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Proficiency test SPIL-1 (2022)

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

Quality Documentation
May 2022

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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 17 March 2022. 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 20 April 2022.

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 1 April 2022. All participants except laboratory no. 19, 36, 47 and 48 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" (2019) /2/ and as described in detail in Spliid (1992) /3/. A short introduction to the statistics and a list of symbols and abbreviations used is given in Eurofins document "Schedule for a proficiency test", which is available at Eurofins' home page /4/.

The statistical model used is based on the assumption that the variances for the two samples in a sample pair are identical. The assumption was tested (F-test, 95% confidence level) and the result was that the two variances may be assumed to be identical for all parameters.

2.3 Assigned and spike value

An overview of the concentrations in the samples (the assigned values) and the difference in concentration between the two samples of a sample pair (spike value) are shown in Table 2 compared to the range of concentrations normally encountered in effluent. The table also gives the expanded uncertainty of the assigned values.

An error was made in some of the preparation instructions for B1 COD/NVOC. A corrected preparation instruction was sent to the affected laboratories on 17 May. The affected laboratories were asked to write the dilution for A1 and B1 COD/NVOC.

If the incorrect preparation instruction was used it would result in reverse split and such results would be excluded as Cocran outliers and would therefore not affect the calculation of the assigned value.

One laboratory had used the incorrect preparation instruction for COD. An alternative nominal and spike value were calculated for COD in the case were the incorrect preparation instruction was used.

Table 2 Assigned and spike value

Parameter	Abbreviation	Unit	Typical Range	Assigned value	Uncertainty of assigned value	Spike value
Chemical oxygen demand – dihromate method	COD_{Cr}	mg/L O_2	5-75	55	4.0	11
Chemical oxygen demand – dihromate method	*COD_{Cr}	mg/L O_2	5-75	*38	*3.6	*17
Five day biochemical oxygen demand w. ATU	BOD_5 w. ATU	mg/L O_2	2-6	3.4	1.5	0.8
Seven day biochemical oxygen demand w. ATU	BOD_7 w. ATU	mg/L O_2	2-6	4.5	1.6	0.8
Non-volatile organic carbon	NVOC/TOC	mg/L C	2-30	23.0	1.1	4.5
Total phosphorus	TP	mg/L P	0.2-2	0.399	0.0044	0.062
Chloride	Cl	mg/L	50-700	114	1.8	25
Sulphate	SO_4	mg/L	20-200	121	4.6	28
Total suspended matter	TSS	mg/L	20-100	54.9	2.4	8.9

* Alternative result if incorrect preparation instruction was used.

2.3.1 Assigned and spike values

The content of each parameter in each sample is given an assigned value for the sample with the lower content and a spike value, the spike value being the difference in concentration between the two samples of the sample pair.

In order to ensure optimal use of the data, the assigned value is calculated as the average of the median for both samples in the sample pair after subtraction of the spike value. The spike values are calculated from sample preparation.

The assigned values for all parameters except Cl and SO_4 are operationally defined and are consensus values based upon the median for method no. 62, 76, 77 (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_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 BOD_5 Cl and SO_4 are consensus values for all accepted laboratories based on the median.

2.3.2 Test of spike values

A comparison was made (t-test, 95% confidence level) between the spike value and the difference in concentration between the two samples in the sample pair found from the laboratories' results, see Appendix C. The test showed no significant difference between the two.

2.3.3 Test of assigned values

The assigned value and the average of the results obtained from all laboratories were also compared (t-test, 95% confidence level), see Appendix D. The test showed no significant difference between the two and the control of assigned value at Eurofins confirmed the value (Appendix E). The test revealed a significant difference between the two for TP. Average recovery was 102.7 % 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. 9, 41, 41B, 42, 42A, 42B and 71 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	Combined homogeneity and stability 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 * 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.

One laboratory reported COD results from samples prepared using an incorrect preparation instruction. There results were assessed using an alternative nominal and spike value for COD.

For TP 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 (2022)*, Report to participants, April 2022.

/2/ ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*, 2019.

/3/ Spliid, H., *Procedure and analysis of data for proficiency tests and environmental analyses*, Report to Danish Environmental Protection Agency, 1994 (in Danish).

/4/ Eurofins A/S, *Schedule for a proficiency test*, document may be downloaded from www.eurofins.dk/proficiencytest.

