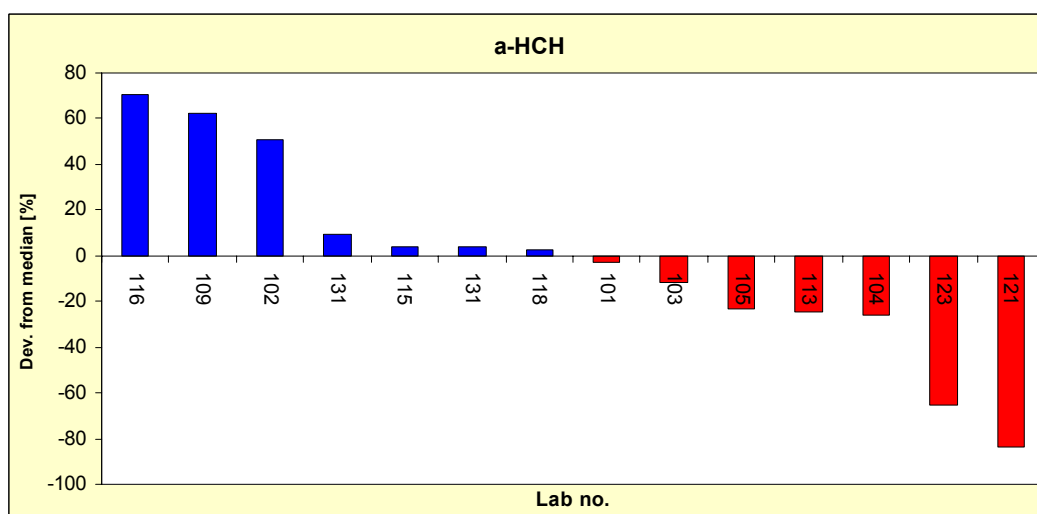


EMEP POP laboratory comparison 2000–2002

Stein Manø and Jan Schaug



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**EMEP Co-operative Programme for Monitoring and Evaluation
of the Long-range Transmission of Air Pollutants
in Europe**

**EMEP POP laboratory comparison
2000–2002**

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1. Introduction

The first collection of POP data in EMEP was reported in 1996 (Berg et al.), while the more formal inclusion in the EMEP measurement programme came in 1999. The activity on POPs had been initiated with the “Workshop on emission inventories and modelling of heavy metals and persistent organic pollutants”, in Bilthoven, Netherlands, May 1994, and the Steering Body to EMEP instructed the CCC to start the collection of POPs and heavy metal data later that year.

The “EMEP Expert meeting on measurements of POP in air and precipitation” in Lillehammer, Norway, November 1997 (Lükewille, 1998), concluded that an analytical comparison for laboratories before the (POP) network was put in operation was essential, and that a comparison should be arranged. The Steering Body agreed to this later that year and the preparations were started.

After a period with procurement of standards and other necessities and preparations, the first round of samples were distributed in November 2000 while the second round with samples were sent to the participants in August 2001.

2. Organisation of the laboratory comparison

27 laboratories responded to the invitation and indicated that they would take part in the exercise. A few laboratories asked for more than one set of samples to be distributed to different laboratories.

Table 1 shows the 19 names of the polycyclic aromatic hydrocarbons (PAH) and the 14 organochlorine compounds included in this comparison.

The comparison was carried out as a two-step exercise. During the first round each laboratory received two ampoules with the chlorinated compounds and two ampoules with a PAH mixture. One of the two ampoules from each group of components contained standards with known concentrations; a list of components in these solutions was distributed separately. The other two ampoules contained the same components but at concentrations unknown to the laboratories. The upper and lower limits of the concentrations in these unknown mixtures were also given to the laboratories.

This first round should therefore be a pure analytical exercise with no need for pre-concentrating or clean-up. The laboratories were asked to analyse the two unknown mixtures using their own standards in triplicate and to forward all the results to the CCC. The known standards were intended for a check on the laboratories own standards, but these results should not be sent the CCC. The laboratories were also asked to give a brief description of their analytical methods (Annex 2) with estimates of detection limits and uncertainties.

Table 1: PAH and organochlorine compounds measured in the laboratory comparison.

PAHs	Organochlorine compound
Naphtalene	p,p'-DDT
Acenaphthylene	p,p'-DDE
Acenaphthene	γ -Chlordane
Fluorene	α -Chlordane
Phenanthrene	Hexachlorocyclohexanes, HCH:
Anthracene	γ -HCH
Fluoranthene	α -HCH
Pyrene	Hexachlorobenzene, HCB
Benzo[a]anthracene	Polychlorinated biphenyls:
Chrysene	PCB 28
Benzo[b]fluoranthene	PCB 52
Benzo[k]fluoranthene	PCB 101
Benzo[a]pyrene	PCB 118
Indeno[1,2,3-cd]pyrene	PCB 138
Dibenzo[a,h]anthracene	PCB 153
Benzo[ghi]perylene	PCB 180
Biphenyl	
Perylene	
Benzo[e]pyrene	

3. Preparation of samples for round 1

Pre-experiments with flame sealing of ampoules showed a large tendency to soot formation below the sealing point, inside the ampoule, if it contained the solvents hexane or cyclohexane. By repeating the test with ampoules containing the less volatile solvent isooctane soot formation was avoided. Hence it was decided to use isooctane as solvent in round 1. This, however, caused a difficulty for laboratories using HPLC for the determination of PAHs, where polar solvents like acetonitrile or methanol are preferred, since a solvent change had to be made.

Solid standard compounds for all compounds but perylene were dissolved in isooctane to produce primary standard solutions. For perylene, which was difficult to dissolve in isooctane, a mixture of isooctane and toluene was used.

From the primary homemade standards and the purchased liquid standards, volumes were taken out using syringes to produce a secondary standard. The actual amount taken out from each primary standard to the secondary standard was determined by weighing each time, before the final dilution with isooctane. The ampoules were filled and flame sealed using a propane gas burner.

The ampoules were packed in sealed plastic boxes filled with shock absorbing plastic foil. A test was performed where a box containing filled ampoules was dropped from the third floor onto a concrete surface on the ground without causing any damage on the ampoules.

Finally a transport agency packed the boxes with ampoules in accordance with the safety regulations for transport of inflammable liquids with air cargo before the shipment.

In spite of shipping the samples in accordance to all rules (shipping and custom) several participants had problems with both shipping companies and custom authorities.

4. Quality assurance

Table 2 shows the purity of the standard compounds used in round 1 and the name of the company, which supplied them.

Table 2: Standard compounds used for round 1 and their purity.

Compound	Purity %	Solution/solid standard	Supplier
Naphthalene	99	Solution with certificate	Restek
Acenaphthylene	99	Solution with certificate	Restek
Acenaphthene	99	Solution with certificate	Restek
Fluorene	99	Solution with certificate	Restek
Phenanthrene	99	Solution with certificate	Restek
Anthracene	99	Solution with certificate	Restek
Fluoranthene	98	Solution with certificate	Restek
Pyrene	99	Solution with certificate	Restek
Benzo[a]anthracene	99	Solution with certificate	Restek
Chrysene	99	Solution with certificate	Restek
Benzo[b]fluoranthene	99	Solution with certificate	Restek
Benzo[k]fluoranthene	99	Solution with certificate	Restek
Benzo[a]pyrene	99	Solution with certificate	Restek
Indeno[1,2,3-cd]pyrene	99	Solution with certificate	Restek
Dibenzo[a,h]anthracene	99	Solution with certificate	Restek
Benzo[ghi]perylene	99	Solution with certificate	Restek
Biphenyl	>99	Solid*	AccuStandard
Perylene	>99	Solid*	AccuStandard
Benzo[e]pyrene	>99	Solid*	AccuStandard
p,p'-DDT	99	Solution with certificate	Restek
p,p'-DDE	99	Solution with certificate	Restek
γ-chlordane	99	Solution with certificate	Restek
α-chlordane	99	Solution with certificate	Restek
γ-HCH	99	Solution with certificate	Restek
α-HCH	99	Solution with certificate	Restek
Hexachlorobenzene, HCB	99	Solution with certificate	Restek
PCB 28	>99	Solid*	Promochem
PCB 52	>99	Solid*	Promochem
PCB 101	>99	Solid*	Promochem
PCB 118	>99	Solid*	Promochem
PCB 138	>99	Solid*	Promochem
PCB 153	>99	Solid*	Promochem
PCB 180	>99	Solid*	Promochem

* All solid standards were controlled on purity by NILU using GC/MS in scan and EI mode in mass range: 50-550. The standard compound peak area was 99% of total ion chromatogram area or better.

1st round:

- The ampoules were weighed after sealing and weighed again one week later to detect leaking ampoules.
- Some ampoules were analysed at the CCC using GC/MS and isotopically labelled internal standards before the distribution to the laboratories.

2nd round:

- The ampoules were weighed after sealing and weighed again one week later to detect leaking ampoules.

5. Participating laboratories

Most of the laboratories took part in both round 1 and 2 and measured both PAH and organochlorine compounds. Some laboratories returned results from parts of the exercise only and a few laboratories participated only in one of the rounds. The 21 laboratories which returned results are listed in Table 3. More information is given in Annex 1.

Table 3: Laboratories participating in the POP laboratory comparison.

Country	Participating institution
Austria	Umweltbundesamt, Vienna
Belgium	Vlaamse Milieumaatschapij, Gent
Canada	Meteorological Service of Canada, Downsview
Canada	Freshwater Institute, DFO, Winnipeg
Czech Republic	RECETOX, Brno
France	Lab Nat. d'Essais, Paris
France	Lab. Wolff Environ., Evry
France	Calydra, Paimboeuf
France	Lab. LARA, Toulouse
Germany	UBA Labor für Wasseranalytik, Berlin
Germany	Alfred-Wegener-Inst., Bremerhaven
Germany	IfE Analytik GmbH, Leipzig
Iceland	Dep. Pharm. & Tox., Univ. Iceland, Reykjavik
Ireland	Environmental Pollution Agency, Dublin
Lithuania	Joint Res. Centre, Vilnius
Lithuania	Institute of Physics, Vilnius
Republic of Macedonia	Republic Hydrometeorological Institute, Skopje
Norway	Norwegian Institute for Air Research, Kjeller
United Kingdom	AEA Technology, Culham
United Kingdom	University of Lancaster, Lancaster
Yugoslavia	Federal Hydrometeorological Institute, Belgrade

6. Results from round 1

The results are given below in Table 4–Table 7 and further presented in Annex 3–4. The first round of the comparison gave results that are related to the calibration and the instrumental performance.

Firstly, for all compounds an average value and a standard deviation was calculated from the data sent from all laboratories.

Secondly a range from [average-(2*st.dev.)] to [average+(2*st.dev.)] was computed. Finally a new average value was computed for each compound, excluding all reported values above or below the range computed in step two. This is the average value reported in Annex 3 and 4.

6.1 Results for organochlorine compounds round 1

Simple statistics and the ratios between arithmetic means and medians to the expected concentrations are given in Table 4 below.

*Table 4: Statistical overview for organochlorine compounds in round 1.
Concentration unit: pg/ μ l.*

Organochlorine compounds	Average	Median	Expected	St.dev.	Average/Expected	Median/Expected
p,p'-DDT	21.7	21.9	20.0	6.0	1.08	1.09
p,p'-DDE	40.9	40.1	40.0	10.8	1.02	1.00
γ -Chlordane	29.5	10.7	7.0	57.9	4.21	1.52
α -Chlordane	15.1	14.9	15.0	3.9	1.00	0.99
γ -HCH	275.5	284.3	300.0	53.5	0.92	0.95
α -HCH	155.9	114.7	120.0	180.6	1.30	0.96
HCB	139.3	141.5	150.0	19.6	0.93	0.94
PCB 28	37.9	37.9	36.0	7.8	1.05	1.05
PCB 52	70.0	68.5	76.0	5.9	0.92	0.90
PCB 101	35.3	38.2	42.0	13.8	0.84	0.91
PCB 118	56.1	53.0	53.0	17.1	1.06	1.00
PCB 138	22.9	24.6	24.0	7.3	0.95	1.02
PCB 153	21.7	21.2	22.0	4.5	0.99	0.96
PCB 180	28.5	29.5	30.0	4.7	0.95	0.98

Inspections of the central tendencies in the group of laboratories show that the ratio median to expected is good and vary from 1.10 to 0.90 for the pesticides with the γ -chlordane results as the one exception with a ratio at 1.52. The results for the organochlorine compounds had large outliers particularly for p,p'-DDT, p,p'-DDE, γ -chlordane, and for several PCBs. This is seen from the standard deviation and the ratios average to expected. γ -chlordane, present at low concentration, was the most challenging compound of the organochlorine group to quantify.

The averages of the three single measurements reported from each laboratory are given in Table 5 below and in Annex 3.

Table 5: Round 1; results of the analyses of organochlorine compounds in a mixture of standards. The expected concentrations are given in the lower rightmost column. Unit: pg/μl.

Lab. Code	101	102	103	104	105	108	109	110
p,p'-DDT	19.6	21.8	20.2	26.7	34.4	22.3	6.8	24.0
p,p'-DDE	39.0	47.3	40.1	47.9	66.4	34.7	18.7	
γ-Chlordane	9.8	11.0	10.7	11.7	10.6	7.3	34.7	
α-Chlordane	14.6	19.7	17.3	17.9	13.3	11.0	15.0	
γ-HCH	328	325	295	272	104	279	274	292
α-HCH	118	130	104	112	34	111	104	119
HCB	137	156	151	130	91	155	144	141
PCB 28	36.3	43.1	22.6	39.6	45.3	38.4	31.0	33.7
PCB 52	71.8	77.3	65.7	60.7	68.6	68.3	64.0	66.0
PCB 101	39.6	38.6	29.0	37.8	56.6	43.6	45.7	37.3
PCB 118	51.3	64.8	34.1	53.5	108.5	57.1	65.7	50.7
PCB 138	21.9	28.4	11.4	24.8	36.8	25.2	27.0	24.3
PCB 153	20.4	27.5	15.8	21.4	32.1	23.2	17.7	21.0
PCB 180	29.6	33.1	17.9	28.6	35.9	29.4	28.7	27.7

Lab. code	113	118	121	123	129A	129L	Expected
p,p'-DDT	19.7	18.3	27.0	24.7	22.0	15.9	20.0
p,p'-DDE	40.5	38.7	28.0	48.4	38.0	44.4	40.0
γ-Chlordane		8.1	8.5	220.0	13.0	8.7	7.0
α-Chlordane		13.9	6.0	21.4	16.0	14.8	15.0
γ-HCH	284	291	275	285	230	323	300.0
α-HCH	117	111	58	128	800	138	120.0
HCB	128	155	142	124	120	175	150.0
PCB 28	55.5	34.0	37.5	38.2	29.0	46.2	36.0
PCB 52	77.4	78.9	68.0	71.3	63.0	78.9	76.0
PCB 101	39.3	37.8	7.6	2.8	33.0	45.0	42.0
PCB 118	49.4	53.9	36.7	52.4	44.0	62.9	53.0
PCB 138	22.9	22.3	6.0	26.5	16.0	27.2	24.0
PCB 153	21.8	20.5	13.9	25.7	20.0	23.1	22.0
PCB 180	30.3	30.6	19.7	33.4	25.0	29.6	30.0

The results for HCB, PCB-52, and γ-HCH have the lowest number of results outside 25% from the expected, and the largest numbers of results better than 15% and better than 5% (Table 4, and Annex 3). This may be due to the fact that these compounds are among those with the highest concentrations in the exercise and that the laboratories possess experience with these substances at these concentration levels. Among the compounds with high numbers of results deviating more than 25% from the expected and relatively few good results are γ-chlordane, p,p'-DDT, p,p'-DDE, and PCB-28. These are among the compounds with the lowest concentrations in the first round of the exercise.

The laboratories performance will presumably depend on many factors, one very important being the experience and routines they have, or lack, with respect to

measurements at low concentration levels as in this comparison. As will be seen below, this is even more important in the second part of the comparison than in the first round.

The laboratories with the largest number of result better than 5% from the expected in the first part of the comparison were 101, 113, and 118, followed by 108 and 110.

6.2 Results for PAH round 1

Simple statistics and ratios between arithmetic means and median to the expected concentrations have been given in Table 6 for the PAH.

*Table 6: Statistical overview for PAH in round 1.
Concentration unit: ng/ μ l.*

PAH	Average	Median	Expected	St.dev.	Average/ Expected	Median/ Expected
Naphthalene	7.73	8.21	8.33	2.40	0.93	0.99
Acenaphthylene	2.58	2.73	2.00	0.85	1.29	1.37
Acenaphthene	3.80	4.00	4.17	1.31	0.91	0.96
Fluorene	3.63	3.75	4.00	0.94	0.91	0.94
Phenanthrene	7.72	8.01	8.33	1.76	0.93	0.96
Anthracene	0.38	0.37	0.42	0.09	0.91	0.87
Fluoranthene	3.79	3.89	4.17	0.74	0.91	0.93
Pyrene	3.02	3.38	3.33	0.78	0.91	1.01
Benzo[a]anthracene	0.66	0.54	0.58	0.42	1.13	0.93
Chrysene	2.06	1.39	1.67	2.97	1.23	0.83
Benzo[b]fluoranthene	1.98	2.09	2.18	0.46	0.91	0.96
Benzo[k]fluoranthene	0.56	0.49	0.50	0.23	1.11	0.98
Benzo[a]pyrene	0.44	0.35	0.42	0.23	1.06	0.84
Indeno[1,2,3-cd]pyrene	1.18	1.20	1.33	0.17	0.89	0.90
Dibenzo[a,h]anthracene	0.22	0.16	0.17	0.17	1.28	0.94
Benzo[ghi]perylene	1.48	0.95	1.00	1.94	1.48	0.95
Biphenyl	6.63	7.10	7.98	2.58	0.83	0.89
Perylene	1.12	1.10	1.20	0.25	0.93	0.92
Benzo[e]pyrene	0.53	0.46	0.43	0.26	1.23	1.07

Most of the medians in Table 6 are less than ten per cent from the expected, with the largest deviation seen for acenaphthylene. The three compounds at the end of Table 6 were analysed by 8–9 participants only.

Table 7 show the results of the PAH analyses from all laboratories for all compounds during round 1.

Table 7: Round 1; results of the analyses of PAH in a mixture of standards. The expected concentrations are given in the lower rightmost column.

Unit: ng/ μ l.

(¹): GC/MS, (²): HPLC, Exp.: Expected concentrations.

Lab. code	101	102	103	104	105 ⁽¹⁾	105 ⁽²⁾	107	108	109
Naphthalene	10.33	1.58		5.35	10.61	8.55	8.190	7.99	8.53
Acenaphthylene	3.19	0.22	2.48	1.68	3.57	2.99	2.680	2.60	2.97
Acenaphthene	4.58	0.24		2.53	5.15	4.10	4.045	3.55	4.07
Fluorene	4.17	1.30	3.02	2.16	4.77	4.13	3.670	3.58	3.80
Phenanthrene	9.35	5.28	7.51	4.98	10.60	8.68	7.890	8.01	8.40
Anthracene	0.520	0.274	0.314	0.190	0.510	0.380	0.336	0.354	0.353
Fluoranthene	4.24	2.70	3.52	2.37	5.02	4.16	3.855	3.89	4.07
Pyrene	3.59	2.32	3.21	1.88	4.13	3.45	3.070	3.35	3.43
Benzo[a]anthracene	0.423	0.516	0.535	0.267	0.650	0.630	0.531	0.396	0.547
Chrysene	1.13	1.70	1.28	0.55	1.47	1.66	1.575	1.17	1.53
Benzo[b]fluoranthene	1.75	2.22	2.79	1.10	2.17	2.08	1.850		2.30
Benzo[k]fluoranthene	0.513	0.462	0.476	0.417	0.620	0.520	0.400	0.442	0.530
Benzo[a]pyrene	0.330	0.314	0.347	0.267	0.540	0.420	0.305	0.338	0.393
Indeno[1,2,3-cd]pyrene	0.89	1.24	1.32	0.84	1.15	1.20	1.210	1.15	1.33
Dibenzo[a,h]anthracene	0.117	0.099	0.193	0.100	0.460	0.260	0.125	0.152	0.177
Benzo[ghi]perylene	0.89	1.10	0.81	0.68	0.95	1.07	0.935	0.92	1.10
Biphenyl				5.21	0.70	6.94	6.820		7.27
Perylene				0.82	0.82	1.17	1.305		1.43
Benzo[e]pyrene			0.806	0.333	0.460	0.490	0.380		0.317

Lab. code	110	122	123	129A	129L ⁽¹⁾	129L ⁽²⁾	130	Exp.
Naphthalene			8.16	8.25	7.52	5.82		8.33
Acenaphthylene			2.58	2.86	2.49			2.00
Acenaphthene			5.32	3.93	3.57	3.57		4.17
Fluorene			4.86	3.69	3.23	3.59	4.10	4.00
Phenanthrene		5.70	9.46	8.41	7.15	7.85	4.75	8.33
Anthracene	0.320		0.464	0.520	0.403	0.348		0.420
Fluoranthene	3.70		4.33	3.88	3.50	4.23	2.55	4.17
Pyrene	3.41	1.20	3.40	3.24	2.72	3.49	1.80	3.33
Benzo[a]anthracene	0.557	2.000	1.377	0.503	0.517	0.576	0.350	0.580
Chrysene	1.43	13.50	0.71	1.35	1.20	1.43	0.95	1.67
Benzo[b]fluoranthene	2.09		1.00	2.02	1.79	2.17		2.18
Benzo[k]fluoranthene	0.473		1.377	0.453	0.530	0.492		0.500
Benzo[a]pyrene	0.400	0.990	1.079	0.350	0.353	0.356	0.250	0.420
Indeno[1,2,3-cd]pyrene	1.23		1.35	1.11	1.05			1.33
Dibenzo[a,h]anthracene	0.147	0.083	0.742	0.163	0.263	0.160		0.170
Benzo[ghi]perylene	0.94	8.70	1.24	0.86	0.79	0.97		1.00
Biphenyl			9.78	8.26	6.58			7.98
Perylene			0.93	1.19	1.01		1.10	1.20
Benzo[e]pyrene			1.156	0.377	0.360			0.430

Benzo[k]fluoranthene, benzo[b]fluoranthene, pyrene, and naphthalene have been best measured by the laboratories when judged from the highest number of results not more than 10% from the expected, i.e. 50–70% of the results were very good. These compounds each had not more than one result 50% or higher from the expected concentration (Annex 4). The two compounds which the group of

laboratories have analysed with the lowest accuracy during the first round of the comparison were acenaphthylene and dibenzo[a,h]anthracene.

The results from the first round indicated that the group of participating laboratories had a better performance for the analysis of the PAH than for the organochlorine compounds. The PAH results have less large outliers than the pesticides with a smaller range for the ratio average to expected.

The laboratory results in Table 7 reveal large performance differences among the participants. Five laboratories were able to measure more than half of the individual PAHs better than 10% from the expected value; Lab. 105, 107, 109 with HPLC, 110, 129A, and 129L with HPLC, while two laboratories failed to obtain any results within 10% (Annex 4).

7. Preparation of samples for round 2

The second round in the exercise involved analysis of real sample extracts. The samples analysed were pooled extracts of high volume ambient air samples (glass fibre filters and PUF-plugs) collected at NILU during the period from 13.12.99 to 18.4.01. The filters and PUF adsorbents were extracted in four batches. Two batches, intended for determination of chlorinated compounds, were extracted with hexane (CI-POP1 and CI-POP2). The other two were extracted with cyclohexane (PAH1 and PAH2). For each extraction about 2.5 litres of solvent was used. The raw-extract was pre-concentrated to about 50 ml using a TurboVap 500. The extracts contained some dust and humidity at this stage. Each extract was passed through a column packed with 5 gram of sodium sulphate (pre-flushed with 30 ml of solvent). The dried, dust free sample was collected in an Erlenmeyer flask, which was weighed before (empty) and after collection of sample. The amount of solvent was adjusted, by weight, to about 60 ml. The dried sample extract was filled into 60 single 1 ml glass ampoules, which were sealed. This was repeated for all four pooled extracts. With this volume, each ml would be equivalent to an air sample volume of about 500 m³, ~ 900 m³ for CI-POP2.

The actual sample volumes were:

- CI-POP1:** 30.148 m³, sampling during May 2000
- CI-POP2:** 53.417 m³, sampling during February, March and April 2001
- PAH1:** 30.021 m³, sampling during December 1999, January, February, March 2000
- PAH2:** 38.804 m³, sampling March, April 2001

Since several samples were taken over time intervals much longer than 24 hours and losses by evaporation through the sampler are expected to occur, the analysis of the extract would not give a correct concentration of POPs in the air sampled. Sampling provided, however, realistic real life sample extracts from air samples containing POPs and possible interferences from the sampling materials and/or the air sampled. The purpose of round 2 was to test the laboratories ability to deal with such samples in a quantitative best way.

The problem with sooth formation inside the ampoules mentioned in Chapter 3 was avoided in the following way:

The 1 ml sub-sample for the ampoule was taken out from the Erlenmeyer flask by using a syringe. The vial was filled with nitrogen gas by holding a micropipette connected to a nitrogen gas bottle with a Teflon tube inside the ampoule for some seconds. Then the sample was transferred from the syringe to the ampoule and the lower part of the ampoule was immersed in liquid argon, freezing out the solvent. After freezing out the solvent, the neck of the ampoule was quickly flame sealed using a propane burner.

The ampoules were packed and transported as described for round 1.

In spite of shipping the samples in accordance to all rules (shipping and customs) several participants had problems with both shipping companies and customs authorities. One shipment was returned to CCC from the customs authorities abroad and one shipment disappeared and had to be replaced with a new one, causing delays in the project.

A set of four ampoules was sent to each participant. The samples should be handled as normal air samples for PAH and for organochlorine compounds and had to be analysed through the normal laboratory routines including the quality assurance steps. The second round therefore included the laboratory routines for handling the samples as well as the chemical analysis.

For simplicity an approximate total sampling volume of 30.000 m³ was assigned to each large sample extract and each lab was asked to report the concentration of the compounds determined relative to a sample volume of 500 m³.

8. Results from round 2

The results are given below in Table 8 and Table 11 and further presented in Annex 5–6. The second round of the comparison gave results that throw light on sample handling and clean-up as well as the chemical analysis with possible interferences from other compounds.

Please note that the concentrations in the Annexes are given as reported and do not express the measurement accuracy.

Some laboratories participated in the comparison's second round only.

Internal standards may be used to compensate for changes in detector response during quantification. If added before extraction they will also compensate for sample losses during extraction and clean-up. Otherwise a loss will produce too low results. Determination of internal standard recovery gives information about the applicability of the method. No such data has been reported during this exercise.

8.1 Results for organochlorine compounds round 2

The medians of all results above the detection limit in the second part of the comparison have been given in Table 8. In addition to the laboratories that

quantified the concentrations and contributed to the median, there were a variable number of laboratories which reported the concentrations to be lower than their detection limits. This is quite understandable since the concentrations of some of the compounds in the real samples were quite low. Table 8 shows that the concentrations of some compounds were very low; γ -chlordane, p,p'-DDT, and PCB-180 all had one or both concentrations lower than 1 pg/m^3 .

Table 8: Medians, and numbers of laboratories giving results above their detection limits. Medians in pg/m^3 .

Compound	1 st sample		2 nd sample	
	Median	Number of laboratories	Median	Number of laboratories
p,p'-DDT	0.9	8	1.2	9
p,p'-DDE	1.7	9	2.1	10
γ -Chlordane	0.7	8	0.9	7
α -Chlordane	1.3	6	1.1	8
γ -HCH	25.0	13	16.4	14
α -HCH	13.3	13	22.5	14
HCB	28.9	15	62.1	15
PCB 28	7.6	11	7.3	11
PCB 52	6.7	11	5.4	11
PCB 101	4.1	11	2.8	10
PCB 118	1.7	10	1.2	11
PCB 138	2.2	11	1.2	10
PCB 153	2.8	10	1.8	11
PCB 180	1.2	9	0.7	9

Table 9 shows concentrations of the organochlorine compounds in the sample in round 1 and in the two samples in round 2. The values for round 2 are calculated from the median for each compound, assuming a 500 m^3 sample volume and a final sample extract volume of 100 μl after clean-up and pre-concentration.

Table 9: Comparison of organochlorine compound concentrations in the standard analysed in round 1 and in the samples of round 2.

Compound	Round1 Theoretical pg/ul	Round2 CI-POP1 median pg/ul	Round2 CI-POP2 median pg/ul
p,p'-DDT	20.0	4.5	5.9
p,p'-DDE	40.0	8.5	10.7
γ -Chlordane	7.0	3.7	4.6
α -Chlordane	15.0	6.5	5.7
γ -HCH	300.0	125.0	82.0
α -HCH	120.0	66.3	112.5
HCB	150.0	144.5	310.5
PCB 28	36.0	37.8	36.7
PCB 52	76.0	33.7	27.2
PCB 101	42.0	20.5	13.8
PCB 118	53.0	8.5	6.0
PCB 138	24.0	11.2	6.2
PCB 153	22.0	13.8	9.2
PCB 180	30.0	6.1	3.4

The results from the second round have been evaluated in view of the deviations from the medians of all measurements as the best estimates for the air concentrations. Annex 5 presents the results from the second part in Figures as illustrated in Figure 1 and Figure 2 for α -HCH.

Table 10 gives the air concentrations measured at two sites in year 2000 (Berg et al., 2002) that can be compared with the exercise medians of the organochlorine compounds in Table 8.

Table 10: Air concentrations of POP at sites in the Czech Republic and Sweden in 2000. Results from weekly and monthly samples. Pesticides and PCB units pg/m^3 .

Organochlorine compounds	Košetice CZ0003R			Rörvik SE0002R		
	Min	50%	Max	Min	50%	Max
	Weekly samples			Monthly samples		
	pg/m^3			pg/m^3		
p,p'-DDT	0.50	3	10	0.05	0.80	3.85
p,p'-DDE	4	25	75	0.64	2.27	16.71
γ -HCH	7	41	199	5	17	69
α -HCH	4	20	70	4	10	24
PCB-28	16	28	52	0.96	2.01	5.98
PCB-52	17	31	106	1.29	2.34	11.2
PCB-101	13	22	48	1.06	2.35	7.95
PCB-118	3	5	8	0.36	0.83	2.40
PCB-138	5	14	28	0.62	1.20	3.28
PCB-153	13	21	32	0.69	1.36	3.78
PCB-180	3	4	17	0.24	0.46	1.23

Comments to the results for each compound are given below.

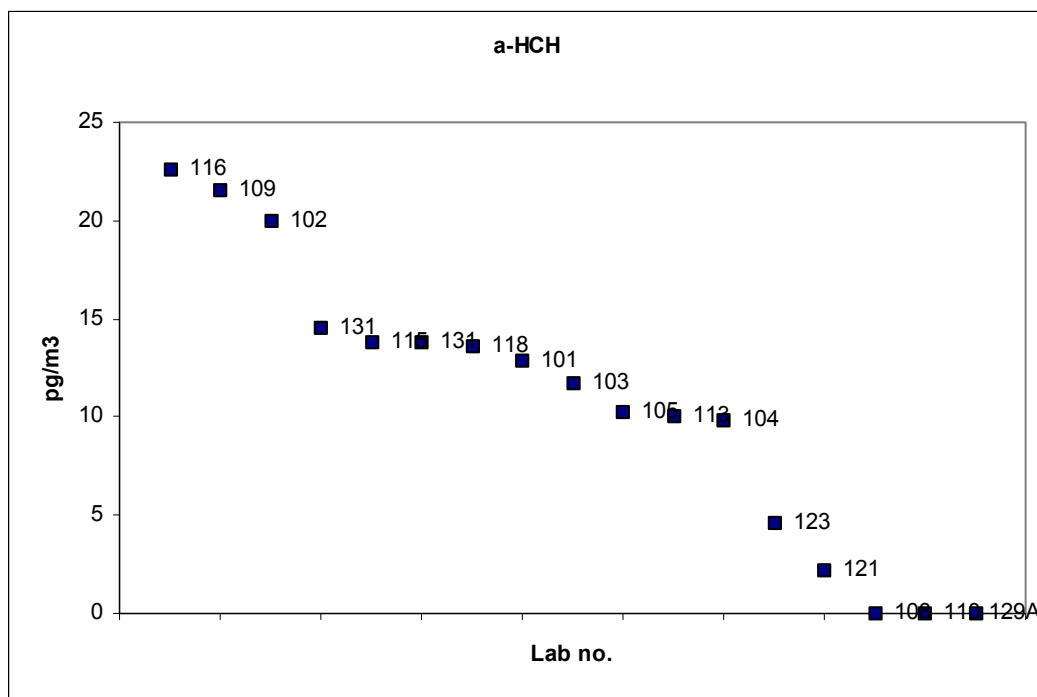


Figure 1: Results for α -HCH measurements in extract 1. Concentrations in pg/m^3 .

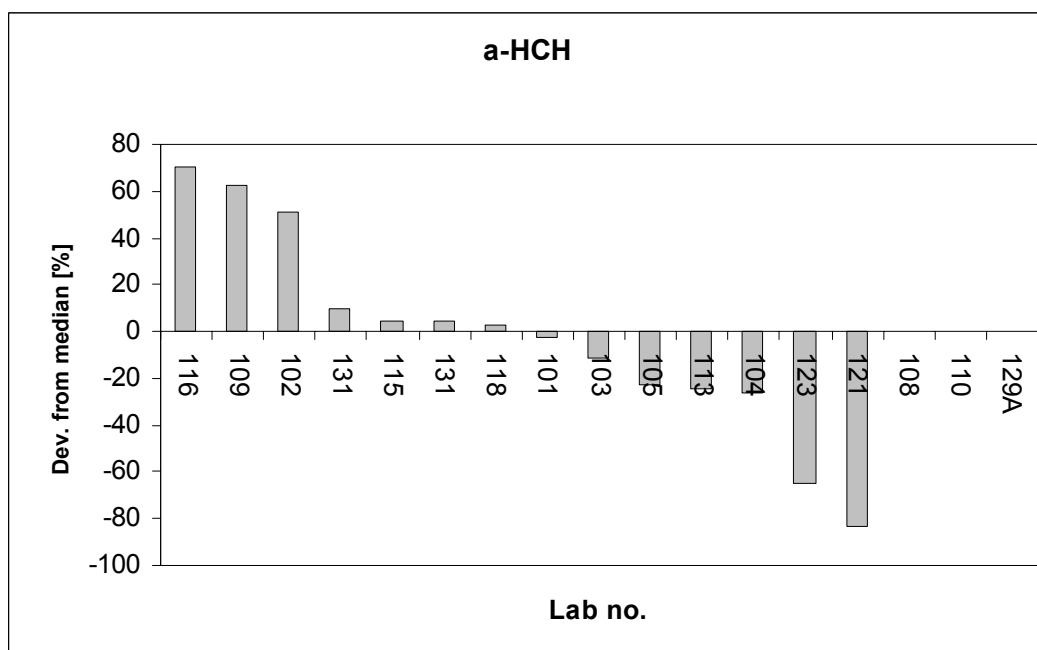


Figure 2: Results for α -HCH measurements in extract 1. Deviation in per cent from the median concentration.

p,p'-DDT

Fifteen laboratories participated, but six laboratories reported the concentrations to be lower than their detection limits. The DDT concentrations in the samples were about 1 pg/m³, a rather typical regional concentration for northern Europe (Table 10), but in the lower end of the central European regional concentrations. The best results were obtained by laboratory 103, which also had good results in the first round of the comparison. Laboratories 101 and 113 obtained excellent results in the first part, but laboratory 101 could not detect the component and laboratory 113 obtained too high results. Laboratories 129A and 121 obtained too high results compared to their good results in round 1.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 103, 118 and 131.

CI-POP 2: Lab. 103 and 113.

p,p'-DDE

Fifteen laboratories took part in the analyses and 6 and 5 laboratories reported the concentration to be lower than their detection limit. The results were similar to the p,p'-DDT results with respect to laboratories with too high detection limits. Laboratories 118 and 103 obtained both results less than 10% from the medians as they did in the first part of the comparison. Laboratories 115 and 131 had results < 20% from the median, none of these laboratories took part in the first part of the comparison. One laboratory reported one result outside 100 % and the other result more than 50% from the median. The concentrations were similar to the p,p'-DDT concentrations.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 103, 104, 105, 109, 115, 118, and 131.

CI-POP 2: Lab. 103, 115, 118, 123 and 131.

 γ -Chlordane (trans-Chlordane)

Fourteen laboratories participated, but only 8 and 7 laboratories respectively reported concentrations higher than the detection limits. The concentrations were less than 1 pg/m³ and four laboratories reported the result as lower than their detection limit, additionally two laboratories reported the compound as not detected. Laboratories 118 and 131 had results near the median, and 115 also had results not more than 20% from the median. Two laboratories reported results more than 100% from the median, and two other laboratories had results deviating more than 50%.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 115, 118, and 131.

CI-POP 2: Lab. 103, 109, 115, 118 and 131.

α -Chlordane (cis-Chlordane)

The number of participants was similar as for γ -chlordane, and 6 and 8 laboratories respectively were able to quantify the concentrations of this compound in the two samples. Laboratories 115, 104, and 103 had both results closer than 20% from the median. The median concentrations were low, 1-2 pg/m³. Laboratory 105 quantified α -chlordane close to the median in one of the two samples but not in the other although the medians for the two samples were quite similar. Five laboratories had too high detection limits, while one another laboratory did not detect the substance, detection limit not given. One laboratory had a result more than 100%, and another laboratory more than 50%, from the medians.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 103, 104, 115, 118 and 129A.

CI-POP 2: Lab. 103, 104, 105, 115 and 131.

γ -HCH

Sixteen laboratories measured γ -HCH and thirteen participants had two results above the detection limit. The concentrations were much higher than for the chlordanes; 15–25 pg/m³, which could be typical for regional European concentrations (Table 10). Two laboratories reported the results wrongly lower than their detection limit; one being laboratory 110 that had very good results in the first part of the comparison. The laboratories that were close to the median had obtained very good results in the first part of the exercise as well; laboratories 101, 118, and 102 had both results less than 10% from the median. Laboratories 103 and 131 obtained results less than 20% away. Six laboratories had one or more result outside 50% from the median, two of the results were more than 100% away.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 101, 102, 103, 113, 115, 116, 118 and 131.

CI-POP 2: Lab. 101, 102, 103, 115, 118, 121 and 131.

α -HCH

Sixteen laboratories took part in the analyses and thirteen participants had two results above the detection limit. The concentrations were similar to those for γ -HCH, and the results both above and lower than the detection limits were quite similar to those of γ -HCH. Laboratory 108 correctly found one of the two concentrations lower than the detection limit while the second was reported far too high, for α -HCH as well as for γ -HCH. Seven laboratories reported one or more results more than 50% from the median, and two results were outside 100% from the median. Laboratories 118, 131, and 115 had both results less than 10% from the median, while laboratories 101 and 103 had results less than 20% from the median.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 101, 103, 115, 118 and 131.

CI-POP 2: Lab. 101, 102, 103, 109, 115, 118 and 131.

HCB

Sixteen laboratories returned HCB results and one of the participants could not detect this compound. Four participants obtained both results not more than 10% from the median; laboratories 118, 103, 116, and 105. The first two of these had obtained results in the first part that were less than five per cent from the expected. Two laboratories were more than 100% away from the median, while these laboratories both had results less than five per cent from the expected in the first part of the comparison. Another four laboratories had one or more results at least 50% from the median.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 101, 102, 103, 105, 113, 116, 118 and 131.

CI-POP 2: Lab. 101, 102, 103, 104, 105, 113, 116 and 118.

PCB

Sixteen laboratories took part in the analyses of the seven PCBs; PCB-28, -52, -101, -118, -138, -153, and -180. Laboratory 123 returned, however, results from PCB-28, -52, -101 and -138 only.

The median concentrations of the first three compounds were in the range 3-8 pg/m^3 (Table 8). PCB-180 had concentrations at about 1 pg/m^3 while the remaining three compounds had medians about 1-2 pg/m^3 . The concentrations could be typical for northern Europe, but could be in the lower end for the central continental parts (Table 10).

Three laboratories reported all seven compounds lower than their detection limits; 102, 110, and 116. Laboratory 108 reported the concentration to be below the detection limit in all but one case where PCB-153 was reported at a far too high concentration. This was also the case for α - and γ -HCH in the same sample. Laboratory 113 found interfering substances in the measurements of PCB-28, and -52, and laboratory 101 could not detect PCB-101, -118, -138, -153, and PCB-180.

The results for the PCBs given below and in the Annex 5 in general reveal that two laboratories were able to obtain both results better than 10% for more than one PCB; laboratories 103 and 118. Laboratories 118, 131, and 105 all had both results for five of the seven PCBs better than 20% from the median. Laboratories 115 and 103 had four of the seven PCBs within 20%.

In the other end of the scale one laboratory had at least one result more than 100% from the median for all seven PCBs, and a different laboratory had six results at more than 100% from the median. Six laboratories had at least one result more

than 100% from the median, and three other laboratories had at least one result deviating 50% or more from the median.

Laboratory 105 commented that use of insufficiently cleaned silica may have given PCB-results up to 20% too high.

PCB-28 (2,4,4'-TriCB)

Three laboratories obtained very good results in this second part; laboratories 118, 101 and 103. The results from laboratories 115 and 104 were likewise near the median. Two laboratories reported concentrations more than 100% from the median, both had however obtained very good results in the first part of the comparison. Two other participants reported both results more than 50% higher than the median.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1 and CI-POP 2: Lab. 101, 103, 104, 115, 118 and 131.

PCB-52 (2,2',5,5'-TetraCB)

Laboratories 103, 104, 131, and 115 had results very near the median. Two of the sixteen laboratories had both results more than 100% from the median, and one laboratory had both results more than 50% from the median.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 101, 103, 104, 115 and 131.

CI-POP 2: Lab. 103, 104, 115 and 131.

PCB-101 (2,2',4,5,5'-PentaCB)

Laboratories 113, 103, 118 and 131 had results very close to the median. Three laboratories obtained results more than 100% from the median, while three other laboratories had results at about 50% from the median. Laboratories 109 and 104 that had around 50% deviation from the median, obtained results at about 10% from the expected in the first part of the comparison.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 103, 109, 113, 115, 118 and 131.

CI-POP 2: Lab. 103, 113, 115, 118, 129A and 131.

PCB-118 (2,3',4,4',5-PentaCB)

The laboratories with results near the median were 104, 109, 115, 118 and 131. Three laboratories had results more than 100% from the median while two other laboratories obtained results that were more than 50% from the median.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1 and CI-POP 2: Lab. 104, 109, 115, 118 and 131.

PCB-138 (2,2',3,4,4',5'-HexaCB)

Three laboratories had both results less than 10% from the median; 104, 118 and 131. Three laboratories had results more than 100% from the median, and three others had results outside 50%.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 103, 104, 109, 118, 129A and 131.

CI-POP 2: Lab. 103, 104, 118, and 131.

PCB-153 (2,2',4,4',5,5'-HexaCB)

Seven single results were less than 10% from the median. Four laboratories had one or two results more than 100% from the median.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 103, 104, 109, 118, 129A and 131.

CI-POP 2: Lab. 104, 118 and 131.

PCB-180 (2,2',3,4,4',5,5'-HeptaCB)

No laboratories had results less than 20 per cent from the median for both samples. Two of the laboratories that obtained the best result for the other PCBs were 26% at most from the median. As seen from Table 8 above ten laboratories only were able to obtain results above their detection limits. Three laboratories deviated more than 100% from the medians while another laboratory had results more than 50% from the median.

Laboratories inside $\pm 20\%$ of the median:

CI-POP 1: Lab. 103, 104 and 118.

CI-POP 2: None.

8.2 Results for PAH round 2

The results from the second part of the comparison were evaluated by comparison with the medians of the laboratory results. Table 11 gives the medians and number of laboratories that found results above their detection limit.

Table 12 shows concentration values for the PAHs in the sample in round 1 and in the two samples in round 2. The values for round 2 are calculated from the median for each compound, assuming a 500 m³ sample volume and a final sample extract volume of 100 μ l after clean-up and pre-concentration.

Table 13 give a few simple statistics on the PAH concentrations measured at two sites in Europe in year 2000 (Berg et al., 2002).

Figure 3 and Figure 4 give the naphthalene results from extract 1. Annex 6 presents the results for all laboratories and compounds in similar figures giving the deviation from the median concentration in concentration units, i.e. ng/m³, and as per cent deviation from the median.

Table 11: Medians and number of laboratories giving results above their detection limits. Medians in ng/m^3 .

Compound	1 st sample		2 nd sample	
	Median	Number of laboratories	Median	Number of laboratories
Naphthalene	9.63	11	0.780	12
Acenaphthylene	3.92	11	0.281	12
Acenaphthene	1.13	12	0.315	13
Fluorene	4.31	12	2.61	13
Phenanthrene	8.23	11	6.68	13
Anthracene	0.800	12	0.48	13
Fluoranthene	2.75	12	2.25	13
Pyrene	2.35	12	1.87	13
Benzo[a]anthracene	0.420	12	0.270	12
Chrysene	0.780	13	0.536	13
Benzo[b]fluoranthene	0.507	11	0.389	12
Benzo[k]fluoranthene	0.226	11	0.177	12
Benzo[a]pyrene	0.365	13	0.240	14
Indeno[1,2,3-cd]pyrene	0.402	13	0.305	13
Dibenzo[a,h]anthracene	0.050	10	0.042	12
Benzo[ghi]perylene	0.460	13	0.355	14
Biphenyl	4.62	6	1.16	5
Perylene	0.0345	5	0.0200	5
Benzo[e]pyrene	0.409	8	0.317	8

Table 12: Comparison of PAH concentrations in the standard analysed in round 1 and in the samples of round 2.

Compound	Round 1 Theoretical $\text{ng}/\mu\text{l}$	Round 2 PAH1 median $\text{ng}/\mu\text{l}$	Round 2 PAH2 median $\text{ng}/\mu\text{l}$
Naphtalene	8.3	48.2	3.9
Acenaphthylene	2.0	19.6	1.4
Acenaphthene	4.2	5.7	1.6
Fluorene	4.0	21.6	13.0
Phenanthrene	8.3	41.1	33.4
Anthracene	0.4	4.0	2.4
Fluoranthene	4.2	13.8	11.2
Pyrene	3.3	11.8	9.4
Benzo[a]anthracene	0.6	2.1	1.4
Chrysene	1.7	3.9	2.7
Benzo[b]fluoranthene	2.2	2.5	1.9
Benzo[k]fluoranthene	0.5	1.1	0.9
Benzo[a]pyrene	0.4	1.8	1.2
Indeno[1,2,3-cd]pyrene	1.3	2.0	1.5
Dibenzo[a,h]anthracene	0.2	0.3	0.2
Benzo[ghi]perylene	1.0	2.3	1.8
Biphenyl	8.0	23.1	5.8
Perylene	1.2	0.2	0.1
Benzo[e]pyrene	0.4	2.0	1.6

Table 13: Air concentrations of PAH at sites in the Czech Republic and Sweden in 2000. Results from weekly and monthly samples. PAH unit ng/m^3 .

PAH	Košetice CZ0003R			Rörvik SE0002R		
	Min	50%	Max	Min	50%	Max
	Weekly samples			Monthly samples		
	ng/m^3			ng/m^3		
Acenaphtene	0.01	0.08	1.51			
Phenanthrene	0.71	3.31	18.56	0.27	1.22	3.05
Anthracene	0.01	0.06	0.69	0.0	0.02	0.07
Pyrene	0.10	0.51	5.76	0.04	0.29	0.78
Benzo[a]anthracene	0.01	0.06	2.23	0.01	0.11	0.24
Benzo[a]pyrene	0.005	0.059	1.757	0.005	0.059	0.267
Indeno[1,2,3-cd]pyrene	0.01	0.07	2.06	0.04	0.07	0.37
Benzo[ghi]perylene				0.01	0.05	0.32

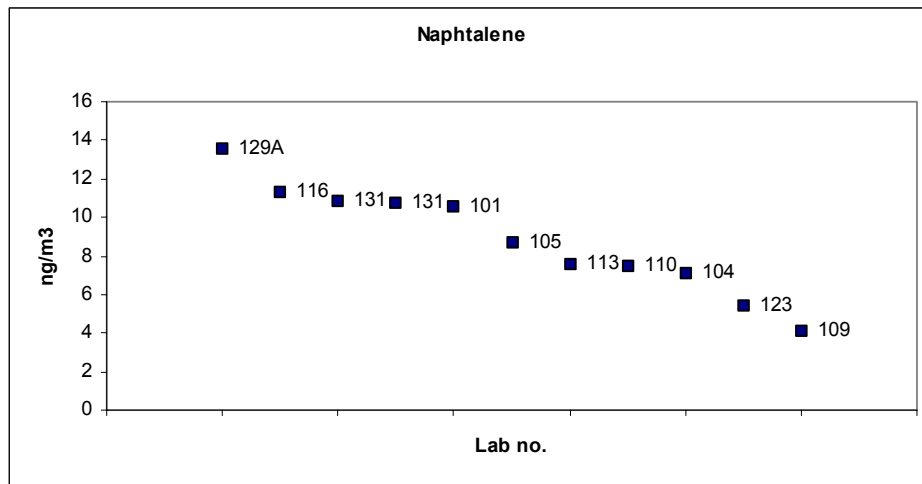


Figure 3: Results of all naphthalene measurements in extract 1 from the second part of the comparison in ng/m^3 .

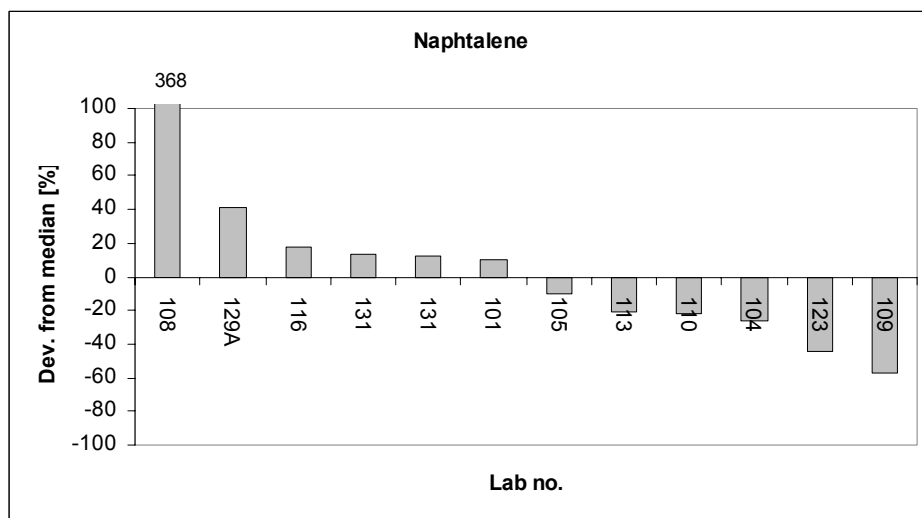


Figure 4: Deviation in percent from the median of all naphthalene measurements in extract 1 of the second part of the comparison.

Comments to the individual compounds are given below.

Naphthalene

The concentrations in the two extracts differed by a factor of 10, the median concentrations were about 9.6 and 0.8 ng/m³. Twelve participants took part in the measurements of naphthalene and three laboratories obtained both results within 20% from the median; laboratories 105, 116, 131. Laboratory 105's results were less than 10% away from the median, and in the first part of the comparison this laboratory was less than 5% from the expected. The two laboratories 116 and 131 did not take part in the first part of the exercise. Three laboratories missed the medians with more than 50%, which may seem surprising since their performance in the first part was very good. One laboratory gave both results more than 100% from the medians.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 105, 116 and 131.

PAH 2: Lab. 105, 110, 116, 129A and 131.

Acenaphthylene

The results of the acenaphthylene measurements in the first part of the comparison were among the least satisfactory in the exercise. The ratio between the acenaphthylene concentrations in the two extracts in this part of the exercise was similar to that of naphthalene, but the concentrations were lower; about 3.9 and 0.3 ng/m³. Three laboratories of the twelve participants obtained both results less than 10% from the median; laboratories 129A, 116, and 101. Neither 129A nor 101 obtained good results in the first part, results they shared with the three laboratories with results more than 50% from the median. Two laboratories gave respectively one and two results more than 100% from the medians.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 109, 116, 123 and 129A.

PAH 2: Lab. 101, 102, 103, 116, 129A and 131.

Acenaphthene

The median concentrations of acenaphthene were about 1.1 and 0.3 ng/m³. These were rather typical weekly concentrations from the central part of Europe (Košetice in the Czech Rep., Table 13) in 2000. Thirteen laboratories measured this compound. Two laboratories, 116 and 131 had both results closer than 10% from the median. Three laboratories had five results outside 50%, and four of these measurements were more than 200% from the median. One of the laboratories outside 200% had excellent results in the first part of the exercise.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 107, 116 and 131.

PAH 2: Lab. 116, 129A and 131.

Fluorene

Thirteen participants have analysed both extracts. Laboratory 102 measured PAH in the low concentration extract only. The median concentrations of fluorene were approximately 4.3 and 2.6 ng/m³. Three participants had both results less than 10% from the medians; laboratories 103, 109, and 116. Lab. 109 had excellent results in the first part as well while Lab. 103 was about 24% from the expected. Three laboratories had results more than 50% away, and one had very large deviations, but very good results in the first part. This is in line with the results above; a good ability to calibrate and analyse a standard is unfortunately no guarantee for good results on real extracts.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 109, 116 and 131.

PAH 2: Lab. 103, 107, 109 and 116.

Phenanthrene

The participants in this measurement were as for fluorene. The phenanthrene medians reached about 6.7 and 8.2 ng/m³. This seems to be higher than one would expect to find in northern Europe but could be rather typical for the central parts (Table 13). The results were without outliers as for some of the compounds above, one laboratory got results between 50% and 60%, and these were the most deviating results. Two laboratories were within 10% from the median; 109 and 131. Laboratory 109 had excellent results in the first part. Another three laboratories found phenanthrene in both extracts less than 20% away from the medians, these were laboratories 103, 105 HPLC and 107 that had similar good results in part 1.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 103, 105, 107, 109, 129A and 131.

PAH 2: Lab. 102, 103, 105, 107, 108, 109 and 131.

Anthracene

The anthracene concentrations were both low, about 0.5 and 0.8 ng/m³. This is higher than one would expect at regional sites in the northern part of Europe and probably in the high end of the Continental regional concentrations (Table 13). This may be the reason for some of the apparent large deviations from the median. It is, however, important to bear in mind that the small concentrations easily give high deviations in per cent for fairly small concentrations differences. Fourteen laboratories measured both concentrations. Two laboratories found concentrations within 10%; laboratories 131 and 110. Three laboratories had outliers more than 300% from the median, and one had results 60–80% too high.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 103, 107, 110 and 131.

PAH 2: Lab. 102, 103, 110 and 131.

Fluoranthene

Thirteen participants returned results for both extracts and one participant had a too high detection limit to measure these concentrations. The median concentrations were higher than anthracene's concentrations, 2.8 and 2.3 ng/m³. Five laboratories obtained both results within 10 % from the median and two more within 20%. These were laboratories 131, 109, 129A, 101, and 103 and 116. No results were outside 100% from the median but two laboratories had results larger than 50%.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 107, 109, 116, 129A and 131.

PAH 2: Lab. 101, 102, 103, 116, 129A and 131.

Pyrene

Pyrene was one of the compounds with the largest number of very good results in the first part of the comparison, and the results from the second part were also good. Fourteen laboratories carried out measurements of both extracts; laboratory 108 had, however, a too high detection limit as for fluoranthene. The medians were 2.4 and 1.9 ng/m³, both concentrations close to this detection limit. Two laboratories gave results within 10% from the median; laboratories 113 and 131. Three results from two laboratories were between 50% and 100% from the median.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 107, 113, 129A and 131.

PAH 2: Lab. 101, 103, 110, 113, 116, 129A and 131.

Benzo[a]anthracene

The concentrations of benzo[a]anthracene were rather low, about 0.4 and 0.3 ng/m³, and could be rather typical for central parts of Europe, but higher than expected in the north (e.g. Table 13). The results in the second part of the comparison were nevertheless good. Twelve participants analysed both extracts and five laboratories returned both results better than 20%, one of which were better than 10% for both samples; laboratory 101. Four single results were more than 50% from the median, two of which were larger than 200%.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 104, 110, 113, 123, 129A and 131.

PAH 2: Lab. 101, 103, 104, 116, 129A and 131.

Chrysene

The concentrations were low, about 0.8 and 0.5 ng/m³. Thirteen participants analysed both samples and five laboratories obtained both results better than 20%; laboratories 103, 113, 131, 129A, and 101. The two first laboratories were not more than 10% away. Four results from two laboratories were more than 100%

from the median. GC-methods may produce high results compared to HPLC-methods because of co-elution with triphenylene.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 113, 129A and 131.

PAH 2: Lab. 101, 102, 103, 113, 116, 129A and 131.

Benzo[b]fluoranthene

The laboratories obtained very good results for this compound in round one. The concentrations in round two corresponds to about 0.5 and 0.4 ng/m³, and eleven participants analysed both samples. Three laboratories reported both results closer than 10% from the median while another participant was 11% and 0% away in the two extracts. The laboratories were laboratories 116, 129A, 103 and 101. One participant was about 90% off in both two results while one laboratory was 60% and 80% away. GC-methods may produce high results compared to HPLC-methods because of co-elution with benzo[j]fluoranthene and benzo[k]fluoranthene. Laboratory 131 reported the sum of benzo[b]fluoranthene and benzo[k]fluoranthene.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 110, 116 and 129A.

PAH 2: Lab. 101, 103, 105, 116 and 129A.

Benzo[k]fluoranthene

Eleven participants analysed both extracts that had medium concentrations about 0.2 ng/m³. Two participants had both results closer than 10%, and two other laboratories measured concentrations not more than 20% off; laboratories 104 and 101, and 103 and 110. Two laboratories measured far too high concentrations. The results for this component and the previous one were not better than those for chrysene and benzo[a]anthracene in contrast to the results from the first part of this exercise where benzo[b]fluoranthene and benzo[k]fluoranthene obtained the largest number of the very best results. GC-methods may produce high results compared to HPLC-methods because of co-elution with benzo[b]fluoranthene and benzo[j]fluoranthene

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 104 and 110.

PAH 2: Lab. 101, 102, 103, 104, 105 and 110.

Benzo[a]pyrene

Thirteen laboratories returned results from both extracts. The concentrations of benzo[a]pyrene were about 0.4 and 0.2 ng/m³. Only laboratory 101 obtained both results less than 10% from the median. One of the two laboratories with strongly deviating results in the analysis of the previous compound had far too high results for this compound as well.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 110, 113, 129A and 131.

PAH 2: Lab. 101, 102, 103, 110, 116, 129A and 131.

Indeno[1,2,3-cd]pyrene

Twelve laboratories analysed both extracts, and three laboratories obtained results less than 10% from the median; laboratories 131, 110 and 129A. Three results from two laboratories were far too high and one result was about 50% too high. The concentrations indeno[1,2,3-cd]pyrene were about 0.3 and 0.4 ng/m³. In Central Europe much higher concentrations may be found (Table 13), but the concentrations are generally lower than this. The concentrations in northern parts of Europe are generally much lower.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 105, 109, 110, 113, 129A and 131.

PAH 2: Lab. 101, 102, 105, 109, 110, 113, 129A and 131.

Dibenzo[a,h]anthracene

Thirteen laboratories returned results for this compound. The median concentrations were quite low, about 0.05 ng/m³, but the results were good with little scatter except from four large outliers. Four laboratories returned both results within 10% from the median; laboratories 101, 131, 105 and 103. In addition to the four large outliers three single results were somewhat higher than 50%. One of the participants with a large deviating result had a too large concentration also in the first part while the other three laboratories obtained results within 20% from the expected. GC-methods may produce high results compared to HPLC-methods because of co-elution with dibenzo[a,c]anthracene.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 105, 113 and 131.

PAH 2: Lab. 101, 103, 105, 116, 129A and 131.

Benzo[ghi]perylene

The medians obtained were between 0.3 and 0.5 ng/m³. Thirteen participants analysed both samples. The concentrations were similar to the highest monthly concentration measured at Rörvik (Table 13) in year 2000. Four participants had both results within 10%; laboratories 131, 113, 101 and 103. Three laboratories had both results more than 50% from the median, all but one single result was <100% from the median.

Laboratories inside $\pm 20\%$ of the median:

PAH 1: Lab. 101, 103, 105, 107, 113, 129A and 131.

PAH 2: Lab. 101, 103, 105, 113, 116, 129A and 131.

Biphenyl and perylene

Only five and six laboratories analysed both samples for biphenyl and perylene respectively. There were three single results between 50% and 100% from the median found for biphenyl, the remaining concentrations being less than 50%. This is in contrast to perylene results where it is seen that one laboratory has two very large outliers, and one laboratory had one large deviating result. The concentrations for perylene were, however, very low 0.02-0.04 ng/m³ only. The biphenyl concentrations were higher, 1-5 ng/m³.

Benzo[e]pyrene

The benzo[e]pyrene median concentrations were about 0.3 to 0.4 ng/m³ that were measured by eight participants only. The results for benzo[e]pyrene are consistent in both samples and have systematic deviations from the median. Results reported by one laboratory were larger than 100% from the median, while those from two other laboratories were between 50% and 100%. The remaining results were mostly below thirty per cent, and results from three laboratories were better than 20%.

Laboratories inside $\pm 20\%$ of the median:

PAH 1 and PAH 2: Lab. 101, 129A and 131.

9. Conclusion

An international laboratory comparison was conducted in order to obtain information on the comparability of results from monitoring data of POPs in air.

The comparison was a two-step exercise:

Round 1: Analysis of a mixture of standards of known composition but with unknown concentrations.

Round 2: Analysis of two raw-extracts from filter and gas phase adsorbents after high volume air sampling.

Two groups of POPs were investigated during the exercise: Organochlorine compounds including pesticides, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

The organochlorine compounds analysed were:

p,p'-DDT, p,p'-DDE, γ -Chlordane, α -Chlordane, Hexachlorocyclohexane (HCH): γ -HCH and α -HCH, HCB, PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180.

The PAHs analysed were:

Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene, Biphenyl, Perylene and Benzo[e]pyrene.

Some laboratories analysed only one compound group.

Results from round 1 are reported as: concentration found in the sample (as pg/ μ l or ng/ μ l) and as deviation from expected value (in %).

The total number of laboratories involved was 21 of which 16 took part in round 1. The results from the first part show that all but one laboratory had at least one result not more than 20 % from the expected, for PAH and for the organochlorine compounds.

Seven laboratories had all, but 3–4 PAH results, better than 20% from the expected, and five laboratories had all except one organochlorine results better than 20%.

Six laboratories had no PAH results, and five laboratories no organochlorine results, more than 50% from the expected in the first part of the comparison.

Results from round 2 are reported as sample concentration found (as pg/m³ or ng/m³, assuming a sample volume of 500 m³) and as deviation from median (in %).

Eighteen laboratories took part in round 2. Four laboratories had more than twenty single results of PAH within 20% from the median, and two laboratories obtained a similar result for the organochlorine compounds.

The second round showed the importance of using an analytical method and instrumentation able to cope with possible interferences without loss of analyte even while working at low concentrations, while round 1 mainly was a calibration exercise.

In round 2, organochlorine compounds, three laboratories accounted for about 66% of the results deviating from the median with 50% or more. Three laboratories accounted for 53% of the PAH results deviating from the median with 50% or more.

The results give an indication of the laboratory accuracy that can be expected for POPs in air. In an actual monitoring situation the accuracy would also be influenced by sampling method (sampling time, flow, filter materials, sampler type), as well as the analytical precision.

10. References

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Annex 1

List of participants

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Annex 2

Methods

Overview of instrumentation used

PAH:

Lab no.	GC/FID	GC/MS	HPLC	TLC
101		X		
102			X	
103			X	
104		X		
105		X	X	
107		X		
108			X	
109	X		X	
110			X	
113			X	
116		X	X	
122				X
123	X			
129A		X		
129L		X		X
130		X		
131		X		

Chlorinated compounds:

Lab no.	GC/ECD	GC/MS
101		X
102	X	
103		X
104	X	
105	X	
108	X	
109	X	
110		X
113		X
115		X
116	X	
118	X	
120		X
121	X	
123	X	
129A	X	
129L		X
131		X

Lab 101

Method description PAH		Method description CI - POP	
<i>Gas-chromatography</i>		<i>Gas-chromatography</i>	
Column phase	DB 5 MS	Column phase	DB 5 MS
Length (m)	60 m	Length (m)	60 m
Internal diameter (mm)	0,25	Internal diameter (mm)	0,25
Film thickness (µm)	0,25	Film thickness (µm)	0,25
Type of injector	Splitless	Type of injector	Splitless
Injection volume (µl)	2	Injection volume (µl)	2
Injection temperature (°C)	270	Injection temperature (°C)	270
Detector		Detector	
Detector type	Agilent MSD	Detector type	Thermoquest Voyager MS
Detector temperature (°C)	280 °C	Detector temperature (°C)	260

Lab 102

PAHs: HPLC with programmed fluorescence detection (UV for Acenaftalen). Solvent replaced by acetonitrile.

