DANAK
PT Reg.nr. 534
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Proficiency test SPIL-3 (2020)

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

Quality Documentation
November 2020

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Project	Project No
Proficiency test SPIL-3 (2020)	20405-03
Authors Rikke Mikkelsen	Date 2020-11-01
	Approved by Peter Rerup

1.	Quality Documentation Report	FYE3	DPRE	2020-11-23	
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	
Eurofins:	Rikke Mikkelsen, FYE3 Peter Rerup, DPRE Available on web: www.eurofins.dk/

CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater was conducted on 10 September 2020. 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 19 October 2020.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 45 laboratories from Denmark and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 24 September 2020. 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.

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	315	4.3	20
5 day biochemical oxygen demand (w. ATU)	BOD_5 w. ATU	mg/L O_2	50-500	*)	-	-
7 day biochemical oxygen demand (w. ATU)	BOD_7 w. ATU	mg/L O_2	50-500	167	8.4	16
Non-volantile/Total organic carbon	NVOC/TOC	mg/L C	50-800	102	4.4	8
Total phosphorus	TP	mg/L P	5-10	6.1	0.11	1.1
Chloride	Cl	mg/L	50-700	170	5.4	15
Sulphate	SO_4	mg/L	20-200	55	2.6	14
Total suspended solids	TSS	mg/L	100-500	196	3.0	23

*) Only four laboratories reported results for BOD_5 w. ATU using standardized methods and therefore BOD_7 w. ATU was 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. 1, 2, 5 (TP) or method no. 1, 2 (TSS), which are the methods required by the Danish EPA /5/. Assigned values for BOD are based upon standardised methods (method no. 1 - 4). Only 3 laboratories reported results for COD using the methods required by the Danish EPA /5/ the assigned value is the consensus value based upon the median for all methods. A list of method identification numbers is found in the report to participants' /1/. Assigned values for 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 of the parameters.

The test revealed a significant difference between the two for COD_{Cr} 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.

The difference for TP was significant and could not be attributed to specific methods or other conditions. Furthermore, the difference had a significant influence on the general

quality of analyses. It was therefore decided to change the spike value form calculated value based on sample preparation to a value based on consensus between participating laboratories, i.e. the difference between the medians for sample A1 and B1.

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 103.6 %. 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. 41, 42, 42a, 43, 43a, 48, 73 and 9 and now showed no significant difference. Furthermore, the results of control measurements at the laboratory for reference materials and proficiency tests 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:

TP	Combined homogeneity and stability test
SS	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.

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 BOD_5 it was not possible to set an assigned value because too few laboratories have reported a result. The result for BOD_7 was used as an indicative value, but care must be taken when evaluating the BOD_5 results.

For COD_{Cr} and TP the participants could not recover the spiked value. For COD_{Cr} 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. However, for TP the control measurements at the laboratory for reference materials and proficiency tests at Eurofins' confirmed the difference and no error in preparation could be found. It is recommended to evaluate deviations from the assigned value with caution.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-3 (2020)*, Report to participants, october 2020.

/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. 1146 on *quality criteria for environmental measurements,* 24 October 2017 (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
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
Melby Renseanlæg	Liseleje	Denmark
NK-Forsyning A/S	Næstved	Denmark
Nyborg Forsyning & Service	Nyborg	Denmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (5 participants)	Slagelse	Denmark
Svendborg Spildevand A/S, Egsmade/Svenborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
AB Lennart Månsson International	Helsingborg	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Holmen Paper AB, Bravikens Pappersbruk	Norrköping	Sweden
Iggesund Paperboard AB, Iggesunds Bruk, Cell- och Miljölab	Iggesund	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaförbundet	Lidingö	Sweden
Laboratoriet Fillanverket, MittSverige Vatten och Avfall AB	Sundsvall	Sweden
Laboratoriet vid Smedjeholms avolppsreningsverk	Falkenberg	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun, Tekniska Förvaltningen, Vatten och Avfall	Motala	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Nyköpings kommun Vattenlaboratoriet	Nyköping	Sweden
Roslagsvatten AB	Åkersberga	Sweden

