REPORT ON THE HELCOM PLC6 INTERCALIBRATION

Technical Report from DCE – Danish Centre for Environment and Energy No. 27 2013

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Data sheet

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Abstract:	This report presents results from the PLC6 intercalibration on metal and nutrients in fresh water and waste water. The intercalibration was performed in ordre to evaluate the analytical quality of results reported to HELCOM. 17 laboratories participated in the intercalibration.

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Preface

The Danish Centre for Environment and Energy, Aarhus University (DCE) has performed an intercalibration on nutrients and metals on behalf of HELCOM PLC6 in fresh water and waste water in order to evaluate the analytical quality of the data reported into HELCOM.

Layout and template for the statistical design are developed by Marianne Thomsen, Department of Environmental Science and Peter Borgen Sørensen, Department of Bioscience, Aarhus University. Planning and coordination of the intercalibration was performed by Pia Lassen, Department of Environmental Science, Martin M Larsen, Department of Bioscience and Susanne Boutrup, DCE – Danish Centre for Environment and Energy, Aarhus University. Responsible for the statistical evaluation and quality control is Pia Lassen.

In appendix 3 is an addendum to the report. One laboratory was accidental not included in the statistical evaluation for the intercalibration. The results from this laboratory are presented in this addendum and further a comparison of the summary statistics the first evaluation and the second evaluation where the additional laboratory is included.

The intercalibration was financed by HELCOM and Swedish Agency for Marine and Water Management. The participating laboratories have financed the analyses they have performed by themselves.

1 Description of the intercalibration

This report presents results from the PLC6 intercalibration on metal and nutrients in fresh water and waste water. There are reported results from 17 laboratories in fresh water and 15 laboratories in waste water. The participating laboratories are listed in appendix 1. Not all laboratories have reported data for all components. Following components are included in the intercalibration: Nutrients: NH_4, NO_3, NO_2, N-total, PO_4, and P-total. Metals: Cd, Cr, Cu, Ni, Pb, Zn, Hg. The original data from the laboratories can be found in appendix 2. Each laboratory has been given a random code number in order to secure the anonymity of the laboratories. The ranking of laboratories in appendix 2 does not reflect the code numbers.

The results from the laboratories were delivered in different units and setup of the reporting spreadsheet. For the statistical evaluation all data for the nutrients have been corrected to the same units (N and P mg/L) and µg/L for the metals– the revised dataset are reported in the same units below. Data below detection limits (reported as <value) is not included in the statistical analysis. Some laboratories have reported NO_2 and NO_3 as a sum. These are not included in the statistical analysis. Cochran's and Grubb's outlier test are carried out according to ISO 5725-2 (2002), outliers according to these tests are not included in the statistical evaluation.

In chapter 3 the statistical evaluation is dealing with the data of the single laboratories related to the relative standard deviation and the deviation from assigned value. Youden plot, outlier test and summary of statistical parameters are also included for each component. In the table below is a summary of the statistical parameters used in this report. They are also described in more details in the relevant chapters.

For NO_2 in waste water there were only 5 data sets. Reservation is therefore taken for the outlier test and the statistics performed on NO_2 in waste water, as the results are debatable due to the low number of data. This means that the statistical evaluation of NO_2 should only be considered as indicative.

Parameter	Description of the statistical parameters used in this report
Chapter 3 Laboratory results	
Measured values	The data from the laboratory
Assigned values	The total mean of all results from the participating laboratories, outliers excluded
Average	The mean of the laboratory test pair (sample A and B)
Dev. %	The relative deviation between the assigned value and the laboratory average
RSD %	The relative deviation between test pairs (sample A and B)
z-score	Evaluate the results in the relation to the uncertainty of the intercalibration
Chapter 4 Statistical evaluation	
Cochran's outlier test	Evaluate if the test pair A and B of the single laboratory can be regarded as a duplicate compared to the deviation of test pair for all laboratories
Grubb's singe outlier test	Evaluate if the mean of test pairs (A and B) of the single laboratories is statistically different from the mean of all laboratories with respect to the deviation of the intercalibration
Grubb's double outlier test	The Grubb's double outlier test is performed on the two most extreme (highest and / or lowest) test pairs but after the same principle as above.
Youden plot	Show the test pairs (A and B) from the laboratories, assigned values and cut off values for the outlier tests is also shown
Summary statistical parameters	
p: Number of laboratories	Number of laboratories included in the statistics. Outliers are excluded
m: mean value	The mean value of the laboratories' results without outliers. m is used as assigned value in the intercalibration
S(L): Laboratory deviation	The deviation between the laboratories
S(r): repeatability	The deviation between test pairs for all laboratories
S(R): reproducibility	Total deviation for the intercalibration, $S(R)^2 = (S(L)^2+S(r)^2$
r: Repeatability limit	The value equal to or below which the absolute difference between test pairs that may be expected to occur with a probability of 95% (r = S(r)*2.8)
R: Reproducibility limit	The value equal to or below which the absolute difference between two laboratories may be expected to occur with a probability of 95% (R = S(R)*2.8)
CV(r): Coefficient of laboratory variation	The relative value (in %) of repeatability, S(r)
CV(R): Coefficient of total variation	The relative value (in %) of reproducibility, S(R), the total derivation

2 Preparation and evaluation of samples used for the intercalibration

The fresh water samples used for this intercalibration were collected from Hove Å, North Zealand, Denmark in the season with thawing of snow contributing to the water flow.

The waste water samples were effluent water collected from Skævinge Waste Water Treatment Plant, North Zealand, Denmark.

Metal samples were conserved with nitric acid (2%) in 30 liter polyethylene (PE) containers, nutrient samples in 30 liter PE containers were not conserved, apart from storing in refrigerator until distribution.

Waste water samples were sent to Holland for sterilization, homogenization and bottling. Due to the low concentration of metals, which were below the detection limits of several of the participating laboratories, it was found necessary to pool the samples, spike with metals and afterwards re-homogenize and rebottling at Aarhus University, Roskilde, before final distribution to participating laboratories.

The fresh water samples were filtered in order to secure homogeneity and increase the stability of the nutrients. For the metals the A and B samples were spiked at the same concentration level whereas the C samples were spiked at a higher concentration level. For the nutrients the C samples were spiked. After homogenization the samples were bottled.

Waste water samples for nutrients were bottled in glass bottles, whereas waste water samples for metals, and all fresh water samples were bottled in PE bottles.

2.1 Samples used for metals

2.1.1 Homogenity test

A selection of samples was tested before the samples were distributed to the laboratories, to check homogeneity. 11 subsamples of 15 ml were collected during bottling of the spiked freshwater and waste water samples, at regular intervals within the period where the laboratories analyzed the received samples. Except for mercury (Hg) none of the elements indicated a substantial trend over time compared to the average concentration (set to 100%, See figure 1 below). For freshwater, the relative standard deviation was <3.5% for all elements except Pb (7%) and Hg (13%). For waste water, the relative standard deviation was below 2.5% for all elements except Cr (8.6%) and Hg (20%). All elements was measured on ICP-MS, some of the Hg trend could be due to carry over from the calibration standard, as Hg is known to have very long wash-out times on ICP-MS.

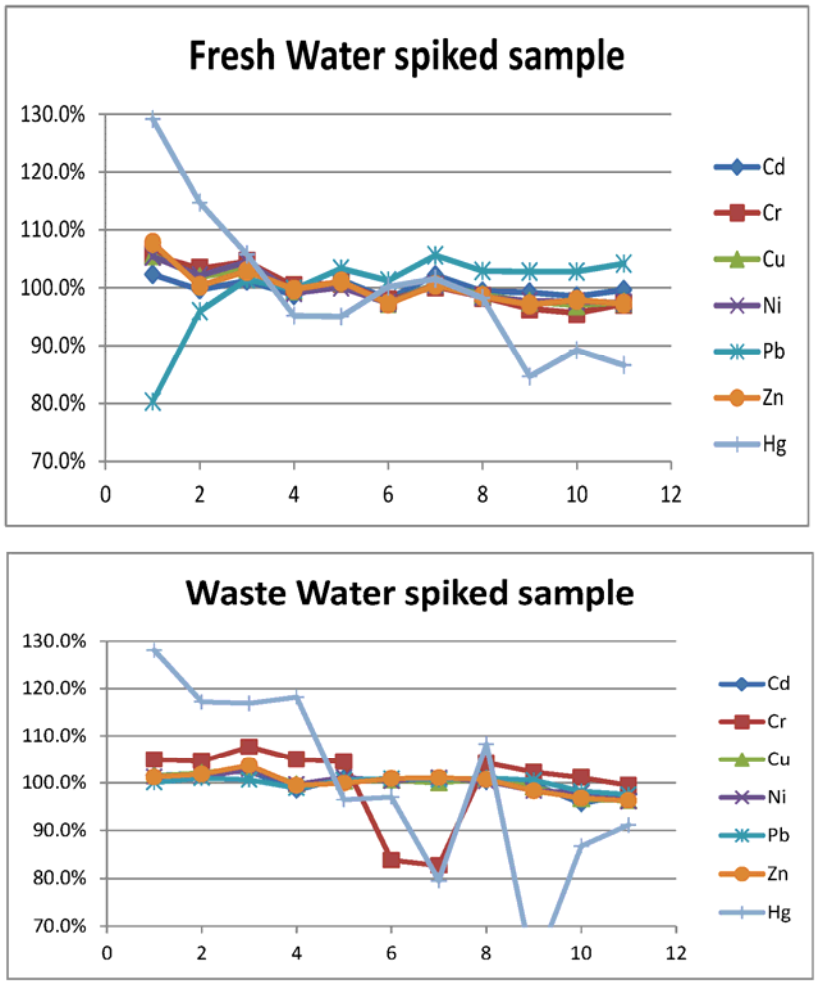


Figure 1. Analysis during bottling – verification of homogeneity shown as the relative standard deviation on the analyses of test samples. Average concentration is set as 100%.

2.1.2 Stability test

After the initial test for homogeneity, further stability test of samples stored during the proficiency test time range was performed, and these gave no indication of bottle contamination or instability. Relative standard deviation for the different samples is shown in table 1.

Table 1. Verification of stability. Relative standard deviation of stored bottles (for fresh water A and B sample both as individual and combined for both, shown in bold). Mercury analyzed only by ICP-MS, so no results available for freshwater (<detection limit, LOD).

ID	n	Cd	Cr	Cu	Ni	Pb	Zn	Hg
Freshwater								
FW A	4	7.4%	3.5%	1.5%	2.9%	7.0%	1.3%	<LOD
FW B	4	4.3%	0.7%	6.1%	2.2%	2.4%	2.9%	<LOD
FW A+B	8	7.2%	4.6%	4.3%	4.8%	5.7%	2.1%	<LOD
FW C	10	2.6%	1.4%	2.7%	2.7%	4.2%	1.6%	<LOD
Wastewater								
WW A	14	3.3%	2.5%	1.6%	2.1%	1.3%	1.6%	5.2%
WW B	13	3.6%	1.4%	1.6%	1.5%	1.2%	2.1%	2.9%

2.2 Samples used for Nutrients

The samples were only tested after spiking, bottling and distribution to the participating laboratories by analysing. The samples were analyzed for NH_4-N and PO_4-P on a Skalar apparatus.

2.2.1 Homogenity test

The homogeneity test showed that the relative standard deviation on the NH_4 concentration ranged between 6-9% whereas it was low for the PO_4 concentration in waste water (1%) but relative high for fresh water 15-21% (figure 2). The latter was primarily caused by very low concentrations of PO_4 in fresh water.

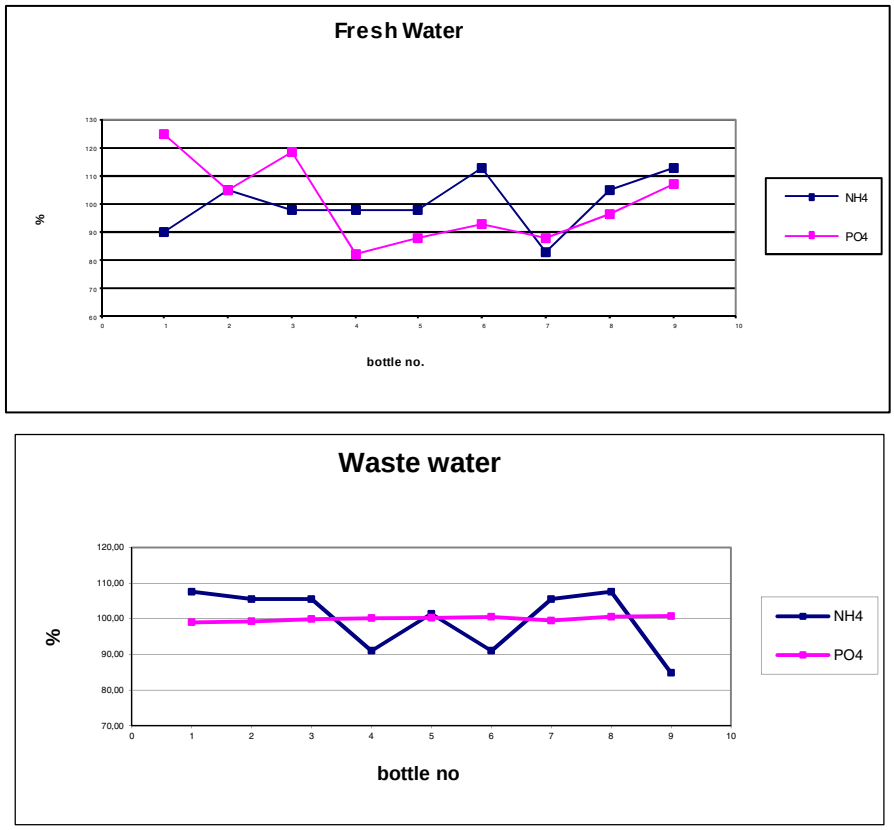


Figure 2. Analysis during bottling – verification of homogeneity shown as the relative standard deviation on the analyses of test samples. The average concentration is set as 100 %.

2.2.2 Stability test

The stability test of samples stored was performed within the period where the laboratories analyzed the received samples. The results gave for PO_4 in fresh water and waste water and NH_4 in waste water no indications of instability. The standard deviations were in the same range as for the homogeneity test and no decreasing tendency. However, NH_4 in fresh water appear to be unstable during the period. Relative standard deviation for the different samples is shown in table 2.

Table 2. Verification of stability. Relative standard deviation of stored bottles.

ID	n	NH_4-N	PO_4-P
Freshwater			
FW A+B	9	34.1%	14.7%
FW C	7	30.1%	21.5%
Wastewater			
WW A/B	9	8.7%	5.7%

2.3 Conclusion

The distributed samples are fit for the purpose, except for NH_4 in fresh water. However, the samples sent out to the laboratories might have been stored under other conditions during the intercalibration period e.g. during transportation which means that samples used in the intercalibration could have higher variation.

The expected uncertainty for metals are <7.5% in fresh water, and <4% in waste water samples with regard to metal analysis.

The expected uncertainty for nutrients are higher than the metals; <9% for NH_4 and <25% for PO_4 in fresh water, and <9% in waste water samples.

3 Laboratory results for the statistical analysis

3.1 Description of the tables

In section 3.2 and 3.3 the single laboratories' results corrected to same units are shown. The following terms are used in the tables:

Measured values are the results from the laboratory

Assigned values are calculated as the total mean of all results from the participating laboratories results without outliers (see 4.1)

Average is the mean of the test pairs (sample A and B)

Dev % is the relative deviation between the assigned value and the laboratory average

RSD % is the relative deviation between test pairs (sample A and B)

z-score is a simple way to evaluate the results in the relation to the uncertainty of the intercalibration; z-scores between -2 and 2 is regarded satisfactory. From -3 to -2 and 2 to 3 is regarded as questionable results. z-scores below -3 and higher than 3 is regarded as not acceptable. z-scores are calculated by the following equation (according to ISO 13528:2005):

$$z=(x-m)/\sigma$$

where x is the average of the laboratory result (sample A and B), m is the assigned value and σ is the standard deviation for evaluation of the intercalibration. In the present intercalibration the reproducibility is used as σ (see also 4.1). As mentioned earlier the assigned values are the means of all laboratories results, outliers excluded.

3.2 Fresh water

Laboratory Code no.: 1

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.101	0.101	0.128	0.128	0.101	-21.1	0.0	-0.4
NO_3-N, mg/L	5.42	5.20	5.01	5.01	5.31	5.9	3.0	1.2
NO_2-N, mg/L	0.164	0.149	0.140	0.140	0.157	12.0	6.9	0.6
N-total, mg/L	6.50	6.50	6.04	6.04	6.50	7.6	0.0	1.5
PO_4-P, mg/L	0.034	0.032	0.028	0.028	0.033	17.6	2.8	0.5
P-total, mg/L	0.051	0.051	0.047	0.047	0.051	9.5	0.0	0.3
Cd, µg/L	0.336	0.325	0.312	0.312	0.331	6.0	2.4	0.6
Cr, µg/L	3.64	3.57	4.22	4.22	3.61	-14.6	1.4	-1.3
Cu, µg/L	4.68	4.64	6.84	6.84	4.66	-31.9	0.6	-1.9
Ni, µg/L	7.69	7.56	8.72	8.72	7.63	-12.6	1.2	-1.0
Pb, µg/L	1.20	1.23	3.00	3.00	1.22	-59.5	1.7	-6.0
Zn, µg/L	12.70	12.80	15.12	15.12	12.75	-15.7	0.6	-1.3
Hg, µg/L	0.020	0.020	0.023	0.023	0.020	-13.0	0.0	-0.3

No. components	13	13

Laboratory Code no.: 1

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev %
NH_4-N, mg/L	0.194	0.216	-10.2
NO_3-N, mg/L	5.20	5.02	3.4
NO_2-N, mg/L	0.213	0.207	3.1
N-total, mg/L	6.70	6.30	6.4
PO_4-P, mg/L	0.134	0.137	-2.1
P-total, mg/L	0.198	0.184	7.7
Cd, µg/L	1.32	1.261	4.7
Cr, µg/L	6.12	6.82	-10.3
Cu, µg/L	12.4	14.8	-16.1
Ni, µg/L	16.7	18.8	-11.0
Pb, µg/L	6.62	12.8	-48.2
Zn, µg/L	29.6	34.3	-13.7
Hg, µg/L	0.068	0.073	-7.1

No. components	13

Laboratory

Code no.: 2

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.128	0.128				
NO_3-N, mg/L	5.34	5.32	5.01	5.01	5.33	6.3	0.3	1.3
NO_2-N, mg/L	0.277	0.255	0.140	0.140	0.266	90.0	5.8	4.7
N-total, mg/L	5.81	5.80	6.04	6.04	5.81	-3.9	0.1	-0.8
PO_4-P, mg/L	0.038	0.036	0.028	0.028	0.037	32.1	3.8	1.0
P-total, mg/L	0.05	0.04	0.047	0.047	0.045	-3.3	15.7	-0.1
Cd, µg/L			0.312	0.312				
Cr, µg/L			4.22	4.22				
Cu, µg/L			6.84	6,84				
Ni, µg/L			8.72	8.72				
Pb, µg/L			3.00	3.00				
Zn, µg/L			15.12	15.12				
Hg, µg/L	0.025	0.024	0.023	0.023	0.025	6.5	2.9	0.2

No. components	6	6

Laboratory

Code no.: 2

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev %
NH_4-N, mg/L		0.216	
NO_3-N, mg/L	5.55	5.02	10.5
NO_2-N, mg/L	0.432	0.207	109.0
N-total, mg/L	6.00	6.30	-4.7
PO_4-P, mg/L	0.174	0.137	27.4
P-total, mg/L	0.19	0.184	3.3
Cd, µg/L		1.26	
Cr, µg/L		6.82	
Cu, µg/L		14.8	
Ni, µg/L		18.8	
Pb, µg/L		12.8	
Zn, µg/L		34.3	
Hg, µg/L	0.088	0.073	

No. components	6

Laboratory
Code no.: 3

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.027	0.114	0.128	0.128	0.071	-44.9	87.3	-0.9
NO_3-N, mg/L	5.22	5.41	5.01	5.01	5.31	6.0	2.6	1.2
NO_2-N, mg/L	0.164	0.152	0.140	0.140	0.158	13.0	5.4	0.7
N-total, mg/L	6.36	6.17	6.04	6.04	6.27	3.7	2.1	0.7
PO_4-P, mg/L	0.021	0.019	0.028	0.028	0.020	-27.6	8.0	-0.8
P-total, mg/L	0.051	0.048	0.047	0.047	0.050	6.5	3.2	0.2
Cd, µg/L			0.312	0.312				
Cr, µg/L			4.22	4.22				
Cu, µg/L			6.84	6.84				
Ni, µg/L			8.72	8.72				
Pb, µg/L			3.00	3.00				
Zn, µg/L			15.12	15.12				
Hg, µg/L			0.023	0.023				

No. components	6	6

Laboratory
Code no.: 3

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev %
NH_4-N, mg/L	0.033	0.216	-84.9
NO_3-N, mg/L	5.103	5.02	1.6
NO_2-N, mg/L	0.289	0.207	39.8
N-total, mg/L	6.34	6.30	0.7
PO_4-P, mg/L	0.137	0.137	0.1
P-total, mg/L	0.214	0.184	16.4
Cd, µg/L		1.26	
Cr, µg/L		6.82	
Cu, µg/L		14.8	
Ni, µg/L		18.8	
Pb, µg/L		12.8	
Zn, µg/L		34.3	
Hg, µg/L		0.073	

No. components	6

Laboratory
Code no.: 4

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.05	0.048	0.128	0.128	0.049	-61.7	2.9	-1.2
NO_3-N, mg/L	4.98	4.96	5.01	5.01	4.97	-0.9	0.2	-0.2
NO_2-N, mg/L	0.164	0.165	0.140	0.140	0.165	17.5	0.4	0.9
N-total, mg/L	6.25	6.08	6.04	6.04	6.16	2.0	2.0	0.4
PO_4-P, mg/L	0.0234	0.0236	0.028	0.028	0.024	-16.1	0.6	-0.5
P-total, mg/L	0.0432	0.0441	0.047	0.047	0.044	-6.2	1.5	-0.2
Cd, µg/L	0.322	0.325	0.312	0.312	0.323	3.6	0.6	0.4
Cr, µg/L	4.39	4.37	4.22	4.22	4.38	3.7	0.3	0.3
Cu, µg/L	6.65	6.58	6.84	6.84	6.62	-3.3	0.7	-0.2
Ni, µg/L	9.07	9.00	8.72	8.72	9.03	3.6	0.5	0.3
Pb, µg/L	2.94	2.95	3.00	3.00	2.94	-1.8	0.2	-0.2
Zn, µg/L	15.89	15.89	15.12	15.12	15.89	5.1	0.0	0.4
Hg, µg/L			0.023	0.023				

No. components	12	12

Laboratory
Code no.: 4

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L	0.102	0.216	-52.8
NO_3-N, mg/L	4.96	5.02	-1.4
NO_2-N, mg/L	0.244	0.207	18.0
N-total, mg/L	6.84	6.30	8.6
PO_4-P, mg/L	0.131	0.137	-4.1
P-total, mg/L	0.190	0.184	3.3
Cd, µg/L	1.32	1.26	5.0
Cr, µg/L	7.11	6.82	4.3
Cu, µg/L	15.0	14.8	1.8
Ni, µg/L	19.3	18.8	2.8
Pb, µg/L	12.7	12.8	-0.6
Zn, µg/L	34.7	34.3	1.0
Hg, µg/L		0.073	

