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Second JRC Polycyclic Aromatic Hydrocarbons Inter-laboratory Comparison on Particulate Matter Quartz Filters

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harmonisation programme
for Air Quality
Measurements*

Pérez Ballesta P.

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Foreword

The knowledge of the composition and the chemical characterisation of particulate matter will become the cornerstone of the future regulatory policy, since the particles are in some way representing the final step of reduction of our substance and acts. Therefore, by comparing our measurements we are more than ever harmonising our points of view.

"Y mientras cree tocar enardecido
el oro aquel que matará la muerte,
Dios, que sabe de alquimia, lo convierte
en polvo, en nadie, en nada y en olvido."

"And while he dreams of finding in the fire
that true gold that will put an end to dying,
God, who knows His alchemy, transforms him
to no one, dust, oblivion."

("*El alquimista*", J.L. Borges, Translation by Alastair Reid)

"El análisis todo a polvo lo reduce"

"The analysis all to dust reduces it"

("*El héroe delincuente*", Emilio Bobadilla)

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Abstract

This report provides the results of the second inter-laboratory comparison for analysis of polycyclic aromatic hydrocarbons (PAHs) in particulate matter (PM) quartz filters carried out in Ispra from the 1st to the 15th of February 2018. Fifteen laboratories from different member states of the European Union participated in this exercise. The main comparison was based on the analysis of sections of four filters from a high-volume sampler and two blanks representing the daily concentration range of PAHs collected in an equivalent low volume sampling filter, which would be operating during the period of comparison. The exercise allowed the comparison between high and low volume sampling, which was carried out by three of the participating laboratories.

The comparison was performed on the analysis of 15 PAHs from phenanthrene to benzo[g,h,i]perylene, including benzo[a]pyrene as regulatory compound. The median of the inter-compound robust repeatability uncertainty and reproducibility was 14%, while the robust overall expanded uncertainty was \pm 30% for the exercise. This value, being representative of a robust best method performance, can fulfil the method expectation for the analysis of PAHs and in line with the data quality objectives (DQO) defined in the Directive 2004/107/EC.

1. Introduction

The EU Directive 2004/107/EC provides Member States with a guide for the measurements of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in ambient air particulate matter. These compounds are of high importance in the characterisation of the toxicity of the particulate with negative impact on the health of the exposed population. PAHs are ubiquitous in the environment and result in measurable background levels. Their concentrations in ambient air also represent a direct means of exposure. Some of these PAHs have already been identified as carcinogenic to humans, in particular benzo[a]pyrene (B[a]P), benzo[a]anthracene (B[a]A), benzo[b,j,k]fluranthenes (B[bjk]F), and dibenzo[a,h]anthracene (DB[ah]A), are classified as 2A by the IARC¹.

The afore-mentioned Directive requests the measurement of B[a]P in particulate matter (PM) and recommends the monitoring of other relevant PAHs, including at least: B[a]A; B[bjk]F, indeno[1,2,3-c,d]pyrene (Ind[123cd]P) and DB[ah]A. Furthermore, Member States are obliged to use reference or equivalent methods for sampling and analysis with data quality objectives that consider maximum uncertainty values of 50% for their measurements.

The implementation of effective quality assurance at EU level involves the organisation of inter-laboratory comparisons between Member States that ensure the harmonisation of measurements, their traceability at international level and testing of their uncertainty estimations.

This report shows the results of the second inter-laboratory comparison of PAHs in particulate matter carried out at European level among the Air Quality Reference Laboratories in Europe (AQUILA).

¹ International Agency for Research on Cancer. WHO.

2. Inter-laboratory comparison strategy

This exercise is the second inter-laboratory comparison carried out by the Joint Research Centre (JRC) since the publication of the Directive 2004/107/EC. The study is part of a quality assurance and quality control (QAQC) programme lead by the European Commission to guarantee traceability and harmonisation of the measurements and to support the activity of the reference laboratories and air quality networks of the Member States.

The comparison aimed to evaluate the sampling and analytical performance of the participating laboratories. To this purpose, a two week PAHs sampling period, from the 1st to the 15th of February 2018, was organised in parallel with a PM10 inter-laboratory comparison exercise carried out in Ispra during the first two months of 2018. During these two weeks, laboratories were invited to perform their own PM sampling for the analysis of PAHs. In addition, the JRC took daily PM samples to select a representative set of samples for comparison.

2.1. Participating laboratories

Fifteen laboratories from AQUILA were involved in this inter-laboratory exercise. Whilst all participants received sections of the HVS filter, only three of them were sampling in parallel with their own devices. Names of the laboratories and personnel involved are listed in Table 1.

Table 1 - List of participating laboratories

Laboratory	Acronyms	Country	Contact/Responsible
Aarhus University Department of Environmental science	AU_ENVS	Denmark	Rossana Bossi
Czech Hydrometeorological Institute	CHMI	Czech Republic	Stepan Rychlik, Helena Placha, Irina Nikolova
Finnish Meteorological Institute	FMI	Finland	Mika Vestenius
Hungarian Meteorological Service	HMS	Hungary	Viktor Dezsi, Attila Machon, Gegő Farkas
Institute for Medical Research and Occupational Health	IMROH	Croatia	Ivana Jakovljević, Ivan Bešlić, Zdravka Sever Štrukil
Institut National de l'Environnement industriel et des Risques	INERIS	France	Hugues Biaudet
Instituto de Salud Carlos III	ISCIII	Spain	Pilar Morillo Gómez, David Galán Madruga, Regina Muñoz Úbeda
IVL Swedish Environmental Institute	IVL	Sweden	Annika Potter, Erika Rehngren
Landesumweltamt für Natur, Umwelt und Verbraucherschutz NRW	LANUV	Germany	Dieter Gladtke, Anja Olszewski, Simone Muratyan
Norwegian Institute for Air Research	NILU	Norway	Stine Marie Bjørneby, Ellen Katrin Enge, Anne Karine Halse
Laboratory of Latvian Environment, Geology and Meteorology Centre	LEGMC	Latvia	Valentina Malecka, Olga Grīzele, Viktors Žilinskis
Amt der oberösterreichischen Landesregierung - Abteilung: Umweltschutz	OOE	Austria	Adolf Schinerl
Slovenian Environment Agency	SEA	Slovenia	Karla Hrovat, Irena Kranjc
Umweltbundesamt GmbH	UBA	Austria	Katharina Braun
Vlaamse Milieumaatschappij	VMM	Belgium	Leen Vandekerckhove, Jordy Vercauteren
European Commission, Joint Research Centre	JRC	Italy	Pascual Pérez Ballesta

2.2. Sampling Strategy

The sampling strategy was designed to produce a sufficient number PM high volume samples to cover a representative range of PAHs concentrations in filters. Two weeks daily sampling was considered sufficient to fulfil such a purpose.

An Andersen HVS with a PM2.5 head was used to provide daily PAH samples during the campaign. PM2.5 was collected on quartz filters (Whatman QM-A) previously heated at 400 °C for a minimum of six hours. Filters were wrapped in aluminium foil before being heated. After the heat treatment, they were left to cool down at room temperature in a controlled temperature balance room (20°C, 50% RH). These filters were only unwrapped at the start of the sampling.

Four low volume samplers (LVS) with PM10 heads were operated in pairs on alternate days at the same location to get duplicate samples. The LVS filters (Whatman QM-A) were treated in the same way that was previously described for the HVS filters.

After sampling HVS filters were subdivided and sealed in an envelope of heat-treated aluminium foil. They were kept at -20°C before being distributed between participants. Blanks filters followed the same procedure, but excluding the sampling step. The two blank filters included in the travelling envelope were prepared at the beginning and end of the sampling campaign.

From each PM2.5 HVS filter, 20 pieces of diameter circa 39.5 mm equivalent to a LVS filter area were obtained. In addition, two PM10 low volume filter samples were also available for JRC analysis. Participating laboratories received the corresponding filters together with a "Guide to operation" (included in annex I). Participants were requested to provide information concerning the analytical method and the uncertainty evaluation of the measurements. Laboratories should perform a minimum of 3 replicate injections for each sample and calculate the uncertainty associated with the average reported analytical value.

Fifteen different PAHs were indicated for analysis, from which seven of them are considered as of major interest in the Directive 2004/107/EC (see Table 2).

Table 2 - List of compounds to be quantified on the filter

N.	Compounds	Acronym	N.	Compounds	Acronym
1	Phenanthrene	Phe	9	Benzo(k)fluoranthene	B[k]F
2	Anthracene	Anth	10	Benzo(e)pyrene	B[e]P
3	Fluoranthene	Flu	11	Benzo(a)pyrene	B[a]P
4	Pyrene	Pyr	12	Perylene	Per
5	Benzo(a)anthracene	B[a]A	13	Indeno(1,2,3-c,d)pyrene	Ind[123cd]P
6	Chrysene	Chry	14	Dibenzo(a,h)anthracene	DB[ah]A
7	Benzo(b)fluoranthene	B[b]F	15	Benzo(g,h,i)perylene	B[ghi]P
8	Benzo(j)fluoranthene	B[j]F			
N.	Combination of isomers			Acronym	
A	*Chrysene+triphenylene			Chry+Tph	
B	*Benzo(b,j,k)fluoranthene			B[bjk]F	

Highlighted in bold: priority compounds for the inter-laboratory comparison

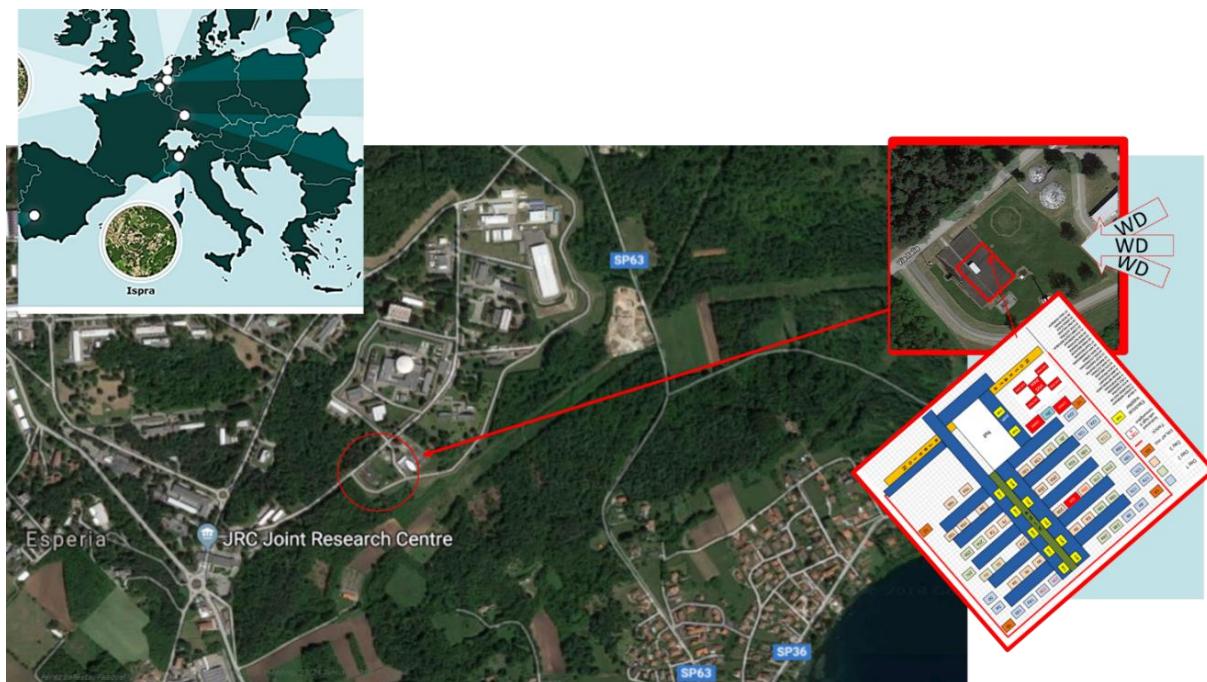
2.2.1. Sampling programme

The PM sampling campaign started on the 15th of January 2018, two weeks before the PAHs comparison exercise. Participating laboratories were also invited to take their own PM samples for PAH analysis during the course of the campaign. However, this offer was only accepted by three laboratories: VMM, SEA and CHMI. Such a low number of laboratories participating with their own samplers limited the representativeness of this part of the comparison.

2.2.2. Measurement site and sampling position

A restricted area inside of the JRC was chosen for PM inter-laboratory comparison exercise. Figure 1 shows in detail the exact position of the PAH samplers (in red colour). Preference wind directions during the sampling period are shown in the upper right-hand side of the picture by the corresponding arrows. Homogeneity of the sampling area was demonstrated in a previous PM comparison campaign (EUR 28107, 2016).

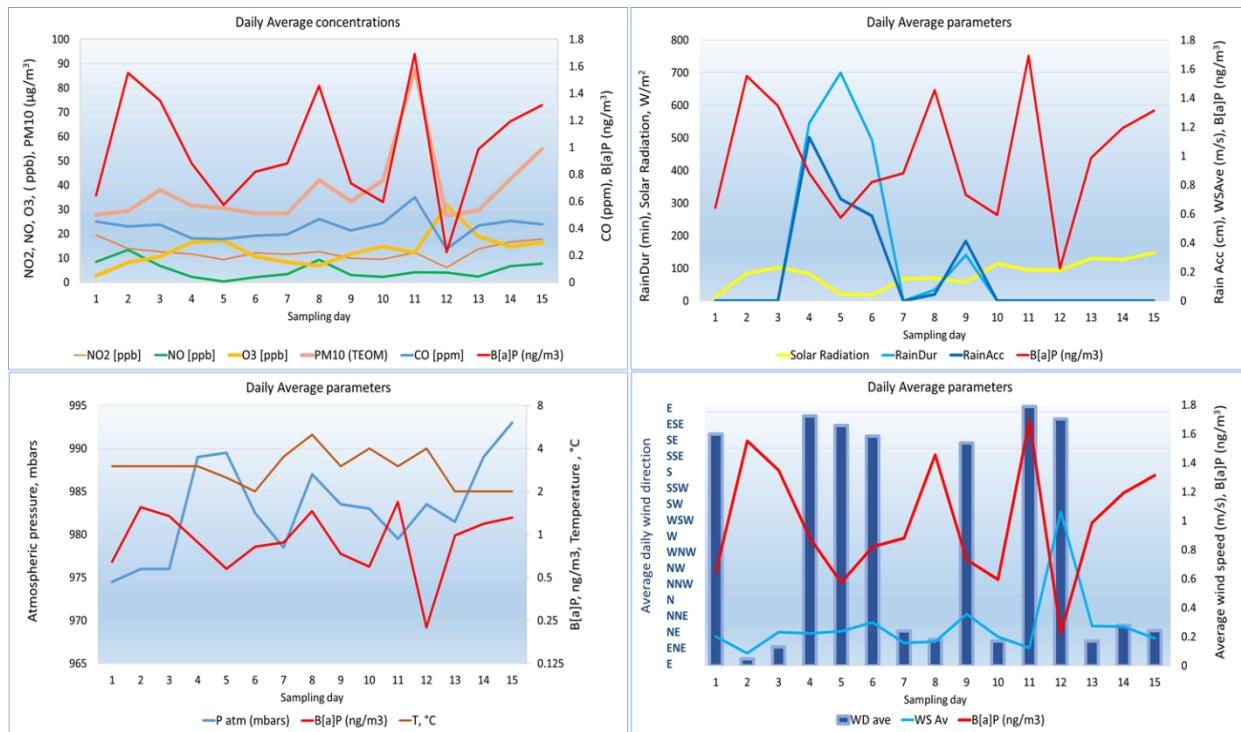
Figure 1 - Location of the PAH samplers (in red)



2.2.3. Meteorological conditions

Meteorological conditions were measured at the EMEP station located a few hundred meters from the sampling site. Daily average values of meteorological parameters and main pollutants measured in the EMEP station are represented in Figure 2.

Figure 2 - Daily average values of temperature, atmospheric pressure, solar radiation, rainfall, wind velocity and direction. Daily average concentrations of NO₂, NO, O₃, PM10 and B[a]P



Meteorological conditions were typical of recent winters. Table 3 shows average, maximum, minimum and variability (coefficient of variation, CV) for the two weeks sampling period of the daily average meteorological parameters and concentration of pollutants measured.

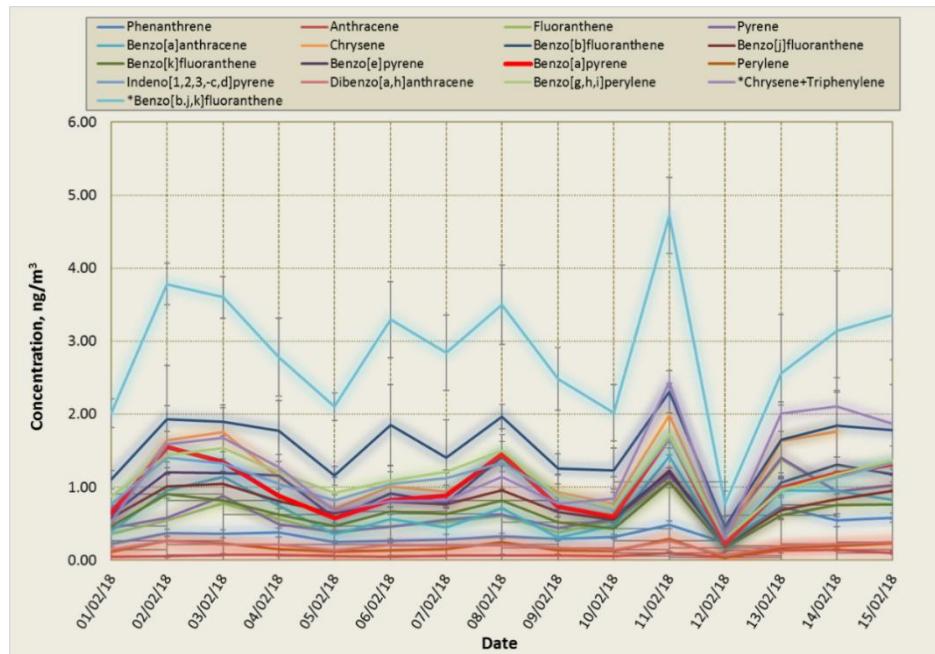
Table 3 - Maximum, minimum and average daily values of pollutants and meteorological parameters

Period: 1 st to 15 th February 2018	Average	Coefficient of Variation, CV %	min	max
NO ₂ , ppb	12.64	27.18	6.16	19.54
NO, ppb	5.09	69.44	0.31	13.39
O ₃ , ppb	13.41	50.09	2.73	31.70
PM10, µgm ³	38.22	41.19	27.40	87.66
CO, ppm	0.41	21.32	0.25	0.63
B[a]P, ng/m ³	0.99	42.14	0.17	1.74
Solar Radiation, W/m ²	81.66	50.79	12.30	147.66
Rain duration, min	127.50	188.31	0.00	700.00
Wind Speed, m/s	0.52	42.13	0.32	1.22
Rain cm	0.19	183.44	0.00	1.13
P atm (mbars)	983.07	0.57	974.50	993.00
Temperature, °C	3.00	28.87	2.00	5.00

2.3. Concentrations and selection of filters for comparison

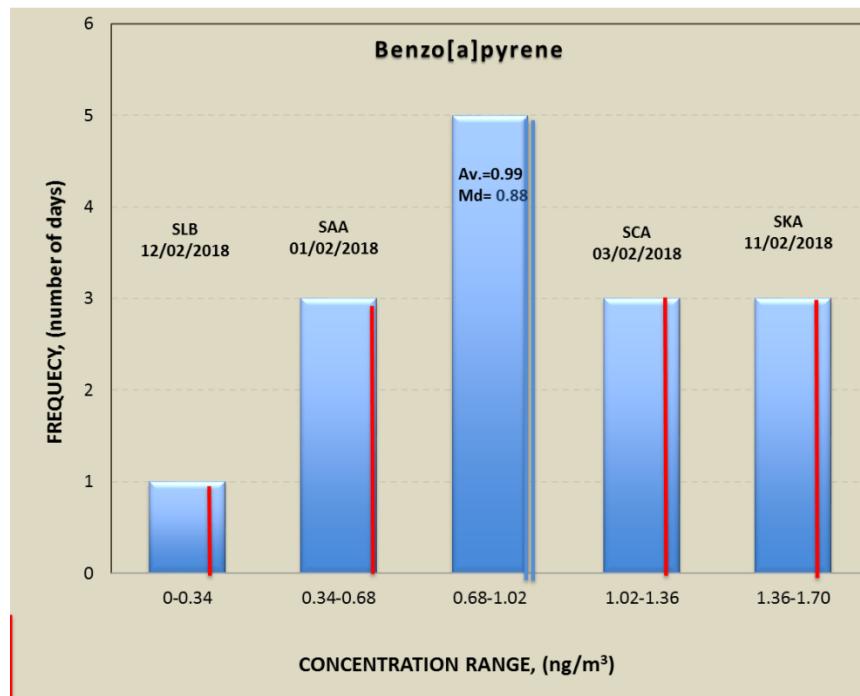
To understand the PAH concentration levels during the campaign, analyses of the daily filters were performed by JRC. Consequently, according to the PAHs concentration profile (see Figure 3), four filters were selected for the comparison. These filters represented the maximum, minimum, 25 and 75 percentiles of the Ba[a]P concentration in the samples.

Figure 3 - PAHs concentration trend during the comparison exercise



The Ba[a]P concentration frequency distribution during the exercise is represented by the histogram in Figure 4, in which concentrations, assigned codes and dates for the selected filters are indicated.

Figure 4 - Frequency distribution of Ba[a]P concentration in air for the selected filter samples



2.4. Filters management, homogeneity and blanks

Whatman QM-A Quartz microfiber filters (20.3 x 25.4 cm cat. No.1851 865) were used for sampling in an Andersen HVS fitted with a PM2.5 sampling head. The filters had an effective sampling area of 406 cm², from which 20 filters of 4 cm diameter can be sectioned.

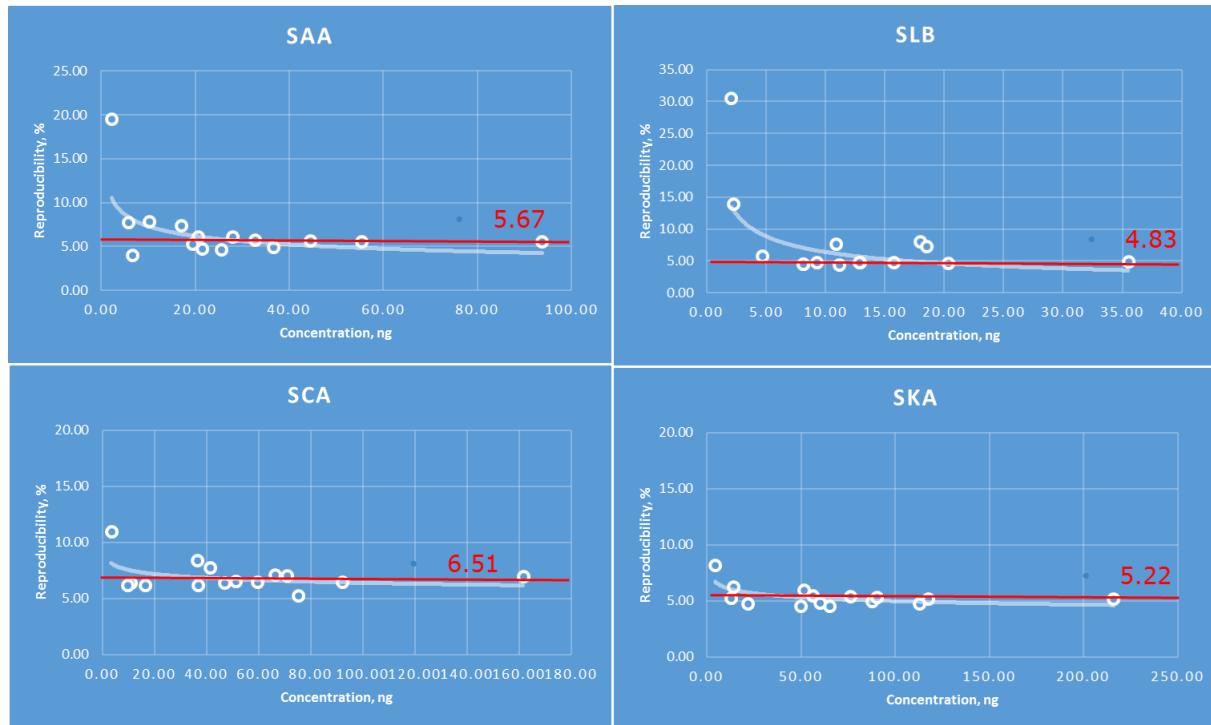
After sampling the high-volume filters were cut by means of a mould specifically designed for this purpose (see Figure 5). The sections were individually packed in a heat-treated aluminium foil, plasticized and codified. These filters were kept in the freezer at -20 °C waiting for shipping to the participants.

Figure 5 - Mould and tools for the subdivision of the high volume filter



After the selection of the filters for comparison, the analysis of the filter was performed on several random 2.5 mm diameter sections by comparing analytical reproducibility. A homogeneity value was derived from the averaged analytical reproducibility of the considered PAHs. In general, such reproducibility values ranged between 4.8% and 6.5% among the filters under consideration. Reproducibility versus concentration of analytes for the considered filters is represented in Figure 6.

Figure 6 - Homogeneity of the high-volume filter: analytical reproducibility of randomly selected sections



Blank filters were carefully prepared in a similar way than the sampled filters. The only difference between sampled and blank filters was the absence of sampling time for the blanks. The blanks not only provided information of a potential contamination of the samplers during storage or transport, but they also acted as indicators of possible problems in the analytical blanks of the participants.

