REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 11 | 2018

Interlaboratory Proficiency Test 03/2018

Alkalinity, pH, nutrients and conductivity in natural waters

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

Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 11 | 2018

Interlaboratory Proficiency Test 03/2018

Alkalinity, pH, nutrients and conductivity in natural waters

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

Proftest
SYKE

FINAS
Finnish Accreditation Service
PT01 (EN ISO/IEC 17043)

Helsinki 2018
Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 11 | 2018
Finnish Environment Institute SYKE
Proftest SYKE

Layout: Markku Ilmakunnas

The publication is also available in the Internet: www.syke.fi/publication | helda.helsinki.fi/syke

ISBN 978-952-11-4927-6 (pbk.)
ISBN 978-952-11-4928-3 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)

Author(s): Mirja Leivuori, Riitta Koivikko, Mika Sarkkinen, Keijo Tervonen, Sari Lanteri,
Ritva Väisänen and Markku Ilmakunnas

Publisher and financier of publication: Finnish Environment Institute (SYKE)
P.O. Box 140, FI-00251 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2018

SYKE

ABSTRACT

Interlaboratory Proficiency Test 03/2018

Proftest SYKE carried out the proficiency test for the determination of alkalinity, nutrients, pH and conductivity in natural waters in February 2018. In total, 30 participants joined in the proficiency test.

The calculated concentration, the robust mean or the median of the results reported by the participants was chosen to be the assigned value for the measurands. The performance of the participants was evaluated by using z scores. In this proficiency test 85 % of the results were satisfactory when deviation of 0.2 pH units (for pH determination) and 5–20 % (for other determinations) from the assigned value was accepted.
Warm thanks to all the participants of this proficiency test!

Keywords: water analysis, alkalinity, nutrients, pH, conductivity, water and environmental laboratories, proficiency test, interlaboratory comparisons, Proftest

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 03/2018

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen helmikuussa 2018. Pätevyyskokeessa määritettiin alkaliniteetti, pH, ravinteet ja sähkönjohtavuus luonnonvesistä. Pätevyyskokeeseen osallistujia oli 30.

Testisuureen vertailuarvona käytettiin teoreettista (laskennallista) pitoisuutta, osallistujien tulosten robustia keskiarvoa tai mediaania. Tulosten arviointi tehtiin z-arvon perusteella, jolloin pH-määrityksessä sallittiin 0,2 pH-yksikön ja muissa määrityksissä 5–20 %:n poikkeama vertailuarvosta. Koko aineistossa hyväksyttäviä tuloksia oli 85 %.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, alkaliniteetti, N_{NH4}, $N_{NO3+NO2}$, N_{tot}, P_{PO4}, P_{tot}, pH, sähkönjohtavuus, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus, Proftest

SAMMANDRAG

Provningsjämförelse 03/2018

Under februari 2018 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av alkalinitet, näringsämnen, pH och ledningsförmåga i naturvatten. Proven sändes ut till 30 deltagarna.

Som referensvärde av analytens koncentration användes det teoretiska värdet, robust medelvärdet eller median av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. Resultatet var tillfredsställande, om det devierade mindre än 0,2 pH enhet eller 5–20% från referensvårdet. I denna jämförelse var 85 % av alla resultaten tillfredsställande.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, alkalinitet, näringsämnen, pH, ledningsförmåga, provningsjämförelse, vatten- och miljölaboratorier, Proftest

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT, NW 03/2018) for analysis of alkalinity, conductivity, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, $P_{tot,}$ $P_{PO4,\ dissolved}$, $P_{tot,\ dissolved}$, and pH in natural waters in February 2018. A total of 30 participants took part in the PT. 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. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it 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 guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, https://www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer:

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4 (formerly Hakuninmaantie 6), FI-00430 Helsinki, Finland
Phone: +358 295 251 000
E-mail: proftest@environment.fi

The responsibilities in organizing the proficiency test were as follows:

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

2.2 Participants

In total 30 laboratories participated in this proficiency test, 27 from Finland and 3 from abroad (Appendix 1). Altogether 77 % 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/sites/en) has the code 21 (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 alkalinity, conductivity, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, $P_{tot,}$ $P_{PO4,\ dissolved}$, $P_{tot,\ dissolved}$, and pH.

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 analyzing P_{PO4}, N_{NH4} or conductivity for phosphoric, nitrogen, and other compounds, respectively. According to the test results all used vessels fulfilled the purity requirements.

The synthetic samples were mainly prepared by diluting from reagents produced by Merck or by BDH Prolab. The synthetic samples A1A, A1N and A1P for alkalinity, ammonium nitrogen (N_{NH4}), nitrate+nitrite nitrogen ($N_{NO2+NO3}$), total nitrogen (N_{tot}) and phosphate phosphorus (P_{PO4}) analysis were prepared from the NIST traceable reference solutions. Brackish water was collected from the coastal area of the Gulf of Finland, in front of Porvoo. The lake water sample was collected from the Lake Lohjanjärvi. The sample preparation is described in details in the Appendix 2.

The samples were delivered to the participants latest on 13 February 2018 and they mainly arrived to the participants on the next day.

The samples were requested to be measured as follows:

alkalinity	15.2.2018
pH, conductivity	15.2.2018
N_{NH4}, $N_{NO2+NO3}$, P_{PO4}, $P_{PO4,\ dissolved}$	15.2.2018
N_{tot}, $P_{tot,}$ $P_{tot,\ dissolved}$	not later than 26.2.2018

The results were mainly reported latest on 27 February 2018 as requested. One participant reported the results two days later. The preliminary results were delivered to the participants on 5 February 2018.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing alkalinity, N_{NH4}, N_{tot}, $P_{tot,}$ and pH. More 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 pH, N_{NH4}, and P_{PO4} from the samples stored at the room temperature for one day. The measurement values were checked against the results of the samples stored at 4 °C. According to the test all samples were considered as stable.

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 the control sample was mainly ≤ 12 °C, and only one participant reported higher temperature. It is crucial to measure the temperature of the control sample rather soon after the sample package has arrived, especially when the package is not stored in refrigerator after the arrival. The warming of samples was taken into account, when needed, in the evaluation of results.

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 their results reporting and the background information of one assigned value. The comment from the provider focused to the missing sample arrival documents. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results which differed more than s_{rob} × 5 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.

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

2.6.2 Assigned values

The assigned values and their uncertainties are presented in Appendix 6. Mainly the NIST traceable calculated concentrations were used as the assigned values for the synthetic samples of alkalinity, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, and P_{tot} (not NIST traceable). For the calculated assigned values the expanded measurement uncertainty (k=2) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

For the other samples and measurements the robust mean or the median (n(stat)<12, $P_{tot,\ dissolved}$, N5P) of the results reported by the participants was used as the assigned value. The uncertainty of the assigned value was calculated using the robust standard deviation or standard deviation

of the reported results [2, 4]. The assigned values based on the robust mean or median are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values. The reliability of the assigned value was statistically tested [2, 3].

The uncertainty of the calculated assigned values was less than 1 %. When using the robust mean or the median of the participant results as the assigned value, the uncertainties of the assigned values varied between 0.4 % and 6.4 % (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's 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 for pH and to 5–20 % 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 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 [2, 3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability 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 of the reported results (s_{rob}) [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was mainly fulfilled.

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

Sample	Measurand
B2N	N_{NH4}[1]
N3N	N_{NH4}[1,2]
B2P	P_{PO4}[1]
N3P	P_{PO4}[1]
N5P	$P_{PO4, dissolved}$[1,2]
B4P	$P_{tot, dissolved}$[1,2]
N5P	$P_{tot, dissolved}$[1,2]

3 Results and conclusions

3.1 Results

The terms in the results table are explained in the 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 deviations of the results varied from 1.2 to 17.6 % (Table 1).The robust standard deviation was lower than 5 % for 39 % of the results and lower than 10 % for 79 % of the results (Table 1). The robust standard deviations were somewhat higher than in the previous similar proficiency test NW 03/2016, where the deviations varied from 0.8 % to 10.7 % [5].

Table 1. The summary of the results in the proficiency test NW 03/2018.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n (all)	Acc z %
Alkalinity	A1A	mmol/l	0.11	0.11	0.11	0.11	0.01	5.1	7.5	20	80
	B2A	mmol/l	1.36	1.36	1.36	1.36	0.04	2.6	7.5	16	100
	N3A	mmol/l	0.51	0.51	0.50	0.50	0.02	4.3	7.5	20	95
Conductivity 25	A1J	mS/m	3.52	3.52	3.52	3.51	0.06	1.8	5	24	92
	B2H	mS/m	850	850	850	853	14	1.7	5	19	84
	N3H	mS/m	10.2	10.2	10.2	10.2	0.1	1.3	5	23	87
N_{NH4}	A1N	µg/l	15.5	17.1	17.9	17.0	3.2	17.6	20	23	59
	B2N	µg/l	22.1	22.1	22.1	22.9	2.7	12.3	25	19	68
	N3N	µg/l	109	109	109	108	11	10.2	15	22	91
$N_{NO2+NO3}$	A1N	µg/l	136	136	136	135	9	7.0	10	22	77
	B2N	µg/l	138	138	138	137	6	4.2	10	20	80
	N3N	µg/l	478	479	478	472	23	4.9	10	21	95
N_{tot}	A1N	µg/l	304	293	293	294	15	5.0	10	21	81
	B2N	µg/l	423	424	423	430	35	8.2	15	20	85
	N3N	µg/l	1042	1042	1042	1047	30	2.9	10	21	90
pH	A1H		6.55	6.56	6.55	6.56	0.04	0.6	3.1	26	100
	B2H		7.89	7.90	7.89	7.90	0.05	0.6	2.5	22	100
	N3H		7.40	7.39	7.40	7.40	0.09	1.2	2.7	24	83
P_{PO4}	A1P	µg/l	6.52	6.14	6.19	6.30	0.86	13.9	15	19	74
	B2P	µg/l	24.4	24.3	24.4	24.6	1.5	6.0	10	18	89
	N3P	µg/l	19.4	19.3	19.4	19.1	1.7	8.6	15	18	89
$P_{PO4, dissolved}$	B4P	µg/l	24.4	24.2	24.4	24.2	1.8	7.3	15	14	93
	N5P	µg/l	16.4	16.4	16.4	16.3	2.6	15.6	20	15	87
P_{tot}	A1P	µg/l	11.8	11.5	11.6	11.8	1.0	8.7	10	21	67
	B2P	µg/l	31.1	31.2	31.1	31.0	2.4	7.9	15	20	95
	N3P	µg/l	37.7	37.6	37.7	38.3	1.9	5.2	15	20	90
$P_{tot, dissolved}$	B4P	µg/l	30.1	30.1	30.1	30.3	3.0	9.9	15	14	79
	N5P	µg/l	32	32.0	32.0	32.0	5.5	17.2	20	15	60

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

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.

Alkalinity

Total alkalinity was measured using titration with two or more end points by 11-13 participants, depending on the sample type. Only from two to five participants reported alkalinity results based on one end point titration depending on the sample type (Appendix 12). Three participants reported the use of other methods. These were internal methods and one participant used the standard ASTM D1067-16. There were no statistical significant differences between potentiometric titration HCl to pH values 4.2 and 4.5 (EN-ISO 9963-1) with the Gran alkalinity method. Based on visual evaluation of the results the titration method to pH value 4.5 gave somewhat higher results than the titration method to two end points and three participants from four gained z score above 2 for the synthetic sample A1A (Appendix 12).

Conductivity

Conductivity was measured by 20 participants according to the standard method EN 27888 and one participant used other method (ASTM 1125-14, Appendix 12).

Ammonium nitrogen, N_{NH4}

Most participants (43 %) determined ammonium nitrogen using the standard method SFS 3032 (manual indophenol blue spectrophotometric method) and 23 % of the participants used the corresponding automatic standard method EN ISO 11732. Depending on the sample, two to three participants used the spectrophotometric salicylate method modified for Aquachem technique and 3–6 participants used some other method, for example based on SFS-EN ISO 14911 or ISO 7150 (Appendix 12). In the statistical comparison between the methods no statistically significant differences were observed.

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

Nitrate+nitrite nitrogen was determined using several methods. In average ca. 68 % of the participants used the standard method EN ISO 13395. The standard method 3030, the standard method EN ISO 10304, and the sulfanilamide spectrophotometric method after hydrazine reduction modified for Aquachem technique were used by 1 to 2 participants depending on the sample (Appendix 12). Other method was used by 1 to 2 participants depending on the sample. In the statistical comparison between the methods no statistically significant differences were observed.

Total nitrogen, N_{tot}

Most participants (67 %) determined total nitrogen according to the standard method EN ISO 11905. Depending of the sample from 6 to 7 participants used other method, for

example based on standards SFS 3031, ISO 29441 or SFS-EN 12260 (Appendix 12). In the statistical method comparison no significant differences were observed between the methods.

pH

Approximately 54 % of the participants measured pH using universal electrode and 35 % of the participants used an electrode for low ionic waters. A specific other electrode was used by one or three participants depending of the sample (Appendix 12). In the statistical method comparison significant differences were observed between the universal pH electrode (mean±sd, 6.55±0.03) and the electrode for low ionic waters (6.57±0.02) for the synthetic sample A1H. The number of results is quite low for the statistical comparison, and the noticed difference is within the analytical error.

Phosphate phosphorus, P_{PO4}

Approximately 51 % of the participants determined phosphate phosphorus using the standard method EN ISO 15681 (Automatic (CFA, FIA) ammonium molybdate method). Two to three participants used the withdrawn Finnish standard method 3025 depending on the sample. The ammonium molybdate spectrophotometric method modified for Aquachem technique was used by 24 % of the participants, in average. Two participants used the standard method EN ISO 6878 (manual spectrophotometric method, Appendix 12). In the statistical method comparison no significant differences were observed between the methods.

Total phosphorus, P_{tot}

Approximately 46 % of the participants determined total phosphorus using the standard method EN ISO 15681. Three participants used the withdrawn standard method SFS 3026. The manual standard method EN ISO 6878 was used by four participants. Ammonium molybdate method modified for Aquachem technique was used by three or four participants depending on the sample (Appendix 12). Based on the visual estimation between the methods no clear differences were observed.

Dissolved phosphorus compounds, $P_{PO4,\ dissolved}$, $P_{tot,\ dissolved}$

The share of used analytical methods for dissolved phosphorus compounds were almost similar than for the non-filtered samples (Appendix 12). Based on the visual estimation between the methods no clear differences were observed.

Noticeable is that for the sample N5P the deviation of dissolved phosphorus compounds' results was higher than in the previous similar kind of proficiency test NW 03/2016, and thus the standard deviation for proficiency assessment increased from 15 % to 20 % in the present proficiency test [5]. One reason for the variation can be the used filter and its pore size in the sample preparation. The national quality recommendations for data entered into water quality registers have been published in Finland, in order to promote the enhancement of environmental measurements' quality standards and traceability [6]. There the recommendation is to use Nuclepore polycarbonate filter 0.4 µm for pretreatment of water samples for dissolved nutrients. In the future PT, the provider will consider to collect the information of the used filter type for dissolved nutrients determination.

3.3 Uncertainties of the results

About 71 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 2, Appendix 13). The range of the reported uncertainties varied between the measurements and the sample types. Expanded measurement uncertainty below 5 % is not common for routine laboratories. Also measurement uncertainty over 50 % should not exist, unless the measured concentration is near to the limit of quantification.

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data entered into water quality registers have been published in Finland [6]. The recommendations for measurement uncertainties for most of the tested measurands in natural waters are from 5 % to 15 % and for pH 0.2 pH unit. In this proficiency test some of participants had their measurement uncertainties within these limits, while some did not achieve them. Nevertheless, harmonization of the uncertainties estimation should be continued.

Several approaches were used for estimating of measurement uncertainty (Appendix 13). The most used approaches were based on the internal quality control (IQC) data from synthetic samples with routine sample replicates and IQC data with the results obtained in proficiency tests. At maximum nine participants used MUkit measurement uncertainty software for the estimation of their uncertainties. The free software is available on the webpage: www.syke.fi/envical/en [7]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 2. The range of the expanded measurement uncertainties (k=2, U_i%)) reported by the participants and recommendations for natural waters [6].

Measurand/ Water type	Synthetic, U_i%	Brackish, U_i%	Lake, U_i%	Recommendation, U%
Alkalinity	1.66-47	2-15	5-22	10
Conductivity 25	0.54-20	2-10	2-10	5
N_{NH4}	9-75	9-38	9-22	15
$N_{NO2+NO3}$	4-20	4-20	4-20	15
N_{tot}	6-22	6-20	6-17	15
pH	0.33-5	2-5	2-5	0.2 pH unit
P_{PO4}	10-43	10-25	10-25	15
$P_{PO4, dissolved}$	-	10-25	10-25	15
P_{tot}	9-35	9-23	9-23	15
$P_{tot, dissolved}$	-	9-22	9-22	15

4 Evaluation of the results

The evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for 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 (for pH) and 5–20 % (for the other measurands) from the assigned values was accepted (Appendix 10). Altogether 77 % of the participants used accredited analytical methods at least for a part of the measurements and 87 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar proficiency test NW 03/2016, the performance was satisfactory for 88 % of the all participants when deviation of 0.2 pH units for pH and for the others 5–15 % from the assigned values was accepted [5]. All samples passed the stability test and, thus, no estimation was needed for the effect of increased temperature during the sample transportation.

Table 3. Summary of the performance evaluation in the proficiency test NW 03/2018.

Measurand	2 × s_{pt}, %	Satisfactory results, %	Assessment
Alkalinity	7.5	92	Good performance. In the PT NW 03/16 83 % of the results were satisfactory [5].
Conductivity 25	5	88	In the PTs NW 03/16 and NW 02/17 90 % of the results were satisfactory [5, 8].
N_{NH4}	15–25	73	Some difficulties in the measurements of samples A1N and B2N, < 80 % of the satisfactory results. The evaluation for the samples B2N and N3N is only approximate due to high variation in the results. In the PT NW 03/16 85 % of the results were satisfactory when deviation of 15 % from the assigned value was accepted [5]. In the PT NW 02/17 66 % of the results were satisfactory when deviation of 20-30 % from the assigned value was accepted [8].
$N_{NO2+NO3}$	10	84	Some difficulties in the measurements of sample A1N, < 80 % of the satisfactory results. In the PT NW 03/16 87 % of the results were satisfactory [5]. In the PT NW 02/17 85 % of the results were satisfactory when deviation of 8-10 % from the assigned value was accepted [8].
N_{tot}	10–15	85	In the PT NW 03/16 93 % of the results were satisfactory when deviation of 10 % from the assigned value was accepted [5]. In the PT NW 02/17 89 % of the results were satisfactory [8].
pH	2.5–3.1	94	Good performance. In the PT NW 03/16 the performance was satisfactory for 99 % of the results were satisfactory when deviation of 2.5–2.7 % from the assigned value was accepted [5]. In the PT NW 02/17 88 % of the results were satisfactory when deviation of 2.6–4.5 % from the assigned value was accepted [8].
P_{PO4}	10–15	84	Some difficulties in the measurements of sample A1P, < 80 % of the satisfactory results. The evaluation for the samples B2P and N3P is only approximate due to high variation in the results. In the PT NW 03/16 83 % of the results were satisfactory [5]. In the PT NW 02/17 70 % of the results were satisfactory when deviation of 10–20 % from the assigned value was accepted [8].
$P_{PO4, dissolved}$	15–20	90	The evaluation for the samples B4P and N5P is only approximate due to variability in the results. In the PT NW 03/16 88 % of the results were satisfactory when deviation of 15 % from the assigned value was accepted [5].
P_{tot}	10–15	84	Some difficulties in the measurements of sample A1P, < 80 % of the satisfactory results. In the PT NW 03/16 81 % of the results were satisfactory [5]. In the PT NW 02/17 83 % of the results were satisfactory when deviation of 15 % from the assigned value was accepted [8].
$P_{tot, dissolved}$	15–20	69	Some difficulties in the measurements of samples B4P and N5P, < 80 % of the satisfactory results. The evaluation for the samples B4P and N5P is only approximate due to high variation in the results. In the PT NW 03/16 87 % of the results were satisfactory when deviation of 15 % from the assigned value was accepted [5].

5 Summary

The Proftest SYKE carried out the proficiency test (PT) for analysis of alkalinity, conductivity, N_{NH4}, $N_{NO2+NO3}$, N_{tot}, P_{PO4}, $P_{tot,}$ $P_{PO4,\ dissolved}$, $P_{tot,\ dissolved}$, and pH in natural waters in February 2018. One synthetic sample, one river water sample and one brackish water sample were distributed. In total, 30 participants joined in this PT.

The theoretical concentration, the robust mean or 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 generally lower than 1 % for the calculated assigned values and for assigned values based on the robust mean or the median it was between 0.4–6.4 %.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for 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 unit in the pH determinations and 5–20 % in the other determinations.

6 Summary in Finnish

Proftest SYKE järjesti luonnonvesiä analysoiville laboratorioille pätevyyskokeen helmikuussa 2018. Pätevyyskokeessa määritettiin alkaliniteetti, ravinteet ja sähkönjohtavuus synteettisistä näytteistä, rannikko- ja järvivedestä. Pätevyyskokeeseen osallistui yhteensä 30 laboratoriota.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa tai mediaania. Vertailuarvolle laskettiin mittausepävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli alle 1 % laskennallista pitoisuutta vertailuarvona käytettäessä ja muilla välillä 0.4–6.4 %.

Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta pH-määrityksessä 0.2 pH-yksikköä ja muissa määrityksissä 5–20 %. Koko aineistossa hyväksyttäviä tuloksia oli 85 %.

REFERENCES

1. SFS-EN ISO 17043, 2010. Conformity assessment – General requirements for Proficiency Testing.

2. ISO 13528, 2015. Statistical methods for use in proficiency testing by interlaboratory comparisons.

3. Thompson, M., Ellison, S. L. R., Wood, R., 2006. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC Technical report). Pure Appl. Chem. 78: 145-196, www.iupac.org.

4. Proftest SYKE Guide for laboratories: www.syke.fi/proftest/en → Running proficiency test www.syke.fi/download/noname/%7B3FFB2F05-9363-4208-9265-1E2CE936D48C%7D/39886.

5. Leivuori, M., Koivikko, R., Näykki, T., Tervonen, K., Lanteri, S, Väisänen, R. and Ilmakunnas, M. 2016. Interlaboratory proficiency test 03/2016. Alkalinity, pH, nutrients and conductivity in natural waters. Reports of Finnish Environment Institute 18/2016. 74 pp. http://hdl.handle.net/10138/161390.

6. Näykki, T. and Väisänen, T. (Eds.) 2016. Laatusuositukset ympäristöhallinnon vedenlaaturekistereihin vietävälle tiedolle: Vesistä tehtävien analyyttien määritysrajat, mittausepävarmuudet sekä säilytysajat ja –tavat. - 2. uudistettu painos. (Quality recommendations for data entered into the environmental administration's water quality registers: Quantification limits, measurement uncertainties, strorage times and methods associated with analytes determined from waters). Suomen ympäristökeskuksen raportteja 22/2016. 57 pp. (In Finnish). http://hdl.handle.net/10138/163532.

7. Näykki, T., Virtanen, A. and Leito, I., 2012. Software support for the Nordtest method of measurement uncertainty evaluation. Accred. Qual. Assur. 17: 603-612. Mukit website: www.syke.fi/envical.

8. Leivuori, M., Koivikko, R., Sarkkinen, M., Tervonen, K., Lanteri, S, Väisänen, R. and Ilmakunnas, M. 2017. Interlaboratory proficiency test 02/2017. Chlorophyll *a*, colour, conductivity, nutrients, pH and turbidity in natural waters. Reports of Finnish Environment Institute 14/2017. 86 pp. http://hdl.handle.net/10138/185256.

9. Magnusson B., Näykki T., Hovind H., Krysell M., Sahlin E., 2017. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. Nordtest Report TR 537 (ed. 4). www.nordtest.info.

APPENDIX 1: Participants in the proficiency test

Country	Institute
Finland	Eurofins Ahma Oy Seinäjoki
	Eurofins Ahma Oy, Rovaniemi
	Eurofins Environment Testing Finland Oy, Lahti
	Eurofins Nab Labs Oy Jyväskylä
	Eurofins/Nab Labs Oy Kokkolan yksikkö
	HSY Käyttölaboratorio Pitkäkoski Helsinki
	HY, Tvärminnen eläintieteellinen asema, Hanko
	HY/Ympäristötieteidenlaitos/Almalab
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötukimus Oy, Turku
	Luonnonvarakeskus, Viikki B2-laboratorio
	Länsi-Uudenmaan vesi ja ympäristö ry, Lohja
	MetropoliLab Oy
	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
	SGS Finland Oy, Kotka
	SYKE Oulun toimipaikka
	SYKE/Merikeskus
	SYNLAB Analytics & Services Finland Oy
	Teollisuuden Voima Oyj
	Yara Suomi Oy, Uusikaupunki
	ÅMHM laboratoriet. Jomala. Åland
Kingdom of Saudi Arabia	Sedres Chemicals Solutions MFG. CO.
Sweden	ACES, Stockholm University
	Stockholm University, Department of Ecology, Environment and Plant Sciences

APPENDIX 2: Preparation of the samples

Measurand	Sample	Initial concentration	Addition (Dilution)	Assigned value
γ_{25} [µS/cm]	A1J	-	2.2 KCl	3.52
	B2H	850	-	850
	N3H	10	-	10.2
pH pH unit	A1H	-	pH 6.5 buffer solution	6.55
	B2H	7.7	-	7.89
	N3H	7.1	-	7.40
Alkalinity [mmol/l]	A1A	-	0.11 Na_2CO_3	0.11
	B2A	1.35	-	1.36
	N3A	0.51	-	0.51
$N_{NO2+NO3}$ [µg/l]	A1N	-	136 $NaNO_3$	136
	B2N	97	-	138
	N3N	420	-	478
N_{NH4} [µg/l]	A1N	-	15.5 NH_4Cl	15.5
	B2N	24	-	22.1
	N3N	< 2	78	109
N_{tot} [µg/l]	A1N	-	304 $NaNO_3$ + NH_4Cl + Na_2-EDTA	304
	B2N	408	-	423
	N3N	980	78	1042
P_{PO4} [µg/l]	A1P	-	6.5 KH_2PO_4	6.52
	B2P	23	-	24.4
	N3P	16	-	19.4
$P_{PO4, dissolved}$	A1P	-	-	-
	B4P	24	-	24.4
	N5P	15	-	16.4
P_{tot} [µg/l]	A1P	-	11.7 KH_2PO_4 + $C_3H_7Na_2O_6P$	11.8
	B2P	31	-	31.1
	N3P	37	-	37.7
$P_{tot, dissolved}$	A1P	-	-	-
	B4P	29	-	30.1
	N5P	37	-	32

First letter of the sample code indicates the sample matrix:

A = Synthetic sample

B = Brackish water

N = Natural water

APPENDIX 3: Homogeneity of the samples

The homogeneity was checked for the selected samples (6-8) and test items as duplicate measurements.

