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Proficiency test SPIL-3 (2015)

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

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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 3 September 2015. 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 5 October 2015.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 63 laboratories from Denmark and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 18 September 2015. All participants, except laboratory no. 15, 25 and 34 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 synthetic wastewater, effluent. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	COD_{Cr}, BOD, NVOC
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 synthetic wastewater, 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	23.6	0.31	14.2
Five day biochemical oxygen demand	BOD_5 (w. ATU)	mg/L O_2	2 – 6	3	1.0	1
Seven day biochemical oxygen demand	BOD_7 (w. ATU)	mg/L O_2	2 – 6	2.8	0.37	1.2
Non-volatile organic carbon	NVOC/TOC	mg/L C	2 – 30	9.3	0.12	5.6
Total phosphorus	TP	mg/L P	0.2 – 2	0.607	0.0047	0.099
Chloride	Cl	mg/L	50 – 700	110.3	0.70	0.0
Sulphate	SO_4	mg/L	20 – 200	49.2	0.31	6.6
Total suspended solids	TSS	mg/L	20 - 100	23.1	0.79	4.5

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.

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. The assigned and spike values are both calculated from sample preparation except for BOD and TSS where spike values are calculated from sample preparation and assigned values are consensus values for laboratories using standardised methods (method no. 1 - 4), based on the median.

2.3.2 Test of spike values

A comparison was made (t-test, 95% confidence level) between the spike value and the difference in concentration between the two samples in the sample pair found from the laboratories' results, see Appendix C. The test revealed a significant difference between the two for COD_{Cr}, NVOC and TP. However, the difference is numerically small and has insignificant influence on the general quality of analyses estimated from the data as well as on the evaluation of accuracy of participating laboratories.

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. For most parameters the test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E). However, a significant difference between the two was found for Cl and TSS.

For Cl the average recovery was 94%. The difference could be attributed to influence from laboratories using method 52, which has previously been shown to give low results. The test was repeated after exclusion of the results for method no. 52 and now showed no significant difference. The assigned value is therefore kept unchanged.

Average recovery for TSS was 96%. A number of the participants noted that the solids were hard to bring into suspension and to some extent stuck to the walls of the con-

tainer. This is a probable cause for the low recovery and caution is therefore recommended when evaluating results for this parameter.

3 HOMOGENEITY OF SAMPLES

The homogeneity of samples was tested using the following parameters as indicators:

TP	Homogeneity test
TSS	Homogeneity 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).

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/. This test ensures that heterogeneity 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 homogeneity show that the samples are homogeneous.

4 CONCLUSION

The quality control performed, including test of sample homogeneity as well as test of recovery of spike and assigned values, shows that the samples and their assigned values are suitable for testing the proficiency of the participating laboratories for all parameters. The results are also suitable for estimation of the general quality of analyses among all participating laboratories.

For COD_{Cr}, NVOC and TP 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 Cl and TSS the participants did not recover the assigned value. Eurofins' scrutiny of the combined evidence gave the conclusion that the assigned value for Cl is correct as the difference could be attributed to results for method no. 52, which has previously been shown to give low values. The assigned value for Cl is therefore kept unchanged and it is recommended as the basis for evaluation of participating laboratories.

For TSS a number of the participants noted that the solids were hard to bring into suspension and to some extent stuck to the walls of the container. This is a probable cause for the low recovery and caution is therefore recommended when evaluating results for this parameter.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-3 (2015)*, Report to participants, October 2015.

