DANAK
PT Reg.No. 534
Member of EA MLA

eurofins

Proficiency test SPIL-3 (2022)

Organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater (untreated sewage)

Proficiency test SPIL-3 (2022)
Quality Documentation

November 2022

Eurofins Miljø A/S
Smedeskovvej 38
DK-8464 Galten
Denmark

Tlf: +45 7022 4266
e-mail: proficiency@eurofins.com
Web: www.eurofins.dk

Client	Client's representative
Environmental laboratories	

Project	Project No
Proficiency test SPIL-3 (2022)	20405-23
Authors Rikke Mikkelsen	Date 29 November 2022
	Approved by Peter Rerup

1	Quality Documentation Report	FYE3	DPRE	30 NOV 2022
Revision	Description	By	Approved	Date

Key words	Classification
Analytical quality, assigned value, precision, trueness, homogeneity, stability, COD, BOD5 (w. ATU), BOD7 (w. ATU), NVOC/TOC, total phosphorus, chloride, sulphate, suspended matter, wastewater	☒ Open ☐ Internal ☐ Proprietary

Distribution	
Online:	www.eurofins.dk/miljoe/voresydelser/praestationsproevninger/
DANAK	
Eurofins:	Rikke Mikkelsen, Peter Rerup

CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater was conducted on 15 September 2022. The proficiency test was organised by Eurofins Miljø A/S.

The present report contains Eurofins' documentation for the quality of the proficiency test. Results of the proficiency test including data from participating laboratories and statistical analysis of these data were issued in a report to all participants /1/ on 18 October 2022 and a revised edition were issued on 8 November 2022.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 48 laboratories from Denmark and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 30 September 2022. All participants had submitted their results before the dead-line.

2.1 Sample preparation

The parameters covered in the proficiency test are listed in Table 2 as are the abbreviations used in this report.

Six samples were dispatched for the proficiency test. The samples were sample pairs covering the parameters as described in Table 1. The matrix of the samples represented wastewater, in this case untreated sewage. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	COD_{Cr}, BOD (w. ATU) and NVOC/TOC
A2/B2	TP, Cl and SO_4
A3/B3	TSS

2.2 Statistical analysis of participants' data

A split-level design was used. The data analysis was performed in accordance with ISO 5725: "Accuracy (trueness and precision) of measurement methods and results" (2019) /2/ and as described in detail in Spliid (1992) /3/. A short introduction to the statistics and a list of symbols and abbreviations used is given in Eurofins document "Schedule for a proficiency test", which is available at Eurofins' home page /4/.

The statistical model used is based on the assumption that the variances for the two samples in a sample pair are identical. The assumption was tested (F-test, 95% confidence level) and the result was that the two variances may be assumed to be identical for all parameters.

2.3 Assigned and spike value

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in untreated sewage. The table also gives the expanded uncertainty of the assigned values.

Only few laboratories reported values for BOD_5 and SO_4. For this reason, no value has been assigned for the parameters.

Table 2 Assigned and spike value

Parameter	Abbreviation	Unit	Typical Range	Assigned value	Uncertainty of assigned value	Spike value
Chemical oxygen demand - dichromate	COD_{Cr}	mg/L O_2	100-800	212	4.2	19
5 day biochemical oxygen demand (w. ATU)*	BOD_5	mg/L O_2	50-500	-	-	-
7 day biochemical oxygen demand (w. ATU)	BOD_7	mg/L O_2	50-500	98	5.5	13
Non-volantile/Total organic carbon	NVOC/TOC	mg/L C	50-800	64	4.9	7
Total phosphorus	TP	mg/L P	5-10	11.3	0.46	1.0
Chloride	Cl	mg/L	50-700	440	24	60
Sulphate*	SO_4	mg/L	20-200	-	-	-
Total suspended matter	TSS	mg/L	100-500	214	9.5	41

* Only few laboratories reported the parameter. No value is assigned.

2.3.1 Assigned and spike values

The content of each parameter in each sample is given an assigned value for the sample with the lower content and a spike value, the spike value being the difference in concentration between the two samples of the sample pair.

