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Proficiency test SPIL-1 (2020)

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

Quality Documentation
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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 12 March 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 16 April 2020.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 58 laboratories from Denmark and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 26 March 2020. All participants except laboratory no. 2,10, 19, 32, 37, 42, 44, 52 and 58 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" (1994) /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
COD_{Cr}	COD_{Cr}	mg/L O_2	5 - 75	32	1.3	0
BOD5 (w. ATU)	BOD_5 w. ATU	mg/L O_2	2 - 6	*)	-	-
BOD7 (w. ATU)	BOD_7 w. ATU	mg/L O_2	2 - 6	3.9	0,20	0
NVOC/TOC	NVOC/TOC	mg/L C	2 - 30	12.9	0.55	0
Total phosphorus	TP	mg/L P	0,2 – 2	1.53	0.029	0.30
Chloride	Cl	mg/L	50 – 700	158	6.4	9
Sulphate	SO_4	mg/L	20 - 200	61	5.7	8
Total suspended solids	TSS	mg/L	20 - 100	29.0	0.32	5.0

*) Only two laboratories reported results for BOD5 w. ATU using a standardised method and therefore no assigned value is given.

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. 76, 77, 77A (COD_{Cr}), 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/. Assigned values for BOD_7 are based upon standardised methods (method no. 1 - 4). 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. For BOD_5 it was not possible to set an assigned value because only two laboratories had used a standardised method.

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 revealed a significant difference between the two for TP. The difference could be attributed to influence from laboratories using methods other than the one prescribed by the Danish EPA. The test was repeated after exclusion of the results for all methods except methods no. 2 and now showed no significant difference. The spike value is therefore kept unchanged.

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 102,5 %. 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 all methods except methods no. 2 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
P	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.

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 used a standardised method.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-1 (2020)*, Report to participants, April 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*, 1994.

/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 and Food, regulation no. 1071 on *quality criteria for environmental measurements,* 30 October 2019 (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
CP Kelco, QC Analyselab (3 participants)	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
Melby Renseanlæg	Liseleje	Denmark
NK-Forsyning A/S	Næstved	Denmark
Nyborg Forsyning & Service	Nyborg	Denmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	Denmark
RGS Nordic A/S	Skælskør	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (5 participants)	Slagelse	Denmark
Spildevandslaboratoriet (2 participants)	Esbjerg	Denmark
Svendborg Spildevand A/S, Egsmade/Svenborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
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
Holmen Paper AB, Bravikens Pappersbruk	Norrköping	Sweden
Iggesund Paperboard AB, Iggesunds Bruk, Cell- och Miljölab	Iggesund	Sweden
INOVYN Sweden AB	Stenungsund	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Käppalaförbundet	Lidingö	Sweden