2.5. Guide to operation and data reporting sheet

Together with the filters, laboratories received a guide to operation & procedure (annex II) and a data reporting sheet (annex III) for laboratories' identification, instrument description, analytical procedure, data reporting: HVS and LVS, quantification, and uncertainty calculation. The deadline for reporting data was the 15th of June 2018, although a complete ratified dataset, which included all the participants, was only available in November 2018.

3. Analytical methods

No analytical method was suggested to, or imposed on, the participating laboratories. Therefore, the participants were free to use a range of separation techniques, analytical instrumentation, extraction systems, solvents, clean-up techniques and analytical parameters that resulted in the comparison. Table 4 summarises the different techniques and analytical conditions used by the participating laboratories.

There were no significant differences between specific techniques for extraction or analysis. The predominant techniques were those using gas chromatography and mass spectrometry detection; accelerated solvent extraction and the use of lightly polar solvent for extraction, i.e. combination of acetone and hexane. Extraction times of less than one hour, the use of clean up procedures, internal standards, and certified reference material (CRM) were of common practice. Figure 7 shows the percentages of the different techniques applied by participants.

Figure 7 - Statistics of the analytical techniques used by participating laboratories

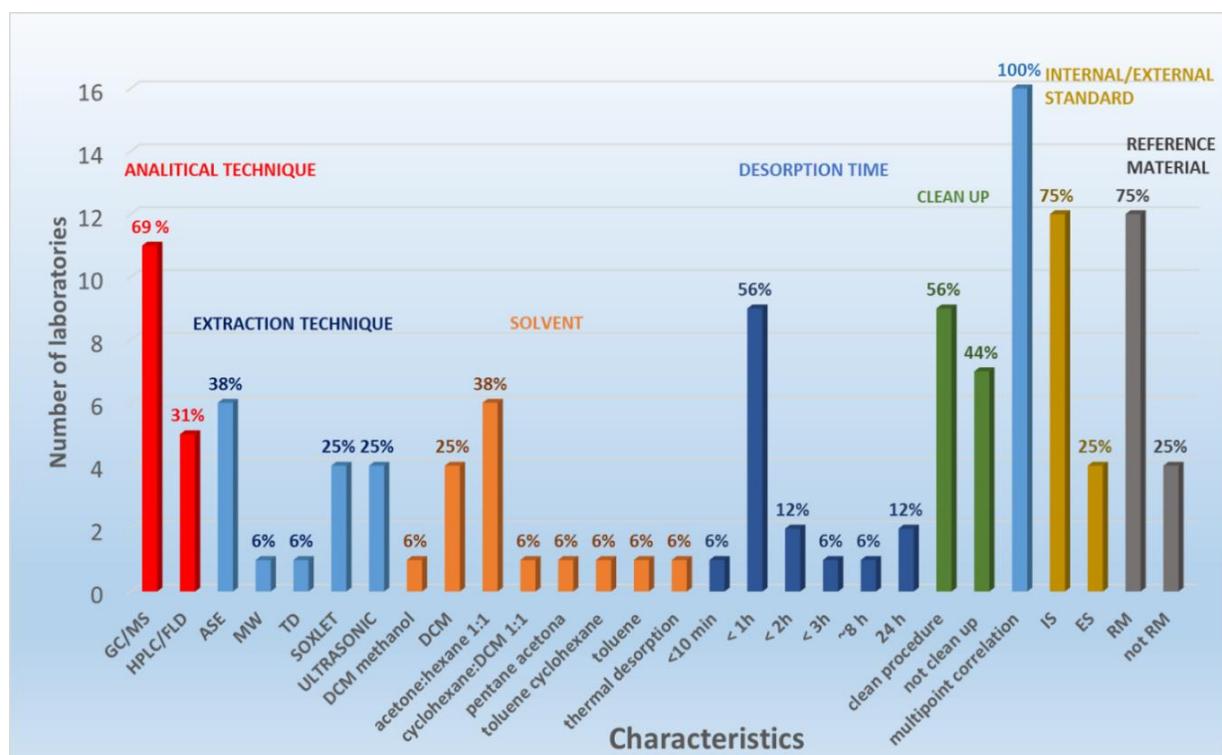


Table 4 - Analytical methods used by the participating laboratories

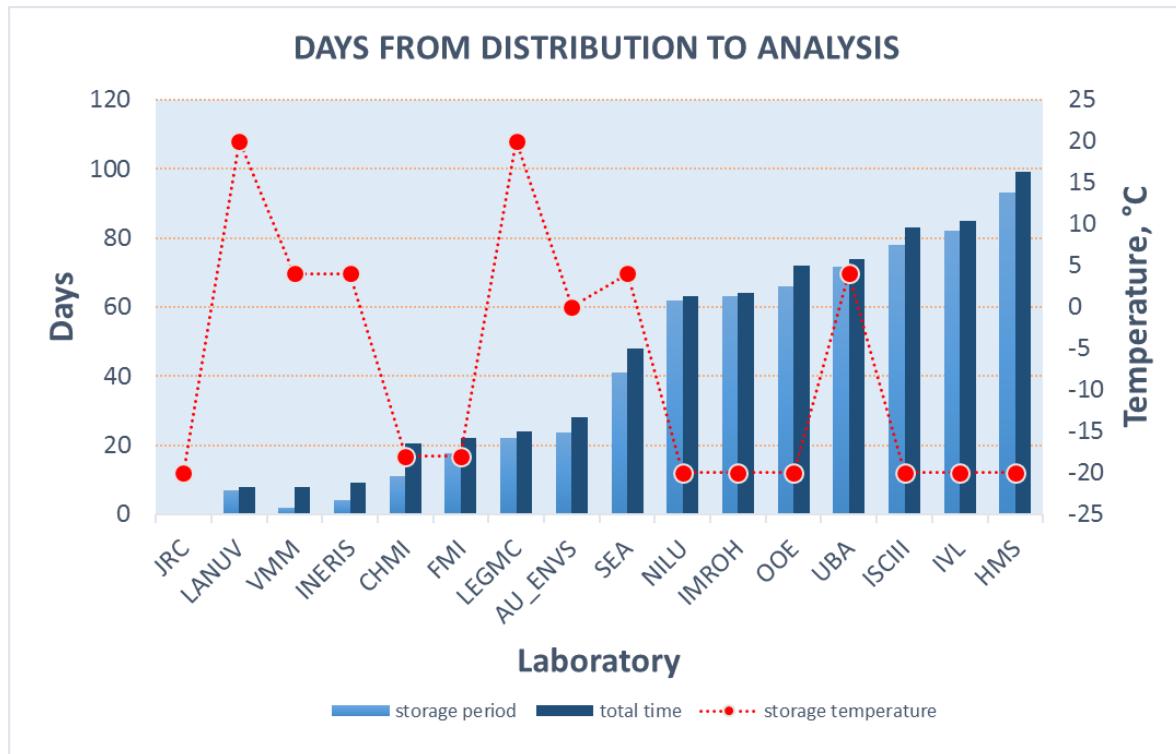
Laborat.	Analytical Method	Column	Extraction Method	Solvent	Time	Clean-up	Correlation	Internal Standard	Certified Reference Material	Standard Solvents
AU_ENVS	GC/MS, Agilent786A/ Agilent 5975C	HP5-MS 30m 0.25 mm i.d., 0.25 µm	ULTRASONIC	DCM	1:30 h:mm	SILICA_ (HEXANE, DCM-TOLUENE)	Linear, multipoint (5-250 pg/µl, 100 pg/µl IS), SIM	Phe-D10, Flu-D10, Pyr-D10, B[a]A-D12, B[a]P-D12, Per-D12, DB[ah]A-D14, B[ghi]P-D12, Chr-D12, B[a]P-D12	Fine Dust (PM10 - Like) BCR (JRC)	chiron, supelco, CIL, Rathburn
CHMI	GC/MS, Agilent 7890 B/ Agilent 5977A	Restek, 30m 0.25mm i.d., 0.1 µm	SOXHLET: Buchi extraction system concentration: biotage TurboVap II	7% Me:DCM	1:25 h:mm	----	Linear, multipoint force (0) (2-200 pg/µl, 100 pg/µl IS), SIM	Napth-D8, Acep-D4, Phe-D10, Pyr-D10, Chr-D12, Per-D12, B[ghi]P-D12	NIST-1649B, ERMCZ100-1VL	Dr. Ehrenstorfer Chromservis Honeywell
FMI	GC/MS, Agilent 6890N/ Agilent 5973	Agilent J&W DB-5MS, 50 m, 0.25 mm i.d., 0.25 µm	SOXHLET: SOXTERM concentration; Buchi Syncore Analyst	DCM	2:55 h:mm	Bond Elut. 12102109 Florisil	using different response factors (50, 100 pg/µl IS), quadratic correlation, SIM	Acep-D4, Chry-D12, Napth-D8, Per-D12, Phe-D10, DB[ah]A-D14	----	----
HMS	GC/MS, Thermo ST1310/ Thermo ISQ LT	TG-5MS, 30 m, 0.25 mm i.d., 0.25 µm	ASE	hexane, acetone	0:28 h:mm	----	Linear, multipoint force 0 (5-1000 pg/µl, 100 pg/µl IS), SIM	Acep-D4, Chry-D12, Napth-D8, Per-D12, Phe-D10	----	Dr. Ehrenstorfer Fisher Scientific, J.T. Baker
IMROH	HPLC/FLD, Agilent_1260 Infinity	Zorbax Eclipse PAH, 0.1 m, 1.6 mm i.d., 3.5 µm particle size	Ultrasonic: Elmasonic S 60H concentration: Organomation NEVAP	toluene, Cyclohexane	1:00 h:mm	Centrifugation, dryness brought to AcN	Linear, multipoint extenal standard, (5-160 pg/µl)	----	NISTH-1649B	Supelco, Merck
INERIS	HPLC/DAD, Agilent_1200 Series	C18, 0.25 m, 3.5 mm i.d., 5 µm particle size	ASE : Diones ASE 200, concentration: turbobap 2	DCM	----	----	Linear, extenal standard, (10-1000 pg/µl)	----	----	Riedel de Haën, Merck
ISCIII	GC/MS, ThermotraceGC Ultra/ Thermo DQS	TG-5MS, 30 m, 0.25 mm i.d., 0.25 µm	ASE, DIONEX ASE200 concentration: HORIZON TECHNOLGOY XcelVap	DCM	0:29 h:mm	500mg Cyano (top)/1000mg SiOH SPE-Bakaerbond J.T. Baker	linear, multipoint, (60-18480 pg/µl, IS 2760 pg/µl), SIM	B[a]A-D12, B[a]P-D12, Per-D12	NIST- SRM 1647F	Dr. Ehrenstofer, Merck, Sigma-Aldrich, LabScan
IVL	HPLC/FLD, Varian Postrar 240	Agilent C18, Pursuit 3PAH, 0.1 m, 3 mm i.d., 3 µm particle size	SOXLET	pentane, acetone	8 h - 24 h	SILICA: silicagel Merck Pentane --> MeOH	linear, multipoint, (10-2500 pg/µl, IS 393 pg/µl)	2,2 binaphthyl	----	NIST, Ultra Scientifiy, Dr. Ehrenstorfer, Rahtburn

LANUV	HPLC/FLD Agilent G1321A ,	Macherey&Nagel Nucelodur C18 PAH, 0.25 m, 4 mm i.d., 3 µm	ULTRASONIC: Bandelin Sonorex Super R 1050 concentration: Barkey Vapotherm mobil S	Toluene	24 h	SPE - Chromabond Florisil 200 mg Machery&Nagel- Vacuum chamber	linear, multipoint, external standard (10 - 200 pg/µl)	----	SRM2060A NIST, ERM-CZ100 IRRM	Ultra VWR	Scientific,	
LEGMC	GC/MS Agilent 7890A, Agilent 5975C	Agilent J&W DB-5MS, 50 m, 0.25 mm i.d., 0.25 µm	ASE, Dionex ASE 350 concentration: Caliper Life Science TurboVap II	1:1 acetone:hexane	0:25 h:mm	SILICA - glass chromatography columns 15 mm i.d. x 300 mm, --> hexane	linear, multipoint, (2-200 pg/µl, IS 500 pg/µl), SIM	Naph-D8, Acen-D10, Phe-D10 , Chr-D12, Per-D12, B[a]P-D12	----	Dr. Ehrenstorfer Merk		
NIU	GC/MS, HP 6890, 5973 MSD	Agilent Select PAH, 30 m , 0.25 mm i.d., 0.15 µm	SOXLET, concentration: Zymark TurboVap500,	1:1 acetone:hexane	8 h	SILICA-COLUM --> hexane	-----, IS , SIM	2MeNap-D10, Acen-d10, anthr-D10, Pyr-D10, B[a]A-D12, B[e]P-D12, B[ghi]P-D12	SRM2260A, SRM1944, SRM1649B (NIST)	Chiron, CIL, VRM		
OOE	GC/MS, Agilent 7890A, Agilent 5973C	supelco SLB-5S, 60 m, 0.25 mm i.d., 0.25 µm	ASE, DIONEX ASE200 concentration: Zymark TurboVap II	1:1 Cyclohexane:D CM	0:30 h:mm	----	linear , multipoint force (0) (10-400 pg/µl, IS 50-100 pg/µl)	Nap-D8, Phe-D10, Ace-D9, Acen-D10, Flu-D10, Pyr-D10, BaA-D12, Chr-D12, B[a]P-D12,B[b]F-D12, B[k]F-D12, Ind[123cd]P-D12, DB[ah]A-D14, B[ghi]P-D12	ERM-CZ100 IRRM	Dr. Ehrenstorfer Merk		
SEA	GC/MS, Agilent 7890B, Agilent 5977A	Agilent J&W, DB-5MS UI, 30 m, 0.25 mm i.d., 0.25 µm	MICROWAVE: Milestone Ethos 1 concentration: LCTech Feestyle systems evaporation	1:1 acetone:hexane	1 h	SILICA (Grace Pure Silica) -LCTech Freestyle sytems SPE	linear, multipoint, (3-100 pg/µl, IS 50 pg/µl), SIM	BaA-D12, BaP-D12, Ind[123cd]P-D12, B[b]F-D12	ERM-CZ100 IRRM	Dr. Ehrenstorfer Chiron Honeywell, Chem-Lab		
UBA	HPLC/FLD, Agilent_1100 series, Agilent G1321	thermo Hypersil Green PAH, 0.25 m, 3 mm i.d., 5 µm particle size	ULTRASONIC, concentration: Zymark TurboVap II	1:1 acetone:hexane	1 h	----	quadratic force (0) (1-250 pg/µl)	B[a]A-d12, B[k]F-d12, B[a]P-d12, DB[ah]A-d14, Ind[123cd]P-d12	ERM-CZ100 IRRM	Dr. Ehrenstorfer Promochem, Merck, VWR		
VMM	GC/MS, 7890B	Agilent	DB5 30 m, 0.25 mm i.d., 0.25 µm	ASE, Thermo Scientific, Dionex ASE 350 concentration: Biotage TurboVap II	1:1 acetone:hexane	0:30 h:mm	----	quadratic 1/x, multipoint, (1-250 pg/µl, IS 25 pg/µl), SIM	Flu-D10, Pyr-D10, BaA-D12, BbF-D12, BkF-D12, ind123cdPyr-D12, DBahA-D14, BghiP-D12	SRM1647F NIST	Dr. Ehrenstorfer Chem Lab Merk	
JRC	GC/MS, 6890, 5975C	Agilent	Rxi-17 Sil MS , 30 m, 0.25 mm i.d., 0.25 µm	Thermal desorption. Gerstel CIS-TD5	----	10 min	----	linear, multipoint (30-3400 pg/µl, 460 pg/µl IS), SIM	Nap-D8, Phe-D10, Ace-D9, Acen-D10, Flu-D10, Pyr-D10, B[a]A-D12, Chr-D12, B[a]P-D12,B[b]F-D12, B[k]F-D12, Ind[123cd]P-D12, DB[ah]A-D14, B[ghi]P-D12	Robust average value ISO-13528	Dr.. Ehrenstorfer Supelco, fluka analytica	

4. Travelling time, storage and date of analysis

Filters were stored from two to four weeks at -20°C before distribution on the 21st of March 2019. Travelling time varied from one to eight days, being four days the average time. While the time that laboratories stored the samples before analysis varied from two to 93 days with an average period of 41 days. The storages temperatures varied between -20°C and 20°C. Figure 8 shows the total time from distribution to analysis, the period of storage after reception of the filters and the storage temperature.

Figure 8 - Total time and storage period and temperature of the filters from their distribution



5. Reference Values

The reference value was determined based on the robust average results of the best performing laboratories. The selection of these laboratories was based on the number of outliers reported by each laboratory with respect to a robust average calculated on the basis of the ISO-13528. Therefore, robust average, \bar{C}_i^* , and standard deviation, s^* , of the p input laboratories, are derived from a convergence process of the following equation:

$$\bar{C}_i^* = \frac{\sum C_i^*}{p}$$

Eq. 1

$$s^* = 1.134 \cdot \sqrt{\frac{\sum (C_i - \bar{C}_i^*)^2}{(p - 1)}}$$

Eq. 2

Where recurrent values are calculated from these equations:

$$C_i^* = \begin{cases} \bar{C}_i^* - 1.5 \cdot s^* & \text{if } C_i < \bar{C}_i^* - 1.5 \cdot s^* \\ \bar{C}_i^* + 1.5 \cdot s^* & \text{if } C_i > \bar{C}_i^* + 1.5 \cdot s^* \\ C_i^* & \text{otherwise} \end{cases}$$

Eq. 3

The initial values are calculated as:

$$\begin{aligned} \bar{C}_i^* &= \text{median of } C_i (i = 1, 2, \dots, p) \\ s^* &= 1.483 \cdot \text{median of } |C_i - \bar{C}_i^*| (i = 1, 2, \dots, p) \end{aligned}$$

Eq. 4

By assuming normal distribution for the bias, $C_i - \bar{C}_i^*$, the associated standard uncertainty is estimated as:

$$u_{bias} = \sqrt{\frac{(1.25 \cdot s^*)^2}{p} + u_{C_i}^2}$$

Eq. 5

Where u_{C_i} is the uncertainty of the reported value from laboratory i.

The null hypothesis for a bias equal to zero can be evaluated using the two tails statistical test of normal distribution of the random variable, Z, defined as:

$$Z = \frac{C_i - \bar{C}_i^*}{u_{bias}}$$

Eq. 6

In light of this statistic, where Z values higher than 3 were considered as outliers, a first evaluation of results was carried out. The output of this first evaluation in terms of overall reported data and outliers are shown in Table 5.

Laboratories with an overall ratio outlier/reported higher than 15% were excluded from the estimation of the robust average value, i.e. the reference value of the inter-laboratory comparison (i.e. HMS, INERIS and ISCIII). Robust average values from the best performance laboratories and associated expanded uncertainties ($k=2$) are given in

Table 6. Those values were considered as reference values for the final evaluation purpose of the exercise.

Table 5 - Total reported values and outliers from participating laboratories

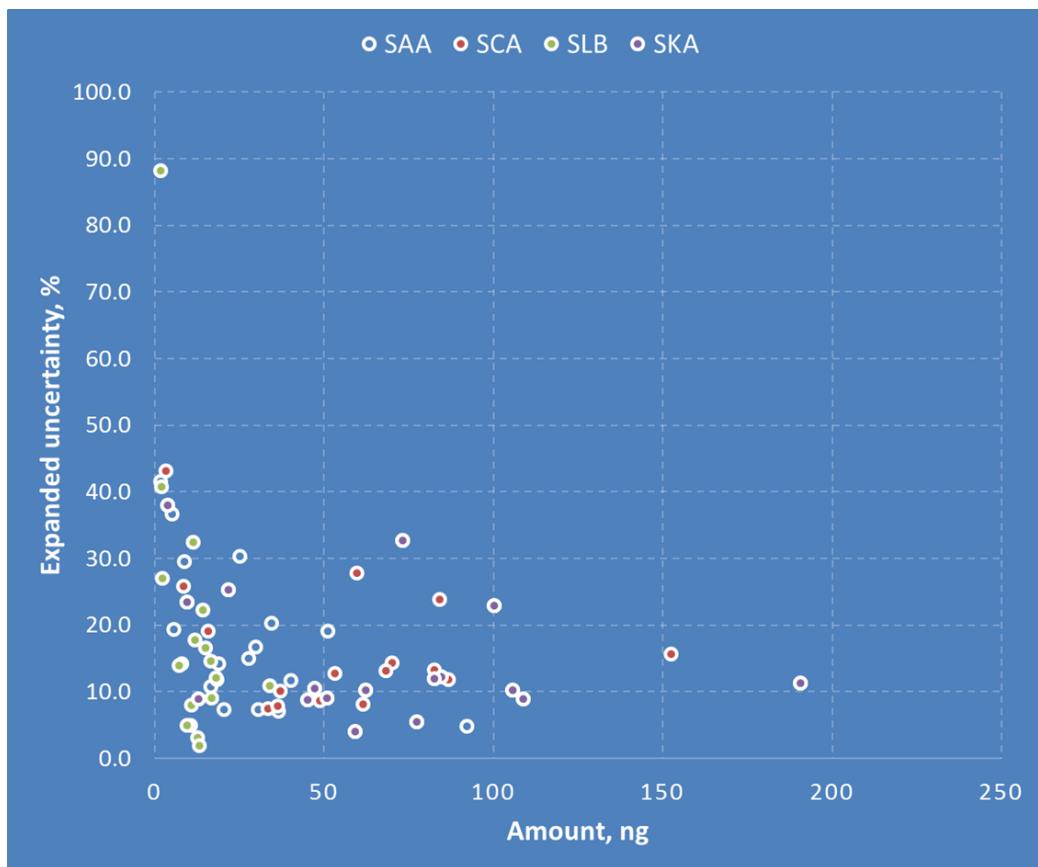
laboratories	Compounds			
	reported	outliers	% reported values vs total	% outliers vs reported
AU_ENVS	42	3	65.6	7.1
CHMI	64	0	100.0	0.0
FMI	44	1	68.8	2.3
HMS	56	45	87.5	80.4
IMROH	46	1	71.9	2.2
INERIS	50	14	78.1	28.0
ISCIII	27	20	42.2	74.1
IVL	52	1	81.3	1.9
LANUV	32	0	50.0	0.0
LEGMC	44	4	68.8	9.1
NILU	61	0	95.3	0.0
OOE	60	1	93.8	1.7
SEA	18	0	28.1	0.0
UBA	57	2	89.1	3.5
VMM	48	6	75.0	12.5
JRC	64	2	100.0	3.1

Table 6 - Reference values and corresponding expanded uncertainties

Filter	SAA		SCA		SKA		SLB	
	(01/02/2018)	(03/02/2018)	(11/02/2018)	(12/02/2018)	Amount ng	EU, %	Amount ng	EU, %
Compound	Amount ng	EU, %	Amount ng	EU, %	Amount ng	EU, %	Amount ng	EU, %
Phenanthrene	8.72	29.5	15.50	19.1	21.65	25.4	11.31	32.5
Anthracene	1.74	41.6	3.14	43.2	3.64	38.0	1.51	88.2
Fluoranthene	16.29	10.8	33.19	7.6	47.00	10.6	16.38	14.7
Pyrene	18.76	14.3	36.95	10.1	50.77	9.2	17.88	12.2
Benzo[a]anthracene	18.11	11.9	53.07	12.8	62.13	10.4	7.92	14.3
Chrysene	29.69	16.8	83.90	23.9	100.00	22.9	13.96	22.4
Benzo[b]fluoranthene	50.91	19.2	86.55	11.9	105.52	10.4	16.78	9.1
Benzo[j]fluoranthene	27.70	15.0	48.50	8.8	59.11	4.0	9.33	5.0
Benzo[k]fluoranthene	20.21	7.4	36.23	7.9	44.95	8.9	6.96	14.0
Benzo[e]pyrene	34.36	20.4	59.46	27.9	73.07	32.8	11.75	17.9
Benzo[a]pyrene	30.53	7.5	69.96	14.4	84.50	12.3	10.59	8.0
Perylene	5.57	19.5	10.45	5.0	12.85	9.0	2.25	27.1
Indeno[1,2,3,-c,d]pyrene	36.45	7.1	61.45	8.2	77.21	5.5	12.57	3.2
Dibenzo[a,h]antracene	4.92	36.8	8.25	25.9	9.29	23.5	1.82	40.9
Benzo[g,h,i]perylene	39.96	11.7	68.14	13.3	82.50	12.1	14.92	16.6
*Chrysene+Triphenylene	24.96	30.4	82.46	13.3	108.50	9.0	12.92	2.0
*Benzo[b,j,k]fluoranthene	92.06	4.9	152.31	15.7	190.49	11.4	33.91	11.0

It is noted that for most of the compounds considered, the uncertainty of the reference value mainly depended on the concentration level, as uncertainties were larger when concentrations approached the detection limit of the method (see Figure 9). The median value of the expanded uncertainty for all compounds was 14%. In the case of B[a]P with concentrations in the filter between 10.6 ng and 84.5 ng, their expanded uncertainty values ranged between 7.5% and 12.3%.

Figure 9 - Expanded uncertainty versus amount of analytes in the filter



6. Evaluation of the laboratory results

Robust repeatability and reproducibility for the exercise were estimated following procedures indicated in ISO 5725. These values were obtained after elimination of outliers identified by the Mandel's k and h statistic. Therefore, the uncertainty of the inter-laboratory average value, \bar{C} , is determined by the combination of the inter-laboratory variance, S_L^2 , and the intra-laboratory variance (repeatability variance of uncertainties), S_r^2 . The addition of both variances represents the reproducibility variance, S_R^2 , in this case being the variance associated with the uncertainty of the method:

$$u = \sqrt{S_L^2 + S_r^2} = S_R$$

Eq. 7

Being

$$S_r^2 = \frac{1}{p} \sum_i^p S_i^2$$

Eq. 8

$$S_R^2 = \frac{1}{2} \sum_i^p (\bar{C}_i - \bar{C})^2 + \left(1 - \frac{1}{n}\right) \cdot S_r^2$$

Eq. 9

where 'p' is the number of laboratories; 'n' is the number of replicated analyses done by each laboratory; S_i and C_i are the standard deviation and average value corresponding to the laboratory 'i'.

