REPORT ON THE HELCOM PLC-7 INTERCALIBRATION

Technical Report from DCE – Danish Centre for Environment and Energy No. 135 2019

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Abstract: This report presents results from the PLC-7 intercalibration on metal and nutrients in freshwater and waste water. The intercalibration was performed in order to evaluate the analytical quality of results reported to HELCOM. 29 laboratories participated in the intercalibration.

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Preface

The Danish Centre for Environment and Energy, Aarhus University (DCE) has in 2018 performed an intercalibration on nutrients and metals in freshwater and waste water as a part of the HELCOM PLC-7 project 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.

The intercalibration was financed by HELCOM and DCE – Danish Centre for Environment and Energy. The participating laboratories have financed the analyses they have performed by themselves.

1. Description of the intercalibration

The Seventh Baltic Sea Pollution Load Compilation Project (PLC-7) includes an intercalibration of chemical analyses. The intercalibration is a part of the quality assurance of the estimation of the waterborne pollution load of the Baltic Sea. The intercalibration consists of freshwater and waste water for nutrients and metals.

As homogeneity and stability is essential for an intercalibration test the samples were treated differently compared to natural samples. Both freshwater and waste water were filtered (glass beads and glass wool) in order to remove particulate matter and the waste water was sterilized.

Further, to make sure that as many laboratories as possible could report data above detection limits the samples were spiked with nutrients in freshwater and with metals in both freshwater and waste water. This implies that the concentration levels do not necessarily reflect the natural concentration levels in rivers and lakes, and in waste water from treatment plants and industry for all components. For freshwater the samples were spiked at two levels; Sample A and B were spiked to the same concentration and sample C to a higher level. This makes it possible to estimate a recovery of the component based on the known spike amount and the difference in concentration between A / B and C samples.

This report presents results from the PLC-7 intercalibration. There are reported results from 20 laboratories on freshwater and 27 laboratories on 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: NO_3 and NO_2 or NO_{2+3}, 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 1 does not reflect the code numbers.

The laboratories were expected to have quality assured the data before submitting results to DCE. Data below detection limits (reported as "<value") 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. Z-score 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. This report do not comment on the performance of single laboratories. The laboratories and the representative from the single member states are expected to do that.

Data on NO_{2+3} in freshwater have been included in the statistical analysis and assessment, if the parameter has been measured as $NO_{2+3.}$ Data on NO_{2+3} which are the sum of measured NO_2 and measured NO_3 are not included. It means that there were only five data sets on NO_{2+3}. Reservation is therefore taken for the outlier test and the statistics performed on NO_{2+3} in freshwater, as the results are debatable due to the low number of data. This means that the statistical evaluation of NO_{2+3} 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 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 extreme (highest and / or lowest) test pairs but after the same principle as above.
z-score	The z-score is shown visually for each component across the laboratories
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 freshwater samples used for this intercalibration were collected from a Danish lake in Zealand.

The waste water samples were effluent water collected from a waste water treatment plant in Zealand, Denmark.

Both freshwater and waste water were collected in 30 litres polyethylene (PE) containers.

Waste water samples were sent to Holland for filtration, sterilization, spiking homogenization and bottling. For the metals, the A and B samples were spiked to the same concentration. The nutrient samples were not spiked.

The freshwater samples were filtered in order to secure homogeneity and increase the stability of the nutrients. Both samples for metal and nutrient analysis were spiked. A and B samples were spiked to the same concentration whereas the C samples were spiked to a higher concentration.

Samples for nutrients and metals were bottled in HPE bottles, whereas Hg samples were bottled in glass bottles.

Waste water samples for metals were conserved with nitric acid (2%), all samples for nutrients and freshwater samples for metals were not conserved, apart from storing in refrigerator until distribution. The samples were transported by courier, TNT, and the transportation time varied from one to three days. The samples were sendt out the 19th of February. The laboratories had approximately 3 weeks for the analysis to mid March.

2.1 Stability and homogeneity

2.1.1 Samples used for metals

Stability and homogeneity of fresh water and waste water samples for metals was tested in Denmark by DCE. 6-10 samples were analysed each time. Tests was performed for mercury using Hg-AFS detector according to US-EPA method 1631, zinc and copper was tested using flame atomic absorption according to DS 259.

The samples was analysed two times, shortly after preparation of the samples in mid-February, and at the end of March for the metals. Recovery was calculated as the difference between the measured values from February to March.

Zn [µg/L]	FW A+B	FW C	WW
PLC 7 result	**77.16±7.22**	**168.5±41.87**	**435.6±33.1**
March	78	167	445
Std.dev.	1	1	2
RSD %	1.7%	0.8%	0.4%
February:	82	185	463
Recovery	95%	90%	96%

The reproducibility of the Zn measurements indicated that the samples was homogeneous (n=10 for each sample type in March). In February, only six bottles of each was tested. The estimated detection limit of Zn using the flame AAS is 10 µg/l. Long-term stability was better than 10% in all cases.

Cu [µg/L]	FW A+B	FW C	WW
PLC 7 result	**29.3±4.9**	**47.38±6.9**	**142.4±8.3**
March	30	44	133
Std.dev.	1	3	4
RSD %	2.2%	7.4%	3.3%
February:	30	51	152
Recovery	100%	87%	87%

The reproducibility of the Cu measurements indicated that the samples was homogeneous (n=10 for each sample type in March). In February, only six bottles of each was tested. The estimated detection limit of Cu using the flame AAS is 10 µg/l, so the RSD are acceptable, but there could possibly be a slight loss of Cu during the 5 weeks between the analyses. Long-term stability was better than 15% in all cases.

Hg [µg/l]	FW A	FW B	FW C	WW
PLC 7 result	**0.174±0.017**	**0.174±0.017**	**0.662±0.102**	**0.385±0.045**
March	0.11	0.11	0.47	0.334
Std.dev.	0.035	0.025	0.146	0.014
RSD %	31.7%	22.2%	31.1%	4.3%

Mercury bottles was only tested one time in March due to problems with the instrumentation. The results for the WW indicated that the WW was homogenous, but the FW bottles was very variable between samples (10 bottles each of A, B and C was analysed, but no difference was found between A and B samples). Further, comparing the result from the participants for the FW showed that Hg probably was not stable possibly because the samples were not acidified.

2.2 Samples used for Nutrients

Homogeneity test of nutrient samples was performed on 6-10 samples. The samples were only tested after spiking, bottling and distribution. The samples were analyzed for NO_2-N, NT-N, PO_4-P and TP-P on a Skalar apparatus.

NO2-N mg/L	FW A+B	FW C	WW
PLC 7 result	**0.036±0.006**	**0.042±0.007**	**0.045±0.005**
Average	0.032	0.039	0.047
Std.dev.	0.003	0.004	0.0003
RSD %	8.0	11.6	0.7

TN-N mg/L	FW A+B	FW C	WW
PLC 7 result	**3.44±0.22**	**6.05±0.56**	**7.23±0.34**
Average	3.55	6.44	7.07
Std.dev.	0.03	0.17	0.06
RSD %	0.8	2.6	0.9

PO4-P mg/L	FW A+B	FW C	WW
PLC 7 result	**0.209±0.014**	**0.347±0.038**	**0.0096±0.003**
Average	0.206	0.354	0.006
Std.dev.	0.008	0.005	0.001
RSD %	3.8	1.3	12.8

TP-P mg/L	FW A+B	FW C	WW
PLC 7 result	**0.361±0.019**	**0.824±0.039**	**0.025±0.013**
Average	0.369	0.800	0.019
Std.dev.	0.010	0.021	0.001
RSD %	2.7	2.7	5.3

The homogeneity test showed that the homogeneity in general was better for waste water. A reason for that could be that the waste water has been sterilized, which the fresh water has not. The relative standard deviation were high for some of the nutrients. This was primarily caused by very low concentrations.

3. Laboratory results for the statistical analysis

3.1 Description of the tables

In section 3.2 and 3.3 the single laboratories' results 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 measured values 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 the measured values of the test pairs (sample A and B)

z-score is a simple way to evaluate the results in 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 (measured values of 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 (S(R)), which are the total deviation of the intercalibration, is used as σ (see also 4.1). As mentioned earlier the assigned values are the means of all laboratories results, after exclusion of outliers.

3.2 Freshwater

Laboratory
Code no.: **1**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L			0.036	0.036				
NO2+3-N, mg/L	1.53	1.50	1.60	1.60	1.52	-5.2	1.4	-1.0
N-total, mg/L	3.56	3.56	3.44	3.44	3.56	3.5	0.0	0.6
PO4-P, mg/L	0.200	0.202	0.209	0.209	0.201	-3.8	0.7	-0.6
P-total, mg/L	0.360	0.359	0.361	0.361	0.360	-0.4	0.2	-0.1
Cd, µg/L	6.43	6.40	6.42	6.42	6.42	-0.1	0.3	0.0
Cr, µg/L	11.32	11.17	11.68	11.68	11.25	-3.7	0.9	-0.3
Cu, µg/L	32.22	32.16	29.30	29.30	32.19	9.9	0.1	0.6
Ni, µg/L	52.98	53.98	51.04	51.04	53.48	4.8	1.3	0.7
Pb, µg/L	10.59	10.36	11.14	11.14	10.48	-6.0	1.6	-0.5
Zn, µg/L	84.32	84.07	77.16	77.16	84.20	9.1	0.2	1.0
Hg, µg/L	0.139	0.156	0.174	0.174	0.148	-15.2	8.1	-1.6

Laboratory
Code no.: **1**

	Measured value	Assigned Values	
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L		0.042	
NO2+3-N, mg/L	2.25	2.40	-6.1
N-total, mg/L	6.54	6.05	8.2
PO4-P, mg/L	0.318	0.347	-8.4
P-total, mg/L	0.818	0.824	-0.7
Cd, µg/L	9.78	9.90	-1.3
Cr, µg/L	16.95	17.78	-4.7
Cu, µg/L	50.25	47.38	6.1
Ni, µg/L	82.01	80.33	2.1
Pb, µg/L	20.94	21.30	-1.7
Zn, µg/L	169.8	168.5	0.8
Hg, µg/L	0.568	0.662	-14.2

Laboratory
Code no.: **4**

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.64	1.60	1.56	1.56	1.62	3.7	1.5	1.2
NO2-N, mg/L	0.031	0.030	0.036	0.036	0.031	-15.3	2.3	-0.9
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.36	3.32	3.44	3.44	3.34	-2.9	0.8	-0.4
PO4-P, mg/L	0.203	0.204	0.209	0.209	0.204	-2.6	0.3	-0.4
P-total, mg/L	0.344	0.340	0.361	0.361	0.342	-5.3	0.8	-1.0
Cd, µg/L		6.48	6.42	6.42	6.48	0.9		0.2
Cr, µg/L	13.00	13.33	11.68	11.68	13.17	12.8	1.8	1.2
Cu, µg/L	31.50	32.10	29.30	29.30	31.80	8.5	1.3	0.5
Ni, µg/L	52.57	51.36	51.04	51.04	51.97	1.8	1.6	0.3
Pb, µg/L	14.71	14.60	11.14	11.14	14.66	31.6	0.5	2.6
Zn, µg/L			77.16	77.16				
Hg, µg/L	0.191	0.186	0.174	0.174	0.189	8.3	1.9	0.9

Laboratory
Code no.: **4**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.46	2.35	4.7
NO2-N, mg/L	0.032	0.042	-23.8
NO2+3-N, mg/L		2.40	
N-total, mg/L	6.40	6.05	5.8
PO4-P, mg/L	0.358	0.347	3.2
P-total, mg/L	0.791	0.824	-4.0
Cd, µg/L		9.90	
Cr, µg/L		17.78	
Cu, µg/L	52.60	47.38	11.0
Ni, µg/L	80.20	80.33	-0.2
Pb, µg/L		21.30	
Zn, µg/L	0.171	168.5	-99.9
Hg, µg/L		0.662	

Laboratory
Code no.: **5**

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L			0.036	0.036				
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L			3.44	3.44				
PO4-P, mg/L			0.209	0.209				
P-total, mg/L			0.361	0.361				
Cd, µg/L	5.50	6.06	6.42	6.42	5.78	-10.0	6.9	-1.8
Cr, µg/L	10.90	9.53	11.68	11.68	10.22	-12.5	9.5	-1.1
Cu, µg/L	20.05	20.66	29.30	29.30	20.36	-30.5	2.1	-1.8
Ni, µg/L	44.62	45.56	51.04	51.04	45.09	-11.7	1.5	-1.8
Pb, µg/L	12.00	12.87	11.14	11.14	12.44	11.6	4.9	1.0
Zn, µg/L	67.16	65.63	77.16	77.16	66.40	-14.0	1.6	-1.5
Hg, µg/L			0.174	0.174				

Laboratory
Code no.: **5**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L		0.042	
NO2+3-N, mg/L		2.40	
N-total, mg/L		6.05	
PO4-P, mg/L		0.347	
P-total, mg/L		0.824	
Cd, µg/L	8.94	9.90	-9.7
Cr, µg/L	14.52	17.78	-18.3
Cu, µg/L	27.61	47.38	-41.7
Ni, µg/L	77.93	80.33	-3.0
Pb, µg/L	21.58	21.30	1.3
Zn, µg/L	165.1	168.5	-2.0
Hg, µg/L		0.662	

Laboratory
Code no.: 7

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.63	1.55	1.56	1.56	1.59	1.7	3.4	0.5
NO2-N, mg/L	0.037	0.030	0.036	0.036	0.033	-7.6	15.5	-0.5
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.80	3.80	3.44	3.44	3.80	10.5	0.1	1.6
PO4-P, mg/L	0.209	0.208	0.209	0.209	0.209	-0.2	0.2	0.0
P-total, mg/L	0.349	0.347	0.361	0.361	0.348	-3.7	0.4	-0.7
Cd, µg/L	4.62	4.68	6.42	6.42	4.65	-27.6	0.9	-4.9
Cr, µg/L	8.60	8.60	11.68	11.68	8.60	-26.3	0.0	-2.4
Cu, µg/L	20.80	21.00	29.30	29.30	20.90	-28.7	0.7	-1.7
Ni, µg/L	43.70	43.60	51.04	51.04	43.65	-14.5	0.2	-2.2
Pb, µg/L	4.55	4.58	11.14	11.14	4.57	-59.0	0.5	-4.8
Zn, µg/L	64.30	64.52	77.16	77.16	64.41	-16.5	0.2	-1.8
Hg, µg/L			0.174	0.174				

Laboratory
Code no.: 7

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.30	2.35	-2.0
NO2-N, mg/L	0.035	0.042	-16.9
NO2+3-N, mg/L		2.40	
N-total, mg/L	6.60	6.05	9.2
PO4-P, mg/L	0.316	0.347	-9.1
P-total, mg/L	0.789	0.824	-4.3
Cd, µg/L	8.66	9.90	-12.6
Cr, µg/L	13.50	17.78	-24.1
Cu, µg/L	36.30	47.38	-23.4
Ni, µg/L	71.60	80.33	-10.9
Pb, µg/L		21.30	
Zn, µg/L	147.0	168.5	-12.8
Hg, µg/L		0.662	

Laboratory
Code no.: 8

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.55	1.55	1.56	1.56	1.55	-0.9	0.0	-0.3
NO2-N, mg/L	0.032	0.033	0.036	0.036	0.033	-9.7	2.2	-0.6
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.73	3.69	3.44	3.44	3.71	7.8	0.8	1.2
PO4-P, mg/L	0.195	0.195	0.209	0.209	0.195	-6.7	0.0	-1.0
P-total, mg/L	0.377	0.374	0.361	0.361	0.376	4.0	0.6	0.8
Cd, µg/L	6.30	6.19	6.42	6.42	6.25	-2.7	1.2	-0.5
Cr, µg/L	11.40	11.40	11.68	11.68	11.40	-2.4	0.0	-0.2
Cu, µg/L	26.30	24.50	29.30	29.30	25.40	-13.3	5.0	-0.8
Ni, µg/L	53.80	53.00	51.04	51.04	53.40	4.6	1.1	0.7
Pb, µg/L	8.43	8.58	11.14	11.14	8.51	-23.6	1.2	-1.9
Zn, µg/L	87.70	86.90	77.16	77.16	87.30	13.1	0.6	1.4
Hg, µg/L			0.174	0.174				

Laboratory
Code no.: 8

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.37	2.35	1.1
NO2-N, mg/L	0.038	0.042	-9.5
NO2+3-N, mg/L		2.40	
N-total, mg/L	6.60	6.05	9.1
PO4-P, mg/L	0.294	0.347	-15.3
P-total, mg/L	0.847	0.824	2.8
Cd, µg/L	10.00	9.90	1.0
Cr, µg/L	17.20	17.78	-3.3
Cu, µg/L	37.40	47.38	-21.1
Ni, µg/L	80.80	80.33	0.6
Pb, µg/L	16.50	21.30	-22.5
Zn, µg/L	186.0	168.5	10.4
Hg, µg/L		0.662	

Laboratory
Code no.: **13**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L			0.036	0.036				
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L			3.44	3.44				
PO4-P, mg/L			0.209	0.209				
P-total, mg/L			0.361	0.361				
Cd, µg/L	6.51	6.63	6.42	6.42	6.57	2.3	1.3	0.4
Cr, µg/L	13.40	13.20	11.68	11.68	13.30	13.9	1.1	1.3
Cu, µg/L	18.70	18.80	29.30	29.30	18.75	-36.0	0.4	-2.1
Ni, µg/L	50.30	49.60	51.04	51.04	49.95	-2.1	1.0	-0.3
Pb, µg/L	9.53	9.39	11.14	11.14	9.46	-15.1	1.0	-1.2
Zn, µg/L	80.00	84.00	77.16	77.16	82.00	6.3	3.4	0.7
Hg, µg/L	0.160	0.150	0.174	0.174	0.155	-10.9	4.6	-1.1

Laboratory
Code no.: **13**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L		0.042	
NO2+3-N, mg/L		2.40	
N-total, mg/L		6.05	
PO4-P, mg/L		0.347	
P-total, mg/L		0.824	
Cd, µg/L	9.53	9.90	-3.8
Cr, µg/L	19.10	17.78	7.4
Cu, µg/L	52.20	47.38	10.2
Ni, µg/L	80.00	80.33	-0.4
Pb, µg/L	25.10	21.30	17.8
Zn, µg/L	210.0	168.5	24.6
Hg, µg/L	0.660	0.662	-0.3

Laboratory
Code no.: **14**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.57	1.56	1.56	1.56	1.57	0.3	0.5	0.1
NO2-N, mg/L	0.028	0.028	0.036	0.036	0.028	-22.2	0.0	-1.4
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.31	3.36	3.44	3.44	3.34	-3.0	1.1	-0.5
PO4-P, mg/L	0.200	0.200	0.209	0.209	0.200	-4.3	0.0	-0.6
P-total, mg/L	0.400	0.410	0.361	0.361	0.405	12.2	1.7	2.3
Cd, µg/L	6.55	6.80	6.42	6.42	6.68	4.0	2.6	0.7
Cr, µg/L	11.50	12.30	11.68	11.68	11.90	1.9	4.8	0.2
Cu, µg/L	32.90	31.40	29.30	29.30	32.15	9.7	3.3	0.6
Ni, µg/L	54.60	58.20	51.04	51.04	56.40	10.5	4.5	1.6
Pb, µg/L	10.40	10.60	11.14	11.14	10.50	-5.7	1.3	-0.5
Zn, µg/L	77.20	77.80	77.16	77.16	77.50	0.4	0.5	0.0
Hg, µg/L	0.188	0.180	0.174	0.174	0.184	5.7	3.1	0.6

Laboratory
Code no.: **14**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.32	2.35	-1.1
NO2-N, mg/L	0.031	0.042	-26.2
NO2+3-N, mg/L		2.40	
N-total, mg/L	5.76	6.05	-4.7
PO4-P, mg/L	0.320	0.347	-7.8
P-total, mg/L	0.900	0.824	9.2
Cd, µg/L	10.10	9.90	2.0
Cr, µg/L	19.70	17.78	10.8
Cu, µg/L	51.70	47.38	9.1
Ni, µg/L	94.80	80.33	18.0
Pb, µg/L	20.90	21.30	-1.9
Zn, µg/L	162.0	168.5	-3.9
Hg, µg/L	0.714	0.662	7.9

Laboratory
Code no.: **15**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L			0.036	0.036				
NO2+3-N, mg/L	1.63	1.62	1.60	1.60	1.63	1.7	0.4	0.3
N-total, mg/L	3.22	3.16	3.44	3.44	3.19	-7.2	1.3	-1.1
PO4-P, mg/L	0.192	0.192	0.209	0.209	0.192	-8.1	0.0	-1.2
P-total, mg/L	0.365	0.366	0.361	0.361	0.366	1.2	0.2	0.2
Cd, µg/L	6.30	6.30	6.42	6.42	6.30	-1.9	0.0	-0.3
Cr, µg/L	12.00	12.00	11.68	11.68	12.00	2.8	0.0	0.3
Cu, µg/L	31.00	31.00	29.30	29.30	31.00	5.8	0.0	0.3
Ni, µg/L	51.00	51.00	51.04	51.04	51.00	-0.1	0.0	0.0
Pb, µg/L	11.00	12.00	11.14	11.14	11.50	3.2	6.1	0.3
Zn, µg/L	79.00	79.00	77.16	77.16	79.00	2.4	0.0	0.3
Hg, µg/L	0.200	0.200	0.174	0.174	0.200	14.9	0.0	1.5

Laboratory
Code no.: **15**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L		0.042	
NO2+3-N, mg/L	2.38	2.40	-0.7
N-total, mg/L	5.70	6.05	-5.7
PO4-P, mg/L	0.301	0.347	-13.3
P-total, mg/L	0.829	0.824	0.6
Cd, µg/L	9.60	9.90	-3.1
Cr, µg/L	19.00	17.78	6.9
Cu, µg/L	48.00	47.38	1.3
Ni, µg/L	79.00	80.33	-1.7
Pb, µg/L	23.00	21.30	8.0
Zn, µg/L	170.0	168.5	0.9
Hg, µg/L	0.850	0.662	28.4

Laboratory
Code no.: 17

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.56	1.53	1.56	1.56	1.55	-1.0	1.4	-0.3
NO2-N, mg/L	0.041	0.046	0.036	0.036	0.044	20.8	8.1	1.3
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.59	3.60	3.44	3.44	3.60	4.6	0.2	0.7
PO4-P, mg/L	0.225	0.235	0.209	0.209	0.230	10.0	3.1	1.5
P-total, mg/L	0.370	0.380	0.361	0.361	0.375	3.9	1.9	0.7
Cd, µg/L	5.50	5.95	6.42	6.42	5.73	-10.8	5.6	-1.9
Cr, µg/L	10.80	10.30	11.68	11.68	10.55	-9.6	3.4	-0.9
Cu, µg/L	30.40	28.90	29.30	29.30	29.65	1.2	3.6	0.1
Ni, µg/L	49.00	48.10	51.04	51.04	48.55	-4.9	1.3	-0.7
Pb, µg/L	10.40	10.90	11.14	11.14	10.65	-4.4	3.3	-0.4
Zn, µg/L	78.10	76.70	77.16	77.16	77.40	0.3	1.3	0.0
Hg, µg/L	0.164	0.163	0.174	0.174	0.164	-6.0	0.4	-0.6

Laboratory
Code no.: 17

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.29	2.35	-2.4
NO2-N, mg/L	0.057	0.042	35.7
NO2+3-N, mg/L		2.40	
N-total, mg/L	6.46	6.05	6.8
PO4-P, mg/L	0.379	0.347	9.2
P-total, mg/L	0.848	0.824	2.9
Cd, µg/L	9.00	9.90	-9.1
Cr, µg/L	16.30	17.78	-8.3
Cu, µg/L	46.30	47.38	-2.3
Ni, µg/L	73.40	80.33	-8.6
Pb, µg/L	26.50	21.30	24.4
Zn, µg/L	164.0	168.5	-2.7
Hg, µg/L	0.697	0.662	5.3