Laboratory	Town	Country
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Tekniska Verken i Linköping AB (publ)	Linköping	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	15.00 g 15.00 g	D-glucose L-glutamic acid milli-Q water up to 13000 g	COD_{Cr}: 2.360 g/kg BOD: 1.615 g/kg NVOC: 0.932 g/kg
Concentrate B1	22.20 g 22.20 g	D-glucose L-glutamic acid milli-Q water up to 24000 g	COD_{Cr}: 1.892 g/kg BOD: 1.295 g/kg NVOC: 0.747 g/kg
Stock TP	1.500 g	Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 0.1518 g/kg
Stock Cl	10.002 g	Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.067 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	15.010 g	Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.100 g/kg

Sample	Sample prepared from	COD_{Cr} mg/L O_2	BOD (w. ATU) mg/L O_2	NVOC mg/L C	TP mg/L P	Cl mg/L	SO_4 mg/L	TSS mg/L
A1-COD/BOD/NVOC	At the laboratory 21.00 mL of concentrate A1 is diluted up to 500.0 mL with filtered water from Vejen sewage treatment plant	a + 99.1	b + 67.8	c + 39.2				
B1-COD/BOD/NVOC	At the laboratory 21.00 mL of concentrate B1 is diluted up to 500.0 mL with filtered water from Vejen sewage treatment plant	a + 79.4	b + 54.4	c + 31.4				
A2	300.0 g stock TP 400.0 g stock Cl 600.0 g stock SO_4 Filtered water from Vejen sewage treatment plant up to 70.0 kg				d + 0.650	e + 34.7	f + 29.0	
B2	200.0 g stock TP 200.0 g stock Cl 150.0 g stock SO_4 Sample A2 up to 35.0 kg				0.987 · * (d+0.650) + 0.867	0.987 * (e + 34.7) + 17.3	0.987 * (f + 29.0) + 14.5	
A3	At the laboratory 250.0 mL of filtered water from Vejen sewage treatment plant is added to 3.0 mL stock TSS							g + 178
B3	At the laboratory 250.0 mL of filtered water from Vejen sewage treatment plant is added to 3.4 mL stock TSS							g + 201

ANNEX C CONTROL OF SPIKE VALUES

COD_{Cr}, mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-1.5	
3	-2.0	
4	0.0	
5	-6.0	
6	-8.0	
7	-4.0	
8	-	
9	-2.0	
10	4.0	
11	-	
12	-	
13	2.0	UG
14	5.0	
15	-	
16	-7.0	
17	4.0	
18	0.0	
19	-2.0	
20	-	
21	-	
22	-6.0	
23A	4.0	
23B	-1.0	
24	0.0	
25	15.0	
26	-4.5	
27	-	
28	42.0	UC
29	-6.0	UG
30	-9.0	
31	-5.0	
32	-1.0	
33	-7.0	
34	-5.0	
35	-	
36	-4.0	
37	-	
38	-3.0	
39	-	
40A	-	
40B	-	
41	-1.0	
42	-13.0	
43	-	
44	-2.0	
45	23.0	UC
46	-	
47	0.0	
48	-3.0	
49	-	

No of labs., p	31	
No of repl., n	2	
d	-2.1	
s^2	26.2	
s	5.1	
$t = \sqrt{p} \cdot (d/s)$	-2.2790	
Sign. level, p(t)	0.0299	*

* 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.

BOD_5, mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	4.50
5	-
6	-
7	-
8	-
9	-
10	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-
18	5.30
19	-
20	-
21	-
22	-
23A	-
23B	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-30.90
35	-
36	-
37	-
38	-
39	-
40A	-
40B	-
41	-35.00
42	-
43	-
44	-
45	-
46	-
47	-
48	-
49	-

No of labs., p	4
No of repl., n	2
d	-14.02
s^2	480.45
s	21.92
$t = \sqrt{p} \cdot (d/s)$	-1.2797
Sign. level, p(t)	0.2906

No test statistics were found to be significant

BOD_7, mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8	-14.0
9	0.0
10	-
11	-
12	-
13	-
14	-
15	-9.0
16	-
17	-
18	-
19	4.0
20	-5.2
21	-
22	-
23A	-
23B	-
24	-
25	-
26	-5.5
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	14.0
36	-
37	2.0
38	-
39	-
40A	0.0
40B	-
41	-
42	-
43	16.1
44	-
45	-
46	-2.0
47	-
48	-
49	-4.7

No of labs., p	12
No of repl., n	2
d	-0.4
s^2	75.8
s	8.7
$t = \sqrt{p} \cdot (d/s)$	-0.1426
Sign. level, p(t)	0.8892

