REPORT ON THE HELCOM PLC-9 INTERCALIBRATION ON HEAVY METALS AND NUTRIENTS

Technical Report from DCE – Danish Centre for Environment and Energy No. 362 2025

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

REPORT ON THE HELCOM PLC-9 INTERCALIBRATION ON HEAVY METALS AND NUTRIENTS

Technical Report from DCE – Danish Centre for Environment and Energy No. 362 2025

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

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

AARHUS
UNIVERSITY
DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

Data sheet

Series title and no.:	Technical Report from DCE – Danish Centre for Environment and Energy No. 362
Category:	Scientific advisory report
Title:	Report on the HELCOM PLC-9 intercalibration on heavy metals and nutrients
Authors: Institutions:	Pia Lassen and Martin M. Larsen Aarhus University, Department of Environmental Science and Department of Ecoscience
Publisher: URL:	Aarhus University, DCE – Danish Centre for Environment and Energy © http://dce.au.dk/en
Year of publication: Editing completed:	December 2025 December 2025
Referee:	HELCOM PLC-9 Expert Group
Quality assurance, DCE:	Iben Kongsfelt og Lars M. Svendsen
Financial support:	Helsinki Commission (HELCOM)
Please cite as:	Lassen, P. and Larsen, M.M. 2025. Report on the HELCOM PLC-9 intercalibration on heavy metals and nutrients. Aarhus University, DCE – Danish Centre for Environment and Energy, 101 pp. Technical Report No. 362

Abstract:	This report presents results from the PLC-9 intercalibration on metals and nutrients in freshwater and wastewater. The intercalibration was performed to evaluate the analytical quality of results reported to HELCOM. 17 laboratories participated in the intercalibration.

Keywords:	HELCOM PLC-9 intercalibration, wastewater, freshwater, nutrients, metals
Layout:	Majbritt Pedersen-Ulrich
Front page photo:	Pia Lassen
ISBN: ISSN (electronic):	978-87-7648-013-4 2244-999X
Number of pages:	101

Contents

Preface

The Danish Centre for Environment and Energy, (DCE), Aarhus University has performed an intercalibration on nutrients and heavy metals as a task under the HELCOM PLC-9 project in freshwater and wastewater to evaluate the analytical quality of the data reported by countries to the HELCOM PLC-9 project.

A draft of the report was discussed and commented by the PLC-9 project at IC PLC-9 IG3-2025 in September 2025. The final draft was sent to the SOURCE to Sea working group, and WG Source to Sea 6-2025 in October 2025 and approved for being published also as a HELCOM report.

The intercalibration was financed by HELCOM and in-kind contribution from The Danish Ministry of Environment and Gender Equality and DCE, Aarhus University. The participating laboratories have financed the analyses they have performed by themselves.

1 Description of the intercalibration

The HELCOM Ninth Baltic Sea Pollution Load Compilation Project (PLC-9) includes an intercalibration of chemical analyses as part of the quality assurance of waterborne inputs of nutrients and selected heavy metals to the Baltic Sea. Analyses were conducted on freshwater and wastewater samples 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 wastewater samples were filtered and the wastewater sterilized.

Further, to make sure that as many laboratories as possible could report data, all samples were spiked to be above the detection limit. This implies that the concentration levels do not necessarily reflect the natural concentration levels in rivers and lakes, and in wastewater 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-9 intercalibration on metal and nutrients in freshwater and wastewater. There are reported results from 17 laboratories. One laboratory participated with an additional method. The participating laboratories are listed in appendix 1. Not all laboratories have reported data for all components. The following components are included in the intercalibration:

Nutrients: NO_3, NO_{2+3}, N-total, PO_4, and P-total.

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

As NO_2 has shown instability in the previous intercalibrations, the PLC-9 group decided not to include this component in the present intercalibration.

The original data from the laboratories can be found in appendix 2. Each laboratory was given a random code number to secure the anonymity of the laboratories. The ranking of laboratories in appendix 1 does not reflect the code numbers.

The laboratories were instructed 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 (2022).

In chapter 3 the statistical evaluation presents the data of the single laboratories for the relative standard deviation and the deviation from assigned value and z-score. Chapter 4 present outlier test, z-score plots and summary of statistical parameters for each component. The table below includes a summary

of the statistical parameters used in this report. They are described in further details in the relevant chapters.

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 are 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 significant different from the mean of all laboratories with respect to the deviation of the intercalibration
Grubb's double outlier test	The Grubb's double outlier test is performed on the two most extreme (highest and / or lowest) test pairs but after the same principle as above.
z-score	The Z score is shown visually for each component across the laboratories
Summary statistical parameters	
p: Number of laboratories	Number of laboratories included in the statistics. Outliers are excluded
m: mean value	The mean value of the laboratories' results without outliers. m is used as assigned value in the intercalibration
S(L): Laboratory deviation	The deviation between the laboratories
S(r): repeatability	The deviation between test pairs for all laboratories
S(R): reproducibility	Total deviation for the intercalibration. $S(R)^2 = (S(L)^2+S(r)^2$
r: Repeatability limit	The value equal to or below which the absolute difference between test pairs that may be expected to occur with a probability of 95% (r = S(r)*2.8)
R: Reproducibility limit	The value equal to or below which the absolute difference between two laboratories may be expected to occur with a probability of 95% (R = S(R)*2.8)
CV(r): Coefficient of laboratory variation	The relative value (in %) of repeatability. S(r)
CV(R): Coefficient of total variation	The relative value (in %) of reproducibility. S(R). the total derivation

2 Preparation of the samples

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

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

Wastewater and freshwater samples were filtered. Wastewater was autoclaved. Metal samples were conserved with nitric acid (0.2%). Hg samples were conserved with HCl (0.5%). Nutrient samples were not conserved. All samples were stored at 5°C until distribution.

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. Because of a calculation error, Zn was not spiked in a higher concentration for the C samples.

Wastewater 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.

Samples were sent with DSV as courier. The transportation time varied from two to eight days. The samples were sent out the 28th of April. The laboratories had approximately 2-3 weeks for the analysis until 21st of May. Laboratory no. 2 did not receive the samples, and a new set of samples were sent on the 8th of May, these were received on the 13th. Despite the late arrival of the samples, the laboratory managed to report within the deadline.

2.1 Comments from the laboratories and other remarks

Following comments were received from the laboratories either during the analysis or as comments to the draft statistically report.

A few laboratories remarked that the samples were at room temperature when received.

Laboratory no. 9: Unfortunately, I have found typos for some results (all results for Lead and 2 for Cadmium).

Laboratory no. 12: We have mixed up the samples for nutrients and metals for sample B, wastewater, due to our strange results.

Other remarks: The transportation time of the samples to some of the laboratories were up to eight days which was longer than the previous PLC intercalibrations. However, the results did not seem to be affected by this, as there appeared to be no connection between the results from the laboratories and the transportation time.

2.2 Stability and homogeneity

2.2.1 Samples for metals

Stability and homogeneity of freshwater and wastewater samples for metals were tested in Denmark by DCE. 3-6 samples were analysed each time. Hg was analysed using a Hg-AFS detector in accordance with US-EPA method 1631; other metals were analysed by ICP-MS.

The metal samples were analysed two times, six samples as test for homogeneity at the same time as the samples were sent out to the laboratories and three samples approximately three weeks later for stability. By mistake the homogeneity for Hg in freshwater AB were only tested for 3 samples. The stability data for metals and Hg showed an error in the analysis, as only a tenth of the concentration was detected. The samples were reanalysed again but nearly four months later by DCE.

Table 2.1. Stability and homogeneity for metals in freshwater A/B samples analysed by DCE. For the stability the reanalysed data are shown.

		Homogeneity		Stability	
Freshwater A/B	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss
Cd µg/L	1.37	0.013	0.9%	1.22	11%
Cr µg/L	6.59	0.061	0.9%	6.07	8%
Cu µg/L	13.02	0.156	1.2%	12.36	5%
Ni µg/L	2.13	0.046	2.1%	2.01	5%
Pb µg/L	1.64	0.184	11.2%	1.40	14%
Zn µg/L	25.65	0.195	0.8%	22.17	14%
Hg µg/L	0.077	0.007	9.2%	nd	nd

Table 2.2. Stability and homogeneity for metals in freshwater C samples analysed by DCE. For the stability the reanalysed data are shown.

		Homogeneity		Stability	
Freshwater c	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss
Cd µg/L	1.94	0.028	1.4%	1.22	11%
Cr µg/L	9.15	0.098	1.1%	6.07	8%
Cu µg/L	17.60	0.282	1.6%	12.36	5%
Ni µg/L	2.56	0.040	1.6%	2.01	5%
Pb µg/L	1.80	0.015	0.8%	1.40	14%
Zn µg/L	24.13	0.253	1.0%	22.17	14%
Hg µg/L	0.121	0.012	9.6%	nd	nd

Table 2.3. Stability and homogeneity for metals in wastewater A/B samples analysed by DCE. For the stability the reanalysed data are shown.

		Homogeneity		Stability	
Wastewater A/B	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss
Cd µg/L	5.07	0.070	1.4%	4.59	10%
Cr µg/L	10.94	0.161	1.5%	10.05	8%
Cu µg/L	23.78	0.286	1.2%	22.28	6%
Ni µg/L	41.42	0.291	0.7%	39.03	6%
Pb µg/L	1.73	0.015	0.9%	1.59	8%
Zn µg/L	83.63	0.812	1.0%	72.19	14%
Hg µg/L	1.157	0.013	1.1%	1.08	7%

The samples for the metal and Hg analysis are homogenous.

The stability tests showed minor loss or instability, however, the stability tests were performed approximately four months later. It should also be noted that Hg is stable in the wastewater samples, which is not always the case.

However, based on the results from the laboratories, the metals and Hg samples were considered stable within the timeframe where the laboratories performed the analysis.

2.2.1 Samples used for nutrients

Stability and homogeneity of freshwater and wastewater samples for nutrients were tested in Denmark by DCE. 3-6 samples were analysed each time.

The nutrient samples were analysed twice: first, six samples were tested for homogeneity at the time of dispatch to the laboratories; subsequently, three samples were analysed approximately three weeks later to assess stability. 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.

Table 2.4 Stability and homogeneity for nutrients in freshwater A/B samples analysed by DCE.

		Homogeneity		Stability	
Freshwater A/B	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss
NO_3-N mg/L	0.64	0.010	1.6%	0.65	-0.4%
N-total mg/L	2.20	0.011	0.5%	2.39	-8.5%
PO_4-P mg/L	0.36	0.001	0.3%	0.37	-2.5%

Table 2.5. Stability and homogeneity for nutrients in freshwater C samples analysed by DCE.

		Homogeneity		Stability	
Freshwater C	Measured conc.	Standard deviation	Rel. deviation	Measured conc. for stability	%Loss
NO_3-N mg/L	1.18	0.008	0.7%	1.17	0.7%
N-total mg/L	2.96	0.017	0.6%	2.68	9.4%
PO_4-P mg/L	0.48	0.001	0.2%	0.48	0.1%

Table 2.6. Stability and homogeneity for nutrients in wastewater 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.

	Homogeneity			Stability	
Wastewater A/B	**Measured conc.**	**Standard deviation**	**Rel. deviation**	**Measured conc. for stability**	**%Loss**
NO_3-N mg/L	2.65	0.046	1.7%	2.60	1.9%
N-total mg/L	6.85	0.047	0.7%	6.71	2.1%
PO_4-P mg/L	0.56	0.004	0.6%	0.55	0.9%

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

3 Laboratory results for the statistical analysis

3.1 Description of the tables

The results for the single laboratories are shown for freshwater (section 3.2) and wastewater (section 3.3). Not all laboratories analysed all samples. Only tables with reported data are shown for the single laboratories. There is no evaluation of the data from the single laboratories in this chapter, but comments from laboratories, which were received after submission of data, are inserted together with the results of the laboratory.

The following terms are used in the tables:

Measured values are the results from the laboratory.

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

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

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

RSD % is the relative deviation between test pairs (sample A and B) reported by the laboratories.

Z-score is a simple way to evaluate the results of the single laboratories in the based on the uncertainty of the intercalibration. For z-scores between -2 and 2 the result is regarded satisfactory. From -3 to -2 and 2 to 3 is regarded as questionable results. Z-scores below -3 and higher than 3 are regarded as not acceptable results. Z-scores are calculated by the following equation (according to ISO 13528:2022):

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

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

3.2 Freshwater

Laboratory								
Code no:	1							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.58	0.59	0.60	0.60	0.59	-2.3	1.2	-0.8
NO2+3-N, mg/L	0.59	0.59	0.61	0.61	0.59	-2.5	0.0	-0.9
N-total, mg/L	2.35	2.36	2.23	2.23	2.36	5.6	0.3	0.8
PO4-P, mg/L	0.40	0.41	0.39	0.39	0.40	2.9	0.9	0.9
P-total, mg/L	0.46	0.46	0.43	0.43	0.46	7.0	0.0	1.5
Cd, µg/L	1.38	1.38	1.40	1.40	1.38	-1.4	0.0	-0.3
Cr, µg/L	6.59	6.80	6.67	6.67	6.70	0.4	2.2	0.2
Cu, µg/L	13.95	13.82	13.84	13.84	13.89	0.3	0.7	0.1
Ni, µg/L	2.23	2.13	2.25	2.25	2.18	-2.9	3.2	-0.5
Pb, µg/L	1.68	1.65	1.69	1.69	1.67	-1.7	1.3	-0.3
Zn, µg/L	24.30	24.00	25.01	25.01	24.15	-3.4	0.9	-1.0
Hg, µg/L	0.09	0.091	0.081	0.081	0.091	11.7	0.8	0.5

Laboratory			
Code no.:	1		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.12	1.14	-1.3
NO2+3-N, mg/L	1.12	1.14	-2.1
N-total, mg/L	3.17	2.89	9.7
PO4-P, mg/L	0.53	0.52	3.1
P-total, mg/L	0.58	0.55	6.0
Cd, µg/L	1.97	1.99	-0.9
Cr, µg/L	9.42	9.62	-2.1
Cu, µg/L	18.91	19.59	-3.5
Ni, µg/L	2.75	2.70	2.0
Pb, µg/L	1.98	2.00	-0.8
Zn, µg/L	22.70	23.78	-4.6
Hg, µg/L	0.130	0.116	12.1

Laboratory								
Code no:	**3**							
	Measured data		**Assigned values**		**Statistics**			
Components	**Freshwater A**	**Freshwater B**	**Freshwater A**	**Freshwater B**	**Average**	**Dev. %**	**RSD %**	**z-score**
NO3-N, mg/L			0.60	0.60				
NO2+3-N, mg/L	0.606	0.598	0.61	0.61	0.60	-0.5	0.9	-0.2
N-total, mg/L	2.29	2.27	2.23	2.23	2.28	2.2	0.6	0.3
PO4-P, mg/L	0.38	0.38	0.39	0.39	0.38	-4.1	0.8	-1.2
P-total, mg/L	0.391	0.388	0.43	0.43	0.39	-9.4	0.5	-2.0
Cd, µg/L	1.33	1.31	1.40	1.40	1.32	-5.6	1.1	-1.2
Cr, µg/L	6.52	6.54	6.67	6.67	6.53	-2.1	0.2	-0.9
Cu, µg/L	14.45	14.3	13.84	13.84	14.38	3.9	0.7	0.8
Ni, µg/L	2.2	2.2	2.25	2.25	2.20	-2.0	0.0	-0.3
Pb, µg/L	1.61	1.59	1.69	1.69	1.60	-5.5	0.9	-1.0
Zn, µg/L	25.60	25.50	25.01	25.01	25.55	2.2	0.3	0.6
Hg, µg/L	<0.0015	<0.0015	0.081	0.081				

Laboratory			
Code no.:	**3**		
	Measured values	**Assigned values**	**Statistics**
Components	**Freshwater C**	**Freshwater C**	**Dev. %**
NO3-N, mg/L		1.14	
NO2+3-N, mg/L	1.16	1.14	1.4
N-total, mg/L	2.97	2.89	2.8
PO4-P, mg/L	0.52	0.52	-0.4
P-total, mg/L	0.51	0.55	-7.5
Cd, µg/L	1.88	1.99	-5.4
Cr, µg/L	9.23	9.62	-4.1
Cu, µg/L	19.90	19.59	1.6
Ni, µg/L	2.70	2.70	0.1
Pb, µg/L	1.91	2.00	-4.3
Zn, µg/L	23.90	23.78	0.5
Hg, µg/L	<0.0015	0.116	

Laboratory Code no:	4							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.64	0.64	0.60	0.60	0.64	6.8	0.0	2.4
NO2+3-N, mg/L	0.64	0.65	0.61	0.61	0.65	6.6	1.1	2.5
N-total, mg/L	2.4	2.5	2.23	2.23	2.45	9.9	2.9	1.4
PO4-P, mg/L	0.39	0.41	0.39	0.39	0.40	1.8	3.5	0.5
P-total, mg/L	0.43	0.41	0.43	0.43	0.42	-2.3	3.4	-0.5
Cd, µg/L	1.31	1.32	1.40	1.40	1.32	-6.0	0.5	-1.3
Cr, µg/L	6.61	6.55	6.67	6.67	6.58	-1.3	0.6	-0.6
Cu, µg/L	13.66	13.82	13.84	13.84	13.74	-0.7	0.8	-0.2
Ni, µg/L	2.20	2.24	2.25	2.25	2.22	-1.1	1.3	-0.2
Pb, µg/L	1.84	1.81	1.69	1.69	1.83	7.7	0.9	1.4
Zn, µg/L	24.57	25.06	25.01	25.01	24.81	-0.8	1.4	-0.2
Hg, µg/L	0.067	0.071	0.081	0.081	0.069	-14.8	4.1	-0.6

Laboratory Code no.:	4		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.20	1.14	5.7
NO2+3-N, mg/L	1.20	1.14	4.9
N-total, mg/L	3.02	2.89	4.5
PO4-P, mg/L	0.55	0.52	6.4
P-total, mg/L	0.56	0.55	2.4
Cd, µg/L	1.87	1.99	-5.7
Cr, µg/L	9.26	9.62	-3.7
Cu, µg/L	18.94	19.59	-3.3
Ni, µg/L	2.71	2.70	0.5
Pb, µg/L	2.17	2.00	8.9
Zn, µg/L	23.54	23.78	-1.0
Hg, µg/L	0.093	0.116	-19.8

Laboratory Code no:	5							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.61	0.61	0.60	0.60	0.61	1.8	0.0	0.6
NO2+3-N, mg/L	0.61	0.61	0.61	0.61	0.61	0.8	0.0	0.3
N-total, mg/L	2.2	2.2	2.23	2.23	2.20	-1.3	0.0	-0.2
PO4-P, mg/L	0.4	0.4	0.39	0.39	0.40	1.8	0.0	0.5
P-total, mg/L	0.46	0.44	0.43	0.43	0.45	4.7	3.1	1.0
Cd, µg/L	1.35	1.37	1.40	1.40	1.36	-2.8	1.0	-0.6
Cr, µg/L	6.7	6.74	6.67	6.67	6.72	0.8	0.4	0.3
Cu, µg/L	14.4	14.3	13.84	13.84	14.35	3.7	0.5	0.7
Ni, µg/L	2.21	2.31	2.25	2.25	2.26	0.7	3.1	0.1
Pb, µg/L	1.77	1.74	1.69	1.69	1.76	3.6	1.2	0.7
Zn, µg/L	26.1	26.1	25.01	25.01	26.10	4.4	0.0	1.2
Hg, µg/L	0.049	0.055	0.081	0.081	0.052	-35.9	7.1	-1.6

Laboratory Code no.:	5		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.10	1.14	-3.1
NO2+3-N, mg/L	1.10	1.14	-3.8
N-total, mg/L	2.90	2.89	0.3
PO4-P, mg/L	0.53	0.52	2.5
P-total, mg/L	0.53	0.55	-3.1
Cd, µg/L	2.00	1.99	0.7
Cr, µg/L	9.62	9.62	0.0
Cu, µg/L	20.10	19.59	2.6
Ni, µg/L	2.72	2.70	0.9
Pb, µg/L	2.09	2.00	4.7
Zn, µg/L	25.00	23.78	5.1
Hg, µg/L	0.0849	0.116	-26.8

