

REPORTS OF FINNISH ENVIRONMENT
INSTITUTE 11 | 2012

Proficiency Test SYKE 10/2011

Heavy metals in surface waters

Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho,
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Helsinki 2012

Finnish Environment Institute



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Finnish Environment Institute SYKE

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CONTENT

ALKUSANAT/PREFACE	4
1 INTRODUCTION	5
2 ORGANIZING THE PROFICIENCY TEST	5
2.1 Responsibilities	5
2.2 Participants	5
2.3 Samples and delivery	6
2.4 Homogeneity studies	7
2.5 Feedback from the proficiency test	7
2.6 Processing of the data	7
2.6.1 Pretesting of the data	7
2.6.2 Assigned value and their uncertainties	7
2.6.3 Standard deviation for proficiency assessment and z score	8
3 RESULTS AND CONCLUSIONS	9
3.1 Results	9
3.2 Analytical methods and status to the results	11
3.3 Uncertainties of the results	11
4 EVALUATION OF PERFORMANCE	12
5 SUMMARY	12
6 YHTEENVETO	13
REFERENCES	14
 APPENDICES	
Appendix 1 Participants	15
Appendix 2 Preparation of the samples	16
Appendix 3 Testing of homogeneity	17
Appendix 4 Feedback from the proficiency test	18
Appendix 5 Assigned values and their uncertainties	19
Appendix 6 Terms in the result tables	20
Appendix 7 Results of each participant	21
Appendix 8 Results and their uncertainties	41
Appendix 9 Summary of the z scores	54
Appendix 10.1 Analytical methods	56
Appendix 10.2 Results grouped according to the measurement methods	57
Appendix 11 Examples of measurement uncertainties reported by the laboratories	69
DOCUMENTATION PAGE	77
KUVAILULEHTI	78
PRESENTATIONS BLAD	79

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 Profitest 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 inter-laboratory 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 Profitest 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 2 huhtikuuta 2012 / Helsinki 2 April 2012



Marja Luotola

Laboratorionjohtaja / Chief of Laboratory

1 Introduction

Profest SYKE carried out the proficiency test (PT) for the analysis of elements in waters in November 2011–January 2012 in the frame of the joint PT-WFD program 2011. The principal aim of the proficiency test was to test the chemical analysis of priority and other substances in the context of chemical monitoring for the European Water Framework Directive (WFD), especially for compliance of surface waters with Environmental Quality Standards (EQS). The main measurements were the priority substances: Cd, Hg, Pb and Ni. Additionally it was possible to test voluntary elements: Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Sb, Se, V and Zn. The sample types were artificial and natural surface water.

The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical Report [3]. The Profest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi). Profest SYKE is the accredited proficiency test provider on the field of the present test.

2 Organizing the proficiency test

2.1 Responsibilities

The main organizing laboratory was:

Profest 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 proficiency test were as follows:

Mirja Leivuori, coordinator

Kaija Korhonen-Ylönen, substitute of coordinator

Keijo Tervonen, technical assistant

Sari Lanteri, technical assistant

Ritva Väisänen, technical assistant

Markku Ilmakunnas, technical assistant and lay-out of the report

The analytical experts were:

Timo Sara-Aho heavy metal analyses (ICP-OES, ICP-MS, ID-ICP-MS)

Teemu Näykki Hg-analyses, ID-ICP-MS

The co-operation partners were accomplished in the cooperation with the following organizations of the “PT-WFD” network (<http://www.pt-wfd.eu/>):

IWW Water Centre, Germany (www.iww-online.de)

LGC Standards - Proficiency Testing, United Kingdom, (www.lgcpt.com)

VITUKI Non-profit Ltd., Quality Assurance and Control, Hungary (<http://www.vituki.hu>)

2.2 Participants

35 laboratories from the four cooperating proficiency test providers participated in the proficiency test (Appendix 1, Table 1). One of participants reported their results 10 days after the deadline. The evaluation for the laboratory was performed, but the data was not included in the statistical treatment of the reported results. One laboratory reported the data measured by two different analytical methods. Six of the Finnish participating laboratories provide data for use of the Finnish environmental authorities.

Table 1. The participants of the cooperating proficiency test providers.

Proficiency test provider	Number of participants
Proftest SYKE	8
IWW	15
LGC	7
VITUKI	1
Total	35

About 81 % of the participating laboratories used accredited analytical methods for at least a part of the measurements.

The organizing laboratory (SYKE) has the code 3 in the result tables. For lead the metrologically traceable assigned value has been measured by ID-ICP-MS in SYKE laboratory and the laboratory code is 6.

2.3 Samples and delivery

The preparation of the samples is presented in more detail in Appendix 2. The main parameters were taken from the list of the priority substances in the context of chemical monitoring for the European Water Framework Directive (WFD). The concentrations of the measurements of the samples were based on the European EQS Directive 2008/105/EC [4]. This directive sets Environmental Quality Standards (EQS) for different substances. The allowed annual average – EQS (AA-EQS) for the above mentioned parameters in the matrix inland surface water are given in the Table 2.

Table 2. Environmental Quality Standards (EQS) for the tested priority substances [4].

Parameter (CAS-number)	AA-EQS ($\mu\text{g/l}$)
Cadmium (CAS 7440-43-9)	0.09
Lead (CAS 7439-92-1)	7.2
Mercury (CAS 7439-97-6)	0.05
Nickel (CAS 7440-02-0)	20

In the PT two different artificial samples were delivered. The sample A1M was prepared using metrologically traceable NIST SRM 1643e and single element Merck CertiPUR[®] Reference material solutions. The Merck Certipur RMs were traceable to the several NIST SRMs. The sample A1Hg was diluted from the Romil PrimAg[®]-plus CRM Hg-solution (traceable to SI unit via ultrapure primary reference silver). The artificial samples were acidified with nitric acid. During the proficiency test the concentration of mercury in the sample A1Hg was not stable. Due to this the performance evaluation of the sample A1Hg was not performed.

For the samples N1M and N2M real surface water including natural suspended solids was used (whole water samples). The surface water was collected from River Mustionjoki in southern Finland. The surface water sample did not contain any visible suspended solids. The samples N1M and N2M were prepared with additions of single element Merck CertiPUR[®] Reference material solutions (traceable to the several NIST SRMs, Appendix 2). Also the purity of the laboratory vessels used in the sample preparation was tested. According to the test the sample vessels fulfilled the purity requirements.

The samples were delivered 10 November to the cooperation proficiency test providers and for the others 15 November 2011. Mercury was requested to be measured 24 November 2011 at the latest. All the samples were requested to be analysed and reported 4 January 2012 at the latest.

2.4 Homogeneity studies

The homogeneity of the samples was studied by measuring Cd, Cu, Hg, Mn, Ni, Pb and Hg. The samples were additionally tested measuring metrologically traceable lead (ID-ICP-MS) in the all studied samples. According to the homogeneity test results the samples were considered to be homogenous. More detailed information of homogeneity studies is in Appendix 3.

2.5 Feedback from the proficiency test

Appendix 4 contains the feedback from the proficiency test. The comments deal with the sample stability (Hg) and the errors with reporting of the results. The provider gives some comments to the participants considering mainly the reporting of the results. These are mainly focused to the lacking conversancy to the given information with the samples.

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 case that the result was reported erroneously (e.g. in wrong unit). The replicate results were tested using the Cochran test (C in the result sheets). If the result was reported < DL (detection limit), it has not been included in calculation of the results (H in the results sheets). More detailed information of the testing and statistical treatment of the proficiency data is available on the internet in the guide for participating laboratories in Profest SYKE proficiency testing schemes (www.environment.fi/syke/proftest).

2.6.2 Assigned value and their uncertainties

The assigned values and their uncertainties are presented in Appendix 5. For the artificial sample A1M the calculated concentrations were used as the assigned value with exceptions of cobalt, antimony and vanadium. The assigned values based on the calculated concentrations are traceable to several NIST SRMs. For these calculated assigned values the expanded combined uncertainty based on the combination of uncertainties associated with individual operations involved in the preparation of the sample. The main individual resource of the uncertainty was the uncertainty of the concentration in the stock solution.

For lead the metrologically traceable assigned value has been used for samples A1M, N1M and N2M. The assigned values for lead in these samples are based on results analyzed by a metrologically traceable isotope dilution ID-ICP-MS method. The method used for analyzing lead by ID-ICP-MS has been accredited for dissolved lead in natural waters in the scope of calibration laboratory (K054; www.finass.fi). For the metrologically traceable lead results, the uncertainty is the expanded measuring uncertainty of the ID-ICP-MS method.

For the other samples and measurements the robust mean of the participant's results was used as the assigned value. For the robust mean metrological traceability is not available. In the calculation of robust mean single results were excluded as replicate results were requested (i.e. Labs 18, 19, 32). The uncertainty of the assigned value was calculated using the robust standard deviation of the reported results using the formula presented in Appendix 5.

The uncertainty of the calculated assigned value and the metrologically traceable value for metals in the artificial sample A1M varied between 0.5 and 3.8 %. When using the robust mean of the participant results as the assigned value, the uncertainties of the assigned values varied between

between 1.4 % and 9 % (Appendix 5).

After reporting of the preliminary results no corrections to the assigned values have been done.

2.6.3 Standard deviation for proficiency assessment and z score

The performance evaluation was carried out by using z scores (Appendix 6). The total standard deviation for calculation of z score was set according to the consensus of the PT-WFD network members for the priority substances as follows: lead, nickel (10 %) and for mercury, cadmium (25%). For the voluntary elements the total standard deviation for proficiency assessment was set according to the type of the sample, the results of the proficiency test, the uncertainty of the assigned values, the concentrations of the samples, the variability of result within the used methods and the long-term variation in the former proficiency tests. In addition, the homogeneity of the samples was used as background data.

The reliability of the assigned value was tested according to the criterion [3]:

$u/s_p \leq 0.3$, where

u is the standard uncertainty of the assigned value

(the expanded uncertainty of the assigned value (U) divided by 2),

s_p the standard deviation for proficiency assessment (total standard deviation divided by 2)

In the testing of the reliability of the assigned value the criterion was met in every case and the assigned values were reliable.

The reliability of the target value for total deviation and the reliability of the corresponding z score were estimated by comparing the deviation for proficiency assessment (s_p) with the robust standard deviation of the reported results (s_{rob}) [3]. The criterion $s_{rob} < 1.2*s_p$ was met in all cases. As the conclusion the evaluation of performance could be considered reliable.

After reporting of the preliminary results no corrections to the total standard deviation for proficiency assessment have been done.

3 Results and conclusions

3.1 Results

The results and the performance of each laboratory are presented in Appendix 7 and the reported results and their uncertainties in Appendix 8. The summary of the proficiency test results is in Table 3. The summary of z scores is shown in Appendix 9.

The robust standard deviation of the results was lower than 5 % for 62 % of the results and lower than 10 % for 92 % of the results. Standard deviations higher than 10 % apply mainly to the surface water sample of mercury measurements (Table 3).

The increased variability of the results can be caused by the very low concentration level of measurements and by the use of different analytical instruments and pretreatment methods.

Table 3. Summary of the results in the proficiency test 10/2011.

Analyte	Sample	Unit	Ass. val.	Mean	Mean rob.	Md	SD rob	SD rob, %	Num. of labs	2·Targ SD%	Accepted z-val%
Al	A1M	µg/l	314	312.07	311.78	315.00	11.74	3,8	29	10	93
	N2M	µg/l	654	655.65	653.56	663.40	32.31	4,9	29	15	97
As	A1M	µg/l	6,05	5.98	5.98	5.89	0.39	6,5	30	15	86
	N2M	µg/l	10,6	10.54	10.57	10.55	0.49	4,7	30	15	93
B	A1M	µg/l	20,8	20.93	21.16	21.19	1.27	6	25	15	91
	N2M	µg/l	40,9	40.90	40.93	41.30	3.05	7,4	25	15	96
Cd	A1M	µg/l	0,66	0.66	0.66	0.66	0.036	5,5	35	25	97
	N1M	µg/l	0,17	0.16	0.17	0.16	0.008	4,8	35	25	97
	N2M	µg/l	0,64	0.64	0.63	0.64	0.034	5,4	35	25	97
Co	A1M	µg/l	5,05	5.07	5.05	5.07	0.20	4	29	15	93
	N2M	µg/l	9,87	9.90	9.87	9.93	0.31	3,1	29	15	97
Cr	A1M	µg/l	18,7	18.79	18.73	18.79	0.75	4	32	10	94
	N2M	µg/l	7,14	7.15	7.14	7.16	0.27	3,7	32	10	97
Cu	A1M	µg/l	27,3	27.43	27.44	27.30	1.28	4,7	32	15	91
	N2M	µg/l	2,64	2.64	2.64	2.62	0.19	7,4	32	20	88
Fe	A1M	µg/l	343	339.95	337.99	339.80	11.85	3,5	30	10	93
	N2M	µg/l	461	462.16	461.06	465.00	19.90	4,3	30	10	93
Hg	A1Hg	µg/l		0.022	0.023	0.022	0.011	49	24		
	N1Hg	µg/l	0,068	0.066	0.068	0.072	0.011	15,7	27	25	74
Mn	A1M	µg/l	171	169.83	168.90	169.30	5.02	3	31	10	97
	N2M	µg/l	89,2	89.08	89.21	89.70	3.16	3,5	30	10	100
Mo	A1M	µg/l	15,4	15.09	15.11	15.11	0.51	3,4	27	15	93
	N2M	µg/l	17	16.87	16.98	17.00	0.59	3,5	27	15	96
Ni	A1M	µg/l	14,6	14.25	14.19	14.20	0.57	4	35	10	94
	N1M	µg/l	17,7	17.75	17.75	17.75	0.82	4,6	35	10	94
	N2M	µg/l	27,1	27.12	27.07	27.25	1.11	4,1	35	10	94
Pb	A1M	µg/l	6,941	6.81	6.82	6.84	0.32	4,7	36	10	89
	N1M	µg/l	7,139	6.99	7.00	7.00	0.28	4,1	36	10	97
	N2M	µg/l	17,18	16.80	16.81	16.92	0.72	4,3	36	10	97
Sb	A1M	µg/l	13,3	13.10	13.34	13.35	0.85	6,4	28	20	86
	N2M	µg/l	16,2	16.16	16.23	16.25	1.05	6,5	28	20	93
Se	A1M	µg/l	34,5	34.25	34.41	34.20	1.90	5,5	27	10	85
	N2M	µg/l	16,7	16.71	16.67	16.70	0.85	5,1	27	10	93
V	A1M	µg/l	8,47	8.48	8.47	8.54	0.24	2,9	27	10	96
	N2M	µg/l	10,7	10.77	10.74	10.73	0.29	2,7	27	10	93
Zn	A1M	µg/l	175	175.43	175.45	173.41	10.75	6,1	31	10	84
	N2M	µg/l	30,5	30.61	30.53	30.30	2.11	6,9	30	15	87

Ass. Val.- the assigned value, Mean - the mean value, Mean rob - robust mean, Md - the median value, SD % - the standard deviation as percent, SD rob - the robust standard deviation, SD rob % - the robust standard deviation as percents, Num of Labs - the number of participants, 2·Targ. SD% - the total standard deviation for proficiency assessment at 95 % confidence level ($2 \cdot s_p$), Accepted z-val% - the satisfactory z scores: the results (%), where $|z| \leq 2$.

In this PT the participants were requested to report duplicate results for all measurements. The participants reported the replicates with the exception of three laboratories (Labs 18, 19, 32, 36). The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 4.

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 1.5 to 9 times higher than the repeatability (s_w). For the robust methods the ratio s_b/s_w , should not exceed 3.

Table 4. 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	Accepted. z-val %
Al	A1M	µg/l	314	311,1	314,6	4,504	13,1	13,86	1,4	4,2	4,5	10	29	90
	N2M	µg/l	654	653,7	663,2	9,496	41,15	42,23	1,5	6,3	6,5	15	29	93
As	A1M	µg/l	6,05	5,983	5,875	0,1476	0,4754	0,4978	2,5	7,9	8,3	15	29	83
	N2M	µg/l	10,6	10,55	10,53	0,2246	0,4206	0,4768	2,1	4	4,5	15	30	90
B	A1M	µg/l	20,8	20,93	21	0,4744	0,9823	1,091	2,3	4,7	5,2	15	23	83
	N2M	µg/l	40,9	40,9	41,35	1,25	2,767	3,036	3,1	6,8	7,4	15	25	92
Cd	A1M	µg/l	0,66	0,659	0,655	0,01797	0,04099	0,04476	2,7	6,2	6,8	25	33	94
	N1M	µg/l	0,17	0,1629	0,164	0,006419	0,01676	0,01795	3,9	10	11	25	33	94
	N2M	µg/l	0,64	0,6394	0,637	0,01554	0,03357	0,037	2,4	5,3	5,8	25	33	94
Co	A1M	µg/l	5,05	5,071	5,075	0,04979	0,1678	0,175	0,98	3,3	3,5	15	29	86
	N2M	µg/l	9,87	9,889	9,915	0,1371	0,2851	0,3163	1,4	2,9	3,2	15	29	93
Cr	A1M	µg/l	18,7	18,77	18,77	0,3024	0,7128	0,7743	1,6	3,8	4,1	10	32	91
	N2M	µg/l	7,14	7,142	7,155	0,1075	0,2434	0,2661	1,5	3,4	3,7	10	32	94
Cu	A1M	µg/l	27,3	27,45	27,25	0,4187	1,327	1,391	1,5	4,8	5,1	15	32	88
	N2M	µg/l	2,64	2,637	2,6	0,06891	0,1782	0,1911	2,6	6,8	7,2	20	32	84
Fe	A1M	µg/l	343	339,4	337,9	2,951	14,42	14,72	0,87	4,2	4,3	10	30	90
	N2M	µg/l	461	461,5	464	7,299	17,4	18,87	1,6	3,8	4,1	10	30	93
Hg	A1Hg	µg/l		0,02224	0,0204	0,001851	0,01178	0,01192	8,3	53	54		22	
	N1Hg	µg/l	0,068	0,06555	0,0675	0,001092	0,00963	0,009692	1,7	15	15	25	27	70
Mn	A1M	µg/l	171	169,5	169,7	3,071	5,595	6,383	1,8	3,3	3,8	10	31	90
	N2M	µg/l	89,2	88,99	89,6	0,7877	2,904	3,009	0,89	3,3	3,4	10	30	93
Mo	A1M	µg/l	15,4	15,14	15,15	0,3855	0,8934	0,973	2,5	5,9	6,4	15	27	89
	N2M	µg/l	17	16,91	17	0,3068	0,7731	0,8317	1,8	4,6	4,9	15	27	93
Ni	A1M	µg/l	14,6	14,22	14,2	0,243	0,5639	0,614	1,7	4	4,3	10	35	91
	N1M	µg/l	17,7	17,75	17,7	0,3808	0,7458	0,8374	2,1	4,2	4,7	10	35	91
	N2M	µg/l	27,1	27,12	27,2	0,4121	1,058	1,135	1,5	3,9	4,2	10	35	91
Pb	A1M	µg/l	6,941	6,811	6,872	0,1295	0,3032	0,3297	1,9	4,5	4,8	10	35	86
	N1M	µg/l	7,139	7	7	0,1932	0,2536	0,3188	2,8	3,6	4,6	10	35	94
	N2M	µg/l	17,18	16,8	16,95	0,3006	0,6206	0,6896	1,8	3,7	4,1	10	36	94
Sb	A1M	µg/l	13,3	13,16	13,4	0,3776	1,065	1,13	2,9	8,1	8,6	20	28	82
	N2M	µg/l	16,2	16,22	16,3	0,2712	1,137	1,169	1,7	7	7,2	20	28	86
Se	A1M	µg/l	34,5	34,25	34,15	0,4402	2,123	2,168	1,3	6,2	6,3	10	27	74
	N2M	µg/l	16,7	16,69	16,7	0,4211	0,7103	0,8258	2,5	4,3	4,9	10	27	89
V	A1M	µg/l	8,47	8,474	8,54	0,158	0,2179	0,2692	1,9	2,6	3,2	10	27	93
	N2M	µg/l	10,7	10,77	10,7	0,1661	0,3258	0,3657	1,5	3	3,4	10	27	89
Zn	A1M	µg/l	175	175,6	173,2	4,541	10,57	11,5	2,6	6	6,6	10	31	81
	N2M	µg/l	30,5	30,61	30,23	0,413	2,202	2,24	1,3	7,2	7,3	15	30	83

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

3.2 Analytical methods and status to the results

It was allowed to use different analytical methods for the measurements in the PT. The used analytical methods of the participants are shown in more detail in Appendix 10.1 and the reported results grouped according to the measurement methods are shown in Appendix 10.2.

In mercury analyses KBr/KBrO_3^- , $\text{K}_2\text{Cr}_2\text{O}_7^-$, BrCl^- or $\text{HNO}_3/\text{H}_2\text{O}_2$ were used as the oxidant from waters at room temperature, in water bath or in microwave oven. Mercury was measured mostly using cold vapor CV-AAS or CV-AFS instruments and ICP-MS instruments.

Cadmium, lead and nickel were mainly measured using ICP-MS instruments, while only a few laboratories used GAAS and ICP-OES instruments. The voluntary elements were mainly measured using ICP-MS or ICP-OES instruments.

The difference between the average concentrations of metals measured by different measurement methods was tested using the t-test in case when the number of the results was 3 or more. There were no statistically significant differences between the results obtained using different methods.

3.3 Uncertainties of the results

At maximum about 80 % of participants reported the expanded uncertainties with their results for some measurements (Table 5, Appendix 11). The range of the reported uncertainties varied greatly between the measurements and the sample types. Very low uncertainties can be considered questionable, if they were lower than the repeatability (the within-laboratory standard deviation, s_w , Table 4).

Several approaches were used for estimating of measurement uncertainty (Appendix 11). The approach based on existing IQC data from synthetic control sample and/or CRM (Meth 1) and data obtained in method validation (Meth 4) were the most common. Also the approach based on existing IQC data from synthetic sample together with the IQC data from routine sample replicates (Meth 2) and the modeling approach (GUM, Meth 5) were used in a few laboratories. Generally, the approach for estimating measurement uncertainty has not made a definite impact on the uncertainty estimates. Thus, harmonization in the estimating of uncertainties should be continued.

The reported measurement uncertainties have been used in the calculation of the zeta values in the preliminary data handling. The results of the comparison of z and zeta values have been delivered to the participants with the preliminary results. The performance evaluation of participants has only been done based in z values, thus the zeta values have not been re-reported in the final report.

Table 5. The range of the expanded measurement uncertainties (%) reported with the results by the participants.

Metal	A1M, %	N1M/ N1Hg, %	N2M, %	Metal	A1M, %	N1M/ N1Hg, %	N2M %
Al	6-44	-	6-44	Mn	3.75-44	-	5-44
As	3.15-44	-	7-44	Mo	7.68-30	-	8-30
B	5.7-44	-	5.7-44	Ni	3.41-44	6-44	6-44
Cd	2.63-44	7-57	7-44	Pb	3.18-44	3-44	3-44
Co	2.84-44	-	6-44	Sb	2.69-44	-	10-44
Cr	4.16-44	-	5-44	Se	5.66-44	-	10-44
Cu	3.21-44	-	5-44	V	3.96-44	-	10-44
Fe	5.47-44	-	8-44	Zn	3.9-44	-	8-44
Hg	-	7-96	-				

4 Evaluation of performance

The evaluation of performance is based on z scores. The calculated z scores are presented with the results of each participant in Appendix 8 and the summary of z scores is presented in Appendix 9.

In the performance evaluation z scores were interpreted as follows:

z score	Interpretation
$ z \leq 2$	satisfactory results
$2 < z < 3$	questionable results
$ z \geq 3$	unsatisfactory results

The total number of laboratories participating in this proficiency test was 35. The robust standard deviation of the results was mostly (92 % of the results) lower than 10 %.

In the artificial sample A1M the concentrations of the priority substances, Cd, Ni, Pb, were fairly low and 93 % of the results were satisfactory, when accepting deviations of 10–25 % from the assigned values. For the voluntary elements 91 % of the results were satisfactory, when accepting deviations of 10-20 % from the assigned value.

Unfortunately, the artificial sample A1Hg was not stable during the test period and the evaluation of the results was not possible.

For the surface water samples N1M and N1Hg the concentrations of priority substances were near the allowed annual average Environmental Quality Standards (AA-EQS, table 1). For the results of Cd, Ni and Pb 96 % of the results were satisfactory, when deviations of 10–25 % from the assigned value were accepted. In measurements of Hg from the surface water sample (N1Hg) was some difficulties as less than 74 % of the results were satisfactory, when deviation of 25 % from the assigned value was accepted. The mercury concentration of the surface water sample (N1Hg) was very low, which caused higher variability between the results (robust standard deviation 15.7 %) than within the other tested elements. The variety of measurement and pretreatment techniques used by the laboratories caused differences in analysis results.

In the surface water sample (N2M) with somewhat higher priority substance (Cd, Ni, Pb) concentrations 96 % of the results were satisfactory, when deviations of 10–25 % from the assigned value were accepted. For the voluntary elements 94 % of the results were satisfactory, when accepting deviations of 10-20 % from the assigned value.

In total, 93 % of the results in this proficiency test were satisfactory. About 81 % of the participants used accredited methods and 93 % of their results were satisfactory. 92 % of the results measured using non-accredited methods were satisfactory.

5 SUMMARY

Profest SYKE carried out the proficiency test (PT) for the analysis of elements in waters in November 2011–January 2012 in the frame of the joint PT-WFD program 2011. The principal aim of the proficiency test was to test the chemical analysis of priority and other substances in the context of chemical monitoring for the European Water Framework Directive (WFD), especially for compliance of surface waters with Environmental Quality Standards (EQS). The main measurements concerned the priority substances: Cd, Hg, Pb and Ni. Additionally it was possible to test voluntary elements: Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Sb, Se, V and Zn. The sample types were artificial and natural surface water. In total of 35 laboratories participated in the proficiency test.

The calculated concentrations or the robust mean of the results reported by the participants were used as the assigned values for measurements, with the exception of Pb in surface water samples. For Pb metrologically traceable assigned values were used for samples A1M, N1M and N2M. The uncertainties of the calculated assigned values and metrologically traceable values varied between 0.5 and 3.8 %. The uncertainties of the consensus assigned values (the robust mean) varied from 1.4 % to 9 %.

The evaluation of the performance of the participants was carried out using z scores. For the mercury in the artificial sample (A1Hg) the evaluation was not possible due to the instability of the sample. In total, 93 % of the results in this proficiency test were satisfactory when deviations of 10–25 % from the assigned values were accepted. About 81 % of the participants used accredited methods and 93 % of their results were satisfactory.

6 YHTEENVETO

Profest SYKE järjesti pätevyyskokeen ympäristönäytteitä analysoiville laboratorioille joulukuussa 2011 yhteistyössä Euroopan pätevyyskoejärjestäjien verkoston PT-WFD kanssa (www.pt-wfd.eu). Verkosto järjestää pätevyyskokeita vesipuitedirektiivin (WFD) prioriteetti- ja muiden aineiden kemiallisille määrityksille, joilla seurataan ympäristölaatumien (Environmental Quality Standards, EQS) toteutumista. Tässä pätevyyskokeessa testattiin pintavedestä vesipuitedirektiivin prioriteettiaineista kadmium, lyijy, elohopea ja nikkeli. Lisäksi oli mahdollista testata seuraavat alkuaineet: Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Sb, Se, V ja Zn. Näytteinä olivat synteettinen näyte sekä pintavedet.

Pätevyyskokeeseen osallistui yhteensä 35 laboratoriota, joista pääosa ulkomaisia laboratorioita (62 %). Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla ja sen laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat välillä 10–25 %. Mittaussuureen vertailuarvona käytettiin pääsääntöisesti laskennallista pitoisuutta tai osallistujien ilmoittamien tulosten robustia keskiarvoa. Lyijylle käytettiin metrologisesti jäljitettävää tavoitearvoa. Tavoitearvon epävarmuus synteettisille näytteille ja metrologisesti jäljitettävälle arvolle vaihteli 0.5 ja 3.8 % välillä. Robustia keskiarvoa käytettäessä tavoitearvon epävarmuus vaihteli 1.4 % ja 9 % välillä. Synteettinen elohopeanäyte ei pystynyt stabiilina testauksen aikana, jolloin sen arviointia ei voitu tehdä. Eri analyysimenetelmillä saatujen tulosten pitoisuuksissa ei havaittu tilastollisesti merkittäviä eroja.

Koko tulosaineistossa hyväksyttäviä tuloksia oli 93 %, kun vertailuarvosta sallittiin 10–25 %:n poikkeama. Osallistujista noin 81 % käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 93 %.

REFERENCES

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2. ISO 13528, 2005. Statistical methods for use in proficiency testing by interlaboratory comparisons.
3. Thompson, M., Ellison, S.L. R., Wood, R., 2006. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC Technical report). *Pure Appl. Chem.* 78: 145-196 (<http://www.iupac.org/publications/pac/2006/pdf/7801x0145.pdf>).
4. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council.

PARTICIPANTS

Co-operation partner	Country	Number/Name of participant
Proftest SYKE	Finland	Jyväskylän yliopisto, ympäristöntutkimuskeskus, Jyväskylä Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku Metla, Vantaa Ramboll Analytics, Lahti SGS Inspection Services Oy, Kotka Suomen ympäristöpalvelu Oy, Oulu SYKE, Laboratoriot, Helsinki Viljavuuspalvelu Oy, Mikkeli
	Sweden	ALS Scandinavia AB, Luleå Stockholm University, ITM, Stockholm
IWW	Germany	7
	Belgium	2
	France	1
	Italy	2
	Sweden	2
	Russia	1
LGC	The Netherlands	1
	United Kingdom	1
	Spain	1
	Sweden	1
	Denmark	1
	Republic of Ireland	2
VITUKI	Hungary	1

PREPARATION OF THE SAMPLES

The artificial samples A1M was prepared by dilution of metrologically traceable NIST Standard Reference Material 1643e (1:10) and adding of some separate Merck CertiPUR[®] Reference material solutions (traceable to various NIST SRMs) for several tested measurements. In diluting acidified water was used. The artificial sample A1Hg was prepared by diluting the Romil PrimAg[®]-plus Hg CRM solution (traceable to SI unit via ultrapure primary reference silver) with acidified water. The water samples N1M, N2M and N1Hg were prepared by adding Merck CertiPUR[®] Reference material solutions (traceable to various NIST SRMs) into the original water sample.

Analyte		A1M µg/l	N1M µg/l	N2M µg/l	A1Hg µg/l	N1Hg µg/l	Analyte		A1M µg/l	N1M µg/l	N2M µg/l
Al	Original	141.8	-	33	-	-	Mn	Original	38.97	-	0.80
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	300	-	400	-	-		Addition	166.7	-	66.7
	Ass. value	314	-	654	-	-		Ass. value	171	-	89.2
As	Original	60.45	-	0.49	-	-	Mo	Original	121.4	-	0.30
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	-	-	10	-	-		Addition	3.3	-	16.7
	Ass. value	6.05	-	10.6	-	-		Ass. value	15.4	-	17
B	Original	157.9	-	25	-	-	Ni	Original	62.41	1,2	1
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	5	-	16.7	-	-		Addition	8.3	16,6	26.7
	Ass. value	20.8	-	40.9	-	-		Ass. value	14.6	17,7	27.1
Cd	Original	6.568	0.02	0.59	-	-	Pb	Original	19.63	0,36	0.35
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	-	0.1	0.6	-	-		Addition	5	5	16.7
	Ass. value	0.66	0.17	0.64	-	-		Ass. value	6.941	7,139	17.18
Co	Original	27.06	-	0.03	-	-	Sb	Original	58.30	-	0.08
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	2.5	-	10	-	-		Addition	8.3	-	16.7
	Ass. value	5.05	-	9.87	-	-		Ass. value	13.3	-	16.2
Cr	Original	20.40	-	0.22	-	-	Se	Original	11.97	-	0.30
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	16.7	-	6.7	-	-		Addition	33.3	-	16.7
	Ass. value	18.7	-	7.14	-	-		Ass. value	34.5	-	16.7
Cu	Original	22.76	-	7.1	-	-	V	Original	37.86	-	0.33
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	25	-	-	-	-		Addition	5	-	10
	Ass. value	27.3	-	2.64	-	-		Ass. value	8.47	-	10.7
Fe	Original	98.1	-	39	-	-	Zn	Original	78.5	-	2.7
	Dilution	1:10	-	-	-	-		Dilution	1:10	-	-
	Addition	333	-	267	-	-		Addition	166.7	-	26.7
	Ass. value	343	-	461	-	-		Ass. value	175	-	30.5
Hg	Original	-	-	-	-	< 0.002					
	Dilution	-	-	-	-	-					
	Addition	-	-	-	0.087	0.07					
	Ass. value	-	-	-	-	0.068					

Original = the original concentration; Dilution = the ratio of dilution; Addition = the addition concentration;
Ass. value = the assigned value

TESTING OF HOMOGENEITY

Measurement/ sample	Concentration ($\mu\text{g l}^{-1}$)	s_h %	s_p %	s_h	s_a	s_a/s_h	Is $s_a/s_h < 0.5$?	s_{bb}	s_{bb}^2	c	Is $s_{bb}^2 < c$?
Cd/N1M	0.17	4.5	12.5	0.008	0.004	0.47	YES	0.003	0.00001	0.00002	YES
Hg/N1M	0.089	7.5	12.5	0.007	0.002	0.30	YES	0.0012	0.000001	0.00001	YES
Ni/N1M	18.7	2.5	5	0.47	0.19	0.41	YES	0.134	0.018	0.073	YES
Pb/N1M	7.29	2	5	0.146	0.067	0.455	YES	0.042	0.002	0.008	YES
Cd/N2M	0.65	4	12.5	0.026	0.012	0.465	YES	0.009	0.0001	0.0003	YES
Cu/N2M	2.69	3	5	0.081	0.036	0.444	YES	0.025	0.0006	0.002	YES
Mn/N2M	90.6	2	5	1.81	0.734	0.405	YES	0.369	0.136	1.10	YES
Ni/N2M	27.8	2	5	0.555	0.235	0.422	YES	0.166	0.028	0.108	YES
Pb/N2M	17.96	2.5	5	0.449	0.186	0.413	YES	0.246	0.061	0.069	YES
Zn/N2M	29.8	2.5	7.5	0.744	0.139	0.187	YES	0.282	0.080	0.113	YES
ID-ICP-MS testing (n=6 A1M or 8 N1M, N2M)											
Pb/A1M	6.93	1	5	0.069	0.026	0.37	YES	0.018	0.0003	0.002	YES
Pb/N1M	7.13	0.5	5	0.036	0.016	0.44	YES	0.004	0.0000	0.0002	YES
Pb/N2M	17.15	0.5	5	0.086	0.033	0.38	YES	0.029	0.0008	0.003	YES

s_p % = standard deviation for proficiency assessment

s_h % = standard deviation for testing of homogeneity

s_a = analytical deviation, standard deviation of the results in a sub sample

s_{bb} = between-sample deviation, standard deviation of the results between sub samples

$$c = F1 \cdot s_{all}^2 + F2 \cdot s_a^2$$

where:

$$s_{all}^2 = (0.3 \cdot s_p)^2$$

F1 = 1.88/2.01/2.21 and

F2 = 1.01/1.25/1.69, when the number of sub samples is 10/8/6

The analytical deviation filled up the criteria $s_a/s_p < 0.5$ for each sample. Also in the each case the s_{bb}^2 was smaller than the criteria c.

Conclusion: The samples could be regarded as homogenous.

FEEDBACK FROM THE PROFICIENCY TEST

COMMENTS SENT BY THE PARTICIPANTS

Laboratory	Comments on samples	Action/Profest
24	The participants found Re in the sample A1M and this caused problems in the internal standardisation of their ICP-MS method.	The NIST SRM 1643e with a Re concentration of 113 µg/l before dilution was used in the preparation of the artificial sample A1M. This unfortunately precludes the use of Re as an internal standard. However, the sample is synthetic and does not necessarily need compensation for matrix effects. This point will be taken into account in future sample preparations.
3	The concentration of the artificial sample A1Hg was lower than expected.	The artificial sample was not stable during the test period. Also other participant from the co-operation partners informed about the decreased concentration. The reason for the decrease has not been found. In the future this will be studied more detail in the sample preparation of low mercury concentration. The sample A1Hg was not evaluated in this proficiency test.

Laboratory	Comments on results	Action/Profest
13	The laboratory was reported wrong method code for some tested measurements.	The code was corrected to the final handling as the correct information was needed for the method comparison of data.
17	The laboratory informed that they were reported Hg results in wrong unit. The laboratory informed that in the result sheet Sn was included in the test parameters.	The results were not corrected in the original database. If the results should have been reported correctly they would have been satisfactory (the sample N1Hg). The participant can re-calculate z scores according to the guide for participating laboratories in Profest proficiency testing schemes (www.environment.fi/syke/profest). In the result sheet of the co-operation partners Sn was erroneously included in the reported test parameters. The participants were instructed to leave this parameter unfilled in the result sheet and the provider corrected the results sheets before transferring the data for the statistical handling.
26, 31	In the reported preliminary results the data of laboratories is not available in Annex 4.	In the preliminary results Annex 4 presented the comparison of z and zeta values. In calculation of zeta values of participants the reported measurement uncertainties were used. The mentioned laboratories have not reported their uncertainties, so their data was not included in the Annex 4.

COMMENTS TO THE PARTICIPANTS

Laboratory	Comments on results
18, 19, 32, 36	Laboratories reported only one result in their whole dataset or partly of it, though replicate results were requested. These results were not included in the calculation of assigned values.
22	The laboratory reported three parallel results, though replicate results were requested. From the results the two first results were included in the database.
16, 25, 26, 31, 36	The laboratory is accredited, but it did not report the total measurement uncertainty for their results.
36	The laboratory provided the results 10 days after the deadline. The results was included in the database, but not used in the calculation of assigned value. Only the performance of the laboratory was provided.

ASSIGNED VALUES AND THEIR UNCERTAINTIES

Analyte	Sample	Assigned value	Evaluation of the assigned value	Expanded uncertainty of the assigned value, U
Al	A1M	314 µg/l	Calculated value	3.8 %
	N2M	654 µg/l	Robust mean	2.4 %
As	A1M	6.05 µg/l	Calculated value	1.2 %
	N2M	10.6 µg/l	Robust mean	2.2 %
B	A1M	20.8 µg/l	Calculated value	2.1 %
	N2M	40.9 µg/l	Robust mean	3.9 %
Cd	A1M	0.66 µg/l	Calculated value	1.1%
	N1M	0.17 µg/l	Robust mean	2.9 %
	N2M	0.64 µg/l	Robust mean	2.2 %
Co	A1M	5.05 µg/l	Robust mean	0.5 %
	N2M	9.87 µg/l	Robust mean	1.5 %
Cr	A1M	18.7 µg/l	Calculated value	1.3 %
	N2M	7.14 µg/l	Robust mean	1.8 %
Cu	A1M	27.3 µg/l	Calculated value	1.4 %
	N2M	2.64 µg/l	Robust mean	3.6 %
Fe	A1M	343 µg/l	Calculated mean	1.5 %
	N2M	461 µg/l	Robust mean	2.1 %
Hg	A1Hg	-	-	-
	N1Hg	0.068 µg/l	Robust mean	9.0 %
Mn	A1M	171 µg/l	Calculated value	1.2 %
	N2M	89.2 µg/l	Robust mean	1.7 %
Mo	A1M	15.4 µg/l	Calculated value	1.2 %
	N2M	17.0 µg/l	Robust mean	1.8 %
Ni	A1M	14.6 µg/l	Calculated value	1.2 %
	N1M	17.7 mg/kg	Robust mean	2.1 %
	N2M	27.1 µg/l	Robust mean	1.9 %
Pb	A1M	6.941 µg/l	ID-ICP-MS	3.0 %
	N1M	7.139 mg/kg	ID-ICP-MS	3.0 %
	N2M	17.18 µg/l	ID-ICP-MS	3.0 %
Sb	A1M	13.3 µg/l	Robust mean	3.3 %
	N2M	16.2 µg/l	Robust mean	3.4 %
Se	A1M	34.5 µg/l	Calculated value	1.1 %
	N2M	16.7 µg/l	Robust mean	2.7 %
V	A1M	8.47 µg/l	Robust mean	1.5 %
	N2M	10.7 µg/l	Robust mean	1.4 %
Zn	A1M	175 µg/l	Calculated value	2.2 %
	N2M	30.5 µg/l	Robust mean	3.8 %

1. Samples A1M the uncertainty was estimated on the basis of the sample preparation, with the exceptions for cobalt, antimony and vanadium.
2. Other samples – the uncertainty was estimated using the data of the results as follows:

$$U\% = \frac{100 \times \left(\frac{2 \times 1.25 \times s_{rob}}{\sqrt{n}} \right)}{AV}, \text{ where:}$$

U% = the expanded uncertainty of the assigned value

n = the number of the results

s_{rob} = the robust standard deviation

AV = the assigned value

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 (<i>the assigned value</i>) 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 (a test for the mean value) In addition, in robust statistics some results deviating from the original robust mean have been rejected
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 $2 * s_p$
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 $2 * s_p$ from the assigned value

q – questionable ($-3 > z > -2$), negative error, the result deviates more than $2 * s_p$ from the assigned value

U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than $3 * s_p$ from the assigned value

u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than $3 * s_p$ from the assigned value

Robust analysis:

$X^* = \text{median of } x_i \quad (i = 1, 2, \dots, p)$

The items of data is sorted into increasing order, $x_1, x_2, x_i, \dots, x_p$.