Laboratory	Town	Country
Kristianstad Kommun	Kristianstad	Sweden
Laboratoriet Fillanverket, MittSweden Vatten och Avfall AB	Sundsvall	Sweden
Laboratoriet vid Smedjeholms avolppsreningsverk	Falkenberg	Sweden
Ljungby Kommun, Avloppsreningsverket	Ljungby	Sweden
Motala Kommun, Tekniska Förvaltningen, Vatten och Avfall	Motala	Sweden
Nordic Sugar, Örtofta Sockerbruk	Eslöv	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Perstorp Oxo AB	Ödsmål	Sweden
Preem AB Göteborg	Göteborg	Sweden
Roslagsvatten AB	Åkersberga	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
St1 Refinery AB	Göteborg	Sweden
Uddebo Laboratorium	Luleå	Sweden
VALAB, Vatten och Avloppslaboratoriet, VAL AB	Norrtälje	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Vattenfall Heat Uppsala, Kemilaboratoriet	Uppsala	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**		**Concentration**
Concentrate A1 BOD	22.2 g 22.2 g	D-glucose L-glutamic acid milli-Q water up to 24000 g	BOD: 1.295 g/kg
Concentrate B1 BOD	22.2 g 22.2 g	D-glucose L-glutamic acid milli-Q water up to 24000 g	BOD: 1.295 g/kg
Concentrate A1 COD/NVOC	22.2 g 22.2 g	D-glucose L-glutamic acid milli-Q water up to 24000 g	COD_{Cr}: 1.892 g/kg NVOC: 0.747 g/kg
Concentrate B1 COD/NVOC	22.2 g 22.2 g	D-glucose L-glutamic acid milli-Q water up to 24000 g	COD_{Cr}: 1.892 g/kg NVOC: 0.747 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	10.001 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	10.000 g	Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 10.000 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 2.00 mL of concentrate A1 is diluted up to 200.0 mL with filtered water from Holsted sewage treatment plant	a + 40.9	b + 12.5					
B1-COD/NVOC	At the laboratory 2.00 mL of concentrate B1 is diluted up to 200.0 mL with filtered water from Holsted sewage treatment plant	a + 40.9	b + 12.5					
A1-BOD	At the laboratory 2.00 mL of concentrate A1 is diluted up to 1000.0 mL with filtered water from Holsted sewage treatment plant			c + 4.59				
B1-BOD	At the laboratory 2.00 mL of concentrate B1 is diluted up to 1000.0 mL with filtered water from Holsted sewage treatment plant			c + 4.59				
A2	75.0 g stock TP 80.0 g stock Cl 100.0 g stock SO_4 Sample B2 up to 40.0 kg				0.994 · (d+0.542) + 0.285	0.994 · (e + 78.0) + 12.1	0.994 · (f + 24.2) + 8.45	
B2	250.0 g stock TP 900.0 g stock Cl 500.0 g stock SO_4 Filtered water from Holsted sewage treatment plant up to 70.0 kg				d + 0.542	e + 78.0	f + 24.2	
A3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 3.0 mL stock TSS							g + 29.9
B3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 3.5 mL stock TSS							g + 34.9

ANNEX C CONTROL OF SPIKE VALUES

COD, mg/L O_2
Control of differences within sample pairs

Laboratory	Difference AB	
1	0.30	
3	-0.50	
4	-	
5	-	
6	-0.60	
7	-0.20	
8	-2.50	
9	-2.65	
11	0.90	
12	-	
13	-	
14	-	
15	2.30	
16	2.90	
17	-	
18	0.00	
20	-0.50	
21	-	
22	-	
23	-0.75	
24	0.30	
25	-	
26	7.30	UC
27	-	
28	-0.10	
29	-0.40	
30	0.20	
31	-	
33	-	
34	0.80	
35	2.00	
36	-0.60	
38	1.90	
39	3.10	
40	5.30	
41	-	
43	-0.40	
45	-	
46	-	
47	-1.00	
48	-0.70	
49	1.80	
50	-	
51	2.20	
53	-	
54	0.50	
55	-	
56	-3.20	
57	-1.50	
58	0.60	

Laboratory	Difference AB
No of labs., p	31
No of repl., n	2
d	0.31
s^2	3.20
s	1.79
$t = \sqrt{p} \cdot (d/s)$	0.9545
Sign. level, p(t)	0.3475

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

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

Laboratory	Difference AB	
1	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
11	-	
12	-	
13	-0.05	
14	-	
15	-	
16	-	
17	-	
18	-	
20	4.00	UC
21	-	
22	-	
23	-	
24	-	
25	-	
26	0.20	
27	-	
28	-0.10	
29	-1.48	
30	-1.00	
31	-	
33	-	
34	-	
35	-	
36	-	
38	-	
39	-	
40	-	
41	-0.30	
43	0.66	
45	-	
46	-	
47	-	
48	-	
49	-	
50	-	
51	-0.10	
53	-	
54	-	
55	-	
56	-	
57	-0.10	
58	-	

Laboratory	Difference AB
No of labs., p	9
No of repl., n	2
d	-0.25
s^2	0.40
s	0.63
$t = \sqrt{p} \cdot (d/s)$	-1.1911
Sign. level, p(t)	0.2678

