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Proficiency test SPIL-1 (2021)

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

Quality Documentation
May 2021

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CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater was conducted on 11 Marts 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 13 April 2021.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 54 laboratories from Denmark, Germany, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 26 March 2021. 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 effluent. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1 BOD	BOD_5 w. ATU, BOD_7 w. ATU
A1/B1 COD/NVOC	COD_{Cr}, NVOC/TOC
A2/B2	TP, Cl, 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 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	5-75	39	1.7	8
Five day biochemical oxygen demand w. ATU	BOD_5 w. ATU	mg/L O_2	2-6	*)	-	-
Seven day biochemical oxygen demand w. ATU	BOD_7 w. ATU	mg/L O_2	2-6	3.5	1.2	0.8
Non-volatile organic carbon	NVOC/TOC	mg/l C	2-30	15.7	0.59	3.0
Total phosphorus	TP	mg/l P	0.2-2	0.336	0.0041	0.071
Chloride	Cl	mg/l	50-700	910	19	40
Sulphate	SO_4	mg/l	20-200	185	9.0	14
Total suspended solids	TSS	mg/l	20-100	51.2	0.65	14.9

*) Few laboratories reported results for BOD_5 w. ATU using a standardized method. The Assigned value for BOD_7 w. ATU is therefore used as indicative value.

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), method no. 2 (TP), or method no.1 and 2 (TSS), which are the methods required by the Danish EPA /5/. Only few laboratories reported COD_{Cr} using the method required by the Danish EPA /5/. Assigned values for BOD_7 are based upon standardised methods (method no. 1 and ISO 5815-1). A list of method identification numbers is found in the report to participants /1/. Assigned values for COD, Cl and SO_4 are consensus values for all laboratories 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 for most parameters, but the test revealed a significant difference between the two for the following parameters: COD_{Cr}, Cl and TP.

For COD and Cl the differences are 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.

For TP 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. 9, 42, 42A, 42B and 71 and now showed no significant difference.

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 for most parameters 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 102.9 %. 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. 9, 42, 42A, 42B and 71 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.

3 HOMOGENEITY AND STABILITY OF SAMPLES

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

COD_{Cr}	Combined homogeneity and stability 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 tests for stability and homogeneity show that the samples are stable and homogeneous. However, the test for TP indicated instability. The standard deviation between days (s_b) for the method used in the test was taken into account and the difference between /*x-y*/ and ($0.3 \cdot \hat{\sigma}$) is found to be marginal.

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 COD_{Cr} and Cl 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 TP the participants did not recover the spike value or 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 value given for BOD_5 w. ATU is only indicative because the number of participants reporting a results is small. The assigned value is therefore uncertain.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-1 (2021)*, Report to participants, April 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
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
Nyborg Forsyning & Service	Nyborg	Denmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	Denmark
Rensningsanlæg Øst, Spildevandslaboratoriet	Esbjerg	Denmark
RGS Nordic A/S	Skælskør	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
Svendborg Spildevand A/S, Svenborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
Eurofins Umwelt West GmbH	Wesseling	Germany
SYNLAB Analytics AS Norway (Hamar)	Hamar	Norway
AB Borlänge Energi, Borlänge Reningsverk	Borlänge	Sweden
AB Lennart Månsson International	Helsingborg	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Hallstavik	Sweden
Hammargårds ARV, Kungsbacka kommun (2 participants)	Kungsbacka	Sweden
Holmen Paper AB, Bravikens Pappersbruk	Norrköping	Sweden
INOVYN Sverige AB	Stenungsund	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Klippans Reningsverk	Klippan	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
Laboratoriet Fillanverket, MittSverige Vatten och Avfall AB	Sundsvall	Sweden
Laboratoriet vid Smedjeholms avloppsreningsverk	Falkenberg	Sweden
Ljungby Kommun, Avloppsreningsverket, VA-labb	Ljungby	Sweden
Mjölby Kommun	Mjölby	Sweden

