

**University of Stuttgart**  
Germany



# Analytische Qualitätssicherung Baden-Württemberg

## PT-WFD

**Proficiency Test 6/10**  
**Polybrominated diphenylether in surface water**

BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154

provided by  
AQS Baden-Württemberg at  
Institute for Sanitary Engineering, Water Quality and Solid Waste Management,  
University of Stuttgart  
Bandtäle 2, 70569 Stuttgart-Büsnau, Germany

**AQS** Baden-  
Württemberg

**in cooperation with other European PT providers**

**Stuttgart, in January 2011**

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## 1. General

This PT was provided by AQS Baden-Württemberg in the context of the “PT-WFD” network of European PT providers for the determination of:

- 2,4,4-Tribromodiphenylether (BDE 28)
- 2,2,4,4-Tetrabromodiphenylether (BDE 47)
- 2,2,4,4,5-Pentabromodiphenylether (BDE 99)
- 2,2,4,4,6-Pentabromodiphenylether (BDE 100)
- 2,2,4,4,5,5-Hexabromodiphenylether (BDE 153)
- 2,2,4,4,5,6-Hexabromodiphenylether (BDE 154)

The PT met the requirements of the water framework directive and the related environmental quality standards for the determination of priority substances in surface water. More information about this network can be found on the webpage <http://www.pt-wfd.eu>.

The PT was organized in collaboration with the following other PT providers in Europe:

**BIPEA**, 6-14 avenue Louis Roche, F-92230 Gennevilliers, FRANCE, Tel.: +33 1 47 33 54 60, Fax : +33 1 40 86 92 59, [contact@bipea.org](mailto:contact@bipea.org)

**LGC Standards Proficiency Testing**, Europa Business Park, Barcroft Street, Bury, Lancashire, BL9 5BT, UK, Telephone: +44 (0) 161 762 2500, Fax: +44 (0) 161 762 2501, Email: [customerservices@lqcpt.com](mailto:customerservices@lqcpt.com)

**Kemijski inštitut** Ljubljana Slovenija, SI-1001 Ljubljana, Hajdrihova 19, p.p.660, Tel.: 01/476 02 00, Faks: 01/476 03 00, mail: [info@ki.si](mailto:info@ki.si)

**QualityConsult**, Via G. Bettolo 4, (00195) Rome Italy, Tel.: +39 320-6905464, Fax: +39 0697840718, [qualityconsult@aqc.it](mailto:qualityconsult@aqc.it)

**VITUKI Nonprofit Ltd.**, Quality Assurance and Control, 1095 Budapest, Kvassay J. 1., HUNGARY, Tel: +36 1 215-6140/ext. 2199, Fax: +36 1 215-6046, [mecs@vituki.hu](mailto:mecs@vituki.hu)

**SYKE Finnish Environment Institute**, Laboratories, Hakuninmaantie 6, 004300 Helsinki, FINLAND, Tel: +358 20 610 123, Fax: +358 9 448 320, [profest@environment.fi](mailto:profest@environment.fi)

The PT was executed and evaluated due to the requirements of the PT-WFD network.

## 2. PT design

Each participant received the following samples:

- 3 x 2 samples for the determination of the mentioned parameters in 1000-ml-ground glass bottles. The samples were stabilised by cooling.

3 different concentration levels/batches were produced. All participants received the same concentration levels.

## 3. Sample preparation

The samples were based on a real surface water.

The surface water was filtered by using 5 µm and 1 µm filter cartridges to eliminate coarse particles. To reduce germs, the surface water was irradiated with ultraviolet light.

For preparation of the samples, each bottle was spiked with a solution of the substances dissolved in DMF.

The concentrations of the analytes of the spiked samples were chosen according to the Environmental Quality Standard (Directive 2008/105/EG on environmental quality standards in the field of water policy):

parameter	AA-EQS [ng/l]
2,4,4-Tribromodiphenylether (BDE 28)	0.5
2,2,4,4-Tetrabromodiphenylether (BDE 47)	0.5
2,2,4,4,5-Pentabromodiphenylether (BDE 99)	0.5
2,2,4,4,6-Pentabromodiphenylether (BDE 100)	0.5
2,2,4,4,5,5-Hexabromodiphenylether (BDE 153)	0.5
2,2,4,4,5,6-Hexabromodiphenylether (BDE 154)	0.5

AA: annual average

The samples were cooled directly after preparation. The samples were dispatched with freezer packs added to the packages.

## 4. Sample distribution

The samples were dispatched on 13<sup>th</sup> October 2010 by express service. Laboratories outside Germany received their samples from one of the cooperating PT provider.

The participants were requested to start with the analysis one day after receipt of the samples at the latest.

## 5. Analytical methods

The participants were free to choose a suitable method, but a limit of quantification for all parameters of 0.15 ng/l was required. The limit originates from the requirements of article 4 of the commission directive 2009/90/EC of the European communities for the technical specifications for chemical analysis and monitoring of water status in the context of the water framework directive. The limit corresponds to 30% of the environmental standards of the directive 2008/105/EG on environmental quality standards in the field of water policy.

The samples had to be analysed in duplicate over the complete method (sample preparation and measurement). The participants were asked to submit the results as average values in ng/l with four significant digits.

## 6. Submission of results

The deadline for the submission of results was on 13<sup>th</sup> November 2010.

## 7. Evaluation and assessment

According to the agreements in the PT-WFD network the following procedure was used for the evaluation and assessment of the PT round: The reference values (see chapter "Traceable reference values") were used as assigned value X.

A fixed value of 25% of the assigned value was used as standard deviation for proficiency assessment  $\hat{\sigma}$ . For each measurement result of the participant a z-score was calculated using the following formula:

$$z = \frac{x - X}{\hat{\sigma}}$$

for the assessment the following criteria were used:

	$ z  \leq 2,0$	satisfactory
2,0 <	$ z  < 3,0$	questionable
	$ z  \geq 3,0$	unsatisfactory

## 8. Participation

Number of participants (total): 28

Registration via:

AQS Baden-Württemberg, Germany:	15
BIPEA	3
LGC Standards, UK:	5
Kemijski inštitut, Slowenien:	0
QualityConsult, Italien:	2
VITUKI, Ungarn:	0
SYKE, Finland:	3

Table 1 shows the number of satisfactory, questionable, unsatisfactory results and the number of not participating laboratories for each parameter. Figure 1 shows the percentage of satisfactory, questionable, unsatisfactory results and not submitted results.

Table 1: Number of values per parameter assessed as satisfactory, questionable, unsatisfactory and not submitted results.

parameter	satisfactory	questionable	unsatisfactory	no participation
BDE 28	53	2	4	25
BDE 47	47	8	4	25
BDE 99	45	6	9	24
BDE 100	45	7	8	24
BDE 153	40	12	8	24
BDE 154	48	13	5	18

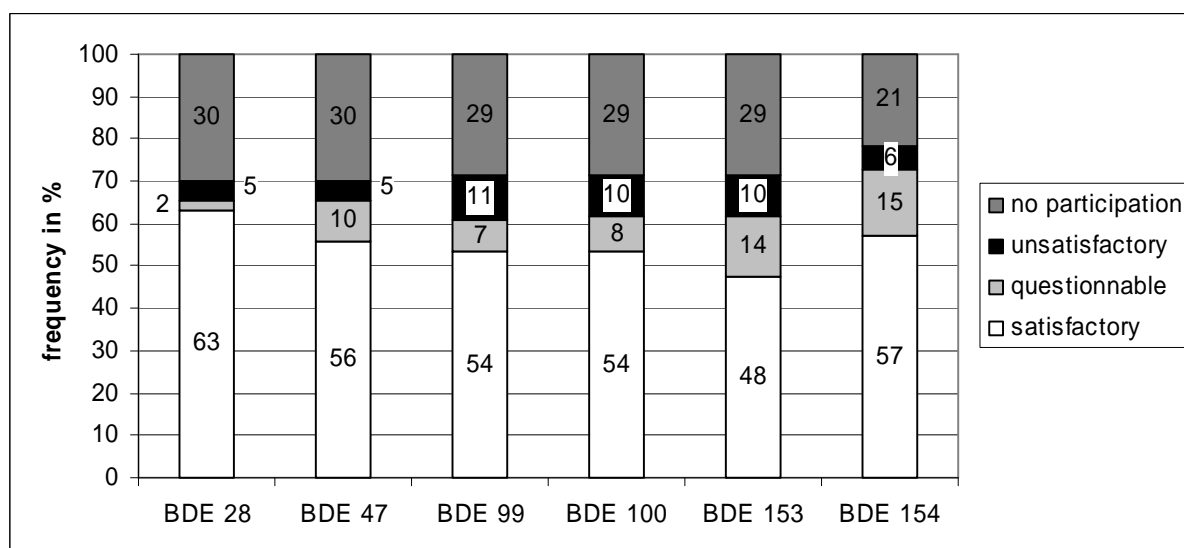


Figure 1: Percentage of satisfactory, questionable, unsatisfactory and not submitted results.

## 9. Explanation of Appendix A

Appendix A contains for each parameter

- parameter tables
- a figure of participants' means (calculated with Algorithm A) versus the spiked amounts for the determination of the recovery rate and the matrix content
- a figure of the relative standard deviations versus the concentrations
- a figure of the tolerance limits in the PT versus the concentrations
- the frequency of application of analytical methods
- the method specific evaluation
- a comparison of mean and reference values for each concentration level
- a comparison of the relative standard deviations of the different methods
- the statistical characteristics of the method specific evaluation
- a tabular comparison of the means with the reference values and their uncertainties

### Parameter tables

In these tables the following values for each concentration level are listed:

- assigned value
- expanded uncertainty of the assigned value in % (see chapter "Traceable reference values")
- standard deviation, calculated using robust statistical method (Q-method)

- standard deviation for proficiency assessment in ng/l for the calculation of z-scores (25 % of the assigned value)
- rel. standard deviation for proficiency assessment in %
- tolerance limits above and below in ng/l and %
- number of values in this level
- number of not satisfactory values below and above the assigned value and the percentage of these values in total.

### Determination of recovery rate

In the diagrams of the assigned values versus the spiked amount of analyte a linear regression line was calculated using a generalized least square regression which takes into account the uncertainties of the values in both directions. From these values the recovery rate for each parameter was determined (see diagrams). The slope of the line indicates the average recovery rate. The diagrams also contain the expanded uncertainty ( $k=2$ ) of the mass values and the assigned values.

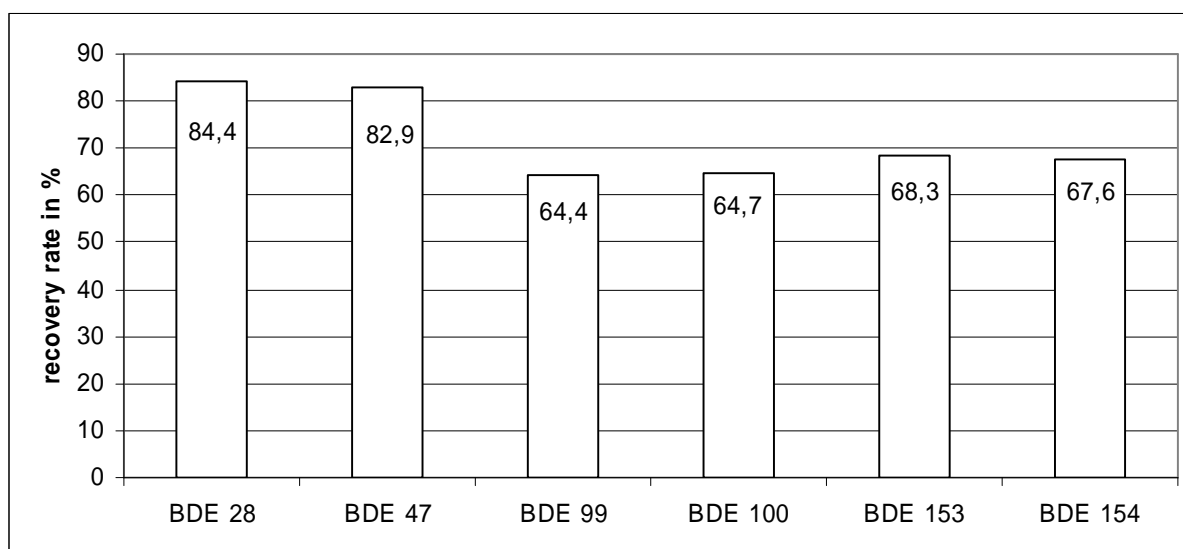


Figure 2: Average recovery rates for all parameters

### Relative standard deviation and tolerance limit

The diagrams for the rel. standard deviation vs. the assigned value show the values compared to the fixed standard deviation for proficiency assessment (horizontal line at 25%) and the concentration dependence. The diagrams with the tolerance limits show the limits in percent.

### Method specific evaluation

For each parameter the methods used by the participants are shown in a diagram. In a second diagram for each method values are sorted in 5 categories:

too low	results with z-score < -2
low	results with $-2 \leq \text{z-score} < -1$
correct	results with $-1 \leq \text{z-score} \leq +1$
high	results with $+1 < \text{z-score} \leq +2$
too high	results with z-score > +2

No conclusion can be drawn from the diagrams of the methods specific evaluation, because it only could show the differences between GC-MS and GC-MSMS. This seems not be the problem. Probably incomplete extraction is the most serious problem in this kind of analysis, also leading to reduced recoveries on average.

### Comparison of means and reference values for each concentration level

Finally the mean value calculated from all results (used as assigned value) is compared with mean values calculated for all methods separately (in this case using the Hampel estimator described in ISO/TS 20612). Mean values were calculated only, if more than 7 results were within a z-score-range of  $\pm 2$ . The means are reported with their expanded uncertainty calculated according to ISO 13528.

## 10. Explanation of Appendix B

Participants were asked to report expanded uncertainties of their results on a voluntary basis. In this diagram for each parameter the reported uncertainties for all concentration levels with the reproducibility standard deviation (horizontal line) are displayed. Values which deviate from the reproducibility standard deviation with a factor more than 2 are usually not realistic.

## 11. Explanation of Appendix C

In the last part of the report, for all concentration levels the results of all participants are illustrated. Confidentiality of participants is ensured by using lab codes. The lab codes were sent to participants with the certificates.

In detail Appendix C contains:

- a table with all data
- figures with
  - all reported results
  - all z-scores
  - all reported expanded uncertainties
  - all  $\zeta$ -scores

### Table with all data

The assigned value with the expanded uncertainty and the tolerance limits for the concentration level is illustrated in the table. For each participant the following data are given:

- lab code
- reported result
- measurement uncertainty of the value (if reported)
- $\zeta$ -score for this value, calculated with the following formula

$$\zeta = \frac{x - \bar{x}}{\sqrt{u_{lab}^2 + u_{ref}^2}}, \text{ with}$$

$x - \bar{x}$  = difference from the measured value and the assigned value

- $u_{lab}$  = standard uncertainty of the value, reported by the participant
- $u_{ref}$  = standard uncertainty of the assigned value
- z-score for proficiency assessment
- assessment of the value according to its z-score

### Meaning of $\zeta$ -scores:

The assessment of  $\zeta$ -scores is similar to that of z-scores. If the data are normally distributed and the uncertainties are well estimated,  $\zeta$ -scores will lie between -2 and +2 with a probability of around 95 %.

$\zeta$ -scores are mainly influenced by the measurement uncertainties reported by the laboratory. Therefore  $\zeta$ -scores are usually not appropriate for the assessment of the reported results, unless the reported measurement uncertainty is checked for fitness-for-purpose.

Therefore we do not use the  $\zeta$ -scores for the assessment of the laboratories. Nevertheless  $\zeta$ -scores are appropriate to check the plausibility of the reported measurement uncertainty:

If the z-score of a result is within the tolerance limit and the  $\zeta$ -score is outside, then the measurement uncertainty is underestimated.

If the z-score is outside the tolerance limits and the absolute value of the  $\zeta$ -score is lower than two, then the requirements of the proficiency test were stronger compared with the reported measurement uncertainty.

### Diagrams of uncertainty data

In the first figure for all lab codes the measurement uncertainty (together with the reproducibility standard deviation) is illustrated. The second figure shows the associated  $\zeta$ -scores.

## 12. Measurement uncertainty

8 (36,4%) out of 22 laboratories with valid values reported measurement uncertainties. In total 142 (39%) out of 364 valid values were given with the measurement uncertainty.

The following table displays the number of values with measurement uncertainty against the accreditation status.

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	77	39 (50,6%)
not accredited	221	88 (39,8%)
not specified	54	15 (27,8%)

We would like to put emphasis on the fact that reporting of measurement uncertainties in our PT scheme is absolutely voluntary. The only objective is to help all participants to reasonably handle measurement uncertainties and their estimation.

The diagrams show that the spread of reported uncertainties in some cases is vast, in many case unrealistically low values. A plausibility check using reproducibility standard deviations of the PT round could be helpful here.

If measurement uncertainties are underestimated values assessed as “satisfactory” in the PT ( $|z| \leq 2$ ), will have a large  $\zeta$ -score.  $|\zeta| > 2$  means that the “own” requirements (defined in terms of estimated uncertainty) are not fulfilled.

39 (27,5%) of the 142 values reported with uncertainties and having a z-score  $|z| \leq 2.0$  had a  $\zeta$ -score  $> 2.0$ . This means that the requirements of the PT scheme have been fulfilled, but not the “own” requirements, the uncertainty is underestimated.

## 13. Traceable reference values

Traceability of analytical results to national and international references is of increasing importance in all laboratories. This is not easy to realise for chemical analyses and often can only be done by analysing certified reference materials. But availability of these reference materials in the water sector is very limited. Therefore we try to provide reference values for the proficiency test samples, traceable to national and international references.

Since our PT samples without exception are spiked, real water samples, reference values can be calculated from the sum of matrix content and spiked amount of analyte. For both summands traceable values and their uncertainty have to be determined. Thereby we assume that no unrecognised bias resulting from sample preparation and transport is present and that we recognise all uncertainty components.

### Determination of the spiked amount and its uncertainty

All spiking of samples was controlled gravimetrically. Conversion to concentration was done by measuring the density of the resulting samples using a pycnometer. This procedure allows the preparation of a complete uncertainty budget. The first step is the specification of the measurand with a formula. This shows the links between the result and all influence quantities

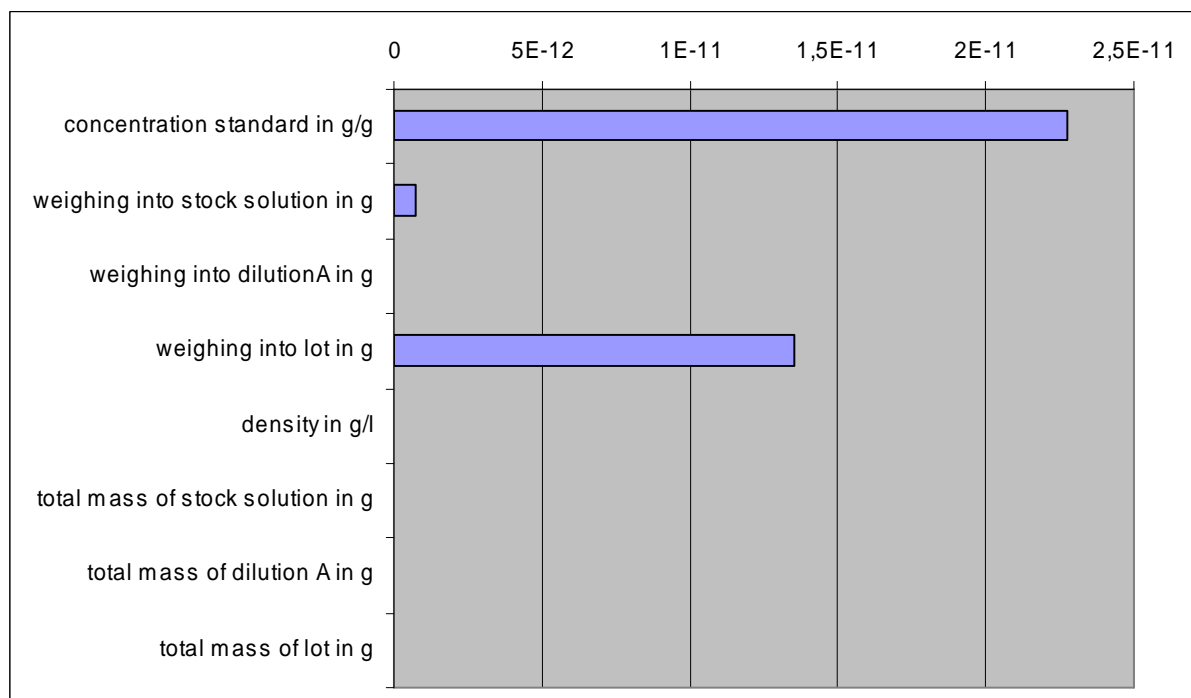
$$C_{lot} = \frac{C_{Stand} \cdot m_{Stand\_ss} \cdot m_{ss\_dilA} \cdot m_{dilA\_lot} \cdot \rho_{lot}}{m_{ss} \cdot m_{dilA} \cdot m_{lot}}$$

with:

$C_{lot}$	concentration of the analyte in the lot resulting from the spike in g/l
$C_{Stand}$	concentration of the standard solution in g/g
$m_{Stand\_ss}$	mass of standard solution added for preparation of the stock solution in g
$m_{ss\_dilA}$	mass of stock solution added for preparation of dilution A in g
$m_{dilA\_lot}$	mass of dilution A added for preparation of the lot in g
$m_{ss}$	total mass of stock solution in g
$m_{dilA}$	total mass of dilution A in g
$m_{lot}$	total mass of the lot in g
$\rho_{lot}$	density of the lot in g/l

Based on this formula the uncertainty budget can be prepared and all components be quantified. The following figure shows a typical distribution of the contributions, here for BDE 28 as an example.

The main contribution results from the uncertainty of the concentration of the standard solution and the weighing of dilution A into the lot. The uncertainty of the concentration was taken from the certificate of the supplier. The uncertainty from the weighing into lot is due to the bottle-by-bottle spiking. The average of the weighing of the dilution A into the lot and the standard deviation was calculated.



All weighings were done as difference weighings. The precision of these weighings was determined in experiments by multiple (20fold) measurements of mass pieces with similar masses as a type A uncertainty. The trueness of the weighing, that has to be considered twice for each weighing, was taken from the calibration certificate of the balance. Maintaining of these tolerances is assured by regular maintenance of the balances by a calibration laboratory and by supervision with our mass pieces (calibrated by an accredited calibration laboratory).

The determination of the density was also made using weighings (of the pycnometer). The above said also applies here.

Temperature measurement was made with a calibrated thermometer.

The purity of the used benzene was taken from the certificate of the manufacturer.

With all these uncertainty components the combined uncertainty, as described in the EURACHEM/CITAC-Guide „Quantifying Uncertainty in Analytical Measurement“, was calculated using the sensitivity coefficients determined by partial derivation of the formula to the respective influence quantities.

So traceability was assured by using calibrated balances and thermometers.

### Determination of the matrix content

Because the same matrix was used for preparation of all samples, the matrix content could be calculated from the mean values of the participants and the spiked amounts in a standard-addition-like way<sup>1,2</sup>.

The uncertainties of the spiked amounts were known from the uncertainty budgets.

The expanded uncertainties of the mean values of participants' result were calculated according to ISO 13528 (Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons) as

$$u_{mean} = 2 \cdot 1,25 \cdot \frac{s_R}{\sqrt{n}}$$

with:

$s_R$  reproducibility standard deviation

$n$  number of data for this level

2 coverage factor for the expanded uncertainty

1,25 correction factor (according to ISO 13528 to be used for robust methods)

The content of the matrix can be derived from a linear regression of means vs. spiked amounts. Since uncertainties of all data points were available for x- as well as y-direction a generalised least square regression was used as described in DIN EN 6143. The computer program B\_LEAST (from BAM) was used for this purpose.

With this method a value for matrix and its uncertainty are obtained.

Because of statistical variation of the input values the calculated matrix content might result in a negative value. From a scientific point of view this of course is nonsense. In those cases the matrix content is set to zero.

The lower end of the uncertainty range of the matrix content also might be negative.

Therefore the expanded uncertainty of the matrix content was set to the matrix content itself in this case.

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<sup>1</sup> Rienitz, O., Schiel, D., Güttler, B., Koch, M., Borchers, U.: A convenient and economic approach to achieve SI-traceable reference values to be used in drinking-water interlaboratory comparisons. *Accred Qual Assur* (2007) 12: 615-622.

<sup>2</sup> Koch, M., Baumeister, F.: Traceable reference values for routine drinking water proficiency testing: first experiences. *Accred Qual Assur* (2008) 13: 77-82.

The matrix content is not directly traceable to national or international references, but it does not considerably compromise the traceability of the final content due to its comparably low contribution.

#### **14. Internet**

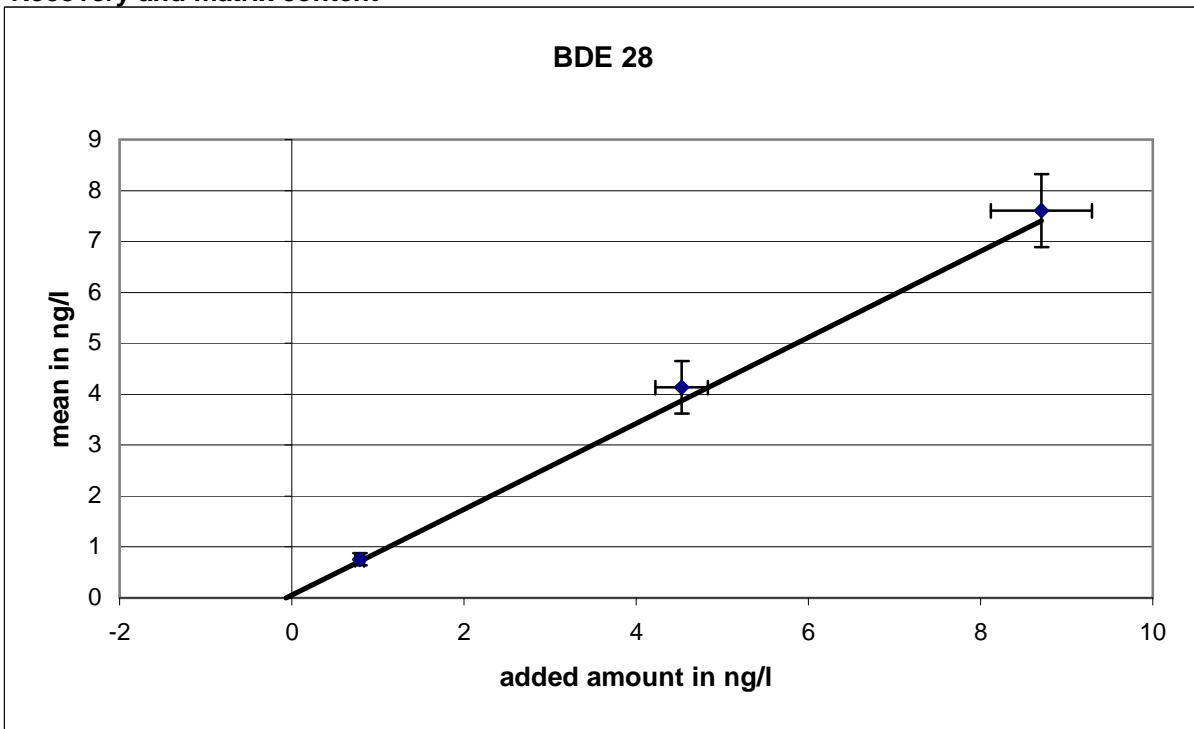
This report also is available from the following internet address:

<http://www.aqsbw/pdf/report610.pdf>

# BDE 28

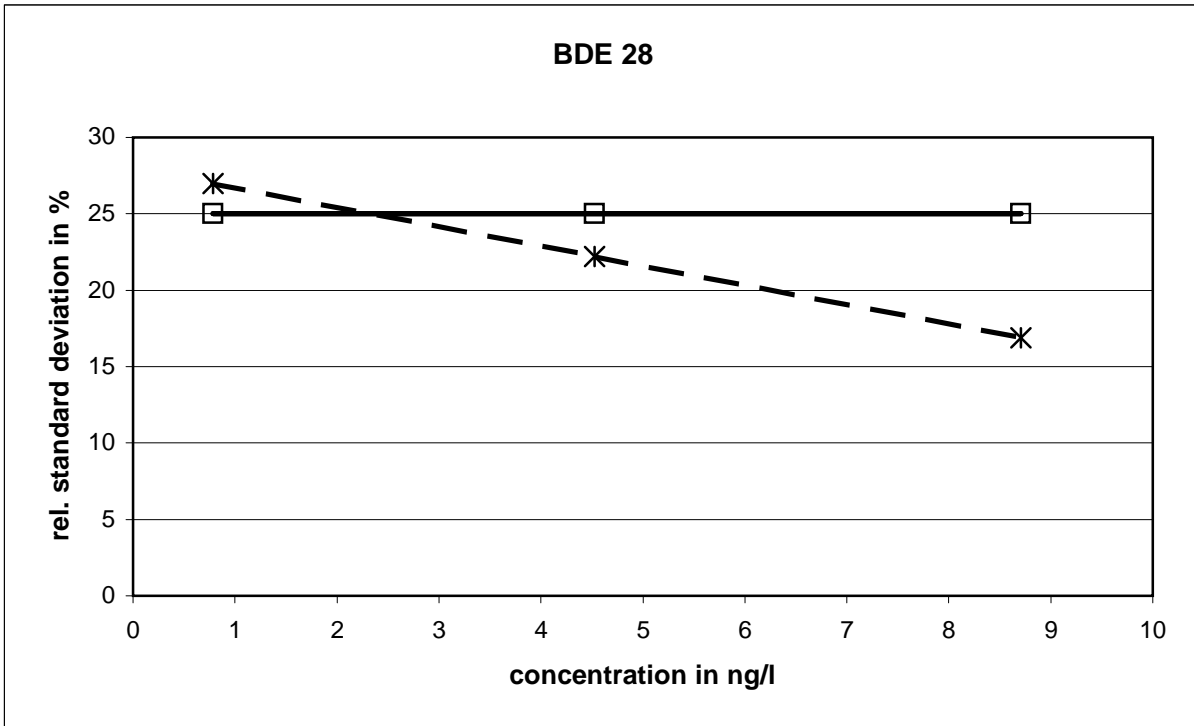
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,7877	6,72	0,2047	0,1969	25,00	1,182	0,3939	50,00	-50,00	19	1	1	10,5
2	4,527	6,72	0,9181	1,132	25,00	6,790	2,263	50,00	-50,00	20	1	1	10,0
3	8,706	6,72	1,282	2,176	25,00	13,06	4,353	50,00	-50,00	20	2	0	10,0
sum										59	4	2	10,2

## Recovery and matrix content

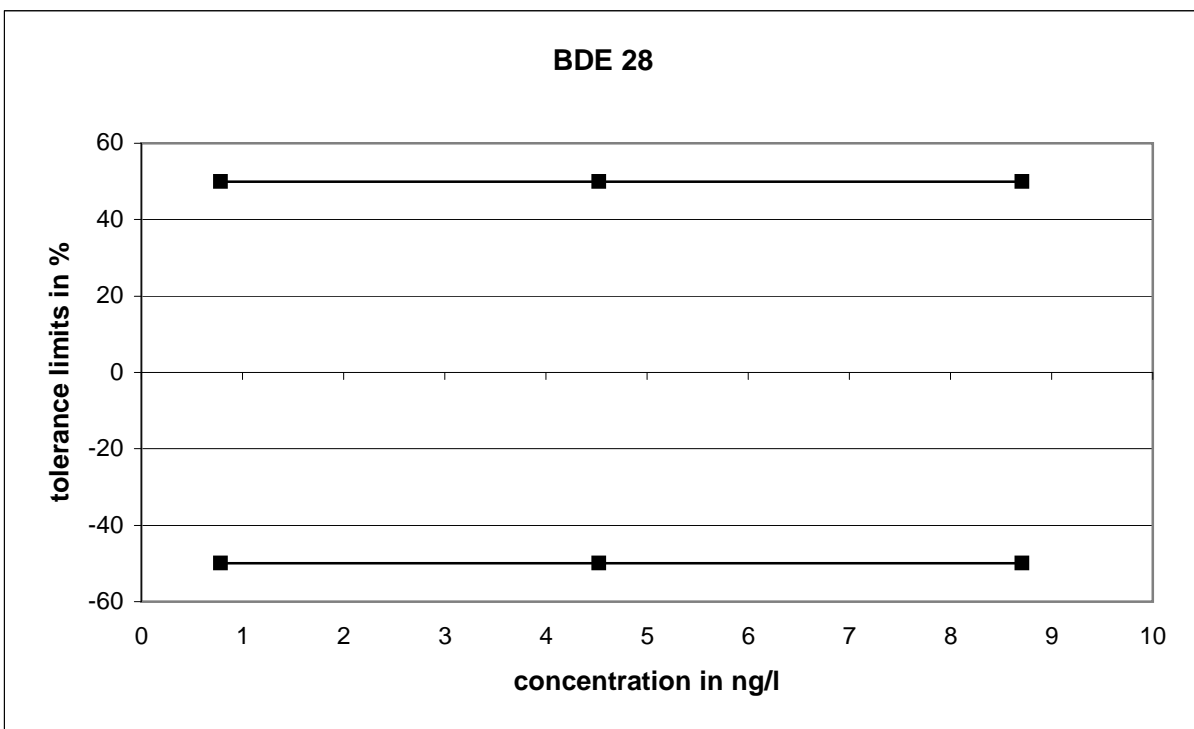


Slope of the regression line: 0,8443, recovery: 84,4 %  
 neg. x-axis-intercept = matrix content: 0,0656 ng/l  
 expanded uncertainty of the matrix content: 0,0656 ng/l =100 %

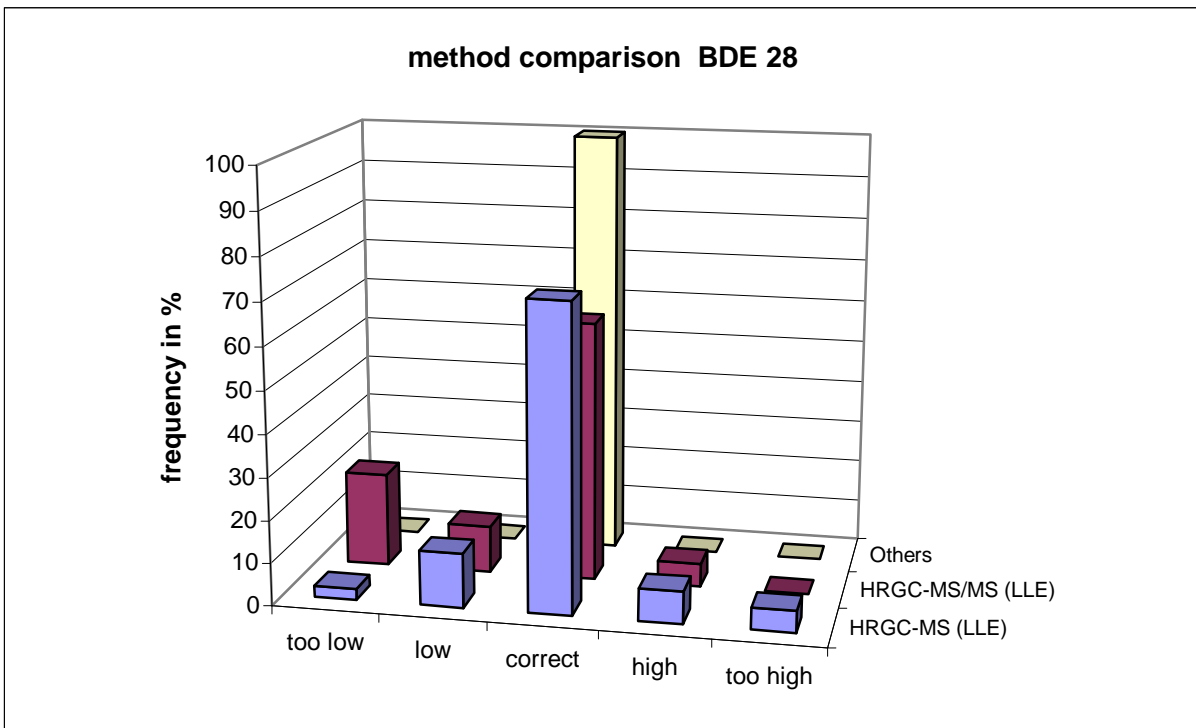
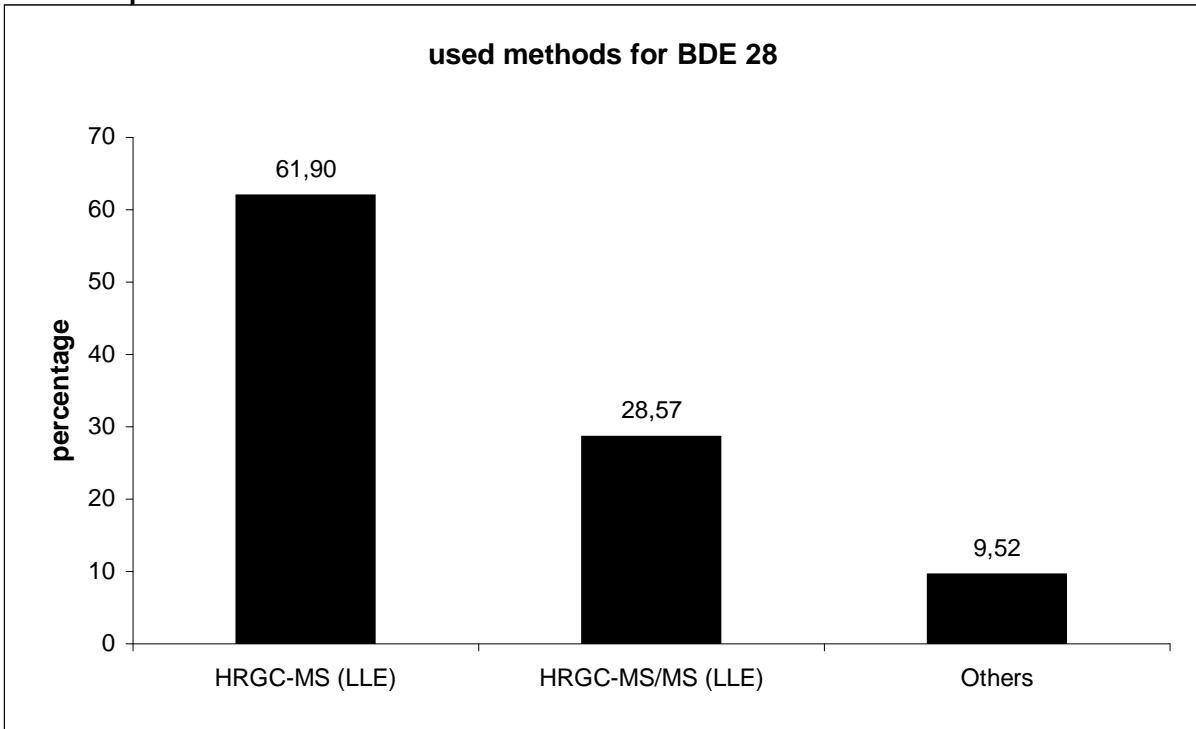
**Relative standard deviation and tolerance limits**



The relative standard deviation, calculated with Algorithm A, reached the standard deviation for proficiency assessment of 25 % at the lowest concentration level.

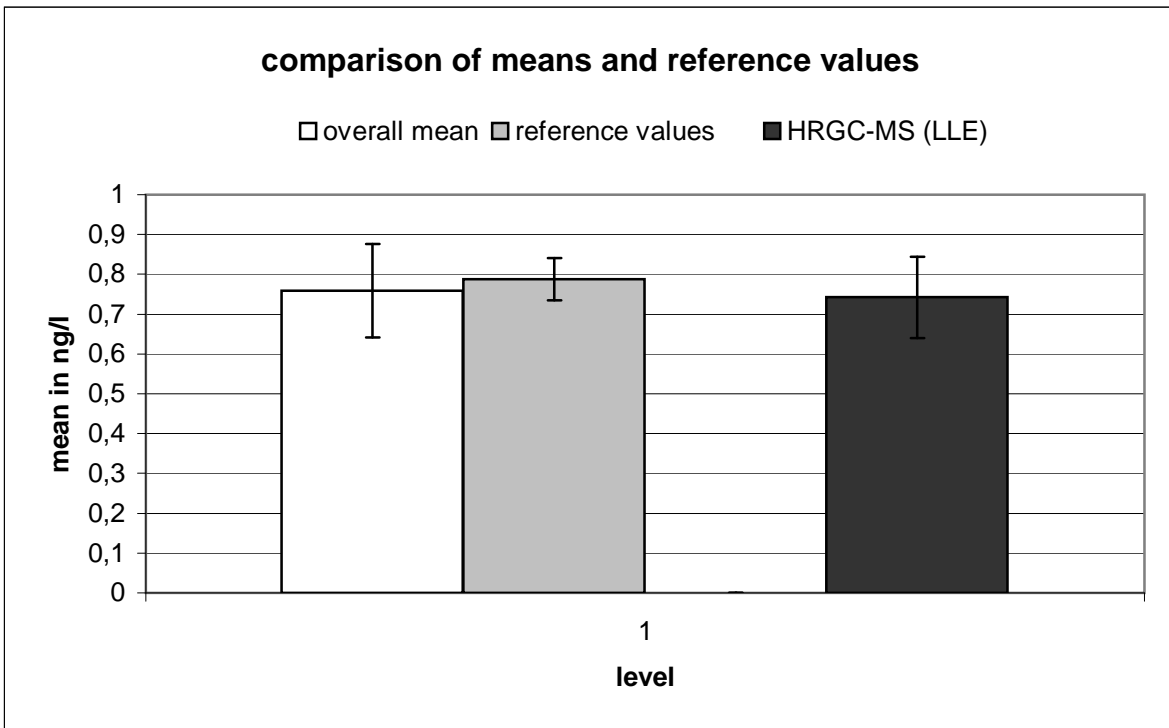


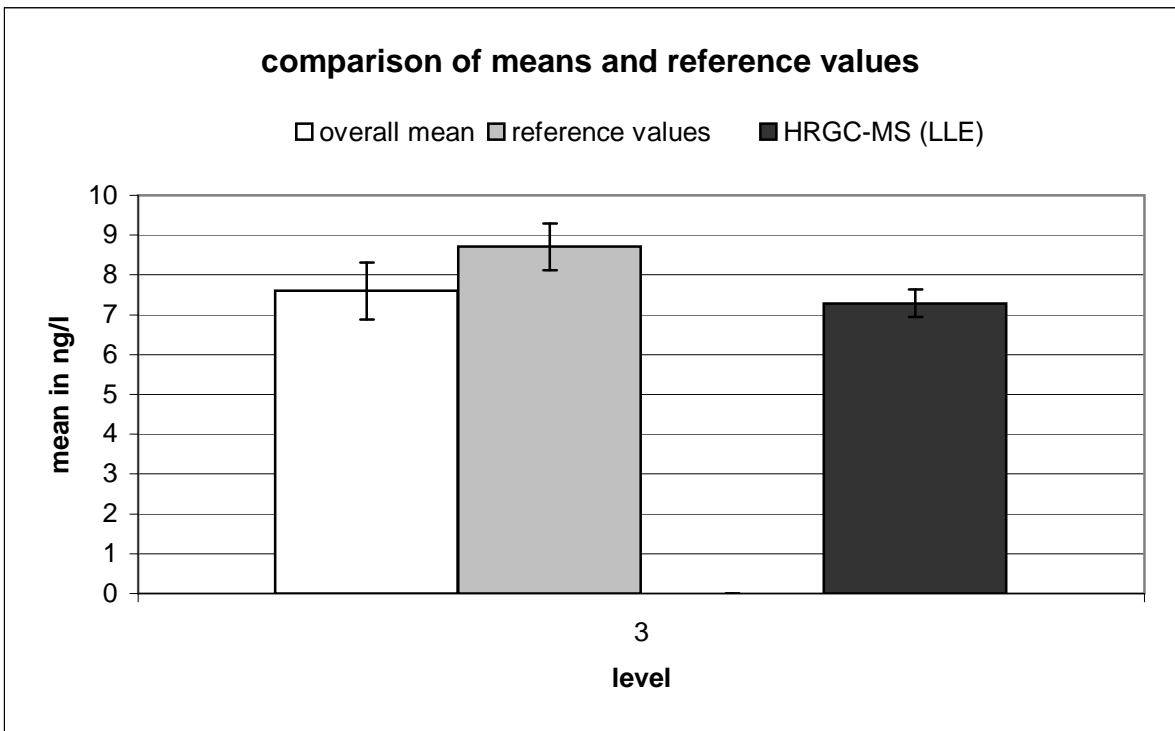
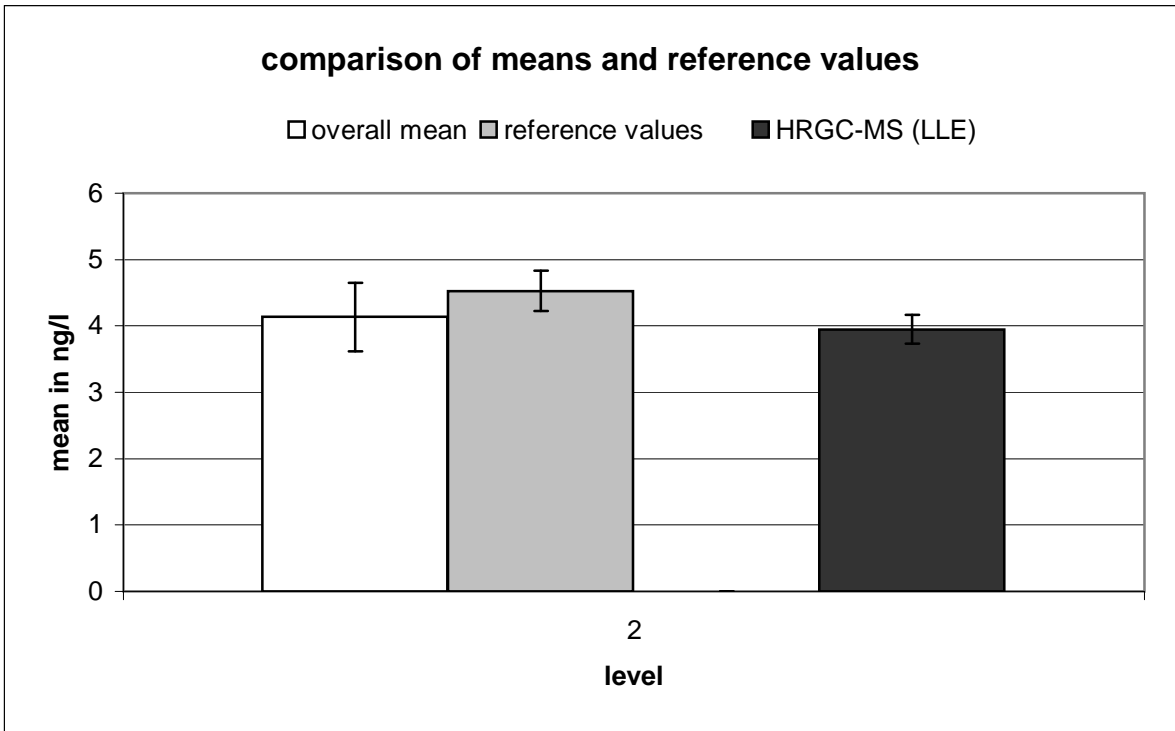
Method specific evaluation

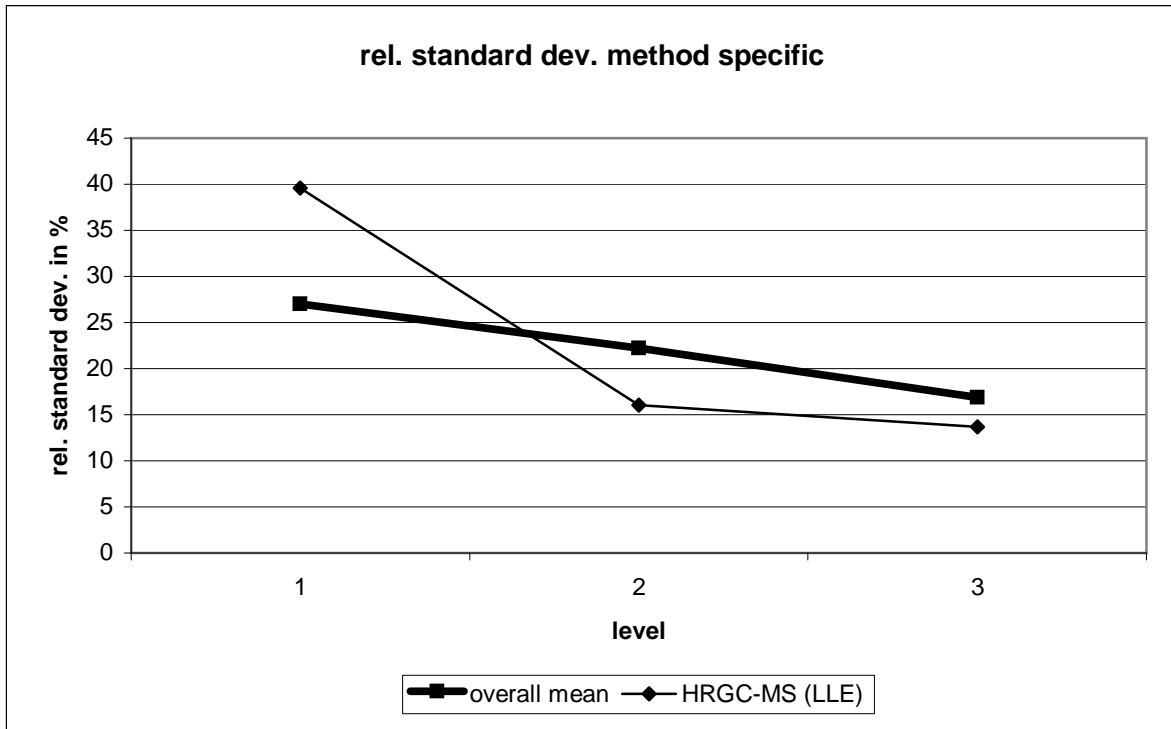


**Comparison of means and reference values**

level	mean [ng/l]			reference value [ng/l]		
	mean [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]	reference value [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]
1	0,7585	0,1174	15,5	0,7877	0,0529	6,7
2	4,135	0,513	12,4	4,527	0,304	6,7
3	7,603	0,717	9,4	8,706	0,585	6,7





