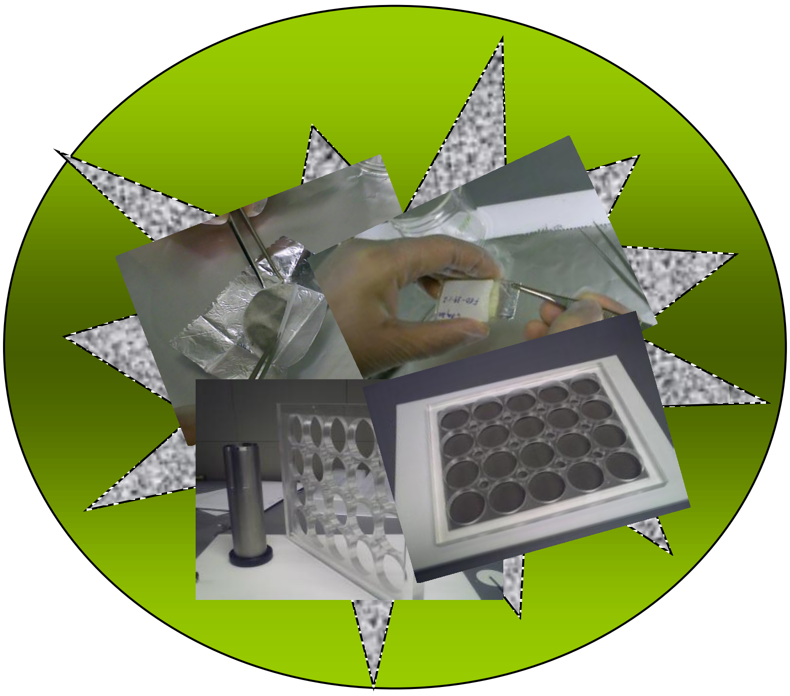
JRC Scientific and Technical Reports

First EC-JRC PAHs inter-laboratory comparison on PM10 quartz filters

Emanuela Grandesso, Konrad Kowalewski, Pascual Pérez Ballesta



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EUR 25170 EN -2012

JRC
EUROPEAN COMMISSION

Institute for Environment and Sustainability

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European Commission
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JRC 67695

EUR 25170 EN

ISBN 978-92-79-22782-0 (pdf) ISBN 978-92-79-22781-3 (print)
ISSN 1831-9494 ISSN 1018-5593
DOI 10.2788/63064

Luxembourg: Office for Official Publications of the European Communities

Printed in Italy

Executive Summary

This report presents the results of the first inter-laboratory comparison for PAHs analysed on quartz filters carried out by the JRC between April and December 2010. Seventeen national reference laboratories participated in this exercise.
Four different filters representing winter and summer periods in two different locations (Madrid and Prague) and two blanks were tested during the exercise. 15 PAHs were considered for analysis from phenanthrene to benzo(g,h,i)perylene, including benzo(a)pyrene.

In general, the results of the exercise showed median overall uncertainties ranging from 10 to 90 %, depending on the compound and the analysed concentration. Median benzo(a)pyrene overall uncertainty ranged between 30 and 50 %, increasing with the decrease of the concentration. The exercise demonstrates the validity of the current methodology for organising PAHs inter-laboratory comparison exercises on PM10 filters. Laboratories exhibited better performance in the analysis of those compounds where reference material was found on the market. The need for implementing a consistent traceability system for measurements is deduced from the systematic biases associated with laboratory behaviour.

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Nomenclature and abbreviations

ABUM: Amt der oberösterreichischen Landesregierung. Abteilung:Umweltschutz
AEA : AEA Technology
APA-LRA: Agência Portuguesa do Ambiente
AQUILA: Air Quality Reference Laboratories
ASE: accelerated solvent extraction
AWEL: Gewässerschutzlabor Kanton Zürich

BaA: benzo(a)anthracene
BaP: benzo(a)Pyrene
BaP-D: benzo(a)pyrene deuterated
BeP: benzo(e)pyrene
DBahA: dibenzo(a,h)anthracene
DBahA-D: dibenzo(a,h)anthracene deuterated
BbjkFlu: benzo(b,j,k)fluoranthene
BbFlu: benzo(b)fluoranthene,
BghiPe: benzo(g,h,i)perylene
BghiPer-D: benzo(g,h,i)perylene deuterated
BjFlu: benzo(j)fluranthene
BkFlu: benzo(k)fluoranthene
$blank_{i:}$: is the system blank level associated with the analysis of the filter i. (eq. 2)

Chr: chrysene
C_i: concentration reported by laboratory i
$\overline{C}_i^*$: robust concentration average (eq. 3)
$\overline{C_{lab}}$ *:* average concentration of the reported values by a laboratory (eq. 10)
C_{ref} *:* reference concentration (eq. 10)

EEA: Executive Environmental Agency
EERC: Estonian Environmental Research Centre
$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$, eq (9)
EPA-ie: Environmental Protection Agency, Ireland
ERLAP : European Reference Laboratory of Air Pollution
ESG: Scientifics part of Environmental Scientifics Group
EU: European Union

F21: code for PM10 Prague summer filter
F3: code for PM10 Madrid summer filter
F10: code for PM10 Madrid winter filter
F30: code for PM10 Prague winter filter
$f_{i,j:}$ concentration calculated for the injection j of the filter i (eq. 1)
$\overline{f_{i,j}}$ is the average value of all injections and filters
FLD: Fluorescence detector
Flu: Fluoranthene
FMI: Laboratory of Air Chemistry, Finnish Meteorological Institute

GC-MS: gas chromatography mass spectrometer

HPLC: High Performance Liquid Chromatography

IndPy: indeno(1,2,3-cd)pyrene
IndPy-D: indeno(1,2,3-cd)pyrene deuterated
I.S.: internal standard
ISCIII: Instituto de Salud Carlos III
ISSeP: Institut Scientifique de Service Public
IVL Swedish environmental institute

KAL : Chemical Analytical Laboratory, Slovenia Environment Agency
LANUV: Landesamt für Natur, Umwelt und Verbraucherschutz NRW

m: number of filters (eq. 2)

n: number of injections (eq. 1)
n.a.: non available
NERI: National Environmental Research Institute

OEU: overall expanded uncertainty (eq. 10)
ou: overall uncertainty (eq. 1)

p: number of input laboratories, (eqs. 3, 4, 6, 7)
Per: perylene
Per-D: perylene deuterated
PM: Particular matter
PM10: particular matter under 10 μm
PM2.5: particular matter under 2.5 μm
PM1: particular matter under 1 μm
PAHs: polycyclic aromatic hydrocarbons
Phe: phenanthrene
Phe-D: phenanthrene deuterated
Phe-D: phenanthrene deuterated
Py-D: pyrene deuterated
Py: pyrene

QAQC: quality assurance quality control
TPhe: triphenylene

stdev() : standard deviation
s^*: standard deviation of the robust concentration average (eq. 3)
u_{bias} : standard uncertainty of the bias (eq. 7)
u_{ci} : uncertainty of the reported value from laboratory I (eq. 7).
$u_{cl:}$ uncertainty of the calibration and the reference value (eq. 1)
U_{lab} : expanded uncertainty for the reported value (eq. 9)
U_{ref} : expanded uncertainty for the reference value (eq. 9)

VMM: Vlaamse Milieumaatschappij
Z: random variable of two tails statistic for normal distribution (eq. 8).

Introduction

The pollution caused by particulate matter (PM) is one of the critical issues of the current air quality policy. Numerous studies relate mortality and morbidity with the pollution levels of particulate matter in air. In this context, an appropriated characterization of the particulate is of importance to provide a better health indicator for air quality than PM10, PM2.5 or PM1. Furthermore, this could help in the identification and quantification of the compounds responsible for health disorders.

At EU level, the Directive 2004/107/EC already focuses on the analysis of heavy metals and polycyclic aromatic hydrocarbons (PAHs) as compounds to be analysed in PM10 as responsible for PM toxicity and carcinogenic characteristics. In the case of the PAHs, an annual limit value has been established for benzo(a)pyrene (BaP) (carcinogenic to humans according to the last upgrade of the IARC) as a marker for PAH in particles. Furthermore, other PAHs are recommended to be measured: benzo(a)anthracene, benzo(b)fluoranthene, benzo(j)fluranthene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene and dibenzo(a,h)anthracene.

The tedious methodologies linked to the quantification of PAHs imply relatively high uncertainties in the reported analytical results. This is reflected in the level of expanded uncertainty defined in the afore-mentioned Directive, being for BaP in PM10 or in total deposition, 50 % and 70 %, respectively. Furthermore, the minimum time coverage for these measurements is reduced up to 14 -33 % for fixed measurements.

The implementation of analytical methods that are traceable and QAQC tested becomes an asset for this sort of analysis. Furthermore, the execution of inter-laboratory comparisons represents an important tool for the demonstration of laboratory traceability, showing competence and identifying weak points in their analytical methods.

This report shows the results of the first inter-laboratory comparison of PAHs on PM10 filters carried out at European level among the Air Quality Reference Laboratories in Europe (AQUILA).

Inter-laboratory comparison strategy

This inter-laboratory comparison focussed on the evaluation of the analytical performance of participating laboratories. Any consideration regarding sampling technique or monitoring strategic approach is out of the discussion in this report. Instead, uncertainties, biases or inaccuracies should be linked to analytical issues and to the traceability of the measurements.
Although the testing of laboratory traceability and analytical performance could easily be carried out by means of reference material (i.e. NIST-16492 or CRM-ERM@CZ-100), this may not reflect the response of a laboratory to real samples collected on PM10 filters. For this reason, this exercise was performed on the basis of real samples on PM10 quartz filters.

Participating laboratories

Sixteen laboratories from AQUILA have participated in this inter-laboratory comparison. Names of the laboratories and people involved are listed in Table 1.

Table 1.– List of participating laboratories

Laboratory name	Acronym	Country	Contact/Analytical responsible
IVL Swedish environmental institute	IVL	Sweden	Annika Potter Erika Rehngren
Environmental Research Department of Environmental Protection Agency, EPA	EPA-lt	Lithuania	Daiva Pockeviciute
Agência Portuguesa do Ambiente	APA-LRA	Portugal	Paula Viana João Matos
Vlaamse Milieumaatschappij - Labo Gent VMM - Labo Gent	VMM	Belgium	Eric Wauters Peter Van Caeter Roland De Fleurquin
Landesamt für Natur, Umwelt und Verbraucherschutz NRW	LANUV	Germany	Ulrich Pfeffer Dieter Gladtke Anja Olschewski
AWEL Gewässerschutzlabor Kanton Zürich	AWEL	Switzerland	Robert Gehrig Andreas Wyss Nicole Imboden
Cesky hydrometeorologicky ustav	CHMU	Czech Republic	Helena Placha Jan Abraham Eva Paznerova Irina Nikolova Jiri Novak
Estonian Environmental Research Centre	EERC	Estonia	Toivo Truuts Juhan Tamm
National Environmental Research Institute, Aarhus University	NERI	Denmark	Rossana Bossi
Executive Environmental Agency	EEA	Bulgaria	Borislav Zdravkov Ognian Georgiev
Institut Scientifique de Service Public	ISSeP	Belgium	HENGESCH Valerie CADET Alain LEBRUN Muriel
Environmental Protection Agency EPA	EPA-ie	Ireland	Barbara O'Leary Lin Delaney Simon O'Toole
Amt der oberösterreichischen Landesregierung. Abteilung:Umweltschutz	ABUM	Austria	Adolf Schinerl
Chemical Analytical Laboratory, Slovenian Environment Agency	KAL	Slovenia	Gregor Muri
Laboratory of Air Chemistry, Finnish Meteorological Institute	FMI	Finland	Hannele Hakola Mika Vestenius Heidi Hellen
AEA Technology Scientifics part of Environmental Scientifics Group	AEA ESG	UK	Christopher Connolly Shane O'Leary Joanne Baker
Instituto de Salud Carlos III	ISCIII	Spain	Rosalía Fernandez Patier
Joint Research Centre European Reference Laboratory for Air Pollution	ERLAP	EC	E. Grandesso K. Kowalewski P. Pérez Ballesta

Sampling programme and schedule

The need for real PM10 samples to carry out this exercise was discussed inside the AQUILA. The sampling of PM10 should represent typical operational network monitoring conditions. Two Laboratories Instituto de Salud Carlos III from Spain and the “Cesky hydrometeorologicky ustav” from the Czech Republic voluntarily offered to act as sampling laboratories and were finally responsible for the PM10 sampling.

The sampling was performed according to a defined protocol (see Annex I) by means of Andersen high volume PM10 samplers on quartz filters (Whatman QM-A). Filters were heat-treated prior to sampling and each seasonal batch of samples was sent to the JRC for characterisation.

The sampling was performed during two different seasonal periods, covering the possible range of concentrations that characterised the sampling locations: summer (June-August 2009) and winter (November-January 2010). The corresponding samplers were sited in background monitoring stations of “Sinesio Delgado” (Madrid) and “Libus” (Prague).

Sections of the filters were distributed among participants during the second week of May 2010, with a data collection deadline, beginning of September 2010. The package contained one filter for each season and location, and two blanks (one from each sampling location).

The comparison was based on the amount of compound quantified on the filter, which should be expected to be equivalent to typical amounts found in low volume sampler filters.

Participating laboratories received the filters together with a “Guide to operation” (included in Annex I). They were requested to provide information concerning the analytical method and the uncertainty evaluation of the measurements. Laboratories were requested to report a minimum of 3 replicate injections for each sample.

A list of fifteen different PAHs was provided from which seven of them were marked as priority (See table 2).

Table 2.– List of compounds to be quantified on the filter

Single compound	***Compounds***
1	Phenanthrene
2	Anthracene
3	Fluoranthene
4	Pyrene
5	**Benzo(a)anthracene**
6	Chrysene
7	**Benzo(b)fluoranthene**
8	**Benzo(j)fluoranthene**
9	**Benzo(k)fluoranthene**
10	Benzo(e)pyrene
11	**Benzo(a)pyrene**
12	Perylene
13	**Indeno(1,2,3,-c,d)pyrene**
14	**Dibenzo(a,h)anthracene**
15	Benzo(g,h,i)perylene
Combination of isomers	***Compounds***
A	*Chrysene+triphenylene
C	***Benzo(b.j,k)fluoranthene**

In highlighted print priority compounds for the inter-laboratory comparison

Filters management, characterisation and homogeneity

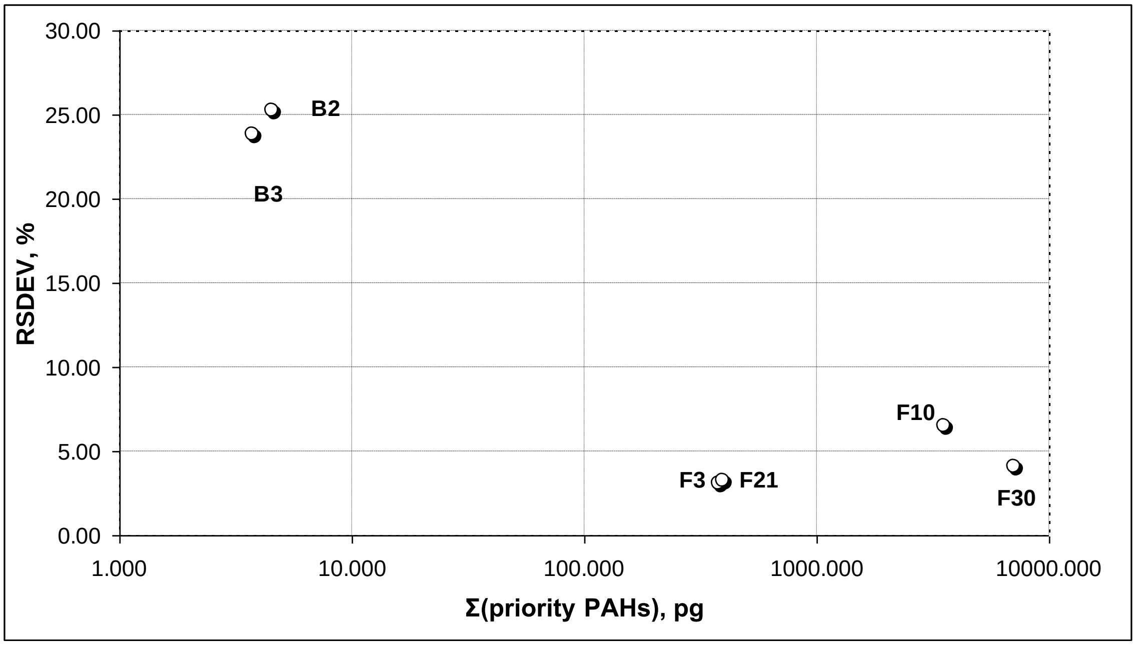
Whatman QM-A Quartz microfiber filter [20.3x 25.4 cm (8x 10 in). Cat. No. 1851 865] were used for sampling in the Andersen high volume PM10 samplers. These filters provide a sampling area of circa 406 cm^2 to be subdivided into smaller filter sections corresponding to low volume filter samples of diameter 4 cm.

The high volume sampled filters that arrived directly from the sampling site were kept in a freezer (at -16 ºC) until the preparation for distribution among participating laboratories. Twenty filter samples of 4 cm diameter were available from each high volume sampled filter. They were systematically cut by means of a mould specifically designed for this purpose (See Figure 1).

Figure 1.– Mould and tools for the subdivision of the high volume sampled filter

The low volume dimension filters were carefully prepared for mailing according to a particular procedure that considered the individual packing and sealing of each sample (Detail of this packing can be observed in Annex I - Guide to operation).

The filters selected for the inter-laboratory comparison were previously tested for homogeneity by means of a thermal desorption methodology, which allowed the quantification of small sections of filters with diameters from 2.5 to 6 mm (Van Drooge et al.).



** Priority PAHs: benzo(a)anthracene, benzo(b,j,k)fluoranthene, benzo(a)pyrene, Indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene*

Figure 2.– Relative standard deviation with respect to priority compounds.

The random analysis of a minimum four small filter sections by thermal desorption shows content relative standard deviations compatible with the needs for the comparison exercise. The relative standard deviations associated with the sum of the priority compound concentrations for the sampled filters ranged between 3.2 and 6.5 %. This is in agreement with previous studies of homogeneity on Andersen high volume sampled filters (A. Baeza et al.).

Table 3 shows sampling parameters and average values for the main ambient variables registered during the sampling of the PM10 in the corresponding locations. As expected PM10 and PM2.5 winter concentrations were higher than those for summer, whilst the highest levels were found in Prague during winter.

Table 3.– Sampling variables for the PM10 collection

Filter code	F3	F21	F10	F30	B2	B3
Location	Madrid	Prague	Madrid	Prague	Madrid	Prague
Sampling Period	6-8/7/2009	27-28/8/2009	25-27/11/2009	21-22/11/2009	-	-
Sampling volume, m^3	3090	1590	3190	1708	-	-
Temperature, ºC	24.9	22.8	9.2	7.28	-	-
Relative Humidity, %	32	63	90	87	-	-
PM10, µg/m^3	30	24.3	21	89	-	-
PM2.5, µg/m^3	11	16.7	n.a.	64	-	-
O$_3$, ppb	37	70	n.a	5	-	-

* n.a.: non available

With the exception of the winter Prague filter, where the concentration of PAHs were significantly high, with concentrations of benzo(a)pyrene of about 7.5 ng/m^3, other filters were much lower, 0.2 ng/m^3 for the winter filter in Madrid and around 50 pg/m^3 of BaP for the summer period in both locations. Graphs from Figure 3 show the estimated PAH air concentration levels during the corresponding sampling days and locations.

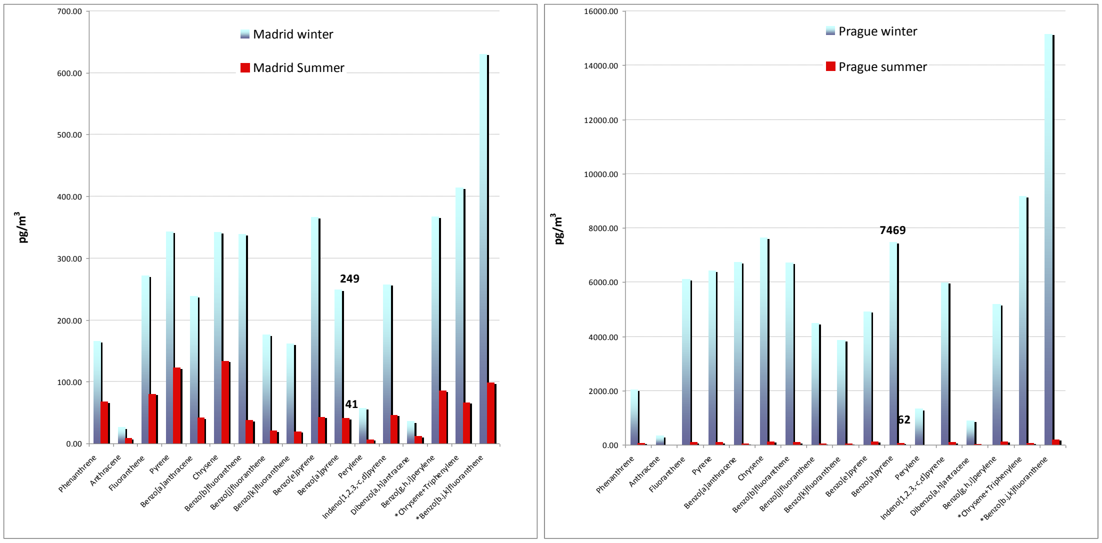
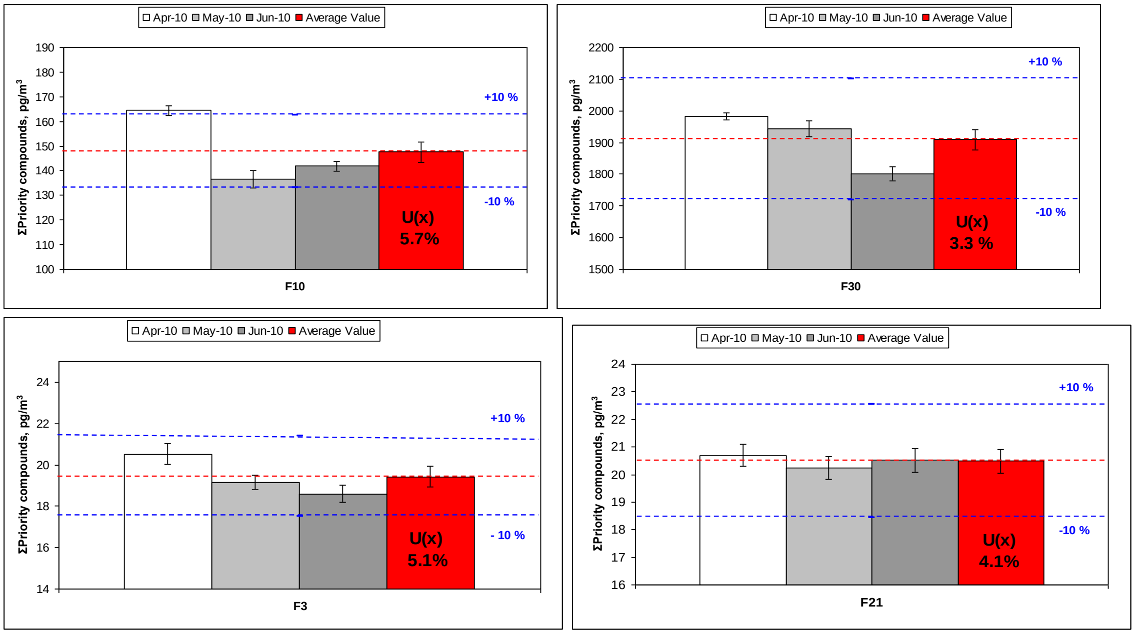


Figure 3.– PAHs air concentration levels during sampling

Filter stability

JRC retained three 4 cm diameter filters for analysis from each sampling batch. One set of filters was sent abroad and return to JRC by courier, simultaneously to the filters of the other participants. The other two filters from the same sampling batch were analysed one month before and one month after the circulating filters. Those filters were stored in freezer.

The analysis of these filters showed variation within ± 10 % of the average value, therefore validating the stability of the filters for the exercise. The sum of the priority PAHs quantified on the filters are shown in Figure 4. It is noted the lower uncertainty associated with filters from Prague when compared to those from Madrid. Similar behaviour was also noted during the homogeneity tests, which could be due to a more volatile composition of the Madrid filters in comparison to Prague or a breakthrough on the Madrid filters caused by the sampling volume being double that of Prague.



** Priority PAHs: benzo(a)anthracene, benzo(b,j,k)fluoranthene, benzo(a)pyrene, Indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene*

Figure 4.– Analysis of the filters before and after the exercise.

Analytical Methods

Each participant was free to choose the analytical method according to their own experience. As a consequence, there were multiple combinations of different separation techniques, detectors, extraction systems, solvents, extraction time, clean up and other analytical parameters. No statistical differences could be associated with a specific technique for extraction or analysis. Table 4 shows the different techniques and relevant analytical conditions used by the participating laboratories.

Table 4.– Analytical method used by the participating laboratories

LABORATORY	ANALYTICAL METHOD	COLUMN	EXTRACTION	SOLVENT	TIME	CLEANUP	CORRELATION	INTERNAL STANDARD
IVL	HPLC /FLD	CHROMSPHERE PAH (VARIAN)	SOXLHET	PENTANE-ACETONE	24 H	SILICA GEL MERK	Multipoint-Linear	b,b-binapthyl
EPA-LT	HPLC /FLD	SUPELCOSILITM LC-PAH	SOXLHET	HEXANE-ACETONE	4 H	SPE CARTRIGE	Multipoint-Linear	external extandard
APA-LRA	HPLC /FLD	C18 REVERSE PHASE	SOXLHET	ACETONITRILE	16 H	-	Multipoint-Linear	external extandard
VMM	HPLC /FLD	ZORBAX ECLIPSE PAH	ASE	DICHLOROMETHANE	35 MIN	-	Multipoint-Linear	external extandard
LANUV	HPLC /FLD	ZORBAX ECLIPSE PAH	ULTRASONIC	TOLUENE	24 H	CHROMABON	Multipoint-Linear through origin	external extandard
AWEL	GC-MS	DB5-30 M	SOXLHET	CYCLOHEXANE-ISOOCTANE-ACETONE	4 H	-	Multipoint-Linear	1,11 dibromodecane
CHMU	GC-MS	DB5-30 M	SOXLHET	METHANOL-DICHLOROMETHANE	1 H	SILICA GEL SUPELCO	Multipoint-Linear through origin	Phe-D, Chry-D, Per-D
EERC	GC-MS	DB5-30 M	SOXLHET	CYLCOHEXANE	16 h	-	Multipoint-Linear	Py-D, Per-D
NERI	GC-MS	DB5-30 M	n.a.	DICHLOROMETHANE	n.a.	-	Multipoint-Linear	BaA-D, Chry-D, BaP-D, Per-D, BghiPer-D, DBahA-D
EEA	GC-MS	DB-XLD- 30 M	ULTRASONIC	DICHLOROMETHANE	1 H	SILICA GEL	Multipoint-Linear	Phe-D, Chry-D, Per-D
ISSeP	GC-MS	DB-17	SOXHLET	CYCLOHEXANE-DIETHYLETHER	16 H	-	Multipoint-Linear	Phe-D, Chry-D, BaP-D
EPA-ie	GC-MS	DB5-30 M	ULTRASONIC	DICHLOROMETHANE	n.a.	FLORASIL	Multipoint-Linear	Chry-D
ABUM	GC-MS	DB5-60 M	ASE	CYCLOHEXANE	30 MIN	SILICA GEL	Multipoint-Linear	corresponding deuterated
KAL	GC-MS	DB5-30 M	MICROWAVE	HEXANE-ACETONE	45 MIN	SILICA	Multipoint-Linear	Phe-D, Py-D, BahA-D, BaP-D, IndPy-D
FMI	GC-MS	DB5-50 M	SOXLHET	DICHLOROMETHANE	8 H	FLORISIL	Multipoint Quadratic	Phe-D, Chry-D, DBahA-D, Per-D
AEA/ESG	GC-MS	ZB-5 30M	ASE	n.a.	n.a.	SPE CARTRIGE	Multipoint-Linear	I.S. non expecified
ERLAP	GC-MS	DB-17 30 M	MICROWAVE	ACETANE-HEXANE	30 MIN	SPE CARTRIGE/ CUPS	Multipoint-Linear	corresponding deuterated
ERLAP#T	GC-MS	DB-17 30 M	THERMAL DESORPTION				Multipoint-Linear	corresponding deuterated

25 % of the participating laboratories used liquid chromatography and FLD detection whilst the rest of the laboratories used gas chromatography separation and mass spectrometry. For gas chromatography separation, a 30 m DB5 was the most frequently used column; other phases such as DB17 or longer lengths were rare. Soxhlet was the most common method for extraction used by 8 laboratories, three laboratories used ultrasonic extraction and another three accelerated soxhlet extraction, 2 laboratories extracted the filter by microwave, whilst only one laboratory used thermal desorption. There was no agreement in the solvent or time for extraction (acetonitrile, pentane, acetone, cyclohexane, isooctane, dichloromethane, toluene and mixtures of these solvents were used by laboratories even with the same extraction technique), with times from minutes to 24 hours. Clean-up was applied by most of the laboratories. All analysis were performed by multipoint calibration. Internal standard method was applied to all GC-MS analysis, while only one laboratory used internal standard for HPLC.

