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Inter-laboratory comparison of methods used for analysing polycyclic aromatic hydrocarbons (PAHs) in soil samples

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Summary. In view of the investigation of contaminated model sites in Baden-Württemberg an inter-laboratory comparison was organized for the methods used for analysing polycyclic aromatic hydrocarbons (PAHs). The laboratories performing chemical and physical analyses at the model sites participated at the request of the Landesanstalt für Umweltschutz, Baden-Württemberg. This inter-laboratory comparison was meant as a first laboratory evaluation, and not as the search for the best method available. Furthermore, it was to show the difficulties in comparing results from different laboratories, which have analysed identical samples. The results of the inter-laboratory comparison between the nine laboratories showed a reproducibility coefficient of variation, for the total of the 16 PAHs according to the EPA, between 48.8 and 61.1% in the concentration range of 5 to 55 mg/kg in the soil samples. One of the laboratories reported significantly lower values compared with the "true value". This was probably due to an ill-suited (sample) preparation method. Although the results of the inter-laboratory comparison are, in general, satisfactory, the reproducibility can be improved by standardizing the analytical method for the determination of PAHs in solid environmental samples.

1 Introduction

When investigating contaminated sites it is often essential to determine specific pollutants in a large number of soil samples. Amongst these sites is a former gasworks at which, due to improper discharging and depositing of e.g. coal gasification tars, soil and groundwater may be contaminated with PAHs. In 1976 the EPA defined 16 PAHs to be monitored and gave concentration limits for water. Nowadays these 16 PAHs are generally analysed as individual compounds when investigating contaminated sites.

A problem with interpreting the analytical results from environmental investigations is not only the inhomogeneity of the samples, but the lack of knowledge on the consistency of results from different laboratories. The absence of standard methods is strongly felt, particularly in the field of solid samples.

2 Defining the problem

In view of the contaminated model sites in Baden-Württemberg (Altlasten-Modellstandorte) [1, 2] problems are being discussed in working groups regarding the sampling and the chemical and physical analyses of solid waste samples. The aim of these discussions is to reach standard procedures for solid waste investigation in Baden-Württemberg. The laboratories performing the analyses participated in this working group as well as state-owned laboratories and some representatives of the administration (section water) of Baden-Württemberg. One of the model sites was the former gasworks at Geislingen. One of the subjects which was discussed was the determination of PAHs in the soil and waste samples from the gasworks.

For the analyses of 6 PAHs according to the German Drinking Water Regulation (TVO) a thin-layer chromatographic method is available as standard procedure [3]. There are also ISO drafts for standard procedures for determining 6 PAHs in water samples [4]. The Bundesland Nordrhein-Westfalen has published a method for analysing water and soil samples, in which HPLC is used with fluorescence detection to determine 12 PAHs [5]. This method is described in more detail in [6]. In this quoted article, a ring test is reported, testing every single step for its reliability.

National or international standard procedures for analysing soil are hard to obtain. A draft standard, the draft NEN 5731, has been published in the Netherlands [7]. Meanwhile several laboratories in Baden-Württemberg are performing analyses on PAHs for the model site projects. These methods differ in the pretreatment of samples (drying, extraction, clean-up, etc.) as well as in the analytical method used for the determination. Table 1 shows the methods used by the laboratories involved in the model sites.

This table clearly shows large differences at the extraction step and the solvent used for the extraction. Acetone, cyclohexane, hexane or mixtures of these solvents were used for the extraction, which can be carried out at room tempera-

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Table 1. Methods used by the laboratories which participated in comparing the analysis on PAHs

Lab. no.	Sample preparation	Method of extraction, solvent	Clean-up	Analytical method
1	Homogenization, trituration with Na_2SO_4	Sonification at ambient temperature, cyclohexane	Silica-gel	GC-MS
2	–	8 h hot extraction, acetone	Deactivated aluminium oxide	GC-MS
3	Trituration with Na_2SO_4	2.5 h Soxhlet, n-hexane	Dilution	GC-MS
4	–	Shaking at ambient temperature, cyclohexane	–	HPLC, fluorescence
5	–	Soxhlet, cyclohexane	Deactivated silica-gel 100	GC-MS
6	Trituration with Na_2SO_4	Shaking at ambient temperature, n-hexane/acetone	Silica-gel	HPLC, UV/fluorescence
7	Trituration with Na_2SO_4	Shaking at ambient temperature, toluene or cyclohexane/acetone (70/30)		GC-MS
8	–	Shaking at ambient temperature, cyclohexane/acetone (70/30)	Deactivated silica-gel 100	HPLC, fluorescence
9	Homogenization	2 h shaking at ambient temperature, acetone/cyclohexane (1:1)	Florisil	GC-FID
Ref. Lab. TAUW	Crusting	Extraction at ambient temperature, acetone/petrolether	Aluminium oxide, 11% H_2O	HPLC, UV/fluorescence

