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Proficiency test SPIL-2 (2021)

Nitrogen parameters in wastewater (untreated sewage)

Quality Documentation
July 2021

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CONTENTS

1 INTRODUCTION

A proficiency test on the analysis of nitrogen parameters in wastewater was conducted on 6 May 2021. 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 8 June 2021.

2 FEATURES OF THE PROFICIENCY TEST

Participants in the proficiency test were a total of 59 laboratories from Denmark, Norway and Sweden. A list of participants is shown in Appendix A.

The closing date for submission of results was 21 May 2021. All participants except laboratory no. 22, 30, 36, 56 and 57 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.

Four 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 untreated sewage. Sample preparation is described in Appendix B.

Table 1 Samples in the proficiency test

Sample name	Parameters
A1/B1	TN, NH_4, NO_{2+3}, NO_3, γ_{25}
A2/B2	pH

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 untreated sewage. 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
Total nitrogen	TN	mg/L N	30 – 80	39.5	0.71	5.29
Ammonium	NH_4	mg/L N	20 – 50	37.1	0.38	4.1
Nitrite+nitrate	NO_{2+3}	mg/L N	< 5	0.24	0.10	0.17
Nitrate	NO_3	mg/L N	< 5	0.21	0.047	0.17
Conductivity	γ_{25}	mS/m	50 – 2000	100	2.4	2
pH	pH	-	6 – 9	6.95	0.029	-

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 γ_{25} where the spike value is the difference between median values for the two samples in the sample pair.

The assigned value for TN is operationally defined and is a consensus value based upon the median for method no. 1, 2, 3, 4 and 5 (TN). A list of method identification numbers is found in the report to participants /1/. Assigned values for NH_4, NO_{2+3}, NO_3, conductivity and pH are consensus values for all 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 for TN and NO_{2+3}. The test revealed a significant difference between the two for NH_4, NO_3 and γ_{25}. However, for NH_4 and γ_{25} 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.

For NO_3 the control measurements at Eurofins confirmed the difference (Appendix E). However, scrutiny of documentation from the sample preparation showed no indications of mistakes in sample preparation. The assigned value is kept unchanged but the value is uncertain and caution is called for when evaluating the 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 for most parameters 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 TN. Average recover was 103.6 %. 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. 6, 9, 71, 71B, 73, 73A and 73B and now showed no significant difference. Furthermore, the results of control measurements at Eurofins confirmed the assigned value (Appendix E). 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:

TN	Combined homogeneity and stability test
NH_4	Combined homogeneity and stability test
NO_2	Combined homogeneity and stability test
NO_3	Combined homogeneity and stability test
pH	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) 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 homogeneity show that the samples are homogeneous.

The tests for stability show that TN and NH_4 in the samples are stable. However, the test shows that NO_2 and NO_3 are not stable. It is therefore recommended to evaluate deviations from the assigned value of these components with caution.

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.

However, for NO_3 the participants did not recover the spiked value and Eurofins' control measurements confirmed the difference. No error in preparation could be found and therefore the assigned value is kept unchanged.

Furthermore, the tests for stability shows that NO_2 and NO_3 are not stable and there is an unusually large deviation and uncertainty on the laboratories results for NO_2 and NO_3. It is therefore recommended to evaluate deviations from the assigned value of NO_2 and NO_3 with caution.

5 REFERENCES

/1/ Eurofins A/S, *Proficiency test SPIL-2 (2021)*, Report to participants, June 2021.

