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Proficiency test SPIL-3 (2021)

Organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater (synthetic wastewater, effluent)

Quality Documentation
November 2021

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Project	Project No
Proficiency test SPIL-3 (2021)	20405-13
Authors Rikke Mikkelsen	Date 2021-11-24
	Approved by Peter Rerup

1	Quality Documentation Report	FYE3	DPRE	2021-11-30
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
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 16 September 2021. 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 2021.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 42 laboratories from Denmark, Norway, Sweden and Singapore. A list of participants is shown in Appendix A.

The closing date for submission of results was 3 October 2021. All participants except laboratory no. 25 and no. 32 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 synthetic wastewater, effluent. 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 (1994) /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 synthetic wastewater, effluent. The table also gives the expanded uncertainty of the assigned values.

Table 2 Assigned and spike value

Parameter	Abbreviation	Unit	Typical Range	Assigned value	Uncertainty of assigned value	Spike value
Chemical oxygen demand – dichromate method	COD_{Cr}	mg/L O_2	100-800	19	0.40	5
5 day biochemical oxygen demand (w. ATU)	BOD_5 w. ATU	mg/L O_2	50-500	2.4	0.58	0.3
7 day biochemical oxygen demand (w. ATU)	BOD_7 w. ATU	mg/L O_2	50-500	2.3	0.38	0.3
Non-volatile/Total organic carbon	NVOC/TOC	mg/L C	50-800	7.5	0.16	1.8
Total phosphorus	TP	mg/L P	5-10	1.30	0.015	0.15
Chloride	Cl	mg/L	50-700	139	1.8	13
Sulphate	SO_4	mg/L	20-200	34	0.39	6
Total suspended matter	TSS	mg/L	100-500	55.3	1.8	59.8

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.

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. The assigned and spike values are both calculated from sample preparation except for BOD.

For BOD_5 the spike value is calculated from sample preparation. The assigned value is calculated using the consensus value after exclusion of laboratory 4 and 30.

For BOD_7 the spike value is calculated from sample preparation and the assigned value is the consensus value for laboratories using standardised methods (method no. 1 - 4), based on the median.

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.

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 and the control of assigned value at Eurofins confirmed the value (Appendix E).

The test revealed a significant difference between the two for TP. Average recovery was 101 %. The difference could be attributed to influence from laboratories using methods other than those prescribed by the Danish EPA. The test was repeated with results from

method no. 1 and no. 2 and now showed no significant difference. Furthermore, the results of control measurements at Eurofins confirmed the assigned value (Appendix E). The assigned value is therefore kept unchanged.

The test revealed a significant difference between the two for TSS. Average recovery was 98.0 %. However, the results of control measurements at Eurofins confirmed the assigned value (Appendix E), and scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. Furthermore, recovery was close to 100%. 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:

NVOC	Homogeneity test (ampoule diluted x100)
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 test for total suspended matter show that the samples are homogeneous. The stability test did not prove the samples to be stable. This is due to the result of sample 50 which is proved to be an outlier using quantiles. When the result for sample 50 is excluded for the calculation for the general average the samples are proved to be stable.

The test for total phosphorous did not prove the samples to be homogenous and stable. The standard deviation between days (sb = 0.053 mg/l) for the method used in the test was taken into account and the between-samples standard deviation, the difference between days /x-y/ and $0.3 \cdot \hat{\sigma}$ is found to be marginal. The laboratories total phosphorous results have been review and no sign of inhomogeneity has been found. The general analytical quality found for total phosphorus and chloride in the proficiency test is comparable with previous proficiency test.

It is concluded, that the heterogeneity and instability of the materials found has not affected the overall evaluation of the laboratories.

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. The results are also suitable for estimation of the general quality of analyses among all participating laboratories.

For TP and TSS 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.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-3 (2021)*, Report to participants, October 2021.

/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. 1770 on *quality criteria for environmental measurements,* 28 October 2020 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2015.