Laboratory
Code no.: **18**

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.56	1.57	1.56	1.56	1.56	0.2	0.3	0.1
NO2-N, mg/L	0.034	0.033	0.036	0.036	0.033	-7.6	1.5	-0.5
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.36	3.31	3.44	3.44	3.33	-3.1	1.2	-0.5
PO4-P, mg/L	0.208	0.210	0.209	0.209	0.209	0.0	0.7	0.0
P-total, mg/L	0.354	0.355	0.361	0.361	0.355	-1.8	0.2	-0.3
Cd, µg/L	6.82	6.86	6.42	6.42	6.84	6.5	0.4	1.2
Cr, µg/L	12.80	12.70	11.68	11.68	12.75	9.2	0.6	0.8
Cu, µg/L	34.90	34.90	29.30	29.30	34.90	19.1	0.0	1.1
Ni, µg/L	53.20	53.30	51.04	51.04	53.25	4.3	0.1	0.7
Pb, µg/L	11.80	11.80	11.14	11.14	11.80	5.9	0.0	0.5
Zn, µg/L	85.90	85.30	77.16	77.16	85.60	10.9	0.5	1.2
Hg, µg/L	0.154	0.145	0.174	0.174	0.150	-14.1	4.3	-1.4

Laboratory
Code no.: **18**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.38	2.35	1.4
NO2-N, mg/L	0.039	0.042	-7.6
NO2+3-N, mg/L		2.40	
N-total, mg/L	5.94	6.05	-1.9
PO4-P, mg/L	0.352	0.347	1.4
P-total, mg/L	0.813	0.824	-1.3
Cd, µg/L	10.50	9.90	6.0
Cr, µg/L	19.60	17.78	10.2
Cu, µg/L	52.00	47.38	9.7
Ni, µg/L	80.70	80.33	0.5
Pb, µg/L	24.60	21.30	15.5
Zn, µg/L	176.0	168.5	4.5
Hg, µg/L	0.593	0.662	-10.4

Laboratory
Code no.: 19

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.55	1.53	1.56	1.56	1.54	-1.3	0.9	-0.4
NO2-N, mg/L	0.039	0.036	0.036	0.036	0.038	4.2	5.7	0.3
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.18	3.14	3.44	3.44	3.16	-8.1	0.9	-1.3
PO4-P, mg/L	0.210	0.210	0.209	0.209	0.210	0.5	0.0	0.1
P-total, mg/L	0.340	0.340	0.361	0.361	0.340	-5.8	0.0	-1.1
Cd, µg/L	6.50	6.60	6.42	6.42	6.55	2.0	1.1	0.4
Cr, µg/L	12.50	13.20	11.68	11.68	12.85	10.1	3.9	0.9
Cu, µg/L	30.50	31.40	29.30	29.30	30.95	5.6	2.1	0.3
Ni, µg/L	53.00	52.50	51.04	51.04	52.75	3.3	0.7	0.5
Pb, µg/L	11.90	10.90	11.14	11.14	11.40	2.3	6.2	0.2
Zn, µg/L	74.80	75.20	77.16	77.16	75.00	-2.8	0.4	-0.3
Hg, µg/L	0.189	0.187	0.174	0.174	0.188	8.0	0.8	0.8

Laboratory
Code no.: 19

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.43	2.35	3.6
NO2-N, mg/L	0.042	0.042	0.0
NO2+3-N, mg/L		2.40	
N-total, mg/L	4.96	6.05	-18.0
PO4-P, mg/L	0.360	0.347	3.7
P-total, mg/L	0.770	0.824	-6.6
Cd, µg/L	10.10	9.90	2.0
Cr, µg/L	19.30	17.78	8.5
Cu, µg/L	51.00	47.38	7.6
Ni, µg/L	80.00	80.33	-0.4
Pb, µg/L	22.00	21.30	3.3
Zn, µg/L	164.0	168.5	-2.7
Hg, µg/L	0.627	0.662	-5.3

Laboratory
Code no.: **22**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L			0.036	0.036				
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L			3.44	3.44				
PO4-P, mg/L	0.210	0.210	0.209	0.209	0.210	0.5	0.0	0.1
P-total, mg/L	0.360	0.350	0.361	0.361	0.355	-1.7	2.0	-0.3
Cd, µg/L	6.68	6.81	6.42	6.42	6.75	5.1	1.4	0.9
Cr, µg/L	11.10	12.30	11.68	11.68	11.70	0.2	7.3	0.0
Cu, µg/L	33.00	34.00	29.30	29.30	33.50	14.3	2.1	0.9
Ni, µg/L	52.20	53.00	51.04	51.04	52.60	3.0	1.1	0.5
Pb, µg/L	11.70	12.00	11.14	11.14	11.85	6.4	1.8	0.5
Zn, µg/L	61.10	60.30	77.16	77.16	60.70	-21.3	0.9	-2.3
Hg, µg/L	0.189	0.186	0.174	0.174	0.188	7.8	1.1	0.8

Laboratory
Code no.: **22**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L		0.042	
NO2+3-N, mg/L		2.40	
N-total, mg/L		6.05	
PO4-P, mg/L	0.370	0.347	6.6
P-total, mg/L	0.870	0.824	5.6
Cd, µg/L	10.50	9.90	6.0
Cr, µg/L	18.50	17.78	4.0
Cu, µg/L	50.30	47.38	6.2
Ni, µg/L	80.00	80.33	-0.4
Pb, µg/L	23.00	21.30	8.0
Zn, µg/L	158.0	168.5	-6.2
Hg, µg/L	0.699	0.662	5.6

Laboratory
Code no.: 26

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.45	1.60	1.56	1.56	1.53	-2.3	7.0	-0.7
NO2-N, mg/L	0.056	0.037	0.036	0.036	0.047	29.2	28.9	1.8
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.20	2.90	3.44	3.44	3.05	-11.3	7.0	-1.8
PO4-P, mg/L	0.220	0.230	0.209	0.209	0.225	7.7	3.1	1.1
P-total, mg/L	0.330	0.350	0.361	0.361	0.340	-5.8	4.2	-1.1
Cd, µg/L	6.69	6.49	6.42	6.42	6.59	2.6	2.1	0.5
Cr, µg/L	11.80	11.70	11.68	11.68	11.75	0.6	0.6	0.1
Cu, µg/L	30.70	30.20	29.30	29.30	30.45	3.9	1.2	0.2
Ni, µg/L	51.20	50.20	51.04	51.04	50.70	-0.7	1.4	-0.1
Pb, µg/L	10.50	10.40	11.14	11.14	10.45	-6.2	0.7	-0.5
Zn, µg/L	79.60	78.70	77.16	77.16	79.15	2.6	0.8	0.3
Hg, µg/L	0.164	0.155	0.174	0.174	0.160	-8.3	4.0	-0.9

Laboratory
Code no.: 26

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.30	2.35	-2.0
NO2-N, mg/L	0.044	0.042	4.8
NO2+3-N, mg/L		2.40	
N-total, mg/L	5.10	6.05	-15.7
PO4-P, mg/L	0.390	0.347	12.4
P-total, mg/L	0.820	0.824	-0.5
Cd, µg/L	10.10	9.90	2.0
Cr, µg/L	17.20	17.78	-3.3
Cu, µg/L	44.90	47.38	-5.2
Ni, µg/L	79.20	80.33	-1.4
Pb, µg/L	21.50	21.30	0.9
Zn, µg/L	162.0	168.5	-3.9
Hg, µg/L	0.697	0.662	5.3

Laboratory
Code no.: **27**

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.60	1.70	1.56	1.56	1.65	5.7	4.3	1.8
NO2-N, mg/L	0.033	0.033	0.036	0.036	0.033	-8.3	0.0	-0.5
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.20	3.50	3.44	3.44	3.35	-2.6	6.3	-0.4
PO4-P, mg/L	0.210	0.210	0.209	0.209	0.210	0.5	0.0	0.1
P-total, mg/L	0.360	0.360	0.361	0.361	0.360	-0.3	0.0	-0.1
Cd, µg/L	6.50	6.30	6.42	6.42	6.40	-0.3	2.2	-0.1
Cr, µg/L	12.90	13.10	11.68	11.68	13.00	11.3	1.1	1.0
Cu, µg/L	32.70	33.00	29.30	29.30	32.85	12.1	0.6	0.7
Ni, µg/L	55.40	56.30	51.04	51.04	55.85	9.4	1.1	1.4
Pb, µg/L	11.20	10.80	11.14	11.14	11.00	-1.2	2.6	-0.1
Zn, µg/L	80.50	79.30	77.16	77.16	79.90	3.5	1.1	0.4
Hg, µg/L			0.174	0.174				

Laboratory
Code no.: **27**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.30	2.35	-2.0
NO2-N, mg/L	0.041	0.042	-2.4
NO2+3-N, mg/L		2.40	
N-total, mg/L	5.90	6.05	-2.4
PO4-P, mg/L	0.350	0.347	0.9
P-total, mg/L	0.820	0.824	-0.5
Cd, µg/L	9.90	9.90	0.0
Cr, µg/L	20.30	17.78	14.2
Cu, µg/L	51.10	47.38	7.8
Ni, µg/L	87.10	80.33	8.4
Pb, µg/L	22.50	21.30	5.6
Zn, µg/L	164.4	168.5	-2.4
Hg, µg/L		0.662	

Laboratory
Code no.: **28**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L	0.041	0.041	0.036	0.036	0.041	13.9	0.0	0.8
NO2+3-N, mg/L	1.70	1.70	1.60	1.60	1.70	6.4	0.0	1.3
N-total, mg/L	3.50	3.30	3.44	3.44	3.40	-1.1	4.2	-0.2
PO4-P, mg/L	0.210	0.210	0.209	0.209	0.210	0.5	0.0	0.1
P-total, mg/L	0.360	0.370	0.361	0.361	0.365	1.1	1.9	0.2
Cd, µg/L			6.42	6.42				
Cr, µg/L			11.68	11.68				
Cu, µg/L			29.30	29.30				
Ni, µg/L			51.04	51.04				
Pb, µg/L			11.14	11.14				
Zn, µg/L			77.16	77.16				
Hg, µg/L	0.170	0.172	0.174	0.174	0.171	-1.7	0.8	-0.2

Laboratory
Code no.: **28**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L	0.050	0.042	19.0
NO2+3-N, mg/L	2.60	2.40	8.5
N-total, mg/L	5.20	6.05	-14.0
PO4-P, mg/L	0.350	0.347	0.9
P-total, mg/L	0.800	0.824	-2.9
Cd, µg/L		9.90	
Cr, µg/L		17.78	
Cu, µg/L		47.38	
Ni, µg/L		80.33	
Pb, µg/L		21.30	
Zn, µg/L		168.5	
Hg, µg/L	0.737	0.662	11.3

Laboratory
Code no.: **29**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L			0.036	0.036				
NO2+3-N, mg/L	1.55	1.55	1.60	1.60	1.55	-3.0	0.0	-0.6
N-total, mg/L	3.56	3.54	3.44	3.44	3.55	3.3	0.4	0.5
PO4-P, mg/L	0.214	0.218	0.209	0.209	0.216	3.3	1.3	0.5
P-total, mg/L	0.349	0.349	0.361	0.361	0.349	-3.3	0.0	-0.6
Cd, µg/L	6.35	6.40	6.42	6.42	6.38	-0.7	0.6	-0.1
Cr, µg/L	11.20	10.70	11.68	11.68	10.95	-6.2	3.2	-0.6
Cu, µg/L	31.90	31.80	29.30	29.30	31.85	8.7	0.2	0.5
Ni, µg/L	51.90	52.20	51.04	51.04	52.05	2.0	0.4	0.3
Pb, µg/L	10.90	10.80	11.14	11.14	10.85	-2.6	0.7	-0.2
Zn, µg/L	80.40	79.30	77.16	77.16	79.85	3.5	1.0	0.4
Hg, µg/L	0.112	0.148	0.174	0.174	0.130	-25.3	19.6	-2.6

Laboratory
Code no.: **29**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L		0.042	
NO2+3-N, mg/L	2.36	2.40	-1.5
N-total, mg/L	6.58	6.05	8.8
PO4-P, mg/L	0.373	0.347	7.5
P-total, mg/L	0.775	0.824	-5.9
Cd, µg/L	9.80	9.90	-1.1
Cr, µg/L	17.40	17.78	-2.1
Cu, µg/L	50.10	47.38	5.7
Ni, µg/L	79.80	80.33	-0.7
Pb, µg/L	22.40	21.30	5.2
Zn, µg/L	167.2	168.5	-0.8
Hg, µg/L	0.411	0.662	-37.9

Laboratory
Code no.: **30**

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.56	1.56	1.56	1.56	1.56	-0.1	0.0	0.0
NO2-N, mg/L	0.038	0.032	0.036	0.036	0.035	-2.8	12.1	-0.2
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.31	3.31	3.44	3.44	3.31	-3.7	0.0	-0.6
PO4-P, mg/L	0.180	0.180	0.209	0.209	0.180	-13.9	0.0	-2.1
P-total, mg/L	0.340	0.330	0.361	0.361	0.335	-7.2	2.1	-1.4
Cd, µg/L	6.28	6.15	6.42	6.42	6.22	-3.2	1.4	-0.6
Cr, µg/L	12.50	12.60	11.68	11.68	12.55	7.5	0.6	0.7
Cu, µg/L	32.40	32.30	29.30	29.30	32.35	10.4	0.2	0.6
Ni, µg/L	50.00	49.00	51.04	51.04	49.50	-3.0	1.4	-0.5
Pb, µg/L	11.20	11.40	11.14	11.14	11.30	1.4	1.3	0.1
Zn, µg/L	78.00	77.60	77.16	77.16	77.80	0.8	0.4	0.1
Hg, µg/L	0.185	0.176	0.174	0.174	0.180	3.6	3.4	0.4

Laboratory
Code no.: **30**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.43	2.35	3.6
NO2-N, mg/L	0.042	0.042	0.0
NO2+3-N, mg/L		2.40	
N-total, mg/L	6.19	6.05	2.4
PO4-P, mg/L	0.280	0.347	-19.3
P-total, mg/L	0.780	0.824	-5.3
Cd, µg/L	9.50	9.90	-4.1
Cr, µg/L	19.10	17.78	7.4
Cu, µg/L	49.50	47.38	4.5
Ni, µg/L	75.20	80.33	-6.4
Pb, µg/L	22.60	21.30	6.1
Zn, µg/L	160.0	168.5	-5.0
Hg, µg/L	0.618	0.662	-6.7

Laboratory
Code no.: **31**

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.52	1.51	1.56	1.56	1.52	-2.8	0.5	-0.9
NO2-N, mg/L	0.046	0.049	0.036	0.036	0.048	32.8	4.1	2.0
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.60	3.59	3.44	3.44	3.60	4.6	0.2	0.7
PO4-P, mg/L	0.240	0.238	0.209	0.209	0.239	14.4	0.6	2.1
P-total, mg/L	0.394	0.385	0.361	0.361	0.390	7.9	1.6	1.5
Cd, µg/L			6.42	6.42				
Cr, µg/L			11.68	11.68				
Cu, µg/L			29.30	29.30				
Ni, µg/L			51.04	51.04				
Pb, µg/L			11.14	11.14				
Zn, µg/L			77.16	77.16				
Hg, µg/L	0.172	0.160	0.174	0.174	0.166	-4.7	5.2	-0.5

Laboratory
Code no.: **31**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.29	2.35	-2.5
NO2-N, mg/L	0.051	0.042	21.0
NO2+3-N, mg/L		2.40	
N-total, mg/L	6.40	6.05	5.8
PO4-P, mg/L	0.425	0.347	22.5
P-total, mg/L	0.893	0.824	8.4
Cd, µg/L		9.90	
Cr, µg/L		17.78	
Cu, µg/L		47.38	
Ni, µg/L		80.33	
Pb, µg/L		21.30	
Zn, µg/L		168.5	
Hg, µg/L	0.748	0.662	13.0

Laboratory
Code no.: 32

	Measured values		Assigned Values		Statistics			
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	1.51	1.52	1.56	1.56	1.52	-2.9	0.5	-0.9
NO2-N, mg/L	0.034	0.035	0.036	0.036	0.035	-4.2	2.0	-0.3
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L	3.52	3.62	3.44	3.44	3.57	3.8	2.0	0.6
PO4-P, mg/L	0.210	0.209	0.209	0.209	0.210	0.2	0.3	0.0
P-total, mg/L	0.370	0.379	0.361	0.361	0.375	3.7	1.7	0.7
Cd, µg/L	6.14	6.19	6.42	6.42	6.17	-3.9	0.6	-0.7
Cr, µg/L	10.57	10.52	11.68	11.68	10.55	-9.7	0.3	-0.9
Cu, µg/L	25.47	29.65	29.30	29.30	27.56	-5.9	10.7	-0.4
Ni, µg/L	48.31	50.92	51.04	51.04	49.61	-2.8	3.7	-0.4
Pb, µg/L	3.22	2.95	11.14	11.14	3.09	-72.3	6.3	-5.9
Zn, µg/L	76.84	80.23	77.16	77.16	78.54	1.8	3.0	0.2
Hg, µg/L	0.195	0.189	0.174	0.174	0.192	10.3	2.2	1.1

Laboratory
Code no.: 32

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L	2.28	2.35	-2.8
NO2-N, mg/L	0.041	0.042	-2.4
NO2+3-N, mg/L		2.40	
N-total, mg/L	6.42	6.05	6.2
PO4-P, mg/L	0.358	0.347	3.2
P-total, mg/L	0.837	0.824	1.6
Cd, µg/L	10.36	9.90	4.6
Cr, µg/L	16.83	17.78	-5.4
Cu, µg/L	53.61	47.38	13.2
Ni, µg/L	81.25	80.33	1.1
Pb, µg/L	6.28	21.30	-70.5
Zn, µg/L	180.3	168.5	7.0
Hg, µg/L	0.655	0.662	-1.1

Laboratory
Code no.: **33**

	Measured values		Assigned Values			Statistics		
	Freshwater	Freshwater	Freshwater	Freshwater				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			1.56	1.56				
NO2-N, mg/L			0.036	0.036				
NO2+3-N, mg/L			1.60	1.60				
N-total, mg/L			3.44	3.44				
PO4-P, mg/L			0.209	0.209				
P-total, mg/L			0.361	0.361				
Cd, µg/L	7.00	7.00	6.42	6.42	7.00	9.0	0.0	1.6
Cr, µg/L			11.68	11.68				
Cu, µg/L	28.00	30.00	29.30	29.30	29.00	-1.0	4.9	-0.1
Ni, µg/L	49.00	49.00	51.04	51.04	49.00	-4.0	0.0	-0.6
Pb, µg/L	11.60	11.20	11.14	11.14	11.40	2.3	2.5	0.2
Zn, µg/L	77.00	77.00	77.16	77.16	77.00	-0.2	0.0	0.0
Hg, µg/L			0.174	0.174				

Laboratory
Code no.: **33**

	Measured value	Assigned Values	Statistics
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		2.35	
NO2-N, mg/L		0.042	
NO2+3-N, mg/L		2.40	
N-total, mg/L		6.05	
PO4-P, mg/L		0.347	
P-total, mg/L		0.824	
Cd, µg/L	12.00	9.90	21.2
Cr, µg/L		17.78	
Cu, µg/L	48.00	47.38	1.3
Ni, µg/L	83.00	80.33	3.3
Pb, µg/L	21.40	21.30	0.5
Zn, µg/L	159.0	168.5	-5.6
Hg, µg/L		0.662	

3.3 Waste water

Laboratory
Code no.: 1

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L	6.14	6.15	6.34	6.34	6.15	-3.1	0.1	-1.0
N-total, mg/L	7.44	7.40	7.23	7.23	7.42	2.6	0.4	0.6
PO4-P, mg/L	0.0077	0.0069	0.0096	0.0096	0.0073	-24.0	7.7	-0.8
P-total, mg/L	0.015	0.015	0.025	0.025	0.015	-41.9	1.9	-0.8
Cd, µg/L	23.74	23.79	23.87	23.87	23.77	-0.5	0.1	-0.1
Cr, µg/L	46.10	45.98	49.01	49.01	46.04	-6.1	0.2	-0.9
Cu, µg/L	145.4	147.4	142.4	142.4	146.4	2.8	1.0	0.5
Ni, µg/L	205.4	206.9	194.4	194.4	206.2	6.0	0.5	0.9
Pb, µg/L	8.29	8.35	8.59	8.59	8.32	-3.1	0.5	-0.2
Zn, µg/L	446.0	448.6	435.6	435.6	447.3	2.7	0.4	0.4
Hg, µg/L	0.315	0.330	0.385	0.385	0.323	-16.2	3.3	-1.4

Laboratory
Code no.: 2

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.85	6.81	6.13	6.13	6.830	11.4	0.4	1.8
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.048	6.7	0.0	0.3
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.26	7.21	7.23	7.23	7.24	0.1	0.5	0.0
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L			0.025	0.025				
Cd, µg/L			23.87	23.87				
Cr, µg/L			49.01	49.01				
Cu, µg/L			142.4	142.4				
Ni, µg/L			194.4	194.4				
Pb, µg/L			8.59	8.59				
Zn, µg/L			435.6	435.6				
Hg, µg/L			0.385	0.385				

Laboratory
Code no.: **4**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.16	6.09	6.13	6.13	6.123	-0.2	0.9	0.0
NO2-N, mg/L	0.04	0.03	0.045	0.045	0.035	-23.3	2.0	-1.1
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	6.47	6.44	7.23	7.23	6.46	-10.7	0.3	-2.3
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L	0.053	0.065	0.025	0.025	0.059	133.2	14.4	2.6
Cd, µg/L	22.50	22.90	23.87	23.87	22.70	-4.9	1.2	-1.0
Cr, µg/L	54.80	55.03	49.01	49.01	54.92	12.1	0.3	1.8
Cu, µg/L			142.4	142.4				
Ni, µg/L	178.5	191.5	194.4	194.4	185.0	-4.9	5.0	-0.7
Pb, µg/L			8.59	8.59				
Zn, µg/L	0.5	0.5	435.6	435.6	0.5	-99.9	2.6	-13.1
Hg, µg/L	0.434	0.424	0.385	0.385	0.429	11.4	1.6	1.0

Laboratory
Code no.: **5**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L			7.23	7.23				
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L			0.025	0.025				
Cd, µg/L	22.84	22.25	23.87	23.87	22.55	-5.6	1.9	-1.1
Cr, µg/L	42.98	42.79	49.01	49.01	42.89	-12.5	0.3	-1.8
Cu, µg/L	133.4	130.9	142.4	142.4	132.1	-7.2	1.3	-1.2
Ni, µg/L	175.5	174.0	194.4	194.4	174.7	-10.1	0.6	-1.5
Pb, µg/L	13.09	13.09	8.59	8.59	13.09	52.4	0.0	2.8
Zn, µg/L	427.0	422.5	435.6	435.6	424.8	-2.5	0.7	-0.3
Hg, µg/L			0.385	0.385				

Laboratory

Code no.: 6

	Measured values		Assigned Values			Statistics		
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L	6.23	6.32	6.34	6.34	6.27	-1.1	1.0	-0.4
N-total, mg/L	7.34	7.30	7.23	7.23	7.32	1.3	0.3	0.3
PO4-P, mg/L	0.0080	0.0068	0.0096	0.0096	0.0074	-22.9	11.5	-0.7
P-total, mg/L	0.026	0.027	0.025	0.025	0.026	3.8	3.5	0.1
Cd, µg/L	23.30	22.40	23.87	23.87	22.85	-4.3	2.8	-0.8
Cr, µg/L	48.10	46.00	49.01	49.01	47.05	-4.0	3.2	-0.6
Cu, µg/L	130.0	125.0	142.4	142.4	127.5	-10.5	2.8	-1.8
Ni, µg/L	185.0	178.0	194.4	194.4	181.5	-6.7	2.7	-1.0
Pb, µg/L	7.91	0.65	8.59	8.59	4.28	-50.2	119.9	-2.7
Zn, µg/L	431.0	413.0	435.6	435.6	422.0	-3.1	3.0	-0.4
Hg, µg/L	0.403	0.404	0.385	0.385	0.404	4.8	0.2	0.4