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

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

Laboratory	Difference AB
1	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
11	0.190
12	-0.100
13	-
14	-
15	-
16	-
17	-
18	-
20	-
21	-
22	0.110
23	-
24	-
25	0.070
26	-
27	-
28	-
29	-
30	-
31	-
33	-
34	-
35	0.000
36	0.080
38	-
39	-
40	-
41	-
43	-
45	-0.058
46	-
47	-
48	-
49	-1.010
50	-
51	-
53	0.390
54	0.100
55	0.530
56	-
57	-
58	-

Laboratory	Difference AB
No of labs., p	11
No of repl., n	2
d	0.027
s^2	0.153
s	0.391
$t = \sqrt{p} \cdot (d/s)$	0.2330
Sign. level, p(t)	0.8205

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	-	
3	-	
4	-	
5	-	
6	1.30	
7	-	
8	-	
9	-0.09	
11	1.76	
12	-0.40	
13	-0.22	
14	-0.49	
15	0.20	
16	-	
17	-	
18	0.53	
20	-	
21	0.20	UG
22	-0.20	
23	-	
24	-	
25	-0.91	
26	-	
27	-	
28	0.10	
29	-	
30	0.00	
31	0.31	
33	-0.40	
34	-	
35	0.20	
36	0.10	
38	0.20	
39	-	
40	0.84	
41	0.10	
43	-	
45	0.11	
46	-1.22	UG
47	0.10	
48	-0.25	
49	-0.38	
50	-	
51	-	
53	0.50	
54	-	
55	-	
56	-	
57	0.01	
58	-	

Laboratory	Difference AB
No of labs., p	25
No of repl., n	2
d	0.12
s^2	0.32
s	0.56
$t = \sqrt{p} \cdot (d/s)$	1.0720
Sign. level, p(t)	0.2944

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

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

Laboratory	Difference AB
1	0.018
3	-0.010
4	-0.124
5	-
6	0.100
7	-0.170
8	0.028
9	0.013
11	0.020
12	0.010
13	-0.020
14	-
15	0.020
16	0.000
17	-0.020
18	0.024
20	-0.020
21	-0.020
22	-0.040
23	-0.050
24	-0.180
25	0.010
26	-0.130
27	-0.050
28	0.000
29	0.010
30	0.040
31	-0.040
33	-0.020
34	-0.130
35	0.060
36	-0.006
38	-0.000
39	-0.031
40	-
41	-
43	-0.035
45	-0.025
46	-0.050
47	-0.030
48	0.002
49	0.020
50	-
51	-0.000
53	0.010
54	-0.030
55	0.040
56	-0.130
57	-0.022
58	-0.180

Laboratory	Difference AB
No of labs., p	45
No of repl., n	2
d	-0.025
s^2	0.004
s	0.062
$t = \sqrt{p} \cdot (d/s)$	-2.7358
Sign. level, p(t)	0.0089 **

* 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)

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	-	
3	27.0	UC
4	2.9	
5	-	
6	-	
7	-	
8	-2.0	
9	-45.1	UC
11	-	
12	1.8	
13	-10.0	
14	-	
15	-	
16	-	
17	2.0	
18	-	
20	-1.0	
21	-4.2	
22	-	
23	5.0	
24	-4.0	
25	-	
26	8.0	UG
27	1.0	
28	-165.3	UC
29	0.0	
30	6.0	
31	-	
33	-	
34	0.0	
35	-	
36	-	
38	-	
39	2.3	
40	-	
41	-	
43	3.0	
45	-	
46	-	
47	0.0	
48	-	
49	-	
50	-	
51	-5.9	UG
53	-	
54	-	
55	-	
56	-	
57	1.2	
58	1.0	

Laboratory	Difference AB
No of labs., p	18
No of repl., n	2
d	0.3
s^2	13.6
s	3.7
$t = \sqrt{p} \cdot (d/s)$	0.3167
Sign. level, p(t)	0.7553