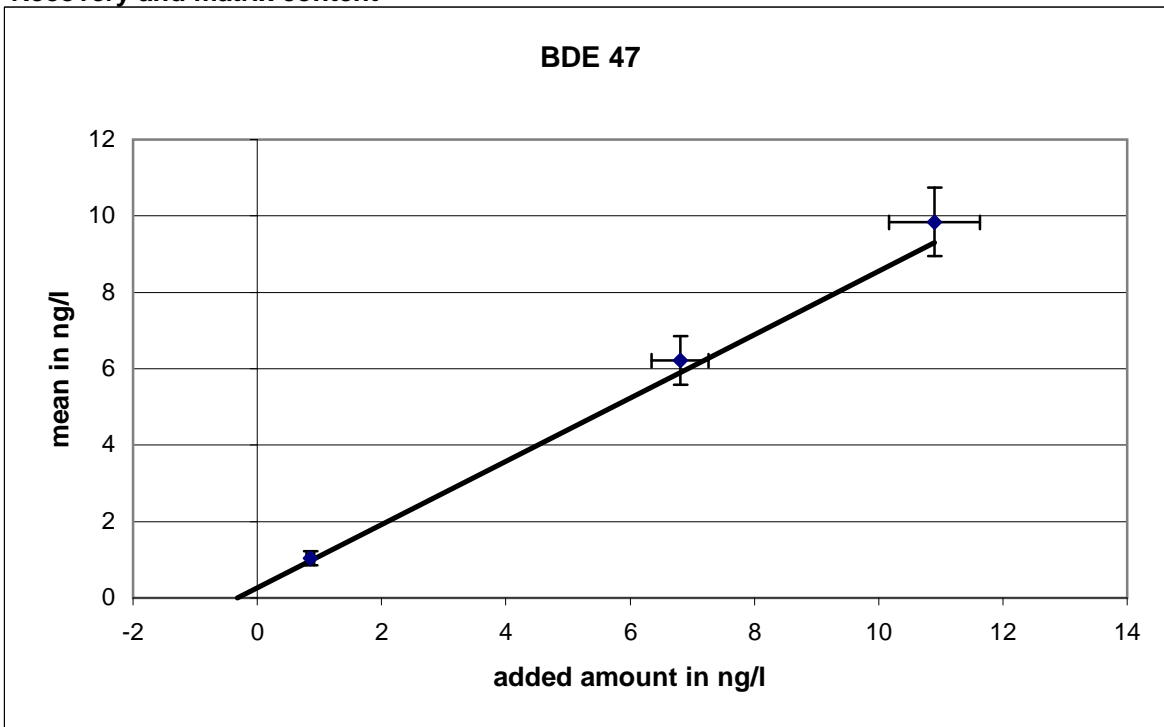


HRGC-MS (LLE)									
level	robust mean [ng/l]	exp. uncertainty of the mean [ng/l]	exp. uncertainty of the mean [%]	robust standard deviation [ng/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,7422	0,1018	13,714	0,2936	39,558	13	2	1	23,08
2	3,948	0,2193	5,5538	0,6325	16,02	13	1	1	15,38
3	7,29	0,3462	4,7491	0,9986	13,699	13	1	2	23,08

# BDE 47

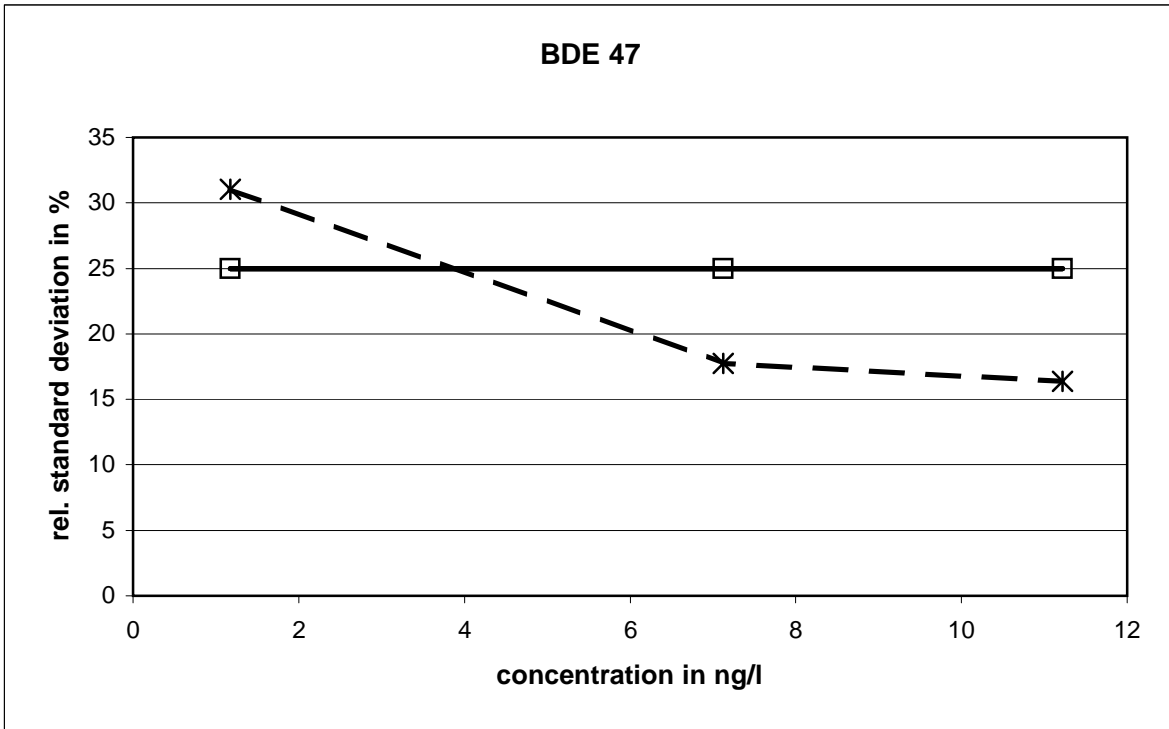
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	1,172	26,40	0,3227	0,2930	25,00	1,758	0,5860	50,00	-50,00	20	3	2	25,0
2	7,124	7,71	1,102	1,781	25,00	10,69	3,562	50,00	-50,00	19	3	0	15,8
3	11,22	7,07	1,611	2,805	25,00	16,83	5,610	50,00	-50,00	20	4	0	20,0
sum										59	10	2	20,3

### Recovery and matrix content

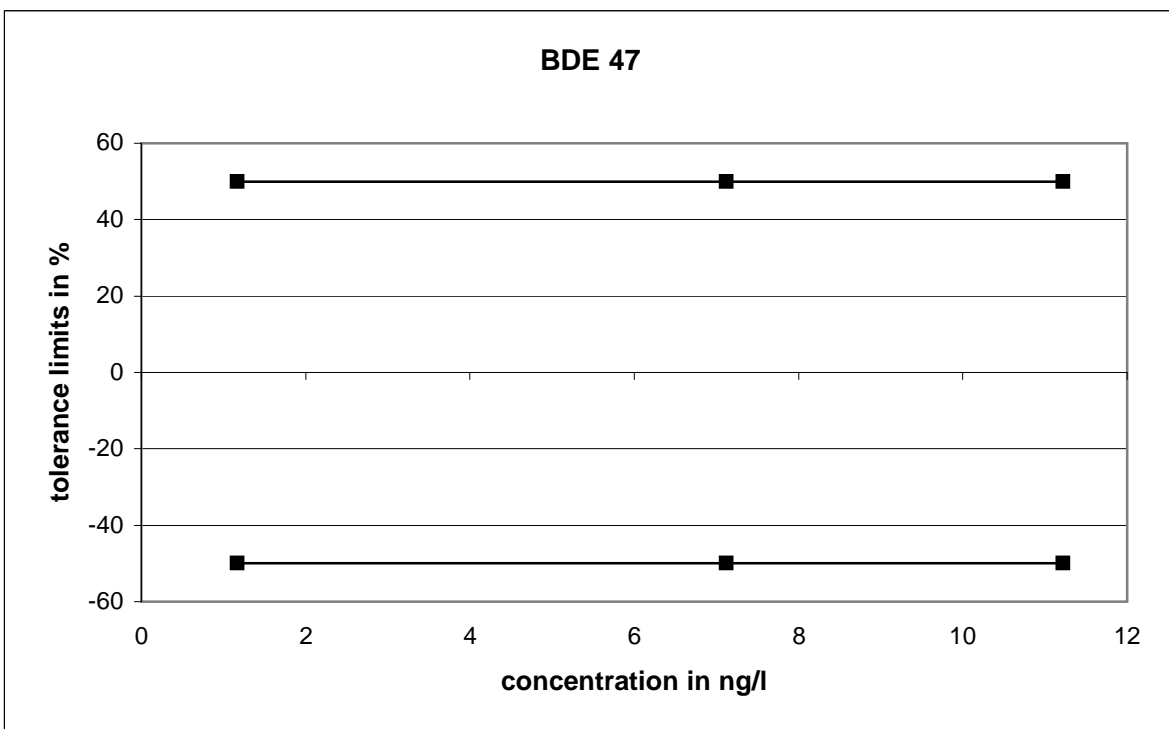


Slope of the regression line: 0,8291, recovery: 84,4 %  
 neg. x-axis-intercept = matrix content: 0,3178 ng/l  
 expanded uncertainty of the matrix content: 0,3040 ng/l = 95,7 %

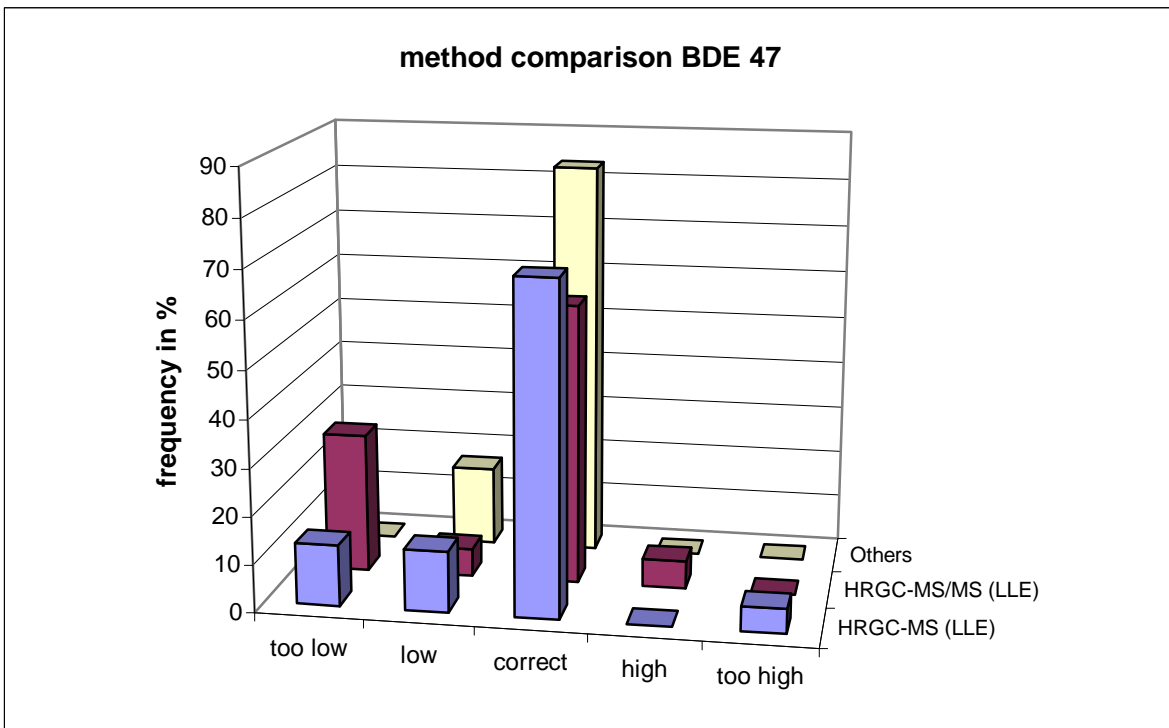
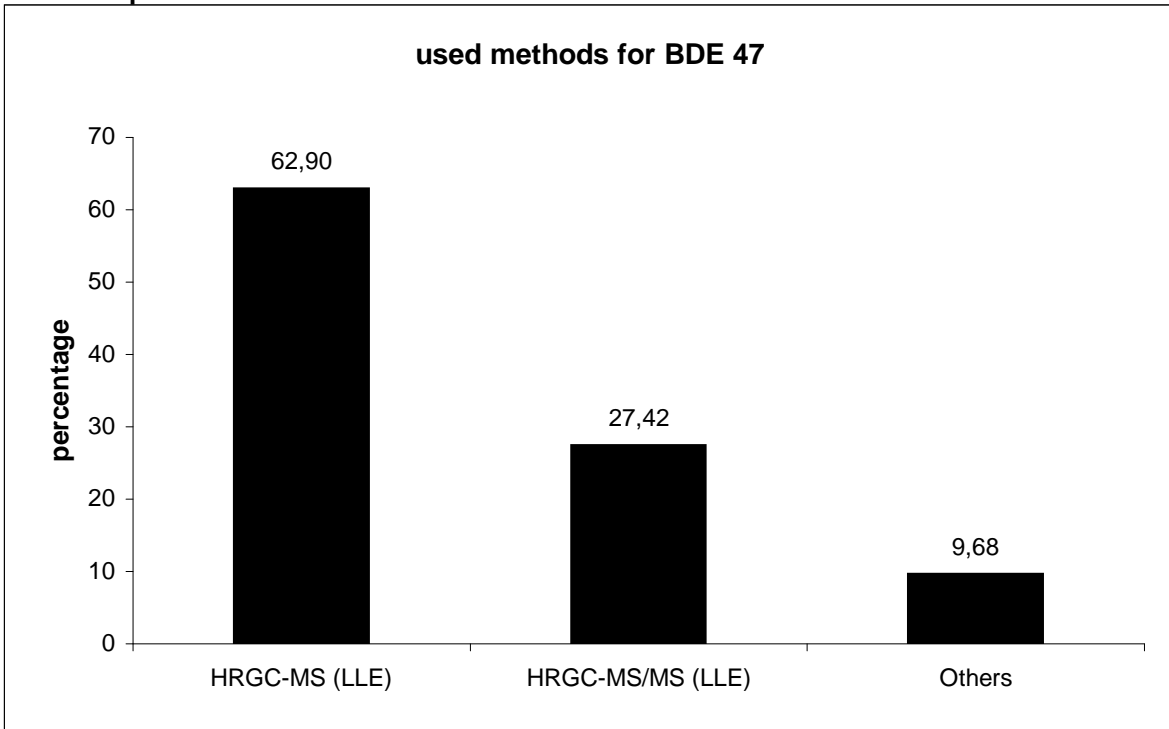
**Relative standard deviation and tolerance limits**



The relative standard deviation, calculated with Algorithm A, reached the standard deviation for proficiency assessment of 25 % at the lowest concentration level.

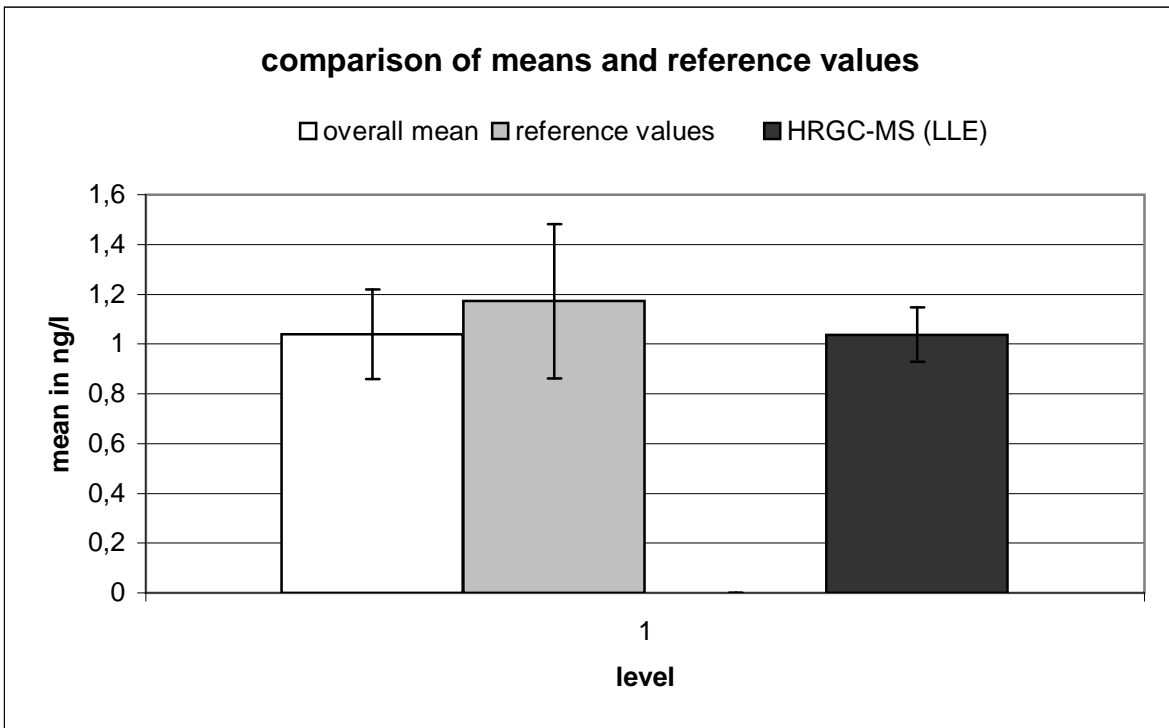


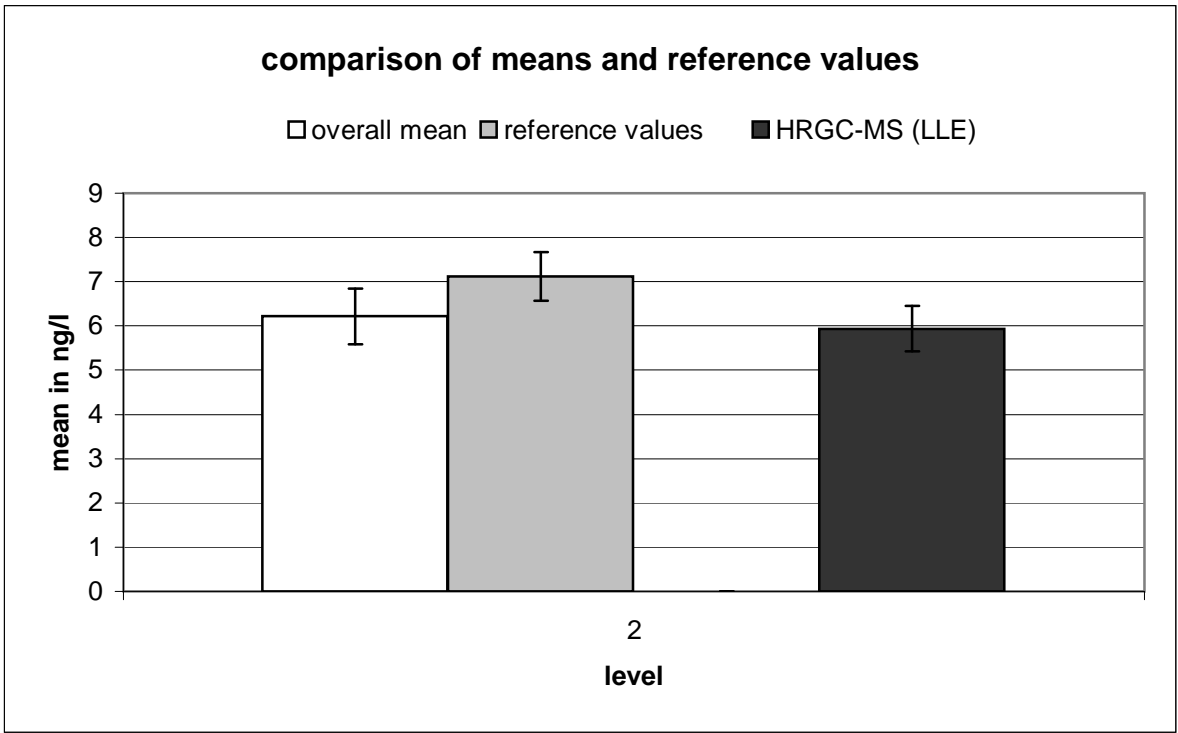
**Method specific evaluation**

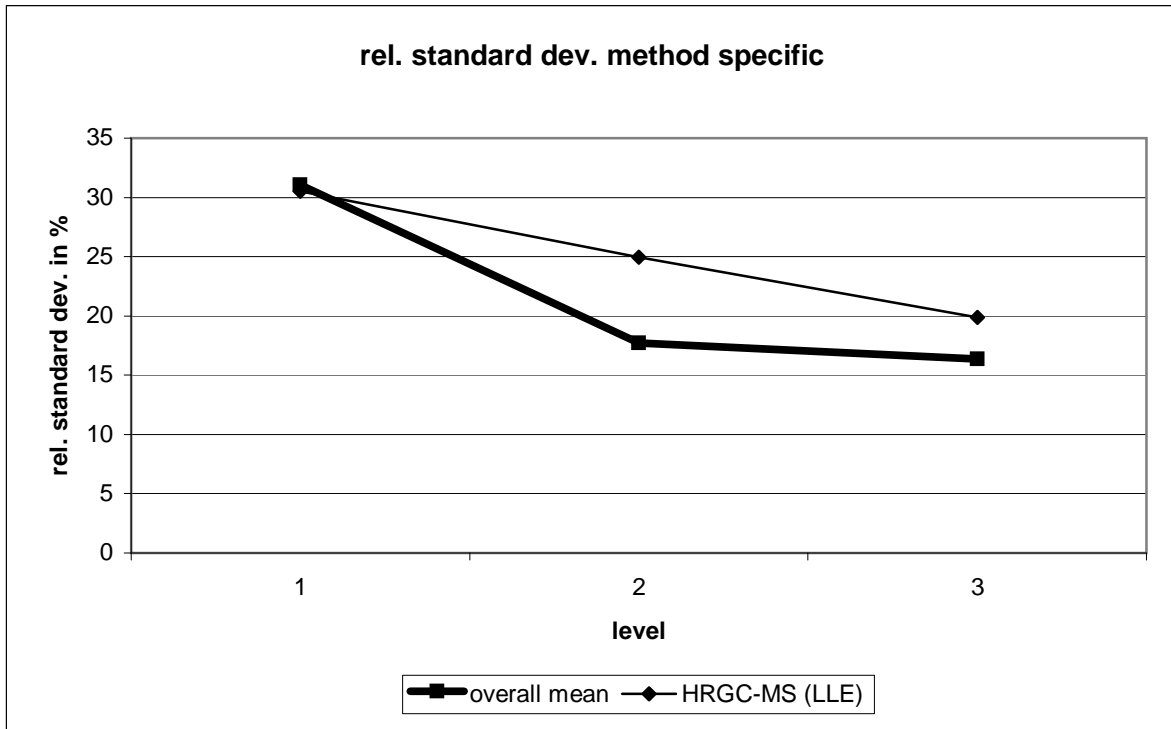


**Comparison of means and reference values**

level	Overall mean			reference values		
	mean [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]	reference value [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]
1	1,040	0,180	17,3	1,172	0,309	26,4
2	6,215	0,632	10,2	7,124	0,549	7,7
3	9,85	0,90	9,1	11,22	0,79	7,1





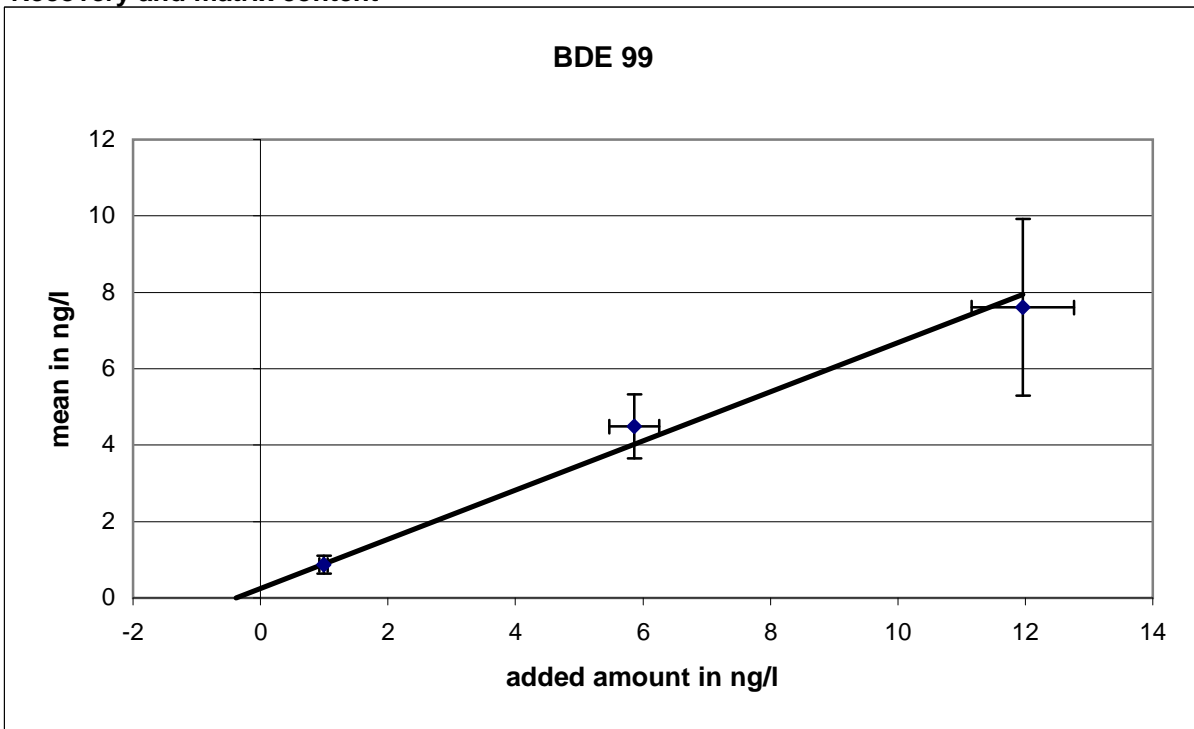


HRGC-MS (LLE)									
level	robust mean [ng/l]	exp. uncertainty of the mean [ng/l]	exp. uncertainty of the mean [%]	robust standard deviation [ng/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	1,038	0,11	10,571	0,3165	30,49	13	1	2	23,08
2	5,934	0,513	8,6473	1,4802	24,94	13	2	0	15,38
3	9,722	0,669	6,8844	1,9307	19,86	13	2	0	15,38

# BDE 99

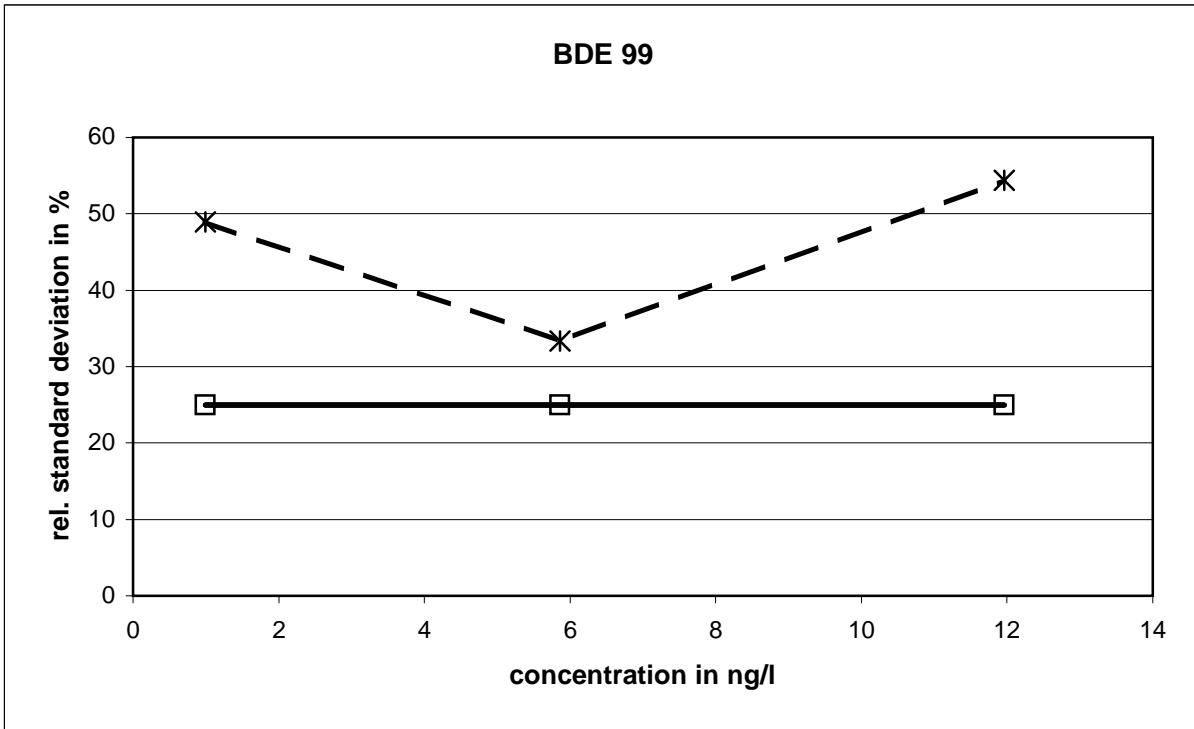
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,9902	6,72	0,4249	0,2476	25,00	1,485	0,4951	50,00	-50,00	20	4	1	25,0
2	5,862	6,72	1,500	1,466	25,00	8,793	2,931	50,00	-50,00	20	4	0	20,0
3	11,96	6,72	4,137	2,990	25,00	17,94	5,979	50,00	-50,00	20	6	0	30,0
sum										60	14	1	25,0

### Recovery and matrix content

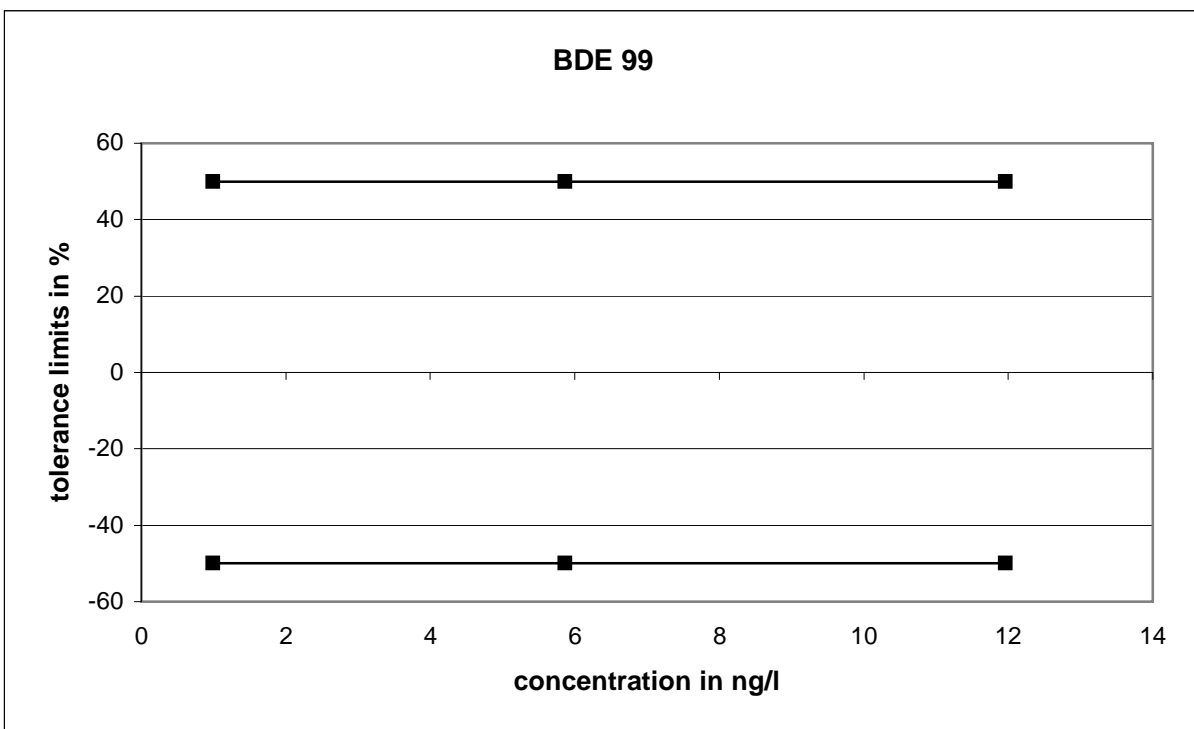


Slope of the regression line: 0,6441, recovery: 64,4 %  
 neg. x-axis-intercept = matrix content: 0,3812 ng/l  
 expanded uncertainty of the matrix content: 0,3812 ng/l = 100 %

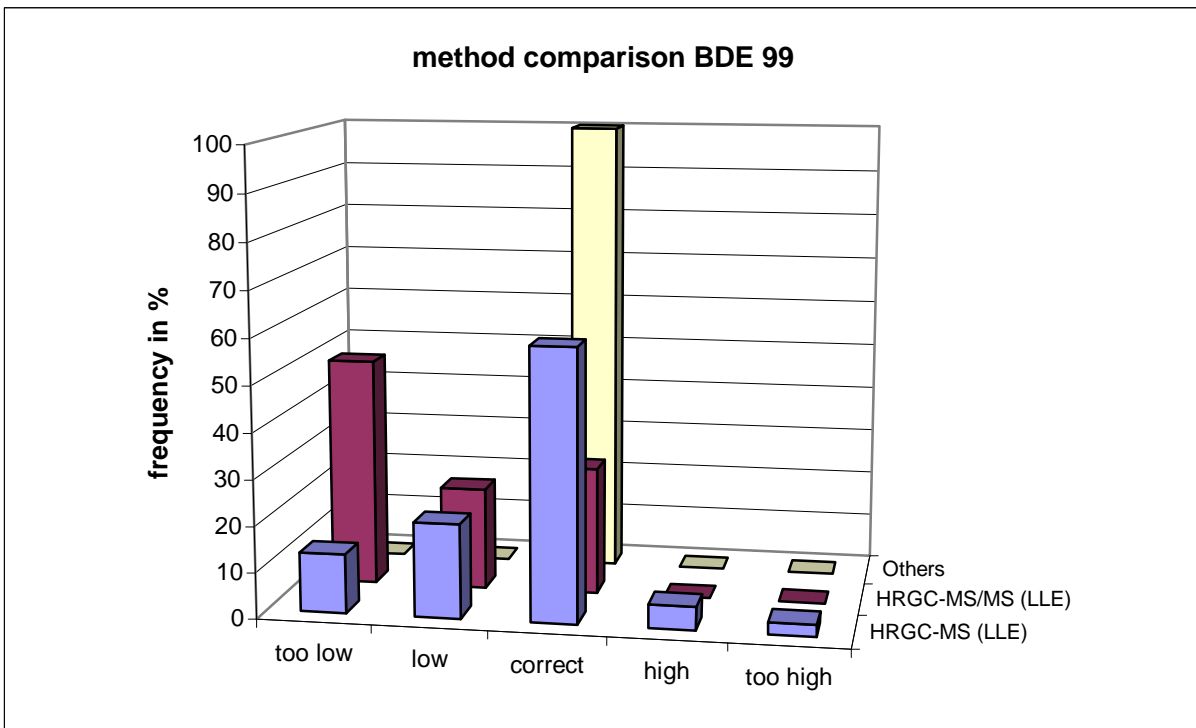
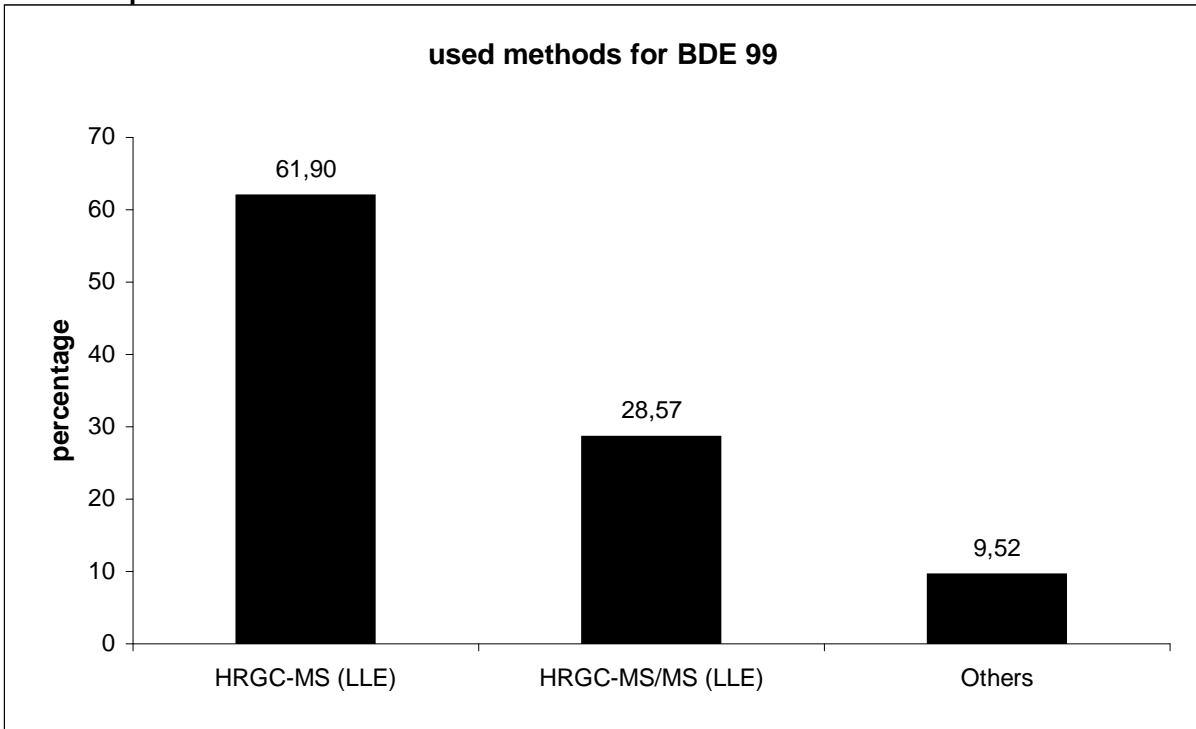
**Relative standard deviation and tolerance limits**



The relative standard deviation, calculated with Algorithm A, reached the standard deviation for proficiency assessment of 25 % at all concentration levels.

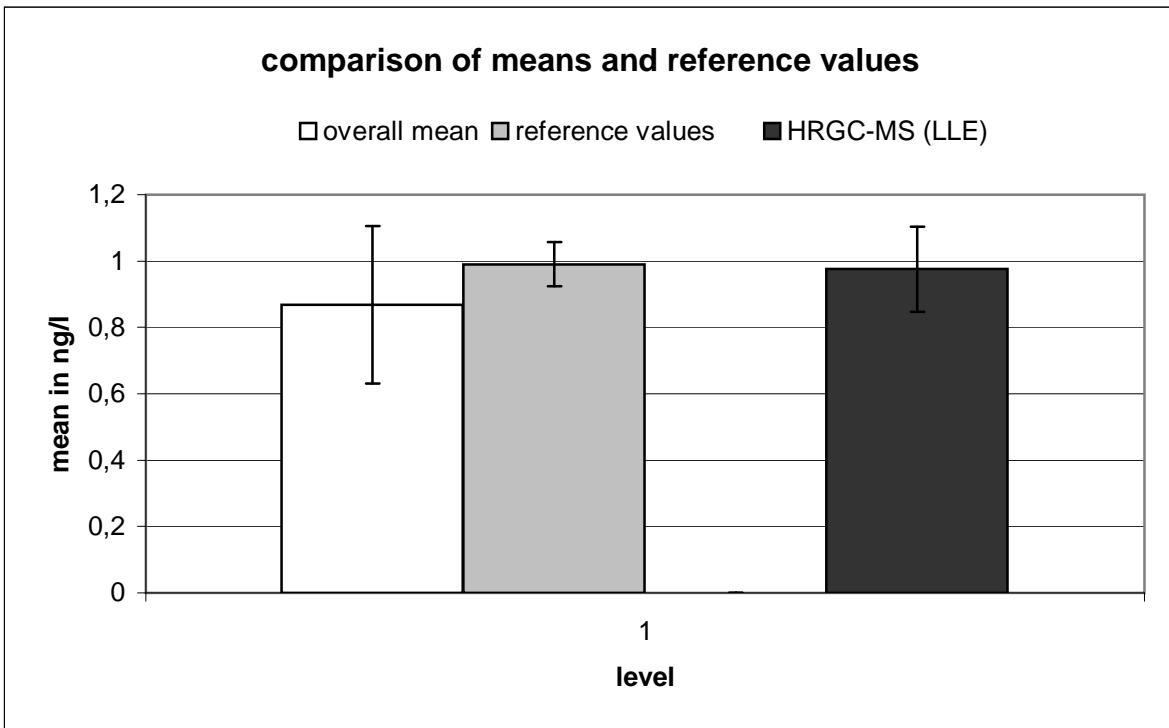


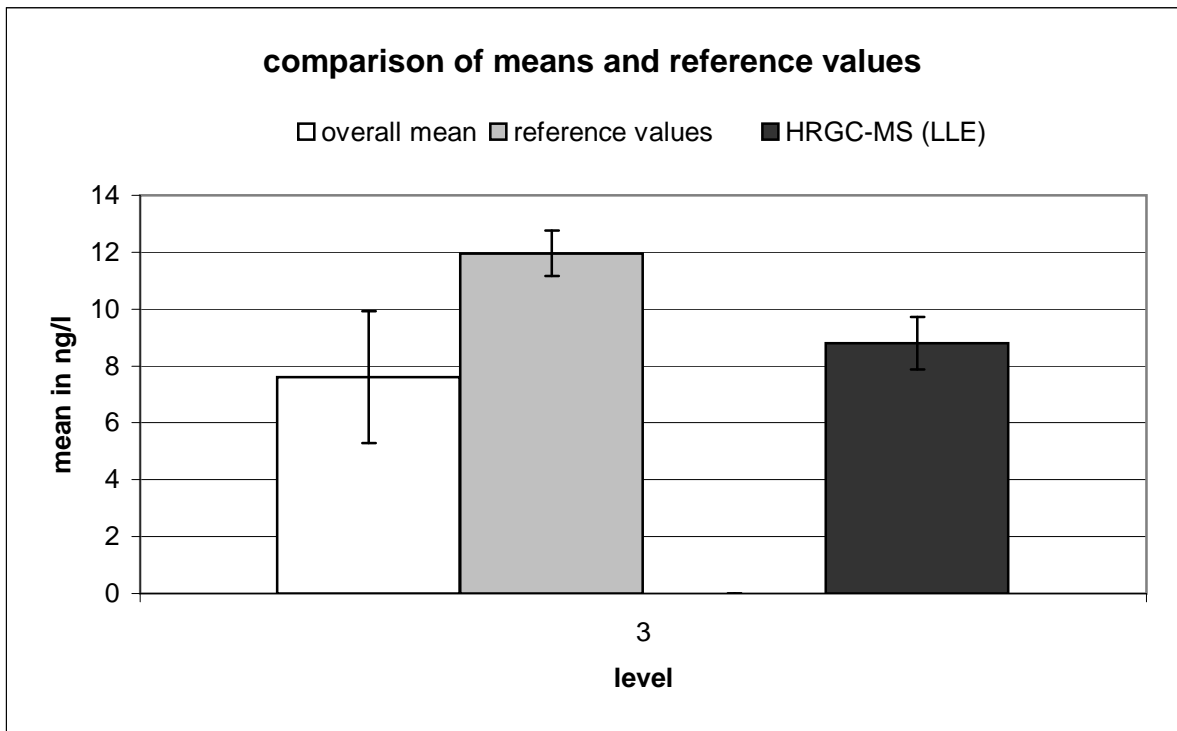
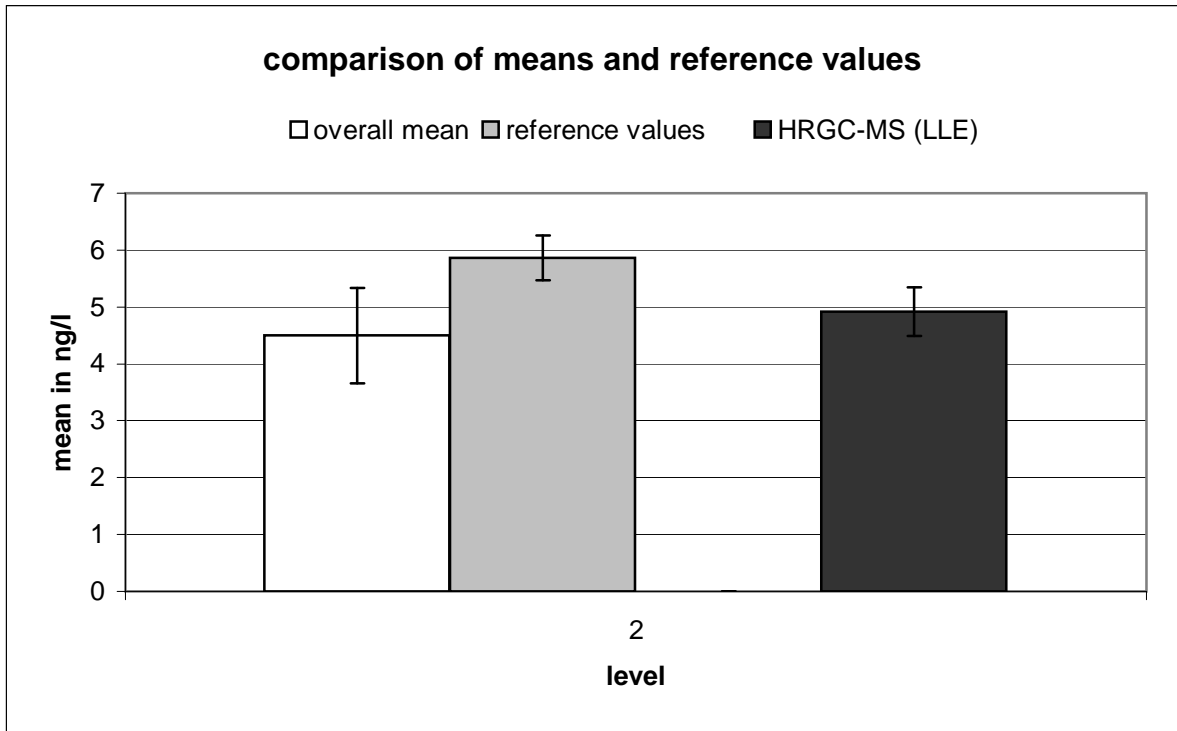
**Method specific evaluation**

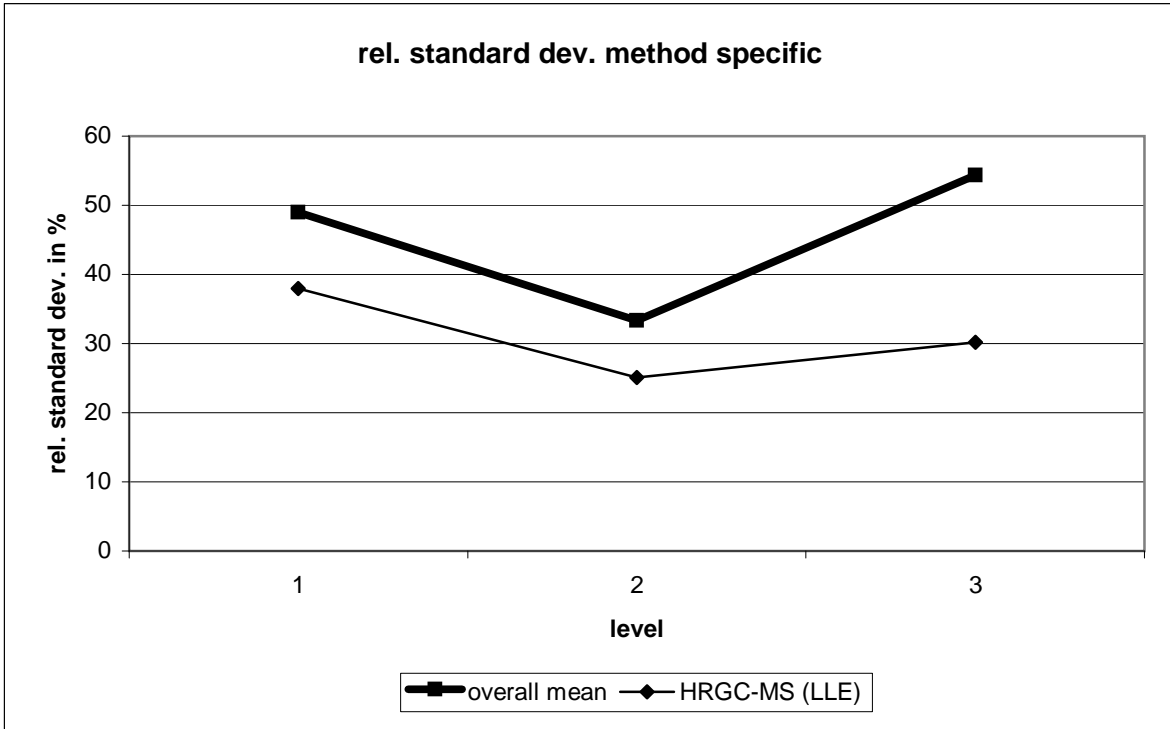


**Comparison of means and reference values**

level	mean [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]	reference value [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]
1	0,8677	0,2375	27,4	0,9902	0,0665	6,7
2	4,498	0,838	18,6	5,862	0,394	6,7
3	7,61	2,31	30,4	11,96	0,80	6,7





