	0.18	0.33	-0.02	0.21	0.13	0.29	0.08	0.30
LNE	2.32	0.77	2.08	0.75	0.45	0.33	1.01	0.44	1.34	0.51
NIST	-0.20	0.56	-0.18	0.30	-0.06	0.20	-0.17	0.23	-0.20	0.28
NMIJ	0.73	0.77	0.27	0.71	0.02	0.25	-0.08	0.31	0.34	0.45

Figure 10: Degrees of equivalence and expanded uncertainties at 95% confidence interval for K50a soil, uniform scaling of the y-axis



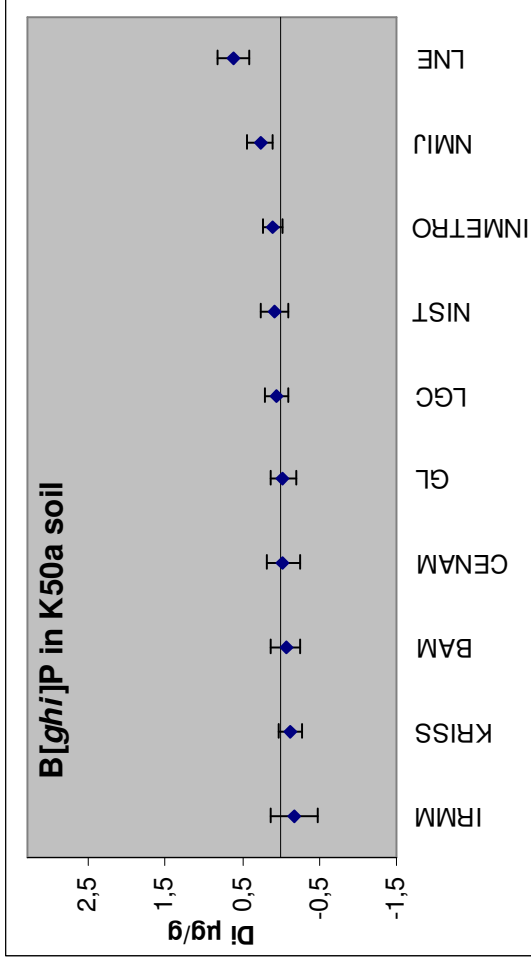
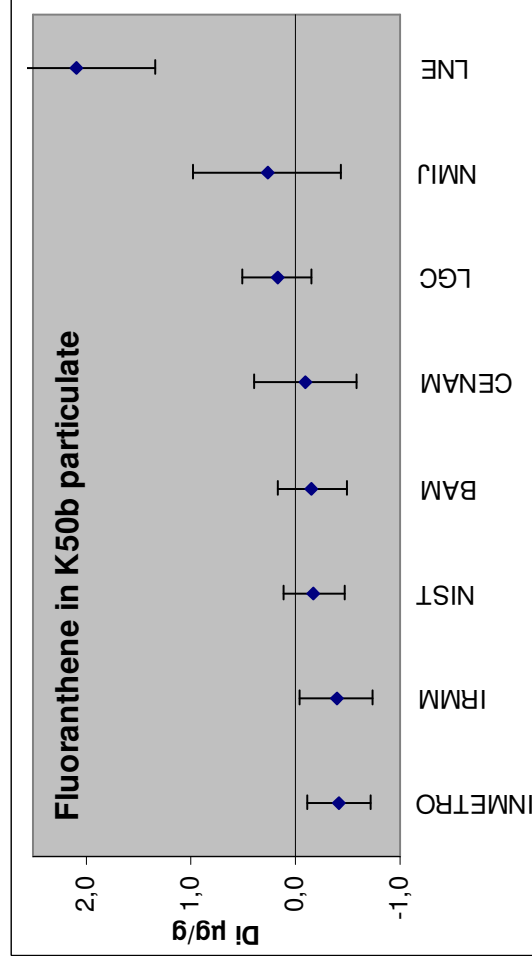
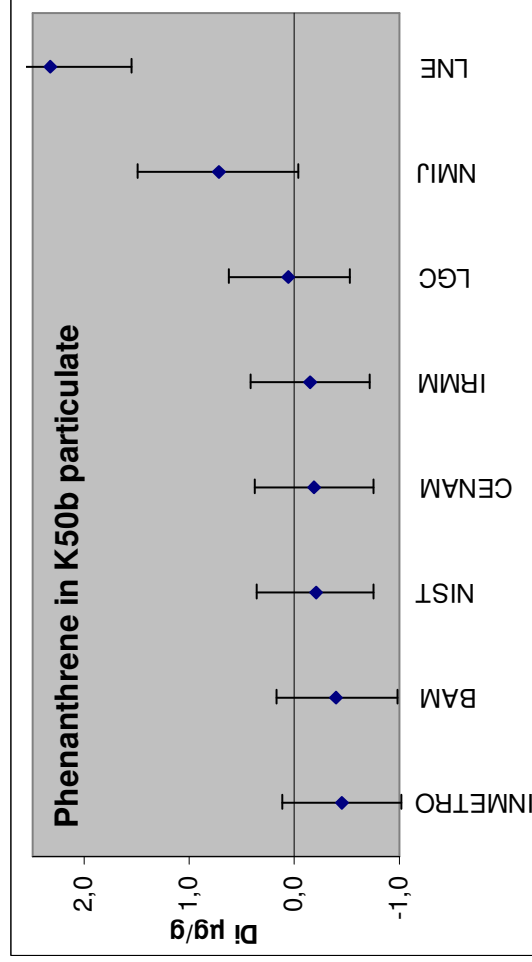
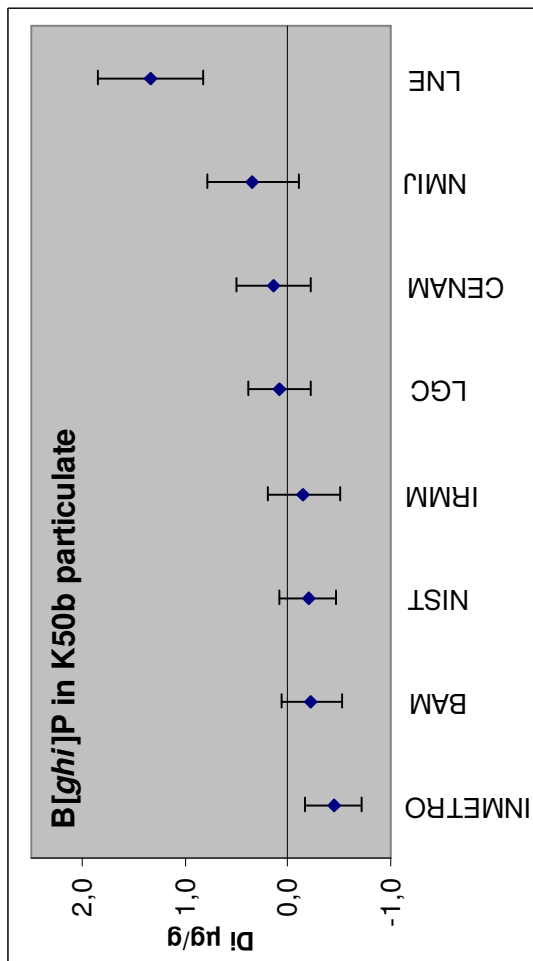
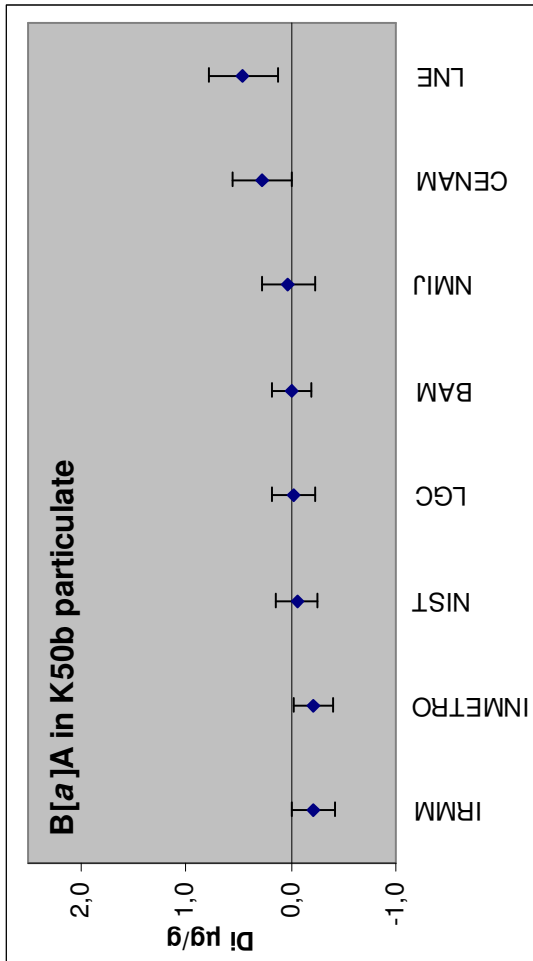
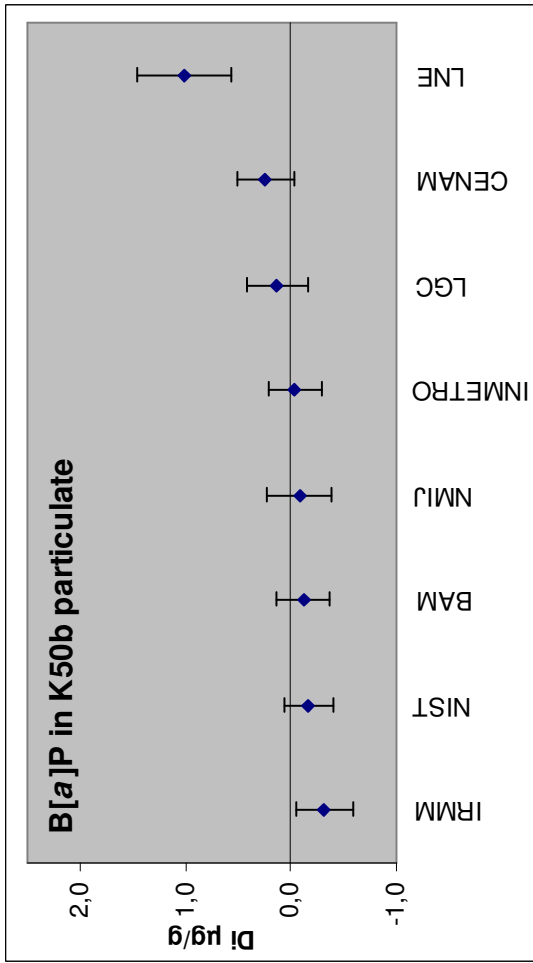


Figure 11: Degrees of equivalence and expanded uncertainties at 95% confidence interval for K50b particulate, uniform scaling of the y-axis





8. Uncertainty estimation

The exercise instructions requested a complete uncertainty budget. A variety of different approaches were used by the participants. The following sources of uncertainty were considered by the majority of labs:

- overall method precision, expressed as standard deviation of the mean of replicate measurements
- concentration of the calibration standard (if a solution was used)
- purity of the calibration standard (if neat chemicals were used)
- dry mass determination

Additional contributions from weightings were considered by LGC, LNE, INMETRO and NMIJ. NMIJ also included sample preparation efficiency and, for the particulate sample, a contribution for inhomogeneity between the two sample jars.