Laboratory	Town	Country
Motala Kommun, Tekniska Förvaltningen, Vatten och Avfall, (2 participants)	Motala	Sweden
Nordic Sugar AB, Örtofta Sockerbruk	Eslöv	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Preemraff AB Göteborg	Göteborg	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Uddebo Laboratorium	Luleå	Sweden
Vallviks Bruk AB	Vallvik	Sweden
VIVAB	Falkenberg	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	0.738 g 0.738 g 	D-glucose L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 1.510 g/kg NVOC: 0.597 g/kg BOD: 1.034 g/kg
Stock TP	1.499 g	Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 151.7 mg/kg
Stock Cl	9.9994 g	Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.066 g/kg
Stock SO_4	5.001 g	Sodium sulphate (Na_2SO_4) milli-Q water up to 1000.0 g	SO_4: 3.382 g/kg
Stock TSS	14.999 g	Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 14.999 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 2.00 mL of concentrate A1 is diluted up to 100.0 mL with filtered water from Varde sewage treatment plant	a + 37.8	b + 14.9					
B1-COD/NVOC	At the laboratory 2.00 mL of concentrate B1 is diluted up to 100.0 mL with filtered water from Varde sewage treatment plant	a + 30.2	b + 11.9					
A1-BOD	At the laboratory 6.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Varde sewage treatment plant			c + 3.9				
B1-BOD	At the laboratory 6.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Varde sewage treatment plant			c + 3.1				
A2	15.0 g stock TP 250.0 g stock Cl 150.0 g stock SO_4 Sample B2 up to 30.0 kg				0.986 · (d+0.258) + 0.057	0.986 · e + 50.6	0.986 · f + 16.9	
B2	85.0 g stock TP 0.0 g stock Cl 0.0 g stock SO_4filtered water from Brørup sewage treatment plant up to 50.0 kg				d + 0.258	e	f	
A3	At the laboratory 1000.0 mL of filtered water from Brørup sewage treatment plant is added to 4.3 mL stock TSS							g + 67.2
B3	At the laboratory 1000.0 mL of filtered water from Brørup sewage treatment plant is added to 3.5 mL stock TSS							g + 52.3

ANNEX C CONTROL OF SPIKE VALUES

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

Laboratory	*Difference AB*	
1	-	
2	-0.40	
3	-2.10	
4	1.10	
5	-	
6	-5.00	
7	-	
8	-3.60	
9	-3.60	
10	-0.50	
11	-	
12	-0.90	
13	-1.40	
14A	-	
14B	2.00	
15	6.60	
16	1.46	
17	-3.00	
18	-2.30	
19	-	
20A	-1.90	
20B	-2.00	
21	2.70	
22	-	
23	-0.70	
24	-	
25	-1.10	
26	-17.70	UC
27	0.40	
28	-0.50	
29	-1.60	
30	0.70	
31	-	
32	-	
33	0.60	
35	-0.60	
36	-	
37	-2.50	
38	-	

Laboratory	*Difference AB*	
39	-	
40	-	
41	-2.90	
42	-2.10	
43	-5.05	
44	-1.60	
45	-	
46	-6.70	
47	0.50	
48	-3.00	
49	-	
50	9.00	
51	-2.80	
52	-	
53	-2.10	
54	-3.70	
No of labs., p	37	
No of repl., n	2	
d	-1.04	
s^2	8.68	
s	2.95	
$t = \sqrt{p} \cdot (d/s)$	-21.535	
Sign. level, p(t)	0.0381	*

* 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

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.