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	Town	Country
Analyseenheden, Institut for Agroøkologi, Aarhus Universitet	Tjele	Denmark
AquaDjurs A/S	Grenaa	Denmark
Biofos A/S	København K	Denmark
Bjergmarken RA, Fors Spildevand Roskilde	Roskilde	Denmark
BlueKolding A/S	Kolding	Denmark
Bornholms Spildevand A/S	Rønne	Denmark
CP Kelco, QC Analyselab.	Ll. Skensved	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Hillerød Spildevand	Hillerød	Denmark
Holbæk RA, Fors Spildevand Holbæk	Holbæk	Denmark
Holstebro Renseanlæg, Vestforsyning Spildevand	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Denmark
NK-Forsyning A/S	Næstved	Denmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	Denmark
Rensningsanlæg Øst, Spildevandslaboratoriet	Esbjerg	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (2 participants)	Slagelse	Denmark
Svendborg Spildevand A/S, Svenborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
SGS Analytics Norway AS (Hamar)	Hamar	Norway
EUROFINS MECHEM PTE. LTD.	Singapore	Singapore
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Hallstavik	Sweden
Iggesund Paperboard AB, Iggesunds Bruk, Cell- och Miljölab	Iggesund	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
MittSverige Vatten och Avfall AB, Fillanverket Laboratoriet	Sundsvall	Sweden

Laboratory	Town	Country
Mjölby Kommun	Mjölby	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Nyköpings kommun Vattenlaboratoriet	Nyköping	Sweden
Perstorp Oxo AB	Ödsmål	Sweden
Preemraff AB Göteborg	Göteborg	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Roslagsvatten AB	Åkersberga	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	Prepared from		Concentration
Concentrate A1	0.925 g 0.925 g 	D-glucose L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 1.892 g/kg NVOC: 0.747 g/kg BOD: 1.295 g/kg
Concentrate B1	1.153 g 1.153 g 	D-glucose L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 2.360 g/kg NVOC: 0.932 g/kg BOD: 1.615 g/kg
Stock TP	1.500 g 	Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 151.8 mg/kg
Stock Cl	20.000 g 	Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 12.133 g/kg
Stock SO_4	5.000 g 	Sodium sulphate (Na_2SO_4) milli-Q water up to 1000.0 g	SO_4: 3.381 g/kg
Stock TSS	15.000 g 	Microcrystalline cellulose milli-Q water up to 1000.0 g	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 1.00 mL of concentrate A1 is diluted up to 100.0 mL with pure water	18.9	7.47					
B1-COD/NVOC	At the laboratory 1.00 mL of concentrate B1 is diluted up to 100.0 mL with pure water	23.6	9.32					
A1-BOD	At the laboratory 2.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Brørup sewage treatment plant			a + 1.30				
B1-BOD	At the laboratory 2.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Brørup sewage treatment plant			a + 1.62				
A2	600.0 g stock TP 800.0 g stock Cl 700.0 g stock SO_4 Milli-Q water up to 70.0 kg				1.30	139	33.8	
B2	35.0 g stock TP 40.0 g stock Cl 60.0 g stock SO4 Sample A2 up to 35.0 kg				1.45	152	39.5	
A3	At the laboratory 1000.0 mL of pure water is added to 4.0 mL stock TSS							59.8
B3	At the laboratory 1000.0 mL of pure water is added to 3.7 mL stock TSS							55.3

ANNEX C CONTROL OF SPIKE VALUES

COD_{Cr}, mg/L O_2
Control of differences within sample pairs

Laboratory	*Difference AB*	
1	-1.00	
2	0.50	
3	1.40	UG
4	24.00	UC
5	-	
6	-	
7	-1.70	
8	-	
9	0.50	
10	-0.60	
11A	1.50	
11B	1.00	
11C	2.90	
12	-	
13	0.50	
14	-0.80	
15	0.90	
16	-2.40	
17	-	
18	0.00	
19	-1.90	
20	-	
21	-	
22	-0.10	
23	0.10	
24	-	
26	-0.90	
27	1.20	
28	-	
29	2.00	
30	-0.10	
31	-8.70	UC
33	1.30	
34	-0.40	
35	-	
36	-	
37	6.50	UC
38	-	
39	16.30	UC
40	0.20	
41	-0.40	
42	1.10	
No of labs., p	25	
No of repl., n	2	
d	0.14	
s^2	1.52	
s	1.23	
$t = \sqrt{p} \cdot (d/s)$	0.5510	
Sign. level, p(t)	0.5867	