Initial values for x^* and s^* are calculated as:

$s^* = 1.483 \text{ median of } |x_i - x^*| \quad (i = 1, 2, \dots, p)$

$x_i^* = x^* - \varphi$ if $x_i < x^* - \varphi$

$x_i^* = x^* + \varphi$ if $x_i > x^* + \varphi$

$x_i^* = x_i$ otherwise

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

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

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

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences.

Ref: Statistical methods for use in proficiency testing by inter laboratory comparisons, Annex C [2].

Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
			-3	-2	-1	0	+1	+2													
Pb	µg/l	A1M	██████████						1,582	yes	6,941	10	7,49	6,872	6,811	0,3274	4,8	30	5	1	36
Laboratory 2																					
Pb	µg/l	N1M	██████████						-0,375	yes	7,139	10	7,005	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M	██████████						0,140	yes	17,18	10	17,3	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M	██████████						3,835	H	13,3	20	18,4	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M	██████████						1,852	yes	16,2	20	19,2	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M	██████████						-2,870	yes	34,5	10	29,55	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M	██████████						-1,796	yes	16,7	10	15,2	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M	██████████						13,770	H	8,47	10	14,3	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M	██████████						8,131	H	10,7	10	15,05	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M	██████████						2,114	yes	175	10	193,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M	██████████						5,552	H	30,5	15	43,2	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 3																					
Al	µg/l	A1M	██████████						0,287	yes	314	10	318,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M	██████████						0,316	yes	654	15	669,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M	██████████						-0,077	yes	6,05	15	6,015	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M	██████████						0,566	yes	10,6	15	11,05	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M	██████████						0,224	yes	20,8	15	21,15	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M	██████████						0,277	yes	40,9	15	41,75	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M	██████████						0,055	yes	0,66	25	0,6645	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M	██████████						-0,188	yes	0,17	25	0,166	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M	██████████						0,412	yes	0,64	25	0,673	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M	██████████						0,356	yes	5,05	15	5,185	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M	██████████						0,783	yes	9,87	15	10,45	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M	██████████						0,588	yes	18,7	10	19,25	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M	██████████						1,261	yes	7,14	10	7,59	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M	██████████						0,611	yes	27,3	15	28,55	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M	██████████						0,701	yes	2,64	20	2,825	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M	██████████						0,291	yes	343	10	348	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M	██████████						0,629	yes	461	10	475,5	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg	██████████							yes			0,0247	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg	██████████						0,882	yes	0,068	25	0,0755	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M	██████████						-0,175	yes	171	10	169,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M	██████████						0,325	yes	89,2	10	90,65	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M	██████████						0,476	yes	15,4	15	15,95	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M	██████████						0,353	yes	17	15	17,45	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M	██████████						0,068	yes	14,6	10	14,65	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M	██████████						1,017	yes	17,7	10	18,6	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M	██████████						1,181	yes	27,1	10	28,7	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M	██████████						0,199	yes	6,941	10	7,01	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M	██████████						0,563	yes	7,139	10	7,34	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M	██████████						0,489	yes	17,18	10	17,6	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M	██████████						0,038	yes	13,3	20	13,35	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M	██████████						-0,247	yes	16,2	20	15,8	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M	██████████						-0,145	yes	34,5	10	34,25	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M	██████████						0,180	yes	16,7	10	16,85	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M	██████████						0,744	yes	8,47	10	8,785	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M	██████████						1,308	yes	10,7	10	11,4	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M	██████████						0,114	yes	175	10	176	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M	██████████						0,066	yes	30,5	15	30,65	30,23	30,61	2,22	7,3	27	3	0	30

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

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fail-ed	Mis-sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 4																				
Al	µg/l	A1M						-0,035	yes	314	10	313,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-0,149	yes	654	15	646,7	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-1,322	yes	6,05	15	5,45	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,126	yes	10,6	15	10,5	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						-0,513	yes	20,8	15	20	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-5,086	H	40,9	15	25,3	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,485	yes	0,66	25	0,62	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,235	yes	0,17	25	0,165	0,164	0,1629	10,9	30	3	2	35	
	µg/l	N2M						-0,313	yes	0,64	25	0,615	0,637	0,6394	5,7	29	4	2	35	
Co	µg/l	A1M						0,132	yes	5,05	15	5,1	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						0,108	yes	9,87	15	9,95	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						1,658	yes	18,7	10	20,25	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						1,008	yes	7,14	10	7,5	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						0,806	yes	27,3	15	28,95	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,341	yes	2,64	20	2,55	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						0,601	yes	343	10	353,3	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						0,985	yes	461	10	483,7	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg							yes			0,048	0,0204	0,02224	0,01173	52,7	18	6	2	24
	µg/l	N1Hg						-0,647	yes	0,068	25	0,0625	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						0,222	yes	171	10	172,9	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,370	yes	89,2	10	90,85	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,390	yes	15,4	15	14,95	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,431	yes	17	15	16,45	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,068	yes	14,6	10	14,55	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,735	yes	17,7	10	18,35	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						0,258	yes	27,1	10	27,45	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-0,550	yes	6,941	10	6,75	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,810	yes	7,139	10	6,85	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,617	yes	17,18	10	16,65	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						-0,038	yes	13,3	20	13,25	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,093	yes	16,2	20	16,35	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						-0,174	yes	34,5	10	34,2	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						0,958	yes	16,7	10	17,5	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						0,661	yes	8,47	10	8,75	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						0,000	yes	10,7	10	10,7	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-2,360	yes	175	10	154,3	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						1,202	yes	30,5	15	33,25	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 5																				
Al	µg/l	A1M						-0,478	yes	314	10	306,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-0,438	yes	654	15	632,5	663,2	653,7	41,86	6,4	28	1	0	29
B	µg/l	A1M						-1,154	yes	20,8	15	19	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-1,190	yes	40,9	15	37,25	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M							H	0,66	25	<0,7	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							H	0,17	25	<0,7	0,164	0,1629	10,9	30	3	2	35	
	µg/l	N2M							H	0,64	25	<0,7	0,637	0,6394	5,7	29	4	2	35	
Cr	µg/l	A1M						-0,535	yes	18,7	10	18,2	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,532	yes	7,14	10	6,95	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,073	yes	27,3	15	27,15	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,151	yes	2,64	20	2,6	2,637	0,1896	7,2	28	4	0	32	
Fe	µg/l	A1M						-0,700	yes	343	10	331	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,694	yes	461	10	445	464	461,5	18,72	4,1	28	2	0	30
Mn	µg/l	A1M						-0,760	yes	171	10	164,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-0,807	yes	89,2	10	85,6	89,6	88,99	2,983	3,4	28	2	0	30
Ni	µg/l	A1M						-1,301	yes	14,6	10	13,65	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,961	yes	17,7	10	16,85	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-1,218	yes	27,1	10	25,45	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						0,890	C	6,941	10	7,25	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						1,712	yes	7,139	10	7,75	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						0,023	yes	17,18	10	17,2	16,95	16,8	0,6855	4,1	35	1	0	36
Zn	µg/l	A1M						-0,571	yes	175	10	170	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						-0,350	yes	30,5	15	29,7	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 6																				
Pb	µg/l	A1M						0,000	yes	6,941	10	6,941	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,001	yes	7,139	10	7,139	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,006	yes	17,18	10	17,18	16,95	16,8	0,6855	4,1	35	1	0	36

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

SYKE - Interlaboratory comparison test 10/2011

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl. fail- ed	Mis- sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 7																				
Al	µg/l	A1M						0,414	yes	314	10	320,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						0,418	yes	654	15	674,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,441	yes	6,05	15	5,85	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,252	yes	10,6	15	10,4	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M							H	20,8	15	<20	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-0,978	yes	40,9	15	37,9	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,200	yes	0,66	25	0,6435	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,471	yes	0,17	25	0,16	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,325	yes	0,64	25	0,614	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,634	yes	5,05	15	4,81	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,615	yes	9,87	15	9,415	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,107	yes	18,7	10	18,6	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,098	yes	7,14	10	7,105	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,464	yes	27,3	15	26,35	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,682	yes	2,64	20	2,46	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,671	yes	343	10	331,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,391	yes	461	10	452	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg							H			0,06815	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						0,835	yes	0,068	25	0,0751	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						-0,877	yes	171	10	163,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-0,605	yes	89,2	10	86,5	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,087	yes	15,4	15	15,3	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						0,314	yes	17	15	17,4	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-1,096	yes	14,6	10	13,8	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,622	yes	17,7	10	17,15	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,775	yes	27,1	10	26,05	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-1,386	yes	6,941	10	6,46	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-1,678	yes	7,139	10	6,54	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-1,723	yes	17,18	10	15,7	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,977	yes	13,3	20	14,6	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,123	yes	16,2	20	16,4	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						-0,261	yes	34,5	10	34,05	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						-0,359	yes	16,7	10	16,4	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						0,189	yes	8,47	10	8,55	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						0,187	yes	10,7	10	10,8	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-0,286	yes	175	10	172,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						-0,787	yes	30,5	15	28,7	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 8																				
Al	µg/l	A1M						-0,924	yes	314	10	299,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-0,500	yes	654	15	629,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M							H	6,05	15	<10	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,252	yes	10,6	15	10,8	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M							H	20,8	15	<40	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						0,244	yes	40,9	15	41,65	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M							H	0,66	25	<1	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							H	0,17	25	<1	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M							H	0,64	25	<1	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-1,320	H	5,05	15	4,55	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,162	yes	9,87	15	9,75	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,160	yes	18,7	10	18,55	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						0,168	yes	7,14	10	7,2	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,195	yes	27,3	15	26,9	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,720	yes	2,64	20	2,45	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,029	yes	343	10	342,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						0,239	yes	461	10	466,5	464	461,5	18,72	4,1	28	2	0	30
Mn	µg/l	A1M						-0,175	yes	171	10	169,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,078	yes	89,2	10	89,55	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-1,255	yes	15,4	15	13,95	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,275	yes	17	15	16,65	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-1,301	yes	14,6	10	13,65	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,735	yes	17,7	10	17,05	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,480	yes	27,1	10	26,45	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M							H	6,941	10	<8	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M							H	7,139	10	<8	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-2,247	yes	17,18	10	15,25	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						-1,692	yes	13,3	20	11,05	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						-1,821	C	16,2	20	13,25	16,3	16,22	1,157	7,1	24	4	0	28

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

Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
			-3	-2	-1	0	+1	+2													
V	µg/l	A1M						0,425	yes	8,47	10	8,65	8,54	8,474	0,2674	3,2	25	2	0	27	
Laboratory 8																					
V	µg/l	N2M						2,056	yes	10,7	10	11,8	10,7	10,77	0,3627	3,4	25	2	0	27	
Zn	µg/l	A1M						-0,286	yes	175	10	172,5	173,2	175,6	11,42	6,5	30	1	0	31	
Zn	µg/l	N2M						-0,131	yes	30,5	15	30,2	30,23	30,61	2,22	7,3	27	3	0	30	
Laboratory 9																					
Al	µg/l	A1M						-1,720	yes	314	10	287	314,6	311,1	13,74	4,4	27	2	0	29	
Al	µg/l	N2M						-1,162	yes	654	15	597	663,2	653,7	41,86	6,4	28	1	0	29	
As	µg/l	A1M						0,584	yes	6,05	15	6,315	5,875	5,983	0,4933	8,2	25	4	1	30	
As	µg/l	N2M						0,880	yes	10,6	15	11,3	10,53	10,55	0,4733	4,5	27	3	0	30	
B	µg/l	A1M						0,994	yes	20,8	15	22,35	21	20,93	1,079	5,2	17	6	2	25	
B	µg/l	N2M						0,848	yes	40,9	15	43,5	41,35	40,9	3,008	7,4	23	2	0	25	
Cd	µg/l	A1M						0,351	yes	0,66	25	0,689	0,655	0,659	0,04445	6,7	29	4	2	35	
Cd	µg/l	N1M						0,212	yes	0,17	25	0,1745	0,164	0,1629	0,01782	10,9	30	3	2	35	
Cd	µg/l	N2M						0,406	yes	0,64	25	0,6725	0,637	0,6394	0,03675	5,7	29	4	2	35	
Co	µg/l	A1M						0,673	yes	5,05	15	5,305	5,075	5,071	0,1733	3,4	25	4	0	29	
Co	µg/l	N2M						0,783	yes	9,87	15	10,45	9,915	9,889	0,3139	3,2	27	2	0	29	
Cr	µg/l	A1M						1,070	yes	18,7	10	19,7	18,77	18,77	0,7685	4,1	29	3	0	32	
Cr	µg/l	N2M						0,924	yes	7,14	10	7,47	7,155	7,142	0,2642	3,7	30	2	0	32	
Cu	µg/l	A1M						0,830	yes	27,3	15	29	27,25	27,45	1,38	5	28	4	0	32	
Cu	µg/l	N2M						0,701	yes	2,64	20	2,825	2,6	2,637	0,1896	7,2	28	4	0	32	
Fe	µg/l	A1M						-1,662	yes	343	10	314,5	337,9	339,4	14,59	4,3	28	2	0	30	
Fe	µg/l	N2M						-1,367	yes	461	10	429,5	464	461,5	18,72	4,1	28	2	0	30	
Hg	µg/l	A1Hg							yes			0,019	0,0204	0,02224	0,01173	52,7	16	6	2	24	
Hg	µg/l	N1Hg						-1,765	yes	0,068	25	0,053	0,0675	0,06555	0,00957	14,6	21	6	0	27	
Mn	µg/l	A1M						-0,234	yes	171	10	169	169,7	169,5	6,338	3,7	28	3	0	31	
Mn	µg/l	N2M						-1,536	yes	89,2	10	82,35	89,6	88,99	2,983	3,4	28	2	0	30	
Mo	µg/l	A1M						-0,087	yes	15,4	15	15,3	15,15	15,14	0,965	6,4	26	1	0	27	
Mo	µg/l	N2M						0,118	yes	17	15	17,15	17	16,91	0,8247	4,9	26	1	0	27	
Ni	µg/l	A1M						0,479	yes	14,6	10	14,95	14,2	14,22	0,6101	4,3	33	2	0	35	
Ni	µg/l	N1M						1,243	yes	17,7	10	18,8	17,7	17,75	0,8323	4,7	33	2	0	35	
Ni	µg/l	N2M						1,107	yes	27,1	10	28,6	27,2	27,12	1,128	4,2	33	2	0	35	
Pb	µg/l	A1M						-0,061	yes	6,941	10	6,92	6,872	6,811	0,3274	4,8	30	5	1	36	
Pb	µg/l	N1M						0,199	yes	7,139	10	7,21	7	7	0,3173	4,5	33	2	1	36	
Pb	µg/l	N2M						0,547	yes	17,18	10	17,65	16,95	16,8	0,6855	4,1	35	1	0	36	
Sb	µg/l	A1M						-0,827	yes	13,3	20	12,2	13,4	13,16	1,119	8,5	24	4	0	28	
Sb	µg/l	N2M						-0,648	yes	16,2	20	15,15	16,3	16,22	1,157	7,1	24	4	0	28	
Se	µg/l	A1M						4,087	H	34,5	10	41,55	34,15	34,25	2,145	6,3	23	4	0	27	
Se	µg/l	N2M						3,713	H	16,7	10	19,8	16,7	16,69	0,8192	4,9	24	3	0	27	
V	µg/l	A1M						1,039	yes	8,47	10	8,91	8,54	8,474	0,2674	3,2	25	2	0	27	
V	µg/l	N2M						0,748	yes	10,7	10	11,1	10,7	10,77	0,3627	3,4	25	2	0	27	
Zn	µg/l	A1M						-0,286	yes	175	10	172,5	173,2	175,6	11,42	6,5	30	1	0	31	
Zn	µg/l	N2M						-0,109	yes	30,5	15	30,25	30,23	30,61	2,22	7,3	27	3	0	30	

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

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl- failed	Mis- sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 10																				
Al	µg/l	A1M						-0,414	yes	314	10	307,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						0,020	yes	654	15	655	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,496	yes	6,05	15	5,825	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,315	yes	10,6	15	10,35	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						1,122	yes	20,8	15	22,55	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						0,538	yes	40,9	15	42,55	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,285	yes	0,66	25	0,6365	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,400	yes	0,17	25	0,1615	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,281	yes	0,64	25	0,6175	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,106	yes	5,05	15	5,09	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						0,162	yes	9,87	15	9,99	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						0,695	yes	18,7	10	19,35	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						0,532	yes	7,14	10	7,33	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						0,293	yes	27,3	15	27,9	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						0,909	yes	2,64	20	2,88	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,729	yes	343	10	330,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,325	yes	461	10	453,5	464	461,5	18,72	4,1	28	2	0	30
Mn	µg/l	A1M						0,058	yes	171	10	171,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-0,347	yes	89,2	10	87,65	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						0,649	yes	15,4	15	16,15	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						0,392	yes	17	15	17,5	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,343	yes	14,6	10	14,35	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,848	yes	17,7	10	18,45	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						0,332	yes	27,1	10	27,55	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-0,334	yes	6,941	10	6,825	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						0,003	yes	7,139	10	7,14	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,268	yes	17,18	10	16,95	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,789	yes	13,3	20	14,35	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,432	yes	16,2	20	16,9	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						0,551	yes	34,5	10	35,45	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						0,060	yes	16,7	10	16,75	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						0,177	yes	8,47	10	8,545	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						0,000	yes	10,7	10	10,7	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-0,914	yes	175	10	167	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						-0,197	yes	30,5	15	30,05	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 11																				
Al	µg/l	A1M						-0,764	yes	314	10	302	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-0,795	yes	654	15	615	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,386	yes	6,05	15	5,875	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,629	yes	10,6	15	11,1	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						0,513	yes	20,8	15	21,6	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						0,326	yes	40,9	15	41,9	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,333	yes	0,66	25	0,6325	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,494	yes	0,17	25	0,1595	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,069	yes	0,64	25	0,6345	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,013	yes	5,05	15	5,045	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,257	yes	9,87	15	9,68	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,107	yes	18,7	10	18,6	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,630	yes	7,14	10	6,915	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						0,415	yes	27,3	15	28,15	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,341	yes	2,64	20	2,55	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						0,467	yes	343	10	351	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,108	yes	461	10	458,5	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg							yes			0,0225	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						0,647	yes	0,068	25	0,0735	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						-0,292	yes	171	10	168,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-0,650	yes	89,2	10	86,3	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,476	yes	15,4	15	14,85	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,275	yes	17	15	16,65	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,205	yes	14,6	10	14,45	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,396	yes	17,7	10	18,05	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,221	yes	27,1	10	26,8	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						0,184	yes	6,941	10	7,005	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						1,123	yes	7,139	10	7,54	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						0,431	yes	17,18	10	17,55	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,338	yes	13,3	20	13,75	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,062	yes	16,2	20	16,3	16,3	16,22	1,157	7,1	24	4	0	28

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

Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Passed	Outl. failed	Missing	Num of labs
			-3	-2	-1	0	+1	+2													
Se	µg/l	A1M							-0,029	yes	34,5	10	34,45	34,15	34,25	2,145	6,3	23	4	0	27
Laboratory 11																					
Se	µg/l	N2M							0,838	yes	16,7	10	17,4	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M							0,142	yes	8,47	10	8,53	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M							-0,654	yes	10,7	10	10,35	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M							0,286	yes	175	10	177,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M							-0,022	yes	30,5	15	30,45	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 12																					
Al	µg/l	A1M							0,127	yes	314	10	316	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M							0,571	yes	654	15	682	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M							-0,838	yes	6,05	15	5,67	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M							-0,748	yes	10,6	15	10,01	10,53	10,55	0,4733	4,5	27	3	0	30
Cd	µg/l	A1M							-0,788	yes	0,66	25	0,595	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							-0,941	yes	0,17	25	0,15	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M							-0,688	yes	0,64	25	0,585	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M							-0,462	yes	5,05	15	4,875	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M							-0,243	yes	9,87	15	9,69	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M							-0,856	yes	18,7	10	17,9	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M							-0,854	yes	7,14	10	6,835	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M							-0,586	yes	27,3	15	26,1	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M							-1,042	yes	2,64	20	2,365	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M							-0,525	yes	343	10	334	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M							0,022	yes	461	10	461,5	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg								yes			0,0485	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg							7,412	H	0,068	25	0,131	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M							-1,111	yes	171	10	161,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M							0,022	yes	89,2	10	89,3	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M							-0,433	yes	15,4	15	14,9	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M							-0,314	yes	17	15	16,6	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M							-1,370	yes	14,6	10	13,6	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M							-0,961	yes	17,7	10	16,85	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M							-0,922	yes	27,1	10	25,85	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M							-10,360	H	6,941	10	3,345	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M							-2,070	yes	7,139	10	6,4	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M							-1,432	yes	17,18	10	15,95	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M							-0,075	yes	13,3	20	13,2	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M							0,062	yes	16,2	20	16,3	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M							-1,130	yes	34,5	10	32,55	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M							0,479	yes	16,7	10	17,1	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M							-0,390	yes	8,47	10	8,305	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M							-0,561	yes	10,7	10	10,4	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M							-2,286	yes	175	10	155	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M							-1,224	yes	30,5	15	27,7	30,23	30,61	2,22	7,3	27	3	0	30

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

SYKE - Interlaboratory comparison test 10/2011

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl-failed	Mis-sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 13																				
Al	µg/l	A1M						0,315	yes	314	10	319	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						0,318	yes	654	15	669,6	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,603	yes	6,05	15	5,777	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,503	yes	10,6	15	10,2	10,53	10,55	0,4733	4,5	27	3	0	30
Cd	µg/l	A1M						-0,194	yes	0,66	25	0,644	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,400	yes	0,17	25	0,1615	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,037	yes	0,64	25	0,637	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,678	yes	5,05	15	5,307	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						0,168	yes	9,87	15	9,994	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						0,316	yes	18,7	10	19	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						0,315	yes	7,14	10	7,252	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,110	yes	27,3	15	27,08	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,589	yes	2,64	20	2,484	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,787	yes	343	10	329,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,260	yes	461	10	455	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg							yes			0,0192	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						0,647	yes	0,068	25	0,0735	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						-0,439	yes	171	10	167,3	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-0,058	yes	89,2	10	88,94	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,026	yes	15,4	15	15,37	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						0,212	yes	17	15	17,27	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,185	yes	14,6	10	14,46	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,328	yes	17,7	10	17,99	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						0,487	yes	27,1	10	27,76	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-0,017	yes	6,941	10	6,935	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,483	yes	7,139	10	6,966	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,308	yes	17,18	10	16,91	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,523	yes	13,3	20	14	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,747	yes	16,2	20	17,41	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						-0,603	yes	34,5	10	33,46	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						-0,222	yes	16,7	10	16,52	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						0,606	yes	8,47	10	8,727	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						0,374	yes	10,7	10	10,9	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-0,509	yes	175	10	170,6	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						-0,900	yes	30,5	15	28,44	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 14																				
Al	µg/l	A1M						0,022	yes	314	10	314,4	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						0,203	yes	654	15	664	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,121	yes	6,05	15	5,995	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,101	yes	10,6	15	10,52	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						0,375	yes	20,8	15	21,38	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						0,142	yes	40,9	15	41,34	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,048	yes	0,66	25	0,656	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,165	yes	0,17	25	0,1665	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,006	yes	0,64	25	0,6395	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,198	yes	5,05	15	5,125	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						0,189	yes	9,87	15	10,01	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,027	yes	18,7	10	18,67	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						0,098	yes	7,14	10	7,175	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						0,029	yes	27,3	15	27,36	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						0,871	yes	2,64	20	2,87	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,793	yes	343	10	329,4	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						0,345	yes	461	10	468,9	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	N1Hg						-2,118	yes	0,068	25	0,05	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						-0,339	yes	171	10	168,1	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,291	yes	89,2	10	90,5	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,658	yes	15,4	15	14,64	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,922	yes	17	15	15,82	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,384	yes	14,6	10	14,32	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,311	yes	17,7	10	17,98	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						0,269	yes	27,1	10	27,46	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						0,084	yes	6,941	10	6,97	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,431	yes	7,139	10	6,985	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						0,460	yes	17,18	10	17,58	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						-2,350	yes	13,3	20	10,18	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,509	yes	16,2	20	17,02	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						-0,093	yes	34,5	10	34,34	34,15	34,25	2,145	6,3	23	4	0	27

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

Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
			-3	-2	-1	0	+1	+2													
	µg/l	N2M						0,030	yes	16,7	10	16,73	16,7	16,69	0,8192	4,9	24	3	0	27	
Laboratory 14																					
V	µg/l	A1M						0,153	yes	8,47	10	8,535	8,54	8,474	0,2674	3,2	25	2	0	27	
	µg/l	N2M						0,421	yes	10,7	10	10,93	10,7	10,77	0,3627	3,4	25	2	0	27	
Zn	µg/l	A1M						0,217	yes	175	10	176,9	173,2	175,6	11,42	6,5	30	1	0	31	
	µg/l	N2M						-0,509	yes	30,5	15	29,34	30,23	30,61	2,22	7,3	27	3	0	30	
Laboratory 15																					
Al	µg/l	A1M						1,242	yes	314	10	333,5	314,6	311,1	13,74	4,4	27	2	0	29	
	µg/l	N2M						0,326	yes	654	15	670	663,2	653,7	41,86	6,4	28	1	0	29	
As	µg/l	A1M						0,496	yes	6,05	15	6,275	5,875	5,983	0,4933	8,2	25	4	1	30	
	µg/l	N2M						0,755	yes	10,6	15	11,2	10,53	10,55	0,4733	4,5	27	3	0	30	
B	µg/l	A1M						0,000	yes	20,8	15	20,8	21	20,93	1,079	5,2	17	6	2	25	
	µg/l	N2M						0,734	yes	40,9	15	43,15	41,35	40,9	3,008	7,4	23	2	0	25	
Cd	µg/l	A1M						9,212	H	0,66	25	1,42	0,655	0,659	0,04445	6,7	29	4	2	35	
	µg/l	N1M						0,000	yes	0,17	25	0,17	0,164	0,01782	10,9	30	3	2	35		
	µg/l	N2M						0,250	yes	0,64	25	0,66	0,637	0,6394	5,7	29	4	2	35		
Co	µg/l	A1M						-11,520	H	5,05	15	0,685	5,075	5,071	0,1733	3,4	25	4	0	29	
	µg/l	N2M						-0,176	yes	9,87	15	9,74	9,915	9,889	0,3139	3,2	27	2	0	29	
Cr	µg/l	A1M						-14,710	H	18,7	10	4,945	18,77	18,77	0,7685	4,1	29	3	0	32	
	µg/l	N2M						-0,560	yes	7,14	10	6,94	7,155	7,142	0,2642	3,7	30	2	0	32	
Cu	µg/l	A1M						-4,347	H	27,3	15	18,4	27,25	27,45	1,38	5	28	4	0	32	
	µg/l	N2M						0,417	yes	2,64	20	2,75	2,6	2,637	0,1896	7,2	28	4	0	32	
Fe	µg/l	A1M						1,166	yes	343	10	363	337,9	339,4	14,59	4,3	28	2	0	30	
	µg/l	N2M						1,345	yes	461	10	492	464	461,5	18,72	4,1	28	2	0	30	
Hg	µg/l	A1Hg							yes			0,01555	0,0204	0,02224	0,01173	52,7	16	6	2	24	
	µg/l	N1Hg						-1,706	yes	0,068	25	0,0535	0,0675	0,06555	0,00957	14,6	21	6	0	27	
Mn	µg/l	A1M						0,760	yes	171	10	177,5	169,7	169,5	6,338	3,7	28	3	0	31	
	µg/l	N2M						0,448	yes	89,2	10	91,2	89,6	88,99	2,983	3,4	28	2	0	30	
Mo	µg/l	A1M						-0,433	yes	15,4	15	14,9	15,15	15,14	0,965	6,4	26	1	0	27	
	µg/l	N2M						-0,510	yes	17	15	16,35	17	16,91	0,8247	4,9	26	1	0	27	
Ni	µg/l	A1M						-1,233	yes	14,6	10	13,7	14,2	14,22	0,6101	4,3	33	2	0	35	
	µg/l	N1M						0,000	yes	17,7	10	17,7	17,7	17,75	0,8323	4,7	33	2	0	35	
	µg/l	N2M						-0,111	yes	27,1	10	26,95	27,2	27,12	1,128	4,2	33	2	0	35	
Pb	µg/l	A1M						-1,588	yes	6,941	10	6,39	6,872	6,811	0,3274	4,8	30	5	1	36	
	µg/l	N1M						-0,473	yes	7,139	10	6,97	7	7	0,3173	4,5	33	2	1	36	
	µg/l	N2M						-0,908	yes	17,18	10	16,4	16,95	16,8	0,6855	4,1	35	1	0	36	
Sb	µg/l	A1M						0,301	yes	13,3	20	13,7	13,4	13,16	1,119	8,5	24	4	0	28	
	µg/l	N2M						0,525	yes	16,2	20	17,05	16,3	16,22	1,157	7,1	24	4	0	28	
Se	µg/l	A1M						0,435	C	34,5	10	35,25	34,15	34,25	2,145	6,3	23	4	0	27	
	µg/l	N2M						1,198	C	16,7	10	17,7	16,7	16,69	0,8192	4,9	24	3	0	27	
V	µg/l	A1M						-0,649	yes	8,47	10	8,195	8,54	8,474	0,2674	3,2	25	2	0	27	
	µg/l	N2M						-0,159	yes	10,7	10	10,62	10,7	10,77	0,3627	3,4	25	2	0	27	
Zn	µg/l	A1M						1,314	yes	175	10	186,5	173,2	175,6	11,42	6,5	30	1	0	31	
	µg/l	N2M						0,940	yes	30,5	15	32,65	30,23	30,61	2,22	7,3	27	3	0	30	

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

SYKE - Interlaboratory comparison test 10/2011

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl- fai- led	Mis- sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 16																				
Al	µg/l	A1M						-0,363	yes	314	10	308,3	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-0,386	yes	654	15	635	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						3,772	H	6,05	15	7,761	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,541	yes	10,6	15	11,03	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						5,260	H	20,8	15	29	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-0,747	yes	40,9	15	38,61	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,364	yes	0,66	25	0,63	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-1,341	yes	0,17	25	0,1415	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,044	yes	0,64	25	0,6365	0,637	0,6394	0,03675	5,7	29	4	2	35
Cr	µg/l	A1M						0,070	yes	18,7	10	18,77	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,646	yes	7,14	10	6,909	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						1223,00	H	27,3	15	2532	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						7130,00	H	2,64	20	1885	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,557	yes	343	10	333,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-1,072	yes	461	10	436,3	464	461,5	18,72	4,1	28	2	0	30
Mn	µg/l	A1M						-0,029	yes	171	10	170,8	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-0,660	yes	89,2	10	86,25	89,6	88,99	2,983	3,4	28	2	0	30
Ni	µg/l	A1M						0,007	yes	14,6	10	14,61	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,045	yes	17,7	10	17,66	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,303	yes	27,1	10	26,69	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-1,941	yes	6,941	10	6,268	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						0,025	yes	7,139	10	7,148	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,268	yes	17,18	10	16,95	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,447	yes	13,3	20	13,89	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,414	yes	16,2	20	16,87	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						1,936	yes	34,5	10	37,84	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						1,162	yes	16,7	10	17,67	16,7	16,69	0,8192	4,9	24	3	0	27
Zn	µg/l	A1M						0,840	yes	175	10	182,3	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						0,654	yes	30,5	15	32	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 17																				
Al	µg/l	A1M						-1,688	yes	314	10	287,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-1,628	yes	654	15	574,1	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,781	yes	6,05	15	5,696	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,566	yes	10,6	15	10,15	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						-0,266	yes	20,8	15	20,38	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-1,392	yes	40,9	15	36,63	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,354	yes	0,66	25	0,6308	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,487	yes	0,17	25	0,1597	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,776	yes	0,64	25	0,5779	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,219	yes	5,05	15	4,967	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,536	yes	9,87	15	9,473	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,455	yes	18,7	10	18,27	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,767	yes	7,14	10	6,866	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,603	yes	27,3	15	26,07	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,642	yes	2,64	20	2,471	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-1,044	yes	343	10	325,1	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-1,256	yes	461	10	432,1	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg							H		25	5,35	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						7774,00	H	0,068	25	66,15	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						-0,731	yes	171	10	164,8	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-0,789	yes	89,2	10	85,68	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,398	yes	15,4	15	14,94	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,357	yes	17	15	16,55	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,877	yes	14,6	10	13,96	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,186	yes	17,7	10	17,54	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,602	yes	27,1	10	26,29	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-0,337	yes	6,941	10	6,824	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,621	yes	7,139	10	6,918	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-1,269	yes	17,18	10	16,09	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,466	yes	13,3	20	13,92	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						-0,929	yes	16,2	20	14,7	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						-1,183	yes	34,5	10	32,46	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						-1,581	yes	16,7	10	15,38	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						-0,898	yes	8,47	10	8,09	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						-0,439	yes	10,7	10	10,46	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-0,983	yes	175	10	166,4	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						-1,152	yes	30,5	15	27,87	30,23	30,61	2,22	7,3	27	3	0	30

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

Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl. fai- led	Mis- sing	Num of labs
			-3	-2	-1	0	+1	+2													
Laboratory 18																					
Cd	µg/l	A1M							-0,400	yes	0,66	25	0,627	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							-0,659	yes	0,17	25	0,156	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M							-0,212	yes	0,64	25	0,623	0,637	0,6394	0,03675	5,7	29	4	2	35
Hg	µg/l	A1Hg								yes			0,017	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg							0,118	yes	0,068	25	0,069	0,0675	0,06555	0,00957	14,6	21	6	0	27
Ni	µg/l	A1M							1,781	yes	14,6	10	15,9	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M							0,452	yes	17,7	10	18,1	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M							0,148	yes	27,1	10	27,3	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M							0,112	yes	6,941	10	6,98	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M							-0,473	yes	7,139	10	6,97	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M							-0,442	yes	17,18	10	16,8	16,95	16,8	0,6855	4,1	35	1	0	36
Laboratory 19																					
Al	µg/l	A1M							1,222	yes	314	10	333,18	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M							1,069	yes	654	15	706,445	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M							-1,327	yes	6,05	15	5,448	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M							-0,879	yes	10,6	15	9,901	10,53	10,55	0,4733	4,5	27	3	0	30
Cd	µg/l	A1M							-0,497	yes	0,66	25	0,619	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							0,235	yes	0,17	25	0,175	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M							-0,075	yes	0,64	25	0,634	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M							0,288	yes	5,05	15	5,159	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M							0,339	yes	9,87	15	10,121	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M							0,369	yes	18,7	10	19,045	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M							0,277	yes	7,14	10	7,239	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M							-0,403	yes	27,3	15	26,474	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M							-0,197	yes	2,64	20	2,588	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M							0,530	yes	343	10	352,091	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M							0,507	yes	461	10	472,680	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	N1Hg							-0,941	yes	0,068	25	0,060	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M							1,205	yes	171	10	181,305	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M							0,208	yes	89,2	10	90,129	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M							-2,633	yes	15,4	15	12,359	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M							-2,212	yes	17	15	14,180	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M							-1,129	yes	14,6	10	13,776	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M							-0,620	yes	17,7	10	17,151	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M							-0,531	yes	27,1	10	26,381	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M							-1,487	yes	6,941	10	6,425	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M							-1,104	yes	7,139	10	6,745	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M							-0,914	yes	17,18	10	16,395	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M							-1,986	yes	13,3	20	10,659	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M							-1,796	yes	16,2	20	13,290	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M							0,191	yes	34,5	10	34,830	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M							0,647	yes	16,7	10	17,240	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M							0,120	yes	8,47	10	8,521	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M							-0,202	yes	10,7	10	10,592	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M							-0,566	yes	175	10	170,05	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M							-0,193	yes	30,5	15	30,058	30,23	30,61	2,22	7,3	27	3	0	30

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

SYKE - Interlaboratory comparison test 10/2011

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl-failed	Mis-sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 20																				
Al	µg/l	A1M						0,236	yes	314	10	317,7	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						0,009	yes	654	15	654,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,029	yes	6,05	15	6,037	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,182	yes	10,6	15	10,75	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						-1,058	yes	20,8	15	19,15	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-1,690	yes	40,9	15	35,72	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						0,000	yes	0,66	25	0,66	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,094	yes	0,17	25	0,168	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,025	yes	0,64	25	0,638	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,623	yes	5,05	15	5,286	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,014	yes	9,87	15	9,86	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,444	yes	18,7	10	18,29	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,571	yes	7,14	10	6,936	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						0,791	yes	27,3	15	28,92	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						0,121	yes	2,64	20	2,672	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,111	yes	343	10	341,1	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,043	yes	461	10	460	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg										<0,015	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						1,176	yes	0,068	25	0,078	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						0,187	yes	171	10	172,6	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,085	yes	89,2	10	89,58	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,004	yes	15,4	15	15,39	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,220	yes	17	15	16,72	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						0,397	yes	14,6	10	14,89	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,463	yes	17,7	10	17,29	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,291	yes	27,1	10	26,7	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-4,089	H	6,941	10	5,522	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,305	yes	7,139	10	7,03	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,349	yes	17,18	10	16,88	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,051	yes	13,3	20	13,37	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						-0,194	yes	16,2	20	15,88	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						0,107	yes	34,5	10	34,69	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						-0,126	yes	16,7	10	16,59	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						0,335	yes	8,47	10	8,612	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						0,056	yes	10,7	10	10,73	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						0,537	yes	175	10	179,7	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						0,017	yes	30,5	15	30,54	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 21																				
Al	µg/l	A1M						-0,573	yes	314	10	305	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						0,622	yes	654	15	684,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						3,085	H	6,05	15	7,45	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,252	yes	10,6	15	10,4	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						0,385	C	20,8	15	21,4	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						0,815	yes	40,9	15	43,4	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						0,000	yes	0,66	25	0,66	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						0,000	yes	0,17	25	0,17	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						0,000	yes	0,64	25	0,64	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,132	yes	5,05	15	5	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,162	yes	9,87	15	9,75	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,963	yes	18,7	10	17,8	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,952	yes	7,14	10	6,8	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,293	yes	27,3	15	26,7	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,341	yes	2,64	20	2,55	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,554	yes	343	10	333,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						0,629	yes	461	10	475,5	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg							yes			0,023	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						-0,235	yes	0,068	25	0,066	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						-0,351	yes	171	10	168	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,336	yes	89,2	10	90,7	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,476	yes	15,4	15	14,85	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						0,039	yes	17	15	17,05	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,747	yes	14,6	10	14,05	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,622	yes	17,7	10	17,15	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,701	yes	27,1	10	26,15	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-2,423	yes	6,941	10	6,1	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-1,650	yes	7,139	10	6,55	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-1,490	yes	17,18	10	15,9	16,95	16,8	0,6855	4,1	35	1	0	36

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

Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl-fai-led	Mis-sing	Num of labs
			-3	-2	-1	0	+1	+2													
Sb	µg/l	A1M							-0,075	yes	13,3	20	13,2	13,4	13,16	1,119	8,5	24	4	0	28
Laboratory 21																					
Sb	µg/l	N2M							-0,247	yes	16,2	20	15,8	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M							-1,478	yes	34,5	10	31,95	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M							-1,557	yes	16,7	10	15,4	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M							-0,283	yes	8,47	10	8,35	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M							0,000	yes	10,7	10	10,7	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M							-1,543	yes	175	10	161,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M							-0,874	yes	30,5	15	28,5	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 22																					
As	µg/l	A1M							2,799	yes	6,05	15	7,32	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M							5,164	H	10,6	15	14,71	10,53	10,55	0,4733	4,5	27	3	0	30
Cd	µg/l	A1M							-0,946	yes	0,66	25	0,582	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							-3,859	yes	0,17	25	0,088	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M							-2,044	H	0,64	25	0,4765	0,637	0,6394	0,03675	5,7	29	4	2	35
Cr	µg/l	A1M							-1,583	yes	18,7	10	17,22	18,77	0,7685	4,1	29	3	0	32	
	µg/l	N2M							0,140	yes	7,14	10	7,19	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M							0,288	yes	27,3	15	27,89	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M							45,970	H	2,64	20	14,78	2,6	2,637	0,1896	7,2	28	4	0	32
Hg	µg/l	A1Hg								H			0,1605	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg							12,590	H	0,068	25	0,175	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M							-5,882	H	171	10	120,7	169,7	169,5	6,338	3,7	28	3	0	31
Ni	µg/l	A1M							-2,144	yes	14,6	10	13,04	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M							-1,328	yes	17,7	10	16,52	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M							-1,380	yes	27,1	10	25,23	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M							0,617	yes	6,941	10	7,155	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M							0,493	yes	7,139	10	7,315	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M							0,792	yes	17,18	10	17,86	16,95	16,8	0,6855	4,1	35	1	0	36
Zn	µg/l	A1M							-1,028	yes	175	10	166	173,2	175,6	11,42	6,5	30	1	0	31
Laboratory 23																					
Al	µg/l	A1M							-0,924	yes	314	10	299,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M							-0,500	yes	654	15	629,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M							2,909	yes	6,05	15	7,37	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M							0,000	yes	10,6	15	10,6	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M							-0,449	yes	20,8	15	20,1	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M							-0,359	yes	40,9	15	39,8	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M							0,097	yes	0,66	25	0,668	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							-0,329	yes	0,17	25	0,163	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M							-0,031	yes	0,64	25	0,6375	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M							0,026	yes	5,05	15	5,06	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M							-0,108	yes	9,87	15	9,79	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M							0,160	yes	18,7	10	18,85	18,77	0,7685	4,1	29	3	0	32	
	µg/l	N2M							-0,420	yes	7,14	10	6,99	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M							-0,220	yes	27,3	15	26,85	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M							0,171	yes	2,64	20	2,685	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M							0,408	yes	343	10	350	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M							0,933	yes	461	10	482,5	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg								yes			0,0186	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg							0,506	yes	0,068	25	0,0723	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M							0,292	yes	171	10	173,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M							0,785	yes	89,2	10	92,7	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M							-0,216	yes	15,4	15	15,15	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M							0,118	yes	17	15	17,15	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M							-0,890	yes	14,6	10	13,95	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M							-0,170	yes	17,7	10	17,55	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M							0,111	yes	27,1	10	27,25	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M							-0,277	yes	6,941	10	6,845	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M							-0,543	yes	7,139	10	6,945	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M							-0,675	yes	17,18	10	16,6	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M							-0,714	yes	13,3	20	12,35	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M							-1,049	yes	16,2	20	14,5	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M							-0,812	yes	34,5	10	33,1	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M							-1,078	yes	16,7	10	15,8	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M							-0,118	yes	8,47	10	8,42	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M							0,000	yes	10,7	10	10,7	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M							1,086	yes	175	10	184,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M							-0,721	yes	30,5	15	28,85	30,23	30,61	2,22	7,3	27	3	0	30