Chlorinated compounds: GC/ECD on HT-8 and CP-SIL 19 columns.

Lab 103**PAHs:**

Each sample was diluted to 2 mL in i-octane, using half of that volume in the analysis.

Cleanup was by silica SPE using Waters cartridges on a Hamilton Microlab Workstation, with elution by dichloromethane and solvent exchange into 1mL of acetonitrile.

Instrumental analysis was by reverse-phase gradient HPLC-FLD using external standardisation. Multiple dilutions of up to 50X were necessary to bring the analyte levels into the usual calibration range of the method used for IADN. The optimum dilution range required was PAH dependent. The relevant vials were injected in triplicate to generate a measure of instrumental precision.

Detection limits were calculated from the estimated instrumental detection limit and converted to "atmospheric equivalent detection limits" using assumptions of the same conditions for the samples in question i.e sample split of 2, final vial volume of 1 mL, air volume nominally 500 m³.

Perylene is not uniquely determined in the MSC method, but (based on the results from EMEP Round 1 and other retention data) it is believed that this species probably co-elutes with benzo[b]fluoranthene and will produce a positive bias in the values reported if it is present in the ambient sample extracts provided.

Chlorinated compounds:

Each of the ampoules was accurately diluted to 2 mL in i-octane, with half of that volume being subjected to analysis.

Florisil column chromatography (60-100 mesh, calcined at 600°C and then deactivated with approximately 2% w/w water) was used to remove interferences and fractionate the sample into three eluates: F1 (eluted with hexane) contained most PCBs plus HCB, heptachlor, aldrin, p,p'-DDE, o,p'-DDT, mirex, photomirex along with t-nonachlor (partial) and p,p'-DDT (partial) and α -chlordane (minor contribution); F2 (eluted with 15% DCM/85% hexane) contained coplanar PCBs plus α -HCH, β -HCH, γ -HCH, oxychlordane, α -chlordane, γ -chlordane, o,p'-DDD, p,p'-DDD along with t-nonachlor (partial) and p,p'-DDT (partial); F3 (eluted with 60% DCM/40% hexane and then DCM alone) contained dieldrin, endrin, heptachlor epoxide, methoxychlor, α -endosulfan, β -endosulfan and δ -HCH. The final extract fractions were concentrated by Turbovap nitrogen blowdown, accurately adjusted to a volume of 1 cm³ and then transferred to autosampler vials fitted with PTFE septa to eliminate silicone interferences. Analysis was performed using a HP5890 GC equipped with dual ⁶³Ni ECDs and dual heated splitless/split injection ports. A 60 m x 0.25 mm i.d. (d_f = 0.25 μ m) DB5 column (J&W Scientific) was used for primary analysis (80°C for 2 min, 15°C/min to 160°C then 2.5°C/min to 265°C and hold for 20 min). A 30 m x 0.25 mm i.d. (d_f = 0.25 μ m) DB-17 column operated under the same temperature program was used to provide confirmatory analysis and/or enhanced separation for certain of the co-elutions on the DB5 column. Splitless-mode injections of 1 μ L (purge on at 2.0min) were made separately onto both columns using an autosampler/autoinjector system (HP 7673 series). Ultra high purity (UHP) He (Praxair) was used as carrier gas in constant-flow mode, with initial column flow-rates of approximately 1.3 mL/min. Injection port and detector were held at 200°C and 350°C, respectively. ECD make-up gas was UHP N₂ (Praxair) at 70 mL/min. External standard calibrated methods were used for quantitation. Note that in the analytical sequence, frequent "bracketing" of the samples with injections of standards was employed to track and correct for response drift.

Lab 104

PAHs: Sample injected on Hewlett Packard 6890 GC with 5973 MSD. Column: J&W DB-5MS 30 x 0.25 μ m.

Chlorinated compounds: The samples were cleaned up and fractionated on a 8g Florisil column (wet packed in hexane). The hexane fraction included PCBs, most HCB and pp-DDE while the 15/85 hexane/DCM fraction included HCHs, chlordanes and pp-DDT. Samples were reduced to 0.5 mL for injection on a GC equipped with an ECD. Detection limits are roughly 0.1 pg/m³ (for PCB 28) or lower.

Lab 105**First Round of the EMEP POP Laboratory Comparison****Sample:** PAH U No. 47 (NILU, Norway)**Remark:**

Lifetime of multiplier is over and, therefore, not all tuning parameters are fulfilled. Detector sensitivity is lower.

GC-MS Equipment: GC Model HP 6890 with Mass Selective Detector HP 5972A, Autosampler HP 6890, HP Enhanced ChemStation G1701AA Version A.03.00 (Hewlett-Packard, FRG).

GC Column: DB-5ms, 58.5 m x 0.25 mm x 0.25 µm film thickness (J&W, USA)

Carrier Gas: Helium, purity 99.9995 %, constant flow 1.5 ml/min

Temperatures: Injector 280°C
Interface 280°C

Temperature programme: 80°C 1 min // 15°C/min to 180°C // 5°C/min to 310°C // 310°C 10 min

Injected Volume: 1 µl splitless

Sample preparation: 200 µl aliquot of PAH U No. 47 solution, 50 µl of internal standard (p-Terphenyl) and 750 µl toluene was added

Standards: Supelprime-HC PAH-Mix (SUPELCO, USA), solution in dichloromethane:benzene (50:50)
Biphenyl Pestanal (Riedel-de Haën, FRG),
Benzo[e]pyrene (Dr. Ehrenstorfer, FRG), Perylene sublimed (Sigma Aldrich, FRG)
Biphenyl, Benzo[e]pyrene and Perylene solutions in acetonitrile prepared by weighing and dilution.

Calibration: Six-level calibration in the range from 0.40 to 10.0 ng/µl

Detection: Mass Selective Detection in Selected Ion Monitoring Mode

Selected Ion Monitoring			
	Target m/z	Qualifier m/z	
Terphenyl I.S.	230	228	215
Naphthalene	128	129	126
Acenaphthylene	152	153	150
Acenaphthene	154	153	155
Fluorene	166	167	164
Phenanthrene	178	179	176
Anthracene	178	179	176
Fluoranthene	202	203	200
Pyrene	202	203	200
Benzo[a]anthracene	228	229	226
Chrysene	228	229	226
Benzo[b]fluoranthene	252	253	250
Benzo[k]fluoranthene	252	253	250
Benzo[a]pyrene	252	253	250
Indeno[1,2,3-cd]pyrene	276	277	274
Dibenzo[a,h]anthracene	278	279	276
Benzo[ghi]perylene	276	277	274
Biphenyl	154	152	155
Perylene	252	253	250
Benzo[e]pyrene	252	253	250

First Round of the EMEP POP Laboratory Comparison

HPLC Determination with UV-VIS Diode-Array Detection:

Remark:

Retention times and, also, peak shapes were affected by the presence of i-octane. Other solvents as e.g., methanol or acetonitrile, would be compatible with HPLC determination.

At standard conditions, fluorescence detection would be used in combination with UV-VIS diode-array detection (for acenaphthylene and chromatographically unresolved peaks of benzo[b]fluoranthene and perylene). Recently, our fluorescence detector (HP 1046A) is out of work - waiting for service.

HPLC Equipment: Model HP 1050 quaternary pump, programmable autosampler, and diode-array detector, model HP 1100 thermostatted column compartment, HP ChemStation Rev. A.07.01 for LCD 3D Systems (all Hewlett-Packard, FRG).

HPLC Column: Narrow-bore Supelcosil LC PAH, 250 x 2.1 mm I.D. (Supelco, USA) packed with 5- μ m octadecyl phase Guard column – SecurityGuard System with C18 cartridges (Phenomenex, USA)

Column Temperature: 20 \pm 0.5°C

Injected Volume: 3.6 μ l

Standards: PAH-Mix 45 (Dr. Ehrenstorfer, FRG), solution in acetonitrile
Biphenyl Pestanal (Riedel-de Haën, FRG),
Biphenyl solutions in acetonitrile prepared by weighing and dilution.

Calibration: Six-level calibration in the range from 0.60 to 10.0 ng/µl

Reagents: Individual polycyclic aromatic hydrocarbons (Supelco, USA)
Acetonitrile, HPLC gradient grade (J. T. Baker, The Netherlands)
Water from Millipore Q185

Gradient elution: Component A: acetonitrile/water 50:50
Component B: acetonitrile
Flow: 0.35 ml/min

Time (min)	% B
0	0
5	0
30	100
47	100

Detection: Signals at 225 nm (20 nm bandwidth), 245 (15), 280 (20), 297 (26), and 425 nm (30) were used for detection as shown in table with results. Reference wavelength 530 nm (50 nm) Spectra taken from 210 to 450 nm

First Round of the EMEP POP Laboratory Comparison

Sample: *Cl-POP U No. 5 (NILU, Norway)*

GC-ECD Equipment: GC Model HP 5890 Series II with Electron Capture Detector, Autosampler HP 7673, HP GC ChemStation Rev A.03.03 (Hewlett-Packard, FRG).

GC Column: Quadrex 007-5, 40m x 0.18mm x 0.25µm film thickness (Quadrex, USA)

Carrier Gas: Helium, purity 99.9995 %, constant flow 0.3 ml/min

Make-up gas: Nitrogen, purity 99.998 %, flow 50 ml/min

Temperatures: Injector 280°C
Detector 310°C

Temperature programme: 80°C 1 min // 20°C/min to 160°C // 3°C/min to 300°C // 300°C 5 min

Injected Volume:	1 µl splitless
Sample preparation:	400 µl aliquot of Cl-POP U No. 5 solution, 50 µl of internal standard (PCB 155) and 550 µl cyclohexane was added
Standards:	PCB-Mix I (Dr.Ehrenstorfer, FRG), solution in cyclohexane PCB 118 (ACU Standards) in isooctane EPA Method 8270A – Chlorinated pesticides (Absolute Standards, USA) Hexachlorobenzene (SUPELCO, USA) in acetone Gama-Chlordane and alfa-Chlordane was calibrated using Cl-POP Standard Nr. 54 (NILU, Norway)
Calibration:	Six-level calibration in the range from 10 to 4000 pg/µl

Second Round of the EMEP POP Laboratory Comparison

PAHs Method Description

Samples: PAH 1 No. 33, PAH 2 No. 4

Sample clean-up:	column chromatography on activated silica (activation 16 hours, 150°C) fraction 15 ml hexane discarded, fraction 15 ml dichloromethane was concentrated and internal standard (p-Terphenyl) was added
GC-MS Equipment:	GC Model HP 6890 with Mass Selective Detector HP 5972A, Autosampler HP 6890, HP Enhanced ChemStation G1701AA Version A.03.00 (Hewlett-Packard, FRG).
GC Column:	DB-5ms, 58 m x 0.25 mm x 0.25 µm film thickness (J&W, USA)
Carrier Gas:	Helium, purity 99.9995 %, constant flow 1.5 ml/min
Temperatures:	Injector 280°C Interface 280°C
Temperature program:	80°C 1 min // 15°C/min to 180°C // 5°C/min to 310°C // 310°C 10 min
Injected Volume:	1 µl splitless
Standards:	Supelpreme-HC PAH-Mix (SUPELCO, USA), solution in dichloromethane:benzene (50:50)
Calibration:	Nine-level calibration in the range from 0.001 to 10.0 ng/µl

Detection: Mass Selective Detection in Selected Ion Monitoring Mode

Selected Ion Monitoring			
	Target m/z	Qualifier m/z	
Terphenyl I.S.	230	228	215
Naphthalene	128	129	126
Acenaphthylene	152	153	150
Acenaphthene	154	153	155
Fluorene	166	167	164
Phenanthrene	178	179	176
Anthracene	178	179	176
Fluoranthene	202	203	200
Pyrene	202	203	200
Benzo[a]anthracene	228	229	226
Chrysene	228	229	226
Benzo[b]fluoranthene	252	253	250
Benzo[k]fluoranthene	252	253	250
Benzo[a]pyrene	252	253	250
Indeno[1,2,3-cd]pyrene	276	277	274
Dibenzo[a,h]anthracene	278	279	276
Benzo[ghi]perylene	276	277	274

CI-POP Method Description

Samples: CI-POP 1 No. 54, CI-POP 2 No. 8

Sample clean-up: column chromatography on activated silica (activation 16 hours, 150°C) modified 44w% H₂SO₄, collected fraction 25 ml hexane:dichloromethane (95:5) was concentrated and internal standard (PCB 155) was added

GC-ECD Equipment: GC Model HP 5890 Series II with Electron Capture Detector, Autosampler HP 7673, HP GC ChemStation Rev A.03.03 (Hewlett-Packard, FRG).

GC Column: Quadrex 007-5, 40m x 0.18mm x 0.25µm film thickness (Quadrex, USA)

Carrier Gas: Helium, purity 99.9995 %, constant flow 0.3 ml/min

Make-up gas: Nitrogen, purity 99.998 %, flow 54 ml/min

Temperatures: Injector 280°C
Detector 310°C

Temperature program: 80°C 1 min // 20°C/min to 160°C // 3°C/min to 300°C // 300°C 5 min

Injected Volume: 1 µl splitless

Standards: PCB-Mix 3 (Dr.Ehrenstorfer, FRG), solution in isooctane
Pesticide-Mix 13 (Dr.Ehrenstorfer, FRG), solution in cyclohexane

Calibration: Eight-level calibration in the range from 1 to 4000 pg/ μ l

Lab 107

PAHs round 1:

Isotopic dilution for each compound / GC-MS

Standard: SRM 2260

Column: (5% - Phenyl) – methylpolysiloxane, 60 m, 0.25 mm, 0.25 μ m

Program temperature: 50°C –2 min
5°C / min \rightarrow 290 °C
290 °C – 30 min

PAHs round 2:

Standard: SRM 2260

Column: (5% - Phenyl) – methylpolysiloxane, 60 m, 0.25 mm, 0.25 μ m

Program temperature: 50°C –2 :min
5°C / min \rightarrow 290 °C
290 °C – 30 min

Ampoule 13:

The extract was analysed by Isotopic Dilution Gas chromatography / Mass Spectrometry (DI GC/MS).

Ampoule 13:

The ampoule was purified on silica and alumina column and eluted with dichloromethane in hexane (20%). The extract was analysed by DI GC/MS.

Lab 108

PAHs:

The solution is analysed by high performance liquid chromatography. The identification and the quantification of the PAH is made with fluorescence and UV detector.

Column: Vydac, length 150mm, internal diameter 4.6mm
Gradient elution (H₂O/CH₃CN) constant flow (1ml/min)
Wavelength programming for the excitation and emission wavelength

UV detection : only for Acenaphtylene.

Limit of detection : 10µg/l.

Uncertainty: around 10%.

Notice that we have co-elution of Benzo (b) fluoranthène and perylene

Chlorinated compounds:

Determination of Organochloro Pesticides :

The solution is analysed by capillary gas chromatography.

GC conditions:

Separation column: Rtx-CLP column, length 60 m, internal diameter 0.25mm, filmthickness 0.25µm.

Oven temperature programmable

Splitless injection

Carrier gas : hydrogen 1ml/min.

Detector : ECD. T = 300°C.

Limit of detection : 5µg/l.

Uncertainty: around 10%

Determination of Polychlorinated biphenyls (PCB) :

The solution is analysed by capillary gas chromatography.

GC conditions:

Separation column: XTI5 (5% phényl)+HT8 (8%phényl) columns, length 50 m, internal diameter 0.25mm, filmthickness 0.25µm.

Oven temperature programmable

Splitless injection

Carrier gas : hydrogen 1ml/min.

Detector : electron capture detector (ECD). T = 300°C.

The PCB are quantified using an internal standard added to the extract.

Limit of detection : 5µg/l.

Uncertainty: around 10%

Lab 109

PAHs:

<i>Compound</i>	<i>Detection</i>
Naphtalene	GC/FID
Acenaphthylene	GC/FID
Acenaphthene	GC/FID
Fluorene	GC/FID
Phenanthrene	GC/FID
Anthracene	HPLC-fluorimétrie
Fluoranthene	GC/FID
Pyrene	GC/FID
Benzo[a]anthracene	HPLC-fluorimétrie
Chrysene	GC/FID

Benzo[b]fluoranthene	GC/FID
Benzo[k]fluoranthene	GC/FID
Benzo[a]pyrene	HPLC-fluorimétrie
Indeno[1,2,3-cd]pyrene	GC/FID
Dibenzo[a,h]anthracene	HPLC-fluorimétrie
Benzo[ghi]perylene	GC/FID
Biphenyl	GC/FID
Perylene	GC/FID
Benzo[e]pyrene	HPLC-fluorimétrie

Uncertainty: 15 %

Chlorinated compounds:

GC/ECD on HP-5 and CP-SIL 19CB.

Uncertainty: 15 %

Impurity overcoat α -chlordane on HP-5 and on CP-SIL 19CB α -chlordane is overcoated by p,p'-DDE.

Lab 110

PAHs:

The samples were evaporated to eliminate cyclohexane and the residue was dissolved in acetonitrile. The extracts obtained were analysed by HPLC with fluorescence detector.

Chlorinated compounds:

GC/MS

Lab 113

Brief description of the method used for PAH:

1) Cleanup

None.

3 different dilutions in acetonitrile/water were prepared: 1:50, 1:100, 1:500.

2) Calibration

Seven point calibration with external standards in the range 0,2- 10 pg/ μ l using a linear calibration function.

3) Analysis

High Pressure Liquid Chromatography

HPLC System Hewlett Packard HP1100 with:

- Binary Gradient Pump G1312A;
- Autosampler G1313A;
- Vacuum-Degasser G1322A,
- Column Thermostat G1316A;

- Fluoreszenzdetektor G1321A;
- Chromatography Software (HP ChemStation for LC 3D Rev. A.08.03 [847]);
- HPLC column: SEPSERV 250 mm * 2 mm Ultrasep ES PAK 6 μm ;
- Precolumn: 10 mm * 2 mm Ultrasep ES PAK 6 μm .

Injection volume: 15 μl

Gradient:

<i>Time in min</i>	<i>% Acetonitril</i>	<i>% Water</i>
0 -5	55	45
5- 30	55 to 100	45 auf 0
30 - 44	100	0
44,01	100 - 55	0 - 45
44,01 - 60	55	45

Wavelength programme:

<i>Time in min</i>	<i>Excitation</i>	<i>Emission</i>	<i>PMT</i>
0,00	275	335	16
13,30	260	369	16
17,40	235	460	16
19,55	250	390	16
22,40	260	400	16
29,00	260	450	15
31,30	290	420	16
34,50	290	420	16
37,80	250	500	16
40,00	270	335	16

4) Limit of detection:

The limits of detection are roughly estimated for pure standard solutions from the calibration functions.

The estimate for Indeno(1,2,3-cd)pyrene is about 0,3 $\text{pg}/\mu\text{l}$ and for all other PAH about 0,1 $\text{pg}/\mu\text{l}$.

5) Uncertainty

From our routinely performed analysis of PAH in rainwater we estimate the uncertainty at the limit of determination to about 40% and in the middle of the calibration range to about 20%.

Brief description of the method used for chlorinated POPs

1) Cleanup

A spatula of sodium sulphate is added on top of a commercially available silica gel column (Chromabond/Mackerey-Nagel) containing 500 mg of silica gel. The column is conditioned by elution with 3 ml acetone (3x), vacuum drying for 5 minutes, elution with 3 ml solvent mixture (70% n-hexane/30% toluene v/v).

500 µl of the extract (sample) and the internal standards δ-HCH and PCB 209 (10pg/µl) are passed through the conditioned silica gel column. Followed by elution with 7 X 2 ml solvent mixture.

The eluat is collected in a 15 ml centrifuge tube.

The eluat is concentrated at 35° C in a Turbo-Vap Evaporator to about 150 µl.

2) Calibration

Six point calibration in the range 0,5-10 pg/µl with two internal standards using a second order calibration function.

δ -HCH (IS II) used as internal standard for HCB, α-HCH, γ-HCH, p,p'-DDE and PCB 101.

PCB 209 (IS I) used for p,p'-DDT, PCB 118, PCB 138, PCB 153 and PCB 180.

3) Analysis

Gas chromatography

Instrument:	HP 6890 Series	Agilent Technologies
Column:	RTX-CLP	Restek
		30 m x 0,25 mm, 0,25 µm
Carrier gas:	Helium	
Pressure:	1,33 bar	
Flow rate:	1,7 ml/min (constant)	

Oven programme:

Start temperature:	115 °C	
Time (isotherm):	2 min	
Heating rate 1:	4 °C/min	Ramp temperature 1: 260 °C
Time(isotherm):	1 min	
Heating rate 2:	30 °C/min	Ramp temperature 2: 320 °C
Time (isotherm):	6 min	

Mass spectrometry:

Instrument:	MSD 5973	Agilent Technologies
Ionisation technique:	NCI	
Reactant gas:	Methane	
Source pressure:	2,4 x 10 ⁻⁴ torr	
Ion source temperature:	120°C	
Electron energy:	179.4 eV	
Emission current:	49,4 µA	
Multiplier voltage:	1895 V	
Acquisition mode:	Selected ion monitoring (SIM)	

SIM-program:

Function	Time window (min)	Mass (amu)		Compound
		Quantification	Qualifier	
1	10,00-15,30	71	255	α -HCH γ -HCH HCB
		71	255	
		283,9	281,9	
2	15,30-19,00	71	255	δ -HCH PCB 28 PCB 52
		221	257	
		292	257	
3	19,00-24,75	325,9	327,9	PCB 101 p, p'-DDE PCB 118
		318	316	
		325,9	327,9	
4	24,75-28,00	359,8	361,8	PCB 153 PCB 138 p, p'-DDT
		359,8	361,8	
		71	248	
5	28,00-36,00	393,8	395,8	PCB 180 PCB 209
		499,7	497,7	

4) Limits of determination and detection

The limit of determination and the limit of detection are estimated for pure standard solutions (using 500 μ l) from the calibration functions.

Compound	Limit of determination in μ g/ μ l	Limit of detection in μ g/ μ l
P, p' DDT	0,5	0,17
P, p' DDE	0,5	0,17
γ -HCH	0,1	0,03
HCB	0,03	0,01
α -HCH	0,1	0,03
PCB 28	5	1,7
PCB 52	5	1,7
PCB 101	0,1	0,3
PCB 118	0,05	0,02
PCB 138	0,05	0,02
PCB 153	0,03	0,01
PCB 180	0,05	0,02

5) Uncertainty

From our routinely performed analysis of chlorinated compounds in human blood we estimate the uncertainty at the limit of determination to about 40-50% and in the middle of the calibration range to about 25%.

Lab 115**Chlorinated compounds:**

The following procedure has been applied to the samples.

- an internal standard of 2.5 ng PCB 6, PCB 65, PCB 207 and e-HCH was added
- two subsamples of 25 perc. were analyzed
- a HPLC fractionation had been performed with the subsamples which led to two fractions :
 1. fraction: PCBs, HCB, pp-DDE
 2. fraction: Chlordanes, HCHs, pp-DDT
- the samples were measured using GC-MS in the MSMS mode. (CP-SIL 8 column, varian saturn 2000 GC-MS)

Detection limits are between 500 fg-1 pg for the target compounds. The analytical precision is in the order of 15 perc. standard deviation. pp-DDT was below the detection limit.

Lab 116**PAHs**

Method 1: HPLC in adaption to ISO/CD 16362

No clean-up

Calibration one point 50 pg/ μ l

Limits of determination:	ng/m ³
Naphthalene, Acenaphthene	0,04
Acenaphthylene	0,08
all others each	0,02

Uncertainty: +/- 25%

Method 2: GC-MS in adaption to DIN ISO 12884, SIM-Mode

No clean-up

Calibration 3-point 100 pg/ μ l to 10 ng/ μ l

Limits of determination:	ng/m ³
all components	0,04

Uncertainty: +/- 25%

Method 1 + 2 comparatively measured against NIST SRM 1647d

Chlorinated compounds:

Method: GC-ECD two-column-technique

in adaption of DIN 38409-F2

no clean-up

Calibration 6-point 10 - 100 pg/ μ l

Limits of determination:	pg/m ³
all components	10

Uncertainty: +/- 25%

Lab 118**Chlorinated compounds:**

In round 1 the solution was diluted with internal standard (TCN) and analysed by GC-ECD using DB5 and DB1701 (JW-Scientific), both 60m, 0.25 mm i.d., 0.25 μ m film.

The estimated uncertainty is close to 10%.

In round 2 the samples were cleaned up with conc. sulphuric acid, evaporated about 50% and redissolved in isooctane containing TCN (ISTD).

Lab 120**Chlorinated compounds:**

GC/MS analysis (round 1 only).

Using working standards at 0.06/0.1 μ g/ml and 0.03/0.05 μ g/ml for the chlorinated pesticides and CB congeners respectively, with SIR detection.

The results are described as very crude, because of instrument difficulties.

Lab 121**Chlorinated compounds:**

Method: GC

Detector: ECD

Column: PE 608, length - 30 m, ID - 0,53 mm.

Lab 122**PAHs:****Method of analysis round 1**

0.2 mL of the "unknown" mixture was fractionated on a thin layer of Al_2O_3 with solvent mixtures of petroleum ether: diethyl ether in the ratio 40:1. PAHs were divided into 4 fractions. Each fraction was eluted by 50 mL of n-hexane. Chromatographic eluates were evaporated to 10 mL. Different PAHs were determined in separate fractions with different R_f . Identification and quantity determination of PAHs was performed by the spectrofluorescent method with luminescent spectrometer CДЛI-2 "JIOMO" using the method of standard addition.

Quantitative analysis of BP was performed by the spectrofluorescent method in liquid nitrogen at 77K. Excitation of BP was performed at $\lambda=298$ nm and fluorescence was recorded at $\lambda=403$ nm. The fluorescent analysis was performed by a diffraction spectrometer (DФC-12 "JIOMO"). The sensitivity of the method: 0.1 ng mL.

The characteristics of analytical method are presented in Table A1.1.

Table A1.1: Characteristics of analytical method.

PAHs Compound	$\lambda_{exc.}$, nm	$\lambda_{fl.}$, nm	Detection limit, $\mu\text{g.mL}$
1. Phenanthrene	255	347	0.1
2. Pyrene	330	372	0.01
3. Chrysene	300	362	0.01
4. Benz(a)Anthracene	280	385	0.1
5. Benzo(a)pyrene	298	403	0.0001
6. Benz(g,h,i)Perylene	300	420	0.1
7. Dibenzo(a,h)Anthracene	300	394	0.01

Method of analysis round 2, B(a)P only

0.2 mL of each extract was fractionated on a thin layer of Al_2O_3 with solvent mixtures of hexene: benzene 6:1. All compounds were divided into 3 fractions. Fraction of BaP was eluted by 50 mL of n-hexane. Chromatographic eluates of BaP fraction were evaporated to 5 mL. Quantitative analysis of BaP was performed by the spectrofluorescent method in liquid nitrogen at 77K using the method of standard addition. Excitation of BP was performed at $\lambda=360$ nm and fluorescence was recorded at $\lambda=403$ nm. The fluorescent analysis was performed by a diffraction spectrometer (ДФС-12 “ЛЮМО”). The sensitivity of the method: 0.1 ng mL.

Lab 123

PAHs

Instrument: Gas Chromatograph HP 5890.
 Column: Supelco PTE-5 30 m x 0.25 mm, 0.25 μm
 Carrier: Hydrogen 1ml/min (constant flow)
 Make up gas: Nitrogen 35 ml/min
 Hydrogen: 30 ml/min
 Air: 360 ml/min
 Injector: Splitless at 280°C
 Detector: FID at 325°C
 Temperature program: 70°C, 1 min
 8°/min
 310°C, 3 min
 Calibration standard: NILU solution

Chlorinated compounds:

Instrument: Gas Chromatograph HP 5890.
 Column: Supelco PTE-5 30 m x 0.25 mm, 0.25 μm
 Carrier: Hydrogen 1 ml/min (constant flow)
 Make up gas: Nitrogen 55 ml/min
 Injector: Splitless at 280°C
 Detector: ECD at 300°C

Temperature program: 120°C, 1 min
30°/min to 180°C
2°/min to 220°C
25°/min to 300°C
300°C, 8 min
Calibration standard: NILU solution

Lab 129A

PAHs: Round 1

The vials were opened and the content was transferred to screw capped vials and weighed. Sub-samples of each solution were spiked with QS internal standards (1000 ng each of D8-naphthalene, D8-acenaphthylene, D10-acenaphthene, D10-anthracene, D10-pyrene, D12-benzo(b)fluoranthene, D14-dibenzo(ah)anthracene), after the addition of RS standard (1000 ng of each of D10-fluorene, D12-chrysene and D12-benzo(ghi)perylene) the 1 ml sample (cleaned up by column chromatography if necessary) was measured by GC/MSD for PAH after the addition of a syringe standard (1000 ng of each of D10-fluoranthene and D12-benzo(a)pyrene)

Measurements were achieved using a HP 5970 GC/MS equipped with a 60m ZB5 0.2 µm film capillary column. The MS was operated in SIM mode.

GC conditions:

Injector temp	280°C
Initial temp	60°C for 0.5 min
First ramp	20°C/min to 240°C
Second ramp	3.5°C/min to 280°C
Third ramp	5°C/min to 300°C
Final temp	300°C for 24 min
Interface temp	275°C

PAHs round 2:

As described above, but the whole extract and clean-up were used:

Each extract was subjected to a normal phase column chromatographic cleanup using alumina and silica. The collected PAH fraction was then concentrated and spiked with a further mixture containing deuterated benzo(a)pyrene and fluoranthene to facilitate measurement of recoveries of the internal standards used for quantitation.

The total amount of each PAH was measured in the clean samples using isotope dilution GC/MS.

Chlorinated compounds:

Round 1

The vials were opened and the content was transferred to screw capped vials and weighed. Sub-samples of each solution were spiked with QS internal standards

(approximately 100 ng each of ¹³C-labelled hexachlorbenzene, PCB-28, p,p'-DDE, DDT, PCB-180)

Measurements were achieved using a HP 5970 GC/MS equipped with a 60m ZB5 0.2µm film capillary column. The MS was operated in SIM mode.

GC conditions:

Injector temp	300°C
Initial temp	60°C for 10 min
First ramp	10°C/min to 180°C
Second ramp	5°C/min to 240°C
Third ramp	8°C/min to 280°C
Final temp	280°C for 12 min
Interface temp	280°C

Round 2

As above, but the whole extract was used.

Lab 129L

PAHs: Round 1 only

The unknown EMEP PAH solution was analysed on HPLC and GC-MS, and quantified using a set of calibration standards made up from the known EMEP solution and using Lancasters calibration standards. The standards used by Lancaster for HPLC quantification and GC-MS quantification were bought at different times, and prepared by different people. For the HPLC analysis two dilutions of the unknown solution were prepared, dilution A was run in duplicate and dilution B in triplicate. A single dilution was run for GC-MS in triplicate.

Chlorinated compounds: Round 1 only

Two separate dilutions (A and B) of the EMEP unknown solution were analysed in duplicate using GC-MS, and quantified using the known EMEP solution and Lancasters calibration standards.

Lab 130

PAHs

Varian 3400 GC equipped with Split/Splitless injector operated at 266⁰. Column Supelco PTE-5 30m, 0.32mm id, 0.25µm film. Carrier gas hydrogen, 1ml/min measured at 210⁰. Column temperature was linearly programmed from 111⁰ to 290⁰ at 4.3⁰/min. Detector FID 310⁰.

Confirmation on:

Ion Trap Detector ITD-705 Finnigan was used with Varian 3400 GC equipped with Split/Splitless injector operated at 266⁰. Column Supelco PTE-5 30m, 0.25mm id, 0.25µm film, inserted directly in Ion Trap via transfer line at 240⁰. Carrier gas hydrogen, 1ml/min measured at 210⁰. Ion manifold and exit nozzle temperatures of 240⁰ were used. Column temperature was linearly programmed

from 60⁰ to 285⁰ at 4.3⁰/min. Scan range was 39-333 Daltons, 1 scan/second (5 micro scans were averaged). Tuning parameters were: 0,50,50,100; AGC on, Background mass 33. Version 3 of ITDS software was used.

Lab 131

PAHs: Round 2

To each extract was added an internal standard containing D10-2-methylnaphthalene, D10-acenaphthene, D10-anthracene, D10-pyrene, D12-benz(a)anthracene, D12-benzo(e)pyrene and D12-benzo(ghi)perylene.

The extract was cleaned up, first using liquid/liquid partitioning between cyclohexane and dimethyl formamide-water.

Secondly the sample was subjected to a normal phase column chromatographic clean-up using silica.

After pre-concentration to about 100µl a recovery standard containing D8-biphenyl, D10-fluoranthene and D12-perylene was added before quantification using HP 5973 GC/MS.

Gas chromatography

Instrument:	HP 6890 Series	Agilent
Column:	CP-SIL 8CB	Varian
		25 m x 0.25 mm, 0.12 µm
Carrier gas:	Helium	
Pressure:	12.6 psi	

1µl sample was injected splitless.

Temperature programme:

Start temperature:	50°C	
Time (isotherm):	1 min	
Heating rate 1:	20°C/min	Ramp temperature 1: 100°C
Heating rate 2:	5°C/min	Ramp temperature 2: 300°C
Time (isotherm):	3.5 min	
Injector temperature:	300°C	
Interface temperature:	310°C	

The MS was operated in SIM mode recording the molecular mass of the PAHs measured.

Uncertainty: +/- 25%
Limits of detection (S/N 3:1): 2-10 pg/m³

Chlorinated compounds: Round 2

To each extract was added an internal standard containing ¹³C labeled α-HCH, HCB, PCB-28, PCB-52, PCB-101, PCB-118, PCB-153, PCB-180, p,p'-DDE, p,p'-DDT and 13C-6D-γ-HCH.

The extracts were treated with concentrated sulphuric acid to oxidize non-persistent compounds before normal phase column chromatographic clean-up using silica.

After pre-concentration to about 100 μ l a recovery standard containing tetrachloronaphtalene.

The HCHs and the chlordanes were analysed using a HP 5989 "ENGINE" GC/MS-system and negative ion chemical ionization.

The column used was a 25m x 0.2mm 0.11 μ m Ultra-2 from J&W.

1 μ l sample was injected splitless.

Uncertainty: +/- 25%

Limits of detection (S/N 3:1): 0.05 pg/m³

DDE and DDT were analysed using a VG AutoSpec with electron impact ionization and mass resolution 10.000.

The column used was a 25m x 0.2mm 0.33 μ m HP-1 from J&W.

1 μ l sample was injected splitless.

Uncertainty: +/- 25%

Limits of detection (S/N 3:1): 0.05 pg/m³

The PCBs were analysed using a VG AutoSpec with electron impact ionization and mass resolution 10.000.

The column used was a 50m x 0.22mm 0.11 μ m HT-8 from SGE.

1 μ l sample was injected splitless.

Uncertainty: +/- 25%

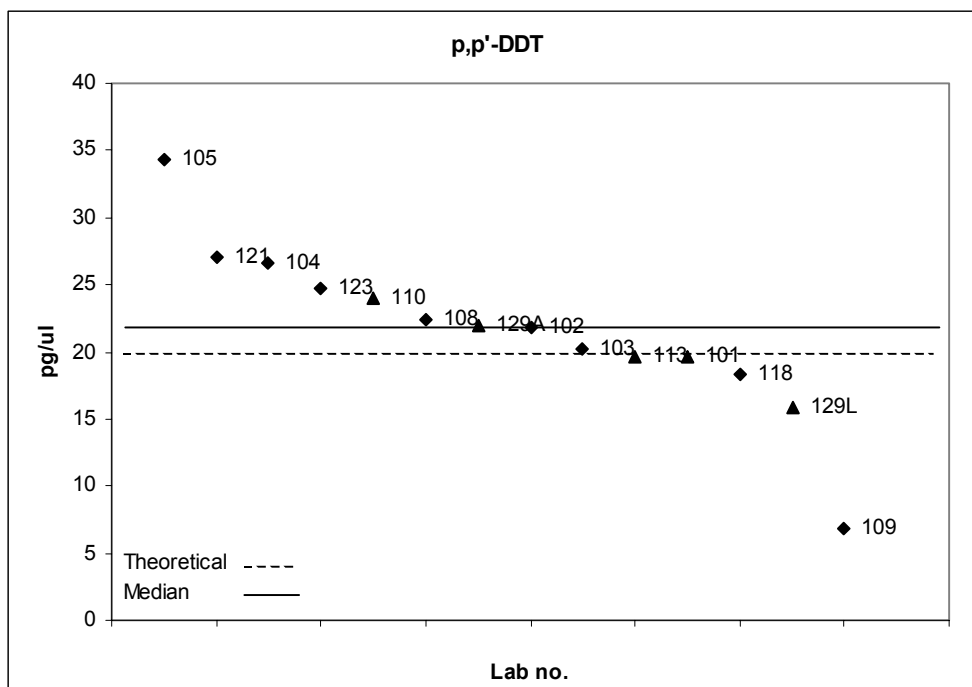
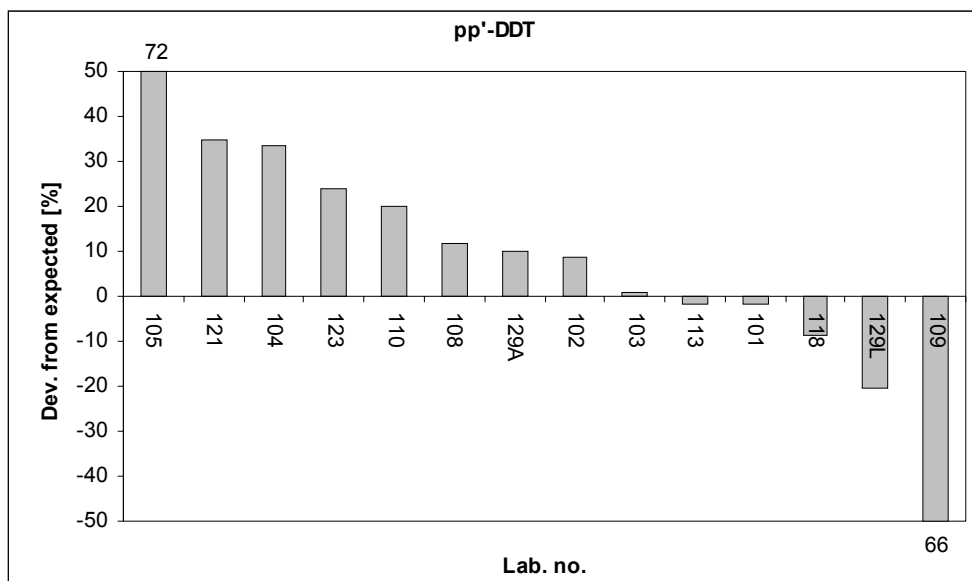
Limits of detection (S/N 3:1): 0.05 pg/m³

Annex 3

Organochlorine compounds, round 1

On the following pages the results from round 1 are shown graphically. The data from each compound is shown as deviation from expected value (upper graph) and as concentration found in the sample (lower graph).

◆	GC/ECD
▲	GC/MS



Results obtained by each laboratory.

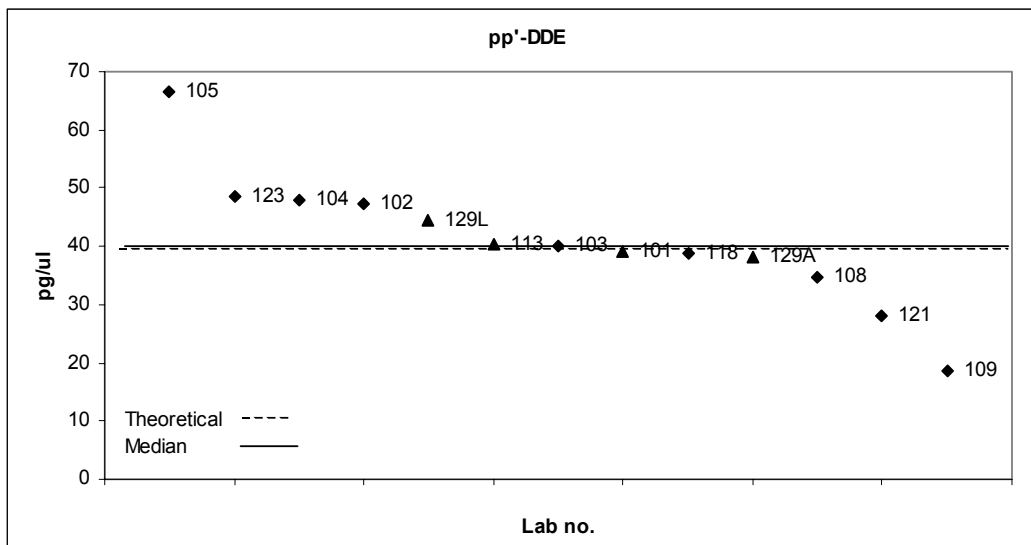
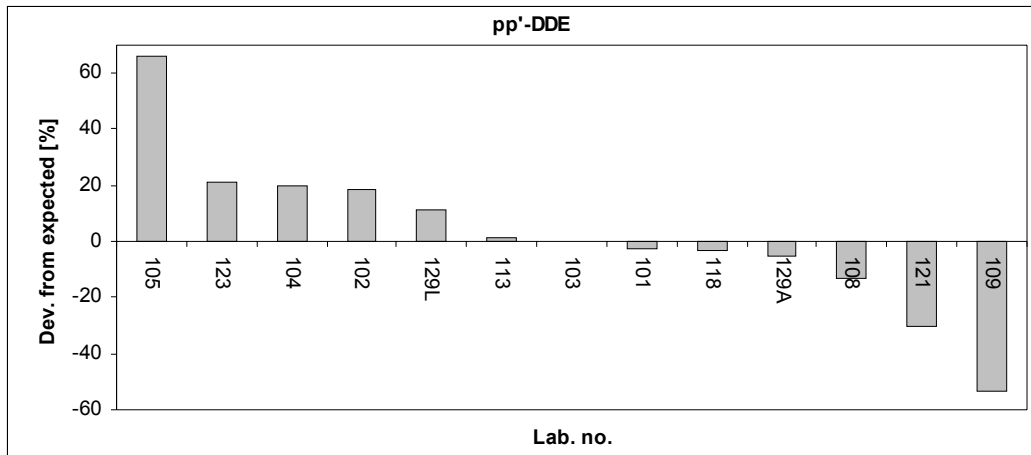
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound:	pp'-DDT
Theoretical value:	20,0
Unit:	pg/ul
Number of laboratories:	14
Aritm. Mean	21,7
Median	21,9

Lab no.	pg/ul	Lab no.	pg/ul
105	34,4	102	21,8
121	27,0	103	20,2
104	26,7	113	19,7
123	24,7	101	19,6
110	24,0	118	18,3
108	22,3	129L	15,9
129A	22,0	109	6,8*

*Not used for determination of mean



Results obtained by each laboratory.

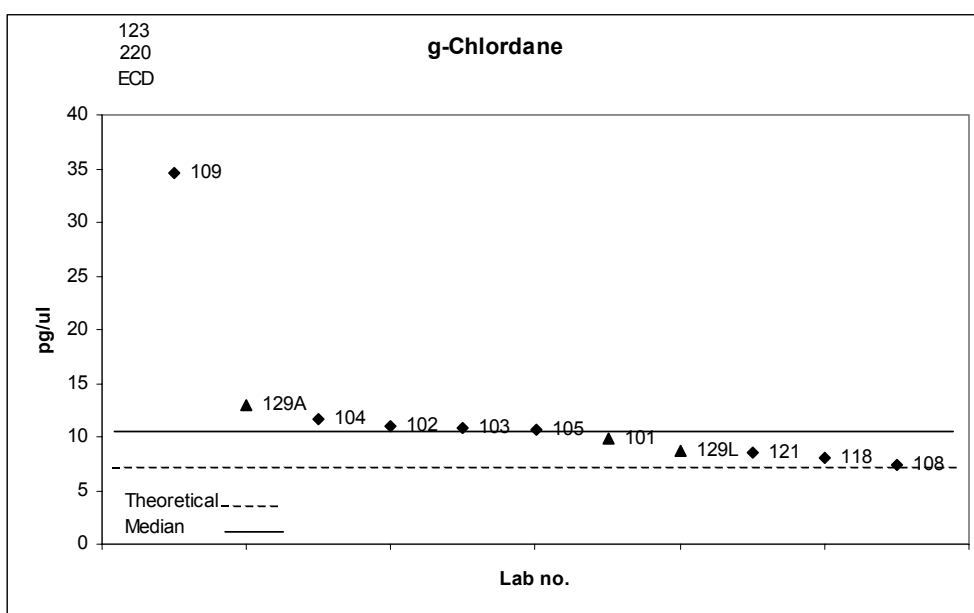
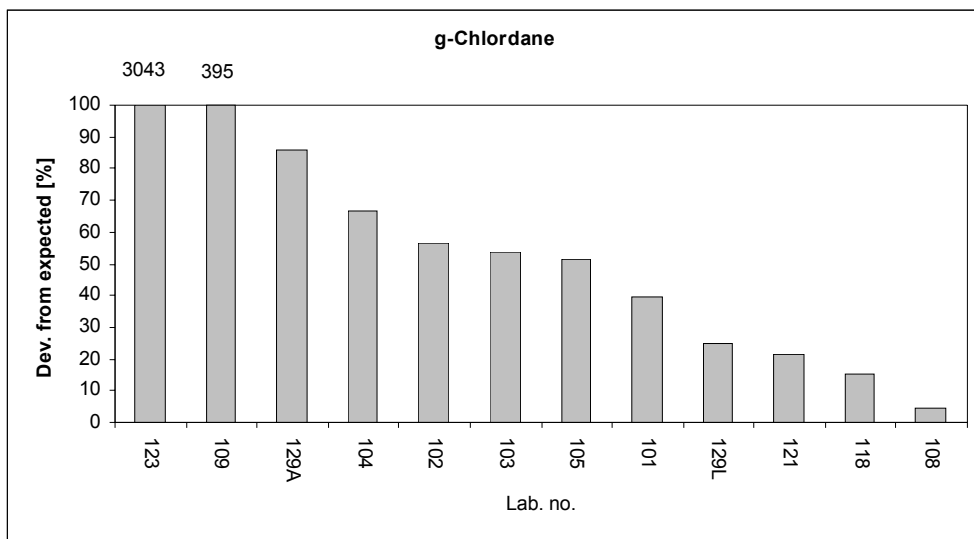
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/ μ l.

Compound: pp'-DDE
 Theoretical value: 40,0
 Unit: pg/ul
 Number of laboratories: 14
 Aritm. Mean: 40,9
 Median: 40,1

Lab no.	pg/ul
105	66,4*
123	48,4
104	47,9
102	47,3
129L	44,4
113	40,5
103	40,1
101	39,0
118	38,7
129A	38,0
108	34,7
121	28,0
109	18,7*

*Not used for determination of mean



Results obtained by each laboratory.

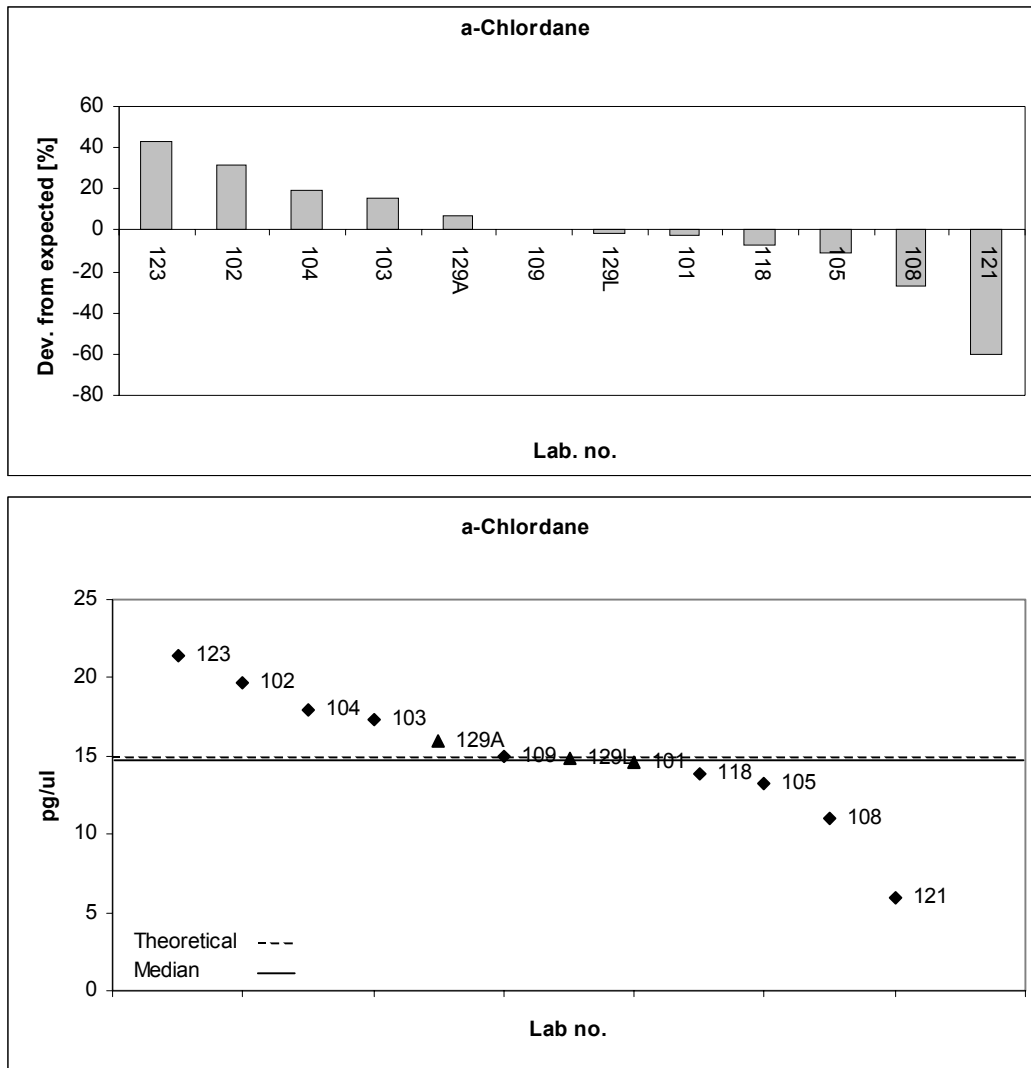
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound:	g-Chlordane
Theoretical value:	7,0
Unit:	pg/ul
Number of laboratories:	12
Aritm. Mean	12,2
Median	10,7

Lab. No.	pg/ul
123	220,0*
109	34,7
129A	13,0
104	11,7
102	11,0
103	10,7
105	10,6
101	9,8
129L	8,7
121	8,5
118	8,1
108	7,3

*Not used for determination of mean



Results obtained by each laboratory.

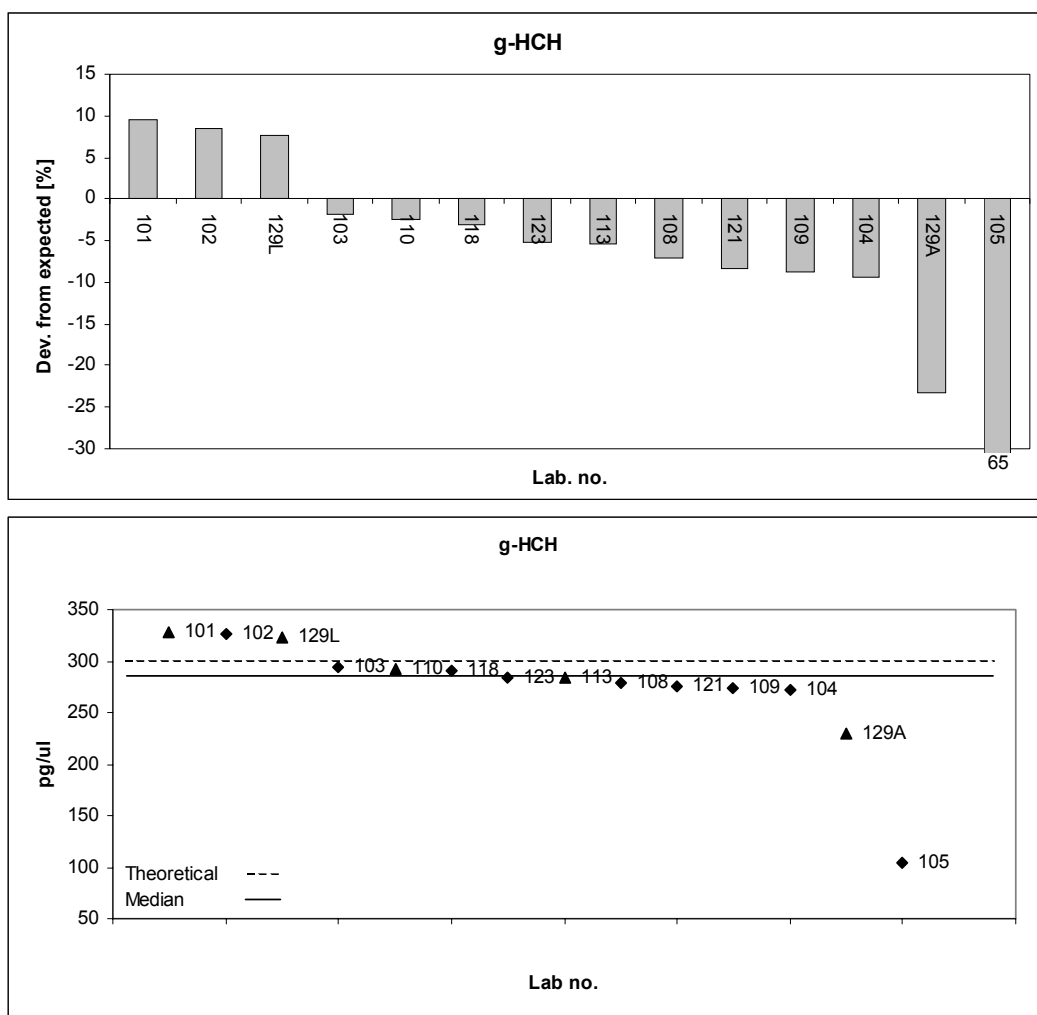
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound: a-Chlordane
 Theoretical value: 15,0
 Unit: pg/ul
 Number of laboratories: 12
 Arithm. Mean: 15,9
 Median: 14,9

Lab. No.	pg/ul
123	21,4
102	19,7
104	17,9
103	17,3
129A	16,0
109	15,0
129L	14,8
101	14,6
118	13,9
105	13,3
108	11,0
121	6,0*

*Not used for determination of mean



Results obtained by each laboratory.

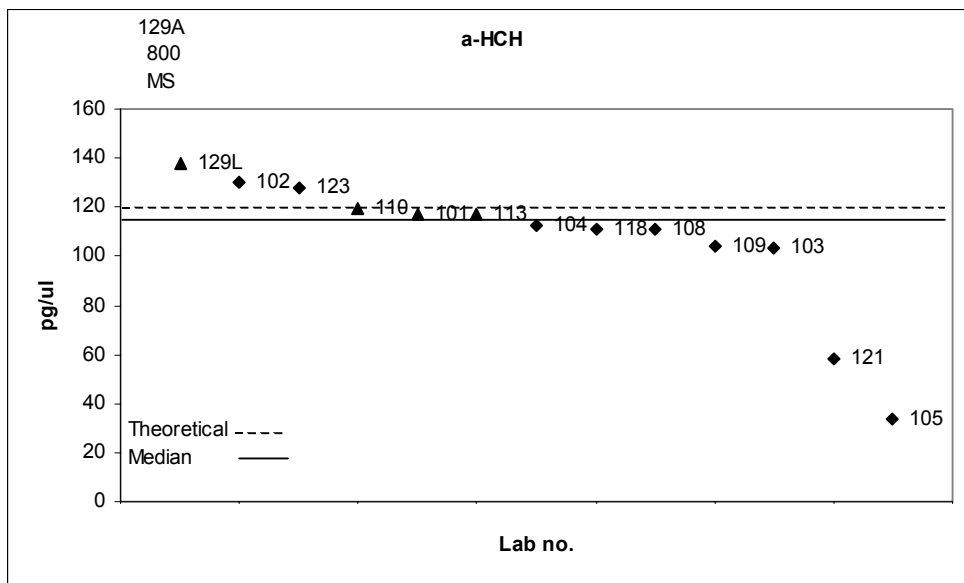
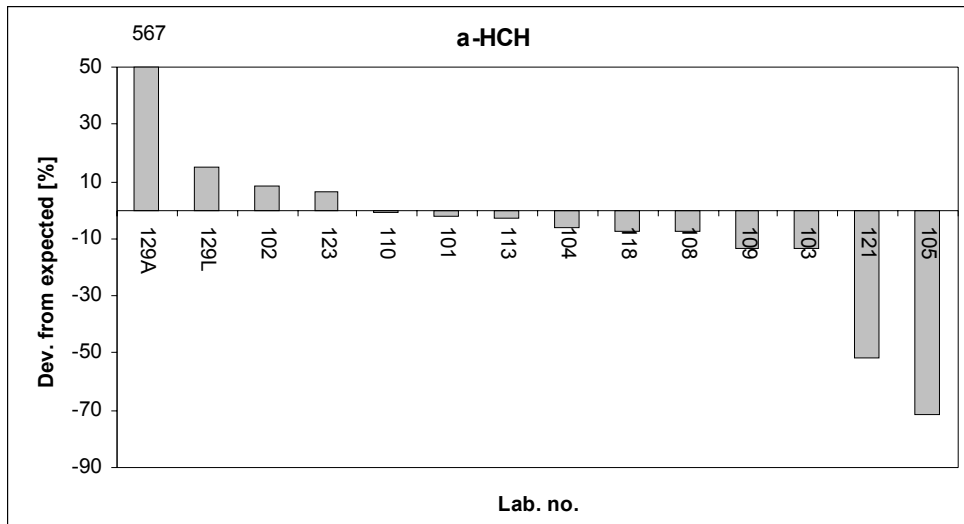
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/ul.

Compound: g-HCH
 Theoretical value: 300
 Unit: pg/ul
 Number of laboratories: 14
 Aritm. Mean: 275
 Median: 284

Lab. No.	pg/ul
120	2300*
101	328
102	325
129L	323
103	295
110	292
118	291
123	284
113	284
108	279
121	275
109	274
104	272
129A	230
105	104*

*Not used for
determination of mean



Results obtained by each laboratory.

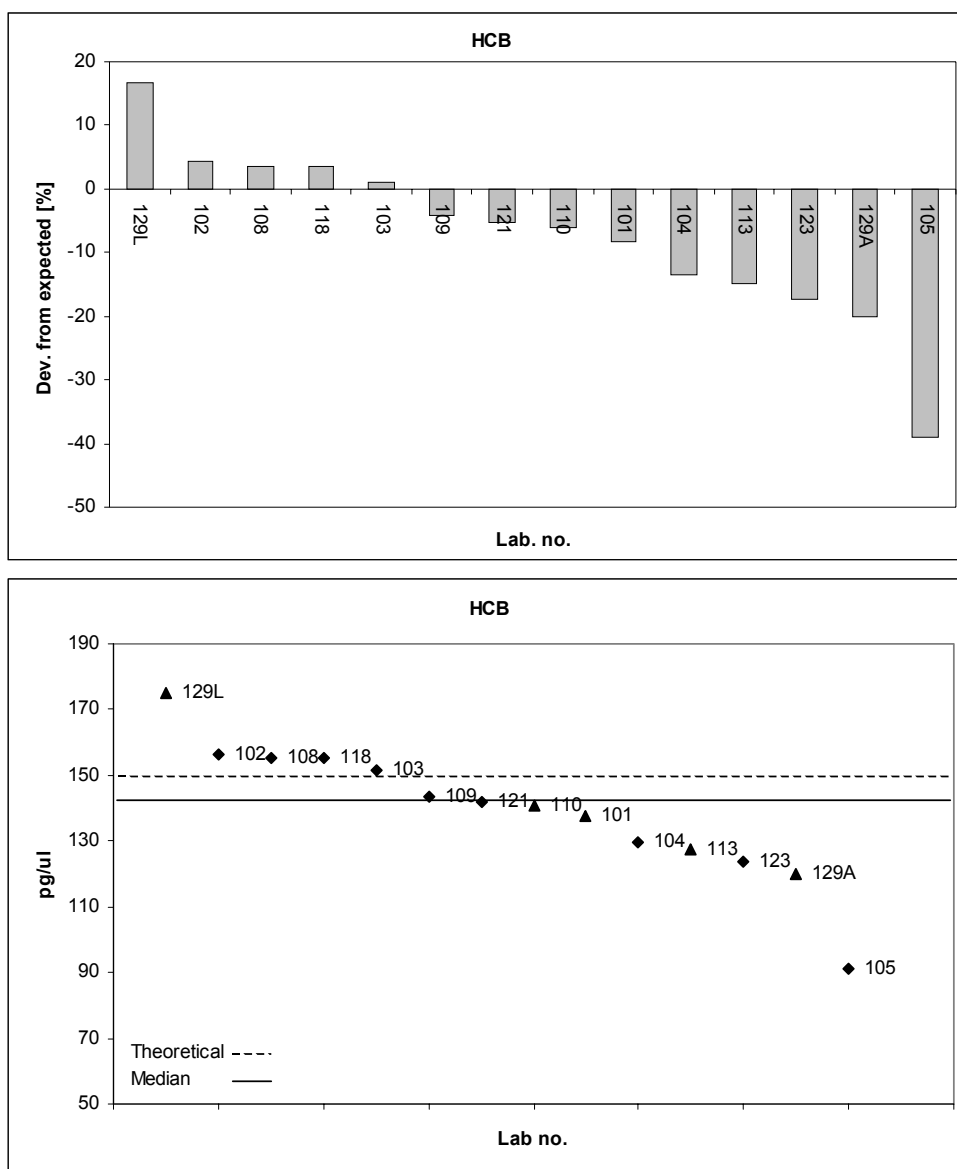
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound: a-HCH
 Theoretical value: 120
 Unit: pg/ul
 Number of laboratories: 14
 Arithm. Mean: 106
 Median: 115

Lab. No.	pg/ul
129A	800*
129L	138
102	130
123	128
110	119
101	118
113	117
104	112
118	111
108	111
109	104
103	104
121	58
105	34

*Not used for determination of mean



Results obtained by each laboratory.

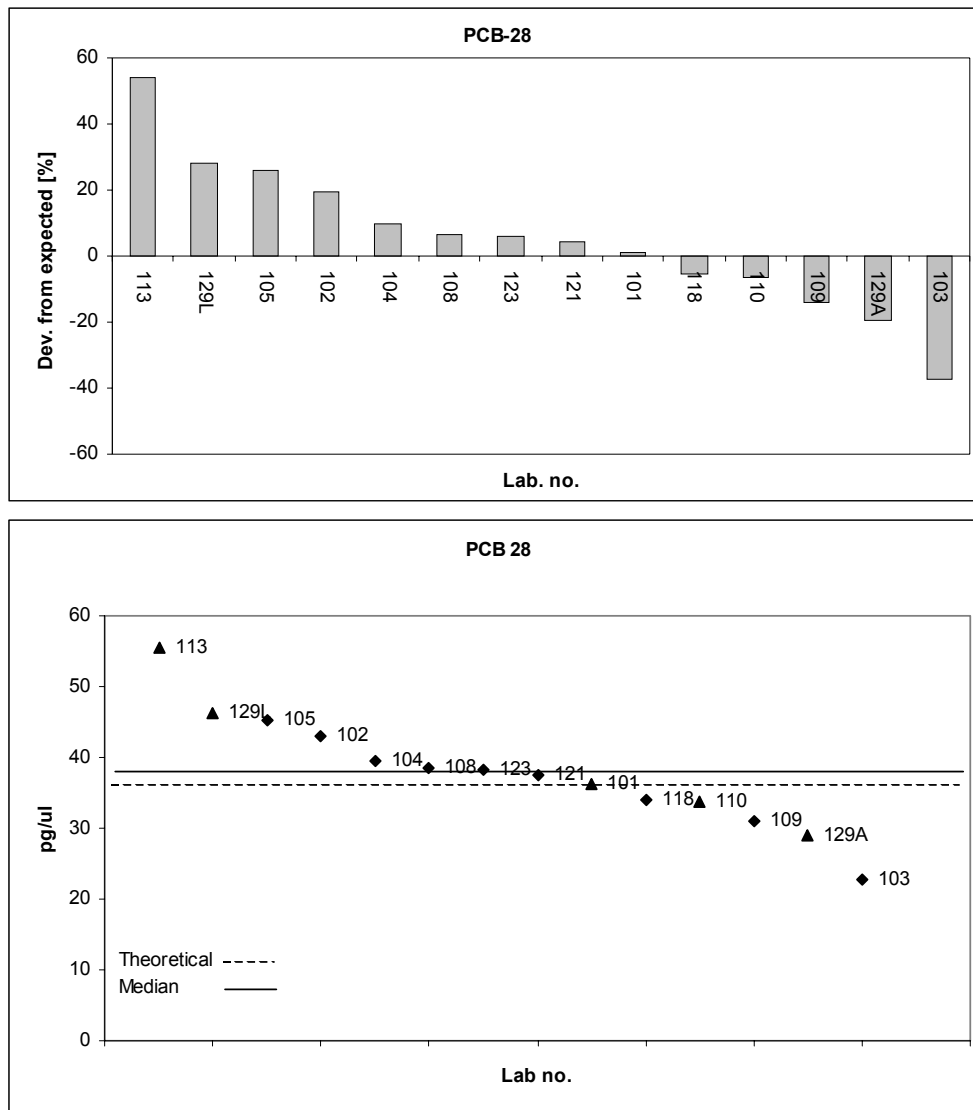
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/ul.