The majority of participants calculated effective degrees of freedom according to the Welch-Satterthwaite equation, resulting in coverage factors between 2 and 3 to give 95% confidence. GL and NMIJ used a coverage factor of 2.

Uncertainty budgets, as reported by the participants, are summarized in appendix 3.

9. Additional investigations

NMIJ results for all samples including the control are systematically higher than the results of the majority of participants or the certified value of the control sample. At the OAWG meeting in November 2007, NMIJ explained this finding with their more drastic extraction conditions (higher temperature and pressure of ASE). NMIJ also presented additional data on the influence of temperature and pressure on extraction efficiency of the soil sample which support this assumption. BAM and NIST agreed to perform additional measurements on the influence of ASE conditions to clarify this finding.

Figure 12 displays results of BAM obtained with the K50a soil sample and figure 13 displays results of NIST obtained with the K50b particulate sample at different extraction temperatures and pressure.

Figure 12: amount of substance, normalized to the value at 110°C/140 bar, obtained at different ASE temperatures, two determinations per temperature, bars are the mean, error bars the two separate results.

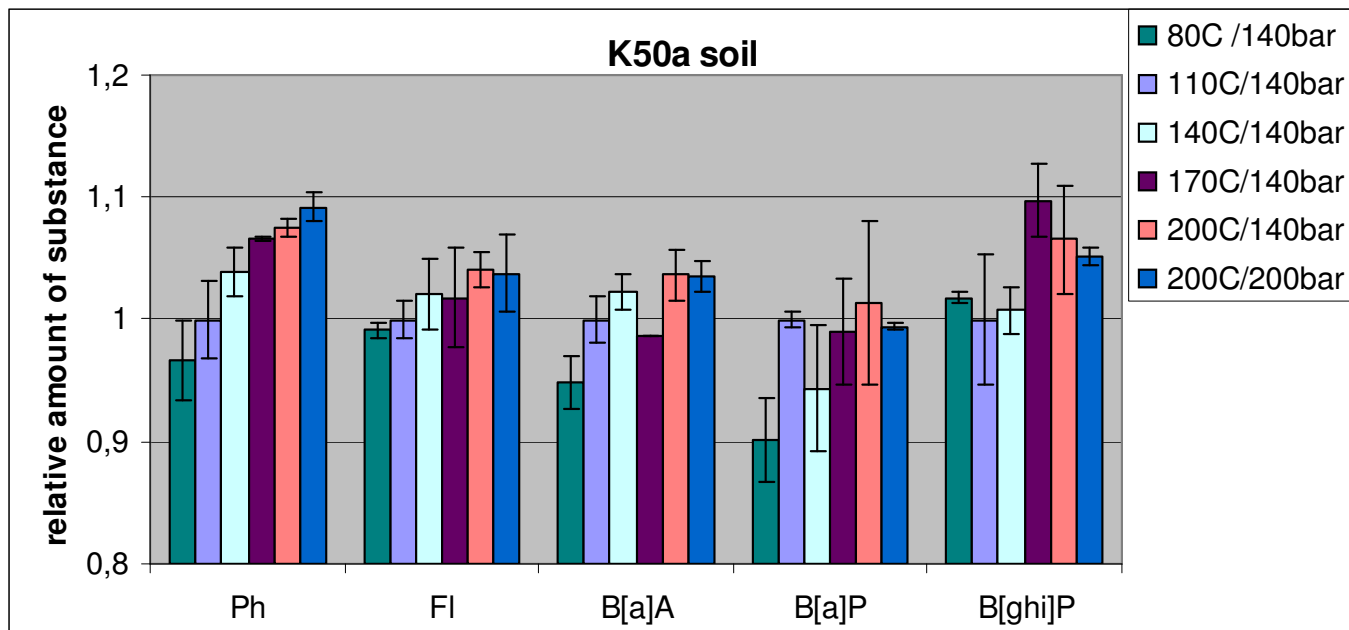
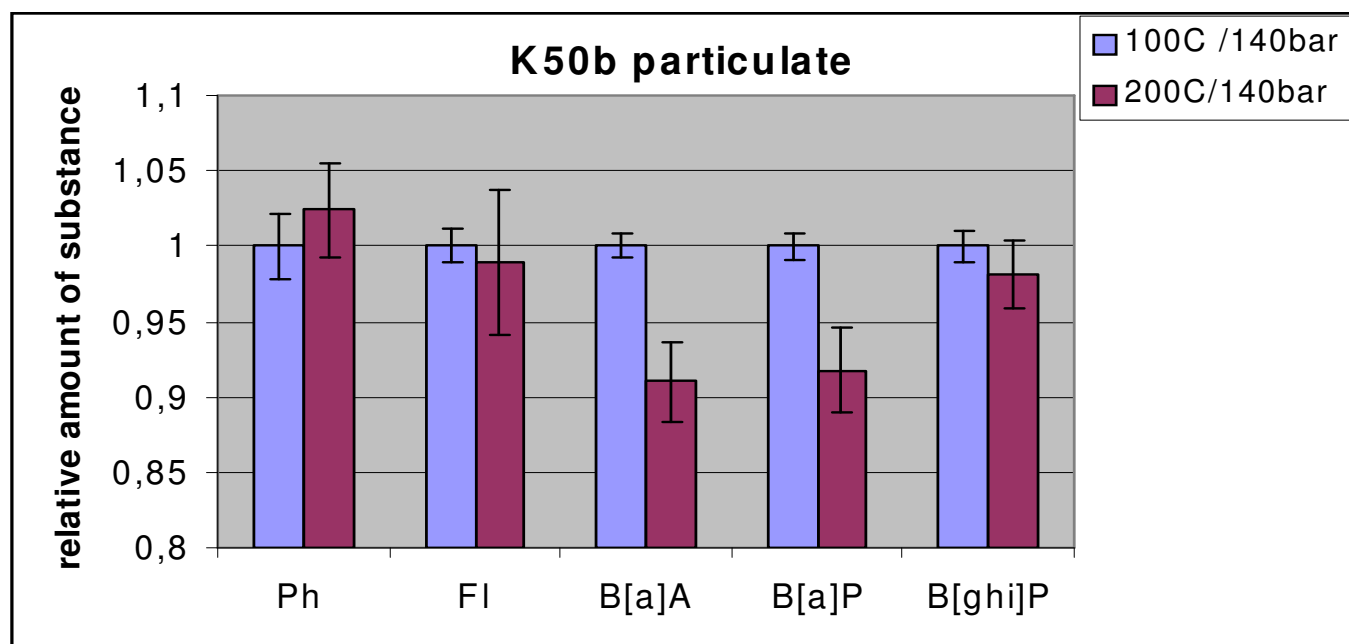


Figure 13: amount of substance, normalized to the value at 100°C/140 bar, obtained at different ASE temperature, three determinations per temperature, bars are the mean, error bars the standard deviation.



Results for the soil sample could be treated by regression analysis. For the air particulate, only measurements at 100°C and 200°C were available. Statistically significant changes have been observed for

- phenanthrene and benz[a]anthracene in the soil sample leading to potentially higher values at higher temperatures and therefore pointing into the claimed direction, and
- benz[a]anthracene and benzo[a]pyrene in the particulate but leading to lower values at higher extraction temperatures, i.e. pointing into the opposite direction.

For the study on the soil samples, the F statistic is given in the table below, and the regression parameters intercept and slope and their uncertainties for those analytes with significant changes. Only results obtained at 140 bar and different temperatures (figure 12) were included in the regression.

Table 14: Results of the regression analysis for the soil sample

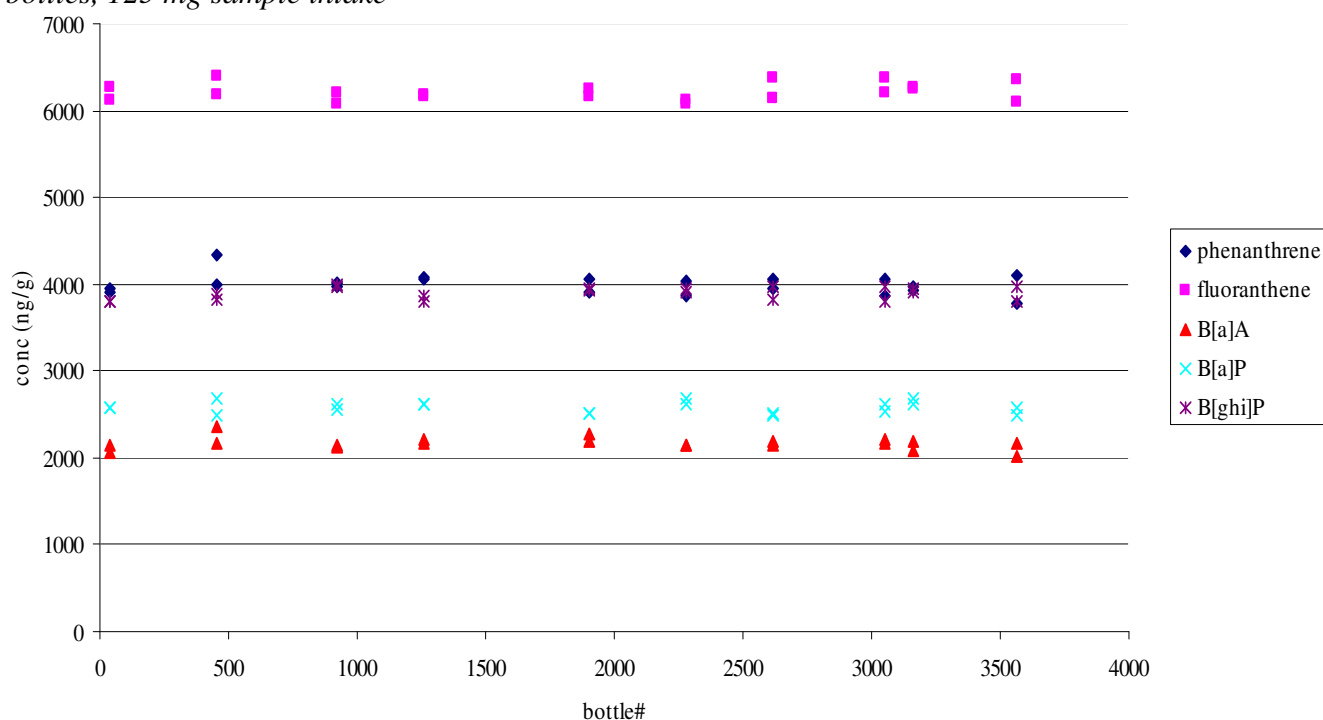
F_krit:	5.317655063				
	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
F	21.91190788	3.54255225	5.991605797	2.602776737	3.137990536
intercept	1.675682938		0.888367094		
slope	0.001770125		0.000520894		
u(inter)	0.055318553		0.031130376		
u(slope)	0.00037815		0.000212803		
cov	-2.00196E-05		-6.33991E-06		