Analytical uncertainties from participating laboratories

Participating laboratories were requested to estimate the associated expanded uncertainties of their analytical results. These values are given in Table 12. Description of the uncertainty evaluation provided by each laboratory is given in annex I.

Several laboratories provided uncertainties on the basis of data from method validations and analysis of reference material, including the bias as an additional source of uncertainty. On the other hand, the 3 analyses per sample requested can only provide an idea about the analytical repeatability, but other sources of uncertainty should be considered in the calculations such as: calibration and standard preparation, blank level, reproducibility, desorption efficiencies, known biases, etc. Furthermore, as the exercise contains different filters with different concentration levels, it is expected that the analytical uncertainty will depend on the concentration level. The lower the analysed concentration, the higher the uncertainty associated with the quantified value. Similarly, the analytical uncertainty will be different from compound to compound, depending on its analytical reproducibility and response, volatility, desorption efficiency, etc. Nevertheless, these aspects not always considered in the reported uncertainties.

Analytical uncertainties from the ERLAP

ERLAP participated in the exercise by analysing the filters using two different techniques: solvent extraction with GC-MS and thermal desorption with GC-MS analysis.

The evaluation of the concentration and the associated budget uncertainty, reported by JRC, was based on the results of the averaging of three filter samples analysed in triplicate by liquid extraction and gas chromatography. The reproducibility uncertainties of these analyses were combined with others sources of uncertainties derived from the standards, calibration and system blank. In a similar way, 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 overall uncertainty, *ou*, was calculated as follows:

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

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 referencies: B.L. Vand Drooge et al. J. Chromatogr. A 1216 (2009) 4030-4039)

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

$f_{i,j}$ is the concentration calculated 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)
$\overline{f_{i,j}}$ is the average value of all injections and filters
$blank_i$, is the system blank level associated with the analysis of the filter i.

Reference values

Due to the nature of this kind of inter-laboratory comparisons, the reference value was determined on the basis of the robust average results from the best performance laboratories. The selection of a best performance laboratory 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, $\overline{C}_i^*$, and standard deviation, s^*, of the p input laboratories, are derived from a convergence process of the following equation:

$$\overline{C}_i^* = \frac{\sum C_i^*}{p} \qquad (3)$$

$$s^* = 1.134 \cdot \sqrt{\frac{\sum (C_i - \overline{C}_i^*)^2}{(p-1)}} \qquad (4)$$

Where recurrent values are calculated from these equations:

$$C_i^* = \begin{cases} \overline{C}_i^* - 1.5 \cdot s^* & \text{if} \quad C_i < \overline{C}_i^* - 1.5 \cdot s^* \\ \overline{C}_i^* + 1.5 \cdot s^* & \text{if} \quad C_i > \overline{C}_i^* + 1.5 \cdot s^* \\ C_i & \text{otherwise} \end{cases} \qquad (5)$$

The initial values are calculated as:

$$\begin{aligned} \overline{C}_i^* &= \text{median of } C_\text{i} \text{ (i} = 1, 2,\text{...p)} \\ s^* &= 1.483 \cdot \text{median of } \left| C_i - \overline{C}_i^* \right| \text{(i} = 1, 2,\text{...p)} \end{aligned} \qquad (6)$$

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

$$u_{bias} = \sqrt{\frac{(1.25 \cdot s^*)^2}{p} + u_{c_i}^2} \qquad (7)$$

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:

$$Z = \frac{C_i - \overline{C}_i^*}{u_{bias}} \qquad (8)$$

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 0.25 were excluded from the estimation of the robust average value, i.e. the reference value of the inter-laboratory comparison. 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.– Outliers versus reported data for all compounds and participating laboratory

Laboratory	**Compounds**			
	reported	**outliers**	**% Reported**	**outlier/reported, %**
IVL	47	11	68	25
EPA-LT	36	9	52	25
APA-LRA	40	9	58	23
VMM	44	9	64	20
LANUV	32	1	46	3
AWEL	29	8	42	**28**
CHMU	44	25	64	**57**
EERC	40	3	58	8
NERI	36	11	52	**31**
EEA	40	24	58	**60**
ISSeP	52	21	75	**40**
EPA-ie	31	16	45	**52**
ABUM	60	8	87	13
KAL	40	4	58	10
FMI	44	8	64	18
AEA/ESG	49	30	71	**61**
ERLAP LIQUID	64	0	93	0
ERLAP THERMAL	64	2	93	3

Table 6.– Reference values and associated expanded uncertainties.

	F21		**F3**		**F10**		**F30**	
	Amount, ng	EU (%)	Amount, ng	EU (%)	Amount, ng	EU (%)	Amount, ng	EU (%)
Phenanthrene	3.9	39.9	6.1	23.0	15.4	20.2	101.3	12.7
Anthracene	0.6	63.9	0.7	40.8	2.4	30.0	16.0	19.8
Fluoranthene	4.2	11.8	7.2	12.1	25.3	13.3	304.9	7.5
Pyrene	4.6	15.9	11.1	10.6	31.9	15.2	320.2	7.7
Benzo(a)anthracene	2.2	29.9	3.7	36.2	22.2	16.1	336.0	5.2
Chrysene	5.1	57.5	12.0	101.3	31.9	31.4	381.5	18.3
Benzo(b)fluoranthene	5.0	18.6	3.3	55.7	31.6	18.0	335.5	12.0
Benzo(j)fluoranthene	2.2	5.9	1.8	5.5	16.4	15.3	223.7	24.7
Benzo(k)fluoranthene	2.2	35.8	1.7	29.1	15.0	24.1	191.3	12.7
Benzo(e)pyrene	5.5	75.2	3.9	65.4	34.1	33.1	245.0	3.8
Benzo(a)pyrene	2.9	16.7	3.7	19.2	23.2	26.6	373.0	7.1
Perylene	0.5	57.0	0.6	25.4	5.3	45.2	65.0	7.1
Indeno(1,2,3,-c,d)pyrene	4.2	14.5	4.2	16.1	24.0	11.4	298.7	11.2
Dibenzo(a,h)anthracene	1.3	66.3	1.1	87.1	3.3	36.7	43.7	15.4
Benzo(g,h,i)perylene	5.4	19.9	7.7	20.1	34.2	14.0	258.9	14.9
***Chrysene+triphenylene**	3.7	30.6	5.9	38.4	38.6	16.2	457.7	14.9
***Benzo(b.j,k)fluoranthene**	8.7	28.9	8.8	36.9	58.8	15.9	756.2	16.0

Evaluation of the laboratory results

Laboratory results were treated according to ISO 5725 to have representative repeatability and reproducibility values for the inter-comparison exercise. Furthermore, in order to evaluate the average results reported by the different laboratories the *En* number as recommended by ISO/EC Guide 43-1:1997, A.2.1.4 item E., was calculated:

$$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}} \tag{9}$$

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

E_n number expresses the validity of the expanded uncertainty estimate associated with each result. The critical value for E_n number is 1. E_n numbers higher than 1 identify results that are incompatible with the reference value after allowing for the stated uncertainties. The overall evaluation of the laboratory results should consider both bias and E_n value, because a low *En* value could be due to a large stated uncertainty. Therefore, to indicate performance an overall expanded uncertainty (OEU), representing 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, is used; the relative OEU % being calculated according to the following expression:

$$OEU\ \% = \left[\left(U_{lab} / \overline{C_{lab}} \right) + \left(\left| \overline{C_{lab}} - C_{ref} \right| \right) / \overline{C_{ref}} \right] \cdot 100 \tag{10}$$

Results and discussion

All the 15 PAHs under consideration in the reporting list were not fully reported by all the laboratories. According to Figure 5, compounds like BaP, BaA, BghiPe, (Chr and Chr+TPhe) and IndPy were reported by 90 % of the laboratories. While 80 % of laboratories reported Phe, Anth, DBahA, Flu, Py and only 60 % of the laboratories reported results for BbFlu, BkFlu, and BbjkFlu. As a result less than 30 % of the laboratories provided results for BjF, Per and BeP.

These reporting percentages are indicative of difficulties linked to the analytical method as well as the capability of these laboratories to analyse these compounds. It is also noted that the highest percentages of reporting correspond to those compounds mentioned in the EU directive 2004/107/EC, in which the laboratories have invested most of their analytical effort.

The blank filters analysed by the participants show the noise level associated with the analytical methodology. Figure 6 shows the average value of the blank level (B) quantified by the participating laboratories in the two filters, as well as the value defined by the best performance laboratories (Blank REF). It is noted that blank levels are generally higher for the more volatile PAHs, which acts as a potential source of contamination for the material of analysis.

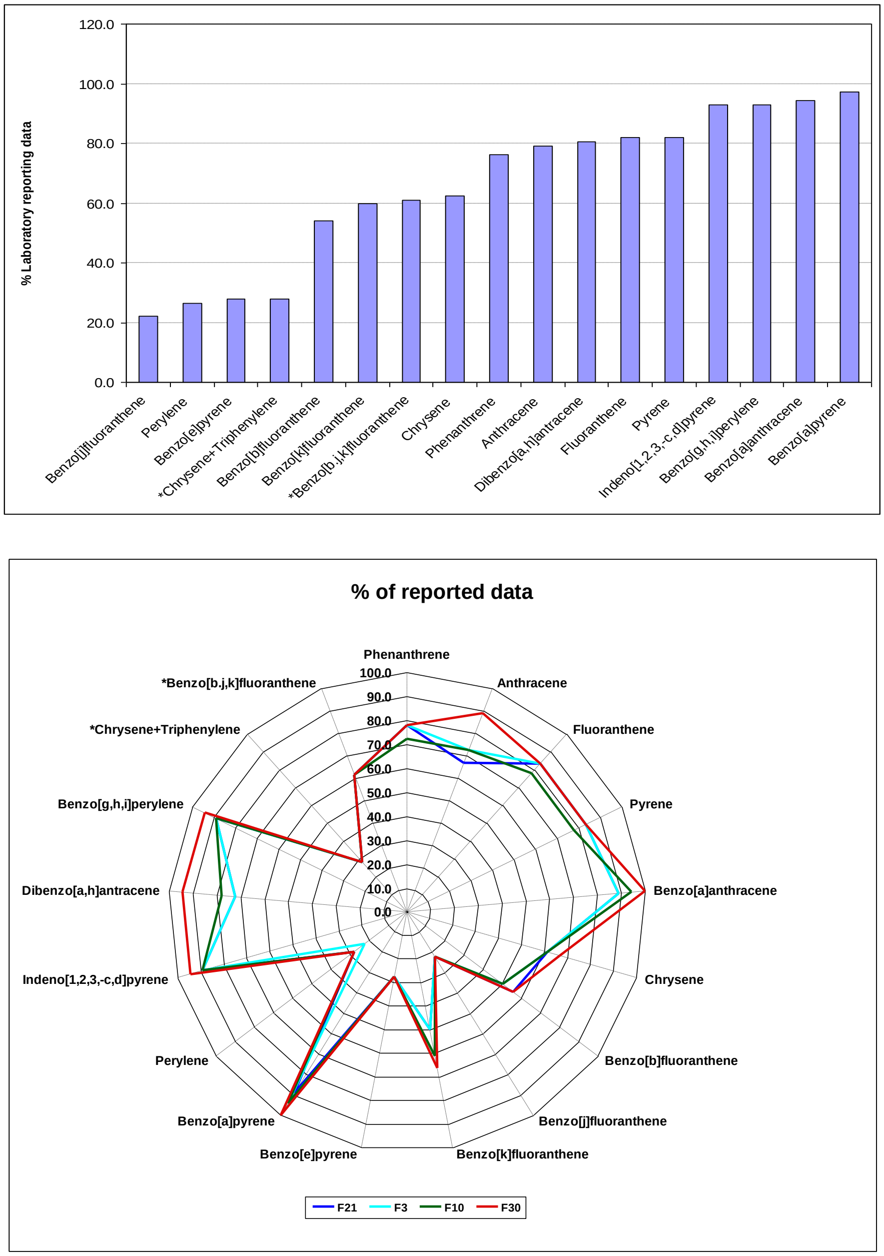


Figure 5.– Percentage of laboratories reporting data for each compound

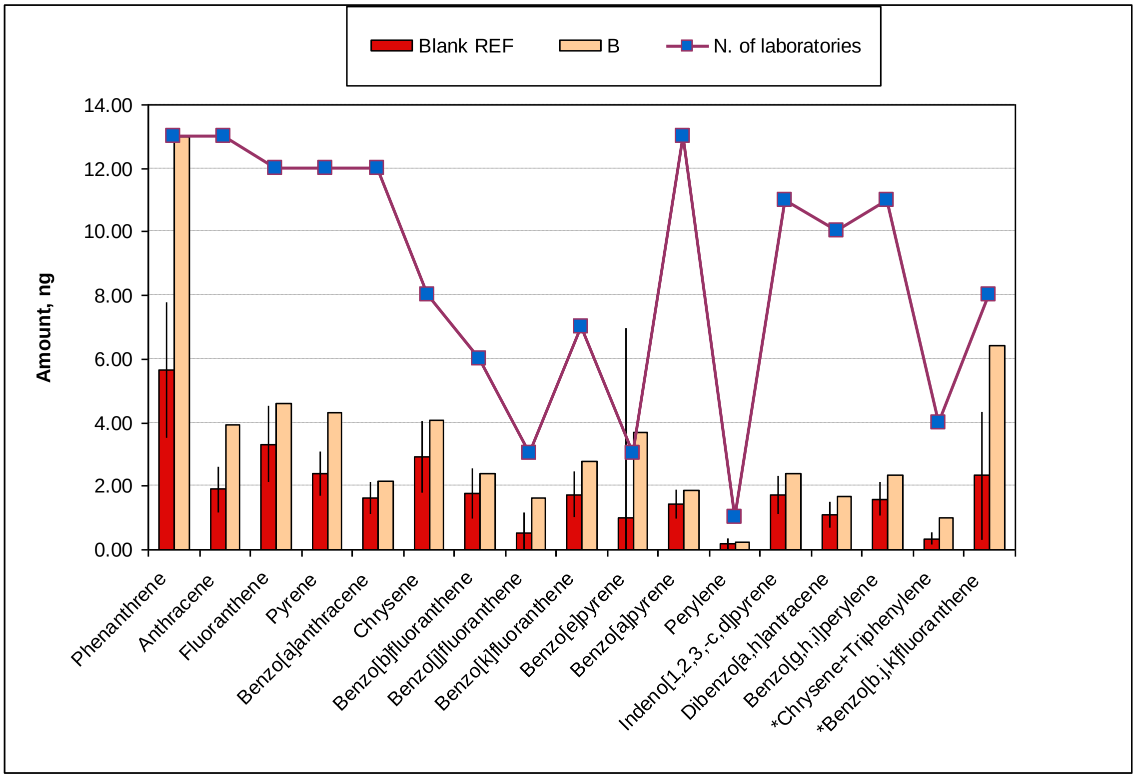


Figure 6.– Average PAH levels for the blank filters of the comparison exercise

Figure 7 shows the amount of compounds quantified in each filter in comparison with the one determined on the blanks by the best performance laboratories. It is noted that filters F21 and F3, corresponding to the summer period in Prague and Madrid, respectively, were probably close to the quantification limit of the method, in particular for the lighter compounds like phenathrene or anthracene where the amounts quantified on the blank and on the filter were similar.

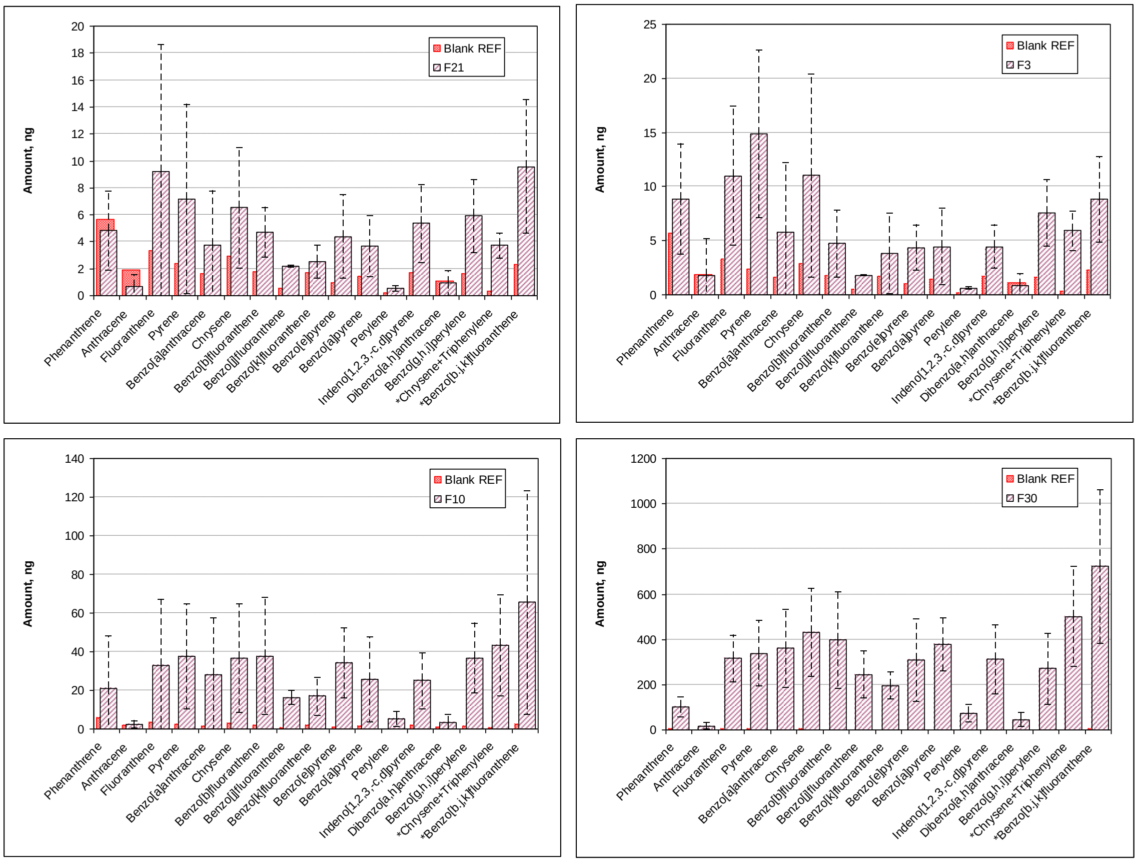
Overall results of the inter-laboratory comparison can be represented in terms of bias with respect to the reference value or deviation of the reference value with respect to the laboratory, when the reference value is higher. This can be represented as follows:

bias (%) = deviation (%) if Laboratory value > Reference value (11)

or

$$\text{bias}(\%) = -\frac{\frac{\text{deviation}(\%)}{100}}{1+\frac{\text{deviation}(\%)}{100}}\cdot 100$$ if Laboratory value < Reference value (12)

Consequently, the sign ‘+’ and ‘-’ makes reference to the ‘over’ and ‘under’ estimation of the reference value.



|-----| *standard deviation of the inter-laboratory average value*

Figure 7.– Blanks versus sampled Filters

Figures 8 to 11 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 is evident that the scattering of the results increase with the decrease in the amount of compounds on the filter.

In order to calculate reproducibility and repeatability for the inter-laboratory exercise, this data was treated according to ISO5725. The results are represented in Figures 12 and 13. These figures show the increase of the repeatability and reproducibility values with the decrease in the concentrations on the filters. Repeatability values over 10 % were observed in compounds like anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene for the lower concentrations. Reproducibility values over the 50 % were systematically obtained for the two summer filters with the lower concentrations. The best reproducibility values were obtained with the filter of highest concentration with average values of circa 20 %.

