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Proficiency test SPIL-1 (2019)

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 28 March 2019. 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 3 May 2019.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 56 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 12 April 2019. All participants except laboratory no. 6, 16 and 35 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
Chemical oxygen demand – dichromate method	COD_{Cr}	mg/L O_2	5 - 75	35	1.2	4
Five day biological oxygen demand (w. ATU)	BOD_5 w. ATU	mg/L O_2	2 - 6	(2.6)*	-	(0.3)*
Seven day biological oxygen demand (w. ATU)	BOD_7 w. ATU	mg/L O_2	2 - 6	2.6	0.36	0.3
Non-volatile organic carbon	NVOC/TOC	mg/L C	2 - 30	14.1	0.37	1.8
Total phosphorus	TP	mg/L P	0,2 - 2	0.75	0.012	0.14
Chloride	Cl	mg/L	50 - 700	192	3.4	35
Sulphate	SO_4	mg/L	20 - 200	105	5.0	20
Total suspended solids	TSS	mg/L	20 - 100	59.4	0.83	12.4

*Indicativ 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 except for COD_{Cr} where the spike value is the difference between median values for the two samples in the sample pair.

The assigned values for all parameters except Cl and SO4 are operationally defined and are consensus values based upon the median for method no. 1 (NVOC), method no. 1 and 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. Only three laboratories have reported COD_{Cr} with the methods required by the Danish EPA. The assigned value for COD_{Cr} is therefore the consensus value for all the laboratories. For BOD_5, only two laboratories used method no. 1, and the assigned value for BOD_7 has therefore been used as an indicative value for BOD_5.

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 COD_{Cr}, TP and SO_4.

The difference for COD_{Cr} 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 from the 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.

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. 1 and 2 and showed no significant difference. The spike value is therefore kept unchanged.

For SO_4 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.

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 102,3 %. 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. 1 and 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}	Combined homogeneity and stability test
TP	Homogeneity 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.

For COD_{Cr} only few laboratories have used a method prescribed by the Danish EPA. The assigned value is the consensus value and it is recommended to evaluate deviations from the assigned value with caution.

For SO_4 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.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-1 (2019)*, Report to participants, May 2019.

/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. 974 on *quality criteria for environmental measurements,* 27 June 2018 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2005.

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
CP Kelco, Spildevandslaboratoriet	Ll. Skensved	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Faxe Forsyning	Faxe	Denmark
Fors Spildevand Holbæk	Holbæk	Denmark
Hillerød Forsyning, Spildevand	Hillerød	Denmark
Holstebro Centralrenseanlæg, Vestforsyning Spildevand	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Denmark
Melby Renseanlæg	Liseleje	Denmark
NK-Spildevand A/S	Næstved	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
Provas	Haderslev	Denmark
RGS Nordic A/S	Skælskør	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Spildevand, Slagelse Renseanlæg	Slagelse	Denmark
Spildevandslaboratoriet	Esbjerg	Denmark
Svendborg Spildevand A/S, Svenborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
Eurofins Environment Testing Norway AS	Moss	Norway
AB Borlänge Energi, Reningsverket	Borlänge	Sweden
AB Lennart Månsson International	Helsingborg	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
Campus Roslagen, Utvecklingscentrum för Vatten	Norrtälje	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Gästrike Vatten AB	Skutskär	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
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
Laboratoriet Fillanverket, MittSweden Vatten och Avfall	Sundsvall	Sweden
Laboratoriet vid Smedjeholms avolppsreningsverk	Falkenberg	Sweden
Nordic Sugar, Örtofta Sockerbruk	Eslöv	Sweden
Nouryon, Akzo Nobel Functional Chemicals AB Cellulosic Specialties QHSE	Örnsköldsvik	Sweden
NSVA/Öresundsverket	Helsingborg	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
Södra Cell AB, Värö	Väröbacka	Sweden
Södra Cell Mörrum	Mörrum	Sweden
Uppsala Vatten och Avfall AB, Vattenlaboratoriet	Uppsala	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	22.20 g 22.20 g 	D-glucose L-glutamic acid milli-Q water up to 24000 g	COD_{Cr}: 1.892 g/kg NVOC: 0.747 g/kg BOD: 1.295 g/kg
Concentrate B1	15.00 g 15.00 g 	D-glucose L-glutamic acid milli-Q water up to 13000 g	COD_{Cr}: 2.360 g/kg NVOC: 0.932 g/kg BOD: 1.615 g/kg
Stock TP	1.500 g 	Na-B.glycerophosphate milli-Q water up to 999.8 g	TP: 151.8 mg/kg
Stock Cl	19.998 g 	Sodium chloride (NaCl) milli-Q water up to 2000.6 g	Cl: 6.064 g/kg
Stock SO_4	5.000 g 	Sodium sulphate (Na_2SO_4) milli-Q water up to 999.9 g	SO_4: 3.382 g/kg
Stock TSS	25.00 g 	Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 25.000 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/kg P	Cl mg/kg	SO_4 mg/kg	TSS mg/kg
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 + 18.9	b + 7.47					
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 + 23.6	b + 9.32					
A1-BOD	At the laboratory 2.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Holsted sewage treatment plant			c + 1.30				
B1-BOD	At the laboratory 2.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Holsted sewage treatment plant			c + 1.62				
A2	40.00 g stock TP 250.0 g stock Cl 250.0 g stock SO_4 Sample B2 up to 40.0 kg				0.986· (d+0.650) + 0.15	0.986· (e+69.3) + 37.9	0.986· (f+19.3) + 21.1	
B2	299.9 g stock TP 799.9 g stock Cl 400.0 g stock SO_4 Filtered water from Holsted sewage treatment plant up to 77.6 kg				d + 0.650	e+69.3	f+19.3	
A3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 2.5 mL stock TSS							g + 62.3
B3	At the laboratory 1000.0 mL of filtered water from Holsted sewage treatment plant is added to 3.0 mL stock TSS							g + 74.8