Laboratory

Code no.: 7

	Measured values		Assigned Values			Statistics		
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.11	6.08	6.13	6.13	6.097	-0.6	0.3	-0.1
NO2-N, mg/L	0.04	0.04	0.045	0.045	0.041	-8.9	0.0	-0.4
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.31	7.30	7.23	7.23	7.30	1.0	0.1	0.2
PO4-P, mg/L	0.0100	0.0070	0.0096	0.0096	0.0085	-11.2	24.9	-0.4
P-total, mg/L	0.015	0.011	0.025	0.025	0.013	-48.5	19.2	-0.9
Cd, µg/L	24.70	24.60	23.87	23.87	24.65	3.3	0.3	0.6
Cr, µg/L	50.30	50.20	49.01	49.01	50.25	2.5	0.1	0.4
Cu, µg/L	143.0	140.0	142.4	142.4	141.5	-0.6	1.5	-0.1
Ni, µg/L	196.0	195.0	194.4	194.4	195.5	0.5	0.4	0.1
Pb, µg/L	8.84	8.70	8.59	8.59	8.77	2.1	1.1	0.1
Zn, µg/L	447.0	443.0	435.6	435.6	445.0	2.1	0.6	0.3
Hg, µg/L			0.385	0.385				

Laboratory

Code no.: 8

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.53	6.53	6.13	6.13	6.533	6.5	0.0	1.0
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.046	1.1	1.6	0.1
NO2+3-N. mg/L			6.34	6.34				
N-total, mg/L	7.45	7.50	7.23	7.23	7.47	3.4	0.4	0.7
PO4-P, mg/L	0.0110	0.0087	0.0096	0.0096	0.0099	2.6	16.5	0.1
P-total, mg/L	0.026	0.024	0.025	0.025	0.025	-1.2	5.7	0.0
Cd, µg/L	24.40	24.70	23.87	23.87	24.55	2.8	0.9	0.6
Cr, µg/L	50.70	50.30	49.01	49.01	50.50	3.0	0.6	0.4
Cu, µg/L	149.0	152.0	142.4	142.4	150.5	5.7	1.4	1.0
Ni, µg/L	212.0	205.0	194.4	194.4	208.5	7.2	2.4	1.1
Pb, µg/L	9.19	8.93	8.59	8.59	9.06	5.5	2.0	0.3
Zn, µg/L	504.0	486.0	435.6	435.6	495.0	13.6	2.6	1.8
Hg, µg/L			0.385	0.385				

Laboratory

Code no.: 10

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.25	6.21	6.13	6.13	6.230	1.6	0.5	0.2
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L	6.98	6.68	6.34	6.34	6.83	7.7	3.1	2.6
N-total, mg/L	7.91	8.16	7.23	7.23	8.04	11.1	2.2	2.4
PO4-P, mg/L	0.0070	0.0070	0.0096	0.0096	0.0070	-27.1	0.0	-0.9
P-total, mg/L	0.016	0.017	0.025	0.025	0.017	-34.8	4.3	-0.7
Cd, µg/L	24.00	24.00	23.87	23.87	24.00	0.5	0.0	0.1
Cr, µg/L	45.00	45.00	49.01	49.01	45.00	-8.2	0.0	-1.2
Cu, µg/L	131.0	131.0	142.4	142.4	131.0	-8.0	0.0	-1.4
Ni, µg/L	180.0	175.0	194.4	194.4	177.5	-8.7	2.0	-1.3
Pb, µg/L	11.00	11.00	8.59	8.59	11.00	28.1	0.0	1.5
Zn, µg/L	407.0	408.0	435.6	435.6	407.5	-6.5	0.2	-0.9
Hg, µg/L			0.385	0.385				

Laboratory
Code no.: **11**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.045	0.0	0.0	0.0
NO2+3-N, mg/L	6.60	6.60	6.34	6.34	6.60	4.0	0.0	1.3
N-total, mg/L	7.10	7.10	7.23	7.23	7.10	-1.8	0.0	-0.4
PO4-P, mg/L	0.0083	0.0069	0.0096	0.0096	0.0076	-20.8	13.0	-0.7
P-total, mg/L			0.025	0.025				
Cd, µg/L			23.87	23.87				
Cr, µg/L			49.01	49.01				
Cu, µg/L			142.4	142.4				
Ni, µg/L			194.4	194.4				
Pb, µg/L			8.59	8.59				
Zn, µg/L			435.6	435.6				
Hg, µg/L			0.385	0.385				

Laboratory
Code no.: **12**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	5.67	5.89	6.13	6.13	5.780	-5.8	2.7	-0.9
NO2-N, mg/L	0.04	0.04	0.045	0.045	0.039	-13.3	0.0	-0.6
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.14	7.60	7.23	7.23	7.37	1.9	4.4	0.4
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L	0.014	0.018	0.025	0.025	0.016	-36.8	17.7	-0.7
Cd, µg/L			23.87	23.87				
Cr, µg/L			49.01	49.01				
Cu, µg/L			142.4	142.4				
Ni, µg/L			194.4	194.4				
Pb, µg/L			8.59	8.59				
Zn, µg/L			435.6	435.6				
Hg, µg/L			0.385	0.385				

Laboratory

Code no.: 13

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L			7.23	7.23				
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L			0.025	0.025				
Cd, µg/L	25.80	25.90	23.87	23.87	25.85	8.3	0.3	1.6
Cr, µg/L	55.00	55.00	49.01	49.01	55.00	12.2	0.0	1.8
Cu, µg/L	160.0	160.0	142.4	142.4	160.0	12.4	0.0	2.1
Ni, µg/L	210.0	210.0	194.4	194.4	210.0	8.0	0.0	1.2
Pb, µg/L	9.81	9.26	8.59	8.59	9.54	11.0	4.1	0.6
Zn, µg/L	530.0	530.0	435.6	435.6	530.0	21.7	0.0	2.9
Hg, µg/L	0.350	0.340	0.385	0.385	0.345	-10.4	2.0	-0.9

Laboratory

Code no.: 14

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	5.48	5.57	6.13	6.13	5.525	-9.9	1.2	-1.6
NO2-N, mg/L	0.04	0.04	0.045	0.045	0.042	-6.7	0.0	-0.3
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	6.55	6.71	7.23	7.23	6.63	-8.3	1.7	-1.8
PO4-P, mg/L	0.0110	0.0120	0.0096	0.0096	0.0115	19.8	6.1	0.6
P-total, mg/L	0.033	0.038	0.025	0.025	0.036	40.3	10.0	0.8
Cd, µg/L	24.40	24.30	23.87	23.87	24.35	2.0	0.3	0.4
Cr, µg/L	48.30	48.10	49.01	49.01	48.20	-1.6	0.3	-0.2
Cu, µg/L	142.0	146.0	142.4	142.4	144.0	1.1	2.0	0.2
Ni, µg/L	201.0	200.0	194.4	194.4	200.5	3.1	0.4	0.5
Pb, µg/L	7.52	7.63	8.59	8.59	7.58	-11.8	1.0	-0.6
Zn, µg/L	401.0	403.0	435.6	435.6	402.0	-7.7	0.4	-1.0
Hg, µg/L	0.403	0.377	0.385	0.385	0.390	1.3	4.7	0.1

Laboratory

Code no.: 17

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.01	6.02	6.13	6.13	6.015	-1.9	0.1	-0.3
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.045	0.0	0.0	0.0
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.25	7.26	7.23	7.23	7.26	0.3	0.1	0.1
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L			0.025	0.025				
Cd, µg/L	21.00	23.00	23.87	23.87	22.00	-7.8	6.4	-1.5
Cr, µg/L	46.50	46.80	49.01	49.01	46.65	-4.8	0.5	-0.7
Cu, µg/L	127.0	132.0	142.4	142.4	129.5	-9.1	2.7	-1.6
Ni, µg/L	175.0	174.0	194.4	194.4	174.5	-10.3	0.4	-1.5
Pb, µg/L	7.42	7.29	8.59	8.59	7.36	-14.4	1.2	-0.8
Zn, µg/L	417.0	414.0	435.6	435.6	415.5	-4.6	0.5	-0.6
Hg, µg/L	0.386	0.382	0.385	0.385	0.384	-0.3	0.7	0.0

Laboratory

Code no.: 18

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.42	6.45	6.13	6.13	6.438	5.0	0.3	0.8
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.047	4.9	0.9	0.2
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	6.92	6.94	7.23	7.23	6.93	-4.2	0.2	-0.9
PO4-P, mg/L	0.0131	0.0111	0.0096	0.0096	0.0121	26.0	11.7	0.8
P-total, mg/L	0.017	0.018	0.025	0.025	0.017	-32.8	4.2	-0.6
Cd, µg/L	23.80	24.30	23.87	23.87	24.05	0.7	1.5	0.1
Cr, µg/L	50.00	50.70	49.01	49.01	50.35	2.7	1.0	0.4
Cu, µg/L	144.0	144.0	142.4	142.4	144.0	1.1	0.0	0.2
Ni, µg/L	198.0	200.0	194.4	194.4	199.0	2.3	0.7	0.4
Pb, µg/L	8.65	8.69	8.59	8.59	8.67	1.0	0.3	0.1
Zn, µg/L	445.0	445.0	435.6	435.6	445.0	2.1	0.0	0.3
Hg, µg/L	0.388	0.427	0.385	0.385	0.408	5.8	6.8	0.5

Laboratory

Code no.: **19**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.34	6.09	6.13	6.13	6.215	1.3	2.8	0.2
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.047	4.4	0.0	0.2
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	6.78	7.74	7.23	7.23	7.26	0.4	9.4	0.1
PO4-P, mg/L	0.0070	0.0090	0.0096	0.0096	0.0080	-16.7	17.7	-0.5
P-total, mg/L	0.036	0.040	0.025	0.025	0.038	50.2	7.4	1.0
Cd, µg/L	23.00	25.00	23.87	23.87	24.00	0.5	5.9	0.1
Cr, µg/L	47.60	48.00	49.01	49.01	47.80	-2.5	0.6	-0.4
Cu, µg/L	145.0	144.0	142.4	142.4	144.5	1.5	0.5	0.3
Ni, µg/L	196.0	197.0	194.4	194.4	196.5	1.1	0.4	0.2
Pb, µg/L	7.60	7.90	8.59	8.59	7.75	-9.8	2.7	-0.5
Zn, µg/L	412.0	421.0	435.6	435.6	416.5	-4.4	1.5	-0.6
Hg, µg/L	0.351	0.379	0.385	0.385	0.365	-5.2	5.4	-0.4

Laboratory

Code no.: **20**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.37	6.47	6.13	6.13	6.420	4.7	1.1	0.7
NO2-N, mg/L	0.04	0.04	0.045	0.045	0.041	-10.0	1.7	-0.5
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.44	7.62	7.23	7.23	7.53	4.1	1.7	0.9
PO4-P, mg/L	0.0140	0.0130	0.0096	0.0096	0.0135	40.6	5.2	1.3
P-total, mg/L	0.033	0.033	0.025	0.025	0.033	29.2	0.4	0.6
Cd, µg/L	22.70	22.30	23.87	23.87	22.50	-5.8	1.3	-1.1
Cr, µg/L	55.40	54.40	49.01	49.01	54.90	12.0	1.3	1.8
Cu, µg/L	147.0	143.0	142.4	142.4	145.0	1.8	2.0	0.3
Ni, µg/L	216.0	213.0	194.4	194.4	214.5	10.3	1.0	1.5
Pb, µg/L	8.87	8.88	8.59	8.59	8.88	3.3	0.1	0.2
Zn, µg/L	437.0	424.0	435.6	435.6	430.5	-1.2	2.1	-0.2
Hg, µg/L	0.421	0.419	0.385	0.385	0.420	9.1	0.3	0.8

Laboratory

Code no.: 22

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	5.52	5.94	6.13	6.13	5.730	-6.6	5.2	-1.0
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.052	15.6	0.0	0.7
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	6.58	7.38	7.23	7.23	6.98	-3.5	8.1	-0.7
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L			0.025	0.025				
Cd, µg/L	24.30	24.40	23.87	23.87	24.35	2.0	0.3	0.4
Cr, µg/L	48.80	48.70	49.01	49.01	48.75	-0.5	0.1	-0.1
Cu, µg/L	143.0	143.0	142.4	142.4	143.0	0.4	0.0	0.1
Ni, µg/L	198.0	211.0	194.4	194.4	204.5	5.2	4.5	0.8
Pb, µg/L	8.07	8.20	8.59	8.59	8.14	-5.3	1.1	-0.3
Zn, µg/L	402.0	404.0	435.6	435.6	403.0	-7.5	0.4	-1.0
Hg, µg/L	0.376	0.361	0.385	0.385	0.369	-4.3	2.9	-0.4

Laboratory

Code no.: 24

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.41	6.44	6.13	6.13	6.425	4.8	0.3	0.7
NO2-N, mg/L	0.05	0.04	0.045	0.045	0.046	1.1	7.8	0.1
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.15	7.21	7.23	7.23	7.18	-0.7	0.6	-0.2
PO4-P, mg/L	0.0090	0.0100	0.0096	0.0096	0.0095	-1.0	7.4	0.0
P-total, mg/L	0.020	0.020	0.025	0.025	0.020	-20.9	0.0	-0.4
Cd, µg/L	25.27	25.47	23.87	23.87	25.37	6.3	0.6	1.2
Cr, µg/L	49.97	49.23	49.01	49.01	49.60	1.2	1.1	0.2
Cu, µg/L	146.4	146.7	142.4	142.4	146.6	2.9	0.1	0.5
Ni, µg/L	202.2	202.9	194.4	194.4	202.6	4.2	0.2	0.6
Pb, µg/L	8.96	8.93	8.59	8.59	8.95	4.2	0.2	0.2
Zn, µg/L	465.7	465.9	435.6	435.6	465.8	6.9	0.0	0.9
Hg, µg/L	0.380	0.384	0.385	0.385	0.382	-0.8	0.7	-0.1

Laboratory

Code no.: **25**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L	6.47	6.49	6.34	6.34	6.48	2.1	0.2	0.7
N-total, mg/L	7.23	7.14	7.23	7.23	7.19	-0.6	0.9	-0.1
PO4-P, mg/L	0.0085	0.0071	0.0096	0.0096	0.0078	-18.8	12.7	-0.6
P-total, mg/L	0.013	0.011	0.025	0.025	0.012	-53.0	10.7	-1.0
Cd, µg/L			23.87	23.87				
Cr, µg/L			49.01	49.01				
Cu, µg/L			142.4	142.4				
Ni, µg/L			194.4	194.4				
Pb, µg/L			8.59	8.59				
Zn, µg/L			435.6	435.6				
Hg, µg/L			0.385	0.385				

Laboratory

Code no.: **26**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.07	6.10	6.13	6.13	6.085	-0.8	0.3	-0.1
NO2-N, mg/L	0.04	0.04	0.045	0.045	0.043	-5.6	1.7	-0.3
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.64	7.10	7.23	7.23	7.37	1.9	5.2	0.4
PO4-P, mg/L	0.0130	0.0100	0.0096	0.0096	0.0115	19.8	18.4	0.6
P-total, mg/L	0.022	0.012	0.025	0.025	0.017	-32.8	41.6	-0.6
Cd, µg/L	23.20	23.30	23.87	23.87	23.25	-2.6	0.3	-0.5
Cr, µg/L	46.80	46.60	49.01	49.01	46.70	-4.7	0.3	-0.7
Cu, µg/L	145.0	147.0	142.4	142.4	146.0	2.5	1.0	0.4
Ni, µg/L	185.0	185.0	194.4	194.4	185.0	-4.9	0.0	-0.7
Pb, µg/L	8.05	7.93	8.59	8.59	7.99	-7.0	1.1	-0.4
Zn, µg/L	434.0	437.0	435.6	435.6	435.5	0.0	0.5	0.0
Hg, µg/L	0.497	0.519	0.385	0.385	0.508	31.9	3.1	2.7

Laboratory

Code no.: 27

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.20	6.20	6.13	6.13	6.200	1.1	0.0	0.2
NO2-N, mg/L	0.04	0.04	0.045	0.045	0.042	-6.7	0.0	-0.3
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	6.90	7.30	7.23	7.23	7.10	-1.8	4.0	-0.4
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L			0.025	0.025				
Cd, µg/L	22.90	22.30	23.87	23.87	22.60	-5.3	1.9	-1.0
Cr, µg/L	51.90	53.40	49.01	49.01	52.65	7.4	2.0	1.1
Cu, µg/L	132.8	135.4	142.4	142.4	134.1	-5.8	1.4	-1.0
Ni, µg/L	204.3	210.3	194.4	194.4	207.3	6.6	2.0	1.0
Pb, µg/L	7.90	8.10	8.59	8.59	8.00	-6.8	1.8	-0.4
Zn, µg/L	408.7	408.9	435.6	435.6	408.8	-6.2	0.0	-0.8
Hg, µg/L			0.385	0.385				

Laboratory

Code no.: 28

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	5.99	5.95	6.13	6.13	5.970	-2.7	0.5	-0.4
NO2-N, mg/L	0.05	0.05	0.045	0.045	0.046	2.2	3.1	0.1
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.21	7.19	7.23	7.23	7.20	-0.4	0.2	-0.1
PO4-P, mg/L	0.0130	0.0140	0.0096	0.0096	0.0135	40.6	5.2	1.3
P-total, mg/L	0.043	0.036	0.025	0.025	0.040	56.1	12.5	1.1
Cd, µg/L			23.87	23.87				
Cr, µg/L			49.01	49.01				
Cu, µg/L			142.4	142.4				
Ni, µg/L			194.4	194.4				
Pb, µg/L			8.59	8.59				
Zn, µg/L			435.6	435.6				
Hg, µg/L	0.346	0.343	0.385	0.385	0.345	-10.5	0.6	-0.9

Laboratory

Code no.: 29

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L	6.23	6.21	6.34	6.34	6.22	-2.0	0.2	-0.7
N-total, mg/L	7.37	7.20	7.23	7.23	7.28	0.7	1.7	0.2
PO4-P, mg/L	0.0070	0.0057	0.0096	0.0096	0.0064	-33.6	14.3	-1.1
P-total, mg/L	0.018	0.014	0.025	0.025	0.016	-37.5	15.2	-0.7
Cd, µg/L	24.30	24.00	23.87	23.87	24.15	1.2	0.9	0.2
Cr, µg/L	46.90	46.80	49.01	49.01	46.85	-4.4	0.2	-0.6
Cu, µg/L	140.2	142.9	142.4	142.4	141.6	-0.6	1.3	-0.1
Ni, µg/L	197.8	198.6	194.4	194.4	198.2	1.9	0.3	0.3
Pb, µg/L	8.61	8.31	8.59	8.59	8.46	-1.5	2.5	-0.1
Zn, µg/L	436.1	435.7	435.6	435.6	435.9	0.1	0.1	0.0
Hg, µg/L	0.394	0.380	0.385	0.385	0.387	0.5	2.6	0.0

Laboratory

Code no.: 30

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.62	6.48	6.13	6.13	6.550	6.8	1.5	1.1
NO2-N, mg/L	0.05	0.04	0.045	0.045	0.046	1.1	10.9	0.1
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.56	7.20	7.23	7.23	7.38	2.1	3.4	0.4
PO4-P, mg/L	0.0087	0.0077	0.0096	0.0096	0.0082	-14.6	8.6	-0.5
P-total, mg/L	0.036	0.038	0.025	0.025	0.037	46.2	3.8	0.9
Cd, µg/L	24.20	24.20	23.87	23.87	24.20	1.4	0.0	0.3
Cr, µg/L	48.80	48.90	49.01	49.01	48.85	-0.3	0.1	0.0
Cu, µg/L	142.0	143.0	142.4	142.4	142.5	0.1	0.5	0.0
Ni, µg/L	179.0	179.0	194.4	194.4	179.0	-7.9	0.0	-1.2
Pb, µg/L	8.00	8.03	8.59	8.59	8.01	-6.7	0.3	-0.4
Zn, µg/L	410.0	412.0	435.6	435.6	411.0	-5.7	0.3	-0.7
Hg, µg/L	0.330	0.334	0.385	0.385	0.332	-13.8	1.0	-1.2

Laboratory

Code no.: 31

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	6.11	6.20	6.13	6.13	6.158	0.4	1.1	0.1
NO2-N, mg/L	0.06	0.06	0.045	0.045	0.058	28.4	0.0	1.3
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.27	7.44	7.23	7.23	7.36	1.7	1.6	0.4
PO4-P, mg/L	0.0189	0.0136	0.0096	0.0096	0.0163	69.3	23.1	2.2
P-total, mg/L			0.025	0.025				
Cd, µg/L			23.87	23.87				
Cr, µg/L			49.01	49.01				
Cu, µg/L			142.4	142.4				
Ni, µg/L			194.4	194.4				
Pb, µg/L			8.59	8.59				
Zn, µg/L			435.6	435.6				
Hg, µg/L	0.407	0.400	0.385	0.385	0.403	4.8	1.3	0.4

Laboratory

Code no.: 32

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	5.27	5.12	6.13	6.13	5.195	-15.3	2.0	-2.4
NO2-N, mg/L	0.04	0.04	0.045	0.045	0.043	-4.4	0.0	-0.2
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L	7.12	7.24	7.23	7.23	7.18	-0.7	1.2	-0.2
PO4-P, mg/L	0.0075	0.0081	0.0096	0.0096	0.0078	-18.8	5.4	-0.6
P-total, mg/L	0.020	0.022	0.025	0.025	0.021	-17.0	6.7	-0.3
Cd, µg/L	23.05	23.21	23.87	23.87	23.13	-3.1	0.5	-0.6
Cr, µg/L	47.40	46.98	49.01	49.01	47.19	-3.7	0.6	-0.5
Cu, µg/L	155.2	153.3	142.4	142.4	154.2	8.3	0.9	1.4
Ni, µg/L	188.0	189.0	194.4	194.4	188.5	-3.1	0.4	-0.5
Pb, µg/L	10.03	8.05	8.59	8.59	9.04	5.3	15.5	0.3
Zn, µg/L	465.2	462.3	435.6	435.6	463.8	6.5	0.4	0.8
Hg, µg/L	0.359	0.351	0.385	0.385	0.355	-7.8	1.6	-0.7

Laboratory

Code no.: **33**

	Measured values		Assigned Values		Statistics			
	Waste Water	Waste Water	Waste Water	Waste Water				
Components	**A**	**B**	**A**	**B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			6.13	6.13				
NO2-N, mg/L			0.045	0.045				
NO2+3-N, mg/L			6.34	6.34				
N-total, mg/L			7.23	7.23				
PO4-P, mg/L			0.0096	0.0096				
P-total, mg/L			0.025	0.025				
Cd, µg/L	27.00	26.00	23.87	23.87	26.50	11.0	2.7	2.2
Cr, µg/L			49.01	49.01				
Cu, µg/L	144.0	144.0	142.4	142.4	144.0	1.1	0.0	0.2
Ni, µg/L			194.4	194.4				
Pb, µg/L	5.10	5.00	8.59	8.59	5.05	-41.2	1.4	-2.2
Zn, µg/L	408.0	408.0	435.6	435.6	408.0	-6.3	0.0	-0.8
Hg, µg/L			0.385	0.385				

4. Evaluation of results

For each chemical component the following statistical analysis has been performed: For sample A and B (freshwater and waste water), table with the data are presented for each component together with outlier test according to Cochran and Grubb, z-score plot and summary table with the statistical parameters. For sample C, freshwater, 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 was carried out according to ISO 5725-2 (2002). Cochran's test is used to determine the uniformity of single laboratory determinations on the test pairs under repeatability conditions (which under specified conditions is regarded as a duplicate). The test pair with highest standard deviation is compared to Cohran's 5% and 1% critical values. If the standard deviation is above the 5% critical value but below the 1% critical value it is a straggler and is still included in the statistics. If it is above the 1% critical value, it is an outlier and is excluded from the further statistics. 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 uniformity of the mean value on the test pairs between the laboratories. The Grubb's single outlier test is performed on the most extreme (highest and / or lowest) test pair. The Grubb's double outlier test is performed on the two most extreme (highest and / or lowest) test pairs. Equal to Cochran's outlier test pairs above 5% but below 1% Grubb's critical values are designated stragglers whereas values above 1% critical are designated outliers and are excluded from the statistics.

