REPORTS OF FINNISH ENVIRONMENT INSTITUTE 7| 2013

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Volatile organic compounds in water and soil

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Helsinki 2013

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Finnish Environment Institute SYKE

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ALKUSANAT

Suomen ympäristökeskus (SYKE) on toiminut ympäristöalan kansallisena vertailulaboratoriona vuodesta 2001 lähtien. Toiminta perustuu ympäristöministeriön määräykseen, mikä on annettu ympäristönsuojelulain (86/2000) nojalla. Vertailulaboratorion tarjoamista palveluista yksi tärkeimmistä on pätevyyskokeiden ja muiden vertailumittausten järjestäminen. SYKEn laboratoriot on FINAS-akkreditointipalvelun akkreditoima testauslaboratorio T003 ja kalibrointilaboratorio K054 (SFS-EN ISO/IEC 17025) sekä vertailumittausten järjestäjä Proftest SYKE PT01 (SFS-EN ISO/IEC 17043, www.finas.fi).

Tämä pätevyyskoe on toteutettu SYKEn vertailulaboratorion pätevyysalueella ja se antaa tietoa osallistujien pätevyyden lisäksi tulosten vertailukelpoisuudesta myös yleisemmällä tasolla. Pätevyyskokeen onnistumisen edellytys on järjestäjän ja osallistujien välinen luottamuksellinen yhteistyö.

Parhaat kiitokset yhteistyöstä kaikille osallistujille

PREFACE

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector by the Ministry of the Environment according to section 24 of the Environment Protection Act (86/2000) since 2001. The duties of the reference laboratory service include providing proficiency tests and other interlaboratory comparisons for analytical laboratories and other producers of environmental information. SYKE laboratories has been accredited by the Finnish Accreditation service as the testing laboratory T003 and the calibration laboratory K054 (EN ISO/IEC 17025) and as the proficiency testing provider Proftest SYKE PT01 (EN ISO/IEC 17043, www.finas.fi).

This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides information about performance of the participants as well as comparability of the results at a more general level. The success of the proficiency test requires confidential co-operation between the provider and participants.

Thank you for your co-operation

Helsingissä 25. helmikuuta 2013 / Helsinki 25 February 2013

Marja Luotola

Laboratorionjohtaja / Chief of Laboratory

1 INTRODUCTION

In October 2012 Proftest SYKE carried out the proficiency test (PT) for the analysis of volatile organic compounds (VOC) in water and soil. The test was carried out in accordance with the international standards, ISO/IEC 17043 [1] and ISO 13528 [2] as well as IUPAC technical report [3]. The SYKE laboratory has been accredited by the Finnish Accreditation Service as a proficiency testing provider Proftest SYKE PT01 on the field of the present PT (www.finas.fi).

2 ORGANIZING OF THE PROFICIENCY TEST

2.1 Responsibilities

Organizing laboratory:
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre,
Hakuninmaantie 6, 00430 Helsinki, Finland
Phone: +358 20 610 123
Fax: +358 9 448 320

The responsibilities in organizing the PT were as follows:

Kaija Korhonen-Ylönen, coordinator
Jari Nuutinen, analytical expert and substitute of coordinator
Helena Tanttu, technical assistant
Markku Ilmakunnas, technical assistant, layout of the report
Keijo Tervonen, technical assistant
Sari Lanteri, technical assistant
Ritva Väisänen, technical assistant

2.2 Participants

In total, 15 laboratories from Czech Republic, Denmark, Finland, Hungary, Norway and Sweden participated in this PT (Appendix 1). One laboratory reported two results measured by different analytical methods. About 75 % of the participating laboratories used accredited analytical methods for at least a part of the measurements. The organizing laboratory (SYKE) has the code 8 in the result tables.

2.3 Samples and their delivery

The synthetic solution A1V and the addition standard solutions for the water sample N2V and the soil sample M3V was prepared gravimetrically from individual compounds by diluting to the final concentration (Appendix 2). Both the soil sample M3V and the water sample N2V were spiked with a known amount of the addition solution. The preparation of the samples is shown more detail in Appendix 2. The concentrations of the aromatic and chlorinated hydrocarbons in the samples A1V and N2V were checked against the NIST-traceable certified calibration solution (Supelco Organics Calibration Mix).

The samples were delivered 16 October 2012. They were requested to be analysed before 19 October 2012. All participants reported their results at the latest 29 October 2012 and the preliminary results were reported to the participants 1 November 2012.

2.4 Homogeneity and stability studies

Homogeneities of the sample N2V and the sample of M3V were tested by analysing all VOC compounds in four replicate determinations from six sub samples (Appendix 3). Although homogenous criteria fulfilled for most VOC compounds in the water sample N2V, the concentration of many VOC compounds decreased during the sample preparation after the sample number 10 and the results of these compounds were not assessed. In the concentrations of 1,2-dichloroethane, dichloromethane, chloroform and oxygenates were not observed any remarkable decrease and these results could be evaluated. According to the homogenous test the sample M3V was considered to be homogenous. Homogeneity of the artificial sample A1V was tested by analysing VOC compounds as duplicates from three samples, because the artifical samples are known to be homogenous according to literature and previous experience. Also according to the homogenous test the between-subsamples standard deviation was insignificant compared to the analytical standard deviation.

The stabilities of the samples A1V and M3V were checked during the sample transport to the participants. The sample vials were weighed at SYKE before the delivering and reweighed at the participating laboratory after the receiving. The differences of these two measurements should be < 0.5 %. One sample A1V and three samples M3V were sent again due to evaporation of solvent during the transport.

The stability test was carried out for all samples A1V, N2V and M3V. One part of the samples was stored at the room temperature and the other part at the temperature 4 °C over night. The samples were analysed 29 October (Appendix 4). The stability of the samples during the transport was mainly adequately good. According to the test the concentration of tetrachloroethene in the sample A1V could increase. This was taken into account in performance evaluation and the results of tetrachloroethene were not assessed. According to the test the concentration of carbontetrachloride and dichloromethane in the sample M3V could increase, if the temperature incresed to 20 °C during the transport. Nine laboratories reported the temperature of the receaved samples to be higher than 10 °C . This was taken into account in performance evaluation (Chapter 4).

Only the results of 1,2-dichloroethane, dichloromethane, chloroform and oxygenates from the water sample N2V was assessed and according to the test these compound were stable.

2.5 Feedback from the proficiency test

Appendix 5 contains the comments sent by the participants as well as the provider´s comments to some participants.

2.6 Processing of the data

2.6.1 Pretesting of the data

Before the statistical treatment, the data was tested according to the Kolmogorov-Smirnov normality test and the possible extreme values were rejected as the outliers according to the Hampel test (H in the results sheets). Also before the robust calculation some extreme outliers were rejected in case that the results deviated from the robust mean more than 50 % or in the case that the results was reported erroneously (e.g. wrong unit).

The replicate results were tested using the Cochran test (C in the result sheets). In case that the result had been reported to be lower than detection limit, it had not been included in the statistical calculation of the results (H in the results sheets). More detailed information of the testing and

statistical treatment of the PT data is available on the internet in the guide for participating laboratories in SYKE proficiency testing schemes (www.environment.fi/syke/proftest).

2.6.2 Assigned value

The assigned values and their uncertainties are presented in Appendix 6. The calculated concentrations were used as the assigned values for the concentrations of all measurements in the artificial sample A1V and the water sample N2V. The expanded uncertainty of the assigned value (k = 2) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. In all cases the uncertainty was < 2 %. The main resource of the uncertainty was impurity of the stock solutions.

The means of the reported results were used as the assigned value for the measurements of the soil sample M3V. The uncertainty of the assigned value was calculated using the standard deviation of the reported results. It was assumed that the uncertainty of mean included the effects of sample inhomogeneity and short term stability. In the sample M3V the uncertainties of the assigned values varied from 5 % to 18 %. After reporting of the preliminary results no changes to the assigned values have been done.

2.6.3 Standard deviation for proficiency assessment and z score

The performance evaluation was based on z score, which was calculated using the estimated standard deviation for proficiency assessment (s_p). The standard deviation for proficiency assessment was estimated on basis of the type of the sample, the concentration of the element, the results of homogeneity and stability testing, the uncertainties of the assigned values and the long-term variation in former proficiency tests. After the preliminary performance evaluation the total standard deviations were changed as follows:

Sample	Analyte / Sample	Change of s_p	Impact on performance evaluation
A1V	**124TCBz**	20 % →15 %	No effect on the number of satisfactory results.
M3V	**DCM**	40 % →30 %	No effect on the number of satisfactory results.
A1V **N2V** **M3V**	**TECEe** **124TCBz, Bz, c12DCEe, CCl4, ETBz, mpXYL, oXYL, t12DCEe, TCEe, TECTe, TOL** **t12DCEe**	s_p could not be estimated reliable	Performance evaluation was not carried out.

The reliability of the assigned value was statistically tested according to the IUPAC Technical report [3]. The criterion was $u/s_p \leq 0.3$, where u is the standard uncertainty of the assigned value and s_p the standard deviation for proficiency assessment. Due to low number of the participants the criterion was not met in every case, which is indicated that the following assigned values had high uncertainty:

Sample	Measurement
M3V	Bz, 124TCBz, 12DCEa, c12DCEe, CHCl3, DCM, ETBE, ETBz, mpXYL, MTBE, oXYL, TAME

3 RESULTS AND CONCLUSIONS

3.1 Results

The results and the performance of each laboratory are presented in Appendix 8 and the summary of the results in Table 1. The results and their uncertainties are presented graphically in Appendix 9. Explanations for the result sheets are presented in Appendix 7. The summary of the performance evaluation (z scores) is presented in Appendix 10.

Table 1. Summary of the proficiency test SYKE 8/2012.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2*Targ SD%	Accepted z-val%
124TCBz	A1V	µg/ml	0,97	0.93	0.98	1.01	0.31	31,5	11	15	45
	M3V	mg/kg	2,35	2.35	2.37	2.28	0.42	17,8	11	30	91
	N2V	µg/l	10,12	8.44	8.49	8.44	2.44	28,8	11		
12DCEa	A1V	µg/ml	2,26	2.11	2.15	2.18	0.19	8,9	11	15	73
	M3V	mg/kg	5,17	5.17	5.12	5.17	0.85	16,6	11	30	91
	N2V	µg/l	23,53	22.17	22.17	21.45	3.02	13,6	11	30	100
Bz	A1V	µg/ml	0,79	0.80	0.81	0.81	0.17	21,1	15	15	60
	M3V	mg/kg	1	1.00	1.00	1.00	0.19	19,3	15	30	87
	N2V	µg/l	2,82	2.40	2.33	2.35	0.44	19	15		
c12DCEe	A1V	µg/ml	3,63	3.46	3.57	3.53	0.45	12,7	10	15	70
	M3V	mg/kg	7,65	7.65	7.65	7.71	1.23	16,1	9	30	100
	N2V	µg/l	37,74	33.87	33.85	32.10	7.74	22,9	10		
CCl4	A1V	µg/ml	0,77	0.73	0.73	0.76	0.14	18,7	13	15	67
	M3V	mg/kg	1,45	1.45	1.45	1.44	0.19	13,4	11	30	80
	N2V	µg/l	8,02	5.88	5.98	6.25	1.60	26,8	13		
CHCl3	A1V	µg/ml	1,06	1.06	1.08	1.06	0.23	21	13	15	50
	M3V	mg/kg	2,23	2.23	2.18	2.24	0.34	15,4	11	30	100
	N2V	µg/l	10,97	10.70	10.70	10.12	2.30	21,5	13	30	100
DCM	A1V	µg/ml	0,95	0.84	0.91	0.87	0.22	24,4	12	15	42
	M3V	mg/kg	1,72	1.72	1.74	1.75	0.40	22,9	10	30	89
	N2V	µg/l	9,85	7.97	7.89	7.76	1.37	17,4	12	30	82
ETBE	A1V	µg/ml	1,21	1.30	1.30	1.34	0.28	21,6	8	15	50
	M3V	mg/kg	2,38	2.38	2.38	2.37	0.46	19,4	7	30	100
	N2V	µg/l	4,54	3.85	3.85	3.97	0.47	12,2	8	30	75
ETBz	A1V	µg/ml	1,06	1.00	1.00	1.07	0.30	30,5	15	15	40
	M3V	mg/kg	1,48	1.48	1.51	1.53	0.34	22,4	15	30	80
	N2V	µg/l	3,79	2.74	2.73	2.86	0.96	35,2	15		
mpXYL	A1V	µg/ml	4,42	4.27	4.24	4.27	0.90	21,3	15	15	53
	M3V	mg/kg	6,38	6.38	6.45	6.43	1.31	20,3	15	30	87
	N2V	µg/l	11,17	11.17	11.27	11.90	3.64	32,3	15		
MTBE	A1V	µg/ml	5,26	5.54	5.41	5.28	1.23	22,8	13	15	46
	M3V	mg/kg	11,53	11.53	11.53	10.70	3.18	27,6	11	30	82
	N2V	µg/l	19,72	18.25	18.07	18.42	3.63	20,1	13	30	85
oXYL	A1V	µg/ml	1,72	1.72	1.71	1.77	0.40	23,5	15	15	53
	M3V	mg/kg	2,68	2.68	2.66	2.70	0.47	17,5	15	30	87
	N2V	µg/l	4,14	4.14	4.14	4.25	1.36	32,7	15		
t12DCEe	A1V	µg/ml	0,98	0.89	0.90	0.89	0.15	16,9	12	15	58
	M3V	mg/kg	1,77	1.77	1.77	1.76	0.62	35	11		
	N2V	µg/l	10,19	8.20	8.12	7.29	2.54	31,3	12		
TAME	A1V	µg/ml	1,83	1.80	1.80	1.76	0.50	27,5	10	15	30
	M3V	mg/kg	3,74	3.74	3.68	3.60	0.81	22,1	10	30	80
	N2V	µg/l	6,86	6.15	6.67	6.03	2.77	41,6	10	30	67
TCEe	A1V	µg/ml	7,88	7.72	7.68	7.69	2.34	30,4	14	15	29
	M3V	mg/kg	12,8	12.80	12.64	13.00	3.40	26,9	12	40	92
	N2V	µg/l	29,56	20.20	21.35	19.99	8.49	39,8	14		
TECEe	A1V	µg/ml	14,22	15.95	15.68	15.85	3.52	22,4	14		
	M3V	mg/kg	19,93	19.93	21.56	20.30	4.29	19,9	12	40	92
	N2V	µg/l	50,85	38.92	39.17	39.17	9.61	24,5	14		
TOL	A1V	µg/ml	3,02	3.00	3.07	3.07	0.35	11,5	15	15	67
	M3V	mg/kg	4,31	4.31	4.32	4.40	0.63	14,7	15	30	87
	N2V	µg/l	10,8	9.33	9.05	8.95	1.70	18,7	15		

Ass. val. -the assigned value, Mean- the mean value, Mean rob- the robust mean, Md- the median value, SD rob- the robust standard deviation, SD rob % - the robust standard deviation as percents, Num of Labs- the number of the participants, 2*Targ. SD%- the total standard deviation for proficiency assessment at the 95% confidence interval (=2*s_p), Accepted z-val% - the amount of satisfactory z scores.

The robust deviations of the assessed results of aromatic compounds varied from 12 % to 32 % and of the assessed results of chlorinated compounds from 9 % to 24 %. The robust deviations of the results of oxygenates were between 12 and 42 % (Table 1).

In this PT the participants were requested to report duplicate results for all measurements. The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 2.

Table 2. Results of the replicate determinations (ANOVA statistics).

Analyte	Sample	Unit	Ass. val.	Mean	Md	sw	sb	st	sw %	sb %	st %	2*Targ SD %	Num of labs	Ac-cepted. z-val %
124TCBz	A1V	µg/ml	0,97	0,9316	0,925	0,02732	0,2311	0,2327	2,9	25	25	15	11	45
	M3V	mg/kg	2,35	2,322	2,28	0,111	0,3995	0,4146	4,8	17	18	30	11	91
	N2V	µg/l	10,12	8,444	8,435	0,3171	2,223	2,246	3,8	26	27		11	
12DCEa	A1V	µg/ml	2,26	2,115	2,11	0,07713	0,1324	0,1532	3,6	6,3	7,2	15	11	73
	M3V	mg/kg	5,17	5,157	5,17	0,3479	0,8427	0,9117	6,7	16	18	30	11	91
	N2V	µg/l	23,53	22,17	21,45	0,6607	2,622	2,704	3	12	12	30	10	100
Bz	A1V	µg/ml	0,79	0,7952	0,7835	0,02166	0,1128	0,1148	2,7	14	14	15	15	60
	M3V	mg/kg	1	0,9955	0,9901	0,03283	0,1839	0,1868	3,3	18	19	30	15	87
	N2V	µg/l	2,82	2,399	2,295	0,08258	0,5295	0,5359	3,4	22	22		14	
c12DCEe	A1V	µg/ml	3,63	3,455	3,5	0,1315	0,3805	0,4026	3,8	11	12	15	10	70
	M3V	mg/kg	7,65	7,621	7,71	0,4283	1,07	1,153	5,6	14	15	30	9	100
	N2V	µg/l	37,74	33,87	32,1	1,101	6,819	6,907	3,3	20	20		10	
CCl4	A1V	µg/ml	0,77	0,7278	0,755	0,02754	0,1306	0,1335	3,8	18	18	15	12	67
	M3V	mg/kg	1,45	1,446	1,44	0,104	0,0922	0,139	7,2	6,4	9,6	30	10	80
	N2V	µg/l	8,02	5,885	6,25	0,191	1,605	1,617	3,2	27	27		12	
CHCl3	A1V	µg/ml	1,06	1,063	1,02	0,06265	0,2175	0,2263	5,9	20	21	15	12	50
	M3V	mg/kg	2,23	2,216	2,31	0,07463	0,2538	0,2645	3,4	11	12	30	10	90
	N2V	µg/l	10,97	10,7	10,12	0,3393	2,016	2,045	3,2	19	19	30	12	100
DCM	A1V	µg/ml	0,95	0,8386	0,8425	0,04076	0,1152	0,1222	4,9	14	15	15	12	42
	M3V	mg/kg	1,72	1,709	1,75	0,05345	0,3906	0,3942	3,1	23	23	30	9	89
	N2V	µg/l	9,85	7,968	7,76	0,2715	1,345	1,372	3,4	17	17	30	11	82
ETBE	A1V	µg/ml	1,21	1,298	1,29	0,04957	0,2447	0,2497	3,8	19	19	15	8	50
	M3V	mg/kg	2,38	2,364	2,37	0,1561	0,3996	0,429	6,6	17	18	30	7	100
	N2V	µg/l	4,54	3,85	3,735	0,2139	0,384	0,4396	5,6	10	11	30	8	75
ETBz	A1V	µg/ml	1,06	1	1,014	0,07276	0,4048	0,4113	7,3	40	41	15	15	40
	M3V	mg/kg	1,48	1,467	1,51	0,03891	0,3129	0,3154	2,7	21	21	30	15	80
	N2V	µg/l	3,79	2,745	2,86	0,1487	0,8711	0,8837	5,4	32	32		14	
mpXYL	A1V	µg/ml	4,42	4,267	4,22	0,2632	0,6743	0,7239	6,2	16	17	15	15	53
	M3V	mg/kg	6,38	6,331	6,294	0,121	1,222	1,228	1,9	19	19	30	15	80
	N2V	µg/l	11,17	11,17	11,9	0,4487	3,386	3,416	4	30	31		15	
MTBE	A1V	µg/ml	5,26	5,537	5,238	0,3202	1,357	1,394	5,8	25	25	15	13	46
	M3V	mg/kg	11,53	11,53	10,7	0,6568	2,838	2,913	5,7	25	25	30	11	82
	N2V	µg/l	19,72	18,25	17,45	0,56	3,546	3,59	3,1	19	20	30	13	85
oXYL	A1V	µg/ml	1,72	1,719	1,745	0,09458	0,3046	0,3189	5,5	18	19	15	15	53
	M3V	mg/kg	2,68	2,654	2,7	0,06553	0,5188	0,5229	2,5	20	20	30	15	80
	N2V	µg/l	4,14	4,143	4,245	0,1568	1,19	1,2	3,8	29	29		14	
t12DCEe	A1V	µg/ml	0,98	0,8947	0,87	0,05821	0,1398	0,1514	6,5	16	17	15	12	58
	M3V	mg/kg	1,77	1,772	1,762	0,1038	0,5564	0,566	5,9	31	32		11	
	N2V	µg/l	10,19	8,198	7,285	0,3061	2,385	2,404	3,7	29	29		11	
TAME	A1V	µg/ml	1,83	1,802	1,723	0,06152	0,4352	0,4395	3,4	24	24	15	10	30
	M3V	mg/kg	3,74	3,715	3,6	0,26	0,8582	0,8967	7	23	24	30	10	80
	N2V	µg/l	6,86	6,149	5,495	0,3372	1,997	2,026	5,5	32	33	30	9	67
TCEe	A1V	µg/ml	7,88	7,721	7,545	0,2184	2,134	2,145	2,8	28	28	15	14	29
	M3V	mg/kg	12,8	12,94	13	0,639	3,282	3,344	4,9	25	26	40	12	92
	N2V	µg/l	29,56	20,2	18,93	0,7793	7,168	7,21	3,9	35	36		14	
TECEe	A1V	µg/ml	14,22	15,95	15,05	0,5897	3,971	4,014	3,7	25	25		14	
	M3V	mg/kg	19,93	19,85	20,3	0,7899	6,818	6,864	4	34	35	40	12	92
	N2V	µg/l	50,85	38,92	39,17	0,9048	10,43	10,47	2,3	27	27		14	
TOL	A1V	µg/ml	3,02	3,002	3,035	0,117	0,2472	0,2734	3,9	8,2	9,1	15	15	67
	M3V	mg/kg	4,31	4,285	4,4	0,1786	0,7446	0,7657	4,2	17	18	30	15	87
	N2V	µg/l	10,8	9,329	8,95	0,2351	2,209	2,222	2,5	24	24		15	

Ass. val. - assigned value, Md - median, sw - repeatability standard error, sb - standard error between laboratories, st - reproducibility standard error

The within-laboratory standard deviation, s_w, describes the repeatability of measurements. While the between-laboratory standard deviation, s_b, describes the reproducibility of measurements. In this PT the reproducibility (s_b) was an average from 2 to 12 times higher than the repeatability (s_w). For the robust methods, the ratio s_b/s_w, should be between 2 and 3.

3.2 Analytical methods and status to the results

The analytical methods used by the participants are presented more detailed in Appendix 11.1.

VOC compounds in water

VOC compound were determined using the methods based on several standards [4-7]. One laboratory extracted VOC compounds from water with pentan extraction. All other participants used either headspace or purge & trap –technique without liquid-liquid extraction. Most participants used GC-MS technique. With the GC-MS technique at least toluene-d8 was used as internal standard (Appendix 11.1). Analytical methods were coded by coordinator based on the measurement technique as follows:

Code	Measurement tecnique	Number of participants
Method 1	GC-MS	11
Method 2	GC-FID+ECD	1
Method 3	GC-FID	2
Method 4	Not specified	1

Statistical comparison between methods was not possible due to the low number of the results, but according to the graphical presentation the unsatisfactory results were not coused based on applied technique (Appendix 11.2).

VOC compounds in soil

Determination of VOC compounds from soil sample mostly based on ISO standard 22155 [7]. Extraction was mostly done by shaking. Only one participant heated the sample in headspace vial and one participant used both shaking and ultrasonication. Most participants used headspace as injection technique and only one split-technique. Equipment technique was mostly GC-MS and only one participant used GC-FID. Analytical methods were coded by coordinator according teh measurement technique as follows:

Code	Measurement tecnique	Number of participants
Method 1	GC-MS	11
Method 2	GC-FID+ECD	-
Method 3	GC-FID	2
Method 4	Not specified	1

Statistical comparison between GC-MS and GC-FID was not possible, but according to the graphical presentation the unsatisfactory results were not due to the applied technique (Appendix 11.2).

3.3 Uncertainties of the results

Most laboratories (85 %) reported the expanded uncertainties with their results (Appendix 9). The reported uncertainties varied greatly, especially in the analysis of water samples (Table 3). Most laboratories estimated uncertainties using the data of validation and internal quality control (Meth 3). The reported evaluation procedures of the uncertainties did not explain the high variation between the reported uncertainties (Appendix 12). It is evident, that harmonization in the estimation of uncertainties should be continued.

Table 3. The range of the expanded measurement uncertainties (k=2) reported with the results in the PT8/2012.

Analyte	A1V %	N2V %	M3V %
Benzene	10–30	10–100	15–36
Ethylbenzene	10–30	10–100	15–40
Toluene	10–30	10–100	15–37
o-Xylene	10–30	10–100	15–42
m/p-Xylene	10–30	10–100	15–41
1,2,4-Trichlorobenzene	20–30	14–100	20–44
Carbontetrachloride	10–50	10–100	20–40
Chloroform	10–50	10–100	20–37
1,2-Dichloroethane	10–30	10–100	20–39
***cis*-1,2-Dichloroethane**	10–30	10–50	15–43
***trans*-1,2-Dichloroethane**	10–30	10–100	15–39
Dichloromethane	10–40	10–100	10–42
Trichloroethene	10–50	10–60	20–41
Tetrachloroethene	10–50	10–60	20–10
ETBE	15–30	15–100	20–38
MTBE	10–30	10–60	20–42
TAME	15–30	20–100	20–41

4 EVALUATION OF PERFORMANCE

The evaluation of the participants was based on z scores, which were calculated using the estimated standard deviation for proficiency assessment. The results were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

The calculated z scores are presented with the results of each participant (Appendix 8) and graphical presentation of the results with their uncertainties is shown in Appendix 9. The summary of z scores is presented in Appendix 10.

In total, 71 % of the total result data in this PT were satisfactory. Three quarters of the participants used accredited methods and 75 % of these results were satisfactory (Appendix 10).

The summary of the performance evaluation is shown in Table 4.

Table 4. Summary of the performance evaluation in the proficiency test 8/2012.

Analyte / Sample	$2 \cdot s_p$	Satisfactory results, %	Remarks
Aromatics / A1V	15	53	A few of the results were questionable and 42 % were unsatisfactory.
Chlorinated hydrocarbons / A1V	15	56	The results of tetrachloroethene were not assessed because of a suspicion of instability of analyte. 30 % of the results were unsatisfactory and 14 % questionable. The results of TeCEe were not assessed.
Oxygenates / A1V	15	42	40 % of the results were unsatisfactory and 18 % questionable. Difficulties especially in measurements of TAME.
Aromatics / N2V	-	-	The results were not assessed by the provider because the decreasing trend in the concentration according to the sub sampling number. The participant can compare one´s results to the assigned values, if the sample bottle number of the sample N2V was <10.
Chlorinated hydrocarbons / N2V	30	94	Only the results of 1,2-dichloroethene, chloroform and dichloromethane were assessed and the performance was mainly good. There were two questionable results and no unsatisfactory result.
Oxygenates / N2V	30	76	21 % of the results were unsatisfactory and only one result was questionable.
Aromatics / M3V	30	87	Only few of the results were questionable and five result were unsatisfactory. Only informative assessment for Bz, 124TCBz, mpXYL, oXYL.
Chlorinated hydrocarbons/ M3V	30–40	92	The performance was mainly good. Only few of the results were questionable and one result was unsatisfactory. The results of t12DCEe were not assessed. Only informative assessment for 12DCEa, c12DCEe, TCEe, TECEe.
Oxygenates / M3V	30	87	Mainly good performance. 13 % of the results were questionable and no unsatisfactory result.

s_p = standard deviation for proficiency assessment.

Satisfactory results for the A1V sample were surprisingly low. The method for the analyzing the A1V sample were not asked from the participants. The sample A1V should have been measured as the calibration standards.

According to the stability test the concentration of carbontetrachloride and dichloromethane in the sample M3V could decrease, if the temperature increased to 20 °C during the transport. Ten laboratories reported the temperature of the samples between 10–17 °C and five of these laboratories had measured carbontetrachloride and dichloromethane. The performance of these laboratories has been studied below:

Analyte	z scores	Conclusions
CCl_4	Four satisfactory results, one z score was 2.46	Duplicate results were 2.39 and 1.58, which indicated large deviation in the measurement.
DCM	Four satisfactory results, one z score was -2.84.	According to the stability test the concentration of DCM in the sample M3V could decrease, if the temperature increased during the transport.

For the priority substances of the European Union surface water directive 2008/105/EC the amount of the accepted z-values of the participants results for N2V sample were from 75 % to 100 % (Tables 1 and 5). Environmental quality standard values (EQS) for the surface waters in the directive are higher than the assigned value in this proficiency test for, DCM and CCl_4, and lower than the assigned value for $CHCl_3$, 124TCBz, 12DCEa, Bz, TCEe and TECEe. The limit of quantitation for the priority substances should be 1/3 of the EQS values.

Table 5. The environmental quality standard (EQS) values for the compounds in surface waters.

Compound	EQS µg/l		Compound	EQS µg/l
Benzene	10		Chloroform	2,5
Trichlorobenzenes	0,4		Carbontetrachloride	12
Tetrachloroethene	10		1,2-Dichloroethane	10
Trichloroethene	10		Dichloromethane	20

5 SUMMARY

Proftest SYKE carried out the proficiency test for the determinations of volatile organic compounds (VOC) in water and soil samples in October 2012. In total, 15 laboratories participated in the proficiency test, from which one laboratory sent two results. One artificial sample (A1V), one river water sample (N2V), and one soil sample (M3V) were delivered to the laboratories.

The calculated concentrations (samples A1V and N2V) or the means of the results reported by the participants (M3V) were used as the assigned values for the measurements. The uncertainties of the calculated assigned values were less than 3 %. Respectively the uncertainties of the consensus assigned values (the mean) were from 5.1 % to 21 %.

In total, 71 % of the total results in this PT were satisfactory when the deviations of 15–40 % from the assigned values were accepted.

5 YHTEENVETO

Proftest SYKE järjesti pätevyyskokeen haihtuvien orgaanisten yhdisteiden määrityksistä vesi- ja maanäytteistä lokakuussa 2012. Vesi- ja maanäytteen lisäksi osallistujalle toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 15 laboratoriota, joista yksi toimitti kahdet tulokset.

Synteettisessä näytteessä A1V ja vesinäytteessä N2V mittaussuureen vertailuarvona käytettiin laskennallista pitoisuutta ja maanäytteessä M3V osallistujien raportoimien tulosten keskiarvoa. VOC-yhdisteiden laskennallisten vertailuarvojen laajennetut epävarmuudet olivat 1–8 %. Yhdisteestä ja raportoitujen tulosten hajonnasta riippuen maanäytteessä vertailuarvon laajennetut epävarmuudet olivat 5–18 % (liite 6).

Synteettisten näytteiden tuloksissa sallittiin 15 %:n poikkeama vertailuarvosta, jolloin aromaattisten yhdisteiden tuloksista hyväksyttäviä oli 53 %, öljyn lisäaineiden tuloksista (ETBE, MTBE ja TAME) 42 % ja kloorattujen hiilivetyjen tuloksista 56 %. Vuoden 2010 vastaavassa vertailussa hyväksyttäviä tuloksia oli enemmän. Silloin aromaattisten hiilivetyjen tuloksista oli hyväksyttäviä 63, öljyn lisäaineiden tuloksista 72 % ja kloorattujen hiilivetyjen tuloksista 64 % [8].

Vesinäytteiden tuloksista arvioitiin ainoastaan dikloorimetaani-, kloroformi- 1,2-dikloorietaani-, ETBE-, MTBE- ja TAME-tulokset. Tuloksissa sallittiin 30 %:n poikkeama vertailuarvosta, jolloin hyväksyttäviä tuloksia oli 85 %.

Maanäytteen tulosten sallittiin poiketa vertailuarvosta 30–40 %, jolloin aromaattisten hiilivetyjen tuloksista oli hyväksyttäviä 87 %, öljyn lisäaineiden tuloksista 87 % ja sekä että kloorattujen hiilivetyjen tuloksia 92 %. Vuoden 2010 vastaavassa vertailussa sekä aromaattisten yhdisteiden tuloksista oli hyväksyttäviä 88 %, öljyn lisäaineiden tuloksista 100 % sekä kloorattujen hiilivetyjen 87 % [8].

Tässä pätevyyskokeessa koko aineistossa hyväksyttäviä tuloksia oli yhteensä 72 %. Osallistujista 75 % käytti määrityksissä akkreditoituja menetelmiä. Heidän tuloksistaan oli hyväksyttäviä 75 %.

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PREPARATION OF THE SAMPLES

Each individual stock solution was prepared by weighting methanol (10 ml) and from 0.15 to 0.34 g of the pure compound into a vial. The concentrations of the analytes in the individual stock solutions have been presented in the table 1.

The ARMixtue was prepared by weighing from 0.5 to 5.0 ml of the individual stock solutions (compounds shown in the table 1) into a vial. The final volume of the ARMixture was 12.4 ml. The CLMixture was prepared by weighing from 0.7 to 4.0 ml of the individual stock solution (compounds shown in the table 1) into a vial. The final volume of the CLMixture was 11.3 ml. The OXMixture was prepared by weighing from 1.5 to 5.8 ml of the individual stock solution (compounds shown in the table 1) into a vial. The final volume of the OXMixture was 14.2 ml.

Table 1. Concentrations of the stock solutions and the mixtures.

Compound producer, purity	**Stock solution, mg/ml**	**ARMixture mg/ml**	**CLMixture mg/ml**	**OXMixture mg/ml**
Benzene Fluka, 99.9 %	17.67	0.72		
Ethylbenzene Fluka, 99.9%	16.99	0.96		
Toluene Fluka, 99.9 %	17.13	2.74		
o-Xylene Fluka, 99.5 %	16.17	1.56		
p-Xylene Fluka, 99.5 %	16.51	4.01		
1,2,4-Trichlorobenzene Fluka, 99.4 %	28.22		2.54	
Carbontetrachloride Ehrenstorfer, 99.9 %	32.04		2.01	
Chloroform Fluka, 99.90%	30.42		2.75	
1,2-Dichloroethane Ehrenstorfer, 99.5 %	24.42		5.90	
cis-1,2-Dichloroethene Fluka, 97 %	26.91		9.46	
trans-1,2-Dichloroethene Fluka, 98.0 %	27.98		2.55	
Dichloromethane Aldrich, 99.9	33.69		2.47	
Trichloroethene Riedel-de Haën, 99.9 %	29.40			9.92
Tetrachloroethene Fluka, 99.0 %	31.52	12.88		
ETBE Fluka, 97.0 %	14.67			1.52
MTBE Sigma Aldrich, 99.8 %	16.36			6.62
TAME Aldrich, 97.0 %	14.94			2.30

PREPARATION OF THE SAMPLES

The addition solution 1 for the sample A1V was prepared by weighting 10 ml of methanol, 1.5 ml of the ARMixture, 0.5 ml of the CLMixture and 1.0 ml of the OXMixture into a vial. The sample A1V was prepared by diluting 1 ml of the addition solution 1 with 100 ml methanol (Table 2).

The addition solution 2 for the sample N2V was prepared by weighting 4 ml of the ARMixture, 4 ml of the CLMixture and 3 ml of the OXMixture into a vial. Addition solution 2 was diluted three times with methanol in ratio 1:10 (v/v) and the final methanol solution (190 ml) was diluted with 20 litre of surface water to produce the sample N2V (Table 2).

The addition solution 3 was prepared by weighting 50 ml of methanol, 2 ml of the ARMixture, 1 ml of the CLMixture and 2 ml of the OXMixture. The sample M3V was made by mixing 20 g of dry soil, 4 ml of water, 1 ml of the addition solution 3 and 20 ml of methanol (Table 2).

Table 2. Concentrations of the addition solutions (1, 2, 3) and the samples (A1V, N2V, M3V).