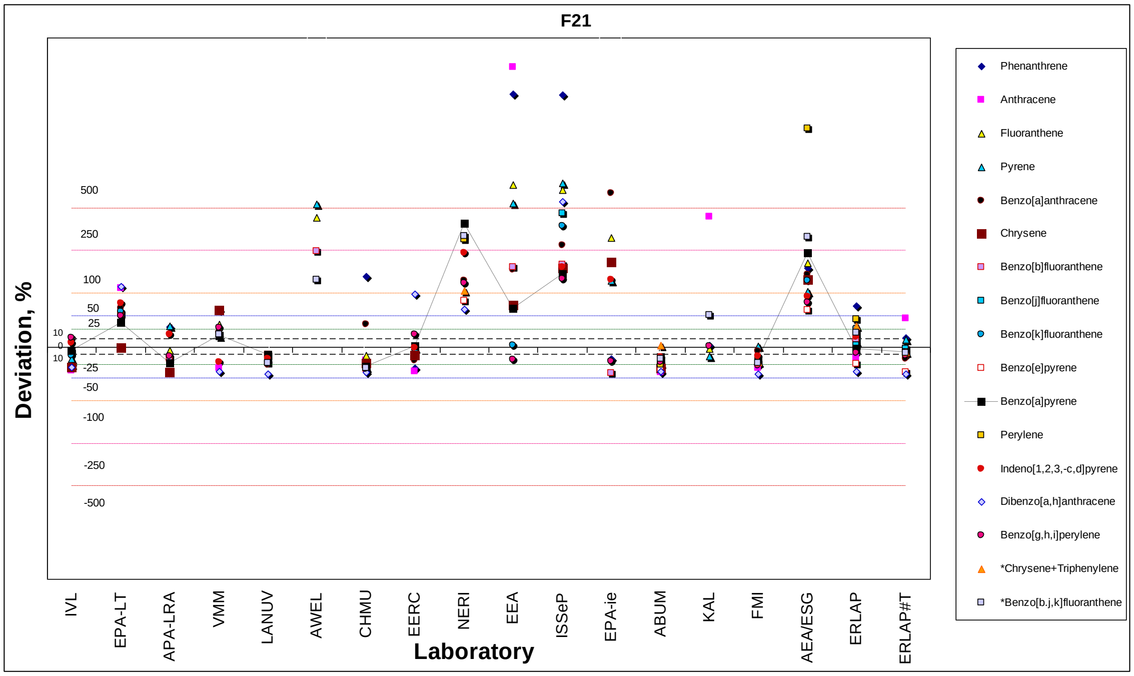


Figure 8.– Inter-laboratory results – Filter F21 – Prague summer period

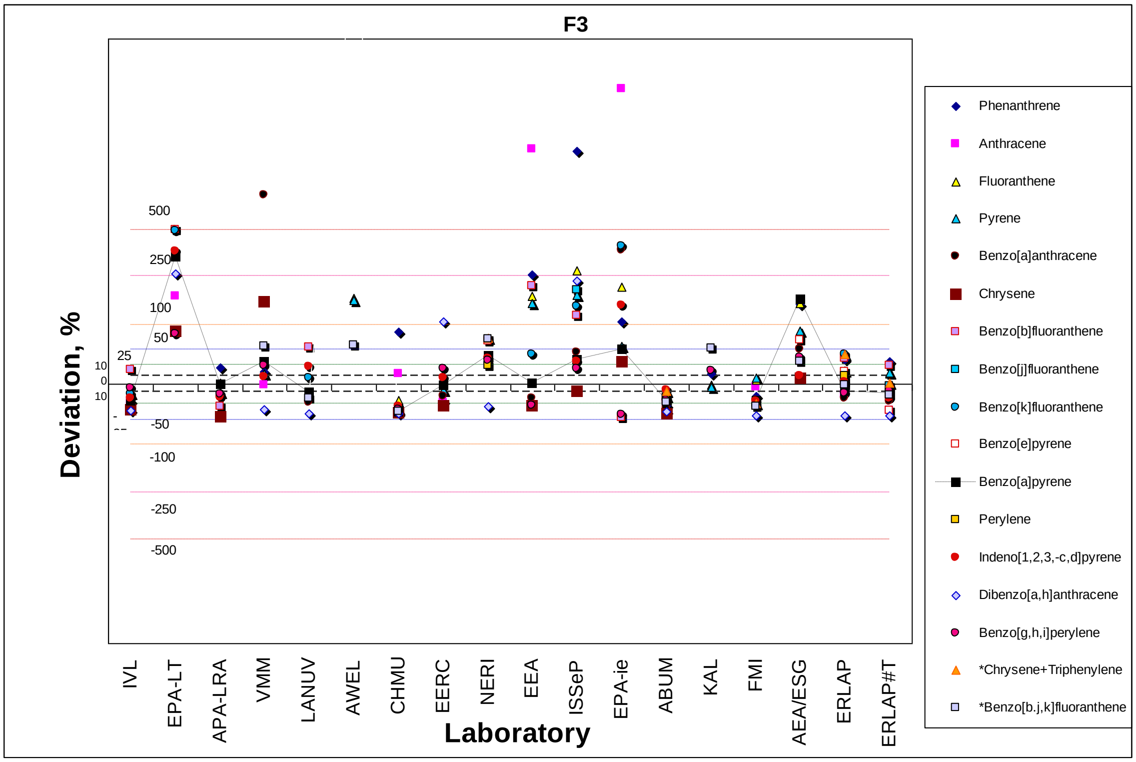


Figure 9.– Inter-laboratory results – Filter F3 – Madrid summer period

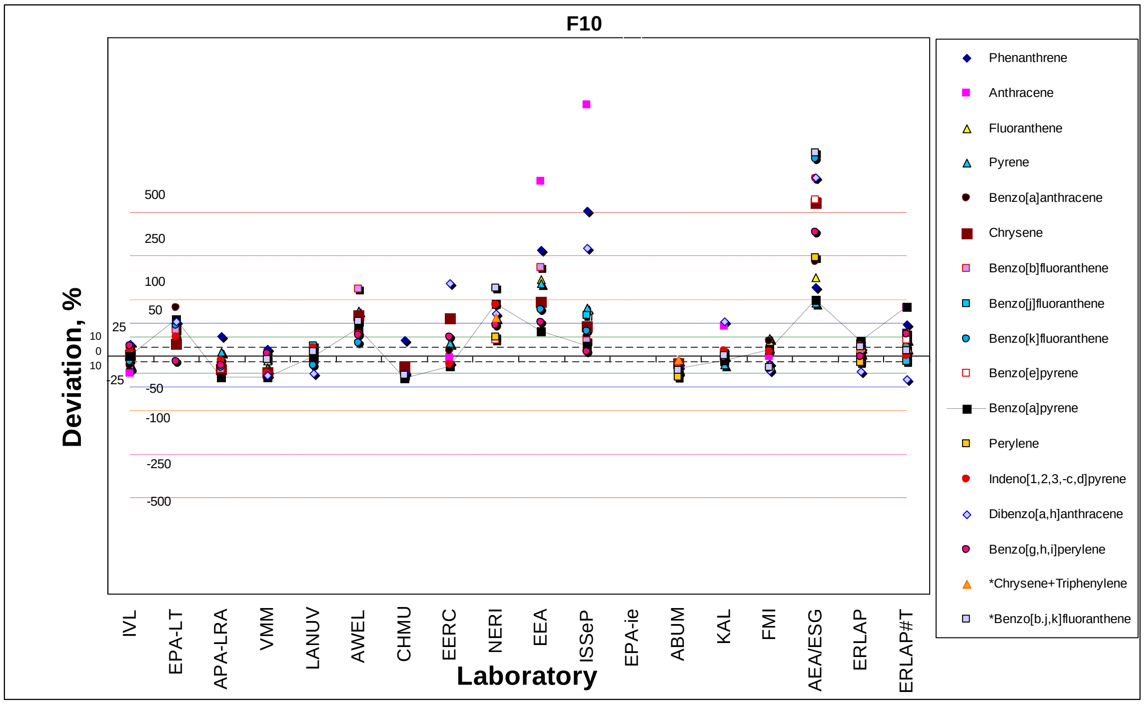


Figure 10.– Inter-laboratory results – Filter F10 – Madrid winter period

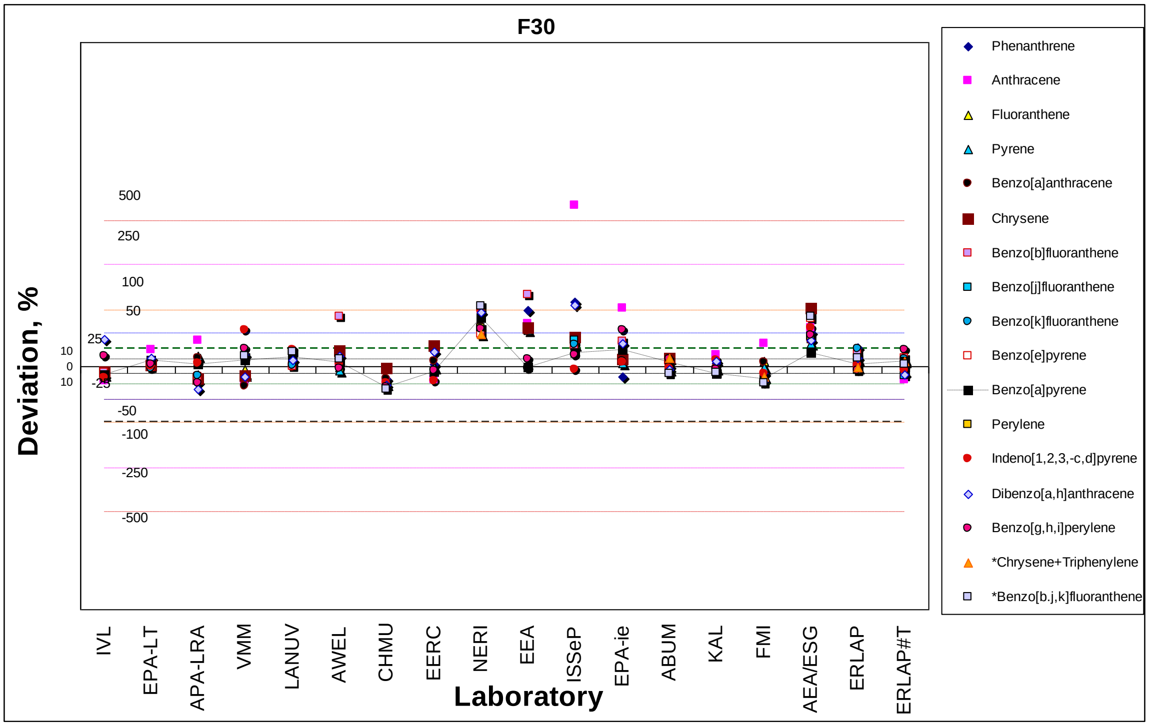


Figure 11.– Inter-laboratory results – Filter F30 – Prague winter period

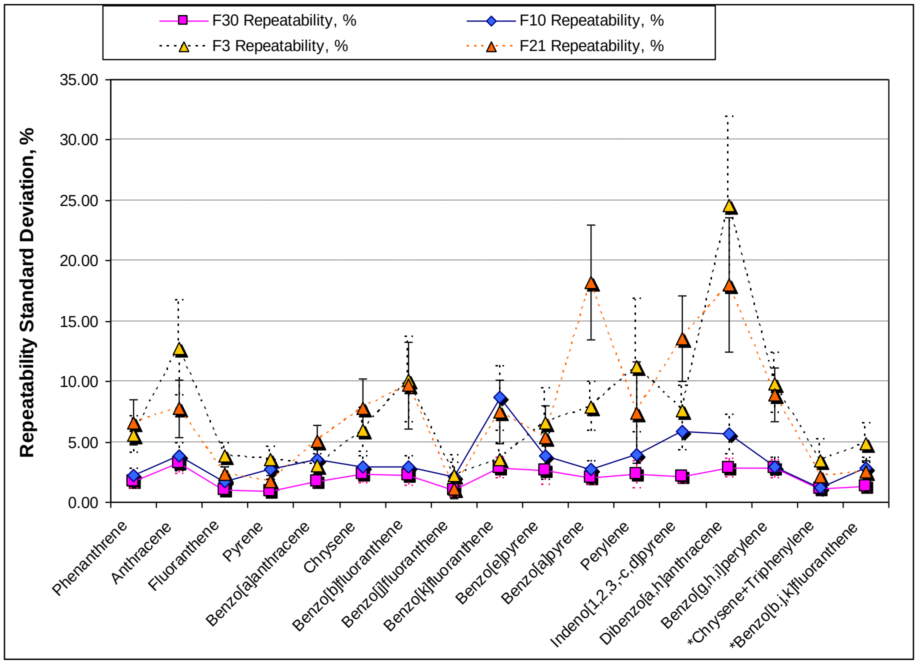


Figure 12.– Repeatability of the inter-laboratory comparison exercise

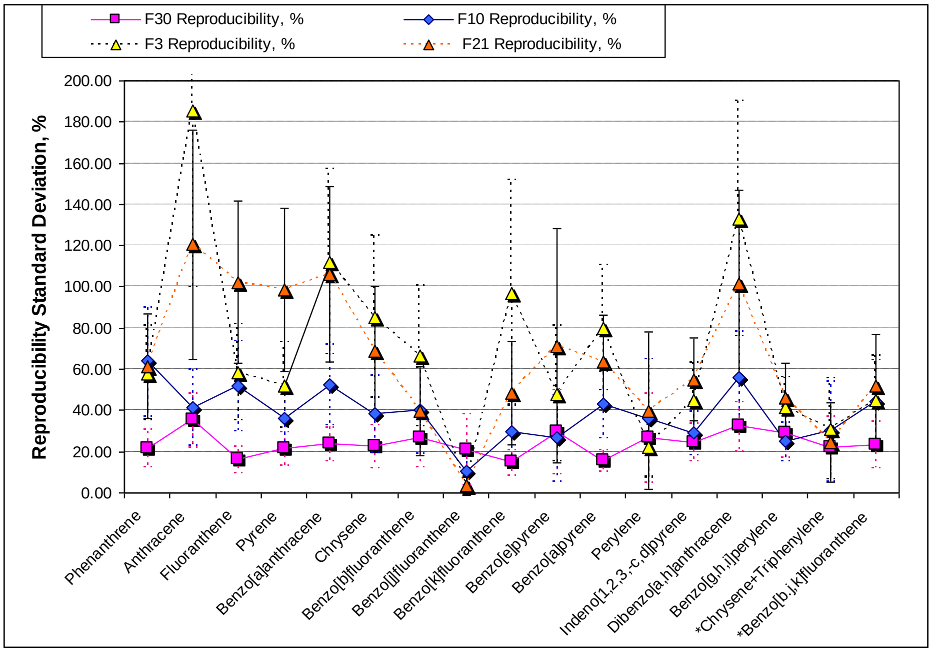


Figure 13.– Reproducibility of the inter-laboratory comparison exercise

Figure 14 represents the median for the repeatability and reproducibility values of all the analysed compounds. In this figure it is possible to see how the repeatability and reproducibility improve with the increase in the concentration levels on the filter. Such an improvement is more significant for the reproducibility values. The robustness of the method is consequently enhanced at higher concentrations.

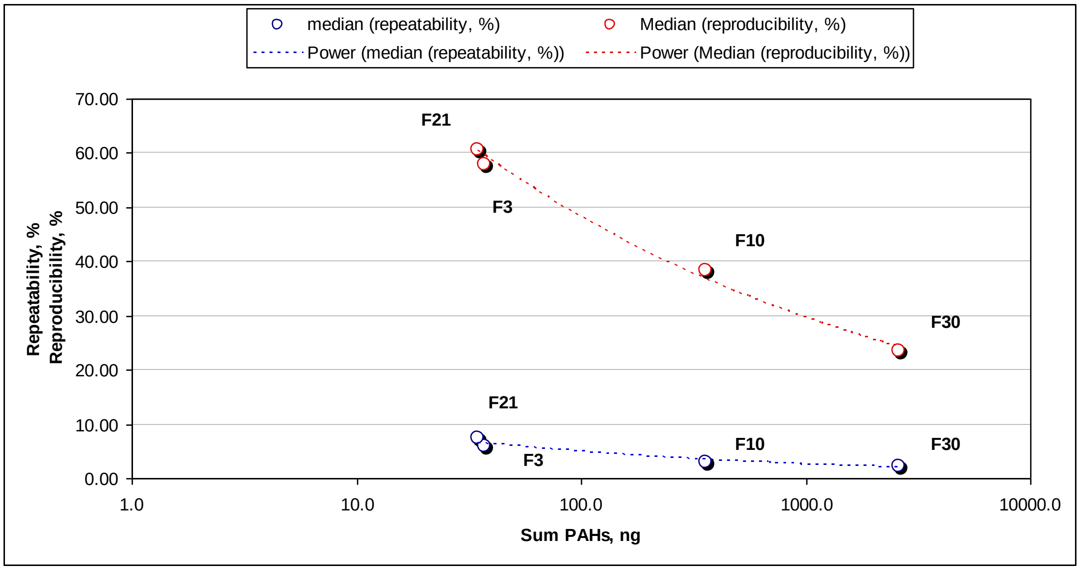


Figure 14.– Median reproducibility and repeatability values versus PAH concentration

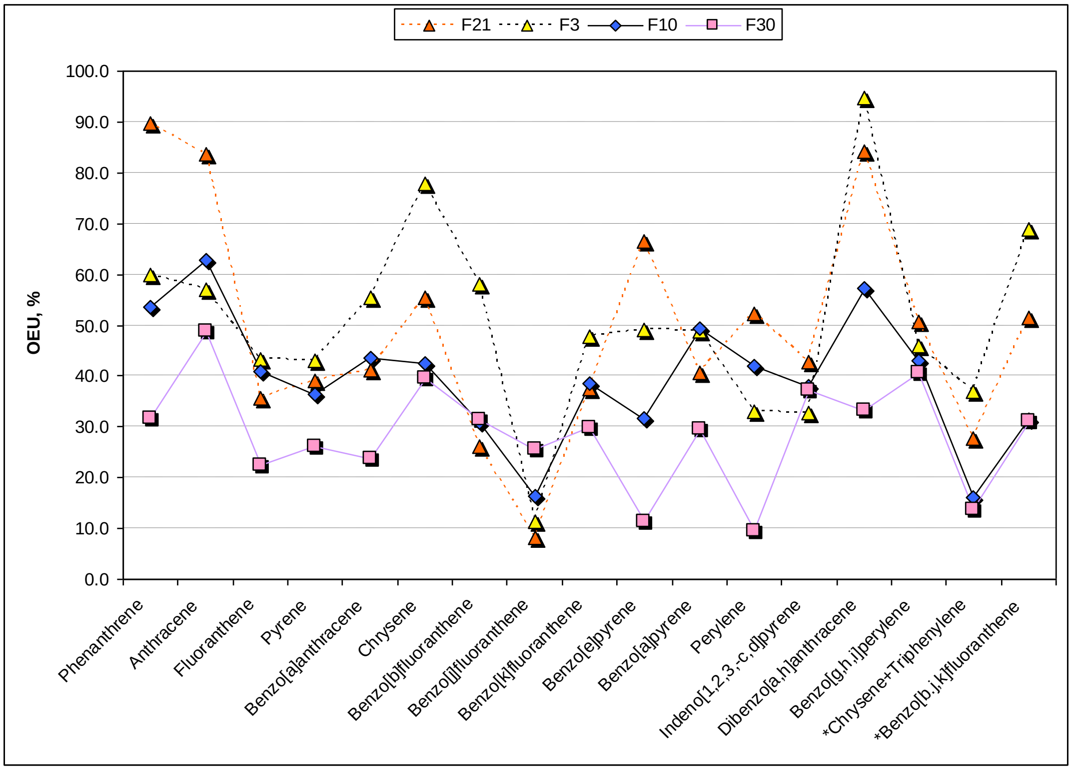


Figure 15.– Median overall expanded uncertainty – excluding outliers

An overall analytical performance for the analysis of each compound, on the basis of this exercise, is given by the median value of the overall expanded uncertainty (OEU), excluding outliers, determined by laboratory according to equation (11). These values are represented in figure 15 for the four filters of the inter-laboratory comparison. The highest concentration filter (F30) shows the lower OEUs, ranging from 10 to 50 %. Those with uncertainties increase with decreasing concentration on the filter. Therefore, from average OEU of circa 29 % for F30 increase to circa 40 % for F10, 51 % for F3 and 52 % for F21 (see table 7).

The results of the inter-laboratory comparison exercise have been evaluated according to ISO 13528 to test the proficiency of each laboratory. All this data was collected from Tables 8 to 12, which shows the average values, expanded uncertainties, bias, En values, and OEU. In addition, an evaluation according to the criteria of En value has been established: warning En>1 and Action En>1.5. En values higher than one imply underestimations of the associated uncertainty or a significant bias of the reported value with respect to the reference's one, not covered by the associated uncertainties.

In general, En values are lower for the higher concentrations, i.e. there is probably a general underestimation of the uncertainty values for the lower concentrations. Excluding outliers, median En values are generally under 1, which represent robust results. Only for a few PAHs (phenanthrene, fluranthene and pyrene) median values were occasionally higher than 1 for the lower concentrations. (see Figure 16).

Table 7.– Inter-laboratory median overall expanded uncertainties for compounds without outliers

median OEU, %	F21	F3	F10	F30
Phenanthrene	89.8	59.9	53.6	31.7
Anthracene	83.8	57.0	62.9	48.8
Fluoranthene	35.6	43.3	41.0	22.4
Pyrene	39.1	43.0	36.4	26.2
Benzo(a)anthracene	46.1	54.4	43.6	23.7
Chrysene	55.3	77.9	42.5	39.7
Benzo(b)fluoranthene	26.2	58.0	30.8	31.4
Benzo(j)fluoranthene	8.3	11.3	16.4	25.7
Benzo(k)fluoranthene	37.6	47.8	38.6	29.7
Benzo(e)pyrene	66.5	49.2	31.6	11.4
Benzo(a)pyrene	45.8	50.2	49.2	29.7
Perylene	52.2	32.9	41.9	9.4
Indeno(1,2,3-c,d)pyrene	47.4	41.8	38.1	37.1
Dibenzo(a,h)anthracene	91.9	94.8	57.3	33.2
Benzo(g,h,i)perylene	50.6	45.9	43.0	40.6
***Chrysene + triphenylene**	27.8	37.0	16.1	13.6
***Benzo(b,j,k)fluoranthene**	51.5	69.0	31.4	31.3

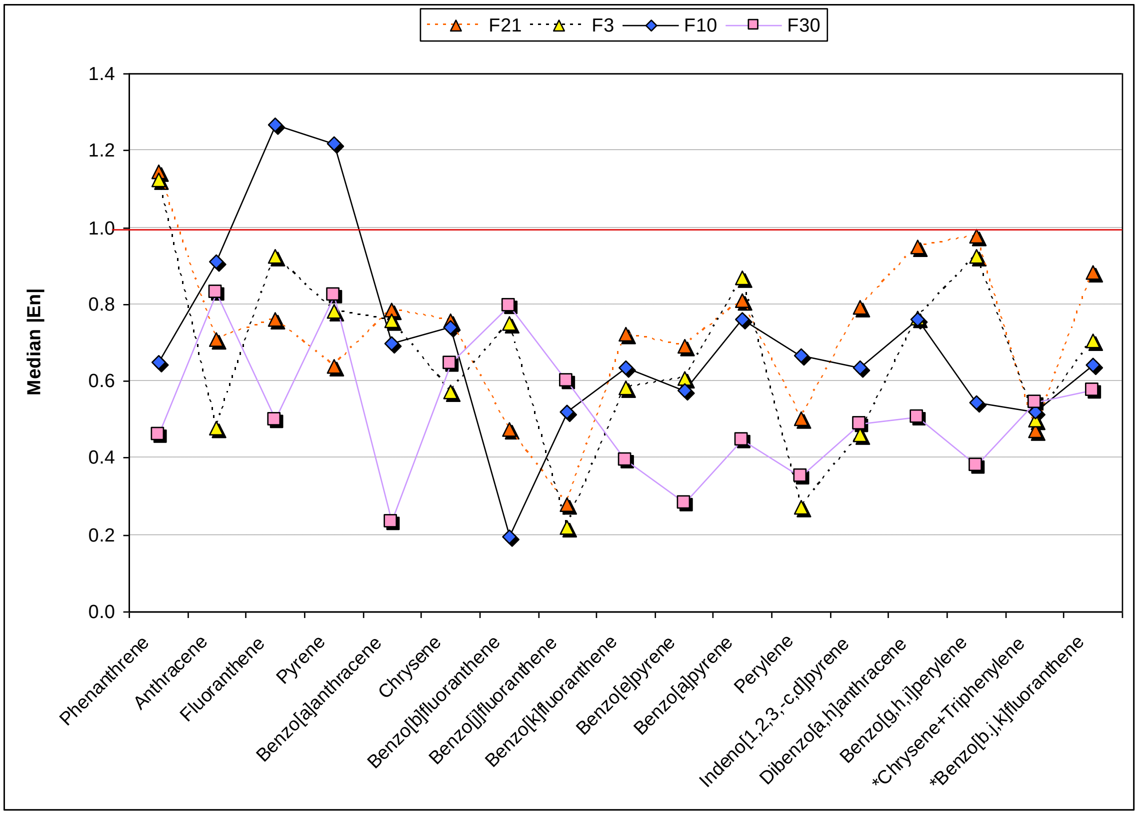


Figure 16.– Median of the absolute En values

Histograms of the results of compounds for the four filters under comparison can be found in the Annex. It is noted that compounds like perylene, benzo(j)fluranthene and benzo(e)pyrene were reported by a very limited number of laboratories. Therefore, no generic conclusions can be draw from these compounds.

Table 8.– Results of the concentrations analysed by each laboratory

REPORTED RESULT	IVL				LANUV				NERI				ABUM				ERLAP			
ng	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	2.6	4.3	11.6	87.9									1.4	3.8	10.2	101.2	6.6	8.1	17.0	128.2
Anthracene	0.3	0.5	1.6	12.0									0.2	0.5	1.4	14.6	0.5	0.6	2.2	15.6
Fluoranthene	4.0	6.1	22.5	263.7									3.1	5.5	19.9	308.8	4.8	7.4	27.1	340.9
Pyrene	3.7	9.8	27.7	281.3									3.2	9.2	24.6	308.7	4.9	12.9	32.9	351.6
Benzo[a]anthracene	1.3		18.7	267.3	1.4	2.6	20.4	333.3	5.2	5.1	42.2	544.3	1.7	2.0	18.3	343.1	2.2	2.9	24.6	339.1
Chrysene	2.9	5.6	31.9	352.0									2.8	3.6	28.2	422.9				
Benzo[b]fluoranthene	4.7	4.0	31.8	306.3	4.5	5.1	30.2	333.7									5.5	4.5	31.9	389.9
Benzo[j]fluoranthene							18.3	266.7									2.2	1.9	15.8	211.6
Benzo[k]fluoranthene	1.9	1.5	13.7	154.0	1.6	1.8	12.8	194.8					1.5	1.2	10.6	174.1	2.8	2.4	17.8	238.2
Benzo[e]pyrene									10.1	6.4	41.4	366.3	2.9	2.9	22.4	252.3	3.8	4.4	31.7	241.8
Benzo[a]pyrene	2.7	2.8	23.0	327.7	2.6	3.3	22.7	419.3	14.2	5.1	44.1	678.0	2.4	2.7	18.0	391.8	2.8	3.4	27.9	380.7
Perylene									2.2	0.8	6.7	105.0	0.4	0.5	2.8	61.6	0.8	0.7	4.8	68.0
Indeno[1,2,3,-c,d]pyrene	4.5	3.3	25.9	247.3	3.4	5.1	26.3	365.2	14.3	5.6	45.0	586.0	3.5	3.8	19.7	289.9	4.8	4.3	27.1	301.2
Dibenzo[a,h]anthracene	0.7	0.5	3.8	60.8	0.4	0.3	2.1	47.1	2.1	0.6	5.6	84.7	0.5	0.4	2.7	41.6	0.5	0.2	2.3	48.8
Benzo[g,h,i]perylene	6.1	7.3	38.7	295.7					12.4	10.1	50.1	411.3	3.9	5.7	28.0	283.9	4.9	6.8	33.4	243.0
*Chrysene+Triphenylene									7.7	10.1	62.1	681.0	3.8	5.4	36.4	507.5	4.9	8.4	42.8	454.2
*Benzo[b.j,k]fluoranthene					6.0	6.9	61.2	904.9	36.5	15.0	136.5	1587.3	7.0	6.1	43.0	684.1	10.5	8.8	65.6	839.8

REPORTED RESULT	EPA-LT				AWEL				EEA				KAL				ERLAP#T			
ng	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene									101.4	21.5	57.9	203.6	3.9	6.9	14.7	105.7	4.3	7.9	22.8	103.8
Anthracene	1.2	2.0	3.4	19.6				16.7	20.6	11.2	21.5	26.9	3.0		3.5	18.5	0.8	0.3	4.4	12.4
Fluoranthene					22.6	19.5	42.9	300.0	34.6	20.0	65.5	485.8	4.1	7.1	23.0	307.0	4.6	8.1	31.0	334.8
Pyrene					28.9	29.4	56.0	300.3	29.3	28.3	79.5	501.3	3.9	10.7	27.6	310.7	5.0	12.6	39.1	350.7
Benzo[a]anthracene	3.6	22.4	40.3	341.3			30.1	348.7	6.0	2.9	41.0	522.6			20.7	328.0	1.8	2.7	27.5	333.7
Chrysene	5.1	22.3	36.9	388.7			52.6	464.0	8.9	7.3	62.2	611.7								
Benzo[b]fluoranthene	7.7	20.0	43.0	329.0	17.4		72.3	618.0	14.2	10.4	95.6	813.5					4.9	4.2	30.8	370.6
Benzo[j]fluoranthene																	2.1	1.8	15.0	192.9
Benzo[k]fluoranthene	3.4	10.1	21.8	185.7			17.5	208.7	2.2	2.4	26.5	186.6					1.9	1.6	16.7	210.4
Benzo[e]pyrene																	2.0	1.8	41.2	240.8
Benzo[a]pyrene	4.0	16.2	36.3	401.7			32.5	393.3	4.7	3.7	31.6	368.2			21.4	336.7	2.7	3.2	42.9	395.6
Perylene																	0.5	0.5	7.0	65.5
Indeno[1,2,3,-c,d]pyrene	7.4	19.3	30.0	298.3			31.1	306.0							25.5	323.3	3.8	3.3	23.9	280.8
Dibenzo[a,h]anthracene	2.8	3.8	5.0	48.6				49.8							5.0	46.5	0.4	0.2	1.6	38.0
Benzo[g,h,i]perylene	8.2	13.7	31.3	265.0			43.9	253.0	4.3	4.6	51.7	282.3	5.5	9.0	33.2	249.7	4.8	7.0	44.5	317.2
*Chrysene+Triphenylene																	3.5	6.0	42.5	486.4
*Benzo[b.j,k]fluoranthene					20.7	13.8	89.7	826.7					13.1	13.5	58.7	687.7	7.9	7.5	62.4	774.0

REPORTED RESULT	APA-LRA				CHMU				ISSeP				FMI			
ng	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	5.0	7.3	19.7	74.3	9.7	11.1	18.7	81.3	100.5	90.5	95.7	225.0	2.6	5.0	13.5	91.4
Anthracene			2.0	22.0	0.4	0.8	1.6	12.0	62.3	46.4	56.1	116.8	0.3	0.7	2.4	21.1
Fluoranthene	4.0	7.3	22.0	266.3	3.7	5.4	18.2	245.7	32.3	26.7	44.3	392.8	4.2	7.5	30.2	327.0
Pyrene	6.0	10.0	33.3	364.0	2.7	5.6	25.2	212.9	37.7	31.1	57.9	418.3	4.6	11.9	39.5	315.9
Benzo[a]anthracene		3.0	19.7	370.3	3.0	2.3	18.3	268.7	8.2	5.4	27.8	417.1	2.1	2.8	26.7	353.7
Chrysene	2.0	2.0	24.0	304.0	3.5	4.4	26.2	368.9	14.2	10.9	46.2	546.2				
Benzo[b]fluoranthene	4.0	2.0	23.7	283.3					14.6	7.4	37.9	430.9				
Benzo[j]fluoranthene									12.3	5.4	27.0	306.7				
Benzo[k]fluoranthene			12.0	164.7					10.4	4.2	20.3	249.0				
Benzo[e]pyrene																
Benzo[a]pyrene	2.0	3.7	12.0	384.7	1.7	1.6	11.2	214.1	7.4	4.9	26.2	439.3	2.3	2.7	24.9	302.5
Perylene																
Indeno[1,2,3,-c,d]pyrene	5.0	3.3	22.0	309.7	1.9	2.4	14.2	213.4	11.9	5.4	25.1	285.1	3.6	3.0	24.9	267.2
Dibenzo[a,h]anthracene				22.0	0.5	0.4	2.1	27.9	8.4	3.5	12.8	93.6	0.4	0.2	2.4	33.4
Benzo[g,h,i]perylene	4.7	6.7	28.7	182.0	2.9	3.7	20.4	154.4	13.1	9.2	35.9	298.8	3.4	4.6	27.0	185.4
*Chrysene+Triphenylene													2.7	4.0	32.5	382.8
*Benzo[b.j,k]fluoranthene					4.6	3.6	35.2	392.7					6.0	5.2	47.3	523.7