In order to ensure optimal use of the data, the assigned value is calculated as the average of the median for both samples in the sample pair after subtraction of the spike value. The spike values are calculated from sample preparation.

The assigned values for all parameters except Cl and SO_4 are operationally defined and are consensus values based upon the median for method no. 1 (NVOC) or method no. 1 and 2 (TP, TSS), which are the methods required by the Danish EPA /5/. The number of laboratories using the method required by the Danish EPA /5/ for COD was insufficient and the assigned value for COD_{Cr} is the consensus value for all laboratories based on the median. The assigned value for BOD_7 is based upon standardised methods (method no. 1 - 4). Not enough data was available to assign a value for BOD_5 and SO_4. The assigned value for Cl is the consensus value for all laboratories based on the median. A list of method identification numbers is found in the report to participants /1/.

2.3.2 Test of spike values

A comparison was made (t-test, 95% confidence level) between the spike value and the difference in concentration between the two samples in the sample pair found from the laboratories' results, see Appendix C. The test showed no significant difference between the two. The test revealed a significant difference between the two for TP. However, the difference is numerically small and has insignificant influence on the general quality of analyses estimated from the data as well as on the evaluation of accuracy of participating laboratories.

2.3.3 Test of assigned values

The assigned value and the average of the results obtained from all laboratories were also compared (t-test, 95% confidence level), see Appendix D. The test showed no significant difference between the two for most parameters and the control of assigned value at Eurofins confirmed the value (Appendix E).

The test revealed a significant difference between the two for NVOC. Average recovery was 104.6 %. The difference could be attributed to influence from laboratories using methods other than those prescribed by the Danish EPA. The test was repeated after exclusion of the results for method no. 42 and 44 and now showed no significant difference. The assigned value is therefore kept unchanged.

3 HOMOGENEITY AND STABILITY OF SAMPLES

The homogeneity and stability of samples were tested using the following parameters as indicators:

COD_{Cr}	Homogeneity test
TP	Combined homogeneity and stability test
TSS	Combined homogeneity and stability test

The results of control measurements are shown in Appendix F. The appendix also gives the results of the statistical evaluation of the control data. The data are analysed by analysis of variance (ANOVA) giving:

1. the standard deviation/variance for replicates (the contribution from analytical variability),

2. the between bottle standard deviation/variance (the contribution from heterogeneity) and

3. the between days concentration difference (the contribution from instability).

Homogeneity is evaluated by comparing the between bottle variance to 0.3 * the standard deviation for evaluation of participants' performance ($0.3 \cdot \hat{\sigma}$) specified by the Danish EPA /5/, whereas the stability is evaluated by comparing the concentration change of the samples to $0.3 \cdot \hat{\sigma}$. This test ensures that heterogeneity and instability will not have negative influence on the evaluation of participant performance /6/.

The appendix also shows the standard deviation within and between laboratories from the proficiency test to allow comparison between tests performed and average quality from participating laboratories.

The homogeneity test for COD_{Cr} showed the samples are homogeneous, however this is not the case for TP and TSS. To accommodate this issue 5 % has been added to the U_{rel} given in the Danish EPA /5/ before calculating the standard deviation for evaluation of participants' performance. All parameters for sample A2, B2, A3 and B3 were treated this way. With this correction samples for TP and TSS are homogeneous according to the above criteria.

The stability test for TP indicated that the samples were not stable. The stability results however agree with the assigned nominal and it is concluded that the sample is still suitable for evaluating the performance of the participants. The stability for TSS show that the samples are stable.

4 CONCLUSION

The quality control performed, including test of sample stability and homogeneity as well as test of recovery of spike and assigned values, shows that the samples and their assigned values are suitable for testing the proficiency of the participating laboratories for all parameters.

For TP the participants could not recover the spike value. The difference between the calculated spike value and that found by the participants is small and the influence on evaluation of participant performance or estimation of general quality of analyses is insignificant.