/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. 1770 on *quality criteria for environmental measurements,* 28 October 2020 (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
Analyseenheden, Institut for Agroøkologi, Aarhus Universitet	Tjele	Denmark
AquaDjurs A/S	Grenaa	Denmark
Arla Foods Nr. Vium (4 participants)	Videbæk	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
Cheminova A/S	Harboøre	Denmark
CP Kelco, QC Analyselab.	Ll. Skensved	Denmark
Eurofins Miljø A/S (2 participants)	Vejen	Denmark
Hillerød Spildevand	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
Rensningsanlæg Øst, Spildevandslaboratoriet	Esbjerg	Denmark
Ringkøbing-Skjern Forsyning A/S	Skjern	Denmark
SK Spildevand A/S, Slagelse Renseanlæg (2 participants)	Slagelse	Denmark
Svendborg Spildevand A/S, Svenborg Centralrenseanlæg	Skårup Fyn	Denmark
Vandmiljø Randers A/S	Randers SØ	Denmark
Vejle Spildevand	Vejle	Denmark
SYNLAB Analytics AS Norway (Hamar)	Hamar	Norway
AB Borlänge Energi, Borlänge Reningsverk	Borlänge	Sverige
AB Lennart Månsson International	Helsingborg	Sverige
Arctic Paper Munkedals AB	Munkedal	Sverige
Ernemar Laboratorium	Oskarshamn	Sverige
GRYAAB AB	Göteborg	Sverige
Hallsta Pappersbruk	Hallstavik	Sverige
Kalmar Vatten AB, VA-lab	Kalmar	Sverige
Klippans Reningsverk	Klippan	Sverige
Kretslopp & Vattens laboratorium, Vänersborgs kommun	Vänersborg	Sverige

Laboratory	Town	Country
Käppalaverket	Lidingö	Sweden
Laboratoriet vid Smedjeholms avloppsreningsverk	Falkenberg	Sweden
Ljungby Kommun, Avloppsreningsverket, VA-labb	Ljungby	Sweden
Mjölby Kommun	Mjölby	Sweden
Motala Kommun, Tekniska Förvaltningen, Vatten och Avfall	Motala	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, Värö	Väröbacka	Sweden
Trollhättan Energi AB	Trollhättan	Sweden
Uddebo Laboratorium	Luleå	Sweden
Vallviks Bruk AB	Vallvik	Sweden
VIVAB	Falkenberg	Sweden
Västervik Miljö & Energi AB, Vattenlaboratoriet	Västervik	Sweden
Östersunds Provningslaboratorium, Göviken reningsverk	Östersund	Sweden

ANNEX B SAMPLE PREPARATION

Stock solution	**Prepared from**		**Concentration**
Stock TN	3.000 g	Disodium edetate, $2H_2O$ milli-Q water up to 1000.0 g	TN: 225.8 mg/kg N
Stock NH_4	5.000 g	Ammonium chloride (NH_4Cl) milli-Q water up to 1000.0 g	NH_4: 1310 mg/kg N
Stock NO_3	2.500 g	Potassium nitrate (KNO_3) milli-Q water up to 1000.0 g	NO_3: 346.4 mg/kg N

Sample	**Sample prepared from**	**TN mg/kg N**	**NH_4 mg/kg N**	**NO_3 mg/kg N**	**Conductivity mS/m**
A1	0 g stock TN 0 g stock NH_4 150.0 g stock NO_3 Filtered water from Vejen sewage treatment plant up to 60.00 kg				
B1	100.0 g stock TN 100.0 g stock NH_4 15.0 g stock NO_3 Sample A1 up to 30.00 kg				

Sample	**Sample prepared from**	**pH**
A2/B2	Filtered untreated wastewater from Vejen sewage treatment plant.	f

ANNEX C CONTROL OF SPIKE VALUES

Total Nitrogen, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB	
1	2.60	
2	-0.50	
3	-0.30	
4	-0.20	
5	-	
6	-3.50	
7	0.85	
8	-0.50	
9	-0.20	
10	-0.30	
11	-0.55	
12	1.10	
13A	0.60	
13B	-	
14	-0.50	
15	-2.90	
16	-	
17	-	
18	0.70	
19	-0.81	
20	-0.30	
21	-0.66	UG
23	-3.30	
24	-0.58	
25	-1.04	
26	-1.00	
27	-4.50	
28	-1.70	UG
29	1.57	
31	-2.50	
32	-0.26	
33	0.30	
34	-0.50	
35	-0.59	
37	0.40	
38	0.00	
39	-0.10	
40	1.30	
41	2.40	
42	-0.79	
43	-0.40	
44	0.00	
45	-0.70	
46	5.70	UG
47	-0.27	
48	0.05	
49	0.40	
50	0.10	
51	2.00	
52	-0.47	

