EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Final Report

Project SA/CEN/ENV/000/2005-32
Standardization work – Measuring methods for the determination of deposition of PAHs

Mandate M/361 EN

CEN/TC 264/WG 21
„Ambient air – Measurement method for benzo[*a*]pyrene”

August 2009

Contents

1 Summary

Council Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, nickel, mercury and polycyclic aromatic hydrocarbons in ambient air requires the measurement of the total deposition of benzo[*a*]pyrene and other relevant polycyclic aromatic hydrocarbons, at least the compounds benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene and dibenz[*a,h*]anthracene, at a limited number of measurement sites within the Member States. In order to ensure the comparability of data measured in the Member States a standard measurement method is necessary.

The European Commission and EFTA have given a mandate to CEN to establish a European Standard which specifies such a method for the determination of the above PAH components. CEN/BT accepted the mandate on 2005-01-27. The Grant Agreements between the European Commission and CEN and between EFTA and CEN were signed in December 2005 and April/May 2006, respectively.

The standardisation work has been carried out by CEN TC 264/WG 21 „Ambient air – Measurement method for benzo[*a*]pyrene". The technical method validation programme comprised three parts:

- Laboratory tests (test and comparison of suitable sample preparation and analysis methods):
  The test demonstrated that both used sample preparation methods, i.e. liquid/liquid extraction and solid-phase extraction, are well suited and that the two analytical methods (GC/MS and HPLC/FLD) are robust and lead to comparable results, with overall reproducibility standard deviations ranging from 5 % to 9 %.
- Degradation test:
  This test should reveal if degradation of the specified PAH compounds occurs during sampling. The used test material (CRM, urban dust) showed no significant degradation under the chosen test conditions.
- Field validation tests (test of 3 different sampler types at 4 sampling sites):
  The test results showed that the funnel-bottle bulk collector is the most appropriate sampling device for the purposes of Directive 2004/107/EC. The uncertainties observed generally meet the 70 % criterion of the Directive. Those cases in which the criterion is exceeded can be explained by atypically high specific analytical uncertainties rather than by the performances of the collectors.

The tests were carried out between January 2006 and March 2009. The draft European Standard prEN 15980 *Air quality – Determination of the deposition of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene* was finalized in May 2009 and submitted to CEN enquiry on 2009-07-30.

The following institutes participated in the work programme:

- ECN Energieonderzoek Centrum Nederland, Petten (The Netherlands)
- INERIS Institut National de l'Environnement Industriel et des Risques, Verneuil-en-Halatte (France)
- LUBW Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, Karlsruhe (Germany)
- NMi Nederlands Meetinstituut, Delft (The Netherlands)
- ORAMIP Observatoire Régional de l'Air en Midi-Pyrénées, Colomiers (France)
- TNO Milieu, Energie en Procesinnovatie, Apeldoorn/Utrecht (The Netherlands)
- Umweltbundesamt GmbH, Wien (Austria)

2 Laboratory Test

The procedure of the laboratory test and the analytical results are given in the report

Method for the determination of the total deposition of PAHs – Results of the laboratory test 1 and 2 (Pages 5 – 66).

The evaluation results of the laboratory tests are given in the report

Method for the determination of the atmospheric deposition of PAH – Evaluation of results of analysis of standards and samples of the laboratory test programme (Pages 67 – 78).

Landesanstalt für Umwelt, Messungen und
Naturschutz Baden-Württemberg

CEN/TC 264/WG 21

Method for the determination of the total deposition of PAHs

-Results of the laboratory test 1 and 2 -

Baden-Württemberg
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CEN/TC 264/WG 21

Method for the determination of the total deposition of PAHs

-RESULTS OF THE LABORATORY TEST 1 AND 2-

WRITTEN BY Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg (LUBW)
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CONTENTS

1 Introduction

Within the framework of CEN/TC 264/WG 21 – Method for the determination of the total deposition of PAHs – LUBW coordinated two laboratory tests for the determination of relevant PAHs.

The laboratory tests included

- check of blank values
- check of detection limits
- check of recovery rate of the surrogate standard
- check of recovery rate using CRM (certified reference material)
- analysis of deposition and rain water samples.

LUBW prepared and distributed the first laboratory test samples at 28. may 2007 and the second laboratory test at 11. march 2008 to the following seven participating laboratories (see also annex 1).

1. Harald Creutznacher, LUBW Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, Germany
2. Dieter Gladtke, LANUV Landesamt für Natur, Umwelt und Verbraucherschutz , Germany
3. B.F. van Egmond, ECN Energieonderzoek Centrum Nederland, the Netherlands
4. Tilman Gocht, UT Universität Tübingen, Germany
5. Marc Houtzager, TNO Environment and Geoscience, the Netherlands
6. Eva Leoz-Garciandia, INERIS L'Institut National de l'Environnement Industriel et des Risques, France
7. Thomas Remesch, UBA Umweltbundesamt, Austria

The following report summarizes the data of the different laboratories. A discussion or an evaluation of the data is not included.

I PART ONE

laboratory test 1

2 Sample preparation and analysis of the test samples

The test samples were prepared and provided by LUBW to the participating laboratories. The test samples included one liquid calibration standard with a known concentration of PAH, two real sample extracts with low and high PAH concentration, three rain water samples and three dust samples (CRM) suspended in water. Additionally 1 ml 6-methyl-chrysene was provided as surrogate standard with the concentration of 10 µg/ml in acetonitrile. It was foreseen that every laboratory shall use this standard as surrogate standard.
Table 2.1 shows the specification of the test samples of the laboratory test.

Table 2.1: Specification of the test samples of the laboratory test

number	sample type	no. of aliquots	solvent	BaP conc.	amount
1	liquid calibration standard	1	dichloromethane	100 ng/ml	ca. 1 ml
2	real sample extract (low PAH conc.)	1	dichloromethane	< 50 ng/ml	ca. 1 ml
3	real sample extract (high PAH conc.)	1	dichloromethane	> 200 ng/ml	ca. 1 ml
4	rain water	3	water + 1% acetone	< 50 ng/ml	ca. 1000 ml
5	dust sample (CRM) suspended in rain water	3	water + 1% acetone+ 75 g NaCl	> 50 ng/ml	ca. 250 ml

The liquid standard was ordered by PAH Research Institute in Greifenberg. The standard included 8 relevant PAH compounds with a concentration of 100 ng/ml and should be used for calibration check.

For the real sample extract 120 PM10 loaded filters of different measurement stations were extracted (sample 3). An aliquot of this sample was diluted to lower the PAH concentration (sample 2).

For the rain water sample (sample 4) the content of different wet-only samplers from different sites in Baden-Württemberg were combined in a big tank and stored cool in the dark.

For sample 5 an aliquot of the wet-only rain water from sample 4 was used. To every small portion of water an amount of a certified reference material was added (NIST, Urban Dust 1649a). Every laboratory got three rain water samples doped with about 40 mg of the NIST material.

The participating laboratories should prepare and analyse the samples according to table 2.2.

Table 2.2: Preparation and analysis of the test samples

number	sample type	Extraction	Quantification	No. of replicate analysis
1	liquid calibration standard	not required	use for calibration check	3
2	real sample extract (low PAH conc.)	not required	following Doc. N 159	3
3	real sample extract (high PAH conc.)	not required	following Doc. N 159	3
4	rain water	following Doc. N 159	following Doc. N 159	3
5	dust sample (CRM) suspended in rain water	following Doc. N 159	following Doc. N 159	3

The analysis comprise the determination of following PAH compounds:

- Benzo(a)pyrene
- Benz(a)anthracene
- Benzo(b)fluoranthene*
- Benzo(j)fluoranthene*
- Benzo(k)fluoranthene*
- Indeno(1,2,3-cd)pyrene
- Dibenz(a,h)anthracene

(* the 3 isomers may be determined as sum)

3 Quality assurance

All samples for the laboratory test were distributed by LUBW on 28. May 2007. The samples arrived in the participating laboratories between 29.05.07 and 05.06.07. Most of the samples were still cool, four samples showed leakage at the outside of the bottle (Ineris, TNO).
Four laboratories prepared the samples according to the CEN-method (liquid-liquid-extraction), three laboratories prepared the samples according to SPE (solid-phase-extraction, Speedisk).
Three participating laboratories analysed the samples with GCMS and four participants analysed the samples with HPLC. The samples were analysed between 11.06. and 05.11.07.
All members used 6-methyl-chrysene as the surrogate standard. The recovery of the surrogate standard on average is in the range of 80 % to 105 %. The lower limit of the working range of the participating laboratories is between 1 ng/ml and 5,5 ng/ml.
The following table 3.1 gives information about the test samples:

Table 3.1 Information about the test samples

laboratories	LUBW	LANUV	INERIS	ECN	UBA	TNO	UT
arrival of the samples	28.05.2007	29.05.2007	01.06.2007	31.05.2007	31.05.2007	30.05.2007	05.06.2007
state of the samples after arriving in the lab	cool	cool	not cool, sample 5.1 crystals at outside of the bottle	cool	cool	not cool, samples 5.1-5.3 showed leakage on the outside of the bottle	not cool
measuring method	GCMS	HPLC	HPLC	GCMS	HPLC	HPLC	GCMS
working up method (samples 4.1 – 5.3)	CEN	CEN	CEN	Speedisk	Speedisk	Speedisk	CEN
date of the analyses	11.-14.06.2007	21.-25.06.2007	21.-23.06.2007	12.07.2007	17.08.2007	29.06.-05.11.2007	17.-21.09.2007
surrogate standard	6-MChr	6-MChr	6-MChr	6-MChr	6-MChr	6-MChr	6-MChr
amount of the added surrogate standard [ng]	100	500	100	500	10	512	100
average recovery rate of the surrogate standard [%]	101	98	81	98	80	101	105
lower limit of the working range [ng/ml]	5	5	1	2,5	1	5,5	4

4 Results of the laboratory test 1

In the following chapters 4.1 to 4.5 the results of the laboratory test 1 are shown.
Every sample had to be analysed threefold to determine the standard deviation. The three isomers Benzo(b)fluoranthene, Benzo(j)fluoranthene and Benzo(k)fluoranthene could be detected as a sum.

4.1 SAMPLE 1: LIQUID CALIBRATION STANDARD

The liquid calibration standard (sample 1, Schmidt) was a mixture of 8 PAH in dichloromethane with a concentration of 100 ng/ml of each compound (Benzo(a)pyrene, Benz(a)anthracene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, Dibenz(a,h)anthracene, Benzo(ghi)perylene). The liquid calibration standard had to be use for calibration check. The following diagrams 4.1.1 to 4.1.5 show the results of all participating laboratories (annex 2).

In all diagrams the continuous line is the target value (100 ng/ml or 300 ng/ml for Benzo(b,j,k)fluoranthene). The whiskers indicate $^{+}/_{-}$ 1 standard deviation of the three replicate analyses.

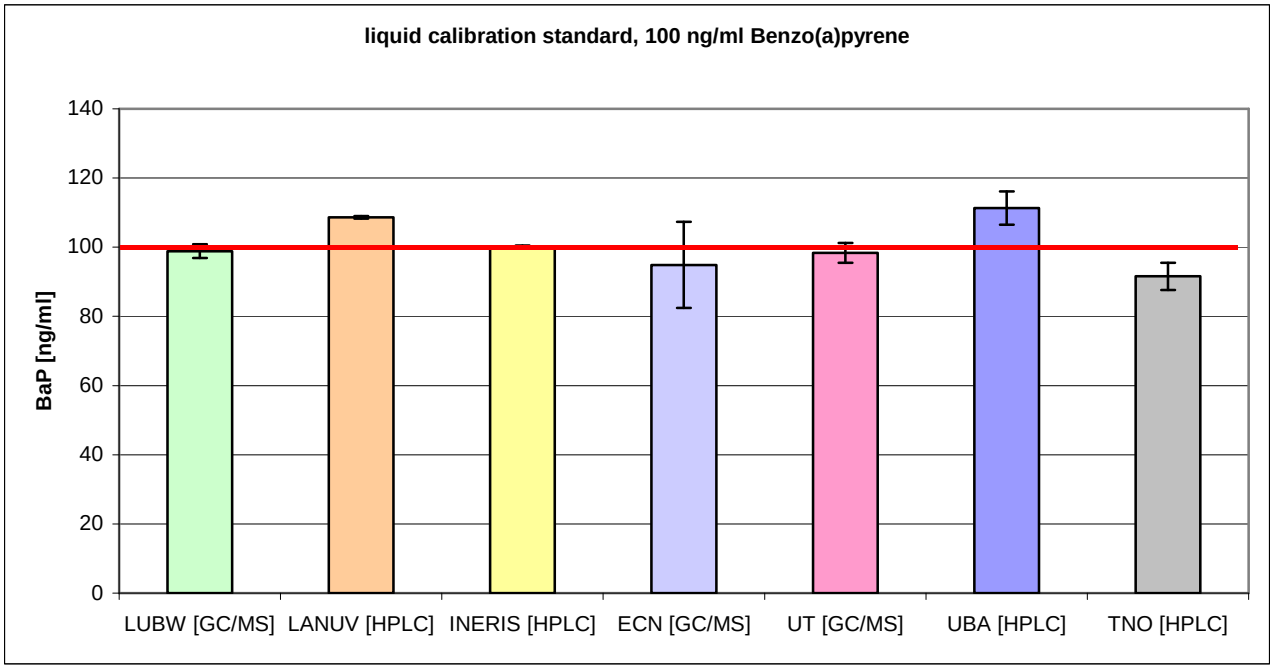

Figure 4.1.1: Liquid calibration standard with the target value of 100 ng/ml Benzo(a)pyrene

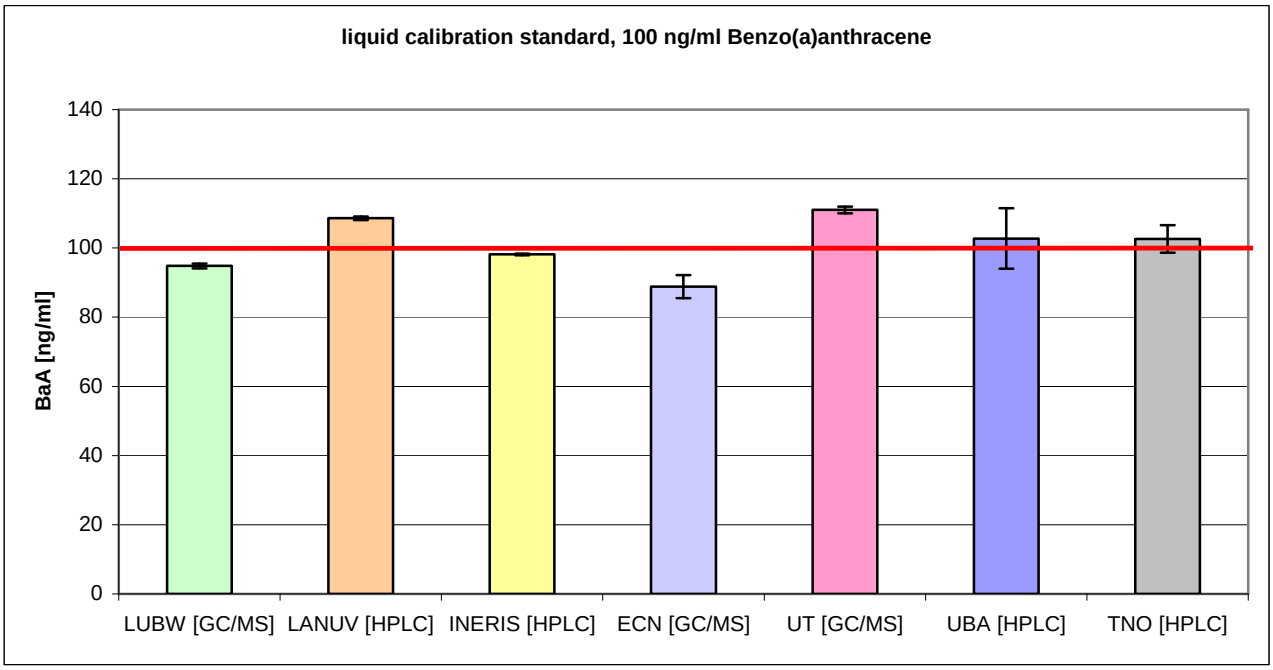

Figure 4.1.2: Liquid calibration standard with the target value of 100 ng/ml Benz(a)anthracene

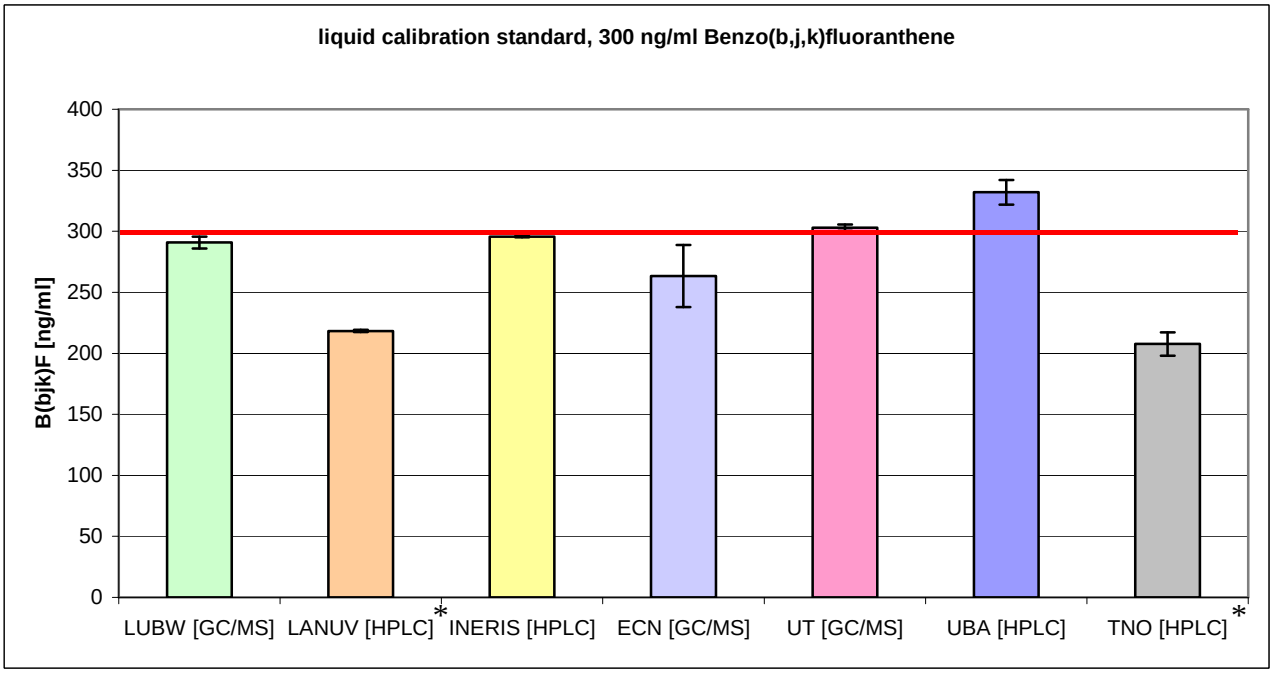

Figure 4.1.3: Liquid calibration standard with the target value of 300 ng/ml Benzo(b,j,k)fluoranthene

*** Benzo(j)fluoranthene not detected**

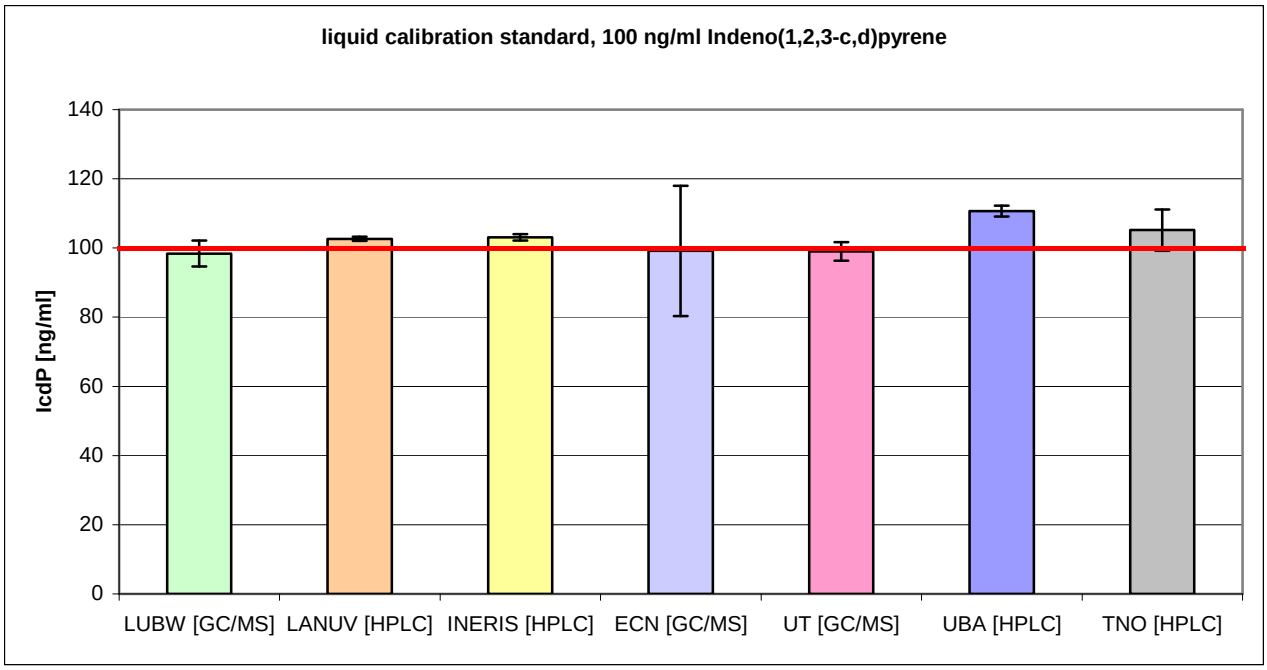

Figure 4.1.4: Liquid calibration standard with the target value of 100 ng/ml Indeno(1,2,3-cd)pyrene

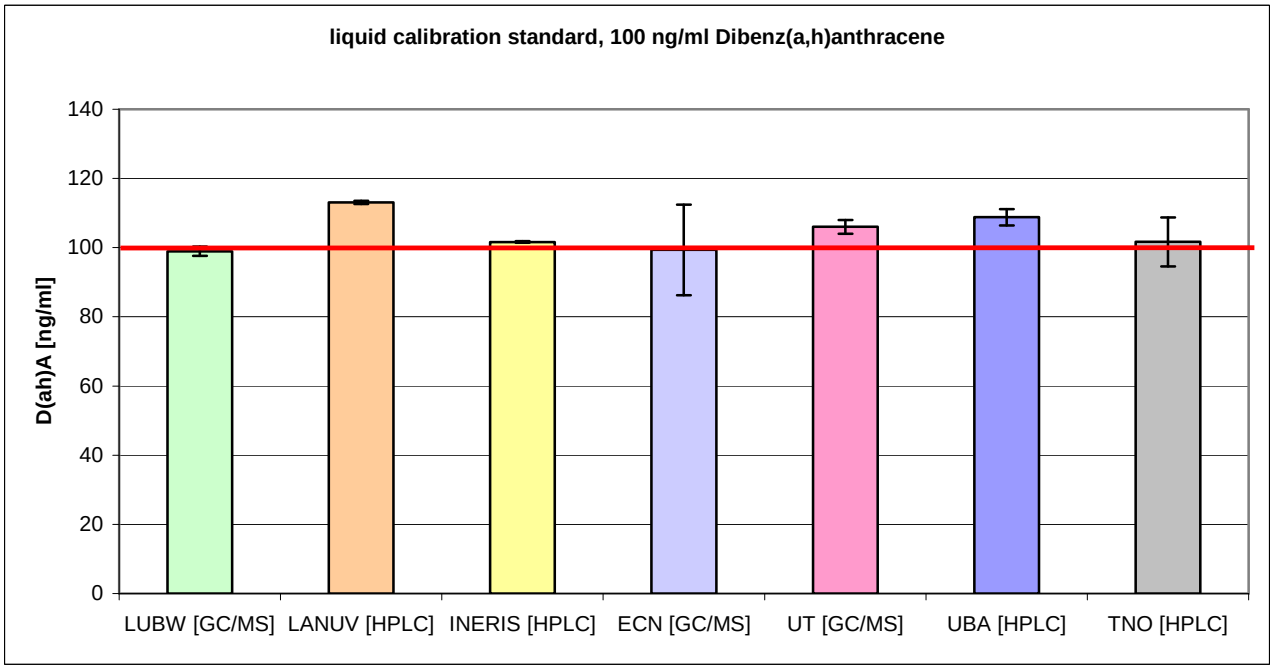

Figure 4.1.5: Liquid calibration standard with the target value of 100 ng/ml Dibenz(a,h)anthracene

4.2 SAMPLE 2: REAL SAMPLE EXTRACT (LOW PAH CONCENTRATION)

For the real sample extract 120 PM10 loaded filters of different measurement stations were extracted. An aliquot of this sample was diluted to lower the PAH concentration.
The following diagrams 4.2.1 to 4.2.5 show the results of all participating laboratories (annex 3).

The continuous line in the diagrams is the average of all results. The whiskers indicate $^{+}/_{-}$ 1 standard deviation of the three replicate analyses. The broken lines show the tolerance area of $^{+}/_{-}$ 2 standard deviation of the average (not possible for Dibenz(a,h)anthracene because of the strongly differences).

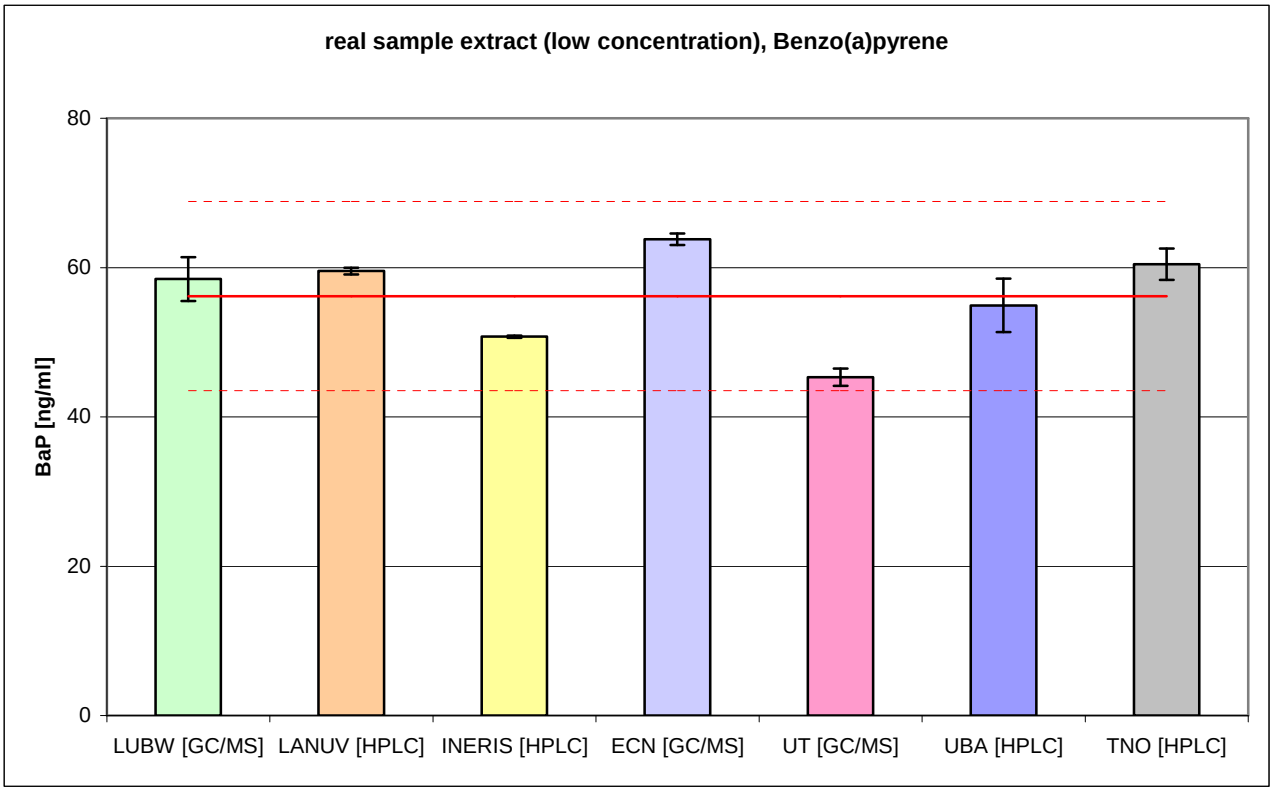

Figure 4.2.1: Real sample extract with a low PAH concentration, Benzo(a)pyrene

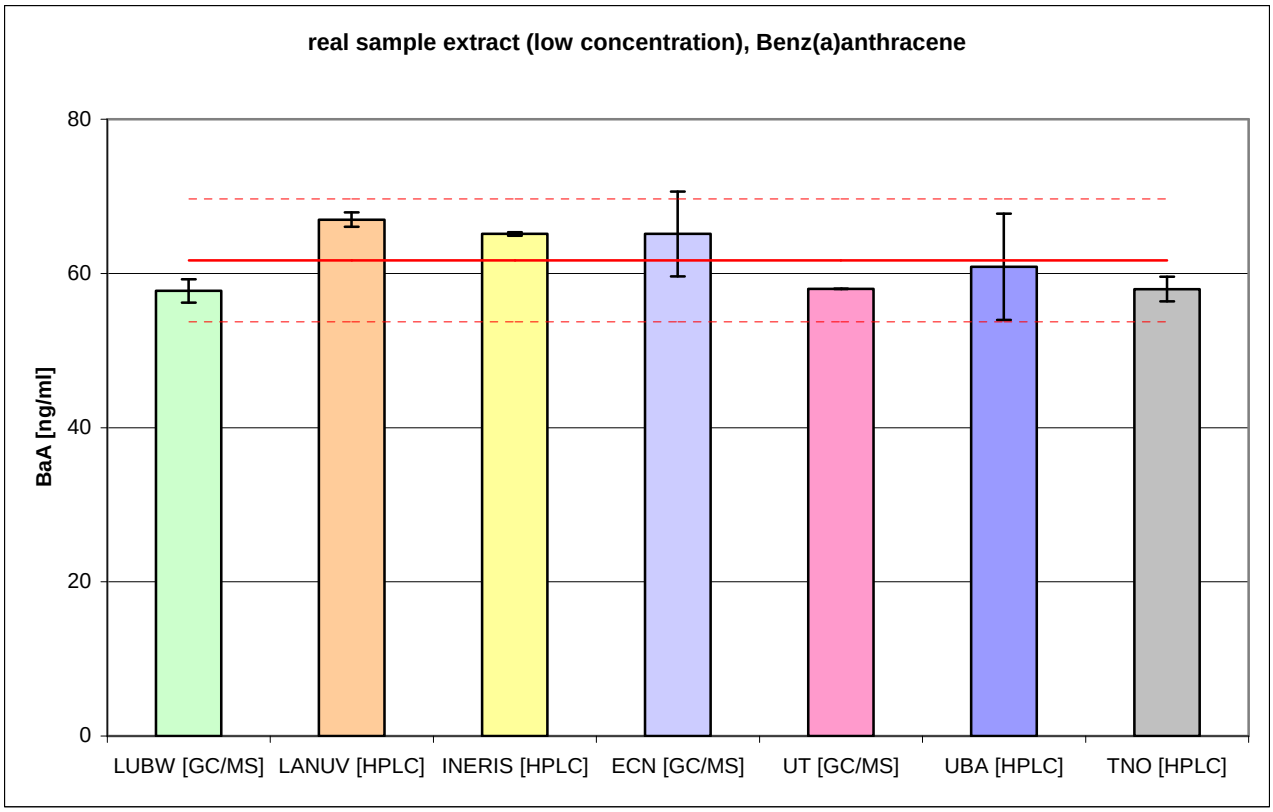

Figure 4.2.2: Real sample extract with a low PAH concentration, Benz(a)anthracene

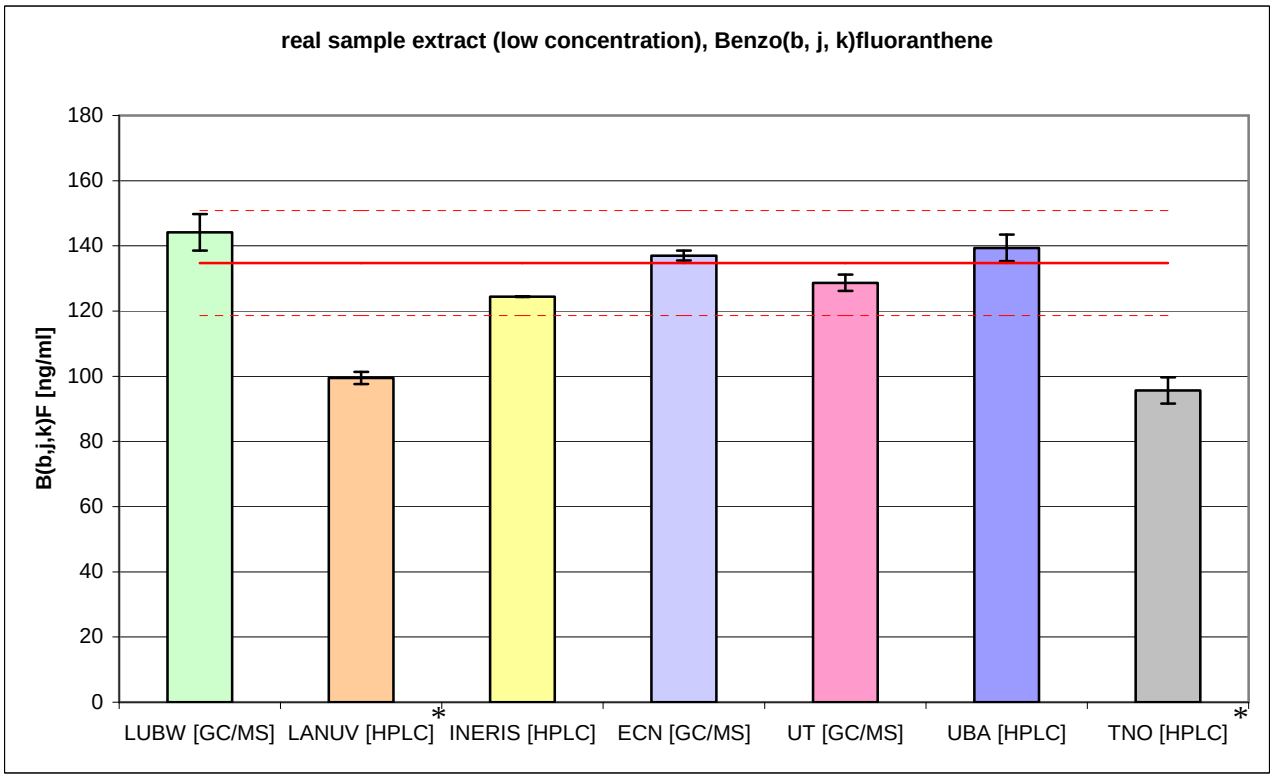

Figure 4.2.3: Real sample extract with a low PAH concentration, Benzo(b,j,k)fluoranthene

*** Benzo(j)fluoranthene not detected**

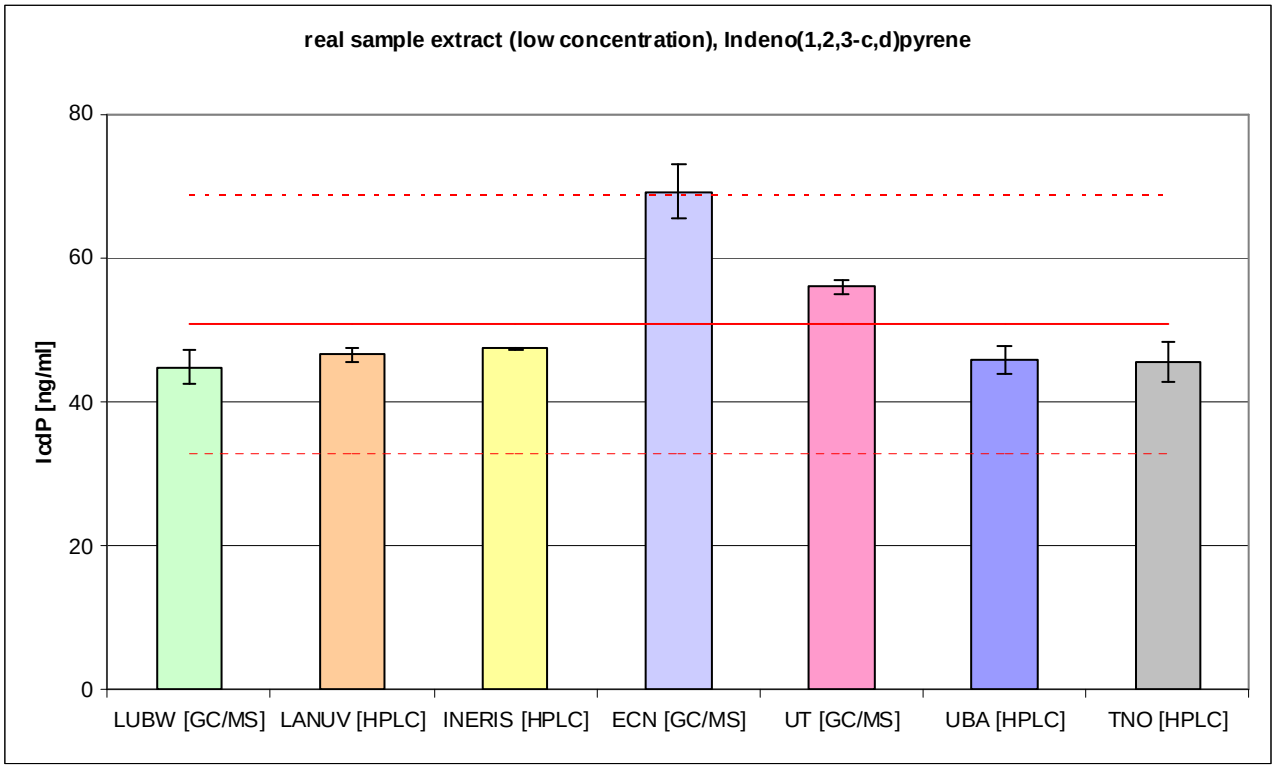

Figure 4.2.4: Real sample extract with a low PAH concentration, Indeno(1,2,3-cd)pyrene

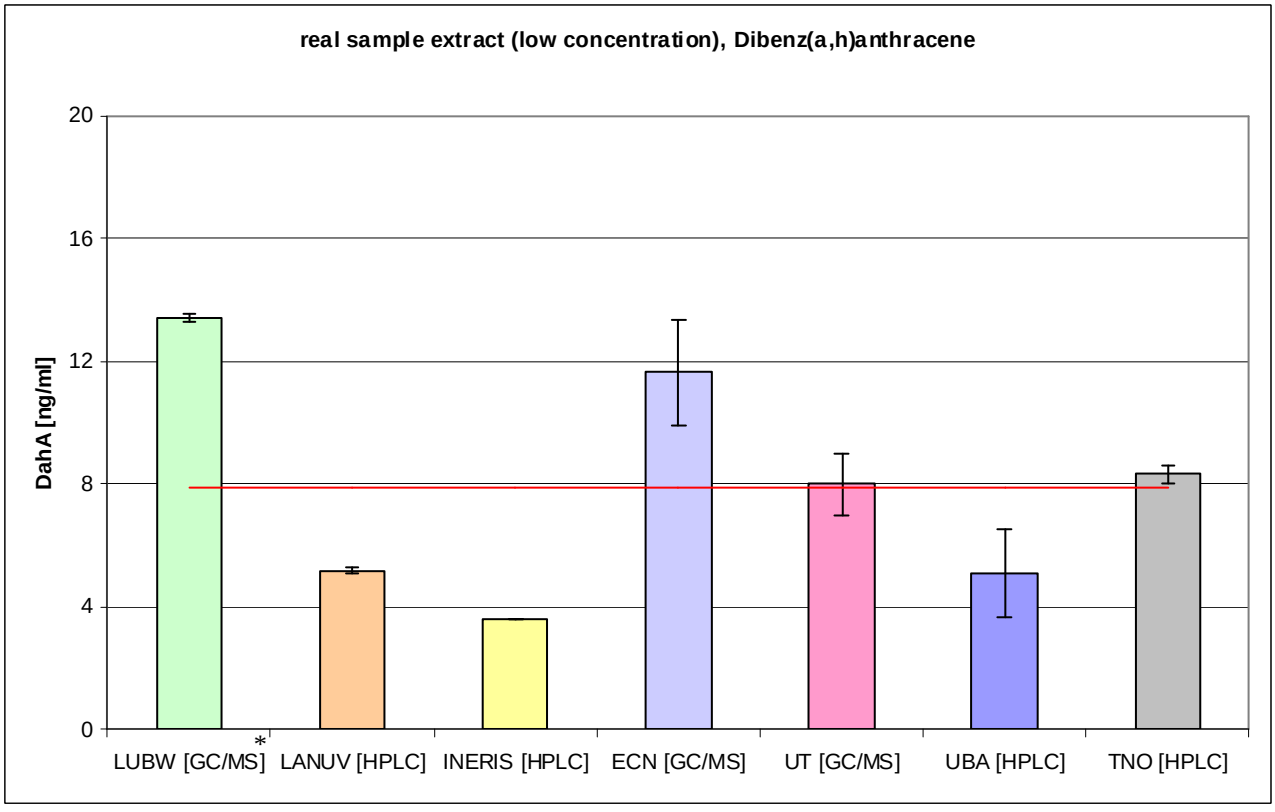

Figure 4.2.5: Real sample extract with a low PAH concentration, Dibenz(a,h)anthracene

*** Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum, we used an calculation factor for determination Dibenz(a,h)anthracene**

4.3 SAMPLE 3: REAL SAMPLE EXTRACT (HIGH PAH CONCENTRATION)

For the real sample extract 120 PM10 loaded filters of different measurement stations were extracted.
The following diagrams 4.3.1 to 4.3.5 show the results of all participating laboratories (annex 4).