Measurement	**Addition solution 1 mg/ml**	**Addition solution 2 mg/ml**	**Addition solution 3 mg/ml**	**A1V µg/ml**	**N2V µg/l**	**M3V mg/kg**
Benzene	0.080	0.259	0.026	0.79	2.82	1.31
Ethylbenzene	0.107	0.348	0.035	1.06	3.79	1.76
Toluene	0.305	0.989	0.100	3.02	10.80	5.01
o-Xylene	0.174	0.562	0.057	1.72	6.14	2.85
p-Xylene	0.447	1.449	0.147	4.42	15.82	7.34
1,2,4-Trichlorobenzene	0.098	0.927	0.048	0.97	10.12	2.40
Carbontetra-chloride	0.078	0.734	0.038	0.77	8.02	1.91
Chloroform	0.107	1.005	0.052	1.06	10.97	2.61
1,2-Dichloroethane	0.229	2.155	0.112	2.26	23.53	5.59
cis-1,2-Dichloroethene	0.367	3.458	0.179	3.63	37.74	8.97
trans-1,2-Dichloroethene	0.099	0.933	0.048	0.98	10.19	2.42
Dichloromethane	0.096	0.903	0.047	0.95	9.85	1.34
Trichloroethene	0.797	2.708	0.356	7.88	29.56	23.59
Tetrachloroethene	1.438	4.659	0.472	14.22	50.85	17.78
ETBE	0.122	0.416	0.055	1.21	4.54	2.73
MTBE	0.532	1.806	0.237	5.26	19.72	11.86
TAME	0.185	0.629	0.083	1.83	6.86	4.13

TESTING OF HOMOGENEITY

The homogeneities of the samples N2V and M3V were tested by analysing six sub samples.

Measurement/ sample N2V	**Concentration ($\mu g\ l^{-1}$)**	**s_h %**	**s_p %**	**s_h**	**s_a**	**s_a/s_h**	**$s_a/s_h<0.5$?**	**s_{bb}**	**s_{bb}^2**	**c**	**$s_{bb}^2<c$?**
Benzene	3.62	11.5	-	0.42	0.022	0.05	YES	0.18	0.033	0.035	YES
Ethylbenzene	4.53	12.5	-	0.57	0.022	0.04	YES	0.25	0.061	0.064	YES
Toluene	9.42	14	-	1.32	0.270	0.20	YES	0.67	0.453	0.469	YES
o-Xylene	6.21	15	-	0.04	0.704	0.04	YES	0.38	0.15	0.17	YES
m+p-Xylene	13.73	18.5	-	2.47	0.063	0.03	YES	1.08	1.17	1.22	YES
1,2,4-Trichlorobenzene	8.60	20	-	8.60	0.118	0.07	YES	0.75	0.56	0.61	YES
Carbontetrachloride	7.10	27	-	1.92	0.091	0.05	YES	1.96	3.86	3.92	YES
Chloroform	10.83	9	15	0.97	0.157	0.16	YES	0.45	0.20	0.23	YES
1,2-Dichloroethane	24.04	2.5	15	0.60	0.29	0.48	YES	0.25	0.06	0.21	YES
cis-1,2-Dichloroethene	32.18	13.5	-	4.34	0.314	0.07	YES	1.96	3.86	3.92	YES
trans-1,2-Dichloroethene	8.41	22	-	1.85	0.84	0.05	YES	0.80	0.64	0.69	YES
Dichloromethane	9.22	5	15	0.46	0.116	0.25	YES	0.24	0.06	0.07	YES
Trichloroethene	23.47	23.5	-	5.52	0.21	0.04	YES	2.46	6.03	6.12	YES
Tetrachloroethene	44.82	28	-	12.6	0.704	0.06	YES	5.59	31.3	32.2	YES
ETBE	5.98	6	15	0.36	0.061	0.17	YES	0.16	0.025	0.032	YES
MTBE	19.36	5	15	0.97	0.23	0.23	YES	0.50	0.25	0.27	YES
TAME	8.25	7	15	0.58	0.07	0.13	YES	0.24	0.06	0.08	YES
Measurement/ sample M3V	**Concentration ($\mu g\ kg^{-1}$)**	**s_h %**	**s_p %**	**s_h**	**s_a**	**s_a/s_h**	**$s_a/s_h<0.5$?**	**s_{bb}**	**s_{bb}^2**	**c**	**$s_{bb}^2<c$?**
Benzene	0.90	18	15	0.16	0.04	0.27	YES	0.09	0.0084	0.0085	YES
Ethylbenzene	1.69	12	15	0.21	0.03	0.16	YES	0.09	0.008	0.01	YES
Toluene	4.44	15	15	0.67	0.13	0.20	YES	0.33	0.11	0.12	YES
o-Xylene	2.79	9	15	0.25	0.03	0.43	YES	0.04	0.001	0.007	YES
m+p-Xylene	6.44	12	15	0.77	0.17	0.22	YES	0.43	0.18	0.17	YES
1,2,4-Trichlorobenzene	2.44	5	15	0.12	0.05	0.42	YES	0.04	0.001	0.008	YES
Carbontetrachloride	1.54	10	15	0.15	0.07	0.46	YES	0.05	0.003	0.016	YES
Chloroform	2.23	10	15	0.22	0.09	0.40	YES	0.15	0.022	0.024	YES
1,2-Dichloroethane	5.40	6	15	0.32	0.14	0.44	YES	0.12	0.015	0.055	YES
cis-1,2-Dichloroethene	8.14	13	15	1.06	0.30	0.29	YES	0.61	0.373	0.377	YES
trans-1,2-Dichloroethene	1.48	35	-	0.52	0.13	0.26	YES	0.28	0.81	0.083	YES
Dichloromethane	1.74	12.5	15	0.22	0.10	0.45	YES	0.16	0.025	0.026	YES
Trichloroethene	14.66	17.5	20	2.57	0.64	0.25	YES	1.39	1.94	0.199	YES
Tetrachloroethene	24.88	19	20	4.72	1.13	0.24	YES	2.54	6.46	6.59	YES
ETBE	2.17	5	15	0.10	0.04	0.41	YES	0.04	0.001	0.006	YES
MTBE	10.58	5.5	15	0.58	0.27	0.47	YES	0.19	0.04	0.19	YES
TAME	3.47	5	15	0.17	0.08	0.44	YES	0.05	0.003	0.016	YES

Criteria for homogeinity:

$s_a/s_h<0.5$ and $s_{bb}^2<c$, where

s_p % = standard deviation for proficiency assessment
s_h % = standard deviation for testing of homogeneity
s_a = analytical deviation, standard deviation of the results within sub samples
s_{bb} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_a^2$, where
$s_{all}^2 = (0.3 \times s_p)^2$
F1 = 2.21 and
F2 = 1.69, when the number of sub samples is 6

Although the homogenous criteria was reached for most measurements in the water sample N2V, the concentration of most VOC compounds decreased during the sample preparation after the sample bottle number 10. However, no remarkable decrease in the concentration of 1, 2-dichloroethane, chloroform, dichloromethane and oxygenates was observed.

Homogenous criteria was reached for most measurements in the soil sample M3V. However, the standard deviation for testing of homogeneity (s_h) was high for the measurement of *trans*-1,2-dichloroethene. So, the results of *trans*-1,2-dichloroethene could not be assessed.

Conclusion: The water sample N2V could be regarded homogenous only for the analysis of 1, 2-dichloroethane, chloroform, dichloromethane and oxygenates (ETBE; MTBE; TAME).
The soil sample M3V could be regarded as homogenous except for the analysis of *trans*-1,2-dichloroethene. The results of *trans*-1,2-dichloroethene were not evaluated.

TESTING OF STABILITY

The samples were distributed 16 October 2012 and they were asked to analyse before 19 October 2012. Stability was tested from the samples A1V, N2N and M3V. The results have been shown in tables 1, 2 and 3.

Criterio for stability: $D < 0.3 \cdot s_p$, where
D = |the difference of results measured from the samples stored at the temperatures 4 and 20 °C|
s_p = standard deviation for proficiency assessment

Table 1. Stability of the sample A1V / concentration µg/ml.

Analyte	Assigned value	16 Oct	19 Oct 4 °C	19 Oct 20 °C	D	$0.3 \cdot s_p$	Test pasted?
Benzene	0.79	0.91	0.796	0.784	-0.01	0.02	yes
Ethylbenzene	1.06	1.09	1.100	1.111	0.01	0.03	yes
Toluene	3.02	3.13	2.969	2.992	0.02	0.07	yes
o-Xylene	1.72	1.86	1.788	1.786	-0.002	0.04	yes
m/p-Xylene	4.42	4.35	3.957	4.007	0.05	0.10	yes
1,2,4-Trichlorobenzene	0.97	0.97	1.038	1.034	-0.004	0.03	yes
Carbontetra-chloride	0.77	0.83	0.826	0.811	-0.015	0.0019	yes
Chloroform	1.06	1.18	0.860	0.858	-0.002	0.024	yes
1,2-Dichloroethane	2.26	2.44	2.204	2.132	-0,07	0.05	no[1)]
cis-1,2-Dichloroethene	3.63	3.83	3.663	3.649	-0.01	0.08	yes
trans-1,2-Dichloroethene	0.98	0,97	0.875	0.880	0.01	0.02	yes
Dichloromethane	0.95	0.95	0.842	0.801	-0.03	0.02	no[1)]
Trichloroethene	7.88	8.42	8.041	8.130	0.09	0.18	yes
Tetrachloroethene	14.22	16.95	17.70	18.25	0.55	0.32	no
ETBE	1.21	1.41	0.999	0.952	-0.05	0.03	no[1)]
MTBE	5.26	5.62	5.264	4.993	-0.27	0.12	no[1)]
TAME	1.83	2.01	1.702	1.626	-0.08	0.06	no[1)]

[1)] However the difference between the difference temperatures was within the daily variation of the method and within the variation between the subsamples. Thus, the stability was concluded to be satisfactory.

Conclusion: The stability of the samples during the transport was mainly good. According to the test the concentration of tetrachloroethene could increase, if the temperature increased to 20 °C during the transport. This was taken into account in performance evaluation and the results of tetrachloroethene were not assessed.

TESTING OF STABILITY

Table 2. Stability of the sample N2V / concentration µg/l.

Analyte	**Assigned value**	**16 Oct**	**19 Oct 4 °C**	**19 Oct 20 °C**	D	**0.3 · s_p**	**Test pasted?**
Benzene	2.82	3.26	3,43	3.29	-0.14	0.15	Yes
Ethylbenzene	3.79	4.12	4.35	4.04	-0.31	0.19	No
Toluene	10,80	9.29	8.99	8.30	-0.69	0.41	No
o-Xylene	4.14	5.14	4.90	4.20	-0,71	0.22	No
m/p-Xylene	11.17	13.12	11.42	10.38	-1.04	0.51	No
1,2,4-Trichlorobenzene	10.12	8.39	8.65	8.16	-0.49	0.39	No
Carbontetra-chloride	8.02	6.99	6.73	6.24	-0.49	0.30	No
Chloroform	10.97	10.72	10.00	9.60	-0.40	0.45	Yes
1,2-Dichloroethane	23.53	23.60	22.25	21.96	-0.30	1.00	Yes
cis-1,2-Dichloroethene	37.74	34.17	33.38	33.02	-1.35	1.50	Yes
trans-1,2-Dichloroethene	10.19	8.22	7.42	6.94	-0.48	0.56	Yes
Dichloromethane	9.85	8.84	7.20	7.01	-0.19	0.32	Yes
Trichloroethene	29.56	24.94	23.92	22.45	-1.47	1.08	No
Tetrachloroethene	50.85	49.74	47.08	44.29	-2.78	2.12	No
ETBE	4.54	6.17	3.77	3.63	-0.14	0.17	Yes
MTBE	19.72	20.32	17.51	17.02	-0.49	0.79	Yes
TAME	6.86	8.49	7.10	6.87	-0.23	0.32	Yes

Conclusion: Only the results of 1,2-dichloroethane, chloroform, dichloromethane and oxygenates (ETBE, MTBE, TAME) were evaluated. The stability of these compounds was good.

TESTING OF STABILITY

Table 3. Stability of the sample M3V / concentration mg/kg.

Analyte	**Assigned value**	**16 Oct**	**19 Oct 4 °C**	**19 Oct 20 °C**	D	**0.3 · s_p**	**Test pasted?**
Benzene	1.00	0.95	0.94	0.97	0.03	0.06	Yes
Ethylbenzene	1.48	1.46	1.58	1.55	-0.06	0.07	Yes
Toluene	4.31	3.87	4.33	4.15	-0.18	0.20	Yes
o-Xylene	2.68	2.54	2.70	2.66	-0.04	0.12	Yes
m/p-Xylene	6.38	5.43	6.08	5.92	-0.16	0.27	Yes
1,2,4-Trichlorobenzene	2.35	2.36	2.29	2.34	0.05	0.10	Yes
Carbontetra-chloride	1.45	1.05	1.35	1.16	-0.19	0.06	No
Chloroform	2.23	1.95	2.11	1.98	0.03	0.10	Yes[1)]
1,2-Dichloroethane	5.17	5.27	5.34	5.16	-0.18	0.24	Yes
cis-1,2-Dichloroethene	7.65	7.51	8.09	7.50	-0.01	0.36	Yes[1)]
trans-1,2-Dichloroethene	1.77	1.64	1.03	1.55	-0.09	0.11	Yes[1)]
Dichloromethane	1.72	1.37	1.46	1.21	-0.26	0.10	No
Trichloroethene	12.80	12.71	14.69	13.86	-0.83	0.88	Yes
Tetrachloroethene	19.93	21.81	26.21	24.63	-1.58	1.57	Yes
ETBE	2.38	1.86	1.82	1.78	-0.04	0.08	Yes
MTBE	11.53	10.76	10.36	10.12	-0.24	0.47	Yes
TAME	3.74	3.15	3.09	3.07	-0.02	0.14	Yes

[1)] D = |the difference of results measured from the samples stored at the temperatures 4 (16 Oct) and 20 °C|

Conclusion: According to the test concentration of carbontetrachloride and dichloromethane could decease, if the temperature increaced to 20 **°C** during the transport. This was taken into consideration in performance evaluation.

FEEDBACK FROM THE PROFICIENCY TEST

Feedback sent by the participants

Lab	Comment on the samples	Action/Proftest
1	The weight of the sample A1V was decreased during the transport more than 0.5 %.	A new sample was sent.
3	The sample A1V does not represent the real samples.	The purpose of the sample A1V was to check calibration. Usefulness of synthetic samples will be discussed in the Proftest steering group.
7, 13, 14	The weight of the sample M3V was decrease during the transport more than 0.5 %.	A new sample was sent.
All	On the electrical result sheet was guided to add the method code, although no method codes were given.	On the web page was added the information to leave method column empty in the result reporting step. The provider added the method codes in the data handling step.
Lab	**Comment on the results**	**Action/Proftest**
3	The laboratory reported the results of the sample A1V in the unit µg/l instead of µg/ml.	The results were handled as outliers in the statistical data treatment. If the results had been reported as the correct units, most of them should have been satisfactory.
10	The laboratory had reported the incorrect TeCEe results for the sample M3V. The correct results were 16.5 and 15.4 mg/kg.	The results were handled as outliers in the statistical data treatment. If the results had been reported correctly, they should have been satisfactory.
16	For calculation of the results in the soil sample M3V was used: 20 g soil and 25 ml of extraction solution (water + methanol).	Calculation has been correctly.

Feedback to the participants

Lab	Comments from the provider
14	The participant reported all results as accredited, but without any information about the used methods. The method code could not be added by the provider.

ASSIGNED VALUES AND THEIR UNCERTAINTIES

Analyte Abbreviation	Sample	Assigned value	Unit	Evaluation of the assigned value	Uncertainty ($U = 2\ u_c$), %
Benzene Bz	A1V	0.79	µg/ml	Calculated	<2
	M3V	1.00	mg/kg	Mean	12
Ethylbenzene ETBz	A1V	1.06	µg/ml	Calculated	<2
	M3V	1.48	mg/kg	Mean	15
Toluene TOL	A1V	3.02	µg/ml	Calculated	<2
	M3V	4.31	mg/kg	Mean	9.4
o-Xylene oXYL	A1V	1.72	µg/ml	Calculated	<2
	M3V	2.68	mg/kg	Mean	11
m/p-Xylene mpXYL	A1V	4.42	µg/ml	Calculated	<2
	M3V	6.38	mg/kg	Mean	13
1,2,4-Trichlorobenzene 124TCBz	A1V	0.97	µg/ml	Calculated	<2
	M3V	2.35	mg/kg	Mean	13
Carbontetrachloride CCl4	A1V	0.77	µg/ml	Calculated	<2
	M3V	1.45	mg/kg	Mean	10
Chloroform CHCl3	A1V	1.06	µg/ml	Calculated	<2
	N2V	10.97-	µg/l	Calculated	<2
	M3V	2.23	mg/kg	Mean	11
1,2-Dichloroethane 12DCEa	A1V	2.26	µg/ml	Calculated	<2
	N2V	23.53	µg/l	Calculated	<2
	M3V	5.17	mg/kg	Mean	12
cis-1,2-Dichloroethene c12DCEe	A1V	3.63	µg/ml	Calculated	<2
	M3V	7.65	mg/kg	Mean	13
trans-1,2-Dichloroethene t12DCEe	A1V	0.98	µg/ml	Calculated	<2
	M3V	1.77	mg/kg	Mean	
Dichloromethane DCM	A1V	0.95	µg/ml	Calculated	<2
	N2V	9.85	µg/l	Calculated	<2
	M3V	1.72	mg/kg	Mean	18
Trichloroethene TCEe	A1V	7.88	µg/ml	Calculated	<2
	M3V	12.8	mg/kg	Mean	19
Tetrachloroethene TECEe	A1V	14.22	µg/ml	Calculated	<2
	M3V	19.93	mg/kg	Mean	16
ETBE	A1V	1.21	µg/ml	Calculated	<2
	N2V	4.54	µg/l	Calculated	<2
	M3V	2.38	mg/kg	Mean	18
MTBE	A1V	5.26	µg/ml	Calculated	<2
	N2V	19.72	µg/l	Calculated	<2
	M3V	11.53	mg/kg	Mean	21
TAME	A1V	1.83	µg/ml	Calculated	<2
	N2V	6.86	µg/l	Calculated	<2
	M3V	3.74	mg/kg	Mean	11

TERMS IN THE RESULT TABLES

Results of each participants

Sample	the code of the sample
z-Graphics	z score - the graphical presentation
z value	calculated as follows: $z = (x_i - X)/s_p$, where x_i = the result of the individual laboratory X = the reference value (*the assigned value*) s_p = the target value of the standard deviation for proficiency assessment
Outl test OK	yes - the result passed the outlier test H = Hampel test (test for the mean value) C = Cochran test (replicate test)
Assigned value	the reference value
2* Targ SD %	the target value of total standard deviation for proficiency assessment (s_p) at the 95 % confidence level, equal $2 \cdot s_p$
Lab's result	the result reported by the participant (the mean value of the replicates)
Md.	Median
Mean	Mean
SD	Standard deviation
SD%	Standard deviation, %
Passed	The results passed the outlier test
Outl. failed	The results not passed the outlier test
Missing	i.e. < DL
Num of labs	the total number of the participants

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than $2 \cdot s_p$ from the assigned value
q – questionable ($-3 > z < -2$), negative error, the result deviates more than $2 \cdot s_p$ from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than $3 \cdot s_p$ from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than $3 \cdot s_p$ from the assigned value

Robust analysis

The data items are sorted in increasing order: $x_1, x_2, \ldots, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as follows:
x^* = median of x_i (i = 1, 2, ...,*p*)
s^* = 1,483 · median of $|x_i - x^*|$ (i = 1, 2, ...,*p*)
The mean x^* and s^* are updated as follows*:*
Calculate $\varphi = 1.5 \cdot s^*$. A new value is then calculated for each result x_i *(i = 1, 2 …p)*:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated as follows:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134 \sqrt{\sum_{i=1}^{p} (x_i^* - x^*)^2 / (p-1)}$$

Ref: Statistical methods for use in proficiency testing by inter laboratory comparisons, Annex C [3].

LIITE 8. RESULTS OF EACH PARTICIPANT

APPENDIX 8.

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 1																
124TCBz	µg/ml	A1V		-1,924	yes	0,97	15	0,83	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		-0,227	yes	2,35	30	2,27	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		7,25	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-1,091	yes	2,26	15	2,075	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		-0,335	yes	5,17	30	4,91	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		-0,575	yes	23,53	30	21,5	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		-1,097	yes	0,79	15	0,725	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		0,467	yes	1	30	1,07	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		2,2	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		-1,286	yes	3,63	15	3,28	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		0,044	yes	7,65	30	7,7	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		29,45	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		-1,645	yes	0,77	15	0,675	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		0,069	yes	1,45	30	1,465	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		5,295	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		-0,880	yes	1,06	15	0,99	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		0,239	yes	2,23	30	2,31	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		-1,012	yes	10,97	30	9,305	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		-2,596	yes	0,95	15	0,765	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		0,194	yes	1,72	30	1,77	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		-1,932	yes	9,85	30	6,995	7,76	7,968	1,341	16,8	10	1	1	12
ETBE	µg/ml	A1V		1,488	yes	1,21	15	1,345	1,29	1,298	0,2403	18,5	7	1	0	8
	mg/kg	M3V		0,616	yes	2,38	30	2,6	2,37	2,364	0,4144	17,5	7	0	0	7
	µg/l	N2V		-0,587	yes	4,54	30	4,14	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		-1,698	yes	1,06	15	0,925	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		0,969	yes	1,48	30	1,695	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		2,43	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-0,453	yes	4,42	15	4,27	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		0,977	yes	6,38	30	7,315	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		10,7	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		0,291	yes	5,26	15	5,375	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		-1,853	yes	11,53	30	8,325	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		-0,835	yes	19,72	30	17,25	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		-0,581	yes	1,72	15	1,645	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		0,709	yes	2,68	30	2,965	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		4,18	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-1,837	yes	0,98	15	0,845	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		1,91	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		6,79	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		3,716	yes	1,83	15	2,34	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		0,677	yes	3,74	30	4,12	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		-0,807	yes	6,86	30	6,03	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		-0,567	yes	7,88	15	7,545	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		0,566	yes	12,8	40	14,25	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		22	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		14,15	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		-0,083	yes	19,93	40	19,6	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		35,85	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		-0,684	yes	3,02	15	2,865	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		0,464	yes	4,31	30	4,61	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		7,985	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 2																
Bz	µg/ml	A1V		0,253	yes	0,79	15	0,805	0,7835	0,7952	0,1122	14,1	11	4	0	15
	µg/l	N2V			yes	2,82		1,835	2,295	2,399	0,5253	21,9	12	2	1	15
CCl4	µg/ml	A1V		-0,165	yes	0,77	15	0,7605	0,755	0,7278	0,1304	17,9	10	2	1	13
	µg/l	N2V			yes	8,02		2,44	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		-0,931	yes	1,06	15	0,986	1,02	1,063	0,2208	20,7	9	3	1	13
	µg/l	N2V		-0,377	yes	10,97	30	10,35	10,12	10,7	2,001	18,7	11	1	1	13
ETBE	µg/ml	A1V		0,992	yes	1,21	15	1,3	1,29	1,298	0,2403	18,5	7	1	0	8
	µg/l	N2V		-1,233	yes	4,54	30	3,7	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		-2,352	yes	1,06	15	0,873	1,014	1	0,4039	40,3	14	1	0	15
	µg/l	N2V			yes	3,79		2,54	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-1,991	yes	4,42	15	3,76	4,22	4,267	0,7101	16,6	12	3	0	15
	µg/l	N2V			yes	11,17		10,64	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		0,659	yes	5,26	15	5,52	5,238	5,537	1,365	24,6	12	1	0	13
	µg/l	N2V		-0,336	yes	19,72	30	18,73	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		-2,287	yes	1,72	15	1,425	1,745	1,719	0,3125	18,1	12	3	0	15
	µg/l	N2V			yes	4,14		4,12	4,245	4,143	1,178	28,4	14	0	1	15
TCEe	µg/ml	A1V		1,058	yes	7,88	15	8,505	7,545	7,721	2,102	27,2	13	1	0	14
	µg/l	N2V			yes	29,56		17,15	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		15,05	15,05	15,95	3,935	24,6	13	1	0	14
	µg/l	N2V			yes	50,85		16,23	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		-0,066	yes	3,02	15	3,005	3,035	3,002	0,2681	8,9	11	4	0	15
	µg/l	N2V			yes	10,8		6,94	8,95	9,329	2,184	23,4	15	0	0	15
Laboratory 3																
124TCBz	µg/ml	A1V		14210,0	H	0,97	15	1035	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		1,617	yes	2,35	30	2,92	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		9,91	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		13760,0	H	2,26	15	2335	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		0,451	yes	5,17	30	5,52	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		-0,320	yes	23,53	30	22,4	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		14060,0	H	0,79	15	834	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		0,933	yes	1	30	1,14	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		2,67	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		13390,0	H	3,63	15	3650	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		0,357	yes	7,65	30	8,06	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		34,3	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		13740,0	H	0,77	15	794,5	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		0,092	yes	1,45	30	1,47	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		7,15	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		14200,0	H	1,06	15	1130	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		0,837	yes	2,23	30	2,51	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		-0,225	yes	10,97	30	10,6	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		12270,0	H	0,95	15	875,5	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		1,008	yes	1,72	30	1,98	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		-1,151	yes	9,85	30	8,15	7,76	7,968	1,341	16,8	10	1	1	12
ETBE	µg/ml	A1V		14310,0	H	1,21	15	1300	1,29	1,298	0,2403	18,5	7	1	0	8
	mg/kg	M3V		0,756	yes	2,38	30	2,65	2,37	2,364	0,4144	17,5	7	0	0	7
	µg/l	N2V		-0,029	yes	4,54	30	4,52	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		13070,0	H	1,06	15	1040	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		1,216	yes	1,48	30	1,75	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		3,155	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		14260,0	H	4,42	15	4730	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		1,484	yes	6,38	30	7,80	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		13,55	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		14160,0	H	5,26	15	5590	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		0,040	yes	11,53	30	11,6	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		0,061	yes	19,72	30	19,9	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		15370,0	H	1,72	15	1985	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		1,866	yes	2,68	30	3,43	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		5,84	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		12800,0	H	0,98	15	941,5	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		1,68	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		8,45	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		14090,0	H	1,83	15	1935	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		0,713	yes	3,74	30	4,14	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		0,029	yes	6,86	30	6,89	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		8684,00	H	7,88	15	5140	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		-1,238	yes	12,8	40	9,63	13	12,94	3,273	25,2	12	0	0	12