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	-
3	-
4	-0.30
5	-
6	-
7	-
8	-
9	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-0.70
18	-
20	-
21	-0.20
22	-
23	-
24	3.00
25	-
26	-
27	-
28	-
29	-
30	-
31	-
33	-
34	-1.00
35	-
36	-
38	-2.80
39	-
40	-
41	-
43	-
45	-
46	-
47	1.00
48	-
49	-
50	-
51	-
53	-
54	-
55	-
56	-
57	0.13
58	-

Laboratory	Difference AB
No of labs., p	8
No of repl., n	2
d	-0.11
s^2	2.77
s	1.66
$t = \sqrt{p} \cdot (d/s)$	-0.1849
Sign. level, p(t)	0.8586

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	-1.20	UG
3	-3.00	UC
4	14.00	UC
5	-	
6	-	
7	-	
8	0.00	
9	0.40	
11	-	
12	-0.50	
13	-	
14	-0.50	
15	1.69	
16	5.90	UC
17	0.40	
18	-0.60	
20	-0.45	
21	0.90	
22	-0.30	
23	-0.60	
24	-	
25	0.10	
26	0.00	
27	1.30	UG
28	-5.20	UC
29	-0.60	
30	0.60	
31	0.00	
33	0.00	
34	-	
35	-0.10	
36	-	
38	-1.00	
39	-0.40	
40	-1.00	
41	0.40	
43	0.15	
45	-0.20	
46	0.00	
47	-	
48	0.00	
49	0.00	
50	0.70	
51	0.00	
53	9.50	UC
54	0.50	
55	-	
56	-	
57	-0.50	
58	-	

Laboratory	Difference AB
No of labs., p	31
No of repl., n	2
d	-0.03
s^2	0.32
s	0.57
$t = \sqrt{p} \cdot (d/s)$	-0.2892
Sign. level, p(t)	0.7744

No test statistics were found to be significant
UC denotes a Cochran outlier
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	31.15	
3	31.75	
4	-	
5	-	
6	31.10	
7	32.30	
8	31.55	
9	36.47	
11	36.35	
12	-	
13	-	
14	-	
15	33.75	
16	34.45	
17	-	
18	33.70	
20	31.25	
21	-	
22	-	
23	36.95	
24	30.75	
25	-	
26	23.65	UC
27	-	
28	30.65	
29	35.20	
30	28.60	
31	-	
33	-	
34	33.90	
35	31.00	
36	33.60	
38	29.15	
39	33.45	
40	35.35	
41	-	
43	31.70	
45	-	
46	-	
47	34.50	
48	36.35	
49	33.50	
50	-	
51	29.50	
53	-	
54	34.05	
55	-	
56	32.10	
57	30.85	
58	27.80	

Laboratory	Sample pair AB
No of labs., p	31
No of repl., n	2
m	32.67
s^2	5.82
s	2.41
Assigned value, μ	32
Recovery, %	102.1
$t = \sqrt{p} \cdot (m-\mu)/s$	1.5462
Sign. level, p(t)	0.1325

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

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

Laboratory	Sample pair AB	
1	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
11	-	
12	-	
13	3.37	
14	-	
15	-	
16	-	
17	-	
18	-	
20	3.00	UC
21	-	
22	-	
23	-	
24	-	
25	-	
26	1.48	
27	-	
28	2.55	
29	3.13	
30	6.50	
31	-	
33	-	
34	-	
35	-	
36	-	
38	-	
39	-	
40	-	
41	6.05	
43	8.68	
45	-	
46	-	
47	-	
48	-	
49	-	
50	-	
51	4.25	
53	-	
54	-	
55	-	
56	-	
57	3.58	
58	-	

Laboratory	Sample pair AB
No of labs., p	9
No of repl., n	2
m	4.40
s^2	5.10
s	2.26
Assigned value, μ	-
Recovery, %	-
$t = \sqrt{p} \cdot (m-\mu)/s$	-
Sign. level, p(t)	-

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

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

Laboratory	Sample pair AB
1	-
3	-
4	-
5	-
6	-
7	-
8	-
9	-
11	3.715
12	3.850
13	-
14	-
15	-
16	-
17	-
18	-
20	-
21	-
22	4.035
23	-
24	-
25	3.805
26	-
27	-
28	-
29	-
30	-
31	-
33	-
34	-
35	3.200
36	4.220
38	-
39	-
40	-
41	-
43	-
45	4.007
46	-
47	-
48	-
49	2.885
50	-
51	-
53	4.055
54	4.450
55	3.235
56	-
57	-
58	-