The data do not show a uniform tendency of PAH concentration with ASE temperature. Instead, it is dependent on the type of sample and analyte. Furthermore, at higher temperatures, processes like decomposition or conversion of higher molecular PAHs into lower molecular PAHs or pyrolysis of organic matter can not be completely excluded. A peculiar smell of burnt organic matter was observed for the soil extracts at 200°C. The total organic carbon content of the soil is rather high ((18.1±0.3) mg/g).

Because of these findings, OAWG agreed to use the mean of eligible participant's results instead of the median as KCRV. This includes the component of any temperature differences observed and assumes all values are credible.

NMIJ also reported a between bottle inhomogeneity of the particulate matter sample of about 4% to 5% depending on the analyte. This could not be confirmed by additional measurements by NIST (figure 14). The material is a candidate NIST CRM and has undergone extensive assessment when bottled, and this degree of heterogeneity was not observed.

Figure 14: Additional homogeneity assessment for K50b particulate, 2 determinations out of 10 bottles, 125 mg sample intake



10. How far does the light shine

Figures 15 to 17 summarize all results, expressed as % deviation from the KCRV or % deviation from the certified value in case of the SRM 1649a sample. Red symbols are results obtained by ASE. Blue symbols are results obtained by Soxhlet extraction.

Figure 15: Deviation from KCRV for K50a soil, blue symbols: ASE, red symbols: Soxhlet

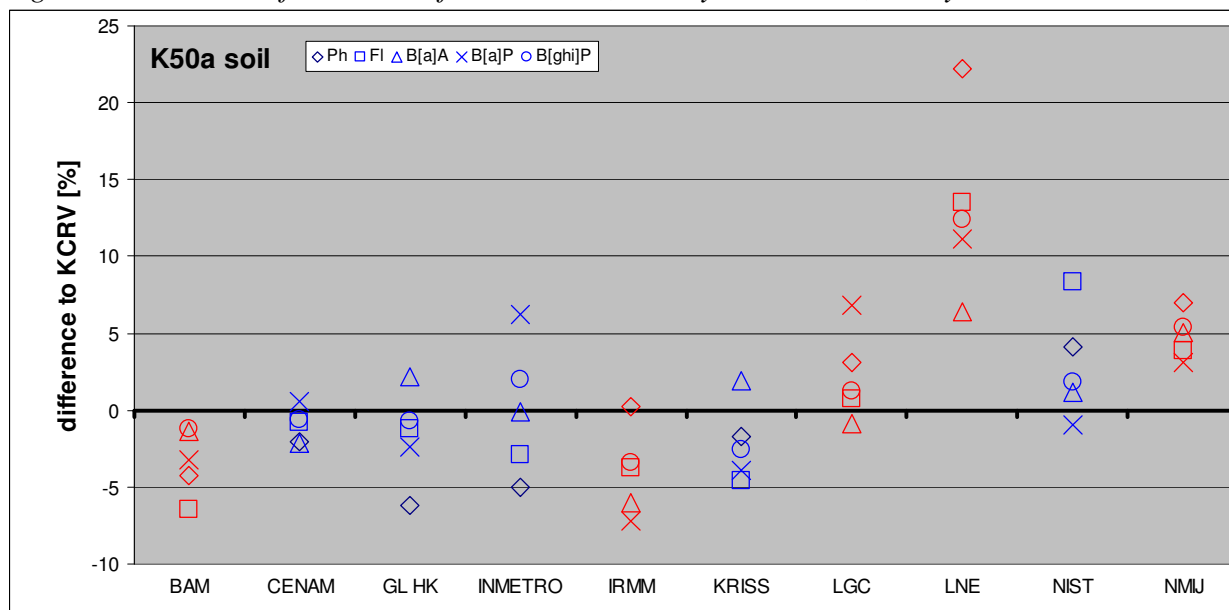


Figure 16: Deviation from KCRV for K50b particulate matter, blue symbols: ASE, red symbols: Soxhlet

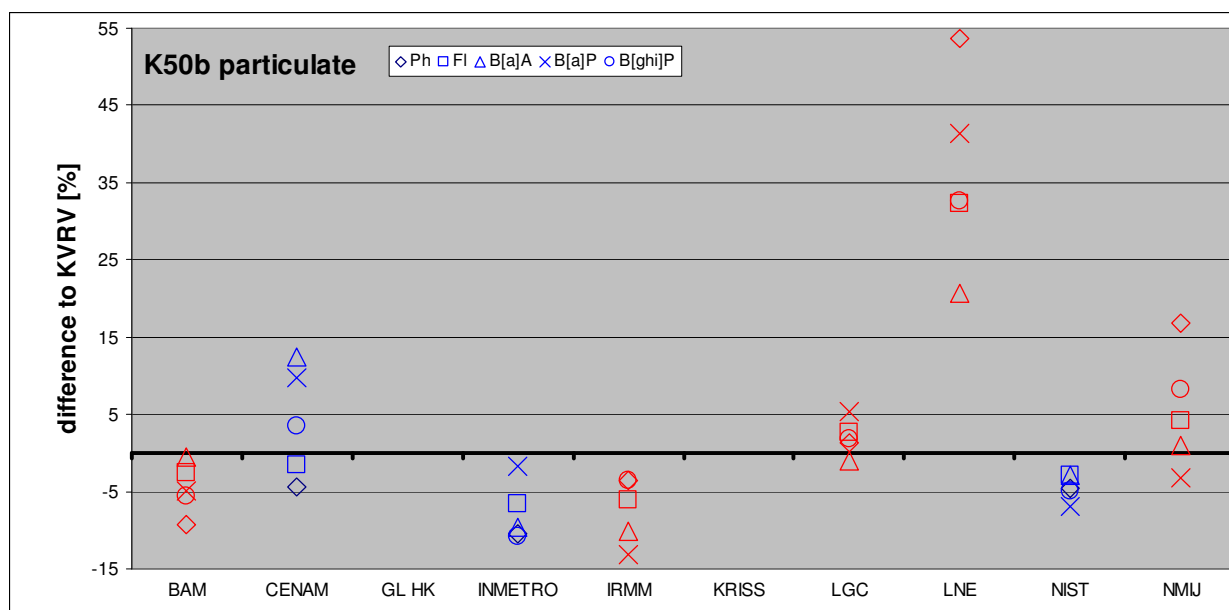
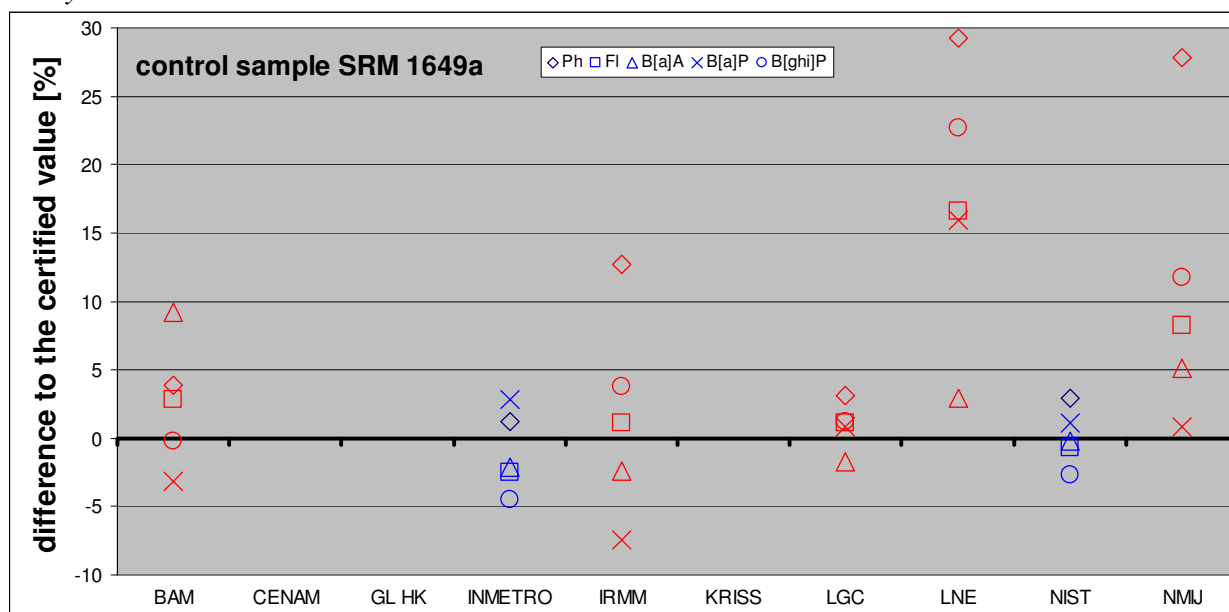


Figure 17: Deviation from the certified value for SRM 1649a control sample, blue symbols: ASE, red symbols: Soxhlet



With a few exceptions, participants agree within the range $\pm 5\%$ from the KCRV for the soil and $\pm 10\%$ from the KCRV for the particulate in analysing five selected PAHs.

CMC claims based on measurements in this study could be applied to other solid matrices (e.g. sediment, sewage sludge, waste) and to extracts of these matrices provided that the concentration range is similar and extraction/clean-up steps are similar to the ones performed in this study. When extending the claim to other solid matrices, extraction efficiency should be studied and it should be demonstrated that extraction efficiency effects are negligible for the particular material.