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

Laboratory	*Difference AB*
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
10	-
11	-
12	-
13	-
14A	-
14B	-
15	-
16	-0.120
17	-
18	-
19	-
20A	-
20B	-
21	-
22	-
23	-
24	-
25	-
26	-
27	0.000
28	-
29	-
30	-
31	-
32	-
33	0.550
35	-
36	-
37	-
38	-
39	-0.480
40	-
41	-
42	-
43	-
44	-0.600
45	-
46	-
47	-
48	0.200
49	-
50	-
51	-
52	-
53	-0.200
54	-0.032
No of labs., p	8
No of repl., n	2
d	-0.085
s^2	0.133
s	0.365
$t = \sqrt{p} \cdot (d/s)$	-0.6615
Sign. level, p(t)	0.5295

No test statistics were found to be significant

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

Laboratory	*Difference*	
	AB	
1	-	
2	-	
3	-	
4	-	
5	0.020	
6	-	
7	0.020	
8	-	
9	-	
10	0.000	
11	0.300	
12	-0.160	
13	-	
14A	-0.070	
14B	0.050	
15	-	
16	-	
17	-	
18	-	
19	-	
20A	-	
20B	-	
21	1.040	UC
22	-	
23	-	
24	-0.100	
25	-	
26	-	
27	-	
28	-	
29	-	
30	-	
31	-	
32	0.200	
33	-	
35	-	
36	0.100	
37	-	
38	-	
39	-	
40	-	

Laboratory	*Difference*
	AB
41	0.240
42	-
43	-0.270
44	-
45	-
46	-
47	-
48	-
49	-
50	-
51	0.020
52	-0.100
53	-
54	-
No of labs., p	14
No of repl., n	2
d	0.018
s^2	0.025
s	0.157
$t = \sqrt{p} \cdot (d/s)$	0.4257
Sign. level, p(t)	0.6773

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

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

Laboratory	*Difference AB*	
1	0.30	
2	-	
3	-	
4	-0.76	
5	0.60	
6	-	
7	-0.01	
8	-	
9	-	
10	0.20	
11	-0.37	
12	-	
13	-0.04	
14A	-	
14B	0.00	
15	-3.59	UC
16	-0.20	
17	0.40	
18	-0.70	
19	0.52	
20A	0.20	
20B	-	
21	-0.50	
22	0.00	
23	-	
24	0.18	
25	-	
26	-	
27	-	
28	-	
29	-	
30	-	
31	-0.55	
32	-0.30	
33	-	
35	0.00	
36	0.05	
37	0.90	
38	0.20	
39	0.20	
40	-0.20	

Laboratory	*Difference AB*
41	-0.10
42	0.20
43	-0.00
44	-
45	-
46	1.00
47	-0.43
48	-
49	-0.12
50	-
51	-
52	0.00
53	0.00
54	-1.30
No of labs., p	33
No of repl., n	2
d	-0.02
s^2	0.21
s	0.46
$t = \sqrt{p} \cdot (d/s)$	-0.2389
Sign. level, p(t)	0.8127

No test statistics were found to be significant

UC denotes a Cochran outlier

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

Laboratory	*Difference AB*	
1	0.0030	
2	0.0070	
3	0.0040	
4	0.0020	
5	-0.0010	
6	0.0090	
7	-0.0450	UC
8	0.0070	
9	0.0000	
10	0.0050	
11	0.0090	
12	0.0060	
13	0.0120	
14A	-	
14B	0.0070	
15	-	
16	0.0140	
17	-0.0190	
18	-0.0030	
19	-	
20A	-0.0030	
20B	-	
21	0.0030	
22	0.0140	
23	-0.0030	
24	0.0020	
25	0.0000	
26	-	
27	0.0080	
28	-0.0080	
29	0.0180	
30	-	
31	-0.0160	
32	-0.0100	
33	0.0120	
35	0.0490	UC
36	0.0010	
37	0.0180	
38	0.0080	
39	-0.0020	
40	0.0250	

Laboratory	*Difference AB*	
41	0.0050	
42	0.0150	
43	0.0050	
44	-0.0070	
45	0.0090	
46	0.0080	
47	0.0070	
48	0.0100	
49	-0.0000	
50	0.0040	
51	0.0010	
52	0.0000	
53	0.0030	
54	0.0060	
No of labs., p	47	
No of repl., n	2	
d	0.0041	
s^2	0.0001	
s	0.0083	
$t = \sqrt{p} \cdot (d/s)$	34.221	
Sign. level, p(t)	0.0013	**

* 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

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.