Table 2. Samples and conditions under which the comparison took place

I	Samples:	1. Soil sample from a former gasworks (54.8 mg/kg PAHs[a]) 2. Soil sample from a former gasworks (33.2 mg/kg PAHs[a]) 3. Soil treated thermally, sample without PAHs (0.18 mg/kg PAHs[a]) 4. Foundry sand (5.2 mg/kg PAHs[a]) 5a. Reference solutions in acetonitrile 5b. Reference solutions in n-hexane
II	Preparation:	Cryogenic trituration – cooling with liquid nitrogen and grinding in a cross-laid mill until the grain size is smaller than 125 μm
III	Analysis of 16 EPA PAHs:	– 5 × by TAUW – 3 × using the usual analytical procedure of each laboratory; TAUW analyses extracts of sample 1 provided by the participating laboratories
IV	Limits of detection:	0.001 – 0.1 mg/kg for each compound 0.01 – 1.0 mg/kg for the total of 16 PAHs

[a] Total of the 16 PAHs on the EPA list:

Compound	Designation in Fig. 1	Compound	Designation in Fig. 1
Naphthalene	NAF	Benz[a]anthracene	BAA
Acenaphthylene	ACY	Chrysene	–
Acenaphthene	ACE	Benzo[b]fluoranthene	BBF
Fluorene	FLU	Benzo[k]fluoranthene	BKF
Phenanthrene	FEN	Benzo[a]pyrene	BAP
Anthracene	ANC	Benzo[ghi]perylene	GHI
Fluoranthene	FLO	Dibenz[a,h]anthracene	DIB
Pyrene	PYR	Indeno[1,2,3-cd]pyrene	IND

ture either by shaking or using the Soxhlet extraction. Most laboratories use GC-MS or GC-FID as an analytical method. HPLC with UV or fluorescence detection is also used. The impact of these different techniques can only be fully investigated when carrying out a large comparative study. However, a simple ring test, as described here, using standardized samples can be seen as a first step in the right direction.