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
	µg/l	N2V			yes	29,56		16,65	18,93	20,2	7,067	34,9	13	1	0	14
Laboratory 3																
TECEe	µg/ml	A1V			H	14,22		15100	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		0,444	yes	19,93	40	21,7	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		44	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		14360,0	H	3,02	15	3255	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		1,021	yes	4,31	30	4,97	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		10,15	8,95	9,329	2,184	23,4	15	0	0	15
Laboratory 4																
124TCBz	µg/ml	A1V		3,711	yes	0,97	15	1,24	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		1,234	yes	2,35	30	2,785	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		12,04	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		0,560	yes	2,26	15	2,355	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		0,264	yes	5,17	30	5,375	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		0,343	yes	23,53	30	24,74	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		-0,759	yes	0,79	15	0,745	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		0,167	yes	1	30	1,025	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		2,425	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		1,286	yes	3,63	15	3,98	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		-0,370	yes	7,65	30	7,225	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		38,98	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		1,299	yes	0,77	15	0,845	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		-0,207	yes	1,45	30	1,405	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		8,015	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		2,075	yes	1,06	15	1,225	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		0,508	yes	2,23	30	2,4	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		1,222	yes	10,97	30	12,98	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		0,772	yes	0,95	15	1,005	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		-0,233	yes	1,72	30	1,66	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		0,501	yes	9,85	30	10,59	7,76	7,968	1,341	16,8	10	1	1	12
ETBz	µg/ml	A1V		0,566	yes	1,06	15	1,105	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		0,135	yes	1,48	30	1,51	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		3,41	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		0,166	yes	4,42	15	4,475	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		0,256	yes	6,38	30	6,625	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		12,86	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		8,948	yes	5,26	15	8,79	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		1,920	yes	11,53	30	14,85	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		8,158	H	19,72	30	43,85	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		1,705	yes	1,72	15	1,94	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		0,274	yes	2,68	30	2,79	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		5,615	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		1,224	yes	0,98	15	1,07	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		1,43	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		9,945	7,285	8,198	2,347	28,6	11	0	1	12
TCEe	µg/ml	A1V		-1,777	yes	7,88	15	6,83	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		-0,586	yes	12,8	40	11,3	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		21,89	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		17,47	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		1,084	yes	19,93	40	24,25	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		49,13	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		1,236	yes	3,02	15	3,3	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		0,626	yes	4,31	30	4,715	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		10,21	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 5																
Bz	µg/ml	A1V		0,262	yes	0,79	15	0,8055	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		-1,700	yes	1	30	0,745	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		2,265	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		6,483	H	3,63	15	5,395	3,5	3,455	0,3904	11,2	8	2	0	10
	µg/l	N2V			yes	37,74		45,65	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		3,524	yes	0,77	15	0,9735	0,755	0,7278	0,1304	17,9	10	2	1	13
	µg/l	N2V			yes	8,02		7,515	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		6,855	yes	1,06	15	1,605	1,02	1,063	0,2208	20,7	9	3	1	13
	µg/l	N2V		1,750	yes	10,97	30	13,85	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		0,800	yes	0,95	15	1,007	0,8425	0,8386	0,1189	14,1	9	3	0	12
	µg/l	N2V		-1,019	yes	9,85	30	8,345	7,76	7,968	1,341	16,8	10	1	1	12
ETBz	µg/ml	A1V		-0,403	yes	1,06	15	1,028	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		-1,577	yes	1,48	30	1,13	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		2,915	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		0,181	yes	4,42	15	4,48	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		-2,116	yes	6,38	30	4,355	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		12,4	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		-1,521	yes	5,26	15	4,66	5,238	5,537	1,365	24,6	12	1	0	13
	µg/l	N2V		-0,412	yes	19,72	30	18,5	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		0,814	yes	1,72	15	1,825	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		-1,779	yes	2,68	30	1,965	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		4,975	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		1,905	yes	0,98	15	1,12	0,87	0,8947	0,1483	16,5	11	1	0	12
	µg/l	N2V			yes	10,19		8,89	7,285	8,198	2,347	28,6	11	0	1	12
TCEe	µg/ml	A1V		2,462	yes	7,88	15	9,335	7,545	7,721	2,102	27,2	13	1	0	14
	µg/l	N2V			yes	29,56		31,35	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		16,55	15,05	15,95	3,935	24,6	13	1	0	14
	µg/l	N2V			yes	50,85		48,95	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		0,773	yes	3,02	15	3,195	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		-2,645	yes	4,31	30	2,6	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		9,01	8,95	9,329	2,184	23,4	15	0	0	15
Laboratory 6																
Bz	µg/ml	A1V		-12,490	H	0,79	15	0,0499	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		-1,640	yes	1	30	0,754	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		1,92	2,295	2,399	0,5253	21,9	12	2	1	15
ETBz	µg/ml	A1V		-12,180	yes	1,06	15	0,092	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		-0,360	yes	1,48	30	1,4	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		3,49	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-12,180	H	4,42	15	0,381	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		-0,930	yes	6,38	30	5,49	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		14,54	11,9	11,17	3,357	30,0	15	0	0	15
oXYL	µg/ml	A1V		-12,110	H	1,72	15	0,1574	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		-0,572	yes	2,68	30	2,45	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		5,23	4,245	4,143	1,178	28,4	14	0	1	15
TOL	µg/ml	A1V		-12,200	H	3,02	15	0,257	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		-1,098	yes	4,31	30	3,6	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		15,76	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 7																
124TCBz	µg/ml	A1V		-0,619	yes	0,97	15	0,925	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		-0,468	yes	2,35	30	2,185	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		7,51	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-1,445	yes	2,26	15	2,015	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		-1,277	yes	5,17	30	4,18	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		-1,412	yes	23,53	30	18,55	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		0,844	yes	0,79	15	0,84	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		-0,333	yes	1	30	0,95	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		2,405	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		-0,698	yes	3,63	15	3,44	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		-1,621	yes	7,65	30	5,79	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		27,1	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		-3,810	yes	0,77	15	0,55	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		-3,103	H	1,45	30	0,775	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		4,015	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		-0,566	yes	1,06	15	1,015	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		-1,629	yes	2,23	30	1,685	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		-1,635	yes	10,97	30	8,28	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		-1,298	yes	0,95	15	0,8575	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		-1,512	yes	1,72	30	1,33	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		-1,909	yes	9,85	30	7,03	7,76	7,968	1,341	16,8	10	1	1	12
ETBE	µg/ml	A1V		-1,433	yes	1,21	15	1,08	1,29	1,298	0,2403	18,5	7	1	0	8
	mg/kg	M3V		-1,303	yes	2,38	30	1,915	2,37	2,364	0,4144	17,5	7	0	0	7
	µg/l	N2V		-1,307	yes	4,54	30	3,65	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		-4,780	yes	1,06	15	0,68	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		-2,748	yes	1,48	30	0,87	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		1,58	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-2,187	yes	4,42	15	3,695	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		-1,740	yes	6,38	30	4,715	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		6,585	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		-2,978	yes	5,26	15	4,085	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		-2,330	yes	11,53	30	7,5	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		-1,711	yes	19,72	30	14,66	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		-3,295	yes	1,72	15	1,295	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		-2,239	yes	2,68	30	1,78	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		2,63	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-3,061	yes	0,98	15	0,755	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		0,935	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		5,645	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		-5,027	yes	1,83	15	1,14	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		-2,406	yes	3,74	30	2,39	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		-2,731	yes	6,86	30	4,05	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		-2,276	yes	7,88	15	6,535	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		-1,113	yes	12,8	40	9,95	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		18,59	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		14,09	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		-0,936	yes	19,93	40	16,2	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		35,46	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		0,508	yes	3,02	15	3,135	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		0,379	yes	4,31	30	4,555	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		8,95	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 8																
124TCBz	µg/ml	A1V		0,825	yes	0,97	15	1,03	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		0,014	yes	2,35	30	2,355	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		8,435	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-0,620	yes	2,26	15	2,155	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		0,516	yes	5,17	30	5,57	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		-0,589	yes	23,53	30	21,45	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		0,051	yes	0,79	15	0,793	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		-0,437	yes	1	30	0,9345	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		3,4	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		-0,055	yes	3,63	15	3,615	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		0,606	yes	7,65	30	8,345	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		32,65	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		0,649	yes	0,77	15	0,8075	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		-0,184	yes	1,45	30	1,41	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		6,49	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		-2,780	yes	1,06	15	0,839	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		-0,090	yes	2,23	30	2,2	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		-0,830	yes	10,97	30	9,605	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		-1,754	yes	0,95	15	0,825	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		-0,562	yes	1,72	30	1,575	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		-2,014	yes	9,85	30	6,875	7,76	7,968	1,341	16,8	10	1	1	12
ETBE	µg/ml	A1V		-2,320	yes	1,21	15	0,9995	1,29	1,298	0,2403	18,5	7	1	0	8
	mg/kg	M3V		-1,485	yes	2,38	30	1,85	2,37	2,364	0,4144	17,5	7	0	0	7
	µg/l	N2V		-1,182	yes	4,54	30	3,735	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		0,566	yes	1,06	15	1,105	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		0,586	yes	1,48	30	1,61	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		4,39	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-1,327	yes	4,42	15	3,98	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		-0,172	yes	6,38	30	6,215	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		11,5	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		0,000	yes	5,26	15	5,26	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		-0,538	yes	11,53	30	10,6	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		-0,835	yes	19,72	30	17,25	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		0,543	yes	1,72	15	1,79	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		0,249	yes	2,68	30	2,78	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		5,09	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-1,469	yes	0,98	15	0,872	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		1,075	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		7,285	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		-0,838	yes	1,83	15	1,715	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		-1,105	yes	3,74	30	3,12	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		0,199	yes	6,86	30	7,065	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		0,195	yes	7,88	15	7,995	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		0,859	yes	12,8	40	15	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		23,45	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		17,5	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		1,811	yes	19,93	40	27,15	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		45,4	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		-0,177	yes	3,02	15	2,98	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		0,178	yes	4,31	30	4,425	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		8,975	8,95	9,329	2,184	23,4	15	0	0	15
Laboratory 9																
Bz	mg/kg	M3V		-0,060	yes	1	30	0,991	0,9901	0,9955	0,1835	18,4	14	1	0	15
ETBz	mg/kg	M3V		-0,586	yes	1,48	30	1,35	1,51	1,467	0,3095	21,1	14	1	0	15
mpXYL	mg/kg	M3V		-0,700	yes	6,38	30	5,71	6,294	6,331	1,205	19,0	14	1	0	15
oXYL	mg/kg	M3V		-0,522	yes	2,68	30	2,47	2,7	2,654	0,5133	19,3	14	1	0	15
TOL	mg/kg	M3V		-0,820	yes	4,31	30	3,78	4,4	4,285	0,7531	17,5	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 10																
124TCBz	µg/ml	A1V		-4,742	yes	0,97	15	0,625	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		-0,184	yes	2,35	30	2,285	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		6,03	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-2,153	yes	2,26	15	1,895	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		-1,135	yes	5,17	30	4,29	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		-0,962	yes	23,53	30	20,14	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		-3,072	yes	0,79	15	0,608	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		-0,407	yes	1	30	0,939	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		1,945	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		-3,563	yes	3,63	15	2,66	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		-1,259	yes	7,65	30	6,205	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		26,13	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		-4,745	yes	0,77	15	0,496	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		2,460	H	1,45	30	1,985	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		4,455	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		-2,686	yes	1,06	15	0,8465	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		-1,540	C	2,23	30	1,715	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		-1,525	yes	10,97	30	8,46	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		-4,435	yes	0,95	15	0,634	0,8425	0,8386	0,1189	14,1	9	3	0	12
	µg/l	N2V		-2,321	yes	9,85	30	6,42	7,76	7,968	1,341	16,8	10	1	1	12
ETBz	µg/ml	A1V		-3,031	yes	1,06	15	0,819	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		0,360	yes	1,48	30	1,56	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		2,235	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-3,650	yes	4,42	15	3,21	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		-0,063	yes	6,38	30	6,32	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		8,75	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		-2,357	yes	5,26	15	4,33	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		-1,278	yes	11,53	30	9,32	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		-1,430	yes	19,72	30	15,49	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		-2,636	yes	1,72	15	1,38	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		0,112	yes	2,68	30	2,725	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		3,475	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-5,041	yes	0,98	15	0,6095	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		1,37	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		5,62	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		-3,024	yes	1,83	15	1,415	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		0,151	yes	3,74	30	3,825	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		-1,890	yes	6,86	30	4,915	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		-3,875	yes	7,88	15	5,59	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		-0,273	yes	12,8	40	12,1	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		18,84	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		9,535	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		-4,502	yes	19,93	40	1,985	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		29,73	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		-3,179	yes	3,02	15	2,3	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		-0,572	yes	4,31	30	3,94	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		7,455	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 11																
124TCBz	µg/ml	A1V		17,880	H	0,97	15	2,271	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		-0,624	yes	2,35	30	2,13	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		10,3	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-1,705	yes	2,26	15	1,971	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		-1,296	yes	5,17	30	4,165	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		0,887	yes	23,53	30	26,66	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		1,511	yes	0,79	15	0,8795	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		0,733	yes	1	30	1,11	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		2,541	2,295	2,399	0,5253	21,9	12	2	1	15
CCl4	µg/ml	A1V		-1,082	yes	0,77	15	0,7075	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		-0,919	yes	1,45	30	1,25	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		7,065	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		18,710	H	1,06	15	2,548	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		-0,628	yes	2,23	30	2,02	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		1,699	yes	10,97	30	13,77	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		8,702	H	0,95	15	1,57	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		-2,837	yes	1,72	30	0,988	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		-1,064	yes	9,85	30	8,278	7,76	7,968	1,341	16,8	10	1	1	12
ETBE	µg/ml	A1V		5,036	yes	1,21	15	1,667	1,29	1,298	0,2403	18,5	7	1	0	8
	mg/kg	M3V		-0,196	yes	2,38	30	2,31	2,37	2,364	0,4144	17,5	7	0	0	7
	µg/l	N2V		4,742	H	4,54	30	7,769	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		-1,000	yes	1,06	15	0,9805	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		-0,608	yes	1,48	30	1,345	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		3,35	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-1,021	yes	4,42	15	4,082	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		-0,961	yes	6,38	30	5,46	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		14,04	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		-0,375	yes	5,26	15	5,112	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		2,295	yes	11,53	30	15,5	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		1,925	yes	19,72	30	25,41	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		-0,124	yes	1,72	15	1,704	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		-0,920	yes	2,68	30	2,31	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		3,425	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-0,238	yes	0,98	15	0,9625	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		2,1	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		12,78	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		-0,120	yes	1,83	15	1,813	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		-1,551	yes	3,74	30	2,87	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		3,431	yes	6,86	30	10,39	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		-3,339	yes	7,88	15	5,906	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		0,332	yes	12,8	40	13,65	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		26,38	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		11,92	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		-0,070	yes	19,93	40	19,65	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		40,54	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		0,024	yes	3,02	15	3,026	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		-0,472	yes	4,31	30	4,005	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		10,63	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 12																
124TCBz	µg/ml	A1V		0,893	yes	0,97	15	1,035	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		0,298	yes	2,35	30	2,455	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		9,75	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-0,826	yes	2,26	15	2,12	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		-0,335	yes	5,17	30	4,91	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		0,587	yes	23,53	30	25,6	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		3,376	C	0,79	15	0,99	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		3,933	H	1	30	1,59	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		3,5	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		0,514	yes	3,63	15	3,77	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		0,689	yes	7,65	30	8,44	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		44,05	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		-1,602	yes	0,77	15	0,6775	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		0,690	yes	1,45	30	1,6	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		6,35	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		-1,296	yes	1,06	15	0,957	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		-0,284	yes	2,23	30	2,135	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		0,899	yes	10,97	30	12,45	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		-2,596	yes	0,95	15	0,765	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		0,717	yes	1,72	30	1,905	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		0,203	yes	9,85	30	10,15	7,76	7,968	1,341	16,8	10	1	1	12
ETBE	µg/ml	A1V		3,802	yes	1,21	15	1,555	1,29	1,298	0,2403	18,5	7	1	0	8
	mg/kg	M3V		1,709	yes	2,38	30	2,99	2,37	2,364	0,4144	17,5	7	0	0	7
	µg/l	N2V		10,370	H	4,54	30	11,6	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		2,956	yes	1,06	15	1,295	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		4,730	H	1,48	30	2,53	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		3,3	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		2,097	yes	4,42	15	5,115	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		1,510	C	6,38	30	7,825	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		15,5	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		3,663	yes	5,26	15	6,705	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		1,255	yes	11,53	30	13,7	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		9,848	H	19,72	30	48,85	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		1,395	yes	1,72	15	1,9	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		0,211	C	2,68	30	2,765	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		4,6	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		0,000	yes	0,98	15	0,98	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		2,715	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		11,6	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		2,332	yes	1,83	15	2,15	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		0,731	yes	3,74	30	4,15	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		5,481	H	6,86	30	12,5	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		2,775	yes	7,88	15	9,52	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		1,582	yes	12,8	40	16,85	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		31,8	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		19,75	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		1,397	yes	19,93	40	25,5	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		58,55	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		0,397	yes	3,02	15	3,11	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		-0,286	yes	4,31	30	4,125	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		10,6	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 13																
124TCBz	µg/ml	A1V		3,643	yes	0,97	15	1,235	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		1,603	yes	2,35	30	2,915	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		10,2	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		9,941	H	2,26	15	3,945	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		2,334	yes	5,17	30	6,98	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V			H	23,53	30	<45	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		4,557	yes	0,79	15	1,06	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		3,067	yes	1	30	1,46	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			H	2,82		<10	2,295	2,399	0,5253	21,9	12	2	1	15
CCl4	µg/ml	A1V			H	0,77	15	<3,00	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V			H	1,45	30	<10	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			H	8,02		<60	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V			H	1,06	15	<2,25	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V			H	2,23	30	<10	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V			H	10,97	30	<45	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		14,110	H	0,95	15	1,955	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V			H	1,72	30	<10	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V			H	9,85	30	<45	7,76	7,968	1,341	16,8	10	1	1	12
ETBz	µg/ml	A1V		4,403	yes	1,06	15	1,41	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		3,018	yes	1,48	30	2,15	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V				3,79		<10	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		4,374	yes	4,42	15	5,87	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		2,727	yes	6,38	30	8,99	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		14,4	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		4,728	yes	5,26	15	7,125	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		1,937	yes	11,53	30	14,88	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		1,312	yes	19,72	30	23,6	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		5,543	yes	1,72	15	2,435	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		2,935	yes	2,68	30	3,86	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V				4,14		<10	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-0,095	yes	0,98	15	0,973	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		2,435	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V				10,19		<15	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		4,517	yes	1,83	15	2,45	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		3,173	yes	3,74	30	5,52	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V				6,86	30	<16	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		4,433	yes	7,88	15	10,5	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		2,656	yes	12,8	40	19,6	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			C	29,56		33,9	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		18,58	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		1,548	yes	19,93	40	26,1	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		41,7	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		4,349	H	3,02	15	4,005	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		2,421	yes	4,31	30	5,875	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		10,45	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 14																
124TCBz	µg/ml	A1V		-1,347	yes	0,97	15	0,872	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		-0,851	yes	2,35	30	2,05	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		7,1	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-0,319	yes	2,26	15	2,206	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		1,199	yes	5,17	30	6,1	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		-1,000	yes	23,53	30	20	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		-0,236	yes	0,79	15	0,776	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		0,667	yes	1	30	1,1	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		2,15	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		-0,933	yes	3,63	15	3,376	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		1,351	yes	7,65	30	9,2	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		31	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		-0,087	yes	0,77	15	0,765	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		0,690	yes	1,45	30	1,6	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		5,8	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		0,528	yes	1,06	15	1,102	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		0,807	yes	2,23	30	2,5	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		-1,106	yes	10,97	30	9,15	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		-2,063	yes	0,95	15	0,803	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		1,667	yes	1,72	30	2,15	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		-1,997	yes	9,85	30	6,9	7,76	7,968	1,341	16,8	10	1	1	12
ETBz	µg/ml	A1V		0,113	yes	1,06	15	1,069	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		0,766	yes	1,48	30	1,65	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		2,85	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-0,042	yes	4,42	15	4,406	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		1,066	yes	6,38	30	7,4	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		12	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		-2,527	yes	5,26	15	4,263	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		-1,087	yes	11,53	30	9,65	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		-1,765	yes	19,72	30	14,5	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		0,760	yes	1,72	15	1,818	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		0,298	yes	2,68	30	2,8	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		4,35	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-2,109	yes	0,98	15	0,825	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		2,05	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		6,6	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		-2,441	yes	1,83	15	1,495	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		-0,428	yes	3,74	30	3,5	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		-1,953	yes	6,86	30	4,85	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		-2,907	yes	7,88	15	6,162	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		0,078	yes	12,8	40	13	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		16,5	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		14,04	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		0,394	yes	19,93	40	21,5	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		37	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		0,389	yes	3,02	15	3,108	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		1,145	yes	4,31	30	5,05	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		8,35	8,95	9,329	2,184	23,4	15	0	0	15

Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
Laboratory 15																
Bz	µg/ml	A1V		13,760	H	0,79	15	1,605	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		-1,467	yes	1	30	0,78	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			H	2,82		8,935	2,295	2,399	0,5253	21,9	12	2	1	15
ETBz	µg/ml	A1V		10,630	yes	1,06	15	1,905	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		0,180	yes	1,48	30	1,52	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		1,36	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		11,030	H	4,42	15	8,075	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		0,167	yes	6,38	30	6,54	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		4,665	11,9	11,17	3,357	30,0	15	0	0	15
oXYL	µg/ml	A1V		11,590	H	1,72	15	3,215	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		0,211	yes	2,68	30	2,765	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		2,21	4,245	4,143	1,178	28,4	14	0	1	15
TCEe	µg/ml	A1V		6,497	yes	7,88	15	11,72	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		-0,994	yes	12,8	40	10,25	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		6,23	18,93	20,2	7,067	34,9	13	1	0	14
TECEe	µg/ml	A1V			yes	14,22		25,41	15,05	15,95	3,935	24,6	13	1	0	14
	mg/kg	M3V		-0,864	yes	19,93	40	16,48	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		29,43	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		11,810	H	3,02	15	5,695	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		-0,657	yes	4,31	30	3,885	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		7,595	8,95	9,329	2,184	23,4	15	0	0	15
Laboratory 16																
124TCBz	µg/ml	A1V		-5,184	yes	0,97	15	0,5928	0,925	0,9316	0,2259	24,2	9	2	0	11
	mg/kg	M3V		-2,426	yes	2,35	30	1,495	2,28	2,322	0,4054	17,4	11	0	0	11
	µg/l	N2V			yes	10,12		4,357	8,435	8,444	2,193	25,9	11	0	0	11
12DCEa	µg/ml	A1V		-0,115	yes	2,26	15	2,241	2,11	2,115	0,1498	7,1	9	2	0	11
	mg/kg	M3V		-0,332	yes	5,17	30	4,912	5,17	5,157	0,893	17,3	11	0	0	11
	µg/l	N2V		-0,815	yes	23,53	30	20,65	21,45	22,17	2,636	11,8	9	1	1	11
Bz	µg/ml	A1V		-1,345	yes	0,79	15	0,7103	0,7835	0,7952	0,1122	14,1	11	4	0	15
	mg/kg	M3V		-0,410	yes	1	30	0,9385	0,9901	0,9955	0,1835	18,4	14	1	0	15
	µg/l	N2V			yes	2,82		1,926	2,295	2,399	0,5253	21,9	12	2	1	15
c12DCEe	µg/ml	A1V		-0,405	yes	3,63	15	3,52	3,5	3,455	0,3904	11,2	8	2	0	10
	mg/kg	M3V		0,172	yes	7,65	30	7,848	7,71	7,621	1,123	14,7	9	0	0	9
	µg/l	N2V			yes	37,74		29,39	32,1	33,87	6,727	19,8	10	0	0	10
CCl4	µg/ml	A1V		-0,370	yes	0,77	15	0,7486	0,755	0,7278	0,1304	17,9	10	2	1	13
	mg/kg	M3V		-0,306	yes	1,45	30	1,383	1,44	1,446	0,1369	9,5	7	3	1	11
	µg/l	N2V			yes	8,02		6,025	6,25	5,885	1,582	26,8	11	1	1	13
CHCl3	µg/ml	A1V		0,039	yes	1,06	15	1,063	1,02	1,063	0,2208	20,7	9	3	1	13
	mg/kg	M3V		0,304	yes	2,23	30	2,332	2,31	2,216	0,2573	11,6	8	2	1	11
	µg/l	N2V		-0,836	yes	10,97	30	9,595	10,12	10,7	2,001	18,7	11	1	1	13
DCM	µg/ml	A1V		-0,900	yes	0,95	15	0,8858	0,8425	0,8386	0,1189	14,1	9	3	0	12
	mg/kg	M3V		1,703	yes	1,72	30	2,159	1,75	1,709	0,3827	22,3	8	1	1	10
	µg/l	N2V		-1,311	yes	9,85	30	7,913	7,76	7,968	1,341	16,8	10	1	1	12
ETBE	µg/ml	A1V		-0,791	yes	1,21	15	1,138	1,29	1,298	0,2403	18,5	7	1	0	8
	mg/kg	M3V		-0,017	yes	2,38	30	2,374	2,37	2,364	0,4144	17,5	7	0	0	7
	µg/l	N2V		-1,737	yes	4,54	30	3,357	3,735	3,85	0,4241	11,0	6	2	0	8
ETBz	µg/ml	A1V		-4,341	yes	1,06	15	0,7149	1,014	1	0,4039	40,3	14	1	0	15
	mg/kg	M3V		-1,532	yes	1,48	30	1,14	1,51	1,467	0,3095	21,1	14	1	0	15
	µg/l	N2V			yes	3,79		1,423	2,86	2,745	0,8677	31,6	14	0	1	15
mpXYL	µg/ml	A1V		-1,696	yes	4,42	15	3,858	4,22	4,267	0,7101	16,6	12	3	0	15
	mg/kg	M3V		0,053	yes	6,38	30	6,431	6,294	6,331	1,205	19,0	14	1	0	15
	µg/l	N2V			yes	11,17		5,458	11,9	11,17	3,357	30,0	15	0	0	15
MTBE	µg/ml	A1V		-0,111	yes	5,26	15	5,216	5,238	5,537	1,365	24,6	12	1	0	13
	mg/kg	M3V		-0,334	yes	11,53	30	10,95	10,7	11,53	2,846	24,6	11	0	0	11
	µg/l	N2V		-1,441	yes	19,72	30	15,46	17,45	18,25	3,506	19,2	11	2	0	13
oXYL	µg/ml	A1V		-1,943	yes	1,72	15	1,469	1,745	1,719	0,3125	18,1	12	3	0	15
	mg/kg	M3V		-0,558	yes	2,68	30	2,456	2,7	2,654	0,5133	19,3	14	1	0	15
	µg/l	N2V			yes	4,14		2,268	4,245	4,143	1,178	28,4	14	0	1	15
t12DCEe	µg/ml	A1V		-2,038	yes	0,98	15	0,8302	0,87	0,8947	0,1483	16,5	11	1	0	12
	mg/kg	M3V			yes	1,77		1,744	1,762	1,772	0,5529	31,2	11	0	0	11
	µg/l	N2V			yes	10,19		6,571	7,285	8,198	2,347	28,6	11	0	1	12
TAME	µg/ml	A1V		-0,919	yes	1,83	15	1,704	1,723	1,802	0,4266	23,6	9	1	0	10
	mg/kg	M3V		-0,020	yes	3,74	30	3,729	3,6	3,715	0,8748	23,5	10	0	0	10
	µg/l	N2V		-1,809	yes	6,86	30	4,999	5,495	6,149	1,959	31,8	8	1	1	10
TCEe	µg/ml	A1V		-6,173	yes	7,88	15	4,232	7,545	7,721	2,102	27,2	13	1	0	14
	mg/kg	M3V		-1,876	yes	12,8	40	7,996	13	12,94	3,273	25,2	12	0	0	12
	µg/l	N2V			yes	29,56		11,75	18,93	20,2	7,067	34,9	13	1	0	14

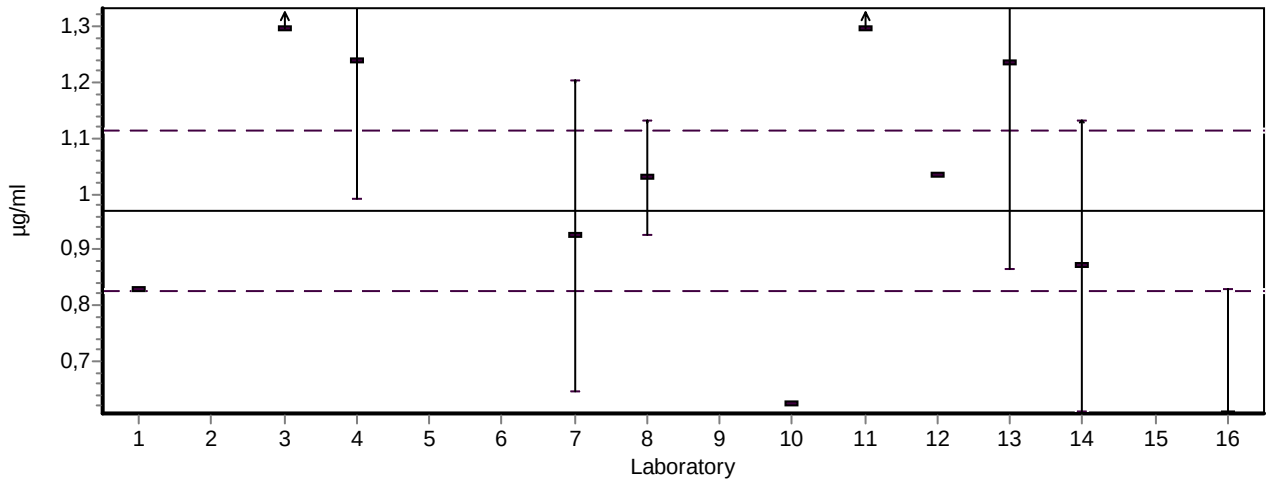
Outlier test failed: C - Cohcran, G1 - Grubbs(1-outlier algorithm), G2 - Grubbs(2-outliers algorithm), H - Hampel, M - manual

Analyte	Unit	Sample	z-Graphics -3 -2 -1 0 +1 +2 +3	Z- value	Outl test OK	Assig-ned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
TECEe	µg/ml	A1V			yes	14,22		13,34	15,05	15,95	3,935	24,6	13	1	0	14
Laboratory 16																
TECEe	mg/kg	M3V		-0,219	yes	19,93	40	19,06	20,3	19,85	6,715	33,8	12	0	0	12
	µg/l	N2V			yes	50,85		32,9	39,17	38,92	10,27	26,3	14	0	0	14
TOL	µg/ml	A1V		-0,098	yes	3,02	15	2,998	3,035	3,002	0,2681	8,9	11	4	0	15
	mg/kg	M3V		0,270	yes	4,31	30	4,485	4,4	4,285	0,7531	17,5	15	0	0	15
	µg/l	N2V			yes	10,8		6,881	8,95	9,329	2,184	23,4	15	0	0	15

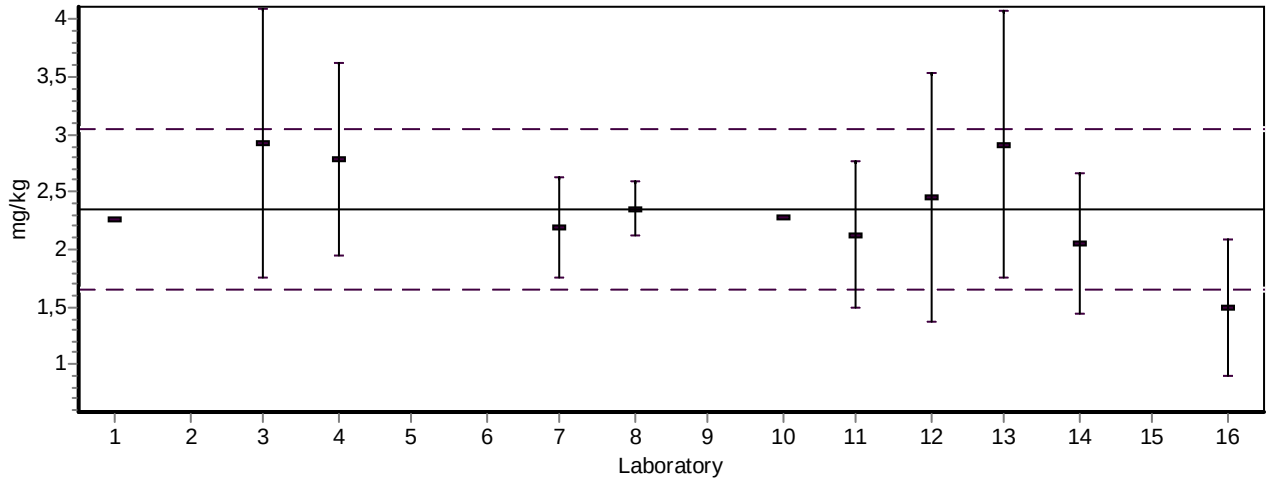
LIITE 9. RESULTS AND THEIR MEASUREMENT UNCERTAINTIES

APPENDIX 9.

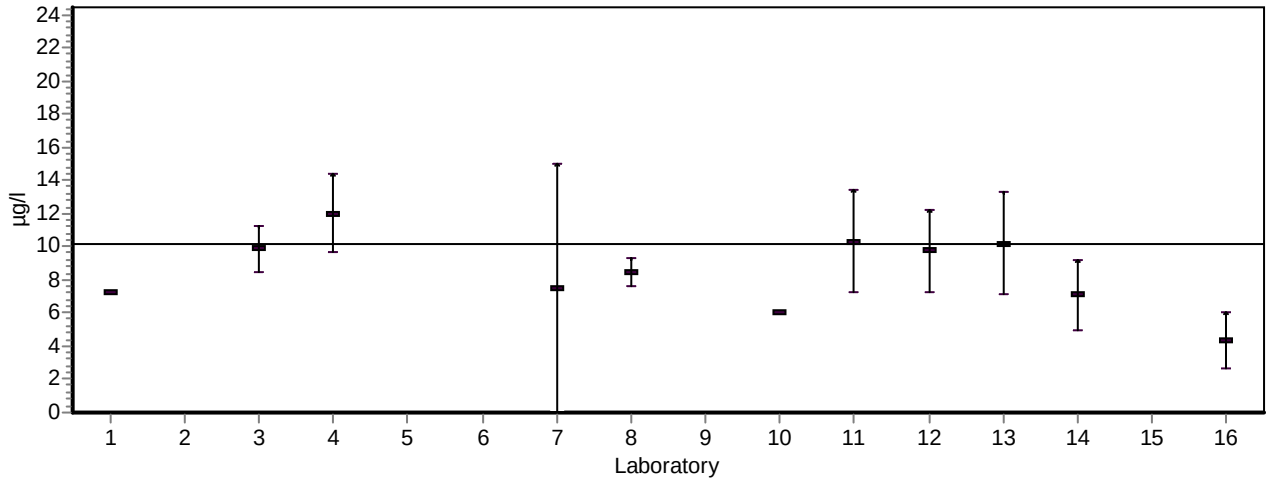
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* A1V



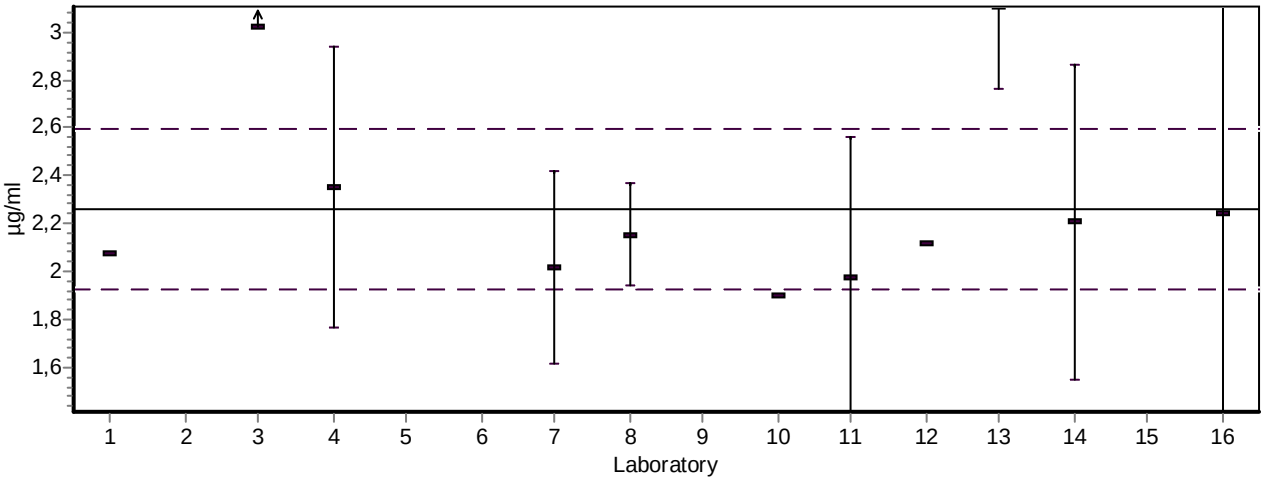
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* M3V



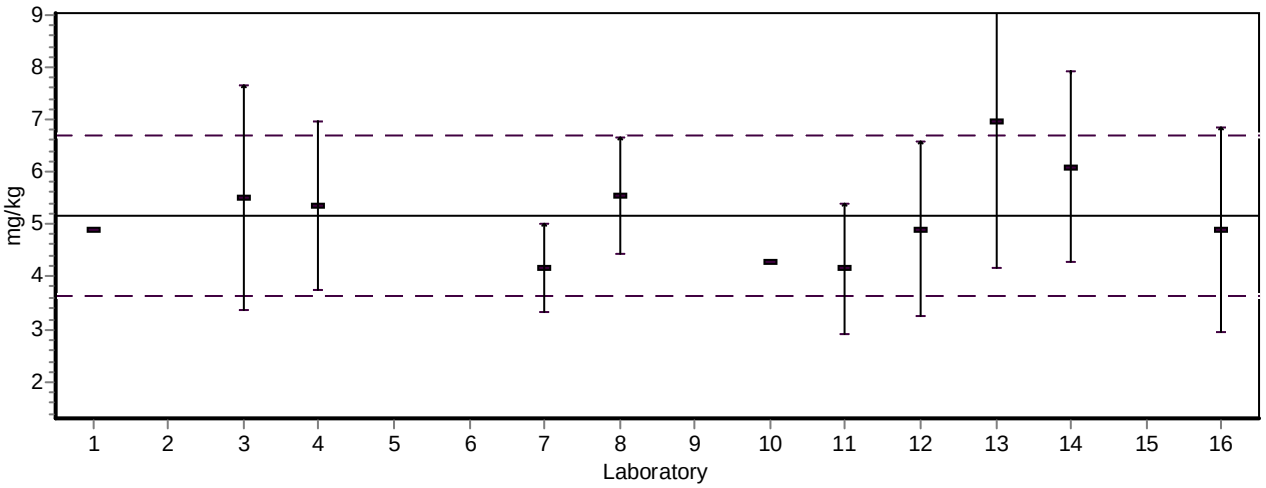
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* N2V



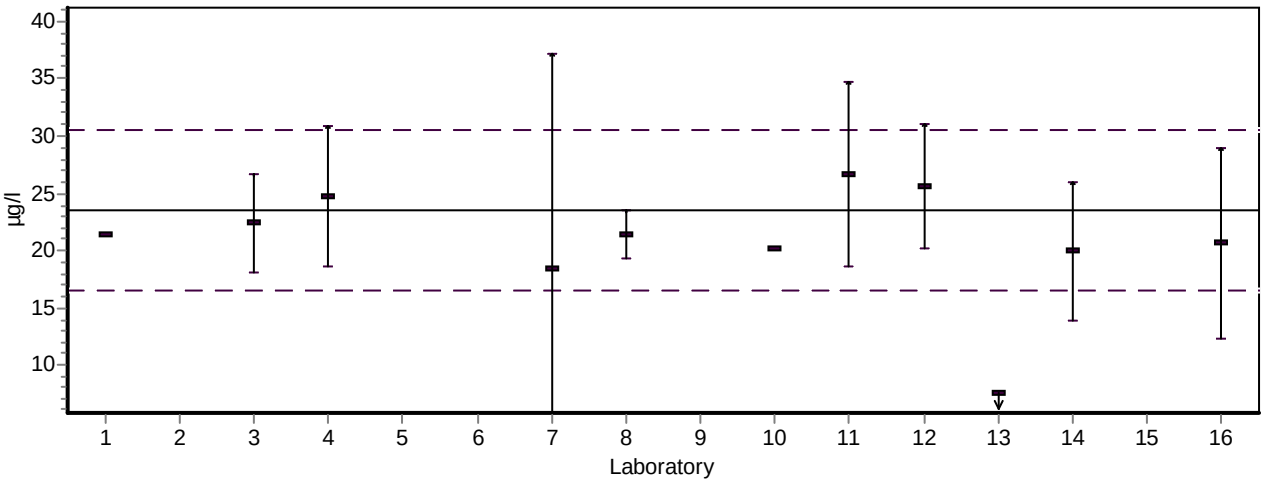
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* A1V



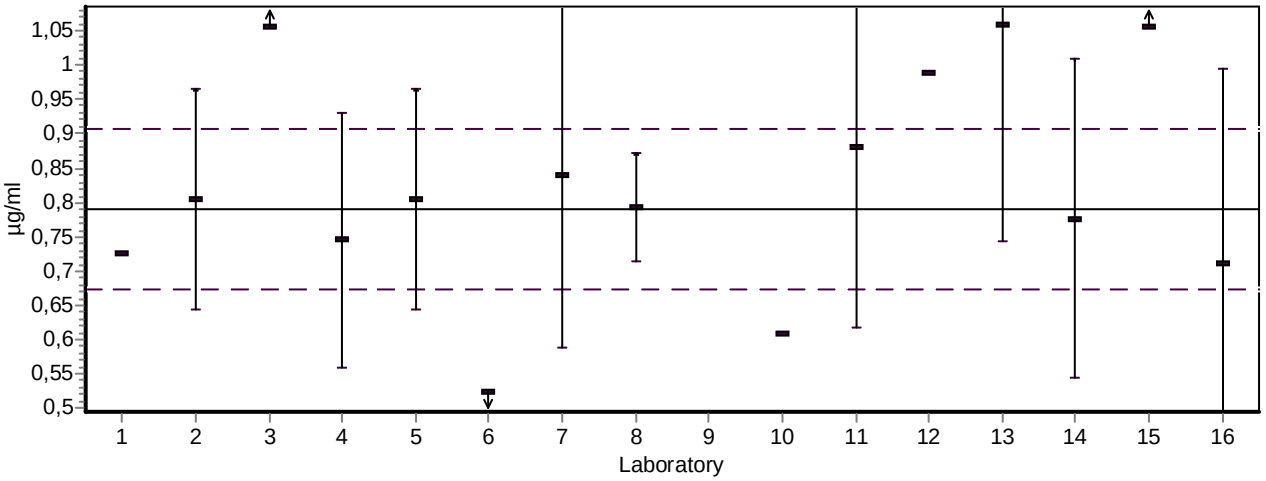
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* M3V



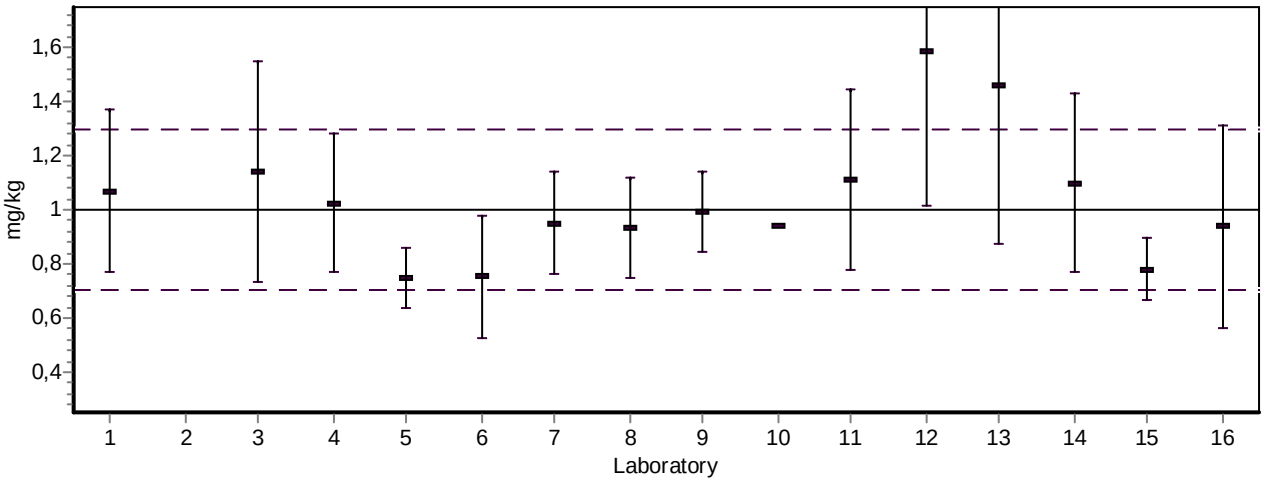
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* N2V



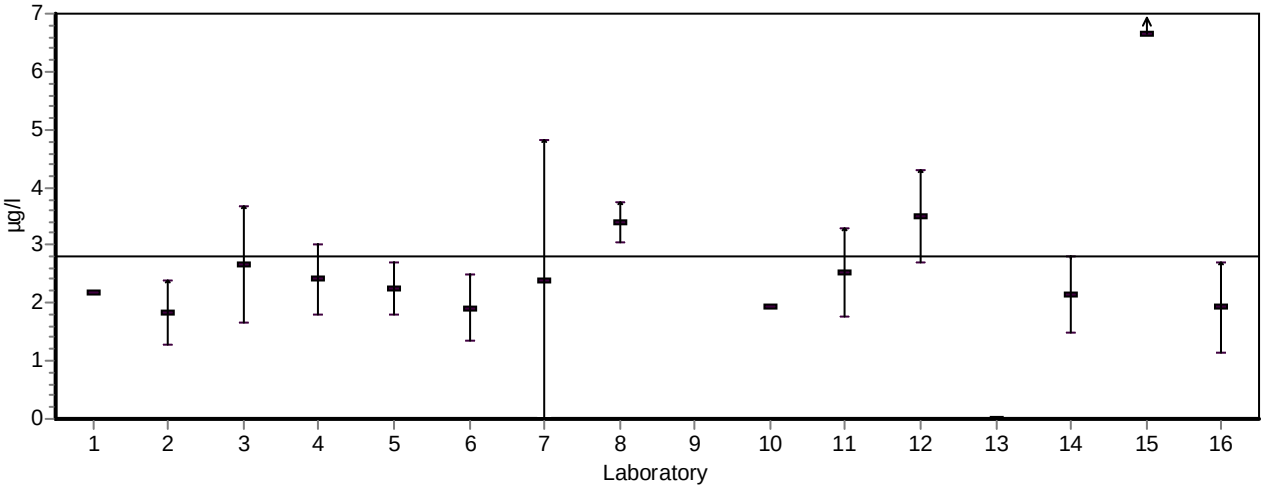
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* A1V