For NVOC the participants did not recover the assigned value. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned value is correct. The assigned value is therefore kept unchanged and it is recommended as the basis for evaluation of participating laboratories.

The stability and homogeneity test indicate larger deviations between samples than the usual evaluation criteria. This is handled by adjusting the standard deviation for evaluation of participants' performance and the samples and their assigned values are suitable for testing the proficiency of the participating laboratories for all parameters.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-3 (2022) ver. 2*, Report to participants, November 2022.

/2/ ISO 5725-2, *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*, 2019.

/3/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).

/4/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.

/5/ Ministry of Environment regulation no. 2362 on *quality criteria for environmental measurements,* 26 November 2021 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2022.

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	**Town**	**Country**
Analyseenheden, Institut for Agroøkologi, Aarhus Universitet	Tjele	Danmark
AquaDjurs A/S	Grenaa	Danmark
Biofos A/S	København K	Danmark
Bjergmarken RA, Fors Spildevand Roskilde	Roskilde	Danmark
BlueKolding A/S	Kolding	Danmark
Bornholms Spildevand A/S	Rønne	Danmark
CP Kelco, QC Analyselab.	Ll. Skensved	Danmark
DIN Forsyning, Laboratorium Rens Øst-Esbjerg	Esbjerg	Danmark
Hillerød Spildevand (2 participants)	Hillerød	Danmark
Holbæk RA, Fors Spildevand Holbæk	Holbæk	Danmark
Holstebro Renseanlæg, Vestforsyning Spildevand	Holstebro	Danmark
Højvang Laboratorier A/S	Dianalund	Danmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Danmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Danmark
NK-Forsyning A/S	Næstved	Danmark
Nyborg Forsyning & Service	Nyborg	Danmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	Danmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Danmark
Svendborg Spildevand A/S, Svenborg Centralrenseanlæg	Skårup Fyn	Danmark
Vandmiljø Randers A/S	Randers SØ	Danmark
Vejle Spildevand	Vejle	Danmark
AB Lennart Månsson International	Helsingborg	Sverige
Ernemar Laboratorium	Oskarshamn	Sverige
Fiskeby Board AB	Norrköping	Sverige

Laboratory	Town	Country
GRYAAB AB	Göteborg	Sverige
Kalmar Vatten AB, VA-lab	Kalmar	Sverige
Kristianstad Kommun	Kristianstad	Sverige
Käppalaverket	Lidingö	Sverige
Laboratoriet Fillanverket, MittSverige Vatten och Avfall AB	Sundsvall	Sverige
Laboratoriet på Vatten och Avloppsavdelningen, SBF, Enköpings Kommun	Enköping	Sverige
Mjölby Kommun (2 participants)	Mjölby	Sverige
Motala Kommun, Tekniska Förvaltningen, Vatten och Avfall	Motala	Sverige
Nordic Sugar AB, Örtofta Sockerbruk	Eslöv	Sverige
NSVA/Öresundsverket	Helsingborg	Sverige
Reningsverket Aggerud	Karlskoga	Sverige
Roslagsvatten AB	Åkersberga	Sverige
Smurfit Kappa Piteå	Piteå	Sverige
St1 Refinery AB	Göteborg	Sverige
Södra Cell AB Mönsterås	Mönsterås	Sverige
Södra Cell AB, Värö	Väröbacka	Sverige
Tekniska Verken i Linköping AB	Linköping	Sverige
Vallviks Bruk AB	Vallvik	Sverige
VIVAB	Falkenberg	Sverige
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sverige
Östersunds Provningslaboratorium, Göviken reningsverk	Östersund	Sverige