The continuous line in the diagrams is the average of all results. The whiskers indicate $^{+}/_{-}$ 1 standard deviation of the three replicate analyses. The broken lines show the tolerance area of $^{+}/_{-}$ 2 standard deviation of the average (not possible for Dibenz(a,h)anthracene because of the strongly differences).

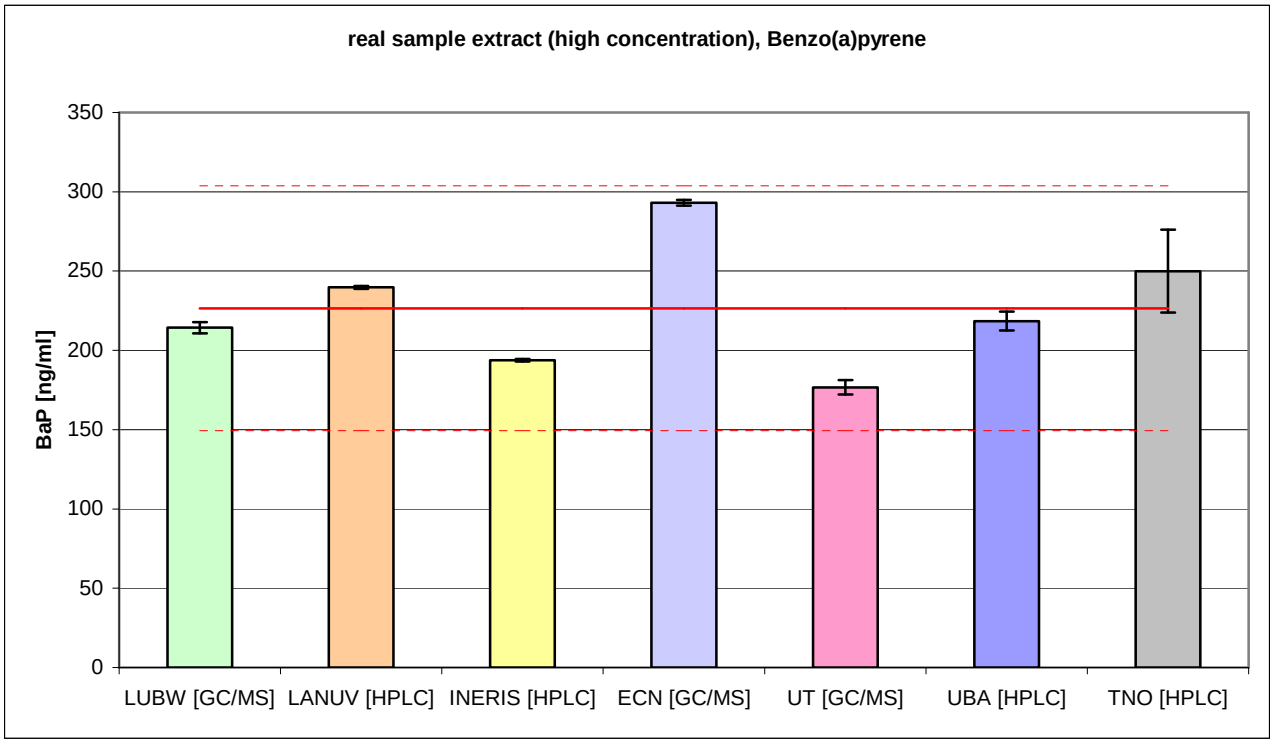

Figure 4.3.1: Real sample extract with a high PAH concentration, Benzo(a)pyrene

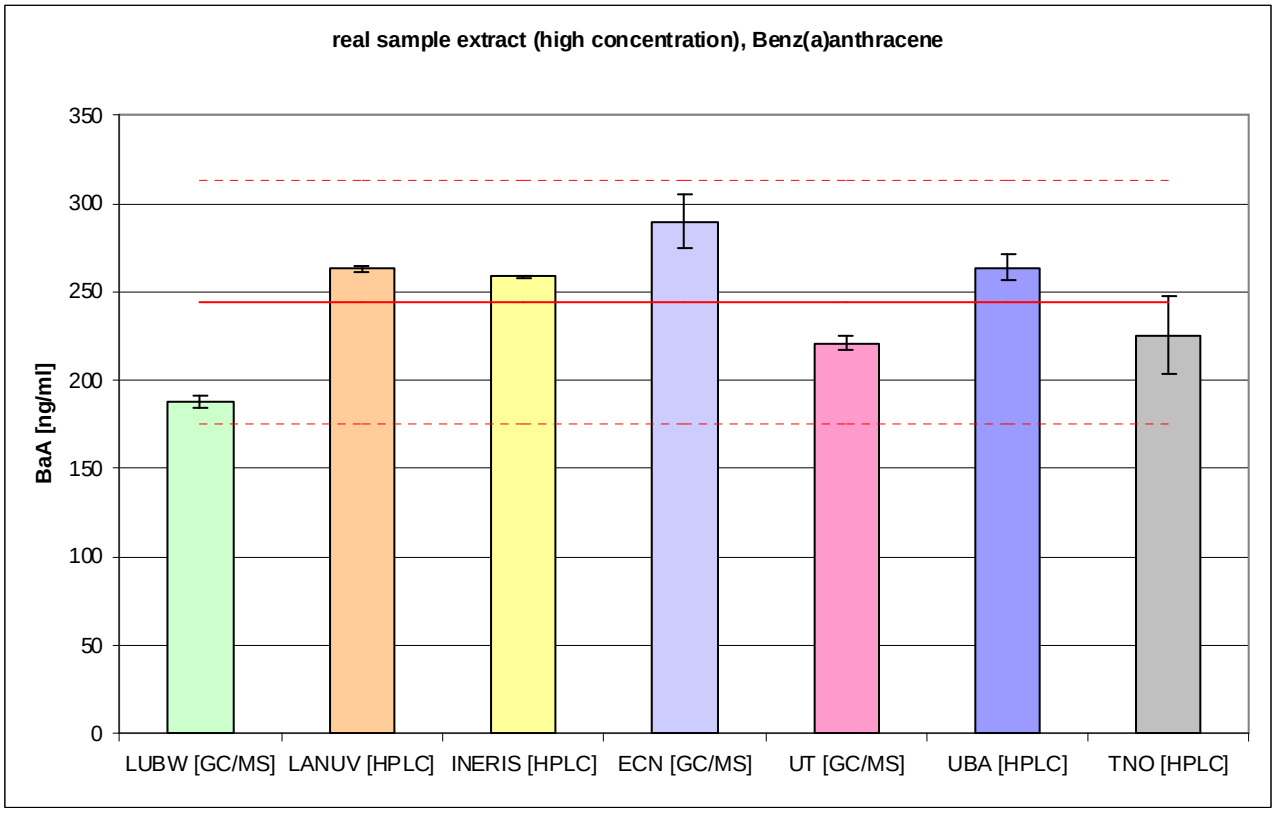

Figure 4.3.2: Real sample extract with a high PAH concentration, Benz(a)anthracene

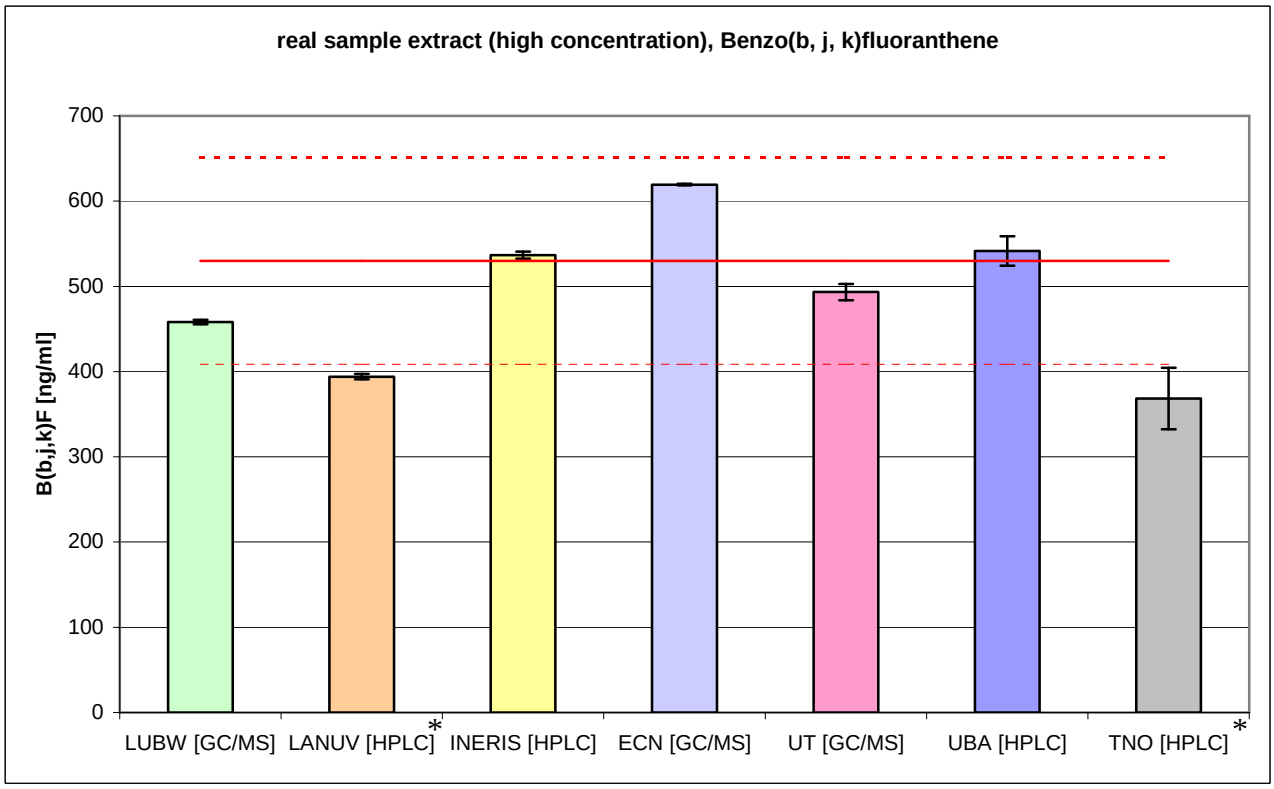

Figure 4.3.3: Real sample extract with a high PAH concentration, Benzo(b,j,k)fluoranthene

***Benzo(j)fluoranthene not detected**

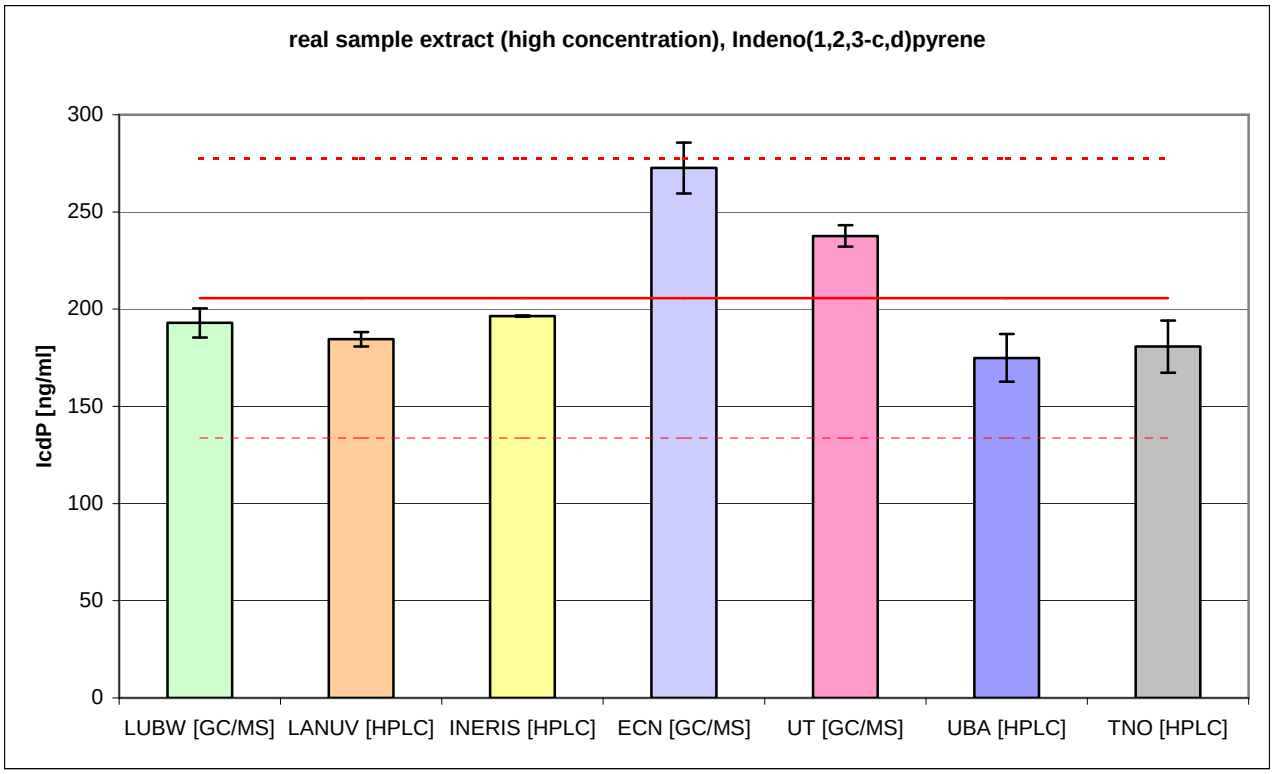

Figure 4.3.4: Real sample extract with a high PAH concentration, Indeno(1,2,3-cd)pyrene

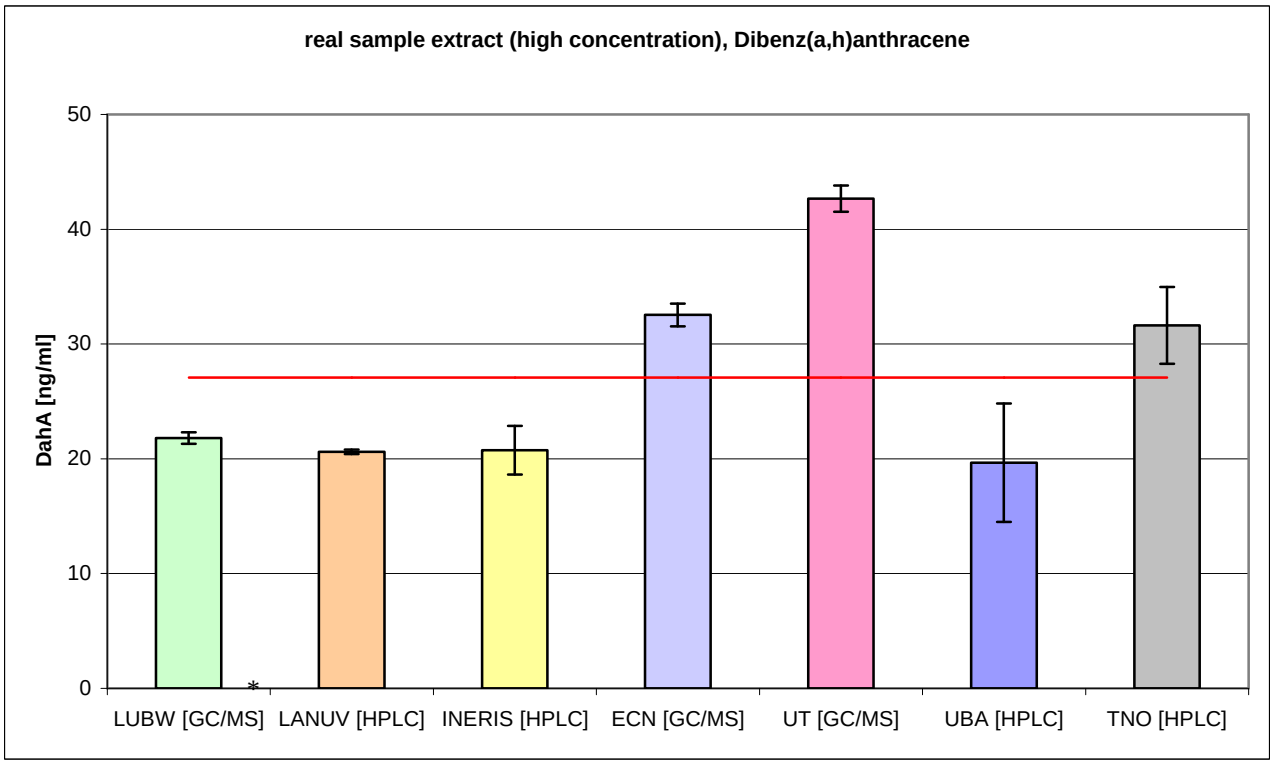

Figure 4.3.5: Real sample extract with a high PAH concentration, Dibenz(a,h)anthracene

*** Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum, we used an calculation factor for determination Dibenz(a,h)anthracene**

4.4 SAMPLE 4: RAIN WATER

For the rain water sample (sample 4) the content of different wet-only samplers from different sites in Baden-Württemberg were combined in a big tank and stored cool in the dark.
The following figures 4.4.1 to 4.4.5 show the results of all participating laboratories (annex 5).

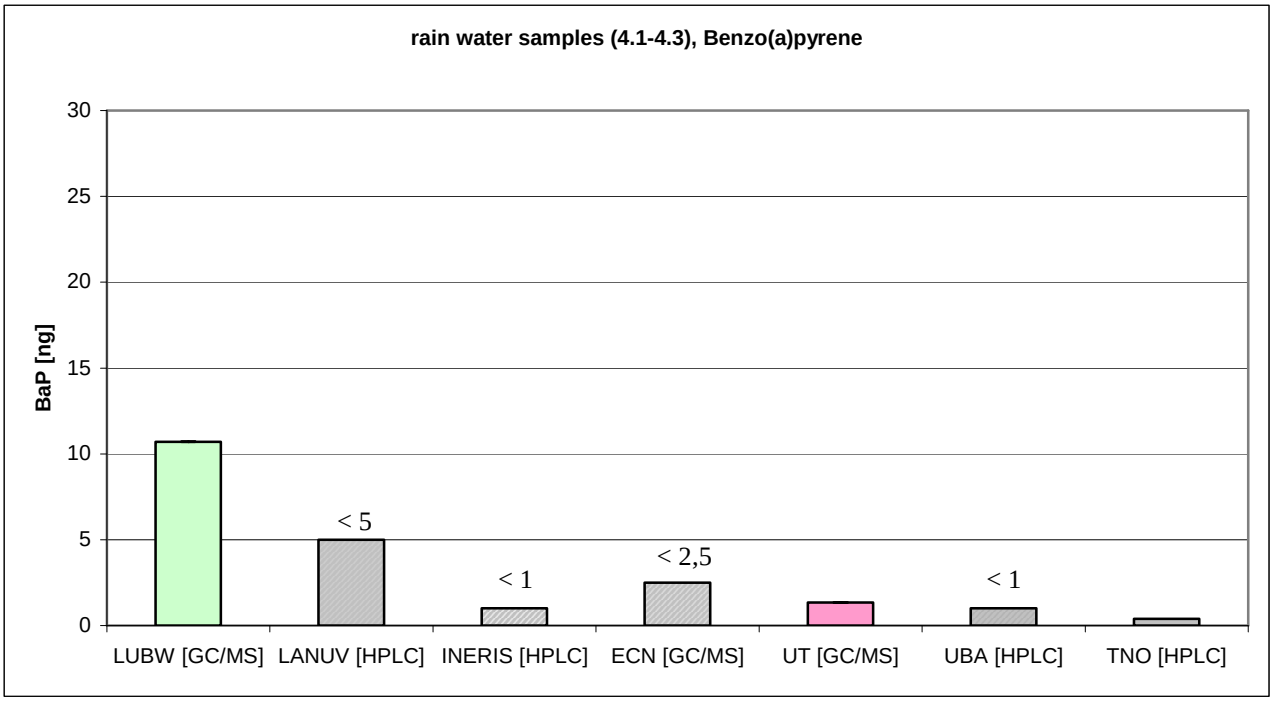

Figure 4.4.1: Rain water, Benzo(a)pyrene

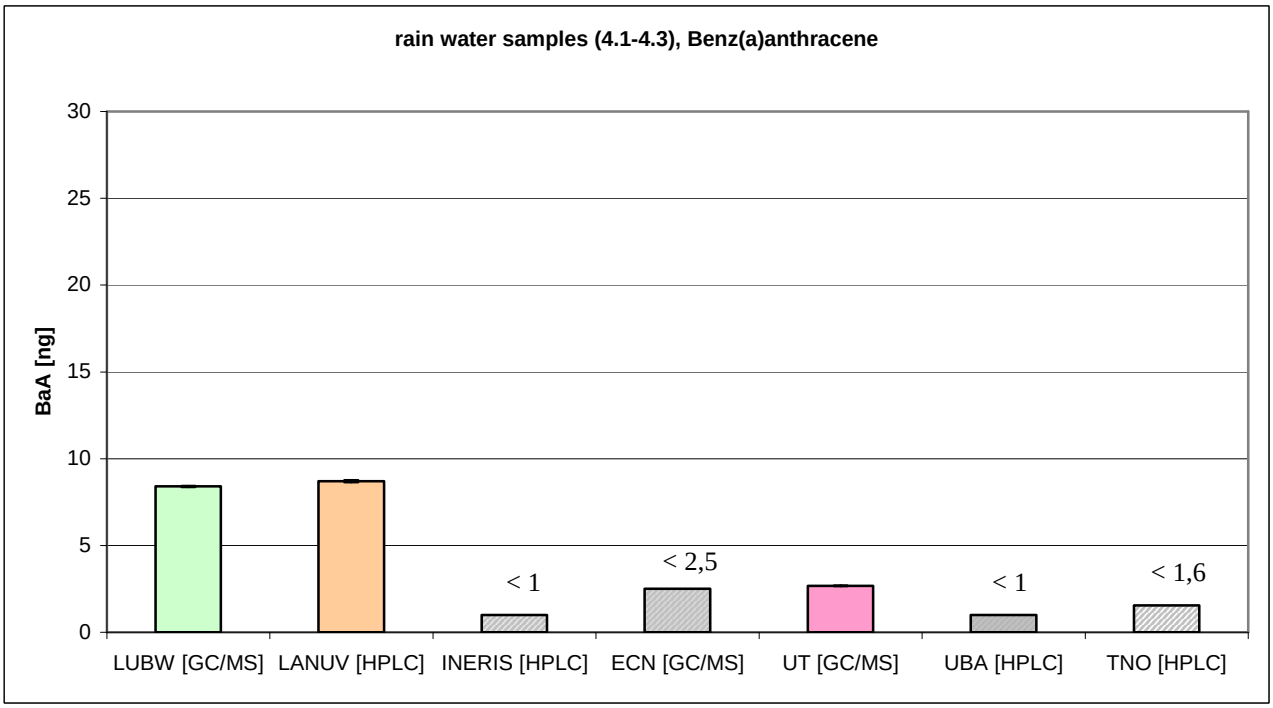

Figure 4.4.2: Rain water, Benz(a)anthracene

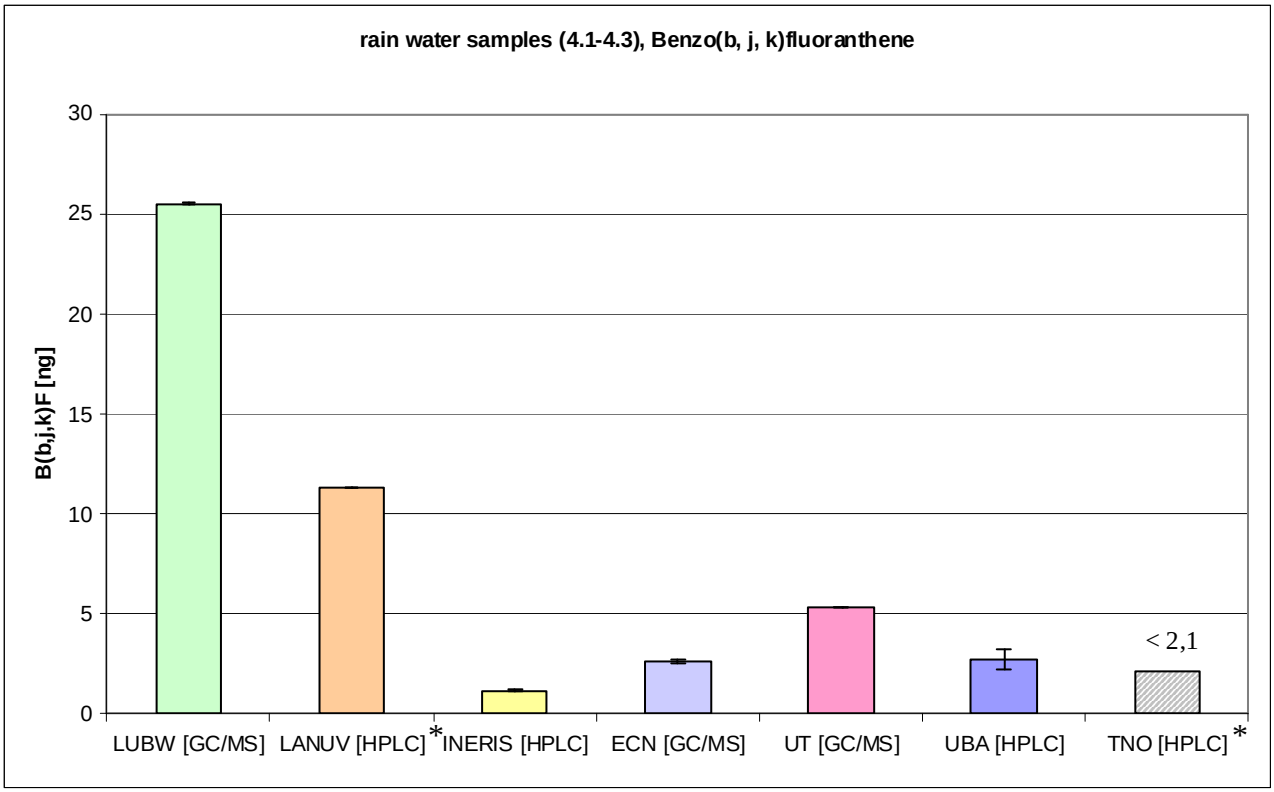

Figure 4.4.3: Rain water, Benzo(b,j,k)fluoranthene

***Benzo(j)fluoranthene not detected**

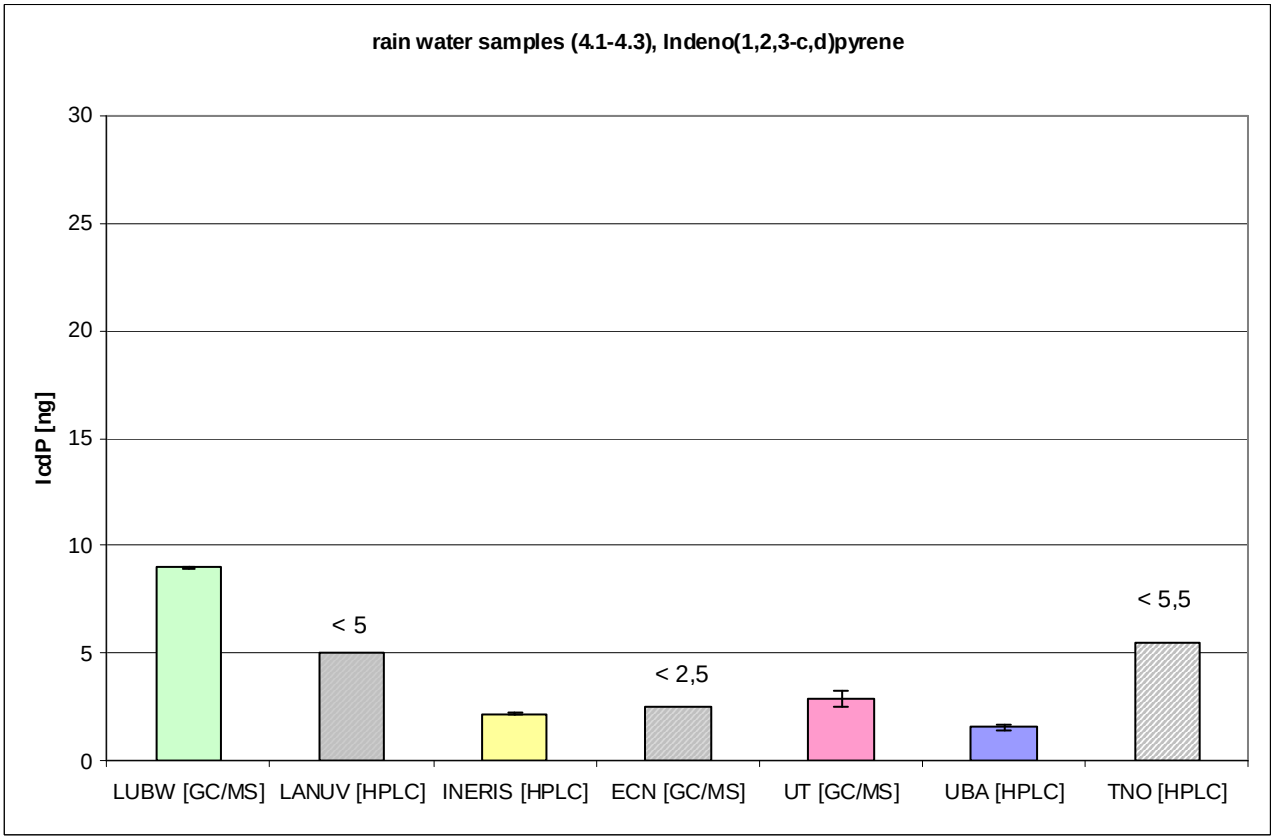

Figure 4.4.4: Rain water, Indeno(1,2,3-cd)pyrene

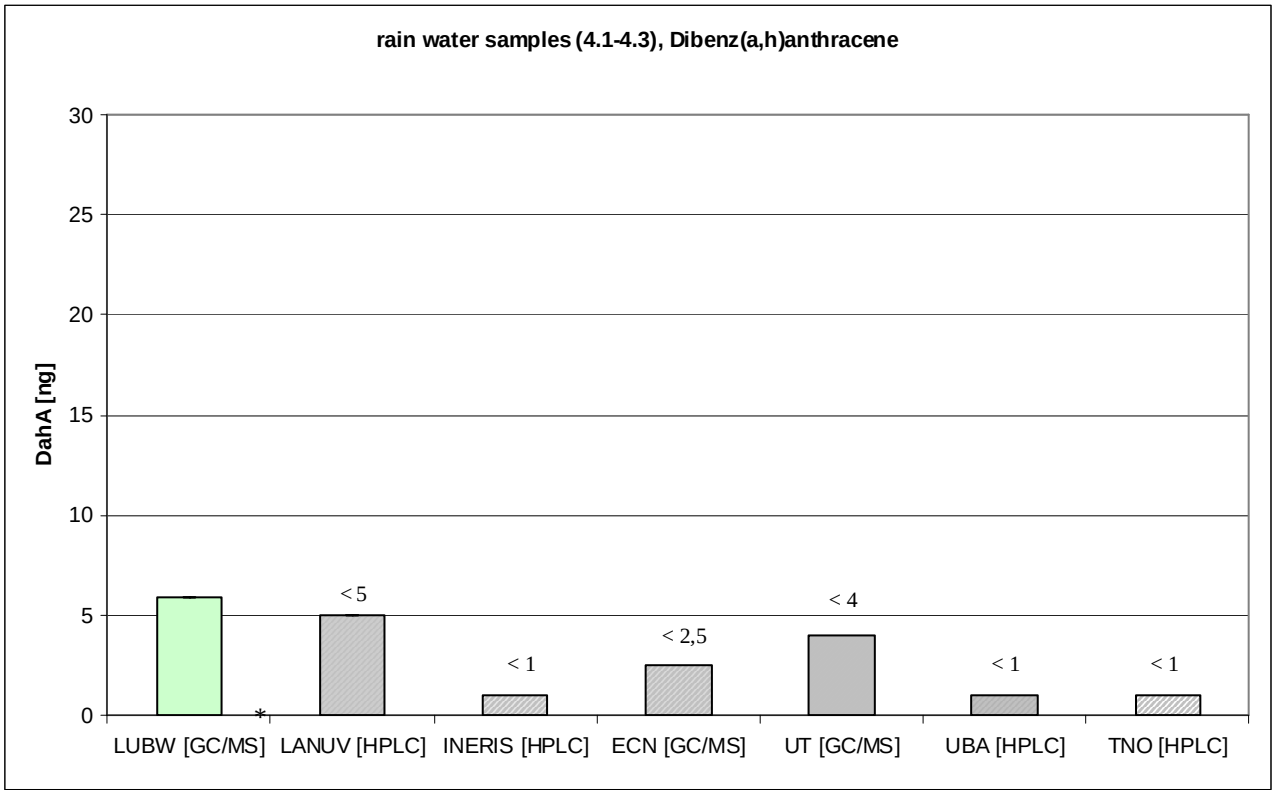

Figure 4.4.5: Rain water, Dibenz(a,h)anthracene

*** Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum, we used an calculation factor for determination Dibenz(a,h)anthracene**

4.5 SAMPLE 5: DUST SAMPLE (CRM) SUSPENDED IN RAIN WATER

For sample 5 an aliquot of the wet-only rain water from sample 4 was used. To every small portion of water an amount of a certified reference material was added (NIST, Urban Dust 1649a). Every laboratory got three samples doped with about 40 mg of the NIST material. In the following table 4.5 the concentrations of the relevant PAHs in 40 mg of the NIST material are shown.

Table 4.5 Concentrations of the relevant PAHs in 40 mg NIST material

PAH compounds	[ng absolute]
Benzo[a]pyrene	100,4
Benz[a]anthracene	88,3
Benzo[b,j]fluoranthene	258,0
Benzo[k]fluoranthene	76,5
Indeno[1,2,3-cd]pyrene	127,2
Dibenz[a,h]anthracene	11,5

The following figures 4.5.1 to 4.5.5 show the recovery rate in % of the doped rain water samples. The whiskers indicate $^{+}/_{-}$ 1 standard deviation of the three replicate analyses (annex 6).