/5/ Ministry of Environment regulation no. 2362 on *quality criteria for environmental measurements,* 26 October 2021 (in Danish).

/6/ ISO 13528, *Statistical methods for use in proficiency testing by interlaboratory comparison*, 2015.

A N N E X E S

ANNEX A LIST OF PARTICIPANTS

Laboratory	Town	Country
AquaDjurs A/S	Grenaa	Denmark
Biofos A/S	København K	Denmark
Bjergmarken RA, Fors Spildevand Roskilde	Roskilde	Denmark
BlueKolding A/S	Kolding	Denmark
Bornholms Spildevand A/S	Rønne	Denmark
CP Kelco, QC Analyselab.	Ll. Skensved	Denmark
DIN Forsyning, Laboratorium Rens Øst-Esbjerg	Esbjerg	Denmark
Eurofins Miljø A/S	Vejen	Denmark
Hillerød Spildevand (2 participants)	Hillerød	Denmark
Holbæk RA, Fors Spildevand Holbæk	Holbæk	Denmark
Holstebro Renseanlæg, Vestforsyning Spildevand	Holstebro	Denmark
Kerteminde Forsyning - Spildevand A/S	Kerteminde	Denmark
Klarforsyning, Køge-Egnens Renseanlæg	Køge	Denmark
NK-Forsyning A/S	Næstved	Denmark
Provas - Haderslev Forsyningsservice A/S	Haderslev	Denmark
RGS Nordic A/S	Skælskør	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (2 participants)	Slagelse	Denmark
Svendborg Spildevand A/S, Svenborg Centralrense-anlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
SGS Analytics Norway AS (Hamar)	Hamar	Norway
AB Lennart Månsson International	Helsingborg	Sweden
Arctic Paper Munkedals AB	Munkedal	Sweden
Borlänge Energi AB, Avloppsreningsverket	Borlänge	Sweden
Ernemar Laboratorium	Oskarshamn	Sweden
Fiskeby Board AB	Norrköping	Sweden
GRYAAB AB	Göteborg	Sweden
Hallsta Pappersbruk	Hallstavik	Sweden
Hammargårds ARV, Kungsbacka kommun (2 participants)	Kungsbacka	Sweden
Holmen Paper Braviken AB, Bravikens Pappersbruk	Norrköping	Sweden
Kalmar Vatten AB, VA-lab	Kalmar	Sweden
Kristianstad Kommun	Kristianstad	Sweden
Käppalaverket	Lidingö	Sweden
Laboratoriet Fillanverket, MittSverige Vatten och Avfall AB	Sundsvall	Sweden
Laboratoriet vid Smedjeholms avloppsreningsverk	Falkenberg	Sweden
Ljungby Kommun, Avloppsreningsverket, VA-labb	Ljungby	Sweden

Laboratory	Town	Country
Mjölby Kommun (2 participants)	Mjölby	Sweden
Nordic Sugar AB, Örtofta Sockerbruk	Eslöv	Sweden
NSVA/Öresundsverket	Helsingborg	Sweden
Perstorp Oxo AB	Ödsmål	Sweden
Preemraff AB Göteborg	Göteborg	Sweden
Preemraff Lysekil	Lysekil	Sweden
Reningsverket Aggerud	Karlskoga	Sweden
Roslagsvatten AB	Åkersberga	Sweden
Smurfit Kappa Piteå	Piteå	Sweden
St1 Refinery AB	Göteborg	Sweden
Södra Cell AB Mönsterås	Mönsterås	Sweden
Södra Cell AB, Värö	Väröbacka	Sweden
Vallviks Bruk AB	Vallvik	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	Prepared from		Concentration
Concentrate A1	0.738 g 0.738 g 	D-glucose L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 1,510 g/kg NVOC: 0.597 g/kg BOD: 1.034 g/kg
Concentrate B1	0.925 g 0.925 g 	D-glucose L-glutamic acid milli-Q water up to 1000 g	COD_{Cr}: 1.892 g/kg NVOC: 0.747 g/kg BOD: 1.295 g/kg
Stock TP	1.500 g 	Na-B.glycerophosphate milli-Q water up to 1000.0 g	TP: 151.8 mg/kg
Stock Cl	10.000 g 	Sodium chloride (NaCl) milli-Q water up to 1000.0 g	Cl: 6.067 g/kg
Stock SO_4	15.000 g 	Sodium sulphate (Na_2SO_4) milli-Q water up to 1000.0 g	SO_4: 10.144 g/kg
Stock TSS	15.000 g 	Microcrystalline cellulose milli-Q water up to 1000.0 g	TSS: 15.000 g/kg

