REPORT ON THE HELCOM PLC-8 INTERCALIBRATION

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

REPORT ON THE HELCOM PLC-8 INTERCALIBRATION

Pia Lassen[1]
Martin M. Larsen[2]

[1] Aarhus University, Department of Environmental Science
[2] Aarhus University, Department of Bioscience

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

Data sheet

Authors:	Pia Lassen[1] and Martin M. Larsen[2]
Institutions:	Aarhus University
	[1]Department of Environmental Science
	[2]Department of Bioscience

Abstract:	This report presents results from the PLC-8 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. 22 laboratories participated in the intercalibration.
Keywords:	HELCOM PLC-8 intercalibration, waste water, freshwater, nutrients, metals

Contents

Preface

The Danish Centre for Environment and Energy. Aarhus University (DCE) has performed an intercalibration on nutrients and metals on behalf of HELCOM PLC-8 in freshwater and waste water in order to evaluate the analytical quality of the data reported into HELCOM.

Layout and template for the statistical design were developed by professor Marianne Thomsen. Department of Environmental Science (ENVS) and senior scientist Peter Borgen Sørensen. Department of Bioscience (BIOS), Aarhus University. Planning and coordination of the intercalibration was done by senior scientist Pia Lassen, ENVS, and senior scientist Martin M Larsen, BIOS. Technician Pia Petersen, ENVS, assisted in preparing the intercalibration. Responsible for the statistical evaluation and quality control is Pia Lassen.

The intercalibration was financed by HELCOM. The participating laboratories have financed the analyses they have performed by themselves.

1.   Description of the intercalibration

The Eighth Baltic Sea Pollution Load Compilation Project (PLC-8) 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 gland sterilized.

Further, to make sure that as many laboratories as possible could report data all samples were spiked to be above thedetection limit. 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-8 intercalibration on metal and nutrients in freshwater and waste water. There are reported results from 22 laboratories. Six laboratories participated with additional methods. 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, NO_{2+3}, N-total, PO_4, and P-total.

Metals: Cd, Cr, Cu, Ni, Pb, Zn and Hg.

The original data from the laboratories can be found in appendix 2. Each laboratory was 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 (2019). Outliers according to these tests are not included in the statistical evaluation. Z-scores are calculated according to ISO 13528 (2015).

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.

For NO_2 in waste water the data is not reliable due to instability. This was also commented by several laboratories. The data therefore cannot be used for evaluation. The same instability was not seen for NO_2 in freshwater.

Parameter	Description of the statistical parameters used in this report
Chapter 3 Laboratory results	
Measured values	The data from the laboratory
Assigned values	The total mean of all results from the participating laboratories. outliers excluded
Average	The mean of the laboratory test pair (sample A and B)
Dev. %	The relative deviation between the assigned value and the laboratory average
RSD %	The relative deviation between test pairs (sample A and B)
z-score	Evaluate the results in the relation to the uncertainty of the intercalibration
Chapter 4 Statistical evaluation	
Cochran's outlier test	Evaluate if the test pair A and B of the single laboratory can be regarded as a duplicate compared to the deviation of test pair for all laboratories
Grubb's single 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. For the evaluation of the z-scores: $z<|2|$ is satifactory, $z=|2|-|3|$ is questionable and $z>|3|$ is not acceptable
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 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 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) of the total derivation

2. Preparation of the samples

The freshwater samples used for this intercalibration was collected from a Danish lake in Zealand. The water was collected in 30 litres polyethylene (PE) containers.

The waste water samples were effluent water collected from a waste water treatment plant in Zealand, Denmark. The water was collected in 30 litres polyethylene (PE) containers.

Waste water and freshwater were filtered and autoclaved in order to secure stability especially for the nutrients. Metal samples were conserved with nitric acid (0.2%). Hg were conserved with HCl (0.2%). Nutrient samples were not conserved further. All samples were stored at 5°C.

The freshwater samples A and B samples were spiked at the same concentration level whereas the C samples were spiked at a higher concentration level.

Waste water samples A and B samples were spiked at the same concentration level.

Nutrients and metals samples were bottled in PE bottles, whereas Hg samples were bottled in glass bottles.

Courier, TNT, transported the samples and the transportation time varied from one to six days. The samples were sent out the 19th of January to most of the laboratories. Samples for the Russian laboratories were sent a week later. The laboratories had approximately 2-3 weeks for the analysis to mid-February.

2.1 Stability and homogeneity

2.1.1 Samples used for metals

Stability and homogeneity of freshwater and waste water samples for metals was tested in Denmark by DCE. 3-8 samples were analysed each time. Tests were performed for mercury using Hg-AFS detector according to US-EPA method 1631, rest of the metals were analysed by ICP-MS.

The metal samples were analysed two times, eight samples as test for homogeneity at the same time as the samples were sent out in late-January and three samples three weeks later in mid-February as test for stability.

Unfortunately, the Hg-AFS broke down, so the homogeneity test at starting time was not possible. Data from the labs has therefore been used as mean value in relation to stability. The stability/homogeneity test was performed on eight samples five weeks after the samples were sent to the laboratories.

Table 2.1. Stability and homogeneity for metals in Freshwater A/B samples. *Loss: negative number indicate a higher measured concentration for the stability test compared to the homogeneity test due to the uncertainty of the analysis.

Freshwater A/B	Homogeneity			Stability	
	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss*
Cd µg/L	1.74	0.012	0.7%	1.75	-0.1%
Cr µg/L	3.30	0.038	1.2%	3.33	-0.7%
Cu µg/L	8.85	0.138	1.6%	9.23	-4.3%
Ni µg/L	13.98	0.132	0.9%	14.78	-5.7%
Pb µg/L	1.67	0.014	0.8%	1.72	-2.7%
Zn µg/L	27.27	0.386	1.4%	29.00	-6.3%

Table 2.2. Stability and homogeneity for metals in Freshwater C samples. *Loss: negative number indicate a higher measured concentration for the stability test compared to the homogeneity test due to the uncertainty of the analysis.

Freshwater c	Homogeneity			Stability	
	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss*
Cd µg/L	2.51	0.034	1.3%	2.50	0.3%
Cr µg/L	4.78	0.081	1.7%	4.74	0.7%
Cu µg/L	13.78	0.150	1.1%	13.83	-0.4%
Ni µg/L	20.40	0.282	1.4%	20.42	-0.1%
Pb µg/L	2.32	0.017	0.8%	2.34	-1.0%
Zn µg/L	46.77	0.474	1.0%	48.30	-3.3%

Table 2.3. Stability and homogeneity for metals in Waste water A/B samples. *Loss: negative number indicate a higher measured concentration for the stability test compared to the homogeneity test due to the uncertainty of the analysis.

Waste water A/B	Homogenity			Stability	
	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss*
Cd µg/L	9.94	0.124	1.3%	9.83	1.1%
Cr µg/L	45.21	0.420	0.9%	43.98	2.7%
Cu µg/L	87.64	0.838	1.0%	86.05	1.8%
Ni µg/L	11.04	0.086	0.8%	11.00	0.4%
Pb µg/L	9.60	0.092	1.0%	9.57	0.3%
Zn µg/L	102.4	1.540	1.5%	103.9	-1.5%

Table 2.4. Stability and homogeneity for Hg in freshwater (FW) and waste water (WW). Mean value is the value from the intercalibration. *Loss: negative number indicate a higher measured concentration for the stability test compared to the homogeneity test due to the uncertainty of the analysis.

Hg, µg/L	Homogeneity			Stability	
	Laboratories Mean conc.	Standard deviation	Rel. Deviation	Measured conc. for stability	%Loss*
FW A/B	0.13	0.018	22.7%	0.08	38%
FW C	0.18	0.040	33.4%	0.12	33%
WW A/B	6.24	0.384	6.1%	6.28	-0.7%

The samples for the metal analysis appeared stable and homogenous and derivations in values are more likely to be due to day-to-day variations in measurements.

Mercury bottles were only tested once in March due to breakdown of the instrument. The results for the measurements in waste water indicated that the waste water samples were homogeneous and stable, but the measurements in freshwater varied between samples. Further, comparing the results from the participants of measurements in freshwater showed that Hg probably was not stable. The reason could be that the samples were not sufficient acidified. Further, the low concentrations of Hg in freshwater gave higher relative derivations.

2.1.2 Samples used for Nutrients

Homogeneity test of nutrient samples was performed on eight samples. The samples were analysed in two rounds: eight samples when the samples were sent out to the laboratories and three samples approx. 1 month later. The samples were analysed for NO_3-N, N-total and PO_4-P on a Skalar apparatus. NO_2-N and P-total were not included in the analysis and must therefore be evaluated based on the laboratories results. Se chapter 5.

Table 2.5. Stability and homogeneity for nutrients in Freshwater A/B samples. *Loss: negative number indicate a higher measured concentration for the stability test compared to the homogeneity test due to the uncertainty of the analysis.

| Freshwater A/B | Homogenity | | | Stability | |
	Measured conc.	Standard deviation	Rel. devia-tion	Measured conc. for stability	%Loss*
NO_3-N mg/L	0.71	0.024	3%	0.66	7.0%
N-total mg/L	3.32	0.150	5%	3.1	6.6%
PO_4-P mg/L	0.21	0.003	2%	0.23	-8.0%

Table 2.6. Stability and homogeneity for nutrients in Freshwater C samples. *Loss: negative number indicate a higher measured concentration for the stability test compared to the homogeneity test due to the uncertainty of the analysis.

| Freshwater C | Homogeneity | | | Stability | |
	Measured conc.	Standard deviation	Rel. devia-tion	Measured conc. for stability	%Loss*
NO_3-N mg/L	1.1	0.036	3%	0.98	10.7%
N-total mg/L	4.46	0.072	2%	4.62	-3.6%
PO_4-P mg/L	0.27	0.004	1%	0.30	-8.5%

Table 2.7. Stability and homogeneity for nutrients in Waste water A/B samples. *Loss: negative number indicate a higher measured concentration for the stability test compared to the homogeneity test due to the uncertainty of the analysis.

| Waste water A/B | Homogenity | | | Stability | |
	Measured conc.	Standard deviation	Rel. devia-tion	Measured conc. for stability	%Loss*
NO_3-N mg/L	6.99	0.154	2%	6.03	13.7%
N-total mg/L	12.02	0.540	4%	10.33	14.1%
PO_4-P mg/L	0.29	0.007	2%	0.26	8.9%

The homogeneity test showed that the homogeneity was the same for both waste water and freshwater. The stability for nutrients in general for freshwater was improved compared to PLC-6 and -7. This could indicate that sterilization improved the stability. For PLC-6 and -7 only the waste water was sterilised, and in both intercalibrations the nutrients appeared more stable in waste water. The only issue was that in PLC-8 the NO_2 appeared very unstable based on the laboratories results. NO_2 was unfortunenately not included in the homogeneity and stability test.

3. Laboratory results for the statistical analysis

3.1 Description of the tables

In section 3.2 and 3.3 the reported data from single laboratories are shown. If on the assigned value are shown in the table, the laboratory did not report data that specific component. 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 the samples), 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**

Components	Measured data Freshwater A	Freshwater B	Assigned values Freshwater A	Freshwater B	Average	Dev. %	Statistics RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L			0.26	0.26				
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L			0.20	0.20				
P-total, mg/L			0.28	0.28				
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L	0.13	0.14	0.13	0.13	0.13	2.1	3.2	0.1

Laboratory
Code no.: **1**

Components	Measured values Freshwater C	Assigned values Freshwater C	Statistics Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L		2.39		
Cr, µg/L		4.91		
Cu, µg/L		14.68		
Ni, µg/L		21.38		
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L	0.18	0.18	-0.82	-0.1

Laboratory

Code no: 2

| Components | Measured data | | Assigned values | | | Statistics | | |
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L			0.26	0.26				
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L	0.18	0.19	0.20	0.20	0.19	-4.6	2.3	-0.7
P-total, mg/L	0.27	0.26	0.28	0.28	0.26	-5.1	2.7	-0.8
Cd, µg/L	1.40	1.51	1.66	1.66	1.45	-12.5	5.3	-1.2
Cr, µg/L	2.84	2.87	3.39	3.39	2.86	-15.8	0.7	-2.2
Cu, µg/L	12.35	12.22	9.77	9.77	12.29	25.7	0.7	2.4
Ni, µg/L	11.83	12.19	15.19	15.19	12.01	-21.0	2.1	-2.5
Pb, µg/L	1.63	1.84	1.71	1.71	1.74	1.5	8.6	0.3
Zn, µg/L	23.30	23.53	27.24	27.24	23.42	-14.0	0.7	-1.8
Hg, µg/L			0.13	0.13				

Laboratory

Code no.: 2

| Components | Measured values | Assigned values | Statistics | |
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L	0.31	0.29	4.02	1.1
P-total, mg/L	0.43	0.42	0.72	0.3
Cd, µg/L	2.05	2.39	-6.98	-1.4
Cr, µg/L	4.09	4.91	-8.36	-2.3
Cu, µg/L	16.34	14.68	5.67	1.3
Ni, µg/L	17.02	21.38	-10.19	-2.3
Pb, µg/L	1.91	2.30	-8.52	-2.1
Zn, µg/L	41.21	46.97	-6.13	-2.7
Hg, µg/L		0.18		

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L			0.26	0.26				
NO2+3-N, mg/L	0.94	0.94	1.05	1.05	0.94	-10.3	0.5	-1.3
N-total, mg/L	3.54	3.51	3.38	3.38	3.53	4.3	0.6	0.6
PO4-P, mg/L	0.18	0.18	0.20	0.20	0.18	-6.9	0.4	-1.1
P-total, mg/L	0.29	0.28	0.28	0.28	0.28	3.2	3.0	0.5
Cd, µg/L	1.70	1.60	1.66	1.66	1.65	-0.8	4.3	-0.1
Cr, µg/L	3.40	3.40	3.39	3.39	3.40	0.2	0.0	0.0
Cu, µg/L	9.40	9.50	9.77	9.77	9.45	-3.3	0.7	-0.3
Ni, µg/L	15.00	15.00	15.19	15.19	15.00	-1.3	0.0	-0.2
Pb, µg/L	1.70	1.70	1.71	1.71	1.70	-0.5	0.0	-0.1
Zn, µg/L	27.00	27.00	27.24	27.24	27.00	-0.9	0.0	-0.1
Hg, µg/L			0.13	0.13				

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L	1.53	1.68	-4.36	-1.2
N-total, mg/L	4.51	4.58	-0.79	-0.2
PO4-P, mg/L	0.25	0.29	-5.94	-1.7
P-total, mg/L	0.43	0.42	1.55	0.6
Cd, µg/L	2.40	2.39	0.31	0.1
Cr, µg/L	4.90	4.91	-0.11	0.0
Cu, µg/L	14.00	14.68	-2.30	-0.5
Ni, µg/L	22.00	21.38	1.46	0.3
Pb, µg/L	2.40	2.30	2.12	0.5
Zn, µg/L	46.00	46.97	-1.03	-0.5
Hg, µg/L		0.18		

Laboratory

Code no: 4

Components	Measured data Freshwater A	Freshwater B	Assigned values Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.83	0.83	0.77	0.77	0.83	8.1	0.1	1.1
NO2-N, mg/L	0.25	0.25	0.26	0.26	0.25	-4.4	0.2	-0.6
NO2+3-N, mg/L	1.08	1.09	1.05	1.05	1.08	3.5	0.1	0.4
N-total, mg/L	3.27	3.29	3.38	3.38	3.28	-3.0	0.4	-0.4
PO4-P, mg/L	0.21	0.21	0.20	0.20	0.21	8.3	0.1	1.4
P-total, mg/L	0.26	0.26	0.28	0.28	0.26	-6.0	0.8	-0.9
Cd, µg/L	1.58	1.60	1.66	1.66	1.59	-4.4	0.9	-0.4
Cr, µg/L	3.17	3.10	3.39	3.39	3.14	-7.6	1.6	-1.1
Cu, µg/L	9.34	9.14	9.77	9.77	9.24	-5.5	1.5	-0.5
Ni, µg/L	15.26	14.94	15.19	15.19	15.10	-0.6	1.5	-0.1
Pb, µg/L	1.63	1.59	1.71	1.71	1.61	-5.9	1.5	-1.0
Zn, µg/L	28.07	27.16	27.24	27.24	27.62	1.4	2.3	0.2
Hg, µg/L	0.08	0.09	0.13	0.13	0.08	-35.8	5.1	-2.1

Laboratory

Code no.: 4

Components	Measured values Freshwater C	Assigned values Freshwater C	Statistics Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L	2.24	2.39	-2.96	-0.6
Cr, µg/L	4.42	4.91	-5.00	-1.4
Cu, µg/L	13.60	14.68	-3.66	-0.8
Ni, µg/L	20.38	21.38	-2.33	-0.5
Pb, µg/L	2.19	2.30	-2.44	-0.6
Zn, µg/L	45.38	46.97	-1.69	-0.7
Hg, µg/L	0.15	0.18	-9.56	-0.6

16

Components	Measured data Freshwater A	Freshwater B	Assigned values Freshwater A	Freshwater B	Average	Dev. %	Statistics RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L			0.26	0.26				
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L			0.20	0.20				
P-total, mg/L			0.28	0.28				
Cd, µg/L	1.74	1.74	1.66	1.66	1.74	4.6	0.0	0.4
Cr, µg/L	3.31	3.32	3.39	3.39	3.32	-2.3	0.2	-0.3
Cu, µg/L	9.20	9.13	9.77	9.77	9.17	-6.2	0.5	-0.6
Ni, µg/L	14.50	14.30	15.19	15.19	14.40	-5.2	1.0	-0.6
Pb, µg/L	1.67	1.67	1.71	1.71	1.67	-2.3	0.0	-0.4
Zn, µg/L	26.80	26.40	27.24	27.24	26.60	-2.3	1.1	-0.3
Hg, µg/L	0.13	0.13	0.13	0.13	0.13	3.6	0.0	0.2

Laboratory

Code no.: 5

Components	Measured values Freshwater C	Assigned values Freshwater C	Statistics Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L	2.51	2.39	2.62	0.5
Cr, µg/L	4.80	4.91	-1.13	-0.3
Cu, µg/L	14.00	14.68	-2.30	-0.5
Ni, µg/L	20.30	21.38	-2.52	-0.6
Pb, µg/L	2.33	2.30	0.60	0.2
Zn, µg/L	45.00	46.97	-2.10	-0.9
Hg, µg/L	0.22	0.18	9.84	0.6

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.66	0.71	0.77	0.77	0.68	-11.5	5.7	-1.5
NO2-N, mg/L	0.27	0.27	0.26	0.26	0.27	2.1	1.3	0.3
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L	2.99	3.03	3.38	3.38	3.01	-10.9	0.9	-1.6
PO4-P, mg/L	0.20	0.20	0.20	0.20	0.20	1.1	0.0	0.2
P-total, mg/L	0.27	0.27	0.28	0.28	0.27	-1.9	0.0	-0.3
Cd, µg/L	1.64	1.63	1.66	1.66	1.64	-1.7	0.4	-0.2
Cr, µg/L	3.47	3.54	3.39	3.39	3.51	3.3	1.4	0.5
Cu, µg/L	8.97	9.06	9.77	9.77	9.02	-7.8	0.7	-0.7
Ni, µg/L	15.01	15.10	15.19	15.19	15.06	-0.9	0.4	-0.1
Pb, µg/L	1.67	1.68	1.71	1.71	1.68	-2.0	0.4	-0.3
Zn, µg/L	25.91	26.55	27.24	27.24	26.23	-3.7	1.7	-0.5
Hg, µg/L	0.16	0.15	0.13	0.13	0.16	20.2	1.4	1.2

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	0.97	1.17	-8.55	-2.1
NO2-N, mg/L	0.44	0.44	0.00	0.0
NO2+3-N, mg/L		1.68		
N-total, mg/L	4.19	4.58	-4.28	-1.2
PO4-P, mg/L	0.29	0.29	-0.17	0.0
P-total, mg/L	0.42	0.42	0.12	0.0
Cd, µg/L	2.37	2.39	-0.31	-0.1
Cr, µg/L	5.16	4.91	2.54	0.7
Cu, µg/L	14.17	14.68	-1.72	-0.4
Ni, µg/L	21.51	21.38	0.31	0.1
Pb, µg/L	2.37	2.30	1.47	0.4
Zn, µg/L	45.61	46.97	-1.45	-0.6
Hg, µg/L	0.24	0.18	14.75	0.9

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.79	0.80	0.77	0.77	0.80	3.1	0.9	0.4
NO2-N, mg/L	0.24	0.24	0.26	0.26	0.24	-9.5	0.0	-1.4
NO2+3-N, mg/L	1.03	1.04	1.05	1.05	1.04	-1.2	0.7	-0.1
N-total, mg/L	3.32	3.52	3.38	3.38	3.42	1.2	4.1	0.2
PO4-P, mg/L	0.19	0.19	0.20	0.20	0.19	-3.0	0.0	-0.5
P-total, mg/L	0.29	0.28	0.28	0.28	0.29	4.3	1.5	0.7
Cd, µg/L	1.72	1.77	1.66	1.66	1.75	4.9	2.0	0.5
Cr, µg/L	3.43	3.48	3.39	3.39	3.46	1.8	1.0	0.3
Cu, µg/L	10.29	9.73	9.77	9.77	10.01	2.4	4.0	0.2
Ni, µg/L	14.54	15.22	15.19	15.19	14.88	-2.1	3.2	-0.2
Pb, µg/L	1.72	1.71	1.71	1.71	1.72	0.3	0.4	0.1
Zn, µg/L	28.20	27.50	27.24	27.24	27.85	2.3	1.8	0.3
Hg, µg/L	0.15	0.15	0.13	0.13	0.15	13.7	1.0	0.8

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.30	1.17	5.60	1.4
NO2-N, mg/L	0.39	0.44	-5.91	-1.7
NO2+3-N, mg/L	1.64	1.68	-1.07	-0.3
N-total, mg/L	4.73	4.58	1.62	0.4
PO4-P, mg/L	0.28	0.29	-1.05	-0.3
P-total, mg/L	0.43	0.42	0.72	0.3
Cd, µg/L	2.53	2.39	3.04	0.6
Cr, µg/L	4.89	4.91	-0.21	-0.1
Cu, µg/L	15.27	14.68	2.03	0.5
Ni, µg/L	22.10	21.38	1.69	0.4
Pb, µg/L	2.19	2.30	-2.44	-0.6
Zn, µg/L	46.80	46.97	-0.18	-0.1
Hg, µg/L	0.21	0.18	6.28	0.4

Laboratory

Code no: **8**

Components	Measured data Freshwater A	Measured data Freshwater B	Assigned values Freshwater A	Assigned values Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.67	0.67	0.77	0.77	0.67	-13.1	0.0	-1.7
NO2-N, mg/L	0.21	0.23	0.26	0.26	0.22	-16.0	6.4	-2.4
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L	3.60	3.70	3.38	3.38	3.65	8.0	1.9	1.2
PO4-P, mg/L	0.19	0.19	0.20	0.20	0.19	-3.0	0.0	-0.5
P-total, mg/L	0.29	0.29	0.28	0.28	0.29	5.4	0.0	0.9
Cd, µg/L	1.70	1.69	1.66	1.66	1.70	1.9	0.4	0.2
Cr, µg/L	3.51	3.46	3.39	3.39	3.49	2.7	1.0	0.4
Cu, µg/L	9.20	9.50	9.77	9.77	9.35	-4.3	2.3	-0.4
Ni, µg/L	16.00	16.00	15.19	15.19	16.00	5.3	0.0	0.6
Pb, µg/L	<5	<5	1.71	1.71				
Zn, µg/L	25.00	26.00	27.24	27.24	25.50	-6.4	2.8	-0.8
Hg, µg/L			0.13	0.13				

Laboratory

Code no.:   **8**

Components	Measured values Freshwater C	Assigned values Freshwater C	Statistics Dev. %	z-score
NO3-N, mg/L	1.10	1.17	-2.95	-0.7
NO2-N, mg/L	0.37	0.44	-7.95	-2.3
NO2+3-N, mg/L		1.68		
N-total, mg/L	4.80	4.58	2.38	0.7
PO4-P, mg/L	0.28	0.29	-1.05	-0.3
P-total, mg/L	0.43	0.42	1.31	0.5
Cd, µg/L	2.40	2.39	0.31	0.1
Cr, µg/L	5.03	4.91	1.21	0.3
Cu, µg/L	14.60	14.68	-0.26	-0.1
Ni, µg/L	22.00	21.38	1.46	0.3
Pb, µg/L	<5	2.30	-	-
Zn, µg/L	45.00	46.97	-2.10	-0.9
Hg, µg/L		0.18		

Laboratory

Code no: 10

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.79	0.79	0.77	0.77	0.79	2.8	0.1	0.4
NO2-N, mg/L	0.28	0.27	0.26	0.26	0.28	5.2	3.8	0.8
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L	3.38	3.36	3.38	3.38	3.37	-0.3	0.3	0.0
PO4-P, mg/L	0.21	0.21	0.20	0.20	0.21	5.1	0.7	0.8
P-total, mg/L	0.26	0.26	0.28	0.28	0.26	-6.9	0.0	-1.1
Cd, µg/L	1.59	1.57	1.66	1.66	1.58	-5.0	0.9	-0.5
Cr, µg/L	3.33	3.31	3.39	3.39	3.32	-2.1	0.4	-0.3
Cu, µg/L	9.10	9.05	9.77	9.77	9.08	-7.1	0.4	-0.7
Ni, µg/L	14.90	14.80	15.19	15.19	14.85	-2.3	0.5	-0.3
Pb, µg/L	1.81	1.76	1.71	1.71	1.79	4.4	2.0	0.7
Zn, µg/L	25.50	25.60	27.24	27.24	25.55	-6.2	0.3	-0.8
Hg, µg/L	0.12	0.12	0.13	0.13	0.12	-6.8	4.1	-0.4