Laboratory	Sample pair AB
No of labs., p	11
No of repl., n	2
m	3.769
s^2	0.228
s	0.477
Assigned value, μ	3.9
Recovery, %	96.6
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.9117
Sign. level, p(t)	0.3834

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	-	
3	-	
4	-	
5	-	
6	13.75	
7	-	
8	-	
9	12.91	
11	13.80	
12	11.80	
13	12.94	
14	13.20	
15	12.60	
16	-	
17	-	
18	13.68	
20	-	
21	6.70	UG
22	13.40	
23	-	
24	-	
25	13.35	
26	-	
27	-	
28	13.65	
29	-	
30	13.40	
31	12.95	
33	13.80	
34	-	
35	13.60	
36	13.05	
38	11.20	
39	-	
40	14.60	
41	12.55	
43	-	
45	12.78	
46	9.24	UG
47	13.15	
48	13.03	
49	12.79	
50	-	
51	-	
53	13.36	
54	-	
55	-	
56	-	
57	12.43	
58	-	

Laboratory	Sample pair AB
No of labs., p	25
No of repl., n	2
m	13.11
s^2	0.48
s	0.69
Assigned value, μ	12.9
Recovery, %	101.6
$t = \sqrt{p} \cdot (m-\mu)/s$	1.5208
Sign. level, p(t)	0.1414

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

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

Laboratory	Sample pair AB
1	1.547
3	1.585
4	1.465
5	-
6	1.550
7	1.465
8	1.650
9	1.611
11	1.710
12	1.532
13	1.530
14	-
15	1.590
16	1.580
17	1.550
18	1.589
20	1.690
21	1.650
22	1.550
23	1.575
24	1.450
25	1.505
26	1.525
27	1.685
28	1.700
29	1.555
30	1.490
31	1.580
33	1.580
34	1.515
35	1.630
36	1.525
38	1.600
39	1.669
40	-
41	-
43	1.593
45	1.499
46	1.535
47	1.575
48	1.513
49	1.680
50	-
51	1.620
53	1.645
54	1.565
55	1.550
56	1.545
57	1.399
58	1.420

Laboratory	Sample pair AB
No of labs., p	45
No of repl., n	2
m	1.568
s^2	0.005
s	0.073
Assigned value, μ	1.53
Recovery, %	102.5
$t = \sqrt{p} \cdot (m-\mu)/s$	3.4930
Sign. level, p(t)	0.0011 **

* 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	-	
3	173.5	UC
4	168.7	
5	-	
6	-	
7	-	
8	168.0	
9	213.6	UC
11	-	
12	157.1	
13	151.0	
14	-	
15	-	
16	-	
17	164.0	
18	-	
20	135.5	
21	140.6	
22	-	
23	139.5	
24	146.0	
25	-	
26	208.0	UG
27	162.5	
28	75.4	UC
29	162.0	
30	150.0	
31	-	
33	-	
34	149.0	
35	-	
36	-	
38	-	
39	160.8	
40	-	
41	-	
43	133.5	
45	-	
46	-	
47	136.0	
48	-	
49	-	
50	-	
51	35.2	UG
53	-	
54	-	
55	-	
56	-	
57	159.0	
58	162.5	

Laboratory	Sample pair AB
No of labs., p	18
No of repl., n	2
m	152.5
s^2	138.5
s	11.8
Assigned value, μ	158
Recovery, %	96.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.9672
Sign. level, p(t)	0.0657

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	-
3	-
4	77.15
5	-
6	-
7	-
8	-
9	-
11	-
12	-
13	-
14	-
15	-
16	-
17	52.95
18	-
20	-
21	62.10
22	-
23	-
24	49.60
25	-
26	-
27	-
28	-
29	-
30	-
31	-
33	-
34	60.70
35	-
36	-
38	53.10
39	-
40	-
41	-
43	-
45	-
46	-
47	65.50
48	-
49	-
50	-
51	-
53	-
54	-
55	-
56	-
57	61.41
58	-