Sample	Sample prepared from	COD_{Cr} mg/L O_2	NVOC mg/L C	BOD (w. ATU) mg/L O_2	TP mg/L P	Cl mg/L	SO_4 mg/L	TSS mg/L
A1-COD/NVOC	At the laboratory 3.00 mL of concentrate A1 is diluted up to 100.0 mL with filtered water from Vejen sewage treatment plant	a + 45.3	b + 17.9					
B1-COD/NVOC	At the laboratory 3.00 mL of concentrate B1 is diluted up to 100.0* mL with filtered water from Vejen sewage treatment plant	a + 56.7	b + 22.4					
A1-BOD	At the laboratory 6.00 mL of concentrate A1 is diluted up to 2000.0 mL with filtered water from Vejen sewage treatment plant			c + 3.1				
B1-BOD	At the laboratory 6.00 mL of concentrate B1 is diluted up to 2000.0 mL with filtered water from Vejen sewage treatment plant			c + 3.9				
A2	15.0 g stock TP 150.0 g stock Cl 100.0 g stock SO_4 Sample B2 up to 35.0 kg				0.992 · (d+0.195) + 0.062	0.992 · (e+26.0) + 25.1	0.992 · (f + 101) + 28.1	
B2	90.0 g stock TP 300.0 g stock Cl 700.0 g stock SO_4 Filtered water from Vejen sewage treatment plant up to 700 kg				d + 0.195	e + 26.0	f + 101	
A3	At the laboratory 1000.0 mL of filtered water from Vejen sewage treatment plant is added to 3.8 mL stock TSS							g + 56.8
B3	At the laboratory 1000.0 mL of filtered water from Vejen sewage treatment plant is added to 4.4 mL stock TSS							g + 65.7

* An error was made in some of the preparation instructions. If the incorrect instruction were followed 200 ml was used for B1-COD/NVOC.

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	3.10	
4	4.20	
5	-5.80	
6	1.00	
7	-4.90	
8	3.10	
9	4.60	
10	1.70	
11	-	
12	-	
13	1.30	
14	2.70	
15	0.60	
16	-0.50	
17	0.00	
18	2.00	
20	-0.30	
21	-	
22	-2.20	
23	-	
24	-3.20	
25	-	
26	-0.60	
27	-	
28	-	
29	-	
30	0.20	
31	-	
32	-0.80	
33	3.20	
34	-	
35	1.10	
37A	1.40	
37B	-0.50	
38	-	
39	-	
40	-	
41	0.50	
42	27.30	UC
43	7.60	
44	2.10	
45A	3.20	
45B	5.00	
46	1.00	
49	-5.30	

Laboratory	Difference AB
50	1.00
51	-5.90
52	3.10
53	-0.30
54	7.10
55	-
56	-1.30
No of labs., p	38
No of repl., n	2
d	0.76
s^2	9.87
s	3.14
$t = \sqrt{p} \cdot (d/s)$	1.4972
Sign. level, p(t)	0.1428

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

BOD_5, mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	0.660
4	-0.500
5	-
6	-
7	0.370
8	0.330
9	-
10	-
11	-
12	-
13	0.300
14	-
15	-0.520
16	-
17	-
18	-
20	-
21	-
22	-
23	-
24	-
25	-
26	2.200
27	-
28	-
29	-
30	-
31	-0.510
32	-
33	-
34	-
35	-
37A	-
37B	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45A	-
45B	-
46	-
49	-

Laboratory	Difference AB
50	1.800
51	-
52	-
53	-0.200
54	-
55	-
56	-
No of labs., p	10
No of repl., n	2
d	0.393
s^2	0.903
s	0.950
$t = \sqrt{p} \cdot (d/s)$	1.3078
Sign. level, p(t)	0.2234

