

Proficiency test SPIL-1 (2017)

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

Proficiency test SPIL-1 (2017) Quality Documentation

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1 INTRODUCTION

A proficiency test on the analysis of organic matter, phosphorus, chloride, sulphate and suspended matter in wastewater was conducted on 16 March 2017. 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 April 2017.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 67 laboratories from Denmark, Sweden, and Åland. A list of participants is shown in Appendix A.

The closing date for submission of results was 30 March 2017. 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.

Eight 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 TOC	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	45	2.8	0
BOD ₅ (w. ATU)	BOD ₅ w. ATU	mg/L O ₂	2 – 6	4.9	0.60	0
BOD ₇ (w. ATU)	BOD ₇ w ATU	mg/L O ₂	2 – 6	6.0	0.32	0
NVOC/TOC	NVOC/TOC	mg/L C	2 – 30	18.3	0.54	0
Total phosphorus	TP	mg/L P	0.2 – 2	1.50	0.044	0.26
Chloride	Cl	mg/L	50 – 700	261	4.3	57
Sulphate	SO ₄	mg/L	20 – 200	63	2.7	12
Total suspended solids	TSS	mg/L	20 - 100	71.0	0.80	11.9

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 SO₄ are operationally defined and are consensus values based upon the median for method no. 77 and 77A (COD_{Cr}), method no. 1 (NVOC), method no. 1 and 2 (TP), or method no. 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). A list of method identification numbers is found in the report to participants /1/. Assigned values for Cl and SO₄ are consensus

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 TSS. 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 method no. 1 and 9 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 revealed a significant difference between the two for COD_{Cr} and NVOC. 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. 71, 71B, 72, 72A, 72B, 74, 78, and 9 (COD_{Cr}) and 42 and 91 (NVOC) and now showed no significant difference. The assigned value is therefore kept unchanged.

3 **HOMOGENEITY AND STABILITY OF SAMPLES**

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

COD _{Cr}	Homogeneity test
TP	Combined homogeneity and stability test
TSS	Combined homogeneity and stability test

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

1. the standard deviation/variance for replicates (the contribution from analytical variability),
2. the between bottle standard deviation/variance (the contribution from heterogeneity) and
3. the between days concentration difference (the contribution from instability).

Homogeneity is evaluated by comparing the between bottle variance to $0.3 \cdot \hat{\sigma}$ 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 TSS 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 COD_{Cr} and NVOC the participants did not recover the assigned value. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned value is correct. The assigned value is therefore kept unchanged and it is recommended as the basis for evaluation of participating laboratories.

5 REFERENCES

- /1/ Eurofins A/S, *Proficiency test SPIL-1 (2017)*, Report to participants, April 2017.
- /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 regulation no. 914 on *quality criteria for environmental measurements*, 27 June 2016 (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 R/A, Fors Spildevand Roskilde	Roskilde	Denmark
BlueKolding A/S	Kolding	Denmark
CP Kelco ApS, Spildevandslaboratoriet	Ll. Skensved	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Faxe Forsyning	Faxe	Denmark
FORCE Technology Holstebro	Holstebro	Denmark
Fors Spildevand Holbæk	Holbæk	Denmark
Hillerød Forsyning Spildevand A/S	Hillerød	Denmark
Holstebro renseanlæg, Vestforsyning, erhverv	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Klarforsyning, Greve Spildevand	Køge	Denmark
Køge-Egnens Renseanlæg	Køge	Denmark
Melby Renseanlæg	Liseleje	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
Næstved Central Renseanlæg, NK-Spildevand	Næstved	Denmark
Provas	Haderslev	Denmark
Randers Spildevand A/S	Randers SØ	Denmark
RGS 90	Skælskør	Denmark
Rønne Renseanlæg	Rønne	Denmark
Slagelse Renseanlæg (5 participants)	Slagelse	Denmark
Spildevandslaboratoriet	Esbjerg	Denmark
Spildevandslaboratoriet, Rens Øst, Esbjerg	Esbjerg	Denmark
Svendborg Centralrenseanlæg	Skårup Fyn	Denmark
Vejle Spildevand A/S	Vejle	Denmark
AB Borlänge Energi, Reningsverket	Borlänge	Sweden
Akzo Nobel Functional Chemicals AB Cellulosic Specialties QHSE	Domsjö	Sweden
Arctic Paper Munkedal AB	Munkedal	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden