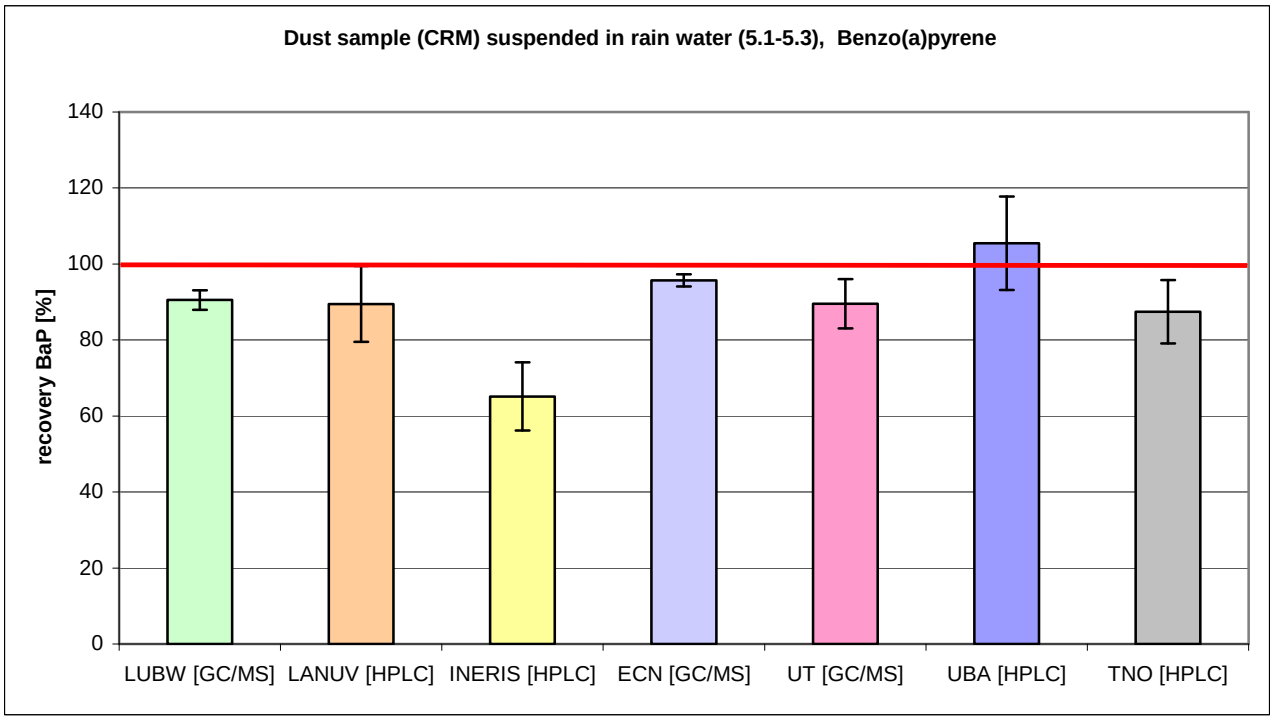

Figure 4.5.1: Dust sample (CRM) suspended in water, Benzo(a)pyrene

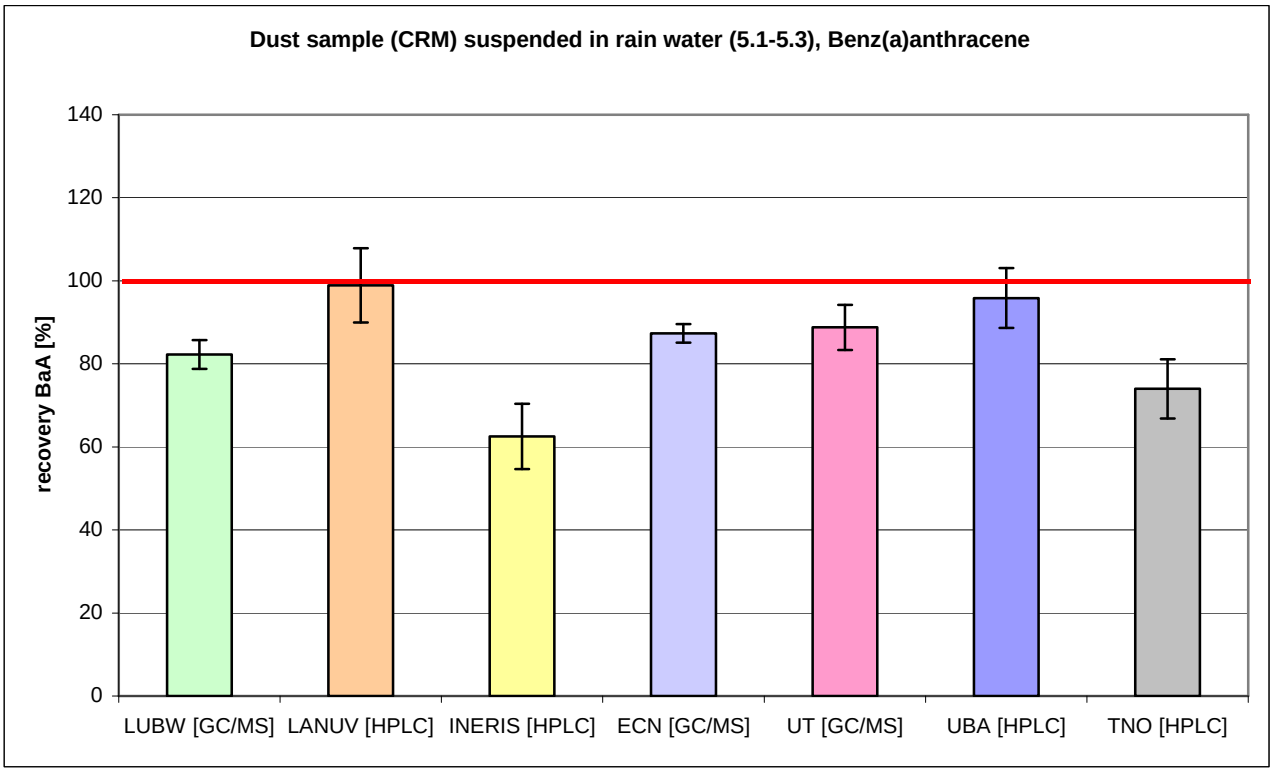

Figure 4.5.2: Dust sample (CRM) suspended in water, Benz(a)anthracene

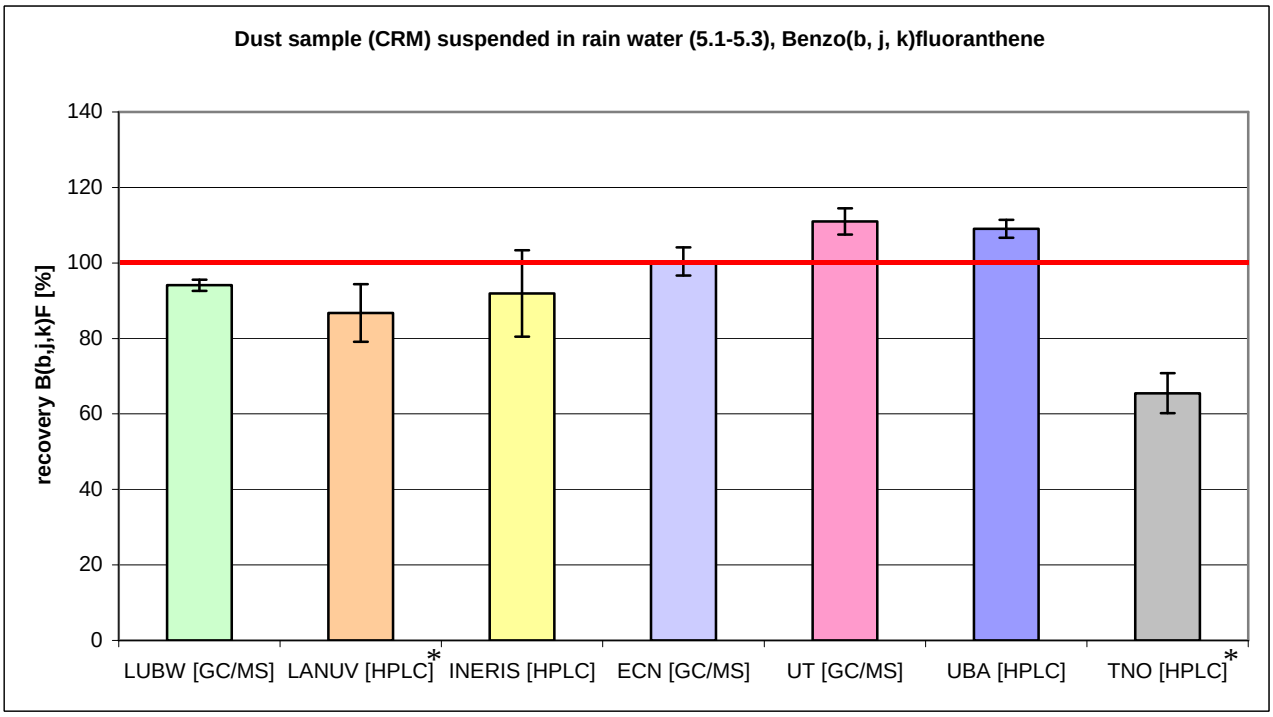

Figure 4.5.3: Dust sample (CRM) suspended in water, Benzo(b,j,k)fluoranthene

***Benzo(j)fluoranthene not detected**

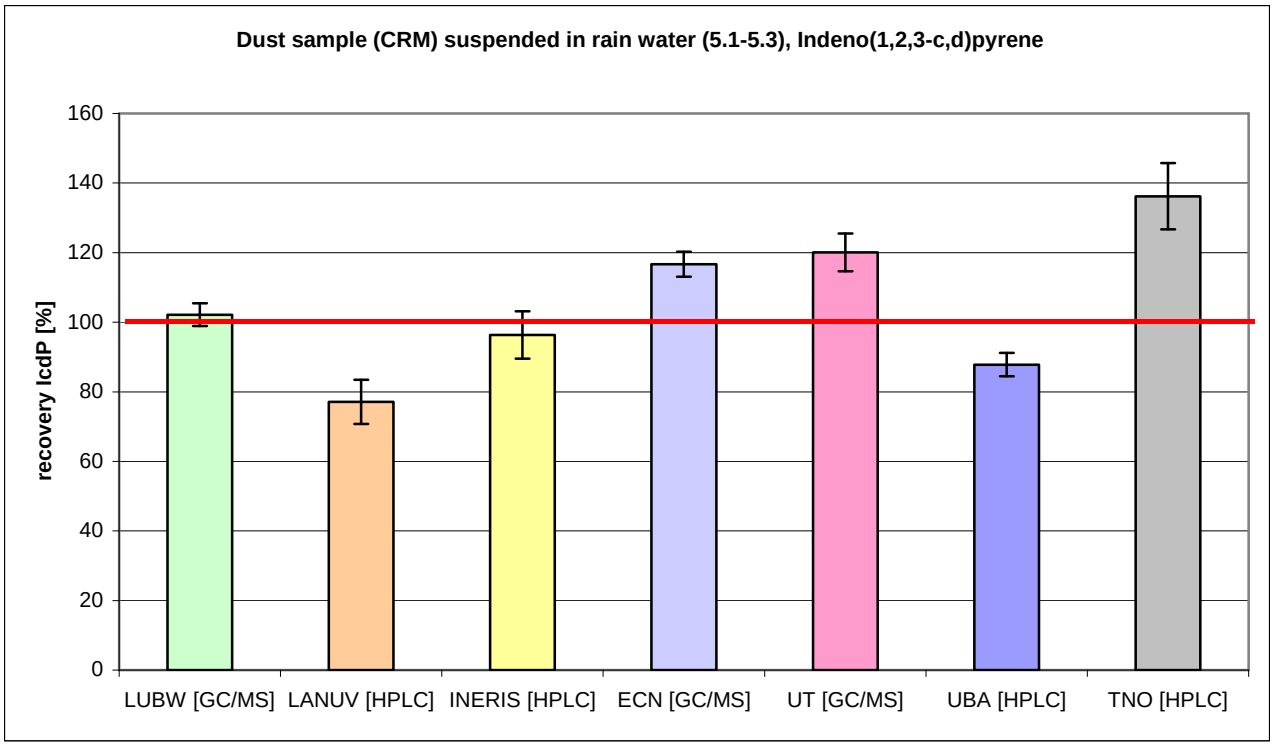

Figure 4.5.4: Dust sample (CRM) suspended in water, Indeno(1,2,3-cd)pyrene

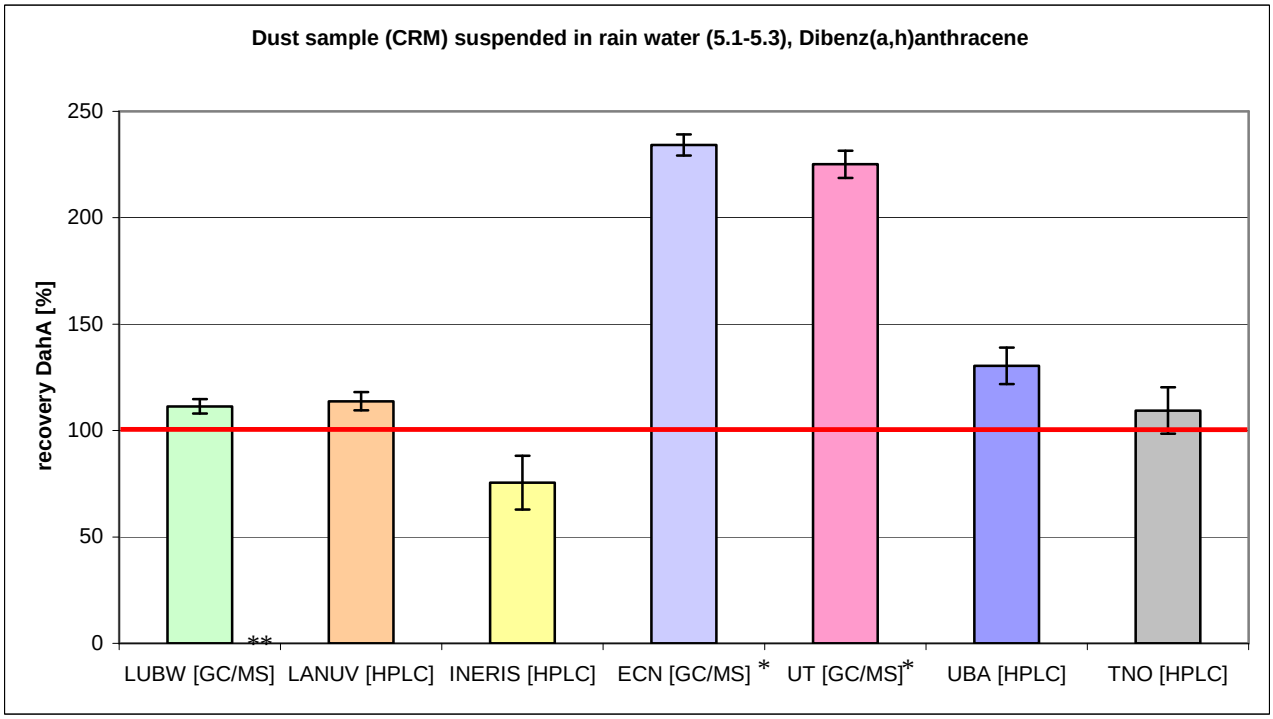

Figure 4.5.5: Dust sample (CRM) suspended in water, Dibenz(a,h)anthracene

*** Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum**

**** Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum, we used an calculation factor for determination Dibenz(a,h)anthracene**

II PART TWO

laboratory test 2

The laboratory test 2 was performed because of the partially insufficient PAH results in the rain water samples in the first laboratory test (sample 4). The concentration of the PAH in the sample 4 was very low and the results were not comparable.
The workgroup (CEN/TC 264/WG 21) decided to repeat this analyses in rain water with a concentration of BaP < 25 ng/sample (sample 7). Because of the low concentration of the rain water the samples were doped with about 10 mg certified reference material (NIST, Urban Dust 1649a).

5 Sample preparation and analysis of the test samples

The test samples were prepared and provided by LUBW to the participating laboratories. The test samples included one liquid calibration standard with a known concentration of PAH and two dust samples (CRM) suspended in rain water. Every laboratory used 6-methyl-chrysene as surrogate standard. Table 5.1 shows the specification of the test samples of the laboratory test.

Table 5.1: Specification of the test samples of the laboratory test

number	sample type	no. of aliquots	solvent	BaP conc.	amount
6	liquid calibration standard	1	toluene	100 ng/ml	ca. 1 ml
7	dust sample (CRM) suspended in rain water	2	water + 1% acetone+ 75 g NaCl	< 25 ng/ml	ca. 1000 ml

The liquid calibration standard included the relevant PAH compounds with a concentration of 100 ng/ml (400 ng/ml for Benzo(b,j,k)fluoranthene) and should be used for calibration check (sample 6).

For sample 7 rain water samples of different wet-only samplers from different sites in Baden-Württemberg were combined in a big tank and stored cool in the dark. One litre of the wet-only rain water was used for one sample. To every portion of water an amount of a certified reference material was added (NIST, Urban Dust 1649a). Every laboratory got two rain water samples doped with about 10 mg of the NIST material.

The participating laboratories should prepare and analyse the samples according to table 5.2.

Table 5.2: Preparation and analysis of the test samples

number	sample type	Extraction	Quantification	No. of replicate analysis
6	liquid calibration standard	not required	use for calibration check	3
7	dust sample (CRM) suspended in rain water	following Doc. N 159	following Doc. N 159	3

The analysis comprise the determination of following PAH compounds:

- Benzo(a)pyrene
- Benz(a)anthracene
- Benzo(b)fluoranthene*
- Benzo(j)fluoranthene*
- Benzo(k)fluoranthene*
- Indeno(1,2,3-cd)pyrene
- Dibenz(a,h)anthracene

(* the 3 isomers may be determined as sum)

6 Quality assurance

All samples for the laboratory test were distributed by LUBW on 11. March 2008. The samples arrived in the participating laboratories between 12.03.08 and 19.03.08.
Four laboratories prepared the samples according to the CEN-method (liquid-liquid-extraction), three laboratories prepared the samples according to SPE (solid-phase-extraction, Speedisk).
Three participating laboratories analysed the samples with GCMS and four participants analysed the samples with HPLC. The samples were analysed between 11.03. and 16.04.08.
All members used 6-methyl-chrysene as the surrogate standard. The recovery of the surrogate standard on average is in the range of 88 % to 118 %. The lower limit of the working range of the participating laboratories is between 1 ng/ml and 48,7 ng/ml.
The following table 6.1 gives information about the test samples:

Table 6.1 Information about the test samples

laboratories	**LUBW**	**LANUV**	**INERIS**	**ECN**	**UBA**	**TNO**	**UT**
arrival of the samples	11.03.2008	12.03.2008	17.03.2008	19.03.2008	12.03.2008	14.03.2008	13.03.2008
state of the samples after arriving in the lab	cool	cool	not cool	little cool	little cool	not cool	not specified
measuring method	GCMS	HPLC	HPLC	GCMS	HPLC	HPLC	GCMS
working up method (samples 7.1 – 7.2)	CEN	CEN	CEN	Speedisk	Speedisk	Speedisk	CEN
date of the analyses	11.03.2008	31.03.-01.04.08	01.-02.04.08	28.03.2008	10.04.2008	11.04.2008	16.04.2008
surrogate standard	6-MChr	6-MChr	6-MChr	6-MChr	6-MChr	6-MChr	6-MChr
amount of the added surrogate standard [ng]	100	54	100	760	100	470	50
average recovery rate of the surrogate standard [%]	118	89	90	88	98	Xaverage (7.1) = 48,85mV Xaverage (7.2) = 64,38mV ?	101
lower limit of the working range [ng/ml]	5	5	1	5	1	between 25,0-48,7 depends on compound	10

7 Results of the laboratory test 2

In the following chapters 7.1 to 7.2 the results of the second laboratory test are shown.
Every sample had to be analysed threefold to determine the standard deviation. The three isomers Benzo(b)fluoranthene, Benzo(j)fluoranthene and Benzo(k)fluoranthene could be detected as a sum.

7.1 SAMPLE 6: LIQUID CALIBRATION STANDARD

The liquid calibration standard (sample 6) was a mixture of 16 PAHs in toluene (Dr. Ehrenstorfer GmbH) with a concentration of 100 ng/ml of each compound (Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)pyrene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, Dibenz(a,h)anthracene, Benzo(ghi)perylene).
Benzo(j)fluoranthene was not included in the mixture so Benzo(j)fluoranthene was added to the standard with a concentration of 200 ng/ml. The liquid calibration standard had to be use for calibration check. The following diagrams 7.1.1 to 7.1.5 show the results of all participating laboratories (annex 7).

In all diagrams the continuous line is the target value (100 ng/ml or 400 ng/ml for Benzo(b,j,k)fluoranthene).
The whiskers indicate $^{+}/_{-}$ 1 standard deviation of the three replicate analyses.

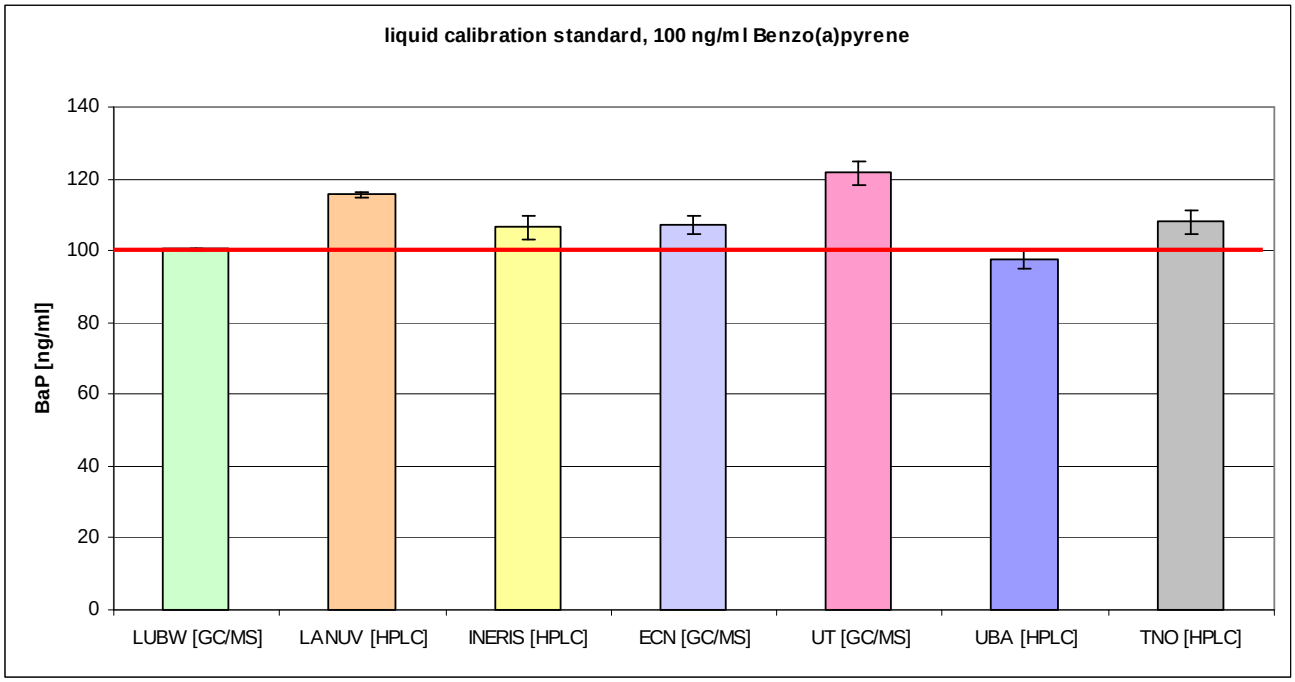

Figure 7.1.1: Liquid calibration standard with the target value of 100 ng/ml Benzo(a)pyrene

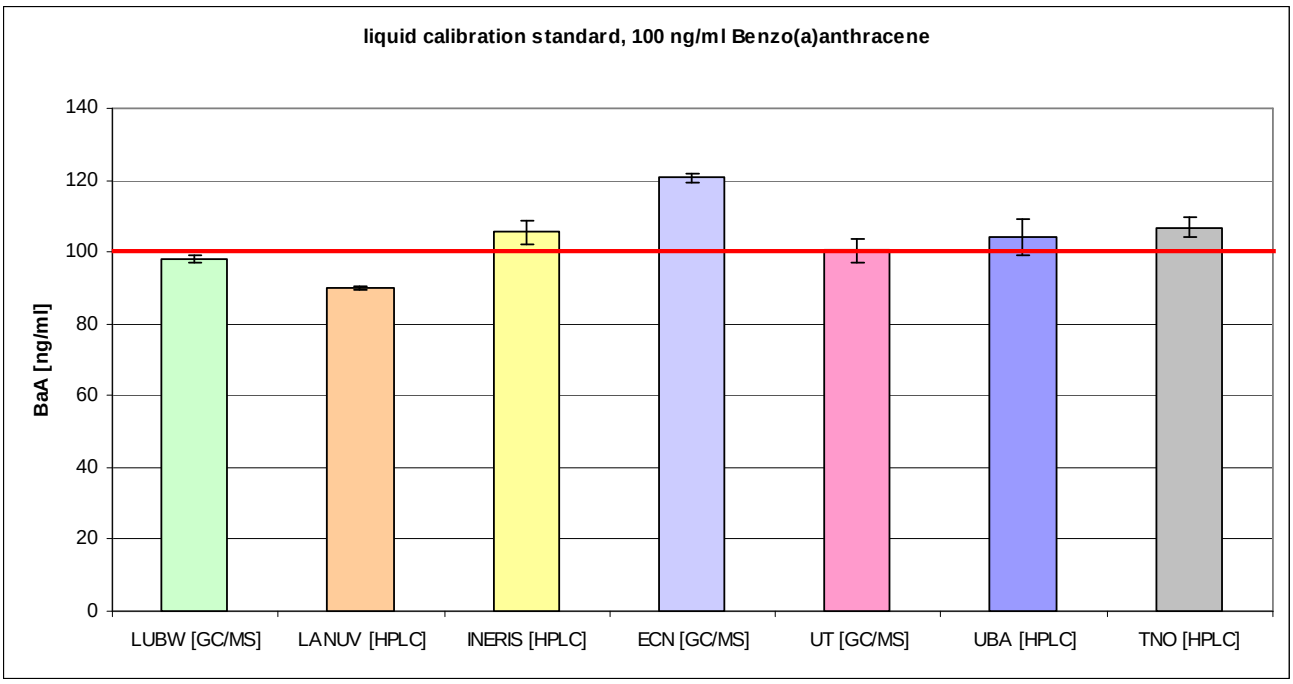

Figure 7.1.2: Liquid calibration standard with the target value of 100 ng/ml Benz(a)anthracene

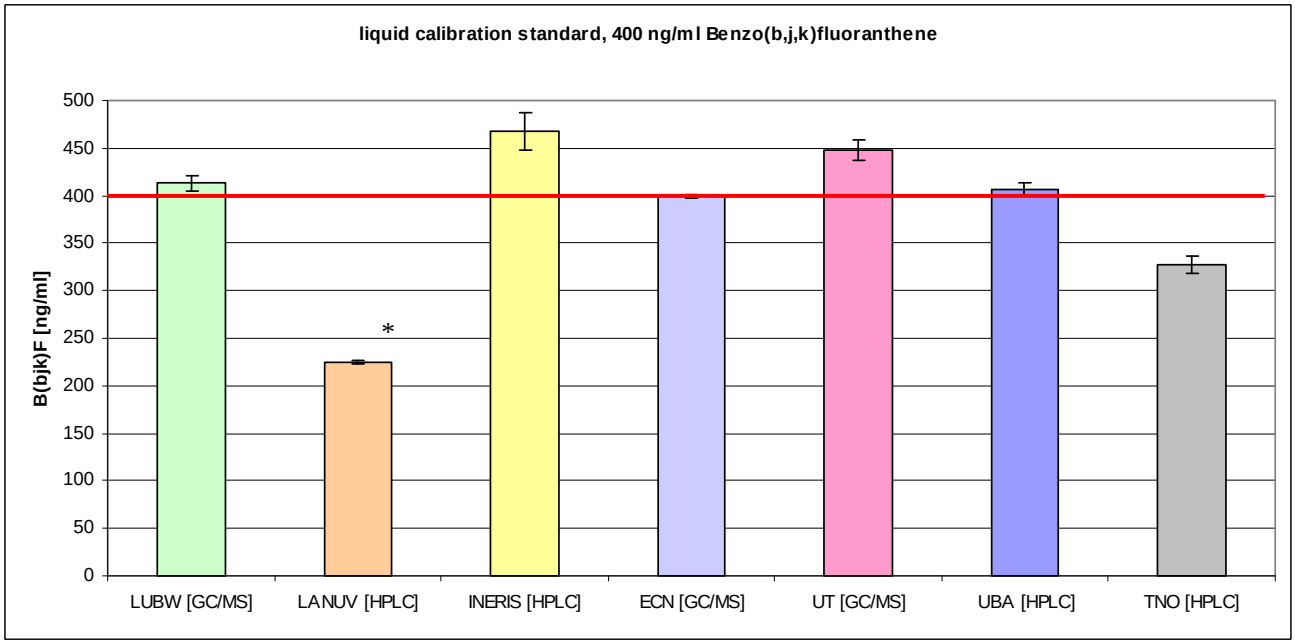

Figure 7.1.3: Liquid calibration standard with the target value of 400 ng/ml Benzo(b,j,k)fluoranthene

***Benzo(j)fluoranthene not detected**

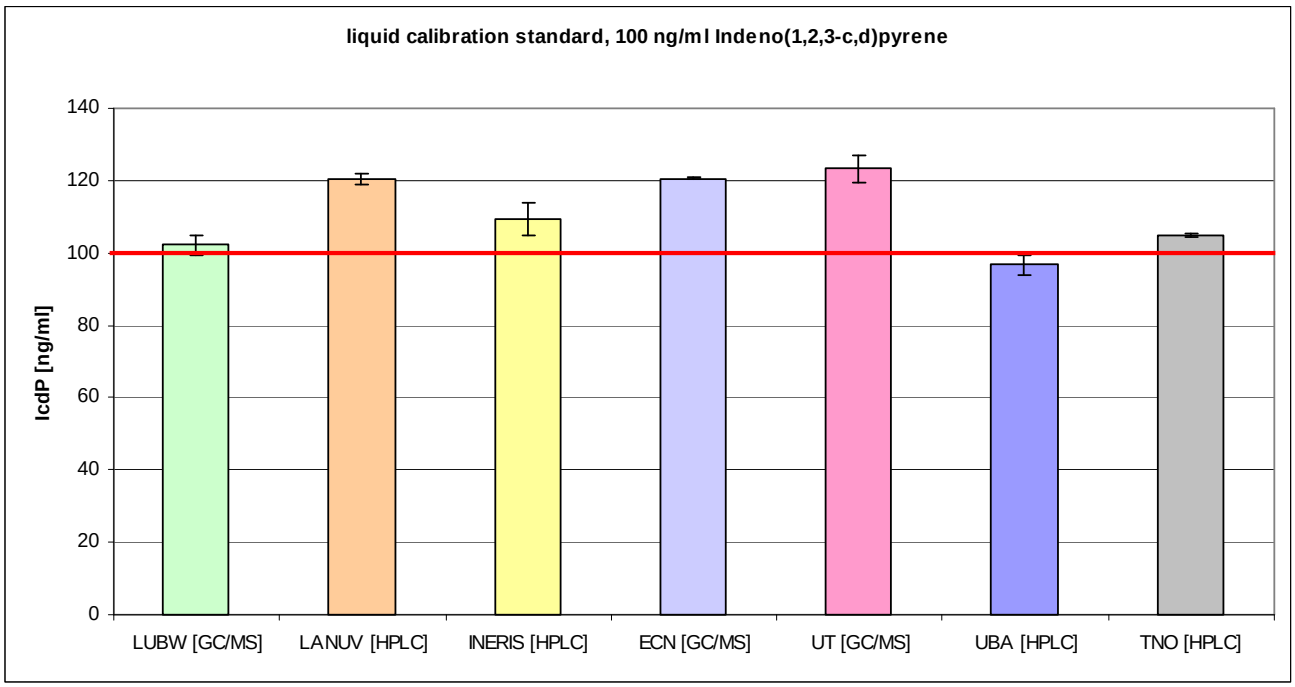

Figure 7.1.4: Liquid calibration standard with the target value of 100 ng/ml Indeno(1,2,3-cd)pyrene

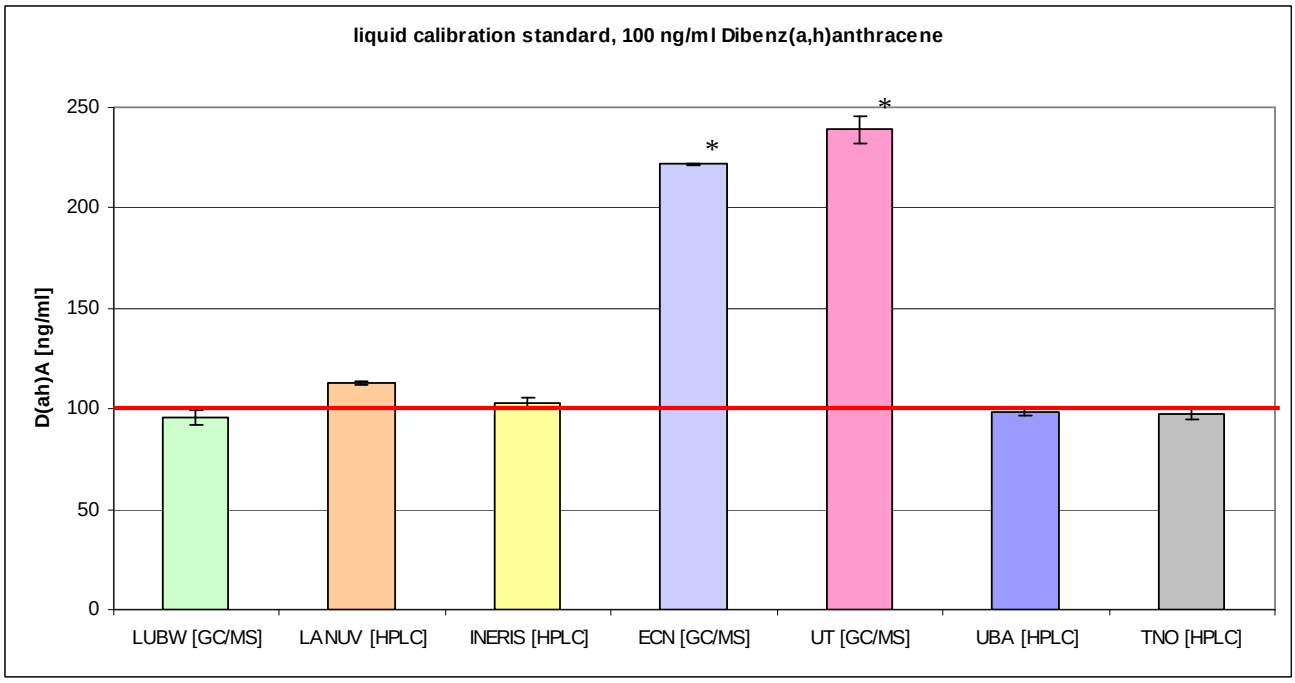

Figure 7.1.5: Liquid calibration standard with the target value of 100 ng/ml Dibenz(a,h)anthracene

*** Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum?? But Dibenz(a,c)anthracene wasn´t include in the standard!!**

7.2 SAMPLE 7: DUST SAMPLE (CRM) SUSPENDED IN RAIN WATER

For sample 7 one litre wet-only rain water was used. To every portion of water an amount of a certified reference material was added (NIST, Urban Dust 1649a). Every laboratory got two samples doped with about 10 mg of the NIST material. In the following table 7.2 the concentrations of the relevant PAHs in 10 mg of the NIST material are shown.

Table 7.2 Concentrations of the relevant PAHs in 10 mg NIST material

PAH compounds	[ng absolute]
Benzo[a]pyrene	25,1
Benz[a]anthracene	22,1
Benzo[b,j]fluoranthene	64,5
Benzo[k]fluoranthene	19,1
Indeno[1,2,3-cd]pyrene	31,8
Dibenz[a,h]anthracene	2,9

The following figures 7.2.1 to 7.2.5 show the recovery rate in % of the doped rain water samples. The whiskers indicate $^{+}/_{-}$ 1 standard deviation of the three replicate analyses (annex 8).