No. components	12

Laboratory
Code no.: **5**

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.141	0.138	0.128	0.128	0.140	9.2	1.6	0.2
NO_3-N, mg/L	4.51	4.49	5.01	5.01	4.50	-10.2	0.2	-2.0
NO_2-N, mg/L	0.166	0.145	0.140	0.140	0.155	10.9	9.7	0.6
N-total, mg/L	5.25	5.23	6.04	6.04	5.24	-13.2	0.3	-2.6
PO_4-P, mg/L	0.030	0.029	0.028	0.028	0.030	6.6	2.3	0.2
P-total, mg/L	0.053	0.052	0.047	0.047	0.053	12.8	1.3	0.4
Cd, µg/L	0.230	0.260	0.312	0.312	0.245	-21.5	8.7	-2.1
Cr, µg/L	3.87	4.41	4.22	4.22	4.14	-1.9	9.2	-0.2
Cu, µg/L	9.71	9.55	6.84	6.84	9.63	40.8	1.2	2.4
Ni, µg/L	7.49	7.07	8.72	8.72	7.28	-16.5	4.1	-1.3
Pb, µg/L	3.59	3.45	3.00	3.00	3.52	17.3	2.8	1.7
Zn, µg/L	10.09	10.51	15.12	15.12	10.30	-31.9	2.9	-2.7
Hg, µg/L	0.003	0.004	0.023	0.023	0.004	-83.9	19.1	-2.0

No. components	13	13

Laboratory
Code no.: **5**

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L	0.238	0.216	9.9
NO_3-N, mg/L	4.48	5.02	-10.8
NO_2-N, mg/L	0.244	0.207	17.8
N-total, mg/L	5.31	6.30	-15.7
PO_4-P, mg/L	0.126	0.137	-7.8
P-total, mg/L	0.196	0.184	6.6
Cd, µg/L	1.15	1.26	-8.8
Cr, µg/L	6.83	6.82	0.1
Cu, µg/L	22.1	14.8	49.2
Ni, µg/L	16.4	18.8	-12.5
Pb, µg/L	12.3	12.8	-4.1
Zn, µg/L	14.9	34.3	-56.7
Hg, µg/L	0.009	0.073	-88.1

No. components	13

Laboratory
Code no.: **6**

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.128	0.128				
NO_3-N, mg/L			5.01	5.01				
NO_2-N, mg/L			0.140	0.140				
N-total, mg/L			6.04	6.04				
PO_4-P, mg/L			0.028	0.028				
P-total, mg/L			0.047	0.047				
Cd, µg/L	0.26	0.26	0.312	0.312	0.260	-16.6	0.0	-1.7
Cr, µg/L	5.00	5.20	4.22	4.22	5.10	20.9	2.8	1.9
Cu, µg/L	6.20	6.00	6.84	6.84	6.10	-10.8	2.3	-0.6
Ni, µg/L	9.40	9.20	8.72	8.72	9.30	6.7	1.5	0.5
Pb, µg/L	3.00	2.90	3.00	3.00	2.95	-1.7	2.4	-0.2
Zn, µg/L	14.90	14.80	15.12	15.12	14.85	-1.8	0.5	-0.1
Hg, µg/L	0.028	0.028	0.023	0.023	0.028	21.7	0.0	0.5

No. components	7	7

Laboratory
Code no.: **6**

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev %
NH_4-N, mg/L		0.216	
NO_3-N, mg/L		5.02	
NO_2-N, mg/L		0.207	
N-total, mg/L		6.30	
PO_4-P, mg/L		0.137	
P-total, mg/L		0.184	
Cd, µg/L	1.00	1.26	-20.7
Cr, µg/L	7.70	6.82	12.9
Cu, µg/L	13.4	14.8	-9.3
Ni, µg/L	19.2	18.8	2.3
Pb, µg/L	12.4	12.8	-3.0
Zn, µg/L	34.2	34.3	-0.3
Hg, µg/L	0.093	0.073	27.1

No. components	7

Laboratory
Code no.: 7

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.269	0.265	0.128	0.128	0.267	108.7	1.2	2.1
NO_3-N, mg/L			5.01	5.01				
NO_2-N, mg/L			0.140	0.140				
N-total, mg/L	136.00	140.00	6.04	6.04	138.00	2184.8	2.0	437.0
PO_4-P, mg/L	0.018	0.019	0.028	0.028	0.019	-33.6	2.5	-1.0
P-total, mg/L	0.074	0.074	0.047	0.047	0.074	58.2	0.3	1.9
Cd, µg/L	0.328	0.327	0.312	0.312	0.328	5.0	0.2	0.5
Cr, µg/L	4.24	4.15	4.22	4.22	4.20	-0.6	1.5	-0.1
Cu, µg/L	6.74	6.59	6.84	6.84	6.67	-2.6	1.6	-0.2
Ni, µg/L	8.82	8.58	8.72	8.72	8.70	-0.2	2.0	0.0
Pb, µg/L	2.90	2.87	3.00	3.00	2.89	-3.8	0.7	-0.4
Zn, µg/L	15.70	15.30	15.12	15.12	15.50	2.5	1.8	0.2
Hg, µg/L	0.060	0.020	0.023	0.023	0.040	73.3	70.4	1.7

No. components	11	11

Laboratory
Code no.: 7

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev %
NH_4-N, mg/L	0.254	0.216	17.5
NO_3-N, mg/L		5.02	
NO_2-N, mg/L		0.207	
N-total, mg/L	142	6.30	2154.3
PO_4-P, mg/L	0.018	0.137	-86.6
P-total, mg/L	0.073	0.184	-60.1
Cd, µg/L	1.29	1.26	2.3
Cr, µg/L	7.17	6.82	5.1
Cu, µg/L	14.8	14.8	0.2
Ni, µg/L	18.4	18.8	-1.9
Pb, µg/L	12.2	12.8	-4.5
Zn, µg/L	38.1	34.3	11.1
Hg, µg/L	0.0783	0.073	7.0

No. components	11

Laboratory
Code no.: **8**

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.074	0.055	0.128	0.128	0.065	-49.6	20.8	-1.0
NO_3-N, mg/L	4.85	4.87	5.01	5.01	4.86	-3.1	0.2	-0.6
NO_2-N, mg/L	0.14	0.117	0.140	0.140	0.129	-8.2	12.7	-0.4
N-total, mg/L	5.95	6.00	6.04	6.04	5.98	-1.1	0.6	-0.2
PO_4-P, mg/L	0.025	0.019	0.028	0.028	0.022	-21.4	19.3	-0.6
P-total, mg/L	0.04	0.034	0.047	0.047	0.037	-20.5	11.5	-0.7
Cd, µg/L	0.33	0.34	0.312	0.312	0.335	7.4	2.1	0.7
Cr, µg/L	3.41	3.54	4.22	4.22	3.48	-17.7	2.6	-1.6
Cu, µg/L	5.50	5.71	6.84	6.84	5.61	-18.1	2.6	-1.1
Ni, µg/L	7.58	7.92	8.72	8.72	7.75	-11.1	3.1	-0.9
Pb, µg/L	3.15	3.16	3.00	3.00	3.16	5.2	0.2	0.5
Zn, µg/L	15.02	15.65	15.12	15.12	15.34	1.4	2.9	0.1
Hg, µg/L	0.020	0.030	0.023	0.023	0.025	8.7	28.3	0.2

No. components	13	13

Laboratory
Code no.: **8**

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev %
NH_4-N, mg/L	0.15	0.216	-30.6
NO_3-N, mg/L	4.83	5.02	-3.8
NO_2-N, mg/L	0.19	0.207	-8.1
N-total, mg/L	6.07	6.30	-3.6
PO_4-P, mg/L	0.128	0.137	-6.3
P-total, mg/L	0.179	0.184	-2.6
Cd, µg/L	1.30	1.26	3.1
Cr, µg/L	5.73	6.82	-16.0
Cu, µg/L	13.0	14.8	-11.9
Ni, µg/L	17.0	18.8	-9.5
Pb, µg/L	13.5	12.8	5.6
Zn, µg/L	34.9	34.3	1.8
Hg, µg/L	0.07	0.073	-4.3

No. components	13

Laboratory
Code no.: **9**

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.166	0.119	0.128	0.128	0.143	11.4	23.3	0.2
NO_3-N, mg/L	4.78	4.82	5.01	5.01	4.80	-4.2	0.6	-0.8
NO_2-N, mg/L	0.11	0.1	0.140	0.140	0.105	-25.0	6.7	-1.3
N-total, mg/L	6.18	6.36	6.04	6.04	6.27	3.8	2.0	0.8
PO_4-P, mg/L			0.028	0.028				
P-total, mg/L			0.047	0.047				
Cd, µg/L	0.289	0.331	0.312	0.312	0.310	-0.6	9.6	-0.1
Cr, µg/L	4.23	4.23	4.22	4.22	4.23	0.2	0.0	0.0
Cu, µg/L	6.48	5.35	6.84	6.84	5.92	-13.5	13.5	-0.8
Ni, µg/L	8.96	8.98	8.72	8.72	8.97	2.9	0.2	0.2
Pb, µg/L	2.54	2.37	3.00	3.00	2.46	-18.2	4.9	-1.8
Zn, µg/L	15.40	15.60	15.12	15.12	15.50	2.5	0.9	0.2
Hg, µg/L	0.021	0.021	0.023	0.023	0.021	-8.7	0.0	-0.2

No. components	11	11

Laboratory
Code no.: **9**

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev %
NH_4-N, mg/L	0.298	0.216	37.9
NO_3-N, mg/L	4.80	5.02	-4.5
NO_2-N, mg/L	0.134	0.207	-35.2
N-total, mg/L	6.12	6.30	-2.8
PO_4-P, mg/L		0.137	
P-total, mg/L		0.184	
Cd, µg/L	1.30	1.26	3.1
Cr, µg/L	6.87	6.82	0.7
Cu, µg/L	13.4	14.8	-9.3
Ni, µg/L	18.6	18.8	-0.9
Pb, µg/L	12.3	12.8	-3.7
Zn, µg/L	32.6	34.3	-4.9
Hg, µg/L	0.086	0.073	17.5

No. components	11

Laboratory
Code no.: **10**

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.128	0.128				
NO_3-N, mg/L	5.17	5.30	5.01	5.01	5.24	4.4	1.8	0.9
NO_2-N, mg/L	0.101	0.09	0.140	0.140	0.096	-31.8	8.1	-1.7
N-total, mg/L	5.40	6.48	6.04	6.04	5.94	-1.7	12.9	-0.3
PO_4-P, mg/L	0.014	0.014	0.028	0.028	0.014	-50.0	0.0	-1.5
P-total, mg/L	0.033	0.032	0.047	0.047	0.033	-30.2	2.2	-1.0
Cd, µg/L	0.35	0.35	0.312	0.312	0.350	12.2	0.0	1.2
Cr, µg/L	4.10	3.90	4.22	4.22	4.00	-5.2	3.5	-0.5
Cu, µg/L	7.80	7.60	6.84	6.84	7.70	12.6	1.8	0.7
Ni, µg/L	7.00	7.00	8.72	8.72	7.00	-19.7	0.0	-1.5
Pb, µg/L	2.80	2.90	3.00	3.00	2.85	-5.0	2.5	-0.5
Zn, µg/L	18.00	17.00	15.12	15.12	17.50	15.8	4.0	1.3
Hg, µg/L			0.023	0.023				

No. components	11	11

Laboratory
Code no.: **10**

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L		0.216	
NO_3-N, mg/L	5.49	5.02	9.3
NO_2-N, mg/L	0.033	0.207	-84.0
N-total, mg/L	7.25	6.30	15.1
PO_4-P, mg/L	0.137	0.137	0.3
P-total, mg/L	0.148	0.184	-19.5
Cd, µg/L	1.20	1.26	-4.8
Cr, µg/L	6.30	6.82	-7.7
Cu, µg/L	15.8	14.8	6.9
Ni, µg/L	18.8	18.8	0.2
Pb, µg/L	14.0	12.8	9.6
Zn, µg/L	34.0	34.3	-0.9
Hg, µg/L		0.073	-100.0

No. components	11

Laboratory
Code no.: **11**

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.1519	0.1689	0.128	0.128	0.160	25.3	7.5	0.5
NO_3-N, mg/L			5.01	5.01				
NO_2-N, mg/L			0.140	0.140				
N-total, mg/L	5.93	5.88	6.04	6.04	5.90	-2.3	0.6	-0.5
PO_4-P, mg/L	0.03052	0.03533	0.028	0.028	0.033	17.6	10.3	0.5
P-total, mg/L	0.045	0.0504	0.047	0.047	0.048	2.5	8.0	0.1
Cd, µg/L	0.3185	0.3319	0.312	0.312	0.325	4.3	2.9	0.4
Cr, µg/L	3.92	4.07	4.22	4.22	4.00	-5.3	2.7	-0.5
Cu, µg/L	6.87	6.97	6.84	6.84	6.92	1.2	1.0	0.1
Ni, µg/L	11.50	11.50	8.72	8.72	11.50	31.9	0.0	2.5
Pb, µg/L	2.88	2.89	3.00	3.00	2.89	-3.8	0.2	-0.4
Zn, µg/L	14.90	15.10	15.12	15.12	15.00	-0.8	0.9	-0.1
Hg, µg/L			0.023	0.023				

No. components	10	10

Laboratory
Code no.: **11**

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L	0.330	0.216	52.5
NO_3-N, mg/L		5.02	
NO_2-N, mg/L		0.207	
N-total, mg/L	5.81	6.30	-7.7
PO_4-P, mg/L	0.146	0.137	7.0
P-total, mg/L	0.204	0.184	10.9
Cd, µg/L	1.28	1.26	1.6
Cr, µg/L	6.65	6.82	-2.5
Cu, µg/L	16.0	14.8	8.3
Ni, µg/L	23.0	18.8	22.6
Pb, µg/L	12.5	12.8	-2.2
Zn, µg/L	33.7	34.3	-1.7
Hg, µg/L		0.073	

No. components	10

Laboratory

Code no.: 13

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.168	0.158	0.128	0.128	0.163	27.4	4.3	0.5
NO_3-N, mg/L	5.07	5.03	5.01	5.01	5.05	0.8	0.6	0.2
NO_2-N, mg/L	0.116	0.108	0.140	0.140	0.112	-20.0	5.1	-1.1
N-total, mg/L	6.24	6.15	6.04	6.04	6.20	2.6	1.0	0.5
PO_4-P, mg/L	0.045	0.043	0.028	0.028	0.044	56.7	2.6	1.7
P-total, mg/L	0.060	0.067	0.047	0.047	0.064	36.4	7.8	1.2
Cd, µg/L			0.312	0.312				
Cr, µg/L	4.04	3.93	4.22	4.22	3.99	-5.6	2.0	-0.5
Cu, µg/L	5.65	5.48	6.84	6.84	5.57	-18.6	2.2	-1.1
Ni, µg/L	9.12	8.94	8.72	8.72	9.03	3.6	1.4	0.3
Pb, µg/L			3.00	3.00				
Zn, µg/L	15.60	15.50	15.12	15.12	15.55	2.9	0.5	0.2
Hg, µg/L	0.029	0.028	0.023	0.023	0.029	23.9	2.5	0.6

No. components	11	11

Laboratory

Code no.: 13

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L	0.325	0.216	50.4
NO_3-N, mg/L	5.05	5.02	0.5
NO_2-N, mg/L	0.141	0.207	-31.8
N-total, mg/L	6.38	6.30	1.3
PO_4-P, mg/L	0.131	0.137	-4.3
P-total, mg/L	0.164	0.184	-10.8
Cd, µg/L	1.32	1.26	4.7
Cr, µg/L	6.22	6.82	-8.8
Cu, µg/L	13.2	14.8	-10.7
Ni, µg/L	18.4	18.8	-2.0
Pb, µg/L	12.2	12.8	-4.5
Zn, µg/L	34.5	34.3	0.6
Hg, µg/L	0.094	0.073	28.5

No. components	13

Laboratory

Code no.: 14

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.128	0.128				
NO_3-N, mg/L	5.01	5.02	5.01	5.01	5.01	0.0	0.1	0.0
NO_2-N, mg/L	0.157	0.162	0.140	0.140	0.160	14.0	2.4	0.7
N-total, mg/L	5.96	6.00	6.04	6.04	5.98	-1.0	0.4	-0.2
PO_4-P, mg/L			0.028	0.028				
P-total, mg/L	0.021	0.022	0.047	0.047	0.021	-54.8	3.0	-1.8
Cd, µg/L	0.32	0.32	0.312	0.312	0.320	2.6	0.0	0.3
Cr, µg/L	4.23	4.29	4.22	4.22	4.26	0.9	1.0	0.1
Cu, µg/L	7.76	7.55	6.84	6.84	7.66	11.9	1.9	0.7
Ni, µg/L	8.58	8.71	8.72	8.72	8.65	-0.9	1.1	-0.1
Pb, µg/L	3.08	2.97	3.00	3.00	3.03	0.8	2.6	0.1
Zn, µg/L	14.50	14.90	15.12	15.12	14.70	-2.8	1.9	-0.2
Hg, µg/L	0.022	0.022	0.023	0.023	0.022	-4.3	0.0	-0.1

No. components	11	11

Laboratory

Code no.: 14

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L		0.216	
NO_3-N, mg/L	5.12	5.02	2.0
NO_2-N, mg/L	0.234	0.207	13.4
N-total, mg/L	6.13	6.30	-2.7
PO_4-P, mg/L	0.166	0.137	21.3
P-total, mg/L	0.166	0.184	-9.7
Cd, µg/L	1.27	1.26	0.7
Cr, µg/L	6.92	6.82	1.4
Cu, µg/L	15.9	14.8	7.6
Ni, µg/L	18.6	18.8	-0.9
Pb, µg/L	12.7	12.8	-0.6
Zn, µg/L	32.8	34.3	-4.4
Hg, µg/L	0.081	0.073	10.7

No. components	12

Laboratory

Code no.: 15

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.128	0.128				
NO_3-N, mg/L	4.86	4.83	5.01	5.01	4.85	-3.3	0.4	-0.7
NO_2-N, mg/L	0.141	0.134	0.140	0.140	0.138	-1.8	3.6	-0.1
N-total, mg/L	6.20	6.10	6.04	6.04	6.15	1.8	1.1	0.4
PO_4-P, mg/L	0.039	0.036	0.028	0.028	0.038	34.0	6.1	1.0
P-total, mg/L	0.059	0.054	0.047	0.047	0.057	21.4	6.3	0.7
Cd, µg/L	0.29	0.36	0.312	0.312	0.325	4.2	15.2	0.4
Cr, µg/L	4.10	4.20	4.22	4.22	4.15	-1.7	1.7	-0.2
Cu, µg/L	7.20	6.90	6.84	6.84	7.05	3.1	3.0	0.2
Ni, µg/L	8.70	9.00	8.72	8.72	8.85	1.5	2.4	0.1
Pb, µg/L	3.05	3.33	3.00	3.00	3.19	6.3	6.2	0.6
Zn, µg/L			15.12	15.12				
Hg, µg/L	0.025	0.029	0.023	0.023	0.027	17.4	10.5	0.4

No. components	11	11

Laboratory

Code no.: 15

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L		0.216	
NO_3-N, mg/L	4.83	5.02	-3.9
NO_2-N, mg/L	0.222	0.207	7.4
N-total, mg/L	6.30	6.30	0.0
PO_4-P, mg/L	0.130	0.137	-4.5
P-total, mg/L	0.20	0.184	8.8
Cd, µg/L	1.41	1.26	11.8
Cr, µg/L	6.70	6.82	-1.8
Cu, µg/L	15.8	14.8	6.9
Ni, µg/L	18.6	18.8	-0.9
Pb, µg/L	13.8	12.8	8.0
Zn, µg/L		34.3	
Hg, µg/L	0.086	0.073	17.5

No. components	11

Laboratory

Code no.: 16

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.128	0.128				
NO_3-N, mg/L	5.04	5.15	5.01	5.01	5.09	1.6	1.6	0.3
NO_2-N, mg/L	0.122	0.115	0.140	0.140	0.119	-15.2	4.4	-0.8
N-total, mg/L	5.61	6.04	6.04	6.04	5.83	-3.6	5.2	-0.7
PO_4-P, mg/L	0.016	0.017	0.028	0.028	0.017	-40.9	4.5	-1.2
P-total, mg/L	0.026	0.026	0.047	0.047	0.026	-43.9	1.1	-1.5
Cd, µg/L	0.273	0.302	0.312	0.312	0.288	-7.8	7.1	-0.8
Cr, µg/L	3.97	4.02	4.22	4.22	4.00	-5.3	0.9	-0.5
Cu, µg/L	7.43	7.58	6.84	6.84	7.51	9.7	1.4	0.6
Ni, µg/L	8.41	8.33	8.72	8.72	8.37	-4.0	0.7	-0.3
Pb, µg/L	3.67	3.38	3.00	3.00	3.53	17.5	5.8	1.8
Zn, µg/L	16.30	16.90	15.12	15.12	16.60	9.8	2.6	0.8
Hg, µg/L	0.014	0.013	0.023	0.023	0.014	-40.4	6.2	-0.9

No. components	12	12

Laboratory

Code no.: 16

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L		0.216	
NO_3-N, mg/L	5.30	5.02	5.4
NO_2-N, mg/L	0.035	0.207	-83.1
N-total, mg/L	6.52	6.30	3.5
PO_4-P, mg/L	0.119	0.137	-12.9
P-total, mg/L	0.141	0.184	-23.2
Cd, µg/L	1.14	1.26	-9.7
Cr, µg/L	6.60	6.82	-3.3
Cu, µg/L	16.2	14.8	9.6
Ni, µg/L	18.1	18.8	-3.5
Pb, µg/L	14.5	12.8	13.2
Zn, µg/L	35.3	34.3	2.9
Hg, µg/L	0.063	0.073	-13.9

No. components	12

Laboratory

Code no.: 17

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.123	0.121	0.128	0.128	0.122	-4.7	0.9	-0.1
NO_3-N, mg/L	4.70	4.74	5.01	5.01	4.72	-5.8	0.7	-1.2
NO_2-N, mg/L	0.188	0.177	0.140	0.140	0.182	30.2	4.4	1.6
N-total, mg/L			6.04	6.04				
PO_4-P, mg/L	0.033	0.022	0.028	0.028	0.027	-2.3	27.7	-0.1
P-total, mg/L	0.057	0.040	0.047	0.047	0.049	4.8	24.6	0.2
Cd, µg/L	0.316	0.302	0.312	0.312	0.309	-0.9	3.2	-0.1
Cr, µg/L	4.90	5.07	4.22	4.22	4.99	18.1	2.4	1.6
Cu, µg/L	6.95	6.83	6.84	6.84	6.89	0.7	1.2	0.0
Ni, µg/L	9.04	9.20	8.72	8.72	9.12	4.6	1.2	0.4
Pb, µg/L	2.90	2.81	3.00	3.00	2.86	-4.8	2.2	-0.5
Zn, µg/L	15.05	14.85	15.12	15.12	14.95	-1.1	0.9	-0.1
Hg, µg/L			0.023	0.023				

No. components	11	11

Laboratory

Code no.: 17

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L	0.238	0.216	10.3
NO_3-N, mg/L	4.59	5.02	-8.7
NO_2-N, mg/L	0.291	0.207	40.8
N-total, mg/L		6.30	
PO_4-P, mg/L	0.118	0.137	-13.6
P-total, mg/L	0.193	0.184	5.0
Cd, µg/L	1.33	1.26	5.5
Cr, µg/L	7.57	6.82	11.0
Cu, µg/L	15.6	14.8	5.7
Ni, µg/L	19.7	18.8	5.2
Pb, µg/L	12.4	12.8	-3.2
Zn, µg/L	33.7	34.3	-1.8
Hg, µg/L		0.073	