Laboratory	Sample pair AB
No of labs., p	8
No of repl., n	2
m	60.31
s^2	76.56
s	8.75
Assigned value, μ	61
Recovery, %	98.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.2220
Sign. level, p(t)	0.8306

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	24.10	UG
3	29.50	UC
4	22.00	UC
5	-	
6	-	
7	-	
8	29.40	
9	29.10	
11	-	
12	28.95	
13	-	
14	29.35	
15	30.21	
16	32.25	UC
17	29.20	
18	26.00	
20	29.17	
21	27.35	
22	29.35	
23	27.63	
24	-	
25	29.15	
26	29.00	
27	24.55	UG
28	27.70	UC
29	28.40	
30	28.50	
31	28.00	
33	29.30	
34	-	
35	29.35	
36	-	
38	28.50	
39	29.00	
40	27.50	
41	28.70	
43	29.18	
45	28.70	
46	27.90	
47	-	
48	29.00	
49	29.00	
50	29.35	
51	28.30	
53	24.75	UC
54	29.25	
55	-	
56	-	
57	29.51	
58	-	

Laboratory	Sample pair AB
No of labs., p	31
No of repl., n	2
m	28.75
s^2	0.68
s	0.82
Assigned value, μ	29
Recovery, %	99.1
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.6779
Sign. level, p(t)	0.1038

No test statistics were found to be significant
UC denotes a Cochran outlier
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	mg/L O2	A1	48-2	28,6	28,9	28,75	28,32	32	1	0
			62-34	27,8	27,5	27,65				
			72,51	28,4	28,7	28,55				
		B1	5-5	29,0	29,0	29,00	28,92	32		
			22-35	28,5	28,8	28,65				
			62-67	29,1	29,1	29,10				
Total phosphorus	mg/L P	A2	8	1,92	1,92	1,92	1,90	1,81	0,28	0,28
			30	1,88	1,88	1,88				
			51	1,89	1,91	1,90				
		B2	32	1,62	1,62	1,62	1,62	1,53		
			41	1,63	1,63	1,63				
			63	1,59	1,60	1,60				
Chloride	mg/L	A2	8	142	144	143,0	143	167	9	9
			30	143	144	143,5				
			51	142	143	142,5				
		B2	32	131	132	131,5	134	158		
			41	135	135	135,0				
			63	133	136	134,5				
Sulphate	mg/L	A2	8	54,7	53,9	54,30	54,0	69	13	8
			30	51,3	51,1	51,20				
			51	56,6	56,1	56,35				
		B2	32	41,4	40,4	40,90	40,6	61		
			41	40,2	40,3	40,25				
			63	37,9 *	36,2*					
Total suspended solids	mg/L	A3	39-13	29,2		29,2	29,2	29,0	4,5	5
			41-46	29,0		29,0				
			54-53	29,5		29,5				
		B3	8-12	32,7		32,7	33,7	34,0		
			48-48	34,4		34,4				
			70-73	34,1		34,1				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-1
Parameter:	COD
Unit:	mg/L O_2
Sigma:	10,8

Responsible for tests: S7MS/HBP

Homogeneity test Date: 2020-02-27

Sample	x(a)	x(b)	aver-age	sd	sd^2
A1-4	32,0	32,1	32,1	0,071	0,005
A1-13	31,9	31,4	31,7	0,354	0,13
A1-20	32,4	32,6	32,5	0,141	0,020
A1-30	32,0	32,0	32,0	0,000	0,000
A1-33	31,2	31,5	31,4	0,212	0,045
A1-45	32,0	32,2	32,1	0,141	0,020
A1-52	28,5	28,7	28,6	0,141	0,020
A1-56	31,9	31,9	31,9	0,000	0,000
A1-63	32,3	32,4	32,4	0,071	0,005
A1-69	32,6	32,9	32,8	0,212	0,045
A1-77	33,8	33,7	33,8	0,071	0,005
A1-80	31,4	31,6	31,5	0,141	0,020