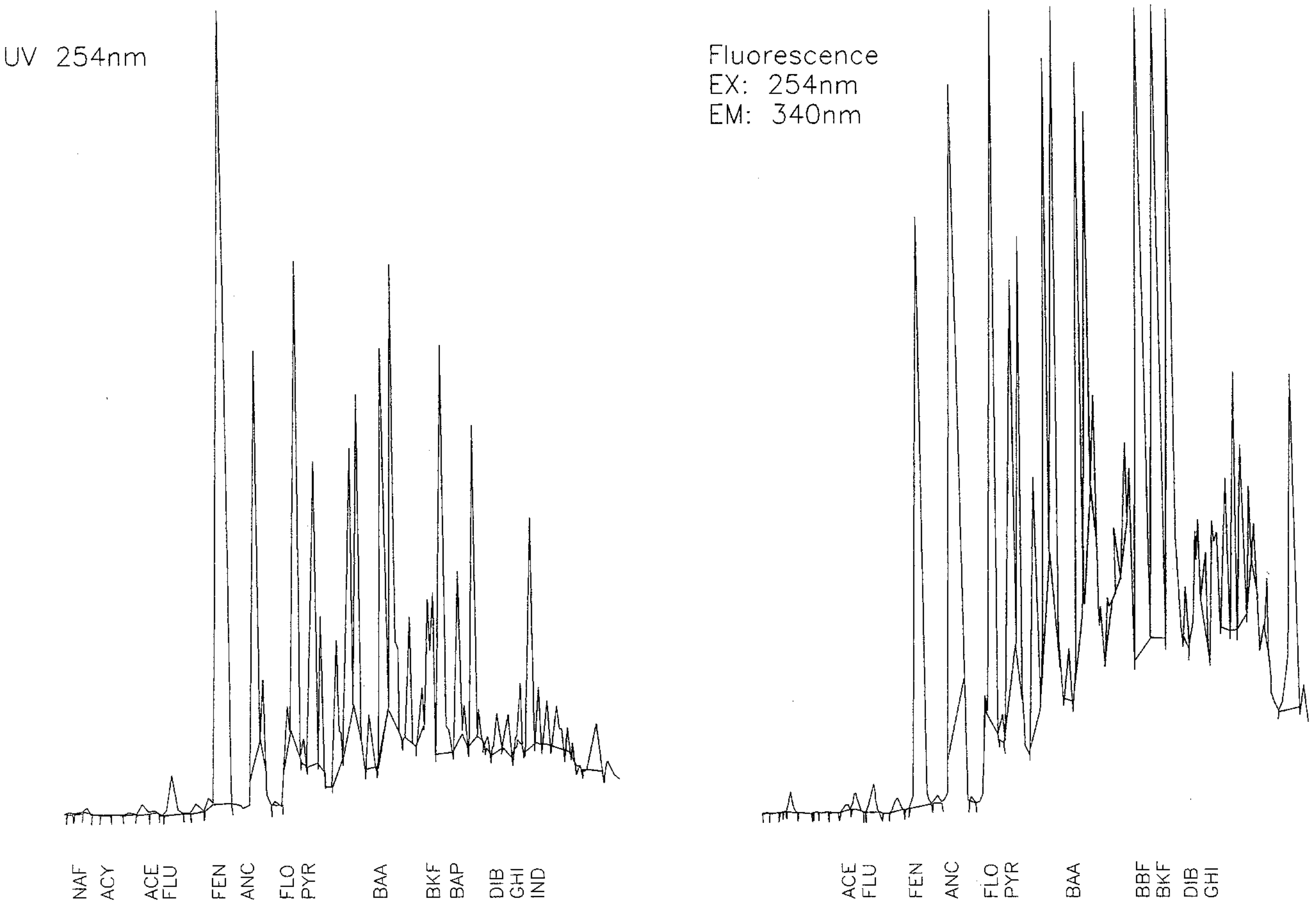

Fig. 1. Analysis of extract of sample 1 using HPLC. HPLC conditions: Column: Vydac 210 TP-5, 5 μm, 25 cm i.d. 4.6 mm; Eluent: Acetonitrile/water 50/50 5 min; Linear gradient to 100% acetronitrile in 15 min; Acetonitrile 100%, 10 min; Flow: 1,5 ml/min; Column temperature: 30 °C; Detection: UV 254 nm; Fluorescence: ex. 254 nm and em. 340 nm

3 Implementing the ring test

The ring test was set up by the Landesanstalt für Umweltschutz Baden-Württemberg, who appointed the laboratory of TAUW Infra Consult B. V. (hereafter referred to as the "reference" laboratory) (Deventer, The Netherlands) to carry out this test. The aim of this ring test was not to point out the best method available for determination of PAHs in soil samples, but to make a comparison of the different methods used by the participating laboratories. The samples had different origins and were homogenized using cryogenic trituration. This step included drying, which implies that the results were directly based upon the percentage of dry matter. Table 2 gives a summary of the samples and the conditions under which they were tested. Six privately owned laboratories, two state-owned laboratories and the laboratory of the Landesanstalt für Umweltschutz Baden-Württemberg participated in the ring test.

The four samples were analysed five-fold by the reference laboratory to test for the homogeneity of the samples. The samples containing PAHs gave repeated coefficients of variation, over the five independent results, ranging from 5–15%, indicating a sufficient homogeneity. The blank sample had a much higher coefficient of variation (28%) due to the low concentrations.

The participating laboratories were asked to analyse each sample in triplicate. Furthermore, the extract from sample 1 was sent to the reference laboratory, where it was reanalysed using their own method. Figure 1 shows a chromatogram obtained from one of the samples analysed by the reference laboratory.

Considering the problems which may be encountered in spiking solid samples, recovery experiments were not included in the ring test. Standard solutions of PAHs in n-hexane and acetonitrile were also included in the test and were analysed.

Statistical data evaluation was performed according to ISO 5725 [8]. Results below the limit of detection were not included in the statistical programme. Outlying results were tested using the Cochran test, testing for a large coefficient of variation within a laboratory. The Dixon outlier test was used to test for an outlier in respect to the general mean.

The following statistical parameters were calculated from the screened set of data:

- Number of outliers: (Cochran and Dixon);
- Number of outlier-free laboratories;
- General mean value;
- Standard deviation and coefficient of variation related to repeatability (only by multiple analyses);
- Standard deviation and coefficient of variation related to reproducibility.

4 Results and discussion

An overview of the results (total of 16 PAHs) is given in Fig. 2, an overview of the calculated parameters from