No test statistics were found to be significant

NVOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	
1	4.80	
2	-3.00	
3	-	
4	-	
5	-0.80	
6	-	
7	10.68	UC
8	-2.40	
9	-	
10	-	
11	-1.30	
12	0.29	
13	-	
14	-	
15	-2.60	
16	0.00	
17	-	
18	-1.00	
19	-1.00	
20	-2.70	
21	-1.19	
22	-	
23A	-0.70	
23B	-	
24	-	
25	-	
26	-1.00	
27	1.70	
28	-	
29	-	
30	-2.00	
31	2.10	
32	-2.30	UG
33	-	
34	-	
35	2.00	
36	-	
37	-1.40	
38	-	
39	-	
40A	-1.00	
40B	-	
41	-	
42	-	
43	-0.60	
44	-	
45	-	
46	1.00	
47	0.00	
48	-	
49	-3.00	

No of labs., p	24
No of repl., n	2
d	-0.58
s^2	3.47
s	1.86
$t = \sqrt{p} \cdot (d/s)$	-1.5118
Sign. level, p(t)	0.1442

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

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

Laboratory	Difference AB	
1	0.200	
2	3.890	UC
3	-	
4	-0.090	
5	-0.270	
6	-0.030	
7	-0.270	
8	-0.010	
9	-0.040	
10	0.010	
11	0.670	
12	0.090	
13	0.060	
14	0.120	
15	-0.140	
16	-0.040	
17	-0.150	
18	0.023	
19	-0.030	
20	-0.000	
21	0.160	
22	-0.270	
23A	-0.010	
23B	-	
24	-0.010	
25	-0.050	
26	0.072	
27	0.100	
28	0.450	
29	-0.240	
30	-0.240	
31	-	
32	0.032	
33	0.320	
34	0.840	UC
35	0.120	
36	-0.450	
37	-0.380	
38	-1.500	UC
39	-1.474	UC
40A	-0.180	
40B	-0.060	
41	0.060	
42	0.010	
43	-0.290	
44	-0.110	
45	-0.060	
46	0.150	
47	0.230	
48	0.120	
49	-0.020	

No of labs., p	44
No of repl., n	2
d	-0.010
s^2	0.043
s	0.207
$t = \sqrt{p} \cdot (d/s)$	-0.3228
Sign. level, p(t)	0.7484

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

Chloride, mg/L
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-1.5	
3	-	
4	5.0	
5	-	
6	-13.0	
7	-1.4	
8	-	
9	-	
10	7.0	
11	-	
12	0.9	
13	-7.0	
14	16.0	UG
15	-1.0	
16	-	
17	-17.0	
18	0.8	
19	-	
20	3.4	
21	-2.0	
22	-	
23A	0.0	
23B	-	
24	-9.0	
25	14.0	
26	-	
27	-0.8	
28	-1.0	
29	15.0	
30	-	
31	-	
32	-3.0	
33	-3.0	
34	-46.0	UC
35	-	
36	2.0	
37	-	
38	9.0	
39	5.0	
40A	1.0	
40B	-	
41	-4.0	
42	-	
43	-	
44	4.0	
45	-3.0	
46	-	
47	-	
48	-13.0	
49	-	

No of labs., p	28
No of repl., n	2
d	-0.5
s^2	53.3
s	7.3
$t = \sqrt{p} \cdot (d/s)$	-0.3263
Sign. level, p(t)	0.7467

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

Sulphate, mg/L

Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-8.30
3	-
4	5.90
5	-
6	-
7	-
8	-
9	-
10	-
11	-
12	1.50
13	-
14	-
15	-
16	-
17	-
18	-1.13
19	-
20	-
21	-
22	-
23A	-27.00
23B	-
24	0.20
25	0.10
26	-
27	-0.80
28	1.30
29	-
30	-
31	-
32	9.10
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40A	30.80
40B	-
41	5.10
42	-
43	-
44	-
45	-
46	-
47	1.60
48	-
49	-

No of labs., p	13
No of repl., n	2
d	1.41
s^2	156.06
s	12.49
$t = \sqrt{p} \cdot (d/s)$	0.4080
Sign. level, p(t)	0.6905