Laboratory	Town	Country
Hallsta Pappersbruk	Hallstavik	Sweden
Holmen Paper AB Bravikens Pappersbruk	Norrköping	Sweden
Iggesund Paperboard AB, Iggesunds Bruk Cell & Miljölab	Iggesund	Sweden
INOVYN Sweden AB	Stenungsund	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Klippans Reningsverk	Klippan	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
Laboratoriet Fillanverket, MittSweden Vatten och Avfall	Sundsvall	Sweden
Norrköping Vatten och Avfall AB, Laboratoriet Slottshagens Reningsverk	Norrköping	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun	Motala	Sweden
Nordic Sugar, Örtofta Sockerbruk	Eslöv	Sweden
Norrköping Vatten och Avfall AB, Laboratoriet Slottshagens Reningsverk	Norrköping	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
PIREVA Sandholmen	Öjebyn	Sweden
Preem AB Göteborg	Göteborg	Sweden
Preemraff Lysekil	Lysekil	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Rottneros Bruk AB	Rottneros	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Stora Enso Paper AB	Hyltebruk	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Södra Cell Mörrum	Mörrum	Sweden
Tekniska förvaltningen, Verksamhetsstöd VA, Laboratoriet	Örebro	Sweden
Uppsala Vatten o. Avfall AB, Vattenlaboratoriet	Uppsala	Sweden
Vallviks Bruk	Vallvik	Sweden
VIVAB	Falkenberg	Sweden
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
ÅMHM laboratoriet	Jomala	Åland

ANNEX B SAMPLE PREPARATION

Stock solution	Prepared from	Concentration
Concentrate A1 and B1, COD/NVOC	7.00 g D-glucose 7.00 g L-glutamic acid milli-Q water up to 24000 g	COD _{Cr} : 1.432 g/kg NVOC: 0.566 g/kg
Concentrate A1 and B1, BOD	17.70 g D-glucose 17.70 g L-glutamic acid milli-Q water up to 10000 g	BOD: 1,033 g/kg
Stock TP	1.50 g Na-B.glycerophosphate milli-Q water up to 1000 g	TP: 151.8 mg/kg
Stock Cl	10.00 g Sodium chloride (NaCl) milli-Q water up to 1000 g	Cl: 6.067 g/kg
Stock SO ₄	5.00 g Sodium sulphate (Na ₂ SO ₄) milli-Q water up to 1000 g	SO ₄ : 3.381 g/kg
Stock TSS	30.03 g Microcrystalline cellulose milli-Q water up to 2000 mL	TSS: 15.015 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 Skovlund sewage treatment plant	a + 28.6	b + 11.3					
B1-COD/NVOC	At the laboratory 2.00 mL of concentrate B1 is diluted up to 100.0 mL with filtered water from Skovlund sewage treatment plant	a + 28.6	b + 11.3					
A1-BOD	At the laboratory 6.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Skovlund sewage treatment plant			c + 3.10				
B1-BOD	At the laboratory 6.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Skovlund sewage treatment plant			c + 3.10				
A2	450.0 g stock TP 600.0 g stock SO ₄ filtered water from Skovlund sewage treatment plant up to 70.0 kg				d + 0.976	e	f + 29.0	
B2	75.01 g stock TP 400.00 g stock Cl 150.03 g stock SO ₄ Sample A2 up to 40.0 kg				0.984 · (d+0.976) + 0.285	0.984 · e + 60.7	0.984 · (f + 29.0) + 12.7	
A3	At the laboratory 1000.0 mL of filtered water from Skovlund sewage treatment plant is added to 4.9 mL stock TSS							g + 73.2
B3	At the laboratory 1000.0 mL of filtered water from Skovlund sewage treatment plant is added to 5.7 mL stock TSS							g + 85.1