ANNEX C CONTROL OF SPIKE VALUES

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

Laboratory	Difference AB
1	-
2	0.20
3	-2.30
4	-
5	-
6	-
7	-0.50
8	-
9	-3.30
10	0.50
11	2.31
12	-
13	-
14	0.10
15	-
16	-
17	-
18	-
19	0.40
20	0.40
21	-1.70
22	-1.60
23	0.20
24	-
25	5.10
26	1.30
27	-
28A	0.30
28B	-3.10
29	-0.50
30	0.60
31	0.20
32	0.10
33	-0.90
34	-
35	-
36	0.00
37	0.85
38	0.80
39	-
40	-2.60
41	-
42	0.50
43	-0.70
44	0.80
45	0.80
46	-2.50
47	1.40
48	-0.70
49	-1.00
50	-
51	0.60
52	-
53	1.45
54	-2.00
55	4.60
56	3.20
No of labs., p	38
No of repl., n	2
d	0.09
s^2	3.36
s	1.83
$t = \sqrt{p} \cdot (d/s)$	0.2931
Sign. level, p(t)	0.7711

No test statistics were found to be significant

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

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5	0.320
6	-
7	-
8	-
9	-
10	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-
18	-
19	-
20	-
21	1.800
22	-
23	-
24	-
25	0.540
26	-
27	-
28A	0.930
28B	-
29	-
30	0.200
31	0.400
32	-
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	0.610
45	-
46	-
47	-
48	0.600
49	-
50	-
51	-
52	-
53	0.700
54	-
55	-
56	-
No of labs., p	9
No of repl., n	2
d	0.389
s^2	0.570
s	0.755
$t = \sqrt{p} \cdot (d/s)$	1.5453
Sign. level, p(t)	0.1609

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	0.200	
2	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
10	-	
11	0.230	
12	0.000	
13	-0.040	
14	-	
15	0.530	
16	-	
17	0.480	
18	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	-	
25	-	
26	-	
27	-0.000	
28A	-	
28B	-	
29	-	
30	-	
31	-	
32	-	
33	-	
34	-	
35	-	
36	-	
37	0.110	
38	0.020	UG
39	-	
40	-	
41	-0.200	
42	-0.200	
43	-	
44	-	
45	-	
46	-0.240	
47	-	
48	-	
49	-	
50	-	
51	-0.070	
52	-	
53	-	
54	0.000	
55	-	
56	-	
No of labs., p	13	
No of repl., n	2	
d	0.062	
s^2	0.059	
s	0.243	
$t = \sqrt{p} \cdot (d/s)$	0.9114	
Sign. level, p(t)	0.3800	