No test statistics were found to be significant

BOD_7, mg/L O_2

Control of differences within sample pairs

Laboratory	Difference AB
1	-0.10
2	-
3	-
4	-
5	0.10
6	-
7	-
8	-
9	-
10	-
11	-0.30
12	-
13	-
14	-
15	-
16	-
17	-
18	-
20	0.20
21	-0.90
22	-
23	-0.00
24	-
25	-
26	-
27	-
28	0.10
29	-
30	-
31	-0.78
32	-0.04
33	-
34	-
35	-
37A	-
37B	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45A	-
45B	0.02
46	-0.20
49	-
50	-
51	-
52	-
53	-
54	-
55	0.00
56	-
No of labs., p	12
No of repl., n	2
d	-0.16
s^2	0.12
s	0.35
$t = \sqrt{p} \cdot (d/s)$	-1.5836
Sign. level, p(t)	0.1416

No test statistics were found to be significant

NVOC, mg/L C

Control of differences within sample pairs

Laboratory	Difference AB
1	0.000
2	-
3	-
4	0.100
5	-
6	-
7	-1.700
8	-
9	-
10	-
11	1.070
12	-
13	-
14	-0.500
15	-
16	-
17	0.400
18	-
20	0.200
21	0.010
22	-0.340
23	-1.500
24	-
25	0.340
26	-0.410
27	-0.340
28	-0.100
29	0.500
30	4.460
31	-
32	-0.350
33	-
34	-0.290
35	-
37A	-
37B	-
38	2.730
39	-
40	-0.880
41	-
42	-
43	4.820
44	-
45A	-
45B	-
46	0.200
49	-
50	-
51	-0.700
52	-0.700
53	0.600
54	-0.500
55	-0.530
56	-
No of labs., p	27
No of repl., n	2
d	0.244
s^2	2.284
s	1.511
$t = \sqrt{p} \cdot (d/s)$	0.8392
Sign. level, p(t)	0.4090

No test statistics were found to be significant

Total phosphorous, mg/L P

Control of differences within sample pairs

Laboratory	Difference AB	
1	0.0000	
2	0.0100	
3	0.0090	
4	0.0010	
5	0.0020	
6	-0.0070	
7	-0.0330	UC
8	0.0130	
9	0.0060	
10	-0.0870	UC
11	-0.0160	
12	-0.0090	
13	0.0060	
14	0.0020	
15	0.0030	
16	-0.0120	
17	-0.0050	
18	0.0030	
20	-0.0060	
21	-0.0040	
22	0.0040	
23	-0.0090	
24	-0.0160	
25	-0.0020	
26	-0.0020	
27	0.0040	
28	0.0040	
29	-0.0040	
30	-0.0100	
31	-	
32	0.0100	
33	0.0120	
34	-0.0060	
35	-0.0020	
37A	0.0030	
37B	0.0020	
38	0.0020	
39	-0.0100	
40	-0.0140	UG
41	-0.0020	
42	0.0030	
43	-0.0060	
44	0.0030	
45A	-	
45B	0.0070	
46	-0.0030	
49	0.0080	

Laboratory	Difference AB
50	0.0220
51	0.0130
52	-0.0060
53	-0.0020
54	0.0090
55	0.0030
56	-0.0120
No of labs., p	49
No of repl., n	2
d	0.0003
s^2	0.0001
s	0.0080
$t = \sqrt{p} \cdot (d/s)$	0.2322
Sign. level, p(t)	0.8173

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

Chloride, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	5.0	UG
4	0.0	
5	-	
6	-12.9	UG
7	-2.6	
8	-3.0	
9	1.0	
10	-67.0	UC
11	-	
12	-	
13	4.0	
14	-	
15	-3.0	
16	-1.8	
17	-	
18	-6.0	
20	-	
21	0.8	
22	1.0	
23	-	
24	-	
25	-	
26	0.0	
27	-	
28	-	
29	2.0	
30	-	
31	0.0	
32	-	
33	9.0	
34	-	
35	-	
37A	-2.0	
37B	-2.0	
38	-	
39	-1.2	
40	-	
41	4.0	
42	3.0	
43	-	
44	3.0	
45A	-	
45B	-	
46	-	
49	-	

Laboratory	Difference AB
50	-
51	0.4
52	5.0
53	0.0
54	-
55	-
56	-1.0
No of labs., p	24
No of repl., n	2
d	0.4
s^2	10.1
s	3.2
$t = \sqrt{p} \cdot (d/s)$	0.6805
Sign. level, p(t)	0.5030