The standard deviation of the average inter-laboratory values, S_L , was used to calculate a robust standard deviation to characterise the analytical performance of each compound. By assuming a linear regression between concentration level and the corresponding inter-laboratory standard deviation of the compared filters, correlation parameters between standard deviations and concentrations were calculated for each compound (see annex IV). The correlation parameters are given in Table 7. The analytical standard deviation calculated through these correlations has been used as the standard deviation for proficiency assessment, σ_{PT} .

In this report, Proficiency testing was based on the following statistics: *Z'-score* for evaluating biases with respect to reference values and *Repeatability-score* for evaluating the uncertainty estimation of the laboratory. In addition, *E_n-scores* were calculated together with an estimation of an *overall standard uncertainty* that represented the contribution of the uncertainty of the measurement and bias with respect to the reference value.

Table 7 - Linear correlation between amount of compound and analytical standard deviation, $\hat{\sigma}_{PT}$

Compound	slope	intercept	R ²
Phenanthrene	0.2246	-0.2946	0.9777
Anthracene	0.0391	0.5174	0.0626
Fluoranthene	0.0469	0.2957	0.9986
Pyrene	0.0346	0.3203	0.9006
Benzo[a]anthracene	0.0517	0.2006	0.9413
Chrysene	0.0967	0.6739	0.8102
Benzo[b]fluoranthene	0.0478	2.2448	0.7230
Benzo[j]fluoranthene	0.0296	1.277	0.1822
Benzo[k]fluoranthene	0.0338	0.2791	0.8879
Benzo[e]pyrene	0.1756	-1.0621	0.9583
Benzo[a]pyrene	0.0622	-0.0517	0.9826
Perylene	0.0743	-0.0493	0.9999
Indeno[1,2,3,-c,d]pyrene	0.0638	-0.4351	0.9018
Dibenzo[a,h]anthracene	0.1501	0.3979	0.9759
Benzo[g,h,i]perylene	0.0793	-0.0478	0.9313
*Chrysene+Triphenylene	0.0509	1.4436	0.6228
*Benzo[b,j,k]fluoranthene	0.0907	-1.3224	0.7023

$$\hat{\sigma}_{PT} = \text{slope} \cdot [\text{amount of analytie in the filter (ng)}] + \text{intercept}$$

6.1. E_n-score

E_n scores were calculated as:

$$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$$

Eq. 10

where C_{lab}, U_{lab} and C_{ref}, U_{ref} are the concentrations and expanded uncertainties for the reported and reference value, respectively.

According to ISO 13528, En-scores with E_n ≥ 1 or E_n ≤ -1 could indicate a need to review the uncertainty estimates, or to correct a measurement issue; similarly -1 < E_n < 1 should be taken as an indicator of successful performance, only if the uncertainties are valid and the deviation (C_{lab}-C_{ref}) is smaller than needed by the participant's customers.

6.2. Z'-score

This statistic is calculated according to ISO13528:2015 as:

$$Z' - score = \frac{C_{lab} - C_{ref}}{\sqrt{\hat{\sigma}_{PT}^2 + u_{ref}^2}}$$

Eq. 11

where u_{ref} is the uncertainty associated with the reference value and $\hat{\sigma}_{PT}$ the standard deviation assigned to the proficiency assessment.

6.3. Repeatability score

A repeatability score based on the ratio between the uncertainty of the laboratory, u_{lab} , and the standard deviation of the proficiency test, $\hat{\sigma}_{PT}$, can be used to monitor the adequacy of the uncertainty estimated by the participating laboratory in the context of the exercise.

$$Repeatability - Score = \frac{u_{lab}}{\hat{\sigma}_{PT}}$$

Eq. 12

6.4. Overall expanded uncertainty

The overall expanded uncertainty, OEU, represents the sum of the expanded uncertainty of the reported result, U_{lab} , and the absolute value of its bias with respect to the reference value. The OEU is calculated according to the following expression:

$$OEU(\%) = \left(\frac{U_{lab}}{C_{lab}} + \frac{|C_{lab} - C_{ref}|}{C_{ref}} \right) \cdot 100$$

Eq. 13

6.5. Robust overall expanded uncertainty for the comparison

For the comparison exercise, a robust overall expanded uncertainty can be calculated as it follows:

$$OEU_R(\%) = \left(2 \cdot \frac{S_R}{C_{ref}} + \frac{|\bar{C} - C_{ref}|}{C_{ref}} \right) \cdot 100$$

Eq. 14

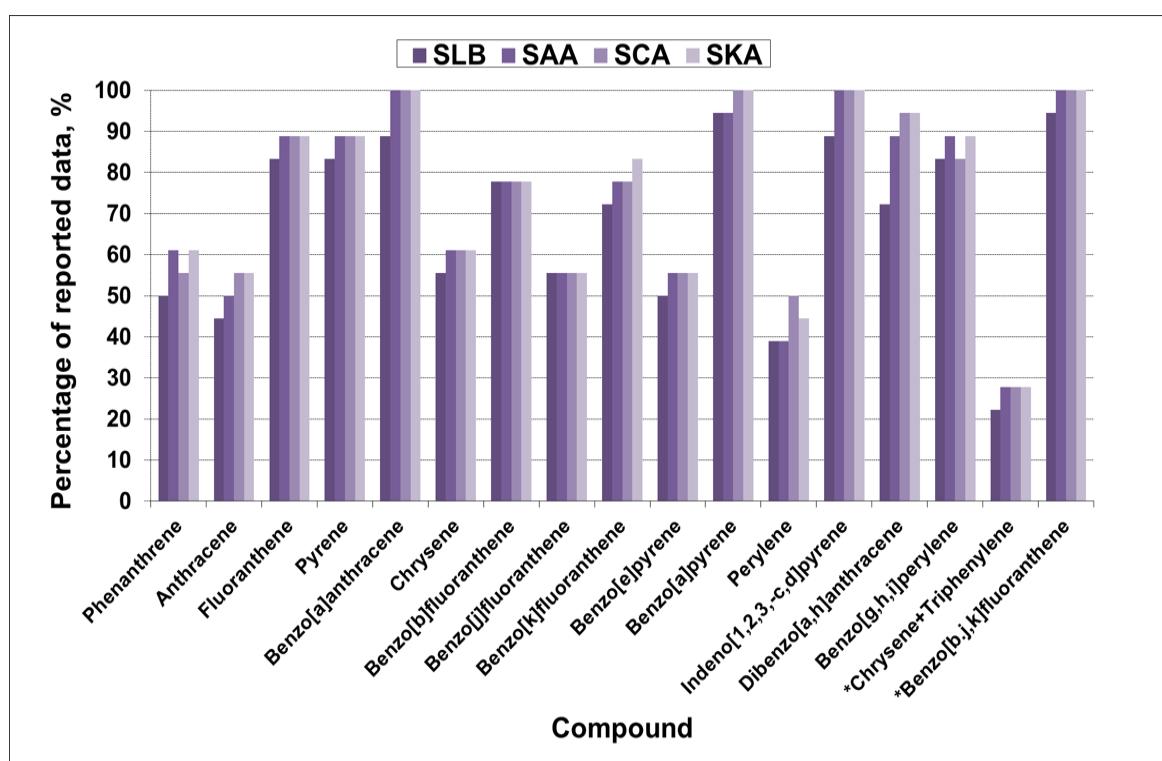
7. Results and discussion

7.1. Data reporting

Not all the laboratories reported the complete list of compounds of Table 2. Phe, Anth, Chry, B[j]F, B[e]P and Per, were reported by only half of the participants. On the other hand, a few laboratories reported other compounds not requested. This was the case of CHMI (reporting Retene, Picene and Coronene), NILU (reporting naphthalene, dibenzofuran, 1,2&9-methylphenanthrenes, retene, benzo[b]fluorene, benzo[g,h,i]fluoranthene, ciclopentane[c,d]pyrene, triphenylene, benzo[a]fluoranthene, dibenzo[a,c]anthracene, coronene, dibenzo[a,e]pyrene).

Figure 10 shows the percentage of reporting PAHs by laboratories. The highest reported percentage corresponded to those compounds mentioned in EU directive 2004/107/EC.

Figure 10 - Percentage of reported data by compounds from all participating laboratories



Laboratories carried out an estimation of their uncertainties, although, in general, the description of the calculation was quite cryptic. The way in which uncertainty was calculated and additional analytical comments from the laboratories are collected in the annex XIII.

Most of the laboratories reported individual values for the isomers of B[bjk]F and Chry+TPh. Nevertheless, some laboratories were not able to separate all isomers and consequently they were reported together or partially separated. Therefore, the statistical analysis of the results for these compounds was limited by a series of statistical assumptions regarding the combination of uncertainties and compounds. Laboratories should take into consideration these assumptions in order to evaluate and interpret their individual results. Details of the reported isomers and treatment are provided in annex V.

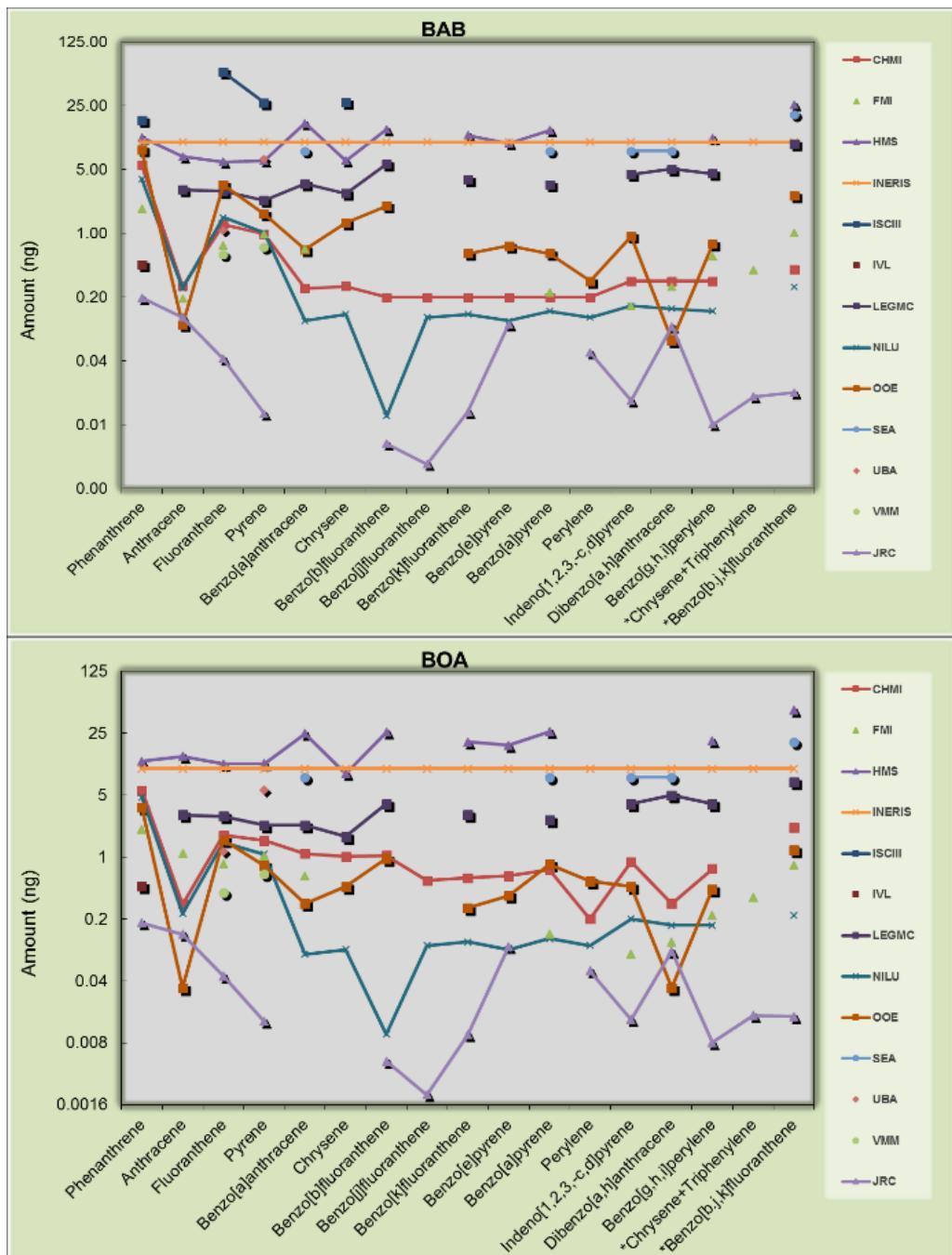
7.2. Blank filters

The blank filters (code BAB and BOA) were a good indication of the noise level associated with the analytical methodology. The reported concentrations for these blank filters are represented in Figure 11. It is noted that the highest blank levels were reported by those

laboratories, which were identified as outlier laboratories in the comparison (see Table 5). In fact, these average blanks decreased by a 70% when identified outliers were removed to estimate a robust blank value.

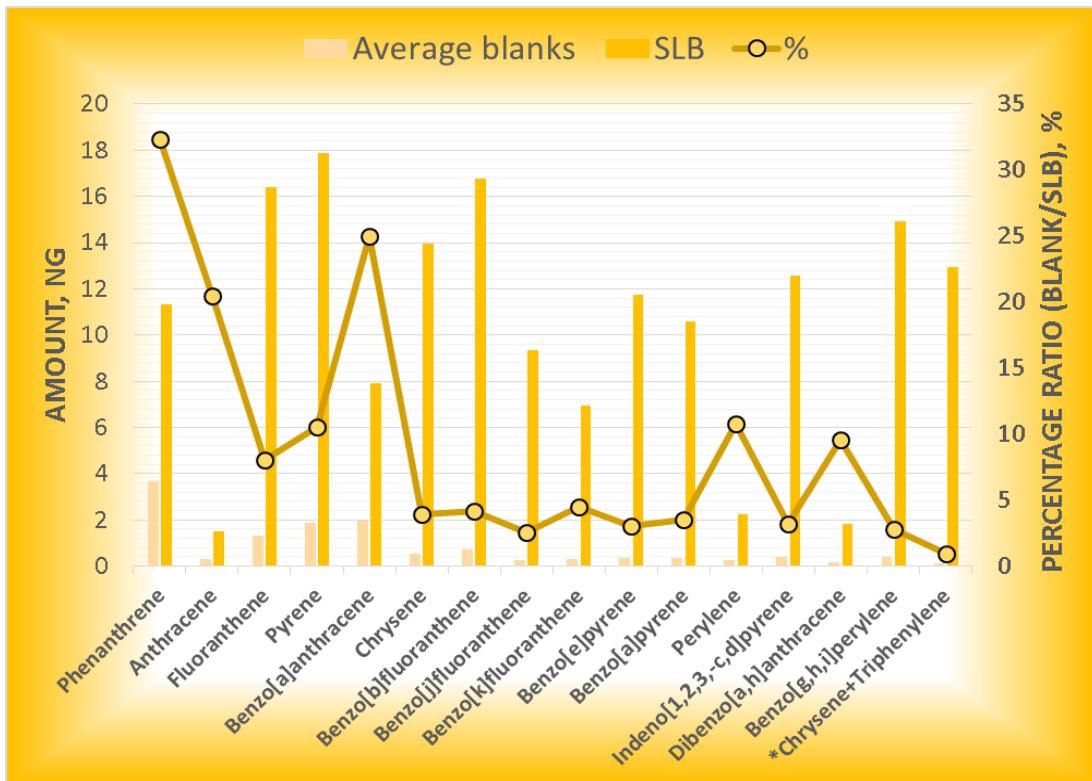
Phe was the compound with the highest amount detected in the blanks (3.6 ng), followed by B[a]A, Pyr and Flu for which their amounts ranged from 2 ng to 1.3 ng in the filters.

Figure 11 - Concentrations of the blank filters



It was noted that for some compounds, the amount detected in the blanks represented a significant amount compared to that analysed in the lower concentration filter (SLB). This was, for instance, the case of Phe (32%), B[a]A (25%), Anth (20%), Per (11%), Pyr (10%) and DB[ah]Anth (10%) (see Figure 12). On the other hand, the outlier blanks were at the same level or higher than the amounts of the lower concentration samples. This could explain the general overestimation of these laboratories during the exercise.

Figure 12 - SLB filter and robust average blank level



7.3. Scattering of laboratory results

The scattering of results of the inter-laboratory comparison were represented in terms of deviation with respect to the lower compared value. Deviations and bias are related according to the following expressions:

$$\text{bias}(\%) = \text{deviation} (\%) \quad \text{if Laboratory value} > \text{Reference value}$$

Eq. 15

or

$$\text{bias}(\%) = -\frac{\frac{\text{deviation}(\%)}{100}}{1 + \frac{\text{deviation}(\%)}{100}} \cdot 100 \quad \text{if Laboratory value} < \text{Reference value}$$

Eq. 16

Consequently, the signs '+' and '-' indicate the 'over' and 'under' estimation of the reference value.

Showing the laboratories' scattering in terms of deviations has the advantage of a symmetrical representation of the over and under estimations with respect to reference values.

Figure 13 to Figure 16. shows the results of the inter-laboratory comparison for the different filters and analysed compounds. The figures include outliers and are expressed in terms of deviation. These figures show how some laboratories are systematically over- or under-estimating the reference concentration. On the other hand, it was evident that the scattering of the results increased with the decrease concentrations on the filter.

Figure 13 - Inter-laboratory result – Filter SAA from 01/02/2018 (75 percentile BaP concentration)

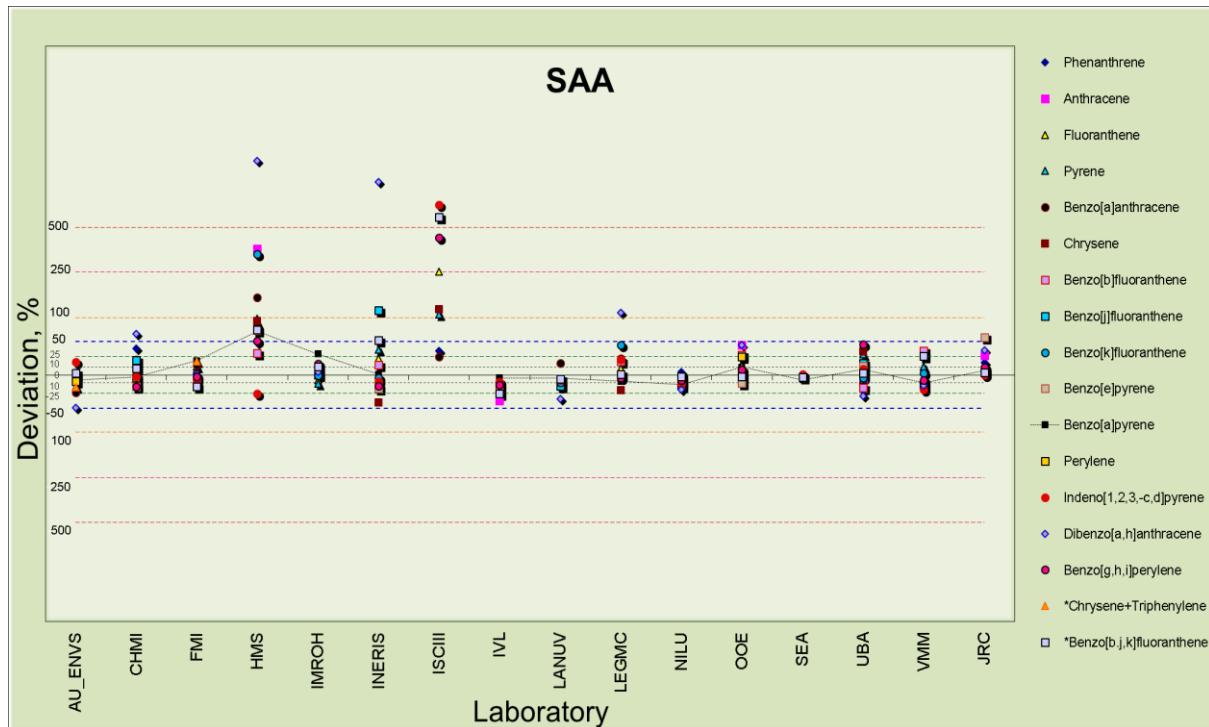


Figure 14 - Inter-laboratory result – Filter SLB from 12/02/2018 (lowest BaP concentration)

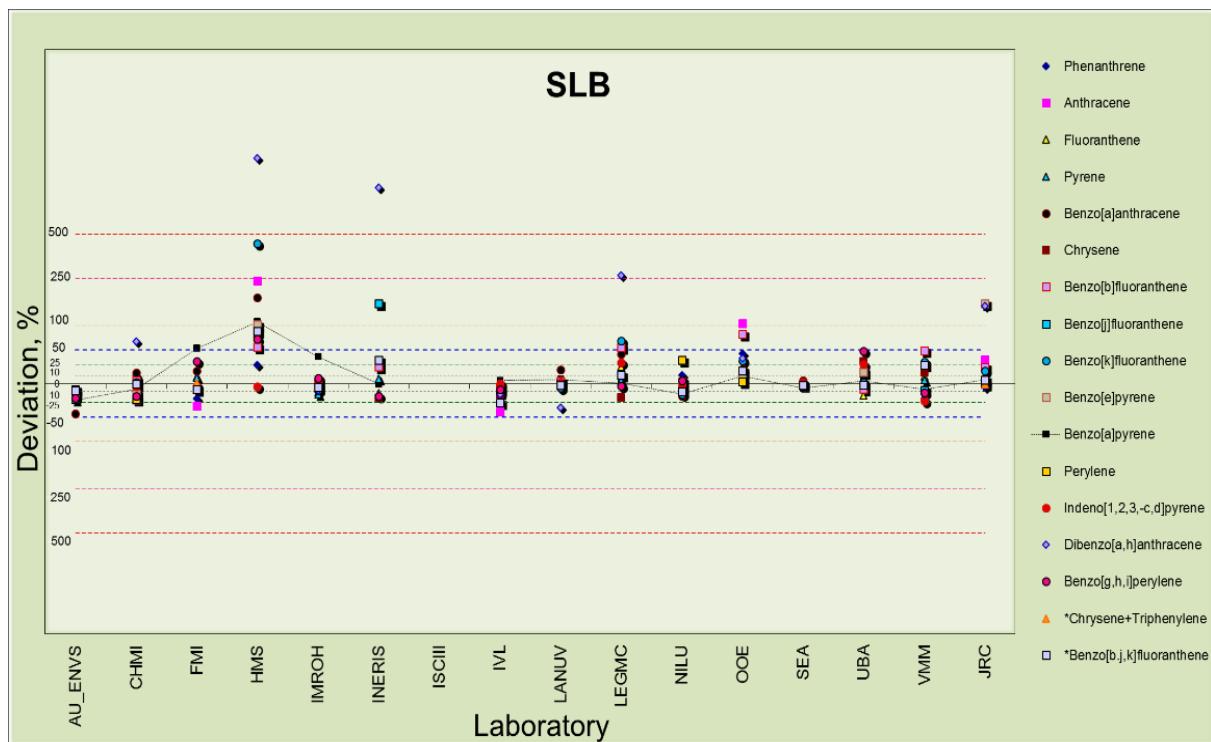


Figure 15 - Inter-laboratory result – Filter SCA from 03/02/2018 (25 percentile BaP concentration)