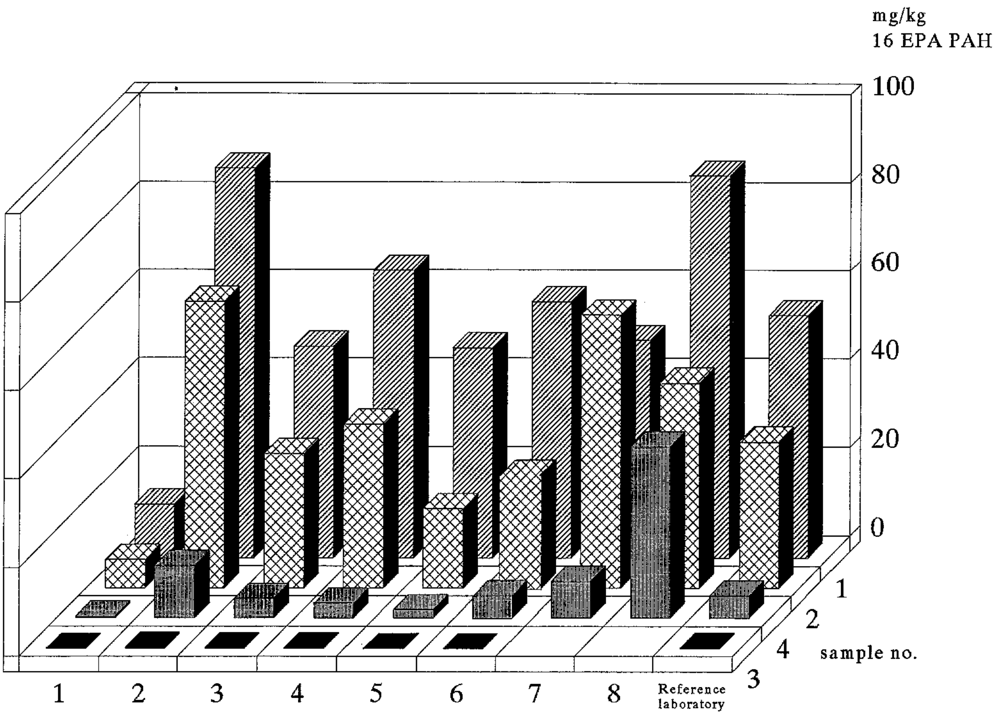

Fig. 2. Overview of results (total of 16 PAHs) from all samples

Table 3. Results of the comparison for sample 1

PAH	No. of outliers		P	Mean of reference lab.[a]	Average from all labs.	SI	VI	SR	VR
	Cochran test	Dixon test							
Naphthalene	–	1	6	0.07	0.07	0.03	42.0	0.05	63.8
Acenaphthylene	–	2	5	< 0.05	0.10	0.05	46.2	0.08	80.8
Acenaphthene	1	–	8	0.74	0.33	0.08	23.8	0.26	80.5
Fluorene	–	1	8	1.24	0.79	0.17	22.1	0.50	63.9
Phenanthrene	–	–	9	8.38	6.68	1.44	21.6	4.06	60.9
Anthracene	–	1	8	1.68	1.74	0.28	16.1	0.95	54.4
Fluoranthene	–	–	9	12.60	9.48	1.59	16.7	4.64	49.0
Pyrene	1	–	8	6.86	4.72	0.66	13.9	2.53	53.5
Benz(a)anthracene	–	–	9	4.40	4.19	0.73	17.3	2.21	52.8
Chrysene	–	–	9	3.44	4.37	0.73	16.8	2.13	48.7
Benzo(b)fluoranthene	–	–	8	3.92	3.70	0.68	18.3	2.29	61.9
Benzo(k)fluoranthene	1	–	7	1.76	1.68	0.20	12.1	0.76	45.2
Benzo(a)pyrene	–	–	9	3.66	3.30	0.51	15.5	1.46	44.1
Dibenz(a,h)anthracene	–	1	8	1.46	0.82	0.19	22.7	0.45	55.0
Benzo(ghi)perylene	–	–	9	1.94	1.95	0.33	17.0	0.94	48.4
Indeno(1,2,3-cd)pyrene	–	–	9	2.20	2.48	0.46	18.5	1.54	61.9
16 EPA PAHs	–	–	9	54.80	53.22	7.89	14.8	26.00	48.8

[a] Mean of five analyses (mg/kg)
P: Number of laboratories without outliers
SI, SR: Standard deviation (mg/kg) for repeatability and reproducibility (respectively)
VI, VR: Coefficient of variation (%) for repeatability and reproducibility (respectively)

samples 1, 2 and 4 is given in Tables 3, 4 and 5. The results of sample 3 (treated soil) were usually reported below the limit of detection which meant that statistical treatment of the results was not useful. No laboratory recorded a false positive result for this sample. The calculated mean value of 0.103 mg/kg corresponds with the results of the reference laboratory of 0.18 mg/kg.

The calculated mean values for the samples 1, 2 and 4 correspond with the values of the reference laboratory. The coefficients of variation for reproducibility of, respectively, 48.8%, 55.3% and 61.1% clearly indicate a relatively large variation in the results. This variation can also be seen in the minimum and maximum values for the sum parameter 16 EPA. Table 6 gives a summary of these results.

When related to the individual components the coefficient of variation for reproducibility for the samples ranged from:

– Sample 1: 44.1% to 80.8% (Table 3);

Table 4. Results of the comparison for sample 2

PAH	No. of outliers		P	Mean of reference lab.[a]	Average from all labs.	SI	VI	SR	VR
	Cochran test	Dixon test							
Naphthalene	1	–	6	0.29	0.36	0.06	15.8	0.55	154.6
Acenaphthylene	1	1	5	<0.2	0.17	0.02	13.7	0.13	75.5
Acenaphthene	2	–	7	0.51	0.15	0.02	10.3	0.10	69.9
Fluorene	–	1	8	0.54	0.44	0.09	19.8	0.38	85.7
Phenanthrene	2	–	7	3.54	2.53	0.13	5.2	1.87	73.9
Anthracene	1	–	8	0.88	0.90	0.12	13.4	0.69	76.6
Fluoranthene	1	–	8	6.08	4.42	0.58	13.1	2.64	59.7
Pyrene	2	–	7	3.74	3.28	0.34	10.3	2.21	67.2
Benz(a)anthracene	1	–	8	2.64	2.40	0.17	7.2	1.44	59.8
Chrysene	1	–	8	2.22	2.71	0.18	6.8	1.48	54.7
Benzo(b)fluoranthene	2	–	6	2.94	2.83	0.17	6.0	1.84	65.1
Benzo(k)fluoranthene	2	–	6	1.70	1.92	0.11	5.8	1.52	78.9
Benzo(a)pyrene	2	–	7	3.18	2.64	0.16	5.9	1.50	56.7
Dibenz(a,h)anthracene	1	–	8	1.14	1.04	0.12	11.3	1.21	116.2
Benzo(ghi)perylene	1	–	8	2.04	1.61	0.25	15.6	0.91	56.4
Indeno(1,2,3-cd)pyrene	1	–	8	1.88	2.23	0.18	8.1	1.45	64.9
16 EPA PAHs	2	–	7	33.20	32.78	0.89	2.7	18.14	55.3

[a] Mean of five analyses (mg/kg)
P: Number of laboratories without outliers
SI, SR: Standard deviation (mg/kg) for repeatability and reproducibility (respectively)
VI, VR: Coefficient of variation (%) for repeatability and reproducibility (respectively)