Laboratory

Code no.: 10

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.25	1.17	3.59	0.9
NO2-N, mg/L	0.44	0.44	0.45	0.1
NO2+3-N, mg/L		1.68		
N-total, mg/L	4.62	4.58	0.45	0.1
PO4-P, mg/L	0.31	0.29	4.90	1.4
P-total, mg/L	0.40	0.42	-2.03	-0.8
Cd, µg/L	2.25	2.39	-2.83	-0.6
Cr, µg/L	4.89	4.91	-0.21	-0.1
Cu, µg/L	14.10	14.68	-1.96	-0.5
Ni, µg/L	21.20	21.38	-0.41	-0.1
Pb, µg/L	2.39	2.30	1.90	0.5
Zn, µg/L	44.70	46.97	-2.42	-1.1
Hg, µg/L	0.16	0.18	-7.10	-0.4

Laboratory
Code no: **11**

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.71	0.70	0.77	0.77	0.71	-8.4	1.3	-1.1
NO2-N, mg/L	0.27	0.27	0.26	0.26	0.27	3.7	0.8	0.5
NO2+3-N, mg/L	0.98	0.97	1.05	1.05	0.98	-6.7	0.7	-0.8
N-total, mg/L	3.40	3.40	3.38	3.38	3.40	0.6	0.0	0.1
PO4-P, mg/L	0.19	0.19	0.20	0.20	0.19	-3.3	0.4	-0.5
P-total, mg/L	0.29	0.28	0.28	0.28	0.29	3.6	2.5	0.6
Cd, µg/L	1.59	1.60	1.66	1.66	1.60	-4.1	0.4	-0.4
Cr, µg/L	3.33	3.44	3.39	3.39	3.39	-0.2	2.3	0.0
Cu, µg/L	9.38	9.01	9.77	9.77	9.20	-5.9	2.8	-0.6
Ni, µg/L	15.60	15.50	15.19	15.19	15.55	2.3	0.5	0.3
Pb, µg/L	1.68	1.68	1.71	1.71	1.68	-1.7	0.0	-0.3
Zn, µg/L	30.70	30.50	27.24	27.24	30.60	12.4	0.5	1.6
Hg, µg/L			0.13	0.13				

Laboratory
Code no.:   **11**

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.12	1.17	-2.31	-0.6
NO2-N, mg/L	0.47	0.44	3.41	1.0
NO2+3-N, mg/L	1.59	1.68	-2.71	-0.8
N-total, mg/L	4.70	4.58	1.29	0.4
PO4-P, mg/L	0.27	0.29	-2.62	-0.7
P-total, mg/L	0.43	0.42	1.31	0.5
Cd, µg/L	2.33	2.39	-1.15	-0.2
Cr, µg/L	5.04	4.91	1.31	0.4
Cu, µg/L	14.10	14.68	-1.96	-0.5
Ni, µg/L	21.80	21.38	0.99	0.2
Pb, µg/L	2.32	2.30	0.38	0.1
Zn, µg/L	50.50	46.97	3.76	1.6
Hg, µg/L		0.18		

Laboratory

Code no: 12

| Components | Measured data | | Assigned values | | | Statistics | | |
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.83	0.80	0.77	0.77	0.81	5.5	2.2	0.7
NO2-N, mg/L	0.26	0.26	0.26	0.26	0.26	-1.5	1.1	-0.2
NO2+3-N, mg/L	1.08	1.06	1.05	1.05	1.07	2.1	1.3	0.3
N-total, mg/L	3.69	3.78	3.38	3.38	3.74	10.5	1.7	1.6
PO4-P, mg/L	0.18	0.19	0.20	0.20	0.19	-5.6	3.8	-0.9
P-total, mg/L	0.27	0.28	0.28	0.28	0.27	-1.9	2.6	-0.3
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L			0.13	0.13				

Laboratory

Code no.: 12

| Components | Measured values | Assigned values | Statistics | |
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.21	1.17	1.75	0.4
NO2-N, mg/L	0.48	0.44	4.09	1.2
NO2+3-N, mg/L	1.68	1.68	0.12	0.0
N-total, mg/L	5.06	4.58	5.22	1.4
PO4-P, mg/L	0.27	0.29	-2.80	-0.8
P-total, mg/L	0.41	0.42	-0.72	-0.3
Cd, µg/L		2.39		
Cr, µg/L		4.91		
Cu, µg/L		14.68		
Ni, µg/L		21.38		
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L		0.18		

Laboratory

Code no: 13

Components	Measured data Freshwater A	Freshwater B	Assigned values Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L	0.27	0.27	0.26	0.26	0.27	2.1	0.8	0.3
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L	0.21	0.22	0.20	0.20	0.22	11.5	3.6	1.9
P-total, mg/L			0.28	0.28				
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µ/L			0.13	0.13				

Laboratory

Code no.: 13

Components	Measured values Freshwater C	Assigned values Freshwater C	Statistics Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L	0.43	0.44	-1.36	-0.4
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L	0.32	0.29	6.47	1.8
P-total, mg/L		0.42		
Cd, µg/L		2.39		
Cr, µg/L		4.91		
Cu, µg/L		14.68		
Ni, µg/L		21.38		
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L		0.18		

Laboratory

Code no: 14

Components	Measured data I		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L	0.25	0.25	0.26	0.26	0.25	-4.7	0.3	-0.7
NO2+3-N, mg/L	1.08	1.08	1.05	1.05	1.08	3.1	0.3	0.4
N-total, mg/L	3.02	3.04	3.38	3.38	3.03	-10.3	0.5	-1.5
PO4-P, mg/L	0.19	0.19	0.20	0.20	0.19	-3.5	0.0	-0.6
P-total, mg/L	0.27	0.27	0.28	0.28	0.27	-1.0	0.8	-0.2
Cd, µg/L	1.60	1.62	1.66	1.66	1.61	-3.2	0.9	-0.3
Cr, µg/L			3.39	3.39				
Cu, µg/L	9.24	8.73	9.77	9.77	8.99	-8.1	4.0	-0.8
Ni, µg/L	14.61	14.99	15.19	15.19	14.80	-2.6	1.8	-0.3
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L	0.15	0.15	0.13	0.13	0.15	12.9	1.0	0.7

Laboratory

Code no.: 14

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L	0.42	0.44	-2.05	-0.6
NO2+3-N, mg/L	1.75	1.68	2.27	0.6
N-total, mg/L	4.03	4.58	-6.02	-1.7
PO4-P, mg/L	0.28	0.29	-1.92	-0.5
P-total, mg/L	0.41	0.42	-1.55	-0.6
Cd, µg/L	2.38	2.39	-0.10	0.0
Cr, µg/L		4.91		
Cu, µg/L	13.04	14.68	-5.57	-1.3
Ni, µg/L	20.66	21.38	-1.67	-0.4
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L	0.20	0.18	4.37	0.3

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.72	0.71	0.77	0.77	0.72	-7.3	0.2	-1.0
NO2-N, mg/L	0.26	0.26	0.26	0.26	0.26	0.4	0.0	0.1
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L	3.56	3.50	3.38	3.38	3.53	4.5	1.2	0.7
PO4-P, mg/L	0.20	0.21	0.20	0.20	0.20	4.4	1.0	0.7
P-total, mg/L	0.25	0.25	0.28	0.28	0.25	-9.3	0.3	-1.5
Cd, µg/L	1.78	1.79	1.66	1.66	1.78	7.1	0.3	0.7
Cr, µg/L	3.54	3.55	3.39	3.39	3.55	4.5	0.3	0.6
Cu, µg/L	10.20	10.08	9.77	9.77	10.14	3.7	0.8	0.4
Ni, µg/L	15.97	15.91	15.19	15.19	15.94	4.9	0.3	0.6
Pb, µg/L	1.88	1.82	1.71	1.71	1.85	8.4	2.4	1.4
Zn, µg/L	27.01	28.44	27.24	27.24	27.72	1.8	3.7	0.2
Hg, µg/L	0.25	0.25	0.13	0.13	0.25	94.5	1.4	5.4

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.14	1.17	-1.33	-0.3
NO2-N, mg/L	0.45	0.44	0.68	0.2
NO2+3-N, mg/L		1.68		
N-total, mg/L	4.47	4.58	-1.19	-0.3
PO4-P, mg/L	0.30	0.29	3.15	0.9
P-total, mg/L	0.37	0.42	-5.73	-2.2
Cd, µg/L	2.57	2.39	3.94	0.8
Cr, µg/L	5.26	4.91	3.56	1.0
Cu, µg/L	15.80	14.68	3.83	0.9
Ni, µg/L	22.58	21.38	2.81	0.6
Pb, µg/L	2.52	2.30	4.64	1.2
Zn, µg/L	46.98	46.97	0.01	0.0
Hg, µg/L	0.29	0.18	29.78	1.9

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.74	0.76	0.77	0.77	0.75	-2.7	2.2	-0.4
NO2-N, mg/L	0.27	0.27	0.26	0.26	0.27	1.2	0.0	0.2
NO2+3-N, mg/L	1.00	1.03	1.05	1.05	1.02	-3.1	2.1	-0.4
N-total, mg/L	3.18	3.24	3.38	3.38	3.21	-5.0	1.3	-0.7
PO4-P, mg/L	0.20	0.20	0.20	0.20	0.20	1.3	1.1	0.2
P-total, mg/L	0.27	0.26	0.28	0.28	0.26	-4.0	0.5	-0.6
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L			0.13	0.13				

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L	2.28	2.39	-2.20	-0.4
Cr, µg/L	4.59	4.91	-3.27	-0.9
Cu, µg/L	13.80	14.68	-2.98	-0.7
Ni, µg/L	20.20	21.38	-2.75	-0.6
Pb, µg/L	2.24	2.30	-1.35	-0.3
Zn, µg/L	43.20	46.97	-4.01	-1.7
Hg, µg/L	0.04	0.18	-39.89	-2.5

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.77	0.76	0.77	0.77	0.77	-0.8	0.9	-0.1
NO2-N, mg/L	0.25	0.26	0.26	0.26	0.25	-3.2	0.8	-0.5
NO2+3-N, mg/L	1.02	1.02	1.05	1.05	1.02	-2.6	0.0	-0.3
N-total, mg/L	3.55	3.46	3.38	3.38	3.51	3.7	1.8	0.6
PO4-P, mg/L	0.18	0.18	0.20	0.20	0.18	-8.1	0.0	-1.3
P-total, mg/L	0.28	0.28	0.28	0.28	0.28	1.8	0.0	0.3
Cd, µg/L	1.40	1.39	1.66	1.66	1.40	-16.1	0.5	-1.5
Cr, µg/L	3.50	3.65	3.39	3.39	3.58	5.4	3.0	0.8
Cu, µg/L	8.92	8.95	9.77	9.77	8.94	-8.6	0.2	-0.8
Ni, µg/L	16.40	16.10	15.19	15.19	16.25	6.9	1.3	0.8
Pb, µg/L	1.52	1.50	1.71	1.71	1.51	-11.6	0.9	-1.9
Zn, µg/L	<50	<50	27.24	27.24				
Hg, µg/L	0.11	0.12	0.13	0.13	0.12	-11.1	2.5	-0.6

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.20	1.17	1.33	0.3
NO2-N, mg/L	0.42	0.44	-2.61	-0.8
NO2+3-N, mg/L	1.58	1.68	-2.86	-0.8
N-total, mg/L	4.98	4.58	4.34	1.2
PO4-P, mg/L	0.28	0.29	-1.05	-0.3
P-total, mg/L	0.42	0.42	0.12	0.0
Cd, µg/L	1.96	2.39	-8.91	-1.8
Cr, µg/L	5.16	4.91	2.54	0.7
Cu, µg/L	13.70	14.68	-3.32	-0.8
Ni, µg/L	24.80	21.38	8.01	1.8
Pb, µg/L	2.04	2.30	-5.70	-1.4
Zn, µg/L	54.50	46.97	8.02	3.5
Hg, µg/L	0.17	0.18	-2.46	-0.2

Laboratory

Code no: 18

| Components | Measured data | | Assigned values | | | Statistics | | |
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.46	0.47	0.77	0.77	0.46	-39.7	0.1	-5.3
NO2-N, mg/L	0.29	0.29	0.26	0.26	0.29	11.5	0.0	1.7
NO2+3-N, mg/L	0.89	0.90	1.05	1.05	0.90	-14.6	0.8	-1.8
N-total, mg/L	3.40	3.40	3.38	3.38	3.40	0.6	0.0	0.1
PO4-P, mg/L	0.21	0.21	0.20	0.20	0.21	8.7	0.7	1.4
P-total, mg/L	0.31	0.33	0.28	0.28	0.32	16.3	4.4	2.6
Cd, µg/L	1.24	1.38	1.66	1.66	1.31	-21.2	7.6	-2.0
Cr, µg/L	3.35	3.27	3.39	3.39	3.31	-2.4	1.7	-0.3
Cu, µg/L	8.92	8.88	9.77	9.77	8.90	-8.9	0.3	-0.8
Ni, µg/L	15.72	15.75	15.19	15.19	15.74	3.6	0.1	0.4
Pb, µg/L	1.17	1.15	1.71	1.71	1.16	-32.3	1.5	-5.4
Zn, µg/L	27.12	27.05	27.24	27.24	27.08	-0.6	0.2	-0.1
Hg, µg/L			0.13	0.13				

Laboratory

Code no.: 18

| Components | Measured values | Assigned values | Statistics | |
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	0.77	1.17	-17.28	-4.3
NO2-N, mg/L	0.48	0.44	4.09	1.2
NO2+3-N, mg/L	1.53	1.68	-4.36	-1.2
N-total, mg/L	4.60	4.58	0.20	0.1
PO4-P, mg/L	0.32	0.29	6.29	1.8
P-total, mg/L	0.48	0.42	7.28	2.8
Cd, µg/L	1.97	2.39	-8.70	-1.7
Cr, µg/L	4.77	4.91	-1.44	-0.4
Cu, µg/L	13.78	14.68	-3.05	-0.7
Ni, µg/L	21.59	21.38	0.50	0.1
Pb, µg/L	1.40	2.30	-19.60	-4.9
Zn, µg/L	47.10	46.97	0.14	0.1
Hg, µg/L		0.18		

Laboratory

Code no: **19**

Components	Measured data Freshwater A	Measured data Freshwater B	Assigned values Freshwater A	Assigned values Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.76	0.76	0.77	0.77	0.76	-1.2	0.2	-0.2
NO2-N, mg/L	0.28	0.27	0.26	0.26	0.27	4.9	0.3	0.7
NO2+3-N, mg/L	1.04	1.04	1.05	1.05	1.04	-1.1	0.1	-0.1
N-total, mg/L	3.27	3.28	3.38	3.38	3.27	-3.2	0.2	-0.5
PO4-P, mg/L	0.18	0.18	0.20	0.20	0.18	-5.9	0.3	-1.0
P-total, mg/L	0.28	0.29	0.28	0.28	0.28	2.9	2.3	0.5
Cd, µg/L	2.01	2.01	1.66	1.66	2.01	20.9	0.1	1.9
Cr, µg/L	4.03	4.02	3.39	3.39	4.02	18.6	0.2	2.6
Cu, µg/L	10.89	10.84	9.77	9.77	10.87	11.2	0.3	1.1
Ni, µg/L	17.83	17.54	15.19	15.19	17.69	16.4	1.1	1.9
Pb, µg/L	1.90	1.89	1.71	1.71	1.89	10.8	0.2	1.8
Zn, µg/L	32.16	32.13	27.24	27.24	32.14	18.0	0.1	2.3
Hg, µg/L	0.10	0.10	0.13	0.13	0.10	-20.7	0.7	-1.2

Laboratory

Code no.: **19**

Components	Measured values Freshwater C	Assigned values Freshwater C	Statistics Dev. %	z-score
NO3-N, mg/L	1.19	1.17	1.09	0.3
NO2-N, mg/L	0.46	0.44	2.10	0.6
NO2+3-N, mg/L	1.65	1.68	-0.69	-0.2
N-total, mg/L	4.54	4.58	-0.47	-0.1
PO4-P, mg/L	0.27	0.29	-3.44	-1.0
P-total, mg/L	0.42	0.42	0.67	0.3
Cd, µg/L	2.90	2.39	10.80	2.1
Cr, µg/L	5.84	4.91	9.46	2.6
Cu, µg/L	16.78	14.68	7.16	1.7
Ni, µg/L	25.51	21.38	9.67	2.2
Pb, µg/L	2.65	2.30	7.64	1.9
Zn, µg/L	54.80	46.97	8.33	3.6
Hg, µg/L	0.12	0.18	-16.12	-1.0

Laboratory

Code no:　　20

| Components | Measured data | | Assigned values | | | Statistics | | |
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.82	0.82	0.77	0.77	0.82	6.4	0.0	0.8
NO2-N, mg/L	0.27	0.27	0.26	0.26	0.27	4.0	0.8	0.6
NO2+3-N, mg/L	1.09	1.10	1.05	1.05	1.10	4.5	0.6	0.6
N-total, mg/L	3.80	3.79	3.38	3.38	3.80	12.3	0.2	1.8
PO4-P, mg/L	0.19	0.19	0.20	0.20	0.19	-3.0	0.0	-0.5
P-total, mg/L	0.29	0.27	0.28	0.28	0.28	1.8	5.1	0.3
Cd, µg/L	1.77	1.77	1.66	1.66	1.77	6.4	0.0	0.6
Cr, µg/L	3.51	3.47	3.39	3.39	3.49	2.9	0.8	0.4
Cu, µg/L	9.40	9.30	9.77	9.77	9.35	-4.3	0.8	-0.4
Ni, µg/L	15.40	15.40	15.19	15.19	15.40	1.4	0.0	0.2
Pb, µg/L	1.72	1.72	1.71	1.71	1.72	0.6	0.0	0.1
Zn, µg/L	27.40	27.40	27.24	27.24	27.40	0.6	0.0	0.1
Hg, µg/L	0.15	0.15	0.13	0.13	0.15	17.5	0.9	1.0

Laboratory

Code no.:　　20

| Components | Measured values | Assigned values | Statistics | |
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.28	1.17	4.75	1.2
NO2-N, mg/L	0.44	0.44	-0.34	-0.1
NO2+3-N, mg/L	1.72	1.68	1.31	0.4
N-total, mg/L	5.15	4.58	6.20	1.7
PO4-P, mg/L	0.27	0.29	-2.80	-0.8
P-total, mg/L	0.42	0.42	0.12	0.0
Cd, µg/L	2.57	2.39	3.88	0.8
Cr, µg/L	5.03	4.91	1.21	0.3
Cu, µg/L	14.40	14.68	-0.94	-0.2
Ni, µg/L	21.60	21.38	0.52	0.1
Pb, µg/L	2.38	2.30	1.69	0.4
Zn, µg/L	47.00	46.97	0.03	0.0
Hg, µg/L	0.20	0.18	4.64	0.3

	Measured data		Assigned values			Statistics		
Components	**Freshwater A**	**Freshwater B**	**Freshwater A**	**Freshwater B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L	0.29	0.28	0.26	0.26	0.29	8.8	2.5	1.3
NO2+3-N, mg/L	1.25	1.27	1.05	1.05	1.26	20.3	1.1	2.5
N-total, mg/L	3.03	3.09	3.38	3.38	3.06	-9.5	1.4	-1.4
PO4-P, mg/L	0.18	0.19	0.20	0.20	0.19	-5.6	3.8	-0.9
P-total, mg/L	0.27	0.27	0.28	0.28	0.27	-1.9	0.0	-0.3
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L	0.13	0.14	0.13	0.13	0.14	4.4	5.2	0.3

Laboratory

Code no.:   **21**

	Measured values	Assigned values	Statistics	
Components	**Freshwater C**	**Freshwater C**	**Dev. %**	**z-score**
NO3-N, mg/L		1.17		
NO2-N, mg/L	0.48	0.44	4.55	1.3
NO2+3-N, mg/L	1.95	1.68	8.17	2.3
N-total, mg/L	3.99	4.58	-6.46	-1.8
PO4-P, mg/L	0.27	0.29	-2.80	-0.8
P-total, mg/L	0.40	0.42	-2.27	-0.9
Cd, µg/L		2.39		
Cr, µg/L		4.91		
Cu, µg/L		14.68		
Ni, µg/L		21.38		
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L	0.19	0.18	1.91	0.1

Laboratory

Code no: **22**

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.80	0.80	0.77	0.77	0.80	3.8	0.0	0.5
NO2-N, mg/L	0.26	0.26	0.26	0.26	0.26	-1.3	0.3	-0.2
NO2+3-N, mg/L	1.06	1.06	1.05	1.05	1.06	1.2	0.0	0.1
N-total, mg/L	3.40	3.40	3.38	3.38	3.40	0.6	0.0	0.1
PO4-P, mg/L	0.21	0.21	0.20	0.20	0.21	6.9	3.0	1.1
P-total, mg/L	0.30	0.30	0.28	0.28	0.30	8.5	1.7	1.4
Cd, µg/L	2.00	2.03	1.66	1.66	2.02	21.2	1.1	1.9
Cr, µg/L	3.24	3.21	3.39	3.39	3.23	-4.9	0.7	-0.7
Cu, µg/L	11.70	12.30	9.77	9.77	12.00	22.8	3.5	2.2
Ni, µg/L	12.51	12.97	15.19	15.19	12.74	-16.2	2.6	-1.9
Pb, µg/L	4.74	4.28	1.71	1.71	4.51	163.9	7.2	27.3
Zn, µg/L	27.77	29.47	27.24	27.24	28.62	5.1	4.2	0.7
Hg, µg/L	0.15	0.12	0.13	0.13	0.14	5.6	13.0	0.3

Laboratory

Code no.:   **22**

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.26	1.17	3.89	1.0
NO2-N, mg/L	0.43	0.44	-1.14	-0.3
NO2+3-N, mg/L	1.69	1.68	0.42	0.1
N-total, mg/L	4.50	4.58	-0.89	-0.2
PO4-P, mg/L	0.30	0.29	2.27	0.6
P-total, mg/L	0.43	0.42	1.31	0.5
Cd, µg/L	2.83	2.39	9.33	1.8
Cr, µg/L	4.71	4.91	-2.05	-0.6
Cu, µg/L	18.00	14.68	11.33	2.6
Ni, µg/L	18.14	21.38	-7.57	-1.7
Pb, µg/L	5.89	2.30	77.92	19.7
Zn, µg/L	47.74	46.97	0.82	0.4
Hg, µg/L	0.20	0.18	4.37	0.3

Laboratory

Code no: 23

Components	Measured data		Assigned values			Statistics		
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.84	0.85	0.77	0.77	0.85	10.0	0.6	1.3
NO2-N, mg/L	0.25	0.25	0.26	0.26	0.25	-4.0	1.4	-0.6
NO2+3-N, mg/L	1.09	1.11	1.05	1.05	1.10	4.9	0.8	0.6
N-total, mg/L	3.25	3.23	3.38	3.38	3.24	-4.1	0.6	-0.6
PO4-P, mg/L	0.21	0.21	0.20	0.20	0.21	7.4	2.4	1.2
P-total, mg/L	0.26	0.26	0.28	0.28	0.26	-6.0	0.1	-1.0
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L			0.13	0.13				

Laboratory

Code no.: 23

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L	1.36	1.17	8.21	2.0
NO2-N, mg/L	0.44	0.44	-0.41	-0.1
NO2+3-N, mg/L	1.80	1.68	3.61	1.0
N-total, mg/L	4.43	4.58	-1.67	-0.5
PO4-P, mg/L	0.28	0.29	-0.35	-0.1
P-total, mg/L	0.40	0.42	-2.35	-0.9
Cd, µg/L		2.39		
Cr, µg/L		4.91		
Cu, µg/L		14.68		
Ni, µg/L		21.38		
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L		0.18		

	Measured data		Assigned values			Statistics		
Components	**Freshwater A**	**Freshwater B**	**Freshwater A**	**Freshwater B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L	0.66	0.68	0.77	0.77	0.67	-13.1	2.1	-1.7
NO2-N, mg/L	0.28	0.28	0.26	0.26	0.28	7.9	0.3	1.2
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L			0.20	0.20				
P-total, mg/L			0.28	0.28				
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L			0.13	0.13				

Laboratory

Code no.:   **25**

	Measured values	Assigned values	Statistics	
Components	**Freshwater C**	**Freshwater C**	**Dev. %**	**z-score**
NO3-N, mg/L	1.22	1.17	2.18	0.5
NO2-N, mg/L	0.47	0.44	2.84	0.8
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L		2.39		
Cr, µg/L		4.91		
Cu, µg/L		14.68		
Ni, µg/L		21.38		
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L		0.18		