ANNEX C CONTROL OF SPIKE VALUES

COD_{Cr}, mg/L O₂

Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	-	
4	1.60	
5A	0.90	
5B	-	
6	-3.70	UG
7	1.00	
8	1.90	
9	-	
10	2.90	
11	-0.70	
12	5.40	
13	-	
14	-	
15	-3.90	
16	0.40	
17	0.20	
18	-1.40	
19	0.80	
20	2.10	
21	0.60	
22	-3.40	UG
23	0.90	
24	-0.30	
25	-	
26	-1.90	
27	1.20	
28	-1.90	
29	0.20	
30	-	
31	-1.40	
32	-	
33	-	
34	-	
35	0.00	
36	6.40	
37	1.00	
38	-	
39	-	
40	-1.60	
41	0.00	
42	1.60	
43	-2.00	
44	-	
45	0.40	
46	-0.70	
47	1.00	
48	-2.70	
49	-0.10	
50	-	

51	-0.60
52	-
53	-0.40
54	-
55	1.00
56	-2.40
57	0.20
58A	-
58B	-
59	1.40
60	-1.05
61	-
62	-
63A	1.70
63B	1.10
64A	0.40
64B	2.00
65	-1.30
66	-
67	-
No of labs., p	45
No of repl., n	2
d	0.31
s ²	3.55
s	1.89
$t = \sqrt{p} \cdot (d/s)$	1.1029
Sign. level, p(t)	0.2761

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

BOD₅ w. ATU, mg/L O₂
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5A	-0.260
5B	0.000
6	-
7	-0.030
8	-
9	-
10	-
11	-0.650
12	-0.540
13	-
14	-
15	-
16	0.200
17	-
18	-
19	-
20	-0.080
21	-
22	-
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	-1.930
36	-
37	-
38	0.180
39	-
40	-
41	-
42	-
43	1.380
44	-
45	-
46	0.000
47	-
48	-
49	-
50	-
51	0.430
52	-
53	-
54	-
55	-1.540

56	-
57	-
58A	-
58B	-
59	-
60	0.000
61	-
62	-
63A	-2.580
63B	-
64A	0.000
64B	-
65	0.440
66	-
67	-
No of labs., p	17
No of repl., n	2
d	-0.293
s ²	0.902
s	0.950
t = $\sqrt{p} \cdot (d/s)$	-1.2715
Sign. level, p(t)	0.2217

No test statistics were found to be significant

BOD₇ w. ATU, mg/L O₂
Control of differences within sample pairs

Laboratory	Difference AB
1	0.280
2	-0.400
3	0.000
4	-
5A	-
5B	-
6	-
7	-
8	-0.010
9	-
10	-
11	-
12	-
13	-
14	-
15	-0.200
16	-
17	-
18	-
19	-
20	-0.080
21	-
22	-
23	-
24	-
25	-
26	-
27	0.970
28	-
29	-0.060
30	-
31	-
32	-0.300
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	0.220 UG
43	-
44	0.200
45	-
46	-
47	0.400
48	-
49	-
50	-
51	-
52	-0.080
53	-
54	-
55	-

56	0.190
57	0.420
58A	-
58B	-
59	-
60	-
61	-0.300
62	-
63A	-
63B	-
64A	-
64B	-
65	-
66	-
67	0.120
No of labs., p	16
No of repl., n	2
d	0.072
s ²	0.117
s	0.343
t = $\sqrt{p} \cdot (d/s)$	0.8393
Sign. level, p(t)	0.4145

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

NVOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB	
1	0.30	
2	1.00	
3	-0.28	
4	-	
5A	-0.20	
5B	-	
6	-	
7	-0.70	
8	0.30	
9	-	
10	-	
11	-	
12	-	
13	-0.91	
14	0.13	UG
15	-	
16	0.10	
17	2.60	UC
18	0.90	
19	-	
20	-	
21	0.00	
22	-	
23	-	
24	-	
25	1.63	
26	-	
27	-	
28	-	
29	-0.80	
30	-0.10	
31	-	
32	0.18	
33	0.40	
34	-	
35	-	
36	-	
37	-	
38	0.48	
39	0.10	
40	-0.40	
41	-	
42	0.40	
43	-	
44	-0.40	
45	-	
46	0.10	
47	-0.70	
48	1.30	
49	-	
50	-	
51	0.20	
52	0.30	UG
53	-	
54	0.55	
55	-	