Table 5. Results of the comparison for sample 4

PAH	No. of outliers		P	Mean of reference lab.[a]	Average from all labs.	SI	VI	SR	VR
	Cochran test	Dixon test							
Naphthalene	2	–	7	1.48	1.17	0.08	7.2	1.10	86.6
Acenaphthylene	–	1	5	<0.2	0.06	0.01	17.5	0.04	54.7
Acenaphthene	[c]	[c]	7	<0.05	0.09	0.01	12.7	0.09	97.9
Fluorene	4	–	5	0.44	0.20	0.01	1.9	0.14	71.0
Phenanthrene	–	–	9	1.38	1.39	0.18	13.2	0.97	69.4
Anthracene	1	1	7	0.40	0.44	0.04	9.3	0.34	75.9
Fluoranthene	–	–	9	1.32	0.62	0.12	20.1	0.34	55.9
Pyrene	–	1	8	0.35[b]	0.53	0.06	11.1	0.37	70.3
Benz(a)anthracene	–	1	7	0.07[b]	0.10	0.02	21.3	0.08	76.3
Chrysene	–	1	7	0.09[b]	0.10	0.04	39.1	0.09	82.9
Benzo(b)fluoranthene	1	1	4	<0.2	0.07	0.01	6.3	0.04	60.9
Benzo(k)fluoranthene	–	1	5	<0.2	0.06	0.01	10.1	0.03	48.4
Benzo(a)pyrene	–	1	5	<0.05[b]	0.09	0.02	22.4	0.07	75.1
Dibenz(a,h)anthracene	–	–	4	<0.05[b]	0.04	0.01	26.8	0.03	76.5
Benzo(ghi)perylene	[c]	[c]	4	<0.05[b]	0.41	0.18	43.9	0.74	179.5
Indeno(1,2,3-cd)pyrene	[c]	[c]	3	<0.05[b]	0.08	0.05	56.4	0.08	93.3
16 EPA PAHs	1	1	7	5.16	4.23	0.31	7.3	2.58	61.1

[a] Mean of five analyses (mg/kg)
[b] Analysis results using an GC-MS
P: Number of laboratories without outliers
SI, SR: Standard deviation (mg/kg) for repeatability and reproducibility (respectively)
VI, VR: Coefficient of variation (%) for repeatability and reproducibility (respectively)
[c] A reliable statistical interpretation of the data was not possible due to the large spreading in the individual laboratory mean values and standard deviations. If all the analyses were carried out, all the laboratories would have been outliers. All the laboratories were included in the interpretation of the statistical results

- Sample 2: 54.7% to 154.6% (Table 4);
- Sample 4: 48.4% to 179.5% (Table 5).

The largest variations were found by the more volatile components, i.e. naphthalene and for components, for which the screened data set was relatively small. A complete summary is given in Table 7. The symbols used are explained in the legend. When examined more closely it can be seen that some laboratories (numbers 2, 7 and 8) produce more outliers than others. When the screened data sets are studied it seems that laboratories 1 and 2 have very different results.

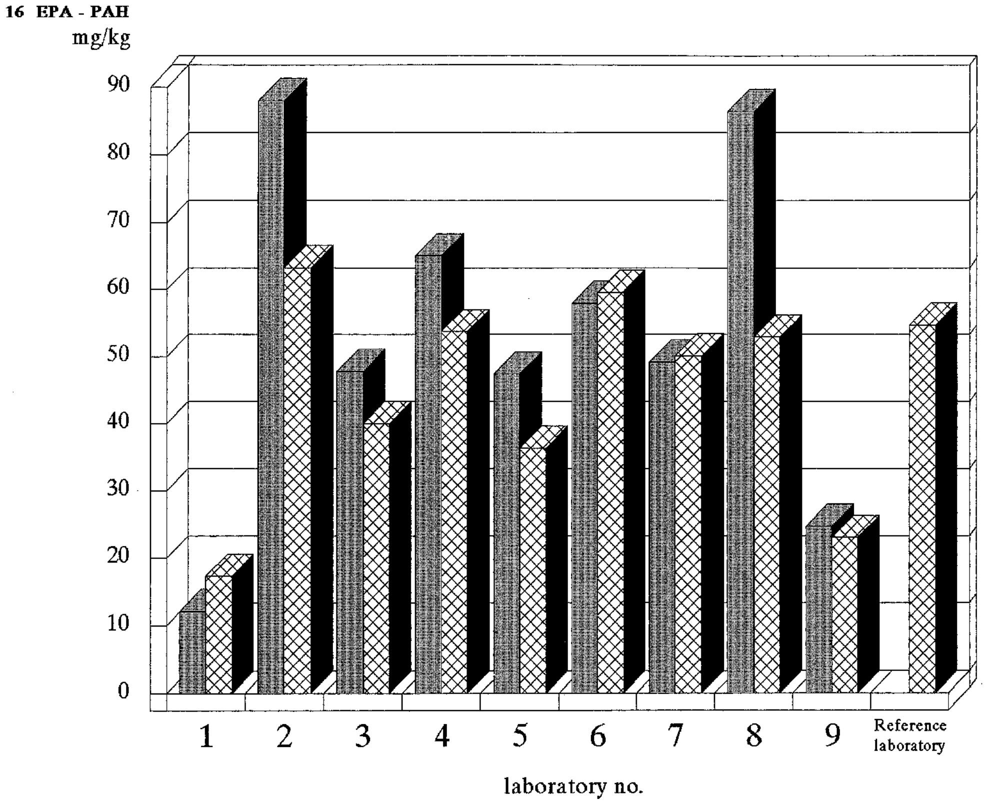

Fig. 3. Comparing the analysis of extract from sample 1 with the nine laboratories and the reference laboratory (TAUW) (hatched columns)