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

SYKE - Interlaboratory comparison test 10/2011

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl-failed	Mis-sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 24																				
Al	µg/l	A1M						-0,064	yes	314	10	313	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M					█	0,601	yes	654	15	683,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,716	yes	6,05	15	5,725	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M					█	-0,440	yes	10,6	15	10,25	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						-0,417	yes	20,8	15	20,15	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M					█	0,277	yes	40,9	15	41,75	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,121	yes	0,66	25	0,65	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,165	yes	0,17	25	0,1665	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M					█	0,181	yes	0,64	25	0,6545	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,383	yes	5,05	15	4,905	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M					█	-0,128	yes	9,87	15	9,775	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,588	yes	18,7	10	18,15	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M					█	0,462	yes	7,14	10	7,305	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,415	yes	27,3	15	26,45	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M					█	-0,265	yes	2,64	20	2,57	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,379	yes	343	10	336,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M					█	0,195	yes	461	10	465,5	464	461,5	18,72	4,1	28	2	0	30
Mn	µg/l	A1M						-0,409	C	171	10	167,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M					█	0,112	yes	89,2	10	89,7	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,606	yes	15,4	15	14,7	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M					█	-0,157	yes	17	15	16,8	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-1,096	yes	14,6	10	13,8	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-2,147	yes	17,7	10	15,8	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M					█	-0,258	yes	27,1	10	26,75	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-0,363	yes	6,941	10	6,815	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-1,398	yes	7,139	10	6,64	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M					█	-1,315	yes	17,18	10	16,05	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,489	yes	13,3	20	13,95	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M					█	0,525	yes	16,2	20	17,05	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						0,696	C	34,5	10	35,7	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M					█	-0,299	yes	16,7	10	16,45	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						-0,803	yes	8,47	10	8,13	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M					█	-0,093	yes	10,7	10	10,65	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						0,971	yes	175	10	183,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M					█	-0,066	yes	30,5	15	30,35	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 25																				
Al	µg/l	A1M						-2,261	yes	314	10	278,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M					█	-2,263	yes	654	15	543	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-1,807	yes	6,05	15	5,23	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M					█	-1,585	yes	10,6	15	9,34	10,53	10,55	0,4733	4,5	27	3	0	30
Cd	µg/l	A1M						0,788	yes	0,66	25	0,725	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						0,706	yes	0,17	25	0,185	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M					█	1,000	yes	0,64	25	0,72	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,621	yes	5,05	15	5,285	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M					█	0,324	yes	9,87	15	10,11	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						1,123	yes	18,7	10	19,75	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M					█	0,644	yes	7,14	10	7,37	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						1,026	yes	27,3	15	29,4	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M					█	0,492	yes	2,64	20	2,77	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						2,303	yes	343	10	382,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M					█	3,709	H	461	10	546,5	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg										<0,05	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg					█	0,235	yes	0,068	25	0,07	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						0,234	yes	171	10	173	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M					█	0,751	yes	89,2	10	92,55	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						0,173	yes	15,4	15	15,6	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M					█	0,627	yes	17	15	17,8	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						0,137	yes	14,6	10	14,7	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						1,073	yes	17,7	10	18,65	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M					█	0,406	yes	27,1	10	27,65	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-1,170	yes	6,941	10	6,535	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,305	yes	7,139	10	7,03	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M					█	-1,432	yes	17,18	10	15,95	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						-0,940	yes	13,3	20	12,05	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M					█	-0,833	yes	16,2	20	14,85	16,3	16,22	1,157	7,1	24	4	0	28
Zn	µg/l	A1M						2,971	yes	175	10	201	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M					█	2,667	yes	30,5	15	36,6	30,23	30,61	2,22	7,3	27	3	0	30

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

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl-failed	Mis-sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 26																				
As	µg/l	A1M						-0,648	yes	6,05	15	5,756	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,131	yes	10,6	15	10,7	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						0,434	yes	20,8	15	21,48	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-1,816	yes	40,9	15	35,33	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						0,131	yes	0,66	25	0,6708	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,125	yes	0,17	25	0,1673	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						0,388	yes	0,64	25	0,6711	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,566	yes	5,05	15	4,836	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,135	yes	9,87	15	9,77	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-0,802	yes	18,7	10	17,95	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,570	yes	7,14	10	6,937	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-1,359	yes	27,3	15	24,52	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-1,054	yes	2,64	20	2,362	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-1,015	yes	343	10	325,6	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,735	yes	461	10	444,1	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg							yes			0,0012	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						-2,553	yes	0,068	25	0,0463	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						-0,716	yes	171	10	164,9	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,621	yes	89,2	10	91,97	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,742	yes	15,4	15	14,54	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,155	yes	17	15	16,8	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-1,691	yes	14,6	10	13,37	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-0,208	yes	17,7	10	17,52	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-0,879	yes	27,1	10	25,91	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						0,650	yes	6,941	10	7,167	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						0,218	yes	7,139	10	7,217	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						0,177	yes	17,18	10	17,33	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,560	yes	13,3	20	14,05	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						0,828	yes	16,2	20	17,54	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						0,438	yes	34,5	10	35,26	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						0,503	yes	16,7	10	17,12	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						-0,190	yes	8,47	10	8,39	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						0,017	yes	10,7	10	10,71	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-0,697	yes	175	10	168,9	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						0,481	yes	30,5	15	31,6	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 27																				
Al	µg/l	A1M						-0,478	yes	314	10	306,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-0,612	yes	654	15	624	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						-0,231	yes	6,05	15	5,945	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,000	yes	10,6	15	10,6	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						1,154	yes	20,8	15	22,6	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						1,206	yes	40,9	15	44,6	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						0,115	yes	0,66	25	0,6695	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						0,024	yes	0,17	25	0,1705	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						0,094	yes	0,64	25	0,6475	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,119	yes	5,05	15	5,095	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						0,311	yes	9,87	15	10,1	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						0,374	yes	18,7	10	19,05	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						0,476	yes	7,14	10	7,31	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						1,929	yes	27,3	15	31,25	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						2,045	yes	2,64	20	3,18	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						0,117	yes	343	10	345	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						0,217	yes	461	10	466	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	N1Hg						-1,529	yes	0,068	25	0,055	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						0,702	yes	171	10	177	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,863	yes	89,2	10	93,05	89,6	88,99	2,983	3,4	28	2	0	30
Ni	µg/l	A1M						1,226	yes	14,6	10	15,49	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						1,949	yes	17,7	10	19,42	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						2,247	yes	27,1	10	30,14	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						0,516	yes	6,941	10	7,12	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						0,619	yes	7,139	10	7,36	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						0,640	yes	17,18	10	17,73	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						-3,169	H	13,3	20	9,085	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						-4,056	H	16,2	20	9,63	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						2,232	yes	34,5	10	38,35	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						1,737	yes	16,7	10	18,15	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						0,118	yes	8,47	10	8,52	8,54	8,474	0,2674	3,2	25	2	0	27

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

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl-failed	Mis-sing	Num of labs
			-3	-2	-1	0	+1													
	µg/l	N2M						0,028	yes	10,7	10	10,71	10,7	10,77	0,3627	3,4	25	2	0	27
Laboratory 27																				
Zn	µg/l	A1M						2,457	yes	175	10	196,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						2,404	yes	30,5	15	36	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 28																				
As	µg/l	A1M						-1,113	yes	6,05	15	5,545	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,761	yes	10,6	15	9,995	10,53	10,55	0,4733	4,5	27	3	0	30
Cd	µg/l	A1M						-0,667	yes	0,66	25	0,605	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,941	yes	0,17	25	0,15	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,563	yes	0,64	25	0,595	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,726	yes	5,05	15	4,775	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,831	yes	9,87	15	9,255	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						-1,059	yes	18,7	10	17,71	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-1,499	yes	7,14	10	6,605	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,464	yes	27,3	15	26,35	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,530	yes	2,64	20	2,5	2,6	2,637	0,1896	7,2	28	4	0	32
Hg	µg/l	A1Hg							yes			0,015	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						-0,059	yes	0,068	25	0,0675	0,0675	0,06555	0,00957	14,6	21	6	0	27
Ni	µg/l	A1M						-1,712	yes	14,6	10	13,35	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						-1,288	yes	17,7	10	16,56	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						-1,185	yes	27,1	10	25,49	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-1,127	yes	6,941	10	6,55	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,641	yes	7,139	10	6,91	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,163	yes	17,18	10	17,04	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						-3,729	H	13,3	20	8,34	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						-4,188	H	16,2	20	9,415	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						-0,707	yes	34,5	10	33,28	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						0,820	yes	16,7	10	17,38	16,7	16,69	0,8192	4,9	24	3	0	27
Laboratory 29																				
Al	µg/l	A1M						0,096	yes	314	10	315,5	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						0,255	yes	654	15	666,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						0,628	yes	6,05	15	6,335	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,189	yes	10,6	15	10,75	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						-0,513	yes	20,8	15	20	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-0,554	yes	40,9	15	39,2	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						-0,261	yes	0,66	25	0,6385	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,494	yes	0,17	25	0,1595	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,463	yes	0,64	25	0,603	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,000	yes	5,05	15	5,05	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						0,149	yes	9,87	15	9,98	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						0,267	yes	18,7	10	18,95	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						0,336	yes	7,14	10	7,26	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						0,073	yes	27,3	15	27,45	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,171	yes	2,64	20	2,595	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-1,778	yes	343	10	312,5	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-1,540	yes	461	10	425,5	464	461,5	18,72	4,1	28	2	0	30
Mn	µg/l	A1M						-1,754	yes	171	10	156	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						-1,413	yes	89,2	10	82,9	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-0,433	yes	15,4	15	14,9	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-0,118	yes	17	15	16,85	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						-0,548	yes	14,6	10	14,2	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,000	yes	17,7	10	17,7	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						0,148	yes	27,1	10	27,3	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-0,378	yes	6,941	10	6,81	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,165	yes	7,139	10	7,08	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-0,035	yes	17,18	10	17,15	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						-0,113	yes	13,3	20	13,15	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						-0,586	yes	16,2	20	15,25	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						-0,464	yes	34,5	10	33,7	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						-0,898	yes	16,7	10	15,95	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						-1,417	yes	8,47	10	7,87	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						-0,467	yes	10,7	10	10,45	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-1,029	yes	175	10	166	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						-0,940	yes	30,5	15	28,35	30,23	30,61	2,22	7,3	27	3	0	30

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

Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
			-3	-2	-1	0	+1	+2													
Laboratory 30																					
Al	µg/l	A1M						0,290	yes	314	10	318,6	314,6	311,1	13,74	4,4	27	2	0	29	
	µg/l	N2M						0,676	yes	654	15	687,2	663,2	653,7	41,86	6,4	28	1	0	29	
B	µg/l	A1M						4,337	H	20,8	15	27,56	21	20,93	1,079	5,2	17	6	2	25	
	µg/l	N2M						1,822	yes	40,9	15	46,49	41,35	40,9	3,008	7,4	23	2	0	25	
Cd	µg/l	A1M						0,545	yes	0,66	25	0,705	0,655	0,659	0,04445	6,7	29	4	2	35	
	µg/l	N1M						-0,235	yes	0,17	25	0,165	0,164	0,1629	0,01782	10,9	30	3	2	35	
	µg/l	N2M						0,250	yes	0,64	25	0,66	0,637	0,6394	0,03675	5,7	29	4	2	35	
Co	µg/l	A1M						0,937	yes	5,05	15	5,405	5,075	5,071	0,1733	3,4	25	4	0	29	
	µg/l	N2M						0,716	yes	9,87	15	10,4	9,915	9,889	0,3139	3,2	27	2	0	29	
Cr	µg/l	A1M						0,572	yes	18,7	10	19,23	18,77	18,77	0,7685	4,1	29	3	0	32	
	µg/l	N2M						0,336	yes	7,14	10	7,26	7,155	7,142	0,2642	3,7	30	2	0	32	
Cu	µg/l	A1M						0,632	yes	27,3	15	28,59	27,25	27,45	1,38	5	28	4	0	32	
	µg/l	N2M						0,701	yes	2,64	20	2,825	2,6	2,637	0,1896	7,2	28	4	0	32	
Fe	µg/l	A1M						0,111	yes	343	10	344,9	337,9	339,4	14,59	4,3	28	2	0	30	
	µg/l	N2M						0,616	yes	461	10	475,2	464	461,5	18,72	4,1	28	2	0	30	
Hg	µg/l	A1Hg							C			0,02	0,0204	0,02224	0,01173	52,7	16	6	2	24	
	µg/l	N1Hg						2,118	C	0,068	25	0,086	0,0675	0,06555	0,00957	14,6	21	6	0	27	
Mn	µg/l	A1M						0,199	yes	171	10	172,7	169,7	169,5	6,338	3,7	28	3	0	31	
	µg/l	N2M						0,693	yes	89,2	10	92,29	89,6	88,99	2,983	3,4	28	2	0	30	
Mo	µg/l	A1M						-0,117	yes	15,4	15	15,27	15,15	15,14	0,965	6,4	26	1	0	27	
	µg/l	N2M						0,020	yes	17	15	17,02	17	16,91	0,8247	4,9	26	1	0	27	
Ni	µg/l	A1M						0,151	yes	14,6	10	14,71	14,2	14,22	0,6101	4,3	33	2	0	35	
	µg/l	N1M						0,977	yes	17,7	10	18,56	17,7	17,75	0,8323	4,7	33	2	0	35	
	µg/l	N2M						0,716	yes	27,1	10	28,07	27,2	27,12	1,128	4,2	33	2	0	35	
Pb	µg/l	A1M						0,775	yes	6,941	10	7,21	6,872	6,811	0,3274	4,8	30	5	1	36	
	µg/l	N1M						0,087	yes	7,139	10	7,17	7	7	0,3173	4,5	33	2	1	36	
	µg/l	N2M						-0,151	yes	17,18	10	17,05	16,95	16,8	0,6855	4,1	35	1	0	36	
V	µg/l	A1M						0,189	yes	8,47	10	8,55	8,54	8,474	0,2674	3,2	25	2	0	27	
	µg/l	N2M						0,523	yes	10,7	10	10,98	10,7	10,77	0,3627	3,4	25	2	0	27	
Zn	µg/l	A1M						0,469	yes	175	10	179,1	173,2	175,6	11,42	6,5	30	1	0	31	
	µg/l	N2M						3,716	H	30,5	15	39	30,23	30,61	2,22	7,3	27	3	0	30	
Laboratory 31																					
Cd	µg/l	A1M						0,345	yes	0,66	25	0,6885	0,655	0,659	0,04445	6,7	29	4	2	35	
	µg/l	N1M						0,329	yes	0,17	25	0,177	0,164	0,1629	0,01782	10,9	30	3	2	35	
	µg/l	N2M						0,256	yes	0,64	25	0,6605	0,637	0,6394	0,03675	5,7	29	4	2	35	
Hg	µg/l	A1Hg							yes			0,0145	0,0204	0,02224	0,01173	52,7	16	6	2	24	
	µg/l	N1Hg						-0,918	yes	0,068	25	0,0602	0,0675	0,06555	0,00957	14,6	21	6	0	27	
Ni	µg/l	A1M						-0,890	yes	14,6	10	13,95	14,2	14,22	0,6101	4,3	33	2	0	35	
	µg/l	N1M						1,469	yes	17,7	10	19	17,7	17,75	0,8323	4,7	33	2	0	35	
	µg/l	N2M						1,476	yes	27,1	10	29,1	27,2	27,12	1,128	4,2	33	2	0	35	
Pb	µg/l	A1M						-0,738	yes	6,941	10	6,685	6,872	6,811	0,3274	4,8	30	5	1	36	
	µg/l	N1M						-0,880	yes	7,139	10	6,825	7	7	0,3173	4,5	33	2	1	36	
	µg/l	N2M						-0,733	yes	17,18	10	16,55	16,95	16,8	0,6855	4,1	35	1	0	36	

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

SYKE - Interlaboratory comparison test 10/2011

Analyte	Unit	Sample	z-Graphics					Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl-failed	Mis-sing	Num of labs
			-3	-2	-1	0	+1													
Laboratory 32																				
Al	µg/l	A1M						1,726	yes	314	10	341,1	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						1,162	yes	654	15	711,0	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						0,375	yes	6,05	15	6,220	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						0,468	yes	10,6	15	10,972	10,53	10,55	0,4733	4,5	27	3	0	30
Cd	µg/l	A1M						0,456	yes	0,66	25	0,6976	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,108	yes	0,17	25	0,1677	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						0,384	yes	0,64	25	0,6707	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						0,272	yes	5,05	15	5,153	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						0,331	yes	9,87	15	10,115	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						1,291	yes	18,7	10	19,907	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						0,297	yes	7,14	10	7,246	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						0,064	yes	27,3	15	27,432	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						0,045	yes	2,64	20	2,652	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						0,886	yes	343	10	358,2	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						1,145	yes	461	10	487,4	464	461,5	18,72	4,1	28	2	0	30
Mn	µg/l	A1M						0,468	yes	171	10	175,0	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,852	yes	89,2	10	93,0	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						0,058	yes	15,4	15	15,467	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						0,299	yes	17	15	17,381	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						0,274	yes	14,6	10	14,800	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,804	yes	17,7	10	18,412	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						0,355	yes	27,1	10	27,581	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						0,233	yes	6,941	10	7,022	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-0,614	yes	7,139	10	6,920	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						0,412	yes	17,18	10	17,534	16,95	16,8	0,6855	4,1	35	1	0	36
Se	µg/l	A1M						-0,546	yes	34,5	10	33,558	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						0,412	yes	16,7	10	17,044	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						0,959	yes	8,47	10	8,876	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						0,506	yes	10,7	10	10,971	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M						-0,182	yes	175	10	173,41	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M						0,245	yes	30,5	15	31,06	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 33																				
Al	µg/l	A1M						0,701	yes	314	10	325	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M						-0,133	yes	654	15	647,5	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M						0,077	yes	6,05	15	6,085	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M						-0,377	yes	10,6	15	10,3	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M						0,417	yes	20,8	15	21,45	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M						-0,033	yes	40,9	15	40,8	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M						0,182	yes	0,66	25	0,675	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M						-0,659	yes	0,17	25	0,156	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M						-0,487	yes	0,64	25	0,601	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M						-0,238	yes	5,05	15	4,96	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M						-0,480	yes	9,87	15	9,515	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M						0,428	yes	18,7	10	19,1	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M						-0,224	yes	7,14	10	7,06	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M						-0,464	yes	27,3	15	26,35	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M						-0,549	yes	2,64	20	2,495	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M						-0,291	yes	343	10	338	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M						-0,456	yes	461	10	450,5	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg						0,01752	yes			0,01752	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg						0,564	yes	0,068	25	0,07279	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M						0,117	yes	171	10	172	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M						0,022	yes	89,2	10	89,3	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M						-1,429	yes	15,4	15	13,75	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M						-1,529	yes	17	15	15,05	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M						0,343	yes	14,6	10	14,85	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M						0,113	yes	17,7	10	17,8	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M						0,406	yes	27,1	10	27,65	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M						-1,026	yes	6,941	10	6,585	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M						-1,314	yes	7,139	10	6,67	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M						-1,490	yes	17,18	10	15,9	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M						0,038	yes	13,3	20	13,35	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M						-0,525	yes	16,2	20	15,35	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M						2,812	yes	34,5	10	39,35	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M						0,778	yes	16,7	10	17,35	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M						-0,378	yes	8,47	10	8,31	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M						-1,028	yes	10,7	10	10,15	10,7	10,77	0,3627	3,4	25	2	0	27

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

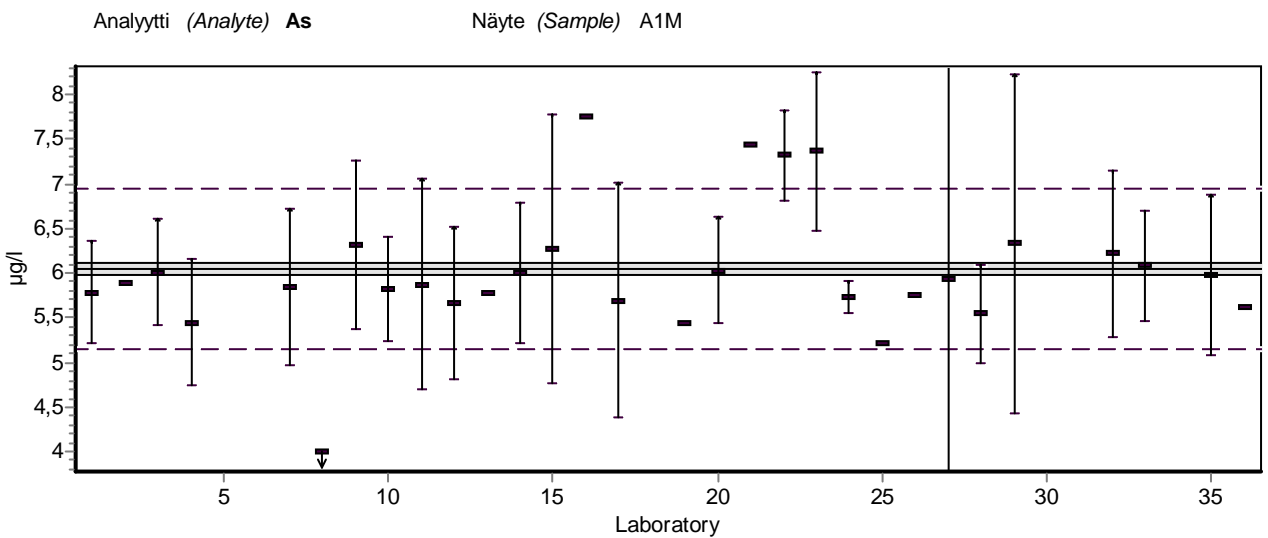
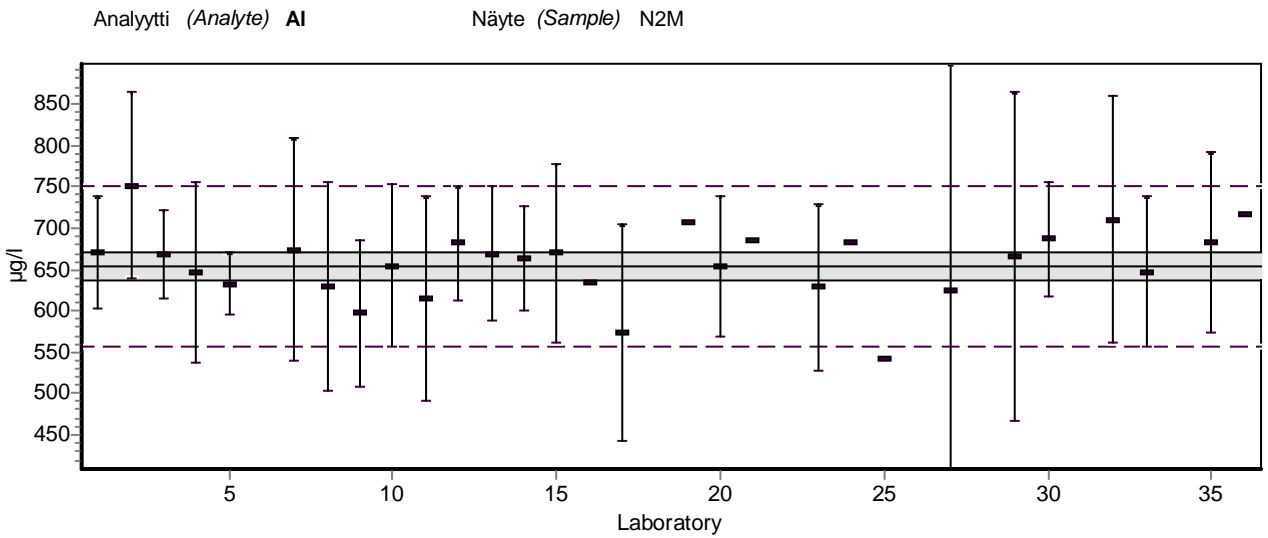
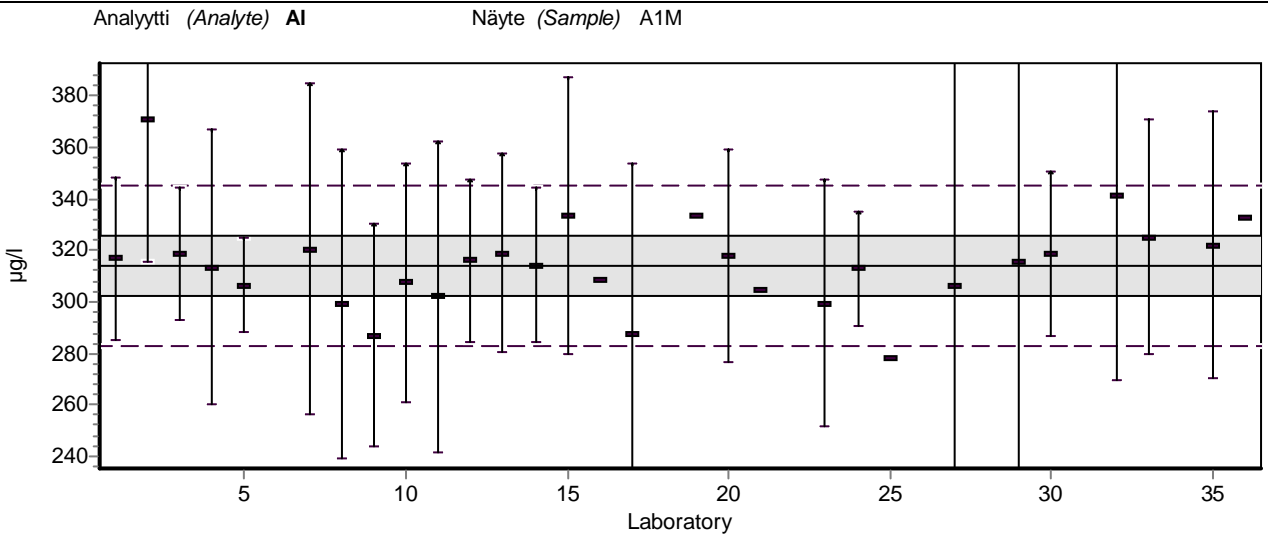
Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas-sed	Outl. fai-led	Mis-sing	Num of labs
			-3	-2	-1	0	+1	+2													
Zn	µg/l	A1M				—			0,743	yes	175	10	181,5	173,2	175,6	11,42	6,5	30	1	0	31
Laboratory 33																					
Zn	µg/l	N2M							-0,044	yes	30,5	15	30,4	30,23	30,61	2,22	7,3	27	3	0	30
Laboratory 34																					
Cd	µg/l	A1M							-0,182	yes	0,66	25	0,645	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M							0,118	yes	0,17	25	0,1725	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M							-0,063	yes	0,64	25	0,635	0,637	0,6394	0,03675	5,7	29	4	2	35
Hg	µg/l	A1Hg								yes			0,025	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg				—			2,235	C	0,068	25	0,087	0,0675	0,06555	0,00957	14,6	21	6	0	27
Ni	µg/l	A1M							-0,137	yes	14,6	10	14,5	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M							0,057	yes	17,7	10	17,75	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M							0,258	yes	27,1	10	27,45	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M				—			0,890	yes	6,941	10	7,25	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M				—			-0,670	yes	7,139	10	6,9	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M				—			-0,442	yes	17,18	10	16,8	16,95	16,8	0,6855	4,1	35	1	0	36
Laboratory 35																					
Al	µg/l	A1M				—			0,510	yes	314	10	322	314,6	311,1	13,74	4,4	27	2	0	29
	µg/l	N2M				—			0,612	yes	654	15	684	663,2	653,7	41,86	6,4	28	1	0	29
As	µg/l	A1M							-0,165	yes	6,05	15	5,975	5,875	5,983	0,4933	8,2	25	4	1	30
	µg/l	N2M							0,566	yes	10,6	15	11,05	10,53	10,55	0,4733	4,5	27	3	0	30
B	µg/l	A1M							-0,032	yes	20,8	15	20,75	21	20,93	1,079	5,2	17	6	2	25
	µg/l	N2M							0,685	yes	40,9	15	43	41,35	40,9	3,008	7,4	23	2	0	25
Cd	µg/l	A1M				—			1,055	yes	0,66	25	0,747	0,655	0,659	0,04445	6,7	29	4	2	35
	µg/l	N1M				—			-0,282	yes	0,17	25	0,164	0,164	0,1629	0,01782	10,9	30	3	2	35
	µg/l	N2M				—			1,206	yes	0,64	25	0,7365	0,637	0,6394	0,03675	5,7	29	4	2	35
Co	µg/l	A1M				—			-0,356	yes	5,05	15	4,915	5,075	5,071	0,1733	3,4	25	4	0	29
	µg/l	N2M				—			0,378	yes	9,87	15	10,15	9,915	9,889	0,3139	3,2	27	2	0	29
Cr	µg/l	A1M				—			1,604	yes	18,7	10	20,2	18,77	18,77	0,7685	4,1	29	3	0	32
	µg/l	N2M				—			1,583	yes	7,14	10	7,705	7,155	7,142	0,2642	3,7	30	2	0	32
Cu	µg/l	A1M				—			-0,366	yes	27,3	15	26,55	27,25	27,45	1,38	5	28	4	0	32
	µg/l	N2M				—			-0,171	yes	2,64	20	2,595	2,6	2,637	0,1896	7,2	28	4	0	32
Fe	µg/l	A1M							-0,058	yes	343	10	342	337,9	339,4	14,59	4,3	28	2	0	30
	µg/l	N2M							0,434	yes	461	10	471	464	461,5	18,72	4,1	28	2	0	30
Hg	µg/l	A1Hg								H			0,08245	0,0204	0,02224	0,01173	52,7	16	6	2	24
	µg/l	N1Hg							-0,171	yes	0,068	25	0,06655	0,0675	0,06555	0,00957	14,6	21	6	0	27
Mn	µg/l	A1M				—			-1,462	yes	171	10	158,5	169,7	169,5	6,338	3,7	28	3	0	31
	µg/l	N2M				—			-0,830	yes	89,2	10	85,5	89,6	88,99	2,983	3,4	28	2	0	30
Mo	µg/l	A1M							0,087	yes	15,4	15	15,5	15,15	15,14	0,965	6,4	26	1	0	27
	µg/l	N2M							0,706	yes	17	15	17,9	17	16,91	0,8247	4,9	26	1	0	27
Ni	µg/l	A1M				—			-0,822	yes	14,6	10	14	14,2	14,22	0,6101	4,3	33	2	0	35
	µg/l	N1M				—			0,565	yes	17,7	10	18,2	17,7	17,75	0,8323	4,7	33	2	0	35
	µg/l	N2M				—			0,443	yes	27,1	10	27,7	27,2	27,12	1,128	4,2	33	2	0	35
Pb	µg/l	A1M				—			-1,069	yes	6,941	10	6,57	6,872	6,811	0,3274	4,8	30	5	1	36
	µg/l	N1M				—			-1,370	yes	7,139	10	6,65	7	7	0,3173	4,5	33	2	1	36
	µg/l	N2M				—			-0,559	yes	17,18	10	16,7	16,95	16,8	0,6855	4,1	35	1	0	36
Sb	µg/l	A1M							-0,113	yes	13,3	20	13,15	13,4	13,16	1,119	8,5	24	4	0	28
	µg/l	N2M							-0,031	yes	16,2	20	16,15	16,3	16,22	1,157	7,1	24	4	0	28
Se	µg/l	A1M							-0,348	yes	34,5	10	33,9	34,15	34,25	2,145	6,3	23	4	0	27
	µg/l	N2M							0,180	yes	16,7	10	16,85	16,7	16,69	0,8192	4,9	24	3	0	27
V	µg/l	A1M							-0,201	yes	8,47	10	8,385	8,54	8,474	0,2674	3,2	25	2	0	27
	µg/l	N2M							0,748	yes	10,7	10	11,1	10,7	10,77	0,3627	3,4	25	2	0	27
Zn	µg/l	A1M				—			1,086	yes	175	10	184,5	173,2	175,6	11,42	6,5	30	1	0	31
	µg/l	N2M				—			0,918	yes	30,5	15	32,6	30,23	30,61	2,22	7,3	27	3	0	30

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

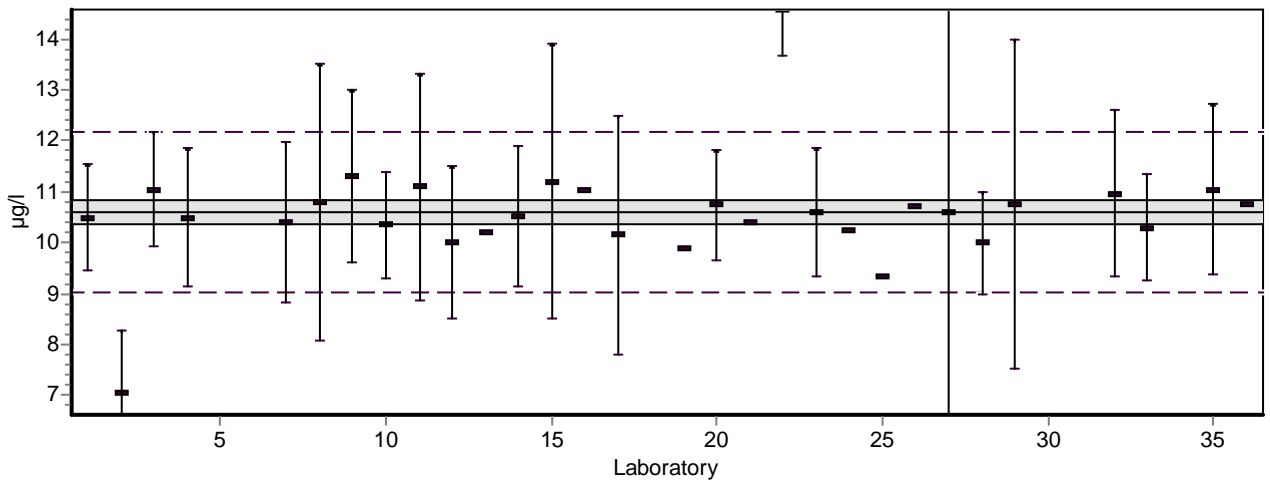
Analyte	Unit	Sample	z-Graphics						Z- value	Outl test OK	Assigned value	2* Targ SD%	Lab's result	Md.	Mean	SD	SD%	Pas- sed	Outl. fai- led	Mis- sing	Num of labs
			-3	-2	-1	0	+1	+2													
Laboratory 36																					
Al	µg/l	A1M						1,192	M	314	10	332,719	314,6	311,1	13,74	4,4	27	2	0	29	
	µg/l	N2M						1,294	M	654	15	717,471	663,2	653,7	41,86	6,4	28	1	0	29	
As	µg/l	A1M						-0,942	M	6,05	15	5,62261	5,875	5,983	0,4933	8,2	25	4	1	30	
	µg/l	N2M						0,205	M	10,6	15	10,7629	10,53	10,55	0,4733	4,5	27	3	0	30	
B	µg/l	A1M						-0,159	M	20,8	15	20,5513	21	20,93	1,079	5,2	17	6	2	25	
	µg/l	N2M						1,000	M	40,9	15	43,9666	41,35	40,9	3,008	7,4	23	2	0	25	
Cd	µg/l	A1M						0,056	M	0,66	25	0,66462	0,655	0,659	0,04445	6,7	29	4	2	35	
	µg/l	N1M						-0,322	M	0,17	25	0,16315	0,164	0,1629	0,01782	10,9	30	3	2	35	
	µg/l	N2M						0,207	M	0,64	25	0,65655	0,637	0,6394	0,03675	5,7	29	4	2	35	
Co	µg/l	A1M						0,687	M	5,05	15	5,31014	5,075	5,071	0,1733	3,4	25	4	0	29	
	µg/l	N2M						0,995	M	9,87	15	10,6062	9,915	9,889	0,3139	3,2	27	2	0	29	
Cr	µg/l	A1M						0,117	M	18,7	10	18,8097	18,77	18,77	0,7685	4,1	29	3	0	32	
	µg/l	N2M						0,025	M	7,14	10	7,14906	7,155	7,142	0,2642	3,7	30	2	0	32	
Cu	µg/l	A1M						0,235	M	27,3	15	27,781	27,25	27,45	1,38	5	28	4	0	32	
	µg/l	N2M						0,091	M	2,64	20	2,664	2,6	2,637	0,1896	7,2	28	4	0	32	
Fe	µg/l	A1M						3,132	M	343	10	396,714	337,9	339,4	14,59	4,3	28	2	0	30	
	µg/l	N2M						3,694	M	461	10	546,156	464	461,5	18,72	4,1	28	2	0	30	
Hg	µg/l	A1Hg							M			0,01283	0,0204	0,02224	0,01173	52,7	16	6	2	24	
	µg/l	N1Hg						-0,974	M	0,068	25	0,05972	0,0675	0,06555	0,00957	14,6	21	6	0	27	
Mn	µg/l	A1M						-0,169	M	171	10	169,555	169,7	169,5	6,338	3,7	28	3	0	31	
	µg/l	N2M						-1,418	M	89,2	10	82,8775	89,6	88,99	2,983	3,4	28	2	0	30	
Mo	µg/l	A1M						-0,330	M	15,4	15	15,0187	15,15	15,14	0,965	6,4	26	1	0	27	
	µg/l	N2M						0,598	M	17	15	17,7619	17	16,91	0,8247	4,9	26	1	0	27	
Ni	µg/l	A1M						-0,239	M	14,6	10	14,4253	14,2	14,22	0,6101	4,3	33	2	0	35	
	µg/l	N1M						-0,007	M	17,7	10	17,6936	17,7	17,75	0,8323	4,7	33	2	0	35	
	µg/l	N2M						0,688	M	27,1	10	28,0317	27,2	27,12	1,128	4,2	33	2	0	35	
Pb	µg/l	A1M						-9,956	M	6,941	10	3,48581	6,872	6,811	0,3274	4,8	30	5	1	36	
	µg/l	N1M						-1,525	M	7,139	10	6,59461	7	7	0,3173	4,5	33	2	1	36	
	µg/l	N2M						-0,650	M	17,18	10	16,6218	16,95	16,8	0,6855	4,1	35	1	0	36	
Sb	µg/l	A1M						0,317	M	13,3	20	13,7212	13,4	13,16	1,119	8,5	24	4	0	28	
	µg/l	N2M						0,185	M	16,2	20	16,5005	16,3	16,22	1,157	7,1	24	4	0	28	
Se	µg/l	A1M						0,304	M	34,5	10	35,0252	34,15	34,25	2,145	6,3	23	4	0	27	
	µg/l	N2M						-2,142	M	16,7	10	14,9115	16,7	16,69	0,8192	4,9	24	3	0	27	
V	µg/l	A1M						0,277	M	8,47	10	8,58744	8,54	8,474	0,2674	3,2	25	2	0	27	
	µg/l	N2M						0,787	M	10,7	10	11,1212	10,7	10,77	0,3627	3,4	25	2	0	27	
Zn	µg/l	A1M						-0,172	M	175	10	173,495	173,2	175,6	11,42	6,5	30	1	0	31	
	µg/l	N2M						0,539	M	30,5	15	31,7328	30,23	30,61	2,22	7,3	27	3	0	30	

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

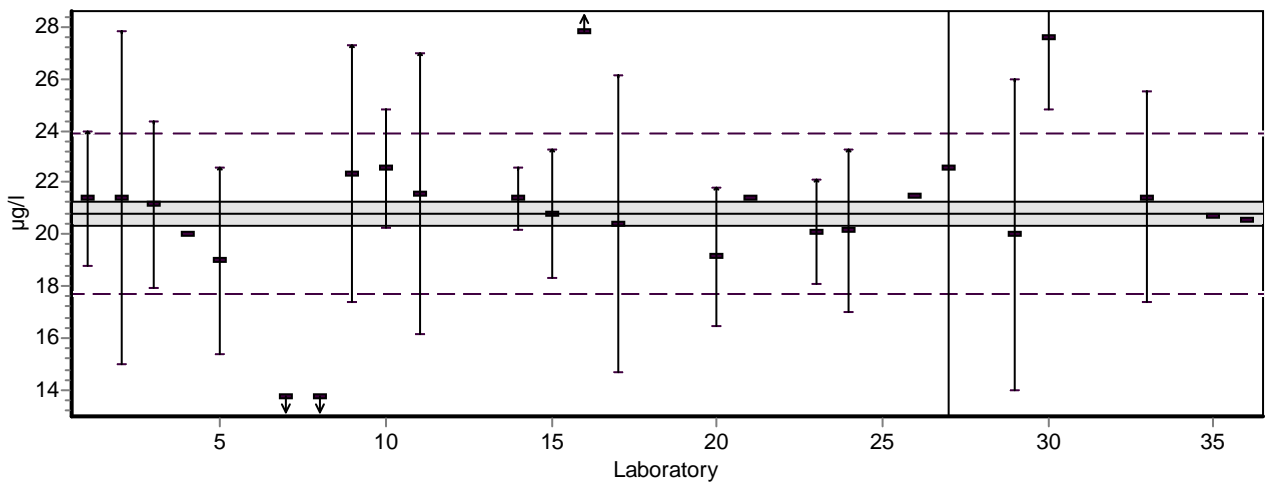
LIITE 8. RESULTS AND THEIR UNCERTAINTIES
APPENDIX 8.