For homogeneity

General average (x)	31,88
Sample average sd (s_x)	1,213
Within-sample sd (s_w):	0,161
Between-samples sd (ss):	1,2078
S_L in the Proficiency Test:	2,24
S_R in the Proficiency Test:	2,57

Stability test Date: 2020-03-12

Sample	x(a)	x(b)
A1-48-2	28,6	28,9
A1-62-34	27,8	27,5
A1-72-51	28,4	28,7

For stability

General average (y):	28,31667
/x-y/ =	3,558333

Conclusions

ss =	1,208	0.3*sigma=	3,24
/x-y/ =	3,558333		
Analytical quality	Is s_w < 0,15*sigma **YES**		
Homogeneity:	Is ss < 0.3*sigma? **YES**		

PT:	SPIL-1
Parameter:	TP
Unit:	mg/L P
Sigma:	0,102

ResponsiAle for tests: S7MS/HBP

Homogeneity test Date: 2020-02-26

Sample	x(a)	x(A)	aver-age	sd	sd^2
A2-3	1,94	1,93	1,94	0,007	0,000
A2-13	1,93	1,92	1,93	0,007	0,00
A2-18	1,92	1,91	1,92	0,007	0,000
A2-28	1,90	1,90	1,90	0,000	0,000
A2-34	1,87	1,87	1,87	0,000	0,000
A2-39	1,84	1,84	1,84	0,000	0,000
A2-43	1,88	1,88	1,88	0,000	0,000
A2-49	1,88	1,88	1,88	0,000	0,000
A2-56	1,88	1,88	1,88	0,000	0,000
A2-66	1,91	1,90	1,91	0,007	0,000
A2-73	1,90	1,89	1,90	0,007	0,000
A2-81	1,88	1,88	1,88	0,000	0,000

For homogeneity

General average (x)	1,89
Sample average sd (s_x)	0,026
Within-sample sd (s_w):	0,005
Between-samples sd (ss):	0,0259
S_L in the Proficiency Test:	0,066
S_R in the Proficiency Test:	0,080

Stability test Date: 2020-03-12

Sample	x(a)	x(A)
A2-8	1,92	1,92
A2-30	1,88	1,88
A2-51	1,89	1,91

For stability

General average (y):	1,9
/x-y/ =	0,007917

Conclusions

ss =	0,026	0.3*sigma= 0,03
/x-y/ =	0,007917	
Analytical quality	Is sw < 0,15*sigma **YES**	
Homogeneity:	Is ss < 0.3*sigma? **YES**	
Stability:	/x-y/ < 0.3*sigma? **YES**	

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

Responsible for tests: S7MS/HBP

Homogeneity test Date: 2020-02-27

Sample	x(a)	x(b)	aver-age	sd	sd^2
B3-4-2	33,9		33,9		
B3-14-10	35,2		35,2		
B3-19-14	34,2		34,2		
B3-25-24	34,4		34,4		
B3-30-28	34,5		34,5		
B3-33-38	34,7		34,7		
B3-44-42	34,7		34,7		
B3-47-53	34,7		34,7		
B3-54-56	34,6		34,6		
B3-57-62	35,0		35,0		
B3-64-69	34,6		34,6		
B3-69-76	34,5		34,5		

For homogeneity

General average (x)	34,6
Sample average sd (s_x)	0,337
Within-sample sd (s_w):	
Between-samples sd (ss):	0,337
S_L in the Proficiency Test:	0,77
S_R in the Proficiency Test:	0,87

Stability test Date: 2020-03-12

Sample	x(a)	x(b)
B3-8-12	32,7	
B3-48-48	34,4	
B3-70-73	34,1	

For stability

General average (y):	33,71533
/x-y/ =	0,847033

Conclusions

ss =	0,34	0.3*sigma=	1,08
/x-y/ =	0,847033		

Homogeneity: Is ss < 0.3*sigma?
YES

Stability: /x-y/ < 0.3*sigma?
YES