Laboratory

Code no: 26

Components	Measured data		Assigned values		Statistics			
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L			0.26	0.26				
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L			0.20	0.20				
P-total, mg/L			0.28	0.28				
Cd, µg/L	1.80	1.49	1.66	1.66	1.65	-1.1	13.3	-0.1
Cr, µg/L	3.93	3.45	3.39	3.39	3.69	8.8	9.2	1.2
Cu, µg/L	11.07	9.78	9.77	9.77	10.43	6.7	8.7	0.6
Ni, µg/L	16.78	14.65	15.19	15.19	15.72	3.4	9.6	0.4
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L			0.13	0.13				

Laboratory

Code no.:   26

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L		1,169.00		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L	2.25	2.39	-2.83	-0.6
Cr, µg/L	4.93	4.91	0.19	0.1
Cu, µg/L	13.99	14.68	-2.33	-0.5
Ni, µg/L	20.63	21.38	-1.74	-0.4
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L		0.18		

Laboratory

Code no: 27

Components	Measured data		Assigned values		Statistics			
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.77	0.77				
NO2-N, mg/L			0.26	0.26				
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L			0.20	0.20				
P-total, mg/L			0.28	0.28				
Cd, µg/L	1.70	1.70	1.66	1.66	1.70	2.2	0.0	0.2
Cr, µg/L	3.30	3.30	3.39	3.39	3.30	-2.7	0.0	-0.4
Cu, µg/L	9.50	9.40	9.77	9.77	9.45	-3.3	0.7	-0.3
Ni, µg/L	15.90	15.80	15.19	15.19	15.85	4.3	0.4	0.5
Pb, µg/L	1.70	1.70	1.71	1.71	1.70	-0.5	0.0	-0.1
Zn, µg/L	24.60	25.40	27.24	27.24	25.00	-8.2	2.3	-1.1
Hg, µg/L			0.13	0.13				

Laboratory

Code no.: 27

Components	Measured values	Assigned values	Statistics	
	Freshwater C	Freshwater C	Dev. %	z-score
NO3-N, mg/L		1.17		
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L	2.40	2.39	0.31	0.1
Cr, µg/L	4.70	4.91	-2.15	-0.6
Cu, µg/L	14.60	14.68	-0.26	-0.1
Ni, µg/L	21.00	21.38	-0.88	-0.2
Pb, µg/L	2.20	2.30	-2.22	-0.6
Zn, µg/L	43.20	46.97	-4.01	-1.7
Hg, µg/L		0.18		

Components	Measured data Freshwater A	Freshwater B	Assigned values Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
						Statistics		
NO3-N, mg/L	0.74	0.76	0.77	0.77	0.75	-2.7	1.9	-0.4
NO2-N, mg/L			0.26	0.26				
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L			0.20	0.20				
P-total, mg/L			0.28	0.28				
Cd, µg/L	1.68	1.64	1.66	1.66	1.66	-0.2	1.7	0.0
Cr, µg/L	3.40	3.30	3.39	3.39	3.35	-1.3	2.1	-0.2
Cu, µg/L	10.50	10.50	9.77	9.77	10.50	7.4	0.0	0.7
Ni, µg/L	16.20	16.30	15.19	15.19	16.25	6.9	0.4	0.8
Pb, µg/L	2.07	<2	1.71	1.71		21.1		3.5
Zn, µg/L	27.40	27.50	27.24	27.24	27.45	0.8	0.3	0.1
Hg, µg/L			0.13	0.13				

Components	Measured values Freshwater C	Assigned values Freshwater C	Dev. %	z-score
			Statistics	
NO3-N, mg/L	1.20	1.17	1.33	0.3
NO2-N, mg/L		0.44		
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L		0.29		
P-total, mg/L		0.42		
Cd, µg/L	2.41	2.39	0.52	0.1
Cr, µg/L	4.92	4.91	0.09	0.0
Cu, µg/L	16.10	14.68	4.86	1.1
Ni, µg/L	23.00	21.38	3.80	0.9
Pb, µg/L	2.38	2.30	1.69	0.4
Zn, µg/L	46.80	46.97	-0.18	-0.1
Hg, µg/L		0.18		

Laboratory
Code no: 29

Components	Measured data		Assigned values		Statistics			
	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.84	0.84	0.77	0.77	0.84	9.5	0.0	1.3
NO2-N, mg/L	0.24	0.25	0.26	0.26	0.24	-7.0	4.4	-1.0
NO2+3-N, mg/L			1.05	1.05				
N-total, mg/L			3.38	3.38				
PO4-P, mg/L	0.19	0.19	0.20	0.20	0.19	-2.3	0.4	-0.4
P-total, mg/L	0.26	0.27	0.28	0.28	0.26	-3.9	1.9	-0.6
Cd, µg/L			1.66	1.66				
Cr, µg/L			3.39	3.39				
Cu, µg/L			9.77	9.77				
Ni, µg/L			15.19	15.19				
Pb, µg/L			1.71	1.71				
Zn, µg/L			27.24	27.24				
Hg, µg/L			0.13	0.13				

Laboratory
Code no.: 29

Components	Measured values Freshwater C	Assigned values Freshwater C	Statistics Dev. %	z-score
NO3-N, mg/L	1.24	1.17	3.17	0.8
NO2-N, mg/L	0.41	0.44	-3.64	-1.0
NO2+3-N, mg/L		1.68		
N-total, mg/L		4.58		
PO4-P, mg/L	0.28	0.29	-1.22	-0.3
P-total, mg/L	0.40	0.42	-1.79	-0.7
Cd, µg/L		2.39		
Cr, µg/L		4.91		
Cu, µg/L		14.68		
Ni, µg/L		21.38		
Pb, µg/L		2.30		
Zn, µg/L		46.97		
Hg, µg/L		0.18		

3.3 Waste water

Laboratory Code no: 1

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	7.05	7.20	7.06	7.06	7.13	0.9	1.5	0.2
NO2-N, mg/L	0.087	0.087	0.19	0.19	0.09	-53.8	0.0	-0.5
NO2+3-N, mg/L	7.14	7.29	7.29	7.29	7.22	-1.1	1.5	-0.3
N-total, mg/L	13.5	14.1	11.9	11.9	13.8	15.5	3.1	2.2
PO4-P, mg/L	0.24	0.24	0.25	0.25	0.24	-2.5	0.0	-0.3
P-total, mg/L	0.52	0.51	0.55	0.55	0.52	-5.9	1.4	-0.8
Cd, µg/L			9.54	9.54				
Cr, µg/L			45.8	45.8				
Cu, µg/L			93.4	93.4				
Ni, µg/L			11.84	11.84				
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L	5.60	6.40	6.24	6.24	6.00	-3.9	9.4	-0.4

Laboratory Code no: 4

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	7.09	7.17	7.06	7.06	7.13	0.9	0.9	0.2
NO2-N, mg/L	0.42	0.42	0.19	0.19	0.42	123.0	0.2	1.2
NO2+3-N, mg/L	7.51	7.59	7.29	7.29	7.55	3.5	0.8	1.1
N-total, mg/L	11.5	11.2	11.9	11.9	11.4	-4.9	1.8	-0.7
PO4-P, mg/L	0.24	0.23	0.25	0.25	0.24	-4.3	1.3	-0.6
P-total, mg/L	0.49	0.49	0.55	0.55	0.49	-11.2	0.1	-1.6
Cd, µg/L	9.49	9.15	9.54	9.54	9.32	-2.3	2.6	-0.3
Cr, µg/L	47.8	47.1	45.8	45.8	47.5	3.7	1.1	0.8
Cu, µg/L	95.7	102.0	93.4	93.4	98.8	5.8	4.4	0.9
Ni, µg/L	12.28	11.82	11.84	11.84	12.1	1.8	2.7	0.3
Pb, µg/L	10.21	10.13	9.88	9.88	10.17	3.0	0.6	0.4
Zn, µg/L	111	114	106	106	112	5.5	1.8	0.9
Hg, µg/L	10.21	6.37	6.24	6.24	8.29	32.8	32.8	3.3

Laboratory
Code no: 5

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L			7.06	7.06				
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L			11.9	11.9				
PO4-P, mg/L			0.25	0.25				
P-total, mg/L			0.55	0.55				
Cd, µg/L	9.76	9.82	9.54	9.54	9.79	2.6	0.4	0.3
Cr, µg/L	44.7	45.2	45.8	45.8	45.0	-1.8	0.8	-0.4
Cu, µg/L	89.2	89.8	93.4	93.4	89.5	-4.2	0.5	-0.6
Ni, µg/L	11.20	11.30	11.84	11.84	11.3	-5.0	0.6	-0.7
Pb, µg/L	9.52	9.51	9.88	9.88	9.52	-3.7	0.1	-0.4
Zn, µg/L	105	105	106	106	105	-1.2	0.0	-0.2
Hg, µg/L	6.47	6.55	6.24	6.24	6.51	4.3	0.9	0.4

Laboratory
Code no: 7

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	6.50	6.44	7.06	7.06	6.47	-8.4	0.7	-1.6
NO2-N, mg/L	0.39	0.40	0.19	0.19	0.39	109.1	1.3	1.1
NO2+3-N, mg/L	6.89	6.84	7.29	7.29	6.87	-5.9	0.5	-1.8
N-total, mg/L	12.4	12.1	11.9	11.9	12.3	2.7	1.5	0.4
PO4-P, mg/L	0.23	0.23	0.25	0.25	0.23	-6.6	0.0	-0.9
P-total, mg/L	0.59	0.62	0.55	0.55	0.61	10.5	3.5	1.5
Cd, µg/L	9.47	9.66	9.54	9.54	9.57	0.3	1.4	0.0
Cr, µg/L	43.7	44.1	45.8	45.8	43.9	-4.1	0.7	-0.9
Cu, µg/L	87.8	88.5	93.4	93.4	88.2	-5.6	0.6	-0.8
Ni, µg/L	11.25	11.47	11.84	11.84	11.4	-4.1	1.4	-0.6
Pb, µg/L	9.41	9.34	9.88	9.88	9.38	-5.1	0.5	-0.6
Zn, µg/L	105	106	106	106	106	-0.8	0.7	-0.1
Hg, µg/L	6.20	7.50	6.24	6.24	6.85	9.7	13.4	1.0

Laboratory
Code no: 8

| | Measured data | | Assigned values | | | Statistics | | |
Components	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver- age	Dev. %	RSD %	z-score
NO3-N, mg/L	6.80	6.90	7.06	7.06	6.85	-3.0	1.0	-0.6
NO2-N, mg/L	0.086	0.085	0.19	0.19	0.09	-54.6	0.8	-0.6
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L	14.0	13.0	11.9	11.9	13.5	13.0	5.2	1.9
PO4-P, mg/L	0.24	0.24	0.25	0.25	0.24	-2.5	0.0	-0.3
P-total, mg/L	0.59	0.59	0.55	0.55	0.59	7.8	0.0	1.1
Cd, µg/L	8.71	9.05	9.54	9.54	8.88	-6.9	2.7	-0.9
Cr, µg/L	43.0	43.0	45.8	45.8	43.0	-6.1	0.0	-1.4
Cu, µg/L	87.0	88.0	93.4	93.4	87.5	-6.3	0.8	-0.9
Ni, µg/L	12.70	12.50	11.84	11.84	12.6	6.4	1.1	0.9
Pb, µg/L	10.00	10.00	9.88	9.88	10.00	1.2	0.0	0.1
Zn, µg/L	95	96	106	106	96	-10.2	0.7	-1.7
Hg, µg/L			6.24	6.24				

Laboratory
Code no: 9

| | Measured data | | Assigned values | | | Statistics | | |
Components	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver- age	Dev. %	RSD %	z-score
NO3-N, mg/L			7.06	7.06				
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L	7.32	7.42	7.29	7.29	7.37	1.0	1.0	0.3
N-total, mg/L	11.2	11.3	11.9	11.9	11.3	-5.8	0.6	-0.8
PO4-P, mg/L	0.27	0.28	0.25	0.25	0.27	10.9	2.6	1.4
P-total, mg/L	0.56	0.57	0.55	0.55	0.56	2.9	0.6	0.4
Cd, µg/L			9.54	9.54				
Cr, µg/L			45.8	45.8				
Cu, µg/L			93.4	93.4				
Ni, µg/L			11.84	11.84				
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L			6.24	6.24				

Laboratory
Code no: **10**

| Components | Measured data | | Assigned values | | | Statistics | | |
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	7.95	8.01	7.06	7.06	7.98	12.9	0.5	2.4
NO2-N, mg/L	0.018	0.021	0.19	0.19	0.02	-89.6	8.7	-0.9
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L	11.8	11.8	11.9	11.9	11.8	-1.1	0.4	-0.2
PO4-P, mg/L	0.29	0.29	0.25	0.25	0.29	16.8	0.2	2.2
P-total, mg/L	0.53	0.52	0.55	0.55	0.52	-4.5	0.9	-0.6
Cd, µg/L	8.82	8.78	9.54	9.54	8.80	-7.7	0.3	-1.0
Cr, µg/L	46.8	46.7	45.8	45.8	46.8	2.1	0.2	0.5
Cu, µg/L	91.0	90.0	93.4	93.4	90.5	-3.1	0.8	-0.5
Ni, µg/L	11.40	11.30	11.84	11.84	11.4	-4.1	0.6	-0.6
Pb, µg/L	10.00	9.91	9.88	9.88	9.96	0.8	0.6	0.1
Zn, µg/L	100	100	106	106	100	-5.9	0.0	-1.0
Hg, µg/L	6.56	6.50	6.24	6.24	6.53	4.6	0.6	0.5

Laboratory
Code no: **11**

| Components | Measured data | | Assigned values | | | Statistics | | |
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	7.26	6.77	7.06	7.06	7.02	-0.7	4.9	-0.1
NO2-N, mg/L	0.056	0.065	0.19	0.19	0.06	-67.8	10.5	-0.7
NO2+3-N, mg/L	7.31	6.83	7.29	7.29	7.07	-3.1	4.8	-0.9
N-total, mg/L	12.0	12.0	11.9	11.9	12.0	0.5	0.0	0.1
PO4-P, mg/L	0.24	0.24	0.25	0.25	0.24	-1.3	0.6	-0.2
P-total, mg/L	0.55	0.55	0.55	0.55	0.55	0.5	0.0	0.1
Cd, µg/L	9.01	9.03	9.54	9.54	9.02	-5.4	0.2	-0.7
Cr, µg/L	46.8	46.9	45.8	45.8	46.9	2.3	0.2	0.5
Cu, µg/L	87.3	87.3	93.4	93.4	87.3	-6.5	0.0	-1.0
Ni, µg/L	11.90	11.90	11.84	11.84	11.9	0.5	0.0	0.1
Pb, µg/L	9.41	9.41	9.88	9.88	9.41	-4.7	0.0	-0.6
Zn, µg/L	114	114	106	106	114	7.2	0.0	1.2
Hg, µg/L	5.57	5.59	6.24	6.24	5.58	-10.6	0.3	-1.1

Laboratory
Code no: 12

| Components | Measured data | | Assigned values | | Statistics | | | |
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	6.88	6.83	7.06	7.06	6.86	-3.0	0.5	-0.6
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L	7.35	7.28	7.29	7.29	7.32	0.3	0.7	0.1
N-total, mg/L	11.6	11.6	11.9	11.9	11.6	-2.9	0.0	-0.4
PO4-P, mg/L	0.22	0.22	0.25	0.25	0.22	-10.7	0.0	-1.4
P-total, mg/L	0.54	0.54	0.55	0.55	0.54	-0.9	0.1	-0.1
Cd, µg/L			9.54	9.54				
Cr, µg/L			45.8	45.8				
Cu, µg/L			93.4	93.4				
Ni, µg/L			11.84	11.84				
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L			6.24	6.24				

Laboratory
Code no: 14

| Components | Measured data I | | Assigned values | | Statistics | | | |
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L			7.06	7.06				
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L	7.20	7.19	7.29	7.29	7.20	-1.4	0.1	-0.4
N-total, mg/L	10.9	10.7	11.9	11.9	10.8	-9.7	1.4	-1.4
PO4-P, mg/L	0.24	0.24	0.25	0.25	0.24	-3.5	0.9	-0.5
P-total, mg/L	0.52	0.53	0.55	0.55	0.53	-3.8	0.7	-0.5
Cd, µg/L	9.98	10.06	9.54	9.54	10.02	5.0	0.6	0.7
Cr, µg/L	42.5	42.6	45.8	45.8	42.5	-7.1	0.2	-1.6
Cu, µg/L	85.5	86.6	93.4	93.4	86.0	-7.9	0.9	-1.2
Ni, µg/L	10.07	10.97	11.84	11.84	10.5	-11.1	6.0	-1.6
Pb, µg/L	11.82	11.78	9.88	9.88	11.80	19.5	0.2	2.3
Zn, µg/L	107	105	106	106	106	-0.5	1.6	-0.1
Hg, µg/L	7.30	7.35	6.24	6.24	7.33	17.3	0.5	1.8

44

Laboratory
Code no: **15**

Components	Measured data		Assigned values			Statistics		
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	7.02	9.96	7.06	7.06	8.49	20.2	24.5	3.8
NO2-N, mg/L	0.0055	0.0048	0.19	0.19	0.01	-97.3	9.6	-1.0
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L	12.5	11.6	11.9	11.9	12.0	0.8	5.1	0.1
PO4-P, mg/L	0.25	0.25	0.25	0.25	0.25	2.1	0.8	0.3
P-total, mg/L	0.50	0.50	0.55	0.55	0.50	-8.2	0.4	-1.2
Cd, µg/L	10.10	10.25	9.54	9.54	10.18	6.7	1.0	0.9
Cr, µg/L	49.0	50.9	45.8	45.8	49.9	9.1	2.7	2.1
Cu, µg/L	98.2	106.1	93.4	93.4	102.1	9.4	5.5	1.4
Ni, µg/L	11.94	12.19	11.84	11.84	12.1	1.9	1.5	0.3
Pb, µg/L	10.27	10.78	9.88	9.88	10.53	6.6	3.4	0.8
Zn, µg/L	107	112	106	106	109	2.9	3.0	0.5
Hg, µg/L	6.80	7.07	6.24	6.24	6.94	11.1	2.7	1.1

Laboratory
Code no: **17**

Components	Measured data		Assigned values			Statistics		
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	6.52	7.21	7.06	7.06	6.87	-2.8	7.1	-0.5
NO2-N, mg/L	0.36	0.36	0.19	0.19	0.36	91.3	0.4	0.9
NO2+3-N, mg/L	6.88	7.57	7.29	7.29	7.23	-1.0	6.8	-0.3
N-total, mg/L	11.2	11.4	11.9	11.9	11.3	-5.4	0.8	-0.8
PO4-P, mg/L	0.26	0.25	0.25	0.25	0.26	3.6	2.8	0.5
P-total, mg/L	0.58	0.60	0.55	0.55	0.59	7.8	2.4	1.1
Cd, µg/L	8.07	8.12	9.54	9.54	8.10	-15.1	0.4	-2.0
Cr, µg/L	49.6	49.4	45.8	45.8	49.5	8.1	0.3	1.8
Cu, µg/L	97.7	97.9	93.4	93.4	97.8	4.7	0.1	0.7
Ni, µg/L	12.10	11.60	11.84	11.84	11.9	0.1	3.0	0.0
Pb, µg/L	9.17	9.30	9.88	9.88	9.24	-6.5	1.0	-0.8
Zn, µg/L	116	106	106	106	111	4.6	6.1	0.8
Hg, µg/L	5.39	5.27	6.24	6.24	5.33	-14.6	1.6	-1.5

Laboratory
Code no: 18

| Components | Measured data | | Assigned values | | Statistics | | | |
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	5.28	5.38	7.06	7.06	5.33	-24.6	1.3	-4.6
NO2-N, mg/L	0.017	0.018	0.19	0.19	0.02	-90.7	4.0	-0.9
NO2+3-N, mg/L	6.08	6.00	7.29	7.29	6.04	-17.2	0.9	-5.2
N-total, mg/L	11.7	11.5	11.9	11.9	11.6	-2.9	1.2	-0.4
PO4-P, mg/L	0.28	0.28	0.25	0.25	0.28	13.7	0.5	1.8
P-total, mg/L	0.60	0.62	0.55	0.55	0.61	11.4	2.3	1.6
Cd, µg/L	9.42	9.44	9.54	9.54	9.43	-1.1	0.1	-0.2
Cr, µg/L	44.0	44.4	45.8	45.8	44.2	-3.4	0.6	-0.8
Cu, µg/L	90.7	90.3	93.4	93.4	90.5	-3.0	0.3	-0.4
Ni, µg/L	11.50	11.67	11.84	11.84	11.6	-2.2	1.0	-0.3
Pb, µg/L	8.22	8.70	9.88	9.88	8.46	-14.4	4.0	-1.7
Zn, µg/L	105	104	106	106	104	-1.8	0.4	-0.3
Hg, µg/L			6.24	6.24				

Laboratory
Code no: 19

| Components | Measured data | | Assigned values | | Statistics | | | |
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	6.96	7.01	7.06	7.06	6.99	-1.1	0.5	-0.2
NO2-N, mg/L	0.37	0.37	0.19	0.19	0.37	97.7	0.8	1.0
NO2+3-N, mg/L	7.37	7.37	7.29	7.29	7.37	1.1	0.0	0.3
N-total, mg/L	12.9	12.7	11.9	11.9	12.8	6.8	1.1	1.0
PO4-P, mg/L	0.24	0.24	0.25	0.25	0.24	-2.5	0.0	-0.3
P-total, mg/L	0.55	0.55	0.55	0.55	0.55	0.3	0.0	0.0
Cd, µg/L	11.22	11.20	9.54	9.54	11.21	17.5	0.1	2.3
Cr, µg/L	57.1	57.3	45.8	45.8	57.2	24.9	0.3	5.7
Cu, µg/L	104.7	106.1	93.4	93.4	105.4	12.9	1.0	1.9
Ni, µg/L	13.85	14.15	11.84	11.84	14.0	18.3	1.5	2.6
Pb, µg/L	10.73	10.61	9.88	9.88	10.67	8.0	0.8	1.0
Zn, µg/L	119	119	106	106	119	12.0	0.1	2.0
Hg, µg/L	6.44	6.30	6.24	6.24	6.37	2.0	1.6	0.2

Laboratory
Code no: 20

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	7.04	6.99	7.06	7.06	7.02	-0.7	0.5	-0.1
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L	7.32	7.31	7.29	7.29	7.32	0.3	0.1	0.1
N-total, mg/L	12.3	12.4	11.9	11.9	12.4	3.4	0.6	0.5
PO4-P, mg/L	0.22	0.22	0.25	0.25	0.22	-10.7	0.0	-1.4
P-total, mg/L	0.58	0.59	0.55	0.55	0.59	6.9	1.2	1.0
Cd, µg/L	10.20	10.00	9.54	9.54	10.10	5.9	1.4	0.8
Cr, µg/L	47.0	46.8	45.8	45.8	46.9	2.5	0.3	0.6
Cu, µg/L	97.1	95.6	93.4	93.4	96.4	3.2	1.1	0.5
Ni, µg/L	11.70	11.50	11.84	11.84	11.6	-2.0	1.2	-0.3
Pb, µg/L	9.80	9.70	9.88	9.88	9.75	-1.3	0.7	-0.2
Zn, µg/L	105	104	106	106	104	-2.1	0.5	-0.4
Hg, µg/L	6.07	6.02	6.24	6.24	6.05	-3.2	0.6	-0.3

Laboratory
Code no: 21

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L			7.06	7.06				
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L			11.9	11.9				
PO4-P, mg/L			0.25	0.25				
P-total, mg/L			0.55	0.55				
Cd, µg/L			9.54	9.54				
Cr, µg/L			45.8	45.8				
Cu, µg/L			93.4	93.4				
Ni, µg/L			11.84	11.84				
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L	6.03	5.99	6.24	6.24	6.01	-3.7	0.5	-0.4

Laboratory
Code no: **22**

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	7.40	7.50	7.06	7.06	7.45	5.5	0.9	1.0
NO2-N, mg/L	0.0037	0.0043	0.19	0.19	0.00	-97.9	10.6	-1.0
NO2+3-N, mg/L	7.40	7.50	7.29	7.29	7.45	2.1	0.9	0.6
N-total, mg/L	12.0	12.0	11.9	11.9	12.0	0.5	0.0	0.1
PO4-P, mg/L	0.25	0.26	0.25	0.25	0.25	2.1	2.0	0.3
P-total, mg/L	0.54	0.56	0.55	0.55	0.55	0.5	2.6	0.1
Cd, µg/L	9.52	9.70	9.54	9.54	9.61	0.7	1.3	0.1
Cr, µg/L	44.9	45.1	45.8	45.8	45.0	-1.6	0.3	-0.4
Cu, µg/L	93.9	94.4	93.4	93.4	94.2	0.8	0.4	0.1
Ni, µg/L	2.30	2.30	11.84	11.84	2.3	-80.6	0.0	-11.4
Pb, µg/L	21.80	21.07	9.88	9.88	21.44	117.0	2.4	14.0
Zn, µg/L	102	101	106	106	101	-4.6	1.0	-0.8
Hg, µg/L	5.72	5.87	6.24	6.24	5.80	-7.2	1.8	-0.7

Laboratory
Code no: **23**

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	7.15	7.17	7.06	7.06	7.16	1.4	0.2	0.3
NO2-N, mg/L	0.43	0.43	0.19	0.19	0.43	130.4	0.3	1.3
NO2+3-N, mg/L	7.59	7.61	7.29	7.29	7.60	4.1	0.2	1.3
N-total, mg/L	11.6	11.5	11.9	11.9	11.5	-3.4	1.0	-0.5
PO4-P, mg/L	0.24	0.25	0.25	0.25	0.24	-2.0	2.4	-0.3
P-total, mg/L	0.49	0.50	0.55	0.55	0.49	-9.9	0.6	-1.4
Cd, µg/L			9.54	9.54				
Cr, µg/L			45.8	45.8				
Cu, µg/L			93.4	93.4				
Ni, µg/L			11.84	11.84				
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L			6.24	6.24				

Laboratory
Code no: 25

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L		6.95	7.06	7.06	6.95	-1.6		-0.3
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L			11.9	11.9				
PO4-P, mg/L			0.25	0.25				
P-total, mg/L			0.55	0.55				
Cd, µg/L			9.54	9.54				
Cr, µg/L			45.8	45.8				
Cu, µg/L			93.4	93.4				
Ni, µg/L			11.84	11.84				
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L			6.24	6.24				

Laboratory
Code no: 26

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L			7.06	7.06				
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L			11.9	11.9				
PO4-P, mg/L			0.25	0.25				
P-total, mg/L			0.55	0.55				
Cd, µg/L	9.61	9.53	9.54	9.54	9.57	0.3	0.6	0.0
Cr, µg/L	47.0	47.0	45.8	45.8	47.0	2.7	0.0	0.6
Cu, µg/L	87.1	87.2	93.4	93.4	87.2	-6.7	0.1	-1.0
Ni, µg/L	11.23	11.22	11.84	11.84	11.2	-5.2	0.1	-0.7
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L			6.24	6.24				

Laboratory
Code no: **28**

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L			7.06	7.06				
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L	11.0	11.2	11.9	11.9	11.1	-7.1	1.3	-1.0
PO4-P, mg/L			0.25	0.25				
P-total, mg/L			0.55	0.55				
Cd, µg/L	9.50	9.50	9.54	9.54	9.50	-0.4	0.0	-0.1
Cr, µg/L	47.0	47.0	45.8	45.8	47.0	2.7	0.0	0.6
Cu, µg/L	99.5	99.3	93.4	93.4	99.4	6.4	0.1	0.9
Ni, µg/L	12.50	12.30	11.84	11.84	12.4	4.7	1.1	0.7
Pb, µg/L	9.20	9.90	9.88	9.88	9.55	-3.3	5.2	-0.4
Zn, µg/L	106	106	106	106	106	-0.6	0.0	-0.1
Hg, µg/L			6.24	6.24				

Laboratory
Code no: **29**

Components	Measured data		Assigned values		Statistics			
	Waste Water A	Waste Water B	Waste Water A	Waste Water B	Aver-age	Dev. %	RSD %	z-score
NO3-N, mg/L	6.88	6.99	7.06	7.06	6.94	-1.8	1.1	-0.3
NO2-N, mg/L			0.19	0.19				
NO2+3-N, mg/L			7.29	7.29				
N-total, mg/L			11.9	11.9				
PO4-P, mg/L	0.24	0.24	0.25	0.25	0.24	-2.5	1.2	-0.3
P-total, mg/L	0.52	0.53	0.55	0.55	0.53	-4.1	0.5	-0.6
Cd, µg/L			9.54	9.54				
Cr, µg/L			45.8	45.8				
Cu, µg/L			93.4	93.4				
Ni, µg/L			11.84	11.84				
Pb, µg/L			9.88	9.88				
Zn, µg/L			106	106				
Hg, µg/L			6.24	6.24				

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 (2019). 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.