CMC claims based on measurements in this study could be applied to other PAHs provided that the concentration range is similar to the one in this study.

Appendix 1: Revised INMETRO data

After initial discussion of the results at the OAWG meeting in Braunschweig in October 2007, INMETRO assessed the purity of their commercial neat chemical PAH standards and recalculated their analytical results with respect to these purity values. Purity assessment was done by GC-FID on two columns with different polarity. Revised data were submitted to the coordinators in February 2008. These data are summarized below.

K50a soil	mean	combined uncertainty	expanded unc. (95% CI)
	[$\mu\text{g/g}$]	[$\mu\text{g/g}$]	[$\mu\text{g/g}$]
Phenanthrene	12.74	0.0689	0.14
Fluoranthene	13.97	0.0699	0.14
Benz[<i>a</i>]anthracene	5.871	0.0319	0.067
Benzo[<i>a</i>]pyrene	5.281	0.0305	0.063
Benzo[<i>ghi</i>]perylene	5.054	0.0241	0.049

K50b particulate	mean	combined uncertainty	expanded unc. (95% CI)
	[$\mu\text{g/g}$]	[$\mu\text{g/g}$]	[$\mu\text{g/g}$]
Phenanthrene	3.853	0.0430	0.095
Fluoranthene	5.99	0.0550	0.12
Benz[<i>a</i>]anthracene	1.957	0.0250	0.054
Benzo[<i>a</i>]pyrene	2.38	0.0594	0.13
Benzo[<i>ghi</i>]perylene	3.632	0.0359	0.078

Control SRM 1649a	mean	combined uncertainty	expanded unc. (95% CI)
	[$\mu\text{g/g}$]	[$\mu\text{g/g}$]	[$\mu\text{g/g}$]
Phenanthrene	4.166	0.0312	0.074
Fluoranthene	6.27	0.0500	0.12
Benz[<i>a</i>]anthracene	2.146	0.0172	0.037
Benzo[<i>a</i>]pyrene	2.57	0.0571	0.14
Benzo[<i>ghi</i>]perylene	3.79	0.0598	0.14

Uncertainties:

K50a soil

Sources of uncertainty	Ph	Fl	B[<i>a</i>]A	B[<i>a</i>]P	B[<i>ghi</i>]P
repeatability of area	3.58E-05	3.59E-08	2.02E-08	1.76E-08	1.54E-08
mass of sample	8.00E-08	8.77E-11	3.68E-11	3.31E-11	3.17E-11
mass of IS added into the sample	2.41E-08	2.52E-08	3.99E-08	2.58E-08	2.47E-08
repeatability of analysis	0.04012	0.04660	0.02679	0.02328	0.01522
calibration curve	0.04592	0.03928	0.009306	0.01475	0.01384
purity of standard	0.03135	0.03427	0.01452	0.01298	0.01251

K50b particulate

Sources of uncertainty	Ph	Fl	B[a]A	B[a]P	B[ghi]P
repeatability of area	1.6870E-08	2.7400E-08	1.144E-08	3.642E-08	2.4640E-08
mass of sample	2.6040E-10	4.0510E-10	1.323E-10	1.610E-10	2.4550E-10
mass of IS added into the sample	1.9370E-08	1.9650E-08	1.081E-08	9.518E-09	1.4510E-08
repeatability of analysis	0.04002	0.05402	0.02209	0.05826	0.03185
calibration curve	0.006852	0.009020	0.01099	0.009404	0.01608
purity of standard	0.01401	0.004447	0.003745	0.006345	0.004437

Control SRM 1649a

Sources of uncertainty	Ph	Fl	B[a]A	B[a]P	B[ghi]P
repeatability of area	3.1180E-08	2.9290E-08	1.360E-08	5.823E-08	6.3500E-08
mass of sample	3.0330E-10	4.5650E-10	1.562E-10	1.867E-10	2.7600E-10
mass of IS added into the sample	2.1210E-08	2.0810E-08	1.200E-08	1.038E-08	1.5340E-08
repeatability of analysis	0.03053	0.04911	0.01371	0.05636	0.05606
calibration curve	0.006422	0.009247	0.01034	0.009087	0.02090
purity of standard	0.0001681	0.0001400	0.0001484	0.0000923	0.0002876

Appendix 2: Alternative Estimation of KCR value and uncertainty

1. Introduction

Degrees of equivalence (DoE) are a measure of laboratory performance and widely used for the assessment of CCQM key comparisons and pilot studies. In a wider sense, they serve as confirmation for CMC claims made by the corresponding laboratories. The DoE of a laboratory result X_{lab} is composed from two single values, namely the difference of the laboratory result and the reference value X_{ref} , and the uncertainty of this difference. Both values can conveniently be combined into an E_n value according to

$$E_n = \frac{X_{ref} - X_{lab}}{2 \cdot u(X_{ref} - X_{lab})} = \frac{X_{ref} - X_{lab}}{2 \cdot \sqrt{u^2(X_{lab}) + u^2(X_{ref}) - 2 \cdot u(X_{lab}, X_{ref})}} \quad (1)$$

being $u(X_{lab}, X_{ref})$ the covariance. The KCR value and uncertainty play a major part in the assignment of DoE's and should thus be most reliable. Self-consistent data assessment following the *Paule-Mandel* [1] or *Birge* [2] approaches using weighted means and direct uncertainty propagation is not appropriate in the case of KC50 given the still considerable biases between laboratories, even in the largest-consistent-subset philosophy developed by *Cox* [3]. Basic ideas of the named approaches can however be taken on board, leading to the following principles of KCR value and uncertainty estimation:

- (1) Only well-performing laboratories shall contribute to the KCR value and uncertainty.
- (2) The maximum possible number of well-performing laboratories (from the total number of participants) shall be the basis for the KCR value and uncertainty.
- (3) Performance of a laboratory shall be assessed by its compatibility with the derived KCR value and uncertainty.
- (4) Performance of a laboratory shall be assessed for all analytes and samples under investigation.
- (5) Except in cases where considerable influence of a physical constraint is to be expected, residual biases of the well-performing and thus contributing laboratories shall be random with decreasing with distance from the centre probabilities of occurrence for the set, i.e. follow a symmetric, bell-shaped distribution. The unbiased location estimator for the KCR value is the classical mean while the classical variance might over- or underestimate the dispersion (depending on the kurtosis of the distribution).
- (6) Non-contributing laboratories are assigned a DoE referring to the KCR value and uncertainty defined by the contributing laboratories.

A measure of compatibility according to principle (3) is a statistic frequently called the *zeta* score ζ

$$\zeta_{lab} = \frac{|X_{ref} - X_{lab}|}{\sqrt{u^2(X_{lab}) + u^2(X_{ref})}} \quad (2)$$

which closely resembles the E_n value (except the sign and the factor of 2 in the denominator). Sums of a certain number v of squared *zeta* scores follow a chi square distribution with v degrees of freedom, a fact which will be used in assessing compatibility of laboratory values with the KCR value and uncertainty. Note that the test statistic for the (single) Grubbs outlier test is different from eqn. 2 since it refers to the standard deviation of the data distribution according to

$$t_{lab} = \frac{|X_{ref} - X_{lab}|}{s_p} \quad (3)$$

The value of this test statistic is then compared with the tabulated critical values for the Grubbs test.

Requirement (4) is a consequence of the fact that the outcome of the KC shall underpin, in a representative manner, CMC claims for PAH measurements and possibly similar other environmental contaminants, but as a minimum for the 16 EPA PAH. A well-performing laboratory shall thus perform on all 5 selected analytes in the manner defined by requirement (3). An analyte-by-analyte inclusion or exclusion of laboratories to or from the group of contributing laboratories is not encouraged here.

Requirement (5) mentions cases with a (physical) constraint. This refers to e.g. ultra-trace (or ultra-high purity) analysis and values obtained close to the LOQ of a method. It may also refer to methods including processes of considerable non-linearity (growth processes as e.g. involved in microbiological methods). In these cases, suitable data transformation is required before an assessment. Experience shows that for a (sub-)set of laboratory values complying with the requirements (3) and (4), most often the normality assumption cannot be rejected on statistical grounds, so not only the (valid for any symmetric distribution) mean but also the classical standard deviation are good estimators.

Note that the requirement of bias randomness for the set of laboratory data does not alter the systematic character of the bias for the individual laboratory. Note also that this KCR value and uncertainty estimation is entirely based on performance criteria and does not refer to any formal criterion (NMI, designated lab, participation in the preceding pilot study etc.).

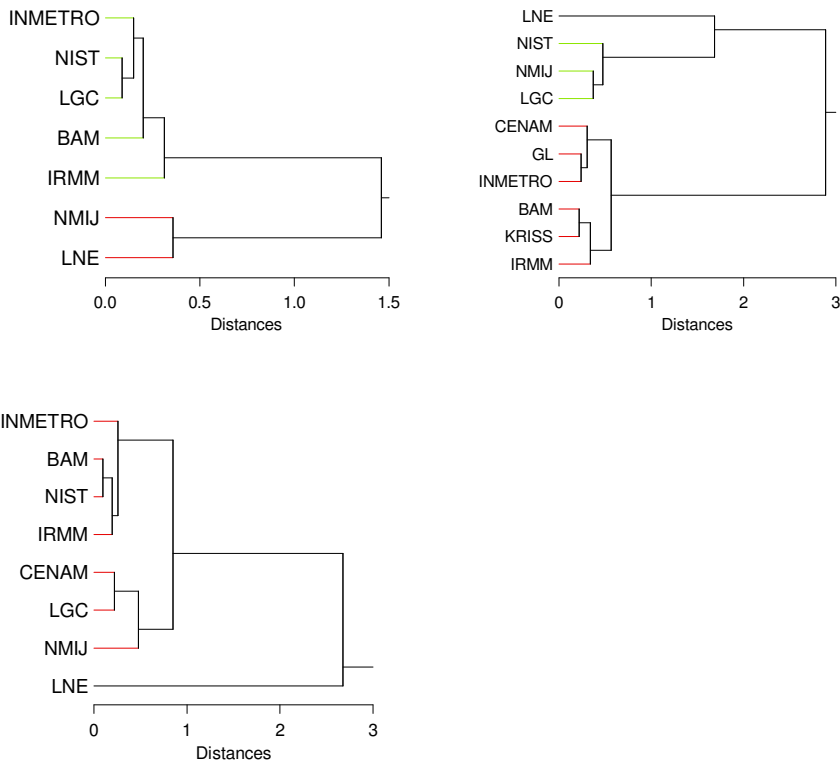
2. Scrutinising the data

Data as given in the KC50 draft A report have been submitted by the participating laboratories for 5 selected PAH in a control sample, a soil and in particulate matter. Numbers of participating laboratories were different for the three samples, with a maximum number for the soil matrix sample.