/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. 231 on *quality criteria for environmental measurements,* 5 March 2014 (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
Analyseenheden, Institut for Agroøkologi	Tjele	Denmark
AquaDjurs - Fornæs Renseanlæg	Grenaa	Denmark
Biofos A/S	København K	Denmark
Bjergmarken R/A, Roskilde Forsyning	Roskilde	Denmark
CP Kelco ApS, Spildevandslaboratoriet	Ll. Skensved	Denmark
Esbjerg Forsyning Spildevandslaboratorium	Esbjerg	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Faxe Forsyning	Faxe	Denmark
FORCE Technology	Holstebro	Denmark
Frederikssund Forsyning	Frederikssund	Denmark
Greve Solrød Forsyning	Greve	Denmark
Halsnæs Spildevand A/S	Liseleje	Denmark
Hedensted Spildevand A/S	Daugård	Denmark
Hillerød Forsyning Spildevand A/S	Hillerød	Denmark
Højmarklaboratoriet	Lem St.	Denmark
Holbæk Forsyning	Holbæk	Denmark
Holstebro Centralrenseanlæg, Vestforsyning A/S	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Køge-Egnens Renseanlæg	Køge	Denmark
Kolding Spildevand A/S	Bjert	Denmark
Middelfart Spildevand A/S	Middelfart	Denmark
Mølleåværkets Driftslaboratorium	Lyngby	Denmark
NK-Spildevand Lab	Næstved	Denmark
Nyborg Renseanlæg	Nyborg	Denmark
Provas Haderslev Forsyningsservice A/S	Haderslev	Denmark
Randers Spildevand A/S	Randers SØ	Denmark
Rønne Renseanlæg	Rønne	Denmark
SK Forsyning, Slagelse Renseanlæg	Slagelse	Denmark
Svendborg Centralrenseanlæg	Skårup Fyn	Denmark
Tårnby Forsyning	Kastrup	Denmark
Vejle Spildevand A/S	Vejle	Denmark
AB Borlänge Energi, Reningsverket	Borlänge	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
Eurofins Environment Testing Sweden AB	Lidköping	Sweden
Fiskeby Board AB	Norrköping	Sweden

Laboratory	Town	Country
Gästrike Vatten AB	Skutskär	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Hallstavik	Sweden
Holmen Paper AB, Bravikens Pappersbruk	Norrköping	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun	Motala	Sweden
Perstorp Oxo AB	Stenungsund	Sweden
Preem AB	Göteborg	Sweden
Preemraff	Lysekil	Sweden
Roslagsvatten AB	Åkersberga	Sweden
Rottneros Bruk AB	Rottneros	Sweden
Ekokem AB	Kumla	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
St1 Refinery AB	Göteborg	Sweden
Uppsala Vatten o. Avfall AB, Vattenlaboratoriet	Uppsala	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Västerviks Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Vattenfall AB Heat Generation Uppsala	Uppsala	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**	**Concentration**
Concentrate A1	12.00 g D-glucose 12.00 g L-glutamic acid milli-Q water up to 13000 g	COD_{Cr}: 1.888 g/kg NVOC: 0.746 g/kg BOD: 1.292 g/kg
Concentrate B1	7.50 g D-glucose 7.50 g L-glutamic acid milli-Q water up to 13000 g	COD_{Cr}: 1.180 g/kg NVOC: 0.466 g/kg BOD: 0.808 g/kg
Stock TP	1.4993 g Na-beta glycerophosphate milli-Q water up to 1000.0 g	TP: 151.8 mg/kg
Stock Cl	10.0003 g Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.067 g/kg
Stock SO_4	5.0002 g Sodium sulphate (Na_2SO_4) milli-Q water up to 1000.0 g	SO_4: 3.381 g/kg
Stock TSS	15.0023 g Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.002 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 Milli-Q water	37.7	14.9					
B1-COD/NVOC	At the laboratory 2.00 mL of concentrate B1 is diluted up to 100.0 mL with Milli-Q water	23.6	9.3					
A1-BOD	At the laboratory 5.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Vejrup sewage treatment plant			c + 3.2				
B1-BOD	At the laboratory 5.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Vejrup sewage treatment plant			c + 2.0				
A2	20.0 g stock PO_4 0 g stock Cl 60.0 g stock SO_4 Sample B2 up to 30,16 kg				0.997 · 0.607 + 0.100	0.997 · 110.3	0.997 ·49.2 + 6.7	
B2	200.0 g stock PO_4 1000.0 g stock Cl 800.0 g stock SO_4 Milli-Q water up to 55,0 kg				0.607	110.3	49.2	
A3	At the laboratory 1000.0 mL of Milli-Q water is added to 1,6 mL stock TSS							24.0
B3	At the laboratory 1000.0 mL Milli-Q water is added to 1,9 mL stock TSS							28.5