REPORTED RESULT	VMM				EERC				EPA-ie				AEA/ESG			
ng	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	6.3	7.0	16.8	116.1	2.1	4.4	13.8	103.3	3.1	12.5		85.0	10.7	15.4	36.5	154.0
Anthracene	0.3	0.7	1.4	11.5	0.2	0.5	2.3	12.6		22.6		32.8				25.7
Fluoranthene	5.6	9.2	23.3	291.9	3.8	6.6	28.9	303.4	17.3	22.2		369.2	12.6	18.3	67.4	433.3
Pyrene	5.2	12.5	25.4	282.9	4.5	10.2	37.2	316.3	10.7	17.2		333.9	9.4	20.5	61.5	426.3
Benzo[a]anthracene	2.6	33.4	12.2	205.3	1.7	3.1	23.4	359.9	16.1	17.6		446.4	5.6	5.6	72.2	461.7
Chrysene	8.2	31.3	21.7	329.4	4.5	7.3	50.4	491.8	15.3	15.7		419.8	12.2	12.9	217.3	786.0
Benzo[b]fluoranthene									1.6	0.3		456.3				
Benzo[j]fluoranthene																
Benzo[k]fluoranthene										8.4		202.7	5.1		178.3	350.7
Benzo[e]pyrene													9.0	6.4	241.3	442.7
Benzo[a]pyrene	3.4	4.8	12.7	402.3	2.9	3.6	19.2	349.3		5.5		457.7	9.7	9.8	46.8	440.7
Perylene													9.1		18.0	93.8
Indeno[1,2,3,-c,d]pyrene	3.1	4.5	15.5	469.6	4.2	4.5	20.5	228.9	10.1	10.4		312.5	8.1	4.6	223.0	482.3
Dibenzo[a,h]anthracene	0.5	0.5	2.0	36.9	2.6	2.2	8.1	52.5				58.0			30.6	60.2
Benzo[g,h,i]perylene	7.0	9.6	34.8	322.8	6.4	9.2	42.8	244.0	4.1	2.1		407.8	9.7	10.5	160.7	381.3
*Chrysene+Triphenylene																
*Benzo[b.j,k]fluoranthene	10.2	13.7	55.3	865.0									36.1	11.4	750.7	1396.7

Table 9.– Expanded uncertainties reported by each laboratory

	IVL				LANUV				NERI				ABUM				ERLAP			
EXPANDED UNCERTAINTY	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	30.0	30.0	30.0	30.0									60.9	24.9	10.8	3.5	32.9	27.1	5.7	9.9
Anthracene	30.0	30.0	30.0	30.0									61.0	9.8	9.9	3.8	36.9	27.9	22.1	12.9
Fluoranthene	30.0	30.0	30.0	30.0									5.1	4.8	1.5	4.7	12.5	40.4	11.8	11.4
Pyrene	30.0	30.0	30.0	30.0									8.3	7.7	2.4	5.1	11.6	27.2	12.7	6.7
Benzo[a]anthracene			30.0	0.0	24.3	24.3	24.3	24.3					9.6	9.0	4.3	7.2	10.2	11.8	13.1	8.3
Chrysene	30.0	30.0	30.0	30.0									10.0	7.2	2.8	4.1				
Benzo[b]fluoranthene	30.0	30.0	30.0	30.0	14.8	14.8	14.8	14.8									8.0	8.7	12.2	7.9
Benzo[j]fluoranthene							13.2	13.2									6.3	12.7	13.1	8.1
Benzo[k]fluoranthene	30.0	30.0	30.0	30.0	10.5	10.5	10.5	10.5					12.2	24.2	15.0	20.7	10.5	15.5	13.8	9.0
Benzo[e]pyrene													18.7	23.1	8.0	6.3	21.0	29.8	15.2	10.7
Benzo[a]pyrene	30.0	30.0	30.0	30.0	14.5	14.5	14.5	14.5					12.4	30.6	16.1	5.7	13.5	15.1	14.9	7.8
Perylene													56.1	82.0	24.4	4.1	9.0	23.2	10.9	10.3
Indeno[1,2,3,-c,d]pyrene	30.0	30.0	30.0	30.0	9.8	9.8	9.8	9.8					42.6	44.5	15.8	7.3	9.5	11.5	15.3	8.4
Dibenzo[a,h]anthracene	30.0	30.0	30.0	30.0	21.7	21.7	21.7	21.7					53.7	41.5	15.2	11.0	14.0	42.4	27.7	15.9
Benzo[g,h,i]perylene	30.0	30.0	30.0	30.0									7.7	4.5	2.4	3.3	13.3	9.4	15.2	10.0
*Chrysene+Triphenylene													4.7	5.6	3.3	4.1	11.0	17.8	20.1	11.5
*Benzo[b.j,k]fluoranthene					13.7	13.7	13.4	11.6					34.2	62.2	4.6	5.3	4.7	6.7	7.7	5.0

	EPA-LT				AWEL				EEA				KAL				ERLAP#T			
EXPANDED UNCERTAINTY	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene									17.2	17.2	17.2	17.2					10.4	8.3	6.0	7.3
Anthracene	25.8	25.8	25.8	25.8					21.5	21.5	21.5	21.5					20.0	36.8	7.3	16.3
Fluoranthene					20.0	20.0	20.0	20.0	6.9	6.9	6.9	6.9					6.2	6.9	5.8	5.4
Pyrene					20.0	20.0	20.0	20.0	17.0	17.0	17.0	17.0					6.2	12.8	5.6	5.5
Benzo[a]anthracene	22.0	22.0	22.0	22.0			20.0	20.0	12.0	12.0	12.0	12.0			18.8	18.9	6.5	5.4	6.8	5.5
Chrysene	20.8	20.8	20.8	20.8			19.9	20.0	30.2	30.2	30.2	30.2								
Benzo[b]fluoranthene	19.3	19.3	19.3	19.3			20.1	20.1	27.6	27.6	27.6	27.6					5.5	5.2	5.8	5.4
Benzo[j]fluoranthene																	5.6	5.5	6.8	5.3
Benzo[k]fluoranthene	25.9	25.9	25.9	25.9			20.0	20.0	33.5	33.5	33.5	33.5					5.9	6.4	6.0	5.4
Benzo[e]pyrene																	13.2	14.9	11.0	9.7
Benzo[a]pyrene	26.1	26.1	26.1	26.1			20.0	20.0	28.2	28.2	28.2	28.2			22.9	22.9	7.5	7.3	11.0	8.5
Perylene																	7.4	6.7	10.4	8.7
Indeno[1,2,3,-c,d]pyrene	22.3	22.3	22.3	22.3			20.0	20.0							34.2	34.0	5.6	7.7	6.9	5.5
Dibenzo[a,h]anthracene	21.2	21.2	21.2	21.2				20.0							38.0	38.0	6.7	8.4	11.0	5.8
Benzo[g,h,i]perylene	17.3	17.3	17.3	17.3			20.0	20.0	29.0	29.0	29.0	29.0					5.4	7.1	7.8	6.1
*Chrysene+Triphenylene																	6.5	9.1	5.9	5.4
*Benzo[b.j,k]fluoranthene					20.0		19.9	2.0					32.8	32.7	33.0	33.0	4.0	3.4	3.7	3.3

	APA-LRA				CHMU				ISSeP				FMI			
EXPANDED UNCERTAINTY	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene					37.3	37.3	37.3	37.3	23.3	23.3	23.3	23.3	85.0	85.0	85.0	25.0
Anthracene					7.7	7.7	7.7	7.7	28.9	28.9	28.9	28.9	54.0	54.0	54.0	47.0
Fluoranthene					32.8	32.8	32.8	32.8	19.1	19.1	19.1	19.1	35.0	35.0	35.0	16.0
Pyrene					14.7	14.7	14.7	14.7	21.4	21.4	21.4	21.4	73.0	73.0	73.0	19.0
Benzo[a]anthracene					23.9	23.9	23.9	23.9	28.1	28.0	28.1	28.1	40.0	40.0	40.0	28.0
Chrysene					14.9	14.9	14.9	14.9	24.0	23.9	23.9	23.9				
Benzo[b]fluoranthene									25.6	25.7	25.6	25.6				
Benzo[j]fluoranthene									18.8	17.1	16.7	18.1				
Benzo[k]fluoranthene									26.7	29.2	29.9	27.7				
Benzo[e]pyrene																
Benzo[a]pyrene					20.3	20.3	20.3	20.3	27.4	27.3	26.3	27.4	25.0	25.0	25.0	11.0
Perylene																
Indeno[1,2,3,-c,d]pyrene					19.8	19.8	19.8	19.8	25.1	25.1	25.1	25.1	53.0	53.0	53.0	48.0
Dibenzo[a,h]anthracene					9.7	9.7	9.7	9.7	28.2	28.2	26.0	28.2	40.0	40.0	40.0	26.0
Benzo[g,h,i]perylene					19.9	19.9	19.9	19.9	26.3	26.3	26.3	26.3	47.0	47.0	47.0	48.0
*Chrysene+Triphenylene													30.0	30.0	30.0	14.0
*Benzo[b.j,k]fluoranthene					23.4	23.4	23.4	23.4					21.0	21.0	21.0	19.0

	VMM				EERC				EPA-ie				AEA/ESG			
EXPANDED UNCERTAINTY	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	14.0	14.0	14.0	14.0	12.0	12.0	12.3	11.6					20.0	20.0	20.0	20.0
Anthracene	21.0	21.0	21.0	21.0	103.0	102.6	102.7	103.4								20.0
Fluoranthene	14.7	14.7	14.7	14.7	5.0	5.0	4.8	4.9					20.0	20.0	20.0	20.0
Pyrene	15.8	15.8	15.8	15.8	8.0	8.0	8.1	7.9					20.0	20.0	20.0	20.0
Benzo[a]anthracene	16.4	16.4	16.4	16.4	11.9	11.9	11.9	11.9					20.0	20.1	19.9	20.0
Chrysene	16.8	16.8	16.8	16.8	13.9	13.7	14.1	14.0					20.0	20.0	20.0	20.0
Benzo[b]fluoranthene																
Benzo[j]fluoranthene																
Benzo[k]fluoranthene													20.1		20.0	20.0
Benzo[e]pyrene													20.0	20.0	20.0	20.0
Benzo[a]pyrene	18.4	18.4	18.4	18.4	48.2	47.1	46.8	46.9					20.0	20.0	20.0	20.0
Perylene													20.0		20.0	20.0
Indeno[1,2,3,-c,d]pyrene	14.9	14.9	14.9	14.9	21.0	21.0	20.5	21.8					20.0	20.0	20.0	20.0
Dibenzo[a,h]anthracene	16.7	16.7	16.7	16.7	207.3	205.8	209.2	207.5							20.0	19.9
Benzo[g,h,i]perylene	19.1	19.1	19.1	19.1	34.6	34.7	35.0	34.8					20.0	20.0	20.0	20.0
*Chrysene+Triphenylene																
*Benzo[b.j,k]fluoranthene	20.8	20.8	20.8	20.8									20.0	20.0	20.0	20.0

Table 10.– bias with respect to the reference value

	IVL				LANUV				NERI				ABUM				ERLAP			
bias %	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	-32.3	-28.8	-25.1	-13.3									-64.3	-37.7	-34.1	-0.1	70.8	32.8	9.9	26.5
Anthracene	-53.8	-27.2	-32.9	-25.0									-64.6	-31.1	-41.7	-8.4	-17.3	-13.2	-9.8	-2.3
Fluoranthene	-5.9	-14.7	-11.0	-13.5									-26.2	-24.1	-21.3	1.3	13.9	3.4	6.9	11.8
Pyrene	-19.2	-12.0	-13.2	-12.1									-30.8	-17.2	-22.9	-3.6	7.1	16.7	3.1	9.8
Benzo[a]anthracene	-38.9		-15.7	-20.4	-34.2	-31.0	-8.3	-0.8	135.0	35.2	89.9	62.0	-24.0	-46.5	-17.8	2.1	-2.1	-21.3	10.9	0.9
Chrysene	-43.7	-53.1	0.1	-7.7									-45.3	-70.0	-11.5	10.9				
Benzo[b]fluoranthene	-6.7	18.4	0.8	-8.7	-11.4	52.9	-4.5	-0.5									9.8	35.4	1.2	16.2
Benzo[j]fluoranthene							11.8	19.2									2.3	2.2	-3.3	-5.4
Benzo[k]fluoranthene	-12.7	-14.4	-8.6	-19.5	-26.9	7.7	-15.1	1.8					-32.2	-27.0	-29.2	-9.0	27.0	40.8	18.5	24.5
Benzo[e]pyrene									82.5	65.6	21.2	49.5	-47.8	-26.1	-34.4	3.0	-32.0	15.1	-7.3	-1.3
Benzo[a]pyrene	-5.3	-24.6	-0.8	-12.1	-11.1	-9.9	-2.1	12.4	394.6	40.2	90.0	81.8	-16.1	-26.8	-22.4	5.1	-2.4	-8.4	20.2	2.1
Perylene									300.1	23.9	25.6	61.5	-34.1	-19.2	-46.6	-5.2	43.2	9.7	-10.4	4.5
Indeno[1,2,3,-c,d]pyrene	5.3	-20.9	8.1	-17.2	-20.1	22.8	9.9	22.2	238.7	34.7	87.8	96.2	-16.7	-8.0	-18.0	-3.0	14.4	3.0	13.1	0.8
Dibenzo[a,h]anthracene	-43.3	-53.7	15.3	39.1	-70.2	-67.2	-35.6	7.8	63.3	-40.1	69.5	93.6	-58.0	-59.0	-17.8	-4.8	-60.5	-78.8	-28.6	11.5
Benzo[g,h,i]perylene	12.2	-5.3	13.0	14.2					128.8	31.0	46.4	58.9	-27.9	-25.4	-18.2	9.7	-9.1	-11.6	-2.3	-6.1
*Chrysene+Triphenylene									106.3	70.9	61.0	48.8	2.5	-9.6	-5.6	10.9	31.5	41.1	11.0	-0.8
*Benzo[b.j,k]fluoranthene					-30.5	-21.5	4.1	19.7	319.9	69.6	132.1	109.9	-19.4	-30.8	-26.8	-9.5	20.9	-0.6	11.6	11.0

	EPA-LT				AWEL				EEA				KAL				ERLAP#T			
bias %	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene									2524.6	254.5	275.0	100.9	1.9	13.1	-4.6	4.3	12.3	29.6	47.7	2.5
Anthracene	112.9	176.0	41.9	22.8				4.2	3612.6	1418.4	789.3	68.5	439.7		44.1	15.5	45.4	-56.3	81.6	-22.7
Fluoranthene					434.4	171.5	69.3	-1.6	719.0	178.9	158.5	59.4	-2.8	-1.4	-9.2	0.7	9.4	13.4	22.4	9.8
Pyrene					533.9	164.9	75.3	-6.2	544.4	155.4	148.8	56.5	-14.5	-3.2	-13.5	-3.0	10.7	14.1	22.3	9.5
Benzo[a]anthracene	65.4	497.0	81.3	1.6			35.6	3.8	172.4	-21.5	84.6	55.5			-6.9	-2.4	-19.0	-27.6	23.9	-0.7
Chrysene	-1.3	85.4	15.7	1.9			65.1	21.6	72.9	-38.8	95.0	60.4								
Benzo[b]fluoranthene	53.6	500.3	36.2	-1.9	246.3		129.0	84.2	181.9	212.1	202.9	142.5					-2.5	24.5	-2.6	10.5
Benzo[j]fluoranthene																	-2.3	-2.2	-8.6	-13.8
Benzo[k]fluoranthene	57.7	492.8	45.3	-3.0			16.2	9.1	2.6	42.2	76.6	-2.5					-12.9	-7.2	11.1	10.0
Benzo[e]pyrene																	-64.5	-54.7	20.6	-1.7
Benzo[a]pyrene	37.6	341.7	56.3	7.7			39.9	5.5	64.5	1.5	36.1	-1.3			-7.7	-9.7	-6.6	-12.8	84.7	6.1
Perylene																	-9.1	-14.4	31.5	0.7
Indeno[1,2,3,-c,d]pyrene	75.8	365.1	25.1	-0.1			29.7	2.4							6.3	8.2	-9.3	-21.4	-0.2	-6.0
Dibenzo[a,h]anthracene	119.1	259.8	53.2	11.2				14.0							52.2	6.4	-69.9	-80.6	-52.6	-13.0
Benzo[g,h,i]perylene	50.3	78.7	-8.7	2.4			28.3	-2.3	-21.6	-39.8	51.1	9.1	1.0	16.9	-2.9	-3.6	-12.2	-8.8	29.9	22.6
*Chrysene+Triphenylene																	-6.6	1.0	10.2	6.3
*Benzo[b.j,k]fluoranthene					138.5	56.8	52.6	9.3					50.7	52.6	-0.1	-9.1	-8.6	-14.9	6.2	2.4

	APA-LRA				CHMU				ISSeP				FMI			
bias %	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	29.4	20.8	27.3	-26.7	149.8	82.9	21.1	-19.8	2499.8	1390.5	519.5	122.0	-33.5	-17.9	-12.5	-9.9
Anthracene			-17.3	37.6	-22.6	13.4	-35.5	-24.8	11113.1	6162.9	2219.6	630.5	-46.9	-2.8	-2.4	31.9
Fluoranthene	-5.3	2.1	-13.1	-12.6	-12.6	-24.9	-28.2	-19.4	665.2	272.2	74.8	28.9	0.3	4.8	19.4	7.3
Pyrene	31.8	-9.8	4.4	13.7	-41.8	-49.4	-21.1	-33.5	728.7	180.7	81.3	30.6	1.1	7.1	23.8	-1.3
Benzo[a]anthracene		-19.9	-11.5	10.2	34.5	-39.9	-17.7	-20.0	272.2	44.7	25.2	24.1	-6.1	-25.5	19.9	5.3
Chrysene	-60.9	-83.3	-24.7	-20.3	-30.8	-63.7	-17.8	-3.3	177.3	-9.5	44.8	43.2				
Benzo[b]fluoranthene	-20.4	-40.1	-25.0	-15.5					190.9	121.8	20.2	28.4				
Benzo[j]fluoranthene									463.0	197.9	65.0	37.1				
Benzo[k]fluoranthene			-20.2	-13.9					377.4	146.4	35.1	30.2				
Benzo[e]pyrene																
Benzo[a]pyrene	-30.5	0.2	-48.3	3.1	-40.2	-57.5	-51.8	-42.6	157.4	33.9	12.6	17.8	-20.8	-26.6	7.2	-18.9
Perylene																
Indeno[1,2,3,-c,d]pyrene	18.1	-19.8	-8.2	3.7	-55.3	-42.6	-40.6	-28.6	181.7	29.4	4.5	-4.6	-13.9	-28.8	4.0	-10.6
Dibenzo[a,h]anthracene				-49.7	-63.2	-66.3	-35.6	-36.2	555.4	232.3	288.1	114.0	-70.4	-78.2	-26.3	-23.7
Benzo[g,h,i]perylene	-14.1	-13.2	-16.3	-29.7	-47.1	-51.8	-40.3	-40.4	141.7	19.6	4.9	15.4	-37.7	-40.2	-21.1	-28.4
*Chrysene+Triphenylene													-27.4	-32.5	-15.6	-16.4
*Benzo[b.j,k]fluoranthene					-46.8	-59.1	-40.1	-48.1					-30.5	-40.6	-19.6	-30.7

	VMM				EERC				EPA-ie				AEA/ESG			
bias %	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	61.9	15.0	8.5	14.6	-46.2	-27.0	-10.7	2.0	-20.5	106.1		-16.1	176.9	153.7	136.1	52.0
Anthracene	-46.0	-1.4	-43.0	-28.0	-59.8	-30.2	-3.4	-21.4		2954.8		105.3				60.7
Fluoranthene	33.6	28.1	-8.2	-4.3	-9.6	-8.2	14.1	-0.5	309.6	209.1		21.1	197.6	155.3	166.0	42.1
Pyrene	14.7	12.3	-20.6	-11.7	-1.0	-8.0	16.6	-1.2	135.3	55.1		4.3	105.4	84.6	92.4	33.1
Benzo[a]anthracene	20.1	792.4	-45.3	-38.9	-23.7	-17.1	5.4	7.1	633.5	369.7		32.8	154.7	50.4	225.0	37.4
Chrysene	60.6	160.5	-31.8	-13.6	-13.0	-39.4	58.0	28.9	199.8	30.4		10.1	138.4	7.1	581.9	106.1
Benzo[b]fluoranthene									-68.2	-91.1		36.0				
Benzo[j]fluoranthene																
Benzo[k]fluoranthene										393.6		6.0	136.2		1086.6	83.3
Benzo[e]pyrene													61.8	65.9	606.8	80.7
Benzo[a]pyrene	16.4	30.3	-45.2	7.9	1.0	-1.4	-17.2	-6.3		50.6		22.7	237.7	166.8	101.5	18.1
Perylene													1583.5		239.8	44.2
Indeno[1,2,3,-c,d]pyrene	-27.9	8.9	-35.4	57.2	-0.8	7.5	-14.4	-23.4	138.5	149.3		4.6	91.3	10.9	830.7	61.5
Dibenzo[a,h]anthracene	-58.5	-51.4	-38.7	-15.6	98.9	106.8	147.4	20.2				32.6			832.5	37.6
Benzo[g,h,i]perylene	27.9	24.3	1.5	24.7	17.2	20.1	25.1	-5.7	-25.0	-72.7		57.5	77.7	36.4	369.3	47.3
*Chrysene+Triphenylene																
*Benzo[b.j,k]fluoranthene	17.3	55.6	-6.0	14.4									314.9	29.6	1176.7	84.7

Table 11.– En values

	IVL				LANUV				NERI				ABUM				ERLAP			
En	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	-0.7	-0.9	-0.8	-0.5									-1.4	-1.4	-1.6	0.0	1.0	0.8	0.5	1.5
Anthracene	-0.8	-0.6	-0.9	-0.8									-1.0	-0.8	-1.4	-0.4	-0.2	-0.3	-0.3	-0.1
Fluoranthene	-0.2	-0.5	-0.4	-0.5									-2.1	-1.9	-1.6	0.1	0.8	0.1	0.4	0.8
Pyrene	-0.7	-0.4	-0.4	-0.4									-1.8	-1.4	-1.5	-0.4	0.4	0.5	0.2	0.9
Benzo[a]anthracene			-0.5	-4.0	-1.0	-0.8	-0.3	0.0					-0.8	-1.3	-1.1	0.2	-0.1	-0.6	0.5	0.1
Chrysene	-0.7	-0.5	0.0	-0.2									-0.8	-0.7	-0.4	0.6				
Benzo[b]fluoranthene	-0.2	0.3	0.0	-0.3	-0.5	0.9	-0.2	0.0									0.5	0.6	0.1	1.1
Benzo[j]fluoranthene							0.6	0.7									0.3	0.2	-0.2	-0.2
Benzo[k]fluoranthene	-0.3	-0.4	-0.2	-0.7	-0.7	0.2	-0.6	0.1					-0.9	-0.8	-1.1	-0.4	0.7	1.1	0.6	1.4
Benzo[e]pyrene													-0.6	-0.4	-1.0	0.4	-0.4	0.2	-0.2	-0.1
Benzo[a]pyrene	-0.2	-0.8	0.0	-0.4	-0.5	-0.4	-0.1	0.7					-0.8	-0.9	-0.8	0.5	-0.1	-0.4	0.6	0.2
Perylene													-0.5	-0.3	-1.0	-0.6	0.7	0.3	-0.2	0.4
Indeno[1,2,3,-c,d]pyrene	0.2	-0.7	0.2	-0.6	-1.2	1.1	0.6	1.4					-0.4	-0.2	-1.0	-0.2	0.8	0.1	0.6	0.1
Dibenzo[a,h]anthracene	-0.6	-0.6	0.3	0.9	-1.1	-0.8	-0.9	0.3					-0.8	-0.7	-0.5	-0.3	-0.9	-0.9	-0.7	0.5
Benzo[g,h,i]perylene	0.3	-0.2	0.4	0.4									-1.4	-1.2	-1.3	0.6	-0.4	-0.5	-0.1	-0.3
*Chrysene+Triphenylene													0.1	-0.2	-0.3	0.7	0.9	0.9	0.4	0.0
*Benzo[b.j,k]fluoranthene					-1.0	-0.6	0.2	0.9					-0.5	-0.5	-1.7	-0.6	0.7	0.0	0.6	0.7

	EPA-LT				AWEL				EEA				KAL				ERLAP#T			
En	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene									5.6	3.9	4.1	2.7					0.3	1.2	2.2	0.2
Anthracene	1.3	2.1	0.9	0.6					4.5	4.3	4.1	1.7					0.6	-1.3	2.5	-1.0
Fluoranthene					4.0	3.1	1.9	-0.1	12.4	7.8	7.1	4.4					0.7	0.9	1.5	1.0
Pyrene					4.2	3.1	2.0	-0.3	4.9	3.5	3.3	2.0					0.6	0.8	1.3	1.0
Benzo[a]anthracene	1.4	3.7	1.9	0.1			1.1	0.2	3.9	-0.6	3.1	2.9			-0.3	-0.1	-0.6	-0.8	1.3	-0.1
Chrysene	0.0	0.8	0.4	0.1			1.4	0.7	0.9	-0.4	1.4	1.2								
Benzo[b]fluoranthene	1.5	3.9	1.1	-0.1			2.6	2.2	2.3	2.1	2.4	2.1					-0.1	0.4	-0.1	0.8
Benzo[j]fluoranthene																	-0.3	-0.3	-0.5	-0.5
Benzo[k]fluoranthene	1.1	3.2	1.0	-0.1			0.5	0.4	0.1	0.8	1.2	-0.1					-0.4	-0.2	0.4	0.7
Benzo[e]pyrene																	-0.9	-0.8	0.6	-0.2
Benzo[a]pyrene	0.9	2.9	1.2	0.3			1.0	0.2	1.3	0.0	0.8	0.0			-0.2	-0.4	-0.4	-0.6	2.5	0.5
Perylene																	-0.2	-0.6	0.7	0.1
Indeno[1,2,3,-c,d]pyrene	1.8	3.5	0.8	0.0			1.0	0.1							0.2	0.2	-0.6	-1.2	0.0	-0.5
Dibenzo[a,h]anthracene	1.5	2.2	1.1	0.4				0.5							0.8	0.1	-1.1	-0.9	-1.4	-0.8
Benzo[g,h,i]perylene	1.5	2.1	-0.4	0.1			1.0	-0.1	-0.7	-1.5	1.1	0.3					-0.6	-0.4	1.7	1.4
*Chrysene+Triphenylene																	-0.2	0.0	0.6	0.4
*Benzo[b.j,k]fluoranthene					2.5		1.5	0.6					0.9	0.8	0.0	-0.3	-0.3	-0.4	0.4	0.1

	APA-LRA				CHMU				ISSeP				FMI			
En	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene					1.5	1.2	0.4	-0.6	4.1	4.0	3.6	2.3	-0.5	-0.2	-0.2	-0.4
Anthracene					-0.4	0.3	-1.2	-1.2	3.4	3.4	3.3	3.0	-0.7	0.0	0.0	0.5
Fluoranthene					-0.4	-0.9	-1.0	-0.7	4.5	3.8	2.1	1.1	0.0	0.1	0.4	0.4
Pyrene					-2.3	-3.8	-1.1	-2.7	4.1	3.0	2.0	1.1	0.0	0.1	0.3	-0.1
Benzo[a]anthracene					0.8	-1.0	-0.7	-1.0	2.5	0.8	0.7	0.7	-0.1	-0.5	0.4	0.2
Chrysene					-0.5	-0.6	-0.5	-0.1	2.0	-0.1	1.0	1.1				
Benzo[b]fluoranthene									2.5	1.5	0.6	0.8				
Benzo[j]fluoranthene									4.4	3.9	2.1	1.1				
Benzo[k]fluoranthene									2.8	1.9	0.7	0.8				
Benzo[e]pyrene																
Benzo[a]pyrene					-1.9	-2.7	-1.8	-3.1	2.2	0.8	0.3	0.5	-0.8	-1.0	0.2	-1.7
Perylene																
Indeno[1,2,3,-c,d]pyrene					-3.3	-2.2	-2.5	-1.6	2.5	0.8	0.2	-0.2	-0.3	-0.7	0.1	-0.2
Dibenzo[a,h]anthracene					-1.0	-0.8	-1.0	-2.2	2.8	1.8	2.7	1.8	-1.0	-0.9	-0.6	-0.9
Benzo[g,h,i]perylene					-2.1	-2.3	-2.2	-2.1	2.1	0.5	0.2	0.5	-1.1	-1.2	-0.5	-0.8
*Chrysene+Triphenylene													-0.7	-0.7	-0.5	-0.9
*Benzo[b.j,k]fluoranthene					-1.5	-1.6	-1.9	-2.4					-0.9	-1.0	-0.8	-1.5

	VMM				EERC				EPA-ie				AEA/ESG			
En	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	1.4	0.5	0.3	0.7	-1.1	-1.1	-0.5	0.1					2.6	2.8	2.7	1.6
Anthracene	-0.7	0.0	-1.3	-1.1	-0.8	-0.4	0.0	-0.3								1.6
Fluoranthene	1.5	1.3	-0.4	-0.3	-0.8	-0.6	1.0	-0.1					3.3	3.0	3.0	1.4
Pyrene	0.6	0.6	-1.0	-0.7	-0.1	-0.6	0.9	-0.1					2.4	2.2	2.2	1.2
Benzo[a]anthracene	0.6	5.3	-2.5	-3.5	-0.8	-0.5	0.3	0.5					2.6	1.1	3.4	1.3
Chrysene	1.0	1.5	-1.0	-0.6	-0.2	-0.4	1.5	1.1					1.9	0.1	4.2	2.4
Benzo[b]fluoranthene																
Benzo[j]fluoranthene																
Benzo[k]fluoranthene													2.3		4.6	2.1
Benzo[e]pyrene													0.8	0.9	4.2	2.2
Benzo[a]pyrene	0.6	1.0	-1.6	0.4	0.0	0.0	-0.4	-0.1					3.4	2.9	2.1	0.7
Perylene													4.6		2.9	1.5
Indeno[1,2,3,-c,d]pyrene	-1.5	0.4	-2.4	2.2	0.0	0.3	-0.7	-1.2					2.2	0.4	4.5	1.8
Dibenzo[a,h]anthracene	-0.9	-0.6	-1.0	-0.7	0.2	0.2	0.3	0.1							4.4	1.2
Benzo[g,h,i]perylene	0.9	0.8	0.1	0.9	0.4	0.4	0.5	-0.2					1.9	1.1	3.9	1.4
*Chrysene+Triphenylene																
*Benzo[b.j,k]fluoranthene	0.5	1.1	-0.2	0.5									3.6	0.7	4.6	2.1

Table 12.– Overall expanded uncertainty.