Criteria for homogeneity:

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

s_{pt} % = standard deviation for proficiency assessment
s_{anal} = analytical deviation, standard deviation of the results within 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 constant of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand/Sample	Concentration [µg/l,mmol/l, pH-unit]	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	21.8	6	12.5	2.72	0.51	0.19	Yes	0.85	1.93	Yes
N_{NH4}/N3N	102	6	7.5	7.62	0.84	0.11	Yes	8.42	12.8	Yes
N_{tot}/B2N	427	6	7.5	32.0	3.59	0.11	Yes	7.56	226	Yes
N_{tot}/N3N	1036	6	5	51.8	20.9	0.40	Yes	435	1276	Yes
pH/B2H	7.93	8	1.25	0.10	0.007	0.07	Yes	0.0002	0.002	Yes
pH/N3H	7.43	8	1.35	0.10	0.01	0.13	Yes	0.0003	0.002	Yes
P_{tot}/B2P	26.0	6	7.5	1.95	0.31	0.16	Yes	0.22	0.92	Yes
P_{tot}/N3P	24.9	6	7.5	2.62	0.47	0.18	Yes	0.71	1.74	Yes
Alkalinity/B2S	1.34	6	3.75	0.05	0.002	0.04	Yes	0	0.0005	Yes
Alkalinity/N3S	0.50	6	3.75	0.002	0.0009	0.05	Yes	0	0.0001	Yes

Conclusion: The criteria were fulfilled in the each case, and thus the samples could be regarded as homogenous.

APPENDIX 4: Stability of the samples

The samples were delivered on 9, 12 or 13 February 2018 and they arrived to the participants mainly on 14 February 2018. The samples were requested to be analysed as follows:

alkalinity	15 February 2018
pH, conductivity	15 February 2018
N_{NH4}, $N_{NO2+NO3}$, P_{PO4}, $P_{PO4,\ dissolved}$	15 February 2018
N_{tot}, P_{tot}, $P_{tot,\ dissolved}$	latest on 26 February 2018

Stability of 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

pH

Sample	Result		Sample	Result		Sample	Result	
Date	15.2. (20 °C)	15.2. (4 °C)	Date	15.2. (20 °C)	15.2. (4 °C)	Date	15.2. (20 °C)	15.2. (4 °C)
A1H	6.54	6.55	B2H	7.91	7.93	N3H	7.37	7.39
D	0.01		D	0.02		D	0.02	
0.3×s_{pt}	0.03		0.3×s_{pt}	0.03		0.3×s_{pt}	0.03	
	D<0.3 × s_{pt}? Yes			D<0.3 × s_{pt}? Yes			D<0.3 × s_{pt}? Yes	

N_{NH4}

Sample	Result [µg/l]		Sample	Result [µg/l]		Sample	Result [µg/l]	
Date	15.2. (20 °C)	15.2. (4 °C)	Date	15.2. (20 °C)	15.2. (4 °C)	Date	15.2. (20 °C)	15.2. (4 °C)
A1N	18.04	17.08	B2N	24.52	23.39	N3N	97.75	98.09
D	0.96		D	1.13		D	0.34	
0.3×s_{pt}	0.47		0.3×s_{pt}	0.83		0.3×s_{pt}	2.45	
	D<0.3 × s_{pt}? No[1)]			D<0.3 × s_{pt}? No[1)]			D<0.3 × s_{pt}? Yes	

P_{PO4}

Sample	Result [µg/l]		Sample	Result [µg/l]		Sample	Result [µg/l]	
Date	15.2. (20 °C)	15.2. (4 °C)	Date	15.2. (20 °C)	15.2. (4 °C)	Date	15.2. (20 °C)	15.2. (4 °C)
A1P	5.02	5.13	B2P	20.61	20.93	N3P	17.33	17.47
D	0.11		D	0.32		D	0.15	
0.3×s_{pt}	0.15		0.3×s_{pt}	0.37		0.3×s_{pt}	0.44	
	D <0.3 × s_{pt}? Yes			D <0.3 × s_{pt}? Yes			D <0.3 × s_{pt}? Yes	

[1)] The difference is within the analytic error

Conclusion: The criteria for stability mainly fulfilled. For N_{NH4} the noticed variation of results is within the analytical error. Thus the samples could be regarded as homogenous.

APPENDIX 5: Feedback from the proficiency test

Participant	Comments on technical excecution	Action / Proftest
30	The sample bottles for alkalinity were not totally full.	Based on the previous experience the possible air space in the sample bottle has not influenced to the alkalinity results.

Participant	Comments to the results	Action / Proftest
19	The pH result was not included in the preliminary results. Participant wondered if that was due to the missing Ui% in their results reporting.	The result of participant was included in the data set, but due to the missing measurement uncertainty value the comparison of z and zeta scores was not possible.
7	The participant asked the background information of the assigned value for N_{NH4} in the sample A1N as it differs from the mean and the median of the results.	The used assigned value is the calculated, NIST traceable concentration based on the sample preparation, and thus it can differ from the values calculated from the reported results.
2	After the delivery of the preliminary report the participant informed that they had used 0.4 µm filter for the $P_{PO4,\ dissolved}$ and $P_{tot,\ dissolved}$ in the sample N5P. They re-measured the measurands with the 0.45 µm filter and reported the new results: N5P $P_{PO4,\ dissolved}$: 16.3 mg/l; $P_{tot,\ dissolved}$: 26.2 mg/l They requested the possibility to change their results for the corrected ones, or to get separate assigned values for the different filter sizes. Further, they also requested that, with results reporting, more detailed information of the used filter would be given.	After publishing the preliminary results we do not take such corrections to the database. There was no question about the pretreatment method for the dissolved nutrients in this PT, and thus separate assigned values for the different pretreatment methods were not possible to provide. The provider will consider the possibilities to include the different sample pretreatment methods for dissolved nutrients in future PTs. The participant can calculate the z scores for the new results according to the Guide for participants [4]. The national quality recommendations for data entered into water quality registers have been published in Finland, in order to promote the enhancement of environmental measurements' quality standards and traceability [6]. There the recommendation is to use Nuclepore polycarbonate filter 0.4 µm for pretreatment of water samples for dissolved nutrients. The organizing laboratory (participant 21) used Nuclepore polycarbonate filter 0.4 µm and their results for dissolved phosphorus compounds in the sample N5P were in accordance with the assigned values.
30	The participant reported erroneously the results of N_{NH4}. Their correct results were: A1N = 19 µg/l N3N = 122 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 result for the sample A1N would have been questionable and for the sample N3N satisfactory. The participant can re-calculate the z score according to the Guide for participants [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
1, 2, 10, 13, 22, 26	The participants did not return the sample arrival document to the provider. Thus their information of the sample arrival temperature missed as well. The participants should follow up the instructions of the provider.

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}
Alkalinity	A1A	mmol/l	0.11	0.00	0.3	Calculated value	0.04
	B2A	mmol/l	1.36	0.02	1.6	Robust mean	0.21
	N3A	mmol/l	0.51	0.01	2.4	Robust mean	0.32
Conductivity 25	A1J	mS/m	3.52	0.03	0.9	Robust mean	0.18
	B2H	mS/m	850	9	1.1	Robust mean	0.22
	N3H	mS/m	10.2	0.1	0.7	Robust mean	0.14
N_{NH4}	A1N	µg/l	15.5	0.1	0.5	Calculated value	0.03
	B2N	µg/l	22.1	2.0	8.9	Robust mean	0.36
	N3N	µg/l	109	6	5.5	Robust mean	0.37
$N_{NO2+NO3}$	A1N	µg/l	136	1	0.6	Calculated value	0.06
	B2N	µg/l	138	3	2.5	Robust mean	0.25
	N3N	µg/l	478	13	2.7	Robust mean	0.27
N_{tot}	A1N	µg/l	304	5	1.8	Calculated value	0.18
	B2N	µg/l	423	20	4.8	Robust mean	0.32
	N3N	µg/l	1042	17	1.6	Robust mean	0.16
pH	A1H		6.55	0.02	0.3	Robust mean	0.10
	B2H		7.89	0.02	0.3	Robust mean	0.12
	N3H		7.40	0.05	0.6	Robust mean	0.23
P_{PO4}	A1P	µg/l	6.52	0.04	0.6	Calculated value	0.04
	B2P	µg/l	24.4	0.9	3.5	Robust mean	0.35
	N3P	µg/l	19.4	1.0	5.2	Robust mean	0.35
$P_{PO4,\ dissolved}$	B4P	µg/l	24.4	1.2	4.9	Robust mean	0.33
	N5P	µg/l	16.4	1.6	10.0	Robust mean	0.50
P_{tot}	A1P	µg/l	11.8	0.1	1.1	Calculated value	0.11
	B2P	µg/l	31.1	1.4	4.4	Robust mean	0.29
	N3P	µg/l	37.7	1.1	3.0	Robust mean	0.20
$P_{tot,\ dissolved}$	B4P	µg/l	30.1	2.2	7.2	Robust mean	0.48
	N5P	µg/l	32	2.9	9.2	Median	0.46

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 reference value
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
sd	Standard deviation
sd%	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_p from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_p from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 × s_p from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 × s_p 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	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		0.48	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-0.35	1.36	7,5	1.34	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-0.16	0.51	7,5	0.51	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.28	3.52	5	3.50	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.27	850	5	856	853	850	14	1.6	16
	mS/m	N3H		-0.33	10.2	5	10.1	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		0.32	15.5	20	16.0	17.0	17.1	2.2	13.0	18
	µg/l	B2N		-0.77	22.1	25	20.0	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-1.29	109	15	98	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		2.35	136	10	152	135	136	8	5.8	20
	µg/l	B2N		0.61	138	10	142	137	138	4	3.2	18
	µg/l	N3N		1.47	478	10	513	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.71	304	10	293	294	293	9	3.2	17
	µg/l	B2N		0.14	423	15	427	430	424	32	7.5	18
	µg/l	N3N		0.21	1042	10	1053	1047	1042	23	2.2	20
pH		A1H		0.34	6.55	3,1	6.59	6.56	6.56	0.03	0.4	26
		B2H		0.41	7.89	2,5	7.93	7.90	7.90	0.04	0.6	22
		N3H		0.75	7.40	2,7	7.48	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-2.99	6.52	15	5.06	6.30	6.14	0.87	14.2	18
	µg/l	B2P		-0.66	24.4	10	23.6	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-0.18	19.4	15	19.1	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	B4P		0.56	24.4	15	25.4	24.2	24.2	1.9	7.8	14
	µg/l	N5P		-0.56	16.4	20	15.5	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		-2.35	11.8	10	10.4	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-1.61	31.1	15	27.3	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-0.90	37.7	15	35.2	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	B4P		0.17	30.1	15	30.5	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-3.00	32	20	22.4	32.0	32.0	4.9	15.2	11

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-0.97	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-1.57	1.36	7,5	1.28	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-1.73	0.51	7,5	0.48	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.91	3.52	5	3.44	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-0.24	850	5	845	853	850	14	1.6	16
	mS/m	N3H		-0.39	10.2	5	10.1	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		0.97	15.5	20	17.0	17.0	17.1	2.2	13.0	18
	µg/l	B2N		0.25	22.1	25	22.8	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-1.44	109	15	97	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		0.00	136	10	136	135	136	8	5.8	20
	µg/l	B2N		-0.29	138	10	136	137	138	4	3.2	18
	µg/l	N3N		-0.59	478	10	464	472	479	22	4.5	20

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
N_{tot}	µg/l	A1N		-0.86	304	10	291	294	293	9	3.2	17
	µg/l	B2N		-1.51	423	15	375	430	424	32	7.5	18
	µg/l	N3N		-0.40	1042	10	1021	1047	1042	23	2.2	20
pH		A1H		0.00	6.55	3,1	6.55	6.56	6.56	0.03	0.4	26
		B2H		-0.51	7.89	2,5	7.84	7.90	7.90	0.04	0.6	22
		N3H		-0.40	7.40	2,7	7.36	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-2.80	6.52	15	5.15	6.30	6.14	0.87	14.2	18
	µg/l	B2P		-0.66	24.4	10	23.6	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-0.34	19.4	15	18.9	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	B4P		-0.82	24.4	15	22.9	24.2	24.2	1.9	7.8	14
	µg/l	N5P		-2.38	16.4	20	12.5	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		-0.34	11.8	10	11.6	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.94	31.1	15	28.9	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-0.95	37.7	15	35.0	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	B4P		-1.37	30.1	15	27.0	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-4.56	32	20	17.4	32.0	32.0	4.9	15.2	11

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		9.70	0.11	7,5	0.15	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		0.98	1.36	7,5	1.41	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		2.09	0.51	7,5	0.55	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		0.34	3.52	5	3.55	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.38	850	5	858	853	850	14	1.6	16
	mS/m	N3H		0.51	10.2	5	10.3	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		8.06	15.5	20	28.0	17.0	17.1	2.2	13.0	18
	µg/l	B2N		29.65	22.1	25	104.0	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-0.12	109	15	108	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-4.26	136	10	107	135	136	8	5.8	20
	µg/l	B2N		-6.38	138	10	94	137	138	4	3.2	18
	µg/l	N3N		-16.11	478	10	93	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-1.64	304	10	279	294	293	9	3.2	17
	µg/l	B2N		0.50	423	15	439	430	424	32	7.5	18
	µg/l	N3N		0.42	1042	10	1064	1047	1042	23	2.2	20
pH		A1H		0.30	6.55	3,1	6.58	6.56	6.56	0.03	0.4	26
		B2H		-0.61	7.89	2,5	7.83	7.90	7.90	0.04	0.6	22
		N3H		-1.80	7.40	2,7	7.22	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-5.15	6.52	15	4.00	6.30	6.14	0.87	14.2	18
	µg/l	B2P		-2.79	24.4	10	21.0	24.6	24.3	1.6	6.5	18
	µg/l	N3P		0.41	19.4	15	20.0	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	B4P		-1.31	24.4	15	22.0	24.2	24.2	1.9	7.8	14
	µg/l	N5P		-2.07	16.4	20	13.0	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		-1.36	11.8	10	11.0	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.90	31.1	15	29.0	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-1.66	37.7	15	33.0	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	B4P		-1.37	30.1	15	27.0	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-4.69	32	20	17.0	32.0	32.0	4.9	15.2	11

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Conductivity 25	mS/m	A1J		-1.25	3.52	5	3.41	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-0.89	850	5	831	853	850	14	1.6	16
	mS/m	N3H		-2.43	10.2	5	9.6	10.2	10.2	0.1	1.0	22
pH		A1H		0.49	6.55	3,1	6.60	6.56	6.56	0.03	0.4	26
		B2H		0.00	7.89	2,5	7.89	7.90	7.90	0.04	0.6	22
		N3H		-2.90	7.40	2,7	7.11	7.40	7.39	0.07	1.0	23

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		1.21	0.11	7,5	0.12	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-0.39	1.36	7,5	1.34	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-0.42	0.51	7,5	0.50	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		1.82	3.52	5	3.68	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-39.86	850	5	3	853	850	14	1.6	16
	mS/m	N3H		0.39	10.2	5	10.3	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		-0.52	15.5	20	14.7	17.0	17.1	2.2	13.0	18
	µg/l	B2N		-0.83	22.1	25	19.8	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-0.49	109	15	105	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		2.21	136	10	151	135	136	8	5.8	20
	µg/l	B2N		3.04	138	10	159	137	138	4	3.2	18
	µg/l	N3N		1.88	478	10	523	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.59	304	10	295	294	293	9	3.2	17
	µg/l	B2N		-0.79	423	15	398	430	424	32	7.5	18
	µg/l	N3N		-0.23	1042	10	1030	1047	1042	23	2.2	20
pH		A1H		0.20	6.55	3,1	6.57	6.56	6.56	0.03	0.4	26
		B2H		1.12	7.89	2,5	8.00	7.90	7.90	0.04	0.6	22
		N3H		1.60	7.40	2,7	7.56	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		0.59	6.52	15	6.81	6.30	6.14	0.87	14.2	18
	µg/l	B2P		1.39	24.4	10	26.1	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-1.44	19.4	15	17.3	19.1	19.3	1.7	8.6	17
$P_{PO4,\ dissolved}$	µg/l	B4P		0.77	24.4	15	25.8	24.2	24.2	1.9	7.8	14
	µg/l	N5P		-1.65	16.4	20	13.7	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		0.34	11.8	10	12.0	11.8	11.5	0.9	7.6	19
	µg/l	B2P		0.09	31.1	15	31.3	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.18	37.7	15	38.2	38.3	37.6	1.9	5.1	18
$P_{tot,\ dissolved}$	µg/l	B4P		0.00	30.1	15	30.1	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-3.19	32	20	21.8	32.0	32.0	4.9	15.2	11

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		0.00	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		0.78	1.36	7,5	1.40	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		0.00	0.51	7,5	0.51	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		1.02	3.52	5	3.61	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.19	850	5	854	853	850	14	1.6	16
	mS/m	N3H		0.78	10.2	5	10.4	10.2	10.2	0.1	1.0	22

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
N_{NH4}	µg/l	A1N		7.87	15.5	20	27.7	17.0	17.1	2.2	13.0	18
	µg/l	B2N		12.20	22.1	25	55.8	22.9	22.1	2.4	11.0	12
	µg/l	N3N		0.82	109	15	116	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		0.88	136	10	142	135	136	8	5.8	20
	µg/l	B2N		-0.72	138	10	133	137	138	4	3.2	18
	µg/l	N3N		0.88	478	10	499	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.66	304	10	294	294	293	9	3.2	17
	µg/l	B2N		1.17	423	15	460	430	424	32	7.5	18
	µg/l	N3N		2.67	1042	10	1181	1047	1042	23	2.2	20
pH		A1H		0.39	6.55	3,1	6.59	6.56	6.56	0.03	0.4	26
		B2H		0.41	7.89	2,5	7.93	7.90	7.90	0.04	0.6	22
		N3H		0.00	7.40	2,7	7.40	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-1.88	6.52	15	5.60	6.30	6.14	0.87	14.2	18
	µg/l	B2P		0.49	24.4	10	25.0	24.6	24.3	1.6	6.5	18
	µg/l	N3P		0.82	19.4	15	20.6	19.1	19.3	1.7	8.6	17
$P_{PO4,\ dissolved}$	µg/l	B4P		1.20	24.4	15	26.6	24.2	24.2	1.9	7.8	14
	µg/l	N5P		1.65	16.4	20	19.1	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		-0.85	11.8	10	11.3	11.8	11.5	0.9	7.6	19
	µg/l	B2P		0.43	31.1	15	32.1	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.35	37.7	15	38.7	38.3	37.6	1.9	5.1	18
$P_{tot,\ dissolved}$	µg/l	B4P		0.89	30.1	15	32.1	30.3	30.1	2.7	9.1	12
	µg/l	N5P		0.44	32	20	33.4	32.0	32.0	4.9	15.2	11

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Conductivity 25	mS/m	A1J		0.00	3.52	5	3.52	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.26	850	5	856	853	850	14	1.6	16
	mS/m	N3H		-0.16	10.2	5	10.2	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		2.58	15.5	20	19.5	17.0	17.1	2.2	13.0	18
	µg/l	B2N		1.56	22.1	25	26.4	22.9	22.1	2.4	11.0	12
	µg/l	N3N		0.64	109	15	114	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-1.03	136	10	129	135	136	8	5.8	20
	µg/l	B2N		-0.75	138	10	133	137	138	4	3.2	18
	µg/l	N3N		-0.20	478	10	473	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.14	304	10	302	294	293	9	3.2	17
	µg/l	B2N		0.63	423	15	443	430	424	32	7.5	18
	µg/l	N3N		0.42	1042	10	1064	1047	1042	23	2.2	20
pH		A1H		-0.20	6.55	3,1	6.53	6.56	6.56	0.03	0.4	26
		B2H		0.10	7.89	2,5	7.90	7.90	7.90	0.04	0.6	22
		N3H		2.20	7.40	2,7	7.62	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-0.04	6.52	15	6.50	6.30	6.14	0.87	14.2	18
	µg/l	B2P		0.49	24.4	10	25.0	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-0.41	19.4	15	18.8	19.1	19.3	1.7	8.6	17
P_{tot}	µg/l	A1P		-3.05	11.8	10	10.0	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.04	31.1	15	31.0	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.67	37.7	15	39.6	38.3	37.6	1.9	5.1	18

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	B2A		-0.06	1.36	7,5	1.36	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-1.10	0.51	7,5	0.49	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	B2H		-0.24	850	5	845	853	850	14	1.6	16
	mS/m	N3H		-0.20	10.2	5	10.2	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	N3N		1.35	109	15	120	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	B2N		0.58	138	10	142	137	138	4	3.2	18
	µg/l	N3N		-0.50	478	10	466	472	479	22	4.5	20
N_{tot}	µg/l	B2N		0.63	423	15	443	430	424	32	7.5	18
	µg/l	N3N		0.40	1042	10	1063	1047	1042	23	2.2	20
pH		B2H		0.91	7.89	2,5	7.98	7.90	7.90	0.04	0.6	22
		N3H		0.40	7.40	2,7	7.44	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	B2P		1.72	24.4	10	26.5	24.6	24.3	1.6	6.5	18
	µg/l	N3P		0.07	19.4	15	19.5	19.1	19.3	1.7	8.6	17
P_{tot}	µg/l	B2P		1.07	31.1	15	33.6	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.25	37.7	15	38.4	38.3	37.6	1.9	5.1	18

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-9.16	0.11	7,5	0.07	0.11	0.11	0.00	3.8	16
Conductivity 25	mS/m	A1J		0.07	3.52	5	3.53	3.51	3.52	0.06	1.8	23
pH		A1H		-1.16	6.55	3,1	6.43	6.56	6.56	0.03	0.4	26

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-0.73	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		0.39	1.36	7,5	1.38	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-0.47	0.51	7,5	0.50	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		0.34	3.52	5	3.55	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.05	850	5	851	853	850	14	1.6	16
	mS/m	N3H		0.39	10.2	5	10.3	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		1.48	15.5	20	17.8	17.0	17.1	2.2	13.0	18
	µg/l	B2N		0.33	22.1	25	23.0	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-2.04	109	15	92	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-2.35	136	10	120	135	136	8	5.8	20
	µg/l	B2N		-0.29	138	10	136	137	138	4	3.2	18
	µg/l	N3N		0.75	478	10	496	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-1.58	304	10	280	294	293	9	3.2	17
	µg/l	B2N		0.09	423	15	426	430	424	32	7.5	18
	µg/l	N3N		-0.29	1042	10	1027	1047	1042	23	2.2	20
pH		A1H		0.00	6.55	3,1	6.55	6.56	6.56	0.03	0.4	26
		B2H		0.30	7.89	2,5	7.92	7.90	7.90	0.04	0.6	22
		N3H		2.60	7.40	2,7	7.66	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		1.53	6.52	15	7.27	6.30	6.14	0.87	14.2	18
	µg/l	B2P		1.15	24.4	10	25.8	24.6	24.3	1.6	6.5	18
	µg/l	N3P		0.96	19.4	15	20.8	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	B4P		0.55	24.4	15	25.4	24.2	24.2	1.9	7.8	14
	µg/l	N5P		0.85	16.4	20	17.8	16.3	16.4	2.3	13.8	15

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
P_{tot}	µg/l	A1P		0.34	11.8	10	12.0	11.8	11.5	0.9	7.6	19
	µg/l	B2P		0.47	31.1	15	32.2	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.42	37.7	15	38.9	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	B4P		1.95	30.1	15	34.5	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-1.84	32	20	26.1	32.0	32.0	4.9	15.2	11

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-0.73	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-0.88	1.36	7,5	1.32	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-1.41	0.51	7,5	0.48	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.23	3.52	5	3.50	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.80	850	5	867	853	850	14	1.6	16
	mS/m	N3H		0.39	10.2	5	10.3	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		2.90	15.5	20	20.0	17.0	17.1	2.2	13.0	18
	µg/l	B2N		6.48	22.1	25	40.0	22.9	22.1	2.4	11.0	12
	µg/l	N3N		1.22	109	15	119	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-1.03	136	10	129	135	136	8	5.8	20
	µg/l	B2N		-0.43	138	10	135	137	138	4	3.2	18
	µg/l	N3N		-0.71	478	10	461	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-1.64	304	10	279	294	293	9	3.2	17
	µg/l	B2N		2.02	423	15	487	430	424	32	7.5	18
	µg/l	N3N		-0.21	1042	10	1031	1047	1042	23	2.2	20
pH		A1H		0.20	6.55	3,1	6.57	6.56	6.56	0.03	0.4	26
		B2H		-0.20	7.89	2,5	7.87	7.90	7.90	0.04	0.6	22
		N3H		0.10	7.40	2,7	7.41	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		0.98	6.52	15	7.00	6.30	6.14	0.87	14.2	18
	µg/l	B2P		0.49	24.4	10	25.0	24.6	24.3	1.6	6.5	18
	µg/l	N3P		1.10	19.4	15	21.0	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	B4P		-0.22	24.4	15	24.0	24.2	24.2	1.9	7.8	14
	µg/l	N5P		-0.24	16.4	20	16.0	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		-3.05	11.8	10	10.0	11.8	11.5	0.9	7.6	19
	µg/l	B2P		0.81	31.1	15	33.0	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.81	37.7	15	40.0	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	B4P		5.71	30.1	15	43.0	30.3	30.1	2.7	9.1	12
	µg/l	N5P		0.00	32	20	32.0	32.0	32.0	4.9	15.2	11

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		1.21	0.11	7,5	0.12	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		1.49	1.36	7,5	1.44	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		1.05	0.51	7,5	0.53	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		0.45	3.52	5	3.56	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.19	850	5	854	853	850	14	1.6	16
	mS/m	N3H		0.00	10.2	5	10.2	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		2.52	15.5	20	19.4	17.0	17.1	2.2	13.0	18
	µg/l	B2N		0.83	22.1	25	24.4	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-0.11	109	15	108	108	109	10	9.0	21