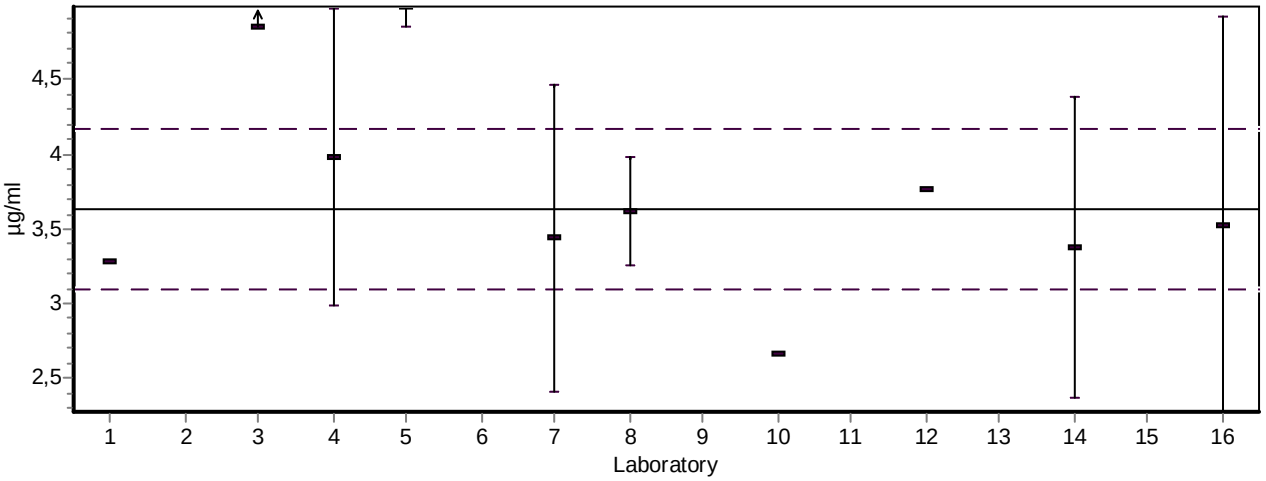
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* M3V



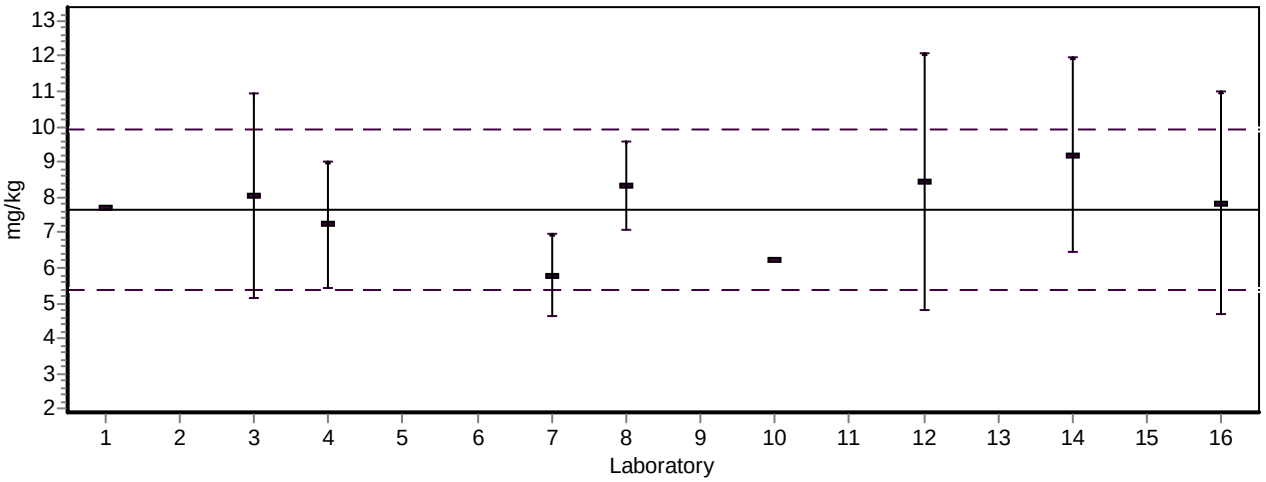
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* N2V



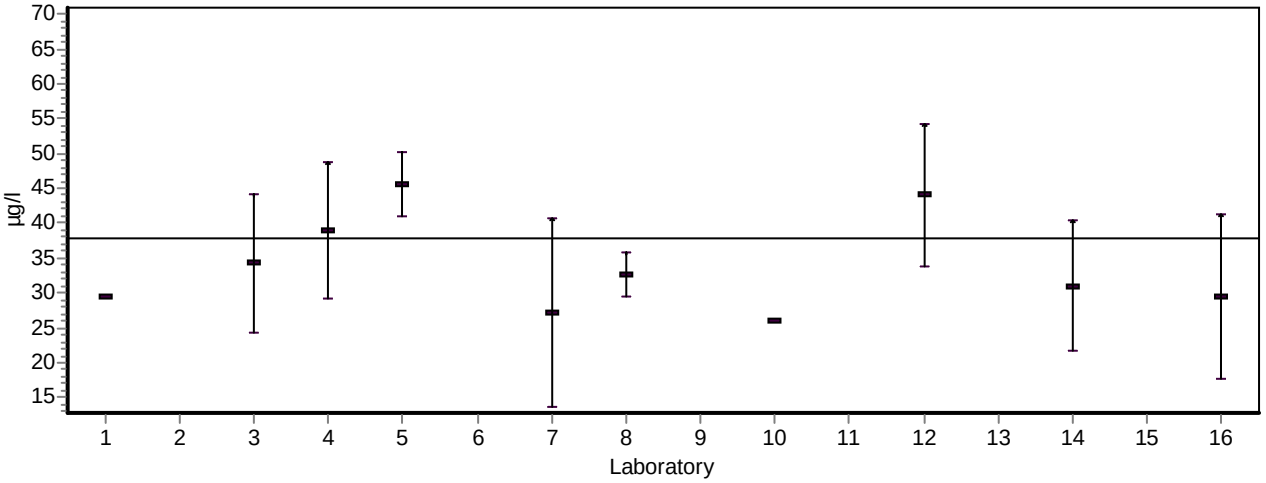
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* A1V



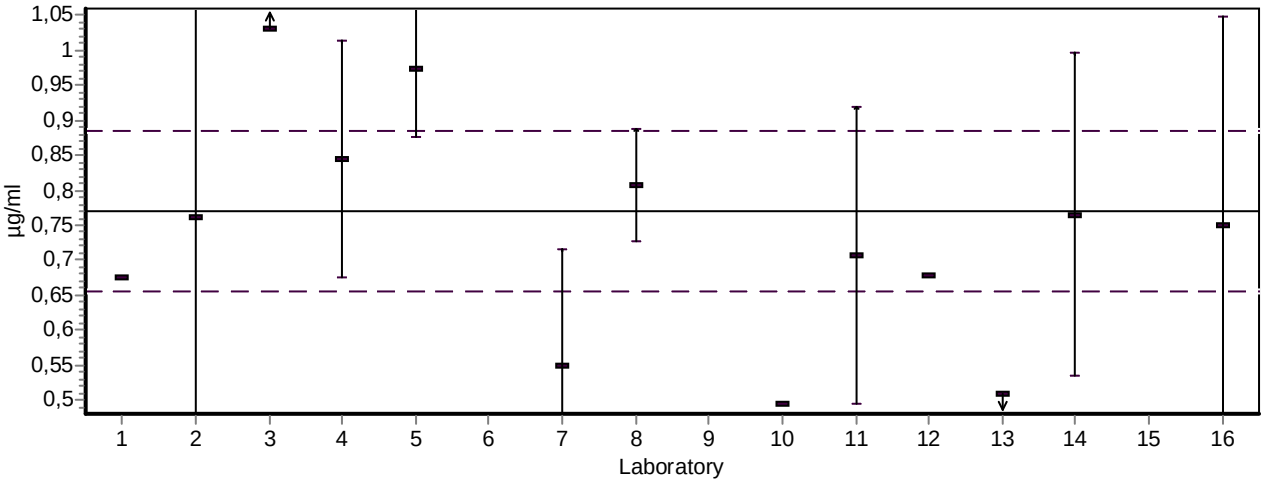
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* M3V



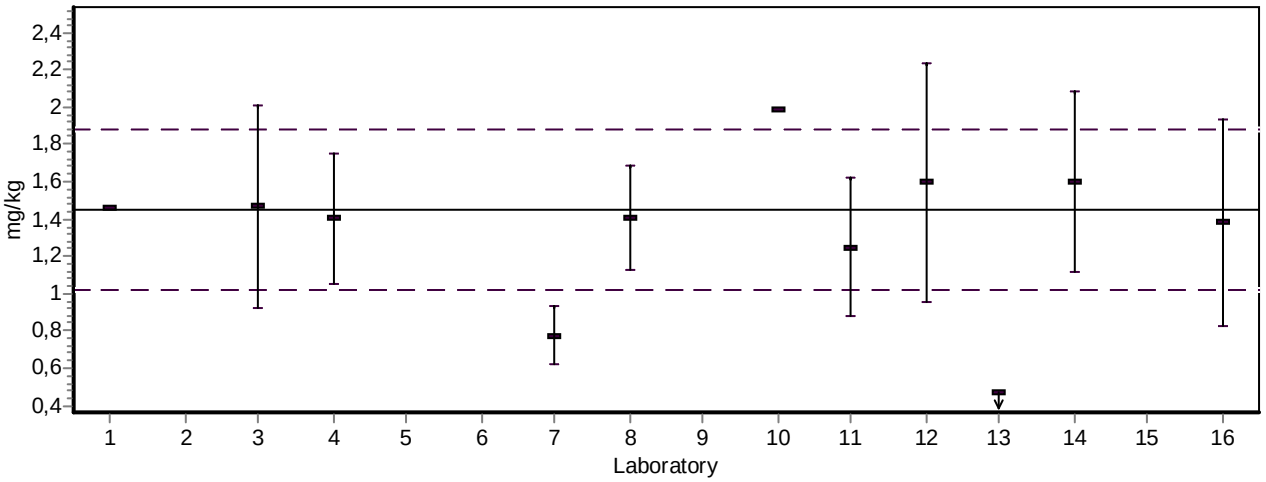
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* N2V



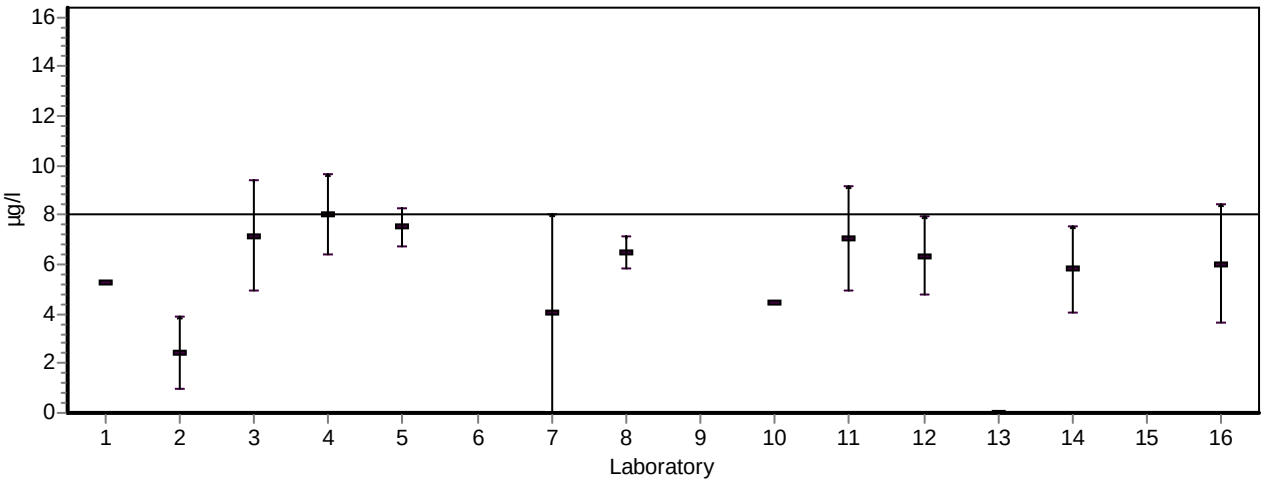
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* A1V



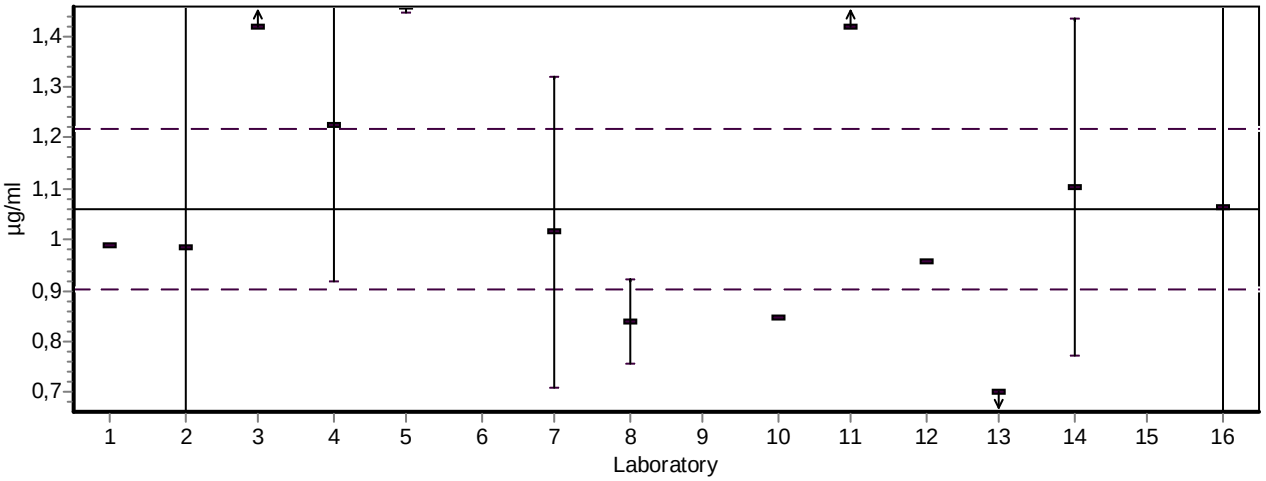
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* M3V



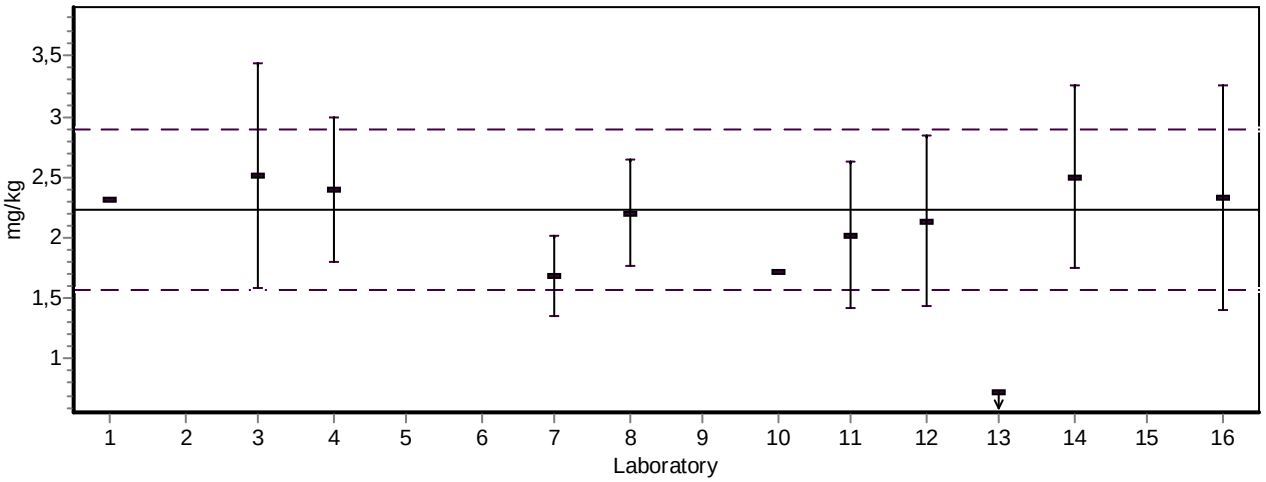
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* N2V



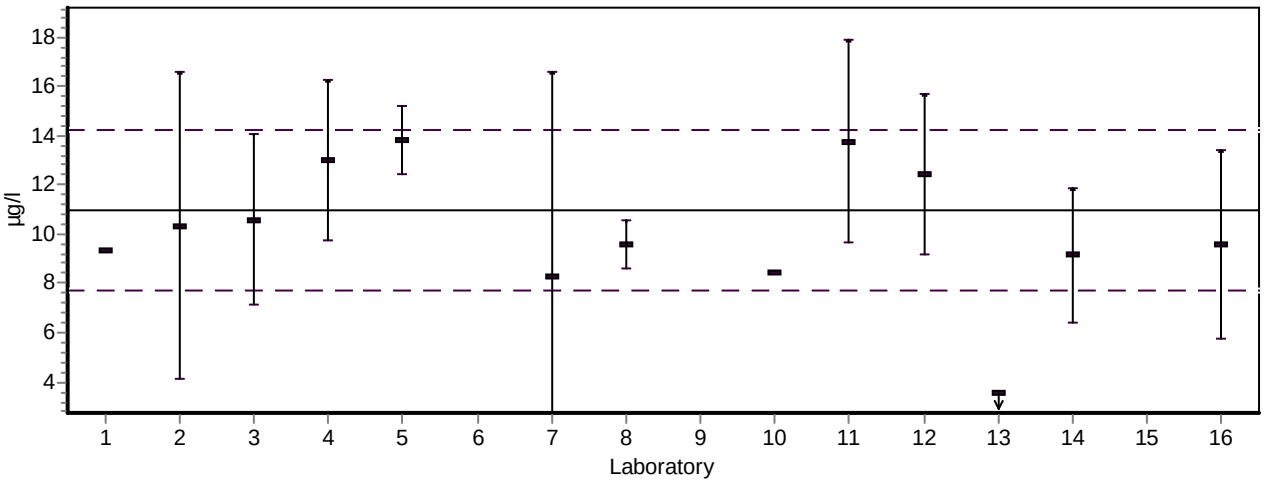
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* A1V



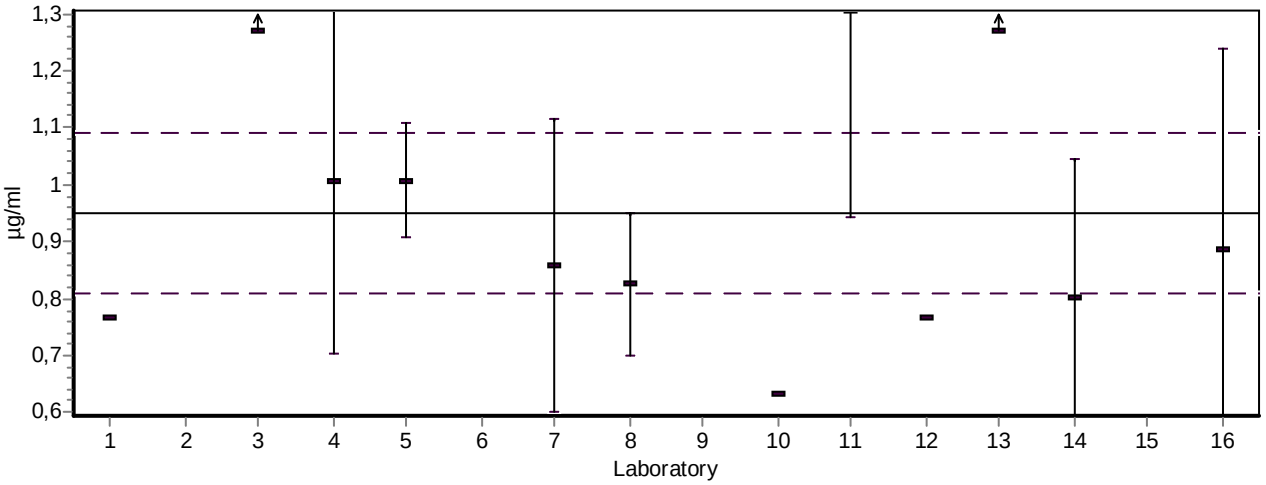
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* M3V



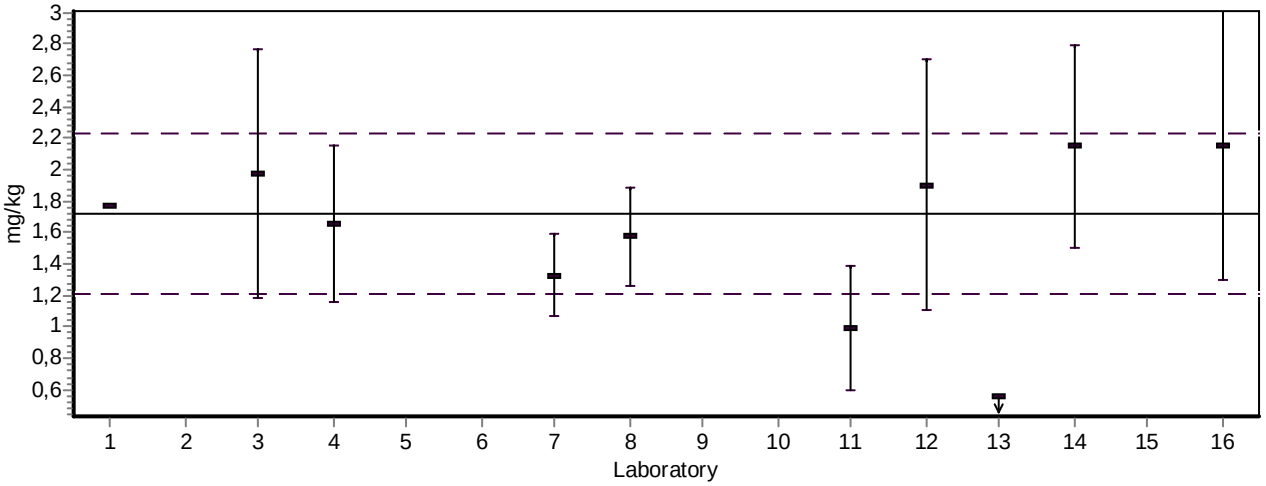
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* N2V



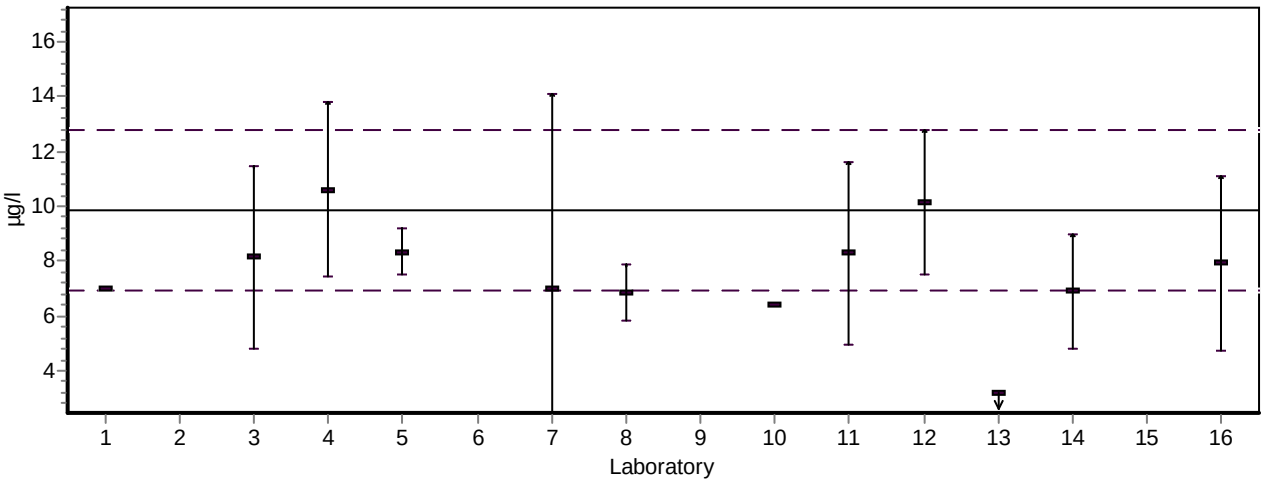
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* A1V



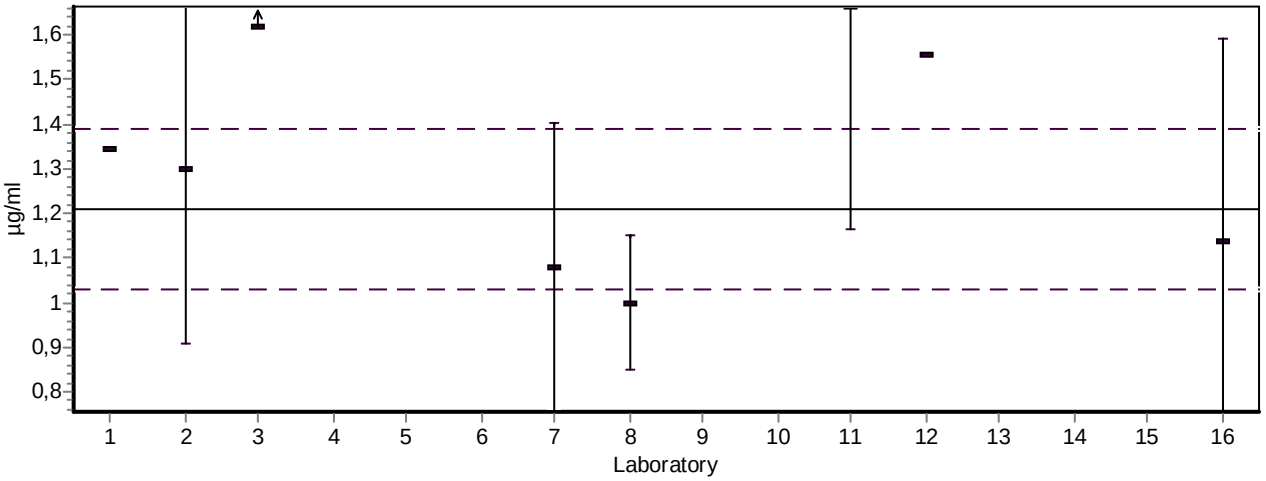
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* M3V



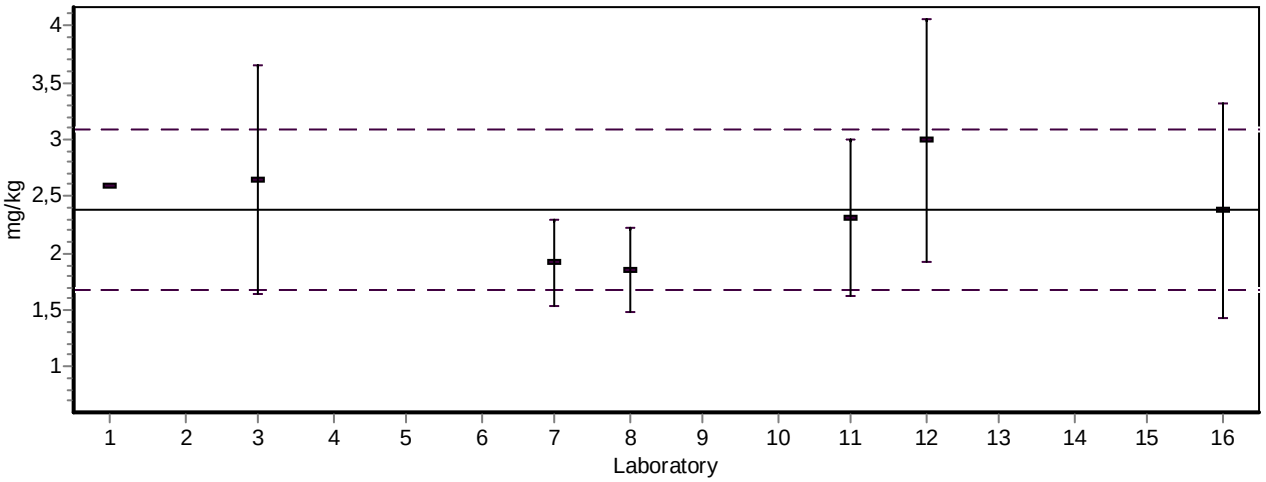
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* N2V



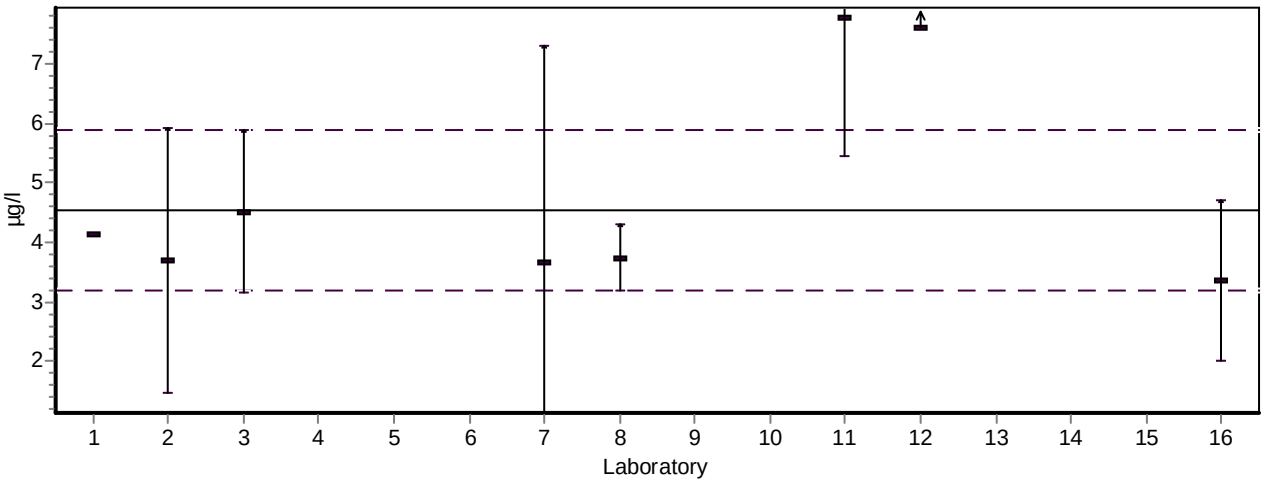
Analyytti *(Analyte)* **ETBE** Näyte *(Sample)* A1V



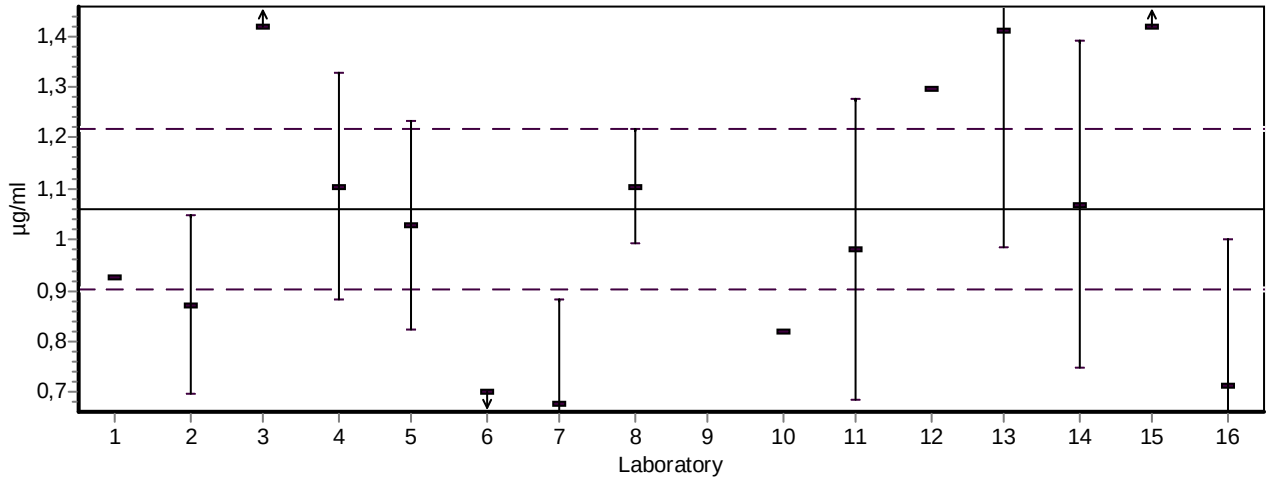
Analyytti *(Analyte)* **ETBE** Näyte *(Sample)* M3V



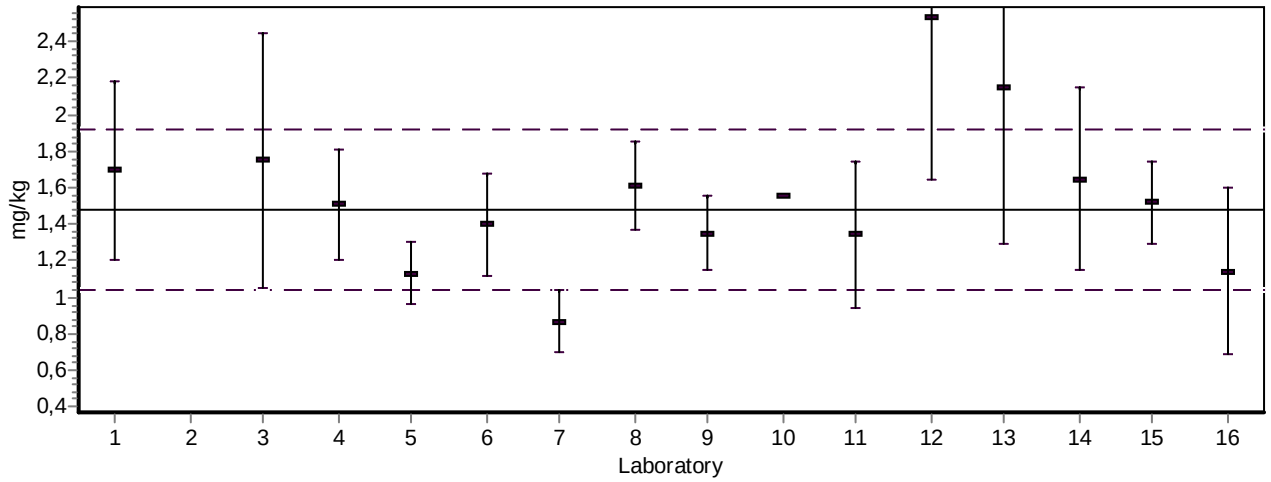
Analyytti *(Analyte)* **ETBE** Näyte *(Sample)* N2V