Basic statistics reveal a considerable deviation from a normal distribution. A Grubbs outlier test according to eqn. (3) identifies the values of LNE for phenanthrene in soil and fluoranthene in air particulate as stragglers (see Table 10, clause 5.1.).

2.1. Checking laboratory performance

Pre-selection of contributing laboratories should identify laboratories revealing systematic bias for all analytes and all matrices. An influence of systematic bias is assumed if a laboratory reports low or high values consistently for all analyte under investigation. This may conveniently be illustrated by a cluster analysis using Euclidean distance as the metric. Laboratories consistently reporting low or high values will be grouped into a separate cluster. Furthermore, cluster analysis shows similarities or dissimilarities between the laboratories. Dendrograms using the 5 analyte values reported as the variables are shown below for the three samples. Ward linkage has been used for collating the clusters.

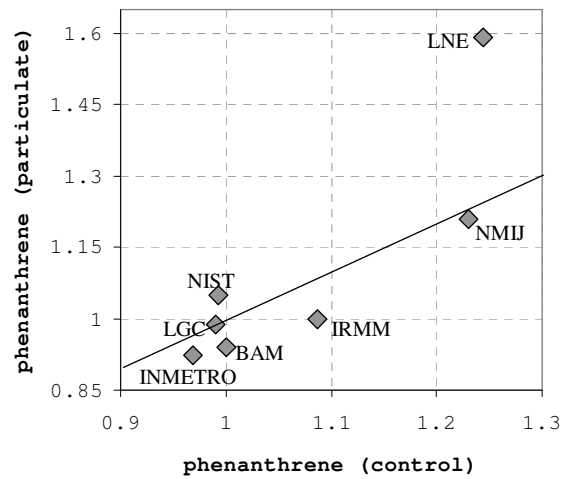
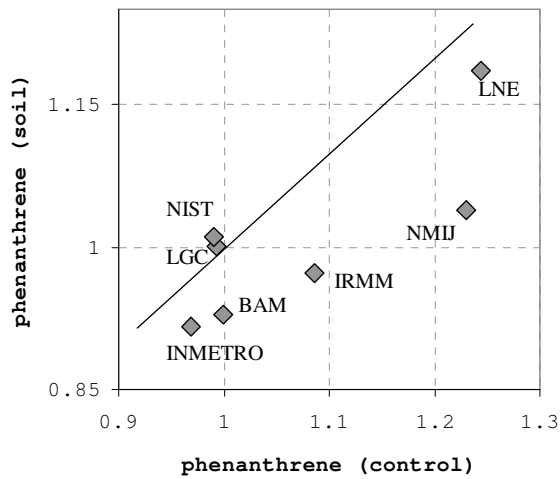


Dendrograms for the three samples: control (left), soil (right), and air particulate (below).

For soil and air particulate, LNE is distant from the main group for all analytes under consideration and should not be included in the group of contributing laboratories. The next candidate for exclusion from this group is NMIJ: For the control sample, its results are similar to those of LNE but for soil and air particulate it is less distant from the main group. As will be discussed below, some of the results submitted by NMIJ satisfactorily agree with the remainder, only the values for phenanthrene and benzo[ghi]perylene make it distant and dissimilar. In accordance with criterion 4, this laboratory should not contribute to the KCR value and uncertainty.

Youden plot analysis is a convenient tool for looking into the method consistency of a laboratory with respect to different matrices analysed. The laboratory results are appropriately normalised and plotted analyte-by-analyte for different matrices, e.g. the soil result versus the result obtained on the control sample. In such a plot, the ideal laboratory is represented by a point at {1,1}. Laboratory bias shifts the point up or down on the diagonal line $y = x$, and an additional influence of the matrix shifts the point off from the diagonal. Well-performing laboratories without any significant laboratory bias and matrix influence should randomly allocate in the vicinity of the ideal point {1,1}.

The figure below shows a *Youden* plot for the phenanthrene results obtained on the soil and the air particulate samples, both plotted versus the result for the control sample. Data were normalised with respect to the median of the set taking into account that some of the distribution are skewed (see clause 5.1.).



Youden plot for phenanthrene in soil and particulate versus the phenanthrene result for the control sample.

Two laboratories, namely LNE and NMIJ reveal systematic laboratory bias (high values for all samples) and an additional influence from the matrix (LNE for the air particulate, NMIJ for the control). For all other analytes, the results of the *Youden* plot analysis are similar. The following tables list the laboratories which are allocated within 10% from the point {1,1} and thus candidates for inclusion in the group of contributing laboratories.

Results of the Youden plot analysis: Well-performing laboratories

soil vs control

phenanthrene	fluoranthene	B (a)A	B (a)P	B (ghi)P
BAM	BAM	BAM	BAM	BAM
INMETRO	INMETRO	INMETRO	INMETRO	INMETRO
IRMM	IRMM	IRMM	IRMM	IRMM
LGC	LGC	LGC	LGC	LGC
NIST	NIST	NIST	NIST	NIST

particulate vs control

phenanthrene	fluoranthene	B (a)A	B (a)P	B (ghi)P
BAM	BAM	BAM	BAM	BAM
INMETRO	INMETRO	INMETRO	INMETRO	INMETRO
IRMM	IRMM	IRMM	IRMM	IRMM
LGC	LGC	LGC	LGC	LGC
NIST	NIST	NIST	NIST	NIST

A core group of only 5 laboratories complies with requirement (4). However, CENAM, KRISS and GL didn't submit values for the control sample (since this was optional), so they couldn't be considered in the above *Youden* plot analysis. But CENAM performs well for both the soil and the particulate. This will be considered separately in clause 3.

2.2. Impact of method layout

The cluster analysis described above revealed a division of the laboratory results into two subgroups (and one distant laboratory). Although all laboratories used GC-MS for separation and detection, the layout of the extraction and clean-up (if applicable) steps was different. If one groups the method layout details into the two clusters, the picture shown in the following two tables is obtained.

For the soil sample, no clear influence of one or a group of method parameters can be derived from the table. Neither the extraction method, the solvent nor the clean-up step may serve as a distinctive criterion between the groups. CENAM, GL, and INMETRO which are closest in the cluster analysis all used Soxhlet extraction but this indication is too weak to be significant. Moreover, in laboratory group 2, Soxhlet has also been used for extraction.

Method details clustered according to the results obtained on the soil and air particulate samples

		soil					
	lab	extraction	solvent	temp, cycles	clean-up	calibration	remarks
group 1	CENAM	soxhlet	toluene	18 h	yes	4 point	deuterated istd
	GL	soxhlet	hexane/acetone	24 h	yes	single point	13C labelled
	INMETRO	soxhlet	dichloromethane	20 h	yes	6 point	deuterated istd
	BAM	ASE	toluene	100, 2	yes	5 point	deuterated istd
	KRISS	soxhlet	hexane/acetone	14 h	none	single point	deuterated istd
	IRMM	ASE	dichloromethane	100, 2	yes	4 point	deuterated istd
group 2	NIST	soxhlet	dichloromethane	20 h	yes	bracketing	deuterated istd
	LGC	ASE	toluene	125, 5	none	exact match	13C labelled
	NMIJ	ASE	toluene	190, 2	yes	single point	deuterated istd

		particulate					
	lab	extraction	solvent	temp, cycles	clean-up	calibration	
group 1	INMETRO	soxhlet	dichloromethane	12 h	yes	8 point	
	BAM	ASE	toluene, dichloromethane	100, 3	yes	5 point	
	NIST	soxhlet	dichloromethane	20 h	yes	bracketing	
	IRMM	ASE	dichloromethane	100, 2	yes	4 point	
group 2	CENAM	soxhlet	toluene	18 h	yes	4 point	
	LGC	ASE	toluene	125, 5	none	exact match	
	NMIJ	ASE	toluene	190, 2	yes	single point	

For the air particulate sample, one might recognise a certain impact of the extraction solvent distinguishing group 1 using dichloromethane from group 2 where toluene has been used.

3. Defining the contributing laboratories on the basis of *zeta* scores

A core group of 5 contributing laboratories, namely BAM, INMETRO, IRMM, LGC and NIST, has been identified on the basis of cluster and *Youden* plot analysis. These laboratories are further scrutinised using the *zeta* score performance measure. The reference value is the mean of means of the laboratories included (requirement 5), and the uncertainty of the difference is combined from the uncertainty statement of the laboratory and the standard deviation of the mean. For all laboratories and all analytes, the *zeta* scores according to equation (2), and the sum

$$\zeta_{lab}^2 = \sum_{k=1}^5 \zeta_{lab,k}^2 \quad (4)$$

of $\zeta_{lab,k}^2$ over all k analytes are calculated. This *zeta* square is assessed against the critical value for a chi square distribution with 5 (= number of terms in the sum) degrees of freedom which is 11.07 at the 95% confidence level. Laboratories grossly exceeding the critical value will be excluded from the group. The remaining laboratories (which were not in the core group at the beginning) are sequentially included in the group using all possible combinations. Assessment of the set of data as a whole is done on the basis of the average ζ^2 over all included laboratories according to

$$\zeta^2 = \frac{\sum_{lab=1}^n \zeta_{lab}^2}{n} \quad (5)$$

(with n being the number of included laboratories) by comparing it with the same critical value given above.

3.1. Control sample

For the control sample, only the core group remains after exclusion for technical reasons of LNE and NMIJ. Mean and standard deviation of the mean are

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
mean	4.3332	6.47	2.2152	2.478	3.982
sd_mean	0.0871	0.0609	0.0496	0.0460	0.0639

and the average ζ square is 9.20, still below the critical value. The reference value for the selected laboratories is in excellent agreement with the values certified for the control sample

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
ref value	4.14	6.45	2.208	2.509	4.01
u(ref value)	0.185	0.09	0.0365	0.0435	0.455
E_n	0.507	0.108	0.058	0.258	0.031

as can clearly be seen from the normalized errors E_n which are all (much) smaller than unity. Individual ζ_{lab}^2 slightly exceed the critical value for IRMM and INMETRO, most probably due to an underestimation of the uncertainty of the laboratory. Replacement of the individual estimate by the average uncertainty stated by all contributing laboratories makes almost all ζ_{lab}^2 smaller than the critical value.