56	-	
57	0.10	UG
58A	-0.18	
58B	-	
59	0.50	
60	0.30	
61	3.80	UC
62	-0.20	
63A	-	
63B	-	
64A	1.00	
64B	-	
65	-	
66	1.00	
67	0.60	
No of labs., p	32	
No of repl., n	2	
d	0.20	
s ²	0.38	
s	0.61	
t = $\sqrt{p} \cdot (d/s)$	1.8655	
Sign. level, p(t)	0.0716	

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

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

Laboratory	Difference AB
1	0.000
2	-0.010
3	-0.017
4	-0.050
5A	0.020
5B	0.020
6	0.001
7	-0.030
8	0.000
9	0.010
10	0.000
11	0.130
12	0.070
13	-
14	0.095
15	0.019
16	0.020
17	0.020
18	-0.010
19	0.040
20	-0.230
21	0.000
22	0.070
23	-0.010
24	-0.010
25	-0.020
26	0.008
27	0.000
28	0.070
29	-0.044
30	-0.010
31	0.060
32	0.000
33	0.100
34	-
35	0.050
36	0.390 UC
37	-0.170
38	0.025
39	-0.020
40	-0.030
41	0.060
42	0.060
43	0.090
44	-0.040
45	-0.110
46	0.020
47	-0.020
48	-0.063
49	0.150
50	0.020
51	0.020
52	-0.002
53	0.060
54	0.020
55	0.030

56	0.090
57	-0.040
58A	-0.004
58B	-0.026
59	-0.060
60	0.000
61	0.057
62	0.000
63A	-0.030
63B	0.110
64A	0.030
64B	-0.140
65	0.010
66	-0.140
67	-0.010
No of labs., p	68
No of repl., n	2
d	0.005
s ²	0.004
s	0.065
t = $\sqrt{p} \cdot (d/s)$	0.5778
Sign. level, p(t)	0.5653

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	-
3	1.3
4	4.2
5A	2.3
5B	2.0
6	-
7	1.7
8	-
9	12.0
10	-
11	-5.0
12	-6.0
13	-0.7
14	-
15	-
16	-10.0
17	2.0
18	-
19	-
20	-35.0
21	-1.0
22	32.0 UG
23	0.1
24	6.0
25	-
26	-8.0
27	-7.0
28	-
29	-
30	-
31	-
32	-3.0
33	0.2
34	-
35	31.0 UG
36	-
37	-50.0
38	3.0
39	-
40	-
41	-
42	-
43	-6.0
44	-
45	11.0
46	6.0
47	-
48	-
49	47.0
50	-50.3
51	-4.0
52	-
53	-12.0
54	-
55	-1.0

56	-
57	-
58A	-
58B	-
59	0.0
60	-3.5
61	2.2
62	-
63A	-4.0
63B	0.0
64A	3.0
64B	-
65	28.0
66	-3.0
67	-
No of labs., p	37
No of repl., n	2
d	-2.1
s ²	277.8
s	16.7
t = $\sqrt{p} \cdot (d/s)$	-0.7647
Sign. level, p(t)	0.4495

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

Sulphate, mg/L
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	0.67
4	-
5A	0.20
5B	-0.20
6	-2.90
7	0.80
8	-
9	-
10	-
11	6.20
12	-
13	-
14	-
15	-
16	-
17	0.00
18	-
19	-
20	-
21	2.20
22	4.40
23	-
24	-2.10
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-1.30
44	-
45	-
46	-
47	-
48	-
49	-
50	-0.20
51	5.10
52	-
53	-2.70
54	-
55	4.80

56	-
57	-
58A	-
58B	-
59	8.90
60	-
61	-
62	-
63A	9.00
63B	-
64A	-
64B	-
65	-
66	-1.00
67	-
No of labs., p	18
No of repl., n	2
d	1.77
s ²	14.09
s	3.75
t = $\sqrt{p} \cdot (d/s)$	2.0014
Sign. level, p(t)	0.0616

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	5.00	
2	3.10	
3	2.90	
4	1.36	
5A	-1.10	
5B	-	
6	-1.45	
7	7.90	
8	-3.00	
9	-1.30	
10	4.90	
11	1.50	
12	5.20	
13	-	
14	0.70	
15	0.90	
16	1.60	
17	-4.10	
18	0.80	
19	-	
20	0.20	
21	-0.10	
22	2.30	
23	1.40	
24	0.90	
25	4.40	
26	11.70	
27	2.50	
28	-	
29	1.30	
30	1.40	
31	2.10	
32	3.00	
33	0.70	
34	9.60	
35	-4.10	
36	-1.50	
37	0.20	UG
38	-	
39	-0.30	
40	-0.10	
41	4.90	
42	4.40	
43	1.60	
44	22.50	UC