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. For all the following calculations are outlier data set not included. The tables includes the following parameters:

p: number of laboratories. Number of laboratories included in the statistics with 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. The deviation between the laboratories.

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

S(R): reproducibility. 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 occur with a probability of 95% (r = S(r)*2.8).

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

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

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

For sample C, freshwater, 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 (%). Deviation between the laboratories relative to the mean value.

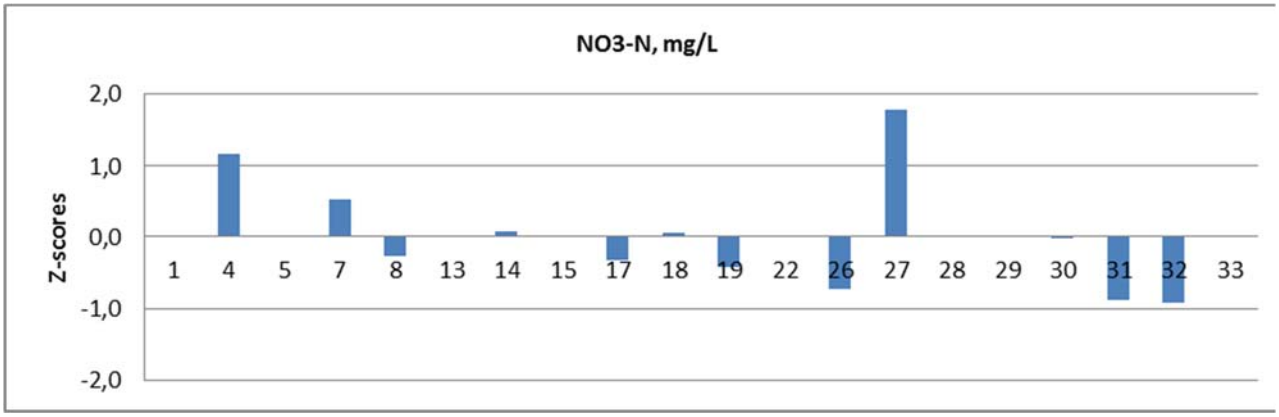
Calculated spike value based on the spike added to the sample.

Measured value of spike [µg/L] based on the assigned value of sample C subtracted the assigned value of samples A / B.

% recovery of spike is measured spike value relative to calculated spike value.

4.2 Statistical data for each component in freshwater

Component			*NO3-N, mgL*						
Assigned value	**1.56**	**1.56**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1									
4	1.64	1.60							
5									
7	1.63	1.55							
8	1.55	1.55							
13									
14	1.57	1.56							
15									
17	1.56	1.53							
18	1.56	1.57							
19	1.55	1.53							
22									
26	1.45	1.60		X					
27	1.60	1.70							
28									
29									
30	1.56	1.56							
31	1.52	1.51							
32	1.51	1.52							
33									

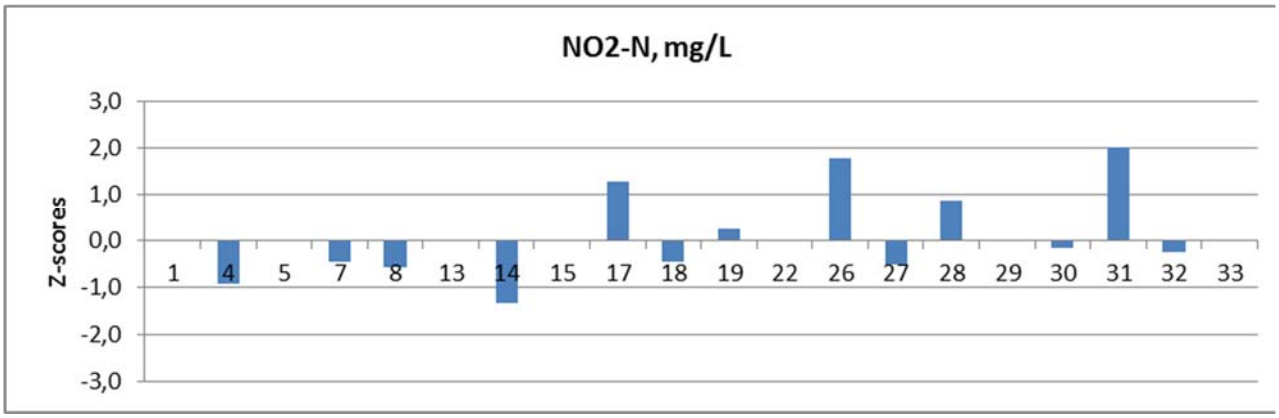


Statistical parameters	NO3-N, A/B Freshwater
p	12
m [mg/L]	1.56
S(L) [mg/L]	0.03
S(r) [mg/L]	0.04
S(R) [mg/L]	0.05
r [mg/L]	0.12
R [mg/L]	0.14
CV(r) [%]	2.8
CV(R) [%]	3.3

Component				*NO3-N, mgL*		
Assigned value	**2.35**	**Grupps single test**		**Grupps double test**		**Excluded in statistical**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1						
4	2.46					
5						
7	2.30					
8	2.37					
13						
14	2.32					
15						
17	2.29					
18	2.38					
19	2.43					
22						
26	2.30					
27	2.30					
28						
29						
30	2.43					
31	2.29					
32	2.28					
33						

Statistical analysis	**Freshwater C NO3-N, mgL**
Assigned value	2.35
Laboratory deviation (S(L)	0.065
Relative laboratory deviation (%)	2.8
Calculated spike value	0.96
Measured value of spike	0.79
% recovery of spike	82

Component	*NO2-N, mgL*								
Assigned value	**0.036**	**0.036**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1									
4	0.031	0.030							
5									
7	0.037	0.030							
8	0.032	0.033							
13									
14	0.028	0.028							
15									
17	0.041	0.046							
18	0.034	0.033							
19	0.039	0.036							
22									
26	0.056	0.037	X	X	-	-	-	-	X
27	0.033	0.033							
28	0.041	0.041							
29									
30	0.038	0.032							
31	0.046	0.049							
32	0.034	0.035							
33									

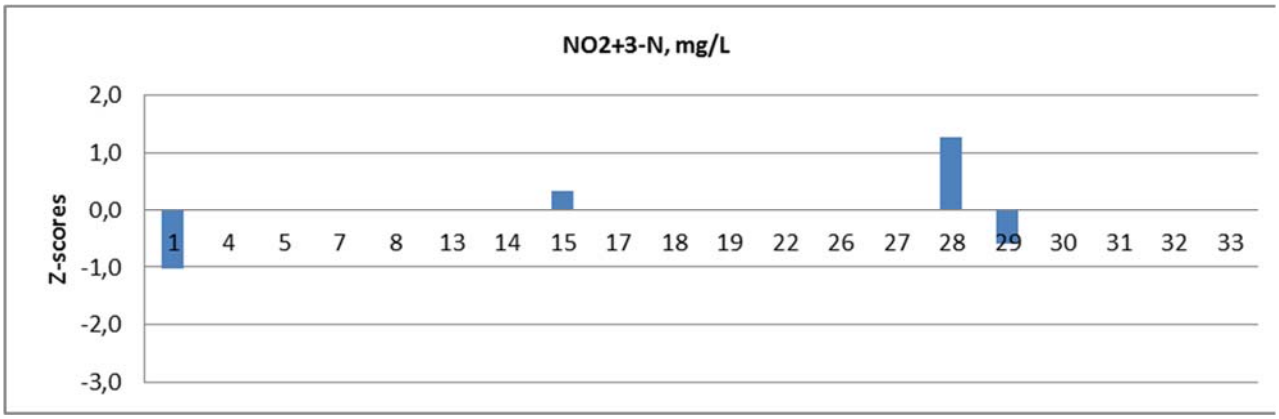


	NO2-N
Statistical parameters	**A/B Freshwater**
p	12
m [mg/L]	0.036
S(L) [mg/L]	0.005
S(r) [mg/L]	0.002
S(R) [mg/L]	0.006
r [mg/L]	0.007
R [mg/L]	0.017
CV(r) [%]	6.8
CV(R) [%]	16.6

Component			*NO2-N, mgL*			
Assigned value	**0.042**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1						
4	0.032					
5						
7	0.035					
8	0.038					
13						
14	0.031					
15						
17	0.057					
18	0.039					
19	0.042					
22						
26	0.044					
27	0.041					
28	0.050					
29						
30	0.042					
31	0.051					
32	0.041					
33						

Statistical analysis	**Freshwater C NO2-N, mgL**
Assigned value	0.042
Laboratory deviation (S(L)	0.007
Relative laboratory deviation (%)	17.8
Calculated spike value	0.010
Measured value of spike	0.006
% recovery of spike	60

Component			*NO2+3-N, mgL*						
Assigned value	**1.60**	**1.60**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	1.53	1.50							
4									
5									
7									
8									
13									
14									
15	1.63	1.62							
17									
18									
19									
22									
26									
27									
28	1.70	1.70							
29	1.55	1.55							
30									
31									
32									
33									

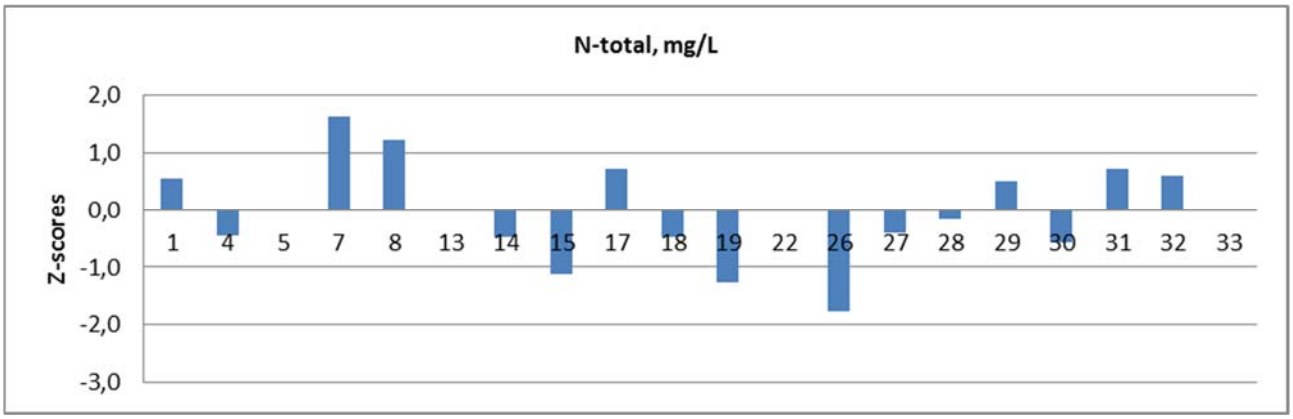


	NO2+3-N
Statistical parameters	**A/B Freshwater**
p	4
m [mg/L]	1.60
S(L) [mg/L]	0.08
S(r) [mg/L]	0.01
S(R) [mg/L]	0.08
r [mg/L]	0.03
R [mg/L]	0.23
CV(r) [%]	0.6
CV(R) [%]	5.2

Component		*NO2+3-N. mgL*				
Assigned value	**2.40**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	2.25					
4						
5						
7						
8						
13						
14						
15	2.38					
17						
18						
19						
22						
26						
27						
28	2.60					
29	2.36					
30						
31						
32						
33						

Statistical analysis	**Freshwater C NO2+3-N, mgL**
Assigned value	2.40
Laboratory deviation (S(L)	0.147
Relative laboratory deviation (%)	6.1
Calculated spike value	0.97
Measured value of spike	0.80
% recovery of spike	83

Component			*N-total, mgL*						
Assigned value	**3.44**	**3.44**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	3.56	3.56							
4	3.36	3.32							
5									
7	3.80	3.80							
8	3.73	3.69							
13									
14	3.31	3.36							
15	3.22	3.16							
17	3.59	3.60							
18	3.36	3.31							
19	3.18	3.14							
22									
26	3.20	2.90							
27	3.20	3.50							
28	3.50	3.30							
29	3.56	3.54							
30	3.31	3.31							
31	3.60	3.59							
32	3.52	3.62							
33									

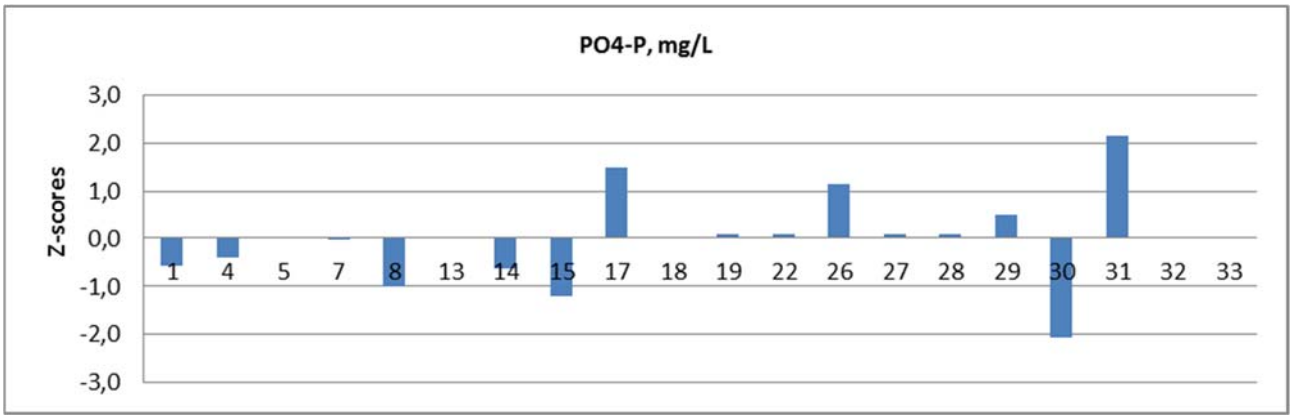


Statistical parameters	N-total A/B Freshwater
p	16
m [mg/L]	3.43
S(L) [mg/L]	0.20
S(r) [mg/L]	0.09
S(R) [mg/L]	0.22
r [mg/L]	0.25
R [mg/L]	0.61
CV(r) [%]	2.6
CV(R) [%]	6.3

Component			*N-total, mgL*			
Assigned value	**6.05**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	6.54					
4	6.40					
5						
7	6.60					
8	6.60					
13						
14	5.76					
15	5.70					
17	6.46					
18	5.93					
19	4.96					
22						
26	5.10					
27	5.90					
28	5.20					
29	6.58					
30	6.19					
31	6.40					
32	6.42					
33						

Statistical analysis	**Freshwater C N-total, mgL**
Assigned value	6.05
Laboratory deviation (S(L)	0.56
Relative laboratory deviation (%)	9.3
Calculated spike value	2.57
Measured value of spike	2.61
% recovery of spike	102

Component				PO4-P, mgL						
Assigned value	0.209	0.209	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Freshwater A	Freshwater B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.200	0.202							
4	0.203	0.204							
5									
7	0.209	0.208							
8	0.195	0.195							
13									
14	0.200	0.200							
15	0.192	0.192							
17	0.225	0.235		X					
18	0.208	0.210							
19	0.210	0.210							
22	0.210	0.210							
26	0.220	0.230							
27	0.210	0.210							
28	0.210	0.210							
29	0.214	0.218							
30	0.180	0.180							
31	0.240	0.238							
32	0.210	0.209							
33									

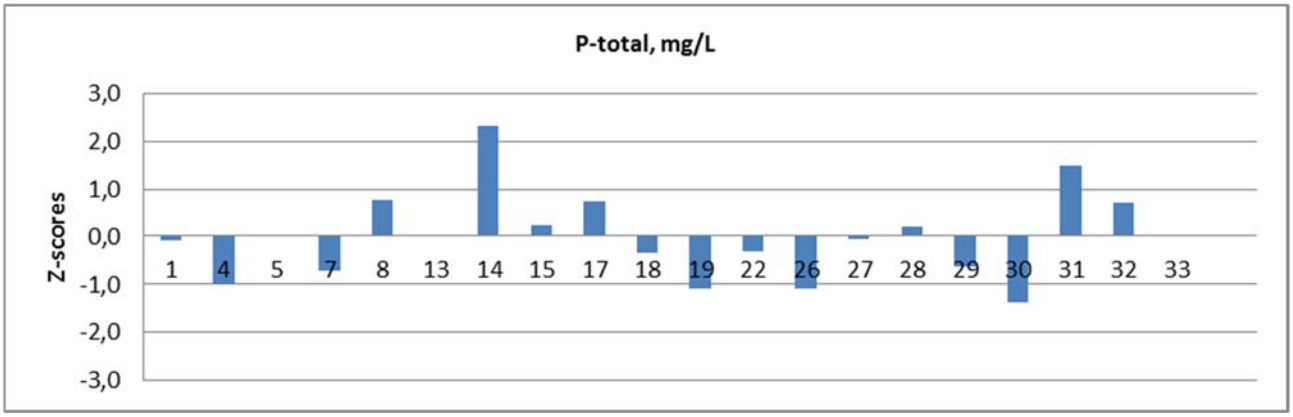


Statistical parameters	PO4-P A/B Freshwater
p	17
m [mg/L]	0.209
S(L) [mg/L]	0.014
S(r) [mg/L]	0.002
S(R) [mg/L]	0.014
r [mg/L]	0.007
R [mg/L]	0.040
CV(r) [%]	1.2
CV(R) [%]	6.8

Component			*PO4-P, mgL*			
Assigned value	**0.347**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	0.318					
4	0.358					
5						
7	0.315					
8	0.294					
13						
14	0.320					
15	0.301					
17	0.379					
18	0.352					
19	0.360					
22	0.370					
26	0.390					
27	0.350					
28	0.350					
29	0.373					
30	0.280					
31	0.425					
32	0.358					
33						

	Freshwater C
Statistical analysis	**PO4-P, mgL**
Assigned value	0.347
Laboratory deviation (S(L)	0.038
Relative laboratory deviation (%)	10.8
Calculated spike value	0.140
Measured value of spike	0.138
% recovery of spike	99

Component			*P-total, mgL*						
Assigned value	**0.361**	**0.361**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	0.360	0.359							
4	0.344	0.340							
5									
7	0.349	0.347							
8	0.377	0.374							
13									
14	0.400	0.410							
15	0.365	0.366							
17	0.370	0.380							
18	0.354	0.355							
19	0.340	0.340							
22	0.360	0.350							
26	0.330	0.350							
27	0.360	0.360							
28	0.360	0.370							
29	0.349	0.349							
30	0.340	0.330							
31	0.394	0.385							
32	0.370	0.379							
33									

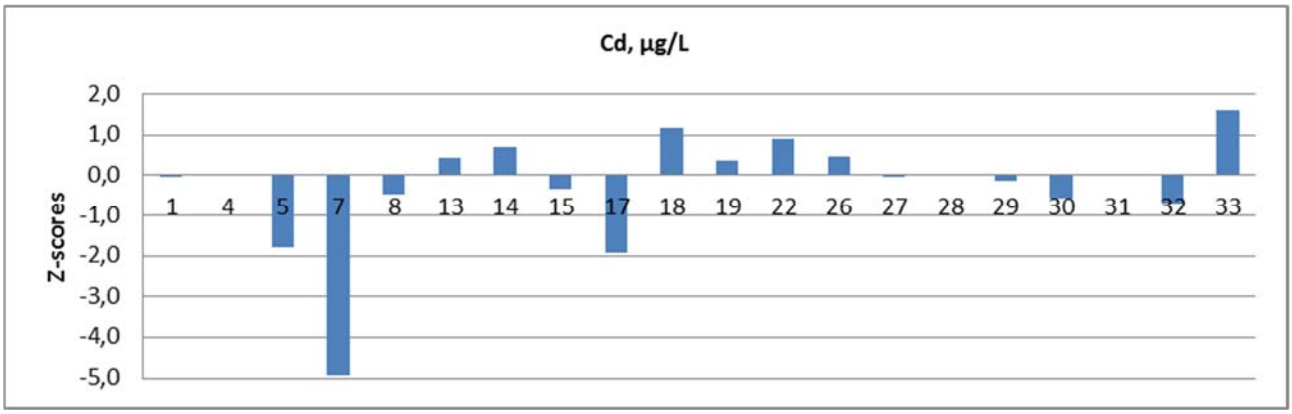


Statistical parameters	P-total A/B Freshwater
p	17
m [mg/L]	0.361
S(L) [mg/L]	0.018
S(r) [mg/L]	0.006
S(R) [mg/L]	0.019
r [mg/L]	0.016
R [mg/L]	0.054
CV(r) [%]	1.6
CV(R) [%]	5.4

Component			*P-total, mgL*			
Assigned value	**0.824**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	0.818					
4	0.791					
5						
7	0.789					
8	0.847					
13						
14	0.900					
15	0.829					
17	0.848					
18	0.813					
19	0.770					
22	0.870					
26	0.820					
27	0.820					
28	0.800					
29	0.775					
30	0.780					
31	0.893					
32	0.837					
33						

	Freshwater C
Statistical analysis	**P-total, mgL**
Assigned value	0.824
Laboratory deviation (S(L)	0.039
Relative laboratory deviation (%)	4.7
Calculated spike value	0.513
Measured value of spike	0.463
% recovery of spike	90

Component					*Cd, µgL*				
Assigned value	**6.42**	**6.42**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	6.43	6.40							
4		6.48							
5	5.50	6.06							
7	4.62	4.68			X	X	-	-	X
8	6.30	6.19							
13	6.51	6.63							
14	6.55	6.80							
15	6.30	6.30							
17	5.50	5.95							
18	6.82	6.86							
19	6.50	6.60							
22	6.68	6.81							
26	6.69	6.49							
27	6.50	6.30							
28									
29	6.35	6.40							
30	6.28	6.15							
31									
32	6.14	6.19							
33	7.00	7.00							

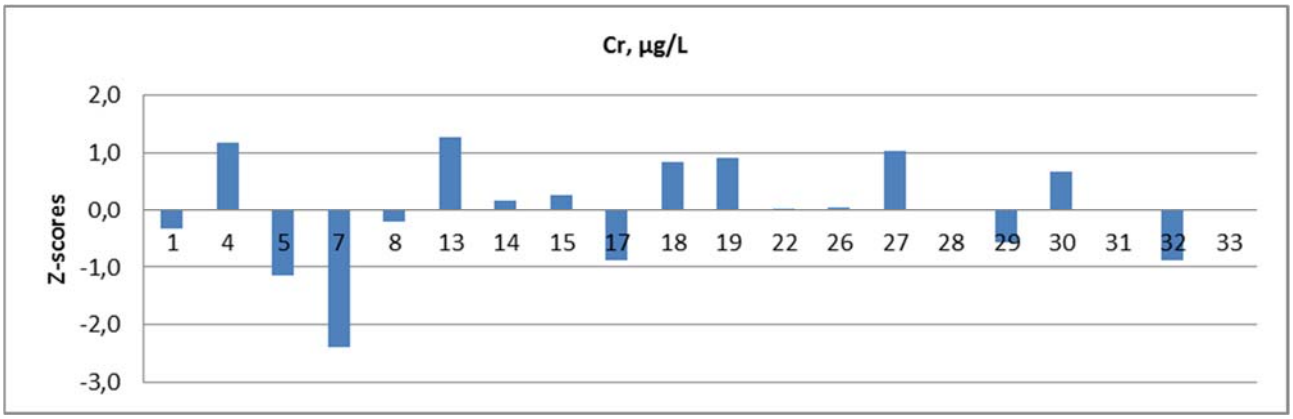


Statistical parameters	Cd A/B Freshwater
p	16
m [µg/L]	6.41
S(L) [µg/L]	0.33
S(r) [µg/L]	0.15
S(R) [µg/L]	0.36
r [µg/L]	0.42
R [µg/L]	1.01
CV(r) [%]	2.3
CV(R) [%]	5.6