Laboratory Code no:	6							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.59	0.59	0.60	0.60	0.59	-1.5	0.0	-0.5
NO2+3-N, mg/L			0.61	0.61				
N-total, mg/L			2.23	2.23				
PO4-P, mg/L	0.39	0.39	0.39	0.39	0.39	-0.8	0.0	-0.2
P-total, mg/L	0.44	0.43	0.43	0.43	0.44	1.2	1.6	0.2
Cd, µg/L	1.44	1.46	1.40	1.40	1.45	3.6	1.0	0.8
Cr, µg/L	6.5	6.8	6.67	6.67	6.65	-0.3	3.2	-0.1
Cu, µg/L	13	12	13.84	13.84	12.50	-9.7	5.7	-2.0
Ni, µg/L	2.3	2.2	2.25	2.25	2.25	0.2	3.1	0.0
Pb, µg/L	1.4	1.7	1.69	1.69	1.55	-8.5	13.7	-1.5
Zn, µg/L	24	24	25.01	25.01	24.00	-4.0	0.0	-1.1
Hg, µg/L	0.078	0.089	0.081	0.081	0.084	3.1	9.3	0.1

Laboratory Code no.:	6		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.13	1.14	-0.4
NO2+3-N, mg/L		1.14	
N-total, mg/L		2.89	
PO4-P, mg/L	0.52	0.52	0.6
P-total, mg/L	0.56	0.55	2.4
Cd, µg/L	1.99	1.99	0.2
Cr, µg/L	10.50	9.62	9.1
Cu, µg/L	18.00	19.59	-8.1
Ni, µg/L	2.50	2.70	-7.3
Pb, µg/L	1.90	2.00	-4.8
Zn, µg/L	24.00	23.78	0.9
Hg, µg/L	0.12	0.116	3.4

Laboratory Code no:	7							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0,60	0,60				
NO2+3-N, mg/L			0.61	0.61				
N-total, mg/L			2.23	2.23				
PO4-P, mg/L			0.39	0.39				
P-total, mg/L			0.43	0.43				
Cd, µg/L	1.4	1.4	1.40	1.40	1.40	0.1	0.0	0.0
Cr, µg/L	11	11	6.67	6.67	11.00	65.0	0.0	28.4
Cu, µg/L	13	13	13.84	13.84	13.00	-6.1	0.0	-1.2
Ni, µg/L	2.4	2.3	2.25	2.25	2.35	4.7	3.0	0.7
Pb, µg/L	1.8	1.8	1.69	1.69	1.80	6.3	0.0	1.1
Zn, µg/L	24	23	25.01	25.01	23.50	-6.0	3.0	-1.7
Hg, µg/L	0.069	0.068	0.081	0.081	0.069	-15.4	1.0	-0.7

Laboratory Code no.:	7		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L		1.14	
NO2+3-N, mg/L		1.14	
N-total, mg/L		2.89	
PO4-P, mg/L		0.52	
P-total, mg/L		0.55	
Cd, µg/L	2.00	1.99	0.7
Cr, µg/L	15.00	9.62	55.9
Cu, µg/L	18.00	19.59	-8.1
Ni, µg/L	3.50	2.70	29.8
Pb, µg/L	2.10	2.00	5.2
Zn, µg/L	22.00	23.78	-7.5
Hg, µg/L	0.093	0.116	-19.8

Laboratory Code no:	8							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.60	0.60				
NO2+3-N, mg/L	0.59	0.59	0.61	0.61	0.59	-2.5	0.0	-0.9
N-total, mg/L	1.89	2.00	2.23	2.23	1.95	-12.8	4.0	-1.8
PO4-P, mg/L	0.39	0.40	0.39	0.39	0.40	0.5	0.4	0.2
P-total, mg/L	0.42	0.43	0.43	0.43	0.42	-1.3	0.5	-0.3
Cd, µg/L	1.42	1.42	1.40	1.40	1.42	1.3	0.1	0.3
Cr, µg/L	6.77	6.88	6.67	6.67	6.82	2.4	1.1	1.0
Cu, µg/L	13.99	13.89	13.84	13.84	13.94	0.7	0.5	0.1
Ni, µg/L	2.25	2.28	2.25	2.25	2.26	0.7	0.9	0.1
Pb, µg/L	1.62	1.60	1.69	1.69	1.61	-4.7	0.9	-0.9
Zn, µg/L	26.05	25.97	25.01	25.01	26.01	4.0	0.2	1.1
Hg, µg/L	0.087	0.086	0.081	0.081	0.087	6.8	0.8	0.3

Laboratory Code no.:	8		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L		1.14	
NO2+3-N, mg/L	1.11	1.14	-3.0
N-total, mg/L	2.61	2.89	-9.7
PO4-P, mg/L	0.53	0.52	1.7
P-total, mg/L	0.55	0.55	0.4
Cd, µg/L	1.98	1.99	-0.2
Cr, µg/L	9.78	9.62	1.7
Cu, µg/L	19.38	19.59	-1.1
Ni, µg/L	2.77	2.70	2.7
Pb, µg/L	1.92	2.00	-4.1
Zn, µg/L	24.28	23.78	2.1
Hg, µg/L	0.120	0.116	3.4

Laboratory Code no:	9							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.59	0.59	0.60	0.60	0.59	-1.5	0.7	-0.5
NO2+3-N, mg/L	0.60	0.59	0.61	0.61	0.59	-2.0	0.7	-0.8
N-total, mg/L	2.24	2.21	2.23	2.23	2.23	-0.1	1.0	0.0
PO4-P, mg/L	0.39	0.39	0.39	0.39	0.39	-0.5	0.0	-0.2
P-total, mg/L	0.44	0.45	0.43	0.43	0.45	3.6	0.4	0.7
Cd, µg/L	1.37	1.55	1.40	1.40	1.46	4.5	8.7	1.0
Cr, µg/L	8.98	8.06	6.67	6.67	8.52	27.8	7.7	12.2
Cu, µg/L	14.89	13.59	13.84	13.84	14.24	2.9	6.5	0.6
Ni, µg/L	2.65	2.37	2.25	2.25	2.51	11.7	7.8	1.8
Pb, µg/L	6.81	6.65	1.69	1.69	6.73	297.2	1.7	54.1
Zn, µg/L	25.20	24.23	25.01	25.01	24.72	-1.1	2.8	-0.3
Hg, µg/L	0.084	0.081	0.081	0.081	0.082	1.7	2.5	0.1

Laboratory Code no.:	9		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.10	1.14	-3.4
NO2+3-N, mg/L	1.10	1.14	-4.0
N-total, mg/L	2.85	2.89	-1.5
PO4-P, mg/L	0.49	0.52	-5.5
P-total, mg/L	0.56	0.55	2.4
Cd, µg/L	2.17	1.99	9.0
Cr, µg/L	11.34	9.62	17.9
Cu, µg/L	22.24	19.59	13.5
Ni, µg/L	3.80	2.70	41.0
Pb, µg/L	7.26	2.00	263.8
Zn, µg/L	24.57	23.78	3.3
Hg, µg/L	0.1172	0.116	1.0

Comment from the laboratory: The Laboratory found typos for some results (all results for Lead and 2 for Cadmium).

Laboratory Code no:	10							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.58	0.58	0.60	0.60	0.58	-2.8	0.5	-1.0
NO2+3-N, mg/L	0.60	0.60	0.61	0.61	0.60	-1.1	0.1	-0.4
N-total, mg/L	2.28	2.25	2.23	2.23	2.27	1.6	0.9	0.2
PO4-P, mg/L	0.41	0.41	0.39	0.39	0.41	4.3	0.0	1.3
P-total, mg/L	0.42	0.43	0.43	0.43	0.43	-1.2	1.7	-0.2
Cd, µg/L	1.01	1.01	1.40	1.40	1.01	-27.7	0.1	-6.1
Cr, µg/L	5.40	5.43	6.67	6.67	5.42	-18.8	0.5	-8.2
Cu, µg/L	13.15	12.99	13.84	13.84	13.07	-5.6	0.9	-1.1
Ni, µg/L	1.59	1.57	2.25	2.25	1.58	-29.5	0.8	-4.6
Pb, µg/L	1.04	1.03	1.69	1.69	1.03	-39.0	0.3	-7.1
Zn, µg/L	20.29	20.36	25.01	25.01	20.33	-18.7	0.2	-5.3
Hg, µg/L	0.046	0.049	0.081	0.081	0.048	-41.4	4.5	-1.8

Laboratory Code no.:	10		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.14	1.14	0.7
NO2+3-N, mg/L	1.15	1.14	0.6
N-total, mg/L	2.90	2.89	0.3
PO4-P, mg/L	0.51	0.52	-1.4
P-total, mg/L	0.55	0.55	0.5
Cd, µg/L	1.41	1.99	-28.9
Cr, µg/L	7.59	9.62	-21.1
Cu, µg/L	17.39	19.59	-11.2
Ni, µg/L	17.39	2.70	545.2
Pb, µg/L	1.22	2.00	-39.1
Zn, µg/L	19.27	23.78	-19.0
Hg, µg/L	0.080	0.116	-31.0

Laboratory Code no:	11							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.59	0.60	0.60	0.60	0.60	-0.3	1.4	-0.1
NO2+3-N, mg/L	0.59	0.60	0.61	0.61	0.60	-1.3	1.4	-0.5
N-total, mg/L	2.07	2.08	2.23	2.23	2.08	-7.0	0.3	-1.0
PO4-P, mg/L	0.37	0.37	0.39	0.39	0.37	-6.4	0.8	-1.9
P-total, mg/L	0.40	0.38	0.43	0.43	0.39	-9.3	3.6	-2.0
Cd, µg/L	1.38	1.39	1.40	1.40	1.39	-0.9	0.8	-0.2
Cr, µg/L	7.34	7.40	6.67	6.67	7.37	10.5	0.6	4.6
Cu, µg/L	14.71	14.88	13.84	13.84	14.79	6.9	0.8	1.4
Ni, µg/L	2.37	2.46	2.25	2.25	2.42	7.6	2.8	1.2
Pb, µg/L	1.60	1.56	1.69	1.69	1.58	-6.7	1.9	-1.2
Zn, µg/L	25.44	25.40	25.01	25.01	25.42	1.7	0.1	0.5
Hg, µg/L	0.108	0.104	0.081	0.081	0.106	30.9	3.0	1.3

Laboratory Code no.:	11		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.14	1.14	0.4
NO2+3-N, mg/L	0.11	1.14	-90.0
N-total, mg/L	2.77	2.89	-4.3
PO4-P, mg/L	0.49	0.52	-4.8
P-total, mg/L	0.50	0.55	-8.6
Cd, µg/L	1.97	1.99	-0.8
Cr, µg/L	10.72	9.62	11.4
Cu, µg/L	20.52	19.59	4.8
Ni, µg/L	3.00	2.70	11.4
Pb, µg/L	1.88	2.00	-5.6
Zn, µg/L	24.59	23.78	3.4
Hg, µg/L	0.151	0.116	29.9

Laboratory Code no:	13							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.60	0.60				
NO2+3-N, mg/L	0.61	0.61	0.61	0.61	0.61	1.3	0.2	0.5
N-total, mg/L	2.07	2.09	2.23	2.23	2.08	-6.7	0.4	-0.9
PO4-P, mg/L	0.38	0.38	0.39	0.39	0.38	-4.3	0.0	-1.3
P-total, mg/L	0.43	0.44	0.43	0.43	0.43	0.9	1.0	0.2
Cd, µg/L	1.43	1.45	1.40	1.40	1.44	2.9	1.0	0.6
Cr, µg/L	6.71	6.79	6.67	6.67	6.75	1.2	0.8	0.5
Cu, µg/L	13.97	14.00	13.84	13.84	13.99	1.0	0.2	0.2
Ni, µg/L	2.28	2.23	2.25	2.25	2.26	0.4	1.6	0.1
Pb, µg/L	1.70	1.70	1.69	1.69	1.70	0.3	0.1	0.0
Zn, µg/L	26.20	26.10	25.01	25.01	26.15	4.6	0.3	1.3
Hg, µg/L	0.0948	0.0965	0.081	0.081	0.096	18.1	1.3	0.8

Laboratory Code no.:	13		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L		1.14	
NO2+3-N, mg/L	1.15	1.14	0.3
N-total, mg/L	2.68	2.89	-7.1
PO4-P, mg/L	0.52	0.52	0.8
P-total, mg/L	0.56	0.55	2.2
Cd, µg/L	1.99	1.99	0.2
Cr, µg/L	9.33	9.62	-3.0
Cu, µg/L	19.50	19.59	-0.4
Ni, µg/L	2.75	2.70	2.0
Pb, µg/L	2.03	2.00	1.7
Zn, µg/L	24.40	23.78	2.6
Hg, µg/L	0.1534	0.116	32.2

Laboratory Code no:	14							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			0.60	0.60				
NO2+3-N, mg/L	0.61	0.6	0.61	0.61	0.61	0.0	1.2	0.0
N-total, mg/L	2.51	2.57	2.23	2.23	2.54	13.9	1.7	2.0
PO4-P, mg/L	0.40	0.40	0.39	0.39	0.40	1.8	0.0	0.5
P-total, mg/L	0.45	0.45	0.43	0.43	0.45	4.7	0.0	1.0
Cd, µg/L			1.40	1.40				
Cr, µg/L			6.67	6.67				
Cu, µg/L			13.84	13.84				
Ni, µg/L			2.25	2.25				
Pb, µg/L			1.69	1.69				
Zn, µg/L			25.01	25.01				
Hg, µg/L			0.081	0.081				

Laboratory Code no.:	14		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L		1.14	
NO2+3-N, mg/L	1.21	1.14	5.8
N-total, mg/L	3.15	2.89	9.0
PO4-P, mg/L	0.53	0.52	2.5
P-total, mg/L	0.56	0.55	2.4
Cd, µg/L		1.99	
Cr, µg/L		9.62	
Cu, µg/L		19.59	
Ni, µg/L		2.70	
Pb, µg/L		2.00	
Zn, µg/L		23.78	
Hg, µg/L		0.116	

Laboratory Code no:	15							
	Measured data		Assigned values		Statistics			
Components	Fresh wter A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.62	0.60	0.60	0.60	0.61	1.3	2.6	0.5
NO2+3-N, mg/L	0.63	0.62	0.61	0.61	0.63	3.4	0.3	1.3
N-total, mg/L	2.08	2.13	2.23	2.23	2.11	-5.6	1.7	-0.8
PO4-P, mg/L	0.38	0.39	0.39	0.39	0.39	-2.0	1.8	-0.6
P-total, mg/L	0.43	0.43	0.43	0.43	0.43	0.0	0.0	0.0
Cd, µg/L	1.53	1.57	1.40	1.40	1.55	10.8	1.8	2.4
Cr, µg/L	6.97	6.63	6.67	6.67	6.80	2.0	3.5	0.9
Cu, µg/L	14.8	14.4	13.84	13.84	14.60	5.5	1.9	1.1
Ni, µg/L	2.01	1.94	2.25	2.25	1.98	-12.0	2.5	-1.9
Pb, µg/L	1.87	1.78	1.69	1.69	1.83	7.7	3.5	1.4
Zn, µg/L	22.70	24.70	25.01	25.01	23.70	-5.2	6.0	-1.5
Hg, µg/L	0.108	0.097	0.081	0.081	0.103	26.5	7.6	1.2

Laboratory Code no.:	15		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.13	1.14	-0.4
NO2+3-N, mg/L	1.17	1.14	2.3
N-total, mg/L	2.77	2.89	-4.2
PO4-P, mg/L	0.52	0.52	0.6
P-total, mg/L	0.55	0.55	0.5
Cd, µg/L	2.13	1.99	7.2
Cr, µg/L	9.70	9.62	0.8
Cu, µg/L	23.90	19.59	22.0
Ni, µg/L	2.50	2.70	-7.3
Pb, µg/L	2.10	2.00	5.2
Zn, µg/L	27.70	23.78	16.5
Hg, µg/L	0.143	0.116	23.3

Laboratory Code no:	16							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.61	0.61	0.60	0.60	0.61	1.6	0.1	0.6
NO2+3-N, mg/L	0.62	0.61	0.61	0.61	0.62	1.7	0.2	0.6
N-total, mg/L	2.26	2.22	2.23	2.23	2.24	0.3	1.1	0.0
PO4-P, mg/L	0.41	0.40	0.39	0.39	0.41	3.2	0.5	0.9
P-total, mg/L	0.43	0.44	0.43	0.43	0.44	1.7	1.1	0.4
Cd, µg/L	1.41	1.41	1.40	1.40	1.41	1.0	0.0	0.2
Cr, µg/L	6.71	6.69	6.67	6.67	6.70	0.5	0.2	0.2
Cu, µg/L	13.45	13.52	13.84	13.84	13.49	-2.5	0.3	-0.5
Ni, µg/L	2.09	2.08	2.25	2.25	2.09	-7.1	0.1	-1.1
Pb, µg/L	1.63	1.62	1.69	1.69	1.62	-4.1	0.2	-0.8
Zn, µg/L	24.91	24.87	25.01	25.01	24.89	-0.5	0.1	-0.1
Hg, µg/L	0.087	0.084	0.081	0.081	0.086	5.6	2.5	0.2

Laboratory Code no.:	16		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.15	1.14	1.1
NO2+3-N, mg/L	1.14	1.14	0.0
N-total, mg/L	2.98	2.89	3.2
PO4-P, mg/L	0.54	0.52	3.5
P-total, mg/L	0.57	0.55	3.7
Cd, µg/L	2.01	1.99	1.2
Cr, µg/L	9.56	9.62	-0.6
Cu, µg/L	18.83	19.59	-3.9
Ni, µg/L	2.58	2.70	-4.2
Pb, µg/L	1.93	2.00	-3.1
Zn, µg/L	23.72	23.78	-0.3
Hg, µg/L	0.114	0.116	-1.7

Laboratory Code no:	17							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.585	0.587	0.60	0.60	0.59	-2.2	0.2	-0.8
NO2+3-N, mg/L	0.585	0.587	0.61	0.61	0.59	-3.1	0.2	-1.2
N-total, mg/L	2.17	2.14	2.23	2.23	2.16	-3.4	1.0	-0.5
PO4-P, mg/L	0.41	0.41	0.39	0.39	0.41	4.3	0.0	1.3
P-total, mg/L	0.43	0.42	0.43	0.43	0.43	-1.2	1.7	-0.2
Cd, µg/L	1.36	1.36	1.40	1.40	1.36	-2.8	0.0	-0.6
Cr, µg/L	6.46	6.38	6.67	6.67	6.42	-3.7	0.9	-1.6
Cu, µg/L	13.8	13.8	13.84	13.84	13.80	-0.3	0.0	-0.1
Ni, µg/L	2.23	2.21	2.25	2.25	2.22	-1.1	0.6	-0.2
Pb, µg/L	1.65	1.65	1.69	1.69	1.65	-2.6	0.0	-0.5
Zn, µg/L	24.7	24.8	25.01	25.01	24.75	-1.0	0.3	-0.3
Hg, µg/L	0.099	0.075	0.081	0.081	0.087	7.0	19.6	0.3

Laboratory Code no.:	17		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.14	1.14	0.4
NO2+3-N, mg/L	1.14	1.14	-0.3
N-total, mg/L	2.73	2.89	-5.5
PO4-P, mg/L	0.48	0.52	-7.2
P-total, mg/L	0.51	0.55	-6.8
Cd, µg/L	1.87	1.99	-5.9
Cr, µg/L	9.01	9.62	-6.3
Cu, µg/L	18.60	19.59	-5.0
Ni, µg/L	2.67	2.70	-1.0
Pb, µg/L	1.94	2.00	-2.8
Zn, µg/L	23.30	23.78	-2.0
Hg, µg/L	0.106	0.116	-8.6