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**		**Concentration**
Concentrate A1	0.925 g 0.925 g milli-Q water up to 1000 g	D-glucose L-glutamic acid	COD_{Cr}: 1.892 g/kg NVOC: 0.747 g/kg BOD: 1.295 g/kg
Concentrate B1	1.154 g 1.154 g milli-Q water up to 1000 g	D-glucose L-glutamic acid	COD_{Cr}: 2.360 g/kg NVOC: 0.932 g/kg BOD: 1.615 g/kg
Stock TP	4.500 g milli-Q water up to 1000.0 g	Na-beta-glycerophosphate	TP: 455.3 mg/kg
Stock Cl	10.000 g milli-Q water up to 1000.0 g	Sodium chloride (NaCl)	Cl: 6.065 g/kg
Stock SO_4	5.000 g milli-Q water up to 1000.0 g	Sodium sulphate (Na_2SO_4)	SO_4: 3.381 g/kg
Stock TSS	15.000 g milli-Q water up to 1000.0 g	Microcrystalline cellulose	TSS: 15.000 g/kg

Sample	Sample prepared from	COD_{Cr} mg/L O_2	NVOC mg/L C	BOD (w. ATU) mg/L O_2	TP mg/L P	Cl mg/L	SO_4 mg/L	TSS mg/L
A1-COD/NVOC	At the laboratory 20.0 mL of concentrate A1 is diluted up to 500.0 mL with filtered water from Holsted sewage treatment plant	a + 75.7	b + 29.9					
B1-COD/NVOC	At the laboratory 20.0 mL of concentrate B1 is diluted up to 500.0 mL with filtered water from Holsted sewage treatment plant	a + 94.4	b + 37.3					
A1-BOD	At the laboratory 20.0mL of concentrate A1 is diluted up to 500.0 mL with filtered water from Holsted sewage treatment plant			c + 51.8				
B1-BOD	At the laboratory 20.0 mL of concentrate B1 is diluted up to 500.0 mL with filtered water from Holsted sewage treatment plant			c + 64.3				
A2	850.0 g stock TP 200.0 g stock Cl 0.0 g stock SO_4 Filtered water from Holsted sewage treatment plant up to 60.0 kg.				d + 6.451	e + 20.215	f	
B2	100.0 g stock TP 450.0 g stock Cl 500.0 g stock SO_4 Sample A2 up to 35 kg.				0.970 · (d+6.451) + 1.301	0.970 · (e+20.215) + 77.977	0.970 · (f+48.307)	
A3	At the laboratory 250.0 mL of filtered water from Holsted sewage treatment plant is added to 3.5 mL stock TSS							g + 207.1
B3	At the laboratory 250.0 mL of filtered water from Holsted sewage treatment plant is added to 4.2 mL stock TSS							g + 247.8

ANNEX C CONTROL OF SPIKE VALUES

Chemical oxygen demand - COD_{Cr}, mg/L O_2
Control of differences within sample pairs

Laboratory	Difference AB	
1	-3.0	
2	1.0	
3	-	
4A	-	
4B	-	
5	0.5	
6	-	
7	2.0	
8	-1.0	
9	-	
10	1.0	
12	1.0	
13	1.0	
14	-4.0	
15A	3.0	
15B	6.0	
15C	-5.0	
16	-	
17	-4.0	
18	-3.0	
19	1.0	
20	30.0	UC
21	-	
22	0.0	
23	3.0	
24	-6.0	
25	-	
26	-	
28	-2.0	
29	-1.0	
30	-	
31	-2.0	
32	-	
33	-6.0	UG
34	16.0	UC
35	-	
36	1.2	
37	-1.0	
38	-	
39	3.0	
40	6.0	
41	-	
42	1.0	
43	-	
44	0.0	
45	-	
46	-	
47	-	

No of labs., p	27
No of repl., n	2
d	-0.0
s^2	8.9
s	3.0
$t = \sqrt{p} \cdot (d/s)$	-0.0836
Sign. level, p(t)	0.9340

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Biochemical oxygen demand - BOD_7, mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4A	0.30
4B	4.80
5	-1.32
6	-
7	-
8	-
9	-
10	-
12	-2.00
13	-
14	-
15A	-
15B	-
15C	-
16	0.00
17	-
18	-
19	-
20	-
21	-1.60
22	-
23	2.90
24	-
25	-
26	3.00
28	1.20
29	-
30	-
31	-
32	-
33	-
34	-
35	19.60
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45	4.00
46	-
47	-12.00