ANNEX C CONTROL OF SPIKE VALUES

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

Laboratory	Difference AB	
1	7.10	
2	-	
3	-	
4	1.10	
5	-4.30	
6	-2.50	
7	2.40	
8A	-2.00	
8B	-	
9	-3.10	
10	-4.20	
11	3.10	
12A	-1.10	
12B	-2.10	
12C	0.90	
12D	-2.80	
13	-6.40	UG
14	-	
16	-3.30	
17A	-	
17B	-	
18	-6.10	
19	-2.90	
20	-3.50	
21	-2.20	
22	0.80	
23	-2.00	
24	6.20	
26	-	
27	-2.90	
28	1.60	
29	-	
30	-	
31	-3.90	
32	-2.10	
33	3.20	
35	-2.10	
36	1.80	
37A	-0.50	
37B	-1.60	
38	-3.00	
39	3.10	
40	-1.20	
41	-1.50	
42	-	
43	-2.20	
44	-	
45	1.20	
46	8.10	
47	-	
48A	-1.10	
48B	-3.70	
49	0.20	
50	0.70	
51	-2.90	
52	-	
53A	-	
53B	-	
54	-2.00	
55	-3.90	
56	-	
57	-1.16	UG
58	-0.10	
59	-	
60	-0.75	
61	-2.10	
62	-3.10	
63	-2.50	
No of labs., p	49	
No of repl., n	2	
d	-0.89	
s^2	8.84	
s	2.97	
$t = \sqrt{p} \cdot (d/s)$	-2.1023	
Sign. level, p(t)	0.0408	*

* 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

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

Laboratory	Difference AB
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8A	0.450
8B	-
9	-
10	-
11	-
12A	0.400
12B	-
12C	0.170
12D	-
13	0.560
14	-
16	-0.170
17A	-
17B	-
18	-0.230
19	-
20	-
21	-0.050
22	-
23	-
24	-
26	-
27	-0.350
28	-
29	-
30	-
31	-0.650
32	0.220
33	-
35	-0.350
36	0.300
37A	-
37B	-
38	-
39	-
40	0.240
41	-0.600
42	-
43	-0.770
44	-
45	-
46	-
47	-
48A	-0.620
48B	-
49	-
50	-
51	0.500
52	-
53A	-
53B	-
54	-
55	0.000
56	-
57	-
58	-
59	-
60	-
61	-
62	9.900 UC
63	-
No of labs., p	18
No of repl., n	2
d	-0.053
s^2	0.188
s	0.433
$t = \sqrt{p} \cdot (d/s)$	-0.5169
Sign. level, p(t)	0.6119

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	Difference AB
1	-
2	0.080
3	-
4	-
5	-
6	-
7	-
8A	-
8B	-
9	-
10	-
11	-
12A	-
12B	-
12C	-
12D	-
13	-
14	-
16	-
17A	-0.200
17B	-
18	-
19	-
20	-
21	-
22	0.520
23	-
24	-
26	-
27	-
28	-
29	-0.100
30	-
31	-
32	-
33	0.050
35	-
36	-
37A	-
37B	-
38	-
39	-
40	-0.050
41	-
42	-
43	-
44	-0.190
45	-
46	-
47	0.340
48A	-
48B	-
49	-0.350
50	-
51	-
52	-
53A	-
53B	-
54	-
55	-
56	-
57	-
58	-
59	-
60	-
61	0.870
62	-
63	-
No of labs., p	10
No of repl., n	2
d	0.097
s^2	0.141
s	0.375
$t = \sqrt{p} \cdot (d/s)$	0.8169
Sign. level, p(t)	0.4350

No test statistics were found to be significant

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

Laboratory	Difference AB	
1	-	
2	0.10	
3	-0.70	
4	-	
5	-	
6	-0.70	
7	-	
8A	-0.36	
8B	-	
9	-	
10	1.00	
11	-	
12A	6.09	UC
12B	-	
12C	-	
12D	-	
13	-	
14	-	
16	-	
17A	-0.59	
17B	-	
18	-	
19	-	
20	-	
21	-0.37	
22	-0.61	
23	-	
24	-0.60	
26	-	
27	-	
28	-0.48	
29	-0.50	
30	-	
31	-	
32	0.00	
33	-0.07	
35	-	
36	-	
37A	-	
37B	0.30	
38	-	
39	-	
40	-	
41	-	
42	-0.28	
43	-	
44	0.31	
45	-0.30	
46	-	
47	-0.10	
48A	-	
48B	-	
49	-	
50	-	
51	-0.20	
52	-	
53A	-0.15	
53B	-	
54	-	
55	-	
56	-0.30	
57	-	
58	-1.04	
59	-	
60	-	
61	-0.76	
62	-3.80	UC
63	-	
No of labs., p	23	
No of repl., n	2	
d	-0.28	
s^2	0.19	
s	0.44	
$t = \sqrt{p} \cdot (d/s)$	-3.0490	
Sign. level, p(t)	0.0059	**