Component			*Cd, µgL*			
Assigned value	**9.90**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	9.78					
4						
5	8.94					
7	8.66					
8	10.00					
13	9.53					
14	10.10					
15	9.60					
17	9.00					
18	10.50					
19	10.10					
22	10.50					
26	10.10					
27	9.90					
28						
29	9.80					
30	9.50					
31						
32	10.36					
33	12.00		X			

	Freshwater C
Statistical analysis	**Cd, µgL**
Assigned value	9.90
Laboratory deviation (S(L)	0.76
Relative laboratory deviation (%)	7.6
Calculated spike value	3.75
Measured value of spike	3.48
% recovery of spike	93

Component					*Cr, µgL*				
Assigned value	**11.68**	**11.68**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	11.32	11.17							
4	13.00	13.33							
5	10.90	9.53							
7	8.60	8.60							
8	11.40	11.40							
13	13.40	13.20							
14	11.50	12.30							
15	12.00	12.00							
17	10.80	10.30							
18	12.80	12.70							
19	12.50	13.20							
22	11.10	12.30							
26	11.80	11.70							
27	12.90	13.10							
28									
29	11.20	10.70							
30	12.50	12.60							
31									
32	10.57	10.52							
33									

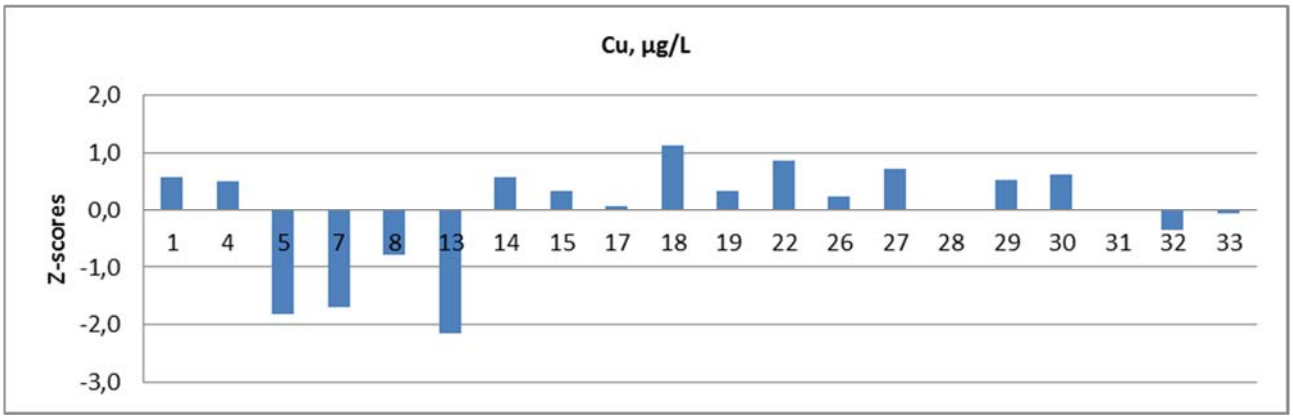


Statistical parameters	Cr A/B Freshwater
p	17
m [µg/L]	11.67
S(L) [µg/L]	1.22
S(r) [µg/L]	0.40
S(R) [µg/L]	1.28
r [µg/L]	1.13
R [µg/L]	3.59
CV(r) [%]	3.4
CV(R) [%]	11.0

Component			*Cr, µgL*			
Assigned value	**17.78**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	16.95					
4						
5	14.52					
7	13.50					
8	17.20					
13	19.10					
14	19.70					
15	19.00					
17	16.30					
18	19.60					
19	19.30					
22	18.50					
26	17.20					
27	20.30					
28						
29	17.40					
30	19.10					
31						
32	16.83					
33						

	Freshwater C
Statistical analysis	**Cr, µgL**
Assigned value	17.78
Laboratory deviation (S(L)	1.91
Relative laboratory deviation (%)	10.7
Calculated spike value	6.90
Measured value of spike	6.11
% recovery of spike	88

Component			*Cu, µgL*						
Assigned value	**29.30**	**29.30**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Freshwater A**	**Freshwater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	32.22	32.16							
4	31.50	32.10							
5	20.05	20.66							
7	20.80	21.00							
8	26.30	24.50							
13	18.70	18.80							
14	32.90	31.40							
15	31.00	31.00							
17	30.40	28.90							
18	34.90	34.90							
19	30.50	31.40							
22	33.00	34.00							
26	30.70	30.20							
27	32.70	33.00							
28									
29	31.90	31.80							
30	32.40	32.30							
31									
32	25.47	29.65	X	X	-	-	-	-	X
33	28.00	30.00							

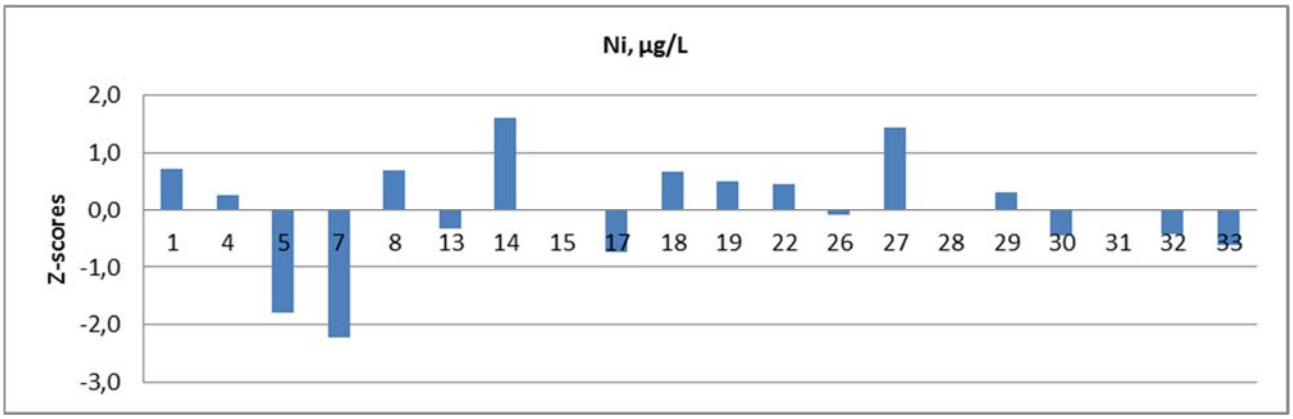


Statistical parameters	Cu A/B Freshwater
p	17
m [µg/L]	29.30
S(L) [µg/L]	4.88
S(r) [µg/L]	0.68
S(R) [µg/L]	4.92
r [µg/L]	1.90
R [µg/L]	13.79
CV(r) [%]	2.3
CV(R) [%]	16.8

Component			*Cu, µgL*			
Assigned value	**47.38**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	50.25					
4	52.60					
5	27.61		X		X	
7	36.30				X	
8	37.40					
13	52.20					
14	51.70					
15	48.00					
17	46.30					
18	52.00					
19	51.00					
22	50.30					
26	44.90					
27	51.10					
28						
29	50.10					
30	49.50					
31						
32	53.61					
33	48.00					

	Freshwater C
Statistical analysis	**Cu, µgL**
Assigned value	47.38
Laboratory deviation (S(L)	6.89
Relative laboratory deviation (%)	14.5
Calculated spike value	18.75
Measured value of spike	18.09
% recovery of spike	96

Component					*Ni, µgL*				
Assigned value	**51.04**	**51.04**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	52.98	53.98							
4	52.57	51.36							
5	44.62	45.56							
7	43.70	43.60							
8	53.80	53.00							
13	50.30	49.60							
14	54.60	58.20		X					
15	51.00	51.00							
17	49.00	48.10							
18	53.20	53.30							
19	53.00	52.50							
22	52.20	53.00							
26	51.20	50.20							
27	55.40	56.30							
28									
29	51.90	52.20							
30	50.00	49.00							
31									
32	48.31	50.92							
33	49.00	49.00							

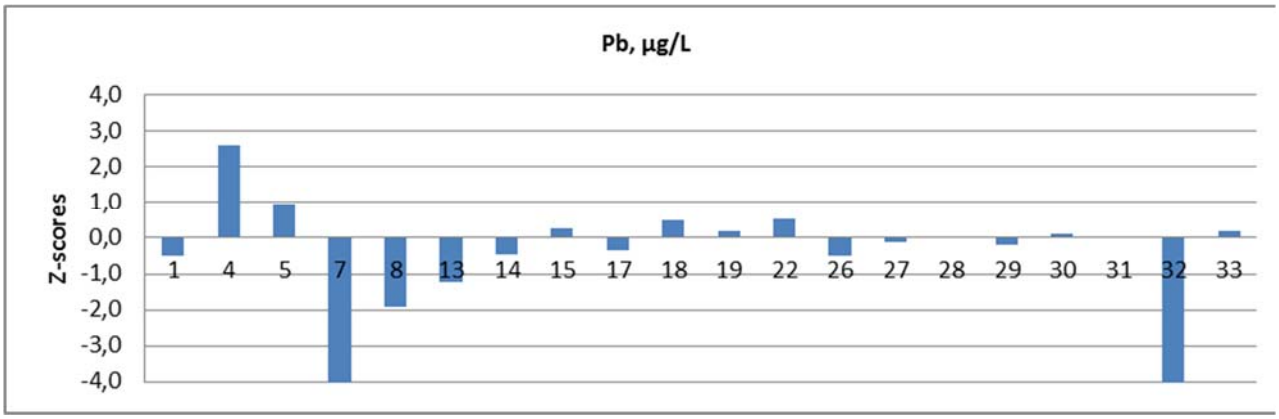


	Ni
Statistical parameters	**A/B Freshwater**
p	18
m [µg/L]	51.04
S(L) [µg/L]	3.20
S(r) [µg/L]	0.91
S(R) [µg/L]	3.33
r [µg/L]	2.54
R [µg/L]	9.33
CV(r) [%]	1.8
CV(R) [%]	6.5

Component	*Ni, µgL*					
Assigned value	**80.33**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	5% level	**tistical analysis**
1	82.01					
4	80.20					
5	77.93					
7	71.60					
8	80.80					
13	80.00					
14	94.80		X		X	
15	79.00					
17	73.40					
18	80.70					
19	80.00					
22	80.00					
26	79.20					
27	87.10				X	
28						
29	79.80					
30	75.20					
31						
32	81.25					
33	83.00					

	Freshwater C
Statistical analysis	**Ni, µgL**
Assigned value	80.33
Laboratory deviation (S(L)	5.01
Relative laboratory deviation (%)	6.2
Calculated spike value	30.00
Measured value of spike	29.29
% recovery of spike	98

Component					*Pb, µgL*				
Assigned value	**11.14**	**11.14**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	10.59	10.36							
4	14.71	14.60							
5	12.00	12.87							
7	4.55	4.58					X	X	X
8	8.43	8.58							
13	9.53	9.39							
14	10.40	10.60							
15	11.00	12.00							
17	10.40	10.90							
18	11.80	11.80							
19	11.90	10.90							
22	11.70	12.00							
26	10.50	10.40							
27	11.20	10.80							
28									
29	10.90	10.80							
30	11.20	11.40							
31									
32	3.22	2.95				X	X	X	X
33	11.60	11.20							



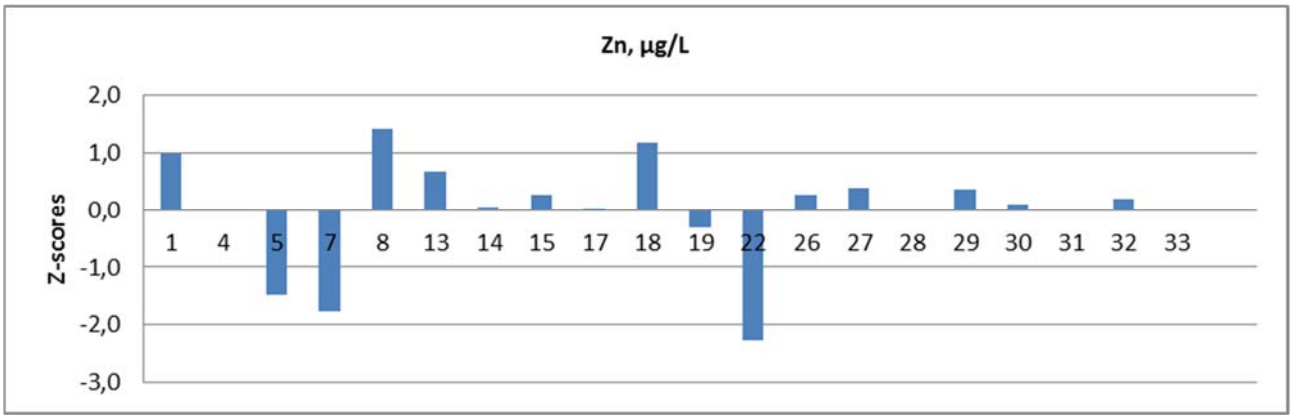
Two z-scores are out of range: Lab 7 (z-score=-4.8) and Lab 32 (z-score =-5.9)

	Pb
Statistical parameters	**A/B Freshwater**
p	16
m [µg/L]	11.14
S(L) [µg/L]	1.31
S(r) [µg/L]	0.35
S(R) [µg/L]	1.36
r [µg/L]	0.97
R [µg/L]	3.80
CV(r) [%]	3.1
CV(R) [%]	12.2

Component			*Pb, µgL*			
Assigned value	**21.30**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	20.94					
4						
5	21.58					
7						
8	16.50		X			
13	25.10					
14	20.90					
15	23.00					
17	26.50					
18	24.60					
19	22.00					
22	23.00					
26	21.50					
27	22.50					
28						
29	22.40					
30	22.60					
31						
32	6.28					
33	21.40					

	Freshwater C
Statistical analysis	**Pb, µgL**
Assigned value	21.30
Laboratory deviation (S(L)	4.56
Relative laboratory deviation (%)	21.4
Calculated spike value	13.66
Measured value of spike	10.16
% recovery of spike	74

Component					*Zn, µgL*				
Assigned value	**77.16**	**77.16**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	84.32	84.07							
4									
5	67.16	65.63							
7	64.30	64.52							
8	87.70	86.90							
13	80.00	84.00							
14	77.20	77.80							
15	79.00	79.00							
17	78.10	76.70							
18	85.90	85.30							
19	74.80	75.20							
22	61.10	60.30							
26	79.60	78.70							
27	80.50	79.30							
28									
29	80.40	79.30							
30	78.00	77.60							
31									
32	76.84	80.23							
33	77.00	77.00							

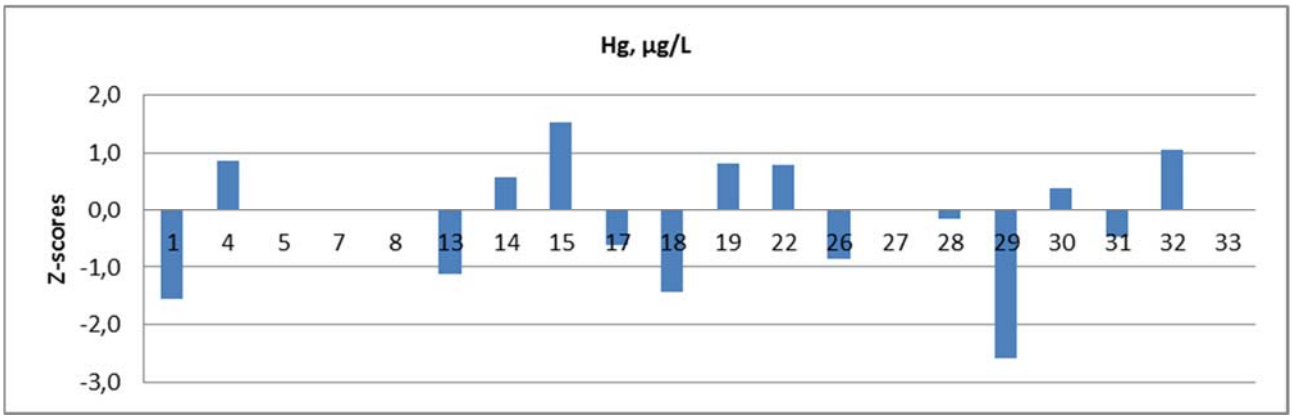


	Zn
Statistical parameters	**A/B Freshwater**
p	17
m [µg/L]	77.16
S(L) [µg/L]	7.14
S(r) [µg/L]	1.08
S(R) [µg/L]	7.22
r [µg/L]	3.04
R [µg/L]	20.23
CV(r) [%]	1.4
CV(R) [%]	9.4

Component			*Zn, µgL*			
Assigned value	**168.5**	**Grupps single test**		**Grupps double test**		**Excluded in stati-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**stical analysis**
1	169.8					
4	0.2	x	x			x
5	165.1					
7	147.0					
8	186.0					
13	210.0					
14	162.0					
15	170.0					
17	164.0					
18	176.0					
19	164.0					
22	158.0					
26	162.0					
27	164.4					
28						
29	167.2					
30	160.0					
31						
32	180.3					
33	159.0					

	Freshwater C
Statistical analysis	**Zn, µgL**
Assigned value	168.5
Laboratory deviation (S(L)	13.96
Relative laboratory deviation (%)	8.3
Calculated spike value	88.72
Measured value of spike	91.3
% recovery of spike	103

Component					*Hg, µgL*				
Assigned value	**0.174**	**0.174**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	0.139	0.156							
4	0.191	0.186							
5									
7									
8									
13	0.160	0.150							
14	0.188	0.180							
15	0.200	0.200							
17	0.164	0.163							
18	0.154	0.145							
19	0.189	0.187							
22	0.189	0.186							
26	0.164	0.155							
27									
28	0.170	0.172							
29	0.112	0.148	X	X	-	-	-	-	X
30	0.185	0.176							
31	0.172	0.160							
32	0.195	0.189							
33									



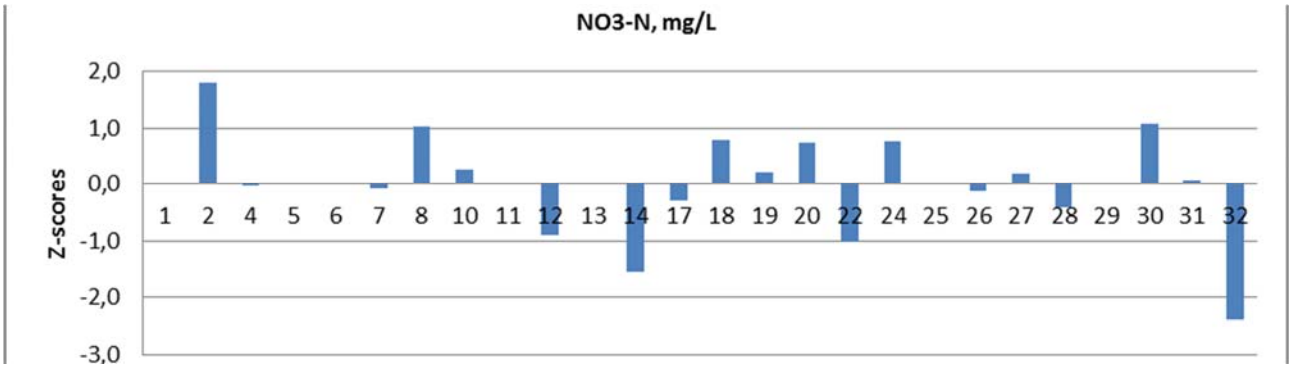
	Hg
Statistical parameters	**A/B Freshwater**
p	14
m [µg/L]	0.174
S(L) [µg/L]	0.017
S(r) [µg/L]	0.005
S(R) [µg/L]	0.017
r [µg/L]	0.015
R [µg/L]	0.049
CV(r) [%]	3.0
CV(R) [%]	10.0

Component			*Hg, µgL*			
Assigned value	**0.662**	**Grupps single test**		**Grupps double test**		**Excluded in sta-**
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**tistical analysis**
1	0.568					
4						
5						
7						
8						
13	0.660					
14	0.714					
15	0.850					
17	0.697					
18	0.593					
19	0.627					
22	0.699					
26	0.697					
27						
28	0.737					
29	0.411					
30	0.618					
31	0.748					
32	0.655					
33						

	Freshwater C
Statistical analysis	**Hg, µgL**
Assigned value	0.662
Laboratory deviation (S(L)	0.102
Relative laboratory deviation (%)	15.4
Calculated spike value	0.577
Measured value of spike	0.488
% recovery of spike	85

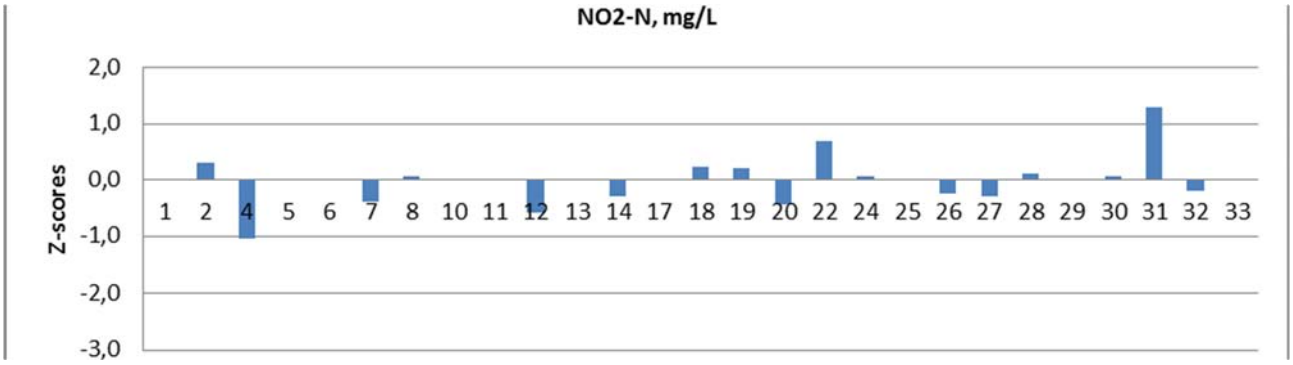
4.3 Statistical data for each component in waste water

Component			*NO3-N, mg/L*						
Assigned value	**6.13**	**6.13**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1									
2	6.85	6.81							
4	6.16	6.09							
5									
6									
7	6.11	6.08							
8	6.53	6.53							
10	6.25	6.21							
11									
12	5.67	5.89							
13									
14	5.48	5.57							
17	6.01	6.02							
18	6.42	6.45							
19	6.34	6.09							
20	6.37	6.47							
22	5.52	5.94		X					
24	6.41	6.44							
25									
26	6.07	6.10							
27	6.20	6.20							
28	5.99	5.95							
29									
30	6.62	6.48							
31	6.11	6.20							
32	5.27	5.12							
33									



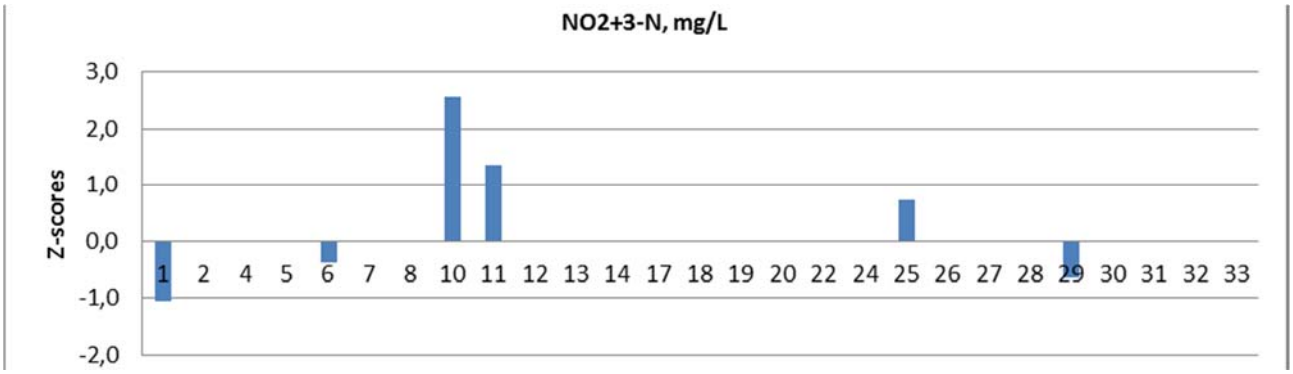
Statistical parameters	NO3-N A/B Waste Water
p	19
m [mg/L]	6.13
S(L) [mg/L]	0.38
S(r)	0.10
S(R)	0.39
r [mg/L]	0.28
R [mg/L]	1.10
CV(r) [%]	1.6
CV(R) [%]	6.4