No of labs., p	12
No of repl., n	2
d	1.57
s^2	51.34
s	7.17
$t = \sqrt{p} \cdot (d/s)$	0.7606
Sign. level, p(t)	0.4629

No test statistics were found to be significant

TOC/NVOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-2.00	
3	-	
4A	1.00	
4B	-1.00	
5	-0.80	
6	0.80	
7	-	
8	-	
9	-0.40	
10	-	
12	-	
13	-	
14	3.98	
15A	-	
15B	-	
15C	-	
16	-3.80	
17	-	
18	-	
19	-0.80	
20	-	
21	-3.00	
22	-	
23	-0.30	
24	-	
25	9.21	
26	0.60	
28	-	
29	-	
30	0.70	
31	-	
32	-3.11	
33	-	
34	-	
35	1.00	
36	-9.70	UG
37	-	
38	2.50	UG
39	-	
40	-	
41	-	
42	-1.30	
43	4.20	
44	-	
45	-0.90	
46	-	
47	-0.10	

No of labs., p	20
No of repl., n	2
d	0.20
s^2	8.59
s	2.93
$t = \sqrt{p} \cdot (d/s)$	0.3040
Sign. level, p(t)	0.7644

No test statistics were found to be significant
UG denotes a Grubbs outlier

Total phosphorus - TP, mg/L P
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.00	
2	0.30	
3	1.25	UG
4A	0.46	
4B	0.26	
5	0.25	
6	-	
7	0.20	
8	0.70	
9	0.38	
10	1.00	
12	0.40	
13	0.40	
14	1.01	UG
15A	0.48	
15B	0.00	
15C	-	
16	0.18	
17	-4.50	UC
18	0.40	
19	0.70	
20	-0.10	
21	0.56	
22	0.10	
23	0.66	
24	-0.10	
25	0.50	
26	0.20	
28	0.30	
29	0.30	
30	-	
31	0.80	
32	-	
33	0.00	
34	0.50	
35	-	
36	-0.11	
37	-0.80	
38	-	
39	0.60	
40	0.40	
41	0.08	
42	0.60	
43	-	
44	1.20	
45	0.47	
46	-0.20	
47	0.21	

No of labs., p	38	
No of repl., n	2	
d	0.32	
s^2	0.13	
s	0.36	
$t = \sqrt{p} \cdot (d/s)$	5.5347	
Sign. level, p(t)	0.0000	***

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Difference for sample pair AB is significantly different from 0,
and data should be corrected with the difference (in spike value),
during execution of Cochran's test.

Chlorid, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	
1	31.0	
2	-	
3	-	
4A	-	
4B	-	
5	-	
6	0.0	
7	-	
8	-	
9	-4.7	
10	-4.0	
12	-	
13	-	
14	5.3	
15A	-21.0	UG
15B	-24.0	
15C	-	
16	-	
17	14.0	
18	-	
19	-	
20	1.0	
21	-	
22	-	
23	-	
24	-11.0	
25	-	
26	-	
28	-1.0	
29	-	
30	-	
31	-	
32	-	
33	8.0	
34	-11.0	
35	-	
36	-3.7	
37	-	
38	-9.3	
39	12.0	
40	-15.0	
41	39.3	
42	-	
43	-	
44	5.0	
45	-	U
46	-15.0	
47	-	

No of labs., p	19
No of repl., n	2
d	0.9
s^2	242.0
s	15.6
$t = \sqrt{p} \cdot (d/s)$	0.2500
Sign. level, p(t)	0.8054

No test statistics were found to be significant
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Total suspended solids - TSS, mg/L
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	1.0
3	6.0
4A	-2.6
4B	-1.0
5	2.7
6	-
7	-
8	1.0
9	-
10	-
12	1.0
13	1.8
14	-0.6
15A	-
15B	-
15C	-
16	3.0
17	-2.2
18	-
19	0.0
20	2.0
21	-13.0
22	-11.0
23	-13.0
24	-8.6
25	-
26	-0.6
28	-5.0
29	-5.0
30	-1.0
31	8.0
32	-
33	-
34	-
35	8.0
36	2.0
37	-
38	-
39	-
40	9.0
41	-1.4
42	2.6
43	-
44	-
45	3.0
46	-4.0
47	-3.0