* 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

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

Laboratory	Difference AB	
1	0.0010	
2	-0.0480	UG
3	-0.0060	
4	-0.0180	
5	-0.0190	
6	0.0010	
7	-0.0040	
8A	-0.0010	
8B	-0.0080	
9	-0.0090	
10	-0.0180	
11	-0.0110	
12A	0.0050	
12B	-0.0033	
12C	-0.0020	
12D	-	
13	0.0080	
14	0.0050	
16	0.0110	
17A	-0.0109	
17B	-0.0030	
18	-0.0140	
19	-0.0100	
20	-0.0030	
21	0.0010	
22	0.0040	
23	-0.0110	
24	0.0210	
26	-	
27	-0.0130	
28	-0.0030	
29	0.0040	
30	-	
31	-0.0290	
32	0.0050	
33	0.0020	
35	-0.0050	
36	-0.0300	
37A	-0.0080	
37B	0.0020	
38	-0.0480	
39	-0.0060	
40	-0.0290	
41	-0.0170	
42	-0.0140	
43	-0.0130	
44	-0.0180	
45	0.0010	
46	-	
47	-0.0030	
48A	0.0110	
48B	-0.0110	
49	-0.0050	
50	-0.0110	
51	0.0090	
52	0.0040	
53A	-	
53B	-	
54	-0.0040	
55	0.0010	
56	-0.0010	
57	0.0450	
58	-0.0160	
59	-0.0080	
60	0.0035	
61	0.0010	
62	0.0130	
63	-0.0010	
No of labs., p	61	
No of repl., n	2	
d	-0.0047	
s^2	0.0002	
s	0.0132	
$t = \sqrt{p} \cdot (d/s)$	-2.7638	
Sign. level, p(t)	0.0076	**

* 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	Difference AB	
1	-5.00	UG
2	-	
3	3.20	
4	3.10	
5	4.20	
6	-3.40	
7	0.00	
8A	-0.50	
8B	-0.50	
9	4.00	
10	1.00	
11	-	
12A	-2.00	
12B	-	
12C	-	
12D	-	
13	-2.00	
14	-	
16	-0.10	
17A	-2.03	
17B	-	
18	-0.60	
19	-46.00	UC
20	-2.00	
21	1.00	
22	-0.50	
23	16.00	UC
24	-1.00	
26	-	
27	-35.00	UC
28	-	
29	-2.08	
30	-	
31	0.60	
32	-0.60	
33	-	
35	-	
36	0.00	
37A	0.00	
37B	1.00	
38	1.00	
39	-	
40	-4.00	
41	1.60	
42	-	
43	-6.90	
44	-	
45	-	
46	-	
47	-	
48A	-4.10	
48B	2.30	
49	-	
50	0.40	UG
51	-1.00	
52	0.39	
53A	-0.52	
53B	1.10	
54	-0.10	
55	-4.70	
56	-	
57	-	
58	-	
59	-3.40	
60	-	
61	-	
62	-1.90	
63	-5.00	
No of labs., p	39	
No of repl., n	2	
d	-0.63	
s^2	6.06	
s	2.46	
$t = \sqrt{p} \cdot (d/s)$	-1.5899	
Sign. level, p(t)	0.1201	

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

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

Laboratory	Difference AB	
1	-	
2	-	
3	-2.30	
4	-	
5	-	
6	-	
7	-15.10	UC
8A	-0.30	
8B	0.60	
9	-	
10	1.55	
11	-	
12A	-	
12B	-	
12C	-	
12D	-	
13	-	
14	-	
16	-7.60	
17A	-1.78	
17B	-	
18	-2.80	
19	-3.60	
20	-	
21	-	
22	-2.70	
23	-	
24	-0.50	
26	-	
27	-	
28	0.30	
29	-	
30	-	
31	2.40	
32	0.20	
33	-	
35	-	
36	-	
37A	-	
37B	-1.70	
38	-	
39	-	
40	-	
41	8.50	
42	-	
43	-	
44	-	
45	-	
46	-	
47	-	
48A	0.30	
48B	-	
49	-	
50	-	
51	-	
52	-0.16	
53A	-0.30	
53B	-	
54	-	
55	-	
56	-	
57	-	
58	-7.10	UG
59	-	
60	-	
61	-	
62	-	
63	2.80	
No of labs., p	19	
No of repl., n	2	
d	-0.37	
s^2	10.21	
s	3.20	
$t = \sqrt{p} \cdot (d/s)$	-0.5088	
Sign. level, p(t)	0.6171	