OEU	IVL				LANUV				NERI				ABUM				ERLAP			
	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	62.3	58.8	55.1	43.3									125.2	62.6	44.9	3.6	103.7	59.9	15.6	36.4
Anthracene	83.8	57.2	62.9	55.0									125.6	40.9	51.6	12.2	54.2	41.1	31.9	15.2
Fluoranthene	35.9	44.7	41.0	43.5									31.3	28.9	22.9	6.0	26.4	43.7	18.7	23.3
Pyrene	49.2	42.0	43.2	42.1									39.1	24.9	25.3	8.7	18.7	43.9	15.8	16.5
Benzo[a]anthracene			45.7	20.4	58.5	55.3	32.6	25.1					33.6	55.5	22.1	9.3	12.3	33.1	23.9	9.3
Chrysene	73.7	83.1	30.1	37.7									55.3	77.2	14.4	15.0				
Benzo[b]fluoranthene	36.7	48.4	30.8	38.7	26.2	67.7	19.3	15.3									17.8	44.1	13.4	24.2
Benzo[j]fluoranthene							25.0	32.4									8.6	15.0	16.4	13.5
Benzo[k]fluoranthene	42.7	44.4	38.6	49.5	37.4	18.2	25.6	12.3					44.4	51.2	44.2	29.7	37.6	56.4	32.4	33.5
Benzo[e]pyrene													66.5	49.2	42.5	9.3	53.0	44.9	22.5	12.0
Benzo[a]pyrene	35.3	54.6	30.8	42.1	25.6	24.4	16.6	26.9					28.6	57.4	38.5	10.8	15.9	23.6	35.1	9.8
Perylene													90.2	101.2	71.0	9.3	52.2	32.9	21.4	14.8
Indeno[1,2,3,-c,d]pyrene	35.3	50.9	38.1	47.2	29.9	32.6	19.7	32.0					59.3	52.5	33.7	10.2	23.9	14.4	28.4	9.2
Dibenzo[a,h]anthracene	73.3	83.7	45.3	69.1	91.9	88.9	57.3	29.5					111.7	100.5	33.0	15.8	74.5	121.2	56.2	27.4
Benzo[g,h,i]perylene	42.2	35.3	43.0	44.2									35.5	30.0	20.6	13.0	22.4	21.0	17.5	16.1
*Chrysene+Triphenylene													7.2	15.2	8.9	14.9	42.5	58.9	31.1	12.3
*Benzo[b.j,k]fluoranthene					44.2	35.1	17.6	31.3					53.6	93.0	31.4	14.8	25.6	7.3	19.3	16.0

OEU	EPA-LT				AWEL				EEA				KAL				ERLAP#T			
	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene									2541.8	271.7	292.2	118.1					22.7	38.0	53.6	9.7
Anthracene	138.7	201.7	67.7	48.5					3634.1	1439.9	810.8	90.0					65.3	93.1	88.9	38.9
Fluoranthene					454.5	191.5	89.3	21.6	725.9	185.9	165.4	66.3					15.5	20.3	28.1	15.2
Pyrene					553.9	184.9	95.3	26.2	561.4	172.4	165.7	73.5					16.9	26.8	27.9	15.0
Benzo[a]anthracene	87.4	519.0	103.3	23.5			55.6	23.8	184.4	33.6	96.7	67.6			25.7	21.3	25.5	33.1	30.7	6.2
Chrysene	22.1	106.2	36.5	22.7			85.1	41.6	103.2	69.1	125.2	90.6								
Benzo[b]fluoranthene	72.9	519.6	55.6	21.3			149.0	104.3	209.5	239.7	230.5	170.1					8.0	29.7	8.4	15.9
Benzo[j]fluoranthene																	7.9	7.7	15.4	19.1
Benzo[k]fluoranthene	83.6	518.7	71.1	28.8			36.2	29.1	36.1	75.6	110.0	35.9					18.9	13.6	17.1	15.4
Benzo[e]pyrene																	77.7	69.5	31.6	11.4
Benzo[a]pyrene	63.7	367.8	82.5	33.8			59.9	25.4	92.7	29.7	64.2	29.4			30.6	32.6	14.2	20.1	95.6	14.6
Perylene																	16.4	21.1	41.9	9.4
Indeno[1,2,3,-c,d]pyrene	98.1	387.5	47.4	22.5			49.6	22.4							40.4	42.2	14.9	29.1	7.1	11.5
Dibenzo[a,h]anthracene	140.3	281.0	74.4	32.3				34.0							90.2	44.5	76.6	89.1	63.5	18.7
Benzo[g,h,i]perylene	67.6	96.0	26.0	19.7			48.3	22.3	50.6	68.8	80.0	38.0					17.7	15.9	37.7	28.7
*Chrysene+Triphenylene																	13.2	10.1	16.1	11.7
*Benzo[b.j,k]fluoranthene					158.5		72.6	11.3					83.5	85.3	33.1	42.1	12.6	18.3	9.8	5.6

OEU	APA-LRA				CHMU				ISSeP				FMI			
	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene					187.1	120.2	58.5	57.1	2523.1	1413.8	542.8	145.3	118.5	102.9	97.5	34.9
Anthracene					30.4	21.2	43.3	32.6	11142.0	6191.8	2248.5	659.4	100.9	56.8	56.4	78.9
Fluoranthene					45.4	57.7	61.0	52.2	684.3	291.3	93.9	48.0	35.3	39.8	54.4	23.3
Pyrene					56.5	64.1	35.8	48.2	750.1	202.1	102.8	52.0	74.1	80.1	96.8	20.3
Benzo[a]anthracene					58.3	63.8	41.6	43.9	300.3	72.7	53.3	52.2	46.1	65.5	59.9	33.3
Chrysene					45.7	78.6	32.7	18.2	201.3	33.4	68.7	67.1				
Benzo[b]fluoranthene									216.6	147.5	45.8	54.1				
Benzo[j]fluoranthene									481.7	215.1	81.8	55.2				
Benzo[k]fluoranthene									404.1	175.5	65.0	57.9				
Benzo[e]pyrene																
Benzo[a]pyrene					60.5	77.8	72.1	62.9	184.8	61.2	39.0	45.2	45.8	51.6	32.2	29.9
Perylene																
Indeno[1,2,3,-c,d]pyrene					75.1	62.3	60.3	48.3	206.8	54.5	29.7	29.7	66.9	81.8	57.0	58.6
Dibenzo[a,h]anthracene					72.9	76.0	45.3	46.0	583.7	260.5	314.1	142.2	110.4	118.2	66.3	49.7
Benzo[g,h,i]perylene					66.9	71.7	60.1	60.2	168.0	45.9	31.2	41.7	84.7	87.2	68.1	76.4
*Chrysene+Triphenylene													57.4	62.5	45.6	30.4
*Benzo[b.j,k]fluoranthene					70.2	82.5	63.6	71.5					51.5	61.6	40.6	49.7

OEU	VMM				EERC				EPA-ie				AEA/ESG			
	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	75.9	29.0	22.5	28.6	58.2	39.0	23.0	13.6					196.9	173.7	156.1	72.0
Anthracene	67.0	22.4	64.0	49.0	162.8	132.8	106.1	124.9								80.7
Fluoranthene	48.3	42.8	22.9	19.0	14.6	13.2	19.0	5.4					217.6	175.3	186.1	62.1
Pyrene	30.5	28.1	36.4	27.5	8.9	16.1	24.6	9.1					125.4	104.6	112.4	53.1
Benzo[a]anthracene	36.5	808.8	61.7	55.3	35.7	29.0	17.4	19.1					174.7	70.4	245.0	57.4
Chrysene	77.4	177.3	48.6	30.4	26.9	53.2	72.1	42.9					158.4	27.1	601.9	126.0
Benzo[b]fluoranthene																
Benzo[j]fluoranthene																
Benzo[k]fluoranthene													156.2		1106.6	103.3
Benzo[e]pyrene													81.8	85.8	626.8	100.7
Benzo[a]pyrene	34.8	48.7	63.6	26.3	49.2	48.5	64.0	53.3					257.7	186.8	121.5	38.1
Perylene													1603.4		259.8	64.3
Indeno[1,2,3,-c,d]pyrene	42.8	23.8	50.3	72.1	21.8	28.6	34.9	45.2					111.3	30.9	850.7	81.5
Dibenzo[a,h]anthracene	75.2	68.1	55.4	32.3	306.2	312.6	356.6	227.6							852.5	57.6
Benzo[g,h,i]perylene	47.0	43.4	20.6	43.8	51.7	54.8	60.1	40.6					97.7	56.4	389.3	67.3
*Chrysene+Triphenylene																
*Benzo[b.j,k]fluoranthene	38.1	76.4	26.8	35.2									334.9	49.6	1196.7	104.7

Table 13.– Evaluation of individual results

	IVL				LANUV				NERI				ABUM				ERLAP			
Evaluation Results	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	OK	OK	OK	OK									warning	warning	Action	OK	warning	OK	OK	warning
Anthracene	OK	OK	OK	OK									OK	OK	warning	OK	OK	OK	OK	OK
Fluoranthene	OK	OK	OK	OK									Action	Action	Action	OK	OK	OK	OK	OK
Pyrene	OK	OK	OK	OK									Action	warning	warning	OK	OK	OK	OK	OK
Benzo[a]anthracene			OK	Action	warning	OK	OK	OK					OK	warning	warning	OK	OK	OK	OK	OK
Chrysene	OK	OK	OK	OK									OK	OK	OK	OK				
Benzo[b]fluoranthene	OK	OK	OK	OK	OK	OK	OK	OK									OK	OK	OK	warning
Benzo[j]fluoranthene							OK	OK									OK	OK	OK	OK
Benzo[k]fluoranthene	OK	OK	OK	OK	OK	OK	OK	OK					OK	OK	warning	OK	OK	warning	OK	warning
Benzo[e]pyrene													OK	OK	warning	OK	OK	OK	OK	OK
Benzo[a]pyrene	OK	OK	OK	OK	OK	OK	OK	OK					OK	OK	OK	OK	OK	OK	OK	OK
Perylene													OK	OK	OK	OK	OK	OK	OK	OK
Indeno[1,2,3,-c,d]pyrene	OK	OK	OK	OK	warning	warning	OK	warning					OK	OK	warning	OK	OK	OK	OK	OK
Dibenzo[a,h]anthracene	OK	OK	OK	OK	warning	OK	OK	OK					OK	OK	OK	OK	OK	OK	OK	OK
Benzo[g,h,i]perylene	OK	OK	OK	OK									warning	warning	warning	OK	OK	OK	OK	OK
*Chrysene+Triphenylene													OK	OK	OK	OK	OK	OK	OK	OK
*Benzo[b.j,k]fluoranthene					warning	OK	OK	OK					OK	OK	Action	OK	OK	OK	OK	OK

	EPA-LT				AWEL				EEA				KAL				ERLAP#T			
Evaluation Results	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene									Action	Action	Action	Action					OK	warning	Action	OK
Anthracene	warning	Action	OK	OK					Action	Action	Action	Action					OK	warning	Action	OK
Fluoranthene					Action	Action	Action	OK	Action	Action	Action	Action					OK	OK	warning	warning
Pyrene					Action	Action	Action	OK	Action	Action	Action	Action					OK	OK	warning	OK
Benzo[a]anthracene	warning	Action	Action	OK			warning	OK	Action	OK	Action	Action			OK	OK	OK	OK	warning	OK
Chrysene	OK	OK	OK	OK			warning	OK	OK	OK	warning	warning								
Benzo[b]fluoranthene	Action	Action	warning	OK			Action	Action	Action	Action	Action	Action					OK	OK	OK	OK
Benzo[j]fluoranthene																	OK	OK	OK	OK
Benzo[k]fluoranthene	warning	Action	warning	OK			OK	OK	OK	OK	warning	OK					OK	OK	OK	OK
Benzo[e]pyrene																	OK	OK	OK	OK
Benzo[a]pyrene	OK	Action	warning	OK			warning	OK	warning	OK	OK	OK			OK	OK	OK	OK	Action	OK
Perylene																	OK	OK	OK	OK
Indeno[1,2,3,-c,d]pyrene	Action	Action	OK	OK			warning	OK							OK	OK	OK	warning	OK	OK
Dibenzo[a,h]anthracene	warning	Action	warning	OK				OK							OK	OK	warning	OK	warning	OK
Benzo[g,h,i]perylene	Action	Action	OK	OK			OK	OK	OK	warning	warning	OK					OK	OK	Action	warning
*Chrysene+Triphenylene																	OK	OK	OK	OK
*Benzo[b.j,k]fluoranthene					Action		Action	OK					OK	OK	OK	OK	OK	OK	OK	OK

	APA-LRA				CHMU				ISSeP				FMI			
Evaluation Results	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene					warning	warning	OK	OK	Action	Action	Action	Action	OK	OK	OK	OK
Anthracene					OK	OK	warning	warning	Action	Action	Action	Action	OK	OK	OK	OK
Fluoranthene					OK	OK	warning	OK	Action	Action	Action	warning	OK	OK	OK	OK
Pyrene					Action	Action	warning	Action	Action	Action	Action	warning	OK	OK	OK	OK
Benzo[a]anthracene					OK	warning	OK	warning	Action	OK	OK	OK	OK	OK	OK	OK
Chrysene					OK	OK	OK	OK	Action	OK	OK	warning				
Benzo[b]fluoranthene									Action	Action	OK	OK				
Benzo[j]fluoranthene									Action	Action	Action	warning				
Benzo[k]fluoranthene									Action	Action	OK	OK				
Benzo[e]pyrene																
Benzo[a]pyrene					Action	Action	Action	Action	Action	OK	OK	OK	OK	warning	OK	Action
Perylene																
Indeno[1,2,3,-c,d]pyrene					Action	Action	Action	Action	Action	OK	OK	OK	OK	OK	OK	OK
Dibenzo[a,h]anthracene					OK	OK	OK	Action	Action	Action	Action	Action	warning	OK	OK	OK
Benzo[g,h,i]perylene					Action	Action	Action	Action	Action	OK	OK	OK	warning	warning	OK	OK
*Chrysene+Triphenylene													OK	OK	OK	OK
*Benzo[b.j,k]fluoranthene					warning	Action	Action	Action					OK	warning	OK	warning

	VMM				EERC				EPA-ie				AEA/ESG			
Evaluation Results	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30	F21	F3	F10	F30
Phenanthrene	warning	OK	OK	OK	warning	warning	OK	OK					Action	Action	Action	Action
Anthracene	OK	OK	warning	warning	OK	OK	OK	OK								Action
Fluoranthene	warning	warning	OK	OK	OK	OK	OK	OK					Action	Action	Action	warning
Pyrene	OK	OK	warning	OK	OK	OK	OK	OK					Action	Action	Action	warning
Benzo[a]anthracene	OK	Action	Action	Action	OK	OK	OK	OK					Action	warning	Action	warning
Chrysene	OK	warning	OK	OK	OK	OK	Action	warning					Action	OK	Action	Action
Benzo[b]fluoranthene																
Benzo[j]fluoranthene																
Benzo[k]fluoranthene													Action		Action	Action
Benzo[e]pyrene													OK	OK	Action	Action
Benzo[a]pyrene	OK	OK	Action	OK	OK	OK	OK	OK					Action	Action	Action	OK
Perylene													Action		Action	warning
Indeno[1,2,3,-c,d]pyrene	Action	OK	Action	Action	OK	OK	OK	warning					Action	OK	Action	Action
Dibenzo[a,h]anthracene	OK	OK	warning	OK	OK	OK	OK	OK							Action	warning
Benzo[g,h,i]perylene	OK	OK	OK	OK	OK	OK	OK	OK					Action	warning	Action	warning
*Chrysene+Triphenylene																
*Benzo[b.j,k]fluoranthene	OK	warning	OK	OK									Action	OK	Action	Action

Conclusions

- The use of high volume samplers to organize inter-laboratory exercise as a valid method to carry out proficiency tests and evaluate overall performance of PAHs analytical methods is demonstrated.
- GC-MS is the predominant technique used in this exercise to analyses PAHs. 75 % of the participating laboratories used GC-MS as the technique for quantification, while the remaining laboratories used HPLC.
- Non statistical differences were found between results reported by HPLC-FLD and GC-MS techniques.
- Only one laboratory used thermal desorption as an extraction technique. Liquid extraction, by soxhlet, microwave, ultrasonic or ASE, was commonly used. There was no agreement on the use of a particular solvent for extraction. Laboratories used different solvents or combination of solvents to extract PAHs from the filter according to their own expertise.
- The performance of the laboratories improved for those compounds mentioned in the Directive 2004/07/EC and for which CRM can be found on the market.
- A difficulty in separating isomers of benzo-fluoranthene in the reporting of results was noted. i.e. only three laboratories provided values for benzo(j)fluoranthene.
- Separation problems between chrysene and triphenylene were also reflected on their overall expanded uncertainty, where the uncertainty for chrysene quantification was higher than that of sum of the two isomers.
- Although no particular analytical problems were highlighted benzo(e)pyrene and perylene were only reported by four laboratories.
- The influence of the blank levels on the quantification of low concentrations generated overestimations, in particular for the more volatile PAHs.
- Some laboratories systematically provided over- or under-estimations of their results for all compounds and filters.
- Repeatability, reproducibility and robustness of the method improved with increased PAH concentration level on the filter.
- Medians of overall expanded uncertainties ranged from 30 % to 50 % among filters and from 15 % to 70 % among compounds.
- As a median value for the inter-laboratory exercise the overall uncertainty for benzo(a)pyrene was lower than 50 % in all the analysed filters.
- With minor exceptions, median En values were lower than 1, which suggests realistic estimations of analytical uncertainties for the reported values.

Remarks

This report does not comment on individual laboratories results, as its purpose is to extract general conclusions on the methodology and the state of the art of PAH measurements. Each participating laboratory is encouraged to interpret its own result. To this respect, comments on analysis or possible interpretations from participating laboratories about outliers are included in the Annex – Comments from laboratories.

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ANNEX I

Protocol for PAHs sampling in high volume samplers and inter-comparison schedule

Guide to operation

Short description of the uncertainty evaluation reported by the participating laboratories

Histogram of results by compounds

Comments from laboratories

Protocol for PAHs sampling in high volume samplers and inter-comparison schedule

Laboratories participating in the PM10 sampling collection

ISCIII
Rosalía Fernandez-Patier
Spain

CHMI
Jiri Novak
Checz Republic

Material

- Andersen high volume sampler
- PM10 sampling head
- Quartz filters: Whatman: QM-A Quartz microfiber filter. 20.3x 25.4 cm (8x 10 in). Cat. No. 1851 865
- pre-cleaned tweezers.
- Petri-disks (Ø 50 mm).
- Freezer -16°C.
- Aluminium foil.

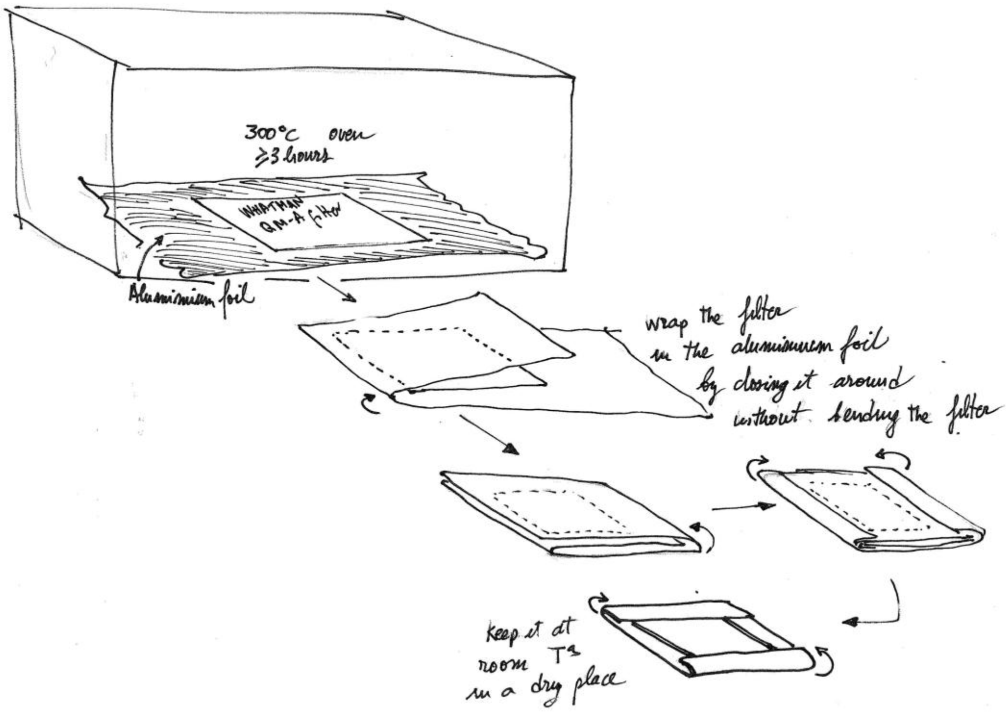
Filter conditioning and handling.

Filters are never to be handled.

Filters are always handled with pre-cleaned tweezers or appropriated gloves and should never be bent.

Tweezers are previously cleaned with hexane (GC quality) and paper tissue and dried in the oven 100 ºC before use.

The filters are heat-treated in an oven at 300 ºC for a -minimum of 3 hours.



Afterwards the filter is wrapped in aluminium foil by bending the edges of the aluminium foil (and not the filter) around the filter. The packet is left to cool to room temperature and placed in a dry environment before sampling.
A sticker over the aluminium foil should be attached indicating the date in which the filter was cleaned, the temperature used and duration of treatment

The filter is unwrapped only at the start of the sampling time. Care must be taken not to place the tweezers in contact with the sampling head.

After sampling, the filter is removed with the cleaned tweezers from the sampling head and wrapped in the same way that was described previously with the aluminium foil.

It is possible to use the same aluminium foils that were used previously if they have not been damaged and if they have been kept in a clean and dry place and free from sources of contamination.

After wrapping the filter sample, another sticker is added with the sampling information:
Date, starting and ending time and sampling location.

The filters are kept in freezers until the sampling campaign is terminated and are then sent to JRC Ispra.

Sampling frequency and location

Sampling should be preferably located in a traffic-oriented or urban background site, in accordance with the availability of additional information such as: meteorological conditions (temperature, relative humidity, and wind velocity), additional measurements as (PM10 level, ozone, and other pollutants).

The sampling will cover two different seasonal conditions, where different concentration levels are expected: summer (between June – August 2009) and winter (between November 09– January 2010).

Sampling laboratories are requested to sample at least 5 filters for each seasonal batch. Laboratories should not weigh the filters; although an indication of the overall sampled volume would be useful

It is up to the sampling laboratory to decide the date for each sampling, which could be done consecutively or spread over the corresponding seasonal period. The following information could be registered for each filter:

Cleaning date :	
Cleaning time:	
Cleaning temperature:	
Starting time and date	
Ending time and date	
Sampling volume (ambient conditions)	
Average atmospheric pressure, KPa	
Average sampling temperature, K	
Average relative humidity, %	
Average inversion layer, m	
Rainfall, mm/h	
Average ozone level (µg/m^3, at standard conditions)*	
PM10 (from parallel measurements)*	
PM2.5 (from parallel measurements)*	
Other pollutants*:	
NOx/CO/BTEX/EC/OC etc….	
Description and location of the sampling site:	

* (If available)

Expedition

Filters are wrapt and kept in the freezer until the campaign is concluded. These filters are then placed in a cardboard box without being bent. This box is wrapped and sent by ***courier express*** to JRC Ispra to the following address:

Pascual Pérez Ballesta
Via Enrico Fermi 2749 - TP-441
Joint Research Centre
21027-Ispra (VA)
Italia

A **blank filter** should be included in each batch dispatched. This blank has been cleaned, treated and wrapt in the same way as the sampled filters, with the only difference that it has not been used for sampling. The filter will be kept in the freezer from the moment that the first sampled filter is introduced until the seasonal sampling batch is completed.

Filters from the **summer period** are expected to be at the JRC Ispra in **September 2009**. Whilst filters from the **winter period** should be sent at the **beginning of February 2010** at the latest.

Distribution of material to participating laboratories

After receiving the second batch of filters. ERLAP will perform the subdivision of the filters for distribution amongst participants. ERLAP will estimate the homogeneity of the different filters and will select the best samples from each place and season to be subdivided and distributed amongst participants.