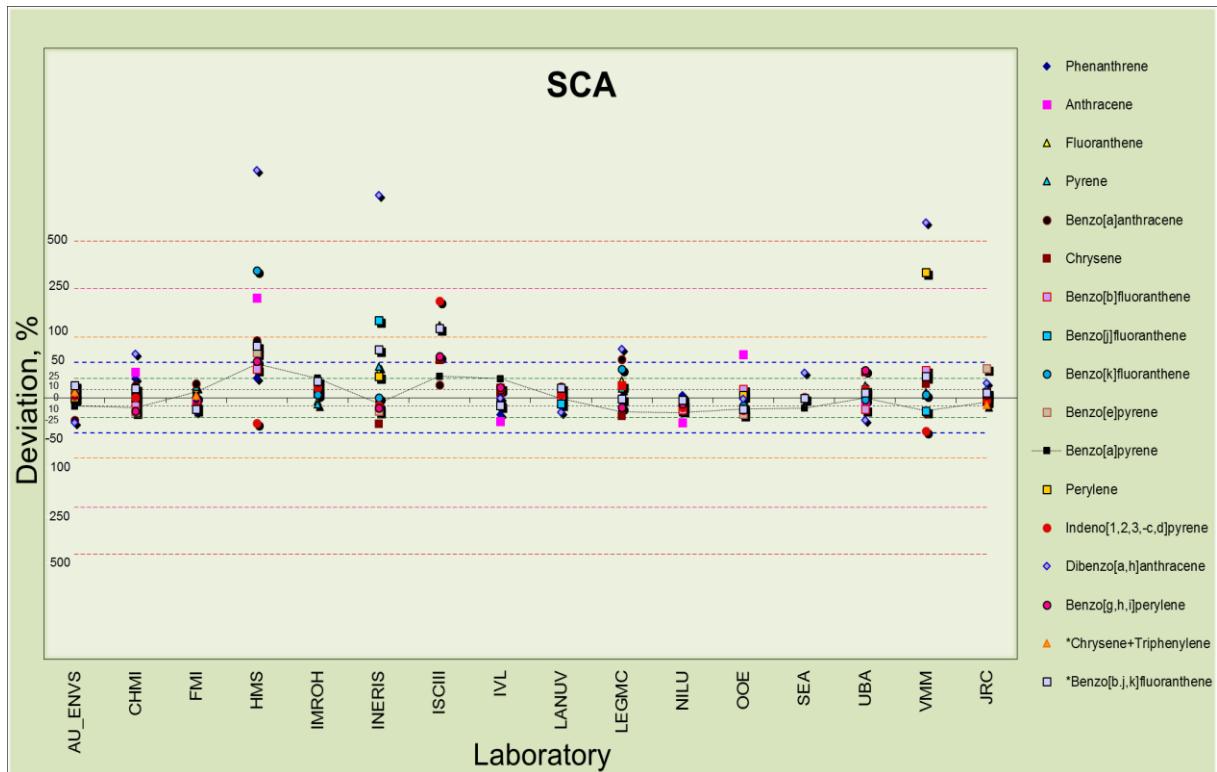
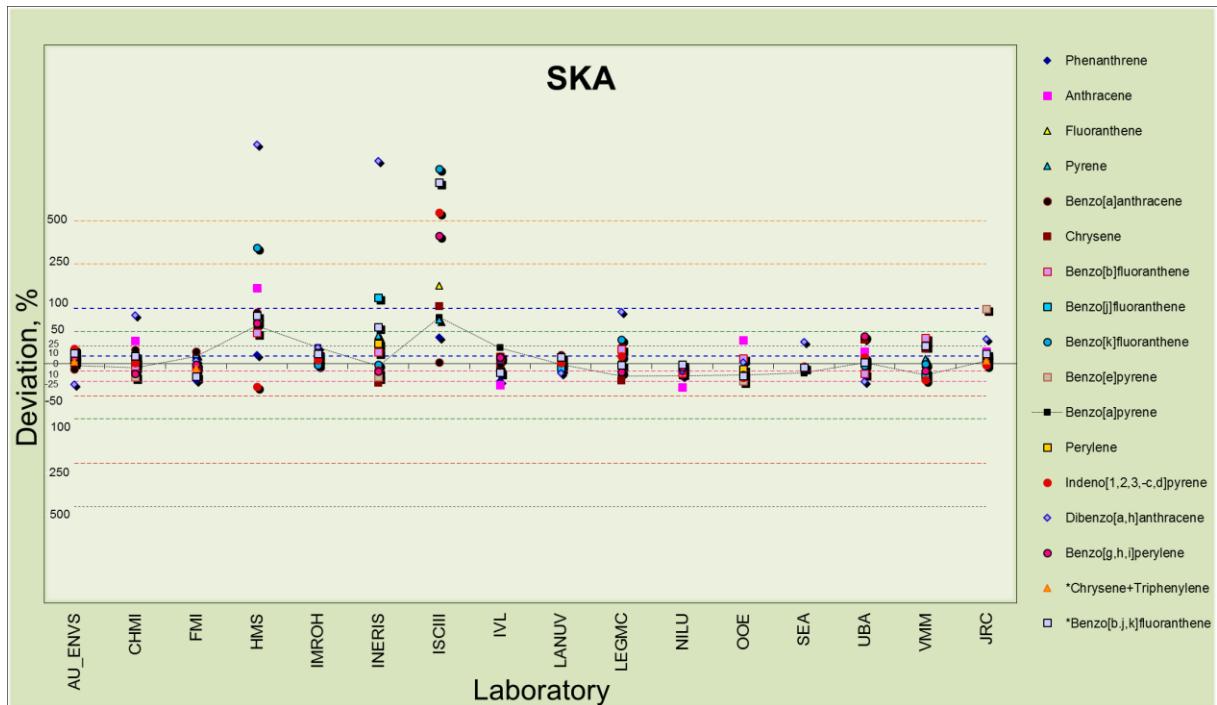


Figure 16 - Inter-laboratory result – Filter SKA from 11/02/2018 (highest BaP concentration)



7.4. Repeatability, reproducibility and overall expanded uncertainty of the comparison exercise

Repeatability and reproducibility values were calculated according to ISO 5725 by considering the laboratory reported uncertainty as the input standard deviation of the reported average value. The convergence of ISO 5725 outlier statistic detection provided robust values for the repeatability uncertainty, the reproducibility and the overall expanded uncertainty (section 6.5) of the comparison.

Average values of the repeatability uncertainty and reproducibility for the four compared filters, as well as the average repeatability standard deviation from replicated analysis are represented in Figure 17. Figure 18 shows the robust overall expanded uncertainty estimated for each filter comparison.

Figure 17 - Average standard deviation, repeatability uncertainty and reproducibility of the filters comparison

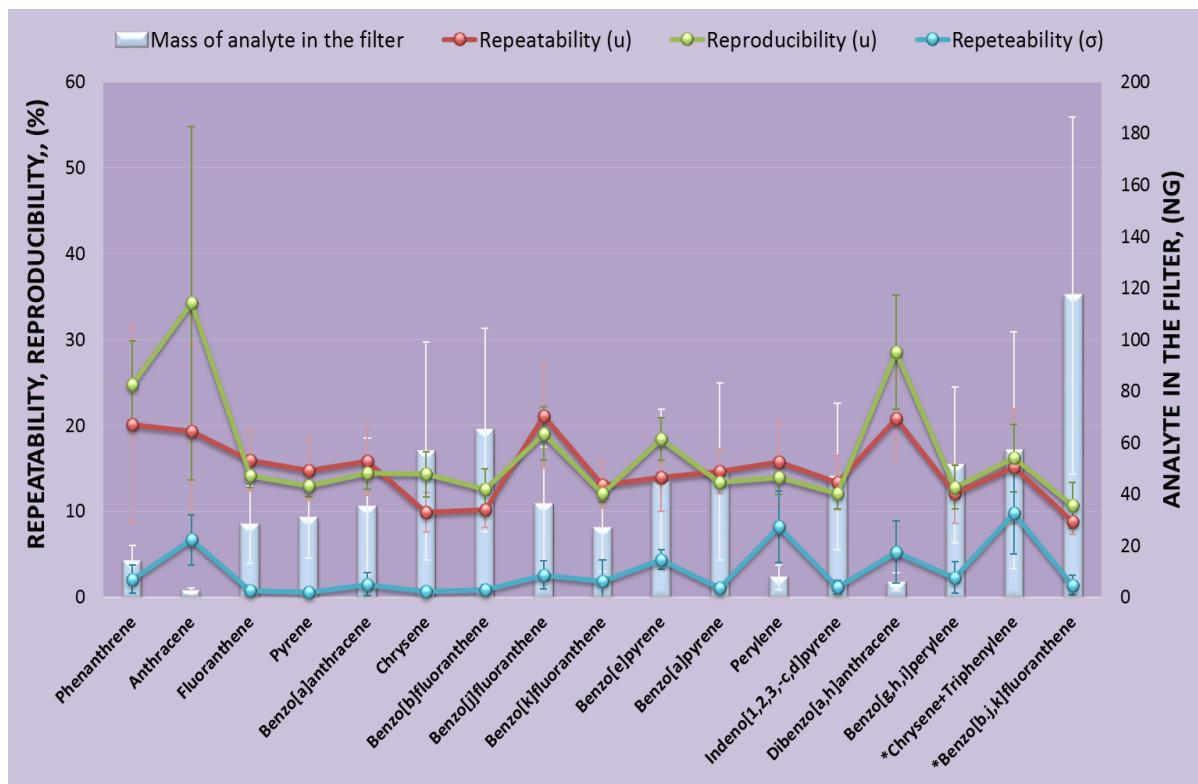
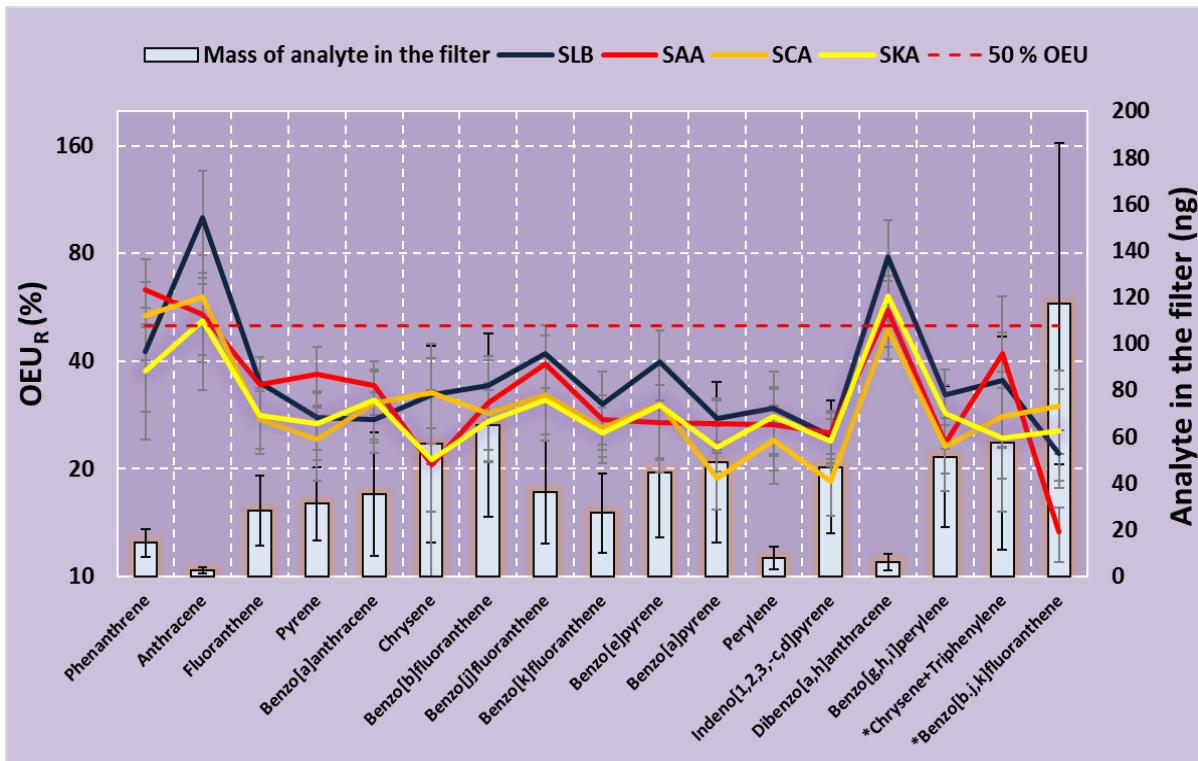


Figure 18 - Robust overall expanded uncertainty for the filters comparison



The median analytical repeatability standard deviation (σ), considering all compared filters and compounds, was circa 1.9%, while repeatability uncertainty and reproducibility median values were around 14.5 %, which confirmed the robustness of the method. The median value for the robust overall expanded uncertainty was of circa 30%. These values were similar to the B[a]P, which showed repeatability and reproducibility values around 14%, an overall expanded uncertainty of 24% and a repeatability standard deviation of around 1%. These results and in particular B[a]P were under the levels of uncertainties requested by the Directive 2004/107/EC for the annual limit value of B[a]P of 50% (Table 8).

Table 8 - Robust overall expanded uncertainty of the compared filters

Compound	Robust overall expanded uncertainty, OEU_R (%)			
	SLB	SAA	SCA	SKA
Phenanthrene	42.6	63.2	53.4	37.4
Anthracene	100.9	54.0	60.4	52.0
Fluoranthene	34.7	34.4	27.5	28.2
Pyrene	27.7	36.7	24.19	26.8
Benzo[a]anthracene	27.3	34.1	30.4	31.0
Chrysene	32.1	20.5	32.6	21.1
Benzo[b]fluoranthene	34.1	30.5	28.6	27.0
Benzo[j]fluoranthene	41.9	39.4	32.1	31.1
Benzo[k]fluoranthene	30.3	27.4	26.0	25.2
Benzo[e]pyrene	39.9	26.9	30.3	30.1
Benzo[a]pyrene	27.6	26.7	18.7	22.9
Perylene	29.5	26.6	24.1	27.9
Indeno[1,2,3,-c,d]pyrene	24.6	25.1	18.4	23.8
Dibenzo[a,h]anthracene	78.4	55.3	49.2	60.6
Benzo[g,h,i]perylene	32.2	23.5	23.0	28.5
*Chrysene+Triphenylene	35.4	41.9	28.0	24.4
*Benzo[b,j,k]fluoranthene	22.0	13.3	29.8	25.5

7.5. Z'-scores

Z'-scores are reported by compounds in annex VI. Between laboratories, the median of the percentage of Z'-scores from reported values ≥ 2 was 11%, while for values ≥ 3 , it was 5%. When the same statistic was considered between compounds, 27% of the values were ≥ 2 , while 19% were ≥ 3 . These results are shown in more detail in Figure 19 and Figure 20.

Figure 19 - Z'-score of reported data by participating laboratories

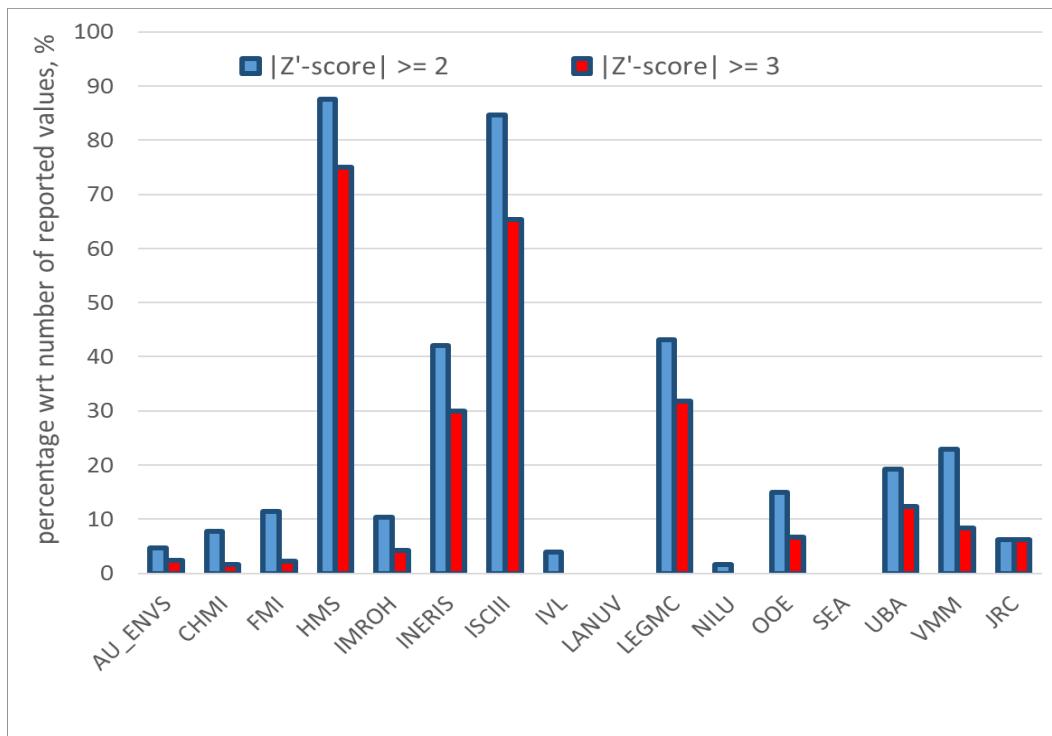
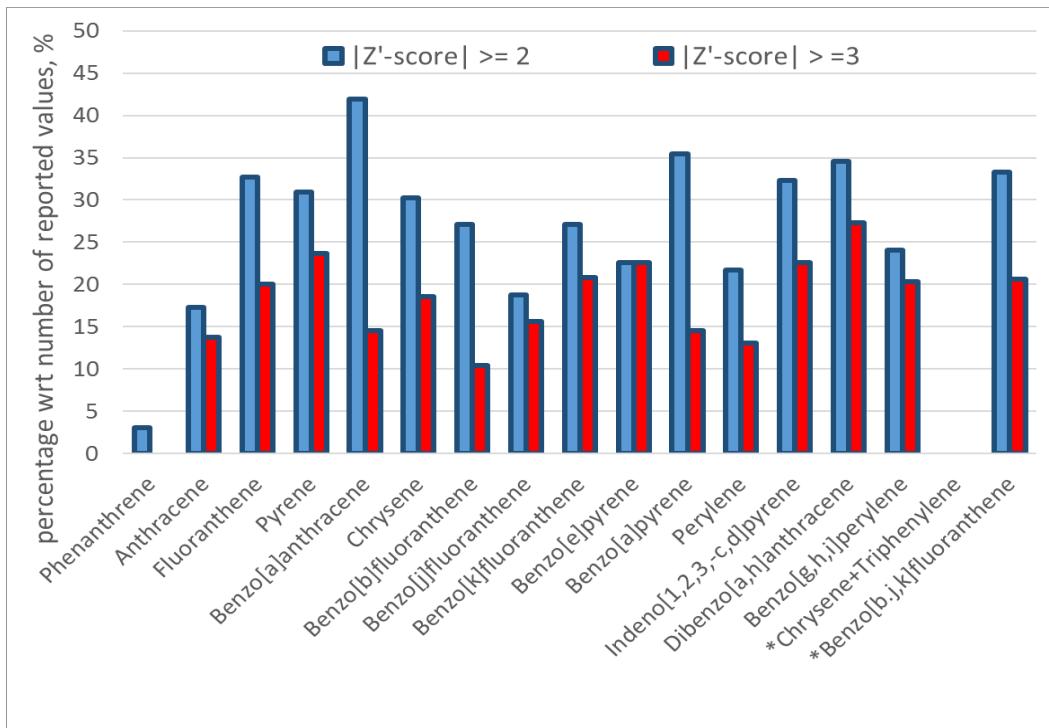


Figure 20 - Z'-score of reported data by analysed compounds



7.6. Repeatability-scores

Repeatability score are reported by compounds in annex VII. Between laboratories, the median percentage of repeatability-scores with reported values ≥ 2 was 18%, while for values ≥ 3 , the percentage was 7 %. When the same statistic was considered between compounds, 12% of the values were ≥ 2 , while 7% were ≥ 3 . These results are illustrated in Figure 21 and Figure 22.

Figure 21 - Repeatability-score by participating laboratories

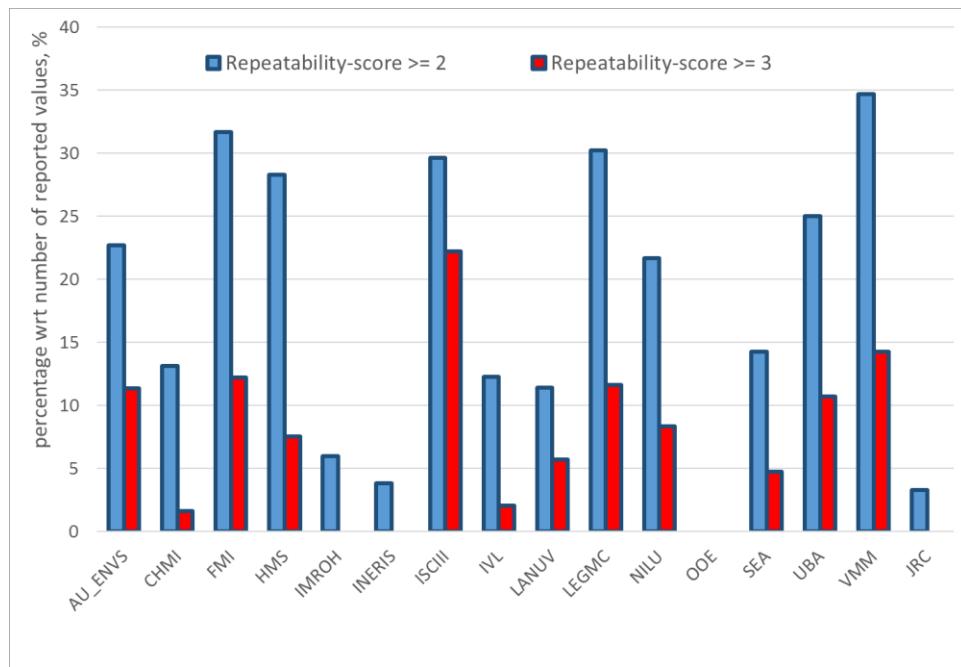
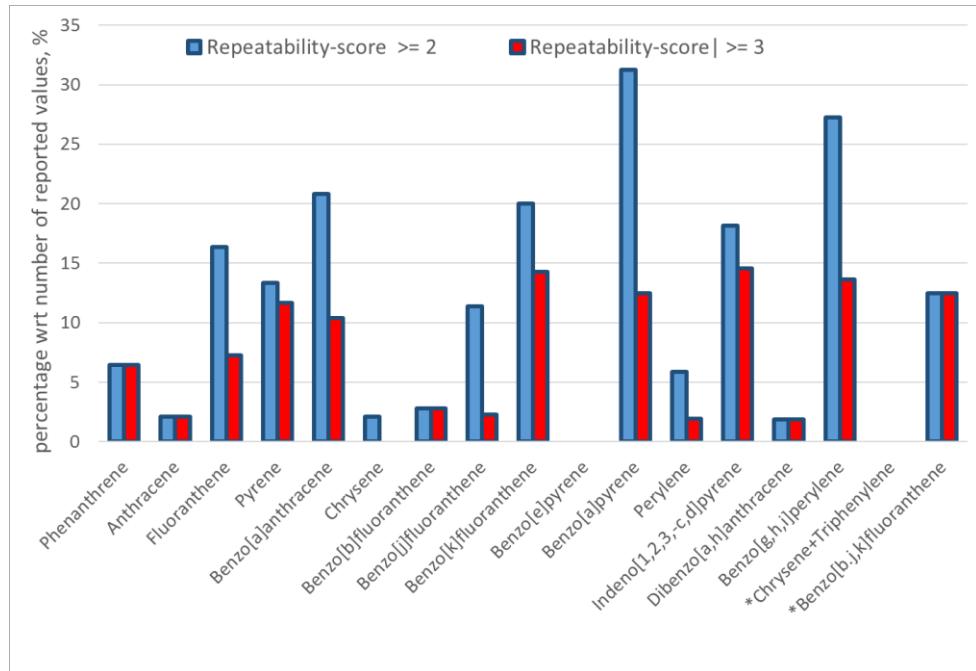


Figure 22 - Repeatability-score by analysed compounds



Those laboratories or compounds with repeatability scores higher than 2 could suffer from an overestimation of the reported uncertainties, which was consistent with the differences between E_n -scores and Z' -scores laboratory ranking.

7.7. E_n-scores

E_n-scores are provided by laboratories in annex VIII. Between laboratories, the median of the percentage of E_n-scores from reported values ≥ 1 was 4%. When the same statistic was considered between compounds, 13% of the values were ≥ 1 . These results are shown in more detail in Figure 23 and Figure 24.

Figure 23 - En-score by participating laboratories

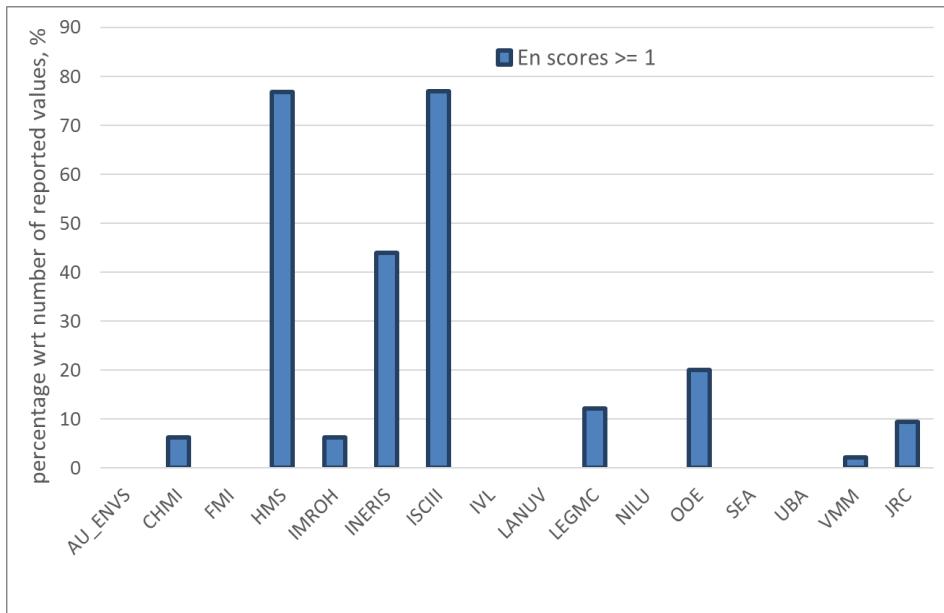
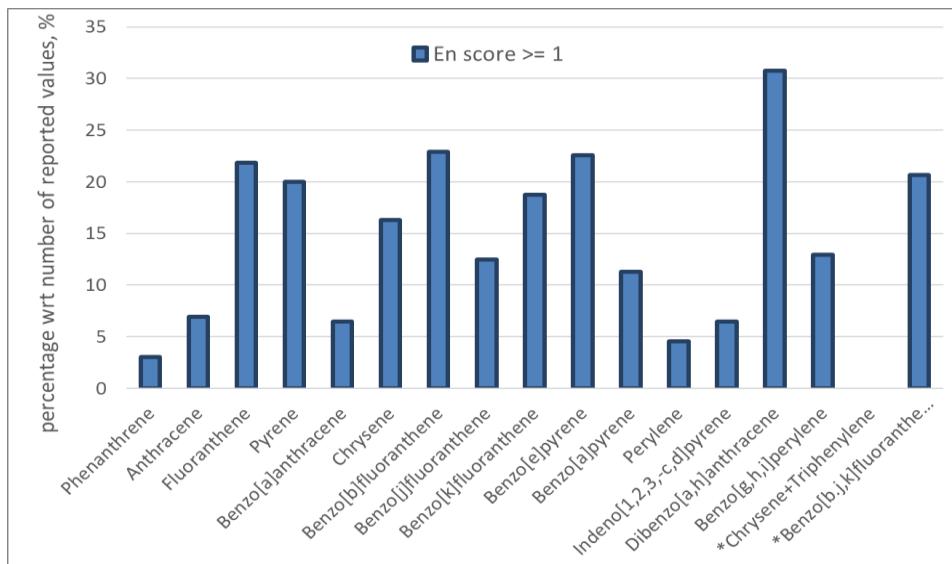


Figure 24 - En-score by analysed compounds



7.8. Overall expanded uncertainties

The overall expanded uncertainties by compounds are given in annex IX. Between laboratories, the median of the percentage of OEU from reported values $\geq 50\%$ was 32 %. When the same statistic is considered between compounds, 33 % of the values were $\geq 50\%$. These results are illustrated in Figure 25 and Figure 26.