Cochran's test value is calculated as:

$$C = \frac{s_{max}^2}{\sum_{i=1}^{p} s_i^2}$$

Where p is the number of standard deviations s_i between test pairs. S_{max} is the highest standard deviation in the dataset. Cochran's critical values can be found in ISO 5725.

Grubb's single outlier test is calculated as

$$G = (x_p - m)/s$$

Where x_p is average of the single test pair, m is the average of all test pairs and s is the standard deviation of all test pairs. Grubb's value is calculated for the highest and lowest test pairs. Grubb's critical values for single outlier test can be found in ISO 5725.

Grubb's double outlier test is calculated as

$$G = s_{p-2}^2/s^2$$

Where s is the standard deviation of all test pairs and s_{p-2} is the standard deviation without the two highest or the two lowest test pairs. Grubb's critical values for double outlier test can be found in ISO 5725.

Table of summary statistics (ISO 5725, 2019):

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 standard deviation between the laboratories.

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

S(R): reproducibility. The total standard 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.

For sample C the summary statistic table 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.

z-scores is calculated for each laboratory as z=(x-m)/S(R), where x is the x is the average of results from all laboratories. For the evaluation of the z-scores: z = |2| is satifactory, z = |2| - |3| is questionable and z > |3| is not acceptable (ISO 13528, 2015).
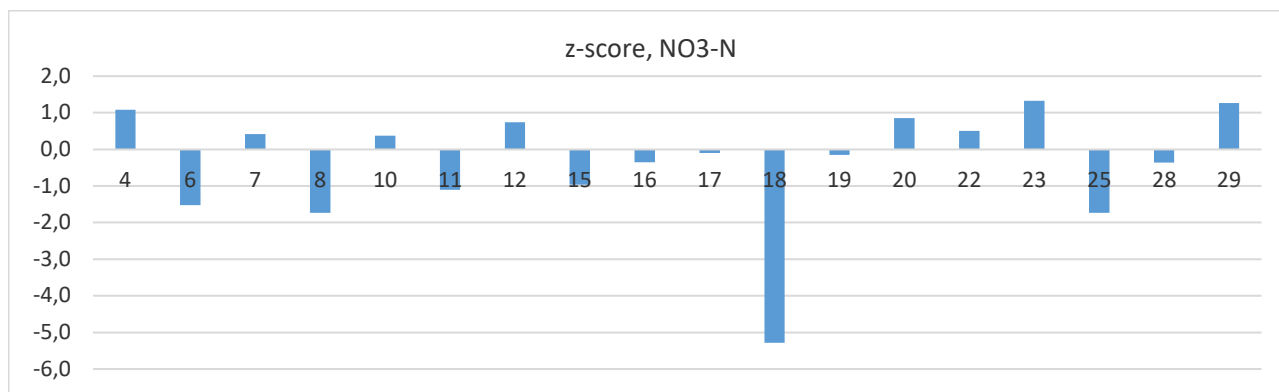
Figures of the z-scores for the participating laboratories for freshwater A/B and waste water A/B, respectively are shown.

4.2 Statistical data for each component in freshwater

4.2.1 NO₃-N

Component:	*NO3-N, mg/L*								
Assigned Laboratory code no.	**0.77 Fresh Water A**	**0.77 Fresh Water B**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
			1% level	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
4	0.83	0.83							
6	0.65	0.71	X	X	-	-	-	-	X
7	0.79	0.80							
8	0.67	0.67							
10	0.79	0.79							
11	0.71	0.70							
12	0.83	0.80							
15	0.72	0.71							
16	0.74	0.76							
17	0.77	0.76							
18	0.46	0.47			X	X	-	-	X
19	0.76	0.76							
20	0.82	0.82							
22	0.80	0.80							
23	0.84	0.85							
25	0.66	0.68							
28	0.74	0.76							
29	0.84	0.84							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	NO3-N A/B Freshwater
p	18
m [mg/L]	0.77
S(L) [mg/L]	0.057
S(r) [mg/L]	0.009
S(R) [mg/L]	0.058
r [mg/L]	0.025
R [mg/L]	0.162
CV(r) [%]	1.1
CV(R) [%]	7.5

Component: *NO3-N, mg/L*

Assigned Laboratory code no.	1.20 Fresh Water C	Grupps single test 1% level	Grupps single test 5% level	Grupps double test 1% level	Grupps double test 5% level	Excluded in statistical ana-lysis
6	0.97					
7	1.30					
8	1.10					
10	1.25					
11	1.12					
12	1.21					
15	1.14					
17	1.20					
18	0.76	X	X	-	-	X
19	1.19					
20	1.28					
22	1.26					
23	1.36					
25	1.22					
28	1.20					
29	1.24					

Statistical analysis	Freshwater C NO3-N, mg/L
Assigned value	1.20
Laboratory deviation (S(L))	0.095
Relative laboratory deviation (%)	7.9
Calculated spike value	0.45
Measured value of spike	0.43
% recovery of spike	96

4.2.2   NO₂-N

Component:	*NO2-N, mg/L*								
Assigned	0.26	0.26	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Fresh Water A	Fresh Water B	1% level	5% level	1% level	5% level	1% level	5% level	
4	0.25	0.25							
6	0.26	0.27							
7	0.24	0.24							
8	0.21	0.23							
10	0.28	0.27							
11	0.27	0.27							
12	0.26	0.26							
13	0.27	0.27							
14	0.25	0.25							
15	0.26	0.26							
16	0.26	0.26							
17	0.25	0.25							
18	0.29	0.29							
19	0.28	0.27							
20	0.27	0.27							
21	0.29	0.28							
22	0.26	0.26							
23	0.25	0.25							
25	0.28	0.28							
29	0.24	0.25							
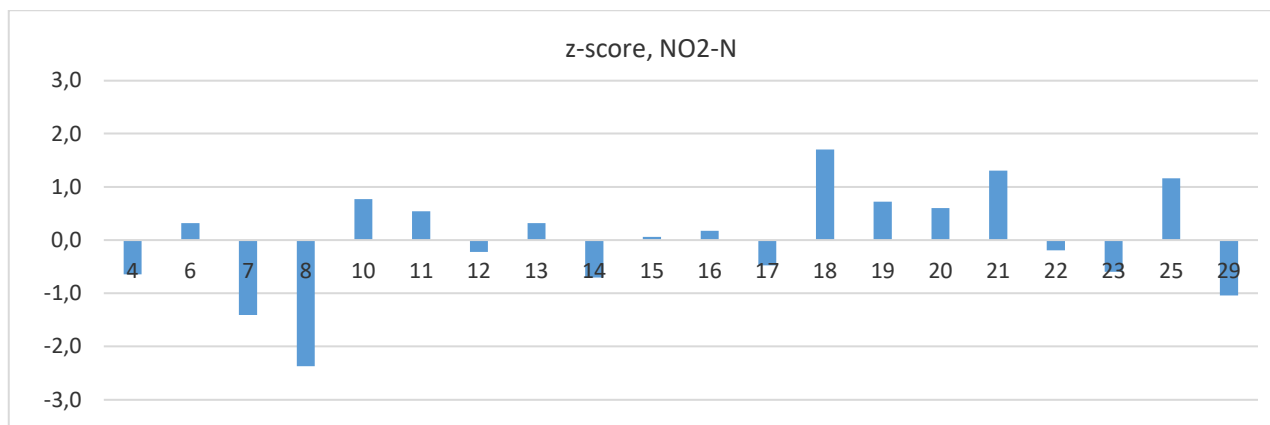
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	NO2-N A/B Freshwater
p	20
m [mg/L]	0.26
S(L) [mg/L]	0.017
S(r) [mg/L]	0.005
S(R) [mg/L]	0.018
r [mg/L]	0.014
R [mg/L]	0.050
CV(r) [%]	2.0
CV(R) [%]	6.8

Compo-nent:	NO2-N, mg/L					
Assigned	0.44	Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Fresh Water C	1% level	5% level	1% level	5% level	
6	0.44					
7	0.39					
8	0.37					
10	0.44					
11	0.47					
12	0.48					
13	0.43					
14	0.42					
15	0.45					
17	0.42					
18	0.48					
19	0.46					
20	0.44					
21	0.48					
22	0.43					
23	0.44					
25	0.47					
29	0.41					

Statistical analysis	Freshwater C NO2-N, mg/L
Assigned value	0.44
Laboratory deviation (S(L))	0.031
Relative laboratory deviation (%)	7.0
Calculated spike value	0.18
Measured value of spike	0.18
% recovery of spike	98

4.2.3 NO$_{2+3}$-N

Component:	*NO2+3-N, mg/L*								
Assigned	**1.05**	**1.05**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Fresh**	**Fresh**							**statistical**
code no.	**Water A**	**Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
3	0.94	0.94							
4	1.08	1.09							
7	1.03	1.04							
11	0.98	0.97							
12	1.08	1.06							
14	1.08	1.08							
16	1.00	1.03							
17	1.02	1.02							
18	0.89	0.90							
19	1.04	1.04							
20	1.09	1.10							
21	1.25	1.27							
22	1.06	1.06							
23	1.09	1.11							
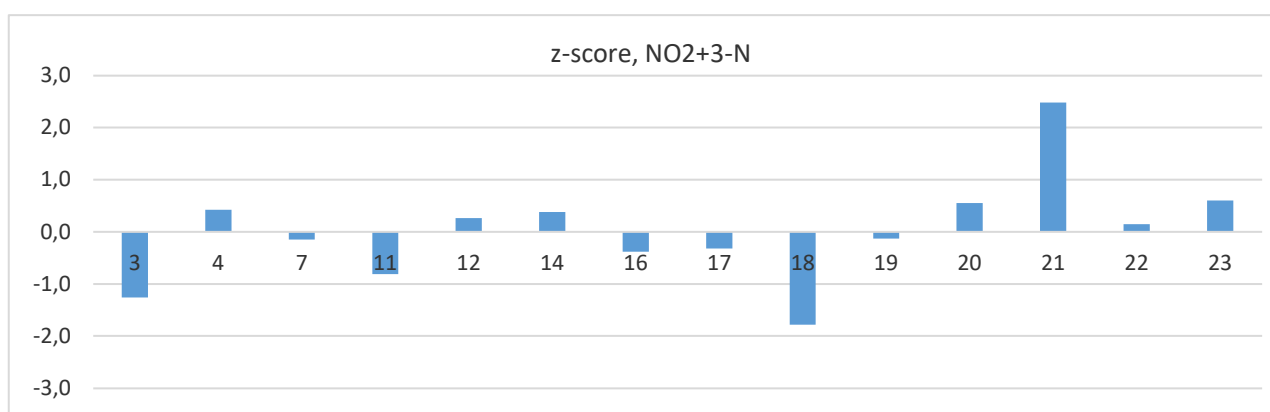
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	NO2+3-N A/B Freshwater
p	14
m [mg/L]	1.05
S(L) [mg/L]	0.085
S(r) [mg/L]	0.009
S(R) [mg/L]	0.086
r [mg/L]	0.024
R [mg/L]	0.240
CV(r) [%]	0.8
CV(R) [%]	8.2

Compo-nent:	NO2+3-N, mg/L					
Assigned	**1.68**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	
3	1.53					
7	1.64					
11	1.59					
12	1.68					
14	1.75					
17	1.58					
18	1.53					
19	1.65					
20	1.72					
21	1.95					
22	1.69					
23	1.80					

Statistical analysis	Freshwater C NO2+3-N, mg/L
Assigned value	1.68
Laboratory deviation (S(L))	0.120
Relative laboratory deviation (%)	7.2
Calculated spike value	0.63
Measured value of spike	0.63
% recovery of spike	100

4.2.4 N-total

Component:	N-total, mg/L								
Assigned	3.38	3.38	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Fresh Water A	Fresh Water B	1% level	5% level	1% level	5% level	1% level	5% level	
3	3.54	3.51							
4	3.27	3.29							
6	2.99	3.03							
7	3.32	3.52		X					
8	3.60	3.70							
10	3.38	3.36							
11	3.40	3.40							
12	3.69	3.78							
14	3.02	3.04							
15	3.56	3.50							
16	3.18	3.24							
17	3.55	3.46							
18	3.40	3.40							
19	3.27	3.28							
20	3.80	3.79							
21	3.03	3.09							
22	3.40	3.40							
23	3.25	3.23							
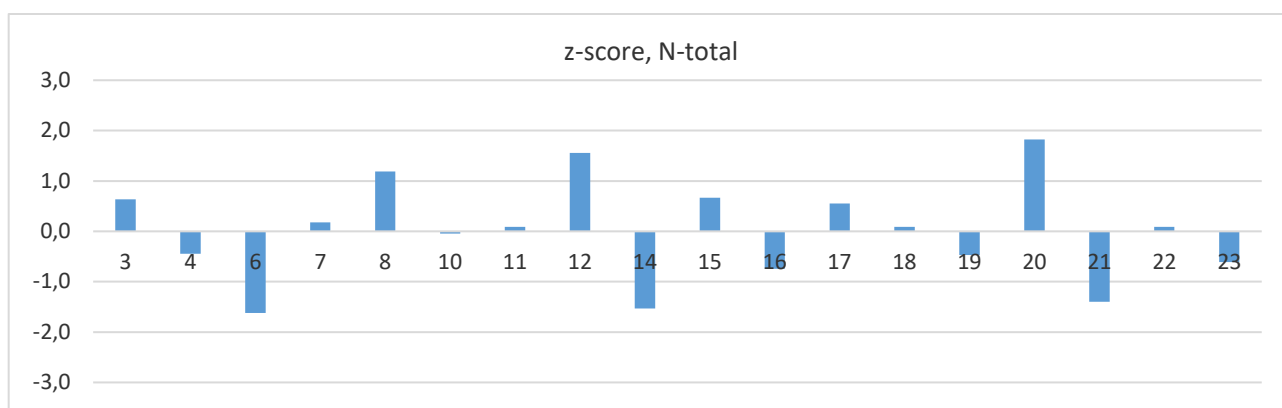
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	N-total A/B Freshwater
p	18
m [mg/L]	3.38
S(L) [mg/L]	0.22
S(r) [mg/L]	0.05
S(R) [mg/L]	0.23
r [mg/L]	0.13
R [mg/L]	0.64
CV(r) [%]	1.4
CV(R) [%]	6.7

Compo-nent:	N-total, mg/L					
Assigned	**4.58**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	
3	4.51					
6	4.19					
7	4.73					
8	4.80					
10	4.62					
11	4.70					
12	5.06					
14	4.03					
15	4.47					
17	4.98					
18	4.60					
19	4.54					
20	5.15					
21	3.99					
22	4.50					
23	4.43					

Statistical analysis	**Freshwater C N-total, mg/L**
Assigned value	4.58
Laboratory deviation (S(L))	0.332
Relative laboratory deviation (%)	7.2
Calculated spike value	1.14
Measured value of spike	1.20
% recovery of spike	105

4.2.5 PO₄-P

Component: *PO4-P, mg/L*

Assigned Laboratory code no.	0.20 Fresh Water A	0.20 Fresh Water B	Cochrans test 1% level	5% level	Grupps single test 1% level	5% level	Grupps double test 1% level	5% level	Excluded in statistical analysis
2	0.18	0.19							
3	0.18	0.18							
4	0.21	0.21							
6	0.20	0.20							
7	0.19	0.19							
8	0.19	0.19							
10	0.21	0.20							
11	0.19	0.19							
12	0.18	0.19							
13	0.21	0.22							
14	0.19	0.19							
15	0.20	0.21							
16	0.20	0.20							
17	0.18	0.18							
18	0.21	0.21							
19	0.18	0.18							
20	0.19	0.19							
21	0.18	0.19							
22	0.20	0.21							
23	0.21	0.21							
29	0.19	0.19							
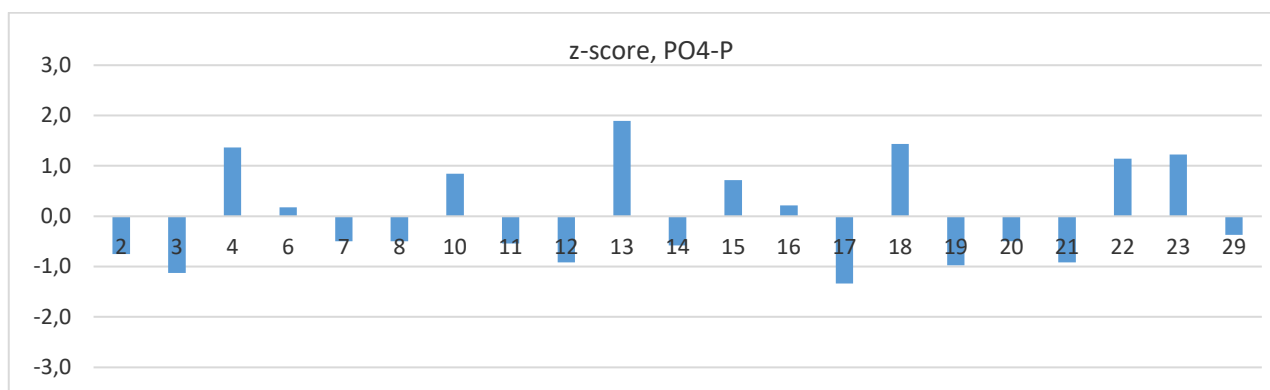
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	PO4-P A/B Freshwater
p	21
m [mg/L]	0.20
S(L) [mg/L]	0.012
S(r) [mg/L]	0.003
S(R) [mg/L]	0.012
r [mg/L]	0.008
R [mg/L]	0.033
CV(r) [%]	1.5
CV(R) [%]	6.1

Compo-						
nent:	*PO4-P, mg/L*					
Assigned	**0.29**	**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
2	0.31					
3	0.25					
6	0.28					
7	0.28					
8	0.28					
10	0.31					
11	0.27					
12	0.27					
13	0.32					
14	0.28					
15	0.30					
17	0.28					
18	0.32					
19	0.27					
20	0.27					
21	0.27					
22	0.30					
23	0.28					
29	0.28					

Statistical analysis	Freshwater C PO4-P, mg/L
Assigned value	0.29
Laboratory deviation (S(L))	0.020
Relative laboratory deviation (%)	7.0
Calculated spike value	0.09
Measured value of spike	0.09
% recovery of spike	100

4.2.6 P-total

Component:	P-total, mg/L								
Assigned	**0.28**	**0.28**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water A**	**Fresh Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
2	0.27	0.26							
3	0.29	0.28							
4	0.26	0.26							
6	0.27	0.27							
7	0.29	0.28							
8	0.29	0.29							
10	0.26	0.26							
11	0.29	0.28							
12	0.26	0.28							
14	0.27	0.27							
15	0.25	0.25							
16	0.26	0.26							
17	0.28	0.28							
18	0.31	0.33							
19	0.28	0.29							
20	0.29	0.27							
21	0.27	0.27							
22	0.29	0.30							
23	0.26	0.26							
29	0.26	0.27							
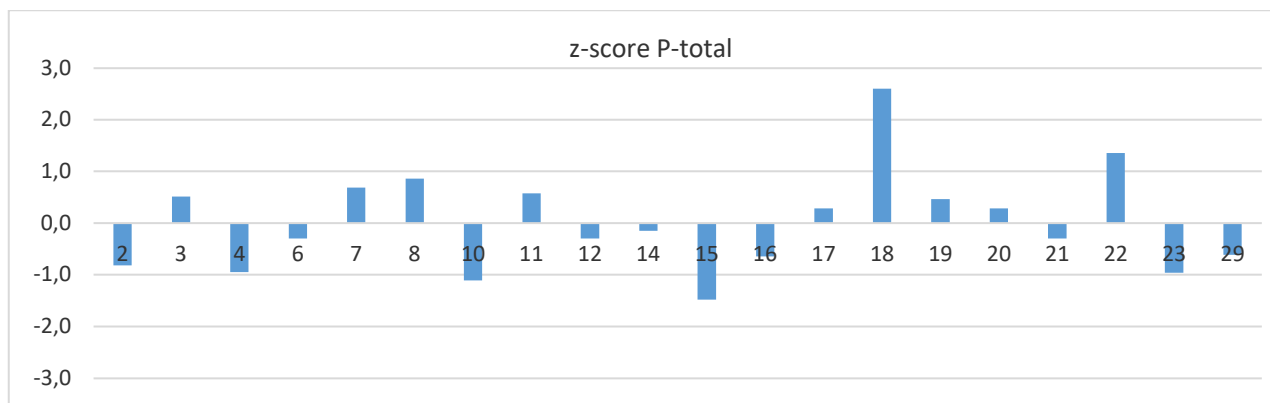
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	P-total A/B Freshwater
p	20
m [mg/L]	0.28
S(L) [mg/L]	0.016
S(r) [mg/L]	0.006
S(R) [mg/L]	0.017
r [mg/L]	0.017
R [mg/L]	0.048
CV(r) [%]	2.3
CV(R) [%]	6.3

Compo-nent:	*P-total, mg/L*					
Assigned	**0.42**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	
2	0.43					
3	0.43					
6	0.42					
7	0.43					
8	0.43					
10	0.40					
11	0.43					
12	0.41					
14	0.41					
15	0.37					
17	0.42					
18	0.48		X			
19	0.42					
20	0.42					
21	0.40					
22	0.43					
23	0.40					
29	0.40					

	Freshwater C
Statistical analysis	**P-total, mg/L**
Assigned value	0.42
Laboratory deviation (S(L))	0.022
Relative laboratory deviation (%)	5.2
Calculated spike value	0.15
Measured value of spike	0.14
% recovery of spike	96