Chloride, mg/L
Control of differences within sample pairs

Laboratory	*Difference AB*	
1	-	
2	-13.0	
3	-	U
4	-19.8	UG
5	-	
6	-	
7	-	
8	-15.5	
9	-40.0	UG
10	-	
11	-6.0	
12	-	
13	3.2	
14A	-	
14B	-	
15	-	
16	-2.5	
17	0.0	
18	-	
19	-	
20A	-19.0	
20B	-	
21	-	
22	-	
23	-4.0	
24	-	
25	-	
26	-	
27	-48.0	
28	-25.0	
29	-	
30	-	
31	-	U
32	-	
33	-1.0	
35	-14.0	
36	-	
37	-	
38	-7.2	
39	-2.0	
40	0.0	

Laboratory	*Difference AB*	
41	-	
42	1.0	
43	-	
44	-4.0	
45	-5.0	
46	-	
47	-	
48	-	
49	-	
50	-9.0	
51	-	
52	-	
53	-	
54	-10.0	
No of labs., p	20	
No of repl., n	2	
d	-9.0	
s^2	137.1	
s	11.7	
$t = \sqrt{p} \cdot (d/s)$	-34.561	
Sign. level, p(t)	0.0026	**

* 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
U denotes data excluded from the data file

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.

Sulphate, mg/L
Control of differences within sample pairs

Laboratory	*Difference AB*
1	-
2	-
3	-
4	1.5
5	-
6	-
7	-
8	-
9	-
10	-
11	0.1
12	-
13	-
14A	-
14B	-
15	-
16	-1.0
17	-
18	-
19	-
20A	-3.0
20B	-
21	-
22	-
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	0.2
32	-
33	-
35	-
36	-
37	4.0
38	2.2
39	-
40	1.0

Laboratory	*Difference AB*
41	-
42	2.6
43	-
44	-6.0
45	-
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	-
54	0.0
No of labs., p	11
No of repl., n	2
d	0.1
s^2	7.7
s	2.8
$t = \sqrt{p} \cdot (d/s)$	0.1699
Sign. level, p(t)	0.8685

No test statistics were found to be significant

Total Suspended Solids, mg/L
Control of differences within sample pairs

Laboratory	*Difference AB*	
1	5.30	
2	1.10	
3	-0.90	
4	-0.50	
5	-0.40	
6	-	
7	0.30	
8	-0.30	
9	-	
10	0.10	
11	-0.50	
12	-	
13	-0.40	
14A	-	
14B	0.30	
15	-8.50	
16	-2.56	
17	0.10	
18	-	
19	-15.75	UG
20A	-	
20B	-	
21	-16.90	
22	0.00	
23	-	
24	-0.80	
25	-	
26	0.30	
27	-0.10	
28	11.10	
29	-	
30	11.10	
31	-1.90	
32	2.00	
33	-5.60	
35	1.10	
36	-0.10	
37	0.10	
38	0.80	
39	-	
40	-0.20	

Laboratory	*Difference AB*	
41	-	
42	-	
43	-1.30	
44	-1.90	
45	-	
46	-	
47	-0.10	
48	6.40	
49	0.10	
50	-3.10	UG
51	-0.50	
52	-1.20	
53	-12.50	
54	0.70	
No of labs., p	38	
No of repl., n	2	
d	-0.43	
s^2	23.82	
s	4.88	
$t = \sqrt{p} \cdot (d/s)$	-0.5404	
Sign. level, p(t)	0.5921	