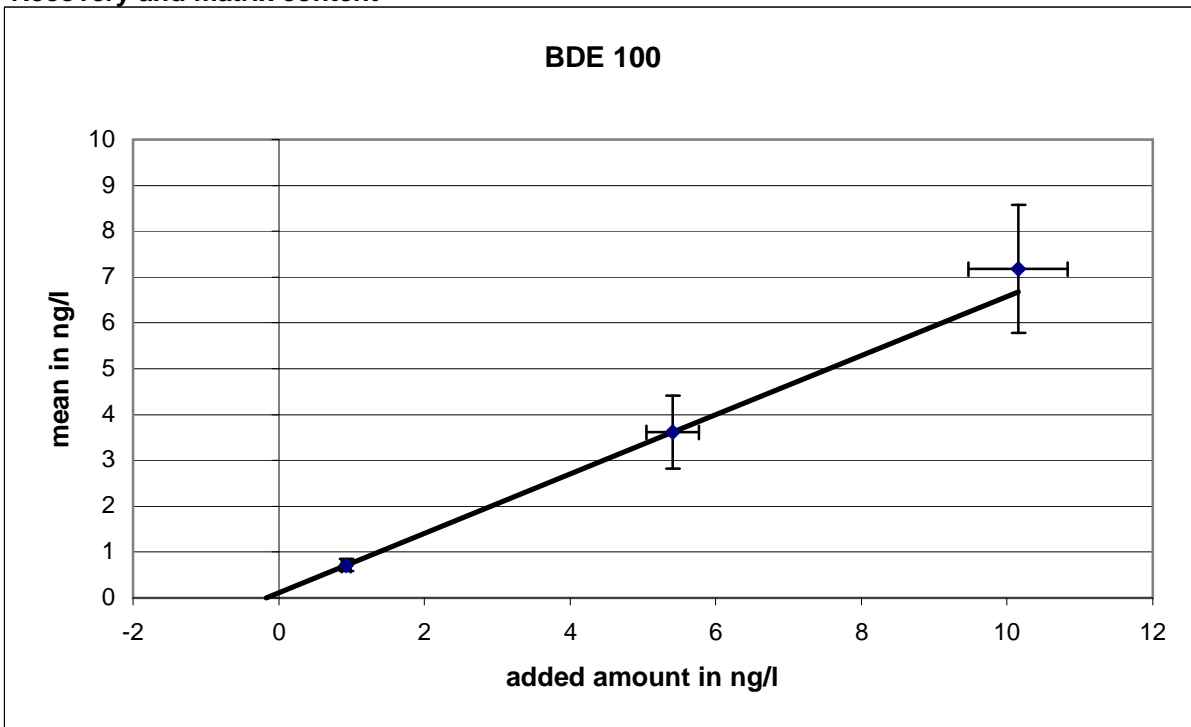


HRGC-MS (LLE)									
level	robust mean [ng/l]	exp. uncertainty of the mean [ng/l]	exp. uncertainty of the mean [%]	robust standard deviation [ng/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,9759	0,1285	13,165	0,3706	37,974	13	1	0	7,692
2	4,9215	0,4285	8,7073	1,2361	25,116	13	1	0	7,692
3	8,8079	0,9225	10,473	2,6608	30,209	13	2	0	15,38

# BDE 100

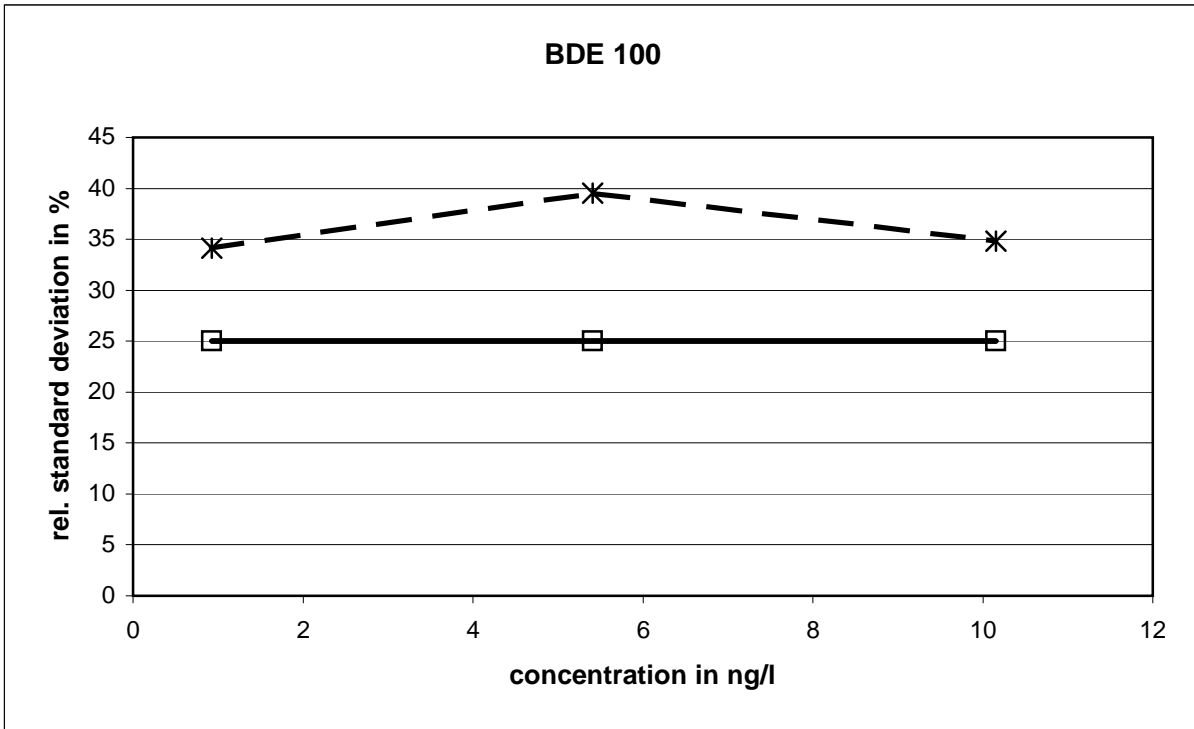
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,9249	6,72	0,2449	0,2312	25,00	1,387	0,4624	50,00	-50,00	20	4	0	20,0
2	5,409	6,72	1,429	1,352	25,00	8,114	2,705	50,00	-50,00	20	6	0	30,0
3	10,15	6,72	2,502	2,538	25,00	15,23	5,076	50,00	-50,00	20	5	0	25,0
sum										60	15	0	25,0

### Recovery and matrix content

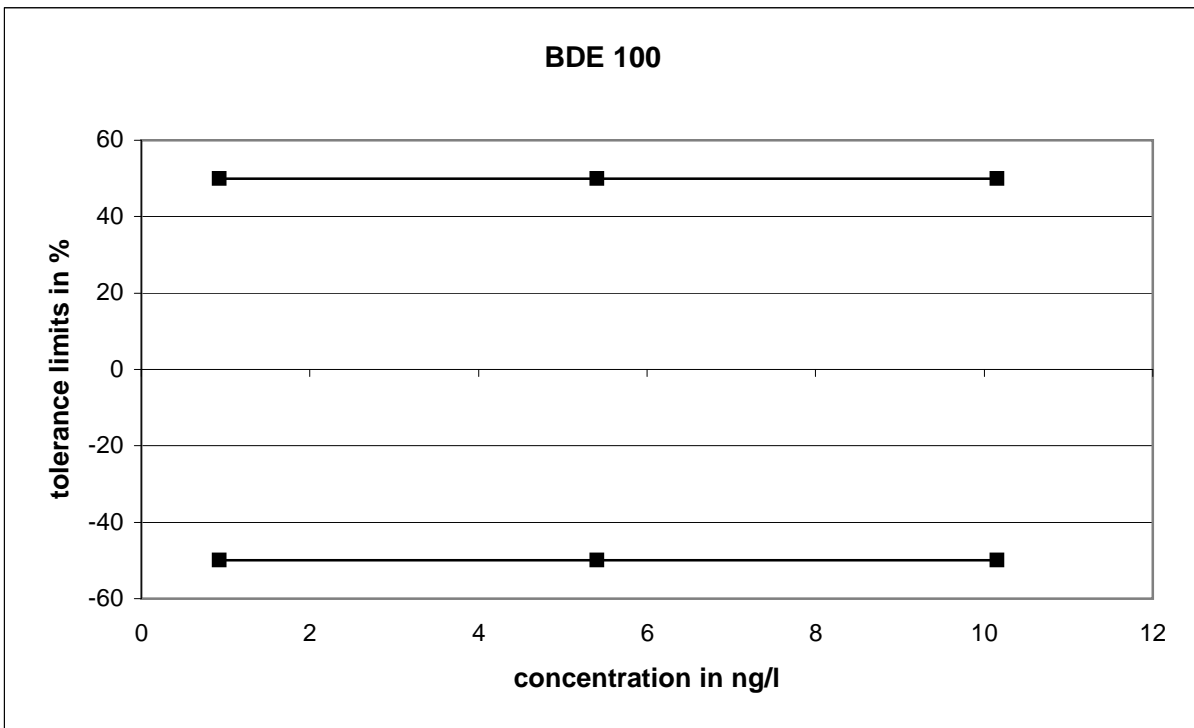


Slope of the regression line: 0,6473, recovery: 64,7 %  
 neg. x-axis-intercept = matrix content: 0,1686 ng/l  
 expanded uncertainty of the matrix content: 0,1686 ng/l = 100 %

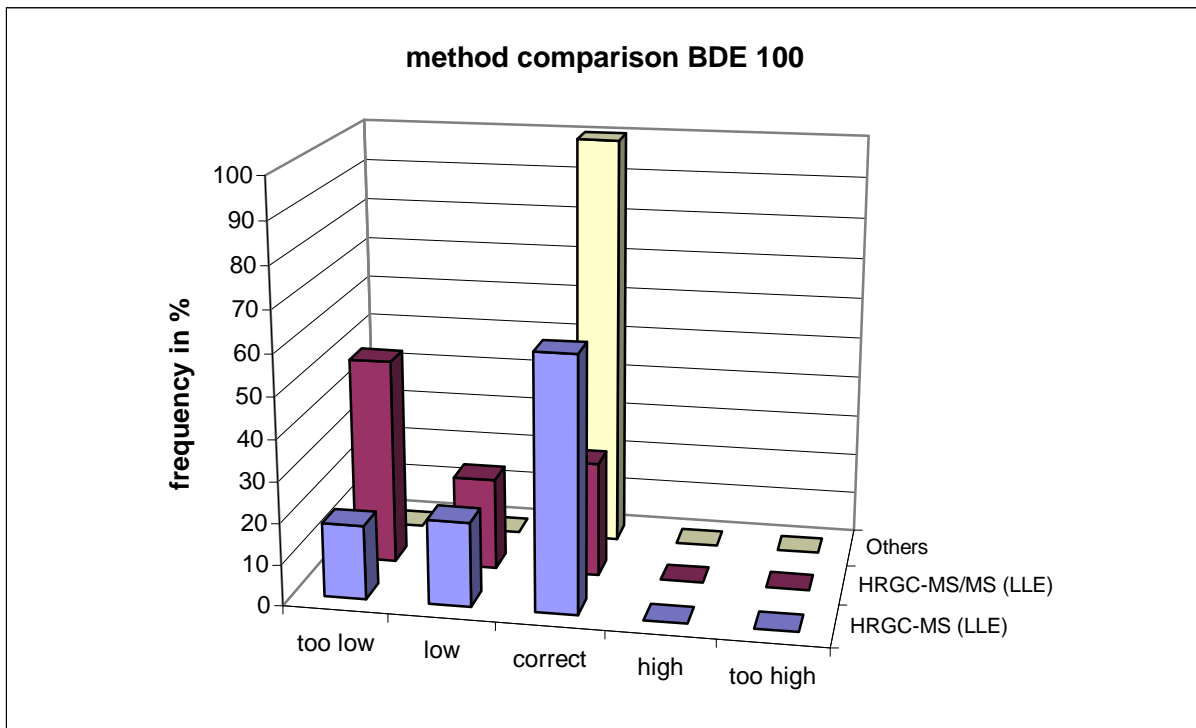
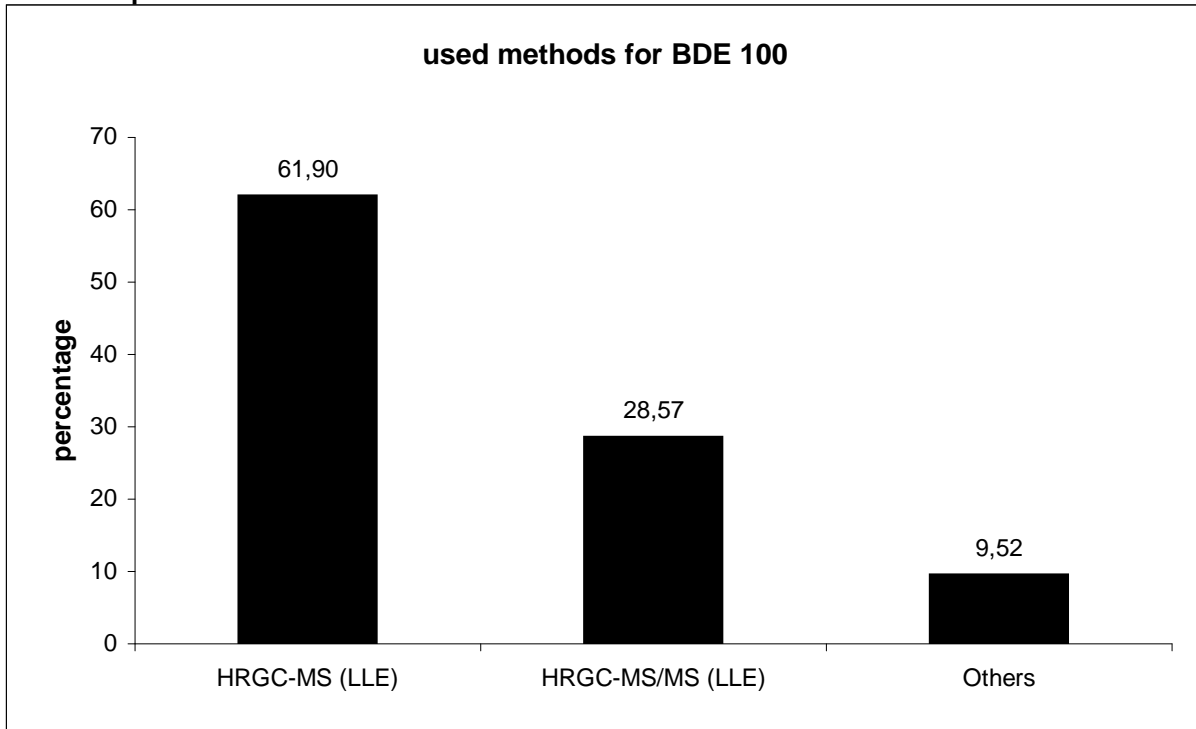
**Relative standard deviation and tolerance limits**



The relative standard deviation, calculated with Algorithm A, reached the standard deviation for proficiency assessment of 25 % at all concentration levels.

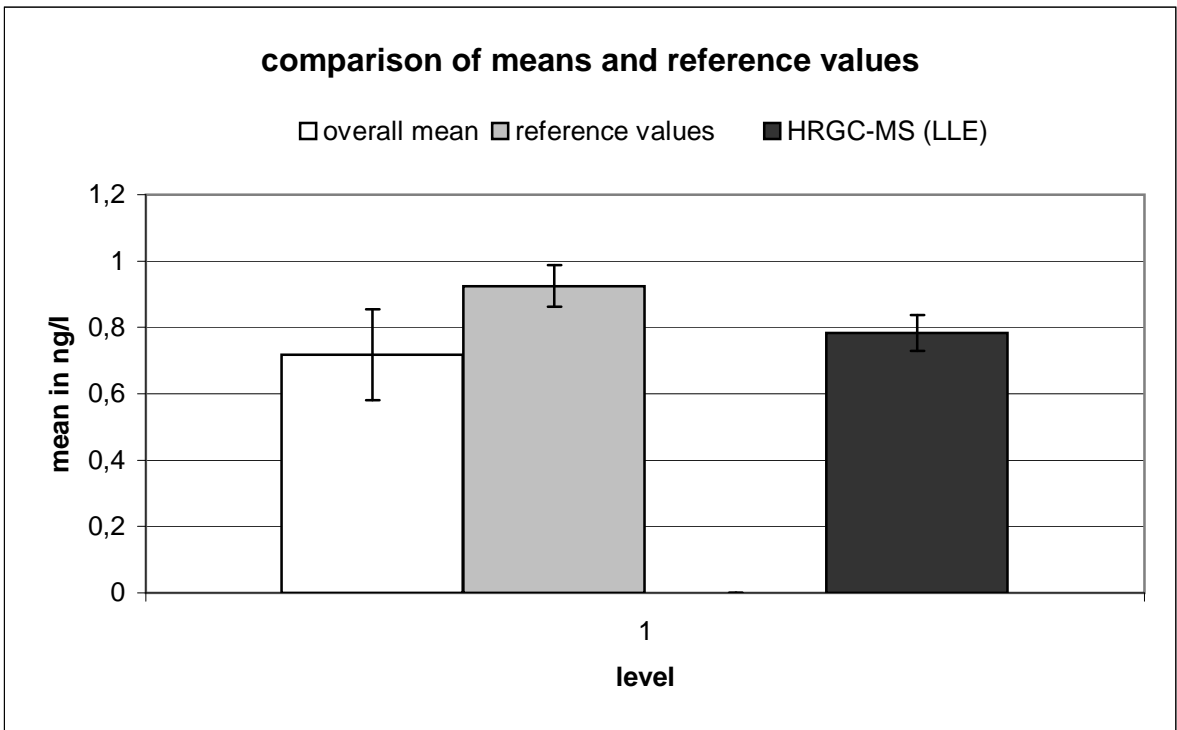


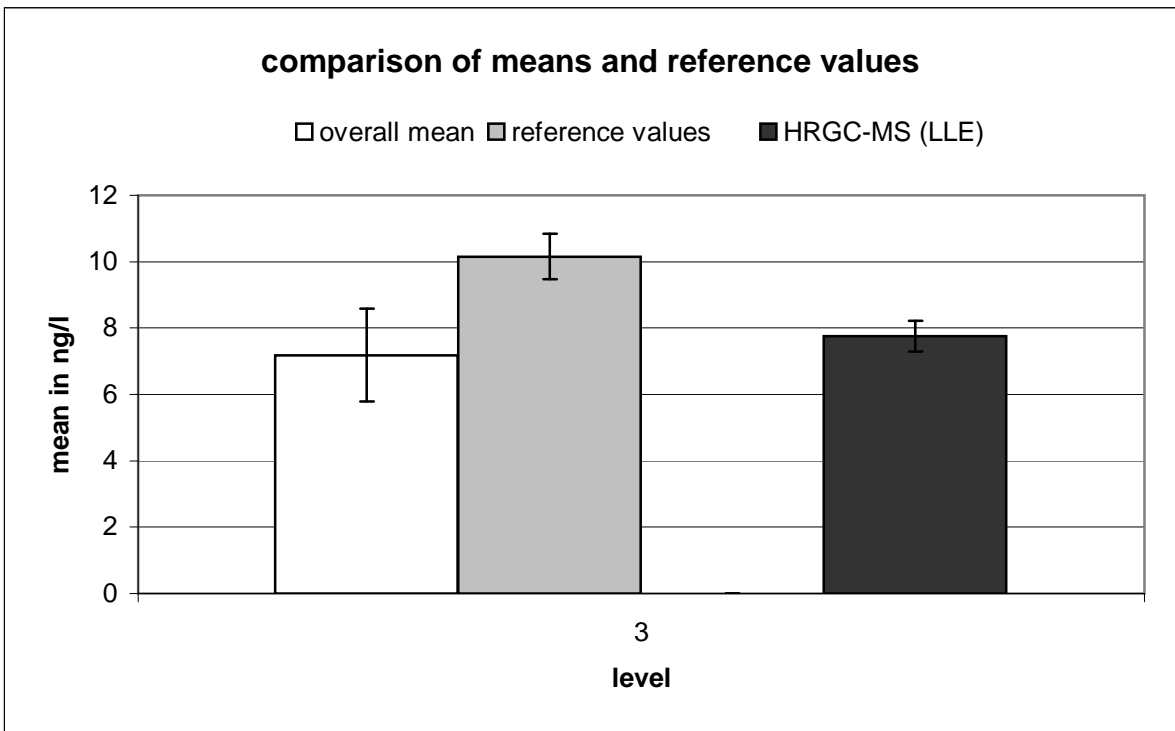
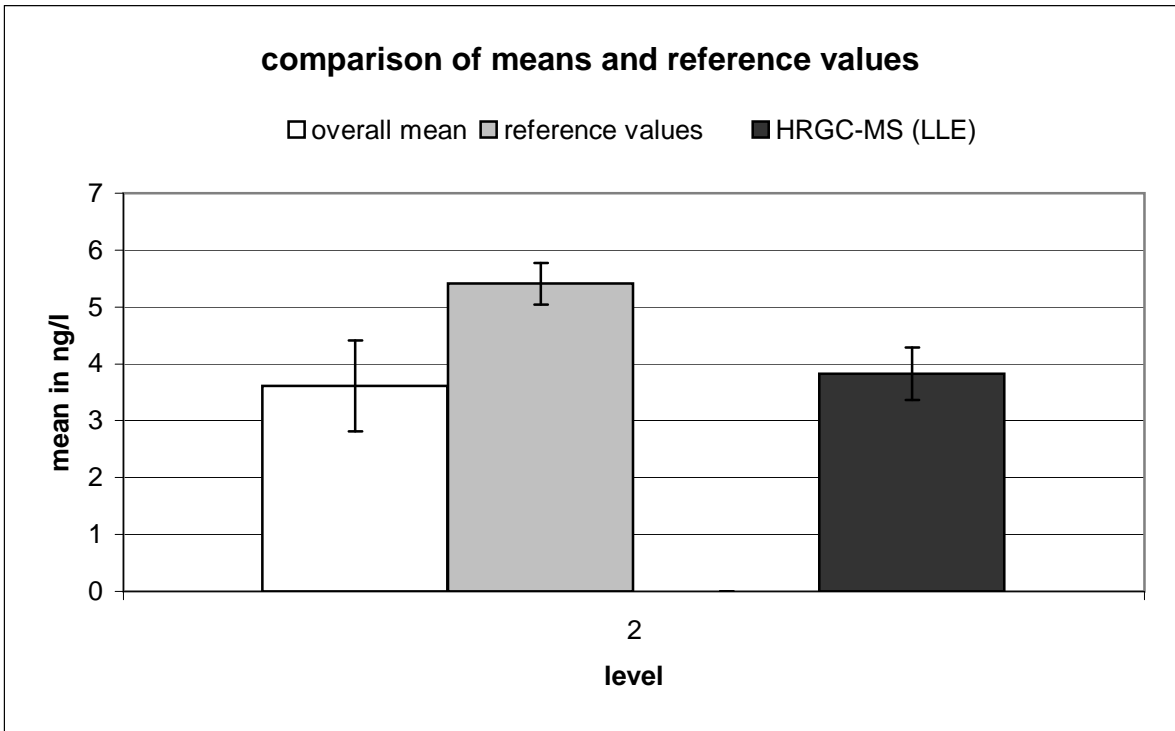
Method specific evaluation

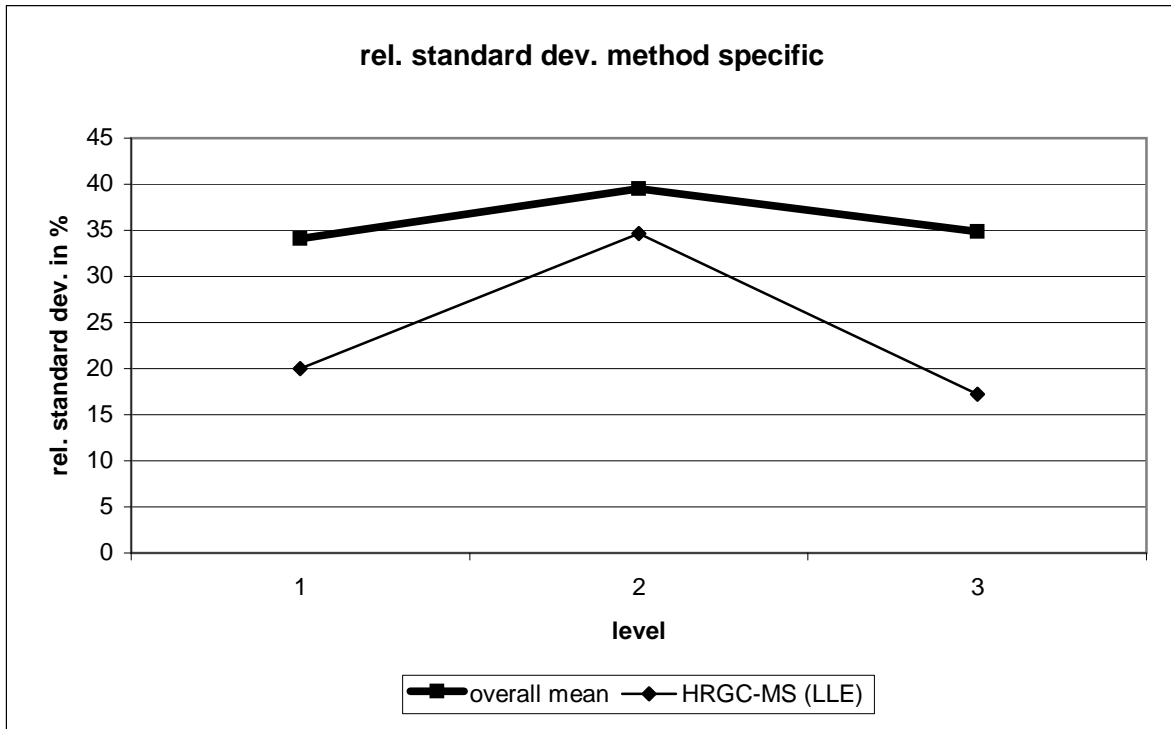


**Comparison of means and reference values**

level	mean [ng/l]			reference value [ng/l]		
	mean [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]	reference value [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]
1	0,7177	0,1369	19,1	0,9249	0,0622	6,7
2	3,614	0,799	22,1	5,409	0,363	6,7
3	7,18	1,40	19,5	10,15	0,68	6,7





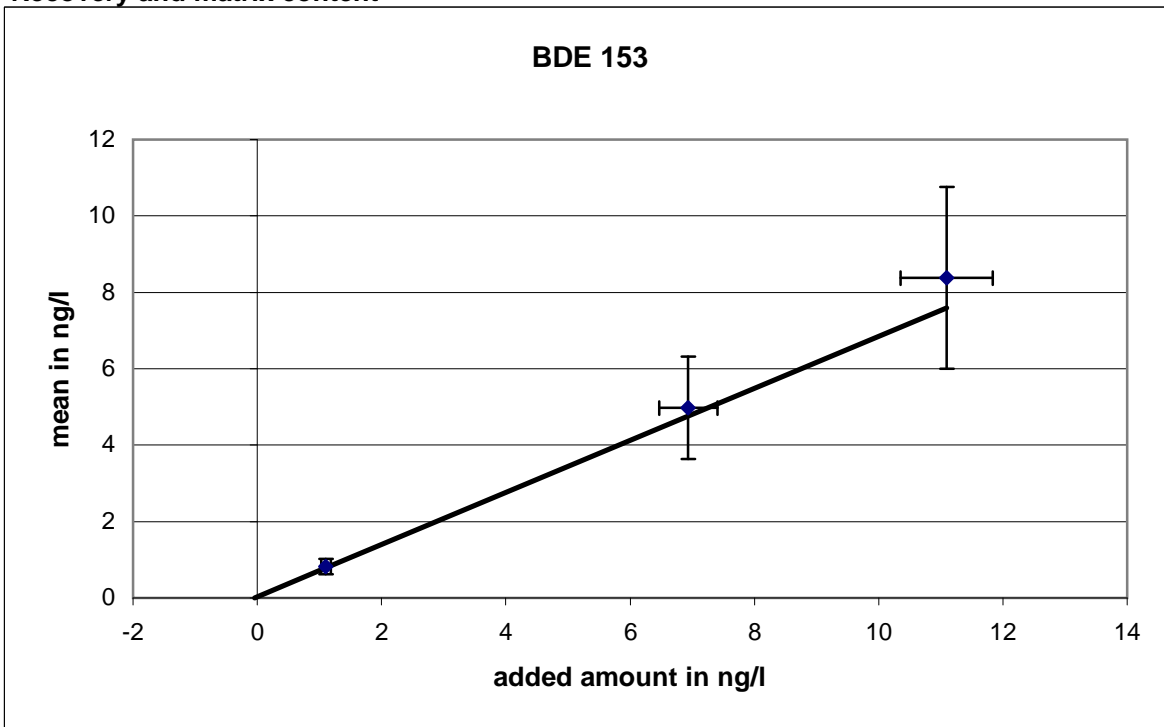


HRGC-MS (LLE)									
level	robust mean [ng/l]	exp. uncertainty of the mean [ng/l]	exp. uncertainty of the mean [%]	robust standard deviation [ng/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,7833	0,0544	6,9439	0,1569	20,029	13	2	0	15,38
2	3,8274	0,4601	12,021	1,327	34,673	13	2	0	15,38
3	7,7548	0,4624	5,9625	1,3337	17,199	13	3	1	30,77

# BDE 153

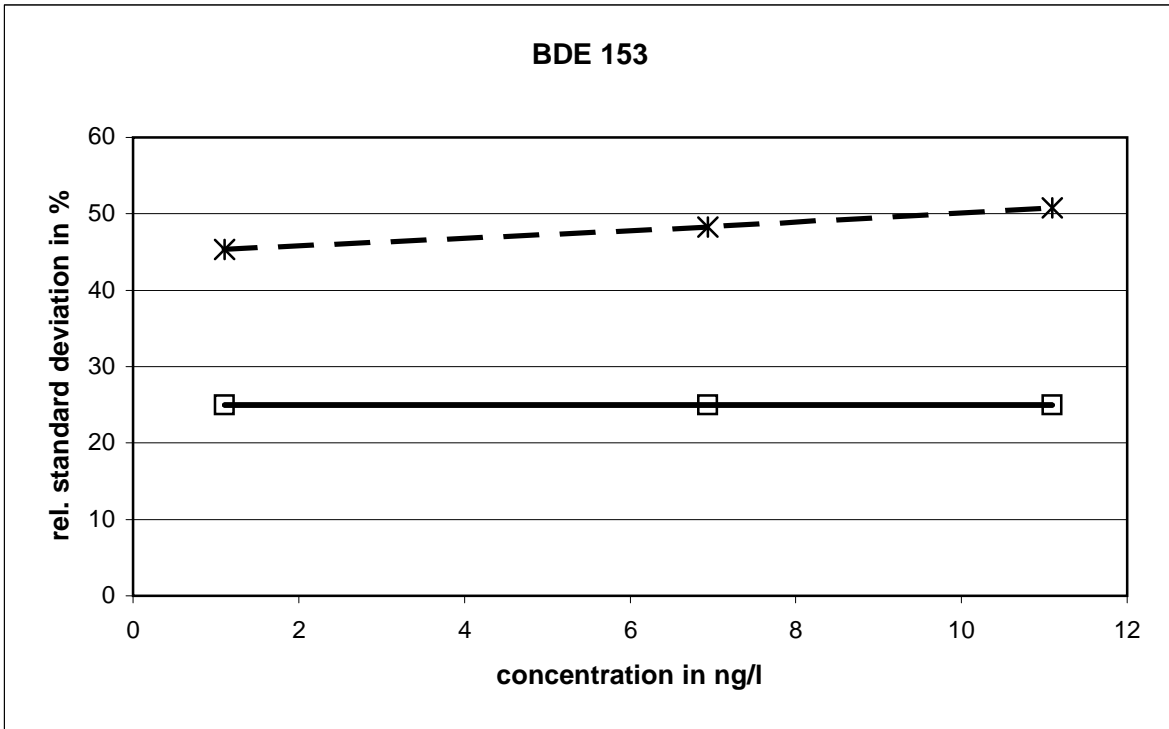
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	1,106	6,72	0,3718	0,2765	25,00	1,659	0,5531	50,00	-50,00	20	6	0	30,0
2	6,936	6,72	2,401	1,734	25,00	10,40	3,468	50,00	-50,00	20	6	1	35,0
3	11,09	6,72	4,257	2,773	25,00	16,64	5,547	50,00	-50,00	20	6	1	35,0
sum										60	18	2	33,3

## Recovery and matrix content

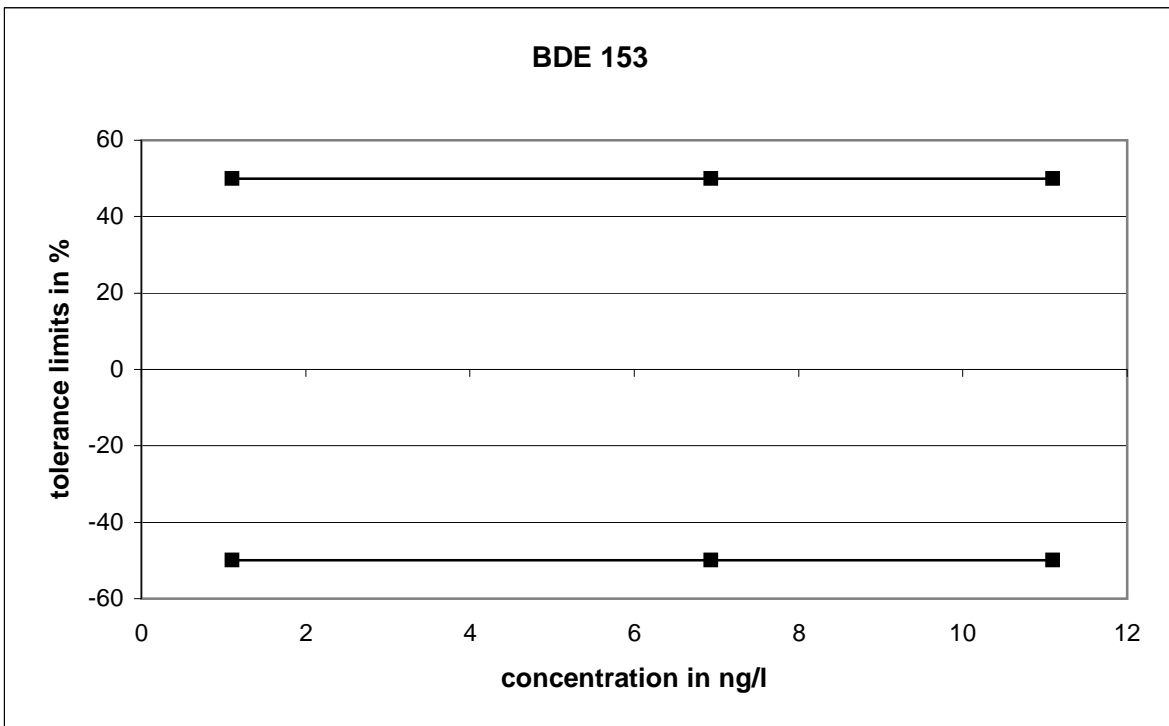


Slope of the regression line: 0,6828, recovery: 68,3 %  
 neg. x-axis-intercept = matrix content: 0,0374 ng/l  
 expanded uncertainty of the matrix content: 0,0374 ng/l = 100 %

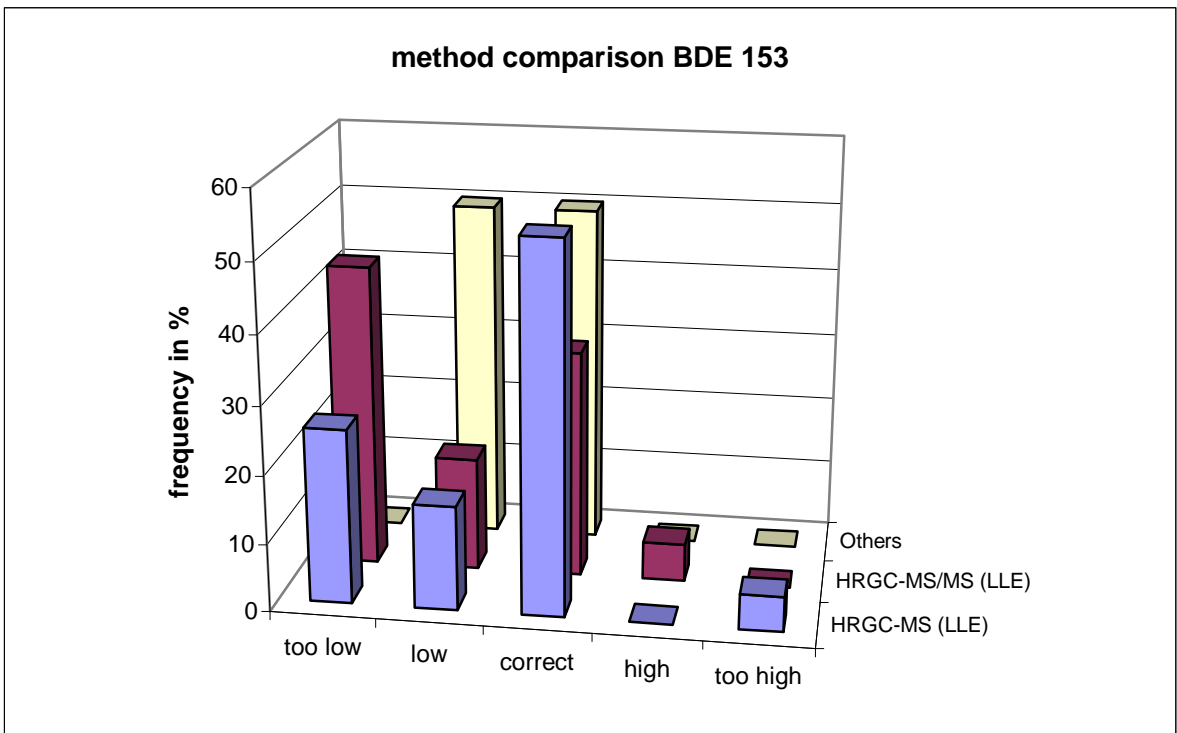
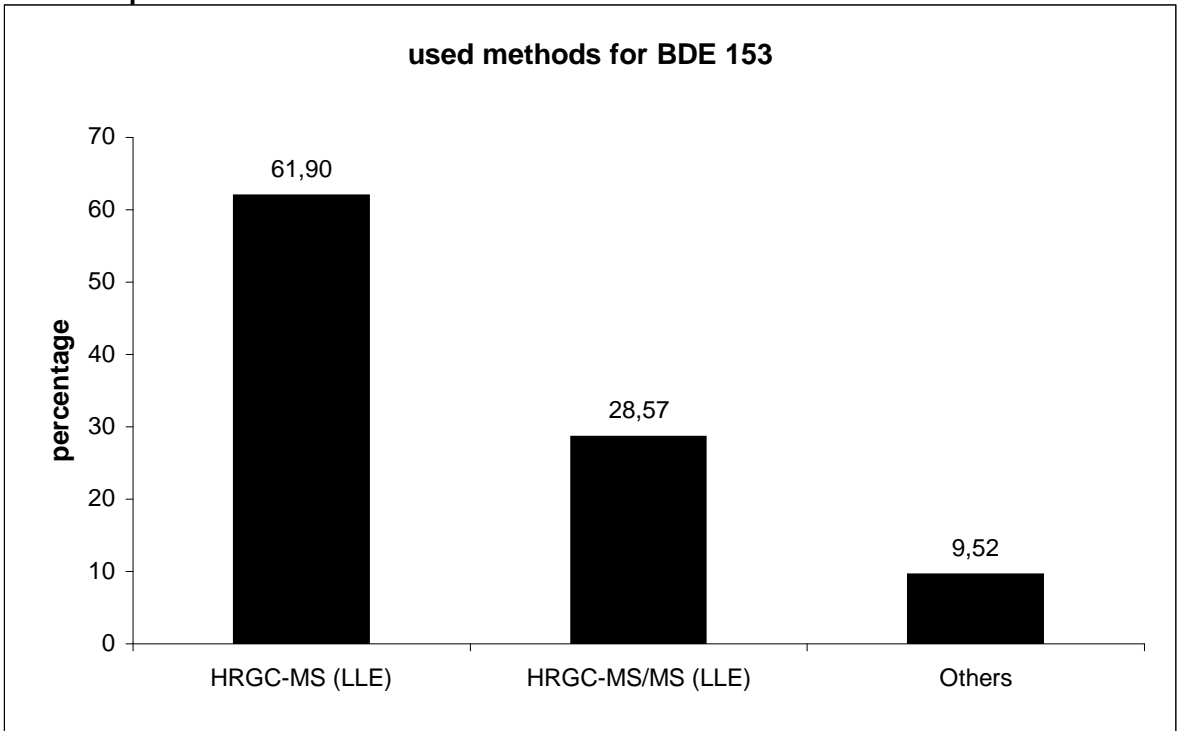
**Relative standard deviation and tolerance limits**



The relative standard deviation, calculated with Algorithm A, reached the standard deviation for proficiency assessment of 25 % at all concentration levels.

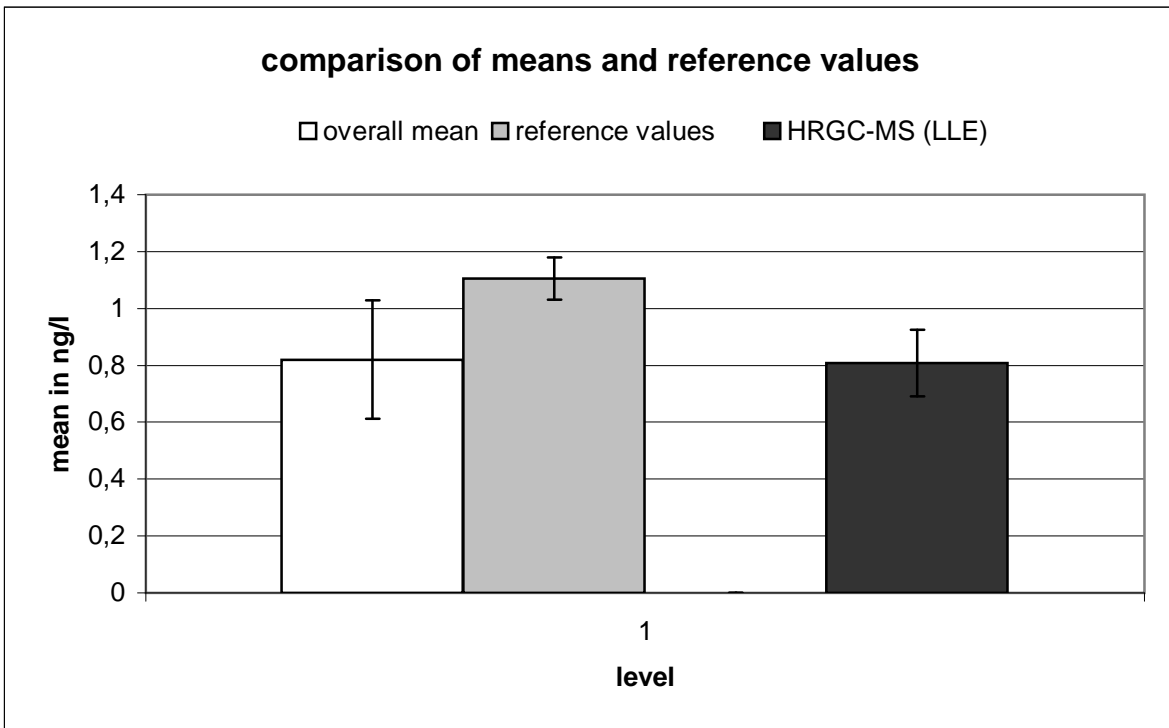


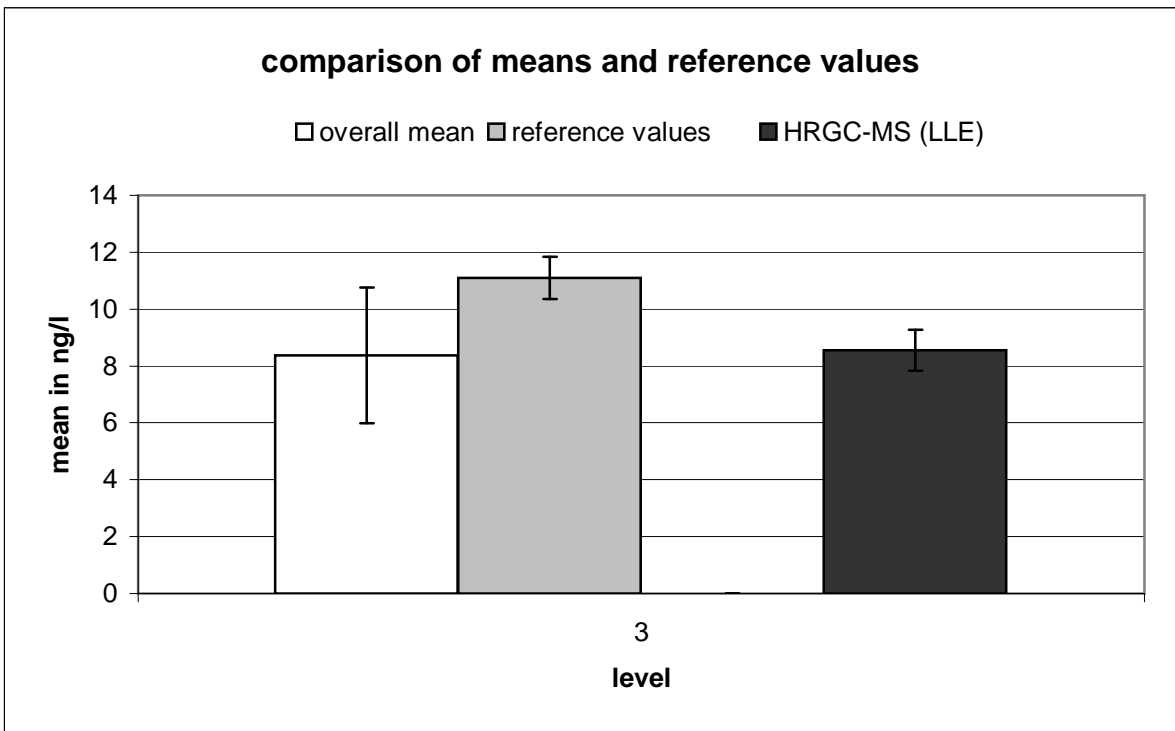
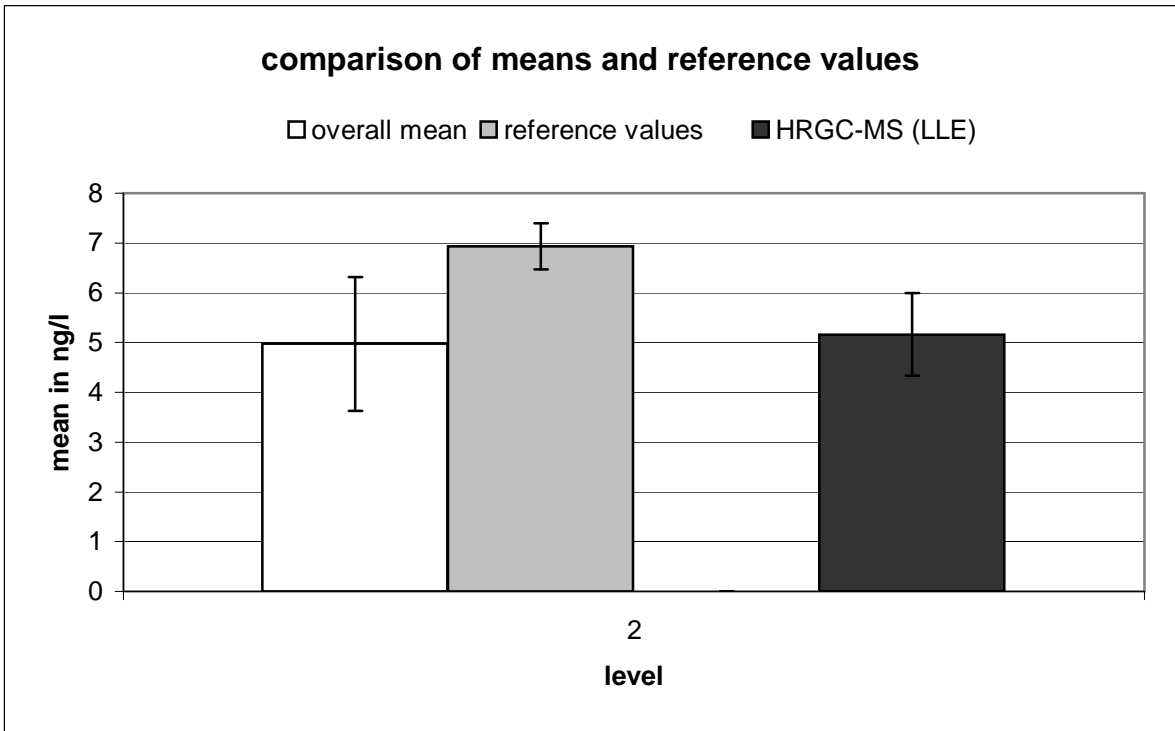
Method specific evaluation