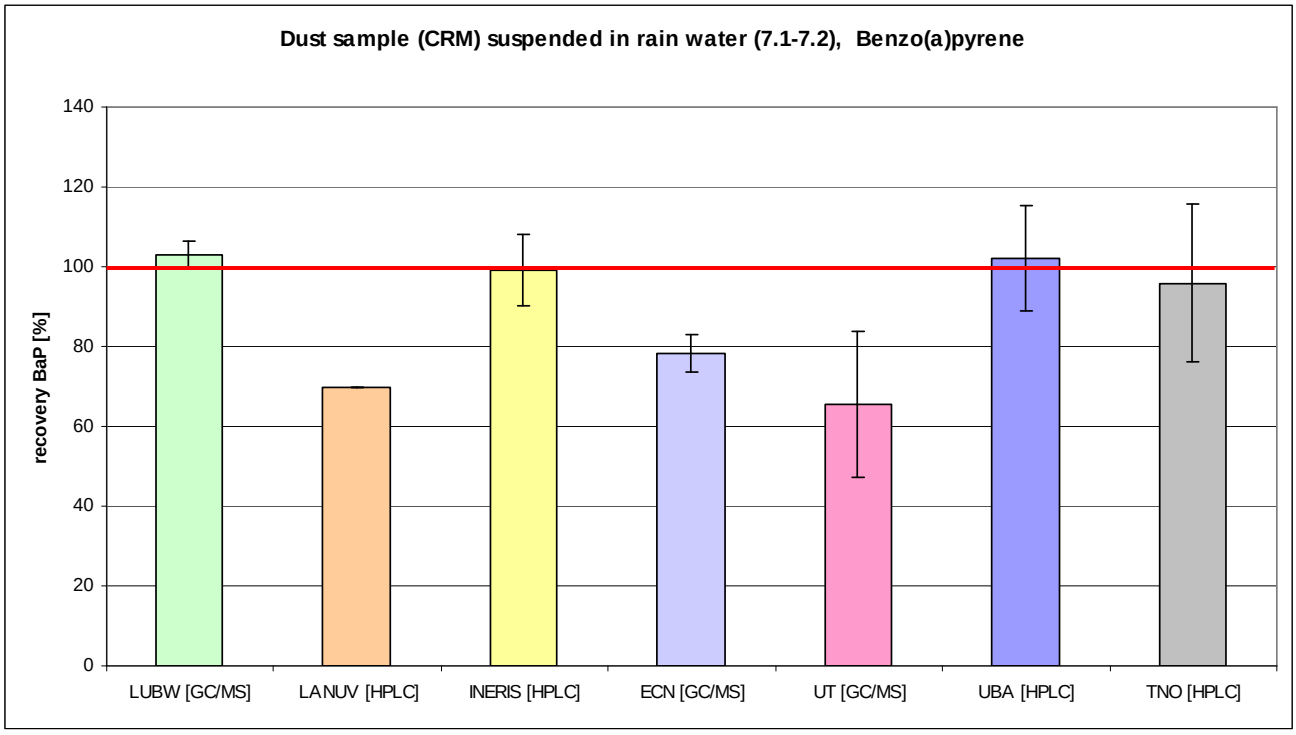

Figure 7.2.1: Dust sample (CRM) suspended in water, Benzo(a)pyrene

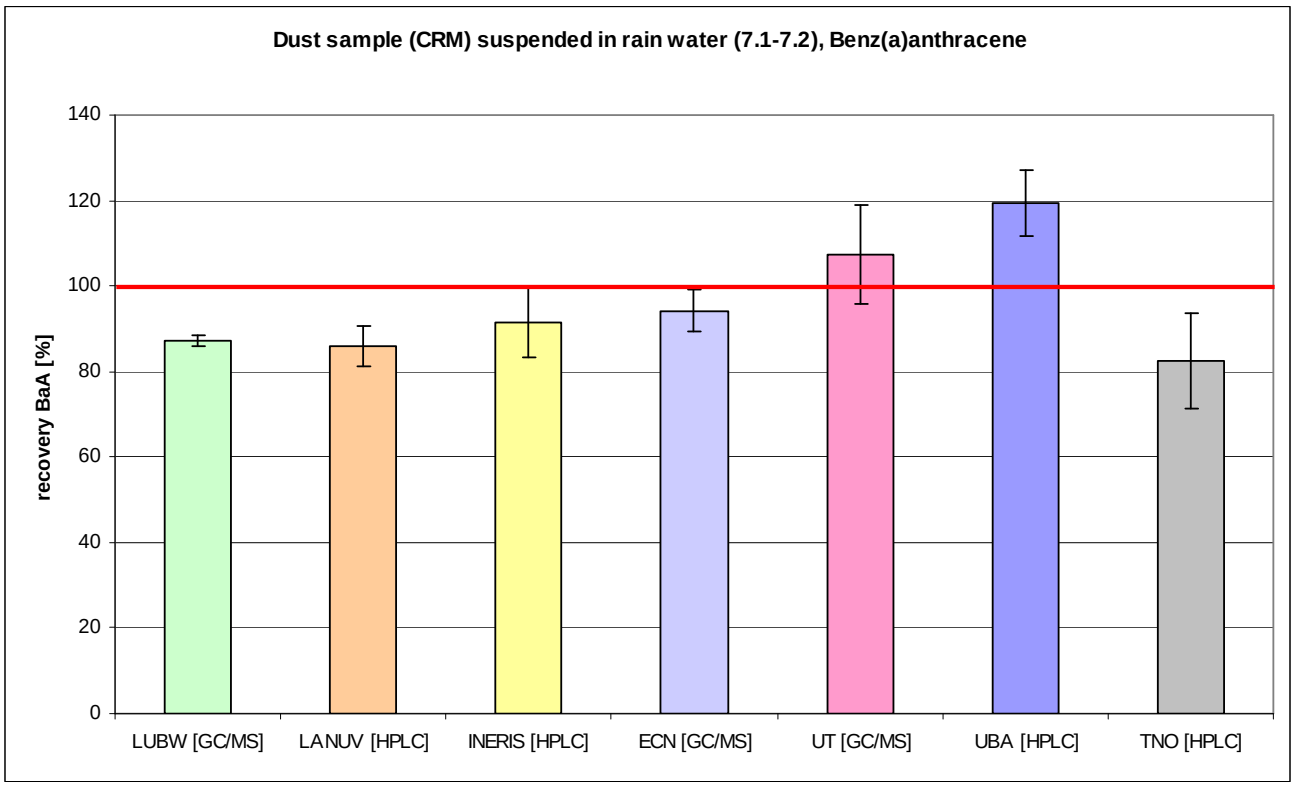

Figure 7.2.2: Dust sample (CRM) suspended in water, Benz(a)anthracene

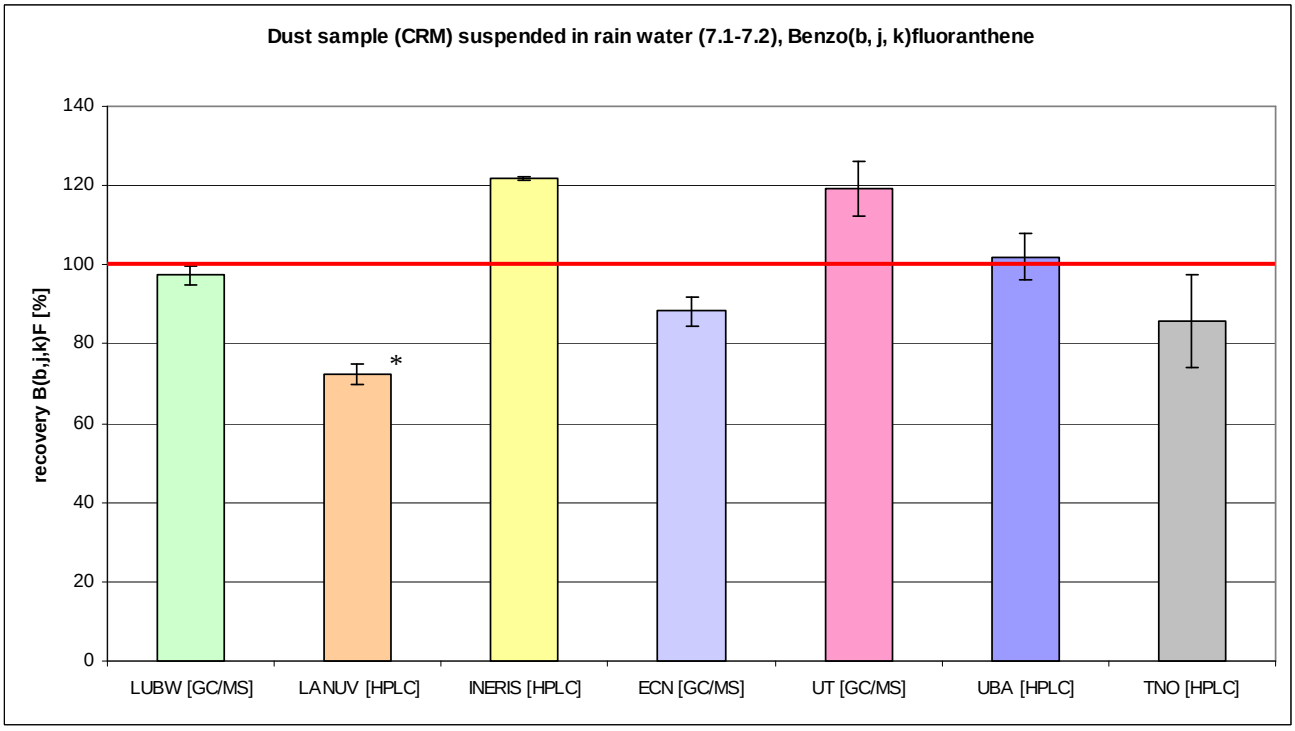

Figure 7.2.3: Dust sample (CRM) suspended in water, Benzo(b,j,k)fluoranthene

***Benzo(j)fluoranthene not detected**

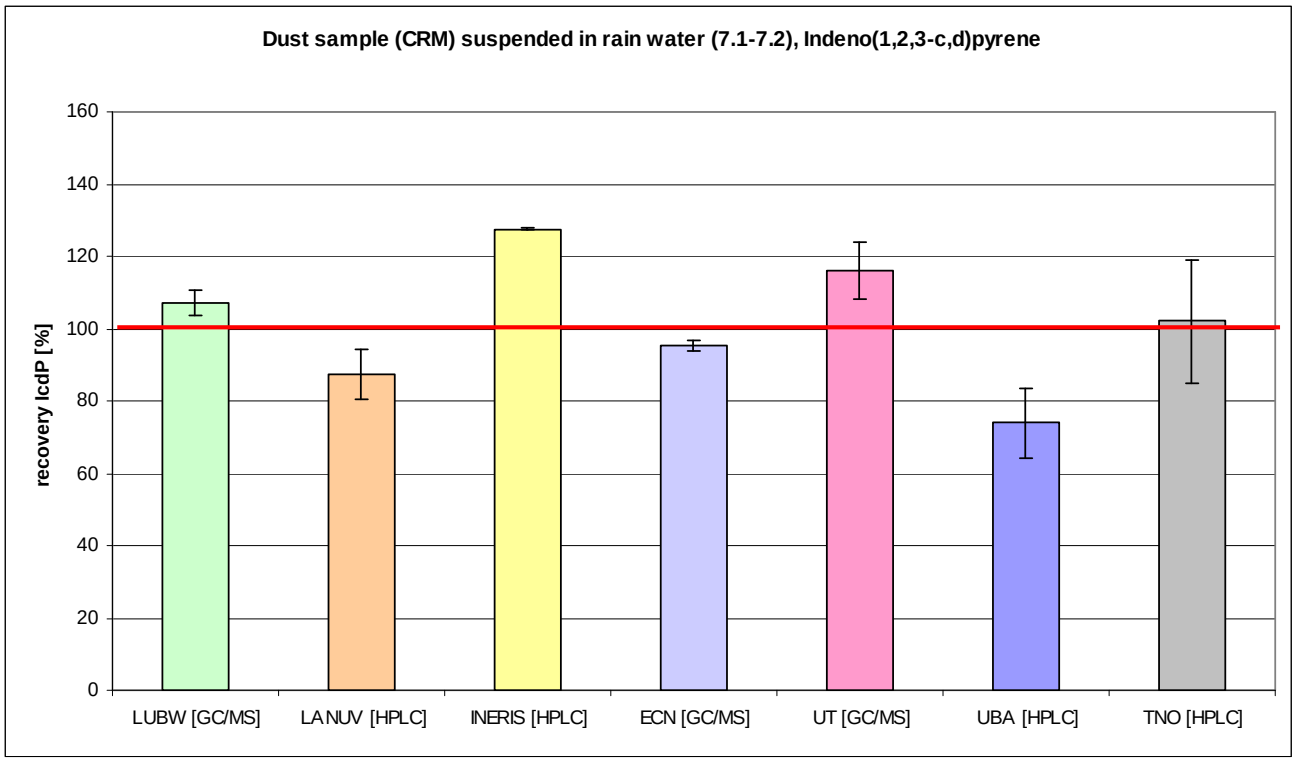

Figure 7.2.4: Dust sample (CRM) suspended in water, Indeno(1,2,3-cd)pyrene

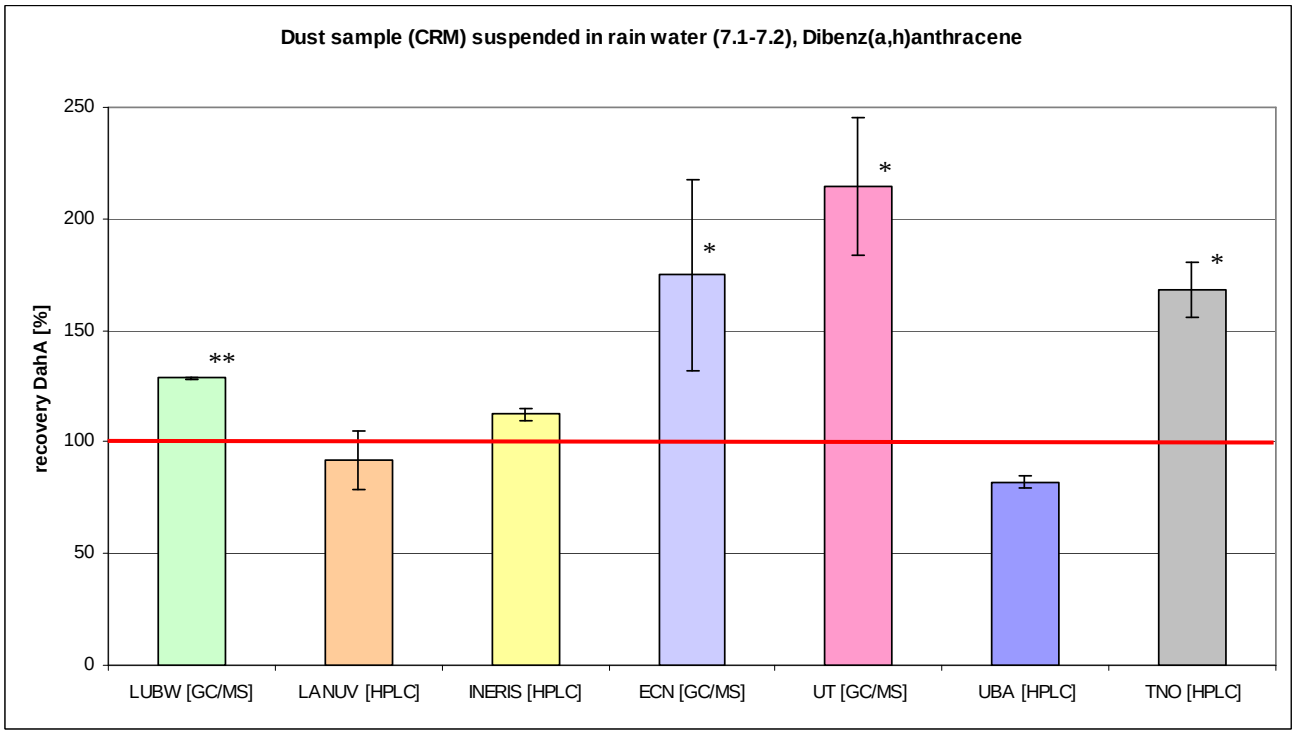

Figure 7.2.5: Dust sample (CRM) suspended in water, Dibenz(a,h)anthracene

Note: The target value of Dibenz(a,h)anthracene is about 2,9 ng absolute (for most laboratories under the working range!)

***Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum**

****** Dibenz(a,c)anthracene and Dibenz(a,h)anthracene detected as a sum, we used an calculation factor for determination Dibenz(a,h)anthracene**

8 Annex

Annex 1: Lab Test Laboratories WG 21

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Annex 2: Results liquid calibration standard (sample 1)

Lab: LUBW	sample 1 [ng/ml]	sample 1 [ng/ml]	sample 1 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	14.06.2007	14.06.2007	14.06.2007		
measuring method	GC/MS	GC/MS	GC/MS		
lower limit of the working range	5	5	5		
Benzo(a)pyrene	99,9	100,1	96,6	98,9	2,0
Benz(a)anthracene	95,6	94,3	94,5	94,8	0,7
Benzo(b)fluoranthene	91,2	95,4	94,8	93,8	2,3
Benzo(j)fluoranthene	96,3	101,9	98,4	98,9	2,8
Benzo(k)fluoranthene	99,3	98,8	96,2	98,1	1,7
sum of Benzo(b,j,k)fluoranthene	286,8	296,1	289,3	290,8	4,8
Indeno(1,2,3-c,d)pyrene	94,1	100,2	100,9	98,4	3,8
Dibenz(a,h)anthracene	99,0	100,3	97,5	98,9	1,4

Lab: LANUV	sample 1 [ng/ml]	sample 1 [ng/ml]	sample 1 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	21.06.2007	22.06.2007	25.06.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	5	5	5		
Benzo(a)pyrene	108,6	109,0	108,2	108,6	0,4
Benz(a)anthracene	108,3	109,2	108,3	108,6	0,5
Benzo(b)fluoranthene	107,0	107,9	107,1	107,3	0,5
Benzo(j)fluoranthene	not detected				
Benzo(k)fluoranthene	110,8	111,6	110,6	111,0	0,5
Indeno(1,2,3-c,d)pyrene	102,7	103,3	102,0	102,7	0,6
Dibenz(a,h)anthracene	112,7	113,6	112,9	113,1	0,5

Lab: INERIS	sample 1 [ng/ml]	sample 1 [ng/ml]	sample 1 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	20.06.2007	20.06.2007	20.06.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	100,2	99,8	100,5	100,2	0,3
Benz(a)anthracene	98,0	98,0	98,4	98,2	0,2
Benzo(b)fluoranthene	96,6	96,0	95,9	96,2	0,4
Benzo(j)fluoranthene	100,4	99,3	100,0	99,9	0,5
Benzo(k)fluoranthene	99,1	99,9	99,4	99,5	0,4
sum of Benzo(b,j,k)fluoranthene	296,2	295,2	295,3	295,6	0,5
Indeno(1,2,3-c,d)pyrene	103,9	103,3	102,1	103,1	1,0
Dibenz(a,h)anthracene	101,6	101,9	101,4	101,6	0,2

Lab: ECN	sample 1 [ng/ml]	sample 1 [ng/ml]	sample 1 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	12.07.2007	12.07.2007	12.07.2007		
measuring method	GCMS	GCMS	GCMS		
lower limit of the working range	2,5	2,5	2,5		
Benzo(a)pyrene	84,1	91,9	108,5	94,9	12,4
Benz(a)anthracene	90,9	85,0	90,5	88,8	3,3
sum of Benzo(b,j,k)fluoranthene	243,1	255,2	291,9	263,4	25,4
Indeno(1,2,3-c,d)pyrene	87,3	89,3	120,8	99,1	18,8
Dibenz(a,h)anthracene	90,6	93,0	114,4	99,3	13,1

Lab: UT	sample 1 [ng/ml]	sample 1 [ng/ml]	sample 1 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	17.09.2007	17.09.2007	17.09.2007		
measuring method	GCMS	GCMS	GCMS		
lower limit of the working range	3	3	3		
Benzo(a)pyrene	100	100	95	98,3	2,9
Benz(a)anthracene	111	110	112	111,0	1,0
sum of Benzo(b,j,k)fluoranthene	304	305	300	303,0	2,6
Indeno(1,2,3-c,d)pyrene	101	100	96	99,0	2,6
Dibenz(a,h)anthracene	108	106	104	106,0	2,0

Lab: UBA	sample 1 [ng/ml]	sample 1 [ng/ml]	sample 1 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	17.08.2007	17.08.2007	17.08.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	114	106	114	111,3	4,8
Benz(a)anthracene	108	93	107	102,8	8,7
Benzo(b)fluoranthene	107	105	105	105,5	1,3
Benzo(j)fluoranthene	116	96	110	107,0	10,3
Benzo(k)fluoranthene	121	126	111	119,5	7,4
sum of Benzo(b,j,k)fluoranthene	343	327	326	331,9	10,0
Indeno(1,2,3-c,d)pyrene	112	110	110	110,7	1,6
Dibenz(a,h)anthracene	111	106	109	108,8	2,3

Lab: TNO	sample 1 [ng/ml]	sample 1 [ng/ml]	sample 1 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	05.11.2007	05.11.2007	05.11.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	5,5	5,5	5,5		
Benzo(a)pyrene	87,0	94,2	93,5	91,6	4,0
Benz(a)anthracene	98,5	106,4	102,9	102,6	4,0
Benzo(b)fluoranthene	97,6	106,5	102,6	102,2	4,5
Benzo(j)fluoranthene	not detected				
Benzo(k)fluoranthene	100,0	110,3	105,9	105,4	5,2
Indeno(1,2,3-c,d)pyrene	98,3	109,3	108,0	105,2	6,0
Dibenz(a,h)anthracene	93,9	107,6	103,5	101,7	7,0

Annex 3: Results real sample extract – low PAH concentration- (sample 2)

Lab: LUBW	sample 2 [ng/ml]	sample 2 [ng/ml]	sample 2 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	11.06.2007	11.06.2007	11.06.2007		
measuring method	GC/MS	GC/MS	GC/MS	GC/MS	GC/MS
lower limit of the working range	5	5	5		
Benzo(a)pyrene	60,8	55,2	59,4	58,5	2,9
Benz(a)anthracene	58,8	56,0	58,4	57,7	1,5
Benzo(b)fluoranthene	66,4	64,7	66,4	65,8	1,0
Benzo(j)fluoranthene	38,0	31,1	36,5	35,2	3,6
Benzo(k)fluoranthene	43,9	42,0	43,4	43,1	1,0
sum of Benzo(b,j,k)fluoranthene	148,4	137,8	146,3	144,1	5,6
Indeno(1,2,3-c,d)pyrene	46,6	42,1	45,7	44,8	2,3
Dibenz(a,h)anthracene	13,5	13,3	13,4	13,4	0,1

Lab: LANUV	sample 2 [ng/ml]	sample 2 [ng/ml]	sample 2 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	21.06.2007	22.06.2007	25.06.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	5	5	5		
Benzo(a)pyrene	59,2	60,0	59,3	59,5	0,44
Benz(a)anthracene	66,0	67,9	67,0	67,0	0,93
Benzo(b)fluoranthene	62,2	63,6	65,4	63,8	1,59
Benzo(j)fluoranthene	not detected				
Benzo(k)fluoranthene	35,4	35,9	35,9	35,7	0,30
Indeno(1,2,3-c,d)pyrene	45,5	47,5	46,6	46,5	0,98
Dibenz(a,h)anthracene	5,0	5,2	5,2	5,2	0,10

Lab: INERIS	sample 2 [ng/ml]	sample 2 [ng/ml]	sample 2 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	20.06.2007	20.06.2007	20.06.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	50,7	50,6	50,9	50,8	0,1
Benz(a)anthracene	65,0	65,0	65,4	65,1	0,2
Benzo(b)fluoranthene	61,6	61,0	61,4	61,3	0,3
Benzo(j)fluoranthene	35,6	36,1	35,6	35,8	0,3
Benzo(k)fluoranthene	27,2	27,4	27,3	27,3	0,1
sum of Benzo(b,j,k)fluoranthene	124,4	124,5	124,4	124,4	0,1
Indeno(1,2,3-c,d)pyrene	47,2	47,4	47,6	47,4	0,2
Dibenz(a,h)anthracene	3,6	3,6	3,6	3,6	0,0

Lab: ECN	sample 2 [ng/ml]	sample 2 [ng/ml]	sample 2 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	12.07.2007	12.07.2007	12.07.2007		
measuring method	GCMS	GCMS	GCMS		
lower limit of the working range	2,5	2,5	2,5		
Benzo(a)pyrene	63,1	63,7	64,6	63,8	0,8
Benz(a)anthracene	74,1	64,4	64,7	67,7	5,5
sum of Benzo(b,j,k)fluoranthene	135,8	136,7	138,7	137,0	1,5
Indeno(1,2,3-c,d)pyrene	73,3	65,9	68,2	69,2	3,7
Dibenz(a,h)anthracene	10,2	11,2	13,5	11,6	1,7

Lab: UT	sample 2 [ng/ml]	sample 2 [ng/ml]	sample 2 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	17.09.2007	17.09.2007	17.09.2007		
measuring method	GCMS	GCMS	GCMS		
lower limit of the working range	3	3	3		
Benzo(a)pyrene	46	44	46	45,3	1,2
Benz(a)anthracene	58	58	58	58,0	0,0
sum of Benzo(b,j,k)fluoranthene	129	126	131	128,7	2,5
Indeno(1,2,3-c,d)pyrene	55	56	57	56,0	1,0
Dibenz(a,h)anthracene	9	7	8	8,0	1,0

Lab: UBA	sample 2 [ng/ml]	sample 2 [ng/ml]	sample 2 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	17.08.2007	17.08.2007	17.08.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	51	55	59	54,9	3,6
Benz(a)anthracene	59	55	68	60,9	6,9
Benzo(b)fluoranthene	58	59	60	58,7	0,9
Benzo(j)fluoranthene	49	52	53	51,3	1,7
Benzo(k)fluoranthene	28	29	31	29,4	1,5
sum of Benzo(b,j,k)fluoranthene	135	140	143	139,4	4,1
Indeno(1,2,3-c,d)pyrene	44	46	48	45,8	1,9
Dibenz(a,h)anthracene	5	4	7	5,1	1,4

Lab: TNO	sample 2 [ng/ml]	sample 2 [ng/ml]	sample 2 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	05.11.2007	05.11.2007	05.11.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	5,5	5,5	5,5		
Benzo(a)pyrene	58,2	62,2	61,0	60,5	2,09
Benz(a)anthracene	56,6	59,7	57,6	58,0	1,61
Benzo(b)fluoranthene	63,5	69,6	65,6	66,2	3,08
Benzo(j)fluoranthene	not detected				
Benzo(k)fluoranthene	28,7	30,6	29,1	29,4	0,99
Indeno(1,2,3-c,d)pyrene	45,7	42,6	48,2	45,5	2,81
Dibenz(a,h)anthracene	8,1	8,6	8,3	8,3	0,28

Annex 4: Results real sample extract – high PAH concentration- (sample 3)

Lab: LUBW	sample 3 [ng/ml]	sample 3 [ng/ml]	sample 3 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	11.06.2007	11.06.2007	11.06.2007		
measuring method	GC/MS	GC/MS	GC/MS	GC/MS	
lower limit of the working range	5	5	5		
Benzo(a)pyrene	218,1	211,2	213,6	214,3	3,5
Benz(a)anthracene	191,0	184,4	188,4	187,9	3,3
Benzo(b)fluoranthene	216,0	201,5	208,3	208,6	7,3
Benzo(j)fluoranthene	122,0	139,5	132,7	131,4	8,9
Benzo(k)fluoranthene	118,7	115,4	120,3	118,1	2,5
sum of Benzo(b,j,k)fluoranthene	456,7	456,4	461,3	458,1	2,7
Indeno(1,2,3-c,d)pyrene	198,7	184,4	195,6	192,9	7,5
Dibenz(a,h)anthracene	22,2	21,3	21,9	21,8	0,5

Lab: LANUV	sample 3 [ng/ml]	sample 3 [ng/ml]	sample 3 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	21.06.2007	22.06.2007	25.06.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	5	5	5		
Benzo(a)pyrene	239,9	240,6	238,7	239,7	1,0
Benz(a)anthracene	261,4	264,6	263,2	263,1	1,6
Benzo(b)fluoranthene	249,7	256,4	252,8	253,0	3,4
Benzo(j)fluoranthene	not detected				
Benzo(k)fluoranthene	141,1	140,4	141,9	141,1	0,7
Indeno(1,2,3-c,d)pyrene	184,0	188,4	181,0	184,5	3,7
Dibenz(a,h)anthracene	20,5	20,5	20,8	20,6	0,2

Lab: INERIS	sample 3 [ng/ml]	sample 3 [ng/ml]	sample 3 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	20.06.2007	20.06.2007	20.06.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	192,8	194,1	194,2	193,7	0,8
Benz(a)anthracene	258,7	258,4	259,3	258,8	0,5
Benzo(b)fluoranthene	262,8	264,0	264,7	263,8	0,9
Benzo(j)fluoranthene	158,1	161,7	164,5	161,4	3,2
Benzo(k)fluoranthene	111,4	110,9	111,5	111,3	0,3
sum of Benzo(b,j,k)fluoranthene	532,4	536,6	540,7	536,5	4,1
Indeno(1,2,3-c,d)pyrene	196,6	196,1	196,7	196,5	0,4
Dibenz(a,h)anthracene	20,6	18,7	22,9	20,7	2,1

Lab: ECN	sample 3 [ng/ml]	sample 3 [ng/ml]	sample 3 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	12.07.2007	12.07.2007	12.07.2007		
measuring methode	GCMS	GCMS	GCMS		
lower limit of the working range	2,5	2,5	2,5		
Benzo(a)pyrene	294,9	291,2	293,1	293,1	1,9
Benz(a)anthracene	307,2	279,2	282,6	289,7	15,3
sum of Benzo(b,j,k)fluoranthene	620,3	618,7	618,8	619,3	0,9
Indeno(1,2,3-c,d)pyrene	287,7	265,4	264,7	272,6	13,1
Dibenz(a,h)anthracene	33,4	31,5	32,7	32,5	1,0

Lab: UT	sample 3 [ng/ml]	sample 3 [ng/ml]	sample 3 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	17.09.2007	17.09.2007	17.09.2007		
measuring methode	GCMS	GCMS	GCMS		
lower limit of the working range	3	3	3		
Benzo(a)pyrene	172	177	181	176,7	4,5
Benz(a)anthracene	217	222	224	221,0	3,6
sum of Benzo(b,j,k)fluoranthene	483	495	502	493,3	9,6
Indeno(1,2,3-c,d)pyrene	232	238	243	237,7	5,5
Dibenz(a,h)anthracene	44	42	42	42,7	1,2

Lab: UBA	sample 3 [ng/ml]	sample 3 [ng/ml]	sample 3 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	17.08.2007	17.08.2007	17.08.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	217	225	213	218,4	6,0
Benz(a)anthracene	259	272	260	263,7	7,5
Benzo(b)fluoranthene	204	218	225	215,7	10,8
Benzo(j)fluoranthene	209	208	210	209,2	0,7
Benzo(k)fluoranthene	109	128	113	116,8	10,0
sum of Benzo(b,j,k)fluoranthene	522	555	548	541,7	17,3
Indeno(1,2,3-c,d)pyrene	171	189	165	174,9	12,3
Dibenz(a,h)anthracene	22	14	23	19,7	5,1

Lab: TNO	sample 3 [ng/ml]	sample 3 [ng/ml]	sample 3 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	05.11.2007	05.11.2007	05.11.2007		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	5,5	5,5	5,5		
Benzo(a)pyrene	221,2	256,5	272,2	250,0	26,1
Benz(a)anthracene	201,0	231,6	243,3	225,3	21,8
Benzo(b)fluoranthene	228,0	265,0	276,7	256,6	25,5
Benzo(j)fluoranthene	not detected				
Benzo(k)fluoranthene	100,0	114,9	120,4	111,8	10,6
Indeno(1,2,3-c,d)pyrene	166,0	183,8	192,4	180,7	13,5
Dibenz(a,h)anthracene	27,9	32,4	34,5	31,6	3,3

LUBW

Annex 5: Rain water (sample 4)

Lab: LUBW	sample 4.1	sample 4.1	sample 4.1	average	s. d.	sample 4.2	sample 4.2	sample 4.2	average	s. d.	sample 4.3	sample 4.3	sample 4.3	average	s. d.
date of the analyses	11.06.2007	11.06.2007	11.06.2007			11.06.2007	11.06.2007	11.06.2007			11.06.2007	11.06.2007	11.06.2007		
measuring method	GC/MS	GC/MS	GC/MS			GC/MS	GC/MS	GC/MS			GC/MS	GC/MS	GC/MS		
lower limit of the working range [ng/ml]	5	5	5			5	5	5			5	5	5		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	100	100	100			100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	114	110	117			58	58	58			96	95	94		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	10,8	10,6	10,8	10,7	0,1	10,7	10,7	10,6	10,7	0,1	10,7	10,8	10,7	10,7	0,1
Benz(a)anthracene [ng/sample]	8,3	8,4	8,4	8,4	0,1	8,4	8,4	8,4	8,4	0,0	8,5	8,5	8,4	8,5	0,0
Benzo(b)fluoranthene [ng/sample]	11,9	11,9	12,0	11,9	0,0	12,1	12,0	12,0	12,0	0,0	12,0	12,0	12,0	12,0	0,0
Benzo(j)fluoranthene [ng/sample]	3,0	3,0	2,9	3,0	0,1	3,2	3,1	3,0	3,1	0,1	3,0	2,9	3,0	3,0	0,1
Benzo(k)fluoranthene [ng/sample]	10,6	10,5	10,5	10,5	0,0	10,6	10,6	10,5	10,6	0,1	10,5	10,4	10,5	10,5	0,1
sum of Benzo(b, j, k) fluoranthene [ng/sample]	25,5	25,5	25,4	25,5	0,1	25,9	25,7	25,4	25,6	0,2	25,6	25,3	25,5	25,5	0,1
Indeno(1,2,3-c,d)pyrene [ng/sample]	9,3	9,1	9,1	9,1	0,1	8,9	8,8	8,8	8,8	0,1	9,0	9,0	9,1	9,0	0,0
Dibenz(a,h)anthracene [ng/sample]	6,0	6,0	6,0	6,0	0,0	5,9	5,9	5,9	5,9	0,0	5,9	5,9	5,9	5,9	0,0

Lab: LANUV	sample 4.1	sample 4.1	sample 4.1	average	s. d.	sample 4.2	sample 4.2	sample 4.2	average	s. d.	sample 4.3	sample 4.3	sample 4.3	average	s. d.
date of the analyses	21.06.2007	22.06.2007	25.06.2007			21.06.2007	22.06.2007	25.06.2007			21.06.2007	22.06.2007	25.06.2007		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	5	5	5			5	5	5			5	5	5		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	501,56	513,07	502,05			478,26	485,90	483,09			450,66	450,92	451,88		
recovery rate of the surrogate standard [%]	100,8	103,1	100,9			96,1	97,6	97,1			90,7	90,8	91,0		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	3,2	3,2	3,3	3,2	0,0	1,7	1,7	1,8	1,7	0,0	1,3	1,3	1,3	1,3	0,0
Benz(a)anthracene [ng/sample]	13,9	14,1	13,8	14,0	0,2	6,5	6,8	6,6	6,6	0,1	5,5	5,6	5,5	5,5	0,1
Benzo(b)fluoranthene [ng/sample]	9,6	9,8	9,7	9,7	0,1	5,6	5,5	5,4	5,5	0,1	4,9	4,9	4,7	4,8	0,1
Benzo(j)fluoranthene [ng/sample]	not detected														
Benzo(k)fluoranthene [ng/sample]	6,6	6,6	6,8	6,7	0,1	3,9	3,9	3,9	3,9	0,0	3,3	3,4	3,4	3,4	0,1
sum of Benzo(b, j, k) fluoranthene [ng/sample]															
Indeno(1,2,3-c,d)pyrene [ng/sample]	4,3	4,3	4,4	4,3	0,0	2,9	3,1	3,0	3,0	0,1	3,0	3,5	2,9	3,1	0,3
Dibenz(a,h)anthracene [ng/sample]	0,6	0,6	0,5	0,6	0,0	0,4	0,5	0,4	0,4	0,0	0,3	0,4	0,3	0,4	0,0

Lab: INERIS	sample 4.1	sample 4.1	sample 4.1	average	s. d.	sample 4.2	sample 4.2	sample 4.2	average	s. d.	sample 4.3	sample 4.3	sample 4.3	average	s. d.
date of the analyses	22.06.07	22.06.07	22.06.07			23.06.07	23.06.07	23.06.07			22.06.07	22.06.07	22.06.07		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	1,0	1,0	1,0			1,0	1,0	1,0			1,0	1,0	1,0		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	100	100	100			100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	82	83	82			73	73	73			81	81	82		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	<1	<1	<1	<1		<1	<1	<1	<1		<1	<1	<1	<1	
Benz(a)anthracene [ng/sample]	<1	<1	<1	<1		<1	<1	<1	<1		<1	<1	<1	<1	
Benzo(b)fluoranthene [ng/sample]	1,3	1,3	1,3	1,3	0,0	1,1	1,1	1,2	1,1	0,1	1,1	1,2	1,1	1,1	0,0
Benzo(j)fluoranthene [ng/sample]	<1	<1	<1	<1		<1	<1	<1	<1		<1	<1	<1	<1	
Benzo(k)fluoranthene [ng/sample]	<1	<1	<1	<1		<1	<1	<1	<1		<1	<1	<1	<1	
sum of Benzo(b, j, k) fluoranthene [ng/sample]	1,3	1,3	1,3	1,3	0,0	1,1	1,1	1,2	1,1	0,1	1,1	1,2	1,1	1,1	0,0
Indeno(1,2,3-c,d)pyrene [ng/sample]	2,3	2,3	2,3	2,3	0,0	2,2	2,1	2,0	2,1	0,1	2,3	2,2	2,2	2,2	0,1
Dibenz(a,h)anthracene [ng/sample]	<1	<1	<1	<1		<1	<1	<1	<1		<1	<1	<1	<1	

Lab: ENC	sample 4.1	sample 4.1	sample 4.1	average	s. d.	sample 4.2	sample 4.2	sample 4.2	average	s. d.	sample 4.3	sample 4.3	sample 4.3	average	s. d.
date of the analyses	12.07.07	12.07.07	12.07.07			12.07.07	12.07.07	12.07.07			12.07.07	12.07.07	12.07.07		
measuring method	GCMS	GCMS	GCMS			GCMS	GCMS	GCMS			GCMS	GCMS	GCMS		
lower limit of the working range [ng/ml]	2,5	2,5	2,5			2,5	2,5	2,5			2,5	2,5	2,5		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	500	500	500			500	500	500			500	500	500		
recovery rate of the surrogate standard [%]	94,5	94,5	94,5			101,8	94,5	94,5			99,9	94,5	94,5		
working up method	Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk		
Benzo(a)pyrene [ng/sample]	0,9	<LOD	<LOD			0,4	<LOD	<LOD			0,6	<LOD	<LOD		
Benz(a)anthracene [ng/sample]	0,8	0,8	0,7	0,8	0,0	0,6	0,5	0,4	0,5	0,1	0,7	0,6	0,7	0,7	0,1
sum of Benzo(b, j, k) fluoranthene [ng/sample]	2,4	2,4	2,4	2,4	0,0	3,2	3,6	3,2	3,3	0,2	2,1	2,0	2,2	2,1	0,1
Indeno(1,2,3-c,d)pyrene [ng/sample]	2,1	2,3	<LOD			1,6	2,2	<LOD			<LOD	<LOD	<LOD	<LOD	
Dibenz(a,h)anthracene [ng/sample]	<LOD	<LOD	<LOD	<LOD		<LOD	<LOD	<LOD	<LOD		<LOD	<LOD	<LOD	<LOD	

Lab: UT	sample 4.1	sample 4.1	sample 4.1	average	s. d.	sample 4.2	sample 4.2	sample 4.2	average	s. d.	sample 4.3	sample 4.3	sample 4.3	average	s. d.
date of the analyses	21.09.07	21.09.07	21.09.07			21.09.07	21.09.07	21.09.07			21.09.07	21.09.07	21.09.07		
measuring method	GCMS	GCMS	GCMS			GCMS	GCMS	GCMS			GCMS	GCMS	GCMS		
lower limit of the working range [ng/ml]	4	4	4			4	4	4			4	4	4		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	100	100	100			100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	107	105	105			106	106	103			103	101	100		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	1,0	1,0	1,0	1,0	0,0	2,0	2,0	2,0	2,0	0,0	1,0	1,0	1,0	1,0	0,0
Benz(a)anthracene [ng/sample]	2,0	2,0	2,0	2,0	0,0	3,0	3,0	3,0	3,0	0,0	3,0	3,0	3,0	3,0	0,0
sum of Benzo(b, j, k) fluoranthene [ng/sample]	5,0	5,0	5,0	5,0	0,0	6,0	6,0	6,0	6,0	0,0	5,0	5,0	5,0	5,0	0,0
Indeno(1,2,3-c,d)pyrene [ng/sample]	1,0	1,0	1,0	1,0	0,0	5,0	5,0	4,0	4,7	0,6	3,0	3,0	3,0	3,0	0,0
Dibenz(a,h)anthracene [ng/sample]	n.d.	n.d.	n.d.	n.d.		1,0	1,0	1,0	1,0	0,0	1,0	n.d.	n.d.	n.d.	