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

ANNEX D CONTROL OF RECOVERY

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

Laboratory	*Sample pair AB*
1	-
2	41.30
3	37.85
4	42.85
5	-
6	22.60
7	-
8	38.10
9	32.40
10	38.15
11	-
12	43.55
13	36.40
14A	-
14B	50.00
15	45.40
16	43.80
17	37.60
18	34.25
19	-
20A	35.65
20B	38.00
21	48.95
22	-
23	41.05
24	-
25	40.15
26	43.45
27	39.60
28	37.95
29	36.40
30	25.85
31	-
32	-
33	35.00
35	36.50
36	-
37	44.05
38	-
39	-
40	-
41	43.35
42	36.95
43	48.92
44	41.10
45	-
46	45.95
47	44.55
48	42.50
49	-
50	41.25
51	38.40
52	-
53	36.55
54	41.35
No of labs., p	37
No of repl., n	2
m	39.57
s^2	31.67
s	5.63
Assigned value, μ	39
Recovery, %	101.5
$t = \sqrt{p} \cdot (m - \mu/s)$	0.6215
Sign. level, p(t)	0.5382

No test statistics were found to be significant

UC denotes a Cochran outlier

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

Laboratory	*Sample pair AB*
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
10	-
11	-
12	-
13	-
14A	-
14B	-
15	-
16	3.710
17	-
18	-
19	-
20A	-
20B	-
21	-
22	-
23	-
24	-
25	-
26	-
27	4.500
28	-
29	-
30	-
31	-
32	-
33	2.915
35	-
36	-
37	-
38	-
39	3.550
40	-
41	-
42	-
43	-
44	1.760
45	-
46	-
47	-
48	4.100
49	-
50	-
51	-
52	-
53	3.100
54	3.416
No of labs., p	8
No of repl., n	2
m	3.381
s^2	0.690
s	0.831
Assigned value, μ	3.5
Recovery, %	96.6
$t = \sqrt{p} \cdot (m - \mu/s)$	-0.4039
Sign. level, p(t)	0.6984

No test statistics were found to be significant

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

Laboratory	*Sample pair AB*	
1	-	
2	-	
3	-	
4	-	
5	4.820	
6	-	
7	4.580	
8	-	
9	-	
10	4.100	
11	4.550	
12	4.990	
13	-	
14A	4.585	
14B	4.525	
15	-	
16	-	
17	-	
18	-	
19	-	
20A	-	
20B	-	
21	3.850	UC
22	-	
23	-	
24	4.350	
25	-	
26	-	
27	-	
28	-	
29	-	
30	-	
31	-	
32	5.000	
33	-	
35	-	
36	4.280	
37	-	
38	-	
39	-	
40	-	
41	4.690	
42	-	

Laboratory	*Sample pair AB*
43	4.255
44	-
45	-
46	-
47	-
48	-
49	-
50	-
51	4.340
52	4.850
53	-
54	-
No of labs., p	14
No of repl., n	2
m	4.565
s^2	0.079
s	0.281
Assigned value, µ	4.5
Recovery, %	101.5
$t = \sqrt{p} \cdot (m - \mu/s)$	0.8711
Sign. level, p(t)	0.3995

No test statistics were found to be significant

UC denotes a Cochran outlier

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

Laboratory	*Sample pair AB*	
1	15.65	
2	-	
3	-	
4	15.92	
5	16.20	
6	-	
7	14.36	
8	-	
9	-	
10	17.10	
11	14.20	
12	-	
13	15.53	
14A	-	
14B	16.30	
15	19.65	UC
16	15.97	
17	16.90	
18	14.95	
19	17.41	
20A	15.40	
20B	-	
21	16.15	
22	16.00	
23	-	
24	15.25	
25	-	
26	-	
27	-	
28	-	
29	-	
30	-	
31	13.56	
32	16.05	
33	-	
35	19.00	
36	16.05	
37	15.75	
38	15.30	
39	15.28	
40	15.80	
41	15.55	
42	16.40	

Laboratory	*Sample pair AB*
43	15.40
44	-
45	-
46	15.40
47	14.80
48	-
49	16.06
50	-
51	-
52	15.10
53	15.50
54	17.05
No of labs., p	33
No of repl., n	2
m	15.80
s^2	1.00
s	1.00
Assigned value, μ	15.7
Recovery, %	100.6
$t = \sqrt{p} \cdot (m - \mu/s)$	0.5662
Sign. level, p(t)	0.5752