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

Sulphate, mg/L

Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-9.00
4	-
5	-
6	-
7	1.30
8	-10.00
9	-
10	-
11	-
12	-
13	-
14	-
15	-
16	-
17	-8.00
18	-
20	-
21	-
22	0.90
23	-
24	-
25	-
26	-
27	-
28	-
29	-0.70
30	-
31	-
32	-
33	-
34	-
35	-
37A	5.00
37B	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45A	-
45B	-
46	-
49	-
50	-
51	-
52	-
53	-4.00
54	-
55	-
56	-2.00
No of labs., p	9
No of repl., n	2
d	-2.94
s^2	26.87
s	5.18
$t = \sqrt{p} \cdot (d/s)$	-1.7041
Sign. level, p(t)	0.1268

No test statistics were found to be significant

TSS, mg/L

Control of differences within sample pairs

Laboratory	Difference AB	
1	2.00	
2	-	
3	-	
4	1.20	
5	-1.10	
6	-	
7	-0.10	
8	-17.50	UC
9	2.90	
10	0.90	
11	0.40	
12	1.20	
13	0.60	
14	-	
15	-3.90	
16	-	U
17	0.10	
18	-0.20	
20	-	
21	-	U
22	1.90	
23	-0.10	
24	-	
25	-	
26	-	
27	-0.80	
28A	-	U
29	0.50	
30	0.30	
31	-0.20	
32	1.00	
33	-	
34	-	
35	-	
37A	-	
37B	-	
38	-0.40	
39	0.90	
40	0.29	
41	-0.10	
42	-	
43	1.70	
44	-	
45A	-	
45B	0.90	
46	3.70	
49	-11.00	UC

Laboratory	Difference AB	
50	0.90	
51	0.00	
52	1.10	
53	-3.50	
54	4.20	
55	-	U
56	0.60	
No of labs., p	32	
No of repl., n	2	
d	0.53	
s^2	2.60	
s	1.61	
$t = \sqrt{p} \cdot (d/s)$	1.8523	
Sign. level, p(t)	0.0735	

No test statistics were found to be significant
UC denotes a Cochran outlier
U denotes data excluded from the data file

ANNEX D CONTROL OF RECOVERY

COD_{Cr}, mg/L O_2

Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	61.60	
3	53.75	
4	53.40	
5	57.40	
6	47.80	
7	55.75	
8	56.25	
9	51.10	
10	52.05	
11	-	
12	-	
13	51.25	
14	48.95	
15	50.20	
16	53.65	
17	64.10	
18	56.00	
20	59.15	
21	-	
22	61.00	
23	-	
24	61.70	
25	-	
26	54.70	
27	-	
28	-	
29	-	
30	57.20	
31	-	
32	52.55	
33	51.80	
34	-	
35	60.05	
37A	52.20	
37B	53.05	
38	-	
39	-	
40	-	
41	52.25	
42	37.45	UC
43	46.50	
44	55.85	
45A	63.10	
45B	61.50	
46	55.30	
49	63.95	

Laboratory	Sample pair AB
50	59.50
51	63.65
52	52.95
53	53.15
54	56.85
55	-
56	55.45
No of labs., p	38
No of repl., n	2
m	55.70
s^2	21.71
s	4.66
Assigned value, μ	55
Recovery, %	101.3
$t = \sqrt{p} \cdot (m-\mu)/s$	0.9278
Sign. level, p(t)	0.3595

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

BOD_5, mg/L O_2

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	3.990
4	3.650
5	-
6	-
7	3.505
8	3.125
9	-
10	-
11	-
12	-
13	4.350
14	-
15	3.630
16	-
17	-
18	-
20	-
21	-
22	-
23	-
24	-
25	-
26	5.400
27	-
28	-
29	-
30	-
31	3.475
32	-
33	-
34	-
35	-
37A	-
37B	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45A	-
45B	-
46	-
49	-

Laboratory	Sample pair AB	
50	5.100	
51	-	
52	-	
53	7.100	
54	-	
55	-	
56	-	
No of labs., p	10	
No of repl., n	2	
m	4.333	
s^2	1.483	
s	1.218	
Assigned value, μ	3.4	
Recovery, %	127.4	
$t = \sqrt{p} \cdot (m-\mu)/s$	2.4219	
Sign. level, p(t)	0.0385	*

* 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)

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

Laboratory	Sample pair AB
1	3.95
2	-
3	-
4	-
5	4.45
6	-
7	-
8	-
9	-
10	-
11	4.63
12	-
13	-
14	-
15	-
16	-
17	-
18	-
20	4.46
21	4.65
22	-
23	4.89
24	-
25	-
26	-
27	-
28	4.55
29	-
30	-
31	3.50
32	3.70
33	-
34	-
35	-
37A	-
37B	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45A	-
45B	4.66
46	4.10
49	-