Laboratory Code no:	18							
	Measured data		Assigned values		Statistics			
Components	Freshwater A	Freshwater B	Freshwater A	Freshwater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	0.60	0.60	0.60	0.60	0.60	-0.4	0.1	-0.1
NO2+3-N, mg/L	0.60	0.61	0.61	0.61	0.60	-0.1	0.5	0.0
N-total, mg/L	2.31	2.31	2.23	2.23	2.31	3.6	0.2	0.5
PO4-P, mg/L	0.39	0.39	0.39	0.39	0.39	-0.9	0.5	-0.3
P-total, mg/L	0.43	0.44	0.43	0.43	0.44	1.2	0.7	0.2
Cd, µg/L			1.40	1.40				
Cr, µg/L			6.67	6.67				
Cu, µg/L			13.84	13.84				
Ni, µg/L			2.25	2.25				
Pb, µg/L			1.69	1.69				
Zn, µg/L			25.01	25.01				
Hg, µg/L			0.081	0.081				

Laboratory Code no.:	18		
	Measured values	Assigned values	Statistics
Components	Freshwater C	Freshwater C	Dev. %
NO3-N, mg/L	1.13	1.14	-0.1
NO2+3-N, mg/L	1.13	1.14	-1.6
N-total, mg/L	2.96	2.89	2.5
PO4-P, mg/L	0.52	0.52	-0.4
P-total, mg/L	0.57	0.55	3.5
Cd, µg/L		1.99	
Cr, µg/L		9.62	
Cu, µg/L		19.59	
Ni, µg/L		2.70	
Pb, µg/L		2.00	
Zn, µg/L		23.78	
Hg, µg/L		0.116	

3.3 Wastewater

Laboratory Code no:	1							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.47	2.48	2.47	2.47	2.48	0.2	0.3	0.1
NO2+3-N, mg/L	2.79	2.80	2.81	2.81	2.80	-0.6	0.3	-0.2
N-total, mg/L	6.49	6.61	6.78	6.78	6.55	-3.3	1.3	-0.8
PO4-P, mg/L	0.48	0.49	0.48	0.48	0.49	1.7	0.6	0.6
P-total, mg/L	0.65	0.64	0.61	0.61	0.65	5.9	1.1	1.7
Cd, µg/L	5.26	5.25	5.26	5.26	5.26	-0.2	0.1	0.0
Cr, µg/L	10.48	10.73	11.13	11.13	10.61	-4.7	1.7	-0.6
Cu, µg/L	23.82	24.21	25.2	25.2	24.0	-4.9	1.1	-1.0
Ni, µg/L	42.18	42.32	43.3	43.3	42.3	-2.5	0.2	-0.5
Pb, µg/L	1.84	1.96	1.90	1.90	1.90	-0.1	4.5	0.0
Zn, µg/L	80.80	80.00	81.65	81.65	80.4	-1.5	0.7	-0.4
Hg, µg/L	1.094	1.128	1.160	1.160	1.111	-4.2	2.2	-0.3

Laboratory Code no:	2							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.31	2.31	2.47	2.47	2.31	-6.4	0.2	-2.2
NO2+3-N, mg/L	2.68	2.69	2.81	2.81	2.69	-4.4	0.3	-1.7
N-total, mg/L	6.50	6.51	6.78	6.78	6.51	-4.0	0.1	-1.0
PO4-P, mg/L	0.48	0.48	0.48	0.48	0.48	0.8	0.1	0.3
P-total, mg/L	0.65	0.64	0.61	0.61	0.64	5.7	0.2	1.6
Cd, µg/L	5.99	5.99	5.26	5.26	5.99	13.8	0.0	1.7
Cr, µg/L	10.63	10.55	11.13	11.13	10.59	-4.8	0.5	-0.6
Cu, µg/L	24.24	24.30	25.2	25.2	24.3	-3.9	0.2	-0.8
Ni, µg/L	41.54	41.26	43.3	43.3	41.4	-4.4	0.5	-0.9
Pb, µg/L	2.08	2.09	1.90	1.90	2.09	9.6	0.3	1.2
Zn, µg/L	84.23	83.79	81.65	81.65	84.0	2.9	0.4	0.8
Hg, µg/L	1.077	1.136	1.160	1.160	1.107	-4.6	3.8	-0.3

Laboratory Code no:	3							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			2.47	2.47				
NO2+3-N, mg/L	2.84	2.85	2.81	2.81	2.85	1.1	0.2	0.4
N-total, mg/L	6.90	6.89	6.78	6.78	6.90	1.8	0.1	0.4
PO4-P, mg/L	0.47	0.47	0.48	0.48	0.47	-1.0	0.0	-0.4
P-total, mg/L	0.60	0.60	0.61	0.61	0.60	-2.1	0.4	-0.6
Cd, µg/L	4.94	4.92	5.26	5.26	4.93	-6.3	0.3	-0.8
Cr, µg/L	11.00	11.10	11.13	11.13	11.05	-0.7	0.6	-0.1
Cu, µg/L	26.40	26.60	25.2	25.2	26.5	5.0	0.5	1.0
Ni, µg/L	43.60	43.70	43.3	43.3	43.7	0.8	0.2	0.2
Pb, µg/L	1.81	1.77	1.90	1.90	1.79	-5.9	1.6	-0.7
Zn, µg/L	84.00	85.00	81.65	81.65	84.5	3.5	0.8	0.9
Hg, µg/L	0.890	0.790	1.160	1.160	0.840	-27.6	8.4	-1.7

Laboratory Code no:	4							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.70	2.90	2.47	2.47	2.80	13.4	5.1	4.6
NO2+3-N, mg/L	3.10	3.20	2.81	2.81	3.15	12.0	2.2	4.5
N-total, mg/L	6.90	7.20	6.78	6.78	7.05	4.1	3.0	1.0
PO4-P, mg/L	0.50	0.49	0.48	0.48	0.50	3.6	1.4	1.3
P-total, mg/L	0.55	0.59	0.61	0.61	0.57	-6.4	5.0	-1.8
Cd, µg/L	4.78	4.87	5.26	5.26	4.82	-8.3	1.4	-1.0
Cr, µg/L	10.18	10.31	11.13	11.13	10.25	-7.9	0.9	-1.0
Cu, µg/L	24.49	24.80	25.2	25.2	24.6	-2.4	0.9	-0.5
Ni, µg/L	41.69	42.18	43.3	43.3	41.9	-3.2	0.8	-0.6
Pb, µg/L	1.74	1.82	1.90	1.90	1.78	-6.6	3.2	-0.8
Zn, µg/L	78.65	78.97	81.65	81.65	78.8	-3.5	0.3	-0.9
Hg, µg/L	1.048	1.100	1.160	1.160	1.074	-7.4	3.4	-0.5

Laboratory Code no:	5							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.50	2.50	2.47	2.47	2.50	1.3	0.0	0.4
NO2+3-N, mg/L	2.80	2.80	2.81	2.81	2.80	-0.5	0.0	-0.2
N-total, mg/L	6.70	6.70	6.78	6.78	6.70	-1.1	0.0	-0.3
PO4-P, mg/L	0.48	0.49	0.48	0.48	0.49	1.5	1.5	0.5
P-total, mg/L	0.58	0.58	0.61	0.61	0.58	-4.8	0.0	-1.3
Cd, µg/L	5.04	5.05	5.26	5.26	5.05	-4.2	0.1	-0.5
Cr, µg/L	11.50	11.40	11.13	11.13	11.45	2.9	0.6	0.4
Cu, µg/L	26.60	26.90	25.2	25.2	26.8	6.0	0.8	1.2
Ni, µg/L	45.30	44.80	43.3	43.3	45.1	4.0	0.8	0.8
Pb, µg/L	2.16	2.10	1.90	1.90	2.13	12.0	2.0	1.5
Zn, µg/L	87.70	87.50	81.65	81.65	87.6	7.3	0.2	2.0
Hg, µg/L	1.260	1.250	1.160	1.160	1.255	8.2	0.6	0.5

Laboratory Code no:	6							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.43	2.43	2.47	2.47	2.43	-1.6	0.0	-0.5
NO2+3-N, mg/L			2.81	2.81				
N-total, mg/L			6.78	6.78				
PO4-P, mg/L	0.47	0.48	0.48	0.48	0.48	-0.6	1.5	-0.2
P-total, mg/L	0.61	0.60	0.61	0.61	0.61	-0.7	1.2	-0.2
Cd, µg/L	<10	<10	5.26	5.26				
Cr, µg/L	11.00	11.00	11.13	11.13	11.00	-1.2	0.0	-0.1
Cu, µg/L	25.00	25.00	25.2	25.2	25.0	-1.0	0.0	-0.2
Ni, µg/L	44.00	45.00	43.3	43.3	44.5	2.7	1.6	0.5
Pb, µg/L	<10	<10	1.90	1.90				
Zn, µg/L	81.00	89.00	81.65	81.65	85.0	4.1	6.7	1.1
Hg, µg/L	1.380	1.460	1.160	1.160	1.420	22.4	4.0	1.4

Laboratory Code no:	7							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			2.47	2.47				
NO2+3-N, mg/L			2.81	2.81				
N-total, mg/L			6.78	6.78				
PO4-P, mg/L			0.48	0.48				
P-total, mg/L			0.61	0.61				
Cd, µg/L	5.10	5.00	5.26	5.26	5.05	-4.1	1.4	-0.5
Cr, µg/L	20.00	21.00	11.13	11.13	20.50	84.2	3.4	10.7
Cu, µg/L	26.00	26.00	25.2	25.2	26.0	3.0	0.0	0.6
Ni, µg/L	47.00	48.00	43.3	43.3	47.5	9.7	1.5	1.9
Pb, µg/L	2.00	2.00	1.90	1.90	2.00	5.2	0.0	0.6
Zn, µg/L	82.00	83.00	81.65	81.65	82.5	1.0	0.9	0.3
Hg, µg/L	0.920	0.910	1.160	1.160	0.915	-21.1	0.8	-1.3

Laboratory Code no:	8							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L			2.47	2.47				
NO2+3-N, mg/L	2.80	2.81	2.81	2.81	2.81	-0.3	0.3	-0.1
N-total, mg/L	6.39	6.62	6.78	6.78	6.51	-4.0	2.5	-1.0
PO4-P, mg/L	0.48	0.49	0.48	0.48	0.48	0.8	0.9	0.3
P-total, mg/L	0.60	0.60	0.61	0.61	0.60	-1.2	0.6	-0.3
Cd, µg/L	5.48	5.49	5.26	5.26	5.49	4.2	0.1	0.5
Cr, µg/L	12.36	12.15	11.13	11.13	12.26	10.1	1.2	1.3
Cu, µg/L	26.00	27.00	25.2	25.2	26.5	5.0	2.7	1.0
Ni, µg/L	42.00	42.00	43.3	43.3	42.0	-3.0	0.0	-0.6
Pb, µg/L	<10	<10	1.90	1.90				
Zn, µg/L	78.80	78.00	81.65	81.65	78.4	-4.0	0.7	-1.1
Hg, µg/L	1.106	1.100	1.160	1.160	1.103	-4.9	0.4	-0.3

Laboratory Code no:	9							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.43	2.44	2.47	2.47	2.43	-1.4	0.2	-0.5
NO2+3-N, mg/L	2.80	2.79	2.81	2.81	2.80	-0.6	0.4	-0.2
N-total, mg/L	6.63	6.44	6.78	6.78	6.53	-3.6	2.0	-0.9
PO4-P, mg/L	0.46	0.47	0.48	0.48	0.46	-2.8	2.0	-1.0
P-total, mg/L	0.62	0.61	0.61	0.61	0.61	0.9	0.6	0.2
Cd, µg/L	5.14	5.08	5.26	5.26	5.11	-2.9	0.9	-0.4
Cr, µg/L	13.23	12.88	11.13	11.13	13.05	17.3	1.9	2.2
Cu, µg/L	26.63	26.77	25.2	25.2	26.7	5.8	0.4	1.2
Ni, µg/L	45.31	46.18	43.3	43.3	45.7	5.6	1.3	1.1
Pb, µg/L	6.98	7.12	1.90	1.90	7.05	270.8	1.4	33.4
Zn, µg/L	81.97	81.43	81.65	81.65	81.7	0.1	0.5	0.0
Hg, µg/L	1.083	1.077	1.160	1.160	1.080	-6.9	0.4	-0.4

Comments from the laboratory: The laboratory found typos for some of the results (all results for Lead).

Laboratory Code no:	10							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.44	2.43	2.47	2.47	2.44	-1.2	0.3	-0.4
NO2+3-N, mg/L	2.70	2.70	2.81	2.81	2.70	-4.0	0.0	-1.5
N-total, mg/L	7.00	6.80	6.78	6.78	6.90	1.8	2.0	0.4
PO4-P, mg/L	0.48	0.47	0.48	0.48	0.48	-0.6	1.5	-0.2
P-total, mg/L	0.58	0.58	0.61	0.61	0.58	-4.8	0.0	-1.3
Cd, µg/L	2.51	2.55	5.26	5.26	2.53	-51.9	1.0	-6.2
Cr, µg/L	6.65	6.66	11.13	11.13	6.65	-40.2	0.1	-5.1
Cu, µg/L	15.17	17.70	25.2	25.2	16.4	-34.9	10.9	-7.1
Ni, µg/L	20.61	17.99	43.3	43.3	19.3	-55.4	9.6	-10.7
Pb, µg/L	0.81	0.81	1.90	1.90	0.81	-57.4	0.6	-7.1
Zn, µg/L	43.36	43.78	81.65	81.65	43.6	-46.6	0.7	-12.6
Hg, µg/L	1.037	1.315	1.160	1.160	1.176	1.4	16.7	0.1

Laboratory Code no:	12							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.24	594.18	2.47	2.47	298.21	11978.3	140.4	4114.3
NO2+3-N, mg/L	0.44	0.17	2.81	2.81	0.30	-89.2	62.6	-33.7
N-total, mg/L	5.77	588.33	6.78	6.78	297.05	4284.6	138.7	1028.5
PO4-P, mg/L	0.43	<0.01	0.48	0.48	0.43			
P-total, mg/L	0.58	0.03	0.61	0.61	0.31	-49.7	128.3	-14.1
Cd, µg/L	5.43	<0.005	5.26	5.26	5.43			
Cr, µg/L	11.87	0.85	11.13	11.13	6.36	-42.9	122.5	-5.4
Cu, µg/L	26.04	0.62	25.2	25.2	13.3	-47.2	134.8	-9.6
Ni, µg/L	45.39	4.42	43.3	43.3	24.9	-42.5	116.3	-8.2
Pb, µg/L	2.02	0.22	1.90	1.90	1.12	-41.0	113.6	-5.1
Zn, µg/L	88.74	65.02	81.65	81.65	76.9	-5.8	21.8	-1.6
Hg, µg/L	1.195	1.196	1.160	1.160	1.195	3.0	0.1	0.2

Comments from the laboratory: The laboratory has mixed up the samples for nutrients and metals for sample B.

Laboratory Code no:	14							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.45	2.37	2.47	2.47	2.41	-2.4	2.3	-0.8
NO2+3-N, mg/L			2.81	2.81				
N-total, mg/L	7.28	7.62	6.78	6.78	7.45	10.0	3.2	2.4
PO4-P, mg/L	0.47	0.47	0.48	0.48	0.47	-2.7	0.0	-1.0
P-total, mg/L	0.64	0.63	0.61	0.61	0.64	4.6	1.6	1.3
Cd, µg/L			5.26	5.26				
Cr, µg/L			11.13	11.13				
Cu, µg/L			25.2	25.2				
Ni, µg/L			43.3	43.3				
Pb, µg/L			1.90	1.90				
Zn, µg/L			81.65	81.65				
Hg, µg/L			1.160	1.160				

Laboratory								
Code no:	15							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.57	2.57	2.47	2.47	2.57	4.1	0.0	1.4
NO2+3-N, mg/L	2.91	2.95	2.81	2.81	2.93	4.2	1.0	1.6
N-total, mg/L	6.59	6.58	6.78	6.78	6.59	-2.8	0.1	-0.7
PO4-P, mg/L	0.47	0.47	0.48	0.48	0.47	-1.7	0.0	-0.6
P-total, mg/L	0.60	0.60	0.61	0.61	0.60	-1.5	0.0	-0.4
Cd, µg/L	6.03	6.21	5.26	5.26	6.12	16.3	2.1	2.0
Cr, µg/L	11.10	11.30	11.13	11.13	11.20	0.6	1.3	0.1
Cu, µg/L	24.00	26.00	25.2	25.2	25.0	-1.0	5.7	-0.2
Ni, µg/L	49.30	45.50	43.3	43.3	47.4	9.4	5.7	1.8
Pb, µg/L			1.90	1.90				
Zn, µg/L	87.00	108.00	81.65	81.65	97.5	19.4	15.2	5.2
Hg, µg/L	1.380	1.370	1.160	1.160	1.375	18.5	0.5	1.1

Laboratory								
Code no:	16							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.48	2.48	2.47	2.47	2.48	0.3	0.1	0.1
NO2+3-N, mg/L	2.90	2.88	2.81	2.81	2.89	2.7	0.6	1.0
N-total, mg/L	6.88	6.83	6.78	6.78	6.86	1.2	0.5	0.3
PO4-P, mg/L	0.50	0.50	0.48	0.48	0.50	5.0	0.0	1.8
P-total, mg/L	0.60	0.60	0.61	0.61	0.60	-1.6	0.7	-0.5
Cd, µg/L	5.26	5.24	5.26	5.26	5.25	-0.2	0.2	0.0
Cr, µg/L	11.06	10.68	11.13	11.13	10.87	-2.3	2.4	-0.3
Cu, µg/L	24.39	23.89	25.2	25.2	24.1	-4.4	1.5	-0.9
Ni, µg/L	43.09	42.12	43.3	43.3	42.6	-1.6	1.6	-0.3
Pb, µg/L	1.78	1.79	1.90	1.90	1.79	-6.1	0.4	-0.8
Zn, µg/L	79.58	79.34	81.65	81.65	79.5	-2.7	0.2	-0.7
Hg, µg/L	1.097	1.106	1.160	1.160	1.102	-5.0	0.6	-0.3

Laboratory Code no:	17							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.52	2.53	2.47	2.47	2.52	2.2	0.3	0.8
NO2+3-N, mg/L	2.88	2.89	2.81	2.81	2.88	2.4	0.3	0.9
N-total, mg/L	6.85	6.84	6.78	6.78	6.84	1.0	0.0	0.2
PO4-P, mg/L	0.48	0.48	0.48	0.48	0.48	0.4	0.0	0.1
P-total, mg/L	0.61	0.61	0.61	0.61	0.61	0.2	0.0	0.0
Cd, µg/L	4.80	4.89	5.26	5.26	4.85	-8.0	1.3	-1.0
Cr, µg/L	10.10	10.10	11.13	11.13	10.10	-9.2	0.0	-1.2
Cu, µg/L	23.40	23.40	25.2	25.2	23.4	-7.3	0.0	-1.5
Ni, µg/L	39.80	39.80	43.3	43.3	39.8	-8.1	0.0	-1.6
Pb, µg/L	1.73	1.77	1.90	1.90	1.75	-8.0	1.6	-1.0
Zn, µg/L	79.80	78.40	81.65	81.65	79.1	-3.1	1.3	-0.8
Hg, µg/L	1.520	1.480	1.160	1.160	1.500	29.3	1.9	1.8

Laboratory Code no:	18							
	Measured data		Assigned values		Statistics			
Components	Wastewater A	Wastewater B	Wastewater A	Wastewater B	Average	Dev. %	RSD %	z-score
NO3-N, mg/L	2.53	2.53	2.47	2.47	2.53	2.4	0.1	0.8
NO2+3-N, mg/L	2.82	2.81	2.81	2.81	2.82	0.1	0.5	0.0
N-total, mg/L	6.71	6.71	6.78	6.78	6.71	-1.0	0.0	-0.2
PO4-P, mg/L	0.45	0.45	0.48	0.48	0.45	-5.5	0.2	-2.0
P-total, mg/L	0.61	0.61	0.61	0.61	0.61	-0.3	0.5	-0.1
Cd, µg/L			5.26	5.26				
Cr, µg/L			11.13	11.13				
Cu, µg/L			25.2	25.2				
Ni, µg/L			43.3	43.3				
Pb, µg/L			1.90	1.90				
Zn, µg/L			81.65	81.65				
Hg, µg/L			1.160	1.160				

4 Evaluation of results

For each component the following statistical analysis have been performed: For sample A and B (freshwater and wastewater): a table with the data presented for each component together with outlier test according to Cochran and Grubb, z-score plot and summary of the statistical parameters. For sample C, freshwater: a 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 individual chemical components together with the outlier tests and the assigned value (in the header of the table).

