REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 23 | 2019

Interlaboratory Proficiency Test 02/2019

Chlorophyll *a*, colour, conductivity, nutrients, pH and turbidity in natural waters

Riitta Koivikko, Mirja Leivuori, Mika Sarkkinen, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

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Proftest SYKE

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ABSTRACT

Interlaboratory Proficiency Test 02/2019

Proftest SYKE carried out the proficiency test for the determination of chlorophyll *a*, colour, conductivity, nutrients, pH, and turbidity in natural waters in February 2019. In total, there were 34 participants in the proficiency test.

Either the calculated concentration, the robust mean or the median of the results reported by the participants was used as the assigned value for the measurands. The overall performance of the participants was evaluated by using z scores. In this proficiency test 85 % of the results were satisfactory when total deviation of 0.2 pH units for pH values and 5–35 % for the other measurands was accepted from the assigned value.
Warm thanks to all participants in this proficiency test!

Keywords: water analysis, chlorophyll *a*, nutrients, pH, conductivity, colour, turbidity, water and environmental laboratories, proficiency test, interlaboratory comparison

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 02/2019

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen helmikuussa 2019. Pätevyyskokeessa määritettiin klorofylli *a*, ravinteet, pH sameus, sähkönjohtavuus ja väri luonnonvesistä. Pätevyyskokeessa oli yhteensä 34 osallistujaa.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta tai osallistujatulosten robustia keskiarvoa tai mediaania. Osallistujien pätevyyden arviointi tehtiin z-arvojen perusteella. Koko aineistossa hyväksyttäviä tuloksia oli 85 %, kun vertailuarvosta sallittiin pH-määrityksissä 0,2 pH-yksikön ja muissa määrityksissä 5–35 %:n poikkeama.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, klorofylli *a*, ravinteet, pH, sähkönjohtavuus, väri, sameus, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 02/2019

Under february 2019 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av klorofyll *a*, näringsämnen (N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, P_{tot}), pH, ledningsförmåga, grumlighet och färg i naturvatten. Proven sändes ut till 34 laboratorier.

Som referensvärde av analytens koncentration användes det teoretiska värdet eller robust medelvärdet eller median av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I denna jämförelsen var 85 % av resultaten tillfredsställande, när 5–35 % och 0,2 pH enhet avvikelsen från referensvärdet accepterades.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, klorofyll *a*, färg, grumlighet, näringsämne, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, P_{tot}, pH, ledningsförmåga, provningsjämförelse, vatten- och miljölaboratorier

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1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of chlorophyll *a*, colour, conductivity (γ_{25}), N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, P_{tot}, pH, and turbidity in brackish and lake waters in February 2019 (NW 02/2019). In the PT the results of Finnish laboratories providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. The proficiency test provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [1], and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest SYKE is a proficiency testing provider PT01 accredited by FINAS Finnish Accreditation Service (www.finas.fi, ISO/IEC 17043). This proficiency test was carried out under the accreditation scope of Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer

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The responsibilities in organizing the proficiency test

Riitta Koivikko	coordinator
Mirja Leivuori	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance

Analytical expert

Mika Sarkkinen

2.2 Participants

In total 34 laboratories participated in this proficiency test, 29 participants were from Finland, five from other European countries (Appendix 1). Altogether 74 % of the participants used accredited analytical methods at least for a part of the measurements. For this proficiency test, the organizing laboratory (T003, www.finas.fi, ISO/IEC 17025) has the code 31 (SYKE, Oulu) in the result tables.

2.3 Samples and delivery

Three types of samples were delivered to the participants; synthetic, brackish and lake water samples for analysis of chlorophyll *a*, colour, conductivity, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, P_{tot}, pH, and turbidity. The synthetic samples A1H, A1J, A1N, and A1P were prepared by diluting from NIST traceable certified reference materials produced by Merck or by BDH Prolab (pH) (Appendix 2). NIST traceable certified reference materials were not available for chlorophyll *a*, turbidity and colour determinations. The synthetic sample A1K for chlorophyll *a* determination was prepared by dissolving the weighted green pigment (Sigma-Aldrich) in ethanol. The synthetic sample A1S for turbidity determination was prepared by diluting Hach Formatzin Turbidity Standard produced by Hach Company. The synthetic sample A1V for colour measurement was prepared from the colour standard produced by Merck. The brackish water was collected from the seashore of Helsinki. The lake water was collected from Espoo, Southern Finland. The sample preparation is described in detail in the Appendix 2.

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after three days by measuring conductivity, N_{NH4} and $P_{PO4.}$ According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered on 11 February 2019 to the participants abroad and on 12 February 2019 to the national participants. The samples arrived to the participants mainly on 13 February 2019. Participant 6 received the samples on 14 February 2019.

The temperature control sample was placed into the sample package and the temperature was requested to be measured immediately after opening the package. The temperature of control sample was ≤ 10 °C for all those participants who returned the sample arrival form.

The samples were requested to be measured as follows:

chlorophyll *a*	14 February 2019
conductivity, pH	14 February 2019
N_{NH4}, $N_{NO2+NO3}$, P_{PO4}	14 February 2019
colour, turbidity	14 February 2019
N_{tot}, P_{tot}	latest on 25 February 2019

The results were requested to be reported latest on 26 February 2019 and the participants delivered the results mainly accordingly. One participant reported their results on 27 February

2019. The preliminary results were delivered to the participants via ProftestWEB and email on 5 March 2019.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing pH, colour, chlorophyll *a*, N_{NH4}, N_{tot}, P_{tot}, and turbidity. Detailed information of homogeneity studies is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous.

The stability of the samples was tested by measuring chlorophyll *a*, N_{NH4}, pH, and P_{PO4} from the samples stored at the room temperature for one day (Appendix 4). The measurement values were checked against the results of the samples stored at 4 °C. According to the test results, the concentration of N_{NH4} could slightly decrease in the samples, if their temperature increased during the sample distribution. Based on the reported temperatures of the control sample, the maximum arrival temperature was 10 °C, thus the samples were regarded stable under the sample distribution conditions. According to the test other samples were considered stable.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. The comments from the participants mainly dealt with sample delivery, reporting errors or difficulties in the result reporting. The comments from the provider were recommendations related to the reporting the sample arrival temperature. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs or the Hampel test before calculating the mean. The results, which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

The participants reported replicate results for the measurements of N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, and P_{tot}. The replicate results were tested using the Cochran test. When two results were to be reported for the analysis and the participant reported only one, the result was not included in the statistical calculations and it was not evaluated. If needed, the participant can calculate the z score [4].

More information about the statistical handling of the data is available from the Guide for participant [4].

2.6.2 Assigned values

The calculated values (NIST traceable) were used as the assigned values for $N_{NO2+NO3}$, N_{tot}, P_{PO4}, and P_{tot} in the synthetic samples. For the other samples and measurands the robust mean or median (A1S, B2S, N3H: conductivity, N3S) of the results reported by the participants were used as the assigned value.

For the calculated assigned values the expanded uncertainty (k=2) was estimated using standard uncertainties associated with individual operations involved in the sample preparation. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution. When the robust mean or the median of the participant results was used as the assigned value, the uncertainty was calculated using the robust standard deviation or the standard deviation, respectively [2, 4]. **After reporting the preliminary results no changes have been done for the assigned values.**

The expanded uncertainty of the calculated assigned values (U_{pt}, k=2) was less than or equal to 1.1 %. When using the robust mean or the median of the participant results as the assigned value, the expanded uncertainties of the assigned values were mainly between 0.4 and 10 %, while for turbidity in the brackish water sample it was 16 % and for $Colour_{Visual}$ in the synthetic sample it was 17 % and in the brackish water sample 18 % (Appendix 6).

2.6.3 Standard deviation for proficiency assessment and z score

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 0.2 pH units and to 5–35 % for the other measurements. **After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.**

When using the robust mean or the median as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation for proficiency assessment and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation or the standard deviation (s) of the reported results (s_{rob}) [3]. The criterion s_{rob} (or s)/ $s_{pt} < 1.2$ was mainly fulfilled.

In the following cases, the criterion for the reliability of the assigned value[1] and/or for the reliability of the standard deviation for performance assessment[2] was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurement
A1V	$Colour_{Visual}$[1,2],$Color_{Spectrofotometric}$[1],
B2N	N_{tot}[1]
B2S	$Colour_{Visual}$[1,2], Turbidity[1,2]
N3S	$Colour_{Visual}$[1,2]

3 Results and conclusions

3.1 Results

The terms used in the results tables are shown in Appendix 7. The results and the performance of each participant are presented in Appendix 8 and the summary of the results in Table 1. The reported results with their expanded uncertainties (k=2) are presented in Appendix 9. The summary of the z scores is shown in Appendix 10 and z scores in the ascending order in Appendix 11.

The robust standard deviation (s_{rob} %) for chlorophyll *a*, conductivity, $N_{NO2+NO3}$ and pH in the synthetic samples was below 4.3 % (Table 1). In general, s_{rob} % was lower than 10 % for 70 % of the reported results (Table 1). In the sample N3S the turbidity concentration was quite low and, in general, the s_{rob} % was higher for turbidity results than in the previous similar PT [5].

Table 1. The summary of the results in the proficiency test NW 02/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n_{all}	Acc z %
Chlorophyll *a*	A1K	abs/cm	0.104	0.104	0.104	0.104	0.001	1.4	10	15	87
	B2K	µg/l	17.3	17.2	17.3	17.5	1.3	7.3	20	16	81
	N3K	µg/l	8.34	8.40	8.34	8.35	0.53	6.4	20	16	88
$Colour_{Visual}$	A1V	mg/l, Pt	15.0	15.0	15.0	15.0	3.4	22.8	25	12	67
	B2S	mg/l, Pt	10.0	9.7	10.3	10.0	3.4	33.0	35	9	78
	N3S	mg/l, Pt	20.0	19.6	20.0	20.0	0.0	0.0	20	12	75
$Colour_{Spectrophotometric}$	A1V	mg/l, Pt	15.7	15.7	15.7	15.9	1.2	7.9	15	13	92
	B2S	mg/l, Pt	10.3	10.3	10.3	10.3	1.8	17.2	35	10	90
	N3S	mg/l, Pt	20.1	20.0	20.9	20.1	3.2	15.5	25	13	85
Conductivity 25	A1J	mS/m	10.5	10.5	10.5	10.5	0.1	1.2	5	25	88
	B2H	mS/m	972	977	972	976	19	2.0	5	21	86
	N3H	mS/m	3.21	3.22	3.26	3.21	0.15	4.6	8	25	64
N_{NH4}	A1N	µg/l	15.8	15.6	15.8	15.5	1.7	10.8	20	26	87
	B2N	µg/l	30.4	29.8	30.4	29.4	3.0	10.0	20	18	82
	N3N	µg/l	75.7	76.2	75.7	76.0	4.6	6.1	20	24	91
$N_{NO2+NO3}$	A1N	µg/l	214	214	213	214	9	4.2	8	25	83
	B2N	µg/l	199	199	199	198	17	8.7	15	19	100
	N3N	µg/l	319	318	319	317	14	4.3	8	22	81
N_{tot}	A1N	µg/l	317	318	314	316	26	8.3	15	23	82
	B2N	µg/l	469	465	469	464	55	11.8	20	20	89
	N3N	µg/l	612	620	612	610	48	7.9	15	21	85
pH	A1H		6.54	6.54	6.54	6.56	0.05	0.8	3.1	27	100
	B2H		7.95	7.95	7.95	7.96	0.07	0.8	2.5	24	100
	N3H		6.39	6.36	6.39	6.36	0.08	1.2	3.1	27	85
P_{PO4}	A1P	µg/l	8.15	8.02	8.23	8.16	0.78	9.5	10	25	70
	B2P	µg/l	27.0	27.1	27.0	27.1	1.9	7.0	15	19	83
	N3P	µg/l	78.4	78.2	78.4	78.6	2.6	3.4	10	22	95
P_{tot}	A1P	µg/l	12.1	12.4	12.2	12.3	1.1	9.2	15	24	90
	B2P	µg/l	35.2	35.4	35.2	35.6	1.4	3.8	15	20	88
	N3P	µg/l	118	117	118	117	6	4.9	10	21	90
Turbidity	A1S	FNU	0.29	0.30	0.31	0.29	0.05	14.7	20	23	74
	B2S	FNU	0.31	0.32	0.31	0.31	0.07	23.4	30	16	75
	N3S	FNU	0.47	0.47	0.47	0.47	0.07	14.9	25	22	86

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{rob} %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, Acc z %: the results (%), where $|z| \leq 2$, n_{all}: the number of the participants.

In this PT the participants were requested to report duplicate results for nutrient measurements. The results of the replicate determinations based on the ANOVA statistical handling are presented in Table 2. The estimation of the robustness of the methods could be done by the ratio s_b/s_w. The ratio s_b/s_w should not exceed 3 for robust methods. For samples B2N and N3N the criterion was fulfilled as well as for $N_{NO2+NO3}$ and N_{tot} in A1N. In other cases the robustness criterion was not fulfilled (Table 2).

Table 2. The summary of repeatability on the basis of replicate determinations (ANOVA statistics).

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
N_{NH4}	A1N	µg/l	15.8	15.6	0.558	2.10	2.18	3.5	13	14	3.8
	B2N	µg/l	30.4	29.8	0.436	3.78	3.80	1.4	12	12	8.7
	N3N	µg/l	75.7	76.2	0.983	5.25	5.34	1.3	6.9	7.0	5.3
$N_{NO2+NO3}$	A1N	µg/l	214	214	2.85	9.29	9.71	1.3	4.3	4.5	3.3
	B2N	µg/l	199	199	2.25	15.2	15.3	1.1	7.6	7.7	6.7
	N3N	µg/l	319	318	3.18	16.7	17.0	0.99	5.2	5.3	5.2
N_{tot}	A1N	µg/l	317	318	7.57	35.3	36.1	2.5	11	12	4.7
	B2N	µg/l	469	465	8.42	58.7	59.3	1.8	13	13	7.0
	N3N	µg/l	612	620	6.56	66.7	67.0	1.1	11	11	10
P_{PO4}	A1P	µg/l	8.15	8.02	0.461	1.55	1.62	5.4	18	19	3.4
	B2P	µg/l	27.0	27.1	0.736	2.55	2.66	2.7	9.4	9.8	3.5
	N3P	µg/l	78.4	78.2	1.57	2.51	2.96	2.0	3.2	3.8	1.6
P_{tot}	A1P	µg/l	12.1	12.4	1.69	0.913	1.92	14	7.5	16	0.54
	B2P	µg/l	35.2	35.4	0.760	1.84	1.99	2.2	5.3	5.7	2.4
	N3P	µg/l	118	117	2.33	6.43	6.84	2.0	5.5	5.8	2.8

s_w**:** repeatability standard error; s_b**:** between participants standard error; s_t: reproducibility standard error.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 12. In this PT the statistical comparison of the analytical method was possible only for very few measurands and samples, and thus the comparison is based partly on the graphical result evaluation.

Chlorophyll *a*

The participants determined chlorophyll *a* mainly by spectrophotometric determination and one participant used fluorometric determination (Appendix 12). The laboratories that use the fluorometer for chlorophyll *a* determination could use the synthetic sample as external assurance for spectrophotometer, which is used in the calibration of the fluorescence spectrophotometer. Along with the proficiency test NW 04/2014 additional test for measurement of the chlorophyll *a* in brackish water sample was performed [6]. There it was concluded that folding of the filter was more important than shaking and the filter should not be folded tightly. Further, it should be noted that shaking is performed properly, i.e. that the bottle is e.g. not too full. Light exposure had significant effect only if the exposure was for several hours.

Colour

Determination of colour was grouped into two groups: visual comparator method using a comparator ($Colour_{Visual}$) and spectrophotometric method ($Colour_{Spectophotometric}$). Depending on the sample 9–12 participants used visual method and 9–13 participants used spectrophotometric method (EN ISO 7887, Appendix 12). For the synthetic sample A1V, the concentration was lower than in the previous similar PTs and, therefore, especially for $Colour_{Visual}$ the deviation of the participant results is very high. In general, as the scale for visual comparator method is

stepped, the results are not normally distributed and the performance evaluation for $Colour_{Visual}$ results is only approximate.

In the previous similar PT the river water sample had high turbidity and was clearly coloured causing difficulties for the determination of colour [5]. Information of the sample pretreatment methods was collected and evaluated. Based on the information it was evident, that for determination of colour, the pretreatment procedures for coloured samples having high turbidity need harmonization among the national laboratories.

Due to high variation of the results in the previous similar PT, also here the participants were requested to describe their pretreatment procedure together with their results. Eight participants described their pretreatment procedures for determination of colour as requested and the used procedures were filtration, turbidity correction and no pretreatment (Table 3). In this PT the river water sample was not clearly coloured and turbidity was lower, thus the sample was not as challenging as in the previous similar PT [5]. In this PT no clear influence of used pretreatment method for sample N3S was observed.

Table 3. The pretreatment methods used for the colour measurements and participants' result for the river sample N3S.

Participant	Pretreatment N3S	$Colour_{Spectrophotometric}$ (mg/l Pt)	$Colour_{Visual}$ (mg/l Pt)
4	Filtratrion with 0.45 µm PES filter	19	
5	Filtration through Millipore Membrane filter 0.45 µm (Mixed cellulosa ester filter)	32.4	
15	Filtration, 25mm PES 0.45µm	21.6	
32	Filtration with 0.45µm IC Acrodisc syringe filter	19	
2	No pretreatment		15
23	No pretreatment		20
25	No pretreatment	16	20
27	No pretreatment. For $Colour_{Spectrophotometric}$: Turbidity correction with secondary wavelenght 750 nm	20.5	20

Conductivity 25

The participants measured conductivity mostly by using the standard method EN 27888 (Appendix 12). One participant used multiparameter meter with conductivity probe.

Ammonium nitrogen, N_{NH4}

Depending on the sample up to 10 participants determined ammonium nitrogen using the standard method SFS 3032 (manual indophenol blue spectrophotometric method) and up to 7 participants used the corresponding automatic standard method EN ISO 11732 (Appendix 12). Depending on the sample up to three participants used the spectrophotometric salicylate method modified for Aquachem technique and 2–6 participants used some other method (e.g. CFA with fluorometric determination, IC method or Hach Lange tube method). In the statistical comparison between the methods no statistically significant differences were observed (Appendix 12).

Nitrate + nitrite nitrogen, $N_{NO2+NO3}$

The participants used mostly (13–16 participants, depending on the sample) the standard method EN ISO 13395. IC method based on EN ISO 10304 was used by 1–3 participants and the sulfanilamide spectrophotometric method after hydrazine or Cd/Cu reduction modified for Aquachem technique was used by 2–3 participants. Some other methods were used by 1-2 participants (e.g. colorimetric vanadium-chloride method with Aquachem technique). In the visual method comparison no significant differences between the methods were observed (Appendix 12).

Total nitrogen, N_{tot}

The participants determined the total nitrogen mostly (11–12 participants, depending on the sample) according to the standard method EN ISO 11905. Depending on the sample 2 or three participants used Hach Lange tube method. Other methods were used by 6–8 participants (Appendix 12). The other used methods were e.g. SFS EN 12260 (four participants), SFS 3031 (withdrawn) and colorimetric vanadium-chloride method with Aquachem technique. In the visual method comparison no significant differences between the methods were observed.

pH

The participants measured pH mostly (14–15 participants, depending on the sample) by using universal electrode and 9–11 participants used an electrode for low ionic waters. One participant used tris electrode (Appendix 12). In the statistical method comparison no significant differences were observed between the electrode for low ionic waters and universal electrode (Appendix 12).

Phosphate phosphorus, P_{PO4}

Phosphate phosphorus was mostly (9–11 participants, depending on the sample) determined using the standard method EN 15681. The standard method EN ISO 6878 (manual spectrophotometric method) was used by 2 participants. The withdrawn Finnish standard method 3025 was used by 4 participants. The ammonium molybdate spectrophotometric method modified for Aquachem technique was used by 4 participants. Three participants used some other method, e.g. Hach Lange tube method or IC method (Appendix 12). In the visual method comparison no significant differences were observed between the methods.

Total phosphorus, P_{tot}

The participants determined total phosphorus mostly (7–8 participants) using the standard method EN ISO 15681. The manual standard method EN ISO 6878 was used by 3–4 participants. The withdrawn Finnish standard method SFS 3026 was used by 3–5 participants. Ammonium molybdate method modified for Aquachem technique was used by 3 participants and tube method was used by 1–3 participants, depending on the sample (Appendix 12). In the visual comparison between the methods no statistically significant differences were observed.

Turbidity

The participants measured turbidity mostly (13–20 participants) with an apparatus based on diffuse radiation measurement. Two participants used an apparatus based on attenuation of a radiation flux measurement and one participant used other method (Appendix 12).

3.3 Uncertainties of the results

Altogether 74 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 4, Appendix 13). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for estimating of measurement uncertainty (Appendix 13). The participants mainly used the internal quality control (IQC) data and the results obtained in proficiency tests followed by the IQC data from both synthetic control samples and routine sample replicates. Also for some measurands the approach based on the data obtained from method validation was used. Depending on the sample and measurand, up to eight participants used MUkit measurement uncertainty software for the estimation of their uncertainties [7]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 4. The range of the expanded measurement uncertainties (U_i%, k=2) reported by the participants and recommendations for natural waters [8].

Measurand	Synthetic sample, U_i%	Brackish water, U_i%	Lake water, U_i%	Recommendation, % [8]
Chlorophyll *a*	10-26	10-26	10-26	20
$Colour_{Visual}$	5-50	5-67 [1)]	5-33	20
$Colour_{Spectrophotometric}$	10-37	10-37	10-37	20
Conductivity 25	1-8	2-8	1-10	5
N_{NH4}	9-79	9-31	9-22	15
$N_{NO2+NO3}$	9-22	9-22	9-20	15
N_{tot}	8-23	8-18	8-23	15
pH	0.2-0.3 pH unit	0.003-0.4 pH unit	0.2-0.3 pH unit	0.2 pH unit
P_{PO4}	8-40	8-25	8-25	15
P_{tot}	11-35	8-35	8-27	15
Turbidity	10-150	10-129	10-89	20

[1)] In table with bold the values of expanded measurement uncertainty over 50 %

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for the data entered into the water quality registers have been published in Finland [8]. The recommendations for measurement uncertainties for the tested measurands in natural waters vary from 5 % to 20 % (for pH measurement 0.2 pH units, see Table 4). In this proficiency test some of participants had their measurement uncertainties within these limits, while some did not achieve them. One participant reported very high measurement uncertainties for turbidity measurements (U_i % = 89 – 150 %). Within the optimal measuring range, the expanded measurement uncertainty (k=2) should typically be 20 – 40%. Close to the limit of quantification the relative measurement uncertainty is higher. Further, the expanded uncertainties below 5% could commonly be considered unrealistic uncertainty value for routine laboratories. Harmonization of the uncertainties estimation should be continued.

4 Evaluation of the results

The performance evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for the performance assessment (Appendix 7). The z scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

In total, 85 % of the results were satisfactory when deviation of 0.2 pH units and for the other measurements 5 – 35 % from the assigned value was accepted (Appendix 10). In the sample N3S the turbidity concentration was quite low and, in general, for turbidity results of all the samples the deviation was high.

Altogether 74 % of the participants used accredited analytical methods at least for a part of the measurements and 88 % of those results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 5. In the previous similar proficiency test NW 02/2017, the performance was satisfactory for 83 % of the all participants, when deviation of 10 – 35 % and 0.2 pH units from the assigned values was accepted [5].

Table 5. Summary of the performance evaluation in the proficiency test NW 02/2019.

Measurand	2 × s_{pt}, %	Satisfactory results, %	Assessment
Chlorophyll *a*	10-20	85	The performance was better than in the PT NW 02/2017 where the performance was satisfactory for 77 % of the results [5].
$Colour_{Visual}$	20-35	73	The performance evaluation is only approximate. In the PT NW 02/2017 the performance was satisfactory for 83 % of the results when deviation of 15-35 % from the assigned value was accepted [5].
$Colour_{Spectophotometric}$	15-35	89	The performance evaluation for the samples A1V is only approximate. In the PT NW 02/2017 the performance was satisfactory for 100 % of the results when deviation of 15-30 % from the assigned value was accepted [5].
Conductivity 25	5-8	79	Concentration of the sample N3H was quite low and only 64 % of the results were satisfactory. In the PT NW 02/2017 the performance was satisfactory for 90 % of the results when deviation of 5 % from the assigned value was accepted [5].
N_{NH4}	20	87	The performance was better than in the PT NW 02/2017 where the performance was satisfactory for 66 % of the results when deviation of 20-30 % from the assigned value was accepted [5].
$N_{NO2+NO3}$	8-15	88	In the PT NW 02/2017 the performance was satisfactory for 85 % of the results when deviation of 8-10 % from the assigned value was accepted [5].
N_{tot}	15-20	85	The performance evaluation for the sample B2N is only approximate. In the PT NW 02/2017 the performance was satisfactory for 89 % of the results when deviation of 10-15 % from the assigned value was accepted [5].
pH	2.5-3.1	95	Good performance. In the PT NW 02/2017 the performance was satisfactory for 88 % of the results when deviation of 2.6-4.5 % from the assigned value was accepted [5].
P_{PO4}	10-15	83	The performance was better than in the PT NW 02/2017 where the performance was satisfactory for 70 % of the results when deviation of 10-20 % from the assigned value was accepted [5].
P_{tot}	10-15	89	In the PT NW 02/2017 the performance was satisfactory for 83 % of the results when deviation of 15 % from the assigned value was accepted [5].
Turbidity	20-30	78	Difficulties in turbidity measurements. The evaluation for the sample B2S is only approximate. In the PT NW 02/2015 the performance was satisfactory for 91 % of the results when deviation of 15-30 % from the assigned value was accepted [5].

5 Summary

The Proftest SYKE carried out the proficiency test (PT) for analysis of colour, conductivity, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, P_{tot}, pH, and turbidity in brackish and river waters in February 2019 (NW 02/2019). In total, 34 laboratories participated in this PT.

Either the calculated concentration or the robust mean or the median of the results reported by the participants was chosen to be the assigned value for the measurand. The uncertainty for the assigned value was estimated at the 95 % confidence level and it was less than or equal to 1.1 % for the calculated assigned values. For the assigned values based on the robust mean or the median it was between 0.4–10 %, while for turbidity in the brackish water sample it was 16 % and for $Colour_{Visual}$ in the synthetic sample it was 17 % and in the brackish water sample 18 %.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for the proficiency assessment at 95 % confidence level. In this proficiency test 85 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value 0.2 pH units for pH measurement and 5 to 35 % for the other determinations.

6 Summary in Finnish

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen helmikuussa 2019 (NW 02/2019). Pätevyyskokeessa määritettiin klorofylli *a*, väri, sähkönjohtavuus, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, P_{tot}, pH ja sameus synteettisistä näytteistä, jokivedestä ja murtovedestä. Pätevyyskokeeseen osallistui yhteensä 34 laboratoriota.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujatulosten robustia keskiarvoa tai mediaania. Vertailuarvolle laskettiin mittausepävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli $\leq$ 1,1 % laskennallista pitoisuutta vertailuarvona käytettäessä ja muutoin pääasiassa välillä 0,4–10 %. Murtoveden sameuden määritykselle vertailuarvon laajennettu epävarmuus oli 16 % ja visuaaliselle värinmääritykselle 17 % (synteettinen näyte) ja 18 % (murtovesinäyte).

Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta 0,2 pH-yksikköä ja muilla testisuureilla 5–35 %. Koko aineistossa hyväksyttäviä tuloksia oli 85 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Estonia	Marine system institute at Tallinn university of Technology
Finland	BewiSynbra RAW Oy, Porvoo
	Eurofins Ahma Oy Seinäjoki
	Eurofins Ahma Oy, Rovaniemi
	Eurofins Environment Testing Finland Oy, Lahti
	HSY Käyttölaboratorio Pitkäkoski Helsinki
	HY, Tvärminnen eläintieteellinen asema, Hanko
	KVVY Tutkimus Oy, Tampere
	KVVY-Botnialab, Vaasa
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	Luonnonvarakeskus, Viikki B2-laboratorio
	MetropoliLab Oy
	Neste Oyj / Laadunvarmistus, Naantali
	Neste Oyj, Tutkimus ja kehitys/Vesilaboratorio, Kulloo
	Oulun Vesi Liikelaitos
	Saimaan Vesi- ja Ympäristötutkimus Oy, Lappeenranta
	Savo-Karjalan Ympäristötutkimus Oy, Joensuu
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	ScanLab Oy
	SeiLab Oy Haapaveden toimipiste
	SeiLab Oy Seinäjoen toimipiste
	SGS Finland Oy, Kotka
	SYKE Oulun toimipaikka
	SYKE/Merikeskus
	SYNLAB Analytics & Services Finland Oy
	Tampereen Vesi/Viemärilaitoksen laboratorio
	Teollisuuden Voima Oyj
	Yara Suomi Oy, Uusikaupunki
	ÅMHM laboratoriet, Jomala, Åland
Germany	Landesamt für Umwelt und Naturschutz und Geologie M-V
Lithuania	Environment Research Department, Environmental Protection Agency
Sweden	ACES, Stockholm University
	Umeå Marine Sciences Centre

APPENDIX 2: Sample preparation

Measurand	Sample	Initial concentration	Added compoud (Producer) Addition	Assigned value
Chlorophyll *a* [abs/cm] [µg/l]	A1K	-	Chlorophyll *a* 2 mg (Sigma) / 1.5 litres ethanol	0.104
	B2K	2	16.0	17.3
	N3K	2	7.9	8.34
N_{NH4} [µg/l]	A1N	-	NH_4Cl (Merck) 14.0	15.8
	B2N	44	-	30.4
	N3N	32	-	75.7
$N_{NO2+NO3}$ [µg/l]	A1N	-	$NaNO_3$ (Merck) 214	214
	B2N	133	-	199
	N3N	87	232	319
N_{tot} [µg/l]	A1N	-	$NaNO_3$ + NH_4Cl + Na_2-EDTA (Merck) 316	317
	B2N	489	-	469
	N3N	423	232	612
pH pH unit	A1H	-	Buffer solution pH 6.0 (BDH Prolabo)	6.54
	B2H	7.7	-	7.95
	N3H	6.1	-	6.39
P_{PO4} [µg/l]	A1P	-	KH_2PO_4 (Merck) 8.1	8.15
	B2P	21	-	27.0
	N3P	0	29.0	78.4
P_{tot} [µg/l]	A1P	-	KH_2PO_4 + $C_3H_7Na_2O_6P$ (Merck) 12.1	12.1
	B2P	33	-	35.2
	N3P	10	118	118
γ_{25} [mS/m]	A1J	-	KCl (Merck) 8.8	10.5
	B2H	931	-	972
	N3H	2.9	-	3.21
Turbidity [FNU]	A1S	-	Hach Formazin 0.25	0.29
	B2S	2	-	0.31
	N3S	1.7	-	0.47
Colour [mg/l, Pt]	A1V	-	Platinum Cobalt-solution (Merck) 15	15.0/15.7
	B2S	5	5	10.0/10.3
	N3S	25	-	20.0/20.1

First letter of the sample code indicates the sample type:

A = Synthetic sample

B = Brackish water

N = Natural water (lake water)

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested from duplicate measurements of selected measurement from six samples of each sample types.