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	-0.090	
2	0.410	
3	-	
4	-0.362	
5	-8.460	UC
6	-	
7	-	
8	0.100	
9	1.000	
10	-	
11	0.370	
12	0.500	
13	0.210	
14	-	
15	-	
16	-	
17	-	
18	0.230	
19	1.100	
20	-	
21	-	
22	-	
23	-1.100	
24	-0.160	
25	-	
26	0.300	
27	0.100	
28A	-	
28B	-	
29	-	
30	-0.070	UG
31	0.300	
32	-	
33	-	
34	0.000	
35	-	
36	-0.220	
37	0.250	
38	-	
39	-0.390	
40	-	
41	-0.100	
42	0.250	
43	0.300	
44	0.800	
45	-	
46	-	
47	-	
48	-0.700	
49	-0.640	UG
50	0.000	
51	-1.000	
52	0.300	
53	-0.400	
54	-0.300	
55	-	
56	0.350	
No of labs., p	30	
No of repl., n	2	
d	0.068	
s^2	0.252	
s	0.502	
$t = \sqrt{p} \cdot (d/s)$	0.7445	
Sign. level, p(t)	0.4626	

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	-0.0320	
2	0.0120	
3	0.0090	
4	0.0070	
5	0.0000	
6	-	
7	-0.0030	
8	0.0050	
9	0.0100	
10	0.0060	
11	-0.0430	UG
12	0.0010	
13	-0.0010	
14	0.0110	
15	0.0100	
16	-	
17	0.0150	
18	0.0180	
19	0.0160	
20	0.0100	
21	0.0190	
22	0.0140	
23	0.0080	
24	-	
25	0.0130	
26	-0.0040	
27	0.0110	
28A	-0.0020	
28B	-0.0120	
29	0.0230	
30	-0.0070	
31	0.0090	
32	0.0200	
33	0.0300	
34	-0.0250	
35	-	
36	0.0140	
37	0.0152	
38	-0.0310	
39	-	
40	-0.0200	
41	0.0120	
42	0.0510	
43	0.0030	
44	0.0240	
45	-0.0130	
46	0.0230	
47	0.0040	
48	0.0570	
49	-	
50	0.0140	
51	0.0200	
52	0.0140	
53	0.0200	
54	0.0070	
55	0.0250	
56	0.0040	
No of labs., p	50	
No of repl., n	2	
d	0.0087	
s^2	0.0003	
s	0.0166	
$t = \sqrt{p} \cdot (d/s)$	3.7067	
Sign. level, p(t)	0.0005	***

* 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

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	4.0	
2	-4.5	
3	-2.0	
4	-	
5	-2.0	
6	-	
7	-	
8	-1.0	
9	2.0	
10	6.0	
11	-	
12	-	
13	-	
14	-19.0	UG
15	-	
16	-	
17	-	
18	-	
19	-	
20	13.0	
21	12.0	
22	-	
23	-4.0	
24	-	
25	-4.0	
26	-4.0	
27	-2.2	
28A	17.0	
28B	3.0	
29	-	
30	-0.6	
31	1.0	
32	46.0	UC
33	5.0	
34	-	
35	-	
36	-	
37	-	
38	5.0	
39	4.1	
40	-3.0	
41	-	
42	-	
43	-	
44	-1.0	
45	-4.5	
46	-	
47	-	
48	-	
49	-	
50	-	
51	-	
52	-1.0	
53	0.5	
54	-	
55	-	
56	-	
No of labs., p	25	
No of repl., n	2	
d	1.6	
s^2	32.9	
s	5.7	
$t = \sqrt{p} \cdot (d/s)$	1.3535	
Sign. level, p(t)	0.1885	