45	5.90	
46	2.00	
47	-8.50	
48	-4.50	
49	-0.70	
50	1.90	
51	-0.10	
52	-4.10	
53	-	
54	3.20	
55	-2.50	
56	-17.00	UC
57	4.40	
58A	2.37	
58B	-	
59	-	
60	1.50	
61	18.90	UC
62	-0.60	
63A	2.70	
63B	-	
64A	-4.70	
64B	-	
65	0.90	
66	2.90	
67	3.40	
No of labs., p	57	
No of repl., n	2	
d	1.35	
s ²	12.23	
s	3.50	
$t = \sqrt{p} \cdot (d/s)$	2.9048	
Sign. level, p(t)	0.0053	**

* 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.

ANNEX D CONTROL OF RECOVERY

COD_{Cr}, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	45.00
5A	47.65
5B	-
6	96.75 UG
7	43.80
8	54.55
9	-
10	55.05
11	40.15
12	51.70
13	-
14	-
15	52.05
16	45.50
17	55.70
18	52.30
19	45.60
20	51.15
21	48.65
22	18.00 UG
23	55.75
24	42.85
25	-
26	44.55
27	47.60
28	47.85
29	49.50
30	-
31	52.30
32	-
33	-
34	-
35	37.00
36	37.10
37	45.10
38	-
39	-
40	50.10
41	47.80
42	52.30
43	35.80
44	-
45	42.20
46	45.75
47	52.50
48	49.25
49	44.75
50	-

51	42.80
52	-
53	43.00
54	-
55	42.60
56	50.90
57	49.00
58A	-
58B	-
59	46.40
60	43.98
61	-
62	-
63A	44.55
63B	54.75
64A	44.10
64B	45.40
65	44.75
66	-
67	-
No of labs., p	45
No of repl., n	2
m	47.14
s ²	24.72
s	4.97
Assigned value, μ	45
Recovery, %	104.7
$t = \sqrt{p} \cdot (m - \mu) / s$	2.8823
Sign. level, p(t)	0.0061 **

* 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

BOD₅ w. ATU, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5A	5.180
5B	4.600
6	-
7	4.455
8	-
9	-
10	-
11	5.325
12	4.450
13	-
14	-
15	-
16	5.200
17	-
18	-
19	-
20	6.350
21	-
22	-
23	-
24	-
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	5.095
36	-
37	-
38	5.480
39	-
40	-
41	-
42	-
43	6.070
44	-
45	-
46	4.900
47	-
48	-
49	-
50	-
51	2.445
52	-
53	-
54	-
55	6.420

56	-
57	-
58A	-
58B	-
59	-
60	8.000
61	-
62	-
63A	3.950
63B	-
64A	7.000
64B	-
65	4.450
66	-
67	-
No of labs., p	17
No of repl., n	2
m	5.257
s ²	1.624
s	1.274
Assigned value, μ	4.9
Recovery, %	107.3
$t = \sqrt{p} \cdot (m-\mu)/s$	1.1553
Sign. level, p(t)	0.2649

No test statistics were found to be significant

BOD₇ w. ATU, mg/L O₂

Control of recovery, average of results

Laboratory	Sample pair AB
1	5.740
2	6.100
3	5.500
4	-
5A	-
5B	-
6	-
7	-
8	4.765
9	-
10	-
11	-
12	-
13	-
14	-
15	6.300
16	-
17	-
18	-
19	-
20	5.550
21	-
22	-
23	-
24	-
25	-
26	-
27	6.885
28	-
29	4.950
30	-
31	-
32	5.650
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	8.890 UG
43	-
44	6.100
45	-
46	-
47	6.200
48	-
49	-
50	-
51	-
52	6.360
53	-
54	-
55	-

56	6.605
57	5.670
58A	-
58B	-
59	-
60	-
61	5.650
62	-
63A	-
63B	-
64A	-
64B	-
65	-
66	-
67	6.070
No of labs., p	16
No of repl., n	2
m	5.881
s ²	0.314
s	0.560
Assigned value, μ	6.0
Recovery, %	98.0
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.8500
Sign. level, p(t)	0.4087