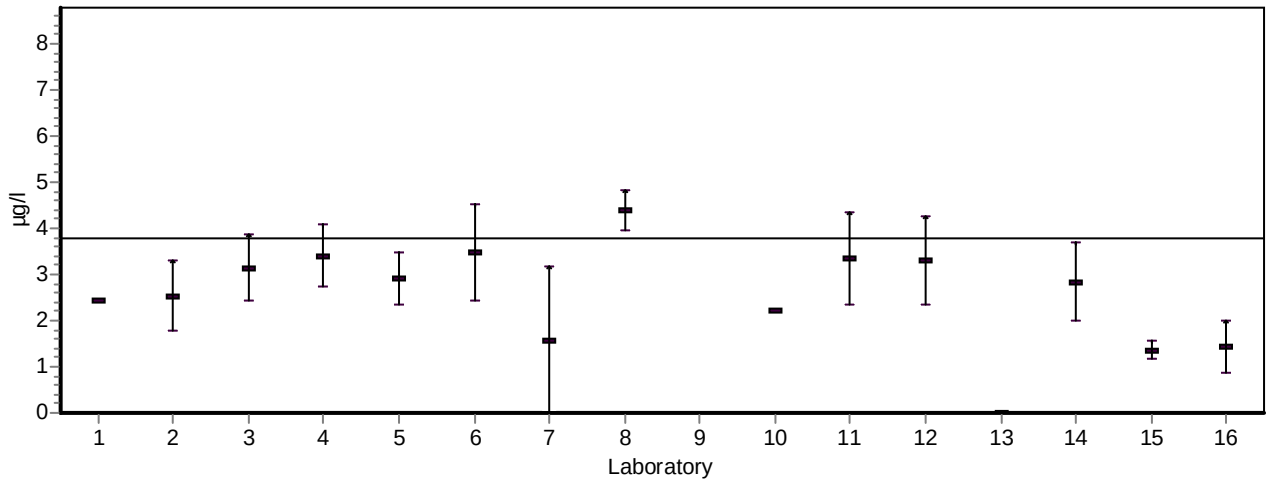
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* A1V



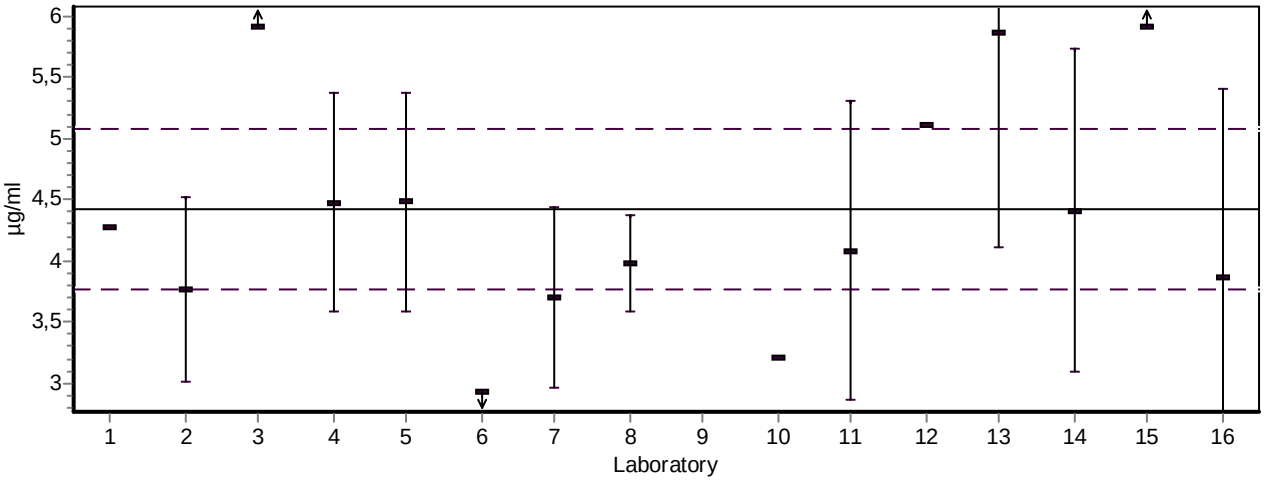
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* M3V



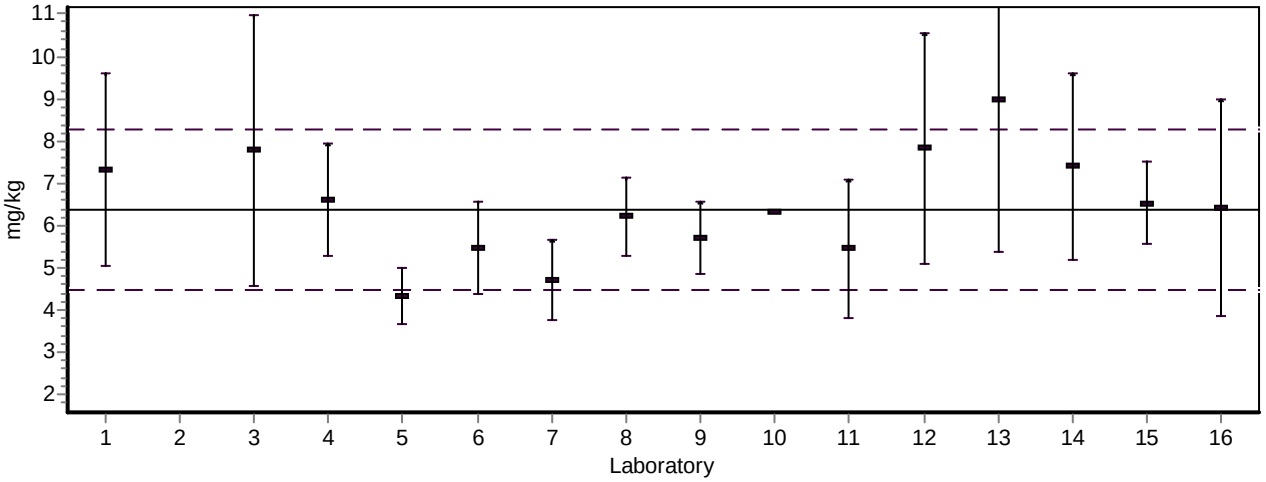
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* N2V



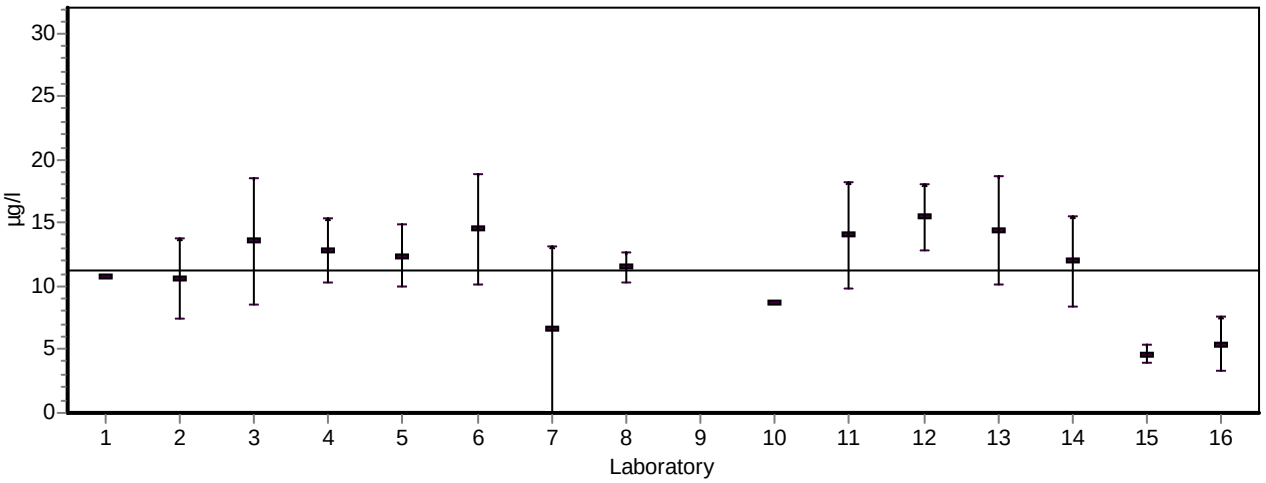
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* A1V



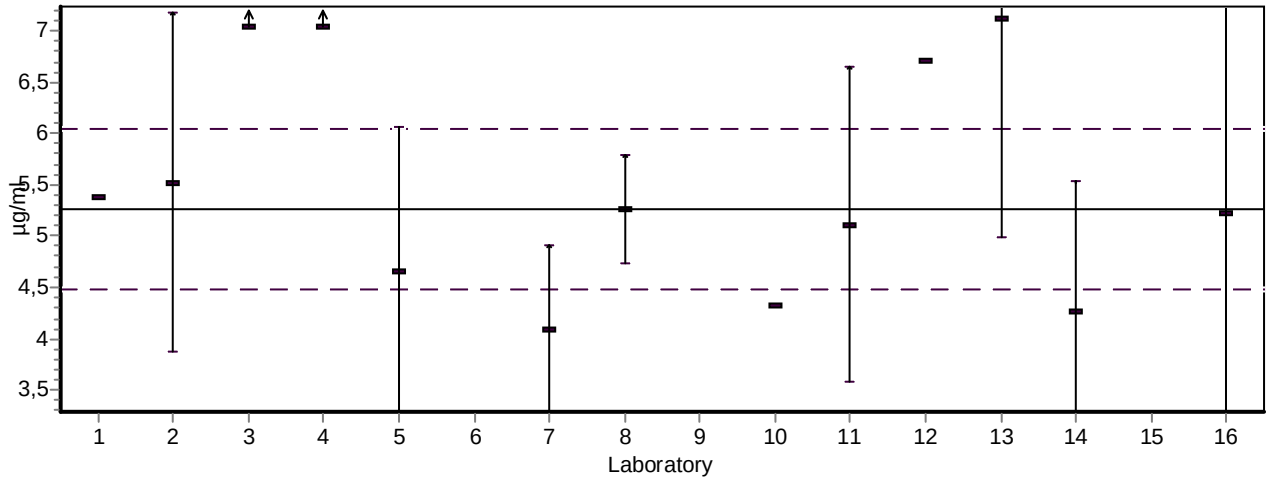
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* M3V



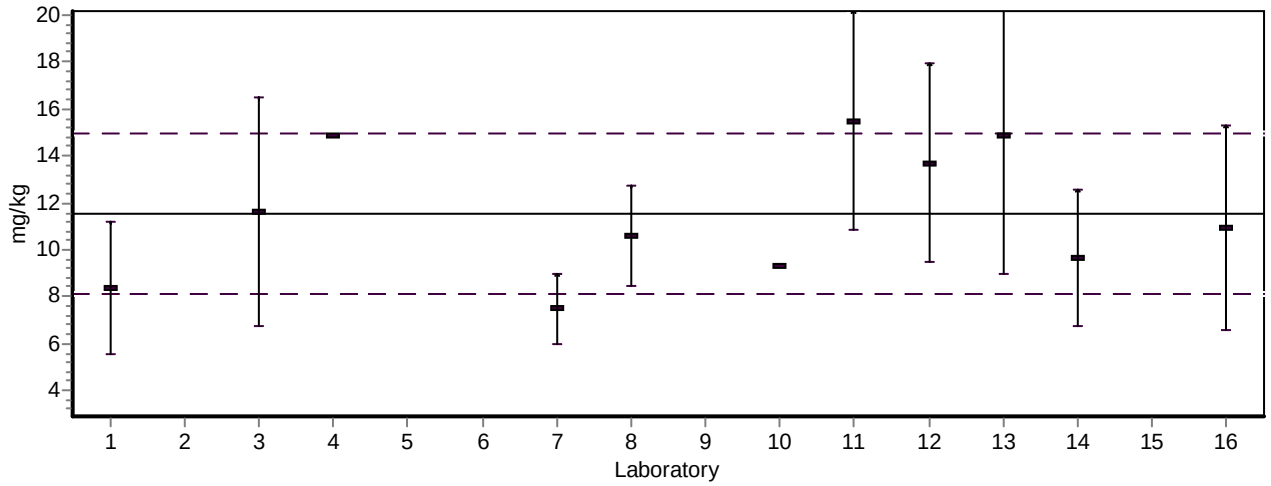
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* N2V



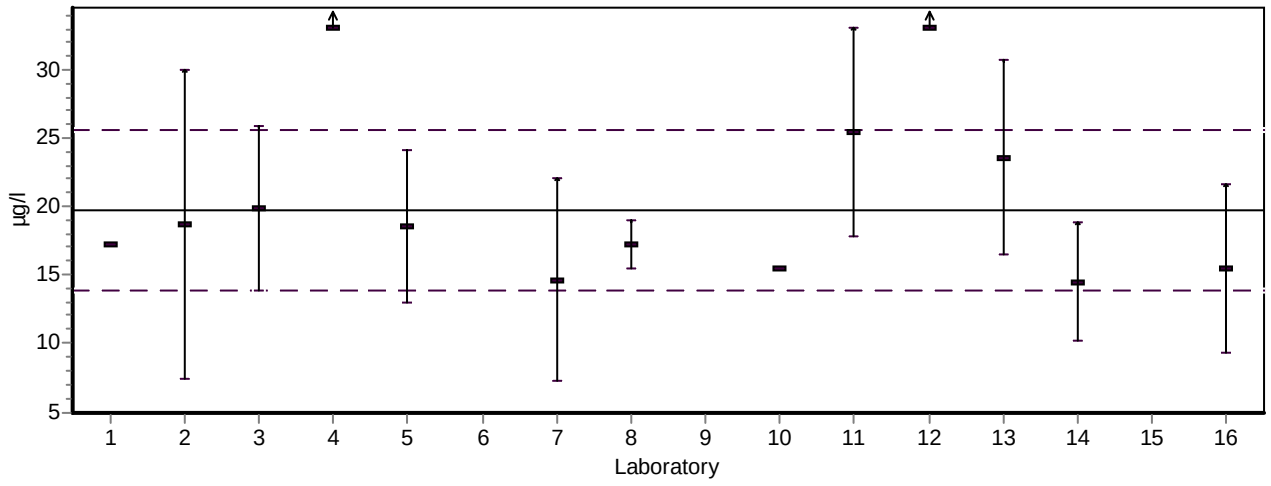
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* A1V



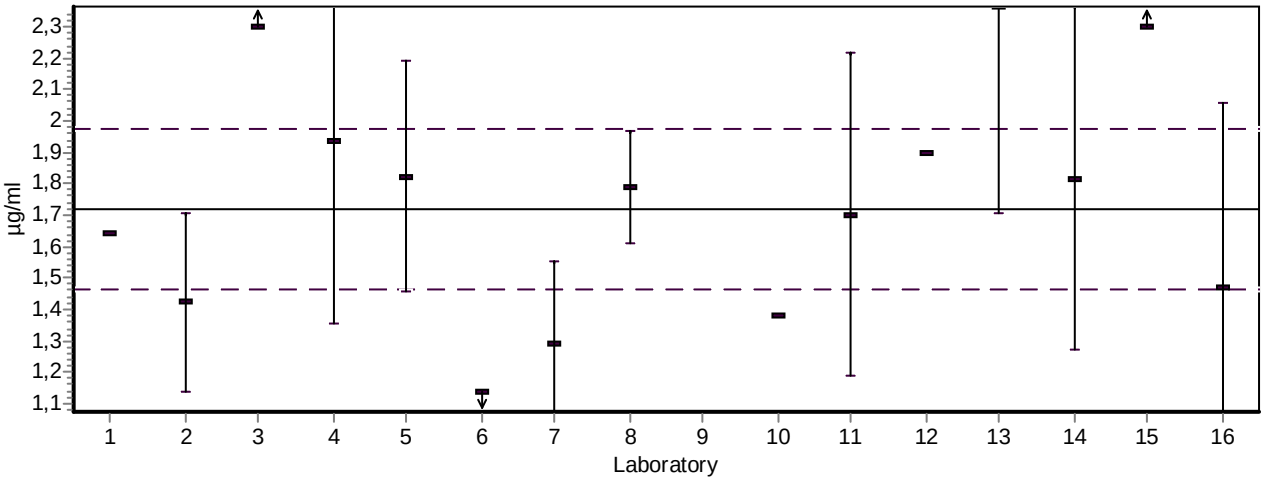
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* M3V



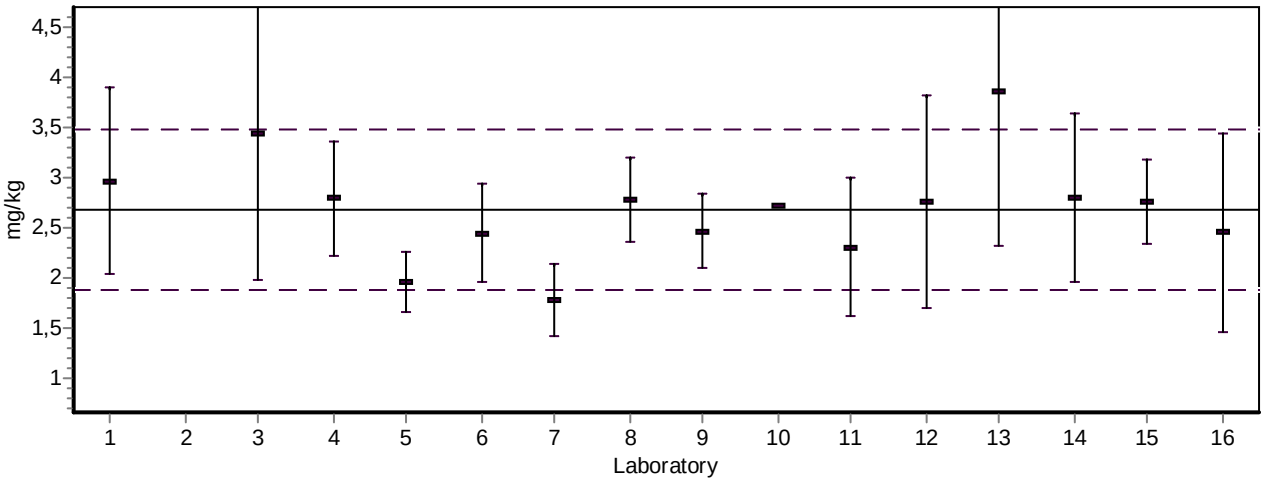
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* N2V



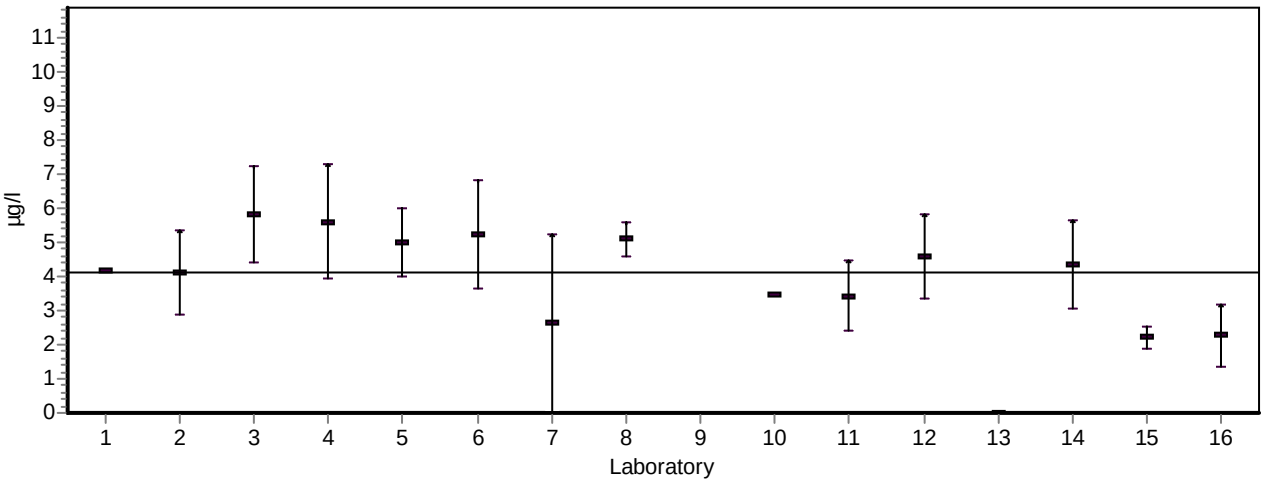
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* A1V



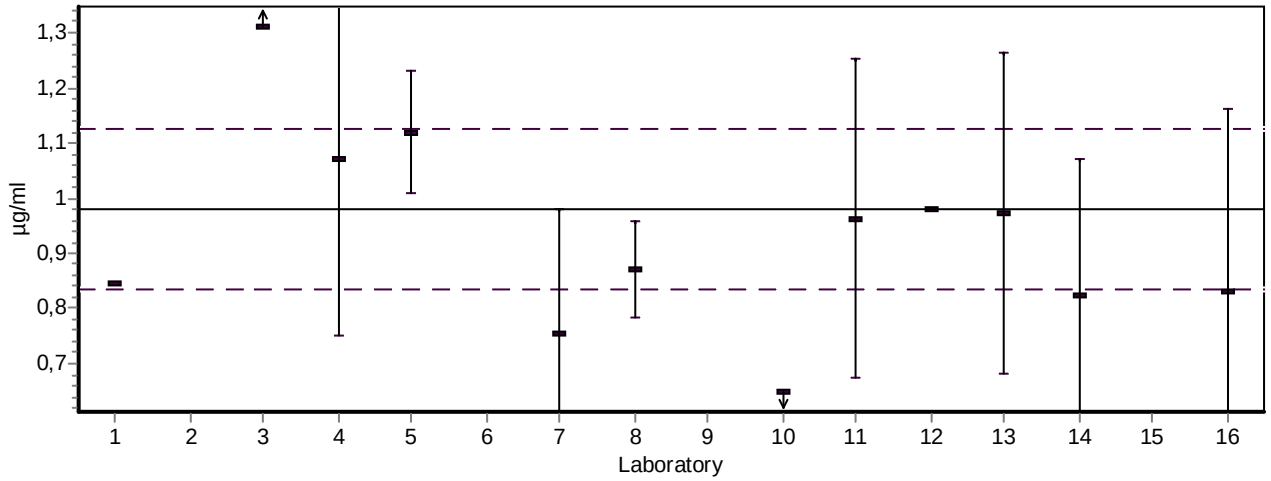
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* M3V



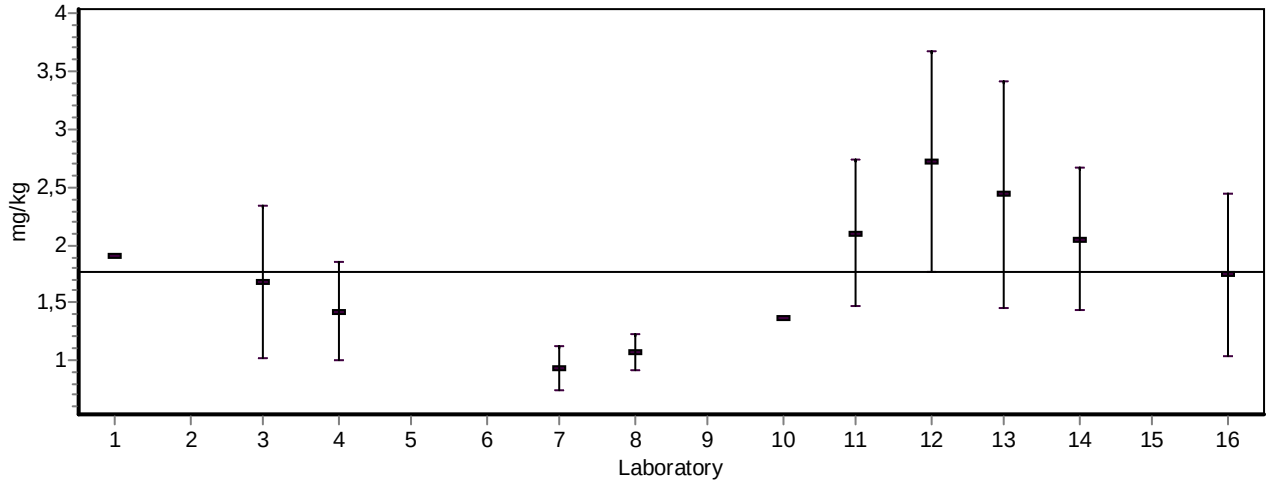
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* N2V



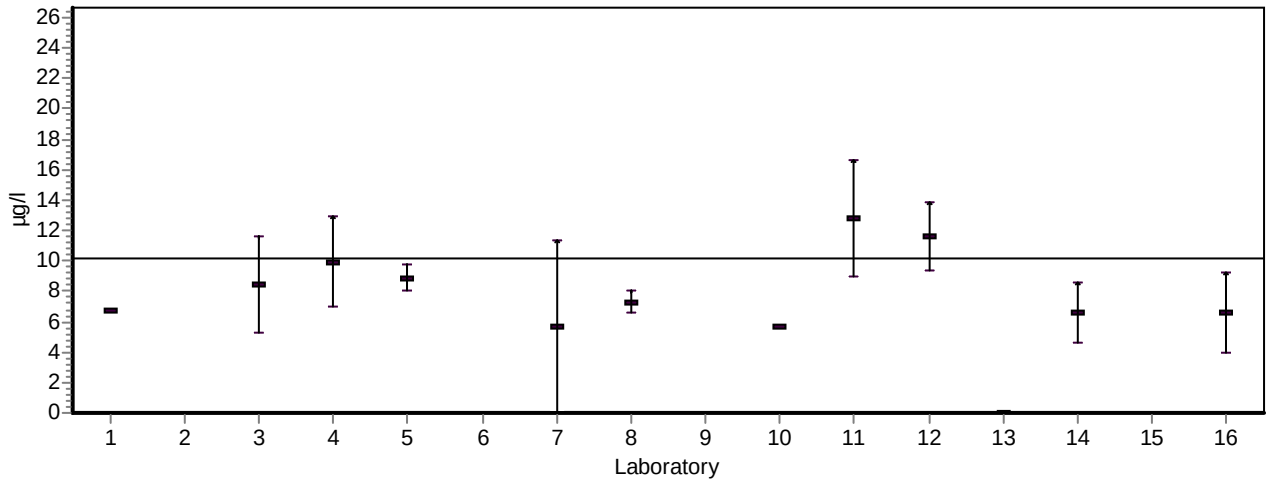
Analyytti *(Analyte)* **t12DCEe** Näyte *(Sample)* A1V



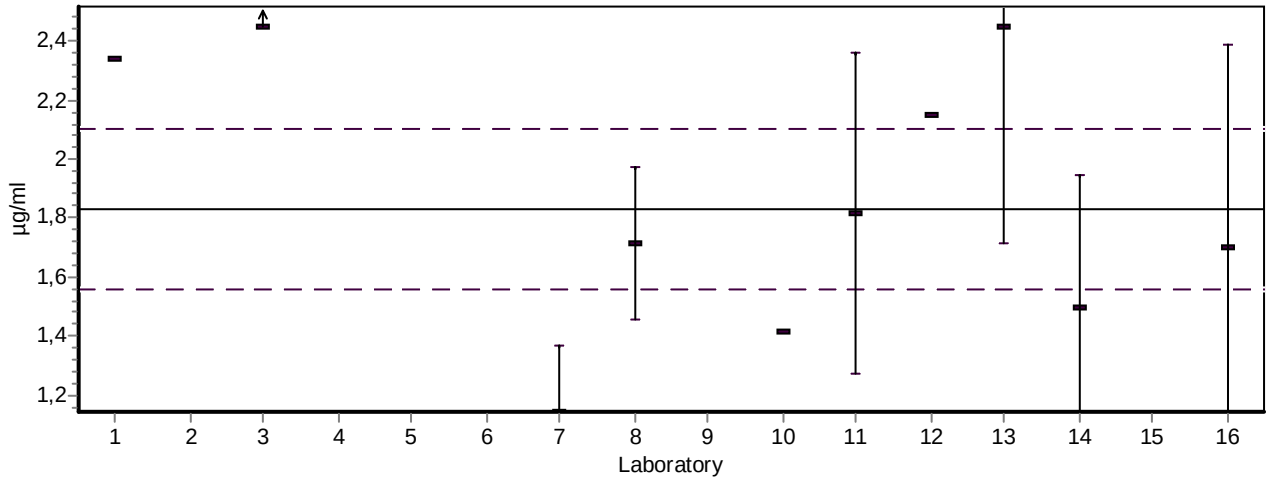
Analyytti *(Analyte)* **t12DCEe** Näyte *(Sample)* M3V



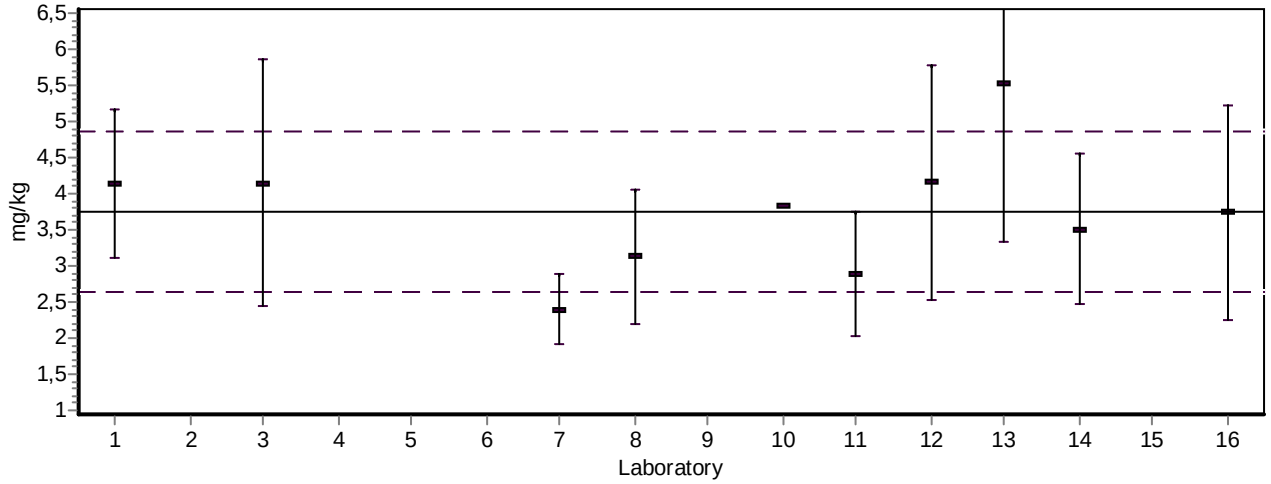
Analyytti *(Analyte)* **t12DCEe** Näyte *(Sample)* N2V



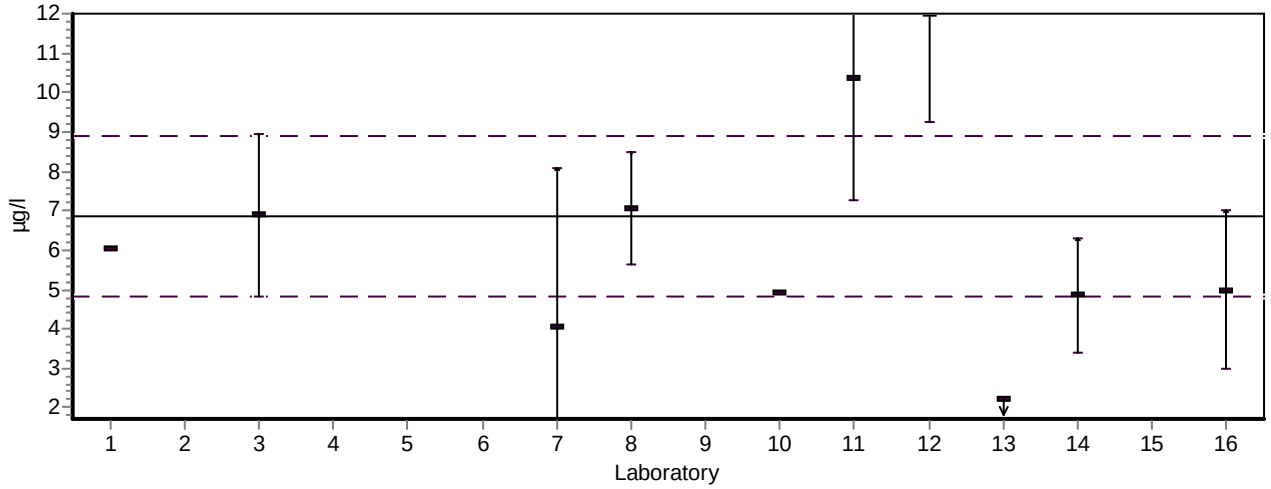
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* A1V



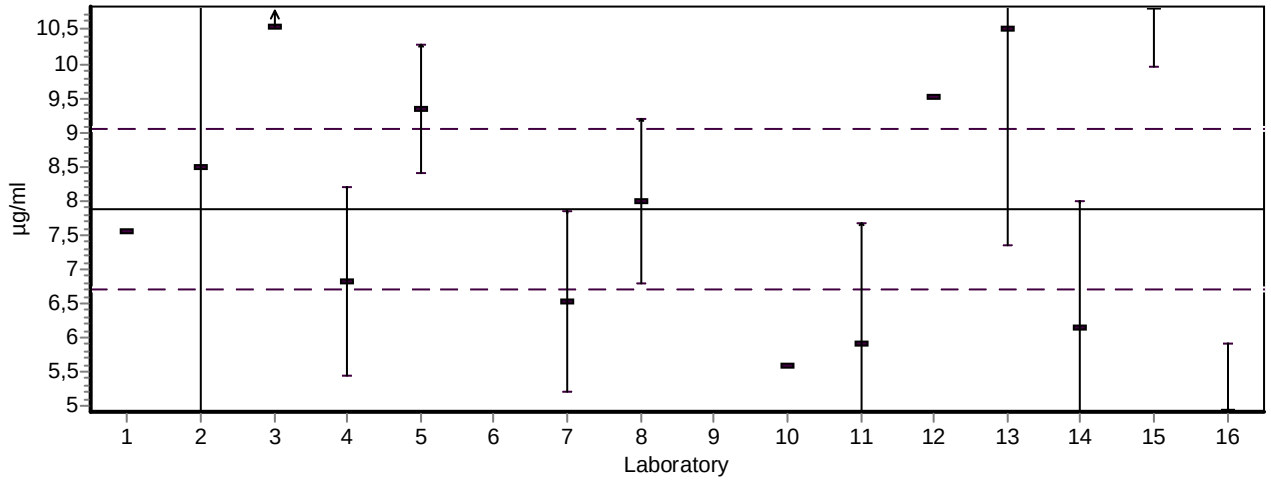
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* M3V



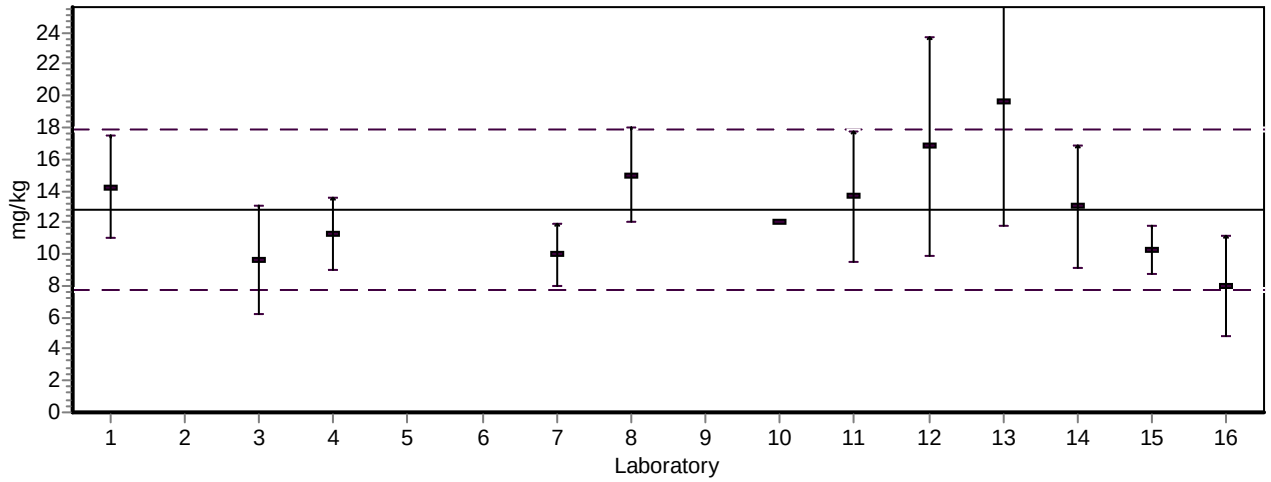
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* N2V