Lab: UBA	sample 4.1	sample 4.1	sample 4.1	average	s. d.	sample 4.2	sample 4.2	sample 4.2	average	s. d.	sample 4.3	sample 4.3	sample 4.3	average	s. d.
date of the analyses	17.08.07	17.08.07	17.08.07			17.08.07	17.08.07	17.08.07			17.08.07	17.08.07	17.08.07		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	1,0	1,0	1,0			1,0	1,0	1,0			1,0	1,0	1,0		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	10	10	10			10	10	10			10	10	10		
recovery rate of the surrogate standard [%]	113	110	114			88	92	91			105	113	105		
working up method	Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk		
Benzo(a)pyrene [ng/sample]	1,2	< 1	< 1	< 1		1,0	< 1	< 1	< 1		1,1	< 1	< 1	< 1	
Benz(a)anthracene [ng/sample]	< 1	< 1	< 1	< 1		< 1	< 1	< 1	< 1		< 1	< 1	< 1	< 1	
Benzo(b)fluoranthene [ng/sample]	1,5	1,3	1,1	1,3	0,2	1,7	< 1	< 1	< 1		2,0	1,6	1,2	1,6	0,4
Benzo(j)fluoranthene [ng/sample]	1,9	1,9	1,6	1,8	0,2	2,3	2,4	1,3	2,0	0,6	2,4	2,0	1,5	2,0	0,5
Benzo(k)fluoranthene [ng/sample]	< 1	< 1	< 1	< 1		< 1	< 1	< 1	< 1		< 1	< 1	< 1	< 1	
sum of Benzo(b, j, k) fluoranthene [ng/sample]	3,4	3,2	2,7	3,1	0,4	3,9	2,4	1,3	1,6	1,4	4,5	3,6	2,6	3,6	0,9
Indeno(1,2,3-c,d)pyrene [ng/sample]	1,8	1,3	2,3	1,8	0,5	1,4	< 1	1,8	1,0	0,3	2,0	1,3	2,3	1,9	0,6
Dibenz(a,h)anthracene [ng/sample]	< 1	< 1	< 1	< 1		1,0	< 1	< 1	< 1		< 1	< 1	< 1	< 1	

Lab: TNO	Sample 4.1	Sample 4.2	Sample 4.3
date of the analyses	29.06.07	29.06.07	29.06.07
measuring method	HPLC	HPLC	HPLC
lower limit of the working range [ng/ml]	5,5	5,5	5,5
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr
amount of the added surrogate standard [ng]	512	512	512
recovery rate of the surrogate standard [%]	87	73	101
working up method	Speedisk	Speedisk	Speedisk
Benzo(a)pyrene [ng/sample]	0,43	0,36	0,40
Benz(a)anthracene [ng/sample]	0,95	0,75	< 1,6
Benzo(b)fluoranthene [ng/sample]	0,89	< 1,9	< 1,9
Benzo(j)fluoranthene [ng/sample]	not detected		
Benzo(k)fluoranthene [ng/sample]	0,59	< 0,2	< 0,2
Indeno(1,2,3-c,d)pyrene [ng/sample]	< 5,5	< 5,5	< 5,5
Dibenz(a,h)anthracene [ng/sample]	0,95	< 1,0	< 1,0

Annex 6: Dust sample (CRM) suspended in water (sample 5)

Lab: LUBW	sample 5.1	sample 5.1	sample 5.1	average	target value 5.1	sample 5.2	sample 5.2	sample 5.2	average	target value 5.2	sample 5.3	sample 5.3	sample 5.3	average	target value 5.3
date of the analyses	11.06.2007	11.06.2007	11.06.2007			11.06.2007	11.06.2007	11.06.2007			11.06.2007	11.06.2007	11.06.2007		
measuring method	GC/MS	GC/MS	GC/MS			GC/MS	GC/MS	GC/MS			GC/MS	GC/MS	GC/MS		
lower limit of the working range [ng/ml]	5	5	5			5	5	5			5	5	5		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	100	100	100			100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	130	120	119			96	99	99			117	117	118		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	90,8	85,9	90,5	89,1	101,3	93,7	92,0	94,1	93,2	102,8	95,4	96,0	96,0	95,8	103,0
Benz(a)anthracene [ng/sample]	68,4	69,8	72,4	70,2	89,2	75,2	73,6	74,9	74,6	90,5	77,5	78,0	77,5	77,6	90,6
Benzo(b)fluoranthene [ng/sample]	182,4	171,5	178,9	177,6	260,5	187,9	183,2	186,6	185,9	264,3	185,7	188,1	192,2	188,7	264,8
Benzo(j)fluoranthene [ng/sample]	72,1	64,7	65,5	67,4		68,5	70,9	66,3	68,6		65,9	66,1	64,8	65,6	
Benzo(k)fluoranthene [ng/sample]	69,2	65,1	67,3	67,2	77,3	68,9	69,4	69,9	69,4	78,4	72,3	73,9	72,8	73,0	78,5
sum of Benzo(b, j, k) fluoranthene [ng/sample]	323,7	301,3	311,7	312,2	337,8	325,4	323,5	322,8	323,9	342,6	323,9	328,0	329,8	327,2	343,3
Indeno(1,2,3-c,d)pyrene [ng/sample]	128,5	123,8	130,9	127,8	128,4	130,6	130,3	135,0	132,0	130,3	136,0	138,8	139,4	138,0	130,5
Dibenz(a,h)anthracene [ng/sample]	12,6	12,2	12,7	12,5	11,6	13,0	13,2	13,3	13,2	11,8	13,6	13,5	13,5	13,5	11,8

Lab: LANUV	sample 5.1	sample 5.1	sample 5.1	average	target value 5.1	sample 5.2	sample 5.2	sample 5.2	average	target value 5.2	sample 5.3	sample 5.3	sample 5.3	average	target value 5.3
date of the analyses	21.06.2007	22.06.2007	25.06.2007			21.06.2007	22.06.2007	25.06.2007			21.06.2007	22.06.2007	25.06.2007		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	5	5	5			5	5	5			5	5	5		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	485,2	487,0	491,8			479,0	484,2	484,1			531,7	549,6	551,5		
recovery rate of the surrogate standard [%]	98,6	98,9	99,9			92,0	93,0	92,9			104,2	107,8	108,1		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	82,2	80,4	80,7	81,1	100,9	87,2	87,4	87,1	87,3	99,3	105,8	106,9	108,1	106,9	106,8
Benz(a)anthracene [ng/sample]	82,0	81,4	81,5	81,6	88,8	83,1	84,5	83,4	83,6	87,4	100,4	103,1	103,7	102,4	94,0
Benzo(b)fluoranthene [ng/sample]	198,7	197,3	192,3	196,1		216,5	207,8	200,5	208,3		239,2	252,3	251,3	247,6	
Benzo(j)fluoranthene [ng/sample]	not detected														
Benzo(k)fluoranthene [ng/sample]	72,4	71,8	72,4	72,2	76,9	75,3	75,4	73,7	74,8	75,7	88,4	90,2	92,2	90,3	81,4
sum of Benzo(b, j, k) fluoranthene [ng/sample]															
Indeno(1,2,3-c,d)pyrene [ng/sample]	90,1	88,1	91,8	90,0	127,8	98,1	96,4	99,7	98,1	125,9	112,1	112,2	112,8	112,4	135,3
Dibenz(a,h)anthracene [ng/sample]	12,9	12,8	13,0	12,9	11,6	13,5	13,6	13,7	13,6	11,4	16,1	16,2	16,8	16,4	12,3

Lab: INERIS	sample 5.1	sample 5.1	sample 5.1	average	target value 5.1	sample 5.2	sample 5.2	sample 5.2	average	target value 5.2	sample 5.3	sample 5.3	sample 5.3	average	target value 5.3
date of the analyses	23.06.2007	23.06.2007	23.06.2007			23.06.2007	23.06.2007	23.06.2007			23.06.2007	23.06.2007	23.06.2007		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	1	1	1			1	1	1			1	1	1		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	100	100	100			100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	88	88	87			75	75	75			85	84	85		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	77,0	76,7	75,7	76,5	110,2	55,9	56,5	56,7	56,4	102,8	76,7	76,1	76,2	76,3	107,2
Benz(a)anthracene [ng/sample]	65,5	64,4	64,4	64,8	97,0	48,6	47,6	48,9	48,4	90,5	63,3	63,3	63,8	63,5	94,3
Benzo(b)fluoranthene [ng/sample]	234,0	224,7	222,6	227,1	283,2	182,4	183,3	183,8	183,2	264,4	224,9	221,9	220,6	222,5	275,6
Benzo(j)fluoranthene [ng/sample]	52,9	56,7	54,6	54,7		54,5	38,4	46,3	46,4		84,3	87,8	83,9	85,3	
Benzo(k)fluoranthene [ng/sample]	58,5	57,6	57,5	57,9	84,0	45,2	45,1	45,2	45,2	78,4	58,4	62,1	60,6	60,4	81,7
sum of Benzo(b, j, k) fluoranthene [ng/sample]	345,4	339,0	334,7	339,7	367,2	282,1	266,8	275,3	274,7	342,8	367,6	371,8	365,1	368,2	357,4
Indeno(1,2,3-c,d)pyrene [ng/sample]	133,4	142,2	141,1	138,9	139,6	113,1	118,1	114,8	115,3	130,3	138,9	135,9	136,6	137,1	135,9
Dibenz(a,h)anthracene [ng/sample]	11,9	8,5	8,9	9,8	12,6	9,7	5,5	6,8	7,3	11,8	12,9	9,7	9,6	10,7	12,3

Lab: ECN	sample 5.1	sample 5.1	sample 5.1	average	target value 5.1	sample 5.2	sample 5.2	sample 5.2	average	target value 5.2	sample 5.3	sample 5.3	sample 5.3	average	target value 5.3
date of the analyses	12.07.2007	12.07.2007	12.07.2007			12.07.2007	12.07.2007	12.07.2007			12.07.2007	12.07.2007	12.07.2007		
measuring method	GCMS	GCMS	GCMS			GCMS	GCMS	GCMS			GCMS	GCMS	GCMS		
lower limit of the working range [ng/ml]	2,5	2,5	2,5			2,5	2,5	2,5			2,5	2,5	2,5		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	500	500	500			500	500	500			500	500	500		
recovery rate of the surrogate standard [%]	104,7	104,7	104,7			95,0	95,0	95,0			102,5	102,5	102,5		
working up method	Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk		
Benzo(a)pyrene [ng/sample]	106,0	104,5	103,6	104,7	108,2	108,6	106,6	105,3	106,8	110,8	102,0	97,4	98,1	99,1	105,6
Benz(a)anthracene [ng/sample]	93,0	81,5	80,6	85,0	95,2	88,1	78,6	81,7	82,8	97,5	87,1	79,7	78,2	81,7	93,0
sum of Benzo(b, j, k) fluoranthene [ng/sample]	389,5	377,2	365,6	377,5	360,7	376,7	355,7	362,5	365,0	369,3	357,4	339,9	334,6	344,0	352,1
Indeno(1,2,3-c,d)pyrene [ng/sample]	176,7	163,0	157,4	165,7	137,2	172,1	157,1	155,2	161,5	140,4	168,6	146,0	144,2	152,9	133,9
Dibenz(a,h)anthracene [ng/sample]	30,8	27,0	29,2	29,0	12,4	26,8	30,2	30,4	29,1	12,7	27,3	28,4	31,2	29,0	12,1

Lab: UT	sample 5.1	sample 5.1	sample 5.1	average	target value 5.1	sample 5.2	sample 5.2	sample 5.2	average	target value 5.2	sample 5.3	sample 5.3	sample 5.3	average	target value 5.3
date of the analyses	21.09.2007	21.09.2007	21.09.2007			21.09.2007	21.09.2007	21.09.2007			21.09.2007	21.09.2007	21.09.2007		
measuring method	GCMS	GCMS	GCMS			GCMS	GCMS	GCMS			GCMS	GCMS	GCMS		
lower limit of the working range [ng/ml]	4	4	4			4	4	4			4	4	4		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	100	100	100			100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	107	104	104			110	110	105			105	105	108		
working up method	CEN	CEN	CEN			CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	87,0	90,0	94,0	90,3	107,2	95,0	93,0	98,0	95,3	108,9	105,0	105,0	106,0	105,3	108,9
Benz(a)anthracene [ng/sample]	78,0	80,0	82,0	80,0	94,4	82,0	84,0	83,0	83,0	95,8	91,0	92,0	90,0	91,0	95,8
sum of Benzo(b, j, k) fluoranthene [ng/sample]	368,0	388,0	396,0	384,0	357,4	401,0	402,0	408,0	403,7	363,0	416,0	418,0	411,0	415,0	362,9
Indeno(1,2,3-c,d)pyrene [ng/sample]	148,0	160,0	163,0	157,0	135,9	159,0	165,0	167,0	163,7	138,0	176,0	175,0	171,0	174,0	138,0
Dibenz(a,h)anthracene [ng/sample]	26,0	29,0	26,0	27,0	12,3	26,0	28,0	30,0	28,0	12,5	29,0	29,0	29,0	29,0	12,5

Lab: UBA	sample 5.1	sample 5.1	sample 5.1	average	target value 5.1	sample 5.2	sample 5.2	sample 5.2	average	target value 5.2	sample 5.3	sample 5.3	sample 5.3	average	target value 5.3
date of the analyses	17.08.2007	17.08.2007	17.08.2007			17.08.2007	17.08.2007	17.08.2007			17.08.2007	17.08.2007	17.08.2007		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	1	1	1			1	1	1			1	1	1		
Which surrogate standard did you use?	6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr			6-MChr	6-MChr	6-MChr		
amount of the added surrogate standard [ng]	10	10	10			10	10	10			10	10	10		
recovery rate of the surrogate standard [%]	32	30	35			19	23	21			120	115	115		
working up method	Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk		
Benzo(a)pyrene [ng/sample]	120,8	143,5	107,5	123,9	109,9	130,2	111,9	106,5	116,2	103,4	82,7	90,7	91,8	88,4	96,9
Benz(a)anthracene [ng/sample]	96,3	109,4	96,5	100,8	96,7	78,6	79,3	93,5	83,8	91,0	68,8	88,3	76,7	77,9	85,3
Benzo(b)fluoranthene [ng/sample]	219,9	228,2	192,6	213,6	282,5	210,9	170,2	201,2	194,1	265,9	172,0	188,6	185,7	182,1	249,1
Benzo(j)fluoranthene [ng/sample]	108,8	111,0	100,4	106,7		107,9	90,0	103,8	100,6		89,4	84,5	100,7	91,5	
Benzo(k)fluoranthene [ng/sample]	84,9	102,1	76,3	87,8	83,8	90,5	78,0	76,7	81,7	78,9	66,6	79,3	66,7	70,9	73,9
sum of Benzo(b, j, k) fluoranthene [ng/sample]	413,6	441,4	369,3	408,1	366,3	409,3	338,2	381,7	376,4	344,8	328,0	352,4	353,0	344,5	323,0
Indeno(1,2,3-c,d)pyrene [ng/sample]	133,4	139,3	107,5	126,7	139,3	130,3	108,9	107,5	115,5	131,1	108,0	104,1	98,4	103,5	122,8
Dibenz(a,h)anthracene [ng/sample]	17,2	18,1	14,6	16,6	12,6	18,6	11,8	18,9	16,4	11,9	13,3	13,9	13,3	13,5	11,1

Lab: TNO	sample 5.1	target value 5.1	sample 5.2	target value 5.2	sample 5.3	target value 5.3
date of the analyses	29.06.2007		29.06.2007		29.06.2007	
measuring method	HPLC		HPLC		HPLC	
lower limit of the working range [ng/ml]	5,5		5,5		5,5	
Which surrogate standard did you use?	6-MChr		6-MChr		6-MChr	
amount of the added surrogate standard [ng]	512		512		512	
recovery rate of the surrogate standard [%]	122		110		114	
working up method	Speedisk		Speedisk		Speedisk	
Benzo(a)pyrene [ng/sample]	92,6	95,4	85,2	104,7	85,7	102,1
Benz(a)anthracene [ng/sample]	68,3	84,0	61,8	92,1	66,0	89,8
Benzo(b)fluoranthene [ng/sample]	172,4	245,4	164,6	269,2	163,1	262,5
Benzo(j)fluoranthene [ng/sample]	not detected		not detected		not detected	
Benzo(k)fluoranthene [ng/sample]	55,2	72,8	51,3	79,8	51,4	77,8
sum of Benzo(b,j,k)fluoranthene [ng/sample]	227,7	318,1	216,0	349,0	214,5	340,3
Indeno(1,2,3-c,d)pyrene [ng/sample]	177,9	121,0	175,6	132,7	167,3	129,4
Dibenz(a,h)anthracene [ng/sample]	13,1	11,0	13,4	12,0	11,4	11,7

Annex 7: Results liquid calibration standard (sample 6)

Lab: LUBW	sample 6 [ng/ml]	sample 6 [ng/ml]	sample 6 [ng/ml]]	average [ng/ml]	s. d.
date of the analyses	11.03.2008	11.03.2008	11.03.2008		
measuring method	GC/MS	GC/MS	GC/MS		
lower limit of the working range	5	5	5		
Benzo(a)pyrene	100,3	100,3	100,5	100,4	0,1
Benz(a)anthracene	96,7	98,3	98,6	97,8	1,0
Benzo(b)fluoranthene	94,5	99,6	95,7	96,6	2,7
Benzo(j)fluoranthene	215,2	218,7	223,9	219,3	4,4
Benzo(k)fluoranthene	94,6	99,7	97,7	97,3	2,6
sum of Benzo(b,j,k)fluoranthene	404,3	418,0	417,3	413,2	7,7
Indeno(1,2,3-c,d)pyrene	102,3	99,6	105,1	102,3	2,8
Dibenz(a,h)anthracene	93,5	99,9	94,1	95,9	3,5

Lab: LANUV	sample 6 [ng/ml]	sample 6 [ng/ml]	sample 6 [ng/ml]]	average [ng/ml]	s. d.
date of the analyses	31.03.2008	31.03.2008	01.04.2008		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	5	5	5		
Benzo(a)pyrene	114,8	115,9	115,8	115,5	0,6
Benz(a)anthracene	89,6	90,2	90,2	90,0	0,3
Benzo(b)fluoranthene	113,9	115,4	115,7	115,0	1,0
Benzo(j)fluoranthene	not detected				
Benzo(k)fluoranthene	109,3	110,3	110,3	110,0	0,6
Indeno(1,2,3-c,d)pyrene	119,0	120,8	122,0	120,6	1,5
Dibenz(a,h)anthracene	112,8	113,3	111,9	112,7	0,7

Lab: INERIS	sample 6 [ng/ml]	sample 6 [ng/ml]	sample 6 [ng/ml]]	average [ng/ml]	s. d.
date of the analyses	01.04.2008	01.04.2008	01.04.2008		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	102,7	107,5	109,3	106,5	3,4
Benz(a)anthracene	102,4	105,2	108,6	105,4	3,1
Benzo(b)fluoranthene	130,2	132,1	136,5	132,9	3,2
Benzo(j)fluoranthene	210,7	233,8	236,9	227,1	14,3
Benzo(k)fluoranthene	103,8	107,2	110,2	107,1	3,2
sum of Benzo(b,j,k)fluoranthene	444,7	473,1	483,6	467,1	20,1
Indeno(1,2,3-c,d)pyrene	105,3	109,0	114,0	109,4	4,4
Dibenz(a,h)anthracene	100,4	102,8	105,2	102,8	2,4

Lab: ECN	sample 6 [ng/ml]	sample 6 [ng/ml]	average [ng/ml]	s. d.
date of the analyses	28.03.2008	28.03.2008		
measuring method	GCMS	GCMS		
lower limit of the working range	5	5		
Benzo(a)pyrene	105,3	109,0	107,2	2,6
Benz(a)anthracene	121,6	119,8	120,7	1,3
sum of Benzo(b,j,k)fluoranthene	401,1	398,1	399,6	2,1
Indeno(1,2,3-c,d)pyrene	120,3	120,6	120,5	0,2
Dibenz(a,h)anthracene	222,3	221,5	221,9	0,5

Lab: UT	sample 6 [ng/ml]	sample 6 [ng/ml]	sample 6 [ng/ml]]	average [ng/ml]	s. d.
date of the analyses	21.04.2008	21.04.2008	21.04.2008		
measuring method	GCMS	GCMS	GCMS		
lower limit of the working range	10	10	10		
Benzo(a)pyrene	118,0	123,0	124,0	121,7	3,2
Benz(a)anthracene	103,0	101,0	97,0	100,3	3,1
sum of Benzo(b,j,k)fluoranthene	436,0	452,0	457,0	448,3	11,0
Indeno(1,2,3-c,d)pyrene	119,0	126,0	125,0	123,3	3,8
Dibenz(a,h)anthracene	231,0	243,0	243,0	239,0	6,9

Lab: UBA	sample 6 [ng/ml]	sample 6 [ng/ml]	sample 6 [ng/ml]]	average [ng/ml]	s. d.
date of the analyses	10.04.2008	10.04.2008	10.04.2008		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	1	1	1		
Benzo(a)pyrene	99,6	94,9	98,4	97,6	2,4
Benz(a)anthracene	108,0	98,6	105,8	104,1	4,9
Benzo(b)fluoranthene	89,1	109,2	90,1	96,1	11,3
Benzo(j)fluoranthene	202,3	196,2	204,2	200,9	4,2
Benzo(k)fluoranthene	107,1	107,6	112,4	109,0	2,9
sum of Benzo(b,j,k)fluoranthene	398,4	412,9	406,8	406,0	7,3
Indeno(1,2,3-c,d)pyrene	99,4	94,1	96,4	96,7	2,6
Dibenz(a,h)anthracene	201,5	199,3	202,8	201,2	1,7

Lab: TNO	sample 6 [ng/ml]	sample 6 [ng/ml]	sample 6 [ng/ml]]	average [ng/ml]	s. d.
date of the analyses	11.04.2008	11.04.2008	11.04.2008		
measuring method	HPLC	HPLC	HPLC		
lower limit of the working range	25,0 - 48,7	25,0 - 48,7	25,0 - 48,7		
Benzo(a)pyrene	105,0	107,4	111,5	108,0	3,3
Benz(a)anthracene	103,7	107,1	109,3	106,7	2,8
Benzo(b)fluoranthene	112,9	114,6	118,5	115,3	2,9
Benzo(j)fluoranthene	104,8	104,8	109,9	106,5	2,9
Benzo(k)fluoranthene	102,9	104,8	108,1	105,3	2,6
sum of Benzo(b,j,k)fluoranthene	320,6	324,3	336,5	327,1	8,3
Indeno(1,2,3-c,d)pyrene	104,4	104,5	105,5	104,8	0,6
Dibenz(a,h)anthracene	95,4	96,7	100,1	97,4	2,4

Annex 8: Dust sample (CRM) suspended in rain water (sample 7)

Lab: LUBW	sample 7.1	sample 7.1	sample 7.1	average	target value 7.1	sample 7.2	sample 7.2	sample 7.2	average	target value 7.2
date of the analyses	11.03.2008	11.03.2008	11.03.2008			11.03.2008	11.03.2008	11.03.2008		
measuring method	GCMS	GCMS	GCMS			GCMS	GCMS	GCMS		
lower limit of the working range [ng/ml]	5	5	5			5	5	5		
Which surrogate standard did you use?	6-M-Ch	6-M-Ch	6-M-Ch			6-M-Ch	6-M-Ch	6-M-Ch		
amount of the added surrogate standard [ng]	100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	114	121	124			114	114	119		
working up method	CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	24,9	24,8	26,6	25,5	25,3	26,5	26,5	26,4	26,5	25,1
Benz(a)anthracene [ng/sample]	19,6	19,4	18,6	19,2	22,3	19,7	19,3	19,4	19,5	22,1
Benzo(b)fluoranthene [ng/sample]	47,4	48,1	48,9	48,1	65,0	49,0	49,0	46,7	48,2	64,5
Benzo(j)fluoranthene [ng/sample]	12,9	10,7	13,7	12,4		12,1	16,5	13,5	14,0	
Benzo(k)fluoranthene [ng/sample]	20,0	20,5	20,0	20,1	19,3	20,8	20,6	20,1	20,5	19,1
sum of Benzo(b, j, k) fluoranthene [ng/sample]	80,2	79,3	82,6	80,7	84,3	89,5	88,9	86,2	88,2	83,6
Indeno(1,2,3-c,d)pyrene [ng/sample]	32,5	33,0	35,2	33,5	32,1	36,1	33,9	34,7	34,9	31,8
Dibenz(a,h)anthracene [ng/sample]	3,7	3,7	3,8	3,7	2,9	3,7	3,8	3,7	3,7	2,9

Lab: LANUV	sample 7.1	sample 7.1	sample 7.1	average	target value 7.1	sample 7.2	sample 7.2	sample 7.2	average	target value 7.2
date of the analyses	31.03.2008	31.03.2008	01.04.2008			31.03.2008	31.03.2008	01.04.2008		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	5	5	5			5	5	5		
Which surrogate standard did you use?	6-M-Ch	6-M-Ch	6-M-Ch			6-M-Ch	6-M-Ch	6-M-Ch		
amount of the added surrogate standard [ng]	54	54	54			54	54	54		
recovery rate of the surrogate standard [%]	89	90	90			88	88	89		
working up method	CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	18,1	17,9	17,6	17,9	25,6	19,0	18,9	19,1	19,0	27,3
Benz(a)anthracene [ng/sample]	19,9	20,3	20,1	20,1	22,5	20,0	19,5	20,0	19,8	24,0
Benzo(b)fluoranthene [ng/sample]	44,8	45,3	44,4	44,9		46,1	45,9	46,2	46,1	
Benzo(j)fluoranthene [ng/sample]	not detected									
Benzo(k)fluoranthene [ng/sample]	18,2	18,7	18,7	18,5	19,5	18,0	18,2	18,4	18,2	20,8
sum of Benzo(b, j, k) fluoranthene [ng/sample]										
Indeno(1,2,3-c,d)pyrene [ng/sample]	30,1	30,1	29,8	30,0	32,4	28,9	28,5	28,5	28,6	34,6
Dibenz(a,h)anthracene [ng/sample]	2,9	3,0	3,1	3,0	2,9	2,6	2,7	2,8	2,7	3,1

Lab: INERIS	sample 7.1	sample 7.1	sample 7.1	average	target value 7.1	sample 7.2	sample 7.2	sample 7.2	average	target value 7.2
date of the analyses	01.04.2008	01.04.2008	01.04.2008			02.04.2008	02.04.2008	02.04.2008		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	1	1	1			1	1	1		
Which surrogate standard did you use?	6-M-Ch	6-M-Ch	6-M-Ch			6-M-Ch	6-M-Ch	6-M-Ch		
amount of the added surrogate standard [ng]	100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	85	90	90			92	90	91		
working up method	CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	22,6	23,5	24,1	23,4	25,2	27,3	26,9	27,3	27,2	25,8
Benz(a)anthracene [ng/sample]	20,8	22,1	21,9	21,6	22,2	21,0	18,1	19,3	19,5	22,7
Benzo(b)fluoranthene [ng/sample]	58,9	63,9	63,9	62,2	64,8	62,6	60,4	61,7	61,6	66,2
Benzo(j)fluoranthene [ng/sample]	20,0	20,7	20,6	20,4		23,5	22,5	23,9	23,3	
Benzo(k)fluoranthene [ng/sample]	19,1	20,4	20,3	19,9	19,2	19,9	19,2	19,6	19,6	19,6
sum of Benzo(b, j, k) fluoranthene [ng/sample]	98,0	105,0	104,8	102,6	84,0	106,0	102,1	105,2	104,4	85,9
Indeno(1,2,3-c,d)pyrene [ng/sample]	38,6	41,5	42,0	40,7	31,9	45,8	40,0	39,3	41,7	32,7
Dibenz(a,h)anthracene [ng/sample]	3,1	3,3	3,5	3,3	2,9	3,2	3,1	3,5	3,3	3,0

Lab: ECN	sample 7.1	sample 7.1	average	target value 7.1	sample 7.2	sample 7.2	average	target value 7.2
date of the analyses	28.03.2008	28.03.2008			28.03.2008	28.03.2008		
measuring method	GCMS	GCMS			GCMS	GCMS		
lower limit of the working range [ng/ml]	5	5			5	5		
Which surrogate standard did you use?	6-M-Ch	6-M-Ch			6-M-Ch	6-M-Ch		
amount of the added surrogate standard [ng]	760	760			760	760		
recovery rate of the surrogate standard [%]	82	93			82	93		
working up method	Speedisk	Speedisk			Speedisk	Speedisk		
Benzo(a)pyrene [ng/sample]	21,0	21,0	21,0	25,7	20,4	20,5	20,5	27,3
Benz(a)anthracene [ng/sample]	21,8	22,5	22,1	22,6	21,6	21,9	21,8	24,0
sum of Benzo(b, j, k) fluoranthene [ng/sample]	81,6	74,4	78,0	85,7	79,6	76,0	77,8	91,0
Indeno(1,2,3-c,d)pyrene [ng/sample]	31,9	31,0	31,4	32,6	32,0	33,3	32,7	34,6
Dibenz(a,h)anthracene [ng/sample]	5,7	6,4	6,1	3,0	4,9	4,2	4,5	3,1

Lab: UT	sample 7.1	sample 7.1	sample 7.1	average	target value 7.1	sample 7.2	sample 7.2	sample 7.2	average	target value 7.2
date of the analyses	21.04.2008	21.04.2008	21.04.2008			21.04.2008	21.04.2008	21.04.2008		
measuring method	GCMS	GCMS	GCMS			GCMS	GCMS	GCMS		
lower limit of the working range [ng/ml]	10	10	10			10	10	10		
Which surrogate standard did you use?	6-M-Ch	6-M-Ch	6-M-Ch			6-M-Ch	6-M-Ch	6-M-Ch		
amount of the added surrogate standard [ng]	50	50	50			50	50	50		
recovery rate of the surrogate standard [%]	96	97	96			105	104	105		
working up method	CEN	CEN	CEN			CEN	CEN	CEN		
Benzo(a)pyrene [ng/sample]	14,0	14,0	15,0	14,3	27,2	19,0	19,0	20,0	19,3	24,6
Benz(a)anthracene [ng/sample]	23,0	24,0	24,0	23,7	23,9	25,0	25,0	25,0	25,0	21,7
sum of Benzo(b, j, k) fluoranthene [ng/sample]	102,0	104,0	105,0	103,7	90,6	102,0	102,0	101,0	101,7	82,0
Indeno(1,2,3-c,d)pyrene [ng/sample]	37,0	38,0	39,0	38,0	34,4	38,0	38,0	38,0	38,0	31,2
Dibenz(a,h)anthracene [ng/sample]	6,0	6,0	6,0	6,0	3,1	7,0	7,0	6,0	6,7	2,8

Lab: UBA	sample 7.1	sample 7.1	sample 7.1	average	target value 7.1	sample 7.2	sample 7.2	sample 7.2	average	target value 7.2
date of the analyses	10.04.2008	10.04.2008	10.04.2008			10.04.2008	10.04.2008	10.04.2008		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	1	1	1			1	1	1		
Which surrogate standard did you use?	6-M-Ch	6-M-Ch	6-M-Ch			6-M-Ch	6-M-Ch	6-M-Ch		
amount of the added surrogate standard [ng]	100	100	100			100	100	100		
recovery rate of the surrogate standard [%]	94	98	99			99	98	102		
working up method	Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk		
Benzo(a)pyrene [ng/sample]	23,9	25,6	25,9	25,1	27,1	27,9	28,5	29,1	28,5	25,6
Benz(a)anthracene [ng/sample]	27,4	27,5	26,8	27,2	23,8	28,6	27,2	28,7	28,2	22,5
Benzo(b)fluoranthene [ng/sample]	55,3	57,4	56,7	56,4	69,7	54,5	58,9	59,5	57,6	65,8
Benzo(j)fluoranthene [ng/sample]	15,5	15,0	14,1	14,8		15,4	18,1	16,9	16,8	
Benzo(k)fluoranthene [ng/sample]	16,8	17,5	17,1	17,1	20,7	16,4	15,7	15,9	16,0	19,5
sum of Benzo(b, j, k) fluoranthene [ng/sample]	87,6	89,9	87,8	88,4	90,3	86,3	92,8	92,3	90,4	85,3
Indeno(1,2,3-c,d)pyrene [ng/sample]	21,4	24,0	23,7	23,0	34,3	25,4	26,5	26,5	26,1	32,4
Dibenz(a,h)anthracene [ng/sample]	3,5	4,0	4,0	3,9	3,1	4,4	4,7	4,9	4,7	2,9

Lab: TNO	sample 7.1	sample 7.1	sample 7.1	average	target value 7.1	sample 7.2	sample 7.2	sample 7.2	average	target value 7.2
date of the analyses	11.04.2008	11.04.2008	11.04.2008			11.04.2008	11.04.2008	11.04.2008		
measuring method	HPLC	HPLC	HPLC			HPLC	HPLC	HPLC		
lower limit of the working range [ng/ml]	25 - 48,7	25 - 48,7	25 - 48,7			25 - 48,7	25 - 48,7	25 - 48,7		
Which surrogate standard did you use?	6-M-Ch	6-M-Ch	6-M-Ch			6-M-Ch	6-M-Ch	6-M-Ch		
amount of the added surrogate standard [ng]	470	470	470			470	470	470		
recovery rate of the surrogate standard [%]	Xaverage = 48,85mV					Xaverage = 64,38mV				
working up method	Speedisk	Speedisk	Speedisk			Speedisk	Speedisk	Speedisk		
Benzo(a)pyrene [ng/sample]	22,6	22,5	16,4	20,5	25,0	28,6	29,6	31,2	29,8	27,1
Benz(a)anthracene [ng/sample]	16,4	16,4	16,4	16,4	22,0	20,9	21,5	22,3	21,5	23,9
Benzo(b)fluoranthene [ng/sample]	44,7	44,4	44,5	44,5	64,3	57,1	58,6	60,7	58,8	69,8
Benzo(j)fluoranthene [ng/sample]	6,0	6,0	5,4	5,8		7,7	7,8	7,9	7,8	
Benzo(k)fluoranthene [ng/sample]	14,6	14,4	14,4	14,5	19,1	18,0	18,6	19,2	18,6	20,7
sum of Benzo(b, j, k) fluoranthene [ng/sample]	65,3	64,8	64,3	64,8	83,4	82,8	84,9	87,7	85,1	90,5
Indeno(1,2,3-c,d)pyrene [ng/sample]	28,0	28,1	29,5	28,5	31,7	39,0	39,1	39,6	39,2	34,4
Dibenz(a,h)anthracene [ng/sample]	4,4	4,8	4,6	4,6	2,9	5,5	5,5	5,5	5,5	3,1

CEN TC 264 WG 21
'METHOD FOR THE DETERMINATION OF THE ATMOSPHERIC DEPOSITION OF PAH'

Evaluation of results of analysis of standards and samples of the laboratory test programme

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Introduction

Within the frame of the validation of a method for the determination of the total atmospheric deposition of polycyclic aromatic hydrocarbons (PAH), a validation programme based on a series of laboratory and field tests has been designed (document CEN/TC264 WG21 N173).

In the laboratory tests, attention is focused on studying the feasibility and comparability of the proposed analytical methodologies for the analysis of deposition samples.
The laboratory tests have consisted of two parts in which a total of 7 samples have been analyzed. In laboratory test programme 1, the following samples have been analyzed:

1. A calibration standard with known concentrations of PAH to in acetone/n-hexane
2. A real sample extract at low PAH levels in dichloromethane
3. A real sample extract at high PAH levels in dichloromethane
4. Rain water samples
5. A sample of NIST SRM 1649a suspended in subsamples of sample 4 with added 1% acetone and sodium chloride, with known levels of PAH.

In laboratory test programme 2, the following additional samples have been analyzed:

6. A calibration standard with known concentrations of PAH to in acetone/n-hexane
7. A sample of NIST SRM 1649a suspended in rain water + 1% acetone + sodium chloride with known levels of PAH.

Participating laboratories have performed the analyses according to their own methods based on EN 15549, ISO 12884 and ISO 16362. The extraction procedure to be followed in principle is described in document CEN/TC264 WG21 N159. As an alternative to the liquid/liquid extraction procedure proposed in N159, a number of laboratories have applied a novel form of combined filtration and solid-phase extraction. The following PAH have been determined:

- Benzo[a]pyrene
- Benzo[a]anthracene
- Benzo[b]fluoranthene*
- Benzo[j]fluoranthene*
- Benzo[k]fluoranthene*
- Indeno(1,2,3-c,d)pyrene
- Dibenzo(a,h)anthracene.

* or the sum of the 3 isomers.

Full details of the sample preparation and analytical results can be found in document CEN/TC264 WG21 N214.

This report concentrates on the statistical evaluation of the results from the analyses of the above samples. The evaluation serves a number of purposes, namely:

- Estimation of uncertainty sources by assessment of within- and between-laboratory variances due to different approaches of individual laboratories, particularly in sample processing and calibration by applying ISO 5725 statistics
- The comparison of the two different approaches for sample extraction for samples 4, 5 and 7.

Although strictly speaking ISO 5725 statistics are meant to be used for the evaluation of uncertainty of a single method, these statistics are useful to reveal potential 'macro' sources of measurement uncertainty and their magnitudes. In addition, these results can be used to evaluate whether between-laboratory contributions to uncertainty will be sufficiently low not to significantly influence the outcome of the field validation tests. Lastly, the reproducibility standard deviations for samples 4, 5 and 7 are measures of the uncertainties to be expected when applying the method under evaluation.

Data processing

Data submitted

The following data have been used for the evaluation:

- Samples 1, 2 and 3: 3 replicate results for each PAH
- Samples 4 and 5: 3 replicate results for 3 subsamples each for each PAH*
- Sample 6: 3 replicate results for each PAH
- Sample 7: 3 replicate results for 2 subsamples each for each PAH.

* One laboratory has submitted mean results for the 3 subsamples only.