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	1.0	
2	-	
3	-18.3	UC
4	0.0	
5	3.0	
6	-	
7	-5.0	
8	-1.0	
9	5.0	
10	-	
11	-	
12	-	
13	3.0	
14	3.0	
15	-5.0	
16	-2.0	
17	-	
18	-2.2	
19	-5.0	
20	-7.7	
21	-14.0	
22	-	
23A	-	
23B	-	
24	37.0	UC
25	-5.0	
26	-6.4	
27	-6.5	
28	0.6	
29	1.4	
30	-	
31	-4.0	
32	-3.0	
33	-	
34	2.0	
35	6.0	
36	66.2	UC
37	1.3	
38	43.0	UC
39	-0.2	
40A	-3.0	
40B	-	
41	4.0	
42	-	
43	3.8	
44	29.0	UC
45	-	
46	-3.0	
47	0.0	
48	-3.0	
49	-3.4	

No of labs., p	32
No of repl., n	2
d	-1.4
s^2	18.6
s	4.3
$t = \sqrt{p} \cdot (d/s)$	-1.8590
Sign. level, p(t)	0.0725

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	-	
2	319.3	
3	319.0	
4	316.0	
5	286.0	
6	294.0	
7	297.0	
8	-	
9	312.0	
10	334.0	
11	-	
12	-	
13	208.0	UG
14	306.5	
15	-	
16	298.5	
17	323.0	
18	332.0	
19	312.0	
20	-	
21	-	
22	319.0	
23A	328.0	
23B	315.5	
24	309.0	
25	312.5	
26	315.8	
27	-	
28	348.0	UC
29	210.0	UG
30	311.5	
31	306.5	
32	328.5	
33	295.5	
34	306.5	
35	-	
36	316.0	
37	-	
38	306.5	
39	-	
40A	-	
40B	-	
41	309.5	
42	331.5	
43	-	
44	316.0	
45	344.5	UC
46	-	
47	321.0	
48	294.5	
49	-	

No of labs., p	31
No of repl., n	2
m	312.7
s^2	144.3
s	12.0
Assigned value, μ	315
Recovery, %	99.3
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.0841
Sign. level, p(t)	0.2870

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

BOD_5, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	134.25
5	-
6	-
7	-
8	-
9	-
10	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-
18	162.25
19	-
20	-
21	-
22	-
23A	-
23B	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	180.45
35	-
36	-
37	-
38	-
39	-
40A	-
40B	-
41	147.50
42	-
43	-
44	-
45	-
46	-
47	-
48	-
49	-

No of labs., p	4
No of repl., n	2
m	156.11
s^2	394.04
s	19.85
Assigned value, μ	168
Recovery, %	92.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.1977
Sign. level, p(t)	0.3170

No test statistics were found to be significant

BOD_7, mg/L O_2
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8	153.0
9	167.0
10	-
11	-
12	-
13	-
14	-
15	170.5
16	-
17	-
18	-
19	164.0
20	174.9
21	-
22	-
23A	-
23B	-
24	-
25	-
26	167.3
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	165.0
36	-
37	175.0
38	-
39	-
40A	196.0
40B	-
41	-
42	-
43	160.6
44	-
45	-
46	155.0
47	-
48	-
49	153.6

No of labs., p	12
No of repl., n	2
m	166.8
s^2	141.4
s	11.9
Assigned value, μ	167
Recovery, %	99.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.0522
Sign. level, p(t)	0.9593

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	83.60	
2	103.50	
3	-	
4	-	
5	88.00	
6	-	
7	108.30	UC
8	107.70	
9	-	
10	-	
11	94.25	
12	91.02	
13	-	
14	-	
15	109.00	
16	102.00	
17	-	
18	86.00	
19	103.50	
20	94.05	
21	95.00	
22	-	
23A	78.95	
23B	-	
24	-	
25	-	
26	106.50	
27	103.55	
28	-	
29	-	
30	104.00	
31	102.15	
32	174.15	UG
33	-	
34	-	
35	103.00	
36	-	
37	103.10	
38	-	
39	-	
40A	104.50	
40B	-	
41	-	
42	-	
43	108.20	
44	-	
45	-	
46	103.50	
47	101.00	
48	-	
49	106.50	

No of labs., p	24
No of repl., n	2
m	99.27
s^2	70.41
s	8.39
Assigned value, μ	102
Recovery, %	97.3
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.5917
Sign. level, p(t)	0.1251