Figure 25 - Bias, reported and overall expanded uncertainty by participating laboratory

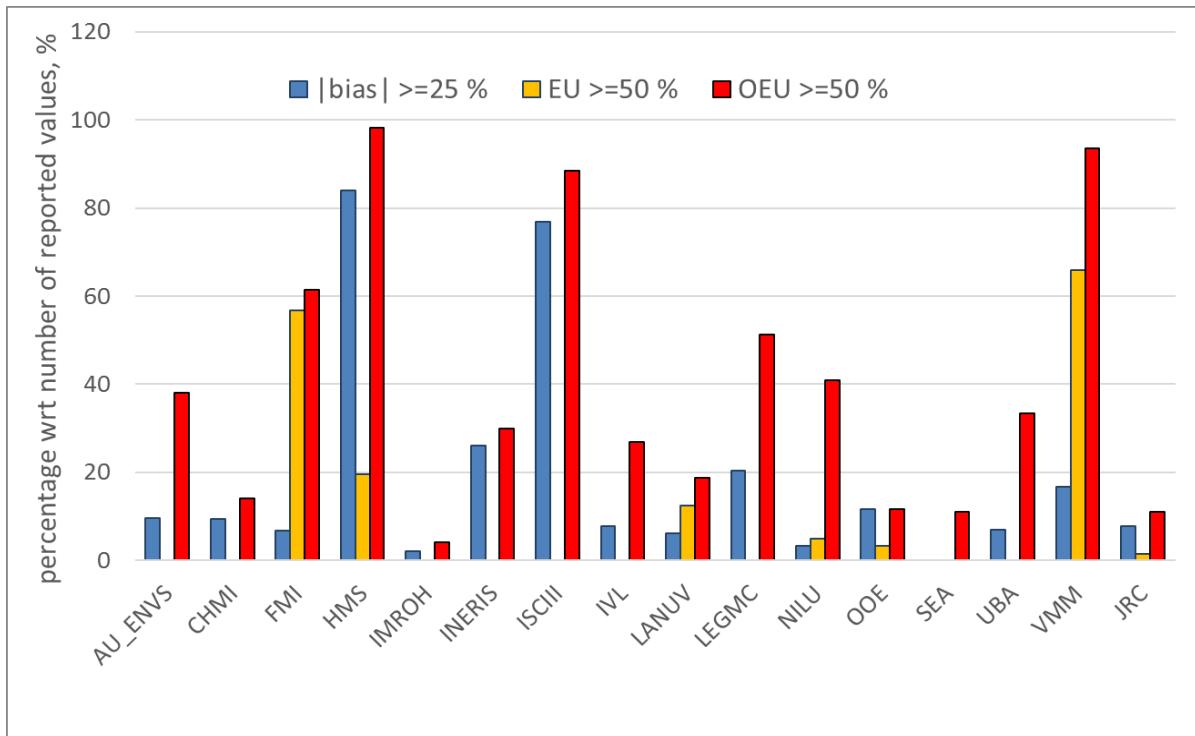
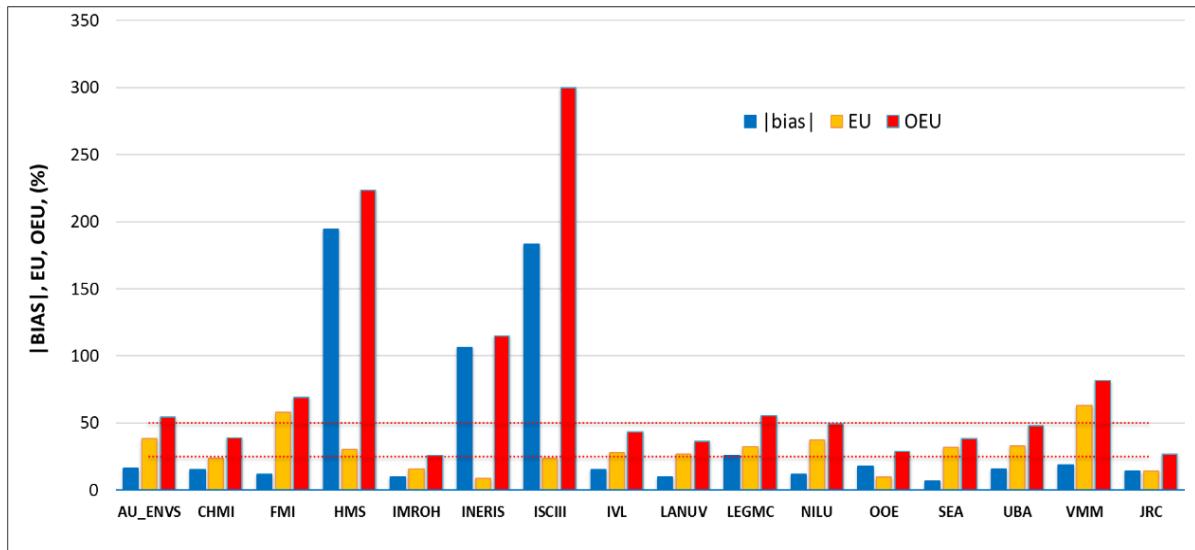


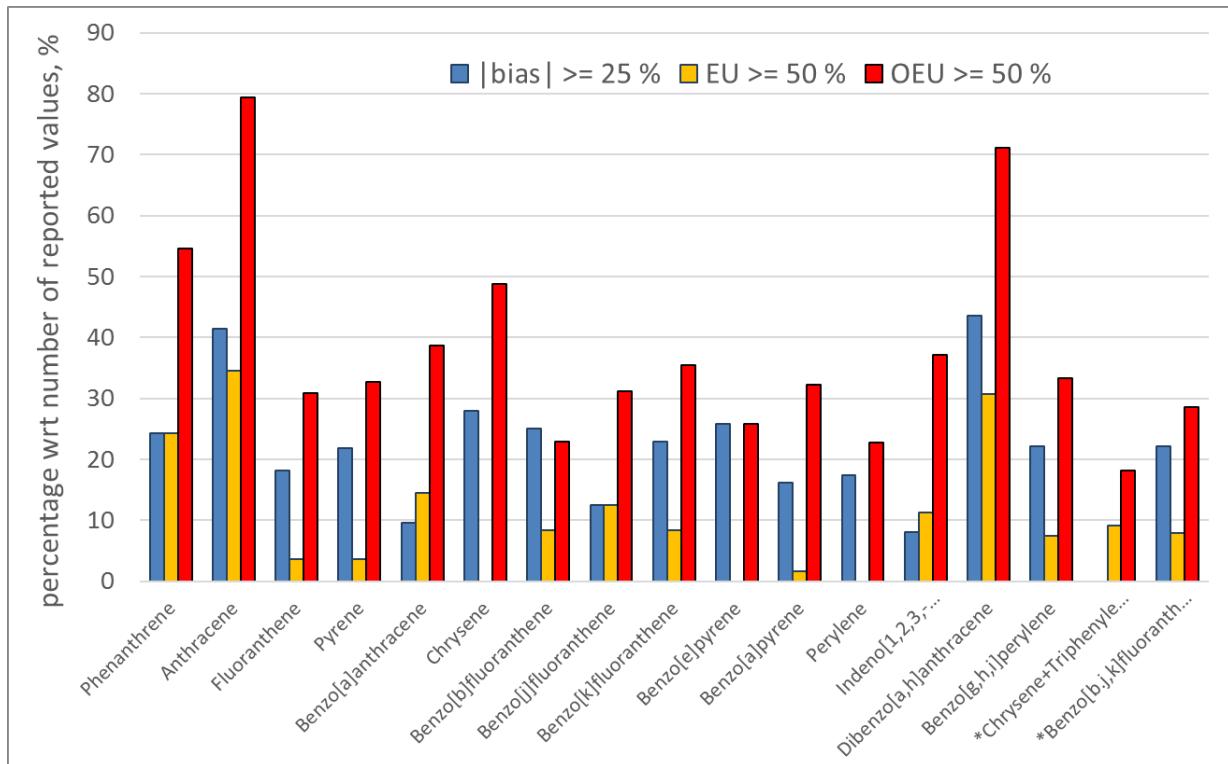
Figure 26 - inter-compound median of the $|\text{bias}|$, EU and OEU by participating laboratories



By observing the overall percentages of bias, EU and OEU in Figure 25 and Figure 27, an over-estimation of the uncertainties for a significant number of reported data from FMI and VMM, was noted. On the other hand, laboratories as HMS, Carlos III or INERIS were characterised by high biases. These observations are consistent with the high values of repeatability-score and the possible divergences between Z'-score and En-score.

It was also noted that when these results were averaged by compounds, the higher biases and OEU corresponded to those analytes present variously at lower concentrations, or with high blank levels, i.e, Phe, Anth or DB[ah]A.

Figure 27 - Bias, reported and overall expanded uncertainty by compounds

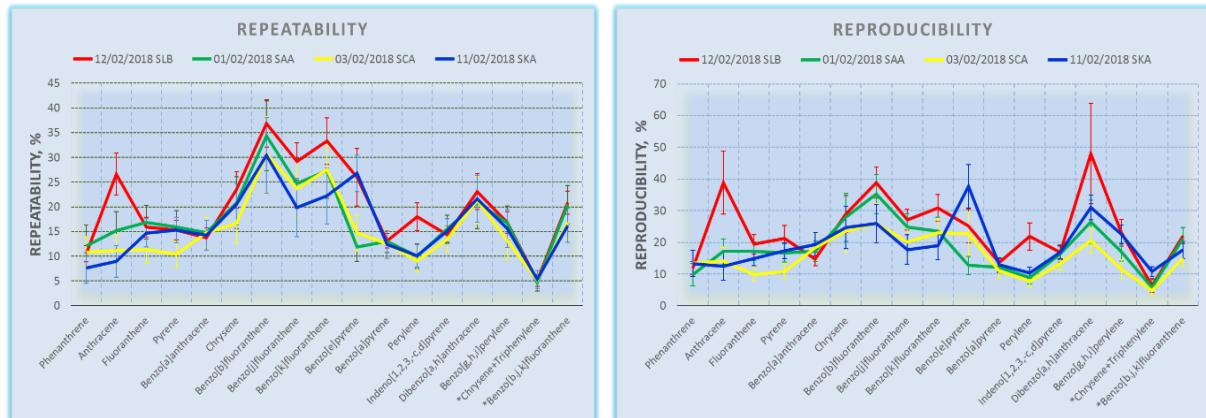


7.9. Low volume sampling comparison

Only three laboratories reported results for the low-volume samplers comparison. This limited participation prevented representative statistics for this sort of sampling. Despite this, their results were also represented in terms of deviation with respect to the robust mean value (annex X). In the case of the sampling days in concomitance with the days of the filters of high-volume sampling, the reference concentrations determined by the robust average value of the HVS filter comparison were used.

To this respect, filters SAA, SCA, SKA and SLB corresponded to sampling days of 01/02/2018, 03/02/2019, 11/02/2018 and 12/02/2018, respectively. Consequently, the data comparison in terms of concentration in air (ng/m^3) allowed the estimation of convergent values of repeatability uncertainty and reproducibility for the samples compared. The results of these analyses are shown in Figure 28, while the robust overall expanded uncertainty is illustrated in Figure 29. The median values of robust repeatability uncertainty and reproducibility were of 15% and 18%. In case of BaP, robust repeatability uncertainty and reproducibility values were of 12.5%, while the robust overall expanded uncertainty was of 39%.

Figure 28 - Repeatability and reproducibility values of the low volume sampling comparison



The values of repeatability, uncertainty and reproducibility were comparable to those calculated from the filter comparison. Consequently, the sampling uncertainty did not contribute significantly to the final overall uncertainty.

When comparing low and high-volume sampling average results (see Figure 30), the bias of the median inter-compound value of the LVS with respect to the HVS value was of -5.6%. This could explain the increase of the median OEU_R to circa 36% instead of the 30% of the HVS filters exercise. This bias, however, did not represent a significant difference between low and high-volume sampling, as this could be overlapped by the sampling and analytical uncertainties.

Figure 29 - Robust overall expanded uncertainty of the low volume sampling comparison

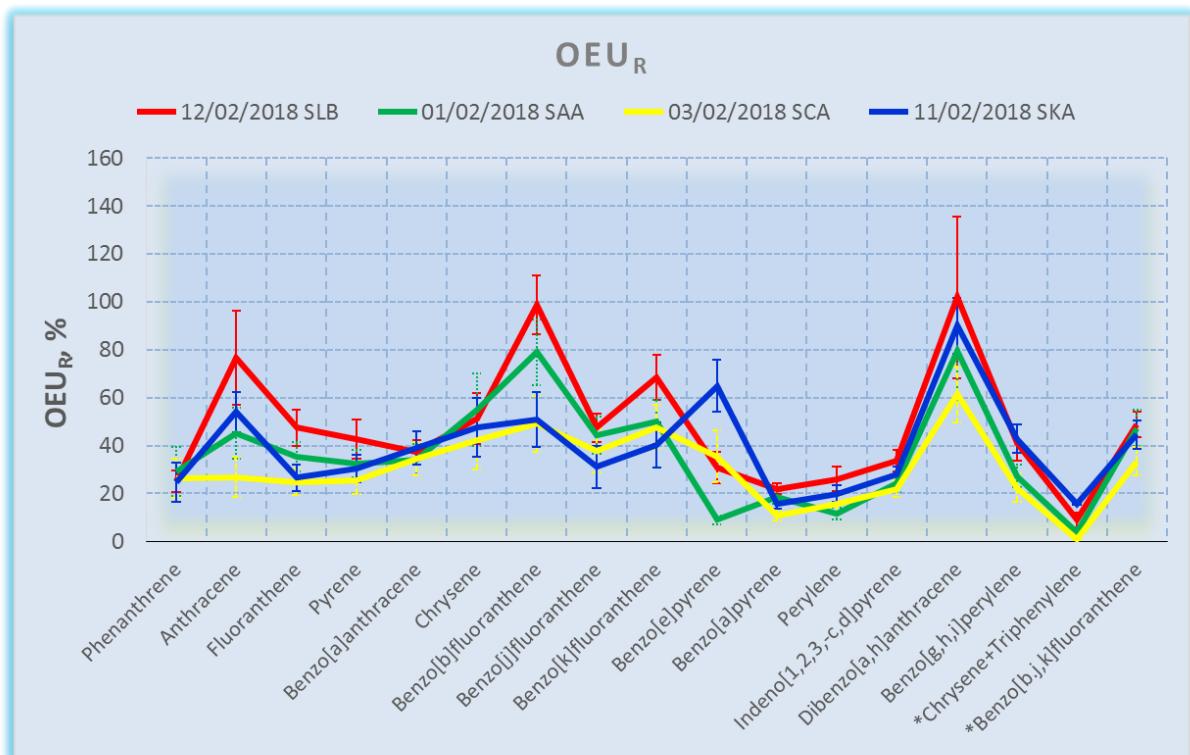
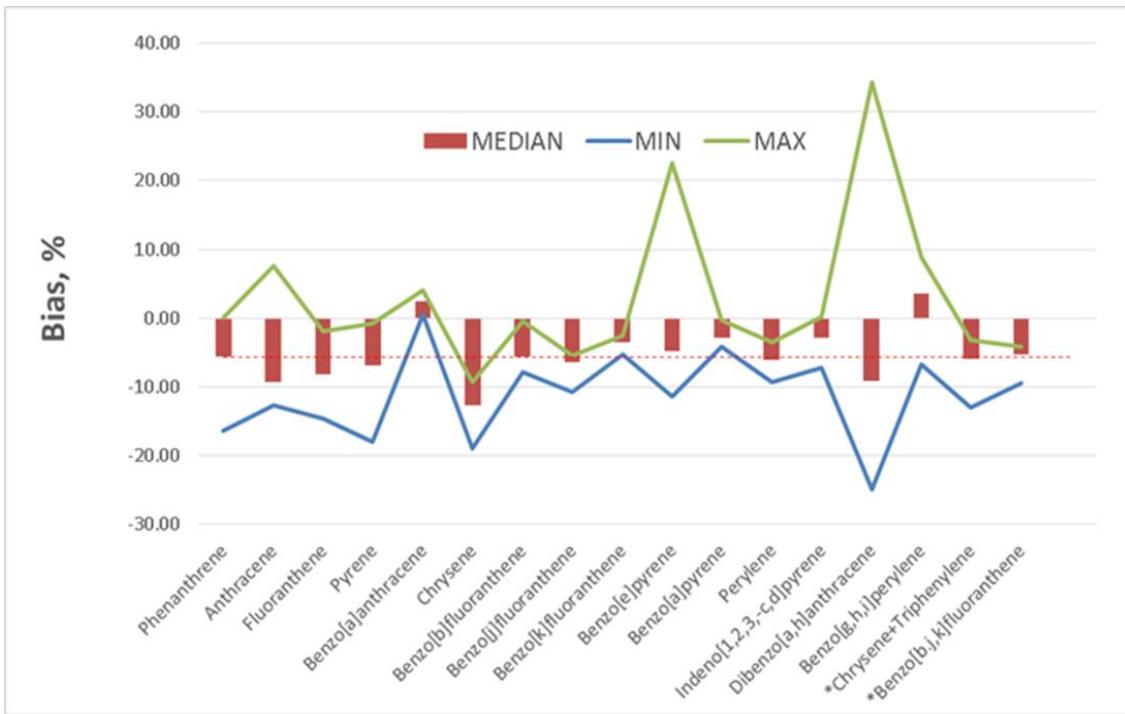
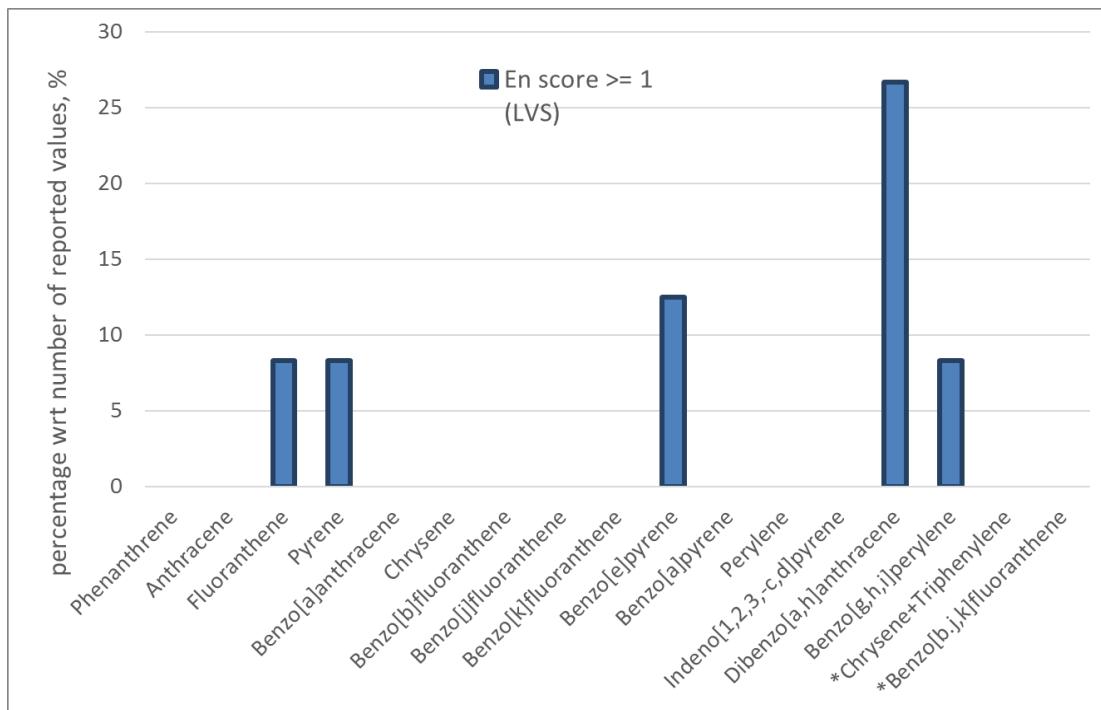


Figure 30 - Bias of the average LVS value with respect to the HVS



The E_n -scores for the low volume sampling data was calculated according to Eq. 12 (see annex XI). For this statistic, only 6.3% of reported values for CHMI and JRC showed E_n scores ≥ 1 . Looking by compounds the highest percentages of E_n -scores ≥ 1 were reported by those compounds found at lower concentration or characterised by poor stability, i.e., DB[ah]A or B[e]P (See Figure 31).

Figure 31 - E_n -scores by analysed compounds



The overall expanded uncertainties calculated by Eq. 13 are shown in annex XII. These results showed an inter-laboratory behaviour similar to the one observed for the LVS filter comparison, the inter-laboratories median of the OEU $\geq 50\%$ was approximately 16%, while the same statistic considered between compounds showed that 33% of the values were $\geq 50\%$ (see Figure 32 and Figure 33).

Figure 32 - Bias, reported and overall expanded uncertainty by participating laboratory

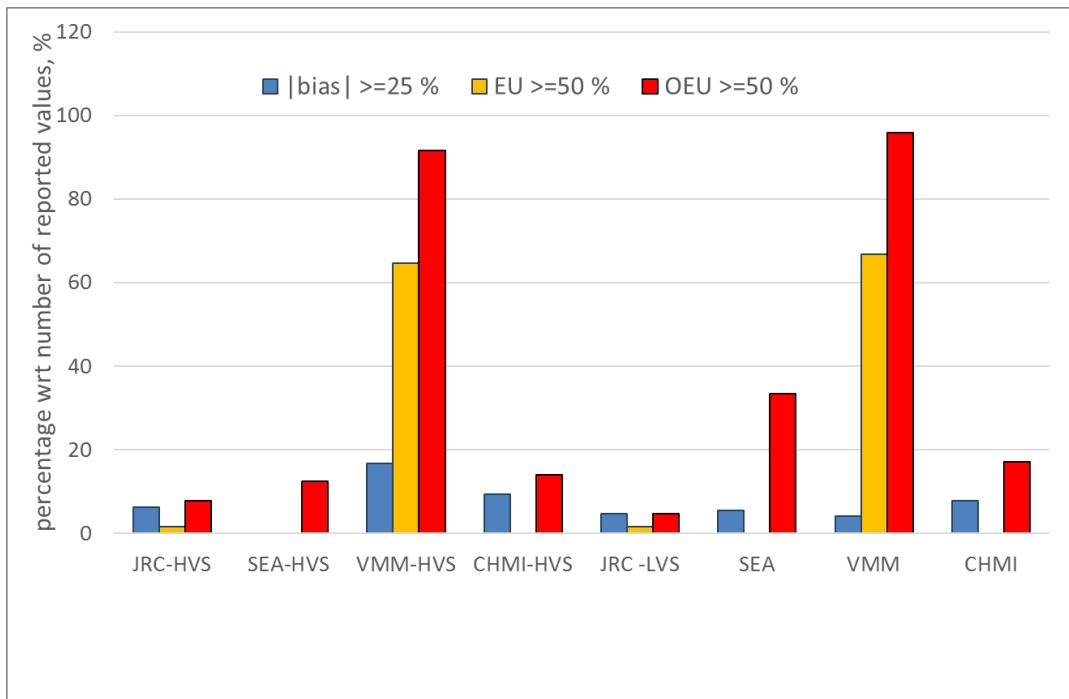


Figure 33 - Bias, reported and overall expanded uncertainty by compounds

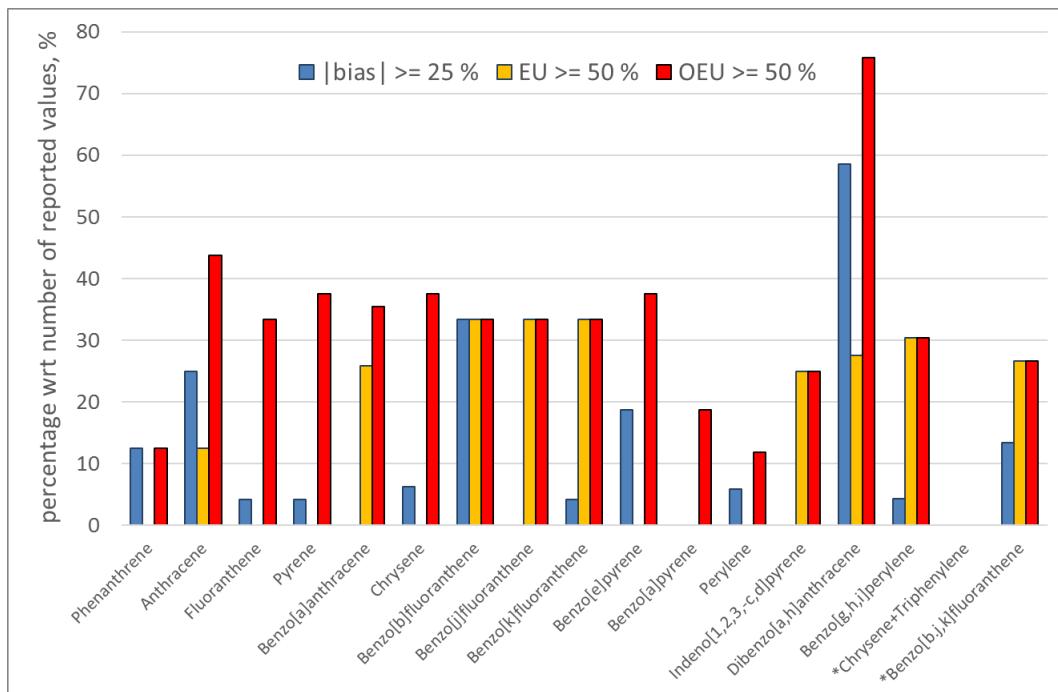


Table 16 - Reported concentrations in ng/m³ and expanded uncertainties of the LVS comparison