In addition, each laboratory has submitted information about the extraction and analytical methodologies used for the sample analysis.

Data pretreatment

Results of analyses of the samples have been processed using ISO 5725 statistics to calculate for each PAH:

- The within-laboratory standard deviation s(r)
- The between-laboratory standard deviation s(L)
- The reproducibility standard deviation s(R).

Prior to evaluation, all data sets have been tested for outliers using Mandel, Cochran and Grubbs statistics. Mandel's k-test and Cochran's test have been used to test for outliers of within-laboratory consistency at the 1% significance level; Mandel's h-test and Grubbs's test have been used to test for outliers of between-laboratory consistency at the 1% significance level.

The test results have been used to indicate potential outliers only. In some cases data have been removed from the dataset on a provisional basis whenever the participant has indicated a clear technical reason for aberrant results. Indications have been taken from document CEN/TC264 WG21 N214.

Results of statistical evaluations

For each of the samples studied the following information is presented in Annexes 1 and 2.

1. A table with a summary of ISO 5725 statistics:
   - *mean* is the mean of all results
   - *s(r)* is the repeatability standard deviation
   - *s(L)* is the between-laboratory standard deviation
   - *s(R)* is the reproducibility standard deviation
   - *p* is the number of participating laboratories.

   Where appropriate, the ratios of the mean values and the nominal levels based on preparation have been given.

2. Two tables with the results of the Mandel h- and k-tests. Figures marked red are qualified as outliers (1% significance level).

3. Two figures with results Mandel tests grouped per laboratory for all PAH.

Legend to tables and figures

BaP	Benzo[a]pyrene
BaA	Benzo[a]anthracene
BbF	Benzo[b]fluoranthene
BjF	Benzo[j]fluoranthene
BkF	Benzo[k]fluoranthene
(BF)	Sum of benzo[x]fluoranthenes
IP	Indeno(1,2,3-c,d)pyrene
DBA	Dibenzo(a,h)anthracene
Nominal level	Level based on preparation of standard or sample
Mean	Mean result of participants'values
Ratio	Ratio of mean and nominal value
s(r)	Relative repeatability standard deviation
s(L)	Relative between-laboratory standard deviation
s(R)	Relative reproducibility standard deviation
p	Number of participating laboratories
Mandels h	Índicator of between-laboratory consistency
Mandel's k	Indicator of within-laboratory consistency
	Lab uses GC-MS
	Lab uses SPE
Figure marked red	Outlier at the 1% level of Mandel's test
Figure marked **red**	Data from lab removed for technical reasons

Conclusions

The results of the statistical evaluations reveal the following.

Laboratory test programme 1

1. Results reported for sample 4 are too variable to be processed with any significance as shown by the standard deviations calculated. This is most likely caused by the low levels of PAH in the rain water samples.

2. For the other samples only one result has been indicated as outlier for between-laboratory consistency. This indicates that – within the uncertainty limits of the methods applied – the mean results for all laboratories are comparable. This – in turn – indicates that no

significant differences can be found between the results for sample 5 obtained using the two different extraction methodologies.

3. In some cases, outliers for within-laboratory consistency have been indicated. However, for these cases no technical reasons for aberrant results have been reported.

4. The standard deviations obtained from the analysis of the calibration standard, sample 1, indicate the robustness of the analytical methods used. The reproducibility standard deviation is between 6% and 8%.

5. The additional steps involved for treatment of the sample extracts lead to an approximate twofold increase of the reproducibility standard deviation. For dibenzo(a,h)anthracene, present at relatively low levels, s(R) increases to 30 - 45%. The within-laboratory standard deviations do not increase, indicating a general lack of robustness in the procedures for the treatment of the extracts.

6. The standard deviations obtained for the SRM suspended in rain water show that the methods used for sample processing are robust. Reproducibility standard deviations are from 12% to 20% with exception of that for dibenzo(a,h)anthracene (45%). This high s(R) is most likely caused by the relatively low level of DBA.

7. The mean recovery of the PAH from the samples – as indicated by the ratio of the mean results and nominal levels – is never significantly different from 1, when taking the reproducibility standard deviation as an indicator of measurement uncertainty.

Laboratory test programme 2

1. On one occasion a result has been indicated as outlier for between-laboratory consistency. This indicates that – within the uncertainty limits of the methods applied – the mean results for all laboratories are generally comparable. This – in turn – indicates that no significant differences can be found between the results for sample 7 obtained using the two different extraction methodologies.

2. In some cases, outliers for within-laboratory consistency have been indicated. One set of results for sample 7 for DBA has been removed as the laboratory has indicated that it has been unable to separate dibenzo(a,h)anthracene from dibenzo(a,c)anthracene. For other cases no technical reasons for aberrant results have been reported, although visual inspection of the data indicates that the two subsamples of sample 7 analyzed by laboratory 5 may have contained different levels of PAH.

3. The standard deviations obtained from the analysis of the calibration standard, sample 6, are at comparable levels to those found for sample 1, with exception of those for benzo[b]- and benzo[j]fluoranthene. In both cases results from one laboratory affect the general performance.

4. Although the nominal levels of PAH are about 25% of those for sample 5, the standard deviations obtained for the SRM suspended in rain water (sample 7) are comparable to those obtained for sample 5, with exception of those for benzo[j]fluoranthene. However, no statistical indication of between-laboratory inconsistency is observed for BjF.

5. Again, recoveries of PAH are not significantly different from 1, indicating the suitability of the extraction methods used.

Overall conclusions

1. Analytical methods used are robust and lead to comparable results, with overall reproducibility standard deviations ranging from about 5% to 9%.

2. Additional steps for sample extract processing apparently lead to a decrease in method robustness; however, this finding from test programme 1 is contradicted by results obtained for determination of PAH in rain water containing suspended NIST SRM 1649a.

3. The determination of PAH in rain water with added suspended NIST SRM 1649a leads to results that are both consistent within and between laboratories, with reproducibility standard deviations ranging from 12% to 20% (with exception of that for dibenzo(a,h)anthracene.

4. No difference can be observed between results obtained by liquid/liquid extraction and solid-phase extraction. An additional quick scan, based on the comparison of the mean-of-means and standard deviations-of-means obtained by both techniques, confirmed this conclusion, although results for this scan are based on relatively few data.

ANNEX 1 – RESULTS OF LABORATORY TEST 1

Bottle **1**
Sample type **Liquid standard**

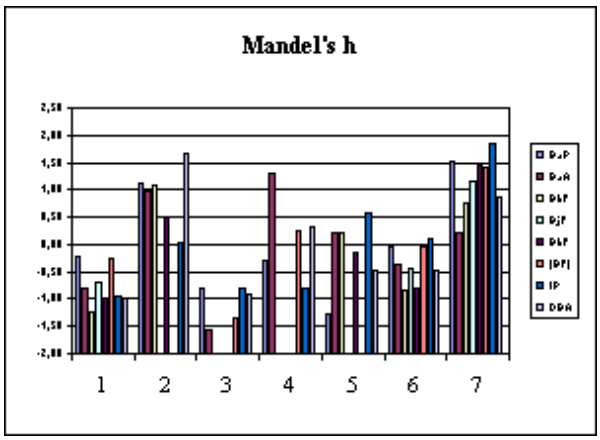
Component	*Nominal level (ng/mL)*	*Mean (ng/mL)*	*Ratio*	*s(r)*	*s(L)*	*s(R)*	*p*
BaP	100	100,5	1,01	5,4%	6,3%	8,3%	7
BaA	100	101,0	1,01	3,8%	7,3%	8,3%	7
BbF	100	101,0	1,01	2,3%	5,6%	6,1%	5
BjF	100	101,9	1,02				3
BkF	100	106,7	1,07	3,9%	7,9%	8,8%	5
(BF)	300	296,9	0,99	4,2%	7,9%	9,0%	5
IP	100	102,6	1,03	7,5%	0,0%	7,5%	7
DBA	100	104,2	1,04	5,5%	3,9%	6,8%	7

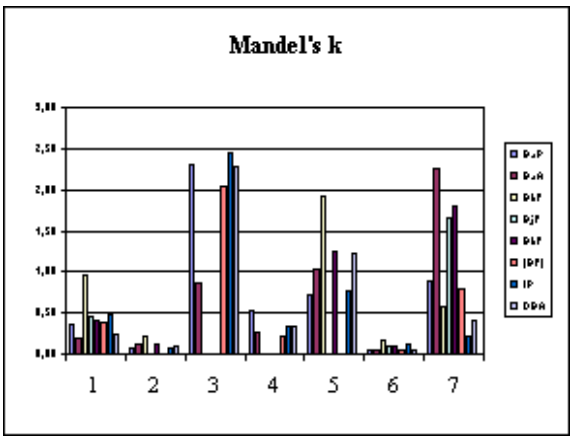
Mandel's h

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	-0,24	-0,80	-1,23	-0,69	-0,98	-0,25	-0,96	-1,00
2	1,14	0,99	1,08		0,49		0,02	1,68
3	-0,80	-1,57				-1,36	-0,79	-0,92
4	-0,31	1,30				0,25	-0,82	0,34
5	-1,26	0,21	0,21		-0,15		0,59	-0,48
6	-0,05	-0,36	-0,83	-0,46	-0,82	-0,06	0,11	-0,49
7	1,52	0,23	0,77	1,15	1,45	1,42	1,85	0,87

Mandel's k

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	0,36	0,18	0,97	0,46	0,40	0,39	0,49	0,24
2	0,07	0,13	0,21		0,12		0,08	0,08
3	2,29	0,85				2,04	2,44	2,27
4	0,53	0,26				0,21	0,34	0,35
5	0,73	1,03	1,91		1,25		0,78	1,22
6	0,06	0,06	0,17	0,09	0,09	0,04	0,12	0,04
7	0,88	2,26	0,57	1,67	1,80	0,80	0,20	0,40





Bottle **2**
Extract
Sample type **LOW**

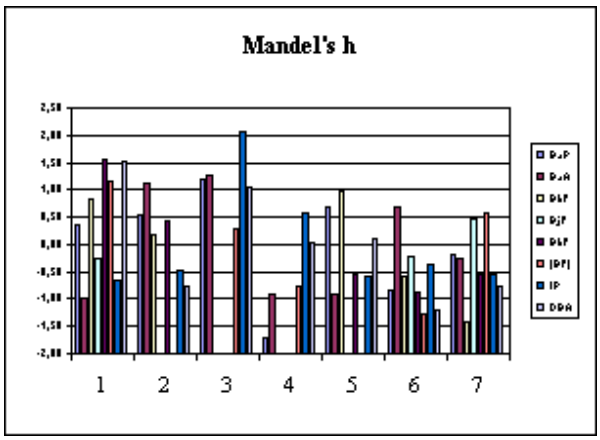
Component	*Nominal level (ng/mL)*	*Mean (ng/mL)*	*s(r)*	*s(L)*	*s(R)*	*p*
BaP		56,2	3,6%	11,1%	11,7%	7
BaA		62,1	5,6%	6,4%	8,5%	7
BbF		63,2	2,6%	4,8%	5,4%	5
BjF		40,8				3
BkF		33,0	2,8%	19,5%	19,7%	5
(BF)		134,7	2,5%	5,8%	6,3%	5
IP		50,7	4,3%	17,5%	18,0%	7
DBA		7,9	11,8%	45,4%	46,9%	7

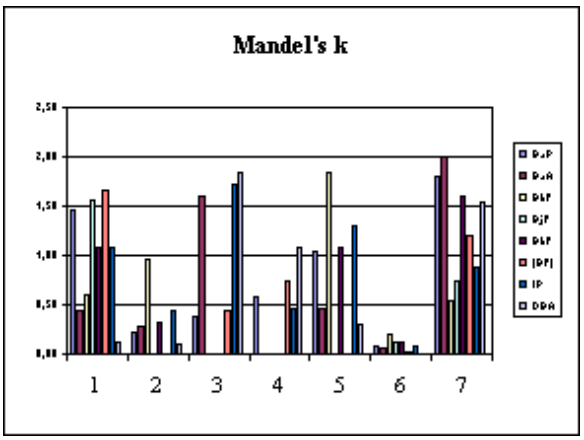
Mandel's h

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	0,36	-0,97	0,84	-0,25	1,56	1,17	-0,66	1,53
2	0,53	1,10	0,18		0,42		-0,47	-0,75
3	1,20	1,27				0,29	2,05	1,04
4	-1,71	-0,91				-0,75	0,59	0,03
5	0,67	-0,92	0,96		-0,55		-0,58	0,12
6	-0,86	0,69	-0,58	-0,23	-0,88	-1,28	-0,37	-1,19
7	-0,20	-0,27	-1,41	0,48	-0,56	0,58	-0,55	-0,77

Mandel's k

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	1,47	0,44	0,60	1,56	1,07	1,67	1,08	0,12
2	0,22	0,27	0,95		0,32		0,45	0,11
3	0,38	1,59				0,44	1,72	1,84
4	0,58	0,00				0,75	0,46	1,07
5	1,05	0,47	1,84		1,07		1,29	0,30
6	0,07	0,07	0,20	0,13	0,11	0,02	0,08	0,01
7	1,79	1,99	0,55	0,75	1,60	1,21	0,89	1,54





Bottle 3
Extract
Sample type HIGH

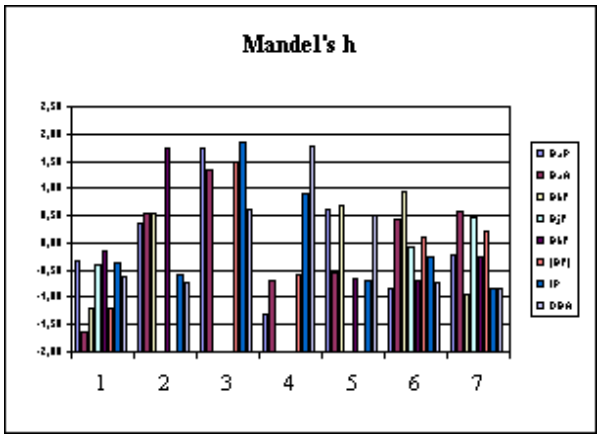
Component	*Nominal level (ng/mL)*	*Mean (ng/mL)*	*s(r)*	*s(L)*	*s(R)*	*p*
BaP		226,6	4,6%	16,8%	17,4%	7
BaA		244,2	4,4%	13,8%	14,5%	7
BbF		239,5	5,4%	10,1%	11,5%	5
BjF		167,3				3
BkF		119,8	5,5%	9,8%	11,2%	5
(BF)		529,8	1,7%	11,4%	11,5%	5
IP		205,7	4,5%	17,3%	17,9%	7
DBA		27,1	9,3%	31,8%	33,1%	7

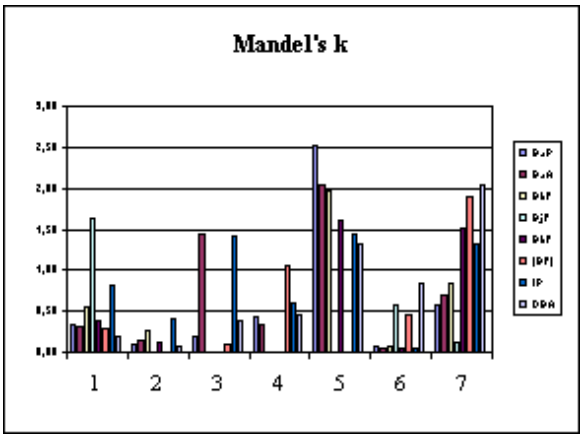
Mandel's h

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	-0,32	-1,64	-1,22	-0,41	-0,14	-1,18	-0,35	-0,61
2	0,34	0,55	0,53		1,73		-0,59	-0,74
3	1,72	1,32				1,48	1,86	0,62
4	-1,29	-0,68				-0,60	0,89	1,78
5	0,61	-0,55	0,67		-0,65		-0,69	0,52
6	-0,85	0,42	0,96	-0,07	-0,69	0,11	-0,26	-0,73
7	-0,21	0,57	-0,94	0,48	-0,25	0,20	-0,86	-0,85

Mandel's k

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	0,34	0,31	0,56	1,63	0,38	0,30	0,81	0,20
2	0,09	0,15	0,26		0,11		0,40	0,08
3	0,18	1,44				0,10	1,41	0,39
4	0,43	0,34				1,05	0,59	0,46
5	2,51	2,05	1,98		1,60		1,45	1,32
6	0,08	0,04	0,07	0,58	0,05	0,45	0,04	0,83
7	0,58	0,71	0,84	0,13	1,51	1,89	1,32	2,04





Bottle **4**
Sample type **Rain water**

Component	*Nominal level (ng/mL)*	*Mean (ng/mL)*	*s(r)*	*s(L)*	*s(R)*	*p*
BaP		3,7	14,2%	123%	124%	6
BaA		4,9	40,4%	82%	91%	5
BbF		5,4	22,0%	94%	96%	5
BjF		2,5				2
BkF		7,2	15,1%	61%	63%	3
(BF)		11,2	4,0%	112%	112%	3
IP		3,8	21,0%	75%	78%	6
DBA		2,6	2,4%	117%	117%	5

Bottle 5

Sample type **Suspended CRM**

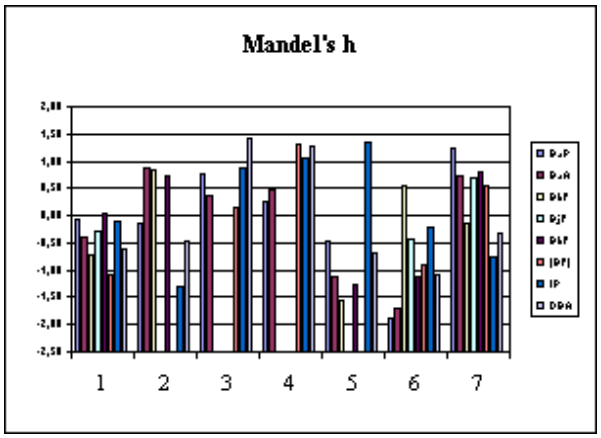
Component	*Nominal level (ng)*	*Mean (ng)*	*Ratio*	*s(r)*	*s(L)*	*s(R)*	*p*
BaP	100,2	93,7	0,94	11,3%	13,6%	17,7%	7
BaA	88,3	78,8	0,89	10,0%	14,2%	17,4%	7
BbF	258,0	199,5	1,07	9,3%	8,2%	12,4%	5
BjF		76,3		15,7%	15,7%	15,7%	3
BkF	76,5	69,5	0,91	11,2%	17,5%	20,8%	5
(BF)	334,5	357,6	1,07	7,8%	9,0%	11,9%	5
IP	127,2	136,0	1,07	7,7%	19,0%	20,5%	7
DBA	11,5	17,9	1,56	10,3%	45,1%	46,2%	7

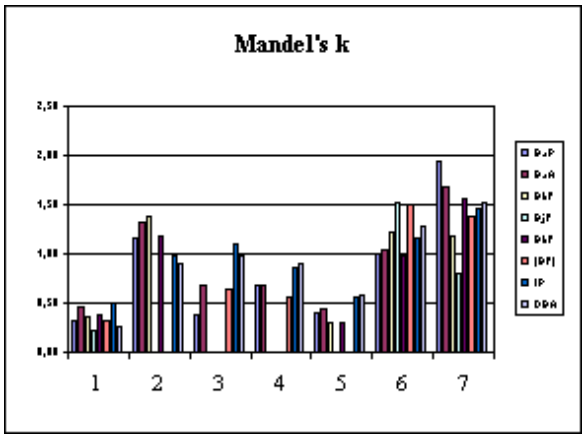
Mandel's h

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	-0,08	-0,40	-0,73	-0,27	0,03	-1,09	-0,12	-0,62
2	-0,15	0,88	0,85		0,72		-1,30	-0,46
3	0,77	0,37				0,14	0,87	1,42
4	0,26	0,49				1,29	1,05	1,29
5	-0,46	-1,14	-1,56		-1,26		1,36	-0,67
6	-1,88	-1,69	0,54	-0,42	-1,12	-0,90	-0,20	-1,10
7	1,24	0,73	-0,14	0,70	0,80	0,56	-0,75	-0,31

Mandel's k

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	0,33	0,45	0,35	0,22	0,38	0,32	0,50	0,27
2	1,16	1,32	1,39		1,18		0,98	0,91
3	0,38	0,67				0,64	1,10	0,99
4	0,69	0,67				0,56	0,87	0,89
5	0,41	0,43	0,29		0,31		0,55	0,59
6	0,99	1,05	1,22	1,52	0,98	1,51	1,16	1,29
7	1,95	1,69	1,17	0,80	1,55	1,38	1,46	1,52





ANNEX 2 – RESULTS OF LABORATORY TEST 2

Bottle 6
Sample type Liquid standard

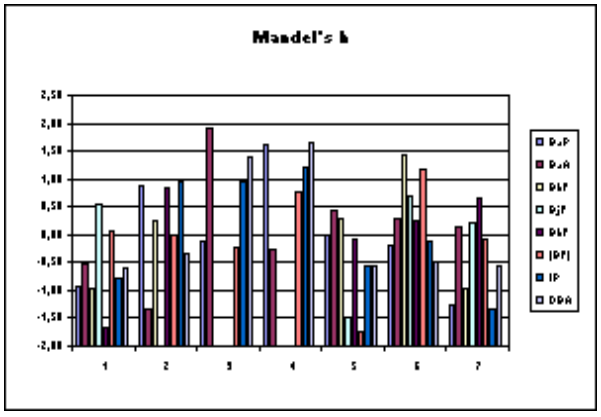
Component	*Nominal level (ng/mL)*	*Mean (ng/mL)*	*Ratio*	*s(r)*	*s(L)*	*s(R)*	*p*
BaP	100	108,2	1,08	2,4%	7,7%	8,1%	7
BaA	100	102,7	1,03	2,8%	8,3%	8,8%	7
BbF	100	111,2	1,11	5,0%	13,5%	14,4%	5
BjF	200	188,5	0,94	4,2%	29,5%	29,8%	4
BkF	100	105,7	1,06	2,4%	4,5%	5,1%	5
(BF)	400	428,8	1,07	2,8%	6,6%	7,2%	5
IP	100	110,6	1,11	2,5%	9,3%	9,7%	7
DBA	100	101,5	1,01	2,3%	6,5%	6,9%	5

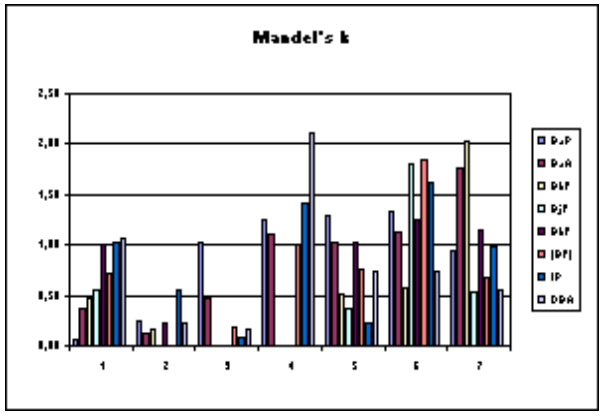
Mandel's h

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	-0,94	-0,52	-0,95	0,55	-1,67	0,05	-0,79	-0,60
2	0,89	-1,34	0,25		0,84	0,00	0,95	-0,34
3	-0,12	1,89				-0,23	0,94	1,38
4	1,63	-0,25				0,77	1,21	1,65
5	-0,02	0,42	0,27	-1,47	-0,09	-1,73	-0,55	-0,58
6	-0,20	0,28	1,41	0,69	0,27	1,16	-0,11	-0,49
7	-1,27	0,15	-0,98	0,22	0,65	-0,10	-1,33	-0,56

Mandel's k

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	0,05	0,37	0,48	0,55	1,00	0,71	1,02	1,07
2	0,24	0,13	0,17		0,23	0,00	0,56	0,22
3	1,02	0,47				0,19	0,08	0,16
4	1,25	1,10				1,01	1,41	2,10
5	1,29	1,02	0,51	0,37	1,03	0,77	0,23	0,73
6	1,33	1,12	0,58	1,81	1,25	1,85	1,62	0,73
7	0,94	1,76	2,03	0,53	1,14	0,67	0,98	0,54





Bottle 7
Sample type **Suspended CRM**

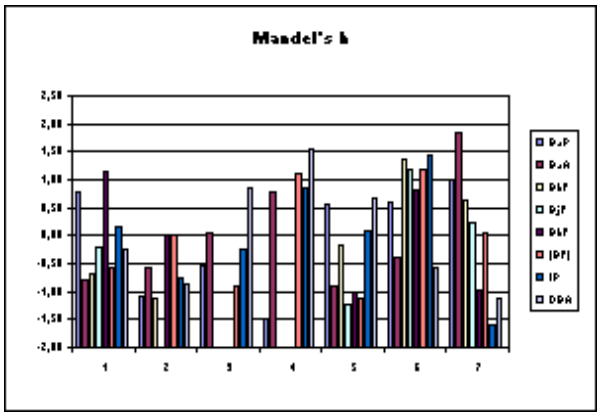
Component	*Nominal level (ng)*	*Mean (ng)*	*Ratio*	*s(r)*	*s(L)*	*s(R)*	*p*
BaP	25,1	22,8	0,91	12,0%	17,2%	20,9%	7
BaA	22,1	21,8	0,99	6,2%	14,7%	15,9%	7
BbF	64,5	52,8	1,04	7,2%	12,3%	14,2%	5
BjF		14,4		10,9%	43,1%	44,5%	4
BkF	19,1	18,3	0,96	6,1%	9,3%	11,1%	5
(BF)	83,6	89,0	1,06	6,0%	13,8%	15,0%	6
IP	31,8	33,4	1,05	8,1%	16,4%	18,3%	7
DBA	2,9	3,9	1,36	8,8%	37,0%	38,1%	6

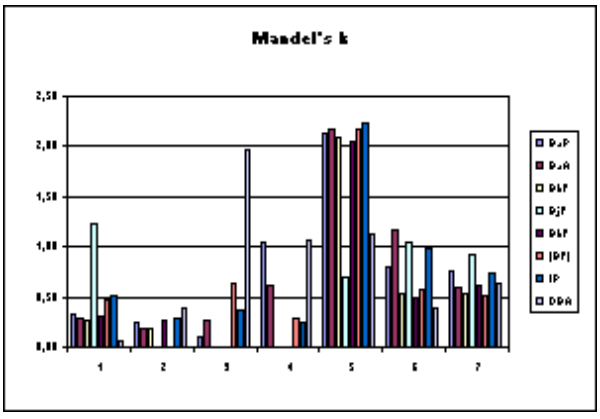
Mandel's h

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	0,78	-0,79	-0,70	-0,19	1,15	-0,58	0,15	-0,25
2	-1,10	-0,59	-1,11		0,03	0,00	-0,75	-0,88
3	-0,53	0,04				-0,89	-0,25	0,84
4	-1,50	0,79				1,10	0,85	1,57
5	0,57	-0,90	-0,18	-1,22	-1,01	-1,13	0,09	0,67
6	0,61	-0,41	1,36	1,19	0,82	1,17	1,43	-0,56
7	0,99	1,85	0,63	0,22	-0,99	0,04	-1,61	-1,12

Mandel's k

Lab	BaP	BaA	BbF	BjF	BkF	(BF)	IP	DBA
1	0,32	0,30	0,26	1,24	0,31	0,47	0,51	0,07
2	0,25	0,19	0,19		0,27	0,00	0,29	0,38
3	0,11	0,27				0,63	0,37	1,98
4	1,05	0,62				0,29	0,24	1,07
5	2,12	2,16	2,08	0,71	2,05	2,17	2,23	1,12
6	0,80	1,18	0,53	1,05	0,49	0,58	0,98	0,38
7	0,76	0,59	0,52	0,93	0,61	0,52	0,74	0,64





3 Degradation Test

This clause contains the report

Determination of the degradation of PAH during sampling of deposition

ECN-I--07-000

CEN/TC 264/WG 21
Method for the determination of the total deposition of PAH

Determination of the degradation of PAH during sampling of deposition

B.F. van Egmond, ECN

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F.P. Bakker, ECN

April 2008

Summary

As it is known that certain PAH compounds may degrade during sampling or upon being collected on a sampling filter a degradation test became part of the method validation programme. This test gave no indication that a statistical significant degradation occurs under the chosen conditions for the tested PAH compounds.

1. Introduction

Within the framework of the CEN/TC 264/WG 21 – Method for the determination of the total deposition of PAH – the following validation tests were performed (as described in CEN/TC 264/WG 21 N173):

1. Laboratory tests
2. Degradation test in the field
3. Field validation test

This report covers item 2, the degradation test, which was performed on the Research Location in Petten (NL). After extraction and work-up the samples were divided between ECN and TNO and analyzed by both laboratories.

2. Description and set-up of the test

2.1 General

Three sampler types were used in the test:

- Wet-only sampler (provided by TNO)
- (Funnel-bottle) bulk sampler (provided by ECN)
- Bergerhoff sampler (provided by UBA Austria)

The sampler containers were filled with a Standard Reference Material, NIST1649a (urban dust, suspended in water). During the test, the sample containers/bottles remained open/exposed to air.

To prevent any real deposition from entering the sample containers the following measures were taken: The wet only samplers were disconnected, so they remained closed all the time. However, the cooling was switched on. The Bergerhoff samplers were placed under a roof and the pots were covered with gauze. The inlet of the bulk sampler funnel was redirected outside the sampling bottle.


Figure 2.1 Wet-only, Bergerhoff and bulk sampler during degradation test

For each sampler 5 samples of artificial rainwater with SRM + 1 field blank were prepared. Exposure of the samples in the field is summarized in Table 2.1.

Table 2.1 Exposure of the samples in the field

Sample	Start date	End date	Work-up	Exposure
1	14-09-07	21-09-07	21-09-07	1 week
2	14-09-07	28-09-07	28-09-07	2 weeks
3	14-09-07	05-10-07	05-10-07	3 weeks
4	14-09-07	12-10-07	12-10-07	4 weeks
5	11-10-07	12-10-07	12-10-07	1 day
Field blank	28-09-07	16-10-07	16-10-07	2.5 weeks

2.2 Experimental data and work-up

Materials:
- NIST SRM1649a Urban Dust
- BAKERBOND Speedisk Extraction Disk H2O-Philic DVB

Each sample contains a suspension of 65 mg – 80 mg NIST SRM1649a in 750 ml Milli-Q-water. This corresponds with 160 ng –200 ng benzo[*a*]pyrene per sample.

The extraction of the sample and desorption of the Speedisk was done at the same day that the exposure in the field was ended. Before extraction with Speedisk, 75 g of sodium chloride and surrogate standard 6-methylchrysene were added to the sample.

Speedisk protocol and analysis

Conditioning of the Speedisk:
- 20 ml DCM
- 10 ml acetone
- 20 ml Milli-Q-water

Extraction over Speedisk:
- 1 sample in 30 min – 45 min.
- The bottle is shaken with 2 x 15 ml hexane. This is added to the rest of the extract.

Figure 2.2 Extraction over Speedisk

Desorption of Speedisk:

- 15 ml DCM
- 4 x 5 ml hexane

Figure 2.3 Desorption of the Speedisk

- The extract is dried with anhydrous sodium sulphate.
- Concentrating under N_2 until 2.5 ml – 3 ml.

Each extract was weighed and divided into 2 vials for analysis at ECN and TNO. TNO performed solvent exchange to acetonitrile and HPLC analysis. ECN performed solvent exchange to toluene for GC/MS analysis.

3. Results of the degradation test

The results are shown in the following paragraphs. The certified value is set to 100 %.
For GC/MS, some compounds had to be reported as a sum because of co-elution:

- Chrysene and triphenylene
- Benzo[*b*]fluoranthene, benzo[*j*]fluoranthene and benzo[*k*]fluoranthene
- Dibenzo[*ah*]anthracene, dibenzo[*ac*]anthracene and dibenzo[*aj*]anthracene

3.1 Benzo[*a*]anthracene

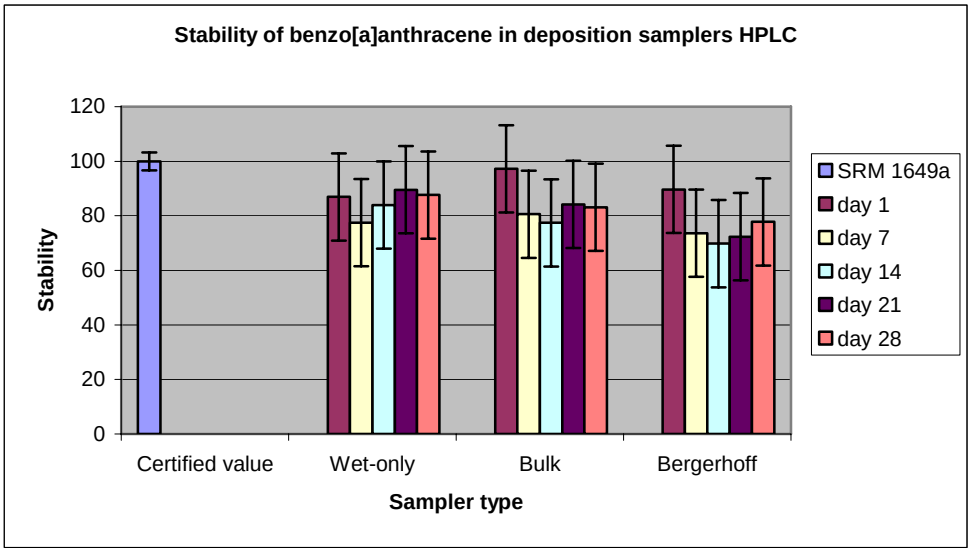

Figure 3.1 HPLC results Benzo[*a*]anthracene

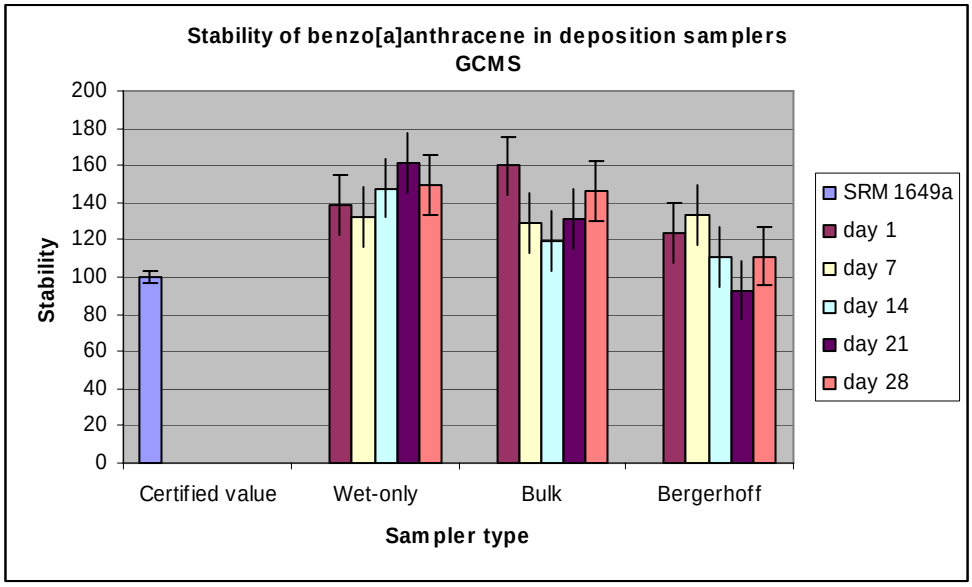

Figure 3.2 GC/MS results Benzo[*a*]anthracene

Table 3.1 HPLC results Benzo[*a*]anthracene

HPLC results	**Benzo[*a*]anthracene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		87	97	90
day 7		77	81	74
day 14		84	77	70
day 21		90	84	72
day 28		88	83	78
95 % level of confidence	3.3	16	16	16

Table 3.2 GC/MS results Benzo[*a*]anthracene

GC/MS results	**Benzo[*a*]anthracene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		139	160	124
day 7		132	129	133
day 14		148	119	111
day 21		161	131	93
day 28		149	146	111
95 % level of confidence	3.3	16	16	16

3.2 Chrysene

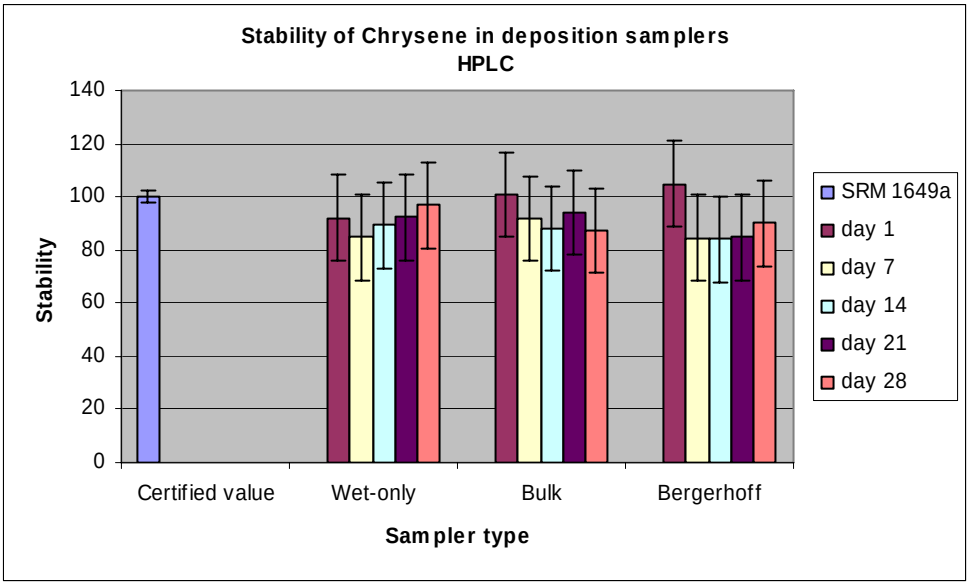

Figure 3.3 HPLC results Chrysene

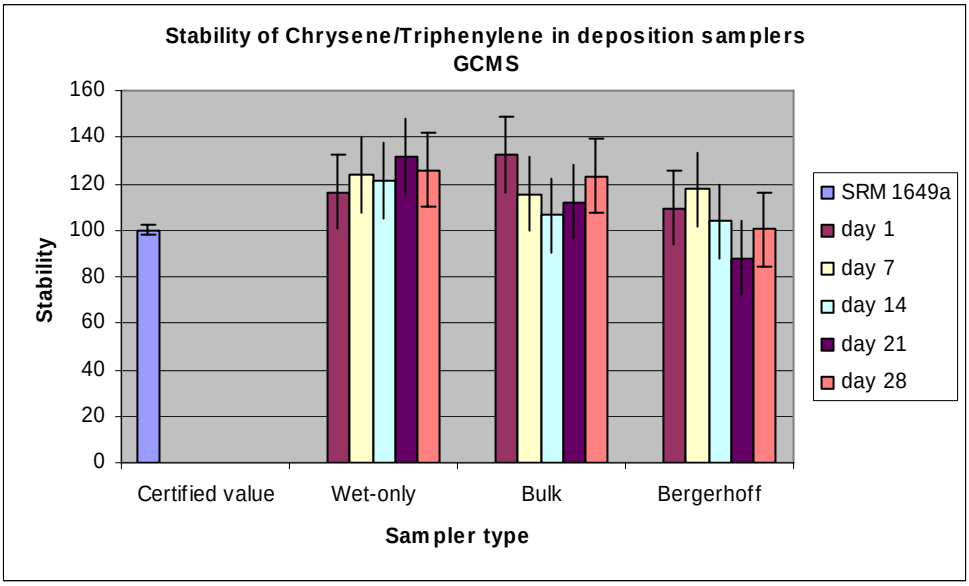

Figure 3.4 GC/MS results Chrysene

Table 3.3 HPLC results Chrysene

HPLC results	**Chrysene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		92	101	105
day 7		85	92	85
day 14		89	88	84
day 21		92	94	85
day 28		97	87	90
95 % level of confidence	2.0	16	16	16