Compound:	HCB
Theoretical value:	150
Unit:	pg/ul
Number of laboratories:	14
Aritm. Mean	143
Median	142

<u>Lab. No.</u>	<u>pg/ul</u>
129L	175
102	156
108	155
118	155
103	151
109	144
121	142
110	141
101	137
104	130
113	128
123	124
129A	120
105	91*

*Not used for determination of mean



Results obtained by each laboratory.

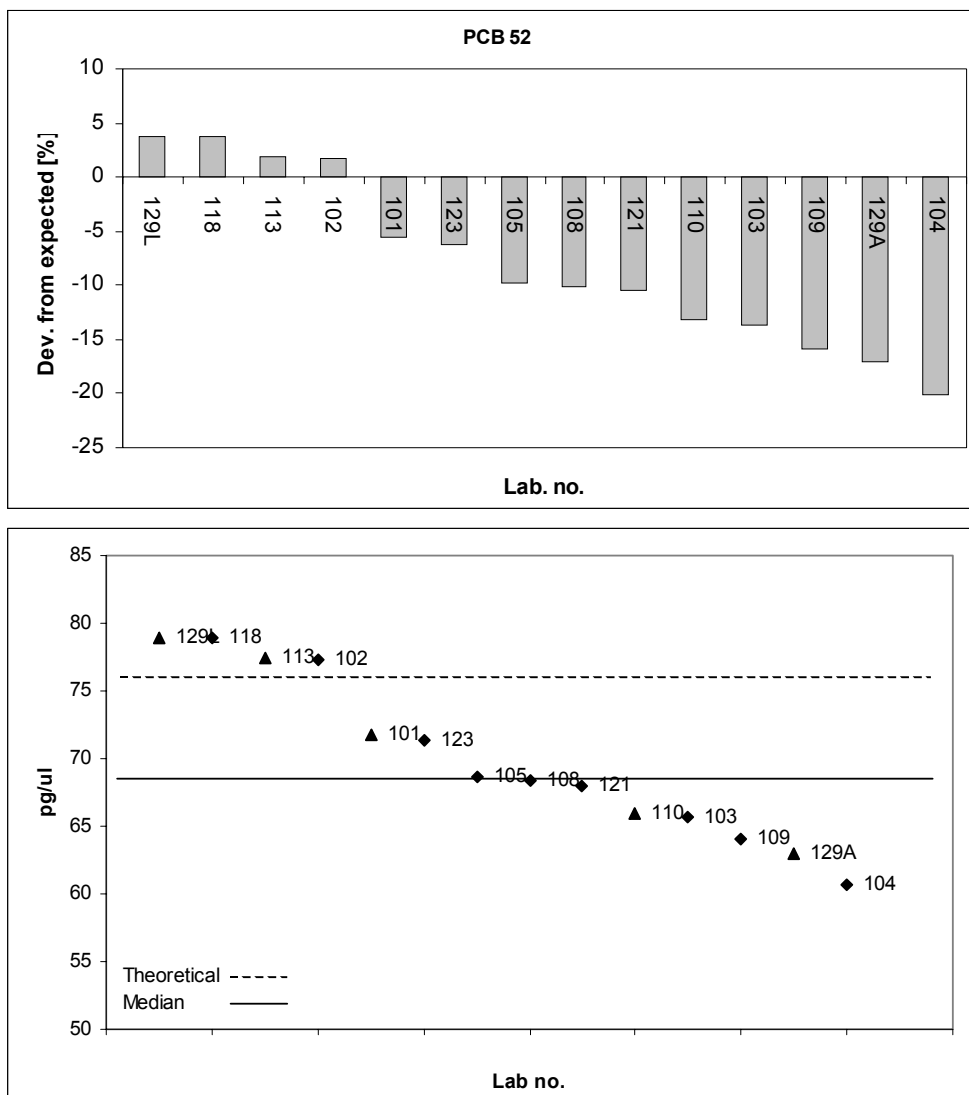
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound: PCB 28
 Theoretical value: 36,0
 Unit: pg/ul
 Number of laboratories: 14
 Arithm. Mean: 36,5
 Median: 37,9

Lab. No.	pg/ul
113	55,5*
129L	46,2
105	45,3
102	43,1
104	39,6
108	38,4
123	38,2
121	37,5
101	36,3
118	34,0
110	33,7
109	31,0
129A	29,0
103	22,6

*Not used for determination of mean



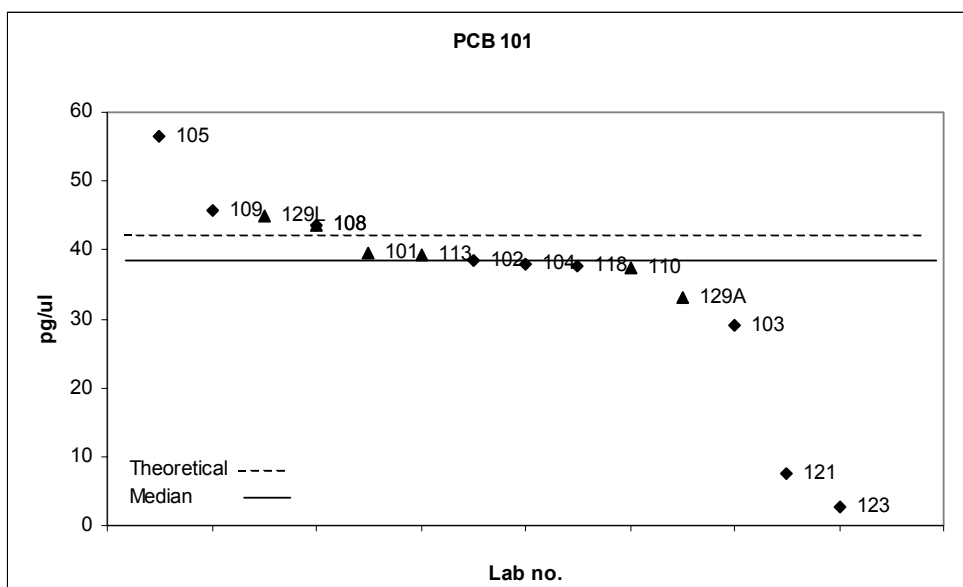
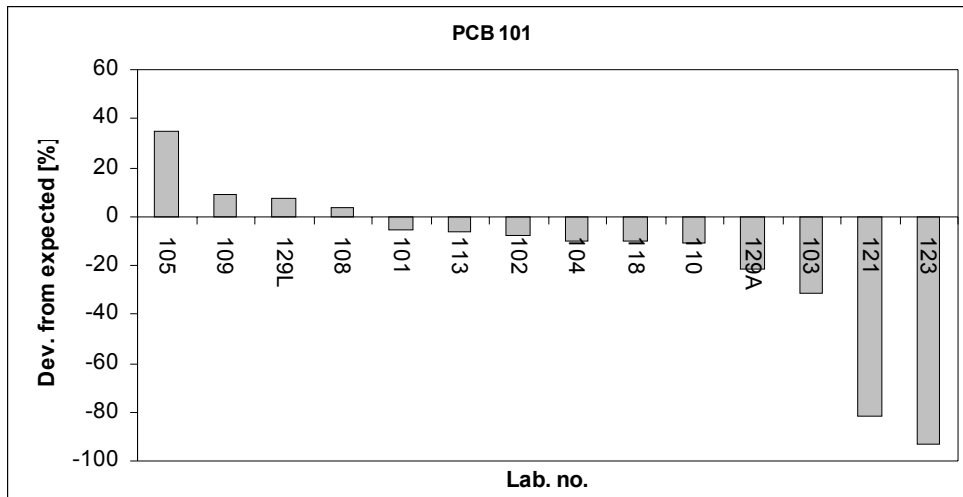
Results obtained by each laboratory.

Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/ul.

Compound:	PCB 52
Theoretical value:	76,0
Unit:	pg/ul
Number of laboratories:	15
Aritm. Mean	70,0
Median	68,5

Lab. No.	pg/ul	Lab. No.	pg/ul
129L	78,9	108	68,3
118	78,9	121	68,0
113	77,4	110	66,0
102	77,3	103	65,7
101	71,8	109	64,0
123	71,3	129A	63,0
105	68,6	104	60,7



Results obtained by each laboratory.

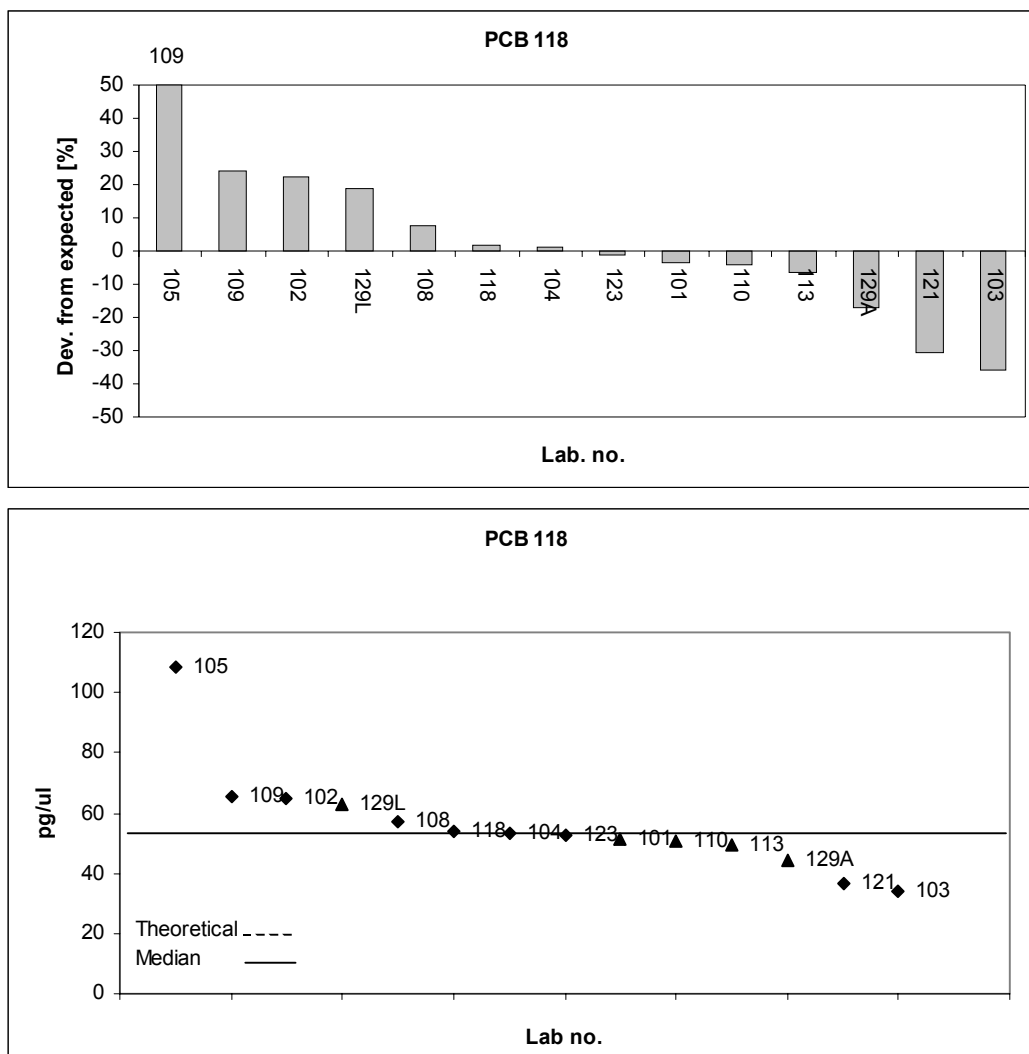
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound: PCB 101
 Theoretical value: 42,0
 Unit: pg/ul
 Number of laboratories: 14
 Aritm. Mean: 40,3
 Median: 38,2

<u>Lab. no.</u>	<u>pg/ul</u>
105	56,6
109	45,7
129L	45,0
108	43,6
101	39,6
113	39,3
102	38,6
104	37,8
118	37,8
110	37,3
129A	33,0
103	29,0
121	7,6*
123	2,8*

*Not used for determination of mean



Results obtained by each laboratory.

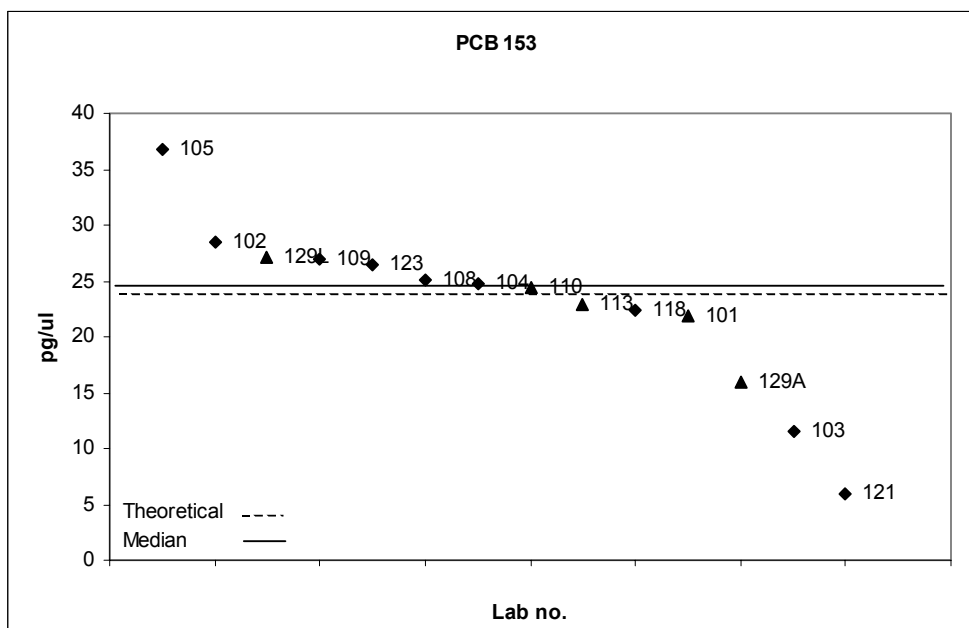
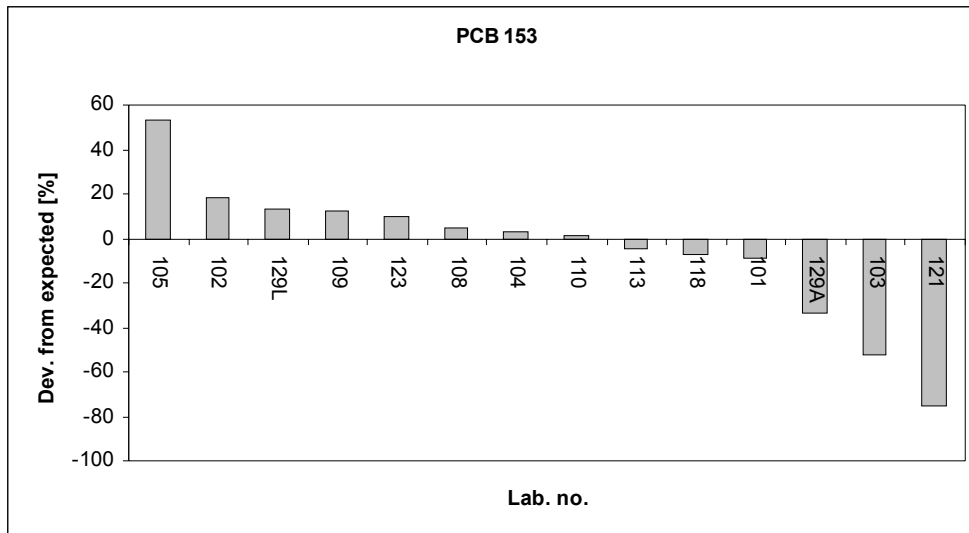
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/ul.

Compound:	PCB 118
Theoretical value:	53,0
Unit:	pg/ul
Number of laboratories:	14
Aritm. Mean	52,0
Median	53,0

Lab. no.	pg/ul
105	108,5*
109	65,7
102	64,8
129L	62,9
108	57,1
118	53,9
104	53,5
123	52,4
101	51,3
110	50,7
113	49,4
129A	44,0
121	36,7
103	34,1

*Not used for determination of mean



Results obtained by each laboratory.

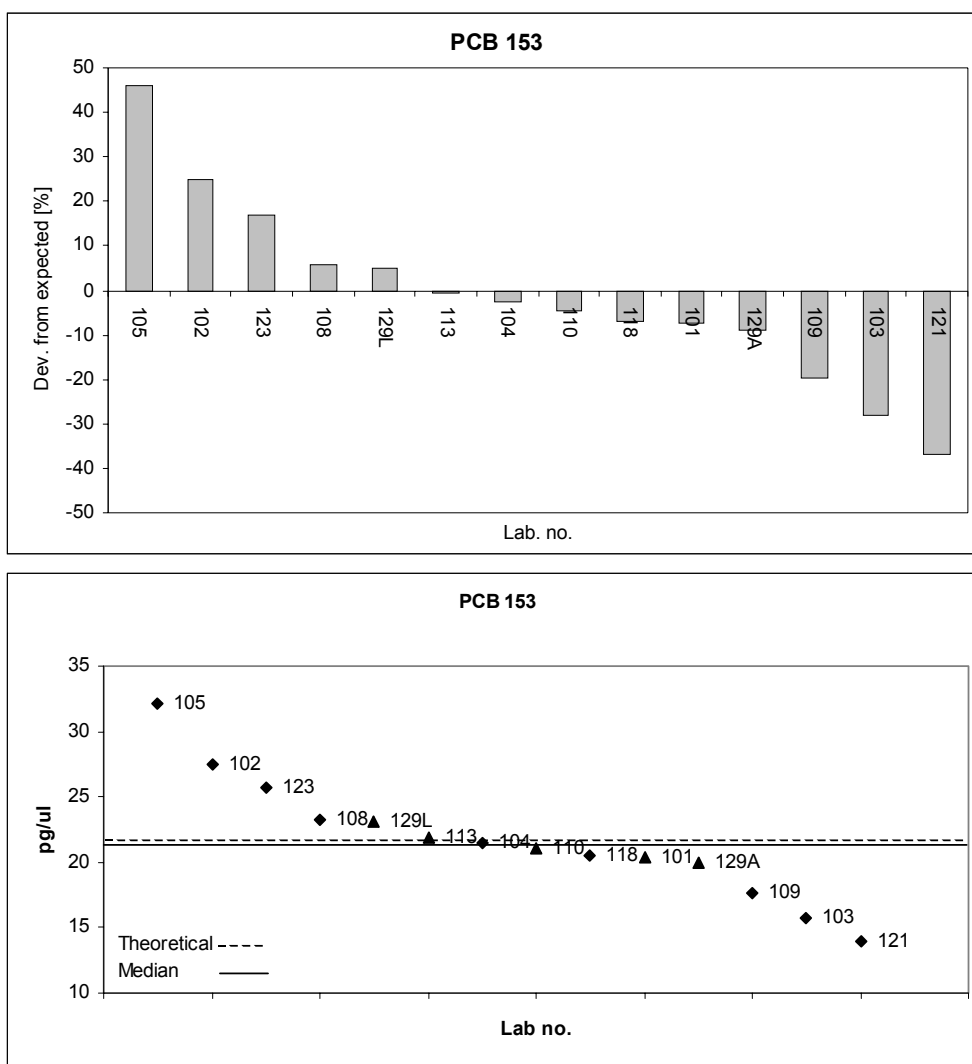
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound:	PCB 138
Theoretical value:	24,0
Unit:	pg/ul
Number of laboratories:	14
Aritm. Mean	24,2
Median	24,6

Lab. no.	pg/ul
105	36,8
102	28,4
129L	27,2
109	27,0
123	26,5
108	25,2
104	24,8
110	24,3
113	22,9
118	22,3
101	21,9
129A	16,0
103	11,4
121	6,0*

*Not used for determination of mean



Results obtained by each laboratory.

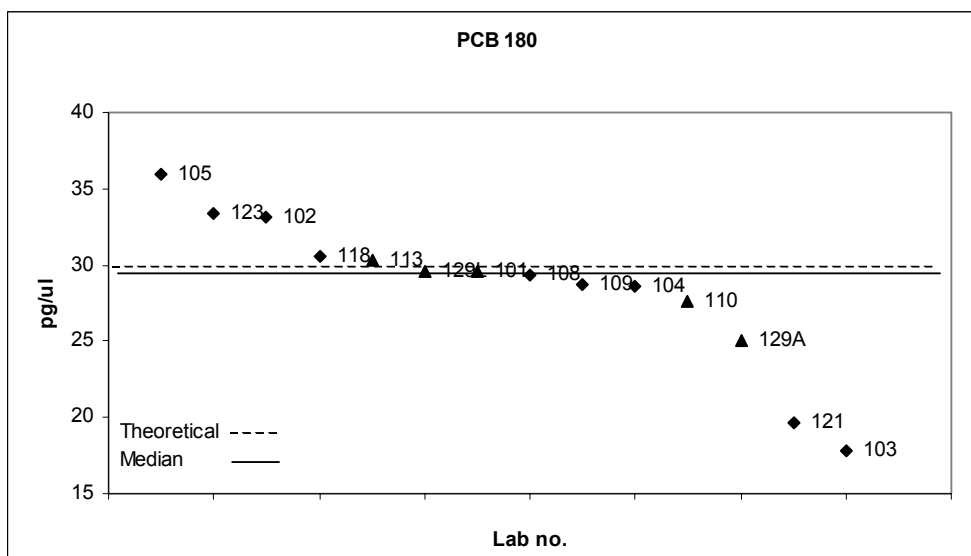
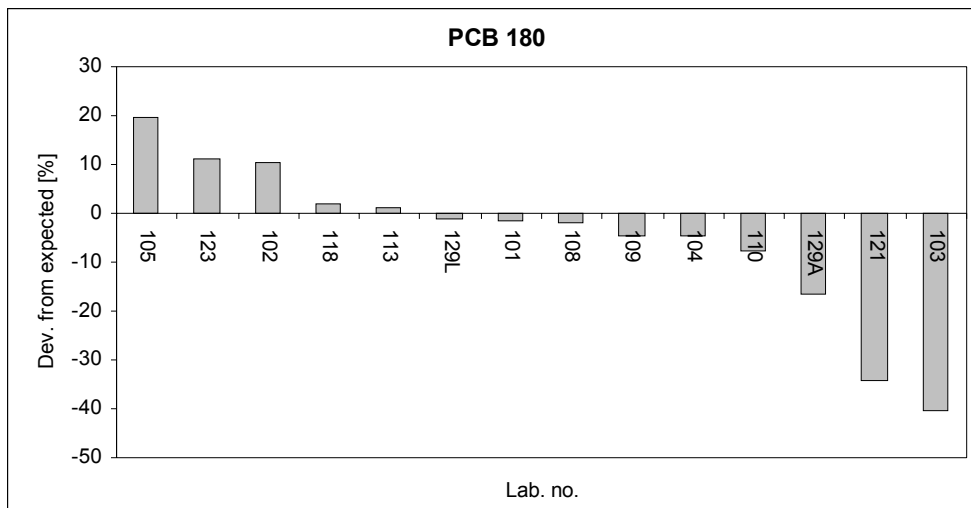
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/ul.

Compound: PCB 153
 Theoretical value: 22,0
 Unit: pg/ul
 Number of laboratories: 14
 Aritm. Mean 20,9
 Median 21,2

Lab. no.	pg/ul
105	32,1*
102	27,5
123	25,7
108	23,2
129L	23,1
113	21,8
104	21,4
110	21,0
118	20,5
101	20,4
129A	20,0
109	17,7
103	15,8
121	13,9

*Not used for determination of mean



Results obtained by each laboratory.

Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/μl.

Compound:	PCB 180
Theoretical value:	30,0
Unit:	pg/ul
Number of laboratories:	14
Aritm. Mean	29,3
Median	29,5

<u>Lab. no.</u>	<u>pg/ul</u>
105	35,9
123	33,4
102	33,1
118	30,6
113	30,3
129L	29,6
101	29,6
108	29,4
109	28,7
104	28,6
110	27,7
129A	25,0
121	19,7*
103	17,9*

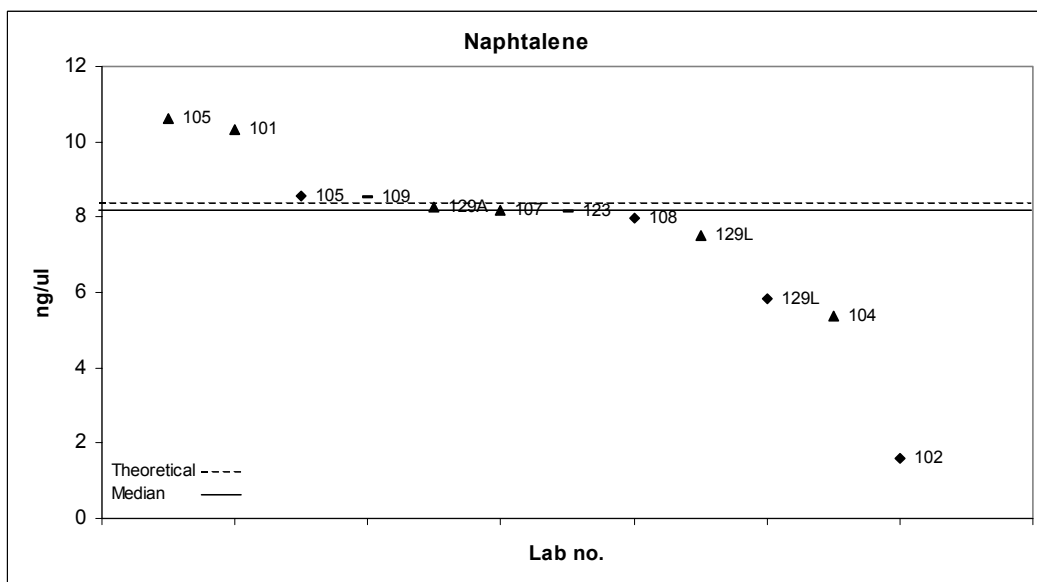
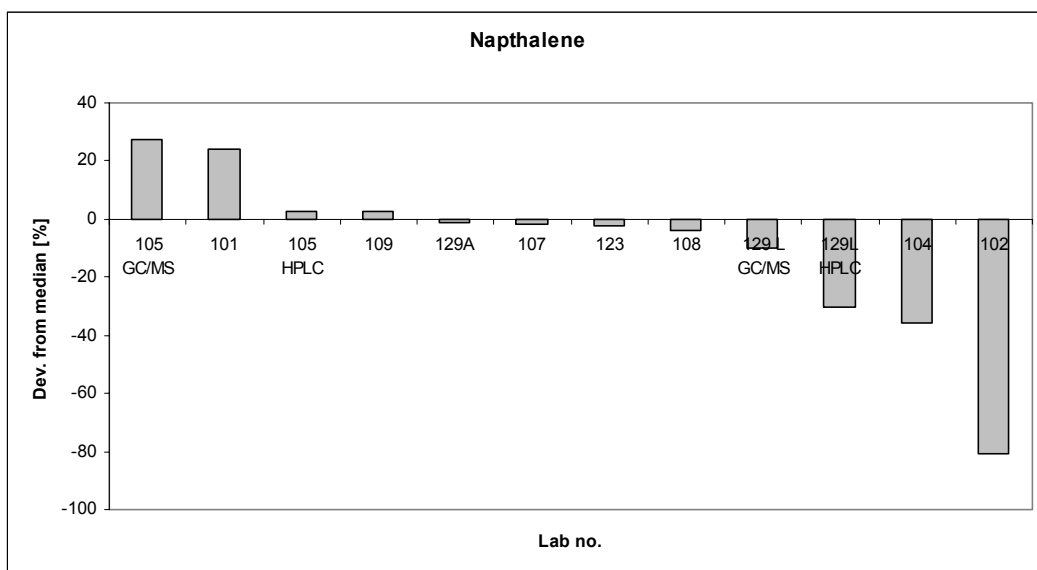
*Not used for determination of mean

Annex 4

PAH compounds, round 1

On the following pages the results from round 1 are shown graphically. The data from each compound is shown as deviation from expected value (upper graph) and as concentration found in the sample (lower graph).

◆	HPLC
▲	GC/MS
—	GC/FID
○	TLC
×	HPLC and GC/MS
■	GC/FID and GC/MS



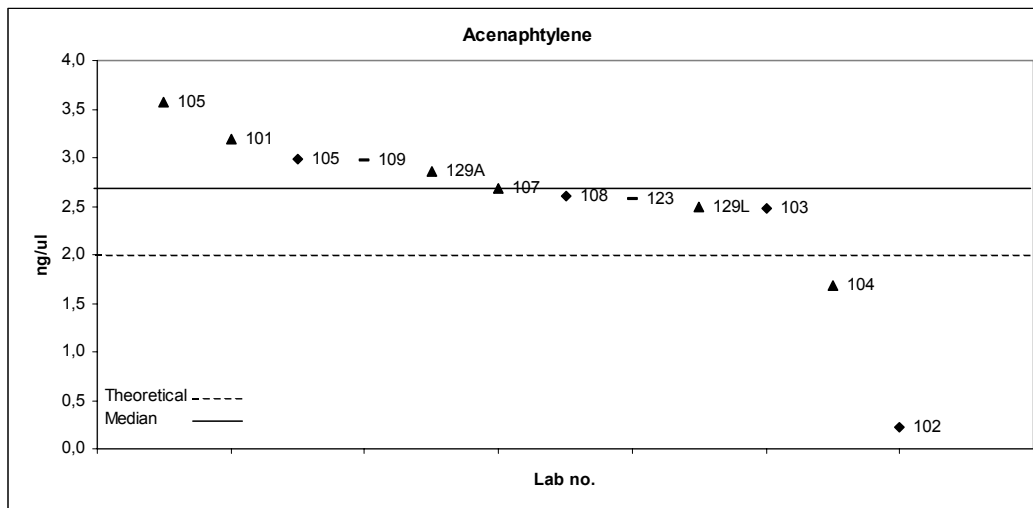
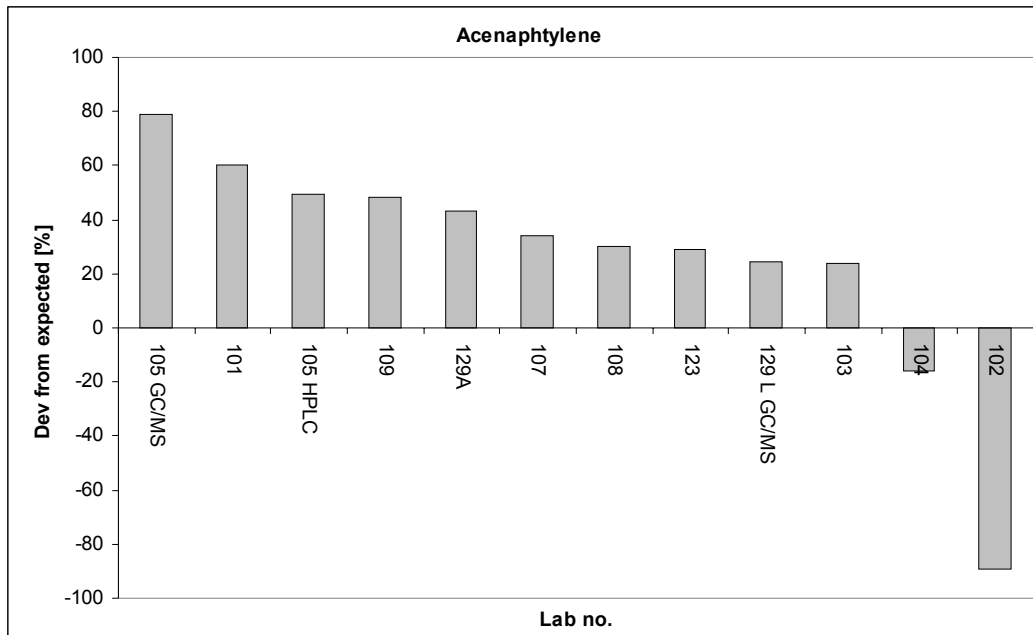
Results obtained by each laboratory.

Upper figure: Deviation from median in %.. Lower figure: Concentrations in ng/μl.

Compound: Naphtalene
 Theoretical value: 8,33
 Unit: ng/ul
 Number of laboratories: 12
 Aritm. Mean: 8,119
 Median: 8,174

Lab. no.	ng/ul
105 GC/MS	10,610
101	10,330
105 HPLC	8,550
109	8,533
129A	8,253
107	8,190
123	8,158
108	7,988
129L GC/MS	7,520
129L HPLC	5,820
104	5,353
102	1,580*

*Not used for determination of mean



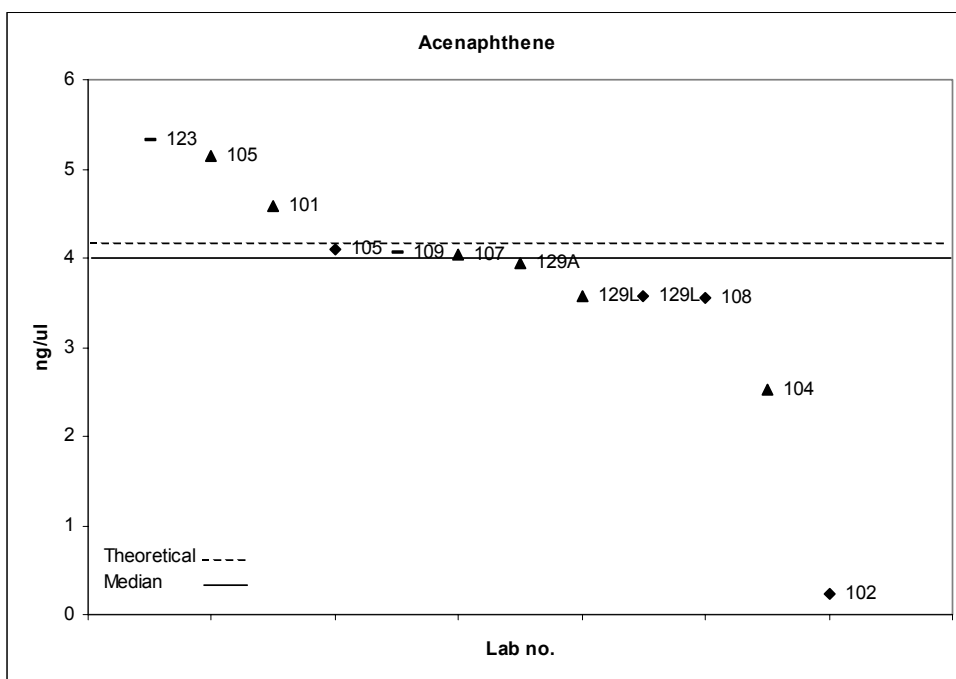
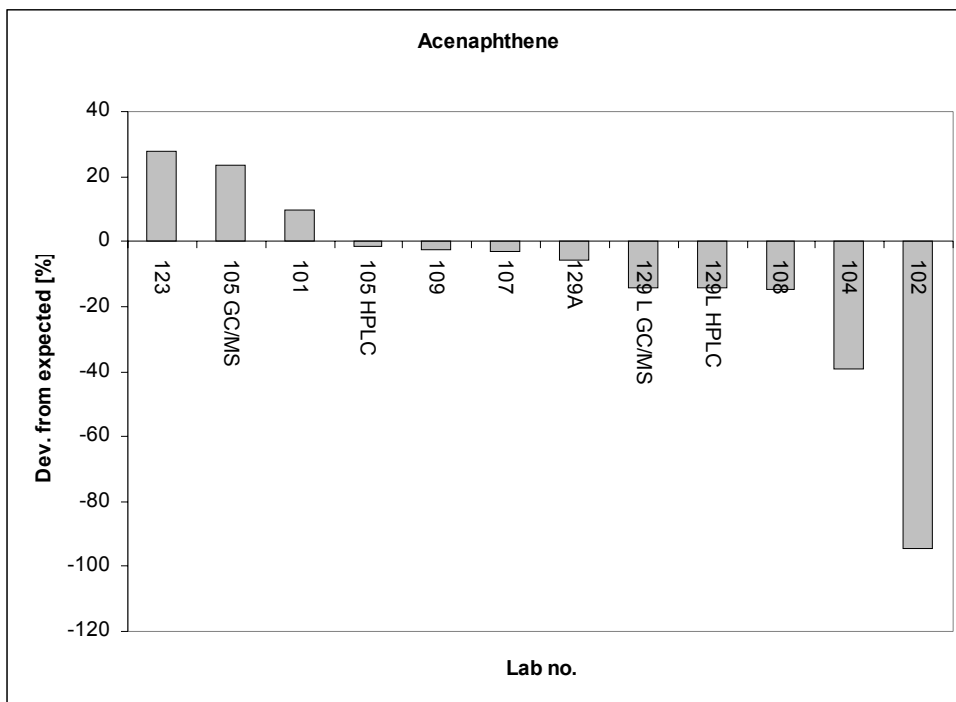
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Acenaphthylene
Theoretical value:	2,00
Unit:	ng/ul
Number of laboratories:	12
Aritm. Mean	2,735
Median	2,680

Lab. no.	ng/ul
105GC/MS	3,570
101	3,190
105 HPLC	2,990
109	2,967
129A	2,863
107	2,680
108	2,600
123	2,577
129L GC/MS	2,493
103	2,477
104	1,680
102	0,222*

*Not used for determination of mean

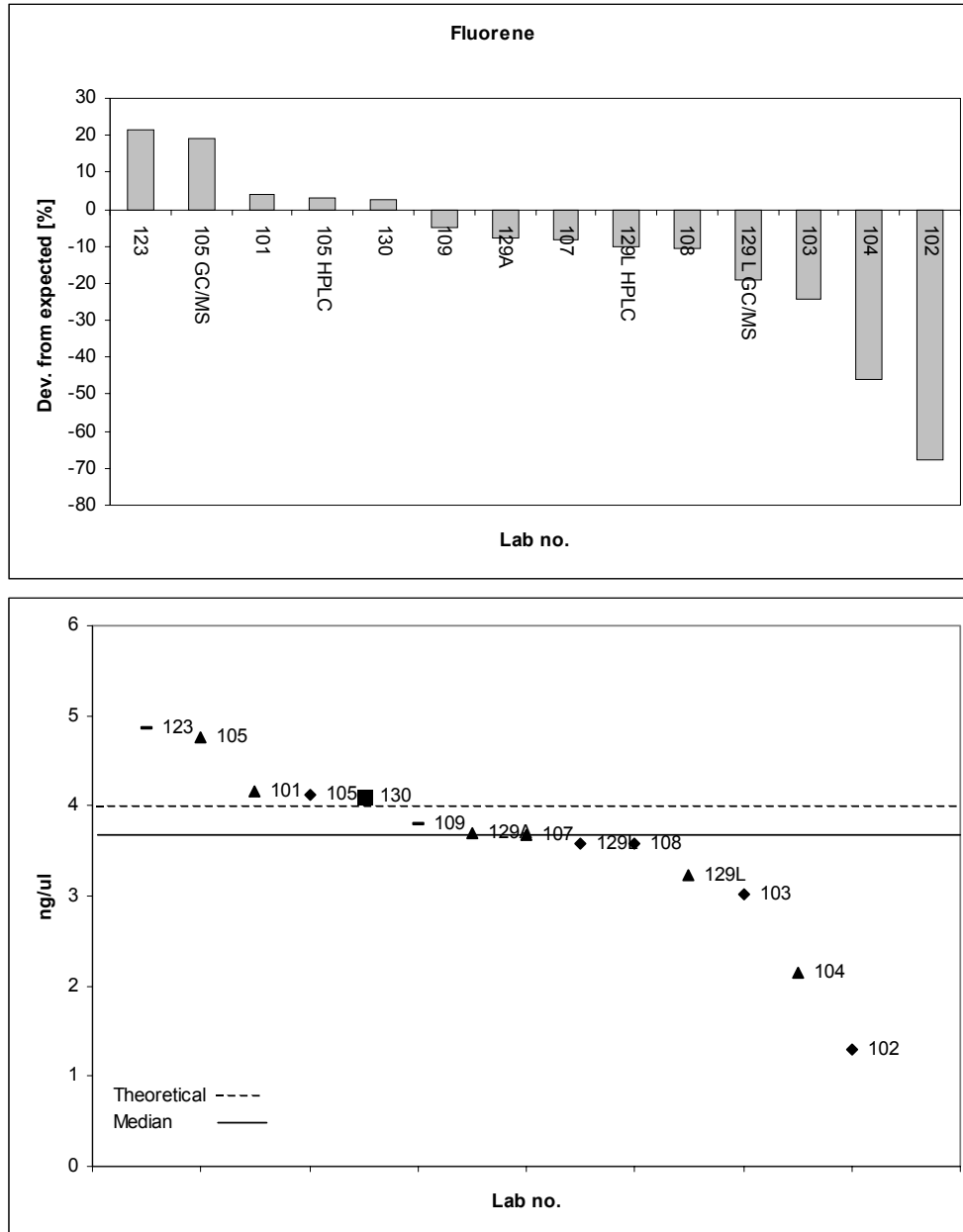


Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Acenaphthene
Theoretical value:	4,17
Unit:	ng/ul
Number of laboratories:	12
Aritm. Mean	4,04
Median	3,99
<u>Lab. no.</u>	<u>ng/ul</u>
123	5,32
105 GC/MS	5,15
101	4,58
105 HPLC	4,10
109	4,07
107	4,05
129A	3,93
129L GC/MS	3,57
129L HPLC	3,57
108	3,55
104	2,53
102	0,24*

*Not used for determination of mean



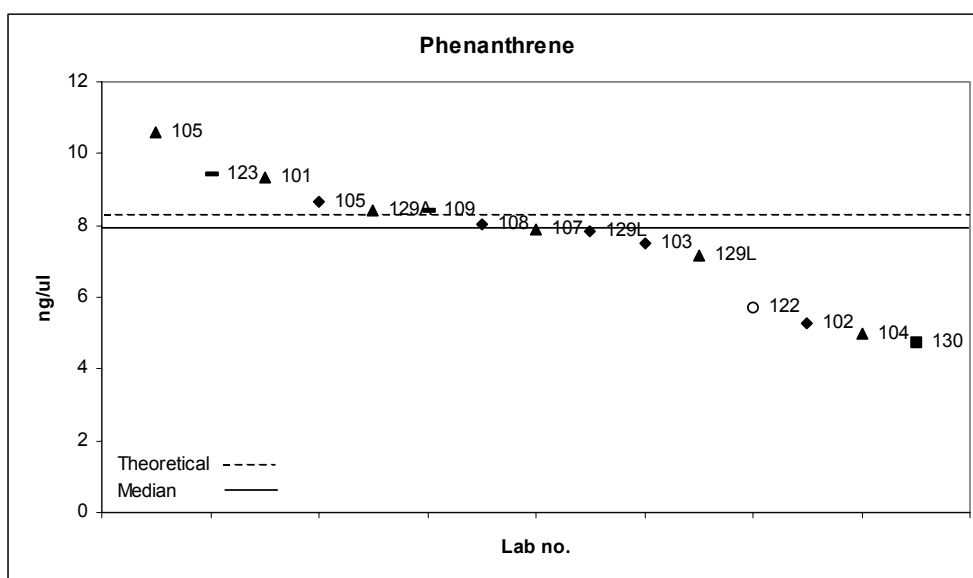
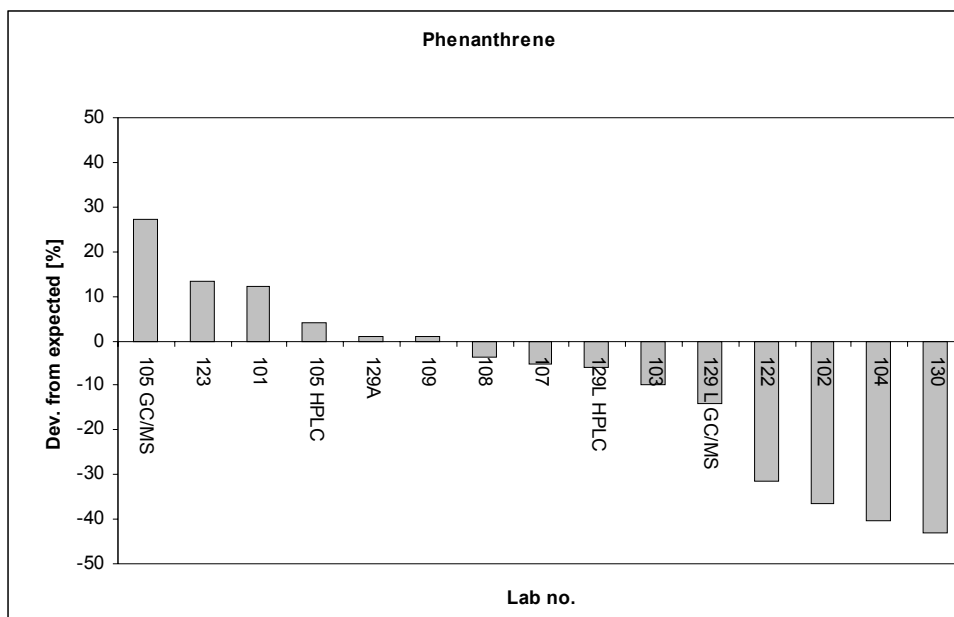
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound: Fluorene
 Theoretical value: 4,00
 Unit: ng/ul
 Number of laboratories: 14
 Arithm. Mean: 3,75
 Median: 3,68

<u>Lab. no.</u>	<u>ng/ul</u>
123	4,86
105 GC/MS	4,77
101	4,17
105 HPLC	4,13
130	4,10
109	3,80
129A	3,69
107	3,67
129L HPLC	3,59
108	3,58
129L GC/MS	3,23
103	3,02
104	2,16
102	1,30*

*Not used for determination of mean

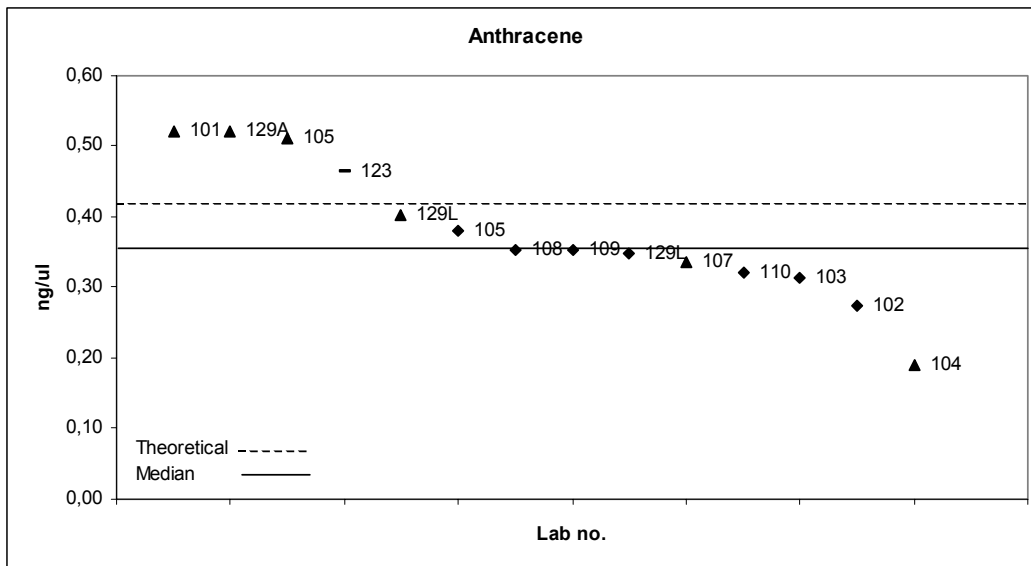
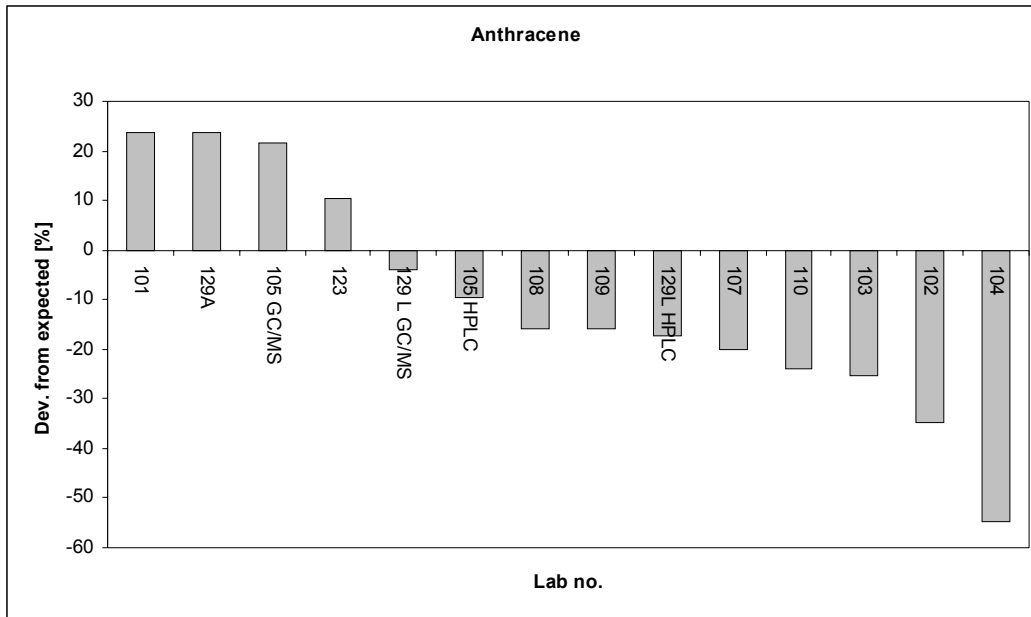


Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Phenanthrene
Theoretical value:	8,33
Unit:	ng/ul
Number of laboratories:	15
Aritm. Mean	7,601
Median	7,890

<u>Lab. no.</u>	<u>ng/ul</u>
105 GC/MS	10,600
123	9,455
101	9,353
105 HPLC	8,680
129A	8,413
109	8,400
108	8,011
107	7,890
129L HPLC	7,846
103	7,513
129L GC/MS	7,147
122	5,700
102	5,280
104	4,983
130	4,750



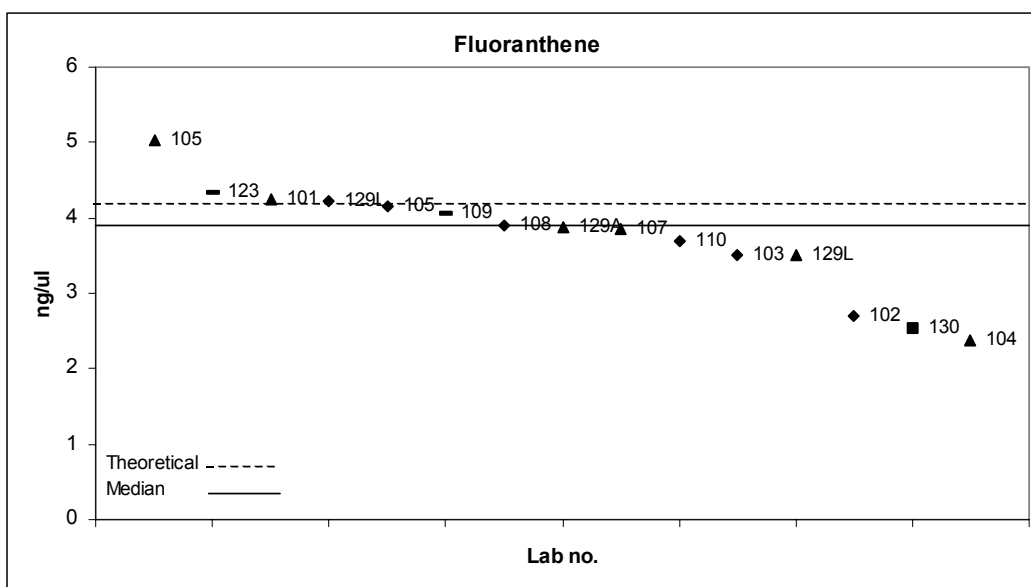
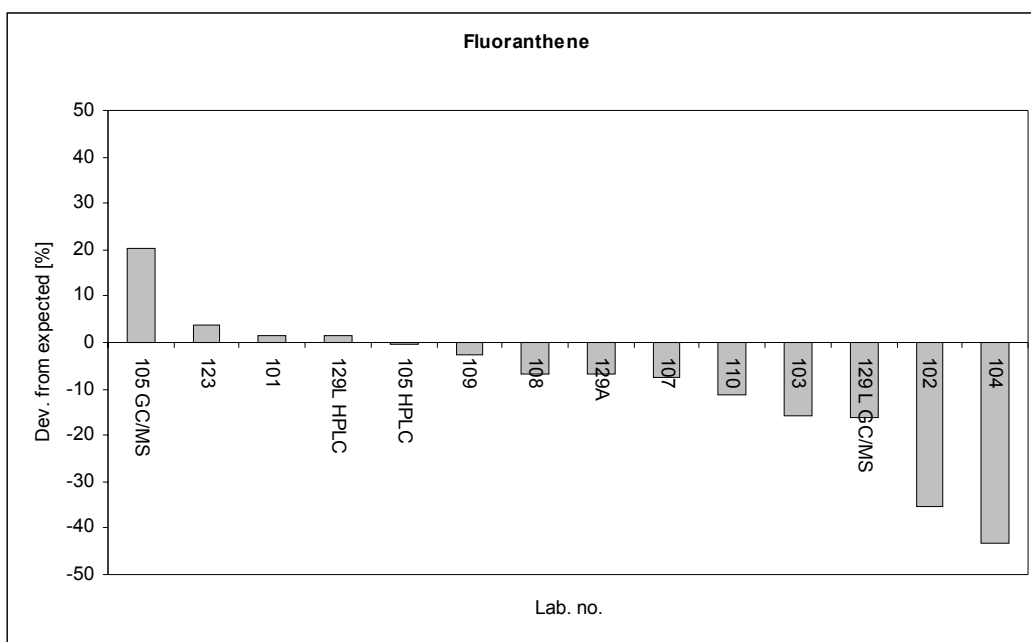
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Anthracene
Theoretical value:	0,42
Unit:	ng/ul
Number of laboratories:	14
Aritm. Mean	0,392
Median	0,354

<u>Lab. no.</u>	<u>ng/ul</u>
101	0,520
129A	0,520
105 GC/MS	0,510
123	0,464
129L GC/MS	0,403
105 HPLC	0,380
108	0,354
109	0,353
129L HPLC	0,348
107	0,336
110	0,320
103	0,314
102	0,274
104	0,190*

*Not used for determination of mean

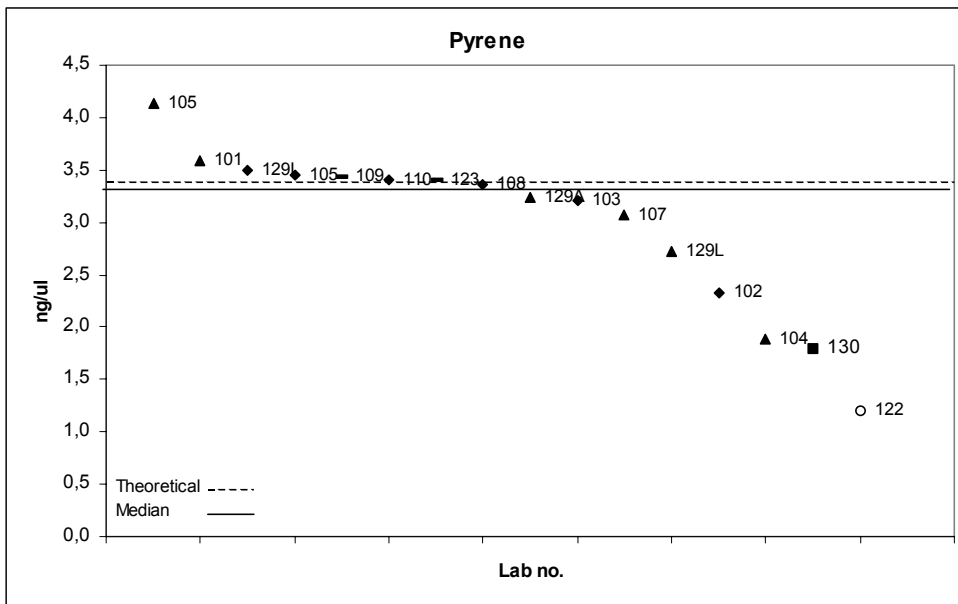
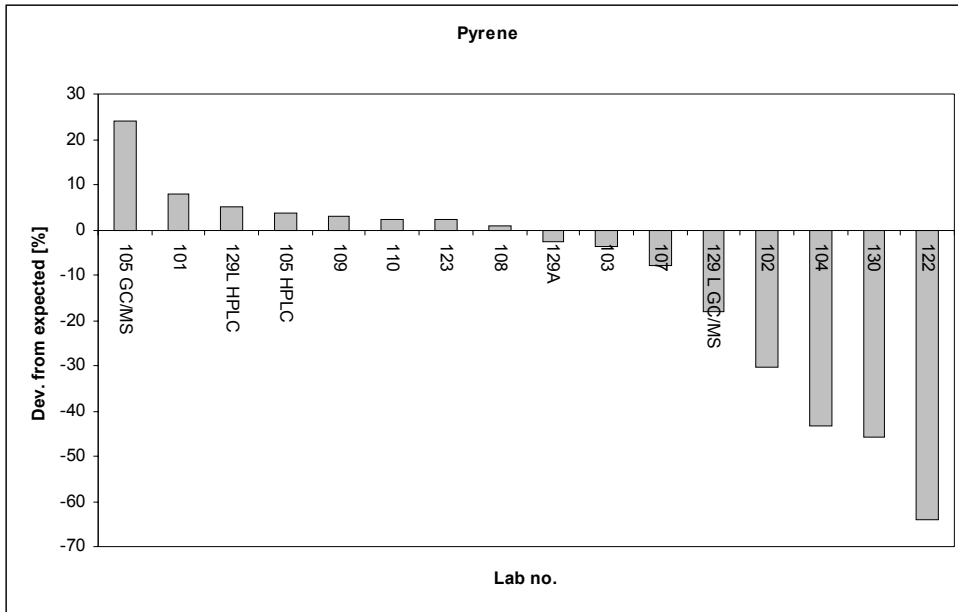


Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Fluoranthene
Theoretical value:	4,17
Unit:	ng/ul
Number of laboratories:	15
Aritm. Mean	3,735
Median	3,880

<u>Lab. no.</u>	<u>ng/ul</u>
105 GC/MS	5,020
123	4,328
101	4,237
129L HPLC	4,234
105 HPLC	4,160
109	4,067
108	3,895
129A	3,880
107	3,855
110	3,703
103	3,516
129L GC/MS	3,500
102	2,700
130	2,550
104	2,373



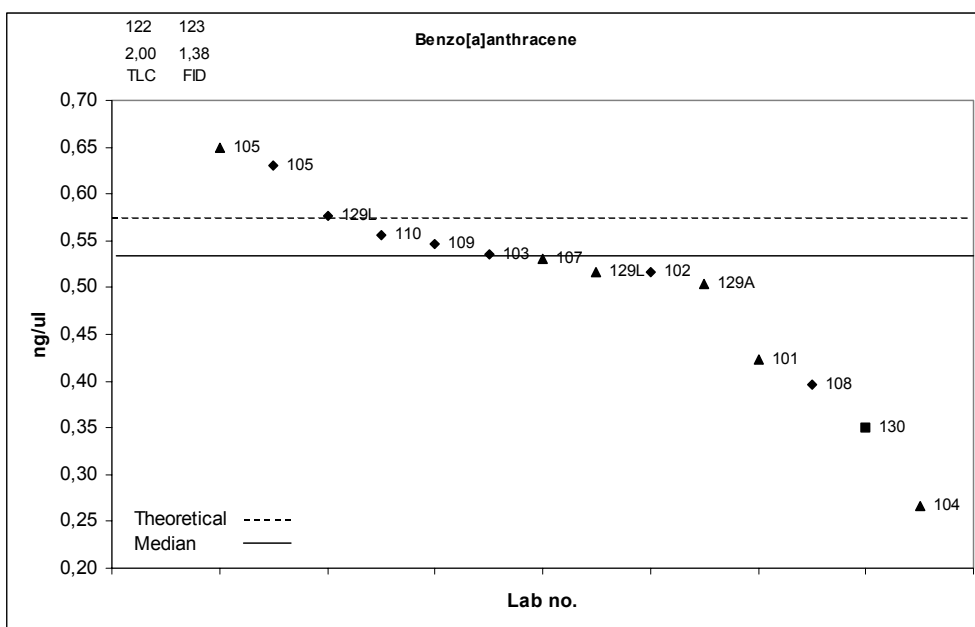
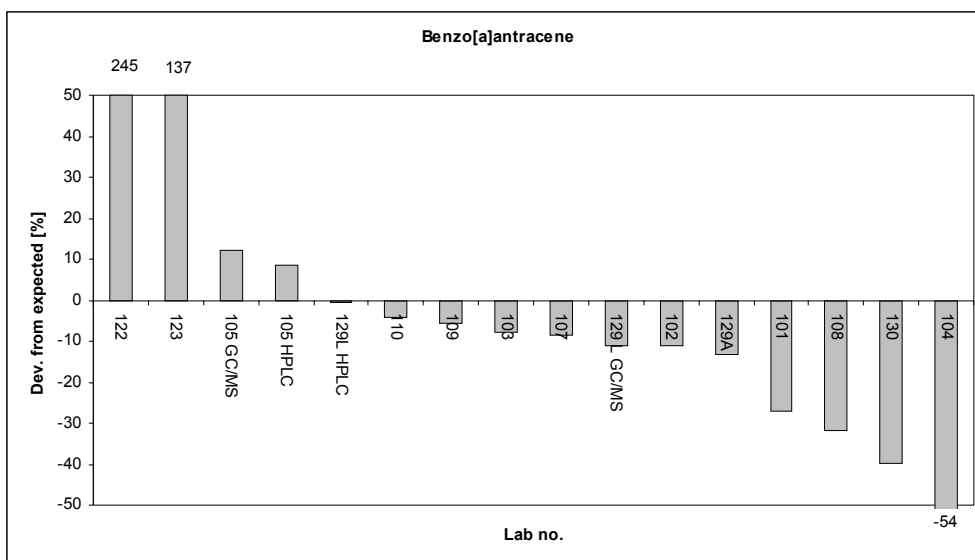
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound: Pyrene
 Theoretical value: 3,33
 Unit: ng/ul
 Number of laboratories: 16
 Aritm. Mean: 3,10
 Median: 3,30

Lab. no.	ng/ul
105 GC/MS	4,13
101	3,59
129L HPLC	3,49
105 HPLC	3,45
109	3,43
110	3,41
123	3,40
108	3,35
129A	3,24
103	3,21
107	3,07
129L GC/MS	2,72
102	2,32
104	1,88
130	1,80
122	1,20*