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	-1.0
2	-
3	-
4	-
5	-
6	-
7	-
8	4.0
9	-3.0
10	-
11	-
12	-
13	-
14	-9.0
15	-
16	-
17	-
18	-
19	-
20	3.0
21	-
22	-
23	0.0
24	-
25	-
26	-8.0
27	-
28A	-5.5
28B	-
29	-
30	-3.0
31	-
32	-
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-7.0
44	-2.1
45	-
46	-
47	-
48	-
49	-
50	-
51	-
52	-6.7
53	-
54	-
55	-
56	-
No of labs., p	12
No of repl., n	2
d	-3.2
s^2	17.8
s	4.2
$t = \sqrt{p} \cdot (d/s)$	-2.6239
Sign. level, p(t)	0.0237 *

* 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.

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

Laboratory	Difference AB	
1	3.20	
2	0.70	
3	-0.70	
4	0.00	
5	-	
6	-	
7	9.20	UG
8	0.20	
9	-1.70	
10	-	
11	-1.70	
12	-0.60	
13	0.10	
14	-6.60	
15	-	
16	-	
17	1.00	
18	-2.70	
19	-0.30	
20	-	
21	4.30	
22	-	
23	-	
24	4.84	
25	0.40	
26	-	
27	10.20	
28A	41.40	UC
28B	-	
29	3.40	
30	1.50	
31	-0.87	
32	-	
33	-2.40	
34	-28.55	UC
35	-	
36	-14.90	
37	1.40	
38	-1.40	
39	-	
40	0.40	
41	23.60	UC
42	4.40	
43	-3.60	
44	-111.60	UC
45	1.70	
46	1.00	
47	0.20	
48	0.40	
49	0.70	
50	13.40	
51	3.60	
52	-0.10	
53	1.20	
54	-3.00	
55	8.40	
56	0.70	
No of labs., p	39	
No of repl., n	2	
d	0.69	
s^2	19.85	
s	4.46	
$t = \sqrt{p} \cdot (d/s)$	0.9621	
Sign. level, p(t)	0.3421	

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	-
2	32.40
3	31.75
4	-
5	-
6	-
7	31.85
8	-
9	35.65
10	31.55
11	25.69
12	-
13	-
14	28.05
15	-
16	-
17	-
18	-
19	29.50
20	27.90
21	31.65
22	36.70
23	30.50
24	-
25	11.25
26	32.25
27	-
28A	29.05
28B	29.35
29	29.85
30	36.30
31	29.50
32	30.75
33	30.45
34	-
35	-
36	35.80
37	39.53
38	27.50
39	-
40	28.20
41	-
42	31.05
43	43.25
44	27.70
45	23.50
46	31.65
47	34.60
48	27.15
49	29.40
50	-
51	35.30
52	-
53	27.27
54	32.00
55	42.30
56	52.40
No of labs., p	38
No of repl., n	2
m	31.59
s^2	40.72
s	6.38
Assigned value, μ	31
Recovery, %	101.9
$t = \sqrt{p} \cdot (m-\mu)/s$	0.5729
Sign. level, p(t)	0.5702

No test statistics were found to be significant

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

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5	2.510
6	-
7	-
8	-
9	-
10	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-
18	-
19	-
20	-
21	7.100
22	-
23	-
24	-
25	2.030
26	-
27	-
28A	3.345
28B	-
29	-
30	1.700
31	2.300
32	-
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	-
44	9.285
45	-
46	-
47	-
48	4.200
49	-
50	-
51	-
52	-
53	3.350
54	-
55	-
56	-
No of labs., p	9
No of repl., n	2
m	3.980
s^2	6.589
s	2.567
Assigned value, μ	2.6
Recovery, %	153.1
$t = \sqrt{p} \cdot (m-\mu)/s$	1.6129
Sign. level, p(t)	0.1454