Table 3.4 GC/MS results Chrysene

GC/MS results	**Chrysene/Triphenylene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		116	132	110
day 7		124	115	118
day 14		121	106	104
day 21		132	112	88
day 28		126	123	101
95 % level of confidence	2.0	16	16	16

3.3 Benzo[*b*]fluoranthene

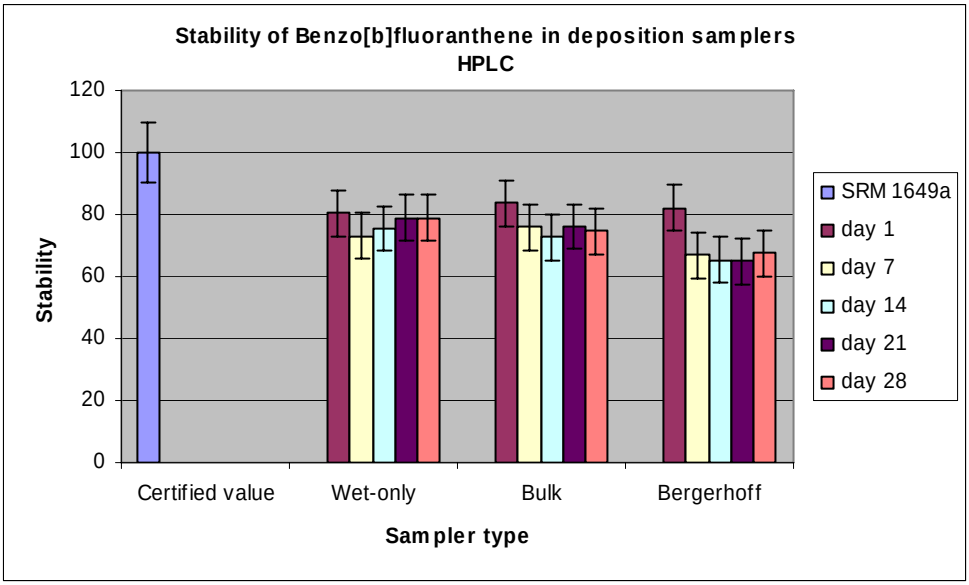

Figure 3.5 HPLC results Benzo[*b*]fluoranthene

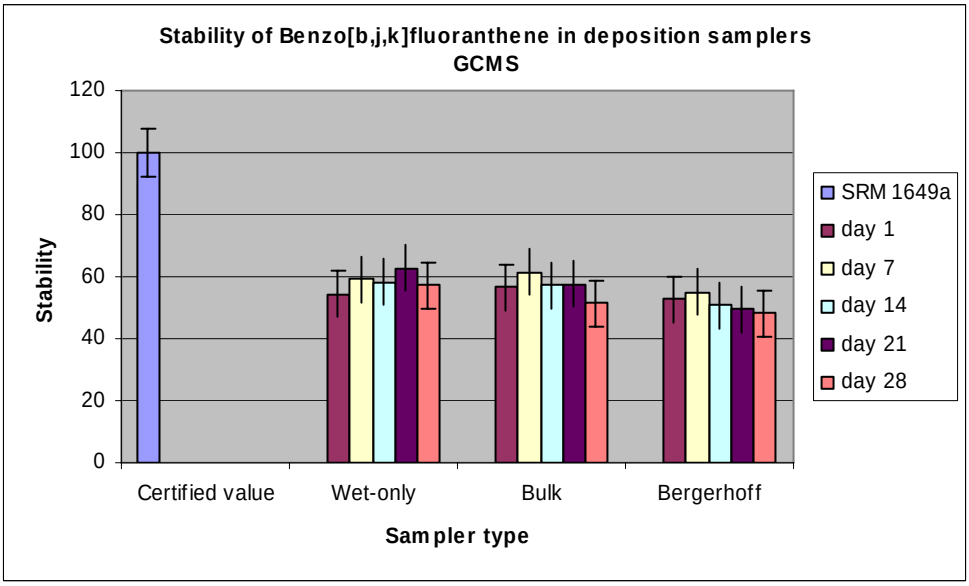

Figure 3.6 GC/MS results Benzo[*b,j,k*]fluoranthene

Table 3.5 HPLC results Benzo[*b*]fluoranthene

HPLC results	**Benzo[*b*]fluoranthene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		80	84	82
day 7		73	76	67
day 14		75	73	65
day 21		79	76	65
day 28		79	75	68
95 % level of confidence	9.9	7.4	7.4	7.4

Table 3.6 GC/MS results Benzo[*b*,*j*,*k*]fluoranthene

GC/MS results	**Benzo[*b,j,k*]fluoranthene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		54	56	53
day 7		59	61	55
day 14		58	57	51
day 21		63	58	50
day 28		57	51	48
95 % level of confidence	7.7	7.4	7.4	7.4

3.4 Benzo[*k*]fluoranthene

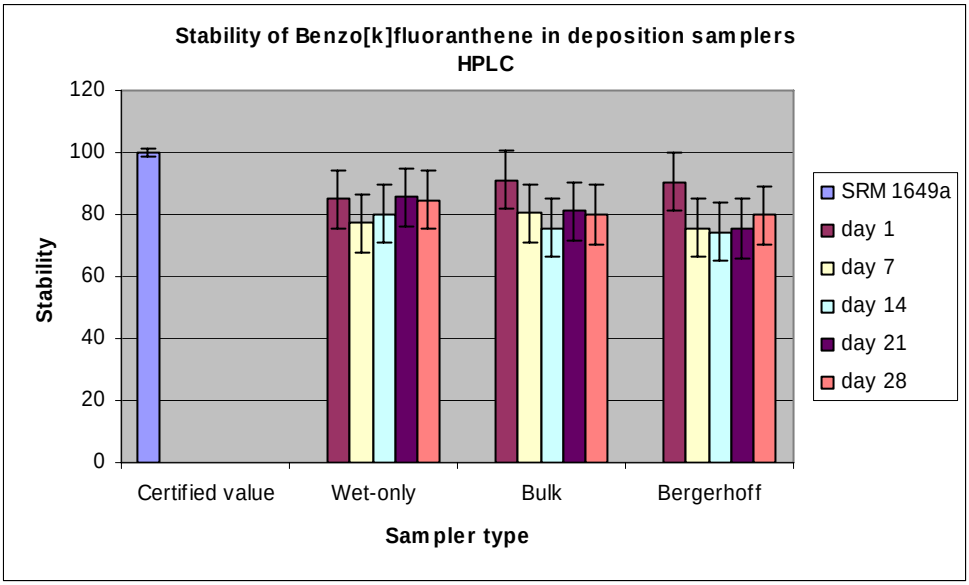

Figure 3.7 HPLC results Benzo[*k*]fluoranthene

Table 3.7 HPLC results Benzo[*k*]fluoranthene

HPLC results	**Benzo[*k*]fluoranthene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		85	91	90
day 7		77	80	76
day 14		80	76	75
day 21		86	81	75
day 28		85	80	80
95 % level of confidence	1.6	9.4	9.4	9.4

3.5 Benzo[*a*]pyrene

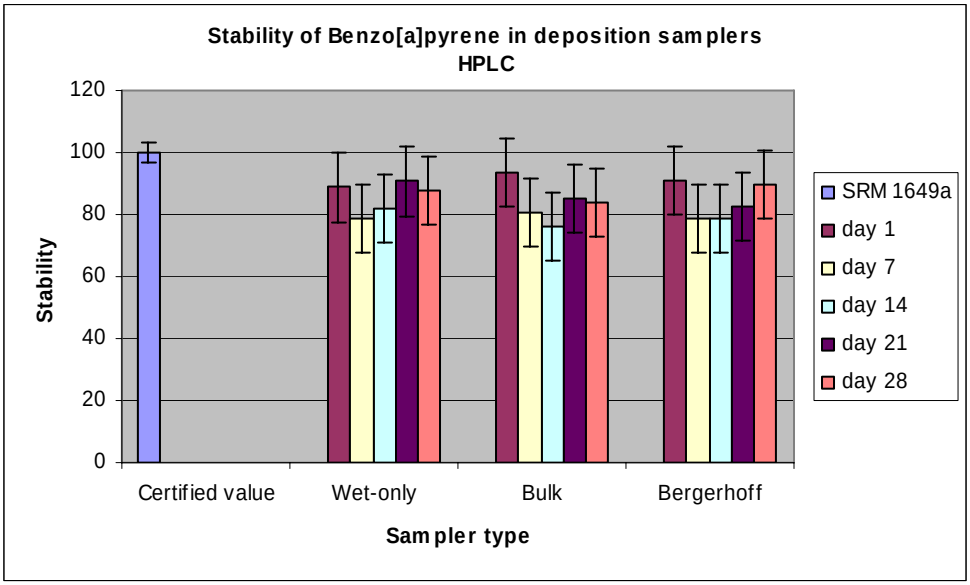

Figure 3.8 HPLC results Benzo[*a*]pyrene

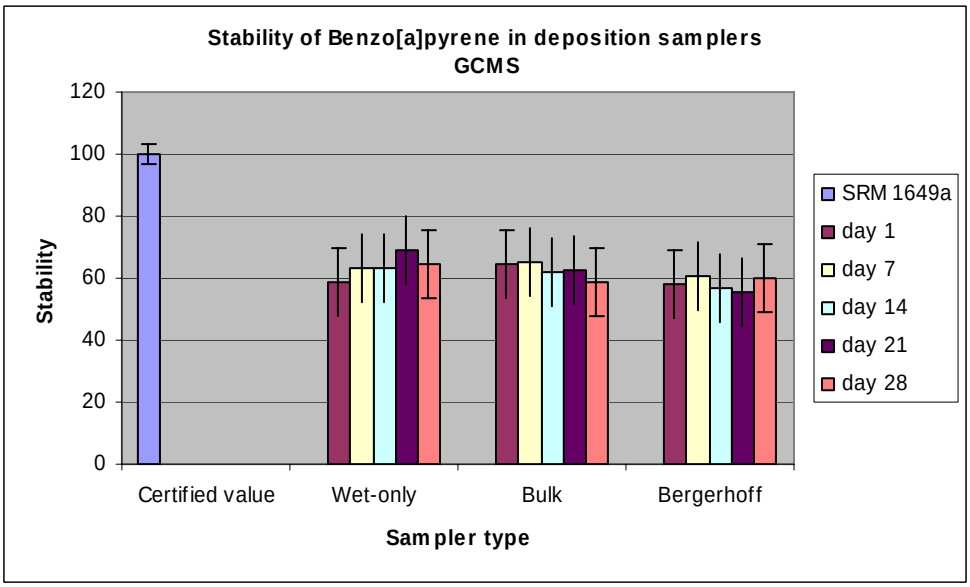

Figure 3.9 GC/MS results Benzo[*a*]pyrene

Table 3.8 HPLC results Benzo[*a*]pyrene

HPLC results	**Benzo[*a*]pyrene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		89	94	91
day 7		79	81	79
day 14		82	76	78
day 21		91	85	82
day 28		88	84	90
95 % level of confidence	3.5	11	11	11

Table 3.9 GC/MS results Benzo[*a*]pyrene

GC/MS results	**Benzo[*a*]pyrene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		59	65	58
day 7		63	65	61
day 14		63	62	57
day 21		69	63	56
day 28		65	58	60
95 % level of confidence	3.5	11	11	11

3.6 Dibenzo[*ah*]anthracene

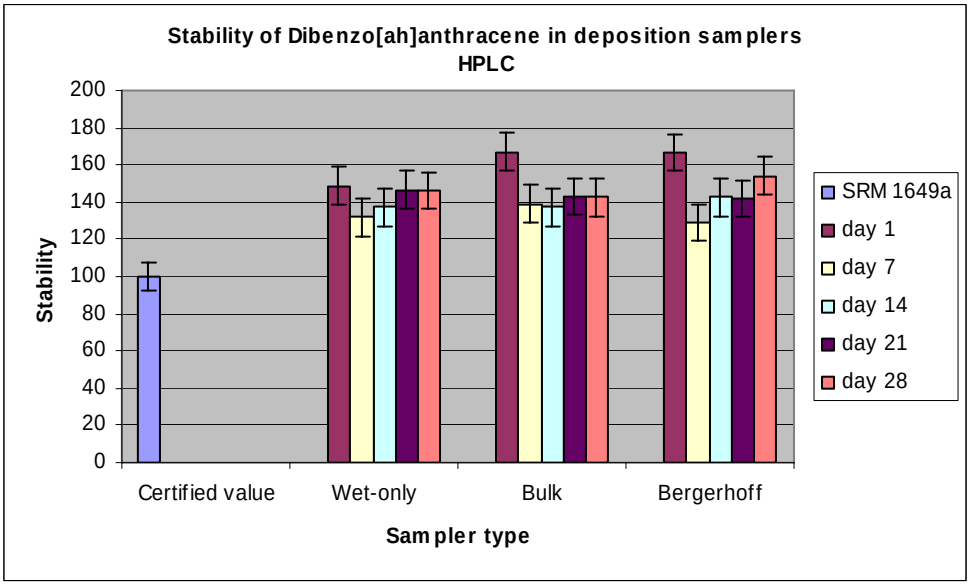

Figure 3.10 HPLC results Dibenzo[*ah*]anthracene

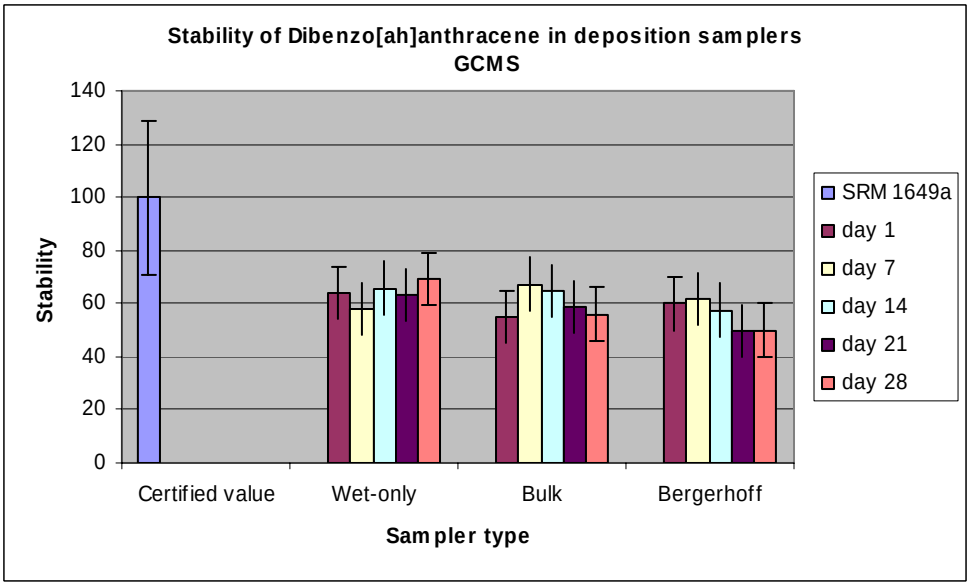

Figure 3.11 GC/MS results Dibenzo[*ah,ac,aj*]anthracene

Table 3.10 HPLC results Dibenzo[*ah*]anthracene

HPLC results	**Dibenzo[*ah*]anthracene**			
	Certified value	Wet-only	Bulk	Bergerhoff
Recovery	%	%	%	%
SRM 1649a	100			
day 1		149	167	167
day 7		132	139	129
day 14		137	137	143
day 21		146	143	142
day 28		146	142	154
95 % level of confidence	8.0	10	10	10

Table 3.11 GC/MS results Dibenzo[*ah*,*ac*,*aj*]anthracene

GC/MS results	**Dibenzo[*ah,ac,aj*]anthracene**			
	Certified value	Wet-only	Bulk	Bergerhoff
Recovery	%	%	%	%
SRM 1649a	100			
day 1		64	55	60
day 7		58	67	62
day 14		66	65	58
day 21		63	59	50
day 28		69	56	50
95 % level of confidence	28.9	10	10	10

3.7 Benzo[*ghi*]perylene

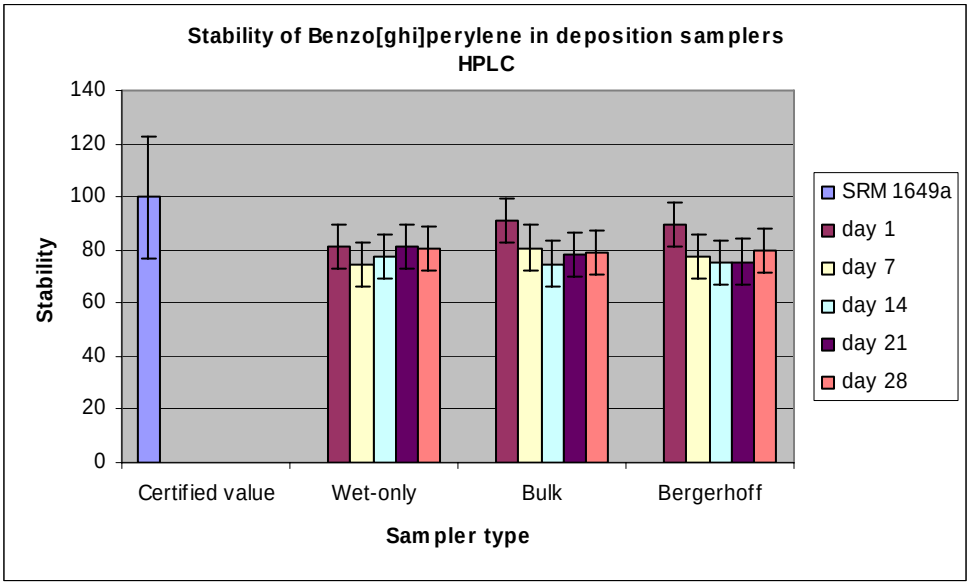

Figure 3.12 HPLC results Benzo[*ghi*]perylene

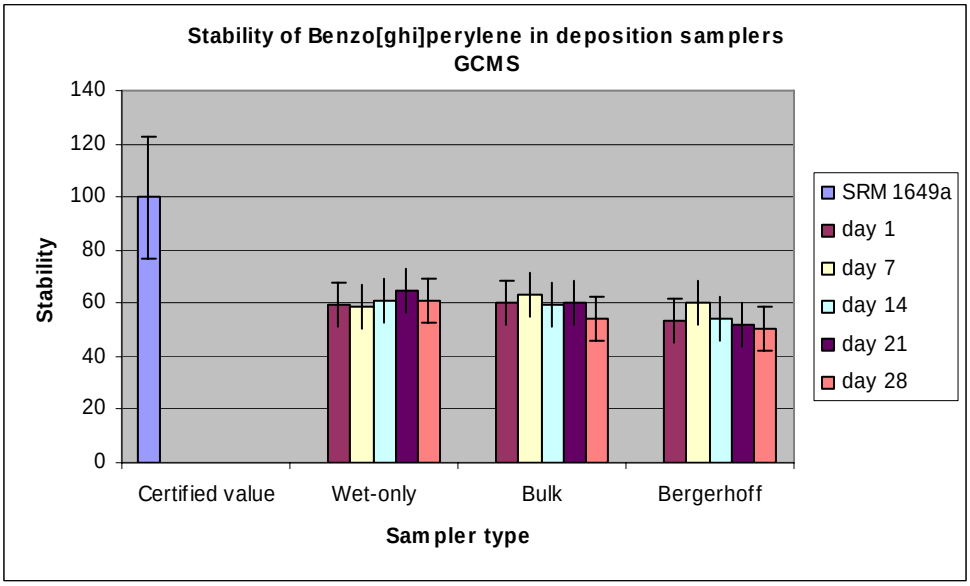

Figure 3.13 GC/MS results Benzo[*ghi*]perylene

Table 3.12 HPLC results Benzo[*ghi*]perylene

HPLC results	**Benzo[*ghi*]perylene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		81	91	90
day 7		74	81	78
day 14		77	75	75
day 21		81	78	76
day 28		81	79	80
95 % level of confidence	23.0	8.3	8.3	8.3

Table 3.13 GC/MS results Benzo[*ghi*]perylene

GC/MS results	**Benzo[*ghi*]perylene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		59	60	54
day 7		59	63	60
day 14		61	60	54
day 21		65	60	52
day 28		61	54	50
95 % level of confidence	23.0	8.3	8.3	8.3

3.8 Indeno[1,2,3-*cd*]pyrene

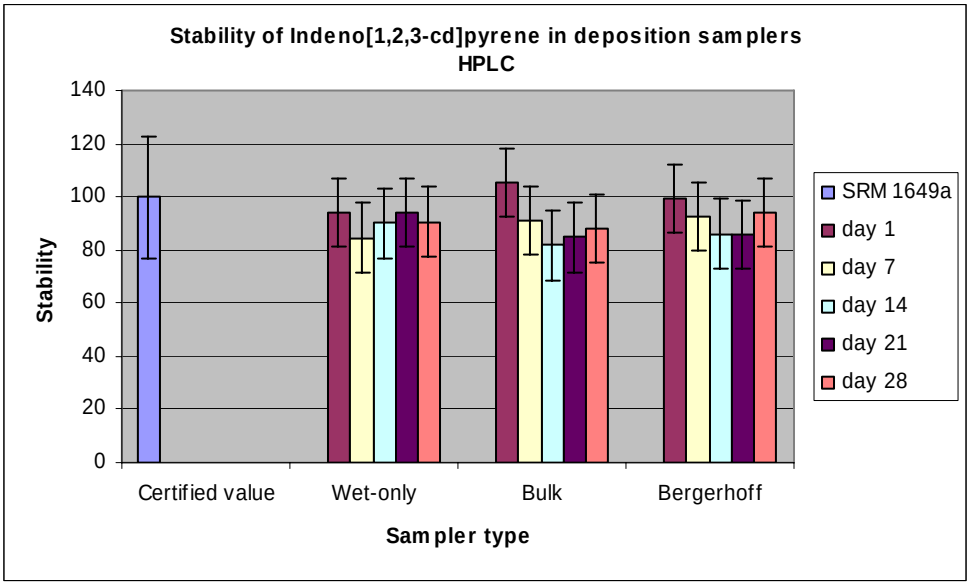

Figure 3.14 HPLC results Indeno[1,2,3-*cd*]pyrene

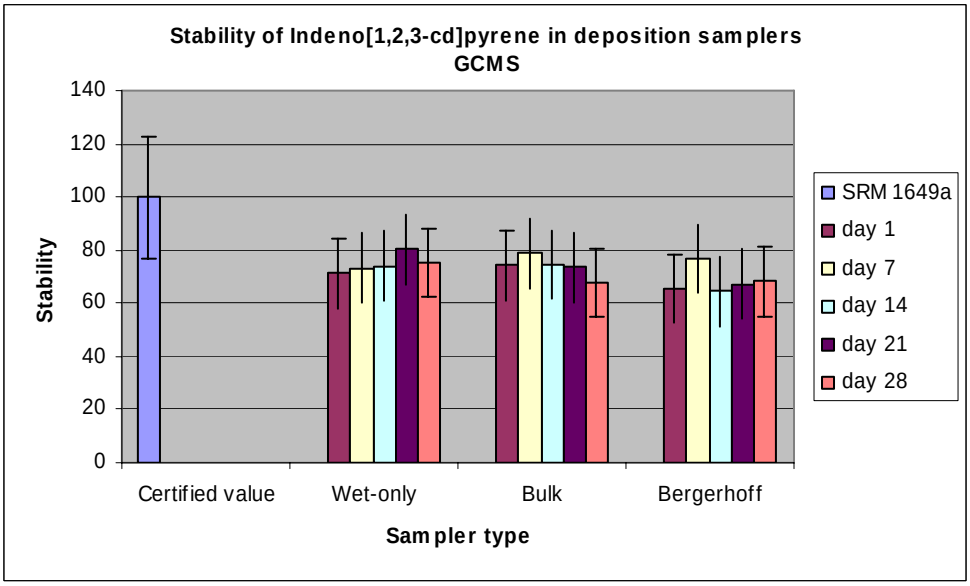

Figure 3.15 GC/MS results Indeno[1,2,3-*cd*]pyrene

Table 3.14 HPLC results Indeno[1,2,3-*cd*]pyrene

HPLC results	**Indeno[1,2,3-*cd*]pyrene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		94	105	99
day 7		84	91	93
day 14		90	82	86
day 21		94	85	86
day 28		91	88	94
95 % level of confidence	23.0	13	13	13

Table 3.15 GC/MS results Indeno[1,2,3-*cd*]pyrene

GC/MS results	**Indeno[1,2,3-*cd*]pyrene**			
	Certified value	Wet-only	Bulk	Bergerhoff
recovery	%	%	%	%
SRM 1649a	100			
day 1		71	74	65
day 7		73	79	77
day 14		74	75	65
day 21		80	73	67
day 28		75	68	68
95 % level of confidence	23.0	13	13	13

3.9 Conclusions

At the first day the determined PAH concentrations were generally within the in the range of ± 20 % of the certified values. The results for the samples which were exposed for longer periods were in most cases well inside the uncertainty range at a confidence interval of 95 % showing that no significant degradation of PAH occurred during the experiments.

Appendix A Meteorological circumstances

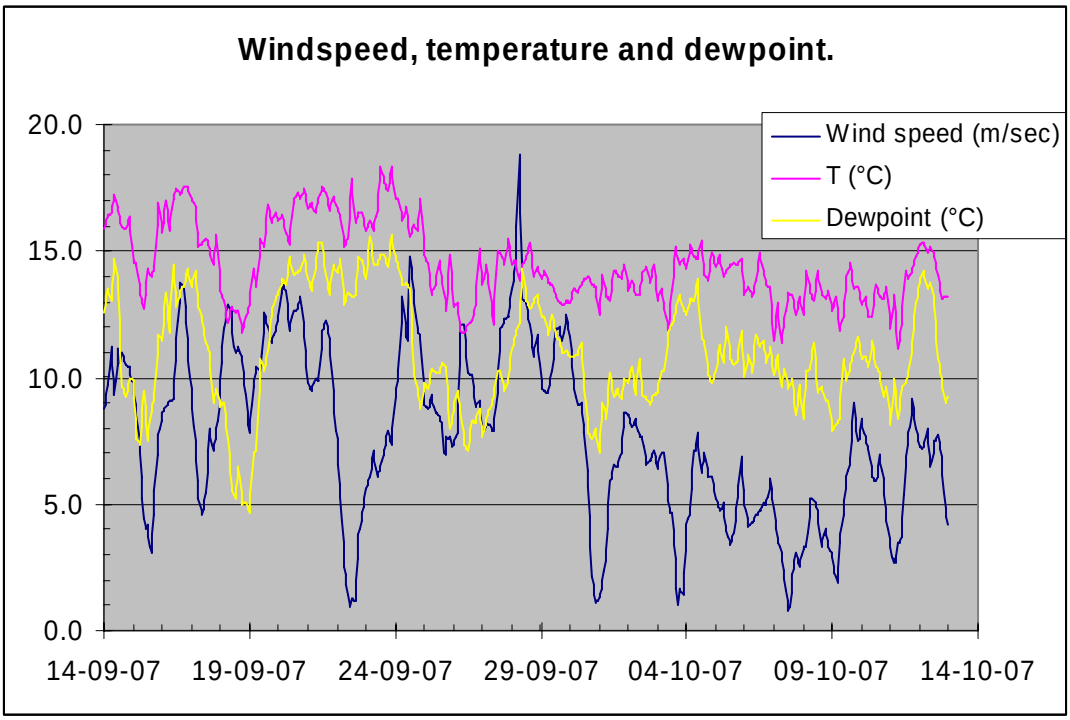

Figure 3.16 Wind speed, temperature and dew point during the degradation test

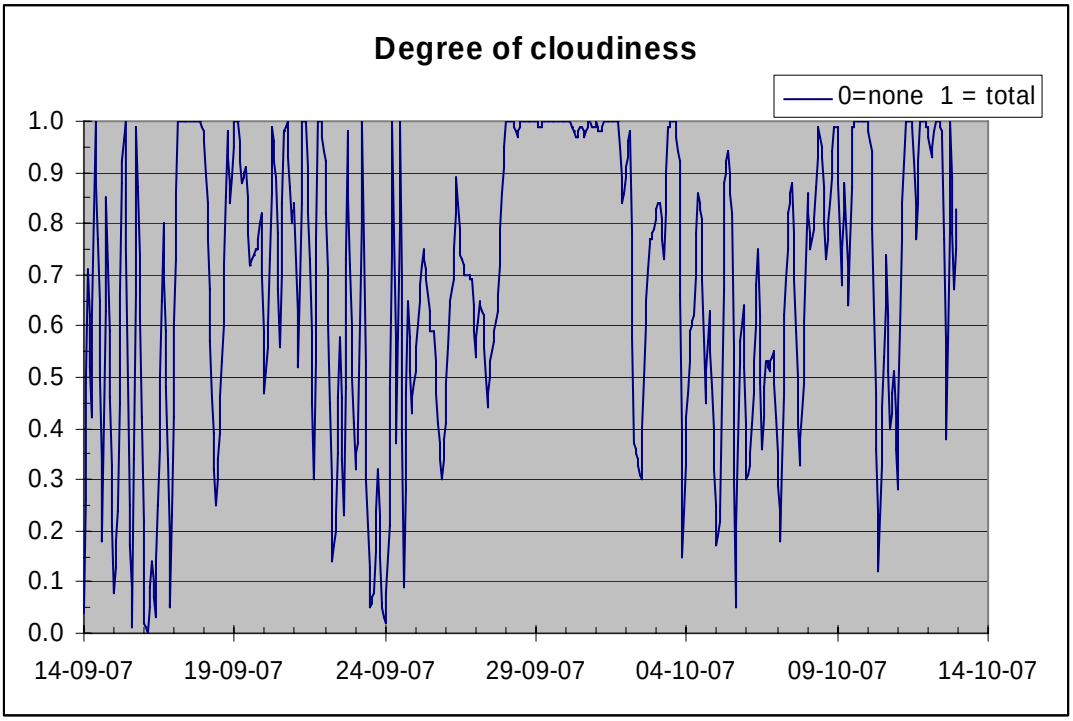

Figure 3.17 Degree of cloudiness during the degradation test

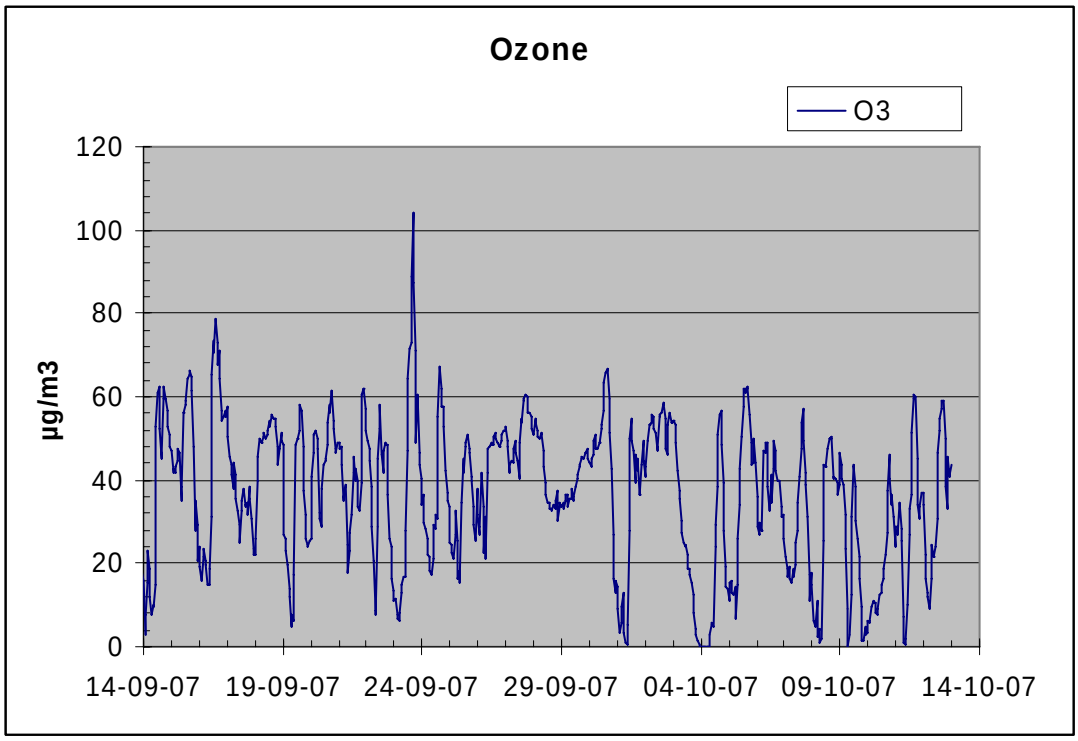

Figure 3.18 Ozone concentrations during the degradation test.
Measurements station at Wieringerwerf, Medemblikkerweg.

4 Field Test

This clause contains a description of the field test sampling sites (Pages 102 – 107) and the report *Evaluation of results of the field test programme* (Pages 108 – 125).

Field Test Sampling Sites

Instrumentation at the sampling sites

8 cylindrical gauges (Bergerhoff bulk collectors)
2 funnel-bottle bulk collectors
2 wet-only collectors

Sampling site I (Industrial site)

Location:
Bottrop (Germany)
Longitude: 6°58´37´´
Latitude: 51°31´37´´
Altitude: 40 m a.s.l.

Sampling period:
2007-07-02 to 2007-12-17

Characteristics:
The site is situated at a school 1500 m east of a highway and a power plant, 1500 m south east of a second power plant, 600 m north-east of a coking plant. The influence of the coking plant gives rise to high concentrations and deposition rates of PAH. Residential areas spread from south-west to north and north-east of the sampling site. Main wind direction is south-west.

Meteorological data (wind speed, wind direction, temperature, precipitation) and the concentration of Benzo[*a*]pyrene (BaP) were determined parallel to the deposition rates. Table 1 gives average values for the meteorological data and the BaP concentration during the sampling periods.

Table 1. Meteorological data and BaP concentrations at sampling site I during the sampling period

Sampling period No.	**1**	**2**	**3**	**4**	**5**	**6**
Date	02.07. – 30.07.	30.07. – 27.08.	27.08. – 24.09	24.09. – 22.10.	22.10. – 19.11.	19.11. – 17.12.
Precipitation in mm/d	5,2	2,7	1,6	1,1	2,8	2,0
Temp. in °C	18,7	17,9	14,7	11,4	7,3	6,2
BaP in ng/m³	1,02	0,97	1,33	1,05	1,15	2,12
Wind speed in m/s	3,0	2,4	2,4	2,0	2,7	3,5
Wind from N in d	1	6	8	10	3	3
Wind from E in d	1	5	0	5	6	5
Wind from S in d	7	4	4	4	2	12
Wind from W in d	17	13	15	9	17	8

Sampling site II (alpine background site)

Location:
Zöbelboden (Austria), A-4462 Reichraming
(EMEP-Code: AT48)
Longitude: 14°26´29´´
Latitude: 47°50´19´´
Altitude: 899 m a.s.l.

Sampling period:
2007-08-08 to 2008-02-21

Characteristics:
Topography: ridge
Settlement pattern: remote area
Local surroundings: wood, grassland
Close surroundings: grassland, trees

The site is situated in an altitude of about 900 m in the national park *Kalkalpen* in Upper Austria, about 6 km south of Reichraming. Gaseous and particle bound air pollutants, precipitations and greenhouse gases are measured there; meteorological data are taken.

The site is part of the national Remote Measuring Network and part of the European EMEP-Network. Beside this long-term measurements within the scope of "Integrated-Monitoring-Programs" of UNECE are carried out there. Figures 1 and 2 give an impression of the sampling site.


Fig. 1 and 2. Sampling site II (alpine background site) in autumn and in winter: Zöbelboden (Austria)

Meteorological data and ozone concentrations were determined parallel to the deposition rates. Table 2 shows average values for precipitation, temperature, wind speed and wind direction data and ozone concentration during the sampling periods.

Table 2. Meteorological data and ozone concentrations at sampling site II during the sampling period

Sampling period No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Date	08.08. – 07.09.	07.09. – 03.10.	03.10. – 31.10	31.10. – 28.11.	28.11. – 27.12.	27.12.07 – 23.01.08	23.01. – 21.02.
Precipitation in mm/d	0,3	0,1	0,1	0,1	0,1	0,1	0,0
Temp. in °C	13,5	10,8	5,7	0,9	- 0,7	1,7	0,7
Wind speed in m/s	0,7	0,7	0,5	1,3	0,8	0,9	1,0
Mean wind direction	SSW	S	S	WSW	SW	SW	SW
Ozone in ppb	38,3	33,4	25,9	28,4	31,3	34,8	34,4

Sampling site III (remote southern site)

Location:
Peyrusse-Grande (France)
Longitude: 0°10´54´´
Latitude: 43°37´50´´
Altitude: 245 m a.s.l.

Sampling period:
2008-08-24 to 2009-02-27

Characteristics:
The site is situated at about 120 km from Toulouse. There are no industries and highways nearby. The sampling station is shown in Fig. 3.

Meteorological conditions were determined parallel to the deposition rates (see Fig. 4 and 5).