*Not used for determination of mean



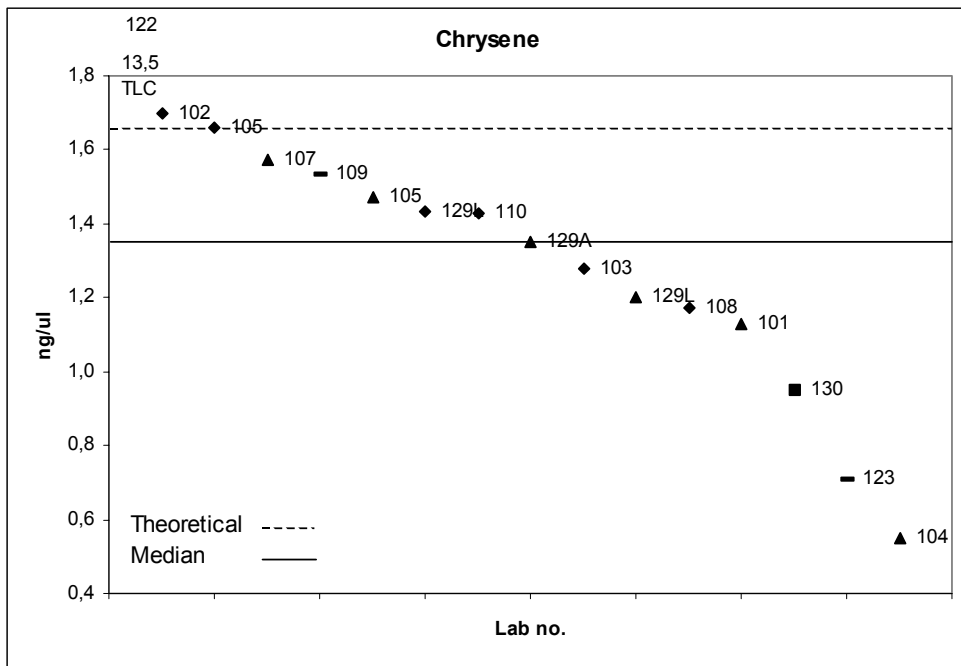
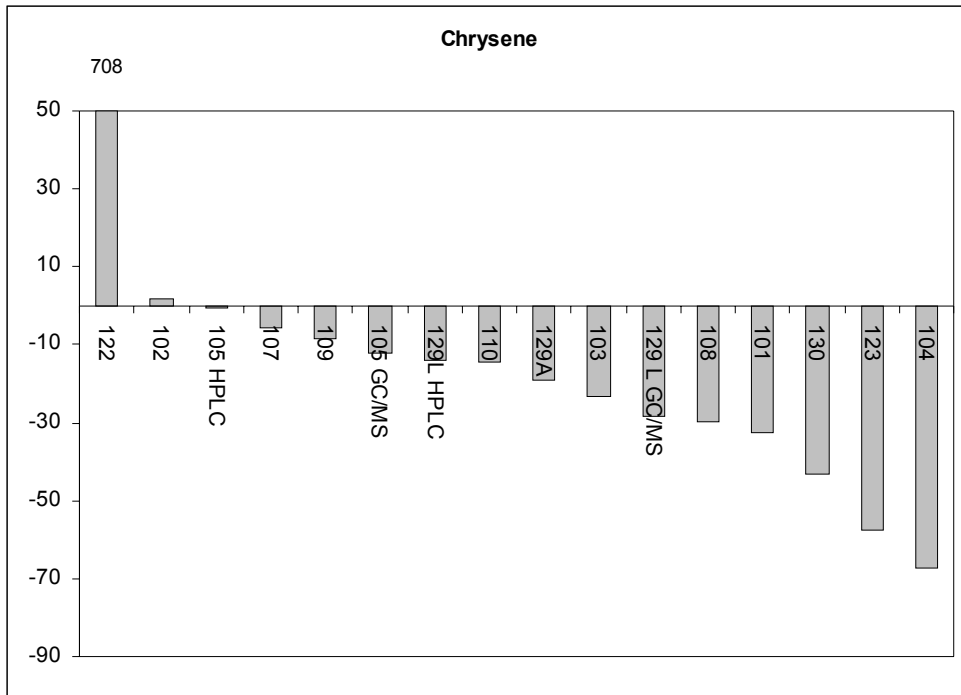
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Benzo[a]anthracene
Theoretical value:	0,58
Unit:	ng/ul
Number of laboratories:	16
Aritm. Mean	0,558
Median	0,533

<u>Lab. no.</u>	<u>ng/ul</u>
122	2,000*
123	1,377
105 GC/MS	0,650
105 HPLC	0,630
129L HPLC	0,576
110	0,557
109	0,547
103	0,535
107	0,531
129L GC/MS	0,517
102	0,516
129A	0,503
101	0,423
108	0,396
130	0,350
104	0,267

*Not used for determination of mean



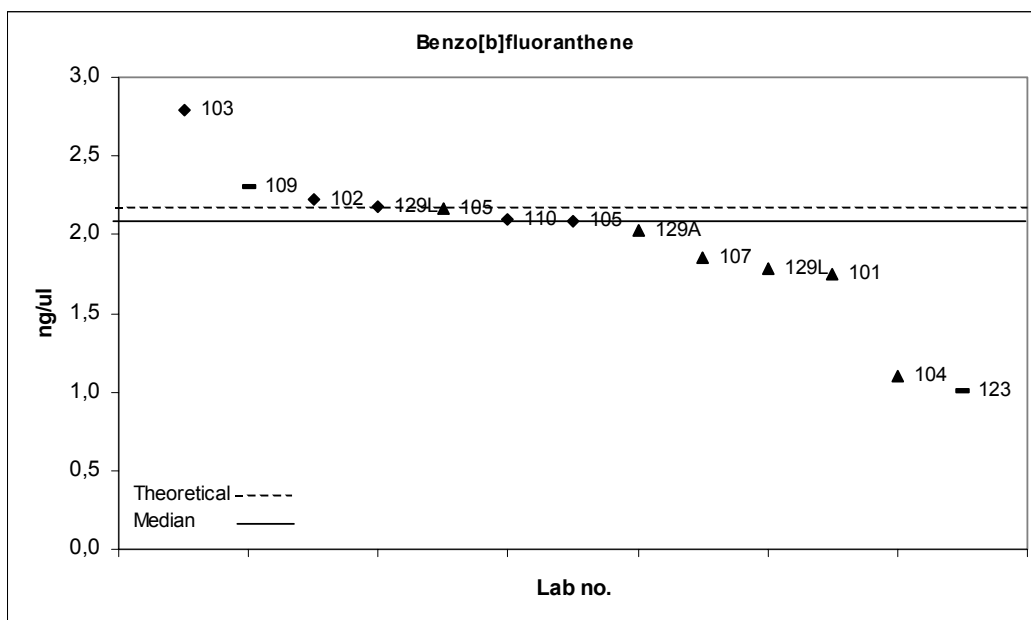
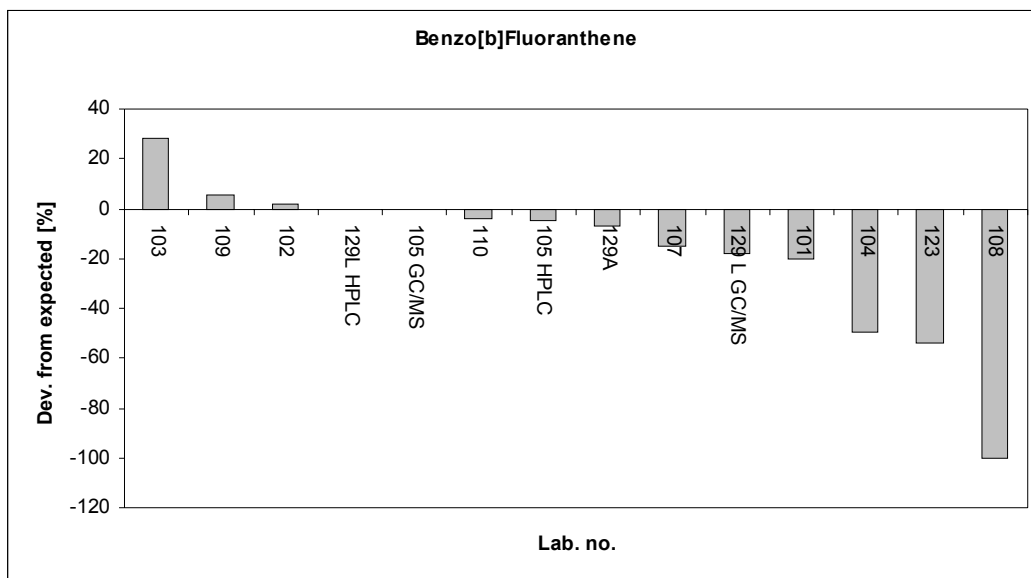
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound: Chrysene
 Theoretical value: 1,67
 Unit: ng/ul
 Number of laboratories: 16
 Arithm. Mean: 1,28
 Median: 1,35

Lab. no.	ng/ul	Lab. no.	ng/ul
122	13,50*	129A	1,35
102	1,70	103	1,28
105 HPLC	1,66	129L GC/MS	1,20
107	1,58	108	1,17
109	1,53	101	1,13
105 GC/MS	1,47	130	0,95
129L HPLC	1,43	123	0,71
110	1,43	104	0,55

*Not used for determination of mean



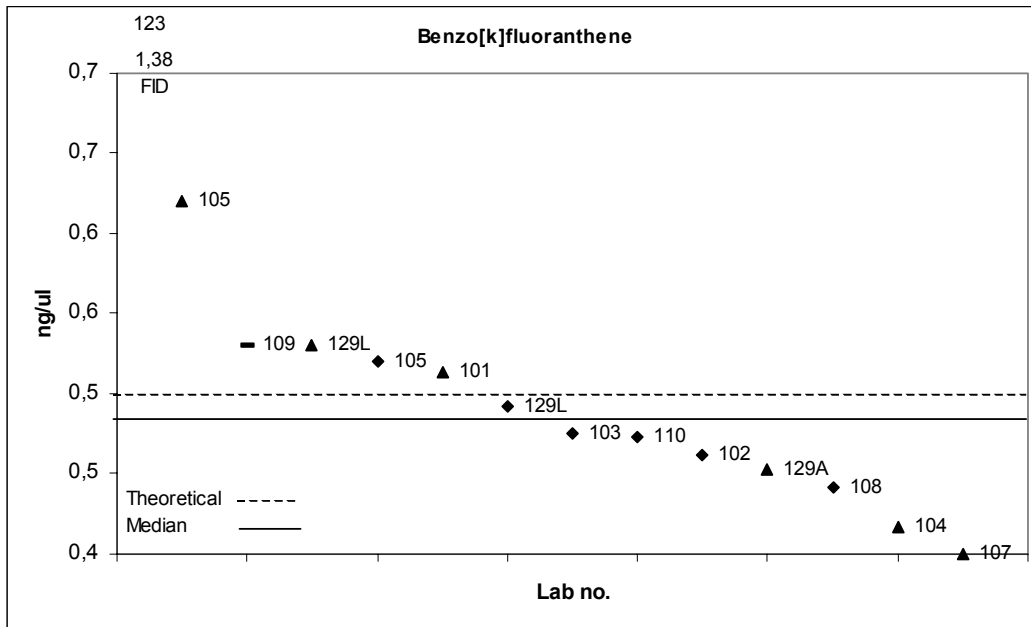
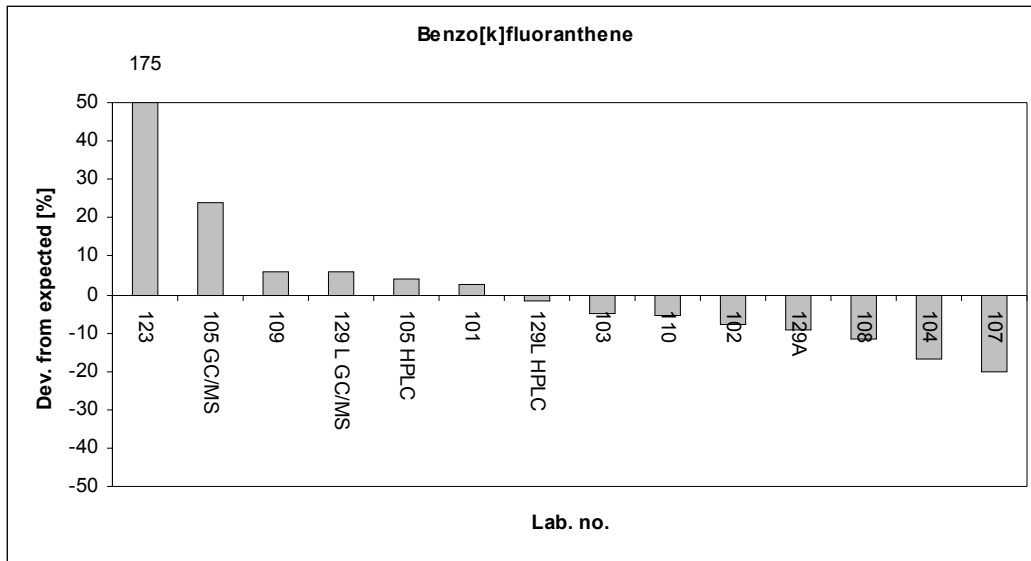
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Benzo[b]fluoranthene
Theoretical value:	2,18
Unit:	ng/ul
Number of laboratories:	13
Aritm. Mean	2,028
Median	2,080

Lab. no.	ng/ul
103	2,791
109	2,300
102	2,220
129L HPLC	2,172
105 GC/MS	2,170
110	2,093
105 HPLC	2,080
129A	2,023
107	1,850
129L GC/MS	1,787
101	1,747
104	1,103
123	1,004*

*Not used for determination of mean



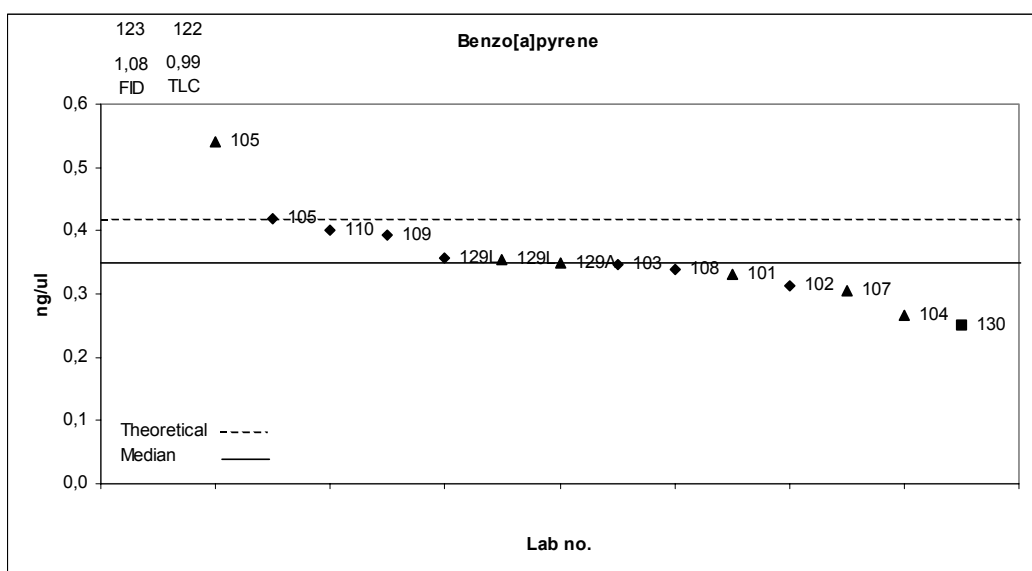
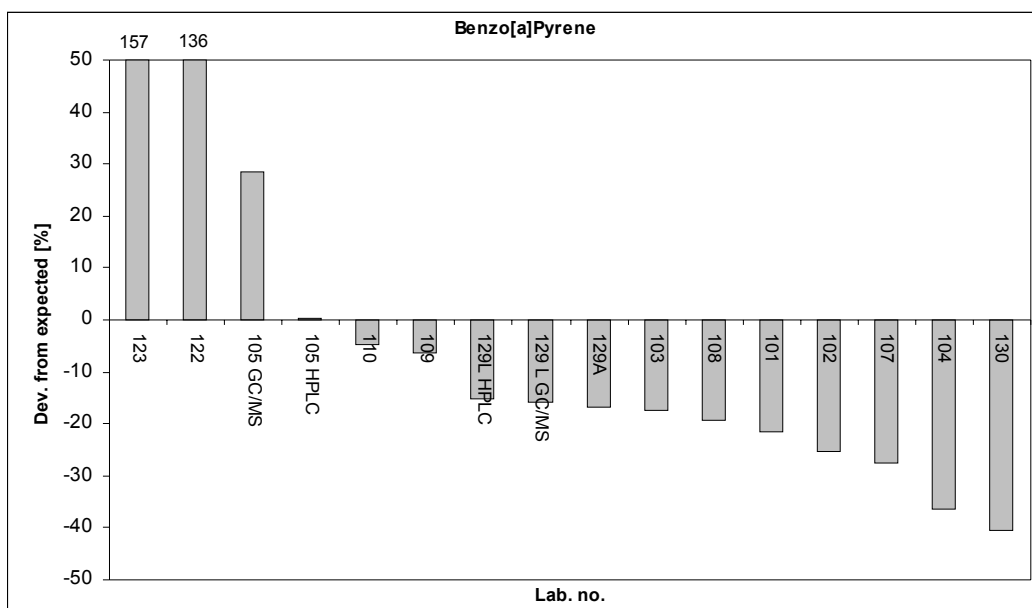
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Benzo[k]fluoranthene
Theoretical value:	0,50
Unit:	ng/ul
Number of laboratories:	14
Aritm. Mean	0,487
Median	0,484

Lab. no.	ng/ul
123	1,377*
105 GC/MS	0,620
109	0,530
129L GC/MS	0,530
105 HPLC	0,520
101	0,513
129L HPLC	0,492
103	0,476
110	0,473
102	0,462
129A	0,453
108	0,442
104	0,417
107	0,400

*Not used for determination of mean



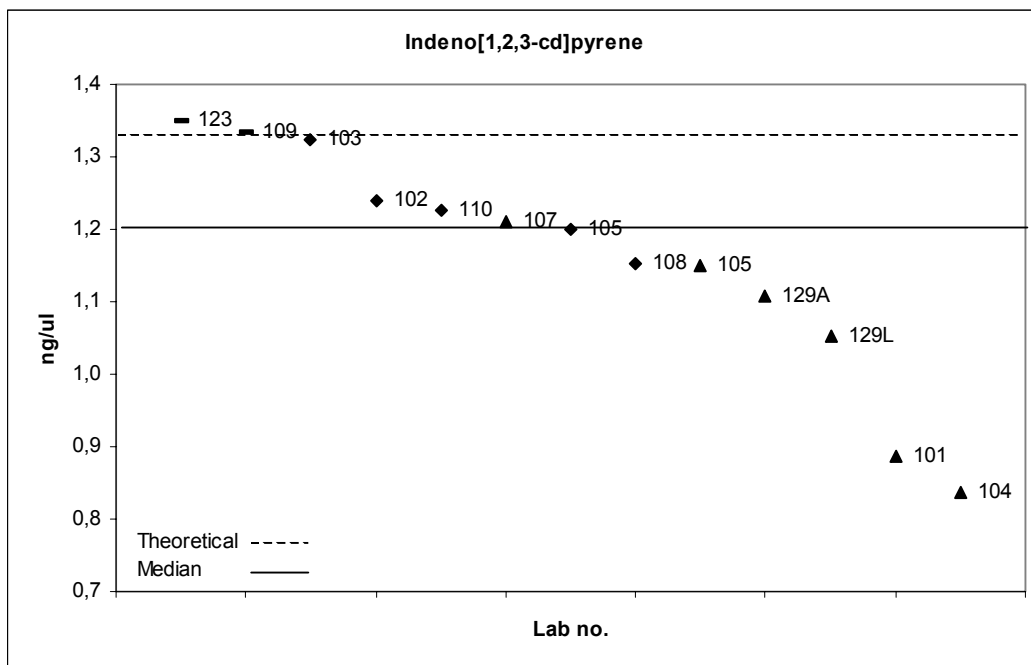
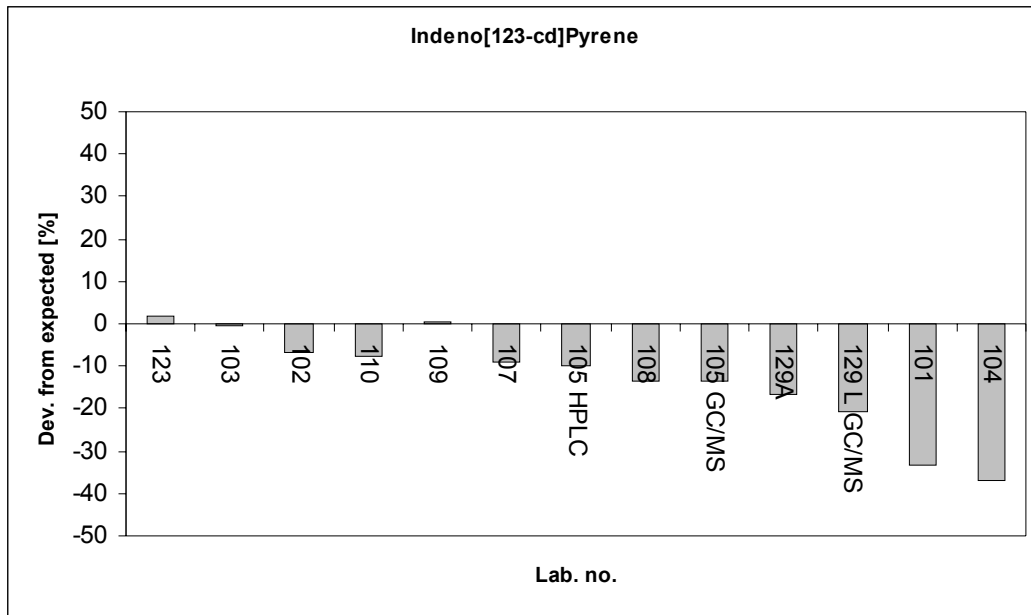
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Benzo[a]pyrene
Theoretical value:	0,42
Unit:	ng/ul
Number of laboratories:	16
Aritm. Mean	0,355
Median	0,348

Lab. no.	ng/ul
123	1,079*
122	0,990*
105 GC/MS	0,540
105 HPLC	0,420
110	0,400
109	0,393
129L HPLC	0,356
129L GC/MS	0,353
129A	0,350
103	0,347
108	0,338
101	0,330
102	0,314
107	0,305
104	0,267
130	0,250

*Not used for determination of mean

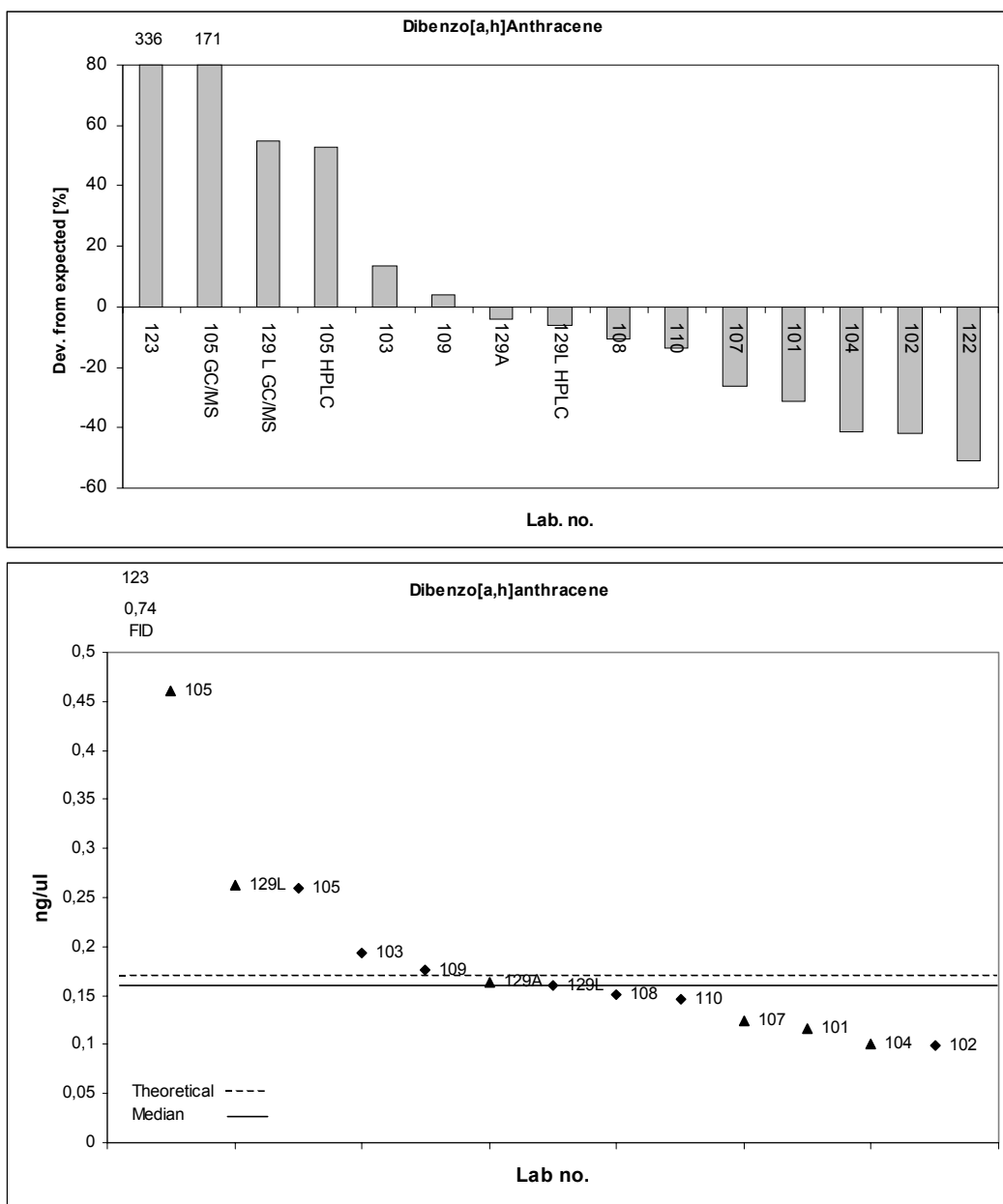


Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Indeno[1,2,3-cd]pyrene
Theoretical value:	1,33
Unit:	ng/ul
Number of laboratories:	13
Aritm. Mean	1,159
Median	1,200

Lab. no.	ng/ul
123	1,351
109	1,333
103	1,324
102	1,240
110	1,227
107	1,210
105 HPLC	1,200
108	1,152
105 GC/MS	1,150
129A	1,107
129L GC/MS	1,053
101	0,887
104	0,837



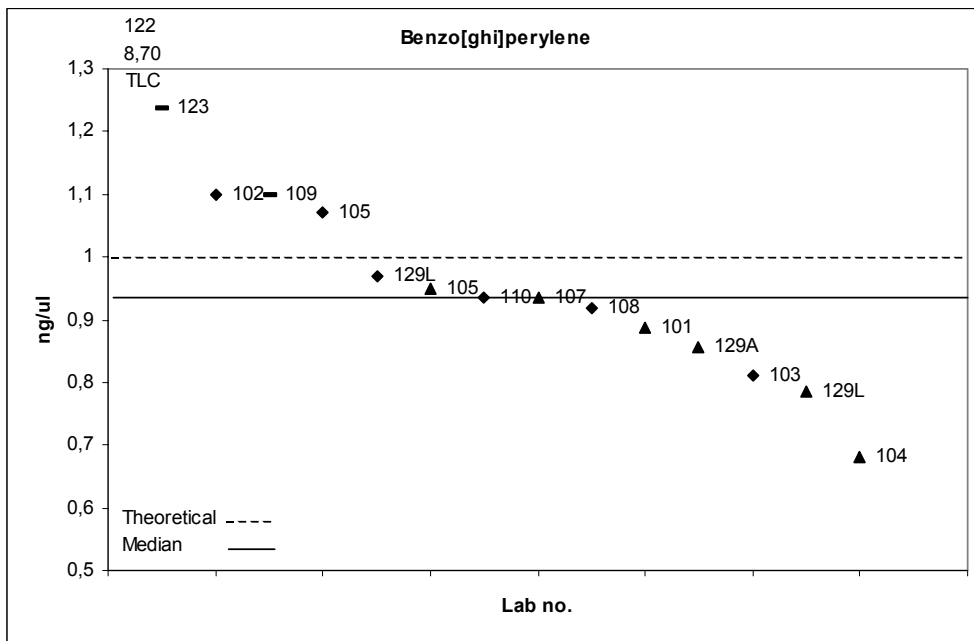
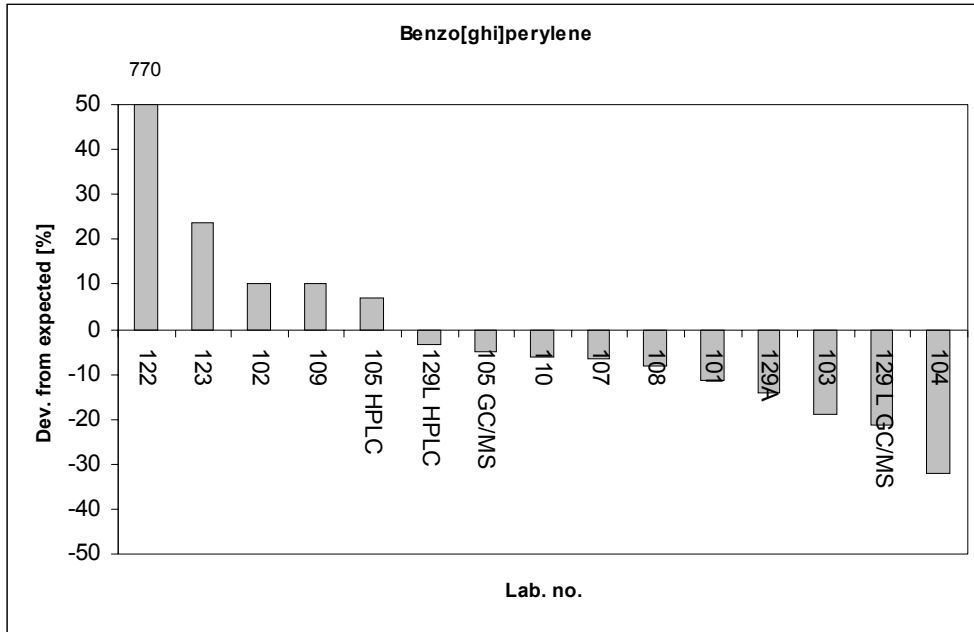
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Dibenzo[a,h]anthracene
Theoretical value:	0,17
Unit:	ng/ul
Number of laboratories:	15
Aritm. Mean	0,178
Median	0,160

Lab. no.	ng/ul
123	0,742*
105 GC/MS	0,460
129L GC/MS	0,263
105 HPLC	0,260
103	0,193
109	0,177
129A	0,163
129L HPLC	0,160
108	0,152
110	0,147
107	0,125
101	0,117
104	0,100
102	0,099
122	0,083

*Not used for determination of mean



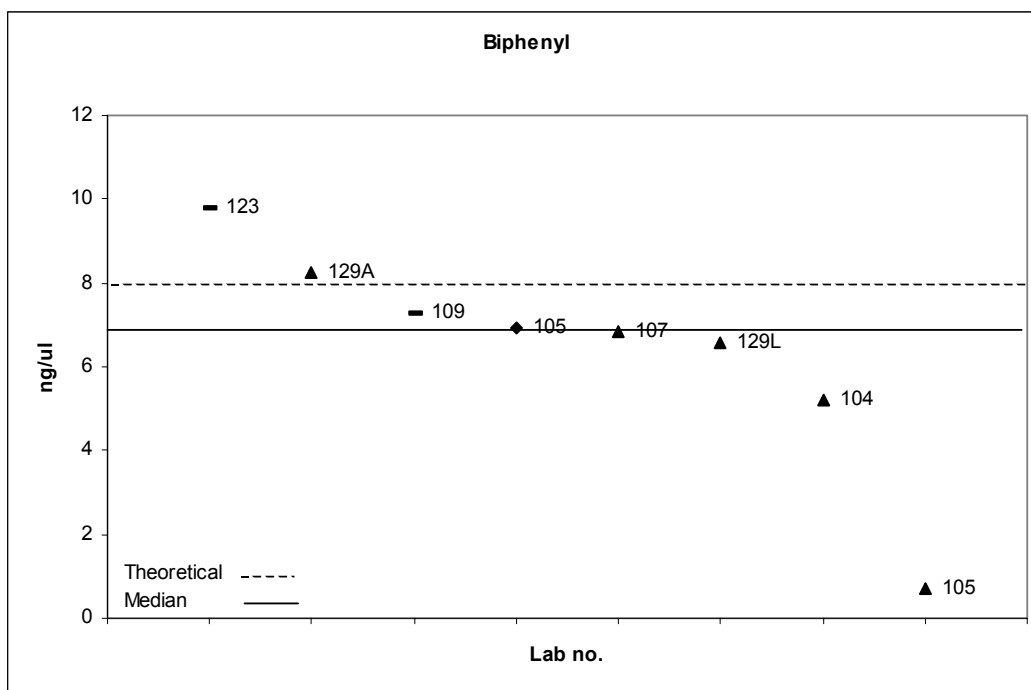
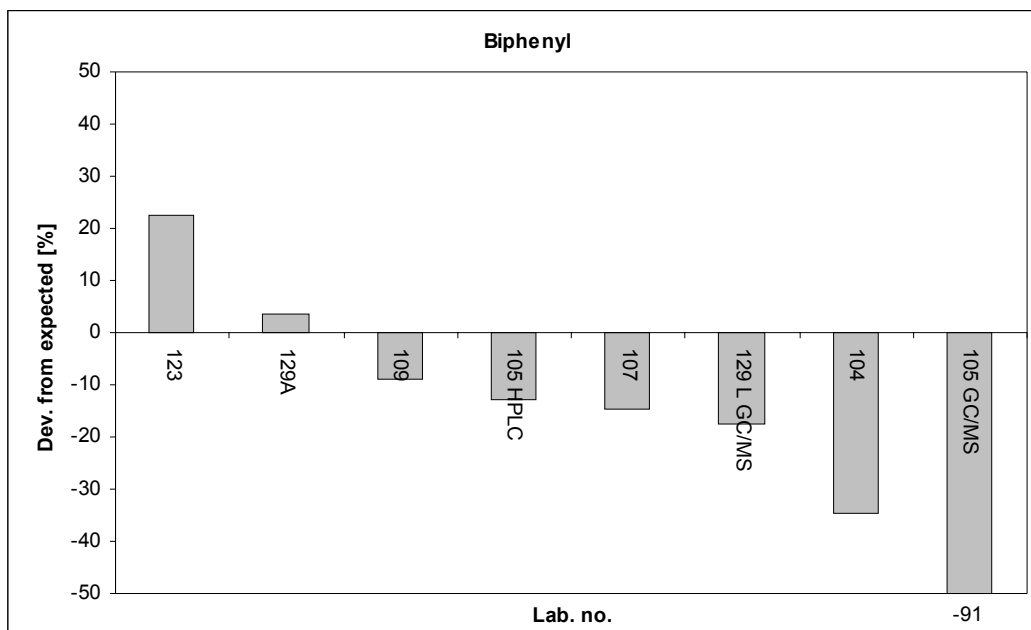
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound: Benzo[ghi]perylene
 Theoretical value: 1,00
 Unit: ng/ul
 Number of laboratories: 15
 Arithm. Mean: 0,946
 Median: 0,937

Lab. no.	ng/ul
122	8,700*
123	1,237
102	1,100
109	1,100
105 HPLC	1,070
129L HPLC	0,968
105 GC/MS	0,950
110	0,937
107	0,935
108	0,919
101	0,887
129A	0,857
103	0,812
129L GC/MS	0,787
104	0,680

*Not used for determination of mean



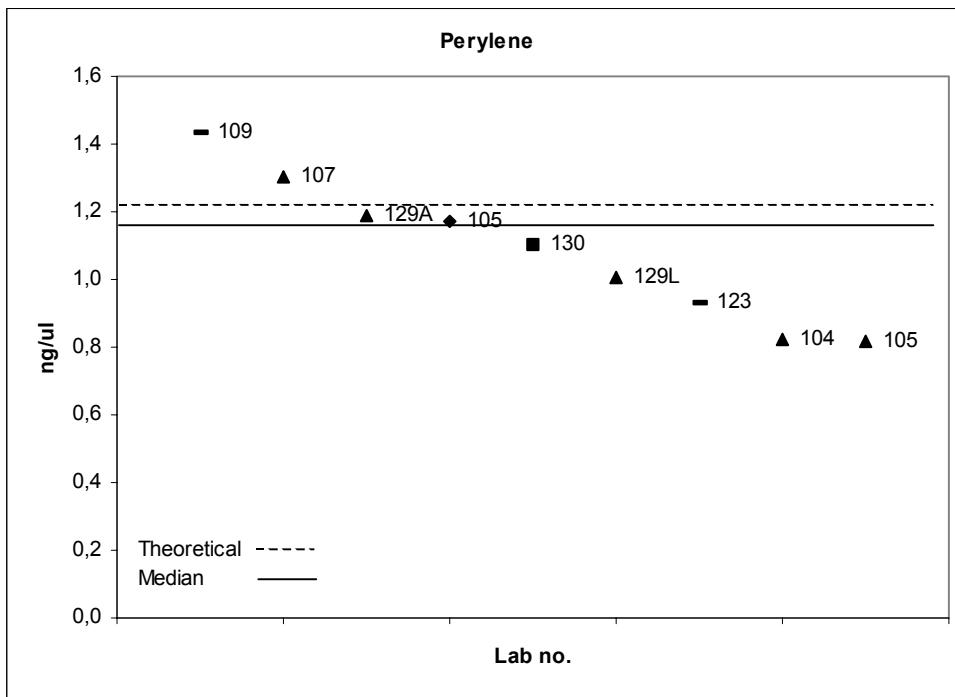
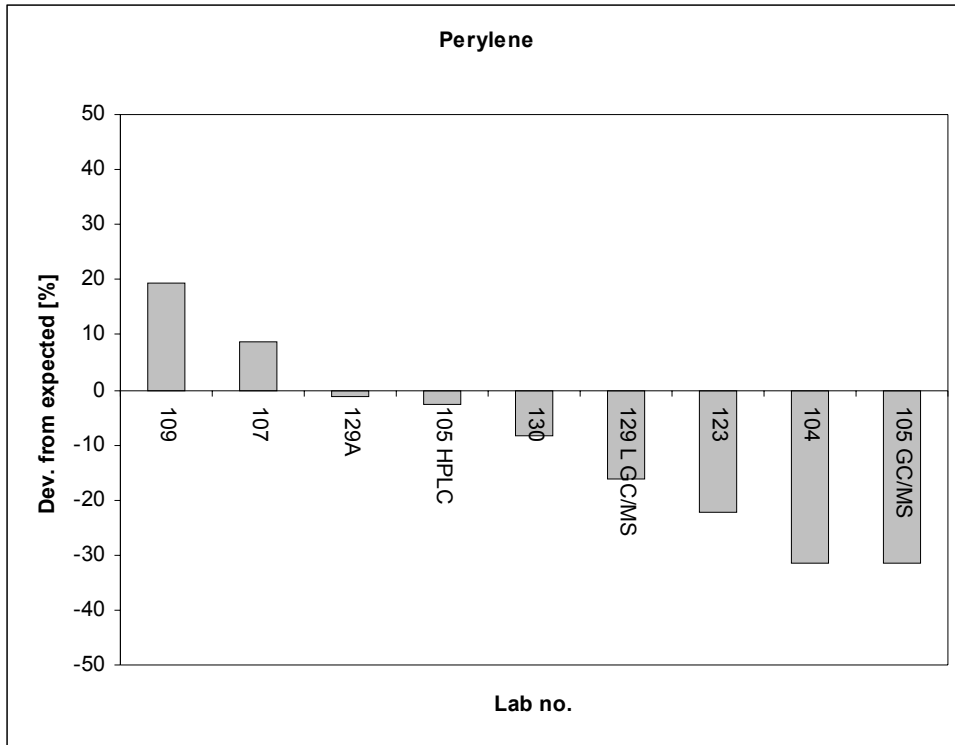
Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Biphenyl
Theoretical value:	7,98
Unit:	ng/ul
Number of laboratories:	8
Aritm. Mean	7,27
Median	6,88

Lab. no.	ng/ul
123	9,78
129A	8,26
109	7,27
105 HPLC	6,94
107	6,82
129L GC/MS	6,58
104	5,21
105 GC/MS	0,70*

*Not used for determination of mean

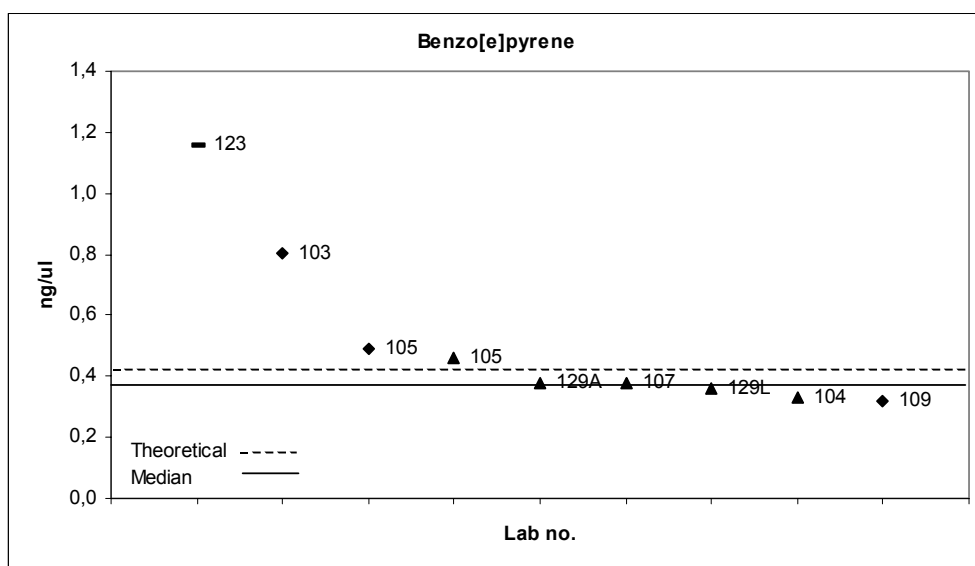
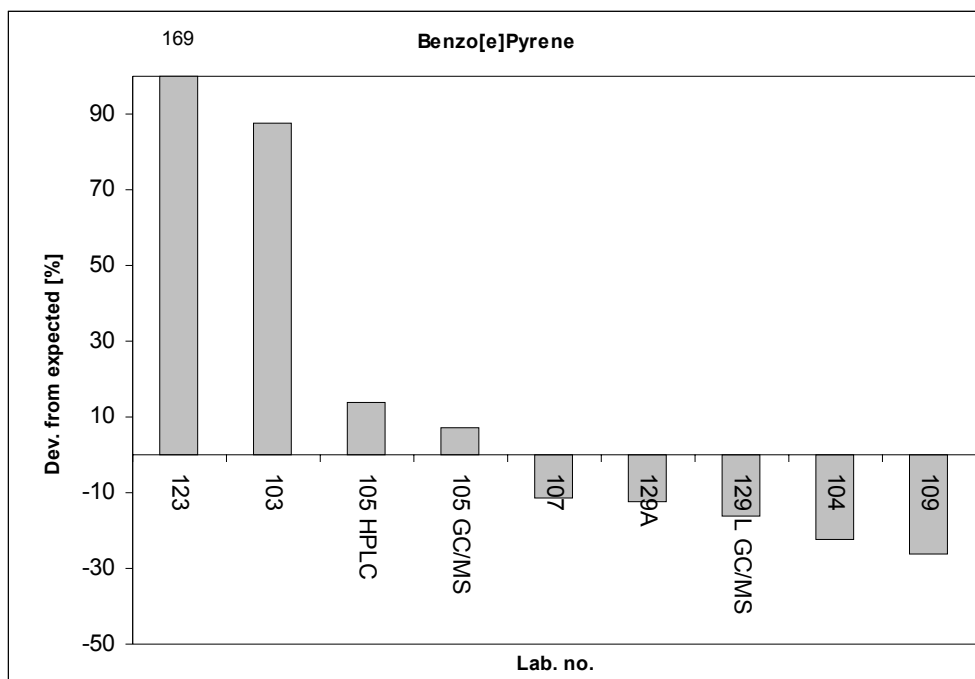


Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Perylene
Theoretical value:	1,20
Unit:	ng/ul
Number of laboratories:	8
Aritm. Mean	1,12
Median	1,14

Lab. no.	ng/ul
109	1,43
107	1,31
129A	1,19
105 HPLC	1,17
130	1,10
129L GC/MS	1,01
123	0,93
104	0,82



Results obtained by each laboratory.

Upper figure: Deviation from median in %. Lower figure: Concentrations in ng/μl.

Compound:	Benzo[e]pyrene
Theoretical value:	0,43
Unit:	ng/ul
Number of laboratories:	9
Aritm. Mean	0,440
Median	0,380

Lab. no.	ng/ul
123	1,156*
103	0,806
105 HPLC	0,490
105 GC/MS	0,460
107	0,380
129A	0,377
129L GC/MS	0,360
104	0,333
109	0,317

*Not used for determination of mean

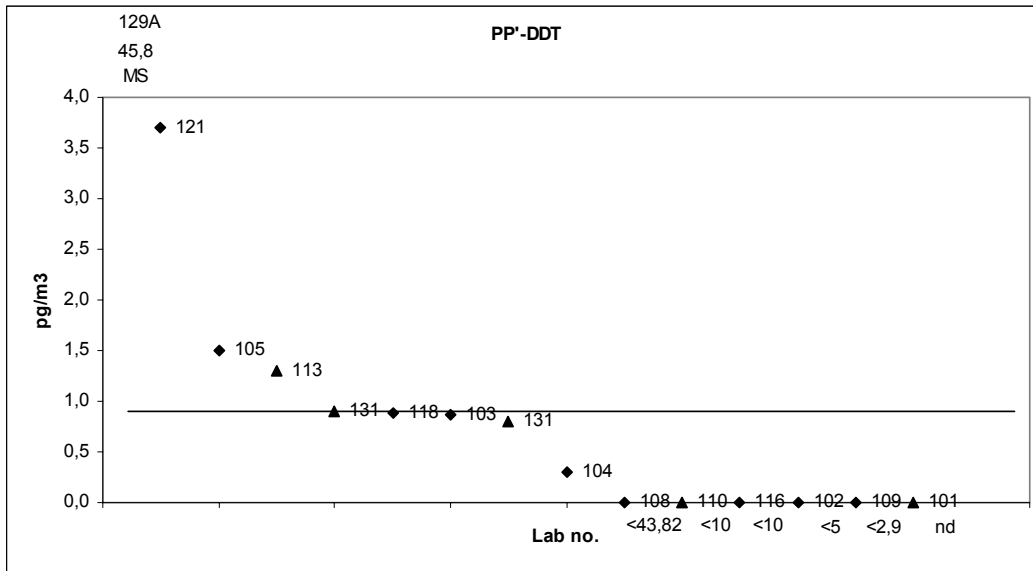
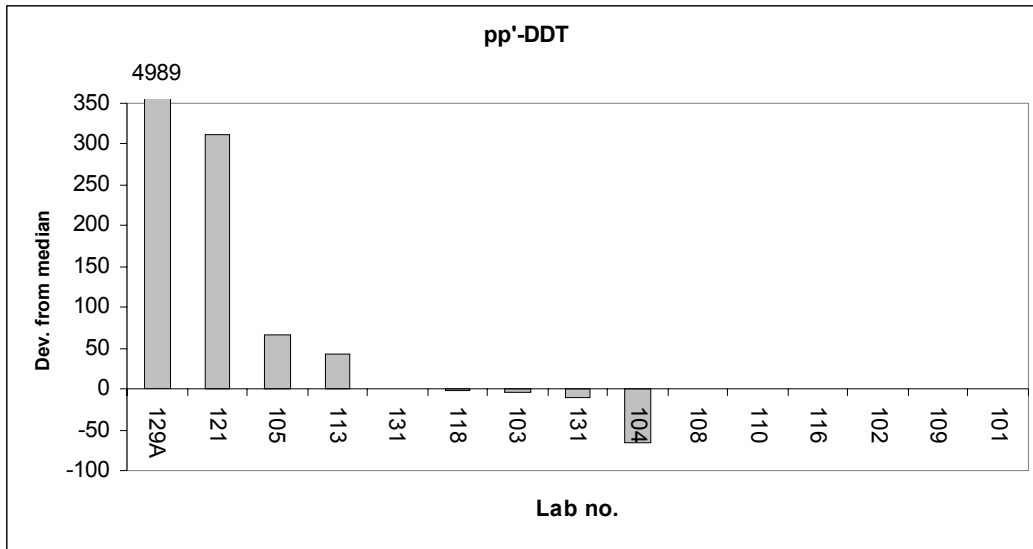
Annex 5

Organochlorine compounds, round 2, sample 1 and 2

The following pages present the results from round 2 graphically. The results for each compound are shown on two pages with the left-hand page giving the sample 1 results and the right-hand side the corresponding data from sample 2.

The results have been given as deviations from the median in per cent (upper graph) and as concentration based on a 500 m³ sample volume (lower graph).

◆	GC/ECD
▲	GC/MS

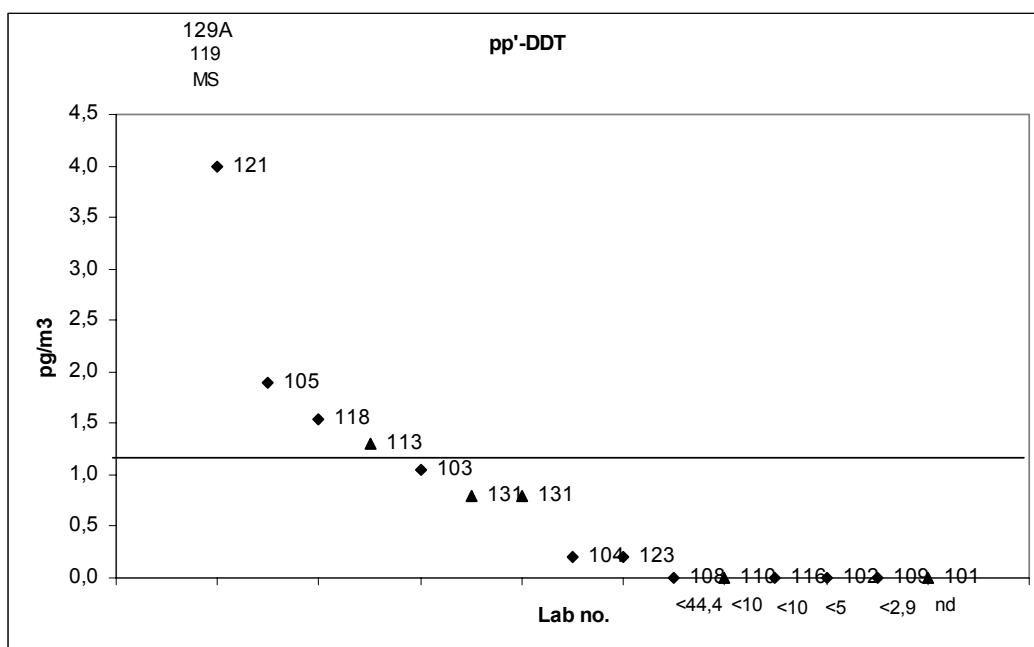
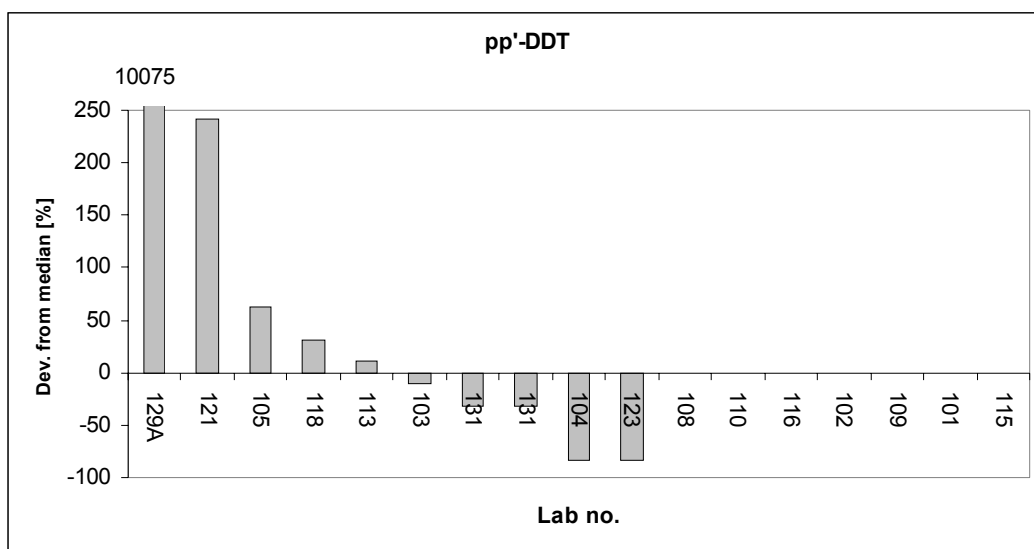


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories:14 Median 0,900

Lab. no.	Dev. f median %	pg/m3
129A	4989	45,8
121	311	3,7
105	67	1,5
113	44	1,292
131	0	0,9
118	-2	0,88
103	-3	0,869333
131	-11	0,8
104	-67	0,3
108		<43,82
110		<10
116		<10
102		<5
109		<2,9
101		n.d

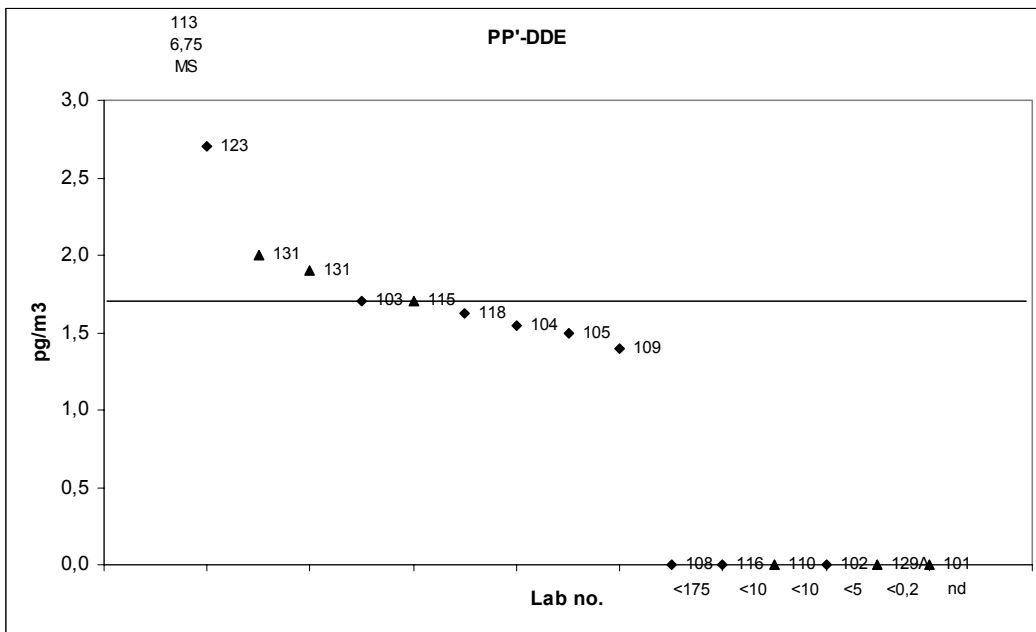
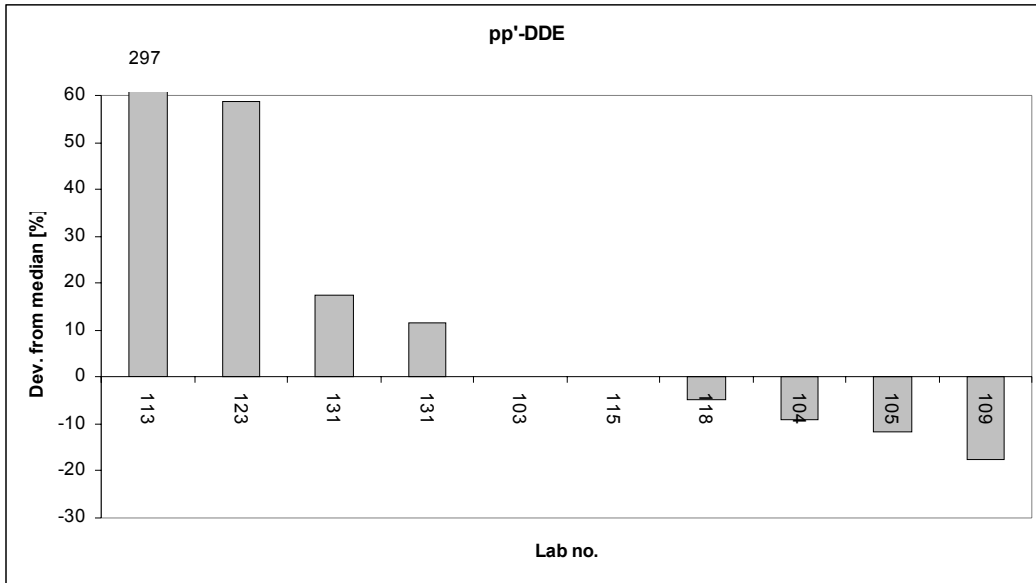


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m³. Median given as a horizontal line.

Number of laboratories: 15 Median 1,17

Lab. no.	Dev. from median %	pg/m ³
129A	10075	119,3
121	241	4
105	62	1,9
118	31	1,54
113	11	1,296
103	-11	1,0489333
131	-32	0,8
131	-32	0,8
104	-83	0,2
123	-83	0,2
108		<44,442
110		<10
116		<10
102		<5
109		<2,9
101		n.d

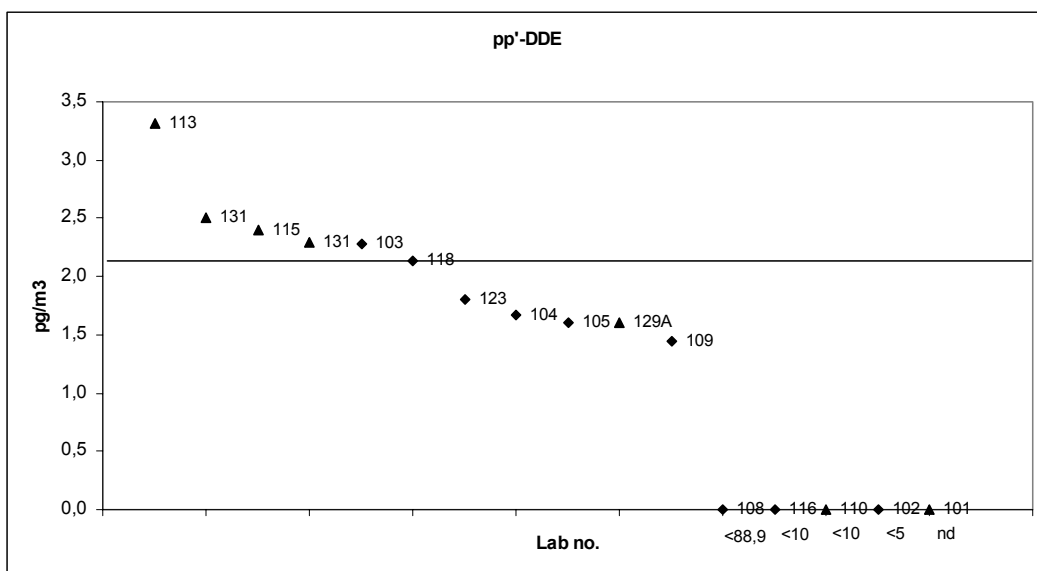
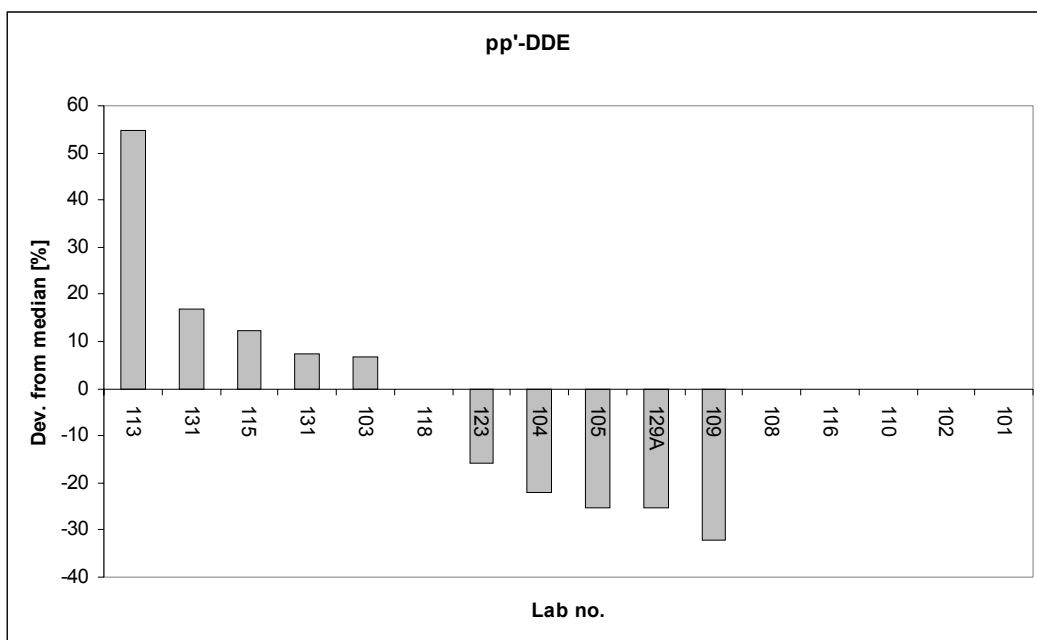


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m³. Median given as a horizontal line.