Laboratory	Difference AB	
53	-7.10	UC
54	-0.10	
55	0.90	
58	-0.60	
59	-2.70	
No of labs., p	47	
No of repl., n	2	
d	-0.33	
s^2	2.00	
s	1.41	
$t = \sqrt{p} \cdot (d/s)$	-1.6193	
Sign. level, p(t)	0.1122	

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

Ammonium, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB	
1	1.61	
2	0.00	
3	0.70	
4	9.40	UC
5	-0.80	
6	0.30	
7	0.30	
8	-1.80	
9	0.10	
10	-1.20	
11	-0.16	
12	-0.90	
13A	-2.00	
13B	-0.90	
14	-0.20	
15	0.60	
16	-	
17	-0.46	
18	-2.40	
19	-	
20	-	
21	-1.23	
23	0.20	
24	1.30	
25	0.14	
26	-	
27	0.40	
28	0.30	
29	-0.58	
31	-0.60	
32	0.25	
33	0.10	
34	-1.10	
35	-1.80	
37	0.10	
38	-	
39	1.10	
40	-0.58	
41	0.00	
42	-2.20	
43	-0.03	
44	0.30	
45	-	
46	-0.70	
47	0.63	
48	-	
49	0.00	
50	0.30	
51	-2.10	
52	-	
53	3.03	UG
54	3.28	UG
55	-	
58	0.40	
59	-0.90	
No of labs., p	43	
No of repl., n	2	
d	-0.31	
s^2	0.90	
s	0.95	
$t = \sqrt{p} \cdot (d/s)$	-2.1677	
Sign. level, p(t)	0.0359	*

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

Difference for sample pair AB is significantly different from 0, and data should be corrected with the difference (in spike value), during execution of Cochran's test.

Nitrite + nitrate, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB	
1	-	
2	-	
3	-	
4	-	
5	-	
6	-	
7	-0.3600	
8	-	
9	-	
10	-	
11	-0.3410	
12	-	
13A	0.2000	
13B	-	
14	-	
15	-	
16	-	
17	-	
18	-	
19	-	
20	-	
21	-	
23	0.0500	
24	-	
25	-0.3220	
26	-0.0710	
27	-0.0200	
28	0.1800	
29	0.1040	
31	-0.1510	
32	-	
33	-	
34	-	
35	-0.2411	
37	-	
38	-	
39	-	
40	-	U
41	-	
42	-	
43	-0.1700	
44	-	
45	-	
46	-	
47	-	
48	-	
49	-	
50	-	
51	0.1500	
52	-	
53	-0.3430	
54	-0.4180	
55	-	
58	-	U
59	-	
No of labs., p	15	
No of repl., n	2	
d	-0.1169	
s^2	0.0472	
s	0.2172	
$t = \sqrt{p} \cdot (d/s)$	-2.0839	
Sign. level, p(t)	0.0560	

No test statistics were found to be significant
U denotes data excluded from the data file

Nitrate, mg/l N
Control of differences within sample pairs

Laboratory	Difference AB
1	-
2	-
3	-
4	0.1900
5	0.1110
6	-
7	-
8	0.0890
9	0.1080
10	-
11	-
12	0.0100
13A	0.1400
13B	-
14	-
15	0.1260
16	-
17	-
18	0.1480
19	-
20	-
21	-
23	-
24	-
25	0.2180
26	-
27	-
28	-
29	0.1700
31	-
32	-
33	-
34	-0.1300
35	0.1700
37	-
38	-
39	0.0900
40	-
41	0.1110
42	-
43	-
44	0.0160
45	0.0100
46	0.0400
47	-
48	-
49	-
50	-
51	-
52	-
53	0.1140
54	0.0020
55	-
58	-
59	-0.3210
No of labs., p	20
No of repl., n	2
d	0.0706
s^2	0.0151
s	0.1228
$t = \sqrt{p} \cdot (d/s)$	2.5715
Sign. level, p(t)	0.0187 *

* 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.