No test statistics were found to be significant

UC denotes a Cochran outlier

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

Laboratory	*Sample pair AB*	
1	0.3355	
2	0.3505	
3	0.3510	
4	0.3410	
5	0.3315	
6	0.3745	
7	0.3235	UC
8	0.3605	
9	0.3260	
10	0.3535	
11	0.3465	
12	0.3370	
13	0.3480	
14A	-	
14B	0.3425	
15	-	
16	0.3780	
17	0.3885	
18	0.3485	
19	-	
20A	0.3595	
20B	-	
21	0.3345	
22	0.3500	
23	0.3605	
24	0.3290	
25	0.3620	
26	0.3350	
27	0.3420	
28	0.3850	
29	0.3630	
30	-	
31	0.3030	
32	0.3390	
33	0.3490	
35	0.3395	UC
36	0.3165	
37	0.3480	
38	0.3540	
39	0.3460	
40	0.3765	
41	0.3345	
42	0.3555	

Laboratory	*Sample pair AB*	
43	0.3429	
44	0.3305	
45	0.3155	
46	0.3410	
47	0.3385	
48	0.2780	
49	0.3370	
50	0.3650	
51	0.3505	
52	0.3330	
53	0.3695	
54	0.3299	
No of labs., p	47	
No of repl., n	2	
m	0.3458	
s^2	0.0004	
s	0.0203	
Assigned value, µ	0.336	
Recovery, %	102.9	
$t = \sqrt{p} \cdot (m - \mu/s)$	32.967	
Sign. level, p(t)	0.0019	**

* 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 outlie

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

Laboratory	*Sample pair AB*	
1	-	
2	836.5	
3	-	U
4	688.8	UG
5	-	
6	-	
7	-	
8	883.3	
9	680.0	UG
10	-	
11	915.0	
12	-	
13	916.0	
14A	-	
14B	-	
15	-	
16	919.3	
17	978.0	
18	-	
19	-	
20A	896.5	
20B	-	
21	-	
22	-	
23	926.0	
24	-	
25	-	
26	-	
27	795.0	
28	972.5	
29	-	
30	-	
31	-	U
32	-	
33	840.5	
35	915.0	
36	-	
37	-	
38	866.8	
39	918.0	
40	928.0	
41	-	
42	937.5	

Laboratory	*Sample pair AB*
43	-
44	872.0
45	937.5
46	-
47	-
48	-
49	-
50	912.5
51	-
52	-
53	-
54	914.0
No of labs., p	20
No of repl., n	2
m	904.0
s^2	1990.7
s	44.6
Assigned value, μ	910
Recovery, %	99.3
$t = \sqrt{p} \cdot (m - \mu/s)$	-0.6024
Sign. level, p(t)	0.5540

No test statistics were found to be significant

UG denotes a Grubbs outlier

U denotes data excluded from the data file

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

Laboratory	*Sample pair AB*
1	-
2	-
3	-
4	188.6
5	-
6	-
7	-
8	-
9	-
10	-
11	186.0
12	-
13	-
14A	-
14B	-
15	-
16	177.5
17	-
18	-
19	-
20A	212.5
20B	-
21	-
22	-
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	179.9
32	-
33	-
35	-
36	-
37	178.0
38	196.6
39	-
40	167.5
41	-
42	196.7
43	-
44	132.0
45	-
46	-
47	-
48	-
49	-
50	-
51	-
52	-
53	-
54	185.0
No of labs., p	11
No of repl., n	2
m	181.8
s^2	417.8
s	20.4
Assigned value, μ	185
Recovery, %	98.3
$t = \sqrt{p} \cdot (m - \mu/s)$	-0.5121
Sign. level, p(t)	0.6197