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	2.500	
2	-	
3	-	
4	-	
5	-	
6	-	
7	-	
8	-	
9	-	
10	-	
11	2.605	
12	2.000	
13	2.500	
14	-	
15	3.315	
16	-	
17	3.630	
18	-	
19	-	
20	-	
21	-	
22	-	
23	-	
24	-	
25	-	
26	-	
27	2.400	
28A	-	
28B	-	
29	-	
30	-	
31	-	
32	-	
33	-	
34	-	
35	-	
36	-	
37	2.175	
38	8.240	UG
39	-	
40	-	
41	2.700	
42	1.900	
43	-	
44	-	
45	-	
46	3.150	
47	-	
48	-	
49	-	
50	-	
51	3.315	
52	-	
53	-	
54	2.200	
55	-	
56	-	
No of labs., p	13	
No of repl., n	2	
m	2.645	
s^2	0.302	
s	0.549	
Assigned value, μ	2.6	
Recovery, %	101.7	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.2979	
Sign. level, p(t)	0.7708	

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

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

Laboratory	Sample pair AB	
1	12.825	
2	13.135	
3	-	
4	11.737	
5	13.250	UC
6	-	
7	-	
8	10.850	
9	12.320	
10	-	
11	12.515	
12	12.250	
13	12.815	
14	-	
15	-	
16	-	
17	-	
18	12.085	
19	12.250	
20	-	
21	-	
22	-	
23	13.600	
24	14.110	
25	-	
26	13.550	
27	11.450	
28A	-	
28B	-	
29	-	
30	7.145	UG
31	12.250	
32	-	
33	-	
34	13.200	
35	-	
36	12.950	
37	12.225	
38	-	
39	12.355	
40	-	
41	12.150	
42	11.455	
43	12.150	
44	12.400	
45	-	
46	-	
47	-	
48	12.050	
49	16.520	UG
50	12.900	
51	15.000	
52	11.350	
53	10.950	
54	13.050	
55	-	
56	12.565	
No of labs., p	30	
No of repl., n	2	
m	12.483	
s^2	0.796	
s	0.892	
Assigned value, μ	12.3	
Recovery, %	101.5	
$t = \sqrt{p} \cdot (m-\mu)/s$	1.1239	
Sign. level, p(t)	0.2703	

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 recovery, average of results

Laboratory	Sample pair AB	
1	0.7620	
2	0.7710	
3	0.7815	
4	0.7365	
5	0.7400	
6	-	
7	0.7365	
8	0.7625	
9	0.7470	
10	0.7560	
11	0.5305	UG
12	0.7595	
13	0.7545	
14	0.7775	
15	0.7350	
16	-	
17	0.7715	
18	0.7400	
19	0.7530	
20	0.7560	
21	0.7985	
22	0.7860	
23	0.7590	
24	-	
25	0.7805	
26	0.8060	
27	0.7535	
28A	0.8160	
28B	0.7180	
29	0.8015	
30	0.7425	
31	0.8075	
32	0.8100	
33	0.7990	
34	0.7725	
35	-	
36	0.7670	
37	0.7657	
38	0.7675	
39	-	
40	0.7900	
41	0.7450	
42	0.7925	
43	0.7535	
44	0.7860	
45	0.7395	
46	0.7685	
47	0.7560	
48	0.7835	
49	-	
50	0.7610	
51	0.7460	
52	0.7660	
53	0.7800	
54	0.7725	
55	0.7645	
56	0.7860	
No of labs., p	50	
No of repl., n	2	
m	0.7676	
s^2	0.0005	
s	0.0224	
Assigned value, μ	0.75	
Recovery, %	102.3	
$t = \sqrt{p} \cdot (m-\mu)/s$	5.5597	
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)
UG denotes a Grubbs outlier

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

Laboratory	Sample pair AB	
1	193.0	
2	191.1	
3	185.0	
4	-	
5	185.0	
6	-	
7	-	
8	189.5	
9	196.0	
10	194.0	
11	-	
12	-	
13	-	
14	830.5	UG
15	-	
16	-	
17	-	
18	-	
19	-	
20	197.5	
21	192.0	
22	-	
23	172.0	
24	-	
25	171.0	
26	205.0	
27	187.3	
28A	229.5	
28B	168.5	
29	-	
30	194.3	
31	198.5	
32	191.0	UC
33	193.5	
34	-	
35	-	
36	-	
37	-	
38	170.5	
39	190.2	
40	178.5	
41	-	
42	-	
43	-	