Conductivity, mS/m
Control of differences within sample pairs

Laboratory	Difference AB	
1	-0.30	
2	-0.30	
3	-	
4	-1.00	
5	-	
6	-	
7	-0.98	
8	-	
9	-	
10	-22.00	UG
11	-1.50	
12	-9.00	UG
13A	1.98	UG
13B	-	
14	-	
15	-	
16	0.30	
17	-	
18	-	
19	-	
20	-29.00	UG
21	-	
23	-	
24	-	
25	-	
26	-0.30	
27	-	
28	-	
29	-	
31	-	
32	-0.20	
33	-0.50	
34	100.13	UC
35	-27.00	UG
37	-	
38	-	
39	-	
40	-1.30	
41	-11.00	UG
42	-1.00	
43	-	
44	1.95	UG
45	-	
46	0.20	
47	-	
48	-0.90	
49	-0.50	
50	-0.80	
51	-	
52	-0.30	

Laboratory	Difference AB	
53	-3.00	UG
54	-	
55	43.90	UC
58	-	
59	-0.80	
No of labs., p	17	
No of repl., n	2	
d	-0.60	
s^2	0.25	
s	0.50	
$t = \sqrt{p} \cdot (d/s)$	-4.9854	
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

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.

pH,
Control of differences within sample pairs

Laboratory	Difference AB
1	0.000
2	-0.080
3	-
4	-0.060
5	-0.110
6	0.070
7	0.000
8	-0.030
9	0.030
10	0.010
11	0.020
12	-
13A	0.030
13B	-
14	-
15	-0.013
16	-0.020
17	-
18	-
19	-
20	0.030
21	0.000
23	-0.040
24	0.004
25	-
26	0.000
27	0.000
28	0.040
29	-0.060
31	0.100
32	-0.020
33	0.030
34	-0.040
35	0.090
37	0.050
38	-0.040
39	-0.020
40	-0.010
41	-0.060
42	0.000
43	-0.010
44	-0.080
45	-0.030
46	0.078
47	-
48	0.020
49	-0.100
50	0.020
51	-0.040
52	0.070

Laboratory	Difference AB
53	-
54	-
55	0.080
58	0.070
59	0.010
No of labs., p	44
No of repl., n	2
d	-0.000
s^2	0.003
s	0.051
$t = \sqrt{p} \cdot (d/s)$	-0.0328
Sign. level, p(t)	0.9740

No test statistics were found to be significant

ANNEX D CONTROL OF RECOVERY

Total Nitrogen, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	44.30	
2	42.10	
3	39.15	
4	39.60	
5	-	
6	40.25	
7	38.53	
8	38.75	
9	39.60	
10	43.55	
11	37.69	
12	42.65	
13A	40.80	
13B	-	
14	39.55	
15	37.05	
16	-	
17	-	
18	41.25	
19	44.12	
20	46.35	
21	48.49	UG
23	41.65	
24	42.39	
25	39.57	
26	38.50	
27	41.05	
28	49.95	UG
29	38.33	
31	42.35	
32	40.96	
33	41.16	
34	40.75	
35	39.14	
37	38.20	
38	40.90	
39	40.45	
40	39.15	
41	43.80	
42	39.55	
43	41.00	
44	40.50	
45	41.25	
46	28.85	UG
47	39.91	
48	42.08	
49	39.80	
50	39.35	
51	44.80	
52	43.17	