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

BOD_5 w. ATU, mg/L O_2
Control of differences within sample pairs

Laboratory	*Difference AB*	
1	-	
2	-0.830	
3	-	
4	-	U
5	-	
6	-	
7	-	
8	-	
9	-0.090	
10	-	
11A	-	
11B	-	
11C	-	
12	-	
13	-	
14	-	
15	-	
16	-	
17	-	
18	-	
19	-	
20	-	
21	-	
22	-	
23	0.200	
24	-	
26	0.310	
27	-	
28	-	
29	-	
30	-	U
31	-	
33	-	
34	-	
35	-	
36	-	
37	-	
38	-	
39	-	
40	-	
41	-	
42	-	
No of labs., p	4	
No of repl., n	2	
d	-0.103	
s^2	0.264	
s	0.514	
$t = \sqrt{p} \cdot (d/s)$	-0.3992	
Sign. level, p(t)	0.7165	

No test statistics were found to be significant.
U denotes data excluded from the data file

BOD_7 w. ATU, mg/L O_2
Control of differences within sample pairs

Laboratory	*Difference AB*
1	-
2	-
3	-
4	-
5	-
6	-0.100
7	-
8	-
9	-
10	-
11A	-
11B	-
11C	-
12	0.080
13	-
14	-
15	-
16	-
17	-
18	-
19	-0.000
20	0.350
21	-
22	-
23	-
24	-
26	-
27	-
28	-
29	-
30	-
31	-
33	-
34	-0.370
35	-
36	0.200
37	-
38	-
39	-
40	-
41	-
42	-
No of labs., p	6
No of repl., n	2
d	0.027
s^2	0.062
s	0.250
$t = \sqrt{p} \cdot (d/s)$	0.2617
Sign. level, p(t)	0.8040

No test statistics were found to be significant

NVOC, mg/L C
Control of differences within sample pairs

Laboratory	*Difference AB*	
1	-	
2	0.760	
3	-	
4	-	
5	-	
6	-0.460	
7	-	
8	-	
9	-	
10	-	
11A	-	
11B	-	
11C	-	
12	-	
13	-	
14	0.209	
15	0.580	
16	-5.640	UC
17	0.610	
18	1.290	
19	-	
20	0.470	
21	-	
22	-	
23	-	
24	-	
26	-0.120	
27	-0.200	
28	0.270	
29	-	

Laboratory	*Difference AB*
30	-
31	-
33	-
34	0.190
35	0.020
36	0.050
37	-0.430
38	-0.078
39	-
40	-
41	-
42	-
No of labs., p	15
No of repl., n	2
d	0.211
s^2	0.223
s	0.472
$t = \sqrt{p} \cdot (d/s)$	17.296
Sign. level, p(t)	0.1057

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

Total phosphorous, mg/L P
Control of differences within sample pairs

Laboratory	*Difference AB*
1	0.010
2	0.000
3	0.030
4	0.020
5	0.010
6	0.050
7	0.010
8	-0.030
9	0.050
10	-0.048
11A	0.010
11B	-
11C	0.010
12	-0.010
13	0.030
14	0.020
15	0.010
16	0.030
17	0.010
18	0.010
19	0.010
20	0.020
21	-0.040
22	-0.060
23	0.000
24	0.030
26	-0.030
27	0.010
28	-
29	0.020
30	0.010
31	0.055
33	0.040
34	-0.040
35	-0.025
36	0.010
37	0.050
38	0.000
39	0.020
40	-0.010
41	0.000
42	-0.020
No of labs., p	40
No of repl., n	2
d	0.007
s^2	0.001
s	0.027
$t = \sqrt{p} \cdot (d/s)$	15.716
Sign. level, p(t)	0.1241