No. components	11

Laboratory

Code no.: **18**

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.128	0.128				
NO_3-N, mg/L	5.15	5.12	5.01	5.01	5.14	2.4	0.4	0.5
NO_2-N, mg/L	0.154	0.148	0.140	0.140	0.151	7.9	2.8	0.4
N-total, mg/L	6.25	6.24	6.04	6.04	6.25	3.4	0.1	0.7
PO_4-P, mg/L	0.034	0.031	0.028	0.028	0.033	16.8	7.4	0.5
P-total, mg/L	0.053	0.047	0.047	0.047	0.050	7.1	7.8	0.2
Cd, µg/L	0.311	0.327	0.312	0.312	0.319	2.3	3.5	0.2
Cr, µg/L	4.78	4.79	4.22	4.22	4.79	13.4	0.1	1.2
Cu, µg/L	7.28	7.19	6.84	6.84	7.24	5.8	0.9	0.3
Ni, µg/L	9.61	9.62	8.72	8.72	9.62	10.3	0.1	0.8
Pb, µg/L	2.73	2.79	3.00	3.00	2.76	-8.0	1.5	-0.8
Zn, µg/L	17.10	17.30	15.12	15.12	17.20	13.8	0.8	1.1
Hg, µg/L	0.043	0.040	0.023	0.023	0.042	80.4	5.1	1.9

No. components	12	12

Laboratory

Code no.: **18**

Components	Measured value	Assigned values	Statistics
	Fresh Water C	C	Dev. %
NH_4-N, mg/L		0.216	
NO_3-N, mg/L	5.05	5.02	0.5
NO_2-N, mg/L	0.192	0.207	-7.1
N-total, mg/L	6.37	6.30	1.1
PO_4-P, mg/L	0.136	0.137	-0.4
P-total, mg/L	0.191	0.184	3.9
Cd, µg/L	1.28	1.26	1.5
Cr, µg/L	7.84	6.82	14.9
Cu, µg/L	16.3	14.8	10.3
Ni, µg/L	20.6	18.8	9.8
Pb, µg/L	11.5	12.8	-10.0
Zn, µg/L	37.8	34.3	10.2
Hg, µg/L	0.062	0.073	-15.3

No. components	12

3.3 Waste water

Laboratory Code no.: 1

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.023	0.023	0.030	0.030	0.023	-21.0	0.0	-0.66
NO_3-N, mg/L	1.36	1.37	1.24	1.24	1.36	10.0	0.2	1.67
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	2.69	2.43	1.91	1.91	2.56	34.0	7.2	2.43
PO_4-P, mg/L	0.147	0.150	0.140	0.140	0.149	6.3	1.4	0.91
P-total, mg/L	0.147	0.149	0.166	0.166	0.148	-10.8	1.0	-0.83
Cd, µg/L	1.49	1.55	1.65	1.65	1.52	-7.9	2.8	-1.58
Cr, µg/L	10.3	9.53	10.24	10.24	9.92	-3.2	5.5	-0.32
Cu, µg/L	81.0	83.0	84.5	84.5	82.0	-3.0	1.7	-0.42
Ni, µg/L	25.8	23.8	28.0	28.0	24.8	-11.5	5.7	-1.28
Pb, µg/L	73.0	74.0	81.5	81.5	73.5	-9.8	1.0	-1.09
Zn, µg/L	93.0	94.0	94.0	94.0	93.5	-0.5	0.8	-0.07
Hg, µg/L	0.16	0.157	0.169	0.169	0.159	-6.2	1.3	-0.62

No. components	12	12

Laboratory Code no.: 2

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.030	0.030				
NO_3-N, mg/L	1.27	1.27	1.24	1.24	1.27	2.4	0.0	0.40
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	1.79	1.75	1.91	1.91	1.77	-7.3	1.6	-0.52
PO4-P, mg/L	0.16	0.16	0.140	0.140	0.160	14.3	0.0	2.04
P-total, mg/L	0.16	0.16	0.166	0.166	0.160	-3.6	0.0	-0.28
Cd, µg/L			1.65	1.65				
Cr, µg/L			10.24	10.24				
Cu, µg/L			84.5	84.5				
Ni, µg/L			28.0	28.0				
Pb, µg/L			81.5	81.5				
Zn, µg/L			94.0	94.0				
Hg, µg/L	0.187	0.189	0.169	0.169	0.188	11.2	0.8	1.12

No. components	5	5

Laboratory Code no.: 3

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.036	0.031	0.030	0.030	0.033	12.7	9.6	0.40
NO_3-N, mg/L	1.24	1.24	1.24	1.24	1.24	0.1	0.3	0.02
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	1.92	1.86	1.91	1.91	1.89	-1.0	2.2	-0.07
PO_4-P, mg/L	0.137	0.144	0.140	0.140	0.141	0.4	3.9	0.05
P-total, mg/L	0.175	0.171	0.166	0.166	0.173	3.9	1.6	0.30
Cd, µg/L			1.65	1.65				
Cr, µg/L			10.24	10.24				
Cu, µg/L			84.5	84.5				
Ni, µg/L			28.0	28.0				
Pb, µg/L			81.5	81.5				
Zn, µg/L			94.0	94.0				
Hg, µg/L			0.169	0.169				

No. components	5	5

Laboratory Code no.: 4

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.023	0.019	0.030	0.030	0.021	-28.8	13.5	-0.90
NO_3-N, mg/L	1.27	1.27	1.24	1.24	1.27	2.6	0.2	0.44
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	1.84	1.85	1.91	1.91	1.85	-3.4	0.2	-0.24
PO_4-P, mg/L	0.138	0.138	0.140	0.140	0.138	-1.4	0.0	-0.20
P-total, mg/L	0.145	0.147	0.166	0.166	0.146	-12.0	1.0	-0.93
Cd, µg/L	1.77	1.73	1.65	1.65	1.75	6.1	2.0	1.21
Cr, µg/L	10.7	10.6	10.24	10.24	10.63	3.8	0.6	0.38
Cu, µg/L	87.0	87.1	84.5	84.5	87.0	3.0	0.1	0.43
Ni, µg/L	27.6	27.6	28.0	28.0	27.6	-1.6	0.0	-0.18
Pb, µg/L	83.2	83.4	81.5	81.5	83.3	2.2	0.1	0.25
Zn, µg/L	96.3	96.2	94.0	94.0	96.3	2.5	0.0	0.35
Hg, µg/L			0.169	0.169				

No. components	11	11

Laboratory
Code no.: 5

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.109	0.091	0.030	0.030	0.100	239.5	13.2	7.49
NO_3-N, mg/L	1.24	1.23	1.24	1.24	1.24	-0.3	0.3	-0.06
NO_2-N, mg/L	0.001	0.001	0.001	0.001	0.001	-4.9	13.2	-0.13
N-total, mg/L	1.68	1.63	1.91	1.91	1.66	-13.4	2.1	-0.95
PO_4-P, mg/L	0.131	0.132	0.140	0.140	0.131	-6.2	0.5	-0.89
P-total, mg/L	0.151	0.147	0.166	0.166	0.149	-10.2	1.9	-0.79
Cd, µg/L	1.49	1.57	1.65	1.65	1.53	-7.3	3.7	-1.45
Cr, µg/L	8.12	8.48	10.24	10.24	8.30	-18.9	3.1	-1.89
Cu, µg/L	98.1	90.6	84.5	84.5	94.4	11.7	5.6	1.67
Ni, µg/L	29.69	26.5	28.0	28.0	28.1	0.3	8.0	0.03
Pb, µg/L	92.2	85.1	81.5	81.5	88.6	8.8	5.7	0.97
Zn, µg/L	81.5	92.5	94.0	94.0	87.0	-7.4	8.9	-1.06
Hg, µg/L	0.0352	0.0419	0.169	0.169	0.039	-77.2	12.3	-7.72

No. components	13	13

Laboratory
Code no.: 6

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.030	0.030				
NO_3-N, mg/L			1.24	1.24				
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L			1.91	1.91				
PO_4-P, mg/L			0.140	0.140				
P-total, mg/L			0.166	0.166				
Cd, µg/L	1.58	1.59	1.65	1.65	1.59	-3.9	0.4	-0.79
Cr, µg/L	10	9.9	10.24	10.24	9.95	-2.8	0.7	-0.28
Cu, µg/L	84.7	84.4	84.5	84.5	84.6	0.1	0.3	0.01
Ni, µg/L	28.9	27.5	28.0	28.0	28.2	0.6	3.5	0.07
Pb, µg/L	80.8	82.0	81.5	81.5	81.4	-0.1	1.0	-0.01
Zn, µg/L	89.3	90.3	94.0	94.0	89.8	-4.4	0.8	-0.63
Hg, µg/L	0.17	0.17	0.169	0.169	0.170	0.6	0.0	0.06

No. components	7	7

Laboratory Code no.: 8

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.019	0.017	0.030	0.030	0.018	-39.0	7.9	-1.22
NO_3-N, mg/L	1.37	1.38	1.24	1.24	1.37	10.7	0.3	1.78
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	1.81	1.82	1.91	1.91	1.82	-5.0	0.4	-0.36
PO_4-P, mg/L	0.14	0.141	0.140	0.140	0.141	0.4	0.5	0.05
P-total, mg/L	0.144	0.147	0.166	0.166	0.146	-12.3	1.5	-0.95
Cd, µg/L	1.8	1.81	1.65	1.65	1.81	9.4	0.4	1.88
Cr, µg/L	8.92	8.67	10.24	10.24	8.80	-14.1	2.0	-1.41
Cu, µg/L	74.7	76.0	84.5	84.5	75.3	-10.9	1.2	-1.55
Ni, µg/L	24.05	24.43	28.0	28.0	24.2	-13.5	1.1	-1.50
Pb, µg/L	74.8	75.8	81.5	81.5	75.3	-7.6	1.0	-0.84
Zn, µg/L	98.8	100.0	94.0	94.0	99.4	5.8	0.8	0.83
Hg, µg/L	0.18	0.19	0.169	0.169	0.185	9.5	3.8	0.95

No. components	12	12

Laboratory Code no.: 9

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.055	0.038	0.030	0.030	0.047	57.6	25.9	1.80
NO_3-N, mg/L	1.23	1.23	1.24	1.24	1.23	-0.8	0.0	-0.13
NO_2-N, mg/L	0.001	0.001	0.001	0.001	0.001	-16.7	0.0	-0.45
N-total, mg/L	2.08	2.35	1.91	1.91	2.22	16.0	8.6	1.14
PO_4-P, mg/L			0.140	0.140				
P-total, mg/L			0.166	0.166				
Cd, µg/L	1.63	1.64	1.65	1.65	1.64	-0.9	0.4	-0.18
Cr, µg/L	10.1	9.84	10.24	10.24	9.97	-2.6	1.8	-0.26
Cu, µg/L	74.0	75.2	84.5	84.5	74.6	-11.7	1.1	-1.67
Ni, µg/L	32.4	28.9	28.0	28.0	30.7	9.4	8.1	1.04
Pb, µg/L	85.8	87.2	81.5	81.5	86.5	6.2	1.1	0.68
Zn, µg/L	91.5	91.9	94.0	94.0	91.7	-2.4	0.3	-0.34
Hg, µg/L	0.169	0.166	0.169	0.169	0.168	-0.9	1.3	-0.09

No. components	11	11

Laboratory Code no.: 11

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.04095	0.0347	0.030	0.030	0.038	28.2	11.7	0.88
NO_3-N, mg/L			1.24	1.24				
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	1.63	1.66	1.91	1.91	1.65	-13.7	1.3	-0.98
PO_4-P, mg/L	0.1469	0.1466	0.140	0.140	0.147	4.8	0.1	0.69
P-total, mg/L	0.1505	0.1568	0.166	0.166	0.154	-7.4	2.9	-0.57
Cd, µg/L	1.631	1.658	1.65	1.65	1.64	-0.3	1.2	-0.07
Cr, µg/L	10.1	10.7	10.24	10.24	10.40	1.6	4.1	0.16
Cu, µg/L	89.7	89.7	84.5	84.5	89.7	6.2	0.0	0.88
Ni, µg/L	34.0	34.1	28.0	28.0	34.1	21.5	0.2	2.39
Pb, µg/L	96.4	82.6	81.5	81.5	89.5	9.8	10.9	1.09
Zn, µg/L	83.5	87.1	94.0	94.0	85.3	-9.2	3.0	-1.32
Hg, µg/L			0.169	0.169				

No. components	10	10

Laboratory Code no.: 13

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.031	0.032	0.030	0.030	0.032	6.8	2.2	0.21
NO_3-N, mg/L	1.20	1.21	1.24	1.24	1.21	-2.8	0.6	-0.47
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	2.14	2.07	1.91	1.91	2.11	10.2	2.4	0.73
PO_4-P, mg/L	0.132	0.129	0.140	0.140	0.131	-6.7	1.6	-0.96
P-total, mg/L	0.145	0.145	0.166	0.166	0.145	-12.7	0.0	-0.97
Cd, µg/L	1.67	1.71	1.65	1.65	1.69	2.4	1.7	0.48
Cr, µg/L	10.52	9.87	10.24	10.24	10.20	-0.4	4.5	-0.04
Cu, µg/L	82.3	79.9	84.5	84.5	81.1	-4.0	2.1	-0.57
Ni, µg/L	27.9	25.1	28.0	28.0	26.5	-5.4	7.5	-0.60
Pb, µg/L	75.1	72.3	81.5	81.5	73.7	-9.5	2.7	-1.06
Zn, µg/L	94.8	90.2	94.0	94.0	92.5	-1.5	3.5	-0.22
Hg, µg/L	0.196	0.180	0.169	0.169	0.188	11.2	6.0	1.12

No. components	12	12

Laboratory
Code no.: **14**

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.030	0.030				
NO_3-N, mg/L	1.30	1.15	1.24	1.24	1.22	-1.3	8.7	-0.22
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	1.79	1.78	1.91	1.91	1.79	-6.5	0.2	-0.47
PO_4-P, mg/L	0.133	0.139	0.140	0.140	0.136	-2.7	3.2	-0.39
P-total, mg/L	0.166	0.173	0.166	0.166	0.170	2.1	2.9	0.16
Cd, µg/L	1.6	1.61	1.65	1.65	1.61	-2.7	0.4	-0.55
Cr, µg/L	10.7	10.8	10.24	10.24	10.75	5.0	0.7	0.50
Cu, µg/L	91.1	90.3	84.5	84.5	90.7	7.3	0.6	1.05
Ni, µg/L	27.5	27.6	28.0	28.0	27.6	-1.7	0.3	-0.19
Pb, µg/L	80.1	80.7	81.5	81.5	80.4	-1.3	0.5	-0.15
Zn, µg/L	92.5	88.0	94.0	94.0	90.3	-3.9	3.5	-0.56
Hg, µg/L	0.17	0.15	0.169	0.169	0.160	-5.3	8.8	-0.53

No. components	11	11

Laboratory
Code no.: **15**

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.027	0.026	0.030	0.030	0.027	-10.2	2.7	-0.32
NO_3-N, mg/L	1.14	1.14	1.24	1.24	1.14	-8.1	0.0	-1.34
NO_2-N, mg/L	0.002	0.002	0.001	0.001	0.002	58.3	0.0	1.58
N-total, mg/L	1.80	1.90	1.91	1.91	1.85	-3.1	3.8	-0.22
PO_4-P, mg/L			0.140	0.140				
P-total, mg/L	0.17	0.16	0.166	0.166	0.165	-0.6	4.3	-0.05
Cd, µg/L	1.78	1.75	1.65	1.65	1.77	7.0	1.2	1.39
Cr, µg/L	10.0	10.0	10.24	10.24	10.00	-2.3	0.0	-0.23
Cu, µg/L	79.6	79.0	84.5	84.5	79.3	-6.2	0.5	-0.88
Ni, µg/L	28.9	27.3	28.0	28.0	28.1	0.3	4.0	0.03
Pb, µg/L	82.1	94.0	81.5	81.5	88.1	8.1	9.6	0.90
Zn, µg/L	106.9	102.8	94.0	94.0	104.9	11.6	2.8	1.66
Hg, µg/L	0.206	0.270	0.169	0.169	0.238	40.8	19.0	4.08

No. components	12	12

Laboratory

Code no.: 16

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.030	0.030				
NO_3-N, mg/L	1.25	1.15	1.24	1.24	1.20	-3.0	6.0	-0.50
NO_2-N, mg/L	0.007	0.008	0.001	0.001	0.008	547.0	8.3	14.78
N-total, mg/L	1.77	1.79	1.91	1.91	1.78	-6.8	0.8	-0.49
PO_4-P, mg/L	0.127	0.127	0.140	0.140	0.127	-9.1	0.0	-1.31
P-total, mg/L	0.120	0.120	0.166	0.166	0.120	-27.7	0.0	-2.13
Cd, µg/L	1.577	1.566	1.65	1.65	1.57	-4.8	0.5	-0.95
Cr, µg/L	10.82	10.72	10.24	10.24	10.77	5.2	0.7	0.52
Cu, µg/L	88.8	90.0	84.5	84.5	89.4	5.8	0.9	0.83
Ni, µg/L	26.7	27.8	28.0	28.0	27.3	-2.7	2.9	-0.31
Pb, µg/L	87.1	88.9	81.5	81.5	88.0	8.0	1.4	0.89
Zn, µg/L	99.1	94.8	94.0	94.0	97.0	3.2	3.1	0.46
Hg, µg/L	0.143	0.138	0.169	0.169	0.141	-16.9	2.5	-1.69

No. components	12	12

Laboratory

Code no.: 17

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L	0.026	0.028	0.030	0.030	0.027	-7.6	5.6	-0.24
NO_3-N, mg/L	1.09	1.24	1.24	1.24	1.16	-6.2	9.1	-1.03
NO_2-N, mg/L	0.001	0.001	0.001	0.001	0.001	-23.6	4.7	-0.64
N-total, mg/L			1.91	1.91				
PO_4-P, mg/L	0.143	0.132	0.140	0.140	0.138	-1.8	5.7	-0.26
P-total, mg/L	0.208	0.199	0.166	0.166	0.204	22.6	3.1	1.74
Cd, µg/L	1.65	1.68	1.65	1.65	1.67	0.9	1.3	0.18
Cr, µg/L	10.82	10.93	10.24	10.24	10.88	6.2	0.7	0.62
Cu, µg/L	85.6	86.5	84.5	84.5	86.1	1.8	0.7	0.26
Ni, µg/L	26.88	27.35	28.0	28.0	27.1	-3.2	1.2	-0.36
Pb, µg/L	77.8	78.6	81.5	81.5	78.2	-4.1	0.7	-0.45
Zn, µg/L	91.2	92.4	94.0	94.0	91.8	-2.3	0.9	-0.32
Hg, µg/L			0.169	0.169				

No. components	11	11

Laboratory

Code no.: **18**

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH_4-N, mg/L			0.030	0.030				
NO_3-N, mg/L	1.25	1.25	1.24	1.24	1.25	0.8	0.0	0.13
NO_2-N, mg/L			0.001	0.001				
N-total, mg/L	1.86	1.87	1.91	1.91	1.87	-2.4	0.4	-0.17
PO_4-P, mg/L	0.149	0.143	0.140	0.140	0.146	4.3	2.9	0.61
P-total, mg/L	0.149	0.15	0.166	0.166	0.150	-9.9	0.5	-0.76
Cd, µg/L	1.61	1.71	1.65	1.65	1.66	0.6	4.3	0.12
Cr, µg/L	12.4	12.8	10.24	10.24	12.60	23.0	2.2	2.30
Cu, µg/L	93.1	95.5	84.5	84.5	94.3	11.6	1.8	1.66
Ni, µg/L	29.7	30.6	28.0	28.0	30.2	7.6	2.1	0.84
Pb, µg/L	71.1	74.6	81.5	81.5	72.9	-10.6	3.4	-1.18
Zn, µg/L	101.0	103.0	94.0	94.0	102.0	8.6	1.4	1.22
Hg, µg/L	0.164	0.158	0.169	0.169	0.161	-4.7	2.6	-0.47

No. components	11	11

4 Evaluation of results

For each component the following statistical analysis has been performed: For sample A and B (fresh water and waste water), table with the data presented for each component together with outlier test according to Cochran and Grubb, Youden plot and summary of the statistical parameters. For sample C, fresh water, table with the data presented for each component together with outlier test according to Grubb and a more limited summary of the statistical parameters. As the main part of the statistical calculations are based on duplicate samples these can obviously not be performed on sample C, freshwater. The statistical parameters are described below.

4.1 Description of the statistical parameters

The first table presents the results of the single components together with the outlier tests and the assigned value.

Cochran's and Grubb's outlier test are carried out according to ISO 5725-2 (2002). Cochran's test used to determine the consistency of single laboratory determinations on the test pair under repeatability conditions (which under specified conditions is regarded as a duplicate). Grubb's single and -double outlier tests are used on the laboratories, which are not outliers according to Cochran's test, in order to evaluate the consistency of the mean value on the test pair between the laboratories. The Grubb's double outlier test is performed on the two most extreme (highest and / or lowest) test pairs. Grubb's test for single or dual outlier tests were carried out for laboratories which are qualified for further statistical analysis, according to Cochran's test.

Youden plot: The aim of Youden plots, presented in this reports is to give an illustrative picture of position of individual laboratories relative to each other. The primary objective of the evaluations of individual round level is also to identify outliers in reported results.

Description of the Youden plots: In the Youden plots the data from the laboratories from sample pairs A and B is shown. The assigned values for test material are depicted with green lines parallel to the y, respectively x-axis. The red line represents y = x. In this presentation of the Youden plots we have chosen to show cut-off lines that represents the threshold for the outlier data and so-called stragglers based on Cochran's outlier test (light blue lines), respectively, Grubb's (yellow lines) single outlier test. A straggler has a data point which, according Cochran's test goes beyond the 5% (thin light blue line) but within 1% (bold light blue bar) levels. Stragglers are included in the further data analysis. Data lying outside the 1% outlier level are disqualified. Similar, for the Grubb's single outlier test for stragglers, that is data points located outside the thin yellow line but within the bold yellow line, are maintained in the further analysis. Data lying outside the bold yellow line deviates significantly from the common laboratory average. Laboratories with the highest precision and accuracy is within the rectangles formed by the thin blue and thin, yellow line, while those lying outside but still within bold lines in future will have an early and clear warning on their performance and demand for improvement. In cases where there is dual outlier according to Grubb's double- outlier these will be specifically marked with blue, bold font on the 5% level, and red, bold, italic font on the 1% level. A

tick means that the laboratory result is identified as an outlier. If the laboratory is determined as being an outlier according to Cochran's test, there will be a line in the cells under the Grubb's outlier test. Line marks the laboratory is not included in following Grubb's tests.

Table of summary statistics: For sample A and B a summary evaluation of the single components across the laboratories present a picture of the general analytical quality – outliers are not included. In the tables the following are shown. The tables consist of following parameters:

p: number of laboratories that is the laboratories that are included in the statistics, outliers excluded.

m: mean values of the results. The total mean value of all results from the participating laboratories without outliers. m is used as assigned value in the intercalibration.

S(L): Laboratory deviation is the deviation between the laboratories.

S(r): repeatability is the deviation between test pairs for all the laboratories.

S(R): reproducibility is the total deviation for the intercalibration ($S(R)^2=S(L)^2+S(r)^2$).

r: Repeatability limit is the value less than or equal to the absolute difference between test pairs that may be expected to be with a probability of 95% (r = S(r)*2.8).