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

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

Laboratory	Difference AB	
1	4.00	UG
2	-0.40	
3	-0.10	
4	-4.20	
5	-	
6	-	
7	-	
8A	-1.10	
8B	-	
9	-	
10	-2.50	
11	-	
12A	0.50	
12B	-	
12C	-	
12D	-	
13	1.50	
14	2.60	
16	1.30	
17A	0.40	
17B	-	
18	0.30	
19	-1.80	
20	-	
21	1.20	
22	0.00	
23	-0.50	
24	0.10	
26	-0.23	
27	5.10	
28	-2.00	
29	-0.60	
30	0.80	
31	0.70	
32	-0.30	
33	9.70	
35	-0.60	
36	-0.30	
37A	-	
37B	-1.50	
38	-	
39	6.50	
40	-3.50	
41	1.70	
42	0.60	
43	-1.00	
44	-1.70	
45	-5.70	
46	4.50	
47	-16.50	UC
48A	-8.70	
48B	-	
49	13.50	UC
50	-0.30	
51	0.70	
52	-	

Laboratory	Difference AB
53A	-
53B	-
54	0.40
55	4.10
56	-1.40
57	-4.50
58	7.50
59	-
60	0.00
61	-1.50
62	2.00
63	-
No of labs., p	46
No of repl., n	2
d	0.17
s^2	10.24
s	3.20
$t = \sqrt{p} \cdot (d/s)$	0.3580
Sign. level, p(t)	0.7220

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	34.85	
2	-	
3	-	
4	23.35	
5	21.85	
6	21.65	
7	22.50	
8A	21.70	
8B	-	
9	23.15	
10	21.30	
11	15.75	
12A	21.35	
12B	21.55	
12C	16.15	
12D	23.30	
13	39.60	UG
14	-	
16	26.35	
17A	-	
17B	-	
18	12.65	
19	19.75	
20	21.55	
21	19.50	
22	27.40	
23	21.00	
24	29.90	
26	-	
27	21.05	
28	19.20	
29	-	
30	-	
31	25.25	
32	19.35	
33	30.50	
35	22.95	
36	18.90	
37A	20.65	
37B	21.50	
38	25.40	
39	27.95	
40	30.40	
41	18.05	
42	-	
43	21.10	
44	-	
45	21.10	
46	28.05	
47	-	
48A	23.05	
48B	27.85	
49	23.40	
50	21.95	
51	19.45	
52	-	
53A	-	
53B	-	
54	22.10	
55	25.55	
56	-	
57	39.44	UG
58	22.72	
59	19.80	
60	23.07	
61	20.55	
62	22.65	
63	25.95	
No of labs., p	49	
No of repl., n	2	
m	22.78	
s^2	16.34	
s	4.04	
Assigned value, μ	23.6	
Recovery, %	96.5	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.4193	
Sign. level, p(t)	0.1623	

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

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

Laboratory	Sample pair AB
1	-
2	-
3	-
4	-
5	-
6	-
7	-
8A	3.575
8B	-
9	-
10	-
11	-
12A	3.300
12B	-
12C	1.825
12D	-
13	4.830
14	-
16	3.545
17A	-
17B	-
18	3.825
19	-
20	-
21	2.355
22	-
23	-
24	-
26	-
27	2.055
28	-
29	-
30	-
31	2.655
32	2.170
33	-
35	3.855
36	2.450
37A	-
37B	-
38	-
39	-
40	3.360
41	3.340
42	-
43	3.395
44	-
45	-
46	-
47	-
48A	3.500
48B	-
49	-
50	-
51	2.250
52	-
53A	-
53B	-
54	-
55	4.000
56	-
57	-
58	-
59	-
60	-
61	-
62	9.150 UC
63	-
No of labs., p	18
No of repl., n	2
m	3.127
s^2	0.659
s	0.812
Assigned value, μ	3
Recovery, %	104.2
$t = \sqrt{p} \cdot (m-\mu)/s$	0.6635
Sign. level, p(t)	0.5159