3.2. Soil

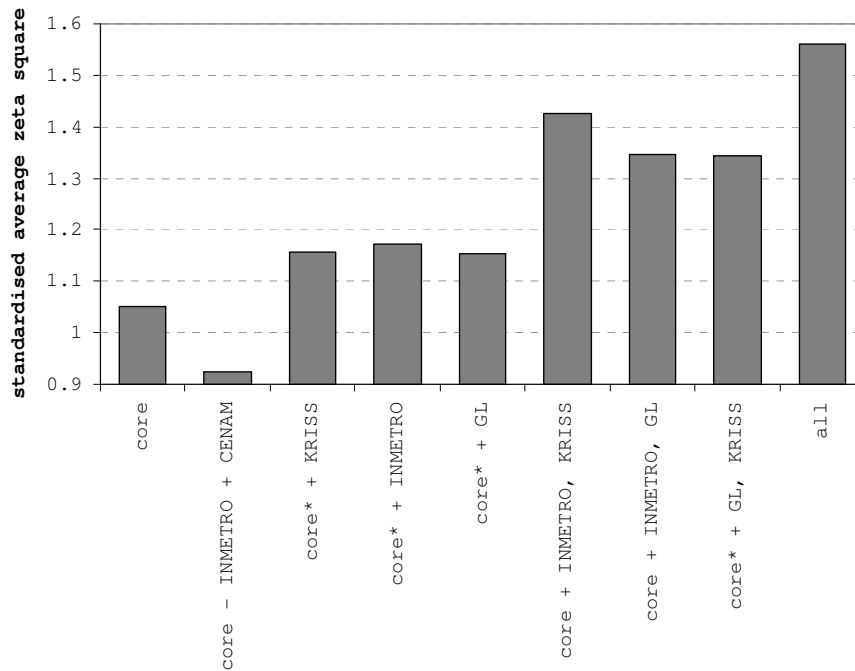
For the core group, the average ζ square is 11.62 and exceeds the critical value. Bearing in mind the fact that CENAM didn't participate in Youden plot analysis but was conveniently accommodated in the main laboratory cluster, INMETRO is excluded, and CENAM included in a new core group (core*). This yields an average ζ square of 10.23 which is satisfactory. The inclusion of more laboratories (according to requirement (1)) increases the average ζ square above the permissible limit as shown in the figure below. The accepted contributing laboratories are BAM, CENAM, IRMM, LGC and NIST, and the KCR values and uncertainties calculated for this core* group of laboratories then are:

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
mean	13.526	14.372	5.812	4.966	4.978
sd_mean	0.2101	0.3617	0.0705	0.1156	0.0462

3.3. Air particulate

Here the same as in the case of the soil sample applies. For the core* group of BAM, CENAM, IRMM, LGC and NIST, an average ζ square of 10.21 is calculated which satisfies the compatibility criterion. If CENAM is replaced by INMETRO, the average ζ square increases to an unsatisfactory level of 12.58. If INMETRO is added to the core* group, this yields average ζ square of 14.34. Thus, the KCR value and uncertainty are calculated from the data of BAM, CENAM, IRMM, LGC and NIST as:

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
mean	4.154	6.3	2.172	2.392	4.038
sd_mean	0.073252986	0.091651514	0.079082236	0.102146953	0.075986841



Standardised (with respect to the critical value) zeta squares for different combinations of contributing laboratories, soil analysis.

4. Assigning degrees of equivalence

Degrees of equivalence are calculated according to equation (1) for all participating laboratories using the KCR values and uncertainties determined under clauses 3.1. to 3.3.

4.1. E_n values for the original data

The following tables display the E_n values for the original data not corrected for any observed influence of temperature on the extraction efficiency.

E_n for the control sample

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
BAM	-0.191	1.313	1.963	-0.522	0.141
INMETRO	-0.903	-1.269	-0.659	0.627	-1.097
IRMM	1.270	0.164	-0.562	-0.943	0.546
LGC	-0.299	0.154	-0.321	0.236	0.287
LNE	1.920	1.662	0.152	0.884	2.047
NIST	-0.420	-0.493	-0.153	0.674	-0.642
NMIJ	4.449	2.311	0.920	0.474	2.908

E_n for soil

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
BAM	-0.866	-1.144	0.151	-0.466	-0.227
CENAM	-0.469	-0.070	-0.046	0.201	-0.040
GL	-1.797	-0.163	0.979	-0.285	-0.056
INMETRO	-1.777	-0.546	0.381	1.317	0.729
IRMM	0.008	-0.581	-1.030	-0.834	-0.471
KRISS	-0.550	-0.777	1.287	-0.641	-0.773
LGC	0.710	0.212	0.335	1.524	0.671
LNE	4.989	2.429	1.994	2.027	3.173
NIST	1.015	1.590	0.639	-0.020	0.668
NMIJ	1.679	0.766	1.886	0.726	1.888

E_n for air particulate

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
BAM	-1.105	-0.123	-0.012	-0.317	-0.765
CENAM	-0.068	0.068	1.026	1.136	0.725
INMETRO	-1.772	-1.450	-1.296	-0.051	-2.416
IRMM	0.137	-0.908	-1.133	-1.098	-0.275
LGC	1.088	1.207	-0.064	0.654	0.689
LNE	4.461	3.054	1.424	2.452	3.033
NIST	-0.152	-0.239	-0.293	-0.586	-0.704
NMIJ	1.642	0.591	0.117	-0.109	1.021

4.2. E_n values for the corrected data

One might be tempted to use the additional information gained during the study into the influence of temperature on the extraction efficiency (see clause 9). For the soil, two dependencies (phenanthrene and benz[*a*]anthracene) turned out to be significant, and correction coefficients (including their uncertainties) could be calculated from the regression parameters.

	phenanthrene	B[<i>a</i>]A
coefficient:	0.920819708	0.952518302
u(coefficient):	0.000261903	0.000356877

If one applies these corrections and their uncertainties to the results and uncertainties submitted by NMIJ (the only laboratory using an extraction temperature substantially different from the rest), one indeed observes a considerable increase in compatibility. The corrected *E_n* values for soil are:

	phenanthrene	fluoranthene	B(a)A	B(a)P	B(ghi)P
BAM	-0.866	-1.144	0.151	-0.466	-0.227
CENAM	-0.469	-0.070	-0.046	0.201	-0.040
GL	-1.797	-0.163	0.979	-0.285	-0.056
INMETRO	-1.777	-0.546	0.381	1.317	0.729
IRMM	0.008	-0.581	-1.030	-0.834	-0.471
KRISS	-0.550	-0.777	1.287	-0.641	-0.773
LGC	0.710	0.212	0.335	1.524	0.671
LNE	4.989	2.429	1.994	2.027	3.173
NIST	1.015	1.590	0.639	-0.020	0.668
NMIJ	-0.435	0.766	0.535	0.726	1.888

This makes NMIJ compatible for all analytes except benzo[*ghi*]perylene where the influence of the extraction temperature turned out to be insignificant. As already explained in clause 9, these corrections do not apply to the air particulate material.

5. Literature

- [1] C.R. Paule and J. Mandel, J Res Natl Bur Stand, 1982, **87**, 377-385.
- [2] R.T. Birge, Phys Rev, 1932, **40**, 207-227.
- [3] M. Cox: CCQM WG approaches to the KCRV and its uncertainty. Presented at the CCQM Workshop on KCRV calculations and their uncertainties, 18 April 2007, Sèvres/F.

Appendix 3: Uncertainty budgets, as reported by the participants

BAM

source	standard uncertainty
method precision	standard deviation of the mean of 6 results
concentration calibrant solution	certified, NIST SRM 1647d
dry mass correction factor	standard deviation of mean of results of Karl-Fischer titration

uncertainty budget K50a soil

	mean µg/g	method precision µg/g	uncertainty calibrant µg/g	uncertainty dry mass µg/g	combined uncertainty µg/g	coverage factor	U _{95%CI} µg/g	U _{95%CI} %
Ph	12,92	0,26	0,10	0,005	0,28	2,45	0,68	5,3
Fl	13,50	0,09	0,08	0,005	0,12	2,14	0,26	1,9
B[a]A	5,84	0,05	0,02	0,002	0,06	2,36	0,13	2,2
B[a]P	4,84	0,05	0,03	0,002	0,07	2,23	0,15	3,1
B[ghi]P	4,94	0,03	0,08	0,002	0,09	1,99	0,17	3,4

uncertainty budget K50b particulate

	mean µg/g	method precision µg/g	uncertainty calibrant µg/g	uncertainty dry mass µg/g	combined uncertainty µg/g	coverage factor	U _{95%CI} µg/g	U _{95%CI} %
Ph	3,93	0,05	0,03	0,002	0,07	2,31	0,15	3,8
Fl	6,27	0,06	0,04	0,002	0,08	2,31	0,17	2,7
B(a)A	2,17	0,01	0,01	0,001	0,02	2,26	0,04	1,8
B(a)P	2,32	0,05	0,02	0,001	0,05	2,45	0,12	5,2
B(ghi)P	3,88	0,03	0,06	0,002	0,07	1,99	0,14	3,6

CENAM

Quantification was done via calibration curves with internal standard using two different columns and via standard addition. The following uncertainty sources were taken into account:

For measurements with calibration curve and internal standard:

- uncertainty of the interpolated value in the calibration curve
- uncertainty of repeatability and reproducibility of sample measurement

For measurements with standard addition, calibration curve and internal standard:

- uncertainty of intercept or target value in the calibration curve
- uncertainty of reproducibility and repeatability of sample measurement
- uncertainty of calibration standard SRM DMR 275a
- uncertainty of preparation of calibration solutions
- uncertainty of quantification method

Government Lab Hong Kong

CCQM-K50a soil	Ph	Fl	B[a]A	B[a]P	B[ghi]P
Measured Value (mean) µg/g	12,66	14,25	6,05	4,88	4,97
Uncertainty components (expressed as relative standard uncertainty)					
Precision of measurements (including sample extraction, cleanup and analysis)	0,007674	0,004233	0,013841	0,008429	0,008896
Calibration standards	0,005186	0,005226	0,008834	0,018047	0,006086
Moisture content	0,000667	0,000667	0,000667	0,000667	0,000667
Rel. Combined Standard Unc.	0,009286	0,006758	0,016433	0,019929	0,010799
Combined Standard Unc. (µg/g)	0,118	0,096	0,099	0,097	0,054
k	2	2	2	2	2
Expanded Uncertainty as %	1,86	1,35	3,29	3,99	2,16
Expanded Uncertainty (µg/g)	0,24	0,19	0,20	0,19	0,11