Laboratory	Sample pair AB	
53	47.95	UC
54	44.55	
55	39.95	
58	40.70	
59	43.05	
No of labs., p	47	
No of repl., n	2	
m	40.92	
s^2	4.26	
s	2.06	
Assigned value, μ	39.5	
Recovery, %	103.6	
$t = \sqrt{p} \cdot (m-\mu)/s$	4.7207	
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

Ammonium, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	38.05	
2	37.80	
3	38.05	
4	42.00	UC
5	36.30	
6	34.75	
7	36.45	
8	37.10	
9	37.95	
10	37.40	
11	37.90	
12	39.55	
13A	35.60	
13B	37.45	
14	37.70	
15	33.60	
16	-	
17	37.00	
18	37.50	
19	-	
20	-	
21	36.38	
23	38.70	
24	37.55	
25	36.30	
26	-	
27	38.40	
28	35.95	
29	37.06	
31	37.00	
32	38.63	
33	38.15	
34	37.15	
35	40.64	
37	37.85	
38	-	
39	37.45	
40	36.92	
41	38.30	
42	36.60	
43	37.23	
44	36.65	
45	-	
46	35.15	
47	37.42	
48	-	
49	35.90	
50	37.05	
51	37.75	
52	-	
53	6.29	UG
54	6.42	UG
55	-	
58	36.70	
59	40.45	
No of labs., p	43	
No of repl., n	2	
m	37.29	
s^2	1.73	
s	1.32	
Assigned value, μ	37.1	
Recovery, %	100.5	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.9491	
Sign. level, p(t)	0.3480	

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

Nitrite + nitrate, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB	
1	-	
2	-	
3	-	
4	-	
5	-	
6	-	
7	0.3000	
8	-	
9	-	
10	-	
11	0.2315	
12	-	
13A	0.2000	
13B	-	
14	-	
15	-	
16	-	
17	-	
18	-	
19	-	
20	-	
21	-	
23	0.2110	
24	-	
25	0.3400	
26	0.0625	
27	0.3000	
28	0.0700	
29	0.3080	
31	0.1705	
32	-	
33	-	
34	-	
35	0.1684	
37	-	
38	-	
39	-	
40	-	U
41	-	
42	-	
43	0.1950	
44	-	
45	-	
46	-	
47	-	
48	-	
49	-	
50	-	
51	0.1350	
52	-	
53	0.3355	
54	0.3150	
55	-	
58	-	U
59	-	
No of labs., p	15	
No of repl., n	2	
m	0.2228	
s^2	0.0084	
s	0.0918	
Assigned value, μ	0.2	
Recovery, %	111.4	
$t = \sqrt{p} \cdot (m-\mu)/s$	0.9628	
Sign. level, p(t)	0.3520	

No test statistics were found to be significant
U denotes data excluded from the data file

Nitrate, mg/l N
Control of recovery, average of results

Laboratory	Sample pair AB
1	-
2	-
3	-
4	0.1050
5	0.1195
6	-
7	-
8	0.2175
9	0.2730
10	-
11	-
12	0.2730
13A	0.1810
13B	-
14	-
15	0.1490
16	-
17	-
18	0.3330
19	-
20	-
21	-
23	-
24	-
25	0.0400
26	-
27	-
28	-
29	-0.0250
31	0.1070
32	-
33	-
34	0.3750
35	-0.0850
37	-
38	-
39	0.1750
40	-
41	0.2515
42	-
43	-
44	0.4310
45	0.2050
46	0.1910
47	-
48	-
49	-
50	-
51	-
52	-

Laboratory	Sample pair AB
53	0.3490
54	0.2420
55	-
58	-
59	0.4005
No of labs., p	20
No of repl., n	2
m	0.2101
s^2	0.0186
s	0.1365
Assigned value, μ	0.21
Recovery, %	100.0
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0016
Sign. level, p(t)	0.9987