Number of laboratories: 15 Median 1,7007

Lab. no.	Dev. from median %	pg/m ³
113	297	6,749
123	59	2,7
131	18	2
131	12	1,9
103	0	1,701333333
115	0	1,7
118	-5	1,62
104	-9	1,545454545
105	-12	1,5
109	-18	1,4
108		<175,28
116		<10
110		<10
102		<5
129A		<0,2
101		n.d

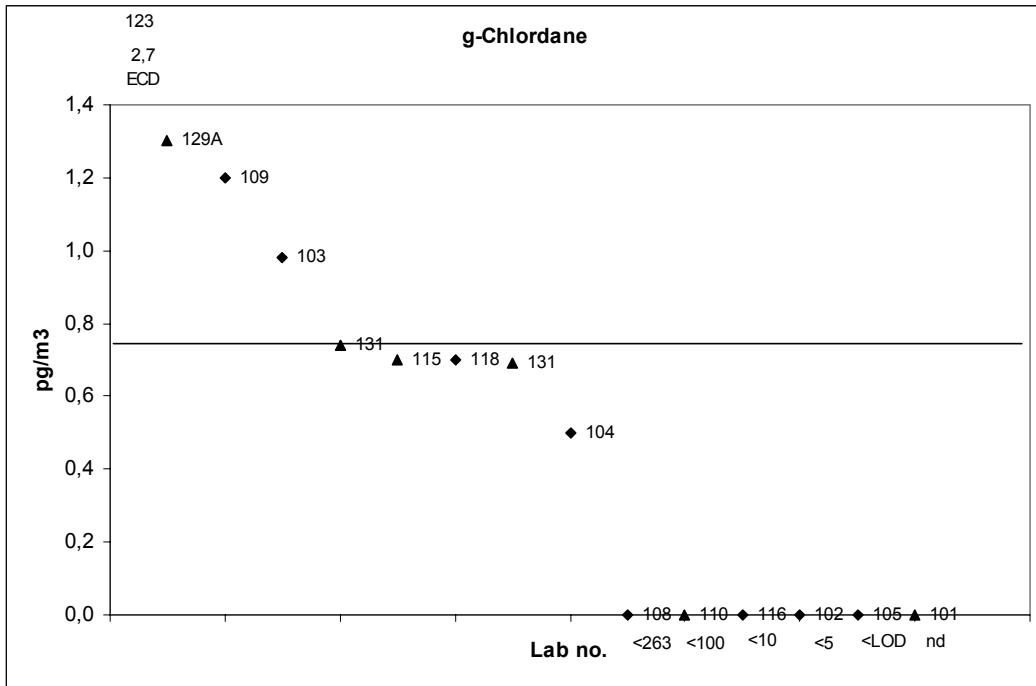
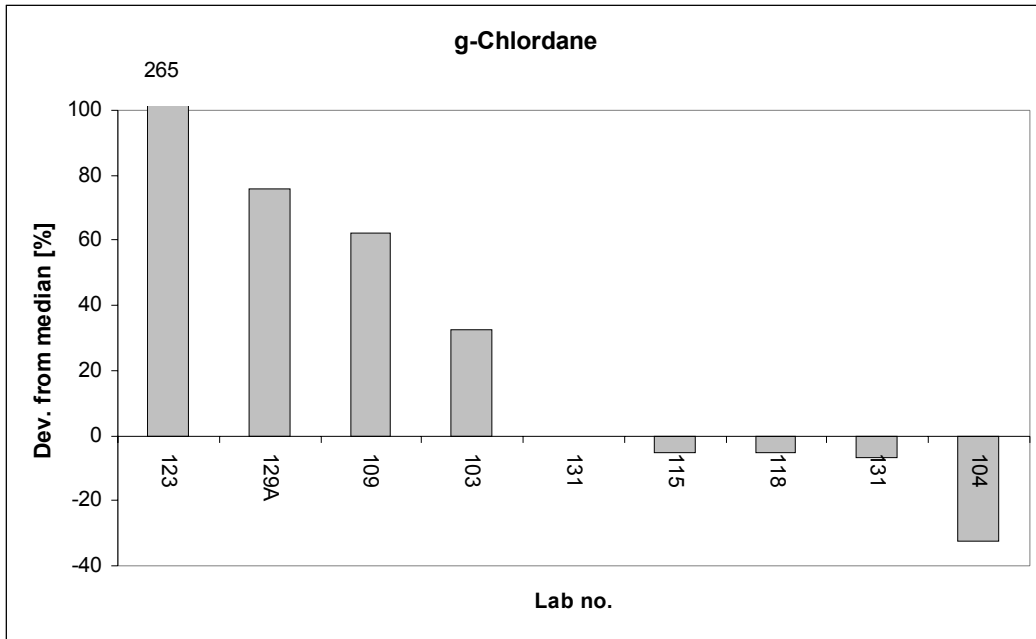


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median 2,14

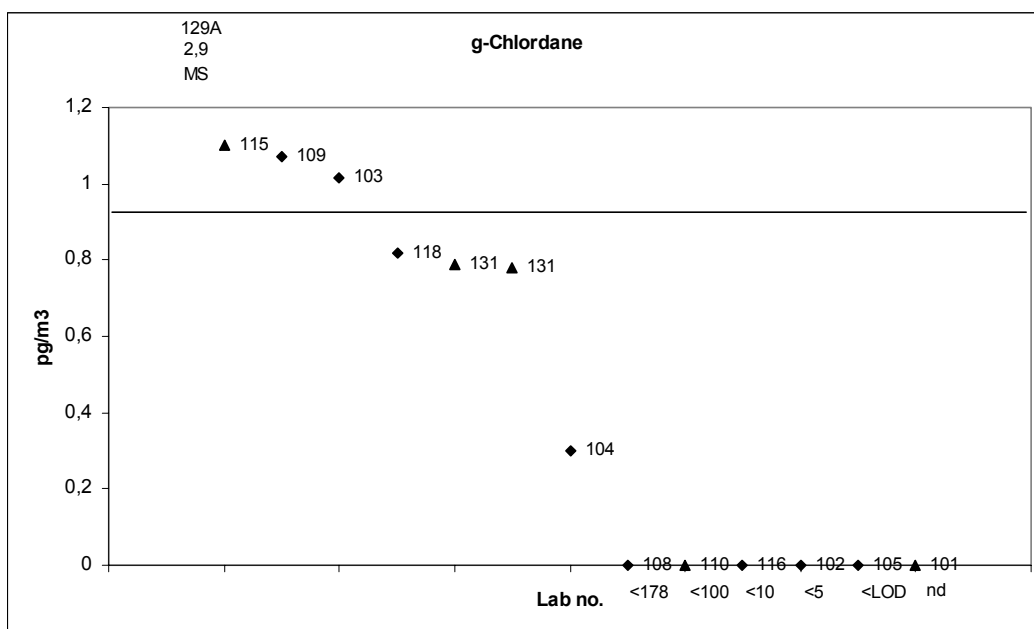
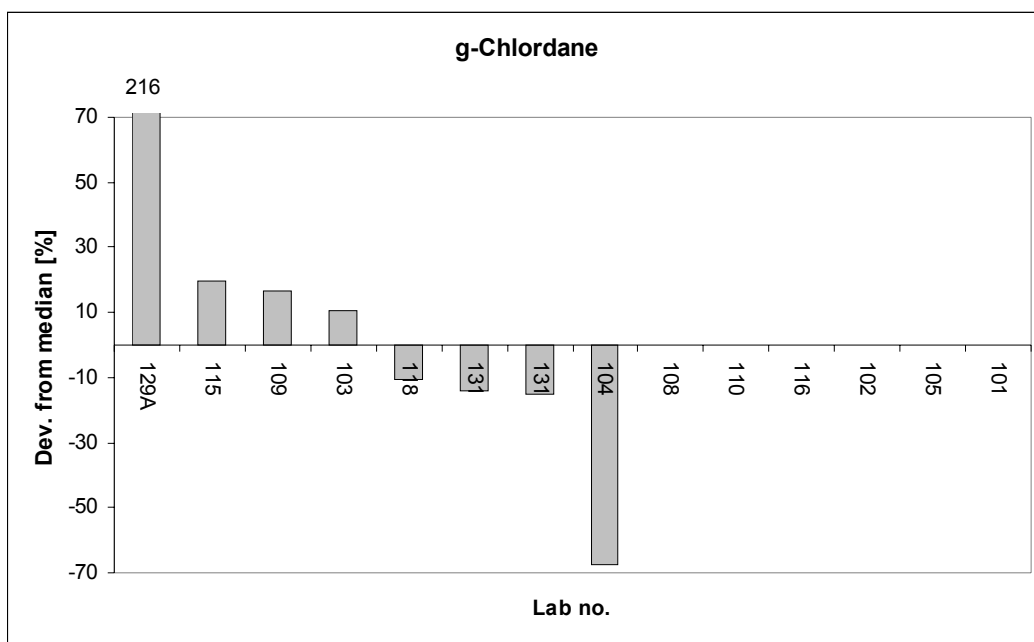
Lab. no.	Dev. from median%	pg/m3
113	55	3,312
131	17	2,5
115	12	2,4
131	7	2,3
103	7	2,281333333
118	0	2,14
123	-16	1,8
104	-22	1,666666667
105	-25	1,6
129A	-25	1,6
109	-32	1,45
108		<88,884
116		<10
110		<10
102		<5
101		n.d



Upper figure: Deviation from median in %.
 Lower figure: Concentrations in pg/m³. Median given as a horizontal line.

Number of laboratories: 14 Median: 0,74

Lab. no.	Dev. from median %	pg/m ³
123	265	2,7
129A	76	1,3
109	62	1,2
103	33	0,981333333
131	0	0,74
115	-5	0,7
118	-5	0,7
131	-7	0,69
104	-32	0,5
108		<262,92
110		<100
116		<10
102		<5
105		<LOD
101		n.d

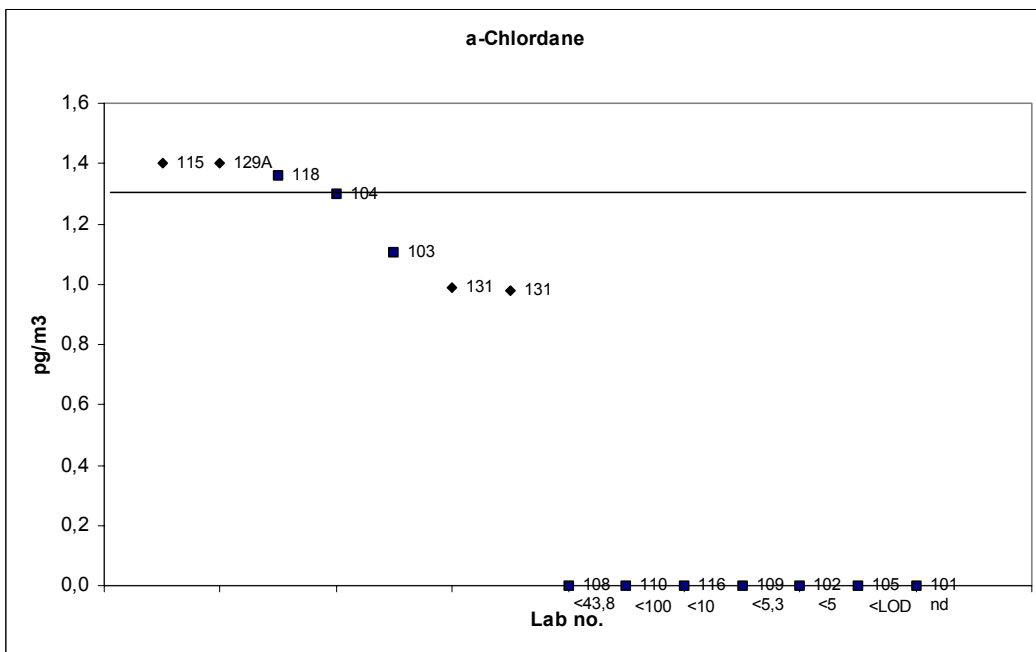
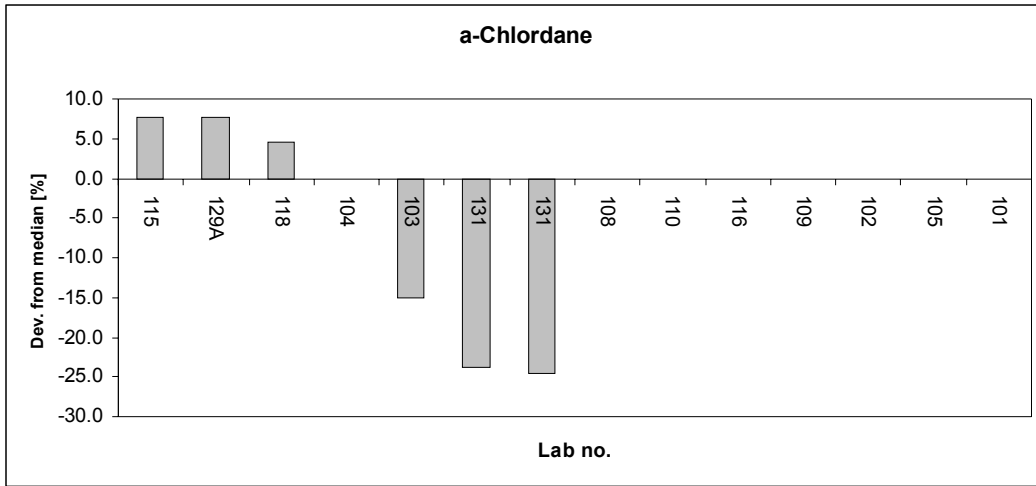


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,92

Lab. no.	Dev. from median %	pg/m ³
129A	216	2,9
115	20	1,1
109	17	1,07
103	11	1,016
118	-11	0,82
131	-14	0,79
131	-15	0,78
104	-67	0,3
108		<177,768
110		<100
116		<10
102		<5
105		<LOD
101		n.d.



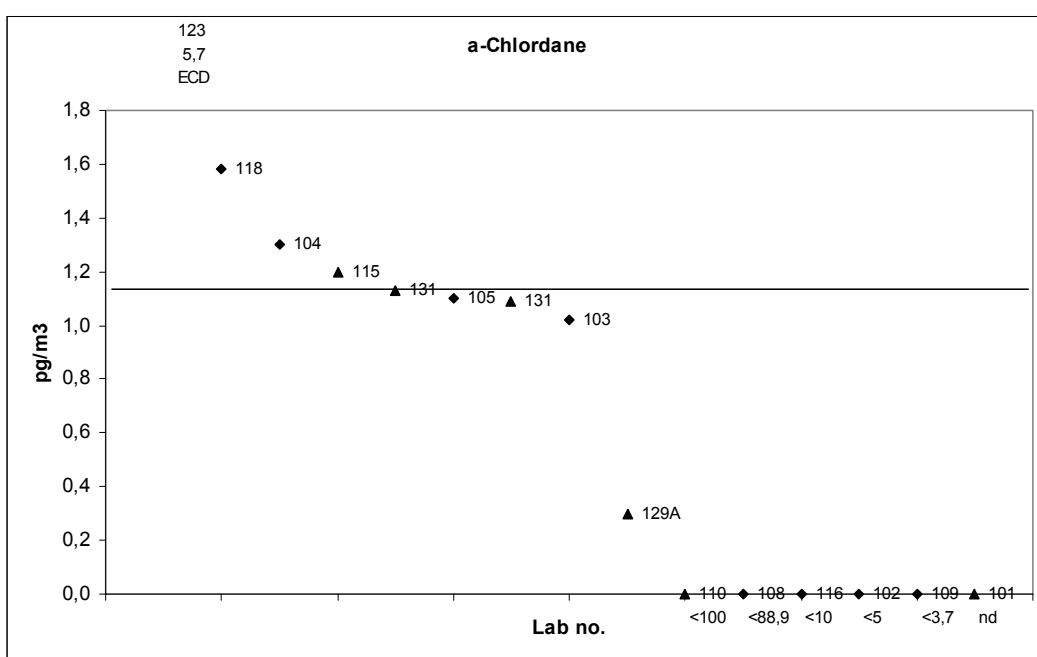
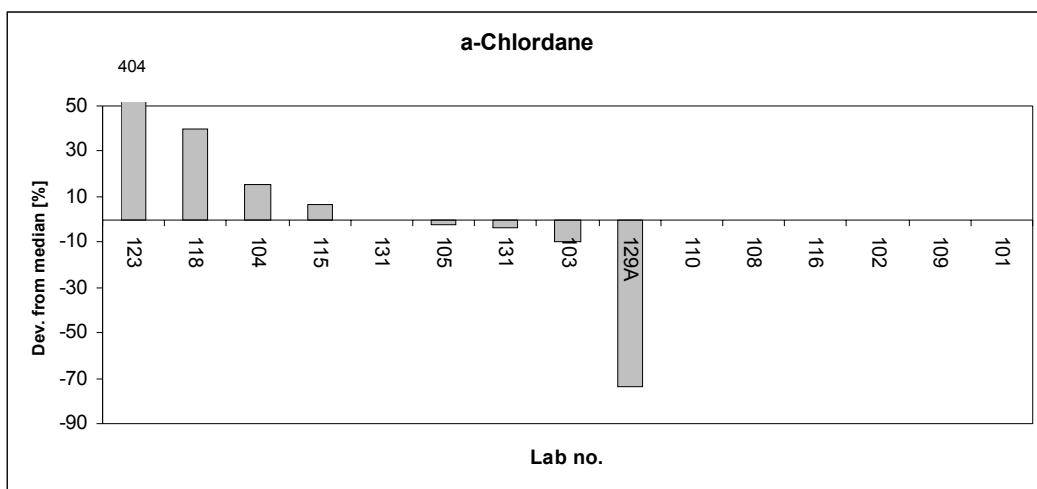
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 1,3

Lab. no.	Dev. from median %	pg/m3
115	7,69	1,4
129A	7,69	1,4
118	4,62	1,36
104	0,00	1,3
103	-14,97	1,105333333
131	-23,85	0,99
131	-24,62	0,98
108		<43,82
110		<100
116		<10
109		<5,3 (1)
102		<5
105		<LOD
101		n.d.

(1) Interference

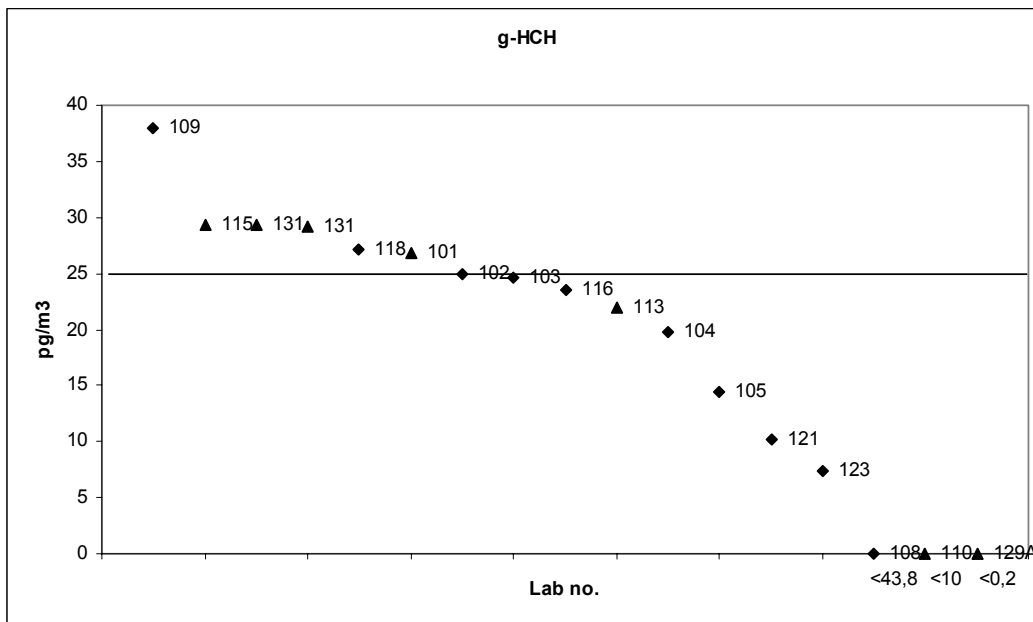
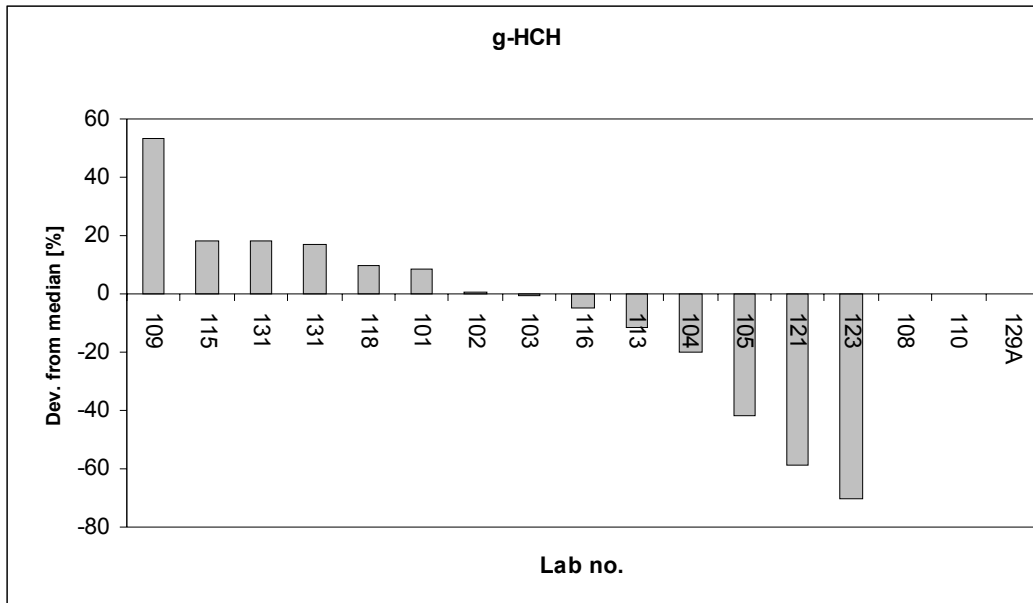


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 14 Median: 1,13

Lab. no.	Dev. from median %	pg/m3
123	404	5,7
118	40	1,58
104	15	1,3
115	6	1,2
131	0	1,13
105	-3	1,1
131	-4	1,09
103	-10	1,02
129A	-73	0,3
110		<100
108		<88,884
116		<10
102		<5
109		<3,7 (1)
101		n.d.



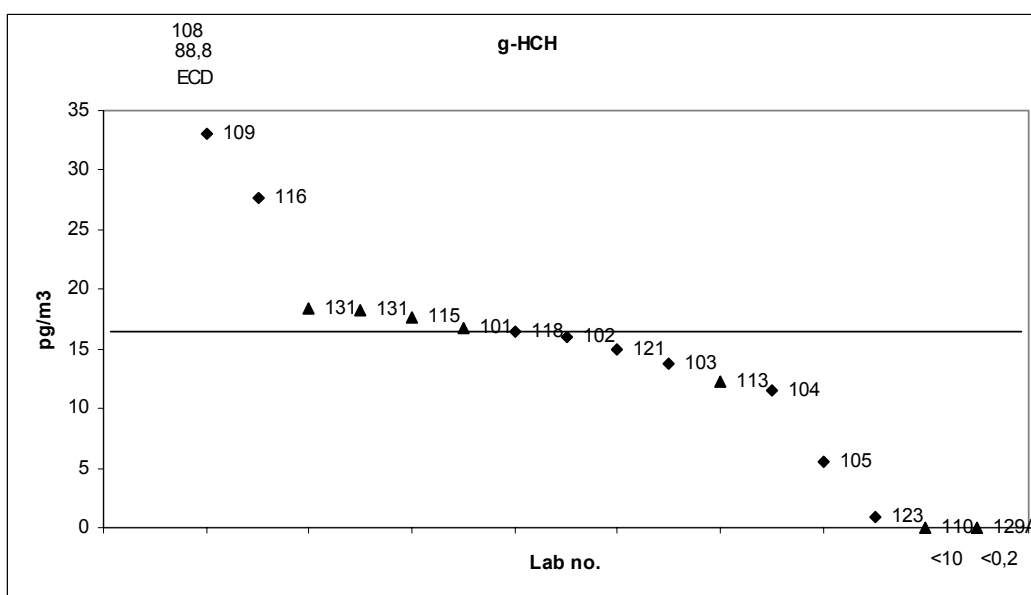
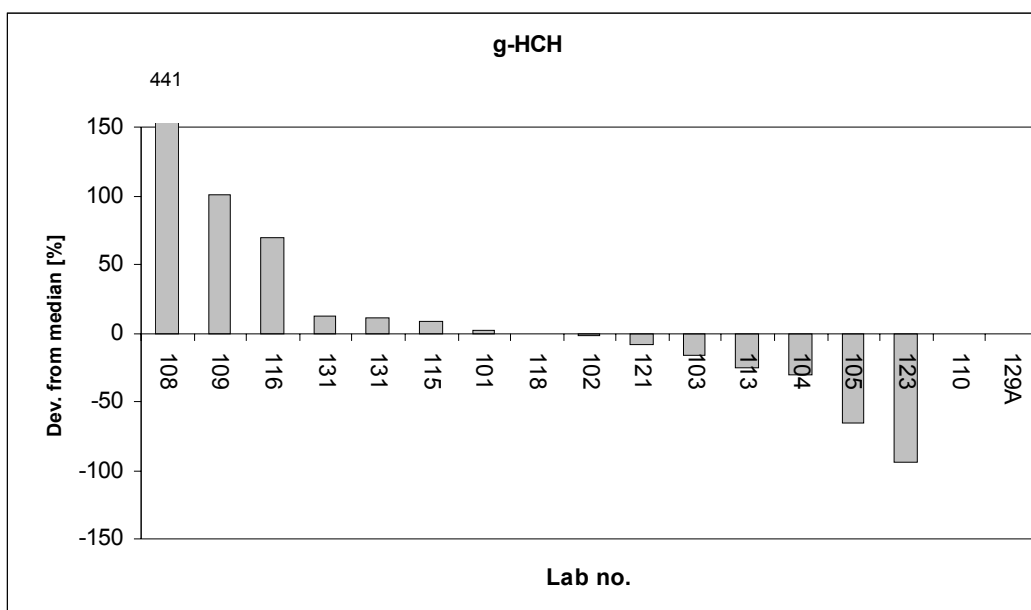
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 24.8

Lab. no.	Dev. from median %	pg/m3
109	53	38
115	18	29,4
131	18	29,3
131	17	29,1
118	10	27,2
101	8	26,9
102	1	25
103	-1	24,64666667
116	-5	23,6
113	-11	22*
104	-20	19,8
105	-42	14,4
121	-59	10,2
123	-70	7,4
108		<43,82
110		<10
129A		<0,2

* out of calibration range

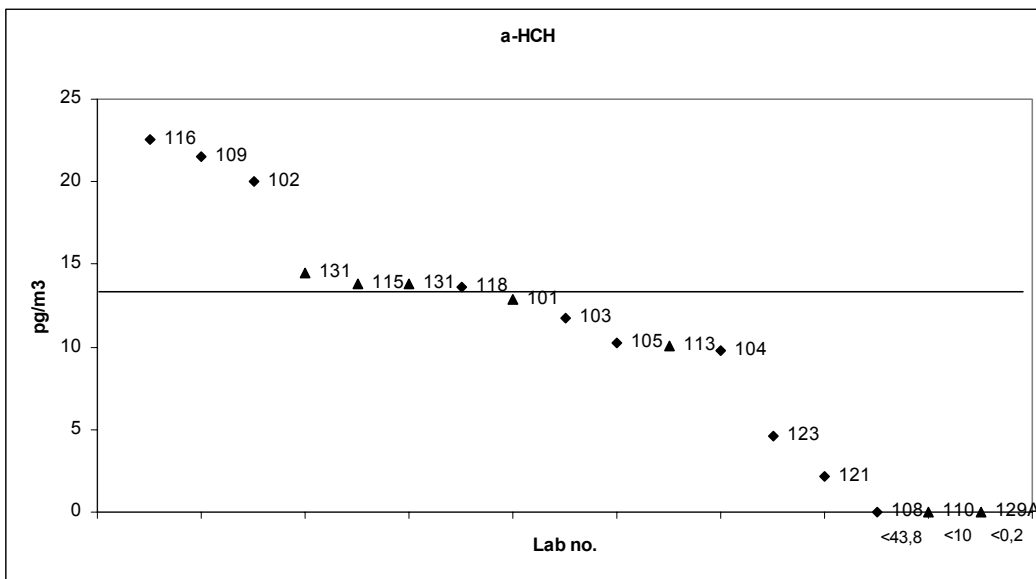
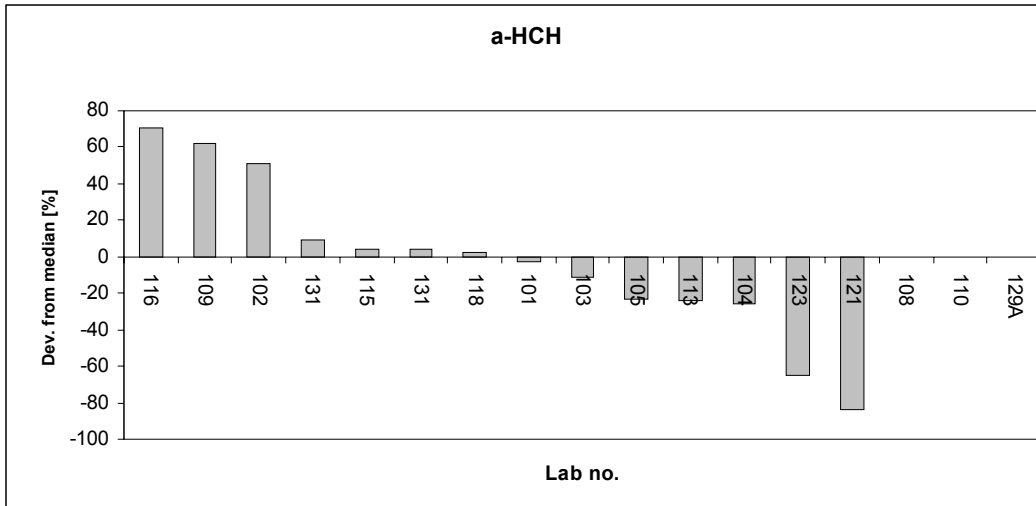


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 16,4

Lab. no.	Dev. from median %	pg/m3
108	441	88,795116
109	101	33
116	69	27,7
131	12	18,4
131	11	18,2
115	8	17,7
101	2	16,7
118	0	16,4
102	-2	16
121	-9	15
103	-16	13,74933333
113	-25	12,336
104	-30	11,5
105	-66	5,6
123	-94	0,92
110		<10
129A		<0,2

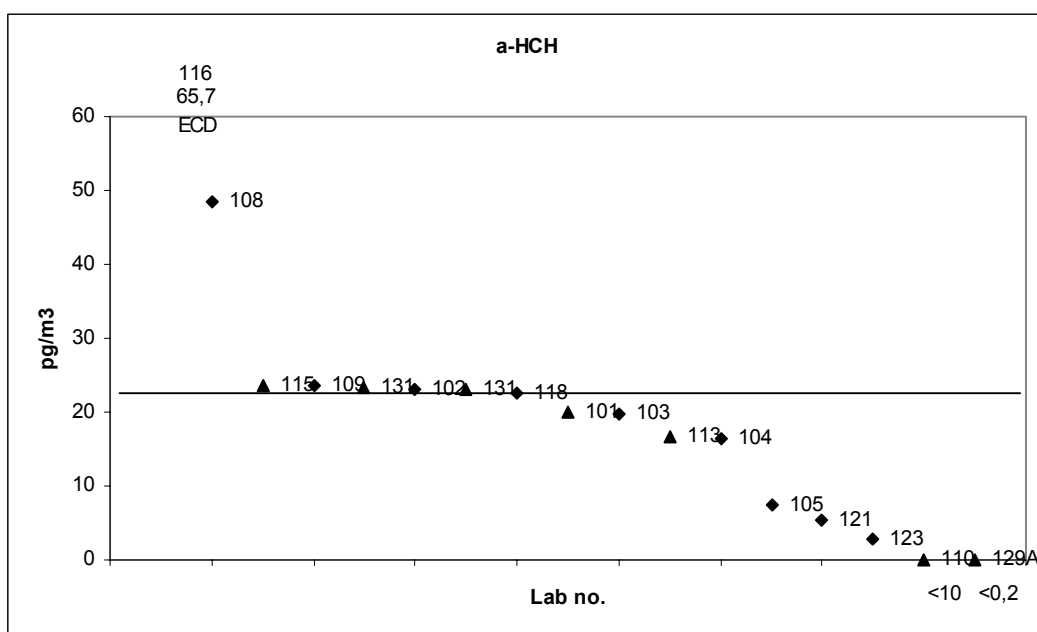
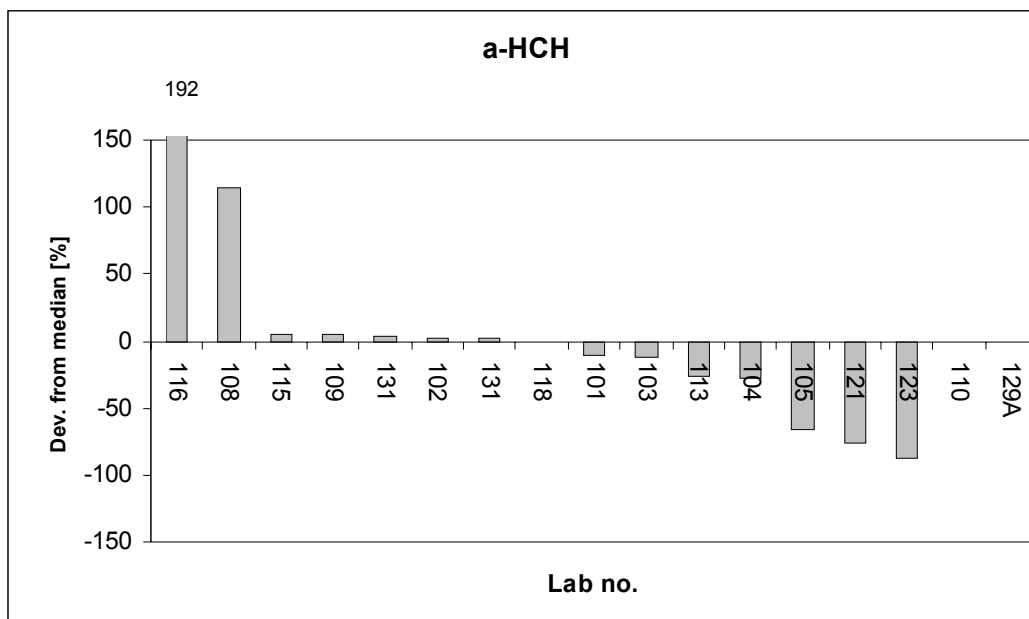


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 13,25

Lab. no.	Dev. from median %	pg/m3
116	71	22,6
109	62	21,5
102	51	20
131	9	14,5
115	4	13,8
131	4	13,8
118	3	13,6
101	-3	12,9
103	-12	11,72266667
105	-23	10,2
113	-24	10,03
104	-26	9,8
123	-65	4,6
121	-83	2,2
108		<43,82
110		<10
129A		<0,2

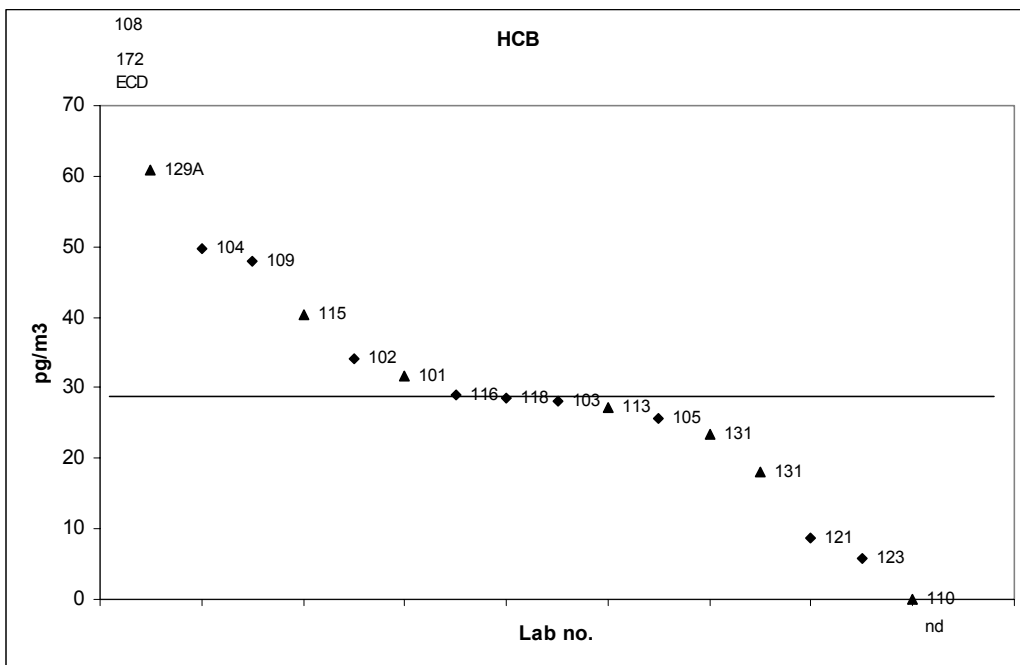
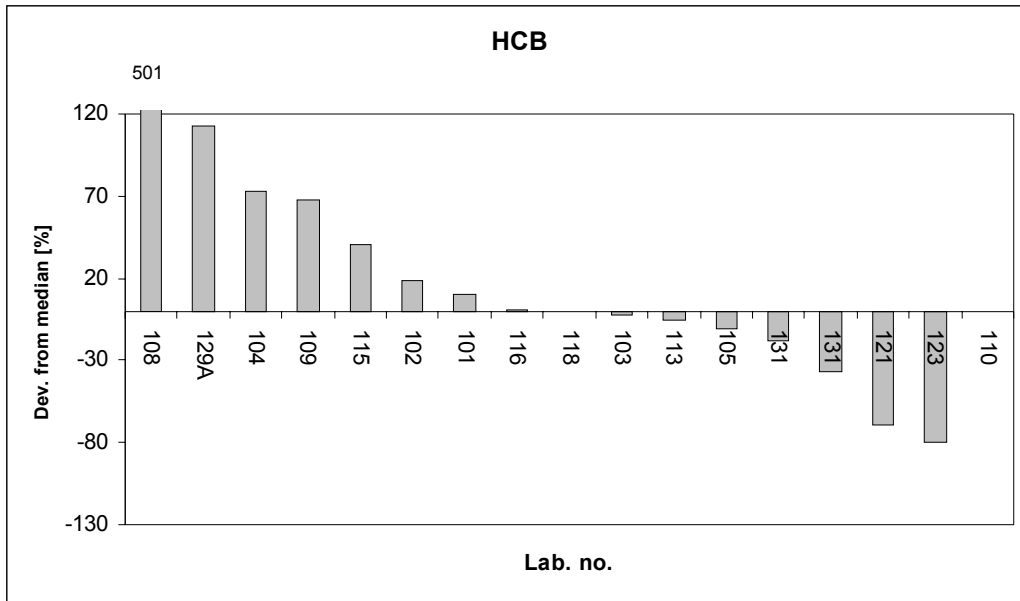


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 22,5

Lab. no.	Dev. from median %	pg/m ³
116	192	65,7
108	115	48,352896
115	5	23,7
109	4	23,5
131	4	23,3
102	2	23
131	2	23
118	0	22,5
101	-11	20,1
103	-12	19,8
113	-26	16,544
104	-27	16,4
105	-67	7,5
121	-76	5,4
123	-88	2,8
110		<10
129A		<0,2

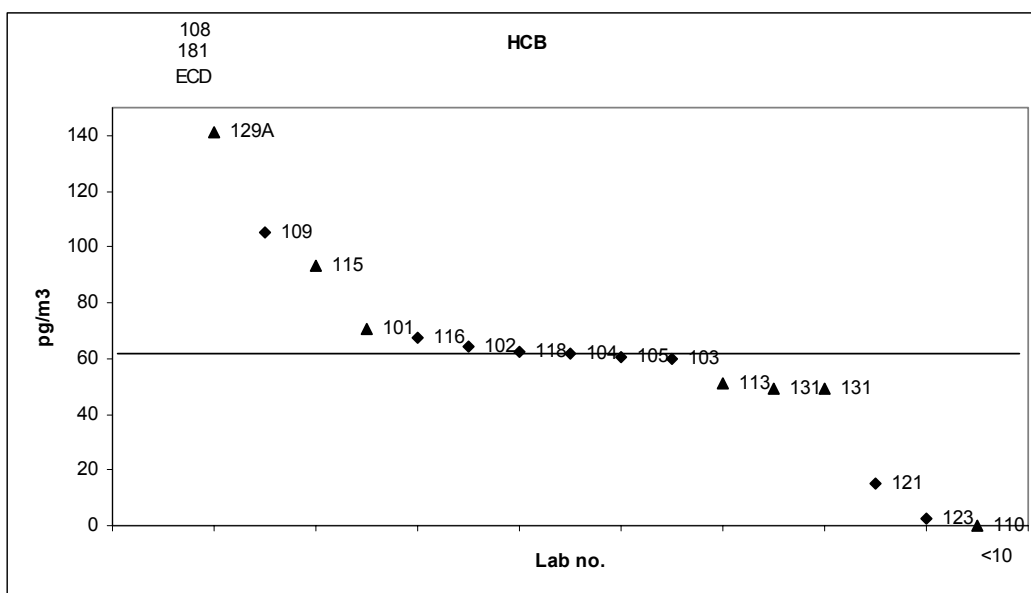
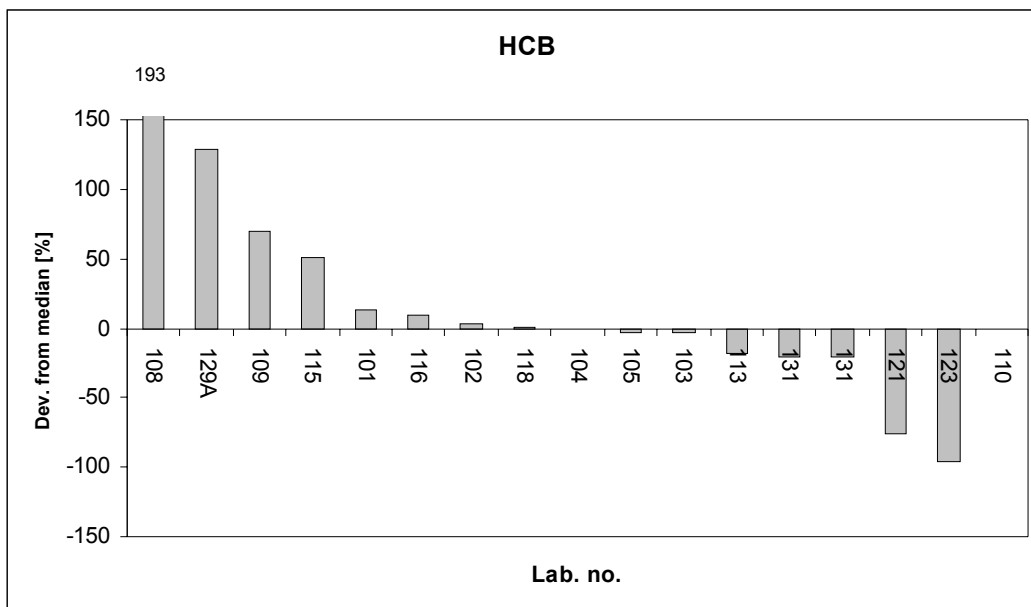


Upper figure: Deviation from median in %.
 Lower figure: Concentrations in pg/m³. Median given as a horizontal line.

Number of laboratories: 16 Median: 28,7

Lab. no.	Dev. from median %	pg/m3
108	501	172,47552
129A	112	60,9
104	73	49,7
109	67	48
115	41	40,4
102	18	34
101	10	31,7
116	1	28,9
118	-1	28,5
103	-3	27,97866667
113	-6	27,1*
105	-10	25,7
131	-18	23,5
131	-37	18,1
121	-69	8,8
123	-80	5,8
110		<10

*Out of calib range

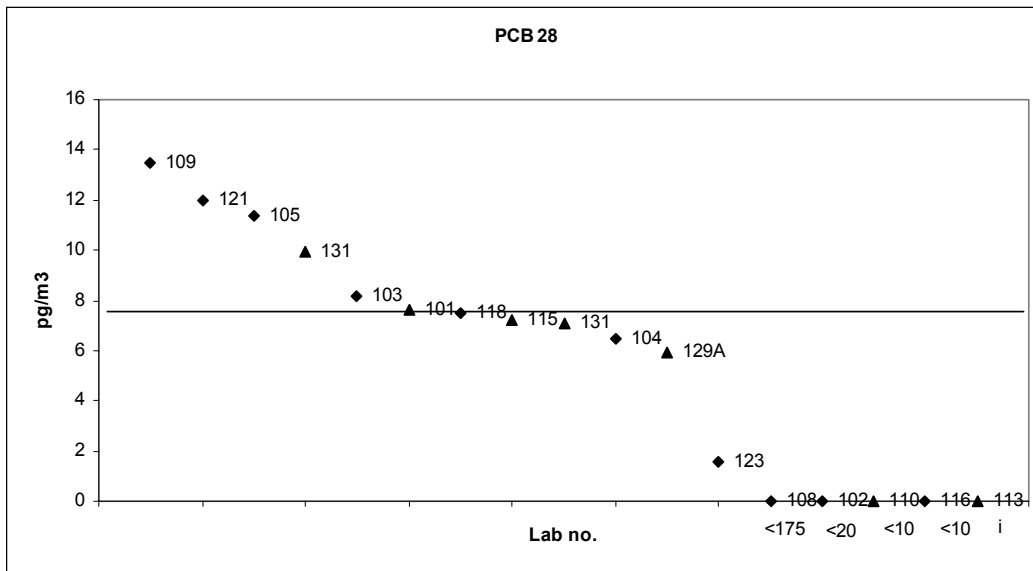
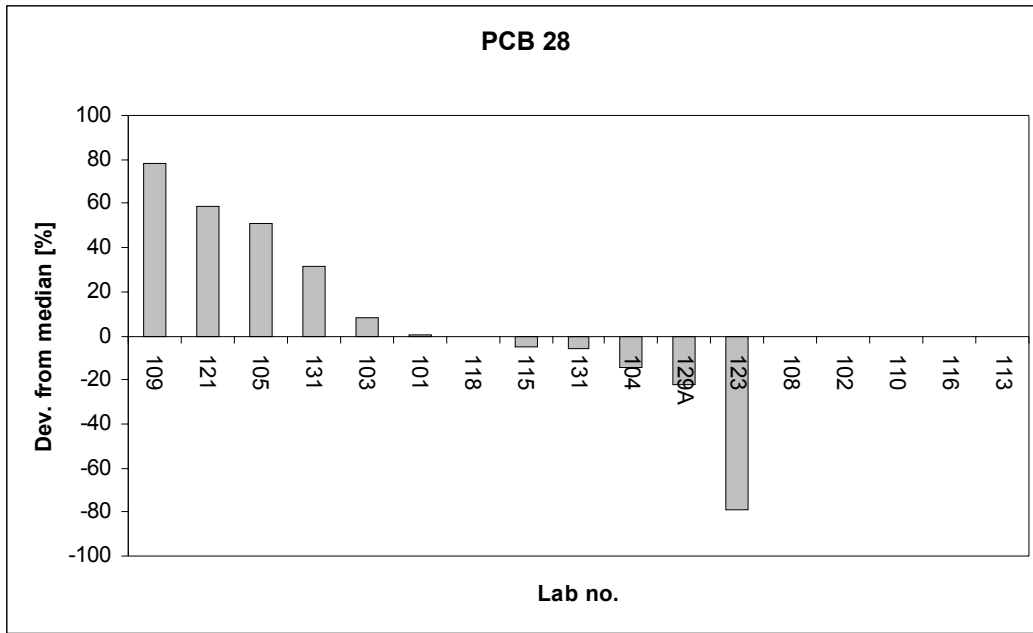


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 61,9

Lab. no.	Dev. from median	pg/m ³
108	193	181,145592
129A	128	141,3
109	70	105
115	50	93,1
101	14	70,3
116	9	67,4
102	3	64
118	0	62,1
104	0	61,7
105	-3	60,3
103	-4	59,69466667
113	-18	50,8
131	-21	49,2
131	-21	49,2
121	-76	15
123	-96	2,7
110		<10

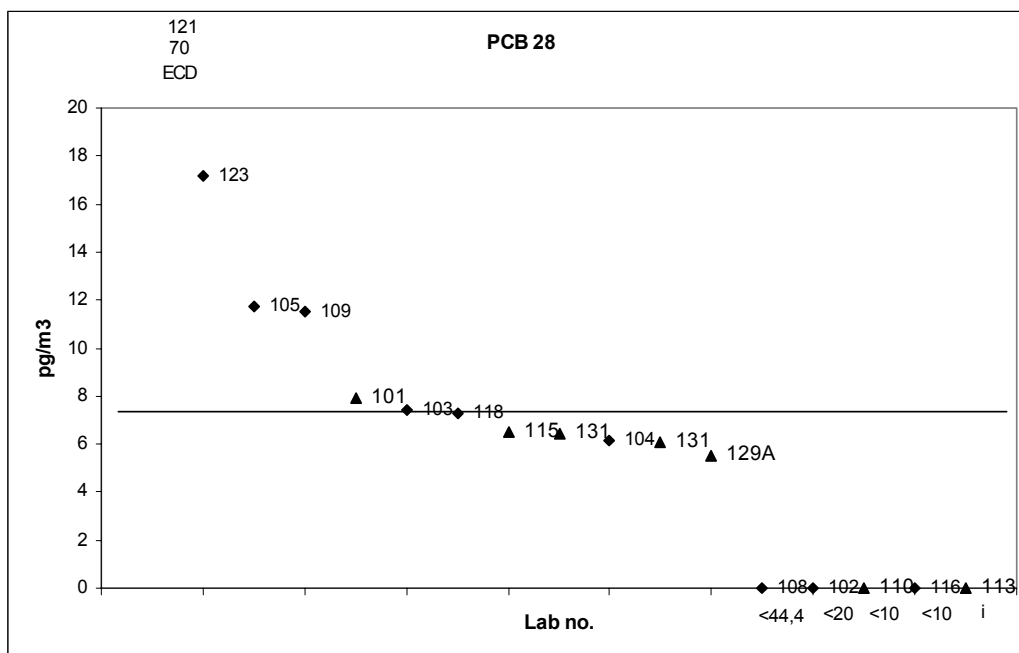
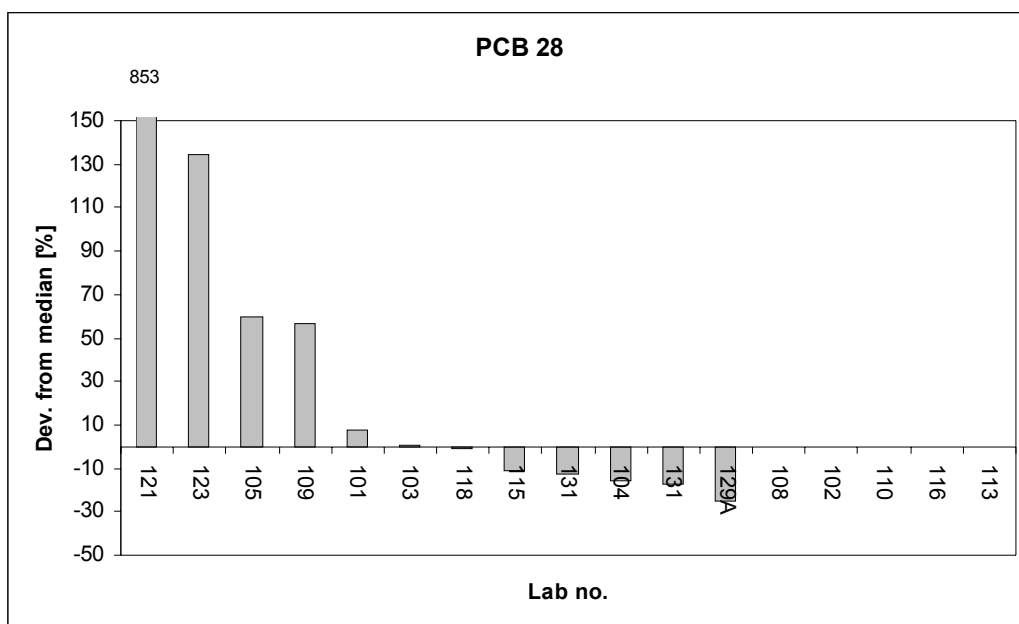


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 7,56

Lab. no.	Dev. from median %	pg/m3
109	79	13,5
121	59	12
105	51	11,4
131	31	9,92
103	8	8,183321067
101	1	7,6
118	-1	7,52
115	-5	7,2
131	-6	7,09
104	-15	6,454545455
129A	-22	5,9
123	-79	1,6
108		<175,28
102		<20
110		<10
116		<10
113		interference



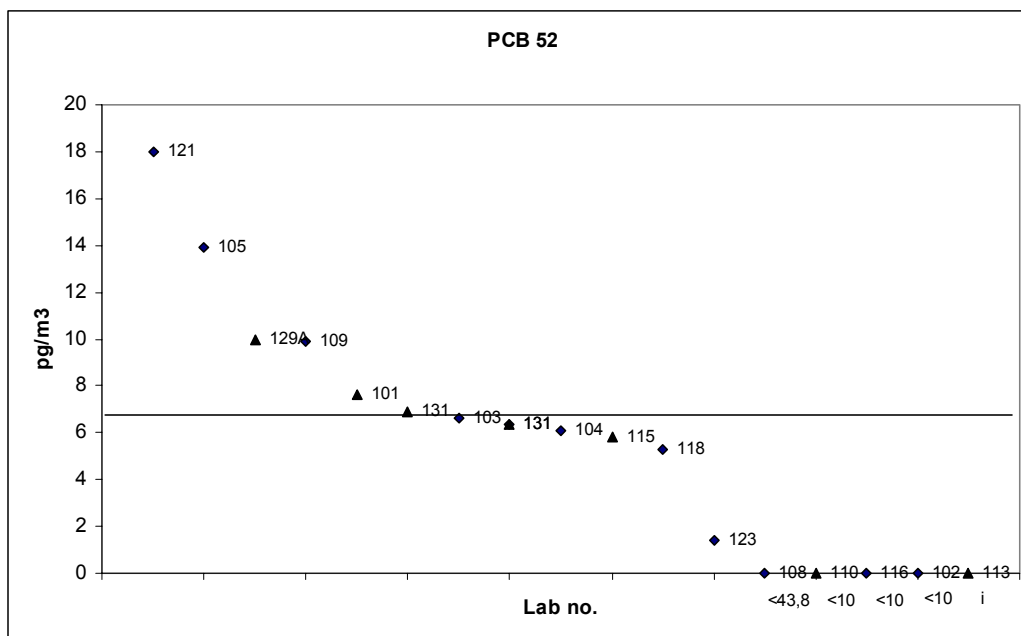
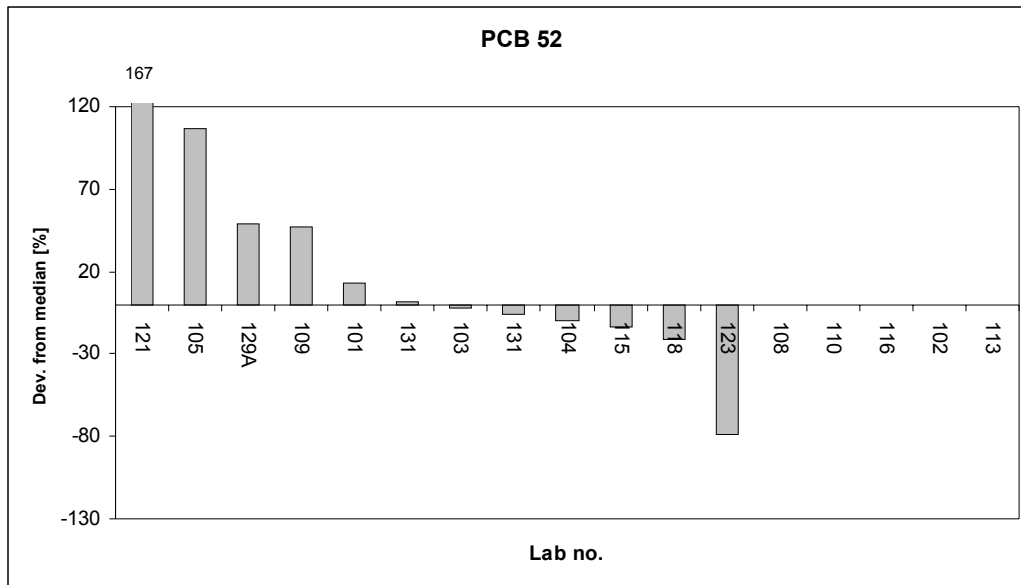
Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16

Median: 7,34

Lab. no.	Dev. from median %	pg/m ³
121	853	70
123	134	17,2
105	59	11,7
109	57	11,5
101	8	7,9
103	1	7,4051152
118	-1	7,28
115	-11	6,5
131	-12	6,44
104	-16	6,166666667
131	-17	6,07
129A	-25	5,5
108		<44,442
102		<20
110		<10
116		<10
113		interference

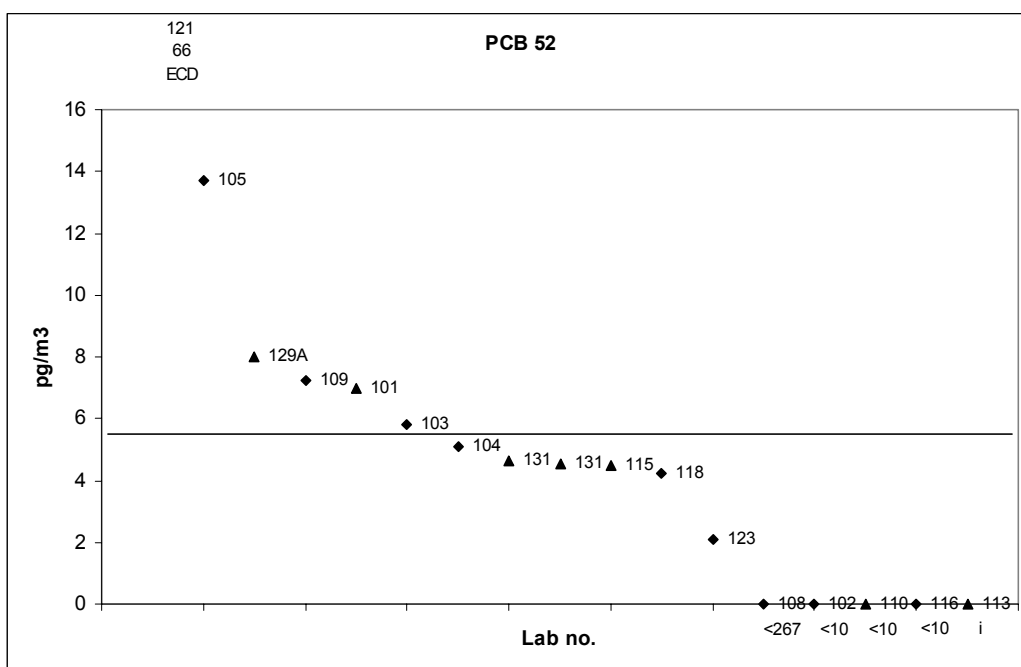
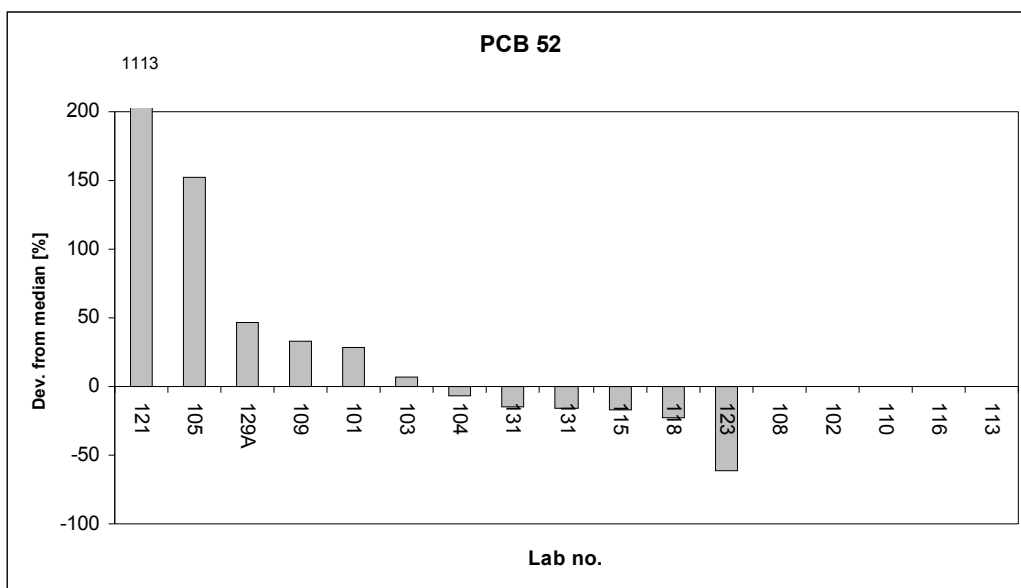


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 6,73

Lab. no.	Dev. from median %	pg/m3
121	167	18
105	106	13,9
129A	49	10
109	47	9,9
101	13	7,6
131	2	6,87
103	-2	6,596784267
131	-6	6,34
104	-10	6,090909091
115	-14	5,8
118	-21	5,3
123	-79	1,4
108		<43,8
110		<10
116		<10
102		<10
113		interference

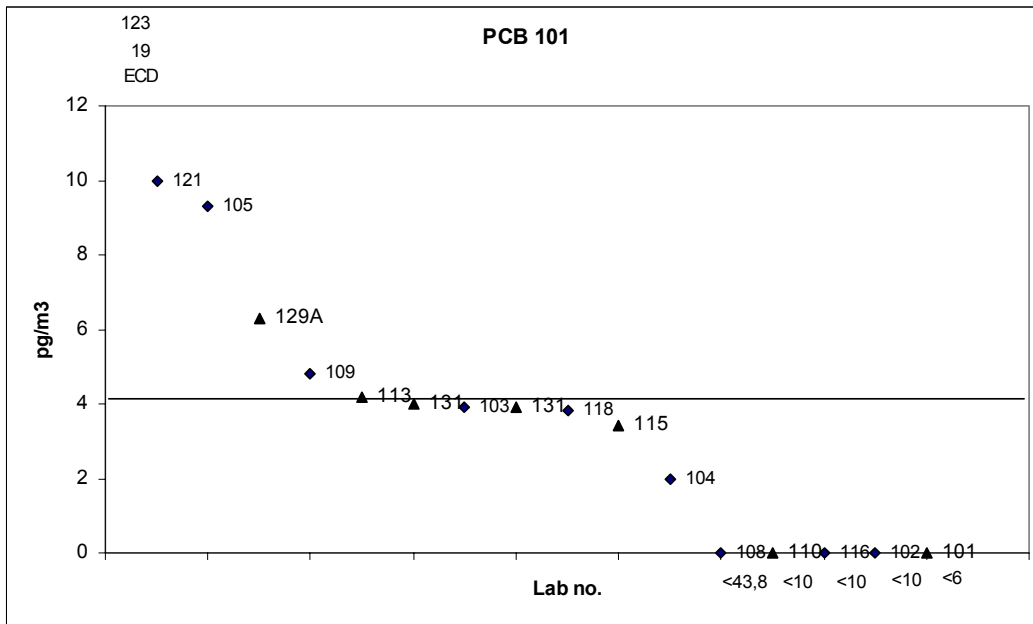
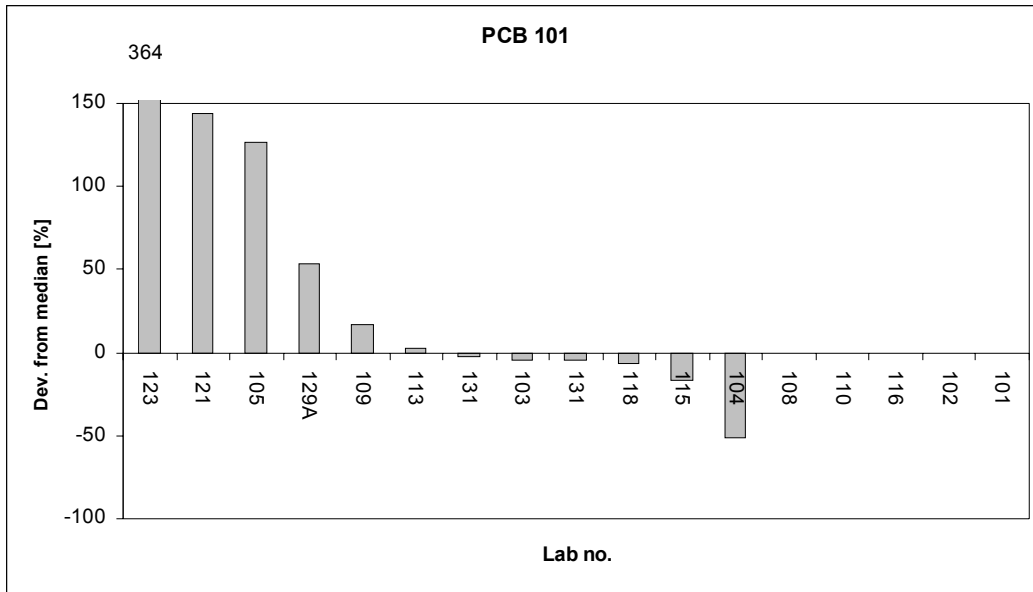


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 5,44

Lab. no.	Dev. from median %	pg/m ³
121	1113	66
105	152	13,7
129A	47	8
109	33	7,25
101	29	7
103	7	5,801125333
104	-7	5,083333333
131	-15	4,62
131	-16	4,56
115	-17	4,5
118	-22	4,22
123	-61	2,1
108		<266,652
102		<10
110		<10
116		<10
113		interference

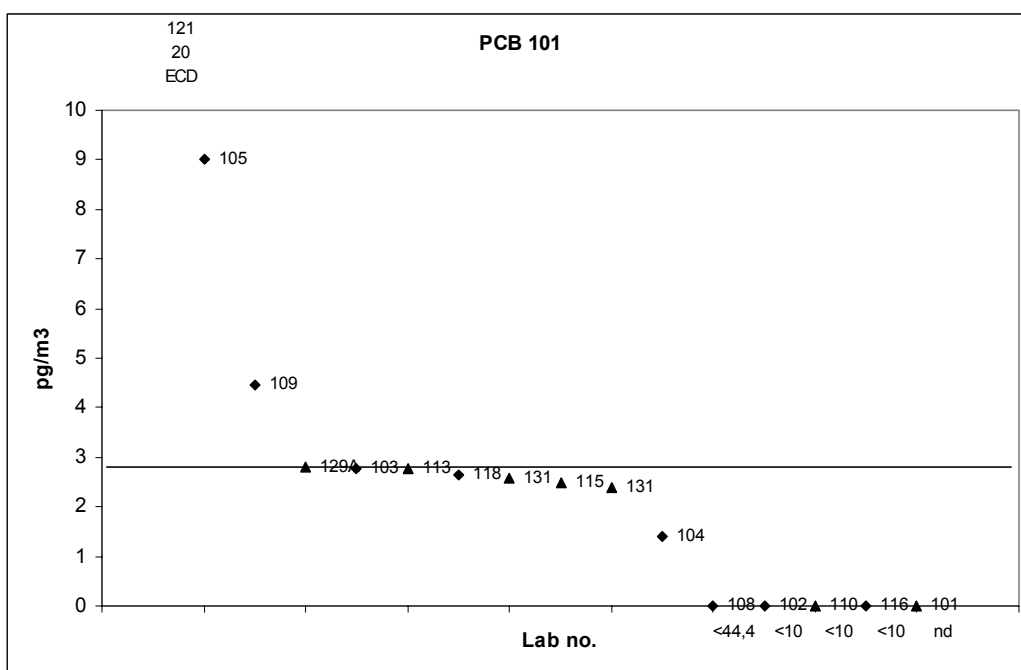
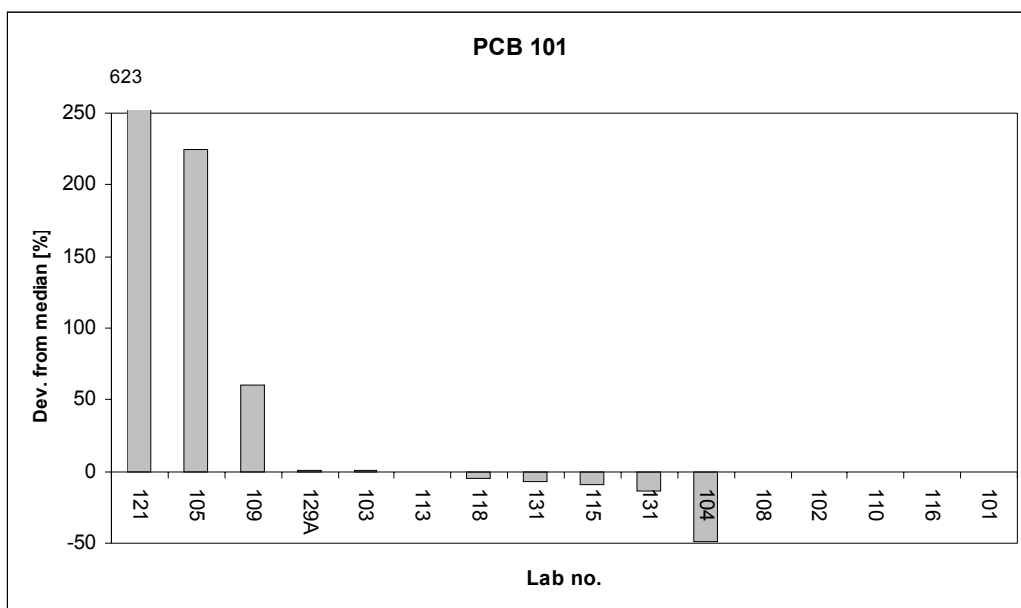


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m³. Median given as a horizontal line.