INMETRO

K50a soil

Sources of uncertainty	Ph	Fl	B[a]A	B[a]P	B[ghi]P
Repeatability of area	3,5996E-08	3,6043E-08	2,0379E-08	1,7713E-08	1,5568E-08
mass of sample	8,0464E-11	8,7959E-11	3,7109E-11	3,3350E-11	3,2008E-11
mass of IS added into the sample	2,4228E-08	2,5240E-08	4,0197E-08	2,5933E-08	2,4890E-08
repeatability of analysis	4,0364E-02	4,6751E-02	2,6985E-02	2,3423E-02	1,5356E-02
calibration curve	4,6202E-02	3,9406E-02	9,3735E-03	1,4841E-02	1,3962E-02
Purity of standard	6,6677E-05	4,8578E-05	1,6121E-04	0,0000E+00	1,1826E-04

K50b particulate

Sources of uncertainty	Ph	Fl	B[a]A	B[a]P	B[ghi]P
Repeatability of area	1,6971E-08	2,7493E-08	1,1522E-08	3,6651E-08	2,4868E-08
mass of sample	2,6194E-10	4,0647E-10	1,3322E-10	1,6196E-10	2,4769E-10
mass of IS added into the sample	1,9488E-08	1,9714E-08	1,0891E-08	9,5770E-09	1,4647E-08
repeatability of analysis	4,0264E-02	5,4197E-02	2,2249E-02	5,8628E-02	3,2137E-02
calibration curve	6,8932E-03	9,0493E-03	1,1069E-02	9,4623E-03	1,6231E-02
purity of standard	2,0161E-05	2,0848E-05	5,3748E-05	0,0000E+00	8,4986E-05

IRMM

$$U = k \cdot c \cdot \sqrt{u(c_{st})^2 + (RSD_{RF})^2 + (RSD_{results})^2}$$

U: expanded uncertainty

k: coverage factor, k=2

c: average concentration of the analyte

u(c_{st}): uncertainty of the standards used

RSD_{RF}: relative standard deviation of response factors determined

RSD_{results}: relative standard deviation of results (analyte concentration)

KRISS

Measurement equation:

$$C = f_{dry} * \frac{M_{is-sol,spiked} * AR_{sample} * M_{s-sol,std} * C_{s-sol}}{M_{sample} * AR_{std} * M_{is-sol,std}}$$

- C* : concentration of analyte in sample
f_{dry}: dry mass correction factor
M_{sample} : weight of sample taken for analysis
M_{is-sol,spiked}: weight of isotope labelled standard solution spiked to sample taken for analysis
C_{s-sol}: concentration of standard solution
M_{s-sol, std}: weight of standard solution added to STD Mix
M_{is-sol,spid}: weight of isotope labelled standard solution added to STD Mix
AR_{sample} : area ratio of the analyte to the isotope labelled analogue from GC/MS-SIM measurement of sample
AR_{std}: area ratio of the analyte peak to the isotope labelled analogue from GC/MS-SIM measurement of STD Mix

Uncertainty sources:

<i>X_i</i>	sources	Rel. unc (%)	v
<i>f_{dry}</i>	Repeated measurement	0,0389	5
<i>M_{sample}</i>	included in between bottle variation	0,003	Large
<i>M_{is-sol,spiked}</i>	included in between bottle variation	0,02	Large
<i>C_{sol}</i>	purity , repeatability of gravimetric preparation	0.1~0.6	Large
<i>M_{s-sol, std}/M_{is-sol, std}</i>	from standard deviation of R.F. of STD Mix	0.2 ~0.5	4
<i>AR_{std}</i>	s/sqrt(n) of 6 repeated GC/MS run	0.05 ~0.5	5
<i>AR_{sample}</i>	s/sqrt(n) of 3 repeated GC/MS run	0.2~1.0	2

Measurement results and uncertainty:

		Ph	Fl	B[a]A	B[a]P	B[ghi]P	
Sample K50-#10	Aliquot 10-1	concentration(mg/g)	12,634	13,080	5,721	4,559	4,622
		unc, rel%	0,78%	1,29%	0,88%	0,92%	1,07%
		veff	10	6	9	10	6
	Aliquot 10-2	concentration(mg/g)	12,546	12,992	5,709	4,533	4,607
		unc, rel%	0,68%	1,01%	0,75%	0,91%	1,07%
		veff	9	8	13	10	6
	Aliquot 10-3	concentration(mg/g)	12,636	13,007	5,745	4,585	4,603
		unc, rel%	0,60%	1,47%	0,69%	0,62%	1,11%
		veff	3	5	5	5	7
pooled unc, rel%		0,57%	0,95%	0,71%	0,80%	0,97%	
veff of pooled unc.		22	19	27	25	19	

Mean (anal2,3)	12,60500	13,02642	5,72497	4,55924	4,61057
RSTD (Anal2,3)	0,4%	0,4%	0,3%	0,6%	0,2%
RSTD of mean	0,2%	0,2%	0,2%	0,3%	0,1%
Combined unc, rel%	0,6%	1,0%	0,7%	0,9%	1,0%
veff of combined unc.	18	19	27	19	19

Dry Mass Correction (f)	1,056	1,056	1,056	1,056	1,056
unc of f	0,0389%	0,0389%	0,0389%	0,0389%	0,0389%
veff	5	5	5	5	5

concentration, corrected	13,31494	13,76010	6,04741	4,81603	4,87025
combined unc	0,6%	1,0%	0,7%	0,9%	1,0%
veff	18	19	27	19	19

		Ph	Fl	B[a]A	B[a]P	B[ghi]P	
Sample K50-#14	Aliquot 14-1	concentration(mg/g)	12,591	13,146	5,707	4,535	4,623
		unc, rel%	0,70%	1,38%	0,72%	0,95%	1,08%
		veff	10	5	11	11	6
	Aliquot 14-2	concentration(mg/g)	12,418	12,948	5,659	4,512	4,604
		unc, rel%	0,70%	1,22%	0,72%	0,84%	1,11%
		veff	10	6	11	9	6
	Aliquot 14-3	concentration(mg/g)	12,517	13,042	5,726	4,579	4,629
		unc, rel%	0,70%	1,14%	0,72%	0,88%	1,05%
		veff	10	8	12	9	5
pooled unc, rel%		0,59%	0,95%	0,67%	0,83%	0,96%	
veff of pooled unc.		30	19	34	29	17	
Mean (anal2,3)		12,50863	13,04539	5,69750	4,54215	4,61869	
RSTD (Anal2,3)		0,7%	0,8%	0,6%	0,7%	0,3%	
RSTD of mean		0,4%	0,4%	0,4%	0,4%	0,2%	
Combined unc, rel%		0,7%	1,0%	0,8%	0,9%	1,0%	
veff of combined unc.	8	14	15	15	17		

Dry Mass Correction (f)	1,056	1,056	1,056	1,056	1,056
unc of f	0,0389%	0,0389%	0,0389%	0,0389%	0,0389%
veff	5	5	5	5	5

concentration, corrected	13,21315	13,78014	6,01840	4,79797	4,87883
combined unc	0,7%	1,0%	0,8%	0,9%	1,0%
veff	8	14	15	15	17

Summary

	Ph	Fl	B[a]A	B[a]P	B[ghi]P
mean of sample#10-#14 (mg/g)	13,264	13,770	6,033	4,807	4,875
RSTD(unc), v=2	0,54%	0,10%	0,34%	0,27%	0,12%
pooled unc. Sample1-2	0,6%	1,0%	0,7%	0,9%	1,0%
veff,pooled	26	33	42	34	36
Combined unc, rel%	0,8%	1,0%	0,8%	0,9%	1,0%
veff of combined unc.	10	33	31	35	37
unc(mg/g)	0,112	0,139	0,049	0,045	0,048
k(95%)	2,23	2,03	2,04	2,03	2,03
Exp. Unc(mg/g)	0,250	0,283	0,101	0,091	0,097

LGC

Measurement equation:

$$c_X = c_Z \cdot \frac{m_{Z,c}}{m_{Y,c}} \cdot \frac{m_Y}{m_X} \cdot \frac{R_B}{R_{B,c}}$$

c_X : mass fraction of PAH in sample X

c_Z : mass fraction of PAH in natural standard Z

m_Y : mass of spike Y added to the sample X to prepare the blend B (=X+Y)

m_X : mass of sample X added to the spike Y to prepare the blend B (=X+Y)

m_{Zc} : mass of primary standard solution Z added to the spike Y to make calibration blend Bc (=Y+ Z)

m_{Yc} : mass of spike Y added to the primary standard solution Z to make calibration blend Bc (=Y+ Z)

R_B : measured isotope amount ratio of sample blend (X+Y)

R_{Bc} : measured isotope amount ratio of calibration blend (Bc=Z+Y)

Uncertainty sources:

The combined standard uncertainty quoted for each PAH was calculated by combining:

- 1) the standard uncertainty of the dry mass correction factor
- 2) the between blend variation; as 6 blends were analysed, this between blend variation uncertainty contribution was calculated as the standard deviation of the mean of the 6 individual results.
- 3) the average uncertainty obtained for each blend; by combining the contributions from the primary standard used, the masses used to prepare the blends and the precision of the method (which corresponds to the precision of the measurement by GC-MS)

The correction factor to convert to the dry mass of the sample was calculated from four determinations. The four values were averaged and one correction factor was used. It was equal to 0.94457 (soil) or 0.954430 (particulate) with an associated standard uncertainty equal to 0.00022 (soil) or 0.00059 (particulate). The standard uncertainties were calculated by combining the standard deviation of the mean of 4 determinations with the standard uncertainty associated with the weightings.

LNE

Uncertainty sources:

Masses

Purity

Ratio measurement in sample

Ratio measurement in standard

Factor of sample dispersion

Calculations were done according to GUM using WINCERT software.