Low volume samplers Laboratory ==> Compound / sample	Reported Concentration ng/m ³				Reported Expanded Uncertainty %			
	SEA				SEA			
	SLB	SAA	SCA	SKA	SLB	SAA	SCA	SKA
Phenanthrene								
Anthracene								
Fluoranthene								
Pyrene								
Benzo[a]anthracene	0.3	0.7	0.8		40.2	40.2	40.2	
Chrysene								
Benzo[b]fluoranthene								
Benzo[j]fluoranthene								
Benzo[k]fluoranthene								
Benzo[e]pyrene								
Benzo[a]pyrene	0.2	0.6	1.2	1.5	24.6	24.6	24.6	24.6
Perylene								
Indeno[1,2,3-c,d]pyrene	0.3	0.8	1.3	1.6	30.6	30.6	30.6	30.6
Dibenzo[a,h]anthracene		0.2	0.2	0.3		45.6	45.6	45.6
Benzo[g,h,i]perylene								
*Chrysene+Triphenylene								
*Benzo[b,j,k]fluoranthene	0.8	1.8	3.2	3.8	24.8	24.8	24.8	24.8
Laboratory ==> Compound / sample	VMM				VMM			
	SLB	SAA	SCA	SKA	SLB	SAA	SCA	SKA
Phenanthrene								
Anthracene								
Fluoranthene	0.3	0.3	0.5	0.7	48.0	48.0	48.0	48.0
Pyrene	0.3	0.4	0.6	0.7	48.0	48.0	48.0	48.0
Benzo[a]anthracene	0.1	0.3	0.9	1.0	53.0	53.0	53.0	53.0
Chrysene	0.3	0.7	1.9	2.3	48.0	48.0	48.0	48.0
Benzo[b]fluoranthene	0.6	1.5	2.7	3.3	91.8	91.3	91.6	91.7
Benzo[j]fluoranthene	0.2	0.5	0.9	1.1	91.8	91.3	91.6	91.7
Benzo[k]fluoranthene	0.2	0.4	0.8	0.9	91.8	91.3	91.6	91.7
Benzo[e]pyrene								
Benzo[a]pyrene	0.2	0.6	1.2	1.3	40.0	40.0	40.0	40.0
Perylene								
Indeno[1,2,3-c,d]pyrene	0.2	0.6	1.1	1.4	50.0	50.0	50.0	50.0
Dibenzo[a,h]anthracene	0.0	0.1	0.2	0.2	76.0	76.0	76.0	76.0
Benzo[g,h,i]perylene	0.3	0.9	1.5	1.8	52.0	52.0	52.0	52.0
*Chrysene+Triphenylene								
*Benzo[b,j,k]fluoranthene	0.9	2.5	4.4	5.3	62.0	62.0	62.0	62.0
Laboratory ==> Compound / sample	CHMI				CHMI			
	SLB	SAA	SCA	SKA	SLB	SAA	SCA	SKA
Phenanthrene	0.3	0.3	0.3	0.4	24.3	24.4	24.3	24.3
Anthracene	0.0	0.0	0.1	0.1	17.1	17.4	17.4	17.6
Fluoranthene	0.4	0.3	0.6	0.9	28.2	28.2	28.2	28.2
Pyrene	0.4	0.4	0.6	0.9	23.8	23.8	23.8	23.8
Benzo[a]anthracene	0.2	0.4	1.3	1.6	20.3	20.3	20.3	20.3
Chrysene	0.2	0.5	1.4	1.8	21.6	21.5	21.5	21.5
Benzo[b]fluoranthene	0.4	1.0	1.7	2.2	27.7	27.7	27.7	27.7
Benzo[j]fluoranthene	0.2	0.6	1.1	1.2	26.9	26.8	26.8	26.8
Benzo[k]fluoranthene	0.2	0.5	0.9	1.1	25.2	25.2	25.2	25.2
Benzo[e]pyrene	0.2	0.6	1.0	1.1	24.1	24.0	24.0	24.0
Benzo[a]pyrene	0.2	0.7	1.4	1.8	22.8	22.8	22.8	22.8
Perylene	0.0	0.1	0.2	0.3	24.3	24.0	24.1	24.0
Indeno[1,2,3-c,d]pyrene	0.3	0.8	1.4	1.9	27.1	27.0	27.0	27.0
Dibenzo[a,h]anthracene	0.1	0.2	0.3	0.5	27.1	27.2	27.2	27.2
Benzo[g,h,i]perylene	0.3	0.7	1.2	1.5	19.7	19.7	19.7	19.7
*Chrysene+Triphenylene								
*Benzo[b,j,k]fluoranthene	0.7	2.2	3.7	4.5	16.7	16.3	16.4	16.5
Laboratory ==> Compound / sample	JRC-LVS				JRC-HVS			
	SLB	SAA	SCA	SKA	SLB	SAA	SCA	SKA
Phenanthrene	0.2	0.2	0.4	0.4	15.9	16.0	12.8	10.2
Anthracene	0.0	0.0	0.1	0.1	61.2	39.3	22.2	16.7
Fluoranthene	0.5	0.4	0.7	0.9	16.4	15.1	17.2	12.5
Pyrene	0.5	0.4	0.8	1.0	14.9	12.6	15.9	11.5
Benzo[a]anthracene	0.2	0.4	1.1	1.2	9.7	11.2	13.6	9.8
Chrysene								
Benzo[b]fluoranthene	0.4	1.1	1.9	2.3	9.8	11.6	13.4	10.9
Benzo[j]fluoranthene	0.2	0.6	1.0	1.2	10.3	12.7	13.3	10.3
Benzo[k]fluoranthene	0.2	0.4	0.8	1.0	9.7	10.1	12.9	9.7
Benzo[e]pyrene	0.4	0.6	1.4	2.0	22.8	24.6	28.6	45.8
Benzo[a]pyrene	0.2	0.6	1.4	1.7	9.5	12.0	14.7	10.6
Perylene	0.0	0.1	0.2	0.3	28.1	16.0	13.2	13.0
Indeno[1,2,3-c,d]pyrene	0.3	0.7	1.2	1.9	10.1	10.4	13.4	11.4
Dibenzo[a,h]anthracene	0.0	0.1	0.2	0.2	12.2	8.8	12.8	11.1
Benzo[g,h,i]perylene	0.4	0.9	1.5	2.4	10.2	11.8	14.6	11.2
*Chrysene+Triphenylene	0.3	0.5	1.6	2.1	10.2	9.9	11.1	10.1
*Benzo[b,j,k]fluoranthene	0.7	1.9	3.4	4.2	9.9	11.5	13.2	11.2

EU≥50 % are highlighted in red

8. Conclusions

- The call for participation for the second JRC PAHs comparison was well supported with 15 participating laboratories from AQUILA. However, at the voluntary sampling exercise, only three laboratories participated with their own LVS.
- Gas chromatography followed by mass spectrometry was the predominant technique for analysis of PAHs, being used by 70% of participants, while the remaining laboratories used HPLC with FLD detection.
- Accelerated solvent extraction, ASE (35%), followed by SOXLET (25%) and ultrasonic (25%) were the preferred extraction techniques of the participants. The use of a variety of solvents or mixture of solvents with different polarities without a clear agreement between applied methodologies was noted. Clean up techniques were however applied by 56% of the participants.
- Most of the participants (75%) used internal standard and CRM.
- No significant biases due to the use of specific techniques for analysis (GC-MS, HPLC-FLD), extraction and the use of solvents or clean-up techniques were observed. Nevertheless, two of the three outlier-laboratories did not report the use of a reference material.
- The homogeneity of the filter was estimated to be around 6%, which was sufficient to allow each of the HVS filters a test comparison by their subdivision between participants.
- Analytical blanks showed an important effect in outliers' production, this was the case of those compounds characterised by their omnipresence or by their low concentration in the filters as: Phe, B[a]A, Per, Anth, Pyr and B[ah]A, with analysed concentrations in the blank between 10% and 30% of the lower filter concentration.
- The average data reporting was of circa 75% of the total considered compounds considered in this exercise, varying from 28% to 100% between laboratories and from 40% to 97% between compounds. Between filters, the total data reporting varied from 68% to 75%.
- By considering all compared filters and compounds, the average of the absolute value of the bias, after excluding the identified outliers' laboratories, was of circa 14%, being the corresponding average for the reported expanded uncertainty of circa 30%. Between laboratories, averaged OEU ranged from 25% to 81%, with a median value of 43%. For LVS filters, the OEU ranged between 22% and 80% with a median value of 38%.
- For the filter comparison, the average robust repeatability uncertainty and reproducibility were around 14.5%, with a robust average overall expanded uncertainty (OEU_R) of 30%. The average repeatability standard deviation for replicated analysis was 1.9%. In the case of B[a]P the robust OEU_R was around 24%.
- In the case of the low volume sampling, robust values of repeatability uncertainty and reproducibility did not differ significantly from those of the filter comparison, being the robust OEU_R of around 36%.
- The bias of the median inter-compound value of the LVS with respect to the HVS value was of circa -5.6%. This was not significant in the context of the comparison, but could justify the slight increase of the robust OEU_R with respect to the filters comparison.
- The robust OEU_R was considered as the best indicator of the method uncertainty used for comparison. The obtained results suggested that the general methodology was able to fulfil the DQO mentioned in the directive 2004/107/EC, at least for individual measurements within the range of concentrations under comparison.

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List of abbreviations and definitions

AcN: acetonitrile

Anth: anthracene

ASE: accelerate solvent extraction

AU_ENVS: Aerhus University Department of Environmental science

B[a]A: benzo[a]anthracene

B[b]F: benzo[b]fluoranthene

B[bjk]F: benzo[b,j,k]fluoranthene

B[j]F: benzo[j]fluoranthene

B[k]F: benzo[k]fluoranthene

B[a]P: benzo[a]pyrene

B[e]P: benzo[e]pyrene

B[ghi]P: benzo[ghi]perylene

blank_i : is the system blank level associated with the analysis of the filter i.

CHMI: Czech Hydrometeorological Institute

Chry: chrysene

Chry+Tph: chrysene + triphenylene

CRM: certified reference material

CO: carbon monoxide

\bar{C} : inter-laboratory average value

C_i : concentration reported by laboratory i

\overline{C}_i^* : robust concentration average, Eq. 1

\overline{C}_{lab} : average concentration of the reported values by a laboratory

C_{ref} : reference concentration

DB[ah]A: dibenzo[a,h]anthracene

DQO: data quality objectives

EMEP: European Monitoring and Evaluation Programme

E_n : E_n -score, Eq. 10

EU: expanded uncertainty

FLD: Fluorescence detector

Flu: fluoranthene

FMI: Finnish Meteorological Institute

$f_{i,j}$: concentration calculated for the injection j of the filter i

$\overline{f}_{i,j}$: is the average value of all injections and filters

GC: gas chromatographer

HMS: Hungarian Meteorological Service

HPLC: high performance liquid chromatography

HVS: high volume sampler
IARC: International Agency for Research on Cancer
IMROH: Institute for Medical Research and Occupational Health
INERIS: Institut National de l'Environnement industriel et des Risques
ISCIII: Instituto de Salud Carlos III
IVL: Swedish Environmental Institute
Ind[123cd]P: indeno[1,2,3,-c,d]pyrene
JRC: Joint Research Centre
LANUV: Landesumweltamt für Natur, Umwelt und Verbraucherschutz NRW
LEGMC: Laboratory of Latvian Environment, Geology and Meteorology Centre
LVS: low volume sampler
MS: mass spectrometry
n: number of replicate analysis.
NILU: Norwegian Institute for Air Research
NO: nitrogen monoxide
NO₂: nitrogen dioxide
OEU: overall expanded uncertainty, Eq. 13
OEUR: robust overall expanded uncertainty, Eq. 14
OOE: Amt der oberösterreichischen Landesregierung - Abteilung: Umweltschutz
O₃: ozone
P: number of laboratories
PAHs: polycyclic aromatic hydrocarbons
Per: perylene
Phe: phenanthrene
PM: particulate matter
PM₁₀: particulate matter under 10 µm
PM_{2.5}: particulate matter under 2.5 µm
P atm: atmospheric pressure
Pyr: pyrene
QAQC: quality assurance quality control
RM: reference material
SEA: Slovenian Environment Agency
SAA: high volume filter code for the 01/02/2018
SBL: high volume filter code for the 12/02/2018
SKA: high volume filter code for the 11/02/2018
SCA: high volume filter code for the 03/02/2018
stdev() : standard deviation
*s**: standard deviation of the robust concentration average, Eq. 2

S_i : standard deviation of replicated measurements of the laboratory i

S_L : standard deviation of the average inter-laboratory value

S_r : repeatability standard deviation, Eq. 8

S_R : reproducibility standard deviation, Eq. 9Eq. 8

UBA: Umweltbundesamt GmbH

u_{bias} : standard uncertainty of the bias, Eq. 5

u_{ci} : uncertainty of the reported value from laboratory I

u_{cl} : uncertainty of the calibration and the reference value

U_{lab} : expanded uncertainty for the reported value

U_{ref} : expanded uncertainty for the reference value

VMM: Vlaamse Milieumaatschappij

WHO: World Health Organization

Z: random variable of two tails statistic for normal distribution P, Eq. 6

Z': Z'-score, Eq. 11

$\hat{\sigma}_{PT}$: Standard deviation for proficiency test

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Annexes

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ANNEX II: Procedure

ANNEX III: Data reporting sheet

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ANNEX XII: Overall expanded uncertainty for the low volume samplers by compounds

ANNEX XIII: Comments on uncertainty calculations and analysis reported by participants

ANNEX I: Guide to operation

This envelope (Fig. a) contains 6 PM2.5 filters pieces with the following characteristics:
two blanks filters from the sampling campaign
four loaded filters at different concentrations

The filters have been carefully packed in such a way that they can be easily kept in the freezer until analysis (Fig. b). Each filter has been wrapped independently for easier management and protection (Fig. c).



Fig. a



Fig. b

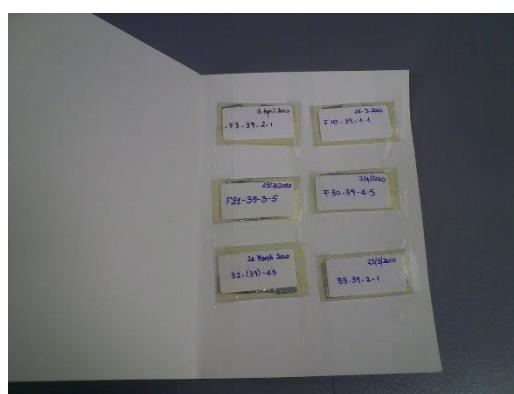


Fig. c

Approximately, the loading of the filters corresponds to the volume sampled by a typical LVS, i.e. 50 m³, the expected B[a]P concentration for the loaded filters would range from 0.1 to 2 ng/m³.

ANNEX II: Procedure

Record and write the arrival date of the package at your laboratory. Keep the filters in the freezer until analysis.

Each filter has been assigned a particular code, written on the individual container: The first letter identifies loaded filters (S) or blanks (B).

To unwrap the filter the following material is needed: gloves, scissors and appropriate tweezers (Fig.1A).

To unwrap the filters proceed carefully as described in Figures 2A to 5A.

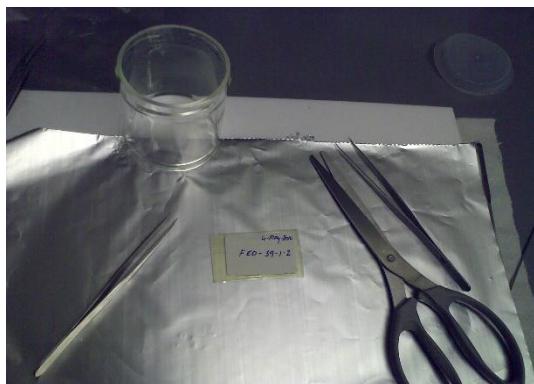


Fig. 1A.- Material



Fig. 2A.- Cut the plastic envelope by the edge

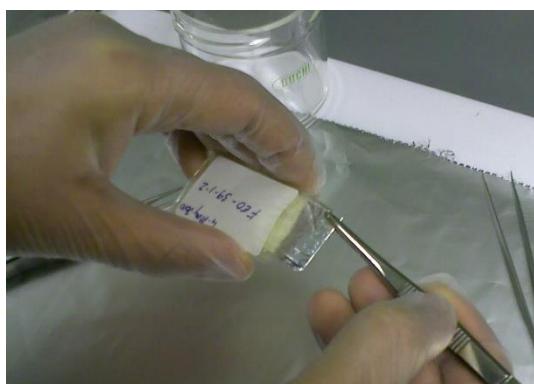


Fig. 3A.- Take out the aluminium envelope from inside



Fig. 4A.- Unwrap the aluminium foil to get the filter



Fig. 5A.- Unfold the filter and introduce it into your container for extraction

Note that the comparison exercise will be based on the amount of compound (ng) quantified on the filter. Therefore, assure that the whole filter is extracted and analysed.

ANNEX III: Data reporting sheet

This file tries to collect all the relevant information that regards the analytical method that you have used to analyse the samples of the current inter-laboratory comparison.

It is very important this information be accurate and complete, as this will be a relevant source of information to interpret your results and compare the methodologies of the different laboratories.

All this information will be collected in the final EUR report and available to all of you. Please try to be clear in the method description and in the calculation of your analytical uncertainty; this may help you in the discussion of the results.

It is kindly requested to the user of this file not to modify the format in order to be able to automate the gathering of the data submitted by the different participants. Nevertheless, if you need to provide information not foreseen in this format, Please insert a new Worksheet #2 with the name corresponding to the sheet that you want to extend, i.e.

Instrument description#2

Method description#2

Analytical procedure#2

Data reporting#2

Data reporting (LVS)#2

Sampling reporting (LVS)#2

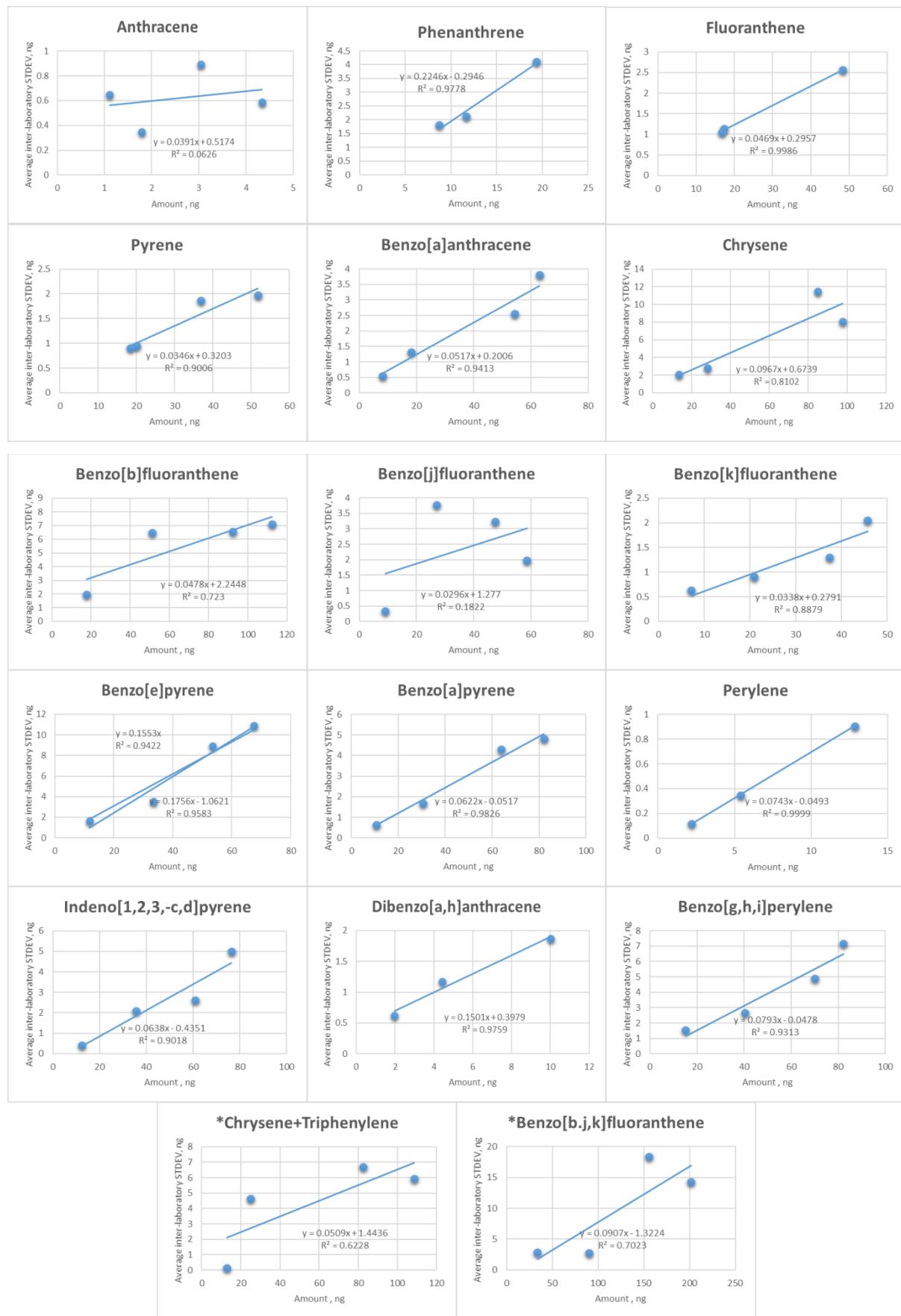
Uncertainty calculation#2

The submission of the results will be only by e-mail to pascual.ballesta@ec.europa.eu

Please note that the deadline for submission of this "data report" file is the **15 June 2018**

<i>Filling check</i>	<i>Pages</i>	<i>Worksheets added by the user</i>
<input type="checkbox"/>	Laboratory identification	1
<input type="checkbox"/>	Instrument description	2
<input type="checkbox"/>	Method description	3
<input type="checkbox"/>	Analytical procedure	2
<input type="checkbox"/>	Data reporting	6
<input type="checkbox"/>	Sampling data - LVS	1
<input type="checkbox"/>	Data reporting - LVS	12
<input type="checkbox"/>	Uncertainty calculation	1
<input checked="" type="checkbox"/>	save and rename of the excel data reporting file by replacing "YOUR-LAB-ACRONYM" by your corresponding laboratory acronym which you indicated in the laboratory identification	

ANNEX IV: Standard deviation of the average inter-laboratory value



ANNEX V: Isomers, reporting data and statistical treatment: benzo[b,j,k]fluoranthene, chrysene + triphenylene

The table below shows the reporting of the corresponding isomers of Benzo[b,j,k]fluranthene and chrysene+triphenylene by the participating laboratories

Table.- Reported and estimated values of concentration and uncertainties for the B[b,j,k] and Chry+TPh isomers

Laboratory	B[b]F	B[j]F	B[k]F	Chry	B[b,j,k]F	Chry + TPh
AU_ENVS	v. & u.	v. & u.	v. & u.	v. & u.	e.v & e.u	n.p.
CHMI	v. & u.	v. & u.	v. & u.	v. & u.	e.v & e.u	n.p.
FMI	n.p.	n.p.	n.p.	n.p.	v. & u.	v. & u.
HMS	v. & u. for B[b,j]F		v. & u.	v. & u.	e.v & e.u	n.p.
IMROH	v. & u.	v. & u.	v. & u.	v. & u.	e.v & e.u	n.p.
INERIS	v. & u.	v. & u.	v. & u.	v. & u.	e.v & e.u	n.p.
ISCIII	v. & u. for B[b,j]F		v. & u.	v. & u.	e.v & e.u	n.p.
IVL	v. & u.	v. & u.	v. & u.	v. & u.	e.v & e.u	n.p.
LANUV	v. & u.	v. & u.	v. & u.	n.p.	e.v & e.u	n.p.
NILU	v. & u.	v. & u.	v. & u.	v. & u.	e.v & e.u	n.p.
LEGMC	v. & u. for B[b,j]F		v. & u.	v. & u.	e.v & e.u	n.p.
OOE	v. & u. for B[b,j]F		v. & u.	v. & u.	e.v & e.u	n.p.
SEA	n.p.	n.p.	n.p.	n.p.	v. & u.	v. & u.
UBA	v. & u.	v. & u.	v. & u.	v. & u.	e.v & e.u	n.p.
VMM	v. & e.u.	v. & e.u.	v. & e.u.	v. & u.	v. & u.	n.p.
JRC	v. & u.	v. & u.	v. & u.	n.p.	e.v & e.u	v. & u.