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

NVOC, mg/L C

Control of recovery, average of results

Laboratory	Sample pair AB	
1	18.80	
2	17.50	
3	18.13	
4	-	
5A	18.20	
5B	-	
6	-	
7	17.75	
8	19.25	
9	-	
10	-	
11	-	
12	-	
13	18.22	
14	12.95	UG
15	-	
16	19.55	
17	23.30	UC
18	17.95	
19	-	
20	-	
21	18.95	
22	-	
23	-	
24	-	
25	18.63	
26	-	
27	-	
28	-	
29	18.40	
30	21.05	
31	-	
32	18.53	
33	17.70	
34	-	
35	-	
36	-	
37	-	
38	17.99	
39	19.15	
40	19.70	
41	-	
42	17.20	
43	-	
44	17.60	
45	-	
46	19.55	
47	19.85	
48	21.53	
49	-	
50	-	
51	18.60	
52	10.55	UG
53	-	
54	17.92	
55	-	

56	-	
57	11.15	UG
58A	19.74	
58B	-	
59	19.55	
60	18.35	
61	54.40	UC
62	19.50	
63A	-	
63B	-	
64A	18.80	
64B	-	
65	-	
66	19.50	
67	19.20	
No of labs., p	32	
No of repl., n	2	
m	18.82	
s ²	0.98	
s	0.99	
Assigned value, μ	18.3	
Recovery, %	102.9	
$t = \sqrt{p} \cdot (m-\mu)/s$	2.9956	
Sign. level, p(t)	0.0053	**

* 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

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

Laboratory	Sample pair AB
1	1.500
2	1.435
3	1.508
4	1.455
5A	1.570
5B	1.380
6	1.442
7	1.545
8	1.470
9	1.395
10	1.490
11	1.405
12	1.465
13	-
14	1.444
15	1.446
16	1.570
17	1.455
18	1.475
19	1.520
20	1.495
21	1.590
22	1.505
23	1.505
24	1.495
25	1.410
26	1.522
27	1.480
28	1.555
29	1.537
30	1.455
31	1.450
32	1.470
33	1.590
34	-
35	1.485
36	1.755
37	1.435
38	1.603
39	1.470
40	1.515
41	1.450
42	1.370
43	1.515
44	1.350
45	1.595
46	1.560
47	1.560
48	1.462
49	1.395
50	1.450
51	1.470
52	1.467
53	1.460
54	1.510
55	1.315

UC

56	1.525
57	1.650
58A	1.528
58B	1.528
59	1.410
60	1.560
61	1.496
62	1.480
63A	1.435
63B	1.305
64A	1.525
64B	1.630
65	1.565
66	1.470
67	1.505
No of labs., p	68
No of repl., n	2
m	1.486
s ²	0.005
s	0.069
Assigned value, μ	1.50
Recovery, %	99.1
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.6226
Sign. level, p(t)	0.1094

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

Chloride, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	262.8
4	265.0
5A	264.4
5B	257.2
6	-
7	259.8
8	-
9	219.0
10	-
11	266.5
12	294.0
13	258.5
14	-
15	-
16	265.0
17	258.0
18	-
19	-
20	291.5
21	261.5
22	181.0 UG
23	259.3
24	322.0
25	-
26	268.0
27	272.5
28	-
29	-
30	-
31	-
32	254.5
33	257.3
34	-
35	182.5 UG
36	-
37	300.0
38	252.5
39	-
40	-
41	-
42	-
43	274.0
44	-
45	236.5
46	261.0
47	-
48	-
49	299.5
50	281.0
51	233.0
52	-
53	271.0
54	-
55	278.5

56	-
57	-
58A	-
58B	-
59	252.0
60	284.8
61	257.5
62	-
63A	286.0
63B	261.0
64A	260.5
64B	-
65	275.0
66	251.5
67	-
No of labs., p	37
No of repl., n	2
m	266.8
s ²	378.0
s	19.4
Assigned value, μ	261
Recovery, %	102.2
$t = \sqrt{p} \cdot (m - \mu) / s$	1.8166
Sign. level, p(t)	0.0776