R: Reproducibility limit is the value less than or equal to the absolute difference between two laboratories that may be expected to be with a probability of 95% (R = S(R)*2.8).

CV(r): Coefficient of laboratory variation is the relative deviation of laboratory variation, CV(r), is CV(r) = S(r)/m*100.

CV(R): Coefficient of total variation is the relative deviation (in %) of total variation, CV(R), is CV(R) = S(R)/ m*100.

For sample C, fresh water, only a revised Grubb's test was performed, which is shown in the first C table. Further the table shows the assigned value as a mean of the results from all laboratories, outliers excluded.

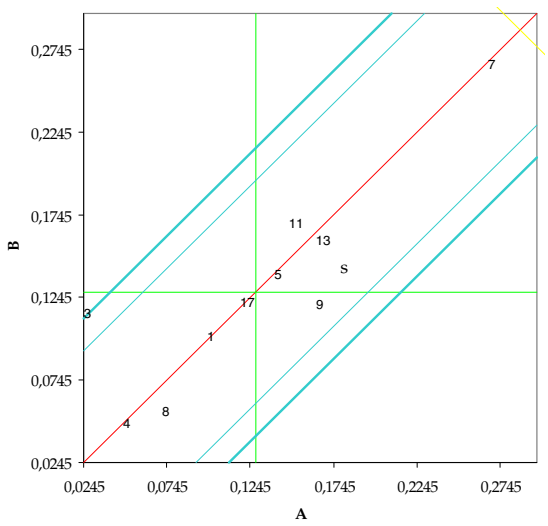
The summary statistic table for sample C consists of:

- **Laboratory deviation (S(L)** between the laboratories.
- **Relative laboratory deviation (%)** between the laboratories which is relative to the mean value.
- **Calculated spike value** based on the spike added to the sample.
- **Measured value of spike [µg/L]** based on measured mean concentration of sample C subtracted the mean concentration of sample A/B, and finally, the percentage recovery of the spike.
- **% recovery of spike** which is measured spike value relative to calculated spike value.

4.2 Statistical data for each component in fresh water

Component	*NH_4-N, mg/L*								
assigned value	0.128	0.128	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.101	0.101							
2									
3	0.027	0.114		X					
4	0.050	0.048							
5	0.141	0.138							
6									
7	0.269	0.265							
8	0.074	0.055							
9	0.166	0.119							
10									
11	0.152	0.169							
13	0.168	0.158							
14									
15									
16									
17	0.123	0.121							
18									

Youden plot for component NH4-N, mg/L



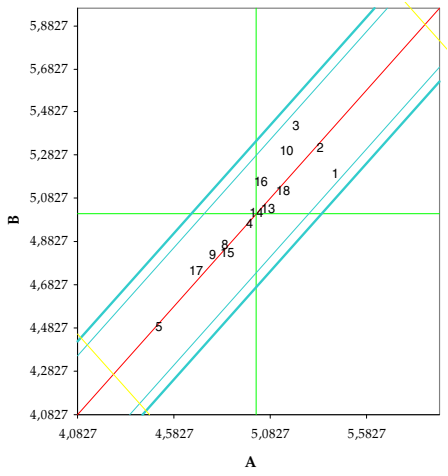
Statistical parameters	A/B fresh water NH_4-N
p	10
m [mg/L]	0.1280
S(L) [mg/L]	0.0612
S(r) [mg/L]	0.0242
S(R) [mg/L]	0.0658
R [mg/L]	0.0677
R [mg/L]	0.1842
CV(r) [%]	18.9
CV(R) [%]	51.0

Component	NH_4-N, mg/L					
assigned value	0.216	Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	C	1% level	5% level	1% level	5% level	
1	0.194					
2						
3	0.033					
4	0.102					
5	0.238					
6						
7	0.254					
8	0.150					
9	0.298					
10						
11	0.330					
13	0.325					
14						
15						
16						
17	0.238					
18						

Statistical analysis	C fresh water NH_4-N
Laboratory deviation (S(L) [mg/L]	0.097
Relative laboratory deviation (%)	45.1
Calculated spike value [mg/L]	0.064
Measured value of spike [mg/L]	0.088
% recovery of spike	138

Component	NO_3-N, mg/L								
assigned value	5.01	5.01	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	5.42	5.20							
2	5.34	5.32							
3	5.22	5.41							
4	4.98	4.96							
5	4.51	4.49							
6									
7									
8	4.85	4.86							
9	4.78	4.82							
10	5.17	5.30							
11									
13	5.07	5.03							
14	5.01	5.02							
15	4.86	4.83							
16	5.04	5.15							
17	4.70	4.74							
18	5.15	5.12							

Youden plot for component NO3-N, mg/L



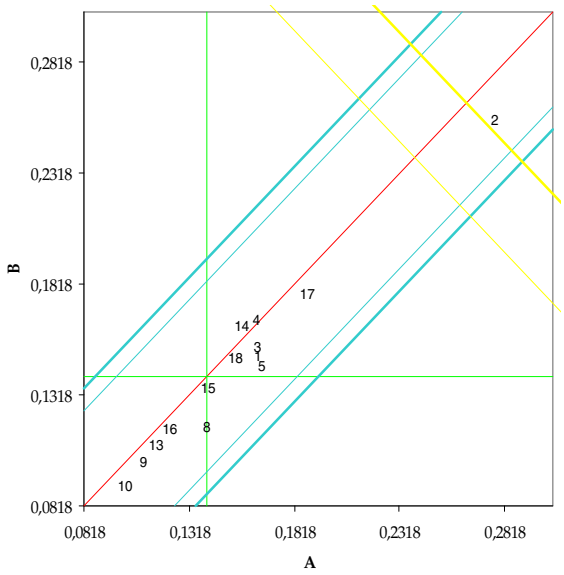
	A/B fresh water
Statistical parameters	NO_3-N
p	14
m [mg/L]	5.0123
S(L) [mg/L]	0.2431
S(r) [mg/L]	0.0696
S(R) [mg/L]	0.2529
r [mg/L]	0.1948
R [mg/L]	0.7080
CV(r) [%]	1.4
CV(R) [%]	5.0

Component	*NO_3-N, mgL*					
assigned value	**5.02**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	5.20					
2	5.55					
3	5.10					
4	4.95					
5	4.48					
6						
7						
8	4.83					
9	4.80					
10	5.49					
11						
13	5.05					
14	5.12					
15	4.83					
16	5.30					
17	4.59					
18	5.05					

Statistical analysis	**C fresh water NO_3-N**
Laboratory deviation (S(L) [mg/L]	0,308
Relative laboratory deviation (%)	6,1
Calculated spike value [mg/L]	0,043
Measured value of spike [mg/L]	spike too low
% recovery of spike	spike too low

Component	*NO_2-N, mgL*								
assigned value	**0.140**	**0.140**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.164	0.149							
2	0.277	0.255			X	X	-	-	X
3	0.164	0.152							
4	0.164	0.165							
5	0.166	0.145							
6									
7									
8	0.140	0.117							
9	0.110	0.100							
10	0.101	0.090							
11									
13	0.116	0.108							
14	0.157	0.162							
15	0.141	0.134							
16	0.122	0.115							
17	0.188	0.177							
18	0.154	0.148							

Youden plot for component NO2-N, mg/L



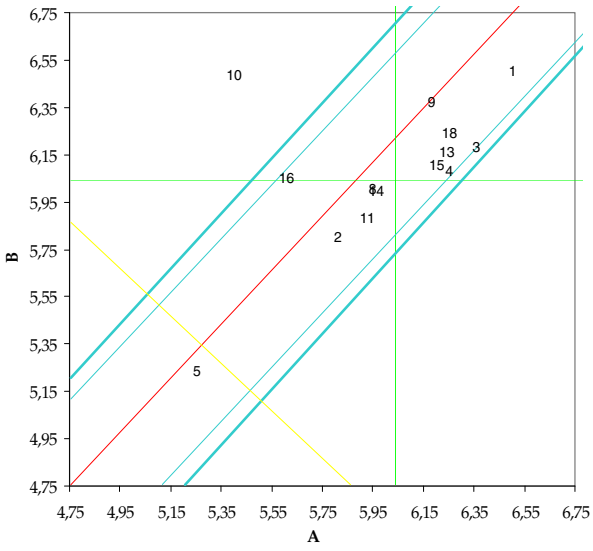
	A/B fresh water
Statistical parameters	**NO_2-N**
p	13
m [mg/L]	0.1404
S(L) [mg/L]	0.0260
S(r) [mg/L]	0.0055
S(R) [mg/L]	0.0266
r [mg/L]	0.0154
R [mg/L]	0.0745
CV(r) [%]	3.9
CV(R) [%]	19.0

Component	NO_2-N, mgL					
assigned value	0.207	Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	C	1% level	5% level	1% level	5% level	
1	0.213					
2	0.432					
3	0.289					
4	0.244					
5	0.244					
6						
7						
8	0.190					
9	0.134					
10	0.033					
11						
13	0.141					
14	0.234					
15	0.222					
16	0.035					
17	0.291					
18	0.192					

Statistical analysis	C fresh water NO_2-N
Laboratory deviation (S(L) [mg/L]	0.103
Relative laboratory deviation (%)	49.9
Calculated spike value [mg/L]	no spike
Measured value of spike [mg/L]	no spike
% recovery of spike	no spike

Component	*N-total, mgL*								
assigned value	6.04	6.04	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	6.50	6.50							
2	5.81	5.80							
3	6.36	6.17							
4	6.25	6.07							
5	5.25	5.23				X			
6									
7	136	140	X	X	-	-	-	-	X
8	5.95	6.00							
9	6.18	6.36							
10	5.40	6.48	X	X	-	-	-	-	X
11	5.93	5.88							
13	6.24	6.15							
14	5.96	5.99							
15	6.20	6.10							
16	5.61	6.04		X					
17									
18	6.25	6.24							

Youden plot for component N-total, mg/L



Laboratory 7 is excluded in the Youden plot of graphic reasons.

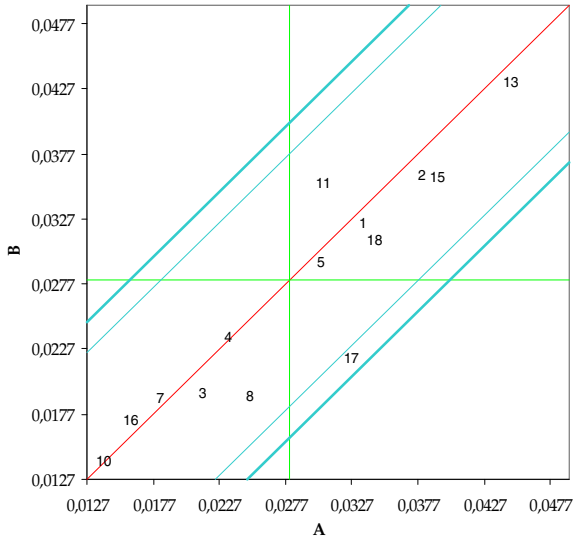
	A/B fresh water
Statistical parameters	**N-total**
p	14
m [mg/L]	6.0396
S(L) [mg/L]	0.3027
S(r) [mg/L]	0.1134
S(R) [mg/L]	0.3232
r [mg/L]	0.3174
R [mg/L]	0.9050
CV(r) [%]	1.9
CV(R) [%]	5.0

Component	*N-total, mgL*					
assigned value	**6.30**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.70					
2	6.04					
3	6.34					
4	6.84					
5	5.31					
6						
7	142.00	X	X	-	-	X
8	6.07					
9	6.12					
10	7.25					
11	5.81					
13	6.38					
14	6.13					
15	6.30					
16	6.52					
17						
18	6.37					

Statistical analysis	**C fresh water N-total**
Laboratory deviation (S(L) [mg/L]	0.465
Relative laboratory deviation (%)	7.4
Calculated spike value [mg/L]	0.273
Measured value of spike [mg/L]	0.259
% recovery of spike	95

Component	*PO_4-P, mgL*								
assigned value	0.028	0.028	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.034	0.032							
2	0.038	0.036							
3	0.021	0.019							
4	0.023	0.024							
5	0.030	0.029							
6									
7	0.018	0.019							
8	0.025	0.019							
9									
10	0.014	0.014							
11	0.031	0.035							
13	0.045	0.043							
14									
15	0.039	0.036							
16	0.016	0.017							
17	0.033	0.022		X					
18	0.034	0.031							

Youden plot for component PO4-P, mg/L



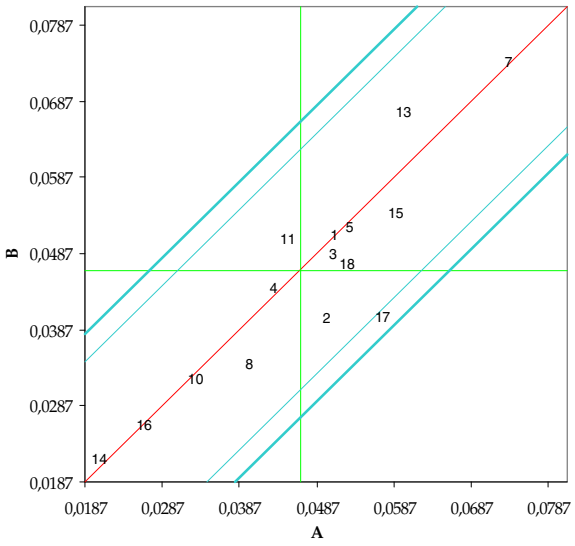
	A/B fresh water
Statistical parameters	**PO_4-P**
p	14
m [mg/L]	0.0278
S(L) [mg/L]	0.0087
S(r) [mg/L]	0.0025
S(R) [mg/L]	0.0091
r [mg/L]	0.0071
R [mg/L]	0.0254
CV(r) [%]	9.1
CV(R) [%]	33.0

Component	*PO_4-P, mgL*					
assigned value	**0.137**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.134					
2	0.174				X	
3	0.137					
4	0.131					
5	0.126					
6						
7	0.018	X	X	-	-	X
8	0.128					
9						
10	0.137					
11	0.146					
13	0.131					
14	0.166				X	
15	0.130					
16	0.119					
17	0.118					
18	0.136					

Statistical analysis	**C fresh water PO_4-P**
Laboratory deviation (S(L) [mg/L]	0.016
Relative laboratory deviation (%)	11.6
Calculated spike value [mg/L]	0.021
Measured value of spike [mg/L]	0.109
% recovery of spike	519

Component	*P-total, mgL*								
assigned value	0.047	0.047	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.051	0.051							
2	0.050	0.040							
3	0.051	0.048							
4	0.043	0.044							
5	0.053	0.052							
6									
7	0.073	0.074							
8	0.040	0.034							
9									
10	0.033	0.032							
11	0.045	0.050							
13	0.060	0.067							
14	0.021	0.022							
15	0.059	0.054							
16	0.026	0.026							
17	0.057	0.040		X					
18	0.053	0.047							

Youden plot for component P-total, mg/L



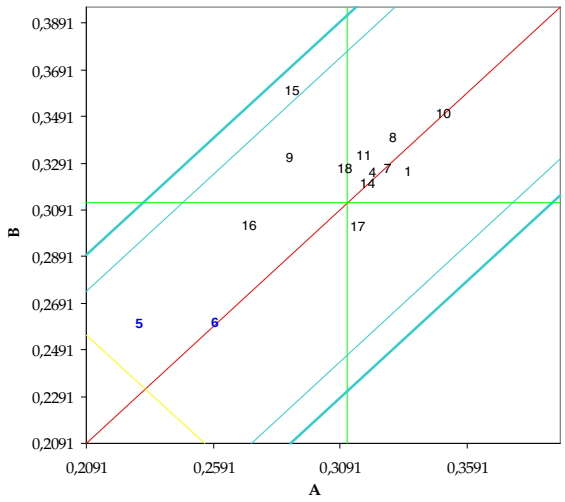
	A/B fresh water
Statistical parameters	**P-total**
p	15
m [mg/L]	0.0466
S(L) [mg/L]	0.0132
S(r) [mg/L]	0.0042
S(R) [mg/L]	0.0139
r [mg/L]	0.0117
R [mg/L]	0.0388
CV(r) [%]	9.0
CV(R) [%]	30.0

Component	*P-total, mgL*					
assigned value	**0.184**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.198					
2	0.190					
3	0.214					
4	0.190					
5	0.196					
6						
7	0.073	X	X	-	-	X
8	0.179					
9						
10	0.148					
11	0.204					
13	0.164					
14	0.166					
15	0.200					
16	0.141					
17	0.193					
18	0.191					

Statistical analysis	**C fresh water P-total**
Laboratory deviation (S(L) [mg/L]	0.021
Relative laboratory deviation (%)	11.7
Calculated spike value [mg/L]	0.154
Measured value of spike [mg/L]	0.137
% recovery of spike	89

Component	*Cd, µgL*								
assigned value	0.312	0.312	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.336	0.325							
2									
3									
4	0.322	0.325							
5	0.230	0.260						X	
6	0.260	0.260						X	
7	0.328	0.327							
8	0.330	0.340							
9	0.289	0.331							
10	0.350	0.350							
11	0.319	0.332							
13									
14	0.320	0.320							
15	0.290	0.360		X					
16	0.273	0.302							
17	0.316	0.302							
18	0.311	0.327							

Youden plot for component Cd, µg/L



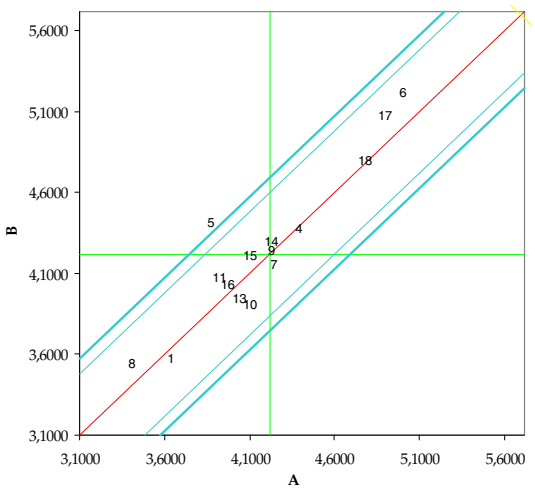
	A/B fresh water
Statistical parameters	**Cd**
p	14
m [µg/L]	0.3119
S(L) [µg/L]	0.0267
S(r) [µg/L]	0.0161
S(R) [µg/L]	0.0312
R [µg/L]	0.0452
R [µg/L]	0.0873
CV(r) [%]	5.2
CV(R) [%]	10.0

Component	*Cd, µgL*					
assigned value	**1.261**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	1.320					
2						
3						
4	1.324					
5	1.150					
6	1.000					
7	1.290					
8	1.300					
9	1.300					
10	1.200					
11	1.281					
13	1.320					
14	1.270					
15	1.410					
16	1.138					
17	1.330					
18	1.280					

Statistical analysis	**C fresh water Cd**
Laboratory deviation (S(L) [µg/L]	0.101
Relative laboratory deviation (%)	8.0
Calculated spike value [µg/L]	1.00
Measured value of spike [µg/L]	0.949
% recovery of spike	95

Component	*Cr, µgL*								
assigned value	4.22	4.22	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	3.64	3.57							
2									
3									
4	4.39	4.37							
5	3.87	4.41	X	X	-	-	-	-	X
6	5.00	5.20							
7	4.24	4.15							
8	3.41	3.54							
9	4.23	4.23							
10	4.10	3.90							
11	3.92	4.07							
13	4.04	3.93							
14	4.23	4.29							
15	4.10	4.20							
16	3.97	4.02							
17	4.90	5.07							
18	4.78	4.79							

Youden plot for component Cr, µg/L



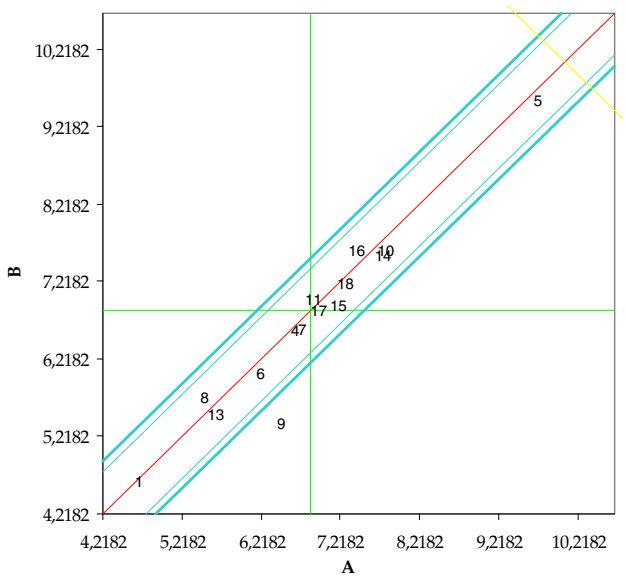
	A/B fresh water
Statistical parameters	**Cr**
p	14
m [µg/L]	4.2241
S(L) [µg/L]	0.4644
S(r) [µg/L]	0.0831
S(R) [µg/L]	0.4718
R [µg/L]	0.2327
R [µg/L]	1.3210
CV(r) [%]	2.0
CV(R) [%]	11.0

Component	*Cr, µgL*					
assigned value	**6.82**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.12					
2						
3						
4	7.11					
5	6.83					
6	7.70					
7	7.17					
8	5.73					
9	6.87					
10	6.30					
11	6.65					
13	6.22					
14	6.92					
15	6.70					
16	6.60					
17	7.57					
18	7.84					

Statistical analysis	**C fresh water Cr**
Laboratory deviation (S(L) [µg/L]	0.598
Relative laboratory deviation (%)	8.8
Calculated spike value [µg/L]	2.67
Measured value of spike [µg/L]	2.602
% recovery of spike	97

Component	*Cu, µgL*								
assigned value	6.84	6.84	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	4.68	4.64							
2									
3									
4	6.65	6.58							
5	9.71	9.55							
6	6.20	6.00							
7	6.74	6.59							
8	5.50	5.71							
9	6.48	5.35	X	X	-	-	-	-	X
10	7.80	7.60							
11	6.87	6.97							
13	5.65	5.48							
14	7.76	7.55							
15	7.20	6.90							
16	7.43	7.58							
17	6.95	6.83							
18	7.28	7.19							

Youden plot for component Cu, µg/L



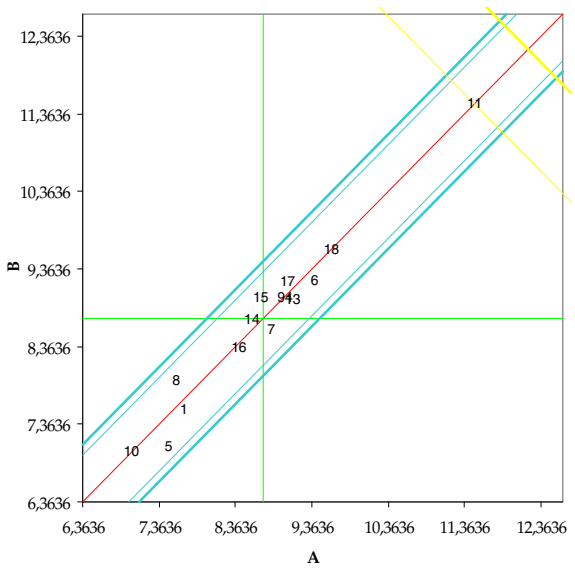
	A/B fresh water
Statistical parameters	**Cu**
p	14
m [µg/L]	6.8427
S(L) [µg/L]	1.1864
S(r) [µg/L]	0.1047
S(R) [µg/L]	1.1910
R [µg/L]	0.2932
R [µg/L]	3.3349
CV(r) [%]	1.5
CV(R) [%]	17.0