Labortory	Sample pair AB
44	197.5
45	197.7
46	-
47	-
48	-
49	-
50	-
51	-
52	185.7
53	187.3
54	-
55	-
56	-
No of labs., p	25
No of repl., n	2
m	190.0
s^2	161.2
s	12.7
Assigned value, μ	192
Recovery, %	99.0
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.7888
Sign. level, p(t)	0.4379

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	105.5
2	-
3	-
4	-
5	-
6	-
7	-
8	107.0
9	110.5
10	-
11	-
12	-
13	-
14	111.5
15	-
16	-
17	-
18	-
19	-
20	115.5
21	-
22	-
23	117.0
24	-
25	-
26	96.0
27	-
28A	95.8
28B	-
29	-
30	105.2
31	-
32	-
33	-
34	-
35	-
36	-
37	-
38	-
39	-
40	-
41	-
42	-
43	102.5
44	90.0
45	-
46	-
47	-
48	-
49	-
50	-
51	-
52	105.7
53	-
54	-
55	-
56	-
No of labs., p	12
No of repl., n	2
m	105.2
s^2	66.1
s	8.1
Assigned value, μ	105
Recovery, %	100.2
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0763
Sign. level, p(t)	0.9405

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	51.20	
2	61.25	
3	59.85	
4	59.20	
5	-	
6	-	
7	42.60	UG
8	60.70	
9	64.95	
10	-	
11	58.65	
12	59.90	
13	60.05	
14	60.30	
15	-	
16	-	
17	58.00	
18	55.05	
19	60.85	
20	-	
21	57.35	
22	-	
23	-	
24	59.75	
25	58.80	
26	-	
27	63.60	
28A	64.30	UC
28B	-	
29	55.30	
30	59.85	
31	61.05	
32	-	
33	62.70	
34	44.95	UC
35	-	
36	47.45	
37	59.10	
38	60.10	
39	-	
40	58.80	
41	49.20	UC
42	57.40	
43	59.80	
44	659.80	UC
45	59.15	
46	57.90	
47	57.10	
48	56.70	
49	60.65	
50	67.60	
51	56.30	
52	59.55	
53	52.20	
54	61.00	
55	50.80	
56	60.65	
No of labs., p	39	
No of repl., n	2	
m	58.73	
s^2	14.08	
s	3.75	
Assigned value, μ	59.4	
Recovery, %	98.9	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.1091	
Sign. level, p(t)	0.2743	

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	23-13	29,00	29,00	29,00	28	31	3	4
			36-33	27,50	27,50	27,50				
			44-58	28,30	28,30	28,30				
		B1	23-14	32,5	31,50	31,50	31	35		
			38-34	30,3	30,40	30,40				
			58-55	31,1	31,20	31,20				
Total phosphorus	mg/L P	A2	5	1,02	1,02	1,02	1,0	0,89	0,16	0,14
			31	1,01	1,02	1,02				
			66	1,10	1,10	1,10				
		B2	3	0,88	0,86	0,87	0,89	0,75		
			35	0,86	0,85	0,85				
			62	0,94	0,94	0,94				
Chloride	mg/L	A2	5	228,00	230,00	229,00	234	227	43	35
			31	235,00	237,00	236,00				
			66	236,00	237,00	236,50				
		B2	3	191,00	192,00	191,50	191	192		
			35	193,00	193,00	193,00				
			62	189,00	190,00	189,50				
Sulphate	mg/L	A2	5	117,00	116,00	116,50	119	125	20	20
			31	122,00	119,00	120,50				
			66	120,00	120,00	120,00				
		B2	3	101,00	99,50	100,25	99	105		
			35	98,30	98,10	98,20				
			62	98,90	95,80	97,35				
Total suspended solids	mg/L	A3	8-6	62,20		62,20	62,1	59,4	12,4	12,4
			38-27	62,20		62,20				
			57-60	61,80		61,80				
		B3	12-9	74,20		74,20	74,5	71,8		
			38-40	74,80		74,80				
			62-56	74,50		74,50				