Criteria for homogeneity:

$\mathbf{s_{anal}/s_{pt}<0.5}$ and $\mathbf{s_{sam}^2<c}$, where

s_{pt} = standard deviation for proficiency assessment
s_{anal} = analytical deviation, standard deviation of the results in a sub samples
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_{pt})^2$
F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand/Sample	Concentration [µg/l], [pH unit] [FNU], [mg/l, Pt]	n	s_{pt} %	s_{pt}	s_{anal}	s_{anal}/s_{pt}	$s_{anal}/s_{pt}<0.5$?	s_{sam}^2	c	$s_{sam}^2<c$?
N_{NH4}/B2N	26.3	6	10	2.63	0.64	0.24	Yes	0.75	2.07	Yes
N_{NH4}/N3N	71.3	6	10	7.13	0.75	0.10	Yes	1.50	11.1	Yes
N_{tot}/B2N	480	6	10	48.0	4.11	0.09	Yes	17.9	487	Yes
N_{tot}/N3N	631	6	7.5	47.3	1.51	0.03	Yes	5.99	450	Yes
pH/B2H	7.97	8	1.25	0.10	0.02	0.21	Yes	0.0004	0.002	Yes
pH/N3H	6.41	8	1.55	0.10	0.01	0.10	Yes	0.0001	0.002	Yes
P_{tot}/B2P	36.0	6	7.5	2.70	0.72	0.27	Yes	0.36	2.33	Yes
P_{tot}/N3P	123	6	5	6.16	2.41	0.39	Yes	6.16	17.4	Yes
Turbidity/B2S	0.25	4	15	0.04	0.004	0.10	Yes	0.00003	0.0004	Yes
Turbidity/N3S	0.49	6	12.5	0.06	0.005	0.08	Yes	0.00004	0.0008	Yes
Colour/B2S	15	4	17.5	2.63	0	0	Yes	0	1.62	Yes
Colour/N3S	25	6	10	2.5	0	0	Yes	0	1.25	Yes

Criterion for homogeneity:

$\mathbf{s_{sam}/s_{pt}} < \mathbf{0.5}$, where

s_{pt} = standard deviation for proficiency assessment
s_{sam} = between-sample deviation, standard deviation of results between sub samples

Measurand/Sample	Concentration [µg/l]	n	s_{pt} %	s_{pt}	s_{sam}	s_{sam}/s_{pt}	$s_{sam}/s_{pt} < 0.5$?
Chlorophyll *a*/B2K	17.5	7	10	1.75	0.62	0.35	Yes
Chlorophyll *a*/N3K	7.85	8	10	0.78	0.31	0.40	Yes

Conclusion: All criteria for homogeneity were fulfilled and the samples could be considered homogenous.

APPENDIX 4: Stability of the samples

The samples were delivered on 11 or 12 February 2019 and they arrived to the participants mainly on 13 February 2019. The samples were requested to be analysed as follows:

chlorophyll *a*	14 February 2019
pH, conductivity	14 February 2019
N_{NH4}, $N_{NO2+NO3}$, P_{PO4}	14 February 2019
colour, turbidity	14 February 2019
N_{tot}, P_{tot}	latest on 25 February 2019

Stability of chlorophyll *a*, pH, N_{NH4} and P_{PO4} was tested by analysing the samples stored at the temperatures 4 ºC and 20 ºC.

Criteria for stability: $D < 0.3 \times s_{pt}$, where
D = |the difference of results measured from the samples stored at the temperatures 4 °C and 20 °C|
s_{pt} = standard deviation for proficiency assessment

Chlorophyll *a*

Sample	Result, abs/cm		Sample	Result, µg/l		Sample	Result, µg/l	
Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)
A1K	0.104	0.104	B2K	18.0	18.4	N3K	8.24	8.37
D	0.000		D	0.4		D	0.13	
$0.3 \times s_{pt}$	0.002		$0.3 \times s_{pt}$	0.5		$0.3 \times s_{pt}$	0.25	
	$D < 0.3 \times s_{pt}$? Yes			$D < 0.3 \times s_{pt}$? Yes		$D < 0.3 \times s_{pt}$? Yes		

pH

Sample	Result		Sample	Result		Sample	Result	
Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)
A1H	6.55	6.55	B2H	7.92	7.95	N3H	7.92	7.95
D	0.003		D	0.025		D	0.027	
$0.3 \times s_{pt}$	0.03		$0.3 \times s_{pt}$	0.030		$0.3 \times s_{pt}$	0.030	
	$D < 0.3 \times s_{pt}$? Yes			$D < 0.3 \times s_{pt}$? Yes		$D < 0.3 \times s_{pt}$? Yes		

N_{NH4}

Sample	Result, µg/l		Sample	Result, µg/l		Sample	Result, µg/l	
Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)
A1N	11.7	13.8	B2N	24.3	27.6	N3N	68.4	71.5
D	2.1		D	3.3		D	3.1	
$0.3 \times s_{pt}$	0.5		$0.3 \times s_{pt}$	0.9		$0.3 \times s_{pt}$	2.3	
	$D < 0.3 \times s_{pt}$? No			$D < 0.3 \times s_{pt}$? No		$D < 0.3 \times s_{pt}$? No		

P_{PO4}

Sample	Result, µg/l		Sample	Result, µg/l		Sample	Result, µg/l	
Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)	Date	14.2. (20 °C)	14.2. (4 °C)
A1P	8.37	8.31	B2P	27.8	28.4	N3P	79.0	75.0
D	0.05		D	0.57		D	4.0	
$0.3 \times s_{pt}$	0.12		$0.3 \times s_{pt}$	0.61		$0.3 \times s_{pt}$	1.2	
	$D < 0.3 \times s_{pt}$? Yes			$D < 0.3 \times s_{pt}$? Yes		$D < 0.3 \times s_{pt}$? No [1)]		

[1)] The difference is within the analytical error.

Conclusion: According to the test results, the concentration of N_{NH4} in the samples A1N, B2N and N3N could slightly decrease, if the temperature increased up to 20°C during the sample transport and storage. However, based on the reported arrival temperatures of the samples (see 2.3), the maximum arrival temperature was 10 °C. Thus the samples were regarded stable under the sample distribution conditions.

Further, the concentration of P_{PO4} in the sample N3N could slightly change during transport and storage, but the difference is within the analytical error, thus the sample could be regarded stable.

Overall, the samples were considered stable in the sample distribution conditions.

APPENDIX 5: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
4	Participant informed that the chlorophyll *a* samples were kept in room temperature for some hours.	The samples should be stored cool (4° C) after the delivery.
6	Participant informed that the temperature sample was not measured at arrival as this procedure was not informed in advance, and per routine the box was put in a cooling room upon arrival. Further the participant noted that according to the Proftest SYKE guide for participants the samples should be delivered within 24 hours but their samples took 6 days to be delivered. The participant was worried about the affected by this delay.	The instructions for "temperature" sample are given both in the information and in the sample letters. If the sample temperature has not elevated, the samples are not affected. The samples for this participant were sent on 11.2. and the delivery time was three days which is fine for these samples. The delivery was ordered on 8.2. and therefore this date was shown on the sample package. The provider chooses the best possible courier to transport the sample for all participants and samples are generally delivered within 24 hours. Special arrangements may be made to govern timely deliveries to e.g. participants abroad.
11	Participant received the samples within one day after the estimated delivery day.	The distributor had difficulties in delivering the samples due to a strike.
12, 28	Problems with logging into ProftestWEB. The system gave a message of wrong username or password.	Unfortunately there was a problem with the server. The problem was fixed rapidly and the participants were informed of the situation.

Participant	Comments to the results	Action / Proftest SYKE
15	Participant reported the results for N_{NH4} ja $N_{NO2+NO3}$ erroneously. The right results were: N_{NH4} A1N: 23.3 µg/l N3N: 110 µg/l $N_{NO2+NO3}$ A1N: 933 µg/l N3N: 1430 µg/l	The results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the results had been reported correctly, the results for would have been unsatisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].
26	Participant reported the results for conductivity erroneously. The right result was: Conductivity B2H: 968 mS/m	The result was outlier in the statistical treatment, and thus did not affect the performance evaluation. If the result had been reported correctly, the result would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].
30	Participant reported the results for conductivity erroneously. The right result was: Conductivity B2H: 970 mS/m	The result was outlier in the statistical treatment, and thus did not affect the performance evaluation. If the result had been reported correctly, the result would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
1, 5, 7, 17, 18, 21, 22, 29	The participants did not return the sample arrival document to the provider. Therefore the information of the sample arrival temperature was not available from all the participants. The participants should follow up the instructions of the provider.
2, 5, 8, 12, 24, 26, 29, 32	For one or more measurands and/or samples the variance of participant's parallel results was significantly higher than the variance of the other participants, i.e. those results were Cochran outliers. The provider recommends the participants to re-validate their accepted deviation of replicate measurements.
3	The participant reported U_i for pH results in pH units, but the request was to report relative U_i %.
4, 26, 32	It is recommended that the participants measure the temperature sample immediately after the sample package arrival.
12	The participant reported lower than value for P_{tot} for sample B2P (<10 µg/l) when the assigned value for the sample was 35.2 µg/l. The participant should re-validate the limit of quantification of their method.
17, 25	The participant didn't report the replicate results for all or some of the nutrient samples as instructed. Therefore the performance evaluation is not done for these measurands.

APPENDIX 6: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Chlorophyll *a*	A1K	abs/cm	0.104	0.001	1.0	Robust mean	0.10
	B2K	µg/l	17.3	0.9	5.1	Robust mean	0.26
	N3K	µg/l	8.34	0.34	4.1	Robust mean	0.21
$Colour_{Visual}$	A1V	mg/l, Pt	15.0	2.5	16.5	Robust mean	0.66
	B2S	mg/l, Pt	10.0	1.8	18.1	Median	0.52
	N3S	mg/l, Pt	20.0	1.5	7.6	Median	0.38
$Colour_{Spectrophotometric}$	A1V	mg/l, Pt	15.7	0.9	5.7	Robust mean	0.38
	B2S	mg/l, Pt	10.3	1.0	10.1	Median	0.29
	N3S	mg/l, Pt	20.1	1.2	6.2	Median	0.25
Conductivity 25	A1J	mS/m	10.5	0.1	0.6	Robust mean	0.12
	B2H	mS/m	972	11	1.1	Robust mean	0.22
	N3H	mS/m	3.21	0.04	1.1	Median	0.14
N_{NH4}	A1N	µg/l	15.8	0.9	5.7	Robust mean	0.29
	B2N	µg/l	30.4	1.9	6.3	Robust mean	0.32
	N3N	µg/l	75.7	2.5	3.3	Robust mean	0.17
$N_{NO2+NO3}$	A1N	µg/l	214	1	0.6	Calculated value	0.08
	B2N	µg/l	199	10	5.1	Robust mean	0.34
	N3N	µg/l	319	8	2.4	Robust mean	0.30
N_{tot}	A1N	µg/l	317	3	1.1	Calculated value	0.07
	B2N	µg/l	469	32	6.9	Robust mean	0.35
	N3N	µg/l	612	28	4.5	Robust mean	0.30
pH	A1H		6.54	0.03	0.4	Robust mean	0.13
	B2H		7.95	0.03	0.4	Robust mean	0.16
	N3H		6.39	0.04	0.6	Robust mean	0.19
P_{PO4}	A1P	µg/l	8.15	0.07	0.8	Calculated value	0.08
	B2P	µg/l	27.0	1.1	4.1	Robust mean	0.27
	N3P	µg/l	78.4	1.5	1.9	Robust mean	0.19
P_{tot}	A1P	µg/l	12.1	0.1	1.0	Calculated value	0.07
	B2P	µg/l	35.2	0.9	2.5	Robust mean	0.17
	N3P	µg/l	118	3	2.7	Robust mean	0.27
Turbidity	A1S	FNU	0.29	0.01	4.8	Median	0.24
	B2S	FNU	0.31	0.05	15.6	Robust mean	0.52
	N3S	FNU	0.47	0.04	8.4	Robust mean	0.34

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 7: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
s	Standard deviation
s %	Standard deviation, %
n_{stat}	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i $(i = 1, 2 \ldots p)$:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 8: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.19	0.104	10	0.105	0.104	0.104	0.001	0.7	13
	µg/l	B2K		0.12	17.3	20	17.5	17.5	17.2	1.2	7.2	13
	µg/l	N3K		0.37	8.34	20	8.65	8.35	8.40	0.43	5.1	15
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		8.57	10.0	35	25.0	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		-0.59	15.7	15	15.0	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		-0.61	10.3	35	9.2	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		0.00	20.1	25	20.1	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		1.90	10.5	5	11.0	10.5	10.5	0.1	1.1	22
	mS/m	B2H		1.15	972	5	1000	976	977	12	1.2	19
	mS/m	N3H		3.82	3.21	8	3.70	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.09	15.8	20	15.7	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.58	30.4	20	28.7	29.4	29.8	2.2	7.2	16
	µg/l	N3N		-0.69	75.7	20	70.5	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-0.35	214	8	211	214	214	10	4.4	22
	µg/l	B2N		-0.50	199	15	192	198	199	15	7.7	18
	µg/l	N3N		-0.55	319	8	312	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.69	317	15	301	316	318	21	6.6	19
	µg/l	B2N		-1.04	469	20	420	464	465	59	12.7	18
	µg/l	N3N		-0.31	612	15	598	610	620	36	5.8	19
pH		A1H		-0.39	6.54	3,1	6.50	6.56	6.54	0.06	0.9	27
		B2H		-0.91	7.95	2,5	7.86	7.96	7.95	0.08	1.0	24
		N3H		2.12	6.39	3,1	6.60	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		0.07	8.15	10	8.18	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-0.25	27.0	15	26.5	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.06	78.4	10	78.7	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		1.76	12.1	15	13.7	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-0.28	35.2	15	34.5	35.6	35.4	1.2	3.5	15
	µg/l	N3P		0.17	118	10	119	117	117	5	4.6	20
Turbidity	FNU	A1S		-0.17	0.29	20	0.29	0.29	0.30	0.03	10.0	17
	FNU	B2S		-0.75	0.31	30	0.28	0.31	0.32	0.07	22.1	14
	FNU	N3S		-0.07	0.47	25	0.47	0.47	0.47	0.06	13.0	20

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Colour_{Visual}$	mg/l, Pt	A1V		2.67	15.0	25	20.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	N3S		-2.50	20.0	20	15.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		356.19	10.5	5	104.0	10.5	10.5	0.1	1.1	22
	mS/m	N3H		224.22	3.21	8	32.00	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.63	15.8	20	14.8	15.5	15.6	1.4	9.2	22
	µg/l	N3N		-0.96	75.7	20	68.4	76.0	76.2	5.3	6.9	21
N_{tot}	µg/l	A1N		-9.13	317	15	100	316	318	21	6.6	19
	µg/l	N3N		-4.62	612	15	400	610	620	36	5.8	19

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
pH		A1H		-0.39	6.54	3,1	6.50	6.56	6.54	0.06	0.9	27
		N3H		-0.91	6.39	3,1	6.30	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		13.74	8.15	10	13.75	8.16	8.02	0.59	7.4	19
	µg/l	N3P		0.59	78.4	10	80.7	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		3.47	12.1	15	15.3	12.3	12.4	1.1	8.8	20
	µg/l	N3P		-0.34	118	10	116	117	117	5	4.6	20
Turbidity	FNU	A1S		1.72	0.29	20	0.34	0.29	0.30	0.03	10.0	17
	FNU	N3S		0.17	0.47	25	0.48	0.47	0.47	0.06	13.0	20

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		0.00	10.0	35	10.0	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		-1.70	15.7	15	13.7	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		0.00	10.3	35	10.3	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		0.28	20.1	25	20.8	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		0.38	10.5	5	10.6	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-0.12	972	5	969	976	977	12	1.2	19
	mS/m	N3H		-0.08	3.21	8	3.20	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-1.08	15.8	20	14.1	15.5	15.6	1.4	9.2	22
	µg/l	B2N		2.58	30.4	20	38.3	29.4	29.8	2.2	7.2	16
	µg/l	N3N		0.22	75.7	20	77.4	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		0.00	214	8	214	214	214	10	4.4	22
	µg/l	B2N		-0.30	199	15	195	198	199	15	7.7	18
	µg/l	N3N		-0.24	319	8	316	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.74	317	15	300	316	318	21	6.6	19
	µg/l	B2N		-0.49	469	20	446	464	465	59	12.7	18
	µg/l	N3N		-0.53	612	15	588	610	620	36	5.8	19
pH		A1H		-0.39	6.54	3,1	6.50	6.56	6.54	0.06	0.9	27
		B2H		-1.91	7.95	2,5	7.76	7.96	7.95	0.08	1.0	24
		N3H		0.20	6.39	3,1	6.41	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-0.12	8.15	10	8.10	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-2.69	27.0	15	21.6	27.1	27.1	1.7	6.3	18
	µg/l	N3P		-0.73	78.4	10	75.6	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		0.50	12.1	15	12.6	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-0.87	35.2	15	32.9	35.6	35.4	1.2	3.5	15
	µg/l	N3P		-0.93	118	10	113	117	117	5	4.6	20
Turbidity	FNU	A1S		20.00	0.29	20	0.87	0.29	0.30	0.03	10.0	17
	FNU	B2S		15.48	0.31	30	1.03	0.31	0.32	0.07	22.1	14
	FNU	N3S		18.04	0.47	25	1.53	0.47	0.47	0.06	13.0	20

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-0.12	0.104	10	0.103	0.104	0.104	0.001	0.7	13
	µg/l	B2K		0.35	17.3	20	17.9	17.5	17.2	1.2	7.2	13
	µg/l	N3K		0.07	8.34	20	8.40	8.35	8.40	0.43	5.1	15
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		-0.59	15.7	15	15.0	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		-0.72	10.3	35	9.0	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		-0.44	20.1	25	19.0	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		-0.50	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-0.13	972	5	969	976	977	12	1.2	19
	mS/m	N3H		-0.86	3.21	8	3.10	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.59	15.8	20	14.9	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.51	30.4	20	28.9	29.4	29.8	2.2	7.2	16
	µg/l	N3N		-0.41	75.7	20	72.6	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		1.49	214	8	227	214	214	10	4.4	22
	µg/l	B2N		-0.41	199	15	193	198	199	15	7.7	18
	µg/l	N3N		0.49	319	8	325	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.76	317	15	299	316	318	21	6.6	19
	µg/l	B2N		-0.11	469	20	464	464	465	59	12.7	18
	µg/l	N3N		0.00	612	15	612	610	620	36	5.8	19
pH		A1H		0.28	6.54	3,1	6.57	6.56	6.54	0.06	0.9	27
		B2H		-0.22	7.95	2,5	7.93	7.96	7.95	0.08	1.0	24
		N3H		-0.38	6.39	3,1	6.35	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-3.82	8.15	10	6.60	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.21	27.0	15	27.4	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.42	78.4	10	80.0	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		-1.18	12.1	15	11.0	12.3	12.4	1.1	8.8	20
	µg/l	B2P		1.05	35.2	15	38.0	35.6	35.4	1.2	3.5	15
	µg/l	N3P		-0.59	118	10	114	117	117	5	4.6	20
Turbidity	FNU	A1S		5.17	0.29	20	0.44	0.29	0.30	0.03	10.0	17
	FNU	B2S		1.94	0.31	30	0.40	0.31	0.32	0.07	22.1	14
	FNU	N3S		1.19	0.47	25	0.54	0.47	0.47	0.06	13.0	20

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.19	0.104	10	0.105	0.104	0.104	0.001	0.7	13
	µg/l	B2K		0.58	17.3	20	18.3	17.5	17.2	1.2	7.2	13
	µg/l	N3K		0.67	8.34	20	8.90	8.35	8.40	0.43	5.1	15
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		1.27	15.7	15	17.2	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		1.28	10.3	35	12.6	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		4.90	20.1	25	32.4	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		-0.11	10.5	5	10.5	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.29	972	5	979	976	977	12	1.2	19
	mS/m	N3H		-0.08	3.21	8	3.20	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.57	15.8	20	14.9	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.41	30.4	20	29.2	29.4	29.8	2.2	7.2	16
	µg/l	N3N		-0.51	75.7	20	71.9	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		0.06	214	8	215	214	214	10	4.4	22
	µg/l	B2N		0.93	199	15	213	198	199	15	7.7	18
	µg/l	N3N		-0.24	319	8	316	317	318	14	4.5	20

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
N_{tot}	µg/l	A1N		0.67	317	15	333	316	318	21	6.6	19
	µg/l	B2N		1.36	469	20	533	464	465	59	12.7	18
	µg/l	N3N		0.96	612	15	656	610	620	36	5.8	19
pH		A1H		0.30	6.54	3,1	6.57	6.56	6.54	0.06	0.9	27
		B2H		0.10	7.95	2,5	7.96	7.96	7.95	0.08	1.0	24
		N3H		-0.71	6.39	3,1	6.32	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-0.37	8.15	10	8.00	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.05	27.0	15	27.1	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.03	78.4	10	78.5	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		0.44	12.1	15	12.5	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-0.23	35.2	15	34.6	35.6	35.4	1.2	3.5	15
	µg/l	N3P		-0.36	118	10	116	117	117	5	4.6	20
Turbidity	FNU	A1S		-1.48	0.29	20	0.25	0.29	0.30	0.03	10.0	17
	FNU	B2S		-0.86	0.31	30	0.27	0.31	0.32	0.07	22.1	14
	FNU	N3S		-1.45	0.47	25	0.39	0.47	0.47	0.06	13.0	20

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
pH		B2H		0.10	7.95	2,5	7.96	7.96	7.95	0.08	1.0	24
Turbidity	FNU	A1S		1.79	0.29	20	0.34	0.29	0.30	0.03	10.0	17

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.00	0.104	10	0.104	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-3.95	17.3	20	10.5	17.5	17.2	1.2	7.2	13
	µg/l	N3K		0.77	8.34	20	8.98	8.35	8.40	0.43	5.1	15
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		0.88	15.7	15	16.7	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		1.08	10.3	35	12.2	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		2.22	20.1	25	25.7	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		-0.38	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-0.25	972	5	966	976	977	12	1.2	19
	mS/m	N3H		4.36	3.21	8	3.77	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.16	15.8	20	15.5	15.5	15.6	1.4	9.2	22
	µg/l	B2N		0.07	30.4	20	30.6	29.4	29.8	2.2	7.2	16
	µg/l	N3N		0.25	75.7	20	77.6	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		0.15	214	8	215	214	214	10	4.4	22
	µg/l	B2N		-0.15	199	15	197	198	199	15	7.7	18
	µg/l	N3N		-0.08	319	8	318	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.13	317	15	314	316	318	21	6.6	19
	µg/l	B2N		-0.25	469	20	457	464	465	59	12.7	18
	µg/l	N3N		-0.04	612	15	610	610	620	36	5.8	19
pH		A1H		0.30	6.54	3,1	6.57	6.56	6.54	0.06	0.9	27
		B2H		0.10	7.95	2,5	7.96	7.96	7.95	0.08	1.0	24
		N3H		0.00	6.39	3,1	6.39	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-2.40	8.15	10	7.17	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-0.49	27.0	15	26.0	27.1	27.1	1.7	6.3	18
	µg/l	N3P		-1.39	78.4	10	72.9	78.6	78.2	2.7	3.5	20

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
P_{tot}	µg/l	A1P		-0.40	12.1	15	11.7	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-0.53	35.2	15	33.8	35.6	35.4	1.2	3.5	15
	µg/l	N3P		-1.34	118	10	110	117	117	5	4.6	20
Turbidity	FNU	A1S		-0.34	0.29	20	0.28	0.29	0.30	0.03	10.0	17
	FNU	B2S		3.23	0.31	30	0.46	0.31	0.32	0.07	22.1	14
	FNU	N3S		0.68	0.47	25	0.51	0.47	0.47	0.06	13.0	20

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
N_{NH4}	µg/l	N3N		-0.09	75.7	20	75.0	76.0	76.2	5.3	6.9	21
N_{tot}	µg/l	N3N		10.74	612	15	1105	610	620	36	5.8	19
pH		A1H		1.58	6.54	3,1	6.70	6.56	6.54	0.06	0.9	27
		N3H		3.13	6.39	3,1	6.70	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-20.00	8.15	10	0.00	8.16	8.02	0.59	7.4	19
	µg/l	N3P		-1.63	78.4	10	72.0	78.6	78.2	2.7	3.5	20

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
N_{NH4}	µg/l	A1N		-0.34	15.8	20	15.3	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.42	30.4	20	29.1	29.4	29.8	2.2	7.2	16
$N_{NO2+NO3}$	µg/l	A1N		-0.59	214	8	209	214	214	10	4.4	22
	µg/l	B2N		-0.01	199	15	199	198	199	15	7.7	18
N_{tot}	µg/l	A1N		-0.44	317	15	307	316	318	21	6.6	19
	µg/l	B2N		0.45	469	20	490	464	465	59	12.7	18
pH		A1H		-1.16	6.54	3,1	6.42	6.56	6.54	0.06	0.9	27
		B2H		-1.79	7.95	2,5	7.77	7.96	7.95	0.08	1.0	24
		N3H		-0.39	6.39	3,1	6.35	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		0.90	8.15	10	8.52	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-0.18	27.0	15	26.6	27.1	27.1	1.7	6.3	18
P_{tot}	µg/l	A1P		-0.53	12.1	15	11.6	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-2.13	35.2	15	29.6	35.6	35.4	1.2	3.5	15

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Conductivity 25	mS/m	A1J		0.27	10.5	5	10.6	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.29	972	5	979	976	977	12	1.2	19
	mS/m	N3H		33.06	3.21	8	7.46	3.21	3.22	0.07	2.2	16
N_{tot}	µg/l	A1N		0.65	317	15	332	316	318	21	6.6	19
	µg/l	B2N		1.50	469	20	539	464	465	59	12.7	18
	µg/l	N3N		1.08	612	15	662	610	620	36	5.8	19
pH		A1H		0.39	6.54	3,1	6.58	6.56	6.54	0.06	0.9	27
		B2H		0.00	7.95	2,5	7.95	7.96	7.95	0.08	1.0	24
		N3H		0.40	6.39	3,1	6.43	6.36	6.36	0.04	0.6	26
P_{tot}	µg/l	A1P		1.54	12.1	15	13.5	12.3	12.4	1.1	8.8	20
	µg/l	B2P		0.30	35.2	15	36.0	35.6	35.4	1.2	3.5	15
	µg/l	N3P		0.08	118	10	119	117	117	5	4.6	20
Turbidity	FNU	A1S		4.48	0.29	20	0.42	0.29	0.30	0.03	10.0	17
	FNU	B2S		6.88	0.31	30	0.63	0.31	0.32	0.07	22.1	14
	FNU	N3S		1.36	0.47	25	0.55	0.47	0.47	0.06	13.0	20

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-1.54	0.104	10	0.096	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-0.92	17.3	20	15.7	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-0.05	8.34	20	8.30	8.35	8.40	0.43	5.1	15
Conductivity 25	mS/m	B2H		-0.08	972	5	970	976	977	12	1.2	19
N_{NH4}	µg/l	A1N			15.8	20	*<50*	15.5	15.6	1.4	9.2	22
	µg/l	N3N		0.03	75.7	20	76.0	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		6.66	214	8	271	214	214	10	4.4	22
	µg/l	N3N		2.78	319	8	355	317	318	14	4.5	20
N_{tot}	µg/l	A1N		0.78	317	15	336	316	318	21	6.6	19
	µg/l	N3N		-0.04	612	15	610	610	620	36	5.8	19
pH		B2H		-0.10	7.95	2,5	7.94	7.96	7.95	0.08	1.0	24
P_{PO4}	µg/l	A1P			8.15	10	*<10*	8.16	8.02	0.59	7.4	19
	µg/l	N3P		-0.08	78.4	10	78.1	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P			12.1	15	*<12*	12.3	12.4	1.1	8.8	20
	µg/l	N3P		0.34	118	10	120	117	117	5	4.6	20

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Conductivity 25	mS/m	A1J		-0.38	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-2.85	972	5	903	976	977	12	1.2	19
	mS/m	N3H		13.08	3.21	8	4.89	3.21	3.22	0.07	2.2	16
N_{tot}	µg/l	A1N		-2.09	317	15	267	316	318	21	6.6	19
	µg/l	B2N			469	20	*450,0*	464	465	59	12.7	18
	µg/l	N3N		-1.32	612	15	551	610	620	36	5.8	19
pH		A1H		-0.39	6.54	3,1	6.50	6.56	6.54	0.06	0.9	27
		B2H		-0.50	7.95	2,5	7.90	7.96	7.95	0.08	1.0	24
		N3H		-0.91	6.39	3,1	6.30	6.36	6.36	0.04	0.6	26
P_{tot}	µg/l	A1P		0.99	12.1	15	13.0	12.3	12.4	1.1	8.8	20
	µg/l	B2P			35.2	15	*<10*	35.6	35.4	1.2	3.5	15
	µg/l	N3P		0.93	118	10	124	117	117	5	4.6	20

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Conductivity 25	mS/m	A1J		0.38	10.5	5	10.6	10.5	10.5	0.1	1.1	22
	mS/m	N3H		0.00	3.21	8	3.21	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N			15.8	20	*<30*	15.5	15.6	1.4	9.2	22
	µg/l	N3N		0.24	75.7	20	77.5	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-1.17	214	8	204	214	214	10	4.4	22
	µg/l	N3N		-1.80	319	8	296	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.72	317	15	300	316	318	21	6.6	19
	µg/l	N3N		-0.33	612	15	597	610	620	36	5.8	19
pH		A1H		-0.99	6.54	3,1	6.44	6.56	6.54	0.06	0.9	27
		N3H		-0.20	6.39	3,1	6.37	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		2.94	8.15	10	9.35	8.16	8.02	0.59	7.4	19
	µg/l	N3P		0.40	78.4	10	80.0	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		-0.50	12.1	15	11.7	12.3	12.4	1.1	8.8	20
	µg/l	N3P		-0.59	118	10	115	117	117	5	4.6	20