Laboratory	Sample pair AB
50	-
51	-
52	-
53	-
54	-
55	4.40
56	-
No of labs., p	12
No of repl., n	2
m	4.33
s^2	0.18
s	0.42
Assigned value, μ	4.5
Recovery, %	96.2
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.4007
Sign. level, p(t)	0.1889

No test statistics were found to be significant

NVOC, mg/L C

Control of recovery, average of results

Laboratory	Sample pair AB
1	24.500
2	-
3	-
4	21.650
5	-
6	-
7	22.850
8	-
9	-
10	-
11	22.365
12	-
13	-
14	22.350
15	-
16	-
17	23.700
18	-
20	22.700
21	21.505
22	24.240
23	23.550
24	-
25	21.530
26	22.845
27	23.130
28	23.770
29	23.150
30	21.890
31	-
32	22.575
33	-
34	23.745
35	-
37A	-
37B	-
38	22.295
39	-
40	23.730
41	-
42	-
43	20.860
44	-
45A	-
45B	-
46	21.200
49	-
50	-
51	24.150
52	24.250
53	23.700
54	24.150
55	23.925
56	-
No of labs., p	27
No of repl., n	2
m	22.974
s^2	1.106
s	1.051
Assigned value, μ	23.0
Recovery, %	99.9
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.1272
Sign. level, p(t)	0.8998

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	0.3980	
2	0.4100	
3	0.4295	
4	0.4315	
5	0.4270	
6	0.4205	
7	0.3815	
		UC
8	0.4375	
9	0.4230	
10	0.4665	
		UC
11	0.4080	
12	0.4035	
13	0.3980	
14	0.4320	
15	0.3955	
16	0.3940	
17	0.3965	
18	0.4375	
20	0.4110	
21	0.3950	
22	0.3990	
23	0.4015	
24	0.4000	
25	0.3980	
26	0.3990	
27	0.4060	
28	0.3940	
29	0.4140	
30	0.4100	
31	-	
32	0.4260	
33	0.4300	
34	0.4170	
35	0.4380	
37A	0.4205	
37B	0.4110	
38	0.3920	
39	0.3760	
40	0.3360	
		UG
41	0.4220	
42	0.4025	
43	0.4020	
44	0.4365	
45A	-	
45B	0.4165	
46	0.4265	
49	0.4140	

Laboratory	Sample pair AB	
50	0.3670	
51	0.4195	
52	0.4030	
53	0.3990	
54	0.4035	
55	0.3885	
56	0.3940	
No of labs., p	49	
No of repl., n	2	
m	0.4097	
s^2	0.0003	
s	0.0163	
Assigned value, μ	0.399	
Recovery, %	102.7	
$t = \sqrt{p} \cdot (m-\mu)/s$	4.5969	
Sign. level, p(t)	0.0000	***

* denotes that there is a significant difference (t-test, 5%-level)
** denotes that there is a significant difference (t-test, 1%-level)
*** denotes that there is a significant difference (t-test, 0.1%-level)
UC denotes a Cochran outlier
UG denotes a Grubbs outlier

Chloride, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	-	
3	142.5	UG
4	120.0	
5	-	
6	63.9	UG
7	109.3	
8	122.5	
9	112.5	
10	291.5	UC
11	-	
12	-	
13	111.0	
14	-	
15	108.5	
16	112.6	
17	-	
18	109.0	
20	-	
21	114.8	
22	118.4	
23	-	
24	-	
25	-	
26	114.0	
27	-	
28	-	
29	113.1	
30	-	
31	113.0	
32	-	
33	122.5	
34	-	
35	-	
37A	97.0	
37B	112.0	
38	-	
39	117.1	
40	-	
41	120.0	
42	110.5	
43	-	
44	112.5	
45A	-	
45B	-	
46	-	
49	-	

Laboratory	Sample pair AB
50	-
51	111.9
52	113.5
53	111.0
54	-
55	-
56	116.5
No of labs., p	24
No of repl., n	2
m	113.5
s^2	28.7
s	5.4
Assigned value, μ	114
Recovery, %	99.5
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.4881
Sign. level, p(t)	0.6301