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

Sulphate, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	64.68
4	-
5A	62.70
5B	69.60
6	62.52
7	62.70
8	-
9	-
10	-
11	50.90
12	-
13	-
14	-
15	-
16	-
17	68.00
18	-
19	-
20	-
21	58.00
22	61.00
23	-
24	75.95
25	-
26	-
27	-
28	-
29	-
30	-
31	-
32	-
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	56.75
44	-
45	-
46	-
47	-
48	-
49	-
50	65.90
51	66.15
52	-
53	64.75
54	-
55	67.00

56	-
57	-
58A	-
58B	-
59	49.25
60	-
61	-
62	-
63A	60.40
63B	-
64A	-
64B	-
65	-
66	61.50
67	-
No of labs., p	18
No of repl., n	2
m	62.65
s ²	40.43
s	6.36
Assigned value, μ	63
Recovery, %	99.4
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.2319
Sign. level, p(t)	0.8194

No test statistics were found to be significant

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

Laboratory	Sample pair AB
1	68.40
2	70.05
3	68.43
4	70.50
5A	73.35
5B	-
6	65.54
7	78.75
8	70.30
9	71.65
10	74.15
11	69.25
12	70.80
13	-
14	68.25
15	71.55
16	70.80
17	64.05
18	71.90
19	-
20	69.90
21	69.45
22	69.35
23	72.20
24	69.55
25	66.60
26	69.15
27	70.05
28	-
29	70.95
30	71.30
31	69.35
32	72.20
33	72.35
34	76.70
35	74.05
36	69.55
37	59.20 UG
38	-
39	72.75
40	70.05
41	62.55
42	71.80
43	70.10
44	70.65 UC
45	67.05
46	69.40
47	65.65
48	69.65
49	72.15
50	72.55
51	72.05
52	69.05
53	-
54	68.20
55	72.05

56	63.30 UC
57	70.55
58A	70.98
58B	-
59	-
60	71.05
61	63.55 UC
62	68.50
63A	69.05
63B	-
64A	70.85
64B	-
65	72.65
66	72.55
67	72.10
No of labs., p	57
No of repl., n	2
m	70.42
s ²	7.22
s	2.69
Assigned value, μ	71.0
Recovery, %	99.2
t = $\sqrt{p} \cdot (m-\mu)/s$	-1.6380
Sign. level, p(t)	0.1070

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	Assigned
COD	mg/L O2	A1	67	43,3	43,0	43,2	43,5	45	-0,4	0
			43	43,6	43,7	43,7				
			16	43,7	43,5	43,6				
		B1	84	43,7	42,9	43,3	43,1	45		
			54	43,1	42,8	43,0				
			3	43,2	42,6	42,9				
Total phosphorus	mg/L P	A2	25	1,49	1,47	1,48	1,51	1,50	0,3	0,26
			52	1,49	1,55	1,52				
			78	1,60	1,48	1,54				
		B2	28	1,84	1,73	1,79	1,77	1,76		
			65	1,75	1,74	1,75				
			96	1,76	1,79	1,78				
Chloride	mg/L	A2	25	265	263	264	264	261	61	57
			52	267	264	266				
			78	263	261	262				
		B2	28	327	323	325	325	318		
			65	323	328	326				
			96	325	323	324				
Sulphate	mg/L	A2	25	56,6	52,1	54,4	53,6	63	14,8	12
			52	53,4	52,7	53,1				
			78	53,3	53,7	53,5				
		B2	28	69,4	67,7	68,6	68,4	75		
			65	67,1	65,1	66,1				
			96	70,4	70,6	70,5				
Total suspended solids	mg/L	A3	21	71,9		71,9	71,0	71,0	12,4	11,9
			61	72,8		72,8				
			75	68,3		68,3				
		B3	25	86,5		86,5	83,4	82,9		
			33	80,8		80,8				
			64	83,0		83,0				