No of labs., p	30
No of repl., n	2
d	-0.7
s^2	31.1
s	5.6
$t = \sqrt{p} \cdot (d/s)$	-0.6846
Sign. level, p(t)	0.4990

No test statistics were found to be significant

ANNEX D CONTROL OF RECOVERY

Chemical oxygen demand - COD_{Cr}, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB	
1	213.5	
2	211.5	
3	-	
4A	-	
4B	-	
5	208.8	
6	-	
7	214.0	
8	204.5	
9	-	
10	211.5	
12	199.5	
13	215.5	
14	203.0	
15A	199.5	
15B	212.0	
15C	221.5	
16	-	
17	214.0	
18	229.5	
19	203.5	
20	267.0	UC
21	-	
22	206.0	
23	191.5	
24	208.0	
25	-	
26	-	
28	204.0	
29	212.5	
30	-	
31	198.0	
32	-	
33	251.0	UG
34	197.0	UC
35	-	
36	208.6	
37	212.5	
38	-	
39	196.5	
40	220.0	
41	-	
42	219.5	
43	-	
44	217.0	
45	-	
46	219.0	
47	-	

No of labs., p	27
No of repl., n	2
m	209.5
s^2	73.5
s	8.6
Assigned value, μ	212
Recovery, %	98.8
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.5303
Sign. level, p(t)	0.1380

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Biochemical oxygen demand - BOD_7, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4A	89.65
4B	83.10
5	99.06
6	-
7	-
8	-
9	-
10	-
12	110.00
13	-
14	-
15A	-
15B	-
15C	-
16	116.00
17	-
18	-
19	-
20	-
21	94.40
22	-
23	91.45
24	-
25	-
26	98.20
28	87.60
29	-
30	-
31	-
32	-
33	-
34	-
35	91.90
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45	99.00
46	-
47	97.00

No of labs., p	12
No of repl., n	2
m	96.45
s^2	85.02
s	9.22
Assigned value, μ	96
Recovery, %	100.5
$t = \sqrt{p} \cdot (m-\mu)/s$	0.1678
Sign. level, p(t)	0.8698

No test statistics were found to be significant

TOC/NVOC, mg/L C
Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	63.50	
3	-	
4A	71.40	
4B	68.70	
5	73.85	
6	70.50	
7	-	
8	-	
9	63.80	
10	-	
12	-	
13	-	
14	59.93	
15A	-	
15B	-	
15C	-	
16	72.50	
17	-	
18	-	
19	73.10	
20	-	
21	59.30	
22	-	
23	74.25	
24	-	
25	68.85	
26	69.20	
28	-	
29	-	
30	62.35	
31	-	
32	68.97	
33	-	
34	-	
35	70.50	
36	114.85	UG
37	-	
38	32.76	UG
39	-	
40	-	
41	-	
42	66.75	
43	57.50	
44	-	
45	68.85	
46	-	
47	55.05	

No of labs., p	20	
No of repl., n	2	
m	66.94	
s^2	32.41	
s	5.69	
Assigned value, μ	64	
Recovery, %	104.6	
$t = \sqrt{p} \cdot (m-\mu)/s$	2.3121	
Sign. level, p(t)	0.0321	*