B[b,j]F was evaluated as B[b,j]F

n.p. : laboratory did not provide any value or uncertainty

v. & u. : laboratory reported value and corresponding uncertainty

v. & e.u.: Laboratory provided values without uncertainties. An estimated uncertainties were assigned.

e.v & e.u.: Laboratory did not provided values or uncertainties:

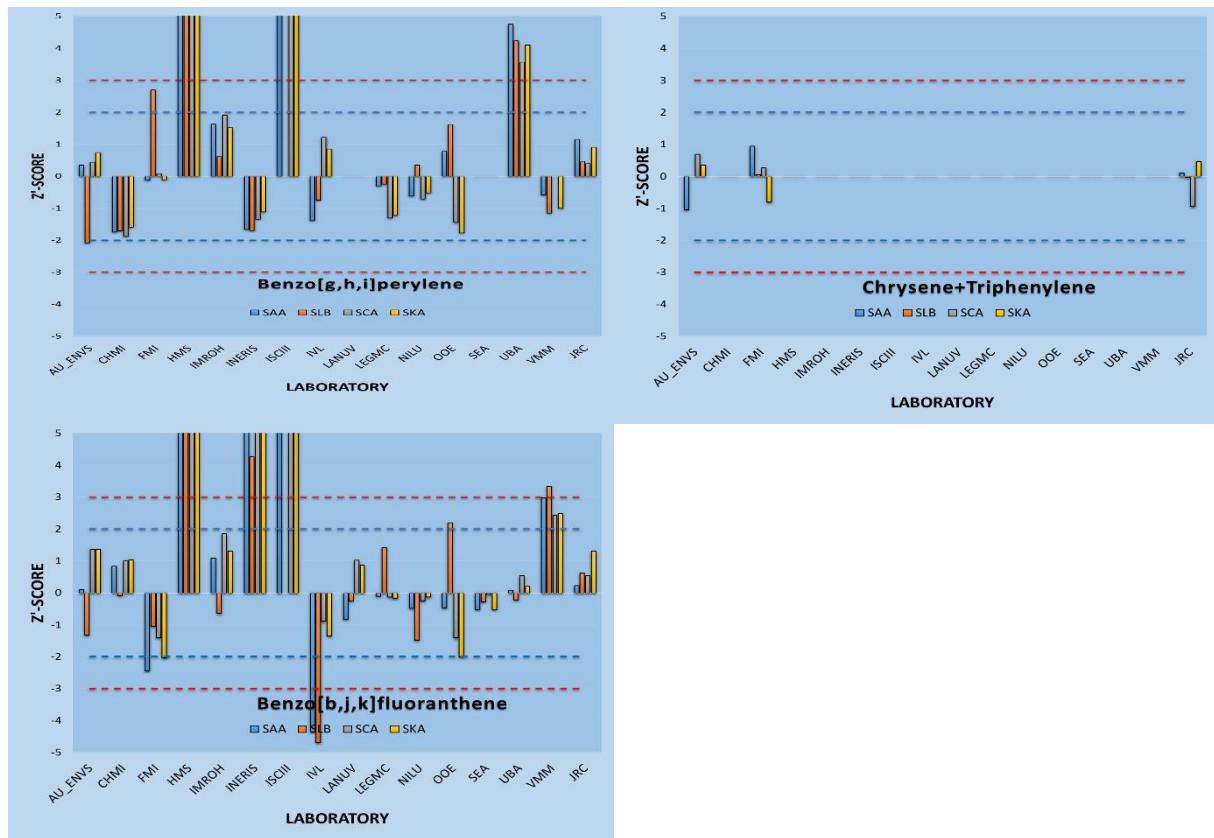
B[b,j,k]F was calculated as the sum of the individual isomers.

Uncertainty variances of B[b,j,k]F were estimated as the square root of the uncertainty variances of the individual compounds

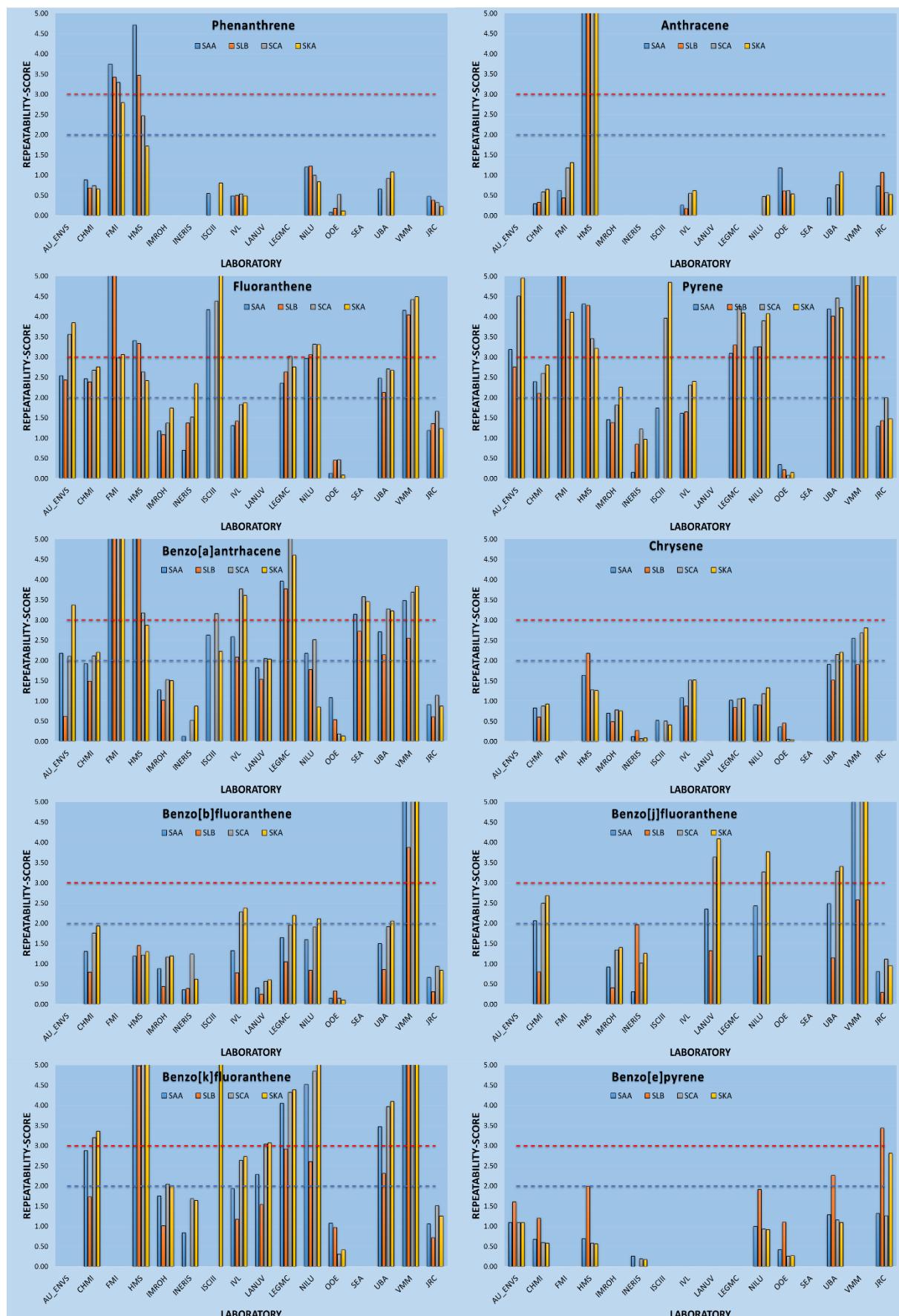
ANNEX VI: Z'-scores. Tests results by compounds

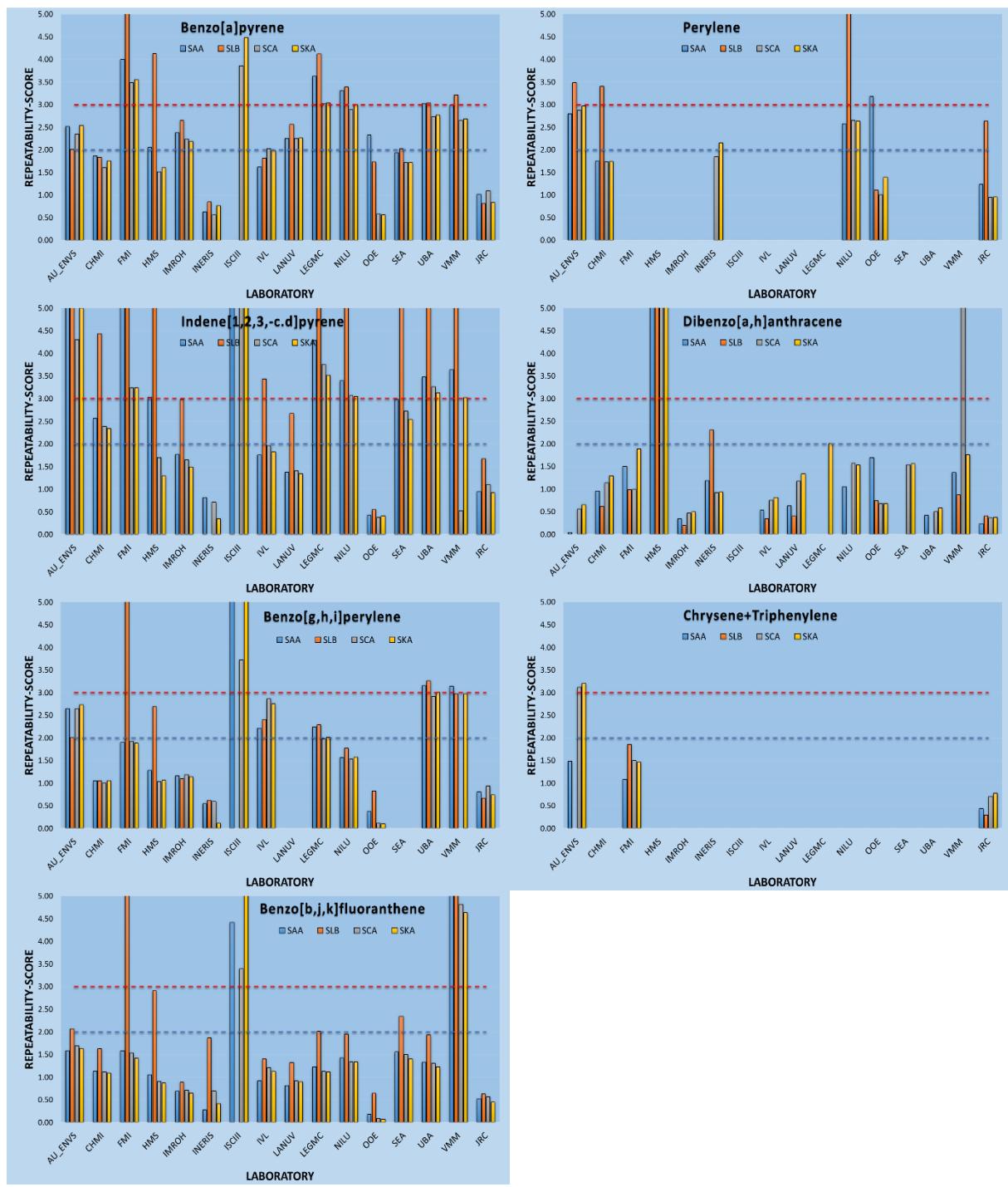




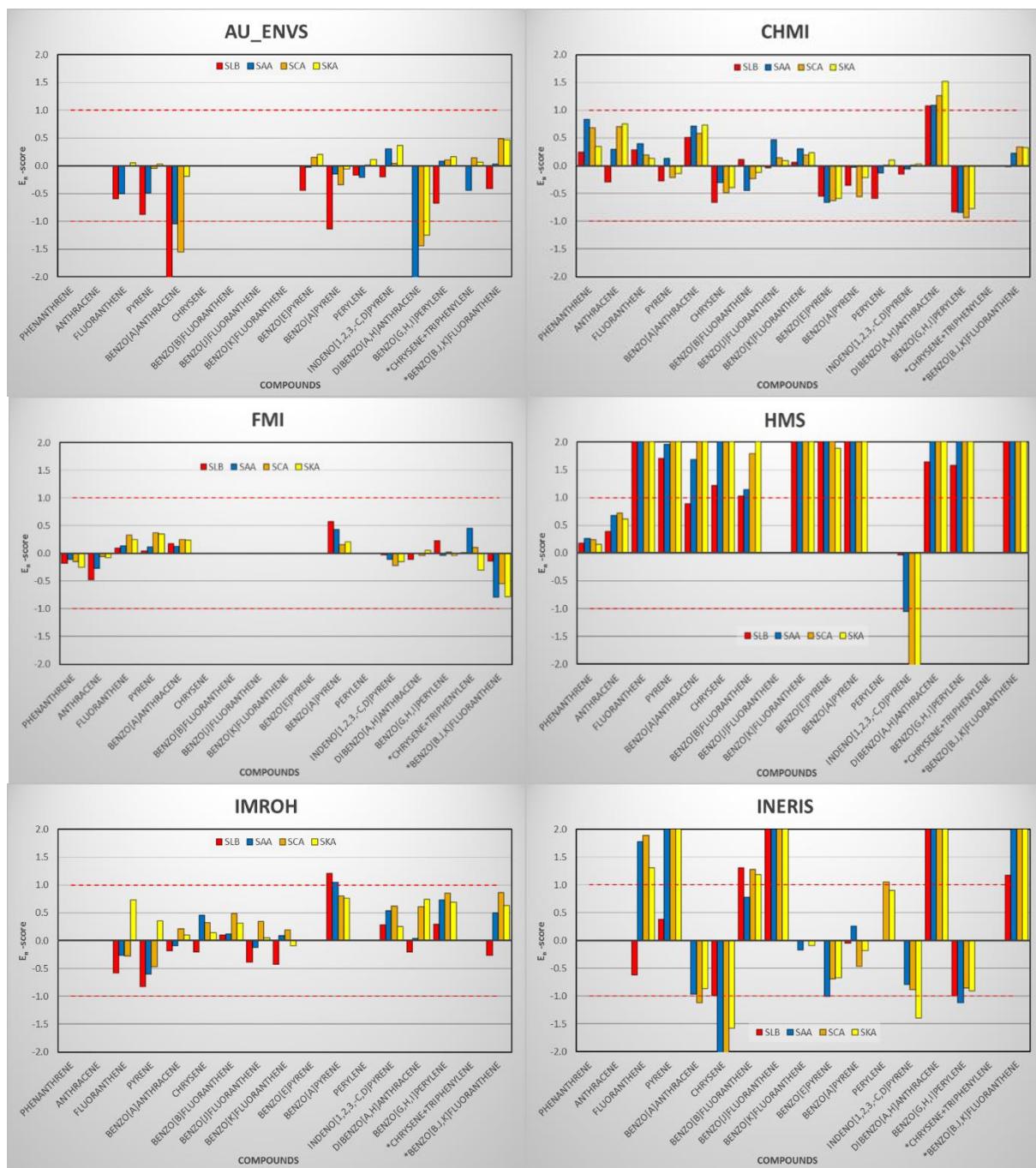


ANNEX VII: Repeatability Score. Test results by compounds

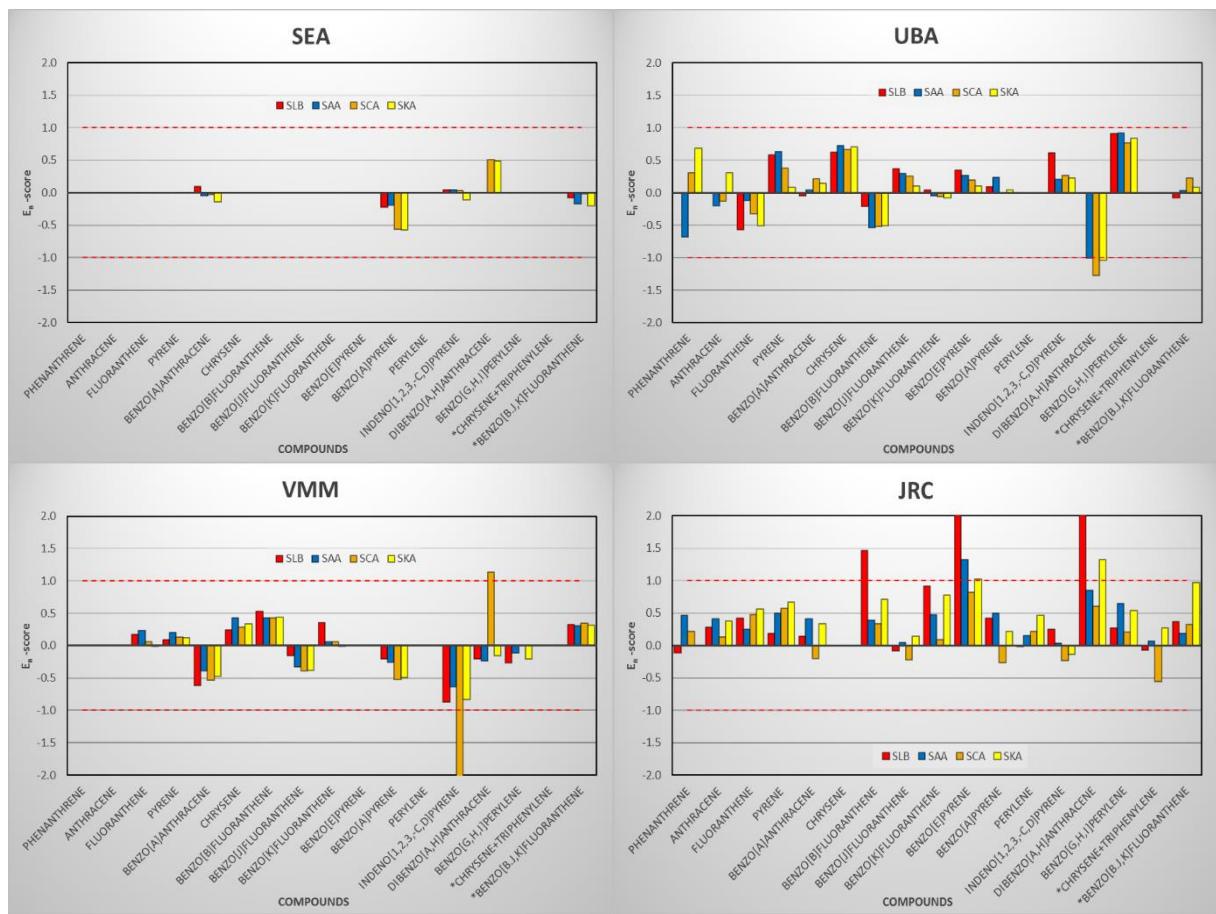




ANNEX VIII: En scores. Test results by laboratories



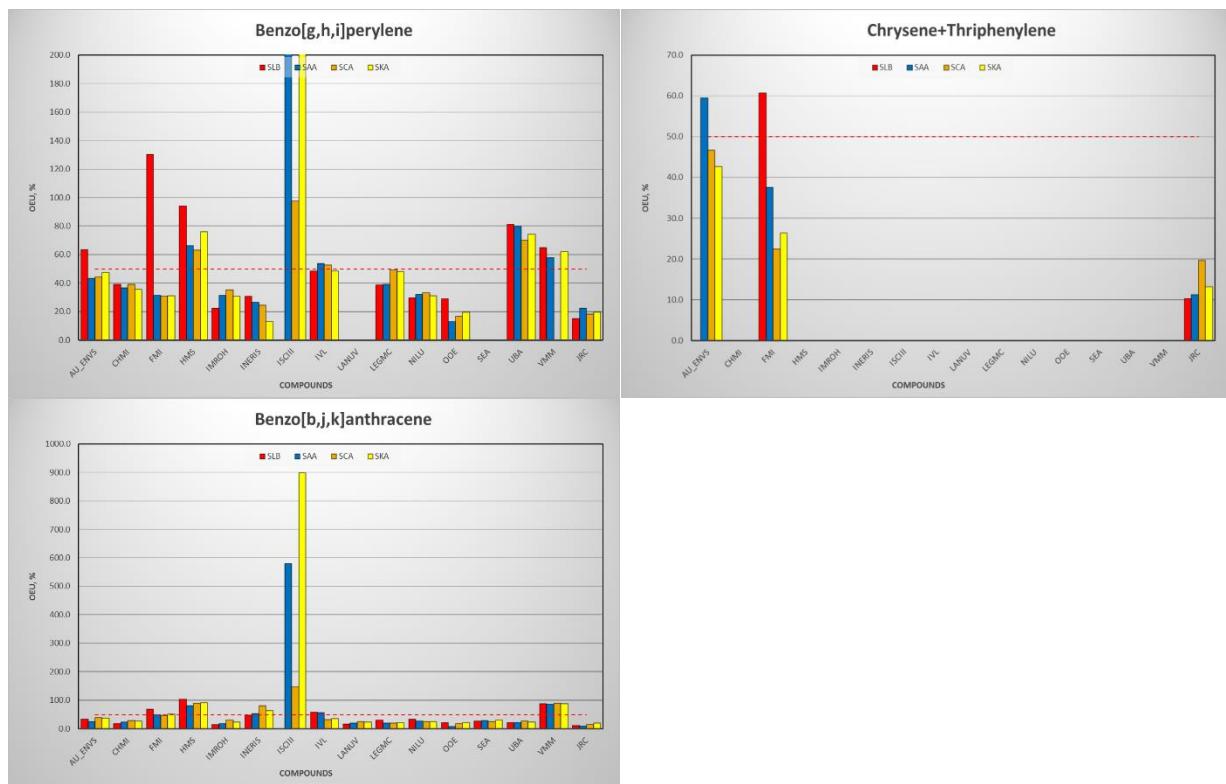




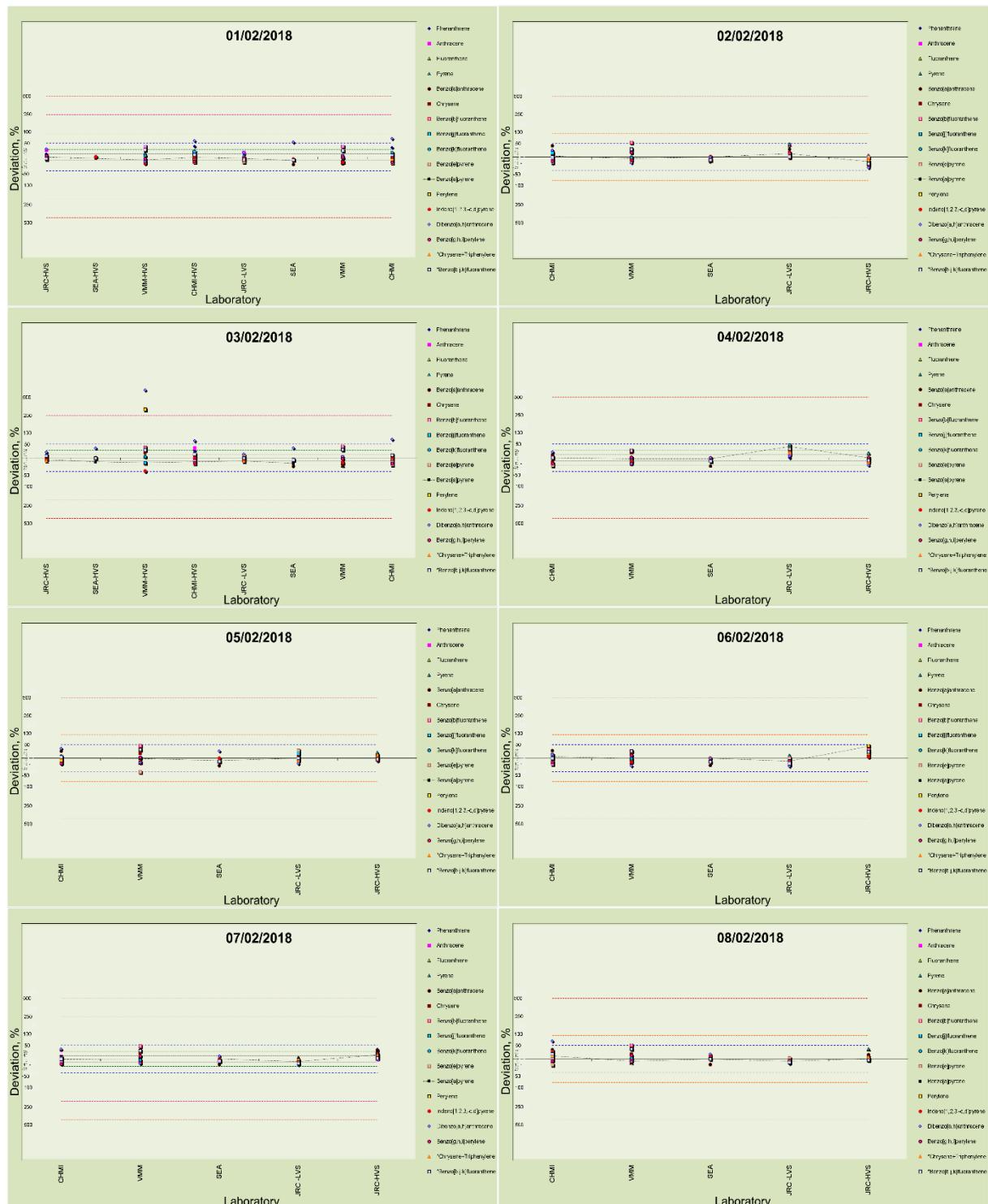
ANNEX IX: Overall expanded uncertainty. Results by compounds