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.

Stragglers and outliers are marked with X in the following outlier tables.

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 satisfactory, z = |2| -|3|is questionable and z > |3|is not acceptable (ISO 13528, 2022). Figures of the z-scores for the participating laboratories for freshwater A/B and wastewater A/B, respectively are located under the tables for outlier tests.

Table of summary statistics (ISO 5725, 2019):

For sample A and B a summary evaluation of the single components across the laboratories in order to present a picture of the general analytical quality. For all the following calculations outlier data are excluded. The tables are located under the z-scores figures and consists of the following parameters:

p: number of laboratories. Number of laboratories included in the statistics, laboratories with outliers are 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.

4.2 Statistical data for each component in freshwater

4.2.1 NO_3-N

Table 4.1. Results of outlier test for freshwater NO_3-N, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***NO3-N, mg/L***								
Assigned value	**0.60**	**0.60**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded**
Laboratory	**Freshwater**	**Freshwater**							**in statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	0.58	0.59							
4	0.64	0.64				X			
5	0.61	0.61							
6	0.59	0.59							
9	0.59	0.59							
10	0.58	0.58							
11	0.59	0.60							
15	0.62	0.60		X					
16	0.61	0.61							
17	0.58	0.59							
18	0.60	0.60							

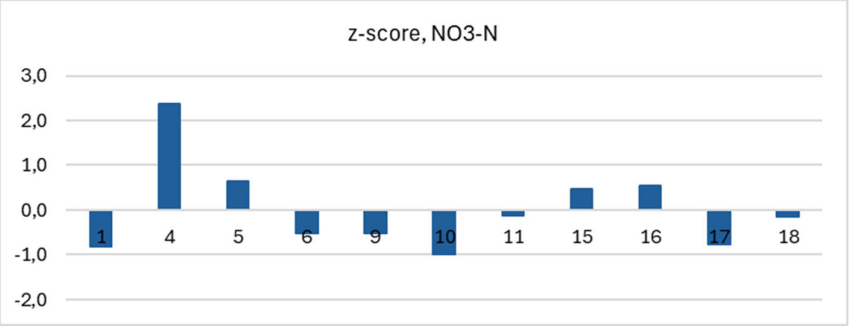


Figure 4.1. Z-scores of the laboratories for freshwater NO_3-N, sample A and B.

Table 4.2. Summary statistics for freshwater NO_3-N, sample A and B.

	NO3-N
Statistical parameters	A/B Freshwater
p	11
m [mg/L]	0.60
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) [%]	1.0
CV(R) [%]	2.9

Table 4.3. Results of outlier tests for freshwater NO_3-N, sample C. Stragglers (5%) and outliers (1%) marked with X.

Component	***NO3-N, mg/L***					
Assigned value	**1.14**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	1.12					
4	1.20		X			
5	1.10					
6	1.13					
9	1.10					
10	1.14					
11	1.14					
15	1.13					
16	1.15					
17	1.14					
18	1.13					

Table 4.4. Summary statistics for freshwater NO_3-N, sample C.

Statistical analysis	**Freshwater C NO_3-N. mg/L**
Assigned value	1.14
Laboratory deviation (S(L)	0.027
Relative laboratory deviation (%)	2.4
Calculated spike value	0.53
Measured value of spike	0.54
% recovery of spike	101%

4.2.2 NO_{2+3}-N

Table 4.5. Results of outlier test for freshwater NO_{2+3}-N, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*NO2+3-N, mg/L*								
Assigned value	**0.605**	**0.605**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Freshwater A**	**Freshwater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	0.59	0.59							
3	0.61	0.60							
4	0.64	0.65							
5	0.61	0.61							
8	0.59	0.59							
9	0.60	0.59							
10	0.60	0.60							
11	0.59	0.60							
13	0.61	0.61							
14	0.61	0.60							
15	0.63	0.62							
16	0.62	0.61							
17	0.58	0.59							
18	0.60	0.61							

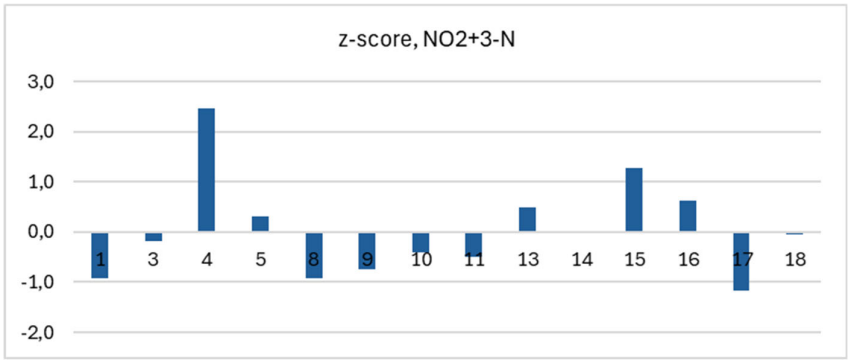


Figure 4.2. Z-scores of the laboratories for freshwater NO_{2+3}-N, sample A and B.

Table 4.6. Summary statistics for freshwater NO_{2+3}-N, sample A and B.

Statistical parameters	**NO2+3-N A/B Freshwater**
p	14
m [mg/L]	0.61
S(L) [mg/L]	0.016
S(r) [mg/L]	0.004
S(R) [mg/L]	0.016
r [mg/L]	0.012
R [mg/L]	0.045
CV(r) [%]	0.7
CV(R) [%]	2.7

Table 4.7. Results of outlier tests for freshwater NO_3-N, sample C. Stragglers (5%) and outliers (1%) marked with X.

Component	***NO2+3-N, mg/L***					
Assigned value	**1.14**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	1.12					
3	1.16					
4	1.20					
5	1.10					
8	1.11					
9	1.10					
10	1.15					
11	0.11	X	X	-	-	X
13	1.15					
14	1.21					
15	1.17					
16	1.14					
17	1.14					
18	1.13					

Tabel 4.8. Summary statistics for freshwater NO_{2+3}-N, sample C.

	Freshwater C
Statistical analysis	**NO2+3-N. mg/L**
Measured spike	1.14
Laboratory deviation (S(L)	0.035
Relative laboratory deviation (%)	3.0
Calculated spike value	0.53
Measured value of spike	0.54
% recovery of spike	102%

4.2.3 N-total

Table 4.9. Results of outlier test for freshwater N-total, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***N-total, mg/L***								
Assigned value	**2.23**	**2.23**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	2.35	2.36							
3	2.29	2.27							
4	2.40	2.50							
5	2.20	2.20							
8	1.89	2.00							
9	2.24	2.21							
10	2.28	2.25							
11	2.07	2.08							
13	2.07	2.09							
14	2.51	2.57							
15	2.08	2.13							
16	2.26	2.22							
17	2.17	2.14							
18	2.31	2.31							

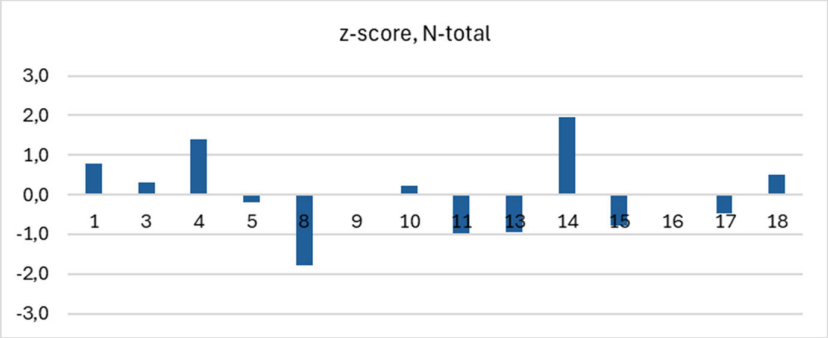


Figure 4.3. Z-scores of the laboratories for freshwater N-total, sample A and B..

Table 4.10. Summary statistics for freshwater N-total, sample A and B.

	N-total
Statistical parameters	**A/B Freshwater**
p	14
m [mg/L]	2.23
S(L) [mg/L]	0.155
S(r) [mg/L]	0.034
S(R) [mg/L]	0.159
r [mg/L]	0.096
R [mg/L]	0.445
CV(r) [%]	1.5
CV(R) [%]	7.1

Table 4.11. Results of outlier tests for freshwater N-total, sample C. Stragglers (5%) and outliers (1%) marked with X

Component	***N-total, mg/L***					
Assigned value	**2.89**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	3.17					
3	2.97					
4	3.02					
5	2.90					
8	2.61					
9	2.85					
10	2.90					
11	2.77					
13	2.68					
14	3.15					
15	2.77					
16	2.98					
17	2.73					
18	2.96					

Table 4.12. Summary statistics for freshwater N-total, sample C.

	Freshwater C
Statistical analysis	**N-total. mg/L**
Measured spike	2.89
Laboratory deviation (S(L)	0.167
Relative laboratory deviation (%)	5.8
Calculated spike value	0.68
Measured value of spike	0.66
% recovery of spike	98%

4.2.4 PO_4-P

Table 4.13. Results of outlier test for freshwater PO_4-P, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*PO4-P, mg/L*								
Assigned value	**0.39**	**0.39**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	0.40	0.41							
3	0.38	0.38							
4	0.39	0.41	X	X	-	-	-	-	X
5	0.40	0.40							
6	0.39	0.39							
8	0.39	0.40							
9	0.39	0.39							
10	0.41	0.41							
11	0.37	0.37							
13	0.38	0.38							
14	0.40	0.40							
15	0.38	0.39		X					
16	0.41	0.40							
17	0.41	0.41							
18	0.39	0.39							

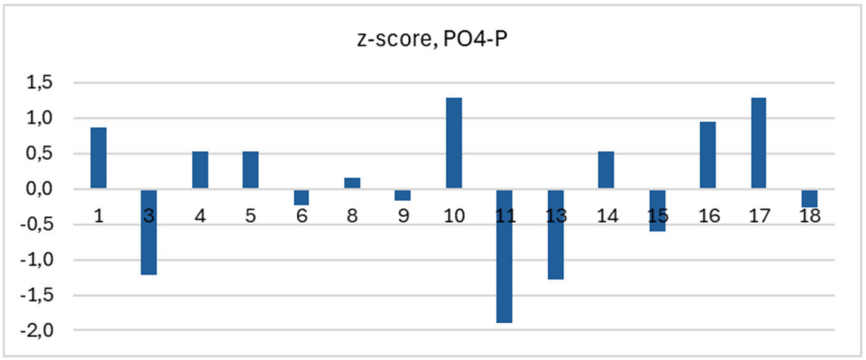


Figure 4.4. Z-scores of the laboratories for freshwater PO_4-P, sample A and B.

Table 4.14. Summary statistics for freshwater PO_4-P, sample A and B.

	PO4-P
Statistical parameters	**A/B Freshwater**
p	14
m [mg/L]	0.39
S(L) [mg/L]	0.013
S(r) [mg/L]	0.003
S(R) [mg/L]	0.013
r [mg/L]	0.007
R [mg/L]	0.037
CV(r) [%]	0.7
CV(R) [%]	3.4

Table 4.15. Results of outlier tests for freshwater PO_4-P, sample C. Stragglers (5%) and outliers (1%) marked with X

Component	***PO4-P, mg/L***					
Assigned value	**0.52**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	0.53					
3	0.51					
4	0.55					
5	0.53					
6	0.52					
8	0.53					
9	0.49					
10	0.51					
11	0.49					
13	0.52					
14	0.53					
15	0.52					
16	0.54					
17	0.48					
18	0.51					

Table 4.16. Summary statistics for freshwater PO_4-P, sample C.

	Freshwater C
Statistical analysis	**PO4-P. mg/L**
Assigned value	0.52
Laboratory deviation (S(L)	0.019
Relative laboratory deviation (%)	3.7
Calculated spike value	0.16
Measured value of spike	0.12
% recovery of spike	79%

4.2.5 P-total

Table 4.17. Results of outlier test for freshwater P-total, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***P-total, mg/L***								
Assigned value	**0.43**	**0.43**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Freshwater A**	**Freshwater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.46	0.46							
3	0.39	0.39							
4	0.43	0.41							
5	0.46	0.44							
6	0.44	0.43							
8	0.42	0.43							
9	0.44	0.45							
10	0.42	0.43							
11	0.40	0.38							
13	0.43	0.44							
14	0.45	0.45							
15	0.43	0.43							
16	0.43	0.44							
17	0.43	0.42							
18	0.43	0.44							

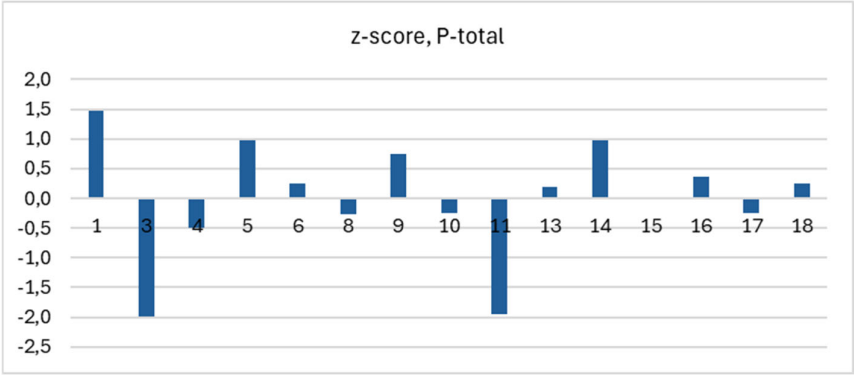


Figure 4.5. Z-scores of the laboratories for freshwater P-total, sample A and B.

Table 4.18. Summary statistics for freshwater P-total, sample A and B.

	P-total
Statistical parameters	**A/B Freshwater**
p	15
m [mg/L]	0.43
S(L) [mg/L]	0.019
S(r) [mg/L]	0.007
S(R) [mg/L]	0.020
r [mg/L]	0.020
R [mg/L]	0.057
CV(r) [%]	1.7
CV(R) [%]	4.7

Table 4.19. Results of outlier tests for freshwater P-total, sample C. Stragglers (5%) and outliers (1%) marked with X.

Component	***P-total, mg/L***					
Assigned value	**0.55**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	0.58					
3	0.51					
4	0.56					
5	0.53					
6	0.56					
8	0.55					
9	0.56					
10	0.55					
11	0.50					
13	0.56					
14	0.56					
15	0.55					
16	0.57					
17	0.51					
18	0.57					

Table 4.20. Summary statistics for freshwater P-total, sample C.

	Freshwater C
Statistical analysis	**P-total. mg/L**
Assigned value	0.55
Laboratory deviation (S(L)	0.024
Relative laboratory deviation (%)	4.4
Calculated spike value	0.12
Measured value of spike	0.12
% recovery of spike	95%

4.2.6 Cd

Table 4.21. Results of outlier test for freshwater Cd, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*Cd, µg/L*								
Assigned value	**1.40**	**1.40**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	1.38	1.38							
3	1.33	1.31							
4	1.31	1.32							
5	1.35	1.37							
6	1.44	1.46							
7	1.40	1.40							
8	1.42	1.42							
9	1.37	1.55	X	X	-	-	-	-	X
10	1.01	1.01			X	X	-	-	X
11	1.38	1.39							
13	1.43	1.45							
15	1.53	1.57							
16	1.41	1.41							
17	1.36	1.36							

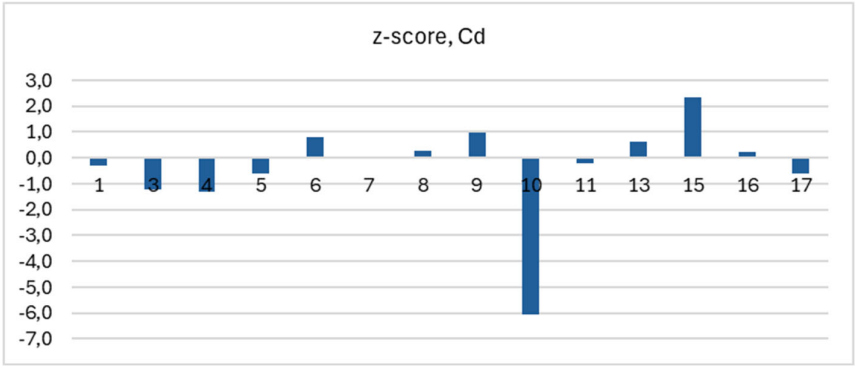


Figure 4.6. Z-scores of the laboratories for freshwater Cd, sample A and B.

Table 4.22. Summary statistics for freshwater Cd, sample A and B.

	Cd
Statistical parameters	**A/B Freshwater**
p	12
m [µg/L]	1.40
S(L) [µg/L]	0.063
S(r) [µg/L]	0.011
S(R) [µg/L]	0.064
r [µg/L]	0.030
R [µg/L]	0.179
CV(r) [%]	0.8
CV(R) [%]	4.6

Table 4.23. Results of outlier tests for freshwater Cd, sample C. Stragglers (5%) and outliers (1%) marked with X

Component	***Cd, µg/L***					
Assigned value	**1.99**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	1.97					
3	1.88					
4	1.87					
5	2.00					
6	1.99					
7	2.00					
8	1.98					
9	2.17					
10	1.41	X	X	-	-	X
11	1.97					
13	1.99					
15	2.13					
16	2.01					
17	1.87					

Table 4.24. Summary statistics for freshwater Cd, sample C.

	Freshwater C
Statistical analysis	**Cd. µg/L**
Measured spike	0.59
Laboratory deviation (S(L)	0.088
Relative laboratory deviation (%)	14.9
Calculated spike value	0.60
Measured value of spike	0.59
% recovery of spike	98%

4.2.7 Cr

Table 4.25. Results of outlier test for freshwater Cr, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***Cr, µg/L***								
Assigned value	**6.67**	**6.67**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Freshwater A**	**Freshwater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.59	6.80							
3	6.52	6.54							
4	6.61	6.55							
5	6.70	6.74							
6	6.50	6.80							
7	11.00	11.00			X	X	-	-	X
8	6.77	6.88							
9	8.98	8.06	X	X	-	-	-	-	X
10	5.40	5.43			X	X	-	-	X
11	7.34	7.40			X	X	-	-	X
13	6.71	6.79							
15	6.97	6.63							
16	6.71	6.69							
17	6.46	6.38							

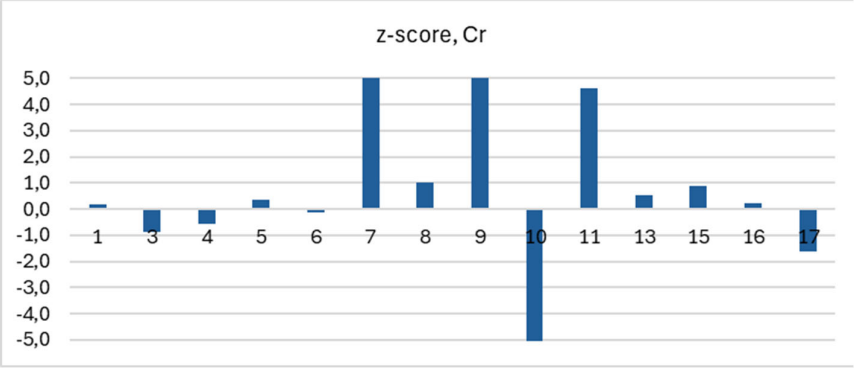


Figure 4.7. Z-scores of the laboratories for freshwater Cr, sample A and B. Laboratory code no. 7 (Z-score 28.4), 9 (Z-score 12.2) and 10 (Z-score -8.2) are outside the range of the figure.