Table 6. Comparison of the minimum and maximum values using the mean from the nine laboratories and the "reference" value (mg/kg 16 EPA-PAHs)

No. of sample	Minimum	Maximum	Mean	"Reference" value
1	12.167	88.133	53.22	54.80
2	6.400	61.733	32.78	33.20
3 (sample without PAHs)	0.010	0.257	0.103	0.18
4	0.533	38.733	4.23	5.16

Table 7. Results of the ring test for the 16 individual components and the 16 EPA sum parameter. The results are coded, in which the laboratory mean value is related to the general mean value

Sample number	Lab. 1					Lab. 2					Lab. 3					Lab. 4					Lab. 5				
	1	2	3	4	Ex.	1	2	3	4	Ex.	1	2	3	4	Ex.	1	2	3	4	Ex.	1	2	3	4	Ex.
Naphthalene	A	A	A	B	G	E	B	B	D	G	A	A	A	A	G	G	G	A	B	G	A	A	A	A	G
Acenaphthylene	A	A	G	G	G	A	B	G	B	G	E	A	*	A	G	G	G	G	G	G	A	A	G	B	G
Acenaphthene	A	A	G	A	G	D	D	G	A	G	B	B	G	A	G	A	B	*	B	G	A	A	G	A	G
Fluorene	B	A	G	B	B	B	B	G	D	B	A	A	A	A	A	A	A	A	A	G	A	A	G	D	G
Phenanthrene	B	B	G	B	B	B	C	A	B	B	A	A	A	A	A	A	A	A	A	B	A	A	G	A	A
Anthracene	B	A	G	B	C	B	C	G	D	A	A	A	D	A	A	A	A	A	A	A	A	A	G	A	A
Fluoranthene	B	B	G	B	C	B	B	G	B	B	A	A	A	A	A	A	A	G	A	A	A	A	G	B	A
Pyrene	B	B	G	B	B	D	B	G	A	B	A	A	A	A	A	A	A	G	B	A	A	A	G	B	A
Benz(a)anthracene	B	B	G	B	B	B	C	G	B	B	A	A	*	A	A	A	A	G	A	A	A	A	G	B	A
Chrysene	B	B	G	A	C	B	B	G	B	B	A	A	A	A	A	B	A	A	A	A	A	A	G	A	A
Benzo(b)fluoranthene	B	B	G	B	B	B	B	G	D	B	A	A	*	A	A	A	A	*	A	A	G	G	G	G	A
Benzo(k)fluoranthene	B	A	G	B	B	D	B	G	A	B	A	A	*	A	A	A	A	*	A	A	G	G	G	G	A
Benzo(a)pyrene	B	B	G	B	B	B	B	G	B	B	A	A	G	A	A	A	A	*	A	A	A	A	G	G	A
Dibenz(a,h)anthracene	A	A	G	G	B	A	A	G	G	G	B	C	G	A	G	E	A	G	B	A	A	A	G	G	A
Benzo(ghi)perylene	A	B	G	G	B	B	B	G	G	A	A	A	*	A	A	A	A	G	A	A	A	A	G	G	A
Indeno(1,2,3-cd)pyrene	A	B	G	G	C	A	A	G	G	B	A	A	*	A	A	B	B	G	G	A	A	A	G	G	A
EPA(16)	B	B	B	B	B	B	B	B	D	B	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A

Table 7 (continued)

	Lab. 6					Lab. 7					Lab. 8					Lab. 9				
	1	2	3	4	Ex.	1	2	3	4	Ex.	1	2	3	4	Ex.	1	2	3	4	Ex.
Naphthalene	G	G	A	D	*	A	D	B	B	G	B	A	G	A	*	A	A	G	A	G
Acenaphthylene	G	G	G	G	*	A	D	G	A	G	E	E	G	E	G	A	A	G	A	G
Acenaphthene	B	B	*	G	G	A	D	G	G	G	A	A	G	A	G	B	A	G	B	G
Fluorene	A	A	A	B	A	A	B	G	D	A	E	E	G	D	A	A	A	B	A	G
Phenanthrene	A	A	A	A	A	A	D	B	A	A	B	D	G	B	A	A	A	A	A	G
Anthracene	A	A	A	B	B	A	D	G	B	A	E	A	G	E	A	A	A	B	A	G
Fluoranthene	A	A	A	A	A	A	D	G	A	A	A	A	G	A	A	A	A	B	A	G
Pyrene	B	A	A	A	A	A	D	G	A	A	B	D	G	E	A	A	A	B	A	G
Benz(a)anthracene	A	A	G	G	A	A	D	G	A	A	A	A	G	E	A	A	A	*	B	G
Chrysene	A	A	G	G	A	A	D	G	A	A	A	A	G	E	A	A	A	A	A	G
Benzo(b)fluoranthene	A	D	G	G	A	A	D	G	G	A	A	A	G	E	A	B	A	G	A	G
Benzo(k)fluoranthene	A	D	G	G	A	B	D	G	G	A	A	A	G	E	A	A	B	G	A	G
Benzo(a)pyrene	A	D	G	G	A	A	D	G	G	A	A	A	G	E	A	A	A	*	A	G
Dibenz(a,h)anthracene	A	A	G	G	B	A	D	G	G	G	B	A	G	B	G	A	A	G	A	G
Benzo(ghi)perylene	A	A	G	G	B	A	D	G	G	A	A	A	G	B	A	B	B	G	A	G
Indeno(1,2,3-cd)pyrene	A	A	G	G	B	A	D	G	G	A	B	A	G	A	A	A	A	G	A	G
EPA(16)	A	D	A	A	A	A	D	G	B	A	B	A	G	E	A	B	A	A	A	G