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	µg/l	B2K		-7.65	17.3	20	4.1	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-7.10	8.34	20	2.42	8.35	8.40	0.43	5.1	15
Conductivity 25	mS/m	A1J		0.08	10.5	5	10.5	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-0.84	972	5	952	976	977	12	1.2	19
	mS/m	N3H		0.70	3.21	8	3.30	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.70	15.8	20	14.7	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-1.42	30.4	20	26.1	29.4	29.8	2.2	7.2	16
$N_{NO2+NO3}$	µg/l	A1N		-2.13	214	8	196	214	214	10	4.4	22
	µg/l	B2N		-1.61	199	15	175	198	199	15	7.7	18
N_{tot}	µg/l	A1N		0.30	317	15	324	316	318	21	6.6	19
	µg/l	B2N		-0.19	469	20	460	464	465	59	12.7	18
pH		A1H		0.59	6.54	3,1	6.60	6.56	6.54	0.06	0.9	27
		B2H		0.40	7.95	2,5	7.99	7.96	7.95	0.08	1.0	24
		N3H		-0.71	6.39	3,1	6.32	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-1.79	8.15	10	7.42	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-0.80	27.0	15	25.4	27.1	27.1	1.7	6.3	18
P_{tot}	µg/l	A1P		0.57	12.1	15	12.6	12.3	12.4	1.1	8.8	20
	µg/l	B2P		0.32	35.2	15	36.0	35.6	35.4	1.2	3.5	15

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Colour$_{Spectrophotometric}$	mg/l, Pt	A1V		-0.25	15.7	15	15.4	15.9	15.7	1.1	7.1	12
	mg/l, Pt	N3S		0.60	20.1	25	21.6	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		0.38	10.5	5	10.6	10.5	10.5	0.1	1.1	22
	mS/m	N3H		-0.08	3.21	8	3.20	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-9.99	15.8	20	0.0	15.5	15.6	1.4	9.2	22
	µg/l	N3N		-9.99	75.7	20	0.1	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-24.89	214	8	1	214	214	10	4.4	22
	µg/l	N3N		-24.89	319	8	1	317	318	14	4.5	20
pH		A1H		0.49	6.54	3,1	6.59	6.56	6.54	0.06	0.9	27
		N3H		0.71	6.39	3,1	6.46	6.36	6.36	0.04	0.6	26
Turbidity	FNU	A1S		-0.34	0.29	20	0.28	0.29	0.30	0.03	10.0	17
	FNU	N3S		0.07	0.47	25	0.47	0.47	0.47	0.06	13.0	20

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Colour$_{Spectrophotometric}$	mg/l, Pt	A1V		-1.44	15.7	15	14.0	15.9	15.7	1.1	7.1	12
	mg/l, Pt	N3S		-0.52	20.1	25	18.8	20.1	20.0	2.1	10.3	11
N_{NH4}	µg/l	A1N		-0.06	15.8	20	15.7	15.5	15.6	1.4	9.2	22
	µg/l	N3N		-0.36	75.7	20	73.0	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-0.76	214	8	208	214	214	10	4.4	22
	µg/l	N3N		-0.74	319	8	310	317	318	14	4.5	20
Turbidity	FNU	A1S		1.38	0.29	20	0.33	0.29	0.30	0.03	10.0	17
	FNU	N3S		0.07	0.47	25	0.47	0.47	0.47	0.06	13.0	20

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-0.67	0.104	10	0.101	0.104	0.104	0.001	0.7	13
	µg/l	B2K		0.29	17.3	20	17.8	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-0.17	8.34	20	8.20	8.35	8.40	0.43	5.1	15
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		0.00	10.0	35	10.0	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		0.91	10.5	5	10.7	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.99	972	5	996	976	977	12	1.2	19
	mS/m	N3H		0.39	3.21	8	3.26	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N			15.8	20	*19*	15.5	15.6	1.4	9.2	22
	µg/l	B2N			30.4	20	*49*	29.4	29.8	2.2	7.2	16
	µg/l	N3N			75.7	20	*74*	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N			214	8	*214*	214	214	10	4.4	22
	µg/l	B2N			199	15	*195*	198	199	15	7.7	18
	µg/l	N3N			319	8	*312*	317	318	14	4.5	20
N_{tot}	µg/l	A1N			317	15	*333*	316	318	21	6.6	19
	µg/l	B2N			469	20	*543*	464	465	59	12.7	18
	µg/l	N3N			612	15	*662*	610	620	36	5.8	19
pH		A1H		-1.97	6.54	3,1	6.34	6.56	6.54	0.06	0.9	27
		B2H		-0.40	7.95	2,5	7.91	7.96	7.95	0.08	1.0	24
		N3H		-0.30	6.39	3,1	6.36	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P			8.15	10	*8*	8.16	8.02	0.59	7.4	19
	µg/l	B2P			27.0	15	*26*	27.1	27.1	1.7	6.3	18
	µg/l	N3P			78.4	10	*79*	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P			12.1	15	*12*	12.3	12.4	1.1	8.8	20
	µg/l	B2P			35.2	15	*48*	35.6	35.4	1.2	3.5	15
	µg/l	N3P			118	10	*117*	117	117	5	4.6	20
Turbidity	FNU	A1S		-0.69	0.29	20	0.27	0.29	0.30	0.03	10.0	17
	FNU	B2S		0.00	0.31	30	0.31	0.31	0.32	0.07	22.1	14
	FNU	N3S		-0.34	0.47	25	0.45	0.47	0.47	0.06	13.0	20

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.00	0.104	10	0.104	0.104	0.104	0.001	0.7	13
	µg/l	B2K		0.86	17.3	20	18.8	17.5	17.2	1.2	7.2	13
	µg/l	N3K		0.71	8.34	20	8.93	8.35	8.40	0.43	5.1	15
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		-1.43	10.0	35	7.5	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		3.54	10.5	5	11.4	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-1.78	972	5	929	976	977	12	1.2	19
	mS/m	N3H		3.58	3.21	8	3.67	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.33	15.8	20	15.3	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.76	30.4	20	28.1	29.4	29.8	2.2	7.2	16
	µg/l	N3N		-0.30	75.7	20	73.4	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-0.11	214	8	213	214	214	10	4.4	22
	µg/l	B2N		1.14	199	15	216	198	199	15	7.7	18
	µg/l	N3N		-0.04	319	8	318	317	318	14	4.5	20

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
N_{tot}	µg/l	A1N		1.29	317	15	348	316	318	21	6.6	19
	µg/l	B2N		0.78	469	20	506	464	465	59	12.7	18
	µg/l	N3N		0.41	612	15	631	610	620	36	5.8	19
pH		A1H		-0.04	6.54	3,1	6.54	6.56	6.54	0.06	0.9	27
		B2H		0.19	7.95	2,5	7.97	7.96	7.95	0.08	1.0	24
		N3H		1.55	6.39	3,1	6.54	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		0.40	8.15	10	8.32	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.22	27.0	15	27.5	27.1	27.1	1.7	6.3	18
	µg/l	N3P		-0.33	78.4	10	77.1	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		-1.32	12.1	15	10.9	12.3	12.4	1.1	8.8	20
	µg/l	B2P		0.37	35.2	15	36.2	35.6	35.4	1.2	3.5	15
	µg/l	N3P		-1.05	118	10	112	117	117	5	4.6	20
Turbidity	FNU	A1S		1.21	0.29	20	0.33	0.29	0.30	0.03	10.0	17
	FNU	B2S		0.86	0.31	30	0.35	0.31	0.32	0.07	22.1	14
	FNU	N3S		0.34	0.47	25	0.49	0.47	0.47	0.06	13.0	20

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Conductivity 25	mS/m	A1J		0.38	10.5	5	10.6	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.21	972	5	977	976	977	12	1.2	19
N_{NH4}	µg/l	A1N		-0.19	15.8	20	15.5	15.5	15.6	1.4	9.2	22
	µg/l	B2N		35.39	30.4	20	138.0	29.4	29.8	2.2	7.2	16
$N_{NO2+NO3}$	µg/l	A1N		-0.58	214	8	209	214	214	10	4.4	22
	µg/l	B2N		-1.51	199	15	177	198	199	15	7.7	18
N_{tot}	µg/l	A1N		-3.89	317	15	225	316	318	21	6.6	19
	µg/l	B2N		-3.29	469	20	315	464	465	59	12.7	18
pH		A1H		0.10	6.54	3,1	6.55	6.56	6.54	0.06	0.9	27
		B2H		1.01	7.95	2,5	8.05	7.96	7.95	0.08	1.0	24
P_{PO4}	µg/l	A1P		6.99	8.15	10	11.00	8.16	8.02	0.59	7.4	19
	µg/l	B2P		3.21	27.0	15	33.5	27.1	27.1	1.7	6.3	18
P_{tot}	µg/l	A1P		-0.11	12.1	15	12.0	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-0.08	35.2	15	35.0	35.6	35.4	1.2	3.5	15

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Colour_{Visual}$	mg/l, Pt	A1V		-2.67	15.0	25	10.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		-0.50	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	N3H		0.00	3.21	8	3.21	3.21	3.22	0.07	2.2	16
$N_{NO2+NO3}$	µg/l	A1N		0.35	214	8	217	214	214	10	4.4	22
	µg/l	N3N		-0.16	319	8	317	317	318	14	4.5	20
P_{PO4}	µg/l	A1P		0.25	8.15	10	8.25	8.16	8.02	0.59	7.4	19
	µg/l	N3P		-0.17	78.4	10	77.8	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		0.22	12.1	15	12.3	12.3	12.4	1.1	8.8	20
	µg/l	N3P		-0.19	118	10	117	117	117	5	4.6	20

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.00	0.104	10	0.104	0.104	0.104	0.001	0.7	13
	µg/l	B2K		0.52	17.3	20	18.2	17.5	17.2	1.2	7.2	13
	µg/l	N3K		0.46	8.34	20	8.72	8.35	8.40	0.43	5.1	15
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		0.25	15.7	15	16.0	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		0.44	10.3	35	11.1	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		-0.28	20.1	25	19.4	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		0.00	10.5	5	10.5	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.62	972	5	987	976	977	12	1.2	19
	mS/m	N3H		0.70	3.21	8	3.30	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		0.54	15.8	20	16.7	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.15	30.4	20	30.0	29.4	29.8	2.2	7.2	16
	µg/l	N3N		0.21	75.7	20	77.3	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		0.06	214	8	215	214	214	10	4.4	22
	µg/l	B2N		0.17	199	15	202	198	199	15	7.7	18
	µg/l	N3N		-0.20	319	8	317	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.04	317	15	316	316	318	21	6.6	19
	µg/l	B2N		-0.84	469	20	430	464	465	59	12.7	18
	µg/l	N3N		-0.44	612	15	592	610	620	36	5.8	19
pH		A1H		0.30	6.54	3,1	6.57	6.56	6.54	0.06	0.9	27
		B2H		0.60	7.95	2,5	8.01	7.96	7.95	0.08	1.0	24
		N3H		-0.30	6.39	3,1	6.36	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-0.98	8.15	10	7.75	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-0.99	27.0	15	25.0	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.10	78.4	10	78.8	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		-5.07	12.1	15	7.5	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-6.46	35.2	15	18.2	35.6	35.4	1.2	3.5	15
	µg/l	N3P		-2.43	118	10	104	117	117	5	4.6	20
Turbidity	FNU	A1S		23.45	0.29	20	0.97	0.29	0.30	0.03	10.0	17
	FNU	B2S		0.22	0.31	30	0.32	0.31	0.32	0.07	22.1	14
	FNU	N3S		3.91	0.47	25	0.70	0.47	0.47	0.06	13.0	20

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		0.08	15.7	15	15.8	15.9	15.7	1.1	7.1	12
	mg/l, Pt	N3S		1.71	20.1	25	24.4	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		-0.23	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	N3H		-0.31	3.21	8	3.17	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		0.13	15.8	20	16.0	15.5	15.6	1.4	9.2	22
	µg/l	N3N		3.41	75.7	20	101.5	76.0	76.2	5.3	6.9	21
pH		A1H		0.30	6.54	3,1	6.57	6.56	6.54	0.06	0.9	27
		N3H		-0.50	6.39	3,1	6.34	6.36	6.36	0.04	0.6	26
Turbidity	FNU	A1S		-1.14	0.29	20	0.26	0.29	0.30	0.03	10.0	17
	FNU	N3S		-1.79	0.47	25	0.37	0.47	0.47	0.06	13.0	20

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Colour_{Visual}$	mg/l, Pt	A1V		2.67	15.0	25	20.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		363.81	10.5	5	106.0	10.5	10.5	0.1	1.1	22
	mS/m	N3H		232.01	3.21	8	33.00	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		3.99	15.8	20	22.1	15.5	15.6	1.4	9.2	22
	µg/l	N3N		1.85	75.7	20	89.7	76.0	76.2	5.3	6.9	21
pH		A1H		0.59	6.54	3,1	6.60	6.56	6.54	0.06	0.9	27
		N3H		2.12	6.39	3,1	6.60	6.36	6.36	0.04	0.6	26
Turbidity	FNU	A1S		-0.34	0.29	20	0.28	0.29	0.30	0.03	10.0	17
	FNU	N3S		-1.19	0.47	25	0.40	0.47	0.47	0.06	13.0	20

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		19.42	0.104	10	0.205	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-0.62	17.3	20	16.2	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-0.74	8.34	20	7.72	8.35	8.40	0.43	5.1	15
$Colour_{Visual}$	mg/l, Pt	A1V		-2.67	15.0	25	10.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		-1.43	10.0	35	7.5	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		-2.50	20.0	20	15.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		-0.15	10.5	5	10.5	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.69	972	5	989	976	977	12	1.2	19
	mS/m	N3H		-0.51	3.21	8	3.14	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		0.22	15.8	20	16.2	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.15	30.4	20	30.0	29.4	29.8	2.2	7.2	16
	µg/l	N3N		-0.67	75.7	20	70.7	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		0.70	214	8	220	214	214	10	4.4	22
	µg/l	B2N		0.17	199	15	202	198	199	15	7.7	18
	µg/l	N3N		0.27	319	8	323	317	318	14	4.5	20
N_{tot}	µg/l	A1N		1.09	317	15	343	316	318	21	6.6	19
	µg/l	B2N		0.36	469	20	486	464	465	59	12.7	18
	µg/l	N3N		1.08	612	15	662	610	620	36	5.8	19
pH		A1H		0.30	6.54	3,1	6.57	6.56	6.54	0.06	0.9	27
		B2H		-0.20	7.95	2,5	7.93	7.96	7.95	0.08	1.0	24
		N3H		0.00	6.39	3,1	6.39	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		0.53	8.15	10	8.37	8.16	8.02	0.59	7.4	19
	µg/l	B2P		2.22	27.0	15	31.5	27.1	27.1	1.7	6.3	18
	µg/l	N3P		-0.15	78.4	10	77.8	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		-0.15	12.1	15	12.0	12.3	12.4	1.1	8.8	20
	µg/l	B2P		0.02	35.2	15	35.3	35.6	35.4	1.2	3.5	15
	µg/l	N3P		0.00	118	10	118	117	117	5	4.6	20
Turbidity	FNU	A1S		1.86	0.29	20	0.34	0.29	0.30	0.03	10.0	17
	FNU	B2S		-1.76	0.31	30	0.23	0.31	0.32	0.07	22.1	14
	FNU	N3S		1.19	0.47	25	0.54	0.47	0.47	0.06	13.0	20

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-0.13	0.104	10	0.103	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-0.35	17.3	20	16.7	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-0.30	8.34	20	8.09	8.35	8.40	0.43	5.1	15
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		0.00	10.0	35	10.0	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		-3.99	15.7	15	11.0	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		-2.94	10.3	35	5.0	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		-1.63	20.1	25	16.0	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		-0.38	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.00	972	5	972	976	977	12	1.2	19
	mS/m	N3H		2.02	3.21	8	3.47	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		1.77	15.8	20	18.6	15.5	15.6	1.4	9.2	22
	µg/l	B2N		3.16	30.4	20	40.0	29.4	29.8	2.2	7.2	16
	µg/l	N3N		1.50	75.7	20	87.1	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		0.70	214	8	220	214	214	10	4.4	22
	µg/l	B2N		0.97	199	15	214	198	199	15	7.7	18
	µg/l	N3N		1.18	319	8	334	317	318	14	4.5	20
N_{tot}	µg/l	A1N		1.32	317	15	349	316	318	21	6.6	19
	µg/l	B2N		2.00	469	20	563	464	465	59	12.7	18
	µg/l	N3N		1.33	612	15	673	610	620	36	5.8	19
pH		A1H		0.10	6.54	3,1	6.55	6.56	6.54	0.06	0.9	27
		B2H		0.50	7.95	2,5	8.00	7.96	7.95	0.08	1.0	24
		N3H		2.02	6.39	3,1	6.59	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-1.35	8.15	10	7.60	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.84	27.0	15	28.7	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.41	78.4	10	80.0	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		1.65	12.1	15	13.6	12.3	12.4	1.1	8.8	20
	µg/l	B2P			35.2	15	*35,8*	35.6	35.4	1.2	3.5	15
	µg/l	N3P		1.44	118	10	127	117	117	5	4.6	20
Turbidity	FNU	A1S		0.79	0.29	20	0.31	0.29	0.30	0.03	10.0	17
	FNU	B2S		-0.65	0.31	30	0.28	0.31	0.32	0.07	22.1	14
	FNU	N3S		-0.10	0.47	25	0.46	0.47	0.47	0.06	13.0	20

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Conductivity 25	mS/m	B2H		-20.74	972	5	468	976	977	12	1.2	19
	mS/m	N3H		-0.08	3.21	8	3.20	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-1.96	15.8	20	12.7	15.5	15.6	1.4	9.2	22
	µg/l	N3N		0.27	75.7	20	77.8	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-0.26	214	8	212	214	214	10	4.4	22
	µg/l	B2N		-0.30	199	15	195	198	199	15	7.7	18
	µg/l	N3N		0.43	319	8	325	317	318	14	4.5	20
pH		B2H		0.91	7.95	2,5	8.04	7.96	7.95	0.08	1.0	24
		N3H		-0.40	6.39	3,1	6.35	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-0.37	8.15	10	8.00	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.74	27.0	15	28.5	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.66	78.4	10	81.0	78.6	78.2	2.7	3.5	20

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Turbidity	FNU	A1S		6.17	0.29	20	0.47	0.29	0.30	0.03	10.0	17
	FNU	N3S		1.74	0.47	25	0.57	0.47	0.47	0.06	13.0	20

Participant 27												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-0.27	0.104	10	0.103	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-0.46	17.3	20	16.5	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-0.16	8.34	20	8.21	8.35	8.40	0.43	5.1	15
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		0.00	10.0	35	10.0	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		0.59	15.7	15	16.4	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		0.44	10.3	35	11.1	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		0.16	20.1	25	20.5	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		0.00	10.5	5	10.5	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.00	972	5	972	976	977	12	1.2	19
	mS/m	N3H		0.00	3.21	8	3.21	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		0.76	15.8	20	17.0	15.5	15.6	1.4	9.2	22
	µg/l	B2N		0.39	30.4	20	31.6	29.4	29.8	2.2	7.2	16
	µg/l	N3N		0.18	75.7	20	77.1	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-1.46	214	8	202	214	214	10	4.4	22
	µg/l	B2N		-1.74	199	15	173	198	199	15	7.7	18
	µg/l	N3N		-2.08	319	8	293	317	318	14	4.5	20
N_{tot}	µg/l	A1N		0.95	317	15	340	316	318	21	6.6	19
	µg/l	B2N		1.18	469	20	525	464	465	59	12.7	18
	µg/l	N3N		1.61	612	15	686	610	620	36	5.8	19
pH		A1H		0.20	6.54	3,1	6.56	6.56	6.54	0.06	0.9	27
		B2H		-0.10	7.95	2,5	7.94	7.96	7.95	0.08	1.0	24
		N3H		-0.40	6.39	3,1	6.35	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		-1.57	8.15	10	7.51	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.20	27.0	15	27.4	27.1	27.1	1.7	6.3	18
	µg/l	N3P		-0.40	78.4	10	76.9	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		0.11	12.1	15	12.2	12.3	12.4	1.1	8.8	20
	µg/l	B2P		0.45	35.2	15	36.4	35.6	35.4	1.2	3.5	15
	µg/l	N3P		0.00	118	10	118	117	117	5	4.6	20
Turbidity	FNU	A1S		-0.14	0.29	20	0.29	0.29	0.30	0.03	10.0	17
	FNU	B2S		0.06	0.31	30	0.31	0.31	0.32	0.07	22.1	14
	FNU	N3S		-0.32	0.47	25	0.45	0.47	0.47	0.06	13.0	20

Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.00	0.104	10	0.104	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-1.58	17.3	20	14.6	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-0.61	8.34	20	7.83	8.35	8.40	0.43	5.1	15
N_{NH4}	µg/l	A1N		1.87	15.8	20	18.8	15.5	15.6	1.4	9.2	22
	µg/l	B2N		1.17	30.4	20	34.0	29.4	29.8	2.2	7.2	16
	µg/l	N3N		0.87	75.7	20	82.3	76.0	76.2	5.3	6.9	21

Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$N_{NO2+NO3}$	µg/l	A1N		1.19	214	8	224	214	214	10	4.4	22
	µg/l	B2N		0.84	199	15	212	198	199	15	7.7	18
	µg/l	N3N		0.65	319	8	327	317	318	14	4.5	20
N_{tot}	µg/l	A1N		0.06	317	15	318	316	318	21	6.6	19
	µg/l	B2N		-0.11	469	20	464	464	465	59	12.7	18
	µg/l	N3N		-0.27	612	15	600	610	620	36	5.8	19
pH		A1H		0.10	6.54	3,1	6.55	6.56	6.54	0.06	0.9	27
		B2H		0.20	7.95	2,5	7.97	7.96	7.95	0.08	1.0	24
		N3H		-0.20	6.39	3,1	6.37	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		0.01	8.15	10	8.16	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-0.17	27.0	15	26.7	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.72	78.4	10	81.2	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		0.84	12.1	15	12.9	12.3	12.4	1.1	8.8	20
	µg/l	B2P		0.25	35.2	15	35.9	35.6	35.4	1.2	3.5	15
	µg/l	N3P		-0.25	118	10	117	117	117	5	4.6	20

Participant 29												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		-2.42	0.104	10	0.091	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-0.29	17.3	20	16.8	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-0.52	8.34	20	7.91	8.35	8.40	0.43	5.1	15
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		0.17	15.7	15	15.9	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		-0.54	10.3	35	9.3	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		0.00	20.1	25	20.1	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		0.38	10.5	5	10.6	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.45	972	5	983	976	977	12	1.2	19
	mS/m	N3H		1.48	3.21	8	3.40	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-0.06	15.8	20	15.7	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.28	30.4	20	29.6	29.4	29.8	2.2	7.2	16
	µg/l	N3N		0.57	75.7	20	80.1	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		2.92	214	8	239	214	214	10	4.4	22
	µg/l	B2N		1.54	199	15	222	198	199	15	7.7	18
	µg/l	N3N		3.21	319	8	360	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.27	317	15	311	316	318	21	6.6	19
	µg/l	B2N		-1.39	469	20	404	464	465	59	12.7	18
	µg/l	N3N		-0.39	612	15	594	610	620	36	5.8	19
pH		A1H		0.30	6.54	3,1	6.57	6.56	6.54	0.06	0.9	27
		B2H		0.81	7.95	2,5	8.03	7.96	7.95	0.08	1.0	24
		N3H		1.92	6.39	3,1	6.58	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		0.53	8.15	10	8.37	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.07	27.0	15	27.2	27.1	27.1	1.7	6.3	18
	µg/l	N3P		0.38	78.4	10	79.9	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		-1.60	12.1	15	10.7	12.3	12.4	1.1	8.8	20
	µg/l	B2P		0.27	35.2	15	35.9	35.6	35.4	1.2	3.5	15
	µg/l	N3P		1.10	118	10	125	117	117	5	4.6	20
Turbidity	FNU	A1S		0.00	0.29	20	0.29	0.29	0.30	0.03	10.0	17
	FNU	B2S		-0.09	0.31	30	0.31	0.31	0.32	0.07	22.1	14
	FNU	N3S		-0.15	0.47	25	0.46	0.47	0.47	0.06	13.0	20

Participant 30												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		-1.43	10.0	35	7.5	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		0.00	20.0	20	20.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		-0.42	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-39.96	972	5	1	976	977	12	1.2	19
	mS/m	N3H		0.23	3.21	8	3.24	3.21	3.22	0.07	2.2	16
pH		A1H		-0.89	6.54	3,1	6.45	6.56	6.54	0.06	0.9	27
		B2H		1.41	7.95	2,5	8.09	7.96	7.95	0.08	1.0	24
		N3H		-0.20	6.39	3,1	6.37	6.36	6.36	0.04	0.6	26
Turbidity	FNU	A1S		0.41	0.29	20	0.30	0.29	0.30	0.03	10.0	17
	FNU	B2S		-1.12	0.31	30	0.26	0.31	0.32	0.07	22.1	14
	FNU	N3S		0.00	0.47	25	0.47	0.47	0.47	0.06	13.0	20

Participant 31												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		0.00	0.104	10	0.104	0.104	0.104	0.001	0.7	13
	µg/l	B2K		0.69	17.3	20	18.5	17.5	17.2	1.2	7.2	13
	µg/l	N3K		0.53	8.34	20	8.78	8.35	8.40	0.43	5.1	15
$Colour_{Visual}$	mg/l, Pt	A1V		0.00	15.0	25	15.0	15.0	15.0	3.0	20.1	12
	mg/l, Pt	B2S		2.86	10.0	35	15.0	10.0	9.7	2.5	25.6	8
	mg/l, Pt	N3S		2.50	20.0	20	25.0	20.0	19.6	2.6	13.1	12
Conductivity 25	mS/m	A1J		-1.14	10.5	5	10.2	10.5	10.5	0.1	1.1	22
	mS/m	B2H		-1.89	972	5	926	976	977	12	1.2	19
	mS/m	N3H		-2.02	3.21	8	2.95	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		-1.33	15.8	20	13.7	15.5	15.6	1.4	9.2	22
	µg/l	B2N		-0.95	30.4	20	27.5	29.4	29.8	2.2	7.2	16
	µg/l	N3N		-0.53	75.7	20	71.7	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		-1.46	214	8	202	214	214	10	4.4	22
	µg/l	B2N		-1.04	199	15	184	198	199	15	7.7	18
	µg/l	N3N		-1.84	319	8	296	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-0.40	317	15	308	316	318	21	6.6	19
	µg/l	B2N		-0.01	469	20	469	464	465	59	12.7	18
	µg/l	N3N		0.34	612	15	628	610	620	36	5.8	19
pH		A1H		0.10	6.54	3,1	6.55	6.56	6.54	0.06	0.9	27
		B2H		-0.10	7.95	2,5	7.94	7.96	7.95	0.08	1.0	24
		N3H		-0.30	6.39	3,1	6.36	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		0.74	8.15	10	8.45	8.16	8.02	0.59	7.4	19
	µg/l	B2P		0.57	27.0	15	28.2	27.1	27.1	1.7	6.3	18
	µg/l	N3P		-0.91	78.4	10	74.9	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P		-0.17	12.1	15	12.0	12.3	12.4	1.1	8.8	20
	µg/l	B2P		-0.04	35.2	15	35.1	35.6	35.4	1.2	3.5	15
	µg/l	N3P		0.85	118	10	123	117	117	5	4.6	20
Turbidity	FNU	A1S		0.34	0.29	20	0.30	0.29	0.30	0.03	10.0	17
	FNU	B2S		-1.72	0.31	30	0.23	0.31	0.32	0.07	22.1	14
	FNU	N3S		-2.04	0.47	25	0.35	0.47	0.47	0.06	13.0	20

Participant 32												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
$Colour_{Spectrophotometric}$	mg/l, Pt	A1V		1.10	15.7	15	17.0	15.9	15.7	1.1	7.1	12
	mg/l, Pt	B2S		-1.28	10.3	35	8.0	10.3	10.3	1.6	15.1	9
	mg/l, Pt	N3S		-0.44	20.1	25	19.0	20.1	20.0	2.1	10.3	11
Conductivity 25	mS/m	A1J		-0.38	10.5	5	10.4	10.5	10.5	0.1	1.1	22
	mS/m	B2H		0.12	972	5	975	976	977	12	1.2	19
	mS/m	N3H		-0.39	3.21	8	3.16	3.21	3.22	0.07	2.2	16
N_{NH4}	µg/l	A1N		2.67	15.8	20	20.0	15.5	15.6	1.4	9.2	22
	µg/l	B2N		1.04	30.4	20	33.6	29.4	29.8	2.2	7.2	16
	µg/l	N3N		-0.19	75.7	20	74.2	76.0	76.2	5.3	6.9	21
$N_{NO2+NO3}$	µg/l	A1N		0.93	214	8	222	214	214	10	4.4	22
	µg/l	B2N		1.38	199	15	220	198	199	15	7.7	18
	µg/l	N3N		0.78	319	8	329	317	318	14	4.5	20
N_{tot}	µg/l	A1N		-4.30	317	15	215	316	318	21	6.6	19
	µg/l	B2N		-1.25	469	20	410	464	465	59	12.7	18
	µg/l	N3N		-2.69	612	15	488	610	620	36	5.8	19
pH		A1H		-0.39	6.54	3,1	6.50	6.56	6.54	0.06	0.9	27
		B2H		-0.50	7.95	2,5	7.90	7.96	7.95	0.08	1.0	24
		N3H		-0.71	6.39	3,1	6.32	6.36	6.36	0.04	0.6	26
P_{PO4}	µg/l	A1P		7.93	8.15	10	11.38	8.16	8.02	0.59	7.4	19
	µg/l	B2P		-1.43	27.0	15	24.1	27.1	27.1	1.7	6.3	18
	µg/l	N3P		5.13	78.4	10	98.5	78.6	78.2	2.7	3.5	20
P_{tot}	µg/l	A1P			12.1	15	*<50*	12.3	12.4	1.1	8.8	20
	µg/l	B2P			35.2	15	*<50*	35.6	35.4	1.2	3.5	15
	µg/l	N3P		2.88	118	10	135	117	117	5	4.6	20
Turbidity	FNU	A1S		11.03	0.29	20	0.61	0.29	0.30	0.03	10.0	17
	FNU	B2S		2.37	0.31	30	0.42	0.31	0.32	0.07	22.1	14
	FNU	N3S			0.47	25	*<0,4*	0.47	0.47	0.06	13.0	20

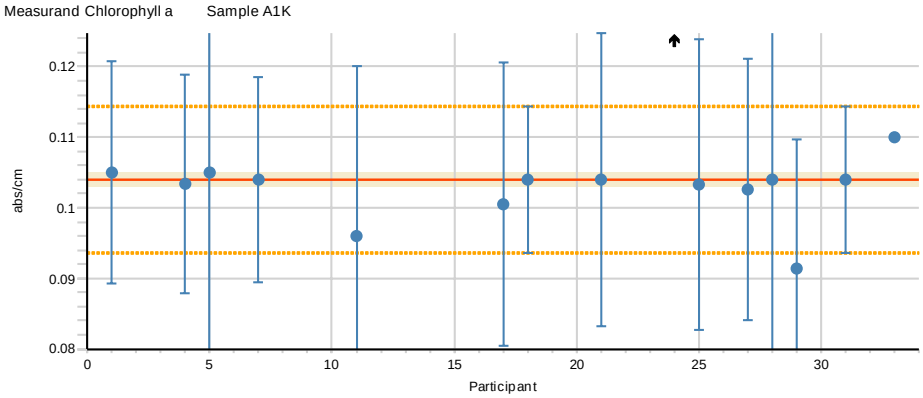
Participant 33												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
Chlorophyll *a*	abs/cm	A1K		1.15	0.104	10	0.110	0.104	0.104	0.001	0.7	13
	µg/l	B2K		-4.12	17.3	20	10.2	17.5	17.2	1.2	7.2	13
	µg/l	N3K		-3.07	8.34	20	5.78	8.35	8.40	0.43	5.1	15