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

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

Laboratory	Sample pair AB	
1	5.950	
2	4.465	UC
3	-	
4	6.375	
5	6.395	
6	6.565	
7	6.115	
8	6.095	
9	6.150	
10	6.705	
11	5.655	
12	6.005	
13	6.500	
14	6.430	
15	6.310	
16	6.650	
17	6.765	
18	5.990	
19	6.265	
20	6.220	
21	5.780	
22	6.445	
23A	6.265	
23B	-	
24	6.635	
25	6.145	
26	6.111	
27	6.260	
28	6.085	
29	6.230	
30	6.480	
31	-	
32	5.989	
33	6.510	
34	6.910	UC
35	6.670	
36	6.755	
37	6.220	
38	20.550	UC
39	5.456	UC
40A	7.140	
40B	6.060	
41	6.500	
42	6.615	
43	6.355	
44	6.595	
45	6.340	
46	6.025	
47	6.075	
48	6.270	
49	6.310	

No of labs., p	44	
No of repl., n	2	
m	6.318	
s^2	0.084	
s	0.290	
Assigned value, μ	6.1	
Recovery, %	103.6	
$t = \sqrt{p} \cdot (m-\mu)/s$	4.9910	
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

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

Laboratory	Sample pair AB	
1	-	
2	173.3	
3	-	
4	136.5	
5	-	
6	157.5	
7	178.9	
8	-	
9	-	
10	157.5	
11	-	
12	167.2	
13	194.5	
14	681.0	UG
15	165.5	
16	-	
17	172.5	
18	169.9	
19	-	
20	172.1	
21	172.7	
22	-	
23A	154.0	
23B	-	
24	190.5	
25	175.0	
26	-	
27	153.4	
28	159.5	
29	149.5	
30	-	
31	-	
32	160.5	
33	181.5	
34	166.0	UC
35	-	
36	179.0	
37	-	
38	191.5	
39	167.5	
40A	169.8	
40B	-	
41	188.0	
42	-	
43	-	
44	179.0	
45	176.5	
46	-	
47	-	
48	143.5	
49	-	

No of labs., p	28
No of repl., n	2
m	169.2
s^2	206.7
s	14.4
Assigned value, μ	170
Recovery, %	99.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.3060
Sign. level, p(t)	0.7620

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

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

Laboratory	Sample pair AB
1	-
2	58.75
3	-
4	52.45
5	-
6	-
7	-
8	-
9	-
10	-
11	-
12	51.68
13	-
14	-
15	-
16	-
17	-
18	56.78
19	-
20	-
21	-
22	-
23A	48.50
23B	-
24	57.60
25	57.05
26	-
27	54.60
28	49.75
29	-
30	-
31	-
32	54.85
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40A	59.30
40B	-
41	50.05
42	-
43	-
44	-
45	-
46	-
47	56.10
48	-
49	-

No of labs., p	13
No of repl., n	2
m	54.42
s^2	12.96
s	3.60
Assigned value, μ	55
Recovery, %	98.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.5810
Sign. level, p(t)	0.5720

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	179.5	
2	-	
3	183.9	UC
4	195.0	
5	188.0	
6	-	
7	203.3	
8	196.5	
9	196.5	
10	-	
11	-	
12	-	
13	170.5	
14	208.5	
15	193.5	
16	193.0	
17	-	
18	196.0	
19	214.5	
20	199.6	
21	186.0	
22	-	
23A	-	
23B	-	
24	191.5	UC
25	195.5	
26	225.5	
27	221.3	
28	202.1	
29	218.5	
30	-	
31	201.0	
32	189.5	
33	-	
34	188.0	
35	204.0	
36	111.7	UC
37	195.8	
38	178.5	UC
39	191.3	
40A	204.5	
40B	-	
41	188.0	
42	-	
43	192.9	
44	1027.5	UC
45	-	
46	203.5	
47	192.0	
48	195.5	
49	194.9	

No of labs., p	32
No of repl., n	2
m	197.6
s^2	131.3
s	11.5
Assigned value, μ	196
Recovery, %	100.8
$t = \sqrt{p} \cdot (m-\mu)/s$	0.8045
Sign. level, p(t)	0.4273