No test statistics were found to be significant

Chloride, mg/L
Control of differences within sample pairs

Laboratory	*Difference AB*
1	-4.0
2	-1.0
3	-15.0
4	-4.0
5	-2.9
6	0.3
7	-
8	-
9	2.0
10	9.0
11A	3.0
11B	-
11C	-2.0
12	-
13	5.0
14	-
15	-
16	-
17	-
18	-1.0
19	-
20	-0.8
21	2.0
22	-
23	-3.0
24	-
26	1.3
27	-4.0
28	-
29	-
30	-3.0
31	-2.3
33	-9.0
34	-
35	-
36	-
37	-
38	-0.6
39	-1.0
40	2.4
41	-
42	-6.0
No of labs., p	24
No of repl., n	2
d	-1.4
s^2	22.2
s	4.7
$t = \sqrt{p} \cdot (d/s)$	-15.006
Sign. level, p(t)	0.1471

No test statistics were found to be significant

Sulphate, mg/L
Control of differences within sample pairs

Laboratory	*Difference AB*
1	-
2	-
3	1.70
4	-
5	0.58
6	0.32
7	-
8	-
9	-
10	-
11A	-2.00
11B	-
11C	-
12	-
13	-
14	-
15	-
16	-
17	-
18	1.10
19	-
20	-
21	-
22	-
23	-
24	-
26	0.22
27	-
28	-
29	-
30	-
31	-
33	-
34	-
35	-
36	-
37	-0.90
38	-
39	-
40	-
41	-
42	-
No of labs., p	7
No of repl., n	2
d	0.15
s^2	1.54
s	1.24
$t = \sqrt{p} \cdot (d/s)$	0.3094
Sign. level, p(t)	0.7675

No test statistics were found to be significant

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

Laboratory	*Difference AB*	
1	-	
2	-2.50	
3	-1.50	
4	-2.50	
5	-	
6	0.00	
7	-	
8	0.10	
9	0.30	
10	-0.40	
11A	-	
11B	-	
11C	-	
12	-7.90	UC
13	-0.50	
14	0.10	
15	-	
16	-8.50	UC
17	-0.80	
18	-1.50	
19	1.50	
20	1.50	
21	0.50	
22	-2.00	
23	0.80	
24	0.60	
26	1.90	
27	-0.50	
28	-	
29	0.50	
30	0.30	
31	-0.10	
33	-	
34	1.80	
35	0.10	
36	1.20	
37	-0.20	
38	-1.10	
39	-0.50	
40	-	
41	-	
42	0.30	
No of labs., p	29	
No of repl., n	2	
d	-0.09	
s^2	1.36	
s	1.17	
$t = \sqrt{p} \cdot (d/s)$	-0.4135	
Sign. level, p(t)	0.6824	

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

ANNEX D CONTROL OF RECOVERY

COD_{Cr}, mg/L O_2
Control of recovery, average of results

Laboratory	*Sample pair AB*	
1	18.50	
2	17.55	
3	4.70	UG
4	34.60	UC
5	-	
6	-	
7	16.45	
8	-	
9	18.65	
10	18.70	
11A	18.55	
11B	16.00	
11C	14.75	
12	-	
13	19.35	
14	13.70	
15	17.05	
16	22.70	
17	-	
18	19.00	
19	19.35	
20	-	
21	-	
22	16.85	
23	19.25	
24	-	
26	16.15	
27	16.20	
28	-	
29	19.00	
30	21.15	
31	19.75	UC
33	20.15	
34	16.90	
35	-	
36	30.00	
37	23.35	UC
38	-	
39	38.65	UC
40	18.60	
41	23.90	
42	22.15	
No of labs., p	25	
No of repl., n	2	
m	18.42	
s^2	5.79	
s	2.41	
Assigned value, μ	19	
Recovery, %	97.0	
$t = \sqrt{p} \cdot (m - \mu/s)$	-11.969	
Sign. level, p(t)	0.2430	