ANNEX F HOMOGENEITY AND STABILITY

PT:SPIL-1
Parameter:COD
Unit:mg/L O ₂
Sigma:10,8

Responsible for tests: IRL/HEW

Homogeneity test Date:2017-03-02

Sample	x(a)	x(b)	average	sd	sd ²
A1-6 88	50,2	50,3	50,3	0,071	0,005
A1-18 3	49,8	50,5	50,2	0,495	0,25
A1-27 46	49,8	50,2	50,0	0,283	0,080
A1-38 62	49,1	49,3	49,2	0,141	0,020
A1-44 24	48,9	49,3	49,1	0,283	0,080
A1-50 13	49,9	49,7	49,8	0,141	0,020
A1-59 38	49,6	50,1	49,9	0,354	0,125
A1-60 32	49,8	48,8	49,3	0,707	0,500
A1-65 75	50,0	49,6	49,8	0,283	0,080
A1-76 54	49,6	49,9	49,8	0,212	0,045
A1-81	49,6	49,6	49,6	0,000	0,000
A1-93 17	50,2	49,8	50,0	0,283	0,080

For homogeneity

General average (x)	49,73
Sample average sd (s _x)	0,369
Within-sample sd (s _w):	0,327
Between-samples sd (ss):	0,2876
S _L in the Proficiency Test:	4,88
S _R in the Proficiency Test:	5,06

Conclusions

ss =0,288	0.3*sigma=3,24
x-y =0	
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:0,096

Responsible for tests: IRL/HEW

Homogeneity test Date:2017-03-01

Sample	x(a)	x(b)	average	sd	sd^2
B2-3	1,77	1,78	1,8	0,007	0,000
B2-11	1,74	1,84	1,8	0,071	0,01
B2-14	1,78	1,87	1,8	0,064	0,004
B2-32	1,76	1,77	1,8	0,007	0,000
B2-39	1,77	1,78	1,8	0,007	0,000
B2-45	1,76	1,78	1,8	0,014	0,000
B2-56	1,77	1,81	1,8	0,028	0,001
B2-68	1,81	1,76	1,8	0,035	0,001
B2-76	1,77	1,76	1,8	0,007	0,000
B2-80	1,74	1,81	1,8	0,049	0,002
B8-88	1,77	1,74	1,8	0,021	0,000
B8-90	1,74	1,77	1,8	0,021	0,000

For homogeneity

General average (x) 1,78
 Sample average sd (s_x) 0,019
 Within-sample sd (s_w): 0,035
 Between-samples sd (ss): 0
 S_L in the Proficiency Test: 0,061
 S_R in the Proficiency Test: 0,076

Stability test Date:2017-03-16

Sample	x(a)	x(b)
B2-28	1,84	1,73
B2-65	1,75	1,74
B2-96	1,76	1,79

For stability

General average (y): 1,768333
 $|x-y| = 0,00875$

Conclusions

	ss =0	0.3*sigma=0,03
	$ x-y =0,00875$	
Analytical quality	Is $s_w < 0,15*\sigma$	NO
Homogeneity:	Is ss < 0.3*sigma?	YES
Stability:	$ x-y < 0.3*\sigma$?	YES

PT:SPIL-1 Parameter:TSS Unit:mg/L Sigma:4,5
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Responsible for tests: HEW

Homogeneity test Date:2017-03-01

Sample	x(a)	x(b)	average	sd	sd^2
B3-2 19	86,1		86,1		
B3-15 41	81,1		81,1		
B3-22 69	84,8		84,8		
B3-31 27	83,9		83,9		
B3-40 49	83,5		83,5		
B3-44 62	83,5		83,5		
B3-52 11	83,3		83,3		
B3-61 57	83,4		83,4		
B3-67 32	89,6*				
B3-73 87	82,7		82,7		
B3-83 79	83,2		83,2		
B3-86 4	82,8		82,8		

For homogeneity

General average (x)	83,5
Sample average sd (s _x)	1,250
Within-sample sd (s _w):	
Between-samples sd (ss):	1,250
S _L in the Proficiency Test:	2,04
S _R in the Proficiency Test:	3,21

*: value excluded as an outlier

Stability test Date:2017-03-16

Sample	x(a)	x(b)
B3-25 84		86,5
B3-33 54		80,8
B3-64 3		83

For stability

General average (y):	83,43333
x-y =	0,048485

Conclusions

ss =1,25		0.3*sigma=1,35
x-y =0,048485		
Analytical quality	Is s _w < 0,15*sigma	No data
Homogeneity:	Is ss < 0.3*sigma?	YES
Stability:	x-y < 0.3*sigma?	YES