4.2.7 Cd

Component:	*Cd, µg/L*								
Assigned	**1.66**	**1.66**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water A**	**Fresh Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
2	1.40	1.51							
3	1.70	1.60							
4	1.58	1.60							
5	1.74	1.74							
6	1.64	1.63							
7	1.72	1.77							
8	1.70	1.69							
10	1.59	1.57							
11	1.59	1.60							
14	1.60	1.62							
15	1.78	1.78							
17	1.40	1.39							
18	1.24	1.38							
19	2.01	2.01							
20	1.77	1.77							
22	2.00	2.03							
26	1.80	1.49	X	X	-	-	-	-	X
27	1.70	1.70							
28	1.68	1.64							
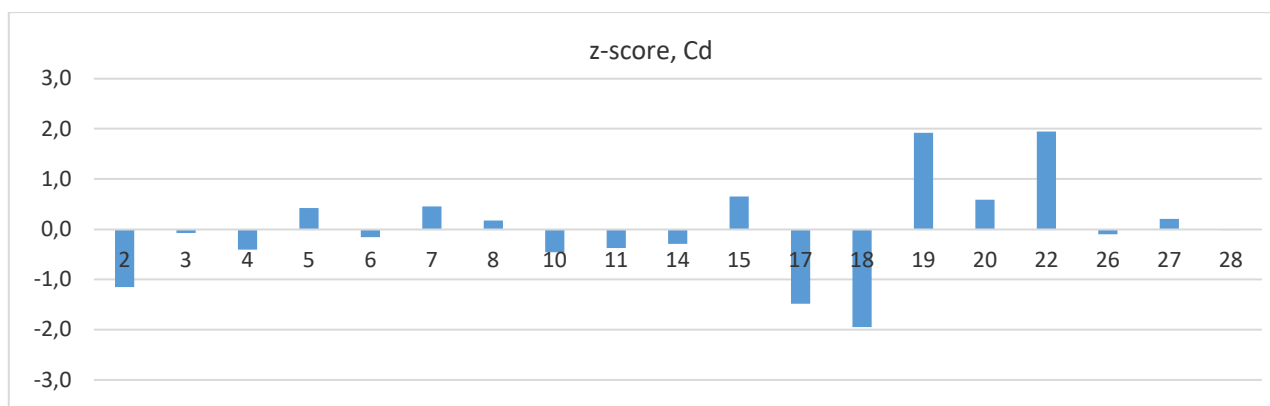
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Cd A/B Freshwater
p	19
m [µg/L]	1.66
S(L) [µg/L]	0.18
S(r) [µg/L]	0.04
S(R) [µg/L]	0.18
r [µg/L]	0.10
R [µg/L]	0.51
CV(r) [%]	2.2
CV(R) [%]	10.9

Compo-nent:	Cd, µg/L					
Assigned	**2.38**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	
2	2.05					
3	2.40					
4	2.24					
5	2.51					
6	2.37					
7	2.53					
8	2.40					
10	2.25					
11	2.33					
14	2.38					
15	2.57					
16	2.28					
17	1.96					
18	1.97					
19	2.90					
20	2.57					
22	2.83					
26	2.25					
27	2.40					
28	2.41					

	Freshwater C
Statistical analysis	**Cd, µg/L**
Assigned value	2.38
Laboratory deviation (S(L))	0.241
Relative laboratory deviation (%)	10.1
Calculated spike value	0.82
Measured value of spike	0.72
% recovery of spike	87

4.2.8 Cr

Component:	*Cr, µg/L*								
Assigned	**3.39**	**3.39**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water A**	**Fresh Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
2	2.84	2.87							
3	3.40	3.40							
4	3.17	3.10							
5	3.31	3.32							
6	3.47	3.54							
7	3.43	3.48							
8	3.51	3.46							
10	3.33	3.31							
11	3.33	3.44							
15	3.54	3.55							
17	3.50	3.65							
18	3.35	3.27							
19	4.03	4.02				X			
20	3.51	3.47							
22	3.24	3.21							
26	3.93	3.45	X	X	-	-	-	-	X
27	3.30	3.30							
28	3.40	3.30							
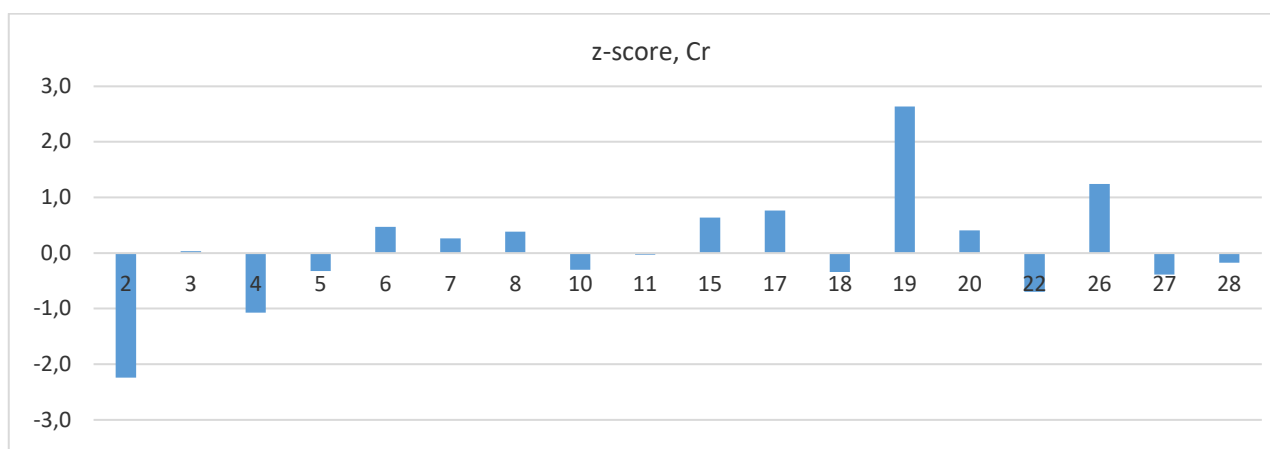
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Cr A/B Freshwater
p	18
m [µg/L]	3.39
S(L) [µg/L]	0.24
S(r) [µg/L]	0.05
S(R) [µg/L]	0.24
r [µg/L]	0.13
R [µg/L]	0.67
CV(r) [%]	1.4
CV(R) [%]	7.1

Component:	Cr, µg/L					
Assigned	**4.90**	**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
2	4.09					
3	4.90					
4	4.42					
5	4.80					
6	5.16					
7	4.89					
8	5.03					
10	4.89					
11	5.04					
15	5.26					
16	4.59					
17	5.16					
18	4.77					
19	5.84					
20	5.03					
22	4.71					
26	4.93					
27	4.70					
28	4.92					

	Freshwater C
Statistical analysis	**Cr, µg/L**
Assigned value	4.90
Laboratory deviation (S(L))	0.357
Relative laboratory deviation (%)	7.3
Calculated spike value	1.65
Measured value of spike	1.51
% recovery of spike	91

4.2.9 Cu

Component:	*Cu, µg/L*									
Assigned	**9.77**	**9.77**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water A**	**Fresh Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
2	12.35	12.22						X	
3	9.40	9.50							
4	9.34	9.14							
5	9.20	9.13							
6	8.97	9.06							
7	10.29	9.73							
8	9.20	9.50							
10	9.10	9.05							
11	9.38	9.01							
14	9.24	8.73							
15	10.19	10.08							
17	8.92	8.95							
18	8.92	8.88							
19	10.89	10.84							
20	9.40	9.30							
22	11.70	12.30						X	
26	11.07	9.78	X	X	-	-	-	-	X
27	9.50	9.40							
28	10.50	10.50							
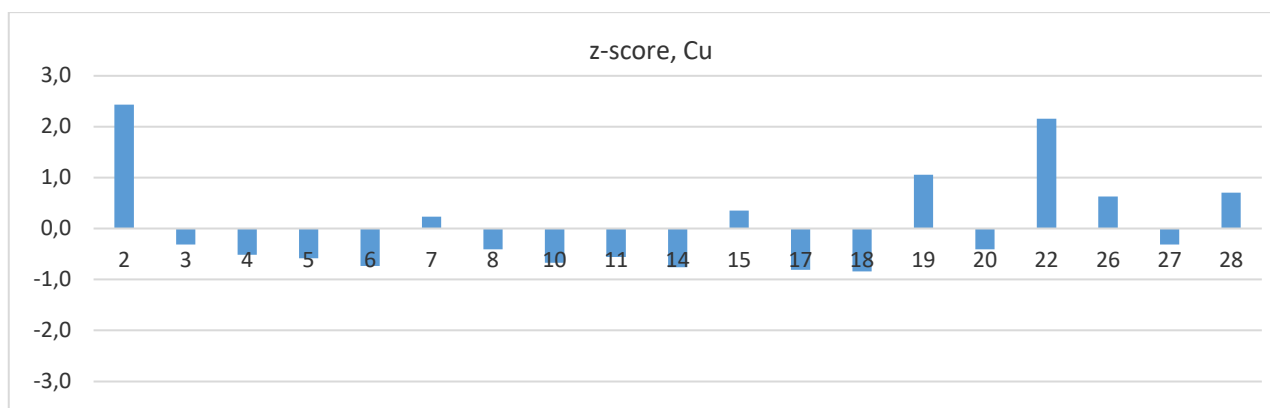
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Cu A/B Freshwater
p	19
m [µg/L]	9.77
S(L) [µg/L]	1.02
S(r) [µg/L]	0.19
S(R) [µg/L]	1.03
r [µg/L]	0.53
R [µg/L]	2.90
CV(r) [%]	1.9
CV(R) [%]	10.6

Compo-nent:	Cu, µg/L					
Assigned	**14.71**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	
2	16.34					
3	14.00					
4	13.60					
5	14.00					
6	14.17					
7	15.27					
8	14.60					
10	14.10					
11	14.10					
14	13.04					
15	15.80					
16	13.80					
17	13.70					
18	13.78					
19	16.78					
20	14.40					
22	18.00					
26	13.99					
27	14.60					
28	16.10					

	Freshwater C
Statistical analysis	**Cu, µg/L**
Assigned value	14.71
Laboratory deviation (S(L))	1.269
Relative laboratory deviation (%)	8.6
Calculated spike value	4.67
Measured value of spike	4.94
% recovery of spike	106

4.2.10 Ni

Component:	*Ni, µg/L*								
Assigned	15.19	15.19	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Fresh Water A	Fresh Water B	1% level	5% level	1% level	5% level	1% level	5% level	
2	11.83	12.19						X	
3	15.00	15.00							
4	15.26	14.94							
5	14.50	14.30							
6	15.01	15.10							
7	14.54	15.22							
8	16.00	16.00							
10	14.90	14.80							
11	15.60	15.50							
14	14.61	14.99							
15	15.97	15.91							
17	16.40	16.10							
18	15.72	15.75							
19	17.83	17.54							
20	15.40	15.40							
22	12.51	12.97						X	
26	16.78	14.65	X	X	-	-	-	-	X
27	15.90	15.80							
28	16.20	16.30							
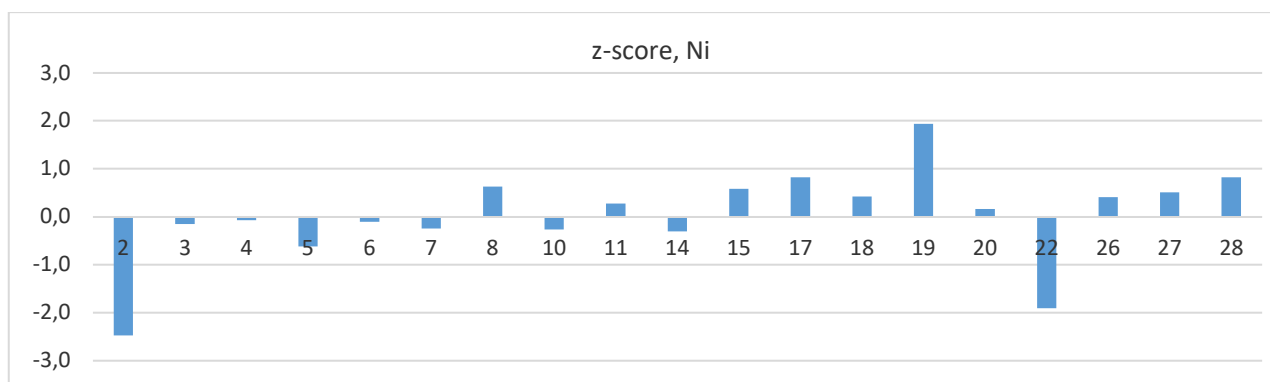
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Ni A/B Freshwater
p	19
m [µg/L]	15.19
S(L) [µg/L]	1.27
S(r) [µg/L]	0.19
S(R) [µg/L]	1.29
r [µg/L]	0.55
R [µg/L]	3.60
CV(r) [%]	1.3
CV(R) [%]	8.5

Compo-nent:	Ni, µg/L	Grupps single test		Grupps double test		Excluded in statistical analysis
Assigned	21.40					
Laboratory code no.	Fresh Water C	1% level	5% level	1% level	5% level	
2	17.02					
3	22.00					
4	20.38					
5	20.30					
6	21.51					
7	22.10					
8	22.00					
10	21.20					
11	21.80					
14	20.66					
15	22.58					
16	20.20					
17	24.80					
18	21.59					
19	25.51					
20	21.60					
22	18.14					
26	20.63					
27	21.00					
28	23.00					

Statistical analysis	Freshwater C Ni, µg/L
Assigned value	21.40
Laboratory deviation (S(L))	1.901
Relative laboratory deviation (%)	8.9
Calculated spike value	6.62
Measured value of spike	6.21
% recovery of spike	94

4.2.11 Pb

Component:	*Pb, µg/L*								
Assigned	**1.71**	**1.71**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water A**	**Fresh Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
2	1.63	1.84	X	X	-	-	-	-	X
3	1.70	1.70							
4	1.63	1.59							
5	1.67	1.67							
6	1.67	1.68							
7	1.72	1.71							
10	1.81	1.76							
11	1.68	1.68							
15	1.88	1.82							
17	1.52	1.50							
18	1.17	1.14			X	X	-	-	X
19	1.90	1.89							
20	1.72	1.72							
22	4.74	4.28	X	X	-	-	-	-	X
27	1.70	1.70							
28	2.07								
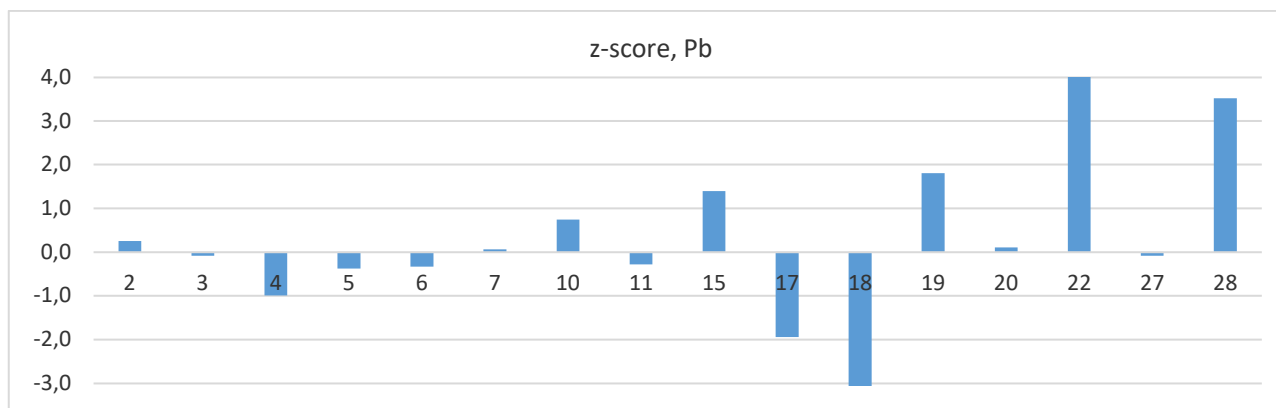
Lab 22 out of range. z-score=27.3.

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Pb A/B Freshwater
p	16
m [µg/L]	1.71
S(L) [µg/L]	0.101
S(r) [µg/L]	0.016
S(R) [µg/L]	0.103
r [µg/L]	0.045
R [µg/L]	0.287
CV(r) [%]	0.9
CV(R) [%]	6.0

Compo-nent:	Pb, µg/L					
Assigned	**2.30**	**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water C**	**1% level**	**5% level**	**1% level**	**5% level**	
2	1.91					
3	2.40					
4	2.19					
5	2.33					
6	2.37					
7	2.19					
10	2.39					
11	2.32					
15	2.52					
16	2.24					
17	2.04					
18	1.40	X	X	-	-	X
19	2.65					
20	2.38					
22	5.89	X	X	-	-	X
27	2.20					
28	2.38					

	Freshwater C
Statistical analysis	**Pb, µg/L**
Assigned value	2.30
Laboratory deviation (S(L)	0.183
Relative laboratory deviation (%)	7.9
Calculated spike value	0.58
Measured value of spike	0.59
% recovery of spike	102

4.2.12 Zn

Component:	*Zn, µg/L*								
Assigned	**27.24**	**27.24**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Fresh Water A**	**Fresh Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
2	23.30	23.53							
3	27.00	27.00							
4	28.07	27.16							
5	26.80	26.40							
6	25.91	26.55							
7	28.20	27.50							
8	25.00	26.00							
10	25.50	25.60							
11	30.70	30.50							
15	27.00	28.44							
18	27.11	27.05							
19	32.16	32.13							
20	27.40	27.40							
22	27.77	29.47							
27	24.60	25.40							
28	27.40	27.50							
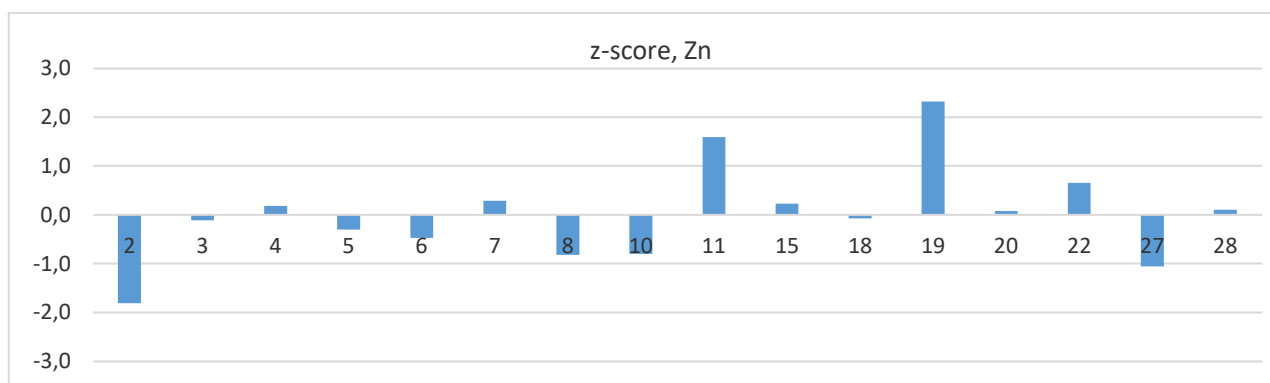
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Zn A/B Freshwater
p	16
m [µg/L]	27.24
S(L) [µg/L]	2.05
S(r) [µg/L]	0.51
S(R) [µg/L]	2.11
r [µg/L]	1.42
R [µg/L]	5.92
CV(r) [%]	1.9
CV(R) [%]	7.8

Compo-nent:	Zn, µg/L					
Assigned	46.75	Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Fresh Water C	1% level	5% level	1% level	5% level	
2	41.21					
3	46.00					
4	45.38					
5	45.00					
6	45.61					
7	46.80					
8	45.00					
10	44.70					
11	50.50	-	-	-	-	X
15	46.98					
16	43.20					
17	54.50			X	X	X
18	47.10					
19	54.80			X	X	X
20	47.00					
22	47.74					
27	43.20					
28	46.80					

Statistical analysis	Freshwater C Zn, µg/L
Assigned value	46.75
Laboratory deviation (S(L))	2.155
Relative laboratory deviation (%)	4.6
Calculated spike value	-
Measured value of spike	18.53
% recovery of spike	-

Recovery is not calculated for Zn as there appeared to be an error in the spiking.

4.2.13 Hg

Component:	Hg, µg/L									
Assigned	0.13	0.13	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Fresh Water A	Fresh Water B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.13	0.14							
4	0.08	0.09							
5	0.13	0.13							
6	0.16	0.15							
7	0.15	0.15							
10	0.12	0.12							
14	0.14	0.15							
15	0.25	0.25			X	X	-	-	X
17	0.11	0.12							
18	0.10	0.10							
20	0.15	0.15							
21	0.13	0.14							
22	0.15	0.12	X	X	-	-	-	-	X
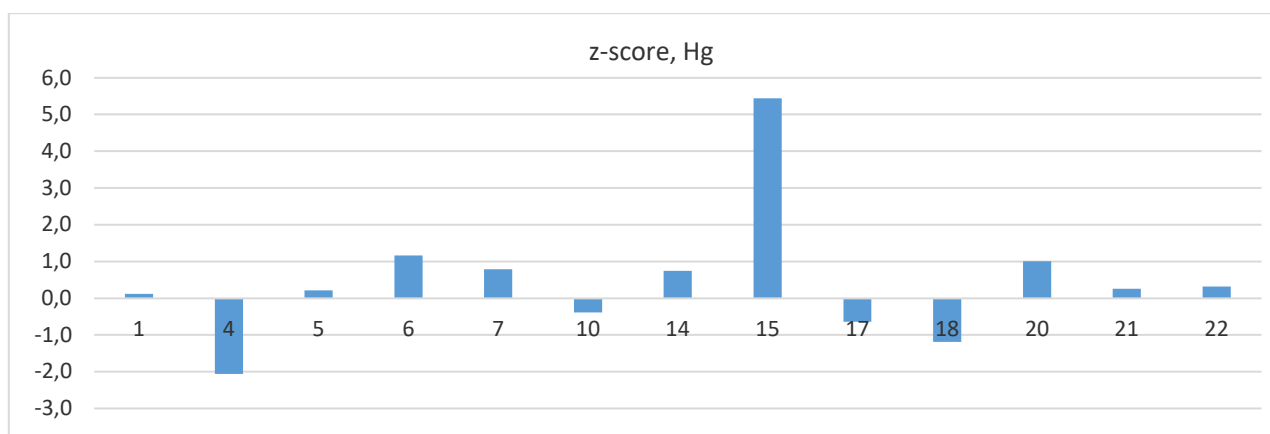
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Hg A/B Freshwater
p	13
m [µg/L]	0.129
S(L) [µg/L]	0.022
S(r) [µg/L]	0.003
S(R) [µg/L]	0.022
r [µg/L]	0.009
R [µg/L]	0.063
CV(r) [%]	2.4
CV(R) [%]	17.4

Compo-nent:	Hg, µg/L					
Assigned	0.18	Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Fresh Water C	1% level	5% level	1% level	5% level	
1	0.18					
4	0.15					
5	0.22					
6	0.24					
7	0.21					
10	0.16					
14	0.20					
15	0.29					
16	0.04					
17	0.17					
19	0.12					
20	0.20					
21	0.19					
22	0.20					

Statistical analysis	Freshwater C Hg, µg/L
Assigned value	0.18
Laboratory deviation (S(L))	0.058
Relative laboratory deviation (%)	31.9
Calculated spike value	0.06
Measured value of spike	0.05
% recovery of spike	94