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

BOD_5 w. ATU, mg/L O_2
Control of recovery, average of results

Laboratory	*Sample pair AB*	
1	-	
2	1.885	
3	-	
4	-	U
5	-	
6	-	
7	-	
8	-	
9	2.375	
10	-	
11A	-	
11B	-	
11C	-	
12	-	
13	-	
14	-	
15	-	
16	-	
17	-	
18	-	
19	-	
20	-	
21	-	
22	-	
23	2.900	
24	-	
26	2.295	
27	-	
28	-	
29	-	
30	-	U
31	-	
33	-	
34	-	
35	-	
36	-	
37	-	
38	-	
39	-	
40	-	
41	-	
42	-	
No of labs., p	4	
No of repl., n	2	
m	2.364	
s^2	0.174	
s	0.417	
Assigned value, μ	2.4	
Recovery, %	98.5	
$t = \sqrt{p} \cdot (m - \mu/s)$	-0.1739	
Sign. level, p(t)	0.8730	

No test statistics were found to be significant
U denotes data excluded from the data file

BOD_7 w. ATU, mg/L O_2
Control of recovery, average of results

Laboratory	*Sample pair AB*
1	-
2	-
3	-
4	-
5	-
6	2.150
7	-
8	-
9	-
10	-
11A	-
11B	-
11C	-
12	2.450
13	-
14	-
15	-
16	-
17	-
18	-
19	2.400
20	2.265
21	-
22	-
23	-
24	-
26	-
27	-
28	-
29	-
30	-
31	-
33	-
34	2.525
35	-
36	2.250
37	-
38	-
39	-
40	-
41	-
42	-
No of labs., p	6
No of repl., n	2
m	2.340
s^2	0.020
s	0.141
Assigned value, μ	2.3
Recovery, %	101.7
$t = \sqrt{p} \cdot (m - \mu/s)$	0.6937
Sign. level, p(t)	0.5188

No test statistics were found to be significant

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

Laboratory	*Sample pair AB*	
1	-	
2	8.320	
3	-	
4	-	
5	-	
6	8.120	
7	-	
8	-	
9	-	
10	-	
11A	-	
11B	-	
11C	-	
12	-	
13	-	
14	7.258	
15	7.810	
16	93.470	UC
17	7.745	
18	7.025	
19	-	
20	6.835	
21	-	
22	-	
23	-	
24	-	
26	7.200	
27	7.220	
28	7.595	
29	-	

Laboratory	*Sample pair AB*
30	-
31	-
33	-
34	6.865
35	6.890
36	8.375
37	7.525
38	8.139
39	-
40	-
41	-
42	-
No of labs., p	15
No of repl., n	2
m	7.528
s^2	0.290
s	0.538
Assigned value, μ	7.5
Recovery, %	100.4
$t = \sqrt{p} \cdot (m - \mu/s)$	0.2022
Sign. level, p(t)	0.8427

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

Total phosphorous, mg/L P
Control of recovery, average of results

Laboratory	*Sample pair AB*
1	1.325
2	1.370
3	1.255
4	1.380
5	1.295
6	1.355
7	1.315
8	1.315
9	1.315
10	1.356
11A	1.315
11B	-
11C	1.295
12	1.295
13	1.395
14	1.290
15	1.335
16	1.265
17	1.285
18	1.365
19	1.265
20	1.300
21	1.400
22	1.280
23	1.290
24	1.275
26	1.315
27	1.255
28	-
29	1.170

Laboratory	*Sample pair AB*	
30	1.365	
31	1.481	
33	1.260	
34	1.340	
35	1.383	
36	1.305	
37	1.275	
38	1.310	
39	1.330	
40	1.365	
41	1.330	
42	1.330	
No of labs., p	40	
No of repl., n	2	
m	1.319	
s^2	0.003	
s	0.053	
Assigned value, μ	1.30	
Recovery, %	101.4	
$t = \sqrt{p} \cdot (m - \mu/s)$	22.225	
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)

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

Laboratory	*Sample pair AB*
1	135.0
2	140.5
3	168.5
4	148.0
5	137.8
6	139.8
7	-
8	-
9	109.0
10	129.5
11A	120.5
11B	-
11C	146.0
12	-
13	107.5
14	-
15	-
16	-
17	-
18	127.5
19	-
20	138.4
21	191.0
22	-
23	118.5
24	-
26	134.3
27	137.0
28	-
29	-