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UG denotes a Grubbs outlier

Total phosphorus - TP, mg/L P
Control of recovery, average of results

Laboratory	Sample pair AB	
1	11.60	
2	11.95	
3	7.81	UG
4A	10.91	
4B	11.03	
5	10.60	
6	-	
7	11.70	
8	12.05	
9	11.11	
10	10.80	
12	11.48	
13	11.20	
14	7.71	UG
15A	9.69	
15B	11.32	
15C	-	
16	11.49	
17	33.25	UC
18	11.80	
19	10.95	
20	12.25	
21	11.12	
22	11.05	
23	10.83	
24	10.85	
25	10.65	
26	11.60	
28	11.45	
29	11.15	
30	-	
31	11.30	
32	-	
33	12.00	
34	11.15	
35	-	
36	12.57	
37	11.20	
38	-	
39	9.90	
40	11.60	
41	11.60	
42	10.10	
43	-	
44	12.00	
45	9.84	
46	11.30	
47	11.25	

No of labs., p	38
No of repl., n	2
m	11.22
s^2	0.42
s	0.64
Assigned value, μ	11.3
Recovery, %	99.3
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.7424
Sign. level, p(t)	0.4625

No test statistics were found to be significant
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Chlorid, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB	
1	476.5	
2	-	
3	-	
4A	-	
4B	-	
5	-	
6	436.0	
7	-	
8	-	
9	415.6	
10	490.0	
12	-	
13	-	
14	399.7	
15A	654.5	UG
15B	512.0	
15C	-	
16	-	
17	470.0	
18	-	
19	-	
20	423.5	
21	-	
22	-	
23	-	
24	401.5	
25	-	
26	-	
28	436.5	
29	-	
30	-	
31	-	
32	-	
33	404.0	
34	497.5	
35	-	
36	429.3	
37	-	
38	437.4	
39	482.0	
40	482.5	
41	419.5	
42	-	
43	-	
44	497.5	
45	-	U
46	417.5	
47	-	

No of labs., p	19
No of repl., n	2
m	448.9
s^2	1386.0
s	37.2
Assigned value, μ	440
Recovery, %	102.0
$t = \sqrt{p} \cdot (m-\mu)/s$	1.0382
Sign. level, p(t)	0.3129

No test statistics were found to be significant
UG denotes a Grubbs outlier
U denotes data excluded from the data file

Total suspended solids - TSS, mg/L
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	214.5
3	210.0
4A	222.9
4B	221.7
5	232.1
6	-
7	-
8	203.5
9	-
10	-
12	216.5
13	221.9
14	219.5
15A	-
15B	-
15C	-
16	220.5
17	210.3
18	-
19	210.5
20	222.0
21	212.5
22	202.2
23	215.5
24	216.7
25	-
26	212.7
28	215.5
29	212.5
30	212.5
31	200.0
32	-
33	-
34	-
35	214.0
36	209.0
37	-
38	-
39	-
40	223.5
41	213.9
42	226.3
43	-
44	-
45	218.5
46	212.0
47	208.5

No of labs., p	30
No of repl., n	2
m	215.1
s^2	50.5
s	7.1
Assigned value, μ	215
Recovery, %	100.0
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0424
Sign. level, p(t)	0.9665

No test statistics were found to be significant

ANNEX E CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total phosphorus	mg/L P	A2	10	11,6	11,6	11,6	11,5	11,3	0,63	1,0
			38	11,3	11,3	11,3				
			58	11,5	11,5	11,5				
		B2	19	12,3	12,3	12,3	12,1	12,3		
			40	11,9	11,9	11,9				
			62	12,1	12,1	12,1				
Chloride	mg/L	A2	10	451,0	453,0	452	444	440	60	60
			38	449	450	450				
			58	431	432	432				
		B2	19	498	498	498	499	500		
			40	499	499	499				
			62	499	500	500				
Sulphate	mg/L	A2	10	< 40	< 40	< 40	< 40	-	-	-
			38	< 40	< 40	< 40				
			58	< 40	< 40	< 40				
		B2	19	68	68	68	68	-		
			40	70	69	70				
			62	66	66	66				
Total suspended solids	mg/L	A3	6-18	214,6		214,6	214,2	214,0	39	41
			40-47	213,8		213,8				
			59-62	214,2		214,2				
		B3	2-18	256,1		256,1	253,2	255,0		
			34-47	254,1		254,1				
			47-62	249,4		249,4				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-3 2022
Parameter:	COD_{Cr} B1
Unit:	mg/L O_2
Sigma:	12.0