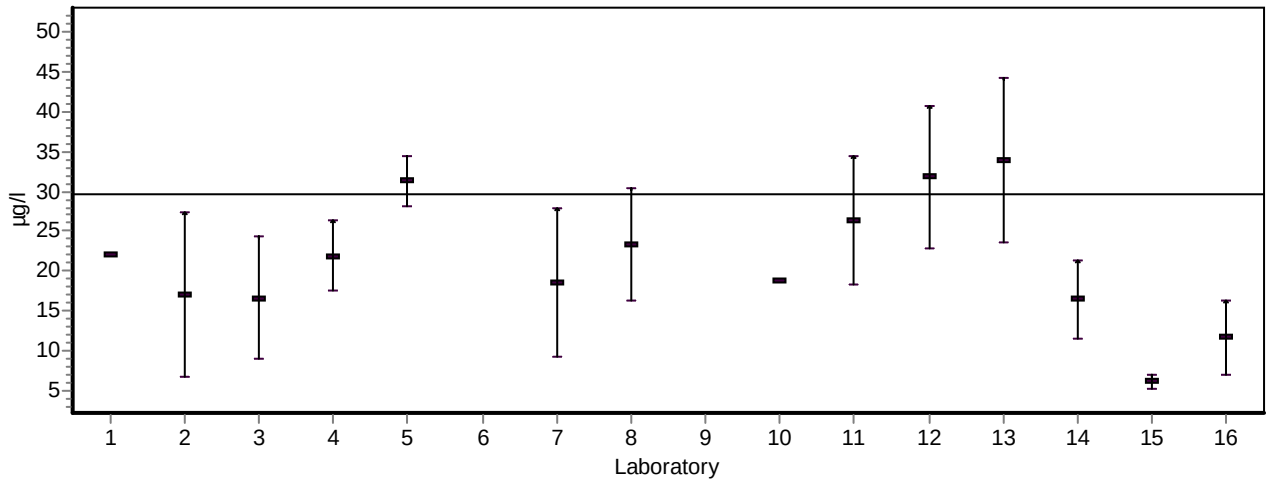
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* A1V



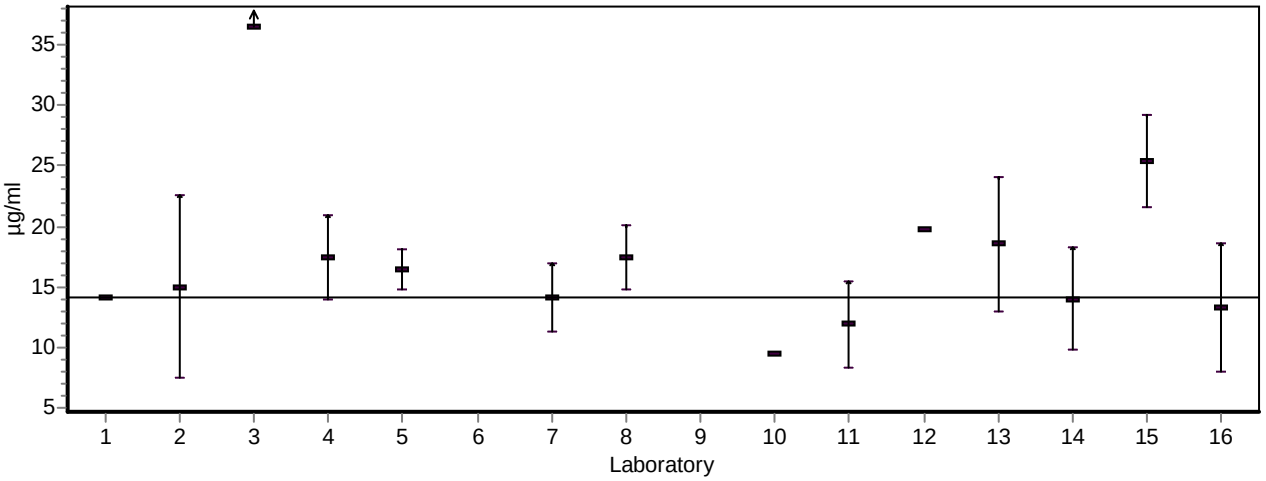
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* M3V



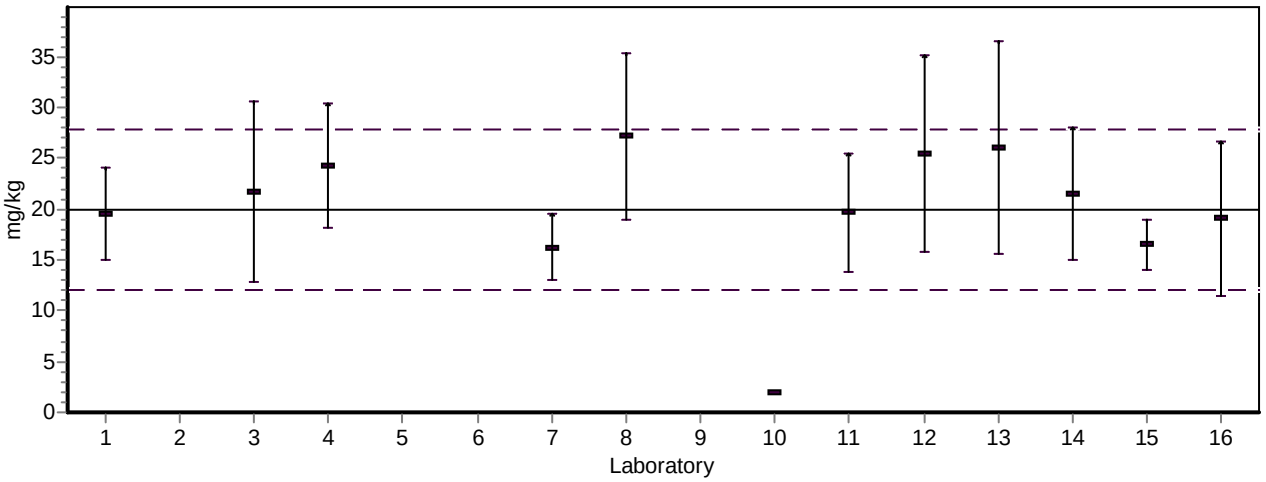
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* N2V



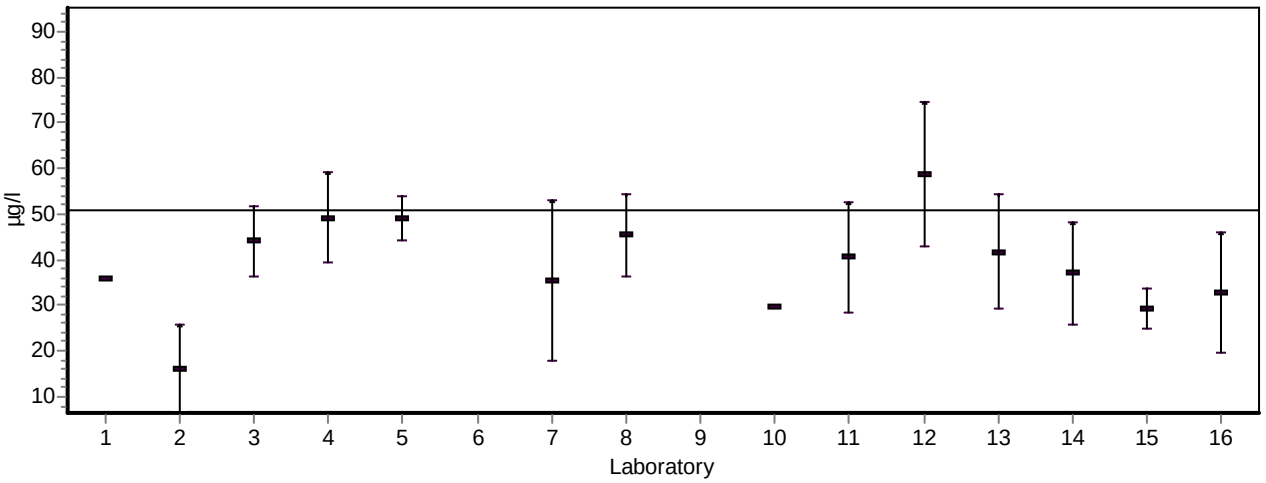
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* A1V



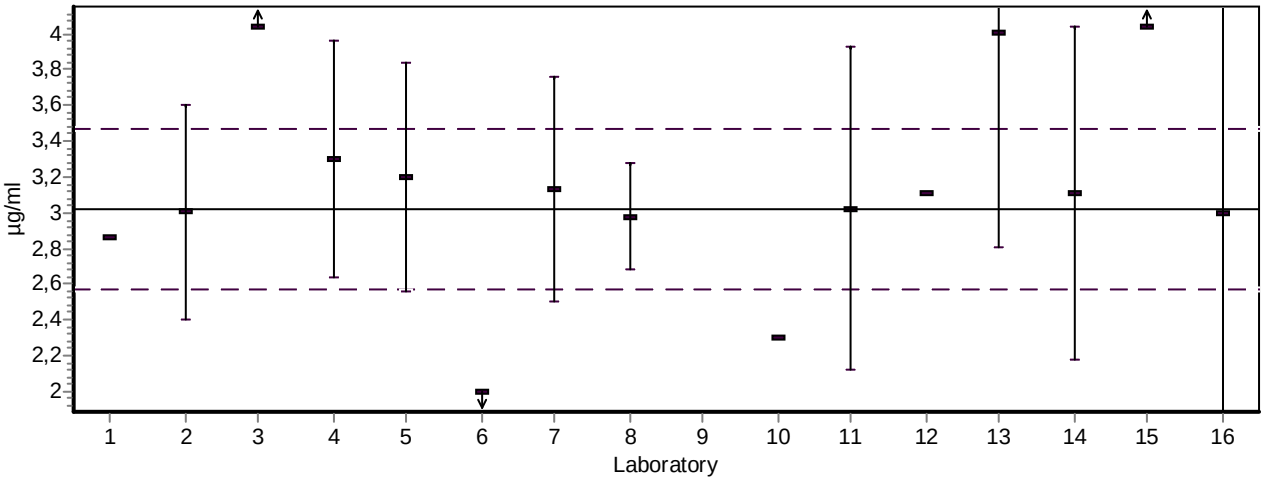
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* M3V



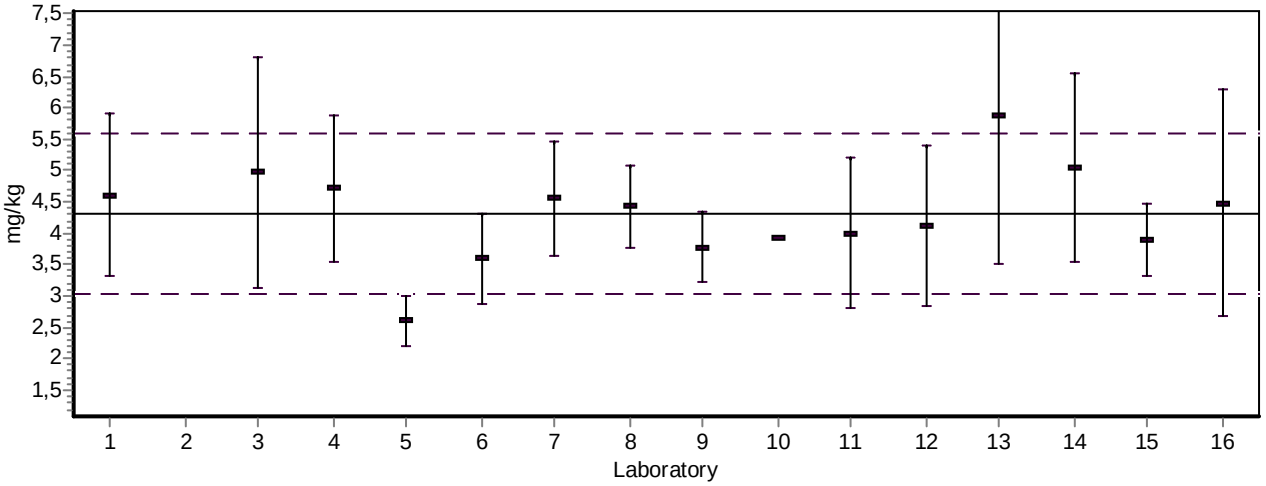
Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* N2V



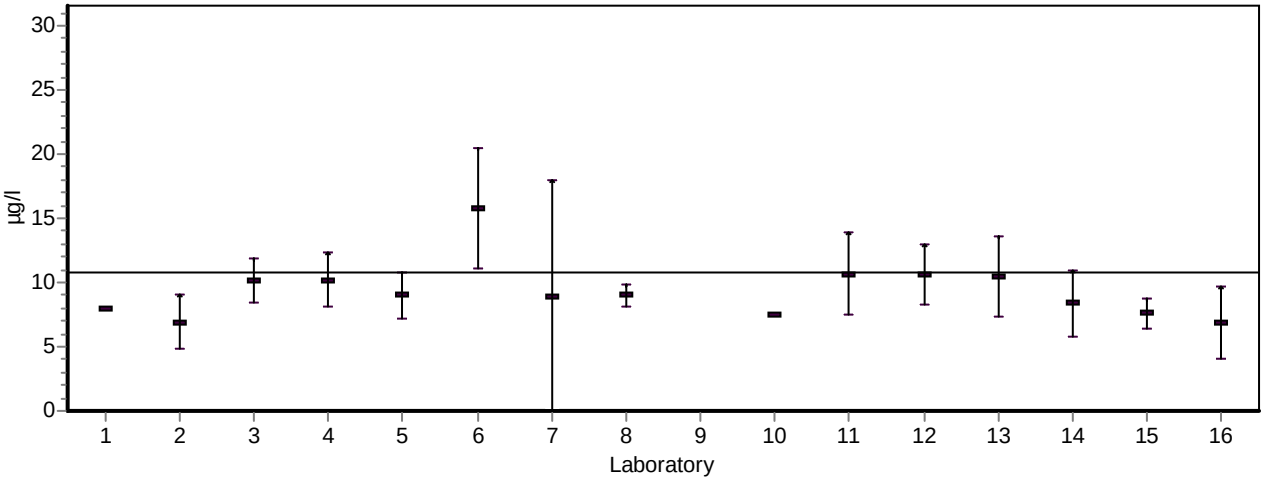
Analyytti *(Analyte)* **TOL** Näyte *(Sample)* A1V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* M3V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* N2V



LIITE 10. SUMMARY OF THE z SCORES

APPENDIX 10.

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	%
124TCBz	A1V	S	.	U	U	.	.	S	S	.	u	U	S	U	S	.	u	45
	M3V	S	.	S	S	.	.	S	S	.	S	S	S	S	S	.	q	91
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
12DCEa	A1V	S	.	U	S	.	.	S	S	.	q	S	S	U	S	.	S	73
	M3V	S	.	S	S	.	.	S	S	.	S	S	S	Q	S	.	S	91
	N2V	S	.	S	S	.	.	S	S	.	S	S	S	.	S	.	S	100
Bz	A1V	S	S	U	S	S	u	S	S	.	u	S	U	U	S	U	S	60
	M3V	S	.	S	S	S	S	S	S	S	S	S	U	U	S	S	S	87
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
c12DCEe	A1V	S	.	U	S	U	.	S	S	.	u	.	S	.	S	.	S	70
	M3V	S	.	S	S	.	.	S	S	.	S	.	S	.	S	.	S	100
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
CCl4	A1V	S	S	U	S	U	.	u	S	.	u	S	S	.	S	.	S	67
	M3V	S	.	S	S	.	.	u	S	.	Q	S	S	.	S	.	S	80
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
CHCl3	A1V	S	S	U	Q	U	.	S	q	.	q	U	S	.	S	.	S	50
	M3V	S	.	S	S	.	.	S	S	.	S	S	S	.	S	.	S	100
	N2V	S	S	S	S	S	.	S	S	.	S	S	S	.	S	.	S	100
DCM	A1V	q	.	U	S	S	.	S	S	.	u	U	q	U	q	.	S	42
	M3V	S	.	S	S	.	.	S	S	.	.	q	S	.	S	.	S	89
	N2V	S	.	S	S	S	.	S	q	.	q	S	S	.	S	.	S	82
ETBE	A1V	S	S	U	.	.	.	S	q	.	.	U	U	.	.	.	S	50
	M3V	S	.	S	.	.	.	S	S	.	.	S	S	.	.	.	S	100
	N2V	S	S	S	.	.	.	S	S	.	.	U	U	.	.	.	S	75
ETBz	A1V	S	q	U	S	S	u	u	S	.	u	S	Q	U	S	U	u	40
	M3V	S	.	S	S	S	S	q	S	S	S	S	U	U	S	S	S	80
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
mpXYL	A1V	S	S	U	S	S	u	q	S	.	u	S	Q	U	S	U	S	53
	M3V	S	.	S	S	q	S	S	S	S	S	S	S	Q	S	S	S	87
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
MTBE	A1V	S	S	U	U	S	.	q	S	.	q	S	U	U	q	.	S	46
	M3V	S	.	S	S	.	.	q	S	.	S	Q	S	S	S	.	S	82
	N2V	S	S	S	U	S	.	S	S	.	S	S	U	S	S	.	S	85
oXYL	A1V	S	q	U	S	S	u	u	S	.	q	S	S	U	S	U	S	53
	M3V	S	.	S	S	S	S	q	S	S	S	S	S	Q	S	S	S	87
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
t12DCEe	A1V	S	.	U	S	S	.	u	S	.	u	S	S	S	q	.	q	58
	M3V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
TAME	A1V	U	.	U	.	.	.	u	S	.	u	S	Q	U	q	.	S	30
	M3V	S	.	S	.	.	.	q	S	.	S	S	S	U	S	.	S	80
	N2V	S	.	S	.	.	.	q	S	.	S	U	U	.	S	.	S	67
TCEe	A1V	S	S	U	S	Q	.	q	S	.	u	u	Q	U	q	U	u	29
	M3V	S	.	S	S	.	.	S	S	.	S	S	S	Q	S	S	S	92
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
TECEe	A1V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	M3V	S	.	S	S	.	.	S	S	.	u	S	S	S	S	S	S	92
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
TOL	A1V	S	S	U	S	S	u	S	S	.	u	S	S	U	S	U	S	67
	M3V	S	.	S	S	q	S	S	S	S	S	S	S	Q	S	S	S	87
	N2V	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
%		95	85	58	88	70	50	63	92	100	47	75	66	21	86	54	87	
Accredited		yes		yes	yes	yes	yes	yes		yes		yes	yes		yes	yes	yes	

S - satisfactory ($-2 \leq z \leq 2$), Q - questionable ($2 < z < 3$), q - questionable ($-3 < z < -2$),
U - unsatisfactory ($z \geq 3$), u - unsatisfactory ($z \leq -3$)

%* - percentage of satisfactory results

Totally satisfactory, % In all: 72 In accredited: 75 In non-accredited: 61

ANALYTICAL METHODS

Water – N2V

Lab	Extraction	Internal standard	Sampling	Equipment	Reference
1	No extraction	Toluene-d8	Headspace	GC-MS	ISO 11423-1
2	No extraction	None	Purge & Trap	GC-FID/EC	?
3	No extraction	Toluene-d8 1,2-Dichlorobenzene-d4	Headspace	GC-MS	modified ISO 22155
4	No extraction	Toluene-d8 Dichlorobenzene-d8	Headspace	GC-MS	In house method
5	No extraction	Fluorobenzene-d5 Tetrahydrofuran-d8 Toluene-d8	Headspace	GC-MS	?
6	Shaking	Bromobenzene o-Terphelyl	Splitless	GC-MS	National standard method
7	No extraction	Toluene-d8	Headspace	GC-MS	In house method
8	No extraction	α,α,α-Trifluorotoluene Toluene-d8	Headspace	GC-MS	ISO 10301
10	No extraction	Toluene-d8	Headspace	GC-MS	In house method
11	No extraction	Toluene-d8 Bromobenzene	Headspace	GC-MS	EN ISO 15680
12	No extraction	1,2-Dichloroethene-d4 Toluene-d8	Headspace	GC-MS	ISO 10301
13	No extraction	None	Headspace	GC-FID	Modified ISO 11423-1
14	?	?	?	?	?
15		Naphtalene-d8 4-Bromo-fluorobenzene	Slit	GC-FID	In house method
16	No extraction	Chlorobenzene-d8	Headspace	GC-MS	?

Soil – M3V

Lab	Extraction	Internal standard	Sampling / Injec-tion	Equipment	Reference
1	Shaking	Toluene-d8	Headspace	GC-MS	ISO 22155
3	Shaking	Toluene-d8 1,2-Dichlorobenzene-d4	Headspace + split	GC-MS	ISO 22155
4	Heating in head-space vial	Toluene-d8 1,4-Dichlorobenzene-d4	Headspace	GC-MS	In house method
5	Shaking	Bromobenzene	Splitless	GC-FID	?
6	Shaking	Bromobenzene o-Terphelyl	Splitless	GC-MS	ISO/DIS 16703
7	Shaking	Toluene-d8	Headspace	GC-MS	In house method
8	Shaking	α,α,α-Trifluorotoluene Toluene-d8	Headspace	GC-MS	ISO 22155
9	Shaking	Bromobenzene	Splitless	GC-MS	?
10	Shaking	Toluene-d8	Split	GC-MS	In house method
11	Shaking	Toluene-d8 Bromobenzene	Headspace	GC-MS	ISO 22155 EN ISO 15680
12	Ultrasonic	Fluorobenzene	Headspace	GC-MS	EN ISO 22155
13	Shaking	None	Headspace	GC-FID	EN ISO 22155
14	?	?	?	?	?
15	Special tecnique	Naphtalene-d8 4-Bromo-fluorobenzene	Headspace + split	GC-FID	In house method
16	Shaking Ultrasonic	Chlorobenzene-d8	Headspace	GC-MS	?

RESULTS GROUPED ACCORDING TO THE MEASUREMENTMETHODS

No statistical comparison between the different techniques could be done because of the low number of the results. In this appendix the results of the participants are grouped according to the instrument tecnique as follows:

Meth 1. GC-MS

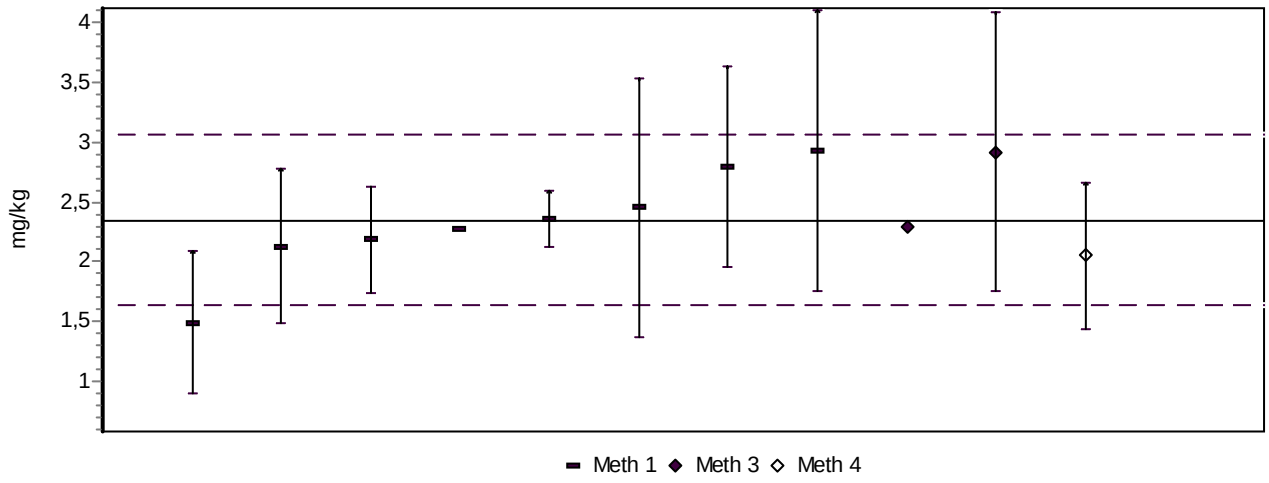
Meth 2. GC-FID+ECD

Meth 3. GC-FID

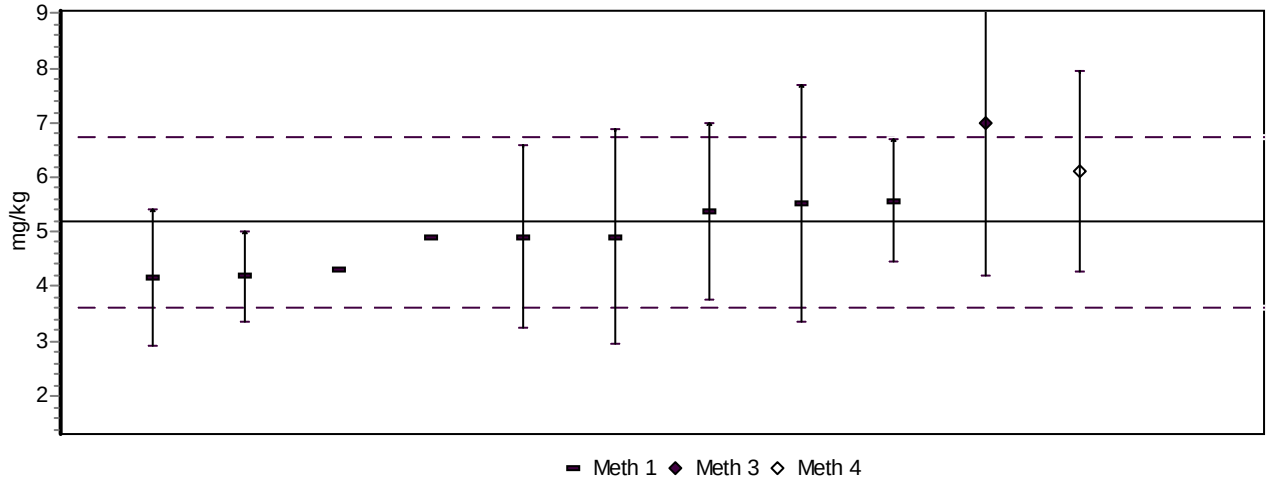
Meth 4. Not specified

LIITE 11.2. RESULTS GROUPED ACCORDING TO THE MEASUREMENTMETHODS
APPENDIX 11.2.

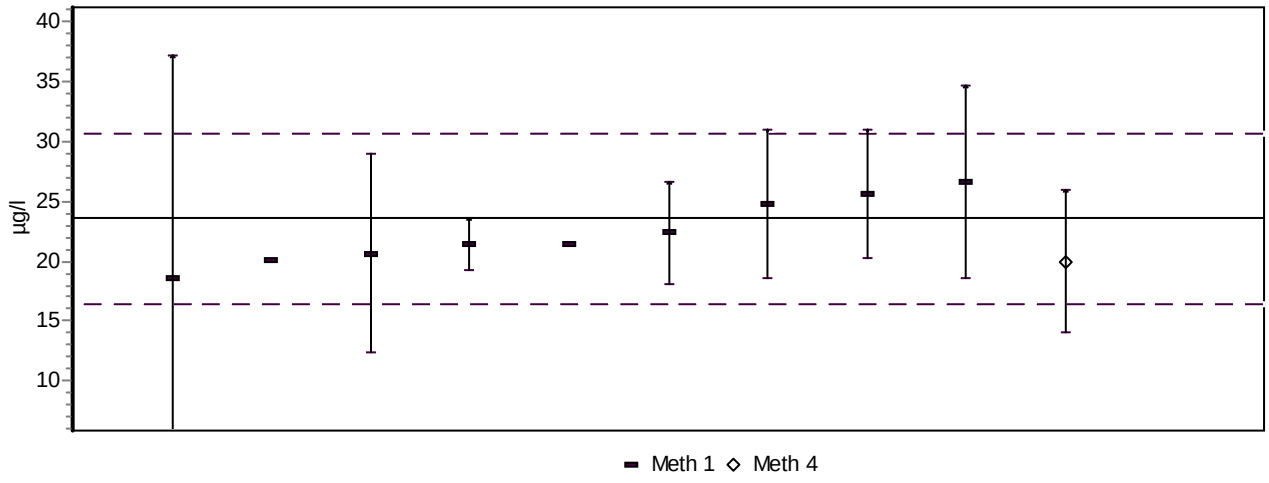
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* M3V



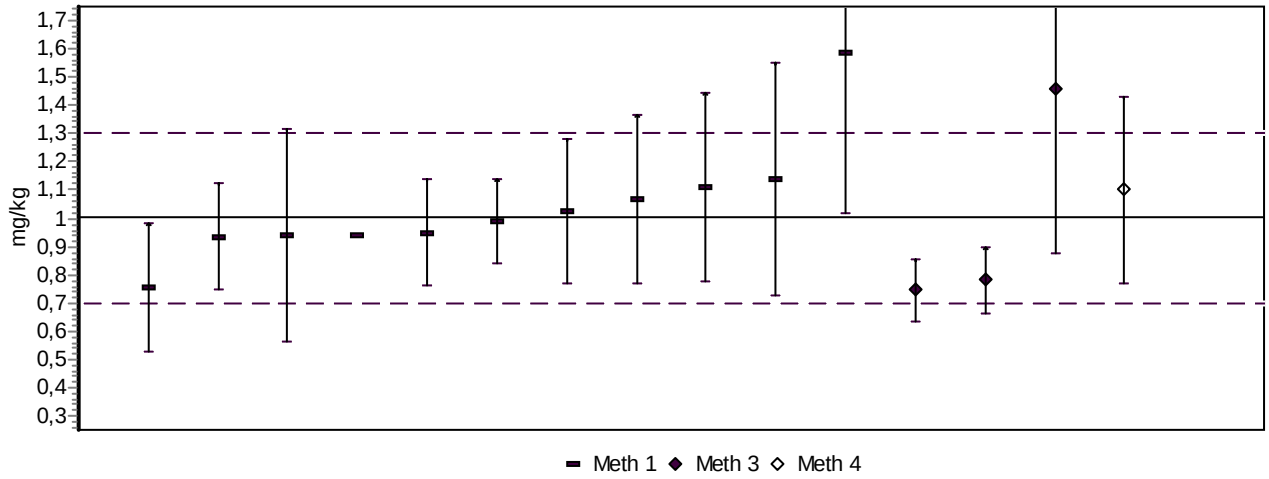
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* M3V



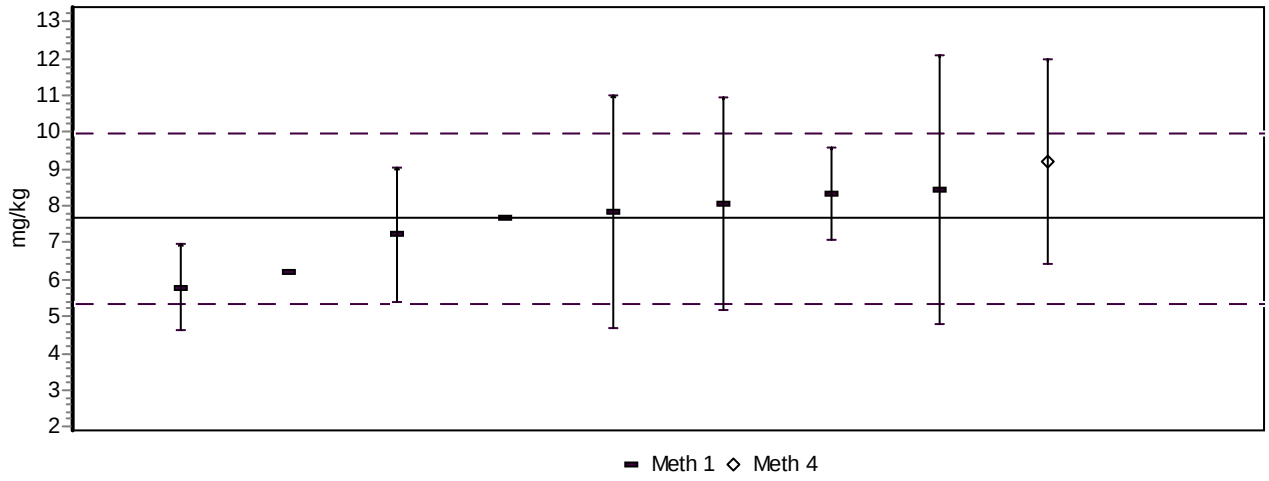
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* N2V



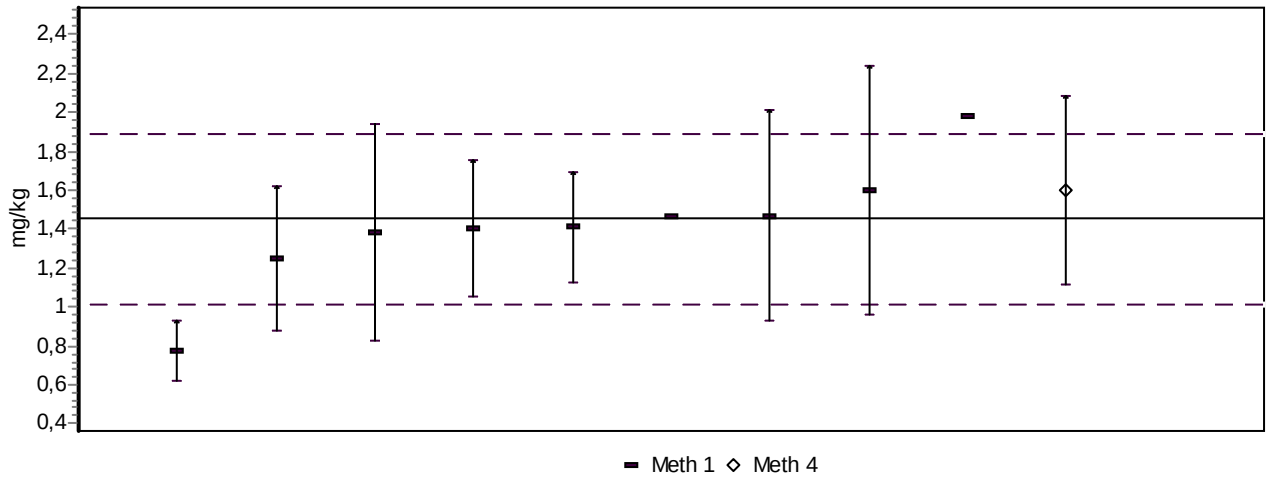
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* M3V



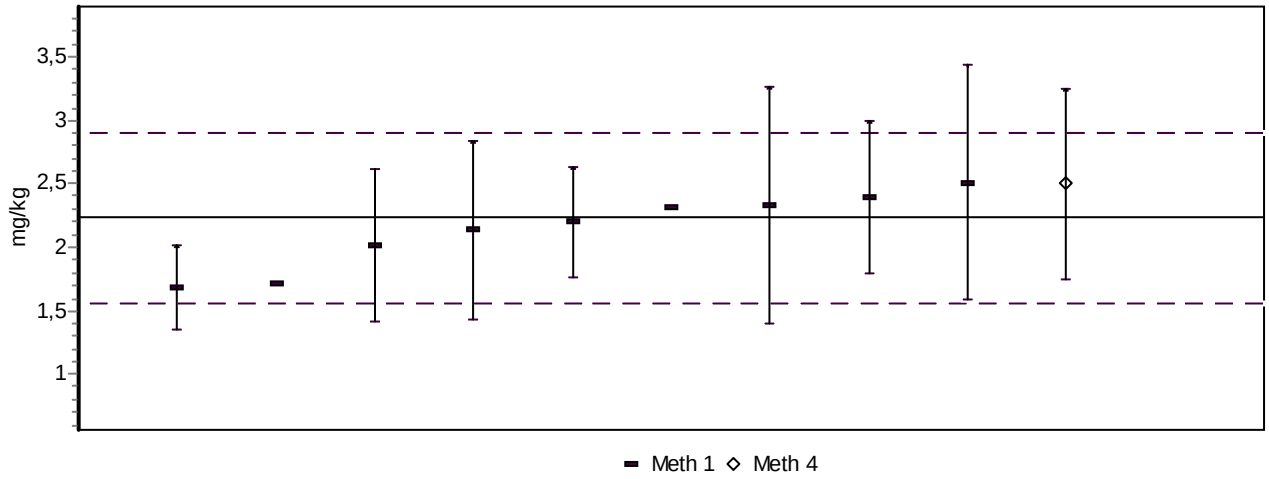
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* M3V