No test statistics were found to be significant

Conductivity, mS/m
Control of recovery, average of results

Laboratory	Sample pair AB	
1	99.15	
2	99.95	
3	-	
4	100.50	
5	-	
6	-	
7	98.71	
8	-	
9	-	
10	1001.00	UG
11	102.95	
12	119.50	UG
13A	0.02	UG
13B	-	
14	-	
15	-	
16	99.95	
17	-	
18	-	
19	-	
20	708.50	UG
21	-	
23	-	
24	-	
25	-	
26	99.85	
27	-	
28	-	
29	-	
31	-	
32	91.20	
33	97.45	
34	49.13	UC
35	1000.50	UG
37	-	
38	-	
39	-	
40	99.35	
41	120.50	UG
42	101.40	
43	-	
44	0.07	UG
45	-	
46	87.10	
47	-	
48	93.05	
49	100.25	
50	99.70	
51	-	
52	100.35	
53	121.50	UG
54	-	
55	71.85	UC
58	-	
59	96.60	
No of labs., p	17	
No of repl., n	2	
m	98.09	
s^2	16.38	
s	4.05	
Assigned value, μ	100	
Recovery, %	98.1	
$t = \sqrt{p} \cdot (m-\mu)/s$	-1.9468	
Sign. level, p(t)	0.0693	

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

pH,
Control of recovery, average of results

Laboratory	Sample pair AB
1	7.020
2	6.920
3	-
4	6.960
5	6.555
6	7.035
7	7.010
8	6.735
9	6.995
10	7.005
11	7.030
12	-
13A	6.955
13B	-
14	-
15	6.801
16	6.940
17	-
18	-
19	-
20	6.965
21	7.010
23	6.950
24	6.982
25	-
26	6.900
27	7.140
28	6.880
29	6.880
31	7.020
32	6.940
33	6.925
34	6.860
35	7.285
37	6.995
38	7.470
39	6.910
40	6.975
41	6.610
42	6.870
43	6.915
44	6.900
45	7.125
46	6.806
47	-
48	6.890
49	7.040
50	6.930
51	6.720
52	7.185

Laboratory	Sample pair AB
53	-
54	-
55	6.910
58	7.015
59	6.875
No of labs., p	44
No of repl., n	2
m	6.951
s^2	0.024
s	0.154
Assigned value, μ	6.95
Recovery, %	100.0
$t = \sqrt{p} \cdot (m-\mu)/s$	0.0388
Sign. level, p(t)	0.9693

No test statistics were found to be significant

ANNEX E CONCENTRATION LEVEL

Concentration level **SPIL-2 (2021)**

Parameter	Unit	Sample	Bottle no.	I	II	Bottle Average	Sample Average	Assigned value	Spike Measured	Spike Assigned
Total nitrogen	mg/L N	A1	6	40.60	40.70	40.65	40.8	39.5	4.92	5.0
			30	41.40	41.50	41.45				
			58	40.30	40.30	40.30				
		B1	1	44.80	45.20	45.00	45.7	44.5		
			46	47.20	47.10	47.15				
			74	44.90	45.10	45.00				
Ammonium	mg/L N	A1	6	37.2	37.3	37.25	37.62	37.100	4.583	4.1
			30	38.0	38.0	38.00				
			58	37.6	37.6	37.60				
		B1	1	42.50	42.50	42.50	42.20	41.200		
			46	42.00	42.00	42.00				
			74	42.10	42.10	42.10				
Nitrate	mg/L N	A1	6	0.317	0.301	0.31	0.30	0.21	0.09	0.17
			30	0.314	0.322	0.32				
			58	0.276	0.277	0.28				
		B1	1	0.37	0.36	0.37	0.39	0.38		
			46	0.39	0.39	0.39				
			74	0.41	0.41	0.41				
pH		A2	12	7.13	7.18	7.16	7.10	6.95	-0.03	0
			41	7.04	7.11	7.08				
			58	7.05	7.08	7.07				
		B2	14	7.04	7.10	7.07	7.07	6.95		
			42	7.06	7.08	7.07				
			61	7.08	7.08	7.08				