4.3 Statistical data for each component in waste water

4.3.1 NO₃-N

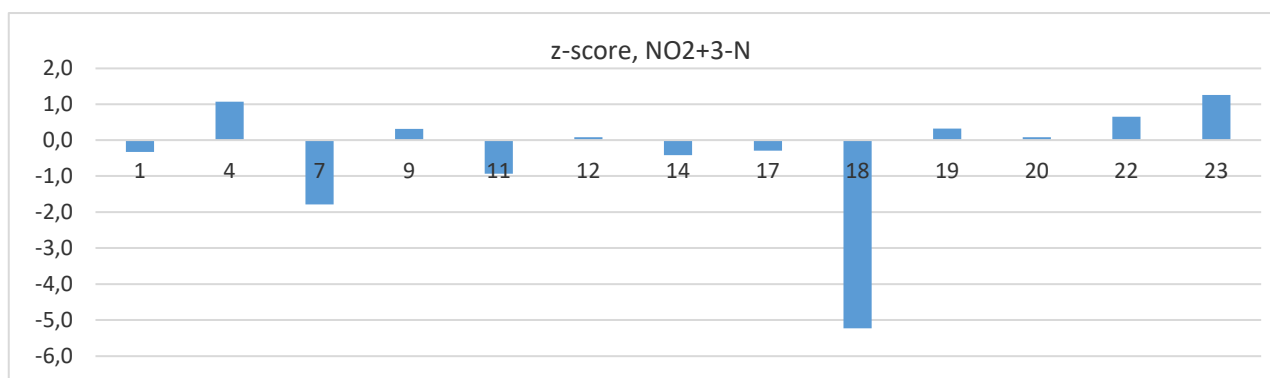| Component:	*NO3-N, mg/L*								
Assigned Laboratory code no.	**7.06** Waste Water A	**7.06** Waste Water B	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
			1% level	5% level	1% level	5% level	1% level	5% level	
1	7.05	7.20							
4	7.09	7.17							
7	6.50	6.44							
8	6.80	6.90							
10	7.95	8.01				X			
11	7.26	6.77							
12	6.88	6.83							
15	7.02	9.96	X	X	-	-	-	-	X
17	6.52	7.21		X					
18	5.28	5.38			X	X	-	-	X
19	6.96	7.01							
20	7.04	6.99							
22	7.40	7.50							
23	7.15	7.17							
25		6.95							
29	6.88	6.99							
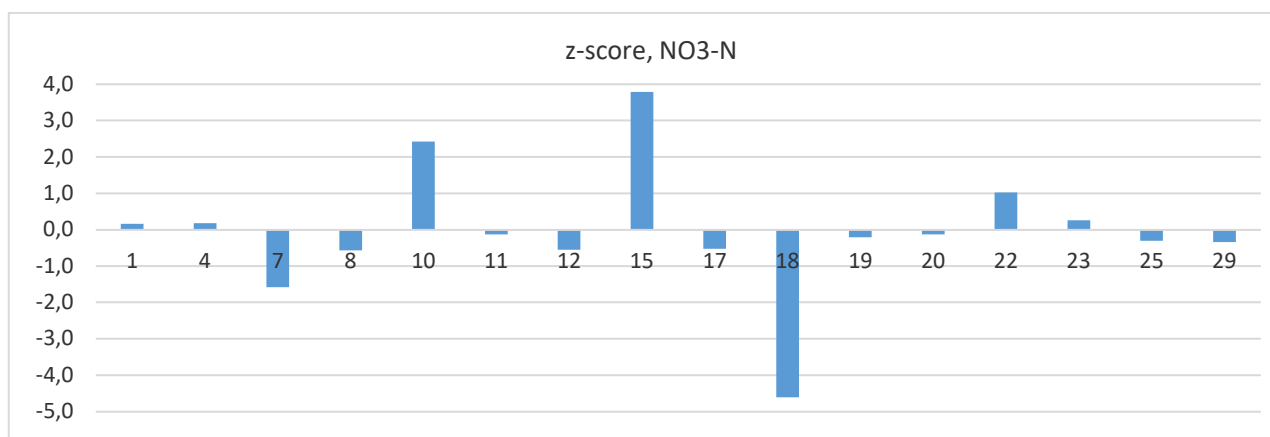
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	NO3-N A/B Waste Water
p	15
m [mg/L]	7.06
S(L) [mg/L]	0.33
S(r) [mg/L]	0.18
S(R) [mg/L]	0.38
r [mg/L]	0.50
R [mg/L]	1.1
CV(r) [%]	2.5
CV(R) [%]	5.3

4.3.2 NO₂-N

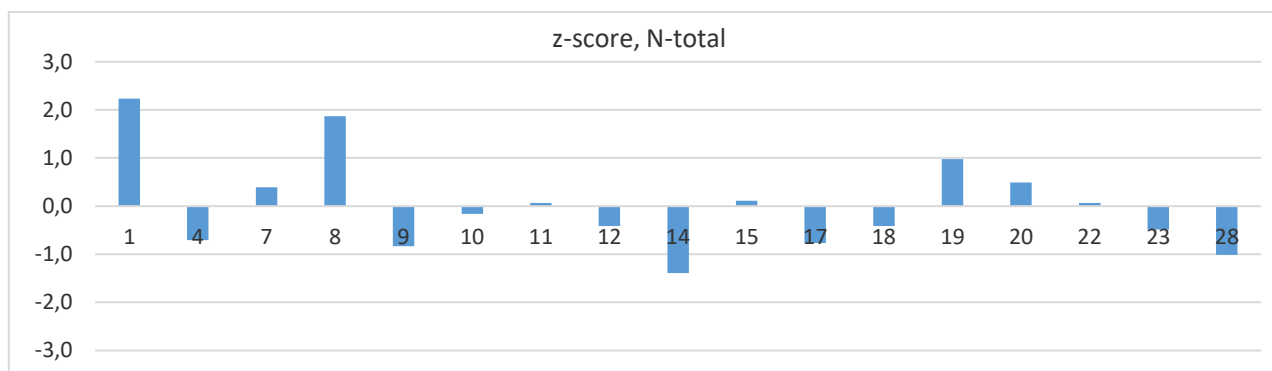| Component:	*NO2-N, mg/L*								
Assigned	**0.188**	**0.188**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Waste Water A**	**Waste Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.087	0.087							
4	0.420	0.419							
7	0.390	0.397							
8	0.086	0.085							
10	0.018	0.021							
11	0.056	0.065							
15	0.0055	0.0048							
17	0.359	0.361							
18	0.017	0.018							
19	0.370	0.374							
22	0.0037	0.0043							
23	0.434	0.433							
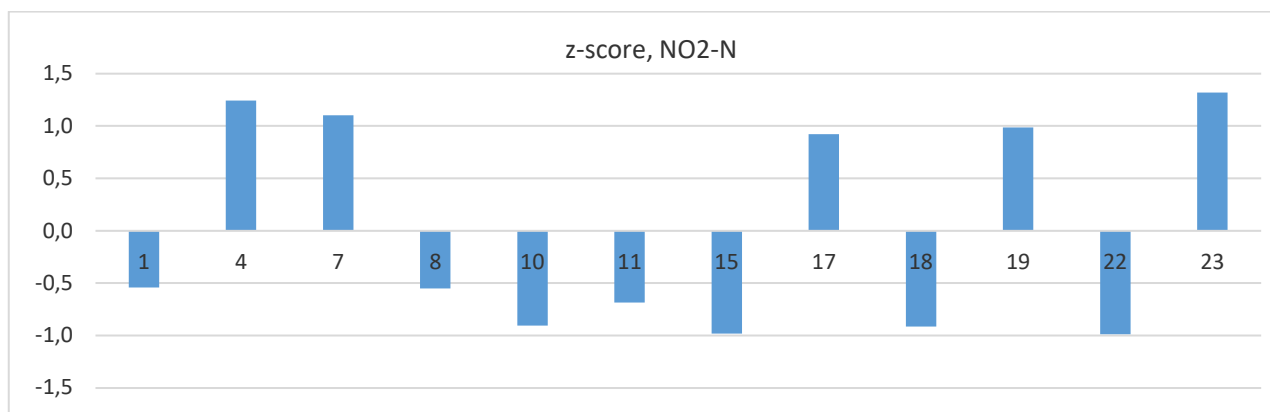
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	NO2-N A/B Waste Water
p	12
m [mg/L]	0.188
S(L) [mg/L]	0.186
S(r) [mg/L]	0.002
S(R) [mg/L]	0.186
r [mg/L]	0.007
R [mg/L]	0.5
CV(r) [%]	1.3
CV(R) [%]	99.0

4.3.3 NO₂₊₃

Component: *NO2+3-N, mg/L*

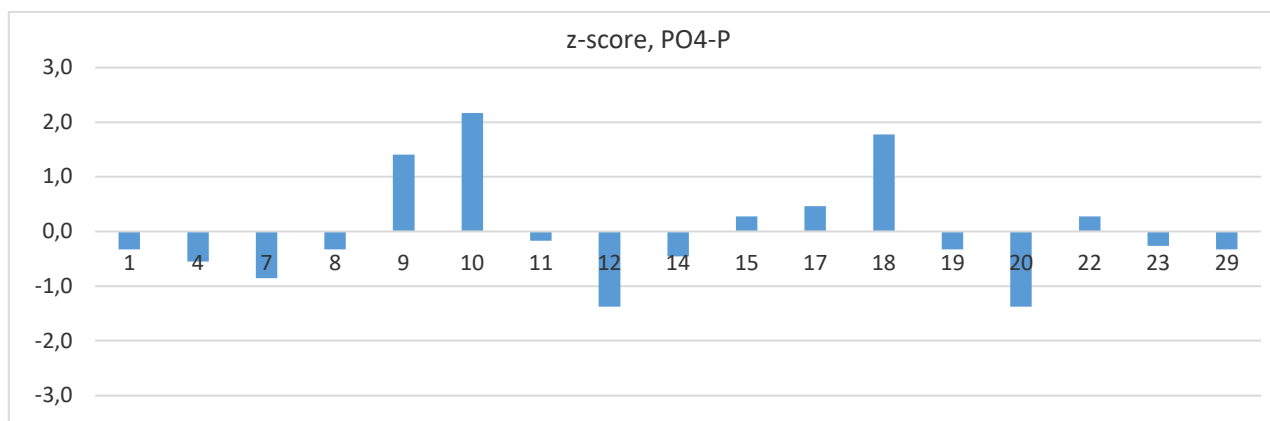| Assigned Laboratory code no.	7.29 Waste Water A	7.29 Waste Water B	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
			1% level	5% level	1% level	5% level	1% level	5% level	
1	7.14	7.29							
4	7.51	7.59							
7	6.89	6.84							
9	7.32	7.42							
11	7.31	6.83							
12	7.35	7.28							
14	7.20	7.19							
17	6.88	7.57		X					
18	6.08	6.00			X	X	-	-	X
19	7.37	7.37							
20	7.32	7.31							
22	7.40	7.50							
23	7.59	7.61							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	NO2+3-N A/B Waste Water
p	13
m [mg/L]	7.29
S(L) [mg/L]	0.15
S(r) [mg/L]	0.18
S(R) [mg/L]	0.24
r [mg/L]	0.51
R [mg/L]	0.7
CV(r) [%]	2.5
CV(R) [%]	3.3

4.3.4   N-total

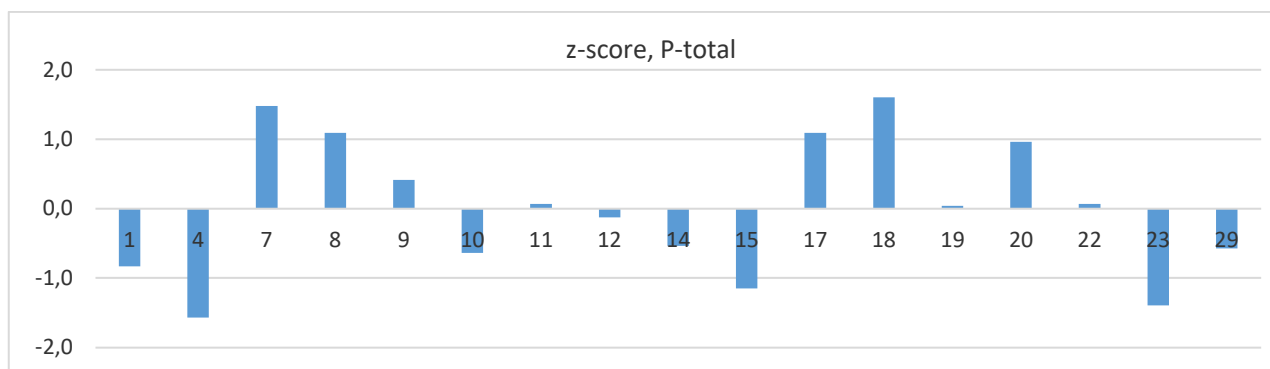| Assigned Laboratory code no.	11.9 Waste Water A	11.9 Waste Water B	Cochrans test 1% level	Cochrans test 5% level	Grupps single test 1% level	Grupps single test 5% level	Grupps double test 1% level	Grupps double test 5% level	Excluded in statistical analysis
Component: *N-total, mg/L*									
1	13.5	14.1							
4	11.5	11.2							
7	12.4	12.1							
8	14.0	13.0							
9	11.2	11.3							
10	11.8	11.8							
11	12.0	12.0							
12	11.6	11.6							
14	10.9	10.7							
15	12.5	11.6							
17	11.2	11.4							
18	11.7	11.5							
19	12.9	12.7							
20	12.3	12.4							
22	12.0	12.0							
23	11.6	11.4							
28	11.0	11.2							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	N-total A/B Waste Water
p	17
m [mg/L]	11.94
S(L) [mg/L]	0.79
S(r) [mg/L]	0.27
S(R) [mg/L]	0.83
r [mg/L]	0.75
R [mg/L]	2.3
CV(r) [%]	2.2
CV(R) [%]	7.0

4.3.5 PO₄-P

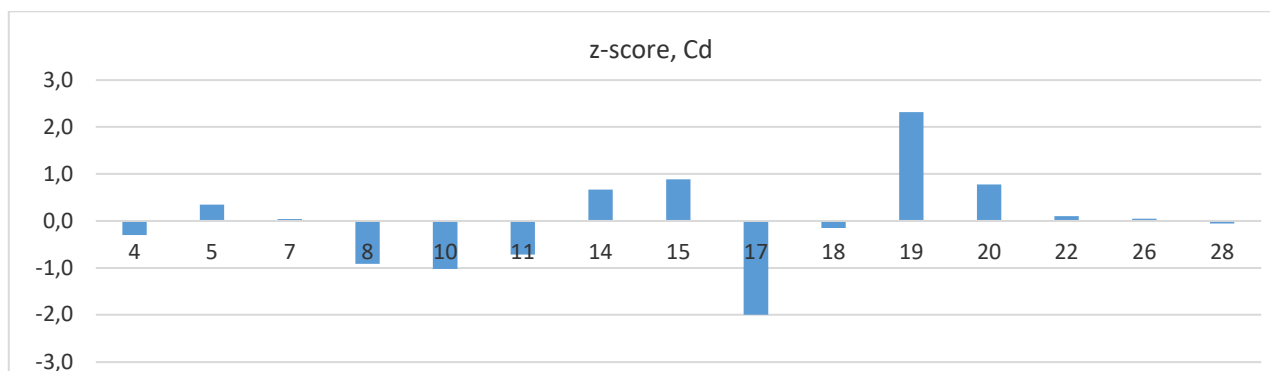| Component:	*PO4-P, mg/L*								
Assigned	**0.25**	**0.25**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Waste Water A**	**Waste Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.24	0.24							
4	0.24	0.23							
7	0.23	0.23							
8	0.24	0.24							
9	0.27	0.28							
10	0.29	0.29							
11	0.24	0.24							
12	0.22	0.22							
14	0.24	0.24							
15	0.25	0.25							
17	0.26	0.25							
18	0.28	0.28							
19	0.24	0.24							
20	0.22	0.22							
22	0.25	0.25							
23	0.24	0.25							
29	0.24	0.24							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	PO4-P A/B Waste Water
p	17
m [mg/L]	0.25
S(L) [mg/L]	0.02
S(r) [mg/L]	0.00
S(R) [mg/L]	0.02
r [mg/L]	0.01
R [mg/L]	0.1
CV(r) [%]	1.4
CV(R) [%]	7.7

4.3.6 P-total

Component:	*P-total, mg/L*								
Assigned	**0.55**	**0.55**	**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	0.52	0.51							
4	0.49	0.49							
7	0.59	0.62							
8	0.59	0.59							
9	0.56	0.57							
10	0.53	0.52							
11	0.55	0.55							
12	0.54	0.54							
14	0.52	0.53							
15	0.50	0.50							
17	0.58	0.60							
18	0.60	0.62							
19	0.55	0.55							
20	0.58	0.59							
22	0.54	0.56							
23	0.49	0.50							
29	0.52	0.53							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	P-total A/B Waste Water
p	17
m [mg/L]	0.55
S(L) [mg/L]	0.04
S(r) [mg/L]	0.01
S(R) [mg/L]	0.04
r [mg/L]	0.02
R [mg/L]	0.1
CV(r) [%]	1.4
CV(R) [%]	7.1

4.3.7   Cd

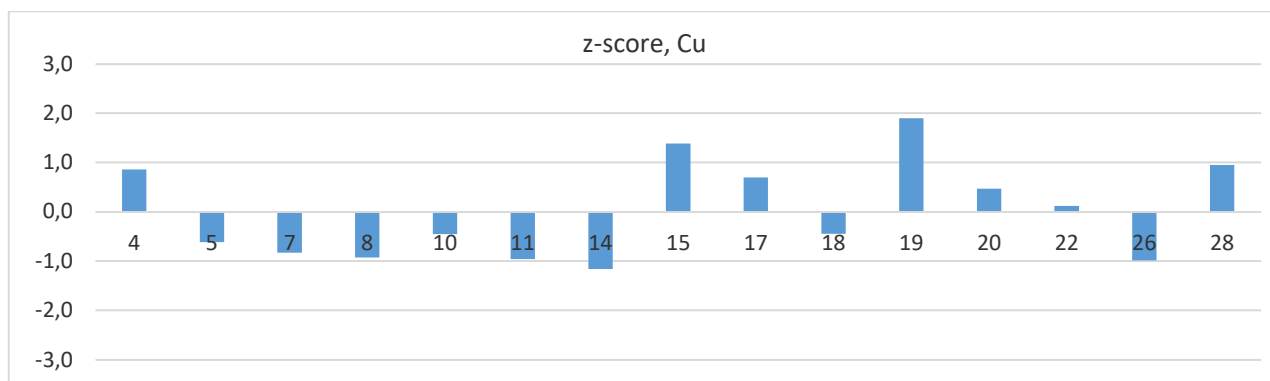| Component:	Cd, µg/L								
Assigned	**9.54**	**9.54**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Waste Water A**	**Waste Water B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
4	9.49	9.15							
5	9.76	9.82							
7	9.47	9.66							
8	8.71	9.05							
10	8.82	8.78							
11	9.01	9.03							
14	9.98	10.06							
15	10.10	10.25							
17	8.07	8.12							
18	9.42	9.44							
19	11.22	11.20							
20	10.20	10.00							
22	9.52	9.70							
26	9.61	9.53							
28	9.50	9.50							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Cd A/B Waste Water
p	15
m [µg/L]	9.54
S(L) [µg/L]	0.71
S(r) [µg/L]	0.12
S(R) [µg/L]	0.72
r [µg/L]	0.32
R [µg/L]	2.0
CV(r) [%]	1.2
CV(R) [%]	7.6

4.3.8   Cr

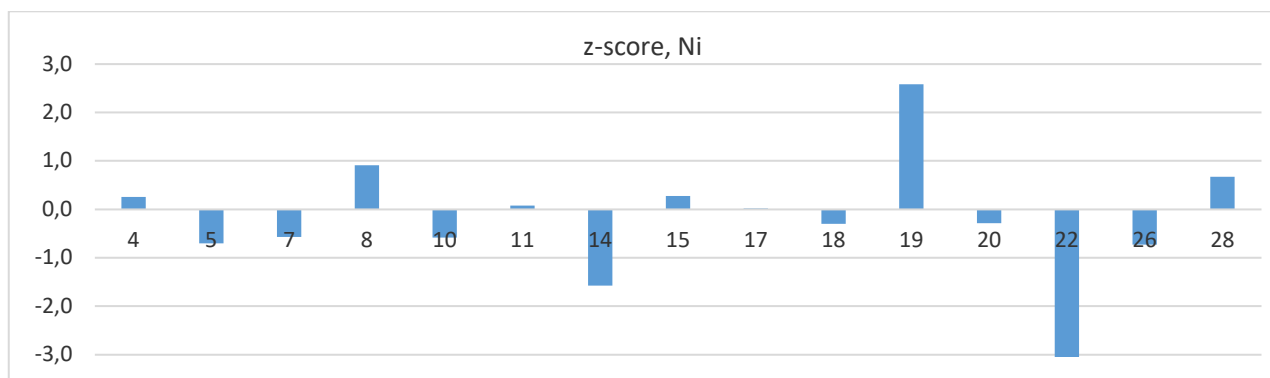| Component:	Cr, µg/L								
Assigned	45.8	45.8	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Waste Water A	Waste Water B	1% level	5% level	1% level	5% level	1% level	5% level	
4	47.8	47.1							
5	44.7	45.2							
7	43.7	44.1							
8	43.0	43.0							
10	46.8	46.7							
11	46.8	46.9							
14	42.5	42.6							
15	49.0	50.9	X	X	-	-	-	-	X
17	49.6	49.4							
18	44.0	44.4							
19	57.1	57.3			X	X	-	-	X
20	47.0	46.8							
22	44.9	45.1							
26	47.0	47.0							
28	47.0	47.0							
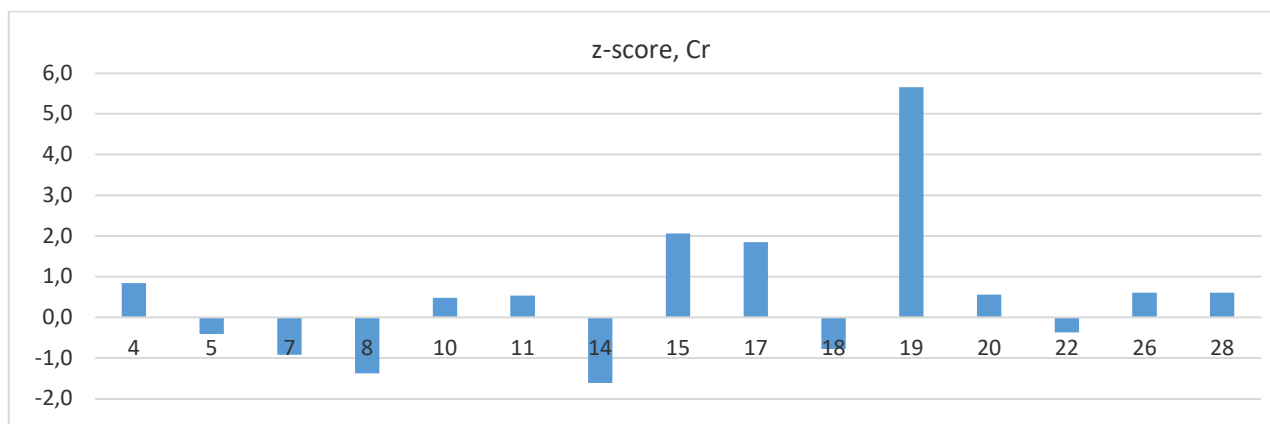
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Cr A/B Waste Water
p	15
m [µg/L]	45.78
S(L) [µg/L]	2.00
S(r) [µg/L]	0.23
S(R) [µg/L]	2.02
r [µg/L]	0.65
R [µg/L]	5.6
CV(r) [%]	0.5
CV(R) [%]	4.4

4.3.9   Cu

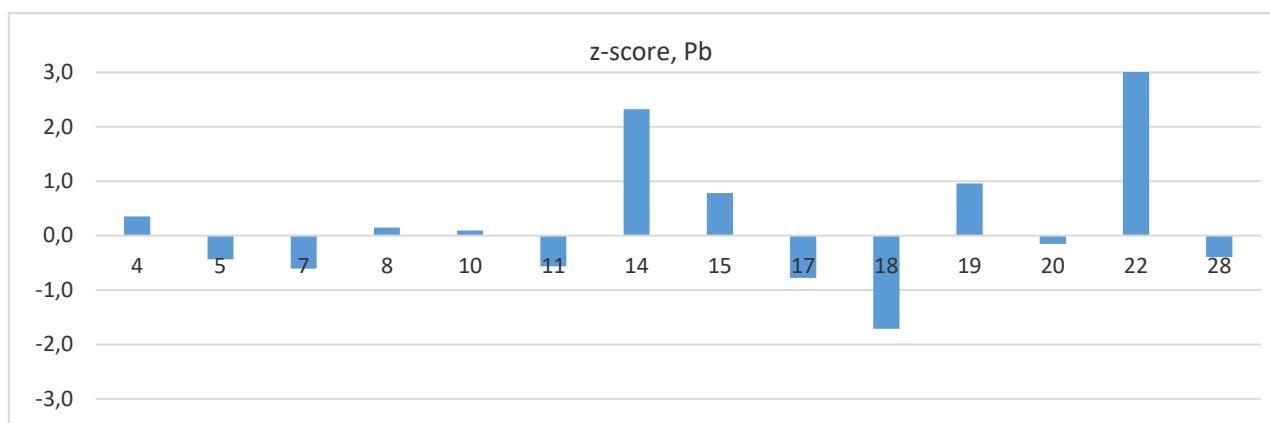| Component:	*Cu, µg/L*								
Assigned Laboratory code no.	93.39 Waste Water A	93.39 Waste Water B	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
			1% level	5% level	1% level	5% level	1% level	5% level	
4	95.74	101.95							
5	89.20	89.80							
7	87.80	88.50							
8	87.00	88.00							
10	91.00	90.00							
11	87.30	87.30							
14	85.50	86.58							
15	98.19	106.11		X					
17	97.70	97.90							
18	90.74	90.35							
19	104.71	106.14							
20	97.10	95.60							
22	93.90	94.40							
26	87.10	87.20							
28	99.50	99.30							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Cu A/B Waste Water
p	15
m [µg/L]	93.4
S(L) [µg/L]	6.08
S(r) [µg/L]	1.81
S(R) [µg/L]	6.34
r [µg/L]	5.06
R [µg/L]	17.8
CV(r) [%]	1.9
CV(R) [%]	6.8

4.3.10 Ni

Component:	*Ni, µg/L*								
Assigned	**11.84**	**11.84**	**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**	
4	12.28	11.82							
5	11.20	11.30							
7	11.25	11.47							
8	12.70	12.50							
10	11.40	11.30							
11	11.90	11.90							
14	10.07	10.97		X					
15	11.94	12.19							
17	12.10	11.60							
18	11.50	11.67							
19	13.85	14.15				X			
20	11.70	11.50							
22	2.30	2.30			X	X	-	-	X
26	11.23	11.22							
28	12.50	12.30							