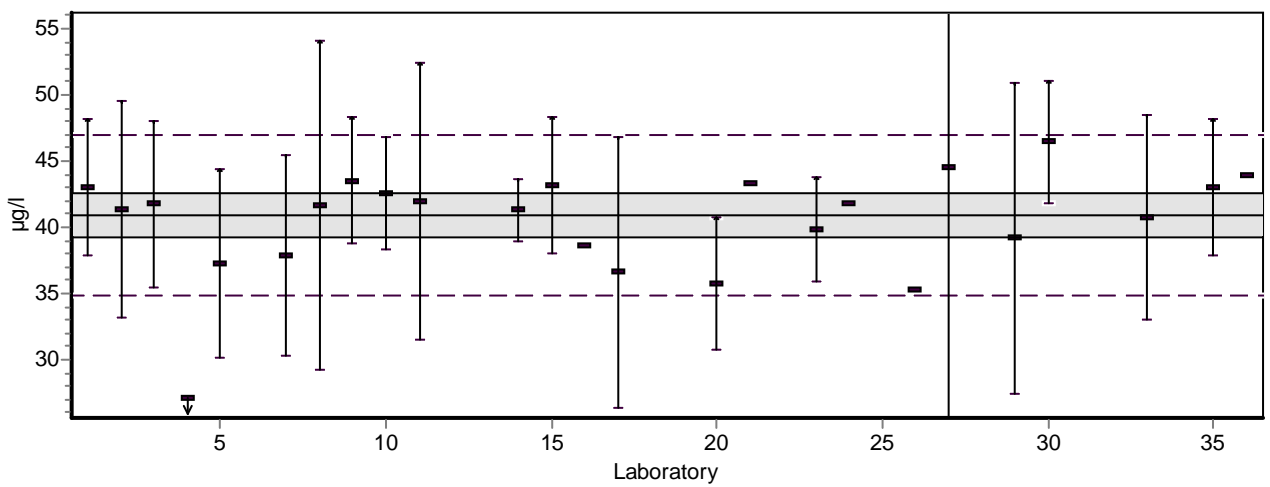
Analyytti (Analyte) **As** Näyte (Sample) **N2M**

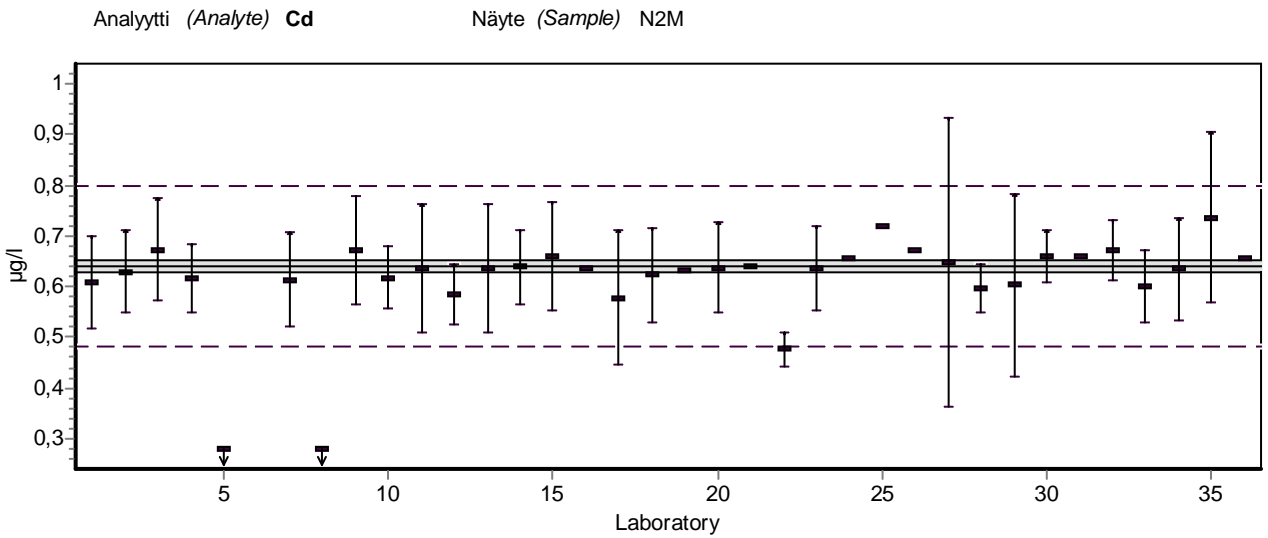
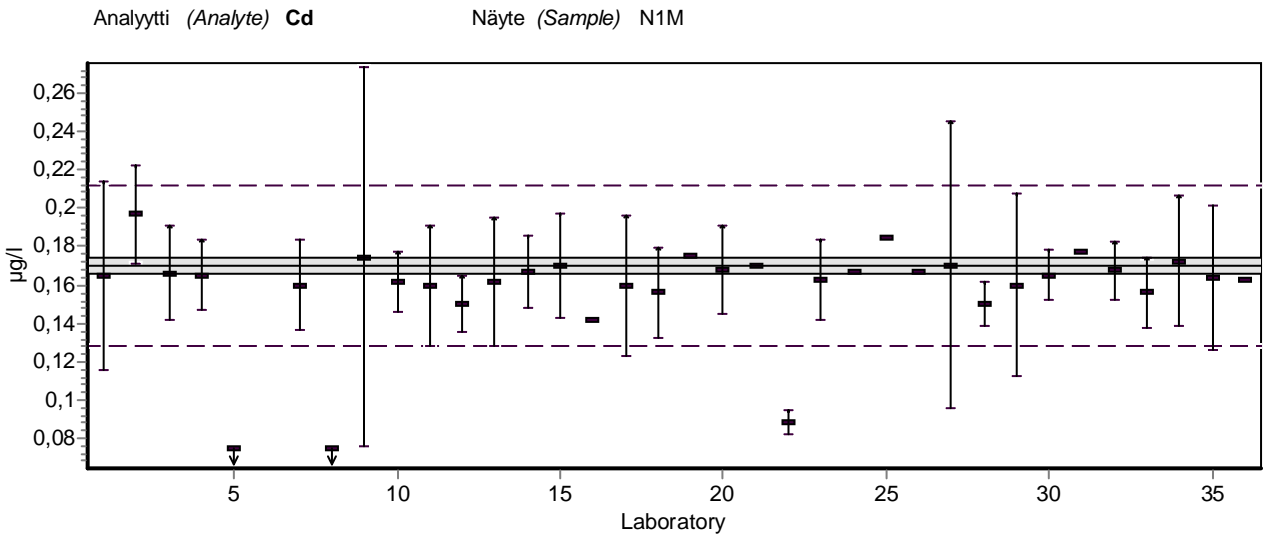
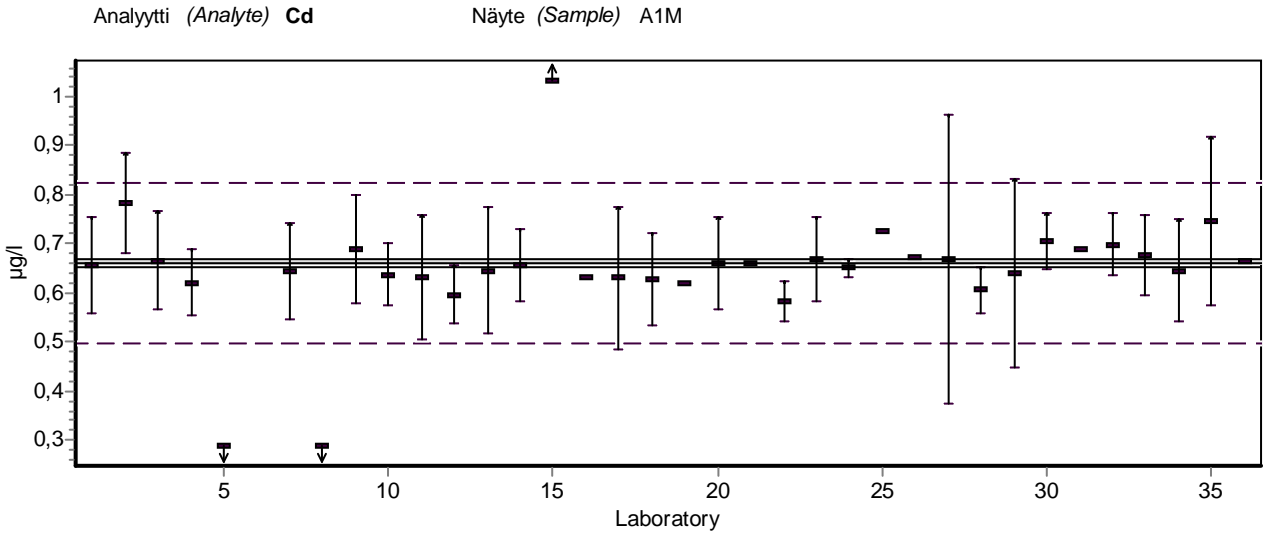


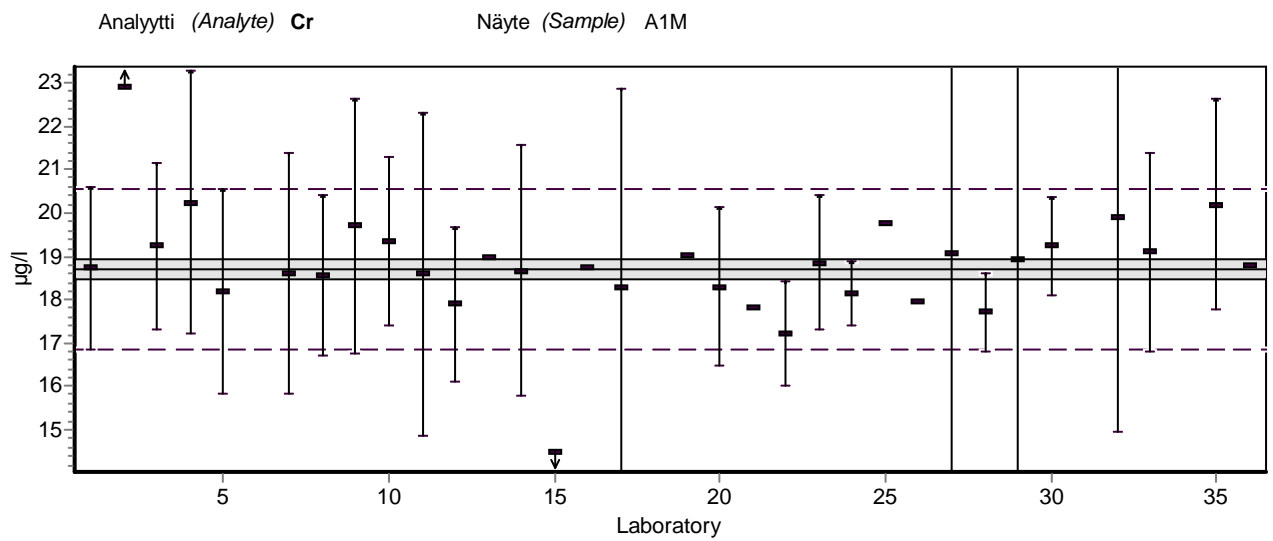
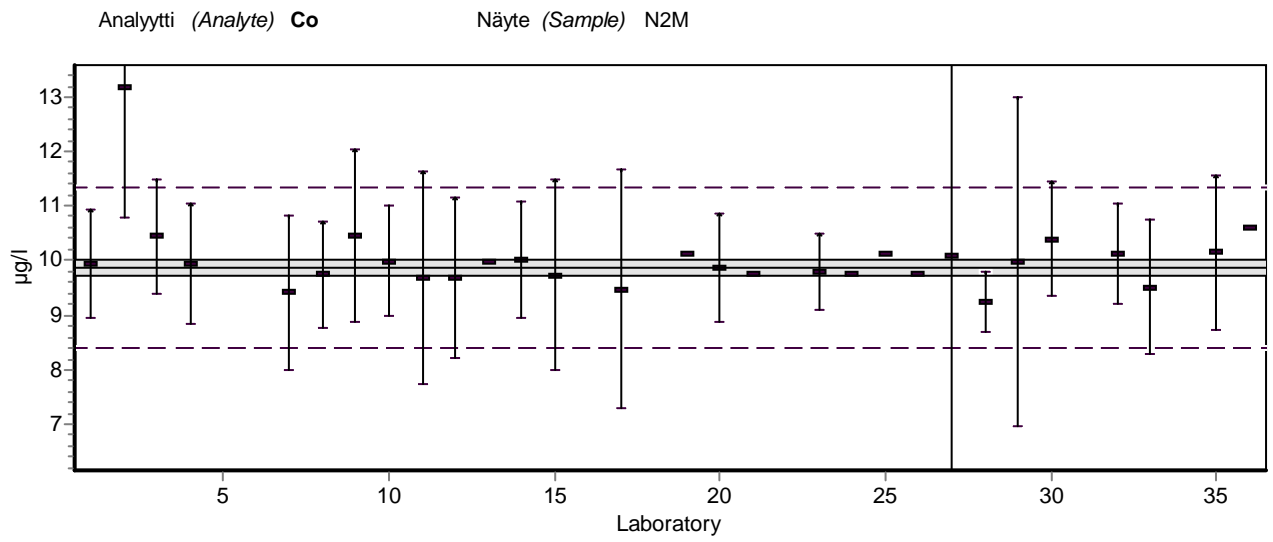
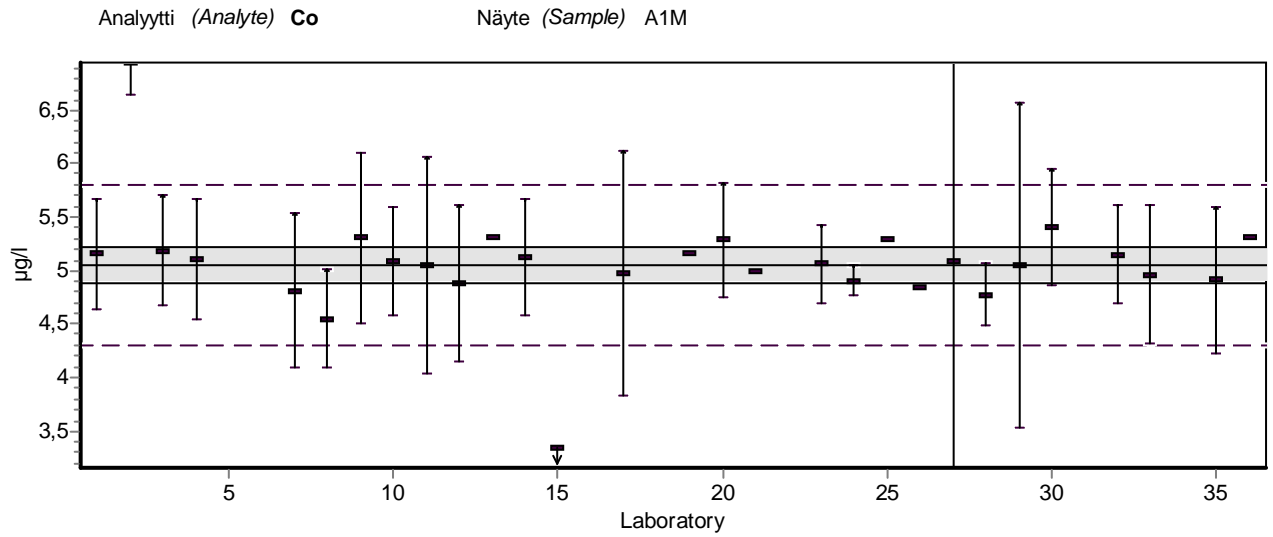
Analyytti (Analyte) **B** Näyte (Sample) **A1M**

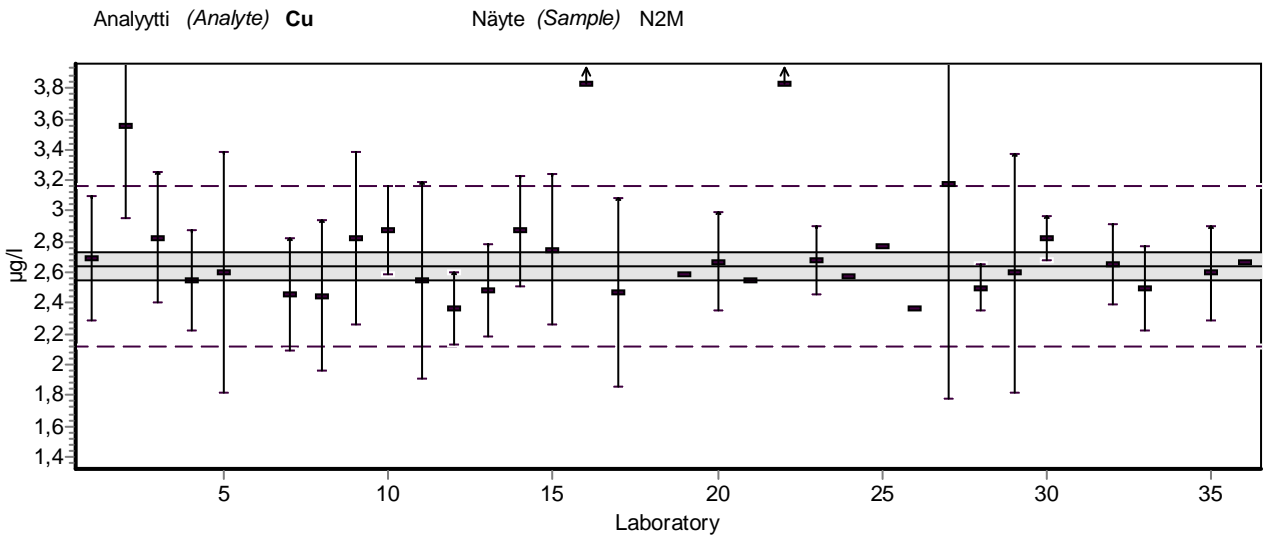
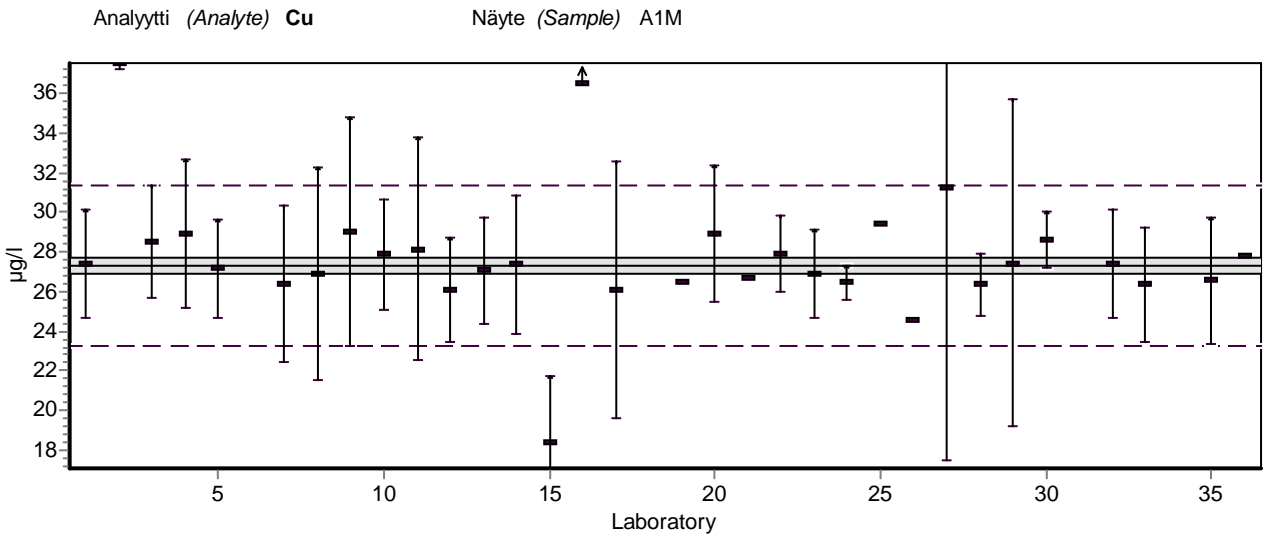
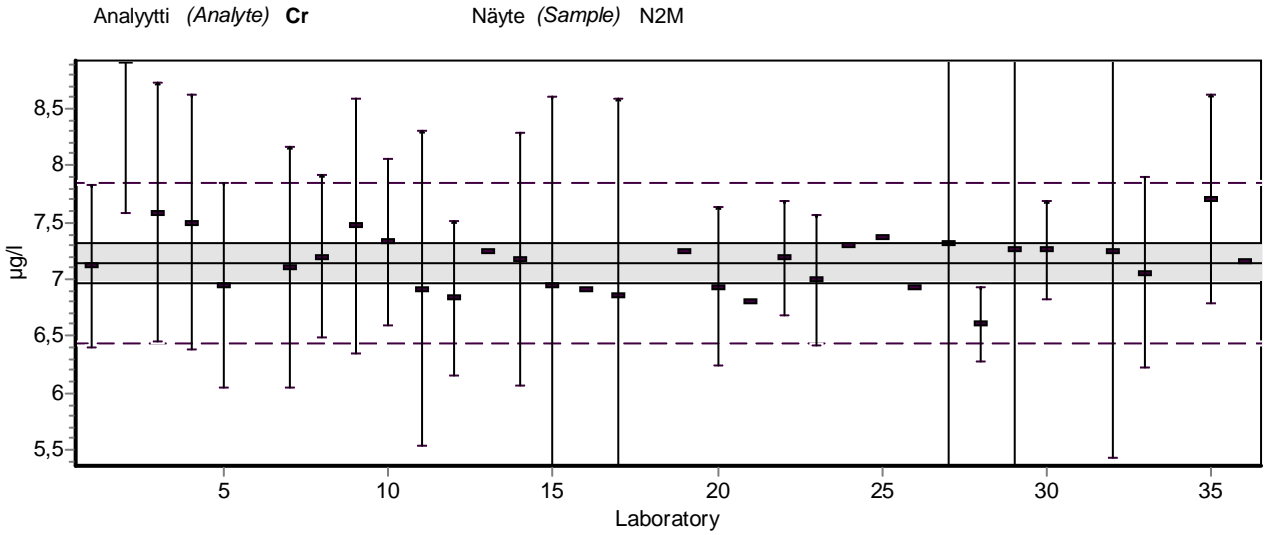


Analyytti (Analyte) **B** Näyte (Sample) **N2M**

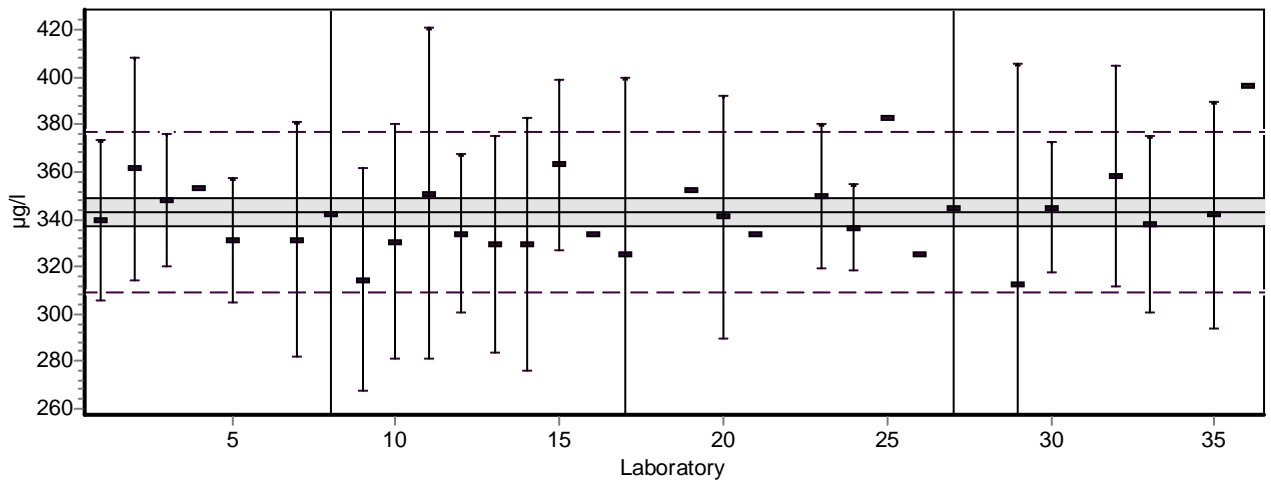




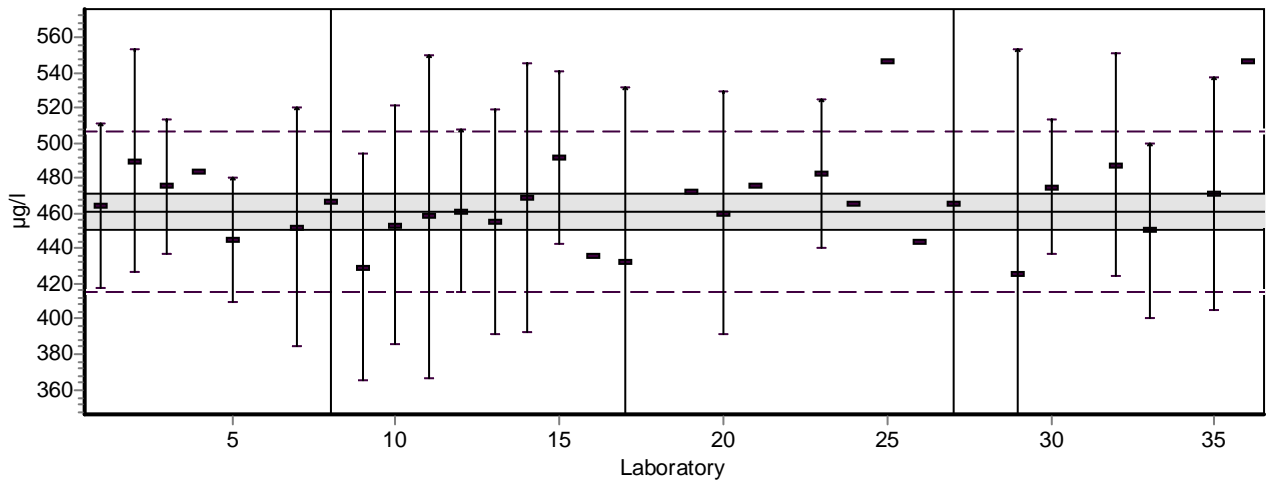


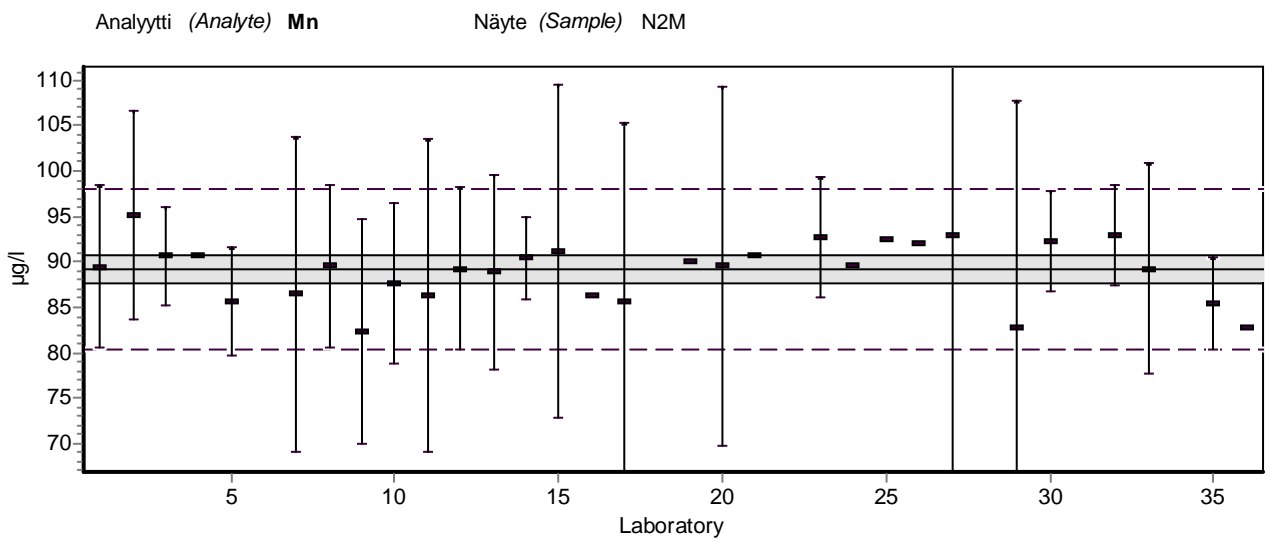
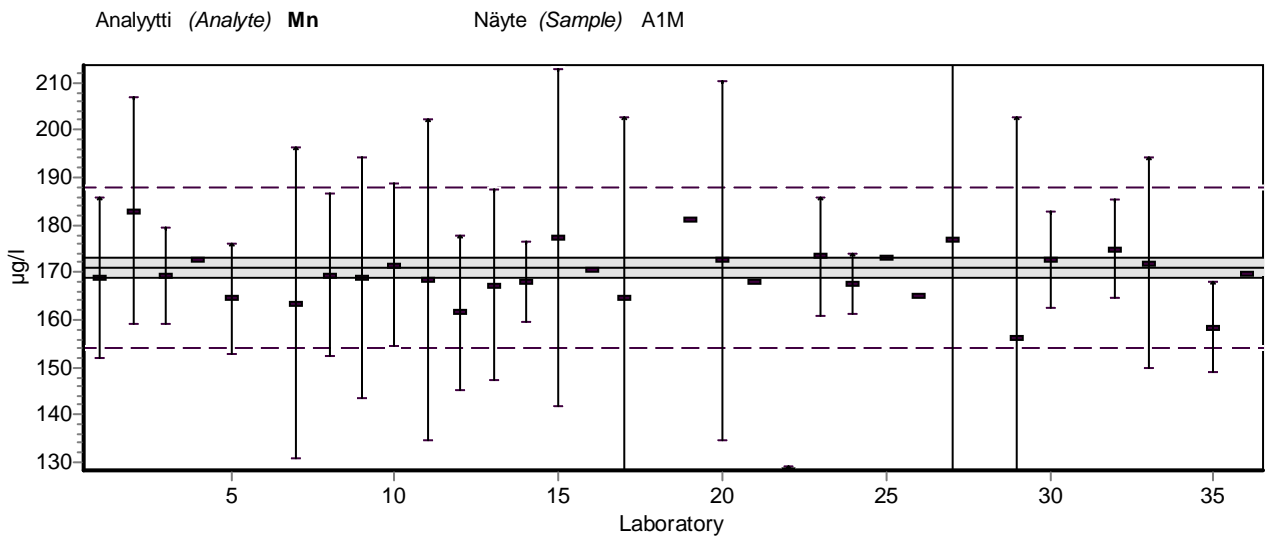
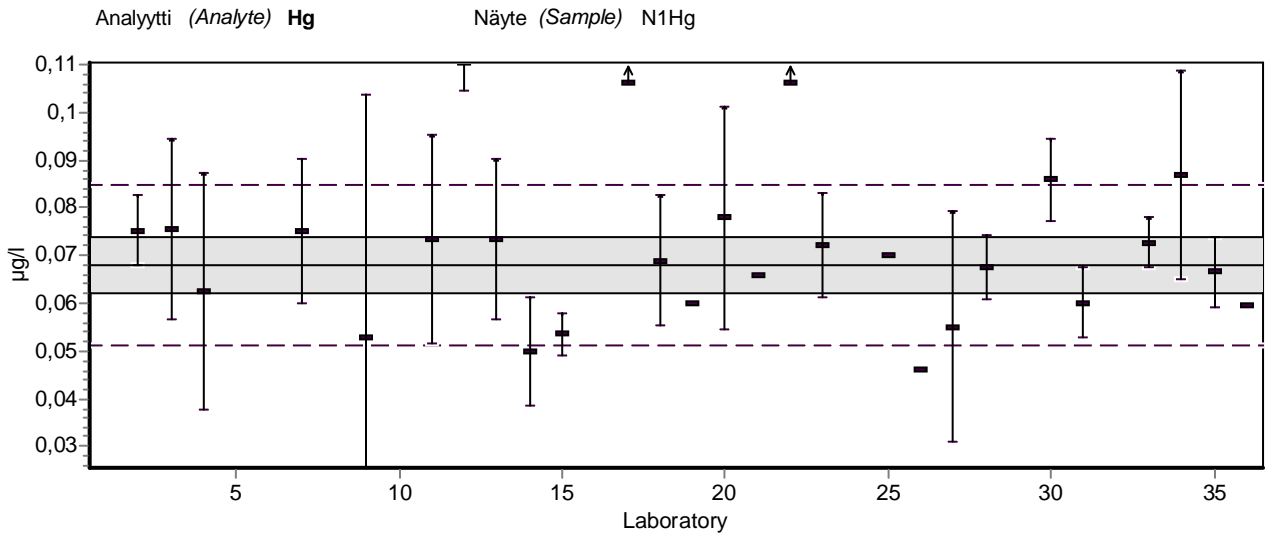


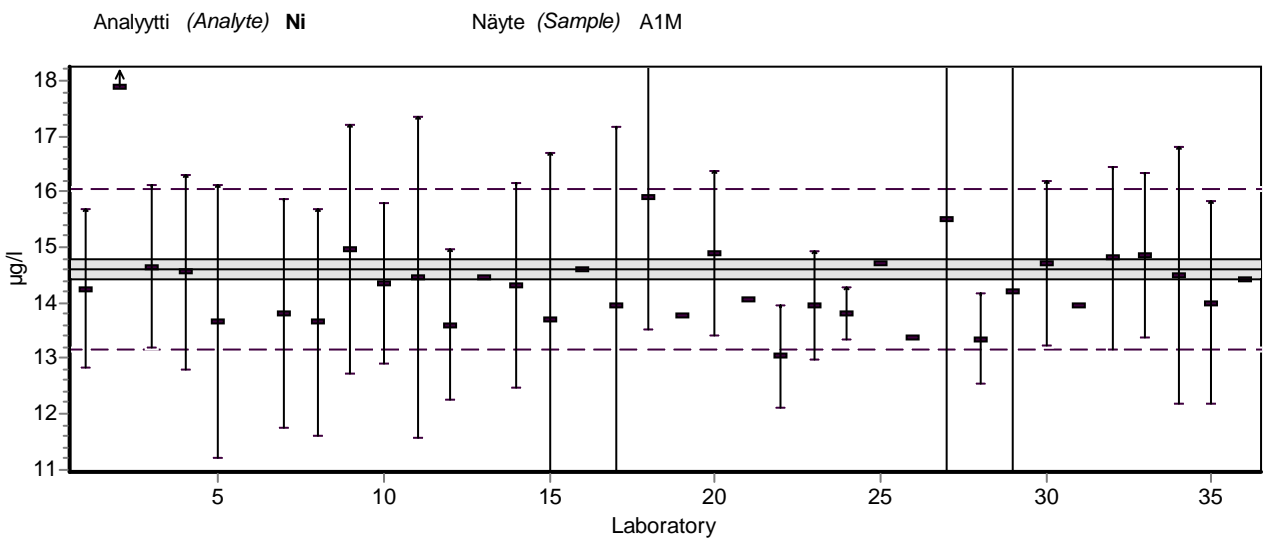
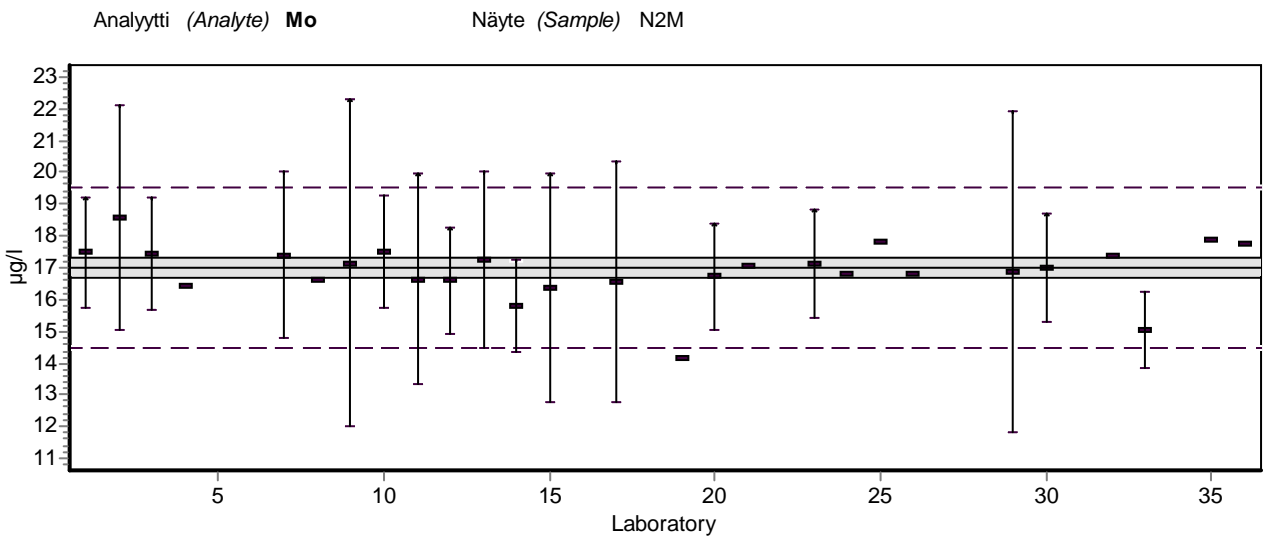
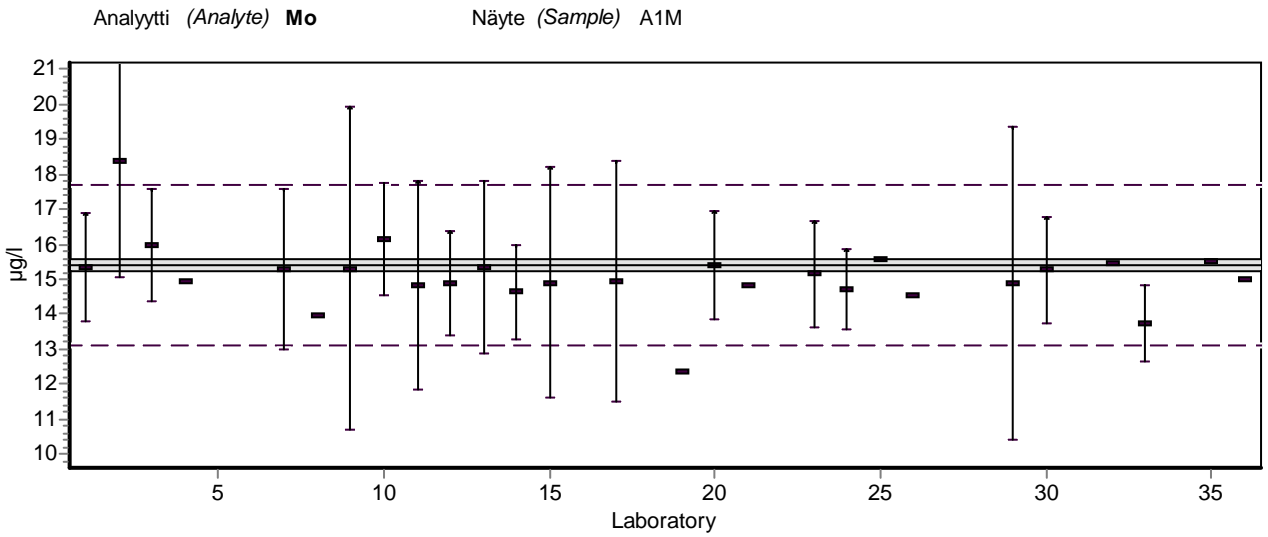
Analyytti (Analyte) Fe Näyte (Sample) A1M