Component	*Cu, µgL*					
assigned value	**14.78**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	12.40					
2						
3						
4	15.04					
5	22.05	X	X	-	-	X
6	13.40					
7	14.80					
8	13.02					
9	13.40					
10	15.80					
11	16.00					
13	13.20					
14	15.90					
15	15.80					
16	16.20					
17	15.62					
18	16.30					

Statistical analysis	**C fresh water Cu**
Laboratory deviation (S(L) [µg/L]	1.387
Relative laboratory deviation (%)	9.4
Calculated spike value [µg/L]	8.3
Measured value of spike [µg/L]	7.937
% recovery of spike	96

Component	*Ni, µgL*								
assigned value	8.72	8.72	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	7.69	7.56							
2									
3									
4	9.07	9.00							
5	7.49	7.07							
6	9.40	9.20							
7	8.82	8.58							
8	7.58	7.92							
9	8.96	8.98							
10	7.00	7.00							
11	11.50	11.50				X			
13	9.12	8.94							
14	8.58	8.71							
15	8.70	9.00							
16	8.41	8.33							
17	9.04	9.20							
18	9.61	9.62							

Youden plot for component Ni, µg/L



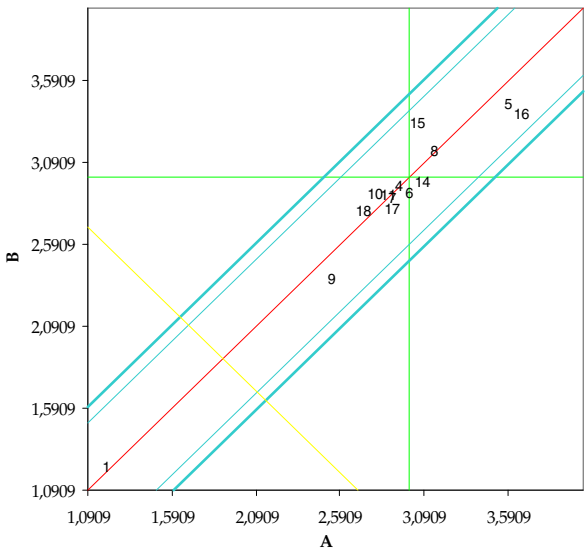
	A/B fresh water
Statistical parameters	**Ni**
p	15
m [µg/L]	8.7193
S(L) [µg/L]	1.0842
S(r) [µg/L]	0.1432
S(R) [µg/L]	1.0936
R [µg/L]	0.4011
R [µg/L]	3.0622
CV(r) [%]	1.6
CV(R) [%]	13.0

Component	*Ni, µgL*					
assigned value	**18.76**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	16.70					
2						
3						
4	19.28					
5	16.42					
6	19.20					
7	18.40					
8	16.98					
9	18.60					
10	18.80					
11	23.00		X			
13	18.39					
14	18.60					
15	18.60					
16	18.10					
17	19.73					
18	20.60					

Statistical analysis	**C fresh water Ni**
Laboratory deviation (S(L) [µg/L]	1.613
Relative laboratory deviation (%)	8.6
Calculated spike value [µg/L]	11.37
Measured value of spike [µg/L]	10.041
% recovery of spike	88

Component	*Pb, µgL*								
assigned value	3.00	3.00	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	1.20	1.23			X	X	-	-	X
2									
3									
4	2.94	2.95							
5	3.59	3.45							
6	3.00	2.90							
7	2.90	2.87							
8	3.15	3.16							
9	2.54	2.37							
10	2.80	2.90							
11	2.88	2.89							
13									
14	3.08	2.97							
15	3.05	3.33							
16	3.67	3.38							
17	2.90	2.81							
18	2.73	2.79							

Youden plot for component Pb, µg/L



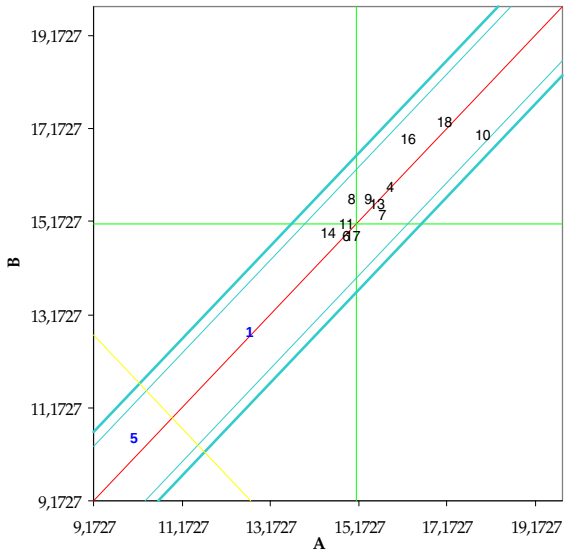
	A/B fresh water
Statistical parameters	**Pb**
p	13
m [µg/L]	3.0000
S(L) [µg/L]	0.2853
S(r) [µg/L]	0.0999
S(R) [µg/L]	0.3023
R [µg/L]	0.2798
R [µg/L]	0.8465
CV(r) [%]	3.3
CV(R) [%]	10.0

Component	*Pb, µgL*					
assigned value	**12.78**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.62	X	X	-	-	X
2						
3						
4	12.70					
5	12.26					
6	12.40					
7	12.20					
8	13.50					
9	12.30					
10	14.00					
11	12.50					
13	12.20					
14	12.70					
15	13.80					
16	14.46					
17	12.37					
18	11.50					

Statistical analysis	**C fresh water Pb**
Laboratory deviation (S(L) [µg/L]	0.836
Relative laboratory deviation (%)	6.5
Calculated spike value [µg/L]	10.3
Measured value of spike [µg/L]	10.041
% recovery of spike	97

Component	*Zn, µgL*								
assigned value	15.12	15.12	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	12.70	12.80						X	
2									
3									
4	15.89	15.89							
5	10.09	10.51				X		X	
6	14.90	14.80							
7	15.70	15.30							
8	15.02	15.65							
9	15.40	15.60							
10	18.00	17.00							
11	14.90	15.10							
13	15.60	15.50							
14	14.50	14.90							
15									
16	16.30	16.90							
17	15.05	14.85							
18	17.10	17.30							

Youden plot for component Zn, µg/L



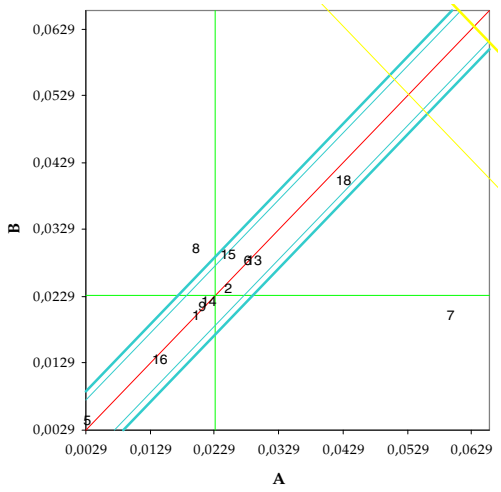
	A/B fresh water
Statistical parameters	Zn
p	14
m [µg/L]	15.1161
S(L) [µg/L]	1.7941
S(r) [µg/L]	0.3025
S(R) [µg/L]	1.8194
R [µg/L]	0.8469
R [µg/L]	5.0942
CV(r) [%]	2.0
CV(R) [%]	12.0

Component	*Zn, µgL*					
assigned value	**34.3**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	29.6					
2						
3						
4	34.7					
5	14.9	X	X	-	-	X
6	34.2					
7	38.1					
8	34.9					
9	32.6					
10	34.0					
11	33.7					
13	34.5					
14	32.8					
15						
16	35.3					
17	33.7					
18	37.8					

Statistical analysis	**C fresh water Zn**
Laboratory deviation (S(L) [µg/L]	2.167
Relative laboratory deviation (%)	6.3
Calculated spike value [µg/L]	19.6
Measured value of spike [µg/L]	19.181
% recovery of spike	98

Component	*Hg, µgL*								
assigned value	0.023	0.023	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.020	0.020							
2	0.025	0.024							
3									
4									
5	0.003	0.004							
6	0.028	0.028							
7	0.060	0.020	X	X	-	-	-	-	X
8	0.020	0.030	X	X	-	-	-	-	X
9	0.021	0.021							
10									
11									
13	0.029	0.028							
14	0.022	0.022							
15	0.025	0.029							
16	0.014	0.013							
17									
18	0.043	0.040							

Youden plot for component Hg, µg/L



	A/B fresh water
Statistical parameters	**Hg**
p	10
m [µg/L]	0.0230
S(L) [µg/L]	0.0099
S(r) [µg/L]	0.0013
S(R) [µg/L]	0.0100
R [µg/L]	0.0036
R [µg/L]	0.0279
CV(r) [%]	5.5
CV(R) [%]	43.0

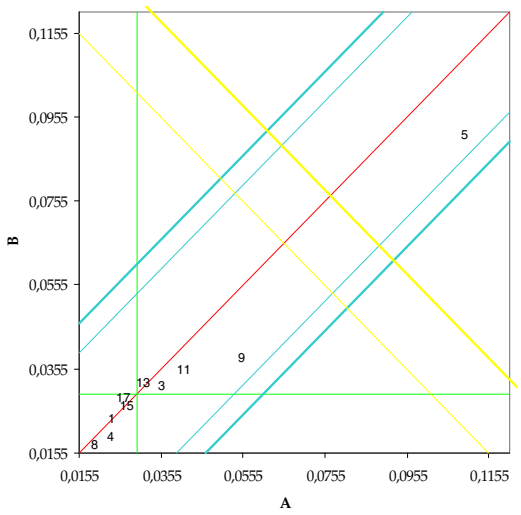
Component	*Hg, µgL*					
assigned value	**0.079**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.068					
2	0.088					
3						
4						
5	0.009	X	X	-	-	X
6	0.093					
7	0.078					
8	0.070					
9	0.086					
10						
11						
13	0.094					
14	0.081					
15	0.086					
16	0.063					
17						
18	0.062					

Statistical analysis	**C fresh water Hg**
Laboratory deviation (S(L) [µg/L]	0.012
Relative laboratory deviation (%)	14.7
Calculated spike value [µg/L]	0.073
Measured value of spike [µg/L]	0.056
% recovery of spike	77

4.3 Statistical data for each component in waste water

Component	*NH_4-N, mgL*								
assigned value	0.030	0.030	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.023	0.023							
2									
3	0.036	0.031							
4	0.023	0.019							
5	0.109	0.091			X	X	-	-	X
6									
8	0.019	0.017							
9	0.055	0.038							
11	0.041	0.035							
13	0.031	0.032							
14									
15	0.027	0.026							
16									
17	0.026	0.028							
18									

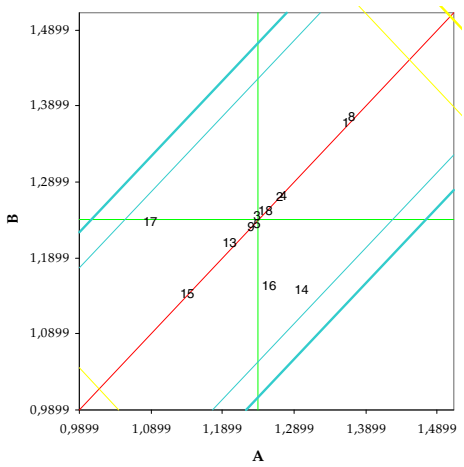
Youden plot for component NH4-N, mg/L



	A/B waste water
Statistical parameters	**NH4-N**
p	9
m [mg/L]	0.0295
S(L) [mg/L]	0.0084
S(r) [mg/L]	0.0041
S(R) [mg/L]	0.0094
r [mg/L]	0.0114
R [mg/L]	0.0262
CV(r) [%]	13.8
CV(R) [%]	32.0

Component	NO_3-N, mgL								
assigned value	1.24	1.24	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	1.36	1.37							
2	1.27	1.27							
3	1.24	1.24							
4	1.27	1.27							
5	1.24	1.23							
6									
8	1.37	1.38							
9	1.23	1.23							
11									
13	1.20	1.21							
14	1.30	1.15							
15	1.14	1.14							
16	1.25	1.15							
17	1.09	1.24							
18	1.25	1.25							

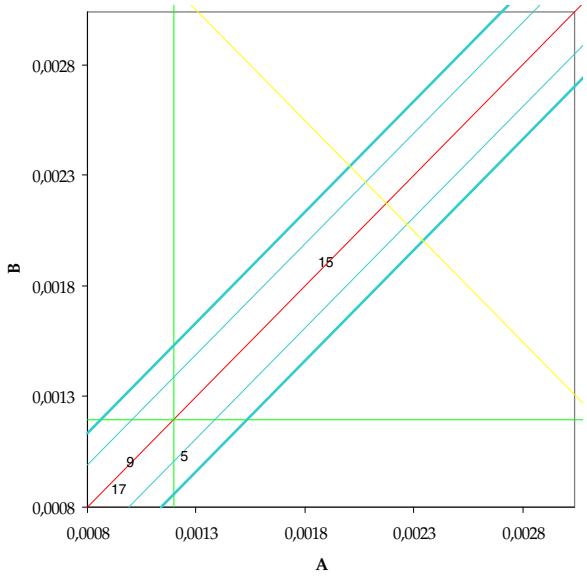
Youden plot for component NO3-N, mg/L



Statistical parameters	A/B waste water NO_3-N
p	13
m [mg/L]	1.2439
S(L) [mg/L]	0.0577
S(r) [mg/L]	0.0479
S(R) [mg/L]	0.0750
r [mg/L]	0.1342
R [mg/L]	0.2101
CV(r) [%]	3.9
CV(R) [%]	6.0

Component	*NO_2-N, mgL*								
assigned value	0.001	0.001	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1									
2									
3									
4									
5	0.001	0.001		X					
6									
8									
9	0.001	0.001							
11									
13									
14									
15	0.002	0.002							
16	0.007	0.008	X	X	-	-	-	-	X
17	0.001	0.001							
18									

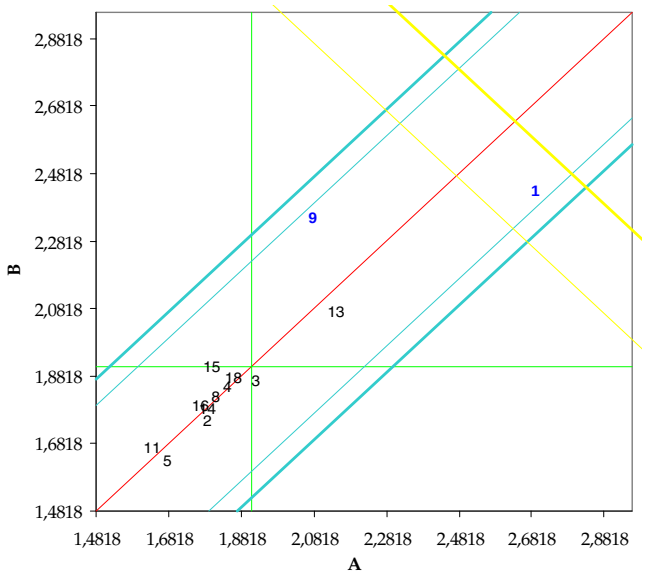
Youden plot for component NO2-N, mg/L



	A/B waste water
Statistical parameters	**NO_2-N**
p	4
m [mg/L]	0,0012
S(L) [mg/L]	0,0004
S(r) [mg/L]	0,0001
S(R) [mg/L]	0,0005
r [mg/L]	0,0002
R [mg/L]	0,0013
CV(r) [%]	5,7
CV(R) [%]	37,0

Component	*N-total, mgL*								
assigned value	1.91	1.91	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	2.69	2.43				X		X	
2	1.79	1.75							
3	1.92	1.86							
4	1.84	1.85							
5	1.68	1.63							
6									
8	1.81	1.82							
9	2.08	2.35						X	
11	1.63	1.66							
13	2.14	2.07							
14	1.79	1.78							
15	1.80	1.90							
16	1.77	1.79							
17									
18	1.86	1.87							

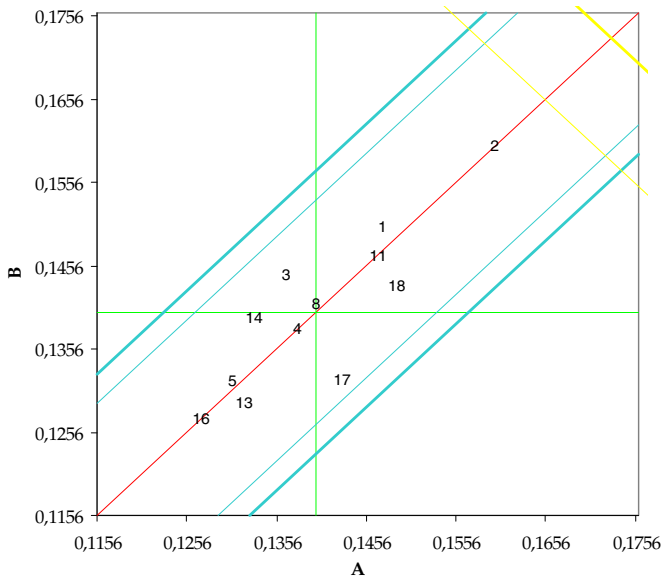
Youden plot for component N-total, mg/L



	A/B waste water
Statistical parameters	**N-total**
p	13
m [mg/L]	1.9065
S(L) [mg/L]	0.2444
S(r) [mg/L]	0.0828
S(R) [mg/L]	0.2580
r [mg/L]	0.2318
R [mg/L]	0.7225
CV(r) [%]	4.3
CV(R) [%]	14.0

Component	*PO₄-P, mgL*								
assigned value	0.140	0.140	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.147	0.150							
2	0.160	0.160							
3	0.137	0.144							
4	0.138	0.138							
5	0.131	0.132							
6									
8	0.140	0.141							
9									
11	0.147	0.147							
13	0.132	0.129							
14	0.133	0.139							
15									
16	0.127	0.127							
17	0.143	0.132							
18	0.149	0.143							

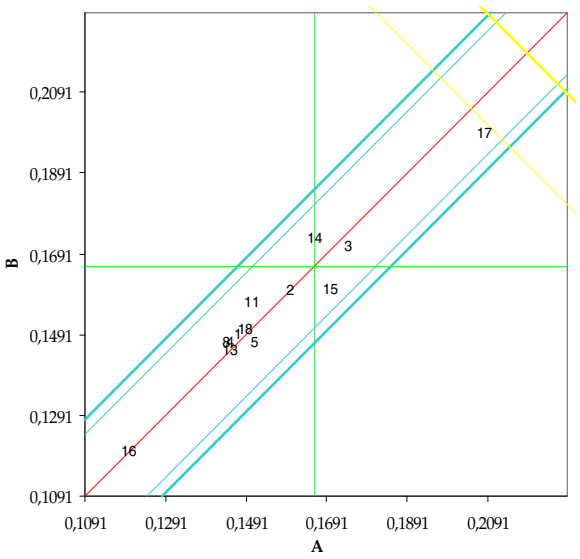
Youden plot for component PO4-P, mg/L



	A/B waste water
Statistical parameters	**PO_4-P**
p	12
m [mg/L]	0.1403
S(L) [mg/L]	0.0088
S(r) [mg/L]	0.0035
S(R) [mg/L]	0.0094
r [mg/L]	0.0099
R [mg/L]	0.0265
CV(r) [%]	2.4
CV(R) [%]	7.0

Component	*P-total, mgL*								
assigned value	0.166	0.166	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.147	0.149							
2	0.160	0.160							
3	0.175	0.170							
4	0.145	0.147							
5	0.151	0.147							
6									
8	0.144	0.147							
9									
11	0.150	0.157							
13	0.145	0.145							
14	0.166	0.173							
15	0.170	0.160							
16	0.120	0.120							
17	0.208	0.199							
18	0.149	0.150							

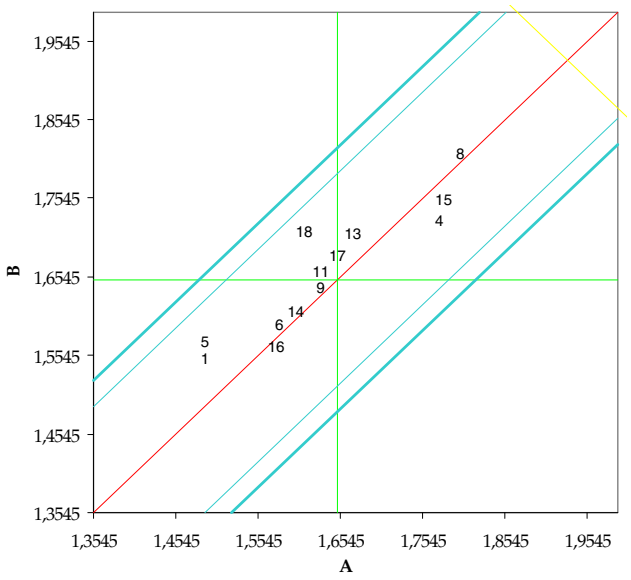
Youden plot for component P-total, mg/L



	A/B waste water
Statistical parameters	**P-total**
p	13
m [mg/L]	0.1559
S(L) [mg/L]	0.0194
S(r) [mg/L]	0.0036
S(R) [mg/L]	0.0197
r [mg/L]	0.0102
R [mg/L]	0.0553
CV(r) [%]	2.3
CV(R) [%]	13.0

Component	*Cd, µgL*								
assigned value	1.65	1.65	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	1.49	1.55							
2									
3									
4	1.77	1.73							
5	1.49	1.57							
6	1.58	1.59							
8	1.80	1.81							
9	1.63	1.64							
11	1.63	1.66							
13	1.67	1.71							
14	1.60	1.61							
15	1.78	1.75							
16	1.58	1.57							
17	1.65	1.68							
18	1.61	1.71							

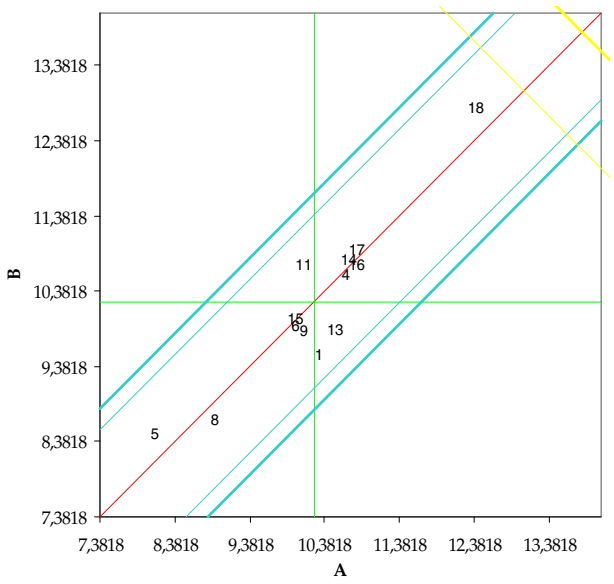
Youden plot for component Cd, µg/L



	A/B waste water
Statistical parameters	**Cd**
p	13
m [µg/L]	1.6481
S(L) [µg/L]	0.0856
S(r) [µg/L]	0.0294
S(R) [µg/L]	0.0905
r [µg/L]	0.0823
R [µg/L]	0.2534
CV(r) [%]	1.8
CV(R) [%]	5.0