Number of laboratories: 16 Median: 4,10

Lab. no.	Dev. from median %	pg/m3
123	364	19
121	144	10
105	127	9,3
129A	54	6,3
109	17	4,8
113	2	4,199
131	-2	4,0
103	-5	3,9060496
131	-5	3,9
118	-6	3,84
115	-17	3,4
104	-51	2
108		<43,82
110		<10
116		<10
102		<10
101		< 6

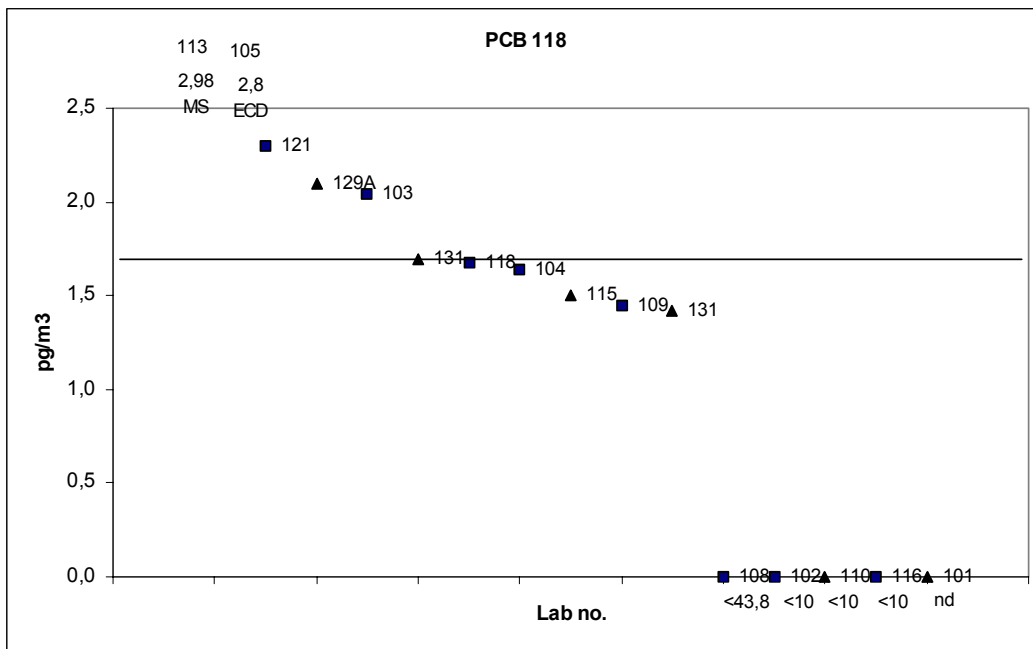
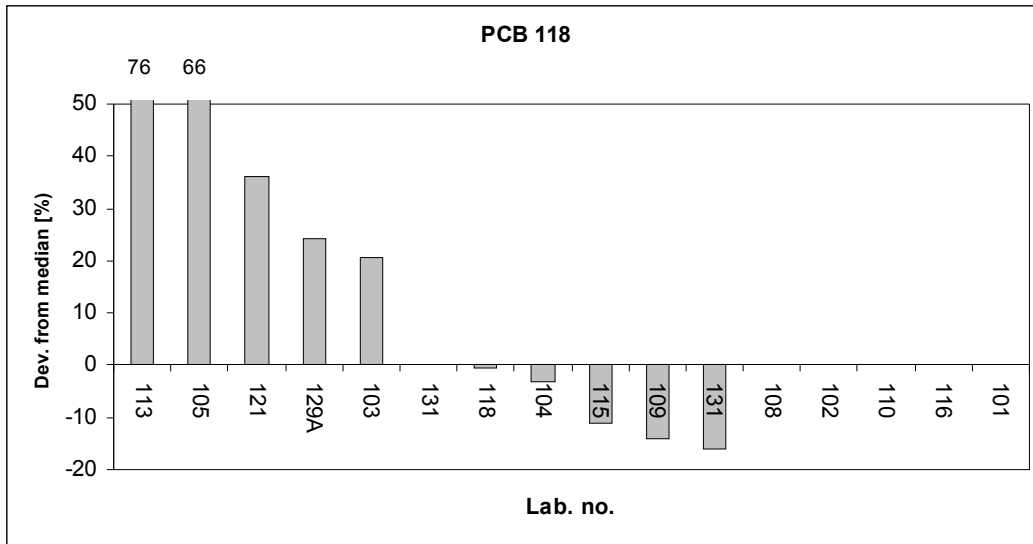


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median: 2,768

Lab. no.	Dev. from median %	pg/m ³
121	623	20
105	225	9
109	61	4,45
129A	1	2,8
103	0	2,7805264
113	0	2,768
118	-5	2,64
131	-7	2,58
115	-10	2,5
131	-14	2,38
104	-49	1,41666667
108		<44,442
102		<10
110		<10
116		<10
101		n.d

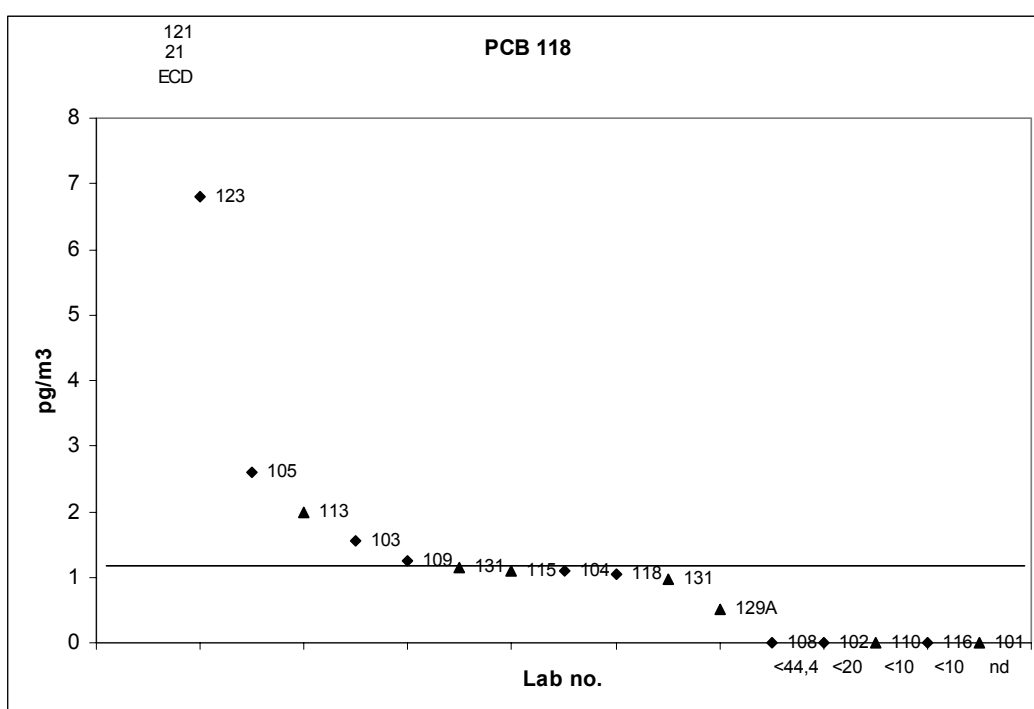
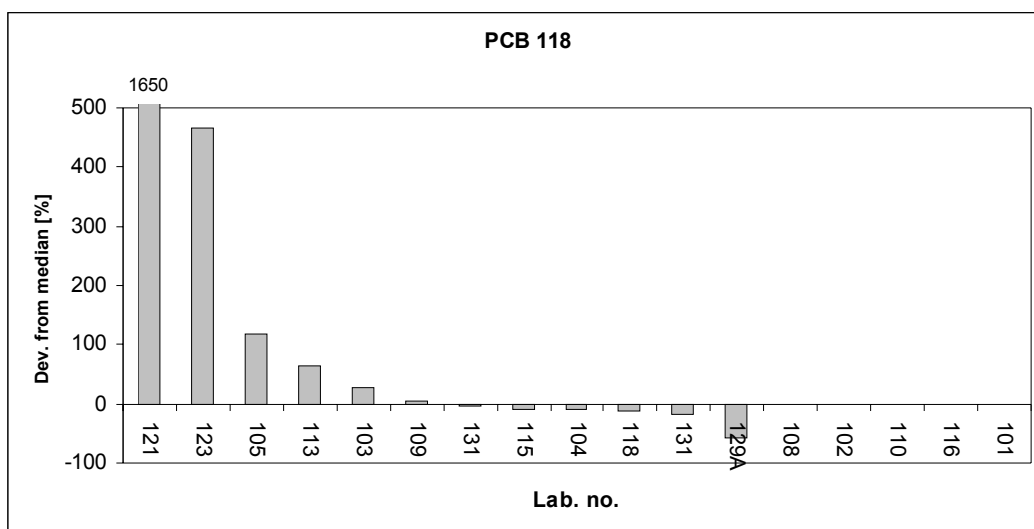


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median: 1,69

Lab. no.	Dev. from median %	pg/m3
113	76	2,975
105	66	2,8
121	36	2,3
129A	24	2,1
103	21	2,039692
131	0	1,69
118	-1	1,68
104	-3	1,636363636
115	-11	1,5
109	-14	1,45
131	-16	1,42
108		<43,82
102		< 20
110		<10
116		<10
101		n.d

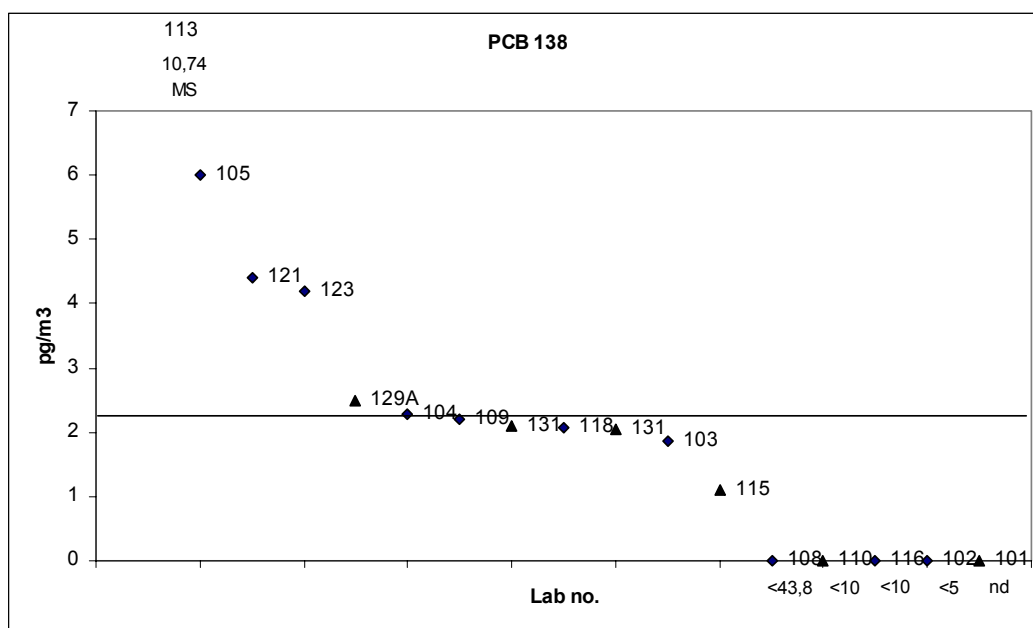
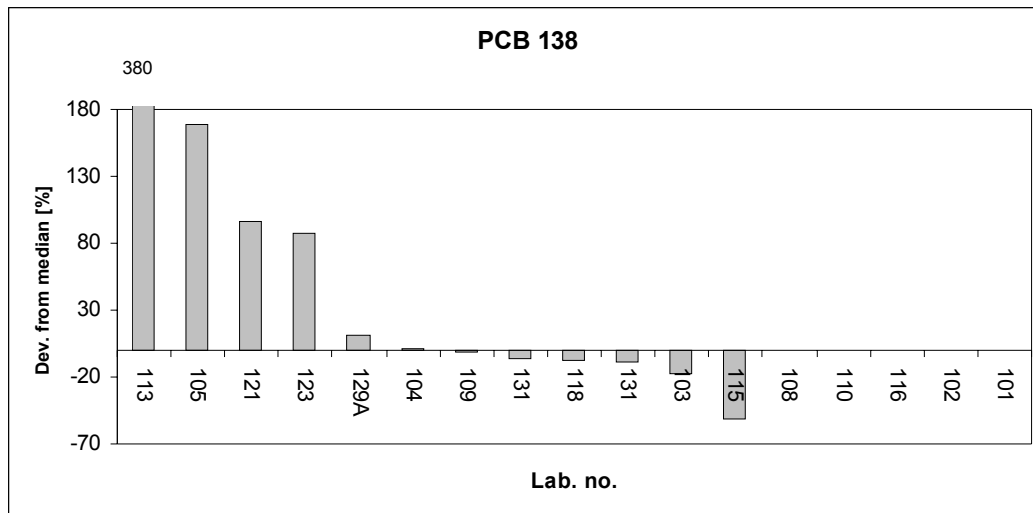


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 1,2

Lab. no.	Dev. from median %	pg/m ³
121	1650	21
123	467	6,8
105	117	2,6
113	65	1,984
103	29	1,543156
109	4	1,25
131	-4	1,15
115	-8	1,1
104	-10	1,083333333
118	-13	1,04
131	-18	0,98
129A	-58	0,5
108		<44,442
102		<20
110		<10
116		<10
101		n.d

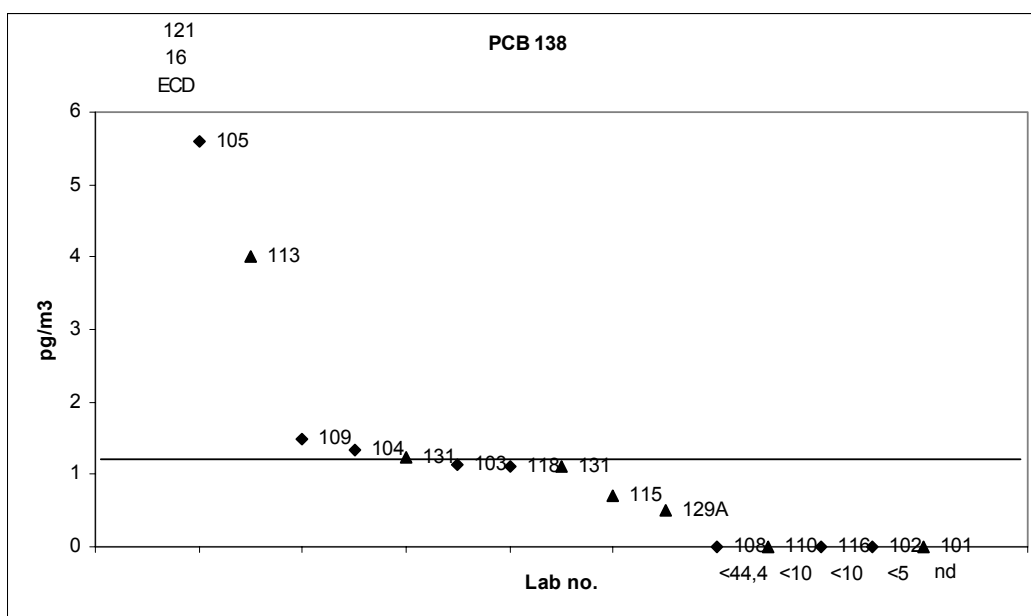
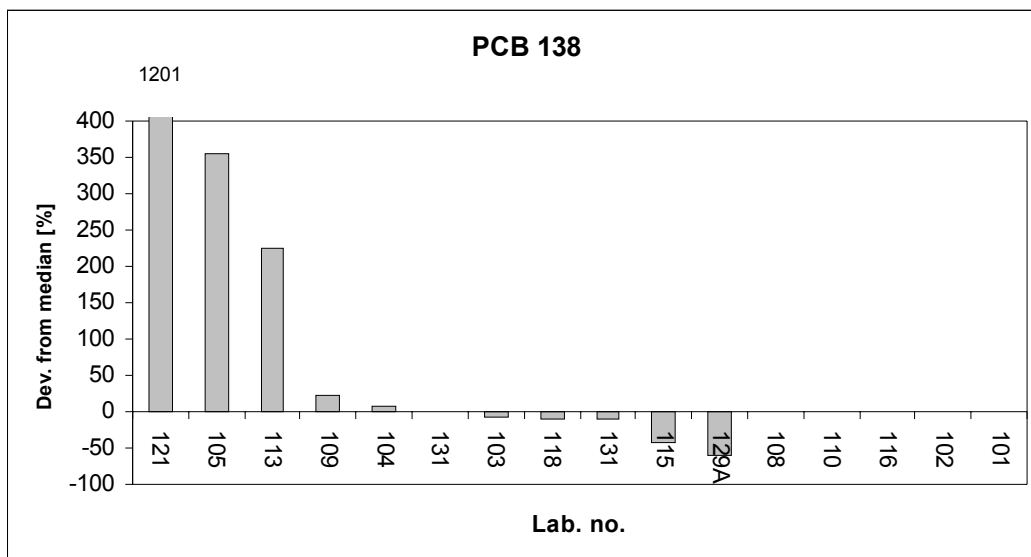


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 16 Median: 2,24

Lab. no.	Dev. from median %	pg/m ³
113	380	10,744
105	168	6
121	97	4,4
123	88	4,2
129A	12	2,5
104	2	2,2727273
109	-2	2,2
131	-7	2,09
118	-8	2,06
131	-9	2,04
103	-17	1,8503672
115	-51	1,1
108		<43,82
110		<10
116		<10
102		< 5
101		n.d

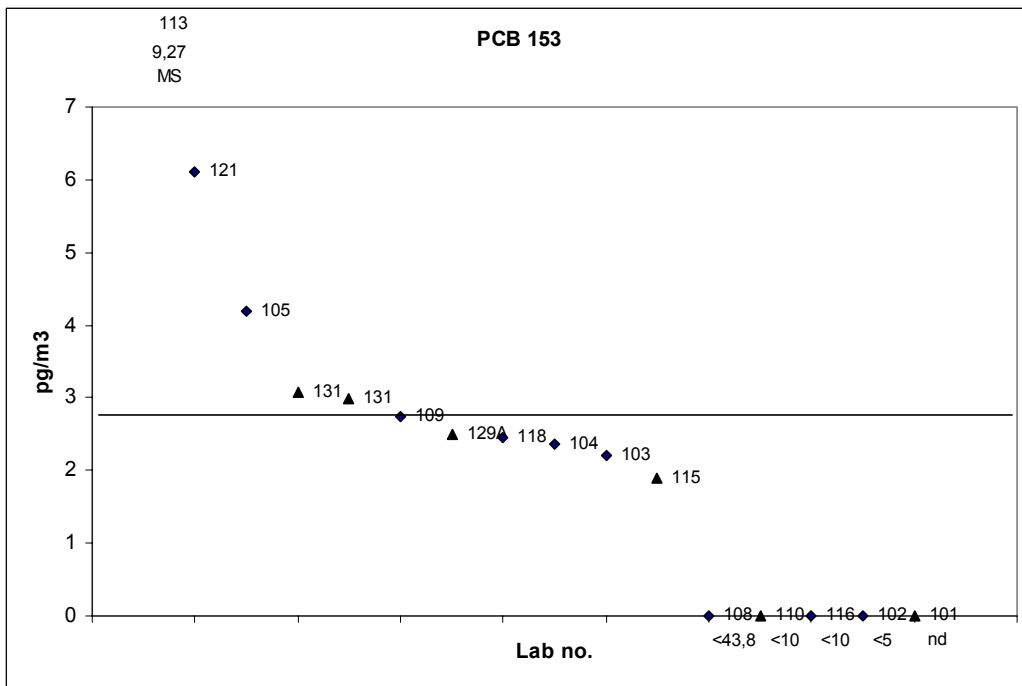
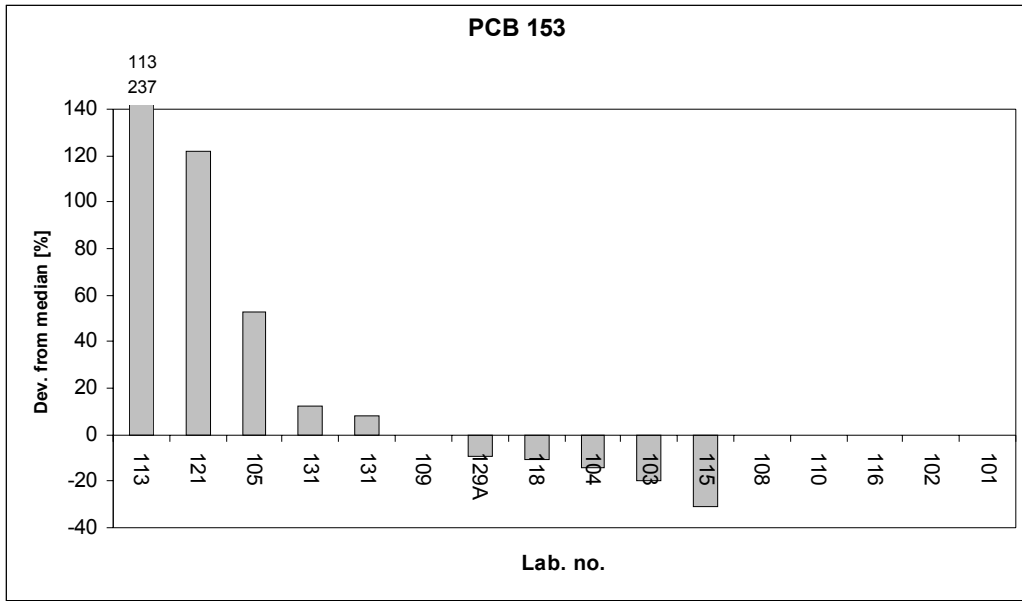


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median: 1,23

Lab. no.	Dev. from median %	pg/m ³
121	1201	16
105	355	5,6
113	225	4
109	22	1,5
104	8	1,333333333
131	0	1,23
103	-7	1,1381128
118	-9	1,12
131	-9	1,12
115	-43	0,7
129A	-59	0,5
108		<44,442
110		<10
116		<10
102		<5
101		n.d

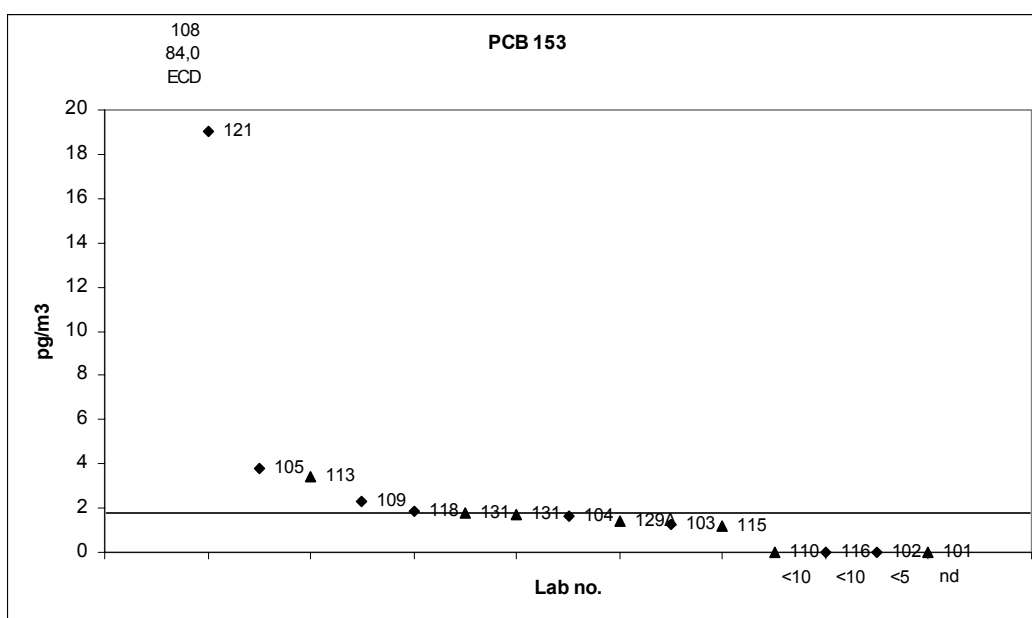
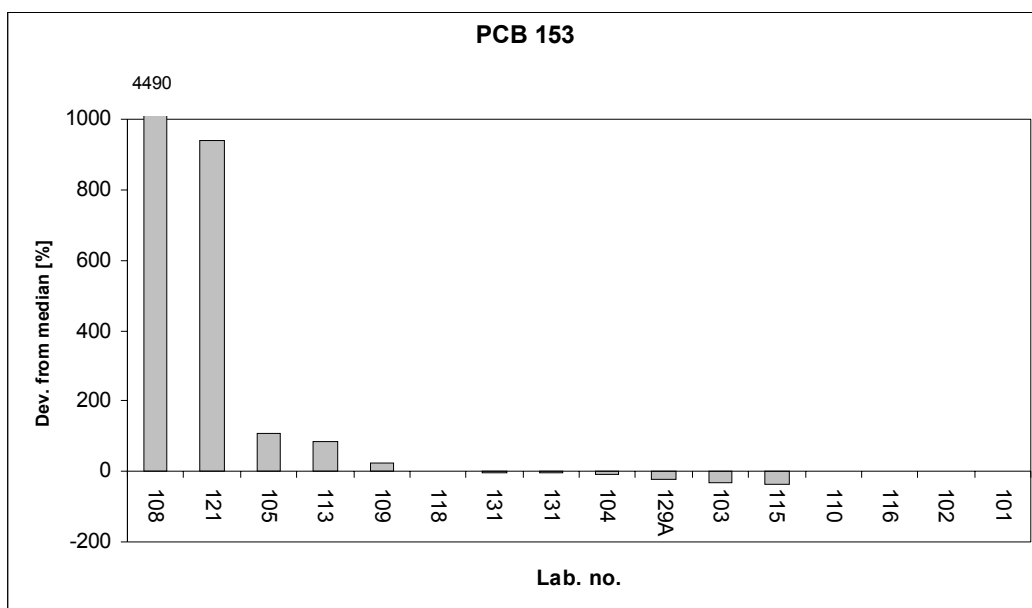


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median: 2,75

Lab. no.	Dev. from median %	pg/m3
113	237	9,265
121	122	6,1
105	53	4,2
131	12	3,08
131	8	2,98
109	0	2,75
129A	-9	2,5
118	-11	2,46
104	-14	2,363636364
103	-20	2,200608
115	-31	1,9
108		<43,82
110		<10
116		<10
102		<5
101		n.d

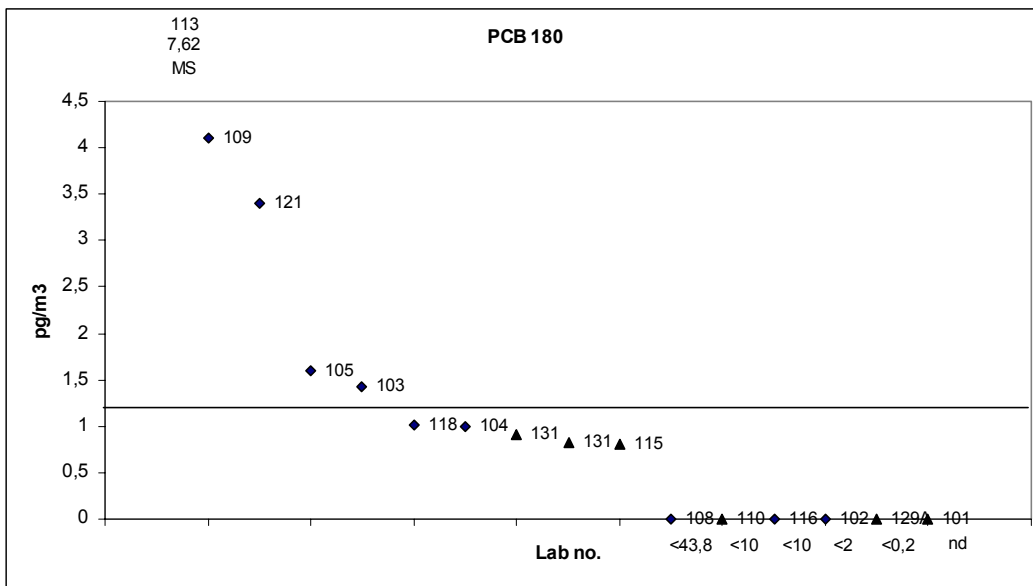
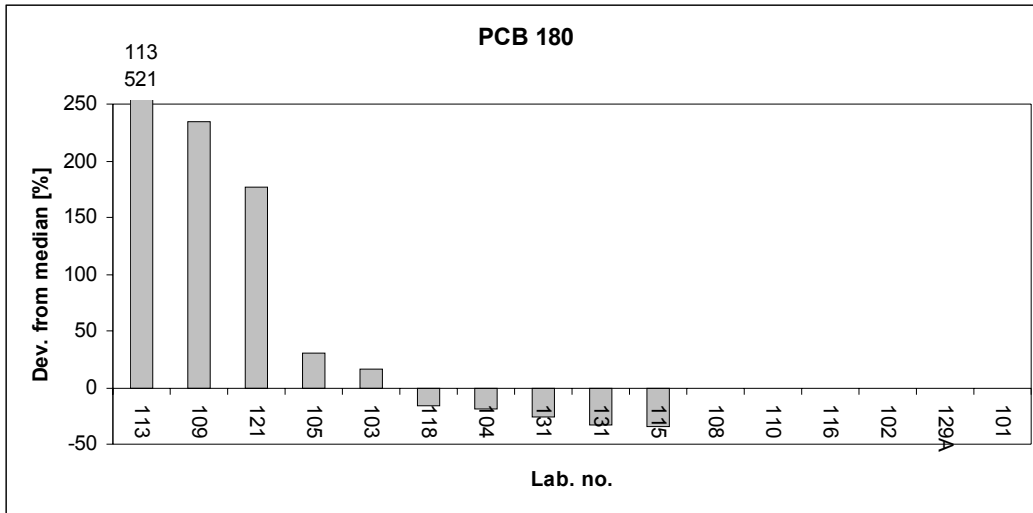


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median: 1,83

Lab. no.	Dev. from median %	pg/m3
108	4490	83,99538
121	938	19
105	108	3,8
113	87	3,424
109	26	2,3
118	2	1,86
131	-2	1,8
131	-5	1,73
104	-9	1,666666667
129A	-23	1,4
103	-31	1,2705984
115	-34	1,2
110		<10
116		<10
102		<5
101		n.d

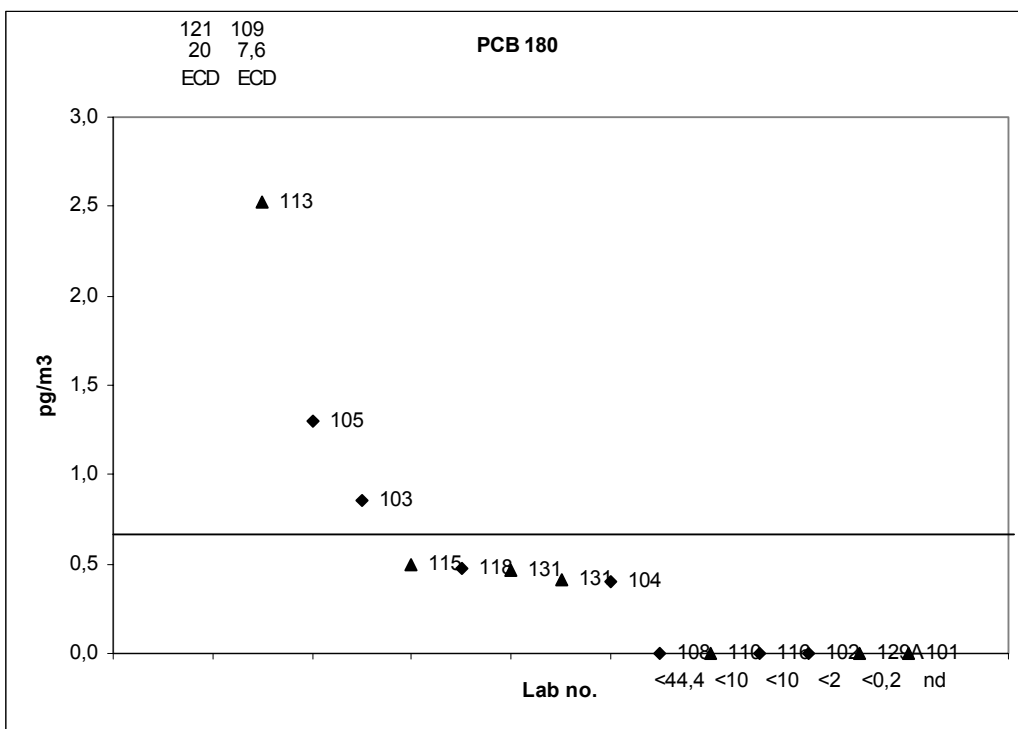
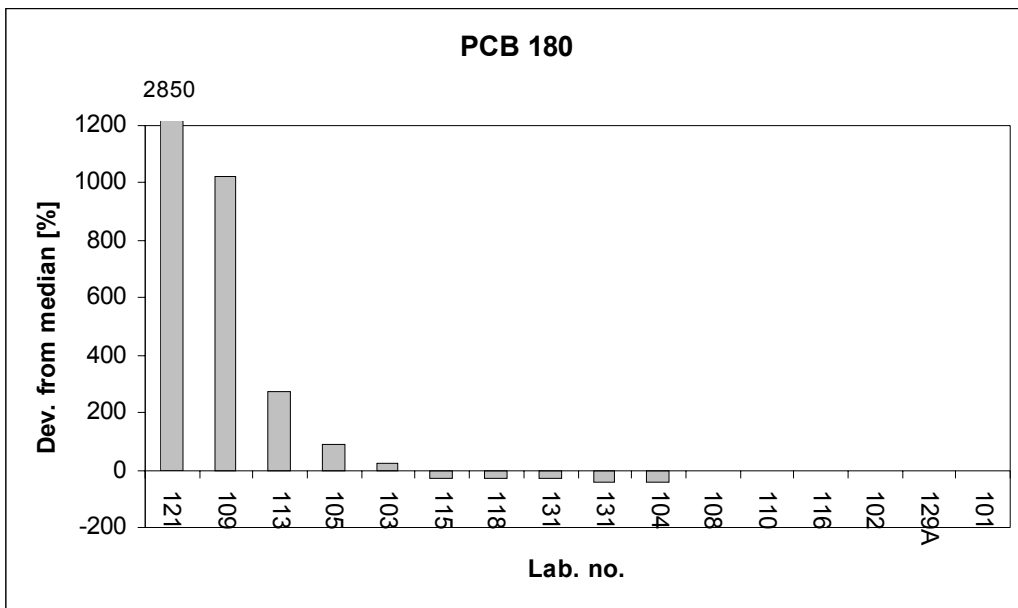


Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median: 1,23

Lab. no.	Dev. from median %	pg/m3
113	521	7,616
109	234	4,1
121	177	3,4
105	30	1,6
103	17	1,433796
118	-17	1,02
104	-18	1
131	-26	0,91
131	-33	0,82
115	-35	0,8
108		<43,82
110		<10
116		<10
102		<2
129A		<0,2
101		n.d



Upper figure: Deviation from median in %.

Lower figure: Concentrations in pg/m^3 . Median given as a horizontal line.

Number of laboratories: 15 Median: 0,68

Lab. no.	Dev. from median %	pg/m3
121	2850	20
109	1021	7,6
113	273	2,528
105	92	1,3
103	26	0,856076
115	-26	0,5
118	-29	0,48
131	-32	0,46
131	-40	0,41
104	-41	0,4
108		<44,442
110		<10
116		<10
102		<2
129A		<0,2
101		n.d.

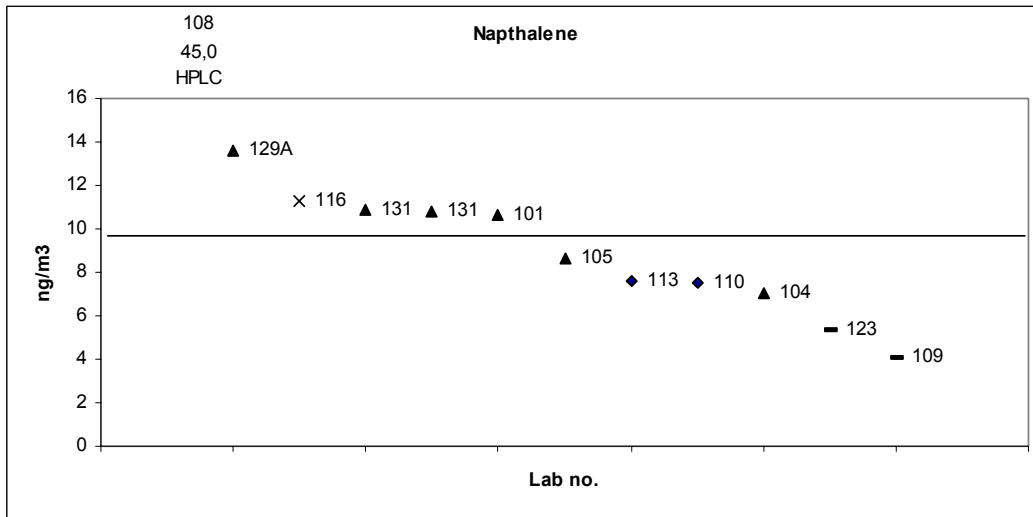
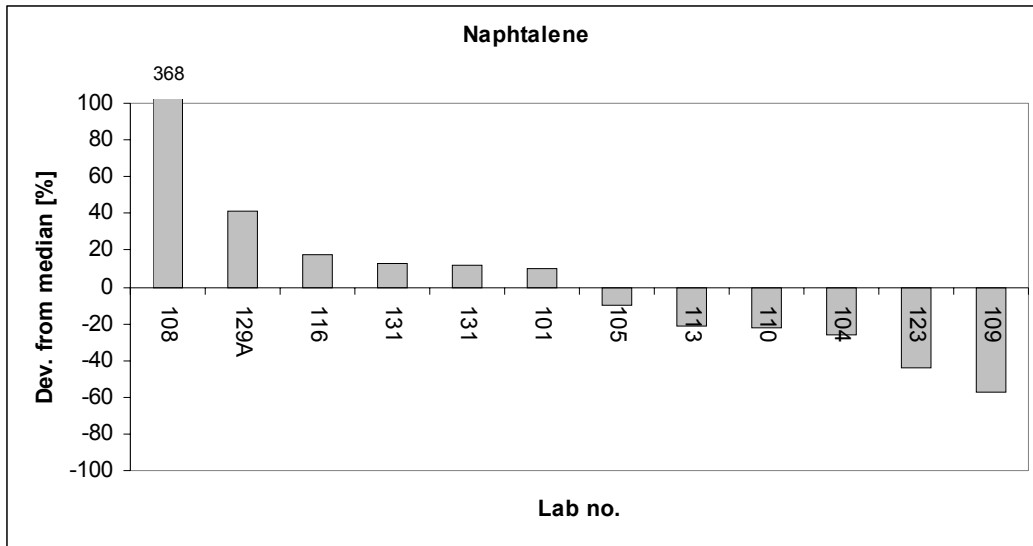
Annex 6

PAH compounds, round 2, sample 1 and 2

The following pages present the results from round 2 graphically. The results for each compound are shown on two pages with the left-hand page giving the sample 1 results and the right-hand side the corresponding data from sample 2.

The results have been given as deviations from the median in per cent (upper graph) and as concentration based on a 500 m³ sample volume (lower graph).

◆	HPLC
▲	GC/MS
■	GC/FID
○	TLC
×	HPLC and GC/MS
■	GC/FID and GC/MS

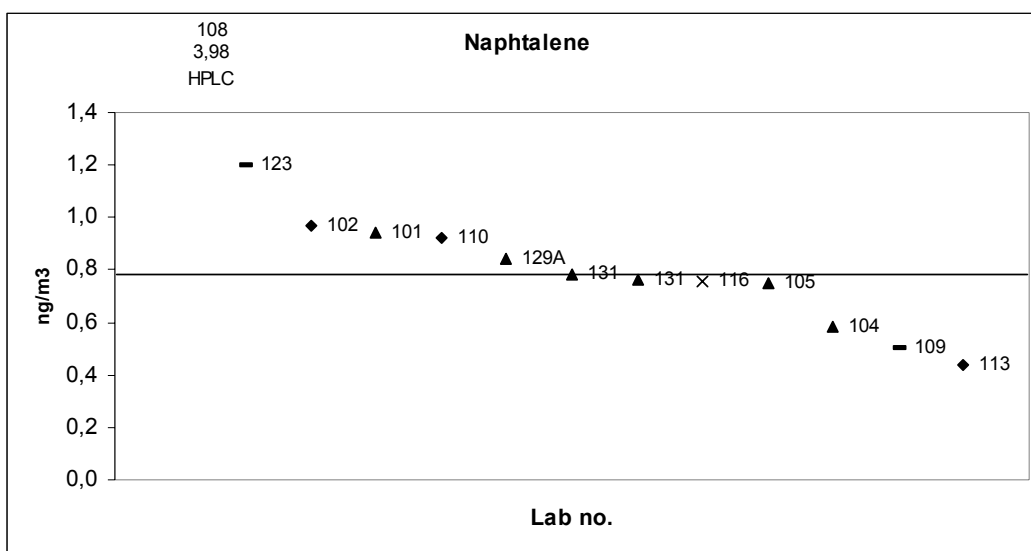
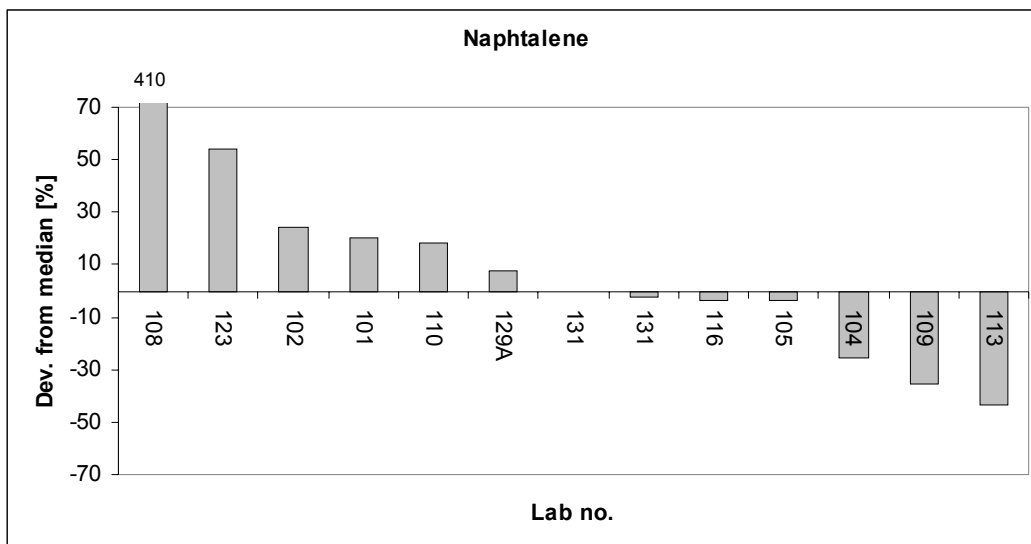


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 11 Median: 9,63

Lab. no.	Dev. from median %	ng/m3
108	368	45,04
129A	41	13,6072
116	17	11,3
131	13	10,9
131	12	10,8
101	10	10,61
105	-10	8,656
113	-21	7,6
110	-22	7,51
104	-27	7,07852
123	-44	5,4
109	-57	4,1

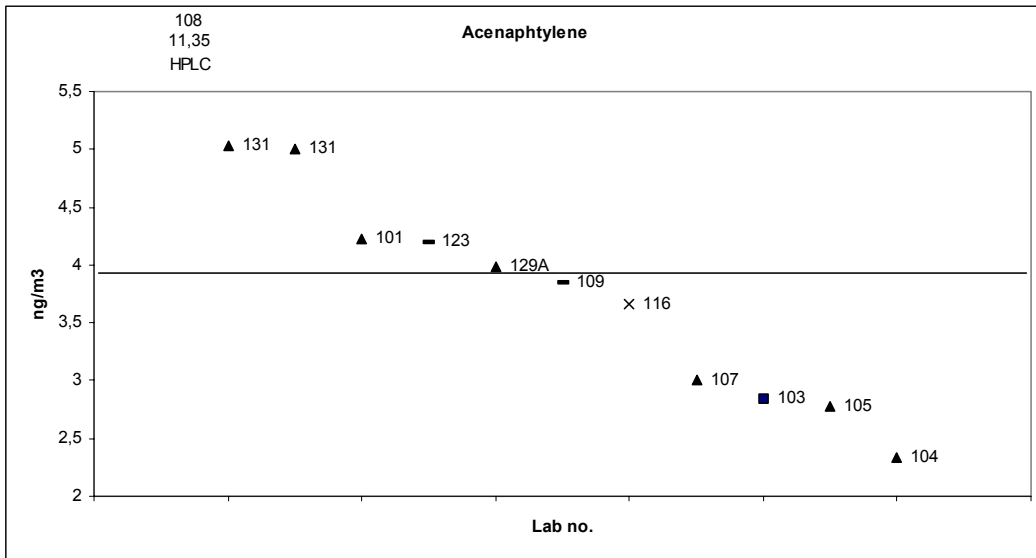
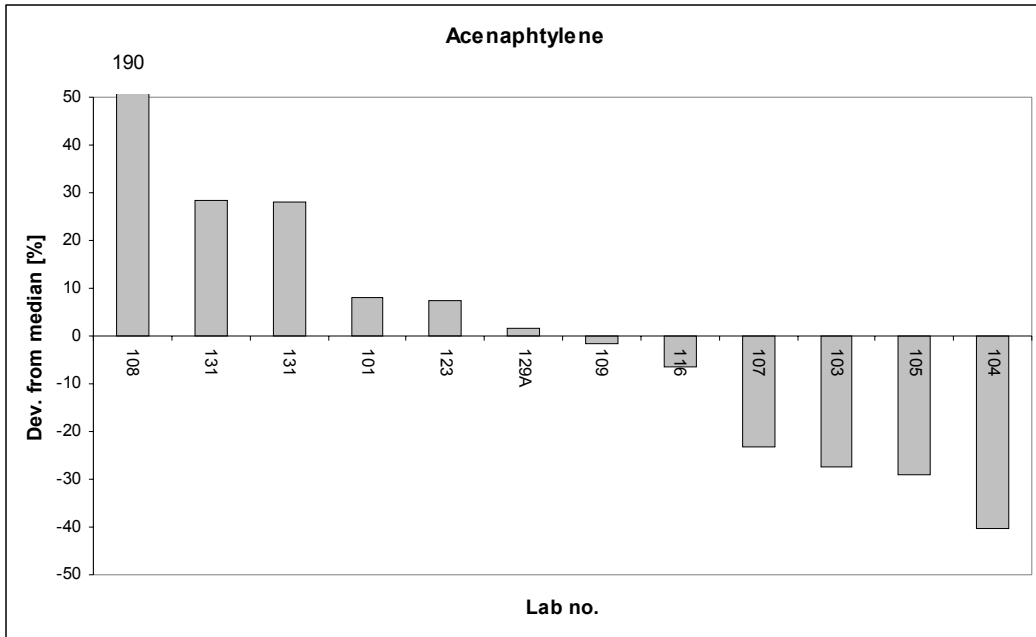


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 12 Median: 0,78

Lab. no.	Dev. from median %	ng/m ³
108	410	3,978918
123	54	1,2
102	24	0,97
101	21	0,94
110	18	0,922
129A	8	0,84
131	0	0,78
131	-3	0,76
116	-3	0,754
105	-4	0,75
104	-25	0,58116
109	-35	0,505
113	-44	0,44

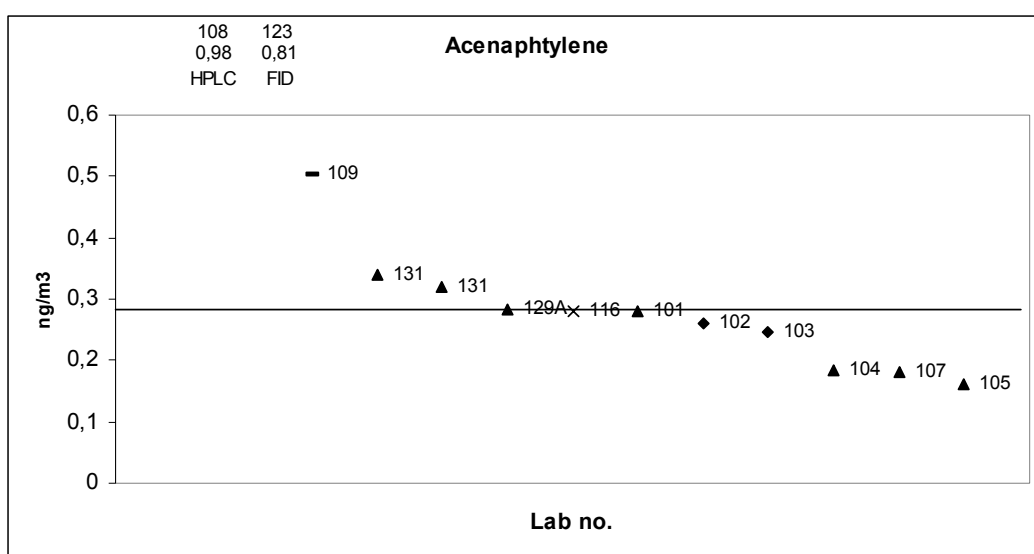
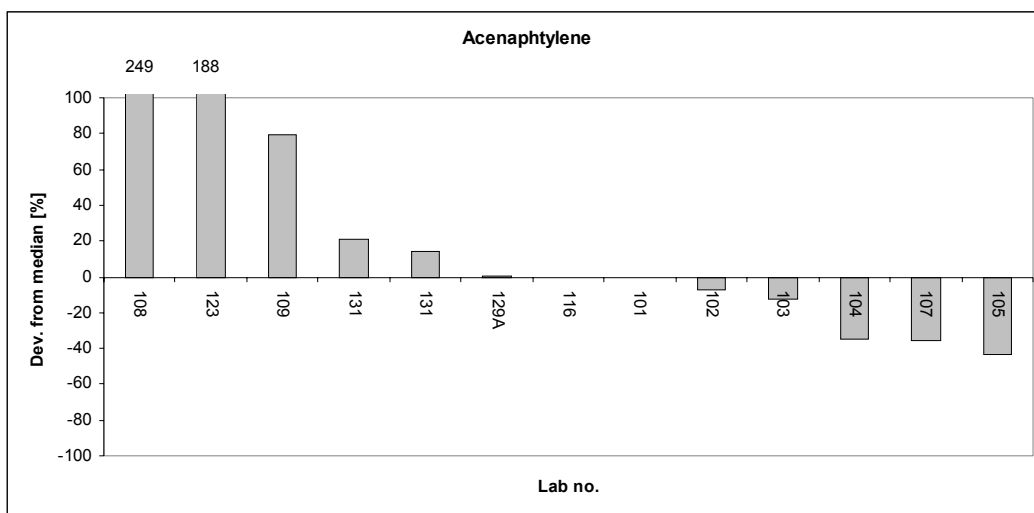


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 11 Median: 3,91

Lab. no.	Dev from median %	ng/m3
108	190	11,35
131	28	5,03
131	28	5,01
101	8	4,23
123	7	4,2
129A	2	3,9806
109	-2	3,85
116	-7	3,66
107	-23	3
103	-27	2,846526667
105	-29	2,774
104	-40	2,33984

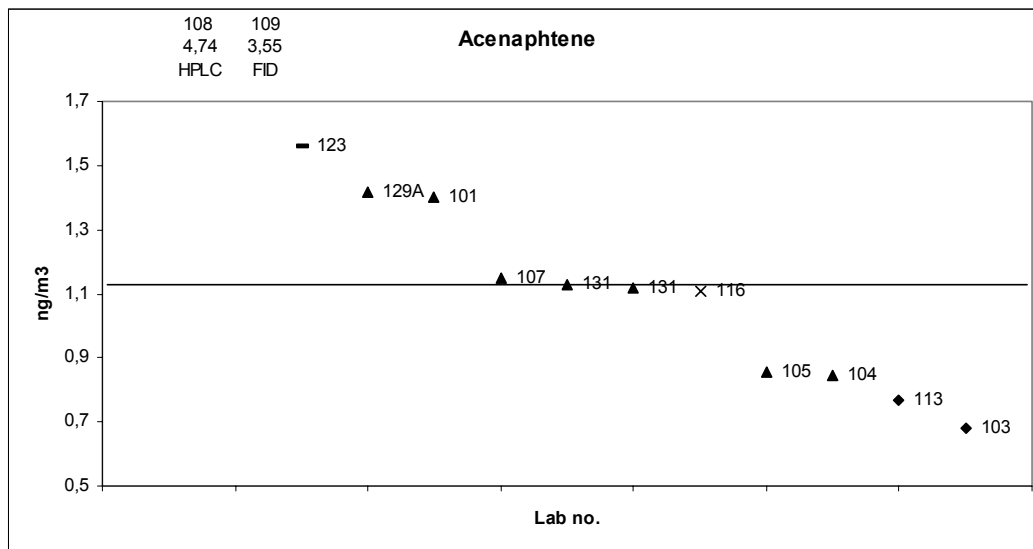
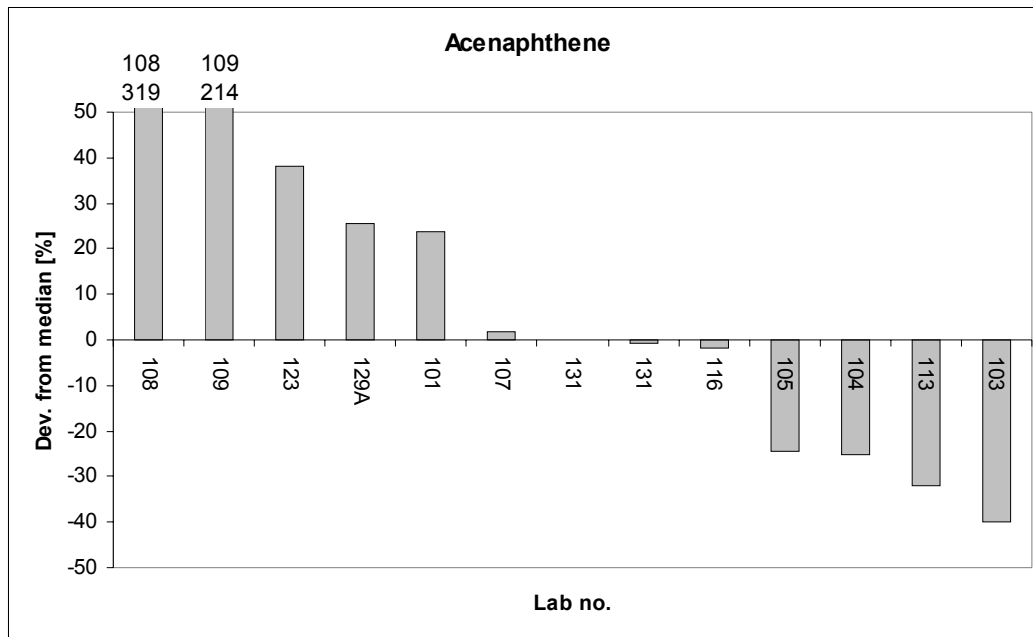


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 12 Median: 0,281

Lab. no.	Dev. from median %	ng/m ³
108	249	0,98
123	188	0,81
109	80	0,505
131	21	0,34
131	14	0,32
129A	1	0,2832
116	0	0,281
101	0	0,28
102	-7	0,26
103	-13	0,244963333
104	-35	0,18259
107	-36	0,18
105	-43	0,16

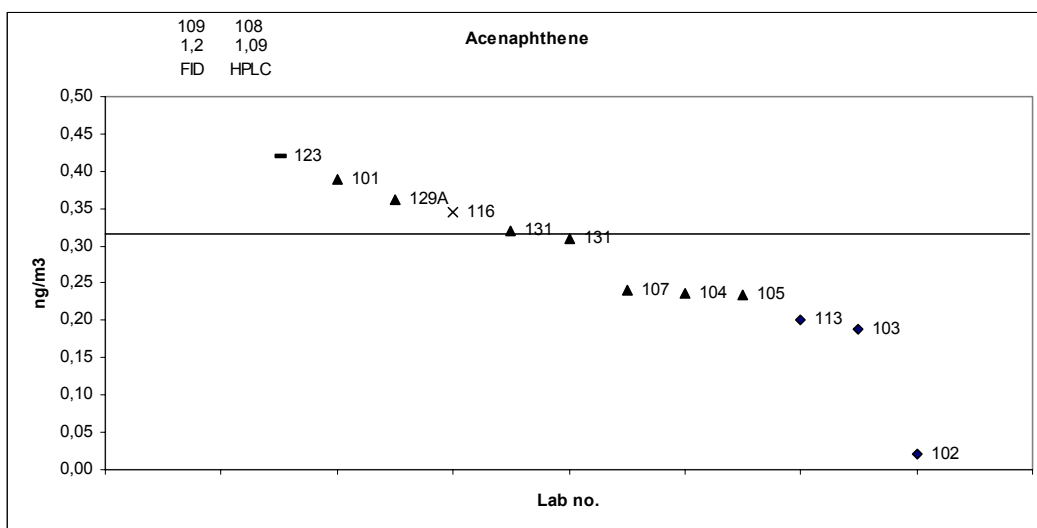
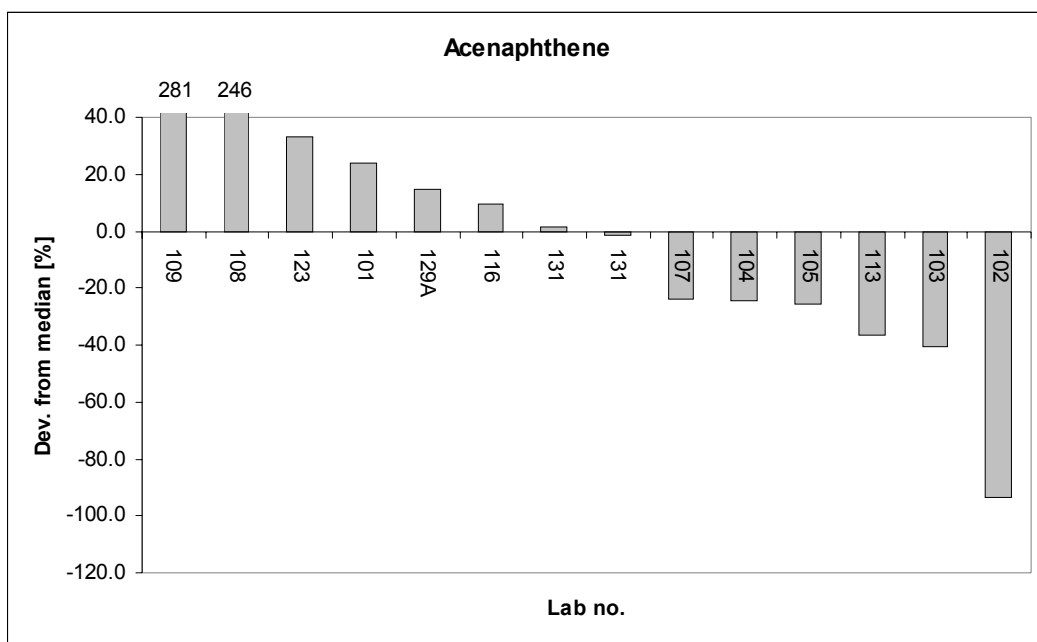


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 12 Median: 1,13

Lab. no.	Dev. from median %	ng/m3
108	319	4,74
109	214	3,55
123	38	1,56
129A	25	1,4172
101	24	1,4
107	2	1,15
131	0	1,13
131	-1	1,12
116	-2	1,11
105	-25	0,853
104	-25	0,84534
113	-32	0,77
103	-40	0,67909

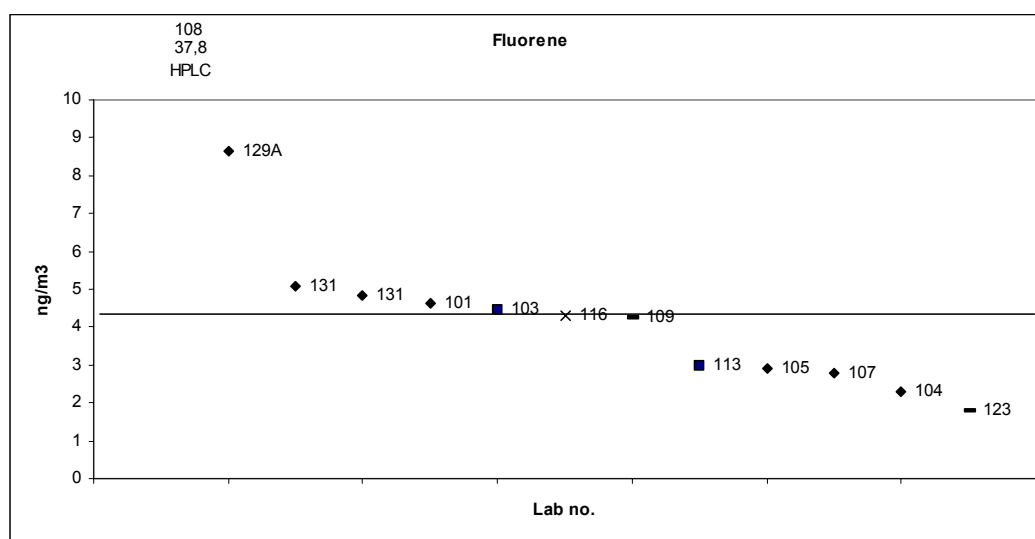
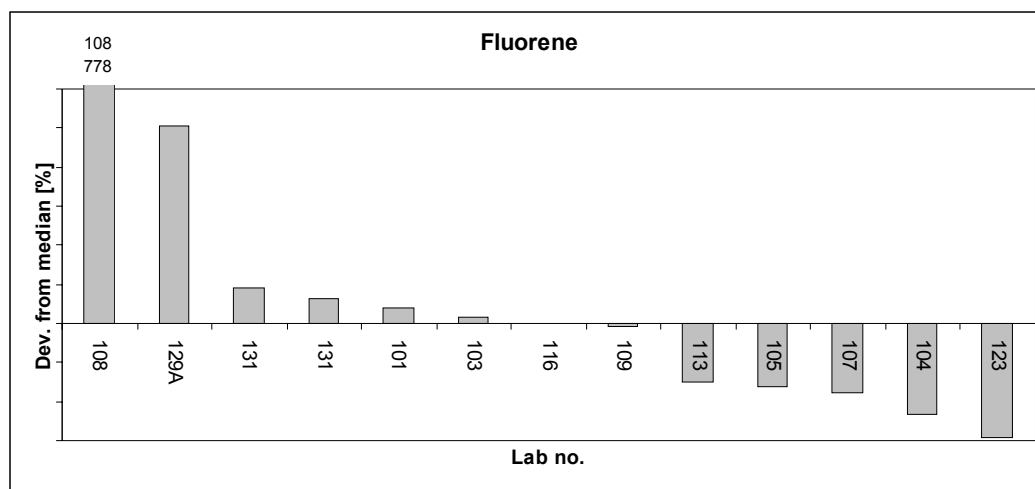