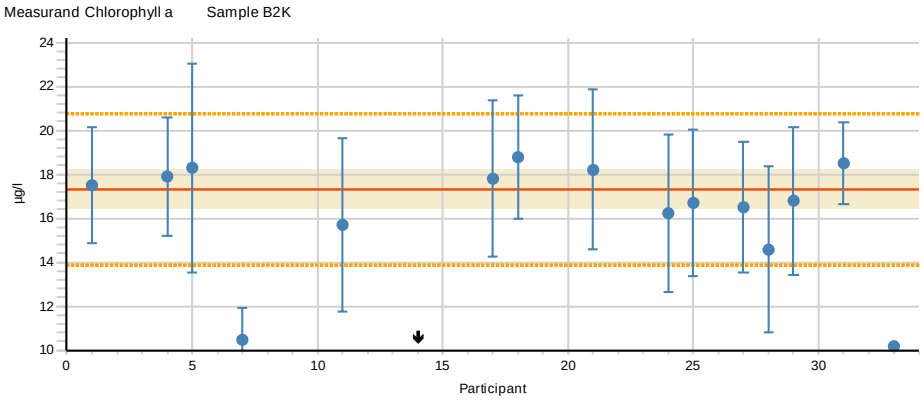
Participant 34												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	$2\times s_{pt}$ %	Participant's result	Md	Mean	s	s %	n_{stat}
$N_{NO2+NO3}$	µg/l	A1N		-0.29	214	8	212	214	214	10	4.4	22
	µg/l	N3N		-0.31	319	8	315	317	318	14	4.5	20
P_{PO4}	µg/l	A1P		0.28	8.15	10	8.27	8.16	8.02	0.59	7.4	19
	µg/l	N3P		1.05	78.4	10	82.5	78.6	78.2	2.7	3.5	20

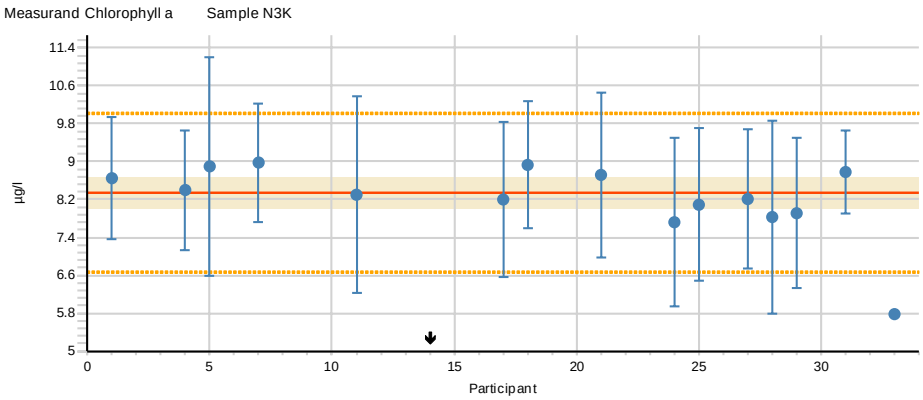
APPENDIX 9: Results of participants and their uncertainties

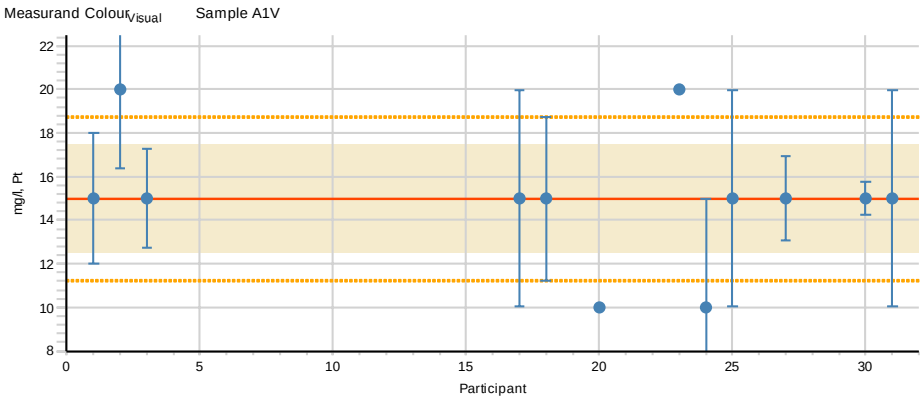
In figures:

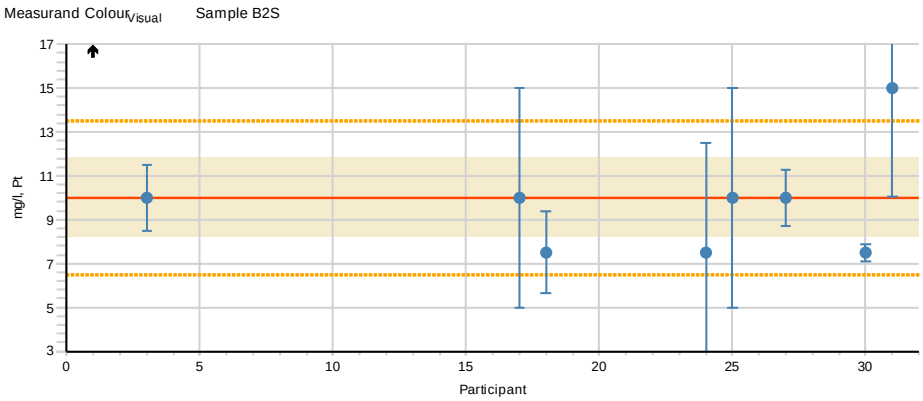
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.

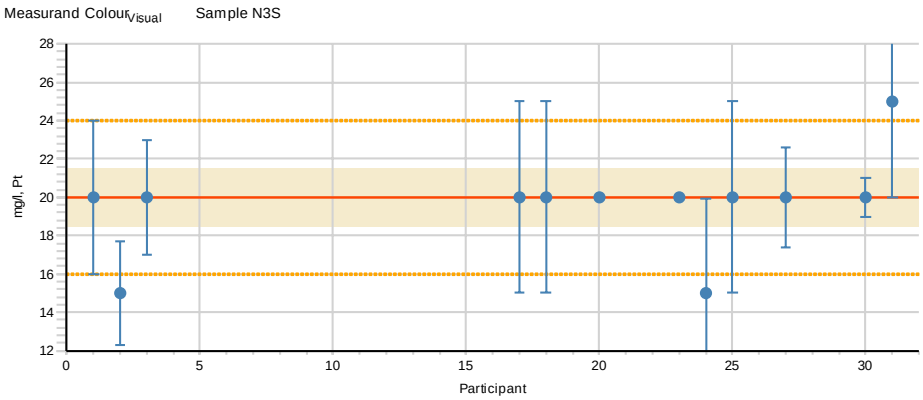


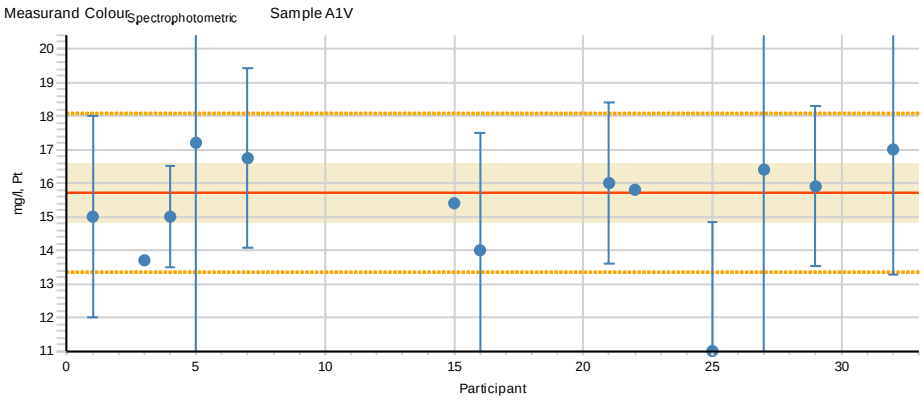


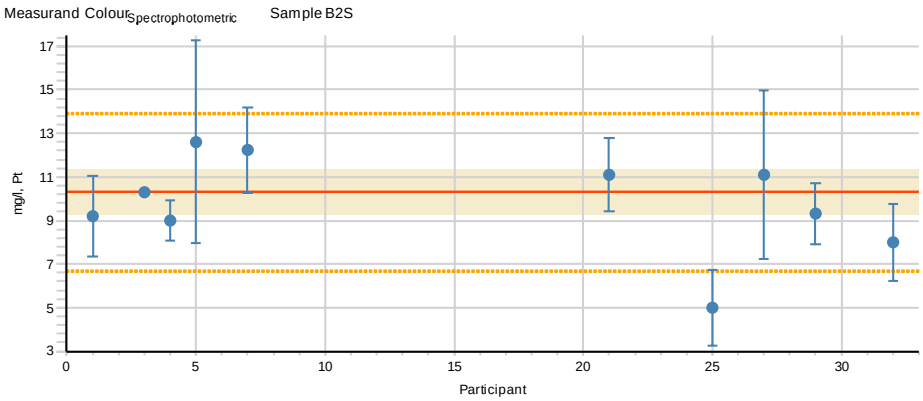


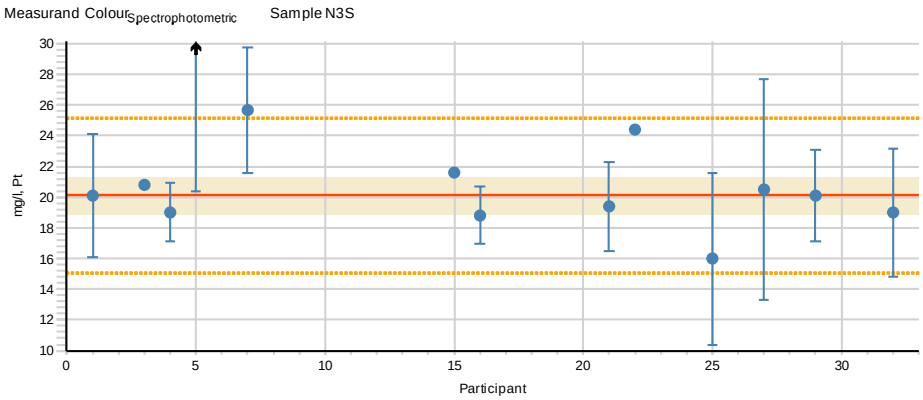

Measurand Colour$_{Visual}$ Sample A1V
mg/l. Pt
Participant


Measurand Colour$_{Visual}$ Sample B2S
mg/l. Pt
Participant

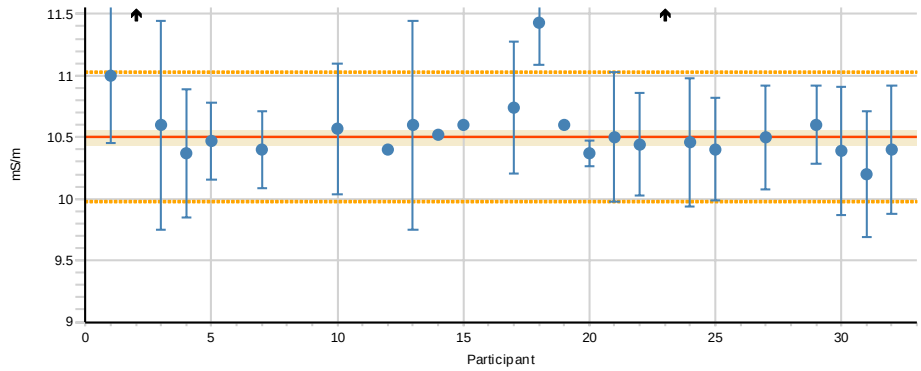

Measurand Colour$_{Visual}$ Sample N3S
mg/l. Pt
Participant


Measurand Colour Spectrophotometric
Sample A1V
mg/l. Pt
Participant

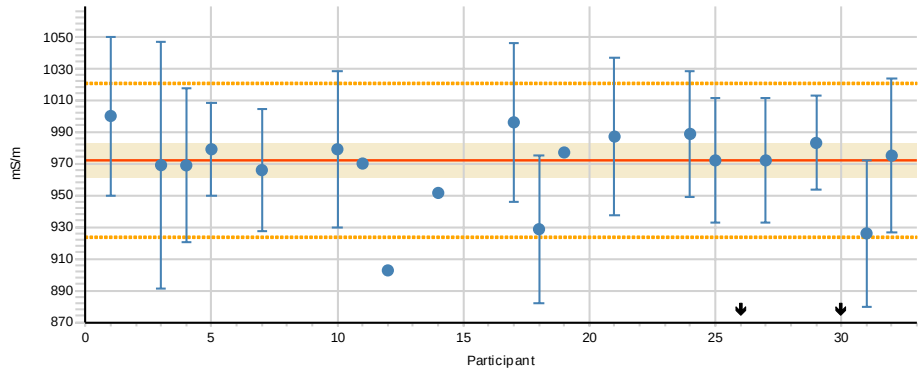

Measurand Colour Spectrophotometric
Sample B2S
mg/l. Pt
Participant


Measurand Colour Spectrophotometric
Sample N3S
mg/l. Pt
Participant

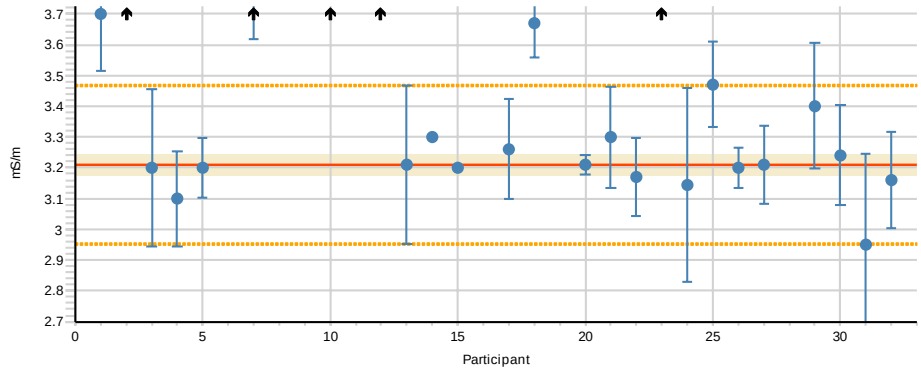
Measurand Conductivity 25 Sample A1J

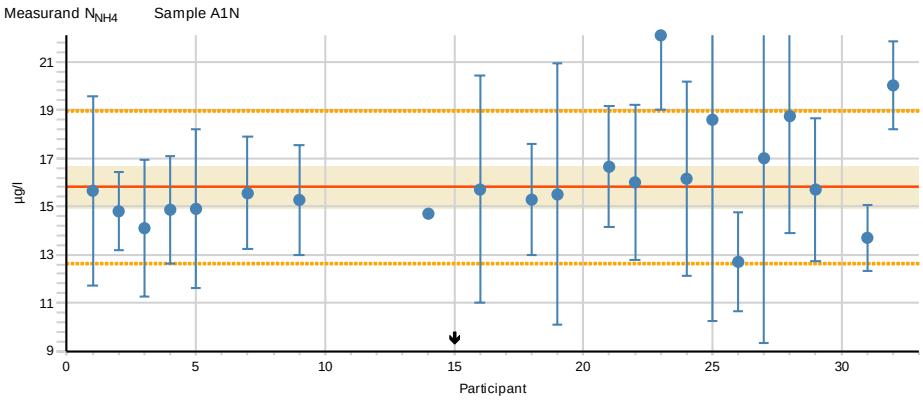


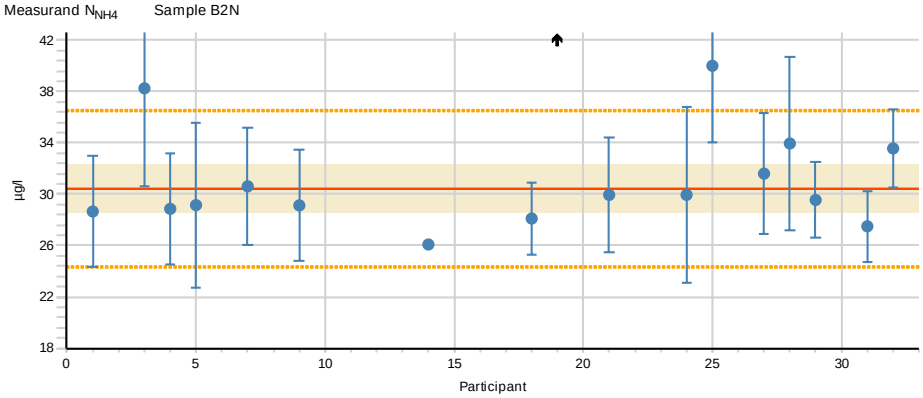
Measurand Conductivity 25 Sample B2H

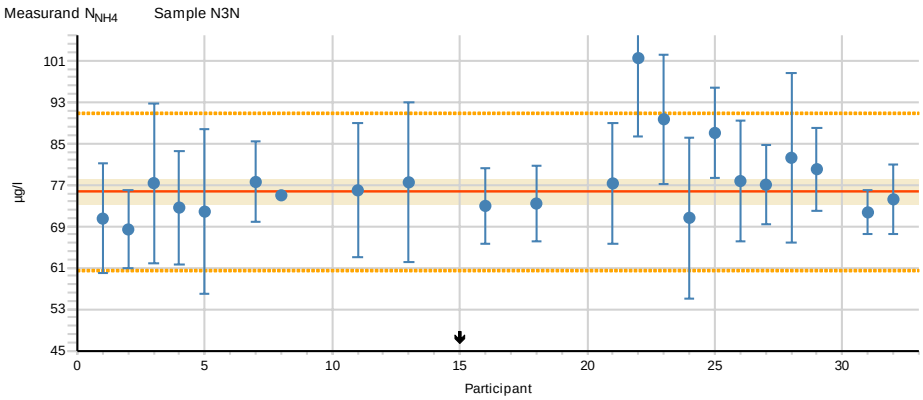


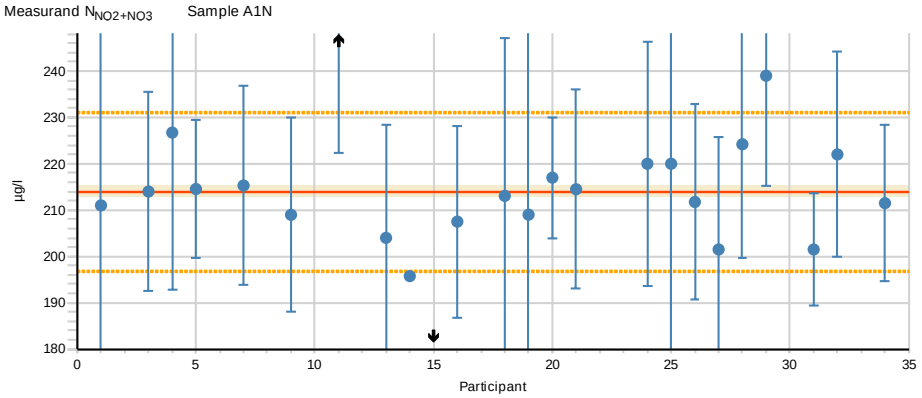
Measurand Conductivity 25 Sample N3H

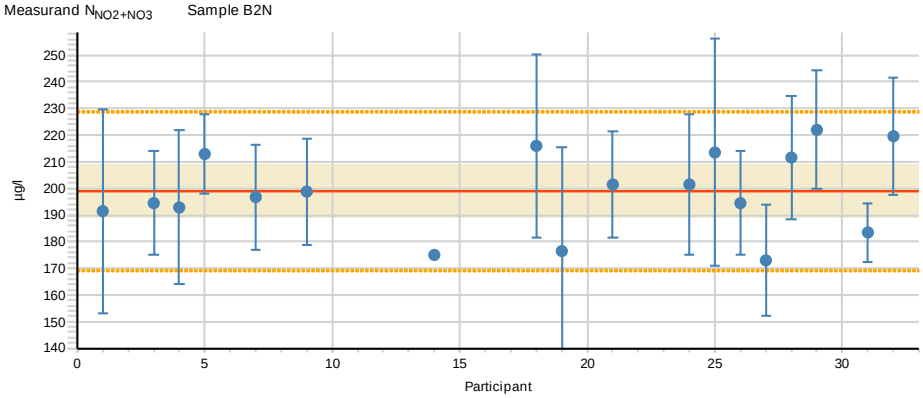


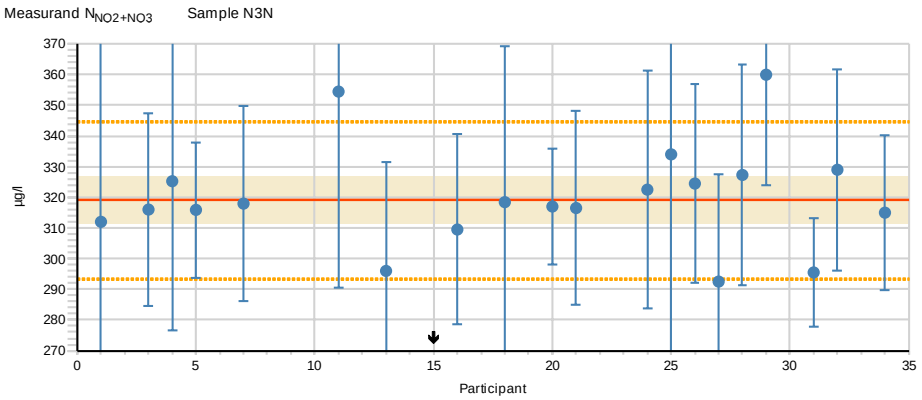

Measurand N_{NH4} Sample A1N
µg/l
21
19
17
15
13
11
9
0
5
10
15
20
25
30
Participant

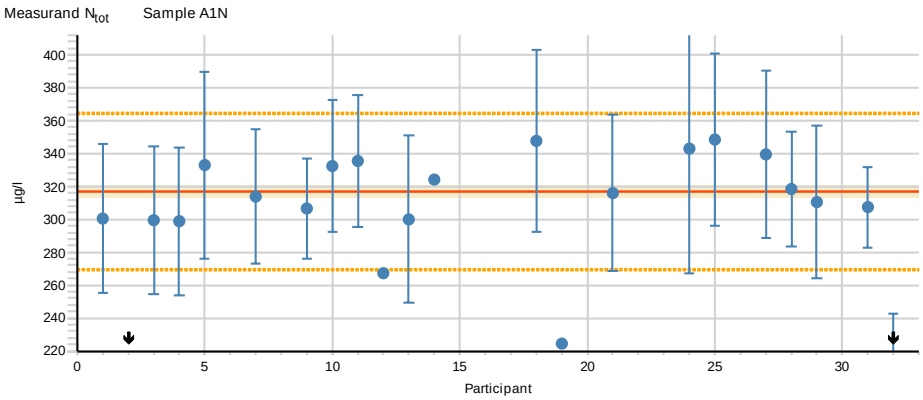

Measurand N_{NH4} Sample B2N
µg/l
42
38
34
30
26
22
18
0
5
10
15
20
25
30
Participant

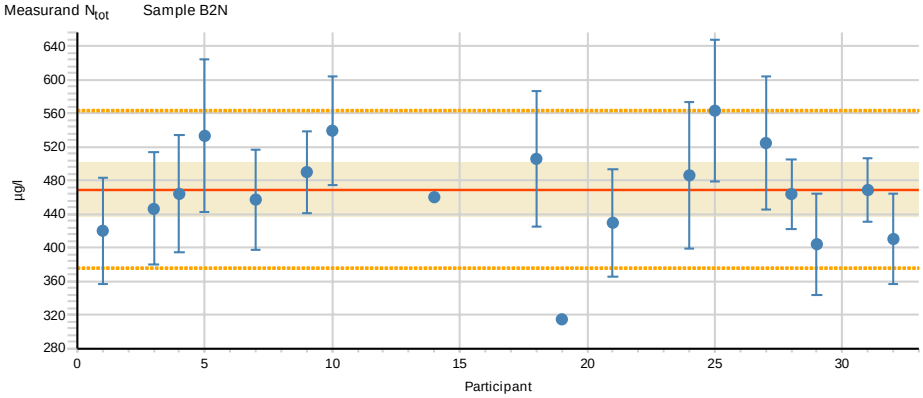

Measurand N_{NH4} Sample N3N
µg/l
101
93
85
77
69
61
53
45
0
5
10
15
20
25
30
Participant

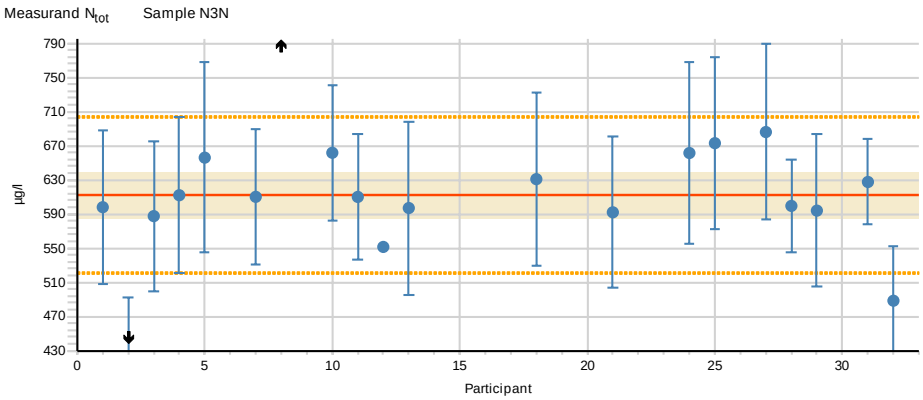

Measurand $N_{NO2+NO3}$
Sample A1N
µg/l
Participant


Measurand $N_{NO2+NO3}$
Sample B2N
µg/l
Participant

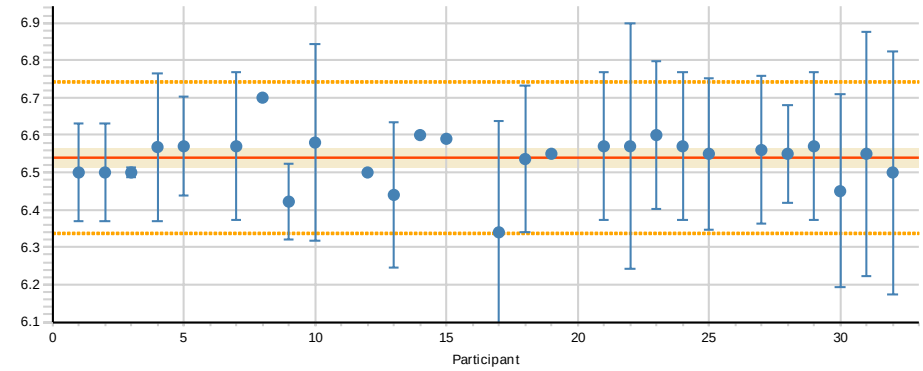

Measurand $N_{NO2+NO3}$
Sample N3N
µg/l
Participant


Measurand N_{tot}
Sample A1N
µg/l
400
380
360
340
320
300
280
260
240
220
0
5
10
15
20
25
30
Participant

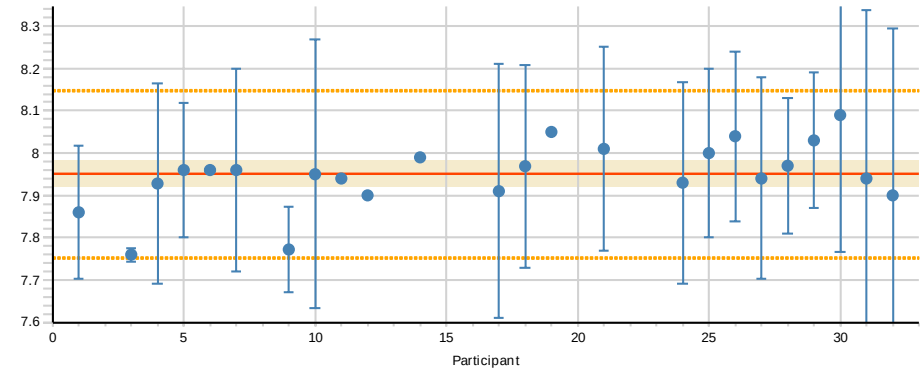

Measurand N_{tot}
Sample B2N
µg/l
640
600
560
520
480
440
400
360
320
280
0
5
10
15
20
25
30
Participant


Measurand N_{tot}
Sample N3N
µg/l
790
750
710
670
630
590
550
510
470
430
0
5
10
15
20
25
30
Participant