Table 4.26. Summary statistics for freshwater Cr, sample A and B.

	Cr
Statistical parameters	**A/B Freshwater**
p	10
m [µg/L]	6.67
S(L) [µg/L]	0.090
S(r) [µg/L]	0.123
S(R) [µg/L]	0.153
r [µg/L]	0.344
R [µg/L]	0.427
CV(r) [%]	1.8
CV(R) [%]	2.3

Table 4.27. Results of outlier tests for freshwater Cr, sample C. Stragglers (5%) and outliers (1%) marked with X

Component	***Cr, µg/L***					
Assigned value	**9.62**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	9.42					
3	9.23					
4	9.26					
5	9.62					
6	10.50					
7	15.00	X	X	-	-	X
8	9.78					
9	11.34					
10	7.59					
11	10.72					
13	9.33					
15	9.70					
16	9.56					
17	9.01					

Table 4.28. Summary statistics for freshwater Cr, sample C.

	Freshwater C
Statistical analysis	**Cr. µg/L**
Measured spike	2.95
Laboratory deviation (S(L)	0.908
Relative laboratory deviation (%)	30.7
Calculated spike value	2.94
Measured value of spike	2.95
% recovery of spike	100%

4.2.8 Cu

Table 4.29. Results of outlier test for freshwater Cu, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*Cu, µg/L*								
Assigned value	**13.84**	**13.84**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Freshwater A**	**Freshwater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	13.95	13.82							
3	14.45	14.30							
4	13.66	13.81							
5	14.40	14.30							
6	13.00	12.00							
7	13.00	13.00							
8	13.99	13.89							
9	14.89	13.59		X					
10	13.15	12.98							
11	14.71	14.88							
13	13.97	14.00							
15	14.80	14.40							
16	13.45	13.52							
17	13.80	13.80							

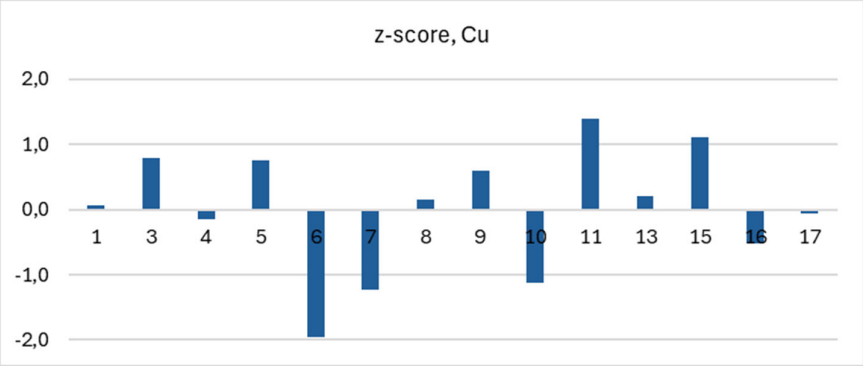


Figure 4.8. Z-scores of the laboratories for freshwater Cu, sample A and B.

Table 4.30. Summary statistics for freshwater Cu, sample A and B.

	Cu
Statistical parameters	**A/B Freshwater**
p	14
m [µg/L]	13.84
S(L) [µg/L]	0.612
S(r) [µg/L]	0.304
S(R) [µg/L]	0.683
r [µg/L]	0.850
R [µg/L]	1.912
CV(r) [%]	2.2
CV(R) [%]	4.9

Table 4.31. Results of outlier tests for freshwater Cu, sample C. Stragglers (5%) and outliers (1%) marked with X

Component	***Cu, µg/L***					
Assigned value	**19.59**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	18.91					
3	19.90					
4	18.94					
5	20.10					
6	18.00					
7	18.00					
8	19.38					
9	22.24				X	
10	17.39					
11	20.52					
13	19.50					
15	23.90				X	
16	18.83					
17	18.60					

Table 4.32. Summary statistics for freshwater Cu, sample C.

	Freshwater C
Statistical analysis	**Cu. µg/L**
Measured spike	5.75
Laboratory deviation (S(L)	1.736
Relative laboratory deviation (%)	30.2
Calculated spike value	5.88
Measured value of spike	5.75
% recovery of spike	98%

4.2.9 Ni

Table 4.33. Results of outlier test for freshwater Ni, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***Ni, µg/L***								
Assigned value	**2.25**	**2.25**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Freshwater A**	**Freshwater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	2.23	2.13							
3	2.20	2.20							
4	2.20	2.24							
5	2.21	2.31							
6	2.30	2.20							
7	2.40	2.30							
8	2.24	2.28							
9	2.65	2.37		X					
10	1.59	1.57			X	X	-	-	X
11	2.37	2.46							
13	2.28	2.23							
15	2.01	1.94							
16	2.09	2.08							
17	2.23	2.21							

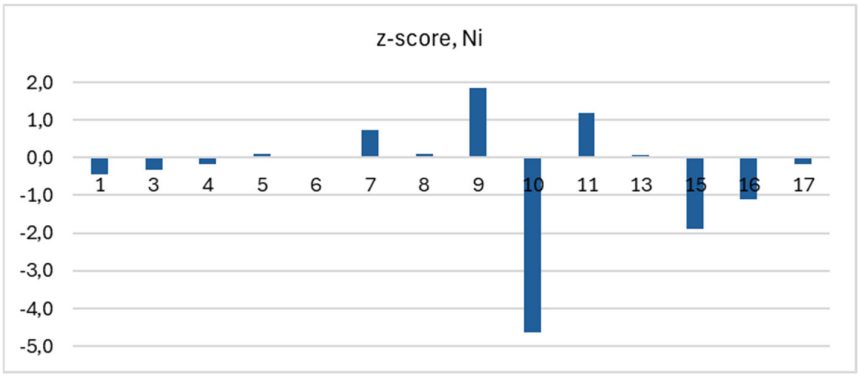


Figure 4.9. Z-scores of the laboratories for freshwater Ni, sample A and B.

Table 4.34. Summary statistics for freshwater Ni, sample A and B.

	Ni
Statistical parameters	**A/B Freshwater**
p	13
m [µg/L]	2.25
S(L) [µg/L]	0.124
S(r) [µg/L]	0.071
S(R) [µg/L]	0.143
r [µg/L]	0.198
R [µg/L]	0.401
CV(r) [%]	3.2
CV(R) [%]	6.4

Table 4.35. Results of outlier tests for freshwater Ni, sample C. Stragglers (5%) and outliers (1%) marked with X

Component	***Ni, µg/L***					
Assigned value	**2.70**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	2.75					
3	2.70					
4	2.71					
5	2.72					
6	2.50					
7	3.50			X	X	X
8	2.77					
9	3.80		X	X	X	X
10	17.39	X	X	-	-	X
11	3.00					
13	2.75					
15	2.50					
16	2.58					
17	2.67					

Table 4.36. Summary statistics for freshwater Ni, sample C.

	Freshwater C
Statistical analysis	**Ni. µg/L**
Measured spike	0.45
Laboratory deviation (S(L)	0.140
Relative laboratory deviation (%)	31.1
Calculated spike value	0.47
Measured value of spike	0.45
% recovery of spike	96%

4.2.10 Pb

Table 4.37. Results of outlier test for freshwater Pb, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***Pb, µg/L***								
Assigned value	**1.69**	**1.69**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Freshwater A**	**Freshwater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	1.68	1.65							
3	1.61	1.59							
4	1.84	1.81							
5	1.77	1.74							
6	1.40	1.70	X	X	-	-	-	-	X
7	1.80	1.80							
8	1.62	1.60							
9	6.81	6.65	X	X	-	-	-	-	X
10	1.03	1.03			X	X	-	-	X
11	1.60	1.56							
13	1.70	1.70							
15	1.87	1.78		X					
16	1.63	1.62							
17	1.65	1.65							

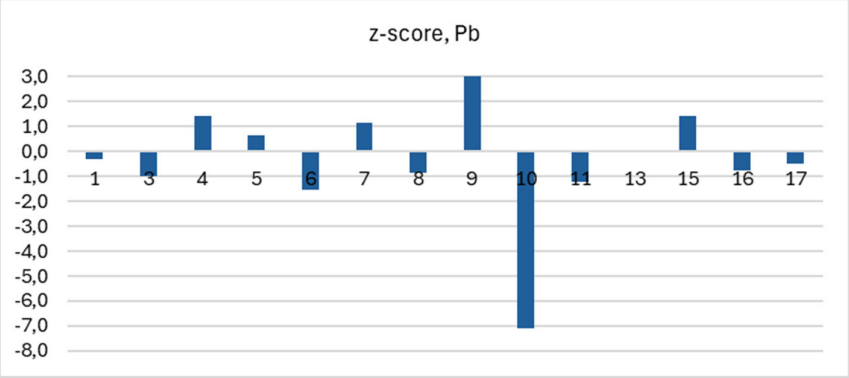


Figure 4.10. Z-scores of the laboratories for freshwater Pb, sample A and B. Laboratory code no. 9 (Z-score 54.1) is outside the range of the figure.

Table 4.38. Summary statistics for freshwater Pb, sample A and B.

	Pb
Statistical parameters	**A/B Freshwater**
p	11
m [µg/L]	1.69
S(L) [µg/L]	0.091
S(r) [µg/L]	0.019
S(R) [µg/L]	0.093
r [µg/L]	0.053
R [µg/L]	0.261
CV(r) [%]	1.1
CV(R) [%]	5.5

Table 4.39. Results of outlier tests for freshwater Pb, sample C. Stragglers (5%) and outliers (1%) marked with X

Component	***Pb, µg/L***					
Assigned value	**2.00**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	1.98					
3	1.91					
4	2.17					
5	2.09					
6	1.90					
7	2.10					
8	1.91					
9	7.26	X	X	-	-	X
10	1.22	X	X	-	-	X
11	1.88					
13	2.03					
15	2.10					
16	1.93					
17	1.94					

Table 4.40. Summary statistics for freshwater Pb, sample C.

	Freshwater C
Statistical analysis	**Pb. µg/L**
Measured spike	0.30
Laboratory deviation (S(L)	0.098
Relative laboratory deviation (%)	32.5
Calculated spike value	0.29
Measured value of spike	0.30
% recovery of spike	102%

4.2.11 Zn

Table 4.41. Results of outlier test for freshwater Zn, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***Zn, µg/L***								
Assigned value	**25.01**	**25.01**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Freshwater**	**Freshwater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	24.30	24.00							
3	25.60	25.50							
4	24.57	25.06							
5	26.10	26.10							
6	24.00	24.00							
7	24.00	23.00							
8	26.05	25.97							
9	25.20	24.23							
10	20.29	20.36			X	X	-	-	X
11	25.44	25.40							
13	26.20	26.10							
15	22.70	24.70	X	X	-	-	-	-	X
16	24.91	24.87							
17	24.70	24.80							

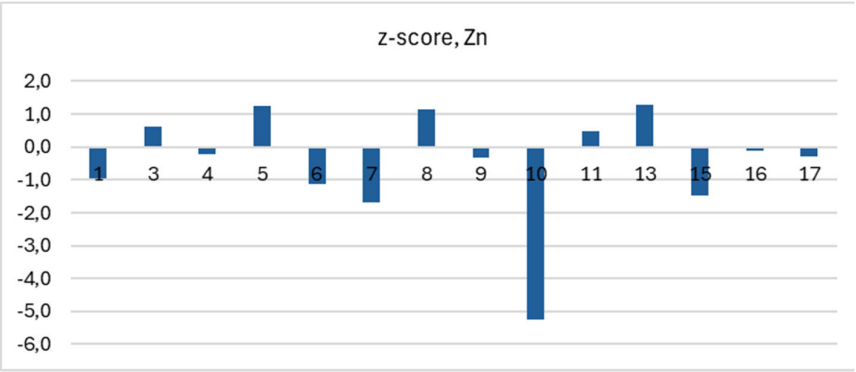


Figure 4.11. Z-scores of the laboratories for freshwater Zn, sample A and B.

Table 4.42. Summary statistics for freshwater Zn, sample A and B.

	Zn
Statistical parameters	**A/B Freshwater**
p	12
m [µg/L]	25.01
S(L) [µg/L]	0.837
S(r) [µg/L]	0.298
S(R) [µg/L]	0.889
r [µg/L]	0.835
R [µg/L]	2.488
CV(r) [%]	1.2
CV(R) [%]	3.6

Table 4.43. Results of outlier tests for freshwater Zn, sample C. Stragglers (5%) and outliers (1%) marked with X.

Component	***Zn, µg/L***					
Assigned value	**23.78**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	22.70					
3	23.90					
4	23.54					
5	25.00					
6	24.00					
7	22.00					
8	24.28					
9	24.57					
10	19.26					
11	24.59					
13	24.40					
15	27.70					
16	23.72					
17	23.30					

Table 4.44. Summary statistics for freshwater Zn, sample C.

	Freshwater C
Statistical analysis	**Zn. µg/L**
Assigned value	23.78
Laboratory deviation (S(L)	1.837
Relative laboratory deviation (%)	7.7
Calculated spike value	-
Measured value of spike	-
% recovery of spike	-

Because of a calculation error, Zn was not spiked in a higher concentration for the C samples.

4.2.12 Hg

Table 4.45. Results of outlier test for freshwater Hg, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*Hg, µg/L*								
Assigned value	0.081	0.081	Cochrans test		Grupps single test		Grupps double test		Excluded in statistical analysis
Laboratory code no.	Freshwater A	Freshwater B	1% level	5% level	1% level	5% level	1% level	5% level	
1	0.090	0.091							
3	<DL	<DL							
4	0.067	0.071							
5	0.049	0.054							
6	0.078	0.089							
7	0.069	0.068							
8	0.087	0.086							
9	0.084	0.081							
10	0.046	0.049							
11	0.108	0.104							
13	0.095	0.097							
15	0.108	0.097							
16	0.087	0.084							
17	0.099	0.075	X	X	-	-	-	-	X

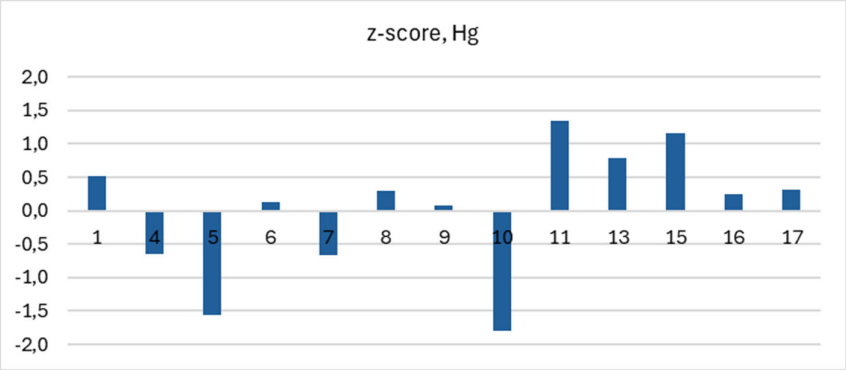


Figure 4.12. Z-scores of the laboratories for freshwater Hg, sample A and B.

Table 4.46. Summary statistics for freshwater Hg, sample A and B.

	Hg
Statistical parameters	**A/B Freshwater**
p	12
m [µg/L]	0.081
S(L) [µg/L]	0.0182
S(r) [µg/L]	0.0039
S(R) [µg/L]	0.0186
r [µg/L]	0.0110
R [µg/L]	0.0521
CV(r) [%]	4.8
CV(R) [%]	23.0

Table 4.47. Results of outlier tests for freshwater Hg, sample C. Stragglers (5%) and outliers (1%) marked with X.

Component	***Hg, µg/L***					
Assigned value	**0.12**	**Grupps single test**		**Grupps double test**		
Laboratory code no.	**Freshwater C**	**1% level**	**5% level**	**1% level**	**5% level**	**Excluded in statistical analysis**
1	0.13					
3	<DL					
4	0.09					
5	0.08					
6	0.12					
7	0.09					
8	0.12					
9	0.12					
10	0.08					
11	0.15					
13	0.15					
15	0.14					
16	0.11					
17	0.11					

Table 4.48. Summary statistics for freshwater Hg, sample C.

	Freshwater C
Statistical analysis	**Hg. µg/L**
Assigned value	0.116
Measured spike	0.035
Relative laboratory deviation (%)	30.2
Calculated spike value	0.04
Measured value of spike	0.04
% recovery of spike	94%

4.3 Statistical data for each component in wastewater

4.3.1 NO_3-N

Table 4.49. Results of outlier test for wastewater NO_3-N, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*NO3-N, mg/L*								
Assigned value	**2.47**	**2.47**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory code no.	**Wastewater A**	**Wastewater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**statistical analysis**
1	2.47	2.48							
2	2.31	2.31							
4	2.70	2.90	X	X	-	-	-	-	X
5	2.50	2.50							
6	2.43	2.43							
9	2.43	2.44							
10	2.44	2.43							
12	2.24	594.18	X	X	-	-	-	-	X
14	2.45	2.37	X	X	-	-	-	-	X
15	2.57	2.57							
16	2.47	2.48							
17	2.52	2.53							
18	2.53	2.53							

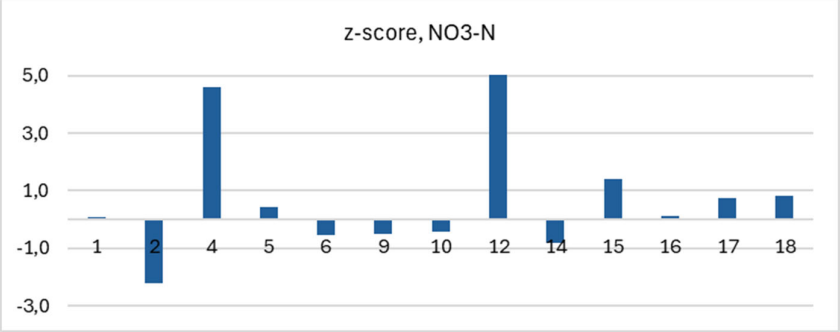


Figure 4.13. Z-scores of the laboratories for wastewater NO_3-N, sample A and B. Laboratory code no. 12 (z-score 4114) is outside the range of the figure.

Table 4.50. Summary statistics for wastewater NO_3-N, sample A and B.

	NO3-N
Statistical parameters	**A/B Wastewater**
p	10
m [mg/L]	2.47
S(L) [mg/L]	0.072
S(r) [mg/L]	0.005
S(R) [mg/L]	0.072
r [mg/L]	0.014
R [mg/L]	0.201
CV(r) [%]	0.2
CV(R) [%]	2.9

4.3.2 NO_{2+3}-N

Table 4.51. Results of outlier test for wastewater NO_{2+3}-N, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***NO2+3-N, mg/L***								
Assigned value	**2.81**	**2.81**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Wastewater A**	**Wastewater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	2.79	2.80							
2	2.68	2.69							
3	2.84	2.85							
4	3.10	3.20	X	X	-	-	-	-	X
5	2.80	2.80							
8	2.80	2.81							
9	2.80	2.79							
10	2.70	2.70							
12	0.44	0.17	X	X	-	-	-	-	X
15	2.91	2.95							
16	2.90	2.88							
17	2.88	2.89							
18	2.82	2.81							

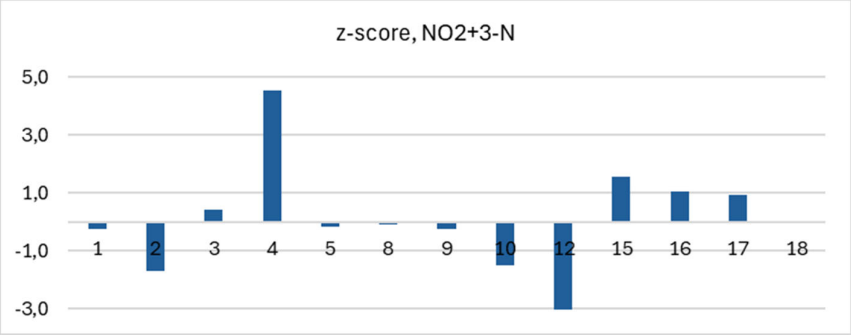


Figure 4.14. Z-scores of the laboratories for wastewater NO_{2+3}-N, sample A and B. Laboratory code no. 12 (z-score -33.7) is outside the range of the figure.