Each participant will consequently receive two sections of filters from each sampling location, corresponding to the summer and winter sampling batch.

It is expected that the filters be distributed amongst the participating laboratories **by April 2010.** The participating laboratories will have **two months** to carry out the corresponding ***analysis and report*** the results to ERLAP according to the protocol, which will be provided with the filters.

Guide to operation

This envelope (Fig. a) contains 6 PM10 filters pieces with the following characteristics:

a) two blanks filters from the sampling campaigns in Spain and the Czech Republic.
b) four loaded filters corresponding to the winter and summer campaigns in the afore-mentioned cities.

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

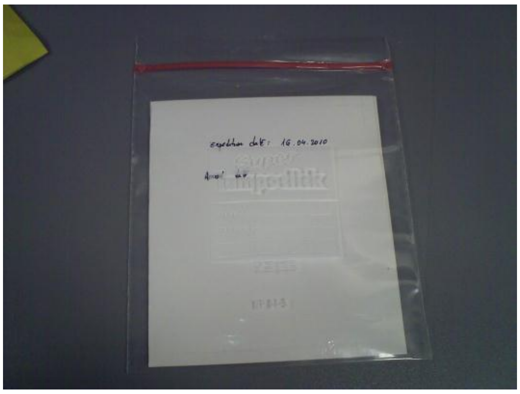


Fig. b

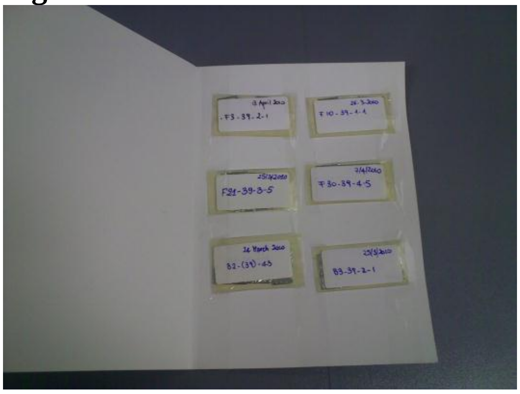


Fig. c

Approximately, the loading of the filters corresponds to the volume sampled by a typical LVS, i.e. 50 m^3, the expected BaP concentration for the loaded filters would range from 0.04 to 10 ng/m^3.

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 (F) or blanks (B).
To unwrap the filter the following material is needed: gloves, scissors and appropriate tweezers (Fig.1).
To unwrap the filters proceed carefully as described in Figures 2 to 5.

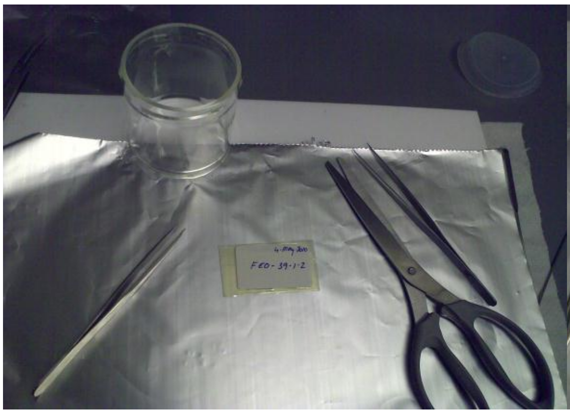


Fig. 1.- Material

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

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

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

Fig. 5.- 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.

Reporting of results

The following information will be requested from the participants (An excel file will be provided to each participant for final reporting):

- Full description of the analytical methodology
- Masses of the quantified PAH compounds on the filter (according to the list below)
- Minimum number of replicate injections for each sample: 3
- Associated expanded uncertainties for each concentration value reported.
- Description and calculations of the measurement uncertainty.

List of compounds to be quantified on the filter

Single compound	***Compounds***
1	Phenanthrene
2	Anthracene
3	Fluoranthene
4	Pyrene
5	**Benzo(a)anthracene**
6	Chrysene
7	**Benzo(b)fluoranthene**
8	**Benzo(j)fluoranthene**
9	**Benzo(k)fluoranthene**
10	Benzo(e)pyrene
11	**Benzo(a)pyrene**
12	Perylene
13	**Indeno[1,2,3-c,d)pyrene**
14	**Dibenzo(a,h)anthracene**
15	Benzo(g,h,i)perylene
Combination of isomers	***Compounds***
A	*Chrysene + triphenylene
C	***Benzo(b.j,k)fluoranthene**

In bolds priority compounds for the interlaboratory comparison

The deadline for submission of results is **August 30th, 2010,** by forwarding the afore-mentioned documents to the following e-mail address: **pascual.ballesta@jrc.ec.europa.eu.**

Ispra, 7 May 2010

Short description of the uncertainty evaluation reported by the participating laboratories

IVL

Description of the methodology- not provided
Uncertainty estimation*:* They provided an overall estimation of 30 % as expanded uncertainty for all averaged measurement values.

EPA-LT

Description of the methodology- 2 x reproducibility standard deviation was chosen for the determination of measurement uncertainty. The statistical data were taken from method validation studies.
Uncertainty estimation*:* Expanded uncertainty was defined as a percentage of the reported concentration, which ranged from 17 to 25 % depending on the compound.

APA-LRA

Description of the methodology- not provided
Uncertainty estimation*:* not provided

VMM

Description of the methodology- The calculation of the combined uncertainty is based on the results of spiked duplo field samples over several years. This procedure is used in general in our laboratory. The used formula is as follows : U = b + 2 CV, where b is bias (measured with certified reference material, and CV is the coefficient of variation. The results are given in the table (at the left) with the uncertainties in %. The table above gives the (+/-) values in pg, calculated from the average concentrations.
Uncertainty estimation*:* Expanded uncertainty was defined as a percentage of the reported concentration, which ranged from 14 to 21 % depending on the compound

LANUV

Description of the methodology- GUM Workbench Pro software was used (Version 2.3.2 beta, Metrodata GmbH).
Uncertainty estimation*:* Expanded uncertainties were different from compound to compounds ranging from 10 to 24 %.

AWEL

Description of the methodology- For each series of measurement there is a qc-sample.
The results of the qc-sample is reported on a qc-chart.
The deviation of this sample is ca. 10% for each PAH.
The uncertainty is the deviation of the qc-sample multiplied with factor 2.
This addicts a uncertainty of 20% each PAH.

Combined standard uncertainty for homogeneous samples:

$u_{rel} = \sqrt{\sum u_{i,rel}^2}$

u_{rel} = ~10% each PAH

Expanded uncertainty for each PAH:

$Urel = k \cdot u_{rel}$ (k = 2, probability 95%)

Expanded uncertainty : 20%

Uncertainty estimation*:* Expanded uncertainties were reported as 100 % of the analysed value for all compounds.

Uncertainty estimation*:* Expanded uncertainties were reported as 20 % of the analysed value for all compounds

CHMU

Description of the methodology*-* Software Effi Validation 3.0. Relative repeatability Measurements. They are weighing averages values.
Uncertainty estimation*:* Expanded uncertainties were different according to the analysed compound ranging from 9.7 to 37.3 %.

EERC

Description of the methodology*-* For the calculation of measurement uncertainty SRM 2585 (Organic Contaminants in House Dust) was analysed repeatedly. Uncertainty was calculated according to the Nord test method. Laboratory measurements repeatability standard deviation, measurements bias and standard uncertainty of certified concentration values were used to calculate the combined standard uncertainty. Values in the table above are presented as expanded combined uncertainty. Some values are quite high due to the high bias value. However, the matrix and the PAH compounds' concentration ranges in SRM 2585 are to some extent different as compared with analysed filters and so the use of these values with the determined PAH concentrations in filters may be questionable..
Uncertainty estimation*:* Expanded uncertainty ranged from approximately 5 to 100 % depending on the compound and concentration level.

NERI

Description of the methodology*-* not provided
Uncertainty estimation*:* not provided

EEA

Description of the methodology*-* The expanded uncertainty for the individual PAH compounds was calculated based on the following uncertainties: 1. uncertainty of the sub-sampling (weighting of SRM 1944 (U of balance; U of unhomogeneity)); 2. uncertainty of the Internal standard addition (U of IS concentration, U of the volume added); 3. uncertainty of the recovery (extraction, clean-up, concentration); 4. uncertainty of repeatability of the measurements; 5. Uncertainty of the GC/MS measurements (U of calibration standards, U of repeated measurements).
Uncertainty estimation*:* Expanded uncertainties ranged from approximately 7 to 34 % of the reported concentration, depending on the compound.

ISSeP

Description of the methodology Our extraction Qcs(1000 ppb) are reported on a Shewhart chart and the given uncertainty equals 2*Standard Deviation. So this uncertainty takes into account also the extraction and reconcentration phases. In routine we are analysing samples with larger sampling volumes and so larger concentrations. The SD is given in % and so to get uncertainty we have this formula: uncertainty(ng)=(2*SD(%)*mean of replicates(ng))/100

Uncertainty estimation: Expanded uncertainties ranged from approximately 16 to 30 % of the reported concentration, depending on the compound.

EPA-ei

Description of the methodology- not provided

Uncertainty estimation: not provided

ABUM

Description of the methodology- calculated with the following software: SQS 2000 - Software for statistical Quality control of analytical data

Uncertainty estimation: Reported expanded uncertainties ranged from approximately 2 to 60 % of the reported concentration, depending on the compound and concentration level.

KAL

Description of the methodology- Measurement uncertainty was assessed only for benzo(a)anthracene, benzo(a)pyrene, benzo(b,j,k)fluoranthene, indeno(1,2,3-cd)pyrene and dibenzo(ah)anthracene. For the assessment of measurement uncertainty, the data from the method validation were used. Two factors were taken into account, i.e., the precision of the method (repeatability and reproducibility) and the bias of the method. For repeatability studies, 7-8 independent replicates of real filter samples were measured in one day, by one analyst. For reproducibility studies, 11 independent replicates of real filter samples were measured in two months period, by two analysts. Repeatability and reproducibility studies were performed for three concentration ranges, i.e. at the lower end of the calibration curve (around 10 pg/uL - at the limit of quantification), in the middle of the calibration curve (around 50 pg/uL) and at the upper end of the calibration curve (around 100 pg/uL). Relative standard deviations were calculated for each concentration range. Furthermore, pooled relative standard deviations were calculated for the whole concentration range (10-100 pg/uL), thus representing standard uncertainties of repeatability and reproducibility. To assess the bias of the method, a Certified Reference Material was used. Trueness of the method was performed only for one concentration range, around 50 pg/uL (the middle of the calibration curve), by measuring 8 independent replicates in one day (for each replicate around 50 mg of CRM was weighed). Standard uncertainty of bias was calculated by taking into account standard deviation of the measured values, average of the measured values, standard uncertainty of the certified value, the certified value and recovery. In the next step, combined standard uncertainty was obtained by calculating the square root of the sum-of-the-squares of individual standard uncertainties of repeatability, reproducibility and bias. In the final step, expanded uncertainty was calculated by multiplying combined standard uncertainty with a coverage factor, i.e. k=2 (for a 95% level of confidence).

Uncertainty estimation: Reported expanded uncertainties ranged from approximately 20 to 40 % of the reported concentration, depending on the compound and concentration level.

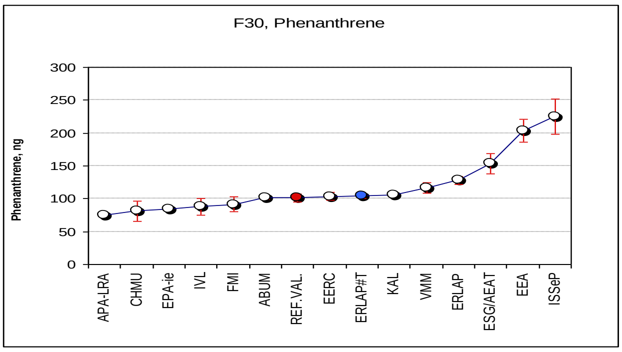
FMI

Description of the methodology- Uncertainties are calculated according to prEN15549 for B(a)P concentrations corresponding to the limit value (1 ngm-3) and low concentrations (0.1 ngm-3). Uncertainty parameters are extraction efficiency, compound mass in extracted sample, B(a)P response factor, IS concentration, response precision and mass of B(a)P in field blank. See sheet uncertainty 2.
Uncertainty estimation*:* reported expanded uncertainties from 11 to 50 % depending on concentration level and compound.

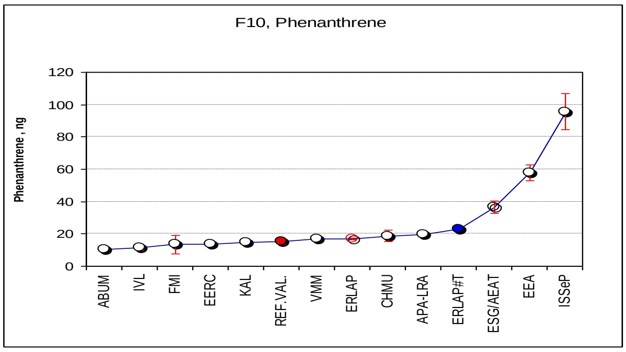
AEAT

Description of the methodology- not provided
Uncertainty estimation*:* Expanded uncertainties were 20 % of the reported concentration.

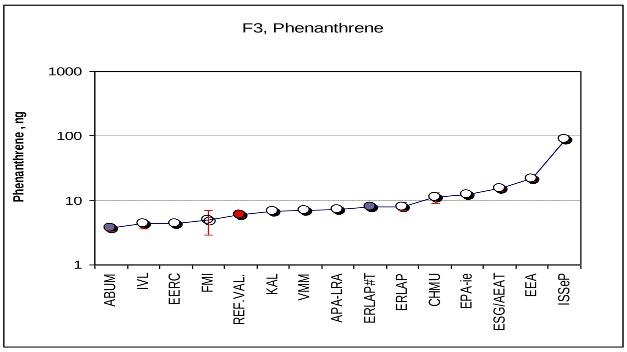
Histogram of results by compounds



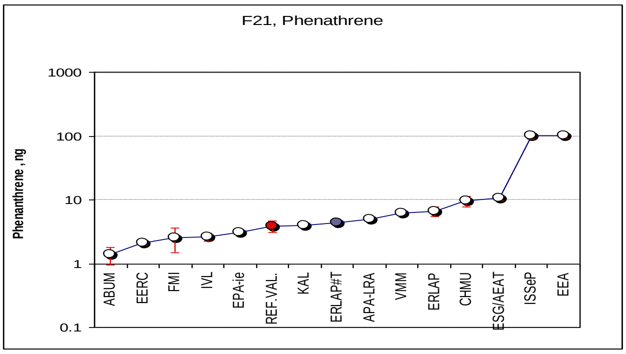
F30, Phenanthrene



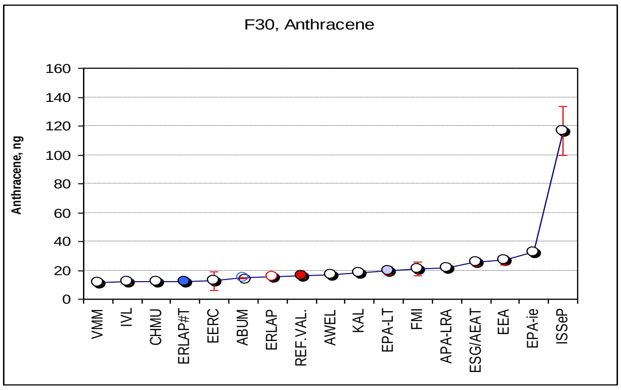
F10, Phenanthrene



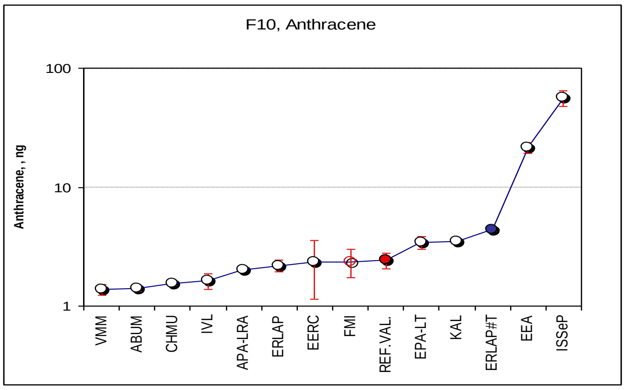
F3, Phenanthrene



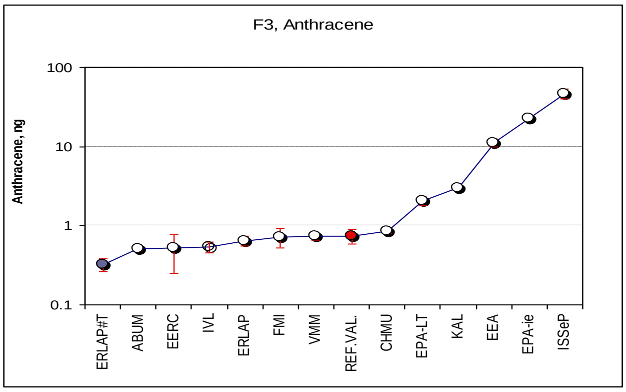
F21, Phenathrene



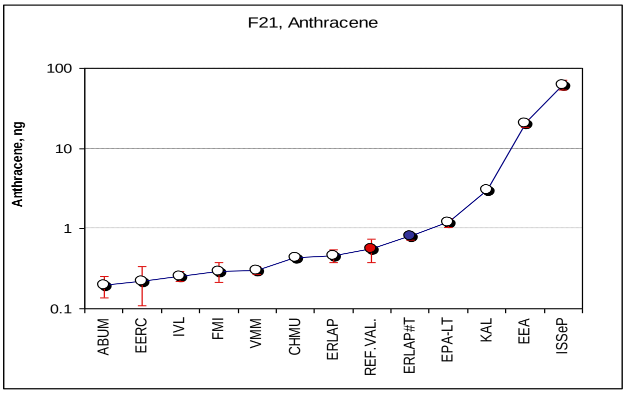
F30, Anthracene



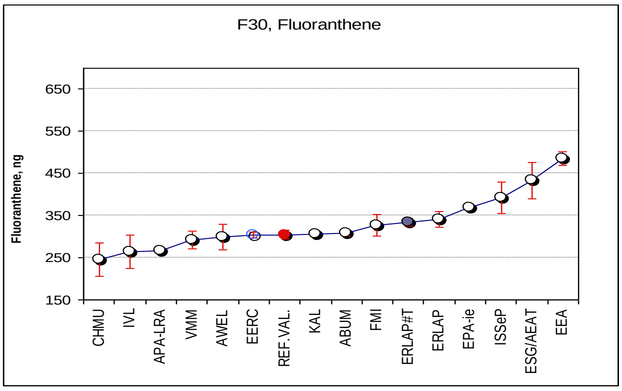
F10, Anthracene

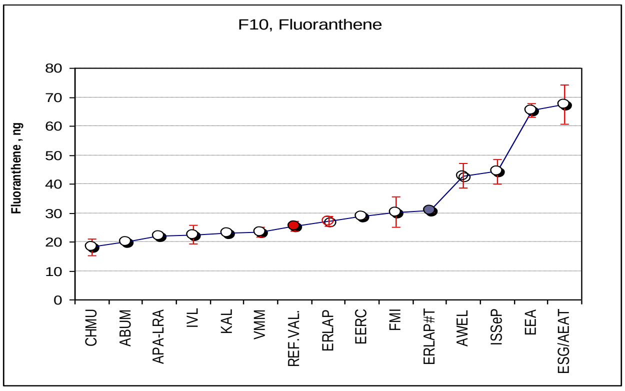


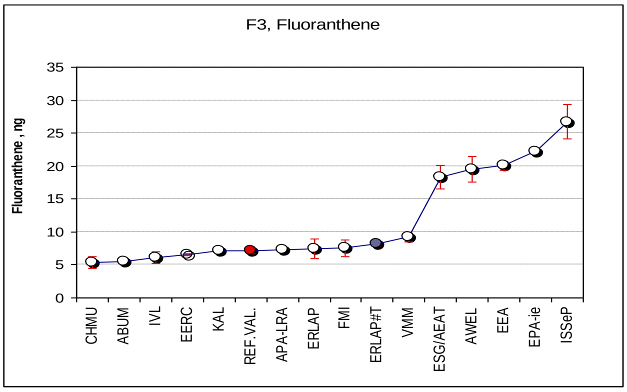
F3, Anthracene

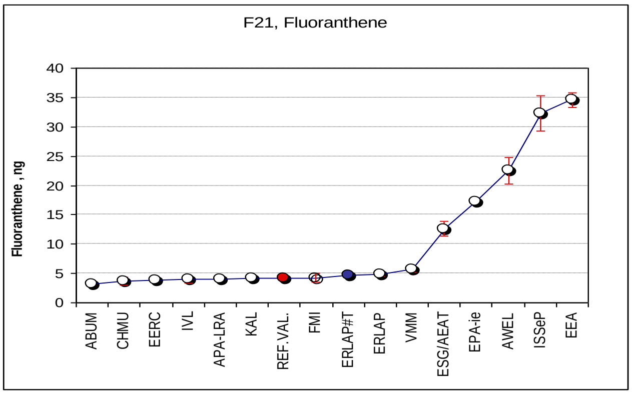


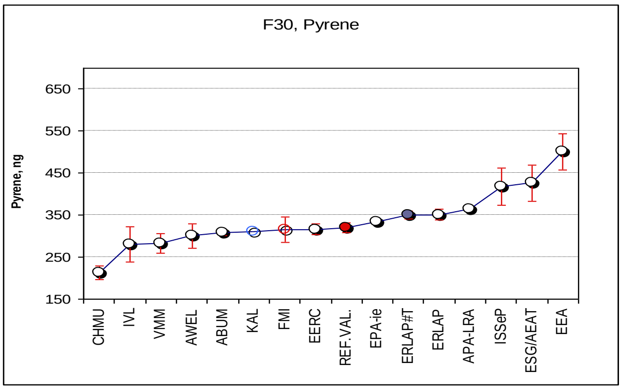
F21, Anthracene

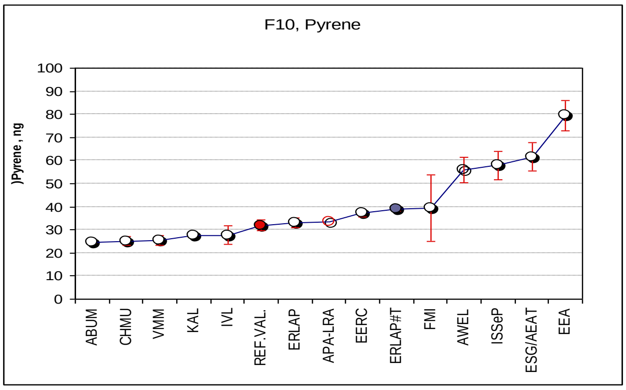

F30, Fluoranthene
Fluoranthene, ng
650
550
450
350
250
150
CHMU
IVL
APA-LRA
VMM
AWEL
EERC
REF. VAL.
KAL
ABUM
FMI
ERLAP#T
ERLAP
EPA-ie
ISSeP
ESG/AEAT
EEA

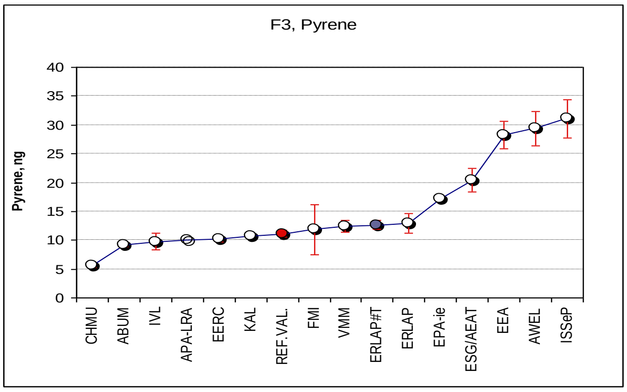

F10, Fluoranthene
Fluoranthene , ng
80
70
60
50
40
30
20
10
0
CHMU
ABUM
APA-LRA
IVL
KAL
VMM
REF. VAL.
ERLAP
EERC
FMI
ERLAP#T
AWEL
ISSeP
EEA
ESG/AEAT

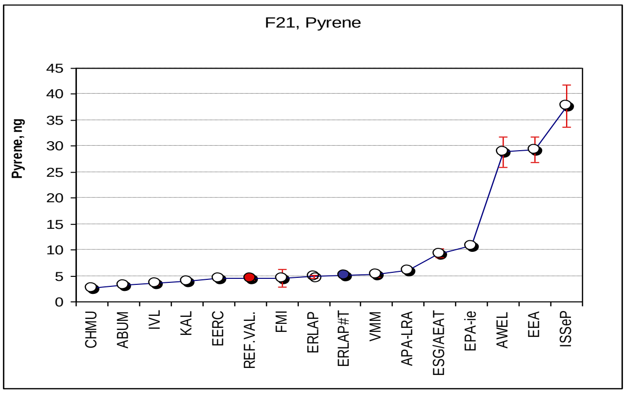

F3, Fluoranthene
Fluoranthene , ng
35
30
25
20
15
10
5
0
CHMU
ABUM
IVL
EERC
KAL
REF. VAL.
APA-LRA
ERLAP
FMI
ERLAP#T
VMM
ESG/AEAT
AWEL
EEA
EPA-ie
ISSeP

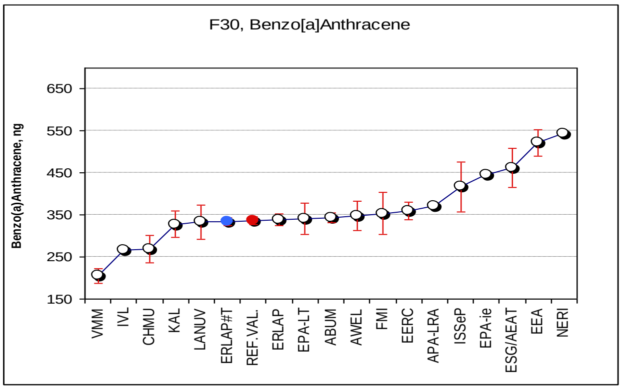

F21, Fluoranthene
Fluoranthene , ng
40
35
30
25
20
15
10
5
0
ABUM
CHMU
EERC
IVL
APA-LRA
KAL
REF. VAL.
FMI
ERLAP#T
ERLAP
VMM
ESG/AEAT
EPA-ie
AWEL
ISSeP
EEA

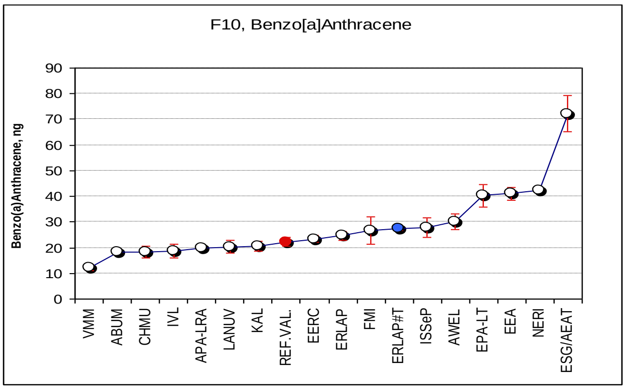

F30, Pyrene
Pyrene, ng
650
550
450
350
250
150
CHMU
IVL
VMM
AWEL
ABUM
KAL
FMI
EERC
REF. VAL.
EPA-ie
ERLAP#T
ERLAP
APA-LRA
ISSeP
ESG/AEAT
EEA