Laboratory	*Sample pair AB*
30	138.5
31	138.4
33	106.5
34	-
35	-
36	-
37	-
38	130.8
39	136.5
40	136.3
41	-
42	111.0
No of labs., p	24
No of repl., n	2
m	134.5
s^2	350.1
s	18.7
Assigned value, μ	139
Recovery, %	96.7
$t = \sqrt{p} \cdot (m - \mu/s)$	-11.904
Sign. level, p(t)	0.2460

No test statistics were found to be significant

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

Laboratory	*Sample pair AB*
1	-
2	-
3	26.75
4	-
5	33.12
6	32.98
7	-
8	-
9	-
10	-
11A	36.00
11B	-
11C	-
12	-
13	-
14	-
15	-
16	-
17	-
18	30.75
19	-
20	-
21	-
22	-
23	-
24	-
26	34.22
27	-
28	-
29	-
30	-
31	-
33	-
34	-
35	-
36	-
37	33.25
38	-
39	-
40	-
41	-
42	-
No of labs., p	7
No of repl., n	2
m	32.44
s^2	8.75
s	2.96
Assigned value, μ	34
Recovery, %	95.4
$t = \sqrt{p} \cdot (m - \mu/s)$	-13.968
Sign. level, p(t)	0.2120

No test statistics were found to be significant

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

Laboratory	*Sample pair AB*	
1	-	
2	49.05	
3	52.25	
4	56.25	
5	-	
6	55.00	
7	-	
8	53.55	
9	54.55	
10	50.90	
11A	-	
11B	-	
11C	-	
12	37.85	UC
13	48.75	
14	52.25	
15	-	
16	54.75	UC
17	52.90	
18	54.25	
19	53.75	
20	55.15	
21	54.25	
22	54.40	
23	55.50	
24	52.90	
26	57.35	
27	55.85	
28	-	
29	55.75	
30	55.25	
31	54.25	
33	-	
34	53.50	
35	55.75	
36	53.80	
37	55.60	
38	55.35	
39	56.75	
40	-	
41	-	
42	56.35	
No of labs., p	29	
No of repl., n	2	
m	54.18	
s^2	4.28	
s	2.07	
Assigned value, μ	55.3	
Recovery, %	98.0	
$t = \sqrt{p} \cdot (m - \mu/s)$	-29.161	
Sign. level, p(t)	0.0069	**

* 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

ANNEX E CONCENTRATION LEVEL

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
COD_{Cr}	mg/L O_2	A1	3	17	17	17	17	19	5	5
			31	16	17	16				
			47	17	17	17				
		B1	7	21	21	21	21	2		
			31	21	21	21				
			49	21	22	21				
Total phosphorus	mg/L P	A2	5	1.30	1.30	1.30	1.30	1.30	0.16	0.15
			33	1.29	1.29	1.29				
			60	1.32	1.32	1.32				
		B2	12	1.47	1.47	1.47	1.46	1.45		
			38	1.48	1.48	1.48				
			53	1.44	1.44	1.44				
Chloride	mg/L	A2	5	116	114	115	112	139	11	13
			33	112	111	112				
			60	111	110	111				
		B2	12	125	125	125	123	152		
			38	123	123	123				
			53	122	122	122				
Sulphate	mg/L	A2	5	<40	<40	<40	<40	34	-	6
			33	<40	<40	<40				
			60	<40	<40	<40				
		B2	12	<40	<40	<40	<40	40		
			38	<40	<40	<40				
			53	<40	<40	<40				
Total suspended solids	mg/L	A3	9	59.8		59.8	60.1	59.8	4.1	4.5
			27	60.1		60.1				
			56	60.5		60.5				
		B3	4	56.3		56.3	56.0	55.3		
			23	55.9		55.9				
			45	55.9		55.9				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-3 2021
Parameter:	NVOC
Unit:	mg/L C
Sigma:	0.5

Responsible for tests: FYE3

Homogeneity test Date: 2020-08-17

Sample	x(a)	x(b)	aver-age	sd	sd^2
A1- xx	8.5	7.5	8.0	0.702	0.493
A1- xx	7.6	7.4	7.5	0.152	0.02
A1- xx	7.6	7.4	7.5	0.113	0.013
A1- xx	8.0	8.1	8.1	0.121	0.015
A1- xx	7.4	7.3	7.4	0.107	0.011
A1- xx	7.4	7.3	7.4	0.027	0.001
A1- xx	7.5	7.4	7.5	0.070	0.005
A1- xx	7.6	7.4	7.5	0.170	0.029
A1- xx	7.7	7.4	7.6	0.225	0.051
A1- xx	7.6	7.4	7.5	0.148	0.022
A1- xx	7.5	7.4	7.4	0.115	0.013
A1- xx	8.0	7.4	7.7	0.461	0.212