Lab 22 out of range. Z-score=-11.4
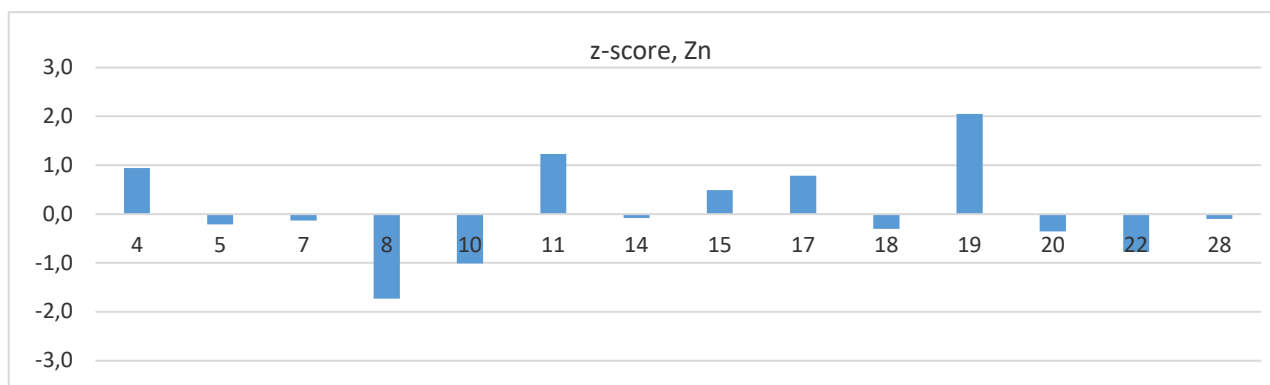
z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Ni A/B Waste Water
p	15
m [µg/L]	11.84
S(L) [µg/L]	0.80
S(r) [µg/L]	0.25
S(R) [µg/L]	0.84
r [µg/L]	0.70
R [µg/L]	2.3
CV(r) [%]	2.1
CV(R) [%]	7.1

4.3.11 Pb

Component: *Pb, µg/L*

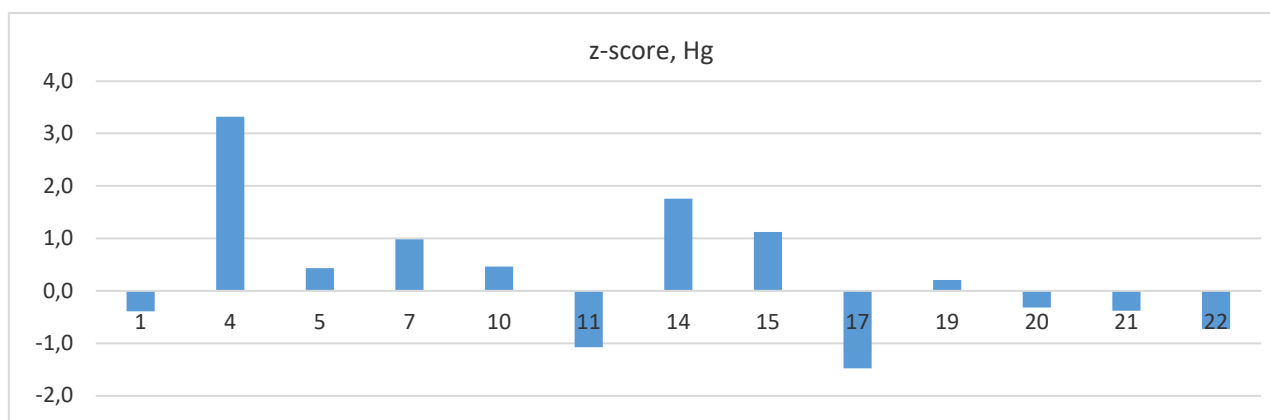| Assigned Laboratory code no.	9.88 Waste Water A	9.88 Waste Water B	Cochrans test 1% level	Cochrans test 5% level	Grupps single test 1% level	Grupps single test 5% level	Grupps double test 1% level	Grupps double test 5% level	Excluded in statistical analysis
4	10.21	10.13							
5	9.52	9.51							
7	9.41	9.34							
8	10.00	10.00							
10	10.00	9.91							
11	9.41	9.41							
14	11.82	11.78							
15	10.27	10.78							
17	9.17	9.30							
18	8.22	8.70							
19	10.73	10.60							
20	9.80	9.70							
22	21.80	21.07			X	X	-	-	X
28	9.20	9.90							

Lab 22 out of range. Z-score=14.0

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Pb A/B Waste Water
p	14
m [µg/L]	9.88
S(L) [µg/L]	0.80
S(r) [µg/L]	0.20
S(R) [µg/L]	0.83
r [µg/L]	0.55
R [µg/L]	2.3
CV(r) [%]	2.0
CV(R) [%]	8.4

4.3.12 Zn

Component:	Zn, µg/L								
Assigned	**106.3**	**106.3**	**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**	
4	110.8	113.6							
5	105.0	105.0							
7	105.0	106.0							
8	95.0	96.0							
10	100.0	100.0							
11	114.0	114.0							
14	107.0	104.6							
15	107.1	111.7		X					
17	116.0	106.4	X	X	-	-	-	-	X
18	104.7	104.1							
19	119.2	119.0							
20	104.5	103.7							
22	102.2	100.8							
28	105.7	105.7							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Zn A/B Waste Water
p	14
m [µg/L]	106.3
S(L) [µg/L]	6.12
S(r) [µg/L]	1.27
S(R) [µg/L]	6.25
r [µg/L]	3.55
R [µg/L]	17.5
CV(r) [%]	1.2
CV(R) [%]	5.9

4.3.13 Hg

Component:	Hg, µg/L								
Assigned	**6.24**	**6.24**	**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	5.60	6.40	X	X	-	-	-	-	X
4	10.21	6.37	X	X	-	-	-	-	X
5	6.47	6.55							
7	6.20	7.50	X	X	-	-	-	-	X
10	6.56	6.50							
11	5.57	5.59							
14	7.30	7.35							
15	6.80	7.07							
17	5.39	5.27							
19	6.44	6.30							
20	6.07	6.02							
21	6.03	5.99							
22	5.72	5.87							

z =|2| is satifactory, z =|2| -|3|is questionable and z >|3|is not acceptable

Statistical parameters	Hg A/B Waste Water
p	13
m [µg/L]	6.24
S(L) [µg/L]	0.61
S(r) [µg/L]	0.09
S(R) [µg/L]	0.62
r [µg/L]	0.25
R [µg/L]	1.7
CV(r) [%]	1.4
CV(R) [%]	9.9

5. Summary and conclusions

5.1 Summary of the intercalibration

The number of participating laboratories is 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.

Component	Freshwater Laboratories included in the statistics	Freshwater Laboratories excluded (</outlier)	Waste water Laboratories included in the statistics	Waste water Laboratories excluded (</outlier)
NO3-N, mg/L	16	0/2	12	0/3
NO2-N, mg/L	20	-	12	-
NO2+3-N, mg/L	14	-	12	0/1
N-total, mg/L	18	-	17	-
PO4-P, mg/L	21	-	17	-
P-total, mg/L	20	-	17	-
Cd, µg/L	18	0/1	15	-
Cr, µg/L	17	0/1	13	0/2
Cu, µg/L	18	0/1	15	-
Ni, µg/L	18	0/1	14	0/1
Pb, µg/L	14	2/2	13	0/1
Zn, µg/L	16	1/0	13	0/1
Hg, µg/L	11	0/2	10	0/3

Only a few laboratories have reported below DL/QL for Pb and Zn in freshwater, see table 5.2. In the PLC-8 intercalibration, all samples have been spiked in order to secure concentration levels at minimum 10 times the recommended detection limits from HELCOM.

A summary of the results from the PLC-8 intercalibration is shown in table 5.2 for freshwater and 5.3 for waste water.

Table 5.2. Freshwater. Mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation and recovery based on the C sample.

Freshwater Component	Mean conc. Sample A/B	S(R) Sample A/B	CV(R) (%) Sample A/B	Sample C recovery of spike
NO$_3$-N mg/L	0.77	0.06	8%	96%
NO$_2$-N mg/L	0.26	0.02	7%	98%
NO2+3	1.05	0.09	8%	100%
N-total mg/L	3.38	0.23	7%	105%
PO$_4$-P mg/L	0.20	0.01	6%	100%
P-total mg/L	0.28	0.02	6%	96%
Cd µg/L	1.66	0.18	11%	87%
Cr µg/L	3.39	0.24	7%	91%
Cu µg/L	9.77	1.03	11%	106%
Ni µg/L	15.19	1.29	8%	94%
Pb µg/L	1.71	0.10	6%	102%
Zn µg/L	27.24	2.11	8%	-
Hg µg/L	0.13	0.02	17%	94%

The recovery of Zn is not calculated as the recovery was high above 100% and it is concluded that there must have been an error in the spiking.

Table 5.3. Waste water. Mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation.

Waste water Component	Mean conc. Sample A/B	S(R) Sample A/B	CV(R) (%) Sample A/B
NO_3-N mg/L	7.06	0.38	5%
NO_2-N mg/L	0.19	0.19	99%
NO2+3	7.29	0.24	3%
N-total mg/L	11.94	0.83	7%
PO_4-P mg/L	0.25	0.02	8%
P-total mg/L	0.55	0.04	7%
Cd µg/L	9.54	0.72	8%
Cr µg/L	45.78	2.02	4%
Cu µg/L	93.39	6.34	7%
Ni µg/L	11.84	0.84	7%
Pb µg/L	9.88	0.83	8%
Zn µg/L	106.3	6.25	6%
Hg µg/L	6.24	0.62	10%

In general, the analytical quality is good and comparable between the laboratories with a few exceptions. For both freshwater and waste water, all components have low deviation, though Hg has a bit higher deviation in waste water and for freshwater and the recovery of Cd is a bit too low.

For NO_2-N in waste water (table 5.3), the samples were clearly unstable and cannot be used for the evaluation of the laboratories. The expected value based on the spiking was 0.8 mg/L, but the laboratories reported data in the range from 0.004-0.44 mg/L. The same was not the case for freshwater. For the freshwater, the average for the A/B samples from the laboratories was near the expected value based on the spiking at 0.25 mg/L. It is unclear what caused this instability in the waste water samples.

For comparison in relation to the analytical quality, the requirements in Danish Statutory Order no 1071 of 28/10/2019 on the analytical quality for environmental measurements from Ministry of Environment are shown in table 5.4.

Table 5.4. The requirements for analytical quality in the Danish Statutory Order no 1071 of 28/10/2019 on quality requirements for environmental analysis for freshwater and waste water. Note there are not requirements for all the components. DL: detection limit, Uabs: the absolute expanded uncertainty at low concentration levels and Urel: the relative expanded uncertainty at high concentration levels.

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%

It is not possible to directly compare table 5.2 and 5.3 with table 5.4 as data in table 5.2 and 5.3 are calculated across the laboratories, whereas table 5.4 shows requirements within each laboratory. However, the deviations in the intercalibration are in the same range as the requirements in Danish Statutory Order, indicating that the monitoring results in overall are reliable.

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.

Figure 5.1. z-score results for freshwater A/B samples, nutrients: z<|2|: 107 results; |3|<z<|2|: 3 results; z>|3|: 1 result. The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|.
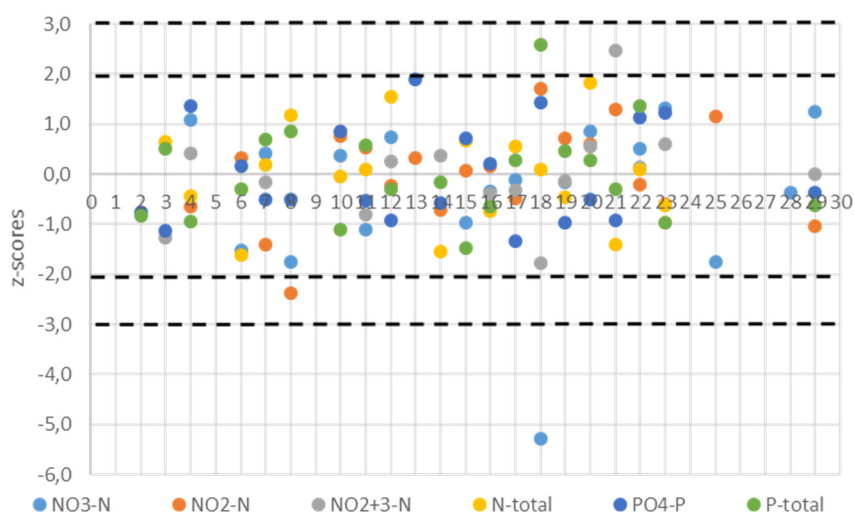
Figure 5.2. z-score results for freshwater, metals: z<|2|: 109 results; |3|<z<|2|: 7 results; z>|3|: 4 results. One z-score not shown (z-score 27.3 for Pb for lab 22). The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|.
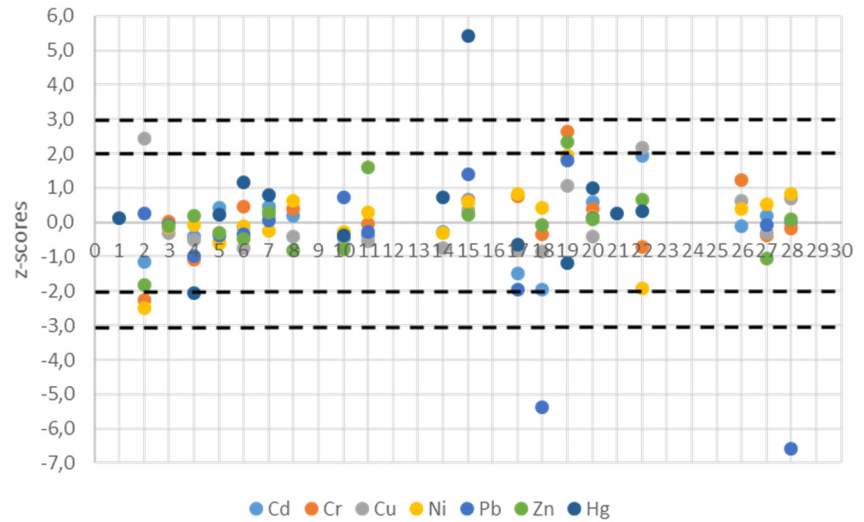

Figure 5.3. z-score results for waste water, nutrients: z<|2|: 85 results; |3|<z<|2|: 3 results; z>|3|: 3 results. The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|.
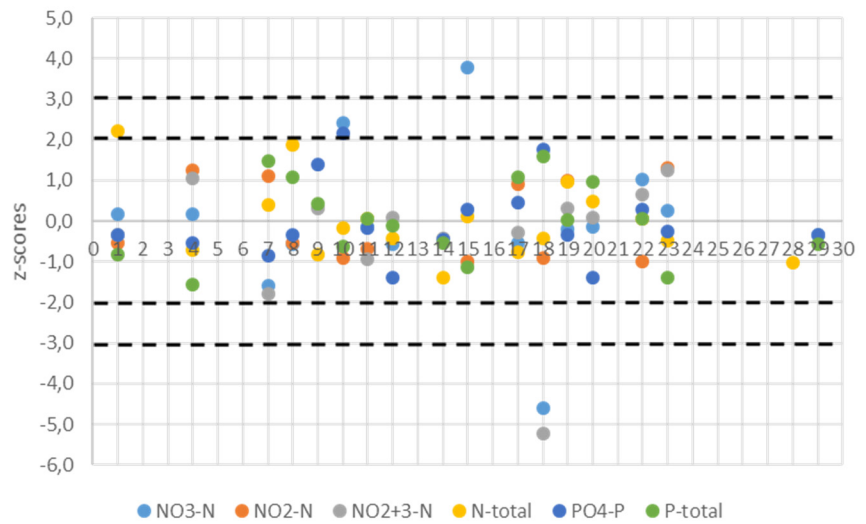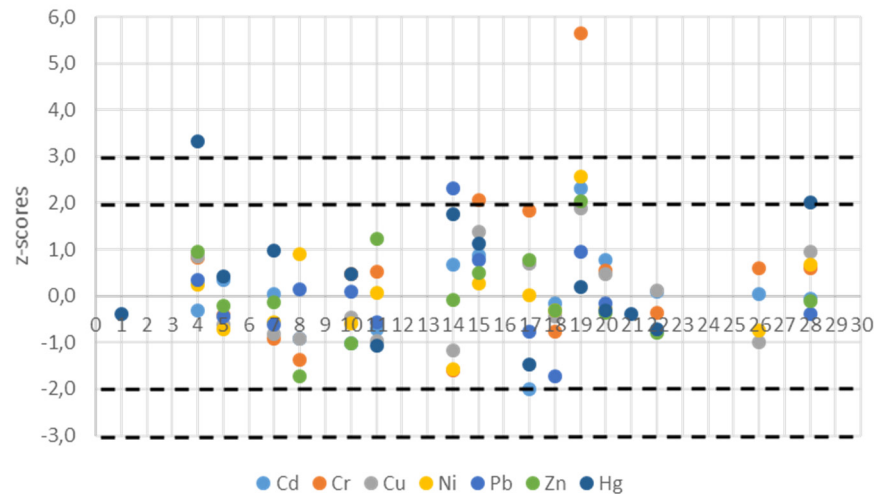

Figure 5.4. z-score results for waste water, metals: z<|2|: 94 results; |3|<z<|2|: 5 results; z>|3|: 4 results. Two z-scores not shown (z-score -11.4 for Ni and 14.0 for Pb for lab 22). The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|.

The results from the laboratories seem uniform. However, as z-scores are calculated from the total deviation of all results in 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 one data point in freshwater and two in waste water for metals are not shown in order to give a better visual comparison. These data points are outliers and are not included in the statistical analysis.

It appears that metals have higher deviation based on z-scores compared to nutrients. For freshwater 3.7% of z-scores were above z=|2| for nutrients and 10.7% for metals, whereas for waste water it was 7.1% for nutrients and 8.5% for metals.

5.3 Comparison PLC-6, PLC-7 and PLC-8

Table 5.5 and 5.6 show comparisons between the intercalibration PLC-6 in 2012, PLC-7 in 2018 and PLC-8 in 2021.

Table 5.5. A comparison of mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation freshwater for PLC-6 (2012), PLC-7 (2018) and PLC-8 (2021).

Component	Freshwater - 2021			Freshwater - 2018			Freshwater - 2012		
	Mean conc.	S(R)	CV(R)	Mean conc.	S(R)	CV(R)	Mean conc.	S(R)	CV(R)
NO_3-N mg/L	0.77	0.06	7.5%	1.56	0.05	3.2%	5.01	0.25	5.0%
NO_2-N mg/L	0.26	0.02	6.8%	0.036	0.006	16.7%	0.14	0.027	19.3%
N-total mg/L	3.38	0.23	6.7%	3.44	0.22	6.4%	6.04	0.32	5.3%
PO_4-P mg/L	0.20	0.01	6.1%	0.209	0.014	6.7%	0.028	0.009	32.1%
P-total mg/L	0.28	0.02	6.3%	0.361	0.019	5.3%	0.047	0.014	29.8%
Cd µg/L	1.66	0.18	10.9%	6.41	0.36	5.6%	0.312	0.031	9.9%
Cr µg/L	3.39	0.24	7.1%	11.67	1.28	11.0%	4.22	0.47	11.1%
Cu µg/L	9.77	1.03	10.6%	29.3	4.92	16.8%	6.84	1.19	17.4%
Ni µg/L	15.19	1.29	8.5%	51.04	3.33	6.5%	8.72	1.09	12.5%
Pb µg/L	1.71	0.10	6.0%	11.14	1.36	12.2%	3.00	0.3	10.0%
Zn µg/L	27.24	2.11	7.8%	77.16	7.22	9.4%	15.12	1.82	12.0%
Hg µg/L	0.13	0.02	17.4%	0.174	0.017	9.8%	0.023	0.01	43.5%

Table 5.6. A comparison of mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation waste water for PLC-6 (2012), PLC-7 (2018) and PLC-8 (2021).

Component	Waste water - 2021			Waste water - 2018			Waste water – 2012		
	Mean conc.	S(R)	CV(R)	Mean conc.	S(R)	CV(R)	Mean conc.	S(R)	CV(R)
NO_3-N mg/L	7.06	0.38	5.3%	6.13	0.39	6.4%	1.24	0.075	6.0%
NO_2-N mg/L	0.19	0.19	99.0%	0.045	0.005	11.1%	0.001	0.0005	50.0%
N-total mg/L	11.94	0.83	7.0%	7.23	0.34	4.7%	1.91	0.26	13.6%
PO_4-P mg/L	0.25	0.02	7.7%	0.010	0.003	30.0%	0.14	0.009	6.4%
P-total mg/L	0.55	0.04	7.1%	0.025	0.013	52.0%	0.166	0.02	12.0%
Cd µg/L	9.54	0.72	7.6%	23.87	1.22	5.1%	1.65	0.091	5.5%
Cr µg/L	45.78	2.02	4.4%	49.01	3.36	6.9%	10.24	1.05	10.3%
Cu µg/L	93.39	6.34	6.8%	142.4	8.3	5.8%	84.5	6.23	7.4%
Ni µg/L	11.84	0.84	7.1%	194.4	13	6.7%	28	2.65	9.5%
Pb µg/L	9.88	0.83	8.4%	8.59	1.62	18.9%	81.5	6.96	8.5%
Zn µg/L	106.3	6.25	5.9%	435.6	33.1	7.6%	94	6.11	6.5%
Hg µg/L	6.24	0.62	9.9%	0.385	0.045	11.7%	0.169	0.017	10.1%

In general, the analytical quality for most parameters appear to be quite stable over the years. Higher relative values of the total variation can be explained by lower concentrations.

NO_2 in waste water appears to be unstable. The same instability was not seen for freshwater. For PLC-6 and PLC-7, the concentrations of NO_2 were very low, but there were no indications of instability. The reason for the present instability is unclear.

Based on recommendation from PLC-7 both freshwater and waste water have been spiked for both nutrients and metals. This has given more data as almost none of the laboratories have reported data under the detection limits especially for nutrients in waste water. Further, the concentration levels have been reduced for some metals and a concentration range have been introduced as a guideline for the laboratories.

In PLC-7 freshwater, the samples for metals were not acidified. In PLC-8 the samples were acidified, which did improve the analytical quality except for Hg. Hg was acidified with HCl and it is possible that a higher acidification than 0.2% is needed.

The autoclavation of freshwater does not seem to have changed variations of the results from the laboratories compared to PLC-7, most likely because they analysed the samples quite fast after receiving them.

5.4   Recommendations for future intercalibration

The motivation for autoclavation of freshwater was to secure the stability of nutrients. However, this did not seem to change the variations for the results, so it could be considered not to do in future intercalibrations as it also changes the matrice. For waste water, it is necessary for safety reasons when transported.

Expect for Hg, the metals appeared stable with respect to acidification. It could be considered to use a higher percent acidification for Hg in order to keep it more stable under transport etc.

NO_2 were very unstable/inhomogenous in waste water. This was not the case for freshwater where the results from the laboratories showed fine homogeneity. It should be tested how to avoid this instability for future intercalibrations.

Appendix 1

List of participating laboratories

The ranking of the laboratories does not reflect the laboratory code numbers.