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2022-08-31

Sample	x(a)	x(b)	average	sd	sd^2
G6-A2	229	229	229.0	0.000	0.000
9-10	224	228	226.0	2.828	8.00
15-16	220	220	220.0	0.000	0.000
21-20	226	227	226.5	0.707	0.500
29-28	224	225	224.5	0.707	0.500
33-31	223	222	222.5	0.707	0.500
38-38	221	223	222.0	1.414	2.000
45-49	223	220	221.5	2.121	4.500
49-53	217	219	218.0	1.414	2.000
53-58	219	221	220.0	1.414	2.000
59-68	219	220	219.5	0.707	0.500
69-72	224	224	224.0	0.000	0.000

For homogeneity

General average (x)	222.79
Sample average sd (s_x)	3.285
Within-sample sd (s_w):	1.307
Between-samples sd (ss):	3.1527
S_L in the Proficiency Test:	8.4
S_R in the Proficiency Test:	8.7

Conclusions

ss =	3.153	0.3*sigma= 3.61
/x-y/ =	0	
Analytical quality	Is s_w < 0.15*sigma	
	YES	
Homogeneity:	Is ss < 0.3*sigma?	
	YES	

PT: SPIL-3 2022
Parameter: TP B2
Unit: mg/L P
Sigma: 0.900

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2022-08-31

Sample	x(a)	x(b)	average	sd	sd^2
8	12.7	12.7	12.7	0.000	0.000
16	12.2	12.3	12.3	0.071	0.01
22	12.2	12.2	12.2	0.000	0.000
26	12.2	12.3	12.3	0.071	0.005
32	12.4	12.5	12.5	0.071	0.005
36	12.6	12.6	12.6	0.000	0.000
42	12.7	12.7	12.7	0.000	0.000
44	12.3	12.3	12.3	0.000	0.000
51	12.3	12.4	12.4	0.071	0.005
58	12.7	12.8	12.8	0.071	0.005
66	12.6	12.6	12.6	0.000	0.000
72	12.8	12.8	12.8	0.000	0.000

For homogeneity

General average (x)	12.5
Sample average sd (s_x)	0.22
Within-sample sd (s_w):	0.05
Between-samples sd (ss):	0.22
S_L in the Proficiency Test:	0.62
S_R in the Proficiency Test:	0.67

Stability test Date: 2022-09-15

Sample	x(a)	x(b)
19	12.3	12.3
40	11.9	11.9
62	12.1	12.1

For stability

General average (y):	12.1
/x-y/ =	0.40

Conclusions

ss = 0.218 0.3*sigma= 0.27
/x-y/ = 0.3958333

Analytical quality	Is s_w < 0.15*sigma **YES**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **NO**

PT:	SPIL-3 2022
Parameter:	TSS Sample A3
Unit:	mg/L
Sigma:	15.3

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2022-08-31

Sample	x(a)	x(b)	aver-age	sd	sd^2
K2-G6	212.6		212.6		
11-9	214.2		214.2		
14-15	215.0		215.0		
16-21	215.4		215.4		
19-29	217.4		217.4		
24-33	215.4		215.4		
28-38	215.4		215.4		
33-45	213.4		213.4		
38-53	207.9		207.9		
41-24	205.5		205.5		
43-59	202.8		202.8		
55-70	211.4		211.4		

For homogeneity

General average (x)	212.2
Sample average sd (s_x)	4.5
Within-sample sd (s_w):	
Between-samples sd (ss):	4.5
S_L in the Proficiency Test:	6.5
S_R in the Proficiency Test:	7.6

Stability test Date: 2022-09-15

Sample	x(a)	x(b)
6-18	214.6	
40-47	213.8	
59-62	214.2	

For stability

General average (y):	214.2
/x-y/ =	2.0

Conclusions

ss =	4.51	0.3*sigma=	4.58
/x-y/ =	2.0040763		

Analytical quality	Is s_w < 0.15*sigma **No data**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **YES**