Table 4.52. Summary statistics for wastewater NO_{2+3}-N, sample A and B.

Statistical parameters	**NO2+3-N A/B Wastewater**
p	11
m [mg/L]	2.81
S(L) [mg/L]	0.073
S(r) [mg/L]	0.013
S(R) [mg/L]	0.074
r [mg/L]	0.036
R [mg/L]	0.208
CV(r) [%]	0.5
CV(R) [%]	2.6

4.3.3 N-total

Table 4.53. Results of outlier test for wastewater N-total, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***N-total, mg/L***								
Assigned value	**6.78**	**6.78**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Wastewater A**	**Wastewater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	6.49	6.61							
2	6.50	6.51							
3	6.90	6.89							
4	6.90	7.20							
5	6.70	6.70							
8	6.39	6.62							
9	6.63	6.44							
10	7.00	6.80							
12	5.77	588	X	X	-	-	-	-	X
14	7.28	7.62				X			
15	6.59	6.58							
16	6.88	6.83							
17	6.85	6.84							
18	6.71	6.71							

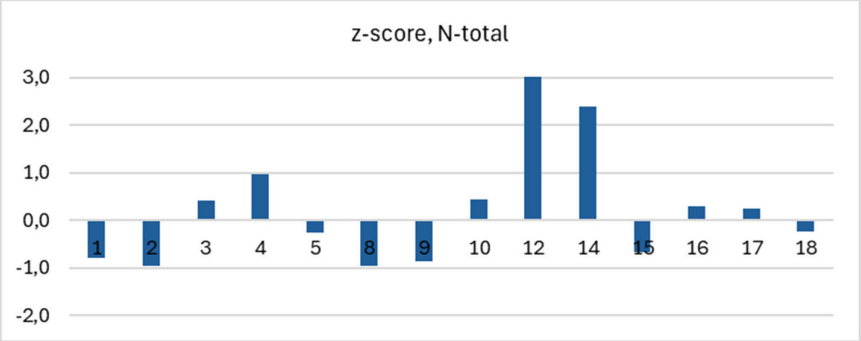


Figure 4.15. Z-scores of the laboratories for wastewater N-total, sample A and B. Laboratory code no. 12 (z-score 1029) is outside the range of the figure.

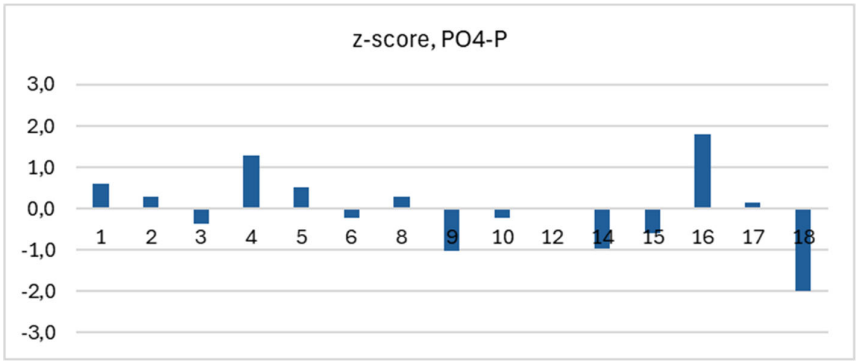
Table 4.54. Summary statistics for wastewater N-total, sample A and B.

Statistical parameters	**N-total A/B Wastewater**
p	13
m [mg/L]	6.78
S(L) [mg/L]	0.257
S(r) [mg/L]	0.117
S(R) [mg/L]	0.282
r [mg/L]	0.327
R [mg/L]	0.790
CV(r) [%]	1.7
CV(R) [%]	4.2

4.3.4 PO_4-P

Table 4.55. Results of outlier test for wastewater PO_4-P, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*PO4-P, mg/L*								
Assigned value	**0.48**	**0.48**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	0.48	0.49							
2	0.48	0.48							
3	0.47	0.47							
4	0.50	0.49							
5	0.48	0.49							
6	0.47	0.48							
8	0.48	0.49							
9	0.46	0.47							
10	0.48	0.47							
12	0.43	<DL							
14	0.47	0.47							
15	0.47	0.47							
16	0.50	0.50							
17	0.48	0.48							
18	0.45	0.45							



Figur 4.16. Z-scores of the laboratories for wastewater PO_4-P, sample A and B.

Table 4.56. Summary statistics for wastewater PO_4-P, sample A and B.

	PO4-P
Statistical parameters	**A/B Wastewater**
p	14
m [mg/L]	0.48
S(L) [mg/L]	0.012
S(r) [mg/L]	0.005
S(R) [mg/L]	0.013
r [mg/L]	0.013
R [mg/L]	0.037
CV(r) [%]	1.0
CV(R) [%]	2.8

4.3.5 P-total

Table 4.57. Results of outlier test for wastewater P-total, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	***P-total, mg/L***								
Assigned value	**0.61**	**0.61**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in statistical analysis**
Laboratory code no.	**Wastewater A**	**Wastewater B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	
1	0.65	0.64							
2	0.64	0.64							
3	0.60	0.60							
4	0.55	0.59	X	X	-	-	-	-	X
5	0.58	0.58							
6	0.61	0.60							
8	0.60	0.60							
9	0.62	0.61							
10	0.58	0.58							
12	0.58	0.03	X	X	-	-	-	-	X
14	0.64	0.63							
15	0.60	0.60							
16	0.60	0.60							
17	0.61	0.61							
18	0.61	0.61							

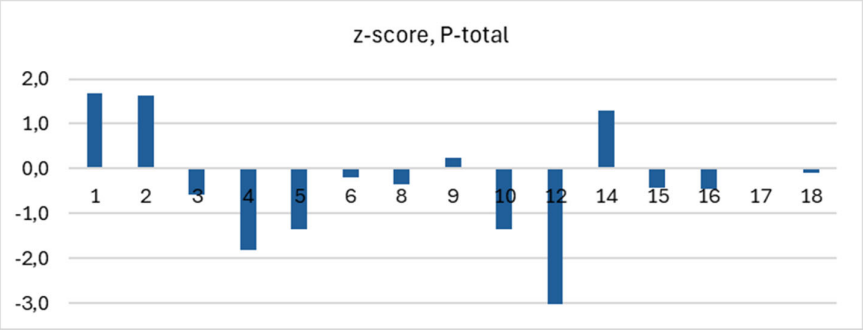


Figure 4.17. Z-scores of the laboratories for wastewater P-total, sample A and B. Laboratory code no. 12 (z-score -14.1) is outside the range of the figure.

Table 4.58. Summary statistics for wastewater P-total, sample A and B.

	P-total
Statistical parameters	**A/B Wastewater**
p	13
m [mg/L]	0.61
S(L) [mg/L]	0.021
S(r) [mg/L]	0.004
S(R) [mg/L]	0.021
r [mg/L]	0.012
R [mg/L]	0.060
CV(r) [%]	0.7
CV(R) [%]	3.5

4.3.6 Cd

Table 4.59. Results of outlier test for wastewater Cd, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*Cd, µg/L*								
Assigned value	**5.26**	**5.26**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	5.26	5.25							
2	5.99	5.99							
3	4.94	4.92							
4	4.78	4.87							
5	5.04	5.05							
6	<DL	<DL							
7	5.10	5.00							
8	5.48	5.49							
9	5.14	5.08							
10	2.51	2.55			X	X	-	-	X
12	5.43	<DL							
15	6.03	6.21							
16	5.26	5.24							
17	4.80	4.89							

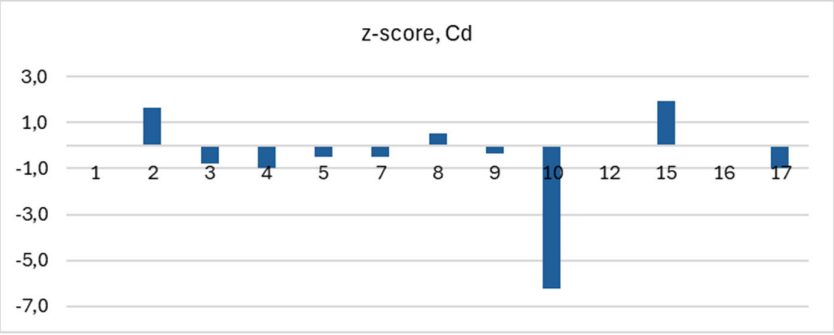


Figure 4.18. Z-scores of the laboratories for wastewater Cd, sample A and B.

Table 4.60. Summary statistics for wastewater Cd, sample A and B.

	Cd
Statistical parameters	**A/B Wastewater**
p	11
m [µg/L]	5.26
S(L) [µg/L]	0.435
S(r) [µg/L]	0.055
S(R) [µg/L]	0.438
r [µg/L]	0.155
R [µg/L]	1.228
CV(r) [%]	1.1
CV(R) [%]	8.3

4.3.7 Cr

Table 4.61. Results of outlier test for wastewater Cr, sample A and B. Stragglers (5%) and outliers (1%) marked with X.

Component	*Cr, µg/L*								
Assigned value	**11.13**	**11.13**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	10.48	10.73							
2	10.63	10.55							
3	11.00	11.10							
4	10.18	10.31							
5	11.50	11.40							
6	11.00	11.00							
7	20.00	21.00	X	X	-	-	-	-	X
8	12.36	12.15							
9	13.23	12.88							
10	6.65	6.66			X	X	-	-	X
12	11.87	0.85	X	X	-	-	-	-	X
15	11.10	11.30							
16	11.06	10.68							
17	10.10	10.10							

Figure 4.19. Z-scores of the laboratories for wastewater Cr, sample A and B. Laboratory code no. 7 (z-score 10,7) is outside the range of the figure.

Table 4.62. Summary statistics for wastewater Cr, sample A and B.

	Cr
Statistical parameters	**A/B Wastewater**
p	11
m [µg/L]	11.13
S(L) [µg/L]	0.864
S(r) [µg/L]	0.148
S(R) [µg/L]	0.876
r [µg/L]	0.415
R [µg/L]	2.454
CV(r) [%]	1.3
CV(R) [%]	7.9

4.3.8 Cu

Table 4.63. Results of outlier test for wastewater Cu, sample A and B. Stragglers (5%) and outliers (1%) marked with X

Component	*Cu, µg/L*								
Assigned value	**25.24**	**25.24**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	23.82	24.21							
2	24.24	24.30							
3	26.40	26.60							
4	24.49	24.80							
5	26.60	26.90							
6	25.00	25.00							
7	26.00	26.00							
8	26.00	27.00							
9	26.63	26.77							
10	15.17	17.70		X	X	X	-	-	X
12	26.04	0.62	X	X	-	-	-	-	X
15	24.00	26.00							
16	24.39	23.89							
17	23.40	23.40							

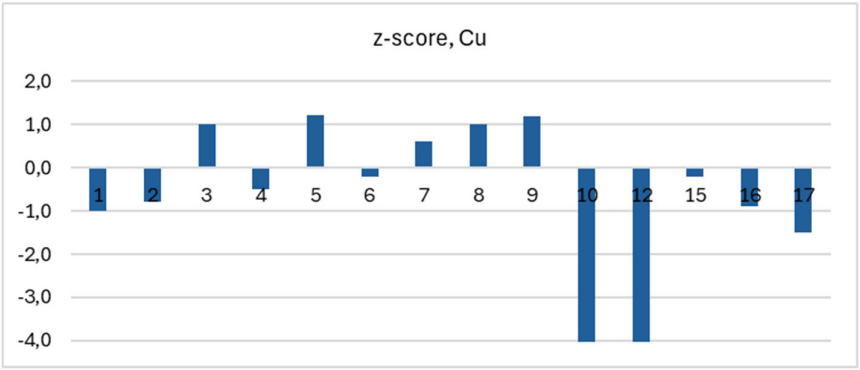


Figure 4.20. Z-scores of the laboratories for wastewater Cu, sample A and B. Laboratory code no. 10 (z-score -7.1) and 12 (z-score -9.6) are outside the range of the figure.

Table 4.64. Summary statistics for wastewater Cu, sample A and B.

	Cu
Statistical parameters	**A/B Wastewater**
p	12
m [µg/L]	25.24
S(L) [µg/L]	1.151
S(r) [µg/L]	0.447
S(R) [µg/L]	1.235
r [µg/L]	1.250
R [µg/L]	3.457
CV(r) [%]	1.8
CV(R) [%]	4.9

4.3.9 Ni

Table 4.65. Results of outlier test for wastewater Ni, sample A and B. Stragglers (5%) and outliers (1%) marked with X

Component	*Ni, µg/L*								
Assigned value	**43.31**	**43.31**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	42.18	42.32							
2	41.54	41.26							
3	43.60	43.70							
4	41.69	42.18							
5	45.30	44.80							
6	44.00	45.00							
7	47.00	48.00							
8	42.00	42.00							
9	45.31	46.18							
10	20.61	17.99			X	X	-	-	X
12	45.39	4.42	X	X	-	-	-	-	X
15	49.30	45.50	X	X	-	-	-	-	X
16	43.09	42.12							
17	39.80	39.80							

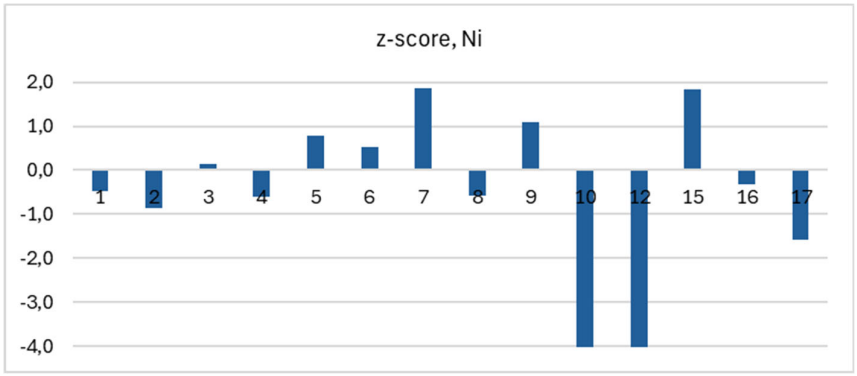


Figure 4.21. Z-scores of the laboratories for wastewater Ni, sample A and B. Laboratory code no. 10 (z-score -10.7) and 12 (z-score -8.2) are outside the range of the figure.

Table 4.66. Summary statistics for wastewater Ni, sample A and B.

	Ni
Statistical parameters	**A/B Wastewater**
p	11
m [µg/L]	43.31
S(L) [µg/L]	2.196
S(r) [µg/L]	0.447
S(R) [µg/L]	2.241
r [µg/L]	1.251
R [µg/L]	6.275
CV(r) [%]	1.0
CV(R) [%]	5.2

4.3.10 Pb

Table 4.67. Results of outlier test for wastewater Pb, sample A and B. Stragglers (5%) and outliers (1%) marked with X

Component	***Pb, µg/L***								
Assigned value	**1.90**	**1.90**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	1.84	1.96							
2	2.08	2.09							
3	1.81	1.77							
4	1.74	1.82							
5	2.16	2.10							
6	<DL	<DL							
7	2.00	2.00							
8	<DL	<DL							
9	6.98	7.12			X	X	-	-	X
10	0.81	0.81			X	X	-	-	X
12	2.02	0.22	X	X	-	-	-	-	X
16	1.78	1.79							
17	1.73	1.77							

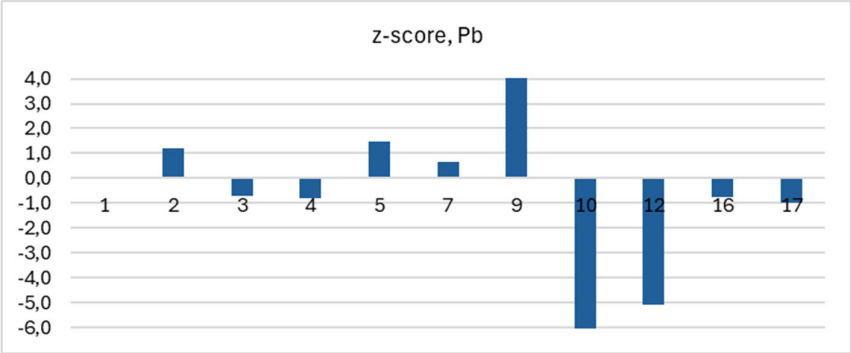


Figure 4.22. Z-scores of the laboratories for wastewater Pb, sample A and B. Laboratory code no. 9 (z-score 33.4) and 10 (z-score -7.1) are outside the range of the figure.

Table 4.68. Summary statistics for wastewater Pb, sample A and B.

	Pb
Statistical parameters	**A/B Wastewater**
p	8
m [µg/L]	1.90
S(L) [µg/L]	0.148
S(r) [µg/L]	0.042
S(R) [µg/L]	0.154
r [µg/L]	0.118
R [µg/L]	0.432
CV(r) [%]	2.2
CV(R) [%]	8.1

4.3.11 Zn

Table 4.69. Results of outlier test for wastewater Zn, sample A and B. Stragglers (5%) and outliers (1%) marked with X

Component	*Zn, µg/L*								
Assigned value	**81.6**	**81.6**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	80.80	80.00							
2	84.23	83.79							
3	84.00	85.00							
4	78.65	78.97							
5	87.70	87.50							
6	81.00	89.00	X	X	-	-	-	-	X
7	82.00	83.00							
8	78.80	78.00							
9	81.97	81.43							
10	43.36	43.78			X	X	-	-	X
12	88.74	65.02	X	X	-	-	-	-	X
15	87.00	108.00			X	X	-	-	X
16	79.58	79.34							
17	79.80	78.40							

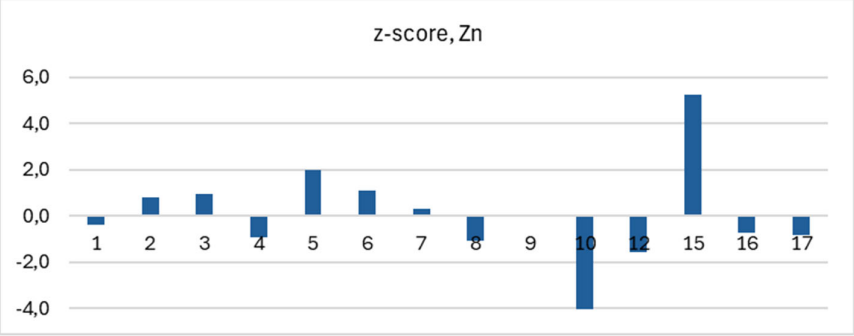


Figure 4.23. Z-scores of the laboratories for wastewater Zn, sample A and B. Laboratory code no. 10 (z-score -12.6) is outside the range of the figure.

Table 4.70. Summary statistics for wastewater Zn, sample A and B.