For homogeneity

General average (x)	7.57
Sample average sd (s_x)	0.224
Within-sample sd (s_w):	0.272
Between-samples sd (ss):	0.1156
S_L in the Proficiency Test:	0.334
S_R in the Proficiency Test:	0.588

Conclusions

ss = 0.116 0.3*sigma= 0,16

/x-y/ = 0

Homogeneity: Is ss < 0.3*sigma?

YES

PT:	SPIL-3 2021
Parameter:	TP
Unit:	mg/L P
Sigma:	0.077

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2021-09-01

Sample	x(a)	x(b)	average	sd	sd^2
2	1.43	1.43	1.43	0.000	0.000
9	1.44	1.44	1.44	0.000	0.000
19	1.44	1.45	1.45	0.007	0.000
22	1.44	1.43	1.44	0.007	0.000
32	1.46	1.46	1.46	0.000	0.000
41	1.39	1.39	1.39	0.000	0.000
42	1.45	1.45	1.45	0.000	0.000
46	1.46	1.47	1.47	0.007	0.000
50	1.46	1.46	1.46	0.000	0.000
55	1.43	1.43	1.43	0.000	0.000
57	1.43	1.44	1.44	0.007	0.000
67	1.38	1.38	1.38	0.000	0.000

For homogeneity

General average (x)	1.435
Sample average sd (s_x)	0.026
Within-sample sd (s_w):	0.004
Between-samples sd (ss):	0.0261
S_L in the Proficiency Test:	0.051
S_R in the Proficiency Test:	0.055
s_b method between-days:	0.053

Quartile 1	1.43
Interquartile Range	0.02
Quartile 3	1.45
Lower fence	1.40
Upper fence	1.49

Outliers: 41, 67

Stability test Date: 2021-09-16

Sample	x(a)	x(b)
12	1.47	1.47
38	1.48	1.48
53	1.44	1.44

For stability

General average (y):	1.463
/x-y/ =	0.028

Conclusions

ss =	0.026	0.3*sigma=	0.023
/x-y/ =	0.028		

Analytical quality	Is s_w < 0.15*sigma **YES**
Homogeneity:	Is ss < 0.3*sigma? **NO. but the difference is marginal**
Stability:	/x-y/ < 0.3*sigma? **No. but the difference is marginal.**

PT:	SPIL-3 2021
Parameter:	TSS
Unit:	mg/L
Sigma:	3.6

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2021-09-01

Sample	x(a)	x(b)	aver-age	sd	sd^2
4	59.2		59.2		
11	58.7		58.7		
15	59.5		59.5		
23	59.7		59.7		
25	58.8		58.8		
31	60.0		60.0		
35	60.0		60.0		
40	58.6		58.6		
45	59.0		59.0		
50	56.6		56.6		
52	58.7		58.7		
59	58.8		58.8		

For homogeneity

General average (x)*	59.1
Sample average sd (s_x)	0.898
Within-sample sd (s_w):	
Between-samples sd (ss):	0.898
S_L in the Proficiency Test:	1.99
S_R in the Proficiency Test:	2.15

* without sample 50

Stability test Date: 2021-09-16

Sample	x(a)	x(b)
5	59.76	
33	60.06	
60	60.46	

For stability

General average (y):	60.09333
/x-y/ =	0.948096

Conclusions

ss =	0.90	0.3*sigma=	1.08
/x-y/ =	0.948096		

Analytical quality	Is s_w < 0.15*sigma **No data**
Homoge-neity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **YES. when sample 50 is ex-cluded from the general aver-age.**

Quartile 1	58.67
Interquartile Range	0.85
Quartile 3	59.51
Lower fence	57.40
Upper fence	60.78