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
$N_{NO2+NO3}$	µg/l	A1N		-0.59	136	10	132	135	136	8	5.8	20
	µg/l	B2N		-0.29	138	10	136	137	138	4	3.2	18
	µg/l	N3N		-0.75	478	10	460	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.79	304	10	292	294	293	9	3.2	17
	µg/l	B2N		0.32	423	15	433	430	424	32	7.5	18
	µg/l	N3N		0.23	1042	10	1054	1047	1042	23	2.2	20
pH		A1H		-0.30	6.55	3,1	6.52	6.56	6.56	0.03	0.4	26
		B2H		0.30	7.89	2,5	7.92	7.90	7.90	0.04	0.6	22
		N3H		0.00	7.40	2,7	7.40	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-0.74	6.52	15	6.16	6.30	6.14	0.87	14.2	18
	µg/l	B2P		0.00	24.4	10	24.4	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-0.27	19.4	15	19.0	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	B4P		-0.16	24.4	15	24.1	24.2	24.2	1.9	7.8	14
	µg/l	N5P		-0.30	16.4	20	15.9	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		0.51	11.8	10	12.1	11.8	11.5	0.9	7.6	19
	µg/l	B2P		1.37	31.1	15	34.3	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.50	37.7	15	39.1	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	B4P		0.84	30.1	15	32.0	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-1.47	32	20	27.3	32.0	32.0	4.9	15.2	11

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		0.48	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		0.02	1.36	7,5	1.36	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		0.52	0.51	7,5	0.52	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		4.32	3.52	5	3.90	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-1.46	850	5	819	853	850	14	1.6	16
	mS/m	N3H		0.78	10.2	5	10.4	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		-1.03	15.5	20	13.9	17.0	17.1	2.2	13.0	18
	µg/l	B2N		-1.34	22.1	25	18.4	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-1.96	109	15	93	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		5.74	136	10	175	135	136	8	5.8	20
	µg/l	B2N		-3.62	138	10	113	137	138	4	3.2	18
	µg/l	N3N		0.63	478	10	493	472	479	22	4.5	20
N_{tot}	µg/l	A1N		3.29	304	10	354	294	293	9	3.2	17
	µg/l	B2N		9.24	423	15	716	430	424	32	7.5	18
	µg/l	N3N		3.19	1042	10	1208	1047	1042	23	2.2	20
pH		A1H		-0.49	6.55	3,1	6.50	6.56	6.56	0.03	0.4	26
		B2H		0.10	7.89	2,5	7.90	7.90	7.90	0.04	0.6	22
		N3H		0.00	7.40	2,7	7.40	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		0.98	6.52	15	7.00	6.30	6.14	0.87	14.2	18
	µg/l	B2P		0.16	24.4	10	24.6	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-0.48	19.4	15	18.7	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	B4P		-0.55	24.4	15	23.4	24.2	24.2	1.9	7.8	14
	µg/l	N5P		1.77	16.4	20	19.3	16.3	16.4	2.3	13.8	15

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
P_{tot}	µg/l	A1P		-1.02	11.8	10	11.2	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.39	31.1	15	30.2	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-0.07	37.7	15	37.5	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	B4P		1.11	30.1	15	32.6	30.3	30.1	2.7	9.1	12
	µg/l	N5P		2.13	32	20	38.8	32.0	32.0	4.9	15.2	11

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Conductivity 25	mS/m	A1J		-0.23	3.52	5	3.50	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-4.52	850	5	754	853	850	14	1.6	16
N_{NH4}	µg/l	A1N		0.97	15.5	20	17.0	17.0	17.1	2.2	13.0	18
	µg/l	B2N		29.57	22.1	25	103.8	22.9	22.1	2.4	11.0	12
$N_{NO2+NO3}$	µg/l	A1N		1.47	136	10	146	135	136	8	5.8	20
	µg/l	B2N		-0.72	138	10	133	137	138	4	3.2	18
pH		A1H		0.00	6.55	3,1	6.55	6.56	6.56	0.03	0.4	26
		B2H		-0.41	7.89	2,5	7.85	7.90	7.90	0.04	0.6	22
P_{PO4}	µg/l	A1P		-0.04	6.52	15	6.50	6.30	6.14	0.87	14.2	18
	µg/l	B2P		-1.15	24.4	10	23.0	24.6	24.3	1.6	6.5	18
P_{tot}	µg/l	A1P		0.68	11.8	10	12.2	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.04	31.1	15	31.0	31.0	31.2	2.5	8.1	20

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-0.48	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	N3A		-0.58	0.51	7,5	0.50	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		0.11	3.52	5	3.53	3.51	3.52	0.06	1.8	23
	mS/m	N3H		0.00	10.2	5	10.2	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N			15.5	20	*<30*	17.0	17.1	2.2	13.0	18
	µg/l	N3N		-0.12	109	15	108	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-0.74	136	10	131	135	136	8	5.8	20
	µg/l	N3N		-1.26	478	10	448	472	479	22	4.5	20
N_{tot}	µg/l	A1N		0.20	304	10	307	294	293	9	3.2	17
	µg/l	N3N		-0.84	1042	10	998	1047	1042	23	2.2	20
pH		A1H		-0.39	6.55	3,1	6.51	6.56	6.56	0.03	0.4	26
		N3H		-0.60	7.40	2,7	7.34	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		16.52	6.52	15	14.60	6.30	6.14	0.87	14.2	18
	µg/l	N3P		0.69	19.4	15	20.4	19.1	19.3	1.7	8.6	17
$P_{PO4, dissolved}$	µg/l	N5P		1.46	16.4	20	18.8	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		13.56	11.8	10	19.8	11.8	11.5	0.9	7.6	19
	µg/l	N3P		0.25	37.7	15	38.4	38.3	37.6	1.9	5.1	18
$P_{tot, dissolved}$	µg/l	N5P		2.16	32	20	38.9	32.0	32.0	4.9	15.2	11

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		0.48	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-0.59	1.36	7,5	1.33	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-0.84	0.51	7,5	0.49	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.23	3.52	5	3.50	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-0.09	850	5	848	853	850	14	1.6	16
	mS/m	N3H		-0.71	10.2	5	10.0	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		0.52	15.5	20	16.3	17.0	17.1	2.2	13.0	18
	µg/l	B2N		0.69	22.1	25	24.0	22.9	22.1	2.4	11.0	12
	µg/l	N3N		0.49	109	15	113	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		0.44	136	10	139	135	136	8	5.8	20
	µg/l	B2N		5.65	138	10	177	137	138	4	3.2	18
	µg/l	N3N		-0.33	478	10	470	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.13	304	10	302	294	293	9	3.2	17
	µg/l	B2N		-1.58	423	15	373	430	424	32	7.5	18
	µg/l	N3N		-0.23	1042	10	1030	1047	1042	23	2.2	20
pH		A1H		0.39	6.55	3,1	6.59	6.56	6.56	0.03	0.4	26
		B2H		0.00	7.89	2,5	7.89	7.90	7.90	0.04	0.6	22
		N3H		-0.30	7.40	2,7	7.37	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-0.25	6.52	15	6.40	6.30	6.14	0.87	14.2	18
	µg/l	B2P		0.08	24.4	10	24.5	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-1.03	19.4	15	17.9	19.1	19.3	1.7	8.6	17
$P_{PO4,\ dissolved}$	µg/l	B4P		-0.05	24.4	15	24.3	24.2	24.2	1.9	7.8	14
	µg/l	N5P		-0.06	16.4	20	16.3	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		0.00	11.8	10	11.8	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-1.33	31.1	15	28.0	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-0.74	37.7	15	35.6	38.3	37.6	1.9	5.1	18
$P_{tot,\ dissolved}$	µg/l	B4P		-2.21	30.1	15	25.1	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-0.91	32	20	29.1	32.0	32.0	4.9	15.2	11

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Conductivity 25	mS/m	A1J		-0.11	3.52	5	3.51	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-0.94	850	5	830	853	850	14	1.6	16
	mS/m	N3H		-0.39	10.2	5	10.1	10.2	10.2	0.1	1.0	22
pH		A1H		0.49	6.55	3,1	6.60	6.56	6.56	0.03	0.4	26
		B2H		0.20	7.89	2,5	7.91	7.90	7.90	0.04	0.6	22
		N3H		0.10	7.40	2,7	7.41	7.40	7.39	0.07	1.0	23
P_{tot}	µg/l	A1P		5.42	11.8	10	15.0	11.8	11.5	0.9	7.6	19
	µg/l	B2P		1.24	31.1	15	34.0	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-4.49	37.7	15	25.0	38.3	37.6	1.9	5.1	18

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
N_{NH4}	µg/l	A1N		10.71	15.5	20	32.1	17.0	17.1	2.2	13.0	18
	µg/l	B2N		9.05	22.1	25	47.1	22.9	22.1	2.4	11.0	12
	µg/l	N3N		1.47	109	15	121	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		1.03	136	10	143	135	136	8	5.8	20
	µg/l	B2N		1.16	138	10	146	137	138	4	3.2	18
	µg/l	N3N		0.96	478	10	501	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-1.38	304	10	283	294	293	9	3.2	17
	µg/l	B2N		-0.98	423	15	392	430	424	32	7.5	18
	µg/l	N3N		0.35	1042	10	1060	1047	1042	23	2.2	20

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	B2A		0.55	1.36	7,5	1.39	1.36	1.36	0.04	2.8	16
pH		B2H		-0.41	7.89	2,5	7.85	7.90	7.90	0.04	0.6	22

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-1.45	0.11	7,5	0.10	0.11	0.11	0.00	3.8	16
	mmol/l	N3A		-0.99	0.51	7,5	0.49	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.45	3.52	5	3.48	3.51	3.52	0.06	1.8	23
	mS/m	N3H		-0.12	10.2	5	10.2	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		0.00	15.5	20	15.5	17.0	17.1	2.2	13.0	18
	µg/l	N3N		0.37	109	15	112	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-0.15	136	10	135	135	136	8	5.8	20
	µg/l	N3N		0.67	478	10	494	472	479	22	4.5	20
pH		A1H		-0.10	6.55	3,1	6.54	6.56	6.56	0.03	0.4	26
		N3H		0.40	7.40	2,7	7.44	7.40	7.39	0.07	1.0	23

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-0.56	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-0.14	1.36	7,5	1.35	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-0.31	0.51	7,5	0.50	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-1.48	3.52	5	3.39	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-0.14	850	5	847	853	850	14	1.6	16
	mS/m	N3H		-2.98	10.2	5	9.4	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		0.97	15.5	20	17.0	17.0	17.1	2.2	13.0	18
	µg/l	B2N		0.40	22.1	25	23.2	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-1.28	109	15	99	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-0.74	136	10	131	135	136	8	5.8	20
	µg/l	B2N		0.00	138	10	138	137	138	4	3.2	18
	µg/l	N3N		-0.50	478	10	466	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.39	304	10	298	294	293	9	3.2	17
	µg/l	B2N		0.50	423	15	439	430	424	32	7.5	18
	µg/l	N3N		-0.04	1042	10	1040	1047	1042	23	2.2	20
pH		A1H		0.00	6.55	3,1	6.55	6.56	6.56	0.03	0.4	26
		B2H		0.20	7.89	2,5	7.91	7.90	7.90	0.04	0.6	22
		N3H		0.10	7.40	2,7	7.41	7.40	7.39	0.07	1.0	23

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
P_{PO4}	µg/l	A1P		-2.90	6.52	15	5.10	6.30	6.14	0.87	14.2	18
	µg/l	B2P		-2.87	24.4	10	20.9	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-1.37	19.4	15	17.4	19.1	19.3	1.7	8.6	17
$P_{PO4,\ dissolved}$	µg/l	B4P		-2.57	24.4	15	19.7	24.2	24.2	1.9	7.8	14
	µg/l	N5P		0.24	16.4	20	16.8	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		0.17	11.8	10	11.9	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.81	31.1	15	29.2	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-0.71	37.7	15	35.7	38.3	37.6	1.9	5.1	18
$P_{tot,\ dissolved}$	µg/l	B4P		-0.66	30.1	15	28.6	30.3	30.1	2.7	9.1	12
	µg/l	N5P		0.34	32	20	33.1	32.0	32.0	4.9	15.2	11

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
N_{NH4}	µg/l	A1N		0.58	15.5	20	16.4	17.0	17.1	2.2	13.0	18
	µg/l	B2N		0.51	22.1	25	23.5	22.9	22.1	2.4	11.0	12
	µg/l	N3N		1.97	109	15	125	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-0.41	136	10	133	135	136	8	5.8	20
	µg/l	B2N		0.01	138	10	138	137	138	4	3.2	18
	µg/l	N3N		-0.96	478	10	455	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.89	304	10	290	294	293	9	3.2	17
	µg/l	B2N		0.32	423	15	433	430	424	32	7.5	18
	µg/l	N3N		0.24	1042	10	1055	1047	1042	23	2.2	20
pH		A1H		-1.67	6.55	3,1	6.38	6.56	6.56	0.03	0.4	26
		B2H		-1.66	7.89	2,5	7.73	7.90	7.90	0.04	0.6	22
		N3H		-1.23	7.40	2,7	7.28	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		1.19	6.52	15	7.10	6.30	6.14	0.87	14.2	18
	µg/l	B2P		-1.23	24.4	10	22.9	24.6	24.3	1.6	6.5	18
	µg/l	N3P		-4.60	19.4	15	12.7	19.1	19.3	1.7	8.6	17
P_{tot}	µg/l	A1P		-1.69	11.8	10	10.8	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.99	31.1	15	28.8	31.0	31.2	2.5	8.1	20
	µg/l	N3P		-3.47	37.7	15	27.9	38.3	37.6	1.9	5.1	18

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-1.45	0.11	7,5	0.10	0.11	0.11	0.00	3.8	16
	mmol/l	N3A		-0.78	0.51	7,5	0.50	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.57	3.52	5	3.47	3.51	3.52	0.06	1.8	23
	mS/m	N3H		-0.39	10.2	5	10.1	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		-2.00	15.5	20	12.4	17.0	17.1	2.2	13.0	18
	µg/l	N3N		-0.61	109	15	104	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-0.88	136	10	130	135	136	8	5.8	20
	µg/l	N3N		-0.84	478	10	458	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-0.53	304	10	296	294	293	9	3.2	17
	µg/l	N3N		-0.46	1042	10	1018	1047	1042	23	2.2	20
pH		A1H		-0.20	6.55	3,1	6.53	6.56	6.56	0.03	0.4	26
		N3H		-0.30	7.40	2,7	7.37	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		-0.65	6.52	15	6.20	6.30	6.14	0.87	14.2	18
	µg/l	N3P		-2.75	19.4	15	15.4	19.1	19.3	1.7	8.6	17

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
$P_{PO4,\ dissolved}$	µg/l	N5P		-1.28	16.4	20	14.3	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		0.34	11.8	10	12.0	11.8	11.5	0.9	7.6	19
	µg/l	N3P		-0.14	37.7	15	37.3	38.3	37.6	1.9	5.1	18
$P_{tot,\ dissolved}$	µg/l	N5P		-1.97	32	20	25.7	32.0	32.0	4.9	15.2	11

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		4.85	0.11	7,5	0.13	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-0.20	1.36	7,5	1.35	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		1.57	0.51	7,5	0.54	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		0.60	3.52	5	3.57	3.51	3.52	0.06	1.8	23
	mS/m	B2H		1.04	850	5	872	853	850	14	1.6	16
	mS/m	N3H		0.20	10.2	5	10.3	10.2	10.2	0.1	1.0	22
N_{tot}	µg/l	A1N		2.04	304	10	335	294	293	9	3.2	17
	µg/l	B2N		2.93	423	15	516	430	424	32	7.5	18
	µg/l	N3N		0.56	1042	10	1071	1047	1042	23	2.2	20
pH		A1H		-1.08	6.55	3,1	6.44	6.56	6.56	0.03	0.4	26
		B2H		-0.10	7.89	2,5	7.88	7.90	7.90	0.04	0.6	22
		N3H		-4.50	7.40	2,7	6.95	7.40	7.39	0.07	1.0	23
P_{tot}	µg/l	A1P		-2.20	11.8	10	10.5	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.47	31.1	15	30.0	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.46	37.7	15	39.0	38.3	37.6	1.9	5.1	18

Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
N_{NH4}	µg/l	A1N		2.13	15.5	20	18.8	17.0	17.1	2.2	13.0	18
	µg/l	B2N		-0.85	22.1	25	19.8	22.9	22.1	2.4	11.0	12
$N_{NO2+NO3}$	µg/l	A1N		-0.09	136	10	135	135	136	8	5.8	20
	µg/l	B2N		-0.47	138	10	135	137	138	4	3.2	18
N_{tot}	µg/l	A1N		-0.69	304	10	294	294	293	9	3.2	17
	µg/l	B2N		1.11	423	15	458	430	424	32	7.5	18
pH		A1H		0.00	6.55	3,1	6.55	6.56	6.56	0.03	0.4	26
		B2H		0.51	7.89	2,5	7.94	7.90	7.90	0.04	0.6	22
P_{PO4}	µg/l	A1P		-1.25	6.52	15	5.91	6.30	6.14	0.87	14.2	18
	µg/l	B2P		-0.18	24.4	10	24.2	24.6	24.3	1.6	6.5	18
$P_{PO4,\ dissolved}$	µg/l	B4P		-0.16	24.4	15	24.1	24.2	24.2	1.9	7.8	14
P_{tot}	µg/l	A1P		0.24	11.8	10	11.9	11.8	11.5	0.9	7.6	19
	µg/l	B2P		0.43	31.1	15	32.1	31.0	31.2	2.5	8.1	20
$P_{tot,\ dissolved}$	µg/l	B4P		0.64	30.1	15	31.5	30.3	30.1	2.7	9.1	12

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		1.45	0.11	7,5	0.12	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		-0.20	1.36	7,5	1.35	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		0.00	0.51	7,5	0.51	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-39.61	3.52	5	0.03	3.51	3.52	0.06	1.8	23
	mS/m	B2H		-39.60	850	5	8	853	850	14	1.6	16
	mS/m	N3H		-39.60	10.2	5	0.1	10.2	10.2	0.1	1.0	22

Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
N_{NH4}	µg/l	A1N		3.55	15.5	20	21.0	17.0	17.1	2.2	13.0	18
	µg/l	B2N		3.95	22.1	25	33.0	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-0.37	109	15	106	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		-0.88	136	10	130	135	136	8	5.8	20
	µg/l	B2N		0.58	138	10	142	137	138	4	3.2	18
	µg/l	N3N		-0.84	478	10	458	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-3.49	304	10	251	294	293	9	3.2	17
	µg/l	B2N		-1.13	423	15	387	430	424	32	7.5	18
	µg/l	N3N		-1.75	1042	10	951	1047	1042	23	2.2	20
pH		A1H		0.10	6.55	3,1	6.56	6.56	6.56	0.03	0.4	26
		B2H		-0.30	7.89	2,5	7.86	7.90	7.90	0.04	0.6	22
		N3H		-1.10	7.40	2,7	7.29	7.40	7.39	0.07	1.0	23

Participant 27												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		-0.73	0.11	7,5	0.11	0.11	0.11	0.00	3.8	16
	mmol/l	N3A		-1.99	0.51	7,5	0.47	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		0.57	3.52	5	3.57	3.51	3.52	0.06	1.8	23
	mS/m	N3H		-0.39	10.2	5	10.1	10.2	10.2	0.1	1.0	22
pH		A1H		0.20	6.55	3,1	6.57	6.56	6.56	0.03	0.4	26
		N3H		-0.20	7.40	2,7	7.38	7.40	7.39	0.07	1.0	23

Participant 28												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
N_{NH4}	µg/l	A1N		0.58	15.5	20	16.4	17.0	17.1	2.2	13.0	18
	µg/l	B2N		1.95	22.1	25	27.5	22.9	22.1	2.4	11.0	12
	µg/l	N3N		1.71	109	15	123	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		0.15	136	10	137	135	136	8	5.8	20
	µg/l	B2N		0.87	138	10	144	137	138	4	3.2	18
	µg/l	N3N		0.84	478	10	498	472	479	22	4.5	20
N_{tot}	µg/l	A1N		-4.34	304	10	238	294	293	9	3.2	17
	µg/l	B2N		-1.17	423	15	386	430	424	32	7.5	18
	µg/l	N3N		-0.69	1042	10	1006	1047	1042	23	2.2	20
P_{PO4}	µg/l	A1P		-0.76	6.52	15	6.15	6.30	6.14	0.87	14.2	18
	µg/l	B2P		1.23	24.4	10	25.9	24.6	24.3	1.6	6.5	18
	µg/l	N3P		1.17	19.4	15	21.1	19.1	19.3	1.7	8.6	17
$P_{PO4,\ dissolved}$	µg/l	B4P		1.37	24.4	15	26.9	24.2	24.2	1.9	7.8	14
	µg/l	N5P		0.91	16.4	20	17.9	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		2.54	11.8	10	13.3	11.8	11.5	0.9	7.6	19
	µg/l	B2P		2.96	31.1	15	38.0	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.07	37.7	15	37.9	38.3	37.6	1.9	5.1	18
$P_{tot,\ dissolved}$	µg/l	B4P		2.52	30.1	15	35.8	30.3	30.1	2.7	9.1	12
	µg/l	N5P		1.72	32	20	37.5	32.0	32.0	4.9	15.2	11

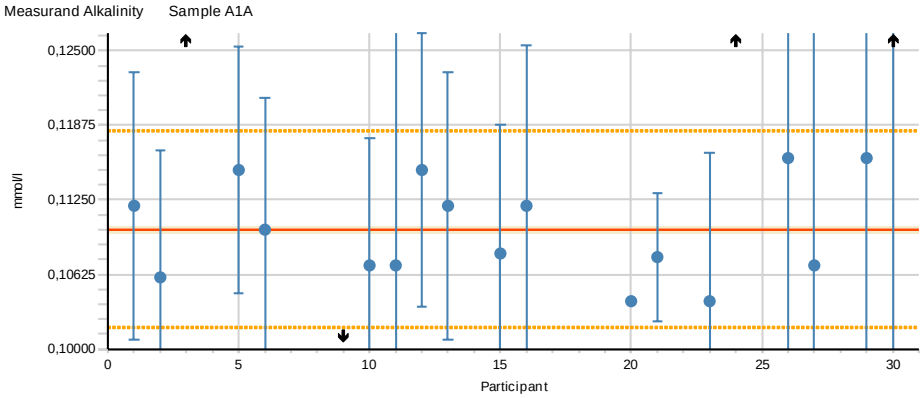
Participant 29												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		1.45	0.11	7,5	0.12	0.11	0.11	0.00	3.8	16
	mmol/l	B2A		0.00	1.36	7,5	1.36	1.36	1.36	0.04	2.8	16
	mmol/l	N3A		-0.26	0.51	7,5	0.51	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.36	3.52	5	3.49	3.51	3.52	0.06	1.8	23
	mS/m	B2H		0.69	850	5	865	853	850	14	1.6	16
	mS/m	N3H		-0.16	10.2	5	10.2	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		1.94	15.5	20	18.5	17.0	17.1	2.2	13.0	18
	µg/l	B2N		-0.72	22.1	25	20.1	22.9	22.1	2.4	11.0	12
	µg/l	N3N		-0.73	109	15	103	108	109	10	9.0	21
$N_{NO2+NO3}$	µg/l	A1N		0.59	136	10	140	135	136	8	5.8	20
	µg/l	B2N		0.87	138	10	144	137	138	4	3.2	18
	µg/l	N3N		-0.17	478	10	474	472	479	22	4.5	20
N_{tot}	µg/l	A1N		0.53	304	10	312	294	293	9	3.2	17
	µg/l	B2N		0.09	423	15	426	430	424	32	7.5	18
	µg/l	N3N		0.69	1042	10	1078	1047	1042	23	2.2	20
pH		A1H		0.10	6.55	3,1	6.56	6.56	6.56	0.03	0.4	26
		B2H		-0.20	7.89	2,5	7.87	7.90	7.90	0.04	0.6	22
		N3H		0.40	7.40	2,7	7.44	7.40	7.39	0.07	1.0	23
P_{PO4}	µg/l	A1P		0.22	6.52	15	6.63	6.30	6.14	0.87	14.2	18
	µg/l	B2P		0.66	24.4	10	25.2	24.6	24.3	1.6	6.5	18
	µg/l	N3P		1.65	19.4	15	21.8	19.1	19.3	1.7	8.6	17
$P_{PO4,\ dissolved}$	µg/l	B4P		0.05	24.4	15	24.5	24.2	24.2	1.9	7.8	14
	µg/l	N5P		1.52	16.4	20	18.9	16.3	16.4	2.3	13.8	15
P_{tot}	µg/l	A1P		1.02	11.8	10	12.4	11.8	11.5	0.9	7.6	19
	µg/l	B2P		-0.09	31.1	15	30.9	31.0	31.2	2.5	8.1	20
	µg/l	N3P		0.60	37.7	15	39.4	38.3	37.6	1.9	5.1	18
$P_{tot,\ dissolved}$	µg/l	B4P		-0.04	30.1	15	30.0	30.3	30.1	2.7	9.1	12
	µg/l	N5P		-0.66	32	20	29.9	32.0	32.0	4.9	15.2	11

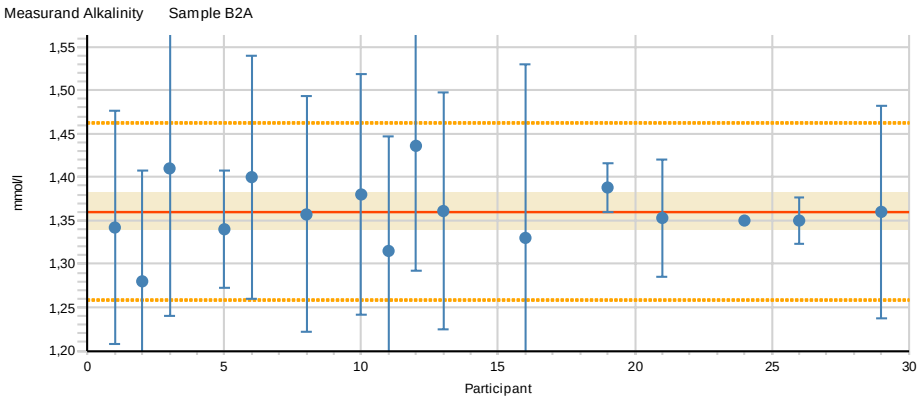
Participant 30												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	sd	sd %	n (stat)
Alkalinity	mmol/l	A1A		7.76	0.11	7,5	0.14	0.11	0.11	0.00	3.8	16
	mmol/l	N3A		1.31	0.51	7,5	0.54	0.50	0.51	0.02	4.1	20
Conductivity 25	mS/m	A1J		-0.23	3.52	5	3.50	3.51	3.52	0.06	1.8	23
	mS/m	N3H		0.12	10.2	5	10.2	10.2	10.2	0.1	1.0	22
N_{NH4}	µg/l	A1N		68.71	15.5	20	122.0	17.0	17.1	2.2	13.0	18
	µg/l	N3N		-11.01	109	15	19	108	109	10	9.0	21
pH		A1H		0.20	6.55	3,1	6.57	6.56	6.56	0.03	0.4	26
		N3H		0.20	7.40	2,7	7.42	7.40	7.39	0.07	1.0	23