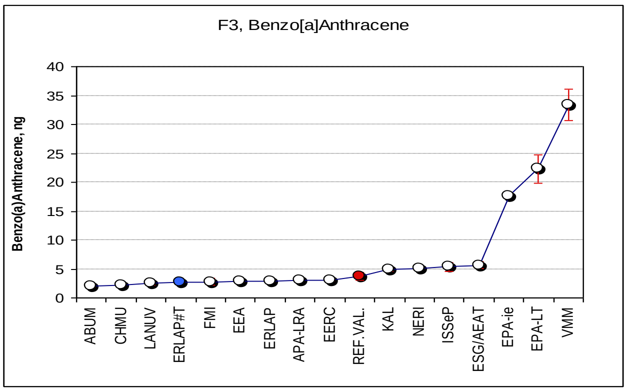

F10, Pyrene
)Pyrene , ng
100
90
80
70
60
50
40
30
20
10
0
ABUM
CHMU
VMM
KAL
IVL
REF. VAL.
ERLAP
APA-LRA
EERC
ERLAP#T
FMI
AWEL
ISSeP
ESG/AEAT
EEA

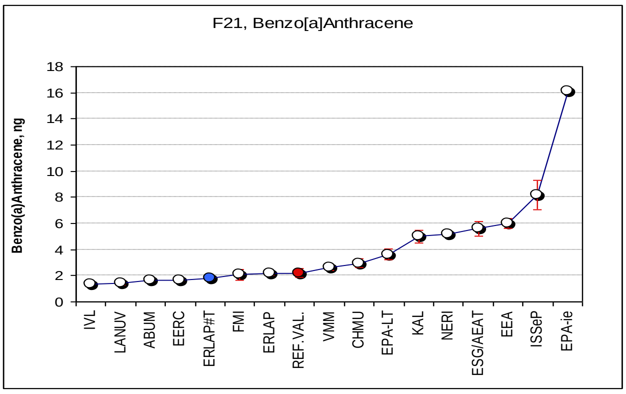

F3, Pyrene
Pyrene, ng
40
35
30
25
20
15
10
5
0
CHMU
ABUM
IVL
APA-LRA
EERC
KAL
REF. VAL.
FMI
VMM
ERLAP#T
ERLAP
EPA-ie
ESG/AEAT
EEA
AWEL
ISSeP

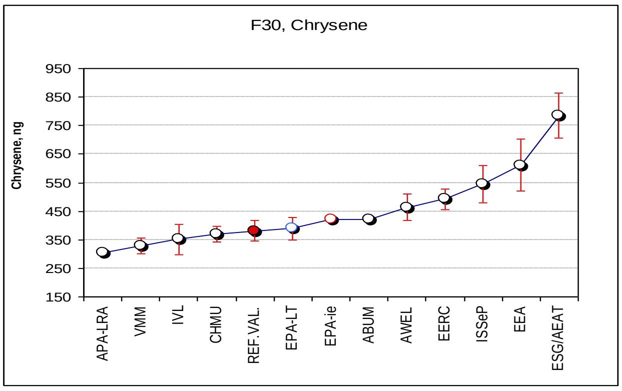

F21, Pyrene
Pyrene, ng
45
40
35
30
25
20
15
10
5
0
CHMU
ABUM
IVL
KAL
EERC
REF. VAL.
FMI
ERLAP
ERLAP#T
VMM
APA-LRA
ESG/AEAT
EPA-ie
AWEL
EEA
ISSeP

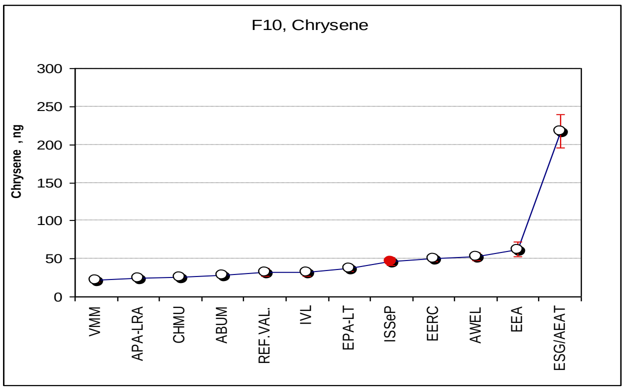

F30, Benzo[a]Anthracene

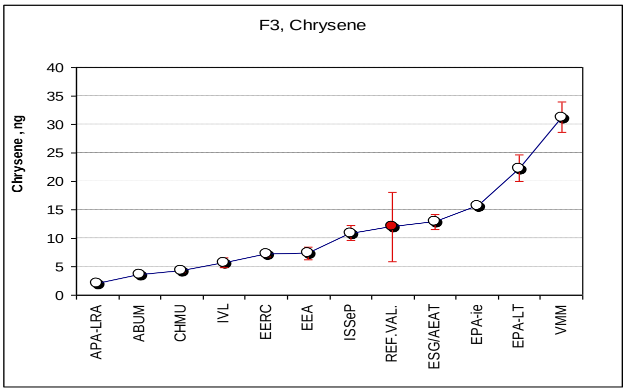

F10, Benzo[a]Anthracene

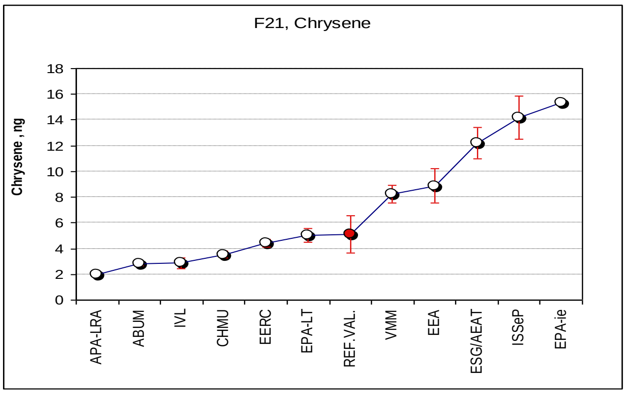

F3, Benzo[a]Anthracene

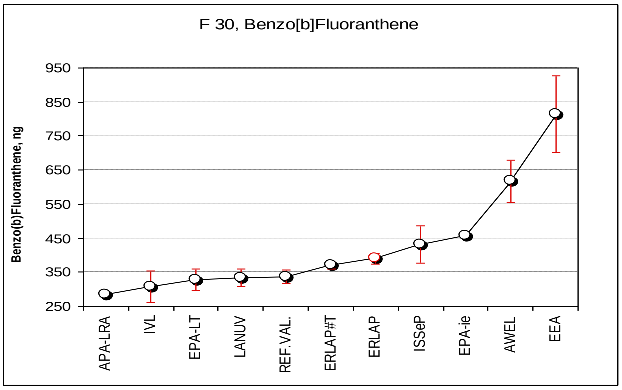

F21, Benzo[a]Anthracene

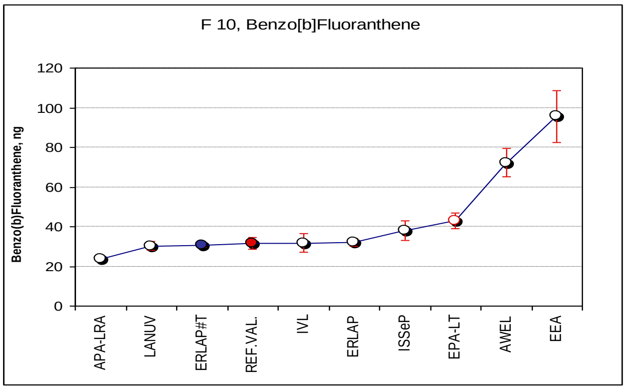

F30, Chrysene

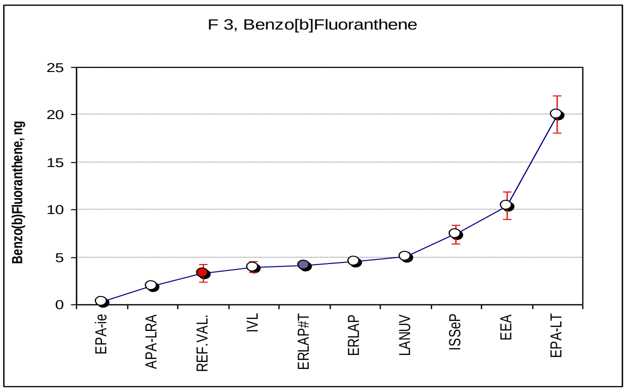

F10, Chrysene

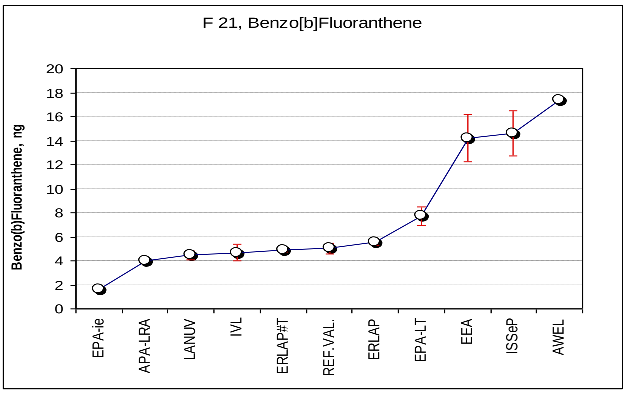

F3, Chrysene

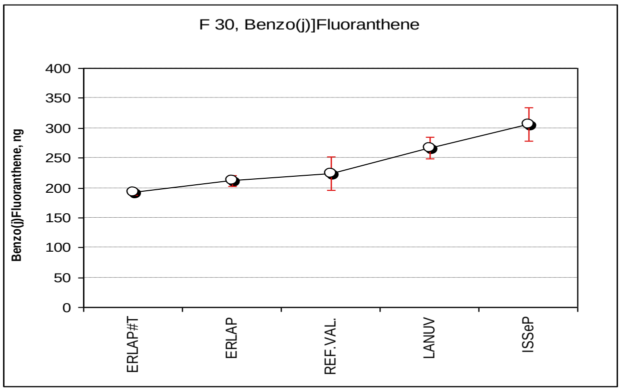

F21, Chrysene

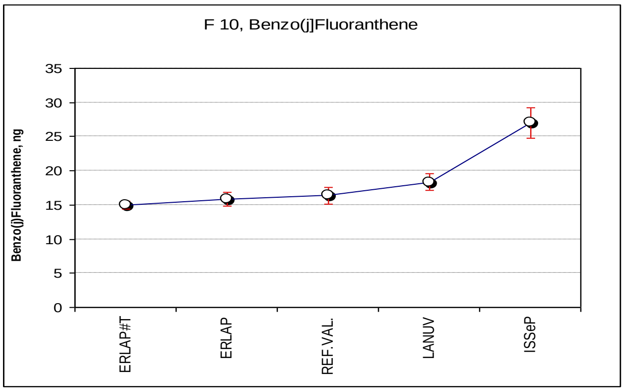

F 30, Benzo[b]Fluoranthene
Benzo(b)Fluoranthene, ng
950
850
750
650
550
450
350
250
APA-LRA
IVL
EPA-LT
LANUV
REF.VAL.
ERLAP#T
ERLAP
ISSeP
EPA-ie
AWEL
EEA

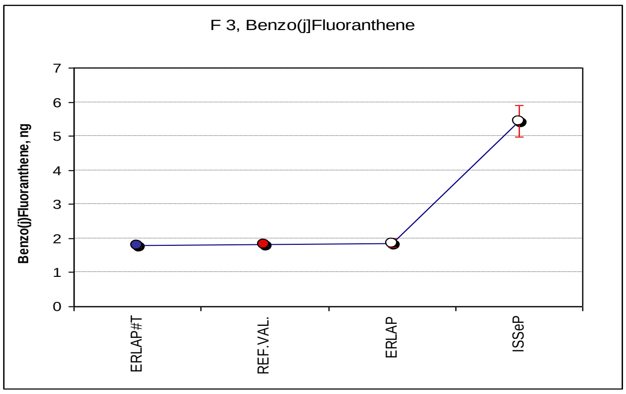

F 10, Benzo[b]Fluoranthene
Benzo(b)Fluoranthene, ng
120
100
80
60
40
20
0
APA-LRA
LANUV
ERLAP#T
REF.VAL
IVL
ERLAP
ISSeP
EPA-LT
AWEL
EEA

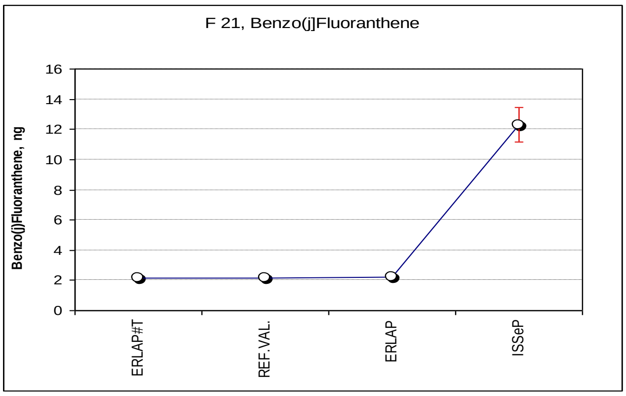

F 3, Benzo[b]Fluoranthene
Benzo(b)Fluoranthene, ng
25
20
15
10
5
0
EPA-ie
APA-LRA
REF.VAL.
IVL
ERLAP#T
ERLAP
LANUV
ISSeP
EEA
EPA-LT

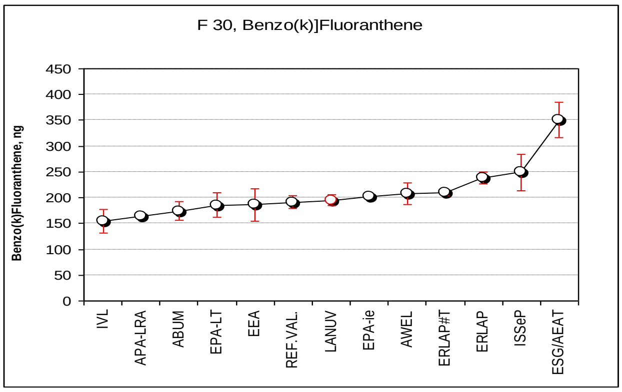

F 21, Benzo[b]Fluoranthene
Benzo(b)Fluoranthene, ng
20
18
16
14
12
10
8
6
4
2
0
EPA-ie
APA-LRA
LANUV
IVL
ERLAP#T
REF.VAL.
ERLAP
EPA-LT
EEA
ISSeP
AWEL


F 30, Benzo(j)]Fluoranthene
Benzo(j)Fluoranthene, ng
400
350
300
250
200
150
100
50
0
ERLAP#T
ERLAP
REF.VAL.
LANUV
ISSeP

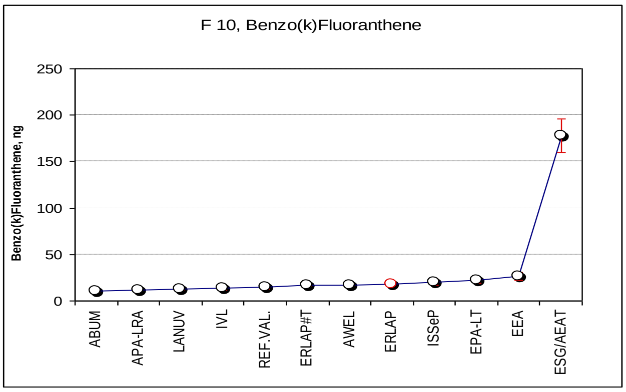

F 10, Benzo(j]Fluoranthene
Benzo(j)Fluoranthene, ng
35
30
25
20
15
10
5
0
ERLAP#T
ERLAP
REF.VAL.
LANUV
ISSeP


F 3, Benzo(j]Fluoranthene
Benzo(j)Fluoranthene, ng
7
6
5
4
3
2
1
0
ERLAP#T
REF.VAL.
ERLAP
ISSeP

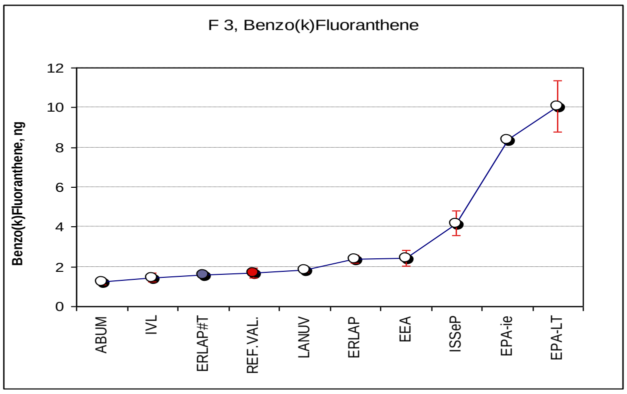

F 21, Benzo(j]Fluoranthene
Benzo(j)Fluoranthene, ng
16
14
12
10
8
6
4
2
0
ERLAP#T
REF.VAL.
ERLAP
ISSeP



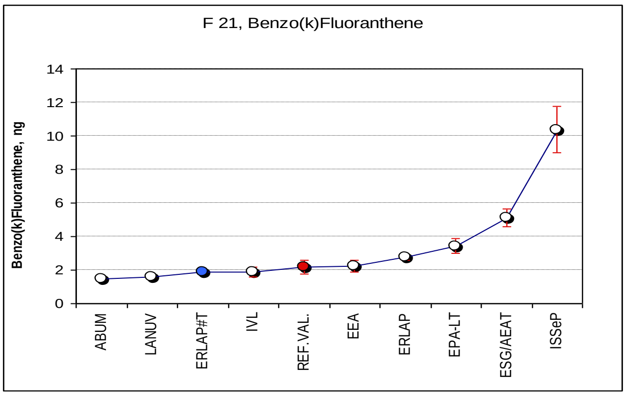
F 30, Benzo(k)]Fluoranthene



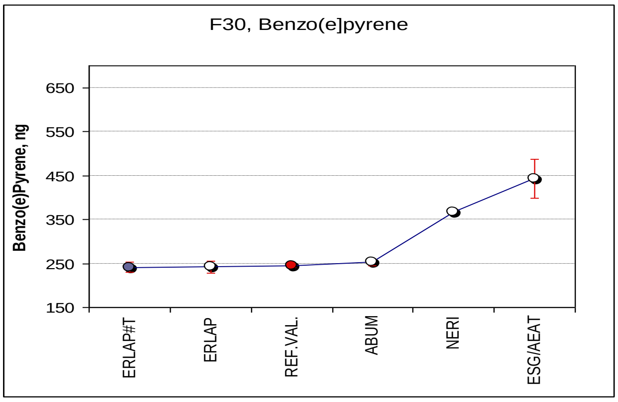
F 10, Benzo(k)Fluoranthene



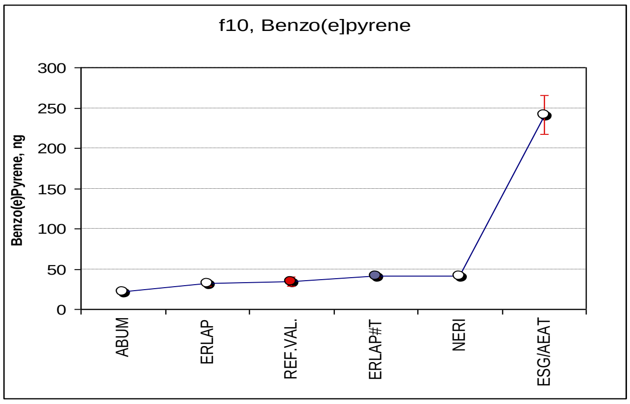
F 3, Benzo(k)Fluoranthene



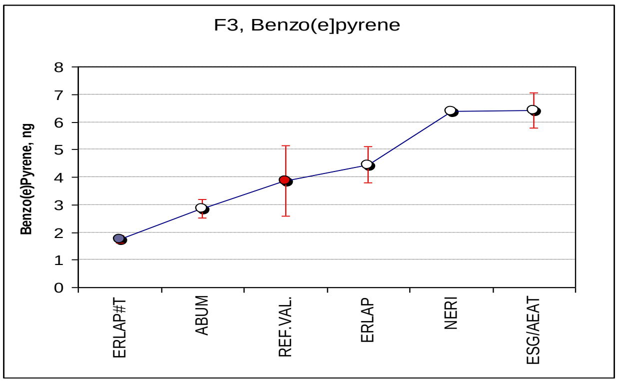
F 21, Benzo(k)Fluoranthene



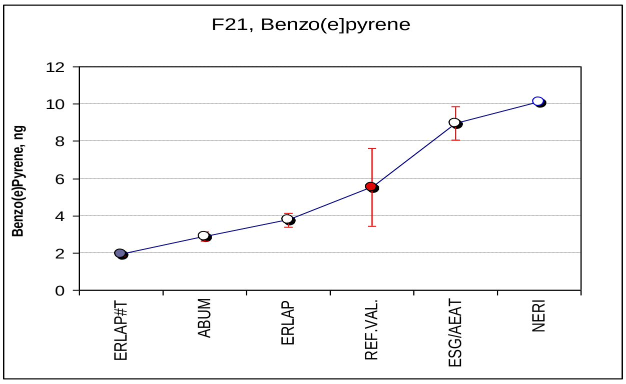
F30, Benzo[e]pyrene



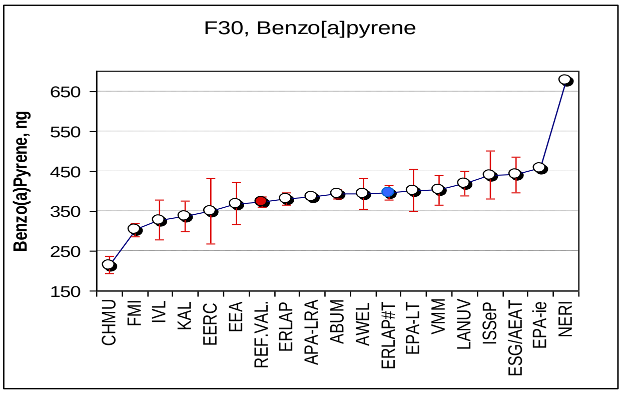
f10, Benzo(e]pyrene

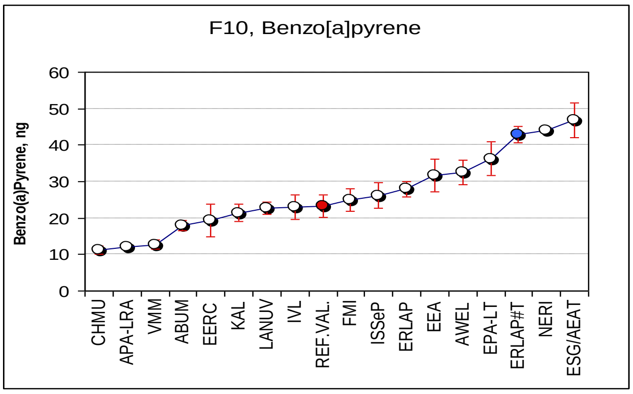


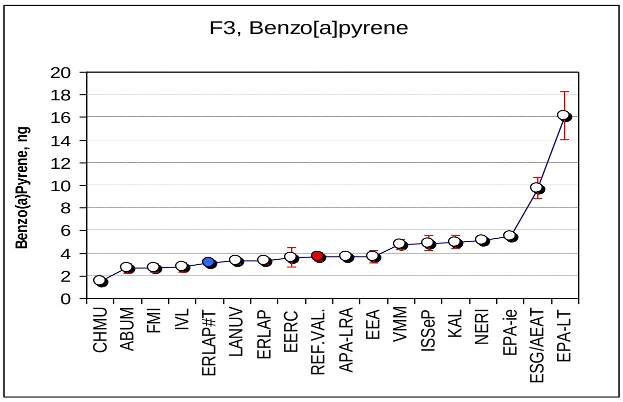
F3, Benzo(e]pyrene

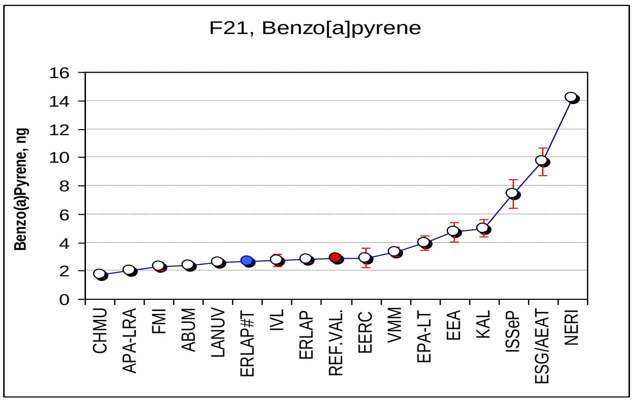


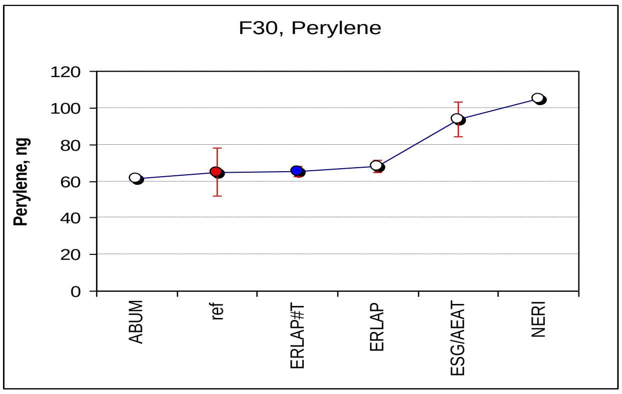
F21, Benzo(e]pyrene

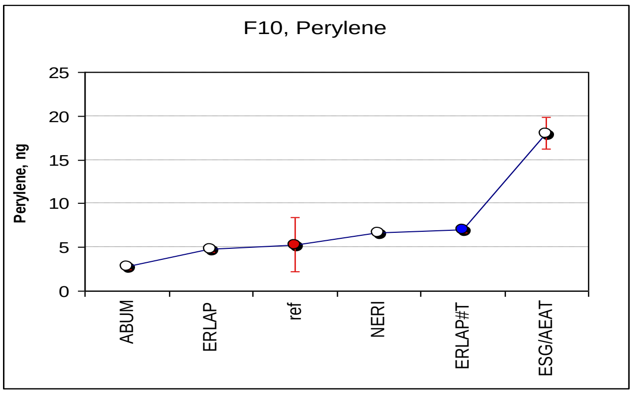

F30, Benzo[a]pyrene
Benzo(a)Pyrene, ng
650
550
450
350
250
150
CHMU
FMI
IVL
KAL
EERC
EEA
REF.VAL.
ERLAP
APA-LRA
ABUM
AWEL
ERLAP#T
EPA-LT
VMM
LANUV
ISSeP
ESG/AEAT
EPA-ie
NERI

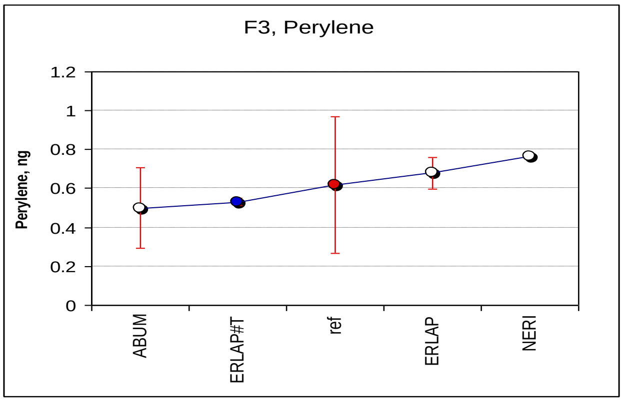

F10, Benzo[a]pyrene
Benzo(a)Pyrene, ng
60
50
40
30
20
10
0
CHMU
APA-LRA
VMM
ABUM
EERC
KAL
LANUV
IVL
REF.VAL.
FMI
ISSeP
ERLAP
EEA
AWEL
EPA-LT
ERLAP#T
NERI
ESG/AEAT