Component	*Cr, µgL*								
assigned value	10.24	10.24	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	10.30	9.53							
2									
3									
4	10.67	10.59							
5	8.12	8.48							
6	10.00	9.90							
8	8.92	8.67							
9	10.10	9.84							
11	10.10	10.70							
13	10.52	9.87							
14	10.70	10.80							
15	10.00	10.00							
16	10.82	10.72							
17	10.82	10.93							
18	12.40	12.80							

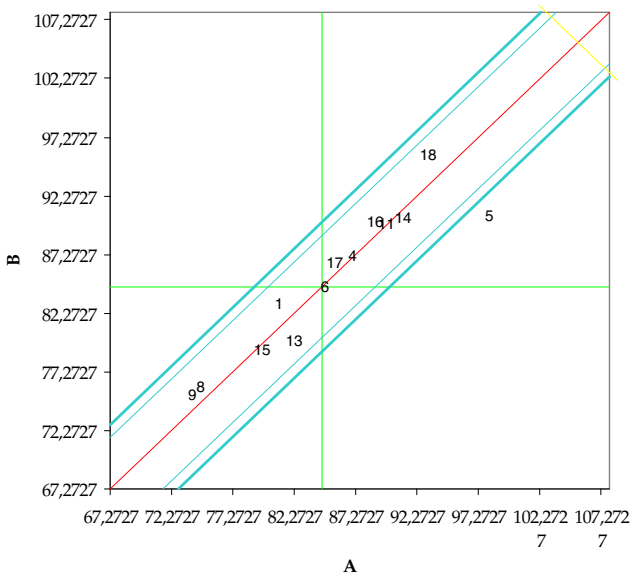
Youden plot for component Cr, µg/L



	A/B waste water
Statistical parameters	**Cr**
p	13
m [µg/L]	10.2422
S(L) [µg/L]	1.0170
S(r) [µg/L]	0.2748
S(R) [µg/L]	1.0535
r [µg/L]	0.7694
R [µg/L]	2.9497
CV(r) [%]	2.7
CV(R) [%]	10.0

Component	*Cu, µgL*								
assigned value	84.5	84.5	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	81.0	83.0							
2									
3									
4	87.0	87.1							
5	98.1	90.6	X	X	-	-	-	-	X
6	84.7	84.4							
8	74.7	76.0							
9	74.0	75.2							
11	89.7	89.7							
13	82.3	79.9							
14	91.1	90.3							
15	79.6	79.0							
16	88.8	90.0							
17	85.6	86.5							
18	93.1	95.5							

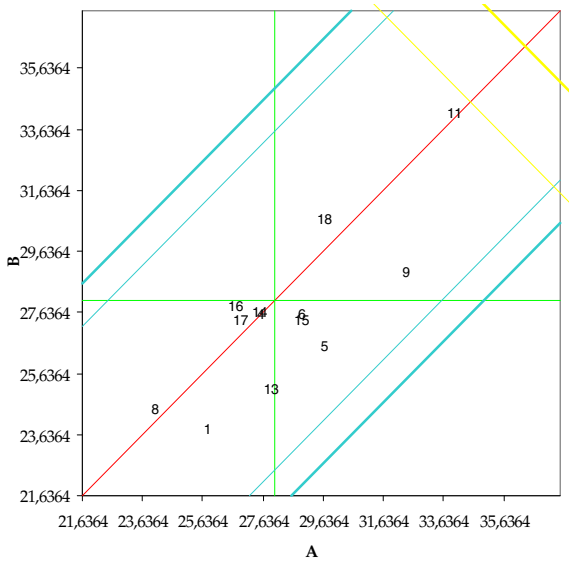
Youden plot for component Cu, µg/L



	A/B waste water
Statistical parameters	Cu
p	12
m [µg/L]	84,5042
S(L) [µg/L]	6,1533
S(r) [µg/L]	0,9512
S(R) [µg/L]	6,2264
r [µg/L]	2,6633
R [µg/L]	17,4339
CV(r) [%]	1,1
CV(R) [%]	7,0

Component	*Ni, µgL*								
assigned value	28.0	28.0	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	25.8	23.8							
2									
3									
4	27.6	27.6							
5	29.7	26.5							
6	28.9	27.5							
8	24.0	24.4							
9	32.4	28.9							
11	34.0	34.1							
13	27.9	25.1							
14	27.5	27.6							
15	28.9	27.3							
16	26.7	27.8							
17	26.9	27.4							
18	29.7	30.6							

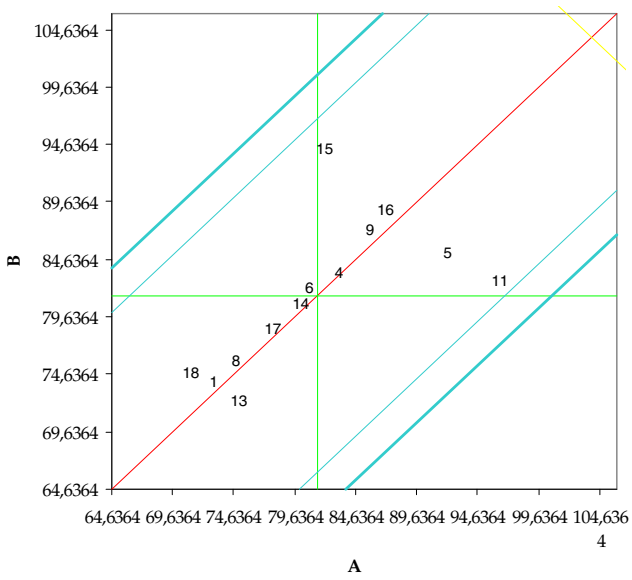
Youden plot for component Ni, µg/L



	A/B waste water
Statistical parameters	**Ni**
p	13
m [µg/L]	28.0206
S(L) [µg/L]	2.3959
S(r) [µg/L]	1.1388
S(R) [µg/L]	2.6528
r [µg/L]	3.1886
R [µg/L]	7.4277
CV(r) [%]	4.1
CV(R) [%]	9.0

Component	*Pb, µgL*								
assigned value	81.5	81.5	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	73.0	74.0							
2									
3									
4	83.2	83.4							
5	92.2	85.1							
6	80.8	82.0							
8	74.8	75.8							
9	85.8	87.2							
11	96.4	82.6							
13	75.1	72.3							
14	80.1	80.7							
15	82.1	94.0							
16	87.1	88.9							
17	77.8	78.6							
18	71.1	74.6							

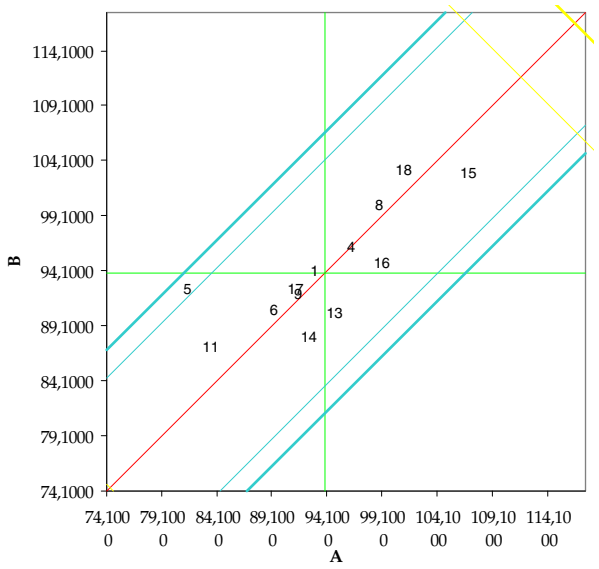
Youden plot for component Pb, µg/L



	A/B waste water
Statistical parameters	Pb
p	13
m [µg/L]	81.4817
S(L) [µg/L]	5.5934
S(r) [µg/L]	4.1451
S(R) [µg/L]	6.9619
r [µg/L]	11.6063
R [µg/L]	19.4934
CV(r) [%]	5.1
CV(R) [%]	9.0

Component	*Zn, µgL*								
assigned value	94.0	94.0	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	93.0	94.0							
2									
3									
4	96.3	96.2							
5	81.5	92.5		X					
6	89.3	90.3							
8	98.8	100.0							
9	91.5	91.9							
11	83.5	87.1							
13	94.8	90.2							
14	92.5	88.0							
15	106.9	102.8							
16	99.1	94.8							
17	91.2	92.4							
18	101.0	103.0							

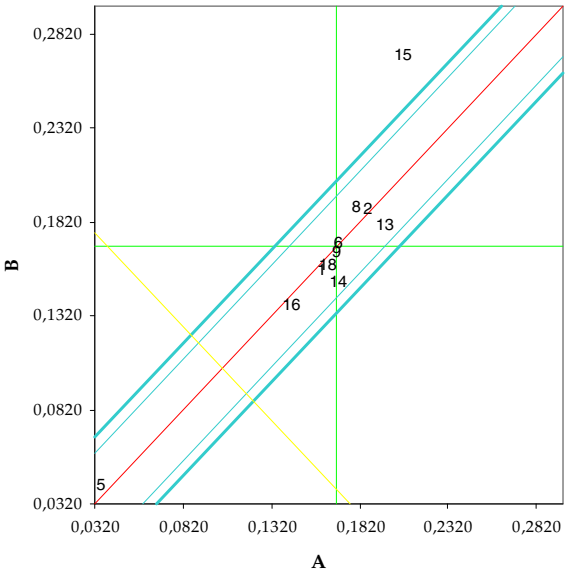
Youden plot for component Zn, µg/L



Statistical parameters	A/B waste water Zn
p	13
m [µg/L]	93.9483
S(L) [µg/L]	5.3192
S(r) [µg/L]	3.0100
S(R) [µg/L]	6.1118
r [µg/L]	8.4281
R [µg/L]	17.1131
CV(r) [%]	3.2
CV(R) [%]	7.0

Component	*Hg, µgL*								
assigned value	0.169	0.169	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.160	0.157							
2	0.187	0.189							
3									
4									
5	0.035	0.042			X	X	-	-	X
6	0.170	0.170							
8	0.180	0.190							
9	0.169	0.166							
11									
13	0.196	0.180							
14	0.170	0.150							
15	0.206	0.270	X	X	-	-	-	-	X
16	0.143	0.138							
17									
18	0.164	0.158							

Youden plot for component Hg, µg/L



Statistical parameters	A/B waste water Hg
p	9
m [µg/L]	0.1687
S(L) [µg/L]	0.0154
S(r) [µg/L]	0.0064
S(R) [µg/L]	0.0166
r [µg/L]	0.0179
R [µg/L]	0.0465
CV(r) [%]	3.8
CV(R) [%]	10.0

5 Conclusions and summary

A summary of the results are shown in table 3.

Table 3. Mean concentrations and relative value of the total variation (CV(R)).

Components	Fresh water			Waste water	
	Mean conc. sample A/B	CV(R) (%) sample A/B	sample C recovery of spike (%)	Mean conc. sample A/B	CV(R) (%) sample A/B
NH_4-N mg/L	0.13	51	138	0.03	32
NO_3-N mg/L	5	5	spike too low	1.2	6
NO_2-N mg/L	0.14	19	no spike	*0.0012**	*37**
N-total mg/L	6	5	95	1.9	14
PO_4-P mg/L	0.028	33	519#	0.14	7
P-total mg/L	0.047	30	89	0.16	13
Cd µg/L	0.31	10	95	1.7	5
Cr µg/L	4.2	11	97	10	10
Cu µg/L	6.8	17	96	85	7
Ni µg/L	8.7	13	88	28	9
Pb µg/L	3	10	97	82	9
Zn µg/L	15	12	98	94	7
Hg µg/L	0.023	43	77	0.17	10

* The statistical data is debatable due to low number of reported data (n=5).

Some PO_4-P could be present in the spike used for P-total

In general the analytical quality is good and comparable between the laboratories with a few exceptions which can be explained by other means. See below.

NH_4-N has high coefficients of total variation (CV(R)) for both fresh water and waste water. This does not necessarily reflect the analytical quality but is more likely to be caused by instability of the component which makes it difficult to include this component in intercalibrations like this. The instability was verified for fresh water but not for waste water in the control analysis (see section 2.2). However, if NH_4 should be included in be included in future intercalibrations it would probably be necessary to prepare NH_4 samples separately as a synthetic sample.

For PO_4-P and P-total in fresh water, the coefficients of total variation (CV(R)) are high but this is an artefact to low concentrations. The corresponding absolute values, reproducibility, S(R), are 0,009-0,014 mg/L which is acceptable. For fresh water sample C the recovery of PO_4-P is far too high. An error in the spiking has been considered but as P-total not has the same high recovery it is considered likely that the reference material used for spiking total-P consists of a not insignificant amount of PO_4-P.

For fresh water Hg has a high deviation for sample A/B and low recovery in sample C. This could be caused by the use of PE bottles instead of glass bottles. Another possibility could be that Hg is more analytical difficult to analyse compared to the rest of the components due to the low concentration levels.

A comparison between data and the analytical methods/apparatus used in the different laboratories was performed. The components were analysed with two to six different methods/apparatus. This comparison showed no bias for specific analytical methods/apparatus. The data is not shown as this could compromise the anonymity of the single laboratories.

Appendix 1

List of participating laboratories

Country	Laboratory
Denmark	Eurofins – Miljø
	AlControl
Estonia	Estinian Environmental Research Institute
Finland	SYKE, Hakuninmaa Laboratory
	MetropoliLab
	Lounais-Suomen vesi- ja ympäristötutkimus Oy
Germany	„Umweltanalytik und Strahlenschutz“ des Landesamtes für Umwelt, Naturschutz und Geologie
Latvia	Laboratory of the Latvian Environment, Geology and Meteorology Center
	Laboratory of Food and Environmental Investigations of the Scientific Institute of Food Safety, Animal Health and Environment „BIOR”
Lithuania	Lithuanian Environmental Protection Agency
	Marine Research Department
Poland	Voivodship Inspectorate for Environmental Protection in Szczecin
	Voivodship Inspectorate for Environmental Protection in Gdańsk
	Voivodship Inspectorate for Environmental Protection in Szczecin
Russia	Surface and Marine water chemistry Laboratory of the FSBO “Saint-Petersburg Center for Hydrometeorology and Environmental Monitoring with regional functions” (FSBO “Saint-Petersburg CHEM–R”)
	Laboratory of the CJSC “Water Research and Control Center”
	Laboratory of the FBI “Center For Laboratory Analysis And Technical Measurements For North-West Federal District”
Sweden	Water Chemistry laboratory
	Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences

Appendix 2

The reported data from the laboratories

Intercalibration under PLC6

Fresh water

Laboratory number: **1**

Skema 1

Components	Measured data		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4, mg/L	0.13	0.13	0.25
NO_3, mg/L	24	23	23
NO_2, mg/L	0.54	0.49	0.7
N-total, mg/L	6.5	6.5	6.7
PO_4, mg/L	0.103	0.099	0.41
P-total, mg/L	0.051	0.051	0.198
Cd, µg/L	0.336	0.325	1.32
Cr, µg/L	3.64	3.57	6.12
Cu, µg/L	4.68	4.64	12.4
Ni, µg/L	7.69	7.56	16.7
Pb, µg/L	1.2	1.23	6.62
Zn, µg/L	12.7	12.8	29.6
Hg, µg/L	0.02	0.02	0.068

No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **1**

Skema 1

Components	Measured data	
	Waste Water sample A	Waste Water sample B
NH_4, mg/L	0.03	0.03
NO_3, mg/L	6.03	6.05
NO_2, mg/L	<0.016	<0.0016
N-total, mg/L	2.69	2.43
PO_4, mg/L	0.452	0.461
P-total, mg/L	0.147	0.149
Cd, µg/L	1.49	1.55
Cr, µg/L	10.3	9.53
Cu, µg/L	81	83
Ni, µg/L	25.8	23.8
Pb, µg/L	73	0.074
Zn, µg/L	93	94
Hg, µg/L	0.16	0.157

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **2**

Skema 1

Components	Measured data [µg/L] Fresh Water sample A	Fresh Water sample B	Fresh Water sample C	
NH_4	< 0.05	< 0.05	< 0.05	mg/l N
NO_3	5.34	5.32	5.55	mg/l N
NO_2	0.277	0.255	0.432	mg/l N
N-total	5.81	5.8	6.04	mg/l
PO4	0.038	0.036	0.174	mg/l P
P-total	0.05	0.04	0.19	mg/l
Cd	-	-	-	
Cr	-	-	-	
Cu	-	-	-	
Ni	-	-	-	
Pb	-	-	-	
Zn	-	-	-	
Hg	0.025	0.024	0.088	

No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **2**

Skema 1

Components	Measured data [µg/L] Waste Water sample A	Waste Water sample B	
NH_4	< 0.05	< 0.05	mg/l N
NO_3	1.27	1.27	mg/l N
NO_2	< 0.01	< 0.01	mg/l N
N-total	1.79	1.75	mg/l
PO_4	0.16	0.16	mg/l P
P-total	0.16	0.16	mg/l
Cd	-	-	
Cr	-	-	
Cu	-	-	
Ni	-	-	
Pb	-	-	
Zn	-	-	
Hg	0.187	0.189	

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **3**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4	0.027	0.114	0.03255
NO_3	5.2158	5.4119	5.1031
NO_2	0.1642	0.1521	0.2889
N-total	6.36	6.17	6.34
PO_4	0.02141	0.01912	0.13667
P-total	0.05071	0.04844	0.214
Cd			
Cr			
Cu			
Ni			
Pb			
Zn			
Hg			
No components	13	13	13

Waste water

Laboratory number: **3**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4	0.0355	0.031
NO_3	1.2385	1.2442
NO_2	0.0004	0.0003
N-total	1.92	1.86
PO_4	0.1366	0.1444
P-total	0.1745	0.1705
Cd		
Cr		
Cu		
Ni		
Pb		
Zn		
Hg		

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **4**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4-N	50	48	102
NO_3-N	4976	4963	4955
NO_2-N	164	165	244
N-total	6250	6075	6840
PO_4-P	23.4	23.6	131
P-total	43.2	44.1	190
Cd	0.322	0.325	1.32
Cr	4.39	4.37	7.11
Cu	6.65	6.58	15.04
Ni	9.07	9.00	19.28
Pb	2.94	2.95	12.70
Zn	15.89	15.89	34.66
Hg	not meas.	not meas.	not meas.

No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **4**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4-N	23	19
NO_3-N	1274	1271
NO_2-N	<1	<1
N-total	1843	1847
PO_4-P	138	138
P-total	145	147
Cd	1.77	1.73
Cr	10.7	10.6
Cu	87.0	87.1
Ni	27.6	27.6
Pb	83.2	83.4
Zn	96.3	96.2
Hg	not meas.	not meas.

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **5**

Skema 1

Components	Measured data [mg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4	0.182	0.178	0.306
NO_3	19.95	19.88	19.83
NO_2	0.545	0.475	0.800
N-total	5.25	5.23	5.31
PO_4	0.093	0.090	0.386
P-total	0.053	0.052	0.196
	[µg/L]		
Cd	0.23	0.26	1.15
Cr	3.87	4.41	6.83
Cu	9.71	9.55	22.05
Ni	7.49	7.07	16.42
Pb	3.59	3.45	12.26
Zn	10.09	10.51	14.86
Hg	0.0032	0.0042	0.0087

No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **5**

Skema 1

Components	Measured data [mg/L]	
	Waste Water sample A	Waste Water sample B
NH_4	0.141	0.117
NO_3	5.48	5.46
NO_2	0.0041	0.0034
N-total	1.68	1.63
PO_4	0.401	0.404
P-total	0.151	0.147
[µg/L]		
Cd	1.49	1.57
Cr	8.12	8.48
Cu	98.10	90.62
Ni	29.69	26.50
Pb	92.17	85.06
Zn	81.51	92.46
Hg	0.0352	0.0419

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **6**

Skema 1

Components	Measured data [µg/L] Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4			
NO_3			
NO_2			
N-total			
PO_4			
P-total			
Cd	0.26±0.03	0.26±0.03	1.00±0.11
Cr	5.0±0.7	5.2±0.7	7.7±1.0
Cu	6.2±0.9	6.0±0.8	13.4±1.9
Ni	9.4±1.4	9.2±1.4	19.2±2.9
Pb	3.0±0.5	2.9±0.5	12.4±2.1
Zn	14.9±1.8	14.8±1.8	34.2±4.1
Hg	0.028±0.0025	0.028±0.0025	0.093±0.0082

No components	7	7	7

Intercalibration under PLC6

Waste water

Laboratory number: **6**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4		
NO_3		
NO_2		
N-total		
PO_4		
P-total		
Cd	1.58±0.17	1.59±0.17
Cr	10±1.1	9.9±1.1
Cu	84.7±6.3	84.4±6.3
Ni	28.9±3.2	27.5±3.0
Pb	80.8±6.8	82±6.9
Zn	89.3±11	90.3±12
Hg	0.17±0.015	0.17±0.015

No components	7	7

Intercalibration under PLC6

Fresh water

Laboratory number: **7**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4	347	341	327
NO_3	140300	139000	139900
NO_2	-	-	-
N-total	136000	140000	142000
PO_4	56	58	56
P-total	73.5	73.8	73.4
Cd	0.328	0.327	1.29
Cr	4.24	4.15	7.2
Cu	6.74	6.59	14.8
Ni	8.82	8.58	18.4
Pb	2.90	2.87	12.2
Zn	15.7	15.3	38.1
Hg	0.0597	0.0200	0.0783

No components	13	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **8**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4-N	74	55	150
NO_3-N	4850	4865	4833
NO_2-N	140	117	190
N-total	5950	6000	6070
PO_4-P	25	19	128
P-total	40	34	179
Cd	0.33	0.34	1.3
Cr	3.41	3.54	5.73
Cu	5.5	5.71	13.02
Ni	7.58	7.92	16.98
Pb	3.15	3.16	13.5
Zn	15.02	15.65	34.93
Hg	0.02	0.03	0.07
Hg + 1% AR	0.06	0.06	0.13
No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **8**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4-N	19	17
NO_3-N	1370	1375
NO_2-N	<0.002	<0.002
N-total	1810	1820
PO_4-P	140	141
P-total	144	147
Cd	1.8	1.81
Cr	8.92	8.67
Cu	74.68	75.96
Ni	24.05	24.43
Pb	74.76	75.81
Zn	98.81	100
Hg	0.12	0.12
Hg + 1% AR	0.18	0.19
No components	13	13

by autoclaving

Components	[µg/L]	
	Waste Water sample A	Waste Water sample B
Cd	1.99	2.06
Cr	9.6	9.84
Cu	82.8	84.69
Ni	26.44	27.02
Pb	91.25	93.55
Zn	111.31	115.39
Hg	0.47	0.48