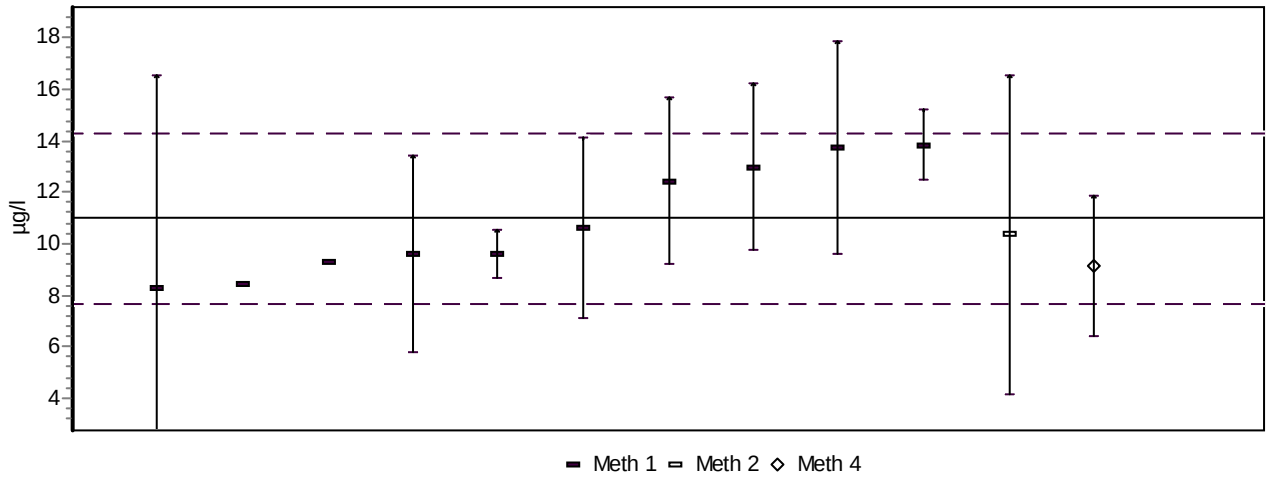
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* M3V



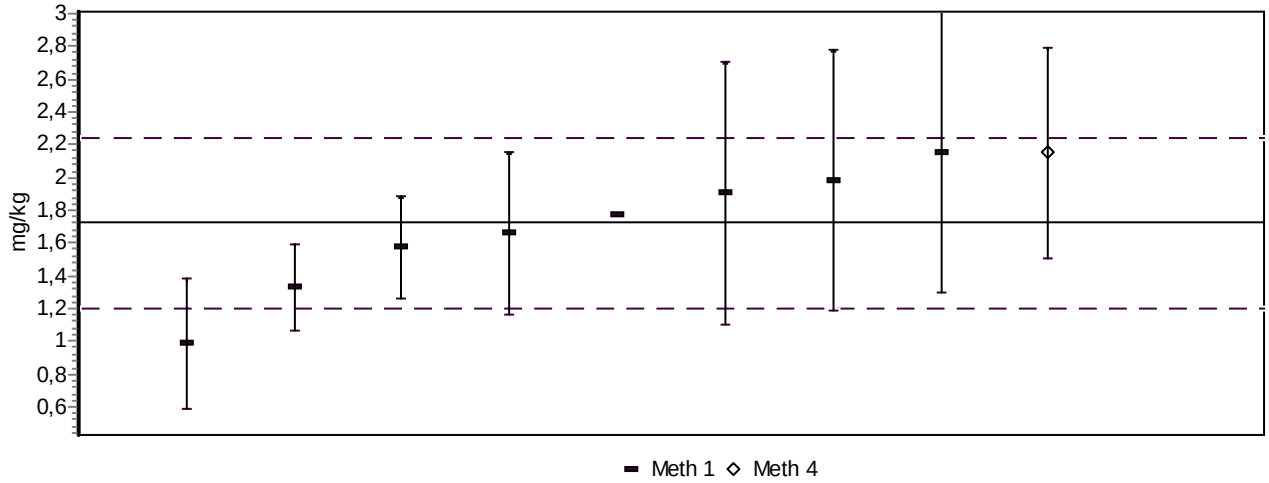
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* M3V



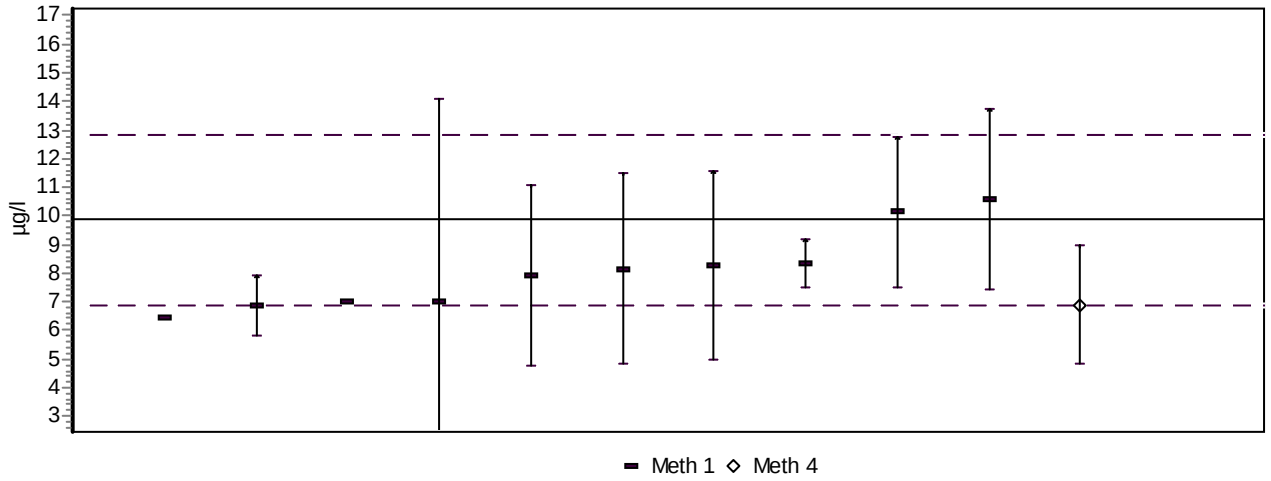
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* N2V



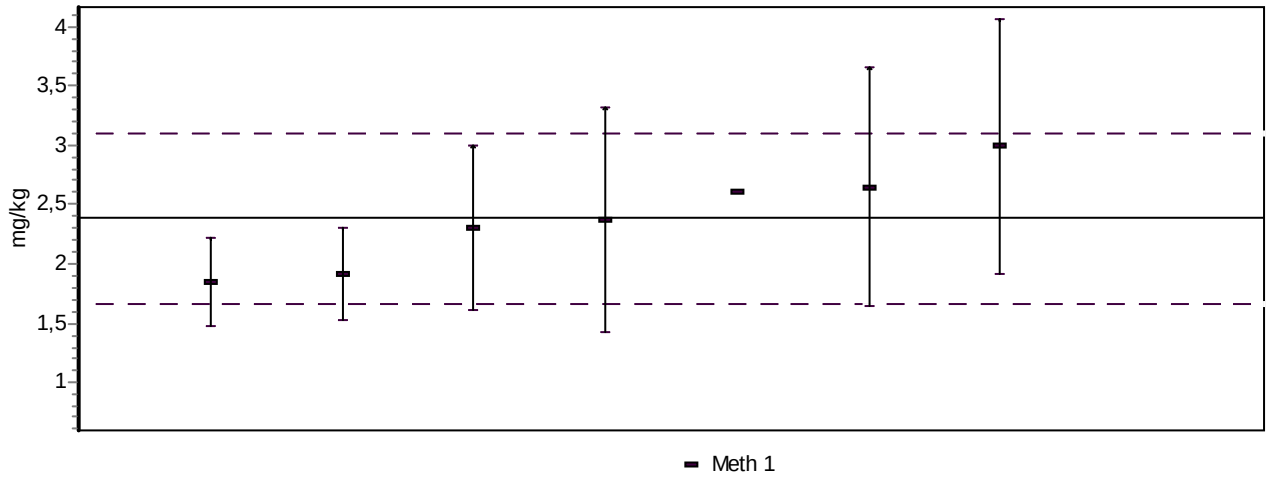
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* M3V



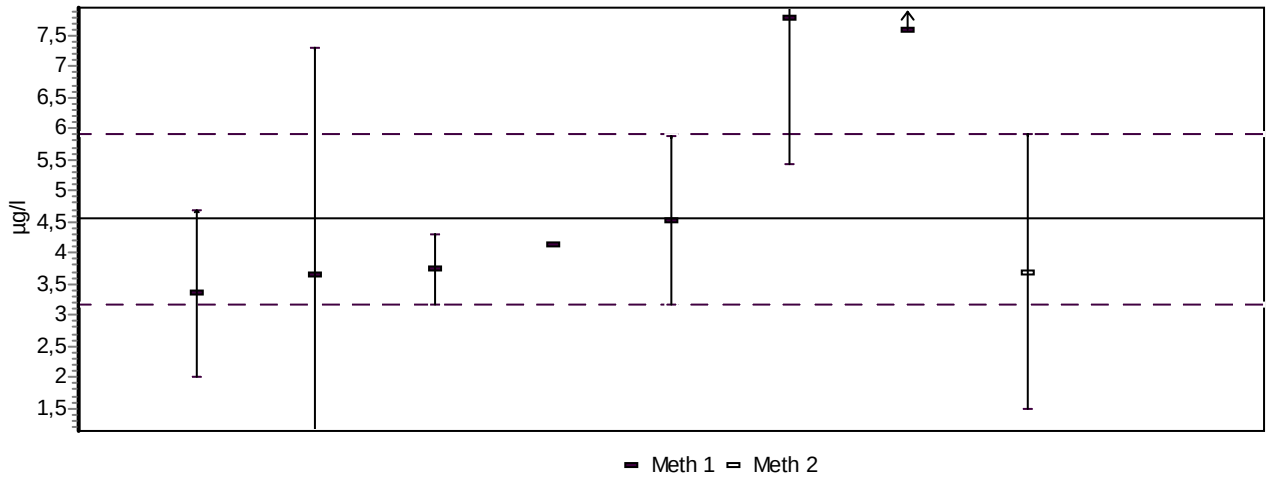
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* N2V



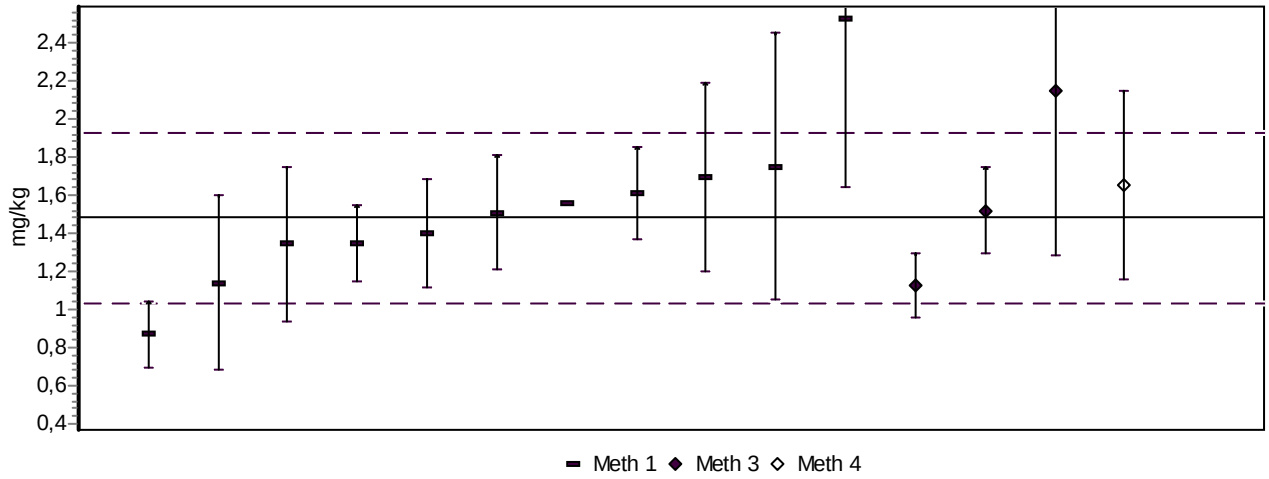
Analyytti *(Analyte)* **ETBE** Näyte *(Sample)* M3V



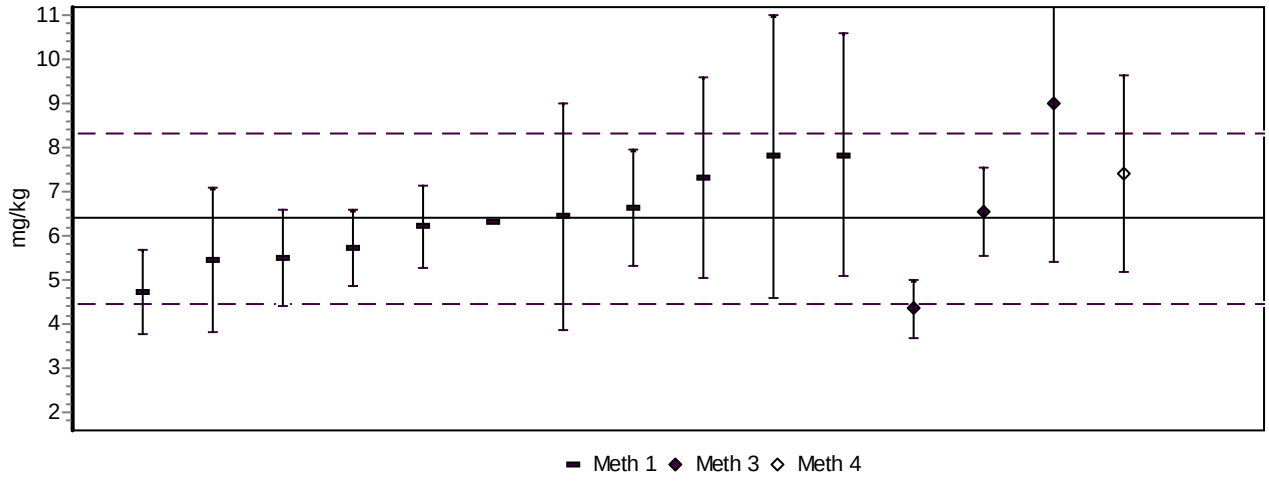
Analyytti *(Analyte)* **ETBE** Näyte *(Sample)* N2V



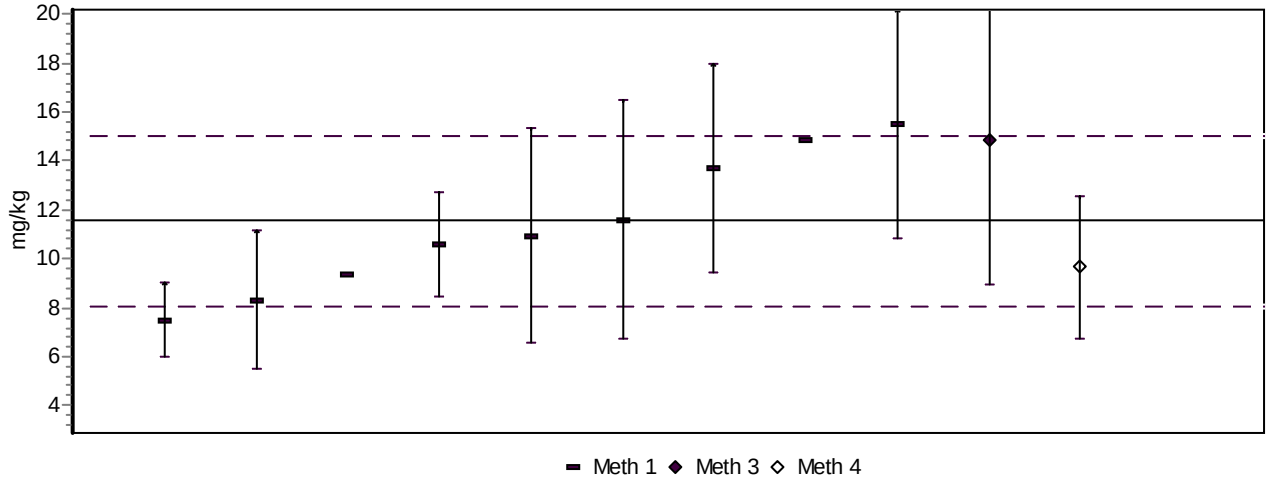
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* M3V



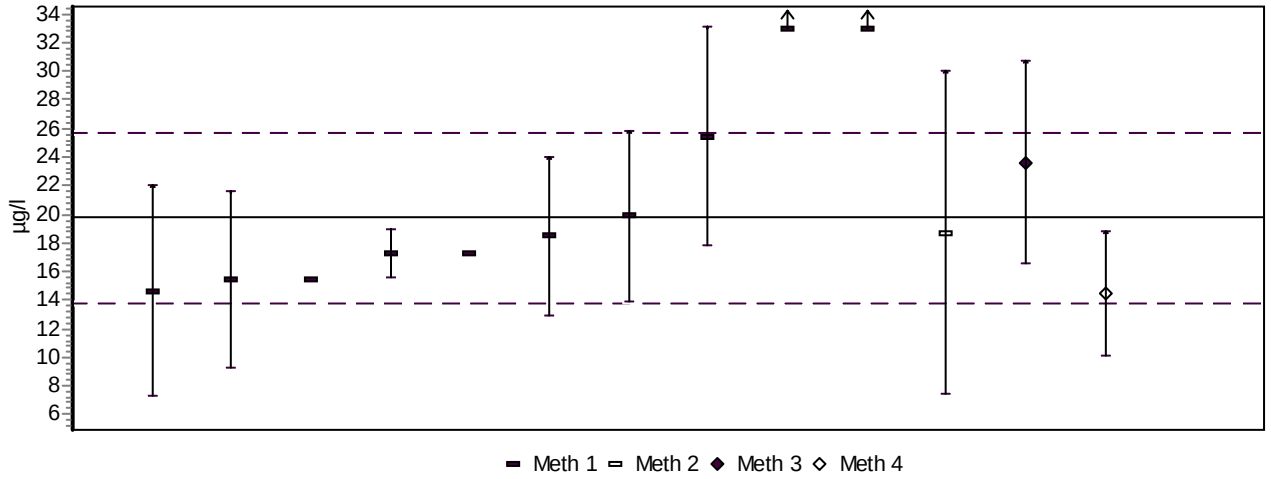
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* M3V



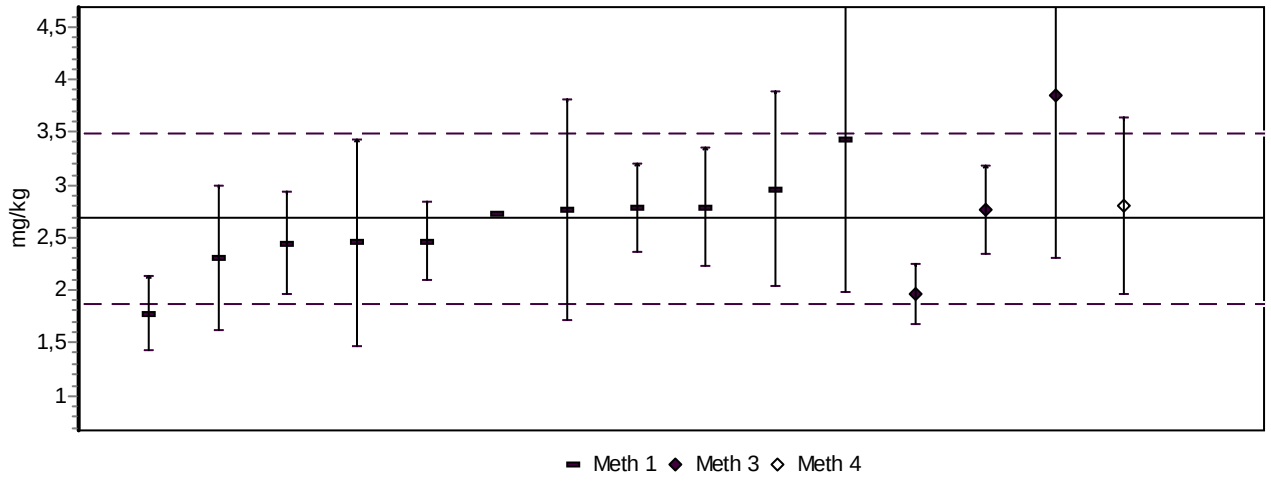
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* M3V



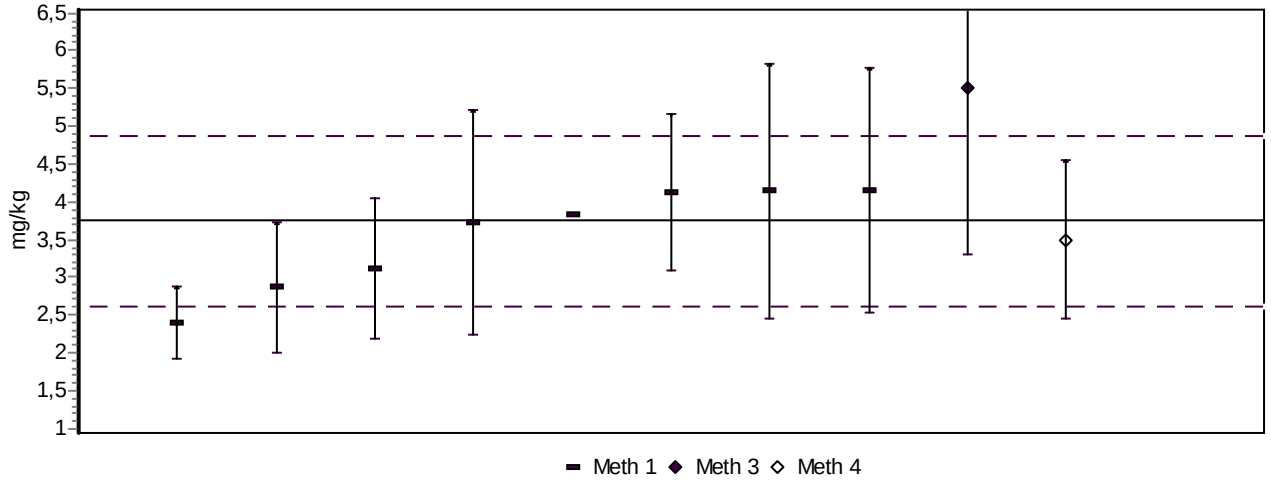
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* N2V



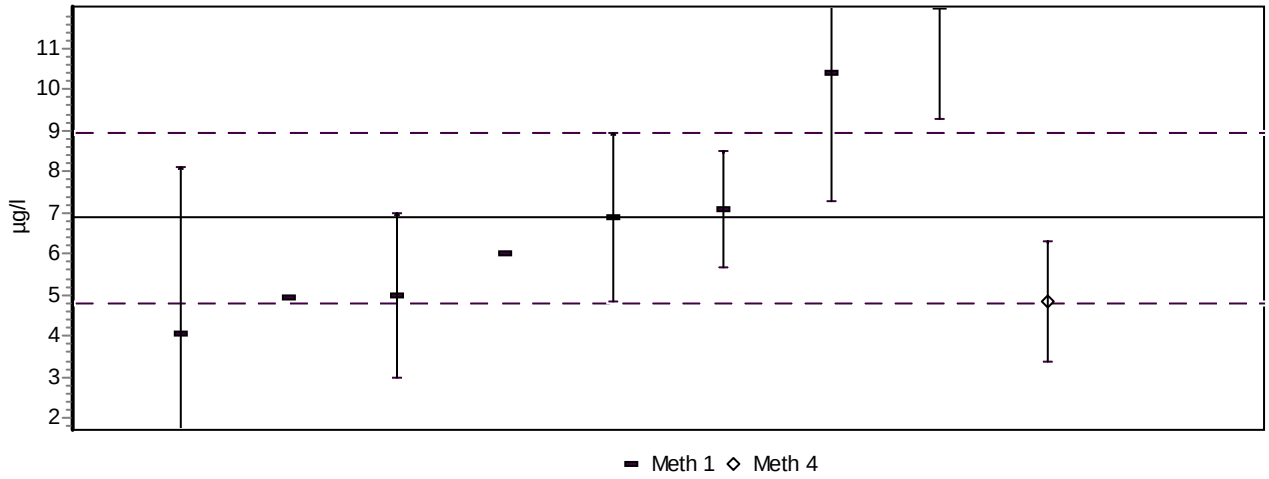
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* M3V



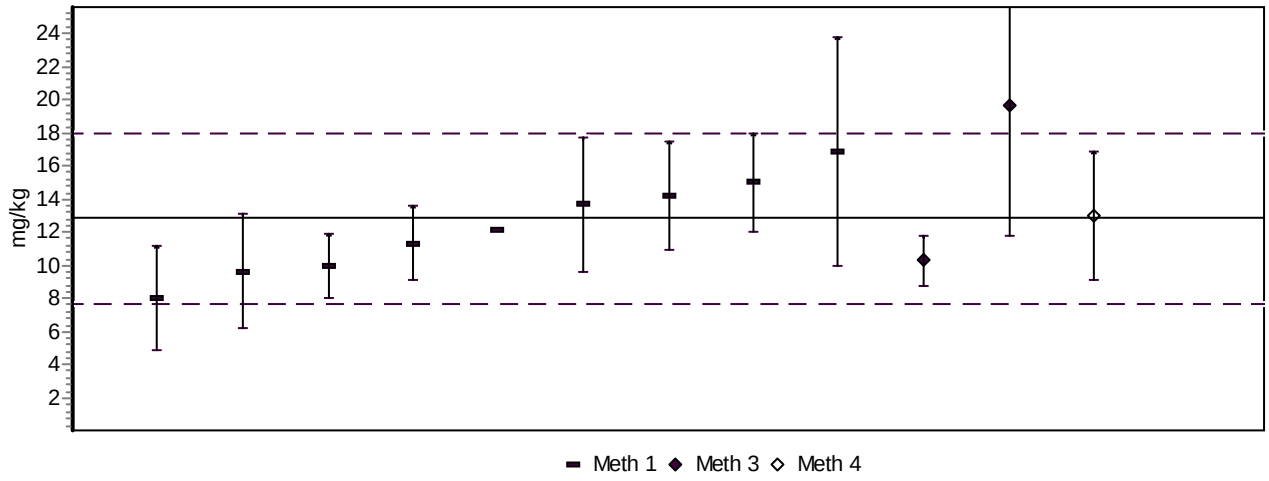
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* M3V



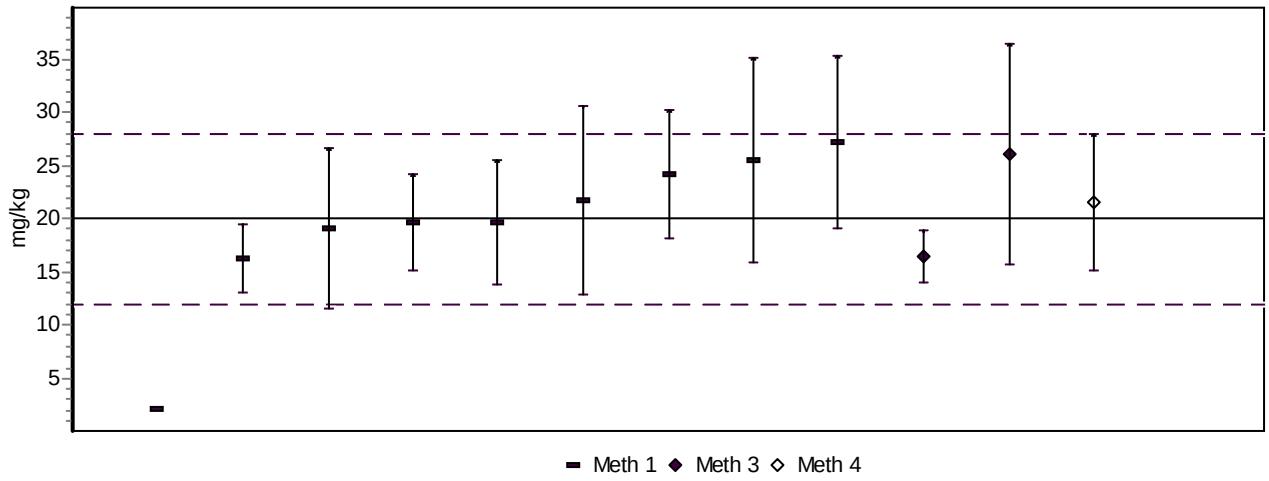
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* N2V



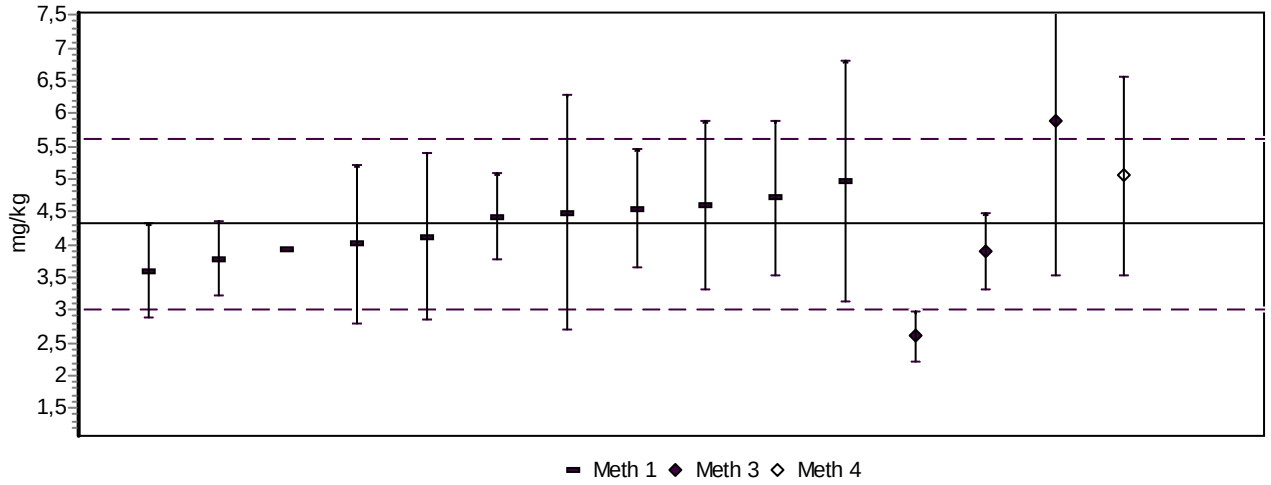
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* M3V



Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* M3V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* M3V



EXAMPLES OF THE MEASUREMENT UNCERTAINTIES REPORTED BY THE LABORATORIES

For evaluation of the measurement uncertainty the participants have used the procedures as follows:

UC No: the procedure used for the estimation of the expanded measurement uncertainty *)
at 95 % confidence level (IQC = internal quality control)

1. Using the IQC data only from synthetic control sample and/or CRM (X-chart), see e.g. NORDTEST TR 537[1)]

2. Using the IQC data from synthetic sample (X-chart) together with the IQC data from routine sample replicates (R-chart or r%-chart), see e.g. NORDTEST TR 537[1)]

3. Using the IQC data and the results obtained in proficiency tests, see e.g. NORDTEST TR 537[1)]

4. Using the data obtained in method validation

5. Using the "modeling approach" (GUM Guide or EURACHEM Guide Quantifying Uncertainty in Analytical Measurement)[2)]

6. Other procedure, please specify

7. No uncertainty estimation

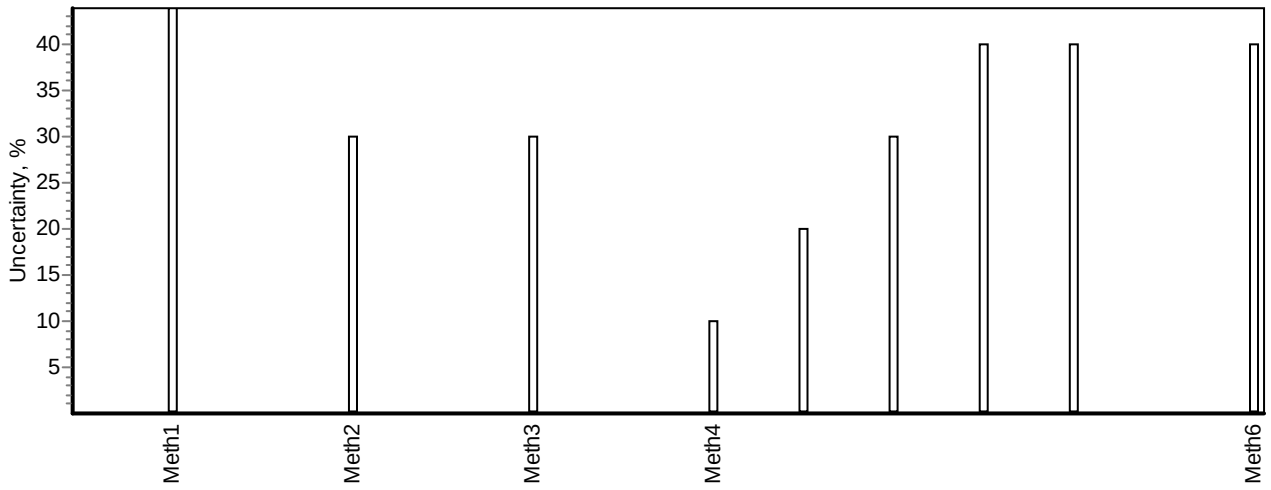
IQC = internal quality control

In the figures the procedures have been presented using the same code number.

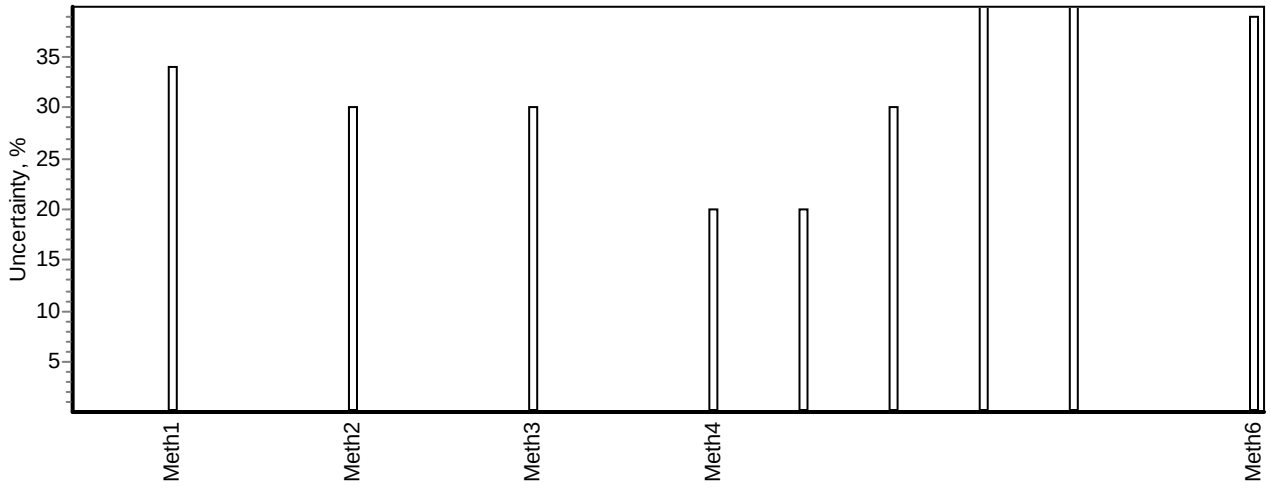
[1)] http://www.nordtest.info
[2)] http://www.eurachem.org

LIITE 12.
APPENDIX 12.