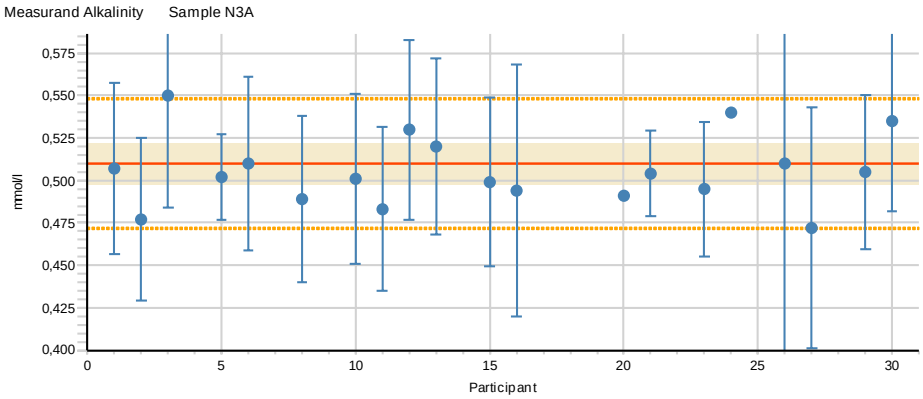
APPENDIX 9: Results of participants and their uncertainties

In figures:

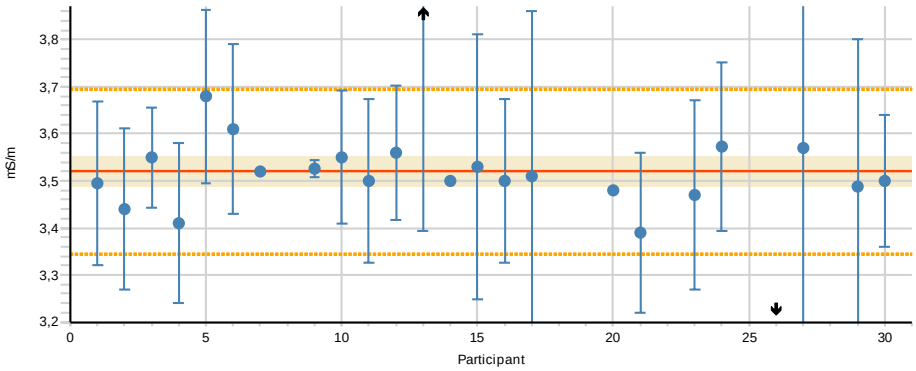
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



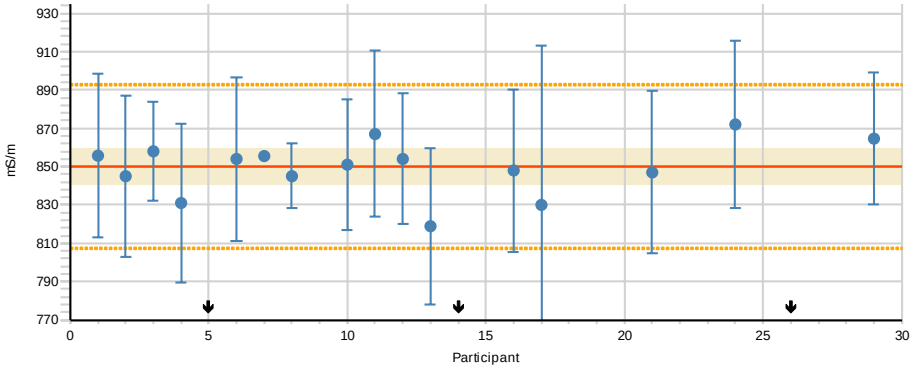




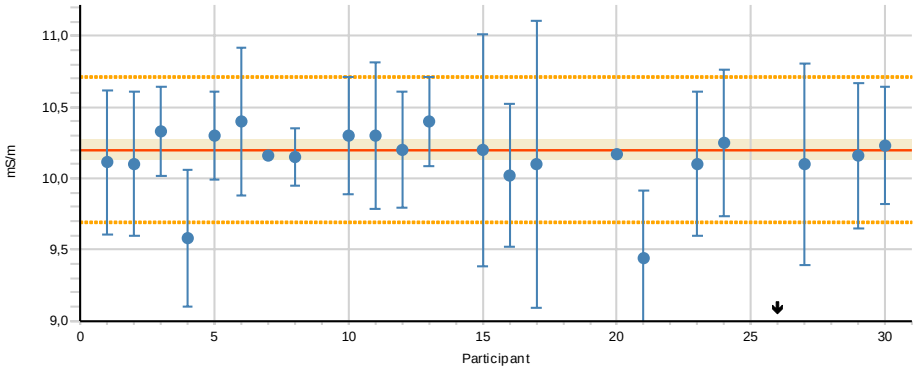
Measurand Conductivity 25 Sample A1J

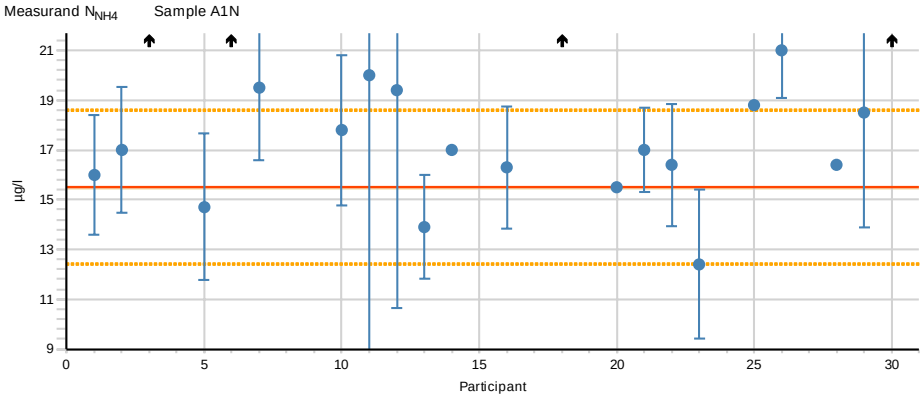


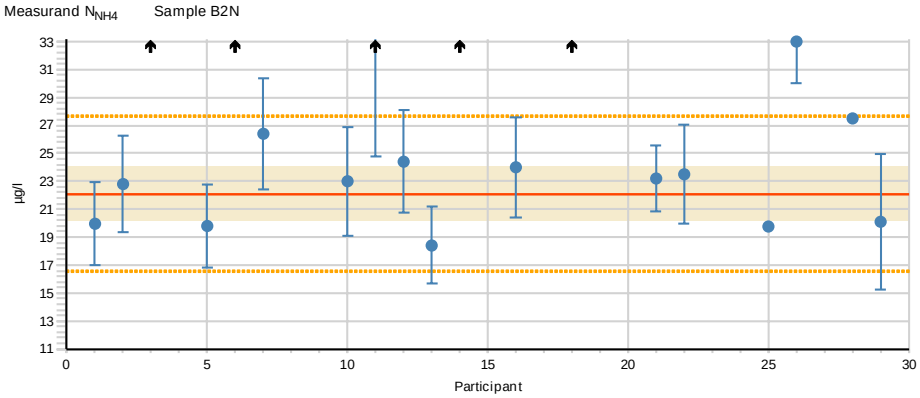
Measurand Conductivity 25 Sample B2H

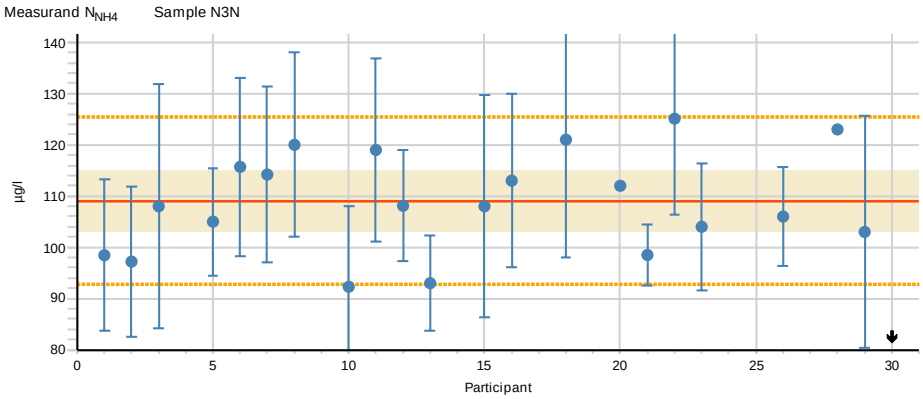


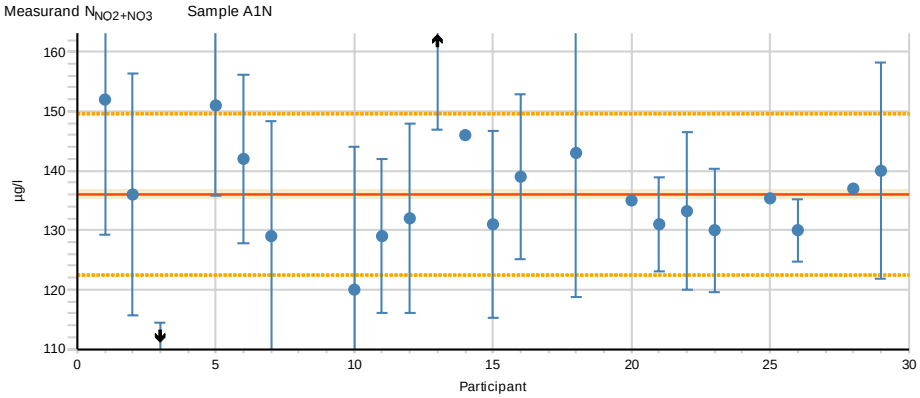
Measurand Conductivity 25 Sample N3H

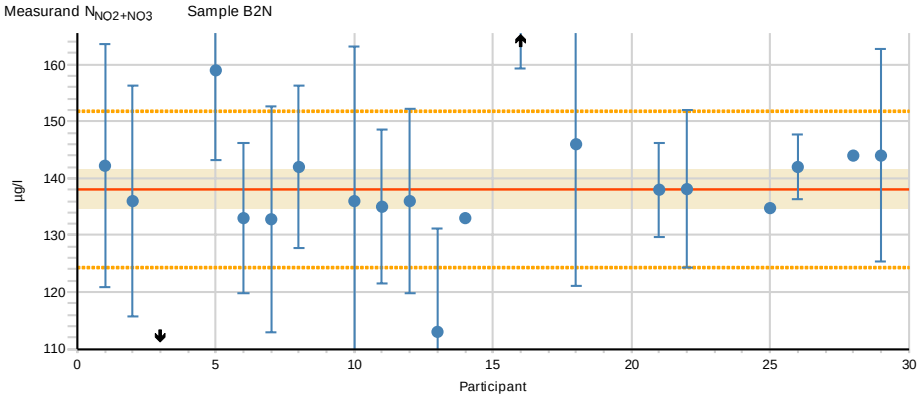


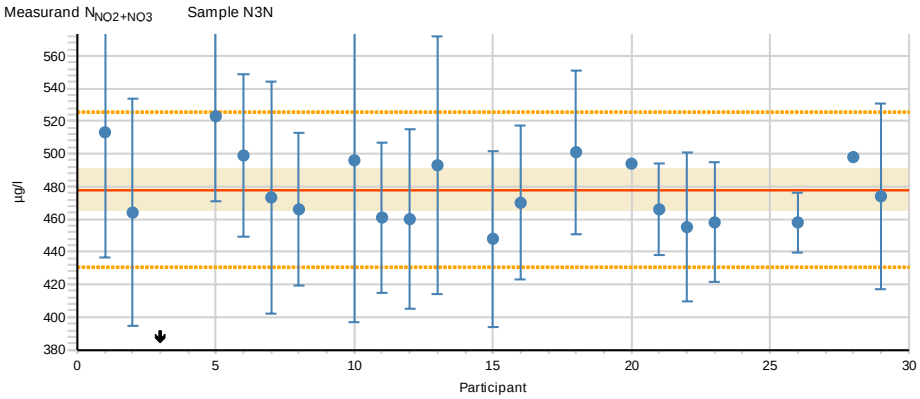

Measurand N_{NH4}
Sample A1N
µg/l
Participant

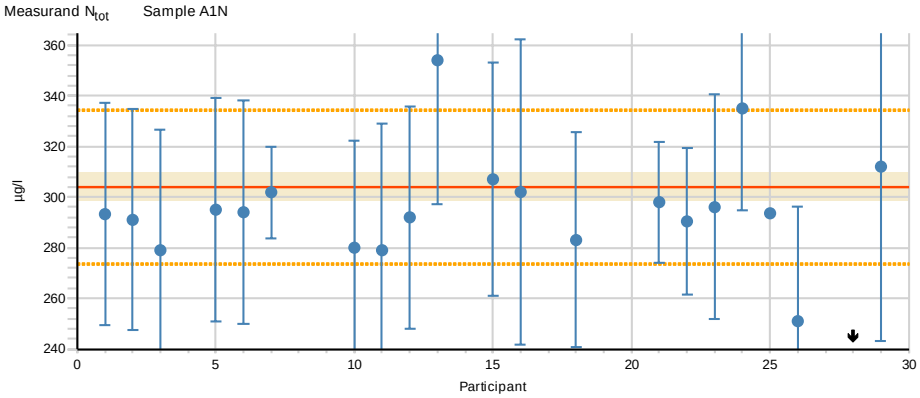

Measurand N_{NH4}
Sample B2N
µg/l
Participant

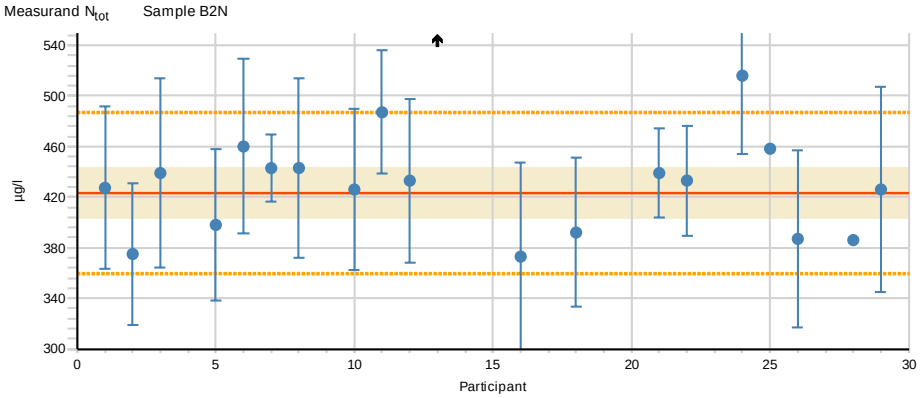

Measurand N_{NH4}
Sample N3N
µg/l
Participant

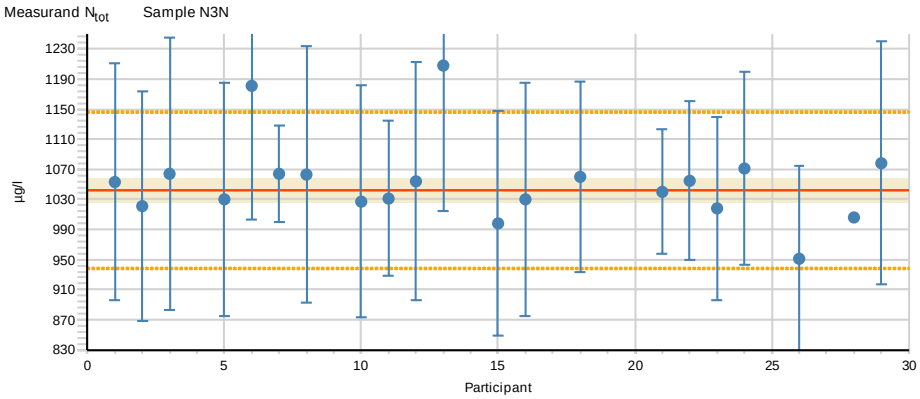

Measurand $N_{NO2+NO3}$
Sample A1N
µg/l
160
150
140
130
120
110
0
5
10
15
20
25
30
Participant

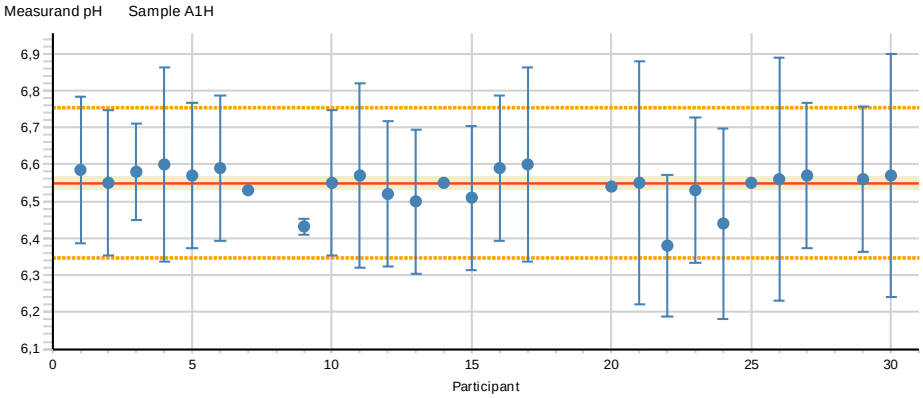

Measurand $N_{NO2+NO3}$
Sample B2N
µg/l
160
150
140
130
120
110
0
5
10
15
20
25
30
Participant

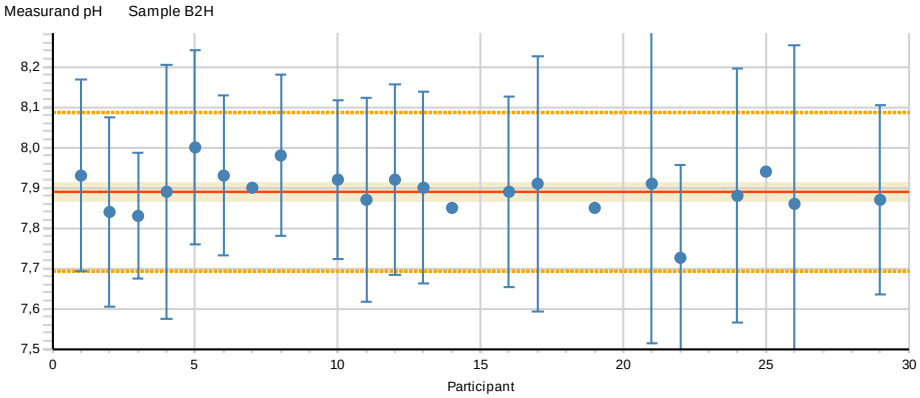

Measurand $N_{NO2+NO3}$
Sample N3N
µg/l
560
540
520
500
480
460
440
420
400
380
0
5
10
15
20
25
30
Participant

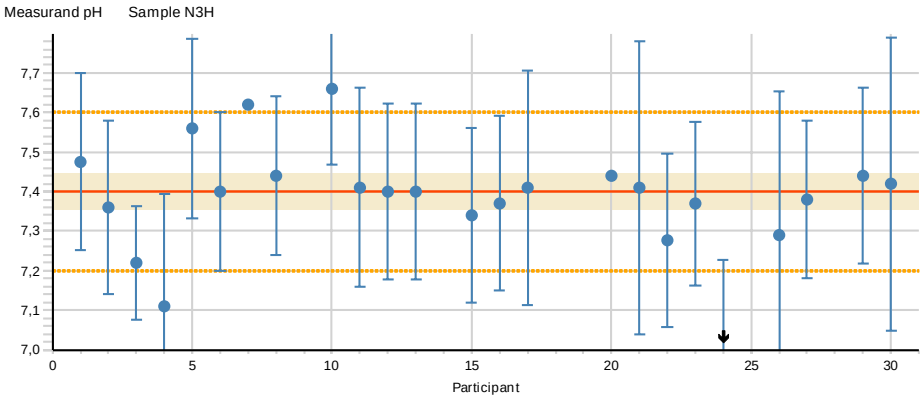

Measurand N_{tot}
Sample A1N
µg/l
360
340
320
300
280
260
240
0
5
10
15
20
25
30
Participant


Measurand N_{tot}
Sample B2N
µg/l
540
500
460
420
380
340
300
0
5
10
15
20
25
30
Participant

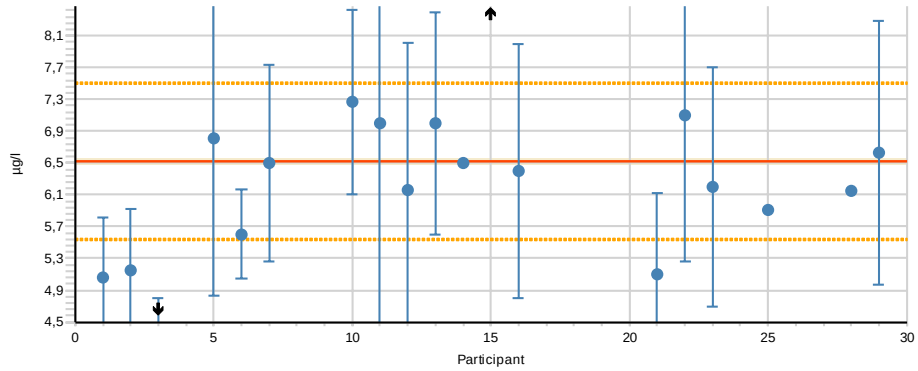

Measurand N_{tot}
Sample N3N
µg/l
1230
1190
1150
1110
1070
1030
990
950
910
870
830
0
5
10
15
20
25
30
Participant


Measurand pH
Sample A1H
6,9
6,8
6,7
6,6
6,5
6,4
6,3
6,2
6,1
0
5
10
15
20
25
30
Participant

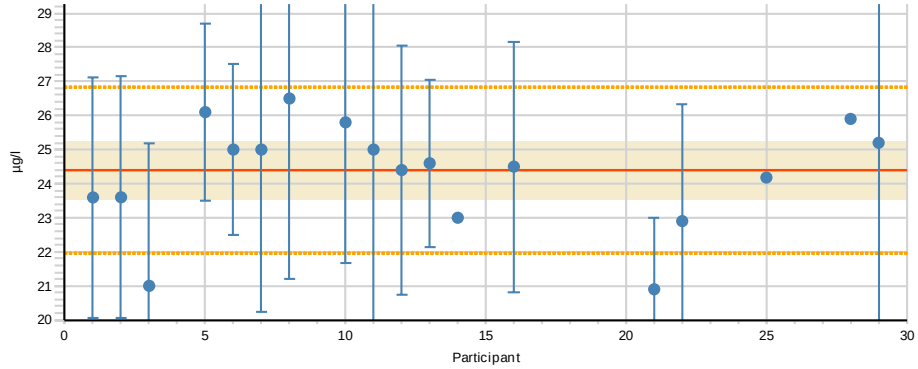

Measurand pH
Sample B2H
8,2
8,1
8,0
7,9
7,8
7,7
7,6
7,5
0
5
10
15
20
25
30
Participant


Measurand pH
Sample N3H
7,7
7,6
7,5
7,4
7,3
7,2
7,1
7,0
0
5
10
15
20
25
30
Participant