Fresh water Intercalibration under PLC6

Laboratory number: **9**

Skema 1

	Measured data		
	06.03-25.03.2013 r.		
Components	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
$N\text{-}NH_4$ [mg/l]	0.166 ± 0.037	0.119 ± 0.026	0.298 ± 0.066
$N\text{-}NH_4$ [mg/l]	0.180 ± 0.029	0.110 ± 0.018	0.310 ± 0.050
$N\text{-}NO_3$ [mg/l]	4.78 ± 0.67	4.82 ± 0.67	4.80 ± 0.67
$N\text{-}NO_2$ [mg/l]	0.110 ± 0.029	0.100 ± 0.026	0.134 ± 0.035
N-total [mg/l]	6.18	6.36	6.12
PO_4	no probe	no probe	no probe
P-total	no probe	no probe	no probe
Cd [µg/l]	0.289 ± 0.124	0.331 ± 0.142	1.30 ± 0.56
Cr [µg/l]	4.23 ± 1.18	4.23 ± 1.18	6.87 ± 1.92
Cu [µg/l]	6.48 ± 1.62	5.35 ± 1.34	13.4 ± 3.4
Ni [µg/l]	8.96 ± 2.78	8.98 ± 2.78	18.6 ± 5.8
Pb [µg/l]	2.54 ± 0.58	2.37 ± 0.55	12.3 ± 2.8
Zn [µg/l]	15.4 ± 2.9	15.6 ± 3.0	32.6 ± 6.2
Zn [µg/l]	<30.0	< 30.0	33.1 ± 6.3
Hg [µg/l]	0.021 ± 0.010	0.021 ± 0.010	0.086 ± 0.041
No components	11	11	11

uncertainty k=2, 95%

Waste water

Laboratory

number: **9**

Skema 1

Components	Measured data 06.03-25.03.2013 r.	
	Waste Water sample A	Waste Water sample B
$N\text{-}NH_4$ [mg/l]	0.055 ± 0.012	0.038 ± 0.008
$N\text{-}NH_4$ [mg/l]		0.040 ± 0.006
$N\text{-}NO_3$ [mg/l]	1.23 ± 0.15	1.23 ± 0.15
$N\text{-}NO_2$ [mg/l]	0.001 ± 0.0003	0.001 ± 0.0003
N-total [mg/l]	2.08	2.35
PO_4	no probe	no probe
P-total	no probe	no probe
Cd [µg/l]	1.63 ± 0.49	1.64 ± 0.49
Cr [µg/l]	10.1 ± 2.6	9.84 ± 2.56
Cu [µg/l]	74.0 ± 14.8	75.2 ± 15.0
Ni [µg/l]	32.4 ± 9.1	28.9 ± 8.1
Pb [µg/l]	85.8 ± 19.7	87.2 ± 20.1
Zn [µg/l]	91.5 ± 17.4	91.9 ± 17.5
Zn [µg/l]	91.1 ± 11.0	93.1 ± 11.2
Hg [µg/l]	0.169 ± 0.081	0.166 ± 0.080
No components	11	11

uncertainty k=2, 95%

Intercalibration under PLC6

Fresh water

Laboratory number: **10**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4 - N	<10	<10	<10
NO_3 - N	5170± 400	5300± 412	5490 ±427
NO_2 - N	101 ±17	90±16	33± 8
N-total - N	5400 ±460	6480±550	7250 ±610
PO_4 - P	14±3	14±3	137±15
P-total - P	33±6	32±6	148±13
Cd	0.35±0.08	0.35±0.08	1.20±0.18
Cr	4.1±1.3	3.9±1.2	6.3±1.8
Cu	7.8±1.7	7.6±1.5	15.8±3.2
Ni	7.0±2.8	7.0±2.8	18.8±4.2
Pb	2.8±1.3	2.9±1.3	14.0±2.7
Zn	18.0±4.1	17.0±3.9	34.0±6.8
Hg			

No components	13	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **11**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water ample A	Fresh Water sample B	Fresh Water sample C
NH_4-N (ug/L)	151.9	168.9	329.6
NO_{23}-N (ug/L)	5010.2	5005.6	4990.6
N-total (ug/L)	5927	5878	5814
PO_4-P (ug/L)	30.52	35.33	146.1
P-total (ug/L)	45.0	50.4	204.0
Cd (ug/L)	0.3185	0.3319	1.281
Cr (ug/L)	3.92	4.07	6.65
Cu (ug/L)	6.87	6.97	16.0
Ni (ug/L)	11.5	11.5	23.0
Pb (ug/L)	2.88	2.89	12.5
Zn (ug/L)	14.9	15.1	33.7
Hg			

No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **11**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4-N (ug/L)	40.95	34.70
NO_{23}-N (ug/L)	1270.3	1273.2
N-total (ug/L)	1634	1664
PO_4-P (ug/L)	146.9	146.6
P-total (ug/L)	150.5	156.8
Cd (ug/L)	1.631	1.658
Cr (ug/L)	10.1	10.7
Cu (ug/L)	89.7	89.7
Ni (ug/L)	34.0	34.1
Pb (ug/L)	96.4	82.6
Zn (ug/L)	83.5	87.1
Hg		

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **13**

Skema 1

Components	Measured data			Uncertainty [%] of result
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C	
$N\text{-}NH_4$ [mg/L]	0.168	0.158	0.325	13
$N\text{-}NO_3$ [mg/L]	5.07	5.03	5.05	13
$N\text{-}NO_2$ [mg/L]	0.116	0.108	0.141	9
N-total [mg/L]	6.24	6.15	6.38	23
PO_4 [mg/L]	0.137	0.132	0.401	12
P-total [mg/L]	0.060	0.067	0.164	12
Cd [µg/L]	<0.5	<0.5	1.32	15
Cr [µg/L]	4.04	3.93	6.22	11
Cu [µg/L]	5.65	5.48	13.2	11
Ni [µg/L]	9.12	8.94	18.39	16
Pb [µg/L]	<4	<4	12.2	16
Zn [µg/L]	15.6	15.5	34.5	8
Hg [µg/L]	0.029	0.028	0.094	20
No components	13	13	13	

Intercalibration under PLC6

Waste water

Laboratory number: **13**

Skema 1

Components	Measured data		
	Waste Water sample A	Waste Water sample B	Uncertainty [%] of result
$N\text{-}NH_4$ [mg/L]	0.031	0.032	13
$N\text{-}NO_3$ [mg/L]	1.20	1.21	13
$N\text{-}NO_2$ [mg/L]	<0.002	<0.002	9
N-total [mg/L]	2.14	2.07	23
PO_4 [mg/L]	0.405	0.396	12
P-total [mg/L]	0.145	0.145	12
Cd [µg/L]	1.67	1.71	15
Cr [µg/L]	10.52	9.87	11
Cu [µg/L]	82.3	79.9	11
Ni [µg/L]	27.9	25.1	16
Pb [µg/L]	75.1	72.3	16
Zn [µg/L]	94.8	90.2	8
Hg [µg/L]	0.196	0.180	20

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **14**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4	<50	<50	<50
NO_3	22170	22210	22675
NO_2	515	533	770
N-total	5964	5995	6132
PO_4	<500	<500	508
P-total	20.6	21.5	166
Cd	0.32	0.32	1.27
Cr	4.23	4.29	6.92
Cu	7.76	7.55	15.9
Ni	8.58	8.71	18.6
Pb	3.08	2.97	12.7
Zn	14.5	14.9	32.8
Hg	0.022	0.022	0.081
No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **14**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4	<50	<50
NO_3	5750	5080
NO_2	<30	<30
N-total	1787	1783
PO_4	408	427
P-total	166	173
Cd	1.6	1.61
Cr	10.7	10.8
Cu	91.1	90.3
Ni	27.5	27.6
Pb	80.1	80.7
Zn	92.5	88
Hg	0.17	0.15

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **15**

Skema 1

Components	Measured data			Filtration
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C	
NH_4 [mg/L N]	_	_	_	_
NO_3 [mg/L N]	4.86 ± 0.49	4.83 ± 0.48	4.83 ± 0.48	Yes
NO_2 [mg/L N]	0.141 ± 0.024	0.134 ± 0.023	0.222 ± 0.038	Yes
N-total [mg/L]	6.2 ± 1.4	6.1 ± 1.4	6.3 ± 1.4	_
PO_4 [mg/L PO_4]	0.12 ± 0.01	0.11 ± 0.01	0.40 ± 0.05	Yes
P-total [mg/L P]	0.059 ± 0.009	0.054 ± 0.009	0.20 ± 0.03	No
Cd [µg/L]	0.29 ± 0.03	0.36 ± 0.04	1.41 ± 0.16	No
Cr [µg/L]	4.1 ± 0.3	4.2 ± 0.3	6.7 ± 0.5	No
Cu [µg/L]	7.2 ± 0.4	6.9 ± 0.4	15.8 ± 0.9	No
Ni [µg/L]	8.7 ± 1.7	9.0 ± 1.7	18.6 ± 3.5	No
Pb [µg/L]	3.05 ± 0.27	3.33 ± 0.30	13.8 ± 1.2	No
Zn [µg/L]	< 50	< 50	< 50	No
Hg [µg/L]	0.025 ± 0.004	0.029 ± 0.005	0.086 ± 0.015	No

No components	12	12	12

Intercalibration under PLC6

Waste water

Laboratory number: **15**

Skema 1

Components	Measured data		Filtration
	Waste Water sample A	Waste Water sample B	
NH_4 [mg/L N]	0.027 ± 0.004	0.026 ± 0.004	Yes
NO_3 [mg/L N]	1.14 ± 0.11	1.14 ± 0.11	Yes
NO_2 [mg/L N]	0.0019 ± 0.0003	0.0019 ± 0.0003	Yes
N-total [mg/L]	1.8 ± 0.4	1.9 ± 0.4	_
PO_4 [mg/L PO_4]	_	_	_
P-total [mg/L P]	0.17 ± 0.03	0.16 ± 0.03	No
Cd [µg/L]	1.78 ± 0.20	1.75 ± 0.19	No
Cr [µg/L]	10.0 ± 0.7	10.0 ± 0.7	No
Cu [µg/L]	79.6 ± 4.8	79.0 ± 4.7	No
Ni [µg/L]	28.9 ± 5.5	27.3 ± 5.2	No
Pb [µg/L]	82.1 ± 7.4	94.0 ± 8.5	No
Zn [µg/L]	106.9 ± 6.4	102.8 ± 6.2	No
Hg [µg/L]	0.206 ± 0.037	0.270 ± 0.049	No

No components	12	12

Intercalibration under PLC6

Fresh water

Laboratory number: **16**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4	<13	<13	<13
NO_3	22295	22810	23440
NO_2	402	378	115
N-total	5610	6040	6520
PO_4	49.1	52.3	365
P-total	26.3	25.9	141.2
Cd	0.273	0.302	1.138
Cr	3.97	4.02	6.60
Cu	7.43	7.58	16.2
Ni	8.41	8.33	18.1
Pb	3.67	3.38	14.46
Zn	16.3	16.9	35.3
Hg	0.014	0.013	0.063
No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **16**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4	<50	<50
NO_3	5550	5100
NO_2	24	27
N-total	1770	1790
PO_4	390	390
P-total	120	120
Cd	1.577	1.566
Cr	10.82	10.72
Cu	88.8	90±3
Ni	26.7	27.8
Pb	87.1	88.9
Zn	99.1	94.8
Hg	0.143	0.138

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **17**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4	158	156	307
NO_3, mg/L	20.8	21.0	20.3
NO_2	617	580	956
N-total, mg/L	<1	<1	<1
PO_4	32.7	22.0	118
P-total	57.3	40.3	193
Cd	0.316	0.302	1.33
Cr	4.90	5.07	7.57
Cu	6.95	6.83	15.62
Ni	9.04	9.20	19.73
Pb	2.90	2.81	12.37
Zn	15.05	14.85	33.68
Hg			
No components	13	13	13

Waste water

Laboratory number: **17**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4	33.7	36.5
NO_3, mg/L	4.82	5.48
NO_2	3.11	2.91
N-total, mg/L	<1	<1
PO_4	143	132
P-total	208	199
Cd	1.65	1.68
Cr	10.82	10.93
Cu	85.6	86.5
Ni	26.88	27.35
Pb	77.80	78.55
Zn	91.23	92.41
Hg		

No components	13	13

Intercalibration under PLC6

Fresh water

Laboratory number: **18**

Skema 1

Components	Measured data [µg/L]		
	Fresh Water sample A	Fresh Water sample B	Fresh Water sample C
NH_4			
NO_3	5150	5120	5050
NO_2	154	148	192
N-total	6250	6240	6370
PO_4	34.4	31.0	136
P-total	52.6	47.1	191
Cd	0.311	0.327	1.28
Cr	4.78	4.79	7.84
Cu	7.28	7.19	16.3
Ni	9.61	9.62	20.6
Pb	2.73	2.79	11.5
Zn	17.1	17.3	37.8
Hg	0.043	0.04	0.062
No components	13	13	13

Intercalibration under PLC6

Waste water

Laboratory number: **18**

Skema 1

Components	Measured data [µg/L]	
	Waste Water sample A	Waste Water sample B
NH_4		
NO_3	1250	1250
NO_2	<3	<3
N-total	1860	1870
PO_4	149	143
P-total	149	150
Cd	1.61	1.71
Cr	12.4	12.8
Cu	93.1	95.5
Ni	29.7	30.6
Pb	71.1	74.6
Zn	101	103
Hg	0.164	0.158

No components	13	13

Appendix 3. Addendum to Report on the HELCOM PLC6 intercalibration

Contents

Preface

This is an addendum to "Report on the HELCOM PLC6 intercalibration". One laboratory was accidential not included in the statistical evaluation for the intercalibration. This addendum presents the results from this laboratory.

Details concerning back ground, statistical parameters, preparation, stability, summary statistics and evaluation of the intercalibration can be found in the main report.

1 Laboratory results for the statistical analysis

1.2 Description of the tables

In section 1.2 and 1.3 the laboratory's results corrected to same units are shown. The following terms are used in the tables:

Measured values are the results from the laboratory

Assigned values are calculated as the total mean of results from the first evaluation from the participating laboratories results without outliers. See the main report.

Average is the mean of the test pairs (sample A and B)

Dev % is the relative deviation between the assigned value and the laboratory average

RSD % is the relative deviation between test pairs (sample A and B)

z-score is a simple way to evaluate the results in the relation to the uncertainty of the intercalibration; z-scores between -2 and 2 is regarded satisfactory. From -3 to -2 and 2 to 3 is regarded as questionable results. z-scores below -3 and higher than 3 is regarded as not acceptable. z-scores are calculated by the following equation (according to ISO 13528:2005):

$z=(x-m)/\sigma$

where x is the average of the laboratory result (sample A and B), m is the assigned value and σ is the standard deviation for evaluation of the intercalibration. In the present intercalibration the reproducibility is used as σ. The assigned values are the means of all laboratories results, outliers excluded.

1.2 Fresh water

Laboratory Code no.: 6

Components	Measured values		Assigned values		Statistics			
	Fresh water A	Fresh water B	Fresh water A	Fresh water B	Average	Dev. %	RSD %	z-score
NH4-N, mg/L	0.026	0.022	0.128	0.128	0.024	-81.2	11.8	-1.6
NO3-N, mg/L	4.5	4.6	5.01	5.01	4.55	-9.2	1.6	-1.8
NO2-N, mg/L	0.26	0.27	0.140	0.140	0.265	89.3	2.7	4.7
N-total, mg/L	4.9	4.9	6.04	6.04	4.90	-18.9	0.0	-3.8
PO4-P, mg/L	0.018	0.016	0.028	0.028	0.017	-39.3	8.3	-1.2
P-total, mg/L	0.050	0.049	0.047	0.047	0.050	6.3	1.4	0.2
Cd, µg/L			0.312	0.312				
Cr, µg/L			4.22	4.22				
Cu, µg/L			6.84	6.84				
Ni, µg/L			8.72	8.72				
Pb, µg/L			3.00	3.00				
Zn, µg/L			15.12	15.12				
Hg, µg/L	0.02	0.02	0.023	0.023	0.020	-13.0	0.0	-0.3

No. components	7	7

Laboratory Code no.: 6

Components	Measured value	assigned value	Statistics
	Fresh Water C	C	dev %
NH4-N, mg/L	0.073	0.216	-66,2
NO3-N, mg/L	4.5	5.02	-10,4
NO2-N, mg/L	0.42	0.207	103,2
N-total, mg/L	5.0	6.30	-20,6
PO4-P, mg/L	0.12	0.137	-12,1
P-total, mg/L	0.16	0.184	-13,0
Cd, µg/L		1.26	
Cr, µg/L		6.82	
Cu, µg/L		14.8	
Ni, µg/L		18.8	
Pb, µg/L		12.8	
Zn, µg/L		34.3	
Hg, µg/L	0.08	0.073	9.3

No. components	7

1.3 Waste water

Laboratory Code no.: 6

Components	Measured values		Assigned values		Statistic			
	Waste water A	Waste water B	Waste water A	Waste water B	Average	Dev. %	RSD %	z-score
NH4-N, mg/L	0.033	0.038	0.030	0.030	0.036	20.3	10.0	0.64
NO3-N, mg/L	1.05	1.05	1.24	1.24	1.05	-15.3	0.0	-2.55
NO2-N, mg/L			0.001	0.001				
N-total, mg/L	1.62	1.63	1.91	1.91	1.63	-14.9	0.4	-1.07
PO4-P, mg/L	0.126	0.125	0.140	0.140	0.126	-10.4	0.6	-1.48
P-total, mg/L	0.15	0.15	0.166	0.166	0.150	-9.6	0.0	-0.74
Cd, µg/L			1.65	1.65				
Cr, µg/L			10.24	10.24				
Cu, µg/L			84.5	84.5				
Ni, µg/L			28.0	28.0				
Pb, µg/L			81.5	81.5				
Zn, µg/L			94.0	94.0				
Hg, µg/L	0.16	0.15	0.169	0.169	0.155	-8.3	4.6	-0.83

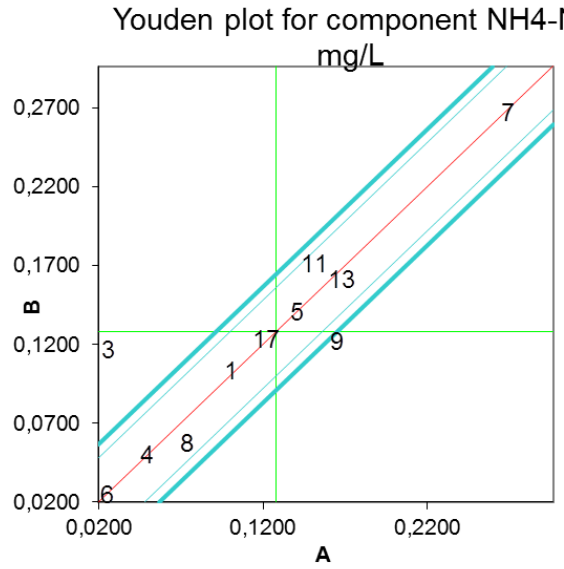
No. components	6	6

2 Evaluation of results

For each component the following statistical analysis has been performed: For sample A and B (fresh water and waste water), table with the data presented for each component together with outlier test according to Cochran and Grubb, Youden plot and summary of the statistical parameters. For sample C, fresh water, table with the data presented for each component together with outlier test according to Grubb and a more limited summary of the statistical parameters. As the main part of the statistical calculations are based on duplicate samples these can obviously not be performed on sample C, freshwater. The statistical parameters are described in the main report chapter 4 and the statistic summary can be found here as well.

2.1 Statistical data for each component in fresh water

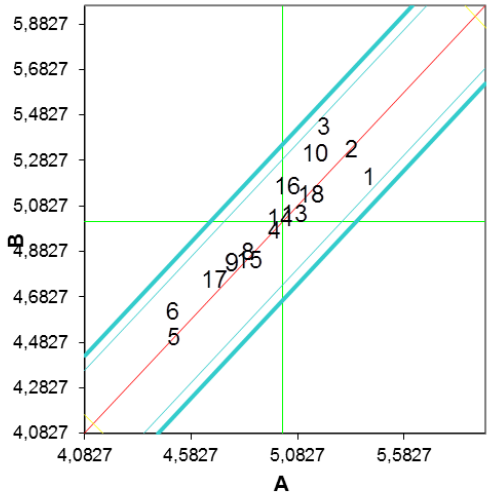
Component	*NH_4-N, mgL*								
Assigned value	0.128	0.128	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% Niveau	5% Niveau	1% Niveau	5% Niveau	1% Niveau	5% Niveau	
1	0.101	0.101							
2									
3	0.027	0.114	X	X	-	-	-	-	X
4	0.050	0.048							
5	0.141	0.138							
6	0.026	0.022							
7	0.269	0.265							
8	0.074	0.055							
9	0.166	0.119	X	X	-	-	-	-	X
10									
11	0.152	0.169							
13	0.168	0.158							
14									
15									
16									
17	0.123	0.121							
18									



Component	NH_4-N, mgL					
Assigned value	0.216	Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	C	1% level	5% level	1% level	5% level	
1	0.194					
2						
3	0.033					
4	0.102					
5	0.238					
6	0.073					
7	0.254					
8	0.150					
9	0.298					
10						
11	0.330					
13	0.325					
14						
15						
16						
17	0.238					
18						

Component	NO_3-N, mgL								
Assigned value	5.012	5.012	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	5.422	5.196							
2	5.340	5.320							
3	5.216	5.412							
4	4.976	4.963							
5	4.507	4.491							
6	4.500	4.600							
7									
8	4.850	4.865							
9	4.780	4.820							
10	5.170	5.300							
11									
13	5.070	5.030							
14	5.008	5.017							
15	4.860	4.830							
16	5.037	5.153							
17	4.699	4.744							
18	5.150	5.120							

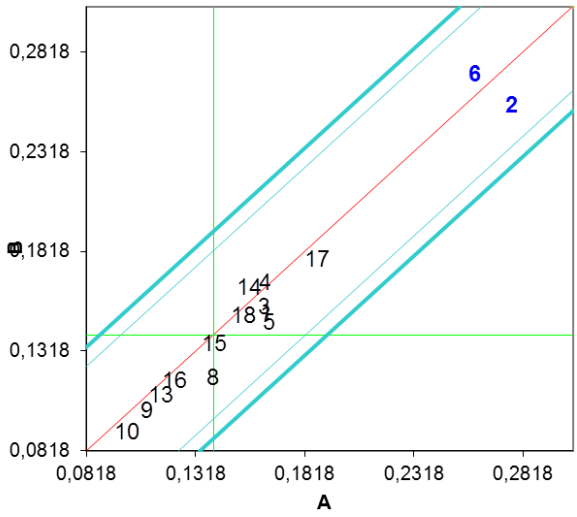
Youden plot for component NO3-N, mg/L



Component	*NO_3-N, mgL*					
Assigned value	**5.024**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	5.196					
2	5.550					
3	5.103					
4	4.955					
5	4.480					
6	4.500					
7						
8	4.833					
9	4.800					
10	5.490					
11						
13	5.050					
14	5.122					
15	4.830					
16	5.295					
17	4.586					
18	5.050					

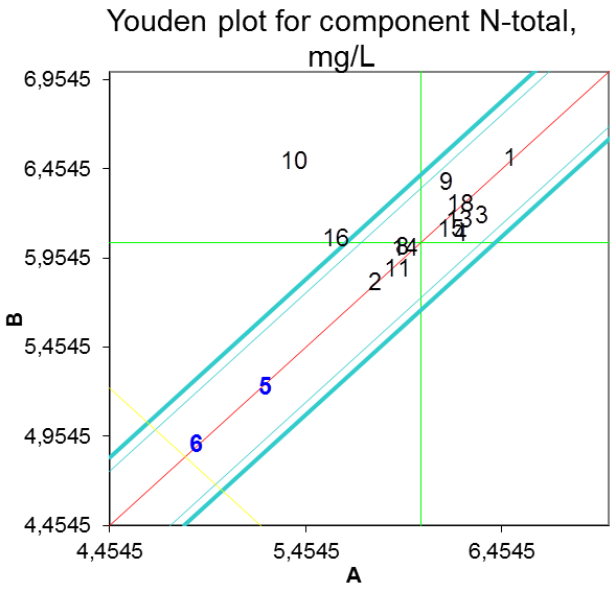
Component	*NO_2-N, mgL*								
Assigned value	**0.140**	**0.140**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.164	0.149							
2	0.277	0.255						X	
3	0.164	0.152							
4	0.164	0.165							
5	0.166	0.145							
6	0.260	0.270						X	
7									
8	0.140	0.117							
9	0.110	0.100							
10	0.101	0.090							
11									
13	0.116	0.108							
14	0.157	0.162							
15	0.141	0.134							
16	0.122	0.115							
17	0.188	0.177							
18	0.154	0.148							