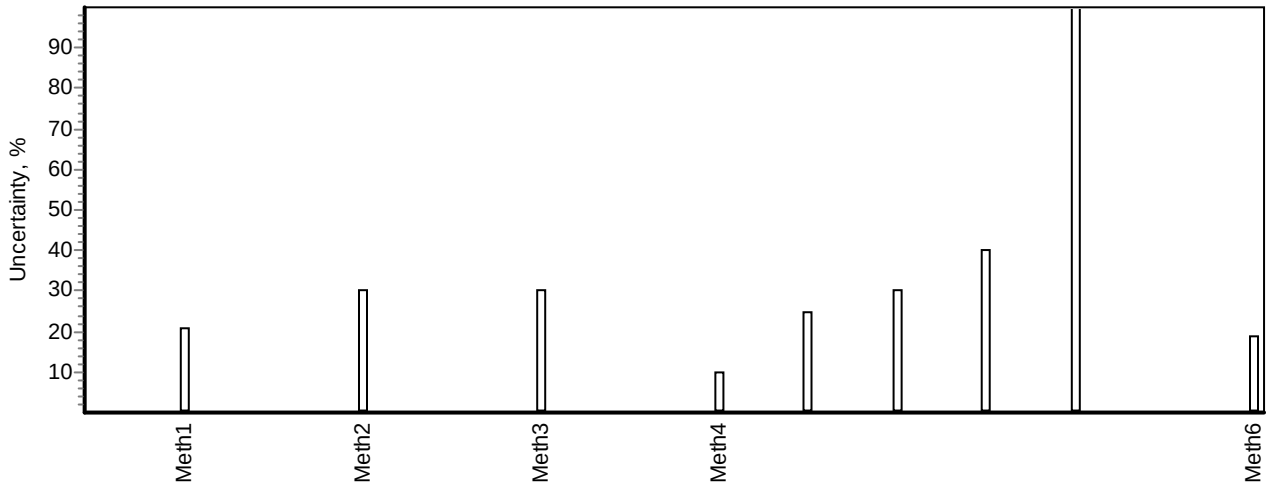
Analyytti *(Analyte)* **124TCBz** Näyte *(Sample)* M3V



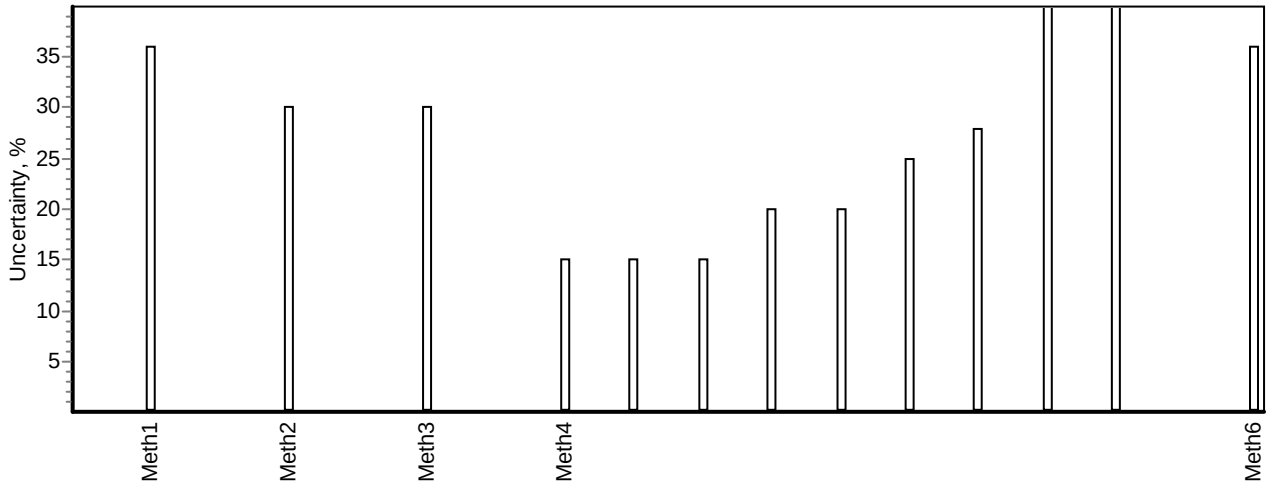
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* M3V



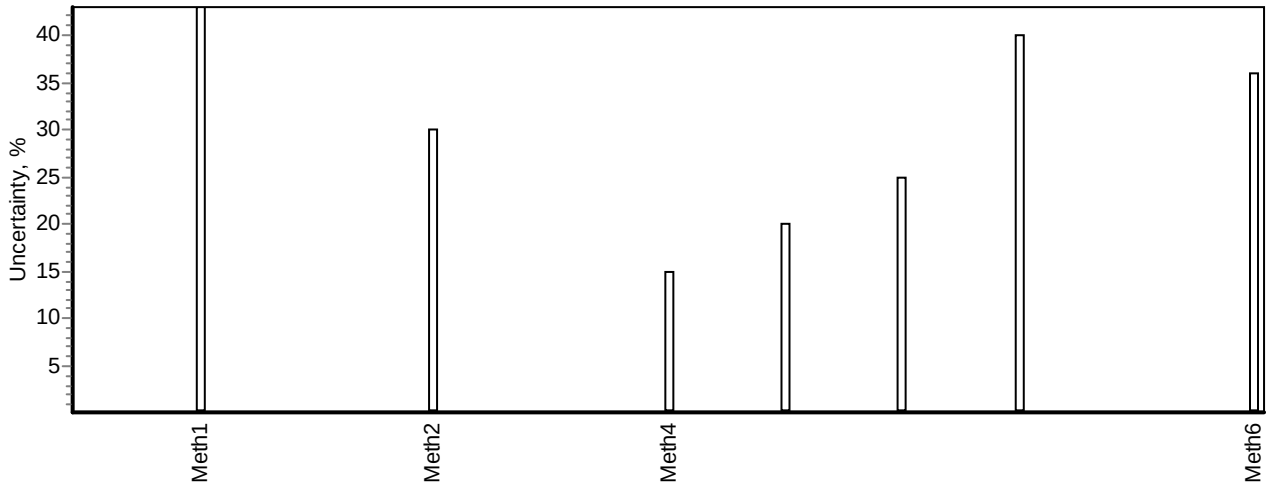
Analyytti *(Analyte)* **12DCEa** Näyte *(Sample)* N2V



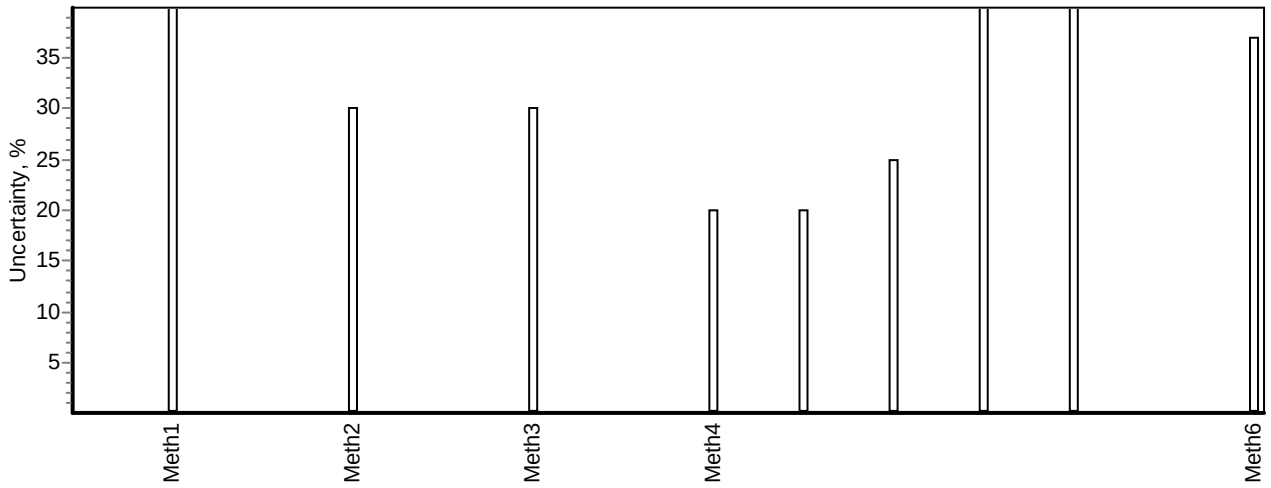
Analyytti *(Analyte)* **Bz** Näyte *(Sample)* M3V



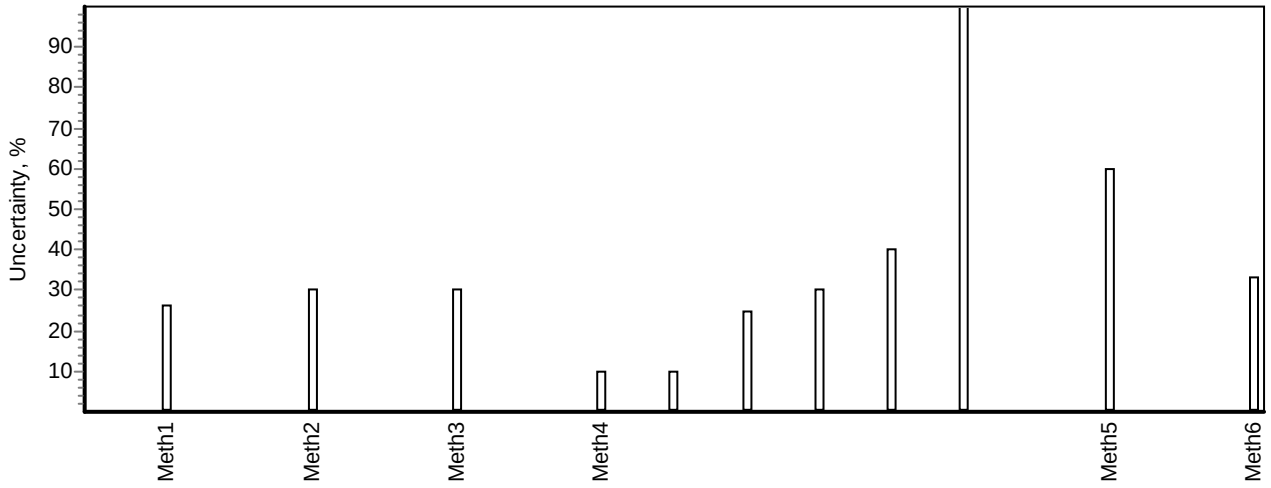
Analyytti *(Analyte)* **c12DCEe** Näyte *(Sample)* M3V



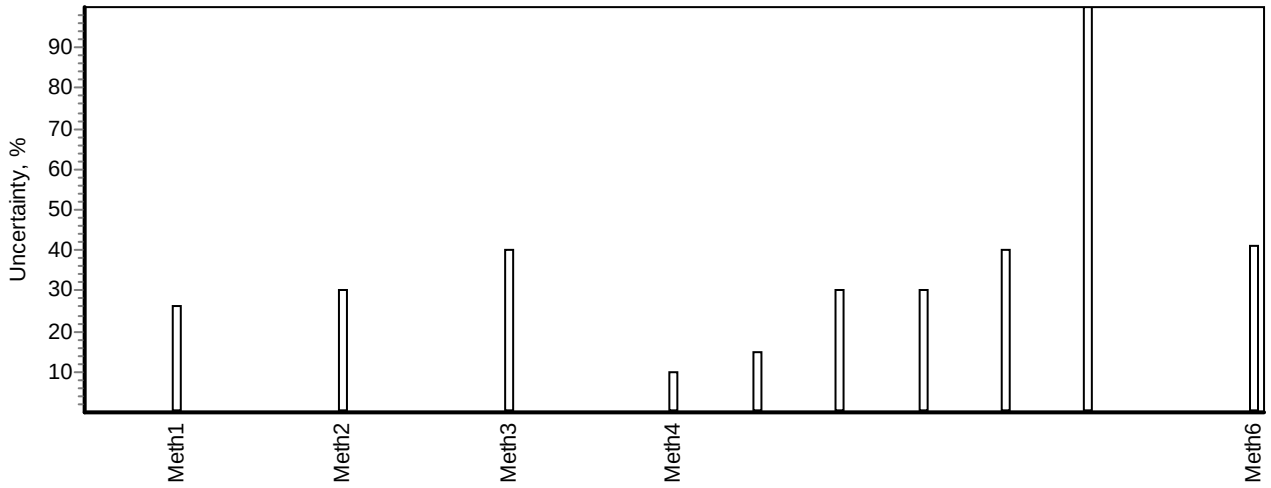
Analyytti *(Analyte)* **CCl4** Näyte *(Sample)* M3V



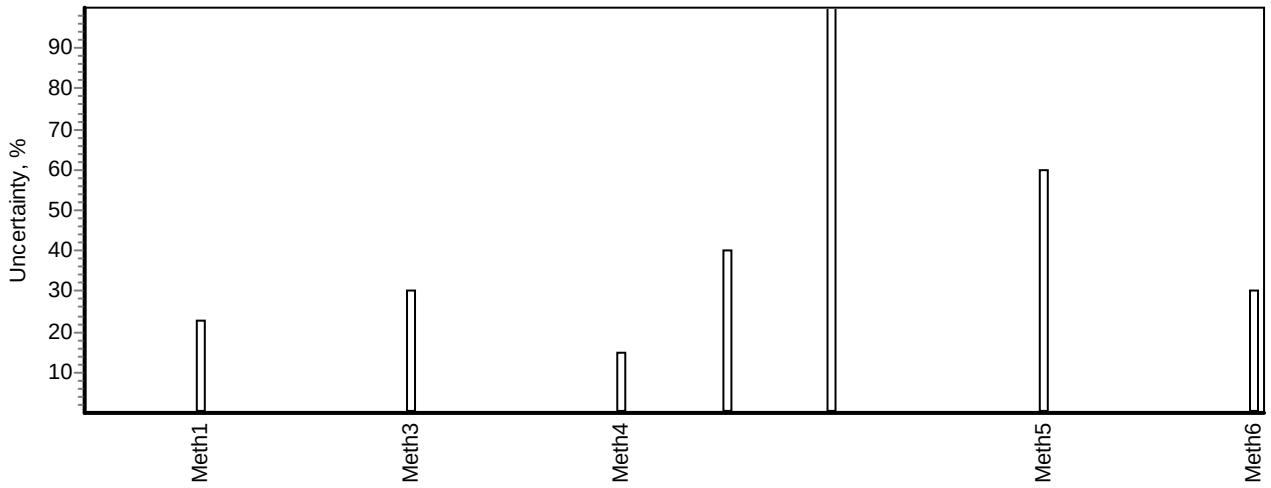
Analyytti *(Analyte)* **CHCl3** Näyte *(Sample)* N2V



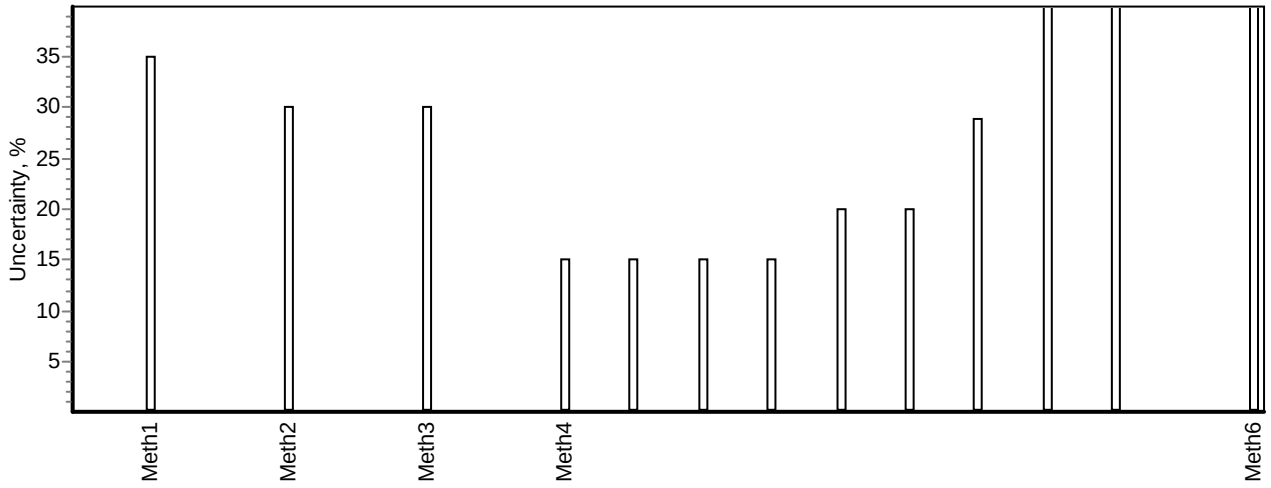
Analyytti *(Analyte)* **DCM** Näyte *(Sample)* N2V



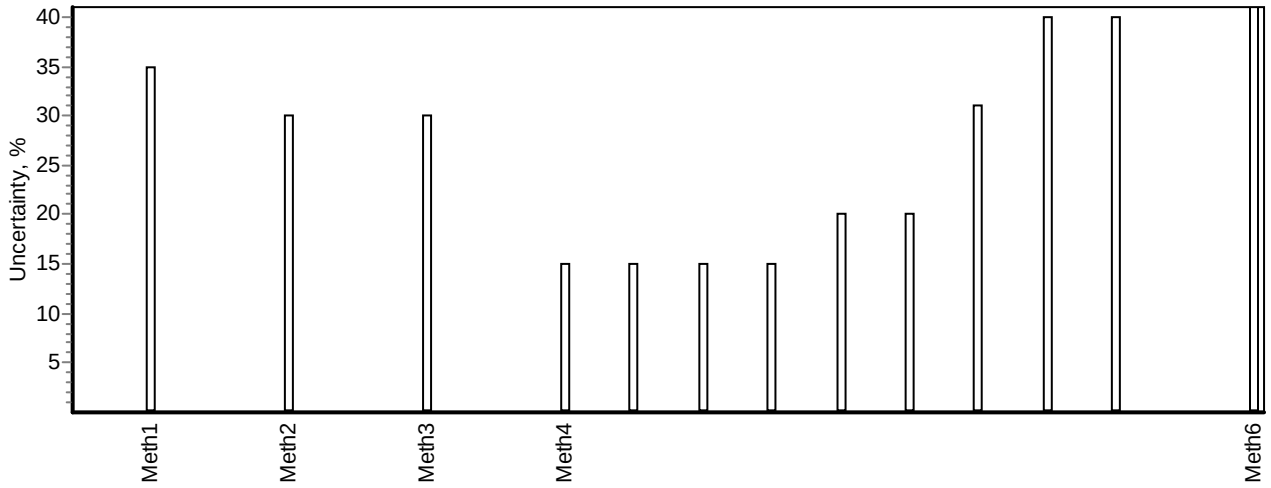
Analyytti *(Analyte)* **ETBE** Näyte *(Sample)* N2V



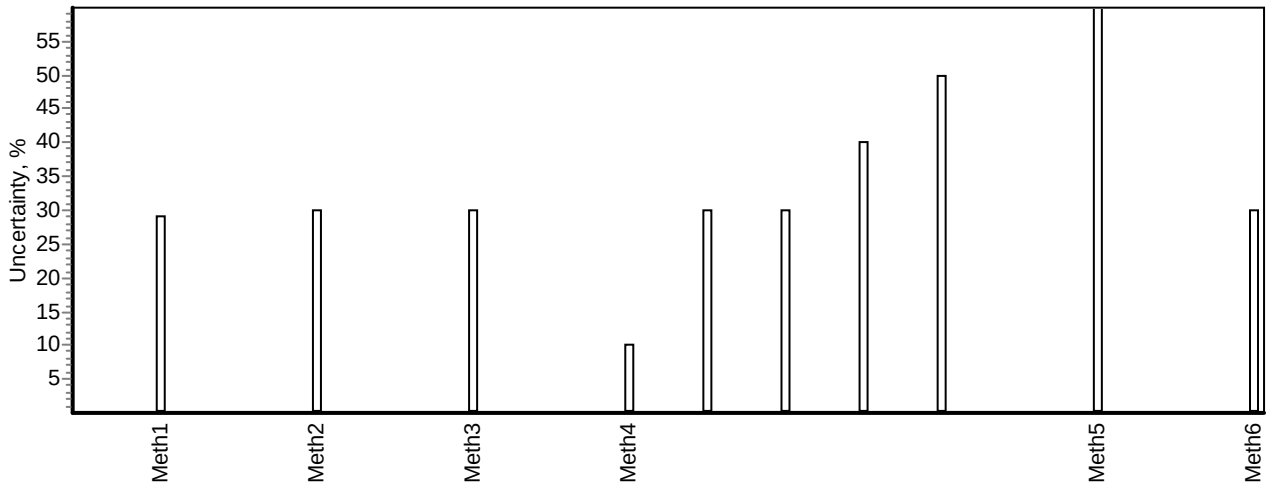
Analyytti *(Analyte)* **ETBz** Näyte *(Sample)* M3V



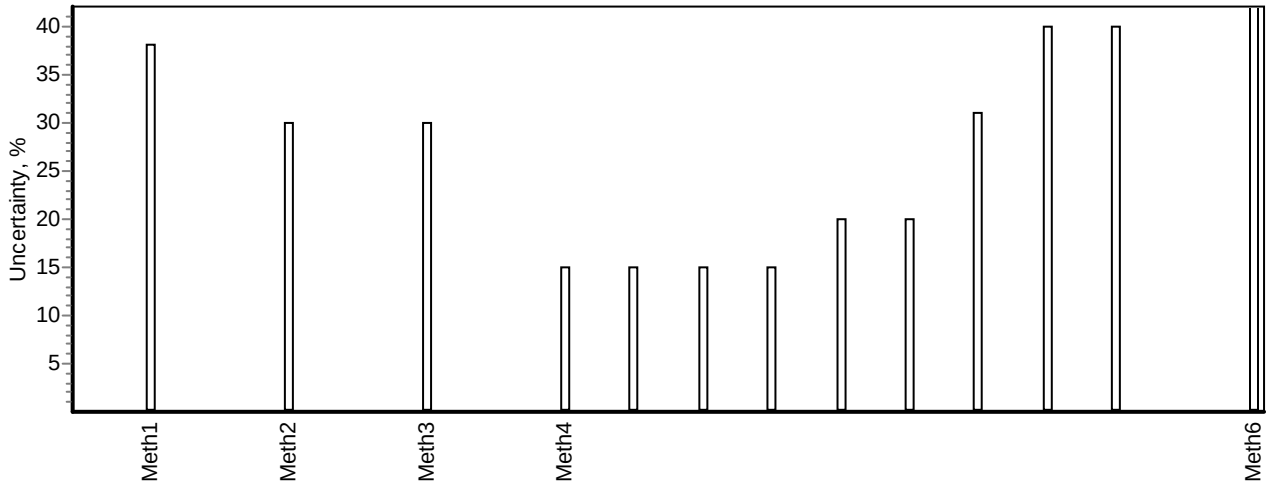
Analyytti *(Analyte)* **mpXYL** Näyte *(Sample)* M3V



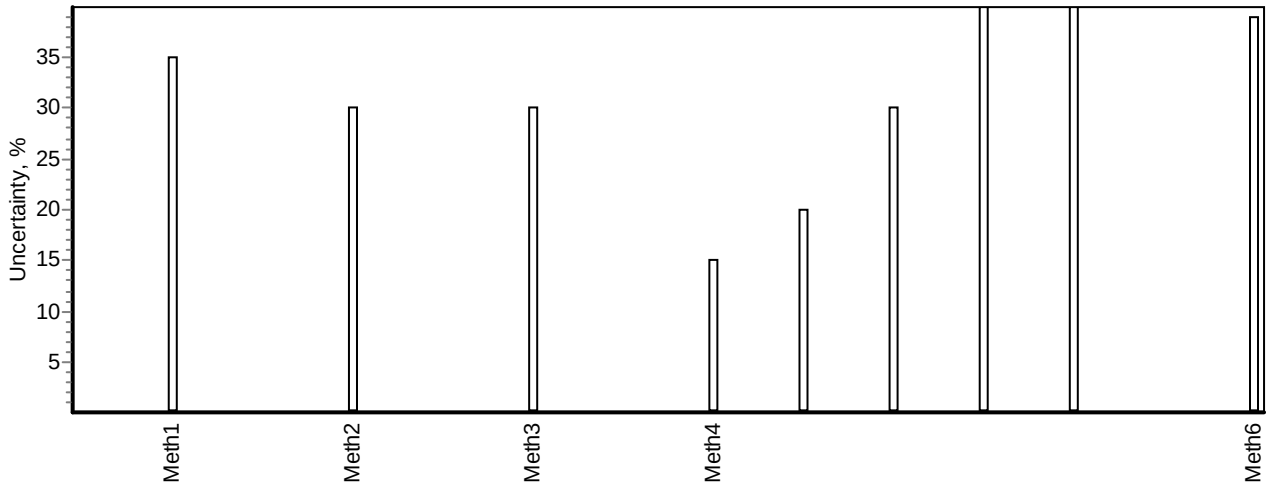
Analyytti *(Analyte)* **MTBE** Näyte *(Sample)* N2V



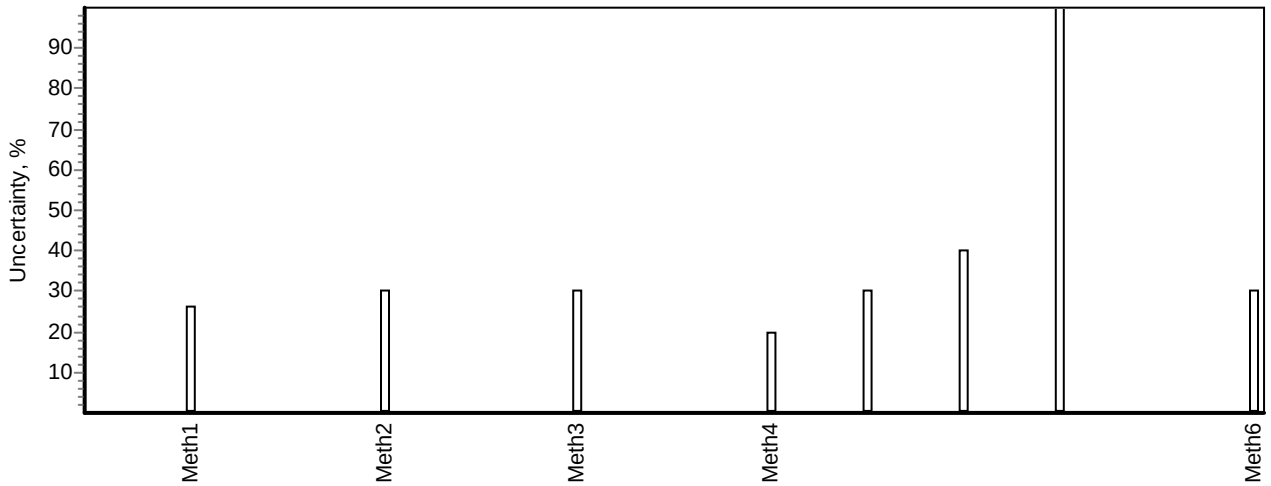
Analyytti *(Analyte)* **oXYL** Näyte *(Sample)* M3V



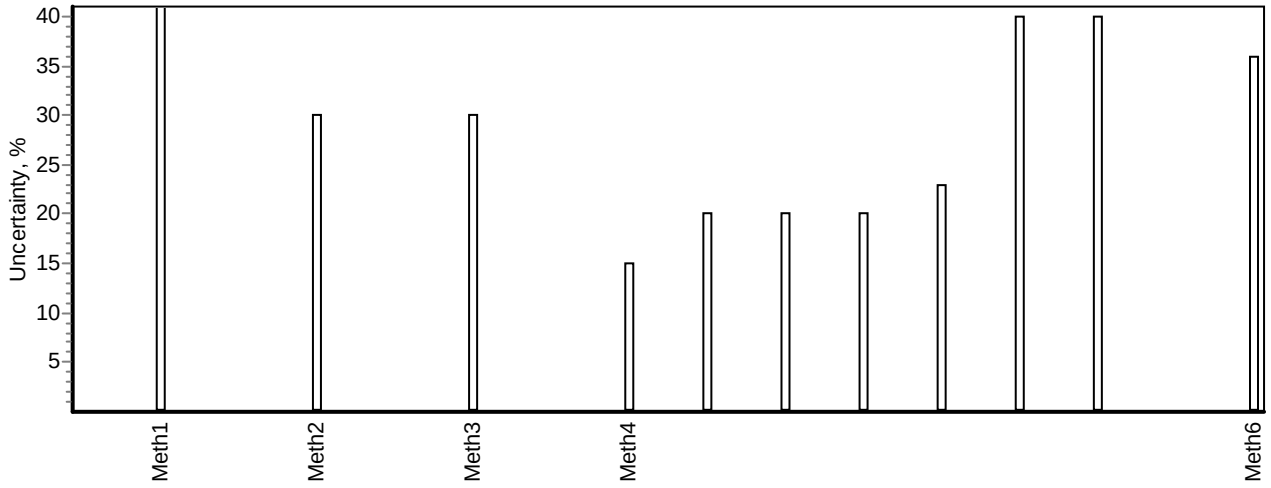
Analyytti *(Analyte)* **t12DCEe** Näyte *(Sample)* M3V



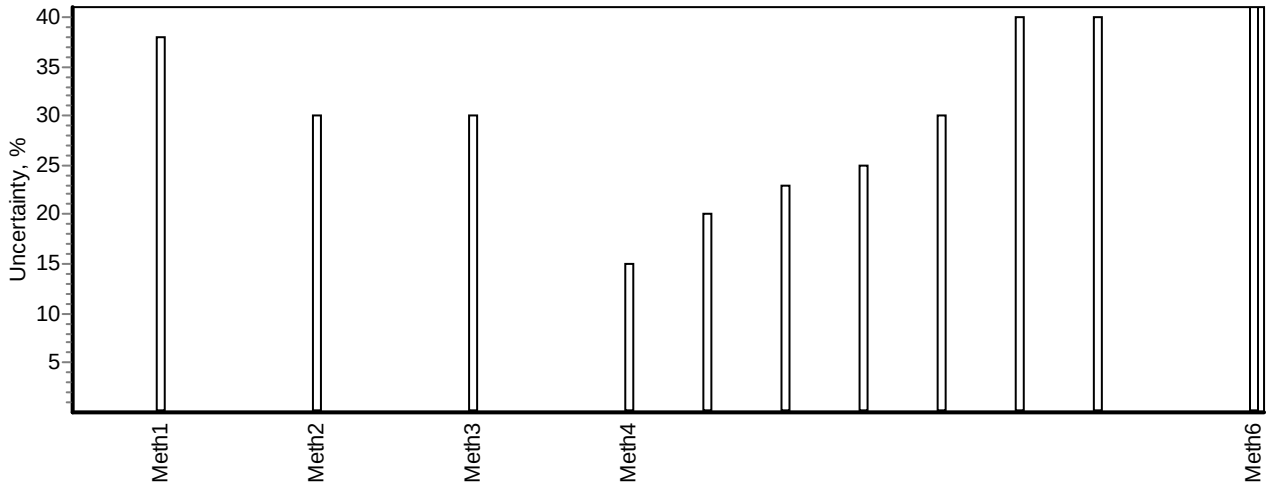
Analyytti *(Analyte)* **TAME** Näyte *(Sample)* N2V



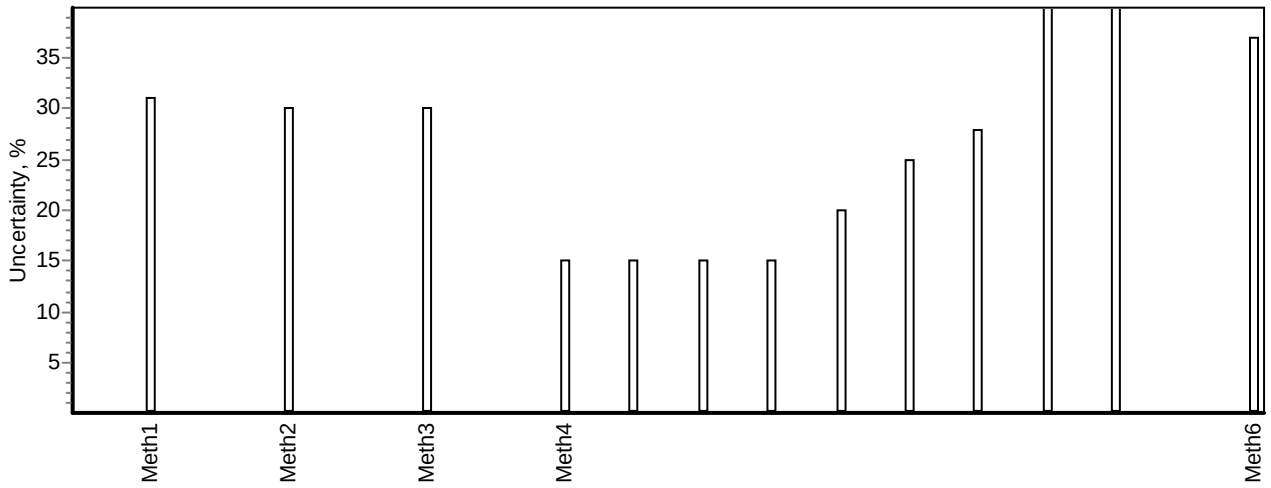
Analyytti *(Analyte)* **TCEe** Näyte *(Sample)* M3V



Analyytti *(Analyte)* **TECEe** Näyte *(Sample)* M3V



Analyytti *(Analyte)* **TOL** Näyte *(Sample)* M3V



Documentation page

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Author(s)	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori and Markku Ilmakunnas	
Title of publication	Proficiency Test SYKE 8/2012 Volatile organic compounds in water and soil.	
Parts of publication/ other project publications	The publication is available only in the internet www.ymparisto.fi/julkaisut.	
Abstract	Proftest SYKE carried out the proficiency test for analysis of volatile organic compounds from water and soil in October 2012. One artificial sample and one river water sample and one soil sample were distributed. In total, 15 laboratories participated in the proficiency test. Either the calculated concentration or the robust mean value was chosen to be the assigned value for the measurement. The performance of the participants was evaluated by using z scores. In this proficiency test 72 % of the results were satisfactory when the deviation of 15–40 % from the assigned value was accepted.	
Keywords	water analysis, soil analysis, volatile organic compounds, VOC, proficiency test, intercomparison	
Publication series and number	Suomen ympäristökeskuksen raportteja 7 / 2013	
Theme of publication		
Project name and number, if any		
Financier/ commissioner		
Project organization		
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Financier of publication	Finnish Environment Institute, P.O.Box 140, FI-00251 Helsinki, Finland	
Printing place and year	Helsinki 2013	
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Tekijä(t)	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori ja Markku Ilmakunnas	
Julkaisun nimi	Proficiency Test SYKE 8/2012 Volatile organic compounds in water and soil.	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä. www.ymparisto.fi/julkaisut	
Tiivistelmä	Proftest SYKE järjesti pätevyyskokeen haihtuvien orgaanisten yhdisteiden määrityksistä vesi- ja maanäytteistä lokakuussa 2012. Vesi- ja maanäytteiden lisäksi osallistujille toimitettiin synteettinen näyte. Pätevyyskokeeseen osallistui yhteensä 15 laboratorioita. Määritettävän yhdisteen vertailuarvona käytettiin laskennallista arvoa tai osallistujien tulosten robustia keskiarvoa. Pätevyyden arvioimisessa käytettiin z-arvoa ja sitä laskettaessa tulokselle sallittiin näytteestä ja yhdisteestä riippuen 15−40 %:n poikkeama vertailuarvosta. Kokonaisuudessaan hyväksyttäviä tuloksia oli 72 %.	
Asiasanat	vesianalyysi, maa-analyysi, haihtuvat orgaaniset yhdisteet, VOC, pätevyyskoe, vertailumittaus	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen raportteja 7 / 2013	
Julkaisun teema		
Projektihankkeen nimi ja projektinumero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
	ISSN 1796-1726 (verkkoj.)	ISBN 978-952-11-4141-6 (PDF)
	Sivuja 77	Kieli englanti
	Luottamuksellisuus Julkinen	Hinta
Julkaisun myynti/ jakaja	Suomen ympäristökeskus, asiakaspalvelu Sähköpostiosoite: neuvonta.syke@ymparisto.fi puh. 020 610 183 faksi 09 5490 2190	
Julkaisun kustantaja	Suomen ympäristökeskus, PL 140, 00251 Helsinki	
Painopaikka ja -aika	Helsinki 2011	
Muut tiedot		

Presentationsblad

Utgivare	Finlands Miljöcentral (SYKE)	Datum Februari 2013
Författare	Kaija Korhonen-Ylönen, Jari Nuutinen, Mirja Leivuori och Markku Ilmakunnas	
Publikationens titel	Proficiency Test SYKE 8/2012 Volatile organic compounds in water and soil.	
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet www.ymparisto.fi/julkaisut	
Sammandrag	Under oktober 2012 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av flyktiga organiska föreningar från älvvatten och från förorenad jord. Proven sändes ut till 15 laboratorier. Som referensvärde av analytens koncentration användes det teoretiska värdet eller robust medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämförelsen var 72 % av alla resultaten tillfredsställande, när 15–40 % totalavvikelsen från referensvärdet accepterades.	
Nyckelord	vattenanalyser, jordanalyser, flyktiga organiska föreningar, VOC, provningsjämförelse, interkalibrering	
Publikationsserie och nummer	Suomen ympäristökeskuksen raportteja 7 / 2013	
Publikationens tema		
Projektets namn och nummer		
Finansiär/ uppdragsgivare		
Organisationer i projektgruppen		
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