	Zn
Statistical parameters	**A/B Wastewater**
p	10
m [µg/L]	81.65
S(L) [µg/L]	2.980
S(r) [µg/L]	0.552
S(R) [µg/L]	3.031
r [µg/L]	1.545
R [µg/L]	8.487
CV(r) [%]	0.7
CV(R) [%]	3.7

4.3.12 Hg

Table 4.71. Results of outlier test for wastewater Hg, sample A and B. Stragglers (5%) and outliers (1%) marked with X

Component	*Hg, µg/L*								
Assigned value	**1.160**	**1.160**	**Cochrans test**		**Grupps single test**		**Grupps double test**		**Excluded in**
Laboratory	**Wastewater**	**Wastewater**							**statistical**
code no.	**A**	**B**	**1% level**	**5% level**	**1% level**	**5% level**	**1% level**	**5% level**	**analysis**
1	1.094	1.128							
2	1.077	1.136							
3	0.890	0.790							
4	1.048	1.100							
5	1.260	1.250							
6	1.380	1.460							
7	0.920	0.910							
8	1.106	1.100							
9	1.082	1.077							
10	1.037	1.315	X	X	-	-	-	-	X
12	1.195	1.196							
15	1.380	1.370							
16	1.097	1.106							
17	1.520	1.480							

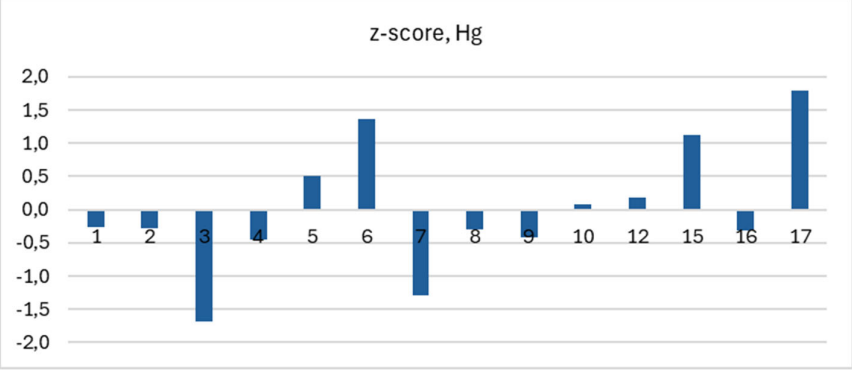


Figure 4.24. Z-scores of the laboratories for wastewater Hg, sample A and B.

Table 4.72. Summary statistics for wastewater Hg, sample A and B.

	Hg
Statistical parameters	**A/B Wastewater**
p	13
m [µg/L]	1.160
S(L) [µg/L]	0.1874
S(r) [µg/L]	0.0326
S(R) [µg/L]	0.1902
r [µg/L]	0.0914
R [µg/L]	0.5327
CV(r) [%]	2.8
CV(R) [%]	16.4

5 Conclusions and summary

5.1 Summary of the intercalibration

The number of participating laboratories for each component 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.

	Freshwater		Wastewater	
Component	**Laboratories included in the statistics**	**Laboratories excluded (</outlier)**	**Laboratories included in the statistics**	**Laboratories excluded (</outlier)**
NO_3-N, mg/L	11	-	10	0/3
NO_{2+3}-N, mg/L	14	-	11	0/2
N-total, mg/L	14	-	13	0/1
PO_4-P, mg/L	14	0/1	14	1/0
P-total, mg/L	15	-	13	0/2
Cd, µg/L	12	0/2	11	2/1
Cr, µg/L	10	0/4	11	0/3
Cu, µg/L	14	-	12	0/2
Ni, µg/L	13	0/1	11	0/3
Pb, µg/L	11	0/3	8	2/3
Zn, µg/L	12	0/2	10	0/4
Hg, µg/L	12	1/1	13	0/1

One laboratory reported below DL/QL for Hg in freshwater. One laboratory reported below DL/LOQ for PO_4-P and two laboratories reported below DL/QL for Pb and Cd in wastewater, see table 5.1. In all cases the laboratories reported below a value and it is not clear if laboratories used DL og LOQ. In the PLC-9 intercalibration, all samples have been spiked to secure concentration levels at minimum 10 times the recommended quantification limits (LOQ) from HELCOM.

The number of outliers could indicate that some laboratories might have analytical issues with some of the metal analysis. Further, one laboratory had mixed up the nutrient sample B and metal sample B, and one laboratory had typed in the wrong values for Cd and Pb. See also 2.1 for comments from the laboratories.

A summary of the results from the PLC-9 intercalibration is shown in table 5.2 for freshwater and in table 5.3 for wastewater, respectively.

Table 5.2. Freshwater. Mean concentration, absolute (S(R)) and relative value (CV(R)%) of the total variation and recovery of spike (CV(R)).

Freshwater Components	Mean Sample A/B	S(R) Sample A/B	CV(R) % Sample A/B	Sample C Recovery of spike
NO_3-N, mg/L	0.60	0.017	2.9%	101%
NO_{2+3}-N, mg/L	0.61	0.016	2.7%	102%
N-total, mg/L	2.23	0.159	7.1%	98%
PO_4-P, mg/L	0.39	0.013	3.4%	79%
P-total, mg/L	0.43	0.020	4.7%	95%
Cd, µg/L	1.40	0.064	4.6%	98%
Cr, µg/L	6.67	0.153	2.3%	100%
Cu, µg/L	13.84	0.683	4.9%	98%
Ni, µg/L	2.25	0.143	6.4%	96%
Pb, µg/L	1.69	0.093	5.5%	102%
Zn, µg/L	25.01	0.89	3.6%	-
Hg, µg/L	0.081	0.0186	23.0%	94%

Table 5.3. Wastewater. Mean concentrations, absolute (S(R)) and relative value of the total variation (CV(R)).

Wastewater Components	Mean Sample A/B	S(R) Sample A/B	CV(R) % Sample A/B
NO_3-N, mg/L	2.47	0.072	2.9%
NO_{2+3}-N, mg/L	2.81	0.074	2.6%
N-total, mg/L	6.78	0.282	4.2%
PO_4-P, mg/L	0.48	0.013	2.8%
P-total, mg/L	0.61	0.021	3.5%
Cd, µg/L	5.26	0.438	8.3%
Cr, µg/L	11.1	0.876	7.9%
Cu, µg/L	25.24	1.235	4.9%
Ni, µg/L	43.31	2.241	5.2%
Pb, µg/L	1.90	0.154	8.1%
Zn, µg/L	81.65	3.031	3.7%
Hg, µg/L	1.160	0.1902	16.4%

In general, the analytical quality is good and comparable between the laboratories. For some laboratories the delivery of the samples was delayed up to 8 days. However, based on comparison of delivery date and the performance of the laboratories, the conclusion is that this does not seem to have affected the stability of the samples.

For comparison in relation to the analytical quality, the requirements in Danish Statutory Order no 811 of 19/06/2024 on the analytical quality for environmental measurements from Ministry of Environment (Miljøministeriet 2024). are shown in table 5.4.

Table 5.4. The requirements for analytical quality in the Danish Statutory Order no 811 of 19/06/2024 (Miljøministeriet 2024) on quality requirements for environmental analysis for freshwater and wastewater. Note there are not requirements for all the chemical 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			Wastewater		
	DL	U abs	U rel	DL	U abs	U rel
NO_3-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%	0.03	0.1	15%
Cd µg/L	0.005	0.03	20%	0.05	0.2	20%
Cr µg/L	0.3	2	20%	0.5	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%	0.5	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 the Danish Statutory Order, indicating that the results of the chemical analysis 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 wastewater.

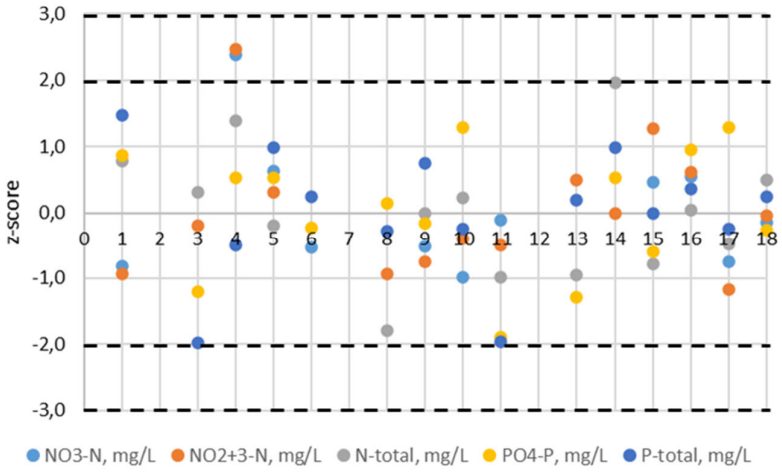


Figure 5.1. z-score results for freshwater A/B samples, nutrients: z<|2|: 67 results; |3|<z<|2|: 2 results; z>|3|: 0 result. The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|. Lab. 2, 7 and 12 did not analyse nutrients in freshwater.

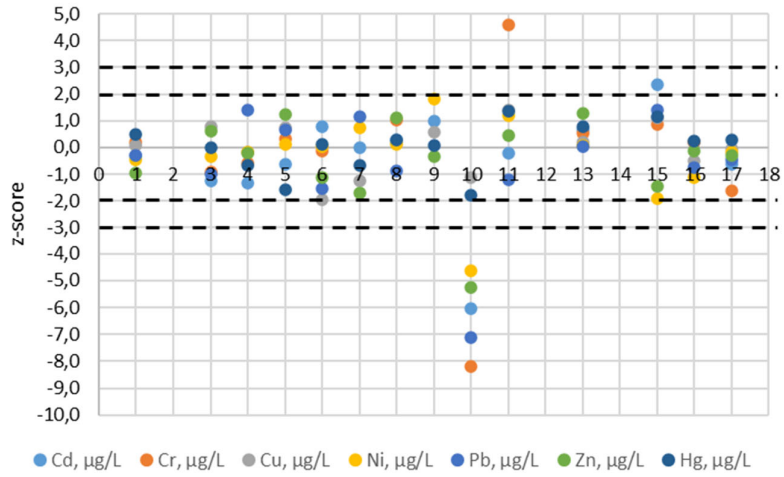


Figure 5.2. z-score results for freshwater, metals: z<|2|: 91 results; |3|<z<|2|: 1 result; z>|3|: 5 results. Three z-score not shown (lab 7: 28.4 for Cr: and lab. 9: 12.2 for Cr and 54.1 for Pb). The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|. Lab. 2,12, 14 and 18 did not analyse metals in freshwater.

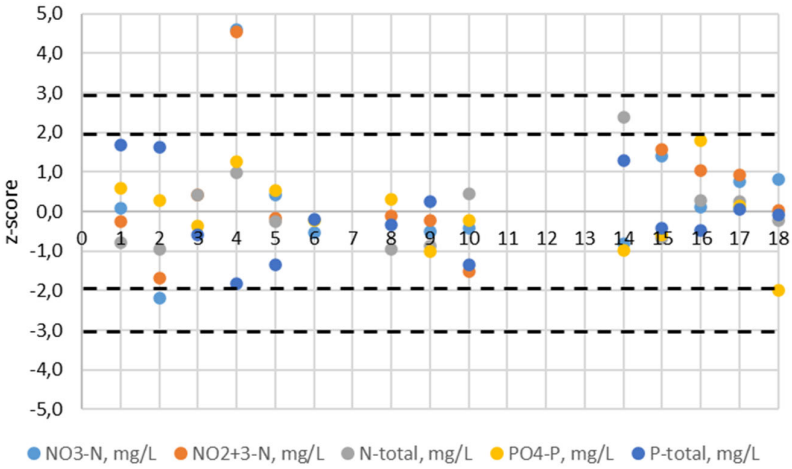


Figure 5.3. z-score results for wastewater, nutrients: z<|2|: 61 results; |3|<z<|2|: 2 results; z>|3|: 6 results. Four z-score not shown (lab 12: NO_3-N, NO_{2+3}, N-total, and P-total). The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|. Lab 7, 11 and 13 did not analyse nutrients in wastewater.

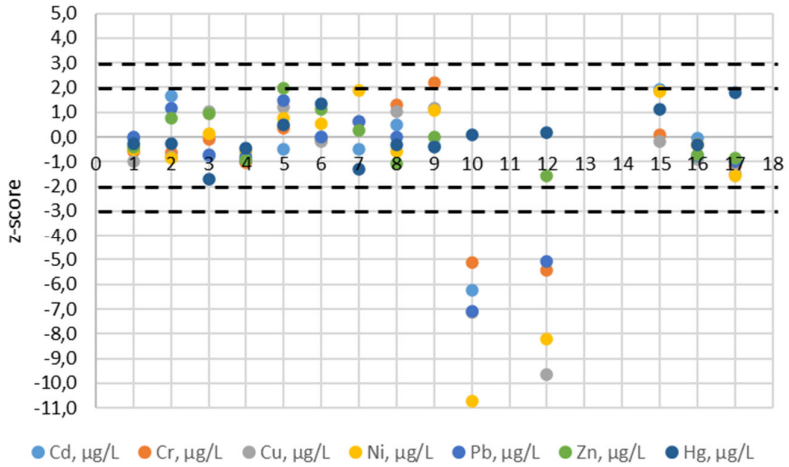


Figure 5.4. z-score results for wastewater, metals: z<|2|: 81 results; |3|<z<|2|: 1 result; z>|3|: 11 results. Three z-scores not shown (lab 7: 10.7 for Cr; lab 9: 33.4 for Pb; lab 10: -12.6 for Zn). The laboratory code numbers are on the x-axis. The dotted lines represent z=|2| and z=|3|. Lab 11, 13 and 18 did not analyse metals in Wastewater.

The results from the laboratories show more outliers in this intercalibration compared to previous PLC intercalibration, especially for the metals. However, the outliers can be related to a few laboratories, where some of them can be pointed out as errors from the laboratories (see 2.1). For a major part of laboratories, the results seem uniform. Note that some data points in freshwater and wastewater are not shown to provide a better visual comparison. These data points are outliers and are not included in the statistical analysis.

5.3 Comparison of PLC-7, PLC-8 and PLC-9

Table 5.5 and 5.6 show comparisons between the intercalibration PLC-7 in 2018, PLC-8 in 2021 and PLC-9 in 2025.

Tabel 5.5. A comparison of mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation for freshwater samples for PLC-7 (2018), PLC-8 (2021) and PLC-9 (2025).

	Freshwater - 2025		Freshwater - 2021		Freshwater - 2018	
Component	**Mean conc.**	**CV(R) (%)**	**Mean conc.**	**CV(R) (%)**	**Mean conc.**	**CV(R) (%)**
NO_3-N mg/L	0.60	2.9	0.77	7.5	1.56	3.3
NO_{2+3}-N mg/L	0.61	2.7	1.05	8.0	1.6	5.2
N-total mg/L	2.23	7.1	3.38	6.7	3.44	6.3
PO_4-P mg/L	0.39	3.4	0.20	6.1	0.209	6.8
P-total mg/L	0.43	4.7	0.28	6.3	0.361	5.4
Cd µg/L	1.40	4.6	1.66	10.9	6.41	5.6
Cr µg/L	6.67	2.3	3.39	7.1	11.67	11.0
Cu µg/L	13.84	4.9	9.77	10.6	29.3	16.8
Ni µg/L	2.25	6.4	15.19	8.5	51.04	6.5
Pb µg/L	1.69	5.5	1.71	6.0	11.14	12.2
Zn µg/L	25.01	3.6	27.24	7.8	77.16	9.4
Hg µg/L	0.08	23.0	0.13	17.4	0.174	10.0

Tabel 5.6. A comparison of mean concentrations, absolute (S(R)) and relative (CV(R)) values of the total variation for wastewater samples for PLC-7 (2018), PLC-8 (2021) and PLC-9 (2025).

	Wastewater – 2025		Wastewater – 2021		Wastewater - 2018	
Component	**Mean conc.**	**CV(R) (%)**	**Mean conc.**	**CV(R) (%)**	**Mean conc.**	**CV(R) (%)**
NO_3-N mg/L	2.47	2.9	7.06	5.3	6.13	6.4
NO_{2+3}-N mg/L	2.81	2.6	7.29	3.0	6.34	3
N-total mg/L	6.78	4.2	11.94	7.0	7.23	4.7
PO_4-P mg/L	0.48	2.8	0.25	7.7	0.010	30.3
P-total mg/L	0.61	3.5	0.55	7.1	0.025	50.4
Cd µg/L	5.26	8.3	9.54	7.6	23.87	5.1
Cr µg/L	11.13	7.9	45.78	4.4	49.01	6.9
Cu µg/L	25.24	4.9	93.39	6.8	142.4	5.8
Ni µg/L	43.31	5.2	11.84	7.1	194.4	6.7
Pb µg/L	1.90	8.1	9.88	8.4	8.59	18.9
Zn µg/L	81.65	3.7	106.3	5.9	435.6	7.6
Hg µg/L	1.16	16.4	6.24	9.9	0.385	11.6

In general, the analytical quality for the parameters appears to be quite stable between the three PLC intercalibrations. Higher relative values of the total variation can be explained by lower concentrations.

5.4 Concluding remarks

The results in the PLC-9 intercalibration from the laboratories show more outliers compared to previous PLC intercalibrations, especially for the metals. However, the outliers can be related to a few laboratories, where some of them can be related to errors from the laboratories (see 2.1). For a major part of laboratories, the results seem uniform.

The samples were spiked at a minimum of ten times above recommended LOQ from the HELCOM guidance document (https://helcom.fi/wp-content/uploads/2022/04/HELCOM-PLC-Water-Guidelines-2022.pdf) to ensure as many positive results as possible. A few laboratories did report below LOD/LOQ for Cr and Pb in wastewater. By mistake Zn was not spiked in a higher concentration for the C samples in freshwater, so recovery could not be evaluated for this component.

As NO_2 has shown instability in previous intercalibration it was decided not including the parameter in the present intercalibration.

In general, the analytical quality appears to be good and quite stable between the laboratories, but few laboratories seem to have challenges with the metal analysis. Compared with previous PLC intercalibrations, the analytical quality also appears to be quite stable over the years.

6 References

ISO (2019). ISO 5725-2:2019 – Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method. International Organization for Standardization, Geneva.

ISO (2022). ISO 13528:2022 – Statistical methods for use in proficiency testing by interlaboratory comparison. International Organization for Standardization, Geneva.

US EPA (2002). Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. EPA-821-R-02-019, United States Environmental Protection Agency.

HELCOM (2022). HELCOM PLC Water Guidelines 2022. https://helcom.fi/wp-content/uploads/2022/04/HELCOM-PLC-Water-Guidelines-2022.pdf

Miljøministeriet (2024). Bekendtgørelse nr. 811 af 19/06/2024 om analysekvalitet for miljømålinger. Miljø- og Ligestillingsministeriet, Danmark.

Lassen, P. & Larsen, M.M. (2018). Report on the HELCOM PLC-7 intercalibration. DCE – Danish Centre for Environment and Energy, Aarhus University. DCE Technical Report No. 135.

Lassen, P. & Larsen, M.M. (2021). Report on the HELCOM PLC-8 intercalibration. DCE – Danish Centre for Environment and Energy, Aarhus University. DCE Technical Report No. 212.

HELCOM (2025). HELCOM PLC-9 project page: objectives, timeline and work packages. https://helcom.fi

HELCOM (2025). HELCOM WG Source to Sea – Working Group on Source-to-Sea Management of Nutrients and Hazardous Substances and Sustainable Agricultural Practices. https://helcom.fier the years.