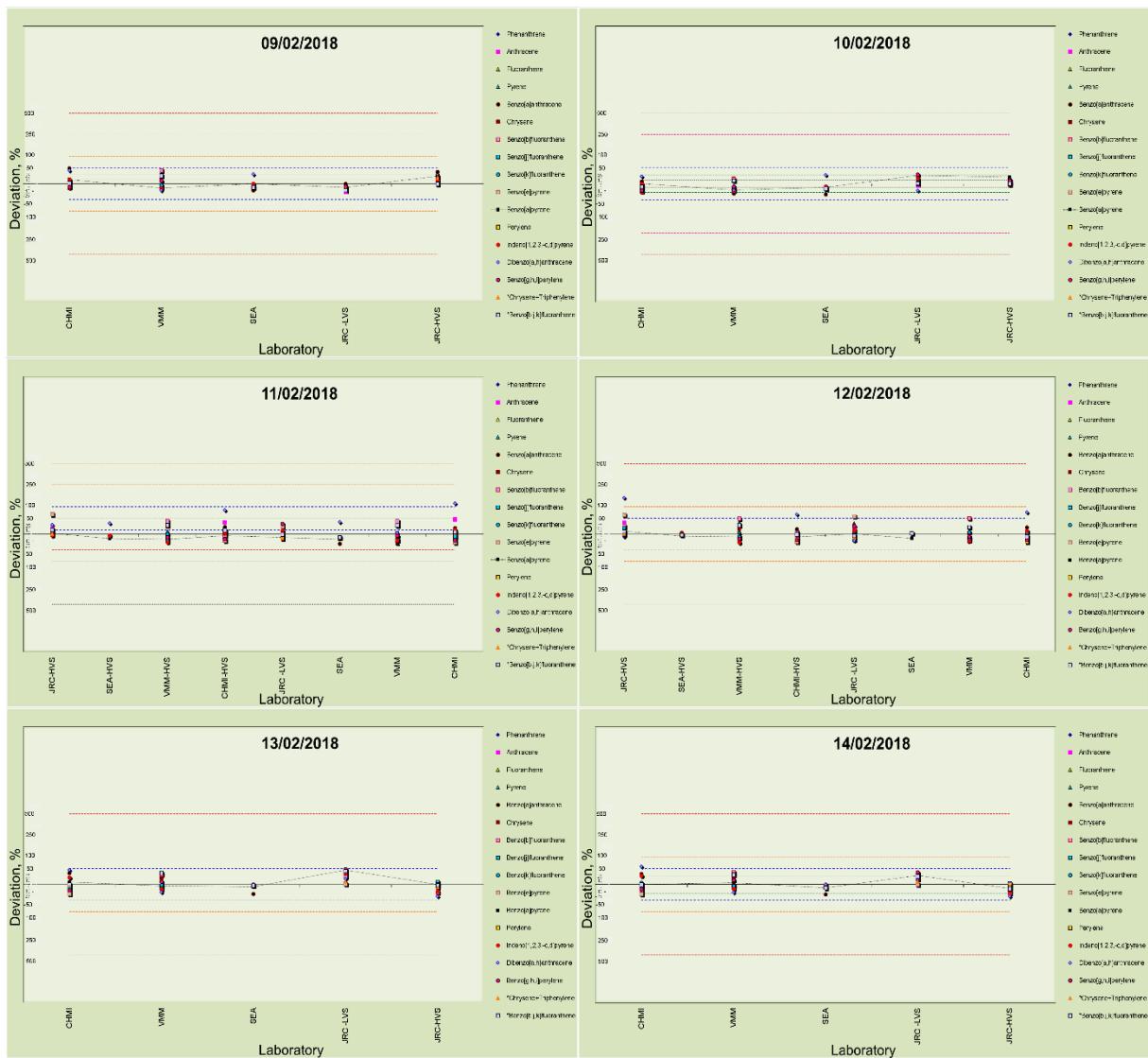




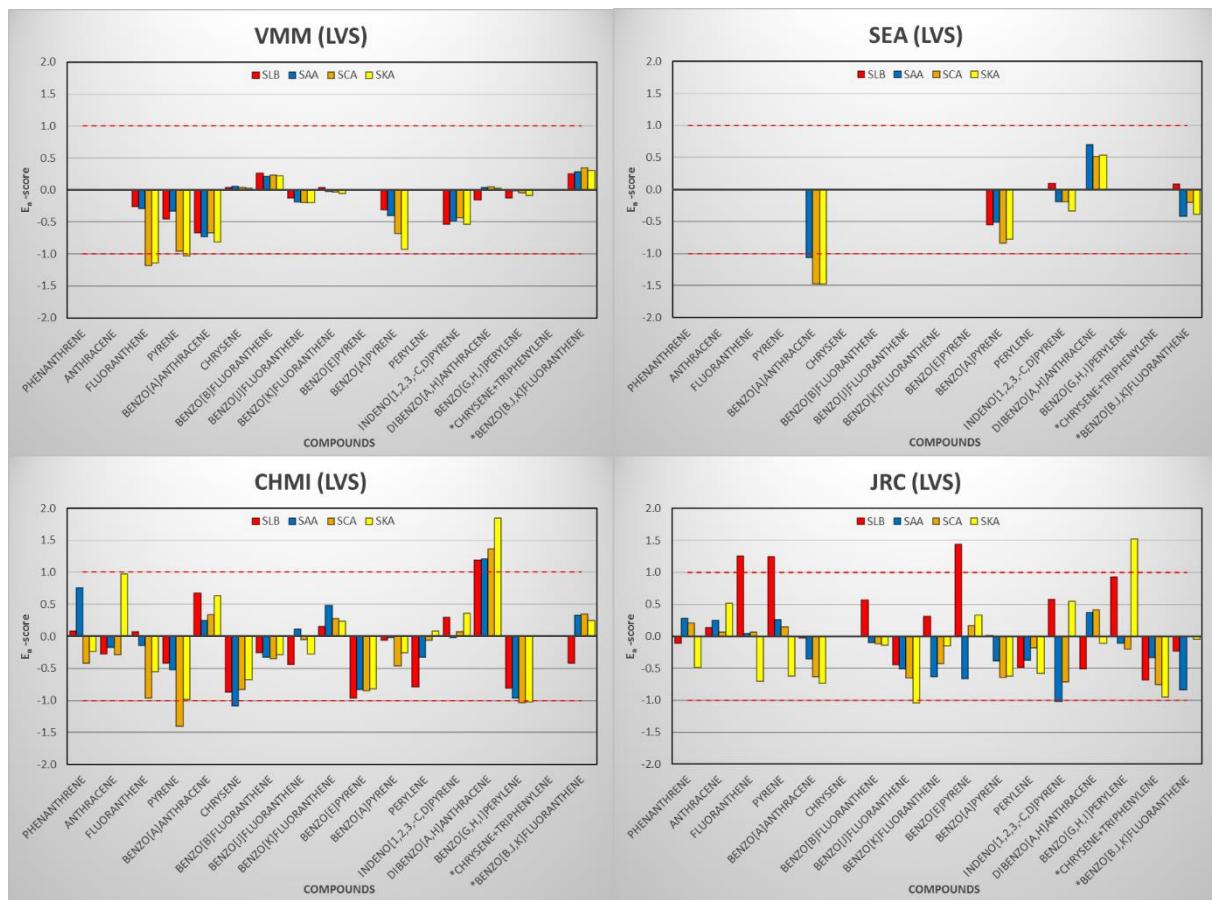


ANNEX X: Low volume sampling scattering results

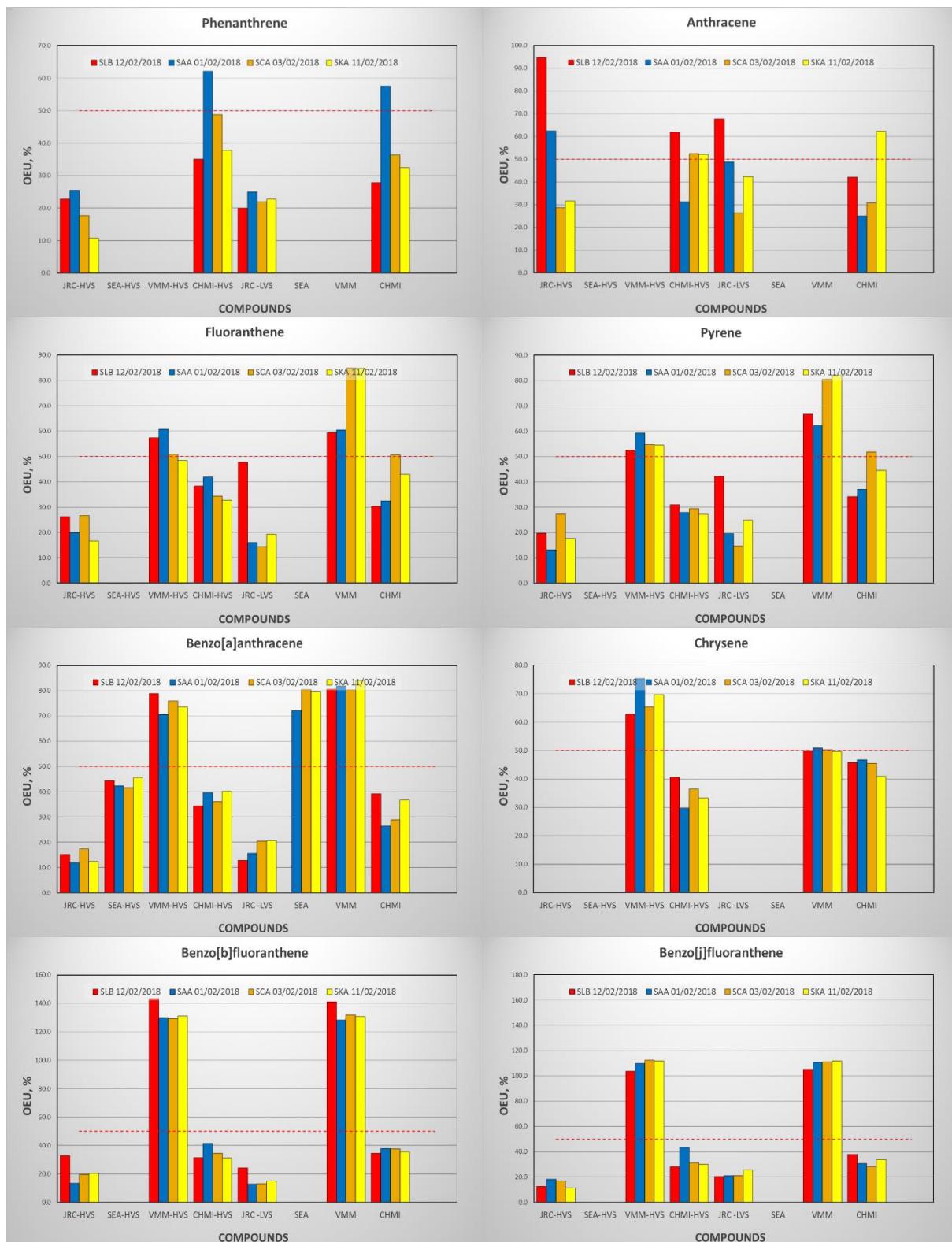


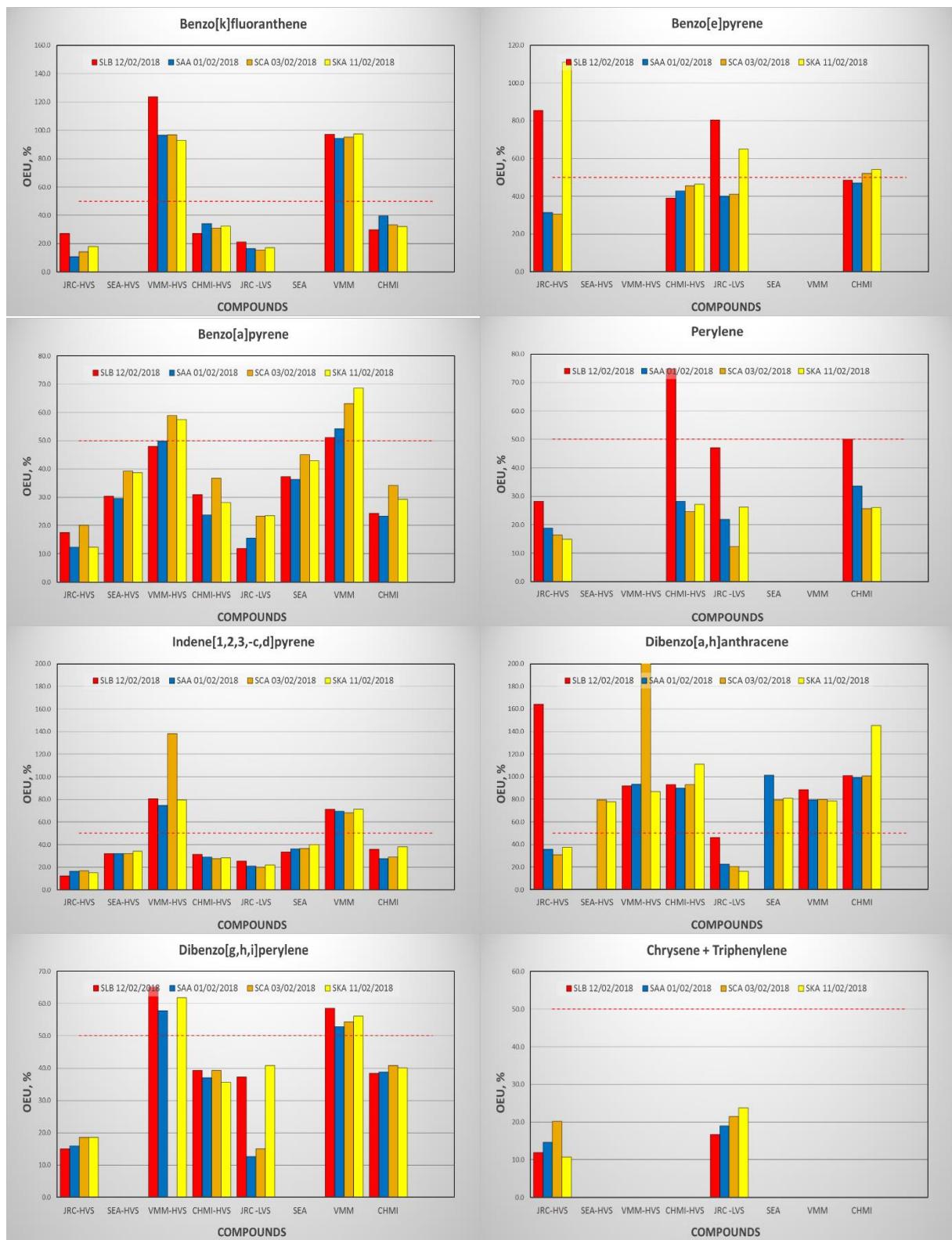


ANNEX XI: En scores for low volume samplers by laboratories



ANNEX XII: Overall expanded uncertainty for the low volume samplers by compounds





ANNEX XIII: Comments on uncertainty calculations and analysis reported by participants

AU_ENVS

Description of uncertainty calculations:

The uncertainty of the method has been estimated on the basis of the analysis of the certified material ERM-CZ100 Fine Dust (BCR). The uncertainty has been estimated using the Measurement Uncertainty Estimation according to Nordtest Technical Report 537 (Handbook for calculation of measurement uncertainty in environmental laboratories). The estimated MU takes into account repeatability and bias.

Comments on the analysis:

Benzo(b,j,k)fluoranthenes were reported together

Chrysene was reported with Triphenylene

CHMI

Description of uncertainty calculations:

Assessment of measurement uncertainty was done with software Effi Validation 4.0. Data from our method validation were used. Combined uncertainty was estimated on the base of the uncertainties of calibration standards preparation, uncertainty of internal standard addition, uncertainty from sample duplicates, uncertainty of repeatability of the measurement and bias of the method. Repeatability studies were performed with standards (at four concentration ranges – 2 pg/µL, 50 pg/µL, 200 pg/µL and 1000 pg/µL) and real samples. Relative standard deviations were estimated and their average value was used for estimation combined uncertainty (to represent repeatability in the whole concentration range). Bias of the method was assessed by using a Certified Reference Material - Urban Dust 1649b and ERM - CZ100 Fine dust. Concentration level of selected PAHs between 20 pg/µL to 200 pg/µL. Combined uncertainty ranged from 9 % to 15 % of the reported concentration depending on the compound. For concentrations close to MDL combined uncertainty is between 18 % to 40 % depends on the compound.

The expanded uncertainty at 95 % confidence was estimated by multiplying combined uncertainty with a coverage factor k=2. Expanded uncertainties ranged from 18 % to 30 % of the reported concentration depending on the compound.

Comments on the analysis:

It was noted that the peak of dibenzo[a,h]anthracene is much wider than the one in the standard - probably an impurity with the same ions

FMI

Description of uncertainty calculations:

B[a]P MU calculations					
based from EN 15549			Target value (1ng/m3) level	medium level (0.4 ng/m3)	low level (10 % of target value)
			B[a]P	B[a]P	B[a]P
<u>partial uncertainties:</u>		requirement	u(x)/x	u(x)/x	u(x)/x
<i>Sample volume (m3)</i>	Usam	<2 %			
sampling time (min)	t	<0.1 %	0.035 %	0.035 %	0.035 %
<i>b(a)p mass in the sample</i>	msam				
sampling efficiency	S	>90 % , MU <3 %			
analytical stability	A	-			
<i>Extraction efficiency</i>	UE/E		7 %	7 %	7 %
<u><i>b(a)p mass in the sample</i></u>	mE				
<u>ISTD-method</u>	mmeas				
b(a)p response factor	Uf	<5 %	1.1 %	0.30 %	4.1 %
ISTD conc	mISE	<2 %	2.3 %	2.3 %	2.3 %
Response measurement accuracy (RSD)	sf		2.5 %	6 %	9 %
selectivity	R	RF>1			
B[a]P extract combined MU	Umeas,	UE	3.6 %	6.4 %	10.4 %
B[a]P mass in lab blank	mbl	<0.55 ng/ml	-	-	-
<u><i>b(a)p mass in field blank</i></u>	mbl	<2.55 ng/ml	0.15 %	0.30 %	1.48 %
<u>Between lab MU</u>			-	-	-
<u>combined MU (sum of squares)</u>			7.9 %	9.5 %	12.6 %
<u>Enhanced MU (k=2)</u>			15.7 %	19.0 %	25.2 %

MU:s with daily filters.					
target value level	low level (<0.4 ng/m ³)				
15 %	85 %	k=2	phenanthrene		
25 %	25 %	k=2	anthracene		
15 %	30 %	k=2	fluoranthene		
15 %	45 %	k=2	pyrene		
30 %	40 %	k=2	benz(a)anthracene		
10 %	25 %	k=2	chrysene/triphenylene		
15 %	20 %	k=2	benzo(k+b+j)fluoranthene		
15 %	20 %	k=2	benzo(ghi)perylene		
20 %	30 %	k=2	indeno(1,2,3-cd)pyrene		
20 %	35 %	k=2	dibenz(a,h+a,c)anthracene		
20 %	25 %	k=2	benzo(a)pyrene		
This corresponds to 22 ng per sample when using LVS.					
(0.4 ng/m ³ * 2.3 m ³ /h * 24h)					

Comments on the analysis:

Benzo(b,j,k)fluoranthenes were reported together

Chrysene was reported with Tripheylene

HMS

Description of uncertainty calculations:

According to: ISO 12884:2003 standard: Ambient air. Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons. Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses

IMROH

Description of uncertainty calculations:

Uncertainty calculation were according to CEN/TS 16645:2014 Annex E

INERIS

Description of uncertainty calculations:

1 écart-type

ISCHII

Description of uncertainty calculations:

The uncertainty has been estimated as follows:

$$U = \sqrt{u_{VR}^2 + \left(\frac{W_R \cdot S_R}{\sqrt{n_M}}\right)^2 + u_{cl}^2}$$

Being

UVR: uncertainty of the standards

WR= factor (2,3)

SR= standard deviation

N: number of repetitions

Ucl: 0.025 x average of all injections

Comments on the analysis:

Benzo(b,j) fluoranthenes were reported together

IVL

Description of uncertainty calculations:

Uncertainty calculations are based on R % for duplicate samples and inter-laboratory variations according to Nordtest 537

Comments on the analysis:

Sample might have been evaporated to harshly

LANUV

Description of uncertainty calculations

The general uncertainty of PAH measurements is estimated according to GUM using the model equation:

$$c_{BaP} = ((m \cdot x) * V_{Multi} * V_{Disp} / V_{Dilu} * E)$$

cBaP - Concentration of Benzo[a]pyrene (or another PAH-compound)

m - Slope of the analytical function

x - Peak area

Vmulti - Volume of Multipette

Vdisp - Volume of Dispensette

Vdilu - Volume of Diluter

E - Extraction yield of Benzo[a]pyrene (or another PAH-compound)

LEGMC

Description of uncertainty calculations:

Uncertainty was estimated using internal quality control data. Combined standard uncertainty can be expressed as: $u^2 = R_w^2 + u(\text{bias})^2$, where R_w is within-laboratory reproducibility, estimated from standard deviation of control samples over a period of time approximately one year and $u(\text{bias})$ is uncertainty component for bias, estimated from recovery tests. $u(\text{bias})$ can be expressed as: $u(\text{bias})^2 = \text{bias}^2 + s_{\text{bias}}^2 / n + u(C_{\text{ref}})^2$, where $\text{bias} = 100 - R$, s_{bias} is recovery standard deviation, n - number of recovery measurements and $u(C_{\text{ref}})$ is the uncertainty of concentration of standard addition used for recovery tests. Estimated values for the standard uncertainty ($k=1$): anthracene $u=11.5\%$, fluoranthene $u=9\%$, pyrene $u=11\%$, benzo(a)anthracene $u=14\%$, chrysene $u=9\%$, benzo(b)fluoranthene $u=9\%$, benzo(k)fluoranthene $u=9\%$, benzo(a)pyrene $u=13\%$, indeno(1,2,3-c,d)pyrene $u=12\%$, dibenzo(a,h)anthracene $u=12\%$, benzo(g,h,i)perylene $u=11\%$.

Comments on the analysis:

No deviations were investigated

NILU

Description of uncertainty calculations:

Uncertainty Calculation for this SLP is based on the method uncertainty estimated for NILUs methods.

A calculation has been made for each component based on our performance in other SLPs and reference materials.

Parameters included in that calculation are $u(C_{\text{ref}})$, $u(\text{bias})$, RMS bias and more.

The calculation has resulted in a % of uncertainty for the method. This % has been used to calculate the uncertainty of the results of this SLP.

Comments on the analysis:

For BAB and BOC: Phenanthrene, anthracene, fluoranthene and pyrene were lower than 10 times method blank, while the rest of the compounds were lower than detection limit at signal:noise 3:1

Phenanthrene was found lower than 10 times method blank for all the samples.

Anthracene was lower than detection limit at signal:noise 3:1 for SAA and SLB

Fluoranthene and pyrene were lower than 10 times method blank for SLB.

OOE

Description of uncertainty calculations:

Comments on the analysis:

Benzo(b,j,k) fluoranthenes were reported together

SEA

Description of uncertainty calculations:

Comments on the analysis:

Benzo(b,j,k) fluoranthenes were reported together

UBA

Description of uncertainty calculations:

The extended uncertainty was carried out according to our VA 021, for the calculation 75 benzo (a) pyrene d12 values were used.

For the Calculation of the combined uncertainty the middle deviation from the setpoint, the fluctuation deviation from the set point and a reference material were used.

$$\frac{u_c}{P_{op}} = \sqrt{u(x_1)^2 + u(x_2)^2 + u(x_3)^2}$$

u_c ... combined uncertainty

P_{op} ... analyte content in the sample

The expanded uncertainty is estimated by multiplying the combined uncertainty by a coverage of 2.

$$U(P_{op}) = u_c(x) \cdot P_{op} \cdot 2 = U \cdot P_{op}$$

$U(P_{op})$... expanded uncertainty

Comments on the analysis:

Samples were diluted prior before injection

VMM

Description of uncertainty calculations:

		estimated uncertain
Fluoranthene	estimate based on average of similar compounds	48%
Pyrene	estimate based on average of similar compounds	48%
Benzo[a]anthracene	middle of the range of field test TS16645:2015 (table F5)	53%
Chrysene	estimate based on average of similar compounds	48%
sum of benzo(b,j,k)fluoranthene	middle of the range of field test TS16645:2015 (table F5)	62%
Benzo[a]pyrene	middle of the range of field test TS16645:2015 (table F5)	40%
Indeno[1,2,3,-c,d]pyrene	middle of the range of field test TS16645:2015 (table F5)	50%
Dibenzo[a,h]antracene	middle of the range of field test TS16645:2015 (table F5)	76%
Benzo[g,h,i]perylene	middle of the range of field test TS16645:2015 (table F5)	52%

Comments on the analysis:

Benzo(b,j,k) fluoranthenes were reported together

JRC

Description of uncertainty calculations:

The evaluation of the concentration and the associated budget uncertainty, reported by JRC, was based on the results of the averaging of at last three filter samples analysed by thermal desorption, gas chromatography and mass spectrometry detection. Uncertainty for the thermal desorption analyses was based on the reproducibility analysis of a number of cuts randomly distributed around the whole high volume filter, plus the corresponding sources of uncertainties related to standards, calibration and system blank. This uncertainty evaluation did not consider uncertainties attributed to biases with respect to the analysis of reference materials.

The final uncertainty, u , was estimated as it follows:

$$u = \sqrt{\sum_{i=1}^m \left(\frac{stdev[f_{i,j}]}{\sqrt{n}} \right)^2 + u_{cl}^2 + u_{blank}^2 + u_{de}^2}$$

Where:

$u_{cl} = 0.025 \cdot \overline{f_{i,j}}$ as an approach value for the uncertainty of the calibration and the reference standard (see references: B.L. Vand Drooge et al. J. Chromatogr. A 1216 (2009) 4030-4039).

$$u_{blank} = \sqrt{\left(\frac{stdev(blank_i)}{\sqrt{m}} \right)^2 + \overline{blank_i^2}}$$

$f_{i,j}$ is the concentration estimated for the injection j of the filter i .

n , is the number of injections ($j = 1$ to n)

m , is the number of filters ($i = 1$ to m)

is the average value of all injections and filters

$blank_i$, is the system blank level associated with the analysis of the filter i .

u_{de} : uncertainty of desorption coefficient derived of the regression between desorbed and reference material.

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