A = Laboratory mean value between general mean value and 1 *SR
B = Laboratory mean value between 1 *SR and 2 *SR
C = Laboratory mean value outside 2 *SR
D = Outlier by result of Cochran test (respective)
E = Outlier by result of Dixon test (reproducibility)
G = No results which could be statistically interpreted
* = Too few results
SR = Coefficient of variation for reproducibility

Table 8. Results of the standard solution in acetonitrile (concentration of PAHs and standard deviation in µg/l)

PAH	Laboratory					No. of outliers Dixon	P	True value[a]	General mean value	SR	VR
	1	4	6	7	8						
Naphthalene	0.88	0.90	0.76	0.66	–	–	4	0.80	0.80	0.11	14.0
Acenaphthylene	0.59	–	0.60	0.55	–	–	3	0.64	0.58	0.03	4.6
Acenaphthene	0.82	0.80	0.75	0.82	–	–	4	0.78	0.80	0.03	4.3
Fluorene	0.18	0.15	0.19	0.25	0.17	–	5	0.19	0.19	0.04	20.0
Phenanthrene	0.14	0.15	0.15	0.11	0.08	–	5	0.14	0.12	0.03	25.6
Anthracene	0.05	0.04	0.05	–	0.15	–	4	0.03	0.07	0.05	72.0
Fluoranthene	0.38	0.50	0.30	0.28	0.32	–	5	0.30	0.36	0.09	25.1
Pyrene	0.40	0.80	0.39	0.31	0.34	–	5	0.33	0.45	0.20	44.7
Benz(a)anthracene	0.16	0.20	0.18	0.16	0.19	–	5	0.15	0.18	0.02	10.0
Chrysene	0.17	0.20	0.17	0.14	0.13	–	5	0.15	0.16	0.03	17.1
Benzo(b)fluoranthene	0.17	0.20	0.18	0.15	0.20	–	5	0.16	0.18	0.02	11.8
Benzo(k)fluoranthene	0.21	0.20	0.20	0.17	0.22	–	5	0.18	0.20	0.02	9.4
Benzo(a)pyrene	0.22	0.20	0.17	0.17	0.23	–	5	0.19	0.20	0.03	14.0
Dibenz(a,h)anthracene	0.17	0.25	0.15	0.11	0.19	–	5	0.15	0.17	0.05	29.8
Benzo(ghi)perylene	0.18	0.25	0.20	0.12	0.12	–	5	0.15	0.17	0.06	31.9
Indeno(1,2,3-cd)pyrene	0.18	0.45	0.16	0.15	0.21	–	5	0.17	0.23	0.13	54.4
16 EPA PAHs	4.90	5.30	4.59	4.20	2.55	–	5	4.52	4.31	1.06	24.7

[a] True value for the PAH Standard Solution, made from NBS 1648a, Certified Standard
P: Number of outlier-free laboratories
SR: Standard deviation for reproducibility
VR: Coefficient of variation for reproducibility (%)

When the results of the extract from sample 1 are compared with the results of the reference laboratory this becomes even more apparent (Fig. 3). The results obtained from the standard solution by laboratory 1 are comparable to the known value, so the different results (see above) can only be accounted for by the extraction technique used.

The other differences are more difficult to explain. Problems can arise in the preparation of the sample, the quantification or the identification of certain components.

The results for the standard solutions in n-hexane (GC) and acetonitrile (HPLC) are given in Tables 8 and 9. The coefficient of variation for sum parameter 16 PAHs accord-

Table 9. Results of the standard solution in n-hexane (concentration and standard deviation in μg/l)