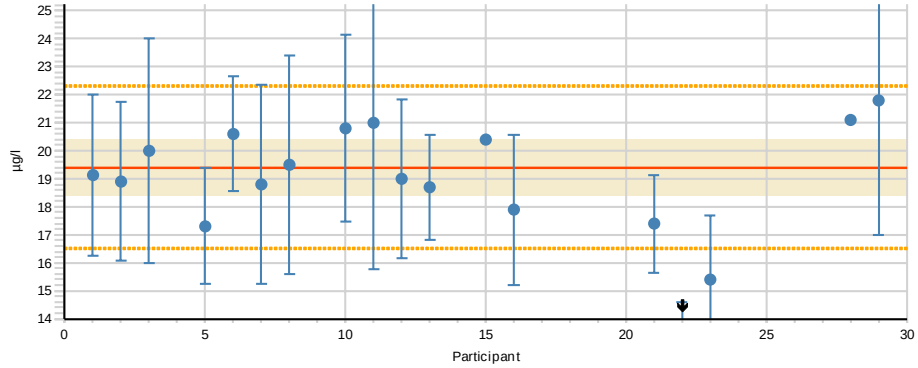
Measurand P_{PO4} Sample A1P

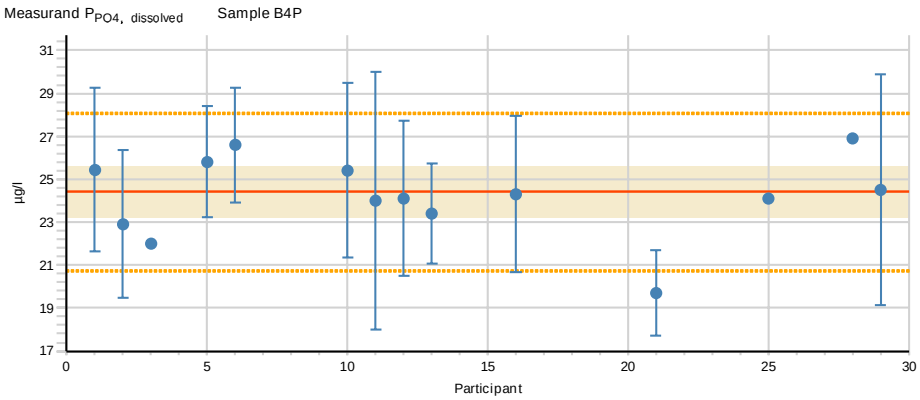


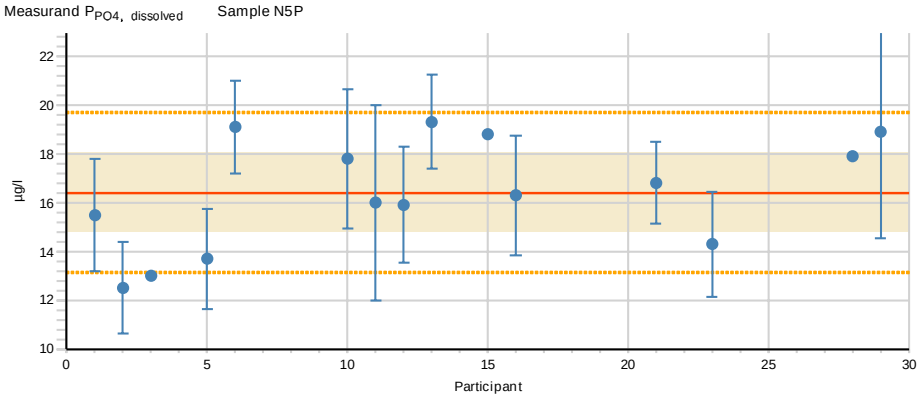
Measurand P_{PO4} Sample B2P

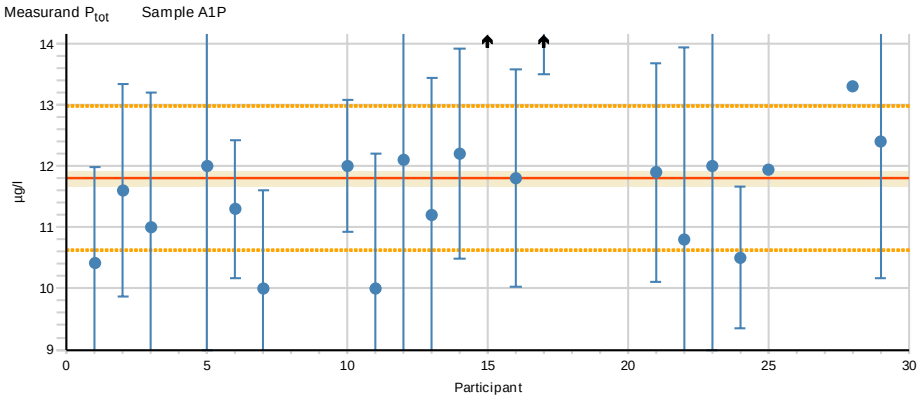


Measurand P_{PO4} Sample N3P

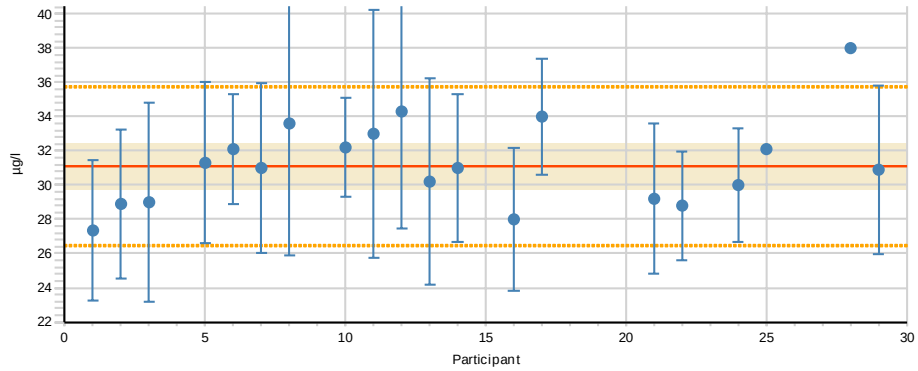



Measurand $P_{PO4,\ dissolved}$ Sample B4P
µg/l
Participant

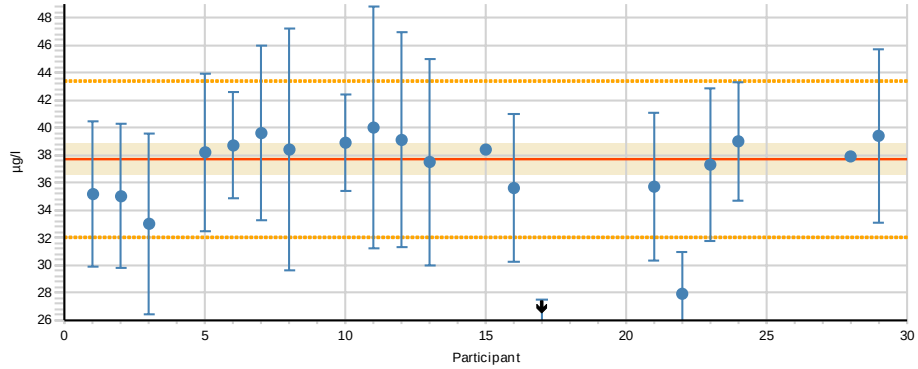

Measurand $P_{PO4,\ dissolved}$ Sample N5P
µg/l
Participant


Measurand P_{tot} Sample A1P
µg/l
Participant

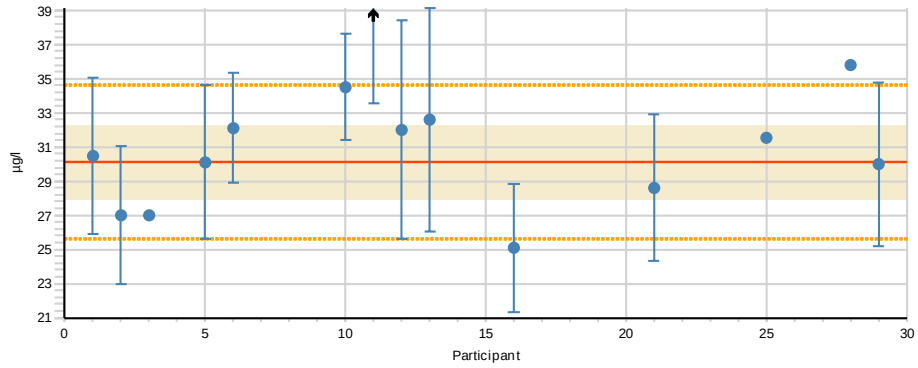
Measurand P_{tot} Sample B2P

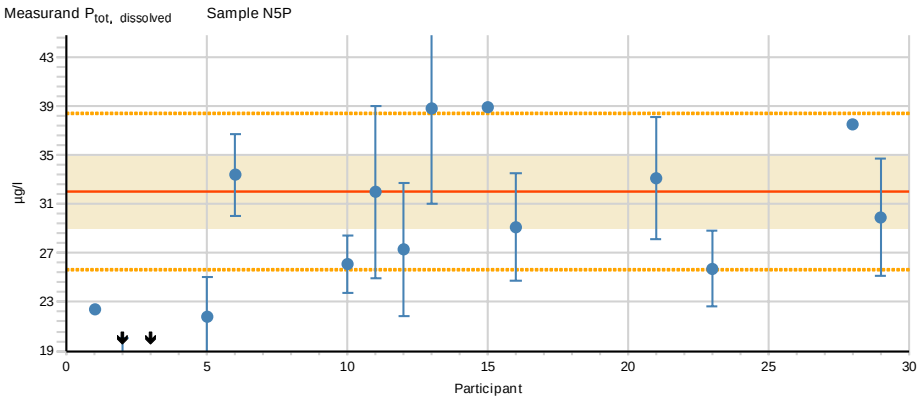


Measurand P_{tot} Sample N3P



Measurand $P_{tot,\ dissolved}$ Sample B4P




Measurand P tot, dissolved
Sample N5P
µg/l
43
39
35
31
27
23
19
0
5
10
15
20
25
30
Participant

APPENDIX 10: Summary of the z scores

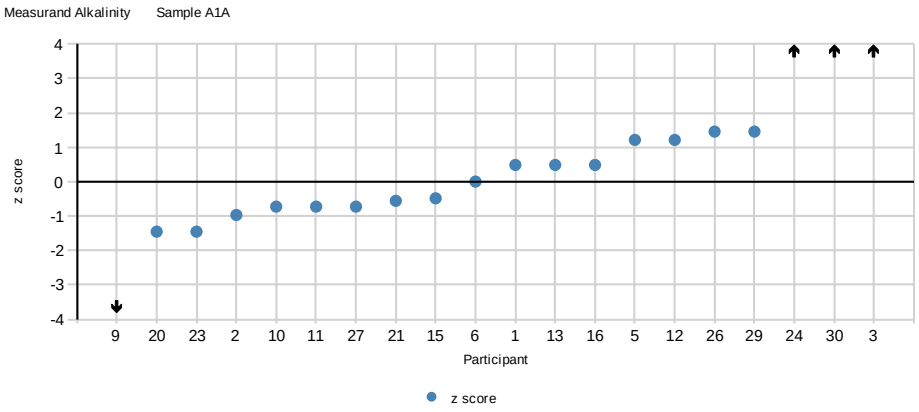
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Alkalinity	A1A	S	S	U	.	S	S	.	.	u	S	S	S	S	.	S	S	.	.	.	S	S	.	S	80.0
	B2A	S	S	S	.	S	S	.	S	.	S	S	S	S	.	.	S	.	.	S	.	S	.	.	100
	N3A	S	S	Q	.	S	S	.	S	.	S	S	S	S	.	S	S	.	.	.	S	S	.	S	95.0
Conductivity 25	A1J	S	S	S	S	S	S	S	.	S	S	S	S	U	S	S	S	S	.	.	S	S	.	S	91.7
	B2H	S	S	S	S	u	S	S	S	.	S	S	S	S	u	.	S	S	.	.	.	S	.	.	84.2
	N3H	S	S	S	q	S	S	S	S	.	S	S	S	S	.	S	S	S	.	.	S	q	.	S	87.0
N_{NH4}	A1N	S	S	U	.	S	U	Q	.	.	S	Q	Q	S	S	.	S	.	U	.	S	S	S	S	59.1
	B2N	S	S	U	.	S	U	S	.	.	S	U	S	S	U	.	S	.	U	.	.	S	S	.	68.4
	N3N	S	S	S	.	S	S	S	S	.	q	S	S	S	.	S	S	.	S	.	S	S	S	S	90.9
$N_{NO2+NO3}$	A1N	Q	S	u	.	Q	S	S	.	.	q	S	S	U	S	S	S	.	S	.	S	S	S	S	77.3
	B2N	S	S	u	.	U	S	S	S	.	S	S	S	u	S	.	U	.	S	.	.	S	S	.	80.0
	N3N	S	S	u	.	S	S	S	S	.	S	S	S	S	.	S	S	.	S	.	S	S	S	S	95.2
N_{tot}	A1N	S	S	S	.	S	S	S	.	.	S	S	S	U	.	S	S	.	S	.	.	S	S	S	81.0
	B2N	S	S	S	.	S	S	S	S	.	S	Q	S	U	.	.	S	.	S	.	.	S	S	.	85.0
	N3N	S	S	S	.	S	Q	S	S	.	S	S	S	U	.	S	S	.	S	.	.	S	S	S	90.5
pH	A1H	S	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	.	S	.	S	S	.	100
	N3H	S	S	S	q	S	S	Q	S	.	Q	S	S	S	.	S	S	S	.	.	S	S	S	S	83.3
P_{PO4}	A1P	q	q	u	.	S	S	S	.	.	S	S	S	S	S	U	S	.	.	.	.	q	S	S	73.7
	B2P	S	S	q	.	S	S	S	S	.	S	S	S	S	S	.	S	.	.	.	.	q	S	.	88.9
	N3P	S	S	S	.	S	S	S	S	.	S	S	S	S	.	S	S	.	.	.	.	S	u	q	88.9
$P_{PO4,\ dissolved}$	B4P	S	S	S	.	S	S	.	.	.	S	S	S	S	.	.	S	.	.	.	.	q	.	.	92.9
	N5P	S	q	q	.	S	S	.	.	.	S	S	S	S	.	S	S	.	.	.	.	S	.	S	86.7
P_{tot}	A1P	q	S	S	.	S	S	u	.	.	S	u	S	S	S	U	S	U	.	.	.	S	S	S	66.7
	B2P	S	S	S	.	S	S	S	S	.	S	S	S	S	S	.	S	S	.	.	.	S	S	.	95.0
	N3P	S	S	S	.	S	S	S	S	.	S	S	S	S	.	S	S	u	.	.	.	S	u	S	90.0
$P_{tot,\ dissolved}$	B4P	S	S	S	.	S	S	.	.	.	S	U	S	S	.	.	q	.	.	.	.	S	.	.	78.6
	N5P	q	u	u	.	u	S	.	.	.	S	S	S	Q	.	Q	S	.	.	.	.	S	.	S	60.0
%		86	89	61	67	86	89	86	100	67	89	82	96	75	83	82	93	78	78	100	100	86	89	94	
accredited		28	28	24	6	28	28		15	3	28	26	28	28		11	28	4	9	2		28	18	18	

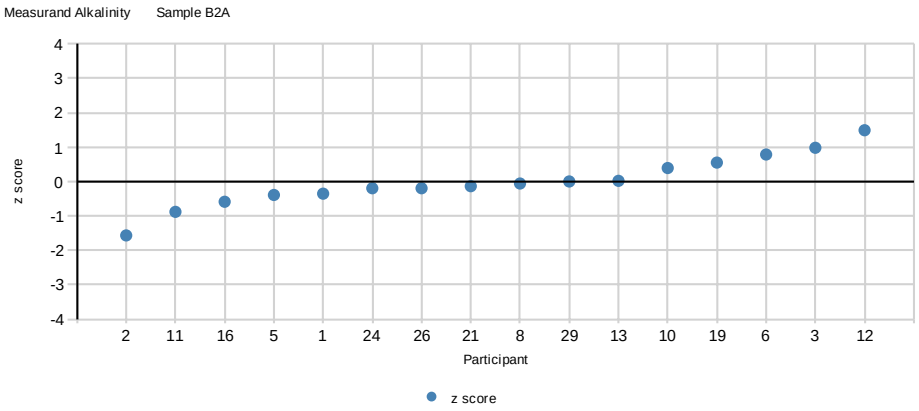
Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	%
Alkalinity	A1A	*U*	.	*S*	S	.	S	U	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	80.0
	B2A	*S*	.	*S*	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	N3A	*S*	.	*S*	S	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	95.0
Conductivity 25	A1J	*S*	.	*u*	S	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	91.7
	B2H	*S*	.	*u*	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	84.2
	N3H	*S*	.	*u*	*S*	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	87.0
N_{NH4}	A1N	.	*Q*	*U*	.	*S*	S	U	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	59.1
	B2N	.	*S*	*U*	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	68.4
	N3N	.	.	*S*	.	*S*	S	u	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.9
$N_{NO2+NO3}$	A1N	.	*S*	*S*	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	77.3
	B2N	.	*S*	*S*	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	80.0
	N3N	.	.	*S*	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	95.2
N_{tot}	A1N	*Q*	*S*	*u*	.	*u*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	81.0
	B2N	*Q*	*S*	*S*	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	85.0
	N3N	*S*	.	*S*	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.5
pH	A1H	*S*	*S*	*S*	S	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2H	*S*	*S*	*S*	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	N3H	*u*	.	*S*	S	.	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	83.3
P_{PO4}	A1P	.	*S*	.	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	73.7
	B2P	.	*S*	.	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	88.9
	N3P	.	.	.	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	88.9
$P_{PO4,\ dissolved}$	B4P	.	*S*	.	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	92.9
	N5P	.	.	.	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	86.7
P_{tot}	A1P	*q*	*S*	.	.	*Q*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	66.7
	B2P	*S*	*S*	.	.	*Q*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	95.0
	N3P	*S*	.	.	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.0
$P_{tot,\ dissolved}$	B4P	.	*S*	.	.	*Q*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	78.6
	N5P	.	.	.	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	60.0
%		67	93	67	100	80	100	63																	
accredited					5		29	8																	

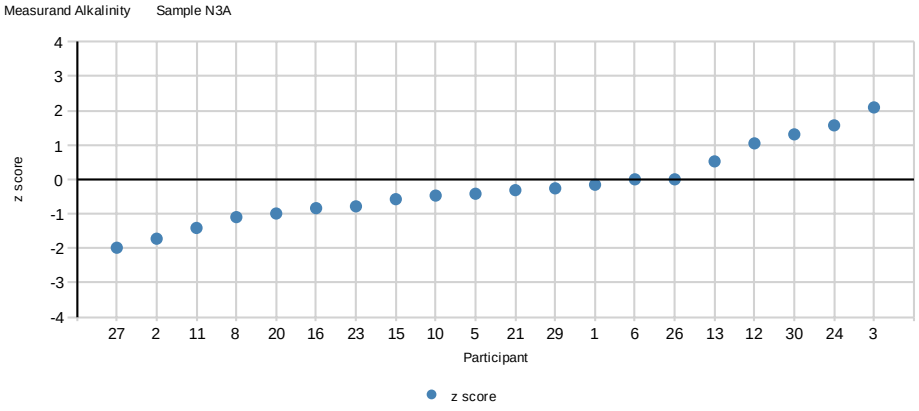
S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - other
% - percentage of satisfactory results

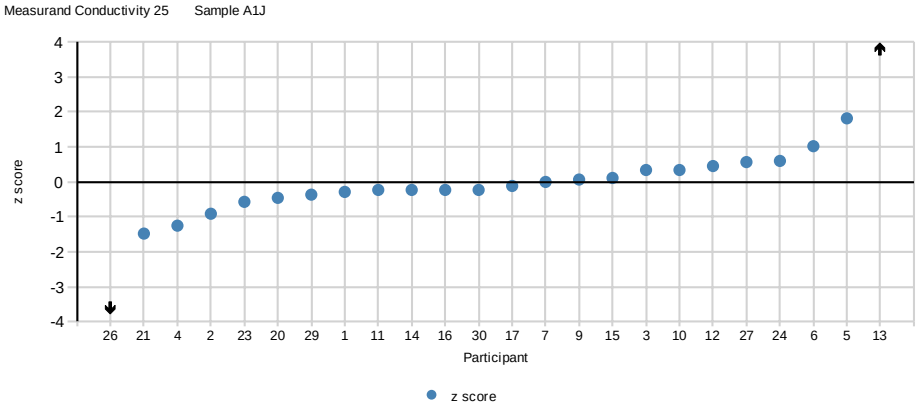
Totally satisfactory, % in all: 85 % in accredited: 87 % in non-accredited: 77

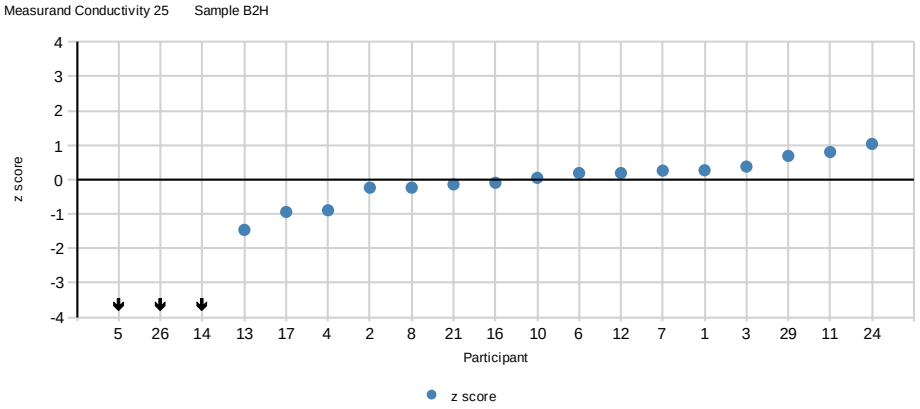
APPENDIX 11: z scores in ascending order

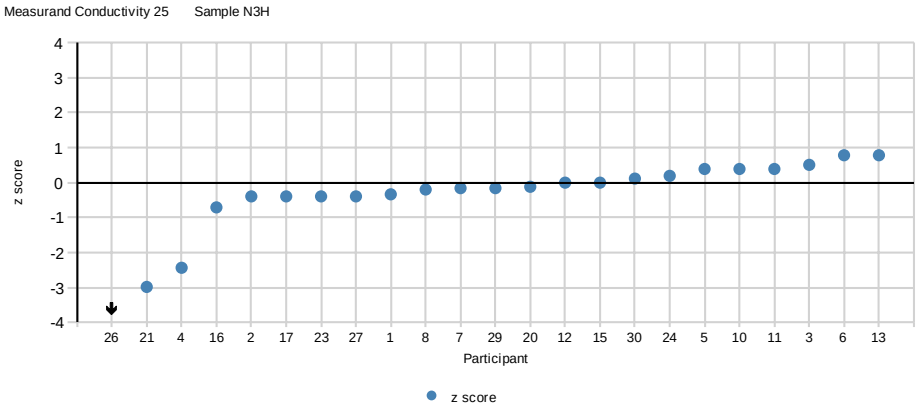


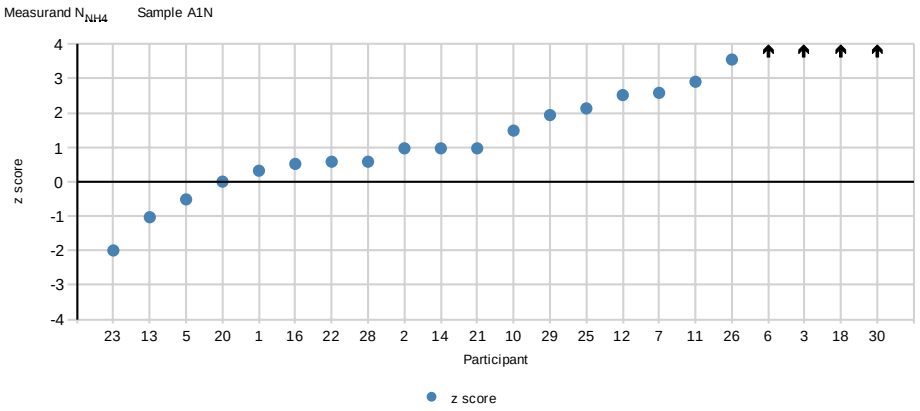


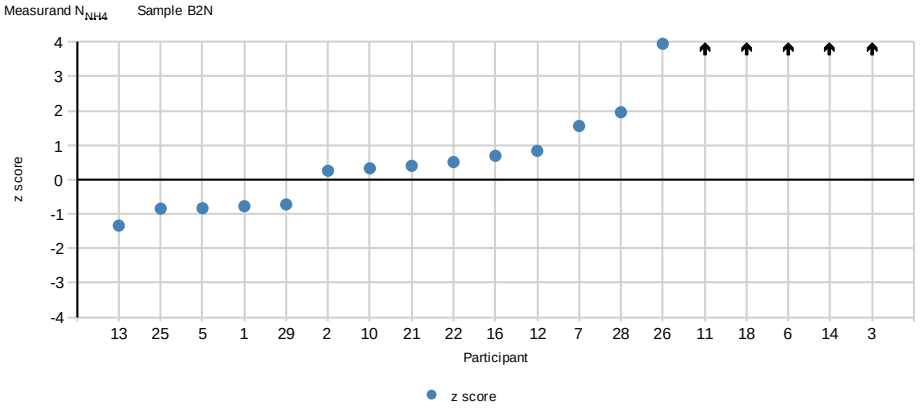


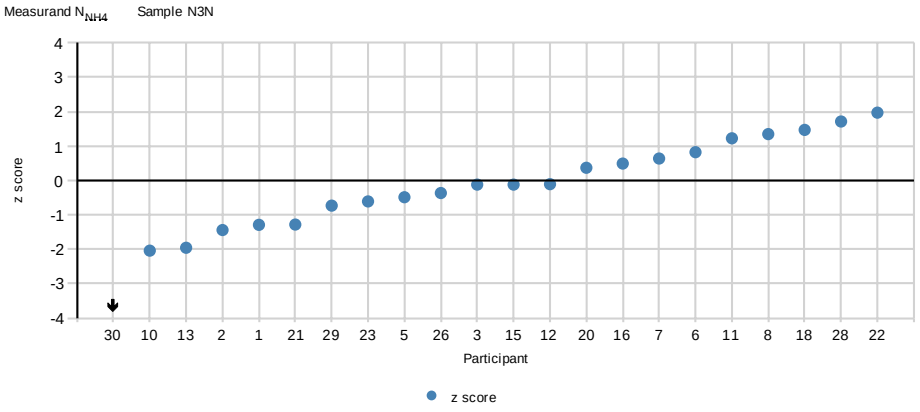

Measurand Conductivity 25 Sample A1J
z score
4
3
2
1
0
-1
-2
-3
-4
26 21 4 2 23 20 29 1 11 14 16 30 17 7 9 15 3 10 12 27 24 6 5 13
Participant
z score

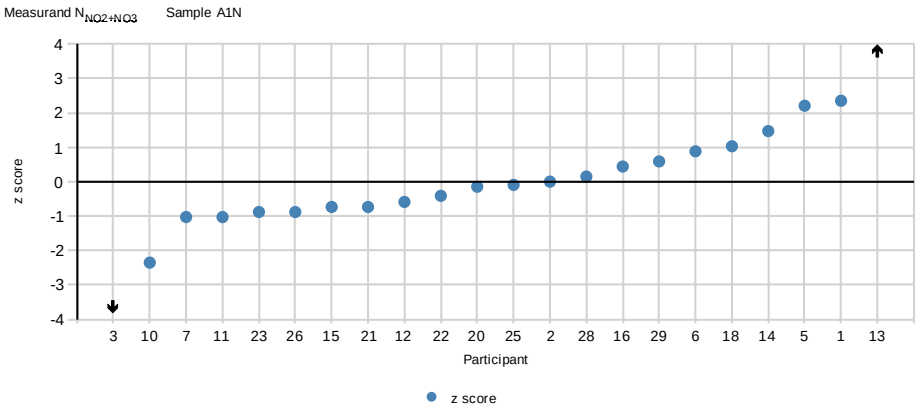

Measurand Conductivity 25 Sample B2H
z score
4
3
2
1
0
-1
-2
-3
-4
5 26 14 13 17 4 2 8 21 16 10 6 12 7 1 3 29 11 24
Participant
z score

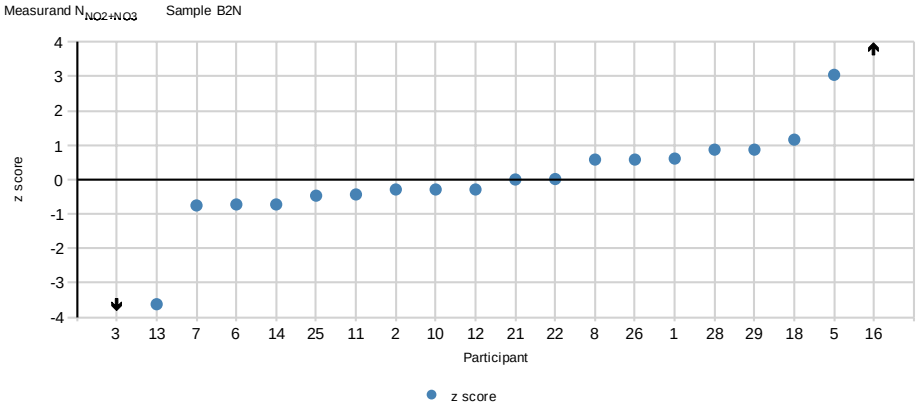

Measurand Conductivity 25 Sample N3H
z score
4
3
2
1
0
-1
-2
-3
-4
26 21 4 16 2 17 23 27 1 8 7 29 20 12 15 30 24 5 10 11 3 6 13
Participant
z score