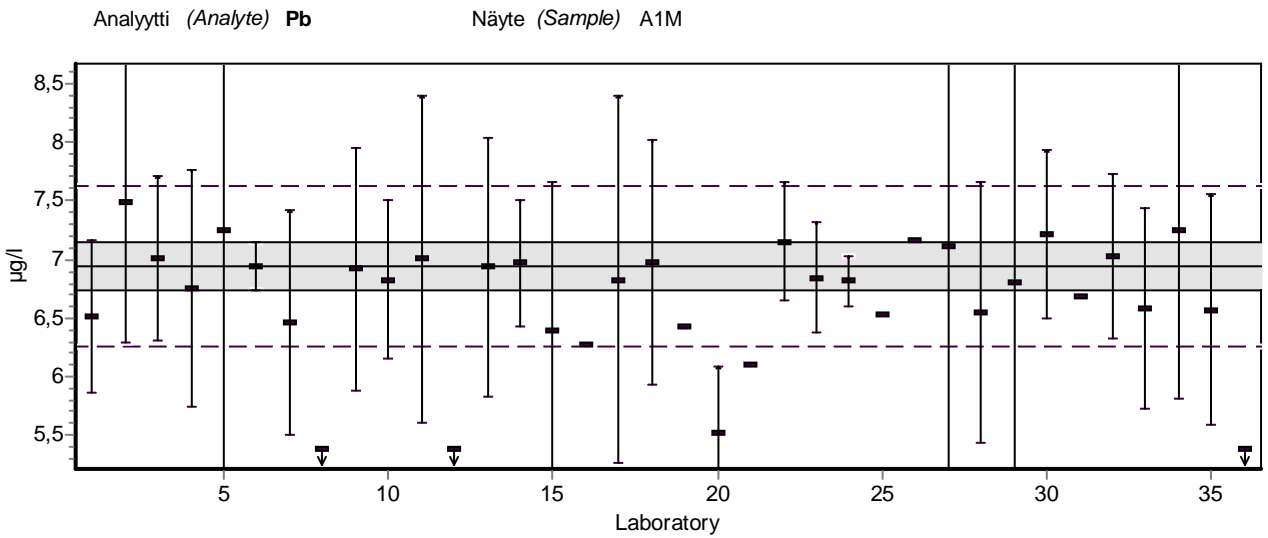
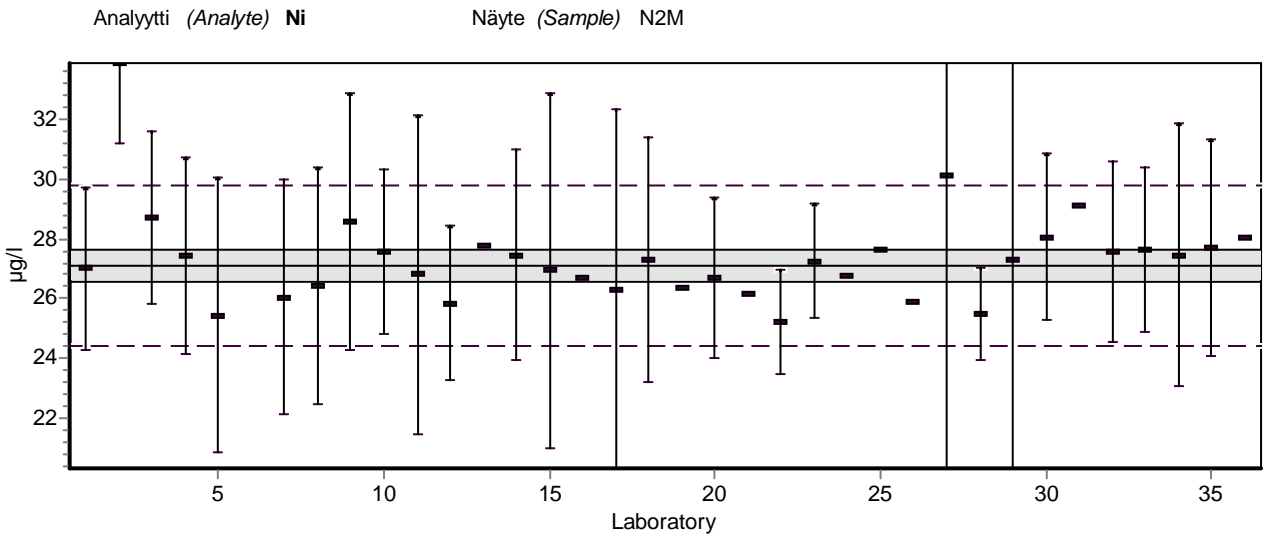
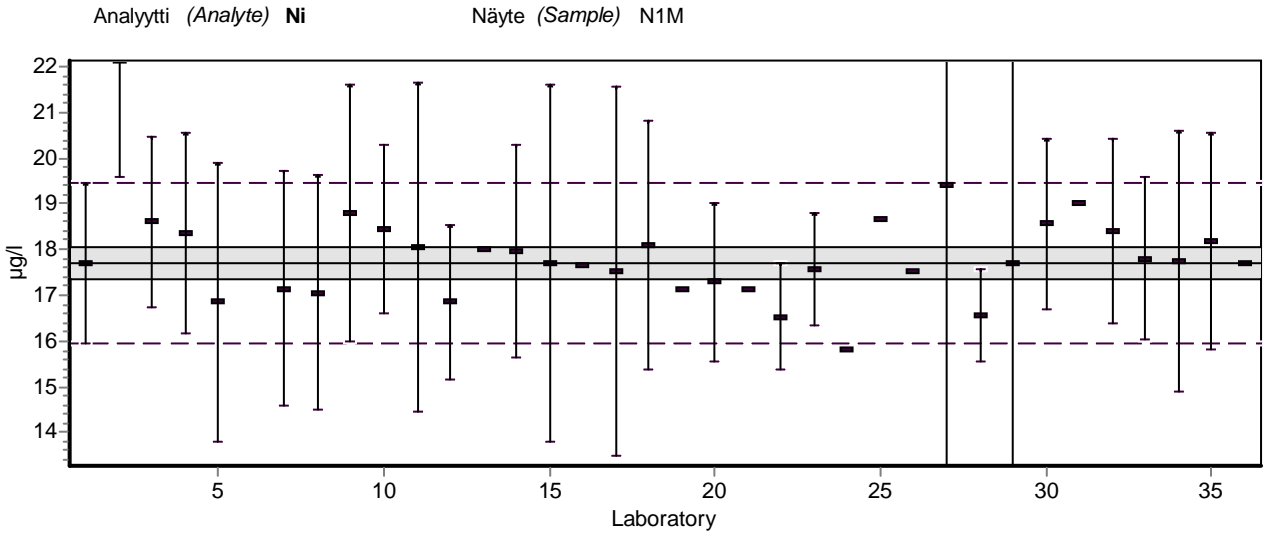


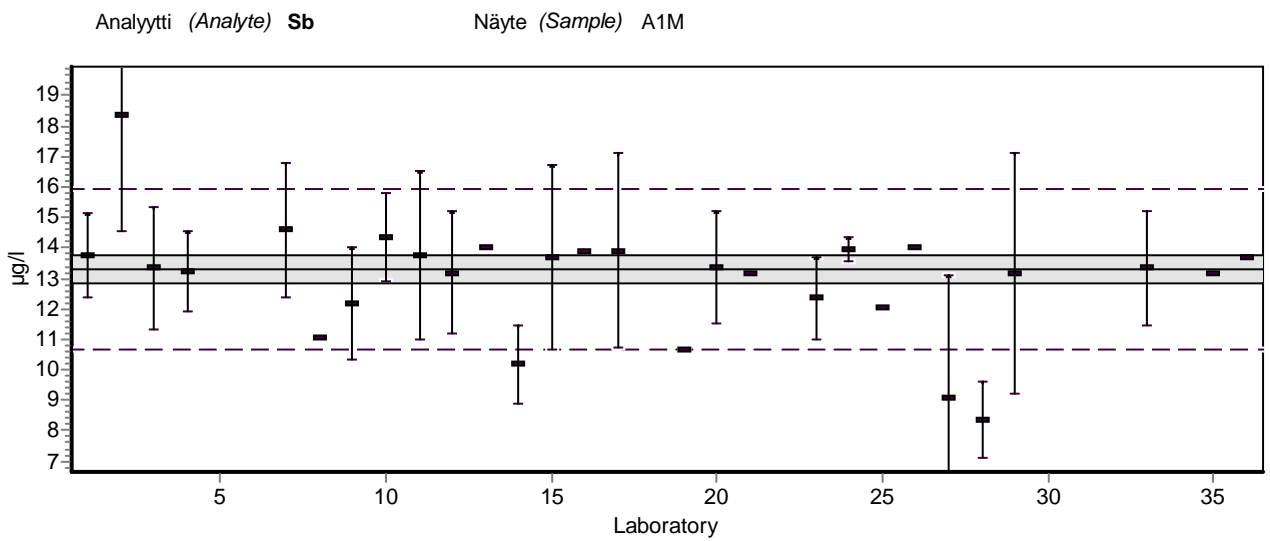
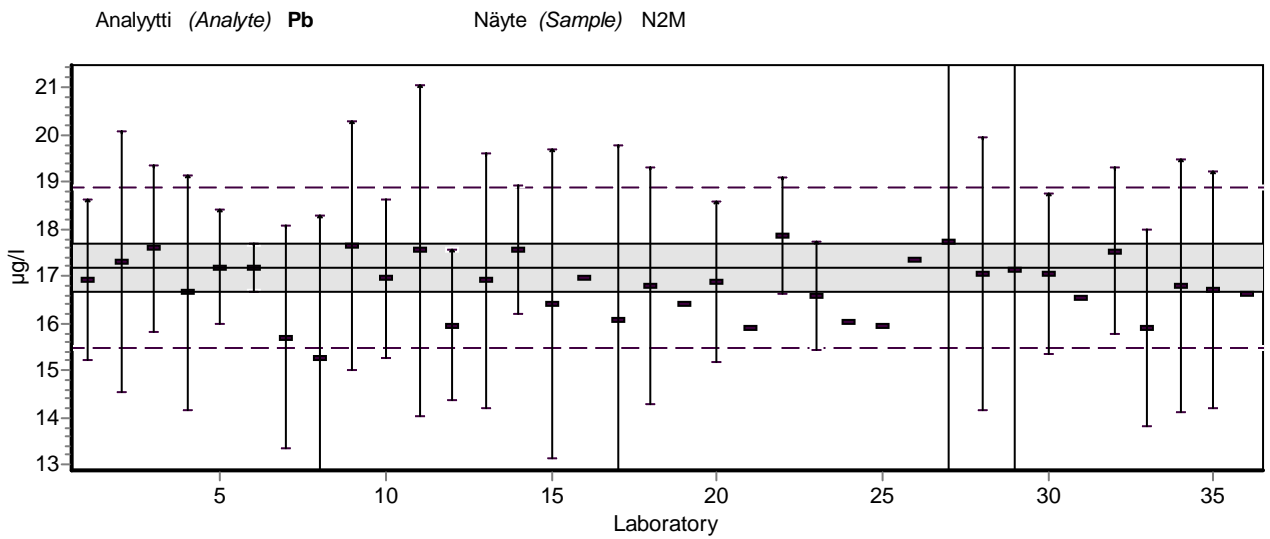
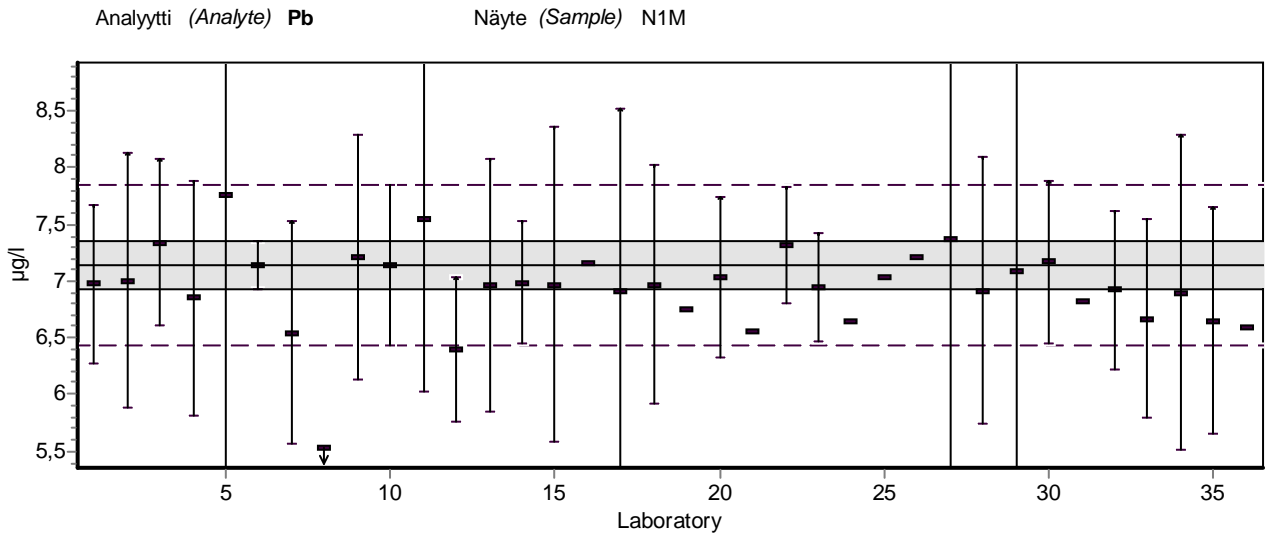
Analyytti (Analyte) Fe Näyte (Sample) N2M



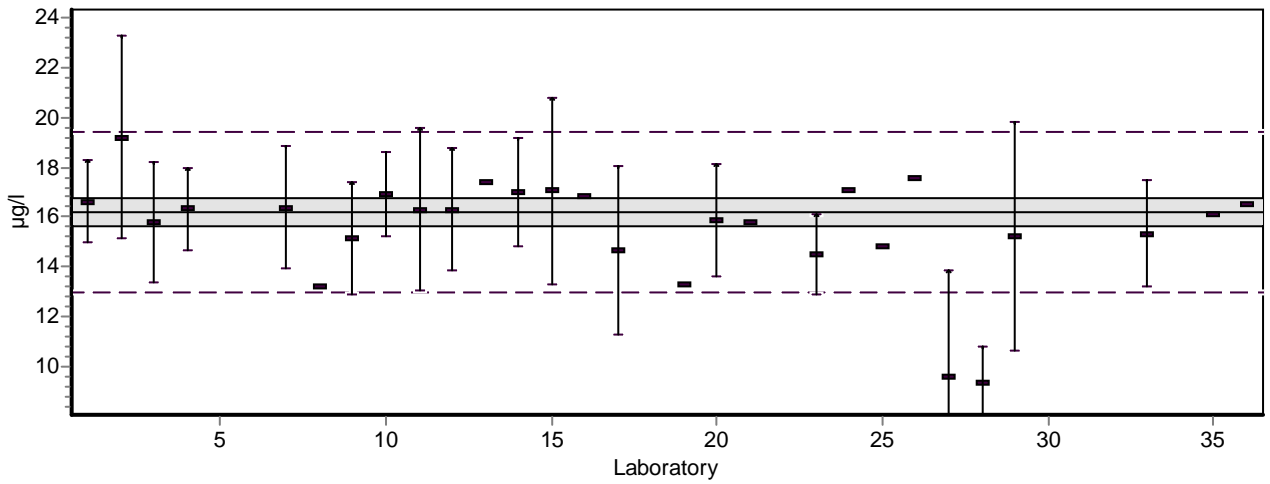




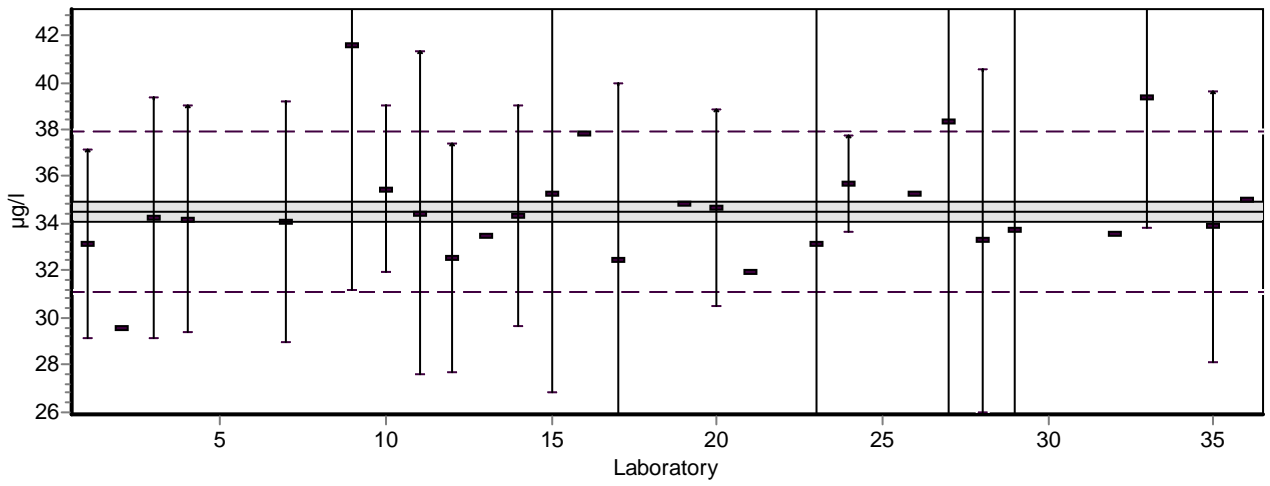




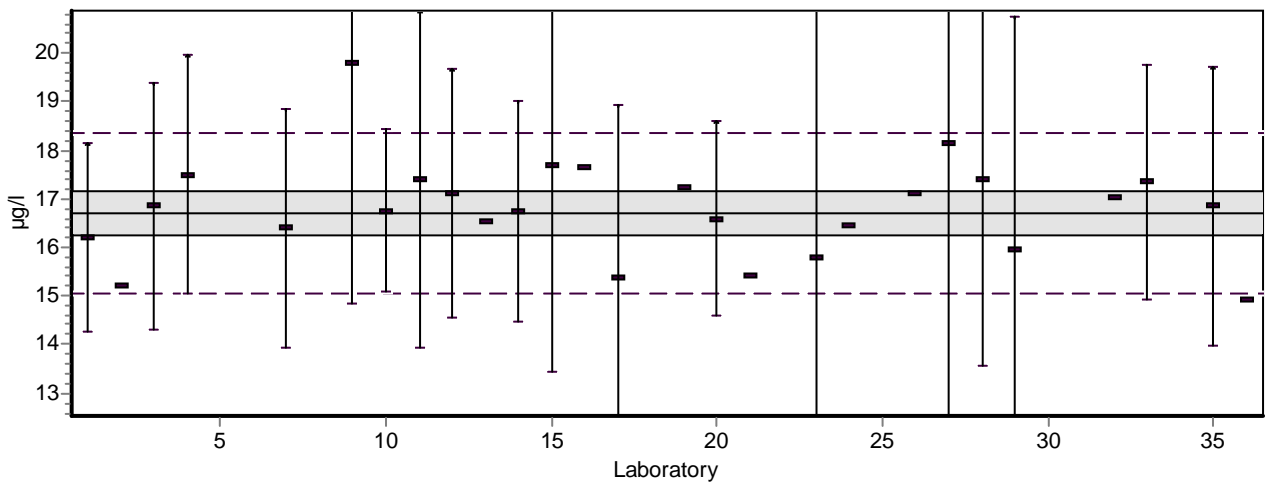
Analyytti (Analyte) **Sb** Näyte (Sample) N2M

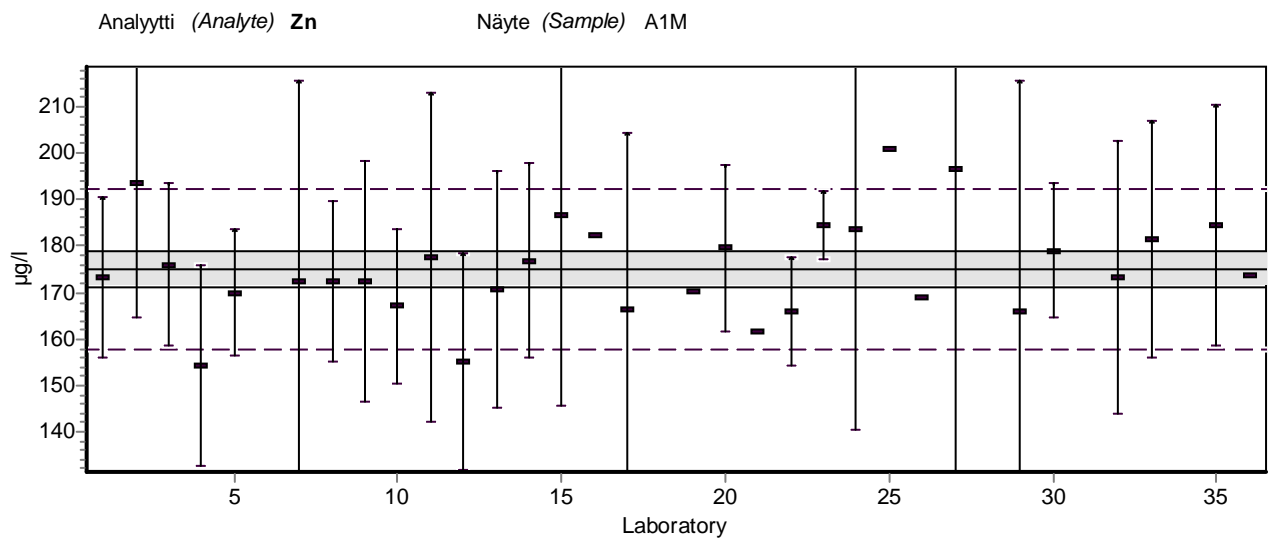
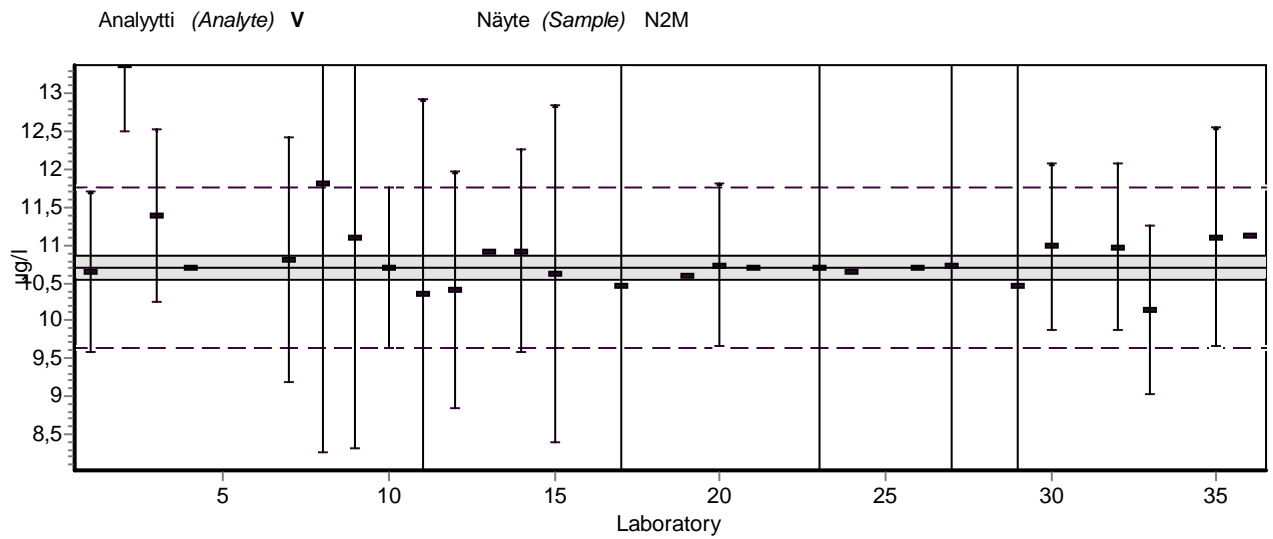
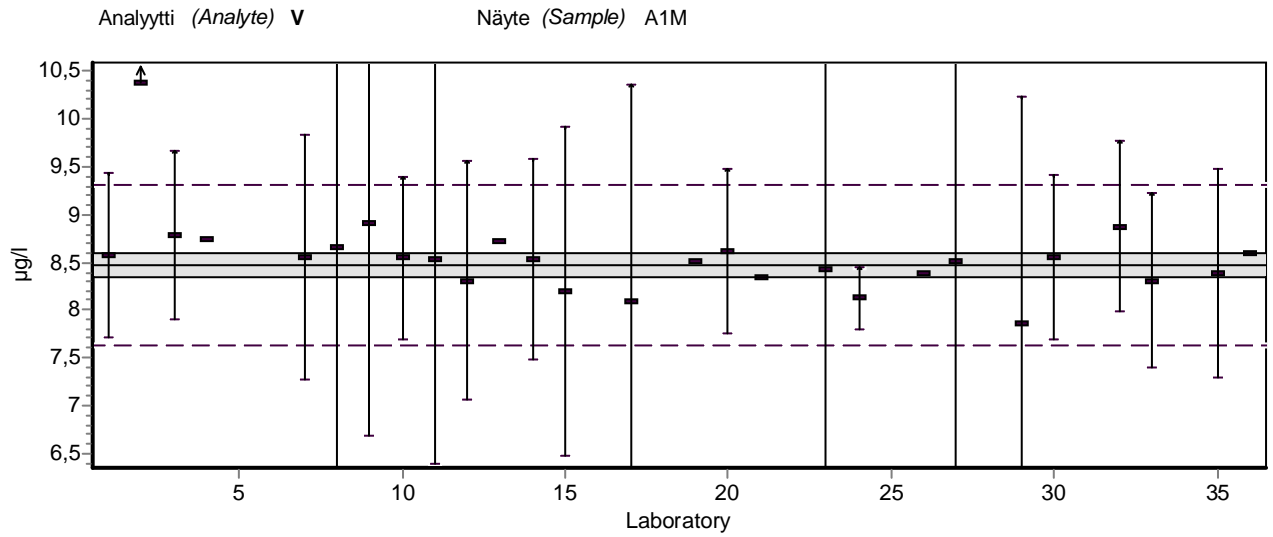


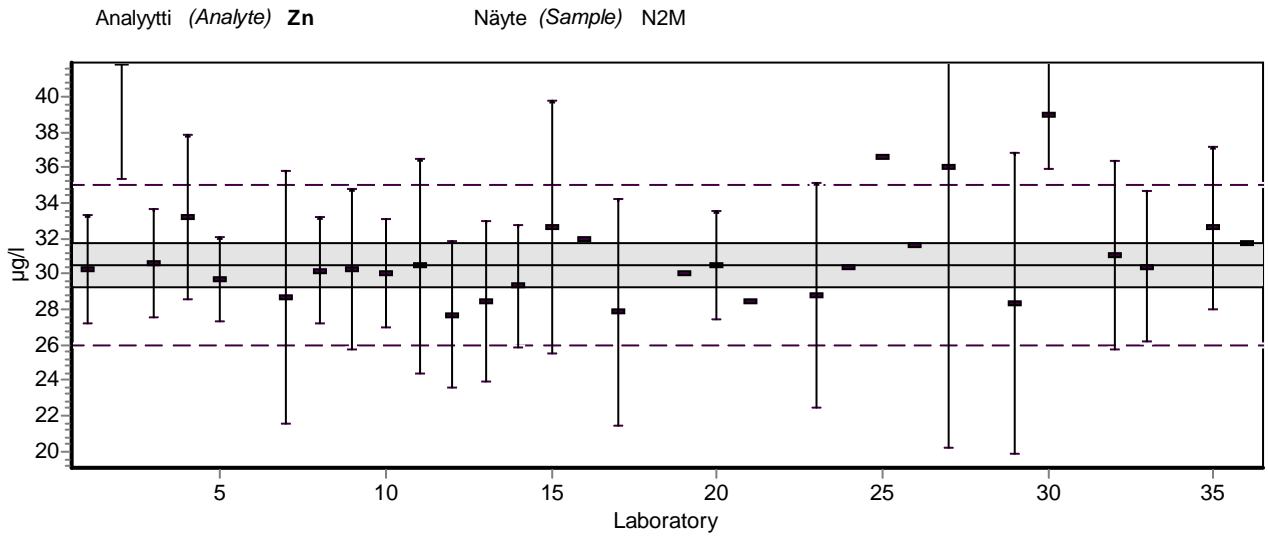
Analyytti (Analyte) **Se** Näyte (Sample) A1M



Analyytti (Analyte) **Se** Näyte (Sample) N2M







LIITE 9. SUMMARY OF THE z SCORES
APPENDIX 9.

Analyte	Sample\Lab	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	
Al	A1M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
	N2M	S	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
As	A1M	S	S	S	S	.	.	S	.	S	S	S	S	S	S	S	S	U	S	.	S	S	U	Q	Q
	N2M	S	u	S	S	.	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	U	S	
B	A1M	S	S	S	S	S	.	.	.	S	S	S	.	.	S	S	U	S	.	.	S	S	.	S	
	N2M	S	S	S	u	S	.	S	S	S	S	S	.	.	S	S	S	S	.	.	S	S	.	S	
Cd	A1M	S	S	S	S	.	.	S	.	S	S	S	S	S	S	S	U	S	S	S	S	S	S	S	S
	N1M	S	S	S	S	.	.	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	u	S
	N2M	S	S	S	S	.	.	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	q	S
Co	A1M	S	U	S	S	.	.	S	S	S	S	S	S	S	S	u	.	S	.	S	S	S	.	S	
	N2M	S	U	S	S	.	.	S	S	S	S	S	S	S	S	S	.	S	.	S	S	S	.	S	
Cr	A1M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	u	S	S	.	S	S	S	S	S	S
	N2M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	S	S	S
Cu	A1M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	u	U	S	.	S	S	S	S	S	S
	N2M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	S	U	S	.	S	S	S	U	S	S
Fe	A1M	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
	N2M	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
Hg	A1Hg
	N1Hg	.	S	S	S	.	.	S	.	S	.	S	U	S	q	S	.	U	S	S	S	S	U	S	
Mn	A1M	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	u	S	
	N2M	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
Mo	A1M	S	Q	S	S	.	.	S	S	S	S	S	S	S	S	S	S	.	S	.	q	S	S	.	S
	N2M	S	S	S	S	.	.	S	S	S	S	S	S	S	S	S	S	.	S	.	q	S	S	.	S
Ni	A1M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	q	S	S
	N1M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
	N2M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Pb	A1M	S	S	S	S	S	S	S	.	S	S	S	u	S	S	S	S	S	S	S	S	u	q	S	S
	N1M	S	S	S	S	S	S	S	.	S	S	S	q	S	S	S	S	S	S	S	S	S	S	S	S
	N2M	S	S	S	S	S	S	q	S	S	S	S	q	S	S	S	S	S	S	S	S	S	S	S	S
Sb	A1M	S	U	S	S	.	.	S	S	S	S	S	S	S	q	S	S	S	.	S	S	S	.	S	
	N2M	S	S	S	S	.	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
Se	A1M	S	q	S	S	.	.	S	.	U	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
	N2M	S	S	S	S	.	.	S	.	U	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
V	A1M	S	U	S	S	.	.	S	S	S	S	S	S	S	S	S	.	S	.	S	S	S	.	S	
	N2M	S	U	S	S	.	.	S	Q	S	S	S	S	S	S	S	.	S	.	S	S	S	.	S	
Zn	A1M	S	Q	S	q	S	.	S	S	S	S	S	q	S	S	S	S	S	.	S	S	S	S	S	S
	N2M	S	U	S	S	S	.	S	S	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	
% Accredited		100	50	100	94	100	100	100	92	94	100	100	88	100	94	89	86	97	100	94	97	94	56	97	
		yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
Analyte	Sample\Lab	24	25	26	27	28	29	30	31	32	33	34	35	36	%										
Al	A1M	S	q	.	S	.	S	S	.	S	S	.	S	S	93										
	N2M	S	q	.	S	.	S	S	.	S	S	.	S	S	97										
As	A1M	S	S	S	S	S	S	.	S	S	.	S	S	86											
	N2M	S	S	S	S	S	S	.	S	S	.	S	S	93											
B	A1M	S	.	S	S	.	S	U	.	S	.	S	S	91											
	N2M	S	.	S	S	.	S	S	.	S	.	S	S	96											
Cd	A1M	S	S	S	S	S	S	S	S	S	S	S	S	S	97										
	N1M	S	S	S	S	S	S	S	S	S	S	S	S	S	97										
	N2M	S	S	S	S	S	S	S	S	S	S	S	S	S	97										
Co	A1M	S	S	S	S	S	S	S	.	S	S	.	S	S	93										
	N2M	S	S	S	S	S	S	S	.	S	S	.	S	S	97										
Cr	A1M	S	S	S	S	S	S	S	.	S	S	.	S	S	94										
	N2M	S	S	S	S	S	S	S	.	S	S	.	S	S	97										
Cu	A1M	S	S	S	S	S	S	S	.	S	S	.	S	S	91										
	N2M	S	S	S	Q	S	S	S	.	S	S	.	S	S	88										
Fe	A1M	S	Q	S	S	.	S	S	.	S	S	.	S	U	93										
	N2M	S	U	S	S	.	S	S	.	S	S	.	S	U	93										
Hg	A1Hg
	N1Hg	.	S	q	S	.	Q	S	.	S	.	Q	S	S	74										
Mn	A1M	S	S	S	S	.	S	S	.	S	S	.	S	S	97										
	N2M	S	S	S	S	.	S	S	.	S	S	.	S	S	100										
Mo	A1M	S	S	S	.	.	S	S	.	S	S	.	S	S	93										
	N2M	S	S	S	.	.	S	S	.	S	S	.	S	S	96										
Ni	A1M	S	S	S	S	S	S	S	S	S	S	S	S	S	94										
	N1M	q	S	S	S	S	S	S	S	S	S	S	S	S	94										
	N2M	S	S	S	Q	S	S	S	S	S	S	S	S	S	94										
Pb	A1M	S	S	S	S	S	S	S	S	S	S	S	u	89											
	N1M	S	S	S	S	S	S	S	S	S	S	S	S	97											
	N2M	S	S	S	S	S	S	S	S	S	S	S	S	97											

Analyte	Sample/Lab	24	25	26	27	28	29	30	31	32	33	34	35	36	%
Sb	A1M	S	S	S	u	u	S	.	.	.	S	.	S	S	86
	N2M	S	S	S	u	u	S	.	.	.	S	.	S	S	93
Se	A1M	S	.	S	Q	S	S	.	.	S	Q	.	S	S	85
	N2M	S	.	S	S	S	S	.	.	S	S	.	S	q	93
V	A1M	S	.	S	S	.	S	S	.	S	S	.	S	S	96
	N2M	S	.	S	S	.	S	S	.	S	S	.	S	S	93
Zn	A1M	S	Q	S	Q	.	S	S	.	S	S	.	S	S	84
	N2M	S	Q	S	Q	.	S	U	.	S	S	.	S	S	87
%		97	80	97	79	91	100	90	100	100	97	90	100	89	
Accredited		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: 93

In accredited: 93

In non-accredited: 92

ANALYTICAL METHODS

Hg/Pretreatment/Measurement

Lab ¹⁾	Sample	Oxidant in pretreatment	Temperature and equipment in oxidation/digestion	Measurement
2	A1Hg, N1Hg	No pretreatment		AFS
3	A1Hg, N1Hg	KBr/KBrO ₃		CV-AFS
12	A1Hg, N1Hg	KBr/KBrO ₃	Cold oxydation digestion	CV-AFS
17	A1Hg, N1Hg	K ₂ Cr ₂ O ₇	PSAnalytical	CV-AFS
20	A1Hg, N1Hg	HNO ₃ + H ₂ O ₂	215°C for 25 min (microwave Mars Xpress)	ICP-MS
33	A1Hg, N1Hg	BrCl	No digestion	CV-AFS
34	A1Hg, N1Hg	KBr/KBrO ₃	Room temperature	CV-AAS
35	A1Hg, N1Hg	KBr/KBrO ₃	Room temperature	CV-AFS

¹⁾Laboratories 4, 7, 9, 11, 13, 14, 15, 18, 19, 21, 22, 23, 25, 26, 27, 28, 30, 31 and 36 didn't report the pretreatment method.