ANNEX F HOMOGENEITY AND STABILITY

PT: SPIL-2
Parameter: TN
Unit: mg/L
Sigma: 2.441

Responsible for tests: HBP/S7SM

Homogeneity test Date: 2021-04-21

Sample	x(a)	x(b)	average	sd	sd^2
2	45.40	45.60	45.5	0.141	0.020
3	45.90	46.10	46.0	0.141	0.02
12	44.70	44.70	44.7	0.000	0.000
17	44.80	44.80	44.8	0.000	0.000
20	44.40	44.50	44.5	0.071	0.005
26	45.50	45.50	45.5	0.000	0.000
30	45.00	44.50	44.8	0.354	0.125
42	44.80	45.00	44.9	0.141	0.020
55	45.90	46.20	46.1	0.212	0.045
58	45.80	46.30	46.1	0.354	0.125
71	45.10	45.30	45.2	0.141	0.020
77	44.40	44.50	44.5	0.071	0.005

For homogeneity

General average (x)	45.20
Sample average sd (s_x)	0.610
Within-sample sd (s_w):	0.179
Between-samples sd (ss):	0.5966
S_L in the Proficiency Test:	1.94
S_R in the Proficiency Test:	2.18

Stability test Date: 2021-05-06

Sample	x(a)	x(b)
1	44.8	45.2
46	47.2	47.1
74	44.9	45.1

For stability

General average (y):	45.71667
/x-y/ =	0.520833

Conclusions

ss =0.597 0.3*sigma=0.73
/x-y/ =0.520833

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-2
Parameter:	NH_4
Unit:	mg/l
Sigma:	2.3

Responsible for tests: HBP/S7MS

Homogeneity test Date: 2021-04-21

Sample	x(a)	x(b)	average	sd	sd^2
3	42.9	42.9	42.9	0.000	0.000
12	43.3	43.3	43.3	0.000	0.00
17	41.9	41.9	41.9	0.000	0.000
20	41.5	41.5	41.5	0.000	0.000
26	42.5	42.5	42.5	0.000	0.000
30	42.1	42.1	42.1	0.000	0.000
42	42.8	42.8	42.8	0.000	0.000
55	41.6	41.6	41.6	0.000	0.000
58	42.1	42.0	42.1	0.071	0.005
68	42.3	42.3	42.3	0.000	0.000
71	43.4	43.5	43.5	0.071	0.005
77	42.3	42.3	42.3	0.000	0.000

For homogeneity

General average (x)	42.39
Sample average sd (s_x)	0.623
Within-sample sd (s_w):	0.029
Between-samples sd (ss):	0.6223
S_L in the Proficiency Test:	1.23
S_R in the Proficiency Test:	1.40

Stability test Date: 2021-05-06

Sample	x(a)	x(b)
1	42.5	42.5
46	42	42
74	42.1	42.1

For stability

General average (y):	42.2
/x-y/ =	0.191667

Conclusions

ss =	0.622	0.3*sigma=	0.69
/x-y/ =	0.191667		

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-2
Parameter:	NO_2
Unit:	mg/L
Sigma:	0.360

Responsible for tests: HBP/S7SM

Homogeneity test Date: 2021-04-21

Sample	x(a)	x(b)	average	sd	sd^2
2	0.23	0.24	0.2	0.004	0.000
3	0.20	0.20	0.2	0.000	0.00
12	0.20	0.20	0.2	0.001	0.000
17	0.23	0.23	0.2	0.004	0.000
20	0.29	0.30	0.3	0.004	0.000
26	0.28	0.28	0.3	0.000	0.000
30	0.21	0.21	0.2	0.000	0.000
42	0.22	0.22	0.2	0.004	0.000
55	0.25	0.26	0.3	0.002	0.000
58	0.21	0.21	0.2	0.002	0.000
68	0.22	0.22	0.2	0.001	0.000
71	0.27	0.26	0.3	0.006	0.000