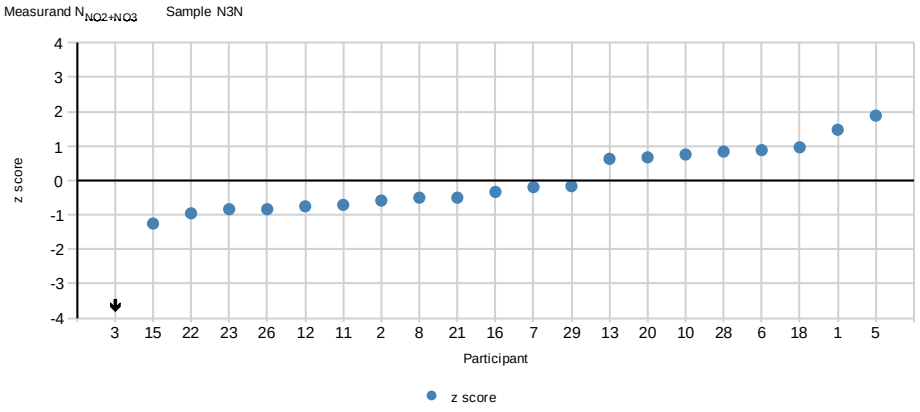

Measurand N_{NH4}
Sample A1N
z score
4
3
2
1
0
-1
-2
-3
-4
23 13 5 20 1 16 22 28 2 14 21 10 29 25 12 7 11 26 6 3 18 30
Participant
z score

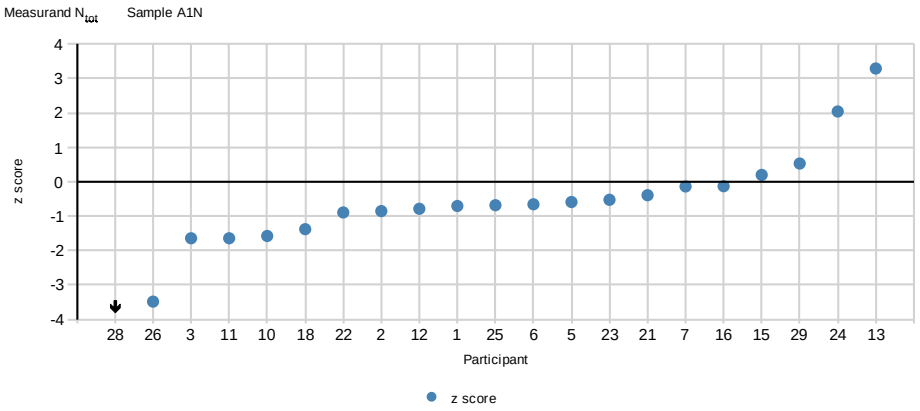

Measurand N_{NH4}
Sample B2N
z score
4
3
2
1
0
-1
-2
-3
-4
13 25 5 1 29 2 10 21 22 16 12 7 28 26 11 18 6 14 3
Participant
z score

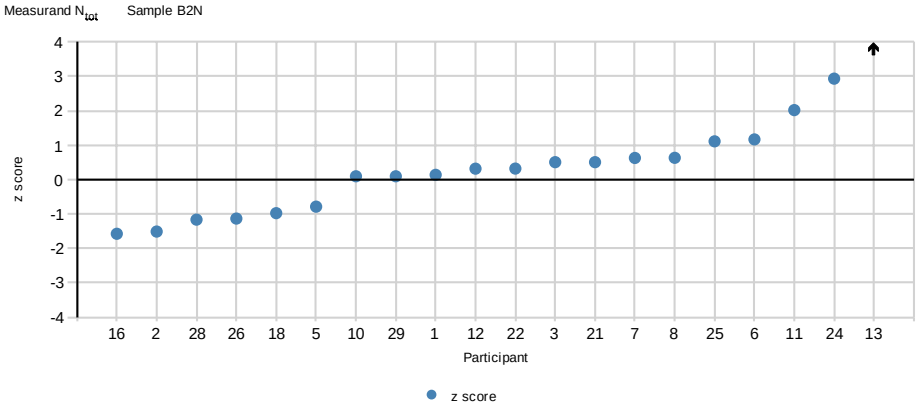

Measurand N_{NH4}
Sample N3N
z score
4
3
2
1
0
-1
-2
-3
-4
30 10 13 2 1 21 29 23 5 26 3 15 12 20 16 7 6 11 8 18 28 22
Participant
z score

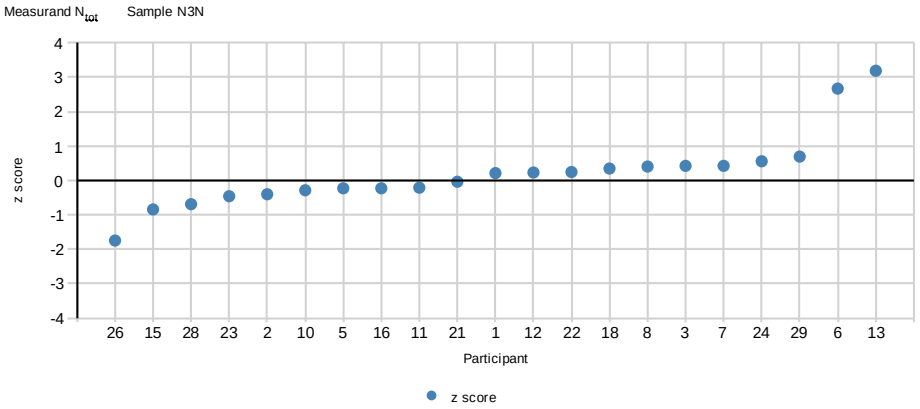

Measurand $N_{NO2+NO3}$
Sample A1N
z score
4
3
2
1
0
-1
-2
-3
-4
3 10 7 11 23 26 15 21 12 22 20 25 2 28 16 29 6 18 14 5 1 13
Participant
z score

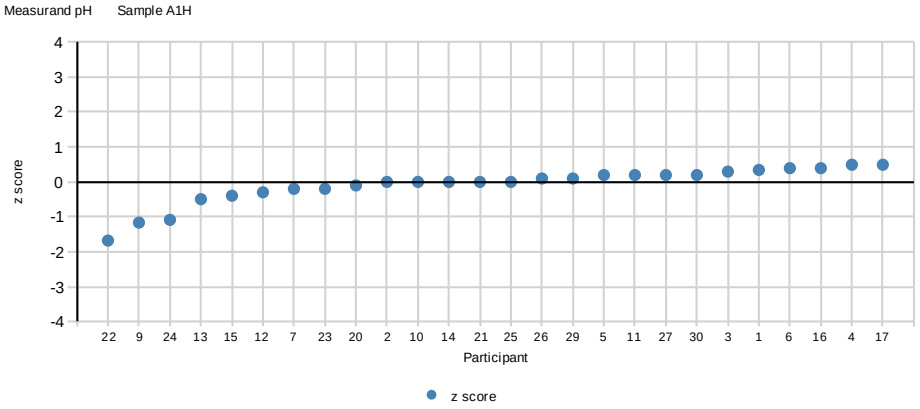

Measurand $N_{NO2+NO3}$
Sample B2N
z score
4
3
2
1
0
-1
-2
-3
-4
3 13 7 6 14 25 11 2 10 12 21 22 8 26 1 28 29 18 5 16
Participant
z score

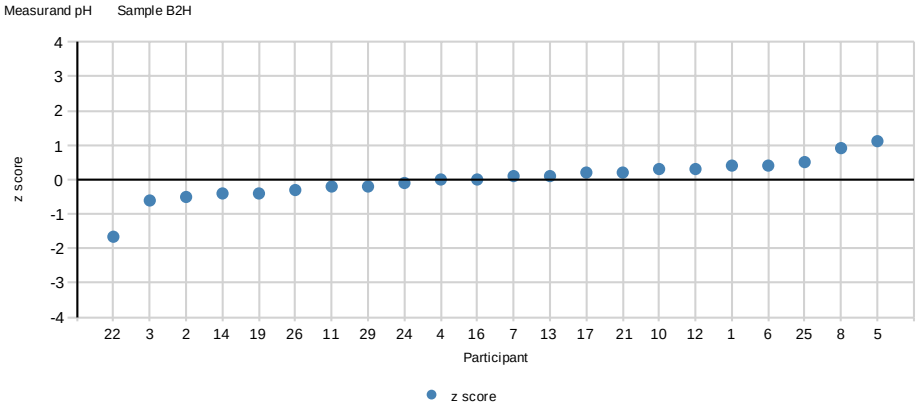

Measurand $N_{NO2+NO3}$
Sample N3N
z score
4
3
2
1
0
-1
-2
-3
-4
3 15 22 23 26 12 11 2 8 21 16 7 29 13 20 10 28 6 18 1 5
Participant
z score

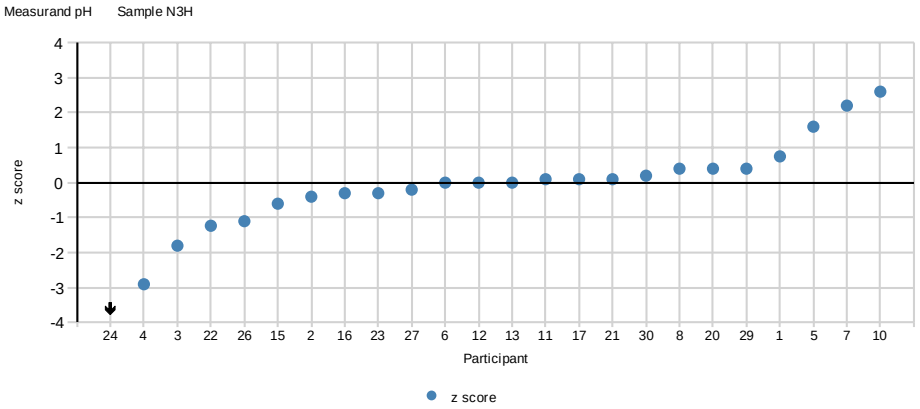

Measurand N_{tot}
Sample A1N
z score
4
3
2
1
0
-1
-2
-3
-4
28 26 3 11 10 18 22 2 12 1 25 6 5 23 21 7 16 15 29 24 13
Participant
z score

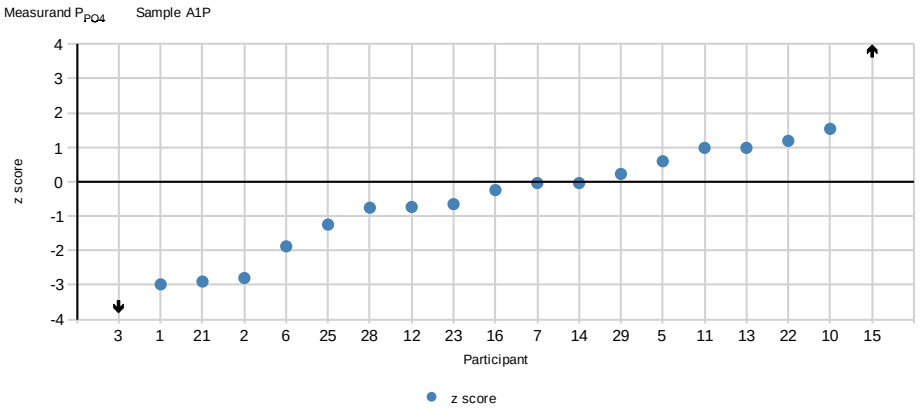

Measurand N_{tot}
Sample B2N
z score
4
3
2
1
0
-1
-2
-3
-4
16 2 28 26 18 5 10 29 1 12 22 3 21 7 8 25 6 11 24 13
Participant
z score

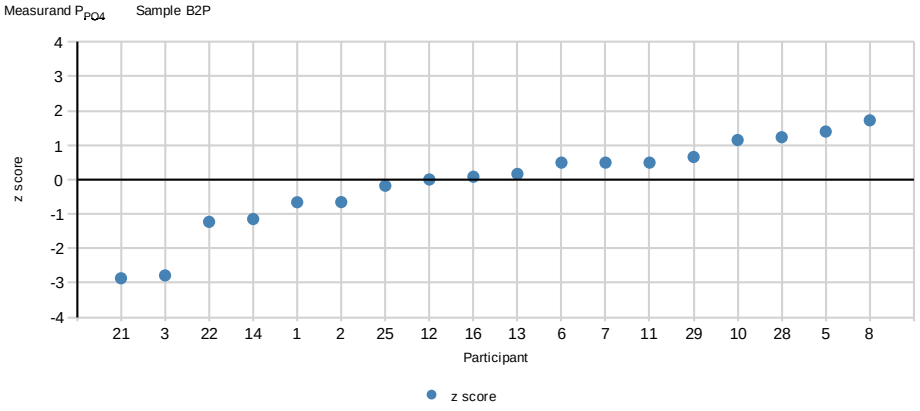

Measurand N_{tot}
Sample N3N
z score
4
3
2
1
0
-1
-2
-3
-4
26 15 28 23 2 10 5 16 11 21 1 12 22 18 8 3 7 24 29 6 13
Participant
z score

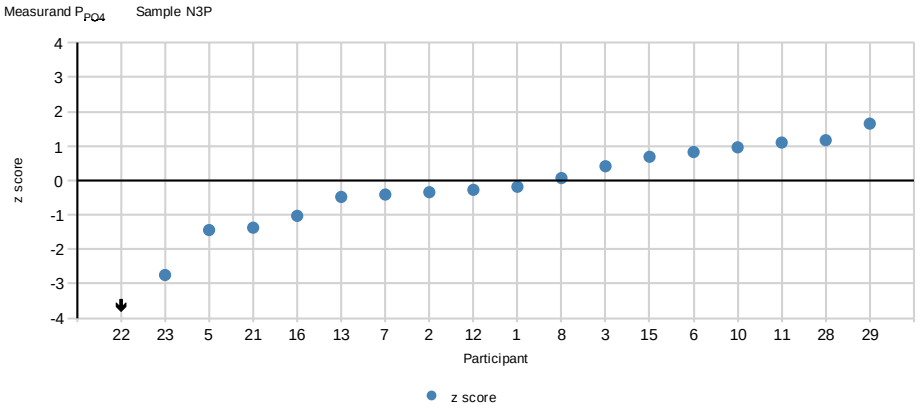

Measurand pH Sample A1H
z score
4
3
2
1
0
-1
-2
-3
-4
22 9 24 13 15 12 7 23 20 2 10 14 21 25 26 29 5 11 27 30 3 1 6 16 4 17
Participant
z score

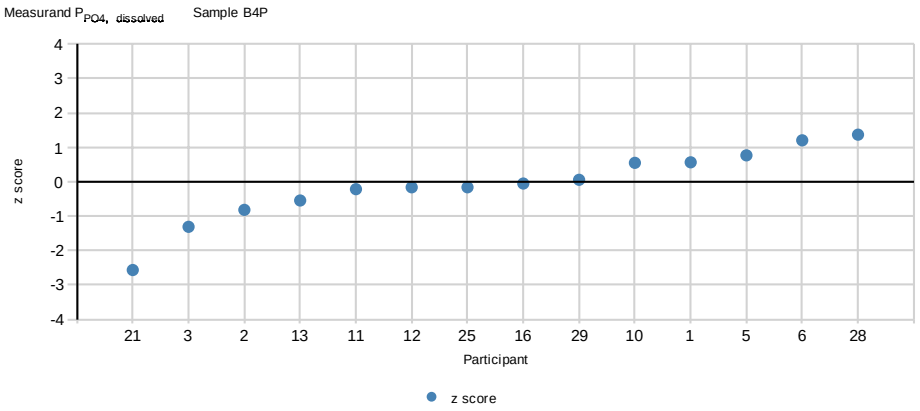

Measurand pH Sample B2H
z score
4
3
2
1
0
-1
-2
-3
-4
22 3 2 14 19 26 11 29 24 4 16 7 13 17 21 10 12 1 6 25 8 5
Participant
z score

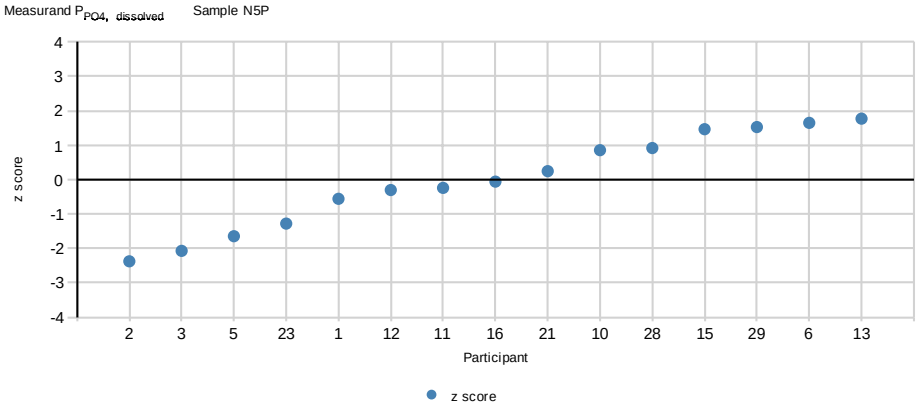

Measurand pH Sample N3H
z score
4
3
2
1
0
-1
-2
-3
-4
24 4 3 22 26 15 2 16 23 27 6 12 13 11 17 21 30 8 20 29 1 5 7 10
Participant
z score

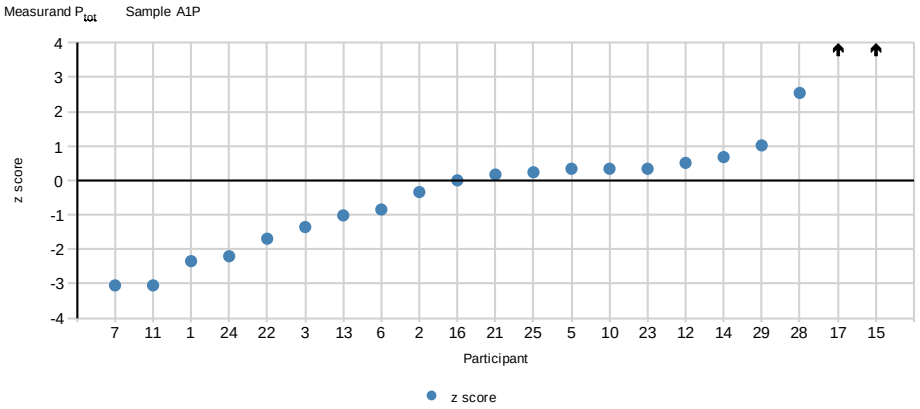

Measurand P_{PO4}
Sample A1P
z score
4
3
2
1
0
-1
-2
-3
-4
3 1 21 2 6 25 28 12 23 16 7 14 29 5 11 13 22 10 15
Participant
z score

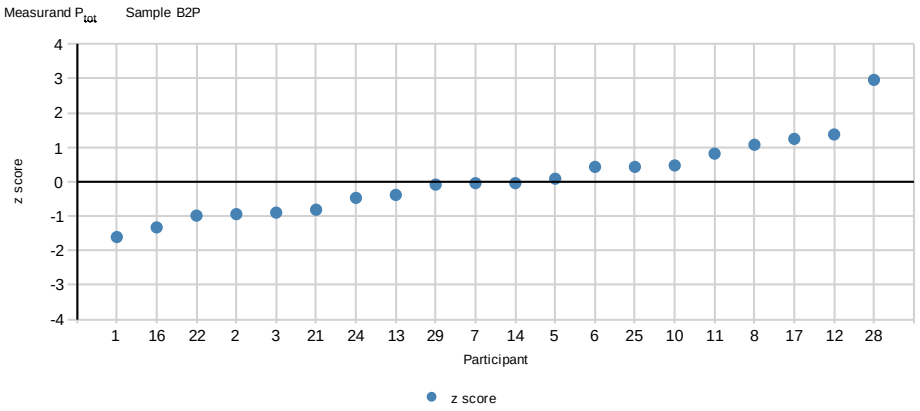

Measurand P_{PO4}
Sample B2P
z score
4
3
2
1
0
-1
-2
-3
-4
21 3 22 14 1 2 25 12 16 13 6 7 11 29 10 28 5 8
Participant
z score

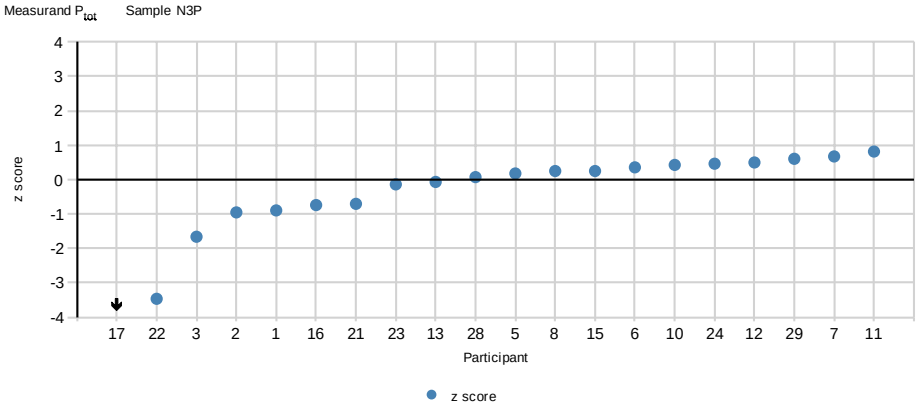

Measurand P_{PO4}
Sample N3P
z score
4
3
2
1
0
-1
-2
-3
-4
22 23 5 21 16 13 7 2 12 1 8 3 15 6 10 11 28 29
Participant
z score

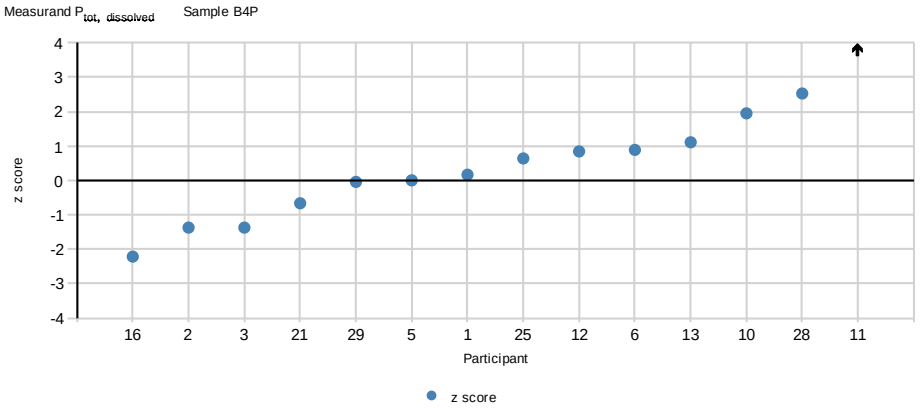

Measurand $P_{PO4,\ dissolved}$ Sample B4P
z score
4
3
2
1
0
-1
-2
-3
-4
21 3 2 13 11 12 25 16 29 10 1 5 6 28
Participant
z score

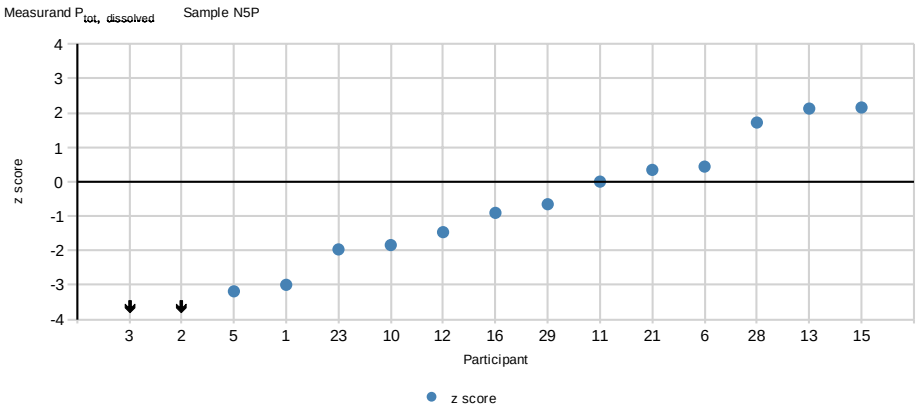

Measurand $P_{PO4,\ dissolved}$ Sample N5P
z score
4
3
2
1
0
-1
-2
-3
-4
2 3 5 23 1 12 11 16 21 10 28 15 29 6 13
Participant
z score


Measurand P_{tot} Sample A1P
z score
4
3
2
1
0
-1
-2
-3
-4
7 11 1 24 22 3 13 6 2 16 21 25 5 10 23 12 14 29 28 17 15
Participant
z score


Measurand P_{tot} Sample B2P
z score
4
3
2
1
0
-1
-2
-3
-4
1 16 22 2 3 21 24 13 29 7 14 5 6 25 10 11 8 17 12 28
Participant
z score

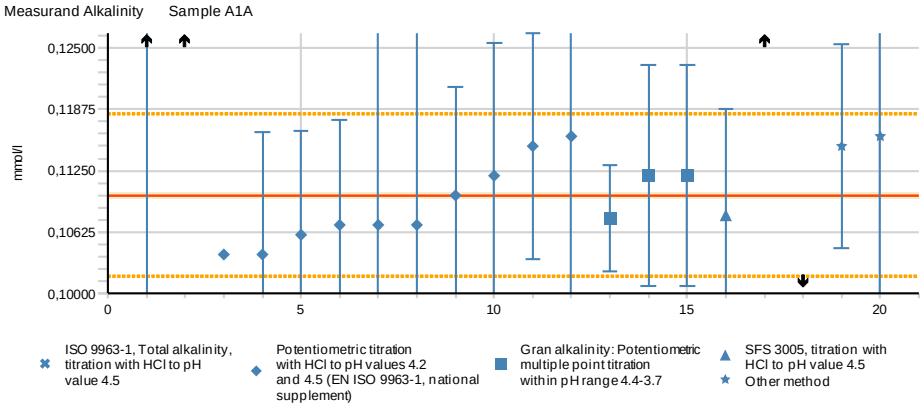

Measurand P_{tot} Sample N3P
z score
4
3
2
1
0
-1
-2
-3
-4
17 22 3 2 1 16 21 23 13 28 5 8 15 6 10 24 12 29 7 11
Participant
z score

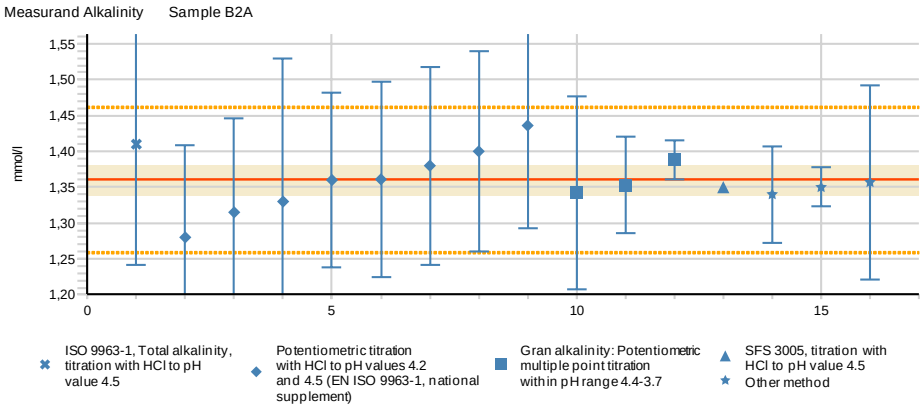

Measurand $P_{tot,\ dissolved}$ Sample B4P
z score
4
3
2
1
0
-1
-2
-3
-4
16 2 3 21 29 5 1 25 12 6 13 10 28 11
Participant
z score

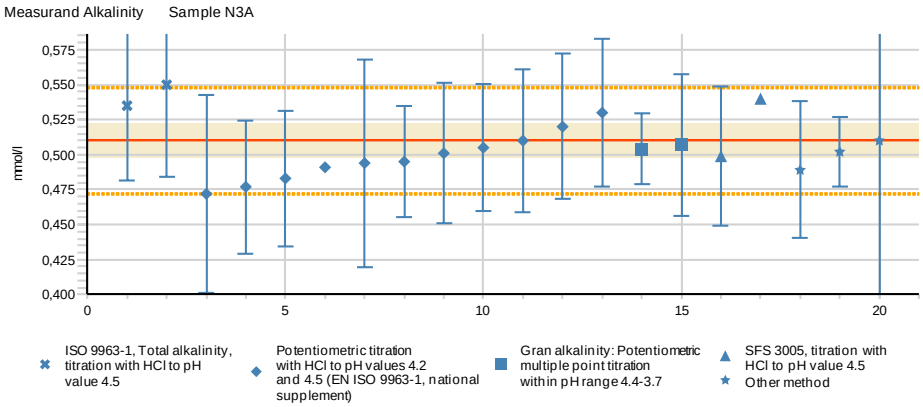

Measurand P tot, dissolved
Sample N5P
z score
4
3
2
1
0
-1
-2
-3
-4
3
2
5
1
23
10
12
16
29
11
21
6
28
13
15
Participant
z score

APPENDIX 12: Results grouped according to the methods

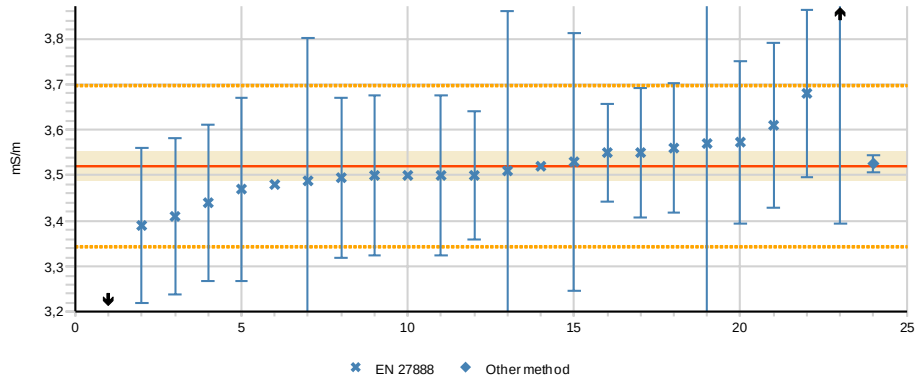
The explanations for the figures are described in the Appendix 9.