Metals/ Measurement from the water samples

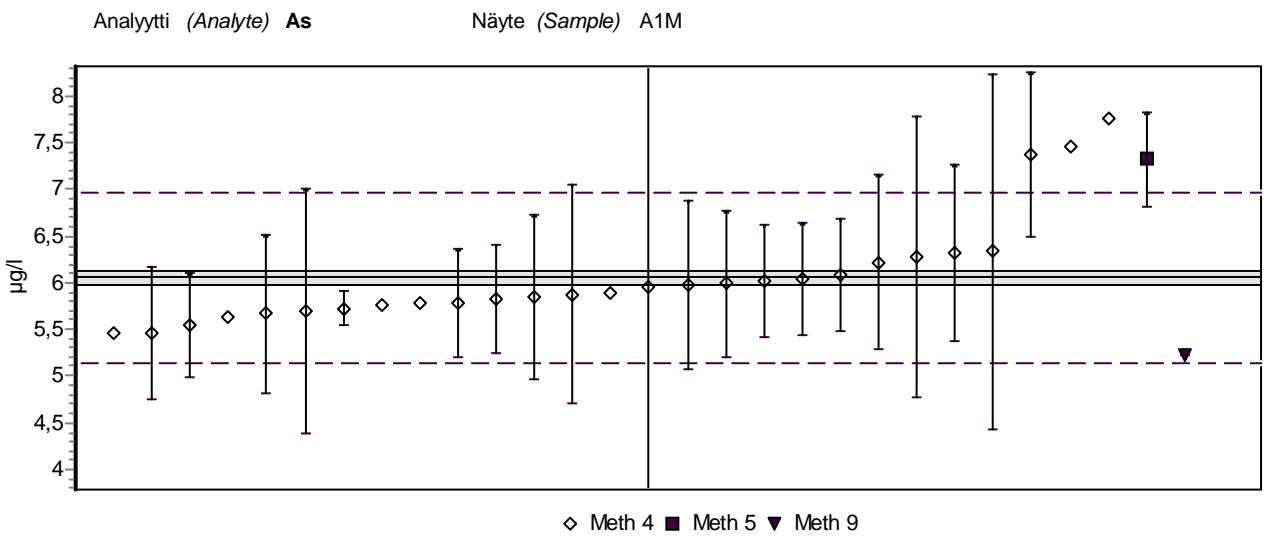
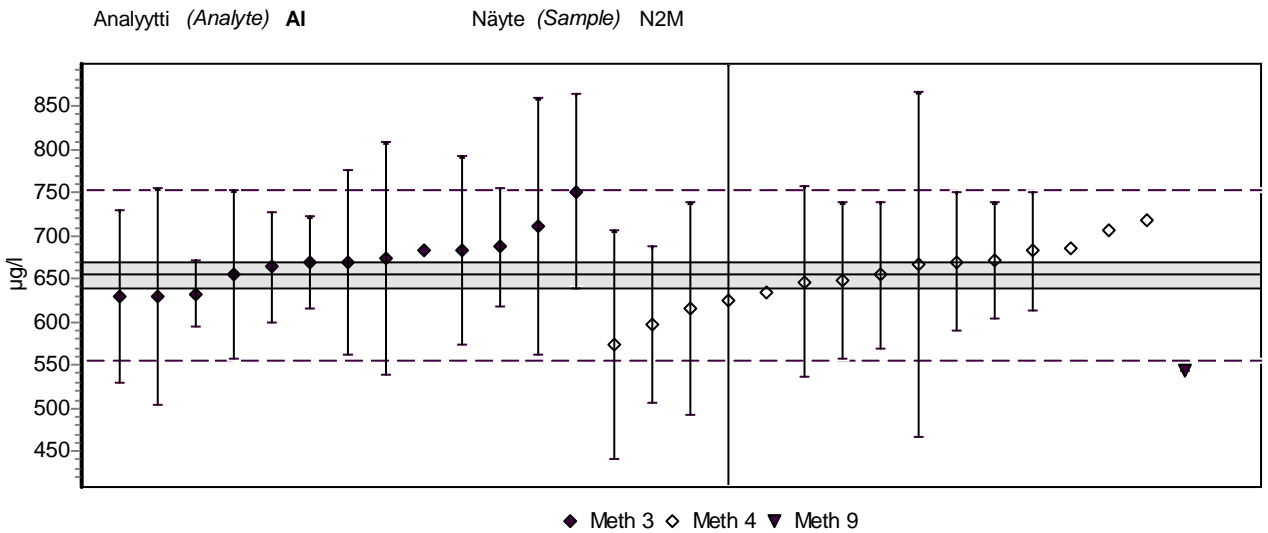
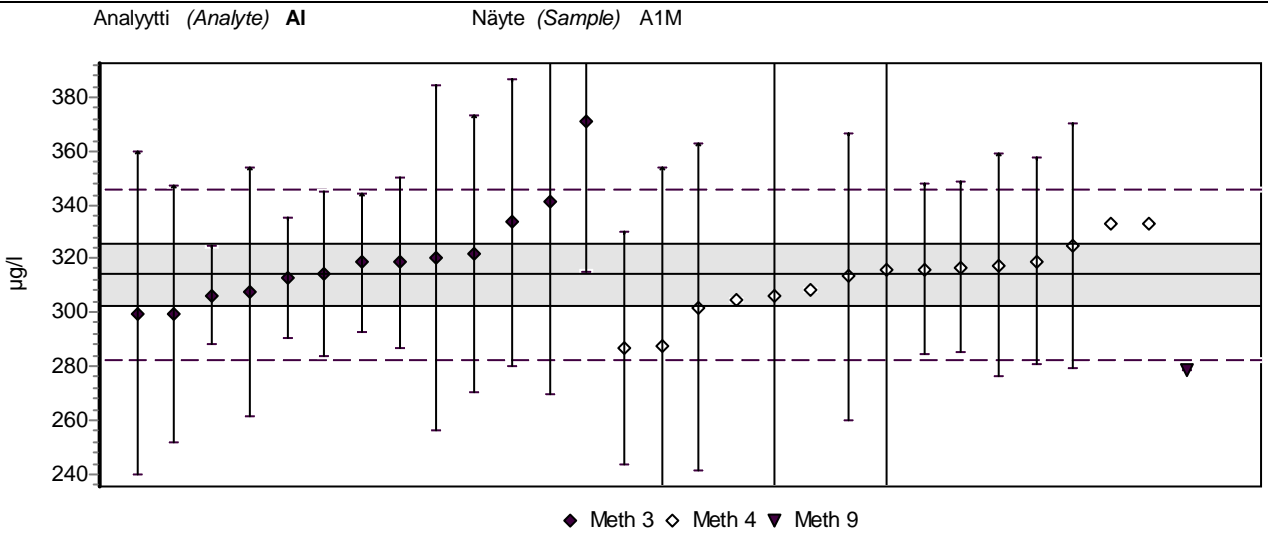
Analyte	Code	Method
Al, As, B, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, V, Zn	1	FAAS
	2	GAAS
	3	ICP-OES
	4	ICP-MS
	5	Hydride generation/AAS
	6	Hydride generation/ICP-OES
	7	Hydride generation/ICP-MS
	8	ID-ICP-MS
	9	Other method, please specify

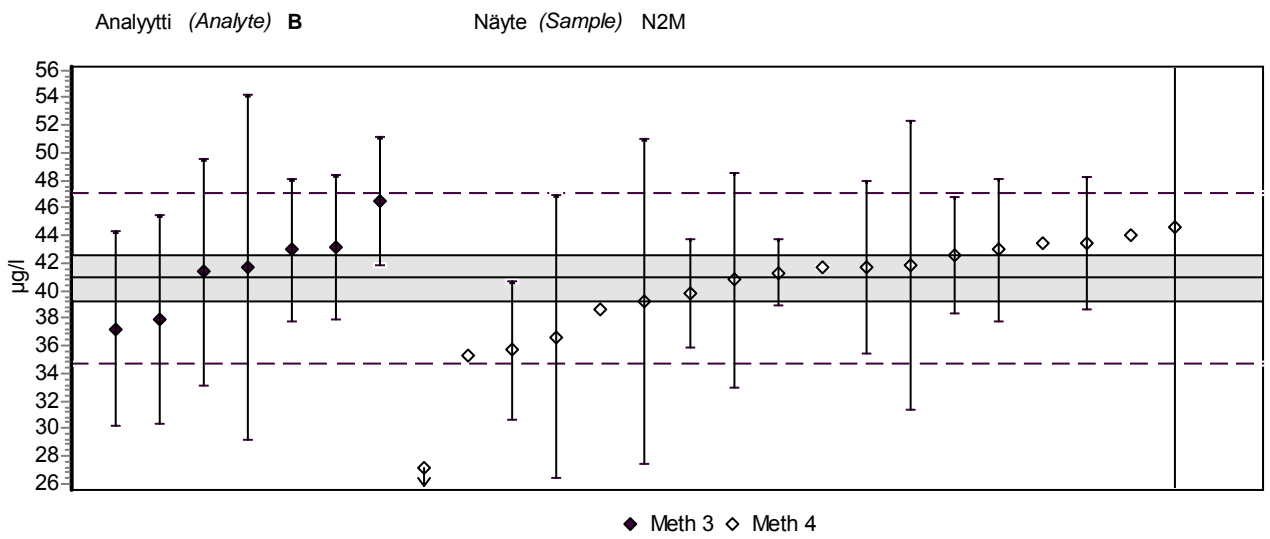
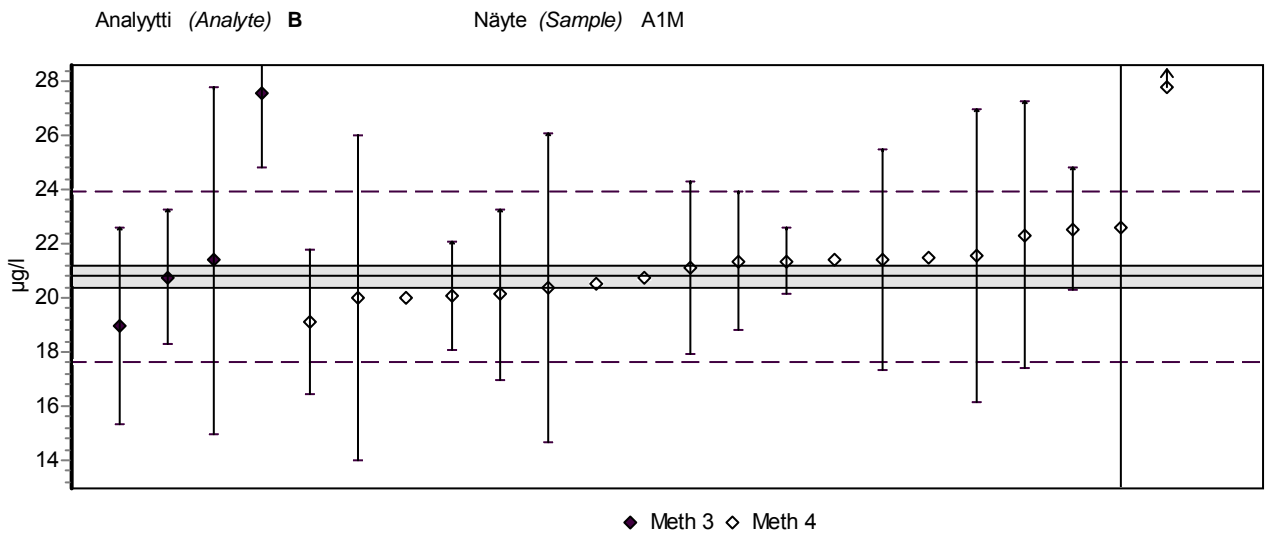
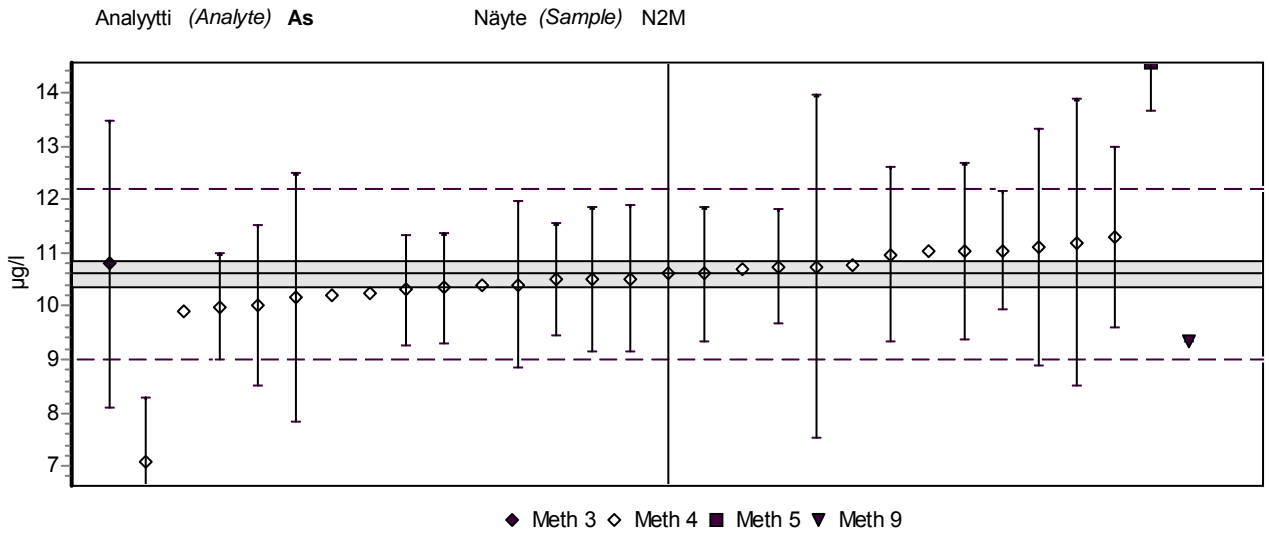
Hg/ Measurement from the water samples

Analyte	Code	Method
Hg	1	CV-AAS
	2	CV-AFS
	3	Hydride generation/AAS
	4	Hydride generation/ICP-OES
	5	Hydride generation/ICP-MS
	6	ICP-OES
	7	ICP-MS
	8	ID-ICP-MS
	9	Oxidation with O ₂ + AAS
	10	Other method, please specify

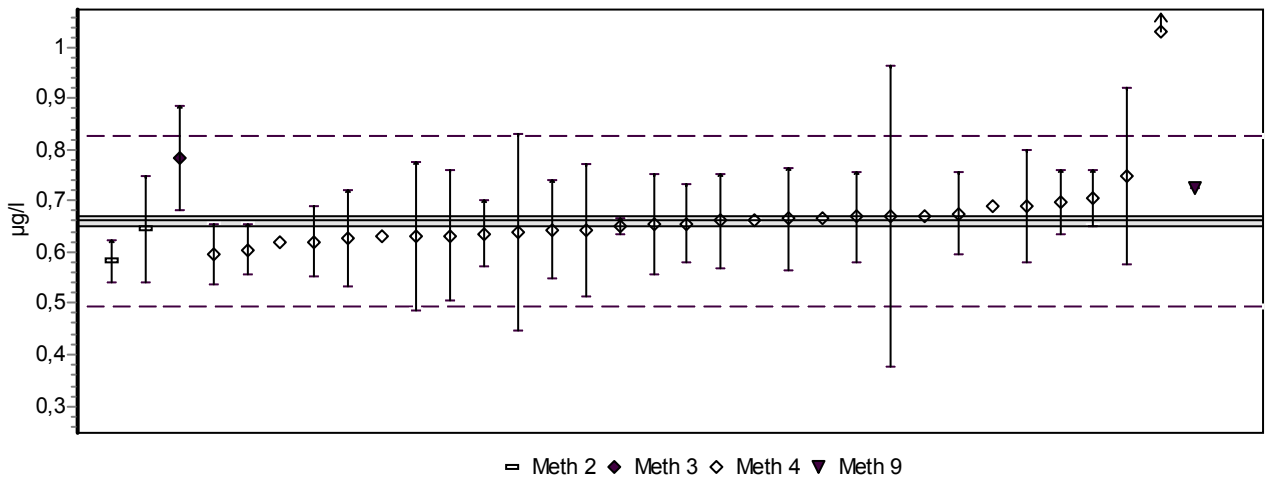
LIITE 10.2. RESULTS GROUPED ACCORDING TO THE METHODS

APPENDIX 10.2. Method code - see the Appendix 10.1

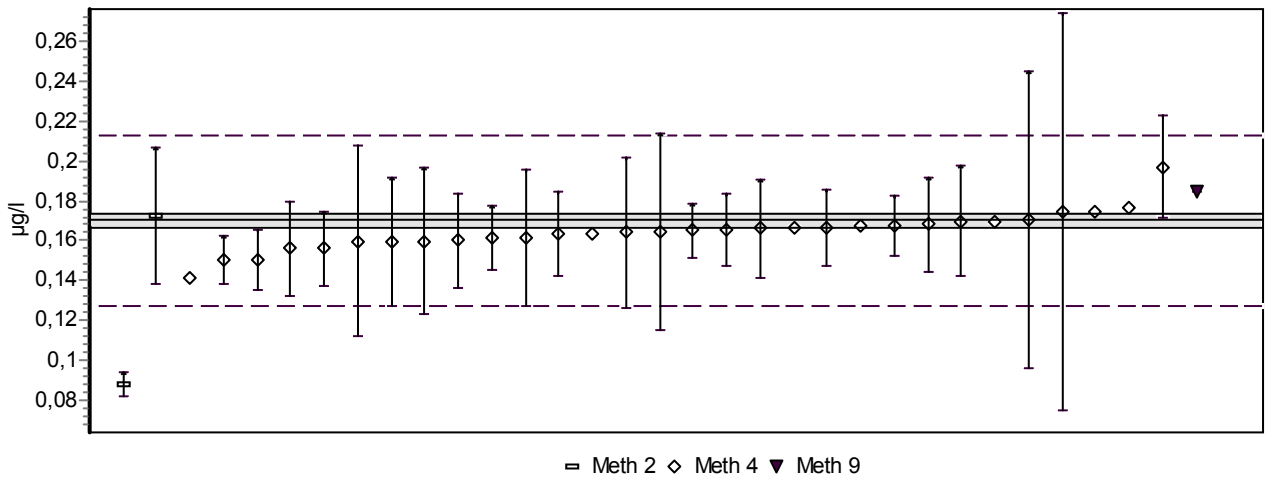




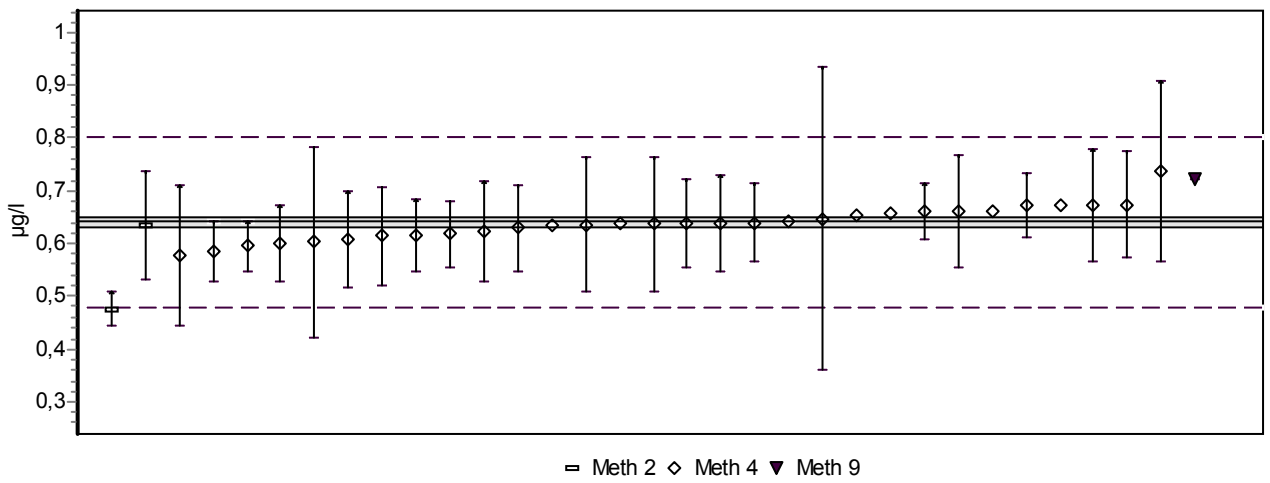
Analyytti (Analyte) Cd Näyte (Sample) A1M

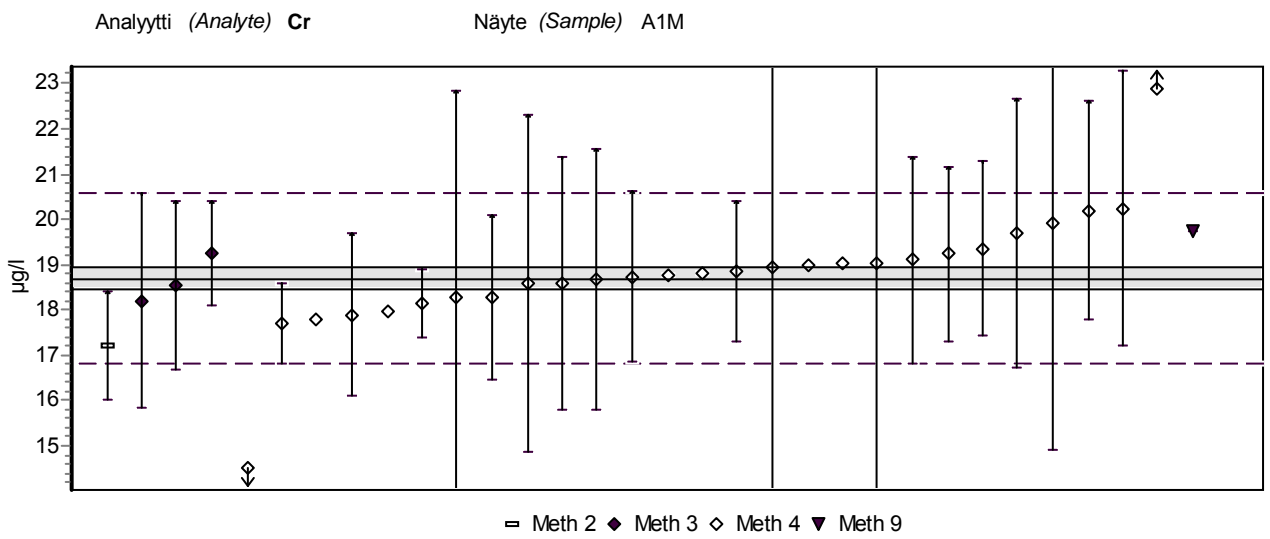
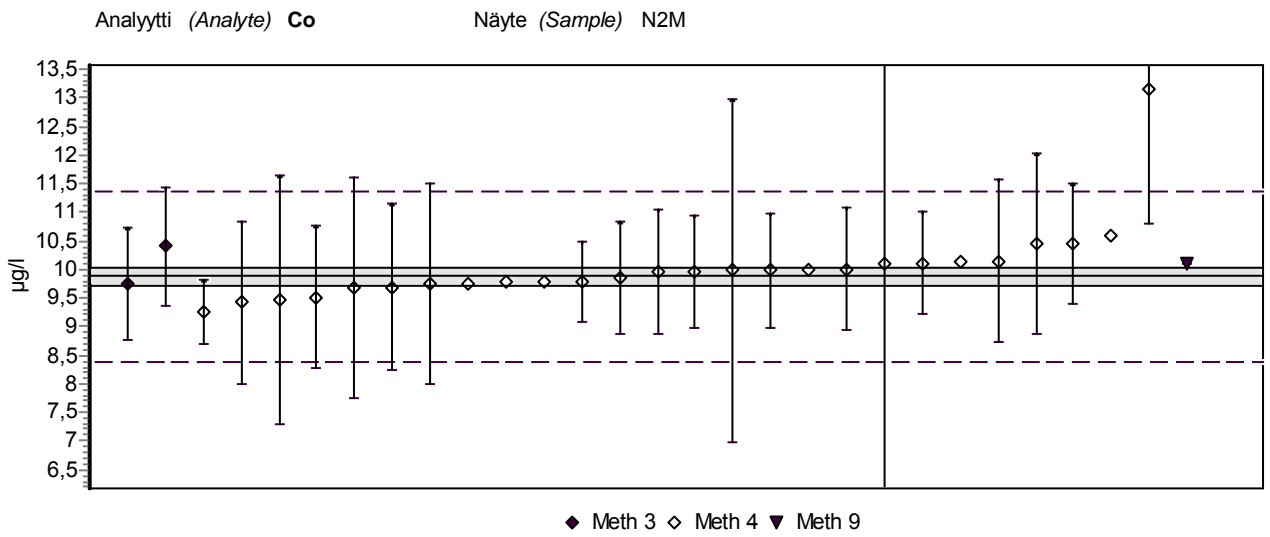
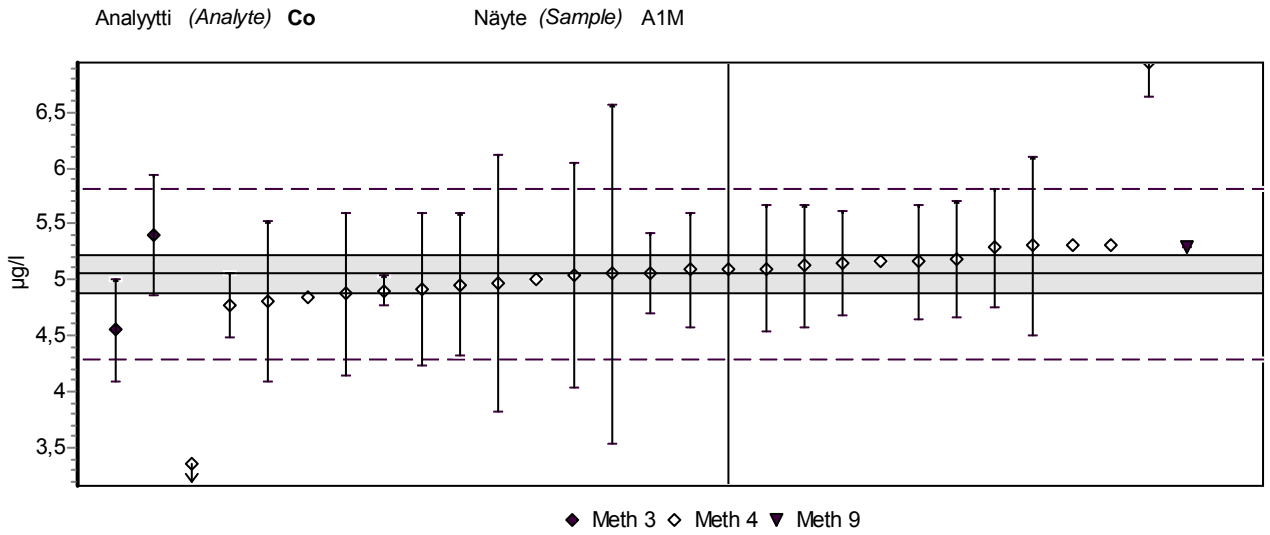


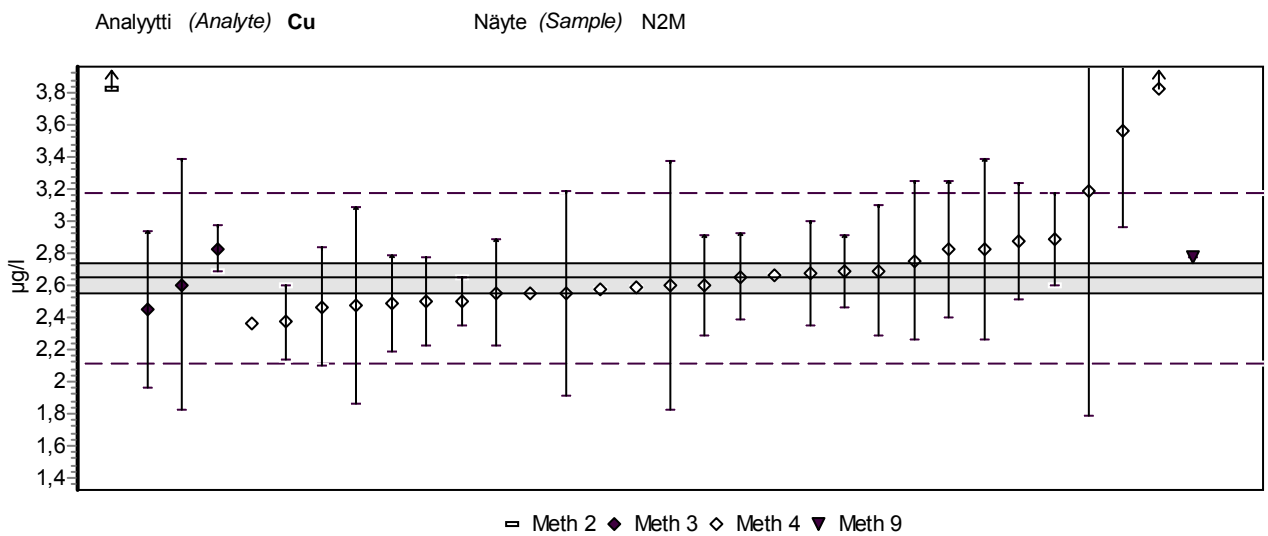
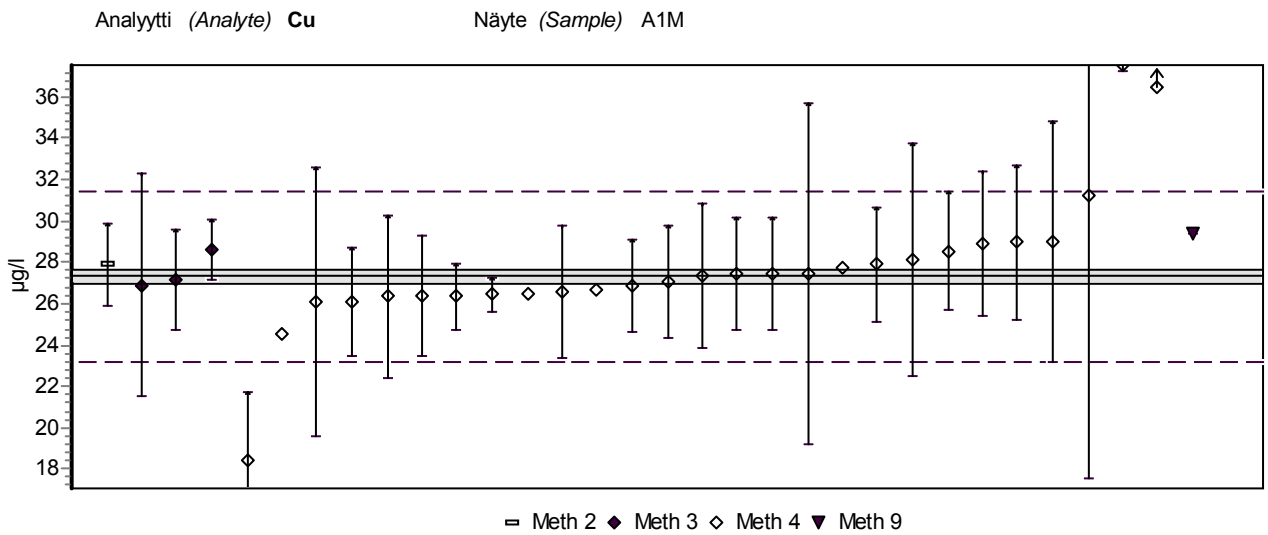
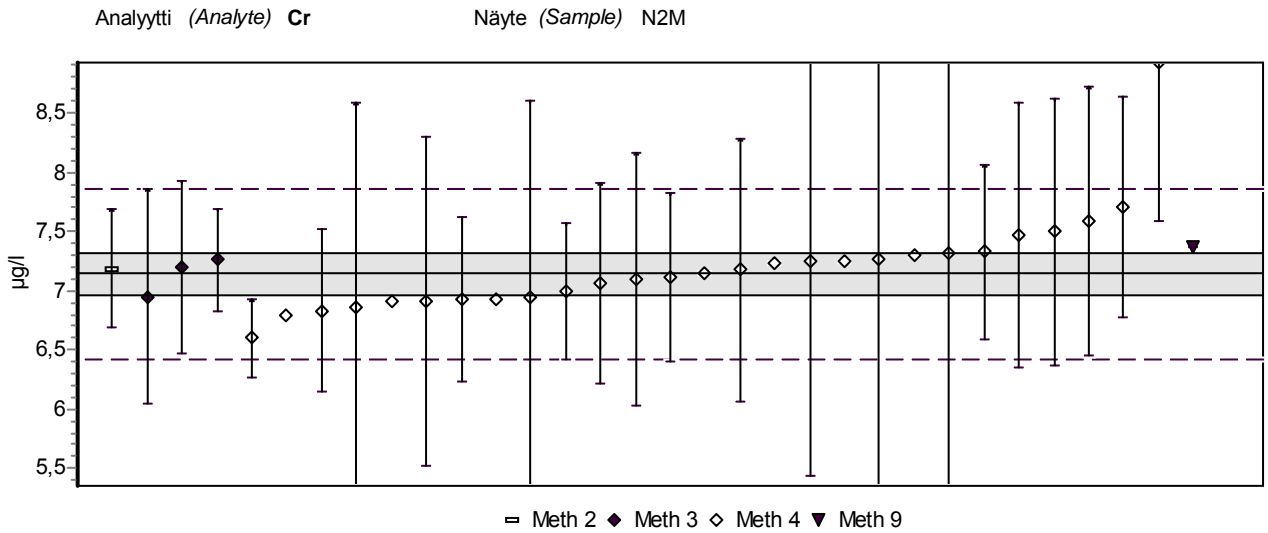
Analyytti (Analyte) Cd Näyte (Sample) N1M

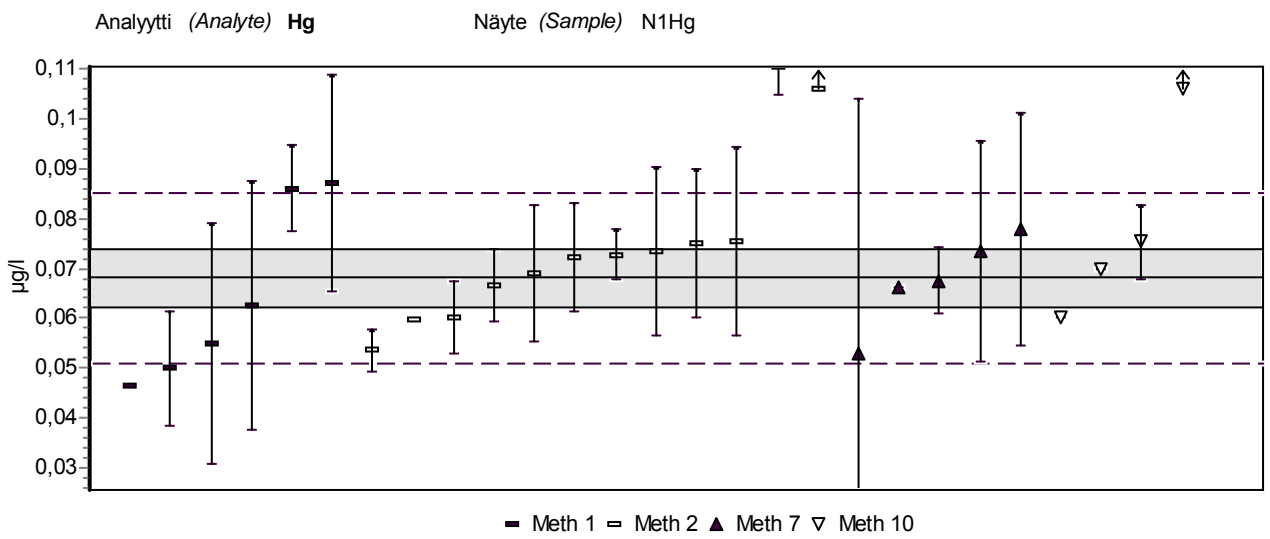
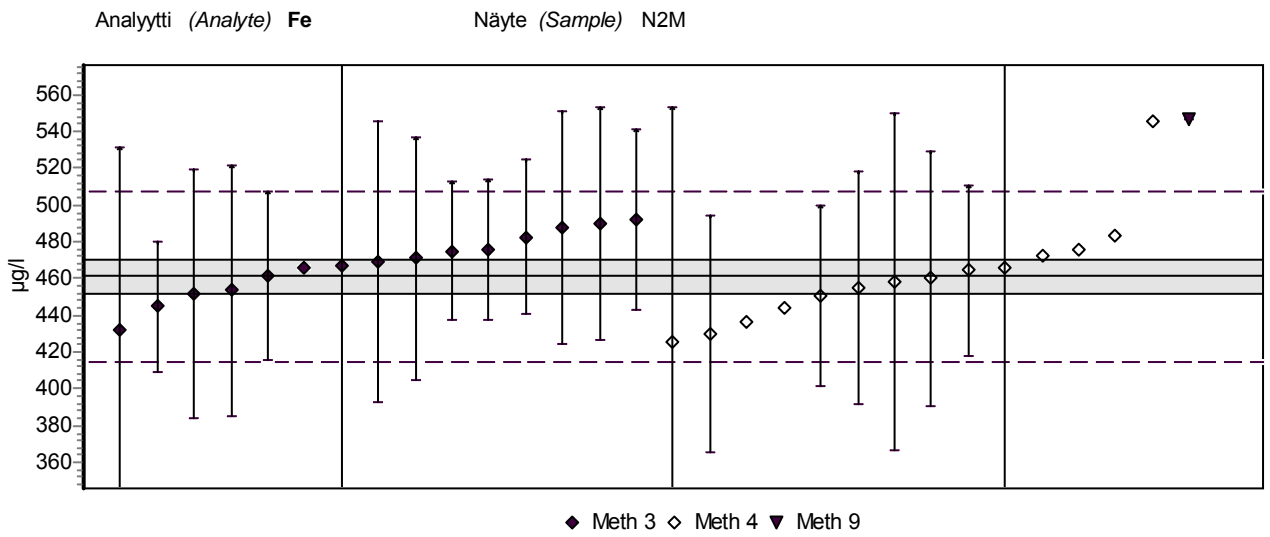
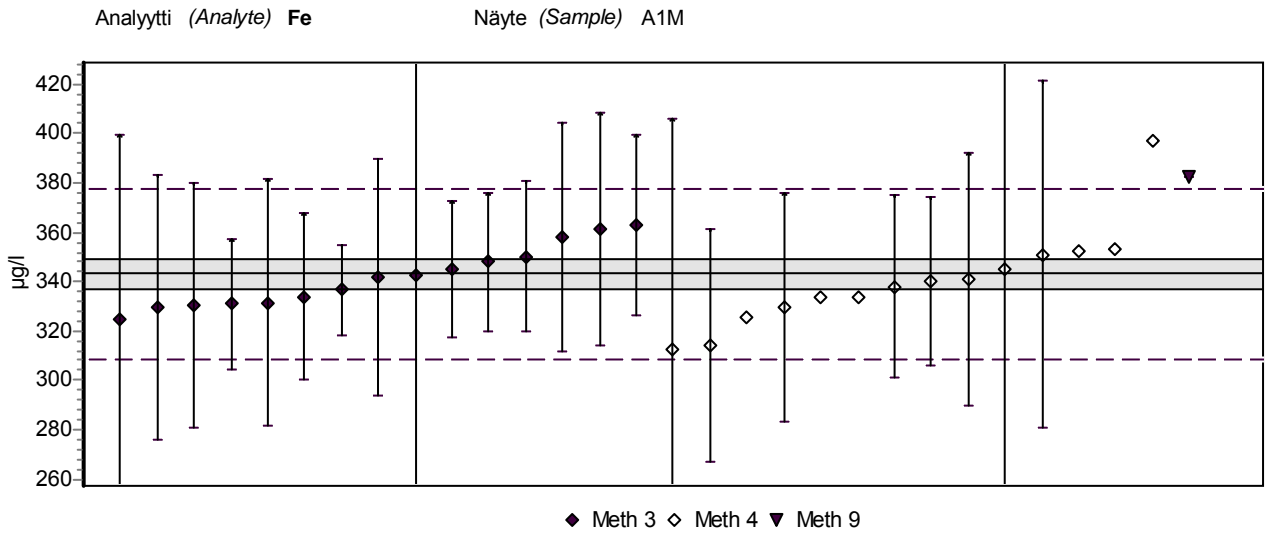


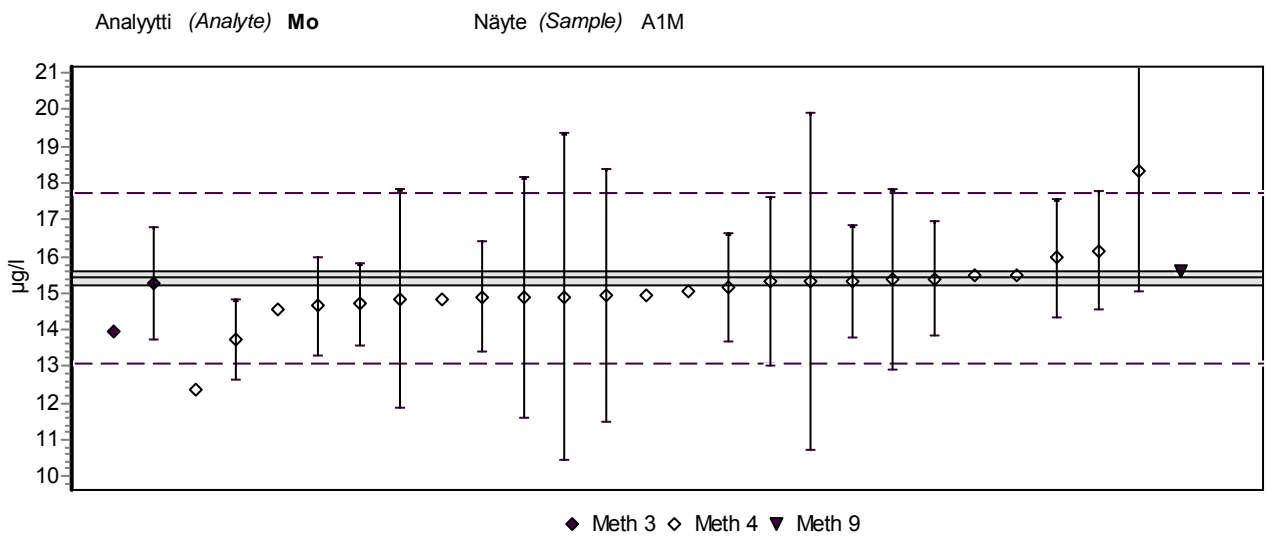
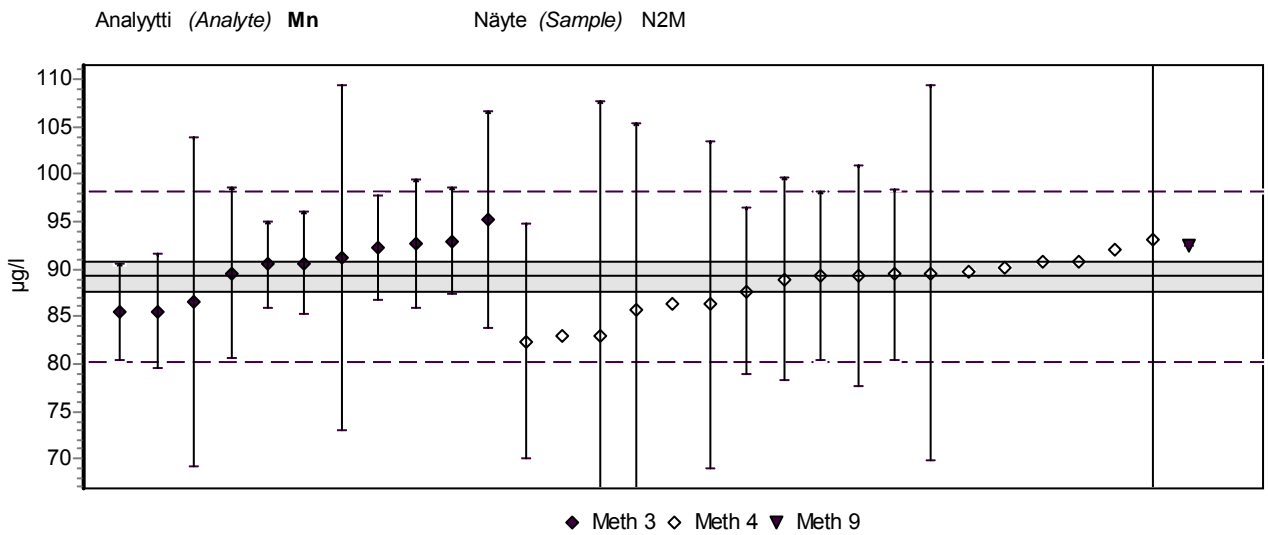
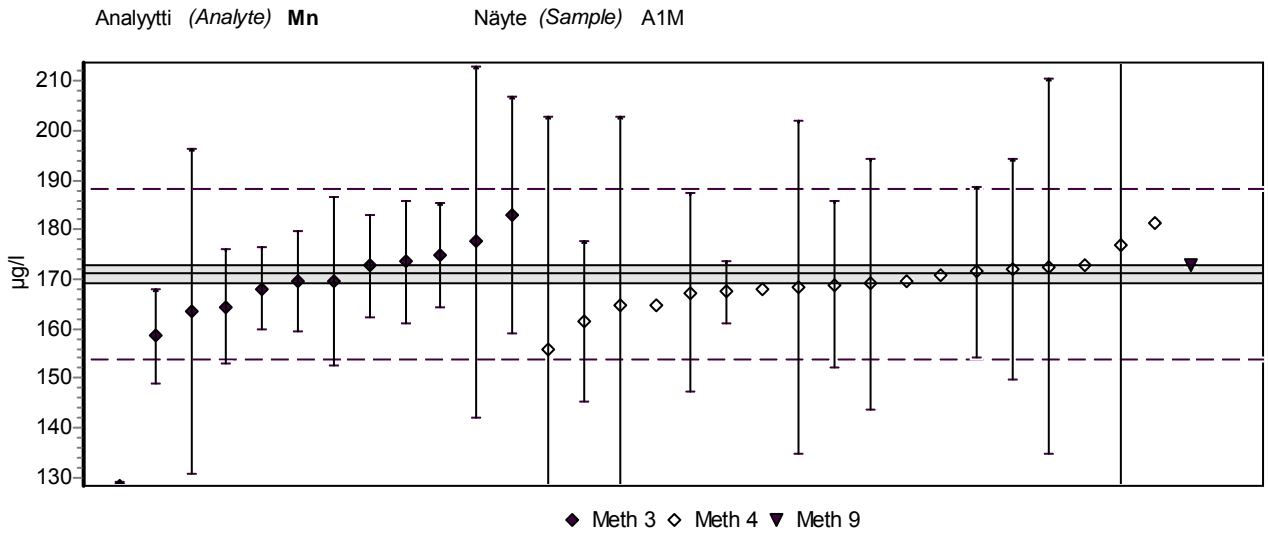
Analyytti (Analyte) Cd Näyte (Sample) N2M