PAH	Laboratory							No. of outliers Dixon	P	True value[a]	General mean value	SR	VR
	1	2	3	4	5	7	9						
Naphthalene	25.0	23.5	19.8	20.0	22.6	23.5	21.0	–	7	20	22.2	2.0	8.9
Acenaphthylene	25.0	22.1	34.5		21.9	24.3	22.0	–	6	20	25.0	4.9	19.4
Acenaphthene	26.0	23.6	9.8a	25,0	21.6	22.9	22.0	1	6	20	23.5	1.7	7.3
Fluorene	22.0	20.7	19.6	16.0	20.3	23.7	22.0	–	7	20	20.6	2.4	11.9
Phenanthrene	21.0	20.3	18.0	25.0	20.4	18.1	21.0	–	7	20	20.5	2.3	11.4
Anthracene	21.0	24.7	17.6	18.0	21.1	19.8	22.0	–	7	20	20.6	2.4	11.8
Fluoranthene	25.0	24.2	19.5	13.0	22.6	18.0	21.0	–	7	20	20.5	4.1	20.1
Pyrene	24.0	22.7	15.0	22.0	20.5	17.2	21.0	–	7	20	20.3	3.2	15.7
Benz(a)anthracene	20.0	24.3	19.0	22.0	20.7	18.1	20.0	–	7	20	20.6	2.0	10.0
Chrysene	24.0	21.5	17.0	22.0	21.2	16.8	20.0	–	7	20	20.4	2.6	13.0
Benzo(b)fluoranthene	24.0	20.8	19.7	19.0	20.2	17.6	19.0	–	7	20	20.0	2.0	10.1
Benzo(k)fluoranthene	30.0	20.7	16.0	20.0	20.7	17.1	22.0	–	7	20	20.9	4.5	21.7
Benzo(a)pyrene	29.0	22.6	18.9	19.0	21.3	17.6	20.0	–	7	20	21.2	3.8	18.0
Dibenz(a,h)anthracene	35.0	19.5	19.8	27.0	22.4	19.2	19.0	–	7	20	23.1	6.0	25.8
Benzo(ghi)perylene	31.0	22.1	18.0	28.0	21.1	16.1	21.0	–	7	20	22.5	5.3	23.6
Indeno(1,2,3-cd)pyrene	34.0	18.9	16.9	34.0	21.4	20.0	19.0	–	7	20	23.5	7.3	31.2
16 EPA PAHs	416.0	352.3	299.0	330.0	340.0	309.9	332.0	–	7	320	339.9	38.0	11.2

[a] True value for the PAH Standard Solution, made from a Supelpreme-HC PAH MIX (Supelco)
a: Dixon Outlier
P: Number of Outlier-free Laboratories
SR: Standard deviation for reproducibility
VR: Coefficient of variation for reproducibility (%)

ing to EPA is 24.7% for the acetonitrile solution and 11.2% for the n-hexane solution. It is obvious that these variations are less than the samples, although some difficulties may be encountered with quantifying by HPLC. Using this method large variations occurred which cannot be accounted for, i.e. the low concentration for anthracene. A possible explanation for these variations may be the different quantifying standards which the laboratories use and which are less consistent than was previously thought.

5 Conclusions

When taking into account the various methods, which the laboratories have used, the overall result of the ring test is quite satisfactory. However, comparing results remains a problem, due to high coefficients of variations, especially for some components (e.g. dibenzo(a,h)anthracene 116.2%, benzo(ghi)perylene 179.5%). These large values indicate differences in analytical methods. Based on the results of the standard solutions, which show smaller coefficients of variation, it can be concluded that the major differences originate in the extraction step and to a lesser extent in the clean-up step, since extraction and clean-up are not carried out in these analyses. This conclusion is backed by the observation that the results of the reanalysed extracts, eliminating the instrumental variations, show large coefficients of variation.

This time the laboratories knew about the samples, which no doubt would have had a positive influence on the variation of the results. Unannounced ring tests would probably show greater variations. In view of the increasing number of soil and waste samples it is necessary to reach standard procedures for these matrices, at least for the sample preparation. The Landesanstalt für Umweltschutz Baden-Württemberg, together with the model site laboratories, will propose guidelines for sample preparation which will be the basis for a new ring test.

References

1. Ministerium für Umwelt Baden-Württemberg (1988) Konzeption zur Behandlung von altlastenverdächtigen Flächen und Altlasten in Baden-Württemberg (Stufenplan). Landtagsdrucksache 10/831, Stuttgart
2. Neifer H (1988) Modellstandortkonzeption Baden-Württemberg. In: Kongreßband Altlastensanierung '88 TNO/BMFT (11.–15. April 1988), Hamburg
3. DIN 38409 (1981) Teil 13. Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Summarische Wirkungs- und Stoffkenngrößen (Gruppe H); Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) im Trinkwasser (H 13)
4. ISO/DIS 7981 (1989) Water quality – Determination of six specified polynuclear hydrocarbons – Part 1: Thin layer chromatographic method, Part 2: High performance liquid chromatographic method
5. Landesamt für Wasser und Abfall Nordrhein-Westfalen (1987) Abfallwirtschaft Nr. 13, Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen in Wasser und Feststoffen (PAK), Entwurf, Düsseldorf
6. Plöger E, Reupert R (1986) Bestimmung von PAK in Wasser, Sedimenten, Schlamm und Abfall mit Hilfe der HPLC. Gewässerschutz-Wasser-Abwasser 88:136–167
7. Ontwerp NEN 5731 (1991) Soil – determination of the content of ten polycyclic aromatic hydrocarbons by high pressure liquid chromatography. NNI, Delft (in press)
8. International Standard ISO-5725 (1990) Precision of test method – determination of repetitive and reproducibility for a standard test method by inter-laboratory test