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	-
2	2.730
3	-
4	-
5	-
6	-
7	-
8A	-
8B	-
9	-
10	-
11	-
12A	-
12B	-
12C	-
12D	-
13	-
14	-
16	-
17A	2.500
17B	-
18	-
19	-
20	-
21	-
22	2.730
23	-
24	-
26	-
27	-
28	-
29	2.650
30	-
31	-
32	-
33	3.635
35	-
36	-
37A	-
37B	-
38	-
39	-
40	3.545
41	-
42	-
43	-
44	3.115
45	-
46	-
47	3.150
48A	-
48B	-
49	2.305
50	-
51	-
52	-
53A	-
53B	-
54	-
55	-
56	-
57	-
58	-
59	-
60	-
61	2.725
62	-
63	-
No of labs., p	10
No of repl., n	2
m	2.908
s^2	0.192
s	0.438
Assigned value, μ	2.8
Recovery, %	103.9
$t = \sqrt{p} \cdot (m-\mu)/s$	0.7828
Sign. level, p(t)	0.4539

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	-	
2	9.15	
3	8.85	
4	-	
5	-	
6	10.25	
7	-	
8A	8.58	
8B	-	
9	-	
10	10.90	
11	-	
12A	12.66	UC
12B	-	
12C	-	
12D	-	
13	-	
14	-	
16	-	
17A	9.44	
17B	-	
18	-	
19	-	
20	-	
21	9.68	
22	9.01	
23	-	
24	11.60	
26	-	
27	-	
28	8.94	
29	7.95	
30	-	
31	-	
32	10.10	
33	9.52	
35	-	
36	-	
37A	-	
37B	10.75	
38	-	
39	-	
40	-	
41	-	
42	9.13	
43	-	
44	9.64	
45	10.25	
46	-	
47	9.55	
48A	-	
48B	-	
49	-	
50	-	
51	9.80	
52	-	
53A	9.37	
53B	-	
54	-	
55	-	
56	8.65	
57	-	
58	7.60	
59	11.50	
60	-	
61	8.13	
62	13.40	UC
63	-	
No of labs., p	23	
No of repl., n	2	
m	9.43	
s^2	0.92	
s	0.96	
Assigned value, μ	9.3	
Recovery, %	101.4	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.6391	
Sign. level, p(t)	0.5294	

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

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

Laboratory	Sample pair AB	
1	0.6305	
2	0.2850	UG
3	0.5730	
4	0.5900	
5	0.6025	
6	0.6005	
7	0.5760	
8A	0.6445	
8B	0.5890	
9	0.6255	
10	0.5940	
11	0.6145	
12A	0.6355	
12B	0.6266	
12C	0.6510	
12D	-	
13	0.6130	
14	0.5655	
16	0.6455	
17A	0.5980	
17B	0.6095	
18	0.6380	
19	0.6200	
20	0.6195	
21	0.5995	
22	0.6140	
23	0.6025	
24	0.5905	
26	-	
27	0.6015	
28	0.5825	
29	0.5870	
30	-	
31	0.6355	
32	0.5875	
33	0.5910	
35	0.5875	
36	0.5890	
37A	0.6040	
37B	0.6150	
38	0.5450	
39	0.5890	
40	0.6255	
41	0.6385	
42	0.6170	
43	0.6105	
44	0.5900	
45	0.5905	
46	-	
47	0.5915	
48A	0.6255	
48B	0.5935	
49	0.5815	
50	0.6005	
51	0.5945	
52	0.5980	
53A	-	
53B	-	
54	0.5860	
55	0.6105	
56	0.5865	
57	0.6165	
58	0.5690	
59	0.5930	
60	0.5893	
61	0.6005	
62	0.6075	
63	0.5385	
No of labs., p	61	
No of repl., n	2	
m	0.6023	
s^2	0.0005	
s	0.0227	
Assigned value, μ	0.607	
Recovery, %	99.2	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.6344	
Sign. level, p(t)	0.1074	