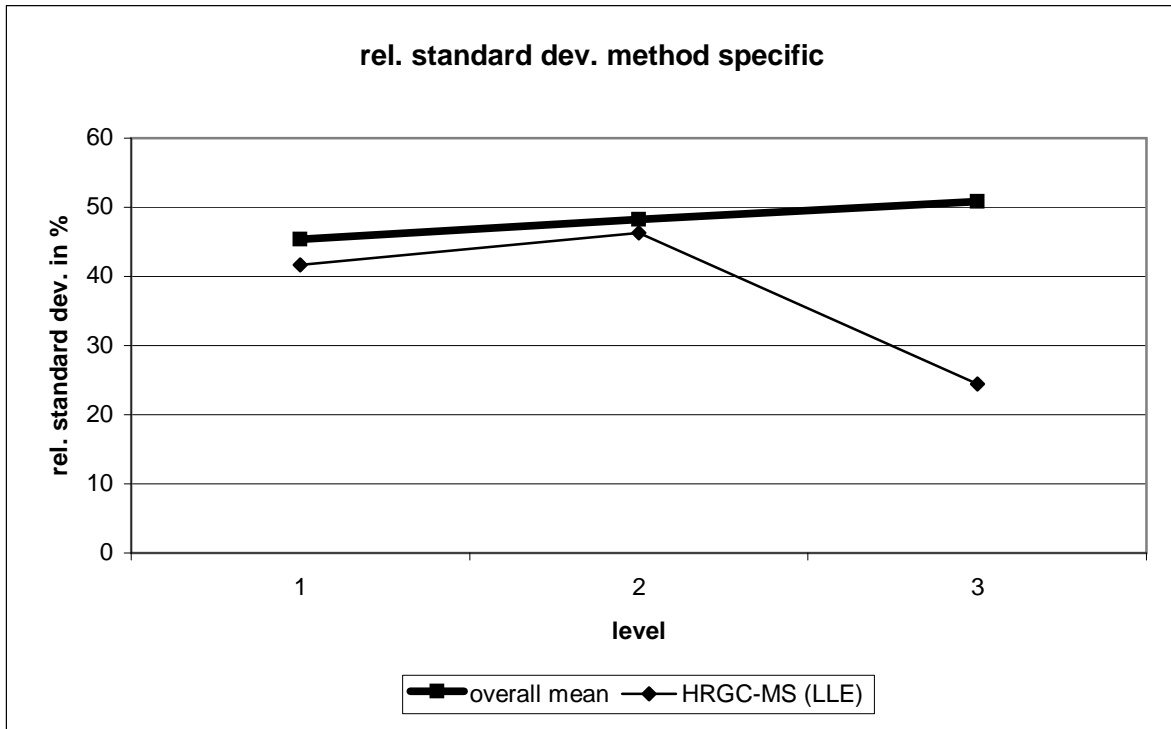


**Comparison of means and reference values**

level	Overall mean			reference values		
	mean [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]	reference value [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]
1	0,820	0,208	25,4	1,106	0,074	6,7
2	4,973	1,342	27,0	6,936	0,466	6,7
3	8,38	2,38	28,4	11,09	0,75	6,7





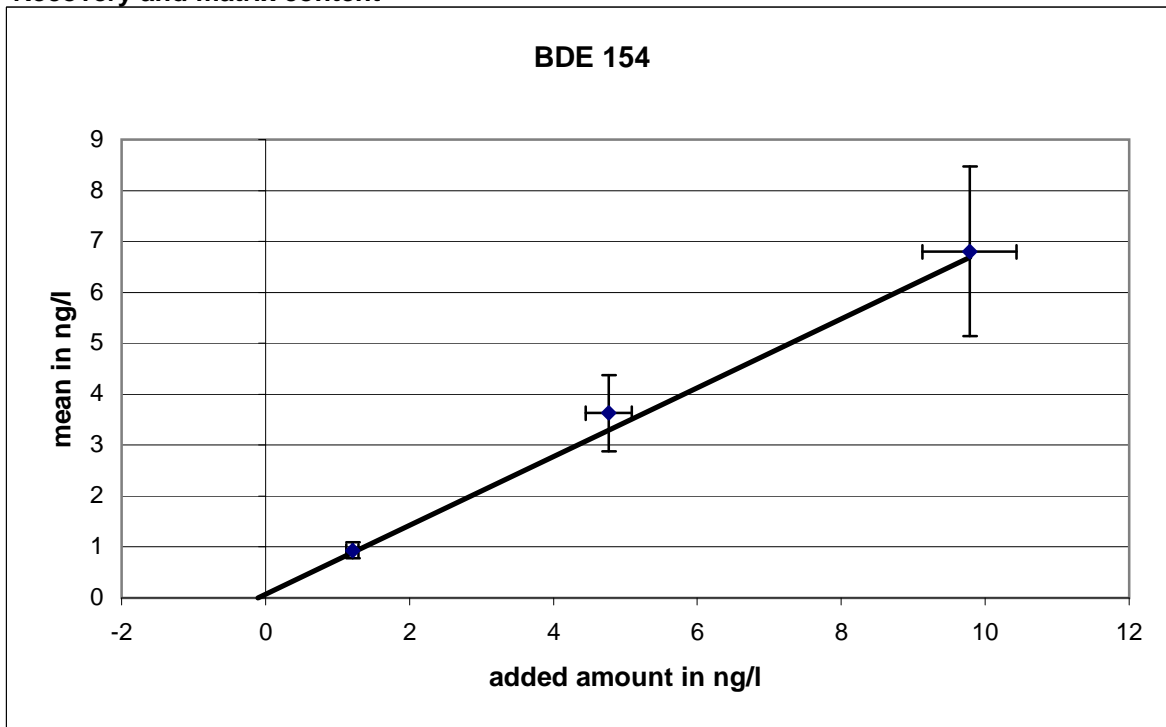


HRGC-MS (LLE)									
level	robust mean [ng/l]	exp. uncertainty of the mean [ng/l]	exp. uncertainty of the mean [%]	robust standard deviation [ng/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,807	0,117	14,454	0,3366	41,69	13	2	0	15,38
2	5,161	0,828	16,039	2,3878	46,26	13	1	1	15,38
3	8,556	0,725	8,4702	2,0904	24,43	13	2	2	30,77

# BDE 154

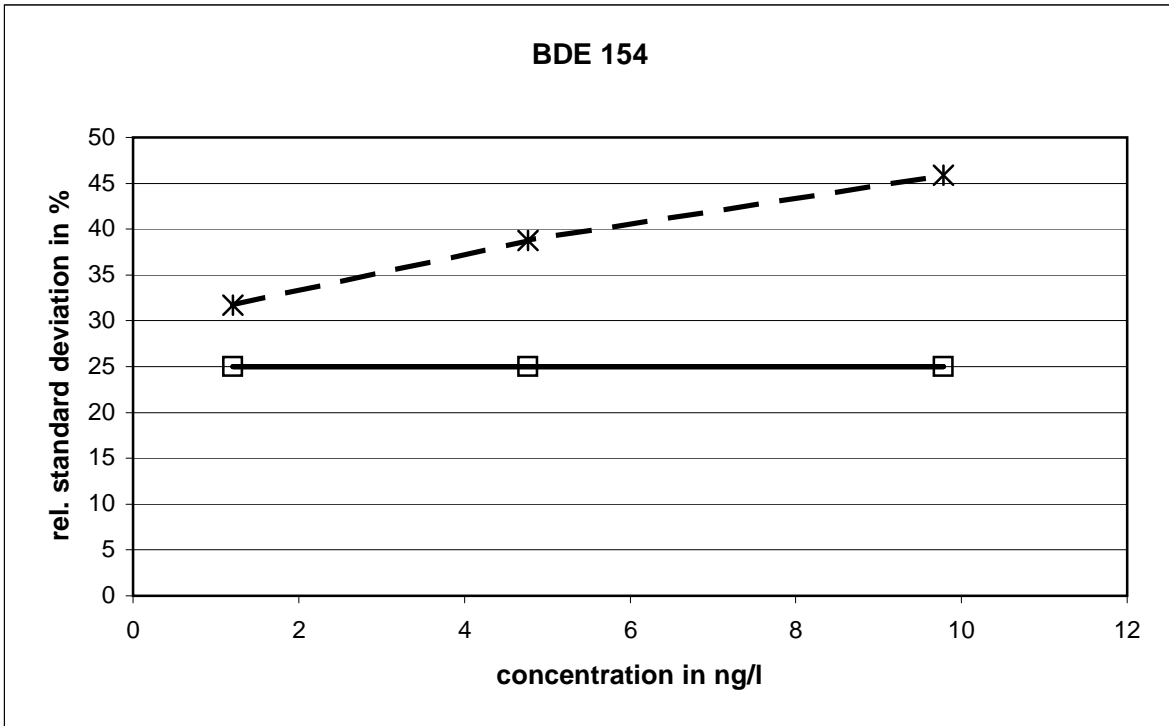
level	assigned value [ng/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [ng/l]	standard deviation for proficiency assessment [ng/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [ng/l]	lower tolerance limit [ng/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	1,207	6,72	0,2964	0,3016	25,00	1,810	0,6033	50,00	-50,00	22	5	0	22,7
2	4,769	6,72	1,406	1,192	25,00	7,154	2,385	50,00	-50,00	22	6	0	27,3
3	9,782	6,72	3,122	2,445	25,00	14,67	4,891	50,00	-50,00	22	7	0	31,8
sum										66	18	0	27,3

## Recovery and matrix content

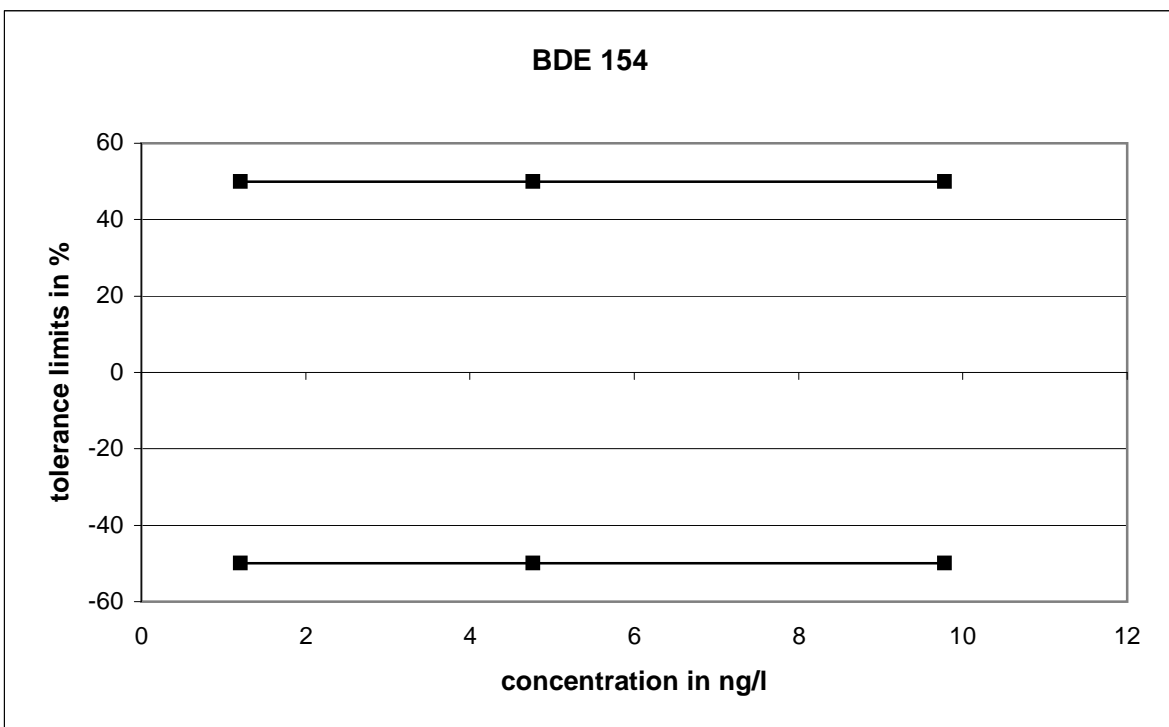


Slope of the regression line: 0,6763, recovery: 67,6 %  
 neg. x-axis-intercept = matrix content: 0,1042 ng/l  
 expanded uncertainty of the matrix content: 0,1042 ng/l = 100 %

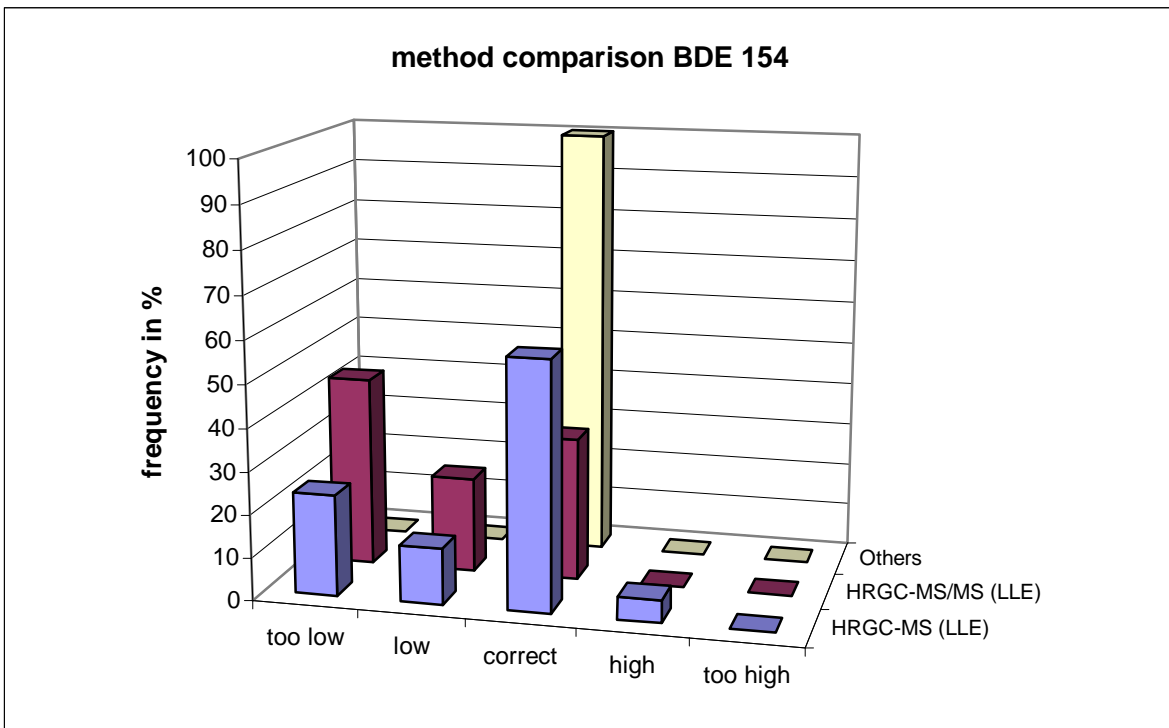
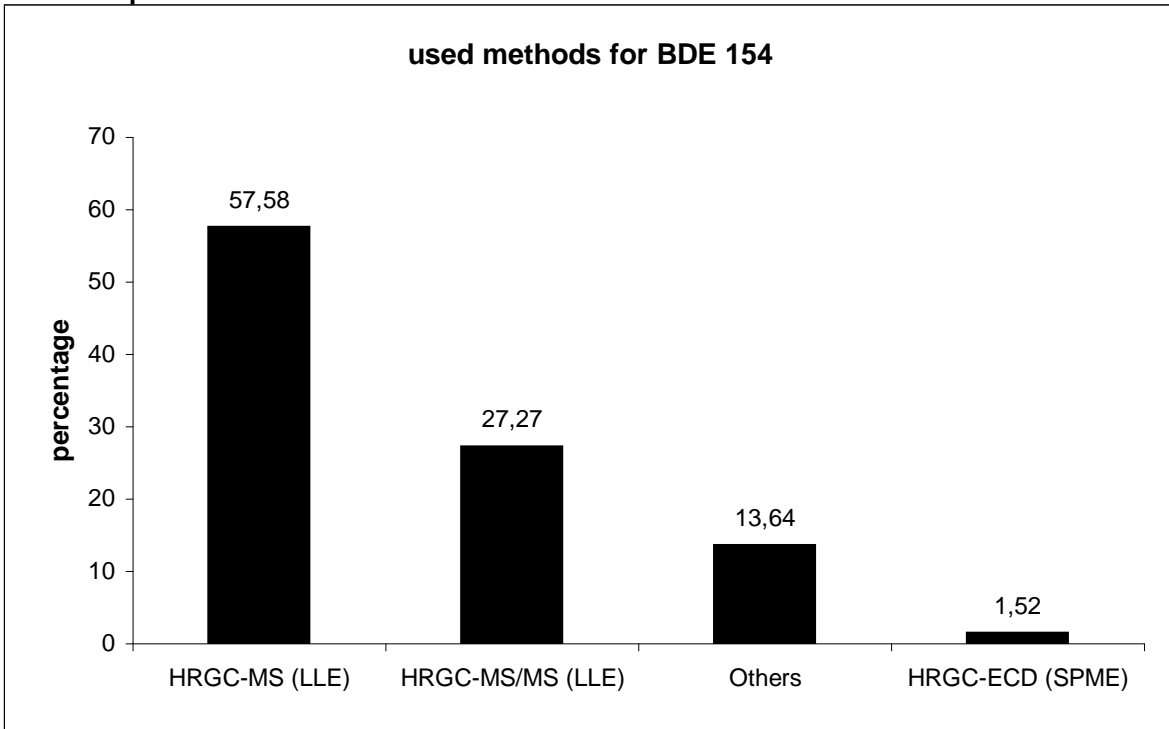
**Relative standard deviation and tolerance limits**



The relative standard deviation, calculated with Algorithm A, reached the standard deviation for proficiency assessment of 25 % at all concentration levels.

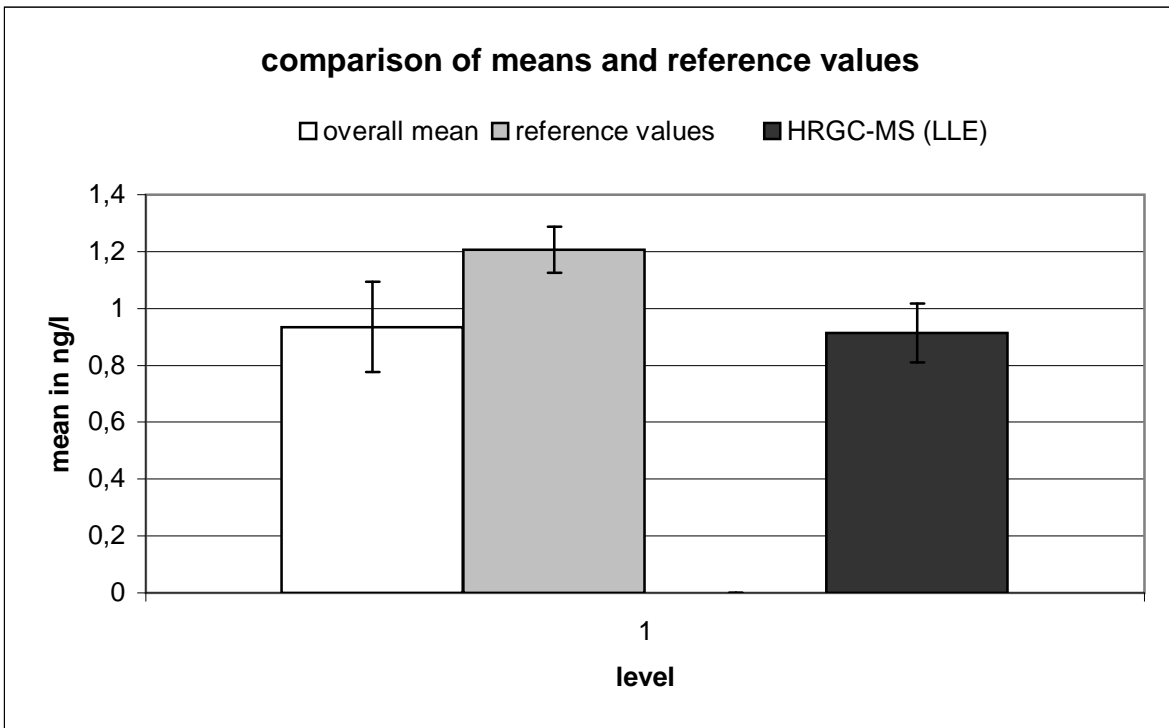


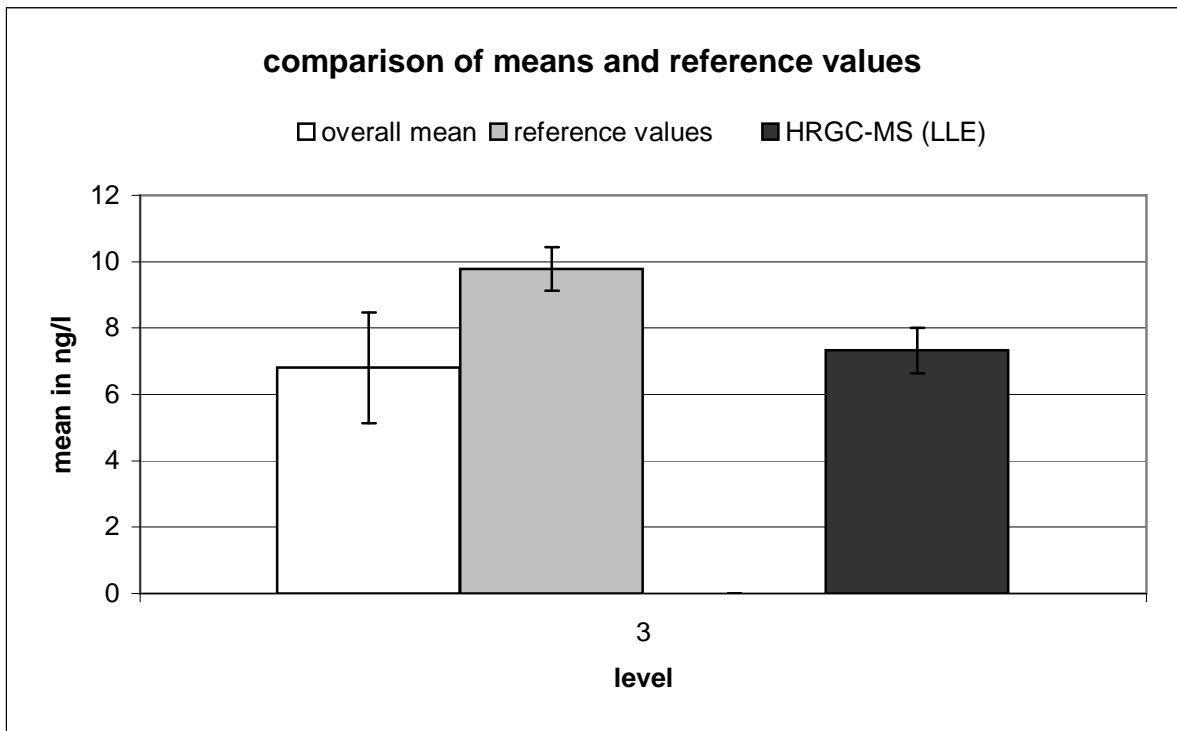
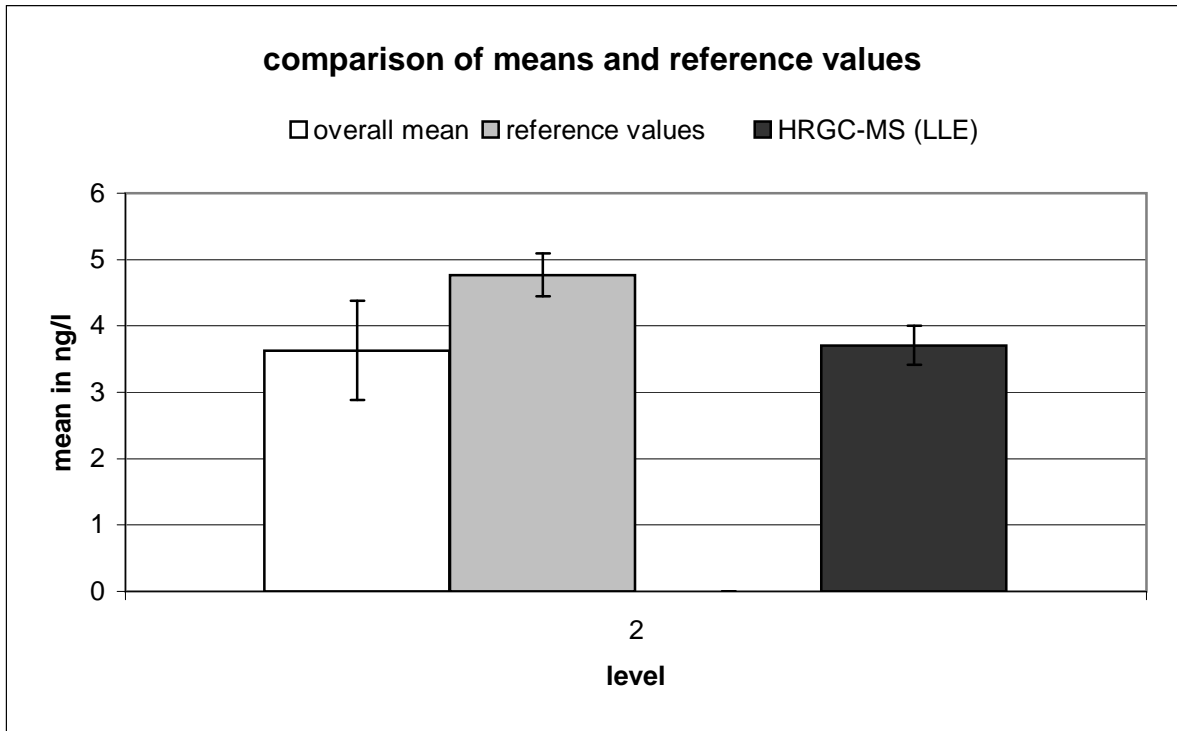
**Method specific evaluation**

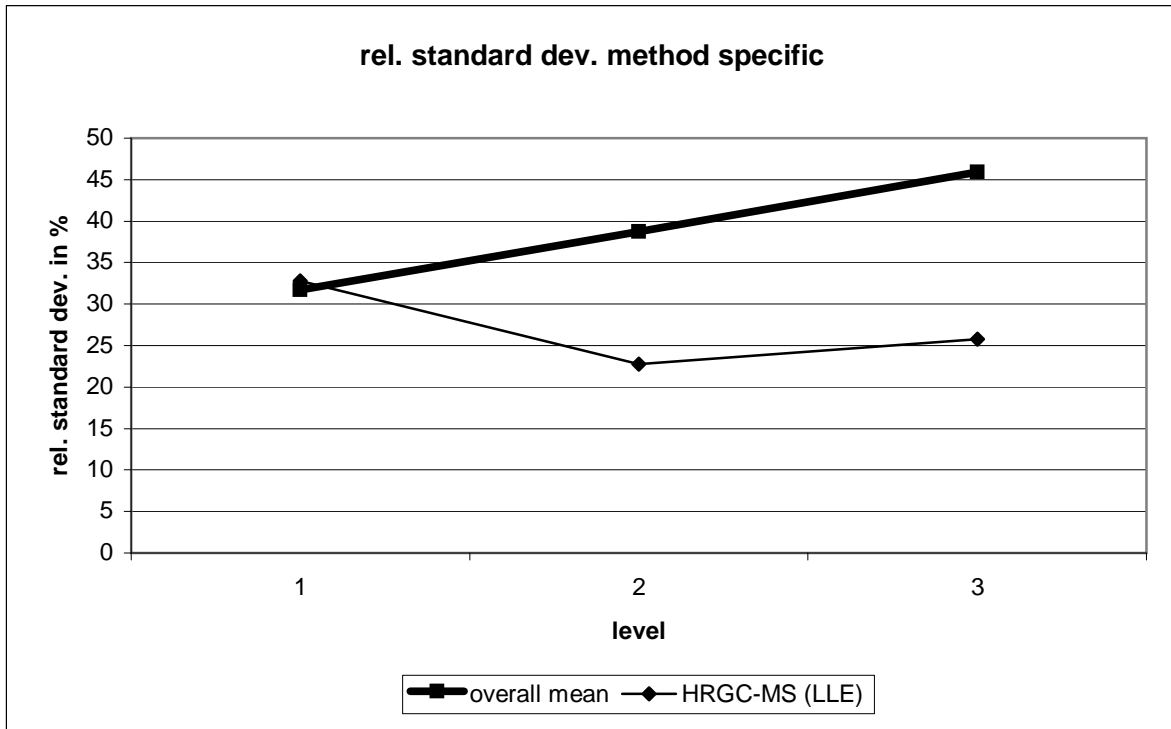


**Comparison of means and reference values**

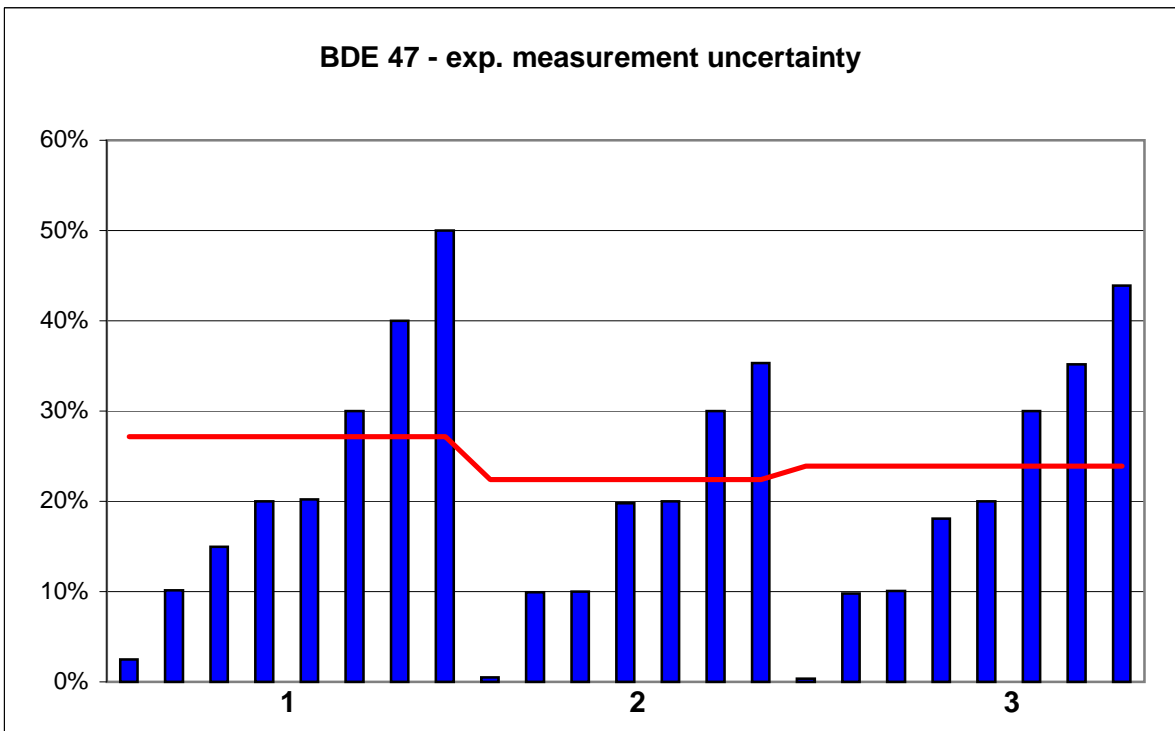
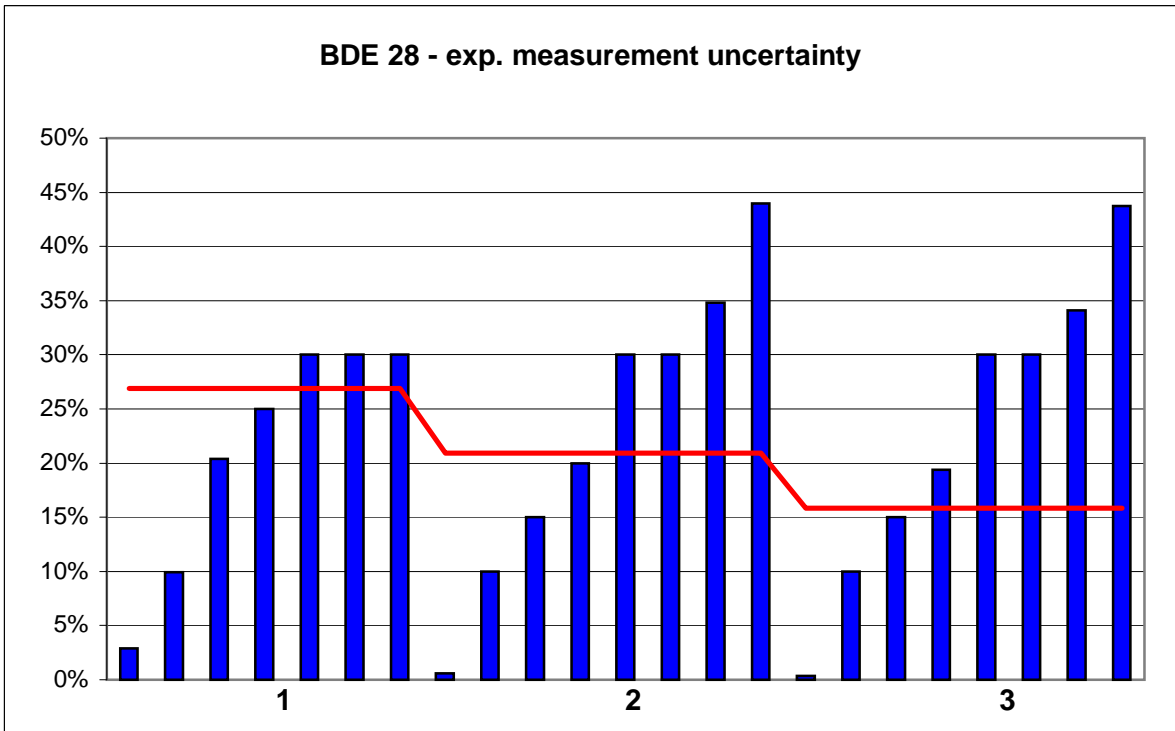
level	Overall mean			reference values		
	mean [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]	reference value [ng/l]	exp. uncertainty [ng/l]	exp. uncertainty [%]
1	0,935	0,158	16,9	1,207	0,081	6,7
2	3,629	0,749	20,6	4,769	0,320	6,7
3	6,803	1,664	24,5	9,782	0,657	6,7

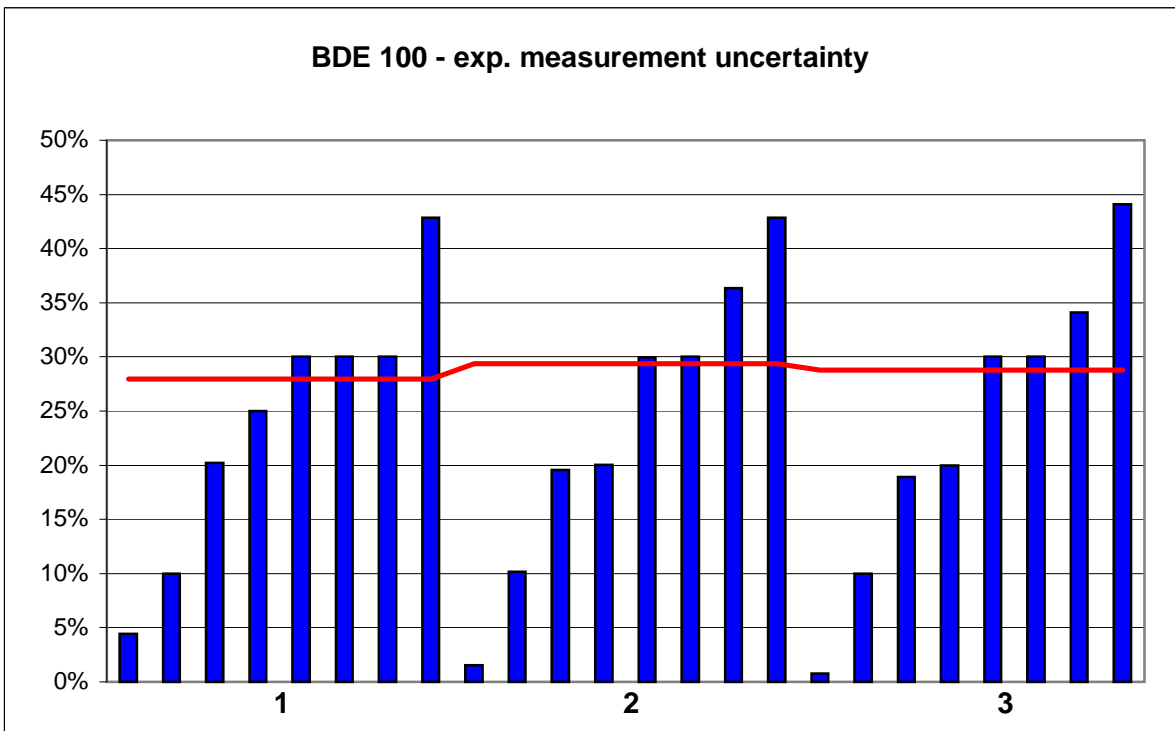
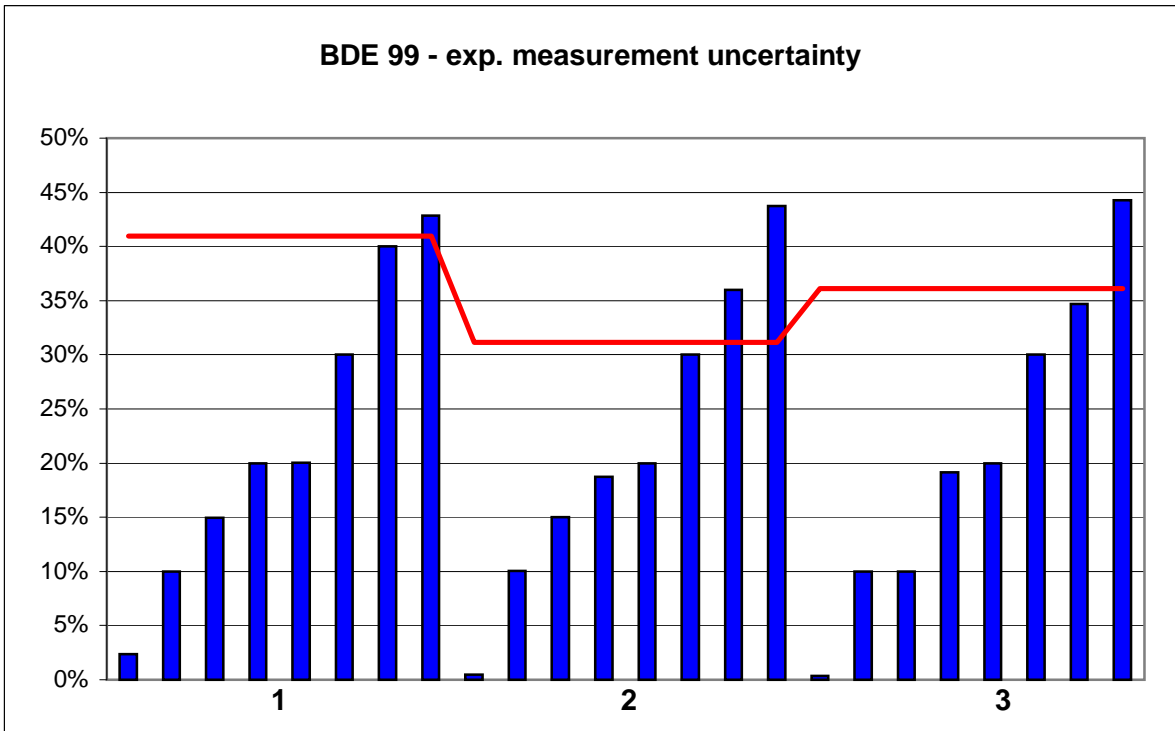


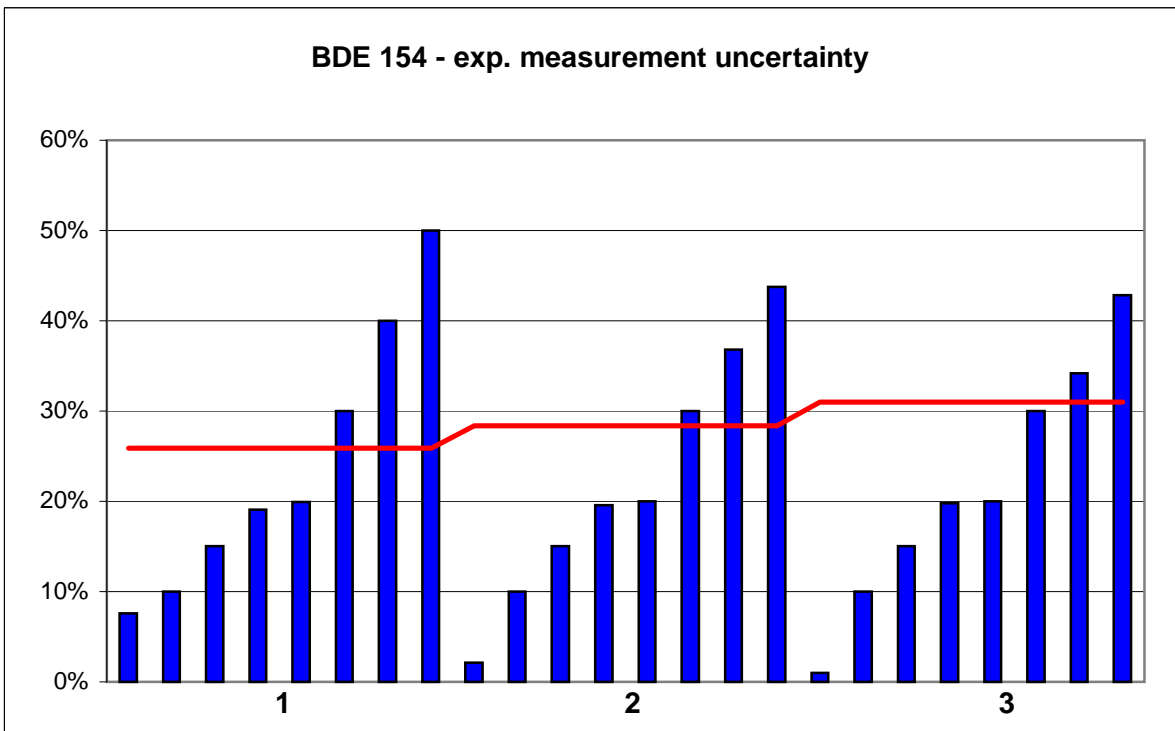
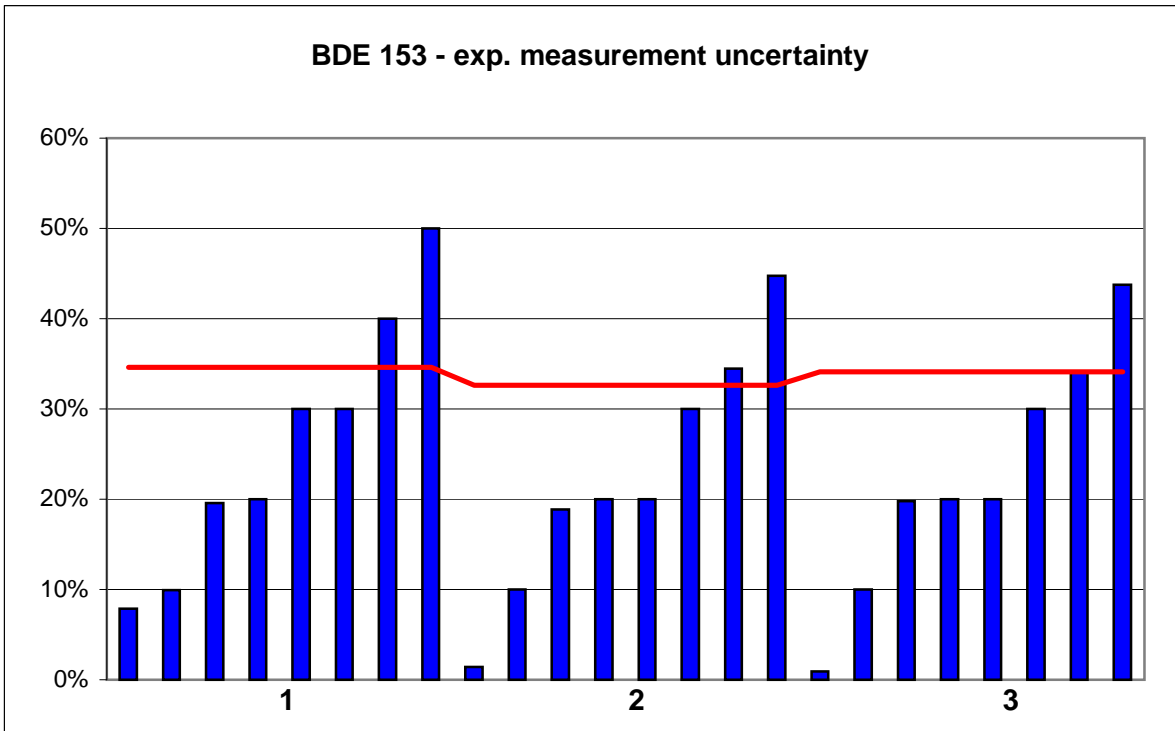




HRGC-MS (LLE)									
level	robust mean [ng/l]	exp. uncertainty of the mean [ng/l]	exp. uncertainty of the mean [%]	robust standard deviation [ng/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,913	0,104	11,357	0,2991	32,76	13	1	0	7,692
2	3,707	0,292	7,8876	0,8433	22,75	13	3	1	30,77
3	7,325	0,681	9,3037	1,8885	25,78	12	2	1	25

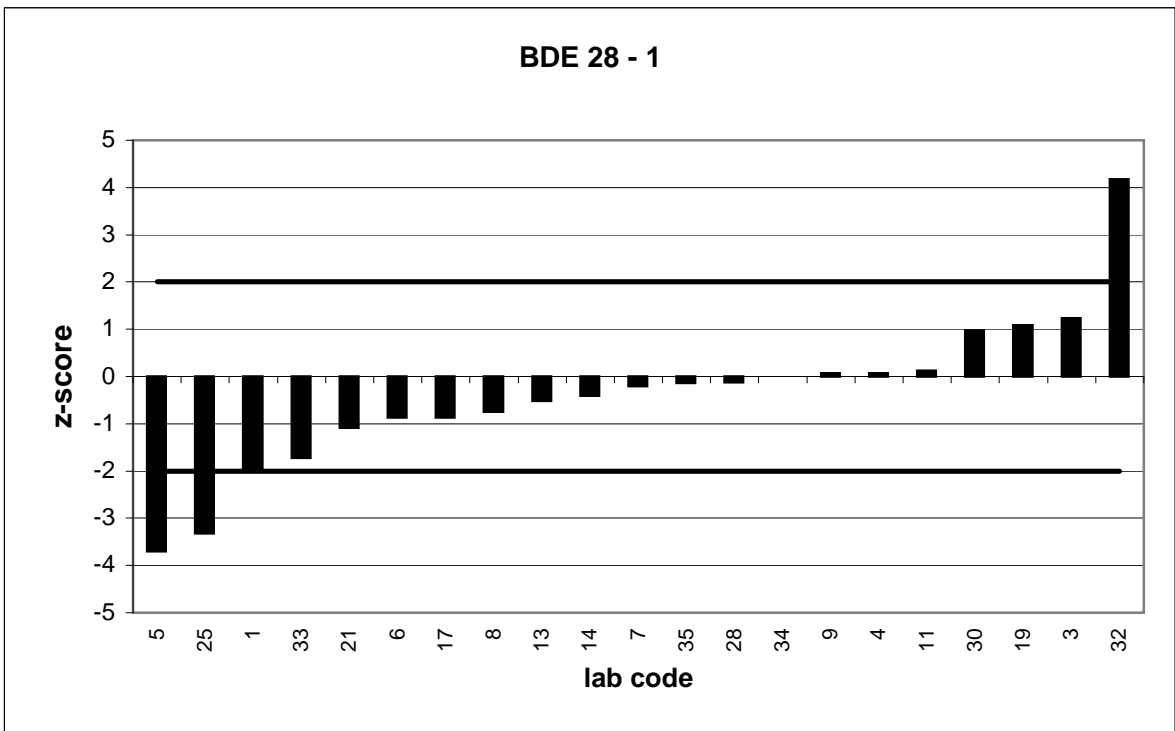
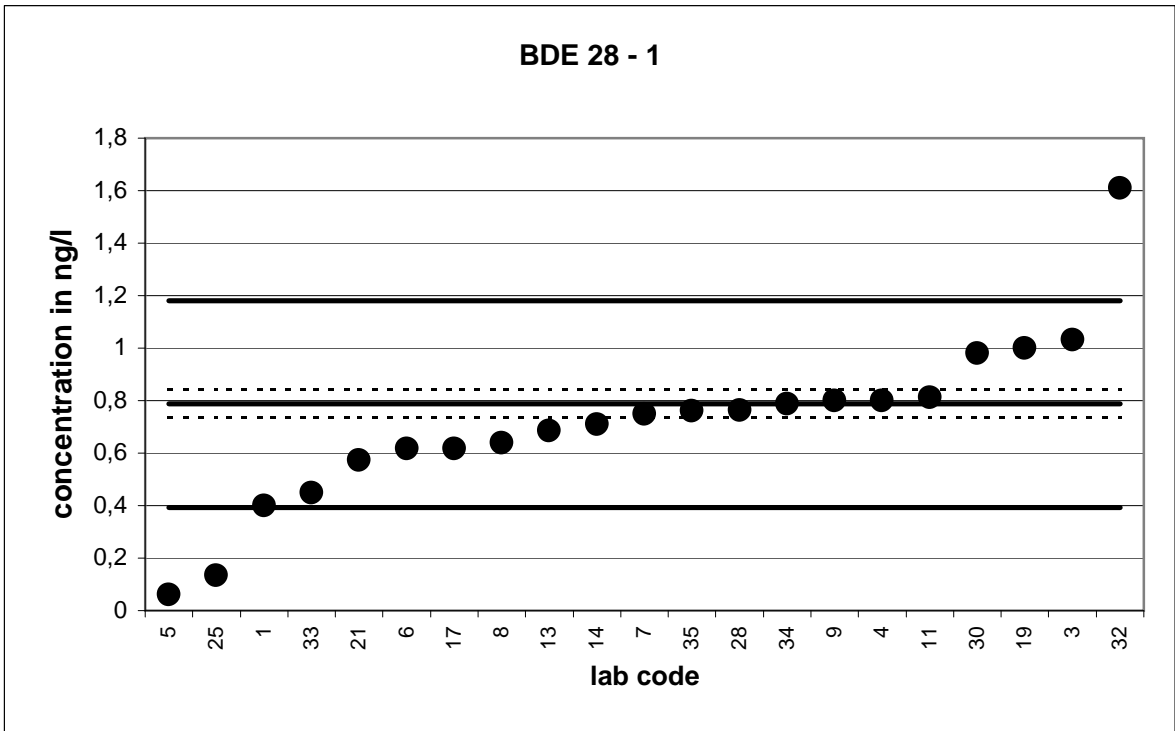