No test statistics were found to be significant

Total Suspended Solids, mg/L
Control of recovery, average of results

Laboratory	*Sample pair AB*	
1	48.25	
2	49.85	
3	51.55	
4	48.05	
5	51.40	
6	-	
7	51.35	
8	52.65	
9	-	
10	53.55	
11	50.95	
12	-	
13	52.30	
14A	-	
14B	51.15	
15	48.75	
16	51.55	
17	51.95	
18	-	
19	39.77	UG
20A	-	
20B	-	
21	43.55	
22	51.00	
23	-	
24	52.90	
25	-	
26	50.55	
27	52.45	
28	50.55	
29	-	
30	46.55	
31	47.05	
32	52.40	
33	48.80	
35	48.95	
36	50.45	
37	51.65	
38	50.60	
39	-	
40	52.20	
41	-	
42	-	
43	52.55	
44	51.05	
45	-	
46	52.40	
47	49.15	
48	55.20	
49	50.85	
50	37.95	UG
51	50.55	
52	52.10	
53	49.85	
54	53.65	
No of labs., p	38	
No of repl., n	2	
m	50.73	
s^2	4.76	
s	2.18	
Assigned value, μ	51.2	
Recovery, %	99.1	
$t = \sqrt{p} \cdot (m - \mu/s)$	-13.154	
Sign. level, p(t)	0.1965	

No test statistics were found to be significant

UG denotes a Grubbs 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 O2	A1	4 - 15	41.9	41.5	41.7	41.9	47	6.1	8
			10 - 45	41.7	42.5	42.1				
			47 - 68	41.6	42.4	42.0				
		B1	29 - 18	36.5	35.8	36.2	35.8	39		
			55 - 39	35.5	35.5	35.5				
			58 - 63	35.7	35.9	35.8				
Total phosphorus	mg/L P	A2	7	0.453	0.452	0.453	0.454	0.407	0.075	0.071
			21	0.458	0.456	0.457				
			65	0.452	0.453	0.453				
		B2	19	0.380	0.379	0.380	0.379	0.336		
			33	0.381	0.383	0.382				
			51	0.375	0.375	0.375				
Chloride	mg/L	A2	7	923	923	923	927	950	29	40
			21	929	928	929				
			65	930	930	930				
		B2	19	898	899	899	898	910		
			33	894	896	895				
			51	899	901	900				
Sulphate	mg/L	A2	7	172.4	173.0	172.7	176.0	199.0	15.9	14.0
			21	177.6	180.0	178.8				
			65	178.0	175.2	176.6				
		B2	19	161.8	163.0	162.4	160.1	185.0		
			33	160.8	159.4	160.1				
			51	156.4	159.4	157.9				
Total suspended solids	mg/L	A3	11	66.20		66.20	66.66	66.10	14.92	14.90
			35	67.19		67.19				
			53	66.60		66.60				
		B3	14	52.11		52.11	51.75	51.20		
			42	52.61		52.61				
			51	50.52		50.52				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-1 2021
Parameter:	COD_{Cr}
Unit:	mg/L O_2
Sigma :	10,8

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2021-02-24

Sample	x(a)	x(b)	aver-age	sd	sd^2
A1-3-6	43,2	43,5	43,4	0,212	0,045
A1-17-9	43,9	43,6	43,8	0,212	0,04
A1-21-16	44,5	47,2	45,9	1,909	3,645
A1-30-21	45,1	43,4	44,3	1,202	1,445
A1-33-25	44,0	42,9	43,5	0,778	0,605
A1-40-38	44,1	44,0	44,1	0,071	0,005
A1-48-41	43,8	44,5	44,2	0,495	0,245
A1-50-44	44,0	45,5	44,8	1,061	1,125
A1-57-53	44,2	44,8	44,5	0,424	0,180
A1-66-67	44,5	44,2	44,4	0,212	0,045
A1-75-72	44,1	43,6	43,9	0,354	0,125
A1-80-82	44,6	44,2	44,4	0,283	0,080