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

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

Laboratory	Sample pair AB	
1	753.50	UG
2	-	
3	102.80	
4	109.45	
5	92.70	
6	91.30	
7	110.00	
8A	108.45	
8B	111.45	
9	108.00	
10	107.50	
11	-	
12A	117.00	
12B	-	
12C	-	
12D	-	
13	118.00	
14	-	
16	86.85	
17A	104.20	
17B	-	
18	93.50	
19	598.00	UC
20	83.40	
21	117.50	
22	109.35	
23	110.00	UC
24	111.50	
26	-	
27	686.50	UC
28	-	
29	109.78	
30	-	
31	89.40	
32	109.40	
33	-	
35	-	
36	110.00	
37A	105.00	
37B	99.00	
38	103.50	
39	-	
40	106.00	
41	90.80	
42	-	
43	81.65	
44	-	
45	-	
46	-	
47	-	
48A	93.25	
48B	99.85	
49	-	
50	53.80	UG
51	117.50	
52	110.93	
53A	109.18	
53B	107.95	
54	110.30	
55	95.95	
56	-	
57	-	
58	-	
59	99.30	
60	-	
61	-	
62	106.15	
63	108.50	
No of labs., p	39	
No of repl., n	2	
m	103.75	
s^2	91.86	
s	9.58	
Assigned value, μ	110.3	
Recovery, %	94.1	
$t = \sqrt{p} \cdot (m-\mu)/s$	-4.2663	
Sign. level, p(t)	0.0001	***

* 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

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

Laboratory	Sample pair AB	
1	-	
2	-	
3	48.25	
4	-	
5	-	
6	40.90	
7	19.35	UC
8A	46.55	
8B	48.70	
9	-	
10	55.02	
11	-	
12A	-	
12B	-	
12C	-	
12D	-	
13	-	
14	-	
16	44.20	
17A	48.66	
17B	-	
18	36.90	
19	52.70	
20	-	
21	-	
22	46.55	
23	-	
24	48.45	
26	-	
27	-	
28	41.85	
29	-	
30	-	
31	51.20	
32	48.20	
33	-	
35	-	
36	-	
37A	-	
37B	37.25	
38	-	
39	-	
40	-	
41	49.25	
42	-	
43	-	
44	-	
45	-	
46	-	
47	-	
48A	50.75	
48B	-	
49	-	
50	-	
51	-	
52	48.59	
53A	47.35	
53B	-	
54	-	
55	-	
56	-	
57	-	
58	72.25	UG
59	39.10	
60	-	
61	-	
62	-	
63	45.40	
No of labs., p	19	
No of repl., n	2	
m	47.15	
s^2	21.17	
s	4.60	
Assigned value, μ	49.2	
Recovery, %	95.8	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.9436	
Sign. level, p(t)	0.0677	

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

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

Laboratory	Sample pair AB	
1	0.30	UG
2	23.20	
3	23.65	
4	21.20	
5	-	
6	-	
7	-	
8A	24.35	
8B	-	
9	-	
10	22.25	
11	-	
12A	23.55	
12B	-	
12C	-	
12D	-	
13	24.25	
14	19.70	
16	22.15	
17A	23.40	
17B	-	
18	22.85	
19	24.20	
20	-	
21	21.40	
22	23.60	
23	23.75	
24	23.05	
26	23.91	
27	19.65	
28	22.70	
29	23.80	
30	21.30	
31	22.85	
32	23.45	
33	23.45	
35	23.20	
36	23.25	
37A	-	
37B	22.35	
38	-	
39	15.75	
40	24.75	
41	17.55	
42	21.00	
43	23.90	
44	22.15	
45	19.35	
46	20.75	
47	234.25	UC
48A	27.15	
48B	-	
49	22.75	UC
50	22.45	
51	20.55	
52	-	
53A	-	
53B	-	
54	23.30	
55	18.75	
56	20.40	
57	22.25	
58	16.25	
59	-	
60	23.10	
61	22.95	
62	23.50	
63	-	
No of labs., p	46	
No of repl., n	2	
m	22.22	
s^2	4.84	
s	2.20	
Assigned value, μ	23.1	
Recovery, %	96.2	
$t = \sqrt{p} \cdot (m-\mu)/s$	-2.7014	
Sign. level, p(t)	0.0097	**