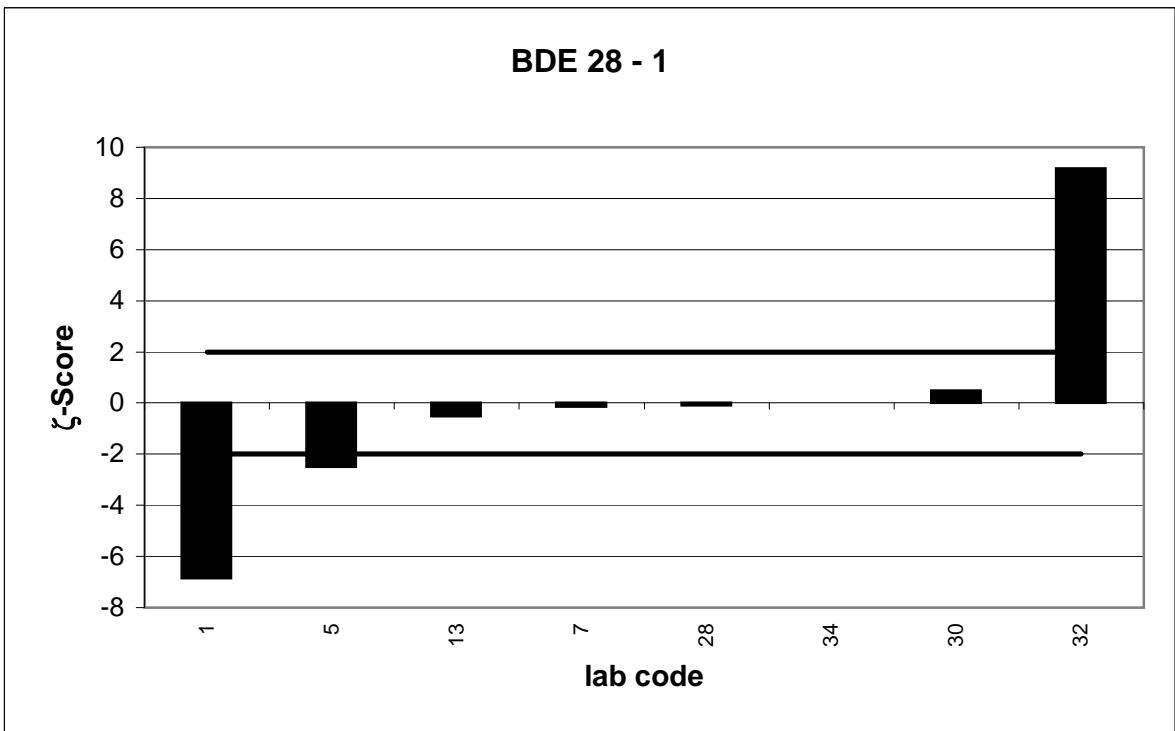
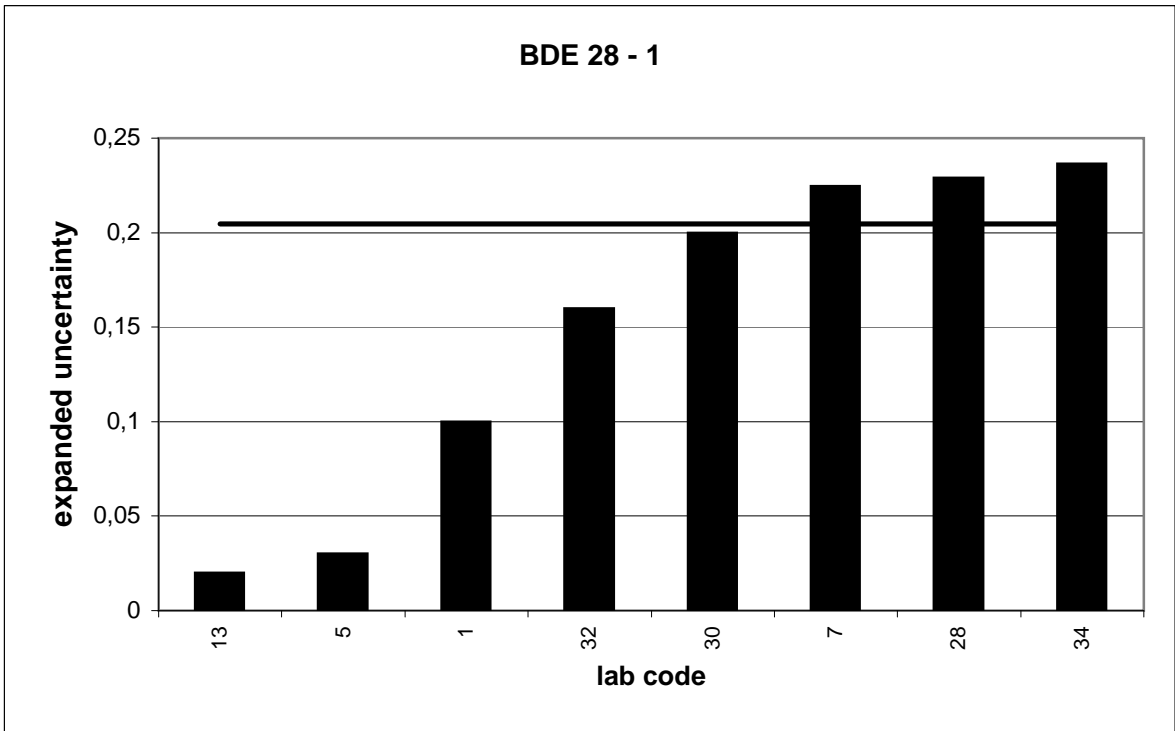




PT 6/10 PT-WFD PBDE		BDE 28 - 1			
assigned value [ng/l]*		0,7877 ± 0,0529			
upper tolerance limit [ng/l]		1,182			
lower tolerance limit [ng/l]		0,3939			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	0,4	0,1	-6,9	-2,0	s
3	1,031			1,2	s
4	0,8008			0,1	s
5	0,06	0,03	-2,5	-3,7	u
6	0,6162			-0,9	s
7	0,7485	0,225	-0,1	-0,2	s
8	0,64			-0,8	s
9	0,8004			0,1	s
11	0,8112			0,1	s
13	0,685	0,02	-0,5	-0,5	s
14	0,709			-0,4	s
17	0,617			-0,9	s
19	1			1,1	s
21	0,574			-1,1	s
25	0,1335			-3,3	u
28	0,763	0,229	-0,1	-0,1	s
30	0,98	0,2	0,5	1,0	s
32	1,61	0,16	9,2	4,2	u
33	0,45			-1,7	s
34	0,7887	0,237	0,0	0,0	s
35	0,76			-0,1	s

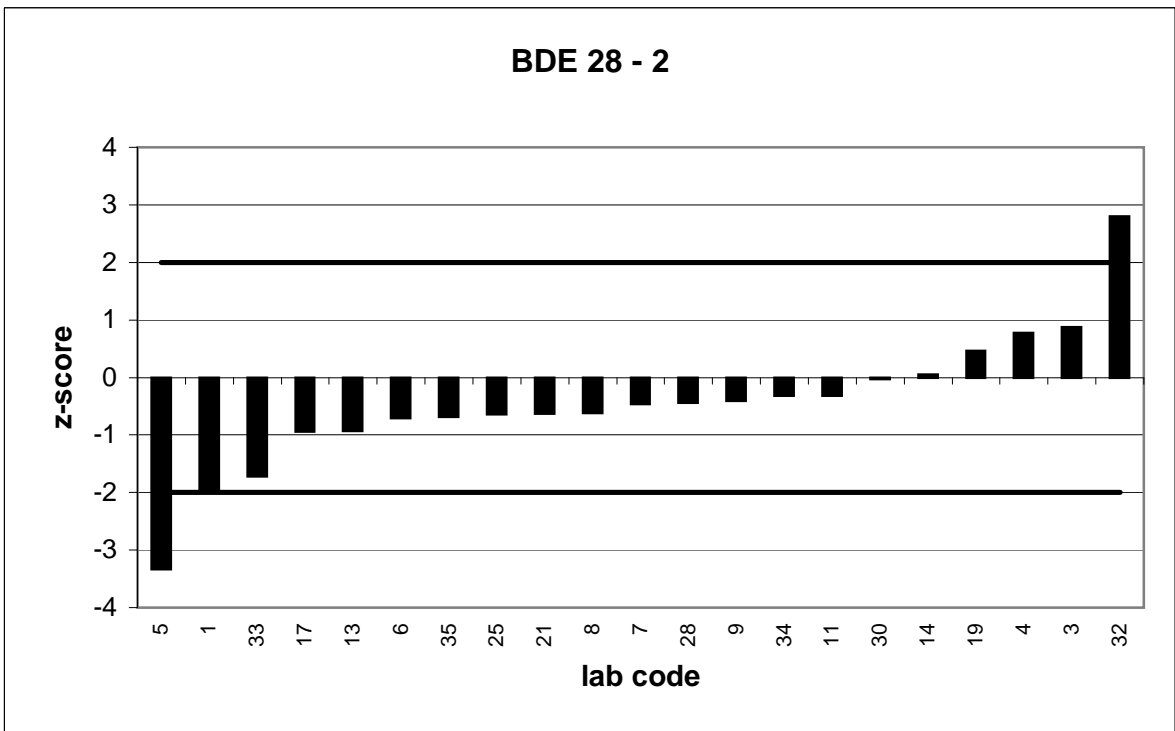
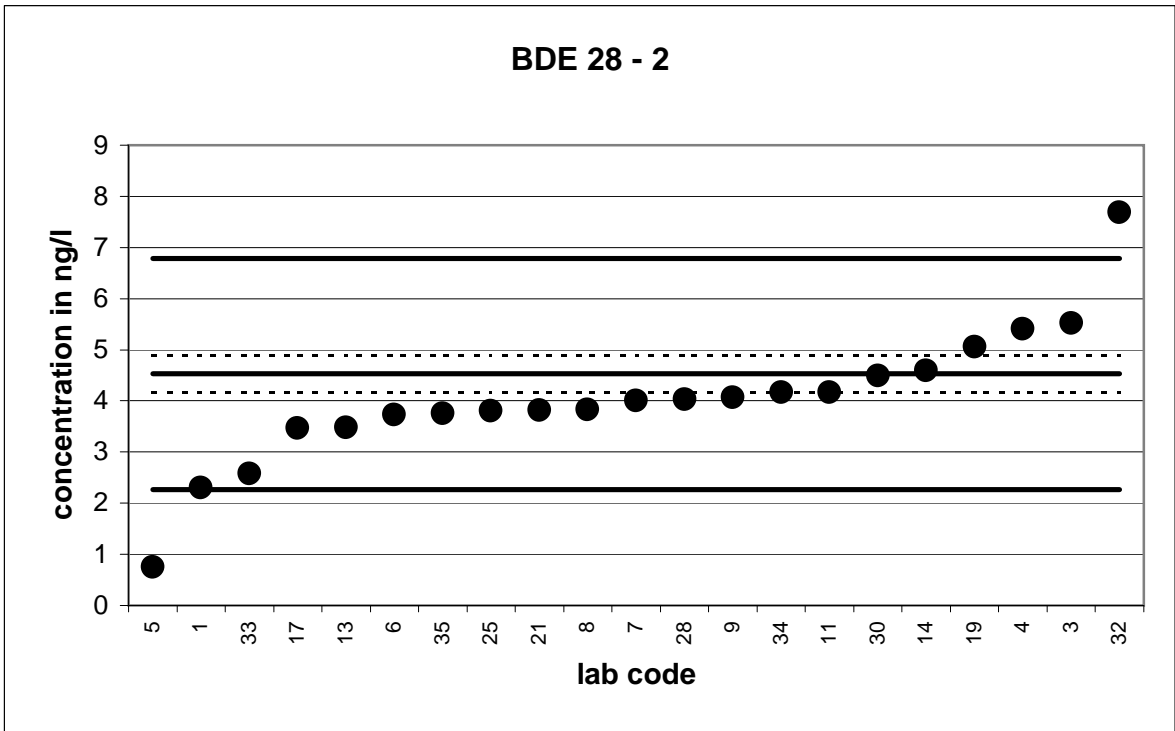
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

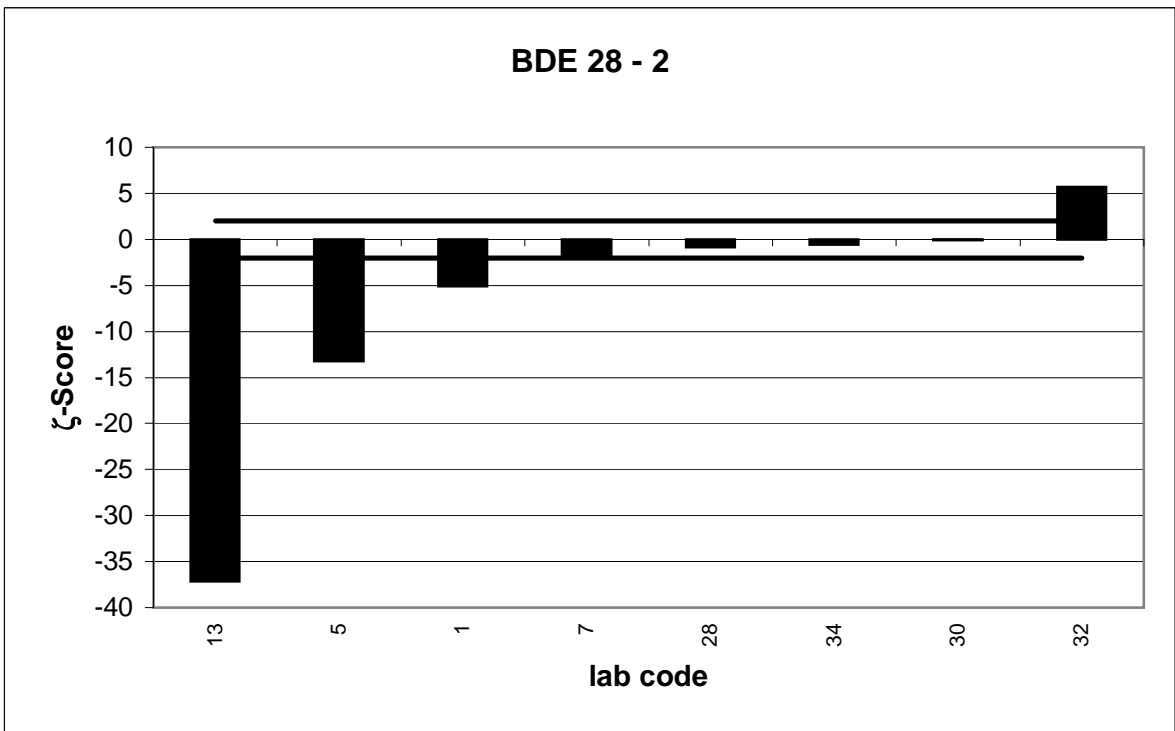
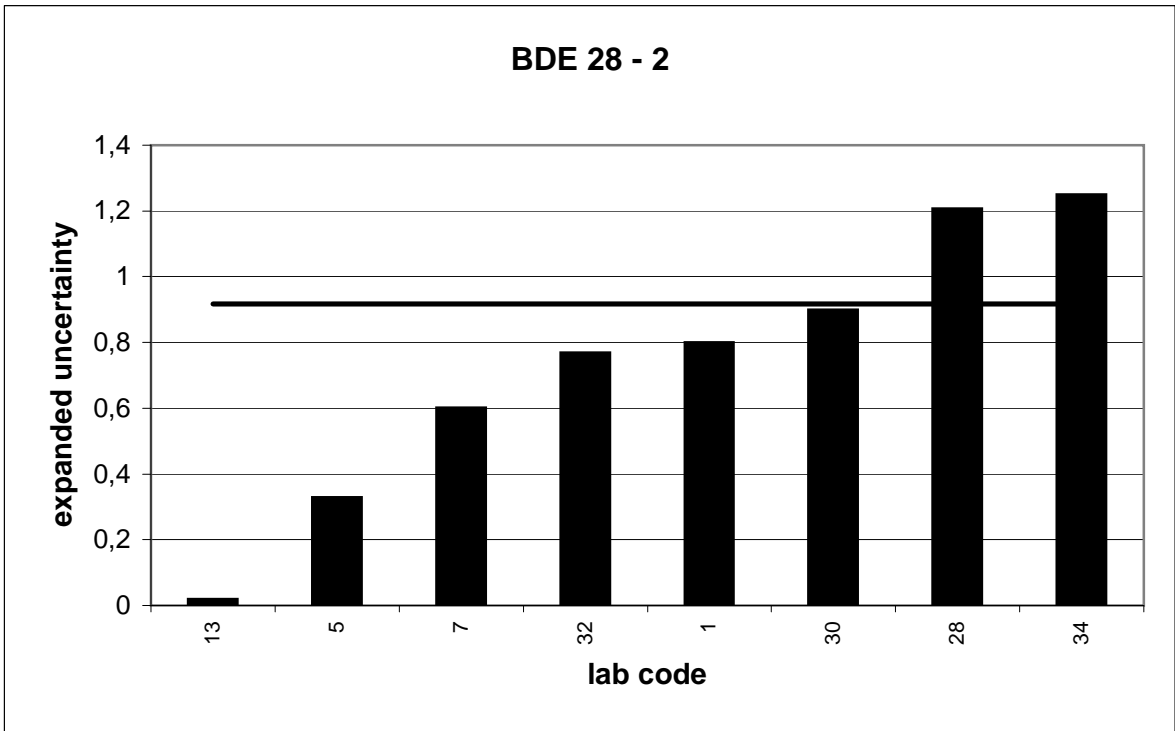




PT 6/10 PT-WFD PBDE		BDE 28 - 2			
assigned value [ng/l]*		4,527 ± 0,363			
upper tolerance limit [ng/l]		6,79			
lower tolerance limit [ng/l]		2,263			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	2,3	0,8	-5,1	-2,0	s
3	5,52			0,9	s
4	5,404			0,8	s
5	0,75	0,33	-13,2	-3,3	u
6	3,724			-0,7	s
7	4,009	0,601	-1,7	-0,5	s
8	3,83			-0,6	s
9	4,073			-0,4	s
11	4,168			-0,3	s
13	3,475	0,02	-37,2	-0,9	s
14	4,589			0,1	s
17	3,464			-0,9	s
19	5,055			0,5	s
21	3,814			-0,6	s
25	3,801			-0,6	s
28	4,026	1,208	-0,8	-0,4	s
30	4,5	0,9	-0,1	0,0	s
32	7,69	0,77	5,7	2,8	q
33	2,58			-1,7	s
34	4,166	1,25	-0,6	-0,3	s
35	3,75			-0,7	s

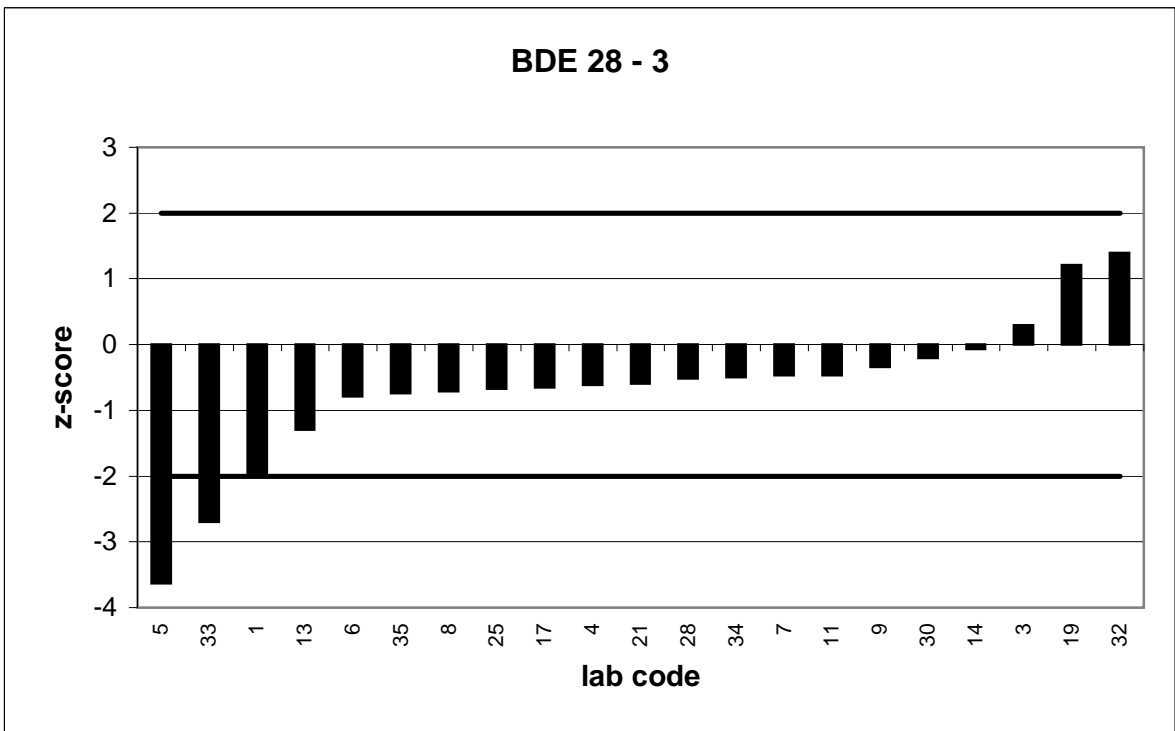
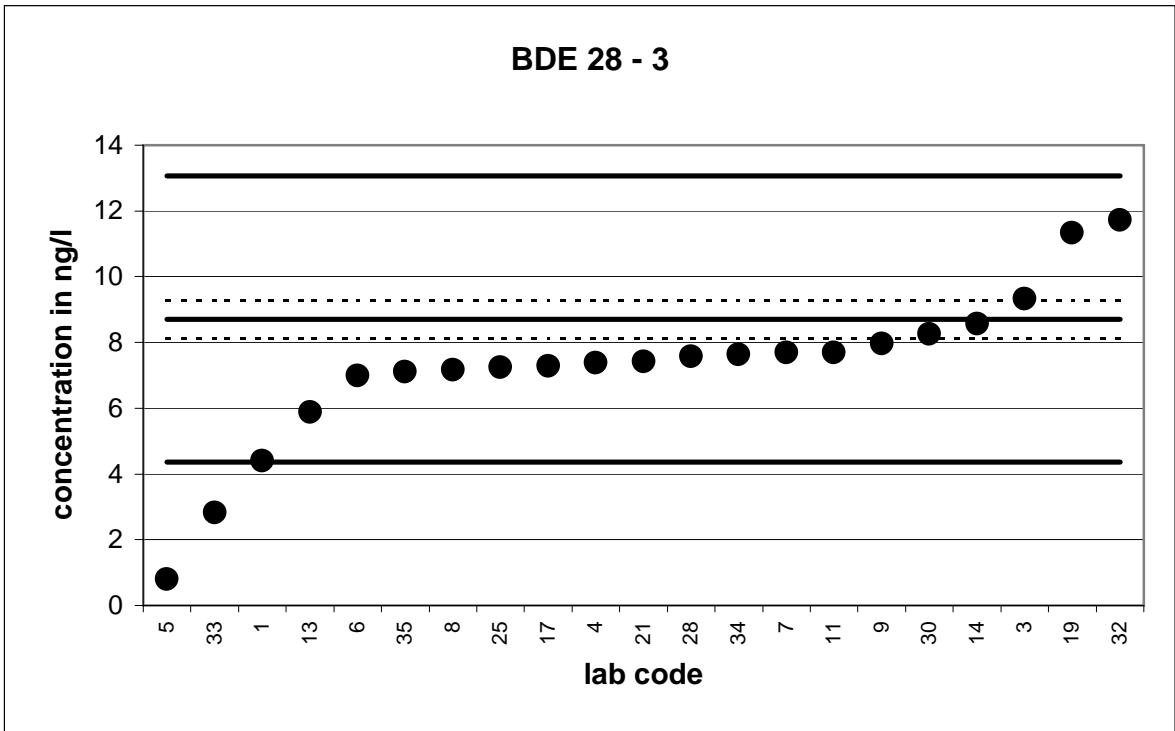
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

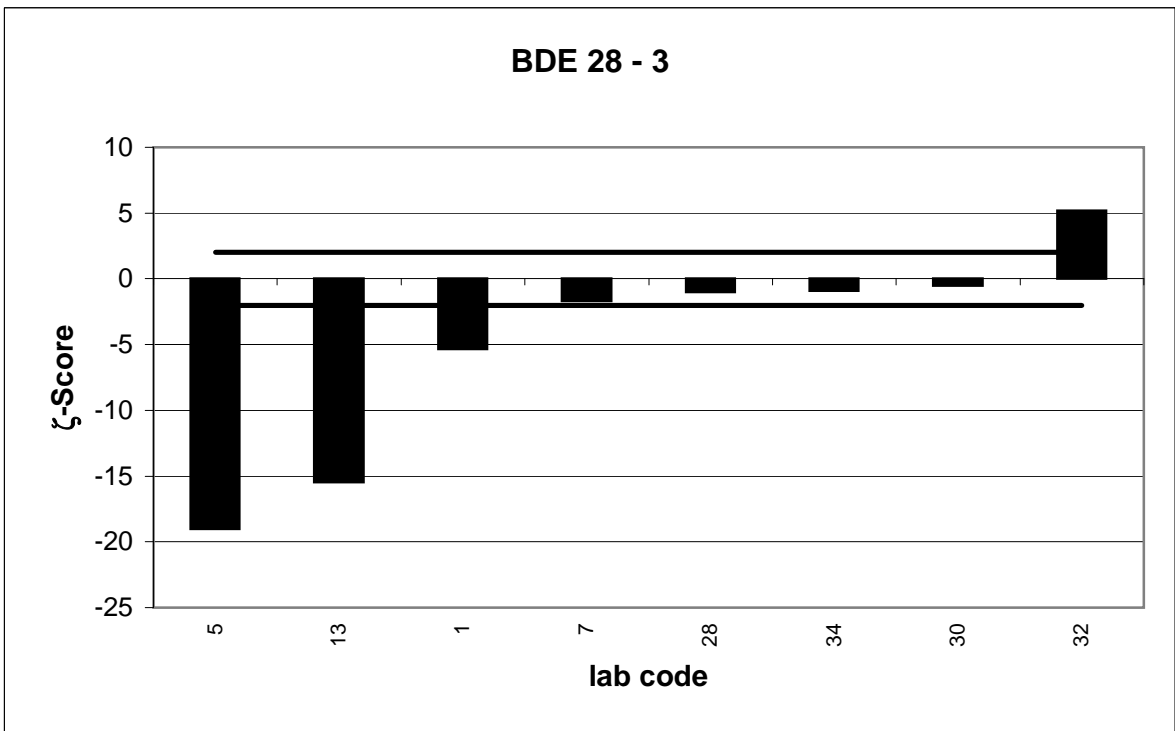
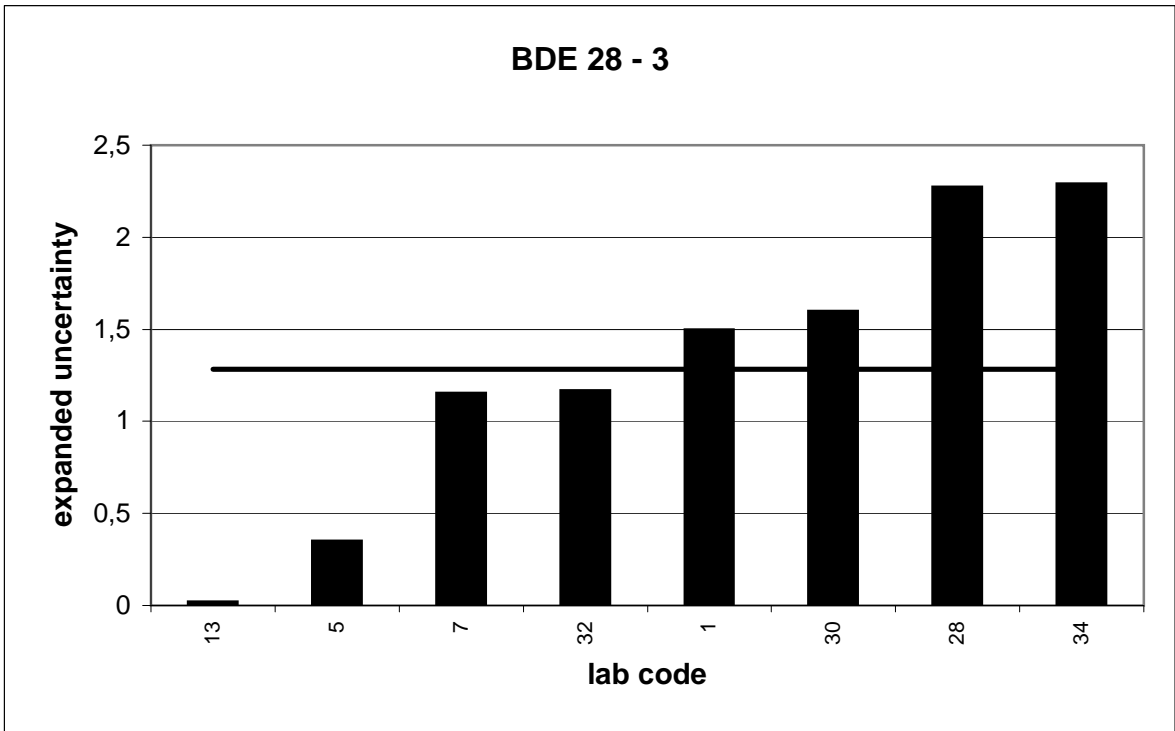




PT 6/10 PT-WFD PBDE		BDE 28 - 3			
assigned value [ng/l]*		8,706 ± 0,585			
upper tolerance limit [ng/l]		13,06			
lower tolerance limit [ng/l]		4,353			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	4,4	1,5	-5,3	-2,0	s
3	9,335			0,3	s
4	7,378			-0,6	s
5	0,8	0,35	-19,0	-3,6	u
6	6,995			-0,8	s
7	7,692	1,154	-1,7	-0,5	s
8	7,16			-0,7	s
9	7,97			-0,3	s
11	7,694			-0,5	s
13	5,89	0,02	-15,5	-1,3	s
14	8,569			-0,1	s
17	7,29			-0,7	s
19	11,33			1,2	s
21	7,412			-0,6	s
25	7,244			-0,7	s
28	7,576	2,273	-1,0	-0,5	s
30	8,26	1,6	-0,5	-0,2	s
32	11,73	1,17	5,2	1,4	s
33	2,83			-2,7	q
34	7,633	2,29	-0,9	-0,5	s
35	7,1			-0,7	s

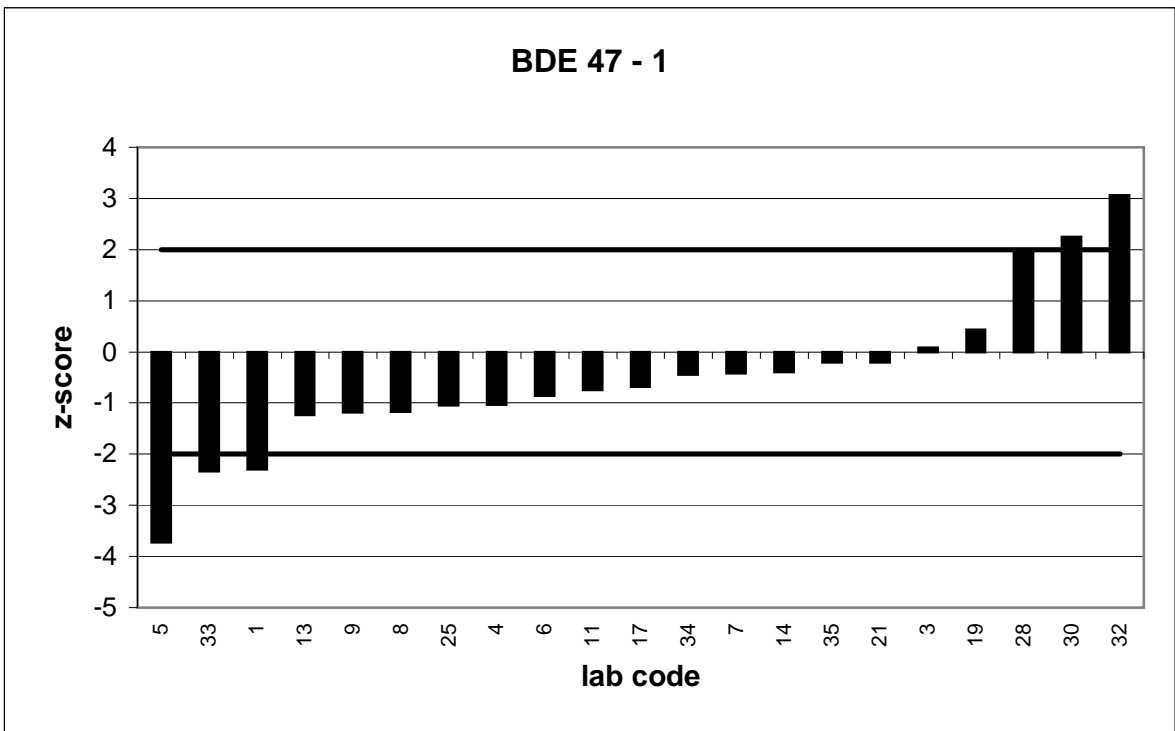
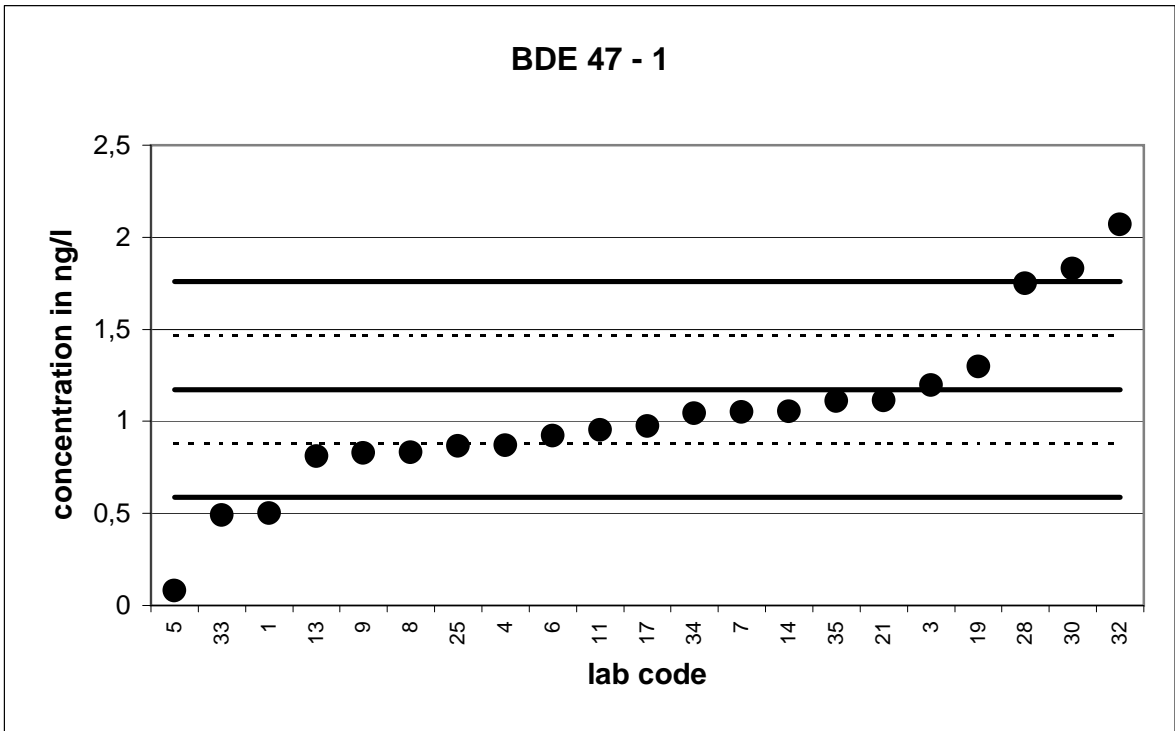
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

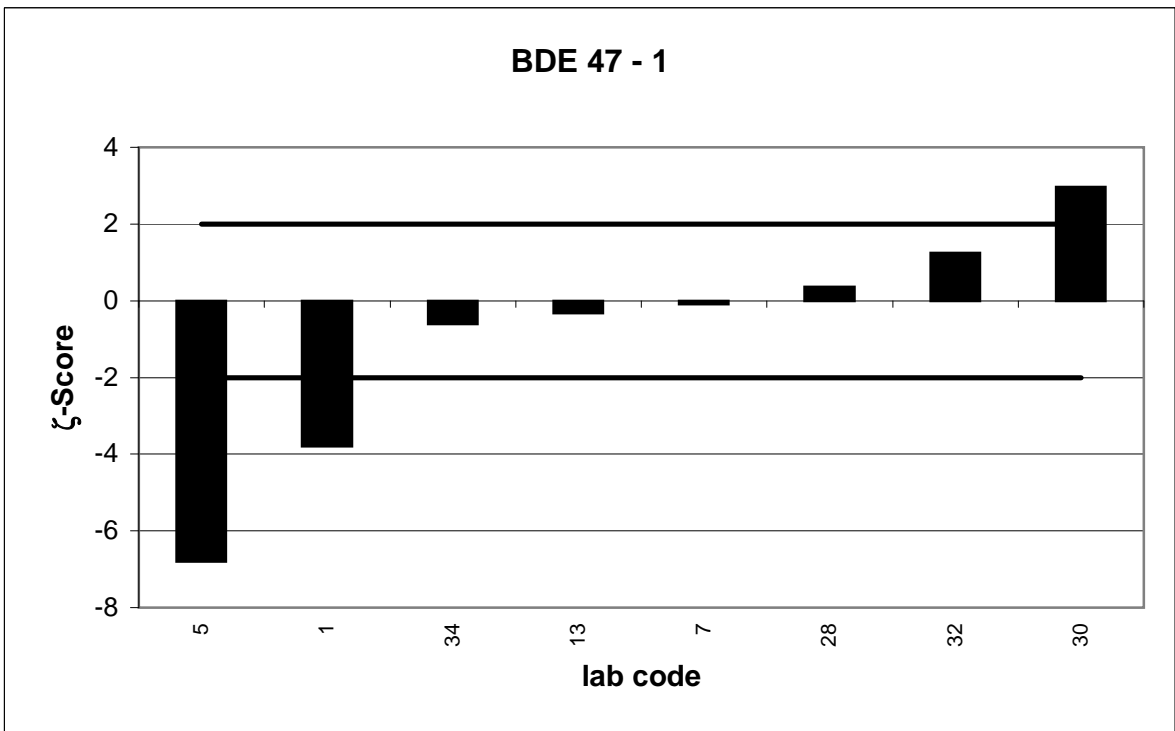
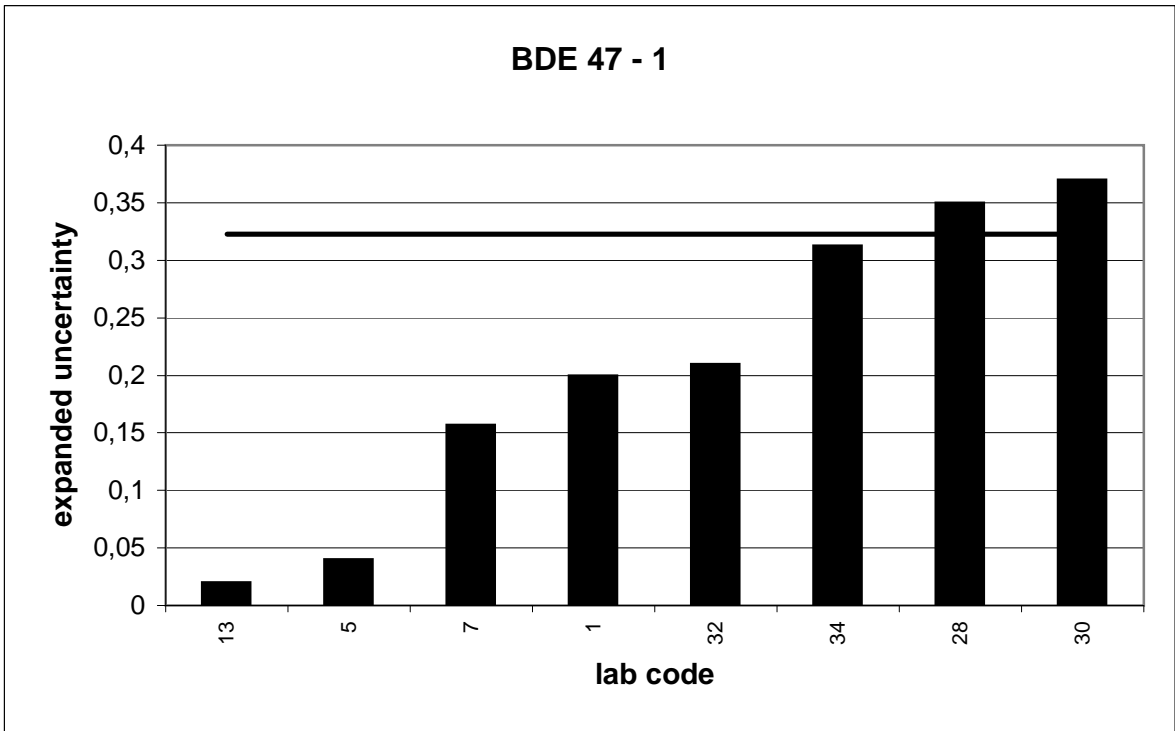




PT 6/10 PT-WFD PBDE		BDE 47 - 1			
assigned value [ng/l]*		1,172 ± 0,292			
upper tolerance limit [ng/l]		1,758			
lower tolerance limit [ng/l]		0,586			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	0,5	0,2	-3,8	-2,3	q
3	1,195			0,1	s
4	0,8685			-1,0	s
5	0,08	0,04	-6,8	-3,7	u
6	0,9206			-0,9	s
7	1,049	0,157	-0,1	-0,4	s
8	0,83			-1,2	s
9	0,8263			-1,2	s
11	0,9526			-0,7	s
13	0,81	0,02	-0,3	-1,2	s
14	1,055			-0,4	s
17	0,972			-0,7	s
19	1,298			0,4	s
21	1,112			-0,2	s
25	0,8649			-1,0	s
28	1,749	0,35	0,4	2,0	s
30	1,83	0,37	3,0	2,2	q
32	2,07	0,21	1,2	3,1	u
33	0,49			-2,3	q
34	1,043	0,313	-0,6	-0,4	s
35	1,11			-0,2	s

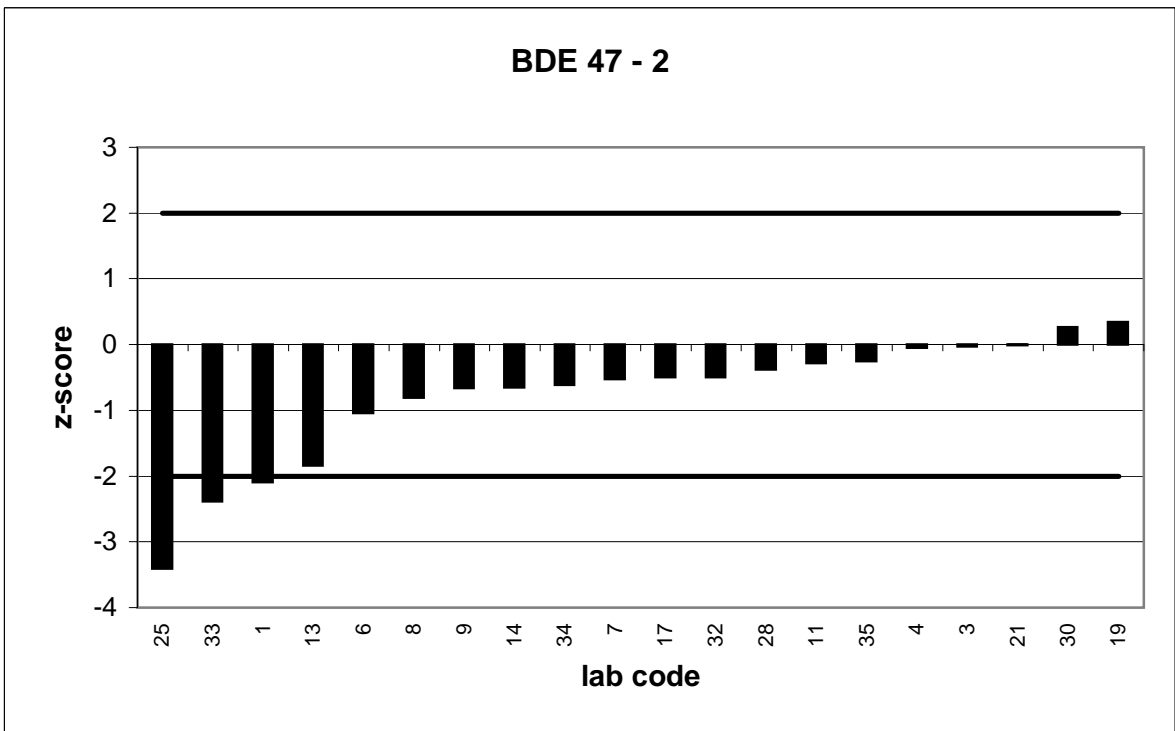
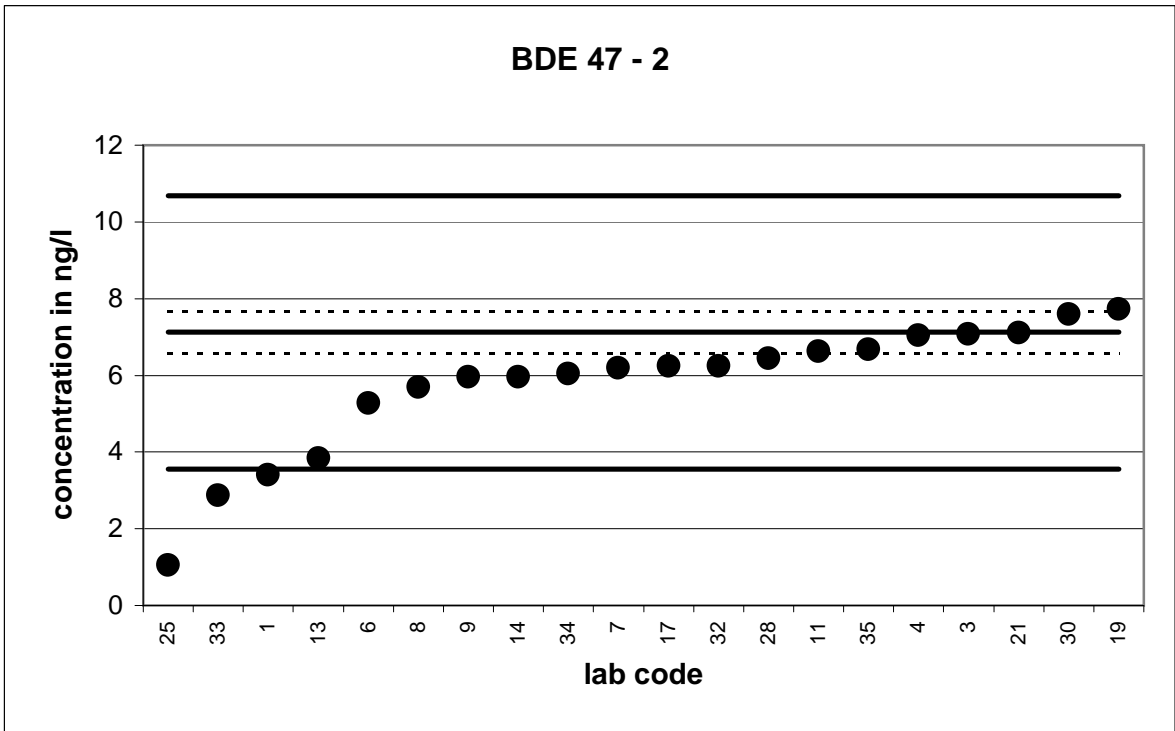
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