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: 2019-03-14

Sample	x(a)	x(b)	average	sd	sd^2
Dunk A1-3	28,9	28,3	28,6	0,424	0,180
Dunk A1-16	29,6	29,7	29,7	0,071	0,00
Dunk A1-20	29,3	29,6	29,5	0,212	0,045
Dunk A1-27	29,5	29,4	29,5	0,071	0,005
Dunk A1-30	29,1	29,2	29,2	0,071	0,005
Dunk A1-45	29,3	29,2	29,3	0,071	0,005
Dunk A1-46	29,2	29,1	29,2	0,071	0,005
Dunk A1-55	27,3	27,1	27,2	0,141	0,020
Dunk A1-63	29,2	29,0	29,1	0,141	0,020
Dunk A1-67	29,4	29,3	29,4	0,071	0,005
Dunk A1-71	29,9	30,0	30,0	0,071	0,005
Dunk A1-75	29,9	30,2	30,1	0,212	0,045

For homogeneity

General average (x)	29,20
Sample average sd (s_x)	0,739
Within-sample sd (s_w):	0,170
Between-samples sd (ss):	0,7295
S_L in the Proficiency Test:	6,32
S_R in the Proficiency Test:	6,45

Stability test Date: 2019-03-28

Sample	x(a)	x(b)
A1-23 13	29	29,0
A1-36 33	27,5	27,5
A1-44 58	28,36	28,3

For stability

General average (y):	28,276667
/x-y/ =	0,9191667

Conclusions

ss =	0,730	0.3*sigma=	3,24
/x-y/ =	0,9191667		

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
Parameter:	TP
Unit:	mg/L P
Sigma:	0,053

Responsible for tests: S7MS/HBP

Homogeneity test Date: 2019-03-14

Sample	x(a)	x(b)	average	sd	sd^2
A2-8	0,98	1,00	0,99	0,013	0,000
A2-	1,00	1,00	1,00	0,001	0,00
A2-15	0,99	1,01	1,00	0,017	0,000
A2-23	0,98	1,00	0,99	0,015	0,000
A2-28	0,99	1,00	1,00	0,005	0,000
A2-33	0,97	1,00	0,98	0,025	0,001
A2-37	1,00	1,01	1,01	0,007	0,000
A2-42	0,98	1,01	1,00	0,021	0,000
A2-46	1,00	1,00	1,00	0,004	0,000
A2-51	0,95	0,96	0,95	0,009	0,000
A2-68	0,95	0,97	0,96	0,008	0,000
A2-77	0,99	0,99	0,99	0,001	0,000

For homogeneity

General average (x)	0,99
Sample average sd (s_x)	0,016
Within-sample sd (s_w):	0,013
Between-samples sd (ss):	0,0129
S_L in the Proficiency Test:	0,0208
S_R in the Proficiency Test:	0,0239

Conclusions

ss = 0,013 0.3*sigma= 0,02

/x-y/ =

Homogeneity: Is ss < 0.3*sigma?

YES

PT:	SPIL-1
Parameter:	TSS
Unit:	mg/L
Sigma:	4,0

Responsible for tests: S7MS/HBP

Homogeneity test Date: 2019-03-14

Sample	x(a)	x(b)	average	sd	sd^2
B3-3-2	73,9		73,9		
B3-15-8	73,9		73,9		
B3-21-14	73,6		73,6		
B3-27-17	74,7		74,7		
B3-30-28	71,5		71,5		
B3-34-34	72,4		72,4		
B3-40-42	74,4		74,4		
B3-42-49	73,1		73,1		
B3-47-51	74,3		74,3		
B3-58-65	71,8		71,8		
B3-67-66	73,4		73,4		

For homogeneity

General average (x)	73,4
Sample average sd (s_x)	1,062
Within-sample sd (s_w):	
Between-samples sd (ss):	1,062
S_L in the Proficiency Test:	1,25
S_R in the Proficiency Test:	1,79

Stability test Date: 2019-03-28

Sample	x(a)	x(b)
B3-12-9	74,2	
B3-38-40	74,8	
B3-62-56	74,5	

For stability

General average (y):	74,5
/x-y/ =	1,1363636

Conclusions

ss = 1,06 0.3*sigma= 1,19

/x-y/ = 1,1363636

Homogeneity: Is ss < 0.3*sigma?
YES

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