Youden plot for component NO2-N, mg/L



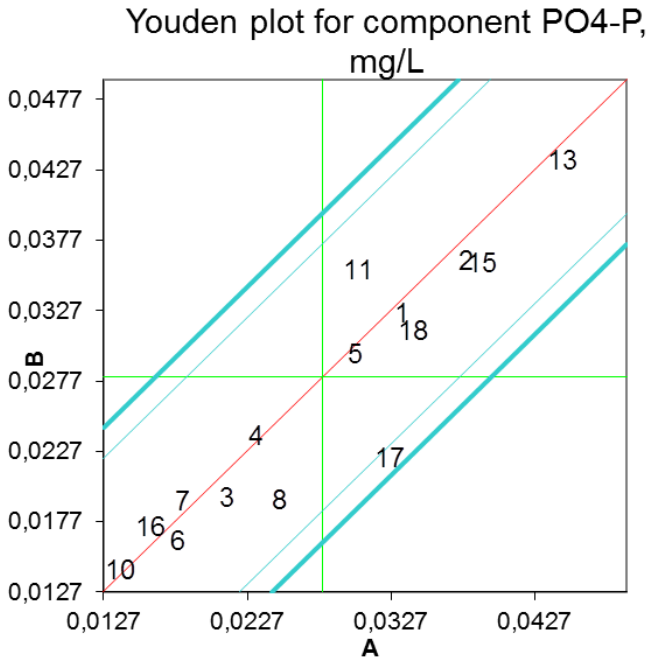
Component	*NO_2-N, mgL*					
Assigned value	**0.207**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.213					
2	0.432					
3	0.289					
4	0.244					
5	0.244					
6	0.420	-	-	-	-	X
7						
8	0.190					
9	0.134					
10	0.033					
11						
13	0.141					
14	0.234					
15	0.222					
16	0.035					
17	0.291					
18	0.192					

Component	*N-total, mgL*								
Assigned value	**6.040**	**6.040**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.500	6.500							
2	5.810	5.800							
3	6.360	6.170							
4	6.250	6.075							
5	5.250	5.230						X	
6	4.900	4.900						X	
7	136.000	140.000	X	X	-	-	-	-	X
8	5.950	6.000							
9	6.180	6.360							
10	5.400	6.480	X	X	-	-	-	-	X
11	5.927	5.878							
13	6.240	6.150							
14	5.964	5.995							
15	6.200	6.100							
16	5.610	6.040	X	X	-	-	-	-	X
17									
18	6.250	6.240							



Component	*N-total, mgL*					
Assigned value	**6.299**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.700					
2	6.040					
3	6.340					
4	6.840					
5	5.310					
6	5.000	-	-	-	-	X
7	142.000	X	X	-	-	X
8	6.070					
9	6.120					
10	7.250					
11	5.814					
13	6.380					
14	6.132					
15	6.300					
16	6.520					
17						
18	6.370					

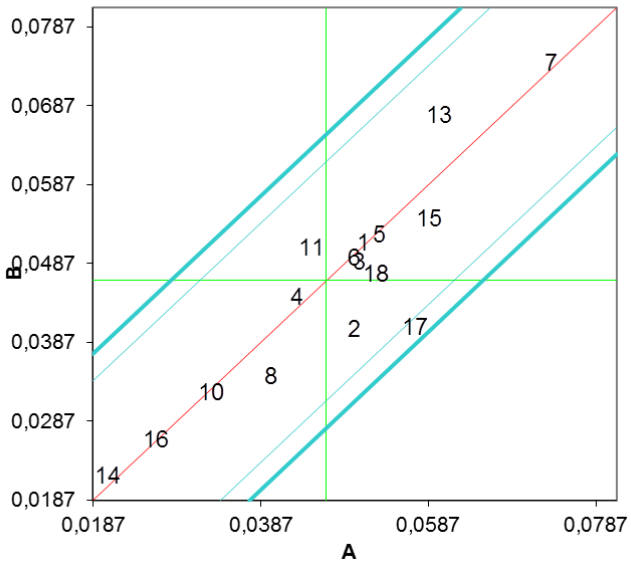
Component	*PO_4-P, mgL*								
Assigned value	**0.028**	**0.028**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.034	0.032							
2	0.038	0.036							
3	0.021	0.019							
4	0.023	0.024							
5	0.030	0.029							
6	0.018	0.016							
7	0.018	0.019							
8	0.025	0.019							
9									
10	0.014	0.014							
11	0.031	0.035							
13	0.045	0.043							
14									
15	0.039	0.036							
16	0.016	0.017							
17	0.033	0.022		X					
18	0.034	0.031							



Compo-nent	PO_4-P, mgL					
Assigned value	0.137	Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	C	1% level	5% level	1% level	5% level	
1	0.134					
2	0.174				X	
3	0.137					
4	0.131					
5	0.126					
6	0.120					
7	0.018	X	X	-	-	X
8	0.128					
9						
10	0.137					
11	0.146					
13	0.131					
14	0.166				X	
15	0.130					
16	0.119					
17	0.118					
18	0.136					

Component	P-total, mgL								
Assigned value	0.047	0.047	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.051	0.051							
2	0.050	0.040							
3	0.051	0.048							
4	0.043	0.044							
5	0.053	0.052							
6	0.050	0.049							
7	0.073	0.074							
8	0.040	0.034							
9									
10	0.033	0.032							
11	0.045	0.050							
13	0.060	0.067							
14	0.021	0.022							
15	0.059	0.054							
16	0.026	0.026							
17	0.057	0.040		X					
18	0.053	0.047							

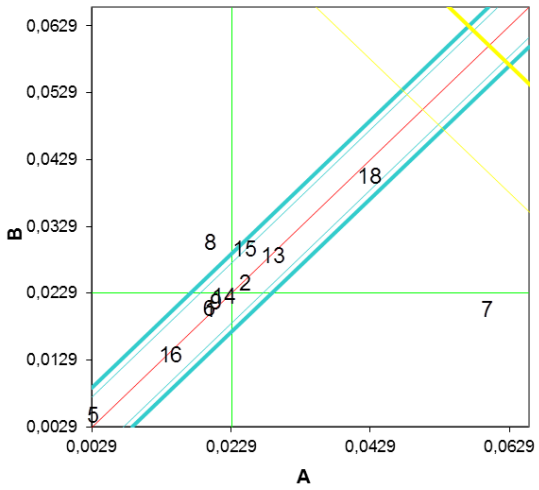
Youden plot for component P-total, mg/L



Component	*P-total, mgL*					
Assigned value	**0.184**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.198					
2	0.190					
3	0.214					
4	0.190					
5	0.196					
6	0.160					
7	0.073	X	X	-	-	X
8	0.179					
9						
10	0.148					
11	0.204					
13	0.164					
14	0.166					
15	0.200					
16	0.141					
17	0.193					
18	0.191					

Component	*Hg, µgL*								
Assigned value	**0.023**	**0.023**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.020	0.020							
2	0.025	0.024							
3									
4									
5	0.003	0.004							
6	0.020	0.020							
7	0.060	0.020	X	X	-	-	-	-	X
8	0.020	0.030	X	X	-	-	-	-	X
9	0.021	0.021							
10									
11									
13	0.029	0.028							
14	0.022	0.022							
15	0.025	0.029							
16	0.014	0.013							
17									
18	0.043	0.040							

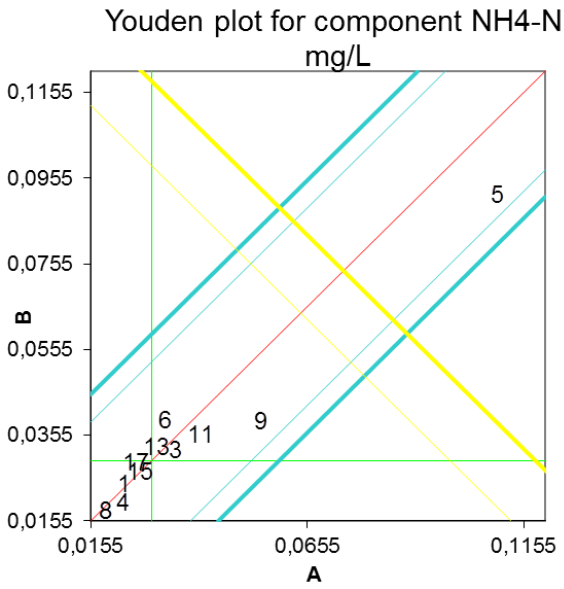
Youden plot for component Hg, µg/L



Component	*Hg, µgL*					
Assigned value	**0.073**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**C**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.068					
2	0.088					
3						
4						
5	0.009	X	X	-	-	X
6	0.080					
7	0.078					
8	0.070					
9	0.086					
10						
11						
13	0.094					
14	0.081					
15	0.086					
16	0.063					
17						
18	0.062					

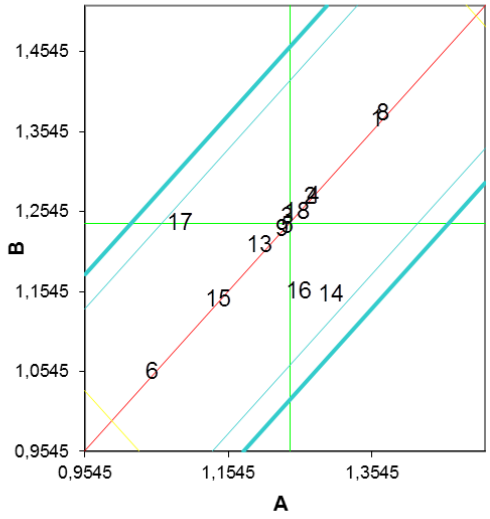
2.2 Statistical data for each component in waste water

Component	*NH_4-N, mgL*								
Assigned value	0.030	0.030	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	A	B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.023	0.023							
2									
3	0.036	0.031							
4	0.023	0.019							
5	0.109	0.091			X	X	-	-	X
6	0.033	0.038							
8	0.019	0.017							
9	0.055	0.038							
11	0.041	0.035							
13	0.031	0.032							
14									
15	0.027	0.026							
16									
17	0.026	0.028							
18									

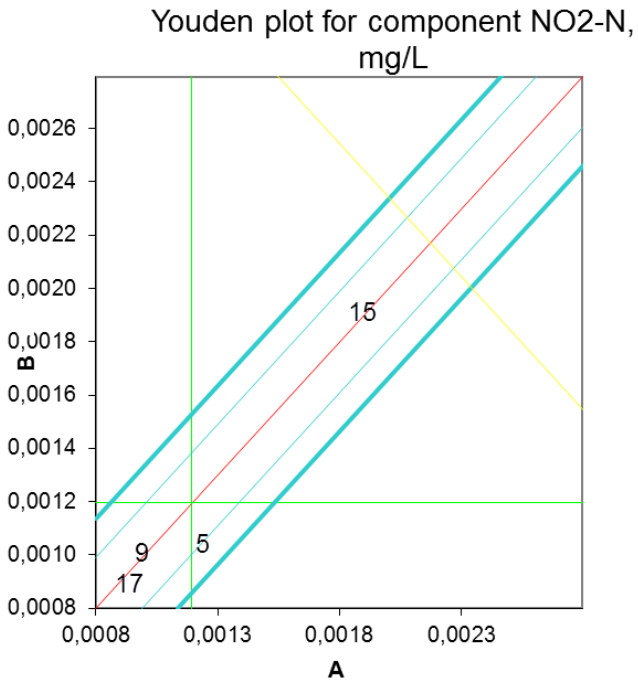


Component	*NO_3-N, mgL*								
Assigned value	**1.240**	**1.240**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	1.362	1.367							
2	1.270	1.270							
3	1.238	1.244							
4	1.274	1.271							
5	1.238	1.233							
6	1.050	1.050							
8	1.370	1.375							
9	1.230	1.230							
11									
13	1.200	1.210							
14	1.299	1.148							
15	1.140	1.140							
16	1.254	1.152							
17	1.089	1.238							
18	1.250	1.250							

Youden plot for component NO3-N, mg/L

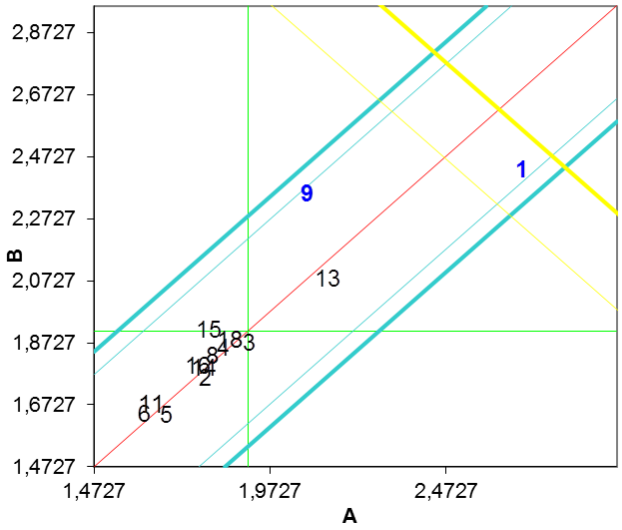


Component	*NO_2-N, mgL*								
Assigned value	**0.001**	**0.001**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1									
2									
3									
4									
5	0.001	0.001		X					
6									
8									
9	0.001	0.001							
11									
13									
14									
15	0.002	0.002							
16	0.007	0.008	X	X	-	-	-	-	X
17	0.001	0.001							
18									

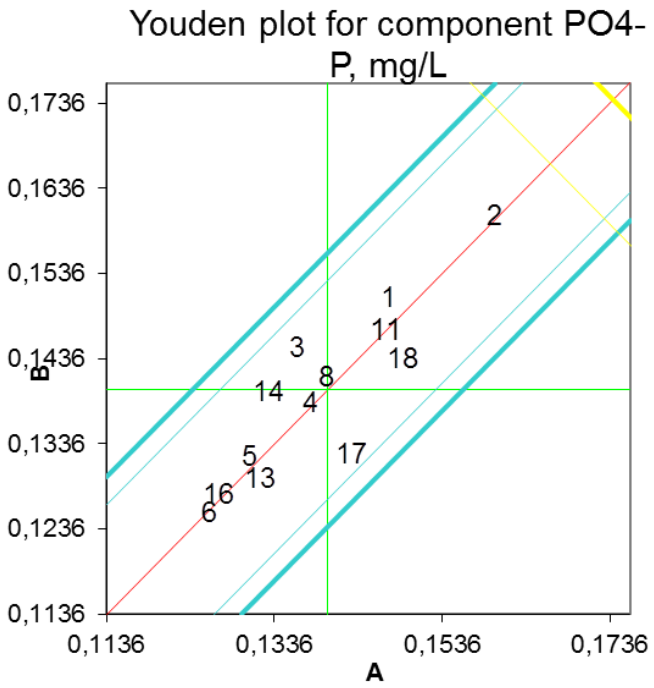


Component	*N-total, mgL*								
Assigned value	**1.910**	**1.910**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	2.690	2.430				X		X	
2	1.790	1.750							
3	1.920	1.860							
4	1.843	1.847							
5	1.680	1.630							
6	1.620	1.630							
8	1.810	1.820							
9	2.080	2.350						X	
11	1.634	1.664							
13	2.140	2.070							
14	1.787	1.783							
15	1.800	1.900							
16	1.770	1.790							
17									
18	1.860	1.870							

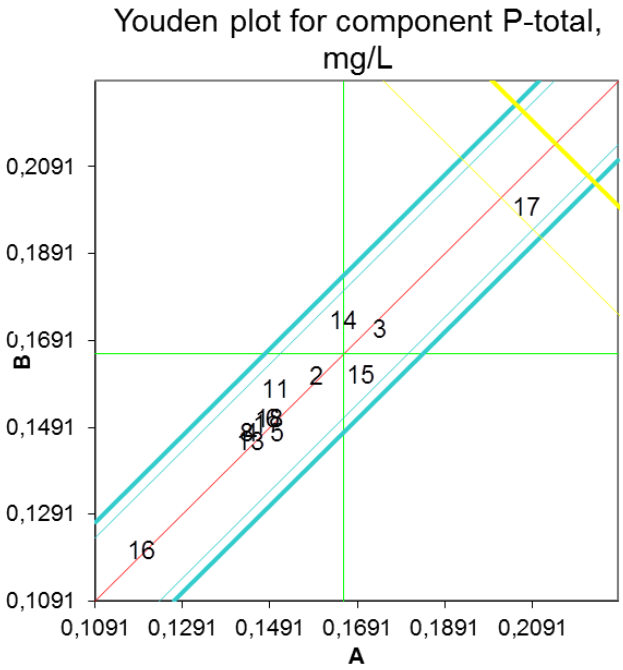
Youden plot for component N-total, mg/L



Component	*PO_4-P, mgL*								
Assigned value	**0.140**	**0.140**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.147	0.150							
2	0.160	0.160							
3	0.137	0.144							
4	0.138	0.138							
5	0.131	0.132							
6	0.126	0.125							
8	0.140	0.141							
9									
11	0.147	0.147							
13	0.132	0.129							
14	0.133	0.139							
15									
16	0.127	0.127							
17	0.143	0.132							
18	0.149	0.143							

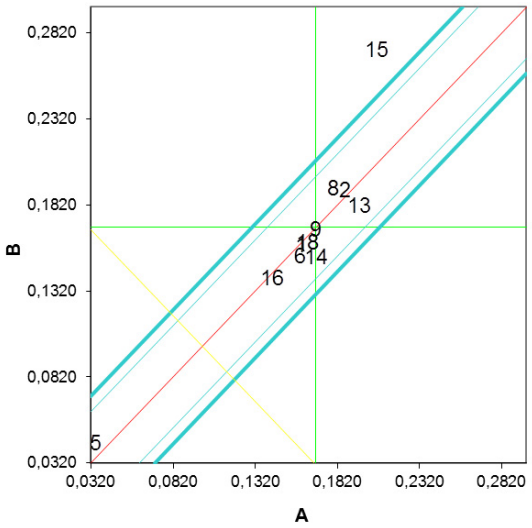


Component	*P-total, mgL*								
Assigned value	**0.166**	**0.166**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.147	0.149							
2	0.160	0.160							
3	0.175	0.170							
4	0.145	0.147							
5	0.151	0.147							
6	0.150	0.150							
8	0.144	0.147							
9									
11	0.150	0.157							
13	0.145	0.145							
14	0.166	0.173							
15	0.170	0.160							
16	0.120	0.120							
17	0.208	0.199				X			
18	0.149	0.150							



Component	*Hg, µgL*								
Assigned value	**0.169**	**0.169**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.160	0.157							
2	0.187	0.189							
3									
4									
5	0.035	0.042			X	X	-	-	X
6	0.160	0.150							
8	0.180	0.190							
9	0.169	0.166							
11									
13	0.196	0.180							
14	0.170	0.150							
15	0.206	0.270	X	X	-	-	-	-	X
16	0.143	0.138							
17									
18	0.164	0.158							

Youden plot for component Hg, µg/L



3 Conclusions

In table 1 and 2 below is a comparison of the summary statistics for for first evaluation and the second evaluation where the additional laboratory is included. The laboratory sent data on the nutrients and Hg. The main changes are highlightet in bold.

Table 1. Fresh water. Comparision of the mean concentrations and relative value of the total variation (CV(R)) from the first evaluation and the second with the additional laboratory is included. # Some PO_4-P could be present in the spike used for P-total.

Components	Freshwater					
	Mean conc. sample A/B	Mean conc. sample A/B Additional lab	CV(R) (%) sample A/B	CV(R) (%) sample A/B Additional lab	sample C recovery of spike (%)	sample C recovery of spike (%) Additional lab
NH_4-N mg/L	0.13	0.12	51	**58**	138	128
NO_3-N mg/L	5	5	5	5	spike too low	spike too low
NO_2-N mg/L	0.14	0.16	19	**36**	no spike	no spike
N-total mg/L	6	6	5	7	95	90
PO_4-P mg/L	0.028	0.027	38	**33**	519#	516#
P-total mg/L	0.047	0.047	30	29	89	88
Cd µg/L	0.31		10		95	
Cr µg/L	4.2		11		97	
Cu µg/L	6.8		17		96	
Ni µg/L	8.7		13		88	
Pb µg/L	3		10		97	
Zn µg/L	15		12		98	
Hg µg/L	0.023	0.022	43	43	77	76

Table 2. Waste water. Comparision of the mean concentrations and relative value of the total variation (CV(R)) from the first evaluation and the second with the additional laboratory is included.

Components	Waste water			
	Mean conc. sample A/B	CV(R) (%) sample A/B Additional lab	CV(R) (%) sample A/B	CV(R) (%) sample A/B Additional lab
NH_4-N mg/L	0.03	0.03	32	31
NO_3-N mg/L	1.2	1.2	6	7
NO_2-N mg/L	0.0012	0.012	37	37
N-total mg/L	1.9	1.9	14	14
PO_4-P mg/L	0.14	0.14	7	7
P-total mg/L	0.16	0.16	13	11
Cd µg/L	1.7		5	
Cr µg/L	10		10	
Cu µg/L	85		7	
Ni µg/L	28		9	
Pb µg/L	82		9	
Zn µg/L	94		7	
Hg µg/L	0.17	0.17	10	10

By adding an additional set of data to the evaluation of the intercalibration the nominel values and the total variation was changed for three compounds in fresh water.

For fresh water, sample A/B the main change was found for NO_2-N where the total variation increased significantly. For NH_4-N and PO_4-P there were minor changes in the total variation. For all three compounds there were

minor changes for the mean concentration. NH_4-N and N-total showed minor changes in the recovery for sample C.

For waste water no changes in the statistics was found by adding an extra set of data.

Overall the conclusions from the first evaluation are still valid with the exception NO_2-N where the uncertainty appears to be higher.

Appendix

The original data from the laboratory

Intercalibration under PLC6

Fresh water

Laboratory number: **6**

Skema 1

Componenets	Measured data			
	Fresh Water sample A	**Fresh Water sample B**	**Fresh Water sample C**	
NH_4-N	0.026	0.022	0.073	mg/L
NO_3-N	4.5	4.6	4.5	mg/L
NO_2-N	0.26	0.27	0.42	mg/L
N-total	4.9	4.9	5.0	mg/L
PO_4-P	0.018	0.016	0.12	mg/L
P-total	0.050	0.049	0.16	mg/L
Cd				
Cr				
Cu				
Ni				
Pb				
Zn				
Hg	0.02	0.02	0.08	µg/L
No components	13	13	13	

Intercalibration under PLC6

Waste water

Laboratory number: **6**

Skema 1

Componenets	Measured data: Waste Water sample A	Measured data: Waste Water sample B	
NH_4-N	0.033	0.038	mg/L
NO_3-N	1.05	1.05	mg/L
NO_2-N	<0.0038	<0.0038	mg/L
N-total	1.62	1.63	mg/L
PO_4-P	0.126	0.125	mg/L
P-total	0.15	0.15	mg/L
Cd			
Cr			
Cu			
Ni			
Pb			
Zn			
Hg	0.16	0.15	µg/L

No components	13	13

REPORT ON THE HELCOM PLC6 INTERCALIBRATION

This report presents results from the PLC6 intercalibration on metal and nutrients in fresh water and waste water. The intercalibration was performed in ordre to evaluate the analytical quality of results reported to HELCOM.
17 laboratories participated in the intercalibration.

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