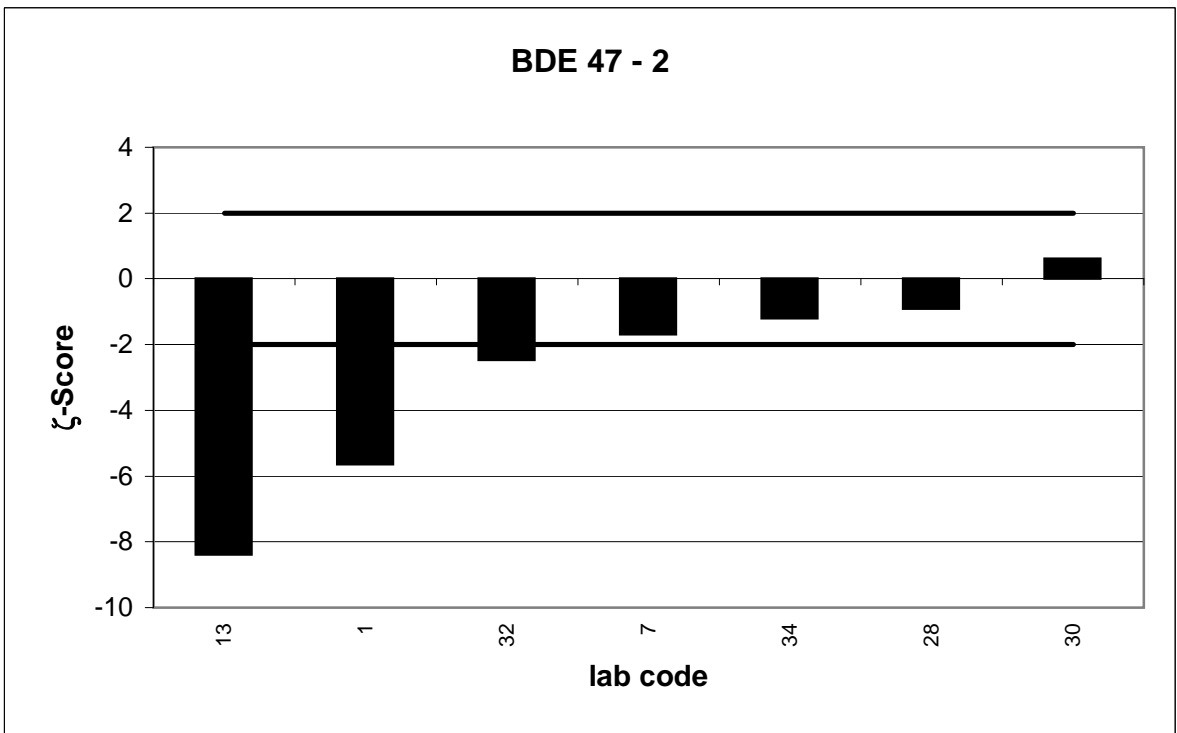
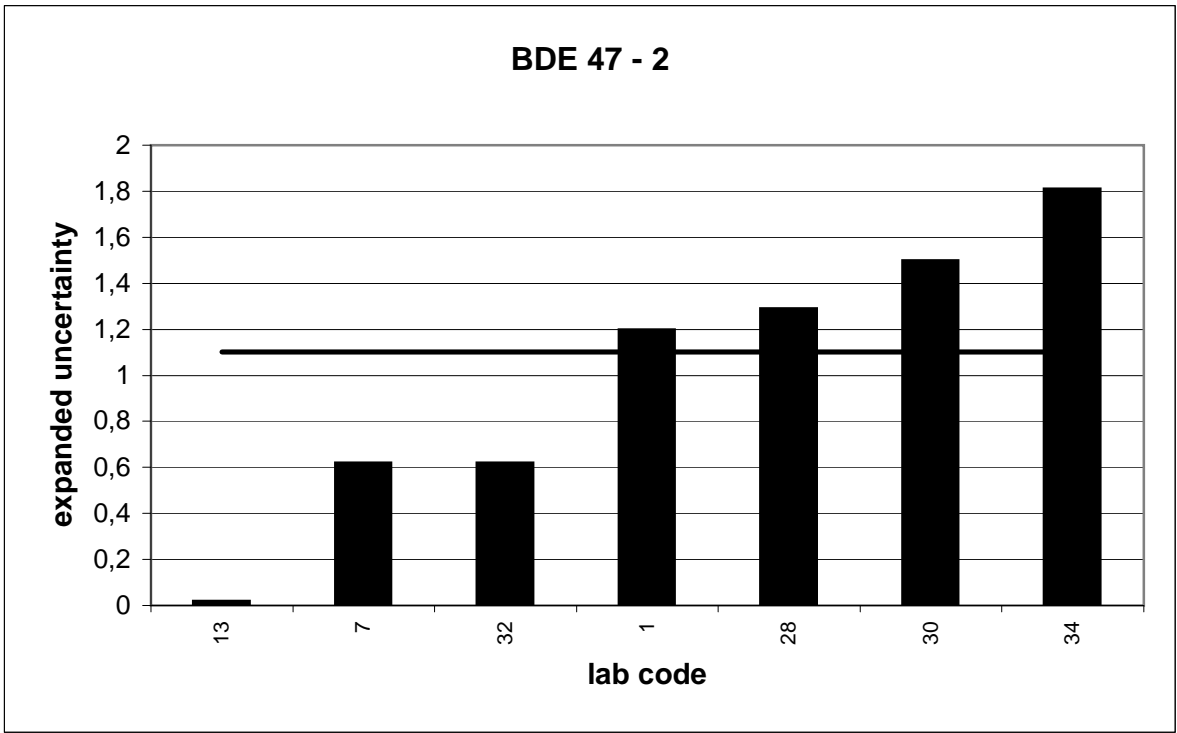




PT 6/10 PT-WFD PBDE		BDE 47 - 2			
assigned value [ng/l]*		7,124 ± 0,549			
upper tolerance limit [ng/l]		10,69			
lower tolerance limit [ng/l]		3,562			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	3,4	1,2	-5,6	-2,1	q
3	7,071			0,0	s
4	7,035			0,0	s
6	5,278			-1,0	s
7	6,187	0,619	-1,7	-0,5	s
8	5,69			-0,8	s
9	5,953			-0,7	s
11	6,62			-0,3	s
13	3,845	0,02	-8,4	-1,8	s
14	5,964			-0,7	s
17	6,234			-0,5	s
19	7,728			0,3	s
21	7,107			0,0	s
25	1,052			-3,4	u
28	6,449	1,29	-0,9	-0,4	s
30	7,59	1,5	0,6	0,3	s
32	6,25	0,62	-2,5	-0,5	s
33	2,87			-2,4	q
34	6,038	1,812	-1,2	-0,6	s
35	6,68			-0,2	s

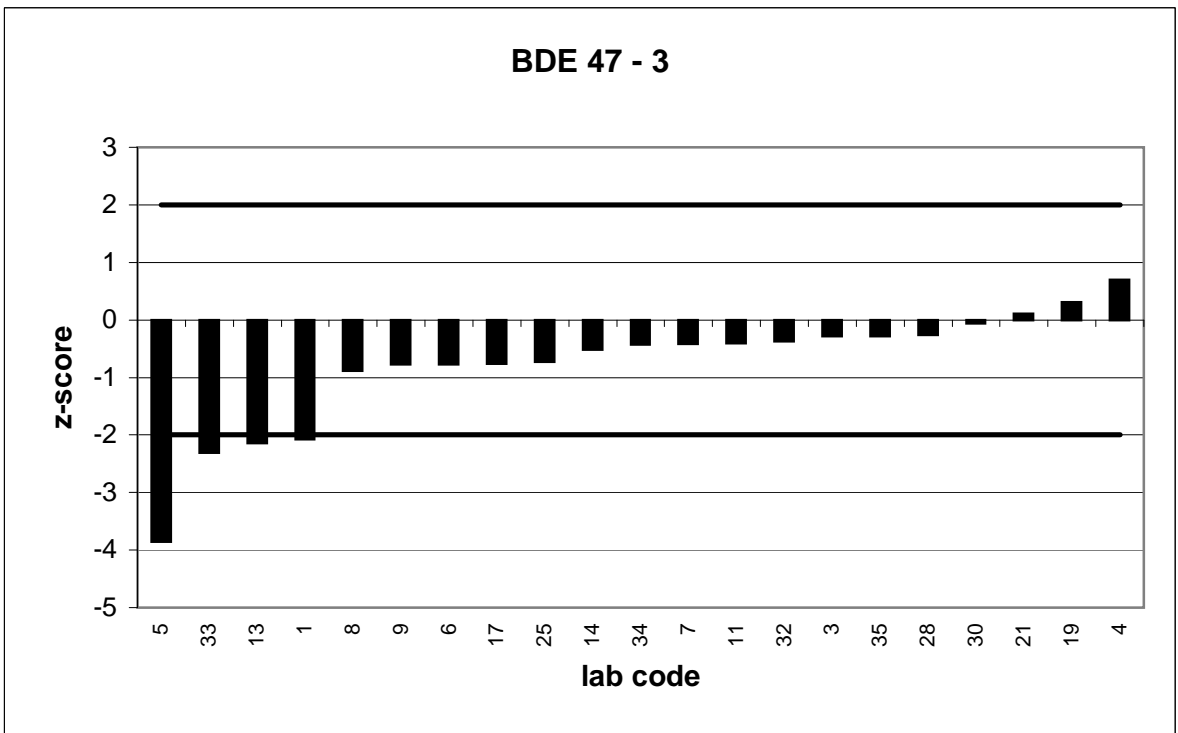
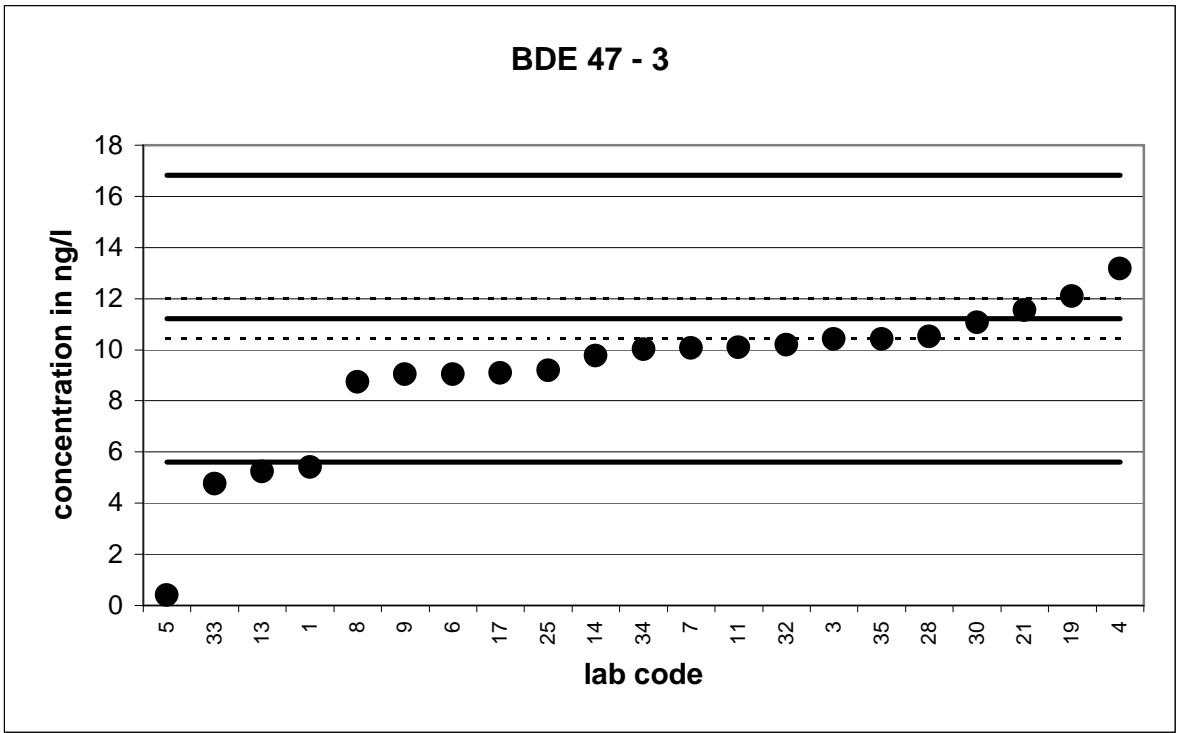
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

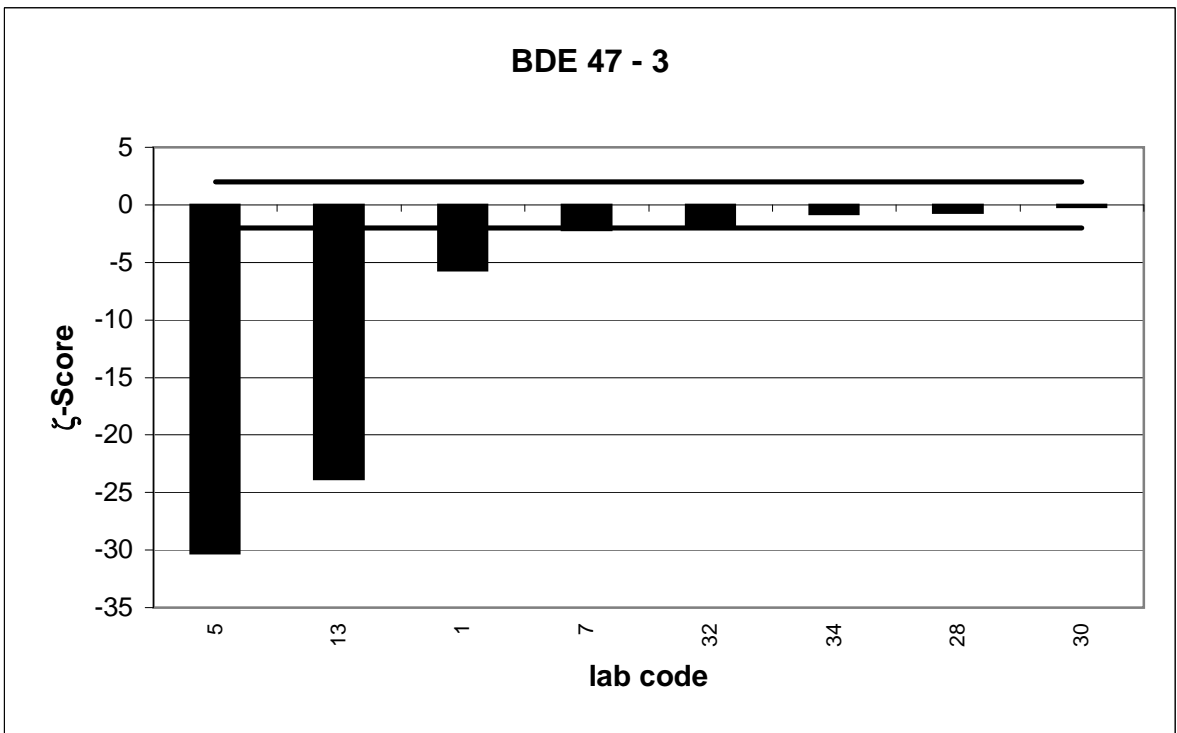
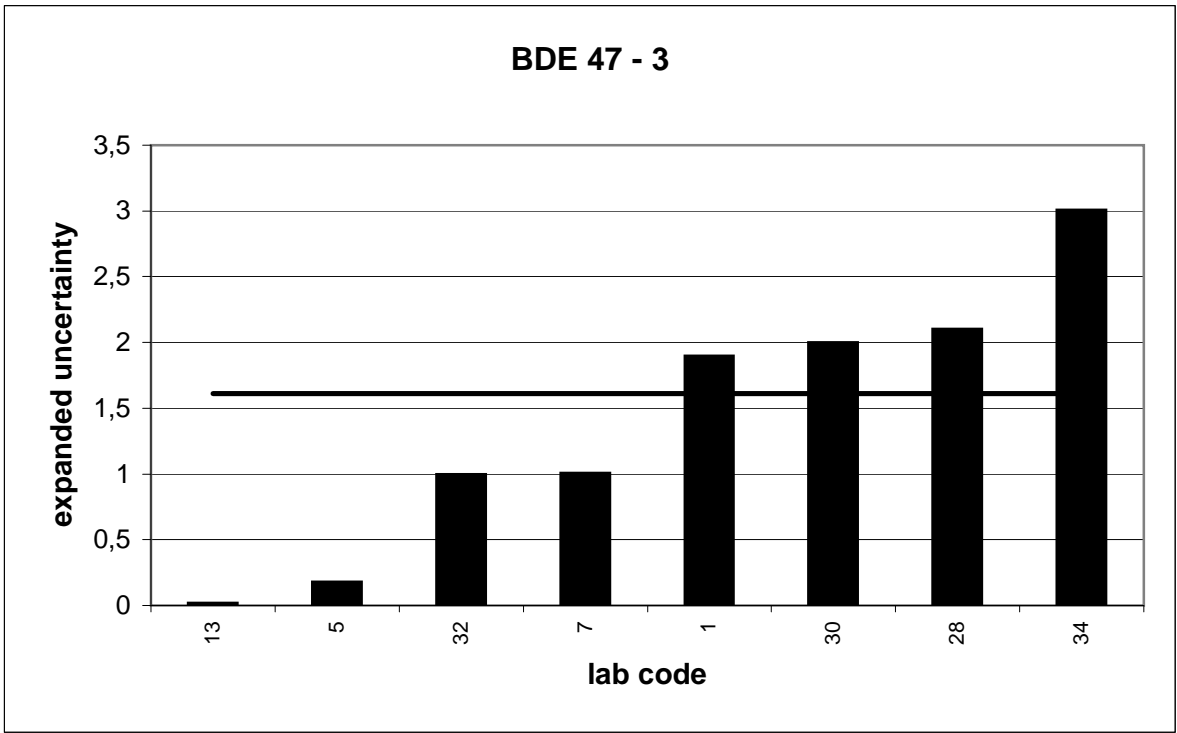




PT 6/10 PT-WFD PBDE		BDE 47 - 3			
assigned value [ng/l]*		11,22 ± 0,78			
upper tolerance limit [ng/l]		16,83			
lower tolerance limit [ng/l]		5,61			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	5,4	1,9	-5,7	-2,1	q
3	10,419			-0,3	s
4	13,17			0,7	s
5	0,41	0,18	-30,3	-3,9	u
6	9,044			-0,8	s
7	10,06	1,01	-2,2	-0,4	s
8	8,73			-0,9	s
9	9,041			-0,8	s
11	10,1			-0,4	s
13	5,22	0,02	-23,8	-2,1	q
14	9,773			-0,5	s
17	9,079			-0,8	s
19	12,08			0,3	s
21	11,53			0,1	s
25	9,194			-0,7	s
28	10,504	2,101	-0,7	-0,3	s
30	11,06	2	-0,2	-0,1	s
32	10,19	1	-2,1	-0,4	s
33	4,76			-2,3	q
34	10,02	3,006	-0,8	-0,4	s
35	10,42			-0,3	s

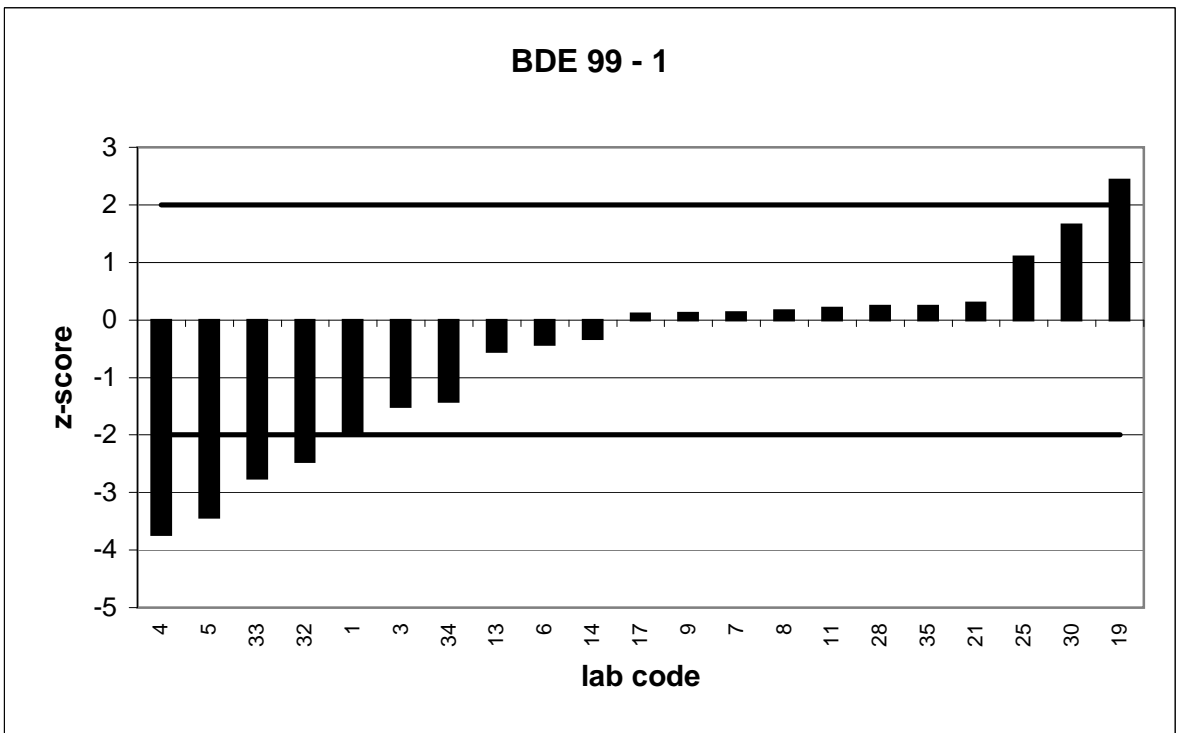
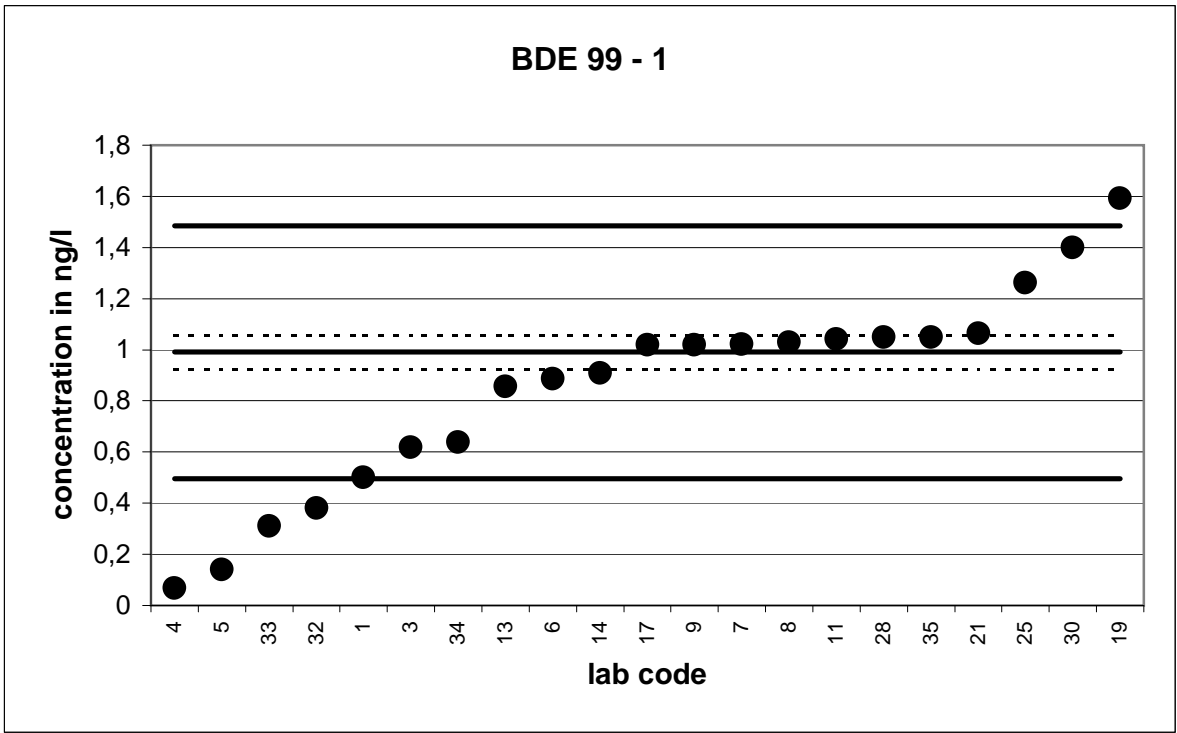
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

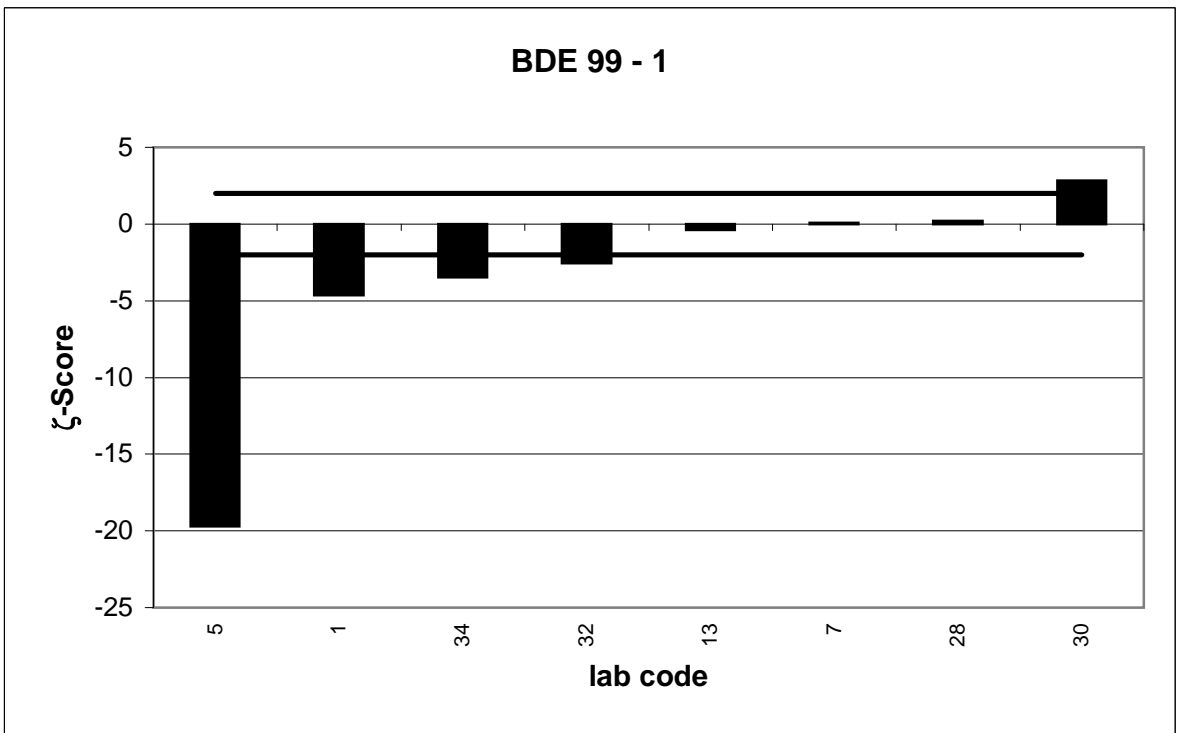
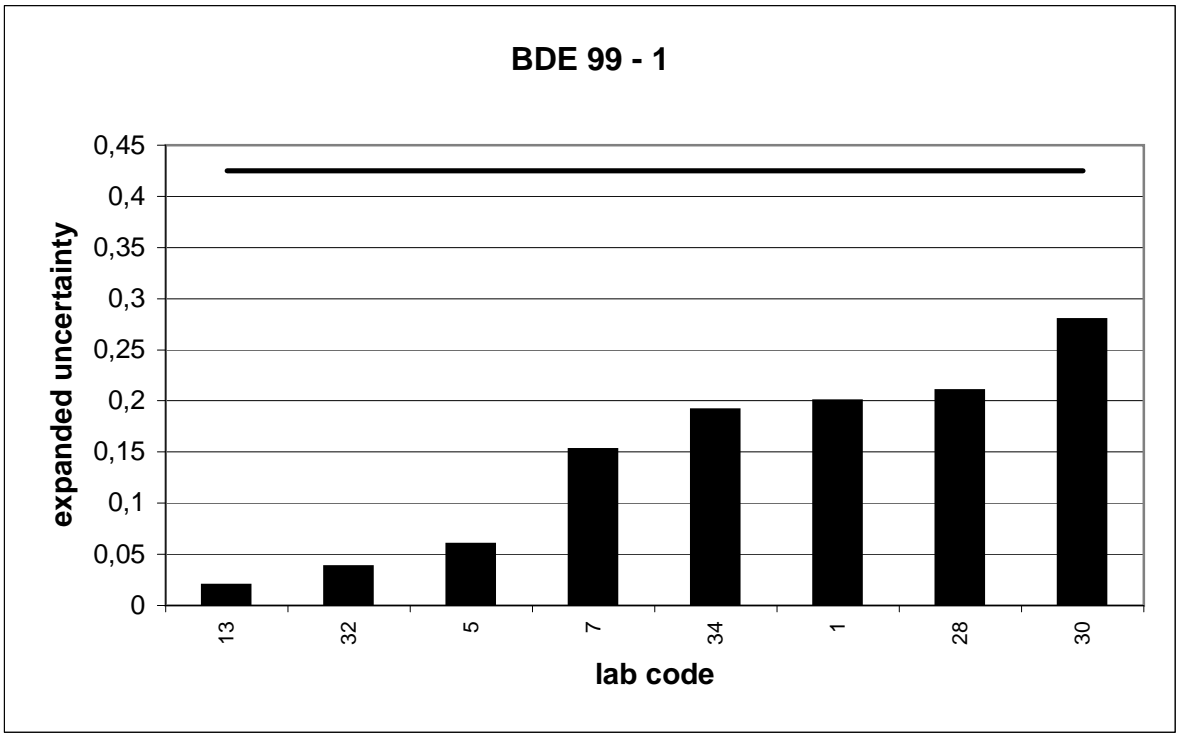




PT 6/10 PT-WFD PBDE		BDE 99 - 1			
assigned value [ng/l]*		0,9902 ± 0,0665			
upper tolerance limit [ng/l]		1,485			
lower tolerance limit [ng/l]		0,4951			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	0,5	0,2	-4,7	-2,0	s
3	0,618			-1,5	s
4	0,06775			-3,7	u
5	0,14	0,06	-19,7	-3,4	u
6	0,8851			-0,4	s
7	1,022	0,153	0,1	0,1	s
8	1,03			0,2	s
9	1,019			0,1	s
11	1,041			0,2	s
13	0,855	0,02	-0,4	-0,5	s
14	0,91			-0,3	s
17	1,018			0,1	s
19	1,593			2,4	q
21	1,063			0,3	s
25	1,262			1,1	s
28	1,049	0,21	0,2	0,2	s
30	1,4	0,28	2,8	1,7	s
32	0,38	0,038	-2,5	-2,5	q
33	0,31			-2,7	q
34	0,638	0,191	-3,5	-1,4	s
35	1,05			0,2	s

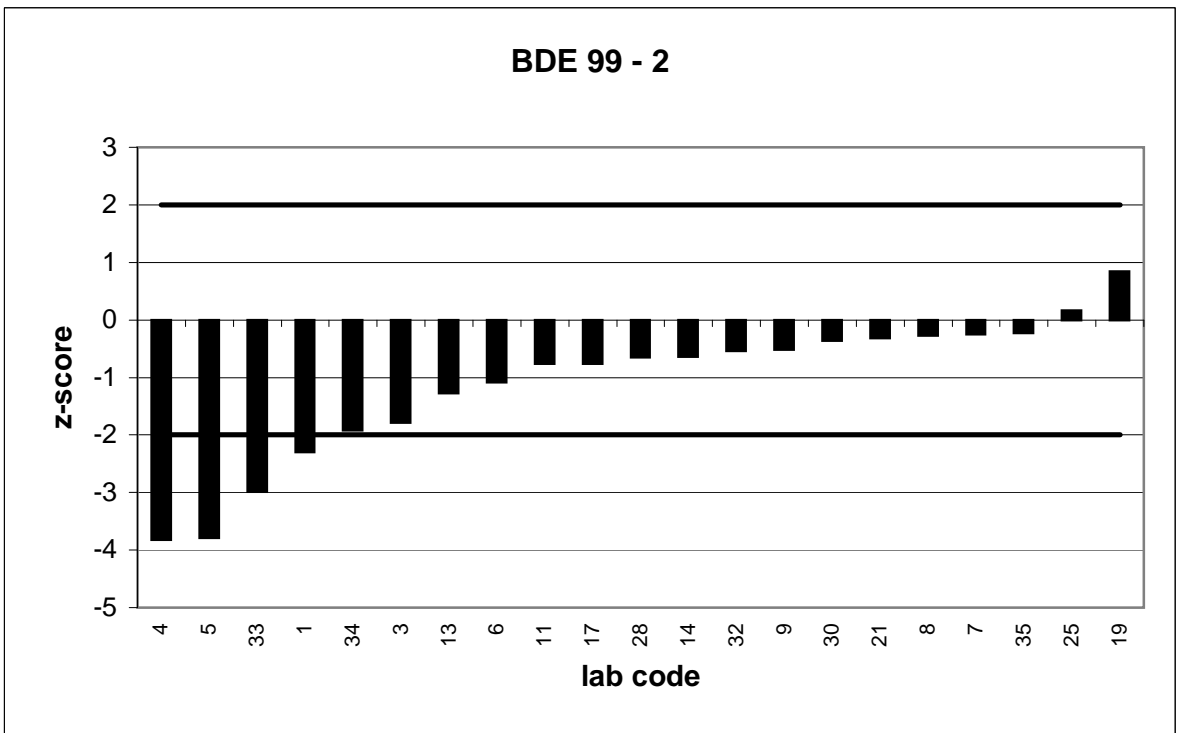
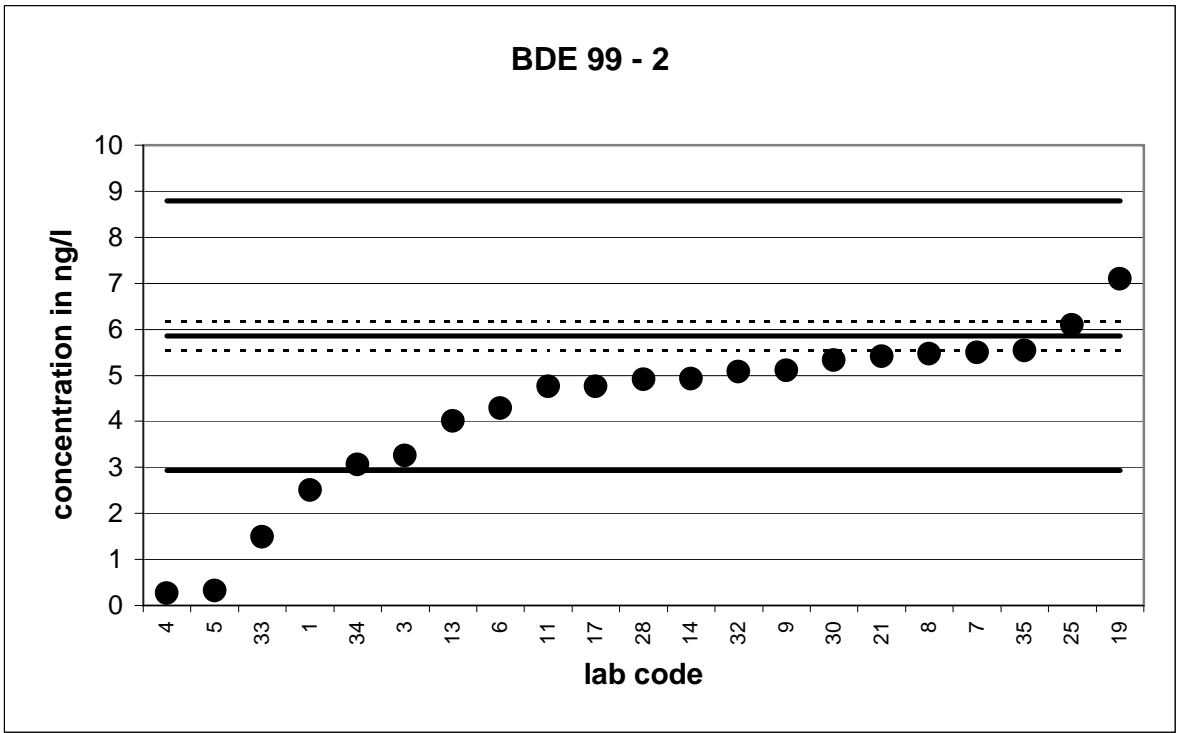
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

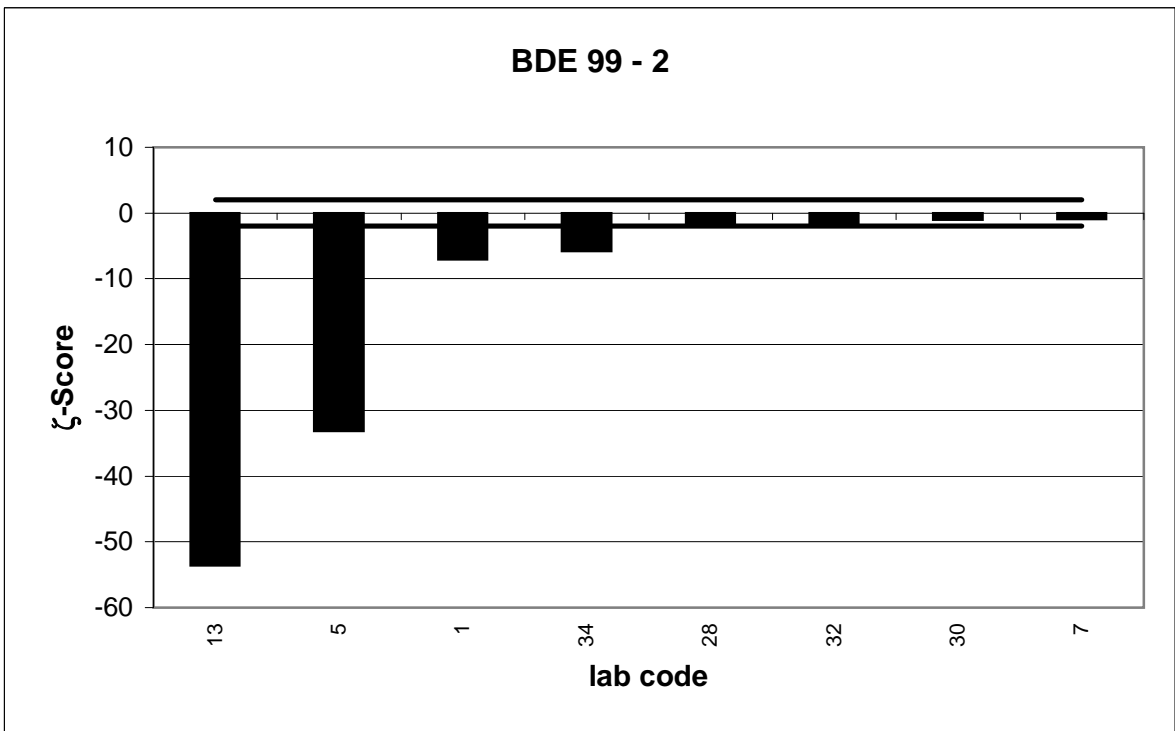
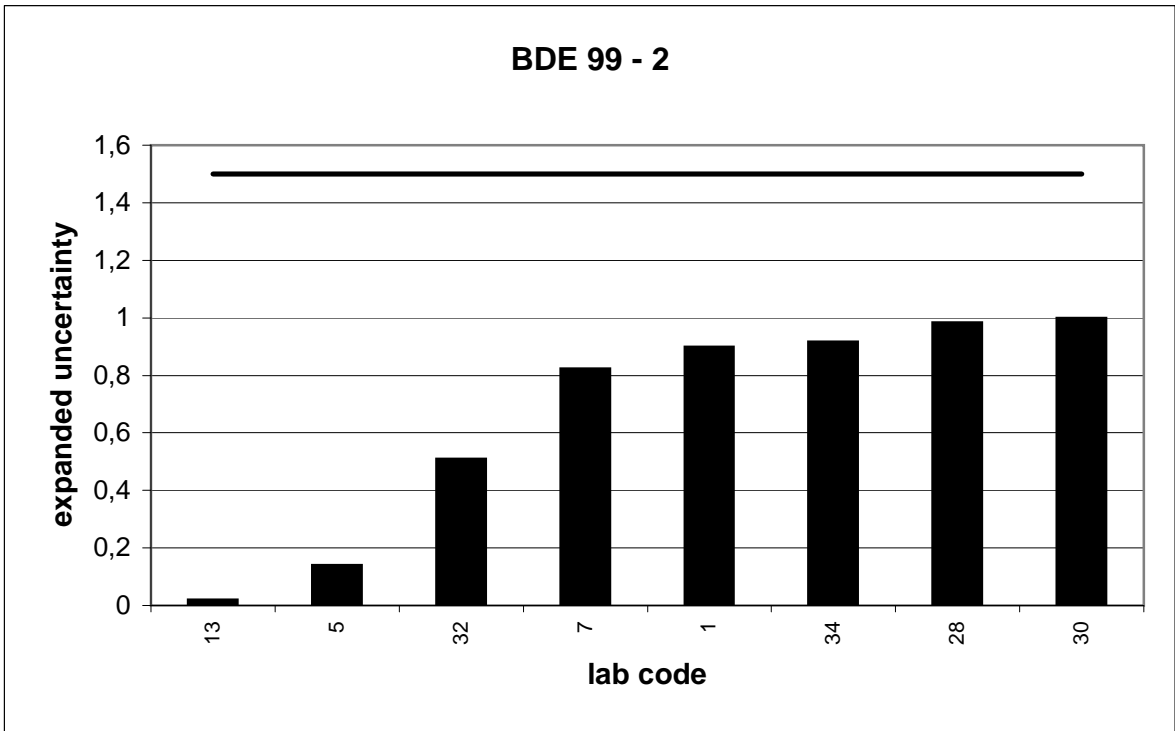




PT 6/10 PT-WFD PBDE		BDE 99 - 2			
assigned value [ng/l]*		5,862 ± 0,32			
upper tolerance limit [ng/l]		8,793			
lower tolerance limit [ng/l]		2,931			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	2,5	0,9	-7,0	-2,3	q
3	3,254			-1,8	s
4	0,2698			-3,8	u
5	0,32	0,14	-33,1	-3,8	u
6	4,28			-1,1	s
7	5,496	0,824	-0,9	-0,2	s
8	5,46			-0,3	s
9	5,108			-0,5	s
11	4,751			-0,8	s
13	4	0,02	-53,6	-1,3	s
14	4,923			-0,6	s
17	4,752			-0,8	s
19	7,095			0,8	s
21	5,407			-0,3	s
25	6,097			0,2	s
28	4,916	0,983	-1,9	-0,6	s
30	5,33	1	-1,0	-0,4	s
32	5,07	0,51	-1,8	-0,5	s
33	1,49			-3,0	u
34	3,057	0,917	-5,8	-1,9	s
35	5,53			-0,2	s

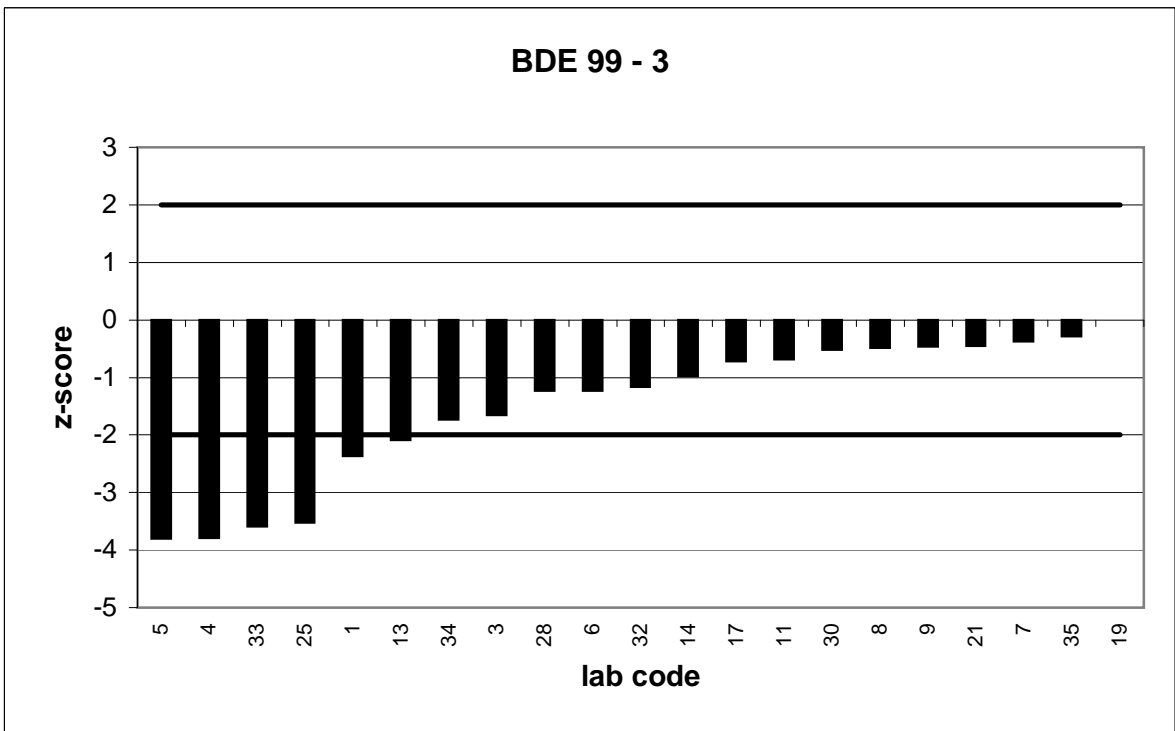
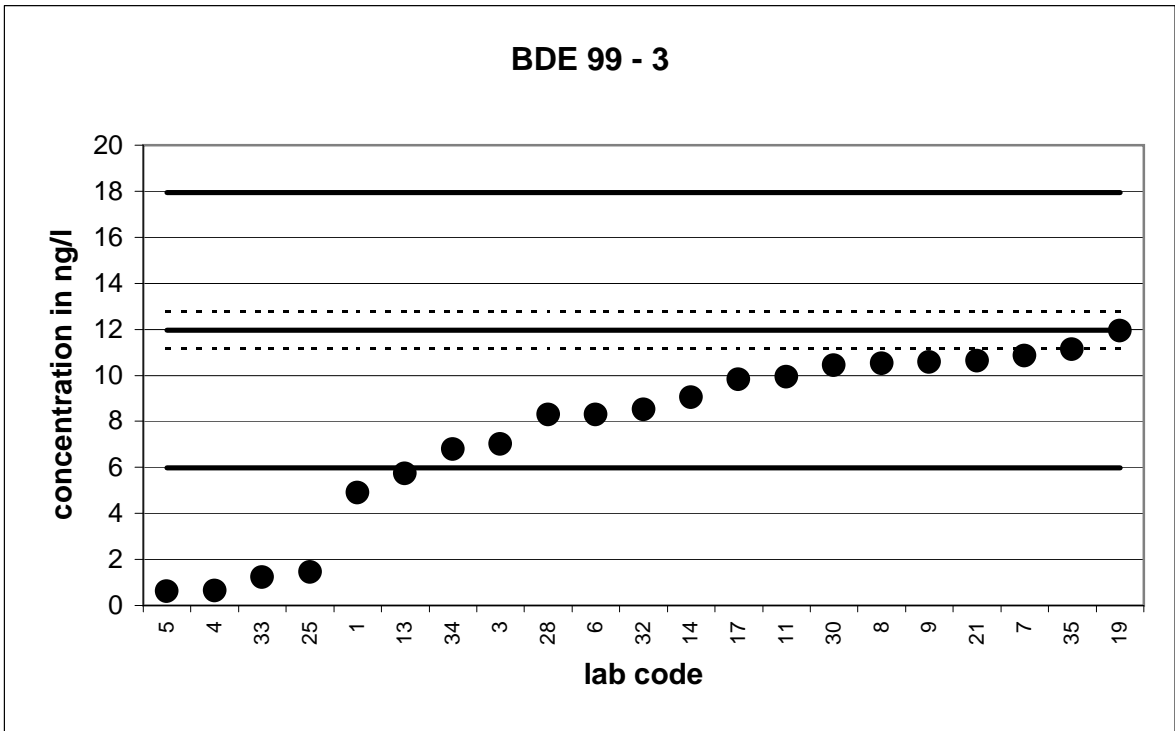
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

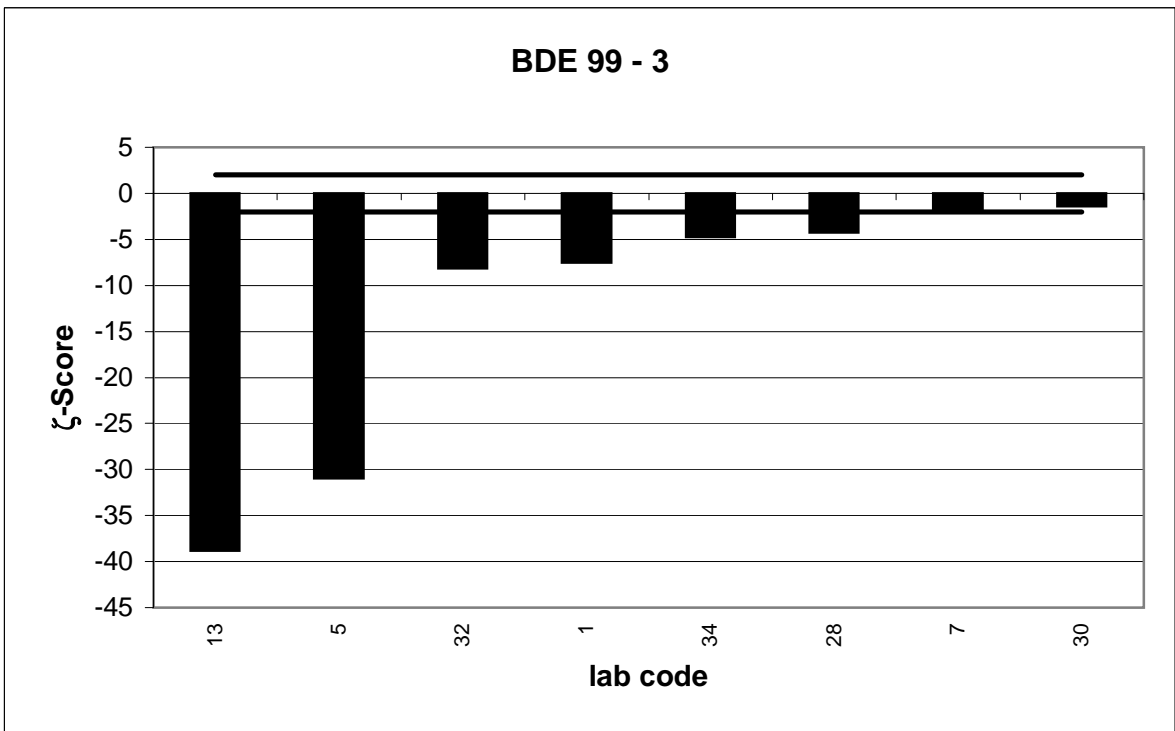
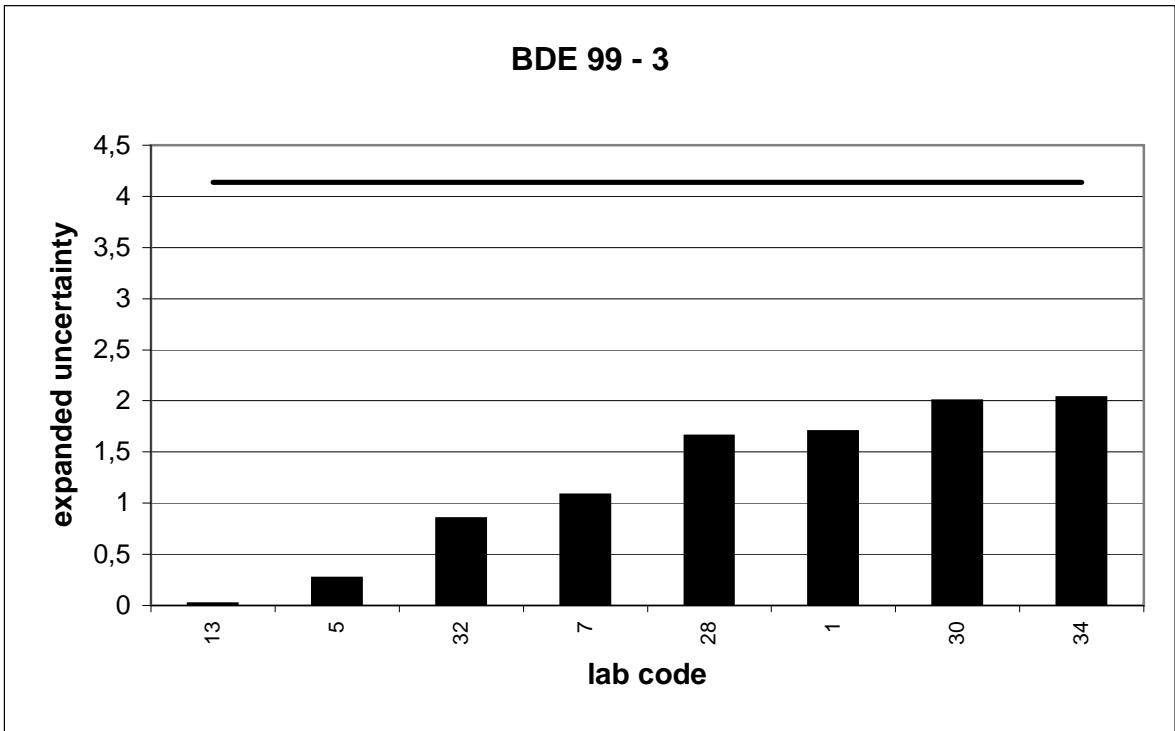