Fig. 3. Sampling station

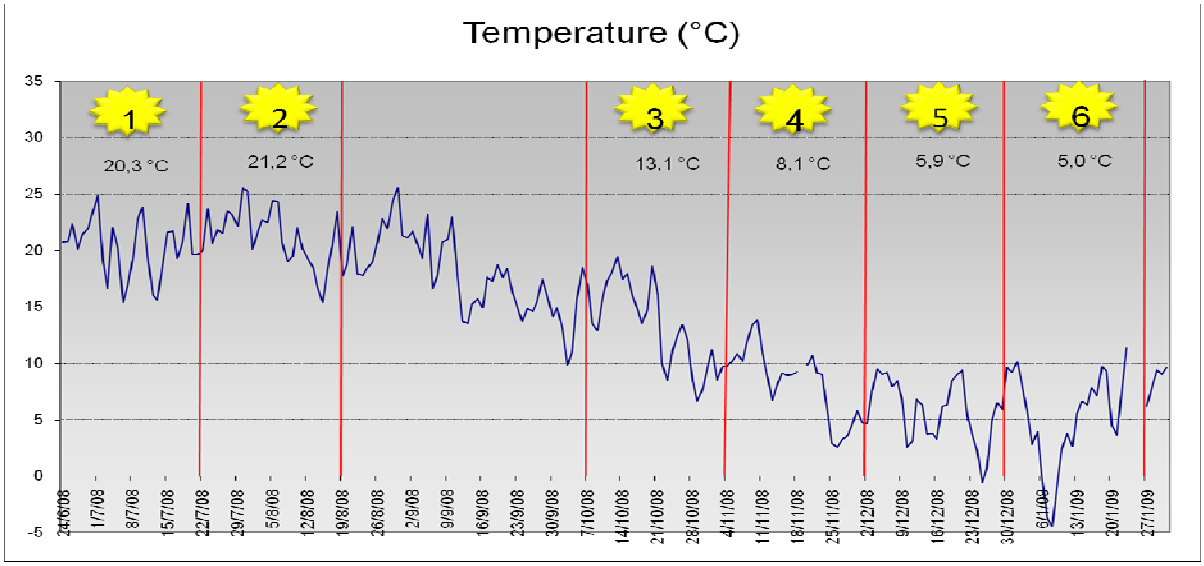

Fig. 4. Ambient air temperature during the sampling period

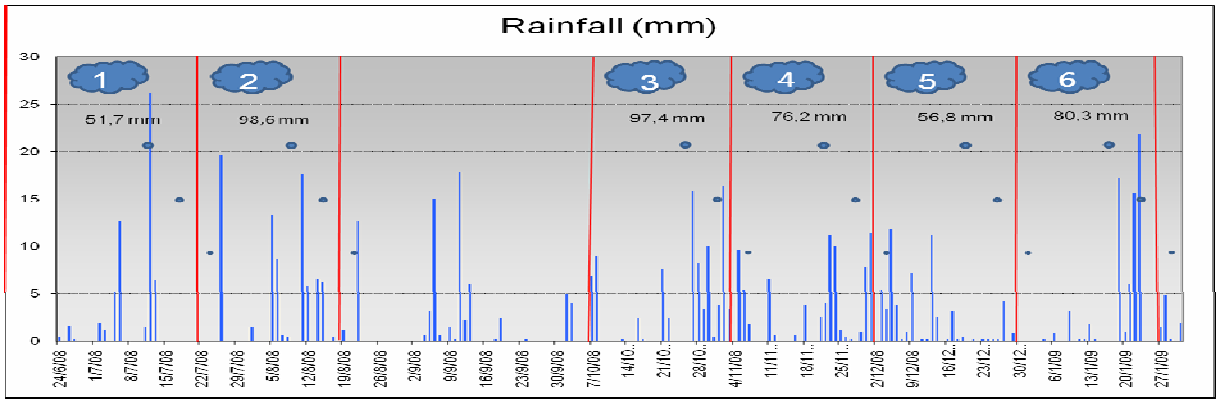

Fig. 5. Precipitation during the sampling period

Sampling site IV (traffic related site)

Location:
De Bilt (The Netherlands)
Latitude: 52°05'56,3" N
Longitude: 5°10'34,3" E
Altitude: 3 m a.s.l.

Sampling period:
2008-04 to 2009-02

Characteristics:
The sampling site is not an official deposition measurement site. It is situated at KNMI (Royal Netherlands Meteorological Institute) near two highways (A27 (E311) and A28 (E30)). Residential areas spread from south-west to north and north-east of the sampling site. Prevailing annual wind direction is south-west. Figure 6 gives an impression of the sampling site.


Fig. 6. Photograph of the sampling equipment at the sampling site

Meteorological data were measured parallel to the deposition rates.

Table 4 shows average values for precipitation, temperature, wind speed and wind direction data and the concentration of BaP during the sampling periods.

Table 4. Meteorological data at sampling site IV during the sampling period

Sampling period No.	**1**	**2**	**3**	**4**	**5**	**6**
Date	09.04. – 14.05.	14.05. – 18.06.	18.06. – 14.07.	14.07. – 13.08.	13.08. – 01.10.	08.01.09 – 04.02.09
Precipitation in mm/period	16.3	64.5	69.9	120.2	176.9	49.7
Precipitation duration in h	18.3	41.6	47.2	63.6	93.8	55.6
Temp. in °C	12.6	15.3	17.1	18.6	14.7	1.3
Wind speed in m/s	3.5	2.9	3.7	3.4	3.2	4.0
Wind from N in d (with prec.)	5 (1)	11 (7)	0 (0)	2 (1)	3 (1)	0 (0)
Wind from E in d	18 (1)	10 (4)	2 (0)	4 (0)	15 (2)	8 (0)
Wind from S in d	10 (6)	3 (1)	9 (8)	12 (10)	19 (13)	18 (9)
Wind from W in d	3 (0)	11 (5)	15 (6)	12 (12)	12 (10)	2 (0)

CEN TC 264 / WG 21
'METHOD FOR THE DETERMINATION OF THE ATMOSPHERIC DEPOSITION OF PAH'

Evaluation of results of the field test programme

July 2009
Author: Theo Hafkenscheid, RIVM (NL)

Introduction

Within the frame of the validation of a method for the determination of the total atmospheric deposition of polycyclic aromatic hydrocarbons (PAH), a validation programme based on a series of laboratory and field tests has been designed [1].

In the laboratory tests, attention was focused on studying the feasibility and comparability of the proposed analytical methodologies for the analysis of deposition samples. In the field test three different collector types were tested side-by-side at four different locations. The collector types were:

1. A funnel-bottle bulk collector
2. A wet-only collector
3. A cylindrical gauge (Bergerhoff collector)

Descriptions of the collectors may be found in Annex A of [2].

The four sampling sites were:

1. A remote site in Central Europe (Austria)
2. An industrial site in Central Europe (Germany)
3. A remote site in Southern Europe (France)
4. An urban site in Western Europe (Netherlands)

At each site two collectors of types (1) and (2) were exposed in parallel, while 2×4 collectors of type (3) were exposed. The contents of 4 collectors of type (3) were combined to one sample, yielding two parallel samples for collector type (3). All collectors were exposed for six consecutive four-week periods; collectors at site (1) were exposed for seven consecutive four-week periods.

The participating laboratories performed their analyses according to their own methods based on EN 15549, ISO 12884 and ISO 16362. The extraction procedures to be followed in principle have been described in detail in documents [1] and [3]. The following PAH were determined:

— Benzo[*a*]anthracene
— Benzo[*b*]fluoranthene
— Benzo[*j*]fluoranthene
— Benzo[*k*]fluoranthene
— Benzo[a*]*pyrene
— Indeno[1,2,3-*cd*]pyrene
— Dibenzo[*a,h*]anthracene

This report concentrates on the statistical evaluation of the results from the analyses of the above samples. The evaluation serves two purposes, namely:

— Estimation and comparison of the uncertainties associated with the use of the different collectors by assessment of between-collector variances
— Calculation of the combined uncertainty for the complete procedure of sampling and analysis by combining results from the laboratory tests [4] with those of the field tests

Data processing

Data submitted

For each of the four sites results were submitted of the mass of each PAH found in each of the collectors for each of the individual exposure periods 'by spreadsheet'. These results were converted into mass deposition rates in units of $mg \cdot m^{-2} \cdot d^{-1}$ by combination with relevant surface area dimensions of the collectors (in m^2) and exposure periods (in days).

In some cases, no results were reported. In other cases, results equal to zero were reported. A careful study of the results submitted learned that – invariably – the latter results could not be explained from zero depositions, as other components were detected and measured in the samples concerned. These reported 'zero' results most likely represented results that were below the limits of detection of the components in the samples concerned. These results were replaced with '*nd'* (not detectable) in the tables of deposition results presented in Annex 1. Consequently, these results were not used for further (statistical) evaluation of uncertainties.

Data treatment

For each site, each collector and each component the mean depositions observed during the consecutive sampling periods were calculated from the results for the individual periods. Further, for each collector and each component the relative between-collector uncertainties were calculated of the results per component per pair of similar collectors exposed in parallel (or combinations of results for four Bergerhoff collectors). These are given in Annex 2. The relative between-collector uncertainties were calculated as

$$w^2_{bs,j} = \frac{\sum_i \left(x_{i,j,1} - x_{i,j,2}\right)^2}{2n \cdot \overline{x_j}} \qquad (1)$$

where

x_1, x_2 = results for collectors 1 and 2 for each exposure period *i* for collector type j
i = individual exposure period
j = collector type
n = number of exposure periods
$\overline{x_j}$ = mean of mean results over period i for collector j.

Uncertainty evaluations

First, values for $w_{bs,i}$ were plotted against the mean depositions reported for all components for each collector type in order to study the relationships between $w_{bs,i}$ and compound deposition. The plots are given in Figures 1 to 3 below. From these figures it is apparent that particularly for the funnel-bottle bulk and wet-only collectors the relationships tend to have the shape of a 'Horwitz-curve' [5], with $w_{bs,i}$ being constant at higher deposition levels and increasing exponentially at low concentrations. For the Bergerhoff collector this relationship is less apparent because of the high scatter observed at the low concentration range.

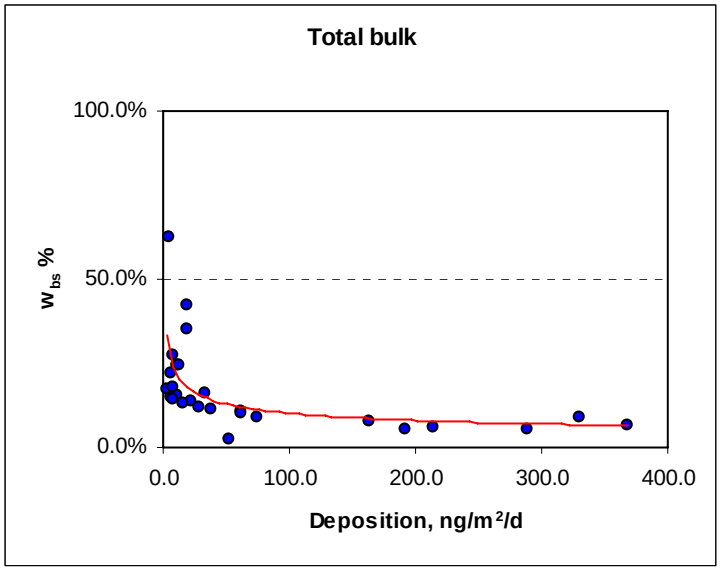

Figure 1. Between-collector uncertainty vs. deposition: funnel-bottle bulk collector

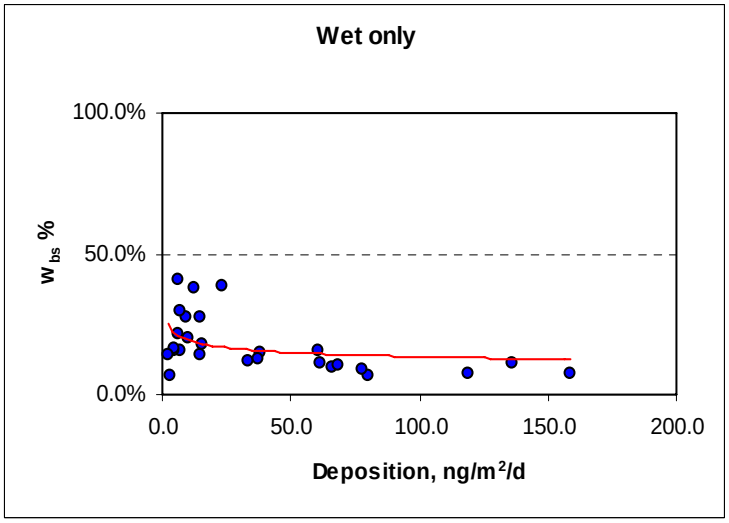

Figure 2. Between-collector uncertainty vs. deposition: wet-only collector

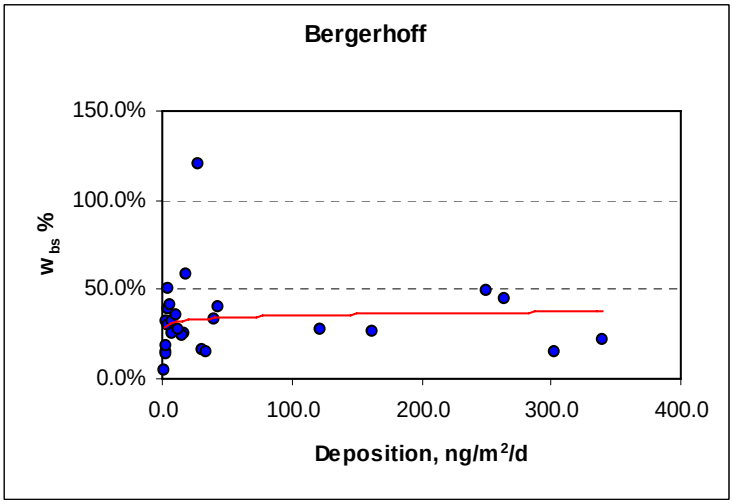

Figure 3. Between-collector uncertainty vs. deposition: Bergerhoff collector

In order to obtain single expressions for all collectors for $w_{bs,i}$ the relationships were fitted to exponential functions of the form

$$w_{bs,j} = a.e^{b.\overline{x_j}} \quad (2)$$

The appropriate values for coefficients *a* and *b* were obtained by minimizing the residuals resulting from the fitting procedure using Excel's solver function. The random relative uncertainties of the fits were calculated from the residual sum-of-squares of the fits as

$$w_{fit}^2 = \frac{rss}{2p} \quad (3)$$

where
rss = residual sum of squares from the fit
p = number of values for $w_{bs,l}$ used for the fitting procedure (p=27).

The following values for a, b and w_{fit} were obtained.

Table 1. Results of exponential fits of $w_{bs,l}$ vs. mean deposition

	Coefficient a	*Coefficient b*	w_{fit}
F-b bulk collector	0,490	-0,342	7,3 %
Wet-only collector	0,277	-0,157	6,4 %
Bergerhoff collector	0,284	0,048	14,9 %

The relationships obtained in this way may be used to estimate the between-collector uncertainty as a function of the deposition measured.

In order to estimate the total random uncertainty of results of the deposition measurements these uncertainties were combined with the uncertainties from the analytical procedures. In doing so it should be born in mind that, in principle, the between-collector uncertainties calculated using equation (1) are built up of contributions from the 'real' between-collector uncertainty and a contribution representing the within-laboratory analytical uncertainty for the component measured. Consequently, when estimating the total uncertainty for the field test results the between-collector uncertainty should be combined with estimates of between-laboratory uncertainty contributions for the analytical procedures used. The uncertainties calculated in this way represent "reproducibility uncertainties".

A selection of results from the laboratory test analyses (see [4]) were used for this. In these tests two samples were analyzed that may be considered representative of real deposition samples (samples 5 and 7 – NIST SRM suspended in water). For the calculation of the total uncertainty the mean results of the analyses of samples 5 and 7 were converted to deposition results by using the appropriate collector surface areas and an exposure period of 28 days. When combining the two contributions by summation in quadrature the following uncertainties resulted (tables 2-7).

Here *s(L)* is the between-laboratory analytical standard deviation, w_c the combined relative uncertainty and *W* the expanded relative uncertainty (95 % confidence level).

Table 2. Results for lab test sample 5 – funnel-bottle bulk collector

	Deposition ($ng \cdot m^{-2} \cdot d^{-1}$)	*s(L)*	w_{bs}	w_c	*W (k=2)*
Benz[*a*]anthracene	57,3	14,2 %	12,3 %	18,8 %	37,5 %
Benz[*b*]fluoranthene	145,1	8,2 %	8,9 %	12,1 %	24,3 %
Benz[*j*]fluoranthene	55,5	15,7 %	12,4 %	20,0 %	40,0 %
Benz[*k*]fluoranthene	50,6	17,5 %	12,8 %	21,7 %	43,4 %
Benz[*a*]pyrene	68,2	13,6 %	11,6 %	17,9 %	35,7 %
Indeno[1,2,3-*cd*]pyrene	98,9	9,0 %	10,2 %	13,6 %	27,2 %
Dibenz[*a,h*]anthracene	13,0	19,0 %	20,4 %	27,9 %	55,7 %

Table 3. Results for lab test sample 5 – wet-only collector

	Deposition ($ng \cdot m^{-2} \cdot d^{-1}$)	*s(L)*	w_{bs}	w_c	*W (k=2)*
Benz[*a*]anthracene	143,5	14,2 %	12,7 %	19,0 %	38,1 %
Benz[*b*]fluoranthene	363,4	8,2 %	11,0 %	13,7 %	27,4 %
Benz[*j*]fluoranthene	139,0	15,7 %	12,8 %	20,2 %	40,5 %
Benz[*k*]fluoranthene	126,6	17,5 %	12,9 %	21,8 %	43,5 %
Benz[*a*]pyrene	170,7	13,6 %	12,4 %	18,4 %	36,7 %
Indeno[1,2,3-*cd*]pyrene	247,7	9,0 %	11,7 %	14,7 %	29,4 %
Dibenz[*a,h*]anthracene	32,6	19,0 %	16,0 %	24,9 %	49,7 %

Table 4. Results for lab test sample 5 – Bergerhoff collector

	Deposition ($ng \cdot m^{-2} \cdot d^{-1}$)	*s(L)*	w_{bs}	w_c	*W (k=2)*
Benz[*a*]anthracene	113,1	14,2 %	35,6 %	38,3 %	76,7 %
Benz[*b*]fluoranthene	286,3	8,2 %	37,2 %	38,1 %	76,3 %
Benz[*j*]fluoranthene	109,5	15,7 %	35,6 %	38,9 %	77,7 %
Benz[*k*]fluoranthene	99,7	17,5 %	35,4 %	39,5 %	79,0 %
Benz[*a*]pyrene	134,5	13,6 %	35,9 %	38,4 %	76,8 %
Indeno[1,2,3-*cd*]pyrene	195,2	9,0 %	36,6 %	37,6 %	75,3 %
Dibenz[*a,h*]anthracene	25,7	19,0 %	33,2 %	38,2 %	76,4 %

Table 5. Results for lab test sample 7 – funnel-bottle bulk collector

	Deposition ($ng \cdot m^{-2} \cdot d^{-1}$)	*s(L)*	w_{bs}	w_c	*W (k=2)*
Benz[*a*]anthracene	15,9	14,7 %	19,0 %	24,0 %	48,1 %
Benz[*b*]fluoranthene	38,4	12,3 %	14,1 %	18,7 %	37,3 %
Benz[*j*]fluoranthene	10,5	43,1 %	21,9 %	48,4 %	96,8 %
Benz[*k*]fluoranthene	13,3	9,3 %	20,2 %	22,2 %	44,5 %
Benz[*a*]pyrene	16,6	17,2 %	18,7 %	25,4 %	50,9 %
Indeno[1,2,3-*cd*]pyrene	24,3	16,4 %	16,5 %	23,3 %	46,5 %
Dibenz[*a,h*]anthracene	3,0	35,1 %	33,8 %	48,7 %	97,4 %

Table 6. Results for lab test sample 7 – wet-only collector

	Deposition ($ng \cdot m^{-2} \cdot d^{-1}$)	*s(L)*	w_{bs}	w_c	*W (k=2)*
Benz[*a*]anthracene	39,7	14,7 %	15,5 %	21,4 %	42,7 %
Benz[*b*]fluoranthene	96,3	12,3 %	13,5 %	18,2 %	36,5 %
Benz[*j*]fluoranthene	26,3	43,1 %	16,6 %	46,2 %	92,4 %
Benz[*k*]fluoranthene	33,3	9,3 %	16,0 %	18,5 %	36,9 %
Benz[*a*]pyrene	41,6	17,2 %	15,4 %	23,1 %	46,2 %
Indeno[1,2,3-*cd*]pyrene	60,8	16,4 %	14,5 %	21,9 %	43,8 %
Dibenz[*a,h*]anthracene	7,4	35,1 %	20,2 %	40,5 %	80,9 %

Table 7. Results for lab test sample 7 – Bergerhoff collector

	Deposition ($ng \cdot m^{-2} \cdot d^{-1}$)	*s(L)*	w_{bs}	w_c	*W (k=2)*
Benz[*a*]anthracene	31,3	14,7 %	33,5 %	36,6 %	73,1 %
Benz[*b*]fluoranthene	75,8	12,3 %	34,9 %	37,0 %	74,0 %
Benz[*j*]fluoranthene	20,7	43,1 %	32,8 %	54,2 %	108,4 %
Benz[*k*]fluoranthene	26,3	9,3 %	33,2 %	34,5 %	68,9 %
Benz[*a*]pyrene	32,8	17,2 %	33,6 %	37,7 %	75,4 %
Indeno[1,2,3-*cd*]pyrene	47,9	16,4 %	34,2 %	37,9 %	75,8 %
Dibenz[*a,h*]anthracene	5,9	35,1 %	30,9 %	46,7 %	93,5 %

Subsequently, the calculated expanded relative uncertainties *W* can be compared with the data-quality objective of 70 % given in Annex IV of Directive 2004/107/EC.

These comparisons show that, generally, uncertainties obtained using the Bergerhoff collectors do not meet the 70 % uncertainty criterion. This is due to the high relative between-collector uncertainty of 30 % – 35 %.

The uncertainties for funnel-bottle bulk collector and wet-only collector meet the 70 % criterion except for benz[*j*]fluoranthene and dibenz[*a,h*]anthracene at low deposition values. However, the exceedances for these cases can be fully explained by the high analytical between-laboratory uncertainties for these components at the low levels of lab test sample 7.

Conclusions

From the results of the field tests the between-collector uncertainties were calculated for the three collector types investigated. These were found to be described more or less by exponential functions of the depositions measured, independent of the components analyzed. The lowest uncertainties and best fits were found for the funnel-bottle bulk collector and the wet-only collector. However, the latter collector generally yields substantially lower deposition values.

Through combination of the between-collector uncertainties with analytical between-laboratory uncertainties for samples from the laboratory validation tests [4] the total uncertainties for the deposition measurement results may be obtained. For the funnel-bottle bulk collector and wet-only collector the uncertainties observed generally meet the 70 % uncertainty criterion given in Directive 2004/107/EC. Those cases in which the criterion is exceeded may simply be explained from the atypically high analytical uncertainties rather than from the performances of the collectors. The uncertainties for the Bergerhoff collector generally do not meet the 70 % criterion.

References

[1] Document CEN/TC264 WG21 N173

[2] Document CEN/TC264 WG21 N232

[3] Document CEN/TC264 WG21 N159

[4] Document CEN/TC264 WG21 N219

[5] Albert R., Horwitz W. (1997): A heuristic derivation of the Horwitz Curve. Anal. Chem. 69, 789 – 790

Annex 1 Deposition results in ng/m^2/d

Site 1 - Austria

Benz[*a*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	31,6	42,5	13,1	14,9	87,6	18,7
2	15,6	20,3	7,3	4,2	12,8	5,2
3	56,6	54,1	49,9	65,4	22,9	13,1
4	54,3	63,0	68,1	78,3	24,7	25,6
5	41,4	37,7	81,7	89,3	120,2	19,9
6	30,1	28,7	12,1	14,4	10,5	9,6
7	25,1	27,6	15,0	15,0	5,0	4,4

Benz[*b*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	48,5	37,5	21,5	20,2	44,9	24,2
2	21,4	35,3	14,2	12,4	48,4	7,9
3	137,6	122,6	108,5	120,4	40,6	28,1
4	85,4	83,7	104,2	116,3	60,8	95,3
5	53,1	46,8	92,8	122,5	91,4	58,9
6	46,5	49,0	22,8	30,8	36,5	36,8
7	41,8	48,2	31,6	35,5	21,4	20,4

Benz[*j*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	60,8	52,1	24,0	22,8	41,3	29,2
2	23,1	28,1	14,2	13,1	6,0	8,5
3	155,2	142,7	114,2	131,6	40,8	31,7
4	99,3	103,0	119,1	122,5	80,6	35,7
5	75,0	62,8	121,6	131,2	91,0	78,5
6	64,4	62,6	22,9	29,1	38,3	39,2
7	47,5	60,7	36,9	51,7	17,4	20,9

Benz[*k*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	22,6	20,0	11,4	10,4	20,6	12,1
2	7,3	8,8	6,4	5,4	5,0	2,0
3	65,3	56,3	59,1	66,4	18,8	12,0
4	41,7	46,5	57,3	64,7	28,3	25,9
5	25,3	21,3	61,4	68,9	37,5	28,1
6	20,9	21,0	10,5	14,5	14,2	14,8
7	16,9	22,4	14,4	20,1	7,3	7,7

Benz[*a*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	27,0	22,6	15,5	13,7	46,4	15,9
2	9,2	20,4	9,2	7,7	3,4	4,6
3	69,2	54,3	56,4	68,4	19,3	13,1
4	46,8	49,9	63,7	73,5	24,9	22,8
5	33,5	29,8	72,4	79,1	52,7	24,3
6	30,7	30,5	12,0	15,0	13,1	14,2
7	23,7	28,3	14,9	19,2	7,2	8,4

Indeno[1,2,3-*cd*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	46,9	41,8	20,8	22,5	38,3	25,4
2	21,1	27,3	15,6	13,0	15,6	7,1
3	140,2	123,3	110,3	123,2	37,2	30,3
4	85,0	89,2	101,0	115,8	50,9	51,8
5	57,9	52,1	109,2	118,7	65,8	56,7
6	46,5	48,6	19,6	27,7	31,7	32,5
7	36,6	47,4	27,8	38,7	16,7	16,8

Dibenz[*a,h*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	5,4	4,0	3,1	2,2	6,1	3,5
2	2,3	3,2	1,9	1,6	3,1	1,1
3	16,1	11,8	13,2	16,0	2,6	3,1
4	7,7	10,1	11,2	13,3	5,2	5,8
5	6,1	6,2	12,8	14,7	10,2	5,4
6	4,7	5,5	2,0	2,4	3,7	3,3
7	3,6	4,7	2,3	3,1	1,8	2,0

Site 2 - Germany

Benz[*a*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1		391,8	230,9	244,7	276,1	329,3
2	298,9	301,0	93,8	86,7	173,7	185,9
3	155,7	168,8	38,7	30,7	181,4	205,1
4	224,4	227,4	68,1	77,8	168,2	169,2
5	246,2	225,6	113,8	93,7	158,6	183,4
6	433,2	392,5	169,6	183,7	362,7	769,0

Benz[*b*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1		478,8	282,1	293,4	448,5	479,3
2	420,4	445,8	149,5	139,9	251,5	220,2
3	207,0	217,1	54,5	45,4	212,1	253,6
4	329,3	341,5	112,6	133,9	274,2	278,8
5	279,3	286,6	146,1	115,5	264,3	274,4
6	503,6	435,7	211,1	220,2	433,0	685,5

Benz[*j*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1						
2	207,8	208,7	79,1	74,9	96,0	93,7
3	105,2	108,8	34,9	29,8	81,7	103,7
4	132,8	137,6	52,2	61,7	93,9	99,7
5	140,4	146,1	71,3	55,8	124,9	129,6
6	245,4	205,2	104,0	101,2	198,9	303,2

Benz[*k*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1		249,1	135,7	142,6	215,7	233,2
2	282,0	292,4	103,6	98,5	117,4	135,5
3	114,8	118,4	35,4	31,0	104,6	119,6
4	158,9	157,8	57,1	65,3	129,4	135,9
5	131,1	131,9	63,7	50,9	116,1	120,0
6	222,2	193,4	87,8	93,1	186,3	330,3

Benz[*a*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1		298,2	157,7	163,1	323,1	365,8
2	220,1	240,4	61,4	60,0	169,5	186,6
3	124,8	143,3	35,0	25,9	161,8	197,3
4	160,6	150,3	46,2	54,5	159,4	160,8
5	174,3	172,9	75,0	58,4	157,4	167,0
6	294,0	264,0	93,1	105,9	266,9	691,2

Indeno[1,2,3-*cd*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1		398,0	216,0	247,4	502,0	519,0
2	443,2	469,6	156,3	141,8	257,9	283,1
3	216,9	230,7	60,3	46,0	219,3	258,2
4	162,6	162,9	57,3	65,9	39,9	39,8
5	292,5	304,5	149,0	119,7	278,6	294,3
6	486,2	396,9	177,8	193,9	393,0	546,3

Dibenz[*a,h*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1					55,3	57,0
2	118,0	118,1	29,3	28,6	22,8	24,1
3	35,3	34,5	11,7	6,0	21,4	24,5
4	53,4	51,9	11,3	13,3	38,6	38,8
5	29,7	31,6	12,6	10,6	23,2	22,8
6	30,0	27,1	9,7	10,8	26,2	10,3

Site 3 - France

Benz[*a*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	2,0	5,3	1,4		7,0	4,6
2	5,6	4,0	2,0	1,6	5,5	6,9
3	3,6	5,3	19,4	13,4	1,6	2,7
4	17,9	12,9	6,0	7,1	1,4	4,0
5		7,7	9,2	3,9	1,7	1,6
6	10,6	8,7	5,7	4,5	2,7	3,0

Benz[*b*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	5,8	10,6	6,7		5,6	3,3
2	16,6	14,9	10,0	10,1	1,6	1,4
3	20,6	22,4	15,9	14,4	1,9	10,9
4	29,3	34,4	19,2	24,6	10,2	8,9
5		23,3	21,5	17,1	4,7	6,2
6	39,7	33,3	24,4	19,3	12,8	14,1

Benz[*j*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	*nd*	*nd*	*nd*		*nd*	*nd*
2	*nd*	*nd*	3,5	1,6	*nd*	*nd*
3	5,6	7,5	5,7	4,2	*nd*	2,6
4	8,9	10,6	6,6	8,1	4,2	4,2
5		11,7	10,0	7,2	*nd*	*nd*
6	16,2	12,9	8,5	7,1	4,6	6,0

Benz[*k*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	2,2	3,5	1,5		1,6	1,7
2	4,0	4,0	2,8	2,8	2,7	1,9
3	5,6	7,1	4,3	3,7	2,7	2,9
4	8,7	10,6	6,0	7,9	4,0	3,0
5		7,7	6,5	5,7	1,6	1,7
6	12,4	10,4	7,1	6,3	4,0	4,3

Benz[*a*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	2,2	3,5	2,3		1,6	1,7
2	5,1	5,5	3,5	3,6	2,7	2,6
3	6,0	7,8	4,2	4,4	2,9	3,0
4	11,1	12,9	6,8	7,8	3,0	3,3
5		7,3	7,2	5,2	1,6	1,9
6	12,9	10,9	7,1	5,7	3,0	4,2

Indeno[1,2,3-*cd*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	4,0	5,6	3,8		1,9	1,7
2	8,9	9,1	6,0	6,1	2,0	2,0
3	14,8	16,8	9,4	8,6	2,0	9,5
4	26,0	29,3	15,4	20,2	7,3	7,0
5		18,6	13,8	11,1	3,2	4,2
6	19,5	14,8	11,9	8,9	5,6	5,7

Dibenz[*a,h*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	*nd*	*nd*	*nd*		*nd*	*nd*
2	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*
3	2,2	2,2	1,5	1,6	1,7	1,7
4	3,5	3,5	2,0	2,3	1,6	1,7
5		3,8	2,3	2,3	*nd*	*nd*
6	3,3	2,0	2,1	1,4	*nd*	*nd*

Site 4 - Netherlands

Benz[*a*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	13,2	9,7	10,6	4,8	4,0	11,2
2	*nd*	3,8	14,2	8,3	7,8	8,7
3	9,3	*nd*	*nd*	*nd*	11,3	11,3
4	10,0	12,2	16,1	15,0	*nd*	*nd*
5	16,0	22,4	10,2	8,6	4,7	2,8
6	11,4	11,7	4,6	4,6	5,8	7,7

Benz[*b*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	11,6	23,7	20,6	11,6	14,0	23,3
2	4,7	9,6	24,0	12,3	23,6	30,2
3	10,7	6,2	36,4	11,1	24,0	25,0
4	39,7	16,7	27,6	17,9	*nd*	3,8
5	27,0	35,1	39,2	34,8	8,9	5,9
6	25,2	20,7	21,8	20,3	12,7	14,9

Benz[*j*]fluoranthene – no data

Benz[*k*]fluoranthene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	8,5	6,4	8,1	4,8	5,7	10,9
2	3,3	4,0	10,3	6,1	10,2	12,6
3	7,2	3,8	3,2	5,5	11,3	12,2
4	7,9	8,0	14,3	10,8	1,1	1,8
5	11,8	14,2	7,0	5,8	4,2	2,5
6	8,0	8,6	3,4	2,1	4,9	6,2

Benz[*a*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	15,7	18,5	17,7	8,7	9,4	21,0
2	5,8	7,0	21,7	10,7	17,6	21,7
3	12,9	6,6	6,2	9,8	14,5	15,1
4	15,3	13,5	26,4	19,7	1,5	2,6
5	19,5	28,1	10,2	9,1	5,3	2,9
6	7,9	9,0	4,5	4,9	5,5	7,3

Indeno[1,2,3-*cd*]pyrene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	*nd*	19,6	26,4	*nd*	7,6	12,8
2	*nd*	*nd*	17,2	*nd*	15,0	23,9
3	*nd*	*nd*	*nd*	*nd*	18,3	20,8
4	*nd*	*nd*	23,5	13,7	*nd*	*nd*
5	13,4	25,3	8,4	7,1	5,5	3,3
6	19,6	14,1	4,6	3,7	8,9	9,3

Dibenz[*a,h*]anthracene

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Sample	*1*	*2*	*1*	*2*	*1*	*2*
1	*nd*	3,5	4,0	*nd*	*nd*	*nd*
2	*nd*	5,4	6,8	*nd*	3,1	4,1
3	*nd*	*nd*	*nd*	*nd*	3,9	4,5
4	*nd*	*nd*	*nd*	*nd*	*nd*	*nd*
5	2,3	4,1	1,7	1,3	1,2	0,6
6	3,9	9,5	0,8	0,6	1,2	1,8

Annex 2 Summary results per component per site – Deposition results in ng/m^2/d

Site 1 - Austria

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Component	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*
Benz[*a*]anthracene	37,8	11,1 %	37,8	14,5 %	27,2	120,3 %
Benz[*b*]fluoranthene	61,2	11,0 %	61,0	15,5 %	44,0	40,6 %
Benz[*j*]fluoranthene	74,1	8,8 %	68,2	10,1 %	39,9	33,0 %
Benz[*k*]fluoranthene	28,3	11,9 %	33,6	11,6 %	16,7	25,6 %
Benz[*a*]pyrene	34,0	16,0 %	37,2	12,8 %	19,3	58,5 %
Indeno[123-*cd*]pyrene	61,7	9,9 %	61,7	11,2 %	34,0	15,1 %
Dibenz[*a,h*]anthracene	6,5	22,0 %	7,1	15,7 %	4,1	38,6 %

Site 2 - Germany

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Component	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*
Benz[*a*]anthracene	288,1	5,2 %	119,4	7,7 %	263,5	45,1 %
Benz[*b*]fluoranthene	368,6	6,4 %	158,7	7,7 %	339,6	22,1 %
Benz[*j*]fluoranthene	163,8	7,9 %	66,5	9,3 %	122,1	27,7 %
Benz[*k*]fluoranthene	191,8	5,1 %	80,4	6,7 %	162,0	26,2 %
Benz[*a*]pyrene	214,3	6,2 %	78,0	9,2 %	250,6	49,3 %
Indeno[123-*cd*]pyrene	330,2	9,1 %	135,9	10,8 %	302,6	15,4 %
Dibenz[*a,h*]anthracene	53,0	2,3 %	14,4	14,3 %	30,4	15,5 %

Site 3 - France

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Component	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*
Benz[*a*]anthracene	7,6	27,5 %	6,3	41,0 %	3,6	32,5 %
Benz[*b*]fluoranthene	22,9	13,5 %	15,8	17,5 %	6,8	40,9 %
Benz[*j*]fluoranthene	10,6	15,7 %	6,3	21,6 %	4,0	30,0 %
Benz[*k*]fluoranthene	7,0	15,1 %	4,7	15,2 %	2,7	14,8 %
Benz[*a*]pyrene	7,7	14,4 %	5,0	16,3 %	2,6	13,7 %
Indeno[123-*cd*]pyrene	15,5	12,9 %	9,9	19,9 %	4,3	50,1 %
Dibenz[*a,h*]anthracene	3,0	17,2 %	1,9	13,9 %	1,7	4,3 %

Benz[*a*]anthracene
Benz[*b*]fluoranthene
Benz[*j*]fluoranthene
Benz[*k*]fluoranthene
Benz[*a*]pyrene

Indeno[123-*cd*]pyrene
Dibenz[*a,h*]anthracene

Site 4 - Netherlands

	Funnel-bottle bulk		*Wet-only*		*Bergerhoff – sum of 4 pots*	
Component	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*	*Mean over all periods*	*Between-collector uncertainty*
Benz[*a*]anthracene	11,1	24,3 %	9,7	27,7 %	7,5	32,4 %
Benz[*b*]fluoranthene	19,3	42,5 %	23,1	38,9 %	15,8	23,9 %
Benz[*j*]fluoranthene						
Benz[*k*]fluoranthene	7,6	17,8 %	6,8	29,6 %	7,0	25,6 %
Benz[*a*]pyrene	13,3	24,5 %	12,5	37,4 %	10,4	35,5 %
Indeno[123-*cd*]pyrene	18,6	35,4 %	14,8	27,5 %	12,5	27,4 %
Dibenz[*a,h*]anthracene	4,7	62,3 %	3,3	6,8 %	2,6	18,9 %