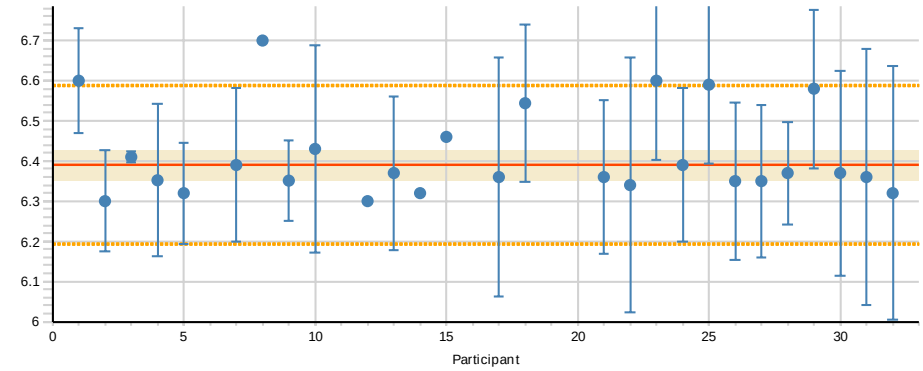
Measurand pH Sample A1H

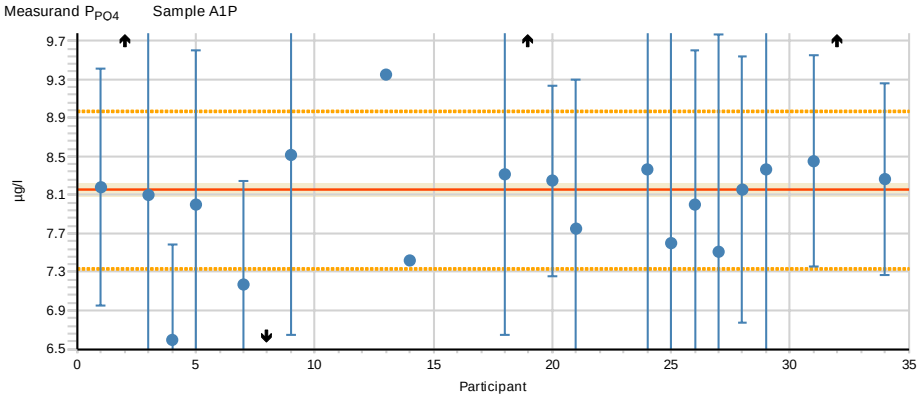


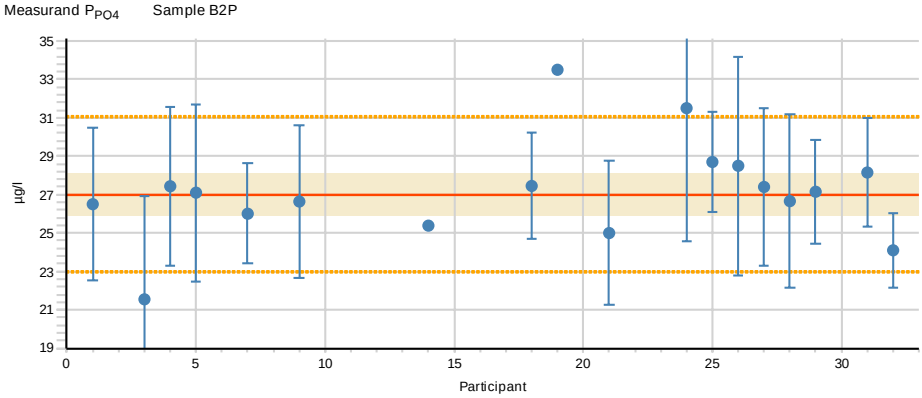
Measurand pH Sample B2H

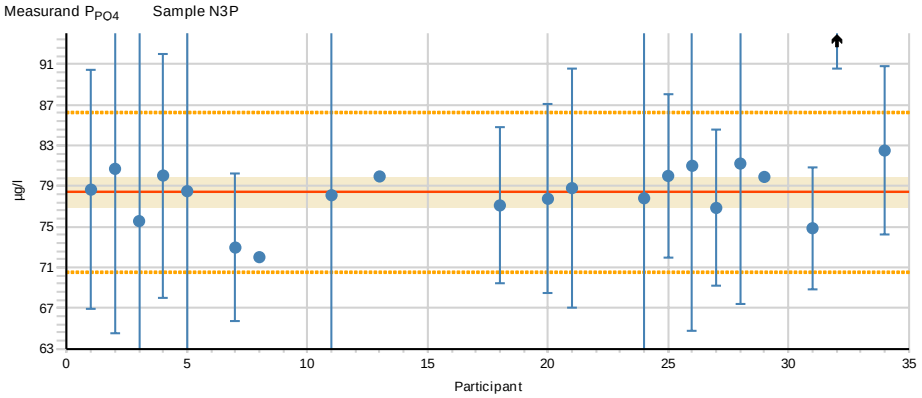


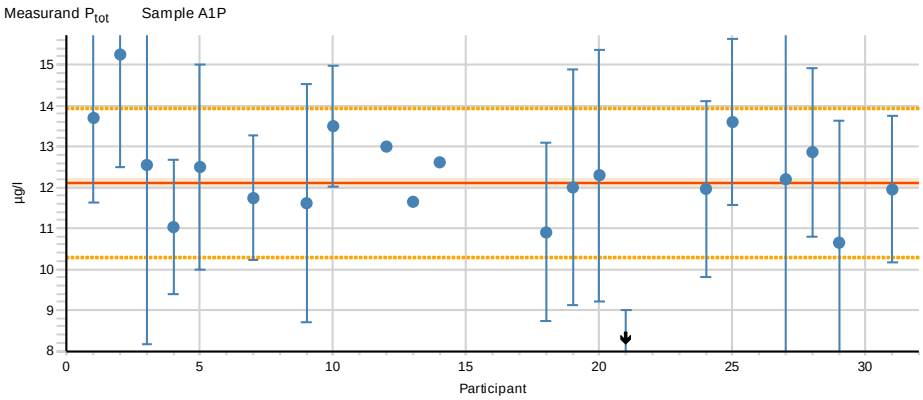
Measurand pH Sample N3H

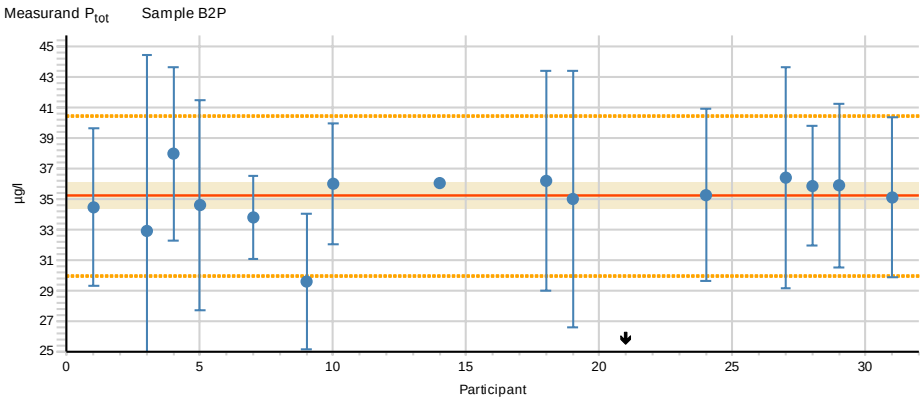


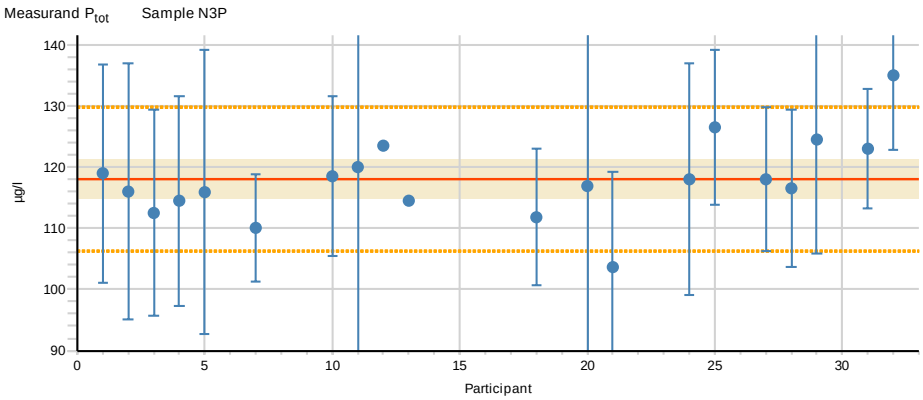

Measurand P_{PO4} Sample A1P
µg/l
9.7
9.3
8.9
8.5
8.1
7.7
7.3
6.9
6.5
0
5
10
15
20
25
30
35
Participant

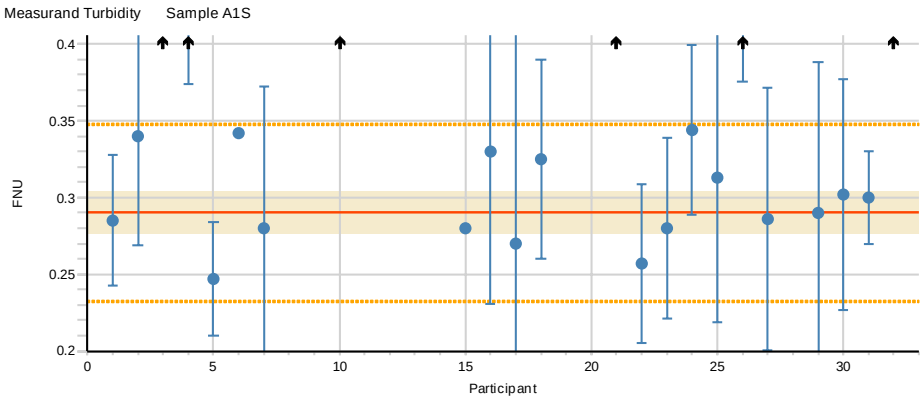

Measurand P_{PO4} Sample B2P
µg/l
35
33
31
29
27
25
23
21
19
0
5
10
15
20
25
30
Participant

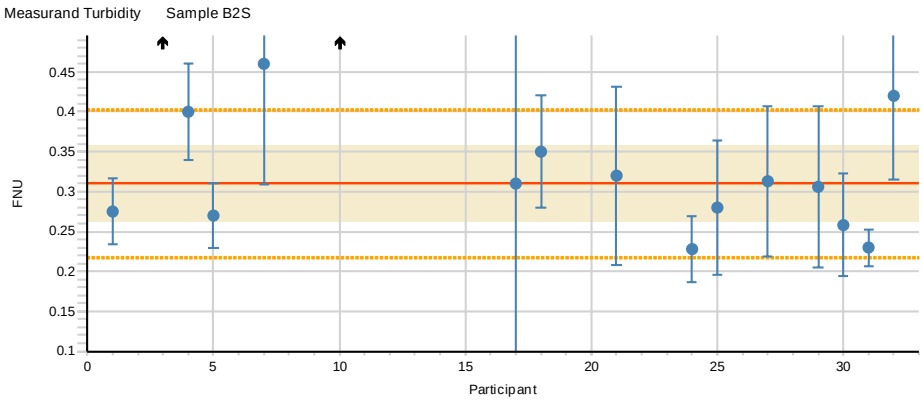

Measurand P_{PO4} Sample N3P
µg/l
91
87
83
79
75
71
67
63
0
5
10
15
20
25
30
35
Participant

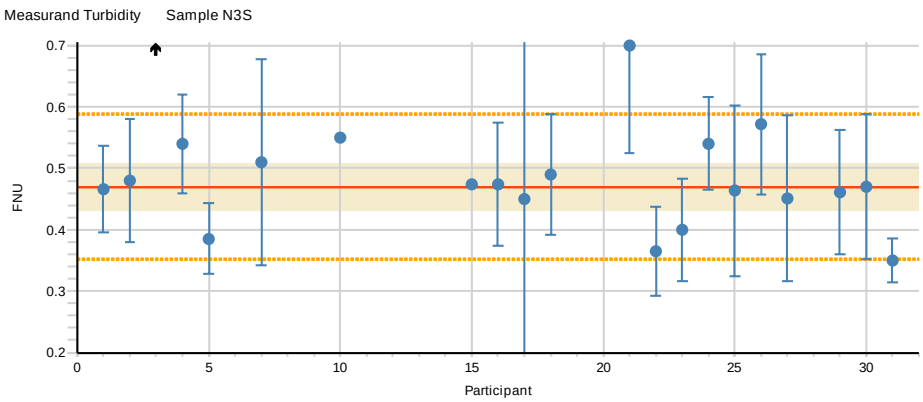

Measurand P_{tot}
Sample A1P
µg/l
Participant


Measurand P_{tot}
Sample B2P
µg/l
Participant


Measurand P_{tot}
Sample N3P
µg/l
Participant


Measurand Turbidity
Sample A1S
FNU
0.4
0.35
0.3
0.25
0.2
0
5
10
15
20
25
30
Participant


Measurand Turbidity
Sample B2S
FNU
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0
5
10
15
20
25
30
Participant


Measurand Turbidity
Sample N3S
FNU
0.7
0.6
0.5
0.4
0.3
0.2
0
5
10
15
20
25
30
Participant

APPENDIX 10: Summary of the z scores

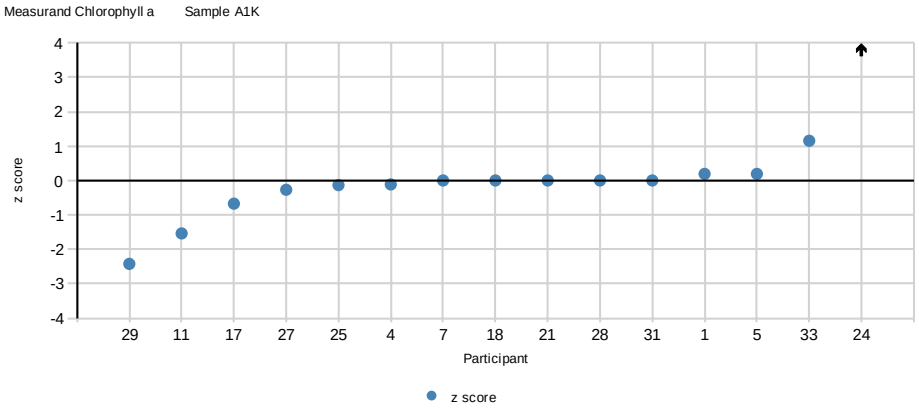
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Chlorophyll *a*	A1K	S	.	.	S	S	.	S	.	.	.	S	.	.	.	.	.	S	S	.	.	S	.	.	86.7
	B2K	S	.	.	S	S	.	u	.	.	.	S	.	.	*u*	.	.	S	S	.	.	S	.	.	81.3
	N3K	S	.	.	S	S	.	S	.	.	.	S	.	.	*u*	.	.	S	S	.	.	S	.	.	87.5
Colour$_{Visual}$	A1V	S	Q	S	.	.	.	.	.	.	.	.	.	.	.	.	.	S	S	.	*q*	.	.	*Q*	66.7
	B2S	U	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	*S*	S	.	.	.	.	.	77.8
	N3S	S	q	S	.	.	.	.	.	.	.	.	.	.	.	.	.	S	S	.	*S*	.	.	*S*	75.0
Colour$_{Spectrophotometric}$	A1V	S	.	S	S	S	.	S	.	.	.	.	.	.	.	*S*	S	.	.	.	.	S	S	.	92.3
	B2S	S	.	*S*	S	S	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	S	.	.	90.0
	N3S	S	.	S	S	U	.	Q	.	.	.	.	.	.	.	*S*	S	.	.	.	.	S	S	.	84.6
Conductivity 25	A1J	S	U	S	S	S	.	S	.	.	*S*	.	*S*	S	S	*S*	.	S	U	S	S	S	S	U	88.0
	B2H	S	.	S	S	S	.	S	.	.	*S*	S	*q*	.	*S*	.	.	S	S	*S*	.	S	.	.	85.7
	N3H	U	U	S	S	S	.	U	.	.	*U*	.	*U*	S	*S*	*S*	.	S	U	.	*S*	S	S	U	64.0
N_{NH4}	A1N	S	S	S	S	S	.	S	.	S	.	.	.	.	*S*	*u*	S	.	S	*S*	.	S	S	U	87.0
	B2N	S	.	Q	S	S	.	S	.	S	.	.	.	.	*S*	.	.	.	S	*U*	.	S	.	.	82.4
	N3N	S	S	S	S	S	.	S	*S*	.	.	S	.	S	.	*u*	S	.	S	.	.	S	U	S	91.3
$N_{NO2+NO3}$	A1N	S	.	S	S	S	.	S	.	S	.	U	.	S	*q*	*u*	S	.	S	*S*	*S*	S	.	.	83.3
	B2N	S	.	S	S	S	.	S	.	S	.	.	.	.	*S*	.	.	.	S	S	.	S	.	.	100
	N3N	S	.	S	S	S	.	S	.	.	.	Q	.	S	.	*u*	S	.	S	.	*S*	S	.	.	81.0
N_{tot}	A1N	S	u	S	S	S	.	S	.	S	*S*	S	*q*	S	*S*	.	.	.	S	*u*	.	S	.	.	81.8
	B2N	S	.	S	S	S	.	S	.	S	*S*	.	.	.	*S*	.	.	.	S	*u*	.	S	.	.	88.9
	N3N	S	u	S	S	S	.	S	*U*	.	*S*	S	*S*	S	.	.	.	.	S	.	.	S	.	.	85.0
pH	A1H	S	S	S	S	S	.	S	*S*	S	*S*	.	S	S	*S*	*S*	.	S	S	*S*	.	S	S	S	100
	B2H	S	.	S	S	S	S	S	.	S	*S*	S	*S*	.	*S*	.	.	S	S	*S*	.	S	.	.	100
	N3H	Q	S	S	S	S	.	S	*U*	S	*S*	.	S	S	*S*	*S*	.	S	S	.	.	S	S	Q	85.2
P_{PO4}	A1P	S	*U*	S	u	S	.	q	*u*	S	.	.	.	*Q*	S	.	.	.	S	*U*	*S*	S	.	.	69.6
	B2P	S	.	q	S	S	.	S	.	S	.	.	.	.	*S*	.	.	.	S	*U*	.	S	.	.	83.3
	N3P	S	*S*	S	S	S	.	S	*S*	.	.	S	.	*S*	.	.	.	.	S	.	*S*	S	.	.	95.2
P_{tot}	A1P	S	U	S	S	S	.	S	.	S	*S*	.	*S*	S	*S*	.	.	.	S	S	S	u	.	.	90.5
	B2P	S	.	S	S	S	.	S	.	q	*S*	.	.	.	*S*	.	.	.	S	*S*	.	u	.	.	87.5
	N3P	S	S	S	S	S	.	S	.	.	*S*	S	*S*	*S*	.	.	.	.	S	.	*S*	q	.	.	90.0
Turbidity	A1S	S	S	U	U	S	*S*	S	.	.	*U*	.	.	.	.	*S*	S	*S*	S	.	.	U	S	S	73.9
	B2S	S	.	U	S	S	.	U	.	.	*U*	.	.	.	.	.	.	*S*	S	.	.	S	.	.	75.0
	N3S	S	S	U	S	S	.	S	.	.	*S*	.	.	.	.	*S*	S	*S*	S	.	.	U	S	S	85.7
%		91	50	83	93	97	100	83	50	92	80	83	70	92	83	67	100	100	93	64	90	83	90	50	
accredited		33	14	27	30	30	1	30		13		12		9			8	9	30			30	8	8	

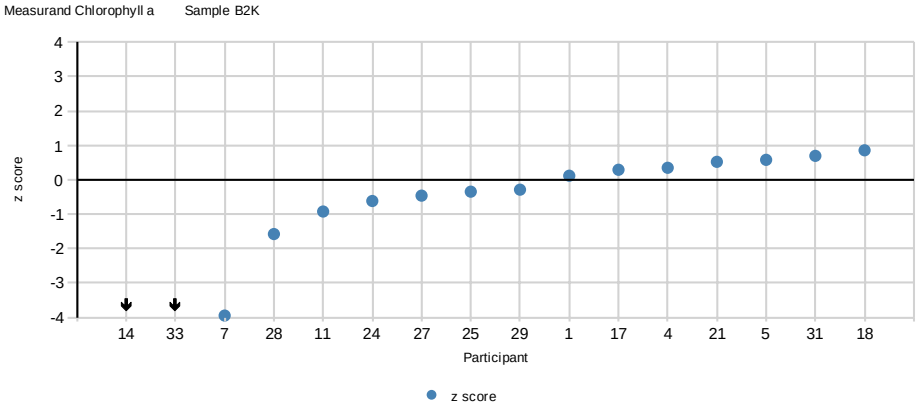
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	%
Chlorophyll *a*	A1K	U	S	.	S	S	q	.	*S*	.	*S*	.	86.7
	B2K	S	S	.	S	S	S	.	*S*	.	*u*	.	81.3
	N3K	S	S	.	S	S	S	.	*S*	.	*u*	.	87.5
$Colour_{Visual}$	A1V	q	S	.	*S*	.	.	*S*	S	.	.	.	66.7
	B2S	S	S	.	*S*	.	.	*S*	Q	.	.	.	77.8
	N3S	q	S	.	*S*	.	.	*S*	Q	.	.	.	75.0
$Colour_{Spectrophotometric}$	A1V	.	u	.	S	.	S	.	.	*S*	.	.	92.3
	B2S	.	q	.	S	.	S	.	.	*S*	.	.	90.0
	N3S	.	S	.	S	.	S	.	.	*S*	.	.	84.6
Conductivity 25	A1J	S	S	.	S	.	S	S	S	*S*	.	.	88.0
	B2H	S	S	u	S	.	S	u	S	*S*	.	.	85.7
	N3H	S	Q	S	S	.	S	S	q	*S*	.	.	64.0
N_{NH4}	A1N	S	S	S	S	S	S	.	S	*Q*	.	.	87.0
	B2N	S	U	.	S	S	S	.	S	*S*	.	.	82.4
	N3N	S	S	S	S	S	S	.	S	*S*	.	.	91.3
$N_{NO2+NO3}$	A1N	S	S	S	S	S	Q	.	S	S	.	S	83.3
	B2N	S	S	S	S	S	S	.	S	*S*	.	.	100
	N3N	S	S	S	q	S	U	.	S	*S*	.	S	81.0
N_{tot}	A1N	S	S	.	S	S	S	.	S	*u*	.	.	81.8
	B2N	S	Q	.	S	S	S	.	S	*S*	.	.	88.9
	N3N	S	S	.	S	S	S	.	S	*q*	.	.	85.0
pH	A1H	S	S	.	S	S	S	S	S	*S*	.	.	100
	B2H	S	S	S	S	S	S	S	S	*S*	.	.	100
	N3H	S	Q	S	S	S	S	S	S	*S*	.	.	85.2
P_{PO4}	A1P	S	S	S	S	S	S	.	S	*U*	.	S	69.6
	B2P	Q	S	S	S	S	S	.	S	*S*	.	.	83.3
	N3P	S	S	S	S	S	S	.	S	*U*	.	S	95.2
P_{tot}	A1P	S	S	.	S	S	S	.	S	.	.	.	90.5
	B2P	S	.	.	S	S	S	.	S	.	.	.	87.5
	N3P	S	S	.	S	S	S	.	S	*Q*	.	.	90.0
Turbidity	A1S	S	S	U	S	.	S	S	S	*U*	.	.	73.9
	B2S	S	S	.	S	.	S	S	S	*Q*	.	.	75.0
	N3S	S	S	S	S	.	S	S	q	.	.	.	85.7
%		87	82	87	97	100	87	92	87	68	33	100	
accredited		31	33	15	31	22	31	9	28			5	

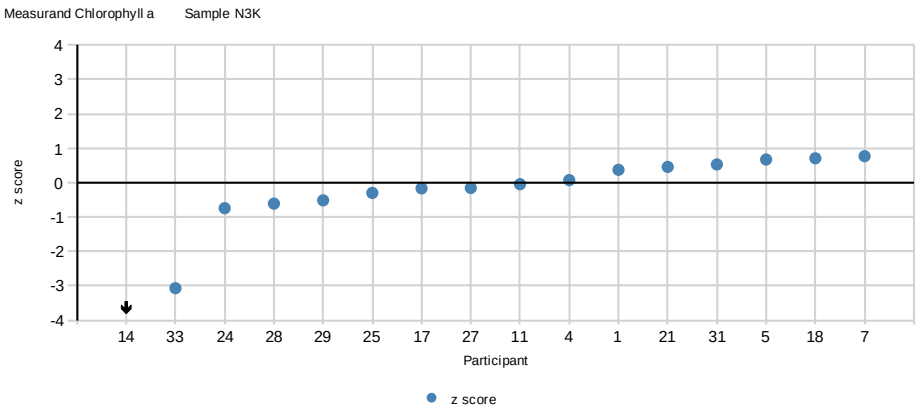
S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited
% - percentage of satisfactory results

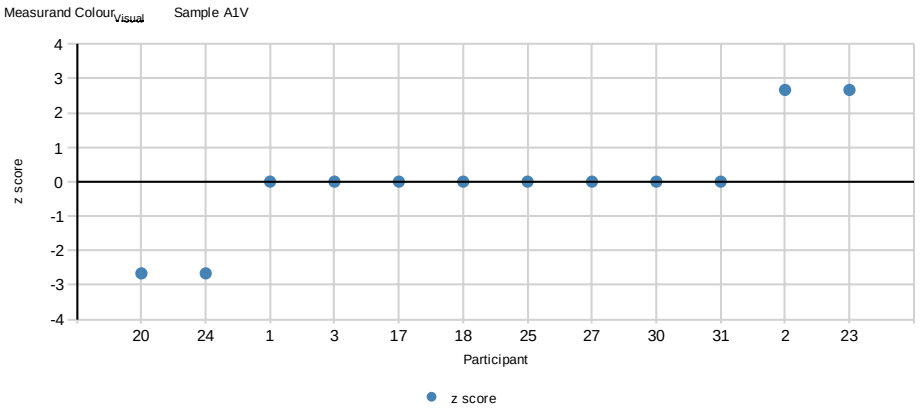
Totally satisfactory, % in all: 85 % in accredited: 88 % in non-accredited: 75

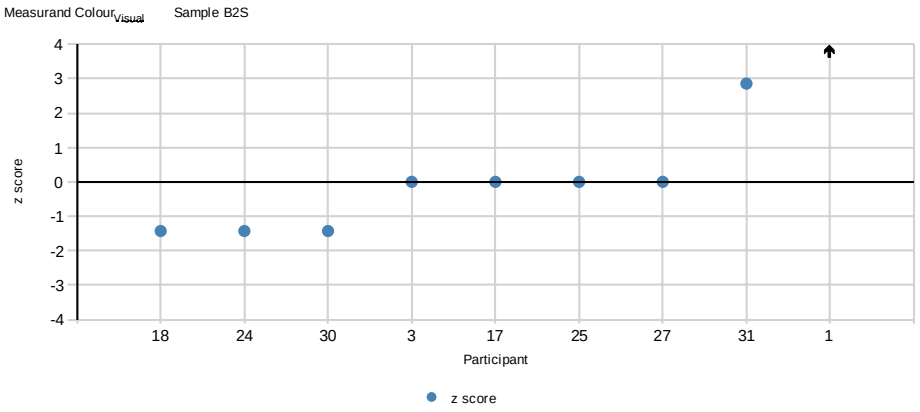
APPENDIX 11: z scores in ascending order

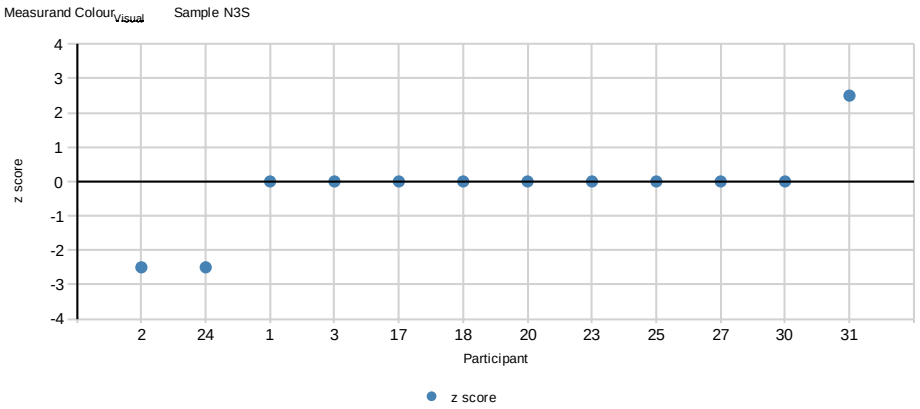


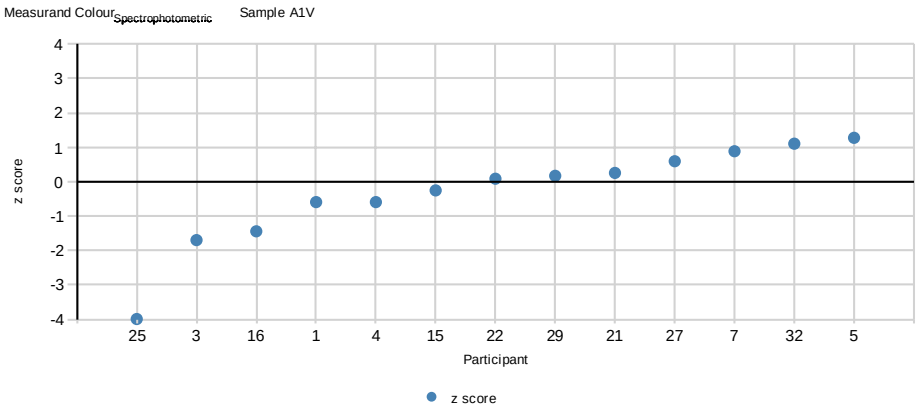


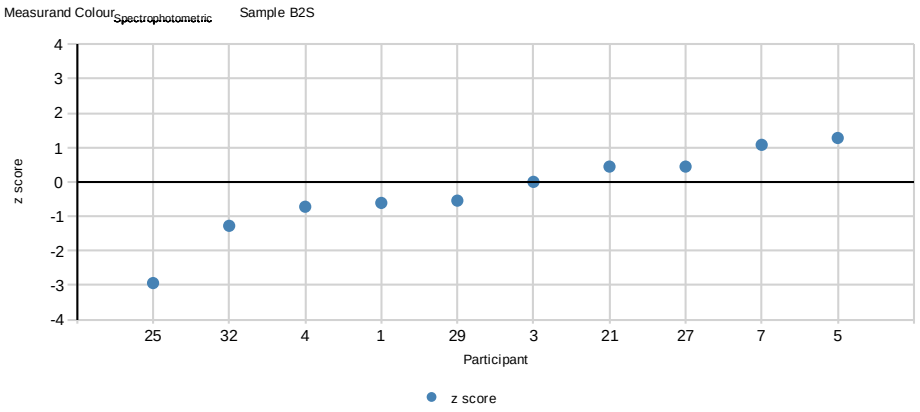


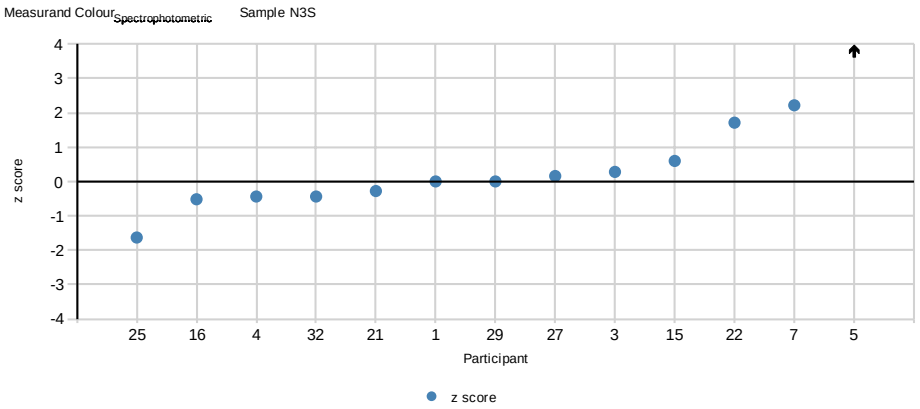

Measurand Colour visual
Sample A1V
z score
4
3
2
1
0
-1
-2
-3
-4
20
24
1
3
17
18
25
27
30
31
2
23
Participant
z score