PT 6/10 PT-WFD PBDE		BDE 99 - 3			
assigned value [ng/l]*		11,96 ± 0,8			
upper tolerance limit [ng/l]		17,94			
lower tolerance limit [ng/l]		5,979			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	4,9	1,7	-7,5	-2,4	q
3	7,019			-1,7	s
4	0,6323			-3,8	u
5	0,61	0,27	-30,9	-3,8	u
6	8,293			-1,2	s
7	10,84	1,08	-1,9	-0,4	s
8	10,51			-0,5	s
9	10,58			-0,5	s
11	9,931			-0,7	s
13	5,735	0,02	-38,8	-2,1	q
14	9,038			-1,0	s
17	9,808			-0,7	s
19	11,94			0,0	s
21	10,63			-0,4	s
25	1,44			-3,5	u
28	8,29	1,658	-4,3	-1,2	s
30	10,43	2	-1,4	-0,5	s
32	8,5	0,85	-8,1	-1,2	s
33	1,22			-3,6	u
34	6,777	2,033	-4,7	-1,7	s
35	11,13			-0,3	s

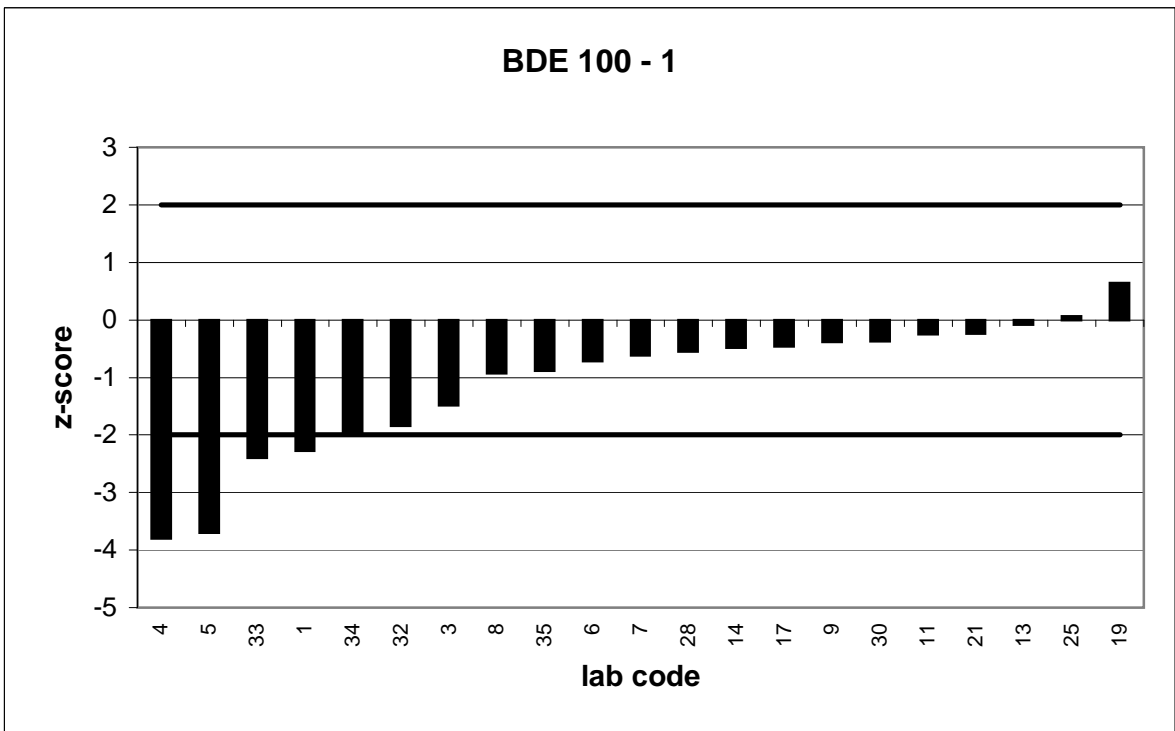
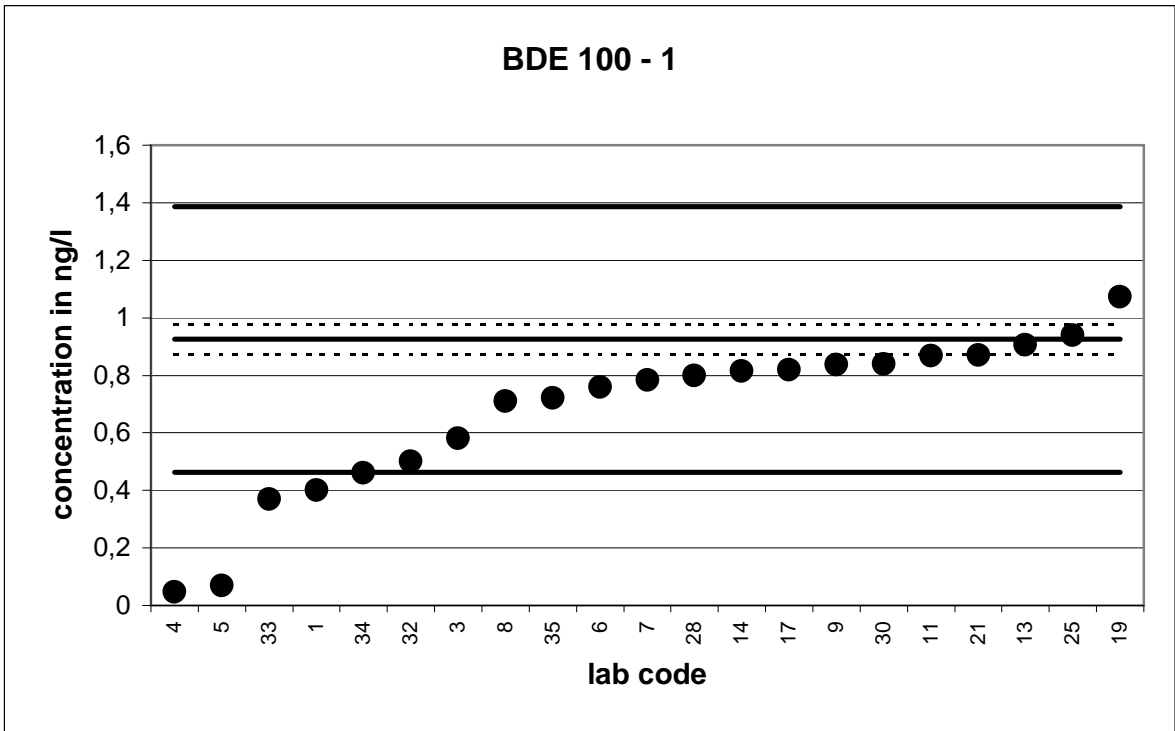
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

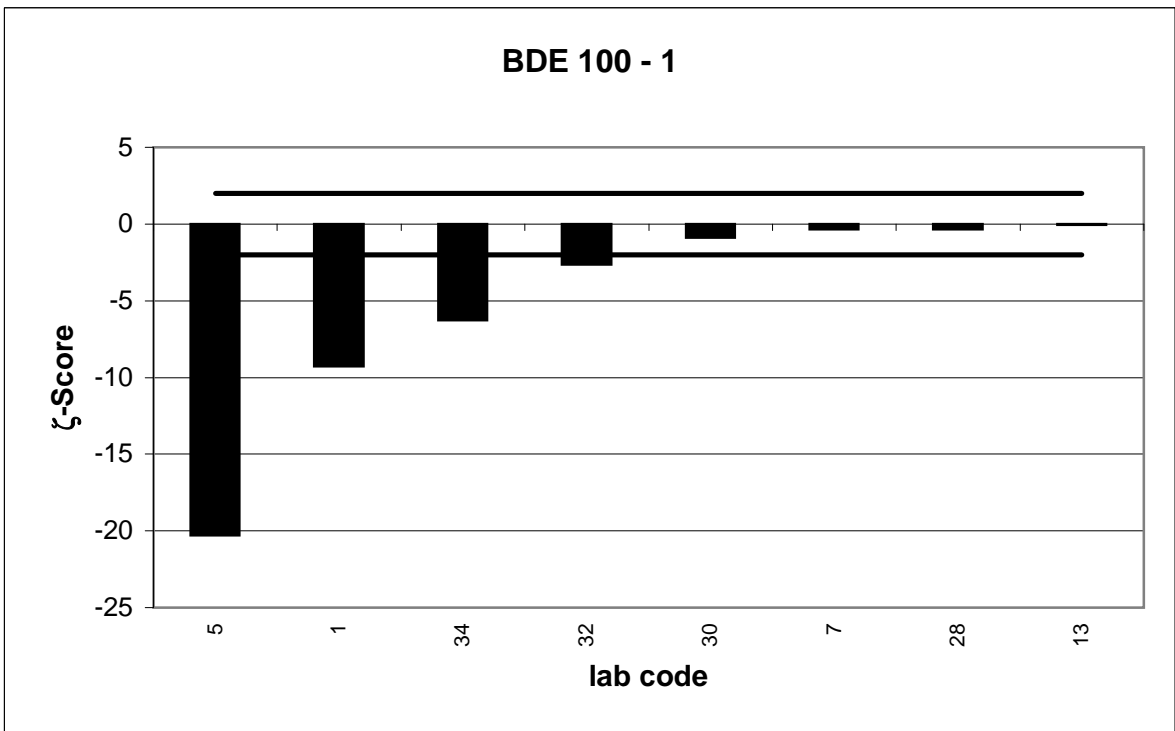
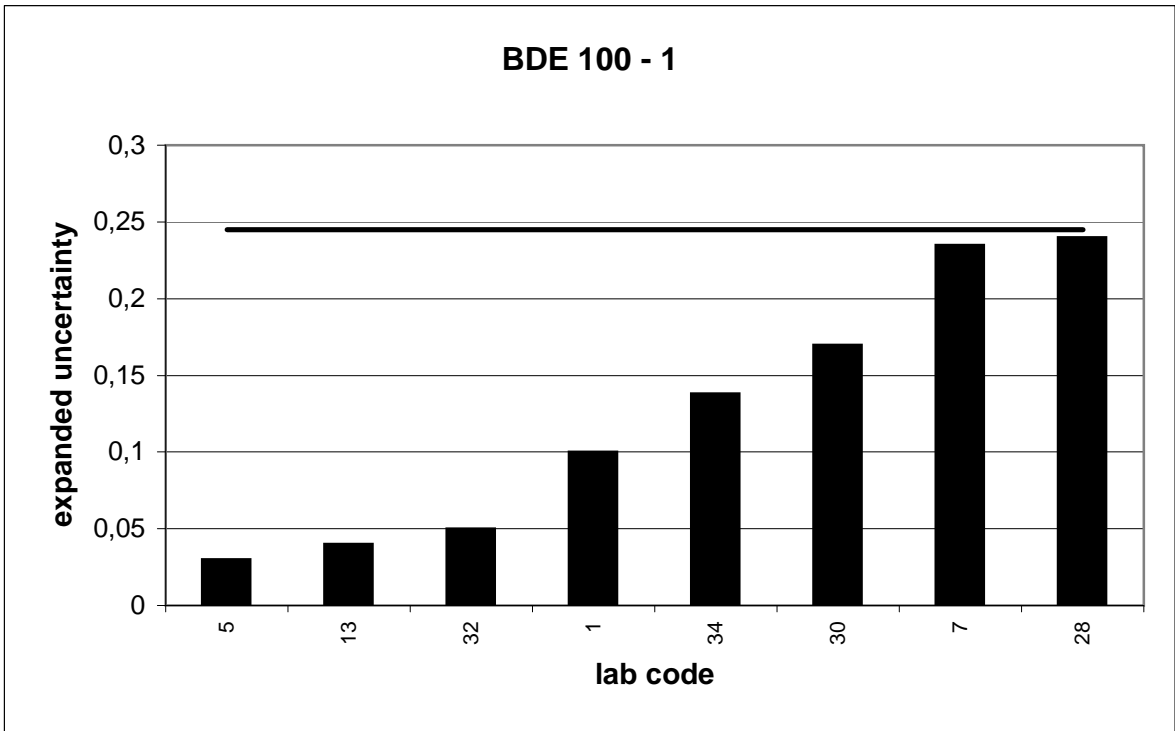




PT 6/10 PT-WFD PBDE		BDE 100 - 1			
assigned value [ng/l]*		0,9249 ± 0,0529			
upper tolerance limit [ng/l]		1,387			
lower tolerance limit [ng/l]		0,4624			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	0,4	0,1	-9,3	-2,3	q
3	0,581			-1,5	s
4	0,04767			-3,8	u
5	0,07	0,03	-20,3	-3,7	u
6	0,7591			-0,7	s
7	0,783	0,235	-0,4	-0,6	s
8	0,71			-0,9	s
9	0,8368			-0,4	s
11	0,8685			-0,2	s
13	0,905	0,04	0,0	-0,1	s
14	0,814			-0,5	s
17	0,819			-0,5	s
19	1,072			0,6	s
21	0,869			-0,2	s
25	0,9392			0,1	s
28	0,799	0,24	-0,3	-0,5	s
30	0,84	0,17	-0,9	-0,4	s
32	0,5	0,05	-2,6	-1,8	s
33	0,37			-2,4	q
34	0,4607	0,138	-6,3	-2,0	s
35	0,72			-0,9	s

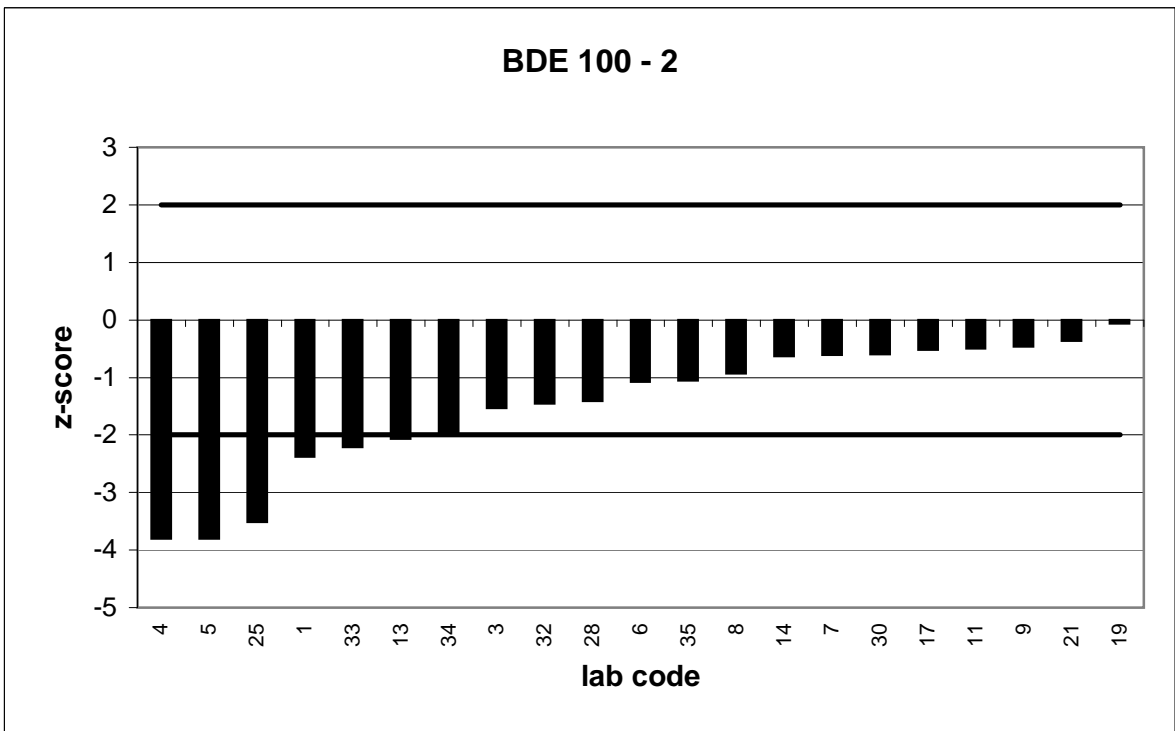
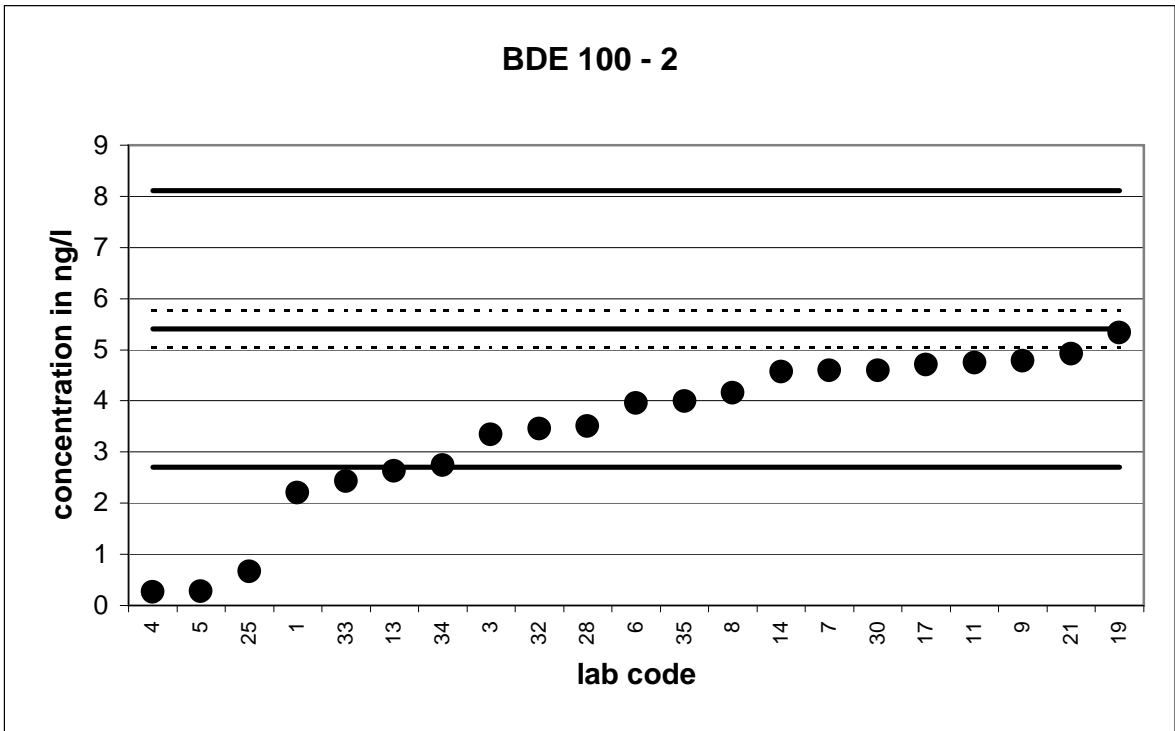
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

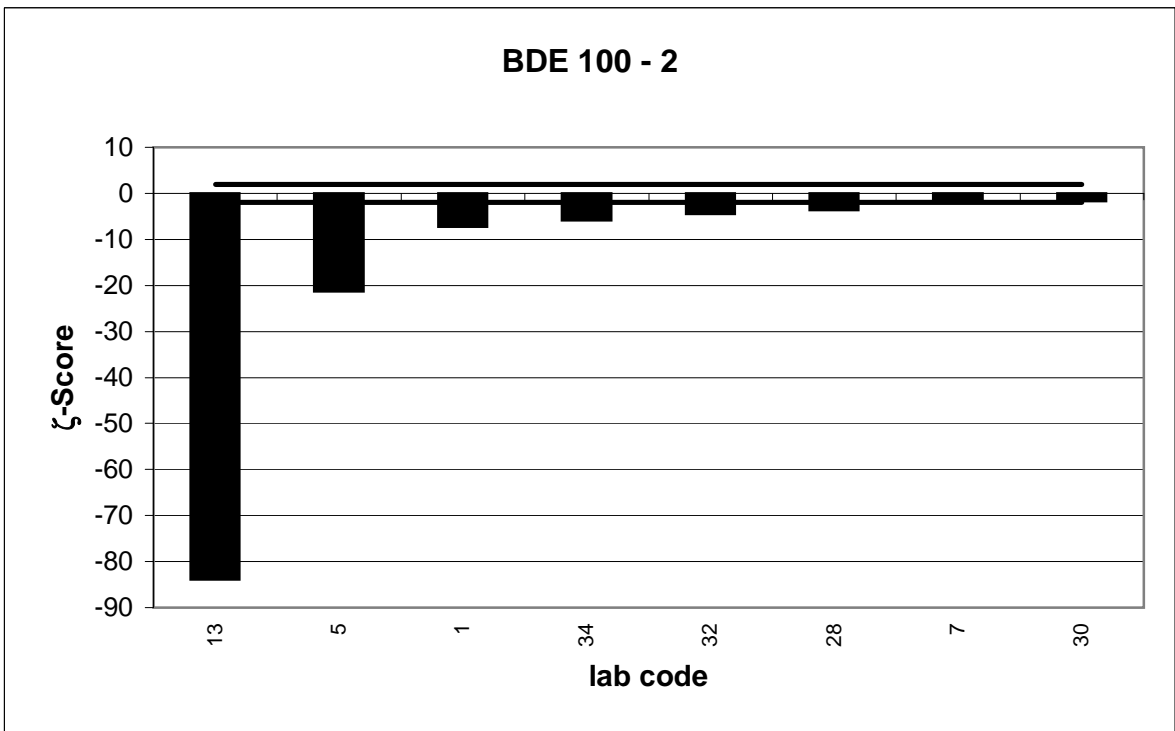
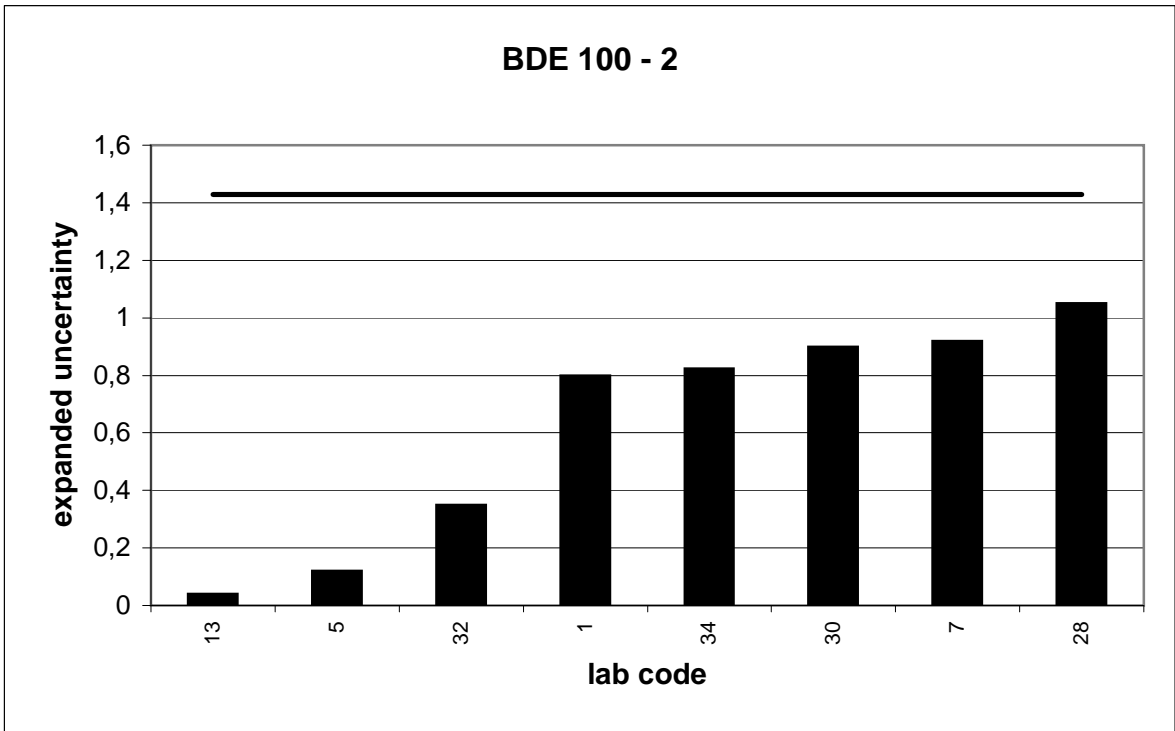




PT 6/10 PT-WFD PBDE		BDE 100 - 2			
assigned value [ng/l]*		5,409 ± 0,363			
upper tolerance limit [ng/l]		8,114			
lower tolerance limit [ng/l]		2,705			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	2,2	0,8	-7,3	-2,4	q
3	3,338			-1,5	s
4	0,2663			-3,8	u
5	0,28	0,12	-21,3	-3,8	u
6	3,953			-1,1	s
7	4,588	0,918	-1,8	-0,6	s
8	4,16			-0,9	s
9	4,786			-0,5	s
11	4,738			-0,5	s
13	2,625	0,04	-83,9	-2,1	q
14	4,565			-0,6	s
17	4,705			-0,5	s
19	5,327			-0,1	s
21	4,918			-0,4	s
25	0,6589			-3,5	u
28	3,501	1,05	-3,6	-1,4	s
30	4,6	0,9	-1,6	-0,6	s
32	3,45	0,35	-4,5	-1,4	s
33	2,43			-2,2	q
34	2,744	0,823	-5,9	-2,0	s
35	3,99			-1,0	s

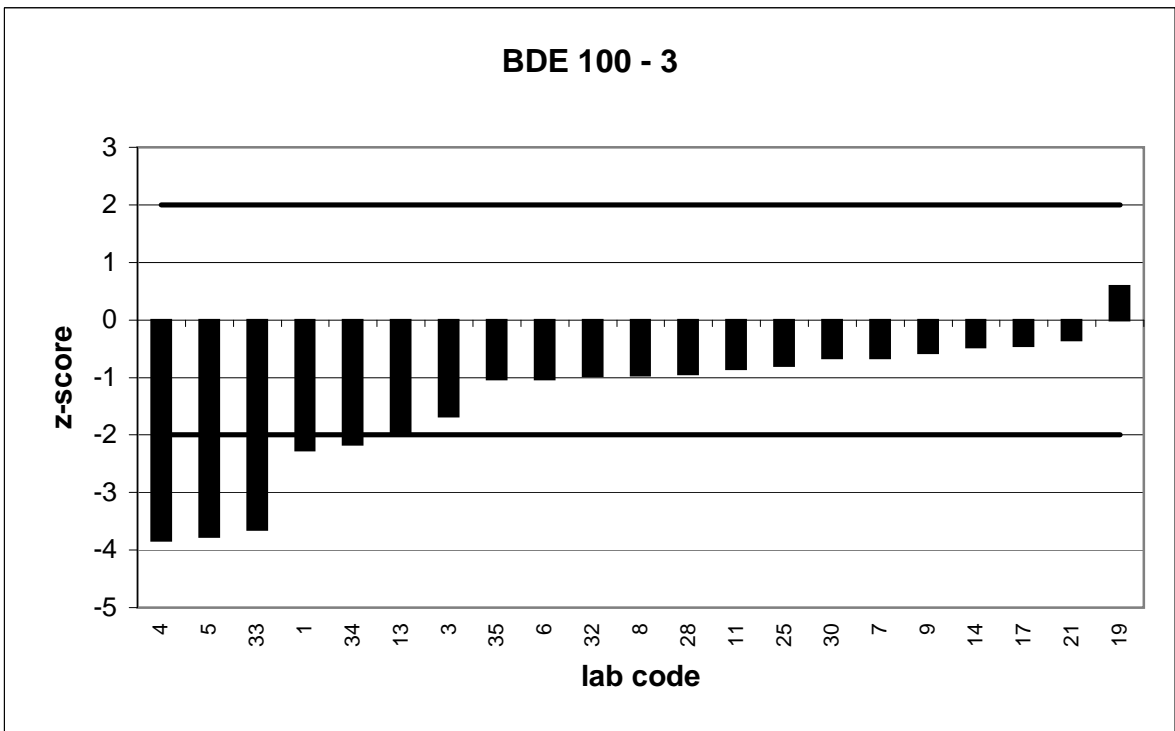
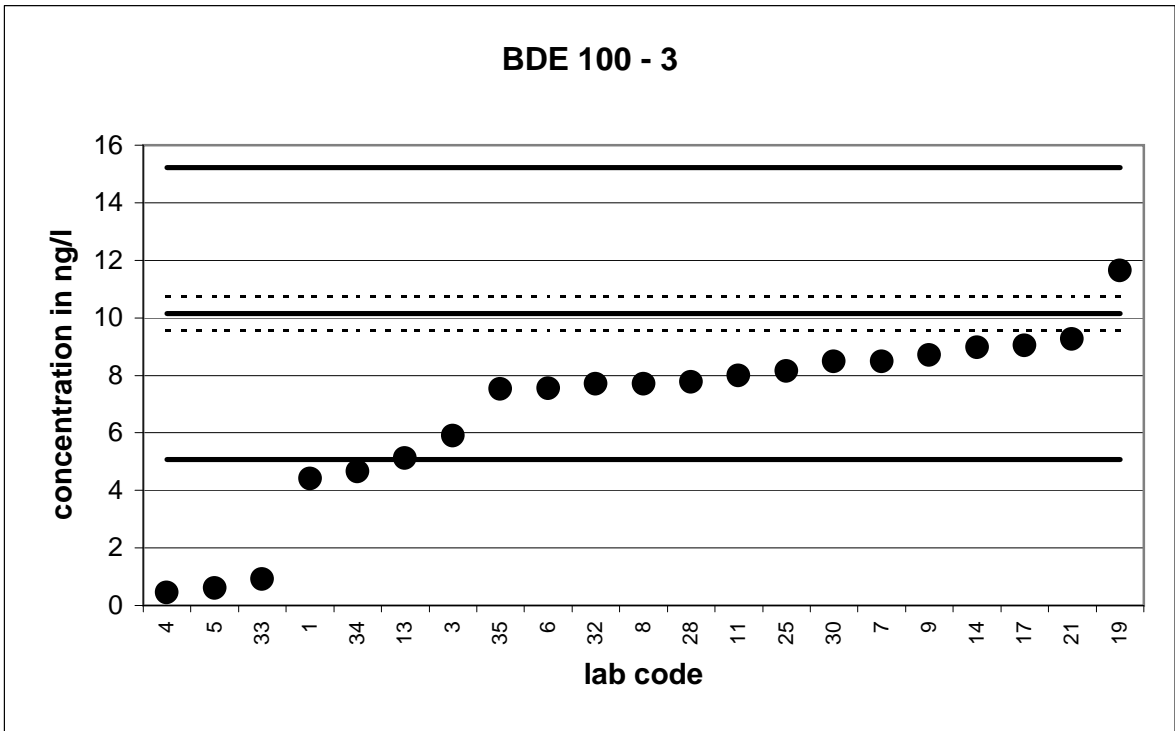
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

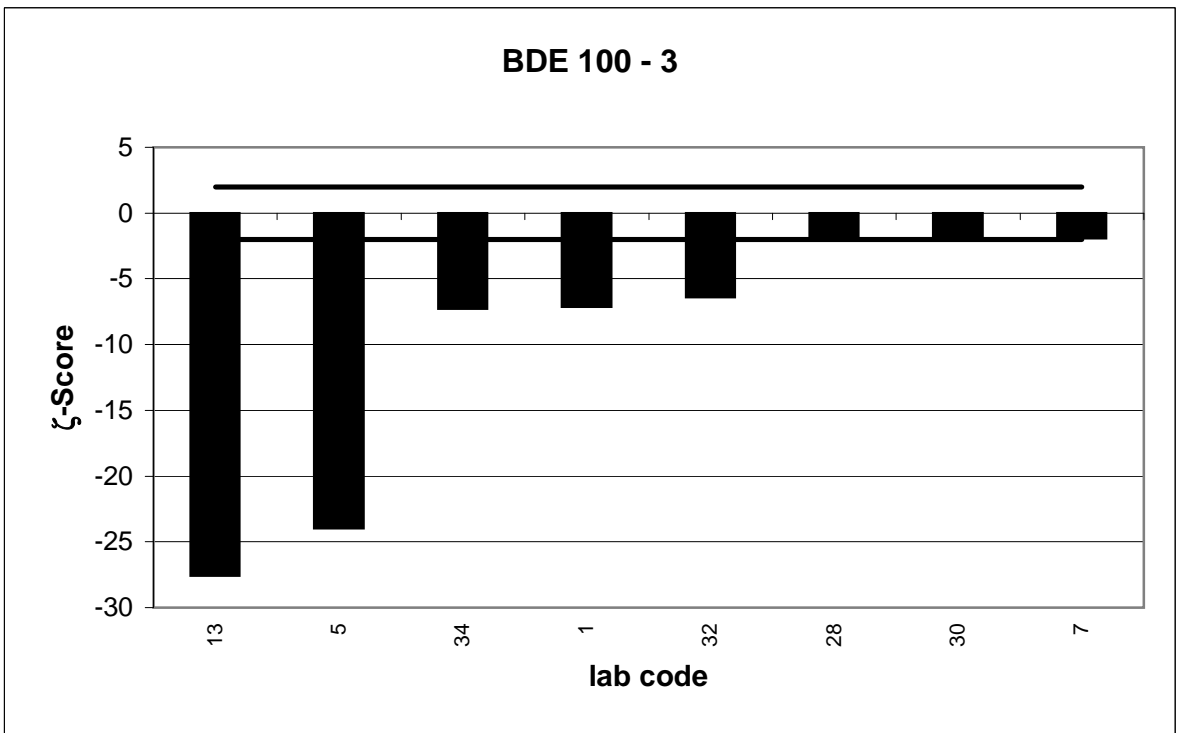
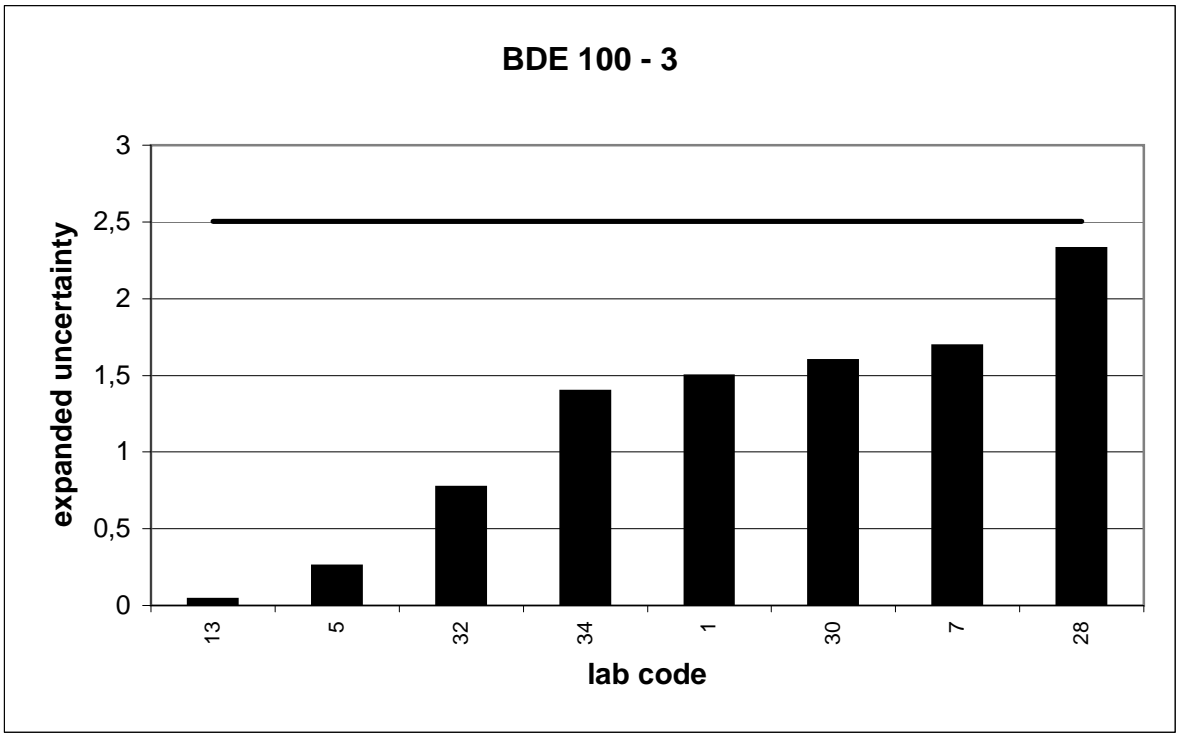




PT 6/10 PT-WFD PBDE		BDE 100 - 3			
assigned value [ng/l]*		10,15 ± 0,58			
upper tolerance limit [ng/l]		15,23			
lower tolerance limit [ng/l]		5,076			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	4,4	1,5	-7,1	-2,3	q
3	5,897			-1,7	s
4	0,436			-3,8	u
5	0,59	0,26	-24,0	-3,8	u
6	7,536			-1,0	s
7	8,476	1,695	-1,9	-0,7	s
8	7,71			-1,0	s
9	8,712			-0,6	s
11	7,986			-0,9	s
13	5,115	0,04	-27,6	-2,0	s
14	8,958			-0,5	s
17	9,024			-0,4	s
19	11,64			0,6	s
21	9,257			-0,4	s
25	8,137			-0,8	s
28	7,766	2,33	-2,0	-0,9	s
30	8,47	1,6	-1,9	-0,7	s
32	7,69	0,77	-6,4	-1,0	s
33	0,91			-3,6	u
34	4,652	1,396	-7,3	-2,2	q
35	7,53			-1,0	s

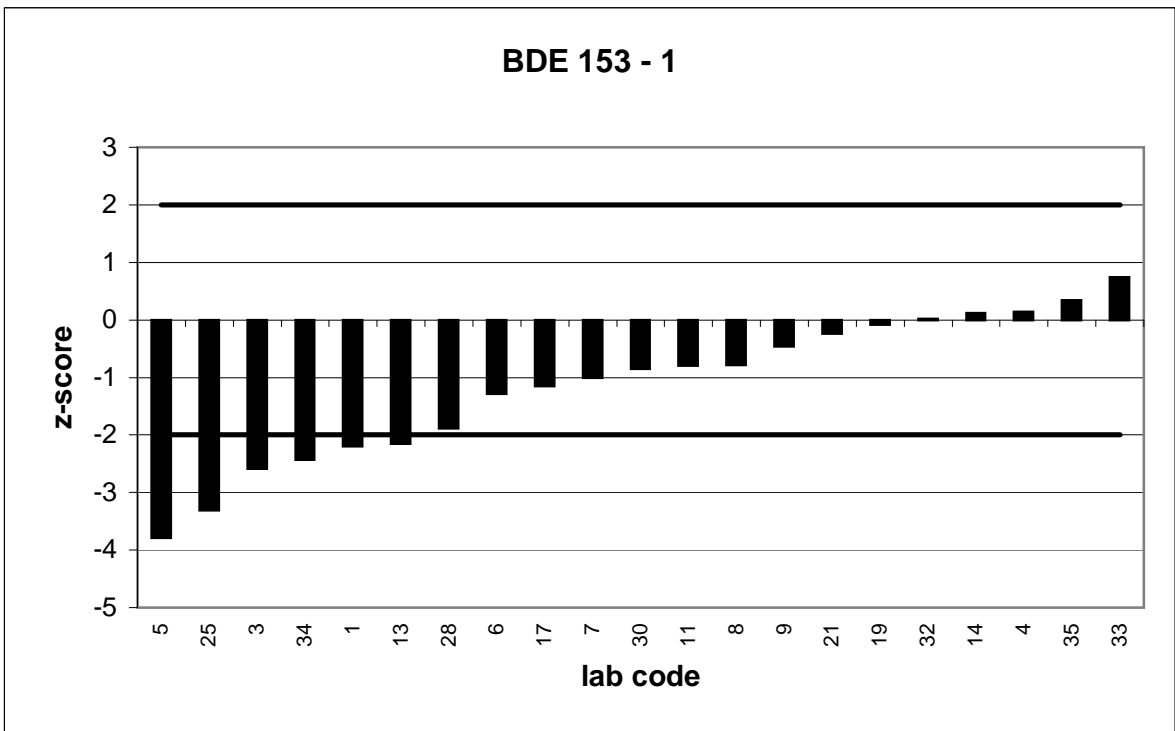
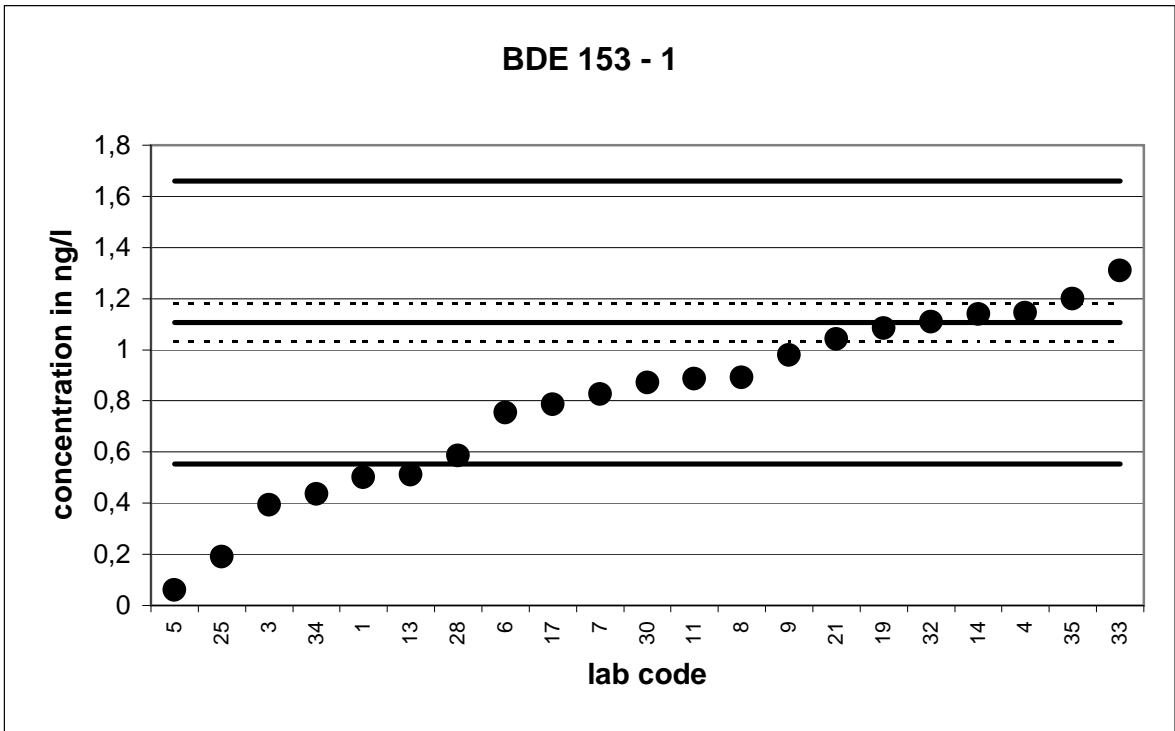
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

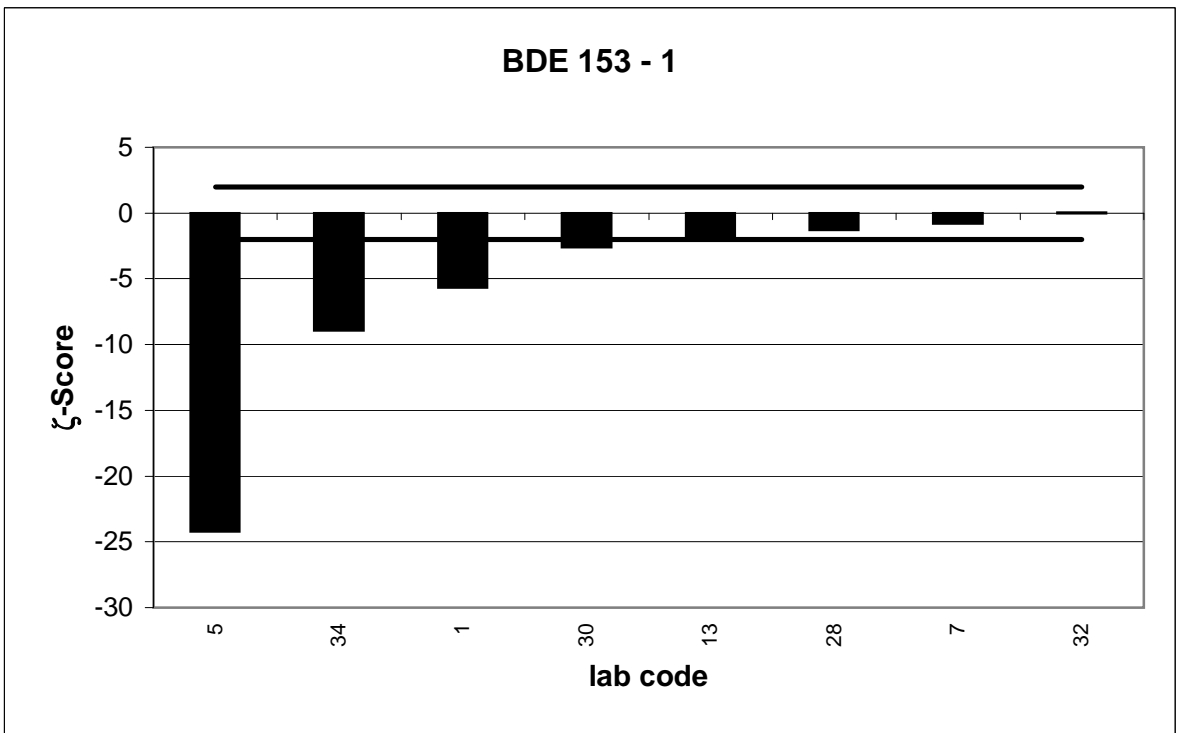
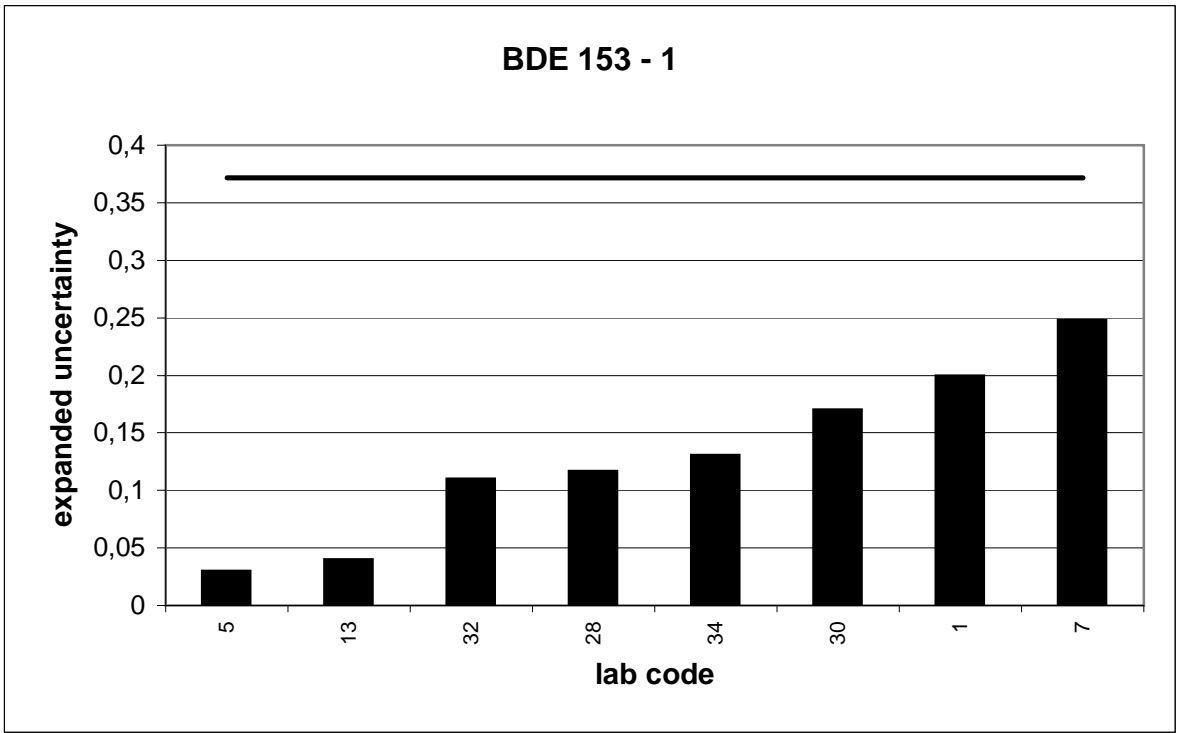




PT 6/10 PT-WFD PBDE		BDE 153 - 1			
assigned value [ng/l]*		1,106 ± 0,074			
upper tolerance limit [ng/l]		1,659			
lower tolerance limit [ng/l]		0,5531			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	0,5	0,2	-5,7	-2,2	q
3	0,392			-2,6	q
4	1,144			0,1	s
5	0,06	0,03	-24,2	-3,8	u
6	0,7526			-1,3	s
7	0,827	0,248	-0,8	-1,0	s
8	0,89			-0,8	s
9	0,9787			-0,5	s
11	0,8863			-0,8	s
13	0,51	0,04	-2,0	-2,2	q
14	1,138			0,1	s
17	0,787			-1,2	s
19	1,083			-0,1	s
21	1,041			-0,2	s
25	0,1907			-3,3	u
28	0,586	0,117	-1,3	-1,9	s
30	0,87	0,17	-2,6	-0,9	s
32	1,11	0,11	0,0	0,0	s
33	1,31			0,7	s
34	0,4356	0,131	-8,9	-2,4	q
35	1,2			0,3	s