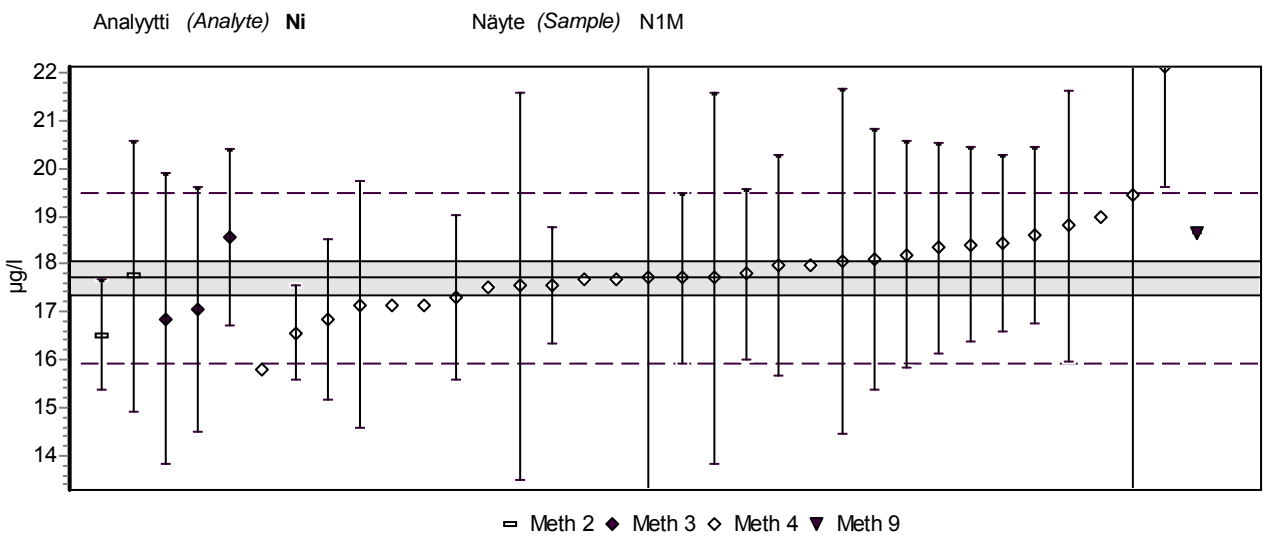
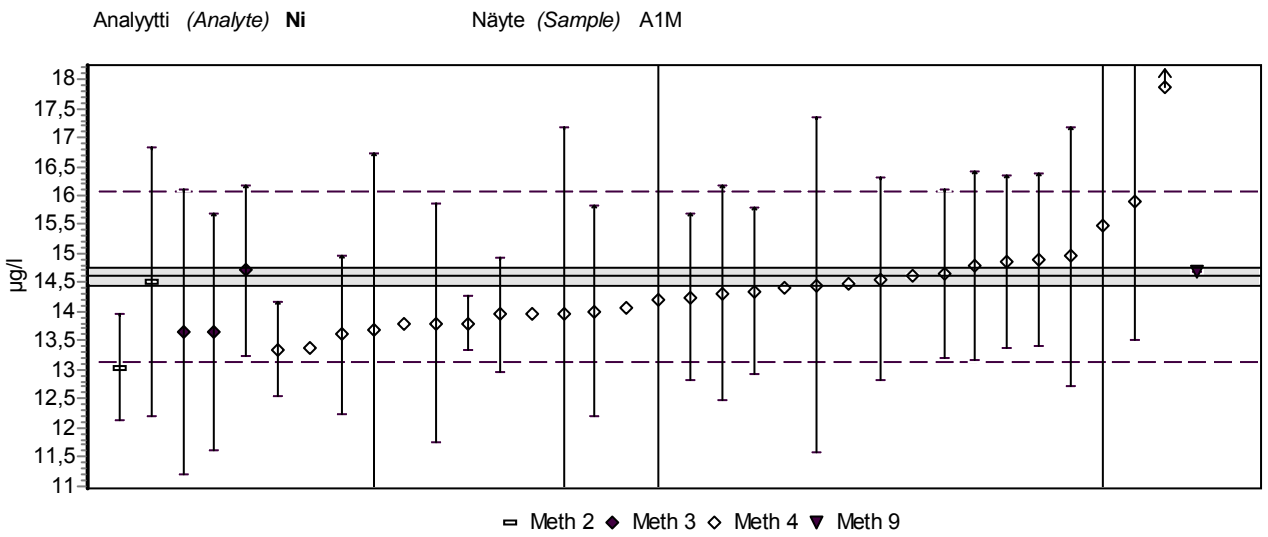
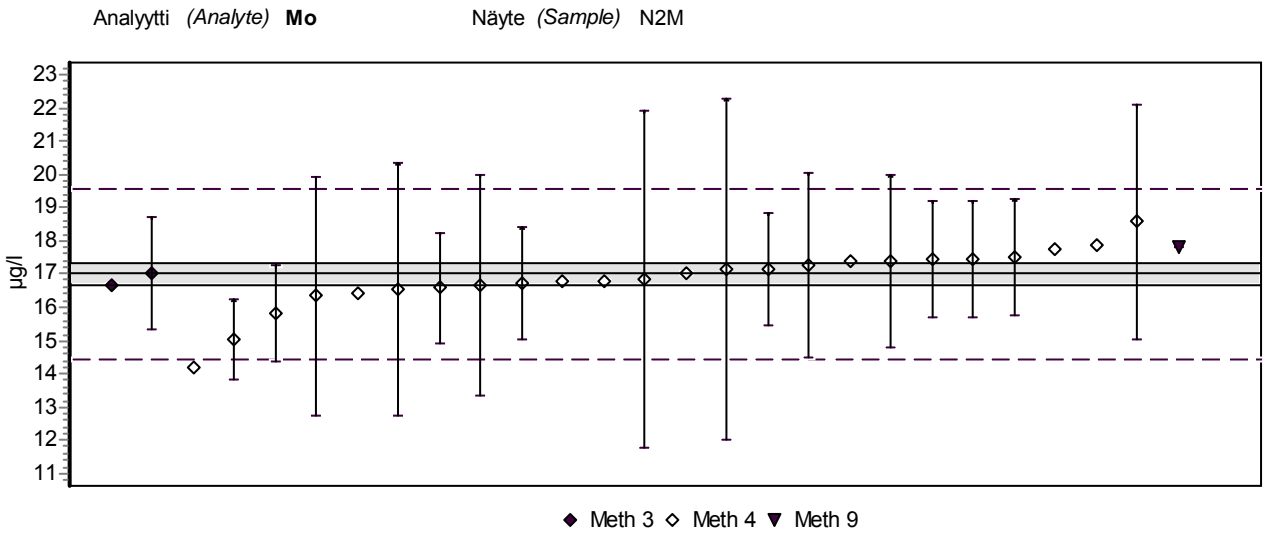






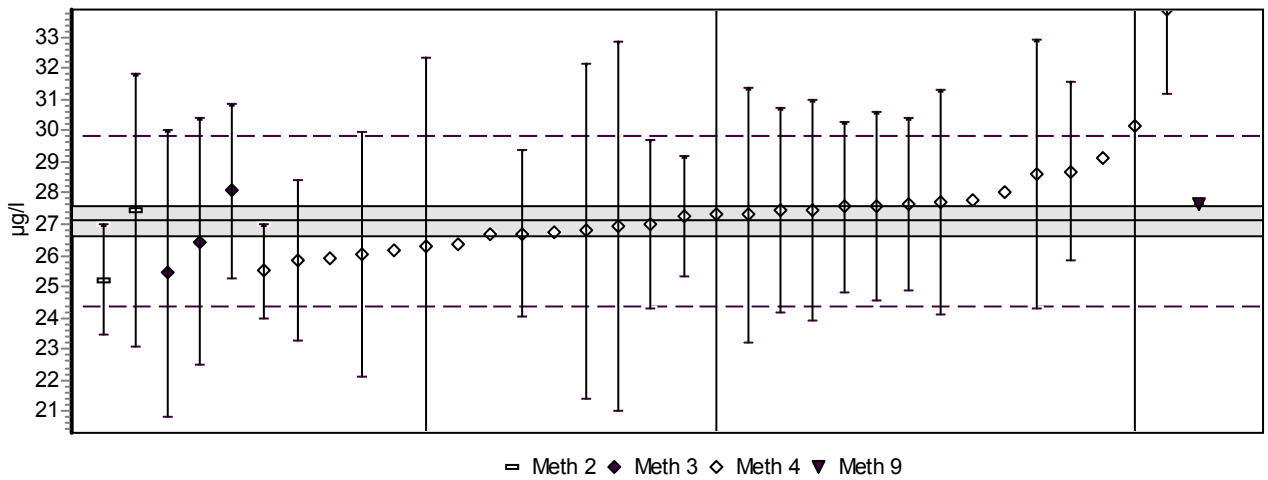






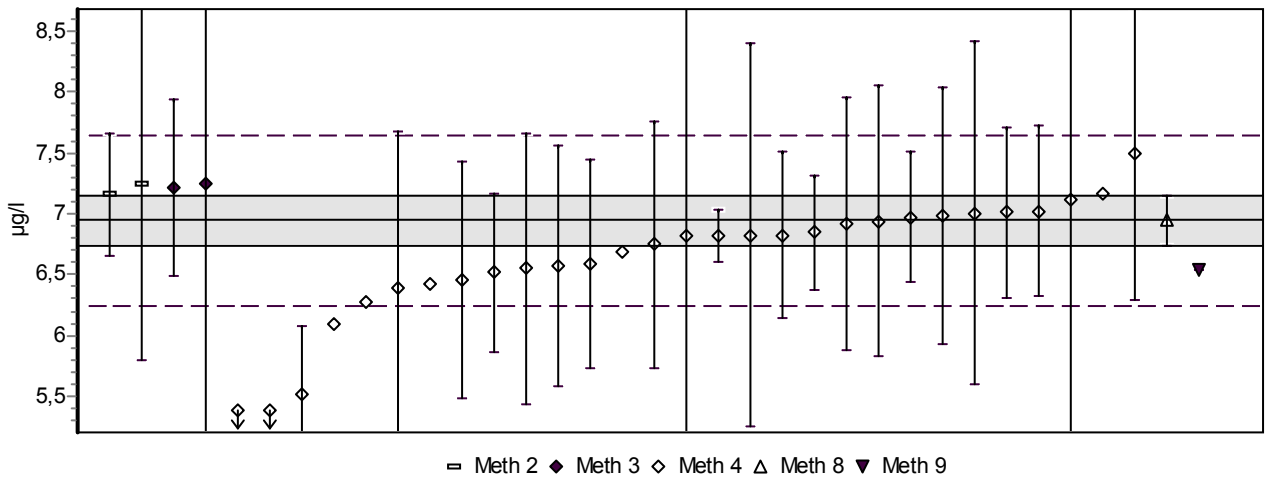
Analyytti (Analyte) Ni

Näyte (Sample) N2M



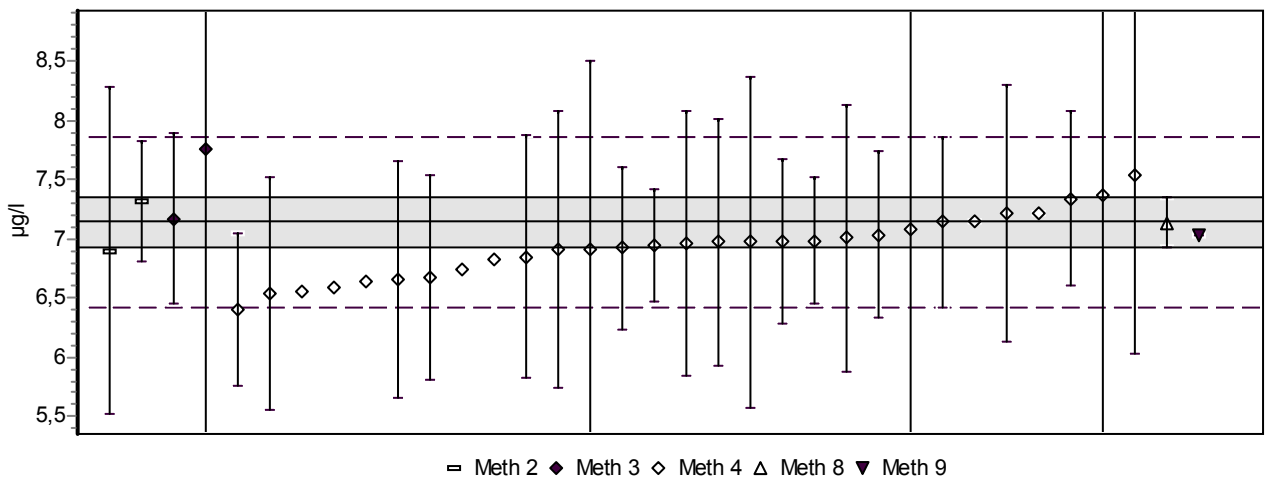
Analyytti (Analyte) Pb

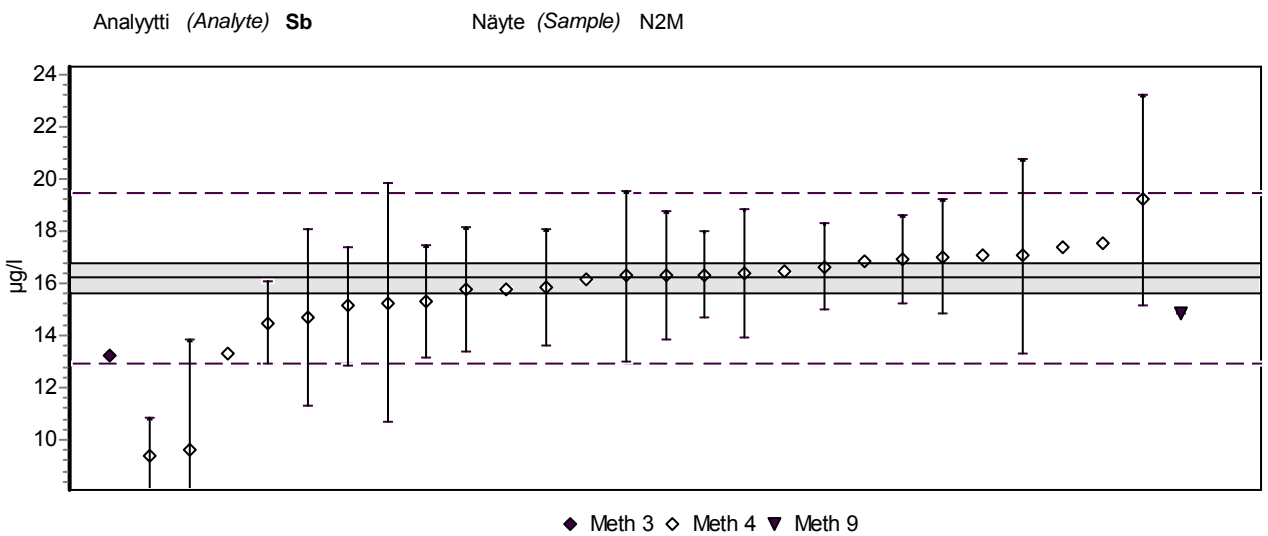
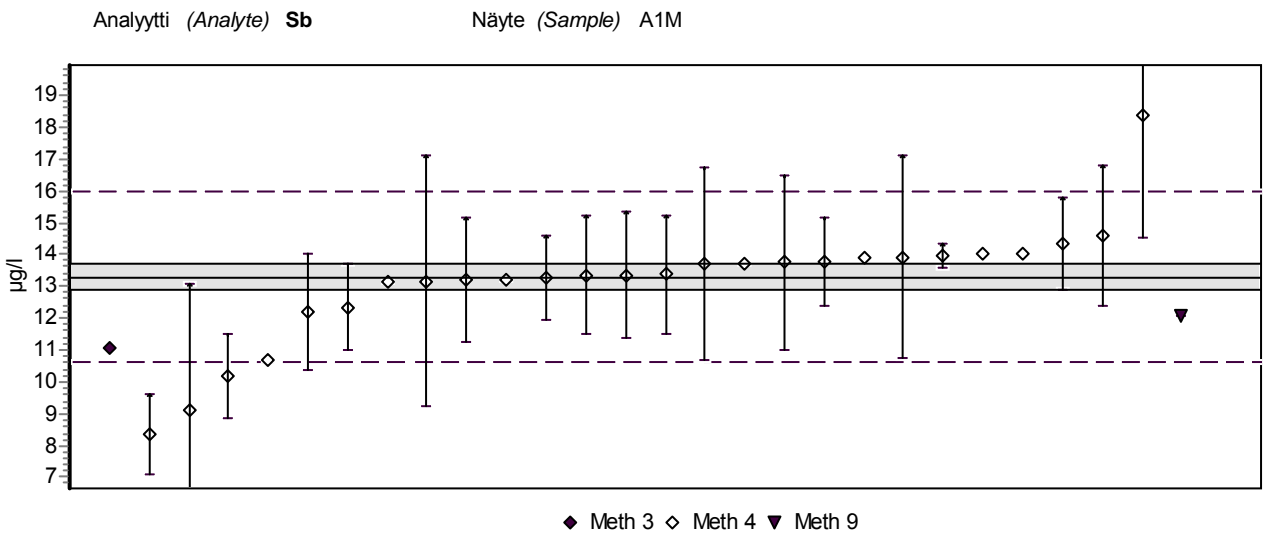
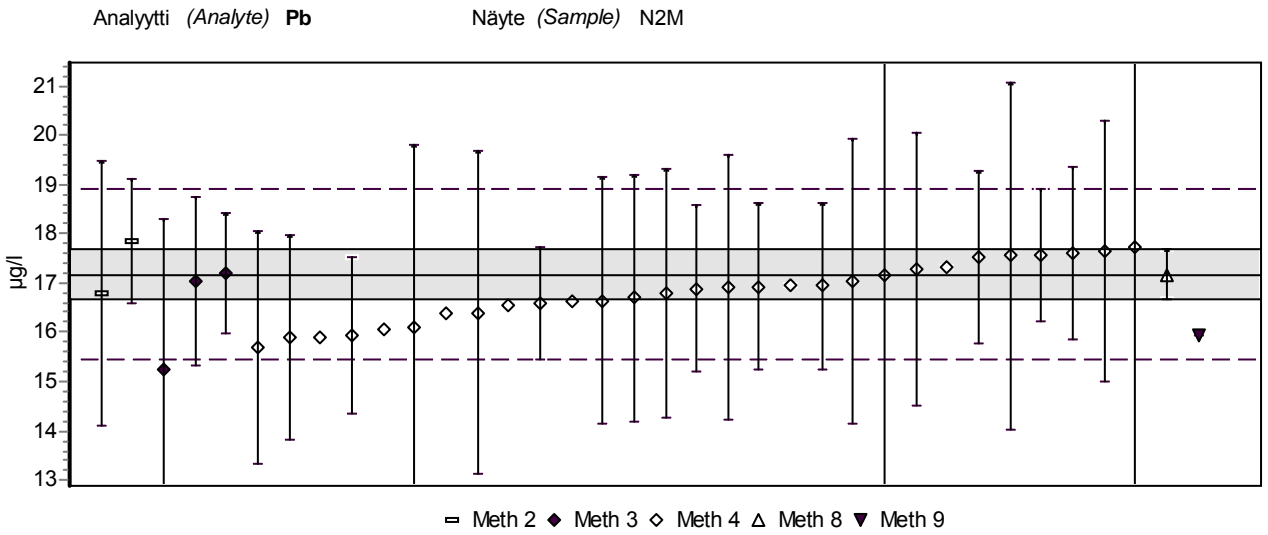
Näyte (Sample) A1M

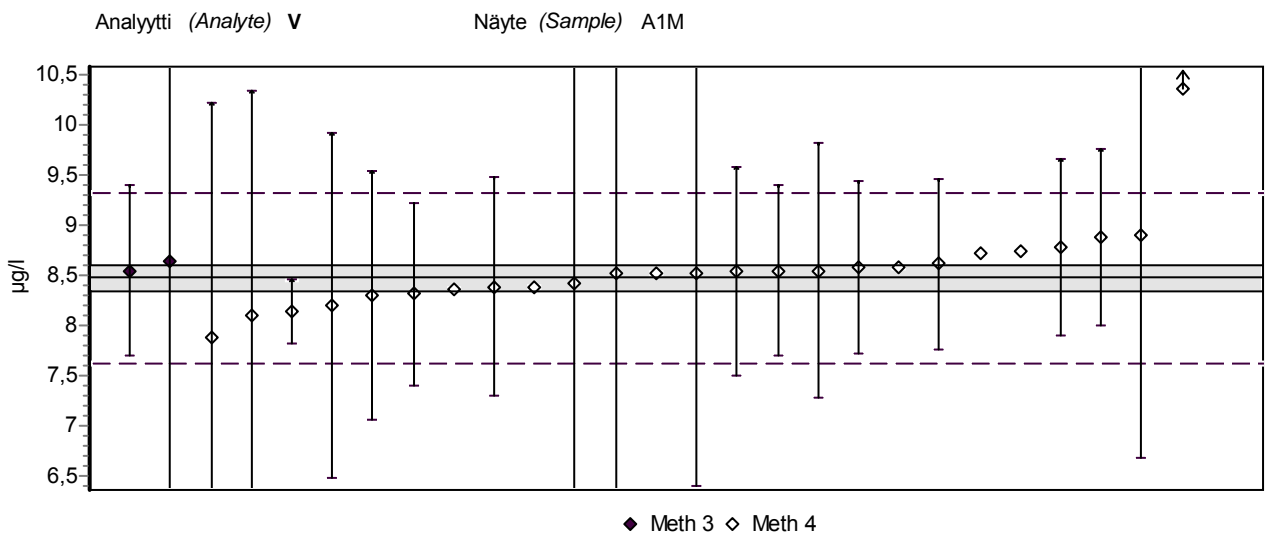
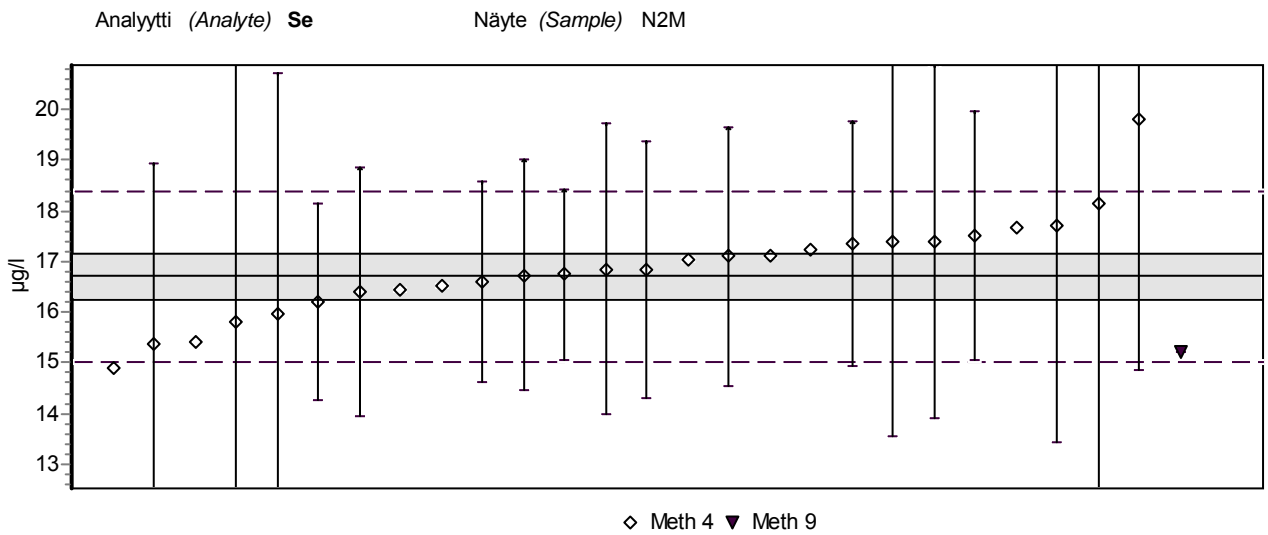
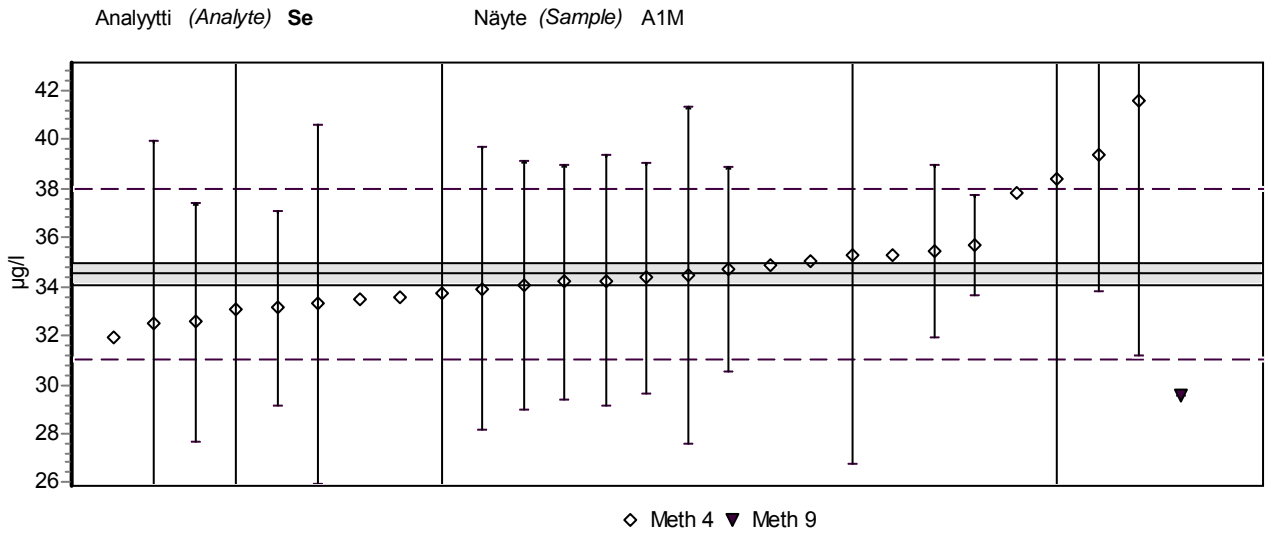


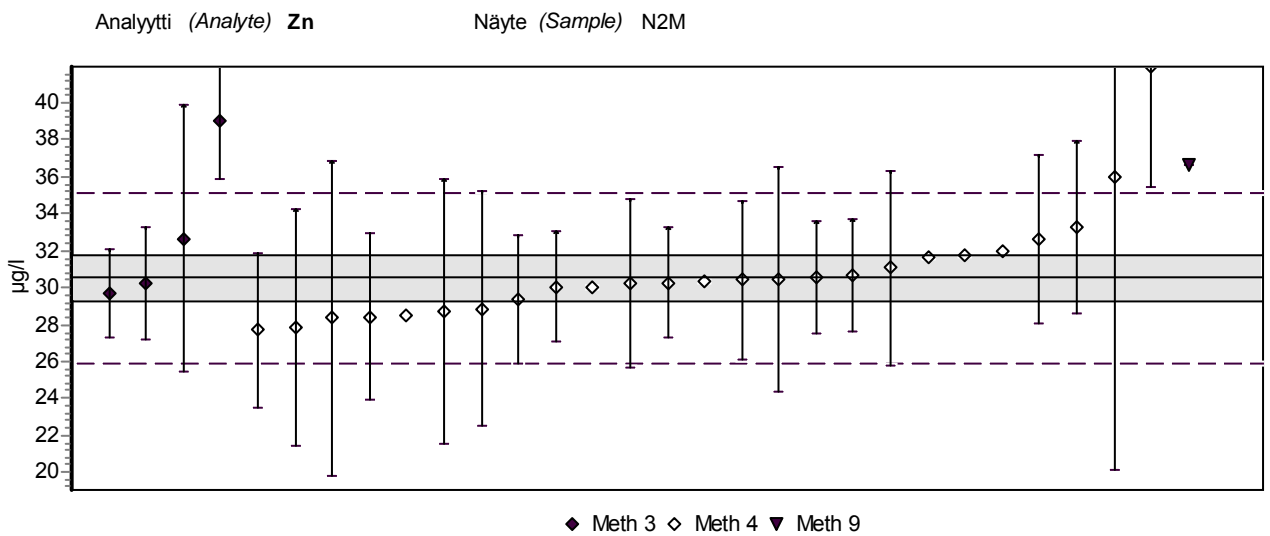
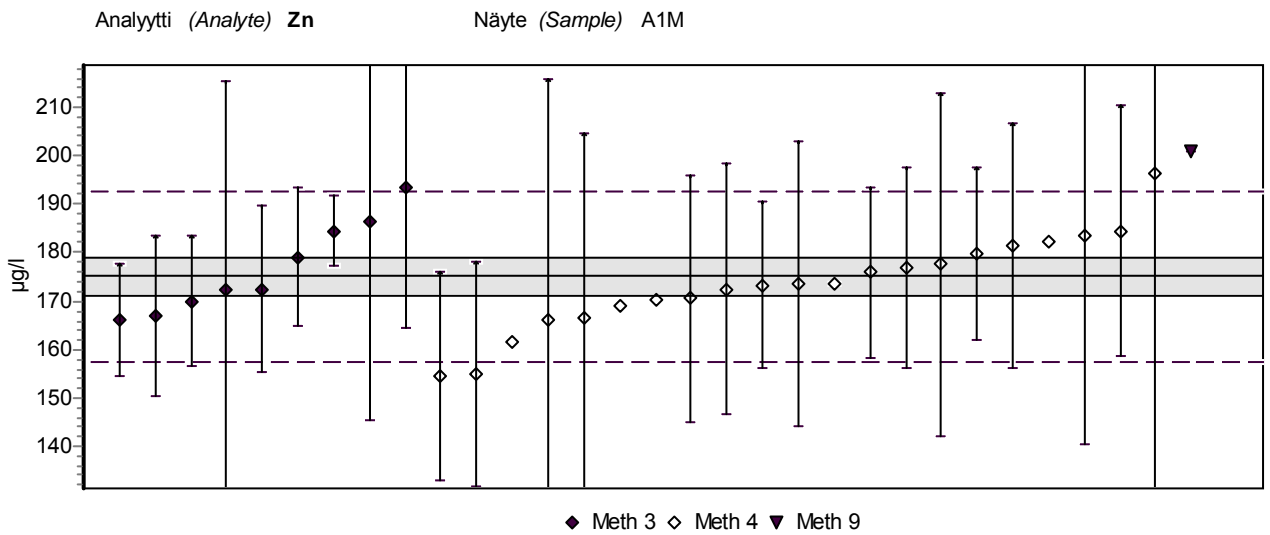
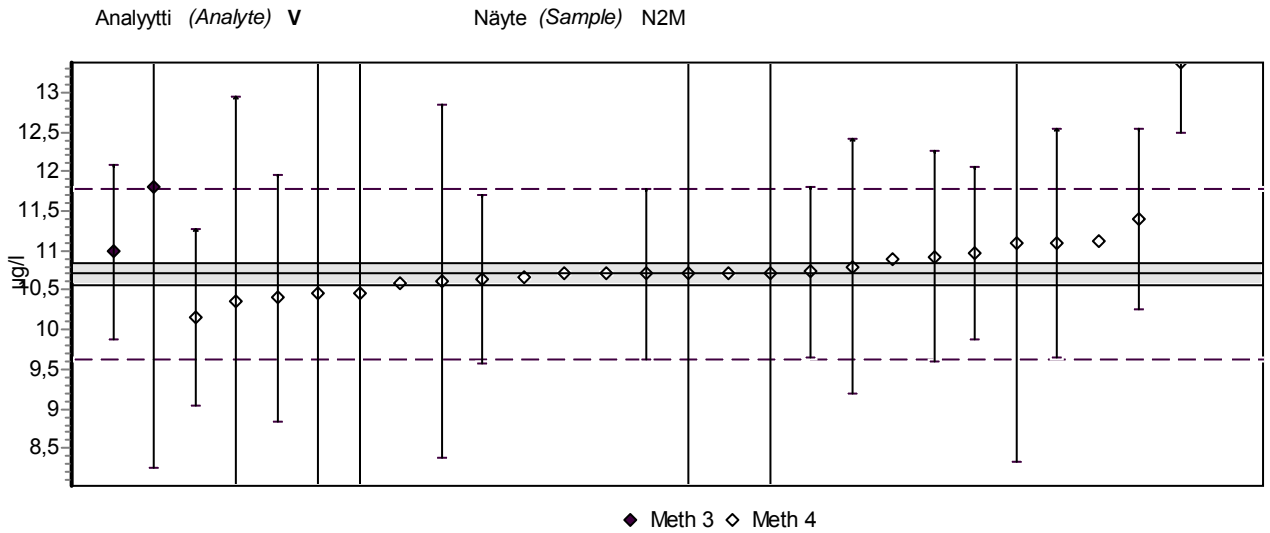
Analyytti (Analyte) Pb

Näyte (Sample) N1M









EXAMPLES OF MEASUREMENT UNCERTAINTIES REPORTED BY THE LABORATORIES

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

1. Using the IQC data only from synthetic control sample and/or CRM (X-chart), see e.g. NORDTEST TR 537¹⁾
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 537¹⁾
3. Using the IQC data and the results obtained in proficiency tests, see e.g. NORDTEST TR 537¹⁾
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

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

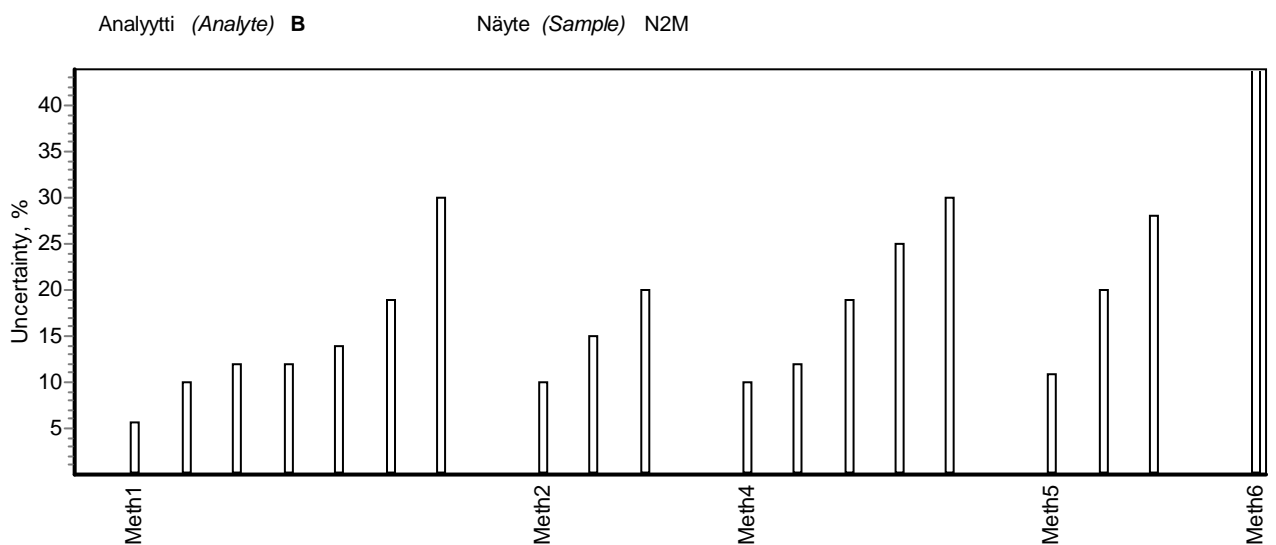
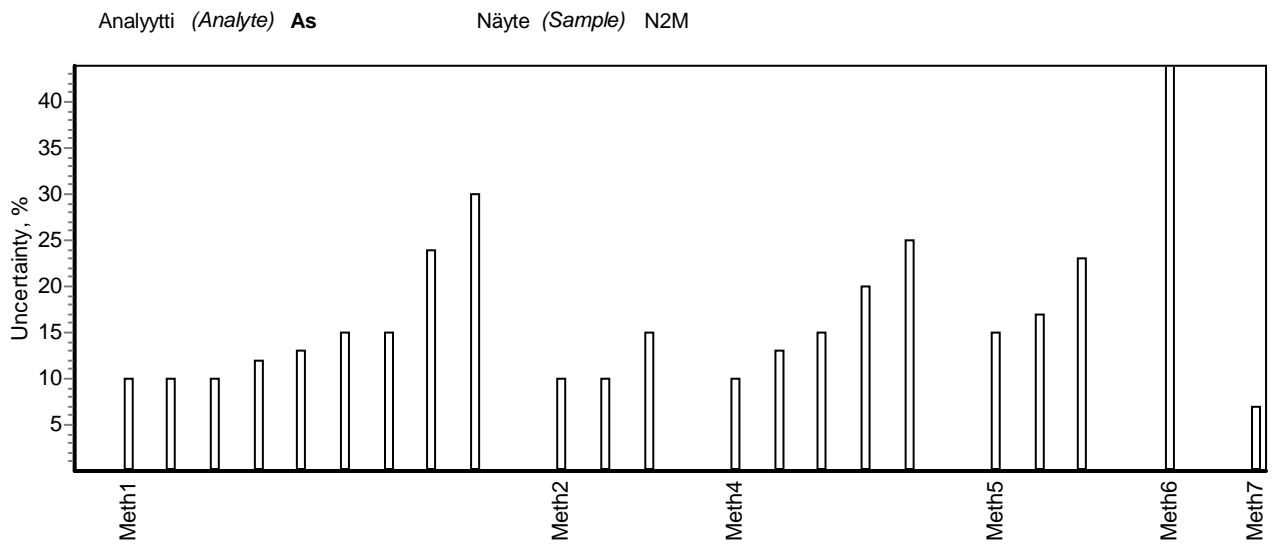
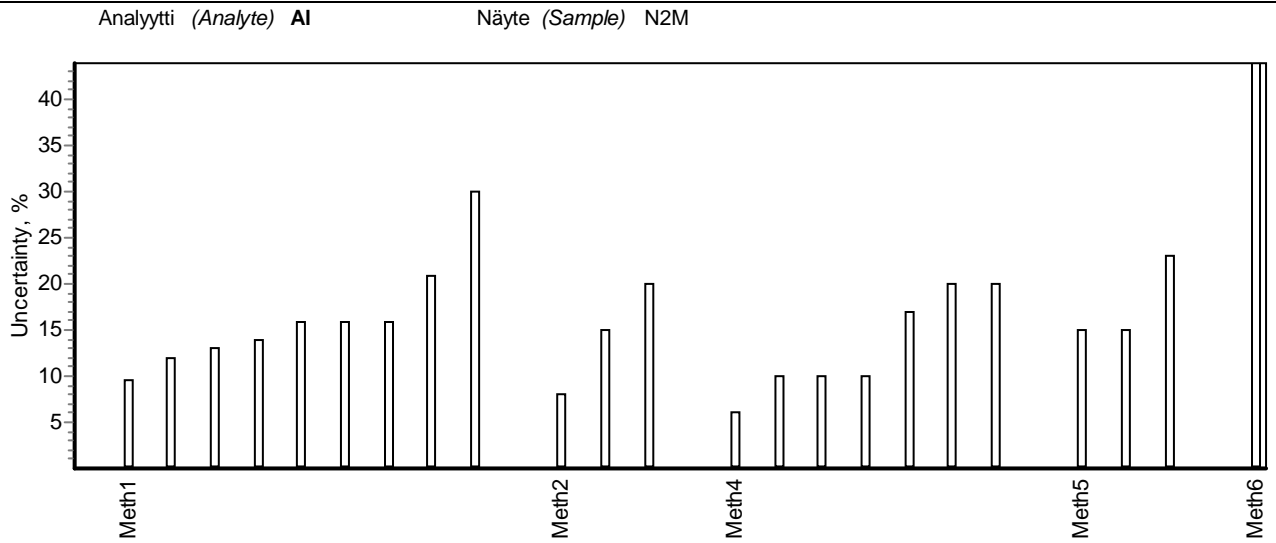
IQC= internal quality control

CRM= certificate reference material

¹⁾ <http://www.nordtest.info>

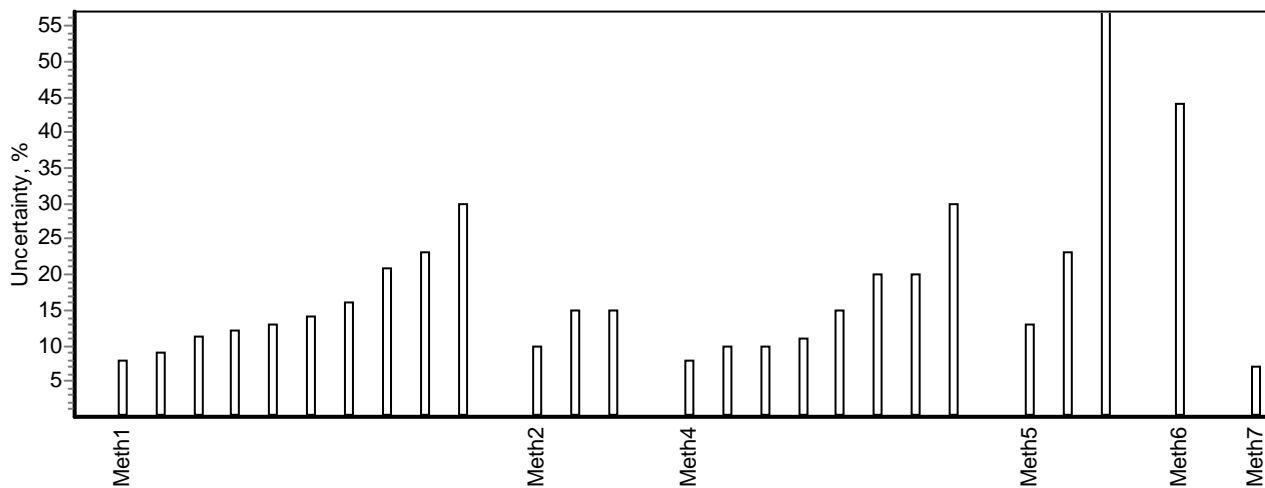
²⁾ <http://www.eurachem.org>

LIITE 11.
APPENDIX 11.