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,315

Lab. no.	Dev. from median %	ng/m3
109	281	1,2
108	246	1,09
123	33	0,42
101	24	0,39
129A	15	0,3612
116	10	0,345
131	2	0,32
131	-2	0,31
107	-24	0,24
104	-25	0,23712
105	-25	0,235
113	-37	0,2
103	-41	0,18725
102	-94	0,02

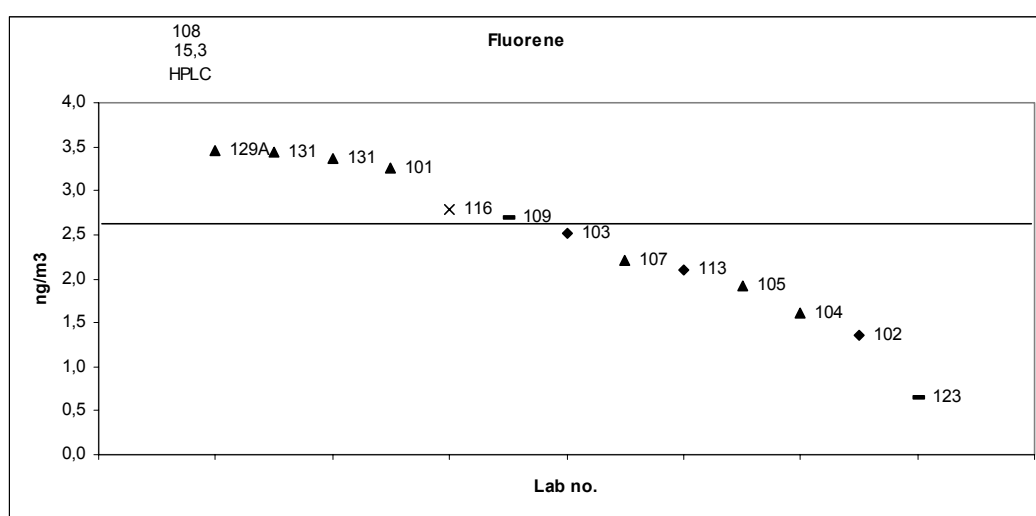
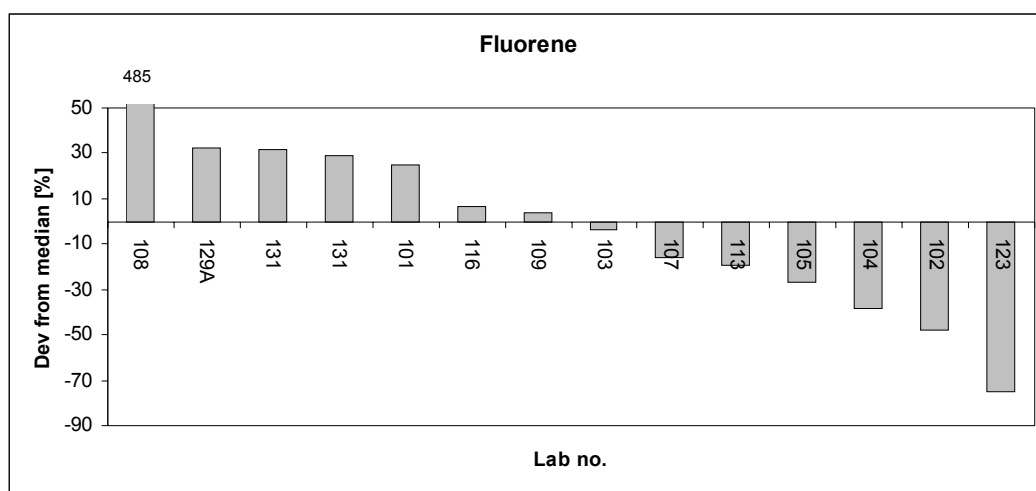


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 12 Median: 4,31

Lab. no.	Dev. from median %	ng/m3
108	778	37,83
129A	101	8,6494
131	18	5,08
131	12	4,84
101	8	4,64
103	4	4,462316
116	0	4,31
109	-1	4,25
113	-30	3
105	-32	2,925
107	-36	2,77
104	-46	2,31453
123	-58	1,8

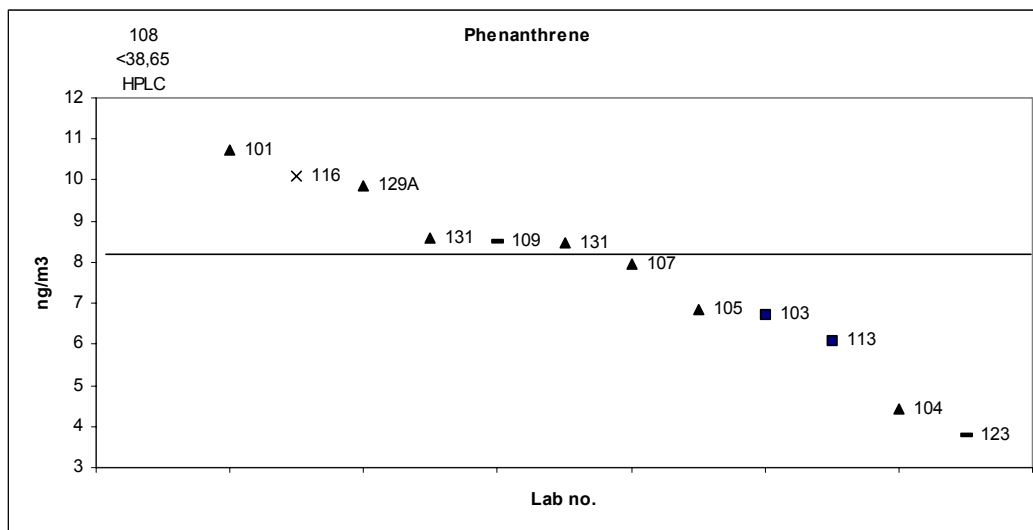
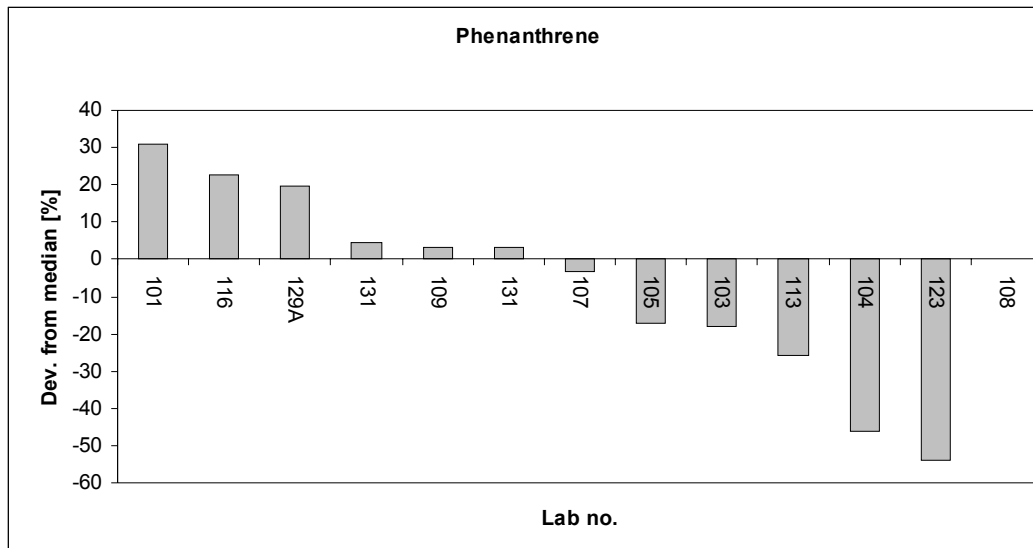


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 13 Median: 2,61

Lab. no.	Dev. from median %	ng/m3
108	485	15,26
129A	32	3,4548
131	31	3,43
131	29	3,36
101	25	3,25
116	7	2,78
109	3	2,7
103	-3	2,517484
107	-16	2,2
113	-20	2,1
105	-27	1,912
104	-38	1,61393
102	-48	1,36
123	-75	0,65



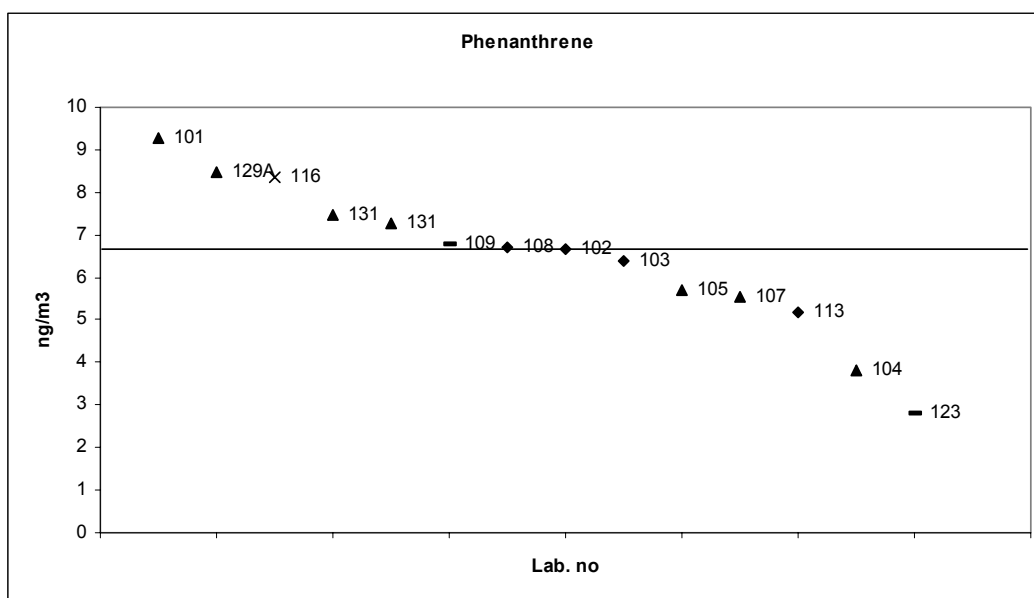
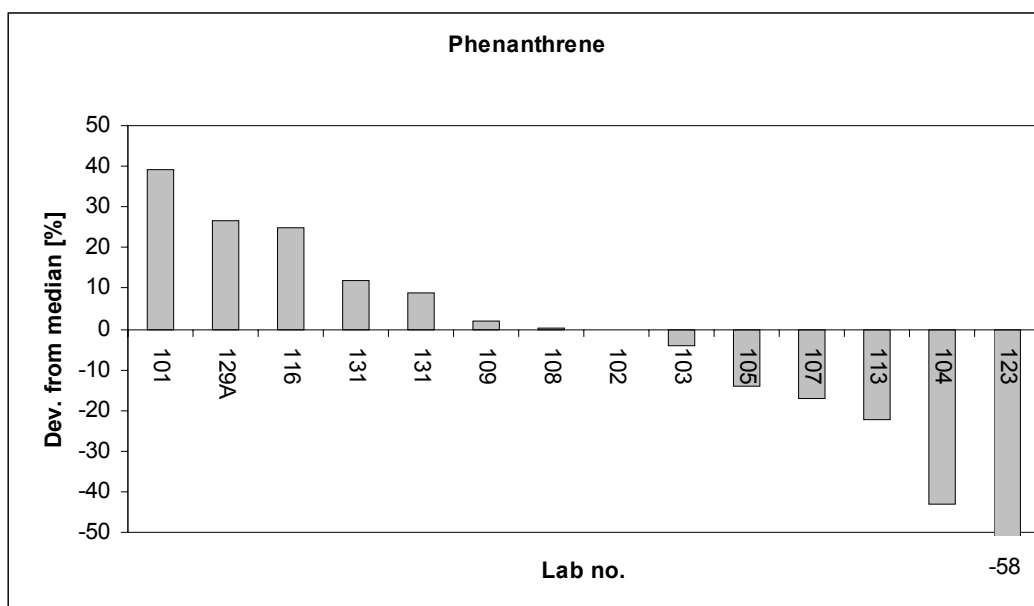
Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 12

Median: 8,23

Lab. no.	Dev. from median %	ng/m ³
101	31	10,75
116	23	10,1
129A	20	9,8418
131	4	8,58
109	3	8,5
131	3	8,48
107	-3	7,97
105	-17	6,826
103	-18	6,739749333
113	-26	6,1
104	-46	4,42796
123	-54	3,8
108		< 38,65

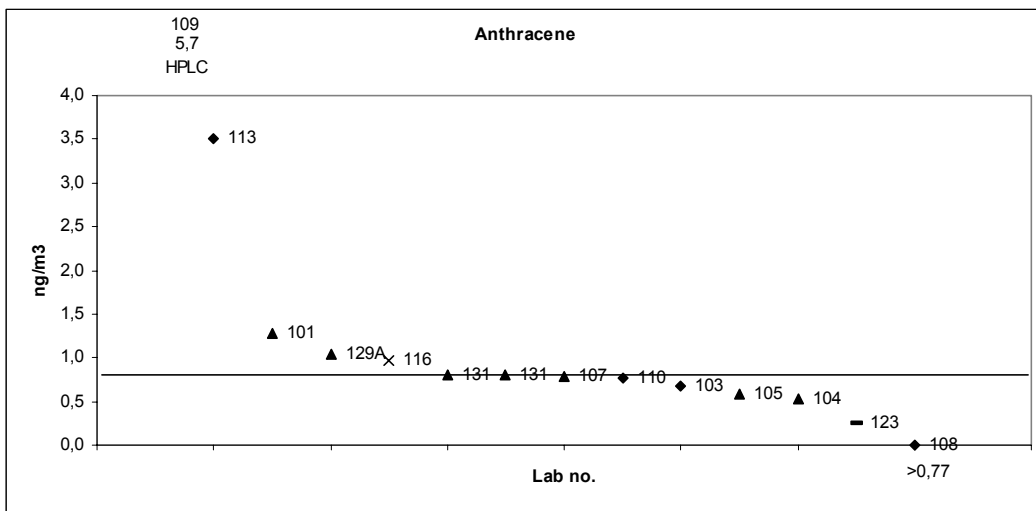
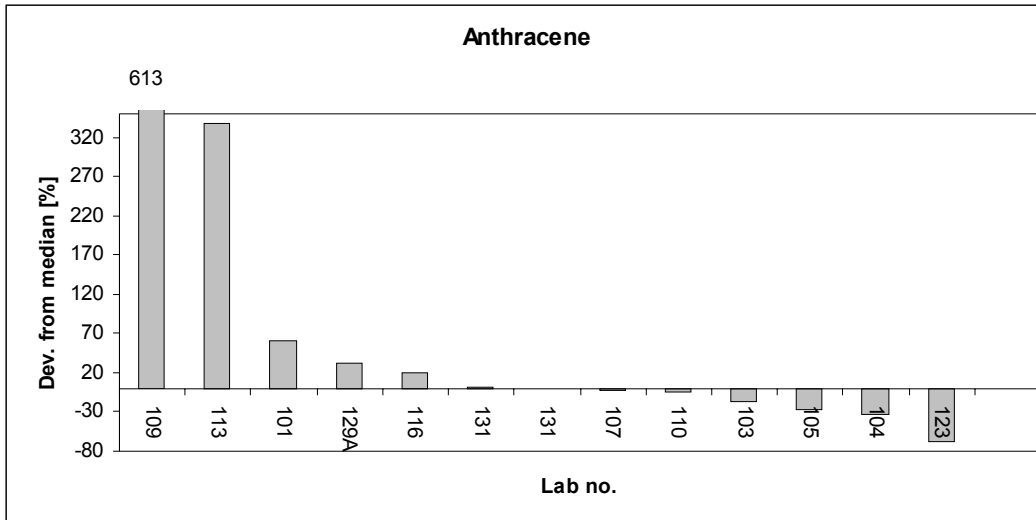


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 6,68

Lab. no.	Dev. from median %	ng/m ³
101	39	9,28
129A	27	8,4546
116	25	8,35
131	12	7,48
131	9	7,27
109	2	6,8
108	0	6,69
102	0	6,66
103	-4	6,402977333
105	-14	5,722
107	-17	5,54
113	-22	5,2
104	-43	3,80953
123	-58	2,8

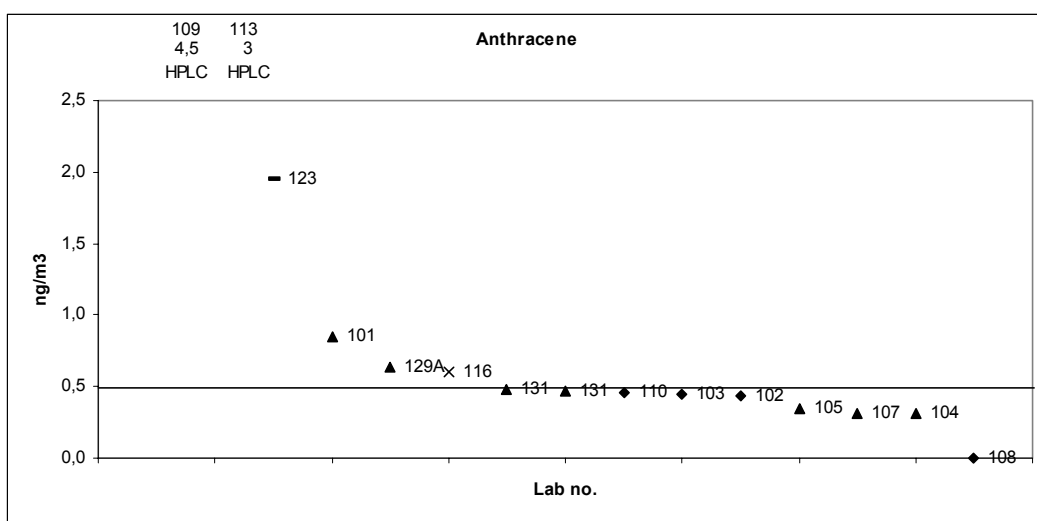
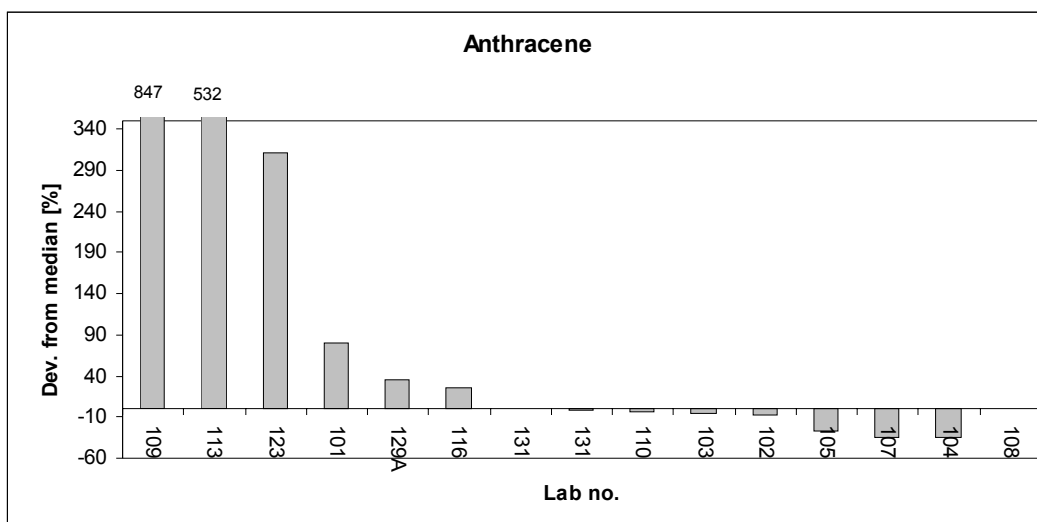


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,80

Lab. no.	Dev. from median %	ng/m3
109	613	5,7
113	338	3,5
101	60	1,28
129A	31	1,0488
116	20	0,963
131	1	0,81
131	0	0,80
107	-3	0,78
110	-5	0,763
103	-17	0,667454667
105	-27	0,583
104	-33	0,53571
123	-69	0,25
108		< 0,77

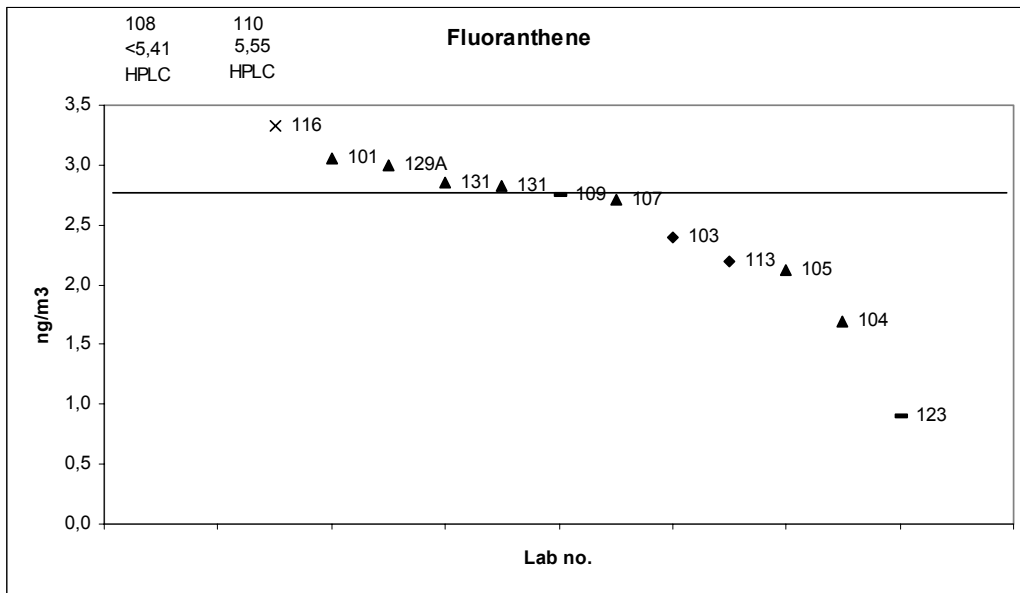
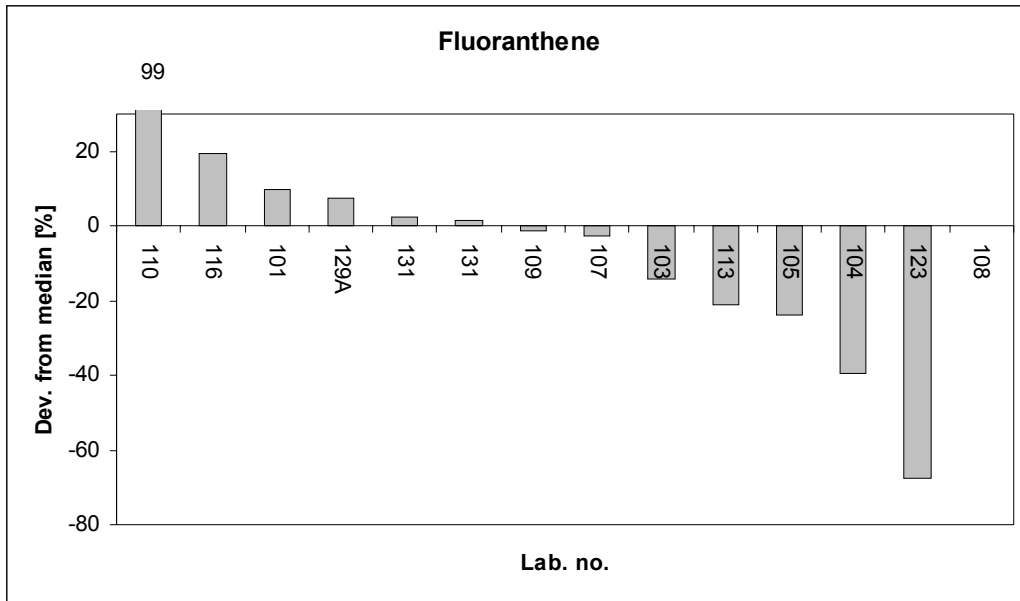


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 14 Median: 0,475

Lab. no.	Dev. from median %	ng/m3
109	847	4,5
113	532	3
123	311	1,95
101	79	0,85
129A	35	0,6414
116	26	0,599
131	1	0,48
131	-1	0,47
110	-4	0,454
103	-6	0,44492
102	-7	0,44
105	-28	0,343
107	-35	0,31
104	-35	0,30811
108		< 0,78

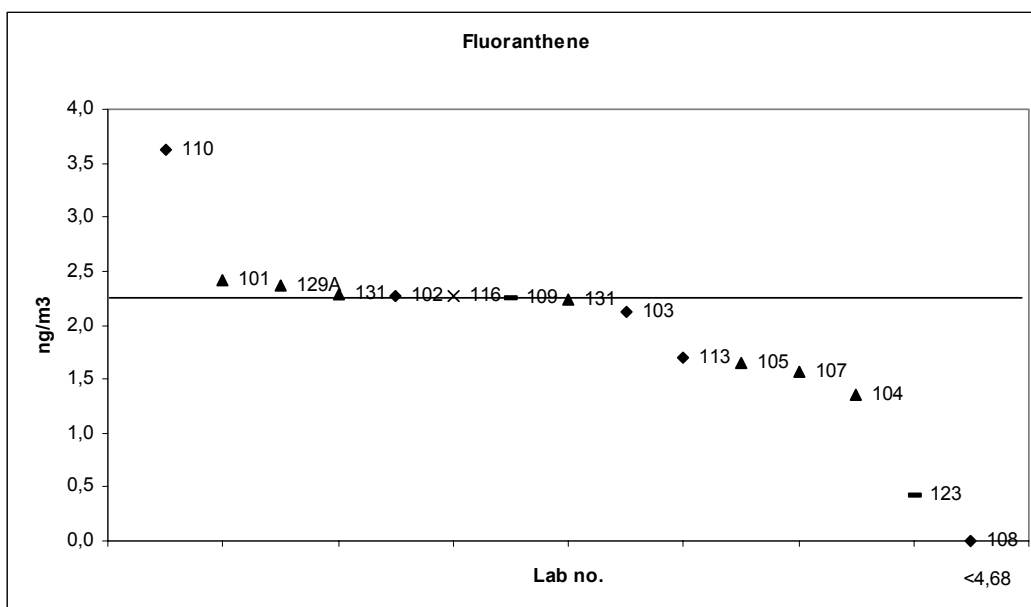
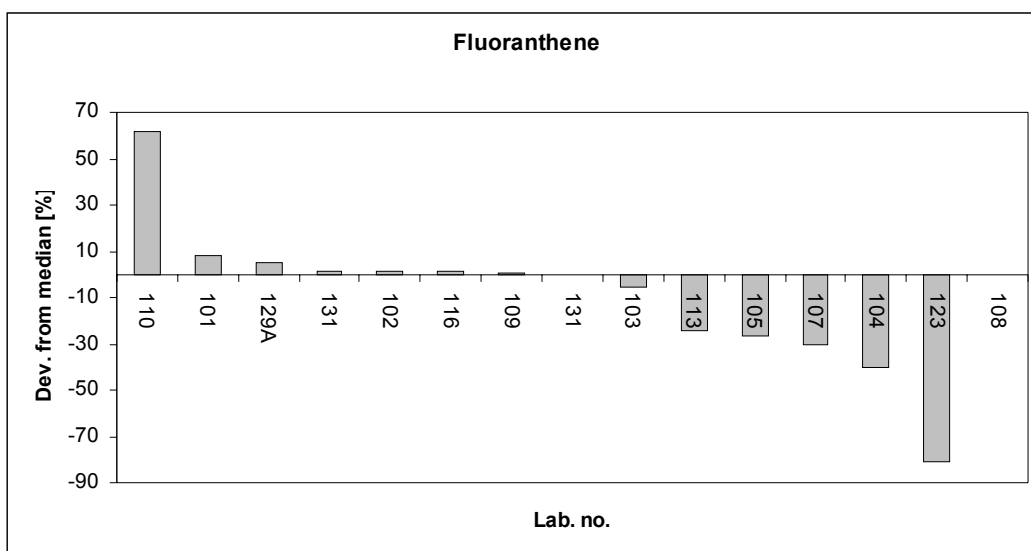


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 2,75

Lab. no.	Dev. from median%	ng/m3
110	99	5,55
116	20	3,33
101	10	3,06
129A	7	2,9914
131	2	2,85
131	1	2,82
109	-1	2,75
107	-3	2,71
103	-14	2,391342667
113	-21	2,2
105	-24	2,123
104	-39	1,68749
123	-68	0,9
108		< 5,41

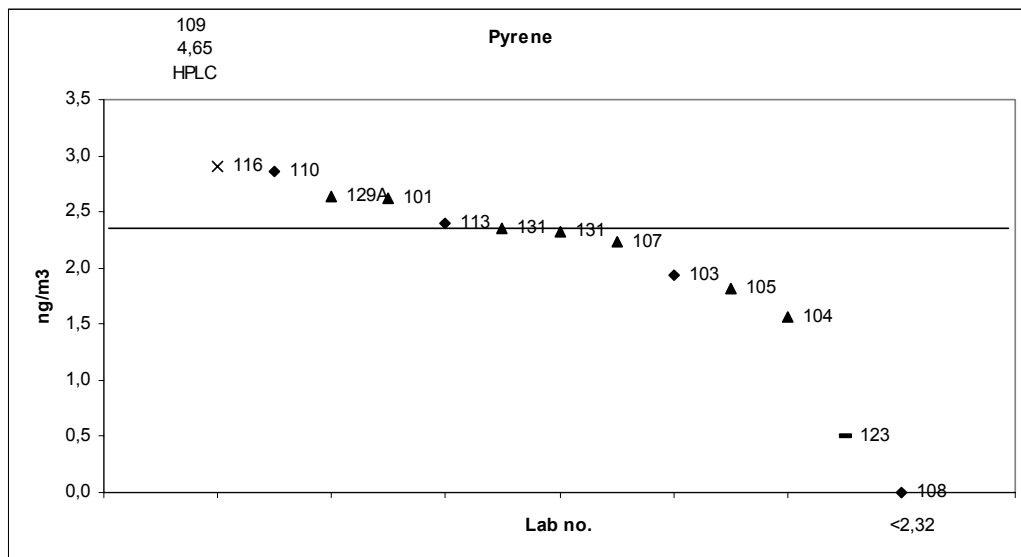
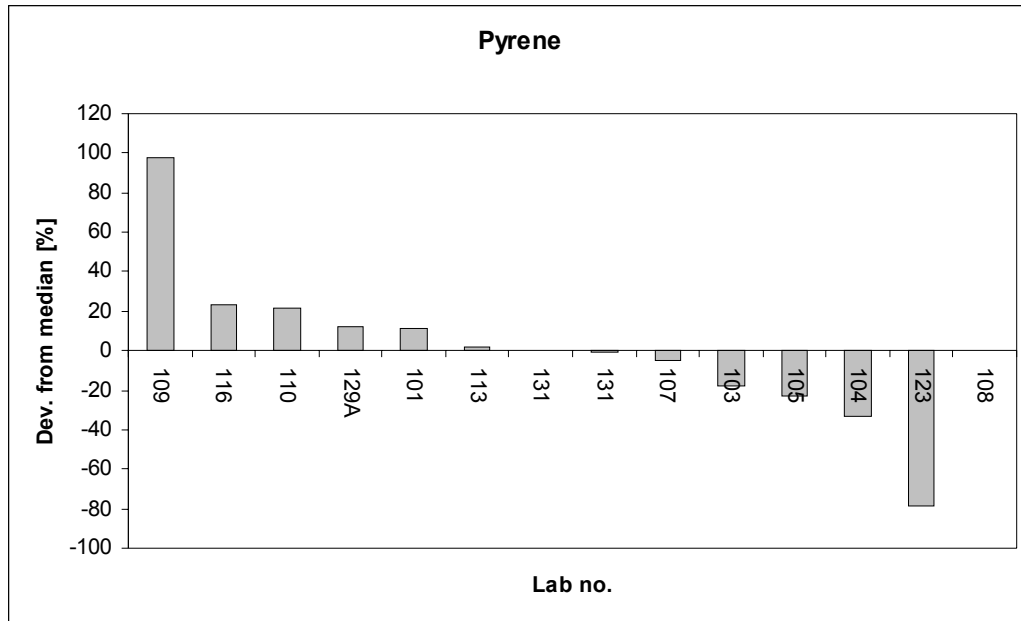


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 14 Median: 2,245

Lab. no.	Dev. from median %	ng/m ³
110	62	3,63
101	8	2,42
129A	5	2,363
131	2	2,28
102	1	2,27
116	1	2,27
109	0	2,25
131	0	2,24
103	-5	2,123284
113	-24	1,7
105	-27	1,649
107	-31	1,56
104	-40	1,34752
123	-81	0,42
108		< 4,68

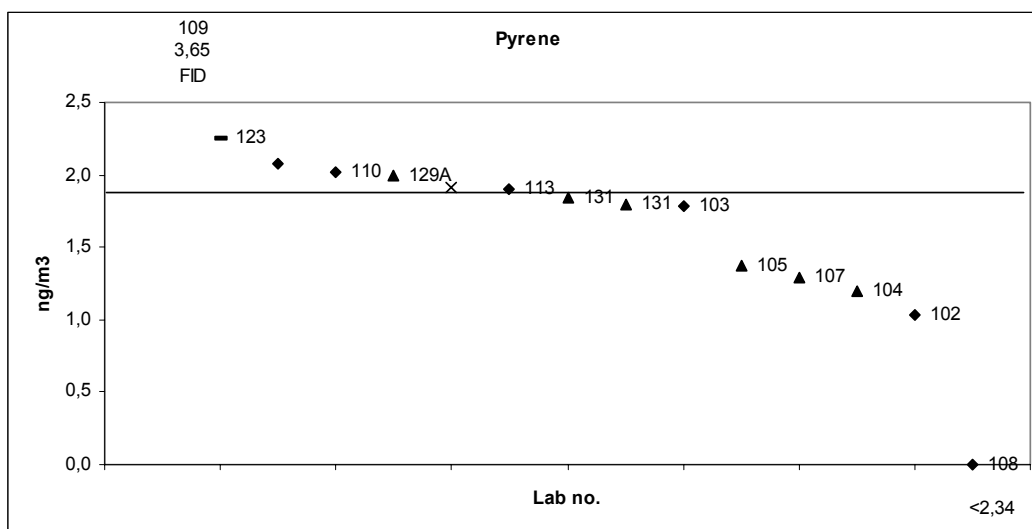
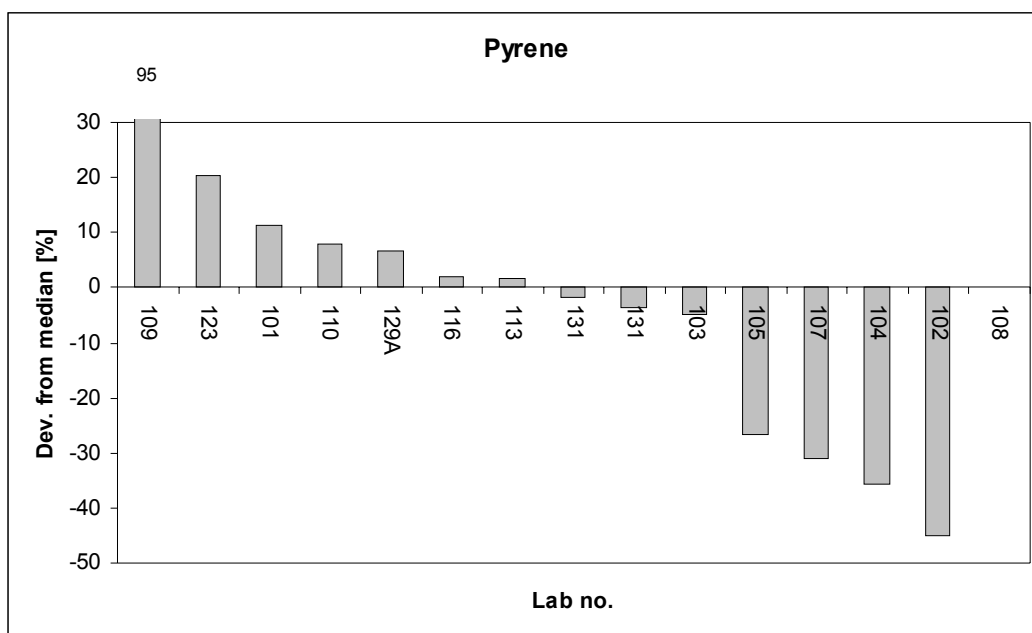


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 2,35

Lab. no.	Dev. from median %	ng/m ³
109	98	4,65
116	23	2,9
110	22	2,86
129A	12	2,6376
101	11	2,62
113	2	2,4
131	0	2,35
131	-1	2,33
107	-5	2,23
103	-18	1,931886667
105	-23	1,81
104	-33	1,56447
123	-79	0,5
108		< 2,32

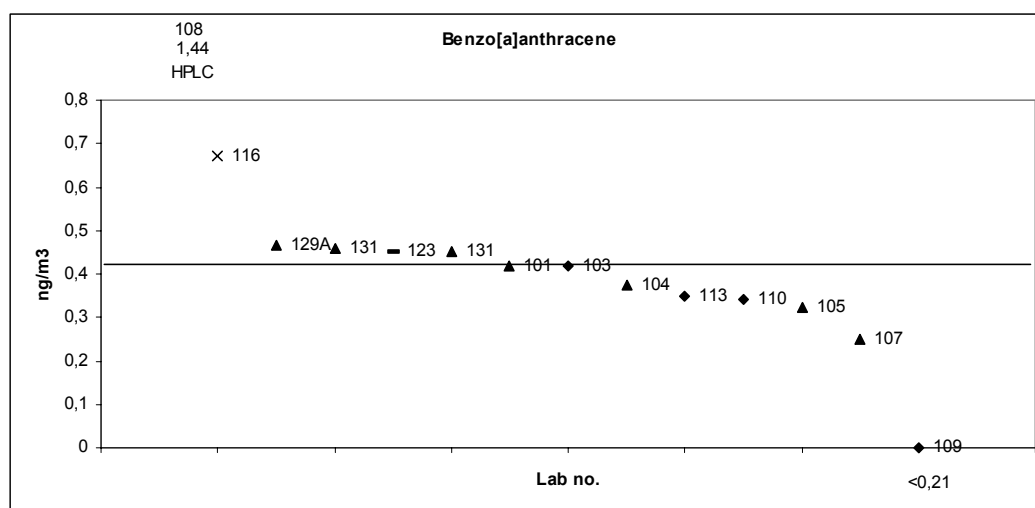
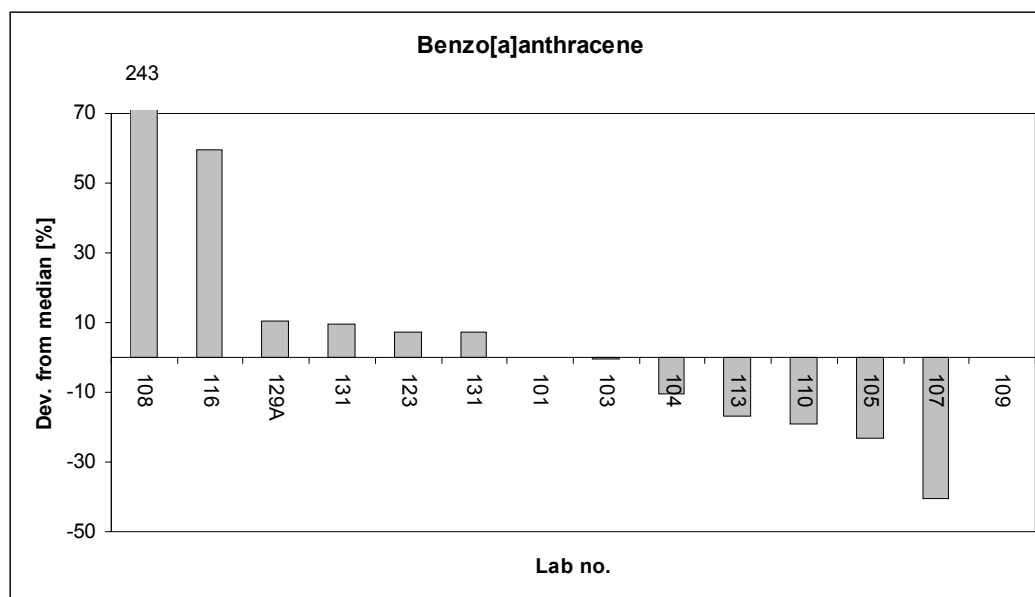


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 14 Median: 1,87

Lab. no.	Dev. from median %	ng/m ³
109	95	3,65
123	20	2,25
101	11	2,08
110	8	2,02
129A	7	1,994
116	2	1,91
113	2	1,9
131	-2	1,84
131	-4	1,8
103	-5	1,779076
105	-27	1,374
107	-31	1,29
104	-36	1,20284
102	-45	1,03
108		< 2,34

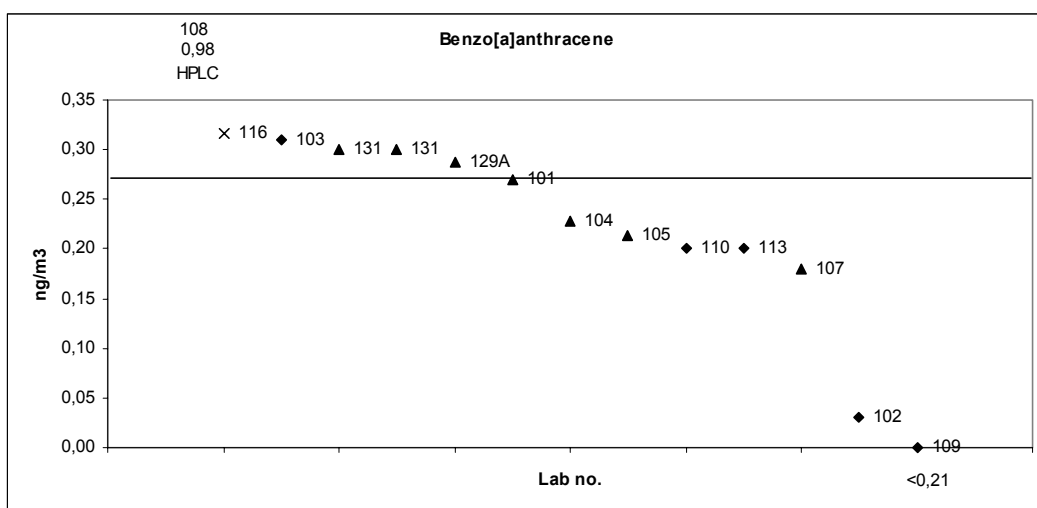
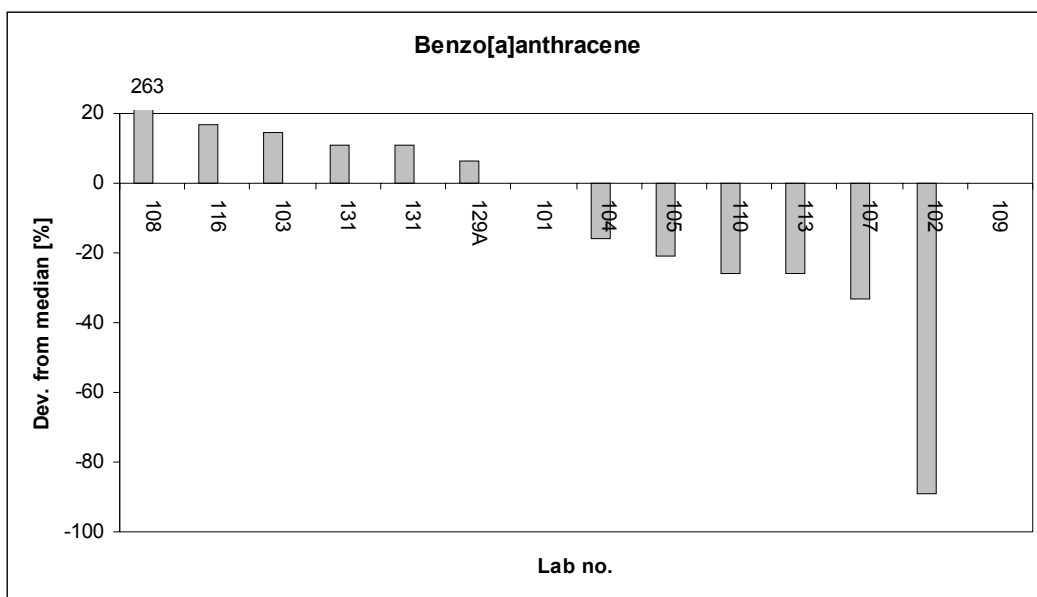


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 13 Median: 0,42

Lab. no.	Dev. from median	ng/m3
108	243	1,44
116	60	0,671
129A	11	0,4648
131	10	0,46
123	7	0,45
131	7	0,45
101	0	0,42
103	-1	0,417665333
104	-11	0,37534
113	-17	0,35
110	-19	0,34
105	-23	0,322
107	-40	0,25
109		<0,21

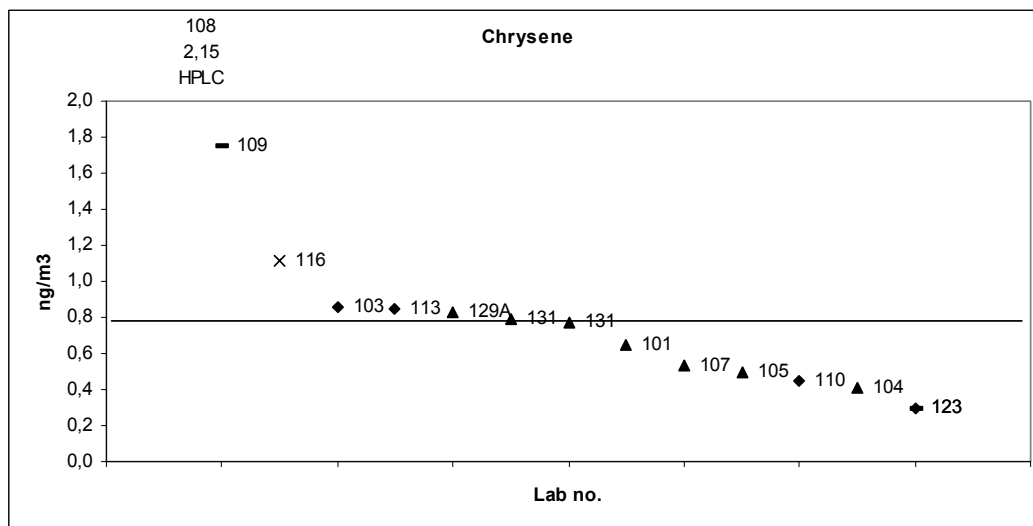
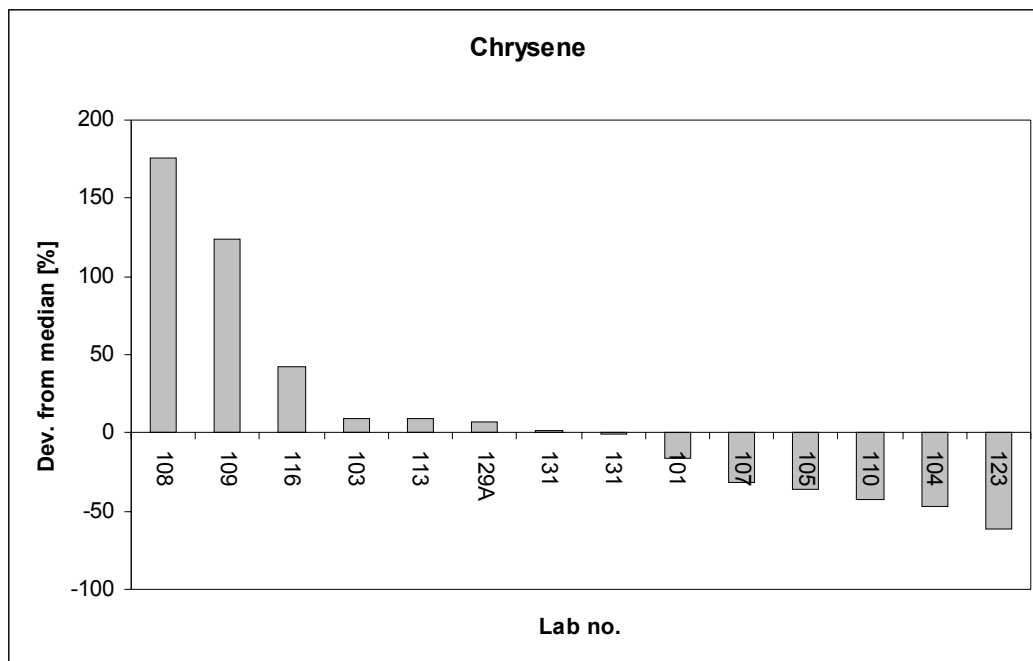


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 13 Median: 0,27

Lab. no.	Dev. from median %	ng/m3
108	263	0,98
116	17	0,316
103	15	0,309314667
131	11	0,3
131	11	0,3
129A	6	0,2874
101	0	0,27
104	-16	0,22721
105	-21	0,214
110	-26	0,2
113	-26	0,2
107	-33	0,18
102	-89	0,03
109		<0,21

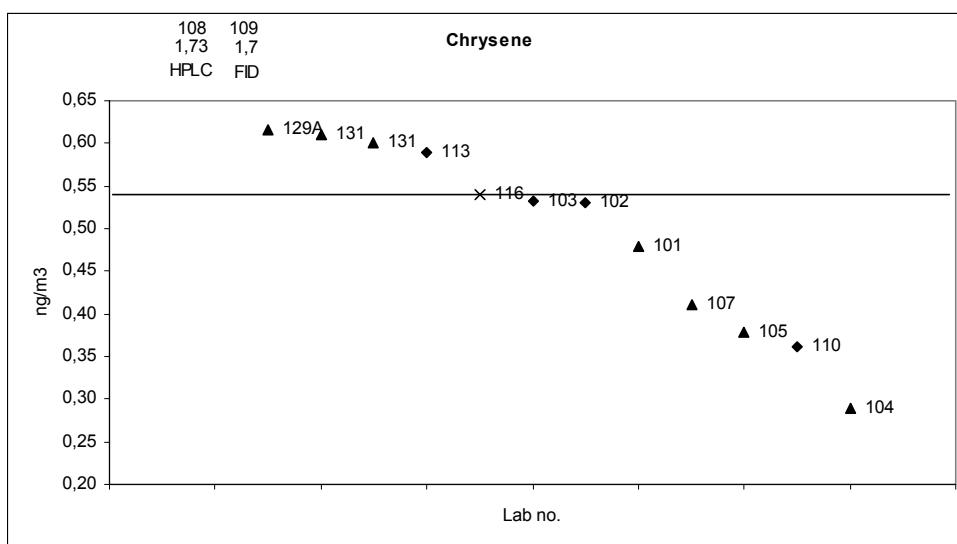
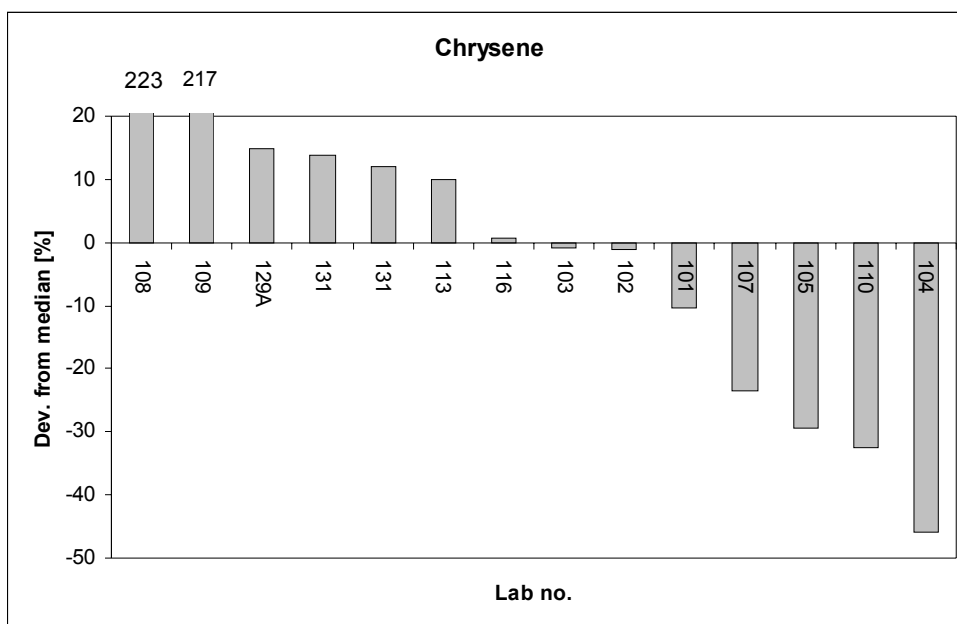


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories:13 Median: 0,78

Lab. no.	Dev. from median %	ng/m3
108	176	2,15
109	124	1,75
116	42	1,11
103	10	0,854905333
113	9	0,85
129A	7	0,8328
131	1	0,79
131	-1	0,77
101	-17	0,65
107	-32	0,53
105	-36	0,498
110	-43	0,448
104	-48	0,40931
123	-62	0,3

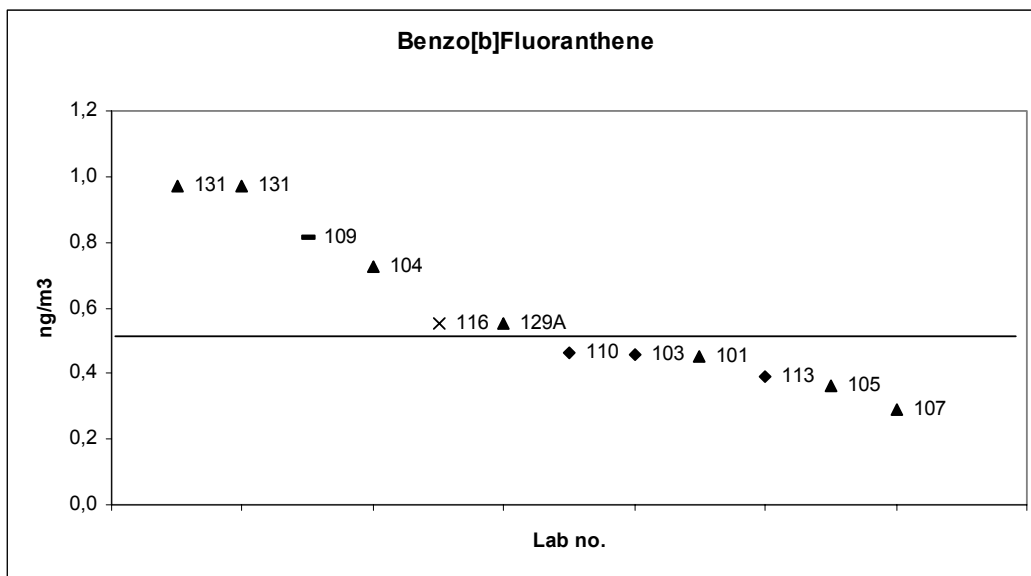
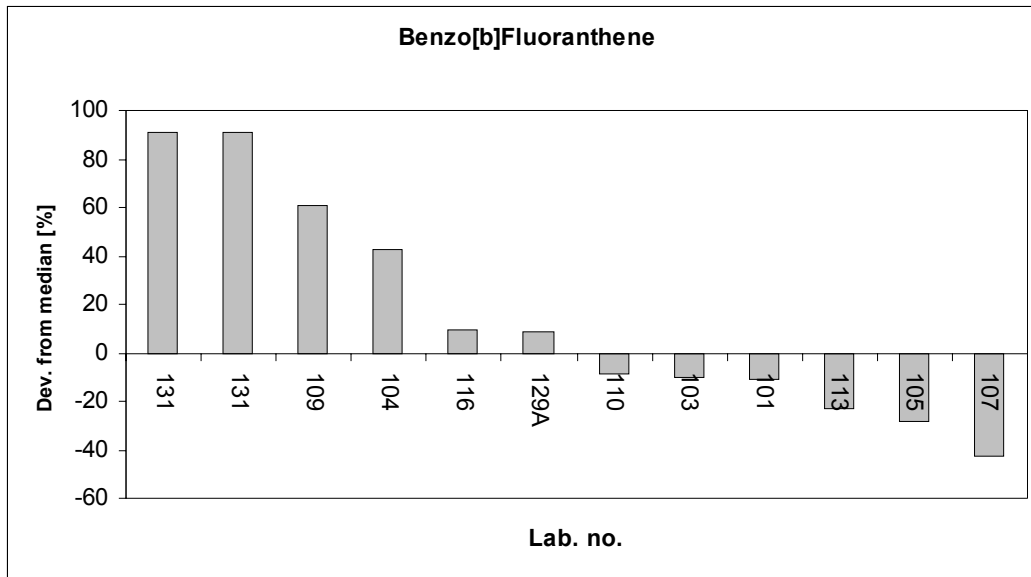


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,536

Lab. no.	Dev. from median %	ng/m3
108	223	1,73
109	217	1,7
129A	15	0,6158
131	14	0,61
131	12	0,6
113	10	0,59
116	1	0,54
103	-1	0,532266667
102	-1	0,53
101	-10	0,48
107	-24	0,41
105	-29	0,379
110	-32	0,362
104	-46	0,29007

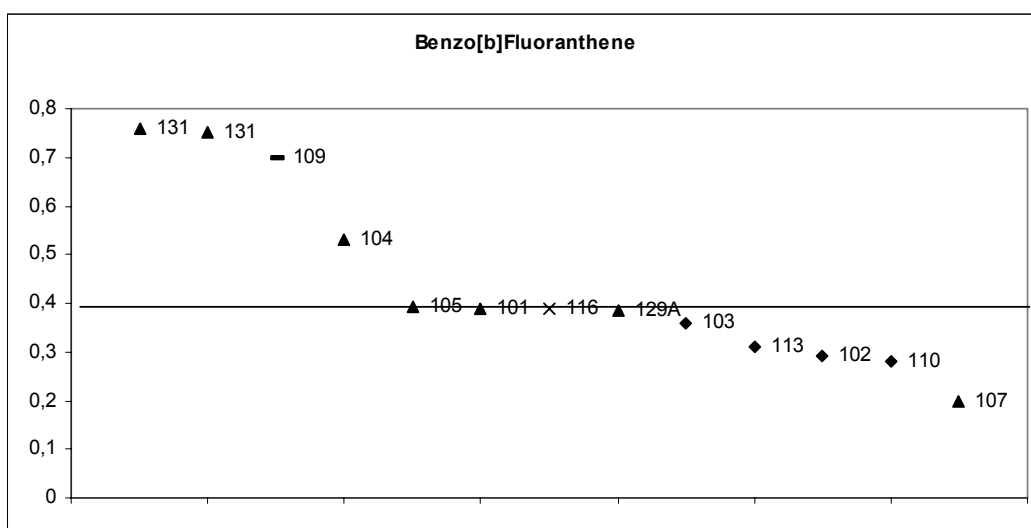
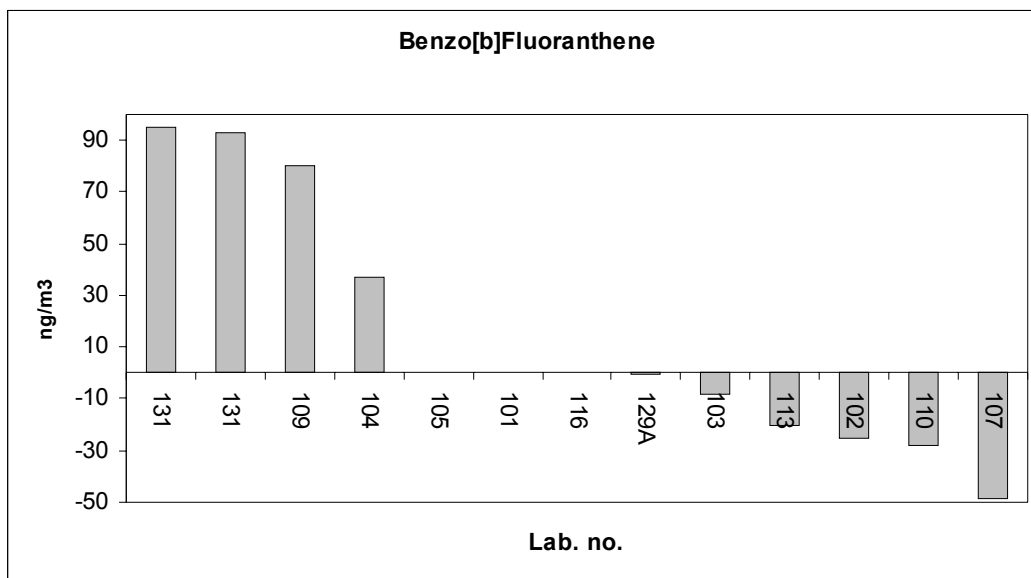


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 11 Median: 0,51

Lab. no.	Dev. from median %	ng/m ³
131	91	0,97
131	91	0,97
109	61	0,815
104	43	0,72282
116	9	0,555
129A	8	0,5502
110	-8	0,464
103	-10	0,457233333
101	-11	0,45
113	-23	0,39
105	-28	0,365
107	-43	0,29

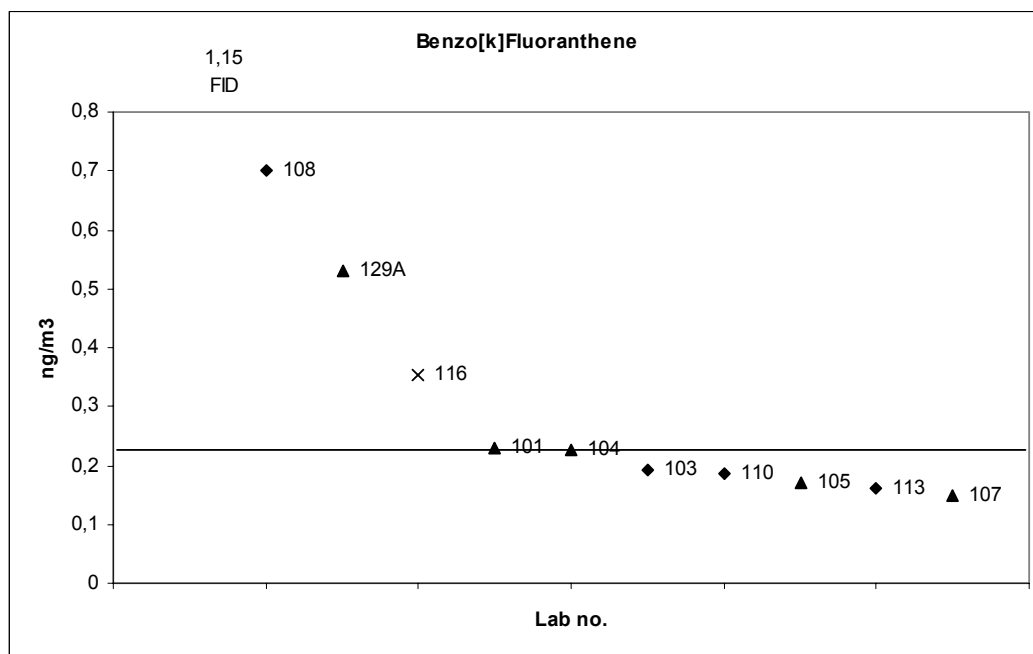
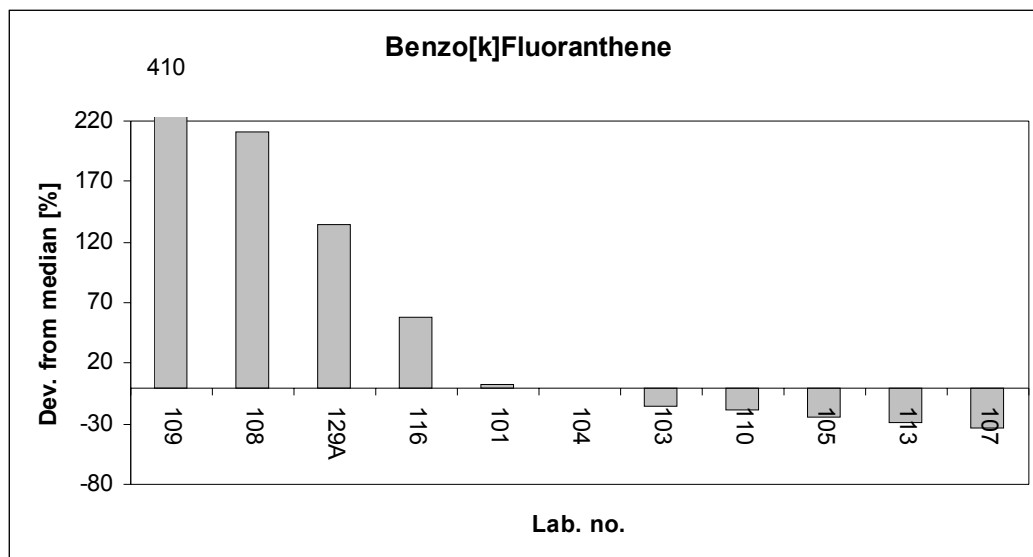