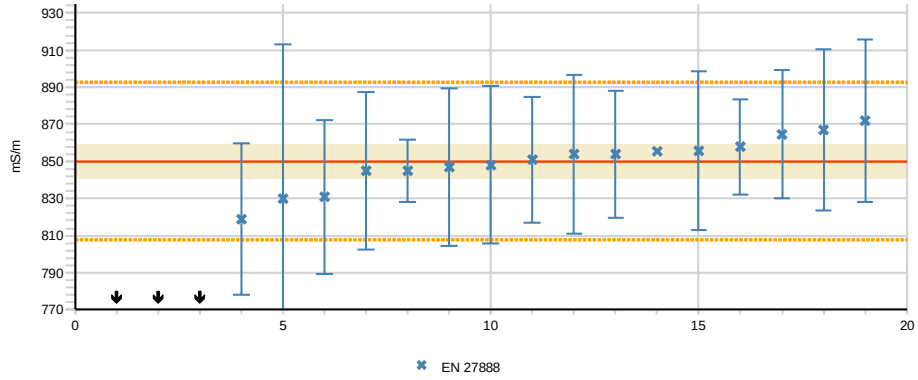




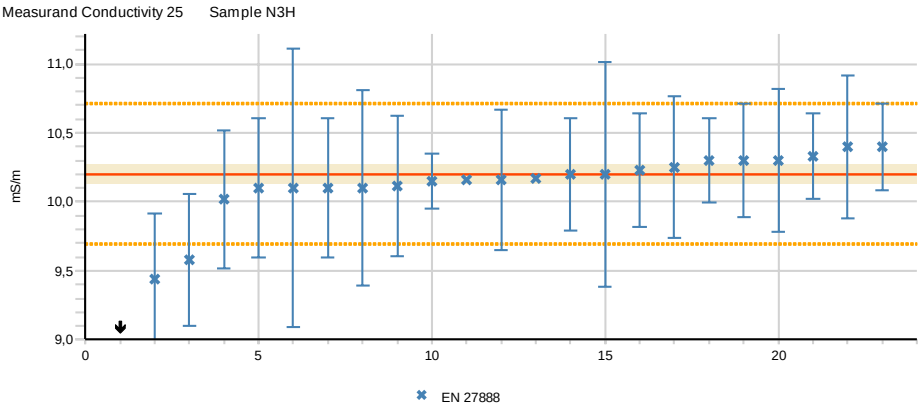
Measurand Conductivity 25 Sample A1J

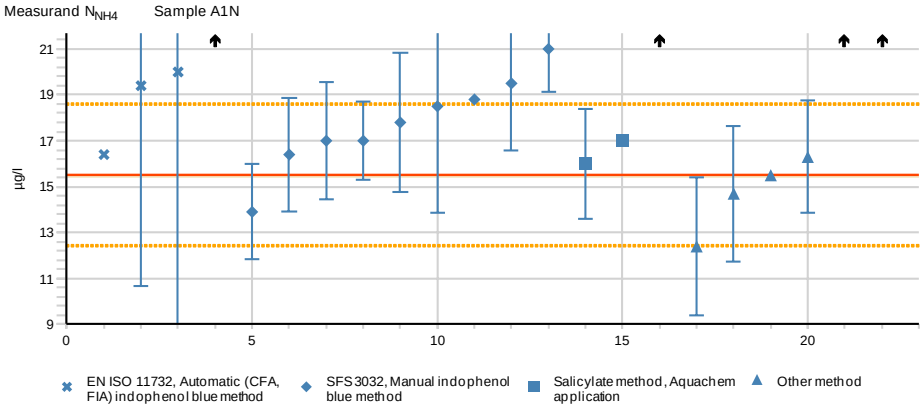


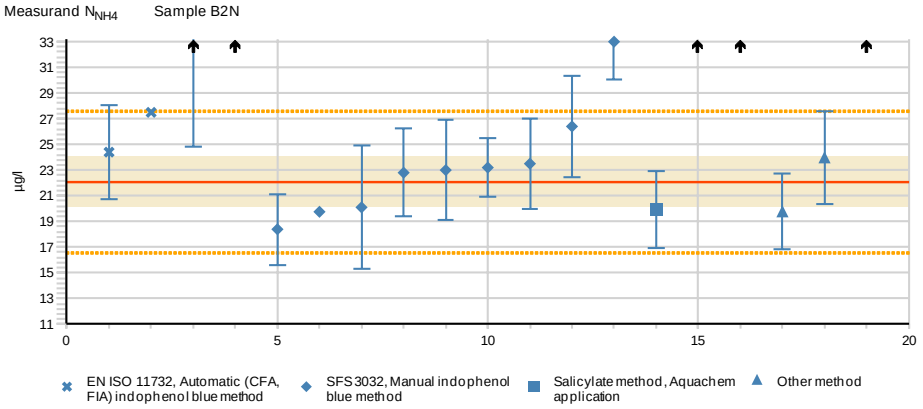
Measurand Conductivity 25 Sample B2H

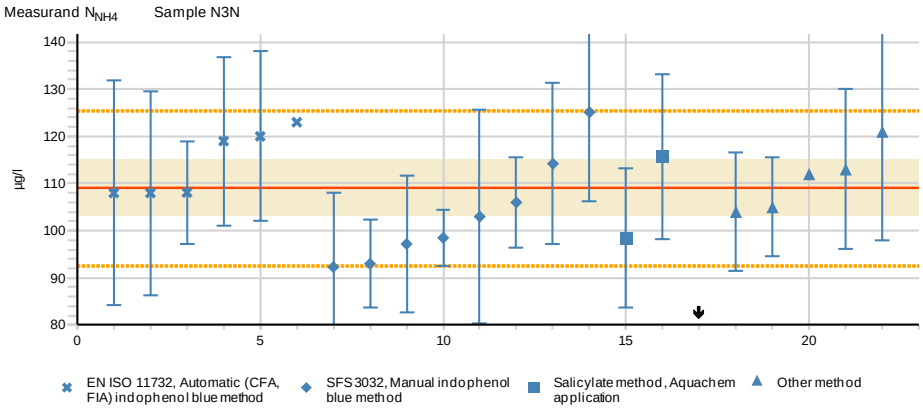


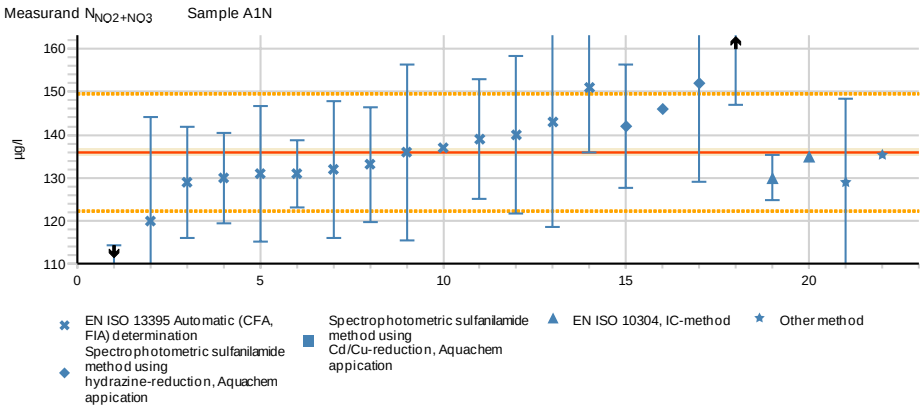
Measurand Conductivity 25 Sample N3H

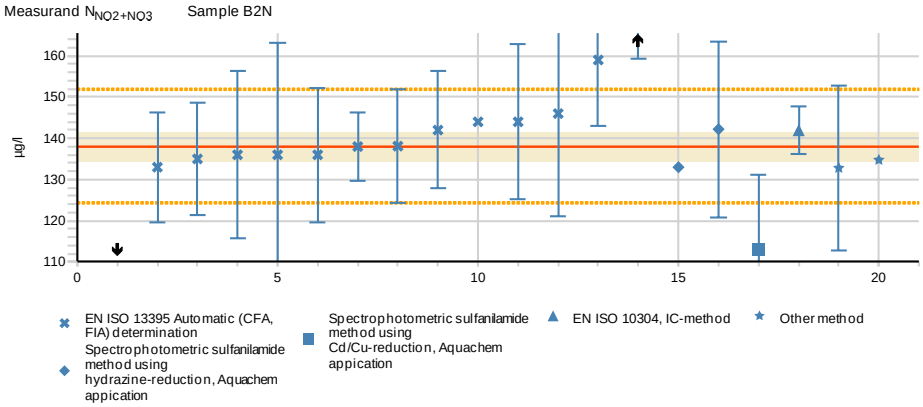


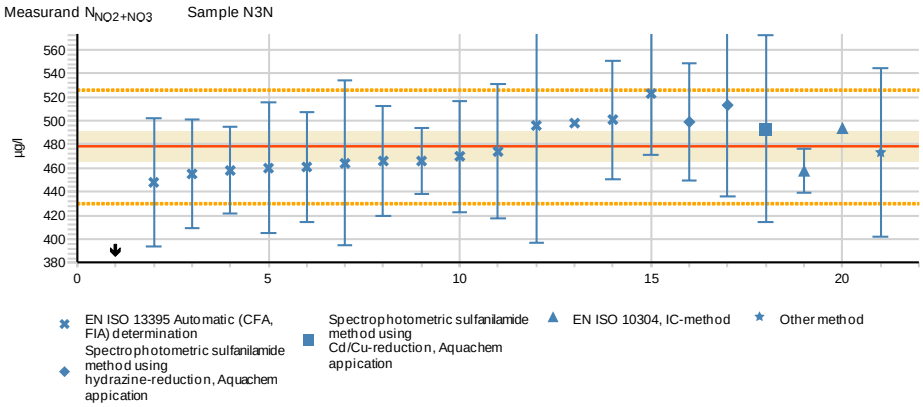

Measurand N_{NH4}
Sample A1N
µg/l
21
19
17
15
13
11
9
0
5
10
15
20
EN ISO 11732, Automatic (CFA, FIA) indophenol blue method
SFS 3032, Manual indophenol blue method
Salicylate method, Aquachem application
Other method

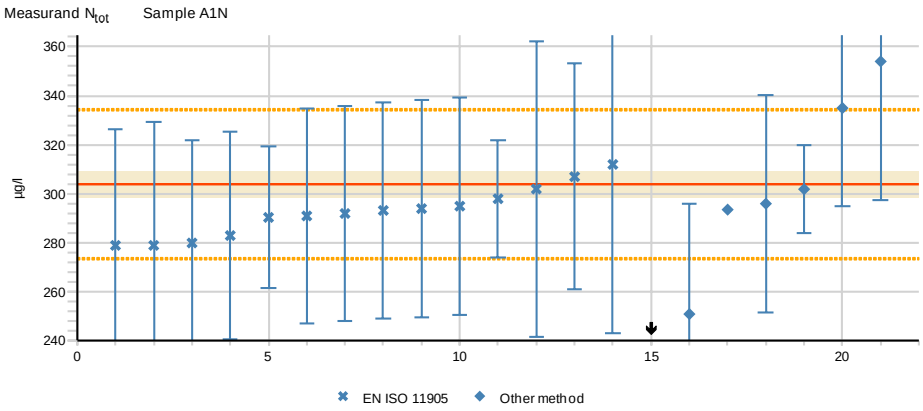

Measurand N_{NH4}
Sample B2N
µg/l
33
31
29
27
25
23
21
19
17
15
13
11
0
5
10
15
20
EN ISO 11732, Automatic (CFA, FIA) indophenol blue method
SFS 3032, Manual indophenol blue method
Salicylate method, Aquachem application
Other method

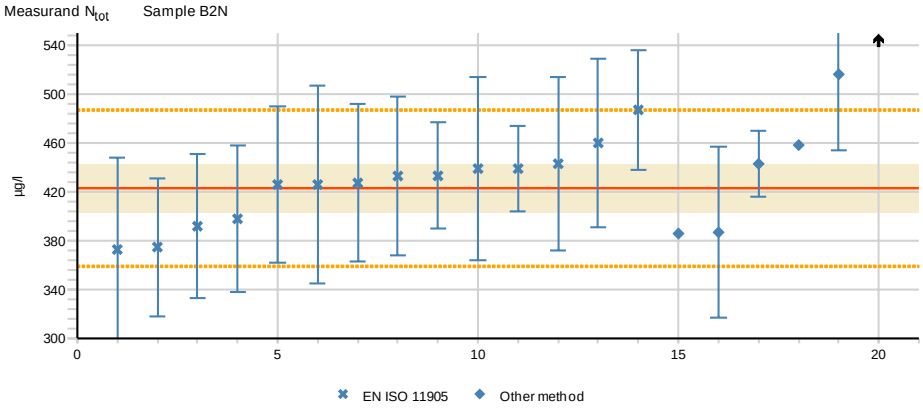

Measurand N_{NH4}
Sample N3N
µg/l
140
130
120
110
100
90
80
0
5
10
15
20
EN ISO 11732, Automatic (CFA, FIA) indophenol blue method
SFS 3032, Manual indophenol blue method
Salicylate method, Aquachem application
Other method

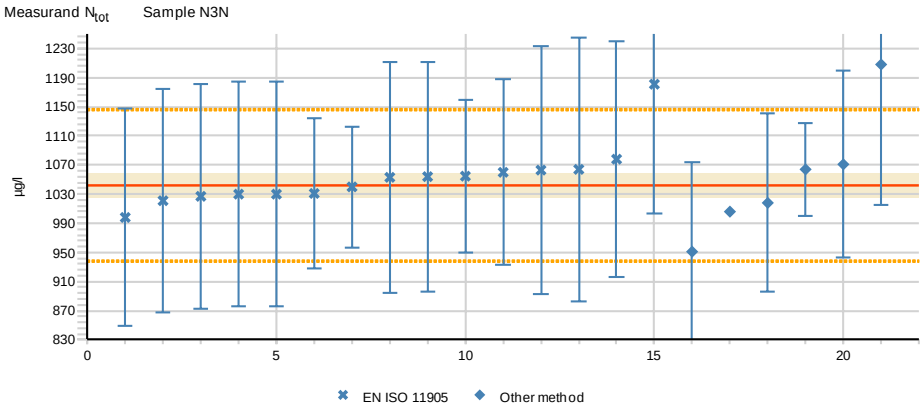

Measurand $N_{NO2+NO3}$
Sample A1N
µg/l
160
150
140
130
120
110
0
5
10
15
20
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
Spectrophotometric sulfanilamide method using Cd/Cu-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method

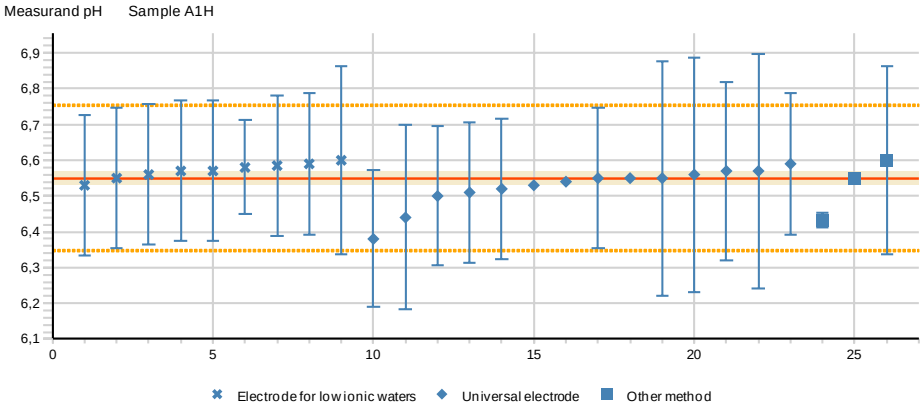

Measurand $N_{NO2+NO3}$
Sample B2N
µg/l
160
150
140
130
120
110
0
5
10
15
20
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
Spectrophotometric sulfanilamide method using Cd/Cu-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method

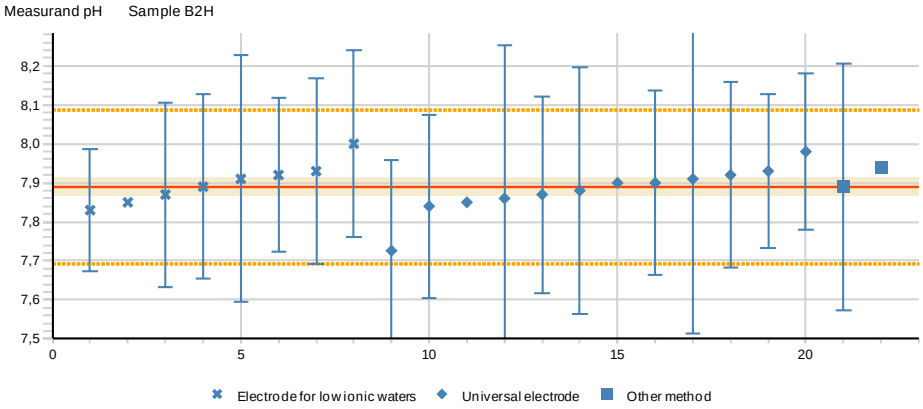

Measurand $N_{NO2+NO3}$
Sample N3N
µg/l
560
540
520
500
480
460
440
420
400
380
0
5
10
15
20
EN ISO 13395 Automatic (CFA, FIA) determination
Spectrophotometric sulfanilamide method using hydrazine-reduction, Aquachem appication
Spectrophotometric sulfanilamide method using Cd/Cu-reduction, Aquachem appication
EN ISO 10304, IC-method
Other method

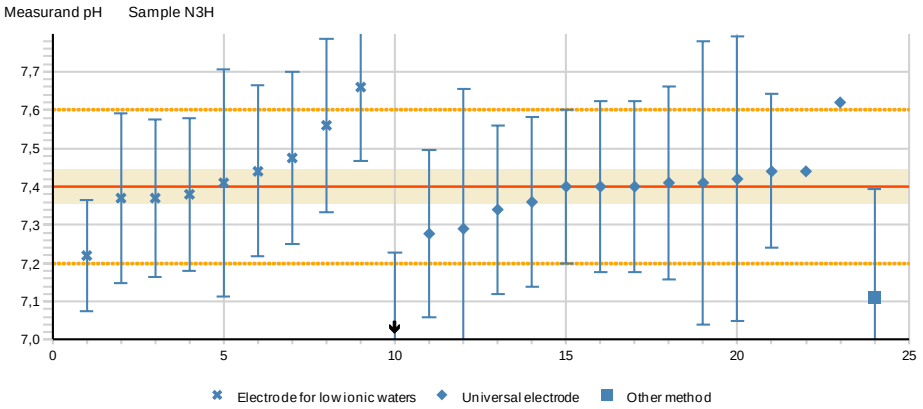

Measurand N_{tot}
Sample A1N
µg/l
360
340
320
300
280
260
240
0
5
10
15
20
EN ISO 11905
Other method

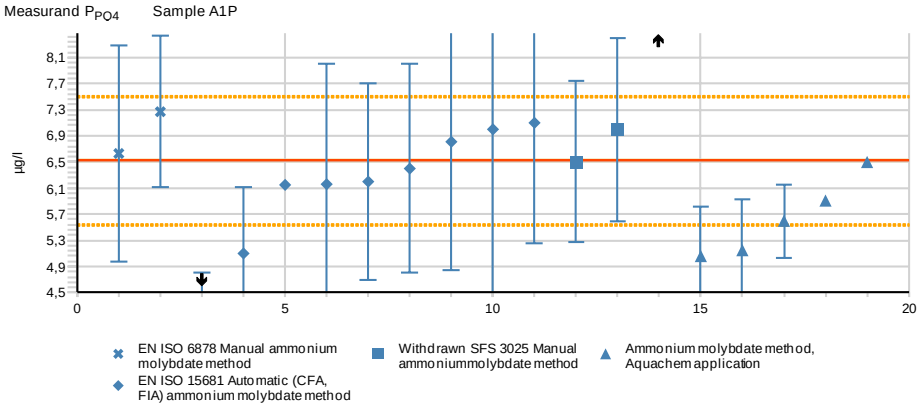

Measurand N_{tot}
Sample B2N
µg/l
540
500
460
420
380
340
300
0
5
10
15
20
EN ISO 11905
Other method

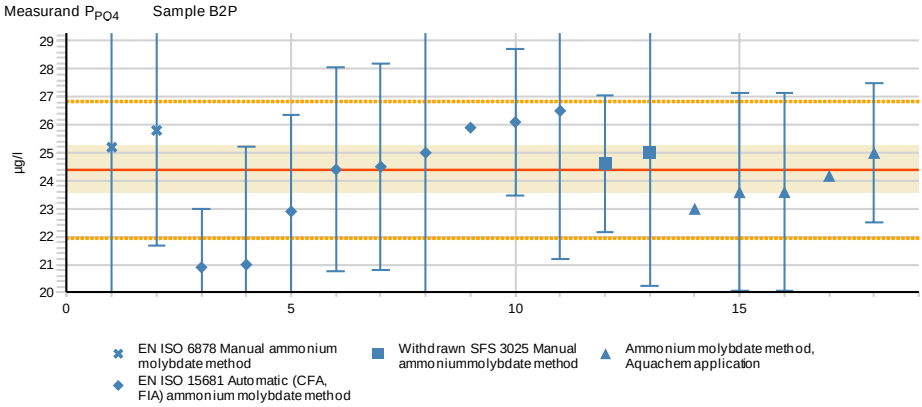

Measurand N_{tot}
Sample N3N
µg/l
1230
1190
1150
1110
1070
1030
990
950
910
870
830
0
5
10
15
20
EN ISO 11905
Other method

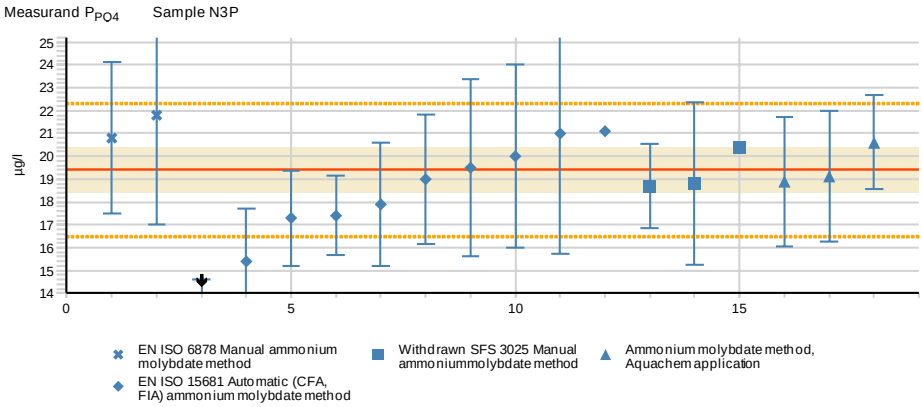

Measurand pH Sample A1H
6,9
6,8
6,7
6,6
6,5
6,4
6,3
6,2
6,1
0
5
10
15
20
25
Electrode for low ionic waters
Universal electrode
Other method