No test statistics were found to be significant
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	mg/L O2	A1	8-3	308	304	306	317	335	12	20
			45-32	318	316	317				
			64-72	328	326	327				
		B1	11-3	292	292	292	305	315		
			27-32	304	300	302				
			72-72	320	320	320				
Total phosphorus	mg/L P	A2	2	6,7	6,6	6,6	6,5	6,1	1,0	1,1
			34	6,5	6,5	6,5				
			58	6,4	6,4	6,4				
		B2	5	7,6	7,6	7,6	7,6	7,2		
			36	7,6	7,6	7,6				
			54	7,6	7,6	7,6				
Chloride	mg/L	A2	2	166	166	166	161	170	17	15
			34	158	158	158				
			58	158	159	159				
		B2	5	175	176	176	178	185		
			36	176	177	177				
			54	181	180	181				
Sulphate	mg/L	A2	2	44	44	44	44	55	23	14
			34	46	46	46				
			58	43	43	43				
		B2	5	68	66	67	67	69		
			36	67	67	67				
			54	66	66	66				
Total suspended solids	mg/L	A3	2-3	206		206	203	196	28	23
			30-32	201		201				
			51-72	202		202				
		B3	4-3	231		231	231	219		
			31-32	233		233				
			56-72	229		229				

ANNEX F HOMOGENEITY AND STABILITY

PT: SPIL-3

Parameter: TP
Unit: mg/L P
Sigma: 0,4

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2020-08-25

Sample	x(a)	x(b)	average	sd	sd^2
A2-3	6,4	6,43	6,4	0,000	0,000
A2-11	6,4	6,37	6,4	0,007	0,000
A2-16	6,5	6,49	6,5	0,000	0,000
A2-25	6,4	6,43	6,4	0,021	0,000
A2-32	6,6	6,6	6,6	0,000	0,000
A2-40	6,5	6,5	6,5	0,007	0,000
A2-45	6,4	6,42	6,4	0,000	0,000
A2-51	6,4	6,39	6,4	0,014	0,000
A2-56	6,4	6,41	6,4	0,042	0,002
A2-62	6,5	6,48	6,5	0,007	0,000
A2-67	6,4	6,43	6,4	0,007	0,000
A2-74	6,4	6,42	6,4	0,000	0,000

For homogeneity

General average (x)	6,4
Sample average sd (s_x)	0,063
Within-sample sd (s_w):	0,015
Between-samples sd (ss):	0,062
S_L in the Proficiency Test:	0,271
S_R in the Proficiency Test:	0,308

Stability test Date: 2020-09-10

Sample	x(a)	x(b)
A2-2	6,65	6,65
A2-34	6,52	6,52
A2-58	6,41	6,4

For stability

General average (y):	6,525
/x-y/ =	0,0795833

Conclusions

ss =0,06 0.3*sigma=0,11
/x-y/ =0,0795833

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-3
Parameter:	TSS
Unit:	mg/L
Sigma:	12,439

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2020-08-25

Sample	x(a)	x(b)	average	sd	sd^2
B3-2-7*)	216,65		216,7		
B3-12-11	233,62		233,6		
B3-16-12	230,45		230,4		
B3-20-23	233,46		233,5		
B3-22-26	228,28		228,3		
B3-30-35	230,27		230,3		
B3-35-42	223,00		223,0		
B3-43-48	228,93		228,9		
B3-47-51	229,50		229,5		
B3-52-62	235,90		235,9		
B3-58-68	231,27		231,3		
B3-61-74	229,21		229,2		

For homogeneity

General average (x)	230,35
Sample average sd (s_x)	3,381
Within-sample sd (s_w):	
Between-samples sd (ss):	3,3815
S_L in the Proficiency Test:	11,3
S_R in the Proficiency Test:	11,7

Stability test Date: 2020-09-10

Sample	x(a)	x(b)
B3-4-3	231,37	
B3-31-32	232,88	
B3-56-72	228,58	

For stability

General average (y):	230,94333
/x-y/ =	0,5895802

Conclusions

ss =	3,381	0.3*sigma=	3,73
/x-y/ =	0,5895802		
Analytical quality	Is s_w < 0,15*sigma **No data**		
Homogeneity:	Is ss < 0.3*sigma? **YES**		
Stability:	/x-y/ < 0.3*sigma? **YES**		

*) The result for sample B3-2-7 has been excluded due to error doing analysis.