Component			*NO2-N, mg/L*						
Assigned value	**0.045**	**0.045**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1									
2	0.048	0.048							
4	0.035	0.034							
5									
6									
7	0.041	0.041							
8	0.045	0.046							
10									
11	0.045	0.045							
12	0.039	0.039							
13									
14	0.042	0.042							
17	0.045	0.045							
18	0.047	0.047							
19	0.047	0.047							
20	0.040	0.041							
22	0.052	0.052							
24	0.048	0.043	X	X	-	-	-	-	X
25									
26	0.043	0.042							
27	0.042	0.042							
28	0.045	0.047		X					
29									
30	0.049	0.042	X	X	-	-	-	-	X
31	0.058	0.058							
32	0.043	0.043							
33									



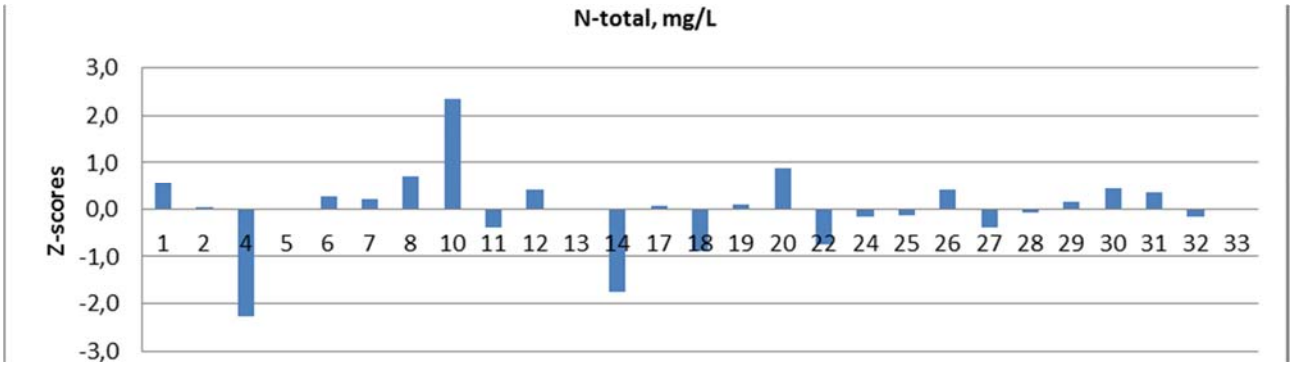
Statistical parameters	NO2-N A/B Waste Water
p	17
m [mg/L]	0.045
S(L) [mg/L]	0.005
S(r)	0.001
S(R)	0.005
r [mg/L]	0.001
R [mg/L]	0.015
CV(r) [%]	1.1
CV(R) [%]	11.8

Component			*NO2+3-N, mg/L*						
Assigned value	**6.34**	**6.34**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.14	6.15							
2									
4									
5									
6	6.23	6.32		X					
7									
8									
10	6.98	6.68	X	X	-	-	-	-	X
11	6.60	6.60							
12									
13									
14									
17									
18									
19									
20									
22									
24									
25	6.47	6.49							
26									
27									
28									
29	6.23	6.21							
30									
31									
32									
33									



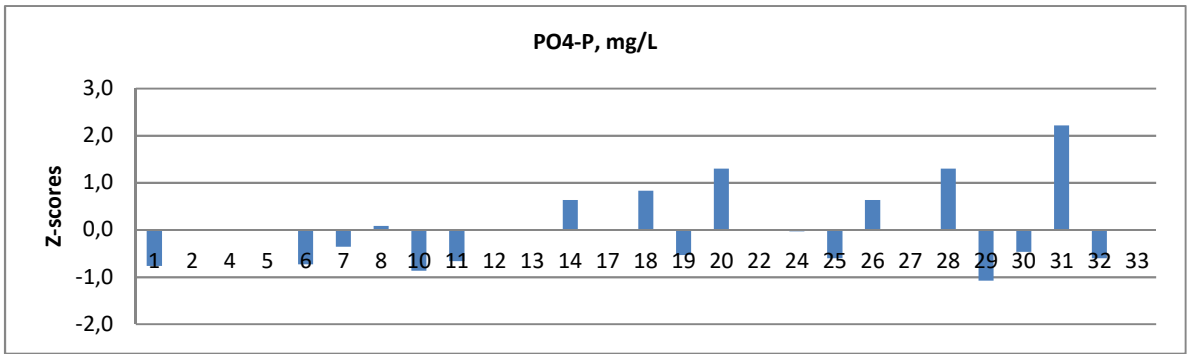
	NO2+3-N
Statistical parameters	**A/B Waste Water**
p	5
m [mg/L]	6.34
S(L) [mg/L]	0.19
S(r)	0.03
S(R)	0.19
r [mg/L]	0.09
R [mg/L]	0.53
CV(r) [%]	0.5
CV(R) [%]	3.0

Component	*N-total, mg/L*								
Assigned value	**7.23**	**7.23**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Waste**	**Waste**							**statistical**
code no.	**water A**	**water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	7.44	7.40							
2	7.26	7.21							
4	6.47	6.44							
5									
6	7.34	7.30							
7	7.31	7.30							
8	7.45	7.49							
10	7.91	8.16							
11	7.10	7.10							
12	7.14	7.60							
13									
14	6.55	6.71							
17	7.25	7.26							
18	6.92	6.93							
19	6.78	7.74		X					
20	7.44	7.62							
22	6.58	7.38							
24	7.15	7.21							
25	7.23	7.14							
26	7.64	7.10							
27	6.90	7.30							
28	7.21	7.19							
29	7.37	7.20							
30	7.56	7.20							
31	7.27	7.44							
32	7.12	7.24							
33									



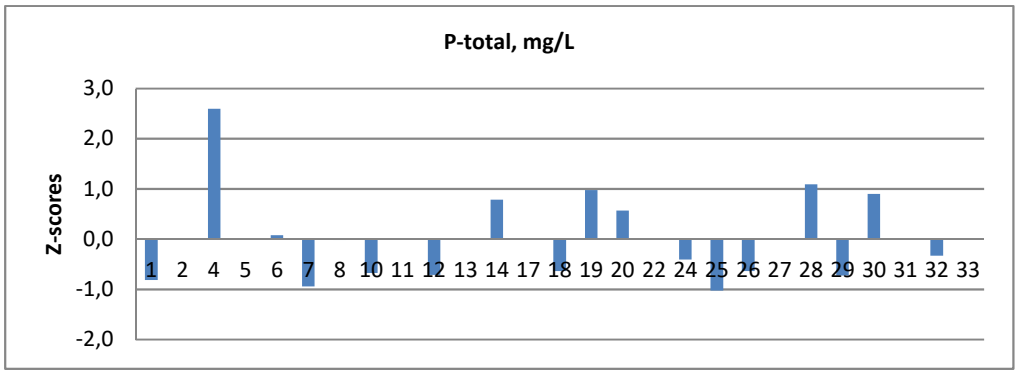
	N-total
Statistical parameters	**A/B Waste Water**
p	24
m [mg/L]	7.23
S(L) [mg/L]	0.26
S(r)	0.23
S(R)	0.34
r [mg/L]	0.63
R [mg/L]	0.95
CV(r) [%]	3.1
CV(R) [%]	4.7

Component			*PO4-P, mg/L*						
Assigned value	**0.010**	**0.010**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	0.008	0.007							
2									
4									
5									
6	0.008	0.007							
7	0.010	0.007							
8	0.011	0.009							
10	0.007	0.007							
11	0.008	0.007							
12									
13									
14	0.011	0.012							
17									
18	0.013	0.011							
19	0.007	0.009							
20	0.014	0.013							
22									
24	0.009	0.010							
25	0.009	0.007							
26	0.013	0.010							
27									
28	0.013	0.014							
29	0.007	0.006							
30	0.009	0.008							
31	0.019	0.014							
32	0.007	0.008							
33									



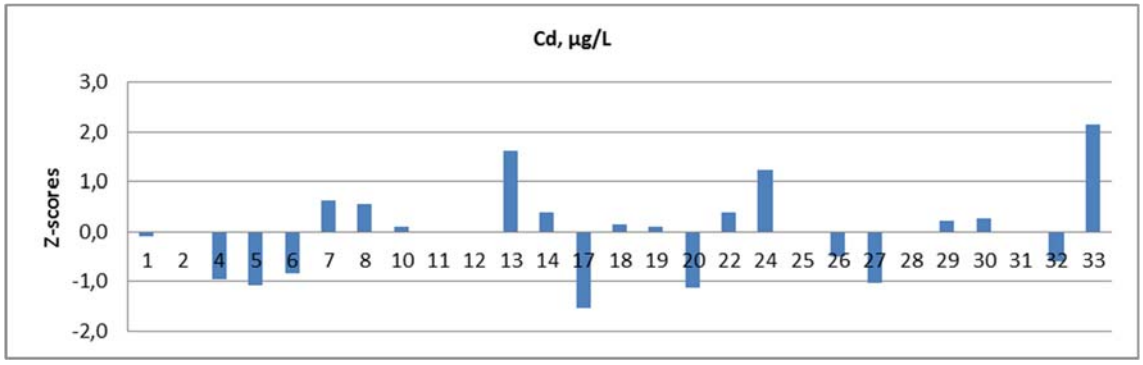
Statistical parameters	PO4-P A/B Waste Water
p	18
m [mg/L]	0.010
S(L) [mg/L]	0.003
S(r)	0.001
S(R)	0.003
r [mg/L]	0.004
R [mg/L]	0.008
CV (r) [%]	13.1
CV (R) [%]	30.3

Component			*P-total, mg/L*						
Assigned value	**0.025**	**0.025**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	0.015	0.014							
2									
4	0.053	0.065				X			
5									
6	0.026	0.027							
7	0.015	0.011							
8	0.026	0.024							
10	0.016	0.017							
11									
12	0.014	0.018							
13									
14	0.033	0.038							
17									
18	0.016	0.018							
19	0.036	0.040							
20	0.033	0.033							
22									
24	0.020	0.020							
25	0.013	0.011							
26	0.022	0.012							
27									
28	0.043	0.036							
29	0.018	0.014							
30	0.036	0.038							
31									
32	0.020	0.022							
33									



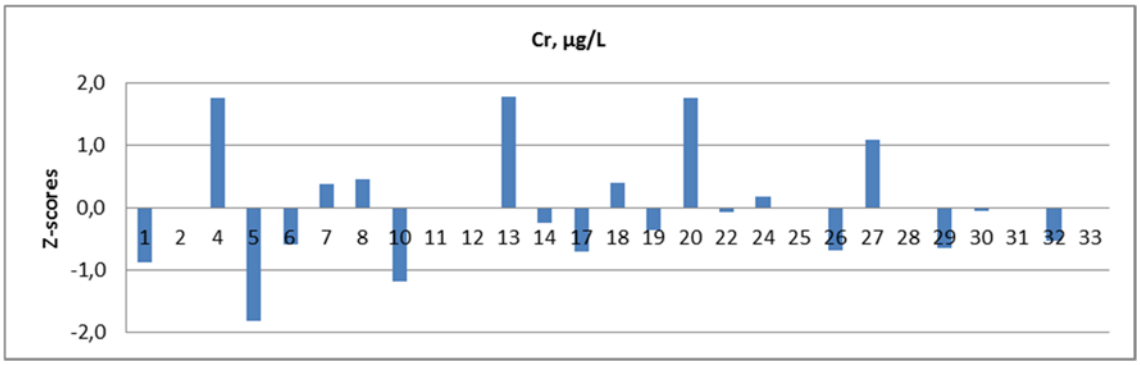
Statistical parameters	P-total A/B Waste Water
p	18
m [mg/L]	0.025
S(L) [mg/L]	0.012
S(r)	0.003
S(R)	0.013
r [mg/L]	0.010
R [mg/L]	0.036
CV(r) [%]	13.4
CV(R) [%]	50.4

Component					*Cd, µg/L*				
Assigned value	**23.87**	**23.87**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	23.74	23.79							
2									
4	22.50	22.90							
5	22.84	22.25							
6	23.30	22.40							
7	24.70	24.60							
8	24.40	24.70							
10	24.00	24.00							
11									
12									
13	25.80	25.90							
14	24.40	24.30							
17	21.00	23.00							
18	23.80	24.30							
19	23.00	25.00							
20	22.70	22.30							
22	24.30	24.40							
24	25.27	25.47							
25									
26	23.20	23.30							
27	22.90	22.30							
28									
29	24.30	24.00							
30	24.20	24.20							
31									
32	23.05	23.21							
33	27.00	26.00							



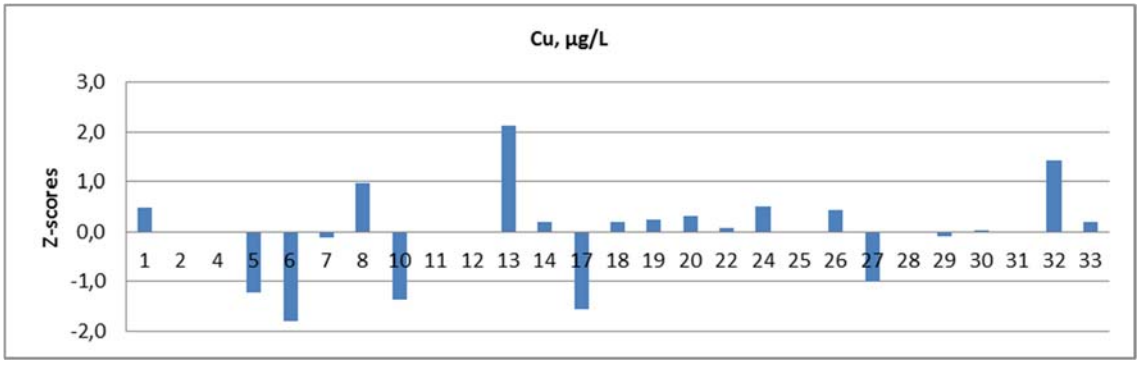
Statistical parameters	Cd A/B Waste Water
p	21
m [µg/L]	23.87
S(L)	1.10
S(r)	0.53
S(R)	1.22
r	1.48
R	3.42
CV(r)	2.2
CV(R)	5.1

Component					*Cr, µg/L*				
Assigned value	**49.01**	**49.01**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	46.10	45.98							
2									
4	54.80	55.03							
5	42.98	42.79							
6	48.10	46.00		X					
7	50.30	50.20							
8	50.70	50.30							
10	45.00	45.00							
11									
12									
13	55.00	55.00							
14	48.30	48.10							
17	46.50	46.80							
18	50.00	50.70							
19	47.60	48.00							
20	55.40	54.40							
22	48.80	48.70							
24	49.97	49.23							
25									
26	46.80	46.60							
27	51.90	53.40							
28									
29	46.90	46.80							
30	48.80	48.90							
31									
32	47.40	46.98							
33									



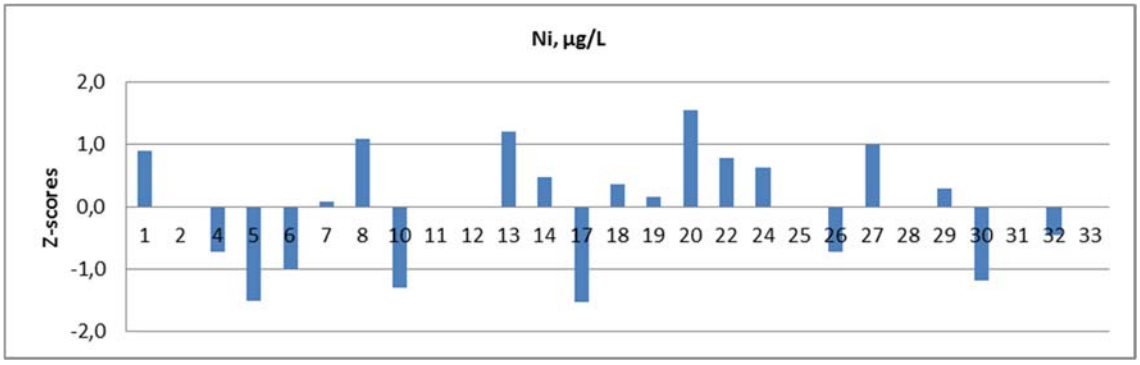
	Cr
Statistical parameters	**A/B Waste Water**
p	20
m [µg/L]	49.01
S(L) [µg/L]	3.32
S(r)	0.49
S(R)	3.36
r [µg/L]	1.38
R [µg/L]	9.40
CV(r) [%]	1.0
CV(R) [%]	6.9

Component			*Cu, µg/L*						
Assigned value	**142.4**	**142.4**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	145.4	147.4							
2									
4									
5	133.4	130.9							
6	130.0	125.0							
7	143.0	140.0							
8	149.0	152.0							
10	131.0	131.0							
11									
12									
13	160.0	160.0							
14	142.0	146.0							
17	127.0	132.0							
18	144.0	144.0							
19	145.0	144.0							
20	147.0	143.0							
22	143.0	143.0							
24	146.4	146.7							
25									
26	145.0	147.0							
27	132.8	135.4							
28									
29	140.2	142.9							
30	142.0	143.0							
31									
32	155.2	153.3							
33	144.0	144.0							



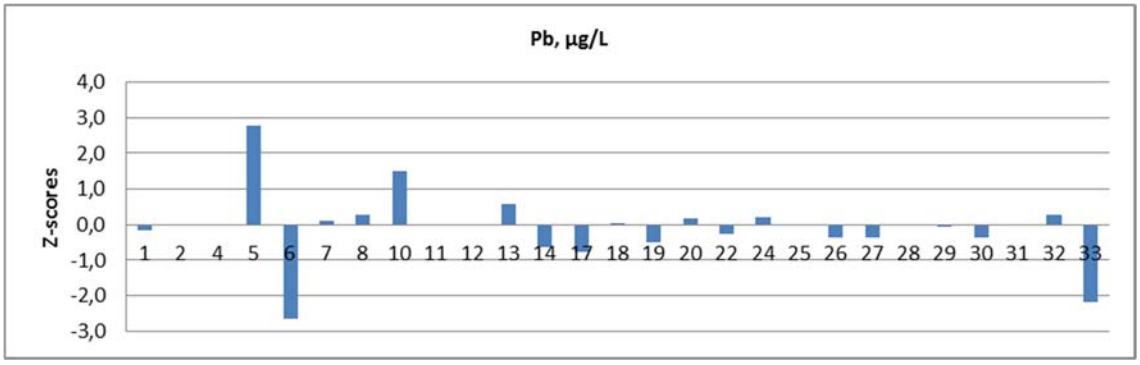
	Cu
Statistical parameters	**A/B Waste Water**
p	20
m [µg/L]	142.4
S(L) [µg/L]	8.1
S(r)	1.9
S(R)	8.3
r [µg/L]	5.2
R [µg/L]	23.2
CV(r) [%]	1.3
CV(R) [%]	5.8

Component					*Ni, µg/L*				
Assigned value	**194.4**	**194.4**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	205.4	206.9							
2									
4	178.5	191.5							
5	175.4	174.0							
6	185.0	178.0							
7	196.0	195.0							
8	212.0	205.0							
10	180.0	175.0							
11									
12									
13	210.0	210.0							
14	201.0	200.0							
17	175.0	174.0							
18	198.0	200.0							
19	196.0	197.0							
20	216.0	213.0							
22	198.0	211.0							
24	202.2	202.9							
25									
26	185.0	185.0							
27	204.3	210.3							
28									
29	197.8	198.6							
30	179.0	179.0							
31									
32	188.0	189.0							
33									



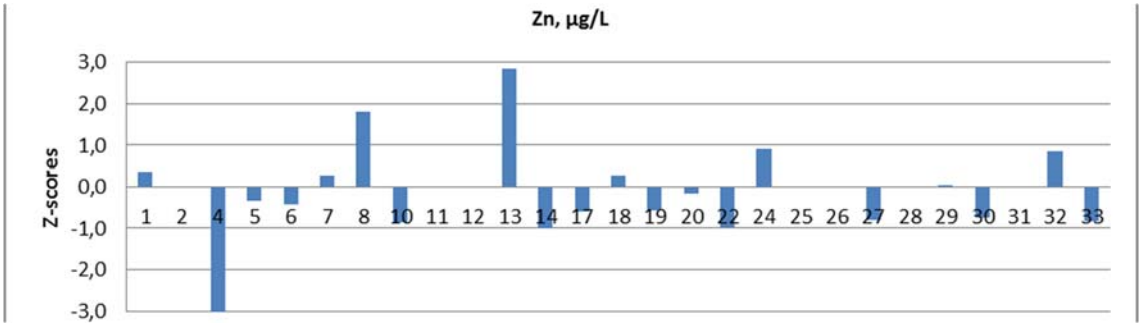
	Ni
Statistical parameters	**A/B Waste Water**
p	20
m [µg/L]	194.4
S(L) [µg/L]	12.5
S(r)	3.7
S(R)	13.0
r [µg/L]	10.3
R [µg/L]	36.4
CV(r) [%]	1.9
CV(R) [%]	6.7

Component					*Pb, µg/L*				
Assigned value	**8.59**	**8.59**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	8.29	8.35							
2									
4									
5	13.09	13.09				X		X	
6	7.91	0.65	X	X	-	-	-	-	X
7	8.84	8.70							
8	9.19	8.93							
10	11.00	11.00						X	
11									
12									
13	9.81	9.26		X					
14	7.52	7.63							
17	7.42	7.29							
18	8.65	8.69							
19	7.60	7.90							
20	8.87	8.88							
22	8.07	8.20							
24	8.96	8.93							
25									
26	8.05	7.93							
27	7.90	8.10							
28									
29	8.61	8.31							
30	8.00	8.03							
31									
32	10.03	8.05	X	X	-	-	-	-	X
33	5.10	5.00							



Statistical parameters	Pb A/B Waste Water
p	18
m [µg/L]	8.59
S(L) [µg/L]	1.62
S(r)	0.14
S(R)	1.62
r [µg/L]	0.39
R [µg/L]	4.54
CV(r) [%]	1.6
CV(R) [%]	18.9

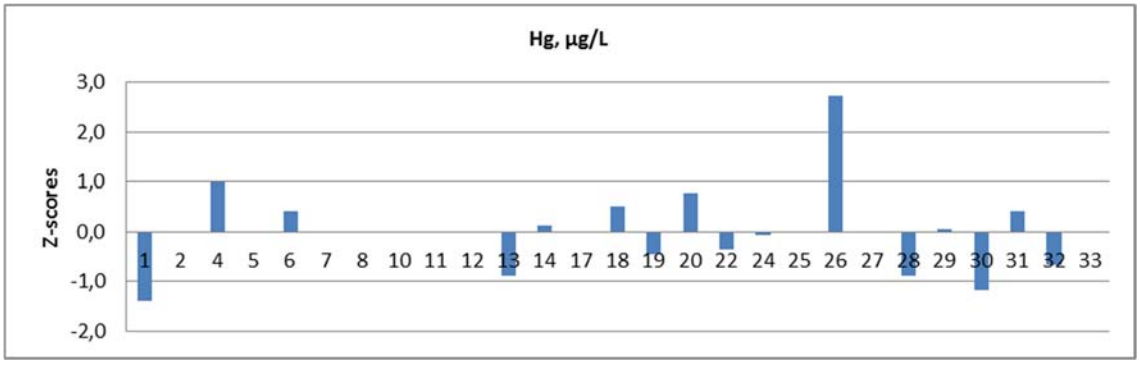
Component					*Zn, µg/L*				
Assigned value	**435.6**	**435.6**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	446.0	448.6							
2									
4	0.5	0.5			X	X	-	-	X
5	427.0	422.5							
6	431.0	413.0							
7	447.0	443.0							
8	504.0	486.0						X	
10	407.0	408.0							
11									
12									
13	530.0	530.0				X		X	
14	401.0	403.0							
17	417.0	414.0							
18	445.0	445.0							
19	412.0	421.0							
20	437.0	424.0							
22	402.0	404.0							
24	465.7	465.9							
25									
26	434.0	437.0							
27	408.7	408.9							
28									
29	436.1	435.7							
30	410.0	412.0							
31									
32	465.2	462.3							
33	408.0	408.0							



One Z-score is out of range: Lab 4 (z-score= -13.1)

Statistical parameters	**Zn A/B Waste Water**
p	20
m [µg/L]	435.6
S(L) [µg/L]	32.8
S(r)	4.8
S(R)	33.1
r [µg/L]	13.6
R [µg/L]	92.7
CV(r) [%]	1.1
CV(R) [%]	7.6

Component					*Hg, µg/L*				
Assigned value	**0.385**	**0.385**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Waste water A**	**Waste water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	0.315	0.330							
2									
4	0.434	0.424							
5									
6	0.403	0.404							
7									
8									
10									
11									
12									
13	0.350	0.340							
14	0.403	0.377							
17	0.386	0.382							
18	0.388	0.427							
19	0.351	0.379							
20	0.421	0.419							
22	0.376	0.361							
24	0.380	0.384							
25									
26	0.497	0.519				X			
27									
28	0.346	0.343							
29	0.394	0.380							
30	0.329	0.334							
31	0.407	0.400							
32	0.359	0.351							
33									



Statistical parameters	Hg A/B Waste Water
p	17
m [µg/L]	0.385
S(L) [µg/L]	0.043
S(r)	0.012
S(R)	0.045
r [µg/L]	0.033
R [µg/L]	0.126
CV(r) [%]	3.1
CV(R) [%]	11.6

5. Conclusions and summary

5.1 Summary of the intercalibration

The number of participating laboratories are shown in table 5.1

Table 5.1. Number of laboratories included in the statistic evaluation for each parameter, column one and three. The second and fourth column indicate the number excluded divided in below detection or quantification limit and outliers.