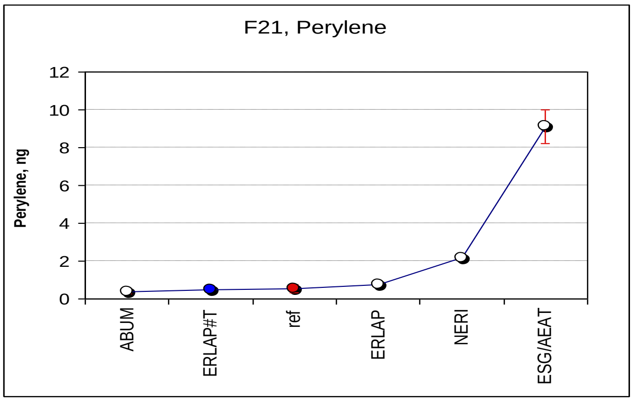

F3, Benzo[a]pyrene
Benzo(a)Pyrene, ng
20
18
16
14
12
10
8
6
4
2
0
CHMU
ABUM
FMI
IVL
ERLAP#T
LANUV
ERLAP
EERC
REF.VAL.
APA-LRA
EEA
VMM
ISSeP
KAL
NERI
EPA-ie
ESG/AEAT
EPA-LT

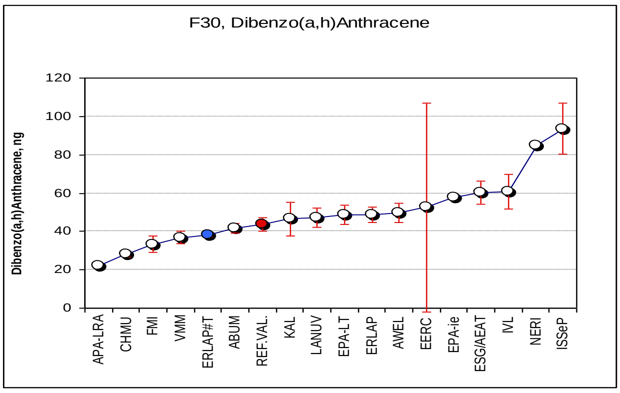

F21, Benzo[a]pyrene
Benzo(a)Pyrene, ng
16
14
12
10
8
6
4
2
0
CHMU
APA-LRA
FMI
ABUM
LANUV
ERLAP#T
IVL
ERLAP
REF.VAL.
EERC
VMM
EPA-LT
EEA
KAL
ISSeP
ESG/AEAT
NERI

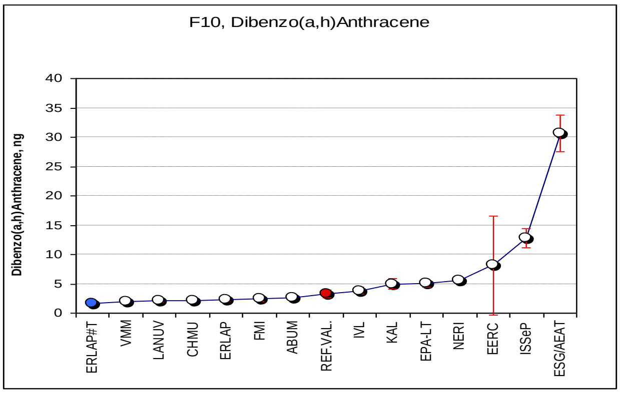

F30, Perylene
Perylene, ng
120
100
80
60
40
20
0
ABUM
ref
ERLAP#T
ERLAP
ESG/AEAT
NERI

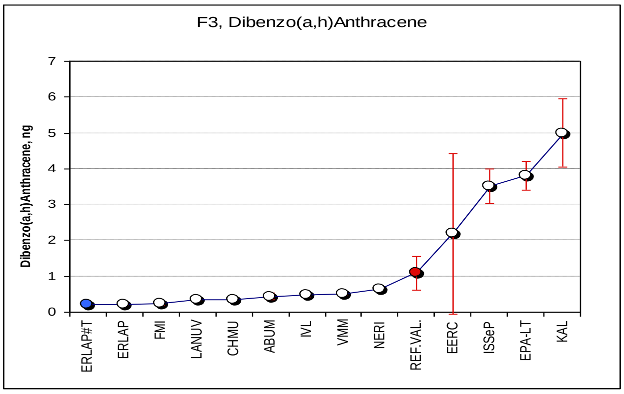

F10, Perylene
Perylene, ng
25
20
15
10
5
0
ABUM
ERLAP
ref
NERI
ERLAP#T
ESG/AEAT

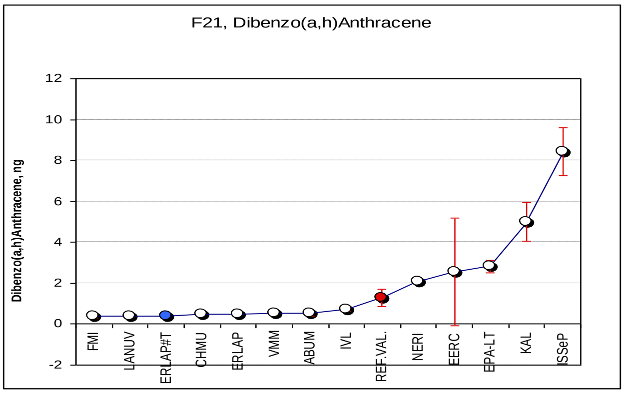

F3, Perylene
Perylene, ng
1.2
1
0.8
0.6
0.4
0.2
0
ABUM
ERLAP#T
ref
ERLAP
NERI

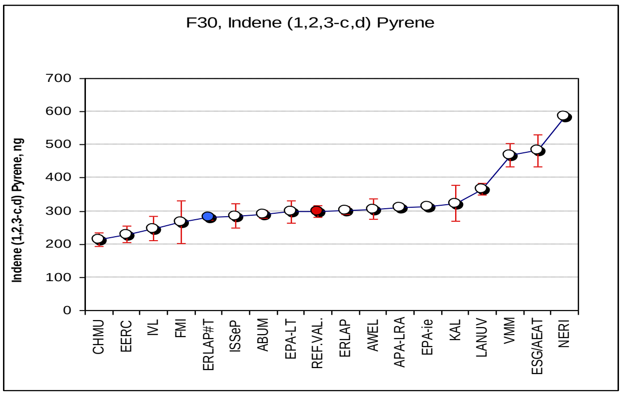

F21, Perylene
Perylene, ng
12
10
8
6
4
2
0
ABUM
ERLAP#T
ref
ERLAP
NERI
ESG/AEAT

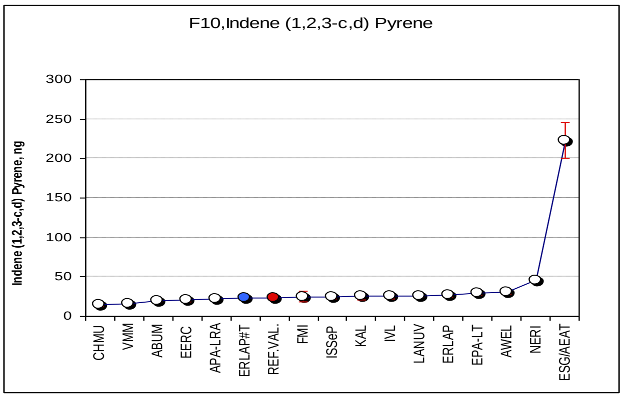

F30, Dibenzo(a,h)Anthracene

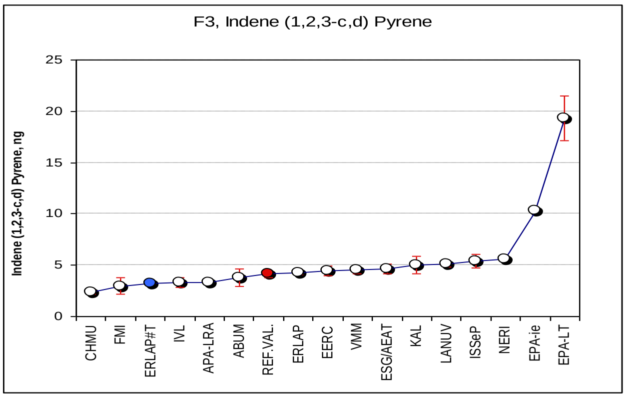

F10, Dibenzo(a,h)Anthracene

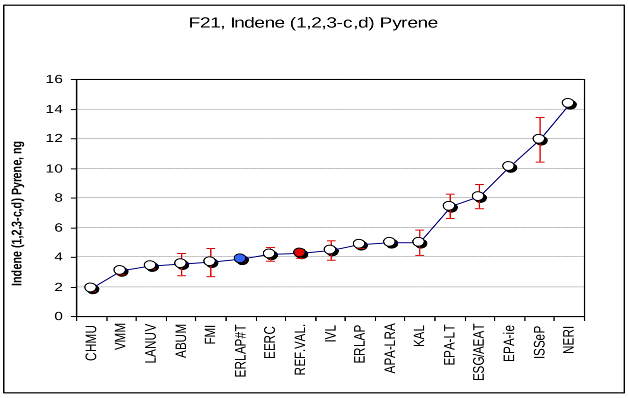

F3, Dibenzo(a,h)Anthracene

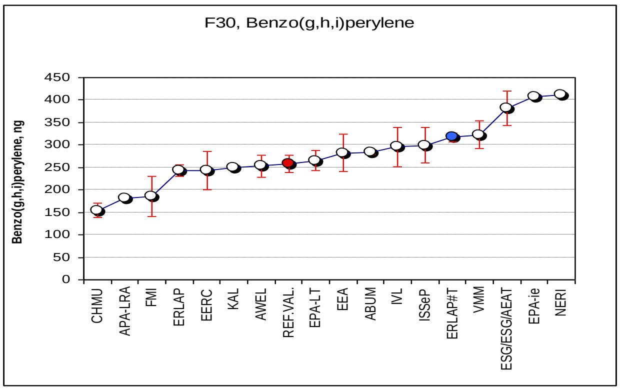

F21, Dibenzo(a,h)Anthracene


F30, Indene (1,2,3-c,d) Pyrene

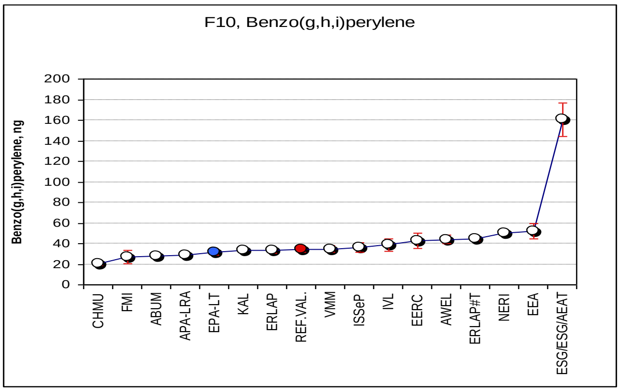

F10,Indene (1,2,3-c,d) Pyrene


F3, Indene (1,2,3-c,d) Pyrene

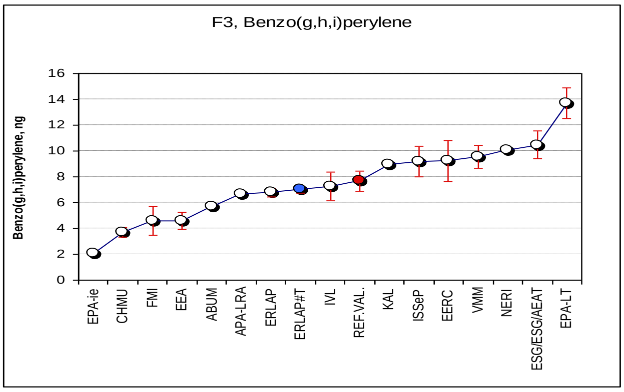

F21, Indene (1,2,3-c,d) Pyrene



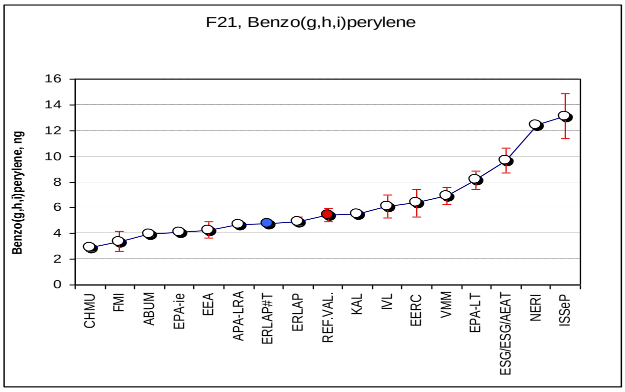
F30, Benzo(g,h,i)perylene



F10, Benzo(g,h,i)perylene



F3, Benzo(g,h,i)perylene



F21, Benzo(g,h,i)perylene

Comments from laboratories

ERLAP:

Chrysene and Triphenylene were reported together.
Dibenzo-ah-Anthracene and Indene-1,2,3-c,d-Pyrene were estimated by the deconvolution of their corresponding overlapped ions 278 and 276.

FM

Average results from 2 injections

LANUV:

Sample F30-39-2-5: The peak of 6-Methylchrysene could not be seperated completely from two peaks eluting shortly before and after the substance, resulting in a too high peak area after integration. We know this phenomenon from other samples with high amounts of PAH. Therefore external calibration was used for quantification.

EEA:

Benzo[j]fluoranthene, Benzo[e]pyrene, Perylene, Benzo[b.j,k]fluoranthene, and Chrysene+Triphenylene: Not present in the calibration mix
Indeno[1,2,3,-c,d]pyrene, Dibenzo[a,h]anthracene: Difficulties in separation

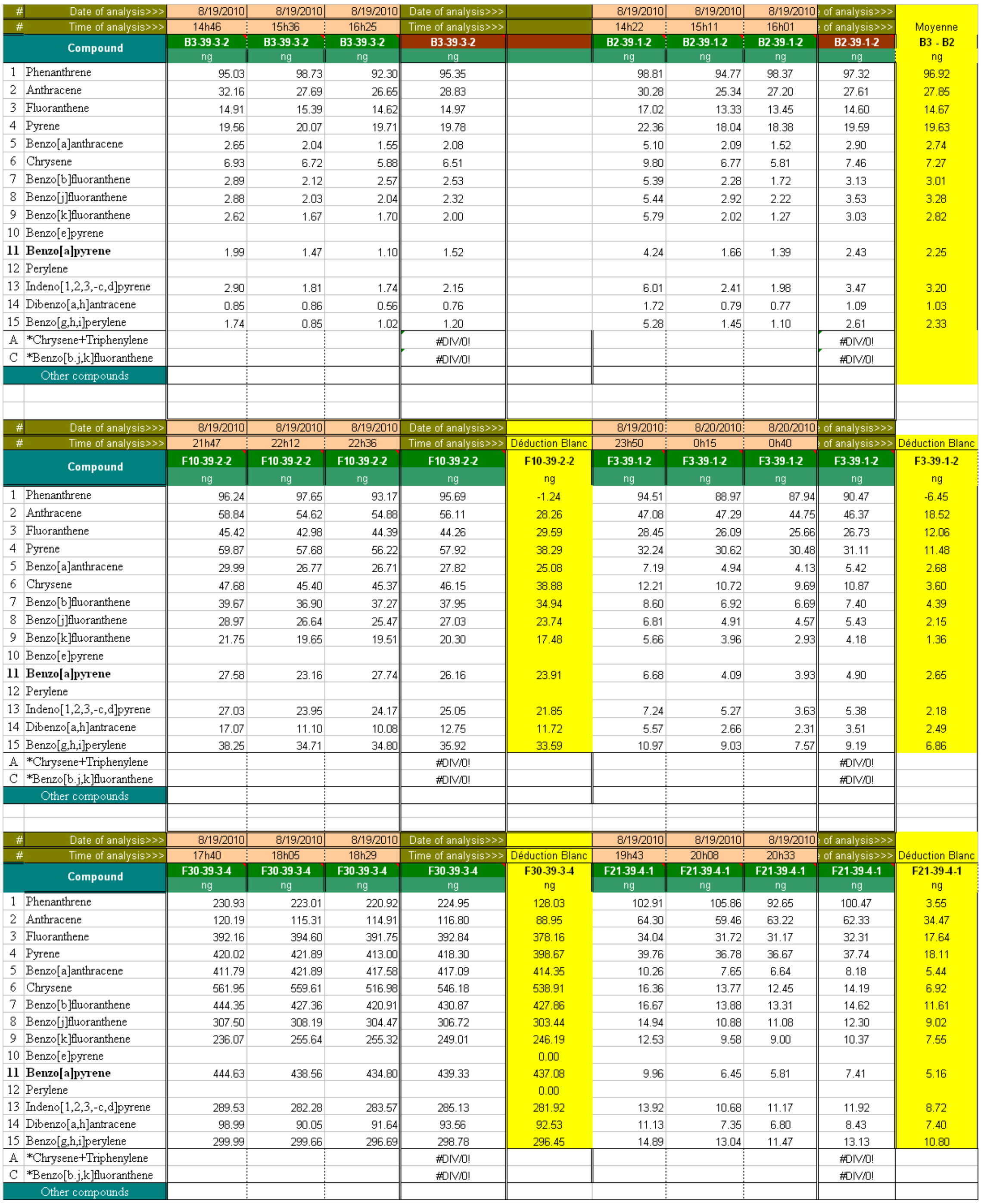
EERC:

Benzo[a]anthracene: B(a)a and Chry partly overlapping; Chrysene: B(a)a and Chry partly overlapping; Benzo[b]fluoranthene Overlapping peaks; Benzo[j]fluoranthene: Compound not calibrated; Benzo[k]fluoranthene: Overlapping peaks; Benzo[e]pyrene: Compound not calibrated; Benzo[a]pyrene: Partly overlapping with unidentified peak; Perylene: Compound not calibrated; Dibenzo[a,h]anthracene: Partly overlapping with unidentified peak.

ISSeP:

ISSeP sent new rectified values on 30/11/2011. These were corrected from laboratory blanks. They suspected a possible contamination from low molecular PAHs. The new results are listed below.

Rectifficatif blancs.xls



#	Date of analysis>>>	8/19/2010	8/19/2010	8/19/2010	Date of analysis>>>		8/19/2010	8/19/2010	8/19/2010	of analysis>>>	
#	Time of analysis>>>	14h46	15h36	16h25	Time of analysis>>>		14h22	15h11	16h01	of analysis>>>	Moyenne
	Compound	B3-39-3-2	B3-39-3-2	B3-39-3-2	B3-39-3-2		B2-39-1-2	B2-39-1-2	B2-39-1-2	B2-39-1-2	B3 - B2
		ng	ng	ng	ng		ng	ng	ng	ng	ng
1	Phenanthrene	95.03	98.73	92.30	95.35		98.81	94.77	98.37	97.32	96.92
2	Anthracene	32.16	27.69	26.65	28.83		30.28	25.34	27.20	27.61	27.85
3	Fluoranthene	14.91	15.39	14.62	14.97		17.02	13.33	13.45	14.60	14.67
4	Pyrene	19.56	20.07	19.71	19.78		22.36	18.04	18.38	19.59	19.63
5	Benzo[a]anthracene	2.65	2.04	1.55	2.08		5.10	2.09	1.52	2.90	2.74
6	Chrysene	6.93	6.72	5.88	6.51		9.80	6.77	5.81	7.46	7.27
7	Benzo[b]fluoranthene	2.89	2.12	2.57	2.53		5.39	2.28	1.72	3.13	3.01
8	Benzo[j]fluoranthene	2.88	2.03	2.04	2.32		5.44	2.92	2.22	3.53	3.28
9	Benzo[k]fluoranthene	2.62	1.67	1.70	2.00		5.79	2.02	1.27	3.03	2.82
10	Benzo[e]pyrene										
11	**Benzo[a]pyrene**	1.99	1.47	1.10	1.52		4.24	1.66	1.39	2.43	2.25
12	Perylene										
13	Indeno[1,2,3,-c,d]pyrene	2.90	1.81	1.74	2.15		6.01	2.41	1.98	3.47	3.20
14	Dibenzo[a,h]antracene	0.85	0.86	0.56	0.76		1.72	0.79	0.77	1.09	1.03
15	Benzo[g,h,i]perylene	1.74	0.85	1.02	1.20		5.28	1.45	1.10	2.61	2.33
A	*Chrysene+Triphenylene				#DIV/0!					#DIV/0!	
C	*Benzo[b.j,k]fluoranthene				#DIV/0!					#DIV/0!	
	Other compounds										

#	Date of analysis>>>	8/19/2010	8/19/2010	8/19/2010	Date of analysis>>>		8/19/2010	8/20/2010	8/20/2010	of analysis>>>	
#	Time of analysis>>>	21h47	22h12	22h36	Time of analysis>>>	Déduction Blanc	23h50	0h15	0h40	of analysis>>>	Déduction Blanc
	Compound	F10-39-2-2	F10-39-2-2	F10-39-2-2	F10-39-2-2	F10-39-2-2	F3-39-1-2	F3-39-1-2	F3-39-1-2	F3-39-1-2	F3-39-1-2
		ng	ng	ng	ng	ng	ng	ng	ng	ng	ng
1	Phenanthrene	96.24	97.65	93.17	95.69	-1.24	94.51	88.97	87.94	90.47	-6.45
2	Anthracene	58.84	54.62	54.88	56.11	28.26	47.08	47.29	44.75	46.37	18.52
3	Fluoranthene	45.42	42.98	44.39	44.26	29.59	28.45	26.09	25.66	26.73	12.06
4	Pyrene	59.87	57.68	56.22	57.92	38.29	32.24	30.62	30.48	31.11	11.48
5	Benzo[a]anthracene	29.99	26.77	26.71	27.82	25.08	7.19	4.94	4.13	5.42	2.68
6	Chrysene	47.68	45.40	45.37	46.15	38.88	12.21	10.72	9.69	10.87	3.60
7	Benzo[b]fluoranthene	39.67	36.90	37.27	37.95	34.94	8.60	6.92	6.69	7.40	4.39
8	Benzo[j]fluoranthene	28.97	26.64	25.47	27.03	23.74	6.81	4.91	4.57	5.43	2.15
9	Benzo[k]fluoranthene	21.75	19.65	19.51	20.30	17.48	5.66	3.96	2.93	4.18	1.36
10	Benzo[e]pyrene										
11	**Benzo[a]pyrene**	27.58	23.16	27.74	26.16	23.91	6.68	4.09	3.93	4.90	2.65
12	Perylene										
13	Indeno[1,2,3,-c,d]pyrene	27.03	23.95	24.17	25.05	21.85	7.24	5.27	3.63	5.38	2.18
14	Dibenzo[a,h]antracene	17.07	11.10	10.08	12.75	11.72	5.57	2.66	2.31	3.51	2.49
15	Benzo[g,h,i]perylene	38.25	34.71	34.80	35.92	33.59	10.97	9.03	7.57	9.19	6.86
A	*Chrysene+Triphenylene				#DIV/0!					#DIV/0!	
C	*Benzo[b.j,k]fluoranthene				#DIV/0!					#DIV/0!	
	Other compounds										

#	Date of analysis>>>	8/19/2010	8/19/2010	8/19/2010	Date of analysis>>>		8/19/2010	8/19/2010	8/19/2010	of analysis>>>	
#	Time of analysis>>>	17h40	18h05	18h29	Time of analysis>>>	Déduction Blanc	19h43	20h08	20h33	of analysis>>>	Déduction Blanc
	Compound	F30-39-3-4	F30-39-3-4	F30-39-3-4	F30-39-3-4	F30-39-3-4	F21-39-4-1	F21-39-4-1	F21-39-4-1	F21-39-4-1	F21-39-4-1
		ng	ng	ng	ng	ng	ng	ng	ng	ng	ng
1	Phenanthrene	230.93	223.01	220.92	224.95	128.03	102.91	105.86	92.65	100.47	3.55
2	Anthracene	120.19	115.31	114.91	116.80	88.95	64.30	59.46	63.22	62.33	34.47
3	Fluoranthene	392.16	394.60	391.75	392.84	378.16	34.04	31.72	31.17	32.31	17.64
4	Pyrene	420.02	421.89	413.00	418.30	398.67	39.76	36.78	36.67	37.74	18.11
5	Benzo[a]anthracene	411.79	421.89	417.58	417.09	414.35	10.26	7.65	6.64	8.18	5.44
6	Chrysene	561.95	559.61	516.98	546.18	538.91	16.36	13.77	12.45	14.19	6.92
7	Benzo[b]fluoranthene	444.35	427.36	420.91	430.87	427.86	16.67	13.88	13.31	14.62	11.61
8	Benzo[j]fluoranthene	307.50	308.19	304.47	306.72	303.44	14.94	10.88	11.08	12.30	9.02
9	Benzo[k]fluoranthene	236.07	255.64	255.32	249.01	246.19	12.53	9.58	9.00	10.37	7.55
10	Benzo[e]pyrene					0.00					
11	**Benzo[a]pyrene**	444.63	438.56	434.80	439.33	437.08	9.96	6.45	5.81	7.41	5.16
12	Perylene					0.00					
13	Indeno[1,2,3,-c,d]pyrene	289.53	282.28	283.57	285.13	281.92	13.92	10.68	11.17	11.92	8.72
14	Dibenzo[a,h]antracene	98.99	90.05	91.64	93.56	92.53	11.13	7.35	6.80	8.43	7.40
15	Benzo[g,h,i]perylene	299.99	299.66	296.69	298.78	296.45	14.89	13.04	11.47	13.13	10.80
A	*Chrysene+Triphenylene				#DIV/0!					#DIV/0!	
C	*Benzo[b.j,k]fluoranthene				#DIV/0!					#DIV/0!	
	Other compounds										

European Commission

EUR 25170 EN – Joint Research Centre – Institute for Environment and Sustainability
Title: First EC-JRC PAHs Inter-laboratory comparison on PM10 quartz filters
Author(s): E. Grandesso, K. Kowaleski, P. Pérez Ballesta
Luxembourg: Office for Official Publications of the European Communities
2012 – 63 pp. – 210 x 297 cm
EUR – Scientific and Technical Research series – ISSN 1831-9424 (on-line) ISSN 1018-5593 (print)
ISBN 978-92-79-22782-0 (pdf) ISBN 978-92-79-22781-3 (print)

DOI 10.2788/63064

Abstract

This report presents the results of the first inter-laboratory comparison for PAHs analysed on quartz filters carried out by the JRC between April and December 2010. Seventeen national reference laboratories participated in this exercise.
Four different filters representing winter and summer periods in two different locations (Madrid and Prague) and two blanks were tested during the exercise. 15 PAHs were considered for analysis from phenanthrene to benzo(g,h,i)perylene, including benzo(a)pyrene. In general, the results of the exercise showed median overall uncertainties ranging from 10 to 90 %, depending on the compound and the analysed concentration. Which in the case of benzo(a)pyrene varied between 30 and 50. The exercise demonstrates the validity of the current methodology for organising PAHs inter-laboratory comparison exercises on PM10 filters. Laboratories exhibited better performance in the analysis of those compounds where reference material was found on the market. The need for implementing a consistent traceability system for measurements is deduced from the systematic biases associated with laboratory behaviour.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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EUROPEAN COMMISSION

LB-NA-25170-EN-N

Publications Office
Publications.europa.eu

ISBN 978-92-79-22782-0
9 789279 227820