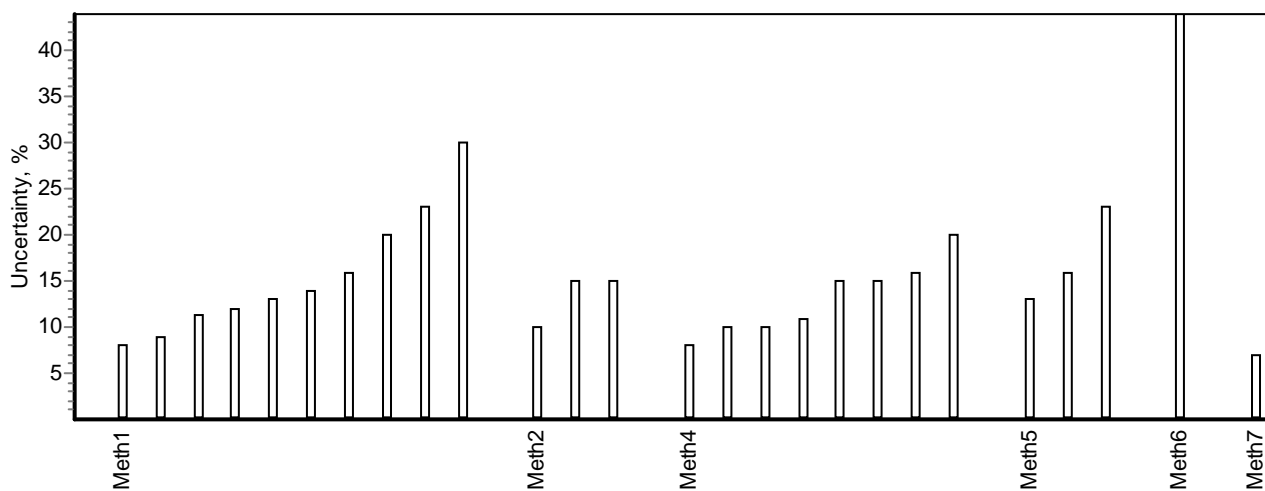
Analyytti (Analyte) Cd

Näyte (Sample) N1M



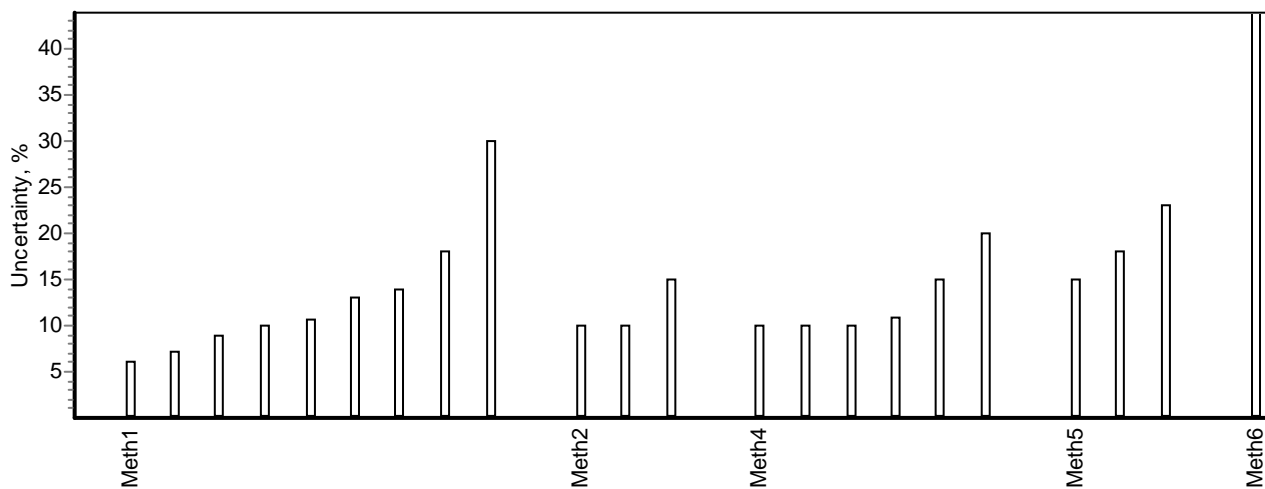
Analyytti (Analyte) Cd

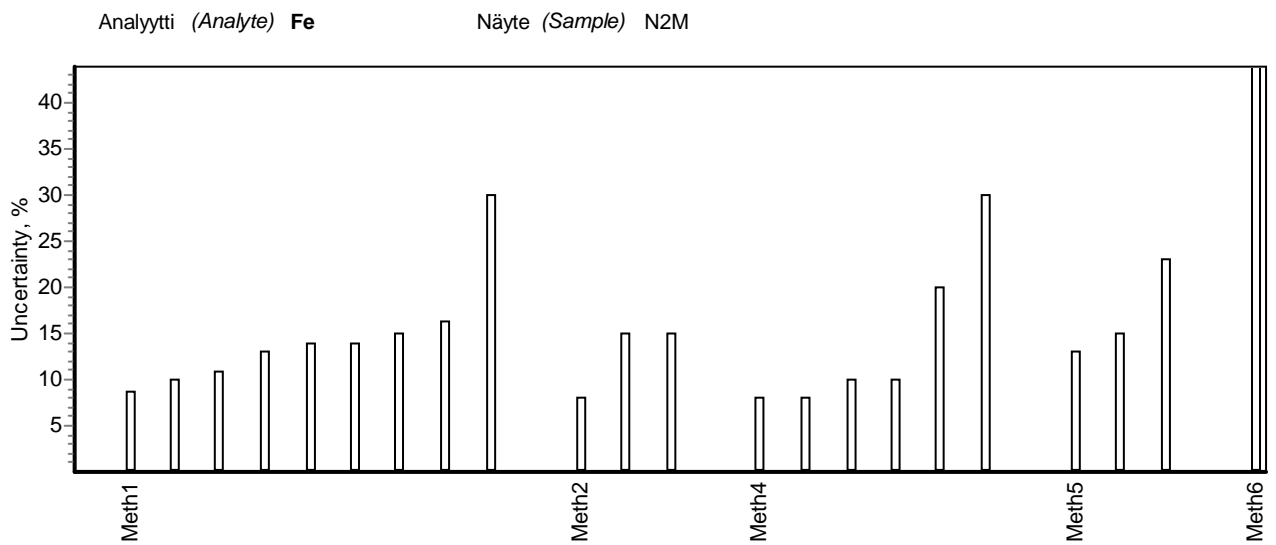
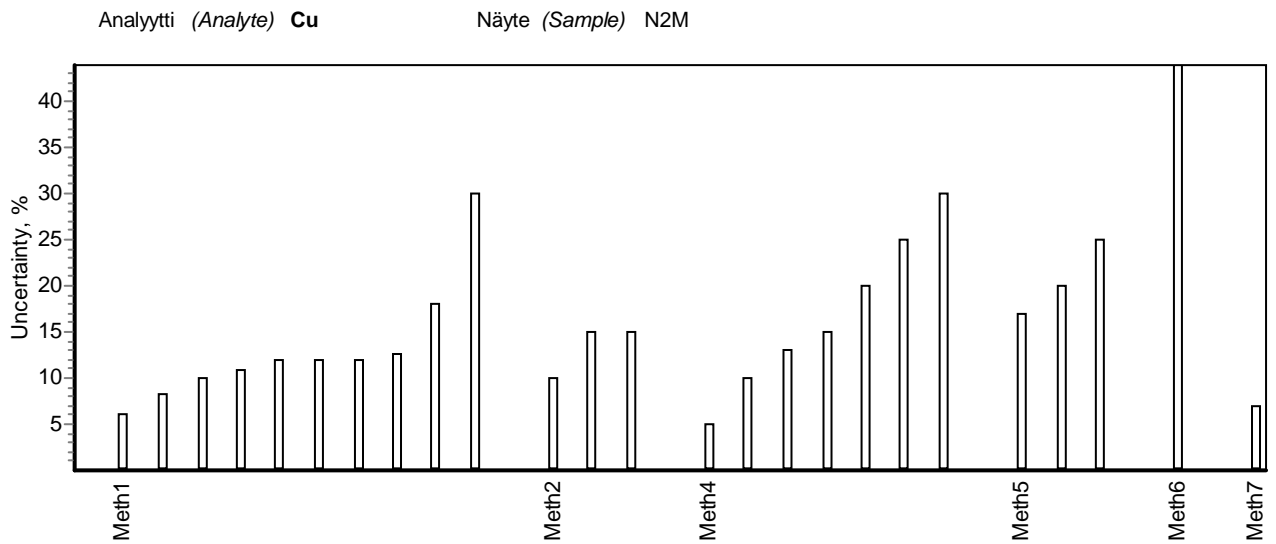
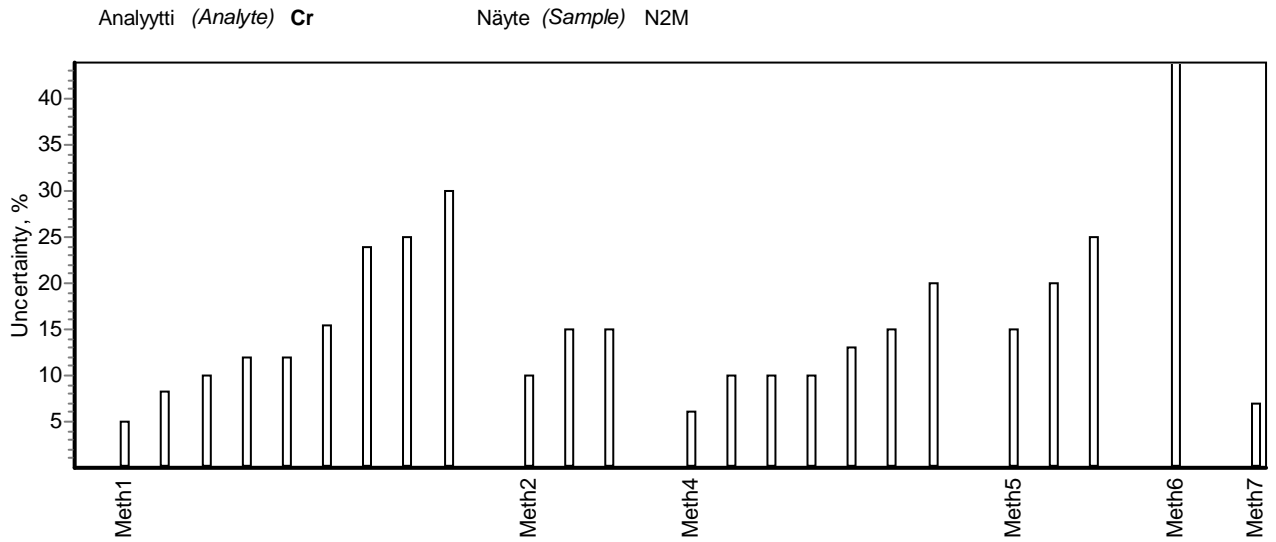
Näyte (Sample) N2M



Analyytti (Analyte) Co

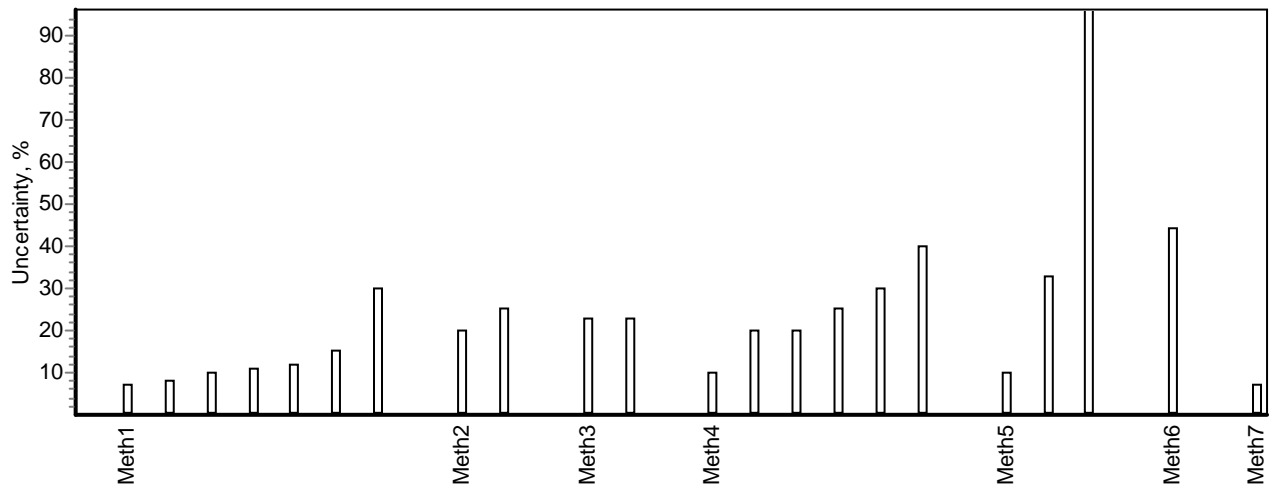
Näyte (Sample) N2M



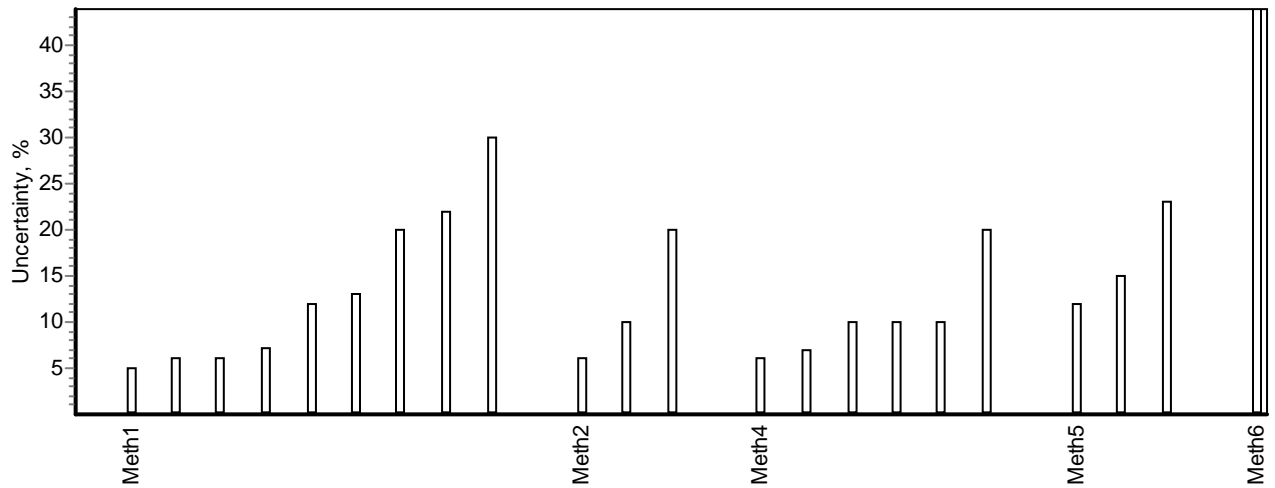


Analyytti (Analyte) **Hg**

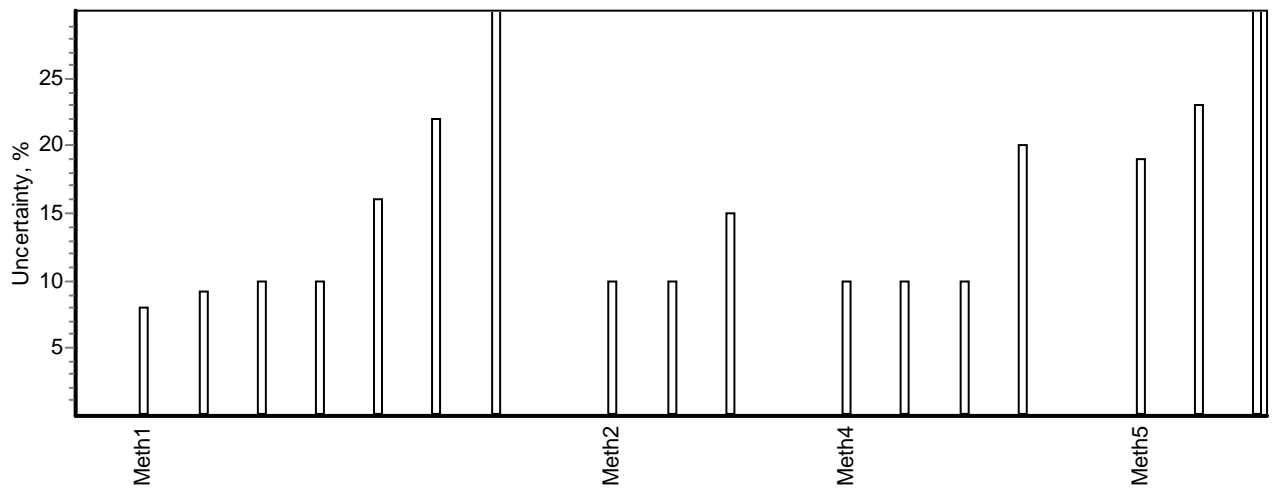
Näyte (Sample) N1Hg

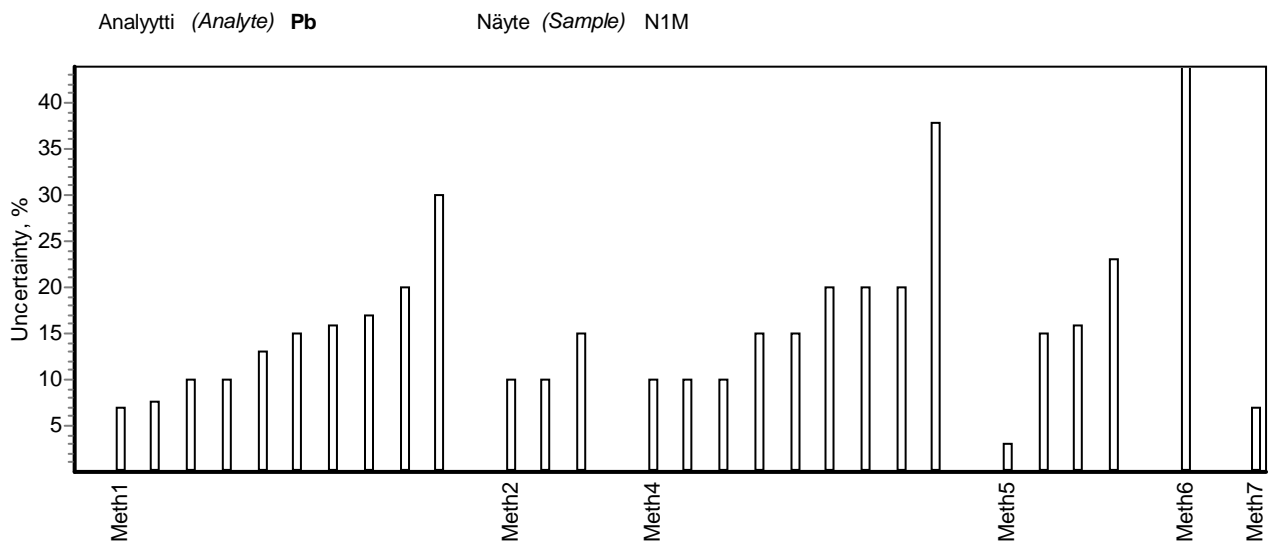
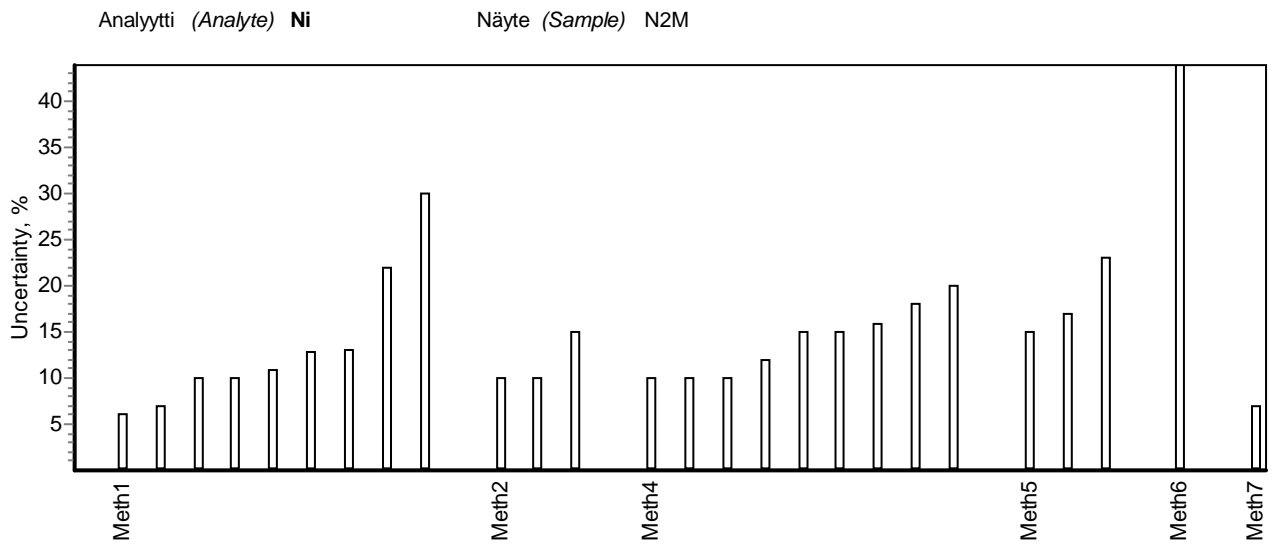
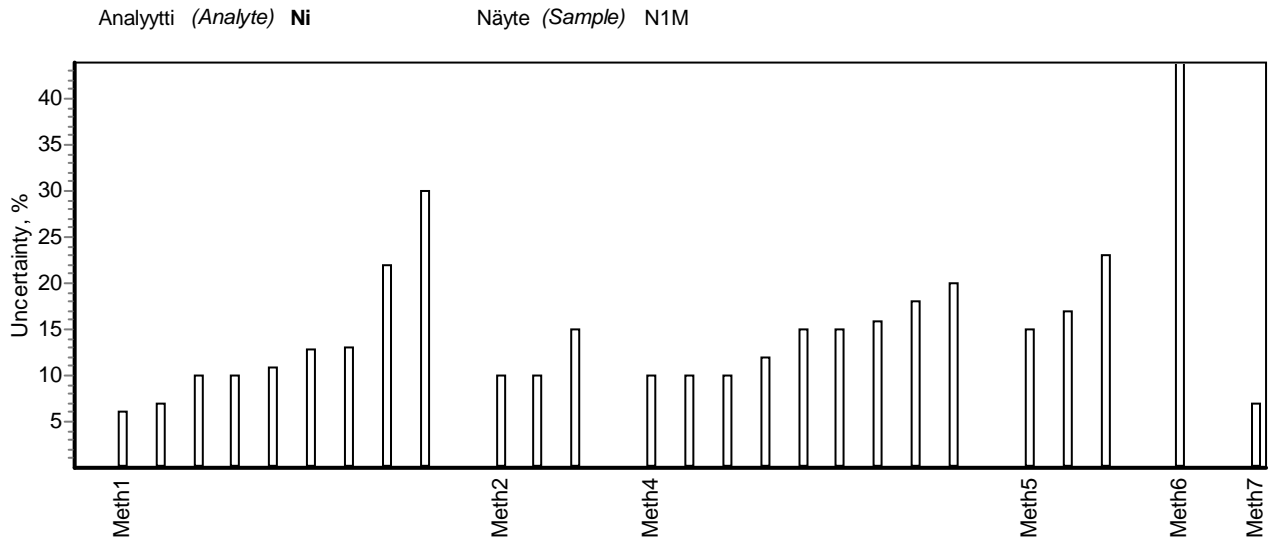
Analyytti (Analyte) **Mn**

Näyte (Sample) N2M

Analyytti (Analyte) **Mo**

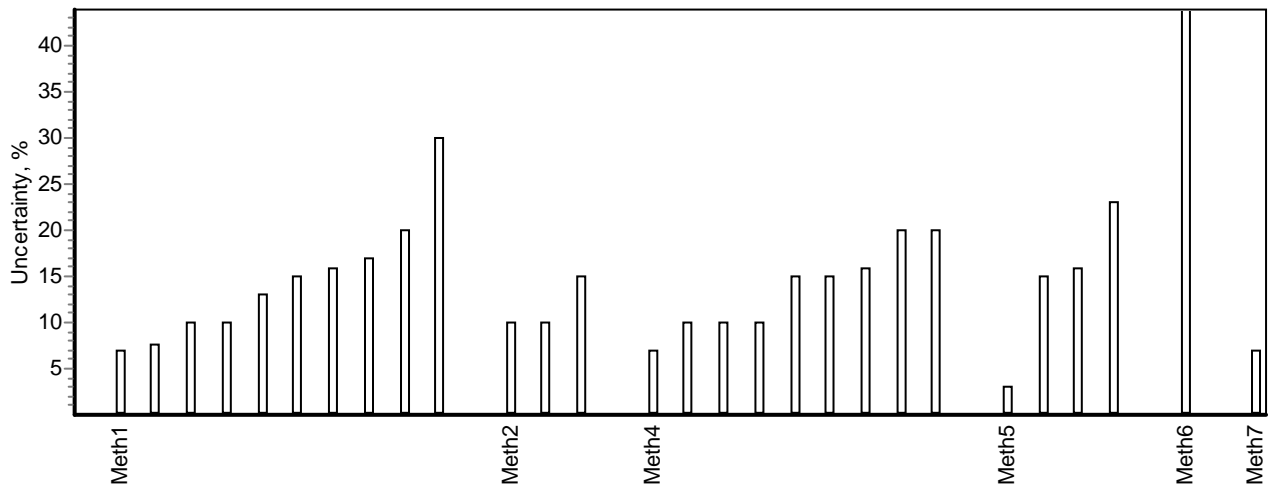
Näyte (Sample) N2M



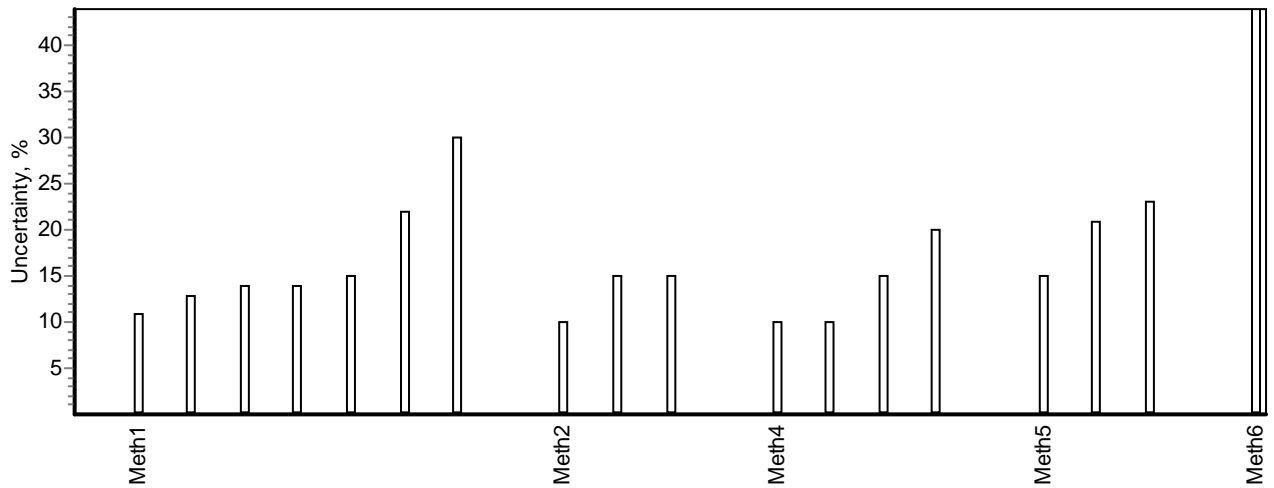


Analyytti (Analyte) **Pb**

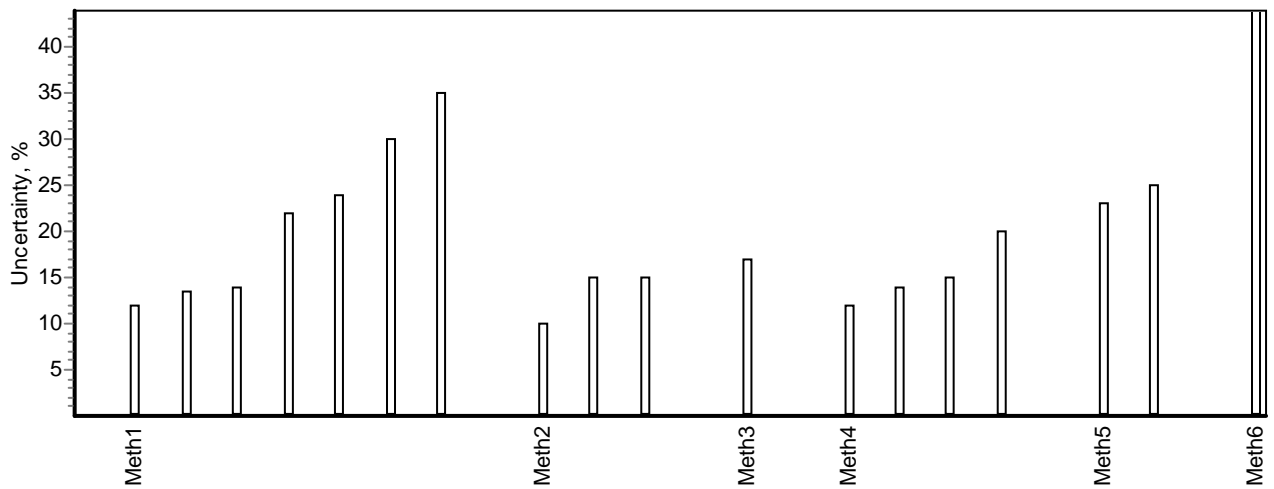
Näyte (Sample) N2M

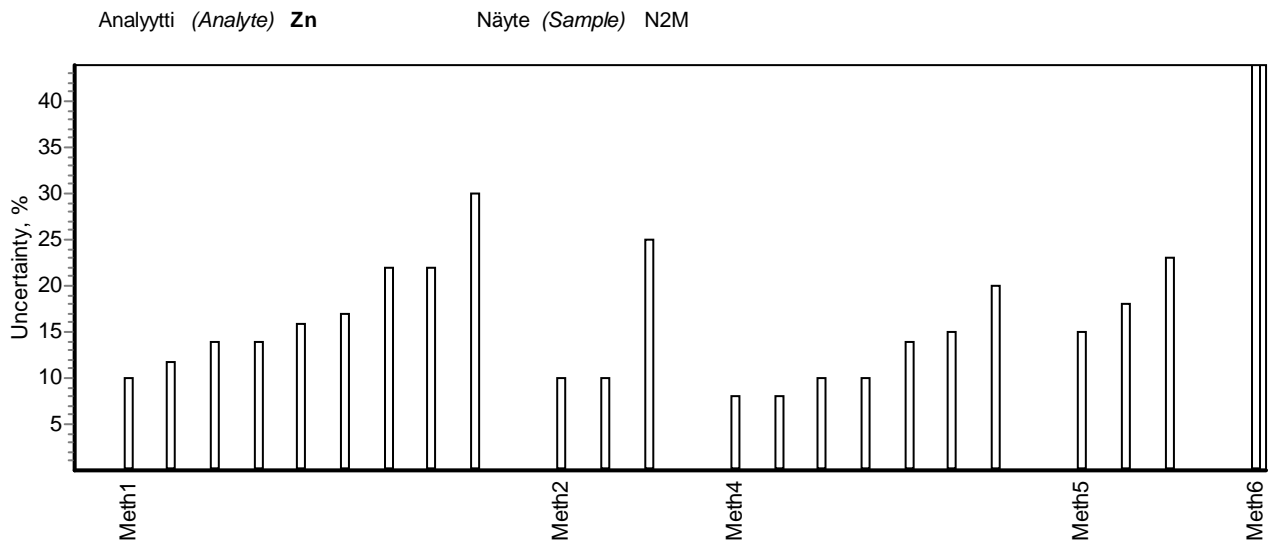
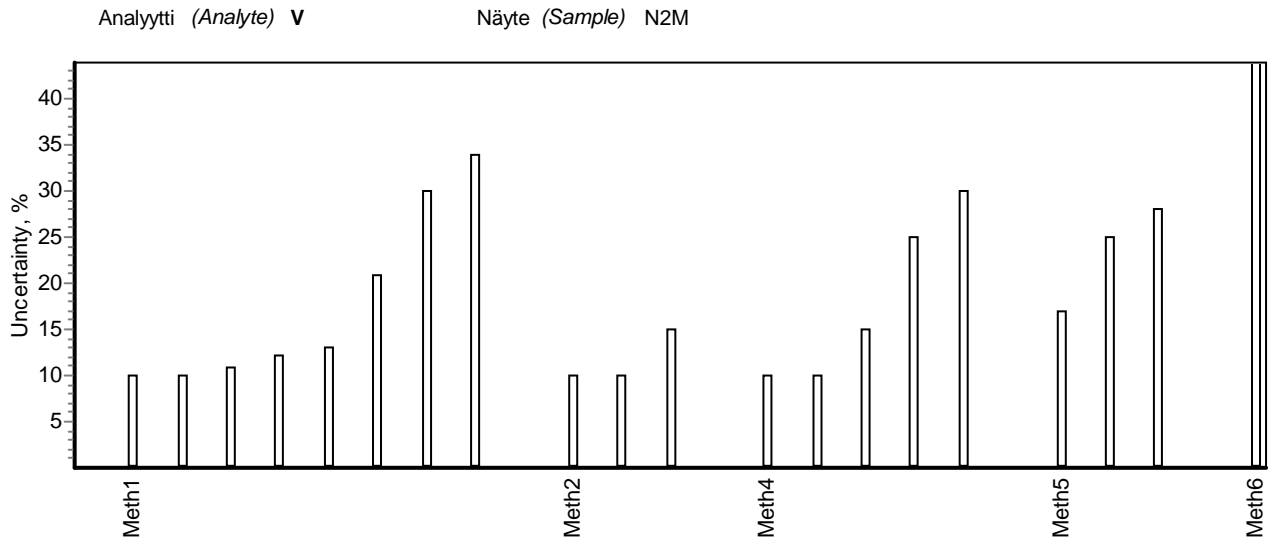
Analyytti (Analyte) **Sb**

Näyte (Sample) N2M

Analyytti (Analyte) **Se**

Näyte (Sample) N2M





Documentation page

Publisher	Finnish Environment Institute (SYKE)	Date	April 2012
Author(s)	Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri and Markku Ilmakunnas		
Title of publication	Proficiency test SYKE 10/2011 Heavy metals in surface waters		
Parts of publication/ other project publications	The publication is available only in the internet www.ymparisto.fi/julkaisut .		
Abstract	<p>Profest SYKE carried out the proficiency test (PT) for the analysis of elements in waters in November 2011–January 2012 in the frame of the joint PT-WFD program 2011. The principal aim of the proficiency test was to test the chemical analysis of priority and other substances in the context of chemical monitoring for the European Water Framework Directive (WFD), especially for compliance of surface waters with Environmental Quality Standards (EQS).</p> <p>The main measurements concerned the priority substances: Cd, Hg, Pb and Ni. Additionally it was possible to test voluntary elements: Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Sb, Se, V and Zn. The sample types were artificial and natural surface water. In total of 35 laboratories participated in the proficiency test.</p> <p>Basically, the metrologically traceable concentration, calculated concentrations or the robust mean of the results reported by the participant were used as the assigned values for measurements. The evaluation of the performance of the participants was carried out using z score. In total, 93 % of the total data in this proficiency test were satisfactory when the deviations of 10–25 % from the assigned values were accepted.</p>		
Keywords	water analysis, metals, Al, As, B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, Zn, water, environmental laboratories, proficiency test, interlaboratory comparisons		
Publication series and number	Reports of Finnish Environment Institute 11/2012		
Theme of publication			
Project name and number, if any			
Financier/ commissioner			
Project organization			
	ISSN 1796-1726 (online)	ISBN 978-952-11-4009-9 (PDF)	
	No. of pages 79	Language English	
	Restrictions Public	Price	
For sale at/ distributor	Finnish Environment Institute, Customer service E-mail: neuvonta.syke@ymparisto.fi Phone +358 20 610 183 Fax +358 9 5490 2190		
Financier of publication	Finnish Environment Institute, P.O. Box 140, FI-00251 Helsinki, Finland		
Printing place and year	Helsinki 2012		
Other information			

Kuvailulehti

Julkaisija	Suomen ympäristökeskus (SYKE)	Julkaisu-aika Huhtikuu 2012
Tekijä(t)	Mirja Leivuori, Kaija Korhonen-Ylönen, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri ja Markku Ilmakunnas	
Julkaisun nimi	SYKE Proficiency Test 10/2011 Heavy metals in surface waters	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä. www.ymparisto.fi/julkaisut	
Tiivistelmä	<p>Profest SYKE järjesti pätevyyskokeen ympäristönäytteitä analysoiville laboratorioille joulukuussa 2011 yhteistyössä Euroopan pätevyyskoejärjestäjien verkoston PT-WFD kanssa (www.pt-wfd.eu). Verkosto järjestää pätevyyskokeita vesipuitedirektiivin (WFD) prioriteetti- ja muiden aineiden kemiallisille määrittämiselle, joilla seurataan ympäristölaatu normien (Environmental Quality Standards, EQS) toteutumista. Tässä pätevyyskokeessa testattiin pintavedestä vesipuitedirektiivin prioriteettiaineista kadmium, lyijy, elohopea ja nikkeli. Lisäksi oli mahdollista testata seuraavat alkuaineet: Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Sb, Se, V ja Zn. Näytteinä olivat syntettilinen näyte sekä pintavedet. Pätevyyskokeeseen osallistui yhteensä 35 laboratoriot.</p> <p>Laboratorioiden pätevyyden arviointi tehtiin z-arvon avulla. Mittausuureen vertailuarvona käytettiin metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta tai osallistujien ilmoittamien tulosten robustia keskiarvoa.</p> <p>Koko tulosaineistossa hyväksyttävää tuloksia oli 93 %, kun vertailuarvosta sallittiin 10–25 %:n poikkeama.</p>	
Asiasanat	vesianalyysi, metallit, Al, As, B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, Zn, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus	
Julkaisusarjan nimi ja numero	Reports of Finnish Environment Institute 11/2012	
Julkaisun teema		
Projektihankkeen nimi ja projektin numero		
Rahoittaja/ toimeksiantaja		
Projektiryhmään kuuluvat organisaatiot		
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Sammandrag	<p>I december år 2011 ordnade SYKE Profest i samarbete med det europeiska nätverket för kompetensprovningar PT-WFD (www.pt-wfd.eu) en kompetensprovning för miljölaboratorier. Nätverket ordnar kompetensprovningar för de kemiska analyser som nämns i ramdirektivet för vatten, med vilka man följer upp hur miljönormer efterföljs (Environmental Quality standards, EQS). I denna kompetensprovning testades följande prioritetsämnen Cd, Pb, Hg och Ni i ytvatten. Dessutom kunde laboratorierna testa följande grundämnen i ett syntetsikt prov och i ytvatten: Al, As, Co, Cr, Cu, Mn, Mo, Sb, Se, V och Zn. I kompetensprovningen deltog totalt 35 laboratorier.</p> <p>Som referensvärde av analytens koncentration användes mest det teoretiska värdet eller robust medelvärde av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I kompetensprovningen var 93 % av alla resultaten tillfredsställande, när total deviation på 10–25 % från referensvärdet accepterades.</p>	
Nyckelord	vattenanalyser, metaller, Al, As, B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, Zn, provningsjämförelse, vatten- och miljölaboratorier	
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