NIST

CCQM-K50a soil	Ph	Fl	B[a]A	B[a]P	B[ghi]P	d.f.	
Measured Value (mean)	14,05	15,63	5,99	4,96	5,09		
Uncertainty Components							
Measurement of Samples	0,136	0,139	0,095	0,090	0,026	5	=sd of the conc divided by sqrt of 6
Measurement of Calib Stds	0,000	0,001	0,000	0,000	0,000	3	=measured value*sqrt[(sd of RF squared/4)]/100
drying factor	0,013	0,014	0,006	0,005	0,005	2	=measured value*sqrt[(sd of DF squared/3)]/100
Certified Conc of Calib Soln	0,069	0,077	0,077	0,019	0,060	inf	=rel std unc of calibration solution* measured value
Combined Standard Unc.	0,153	0,159	0,123	0,092	0,065		=sqrt (sum of squares of above 3)
Effective degrees of freedom	8,07	8,67	13,75	5,47	215,19		=combined std unc to the 4th / (unc meas samples to the 4th/df + meas of calib to the 4th /df)
k (from t-distribution)	2,31	2,31	2,16	2,57	1,97		=inverse of students t distribution of effective degrees of freedom at 95% conf level
Expanded Uncertainty	0,353	0,367	0,265	0,237	0,129		=k * comb std unc
Expanded Unc as %	2,51%	2,35%	4,43%	4,78%	2,53%		

CCQM-K50b particulate matter	Ph	Fl	B[a]A	B[a]P	B[ghi]P	d.f.	
Measured Value (mean)	4,13	6,25	2,12	2,27	3,91		
Uncertainty Components							
Measurement of Samples	0,025	0,039	0,025	0,023	0,023	5	
Measurement of Calib Stds	0,000	0,000	0,000	0,000	0,000	3	
drying factor	0,003	0,004	0,001	0,002	0,003	2	
Certified Conc of Calib Soln	0,020	0,031	0,027	0,009	0,046	inf	
Combined Standard Unc.	0,032	0,050	0,037	0,025	0,052		
Effective degrees of freedom	14,11	13,13	24,40	6,52	118,47		
k (from t-distribution)	2,14	2,16	2,06	2,45	1,98		
Expanded Uncertainty	0,069	0,108	0,076	0,061	0,102		
Expanded Unc as %	1,68%	1,73%	3,60%	2,68%	2,62%		

NMIJ

Measurement equation:

$$\text{Canal} = [\text{Fprep}(\text{sample}) * \text{R}(\text{sample}) - \text{R}(\text{blank})] * [\text{Mcal} * \text{Ccal} * \text{Msur}(\text{sample}) * \text{Fsur}(\text{sample}) * \text{Fsur}(\text{dilute})] / [\text{Fmoist} * \text{Msample} * \text{Msur}(\text{calibration})]$$

Canal:	concentration of analyte in the sample (dry mass-basis),
Fprep(sample):	efficiency of sample preparation,
R(sample):	ratio $R_{\text{sample}} / R_{\text{calibration}}$,
Rsample:	ratio of peak area of analyte / surrogate observed for the sample solution,
Rcalibration:	ratio of peak area of analyte / surrogate observed for the calibration solution,
R(blank):	ratio $R_{\text{blank}} / R_{\text{calibration}}$,
Rblank:	ratio of peak area of analyte / surrogate observed for the blank solution,
Rcalibration:	ratio of peak area of analyte / surrogate observed for the calibration solution,
Mcal:	mass of the standard solution of analytes taken for preparation of the calibration solution, Type A uncertainty (reproducibility of weighing, n=10) and type B uncertainty (linearity of weighing, certificate of calibration) were combined.
Ccal:	concentration of analyte in the calibration solution,
u(Ccal):	uncertainty of concentration in calibration solution prepared from neat chemicals
Msur(sample):	mass of the surrogates solution added to the sample, Type B uncertainties (linearity and reproducibility of weighing, certificate of calibration) were combined.
Fsur(sample):	correction factor of adding surrogates solution on the sample, Type A uncertainty (reproducibility of weighing, n=10) and type B uncertainty (linearity of weighing, certificate of calibration) were combined.
Fsur(dilute):	correction factor of preparing surrogates solution on the sample, Type A uncertainty (reproducibility of weighing, n=10) and type B uncertainty (linearity of weighing, certificate of calibration) were combined.
Fmoist:	correction factor concerning moisture content in the sample, Type A uncertainty (reproducibility, subsamples: n=3 (soil), n=2 particulate) and type B uncertainty (linearity and reproducibility of weighing, certificate of calibration) were combined.
Msample:	mass of the sample taken for analysis, Type B uncertainties (linearity and reproducibility of weighing, certificate of calibration) were combined.
Msur(calibration):	mass of the undiluted surrogates solution taken for preparation of the calibration solution, Type A uncertainty (reproducibility of weighing, n=10) and type B uncertainty (linearity of weighing, certificate of calibration) were combined.

Since there was no significant difference between the two bottles of the soil sample, uncertainties obtained from two bottles were combined.

Budget K50a soil:

	Value, xi	Uncertainty, u(xi)	degree of freedom	type of uncertainty
Fprep(sample): Phenanthrene	1,00000	0,00238	9	A
Fprep(sample): Fluoranthene	1,00000	0,00222	9	A
Fprep(sample): Benz[a]anthracene	1,00000	0,00531	9	A
Fprep(sample): Benzo[a]pyrene	1,00000	0,00391	9	A
Fprep(sample): Benzo[ghi]perylene	1,00000	0,00203	9	A
R(sample): Phenanthrene	0,99665	0,00222	9	A
R(sample): Fluoranthene	1,00880	0,00206	9	A
R(sample): Benz[a]anthracene	0,96759	0,00236	9	A
R(sample): Benzo[a]pyrene	0,95241	0,00417	9	A
R(sample): Benzo[ghi]perylene	0,97965	0,00168	9	A
R(blank): Phenanthrene	0,00026	0,00001	2	A
R(blank): Fluoranthene	0,00036	0,00001	2	A
R(blank): Benz[a]anthracene	0,00034	0,00001	2	A
R(blank): Benzo[a]pyrene	0,00025	0,00001	2	A
R(blank): Benzo[ghi]perylene	0,00032	0,00001	2	A
Mcal: Phenanthrene (mg)	667,72	0,69981	large	A + B
Mcal: Fluoranthene (mg)	667,72	0,28979	large	A + B
Mcal: Benz[a]anthracene (mg)	667,72	0,51498	large	A + B
Mcal: Benzo[a]pyrene (mg)	667,72	0,39725	large	A + B
Mcal: Benzo[ghi]perylene (mg)	667,72	0,25032	large	A + B
Ccal: Phenanthrene (µg/g)	48,312	0,40276	large	A + B
Ccal: Fluoranthene (µg/g)	49,031	0,40876	large	A + B
Ccal: Benz[a]anthracene (µg/g)	21,179	0,17656	large	A + B
Ccal: Benzo[a]pyrene (µg/g)	17,650	0,14714	large	A + B
Ccal: Benzo[ghi]perylene (µg/g)	17,548	0,14629	large	A + B
Msur(sample) (mg)	2456,75	2,9075	large	A + B
Msur(calibration)	405,40	2,2297	large	A + B
Fsur(sample)	1,00000	0,00080	large	A + B
Fsur(dilute)	0,21532	0,00118	large	A + B
Fmoist	0,94958	0,00030	large	A + B
Msample (mg)	3044,92	0,09006	large	B
	Concentration (µg/g)	combined uncertainty (µg/g)	k	expanded uncertainty (µg/g)
Phenanthrene	14,44	0,173	2	0,35
Fluoranthene	14,99	0,178	2	0,36
Benz[a]anthracene	6,22	0,082	2	0,16
Benzo[a]pyrene	5,16	0,067	2	0,13
Benzo[ghi]perylene	5,27	0,062	2	0,12

For the particulate matter sample a significant difference between the results obtained for the two bottles was observed. Therefore, this difference was added to the uncertainty budget.

Budget K50b particulate

	Value, xi	Uncertainty, u(xi)	degree of freedom	type of uncertainty
Fprep(sample): Phenanthrene	1,00000	0,00167	4	A
Fprep(sample): Fluoranthene	1,00000	0,00463	4	A
Fprep(sample): Benz[a]anthracene	1,00000	0,00212	4	A
Fprep(sample): Benzo[a]pyrene	1,00000	0,00372	4	A
Fprep(sample): Benzo[ghi]perylene	1,00000	0,00239	4	A
R(sample): Phenanthrene	1,09126	0,00192	4	A
R(sample): Fluoranthene	1,05364	0,00606	4	A

R(sample): Benz[a]anthracene	1,03539	0,00194	4	A
R(sample): Benzo[a]pyrene	0,99367	0,00334	4	A
R(sample): Benzo[ghi]perylene	1,04387	0,00287	4	A
R(blank): Phenanthrene	0,00187	0,00004	2	A
R(blank): Fluoranthene	0,00071	0,00003	2	A
R(blank): Benz[a]anthracene	0,00070	0,00003	2	A
R(blank): Benzo[a]pyrene	0,00070	0,00001	2	A
R(blank): Benzo[ghi]perylene	0,00063	0,00003	2	A
Mcal: Phenanthrene (mg)	632,96	0,66338	large	A + B
Mcal: Fluoranthene (mg)	632,96	0,27471	large	A + B
Mcal: Benz[a]anthracene (mg)	632,96	0,48817	large	A + B
Mcal: Benzo[a]pyrene (mg)	632,96	0,37657	large	A + B
Mcal: Benzo[ghi]perylene (mg)	632,96	0,23729	large	A + B
Ccal: Phenanthrene (µg/g)	25,577	0,21323	large	A + B
Ccal: Fluoranthene (µg/g)	35,065	0,29233	large	A + B
Ccal: Benz[a]anthracene (µg/g)	11,733	0,09781	large	A + B
Ccal: Benzo[a]pyrene (µg/g)	13,164	0,10974	large	A + B
Ccal: Benzo[ghi]perylene (µg/g)	23,523	0,19611	large	A + B
Msur(sample) (mg)	341,81	0,04521	large	A + B
Msur(calibration) (mg)	725,56	3,99058	large	A + B
Fsur(sample)	1,00000	0,00080	large	A + B
Fsur(dilute)	0,08947	0,00049	large	A + B
Fmoist	0,9558	0,00057	large	A + B
Msample (mg)	152,38	0,09006	large	B
Differences in two bottles: Phenanthrene	5,06	0,25712	8	A
Differences in two bottles: Fluoranthene	6,70	0,31215	8	A
Differences in two bottles: Benz[a]anthracene	2,20	0,08501	8	A
Differences in two bottles: Benzo[a]pyrene	2,36	0,10047	8	A
Differences in two bottles: Benzo[ghi]perylene	4,45	0,17860	8	A
	Concentration (µg/g)	combined uncertainty (µg/g)	k	expanded uncertainty (µg/g)
Phenanthrene	5,06	0,266	2	0,53
Fluoranthene	6,70	0,326	2	0,65
Benz[a]anthracene	2,20	0,090	2	0,18
Benzo[a]pyrene	2,36	0,105	2	0,21
Benzo[ghi]perylene	4,45	0,187	2	0,37