For homogeneity

General average (x)	0.23
Sample average sd (s_x)	0.031
Within-sample sd (s_w):	0.003
Between-samples sd (ss):	0.0309
S_L in the Proficiency Test:	-
S_R in the Proficiency Test:	0.154

Stability test Date: 2021-05-06

Sample	x(a)	x(b)
1	0.481	0.481
46	0.649	0.65
74	0.761	0.762

For stability

General average (y):	0.630667
/x-y/ =	0.39625

Conclusions

ss =	0.031	0.3*sigma= 0.11
/x-y/ =	0.39625	
Analytical quality	Is s_w < 0.15*sigma	**YES**
Homogeneity:	Is ss < 0.3*sigma?	**YES**
Stability:	/x-y/ < 0.3*sigma?	**NO**

PT:	SPIL-2
Parameter:	NO_3
Unit:	mg/L
Sigma:	0.360

Responsible for tests: HBP/S7SM

Homogeneity test Date: 2021-04-21

Sample	x(a)	x(b)	average	sd	sd^2
2	0.23	0.24	0.2	0.004	0.000
3	0.20	0.20	0.2	0.000	0.00
12	0.20	0.20	0.2	0.001	0.000
17	0.23	0.23	0.2	0.004	0.000
20	0.29	0.30	0.3	0.004	0.000
26	0.28	0.28	0.3	0.000	0.000
30	0.21	0.21	0.2	0.000	0.000
42	0.22	0.22	0.2	0.004	0.000
55	0.25	0.26	0.3	0.002	0.000
58	0.21	0.21	0.2	0.002	0.000
68	0.22	0.22	0.2	0.001	0.000
71	0.27	0.26	0.3	0.006	0.000

For homogeneity

General average (x)	0.23
Sample average sd (s_x)	0.031
Within-sample sd (s_w):	0.003
Between-samples sd (ss):	0.0309
S_L in the Proficiency Test:	0.126
S_R in the Proficiency Test:	0.139

Stability test Date: 2021-05-06

Sample	x(a)	x(b)
1	0.37	0.364
46	0.394	0.388
74	0.41	0.409

For stability

General average (y):	0.389167
/x-y/ =	0.15475

Conclusions

ss =	0.031	0.3*sigma=	0.11
/x-y/ =	0.15475		
Analytical quality	Is s_w < 0.15*sigma **YES**		
Homogeneity:	Is ss < 0.3*sigma? **YES**		
Stability:	/x-y/ < 0.3*sigma? **NO**		

PT:	SPIL-2
Parameter:	pH
Unit:	
Sigma:	0.1

Responsible for tests: HBP/S7SM

Homogeneity test Date: 2021-04-21

Sample	x(a)	x(b)	average	sd	sd^2
2	6.93	6.95	6.9	0.014	0.000
7	6.89	6.91	6.9	0.014	0.000
11	6.88	6.9	6.9	0.014	0.000
16	6.88	6.89	6.9	0.007	0.000
21	6.88	6.89	6.9	0.007	0.000
32	6.88	6.9	6.9	0.014	0.000
41	6.87	6.89	6.9	0.014	0.000
49	6.89	6.91	6.9	0.014	0.000
52	6.88	6.9	6.9	0.014	0.000
62	6.87	6.89	6.9	0.014	0.000
68	6.88	6.9	6.9	0.014	0.000
72	6.88	6.93	6.9	0.035	0.001

For homogeneity

General average (x)	6.9
Sample average sd (s_x)	0.016
Within-sample sd (s_w):	0.016
Between-samples sd (ss):	0.012
S_L in the Proficiency Test:	0.152
S_R in the Proficiency Test:	0.156

Conclusions

ss = 0.01 0.3*sigma= 0.02

/x-y/ = 0.17875

Homogeneity: Is ss < 0.3*sigma?

YES