For homogeneity

General average (x)	44,23
Sample average sd (s_x)	0,661
Within-sample sd (s_w):	0,795
Between-samples sd (ss):	0,3476
S_L in the Proficiency Test:	5,43
S_R in the Proficiency Test:	5,82

Stability test Date: 2021-03-11

Sample	x(a)	x(b)
A1-4-15	41,9	41,5
A1-10-45	41,7	42,5
A1-47-68	41,6	42,4

For stability

General average (y):	41,933333
/x-y/ =	2,2916667

Conclusions

ss =	0,348	0.3*sigma=	3,24
/x-y/ =	2,291666 7		

Analytical quality	Is s_w < 0,15*sigma **YES**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **YES**

PT: SPIL-1 2021
Parameter: TP
Unit: mg/L P

Sigma: 0,036

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2021-02-23

Sample	x(a)	x(b)	average	sd	sd^2
A2-2	0,428	0,429	0,429	0,001	0,000
A2-10	0,441	0,442	0,442	0,001	0,00
A2-17	0,444	0,445	0,445	0,001	0,000
A2-25	0,442	0,443	0,443	0,001	0,000
A2-29	0,447	0,448	0,448	0,001	0,000
A2-40	0,439	0,438	0,439	0,001	0,000
A2-45	0,431	0,432	0,432	0,001	0,000
A2-48	0,430	0,429	0,430	0,001	0,000
A2-53	0,441	0,441	0,441	0,000	0,000
A2-57	0,434	0,433	0,434	0,001	0,000
A2-71	0,435	0,435	0,435	0,000	0,000
A2-80	0,427	0,428	0,428	0,001	0,000

For homogeneity

General average (x)	0,437
Sample average sd (s_x)	0,007
Within-sample sd (s_w):	0,001
Between-samples sd (ss):	0,0067
S_L in the Proficiency Test:	0,020
S_R in the Proficiency Test:	0,021

Stability test Date: 2021-03-11

Sample	x(a)	x(b)
A2-7	0,453	0,452
A2-21	0,458	0,456
A2-65	0,452	0,453

For stability

General average (y):	0,454
/x-y/ =	0,017
s_b =	0,025

Conclusions

ss = 0,007 0.3*sigma= 0,011
/x-y/ = 0,01725

Analytical quality	Is s_w < 0,15*sigma **YES**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **No but difference is marginal**

PT:	SPIL-1 2021
Parameter:	TSS
Unit:	mg/L
Sigma:	3,6

Responsible for tests: S7MS/DHBP

Homogeneity test Date: 2021-02-24

Sample	x(a)	x(b)	average	sd	sd^2
B3-7-3	52,4		52,4		
B3-14-8	52,4		52,4		
B3-18-20	52,5		52,5		
B3-21-23	52,7		52,7		
B3-28-26	52,6		52,6		
B3-30-31	51,8		51,8		
B3-39-39	52,2		52,2		
B3-44-48	52,6		52,6		
B3-48-57	52,3		52,3		
B3-53-62	52,7		52,7		
B3-57-66	52,6		52,6		
B3-61-70	52,7		52,7		

For homogeneity

General average (x)	52,5
Sample average sd (s_x)	0,266
Within-sample sd (s_w):	
Between-samples sd (ss):	0,266
S_L in the Proficiency Test:	-
S_R in the Proficiency Test:	3,45

Stability test Date: 2021-03-11

Sample	x(a)	x(b)
B3-11-8	52,11	
B3-35-24	52,61	
B3-53-60	50,52	

For stability

General average (y):	51,746667
/x-y/ =	0,7304966

Conclusions

ss =	0,27	0.3*sigma=	1,08
/x-y/ =	0,7304966		
Analytical quality	ls s_w < 0,15*sigma **No data**		
Homogeneity:	ls ss < 0.3*sigma? **YES**		
Stability:	/x-y/ < 0.3*sigma? **YES**		