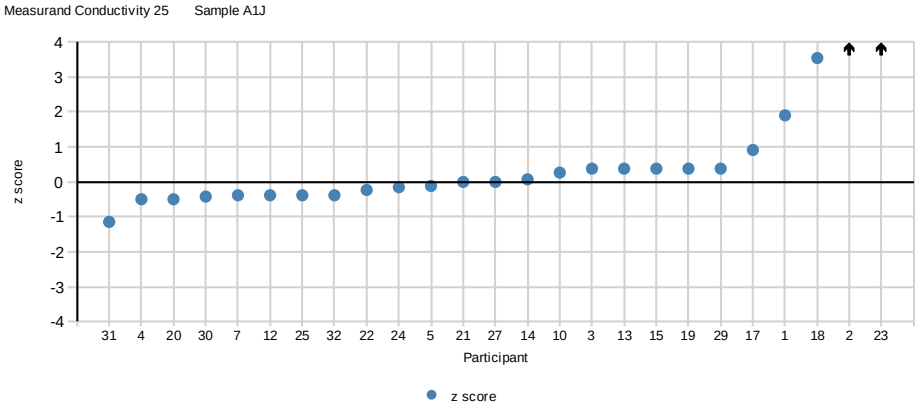

Measurand Colour visual
Sample B2S
z score
4
3
2
1
0
-1
-2
-3
-4
18
24
30
3
17
25
27
31
1
Participant
z score

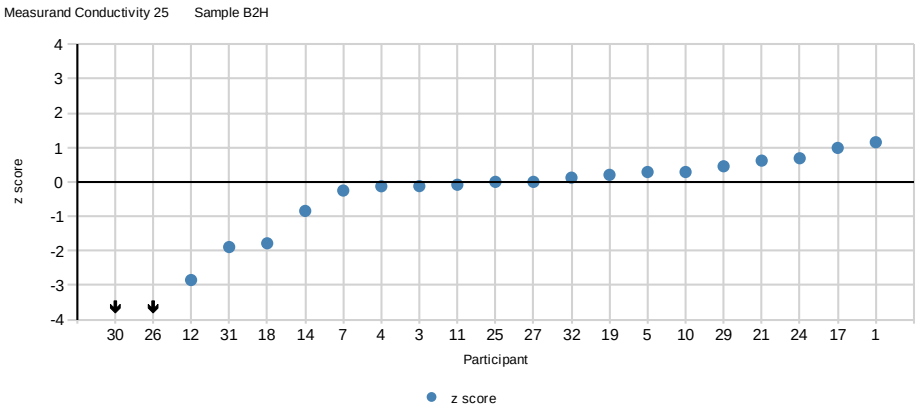

Measurand Colour visual
Sample N3S
z score
4
3
2
1
0
-1
-2
-3
-4
2
24
1
3
17
18
20
23
25
27
30
31
Participant
z score

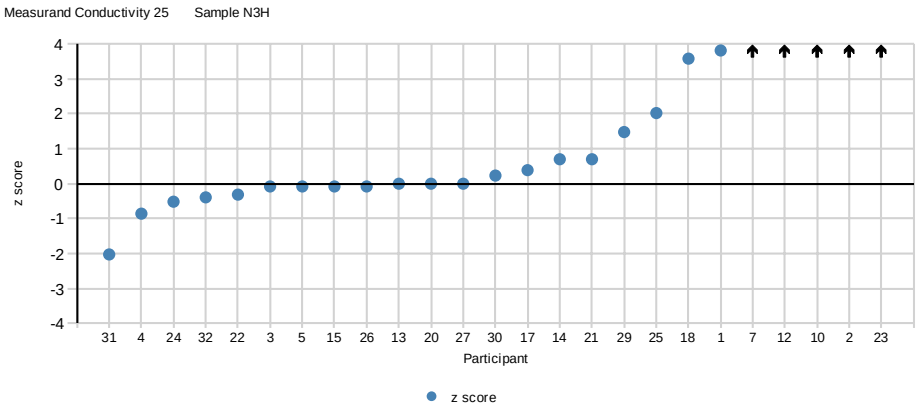

Measurand Colour Spectrophotometric
Sample A1V
z score
4
3
2
1
0
-1
-2
-3
-4
25 3 16 1 4 15 22 29 21 27 7 32 5
Participant
z score

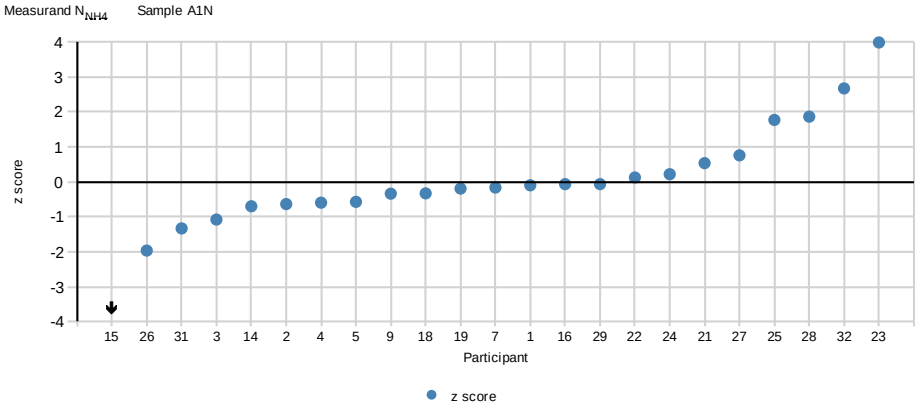

Measurand Colour Spectrophotometric
Sample B2S
z score
4
3
2
1
0
-1
-2
-3
-4
25 32 4 1 29 3 21 27 7 5
Participant
z score

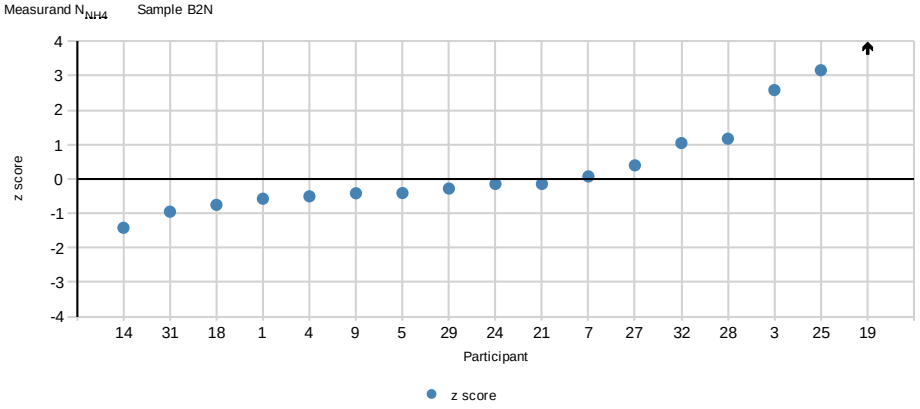

Measurand Colour Spectrophotometric
Sample N3S
z score
4
3
2
1
0
-1
-2
-3
-4
25 16 4 32 21 1 29 27 3 15 22 7 5
Participant
z score

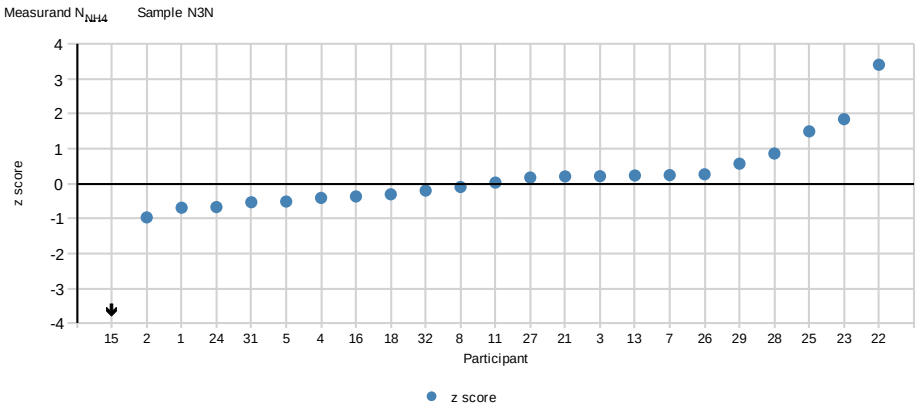

Measurand Conductivity 25 Sample A1J
z score
4
3
2
1
0
-1
-2
-3
-4
31 4 20 30 7 12 25 32 22 24 5 21 27 14 10 3 13 15 19 29 17 1 18 2 23
Participant
z score

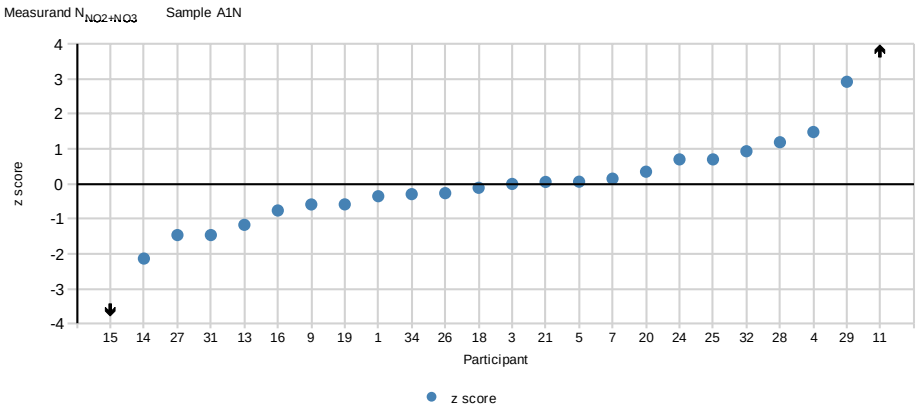

Measurand Conductivity 25 Sample B2H
z score
4
3
2
1
0
-1
-2
-3
-4
30 26 12 31 18 14 7 4 3 11 25 27 32 19 5 10 29 21 24 17 1
Participant
z score

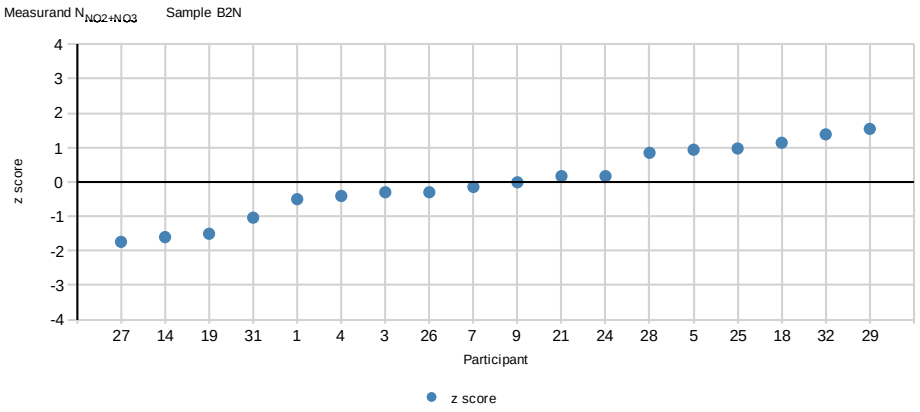

Measurand Conductivity 25 Sample N3H
z score
4
3
2
1
0
-1
-2
-3
-4
31 4 24 32 22 3 5 15 26 13 20 27 30 17 14 21 29 25 18 1 7 12 10 2 23
Participant
z score

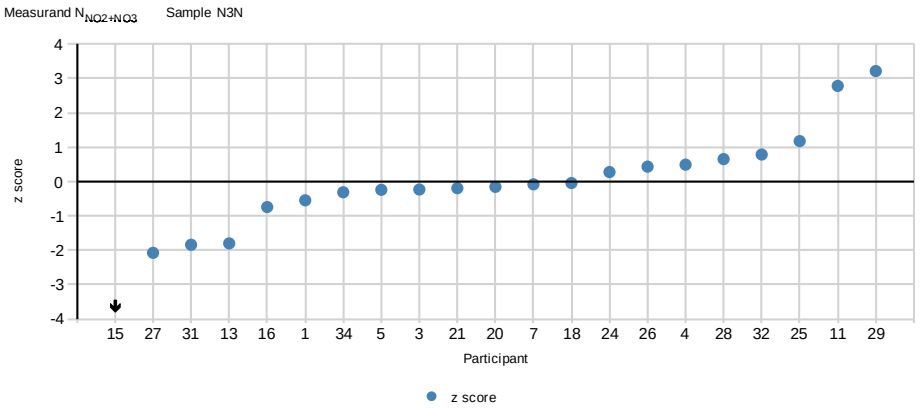

Measurand N_{NH4}
Sample A1N
z score
4
3
2
1
0
-1
-2
-3
-4
15 26 31 3 14 2 4 5 9 18 19 7 1 16 29 22 24 21 27 25 28 32 23
Participant
z score

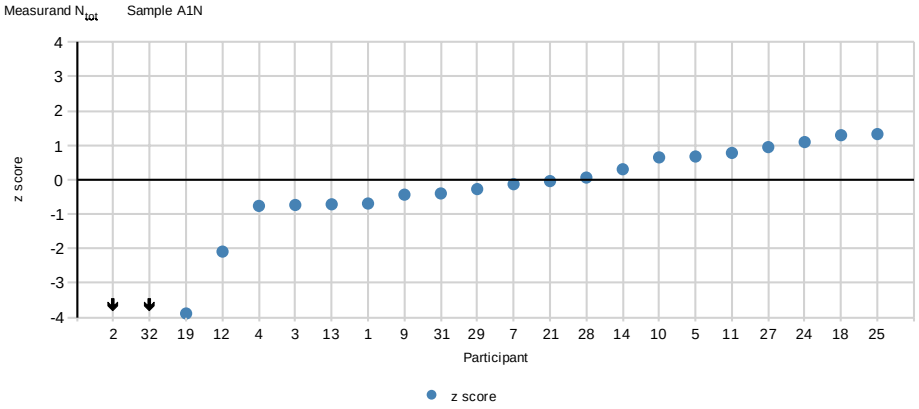

Measurand N_{NH4}
Sample B2N
z score
4
3
2
1
0
-1
-2
-3
-4
14 31 18 1 4 9 5 29 24 21 7 27 32 28 3 25 19
Participant
z score

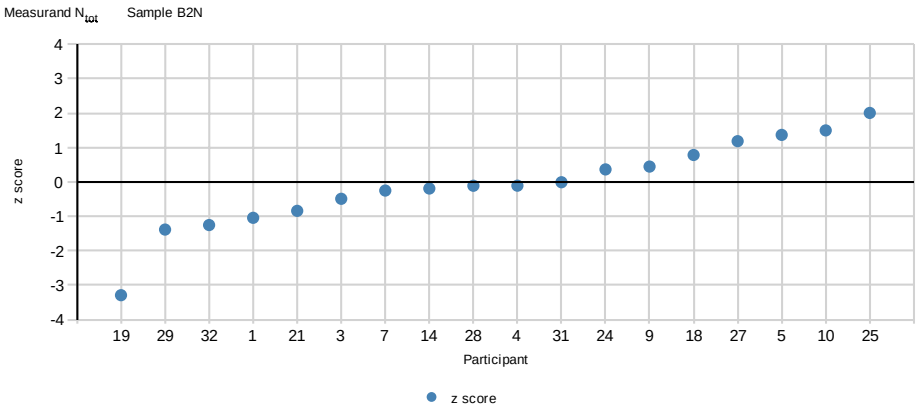

Measurand N_{NH4}
Sample N3N
z score
4
3
2
1
0
-1
-2
-3
-4
15 2 1 24 31 5 4 16 18 32 8 11 27 21 3 13 7 26 29 28 25 23 22
Participant
z score

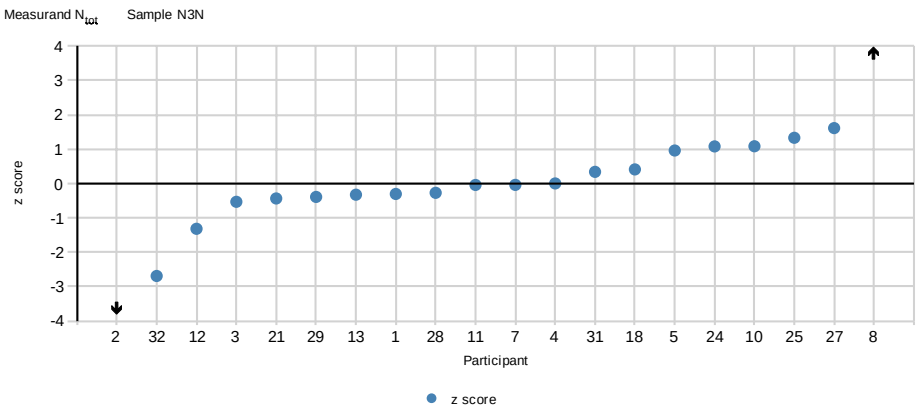

Measurand $N_{NO2+NO3}$ Sample A1N
z score
4
3
2
1
0
-1
-2
-3
-4
15 14 27 31 13 16 9 19 1 34 26 18 3 21 5 7 20 24 25 32 28 4 29 11
Participant
z score

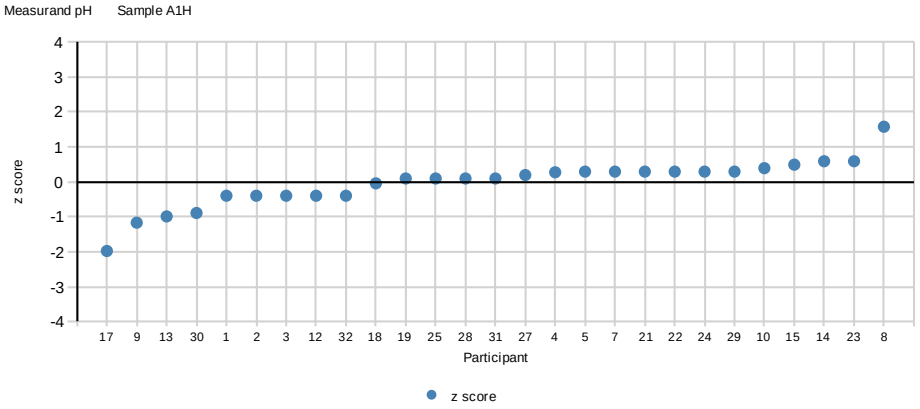

Measurand $N_{NO2+NO3}$ Sample B2N
z score
4
3
2
1
0
-1
-2
-3
-4
27 14 19 31 1 4 3 26 7 9 21 24 28 5 25 18 32 29
Participant
z score

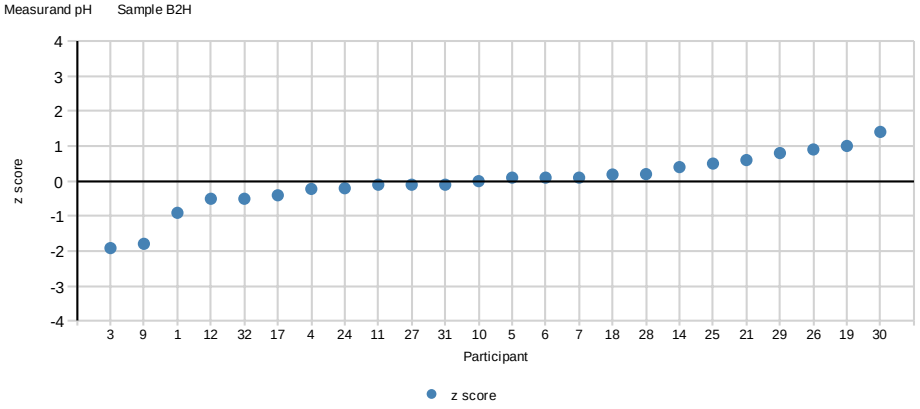

Measurand $N_{NO2+NO3}$ Sample N3N
z score
4
3
2
1
0
-1
-2
-3
-4
15 27 31 13 16 1 34 5 3 21 20 7 18 24 26 4 28 32 25 11 29
Participant
z score

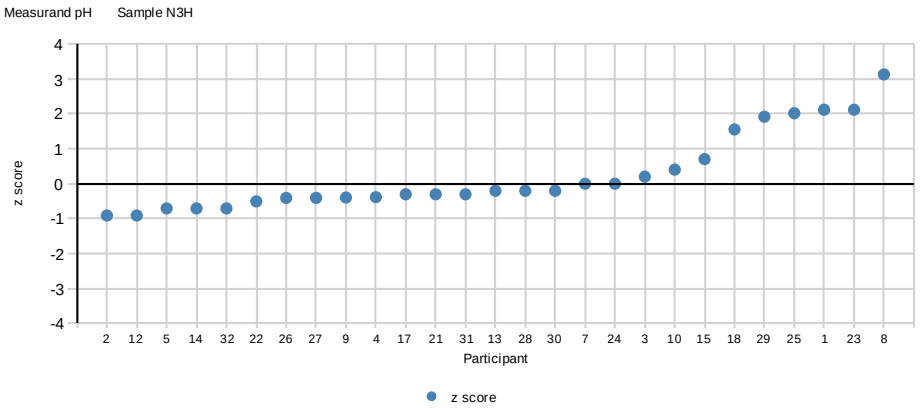

Measurand N_{tot} Sample A1N
z score
4
3
2
1
0
-1
-2
-3
-4
2 32 19 12 4 3 13 1 9 31 29 7 21 28 14 10 5 11 27 24 18 25
Participant
z score

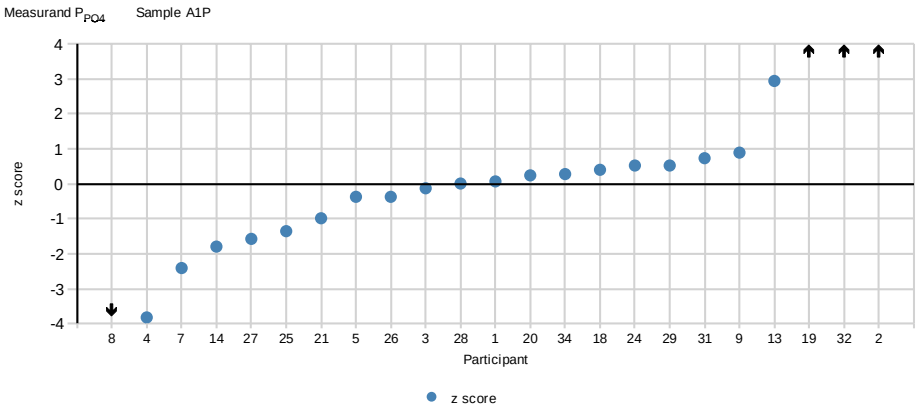

Measurand N_{tot} Sample B2N
z score
4
3
2
1
0
-1
-2
-3
-4
19 29 32 1 21 3 7 14 28 4 31 24 9 18 27 5 10 25
Participant
z score

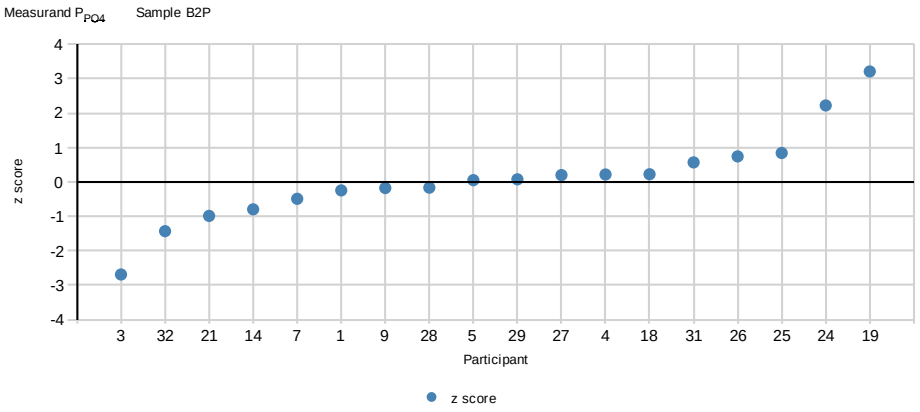

Measurand N_{tot} Sample N3N
z score
4
3
2
1
0
-1
-2
-3
-4
2 32 12 3 21 29 13 1 28 11 7 4 31 18 5 24 10 25 27 8
Participant
z score

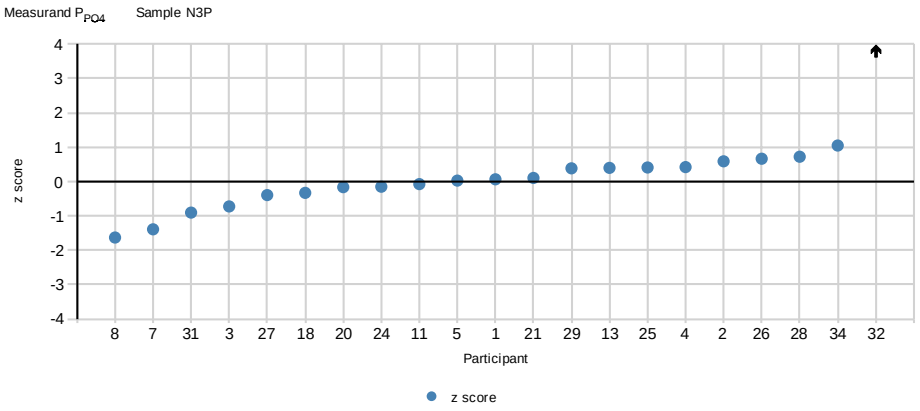

Measurand pH Sample A1H
z score
4
3
2
1
0
-1
-2
-3
-4
17 9 13 30 1 2 3 12 32 18 19 25 28 31 27 4 5 7 21 22 24 29 10 15 14 23 8
Participant
z score

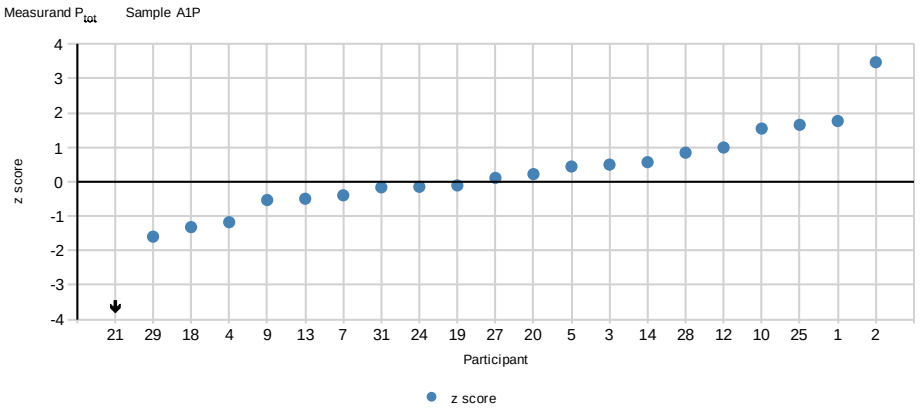

Measurand pH Sample B2H
z score
4
3
2
1
0
-1
-2
-3
-4
3 9 1 12 32 17 4 24 11 27 31 10 5 6 7 18 28 14 25 21 29 26 19 30
Participant
z score

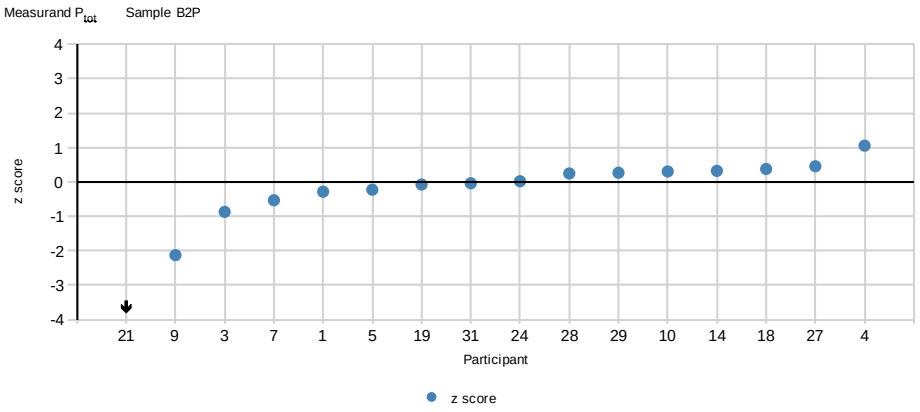

Measurand pH Sample N3H
z score
4
3
2
1
0
-1
-2
-3
-4
2 12 5 14 32 22 26 27 9 4 17 21 31 13 28 30 7 24 3 10 15 18 29 25 1 23 8
Participant
z score

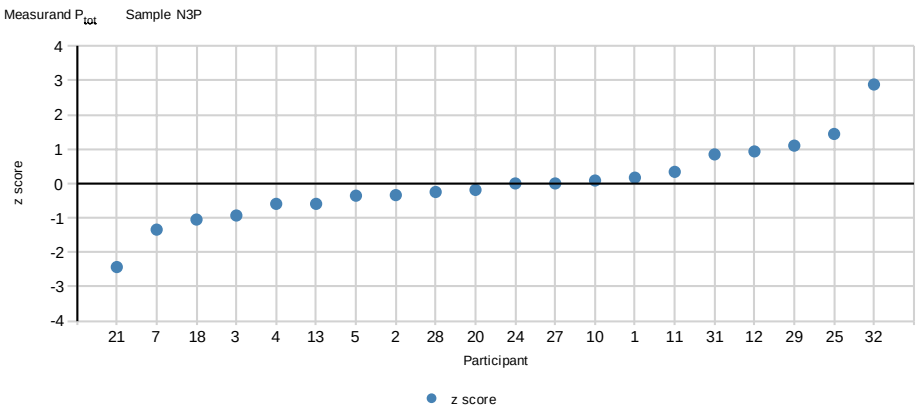

Measurand P_{PO4}
Sample A1P
z score
4
3
2
1
0
-1
-2
-3
-4
8 4 7 14 27 25 21 5 26 3 28 1 20 34 18 24 29 31 9 13 19 32 2
Participant
z score

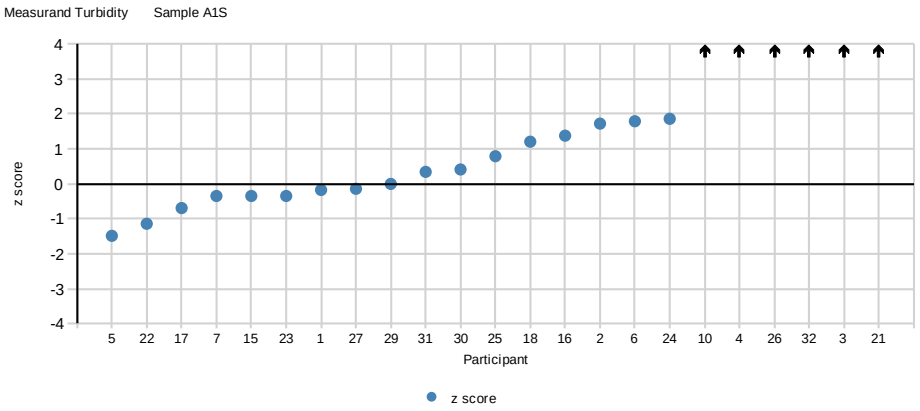

Measurand P_{PO4}
Sample B2P
z score
4
3
2
1
0
-1
-2
-3
-4
3 32 21 14 7 1 9 28 5 29 27 4 18 31 26 25 24 19
Participant
z score