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
Germany	Landeslabor Schleswig-Holstein
	Landesamt für Umwelt, Naturschutz und Geologie M-V
Latvia	LEGMC Laboratory
	Riga Water Ltd Water Quality Control Laboratories
Lituania	Environmental Protection Agency, Chemical research division
	Environmental Protection Agency, Western Lithuania Environment Research division
Poland	GIOŚ , Centralne Laboratorium Badawcze, Oddział w Szczecinie, Pracownia w Szczecinie
	Centralne Laboratorium Badawcze GIOŚ Oddział w Krakowie
	Centralne Laboratorium Badawcze (CLB) GIOŚ, Oddział w Katowicach
	Chief Inspectorate of Environmental Protection, Central Research, Laboratory, branch in Gdansk
Sweden	Eurofins Environment Testing Sweden AB
	IVL Svenska Miljöinstitutet AB
	SLU, Vattenkemiska laboratoriet

Appendix 2

The reported data from the laboratories

Intercalibration under PLC9
Freshwater

Laboratory number: **1**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.58	0.59	1.12
NO2+3-N, mg/L	0.59	0.59	1.12
N-total, mg/L	2.35	2.36	3.17
PO4-P, mg/L	0.402	0.407	0.534
P-total, mg/L	0.46	0.46	0.58
Cd, µg/L	1.38	1.38	1.97
Cr, µg/L	6.59	6.80	9.42
Cu, µg/L	13.95	13.82	18.91
Ni, µg/L	2.23	2.13	2.75
Pb, µg/L	1.68	1.65	1.98
Zn, µg/L	24.3	24.0	22.7
Hg, µg/L	0.09	0.091	0.130

Intercalibration under PLC9
Wastewater

Laboratory number: **1**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.47	2.48
NO2+3-N, mg/L	2.79	2.80
N-total, mg/L	6.49	6.61
PO4-P, mg/L	0.484	0.488
P-total, mg/L	0.65	0.64
Cd, µg/L	5.26	5.25
Cr, µg/L	10.48	10.73
Cu, µg/L	23.82	24.21
Ni, µg/L	42.18	42.32
Pb, µg/L	1.84	1.96
Zn, µg/L	80.8	80.0
Hg, µg/L	1.094	1.128

Intercalibration under PLC9
Wastewater

Laboratory number: **2**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.308	2.314
NO2+3-N, mg/L	2.682	2.694
N-total, mg/L	6.500	6.510
PO4-P, mg/L	0.4821	0.4817
P-total, mg/L	0.6450	0.6429
Cd, µg/L	5.99	5.99
Cr, µg/L	10.63	10.55
Cu, µg/L	24.24	24.3
Ni, µg/L	41.54	41.26
Pb, µg/L	2.081	2.09
Zn, µg/L	84.23	83.79
Hg, µg/L	1.077	1.136

Intercalibration under PLC9
Freshwater

Laboratory number: **3**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2+3-N, mg/L	0.606	0.598	1.16
N-total, mg/L	2.29	2.27	2.97
PO4-P, mg/L	0.375	0.379	0.515
P-total, mg/L	0.391	0.388	0.506
Cd, µg/L	1.33	1.31	1.88
Cr, µg/L	6.52	6.54	9.23
Cu, µg/L	14.45	14.3	19.9
Ni, µg/L	2.2	2.2	2.7
Pb, µg/L	1.61	1.59	1.91
Zn, µg/L	25.6	25.5	23.9
Hg, µg/L	<0.0015	<0.0015	<0.0015

Intercalibration under PLC9
Wastewater

Laboratory number: **3**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L		
NO2+3-N, mg/L	2.84	2.85
N-total, mg/L	6.9	6.89
PO4-P, mg/L	0.473	0.473
P-total, mg/L	0.595	0.598
Cd, µg/L	4.94	4.92
Cr, µg/L	11	11.1
Cu, µg/L	26.4	26.6
Ni, µg/L	43.6	43.7
Pb, µg/L	1.81	1.77
Zn, µg/L	84	85
Hg, µg/L	0.89	0.79

Intercalibration under PLC9
Freshwater

Laboratory number: **4**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.64	0.64	1.2
NO2+3-N, mg/L	0.64	0.65	1.2
N-total, mg/L	2.4	2.5	3.02
PO4-P, mg/L	0.39	0.41	0.55
P-total, mg/L	0.43	0.41	0.56
Cd, µg/L	1.31	1.32	1.874
Cr, µg/L	6.606	6.554	9.261
Cu, µg/L	13.658	13.815	18.94
Ni, µg/L	2.2	2.241	2.709
Pb, µg/L	1.836	1.814	2.174
Zn, µg/L	24.57	25.055	23.543
Hg, µg/L	0.067	0.071	0.093

Intercalibration under PLC9
Wastewater

Laboratory number: **4**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.7	2.9
NO2+3-N, mg/L	3.1	3.2
N-total, mg/L	6.9	7.2
PO4-P, mg/L	0.5	0.49
P-total, mg/L	0.55	0.59
Cd, µg/L	4.778	4.871
Cr, µg/L	10.18	10.311
Cu, µg/L	24.493	24.798
Ni, µg/L	41.69	42.183
Pb, µg/L	1.736	1.817
Zn, µg/L	78.648	78.968
Hg, µg/L	1.048	1.1

Intercalibration under PLC9
Freshwater

Laboratory number: **5**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.61	0.61	1.1
NO2+3-N, mg/L	0.61	0.61	1.1
N-total, mg/L	2.2	2.2	2.9
PO4-P, mg/L	0.40	0.40	0.53
P-total, mg/L	0.46	0.44	0.53
Cd, µg/L	1.35	1.37	2.00
Cr, µg/L	6.70	6.74	9.62
Cu, µg/L	14.4	14.3	20.1
Ni, µg/L	2.21	2.31	2.72
Pb, µg/L	1.77	1.74	2.09
Zn, µg/L	26.1	26.1	25.0
Hg, µg/L	0.0493	0.0545	0.0849

Intercalibration under PLC9
Wastewater

Laboratory number: **5**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.5	2.5
NO2+3-N, mg/L	2.8	2.8
N-total, mg/L	6.7	6.7
PO4-P, mg/L	0.48	0.49
P-total, mg/L	0.58	0.58
Cd, µg/L	5.04	5.05
Cr, µg/L	11.5	11.4
Cu, µg/L	26.6	26.9
Ni, µg/L	45.3	44.8
Pb, µg/L	2.16	2.10
Zn, µg/L	87.7	87.5
Hg, µg/L	1.26	1.25

Intercalibration under PLC9
Freshwater

Laboratory number: **6**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.59	0.59	1.13
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L	0.39	0.39	0.52
P-total, mg/L	0.44	0.43	0.56
Cd, µg/L	1.44	1.46	1.99
Cr, µg/L	6.5	6.8	10.5
Cu, µg/L	13	12	18
Ni, µg/L	2.3	2.2	2.5
Pb, µg/L	1.4	1.7	1.9
Zn, µg/L	24	24	24
Hg, µg/L	0.078	0.089	0.12

Intercalibration under PLC9
Wastewater

Laboratory number: **6**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.43	2.43
NO2+3-N, mg/L		
N-total, mg/L		
PO4-P, mg/L	0.47	0.48
P-total, mg/L	0.61	0.60
Cd, µg/L	<10	<10
Cr, µg/L	11	11
Cu, µg/L	25	25
Ni, µg/L	44	45
Pb, µg/L	<10	<10
Zn, µg/L	81	89
Hg, µg/L	1.38	1.46

Intercalibration under PLC9
Freshwater

Laboratory number: **7**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2+3-N, mg/L			
N-total, mg/L			
PO4-P, mg/L			
P-total, mg/L			
Cd, µg/L	1.4 ± 0.055	1.4 ± 0.055	2.0 ± 0.078
Cr, µg/L	11 ± 0.62	11 ± 0.62	15 ± 0.84
Cu, µg/L	13 ± 0.58	13 ± 0.58	18 ± 0.81
Ni, µg/L	2.4 ± 0.15	2.3 ± 0.14	3.5 ± 0.21
Pb, µg/L	1.8 ± 0.17	1.8 ± 0.17	2.1 ± 0.19
Zn, µg/L	24 ± 0.76	23 ± 0.73	22 ± 0.70
Hg, µg/L	0.069 ± 0.0076	0.068 ± 0.0075	0.093 ± 0.010

Intercalibration under PLC9
Wastewater

Laboratory number: **7**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L		
NO2+3-N, mg/L		
N-total, mg/L		
PO4-P, mg/L		
P-total, mg/L		
Cd, µg/L	5.1 ± 0.20	5.0 ± 0.19
Cr, µg/L	20 ± 1.1	21 ± 1.2
Cu, µg/L	26 ± 1.2	26 ± 1.2
Ni, µg/L	47 ± 2.9	48 ± 2.9
Pb, µg/L	2.0 ± 0.18	2.0 ± 0.18
Zn, µg/L	82 ± 2.6	83 ± 2.6
Hg, µg/L	0.92 ± 0.10	0.91 ± 0.10

Intercalibration under PLC9
Freshwater

Laboratory number: **8**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	-	-	-
NO2+3-N, mg/L	0.59	0.59	1.11
N-total, mg/L	1.89	2.00	2.61
PO4-P, mg/L	0.394	0.396	0.526
P-total, mg/L	0.423	0.426	0.549
Cd, µg/L	1.416	1.419	1.983
Cr, µg/L	6.771	6.878	9.783
Cu, µg/L	13.993	13.885	19.376
Ni, µg/L	2.245	2.275	2.768
Pb, µg/L	1.624	1.604	1.915
Zn, µg/L	26.052	25.971	24.282
Hg, µg/L	0.087	0.086	0.120

Intercalibration under PLC9
Wastewater

Laboratory number: **8**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	-	-
NO2+3-N, mg/L	2.8	2.81
N-total, mg/L	6.39	6.62
PO4-P, mg/L	0.479	0.485
P-total, mg/L	0.599	0.604
Cd, µg/L	5.48	5.49
Cr, µg/L	12.36	12.15
Cu, µg/L	26.0	27.0
Ni, µg/L	42.0	42.0
Pb, µg/L	<10	<10
Zn, µg/L	78.8	78.0
Hg, µg/L	1.106	1.100

Intercalibration under PLC9
Freshwater

Laboratory number: **9**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.5932	0.5873	1.0969
NO2+3-N, mg/L	0.5959	0.5897	1.0984
N-total, mg/L	2.2448	2.2128	2.8457
PO4-P, mg/L	0.3908	0.3910	0.4888
P-total, mg/L	0.444	0.4466	0.5603
Cd, µg/L	1.3719	1.5524	2.1667
Cr, µg/L	8.9844	8.0597	11.3402
Cu, µg/L	14.894	13.5872	22.2372
Ni, µg/L	2.6468	2.369	3.8023
Pb, µg/L	6.8114	6.6468	7.2611
Zn, µg/L	25.2024	24.2336	24.5742
Hg, µg/L	0.0838	0.0809	0.1172

Intercalibration under PLC9
Wastewater

Laboratory number: **9**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.4304	2.4365
NO2+3-N, mg/L	2.8042	2.7874
N-total, mg/L	6.625	6.4395
PO4-P, mg/L	0.4579	0.4709
P-total, mg/L	0.6167	0.6119
Cd, µg/L	5.1423	5.0782
Cr, µg/L	13.2293	12.8758
Cu, µg/L	26.6326	26.7714
Ni, µg/L	45.3052	46.1779
Pb, µg/L	6.9823	7.1227
Zn, µg/L	81.9699	81.4318
Hg, µg/L	1.0825	1.0766

Intercalibration under PLC9
Freshwater

Laboratory number: **10**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.584	0.580	1.143
NO2-N, mg/L	0.0027	0.0026	0.0025
NO2+3-N, mg/L	0.598	0.599	1.151
N-total, mg/L	2.28	2.25	2.9
PO4-P, mg/L	0.41	0.41	0.51
P-total, mg/L	0.42	0.43	0.55
Cd, µg/L	1.011	1.012	1.412
Cr, µg/L	5.396	5.434	7.588
Cu, µg/L	13.150	12.985	17.394
Ni, µg/L	1.591	1.573	17.394
Pb, µg/L	1.035	1.030	1.215
Zn, µg/L	20.293	20.359	19.265
Hg, µg/L	0.046	0.049	0.080

Intercalibration under PLC9
Wastewater

Laboratory number: **10**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.444	2.433
NO2-N, mg/L	0.335	0.335
NO2+3-N, mg/L	2.7	2.7
N-total, mg/L	7.0	6.8
PO4-P, mg/L	0.48	0.47
P-total, mg/L	0.58	0.58
Cd, µg/L	2.514	2.549
Cr, µg/L	6.648	6.660
Cu, µg/L	15.173	17.704
Ni, µg/L	20.610	17.993
Pb, µg/L	0.813	0.806
Zn, µg/L	43.356	43.783
Hg, µg/L	1.037	1.315

Intercalibration under PLC9
Freshwater

Laboratory number: **11**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.591	0.603	1.139
NO2+3-N, mg/L	0.591	0.603	0.1139
N-total, mg/L	2.07	2.08	2.766
PO4-P, mg/L	0.37	0.366	0.492
P-total, mg/L	0.4	0.38	0.5
Cd, µg/L	1.378	1.394	1.972
Cr, µg/L	7.339	7.398	10.719
Cu, µg/L	14.711	14.876	20.517
Ni, µg/L	2.369	2.463	3.003
Pb, µg/L	1.602	1.56	1.884
Zn, µg/L	25.443	25.401	24.591
Hg, µg/L	0.108	0.104	0.151

Intercalibration under PLC9
Wastewater

Laboratory number: **12**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.24	594
NO2+3-N, mg/L	0.438	0.169
N-total, mg/L	5.77	588
PO4-P, mg/L	0.432	<0.010
P-total, mg/L	0.584	0.028
Cd, µg/L	5.43	<0.005
Cr, µg/L	11.9	0.851
Cu, µg/L	26.0	0.622
Ni, µg/L	45.4	4.42
Pb, µg/L	2.02	0.221
Zn, µg/L	88.7	65.0
Hg, µg/L	1.19	1.20

Intercalibration under PLC9
Freshwater

Laboratory number: **13**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2+3-N, mg/L	0.614	0.612	1.147
N-total, mg/L	2.074	2.086	2.684
PO4-P, mg/L	0.376	0.376	0.521
P-total, mg/L	0.431	0.437	0.559
Cd, µg/L	1.43	1.45	1.99
Cr, µg/L	6.71	6.79	9.33
Cu, µg/L	14.0	14.0	19.5
Ni, µg/L	2.28	2.23	2.75
Pb, µg/L	1.70	1.70	2.03
Zn, µg/L	26.2	26.1	24.4
Hg, µg/L	0.0948	0.0965	0.1534

Intercalibration under PLC9
Freshwater

Laboratory number: **14**

Table 1a

Components	07/05/2025		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L			
NO2+3-N, mg/L	0.61±0.02	0.6±0.02	1.21±0.05
N-total, mg/L	2.51±0.10	2.57±0.10	3.15±0.13
PO4-P, mg/L	0.40±0.03	0.40±0.03	0.53±0.039
P-total, mg/L	0.45±0.025	0.45±0.025	0.56±0.031
Cd, µg/L			
Cr, µg/L			
Cu, µg/L			
Ni, µg/L			
Pb, µg/L			
Zn, µg/L			
Hg, µg/L			

Intercalibration under PLC9
Wastewater

Laboratory number: **14**

Table 1b

Components	07/05/2025	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.45 ±0.16	2.37 ±0.15
NO2+3-N, mg/L		
N-total, mg/L	7.28 ±0.80	7.62 ±0.84
PO4-P, mg/L	0.465 ±0.009	0.465 ±0.009
P-total, mg/L	0.644 ±0.022	0.630 ±0.021
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

Intercalibration under PLC9
Freshwater

Laboratory number: **15**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.618	0.596	1.13
NO2+3-N, mg/L	0.627	0.624	1.17
N-total, mg/L	2.08	2.13	2.77
PO4-P, mg/L	0.38	0.39	0.52
P-total, mg/L	0.43	0.43	0.55
Cd, µg/L	1.53	1.57	2.13
Cr, µg/L	6.97	6.63	9.7
Cu, µg/L	14.8	14.4	23.9
Ni, µg/L	2.01	1.94	2.5
Pb, µg/L	1.87	1.78	2.1
Zn, µg/L	22.7	24.7	27.7
Hg, µg/L	0.108	0.097	0.143

Intercalibration under PLC9
Wastewater

Laboratory number: **15**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.57	2.57
NO2+3-N, mg/L	2.91	2.95
N-total, mg/L	6.59	6.58
PO4-P, mg/L	0.47	0.47
P-total, mg/L	0.6	0.6
Cd, µg/L	6.03	6.21
Cr, µg/L	11.1	11.3
Cu, µg/L	24	26
Ni, µg/L	49.3	45.5
Pb, µg/L		
Zn, µg/L	87	108
Hg, µg/L	1.38	1.37

Intercalibration under PLC9
Freshwater

Laboratory number: **16**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.609	0.608	1.148
NO2+3-N, mg/L	0.616	0.614	1.144
N-total, mg/L	2.255	2.219	2.982
PO4-P, mg/L	0.407	0.404	0.535
P-total, mg/L	0.434	0.441	0.567
Cd, µg/L	1.41	1.41	2.01
Cr, µg/L	6.71	6.69	9.56
Cu, µg/L	13.5	13.5	18.8
Ni, µg/L	2.09	2.08	2.58
Pb, µg/L	1.63	1.62	1.93
Zn, µg/L	24.9	24.9	23.7
Hg, µg/L	0.087	0.084	0.114

Intercalibration under PLC9
Wastewater

Laboratory number: **16**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.475	2.479
NO2+3-N, mg/L	2.901	2.878
N-total, mg/L	6.880	6.830
PO4-P, mg/L	0.502	0.502
P-total, mg/L	0.596	0.602
Cd, µg/L	5.26	5.24
Cr, µg/L	11.1	10.7
Cu, µg/L	24.4	23.9
Ni, µg/L	43.1	42.1
Pb, µg/L	1.78	1.79
Zn, µg/L	79.6	79.3
Hg, µg/L	1.097	1.106

Intercalibration under PLC9
Freshwater

Laboratory number: **17**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.585	0.587	1.14
NO2+3-N, mg/L	0.585	0.587	1.14
N-total, mg/L	2.17	2.14	2.73
PO4-P, mg/L	0.41	0.41	0.48
P-total, mg/L	0.43	0.42	0.51
Cd, µg/L	1.36	1.36	1.87
Cr, µg/L	6.46	6.38	9.01
Cu, µg/L	13.8	13.8	18.6
Ni, µg/L	2.23	2.21	2.67
Pb, µg/L	1.65	1.65	1.94
Zn, µg/L	24.7	24.8	23.3
Hg, µg/L	0.0987	0.0747	0.106

Intercalibration under PLC9
Wastewater

Laboratory number: **17**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.517	2.529
NO2+3-N, mg/L	2.876	2.887
N-total, mg/L	6.846	6.842
PO4-P, mg/L	0.48	0.48
P-total, mg/L	0.61	0.61
Cd, µg/L	4.8	4.89
Cr, µg/L	10.1	10.1
Cu, µg/L	23.4	23.4
Ni, µg/L	39.8	39.8
Pb, µg/L	1.73	1.77
Zn, µg/L	79.8	78.4
Hg, µg/L	1.52	1.48

Intercalibration under PLC9
Freshwater

Laboratory number: **18**

Table 1a

Components	Measured data		
	Freshwater sample A	Freshwater sample B	Freshwater sample C
NO3-N, mg/L	0.597	0.596	1.134
NO2+3-N, mg/L	0.602	0.607	1.125
N-total, mg/L	2.313	2.306	2.962
PO4-P, mg/L	0.391	0.388	0.515
P-total, mg/L	0.433	0.437	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 PLC9
Wastewater

Laboratory number: **18**

Table 1b

Components	Measured data	
	Wastewater sample A	Wastewater sample B
NO3-N, mg/L	2.531	2.526
NO2+3-N, mg/L	2.825	2.806
N-total, mg/L	6.711	6.707
PO4-P, mg/L	0.451	0.452
P-total, mg/L	0.605	0.609
Cd, µg/L		
Cr, µg/L		
Cu, µg/L		
Ni, µg/L		
Pb, µg/L		
Zn, µg/L		
Hg, µg/L		

REPORT ON THE HELCOM PLC-9 INTERCALIBRATION ON HEAVY METALS AND NUTRIENTS

This report presents results from the PLC-9 intercalibration on metals and nutrients in freshwater and wastewater. The intercalibration was performed to evaluate the analytical quality of results reported to HELCOM. 17 laboratories participated in the intercalibration.

ISBN: 978-87-7648-013-4
ISSN: 2244-999X