Country	Laboratory name
Denmark	ALS Danmark A/S
	Eurofins Miljø A/S
Estonia	Estonian Environmental Research Centre
Finland	Eurofins Environment Testing Finland Oy
	Finnish Environment Institute SYKE
	MetropoliLab Oy
Germany	Landeslabor Schleswig-Holstein
	Landesamt für Umwelt, Naturschutz und Geologie Mecklenburg-Vorpommen (LUNG-MV)
Latvia	LEGMC Laboratory
	Laboratory "Vides audits" Ltd
Lituania	Lithuanian Environmental Protection Agency, Environment Research Department: West Lithuania Environment Research division, Chemical Analysis Division.
Poland	GIOŚ Centralne Laboratorium Badawcze Oddział w Szczecinie, Pracownia w Szczecinie
	GIOŚ Centralne Laboratorium Badawcze Oddział w Szczecinie, Pracownia w Koszalinie
	GIOŚ, Centralne Laboratorium Badawcze, Oddział w Olsztynie, Pracownia w Olsztynie
	GIOŚ, Centralne Laboratorium Badawcze, Oddział w Olsztynie, Pracownia w Elblągu
	GIOŚ Centralne Laboratorium Badawcze Oddział w Gdańsku, Pracownia w Gdańsku
	GIOŚ Centralne Laboratorium Badawcze Oddział w Gdańsku, Pracownia w Słupsku
Russia	Environmental pollution monitoring laboratory (Kaliningrad Center for Hydro-meteorology and Environmental Monitoring – regional branch of FSBI "North-West AHEM")
	Laboratory of chemistry of surface and sea waters, St.Petersburg (environmental monitoring center of FSBI "North-West AHEM")
	Regional laboratory for analytical control and analysis of the "Baltvodkhoz" - branch of the FSBWI "Tsentrregionvodkhoz"
Sweden	Käppalaförbundet
	SLU-Swedish University of Agricultural Sciences

Appendix 2

The reported data from the laboratories

Intercalibration under PLC-8

Fresh water

Laboratory number: **1**

Table 1a

Componenets	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			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L	0.129	0.135	0.180

Intercalibration under PLC-8

Waste water

Laboratory number: **1**

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.05	7.2
NO2-N, mg/L	0.087	0.087
NO2+3-N, mg/L	7.14	7.29
N-total, mg/L	13.5	14.1
PO4-P, mg/L	0.24	0.24
P-total, mg/L	0.52	0.51
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L	5.6	6.4

Intercalibration under PLC-8
Fresh water

**Laboratory
number:** _____ **2**

Table 1a

Componenets	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	0,184±0,0018	0,190±0,0019	0,309±0,027
P-total, mg/L	0,266±0,021	0,256±0,020	0,425±0,031
Cd, µg/L	1,400±0,45	1,509±0,48	2,052±0,66
Cr, µg/L	2,84±0,74	2,87±0,75	4,09±1,06
Cu, µg/L	12,35±3,21	12,22±3,18	16,34±4,25
Ni, µg/L	11,83±3,08	12,19±3,17	17,02±4,42
Pb, µg/L	1,63±0,41	1,84±0,46	1,91±0,48
Zn, µg/L	23,30±7,92	23,53±8,00	41,21±14,01
Hg, µg/L			

Intercalibration under PLC-8
Fresh water

Laboratory number: _____ **3**

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L			
NO2+3-N, mg/L	0.937	0.943	1.53
N-total, mg/L	3.54	3.51	4.51
PO4-P, mg/L	0.183	0.182	0.252
P-total, mg/L	0.29	0.278	0.432
Cd, µg/L	1.7	1.6	2.4
Cr, µg/L	3.4	3.4	4.9
Cu, µg/L	9.4	9.5	14
Ni, µg/L	15	15	22
Pb, µg/L	1.7	1.7	2.4
Zn, µg/L	27	27	46
Hg, µg/L			

Intercalibration under PLC-8
Fresh water

**Laboratory
number:** _____ **4**

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	x	x	x
NO2-N, mg/L	x	x	x
NO2+3-N, mg/L	x	x	x
N-total, mg/L	x	x	x
PO4-P, mg/L	x	x	x
P-total, mg/L	x	x	x
Cd, µg/L	1.58	1.6	2.244
Cr, µg/L	3.17	3.1	4.42
Cu, µg/L	9.34	9.14	13.6
Ni, µg/L	15.26	14.94	20.38
Pb, µg/L	1.625	1.59	2.19
Zn, µg/L	28.07	27.16	45.38
Hg, µg/L	0.08	0.086	0.148

Intercalibration under PLC-8
Waste water

**Laboratory
number:** _____ **4**

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	x	x
NO2-N, mg/L	x	x
NO2+3-N, mg/L	x	x
N-total, mg/L	x	x
PO4-P, mg/L	x	x
P-total, mg/L	x	x
Cd, µg/L	9.49	9.15
Cr, µg/L	47.84	47.09
Cu, µg/L	95.74	101.95
Ni, µg/L	12.28	11.82
Pb, µg/L	10.21	10.13
Zn, µg/L	110.78	113.62
Hg, µg/L	10.21	6.37

Intercalibration under PLC-8
Fresh water

**Laboratory
number:** 4

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.8328	0.8342	
NO2-N, mg/L	0.2502	0.2508	
NO2+3-N, mg/L	1.083	1.085	
N-total, mg/L	3.269	3.288	
PO4-P, mg/L	0.212	0.2123	
P-total, mg/L	0.26028	0.25719	
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L			

Intercalibration under PLC-8
Waste water

**Laboratory
number:** 4

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.088	7.174
NO2-N, mg/L	0.4203	0.4189
NO2+3-N, mg/L	7.508	7.593
N-total, mg/L	11.5	11.21
PO4-P, mg/L	0.238	0.2335
P-total, mg/L	0.48637	0.486
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	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	1.74	1.74	2.51
Cr, µg/L	3.31	3.32	4.80
Cu, µg/L	9.20	9.13	14.0
Ni, µg/L	14.5	14.3	20.3
Pb, µg/L	1.67	1.67	2.33
Zn, µg/L	26.8	26.4	45.0
Hg, µg/L	0.134	0.134	0.219

Intercalibration under PLC-8
Waste water

Table 1b

Componenets	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	9.76	9.82
Cr, µg/L	44.7	45.2
Cu, µg/L	89.2	89.8
Ni, µg/L	11.2	11.3
Pb, µg/L	9.52	9.51
Zn, µg/L	105	105
Hg, µg/L	6.47	6.55

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.655	0.71	0.969
NO2-N, mg/L	0.265	0.27	0.44
NO2+3-N, mg/L			
N-total, mg/L	2.99	3.03	4.19
PO4-P, mg/L	0.198	0.198	0.285
P-total, mg/L	0.27	0.27	0.42
Cd, µg/L	1.64	1.63	2.37
Cr, µg/L	3.47	3.54	5.16
Cu, µg/L	8.97	9.06	14.17
Ni, µg/L	15.01	15.1	21.51
Pb, µg/L	1.67	1.68	2.37
Zn, µg/L	25.91	26.55	45.61
Hg, µg/L	0.157	0.154	0.237

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.79	0.80	1.30
NO2-N, mg/L	0.237	0.237	0.388
NO2+3-N, mg/L	1.03	1.04	1.64
N-total, mg/L	3.32	3.52	4.73
N-total, mg/L	3.49	3.44	4.54
PO4-P, mg/L	0.19	0.19	0.28
P-total, mg/L	0.29	0.28	0.43
Cd, µg/L	1.72	1.77	2.53
Cr, µg/L	3.43	3.48	4.89
Cu, µg/L	10.29	9.73	15.27
Ni, µg/L	14.54	15.22	22.10
Pb, µg/L	1.72	1.71	2.19
Zn, µg/L	28.2	27.5	46.8
Hg, µg/L	0.148	0.146	0.205

Intercalibration under PLC-8
Waste water

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	6.50	6.44
NO2-N, mg/L	0.390	0.397
NO2+3-N, mg/L	6.89	6.84
N-total, mg/L	12.40	12.14
PO4-P, mg/L	0.23	0.23
P-total, mg/L	0.59	0.62
Cd, µg/L	9.47	9.66
Cr, µg/L	43.70	44.13
Cu, µg/L	87.8	88.5
Ni, µg/L	11.25	11.47
Pb, µg/L	9.41	9.34
Zn, µg/L	105.0	106.0
Hg, µg/L	6.20	7.50

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.67	0.67	1.1
NO2-N, mg/L	0.21	0.23	0.37
NO2+3-N, mg/L	0.88	0.90	1.5
N-total, mg/L	3.6	3.7	4.8
PO4-P, mg/L	0.19	0.19	0.28
P-total, mg/L	0.29	0.29	0.43
Cd, µg/L	1.70	1.69	2.40
Cr, µg/L	3.51	3.46	5.03
Cu, µg/L	9.2	9.5	14.6
Ni, µg/L	16	16	22
Pb, µg/L	<5	<5	<5
Zn, µg/L	25	26	45
Hg, µg/L			

Intercalibration under PLC-8
Waste water

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	6.8	6.9
NO2-N, mg/L	0.086	0.085
NO2+3-N, mg/L	6.9	7.0
N-total, mg/L	14	13
PO4-P, mg/L	0.24	0.24
P-total, mg/L	0.59	0.59
Cd, µg/L	8.71	9.05
Cr, µg/L	43	43
Cu, µg/L	87	88
Ni, µg/L	12.7	12.5
Pb, µg/L	10	10
Zn, µg/L	95	96
Hg, µg/L		

Intercalibration under PLC-8
Waste water

Laboratory
number: 9

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L		
NO2-N, mg/L		
NO2+3-N, mg/L	7.32	7.42
N-total, mg/L	11.2	11.3
PO4-P, mg/L	0.268	0.278
P-total, mg/L	0.561	0.566
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.793	0.792	1.253
NO2-N, mg/L	0.283	0.268	0.444
NO2+3-N, mg/L			
N-total, mg/L	3.377	3.362	4.623
PO4-P, mg/L	0.207	0.205	0.314
P-total, mg/L	0.256	0.256	0.402
Cd, µg/L	1.59	1.57	2.25
Cr, µg/L	3.33	3.31	4.89
Cu, µg/L	9.1	9.05	14.1
Ni, µg/L	14.9	14.8	21.2
Pb, µg/L	1.81	1.76	2.39
Zn, µg/L	25.5	25.6	44.7
Hg, µg/L	0.117	0.124	0.157

Intercalibration under PLC-8
Waste water

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.946	8.008
NO2-N, mg/L	0.0184	0.0208
NO2+3-N, mg/L		
N-total, mg/L	11.78	11.84
PO4-P, mg/L	0.287	0.288
P-total, mg/L	0.526	0.519
Cd, µg/L	8.82	8.78
Cr, µg/L	46.8	46.7
Cu, µg/L	91	90
Ni, µg/L	11.4	11.3
Pb, µg/L	10	9.91
Zn, µg/L	100	100
Hg, µg/L	6.56	6.5

Intercalibration under PLC-8
Fresh water

Laboratory number: __11__

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.713	0.700	1.115
NO2-N, mg/L	0.270	0.273	0.470
NO2+3-N, mg/L	0.983	0.973	1.585
N-total, mg/L	3.4	3.4	4.7
PO4-P, mg/L	0.189	0.190	0.271
P-total, mg/L	0.29	0.28	0.43
Cd, µg/L	1.59	1.60	2.33
Cr, µg/L	3.33	3.44	5.04
Cu, µg/L	9.38	9.01	14.1
Ni, µg/L	15.6	15.5	21.8
Pb, µg/L	1.68	1.68	2.32
Zn, µg/L	30.7	30.5	50.5
Hg, µg/L	-	-	-

Intercalibration under PLC-8
Waste water

Laboratory number: __11__

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.26	6.77
NO2-N, mg/L	0.056	0.065
NO2+3-N, mg/L	7.31	6.83
N-total, mg/L	12	12
PO4-P, mg/L	0.244	0.242
P-total, mg/L	0.55	0.55
Cd, µg/L	9.01	9.03
Cr, µg/L	46.8	46.9
Cu, µg/L	87.3	87.3
Ni, µg/L	11.9	11.9
Pb, µg/L	9.41	9.41
Zn, µg/L	114	114
Hg, µg/L	5.57	5.59

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.826	0.801	1.21
NO2-N, mg/L	0.256	0.260	0.476
NO2+3-N, mg/L	1.08	1.06	1.68
N-total, mg/L	3.69	3.78	5.06
PO4-P, mg/L	0.18	0.190	0.27
P-total, mg/L	0.265	0.275	0.413
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L			

Intercalibration under PLC-8
Waste water

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	6.88	6.83
NO2-N, mg/L		
NO2+3-N, mg/L	7.35	7.28
N-total, mg/L	11.6	11.6
PO4-P, mg/L	0.22	0.22
P-total, mg/L	0.542	0.543
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC-8
Fresh water

Laboratory number: **13**

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L	0,266±0,015	0,269±0,015	0,428±0,015
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L	0,213±0,019	0,224±0,020	0,323±0,029
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 PLC-8
Fresh water

Table 1a

Componenets	Measured data I			Measured data II		
	Freshwater sample A	Freshwater sample B	Freshwater sample C	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L				0.844	0.844	1.243
NO2-N, mg/L	0.249	0.250	0.422	0.236	0.251	0.408
NO2+3-N, mg/L	1.082	1.078	1.752			
N-total, mg/L	3.02	3.04	4.03			
PO4-P, mg/L	0.189	0.189	0.275	0.191	0.192	0.279
P-total, mg/L	0.274	0.271	0.406	0.261	0.268	0.404
Cd, µg/L	1.60	1.62	2.38			
Cr, µg/L						
Cu, µg/L	9.24	8.73	13.04			
Ni, µg/L	14.61	14.99	20.66			
Pb, µg/L						
Zn, µg/L						
Hg, µg/L	0.145	0.147	0.199			

Intercalibration under PLC-8
Waste water

Table 1b

Componenets	Measured data I		Measured data II	
	Waste Water sample A	Waste Water sample B	Waste Water sample A	Waste Water sample B
NO3-N, mg/L			6.881	6.993
NO2-N, mg/L				
NO2+3-N, mg/L	7.20	7.19		
N-total, mg/L	10.89	10.68		
PO4-P, mg/L	0.236	0.239	0.238	0.242
P-total, mg/L	0.524	0.529	0.523	0.527
Cd, µg/L	9.98	10.06		
Cr, µg/L	42.48	42.58		
Cu, µg/L	85.50	86.58		
Ni, µg/L	10.07	10.97		
Pb, µg/L	11.82	11.78		
Zn, µg/L	107.0	104.6		
Hg, µg/L	7.30	7.35		

Intercalibration under PLC-8
Fresh water

Table 1a

	Measured data		
Componenets	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.716	0.714	1.138
NO2-N, mg/L	0.263	0.263	0.446
NO2+3-N, mg/L			
N-total, mg/L	3.561	3.502	4.473
PO4-P, mg/L	0.203	0.206	0.304
P-total, mg/L	0.249	0.250	0.371
Cd, µg/L	1.778	1.785	2.573
Cr, µg/L	3.539	3.552	5.261
Cu, µg/L	10.195	10.082	15.798
Ni, µg/L	15.971	15.911	22.576
Pb, µg/L	1.883	1.821	2.516
Zn, µg/L	27.005	28.438	46.979
Hg, µg/L	0.249	0.254	0.292

Intercalibration under PLC-8
Waste water

Table 1b

	Measured data	
Componenets	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.017	9.959
NO2-N, mg/L	0.0055	0.0048
NO2+3-N, mg/L		
N-total, mg/L	12.473	11.602
PO4-P, mg/L	0.253	0.250
P-total, mg/L	0.504	0.501
Cd, µg/L	10.103	10.252
Cr, µg/L	48.962	50.890
Cu, µg/L	98.191	106.105
Ni, µg/L	11.943	12.192
Pb, µg/L	10.271	10.780
Zn, µg/L	107.099	111.688
Hg, µg/L	6.802	7.069

Intercalibration under PLC-8
Fresh water

Laboratory number: **16**

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.739	0.762	
NO2-N, mg/L	0.265	0.265	
NO2+3-N, mg/L	1.00	1.03	
N-total, mg/L	3.18	3.24	
PO4-P, mg/L	0.197	0.200	
P-total, mg/L	0.265	0.263	
Cd, µg/L			2.28
Cr, µg/L			4.59
Cu, µg/L			13.8
Ni, µg/L			20.2
Pb, µg/L			2.24
Zn, µg/L			43.2
Hg, µg/L			0.037

Intercalibration under PLC-8
Fresh water

**Laboratory
number:** <u>17</u>

Table 1a

	Measured data		
Componenets	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.77	0.76	1.20
NO2-N, mg/L	0.252	0.255	0.417
NO2+3-N, mg/L	1.02	1.02	1.58
N-total, mg/L	3.55	3.46	4.98
PO4-P, mg/L	0.18	0.18	0.28
P-total, mg/L	0.28	0.28	0.42
Cd, µg/L	1.40	1.39	1.96
Cr, µg/L	3.50	3.65	5.16
Cu, µg/L	8.92	8.95	13.7
Ni, µg/L	16.4	16.1	24.8
Pb, µg/L	1.52	1.5	2.04
Zn, µg/L	<50	<50	54.5
Hg, µg/L	0.113	0.117	0.174

Intercalibration under PLC-8
Waste water

**Laboratory
number:** <u>17</u>

Table 1b

	Measured data	
Componenets	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	6.52	7.21
NO2-N, mg/L	0.359	0.361
NO2+3-N, mg/L	6.88	7.57
N-total, mg/L	11.24	11.37
PO4-P, mg/L	0.26	0.25
P-total, mg/L	0.58	0.60
Cd, µg/L	8.07	8.12
Cr, µg/L	49.6	49.4
Cu, µg/L	97.7	97.9
Ni, µg/L	12.1	11.6
Pb, µg/L	9.17	9.3
Zn, µg/L	116.0	106.4
Hg, µg/L	5.39	5.27

Intercalibration under PLC-8
Fresh water

Laboratory number: __18__

Table 1a

	Measured data		
Componenets	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.464	0.465	0.765
NO2-N, mg/L	0.292	0.292	0.476
NO2+3-N, mg/L	0.89	0.9	1.53
N-total, mg/L	3.4	3.4	4.6
PO4-P, mg/L	0.212	0.214	0.322
P-total, mg/L	0.31	0.33	0.48
Cd, µg/L	1.24	1.38	1.97
Cr, µg/L	3.35	3.27	4.77
Cu, µg/L	8.92	8.88	13.78
Ni, µg/L	15.72	15.75	21.59
Pb, µg/L	1.17	1.15	1.40
Zn, µg/L	27.12	27.05	47.1
Hg, µg/L			

Intercalibration under PLC-8
Waste water

Laboratory number: __18__

Table 1b

	Measured data	
Componenets	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	5.28	5.38
NO2-N, mg/L	0.017	0.018
NO2+3-N, mg/L	6.08	6.00
N-total, mg/L	11.7	11.5
PO4-P, mg/L	0.279	0.281
P-total, mg/L	0.60	0.62
Cd, µg/L	9.42	9.44
Cr, µg/L	44.0	44.4
Cu, µg/L	90.7	90.3
Ni, µg/L	11.5	11.7
Pb, µg/L	8.22	8.70
Zn, µg/L	104.7	104.1
Hg, µg/L		

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.761	0.763	1.195
NO2-N, mg/L	0.275	0.274	0.459
NO2+3-N, mg/L	1.036	1.037	1.653
N-total, mg/L	3.269	3.276	4.539
PO4-P, mg/L	0.185	0.184	0.266
P-total, mg/L	0.279	0.288	0.425
Cd, µg/L	2.013	2.009	2.900
Cr, µg/L	4.030	4.017	5.840
Cu, µg/L	10.892	10.84	16.776
Ni, µg/L	17.828	17.544	25.508
Pb, µg/L	1.897	1.891	2.654
Zn, µg/L	32.157	32.127	54.796
Hg, µg/L	0.103	0.102	0.124

Intercalibration under PLC-8
Waste water

**Laboratory
number:** <u>19</u>

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	6.959	7.013
NO2-N, mg/L	0.370	0.374
NO2+3-N, mg/L	7.369	7.374
N-total, mg/L	12.855	12.652
PO4-P, mg/L	0.240	0.240
P-total, mg/L	0.549	0.549
Cd, µg/L	11.215	11.200
Cr, µg/L	57.074	57.299
Cu, µg/L	104.71	106.14
Ni, µg/L	13.851	14.152
Pb, µg/L	10.731	10.605
Zn, µg/L	119.237	119.001
Hg, µg/L	6.443	6.299

Intercalibration under PLC-8
Fresh water

Laboratory number: **20**

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.82	0.82	1.28
NO2-N, mg/L	0.274	0.271	0.437
NO2+3-N, mg/L	1.09	1.10	1.72
N-total, mg/L	3.80	3.79	5.15
PO4-P, mg/L	0.19	0.19	0.27
P-total, mg/L	0.29	0.27	0.42
Cd, µg/L	1.77	1.77	2.57
Cr, µg/L	3.51	3.47	5.03
Cu, µg/L	9.4	9.3	14.4
Ni, µg/L	15.4	15.4	21.6
Pb, µg/L	1.72	1.72	2.38
Zn, µg/L	27.4	27.4	47.0
Hg, µg/L	0.153	0.151	0.20

Intercalibration under PLC-8
Waste water

Laboratory number: **20**

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.04	6.99
NO2-N, mg/L	-	-
NO2+3-N, mg/L	7.32	7.31
N-total, mg/L	12.3	12.4
PO4-P, mg/L	0.22	0.22
P-total, mg/L	0.58	0.59
Cd, µg/L	10.2	10.0
Cr, µg/L	47.0	46.8
Cu, µg/L	97.1	95.6
Ni, µg/L	11.7	11.5
Pb, µg/L	9.8	9.7
Zn, µg/L	104.5	103.7
Hg, µg/L	6.07	6.02

Intercalibration under PLC-8
Fresh water

Laboratory number: **21**

Table 1a

Componenets	Measured data 26-01-2021		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2-N, mg/L	0,29±0,096	0,28±0,096	0,48±0,096
NO2+3-N, mg/L	1,25±0,04	1,27±0,04	1,95±0,04
N-total, mg/L	3,03±0,04	3,09±0,04	3,99±0,04
PO4-P, mg/L	0,18±0,014	0,19±0,015	0,27±0,021
P-total, mg/L	0,27±0,016	0,27±0,016	0,40±0,023
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L	0,13 ± 0,014	0,14 ± 0,015	0,19 ± 0,021

Intercalibration under PLC-8
Waste water

Laboratory number: **21**

Table 1b

Componenets	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		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L	6,03 ± 0,66	5,99 ± 0,66

Intercalibration under PLC-8
Fresh water

Laboratory number: 22

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.80	0.80	1.26
NO2-N, mg/L	0.258	0.259	0.43
NO2+3-N, mg/L	1.06	1.06	1.69
N-total, mg/L	3.4	3.4	4.5
PO4-P, mg/L	0.205	0.214	0.299
P-total, mg/L	0.295	0.302	0.43
Cd, µg/L	2.00	2.03	2.83
Cr, µg/L	3.24	3.21	4.71
Cu, µg/L	11.7	12.3	18.0
Ni, µg/L	12.51	12.97	18.14
Pb, µg/L	4.74	4.28	5.89
Zn, µg/L	27.77	29.47	47.74
Hg, µg/L	0.149	0.124	0.199

Intercalibration under PLC-8
Waste water

Laboratory number: 22

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.4	7.5
NO2-N, mg/L	0.0037	0.0043
NO2+3-N, mg/L	7.4	7.5
N-total, mg/L	12.0	12.0
PO4-P, mg/L	0.248	0.255
P-total, mg/L	0.54	0.56
Cd, µg/L	9.52	9.70
Cr, µg/L	44.94	45.12
Cu, µg/L	93.9	94.4
Ni, µg/L	2.30	2.30
Pb, µg/L	21.80	21.07
Zn, µg/L	102.17	100.75
Hg, µg/L	5.722	5.869

Intercalibration under PLC-8
Fresh water

Laboratory number: 23

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.8441	0.8512	1.361
NO2-N, mg/L	0.2489	0.2538	0.4364
NO2+3-N, mg/L	1.093	1.105	1.797
N-total, mg/L	3.253	3.226	4.429
PO4-P, mg/L	0.2069	0.2141	0.284
P-total, mg/L	0.25872	0.25834	0.39933
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L			

Intercalibration under PLC-8
Waste water

Laboratory number: 23

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L	7.151	7.173
NO2-N, mg/L	0.4344	0.4326
NO2+3-N, mg/L	7.585	7.606
N-total, mg/L	11.62	11.45
PO4-P, mg/L	0.2371	0.2454
P-total, mg/L	0.49088	0.49507
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC-8
Fresh water

Laboratory number: 25

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.66	0.68	1.22
NO2-N, mg/L	0.283	0.282	0.465
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L			
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 PLC-8
Waste water

Laboratory number: 25

Table 1b

Componenets	Measured data	
	Waste Water sample A	Waste Water sample B
NO3-N, mg/L		6.95
NO2-N, mg/L		
NO2+3-N, mg/L		
N-total, mg/L		
PO4-P, mg/L		
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 PLC-8
Fresh water

Laboratory number: **26**

Table 1a

Componenets	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			
N-total, mg/L			
PO4-P, mg/L			
P-total, mg/L			
Cd, µg/L	1.8	1.49	2.25
Cr, µg/L	3.93	3.45	4.93
Cu, µg/L	11.07	9.78	13.99
Ni, µg/L	16.78	14.65	20.63
Pb, µg/L			
Zn, µg/L			
Hg, µg/L			

Intercalibration under PLC-8
Waste water

Laboratory number: **26**

Table 1b

Componenets	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	9.61	9.53
Cr, µg/L	47.00	47
Cu, µg/L	87.1	87.2
Ni, µg/L	11.23	11.22
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC-8
Fresh water

Table 1a

Componenets	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	1.7	1.7	2.4
Cr, µg/L	3.3	3.3	4.7
Cu, µg/L	9.5	9.4	14.6
Ni, µg/L	15.9	15.8	21.0
Pb, µg/L	1.7	1.7	2.2
Zn, µg/L	24.6	25.4	43.2
Hg, µg/L			

Intercalibration under PLC-8
Fresh water

Laboratory number: __28__

Table 1a

Componenets	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.74	0.76	1.20
NO2-N, mg/L			
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L			
P-total, mg/L			
Cd, µg/L	1.68	1.64	2.41
Cr, µg/L	3.40	3.30	4.92
Cu, µg/L	10.5	10.5	16.1
Ni, µg/L	16.2	16.3	23.0
Pb, µg/L	2.07	<2	2.38
Zn, µg/L	27.4	27.5	46.8
Hg, µg/L			

Intercalibration under PLC-8
Waste water

Laboratory number: __28__

Table 1b

Componenets	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	11.0	11.2
PO4-P, mg/L		
P-total, mg/L		
Cd, µg/L	9.5	9.5
Cr, µg/L	47.0	47.0
Cu, µg/L	99.5	99.3
Ni, µg/L	12.5	12.3
Pb, µg/L	9.2	9.9
Zn, µg/L	105.7	105.7
Hg, µg/L		

REPORT ON THE HELCOM PLC-8 INTERCALIBRATION

This report presents results from the PLC-8 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. 22 laboratories participated in the intercalibration.