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

Sulphate, mg/L

Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	111.50
4	-
5	-
6	-
7	123.45
8	112.00
9	-
10	-
11	-
12	-
13	-
14	-
15	-
16	-
17	120.00
18	-
20	-
21	-
22	128.15
23	-
24	-
25	-
26	-
27	-
28	-
29	125.95
30	-
31	-
32	-
33	-
34	-
35	-
37A	146.50
37B	-
38	-
39	-
40	-
41	-
42	-
43	-
44	-
45A	-
45B	-
46	-
49	-

Laboratory	Sample pair AB
50	-
51	-
52	-
53	112.00
54	-
55	-
56	120.00
No of labs., p	9
No of repl., n	2
m	122.17
s^2	121.72
s	11.03
Assigned value, μ	121
Recovery, %	101.0
$t = \sqrt{p} \cdot (m-\mu)/s$	0.3187
Sign. level, p(t)	0.7581

No test statistics were found to be significant

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

Laboratory	Sample pair AB	
1	55.90	
2	-	
3	-	
4	54.10	
5	53.15	
6	-	
7	54.95	
8	31.15	UC
9	55.55	
10	55.55	
11	53.80	
12	56.00	
13	55.20	
14	-	
15	51.65	
16	-	U
17	56.75	
18	54.60	
20	-	
21	-	U
22	56.05	
23	55.05	
24	-	
25	-	
26	-	
27	55.30	
28A	-	U
29	57.15	
30	55.85	
31	54.60	
32	54.70	
33	-	
34	-	
35	-	
37A	-	
37B	-	
38	54.80	
39	53.55	
40	53.95	
41	54.75	
42	-	
43	52.05	
44	-	
45A	-	
45B	55.05	
46	54.75	
49	49.90	UC

Laboratory	Sample pair AB	
50	57.55	
51	56.40	
52	54.95	
53	49.35	
54	58.00	
55	-	U
56	51.20	
No of labs., p	32	
No of repl., n	2	
m	54.76	
s^2	3.34	
s	1.83	
Assigned value, μ	54.9	
Recovery, %	99.7	
$t = \sqrt{p} \cdot (m-\mu)/s$	-0.4409	
Sign. level, p(t)	0.6623	

No test statistics were found to be significant
UC denotes a Cochran outlier
U denotes data excluded from the data file

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	1	49.6	48.1	48.9	49.1	55	8.3	11
			39	49.6	49.4	49.5				
			54	49.4	48.2	48.8				
		B1	5	58.2	56.1	57.2	57.4	66		
			16	58.2	56.6	57.4				
			22	58.0	57.2	57.6				
Total phosphorus	mg/L P	A2	8	0.50	0.50	0.50	0.50	0.461	0.061	0.062
			40	0.49	0.50	0.49				
			75	0.50	0.50	0.50				
		B2	4	0.44	0.44	0.44	0.44	0.399		
			43	0.44	0.44	0.44				
			67	0.44	0.44	0.44				
Chloride	mg/L	A2	8	121	120	121	132	139	40	25
			40	119	199	159				
			75	117	117	117				
		B2	4	94	93	93	93	114		
			43	93	93	93				
			67	91	91	91				
Sulphate	mg/L	A2	8	149	147	148	149	149	24	28
			40	150	147	149				
			75	149	149	149				
		B2	4	124	123	124	124	121		
			43	124	123	124				
			67	126	126	126				
Total suspended solids	mg/L	A3	7	54.49		54.49	55.19	54.90	8.36	8.9
			28	54.69		54.69				
			57	56.39		56.39				
		B3	11	61.83		61.83	63.55	63.80		
			58	63.32		63.32				
			71	65.51		65.51				

ANNEX F HOMOGENEITY AND STABILITY

PT:	SPIL-1
Parameter:	COD
Unit:	mg/L O_2
Sigma:	10.8

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2022-03-02

Sample	x(a)	x(b)	average	sd	sd^2
A1- 3-3	49.7	50.9	50.3	0.849	0.720
A1-15-7	50.9	50.9	50.9	0.000	0.00
A1-22-1	51.5	50.8	51.2	0.495	0.245
A1-26-2	50.6	50.6	50.6	0.000	0.000
A1-40-3	51.3	51.3	51.3	0.000	0.000
A1-47-4	50.9	50.5	50.7	0.283	0.080
A1-50-4	50.5	51.3	50.9	0.566	0.320
A1-59-5	52.0	50.4	51.2	1.131	1.280
A1-61-5	50.7	51.0	50.9	0.212	0.045
A1-68-6	49.6	51.0	50.3	0.990	0.980
A1-73-6	49.8	49.5	49.7	0.212	0.045
A1-80-7	49.6	49.4	49.5	0.141	0.020