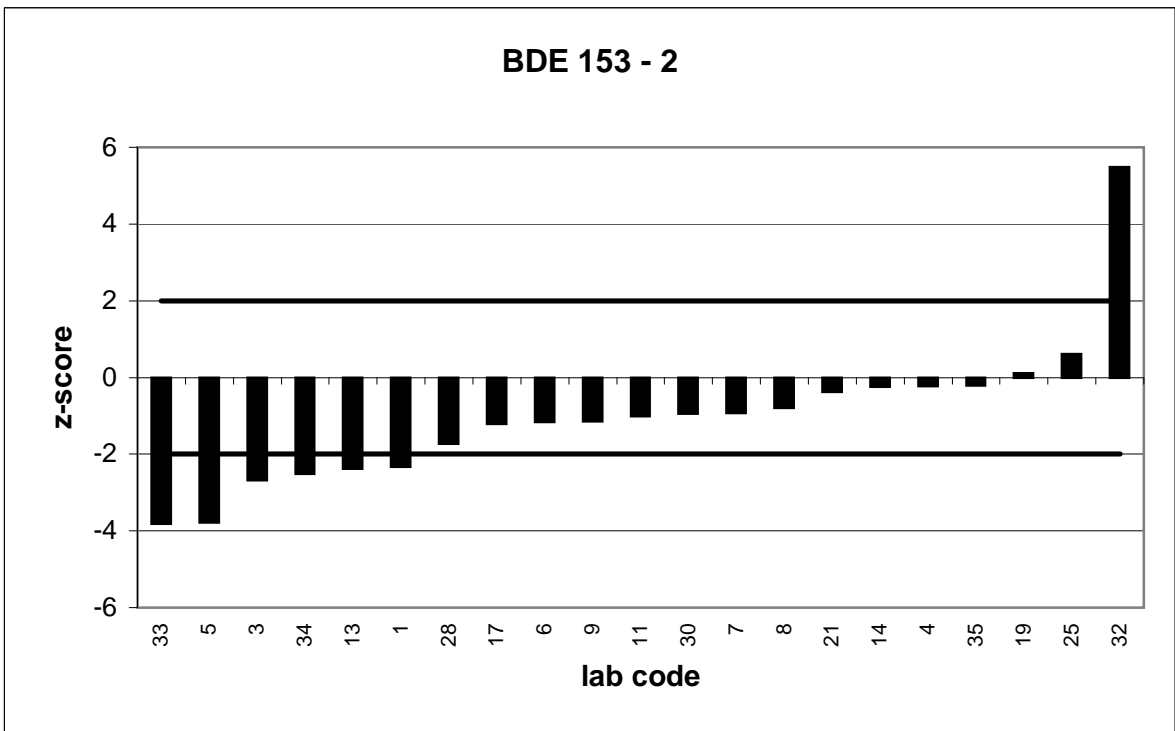
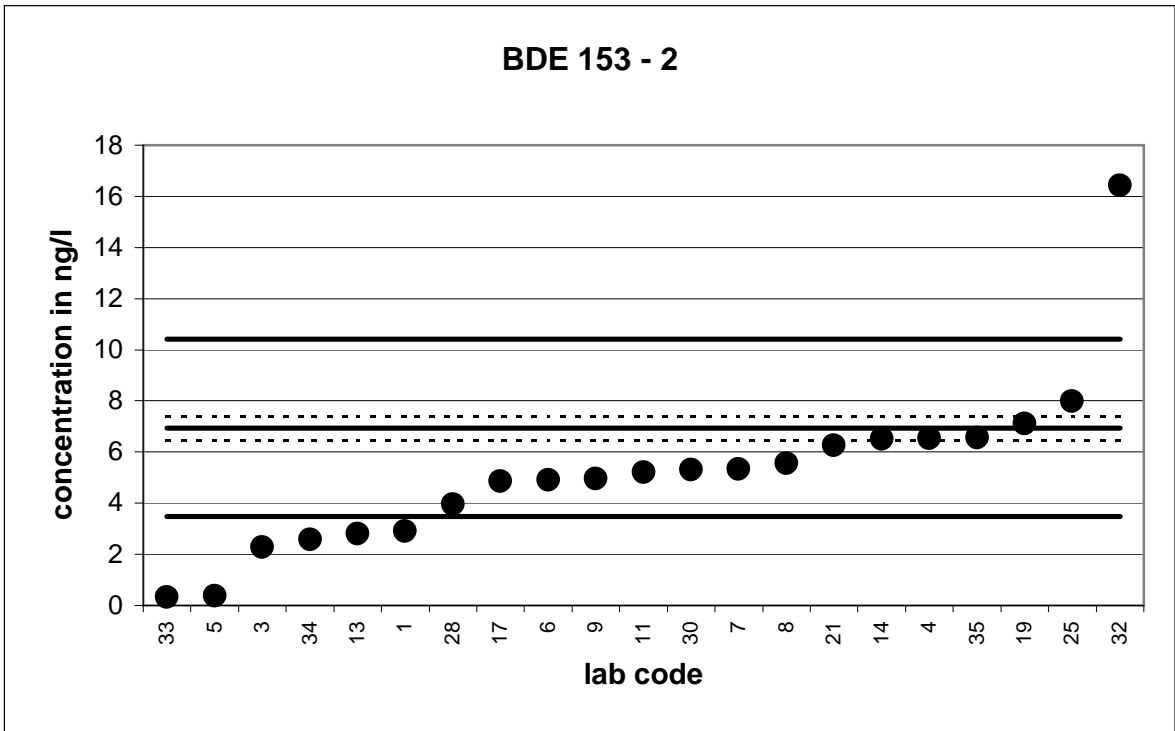
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

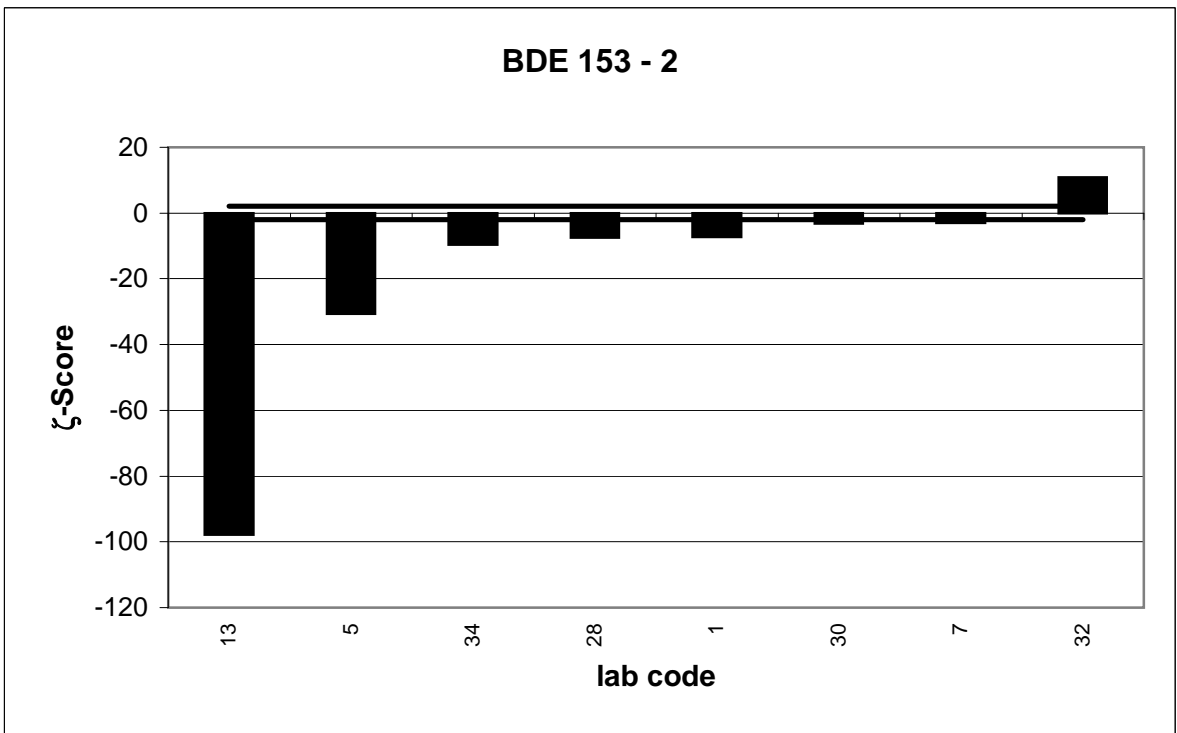
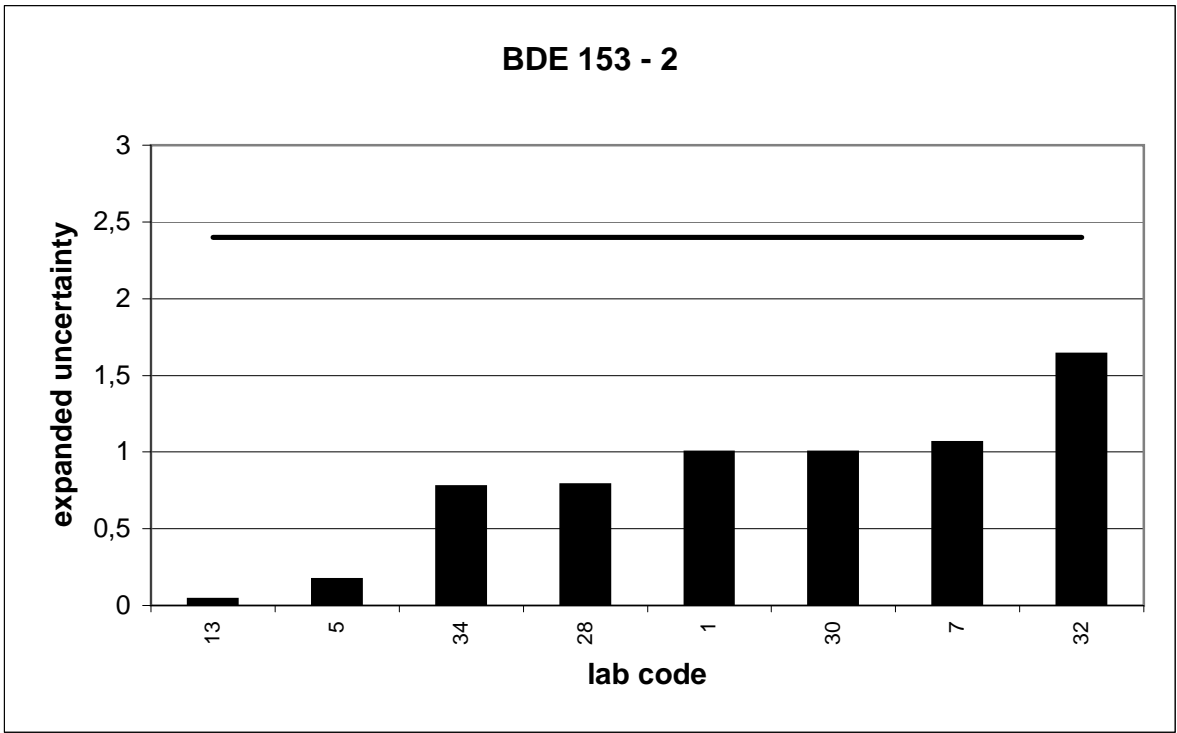




PT 6/10 PT-WFD PBDE		BDE 153 - 2			
assigned value [ng/l]*		6,936 ± 0,479			
upper tolerance limit [ng/l]		10,4			
lower tolerance limit [ng/l]		3,468			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	2,9	1	-7,3	-2,3	q
3	2,277			-2,7	q
4	6,543			-0,2	s
5	0,38	0,17	-30,6	-3,8	u
6	4,918			-1,2	s
7	5,326	1,065	-3,0	-0,9	s
8	5,56			-0,8	s
9	4,957			-1,1	s
11	5,195			-1,0	s
13	2,805	0,04	-97,9	-2,4	q
14	6,515			-0,2	s
17	4,851			-1,2	s
19	7,115			0,1	s
21	6,271			-0,4	s
25	7,993			0,6	s
28	3,949	0,79	-7,5	-1,7	s
30	5,31	1	-3,1	-0,9	s
32	16,43	1,64	10,9	5,5	u
33	0,32			-3,8	u
34	2,584	0,775	-9,6	-2,5	q
35	6,56			-0,2	s

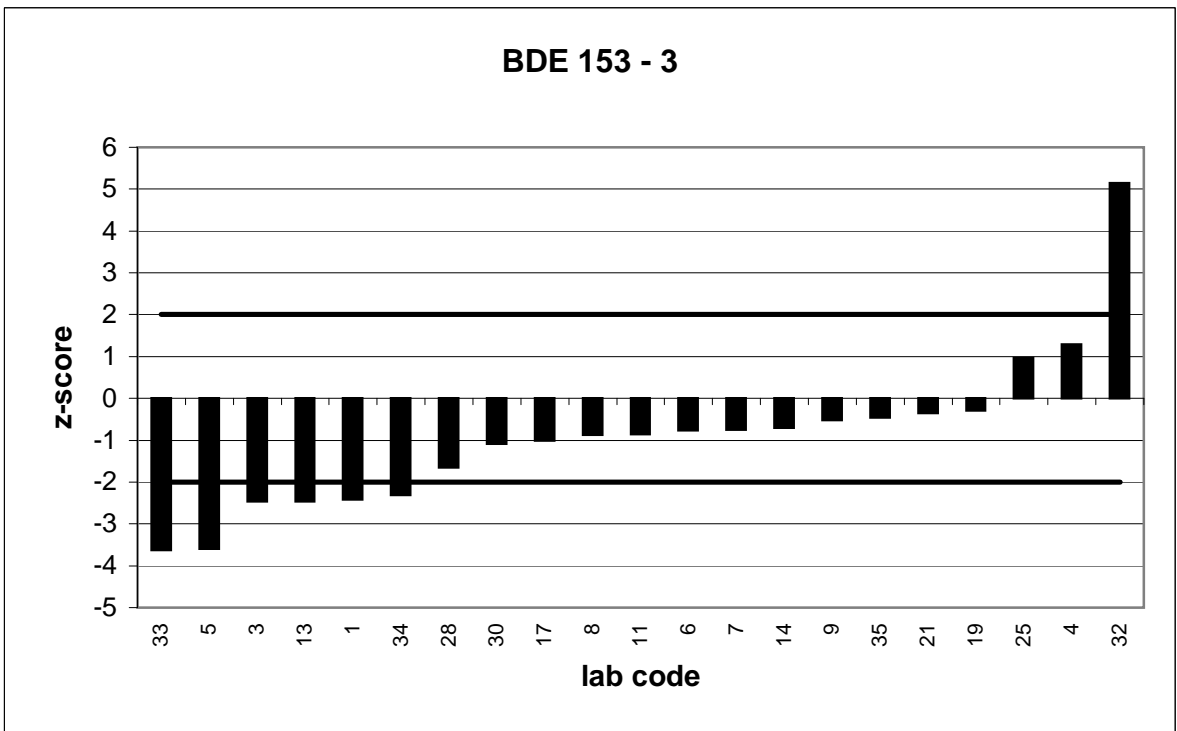
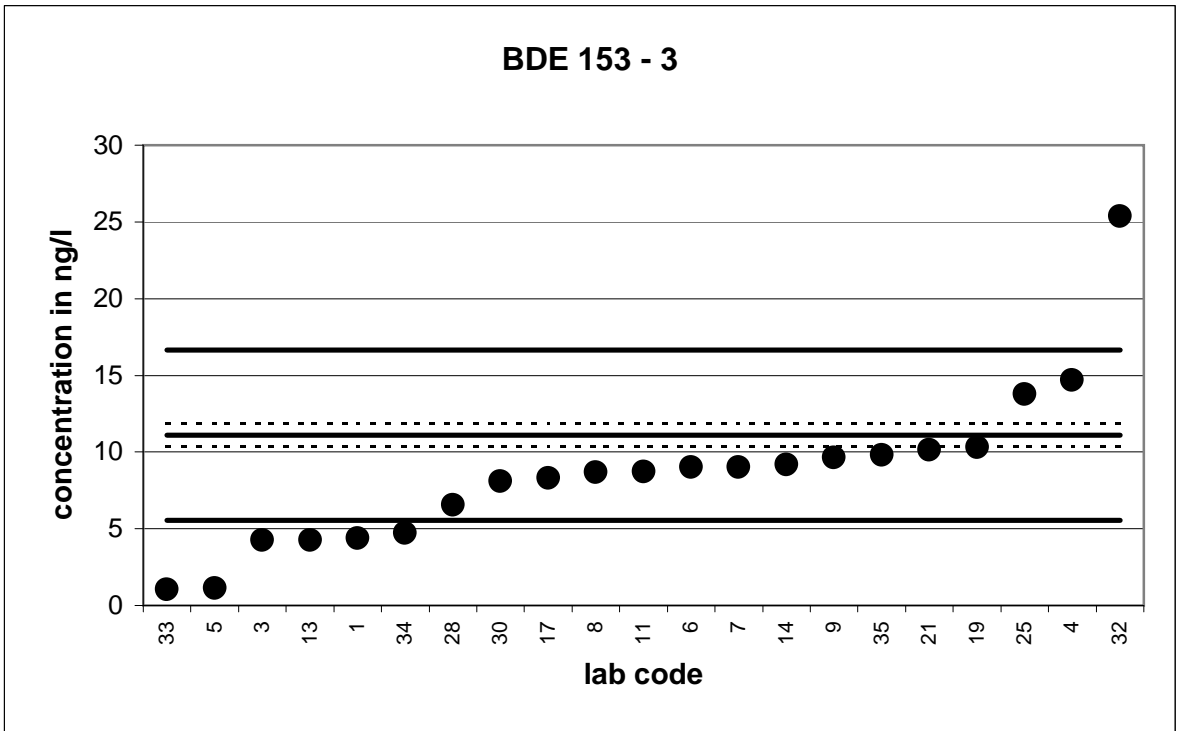
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

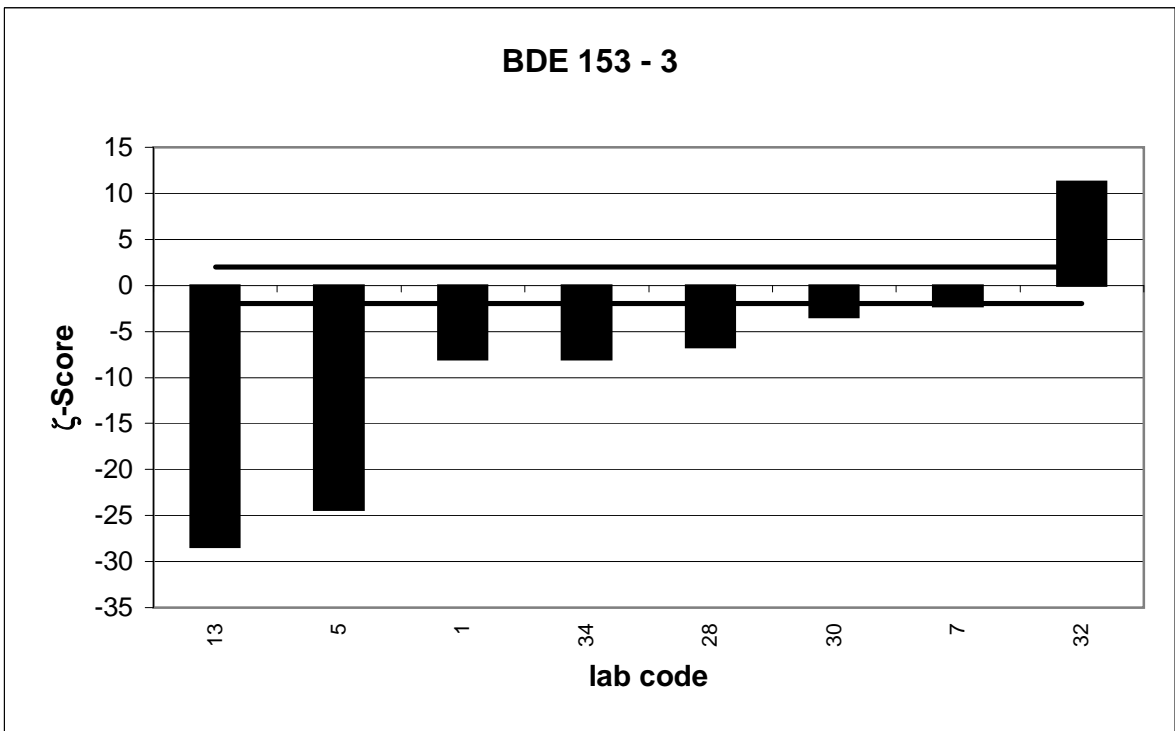
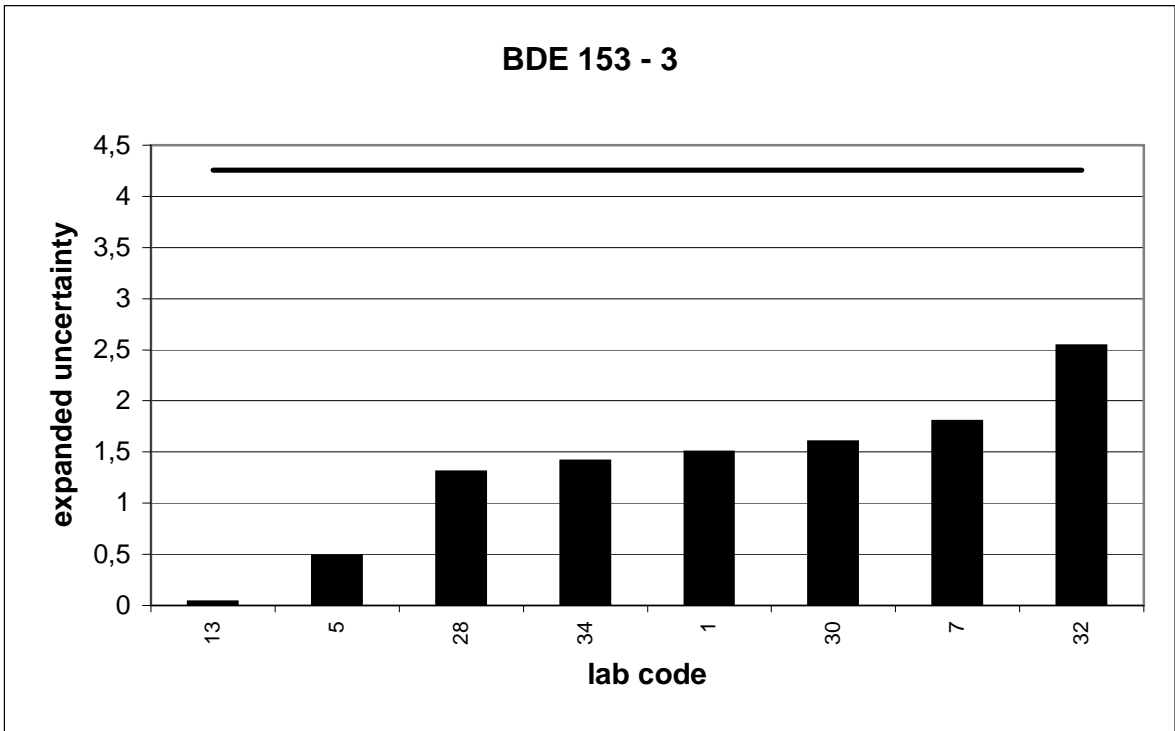




PT 6/10 PT-WFD PBDE		BDE 153 - 3			
assigned value [ng/l]*		11,09 ± 0,75			
upper tolerance limit [ng/l]		16,64			
lower tolerance limit [ng/l]		5,547			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	4,4	1,5	-8,0	-2,4	q
3	4,264			-2,5	q
4	14,67			1,3	s
5	1,12	0,49	-24,3	-3,6	u
6	8,997			-0,8	s
7	9,014	1,803	-2,3	-0,7	s
8	8,68			-0,9	s
9	9,651			-0,5	s
11	8,709			-0,9	s
13	4,275	0,04	-28,4	-2,5	q
14	9,159			-0,7	s
17	8,296			-1,0	s
19	10,31			-0,3	s
21	10,13			-0,3	s
25	13,77			1,0	s
28	6,538	1,308	-6,7	-1,6	s
30	8,1	1,6	-3,4	-1,1	s
32	25,37	2,54	11,2	5,1	u
33	1,06			-3,6	u
34	4,712	1,414	-8,0	-2,3	q
35	9,81			-0,5	s

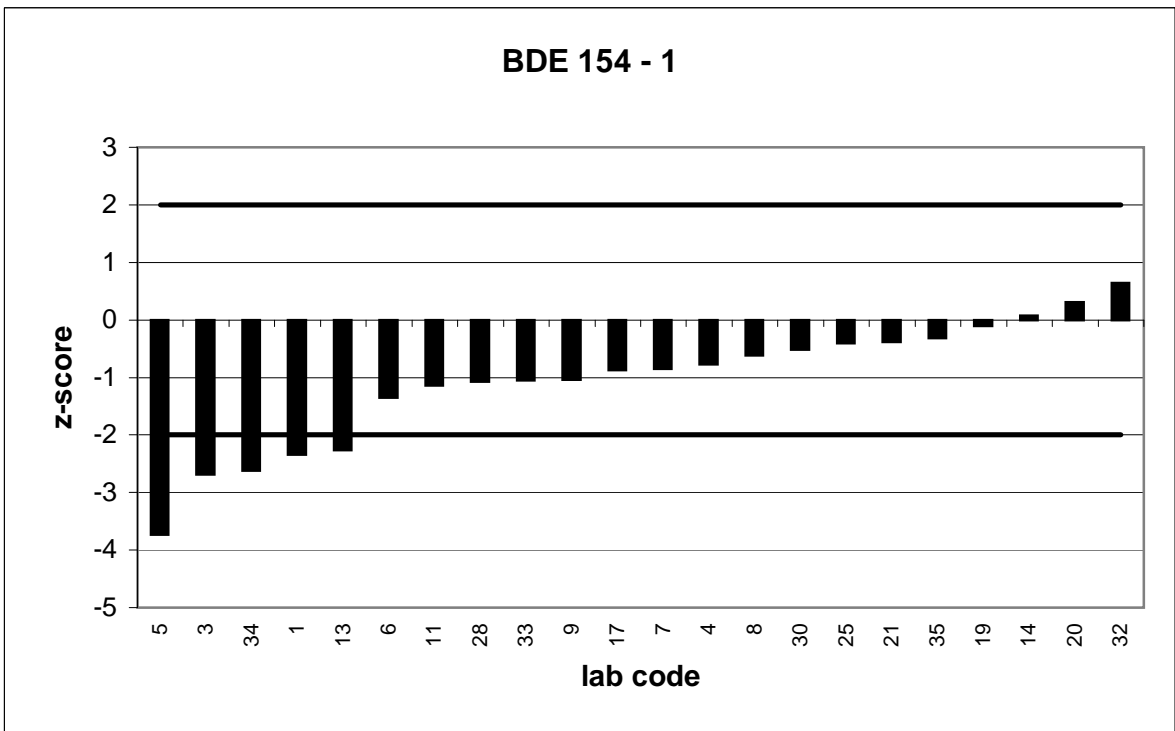
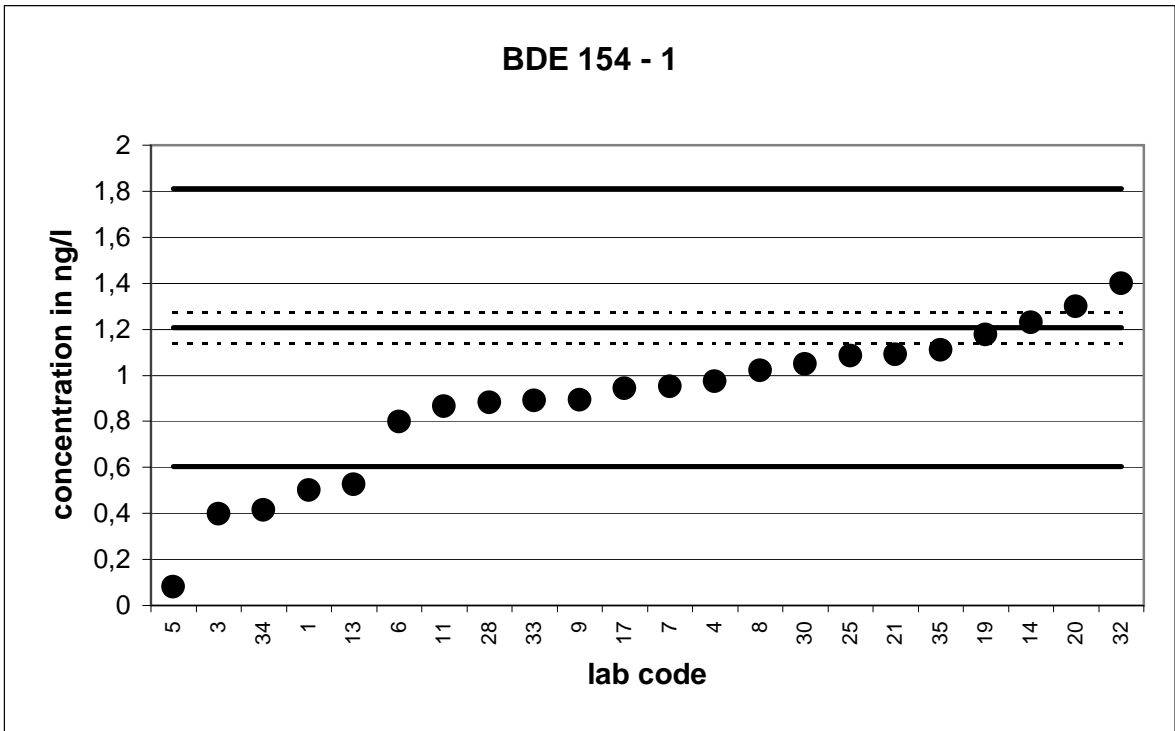
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

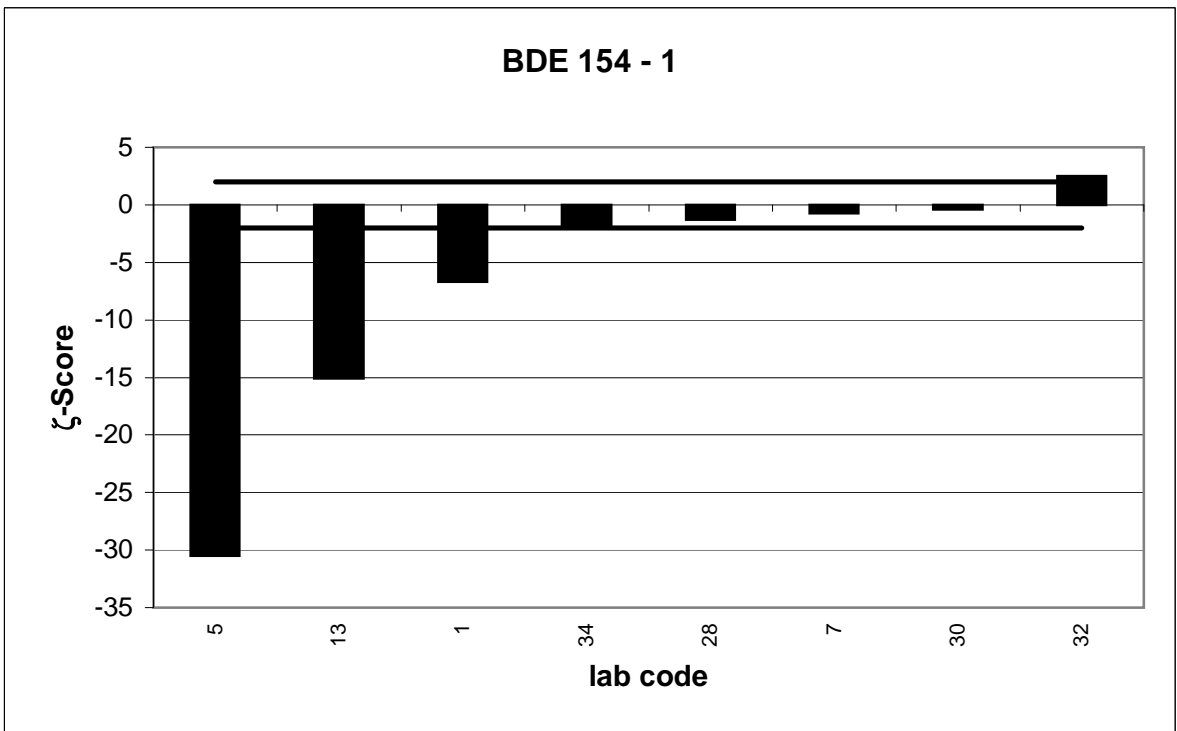
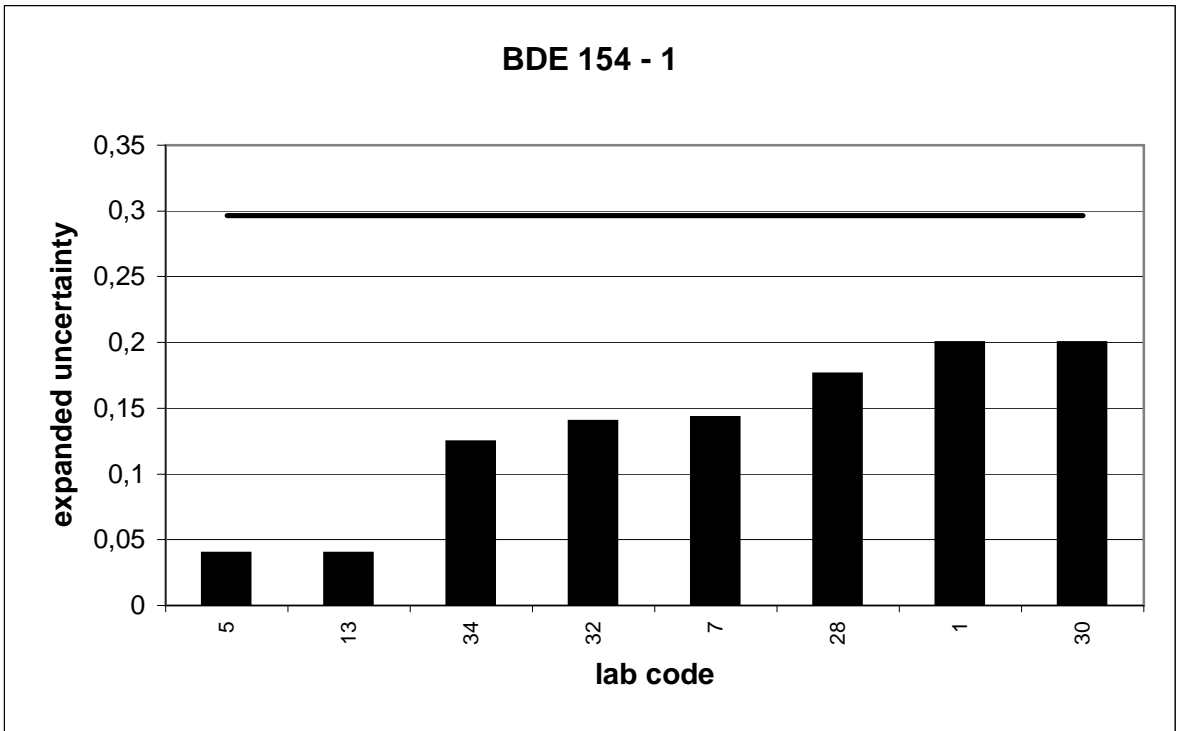




PT 6/10 PT-WFD PBDE		BDE 154 - 1			
assigned value [ng/l]*		1,207 ± 0,067			
upper tolerance limit [ng/l]		1,81			
lower tolerance limit [ng/l]		0,6033			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	0,5	0,2	-6,7	-2,3	q
3	0,397			-2,7	q
4	0,9728			-0,8	s
5	0,08	0,04	-30,5	-3,7	u
6	0,7994			-1,3	s
7	0,9502	0,143	-0,7	-0,8	s
8	1,02			-0,6	s
9	0,8941			-1,0	s
11	0,8642			-1,1	s
13	0,525	0,04	-15,1	-2,3	q
14	1,229			0,1	s
17	0,944			-0,9	s
19	1,176			-0,1	s
20	1,3			0,3	s
21	1,091			-0,4	s
25	1,085			-0,4	s
28	0,882	0,176	-1,3	-1,1	s
30	1,05	0,2	-0,4	-0,5	s
32	1,4	0,14	2,5	0,6	s
33	0,89			-1,0	s
34	0,4156	0,125	-1,9	-2,6	q
35	1,11			-0,3	s

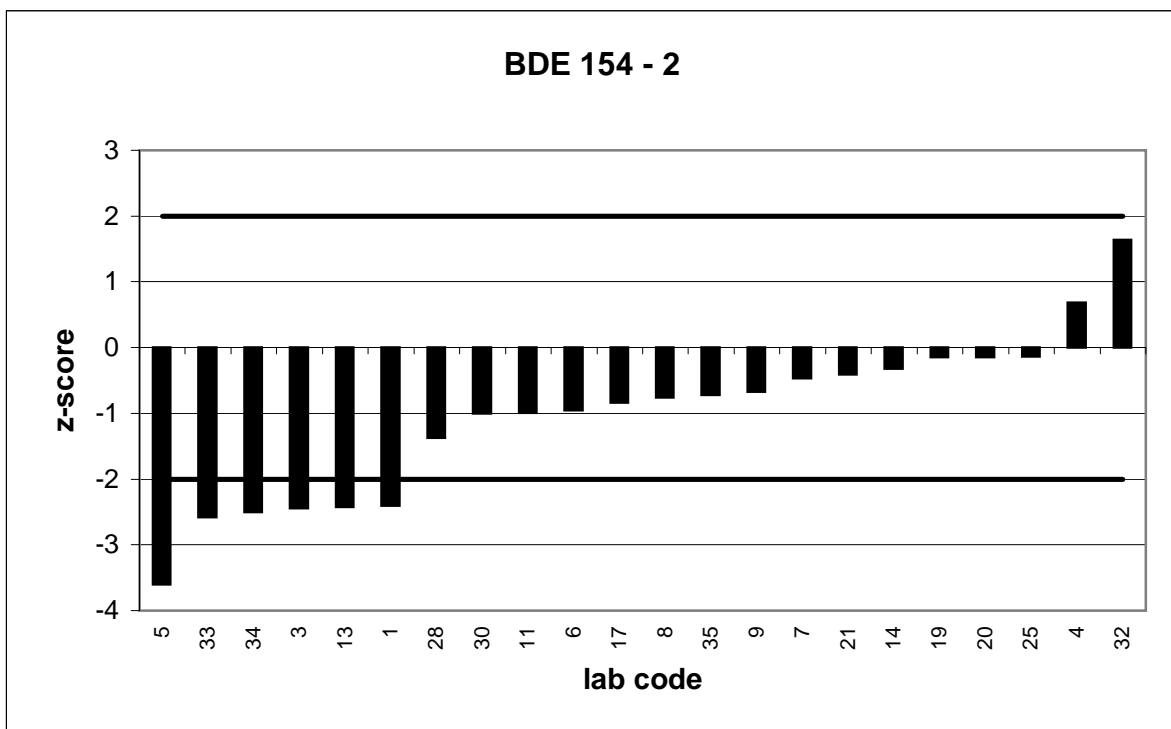
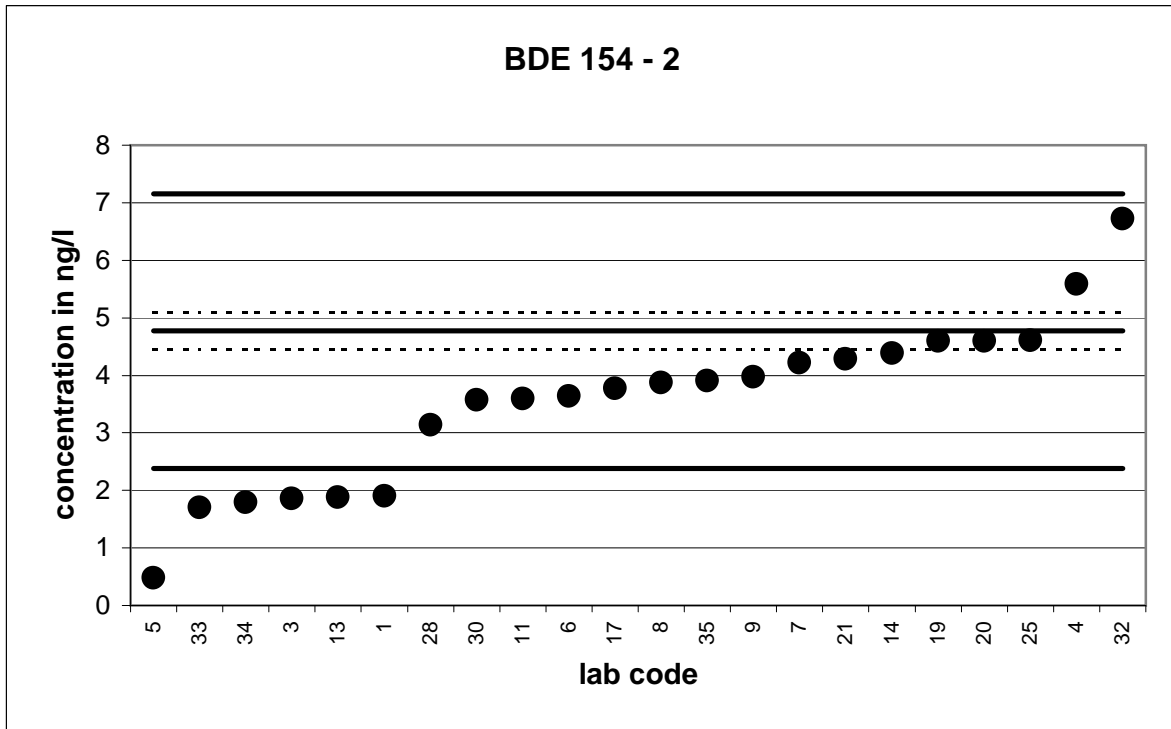
\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

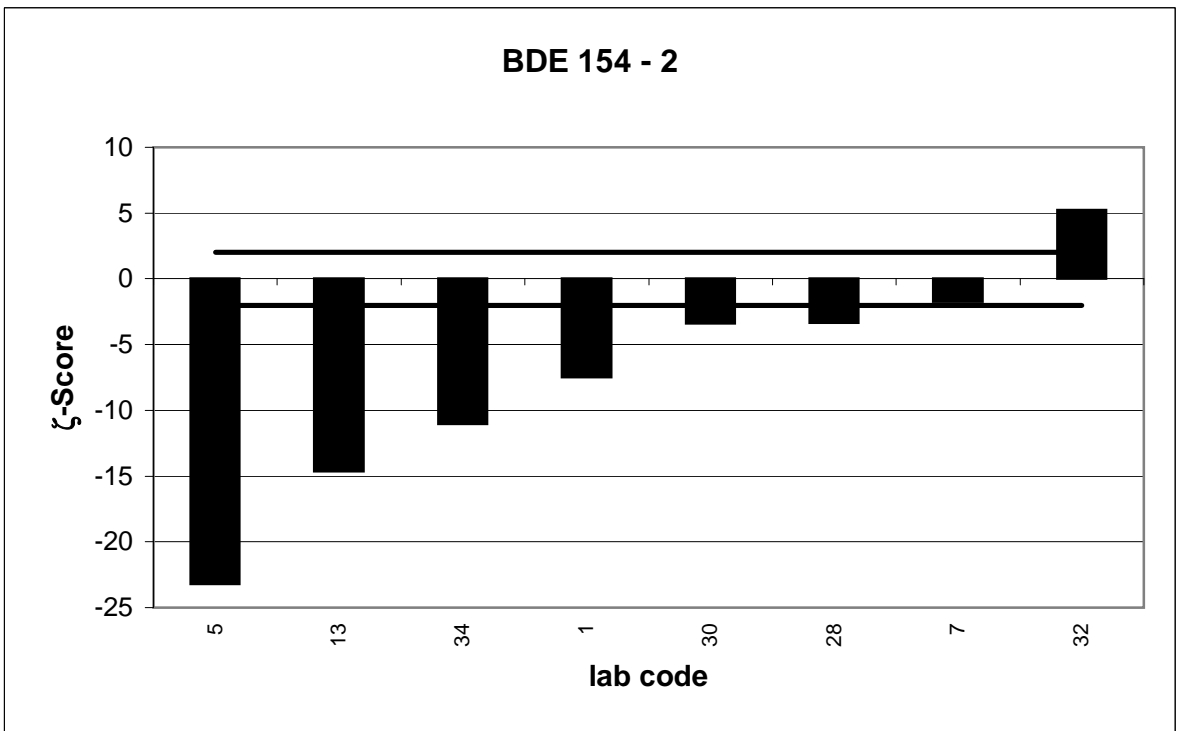
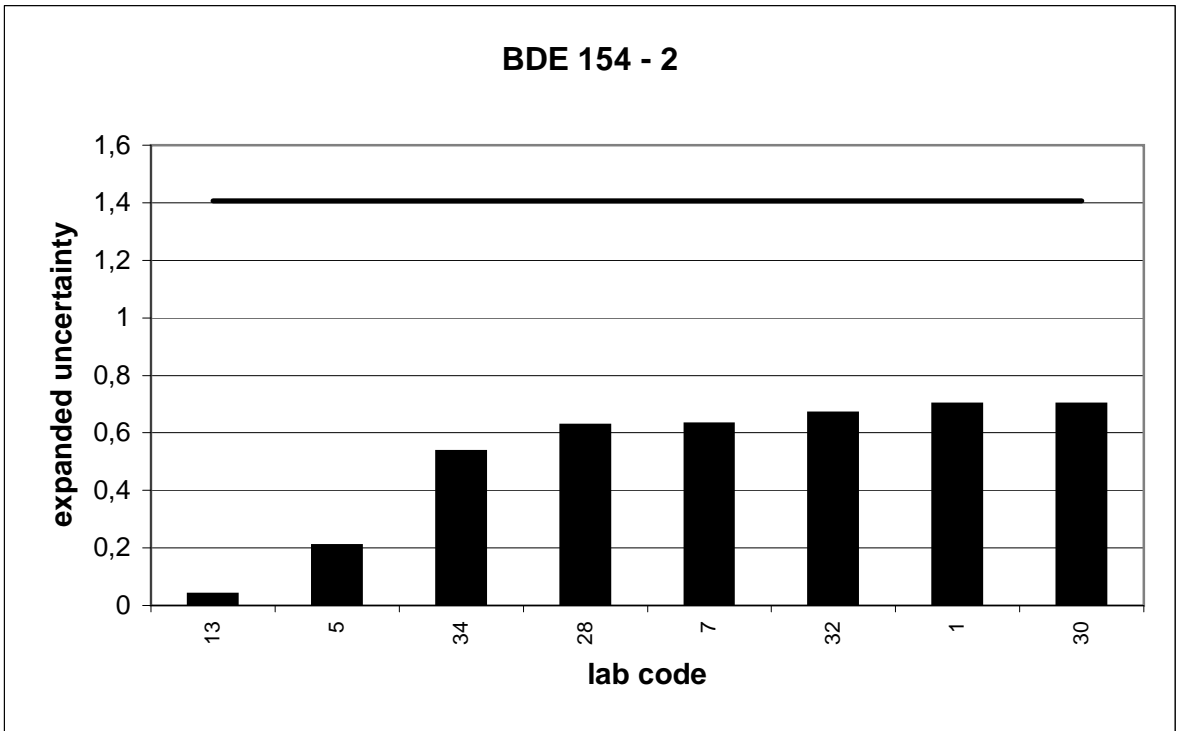




PT 6/10 PT-WFD PBDE		BDE 154 - 2			
assigned value [ng/l]*		4,769 ± 0,32			
upper tolerance limit [ng/l]		7,154			
lower tolerance limit [ng/l]		2,385			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	1,9	0,7	-7,5	-2,4	q
3	1,859			-2,4	q
4	5,589			0,7	s
5	0,48	0,21	-23,2	-3,6	u
6	3,633			-1,0	s
7	4,212	0,632	-1,7	-0,5	s
8	3,87			-0,8	s
9	3,97			-0,7	s
11	3,59			-1,0	s
13	1,875	0,04	-14,6	-2,4	q
14	4,389			-0,3	s
17	3,77			-0,8	s
19	4,598			-0,1	s
20	4,6			-0,1	s
21	4,285			-0,4	s
25	4,604			-0,1	s
28	3,139	0,628	-3,3	-1,4	s
30	3,57	0,7	-3,4	-1,0	s
32	6,72	0,67	5,3	1,6	s
33	1,7			-2,6	q
34	1,791	0,537	-11,0	-2,5	q
35	3,91			-0,7	s

\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%





PT 6/10 PT-WFD PBDE		BDE 154 - 3			
assigned value [ng/l]*		9,782 ± 0,803			
upper tolerance limit [ng/l]		14,67			
lower tolerance limit [ng/l]		4,891			
lab code	result [ng/l]	±	ζ-score	z-score	assessm.
1	3,8	1,3	-7,8	-2,4	q
3	3,716			-2,5	q
4	9,977			0,1	s
5	0,42	0,18	-26,5	-3,8	u
6	6,41			-1,4	s
7	8,671	1,301	-1,6	-0,5	s
8	7,56			-0,9	s
9	7,983			-0,7	s
11	7,385			-1,0	s
13	4,1	0,04	-17,3	-2,3	q
14	8,616			-0,5	s
17	7,487			-0,9	s
19	8,866			-0,4	s
20	9,7			0,0	s
21	8,236			-0,6	s
25	0,7084			-3,7	u
28	6,919	1,384	-4,1	-1,2	s
30	7,59	1,5	-2,8	-0,9	s
32	12,4	1,24	3,5	1,1	s
33	0,39			-3,8	u
34	3,632	1,09	-10,7	-2,5	q
35	8,17			-0,7	s

\* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor  $k=2$  corresponding to a confidence level of about 95%