	Freshwater		Waste water	
	Laboratories included in the statistics	Laboratories excluded (</outlier)	Laboratories included in the statistics	Laboratories excluded (</outlier)
NO3-N mg/L	12	-	19	-
NO2-N mg/L	12	0/1	17	0/2
NO2+3-N mg/L	4	-	5	0/1
N-total mg/L	16	-	24	-
PO4-P mg/L	17	-	18	3/0
P-total mg/L	17	-	18	2/0
Cd µg/L	16	0/1	21	-
Cr µg/L	17	-	20	-
Cu µg/L	17	0/1	20	-
Ni µg/L	18	-	20	-
Pb µg/L	16	0/2	18	0/2
Zn µg/L	17	-	20	0/1
Hg µg/L	14	1/1	17	1/0

It is unclear if the laboratories have reported data as below detection limit (DL) or below quantification limit (QL) as the tradition for this differs between the countries. It has not been possible to clarify this. A request send to the laboratories afterwards whether they have used detection limit (DL) or quantification limit (QL) gave only a few replies. Only a few laboratories have reported below DL / QL even for the parameters present in very low concentrations, such as PO_4-P and P-total in waste water, see table 5.2. However, as it was informed in the DCE introduction letter to the laboratories that reported data under DL would not be included in the assessment of data, it is possible that some laboratories did not report data in that case.

A summary of the results from the PLC7 intercalibration are shown in table 5.2.

In general, the analytical quality is good and comparable between the laboratories with a few exceptions. See below.

For PO_4-P and P-total in waste water, the relative coefficients of total variation (CV(R)) are high which is due to low concentrations. The corresponding absolute values, reproducibility, S(R), are 0.003 and 0.013 mg / L, which is assessed as acceptable.

Table 5.2. Mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation.

Components	Freshwater				Waste water		
	Mean conc. sample A/B	S(R) sample A/B	CV(R) (%) sample A/B	Sample C recovery of spike (%)	Mean conc. sample A/B	S(R) sample A/B	CV(R) (%) sample A/B
NO_3-N mg/L	1.56	0.05	3.3	82	6.13	0.39	6.4
NO_2-N mg/L	0.036	0.006	16.6	60	0.045	0.005	11.8
NO_{2+3}-N mg/L	*1.60**	*0.08**	*5.2**	83	*6.34**	*0.19**	*3.0**
N-total mg/L	3.44	0.22	6.3	102	7.23	0.34	4.7
PO_4-P mg/L	0.209	0.014	6.8	99	0.0096	0.003	30.3
P-total mg/L	0.361	0.019	5.4	90	0.025	0.013	50.4
Cd µg/L	6.42	0.36	5.6	93	23.87	1.22	5.1
Cr µg/L	11.68	1.28	11.0	88	49.01	3.36	6.9
Cu µg/L	29.30	4.92	16.8	96	142.40	8.3	5.8
Ni µg/L	51.04	3.33	6.5	98	194.45	13	6.7
Pb µg/L	11.14	1.36	12.2	74	8.59	1.62	18.9
Zn µg/L	77.16	7.22	9.4	103	435.6	33.1	7.6
Hg µg/L	0.174	0.017	10.0	85	0.385	0.045	11.6

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

Pb showed low recovery and is the only parameter with two outliers in both freshwater and waste water. Further three laboratories were determined as stragglers for Pb in waste water, see outlier tables page 69 and 85. However, one laboratory was determined as outlier in both matrices. The PLC-6 intercalibration from 2012 did not show the same deviation for Pb concerning outliers and recovery.

In freshwater sample C, NO_2-N has low relative recovery. However, the main reason is likely to be due to very low concentration of NO_2-N. The calculated spike value was 0.01 and the measured spike value was 0.006.

According to the Danish Statutory Order no 974 of 27/06/2018 on quality requirements for environmental measurements from Ministry of Environment and Food the laboratories in Denmark must fulfil the following analytical quality: DL: detection limit, Uabs: the absolute expanded uncertainty at low concentrations and Urel: the relative expanded uncertainty at high concentrations. See Table 5.3.

It is not possible direct to compare table 5.2 and 5.3 as data in table 5.2 are across the laboratories, whereas table 5.3 is within the laboratory but it can give some indications om the levels.

Table 5.3. The required analytical quality from the Danish Statutory Order no 974 of 27/06/2018 on quality requirements for environmental measurements for freshwater and waste water. Note there are not requirements for all the components.

Components	Freshwater			Waste water		
	DL	U abs	U rel	DL	U abs	U rel
NO_3-N mg/L	-	-	-	-	-	-
NO_2-N mg/L	-	-	-	-	-	-
NO_{2+3}-N mg/L	0.005	0.01	15%	-	-	-
N-total mg/L	0.05	0.1	15%	0.05	0.1	15%
PO_4-P mg/L	0.005	0.01	15%	-	-	-
P-total mg/L	0.01	0.01	15%	0.3	0.1	15%
Cd µg/L	0.005	0.03	20%	0.05	0.2	20%
Cr µg/L	0.3	2	20%	1	1.5	20%
Cu µg/L	0.1	0.3	20%	1	3	20%
Ni µg/L	0.2	1	20%	1	3	20%
Pb µg/L	0.03	0.1	20%	1	3	20%
Zn µg/L	0.3	1	20%	5	10	20%
Hg µg/L	0.005	0.03	20%	0.05	0.2	20%

5.2 z-scores

Figure 5.1 and 5.2 show Z-scores for freshwater and figure 5.3 and 5.4 for waste water. The laboratory numbers are in the x-axis in the figures.

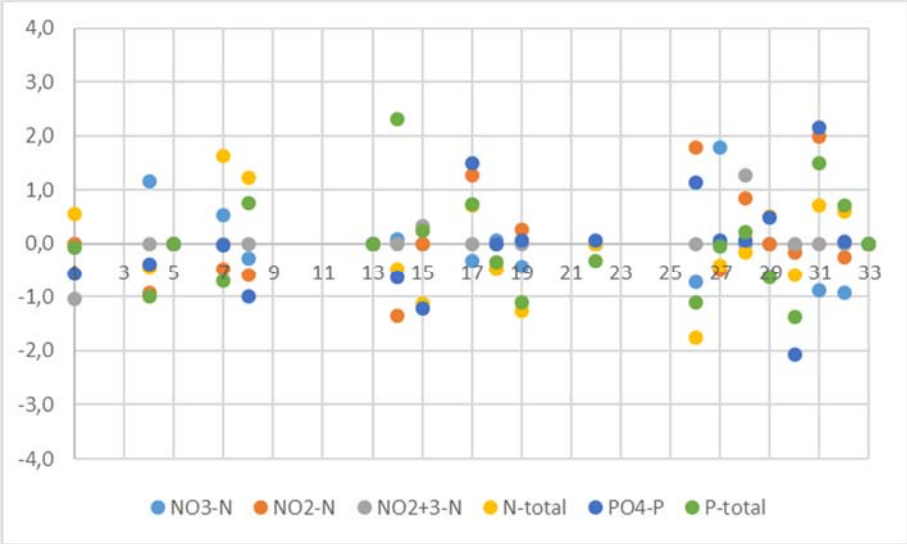


Figure 5.1. z-score results for freshwater, nutrients: z<|2|: 79 results; |3|<z<|2|: 3 results; z>|3|: 0 results..

Figure 5.2. z-score results for freshwater, metals: z<|2|: 109 results; |3|<z<|2|: 6 results; z>|3|: 3 results. Three z-scores not shown (z-score -4.9 Cd and -4.8 Pb for lab 7, and -5.9 Pb for lab 32).

Figure 5.3. z-score results for waste water, nutrients: z<|2|: 104 results; |3|<z<|2|: 4 results; z>|3|: 0 results.

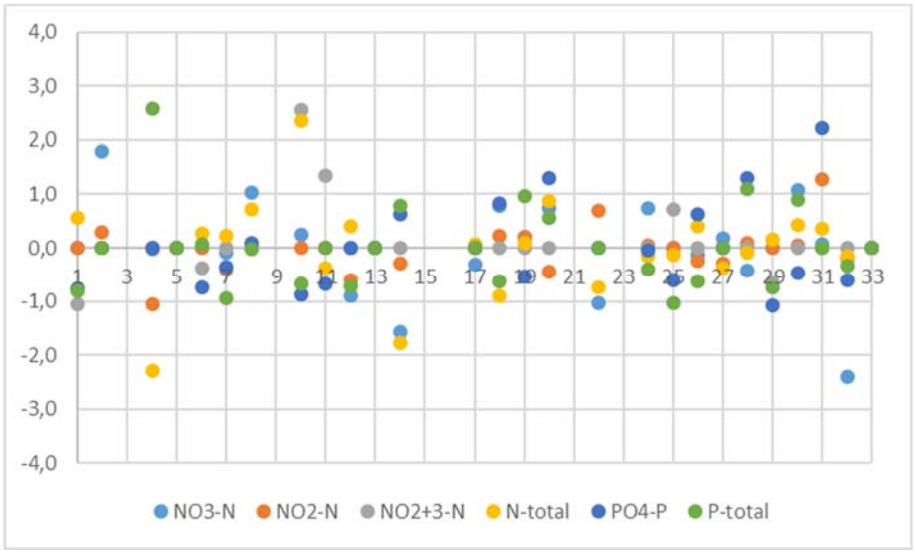


Figure 5.4. z-score results for waste water, metals: z<|2|: 139 results; |3|<z<|2|: 5 results; z>|3|: 1 results. One z-score not shown (z-score 13.1 for lab 4, Zn).

The results from the laboratories seem uniform. However, as z-scores are calculated from the total deviation of the intercalibration, it can reflect the limited number of z-scores above $z=|2|$. Therefore, these figures mainly provides an overview of the intercalibration. Note that three data points in freshwater and one in waste water for metals are not shown in order give to a better visual comparison. These data points are outliers and are not included in the statistical analysis.

It appears that metal have higher deviation based on z-scores compared to nutrients for freshwater. For freshwater 3.7% of z-scores were above $z=|2|$ for nutrients and 7.6% for metals, whereas for waste water it were 3.7% for nutrients and 4.1% for metals.

5.3 Comparison PLC-6 2012 and PLC-7

Table 5.4 and 5.5 is a comparison between the intercalibration PLC-6 in 2012 and PLC-7 in 2018.

Table 5.4. A comparison of mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation for PLC-6 (2012) and PLC-7 (2018) freshwater.

	Freshwater – PLC-7			Freshwater – PLC-6		
	Mean conc.	**S(R)**	**CV(R) (%)**	**Mean conc.**	**S(R)**	**CV(R) (%)**
NO_3-N mg/L	1.56	0.05	3.3	5.01	0.25	5.0
NO_2-N mg/L	0.036	0.006	16.6	0.14	0.027	19.3
N-total mg/L	3.44	0.22	6.3	6.04	0.32	5.3
PO_4-P mg/L	0.209	0.014	6.8	0.028	0.009	32.1
P-total mg/L	0.361	0.019	5.4	0.047	0.014	29.8
Cd µg/L	6.41	0.36	5.6	0.312	0.031	9.9
Cr µg/L	11.67	1.28	11.0	4.22	0.47	11.1
Cu µg/L	29.3	4.92	16.8	6.84	1.19	17.4
Ni µg/L	51.04	3.33	6.5	8.72	1.09	12.5
Pb µg/L	11.14	1.36	12.2	3.00	0.3	10.0
Zn µg/L	77.16	7.22	9.4	15.12	1.82	12.0
Hg µg/L	0.174	0.017	10.0	0.023	0.01	43.5

Table 5.5. A comparison of mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation for PLC-6 (2012) and PLC-7 (2018) waste water.

	Waste water – PLC-7			Waste water – PLC-6		
	Mean conc.	**S(R)**	**CV(R) (%)**	**Mean conc.**	**S(R)**	**CV(R) (%)**
NO_3-N mg/L	6.13	0.39	6.4	1.24	0.075	6.0
NO_2-N mg/L	0.045	0.005	11.8	0.001	0.0005	50.0
N-total mg/L	7.23	0.34	4.7	1.91	0.26	13.6
PO_4-P mg/L	0.010	0.003	30.3	0.14	0.009	6.4
P-total mg/L	0.025	0.013	50.4	0.166	0.02	12.0
Cd µg/L	23.87	1.22	5.1	1.65	0.091	5.5
Cr µg/L	49.01	3.36	6.9	10.24	1.05	10.3
Cu µg/L	142.4	8.3	5.8	84.5	6.23	7.4
Ni µg/L	194.4	13	6.7	28	2.65	9.5
Pb µg/L	8.59	1.62	18.9	81.5	6.96	8.5
Zn µg/L	435.6	33.1	7.6	94	6.11	6.5
Hg µg/L	0.385	0.045	11.6	0.169	0.017	10.1

In general, the analytical quality for most parameters has approved to some extent. For PO_4-P and P-total in waste water the higher CV(R) % in PLC-7 can be explained by very low concentrations. For Pb in both freshwater and waste water the analytical quality seem to have been reduced in 2018, most significant in waste water. There are no obvious explanation for these results.

In PLC-6 Hg in freshwater has a high deviation for sample A/B and low recovery in sample C (77%). It was suggested that this could partly be due to bottling in PE bottles. In PLC-7 glass bottles were used for Hg in both freshwater and waste water. In PLC-7 there was a reduced deviation and the recovery of sample C increased to some extent (85%). In general, analysis of Hg can be challenging.

5.4 Recommendations for future intercalibration

It is not clear whether the laboratories have used limit of quantification, LQ, or limit of detection, LD. There are different tradition for this in the different countries. In the instruction letter from DCE, we asked for LD. However, it is known that some laboratories reported LQ. A request to the laboratories to send information if they have used LQ or LD gave only very few replies. This should be much clearer explained in a next intercalibration.

Spike level nutrients: The fresh water were spiked with nutrients to a higher level but the waste water was not which gave very low concentrations for some nutrients and therefore high relative deviation. In a next intercalibration, the waste water should also be spiked with nutrients in order to generate data that are more robust.

Spike level metals: In order to secure, that most laboratories could detect the parameters the spike level was quite high. It has been debated that the levels where unrealistic high for some of the metals. In a next intercalibration, the spike level should be lowered.

Fresh water samples for metal were not conserved with acid. That should be done next time in order to improve stability.

The waste water were autoclaved in order to secure stability. It could be considered to do the same with fresh water next time.

Appendix 1

List of participating laboratories

The ranking of the laboratories does not reflect the laboratory code numbers. Some laboratories participated with more than one laboratory unit.

Country	Laboratory
Denmark	Eurofins-Miljø A-S
	Højvang Laboratorier A/S
Estonia	AS Pärnu Vesi
	OÜ Eesti Keskkonnauuringute Keskus (EKUK), Tallinn (Estonian Environmental Research Centre Ltd branches) EKUK, Tallinn
	OÜ Eesti Keskkonnauuringute Keskus (EKUK), Tartu (Estonian Environmental Research Centre Ltd branches) EKUK, Tallinn
	OÜ Eesti Keskkonnauuringute Keskus (EKUK), Virumaa
	Terviseamet (keemialabor) (Health Boards Chemistry lab)
Finland	Ahma ympäristö Oy
	Eurofins Environment Testing Finland Oy
Germany	Landeslabor Schleswig-Holstein
	Aqua Service Schwerin. Beratungs- und Betriebsführungsgesellschaft mbH
Latvia	Laboratory of the Latvian Environment. Geology and Meteorology Center
	Vides audits
Lithuania	Environmental Protection Agency of the Republic of Lithuania
	Environmental Protection Agency of the Republic of Lithuania
Polen	WIOŚ Szczecin. Pracownia Chemiczna
	WIOŚ Szczecin. Pracownia w Koszalinie
	WIOŚ Gdańsk. Pracownia w Gdańsku
	Laboratorium WIOŚ w Olsztynie Pracownia w Elblągu
Russia	Centre for Environmental Monitoring (FSBO “North-West Administration for Hydrometeorology and Environmental Monitoring”).
	Laboratory of the Pskov Centre for Environmental Monitoring
	Laboratory of the Novgorod Centre for Environmental Monitoring
Sweden	SLU
	SYNLAB
	Eurofins
	Laboratoriet. Kretslopp och vatten

Appendix 2

The reported data from the laboratories

Intercalibration under PLC7
Freshwater

Laboratory number: 1

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L			
NO2+3-N, mg/L	1.53	1.50	2.25
N-total, mg/L	3.56	3.56	6.54
PO4-P, mg/L	0.200	0.202	0.318
P-total, mg/L	0.360	0.359	0.818
Cd, µg/L	6.43	6.40	9.78
Cr, µg/L	11.32	11.17	16.95
Cu, µg/L	32.22	32.16	50.25
Ni, µg/L	52.98	53.98	82.01
Pb, µg/L	10.59	10.36	20.94
Zn, µg/L	84.32	84.07	169.8
Hg, µg/L	0.139	0.156	0.568

Intercalibration under PLC7
Waste water

Laboratory number: 1

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L		
NO2-N, mg/L		
NO2+3-N, mg/L	6.14	6.15
N-total, mg/L	7.44	7.40
PO4-P, mg/L	0.0077	0.0069
P-total, mg/L	0.0149	0.0145
Cd, µg/L	23.74	23.79
Cr, µg/L	46.10	45.98
Cu, µg/L	145.4	147.4
Ni, µg/L	205.4	206.9
Pb, µg/L	8.29	8.35
Zn, µg/L	446.0	448.6
Hg, µg/L	0.315	0.330

Intercalibration under PLC7
Waste water

Laboratory number: **2**

Table 1

Components	Measured data		Error
	Waste water sample A	Waste water sample B	
NO3-N, mg/L	6.85	6.81	10%
NO2-N, mg/L	0.048	0.048	0.004+0.13*X
NO2+3-N, mg/L	6.9	6.86	
N-total, mg/L	7.26	7.21	18.90%
PO4-P, mg/L	<0.01	<0.01	0.004+0.063*X
P-total, mg/L	<0.02	<0.02	0.004+0.063*X
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L			

Intercalibration under PLC7
Freshwater

Laboratory number: **4**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.637	1.602	2.456
NO2-N, mg/L	0.031	0.030	0.032
NO2+3-N, mg/L			
N-total, mg/L	3.360	3.320	6.400
PO4-P, mg/L	0.203	0.204	0.358
P-total, mg/L	0.344	0.340	0.791
Cd, µg/L		6.480	
Cr, µg/L	13.000	13.330	
Cu, µg/L	31.500	32.100	52.600
Ni, µg/L	52.570	51.360	80.200
Pb, µg/L	14.710	14.600	
Zn, µg/L			0.171
Hg, µg/L	0.191	0.186	

Intercalibration under PLC7
Waste water

Laboratory number: **4**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.161	6.085
NO2-N, mg/L	0.035	0.034
NO2+3-N, mg/L	6.196	
N-total, mg/L	6.470	6.440
PO4-P, mg/L		
P-total, mg/L	0.053	0.065
Cd, µg/L	22.50	22.90
Cr, µg/L	54.800	55.030
Cu, µg/L		
Ni, µg/L	178.50	191.50
Pb, µg/L		
Zn, µg/L	0.459	0.476
Hg, µg/L	0.434	0.424

Intercalibration under PLC7
Freshwater

Laboratory number: **5**

Table 1

Components	06-03-2018		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L			
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L			
P-total, mg/L			
Cd, µg/L	5.5	6.06	8.94
Cr, µg/L	10.9	9.53	14.52
Cu, µg/L	20.05	20.66	27.61
Ni, µg/L	44.62	45.56	77.93
Pb. µg/L	12	12.87	21.58
Zn. µg/L	67.16	65.63	165.1
Hg. µg/L			

Intercalibration under PLC7
Waste water

Laboratory number: **5**

Table 1

Components	06-03-2018	
	Waste water sample A	Waste water sample B
NO3-N, mg/L		
NO2-N, mg/L		
NO2+3-N, mg/L		
N-total, mg/L		
PO4-P, mg/L		
P-total, mg/L		
Cd, µg/L	22.84	22.25
Cr, µg/L	42.98	42.79
Cu, µg/L	133.38	130.9
Ni, µg/L	175.45	174.02
Pb, µg/L	13.09	13.09
Zn, µg/L	427	422.5
Hg, µg/L		

Intercalibration under PLC7
Waste water

Laboratory number: **6**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	No analysis	
NO2-N, mg/L	No analysis	
NO2+3-N, mg/L	6.2262	6.3189
N-total, mg/L	7.3393	7.3039
PO4-P, mg/L	0.0080	0.0068
P-total, mg/L	0.0256	0.0269
Cd, µg/L	No analysis	
Cr, µg/L	No analysis	
Cu, µg/L	No analysis	
Ni, µg/L	No analysis	
Pb, µg/L	No analysis	
Zn, µg/L	No analysis	
Hg, µg/L	No analysis	

Intercalibration under PLC7
Waste water

Laboratory number: **7**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.11	6.083
NO2-N, mg/L	0.041	0.041
NO2+3-N, mg/L	6.151	6.124
N-total, mg/L	7.31	7.299
PO4-P, mg/L	0.01002	0.007024
P-total, mg/L	0.01481	0.01127
Cd, µg/L	24.7	24.6
Cr, µg/L	50.3	50.2
Cu, µg/L	143	140
Ni, µg/L	196	195
Pb, µg/L	8.84	8.7
Zn, µg/L	447	443
Hg. µg/L		

Intercalibration under PLC7
Freshwater

Laboratory number: 7

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.626	1.549	2.3
NO2-N, mg/L	0.0369	0.0296	0.0349
NO2+3-N, mg/L	1.663	1.579	2.335
N-total, mg/L	3.801	3.796	6.604
PO4-P, mg/L	0.2088	0.2082	0.3155
P-total, mg/L	0.3486	0.3465	0.7889
Cd, µg/L	4.62	4.68	8.66
Cr, µg/L	8.6	8.6	13.5
Cu, µg/L	20.8	21	36.3
Ni, µg/L	43.7	43.6	71.6
Pb, µg/L	4.55	4.58	
Zn, µg/L	64.3	64.52	147
Hg, µg/L			