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories:12 Median: 0,389

Lab. no.	Dev. from median %	ng/m3
131	95	0,76
131	93	0,75
109	80	0,7
104	37	0,53254
105	1	0,391
101	0	0,39
116	0	0,389
129A	-1	0,386
103	-8	0,35818
113	-20	0,31
102	-25	0,29
110	-28	0,279
107	-49	0,2

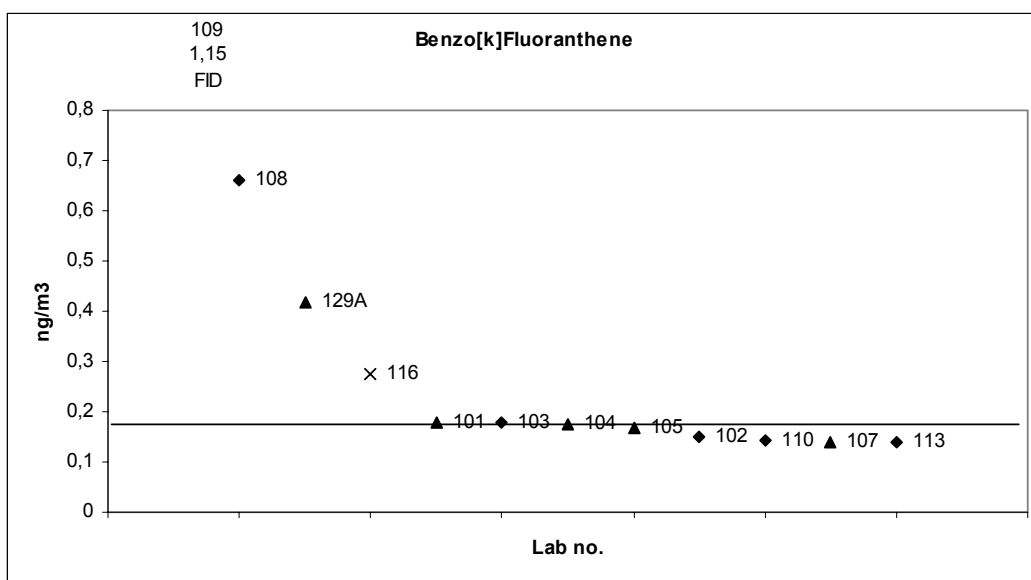
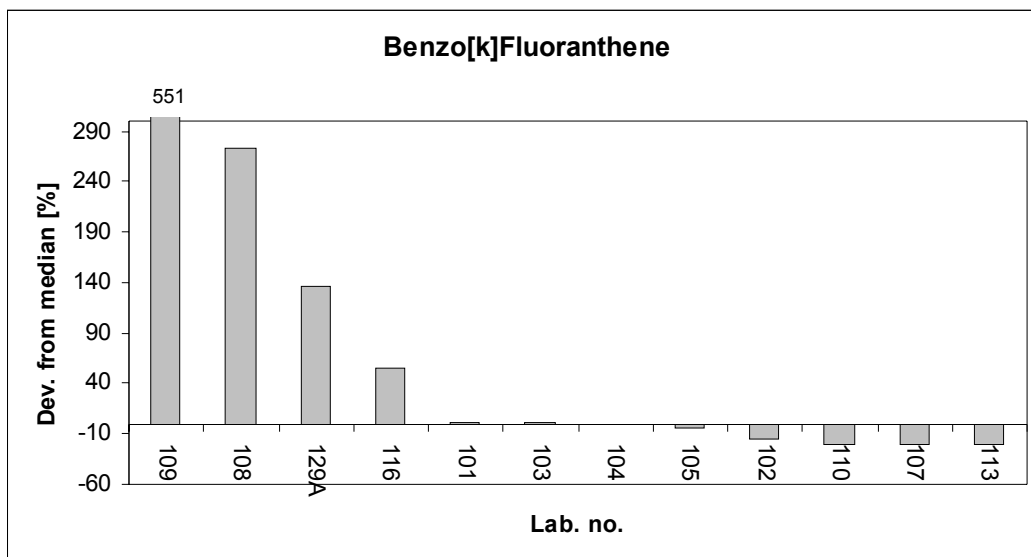


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 11 Median: 0,226

Lab. no.	Dev. from median %	ng/m ³
109	410	1,15
108	210	0,7
129A	135	0,5302
116	57	0,355
101	2	0,23
104	0	0,22559
103	-15	0,190993333
110	-18	0,185
105	-24	0,172
113	-29	0,16
107	-34	0,15

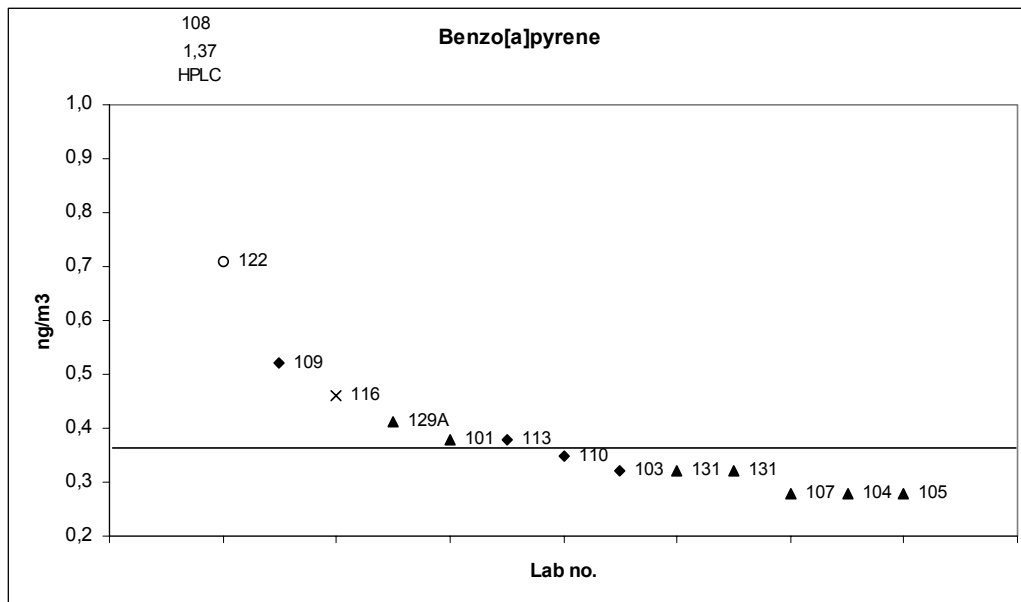
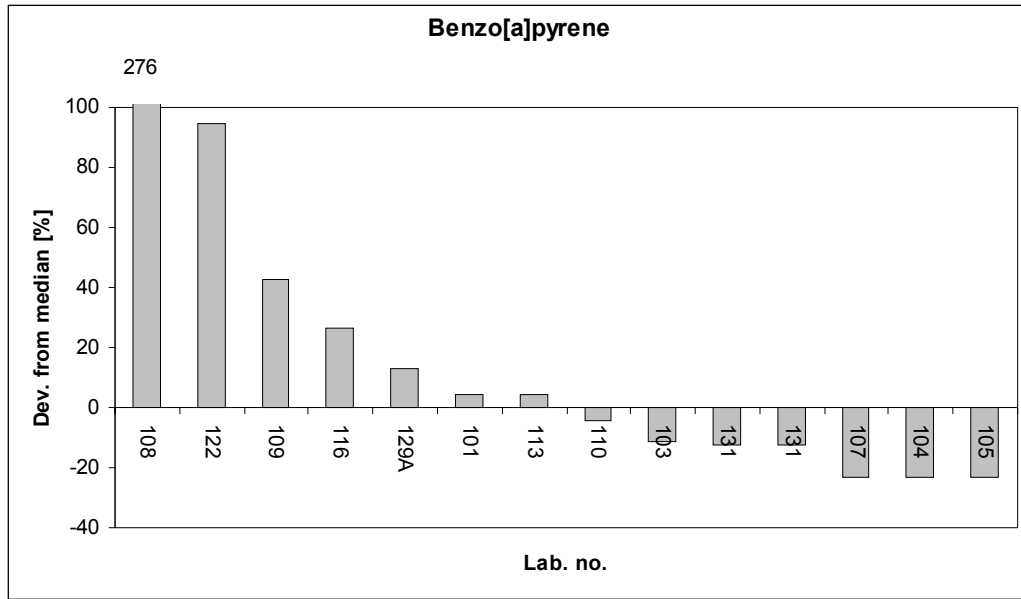


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 12 Median: 0,177

Lab. no.	Dev. from median %	ng/m ³
109	551	1,15
108	273	0,66
129A	136	0,4166
116	55	0,274
101	2	0,18
103	1	0,178508
104	-1	0,17506
105	-5	0,168
102	-15	0,15
110	-20	0,142
107	-21	0,14
113	-21	0,14

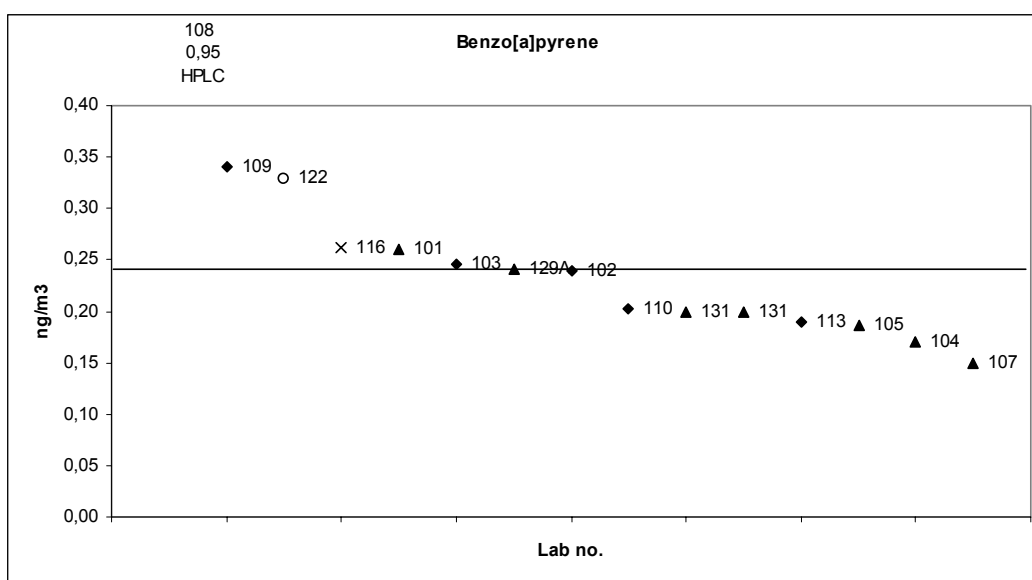
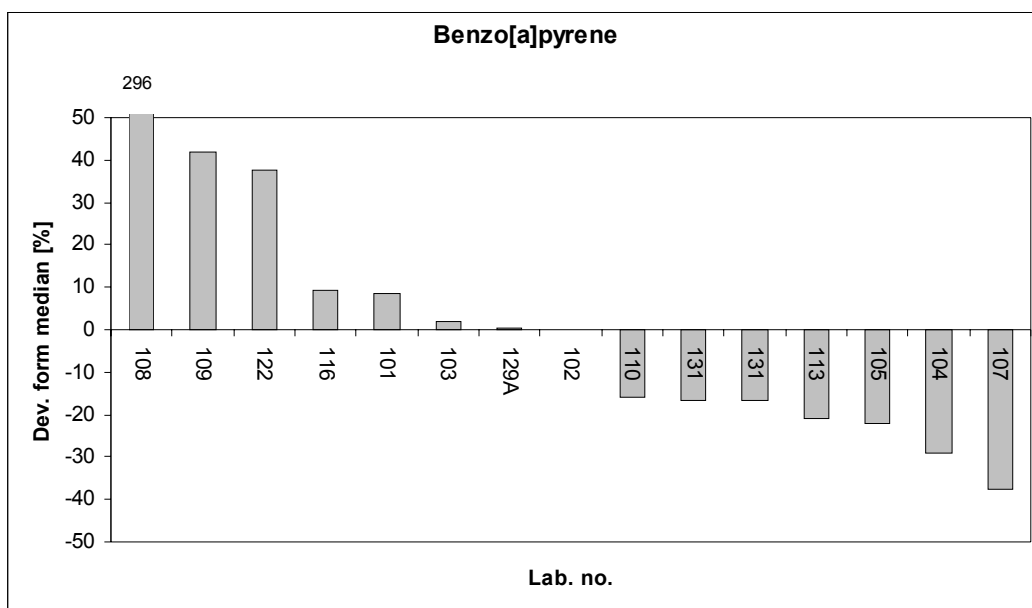


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,36

Lab. no.	Dev. from median %	ng/m ³
108	276	1,37
122	95	0,71
109	43	0,52
116	27	0,462
129A	13	0,4114
101	4	0,38
113	4	0,38
110	-4	0,349
103	-12	0,3223
131	-12	0,32
131	-12	0,32
107	-23	0,28
104	-23	0,2793
105	-23	0,279

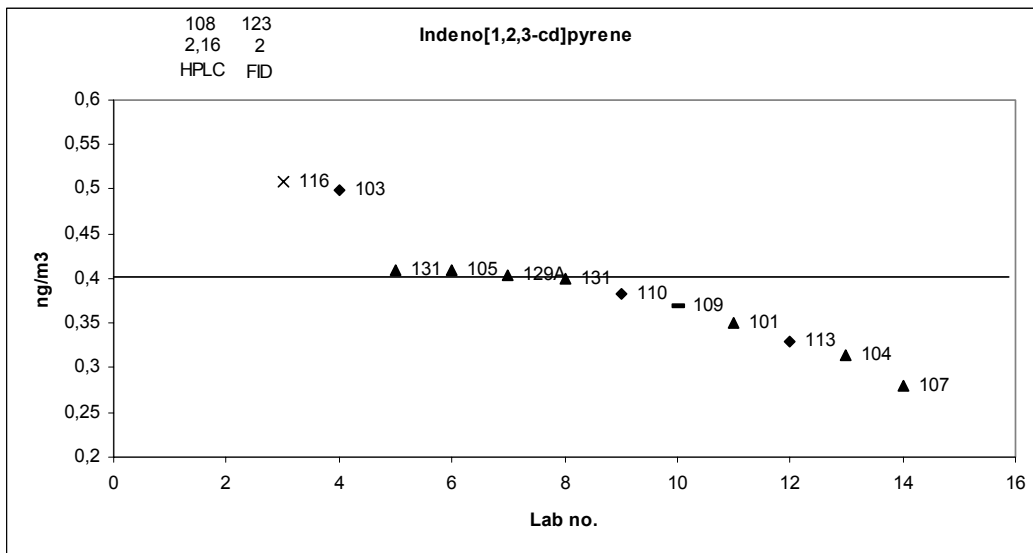
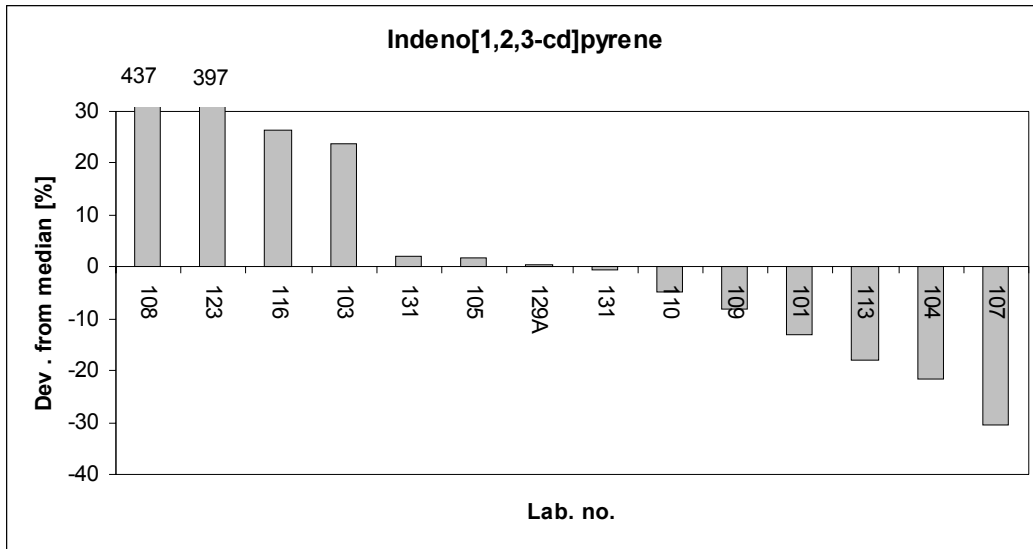


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 14 Median: 0,24

Lab. no.	Dev. from median %	ng/m ³
108	296	0,95
109	42	0,34
122	38	0,33
116	9	0,262
101	8	0,26
103	2	0,245026667
129A	1	0,2412
102	0	0,24
110	-16	0,202
131	-17	0,2
131	-17	0,2
113	-21	0,19
105	-22	0,187
104	-29	0,17022
107	-38	0,15

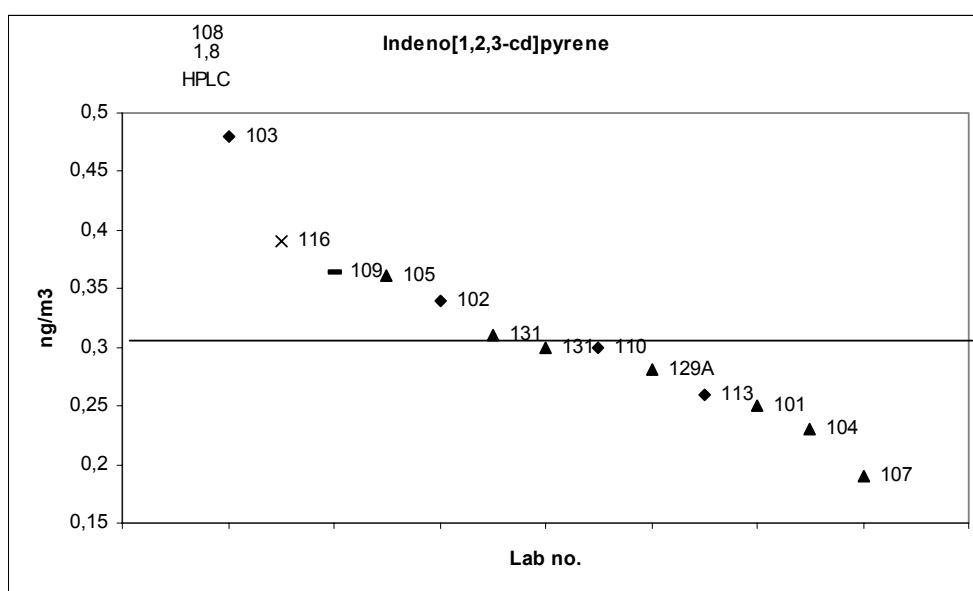
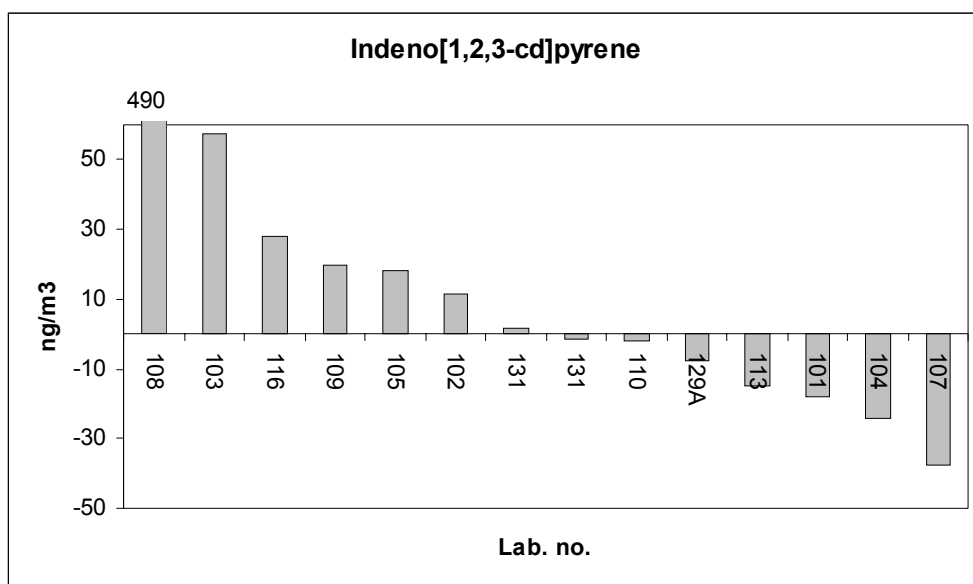


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,402

Lab. no.	Dev. from median %	ng/m ³
108	437	2,16
123	397	2
116	26	0,508
103	24	0,498177333
131	2	0,41
105	2	0,409
129A	1	0,4042
131	-1	0,40
110	-5	0,382
109	-8	0,37
101	-13	0,35
113	-18	0,33
104	-22	0,31502
107	-30	0,28

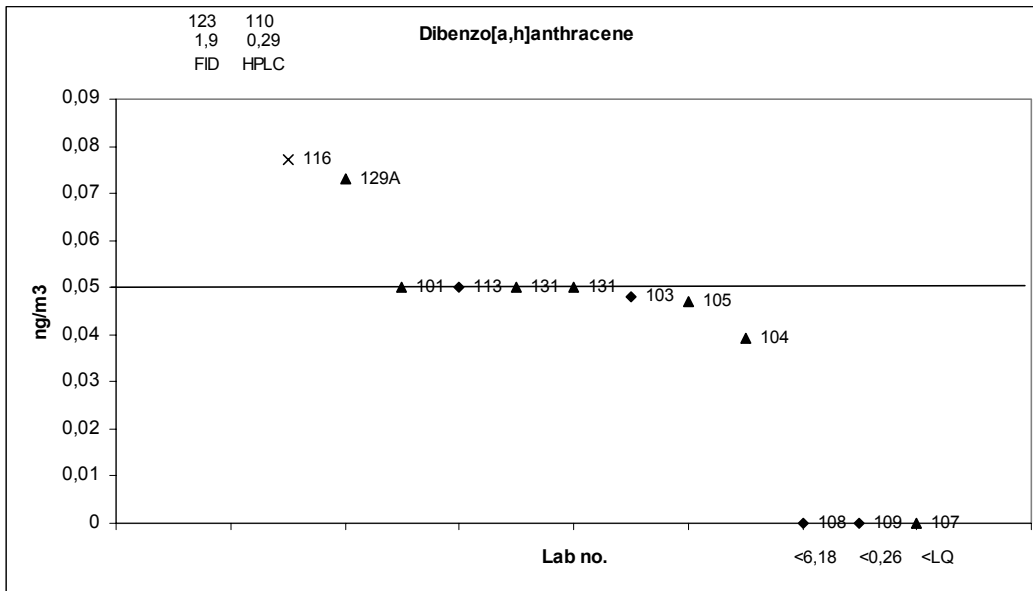
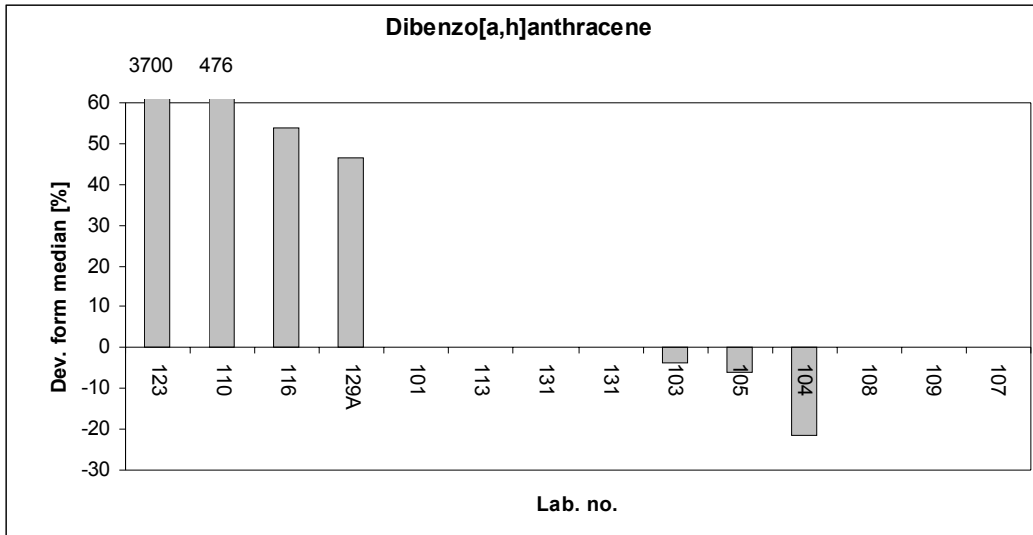


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 13 Median: 0,305

Lab. no.	Dev. from median %	ng/m ³
108	490	1,8
103	57	0,4795
116	28	0,391
109	20	0,365
105	18	0,361
102	11	0,34
131	2	0,31
131	-2	0,3
110	-2	0,299
129A	-8	0,2814
113	-15	0,26
101	-18	0,25
104	-24	0,23082
107	-38	0,19

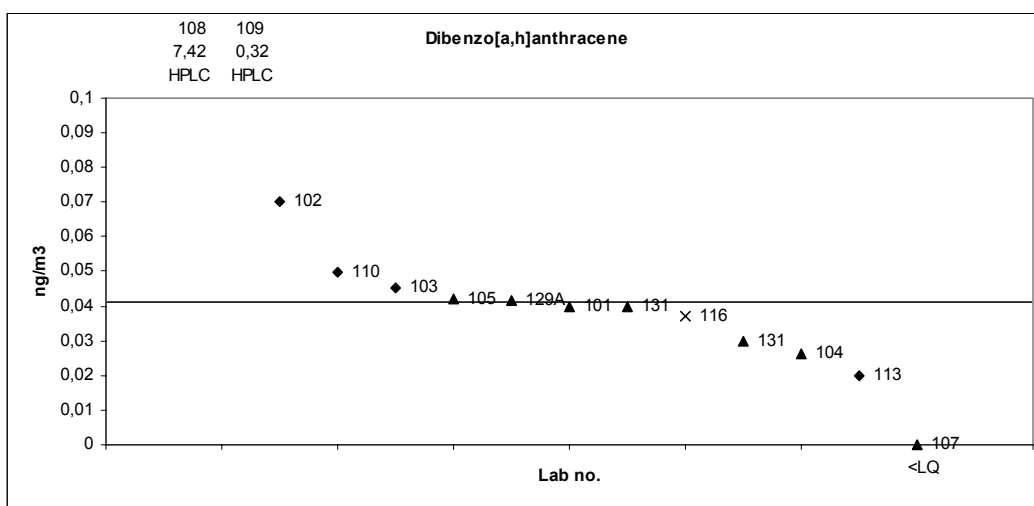
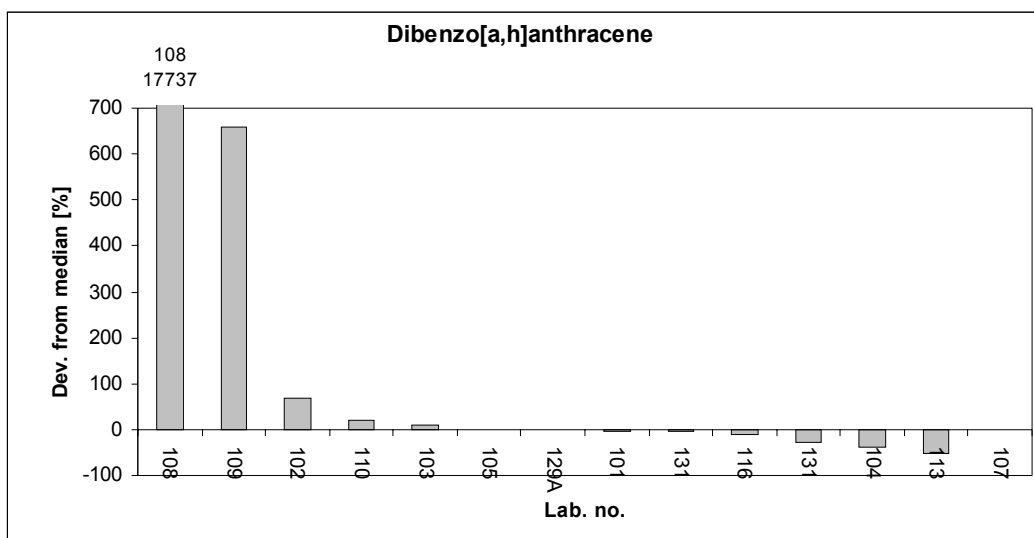


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,05

Lab. no.	Dev. from median %	ng/m ³
123	3700	1,9
110	476	0,288
116	54	0,077
129A	46	0,0732
101	0	0,05
113	0	0,05
131	0	0,05
131	0	0,05
103	-4	0,048069333
105	-6	0,047
104	-22	0,03919
108		< 6,18
109		<0,26
107		<LQ

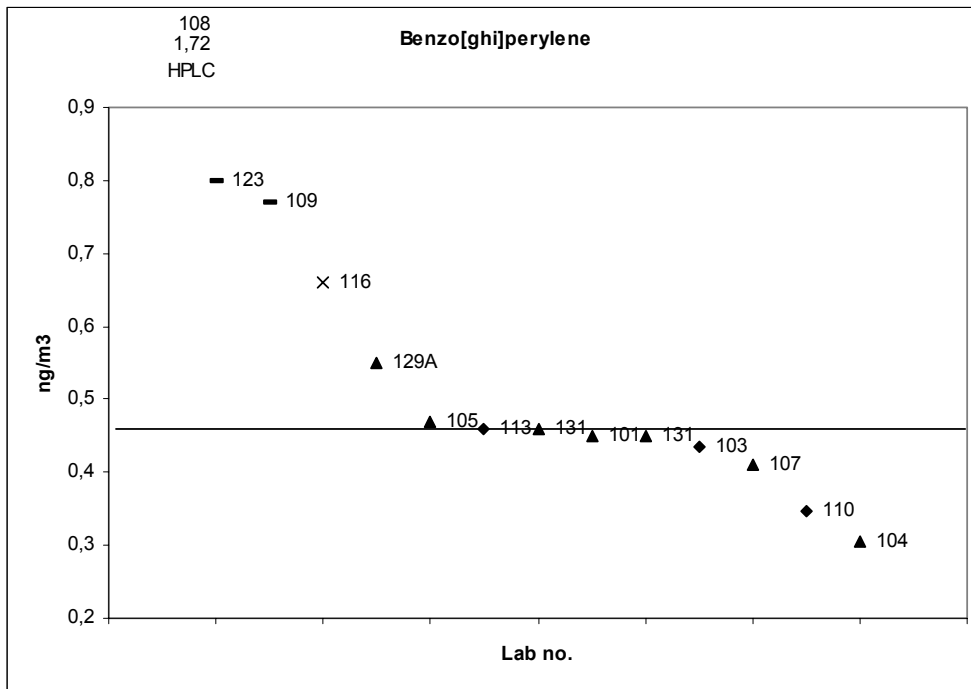
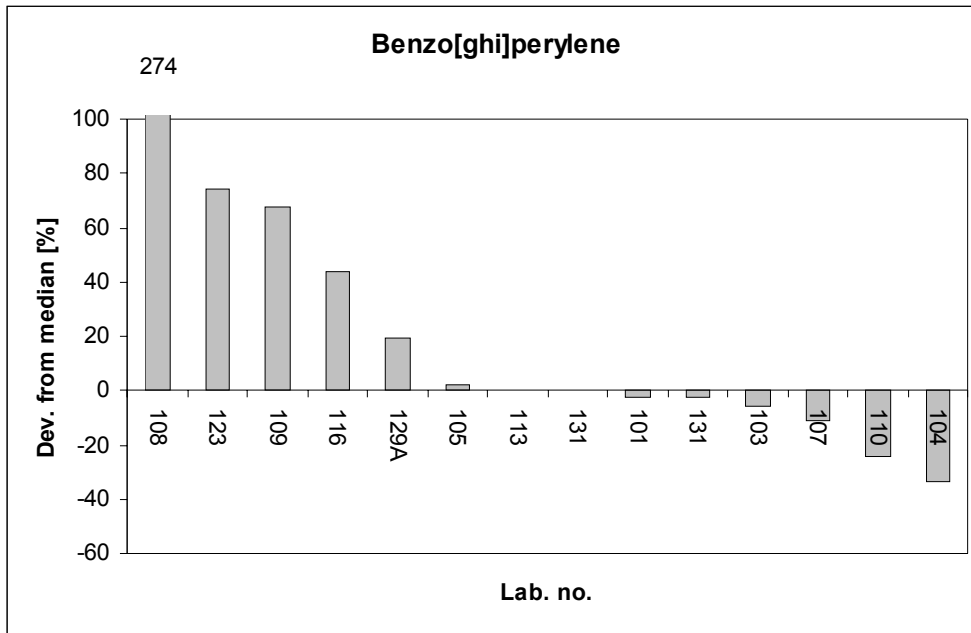


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 13 Median: 0,0416

Lab. no.	Dev. from median %	ng/m3
108	17737	7,42
109	657	0,315
102	68	0,07
110	20	0,05
103	9	0,045304
105	1	0,042
129A	0	0,0416
101	-4	0,04
131	-4	0,04
116	-11	0,037
131	-28	0,03
104	-37	0,02639
113	-52	0,02
107		<LQ

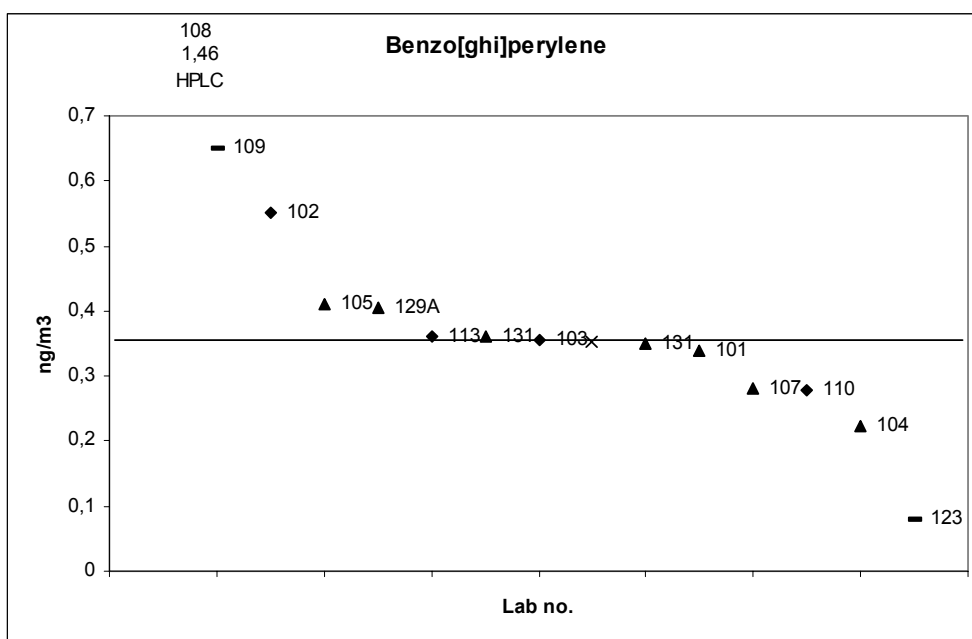
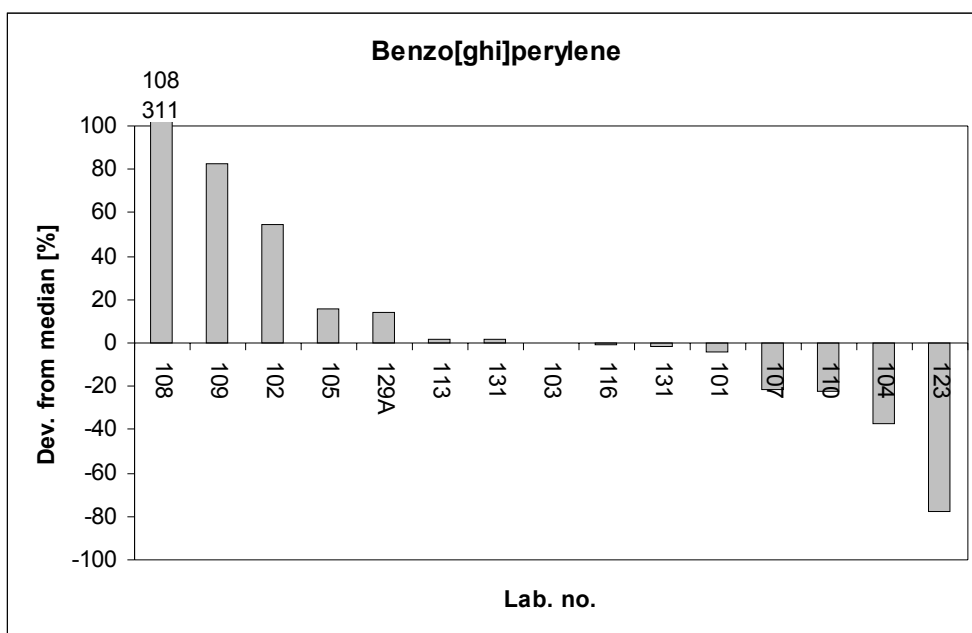


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 13 Median: 0,46

Lab. no.	Dev. from median %	ng/m ³
108	274	1,72
123	74	0,8
109	67	0,77
116	43	0,66
129A	20	0,5504
105	2	0,47
113	0	0,46
131	0	0,46
101	-2	0,45
131	-2	0,45
103	-6	0,434190667
107	-11	0,41
110	-25	0,347
104	-33	0,30642

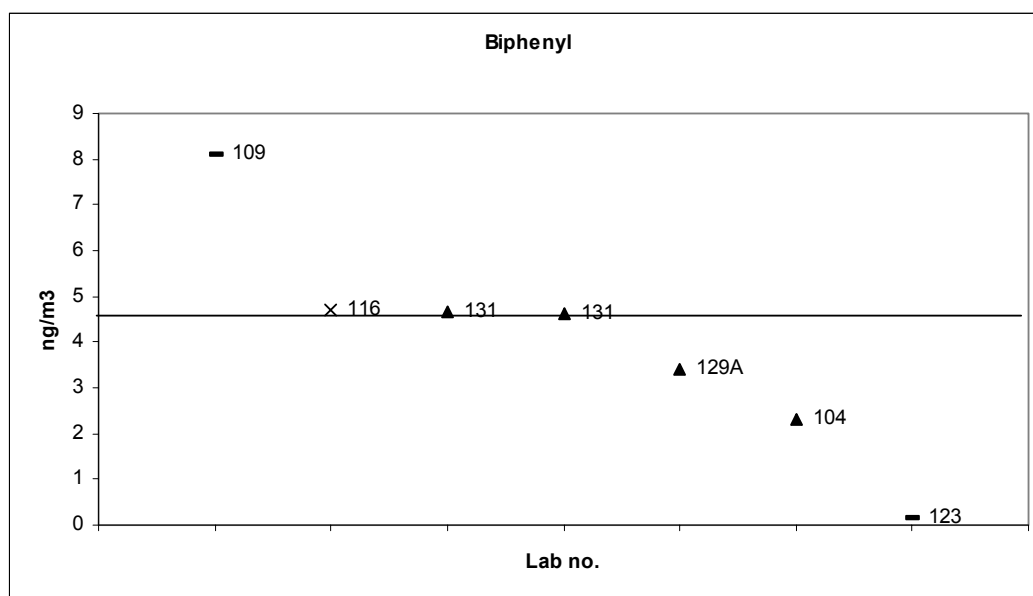
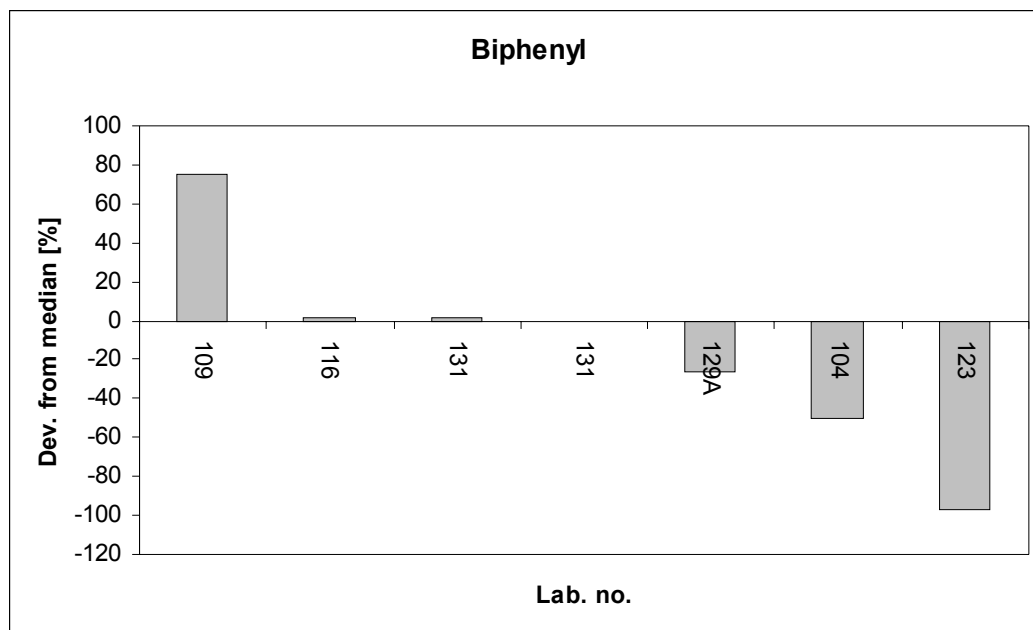


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 14 Median: 0,355

Lab. no.	Dev. from median %	ng/m3
108	311	1,46
109	83	0,65
102	55	0,55
105	15	0,41
129A	14	0,4054
113	1	0,36
131	1	0,36
103	0	0,355498667
116	-1	0,353
131	-2	0,35
101	-4	0,34
107	-21	0,28
110	-22	0,277
104	-37	0,22288
123	-77	0,08

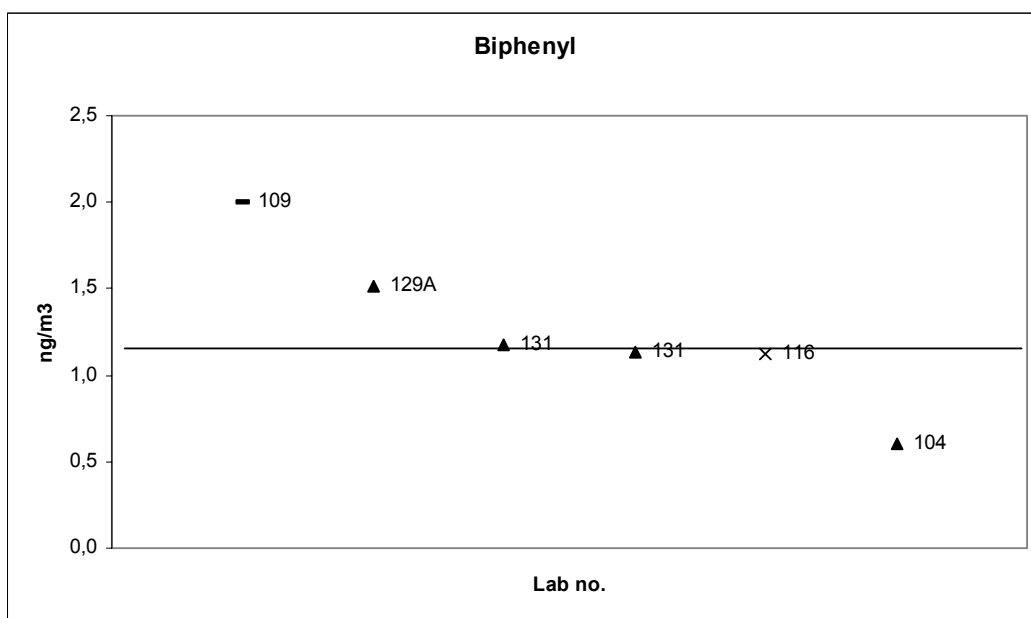
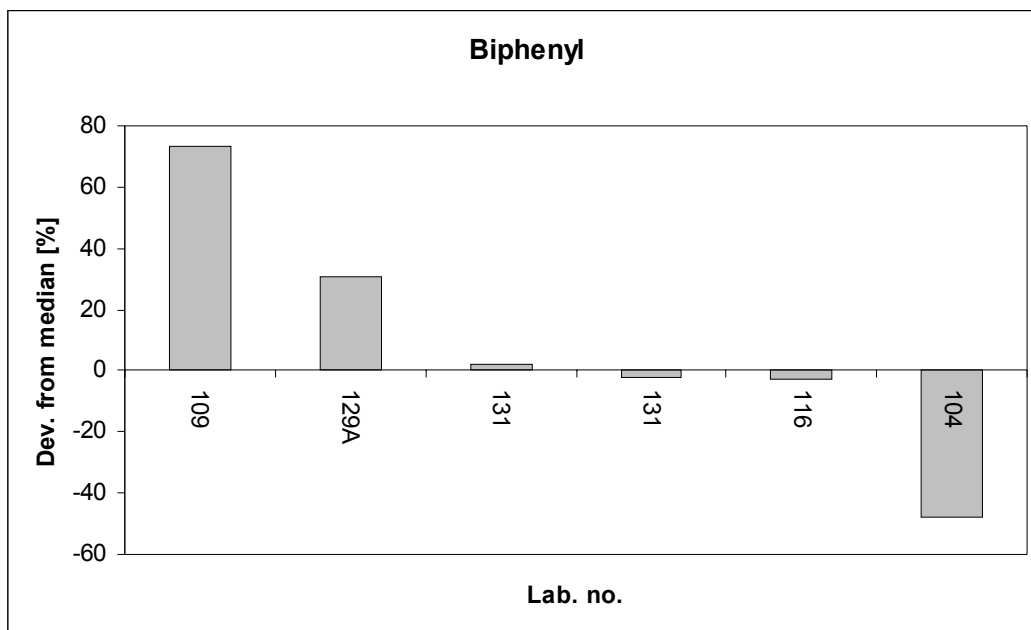


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 6 Median: 4,62

Lab. no.	Dev. from median %	ng/m ³
109	75	8,1
116	2	4,7
131	1	4,68
131	0	4,62
129A	-26	3,3996
104	-50	2,32367
123	-97	0,15

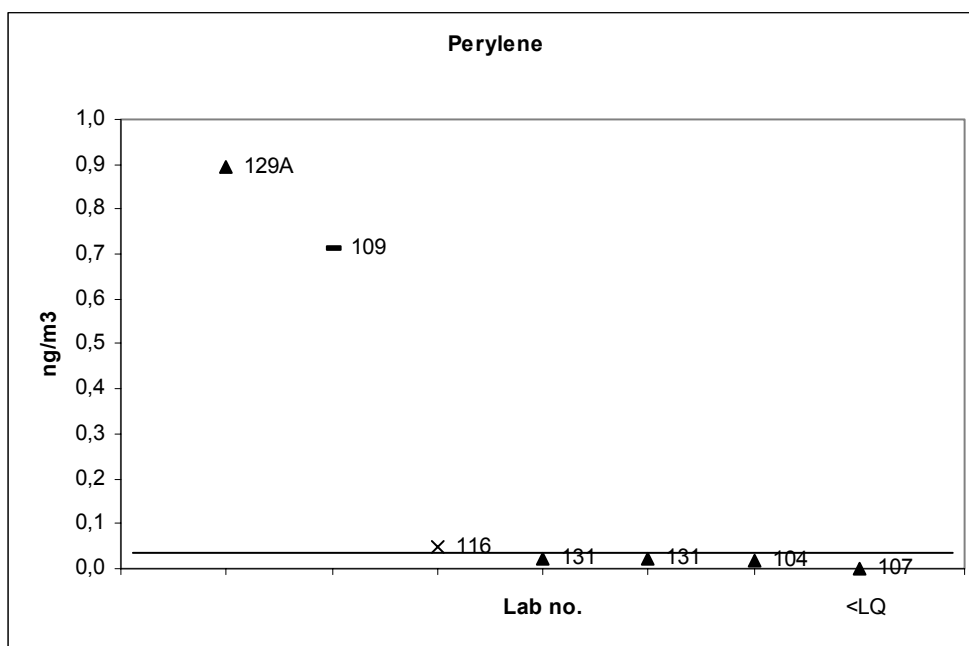
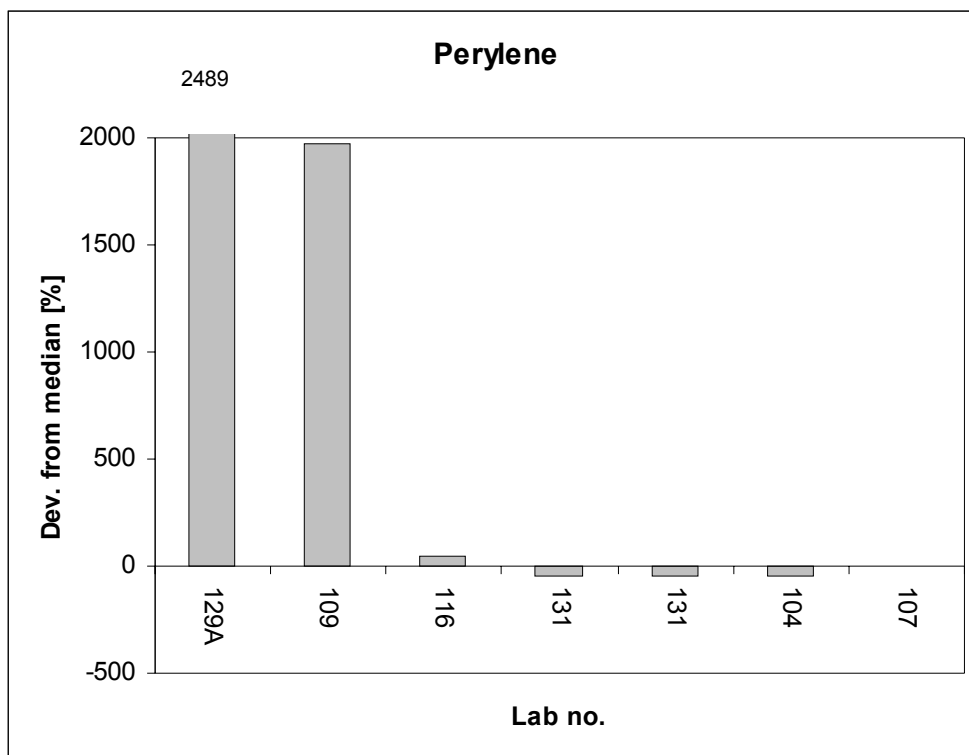


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 5 Median: 1,16

Lab. no.	Dev. from median %	ng/m ³
109	73	2
129A	31	1,5104
131	2	1,18
131	-2	1,13
116	-3	1,12
104	-48	0,60386

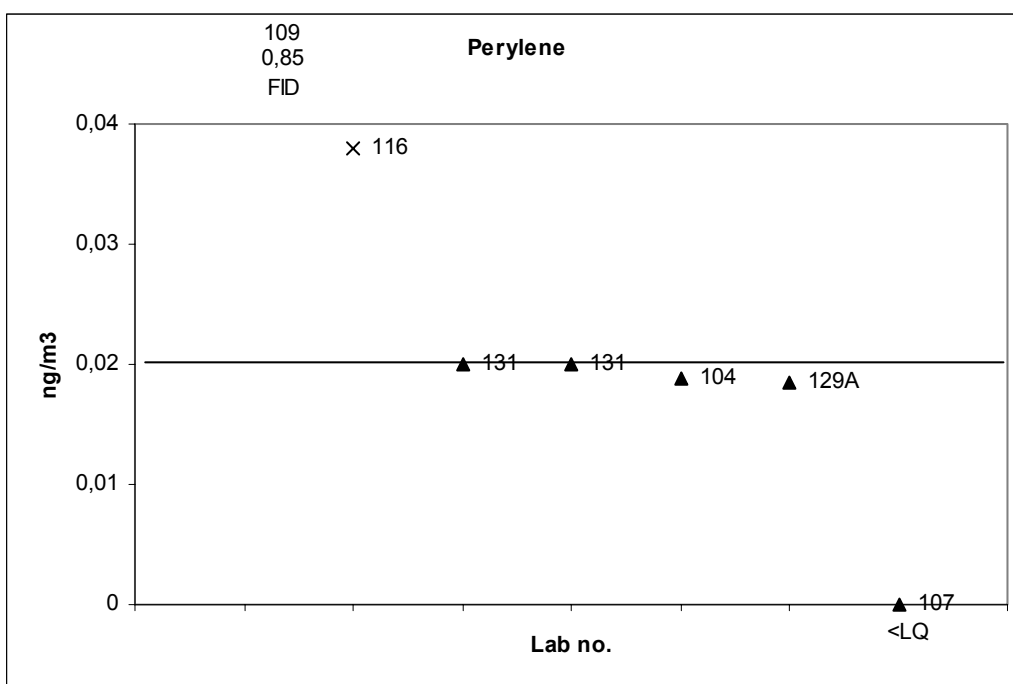
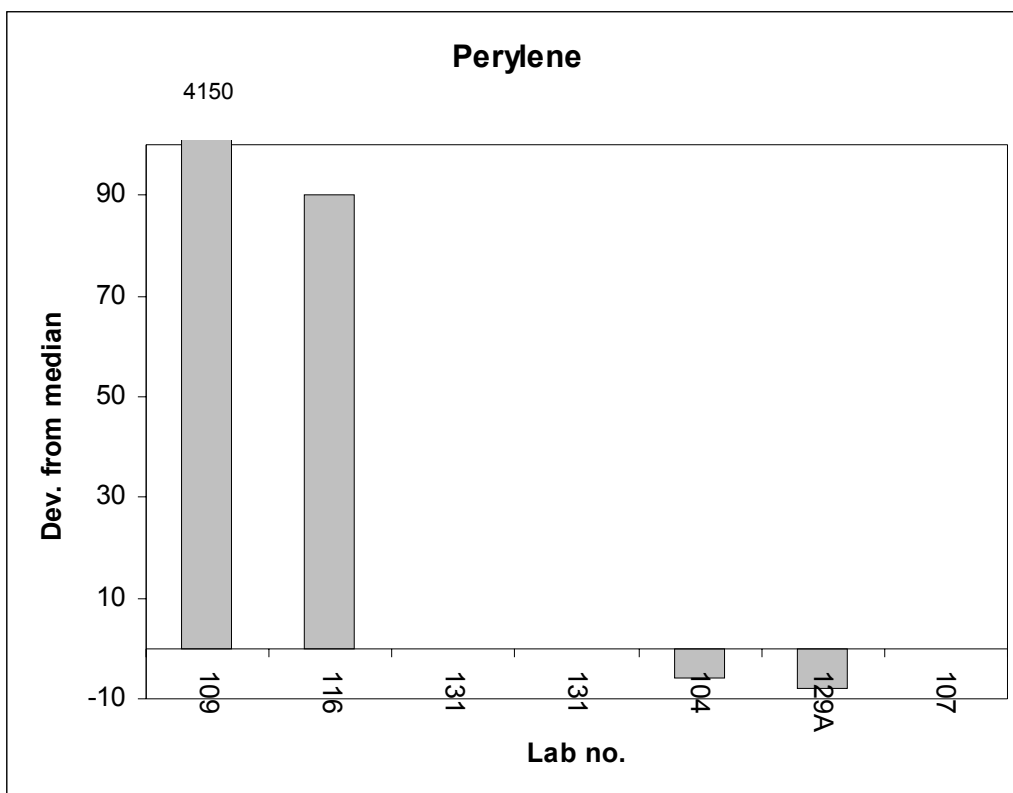


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 6 Median: 0,035

Lab. no.	Dev. from median	ng/m ³
129A	2489	0,8932
109	1972	0,715
116	42	0,049
131	-42	0,02
131	-42	0,02
104	-47	0,01843
107		<LQ

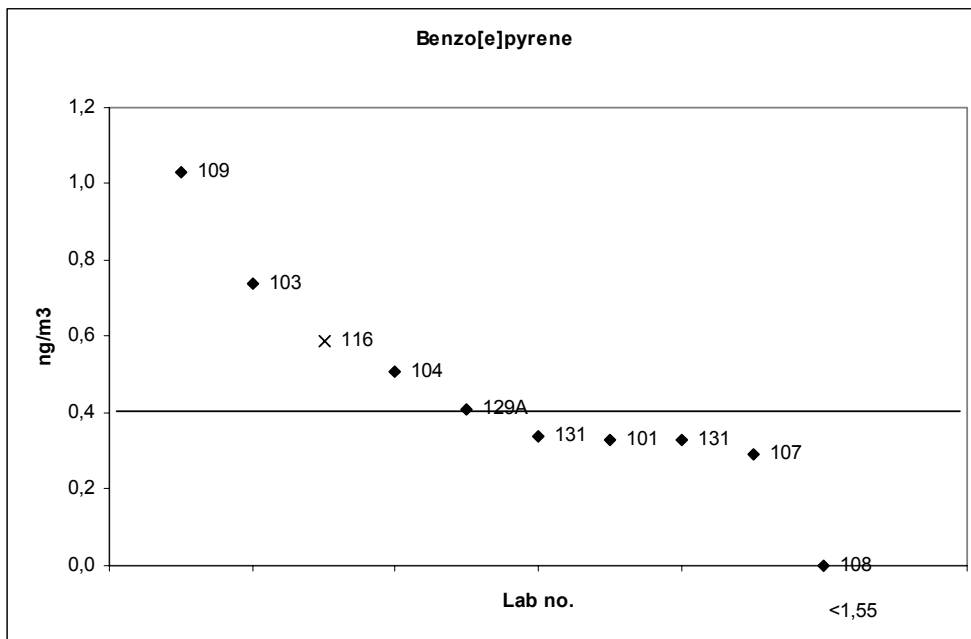
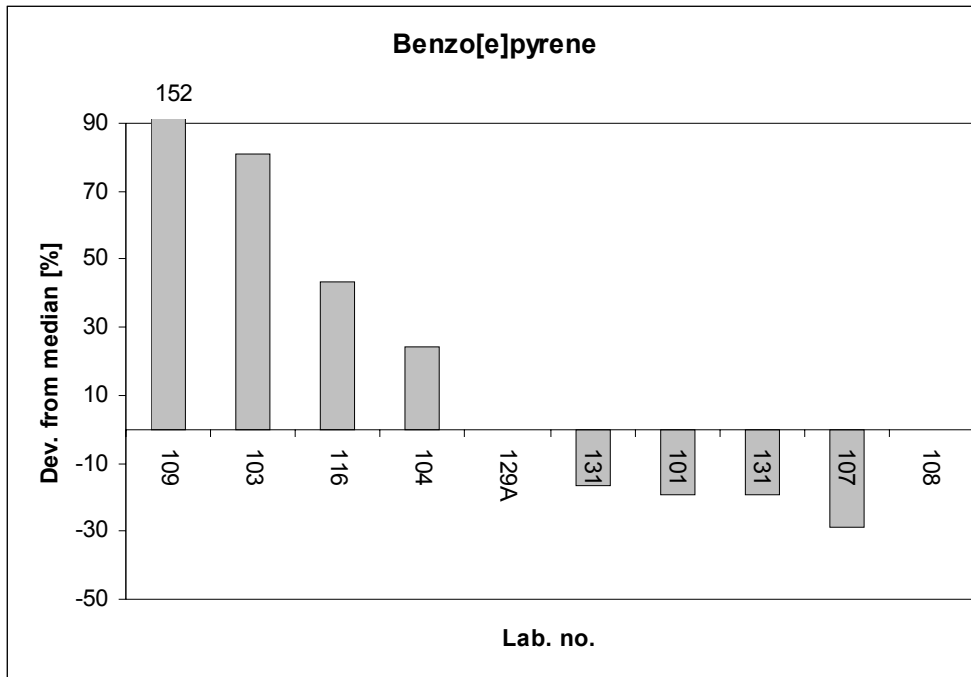


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 6 Median: 0,02

Lab. no.	Dev. from median %	ng/m ³
109	4150	0,85
116	90	0,038
131	0	0,02
131	0	0,02
104	-6	0,01881
129A	-8	0,0184
107		<LQ

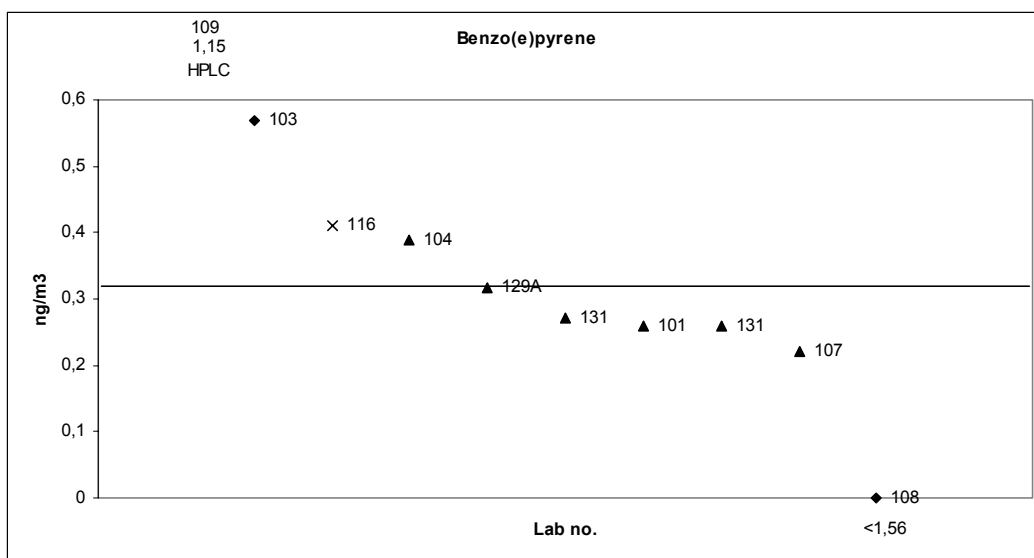
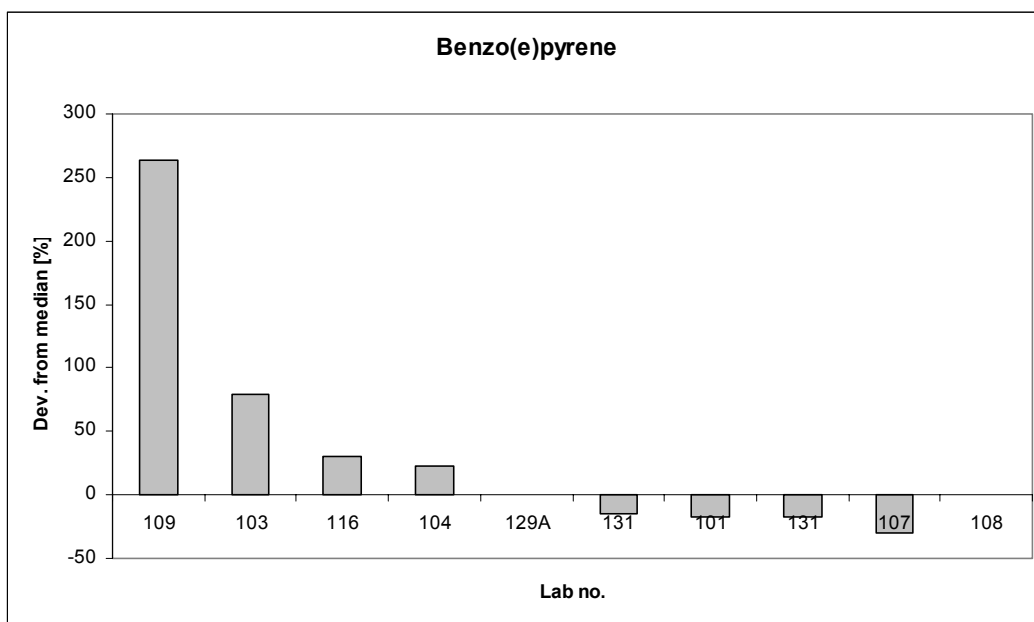


Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m³. Median given as a horizontal line.

Number of laboratories: 9 Median: 0,4086

Lab. no.	Dev. from median %	ng/m ³
109	152	1,03
103	81	0,739625333
116	43	0,586
104	24	0,50804
129A	0	0,4086
131	-17	0,34
101	-19	0,33
131	-19	0,33
107	-29	0,29
108		< 1,55



Upper figure: Deviation from median in %.

Lower figure: Concentrations in ng/m^3 . Median given as a horizontal line.

Number of laboratories: 9 Median: 0,317

Lab. no.	Dev. from median %	ng/m3
109	263	1,15
103	79	0,568157333
116	30	0,411
104	23	0,38935
129A	0	0,3166
131	-15	0,27
101	-18	0,26
131	-18	0,26
107	-31	0,22
108		< 01,56