* 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 markerer en Cochran outlier
UG markerer en 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	27	33.60	33.50	33.55	33,4	37,8	11,8	14,2
			37	32.70	33.10	32.90				
			45	34.20	33.40	33.80				
		B1	1	22.10	21.80	21.95	21,6	23,6		
			18	21.60	21.60	21,.60				
			22	21.20	21.40	21.30				
Total phosphorus	mg/L P	A2	7	0.680	0.676	0.68	0,688	0,706	0,092	0,099
			38	0.704	0.705	0.70				
			81	0.684	0.679	0.68				
		B2	48	0.597	0.590	0.59	0,596	0,607		
			71	0.598	0.597	0.60				
			6	0.595	0.597	0.60				
Chloride	mg/L	A2	7	82.90	86.20	84.55	82,8	110,0	-0,58	0,0
			38	82.0	81.6	81.80				
			81	82.6		82.10				
		B2	48	83.3	83.5	83.40	83,4	110,3		
			71	84.4		84.40				
			6	82.3	82.5	82.40				
Sulphate	mg/L	A2	7	43.2	43.1	43.15	43,3	55,8	8,7	6,6
			38	45.5	42.1	43.80				
			81	43.5	42.5	43.00				
		B2	48	38.2	36.1	37.15	34,6	49,2		
			71	32.6	31.5	32.05				
			6	36.80	32.50	34.65				
Total suspended solids	mg/L	A3	3	23.8		23.80	24,3	23,1	-3,8	4,5
			17	24.1		24.10				
			38	25.1		25.10				
		B3	10	27.2		27.20	28,1	27,6		
			29	28.1		28.10				
			74	29.1		29.10				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-3 2015		
Parameter:	TP		
Unit:	mg/L P		
Sigma:	0,0503	6,5% of x	
		6,5% level or 1,3*$S_{T\ max}$	

Responsible for tests: IRL

Homogeneity test Date: 2015-08-19

Sample	x(a)	x(b)	average	sd	sd^2
A2-41	0,769	0,778	0,774	0,006	0,000
A2-33	0,764	0,787	0,776	0,016	0,00
A2-25	0,785	0,792	0,789	0,005	0,000
A2-18	0,786	0,777	0,782	0,006	0,000
A2-10	0,760	0,775	0,768	0,011	0,000
A2-03	0,771	0,762	0,767	0,006	0,000
A2-*86	0,766	0,756	0,761	0,007	0,000
A2-76	0,784	0,776	0,780	0,006	0,000
A2-61	0,778	0,784	0,781	0,004	0,000
A2-68	0,773	0,783	0,778	0,007	0,000
A2-11	0,770	0,762	0,766	0,006	0,000
A2-12	0,774	0,777	0,776	0,002	0,000

For homogeneity

General average (x)	0,775
Sample average sd (s_x)	0,0080
Within-sample sd (s_w):	0,0077
Between-samples sd (ss):	0,0058
S_L in the Proficiency Test:	
S_R in the Proficiency Test:	

Conclusions

ss =	0,006	0.3*sigma= 0,01
/x-y/ =	0	
Analytical quality	Is s_w < 0,15*sigma **NO**	
Homogeneity:	Is ss < 0.3*sigma? **YES**	

PT:	SPIL-3 2015
Parameter:	TSS
Unit:	mg/L
Sigma:	3,9

$1{,}3*s_{T\,max}$

$6{,}5\%$ level or $1{,}3*S_{T\,max}$

Responsible for tests: IRL

Homogeneity test Date: 2015-08-20

Sample	x(a)	x(b)	average	sd	sd^2
A3-63	28,5		28,5		
A3-66	28,5		28,5		
A3-71	28,0		28,0		
A3-46	27,2		27,2		
A3-53	28,2		28,2		
A3-58	28,3		28,3		
A3-39	28,9		28,9		
A3-34	28,1		28,1		
A3-04	28,6		28,6		
A3-19	28,1		28,1		
A3-13	28,9		28,9		
A3-26	28,9		28,9		

For homogeneity

General average (x)	28,4
Sample average sd (s_x)	0,487
Within-sample sd (s_w):	
Between-samples sd (ss):	0,487
S_L in the Proficiency Test:	
S_R in the Proficiency Test:	

Conclusions

ss =	0,49	0.3*sigma= 1,17
/x-y/ =	0	
Analytical quality	Is $s_w < 0{,}15*$sigma	
	No data	
Homogeneity:	Is ss < 0.3*sigma?	
	YES	