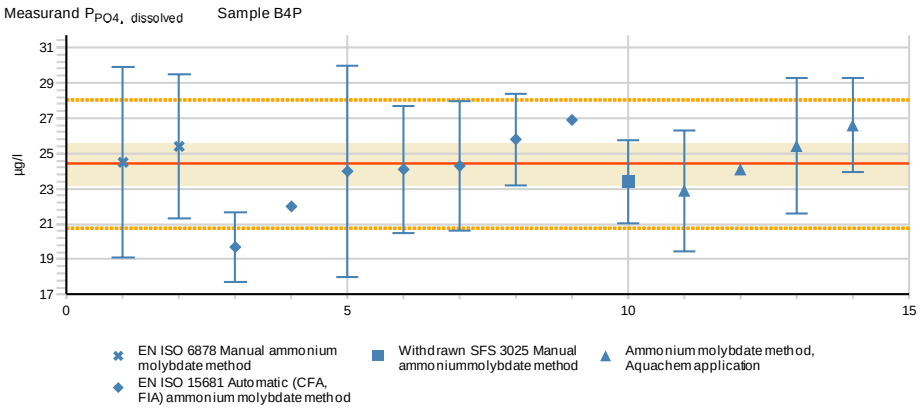

Measurand pH Sample B2H
8,2
8,1
8,0
7,9
7,8
7,7
7,6
7,5
0
5
10
15
20
Electrode for low ionic waters
Universal electrode
Other method

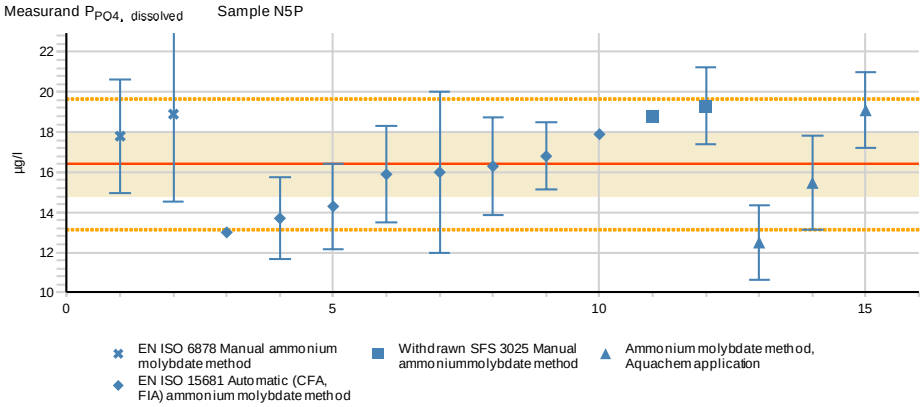

Measurand pH Sample N3H
7,7
7,6
7,5
7,4
7,3
7,2
7,1
7,0
0
5
10
15
20
25
Electrode for low ionic waters
Universal electrode
Other method

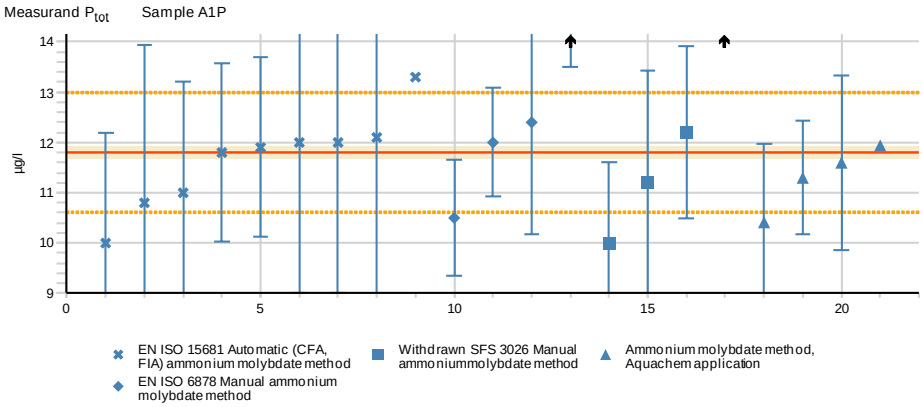

Measurand P_{PO4}
Sample A1P
µg/l
8,1
7,7
7,3
6,9
6,5
6,1
5,7
5,3
4,9
4,5
0
5
10
15
20
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method


Measurand P_{PO4}
Sample B2P
µg/l
29
28
27
26
25
24
23
22
21
20
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method

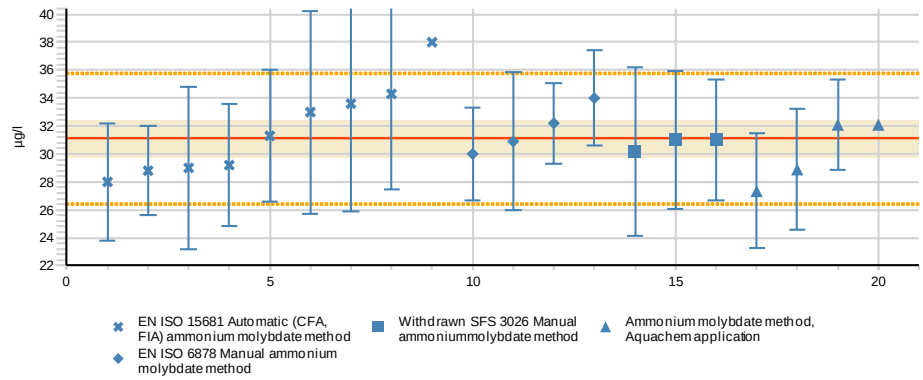

Measurand P_{PO4}
Sample N3P
µg/l
25
24
23
22
21
20
19
18
17
16
15
14
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method


Measurand $P_{PO4,\ dissolved}$ Sample B4P
µg/l
31
29
27
25
23
21
19
17
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method

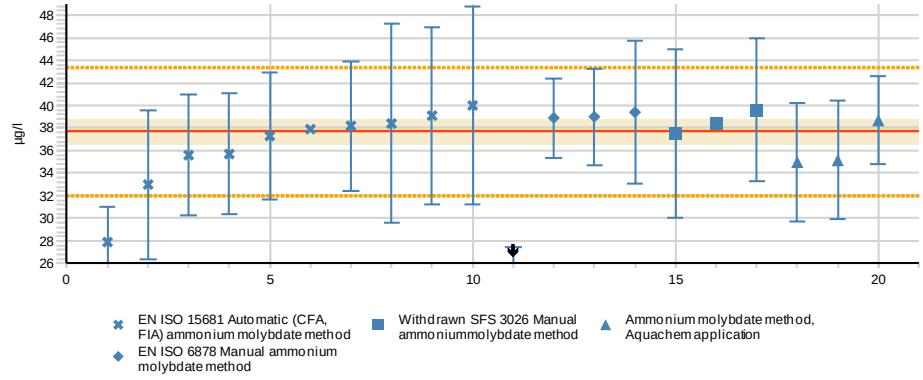

Measurand $P_{PO4,\ dissolved}$ Sample N5P
µg/l
22
20
18
16
14
12
10
0
5
10
15
EN ISO 6878 Manual ammonium molybdate method
Withdrawn SFS 3025 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method


Measurand P_{tot} Sample A1P
µg/l
14
13
12
11
10
9
0
5
10
15
20
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

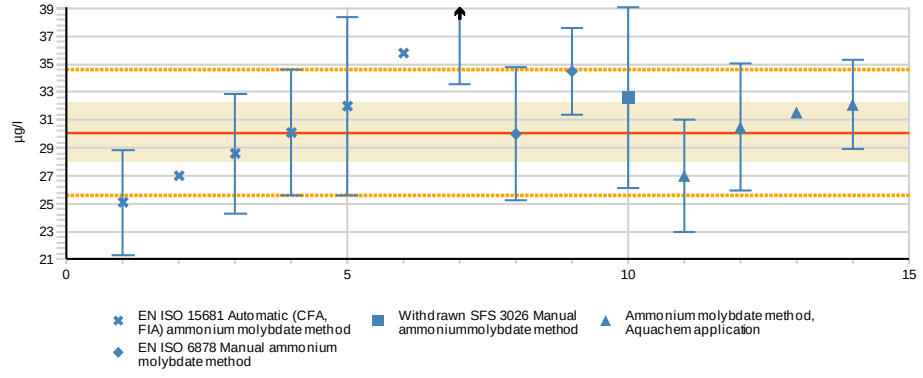
Measurand P_{tot} Sample B2P

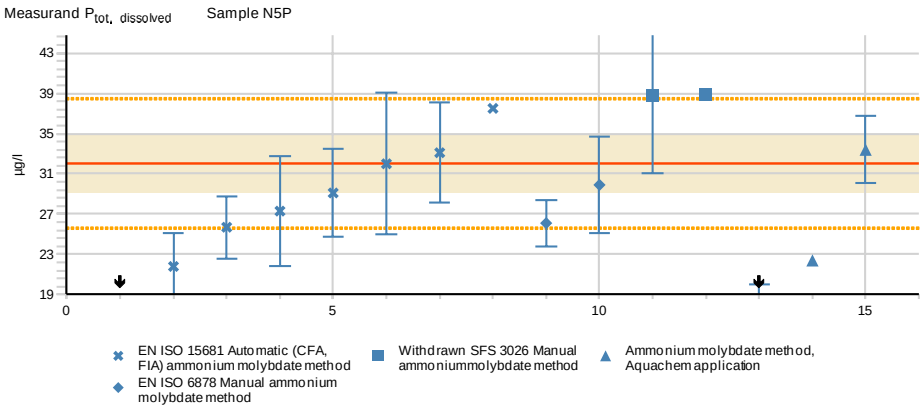


Measurand P_{tot} Sample N3P



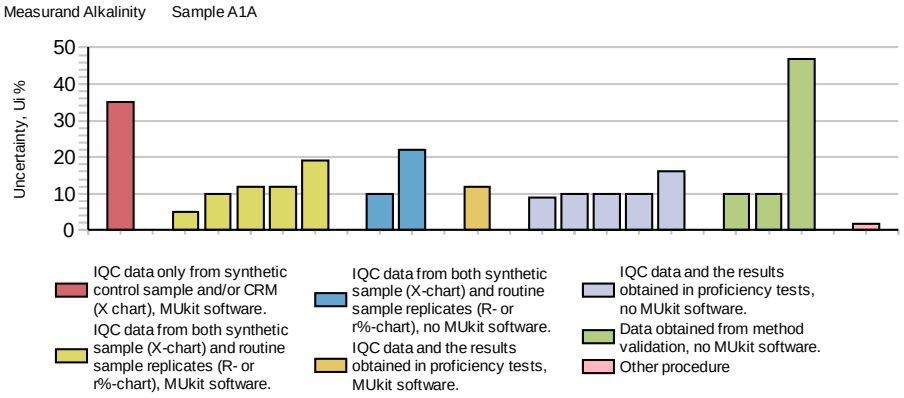
Measurand $P_{tot,\ dissolved}$ Sample B4P

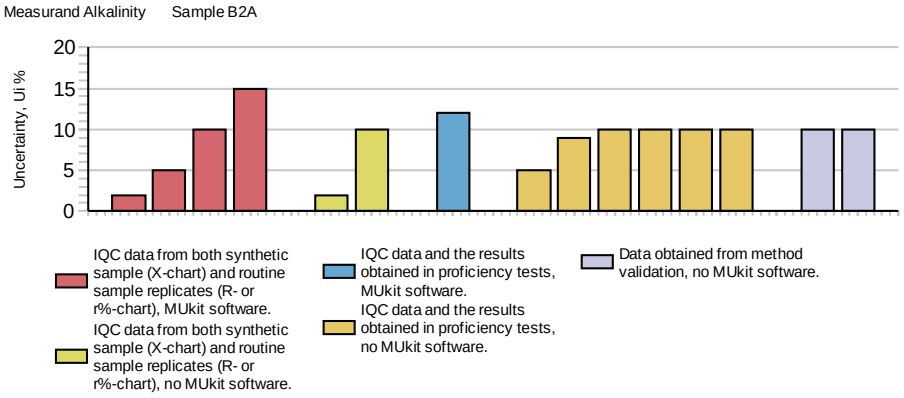


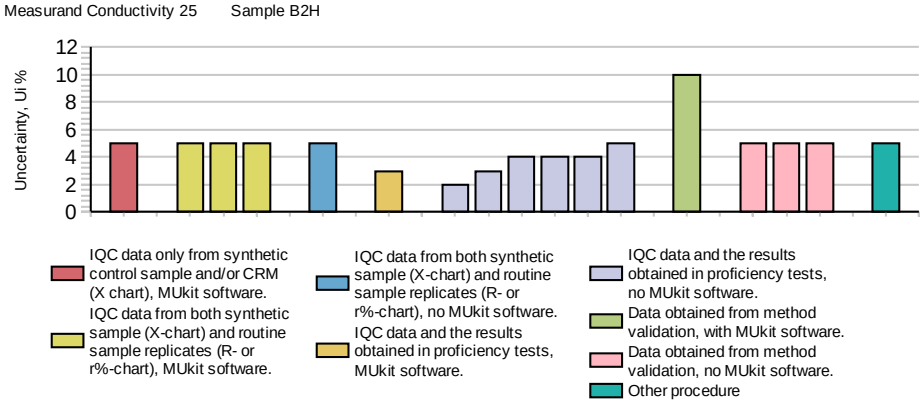

Measurand $P_{tot,\ dissolved}$
Sample N5P
µg/l
43
39
35
31
27
23
19
0
5
10
15
EN ISO 15681 Automatic (CFA, FIA) ammonium molybdate method
Withdrawn SFS 3026 Manual ammoniummolybdate method
Ammonium molybdate method, Aquachem application
EN ISO 6878 Manual ammonium molybdate method

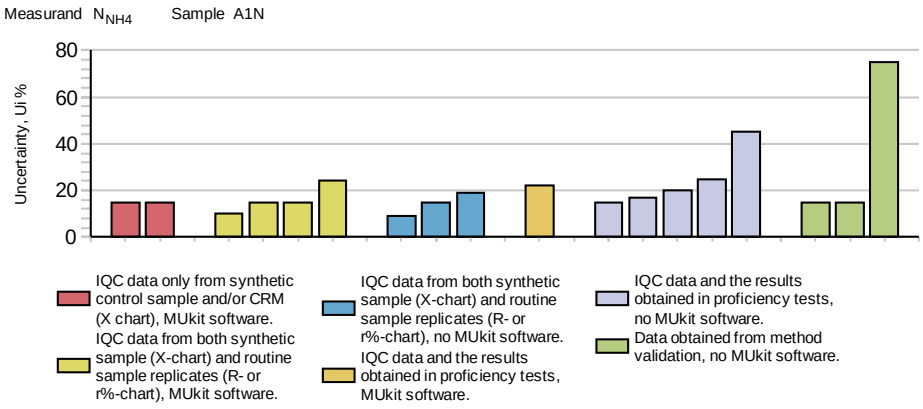
APPENDIX 13: Examples of measurement uncertainties reported by the participants

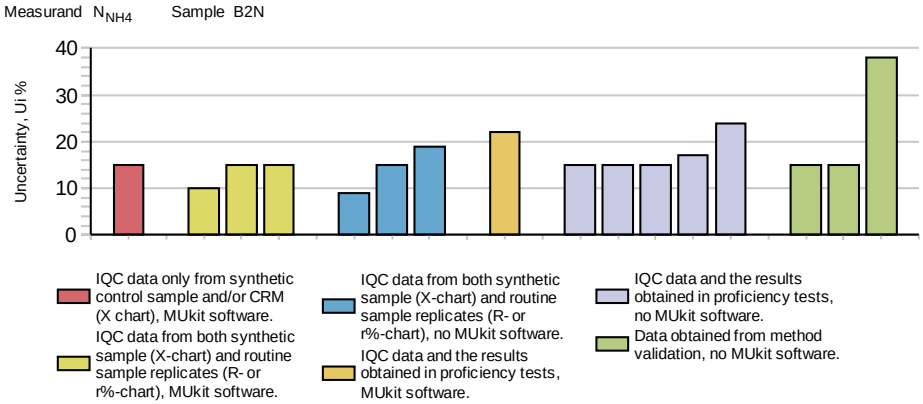
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [7, 9].

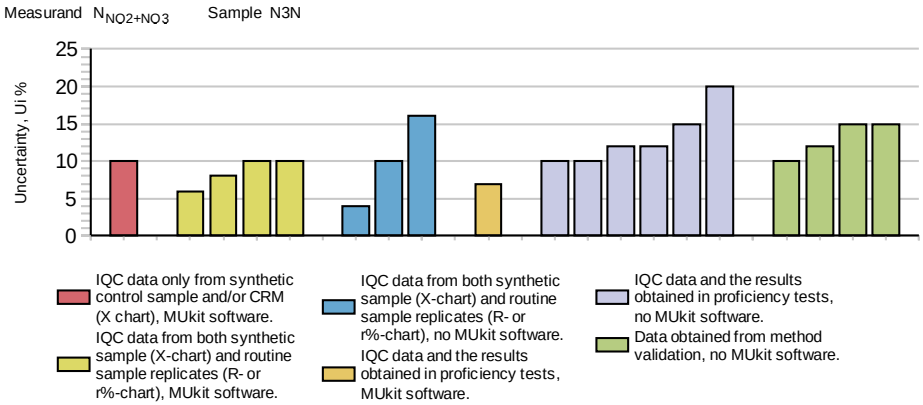




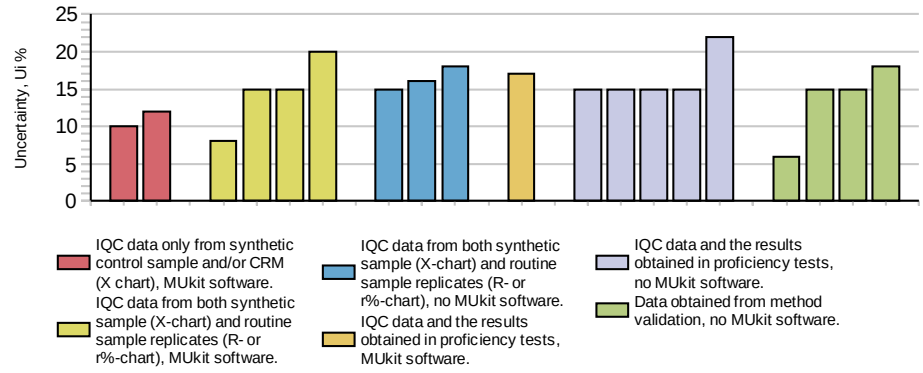



Measurand N_{NH4} Sample A1N
Uncertainty, Ui %
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and 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.


Measurand N_{NH4} Sample B2N
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 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.

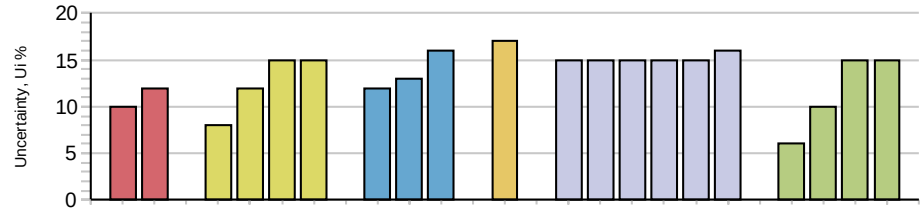

Measurand $N_{NO2+NO3}$ Sample N3N
Uncertainty, Ui %
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) 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.

Measurand N_{tot} Sample A1N



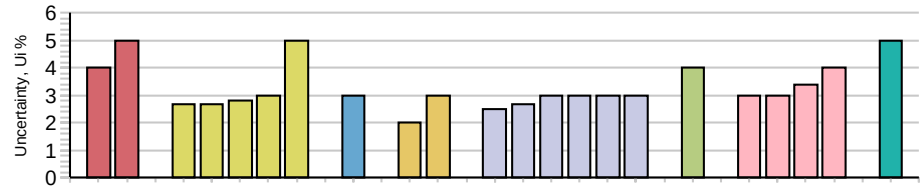
- IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
- IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
- IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit 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.

Measurand N_{tot} Sample N3N

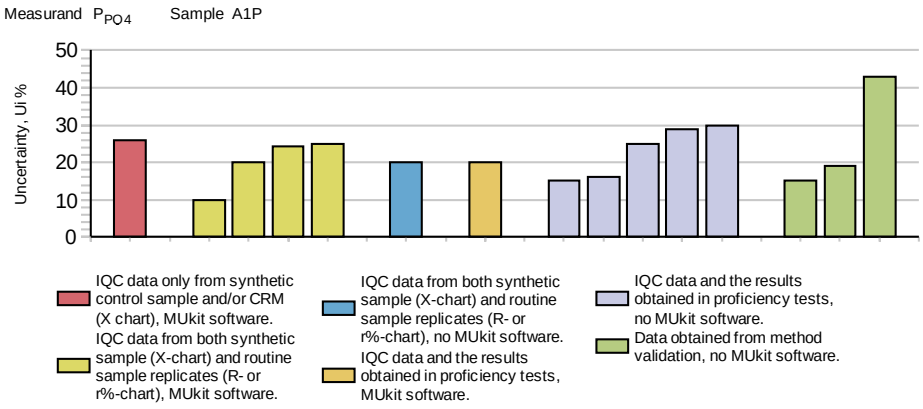


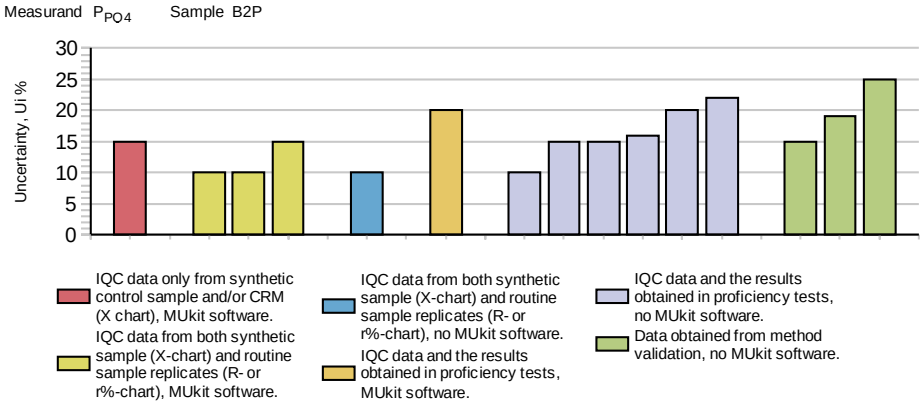
- IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
- IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
- IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit 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.

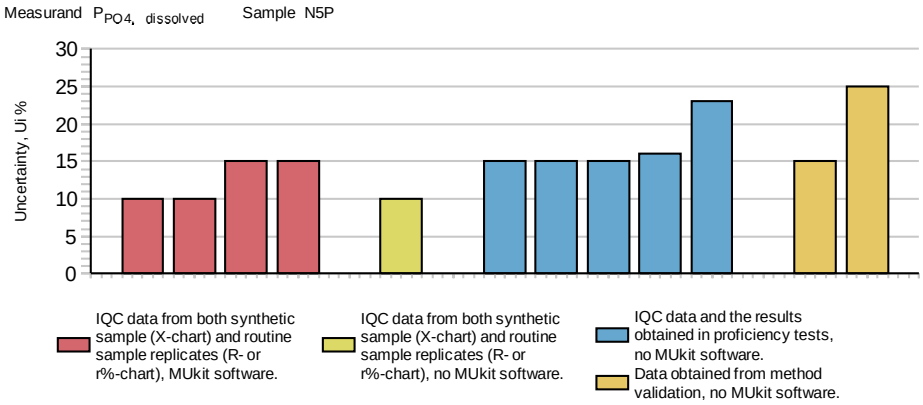
Measurand pH Sample N3H

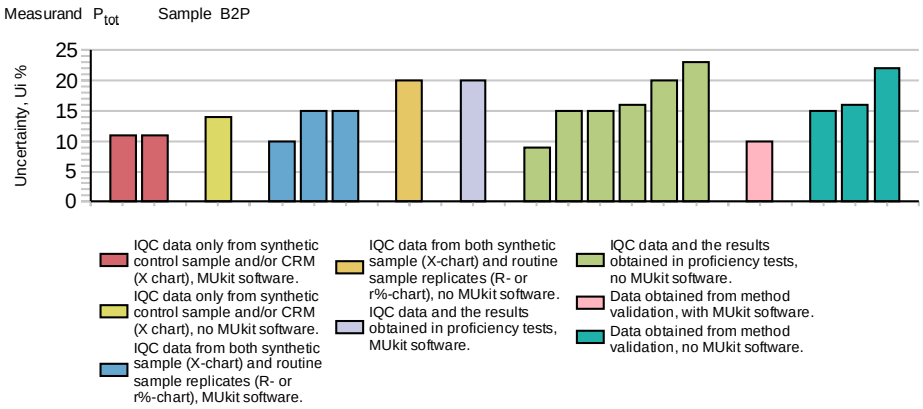


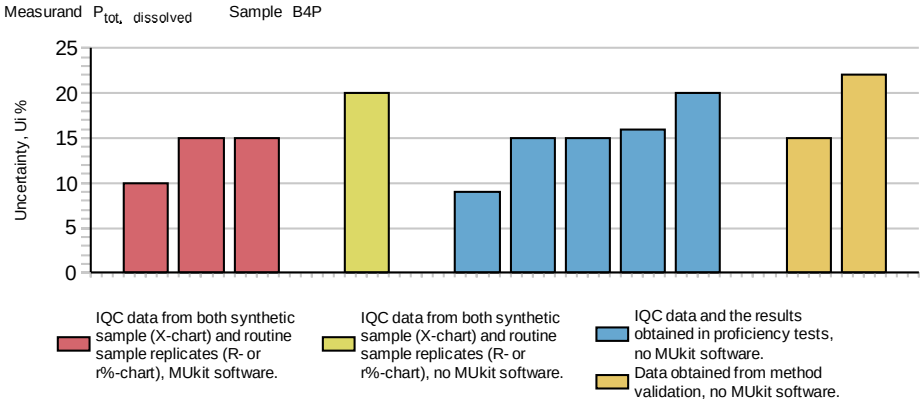
- IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
- IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
- IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit 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, with MUkit software.
- Data obtained from method validation, no MUkit software.
- Other procedure


Measurand P_{PO4} Sample A1P
Uncertainty, Ui %
50
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 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.


Measurand P_{PO4} Sample B2P
Uncertainty, Ui %
30
25
20
15
10
5
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 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.


Measurand $P_{PO4,\ dissolved}$ Sample N5P
Uncertainty, Ui %
30
25
20
15
10
5
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, no MUkit software.
Data obtained from method validation, no MUkit software.


Measurand P_{tot} Sample B2P
Uncertainty, Ui %
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), 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), 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, with MUkit software.
Data obtained from method validation, no MUkit software.


Measurand $P_{tot,\ dissolved}$ Sample B4P
Uncertainty, Ui %
25
20
15
10
5
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, no MUkit software.
Data obtained from method validation, no MUkit software.

INTERLABORATORY PROFICIENCY TEST SYKE 03/2018

FINNISH ENVIRONMENT INSTITUTE

ISBN 978-952-11-4927-6 (pbk.)
ISBN 978-952-11-4928-3 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)