For homogeneity

General average (x)	50.61
Sample average sd (s_x)	0.580
Within-sample sd (s_w):	0.558
Between-samples sd (ss):	0.4247
S_L in the Proficiency Test:	4.39
S_R in the Proficiency Test:	4.92

Stability test Date: 2022-03-17

Sample	x(a)	x(b)
A1- 1-4	49.6	48.1
A1- 39-45	49.6	49.4
A1- 54-79	49.4	48.2

For stability

General average (y):	49.05
/x-y/ =	1.5625

Conclusions

ss =	0.425	0.3*sigma= 3.24
/x-y/ =	1.5625	
Analytical quality	Is s_w < 0.15*sigma	**YES**
Homoge-neity:	Is ss < 0.3*sigma?	**YES**
Stability:	/x-y/ < 0.3*sigma?	**YES**

PT:	SPIL-1
Parameter:	TP
Unit:	mg/L P
Sigma:	0.036

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2022-03-02

Sample	x(a)	x(b)	average	sd	sd^2
A2-9	0.52	0.52	0.5	0.000	0.000
A2-14	0.51	0.51	0.5	0.001	0.00
A2-18	0.51	0.51	0.5	0.000	0.000
A2-22	0.51	0.51	0.5	0.001	0.000
A2-33	0.52	0.52	0.5	0.001	0.000
A2-37	0.51	0.51	0.5	0.002	0.000
A2-43	0.50	0.50	0.5	0.000	0.000
A2-49	0.50	0.50	0.5	0.000	0.000
A2-55	0.51	0.51	0.5	0.001	0.000
A2-61	0.51	0.51	0.5	0.000	0.000
A2-65	0.50	0.50	0.5	0.000	0.000
A2-76	0.51	0.51	0.5	0.001	0.000

For homogeneity

General average (x)	0.51
Sample average sd (s_x)	0.006
Within-sample sd (s_w):	0.001
Between-samples sd (ss):	0.0059
S_L in the Proficiency Test:	0.0158
S_R in the Proficiency Test:	0.0168

Stability test Date: 2022-03-17

Sample	x(a)	x(b)
A2-8	0.498	0.5
A2-40	0.498	0.499
A2-75	0.5	0.499

For stability

General average (y):	0.499
/x-y/ =	0.010625

Conclusions

ss =	0.006	0.3*sigma= 0.01
/x-y/ =	0.010625	
Analytical quality	Is s_w < 0.15*sigma	**YES**
Homoge-neity:	Is ss < 0.3*sigma?	**YES**
Stability:	/x-y/ < 0.3*sigma?	**YES**

PT: SPIL-1
Parameter: TSS
Unit: mg/L
Sigma: 3.6

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2022-03-02

Sample	x(a)	x(b)	average	sd	sd^2
B3-5-4	62.3		62.3		
B3-9-8	64.7		64.7		
B3-14-14	64.7		64.7		
B3-19-19	64.8		64.8		
B3-27-26	65.1		65.1		
B3-31-33	63.4		63.4		
B3-37-38	64.9		64.9		
B3-52-48	65.0		65.0		
B3-57-54	64.9		64.9		
B3-59-56	62.7		62.7		
B3-65-63	62.8		62.8		
B3-72-70	65.0		65.0		

For homogeneity

General average (x)	64.2
Sample average sd (s_x)	1.057
Within-sample sd (s_w):	
Between-samples sd (ss):	1.057
S_L in the Proficiency Test:	1.64
S_R in the Proficiency Test:	2.00

Stability test Date: 2022-03-17

Sample	x(a)	x(b)
B3- 11-12	61.83	
B3- 58-70	63.32	
B3- 71-66	65.51	

For stability

General average (y):	63.55333
/x-y/ =	0.655813

Conclusions

ss =1.06 0.3*sigma=1.08
/x-y/ =0.655813

Analytical quality	Is s_w < 0.15*sigma **No data**
Homogeneity:	Is ss < 0.3*sigma? **YES**
Stability:	/x-y/ < 0.3*sigma? **YES**