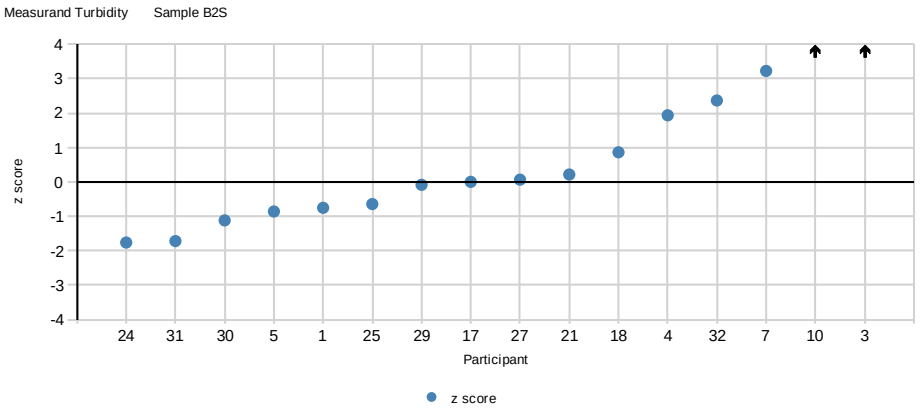

Measurand P_{PO4}
Sample N3P
z score
4
3
2
1
0
-1
-2
-3
-4
8 7 31 3 27 18 20 24 11 5 1 21 29 13 25 4 2 26 28 34 32
Participant
z score

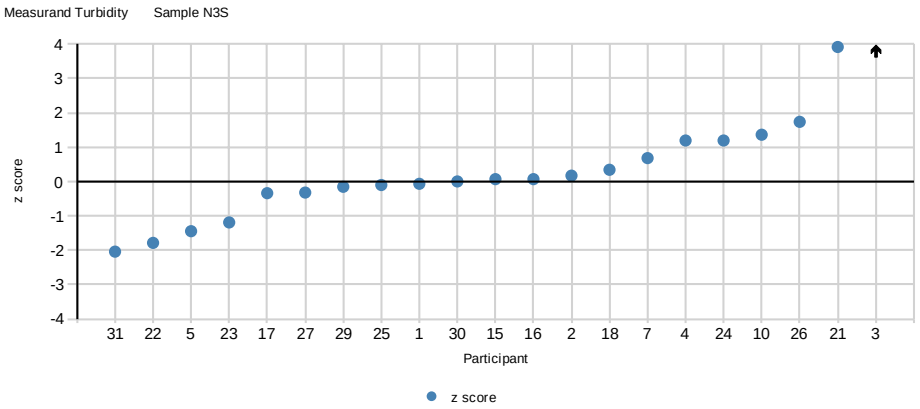

Measurand P_{tot} Sample A1P
z score
4
3
2
1
0
-1
-2
-3
-4
21 29 18 4 9 13 7 31 24 19 27 20 5 3 14 28 12 10 25 1 2
Participant
z score


Measurand P_{tot} Sample B2P
z score
4
3
2
1
0
-1
-2
-3
-4
21 9 3 7 1 5 19 31 24 28 29 10 14 18 27 4
Participant
z score


Measurand P_{tot} Sample N3P
z score
4
3
2
1
0
-1
-2
-3
-4
21 7 18 3 4 13 5 2 28 20 24 27 10 1 11 31 12 29 25 32
Participant
z score

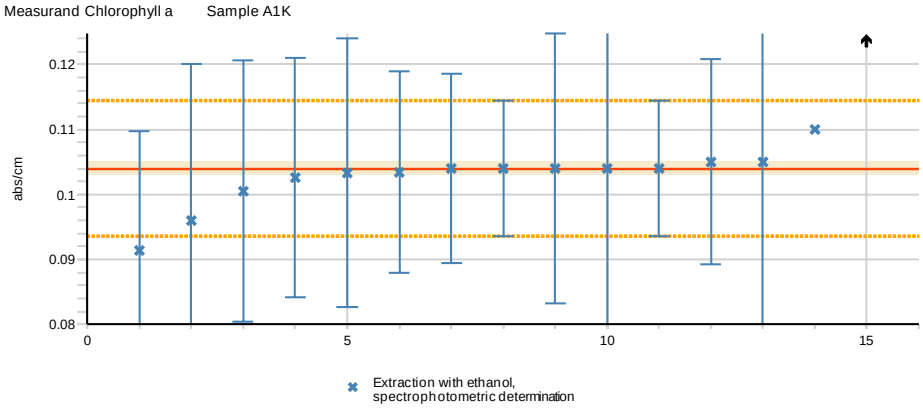

Measurand Turbidity Sample A1S
z score
4
3
2
1
0
-1
-2
-3
-4
5 22 17 7 15 23 1 27 29 31 30 25 18 16 2 6 24 10 4 26 32 3 21
Participant
z score

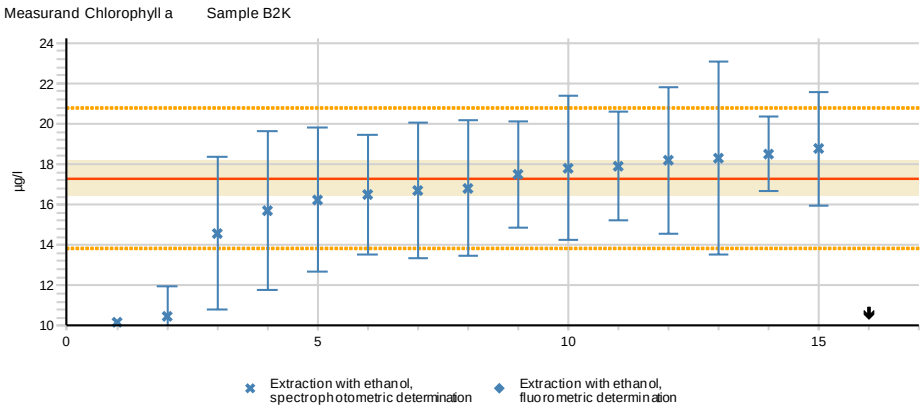

Measurand Turbidity Sample B2S
z score
4
3
2
1
0
-1
-2
-3
-4
24 31 30 5 1 25 29 17 27 21 18 4 32 7 10 3
Participant
z score

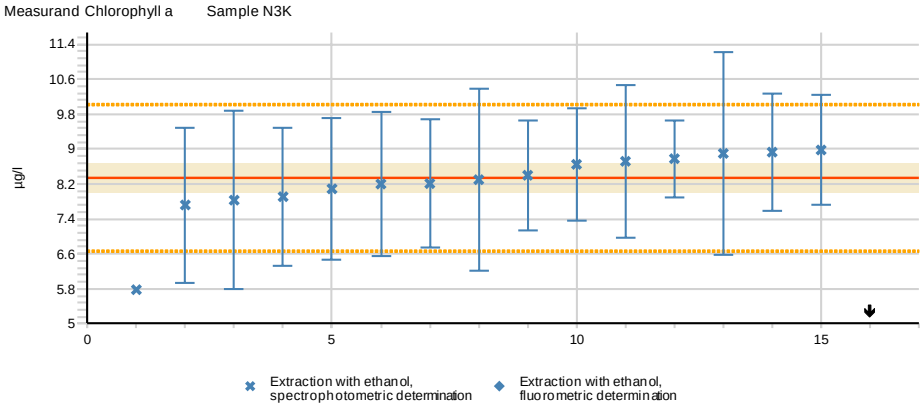

Measurand Turbidity Sample N3S
z score
4
3
2
1
0
-1
-2
-3
-4
31 22 5 23 17 27 29 25 1 30 15 16 2 18 7 4 24 10 26 21 3
Participant
z score

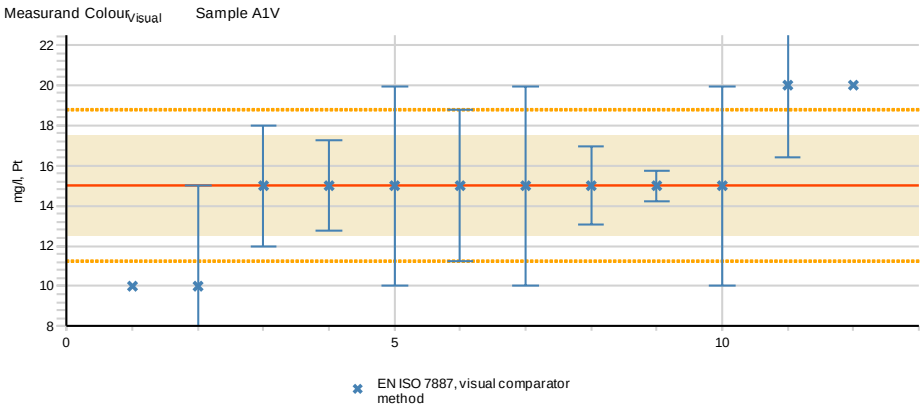
APPENDIX 12: Results grouped according to the methods

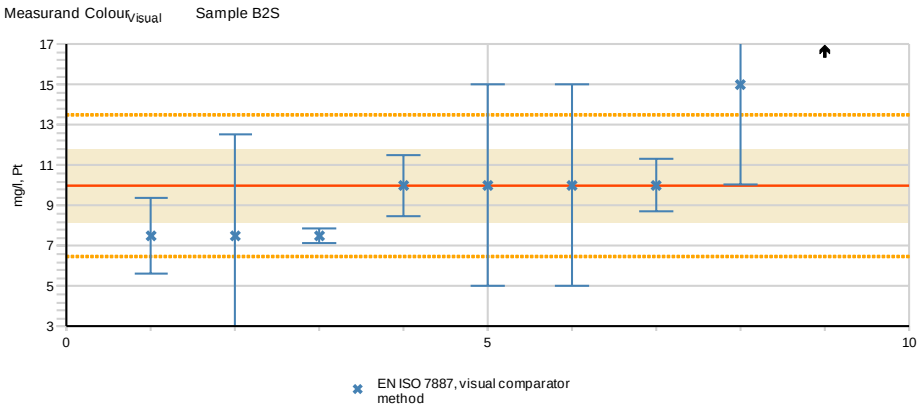
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.

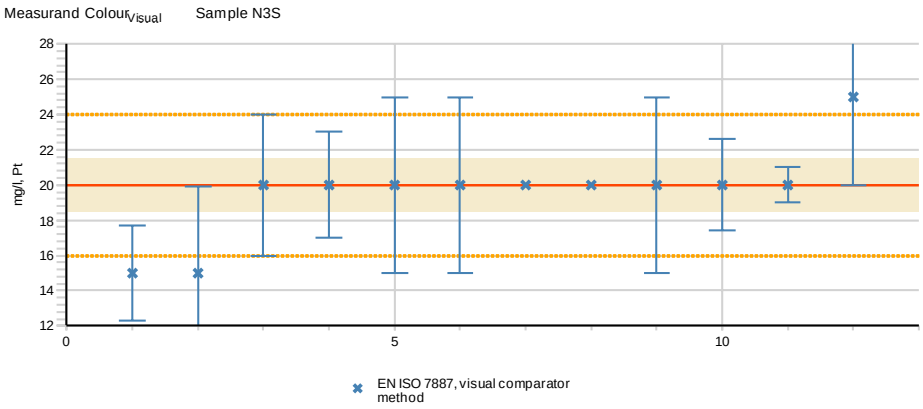


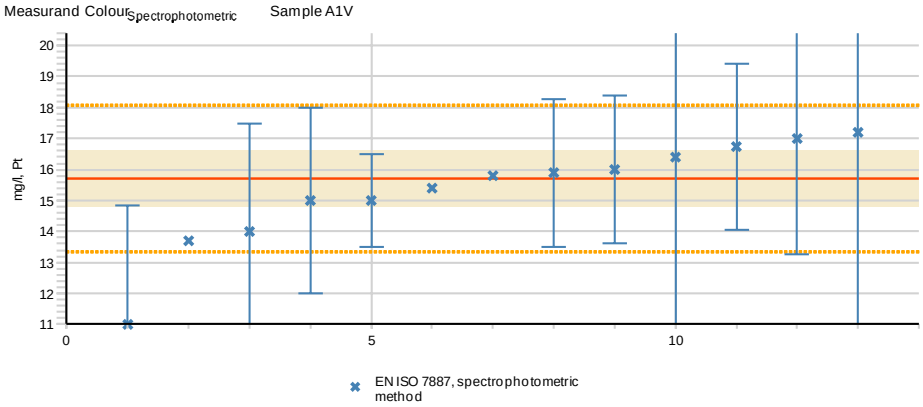


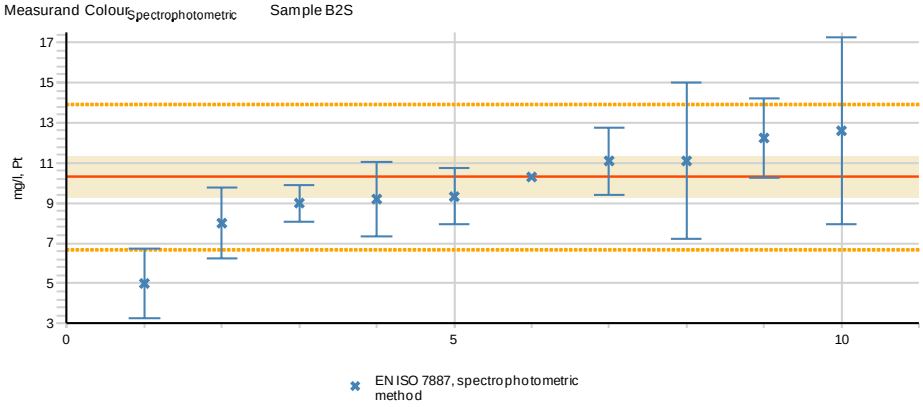


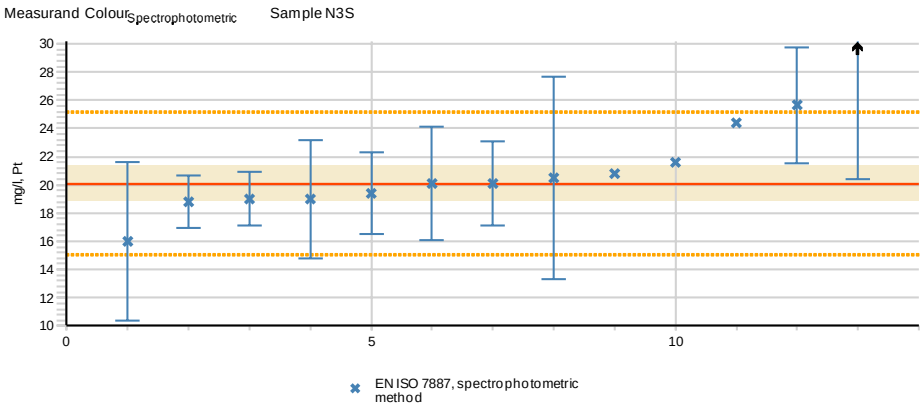

Measurand Colour$_{Visual}$
Sample A1V
mg/l, Pt
22
20
18
16
14
12
10
8
0
5
10
EN ISO 7887, visual comparator method


Measurand Colour$_{Visual}$
Sample B2S
mg/l, Pt
17
15
13
11
9
7
5
3
0
5
10
EN ISO 7887, visual comparator method

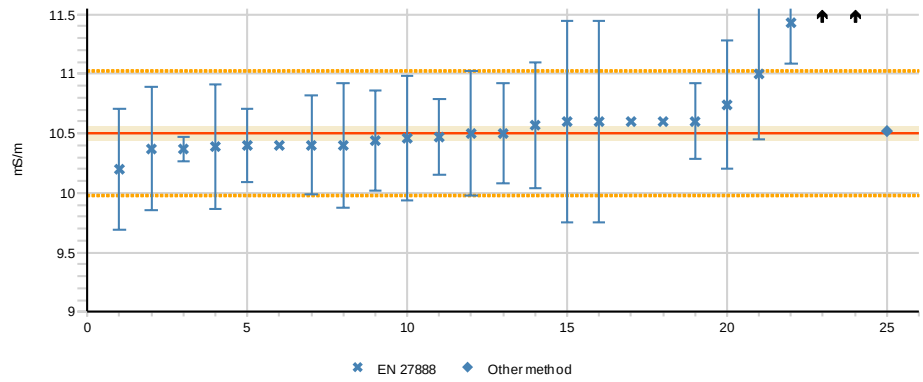

Measurand Colour$_{Visual}$
Sample N3S
mg/l, Pt
28
26
24
22
20
18
16
14
12
0
5
10
EN ISO 7887, visual comparator method


Measurand Colour Spectrophotometric
Sample A1V
mg/l, Pt
20
19
18
17
16
15
14
13
12
11
0
5
10
EN ISO 7887, spectrophotometric method

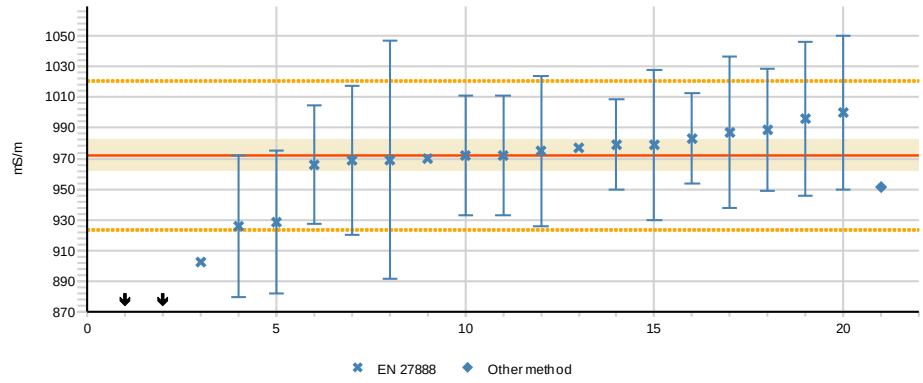

Measurand Colour Spectrophotometric
Sample B2S
mg/l, Pt
17
15
13
11
9
7
5
3
0
5
10
EN ISO 7887, spectrophotometric method


Measurand Colour Spectrophotometric
Sample N3S
mg/l, Pt
30
28
26
24
22
20
18
16
14
12
10
0
5
10
EN ISO 7887, spectrophotometric method

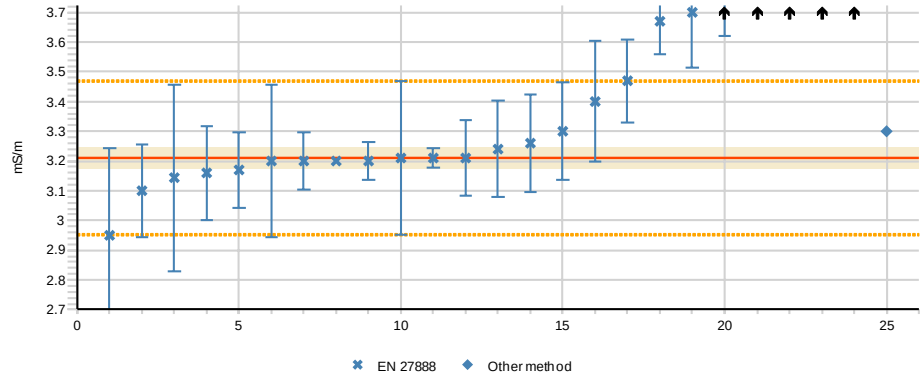
Measurand Conductivity 25 Sample A1J

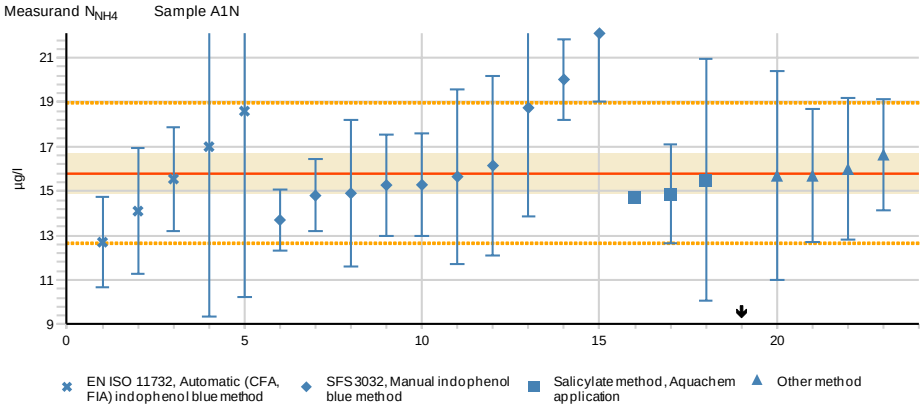


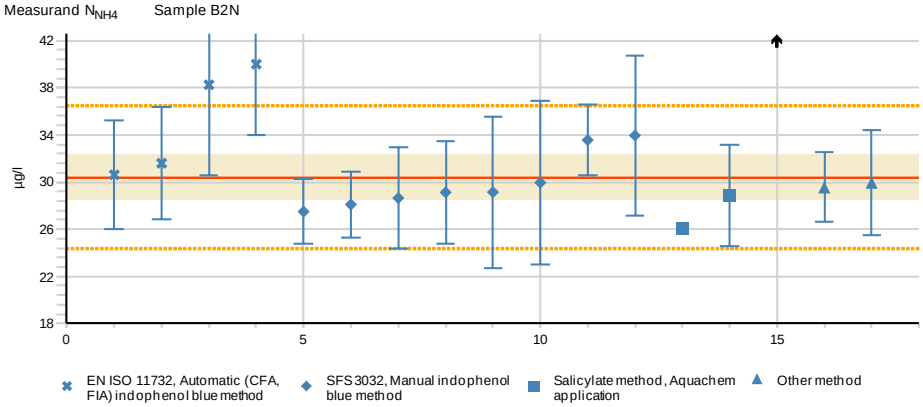
Measurand Conductivity 25 Sample B2H

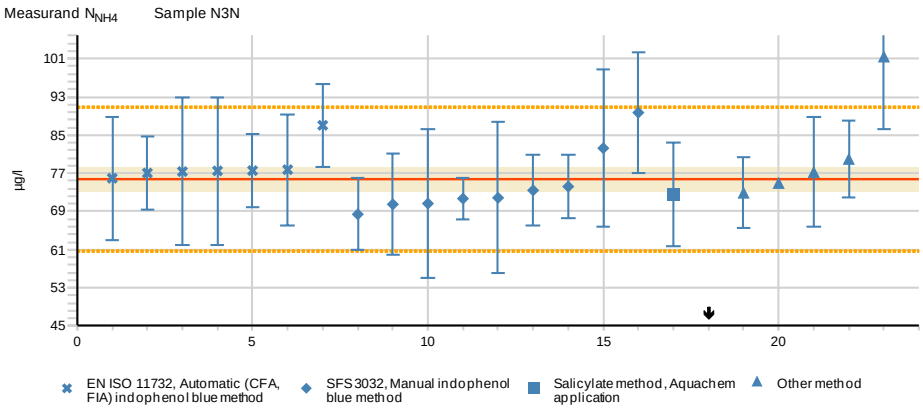


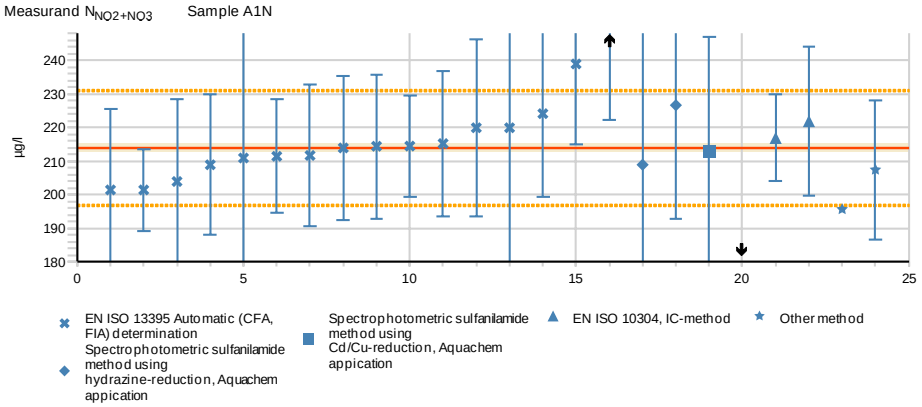
Measurand Conductivity 25 Sample N3H

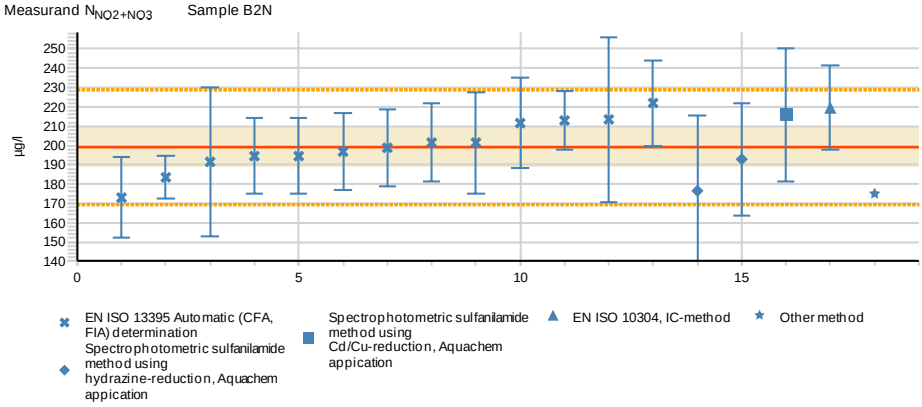


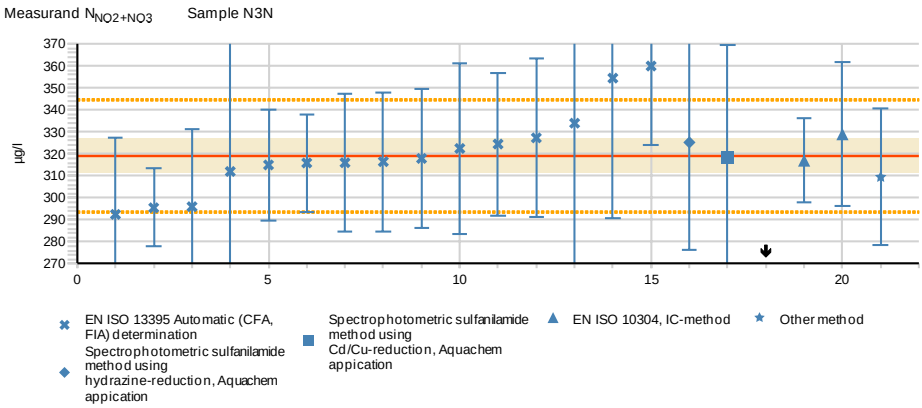

Measurand N_{NH4} Sample A1N
µg/l
21
19
17
15
13
11
9
0
5
10
15
20
EN ISO 11732, Automatic (CFA, FIA) indophenol blue method
SFS 3032, Manual indophenol blue method
Salicylate method, Aquachem application
Other method

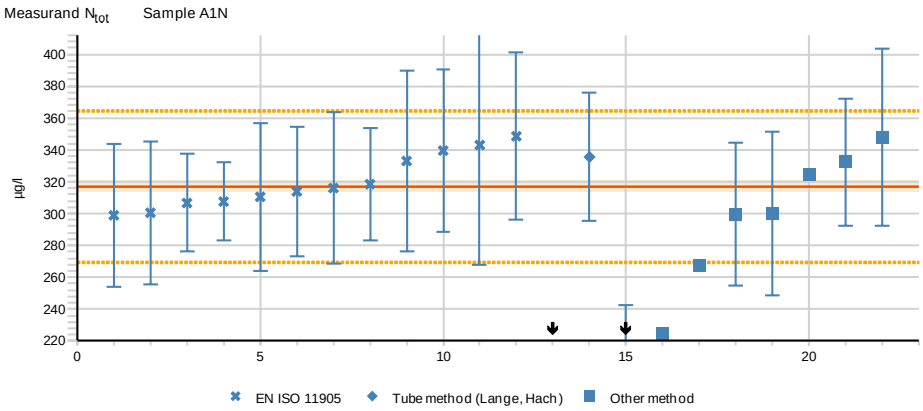

Measurand N_{NH4} Sample B2N
µg/l
42
38
34
30
26
22
18
0
5
10
15
EN ISO 11732, Automatic (CFA, FIA) indophenol blue method
SFS 3032, Manual indophenol blue method
Salicylate method, Aquachem application
Other method

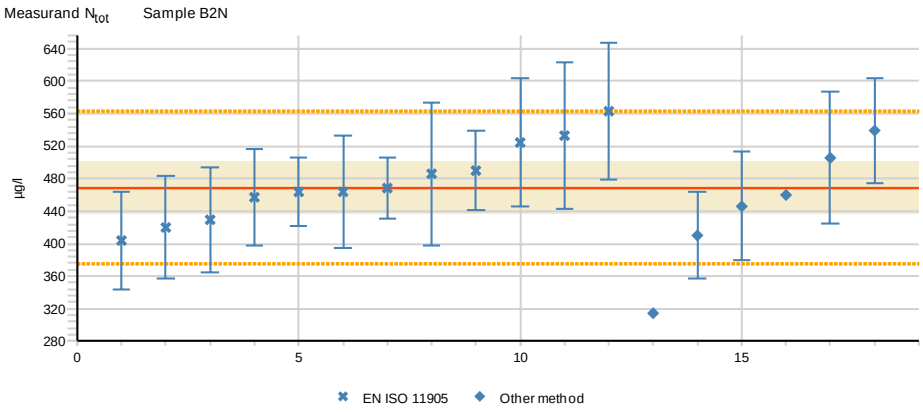

Measurand N_{NH4} Sample N3N
µg/l
101
93
85
77
69
61
53
45
0
5
10
15
20
EN ISO 11732, Automatic (CFA, FIA) indophenol blue method
SFS 3032, Manual indophenol blue method
Salicylate method, Aquachem application
Other method

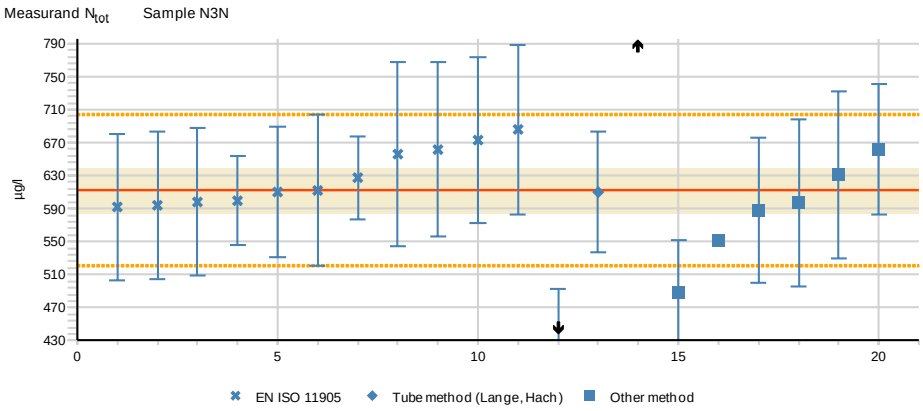

Measurand $N_{NO2+NO3}$
Sample A1N
µg/l
240
230
220
210
200
190
180
0
5
10
15
20
25
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
Spectrophotometric sulfanilamide method using Cd/Cu-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method