Intercalibration under PLC7
Waste water

Laboratory number: 7

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.11	6.083
NO2-N, mg/L	0.041	0.041
NO2+3-N, mg/L	6.151	6.124
N-total, mg/L	7.31	7.299
PO4-P, mg/L	0.01002	0.007024
P-total, mg/L	0.01481	0.01127
Cd, µg/L	24.7	24.6
Cr, µg/L	50.3	50.2
Cu, µg/L	143	140
Ni, µg/L	196	195
Pb, µg/L	8.84	8.7
Zn, µg/L	447	443
Hg. µg/L		

Intercalibration under PLC7
Freshwater

Laboratory number: **8**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.55	1.55	2.37
NO2-N, mg/L	0.032	0.033	0.038
NO2+3-N, mg/L	1.58	1.58	2.41
N-total, mg/L	3.73	3.69	6.60
PO4-P, mg/L	0.195	0.195	0.29
P-total, mg/L	0.38	0.374	0.847
Cd, µg/L	6.30	6.19	10.0
Cr, µg/L	11.4	11.4	17.2
Cu, µg/L	26.3	24.5	37.4
Ni, µg/L	53.8	53.0	80.8
Pb, µg/L	8.43	8.58	16.5
Zn, µg/L	87.7	86.9	186
Hg, µg/L	-	-	-

Intercalibration under PLC7
Waste water

Laboratory number: **8**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.53	6.53
NO2-N, mg/L	0.045	0.046
NO2+3-N, mg/L	6.58	6.58
N-total, mg/L	7.45	7.50
PO4-P, mg/L	0.011	0.0087
P-total, mg/L	0.026	0.024
Cd, µg/L	24.4	24.7
Cr, µg/L	50.7	50.3
Cu, µg/L	149	152
Ni, µg/L	212	205
Pb, µg/L	9.19	8.93
Zn, µg/L	504	486
Hg, µg/L	-	-

Intercalibration under PLC7
Waste water

Laboratory number: **10**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.25	6.21
NO2-N, mg/L		
NO2+3-N, mg/L	6.98	6.68
N-total, mg/L	7.91	8.16
PO4-P, mg/L	0.007	0.007
P-total, mg/L	0.016	0.017
Cd, µg/L	24	24
Cr, µg/L	45	45
Cu, µg/L	131	131
Ni, µg/L	180	175
Pb, µg/L	11	11
Zn, µg/L	407	408
Hg, µg/L		

Intercalibration under PLC7
Waste water

Laboratory number: **11**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L		
NO2-N, mg/L	0.045	0.045
NO2+3-N, mg/L	6.6	6.6
N-total, mg/L	7.1	7.1
PO4-P, mg/L	0.0083	0.0069
P-total, mg/L		
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC7
Waste water

Laboratory number: **12**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	5.67	5.89
NO2-N, mg/L	0.039	0.039
NO2+3-N, mg/L		
N-total, mg/L	7.14	7.60
PO4-P, mg/L	<0.005	<0.005
P-total, mg/L	0.014	0.018
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC7
Freshwater

Laboratory number: 13

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L			
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L			
P-total, mg/L			
Cd, µg/L	6.51±0.86	6.63±0.87	9.53±1.25
Cr, µg/L	13.4±2.4	13.2±2.4	19.1±3.5
Cu, µg/L	18.7±3.5	18.8±3.5	52.2±9.7
Ni, µg/L	50.3±9.0	49.6±8.9	80.0±14.3
Pb, µg/L	9.53±1.45	9.39±1.43	25.1±3.8
Zn, µg/L	80±5.1	84±5.3	210±13
Hg, µg/L	0.16±0.013	0.15±0.013	0.66±0.056

Intercalibration under PLC7
Waste water

Laboratory number: **13**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L		
NO2-N, mg/L		
NO2+3-N, mg/L		
N-total, mg/L		
PO4-P, mg/L		
P-total, mg/L		
Cd, µg/L	25.8±3.4	25.9±3.4
Cr, µg/L	55±5.0	55±5.0
Cu, µg/L	160±6.4	160±6.4
Ni, µg/L	210±17	210±17
Pb, µg/L	9.81±1.49	9.26±1.41
Zn, µg/L	530±34	530±34
Hg, µg/L	0.35±0.029	0.34±0.029

Intercalibration under PLC7
Freshwater

Laboratory number: **14**

Table 1

Components	Measured data 21.02-1.03.2018		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.57 ± 0.27	1.56 ± 0.27	2.32 ± 0.39
NO2-N, mg/L	0.028 ± 0.006	0.028 ± 0.006	0.031 ± 0.007
NO2+3-N, mg/L	1.60	1.59	2.35
N-total, mg/L	3.31 ± 1.29	3.36 ± 1.31	5.76 ± 2.25
PO4-P, mg/L	0.2 ± 0.03	0.2 ± 0.03	0.32 ± 0.05
PO4-P, mg/L	0.19 ± 0.03	0.19 ± 0.03	0.31 ± 0.05
P-total, mg/L	0.4 ± 0.09	0.41 ± 0.09	0.9 ± 0.20
Cd, µg/L	6.55 ± 2.88	6.82 ± 3.00	10.1 ± 4.4
Cr, µg/L	11.5 ± 2.6	12.3 ± 2.8	19.7 ± 4.5
Cu, µg/L	32.9 ± 7.6	31.4 ± 7.2	51.7 ± 11.9
Ni, µg/L	54.6 ± 15.8	58.2 ± 16.9	94.8 ± 27.5
Pb, µg/L	10.4 ± 2.6	10.6 ± 2.6	20.9 ± 5.2
Zn, µg/L	77.2 ± 16.2	77.8 ± 16.3	162 ± 34
Hg, µg/L	0.188 ± 0.058	0.18 ± 0.056	0.714 ± 0.221

uncertainty k=2. 95%

Intercalibration under PLC7
Waste water

Laboratory number: **14**

Table 1

Components	Measured data 21.02-1.03.2018	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	5.48 ± 0.71	5.57 ± 0.72
NO2-N, mg/L	0.042 ± 0.010	0.042 ± 0.010
NO2+3-N, mg/L	5.52	5.61
N-total, mg/L	6.55 ± 2.23	6.71 ± 2.28
PO4-P, mg/L	0.011 ± 0.002	0.012 ± 0.002
PO4-P, mg/L	0.010 ± 0.002	0.011 ± 0.002
P-total, mg/L	0.033 ± 0.005	0.038 ± 0.005
Cd, µg/L	24.4 ± 7.1	24.3 ± 7.0
Cr, µg/L	48.3 ± 10.6	48.1 ± 10.6
Cu, µg/L	142 ± 47	146 ± 48
Ni, µg/L	201 ± 60	200 ± 60
Pb, µg/L	7.52 ± 1.96	7.63 ± 1.98
Zn, µg/L	401 ± 84	403 ± 85
Hg, µg/L	0.403 ± 0.121	0.377 ± 0.113

uncertainty k=2. 95%

Intercalibration under PLC7
Freshwater

Laboratory number: **15**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L			
NO2+3-N, mg/L	1.63	1.62	2.38
N-total, mg/L	3.22	3.16	5.7
PO4-P, mg/L	0.192	0.192	0.301
P-total, mg/L	0.365	0.366	0.829
Cd, µg/L	6.3	6.3	9.6
Cr, µg/L	12	12	19
Cu, µg/L	31	31	48
Ni, µg/L	51	51	79
Pb, µg/L	11	12	23
Zn, µg/L	79	79	170
Hg, µg/L	0.20	0.20	0.85

Intercalibration under PLC7
Freshwater

Laboratory number: **17**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.56	1.53	2.29
NO2-N, mg/L	0.041	0.046	0.057
NO2+3-N, mg/L			
N-total, mg/L	3.59	3.6	6.46
PO4-P, mg/L	0.225	0.235	0.379
P-total, mg/L	0.37	0.38	0.848
Cd, µg/L	5.5	5.95	9
Cr, µg/L	10.8	10.3	16.3
Cu, µg/L	30.4	28.9	46.3
Ni, µg/L	49	48.1	73.4
Pb, µg/L	10.4	10.9	26.5
Zn, µg/L	78.1	76.7	164
Hg, µg/L	0.164	0.163	0.697

Intercalibration under PLC7
Waste water

Laboratory number: **17**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.01	6.02
NO2-N, mg/L	0.045	0.045
NO2+3-N, mg/L		
N-total, mg/L	7.25	7.26
PO4-P, mg/L	<0.02	<0.02
P-total, mg/L	<0.02	<0.02
Cd, µg/L	21	23
Cr, µg/L	46.5	46.8
Cu, µg/L	127	132
Ni, µg/L	175	174
Pb, µg/L	7.42	7.29
Zn, µg/L	417	414
Hg. µg/L	0.386	0.382

Intercalibration under PLC7
Freshwater

Laboratory number: **18**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.561	1.567	2.38
NO2-N, mg/L	0.0336	0.0329	0.0388
NO2+3-N, mg/L	1.595	1.6	2.419
N-total, mg/L	3.36	3.305	5.935
PO4-P, mg/L	0.208	0.21	0.352
P-total, mg/L	0.354	0.355	0.813
Cd, µg/L	6.82	6.86	10.5
Cr, µg/L	12.8	12.7	19.6
Cu, µg/L	34.9	34.9	52
Ni, µg/L	53.2	53.3	80.7
Pb, µg/L	11.8	11.8	24.6
Zn, µg/L	85.9	85.3	176
Hg, µg/L	0.154	0.145	0.593

Intercalibration under PLC7
Waste water

Laboratory number: **18**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.424	6.452
NO2-N, mg/L	0.0475	0.0469
NO2+3-N, mg/L	6.471	6.499
N-total, mg/L	6.920	6.935
PO4-P, mg/L	0.0131	0.0111
P-total, mg/L	0.0165	0.0175
Cd, µg/L	23.8	24.3
Cr, µg/L	50	50.7
Cu, µg/L	144	144
Ni, µg/L	198	200
Pb, µg/L	8.65	8.69
Zn, µg/L	445	445
Hg, µg/L	0.388	0.427

Intercalibration under PLC7
Freshwater

Laboratory number: **19**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.55	1.53	2.43
NO2-N, mg/L	0.039	0.036	0.042
NO2+3-N, mg/L	1.58	1.56	2.47
N-total, mg/L	3.18	3.14	4.96
PO4-P, mg/L	0.21	0.21	0.36
P-total, mg/L	0.34	0.34	0.77
Cd, µg/L	6.5	6.6	10.1
Cr, µg/L	12.5	13.2	19.3
Cu, µg/L	30.5	31.4	51.0
Ni, µg/L	53.0	52.5	80.0
Pb, µg/L	11.9	10.9	22.0
Zn, µg/L	74.8	75.2	164
Hg, µg/L	0.189	0.187	0.627

Intercalibration under PLC7
Waste water

Laboratory number: **19**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/	6.34	6.09
NO2-N, mg/L	0.047	0.047
NO2+3-N, mg/L	6.39	6.14
N-total, mg/L	6.78	7.74
PO4-P, mg/L	0.007	0.009
P-total, mg/L	0.036	0.040
Cd, µg/L	23.0	25.0
Cr, µg/L	47.6	48.0
Cu, µg/L	145	144
Ni, µg/L	196	197
Pb, µg/L	7.6	7.9
Zn, µg/L	412	421
Hg, µg/L	0.351	0.379

Intercalibration under PLC7
Waste water

Laboratory number: **20**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.37	6.47
NO2-N, mg/L	0.040	0.041
NO2+3-N, mg/L	6.41	6.51
N-total, mg/L	7.44	7.62
PO4-P, mg/L	0.014	0.013
P-total, mg/L	0.0326	0.0328
Cd, µg/L	22.7	22.3
Cr, µg/L	55.4	54.4
Cu, µg/L	147	143
Ni, µg/L	216	213
Pb, µg/L	8.87	8.88
Zn, µg/L	437	424
Hg, µg/L	0.421	0.419

Intercalibration under PLC7
Freshwater

Laboratory number: **22**

Table 1

Components	Measured data 01.03-07.03.2018		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L			
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L	0.21 ± 0.03	0.21 ± 0.03	0.37 ± 0.06
P-total, mg/L	0.36 ± 0.07	0.35 ± 0.07	0.87 ± 0.17
Cd, µg/L	6.68 ± 1.60	6.81 ± 1.63	10.5 ± 2.5
Cr, µg/L	11.1 ± 2.3	12.3 ± 2.6	18.5 ± 3.9
Cu, µg/L	33.0 ± 6.9	34.0 ± 7.1	50.3 ± 10.6
Ni, µg/L	52.2 ± 14.6	53.0 ± 14.8	80.0 ± 22.4
Pb, µg/L	11.7 ± 2.6	12.0 ± 2.6	23.0 ± 5.1
Zn, µg/L	61.1 ± 25.1	60.3 ± 24.7	158 ± 65
Hg, µg/L	0.189 ± 0.066	0.186 ± 0.065	0.699 ± 0.245

Intercalibration under PLC7
Waste water

Laboratory number: **22**

Table 1

Components	Measured data 01.03-07.03.2018	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	5.52 ± 0.77	5.94 ± 0.83
NO2-N, mg/L	0.052 ± 0.010	0.044 ± 0.009
NO2+3-N, mg/L		
N-total, mg/L	6.58 ± 1.58	7.38 ± 1.77
PO4-P, mg/L		
P-total, mg/L		
Cd, µg/L	24.3 ± 5.8	24.4 ± 5.9
Cr, µg/L	48.8 ± 10.2	48.7 ± 10.2
Cu, µg/L	143 ± 30	143 ± 30
Ni, µg/L	198 ± 55	211 ± 59
Pb, µg/L	8.07 ± 1.78	8.2 ± 1.80
Zn, µg/L	402 ± 165	404 ± 166
Hg, µg/L	0.376 ± 0.132	0.361 ± 0.126

Intercalibration under PLC7
Waste water

Laboratory number: **24**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.41	6.44
NO2-N, mg/L	0.048	0.043
NO2+3-N, mg/L		
N-total, mg/L	7.15	7.21
PO4-P, mg/L	0.009	0.01
P-total, mg/L	0.02	0.02
Cd, µg/L	25.27	25.47
Cr, µg/L	49.97	49.23
Cu, µg/L	146.4	146.7
Ni, µg/L	202.2	202.9
Pb, µg/L	8.957	8.934
Zn, µg/L	465.7	465.9
Hg, µg/L	0.38	0.384

Intercalibration under PLC7
Waste water

Laboratory number: **25**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L		
NO2-N, mg/L		
NO2+3-N, mg/L	6.47	6.49
N-total, mg/L	7.23	7.14
PO4-P, mg/L	0.0085	0.0071
P-total, mg/L	0.0128	0.011
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Data recieved as pdf file

Intercalibration under PLC7
Freshwater

Laboratory number: **26**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.45	1.6	2.3
NO2-N, mg/L	0.056	0.037	0.044
NO2+3-N, mg/L			
N-total, mg/L	3.2	2.9	5.1
PO4-P, mg/L	0.22	0.23	0.39
P-total, mg/L	0.33	0.35	0.82
Cd, µg/L	6.69	6.49	10.1
Cr, µg/L	11.8	11.7	17.2
Cu, µg/L	30.7	30.2	44.9
Ni, µg/L	51.2	50.2	79.2
Pb, µg/L	10.5	10.4	21.5
Zn, µg/L	79.6	78.7	162
Hg, µg/L	0.164	0.155	0.697

Intercalibration under PLC7
Waste water

Laboratory number: **26**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N., mg/L	6.07	6.1
NO2-N, mg/L	0.043	0.042
NO2+3-N, mg/L		
N-total, mg/L	7.64	7.1
PO4-P, mg/L	0.013	0.01
P-total, mg/L	0.022	0.012
Cd, µg/L	23.2	23.3
Cr, µg/L	46.8	46.6
Cu, µg/L	145	147
Ni, µg/L	185	185
Pb, µg/L	8.05	7.93
Zn, µg/L	434	437
Hg, µg/L	0.497	0.519

Intercalibration under PLC7
Freshwater

Laboratory number: **27 and 33**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.6	1.7	2.3
NO2-N, mg/L	0.033	0.033	0.041
NO2+3-N, mg/L	x	x	x
N-total, mg/L	3.2	3.5	5.9
PO4-P, mg/L	0.21	0.21	0.35
P-total, mg/L	0.36	0.36	0.82
Cd, µg/L 1)	6.5	6.3	9.9
Cd, µg/L 2)	7.0	7.0	12.0
Cr, µg/L 1)	12.9	13.1	20.3
Cu, µg/L 1)	32.7	33.0	51.1
Cu, µg/L 2)	28.0	30.0	48.0
Pb, µg/L 1)	11.2	10.8	22.5
Pb, µg/L 3)	11.6	11.2	21.4
Zn, µg/L 1)	80.5	79.3	164.4
Zn, µg/L 2)	77.0	77.0	159.0
Hg, µg/L 1)	<0.2	<0.2	<0.2
Ni, µg/L 1)	55.4	56.3	87.1
Ni, µg/L 2)	49.0	49.0	83.0

1) ICP-M, 2) FAAS, 3) GFAAS

Intercalibration under PLC7
Waste water

Laboratory number: **27 and 33**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-, /L	6.2	6.2
NO2-N, mg/L	0.042	0.042
NO2+3-N, mg/L	x	x
N-total, mg/L	6.9	7.3
PO4-P, mg/L	< 0.040	< 0.040
P-total, mg/L	< 0.040	< 0.040
Cd, µg/L 1)	22.9	22.3
Cd, µg/L 2)	27.0	26.0
Cr, µg/L 1)	51.9	53.4
Cu, µg/L 1)	132.8	135.4
Cu, µg/L 2)	144.0	144.0
Pb, µg/L 1)	7.9	8.1
Pb, µg/L 3)	5.1	5.0
Zn, µg/L 1)	408.7	408.9
Zn, µg/L 2)	408.0	408.0
Hg, µg/L 1)*	<0.2	<0.2
Ni, µg/L 1)	204.3	210.1

1) ICP-MS, 2) FAAS, 3) GFAAS

Intercalibration under PLC7
Freshwater

Laboratory number: **28**

Table 1

Component,	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L	0.041	0.041	0.050
NO2+3-N, mg/L	1.7	1.7	2.6
N-total, mg/L	3.5	3.3	5.2
PO4-P, mg/L	0.21	0.21	0.35
P-total, mg/L	0.36	0.37	0.80
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L*	0.170	0.172	0.737

* - due to the problems with instrument computer, Hg is measured after the deadline - at the 21st of March 2018

Intercalibration under PLC7
Waste water

Laboratory number: **28**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	5.99	5.95
NO2-N, mg/L	0.045	0.047
NO2+3-N, mg/L		
N-total, mg/L	7.21	7.19
PO4-P, mg/L	0.013	0.014
P-total, mg/L	0.043	0.036
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L*	0.346	0.343

* - due to the problems with instrument computer, Hg is measured after the deadline - at the 21st of March 2018

Intercalibration under PLC7
Freshwater

Laboratory number: **29**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L			
NO2+3-N, mg/L	1.55	1.55	2.36
N-total, mg/L	3.56	3.54	6.582
PO4-P, mg/L	0.214	0.218	0.373
P-total, mg/L	0.349	0.349	0.775
Cd, µg/L	6.35	6.4	9.8
Cr, µg/L	11.2	10.7	17.4
Cu, µg/L	31.9	31.8	50.1
Ni, µg/L	51.9	52.2	79.8
Pb, µg/L	10.9	10.8	22.4
Zn, µg/L	80.4	79.3	167.2
Hg, µg/L	0.112	0.148	0.411

Intercalibration under PLC7
Waste water

Laboratory number: **29**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L		
NO2-N, mg/L		
NO2+3-N, mg/L	6.23	6.21
N-total, mg/L	7.372	7.196
PO4-P, mg/L	0.00702	0.00573
P-total, mg/L	0.0175	0.0141
Cd, µg/L	24.3	24
Cr, µg/L	46.9	46.8
Cu, µg/L	140.2	142.9
Ni, µg/L	197.8	198.6
Pb, µg/L	8.61	8.31
Zn, µg/L	436.1	435.7
Hg, µg/L	0.394	0.38

Intercalibration under PLC7
Freshwater

Laboratory number: **30**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.56	1.56	2.43
NO2-N, mg/L	0.038	0.032	0.042
NO2+3-N, mg/L			
N-total, mg/L	3.31	3.31	6.19
PO4-P, mg/L	0.18	0.18	0.28
P-total, mg/L	0.34	0.33	0.78
Cd, µg/L	6.28	6.15	9.50
Cr, µg/L	12.5	12.6	19.1
Cu, µg/L	32.4	32.3	49.5
Ni, µg/L	50.0	49.0	75.2
Pb, µg/L	11.2	11.4	22.6
Zn, µg/L	78.0	77.6	160
Hg, µg/L	0.185	0.176	0.618

Intercalibration under PLC7
Waste water

Laboratory number: **30**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.62	6.48
NO2-N, mg/L	0.049	0.042
NO2+3-N, mg/L		
N-total, mg/L	7.56	7.2
PO4-P, mg/L	0.0087	0.0077
P-total, mg/L	0.036	0.038
Cd, µg/L	24.2	24.2
Cr, µg/L	48.8	48.9
Cu, µg/L	142	143
Ni, µg/L	179	179
Pb, µg/L	8.00	8.03
Zn, µg/L	410	412
Hg, µg/L	0.330	0.334

Intercalibration under PLC7
Freshwater

Laboratory number: **31**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.522	1.512	2.288
NO3-N, mg/L	1.681	1.663	2.5
NO2-N, mg/L	0.0464	0.0492	0.0508
NO2+3-N, mg/L	1.728	1.712	2.55
N-total, mg/L	3.6	3.59	6.4
PO4-P, mg/L	0.24	0.238	0.425
P-total, mg/L	0.394	0.385	0.893
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L	0.1719	0.1598	0.748

Intercalibration under PLC7
Waste water

Laboratory number: **31**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	6.112	6.204
NO3-N, mg/L	6.478	6.483
NO2-N, mg/L	0.0578	0.0578
NO2+3-N, mg/L	6.535	6.541
N-total, mg/L	7.27	7.44
PO4-P, mg/L	0.0189	0.0136
P-total, mg/L		
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L	0.4072	0.3995

Intercalibration under PLC7
Freshwater

Laboratory number: **32**

Table 1

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	1.51	1.52	2.28
NO2-N, mg/L	0.034	0.035	0.041
NO2+3-N, mg/L	1.55	1.56	2.32
N-total, mg/L	3.52	3.62	6.42
PO4-P, mg/L	0.210	0.209	0.358
P-total, mg/L	0.370	0.379	0.837
Cd, µg/L	6.14	6.19	10.36
Cr, µg/L	10.57	10.52	16.83
Cu, µg/L	25.47	29.65	53.61
Ni, µg/L	48.31	50.92	81.25
Pb, µg/L	3.22	2.95	6.28
Zn, µg/L	76.84	80.23	180.3
Hg, µg/L	0.195	0.189	0.655

Intercalibration under PLC7
Waste water

Laboratory number: **32**

Table 1

Components	Measured data	
	Waste water sample A	Waste water sample B
NO3-N, mg/L	5.27	5.12
NO2-N, mg/L	0.043	0.043
NO2+3-N, mg/L	5.31	5.16
N-total, mg/L	7.12	7.24
PO4-P, mg/L	0.0075	0.0081
P-total, mg/L	0.020	0.022
Cd, µg/L	23.05	23.21
Cr, µg/L	47.40	46.98
Cu, µg/L	155.2	153.3
Ni, µg/L	188.0	189.0
Pb, µg/L	10.03	8.05
Zn, µg/L	465.2	462.3
Hg, µg/L	0.359	0.351

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REPORT ON THE HELCOM PLC-7 INTERCALIBRATION

This report presents results from the PLC-7 intercalibration on metal and nutrients in freshwater and waste water. The intercalibration was performed in order to evaluate the analytical quality of results reported to HELCOM. 29 laboratories participated in the intercalibration.

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