Measurand $N_{NO2+NO3}$
Sample B2N
µg/l
250
240
230
220
210
200
190
180
170
160
150
140
0
5
10
15
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
Spectrophotometric sulfanilamide method using Cd/Cu-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method

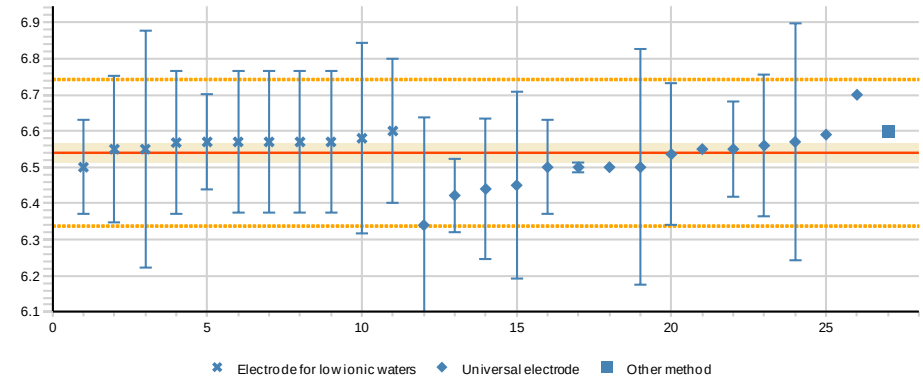

Measurand $N_{NO2+NO3}$
Sample N3N
µg/l
370
360
350
340
330
320
310
300
290
280
270
0
5
10
15
20
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
Spectrophotometric sulfanilamide method using Cd/Cu-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method


Measurand N_{tot}
Sample A1N
µg/l
400
380
360
340
320
300
280
260
240
220
0
5
10
15
20
EN ISO 11905
Tube method (Lange, Hach)
Other method

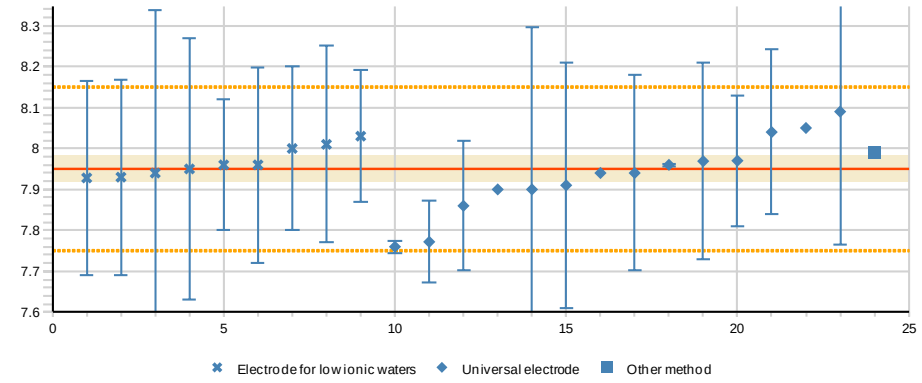

Measurand N_{tot}
Sample B2N
µg/l
640
600
560
520
480
440
400
360
320
280
0
5
10
15
EN ISO 11905
Other method


Measurand N_{tot}
Sample N3N
µg/l
790
750
710
670
630
590
550
510
470
430
0
5
10
15
20
EN ISO 11905
Tube method (Lange, Hach)
Other method

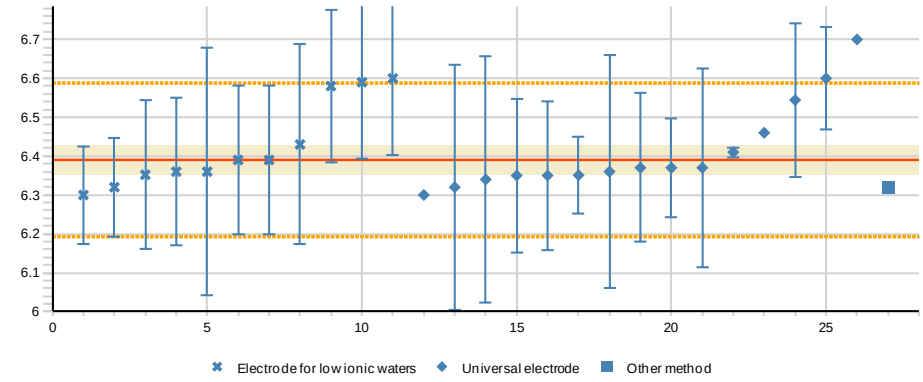
Measurand pH Sample A1H

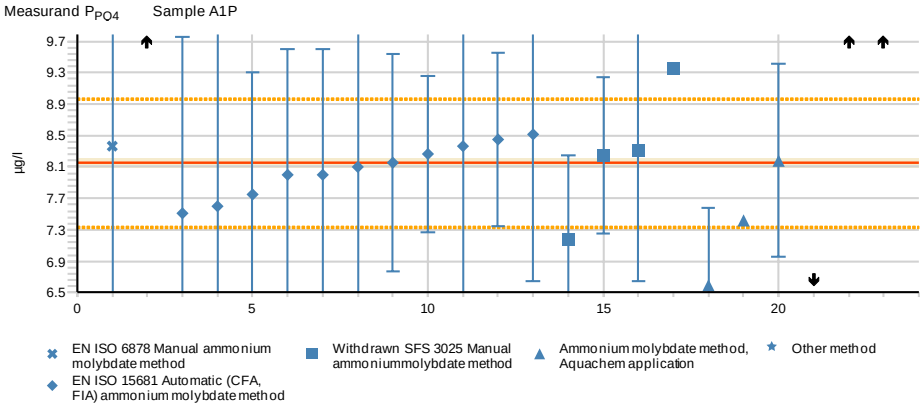


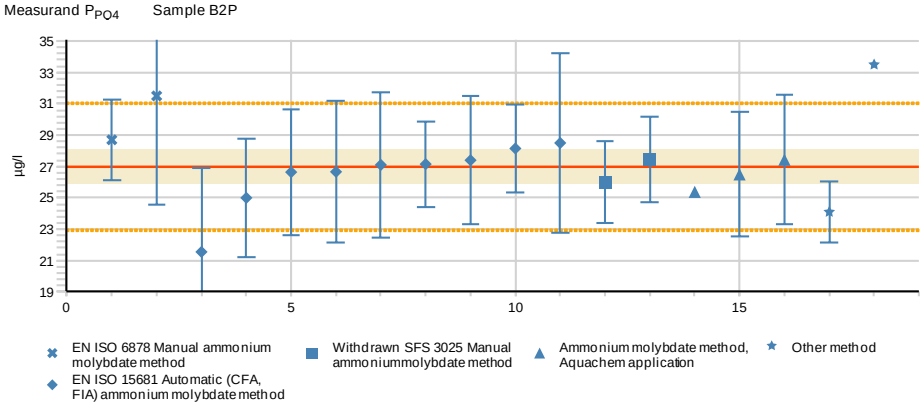
Measurand pH Sample B2H

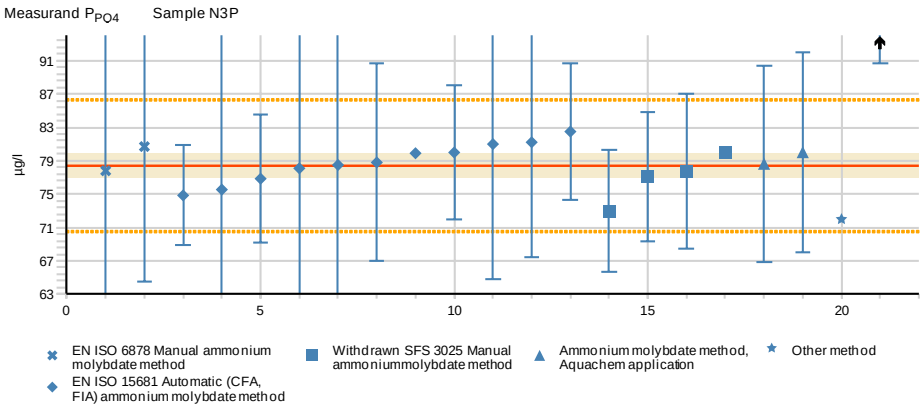


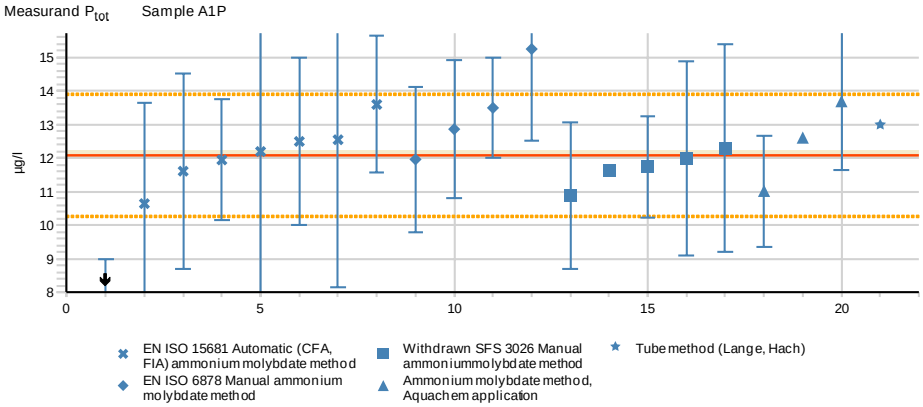
Measurand pH Sample N3H

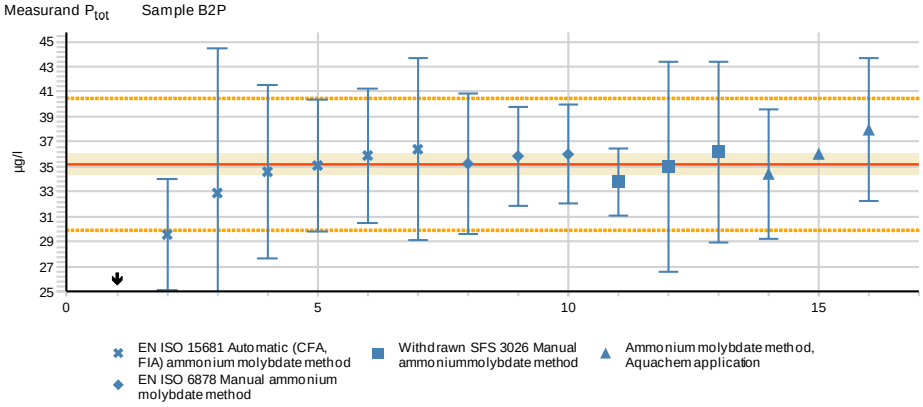


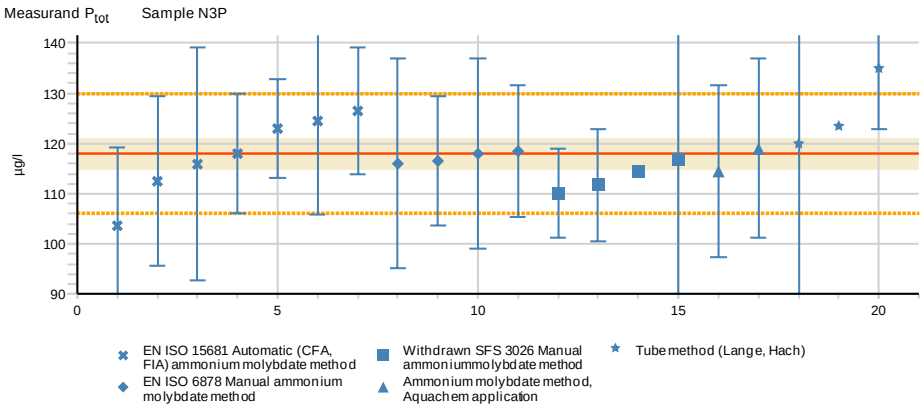

Measurand P_{PO4} Sample A1P
µg/l
9.7
9.3
8.9
8.5
8.1
7.7
7.3
6.9
6.5
0
5
10
15
20
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
Other method
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method

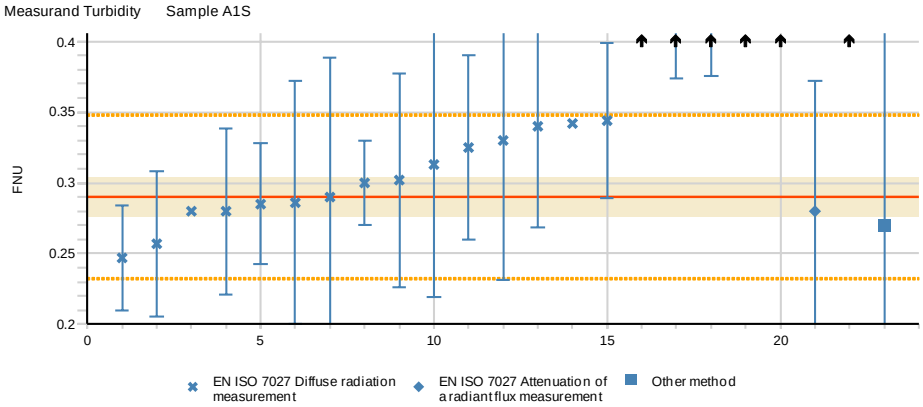

Measurand P_{PO4} Sample B2P
µg/l
35
33
31
29
27
25
23
21
19
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
Other method
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method

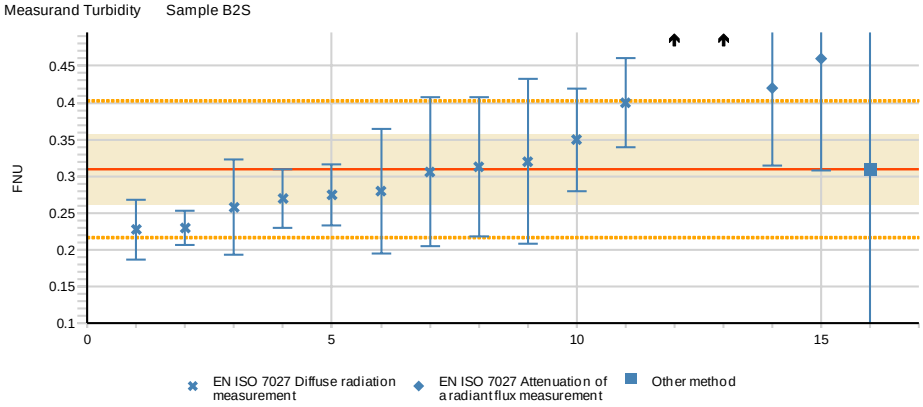

Measurand P_{PO4} Sample N3P
µg/l
91
87
83
79
75
71
67
63
0
5
10
15
20
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
Other method
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method

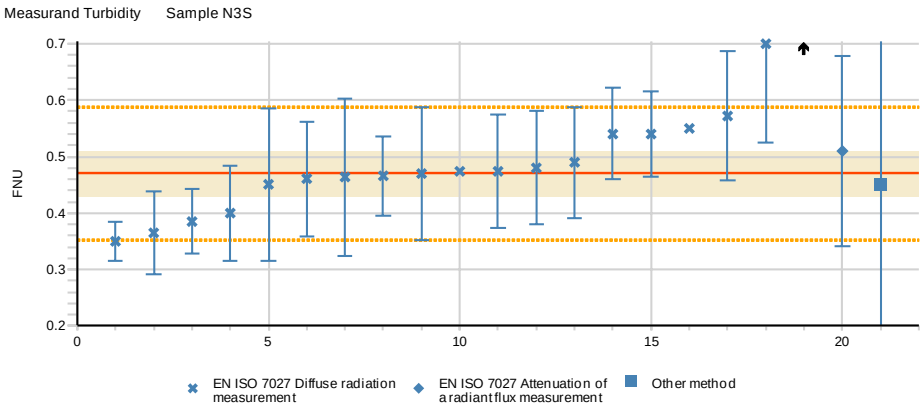

Measurand P_{tot} Sample A1P
µg/l
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Tube method (Lange, Hach)
EN ISO 6878 Manual ammonium molybdate method
Ammonium molybdate method, Aquachem application


Measurand P_{tot} Sample B2P
µg/l
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 6878 Manual ammonium molybdate method


Measurand P_{tot} Sample N3P
µg/l
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Tube method (Lange, Hach)
EN ISO 6878 Manual ammonium molybdate method
Ammonium molybdate method, Aquachem application

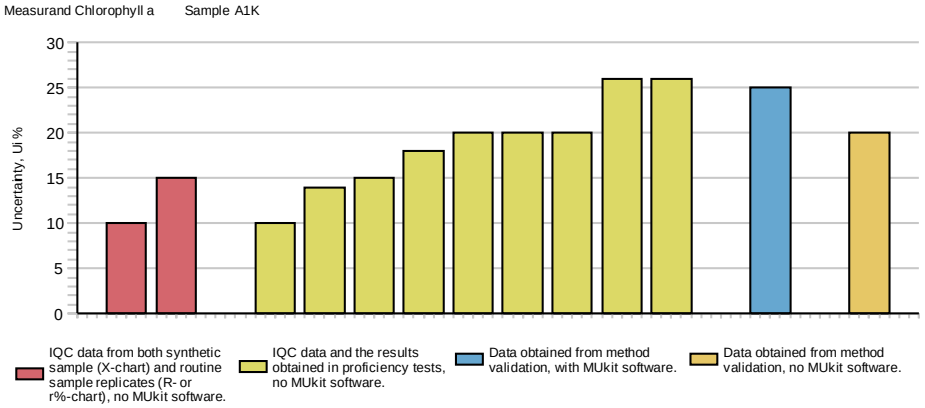

Measurand Turbidity Sample A1S
FNU
0.4
0.35
0.3
0.25
0.2
0
5
10
15
20
EN ISO 7027 Diffuse radiation measurement
EN ISO 7027 Attenuation of a radiant flux measurement
Other method

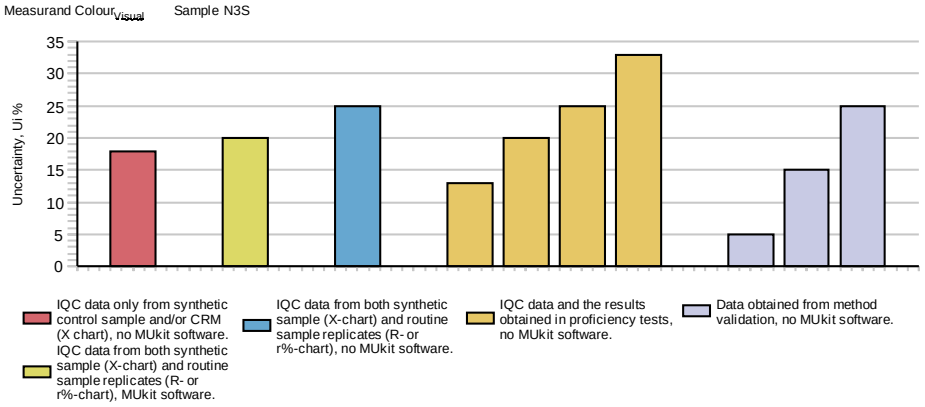

Measurand Turbidity Sample B2S
FNU
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0
5
10
15
EN ISO 7027 Diffuse radiation measurement
EN ISO 7027 Attenuation of a radiant flux measurement
Other method

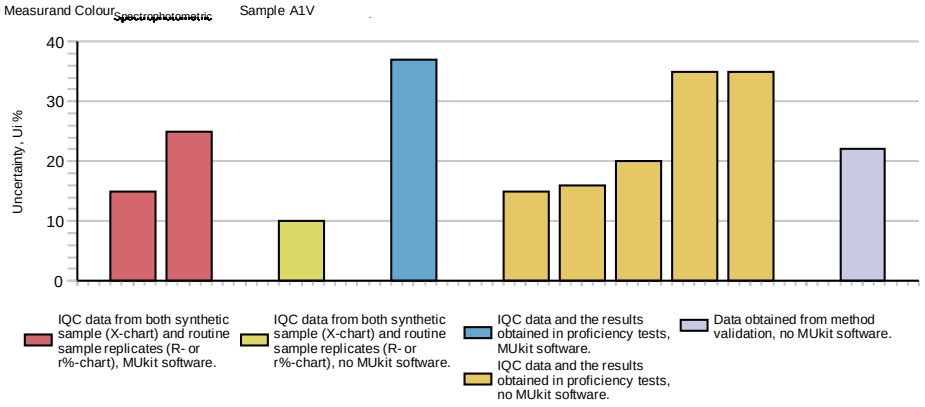

Measurand Turbidity Sample N3S
FNU
0.7
0.6
0.5
0.4
0.3
0.2
0
5
10
15
20
EN ISO 7027 Diffuse radiation measurement
EN ISO 7027 Attenuation of a radiant flux measurement
Other method

APPENDIX 13: Examples of measurement uncertainties reported by the participants

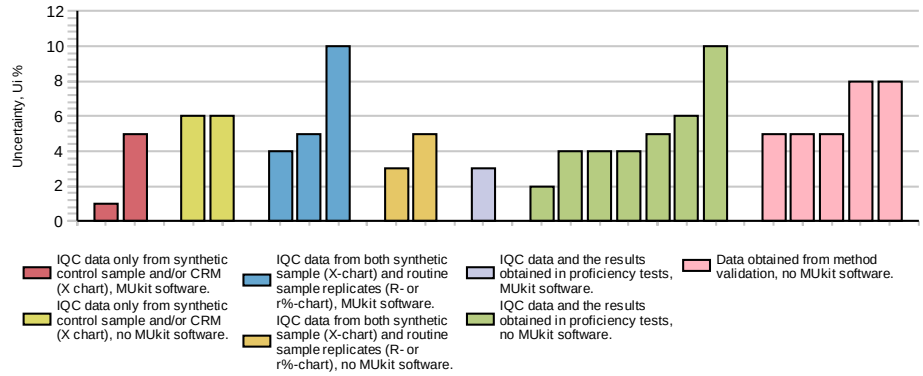
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [9, 10].



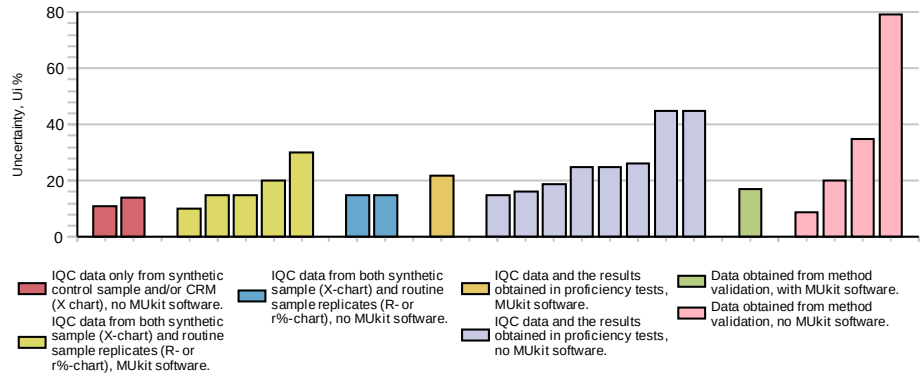




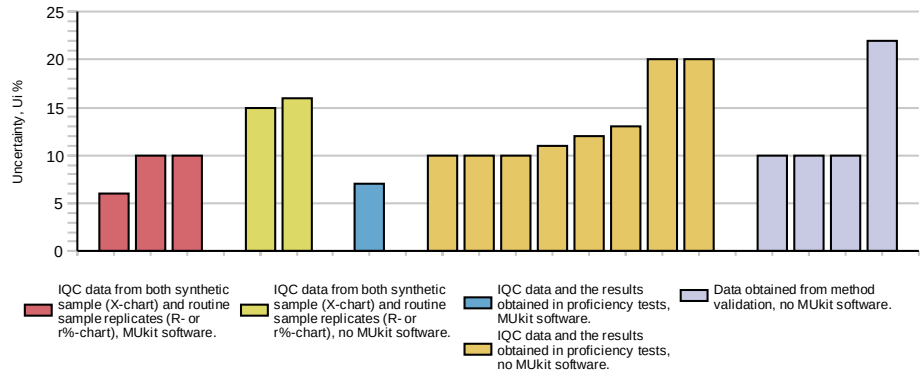
Measurand Conductivity 25 Sample N3H



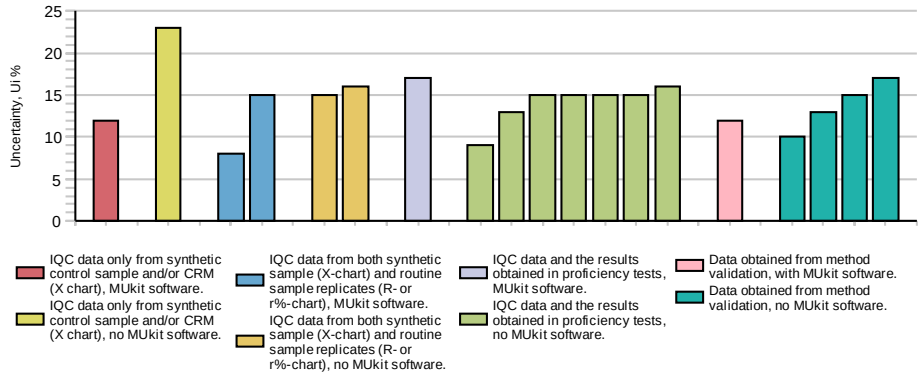
Measurand N_{NH4} Sample A1N



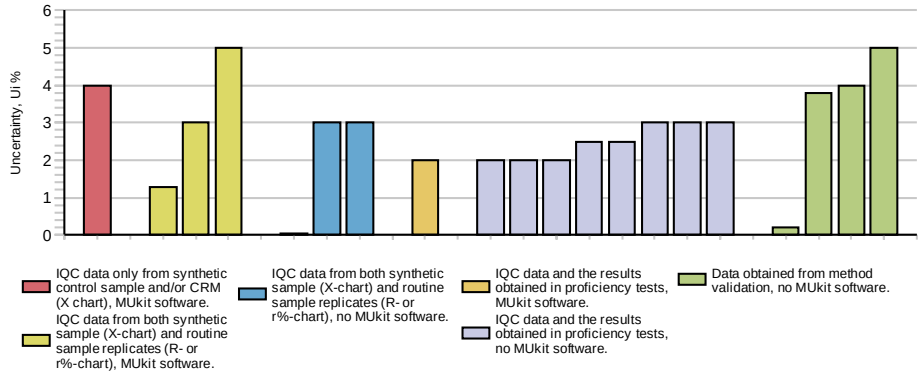
Measurand $N_{NO2+NO3}$ Sample B2N



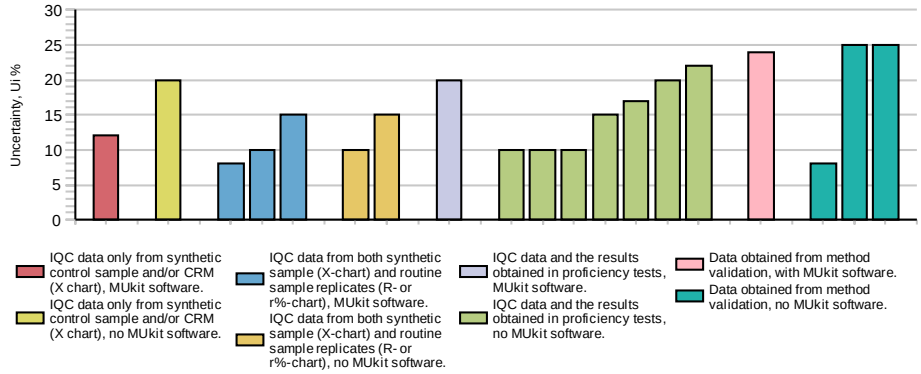
Measurand N_{tot} Sample N3N

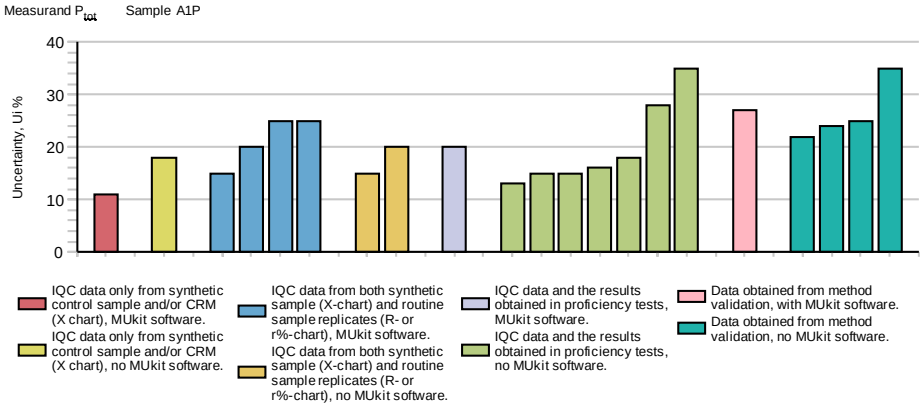


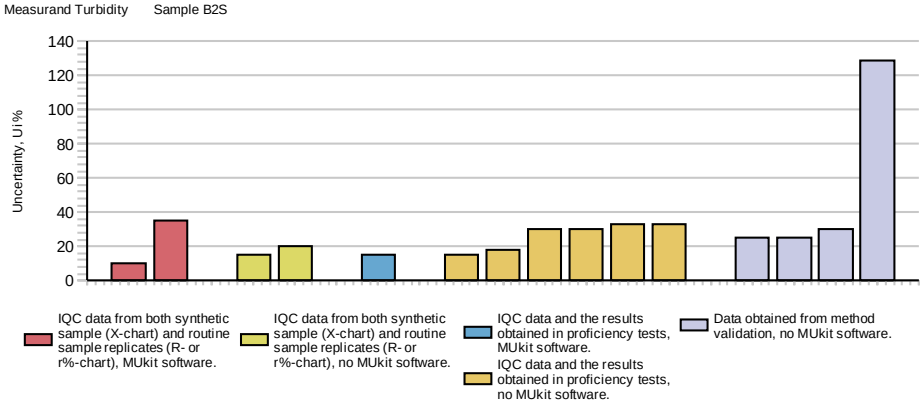
Measurand pH Sample B2H



Measurand P_{PO4} Sample N3P




Measurand P_{tot} Sample A1P
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
Data obtained from method validation, with MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand Turbidity Sample B2S
Uncertainty, Ui %
140
120
100
80
60
40
20
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

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